University of Alberta

Synthesis of Boracyclobutenes by Transmetallation; Insertion and Demetallation Reactions of Boracyclobutenes and Titanacyclobutene Complexes

by

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In memory of my Grandma,

Elsie Bauer

Abstract

A series of new titanacyclobutene complexes were prepared by samarium diiodide-mediated central carbon alkylation of η^3-propargyltitanium complexes. The titanacyclobutenes were synthesized in high yield and completely characterized using NMR spectroscopy and, where applicable, single crystal X-ray analysis. For sterically crowded η^3-(*tert*-butyl)propargyltitanocene, attack at the titanium centre by benzyl radical is also observed.

Migratory insertion of isonitriles to titanacyclobutene complexes was investigated. Treatment with one equivalent of isonitrile affords iminoacyl titanacyclopentene complexes by insertion on the alkyl side. Subsequent treatment with another equivalent of isonitrile produces titanium-diamidate complexes by vinyl-side insertion and reductive cyclization. Demetallation of iminoacyl titanacyclopentene complexes with mCPBA yields homoallylic amides.

Boracyclobutenes were prepared in moderate to excellent yield by the novel transmetallation of titanacyclobutene complexes with dihaloorganoboranes. The transmetallation is efficient with 2-phenyltitanacyclobutenes, however two equivalents of titanacycle are required for clean conversion of 2-methyltitanacyclobutenes. Characterization was achieved using NMR spectroscopy; based on ^{13}C NMR data, there appears to be a 1,3-bonding interaction between boron and the β-ring carbon. A cyclic six-membered borinic ester was synthesized by transmetallation of a 2-oxatitanocenecyclohex-5-ene complex with dichlorophenylborane.

Exposure of boracyclobutenes to protic sources yields products arising from protodeboronation. Lewis acidity, as measured by the Gutmann-Beckett method, is relatively low for a trialkylborane; additionally, stable tetra-coordinate adducts could not be formed upon treatment of boracyclobutenes with anions and amines. Oxidation of boracyclobutenes with dry DABCO·$2H_2O_2$ produces the expected β-hydroxy ketones, however wet oxidation reagents produce mixtures of β-hydroxy ketone and protodeboronation products. Boracyclobutenes react with aldehydes in a non-selective manner, producing butadienes from an intermediate formed by allylboration, as well as 1,2-oxaborins by an uncommon insertion into the sp^3-hybridized carbon-boron bond.

Acknowledgements

I would like to thank my supervisor, Dr. Jeff Stryker, for education, instruction, guidance, suggestions, and everything else. We didn't always agree, but I learned a lot and some pretty decent research was completed. I particularly appreciated the loose autonomy while conducting this research, which probably diverged at least somewhat from the intended directions.

Current and past members of the Stryker group helped in countless obvious and intangible ways, so I would like to thank Dr. Masaki Morita, Dr. Takahiro Saito, Dr. Ross Witherell, Dr. Dave Norman, Dr. Owen Lightbody, Dr. Mee-Kyung Cheung, Dr. Armando Ramirez, Jason Norman, Bryan Chan, Nolan Erickson, Kai Ylijoki, Paul Fancy, Jeremy Gauthier, Jeff Quesnel, Andrew Kirk, Adam McKinty, Bichu Cheng, Shaohui Yu, and Dominique Hebert. Masaki in particular put a large amount of time and effort into my training, and he was an exceptional colleague during the writing of the book chapter.

While the research I conducted at LMU is not included in this dissertation, I would like to express my substantial gratitude to Prof. Dr. Paul Knochel for accepting me into his group, exposing me to chemistry and an atmosphere with a different flavour, and assisting me since I left Munich; I learned a ton of things, and had a great time too. Of course, to all the other people that welcomed me in Germany and made it a fantastic experience: Danke vielmals! That's for Christina, Florian, Guillame, Giuliano, Vicente, Mathias, Marcel, Vladamir, Georg, Georgios, Simon, Fabi, Christoph, Marc, Tom, Cora, Nadege, Murthy, Srinu, Andrei, Milica, Ben, Matt, Albrecht, Christian, Shohei, Armin, Stefan, Felix, Liu, Darunee, Sylvie, Chrissy, Jenny, and everybody I missed. Christina had the misfortune of actually working with me, so she deserves extra kudos.

Incredibly important contributions were made by all the support staff, technical and otherwise, at the University of Alberta. I would particularly like to acknowledge the excellent people in the NMR, MS, and analytical laboratories that made time for a multitude of finicky samples.

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List of Abbreviations

Å	Angstroms
APT	Attached proton test
Bn	Benzyl
Bu	Butyl
Calcd.	Calculated
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Cy	Cyclohexyl
COSY	Correlated spectroscopy
DABCO	1,4-Diazabicyclo[2.2.2]octane
DMAD	Dimethylacetylenedicarboxylate
DMAP	N,N-Dimethyl-4-aminopyridine
DMPU	N,N'-Dimethylpropylene urea
DMSO	Dimethylsulfoxide
Dur	2,3,5,6-Tetramethylphenyl
EHMO	Extended Huckel molecular orbital
equiv	Equivalents
g	Grams
h	Hour(s)
HMBC	Heteronuclear multiple bond coherence
HMPA	Hexamethylphosphoramide
HMQC	Heteronuclear multiple quantum coherence
HOMO	Highest occupied molecular orbital
HRMS	High-resolution mass spectrometry
HSQC	Heteronuclear single quantum correlation
Hz	Hertz
i	iso
IR	Infrared
L	Litre

List of Abbreviations

LUMO	Lowest unoccupied molecular orbital
M	Metal
mCPBA	*m*-Chloroperbenzoic acid
Me	Methyl
Mes	Mesityl
mg	Milligram
mL	Millilitre
MO	Molecular orbital
MS	Mass spectrometry
NOE	Nuclear Overhauser effect
NMP	N-Methyl-2-pyrrolidinone
NMR	Nuclear magnetic resonance
Ph	Phenyl
ppm	Parts per million
Pr	Propyl
R	Alkyl group
SOMO	Singly occupied molecular orbital
t	tert
THF	Tetrahydrofuran
THT	Tetrahydrothiophene
TLC	Thin layer chromatography
TMP	2,2,6,6-Tetramethylpiperidine
TMS	Trimethylsilyl
Tol	Toluene
Tp'	$HB(3,5\text{-dimethylpyrazolyl})_3$
TROESY	Transverse rotational nuclear overhauser effect spectroscopy
X	Halide
η	Hapticity
μL	Microlitre

Chapter 1: Introduction

Organometallic complexes bear metal-carbon bonds that have been exploited in a wide range of transformations. Novel and highly efficient methods have been developed to form carbon-carbon bonds, as well as other main group element-carbon bonds, using organometallic complexes. In many cases, utilizing organometallic chemistry affords access to synthetic pathways unavailable using classical organic chemistry. Therefore, since much of current chemical synthesis is predicated upon adding components to available molecules to create more complex compounds, discovery of new methods and improvement of existing processes using organometallic chemistry contributes to the field of targeted synthetic chemistry.

This dissertation focuses upon the preparation and study of boracyclobutenes **1** and titanacyclobutene complexes **2**, strained four-membered organometallic rings (Figure **1.1**). Compounds of type **1** and **2** are interesting to investigate for potential as boron and titanium synthons; specifically, to combine these organometallic subunits with functional groups of other compounds in a rapid and controllable fashion for use in targeted syntheses. Titanacyclobutene complexes and boracyclobutenes have been prepared and reported upon in the literature, however only a relatively minor amount of attention has been devoted to exploring their reactivity. At this preliminary stage, the majority of the freshly completed research was directed to establishing a feasible synthetic route to the compounds of interest, particularly the boracyclobutenes, and subsequently investigating their reactivity.

Figure **1.1**: A boracyclobutene and a titanacyclobutene complex

1 **2**

Following a general introduction and review of pertinent literature in Chapter 1, new results will be discussed in Chapters 2 through 5. Chapter 2 describes the preparation of titanacyclobutene complexes of type **2** by central carbon alkylation of

η^3-propargyltitanium complexes. This extension of previous work conducted in the Stryker group includes improvement of the preparative methodology and the synthesis of a broader range of titanacyclobutene complexes. Chapter 3 presents the research into single- and double-isonitrile insertion to titanacyclobutene complexes, as well as a new demetallative strategy that yields homoallylic amides.

Chapter 4 describes the synthesis of boracyclobutenes **1** by transmetallation from titanacyclobutene complexes **2**. This methodology is a new approach to the preparation of boracyclobutenes using stable reagents that are easily modified for, conceivably, a large library of compounds for further investigation. Chapter 5 establishes a foundation for future boracyclobutene reactivity studies by probing elementary transformations, investigating Lewis acidic properties, and identifying reaction paths with aldehydes, including an uncommon 1,2-migration of carbon from boron. Chapter 6, the final section, includes all experimental details.

This Introduction is divided into four sections pertinent to the new results that will be presented, so that a critical evaluation can be made with respect to what has been reported in the literature. The first two sections review the reactivity and synthesis of metallacyclobutenes, with a focus on titanacyclobutene complexes. Of particular interest is the selectivity observed for reactions with titanacyclobutenes, as established patterns have bearing on understanding the new work on the boron transmetallation of titanacyclobutene complexes, as well as for insertion of isonitriles. The synthesis of titanacyclobutenes by central carbon alkylation of η^3-propargyltitanium complexes is the starting point for all subsequent research conducted, so this and other synthetic approaches to metallacyclobutenes will be covered in detail in Section 1.2.

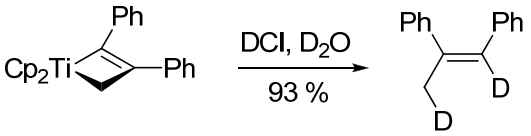
The chemistry of boracyclobutenes is relatively unexplored, with only two preparative routes having been reported, and few synthetic studies conducted. Therefore, the limited knowledge regarding the synthesis and reactivity of boracyclobutenes is presented in Section 1.3. Since this dissertation establishes a novel method for synthesizing boracyclobutenes by transmetallation, the final introductory section reviews transmetallation chemistry, with a focus on mechanism and principles.

1.1 Reactivity of titanacyclobutene complexes

To obtain synthetically useful downstream material from the synthesis of titanacyclobutene complexes, methods for functionalization and decomplexation are necessary. Unfunctionalized alkenes can be obtained from elementary steps: protonation of the metal-carbon bonds results in acyclic material, whereas straightforward reductive elimination, unknown for titanacyclobutenes, would form substituted cyclopropenes. An established technique to enhance the synthetic utility of titanacyclobutene complexes, and metallacycles in general, is the incorporation of new functional groups by migratory insertion. Additionally, reactions of titanium alkylidene complexes, often accessible from titanacyclobutenes, are useful methylenating reagents. A reactivity profile of titanacylobutene complexes, and where necessary other metallacyclobutene complexes, will be provided so that new results reported in this dissertation may be placed in the proper context.

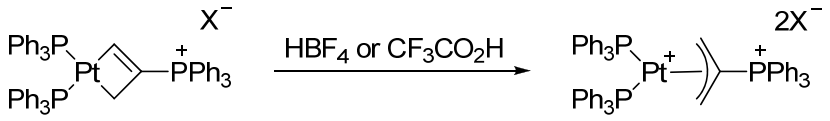
Protonation

Early period metallacyclobutene complexes typically react with protic acids at the metal-carbon bonds. Two equivalents of acid are required for complete liberation of the organic fragment. Titanacyclobutene complexes react with anhydrous HCl gas to form methyl substituted olefins and titanocene dichloride. This is illustrated in Equation **1.1** for the reaction with DCl.[1]



Equation **1.1**

While not achieved with titanacyclobutenes, protonation of the late series metallacyclobutene complexes with one equivalent of acid occurs at the vinyl bond to form metal η^3-allyl species. This is shown for a platinacyclobutene[2] (Equation **1.2**) and is also known for rhenacyclobutenes.[3]



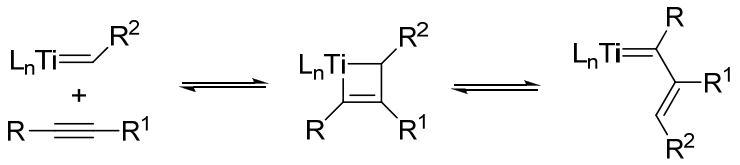
Equation **1.2**

Cycloreversion

A number of detailed studies regarding the cycloreversion of titanacyclobutene and titanacyclobutane complexes have been completed; titanacyclobutanes display this reactivity more prominently and were among the first systems studied for olefin metathesis.[4] Current metathesis research involves mostly late transition metal complexes due to greater functional group compatibility, whereas early transition metals are typically too oxophilic for widespread use.[5-9] However, titanium alkylidene complexes, including vinylcarbene complexes, have a multitude of applications, including: methylenation of carbonyls, cycloaddition as well as polymerization with alkenes and alkynes, and cyclopropanation of olefins.[10-13] In addition to cycloreversion, titanium alkylidene complexes can be prepared by α-hydrogen abstraction from alkyltitanium complexes.[14]

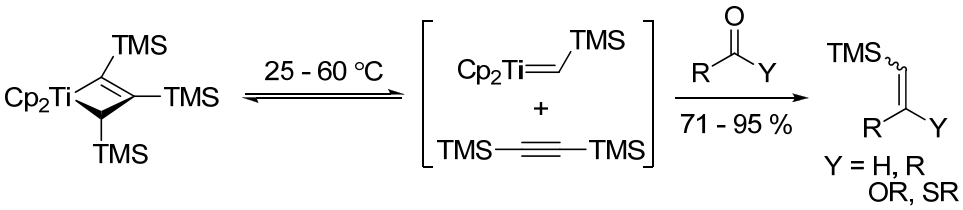
Generally, titanacyclobutanes and –butenes undergo cycloreversion to liberate alkene or alkyne and form titanium alkylidene complexes,[15] although an alternative reaction is ring opening to a vinylalkylidene complex (Scheme **1.1**). While titanacyclobutane complexes readily form titanium alkylidene complexes by extruding alkene, cycloreversion of titanacyclobutenes to the titanium alkylidene and alkyne is not as common. In the presence of diphenylacetylene, $Cp_2Ti[C(TMS)=C(TMS)CH_2]$ is converted to the diphenyl-substituted titanacyclobutene complex in 36 % yield over 6 hours at 85 °C, and the reverse reaction does not occur to an appreciable extent.[16]

Scheme **1.1**



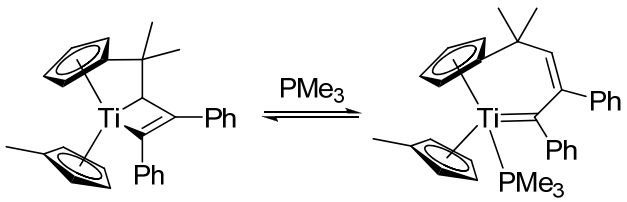
With the more sterically hindered tris(TMS)titanacyclobutene complex, cycloreversion to a titanium alkylidene and alkyne is facile and occurs at room

temperature (Equation **1.3**). Olefination of carbonyl-containing molecules, including aldehydes, ketones, esters, thioesters, and lactones, was complete within minutes at 60 °C or after 1 – 12 hours at 25 °C, although the alkenylsilane *E* : *Z* ratios in the products were poor (1 : 1.3 – 2.2 : 1).[17]



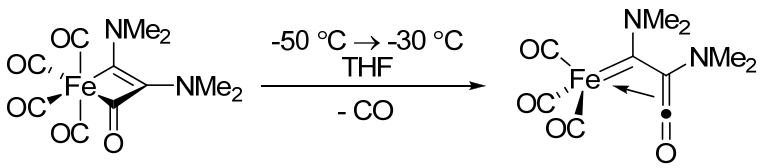
Equation **1.3**

Ring opening to vinylalkylidene complexes is frequently proposed as a reaction step to explain the observed reactivity of metallacyclobutenes, however, this process is rarely observed directly. In a strained titanacyclobutene complex containing a one-carbon linker between the four-membered ring and a cyclopentadienyl (Cp) ancillary ligand, the cycloreversion product is trapped by coordination of trimethylphosphine (Equation **1.4**).[18] In this case, extrusion of alkyne does not occur and PMe_3 stabilizes the titanium vinylalkylidene complex. In general, titanocene-based alkyl complexes are stabilized by electron-rich ancillary ligands like Cp* more so than Cp.[19]



Equation **1.4**

In another example of the transformation from a metallacyclobutene to a vinylalkylidene complex, loss of carbon monoxide drives ring opening of a ferrocyclobutenone (Equation **1.5**).[20] Coordination of the ketene moiety maintains electron density at the metal. Tantalum[21] and ruthenium[22] alkylidene complexes react with alkynes to form vinylalkylidene complexes, likely through an intermediate metallacyclobutene.



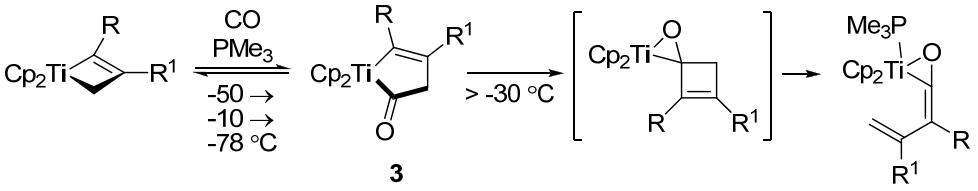
Equation **1.5**

Insertion

The insertion of small molecules into metal-carbon bonds is well established, offering a direct route to functionalized metallacycles and, through downstream transformations, the ability to obtain functionalized organic material. Whereas both metal-carbon bonds in metallacyclobutanes are equivalent (barring significant differences in substituents), metallacyclobutenes have two markedly different sites of reaction in the sp^2- and sp^3-hybridized metal-carbon bonds. Reactions occurring selectively at either site and at both sites have been reported, with the substitution pattern of the metallacycle and the steric and electronic characteristics of the electrophile governing the regioselectivity. Controlling, or at least understanding, the regioselectivity of insertion is key to developing new reactions.

Carbon monoxide is a typical reactive small molecule studied for insertion reactions, with a large number of published examples.[23-25] The mechanism of migratory insertion of carbon monoxide and other small molecules has also been extensively studied, both experimentally and theoretically, and has been reviewed.[26,27] With titanacyclobutenes, carbon monoxide reversibly inserts into the titanium-alkyl bond to form acyl titanacyclopentene complexes (Equation **1.6**).[28] The dimethyl-substituted acyl complex (**3**: R, R^1 = Me) was characterized at low temperature by NMR and IR spectroscopy because decomposition occurs in solution above -30 °C to an oligomeric ketene adduct, although in the presence of PMe_3 the titanium adduct is isolable. The reversibility of carbon monoxide insertion was established by exposing the titanacyclobutene complex to labeled ^{13}CO, then replacing the atmosphere with CO of natural abundance in the presence of PMe_3; ^{13}C NMR spectroscopy proved the loss of the ^{13}C label from the titanium-ketene complex. The presence of an acyl titanacyclopentene, along with a competition experiment between the reversibly-formed acyl complex and *tert*-butyl isonitrile, strongly suggests that the observed ketene adducts are not obtained

from titanocene-vinylalkylidene complexes, but from an intermediate cyclobutenone that undergoes ring opening.

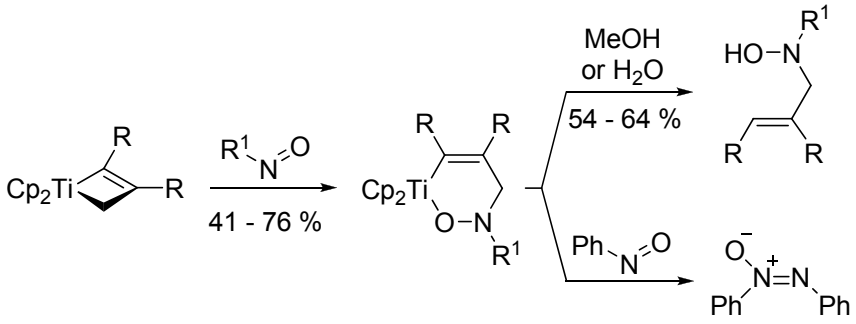


Equation **1.6**

Characterization of the acyl titanacyclopentene **3** as an η^1-complex was determined based on IR data; an intense peak at 1615 cm^{-1} suggests little η^2-character in the acyl bond. In subsequent work by the Stryker group, an acyl titanacyclopentene complex (Equation **1.6**: Cp*, R = CH_3, R^1 = -C≡C-CH_3) was prepared similarly and a solid state structure was obtained.[29] While no further functionalization was attempted, the crystal data confirmed the η^1-bonding mode, showing a long Ti-O distance of 3.07 Å.

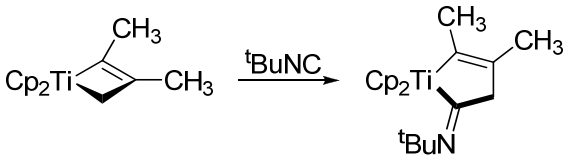
Organonitroso compounds have also been used for insertion to titanacyclobutene complexes. As with carbon monoxide, insertion occurs on the alkyl side to form Ti-O and C-N bonds in a new 2-oxa-3-azatitanacyclohexene complex (Scheme **1.2**). Demetallation was achieved in good yield simply by hydrolysis with either methanol or water to form hydroxylamines. Interestingly, in the presence of an excess of nitrosobenzene, azoxybenzene is formed; no mechanism was proposed for this transformation.[30]

Scheme **1.2**



Reports of isonitrile insertion to both the alkyl and vinylic Ti-C bonds of titanacyclobutene complexes have been made. Grubbs first reported insertion of *tert*-

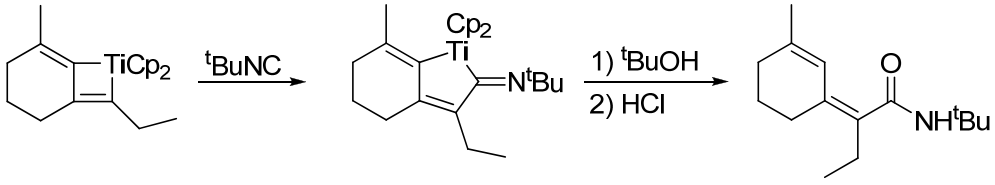
butyl isonitrile to a titanacyclobutene complex, which forms an η^1-iminoacyl titanacyclopentene by insertion on the alkyl side (Equation **1.7**).[28] Isonitrile insertion has also been investigated by the Stryker group, with all such reactions also occurring at the sp^3 Ti-C bond.[29] This chemistry will be discussed further in Chapter 3.

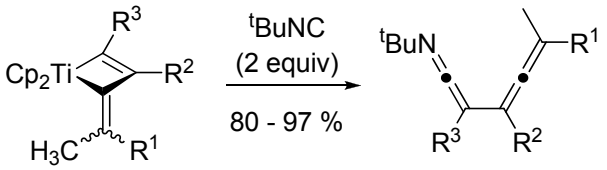


Equation **1.7**

With α-methylenetitanacyclobutene complexes, insertion of isonitriles occurs regioselectively at the endocyclic vinyltitanium bond (Scheme **1.3**). Treatment of the only intermediate iminoacyl complex reported by Whitby with *tert*-butanol followed by acidolysis with HCl gas afforded a conjugated amide in unspecified yield. Alternatively, when monocyclic α-methylenetitanacyclobutene complexes were treated with two equivalents of isonitrile, allenylketenimines were formed (Equation **1.8**). Allenylketenimines were also formed with one equivalent of isonitrile, albeit in lower yield (66 %).[31]

Scheme **1.3**



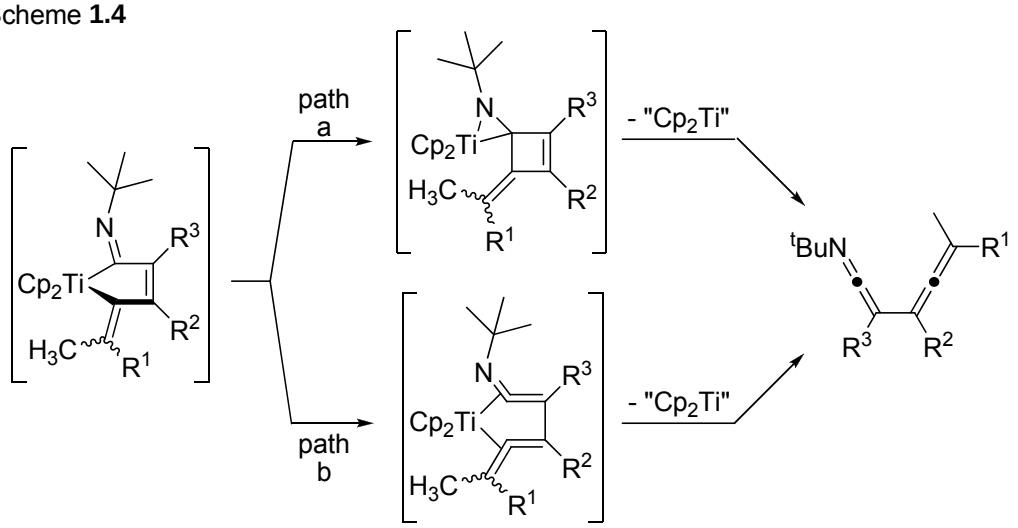


Equation **1.8**

R^1 = Ph, C_5H_{11}
R^2 = H, Ph, C_3H_7, C_5H_{11}
R^3 = Ph, C_3H_7, TMS

The authors provide two potential mechanisms for allenylketenimine formation: in the first, reductive elimination produces an intermediate titanium η^2-iminoacyl complex, which results in the observed product following loss of "titanocene"[32] and electrocyclic ring opening (Scheme **1.4**, path a). This is based on the mechanistic studies by Grubbs for the reaction of CO with titanacyclobutene complexes (see Equation **1.6**).[28] Alternatively, if the organic fragment of the iminoacyl complex is viewed as a chelating allene and ketenimine, simple dissociation of "titanocene" would provide the allenylketenimine product (Scheme **1.4**, path b). Similar products have been obtained from the reaction of a cobaltacyclobutene complex with *tert*-butyl isonitrile or carbon monoxide.[33]

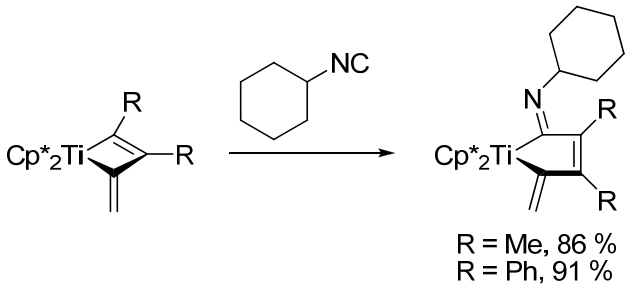
Scheme **1.4**



For two unsubstituted α-methylenetitanacyclobutene complexes, cyclohexyl isonitrile also inserts selectively into the endocyclic vinyltitanium bond (Equation **1.9**).[34] This is the least sterically hindered isonitrile reported for insertion into a titanacyclobutene complex. Reactions with other isonitriles failed, as did corresponding reactions with nitriles and ketones.

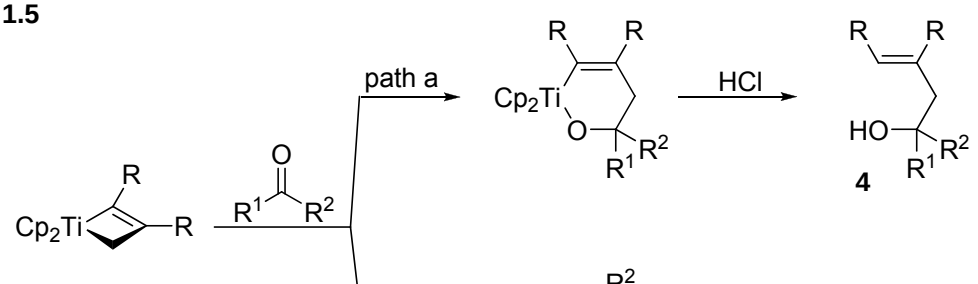
Aldehydes and ketones react non-selectively at the vinylic and alkyl Ti-C bonds of titanacyclobutene complexes (Scheme **1.5**). Insertion on the alkyl side produces a stable vinyltitanium alkoxide, which liberates homoallylic alcohol **4** upon treatment with anhydrous HCl gas (Scheme **1.5**, path a).[35] Alternatively, vinyl-side insertion forms an

allylic titanium alkoxide, which undergoes 6π electron cycloreversion to produce a conjugated diene **5** and oligomeric [Cp_2Ti=O] (Scheme **1.5**, path b).[36,37] The preferred site for insertion of carbonyls is the vinylic titanium bond, unless steric inhibition forces the reaction to occur on the alkyl side. Small methyl- and ethyl-substituted titanacyclobutene complexes react with acetaldehyde almost exclusively on the vinyl side. However, when slightly more bulky acetone is used, the ratio of products is only 66 : 34 in favour of vinyl insertion. With a sterically more hindered bis(phenyl)-substituted titanacyclobutene, exposure to acetaldehyde results in a 50 : 50 mixture of products from insertion on both sides, while acetone inserts exclusively into the sp^3-hybridized Ti-C bond.



Equation **1.9**

Scheme **1.5**

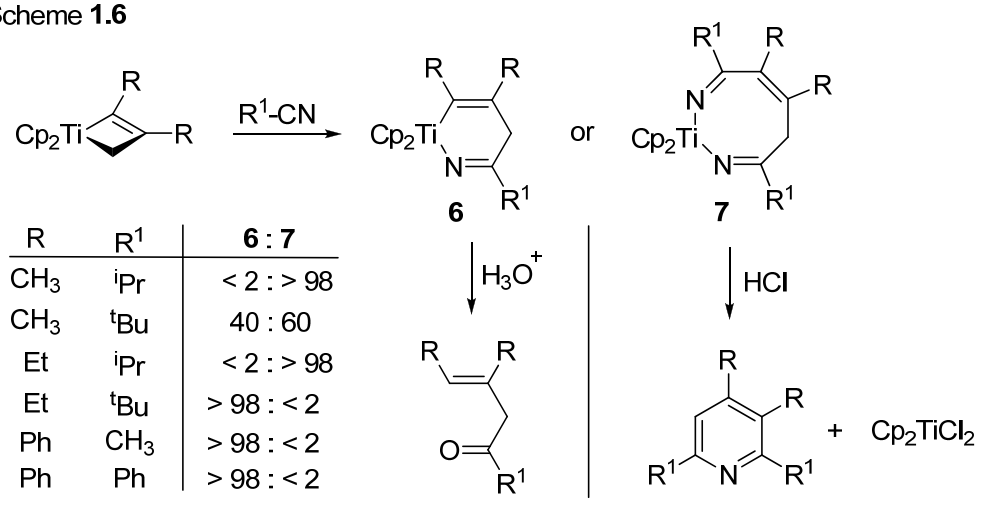


R	R^1	R^2	**4** : **5**
CH_3	CH_3	H	< 2 : > 98
CH_3	CH_3	CH_3	34 : 66
Et	CH_3	H	< 2 : > 98
Ph	CH_3	H	50 : 50
Ph	Ph	H	60 : 40
Ph	CH_3	CH_3	> 98 : < 2

In his initial report of nitrile insertion (*vide infra*) and prior to mechanistic studies of that reaction, Doxsee pointed out the likelihood that the vinyl and alkyl titanium-carbon bonds are more similar in energy than originally believed.[38] Typically a vinyl bond is less reactive due to a combination of π-bonding with metal orbitals and a stronger σ-bond to sp^2-hybridized carbon,[39] but in this case there are no orbitals of low enough energy or correct symmetry on titanium for any appreciable π-interaction.[40,41] Additionally, this reactivity profile is compared to that of the preference for vinyl migration over alkyl migration in the Baeyer-Villager oxidation of α,β-unsaturated ketones.[42] While subsequent work favours a different mechanism for nitrile insertion, the original sentiment may still apply to the insertion of aldehydes and ketones.

α-Methylenetitanacyclobutene complexes reportedly do not react with ketones or nitriles.[34] However, nitrile insertion occurs at both the alkyl and vinyl Ti-C bonds of other titanacyclobutene complexes (Scheme **1.6**). In titanacyclobutene complexes bearing olefinic phenyl substituents or when bulky isonitriles react with less hindered methyl- and ethyl-substituted titanacyclobutenes, insertion occurs preferentially into the Ti-C(sp^3) bond to form 1-aza-2-titana-3,6-cyclohexadiene complexes **6**. [35,36,38] These complexes react with aqueous acid to form β,γ-unsaturated ketones. Alternatively, with less sterically hindered isonitriles and small substituents on the titanacyclobutene ring, a double insertion diazacyclooctatriene product **7** is obtained.[36,38] Upon treatment with anhydrous HCl gas, substituted pyridines are formed, presumably by cyclization of the expected organic diimine.

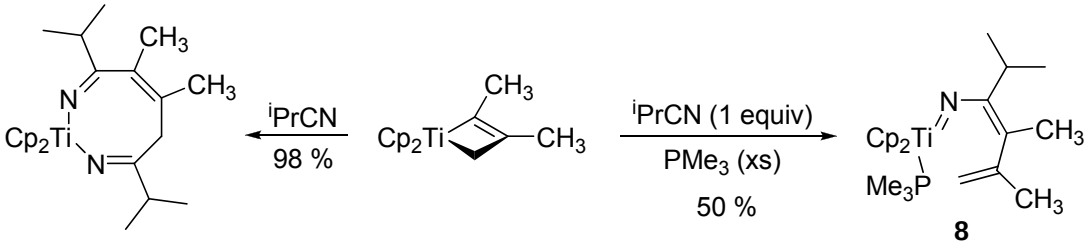
Scheme **1.6**



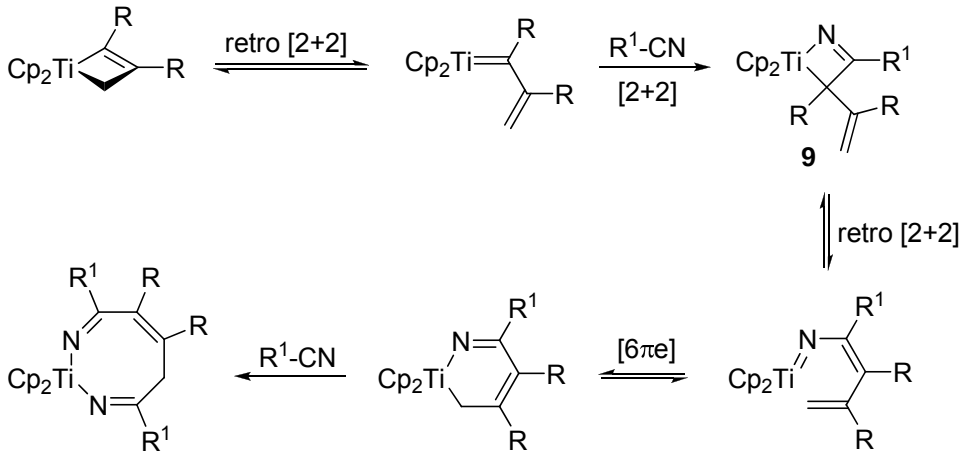
R	R^1	**6 : 7**
CH_3	^iPr	< 2 : > 98
CH_3	^tBu	40 : 60
Et	^iPr	< 2 : > 98
Et	^tBu	> 98 : < 2
Ph	CH_3	> 98 : < 2
Ph	Ph	> 98 : < 2

Mechanistically, the insertion of nitriles to titanacyclobutene complexes is not a simple process.[43] The first noteworthy observation was that the single insertion product **6** can not be converted to the double insertion product **7** in the presence of excess nitrile. When a dimethyl-substituted titanacyclobutene complex is treated with isopropylnitrile, double insertion occurs. However, when this reaction is carried out in the presence of excess trimethylphosphine, (butadienylimido)titanium complex **8** is obtained (Scheme **1.7**). This intermediate is trapped after the initial "insertion" into the vinyl bond, although the mechanism appears to involve a series of steps (Scheme **1.8**). The authors propose ring opening to a titanium vinylalkylidene followed by [2 + 2] cycloaddition with nitrile to form an azatitanacyclobutene intermediate **9**. Cycloreversion results in a (butadienylimido)titanium complex that cyclizes to a 2-aza-1-titana-2,4-cyclohexadiene complex, which then inserts an additional equivalent of nitrile to form the observed double insertion product.

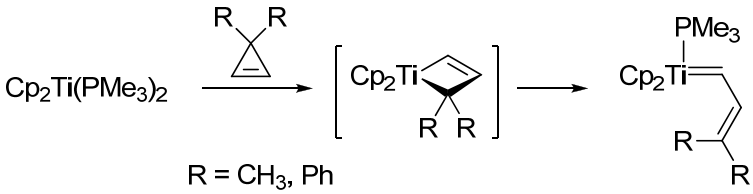
Scheme **1.7**



Scheme **1.8**

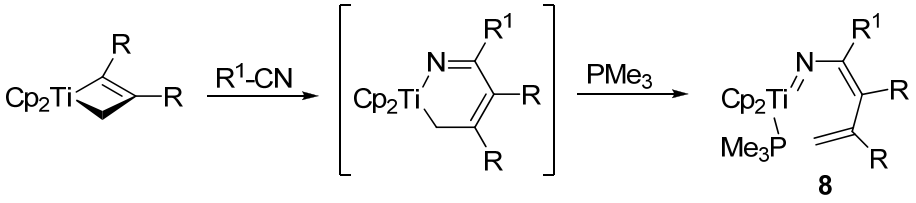


The proposed mechanism calls for ring opening to a titanium vinylalkylidene complex in the first step. However, this intermediate is not trapped by PMe_3 despite the known trapping of similar complexes. The *ansa*-bridged titanacyclobutene complex discussed previously opens to a titanium vinylalkylidene complex that was trapped with PMe_3 (see Equation **1.4**).[18] Additionally, bis(trimethylphosphine)titanocene reacts with 3,3-disubstituted cyclopropenes to form phosphine-coordinated titanium vinyl carbene complexes (Equation **1.10**). The presumed intermediate is a titanacyclobutene formed by insertion into the vinylic C-C bond, although this complex was not observed.[44]



Equation **1.10**

Another possible explanation for the observed (butadienylimido)titanium intermediate **8** is that insertion occurs into the vinylic Ti-C bond and 6π-electron retrocyclization occurs, which is trapped by PMe_3 (Equation **1.11**). This would imply that the product from vinyl insertion is less stable than that from alkyl insertion, and another molecule of nitrile inserts readily.



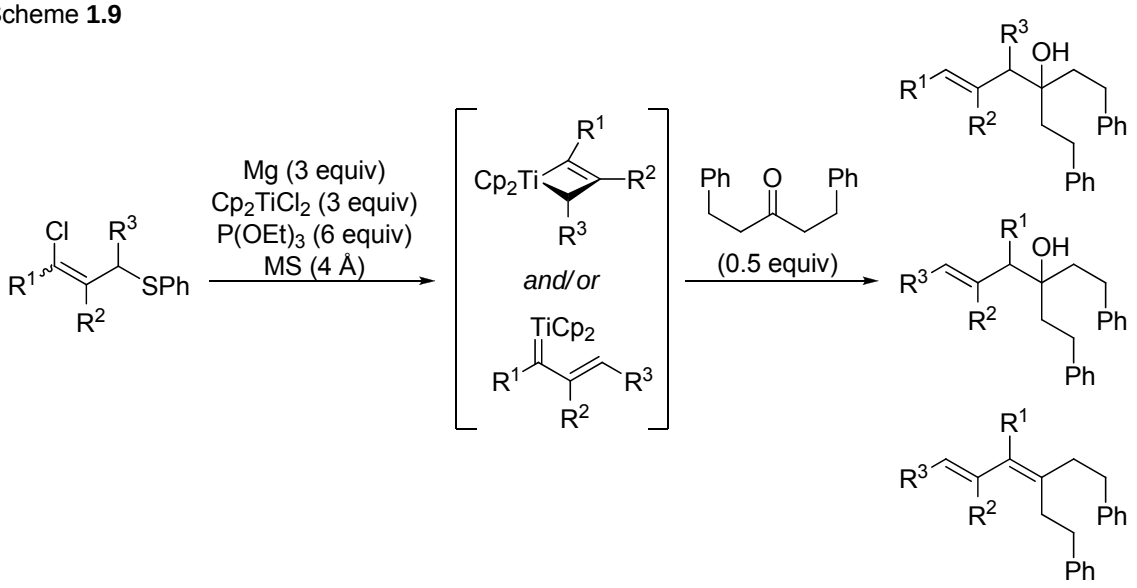
8

Equation **1.11**

Takeda has achieved a number of interesting titanium-mediated functionalizations of substituted alkanes and alkenes, although characterization of the titanium intermediates involved is minimal.[11] Recently, he and his coworkers used the product distribution from various reactions to gain indirect insight into the identity of the reactive intermediates.[45] An example is the synthesis of homoallylic alcohols and dienes, products accessible from titanacyclobutene intermediates, from ketones and γ-chloroallyl sulfides (Scheme **1.9**). The three products reported could be obtained by reaction with a putative

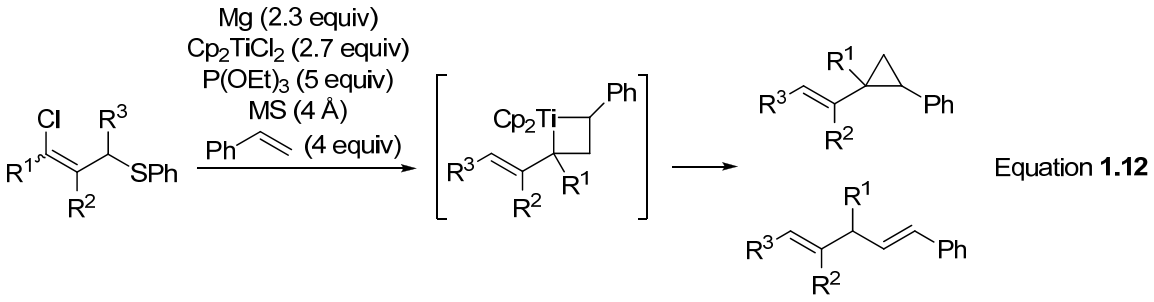
titanacyclobutene intermediate: the two homoallylic alcohols could arise from hydrolysis of the cyclic titanium alkoxide obtained from insertion into the vinyl and alkyl Ti-C bonds, whereas the diene product could be obtained by cycloreversion from the vinyl insertion product (refer to Scheme **1.5**). Alternatively, the products could conceivably be obtained by [4 + 2] cycloaddition or through a series of [2 + 2] cycloaddition/cycloreversion reactions involving a titanium vinylalkylidene intermediate, in a process similar to the proposed reaction route with nitriles (refer to Scheme **1.6**).

Scheme **1.9**



Under the same conditions, the reactive titanium intermediates couple with styrene to form vinyl cyclopropanes and dienes (Equation **1.12**).[45] The only reported reaction of an olefin with a titanacyclobutene complex involves metathesis,[16] whereas intermediates assumed to be titanium vinylalkylidene complexes are known to react with olefins to form cyclopropanes.[46] Thus, the two observed products potentially arise from an intermediate titanacyclobutane formed by [2 + 2] cycloaddition of a vinylalkylidene complex with styrene: direct reductive elimination forms the vinyl cyclopropane, a known reaction of well-characterized titanacyclobutanes.[47] Conversely, β-hydride elimination and reductive elimination from the titanacyclobutane intermediate accounts for the diene product. The parallels to known titanium vinylalkylidene chemistry, combined with the rarity of metallacyclobutene reactions with olefins (for which only

two reports are known[16,48]), support the titanium vinylalkylidene formulation for the reactive titanium species.



Equation **1.12**

The authors intention in these studies was to use the reactivity pattern to determine the identity of the reactive titanium species (as well as to introduce new methodology), and it is suggested that the substituents of the titanium species determine whether a titanium vinylalkylidene or a titanacyclobutene complex is formed. However, there is apparently a contradiction with the earlier work already presented: titanacyclobutene complexes also follow different reaction pathways that are dependent upon the ring substituents. Unfortunately, in this and similar chemistry where the organic product is of primary interest, the reactive titanium intermediates have not been characterized, but converted further *in situ*. Since there are many additional species present in the reaction flask (magnesium turnings, triethyl phosphite, molecular sieves, water, by-products from the initial formation of the reactive titanium species including $MgCl_2$ and Cp_2TiX_2, where X is an electronegative atom displaced from the initial organic substrate), it is difficult to identify what is actually occurring. This is not to say that the work of Takeda in the titanium-mediated synthesis of functionalized organic compounds is not meritorious, only that interpreting these results to gain an understanding of the titanium intermediates is not straightforward.

Thus, it appears to be a general trend that the size of the α-vinyl substituent plays a dominant role in determining the initial reaction site of known titanacyclobutene complexes. This selectivity has been explained in two ways: (1) by invoking titanium vinylalkylidene intermediates obtained through ring opening in the case of nitrile

insertion, or (2) by considering that the vinylic Ti-C bond is not as strong as originally thought and thus more prone to migration.

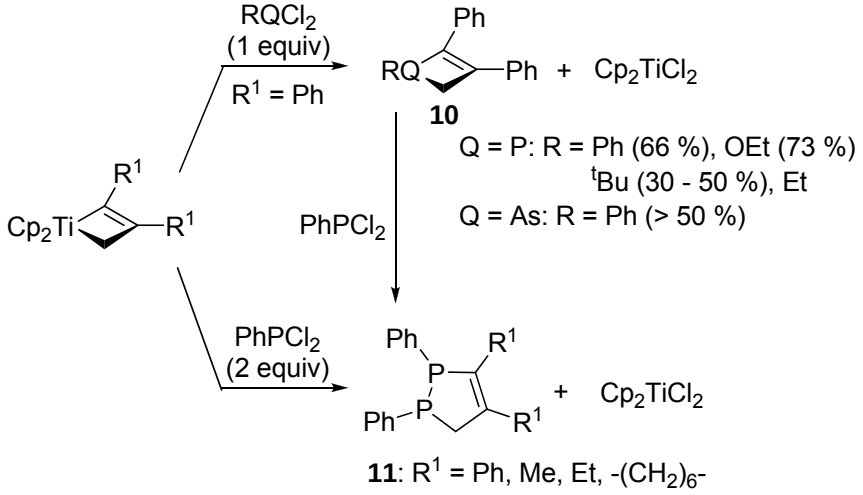
Transmetallation

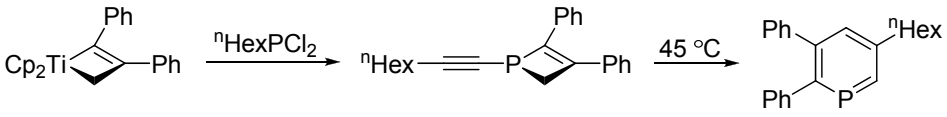
Transmetallation is the transfer of a bound organic moiety from one metal to another, creating a new organometallic complex. In this case, "metal" encompasses a broad definition that includes elements of Groups I - XVI excepting C, N, O, and S. After an organic ligand or fragment is transferred from one metal to another, it exists in a new coordination environment from which different and more efficient reactions may be achieved. Thus, it is particularly useful for diversifying the reactivity of the organic portion. Transmetallation is also useful in the synthesis of complexes difficult to access by other means and, in the context of this thesis, has been used extensively for the synthesis of novel boracyclobutenes.

Only a few reports of transmetallation from titanacylobutene complexes have appeared, and are of limited synthetic utility. Initial reports involved the reaction of titanacyclobutene complexes with dichlorophenylphosphine and dichlorophenylarsine to make the respective main group heterocycles, producing titanocene dichloride as a by-product (Scheme **1.10**).[49-51] Later, it was realized that 1,2-diphosphacyclopent-3-enes **11** were formed in addition to the expected phosphetes **10** when two equivalents of dichlorophenylphosphine were used, but the diphosphine products were formed in low, unspecified, yield (Scheme **1.10**).[52] This product can also be obtained indirectly by addition of $PhPCl_2$ to phosphete.[53] Interestingly, only the diphosphine product is reported for transmetallation to phosphorous starting from the dimethyl-substituted titanacyclobutene complex.

Since then, other transformations to phosphacyclobutenes have been achieved by the same methodology.[45,54] When 1-alkynyldichlorophosphines were used, the resultant phosphete expanded to a phosphinine over four days at 45 °C (Equation **1.13**).[55] Titanocene and zirconocene complexes, and their chemistry related to phosphinines, have been reviewed.[56] Similar to the transmetallation to phosphorous, titanacyclobutene complexes also react with one equivalent of dichlorophenylstibene to form both the analogous stibacyclobutene and distibene product in variable ratios.[52]

Scheme **1.10**

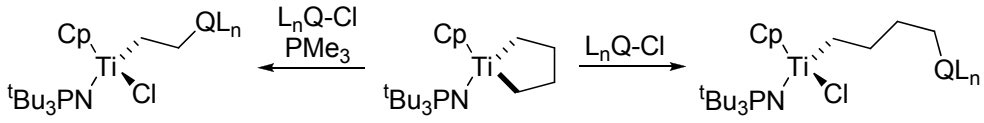




Equation **1.13**

Titanacyclobutene transmetallation is relatively uncommon, but other Group IV metallacycles have been transmetallated and used for the preparation of a range of main group compounds. Unsubstituted titanacyclopentanes react with one equivalent of phosphorous, silicon, boron, and tin chlorides to form ring-opened bimetallic species in moderate to excellent yield (Scheme **1.11**).[57] According to DFT calculations, loss of ethylene occurs in the presence of PMe_3, resulting in isolated complexes with a chain two carbons shorter between titanium and the main group element.

Scheme **1.11**

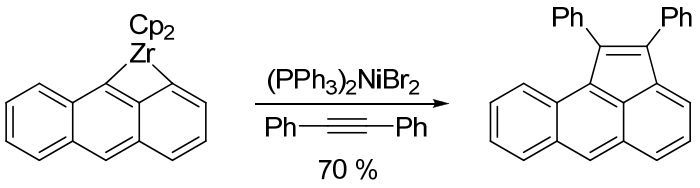


QL_n = $SiCl_3$: 78 %
TMS: 95 %
DPMS: 59 %
$Si(TMS)_3$: 100 %
Bcat: 52 %
PPh_2: 70 %

QL_n = $SiCl_3$: 49 %
$SnMe_3$: 73 %
Bcat: 62 %
PPh_2: 67 %

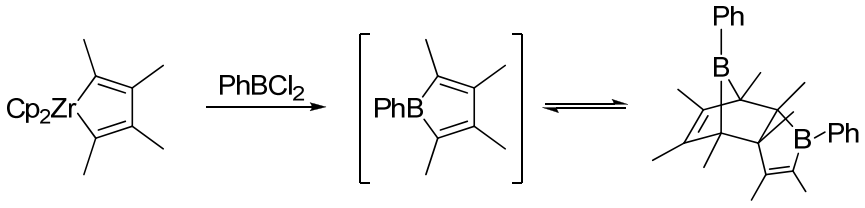
The Ziegler-Natta polymerization of olefins with metallocene catalysts is performed in the presence of alkylaluminum complexes. Studies investigating chain termination found that polymer chain transfer can occur from titanium and zirconium to the methylaluminum cocatalyst through a cyclic transition state.[58]

Transfer of acyclic organic ligands from alkenylzirconium complexes to boron is known.[59-61] Zirconocene 1,9-anthracenediyl reacts with bis(triphenylphosphine)-nickel(II)bromide to form an intermediate nickelacycle, which reductively couples with diphenylacetylene to form 1,2-diphenylaceanthrylene (Equation **1.14**).[62]



Equation **1.14**

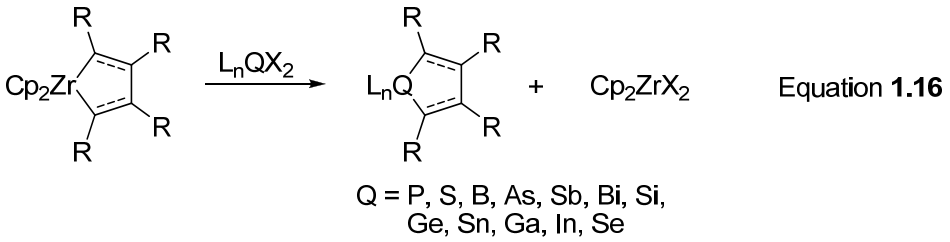
Zirconacyclopentadienes, formed by oxidative cyclization between two equivalents of alkyne and a "Cp_2Zr" synthon, smoothly transmetallate with dichlorophenylborane to form transient boroles that cyclodimerize (Equation **1.15**).[63] Evidence of free borole was not obtained, although the [4 + 2] cycloaddition dimer was characterized completely. In the presence of dienophiles such as alkynes, alkenes, allenes, and dienes, [4 + 2] cycloadducts of 2,3,4,5-tetramethyl-1-phenylborole were readily obtained at 60 – 100 °C, demonstrating that the initial dimerization is reversible.[63]



Equation **1.15**

"Metallacycle transfer" from five-membered zirconacycles with varying substituents is quite general and has been used for the synthesis of a number of other main group heteroles (Q = P, As, Sb, Bi, B, Si, Ge, Sn, Ga, In, S, Se), dihydroheteroles (Q = S, Sn, Se, P), and tetrahydroheteroles (Q = Se, Sn, S) (Equation **1.16**).[64,65] This also

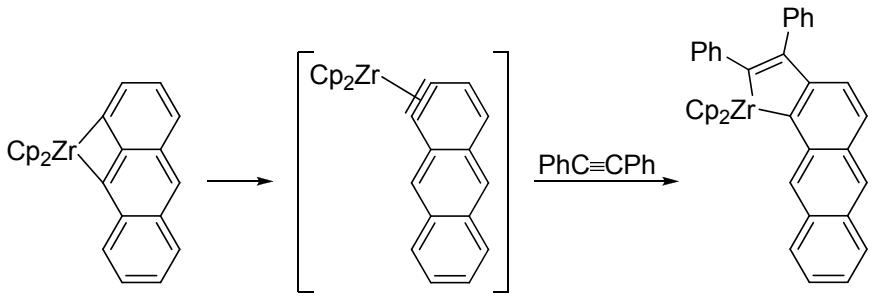
demonstrates the synthetic utility of transmetallation, as numerous heterocycles can be prepared from just a handful of different zirconacycles.



Equation **1.16**

β-hydrogen elimination

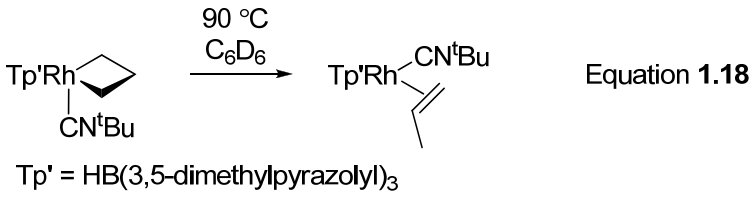
β-Hydrogen elimination is a common process of metal-alkyl species that can adopt the proper orientation, but is not typical of metallacyclobutenes. In planar metallacyclobutenes, a substituent at the β-ring position is not geometrically accessible to the metal. Thus, β-hydrogen elimination from metallacyclobutenes must occur from a substituent at the α-position. While not known for titanacyclobutene complexes, this reaction has been reported for a zirconium complex. Zirconocene 1,9-anthracenediyl reacts with diphenylacetylene to form a 1,2-annulated zirconacyclopentadiene (Equation **1.17**). β-Hydrogen elimination followed by reductive elimination transfers a hydrogen atom from the 2-position to the 9-position, leaving a zirconium-benzyne intermediate; this couples with alkyne to form the observed annulated zirconacycle.[62]



Equation **1.17**

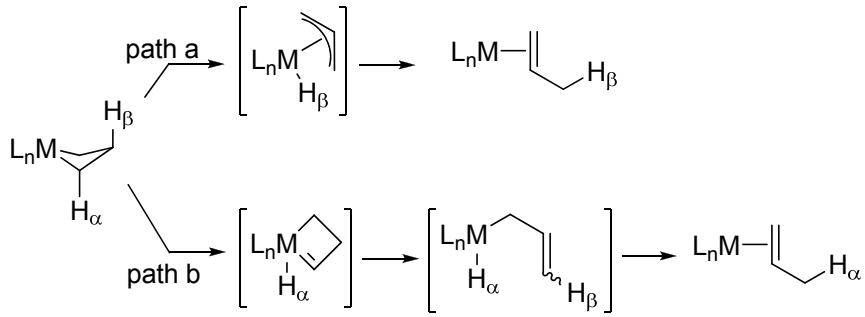
β-Hydride elimination from metallacyclobutanes is also quite rare, although less so. This process has been implicated by computational studies of decomposition pathways of ruthenacyclobutane intermediates formed during alkene metathesis.[66] A recent example is the rearrangement of a rhodacyclobutane complex to a propene-

coordinated rhodium complex at 90 °C (Equation **1.18**),[67] though other cases are known for late and early transition metals.[68] In this and other such reactions, the mechanism remains in question. The most direct route is β-hydride elimination followed by reductive elimination from the intermediate metal-η^3-allyl complex (Scheme **1.12**, path a). Alternatively, in a mechanism known to operate for platinacyclobutanes, the same product is obtained by α-hydride elimination to form a cyclic metal carbene complex; this then undergoes 1,2-hydride migration of the β-hydrogen before reductive elimination from the platinum η^1-allyl complex (Scheme **1.12**, path b).[69,70] β-Carbon elimination is also known for metallacyclobutanes,[71-74] although there are no such reports starting from metallacyclobutene complexes.



Equation **1.18**

Scheme **1.12**



1.2 Synthesis of titanacyclobutene complexes

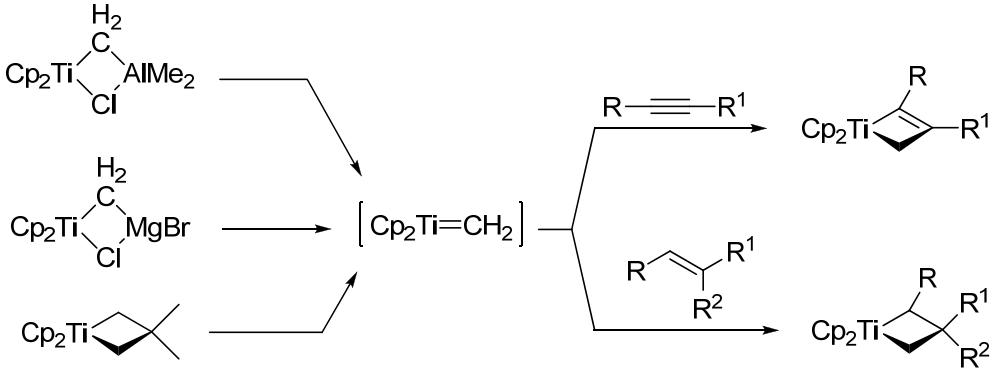
A number of routes have been developed for the synthesis of titanacyclobutene complexes. The most common is [2 + 2] cycloaddition chemistry of titanium-alkylidene complexes and alkynes, as a number of studies were completed related to the mechanism of metathesis reactivity. Nucleophilic addition of doubly metallated organic substrates has also been studied. γ-Hydrogen elimination is an infrequent approach due to the nature of the ligands required. Central carbon alkylation of η^3-propargyl complexes is a

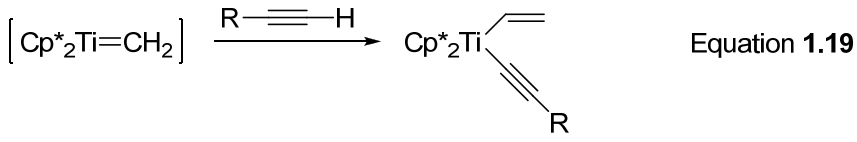
relatively new route for the regioselective preparation of metallacyclobutenes in general, and titanacyclobutenes in particular. The various synthetic methods will now be presented in greater detail, with a focus on central carbon alkylation, the principle focus of Chapter 2.

Cycloaddition

The most common synthetic route to four-membered metallacycles is [2 + 2] cycloaddition between two unsaturated two-atom units, a reaction that is broadly applicable across the transition metal series;[68,75] the synthesis of titanacyclobutene complexes is not an exception. Titanium alkylidene complexes[76] can be prepared from Tebbe's reagent (Cp_2TiCH_2-$Al(CH_3)_2Cl$)[16,77] or a related magnesium analogue (Cp_2TiCH_2-ClMgBr),[78] and from titanacyclobutanes (Scheme **1.13**).[79] Titanium alkylidene complexes readily couple with alkynes and olefins to produce titanacyclobutenes and titanacyclobutanes by cycloaddition (Scheme **1.13**). However, two problems arise from this methodology: for unsymmetric alkynes, a regioisomeric mixture of products may be obtained;[34] also, vinyl titanocene acetylides are formed in reactions with terminal alkynes (Equation **1.19**).[34,80] It should be noted that cycloreversion of four-membered titanacycles with insufficient electron density at the metal is a facile process.

Scheme **1.13**

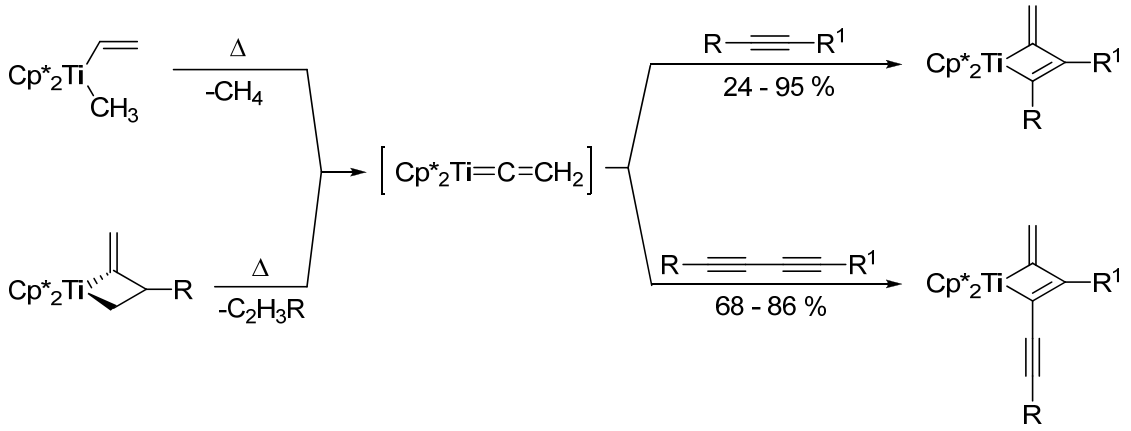




Equation **1.19**

Beckhaus has thoroughly studied α-methylenetitanacyclobutene complexes, which are prepared by [2 + 2] cycloaddition between titanium vinylidene complexes and alkynes (Scheme **1.14**).[34] The authors note that this reaction typically occurs regioselectively, placing bulky substituents preferentially at the β-carbon of the titanacyclobutene complex, and the alkynyl carbon with the greatest electron density, as measured by ^{13}C NMR spectroscopy, at the α-position. Titanacyclobutenes with extended conjugation to ring substituents were prepared by [2 + 2] cycloaddition of a titanium vinylidene complex with diynes, selectively placing the alkyne substituent at the α-position (Scheme **1.14**).[81] There was no interaction between the metal centre and the pendant alkyne observed.

Scheme **1.14**

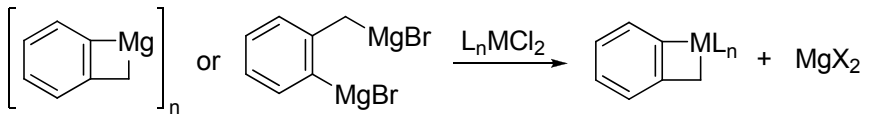


Metallacyclobutene complexes have also been prepared by a formal [2 + 1 + 1] cycloaddition between a metal, CO, and an alkyne, although this can also be viewed as migratory insertion of CO into a metal-alkyne or metallacyclopropene complex.[68] These reactions typically involve mid-to-late transition metals.

Nucleophilic and Electrophilic Alkylation

A number of benzannulated metallacyclobutene complexes, and related naphthalene derivatives, have been prepared by nucleophilic or electrophilic alkylation. Due to the nature of the organic fragment, these complexes do not display the entire range of metallacyclobutene reactivity discussed, such as cycloreversion, although other

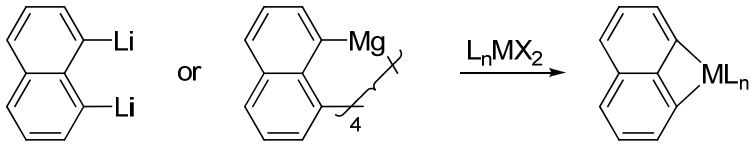
common reactivity patterns have been observed. Synthesis of metallacyclobutene complexes by 1,3-dianionic addition was first achieved from a benzyl moiety, by treating either 1-magnesiacyclobutabenzene or 2-(bromomagnesiamethyl)bromo-magnesiabenzene with dichlorometal complexes (Equation **1.20**: L_nMCl_2 = Cp_2TiCl_2;[82] Cp*Re(O)Cl_2;[83] Me_2SiCl_2, Me_2GeCl_2, Me_2SnCl_2;[84] Cp_2MoCl_2, Cp_2WCl_2;[85] (COD)$PtCl_2$[86]).[75]



Equation **1.20**

L_nM = Cp_2Ti, Cp*ReO, Me_2Si, Me_2Ge, Me_2Sn, Cp_2Mo, Cp_2W, (COD)Pt

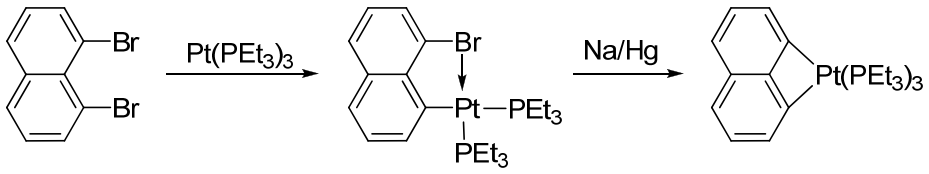
More recently, a series of transition metal 1,8-naphthalenediyl complexes have been prepared by nucleophilic addition of 1,8-dilithionaphthalide, or an analogous magnesiated reagent, to dichlorometal complexes or metals in low oxidation states (Equation **1.21**: Li/Zr and Mg/Ti, Rh, Ir, Pt;[87] Li/Pt[88]).



Equation **1.21**

L_nMX_2 = Cp_2ZrCl_2, $(PEt_3)_2PtCl_2$, Cp_2TiCl_2, Cp*Ir(PPh_3), Cp*Rh(PPh_3),

Analogous Group X complexes of platinum[88] and nickel[89] were prepared from 1,8-dihalonaphthalene, by initial oxidative addition into one carbon-halogen bond, followed by reduction with Na/Hg amalgam (Pt: Equation **1.22**).



Equation **1.22**

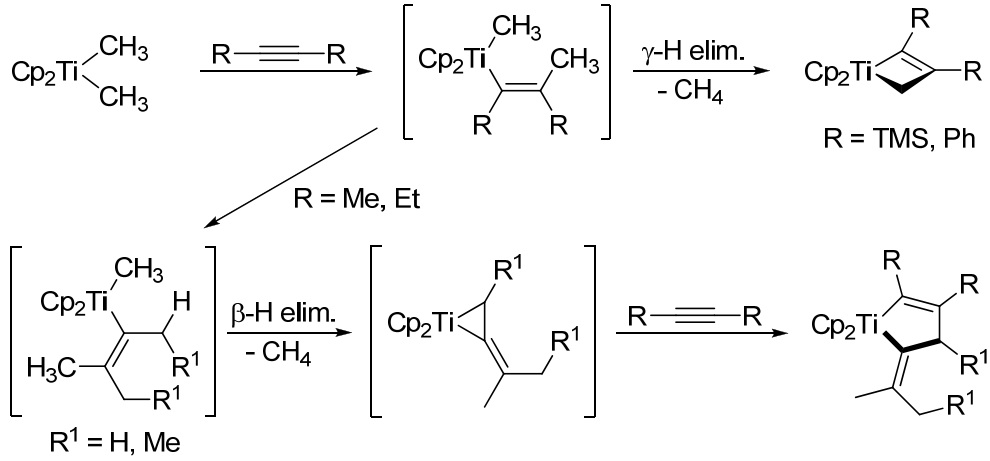
The exact mechanism for Takeda's synthesis of titanacyclobutene complexes from γ-chloroallyl sulfides in the presence of Mg(0) has not been elucidated, but it also must proceed through nucleophilic or electrophilic addition, or a combination of both (refer to Scheme **1.9**).[45]

γ-Hydrogen Elimination

Early and late transition metals can undergo intramolecular γ-hydrogen elimination, forming metallacyclobutene complexes by sp^2- and sp^3-hydrogen elimination. Mechanistically, late transition metals will perform oxidative insertion into the C-H bond in question followed by reductive elimination of HX, where X can be a halide, hydrocarbon, or other anionic ligand. Early transition metals favour a σ-bond metathesis mechanism, often with elimination of hydrocarbon. Presumably, any metal in a high oxidation state will also avoid direct oxidative insertion to a C-H bond. However, elimination of a β-hydrogen is generally favoured over that of a γ-hydrogen because of the proximity and ease of proper orbital alignment. Complexes that exhibit γ-hydrogen elimination reactivity are therefore much less common.

Dimethyltitanocene, also known as Petasis' reagent, was introduced as a carbonyl methenylation reagent in 1990.[90] At that time, evidence suggested that a titanium alkylidene species, accessible by loss of methane through α-hydride abstraction, was not formed. However, this prompted further research into the reactive species. Reactions of dimethyltitanocene with bis(trimethylsilyl)acetylene and diphenylacetylene resulted in the formation of titanacyclobutene complexes, although the latter alkyne required higher temperatures and an intermediate from carbotitanation of the alkyne was observed (Scheme **1.15**).[91] Titanacyclobutene products demonstrate that γ-hydrogen elimination from the allylic position is favoured over activation of a TMS C-H or aromatic C-H bond from the original alkyne. Further studies of reactions between dimethyltitanocene and alkyl-substituted alkynes found that β-hydrogen elimination is favoured over γ-hydrogen elimination, and results in formation of titanacyclopentene products as well as a small amount of titanacyclobutene (Scheme **1.15)**.[92,93]

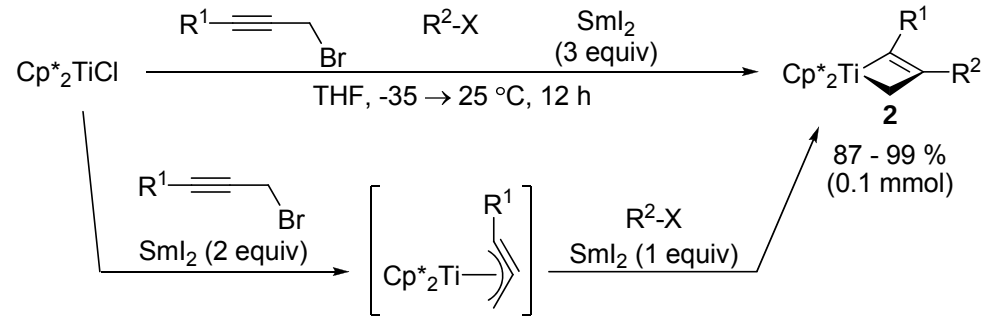
Scheme **1.15**



Central Carbon Alkylation of Metal-Propargyl/Allenyl Species

Central carbon alkylation of η^3-propargyltitanium complexes[94] will be covered in more detail since a contribution to this chemistry is described in Chapter 2. In the presence of one equivalent of samarium diiodide and a sufficiently reactive alkyl halide, alkylation of η^3-propargyltitanium complexes occurs at the central carbon and results in formation of titanacyclobutene complexes **2**. Initial studies involved the use of isolated propargyltitanium complexes, though procedural improvements have led to a one-pot protocol. Thus, titanacyclobutene formation is achieved directly from a propargyl halide, Cp^*_2TiCl, an alkyl halide, and three equivalents of samarium diiodide in high yield (Scheme **1.16**); by this methodology, the propargyltitanium complex is formed with two equivalents of SmI_2 before the final samarium-mediated alkylation.

Scheme **1.16**

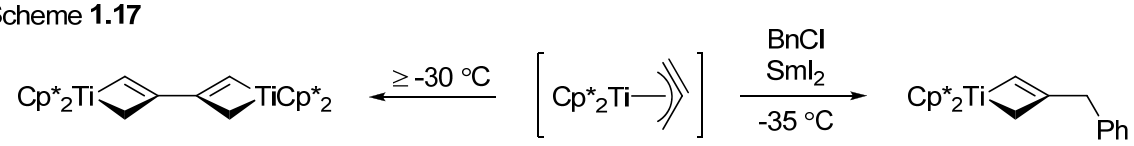


In general, alkylation reagents that form stabilized organic radicals (benzylic, allylic, tertiary alkyl …) can be chlorides and bromides while less stabilized alkyl

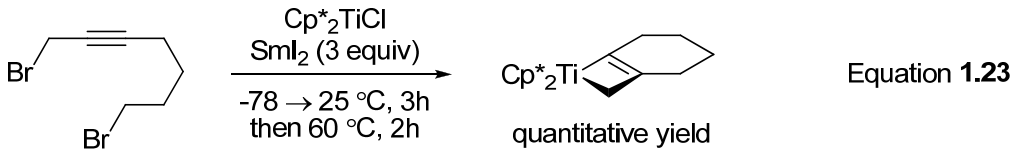
radicals are generated from iodides. Vinylic bromides have also been used successfully in the presence of HMPA or DMPU,[95] which are additives that have been shown to increase the reducing power of SmI_2.[96]

Several interesting titanacyclobutene complexes have been synthesized using central carbon alkylation methodology. The parent unsubstituted η^3-propargyltitanium complex dimerizes above approximately -30 °C, but may be alkylated at low temperature provided the organic radical can be generated (Scheme **1.17**).[94] Thus, alkylation with benzyl radical was possible but monomeric titanacyclobutene complexes were not obtained with less reactive alkyl halides. As noted previously, terminal alkynes react with titanium alkylidene species to form titanium acetylides and are not useful for [2 + 2] cycloaddition chemistry.[34,80]

Scheme **1.17**



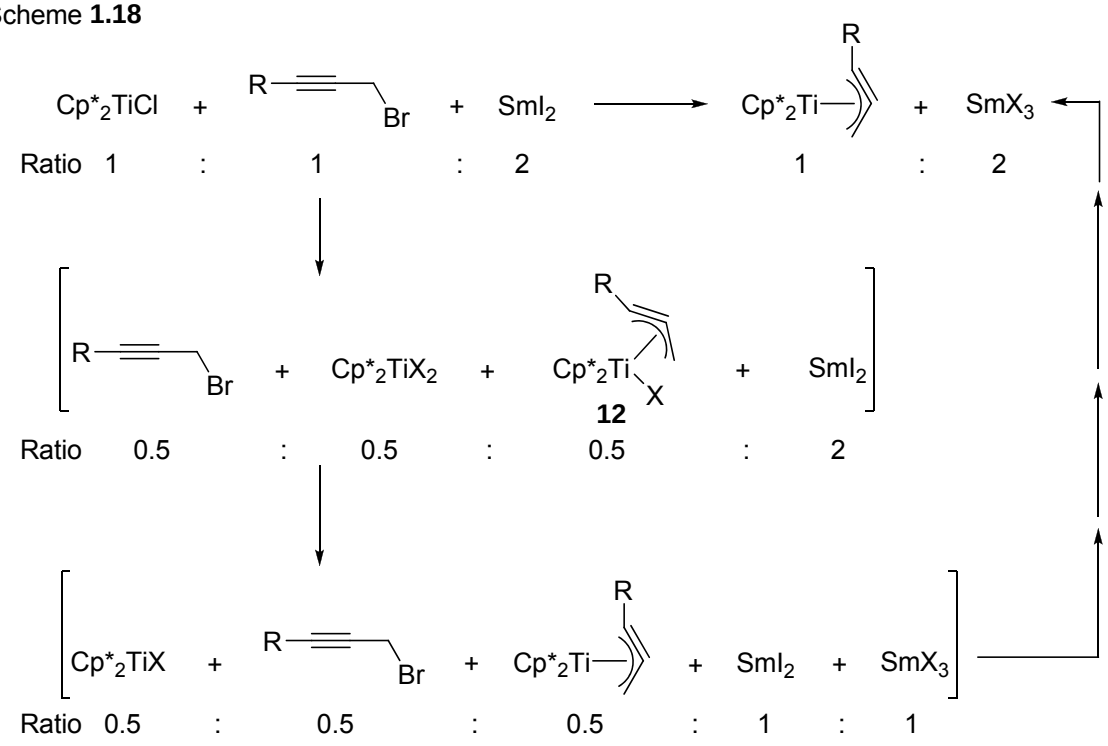
Of particular interest is intramolecular central carbon alkylation and its application to the synthesis of medium to large organic rings. At elevated temperatures α,ω-dibromoalkynes form the requisite propargyltitanium(III) complexes and are alkylated by the pendant alkyl bromide (Equation **1.23**).[95,97] Preliminary investigations suggested that larger ring systems could be obtained using bulkier ancillary ligands, possibly as large as ten- and twelve-membered rings with Cp*. This can be interpreted as similar to a Thorpe-Ingold effect from the sterically large titanium centre. Current research is focused on malonate-derived α,ω-dibromoalkynes bearing a quaternary carbon, so the necessary steric restrictions are a feature of the organic substrate instead of the inorganic moiety; this also accomplishes the long-standing goal of improving functional group compatibility.[98]



Equation **1.23**

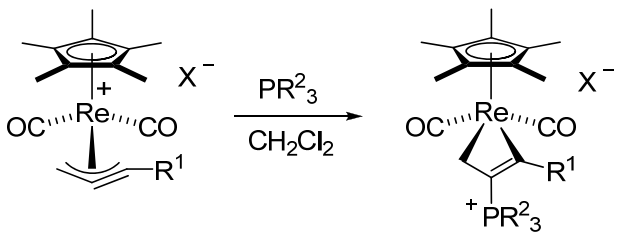
Determining the mechanism for this reaction is complicated by the presence of two halophilic reducing species and the presence and formation of paramagnetic material. Despite these issues, a mechanism for the reaction has been proposed based on visual experimental evidence (Scheme **1.18**).[94] Control experiments indicated that SmI_2 does not react with Cp^*_2TiCl or propargyl bromide separately at low temperature. However, when the three species are combined at -78 °C there is an observable colour change from blue to violet, indicating that Cp^*_2TiCl initially reacts with the propargyl bromide to form two Ti(IV) species: $Cp^*_2TiX_2$ and propargyltitanium(IV) complex. Subsequent reduction of both Ti(IV) species with SmI_2 forms the expected Ti(III) propargyl complex and Cp^*_2TiCl, the latter of which reacts further with remaining propargyl bromide. The alkyl radical necessary for alkylation of the propargyl species could be formed by reaction with SmI_2 or through a similar titanium-mediated process as described above, although with the propargyltitanium(III) intermediate. Alternatively, using the modified procedure (*vide infra*) where the alkyl halide is added at the same time as the propargyl bromide, Cp^*_2TiCl could also be the reductant that forms the alkylating organic radical.

Scheme **1.18**



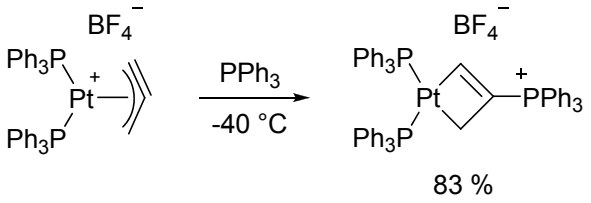
In addition to the pentamethylcyclopentadienyl ligands on titanium, several other ancillary ligand sets have been investigated, at least in a preliminary way. Different Cp analogues have been used (Cp, ^{t}BuCp, Cp*) as well as variously substituted phosphinimide ligands.[29,95,97,99] While titanacyclobutene formation is fairly general, the electronic profile of the ancillary ligands influences the course of the reaction significantly. Electron-rich η^3-propargyltitanium complexes bearing Cp* and phosphinimide ancillary ligands can form stable dimeric titanacyclobutene complexes by coupling of the two central propargyl carbons, sometimes in preference to attack by an organic radical.[94,99] Additionally, uncommon η^1-propargyltitanium complexes have been obtained under the typical conditions with titanium-phosphinimide complexes. The impact of varying the electronic characteristics of the ancillary ligands is still not completely understood.

Prior to the research on propargyltitanium complexes, central carbon addition was reported by Casey and Yi using cationic (η^3-propargyl)rhenium complexes.[100] Following the initial communication, Casey and Chen separately reported similar addition chemistry to cationic rhenium and platinum complexes, respectively. As opposed to the radical processes with titanium, the later period metallacyclobutene complexes were prepared by nucleophilic addition to the central carbon. Thus, addition of soft phosphine nucleophiles to cationic (η^3-propargyl)rhenium complexes, prepared either by hydride abstraction from complexed alkyne with trityl cation or protonation followed by dehydration of complexed propargyl alcohols, results in formation of rhenacyclobutenes (Equation **1.24**).[3,100] Similarly, stable platinacyclobutenes are synthesized upon treatment of a cationic unsubstituted (η^3-propargyl)platinum complex with triphenylphosphine (Equation **1.25**).[2] It was also reported that triphenylphosphine adds to the central carbon of an η^1-allenyliridium complex, resulting in the formation of an iridacyclobutene.[2]



R^1 = H, Me, ^{t}Bu
R^2 = Me, Ph, OMe
X = BF_4, PF_6
Yield: 46 - 100 %

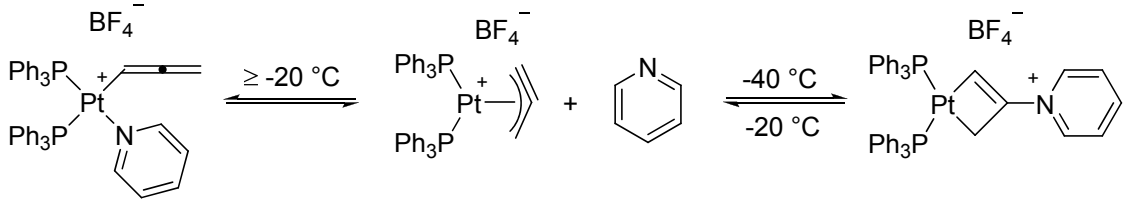
Equation **1.24**



Equation **1.25**

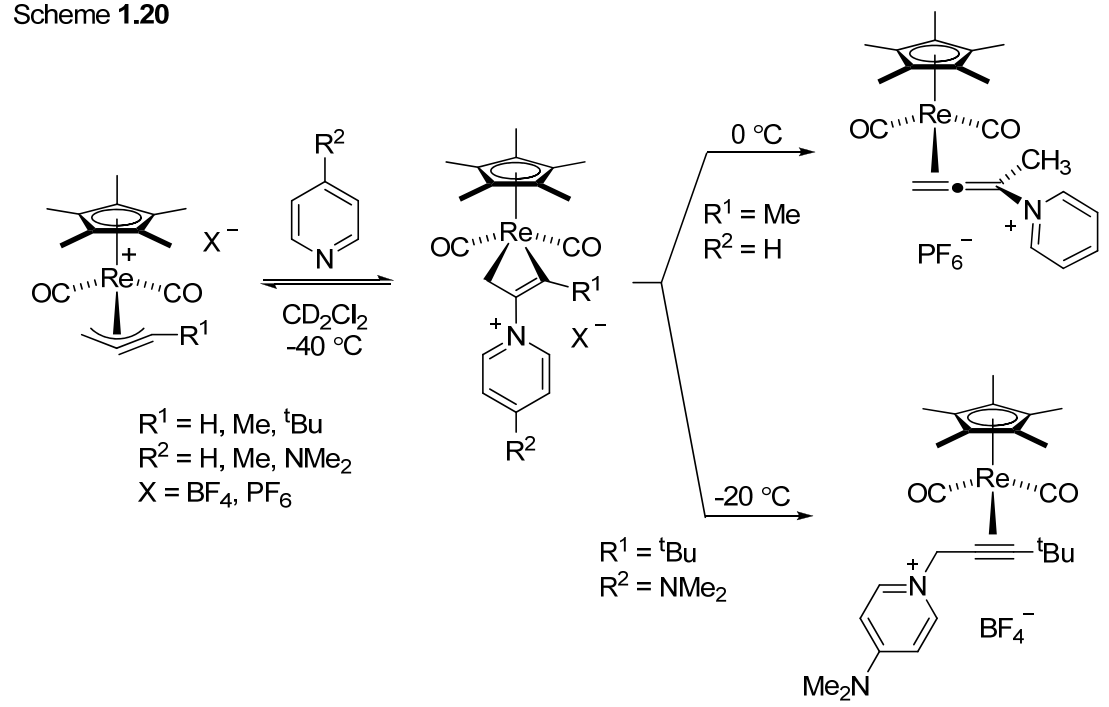
Addition of neutral nitrogen nucleophiles to the same (η^3-propargyl)rhenium and –platinum complexes results in much less stable metallacyclobutene complexes. Triethylamine adds to the central carbon of an unsubstituted (η^3-propargyl)platinum complex but the resulting platinacyclobutene is unstable under vacuum due to removal of the amine. The same complex, when treated with pyridine at -40 °C, forms platinacyclobutene reversibly; upon warming to -20 °C, a new product is formed and free pyridine and the original propargylplatinum complex are observed (Scheme **1.19**). The new thermodynamic product was the only species in solution at 0 °C and was identified as a pyridine-coordinated cationic η^1-allenylplatinum complex. The allenylplatinum complex is also formed reversibly however, as exposure to adventitious water resulted in the formation of multiple products arising from attack at the central carbon.[2]

Scheme **1.19**



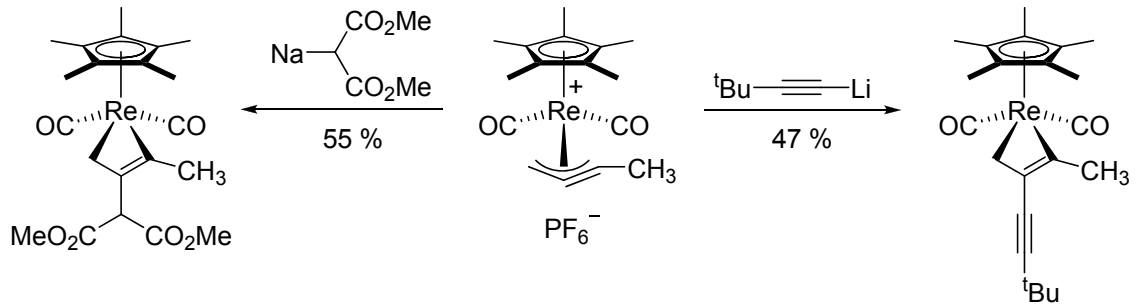
Casey also observed that pyridines add reversibly to the central carbon at -40 °C to form rhenacyclobutenes.[3] In this case, the kinetic product disappears at higher temperatures and addition of the pyridine to one of the terminal carbons occurs, which is not reversible (Scheme **1.20**). Depending upon the size of the propargyl substituent, rhenium complexes bearing coordinated allene or alkyne ligands are produced; a bulky *tert*-butyl group prevents attack at the substituted terminal carbon and the alkyne complex is formed.

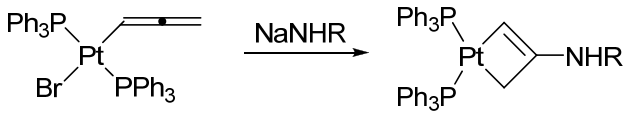
Scheme **1.20**



In addition to neutral nucleophiles, carbanions also attack the central carbon of η^3-propargylrhenium complexes. Two examples have been reported, using malonate and lithium *tert*-butylacetylide to prepare rhenacyclobutenes in moderate yield (Scheme **1.21**).[100] It was noted that after several days in solution, these rhenacyclobutene complexes decomposed to predominantly η^3-allylrhenium complexes by protonation; the corresponding phosphine adducts were thermally more stable.[3] In another example of attack with hard nucleophiles, an η^1-allenylplatinum(II) complex forms platinacyclobutenes upon treatment with sodium amides in reasonable yield, and the product does not equilibrate further (Equation **1.26**).[101]

Scheme **1.21**

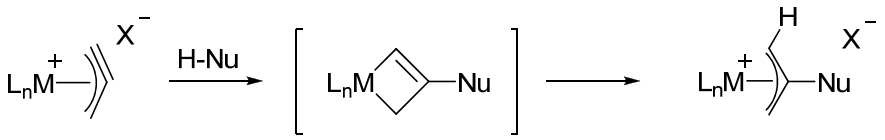




Equation **1.26**

R = SO_2*p*-Tol (72 %)
SO_2Ph (70 %)

Platinum and palladium propargyl complexes have also been shown to react with both strong and weak acids. In these reactions, metallacyclobutenes are formed by nucleophilic attack at the central carbon followed by protonation at the vinyl position to give the observed transition metal allyl complexes (Equation **1.27**).[2,101-108]

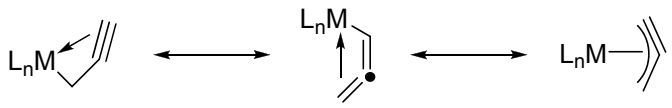


Equation **1.27**

L_nM = $(PPh_3)_2Pt$, $(PPh_3)_2Pd$

Having reviewed some of the chemistry of metal-propargyl complexes, clearly further discussion is required. What factors influence the site of attack and, hence, determine the products obtained? A metal-bound propargyl/allenyl ligand can have three bonding modes: η^1-propargyl, η^1-allenyl, η^3-propargyl/allenyl. As commonly noted in reviews,[109-113] the latter mode may be represented as alkyne- or olefin-coordinated η^1-alkyl species, however it is the combined resonance structure that is typically illustrated (Scheme **1.22**).

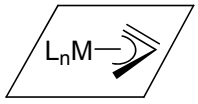
Scheme **1.22**



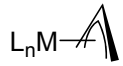
A propargyl ligand is planar, and the metal to which it is coordinated lies in the same plane as the three carbon atoms. The bond angle between the three carbon atoms is typically 146 - 156° (Figure **1.2**).[109,110] Carbon-carbon bond lengths of the propargyl moiety vary, but the C1-C2 distance is between that of a double and triple bond while the

C2-C3 bond length falls between that of a single and double bond. Bond lengths of the propargyl moiety have been used to support the identification of a dominant canonical structure, however, in the absence of solid state data, C-H coupling constants have also been used for the same purpose. Reactions can occur at the central carbon or either of the two terminal carbons, much like that shown in Scheme **1.20**. Therefore, potential products are metallacyclobutenes, allenes, and alkynes.

Figure **1.2**: Structure of metal-propargyl and -allyl complexes



∠ C1-C2-C3: 146 - 156°



∠ C1-C2-C3: ~ 120°

η^3-Propargyl complexes differ markedly from metal-η^3-allyl complexes. For allyl complexes, the angle between the three carbon atoms is approximately 120° and the metal centre is roughly perpendicular to the plane of the allyl moiety, although the central carbon is tilted away from the metal to a varying degree (Figure **1.2**). As with propargyl complexes, reactions can occur at the terminal carbons or the central carbon, forming olefins and metallacyclobutanes, respectively. Controlling stereoselectivity adds an additional level of complexity with allyl chemistry, as nucleophiles can in principle attack either face of the ligand. Stereocontrol is a major concern with allyl chemistry, but it has not prevented the development of significant synthetic applications.[114] Discussing the wealth of allyl chemistry is beyond the scope of this thesis, however some of the theoretical implications are applicable to the observed reactivity of metal-propargyl/allenyl complexes.

In 1978, Davies, Green, and Mingos proposed a set of empirical rules to predict the site of charge-controlled attack on cationic 18-electron complexes.[115] These rules quickly became popularized for their intended predictive purposes as well as for the number of "exceptions" that became known. Despite the limitations, the rules are still significant and are summarized as follows:

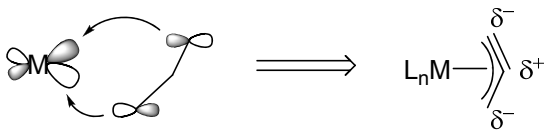
1) Nucleophilic attack occurs preferentially at even-numbered carbon ligands over odd-numbered carbon ligands.

2) Nucleophilic addition to open polyenes is preferred over addition to closed polyene ligands (i.e. cyclic carbon ligands).
3) For even open polyenes, nucleophilic attack occurs at the terminal carbon atom; for odd open polyenes, attack at the terminus occurs only for strongly electron-withdrawing ML_n^+ fragments.

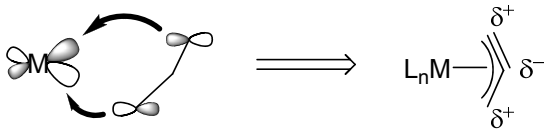
The rules are designed to be applied in hierarchical order. It should be noted that the rules apply only to kinetically-controlled reactions, whereas the thermodynamic products may differ. Thus, because many reactions with propargyl and allyl species (as well as others) are reversible, product composition alone may not indicate whether these rules are indeed accurate.

With respect to how the Davies-Green-Mingos (DGM) rules relate to the regioselectivity of nucleophilic addition to a propargyl ligand, the prediction is attack will occur at the central carbon unless the metal is a strong electron acceptor. The basis behind the prediction is that in a weak electron acceptor, negative charge is centered on the ligand, the HOMO of which has orbitals at the terminal carbons and a node at the central carbon. With a strong electron acceptor metal, the propargyl ligand is somewhat positive and the charge is primarily on the terminal carbons (Figure **1.3**).

Figure **1.3**: Charge distribution for metal-propargyl complexes



Weak electron acceptor ML_n^+



Strong electron acceptor ML_n^+

However, the DGM rules do not predict some reactions, such as why central carbon addition occurs for η^3-propargylrhenium complexes[3,100] and titanocene(IV) allyl cations,[116] (although the latter are not 18-electron complexes). Instead, theoretical studies

indicate that frontier orbital control plays a large role and better rationalizes the observed regioselectivity.

Due to the interest in transition metal-allyl complexes, a number of molecular orbital analyses have been conducted for metallocenes.[41,117,118] In these studies, the molecular orbitals of the metal fragment are combined with the orbitals of the allyl or propargyl fragment based on symmetry characteristics and calculated potential energies to determine the frontier orbitals of the complexes. From this information, it is possible to predict and explain reactivity based on orbital coefficients. Propargyltitanium complexes have not been considered directly, but it is instructive to review the findings for other complexes.

A series of allyl complexes were investigated by EHMO analysis; based on the results obtained, the authors predicted that cationic, pseudo-tetrahedral, d^0 Group IV η^3-allyl complexes might undergo central carbon addition.[118] This turned out to be accurate, as demonstrated by the Stryker group for cationic zirconocene[119,120] and titanocene[120] allyl complexes, although products from attack at the metal centre were obtained for some nucleophiles.

An MO diagram of a d^2 bent metallocene allyl complex is shown in Figure **1.4.**[41,118] (Note: An effort was made to maintain the relative position of the energy levels calculated by Curtis and Eisenstein.[118] Symmetry labels do not account for the lower energy molecular orbitals not shown, so the labels differ from those of Green and co-workers.[41] Frontier orbitals of Cp_2Mo^+ are drawn in perspective, and illustrate the computer-generated orbital isosurfaces provided by Green.) The LUMO is made up of the anti-bonding orbital of the allyl ligand and the $3a_1$ orbital of the metal fragment (similar to a d_{yz} orbital), which is pointed towards the wedge of the allyl. Incoming nucleophiles would then be directed towards the central carbon, which has the largest orbital coefficient on the allyl fragment. Close in energy is an MO made from the non-bonding allyl orbital and the $1a_2$ metal fragment orbital (corresponding to a d_{xz} orbital), which would direct nucleophiles to the terminal carbons.

The MO diagram of a d^0 bent metallocene allyl complex should be similar, albeit with two less electrons (Figure **1.5**).[118] In this case, what was formerly the HOMO becomes the LUMO, a bonding orbital made from a combination of the anti-bonding

orbital from the allyl ligand and the $1a_1$ orbital on the metal. This LUMO is largely metal in character. An incoming nucleophile would be expected to attack the metal unless it is sterically hindered, in which case it would be directed to the central carbon of the allyl moiety.

Figure **1.4**: EHMO energy level diagram for $Cp_2Mo(C_3H_5)^+$

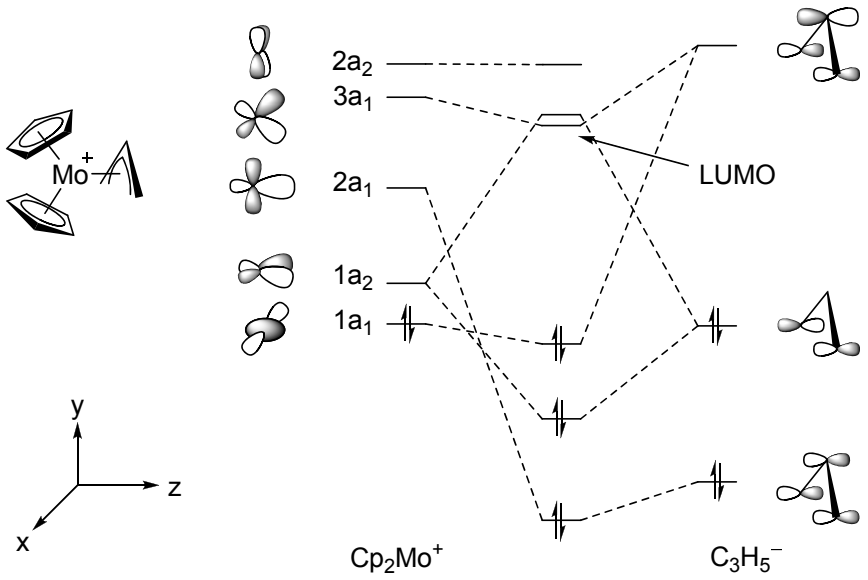
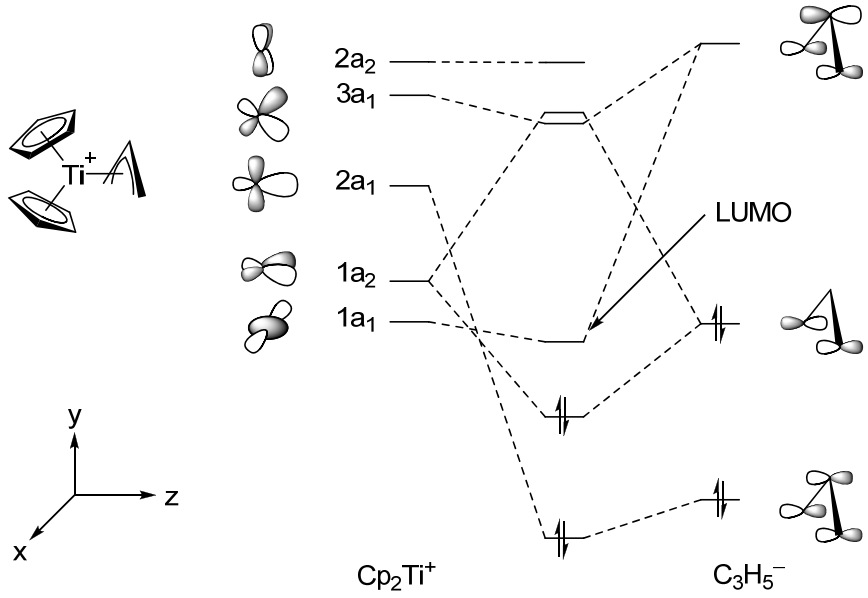
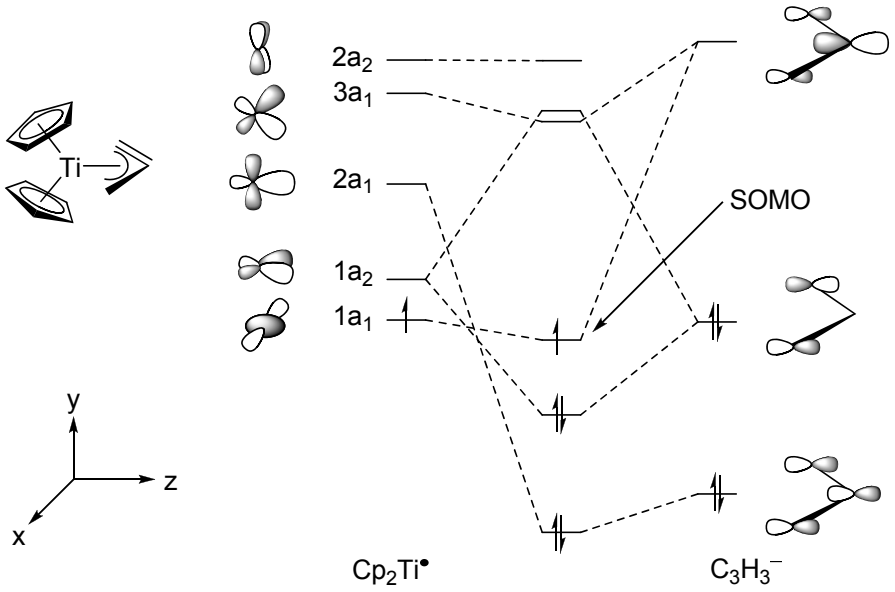


Figure **1.5**: EHMO energy level diagram for $Cp_2Ti(C_3H_5)^+$



What follows is speculation, as no computational MO analysis of a titanocene(III) propargyl complex has been completed. However, assuming that no major perturbations occur in changing to a d^1 propargyl complex, it is possible to compile a reasonable MO picture (Figure **1.6**). This assumption relies on the orthogonal π-bond between C1 and C2 not influencing the orbital picture significantly (and consequently is not shown). The singly-occupied molecular orbital (SOMO) is a combination of the in-plane anti-bonding orbital of the propargyl moiety and the $1a_1$ orbital from the metal again, and is mostly metallic in character. Thus, an incoming radical would attack the metal centre unless sterically inhibited, in which case it would be directed to the central carbon of the propargyl fragment. In comparison to the η^3-allyltitanium complex, an argument could be made that the η^3-propargyltitanium complex has more orbital overlap due to the co-planar relationship of the four atoms in question. Despite the crudeness of the analysis, it provides a rationale for why central carbon alkylation of titanium(III) propargyl complexes is generally observed.

Figure **1.6**: EHMO energy level diagram for $Cp_2Ti(C_3H_3)$



The reactivity of propargyltitanium complexes has not been studied by MO analysis, but it has been investigated for cationic η^3-propargylplatinum and η^3-allylplatinum complexes bearing two model PH_3 ligands using Fenske-Hall and DFT

calculations.[121] In previous experiments, η^3-propargylplatinum complexes reacted with nucleophiles such as PMe_3, Br^-, and CO at the metal centre, forming η^1-propargyl and η^1-allenyl complexes. However, nucleophiles with a transferable proton formed η^3-allyl complexes by initial attack at the central carbon.[102,122] Allylplatinum complexes themselves typically undergo nucleophilic attack at one of the terminal carbons.[114] The molecular orbital analysis determined that the π orbitals between C1 and C2 that are orthogonal to the plane of the three carbon atoms do not interact significantly with the metal. This is true whether the complex is in isolation or undergoing nucleophilic attack, so it appears that making the above assumption for the η^3-propargyltitanium MO analysis is not unreasonable.

The MO description of the allyl and propargyl complexes of platinum were compared to determine the origin of the differences in regioselectivity, and two factors were noted. There is greater charge separation between the terminal and central carbon atoms in the propargyl fragment than in the allyl fragment, meaning the central carbon atom is more positive in the former complexes. This increases the likelihood of charge-controlled attack of η^3-propargylplatinum complexes. It was also found that the propargyl complex has an acceptor orbital predominantly on the organic ligand with a large orbital coefficient for the central carbon that is of low enough energy to be attacked and that produces only minor structural changes (this orbital is the SLUMO in the optimized η^3-propargylplatinum complex, however it becomes the LUMO once the propargyl ligand bends from 152° to 120° upon nucleophilic attack at the central carbon). The allyl species does not have such an orbital and requires greater, albeit still minor, changes in geometry to form a platinacyclobutane. The authors propose that nucleophilic attack at the central carbon of η^3-propargylplatinum complexes is initially a charge-controlled process that, as the complex transitions to a platinacyclobutene, becomes an orbital-controlled interaction.

As predicted by the DGM rules, the site of attack may be influenced by the electronic nature of the metal fragment. *Ab initio* calculations at the Hartree-Fock, MP2, and MP4 level have been conducted on an unsubstituted η^3-allylpalladium complex bearing either two PH_3 or two NH_3 ligands (i.e. η^3-$(H_2CC(H)CH_2)PdL_2$; L = PH_3, NH_3).[123,124] The authors found that the energies of the two lowest lying unoccupied

molecular orbitals are very similar and dependent upon the ancillary ligands. The LUMO of the complex bearing π-acceptor PH_3 ligands is made from a contribution from ψ^2 of the allyl moiety, which has a node at C2. Conversely, the LUMO of the complex with σ-donor NH_3 ligands was made from ψ^3 of the allyl moiety, which has the largest orbital coefficient at the central carbon. These calculations were used to explain the experimentally observed preference for attack at the terminal carbon for complexes with phosphine ligands and attack at the central carbon for nitrogen ligands. It may also be that the difference in reactivity is the result of a change from a charge-controlled process to an orbital-controlled reaction.

A number of methods for the preparation of titanacyclobutene complexes have thus been developed. The most common route involves the reaction of titanium alkylidene reagents with alkynes. Ten years ago, central carbon alkylation was introduced as a regioselective synthetic route and, consequently, a greater range of titanacyclobutenes are now accessible. Although limited, titanacyclobutene complexes have also been prepared by γ-hydride elimination and nucleophilic addition of 1,3-dianionic species.

Titanacyclobutene complexes display a range of reactivity and a range of organic products have been liberated following functionalization. Insertion of reactive small molecules and decomplexation has produced homoallylic alcohols, dienes, pyridines, hydroxylamines and more. Transmetallation of titanacyclobutene complexes has been used in the preparation of main group heterocycles, including phosphorous, arsenic, and stibene analogues. With additional research, the utility of titanacyclobutene complexes should expand beyond this current scope.

This report will detail our investigation of the synthesis of boracyclobutenes by transmetallation from titanacyclobutene complexes. The development of this process provides a new route for the preparation of an interesting class of boracycle that is currently difficult to access. This reaction also enhances our ability to functionalize the organic fragment since it will be part of a new borane complex with different electronic and steric features than the original titanacylobutene complexes.

The following two sections will detail the known chemistry of boracyclobutenes, and introduce chemistry relevant to the intended transmetallation of titanacyclobutene complexes.

1.3 Boracyclobutenes (Boretes)

The boracyclobutene structural motif is not common, and only a few synthetic approaches, none general, have been developed thus far. This is due in part to the high reactivity of the target molecules as well as the limited number of ways to prepare four-membered rings. The two approaches reported in the literature parallel two methods discussed previously for the synthesis of titanacyclobutene rings: 1,3-nucleophilic alkylation of haloboranes and [2 + 2] cycloaddition of boraalkenes (methylene boranes) with alkynes. In this dissertation, new results from the transmetallation of titanacyclobutene complexes will be presented as a potentially more general and convenient route to the synthesis of boracyclobutenes.

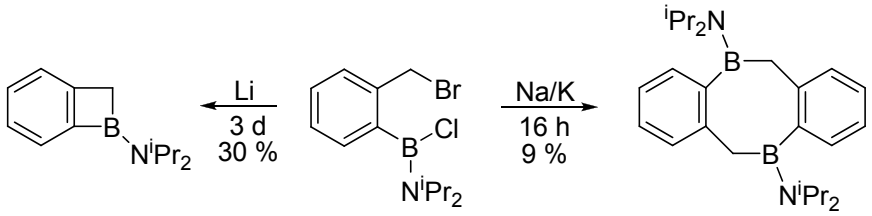
Thus far, the reported reactivity of boracyclobutenes is strongly dependent upon the structure of the rest of the organic fragment, and therefore the initial synthetic approach. For convenience, the known preparation and reactivity of boracyclobutenes will be combined. One note regarding the nomenclature used: IUPAC naming for the B[-C=C-C-] ring is borete, and it will be used interchangeably with boracyclobutene.

The first area covered is the 1,3-nucleophilic alkylation of haloboranes. Benzoboracyclobutene rings have been prepared by reduction of [(2-bromomethyl)phenyl]chloroborane with lithium (Scheme **1.23**).[125] The starting material was obtained through a multi-step synthesis from *o*-dichlorotolylborane,[125] which is easily synthesized from *o*-bromotoluene.[126] Interestingly, the authors found that cyclization only occurred for the diisopropylamino-substituted chloroborane, and not for methyl- or butyl-substituted chloroboranes. When Na/K alloy was used for the cyclization, only the dimeric 8-membered ring product was isolated, in very low yield (Scheme **1.23**).

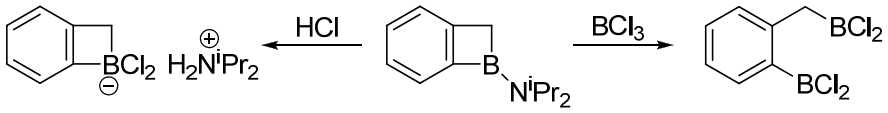
The aminoboracyclobutabenzene product was subsequently treated with two electrophiles: HCl gas and BCl_3 (Scheme **1.24**). Upon treatment with HCl, a

dichloroborate salt was obtained bearing a diisopropylammonium counterion. A ring-opened bis(dichloroborane) was recovered following the reaction with BCl_3.[125]

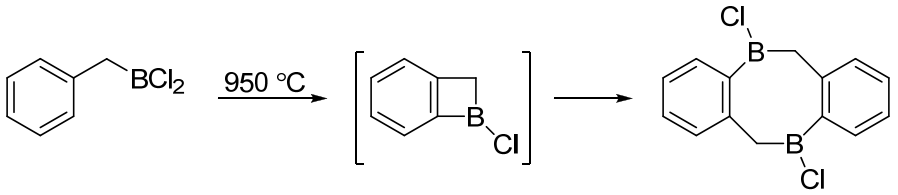
Scheme **1.23**



Scheme **1.24**



At 950 °C, dichlorobenzylborane forms a tetrahydrodibenzo-1,5-diborocine product (Equation **1.28**). The presumed intermediate borete could not be isolated at that temperature.[126]

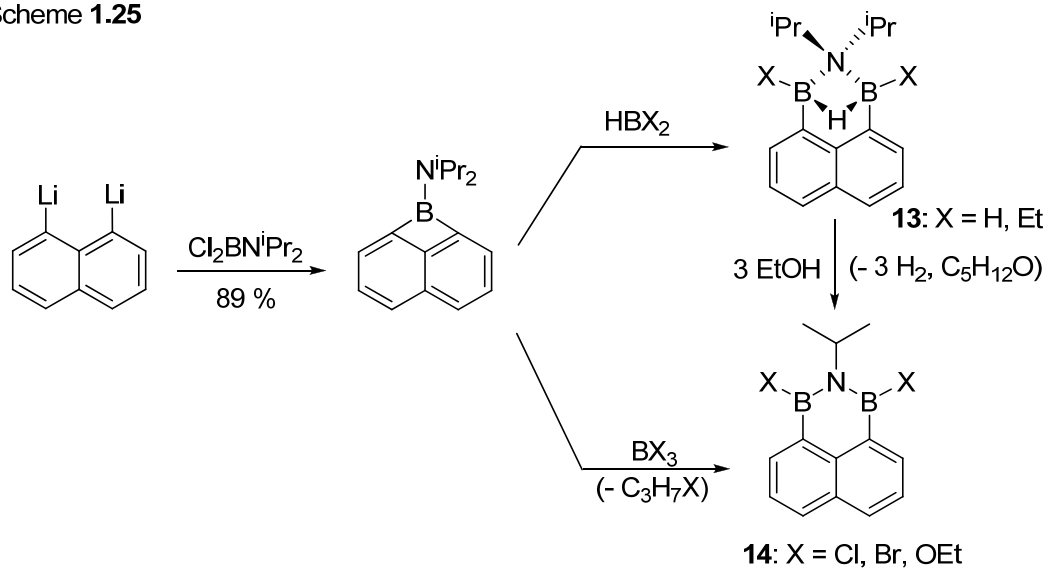


Equation **1.28**

The boracyclobutene moiety has also been incorporated in 1,8-peribridged naphthalenes, which have been used to make bimetallic disubstituted naphthalene derivatives. The first such boracyclobutene synthesis was achieved in 89 % yield by nucleophilic attack of 1,8-dilithionaphthalide on $Cl_2BN^iPr_2$ (Scheme **1.25**).[127] The rigidity of the naphthalene framework imposes additional strain on the boracyclobutene ring, which has three internal bond angles between 85 – 87°. A recent computational study calculated a ring strain of 178.9 kJ/mol for the unsubstituted naphtho[1,8-*bc*]borete.[128] The annulated boracyclobutene reacts with boron trichloride and boron tribromide to form naphtho[1,8-*cd*]azadiborinin **14** products directly.[127] In reactions with

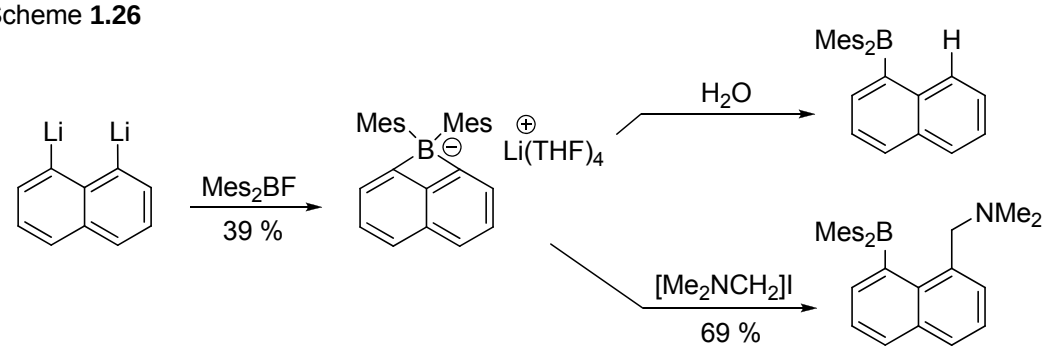
borane and diethylborane, an intermediate hydride-bridged product **13** can be isolated; the intermediacy is demonstrated by reacting the trihydride with three equivalents of ethanol to form the ethoxy-substituted naptho[1,8-*cd*]azadiborinin (Scheme **1.25**).

Scheme **1.25**



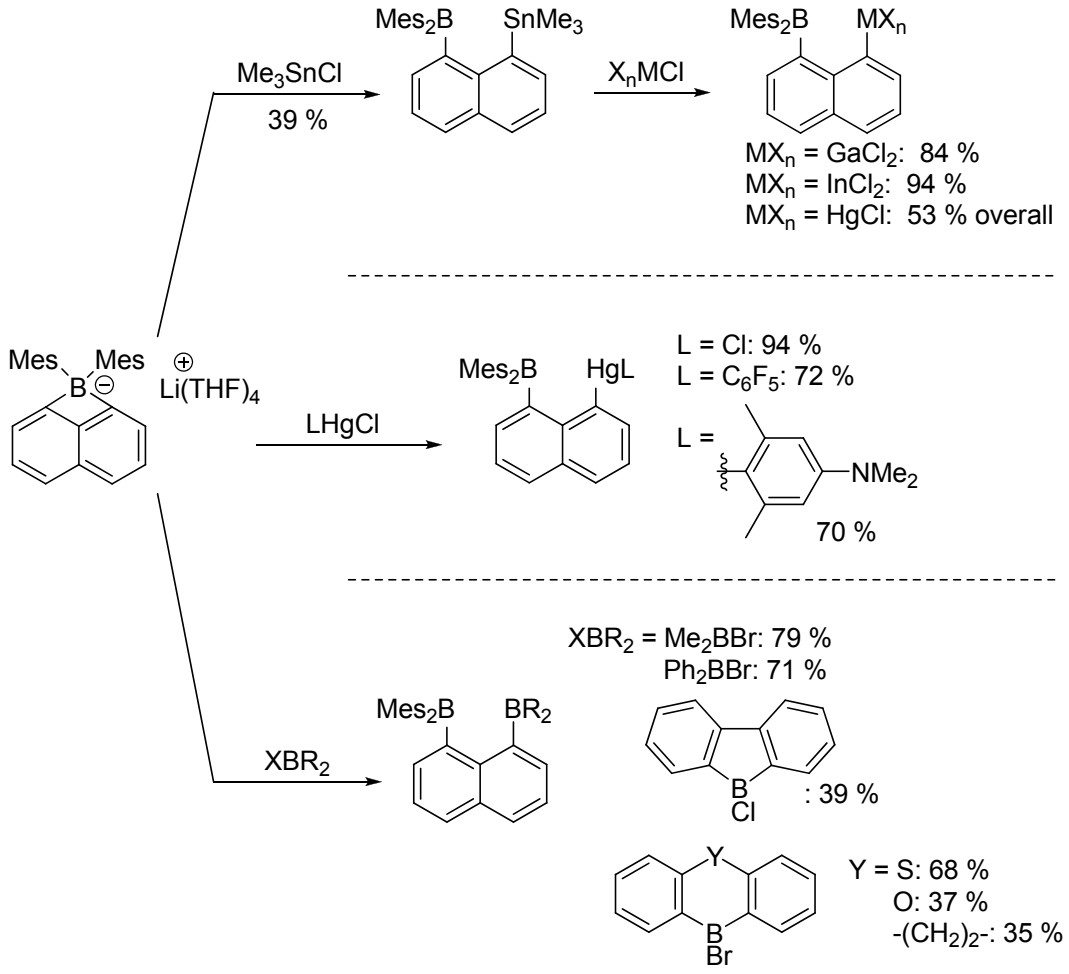
More recently, Gabbaï has used this approach to form anionic boracyclobutene rings by addition of 1,8-dilithionaphthalide to fluorodimesitylborane (Scheme **1.26**).[129] The product is formed in 39 % yield and crystallizes as the THF-solvated lithium salt. As with the other annulated boracyclobutenes, electrophiles react to give ring-opened products: hydrolysis occurs in water,[130] and in the presence of $[Me_2NCH_2]I$, alkylation occurs at the 8-position.[131]

Scheme **1.26**



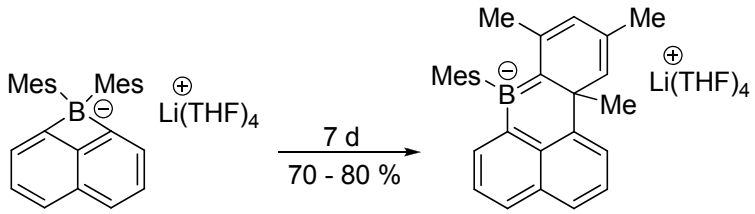
Furthermore, a series of 1,8-bimetallic naphthalene-derivatives were prepared by electrophilic ring opening with mercury,[132-134] boron,[129,130,135,136] and tin[137] halides in yields varying from moderate to excellent (Scheme **1.27**). Substitution at the C-Sn bond was accomplished from the mixed B/Sn species with $GaCl_3$ and $InCl_3$, which formed new bimetallic species. All of these bimetallic naphthalene derivatives have been investigated for fluoride-capture applications, with particular interest in complexation in aqueous solutions. Group XIII-substituted naphthalene derivatives were reviewed in 2002,[138] prior to much of this recent work.[139]

Scheme **1.27**



In addition to electrophilic ring-opening, the anionic naphtho[1,8-*bc*]borete slowly decomposes over 7 days at room temperature to give an anionic tetracyclic

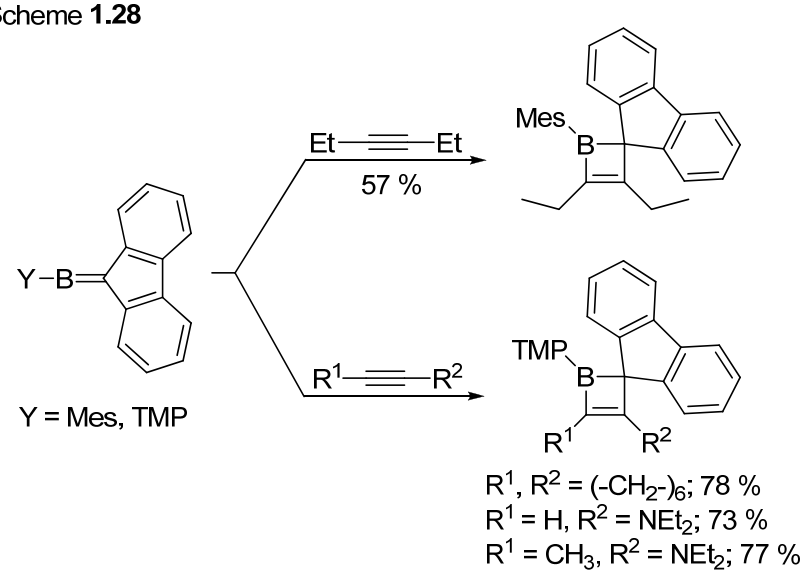
boraalkene (Equation **1.29**). This ring expansion occurs via an apparent 1,3-aryl shift, presumably driven by release of ring strain.[130]



Equation **1.29**

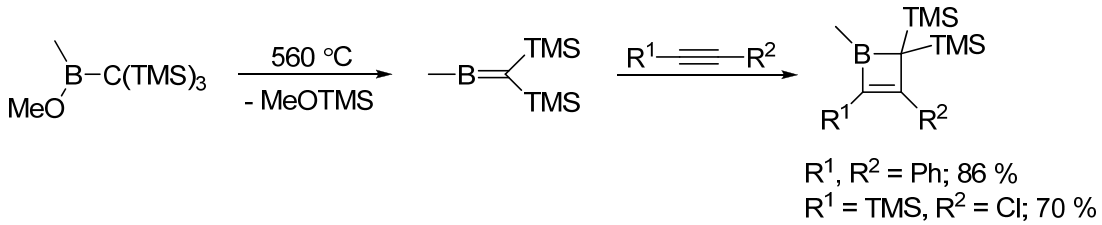
The only other method that has been used for synthesis of boracyclobutenes is [2 + 2] cycloaddition of boraalkenes and alkynes. Boraalkenes are a highly reactive class of compounds, usually formed by elimination of a volatile fragment at elevated temperatures. Due to the high reactivity, bulky substituents and/or electron-donating groups on boron are usually necessary. *C*-Fluorenyl-*B*-mesitylmethyleneborane reacts with 3-hexyne to form a boracyclobutene in good yield (Scheme **1.28**, Y = Mes).[140] Similarly, a boracyclobutene is obtained when a boraalkene bearing a nitrogen-donor substituent on boron is treated with alkynes (Scheme **1.28**, Y = TMP). For this substrate, electronically biased alkynes (i.e. N,N-diethylaminoacetylene) and symmetric alkynes provided pure material, whereas phenylacetylene formed an inseparable regioisomeric mixture of boracyclobutenes.[141]

Scheme **1.28**



An unstabilized boraalkene, synthesized from a tris(trimethylsilyl)borinic ester by elimination of CH_3OTMS at 560 °C,[142] reacted with alkynes efficiently (Scheme **1.29**).[143] No further transformations were reported. Two similar boracyclobutenes have also been prepared.[144]

Scheme **1.29**



R^1, R^2 = Ph; 86 %
R^1 = TMS, R^2 = Cl; 70 %

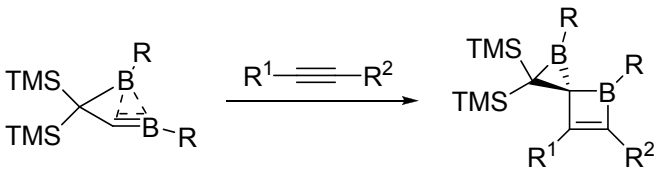
Interestingly, the only reaction between a boraalkene and an olefin reported is with the highly electron rich 1,1-bis(ethoxy)ethylene.[145] A boracyclobutane was also formed when a boraalkene was treated with two equivalents of *tert*-butylisonitrile.[146]

Diboramethylenecyclopropanes, prepared by reduction of sterically hindered *gem*-bis(chloroborane)-*gem*-bis(trimethylsilyl)ethylenes with Na/K alloy,[147] can be considered in both classical and non-classical forms (Figure **1.7**).[148] The non-classical depiction accounts for stabilization of the nominally two-coordinate boron atom by decreasing the electron deficiency through a three-centre two-electron bond with the neighbouring B-C σ-bond. An X-ray crystal structure was obtained and provided a distance of 1.84 Å between the boron atoms, which is long for a single bond but within reason for a bonding interaction.[149] Additional stability for the boraalkene is provided by sterically-isolating substituents on boron.

Figure **1.7**: Bonding in spirocyclic diboraalkenes

In chemistry studied by Berndt *et al*, these boraalkenes react with alkynes at low temperatures to form spirobicyclic boracyclobutenes (Equation **1.30**). Cycloaddition is

regioselective using unsymmetric alkynes, provided there is sufficient steric or electronic bias between the substituents.[147,150-155]



Equation **1.30**

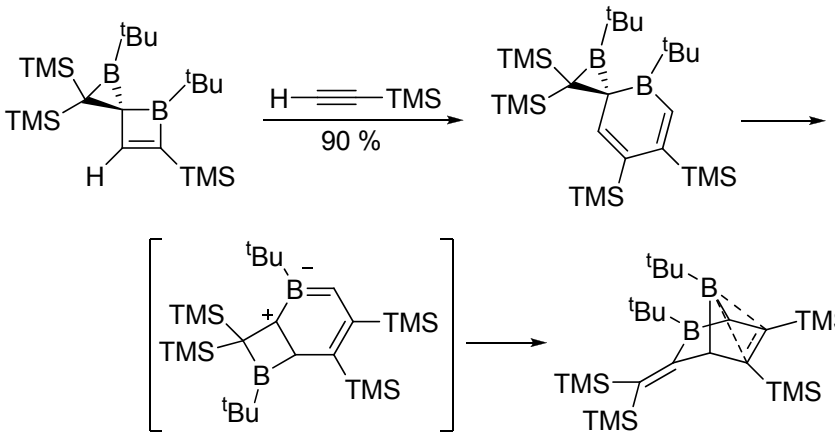
R	R^1	R^2	Temp
^{t}Bu	Ph	Ph	-30 °C
^{t}Bu	Me	Me	-50 °C
^{t}Bu	H	^{t}Bu	-50 °C
Dur	H	TMS	-30 °C
Dur	$SnMe_3$	3,5-(^{t}Bu)$_2$Ph	-20 °C
^{t}Bu	H	TMS	-
Dur	Et	Et	-30 °C
Dur	Me	Me	-30 °C

Dur = 2,3,5,6-tetramethylphenyl

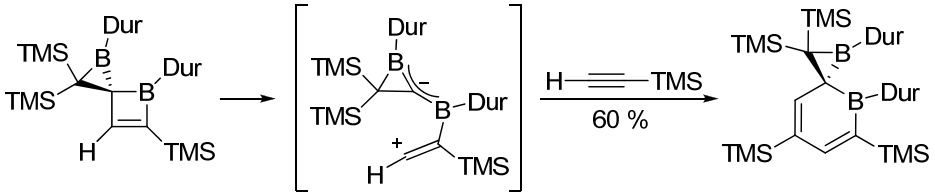
The spiro-diboracyclobutenes were characterized at low temperature to minimize spectral line broadening due to the quadrapolar boron nucleus, and to prevent additional reactions. The reported reactivity involves insertions or rearrangements that relieve ring strain. Insertion into the vinylic B-C bond was observed in the presence of additional (trimethylsilyl)acetylene; the boracyclohexadiene formed then isomerizes to a bridged diborane that is a neutral analogue of a non-classical carbocation (Equation **1.31**).[153] Conversely, with 2,3,5,6-tetramethylphenyl (Dur) substitutuents on boron instead of *tert*-butyl, insertion occurs into the vinylic C-C bond and the resultant boracyclohexadiene was isolated (Equation **1.32**).[151] The initial spiro-diboracyclobutene exhibits fluxional behaviour during variable temperature NMR experiments; the authors account for this by proposing the formation of the ring-opened zwitterionic intermediate pictured (Equation **1.32**), which freely rotates about the vinylic B-C bond. This accounts for the change in regioselectivity.[151]

Other spiro-diboracyclobutenes isomerize upon warming to room temperature. At 10 °C, a diborabicyclo[1,1,1]pentane was characterized; further isomerization to a boron-substituted *gem*-(trimethylsilyl)allene occurs at 25 °C (Equation **1.33**).[154,155] A stannylated analogue also isomerizes to an allene, albeit at lower temperature, and then

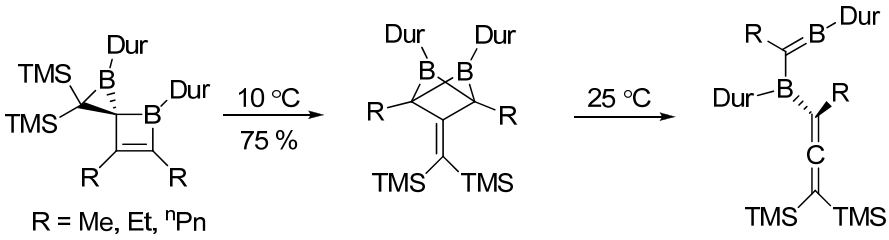
rearranges further at room temperature to an allenyl-1,3-diboracyclobutane (Equation **1.34**).[152]



Equation **1.31**

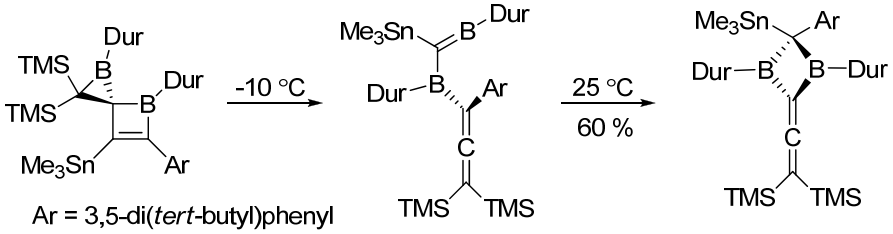


Equation **1.32**



R = Me, Et, ^{n}Pn

Equation **1.33**



Ar = 3,5-di(*tert*-butyl)phenyl

Equation **1.34**

Thus far, the chemistry of boracyclobutenes is relatively unexplored, in part due to the limited number of compounds synthesized. Naphtho[1,8]boretes, prepared from 1,8-dilithionaphthalide, have been studied largely as a means for accessing 1,8-bimetallic or –metalloid naphthalene derivatives. As expected, reactions with electrophiles occur at a B-C bond and the naphthalene system is unchanged. The spiro-diboracyclobutenes derived from Berndt's methodology undergo rearrangements and insertions to relieve ring strain. However, it is difficult to determine what reactivity is characteristic of "simple" boracyclobutenes and what reactivity is a function of the unique character of the spirocycles. The other boracyclobutenes prepared by [2 + 2] cycloaddition required bulky substituents to stabilize the initial boraalkene, and further reactivity was not investigated. Hence, due to the nature of the synthetic protocols, it has not yet been possible to investigate a boracyclobutene moiety free of a strong influence from the rest of the molecule. Clearly, a new synthetic approach to boracyclobutenes must be developed to further explore the potential reactivity of this interesting class of molecule.

1.4 Transmetallation

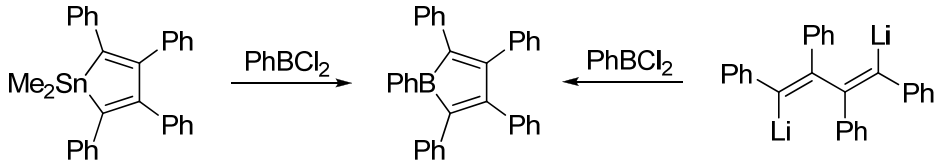
Alkyl- and arylboranes are typically prepared by nucleophilic alkylation of haloboranes with lithium or Grignard reagents; these may also be considered as transmetallation reactions, because the broad definition is the transfer of an organic moiety from one metallic species to another. This alkylative method, while broadly applicable, is limited by the functional group tolerance of the reagents. Additionally, products arising from more than a single alkylation are easily encountered. However, it remains the most common preparation method and has also been used for synthesizing cyclic boranes.

Highly-substituted boroles have also been prepared through transmetallation from tin and lithium complexes. Pentaphenylborole was first prepared by the reaction of 1,4-dilithiotetraphenylbutadienide with dichorophenylborane (Scheme **1.30**) and several other metallacyclopentadienes have been prepared in the same manner.[156] The borole has also been synthesized by transmetallation from the analogous stannole using dichlorophenylborane (Scheme **1.30**).[157-159] The authors note that the boroles studied

easily undergo protodeboronation with a wide range of acidic, neutral, and even basic reagents but that cleavage of both B-C bonds to make the tetrasubstituted diene is a low yielding process.[158] Other tin-to-boron transmetallations of cyclic stannanes are also known.[160-166]

Transmetallation of Group IV metallacycles was discussed in Section 1.1. Titanacyclobutene complexes react with some main group (P, As, Sb) dihalides to form the corresponding four-membered heterocycles (refer to Scheme **1.10**). Additionally, zirconacyclopentadienes, zirconacyclopentenes, and zirconacyclopentanes react with a large number of electrophilic main group reagents with two or more halides, including dichlorophenylborane (refer to Equation **1.16**). Thus, successful transmetallation of titanacyclobutene complexes to boron should not be unexpected.

Scheme **1.30**



Because transmetallation is a major component of the new research to be presented, some further background will be provided. Transmetallation is in theory an equilibrium process, making it possible to design catalytic cycles where transmetallation is not favoured, provided the subsequent steps are relatively favourable. However, many transmetallation reactions occur irreversibly; one such example is in the reaction between titanocene dichloride and two equivalents of methyllithium, where dimethyltitanocene and lithium chloride is formed but the reverse reaction is not known. Two rationales have been used for this observation: using a kinetic argument, the nucleophilicity of the newly formed species is lower than that of the starting material. That is, referring to the example, dimethyltitanocene is not sufficiently nucleophilic to alkylate LiCl. Another explanation involves comparing the stability of the two new bonds formed to those present in the reactants. Thus, transmetallation is thermodynamically favoured when the carbon ligand is transferred to a more electronegative metal and a halogen or hard anion is moved to the less electronegative metal. This applies to transition metals as well as

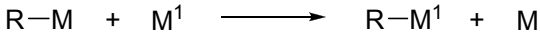
main group elements, although it should be noted that it does not necessarily correlate to the relative stabilities of the M-C and M-X bonds in the reactants and products.[167]

While it would be desirable to make general statements about the direction of organic ligand transfer based on the relative position in the periodic table of the two metallic elements in question, it is often dependent upon the electronic environment of both metallic species. For instance, in the palladium-catalyzed Suzuki-Miyaura cross-coupling of organoboron compounds with organic halides and triflates, an organic group is transferred from boron to palladium.[168,169] However, in the palladium-catalyzed Miyaura boration of aromatic halides with tetraalkoxydiboron compounds, the organic ligand is transferred from palladium to boron.[170,171]

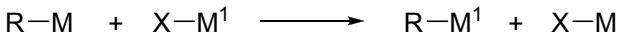
There are four standard ways to prepare organometallic compounds, and two of them involve transmetallation: redox-type exchange (Figure **1.8**, reaction *a*) and metal-exchange (Figure **1.8**, reaction *b*) [the other two methods are redox dehalogenation (Figure **1.8**, reaction *c*) and halogen- or hydrogen-exchange (Figure **1.8**, reaction *d*)].[172]

Figure **1.8**: Preparation of organometallic complexes

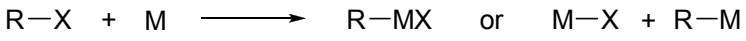
a) Redox transmetallation



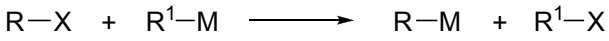
b) Metal exchange



c) Redox dehalogenation



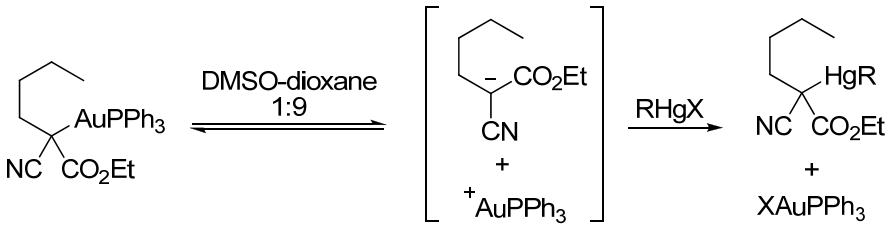
d) Metal-halogen and metal-hydrogen exchange



Transmetallation is typically milder than other preparative methods, particularly the dehalogenation of organic compounds, which is the common route for making lithium and magnesium organometallics. The metal exchange reaction often goes completely to two separate metallic complexes by the complementary swapping of ligands. Conversely, it may also result in the formation of an "ate" complex by transfer of a

hydrocarbyl group from one metal to another without returning a ligand to the first metal [i.e. the charge of both complexes changes ± 1 but not the oxidation states, for example, in this preparation of organocuprates: RLi + Cu(CN) → RCu(CN)Li].

Transmetallation, despite being of fundamental importance in numerous stoichiometric and catalytic processes, is not well-defined mechanistically. This is due in part to the requisite intermediates containing two metallic species, which are nearly always short-lived. That said, a number of mechanisms have been established for various specific systems. Transmetallation is most frequently an associative process as dissociation of hydrocarbyl ligands is unfavourable.[167] However, an S_E1 mechanism has been proposed in the transmetallation of a gold complex to mercury (Equation **1.35**).[173] This proposal is based on the first-order kinetics in gold complex and zero-order kinetics in alkyl mercuric salt observed when the reaction is carried out in a 1 : 9 mixture of DMSO-dioxane. Additionally, the rate constant remains unchanged when the composition of the mercury salt is varied. If the reaction is carried out in dioxane however, it is first-order in both gold and mercury complexes and an S_E2 mechanism was therefore proposed. Several other reactions have been proposed to go through an S_E1 mechanism, though typically in complexes where the carbanion is stabilized by electron withdrawing substituents and not often for Group III-X transition metals.[174]

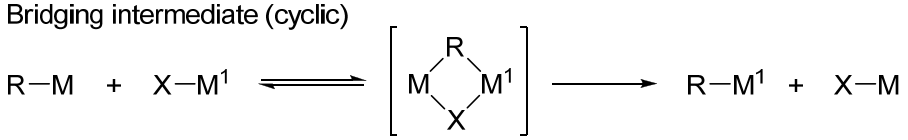


Equation **1.35**

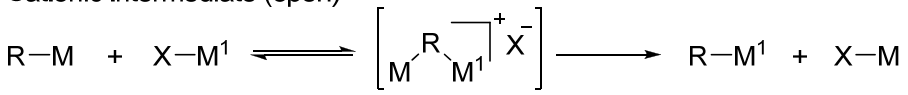
Two associative substitution mechanisms have been proposed, S_E2(open) and S_E2(cyclic) (Figure **1.9**), though most transmetallations likely have some contribution from both.[175,176] Reactions that follow any type of S_E2 mechanism proceed more slowly with large organic groups, due to unfavourable steric interactions between the carbon ligand and the incoming metal.

Figure **1.9**: S_E2 transition states

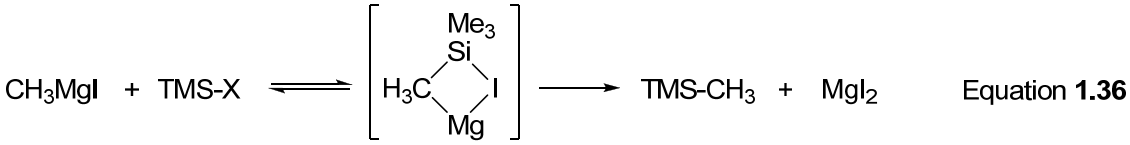
a) Bridging intermediate (cyclic)



b) Cationic intermediate (open)



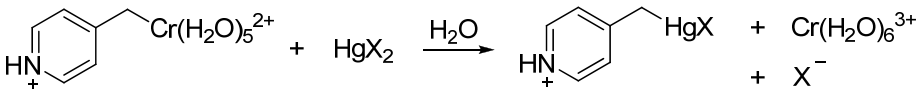
For S_E2 reactions proceeding by cyclic transition states, second-order kinetics are observed, first-order in both RM and M^1X. No kinetic electrolyte effect on the transition state is expected as there is little separation of charge, although an electrolyte effect may be observed if it influences the relative stability of the reactants. A characteristic feature is rate dependence on the halide or anionic ligand that is exchanged, with softer, better-bridging halides reacting faster than harder anions. This was noted, inter alia, during the methylation of halosilanes with Grignard reagents, with the reactivity sequence of trimethylsilicon halides proceeding in the order X = I > Br > Cl > F (Equation **1.36**).[177] Conversely, the opposite order of reactivity is expected from an open transition state because the more electronegative silanes should react faster. Of importance for enantioselective cross-couplings, transmetallations proceeding through an S_E2(closed) transition state demonstrate retention of configuration.



Equation **1.36**

In bimetallic electrophilic substitution reactions proceeding by an open transition state, termed S_E2(open), an alkyl or aryl ligand forms a bridge between the two metal centres. This substitution reaction also displays second order kinetics, first order in both the organometallic and the metal salt. Positive kinetic electrolyte effects are observed, as there is more charge separation in the transition state. Additionally, an S_E2(open) mechanism is clearly in effect when the isolated metal salt following transmetallation

bears different ligands than the initial metal salt (i.e. the "X" ligand is not transferred from M^1 to M). This is observed for the transmetallation of a chromium alkyl species to mercury conducted in water, where the majority of product is the hexaaquachromium salt and not the halogenated pentaaquachromium salt; the species are not interconvertable under the conditions studied (Equation **1.37**).[178] Open transition states lead to inversion of configuration at the carbon centre that is transferred.



Equation **1.37**

One of the most studied transmetallation reactions is between a hydrocarbyl palladium halide and an alkyl stannane, an important step in the Stille (or Migita-Kosugi-Stille) reaction.[179-181] This has been shown to proceed through both closed and open S_E2 mechanisms, with the outcome dependent upon the reaction conditions, particularly the nature of the anion and solvent (Scheme **1.31**). When an alkyl halide and relatively non-coordinating solvent such as chloroform, THT, or NMP are used, the reaction proceeds through a cyclic transition state and retention of stereochemistry is observed. Conversely, for an alkyl halide in HMPA or an alkyl triflate in NMP or HMPA, the reaction proceeds through an open transition state and the stereochemistry is inverted. In the latter reaction, with a poorly bridging ligand and/or a strongly coordinating solvent, the palladium species in solution is actually an ionic salt (i.e. $[PdRL_3]^+X^-$) and bridging is not possible.

Of course, the S_E2(closed) and S_E2(open) mechanisms are two extremes of bimolecular mechanisms and many reactions likely fall between the two, with varying degrees of internal coordination or charge separation. A mechanism has been proposed in which the metals bridge through a hard anionic ligand and not the carbon ligand, the so-called S_E2(co-ord) mechanism (Figure **1.10**).[182] In this substitution, the M^1X salt forms a bimetallic complex by bridging through the hard "X" anion, and the hydrocarbyl ligand is transferred through a 1,3-shift. This reaction may also be viewed as an insertion process.

Scheme **1.31**

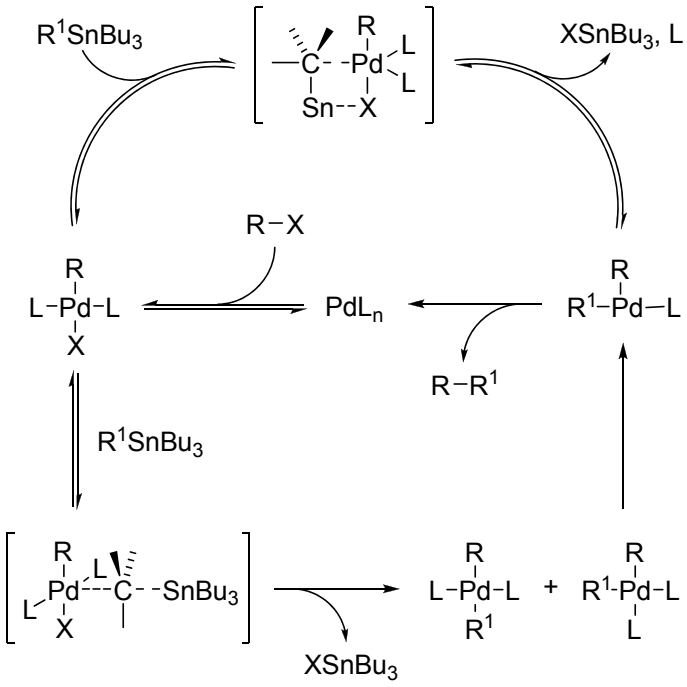
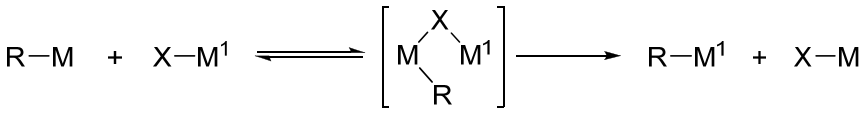
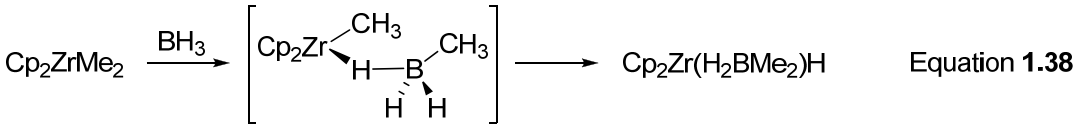


Figure **1.10**: Coordinated transition state



Just such an insertion mechanism is proposed for the methyl-transfer reaction between dimethylzirconocene and borane (Equation **1.38**).[61] Fractions from the titration of dimethylzirconocene with borane provided evidence of intermediates containing $[BH_3Me]^-$ and $[BH_2Me_2]^-$ by ^{11}B NMR spectroscopy. Upon addition of excess BH_3, $Cp_2Zr(BH_4)_2$ is formed and free alkylboranes are detected in solution; the majority of this material is dimethylborane, not methylborane, supporting the contention that a bridged Zr/B intermediate is formed and the reaction proceeds via an insertion mechanism.



Equation **1.38**

The synthetic utility of transmetallation is quite evident in both stoichiometric and catalytic processes. The process has much wider synthetic applicability than covered here, although the main applications have been presented, including (1) the synthesis of new compounds unattainable by other routes, (2) an efficient synthesis of known compounds, (3) an important step in a broad range of catalytic processes, including cross-coupling and polymerization, and (4) to modulate the reactivity of the organic fragment. Current mechanistic understanding of transmetallation lags behind such important applications, but knowledge of the process is improving.

The IUPAC numbering system for heterocyclobutenes begins with the heteroatom at the 1-position and continues around the ring from the olefinic carbons to the sp^3 carbon at the 4-position. For the purposes of this dissertation, atom labels will maintain that numbering convention. Therefore, the α-olefinic carbon will be referred to as C2 and, by adopting this labelling convention, there is no C1 atom (Figure **1.11**).

Figure **1.11**: Heterocyclobutene labelling system

Chapter 2: Central Carbon Alkylation of η^3-Propargyltitanium Complexes

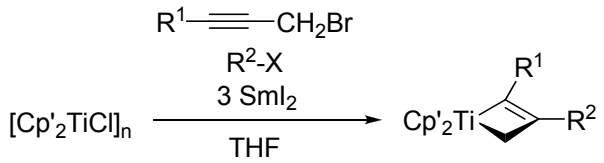
2.1 Introduction

The first reported synthesis of titanacyclobutene complexes was achieved from the reaction of Tebbe's reagent, Cp_2TiCH_2-$Al(CH_3)_2Cl$, with disubstituted alkynes.[16] Subsequent research into this and other titanium alkylidene intermediates established [2 + 2] cycloaddition chemistry as the most common method for preparing titanacyclobutene complexes. γ-Hydrogen elimination, a less general synthetic route, was reported for appropriately substituted vinylic titanium species.[91-93] Benzo- and naphthotitanacyclobutene derivatives were also prepared by 1,3-dianionic addition to titanium dihalides. These synthetic strategies have been discussed in detail in the introduction.

Samarium diiodide-mediated central carbon alkylation of η^3-propargyltitanium complexes also forms titanacyclobutene complexes in high yield.[94] Importantly, this radical process allows for completely regioselective formation of the target molecules. Previously, for both cycloaddition and γ-hydrogen elimination routes, symmetric or sterically- and electronically-biased alkynes were required to avoid the formation of regioisomeric mixtures of titanacyclobutene complexes. Since the first report detailing the synthesis of titanacyclobutenes bearing pentamethylcyclopentadienyl (Cp*) ancillary ligands, numerous other titanacyclobutene complexes have been prepared within the Stryker group.[29,95,97] Equation **2.1** summarizes much of the peer-reviewed and as yet unpublished work conducted in this area. Research into intramolecular cyclization and preparation of bicyclic titanacyclobutenes is ongoing.[98,99]

We had a strong interest in developing the synthesis of additional titanacyclobutene complexes bearing Cp ligands. The reasoning was two-fold: purchase or preparation of the starting material is less cumbersome[183,184] and transmetallation of the complexes was determined to be more efficient. The central addition chemistry was initiated by using the permethyltitanocene system because it was believed that sterically large ligands were required to inhibit competitive attack at the metal. Additionally, based on the inferred MO description presented in the introduction, strong electron-releasing ligands were considered necessary to promote central carbon alkylation. However, Cp*

is not ideal synthetically as it is expensive to purchase and arduous to prepare.[185] Once central carbon alkylation of η^3-propargyltitanium complexes was discovered to be more general than originally thought, there was no need to avoid the more convenient and accessible Cp complexes.



Equation **2.1**

n = 1; 1.0 equiv
n = 2; 0.5 equiv

Cp' = Cp*, ^{t}BuCp, Cp

R^1 = H, Me, Ph, *p*-C_6H_4OMe

R^2 = Bn, ^{i}Pr, CH_2TMS,
$CH_2C{\equiv}CCH_3$, $CH_2C{\equiv}CPh$,
$C(=CH_2)CH_3$, $C(=CH_2)Ph$, $C(=CHCH_3)CH_3$

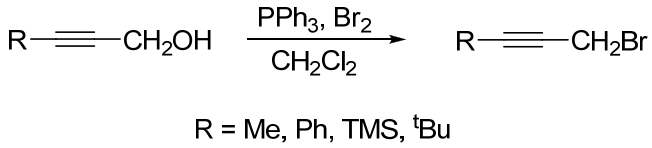
Prior to this work, five titanacyclobutene complexes bearing Cp ancillary ligands were prepared by central carbon alkylation.[29,95,97] As with many other titanacyclobutene complexes, combustion analyses were not within an acceptable range of the theoretical values and HRMS was used instead to confirm the elemental composition. Thus, rigourous characterization of new bis(cyclopentadienyl)titanacyclobutene complexes was necessary in and of itself, but also to ensure that further functionalization and transmetallation reactions occurred from well-defined compounds. Additionally, solid-state structures of titanacyclobutene complexes are uncommon, so crystals suitable for X-ray analysis were sought for structural confirmation and to provide real values for reference in potential future theoretical calculations. However, the primary focus of this chemistry was no longer simply preparation of titanacyclobutenes, but new synthetic transformations of the complexes. Therefore, optimization of the methodology and synthesis of "large" quantities of material was quite essential.

Before presenting our new results for central carbon addition to η^3-propargyltitanium complexes, one important procedural modification with respect to

the use of samarium diiodide has been made. THF-solvated samarium diiodide is used as a halophilic one-electron reducing agent for this chemistry, however it is more widely applied for reducing carbonyl-containing compounds, removing protecting groups, and other reductive organic synthesis.[186-189] The reagent is typically purchased and used as a 0.1 M solution in THF, although SmI_2 solutions of tetrahydropyran,[190] nitriles,[191] and dimethoxyethane[192] are known and a number of additives that promote increased reactivity have been used.[96] Unfortunately, SmI_2 is prohibitively expensive on a molar basis and relatively insoluble, hence the dilute commercial solutions of 0.1 M. To overcome these limitations for the preparation of titanacyclobutene complexes, solid SmI_2•xTHF[192] was prepared from samarium metal and iodine in THF suspension by a modified published procedure.[193] Essentially, once most of the samarium metal is consumed, the solution is filtered to remove $Sm^{(0)}$ and SmI_3 and then washed with THF. Recrystallization or simple removal of the THF furnishes solid SmI_2•xTHF. Titration with iodine in triplicate was used to determine the molecular composition, which typically includes 2 – 3 moles of THF per mole of SmI_2. The solid can be employed in reactions using less solvent than those using 0.1 M solutions of SmI_2, because as the reactions progress and SmI_2 is oxidized to SmX_3 (which precipitates out of solution), more of the suspended SmI_2 enters solution. Despite this modification, reactions are still conducted at approximately 0.11 M in SmI_2, which is near the maximum solubility concentration in THF at 25 °C.

2.2 Results and Discussion

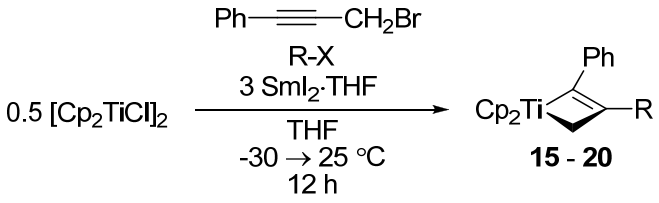
A series of titanacyclobutene complexes bearing methyl, phenyl, trimethylsilyl, and *tert*-butyl substituents at the α-alkenyl (C2) carbon were thus synthesized from the corresponding four propargyl bromide substrates. The propargyl bromides were prepared from the respective alcohols by the standard procedure used for such substitutions, triphenylphosphine and bromine, in 85 – 95 % yield (Equation **2.2**).[194] In all cases, a slight excess of the propargyl alcohol was included to prevent subsequent bromination of the alkyne moiety, which lowers the yield somewhat but makes purification significantly more straightforward.



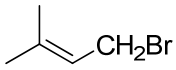
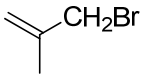
Equation **2.2**

2-Phenyltitanacyclobutene complexes

When phenylpropargyl bromide and a series of alkylating reagents were introduced to a suspension of $[Cp_2TiCl]_2$[184] and SmI_2, titanacyclobutene complexes **15** – **20** were produced in high isolated yields (Equation **2.3**). The alkylating reagents used included secondary and tertiary alkyl iodides, activated allylic bromides, and benzyl chloride.



Equation **2.3**

Complex	R-X	Yield
15	^{i}PrI	81 %
16	CyI	80 %
17	^{t}BuI	76 %
18		75 %
19		84 %
20	BnCl	75 %

A typical procedure involves the addition of one equivalent of both propargyl and alkylating halides to a THF suspension of 0.5 equivalents $[Cp_2TiCl]_2$ and three equivalents SmI_2 at -30 °C (*i.e.* 1 : 1 : 1 : 3 ratio of alkyne, alkyl halide, Ti, and Sm). As the reaction progresses and warms to 25 °C, the solution changes from the dark blue colour of SmI_2 to the dark red colour characteristic of Ti(IV) species, with concomitant formation of samarium(III) trihalide solvate as a yellow precipitate. Isolation of the titanacyclobutene complexes was achieved by a sequence of removal of solvents,

trituration into hexanes, filtration through Celite, and removal of solvents again; the isolated products were obtained as red crystalline solids in good yield (75 – 84 %). Further purification was typically unnecessary, although recrystallization from concentrated hexanes or pentane solutions was possible. The titanacyclobutene complexes are air- and moisture-sensitive, however they remain unchanged over years at room temperature under a dry nitrogen atmosphere. Reaction yields, while near-quantitative on small scale (~ 30 mg), are typically eroded by 10 – 20 % in larger scale reactions (up to 1 g)**.**

For titanacyclobutene complexes **18** and **19** bearing β-allylic substituents, the procedure was modified slightly. In these and other reactions with allylic bromides, the propargyl bromide substrate was added to a mixture of $[Cp_2TiCl]_2$ (0.5 equiv) and samarium diiodide (3 equiv) at -30 °C and stirred at room temperature for 30 minutes. The solution was then cooled to -30 °C again before addition of the allylic bromide, after which the procedure continued as before. This ensured that the desired propargyltitanium intermediate was fully formed prior to addition of the allylic reagent, which may competitively produce allyltitanium species and undesired side products.[116]

Titanacyclobutene complexes **15 - 20** all exhibit similar and characteristic ^{1}H and ^{13}C NMR spectroscopic data, as summarized in Table **2.1**. Specific resonances were assigned based on analysis of 2D NMR data (COSY, HMQC, HMBC) and by analogy to complexes previously synthesized and fully characterized. The α-alkenyl carbon (C2) is observed as a markedly downfield resonance between 204 – 212 ppm, whereas the β-alkenyl carbon (C3) is upfield between 95 – 102 ppm. The sp^3-hybridized ring carbon (C4) is found between 68 – 78 ppm, which is unusually deshielded considering the inherent polarization of Ti-C bonds. Thus, to explain the chemical shifts of the ring carbons it is useful to consider other canonical structures of the titanacyclobutene ring, where both the titanium-vinylalkylidene and -alkylidene/alkyne complexes contribute to the complete molecular picture (Figure **2.1**); agostic bonding between metals and C-C bonds has been noted for metallacyclobutanes.[195,196] The *ipso*-phenyl carbon is observed between 148 – 149 ppm for most of the complexes, although for titanacyclobutene **17** bearing a β-^{t}Bu substituent it is shifted slightly downfield at 151.1 ppm. The ring

hydrogens on C4 are observed as singlets in all cases from 3.13 – 3.39 ppm. Other resonances are dependent upon, and consistent with, the various C3 substituents.

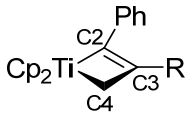
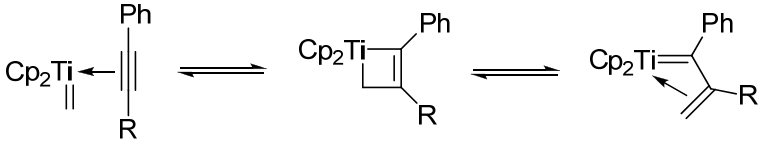


Table **2.1**: ^{1}H and ^{13}C NMR chemical shifts of 2-phenyltitanacyclobutene complexes[a]

Complex	C3 Substituent	C2 (δ)	C3 (δ)	C4 (δ)	C^4H_2 (δ)	*ipso*-Ph (δ)
15	^{i}Pr	210.2	99.7	68.9	3.21	148.9
16	Cy	210.7	99.3	71.1	3.27	148.9
17	^{t}Bu	204.7	101.3	72.1	3.25	151.1
18	$CH_2C(H)=CMe_2$	210.5	95.8	77.6	3.39	148.1
19	2-methylallyl	211.3	95.1	76.1	3.26	148.1
20	Bn	209.9	96.3	75.5	3.13	148.2

a) C_6D_6, 27 °C, ^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz

Figure **2.1**: Canonical structures of titanacyclobutene complexes



The NMR spectra for titanacyclobutene complexes are relatively simple, so HMQC data was used to assign the majority of the carbon resonances. HMBC experiments reveal that the C4 ring hydrogens correlate to both olefinic carbons and typically to the *ipso*-phenyl carbon as well, despite the four-bond distance. To assign accurately the two olefinic carbons, HMBC correlations from hydrogens on the β-sidechain were useful (*i.e.* for complex **15**, the isopropyl CH_3 groups only correlate to the isopropyl carbons and C3). Additionally, C2 is downfield of C3 in other known titanacyclobutene complexes.[16,197]

To provide confirmation of the structure, single crystals of titanacyclobutene complexes **16**, **17**, and **19** were analyzed by X-ray diffraction (ORTEP diagrams in Figures **2.2**, **2.3**, and **2.4**). Bond lengths and angles are similar to those previously

reported by Tebbe.[197] The titanacyclobutene rings are essentially planar, with the exocyclic α-phenyl substituent oriented perpendicular to the four-membered ring to avoid non-bonding repulsions with the β-substituent and ancillary ligands. Titanium-carbon bond lengths to the sp^2- and sp^3-hybridized α-carbon atoms are 2.09 – 2.10 and 2.12 – 2.14 angstroms, respectively. Representative bond lengths and angles of complexes **16**, **17**, and **19** are compiled in Table **2.2**; titanacyclobutenes **17** and **19** crystallized as two crystallographically independent molecules, and data for only one structure of each is included. Additional crystallographic data for **16**, **17**, and **19** can be found in Appendix **1**.

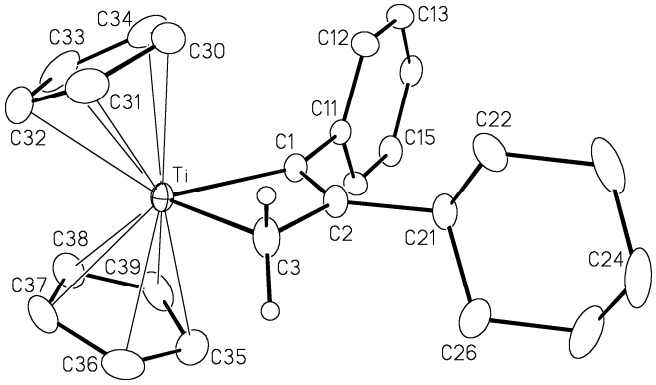


Figure **2.2**: Perspective view of **16**, $Cp_2Ti[PhC{=}C(Cy)CH_2]$. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms bonded to C3 are shown with arbitrarily small thermal parameters. $R_1 = 0.0411$, $R(w) = 0.1119$.

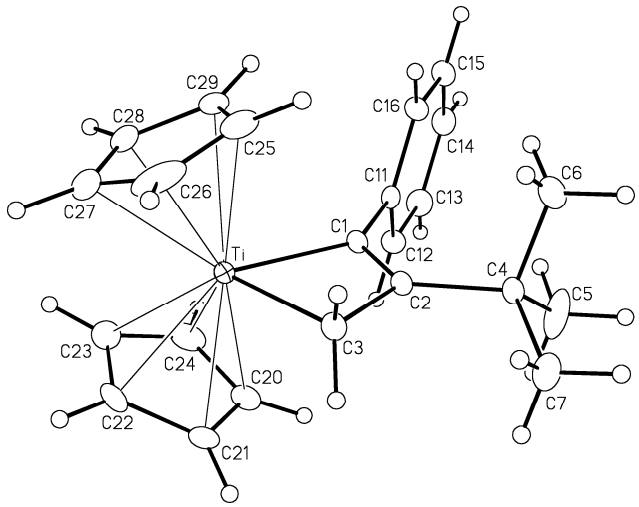


Figure **2.3**: Perspective view of **17**, $Cp_2Ti[PhC{=}C(^tBu)CH_2]$. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. $R_1 = 0.0307$, $R(w) = 0.0830$.

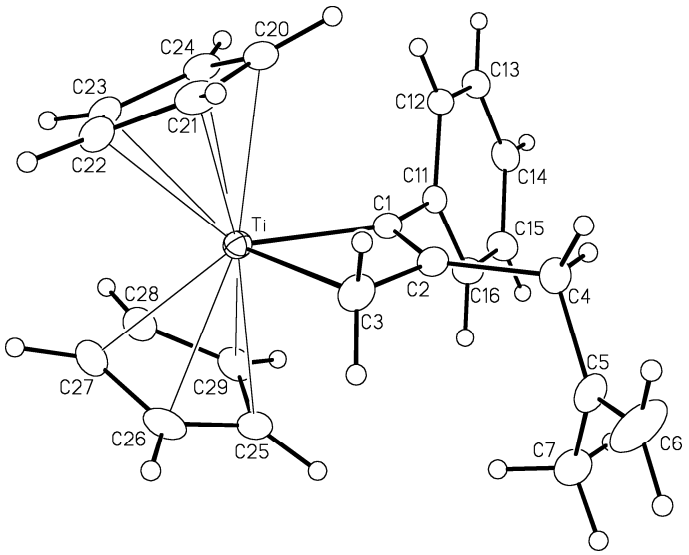


Figure **2.4**: Perspective view of **19**, $Cp_2Ti[PhC{=}C(CH_2C(Me){=}CH_2)CH_2]$. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. $R_1 = 0.0434$, $R(w) = 0.1158$.

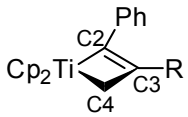
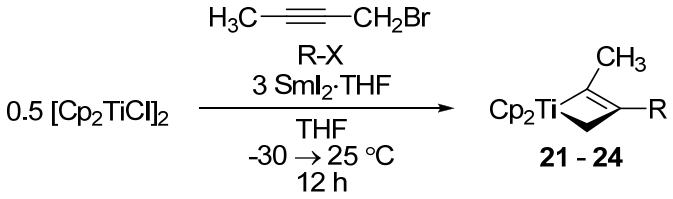


Table **2.2**: Selected bond lengths and angles for 2-phenyltitanacyclobutene complexes[a]

Complex	**16**	**17**	**19**
C3 substituent	Cy	^{t}Bu	2-methylallyl
Bond Length (Å)			
Ti-C2	2.0909(16)	2.0969(14)	2.100(2)
Ti-C4	2.1205(18)	2.1263(17)	2.139(2)
C2-C3	1.340(2)	1.337(2)	1.338(3)
C3-C4	1.536(2)	1.538(2)	1.532(3)
Bond Angle (°)			
C2-Ti-C4	71.57(6)	70.29(6)	70.75(8)
Ti-C2-C3	88.30(11)	90.30(9)	89.00(14)
Ti-C4-C3	82.45(10)	84.11(9)	82.83(12)
C2-C3-C4	117.62(15)	115.30(14)	117.39(18)

2-Methyltitanacyclobutene complexes

A series of new 2-methyltitanacyclobutene complexes were prepared from 1-bromo-2-butyne by the same methodology (Equation **2.4**). Similar complexes have been prepared with Cp* and ^{t}BuCp ancillary ligands,[29,95] and titanacyclobutenes **21** and **22** are known.[97] The products were obtained in good yield (70 – 91 %) as viscous red oils with no spectroscopic evidence of impurities, however none passed elemental analyses; this appears to be a systemic problem for 2-methyltitanacyclobutene complexes in this series.



Equation **2.4**

Complex	R-X	Yield
21	BnCl	78 %
22	^{i}PrI	91 %
23	CyI	70 %
24	^{t}BuI	79 %

The characteristic NMR data for 2-methyltitanacyclobutene complexes **21 - 24** are tabulated in Table **2.3**. Representative ^{1}H and ^{13}C NMR chemical shifts are very similar to those observed for 2-phenyltitanacyclobutenes. C2 is the furthest downfield ^{13}C NMR signal, located between 205 – 213 ppm. The other ring carbons, C3 and C4, are upfield between 91 – 98 ppm and 69 – 76 ppm, respectively. The exocyclic methyl group carbon is observed between 21 – 23 ppm and the hydrogens are observed as a triplet between 2.10 – 2.23 ppm due to long-range coupling to the C4 hydrogens. Consequently, the C4 hydrogens are split into a narrow quartet and observed between 3.05 – 3.14 ppm with five bond coupling constants of 2.0 – 2.1 Hz.

Table **2.3**: ^{1}H and ^{13}C NMR chemical shifts of 2-methyltitanacyclobutene complexes[a]

Complex	C3 substituent	C2	C3	C4	C^4H_2	Ti-C^2-CH_3	Ti-C^2-CH_3
21	Bn	211.2	91.0	75.7	3.05	22.0	2.23
22	^{i}Pr	211.8	94.3	69.1	3.10	21.4	2.10
23	Cy	212.7	93.8	71.2	3.14	21.5	2.13
24	^{t}Bu	205.9	97.6	72.6	3.09	23.0	2.16

a) C_6D_6, 27 °C, ^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz

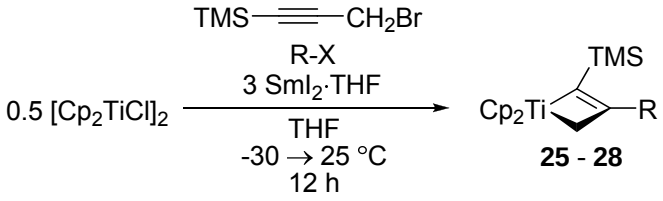
2-(Trimethylsilyl)titanacyclobutene complexes

2-Trimethylsilyl-substituted titanacyclobutene complexes were targeted in order to probe the effect of a sterically bulky α-substituent on transmetallation to boron. Additionally, TMS groups that are incorporated into titanacyclobutene complexes provide a new handle for elaboration or derivatization. 1-Bromo-3-trimethylsilyl-2-propyne [(trimethylsilyl)propargyl bromide] was prepared in two steps from propargyl alcohol.[198] This substrate was subjected to the standard central carbon alkylation conditions and a series of 2-(trimethylsilyl)titanacyclobutene complexes were obtained in good yield (70 – 81 %) and high purity, although only β-benzyl complex **26** passed elemental analysis (Equation **2.5**). Recrystallization from hexanes, which was successful for 2-phenyltitanacyclobutenes, afforded amorphous solid **26** unsuitable for X-ray crystallography; the other complexes were isolated as red oils at room temperature. Such a bulky propargyl substrate could conceivably favour the η^1-bonding mode with titanium over the η^3-bonding mode, however there was no evidence of attack at the metal centre.

The 2-(trimethylsilyl)titanacyclobutene complexes were characterized with 1D and 2D NMR techniques, as before (Table **2.4**). Compared to the other two sets of titanacyclobutenes bearing α-phenyl and α-methyl substituents (Tables **2.1** and **2.3**), the 2-(trimethylsilyl)titanacyclobutene olefinic carbons are less magnetically shielded at 213 – 223 ppm for C2 and 111 – 122 ppm for C3; these are shifted downfield by 8 – 13 ppm and 15 – 25 ppm, respectively. Decreased shielding may be attributable to negative $\pi_{C=C} \rightarrow \sigma^*_{Si-C}$ hyperconjugation[199] and, for C2, β-carbon effects.[200]

Titanacyclobutene complexes bearing both α- and β-trimethylsilyl substituents are known in the literature and, unusually, exhibit cycloreversion reactivity to alkyne and

titanium alkylidene species. Solid state data supports formulation of the bis(trimethylsilyl) complex **29** (Figure **2.5**) as distorted toward a titanium alkylidene/alkyne complex.[16] The only ^{13}C NMR data reported for the olefinic carbons of a TMS-substituted titanacyclobutene is for 1,2,3-tris(trimethylsilyl) complex **30**, where C2 is observed at 250 ppm (Figure **2.5**).[17] Titanacyclobutene complexes **25** and **26** were heated to 65 °C in sealed NMR tubes with diphenylacetylene with no evidence of the metathesis reactivity noted for 1,2-bis(trimethylsilyl)titanacyclobutene **29**.[16]



Equation **2.5**

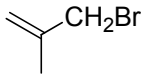
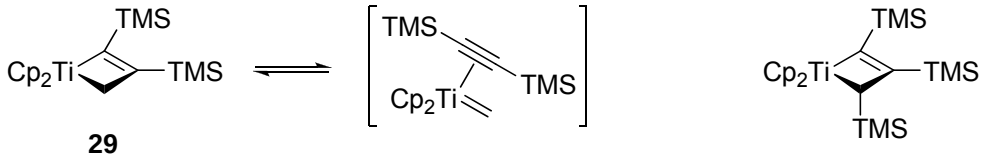
Complex	R-X	Yield
25	^{i}PrI	74 %
26	BnCl	70 %
27	^{t}BuI	74 %
28		81 %

Table **2.4**: ^{1}H and ^{13}C NMR data of 2-(trimethylsilyl)titanacyclobutene complexes[a]

Complex	C3 substituent	C2	C3	C4	C^4H_2
25	^{i}Pr	221.0	117.5	73.2	3.23
26	Bn	220.9	112.7	81.1	3.13
27	^{t}Bu	213.8	121.4	82.0	3.49
28	2-methylallyl	222.3	111.9	81.5	3.31

a) C_6D_6, 27 °C, ^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz

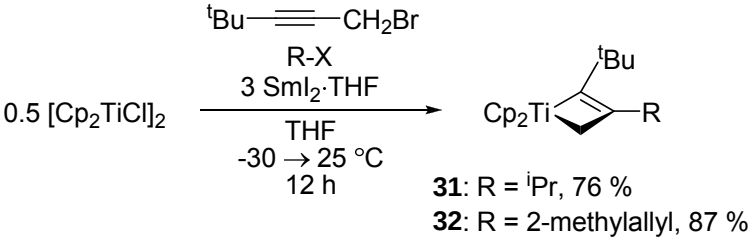
Figure **2.5**: Titanacyclobutene complexes bearing trimethylsilyl substituents



29 **30**

2-(Tert-butyl)titanacyclobutene complexes

To corroborate the results from boron transmetallation of 2-(trimethylsilyl)titanacyclobutene complexes, (2-*tert*-butyl)titanacyclobutene complexes were targeted. 1-Bromo-4,4-dimethyl-2-pentyne (*tert*-butylpropargyl bromide), another sterically bulky substrate, was successfully incorporated into the synthesis of titanacyclobutene complexes. Using the standard procedure for central carbon addition, alkylation with isopropyl iodide and 2-methylallyl chloride formed titanacyclobutene complexes **31** and **32** as red oils in good yield and high purity (Equation **2.6**). There was no spectroscopic evidence for any paramagnetic impurities, however elemental analysis of the products, much like that of many other titanacyclobutene complexes, was not within the accepted limits.

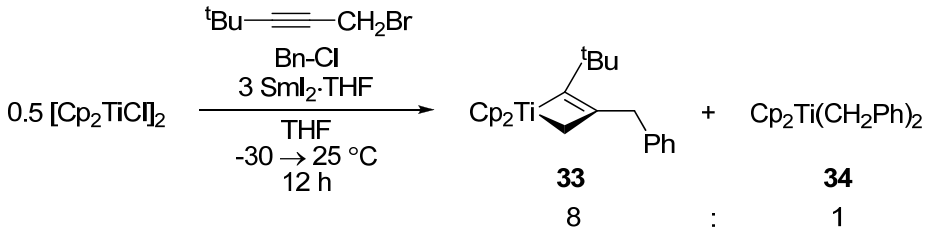


Equation **2.6**

Interestingly, *tert*-butyl iodide and (1-chloroethyl)benzene do not alkylate the titanium *tert*-butylpropargyl intermediate and only paramagnetic green material is returned, probably because the propargyl ligand is too sterically crowded for alkylation with large radicophiles.

Alkylation of the (*tert*-butylpropargyl)titanium complex with benzyl radical led to the formation of minor amounts of 1,1-bis(benzyl)titanocene **34** as well as the desired titanacyclobutene complex **33** (Equation **2.7**). The mixture was characterized by NMR spectroscopy, with HRMS providing confirmation of the identities of both the desired product and by-product. The same bis(benzyl) by-product was also obtained during alkylation with benzyl radical of a (*tert*-butyldimethylsilyl-propargyl)titanium intermediate. To identity the by-product unambiguously, 1,1-bis(benzyl)titanocene **34** was synthesized independently from $[Cp_2TiCl]_2$, 4 equivalents of benzyl chloride, and 6 equivalents of SmI_2 by the same procedure as that used for titanacyclobutene formation;

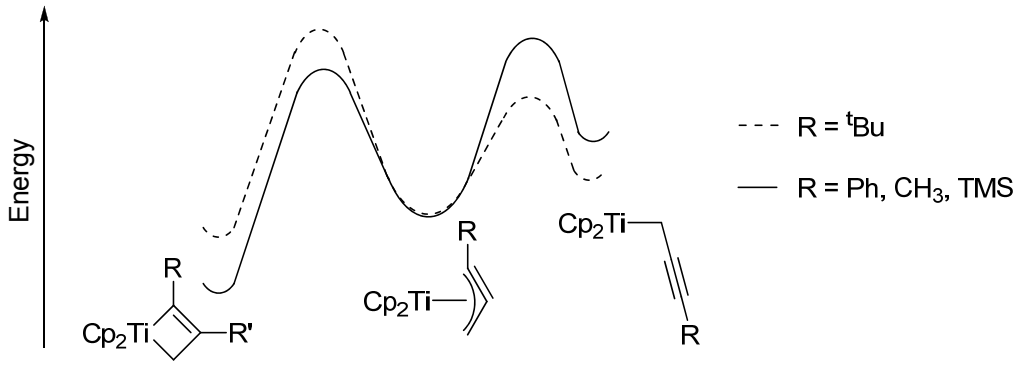
the spectroscopic data matched the reported ^{1}H NMR data[201] for bis(benzyl) complex **34** and the ^{1}H and ^{13}C NMR data observed for the by-product. The ratio of products does not change from 8 : 1 when the η^3-propargyltitanium complex is formed prior to addition of benzyl chloride, nor when the reaction concentration or time is varied.



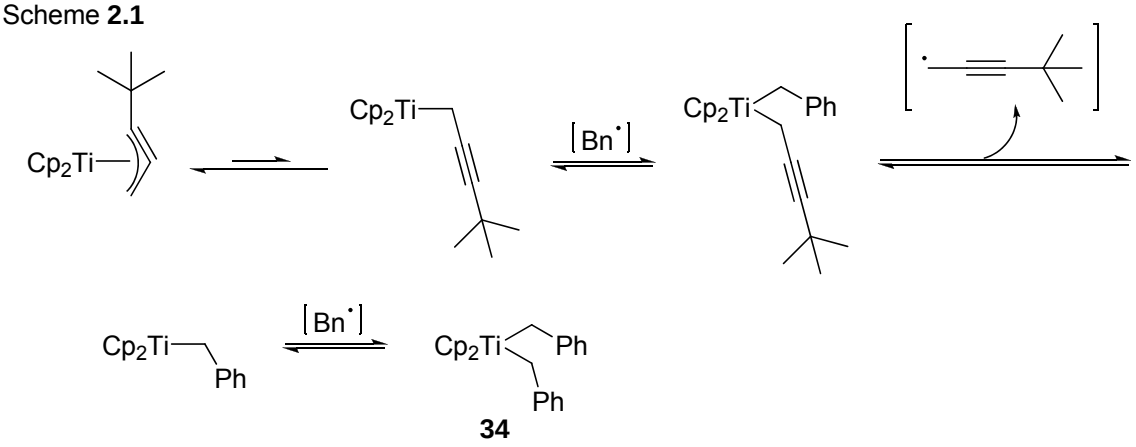
Equation **2.7**

The transition from a titanium(III)-propargyl complex to a titanacyclobutene product requires that which becomes the C2-substituent to move closer to the titanium centre as the angle of the three ring-forming carbons decreases. Larger substituents are expected to result in higher energy barriers to titanacyclobutene formation, while conversely lowering the transition state energy towards equilibrium formation of η^1-propargyltitanium intermediates. This concept is depicted in Figure **2.6**. An η^1-propargyltitanium complex would be electron-poor, coordinatively unsaturated, and susceptible to attack at the metal centre by benzyl radical, leading to eventual formation of the observed bis(benzyl) by-product (Scheme **2.1**). Similar by-products are not observed from isopropyl and 2-methylallyl radicals, presumably because the analogous dialkylated titanium species are not stable towards subsequent β-hydrogen elimination.[202]

Figure **2.6**: Proposed potential energy surface for alkylation of propargyltitanium complexes



Scheme **2.1**



34

Selected NMR data for the 2-(*tert*-butyl)titanacyclobutene complexes are tabulated in Table **2.5**. The compounds exhibit signals for C2 and C4 that are shifted downfield by 10 – 13 ppm and 6 – 8 ppm, respectively, relative to the 2-phenyl and 2-methyltitanacyclobutene complexes, but are close in range to the 2-(trimethylsilyl)-titanacyclobutenes (~ 1 – 2 ppm downfield). The downfield C2 chemical shifts are expected because β-carbon effects similar to the TMS complexes should be present. The C3 resonances of 2-(*tert*-butyl)titanacyclobutene complexes appear 0 – 5 ppm upfield of the analogous 2-phenyl and 2-methyltitanacyclobutenes, and can be attributed to steric compression caused by significant gauche interactions.[200] These signals are 21 – 23 ppm upfield of the corresponding trimethylsilyl-substituted complexes.

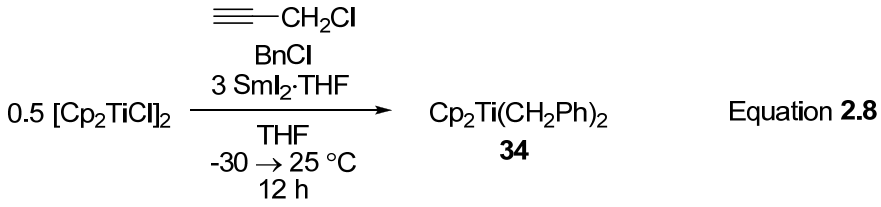
Table **2.5**: ^{1}H and ^{13}C NMR chemical shifts of 2-(*tert*-butyl)titanacyclobutene complexes

Complex	C3 substituent (β)	C2	C3	C4	C^4H_2	$C(CH_3)_3$
31	^{i}Pr	221.7	95.8	74.6	3.29	38.9
32	2-methylallyl	223.0	90.2	83.0	3.32	38.6
33	Bn	222.1	91.3	83.1	3.12	38.8

Limitations to central carbon alkylation of η^3-propargyltitanium complexes

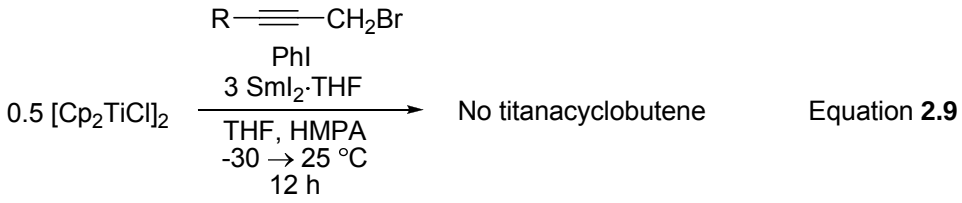
Not all research into central carbon alkylation of η^3-propargyltitanium intermediates went as smoothly as that presented thus far. Terminal alkynes react with titanium alkylidene complexes to form titanium acetylides, so this substrate class is not

useful for preparing titanacyclobutenes by the [2 + 2] cycloaddition route.[34] Stryker and Ogoshi reported the successful incorporation of a terminal alkyne by alkylating the parent permethyltitanocene η^3-propargyl complex with benzyl chloride in the presence of samarium diiodide.[94] The reaction had to be maintained at -35 °C, a temperature that only allowed for use of easily reduced benzyl chloride. However, with less electron-rich Cp ligands only bis(benzyl)titanocene **34** was obtained, with no sign of the desired titanacyclobutene complex (Equation **2.8**).



Equation **2.8**

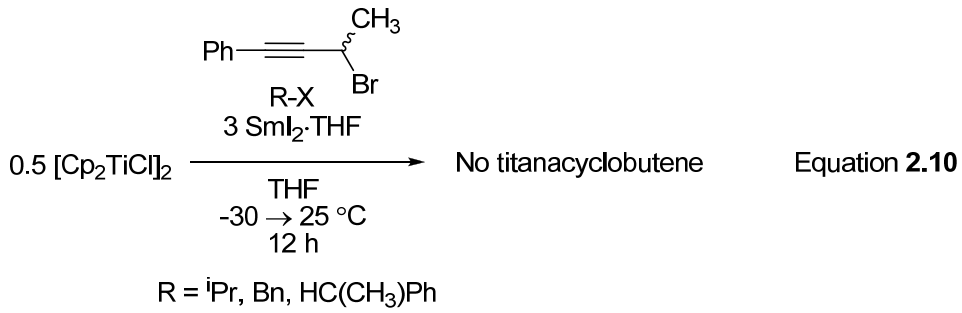
As noted previously, central carbon alkylation of propargyltitanium complexes with a source of phenyl radical is unsuccessful, even in cases where vinyl radical alkylation has been observed.[95] Iodobenzene is known to participate in radical chemistry in the presence of SmI_2 and HMPA under similar conditions.[203] However, titanacyclobutene product was not isolated from any reaction involving $[Cp_2TiCl]_2$, SmI_2, HMPA, PhI, and a propargyl bromide (Equation **2.9**), regardless of the procedure or conditions.



Equation **2.9**

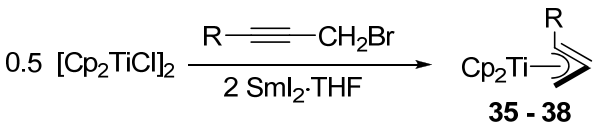
The use of 1-substituted propargyl bromides would result in synthetically valuable titanacyclobutene complexes with a substituent on the sp^3-hybridized carbon, but have thus far proved inaccessible using radical alkylation methodology; reactions with 1-methyl-3-phenylpropargyl bromide and, previously, 1,1-dimethylpropargyl chloride[68] produce no material identifiable as a titanacyclobutene product (Equation **2.10**). Varying

the reaction conditions, such as lower temperatures (-78 °C), a different order of addition of reagents, and changing the concentration of the solution, also failed to produce titanacyclobutene products.



To differentiate whether the problem arises during central carbon alkylation or in the initial formation of the propargyltitanium intermediate, a series of propargyltitanium(III) complexes were prepared. From the reaction of 0.5 equivalents of $[Cp_2TiCl]_2$, one equivalent of propargyl bromide, and two equivalents of samarium diiodide, a range of propargyltitanium species were isolated as green oils (Table **2.6**). Infrared spectroscopy was then performed on the η^3-propargyltitanium complexes, as well as the original substituted propargyl bromides (Table **2.6**). IR samples of the titanium complexes were prepared as THF solutions to approximate the reaction conditions.

Table **2.6**: C≡C stretching frequency for η^3-propargyltitanium complexes



R	C≡C IR stretch (cm^{-1}) R—≡—CH_2Br		C≡C IR stretch (cm^{-1}) Cp_2Ti—(R)
Ph	2261, 2220	**35**	1925
^{t}Bu	2239	**36**	1934, 1923
TMS	2181	**37**	1948, 1933
TBDMS	2179, 2156	**38**	1947, 1932

The typical stretching frequency of an alkyne is between 2100 – 2260 cm^{-1}.[200] The absorptions assigned to the C≡C stretching frequency for the η^3-propargyltitanium complexes are between 1920 – 1950 cm^{-1}.[204] Upon formation of a propargyl radical and complexation with titanium the bond order decreases, which is observed as a lower stretching frequency in the IR spectrum. Many of the alkynes and propargyl species studied show two absorption peaks, one of which is attributed to a Fermi resonance interaction between the fundamental C≡C absorption and the overtone of another vibration.[205,206] When 1-methyl-3-phenylpropargyl bromide (ν = 2236 and 2209 cm^{-1}) was subjected to the same η^3-propargyltitanium complex-forming conditions as before, the expected propargyl infrared absorptions were not observed. Although peaks characteristic of sp^3- and sp^2-hybridized C-H stretches were evident as well as typical C=C stretches, no major absorption appears in the region between 2800 – 1600 cm^{-1}. This suggests that either formation of the disubstituted η^3-propargyltitanium complex does not occur, or it is unstable once synthesized.

Finally, in an effort to decrease the amount of SmI_2 required for this procedure, reactions were conducted with one equivalent of SmI_2 in the presence of various metal co-reductants, including zinc, manganese, samarium, and aluminum. The desired titanacyclobutene complexes were obtained, although in less than 33 % yield and in each case contaminated with metallic by-product(s), as evident by the mass of isolated material. Clearly, the metal additives played no role in the reaction and the titanacyclobutene complexes were produced only from stoichiometric SmI_2. Inclusion of magnesium in the reaction mixture resulted in unknown side reactions and low, highly variable yields.

2.3 Conclusion

As intended, a series of titanacyclobutene complexes bearing simple cyclopentadienyl ancillary ligands have been synthesized and fully characterized. New propargyl substrates bearing bulky *tert*-butyl and trimethylsilyl substituents on the alkyne were successfully incorporated into the titanacyclobutene structural motif, and a wider range of 2-phenyl and 2-methyltitanacyclobutene complexes were prepared, which will allow for a comprehensive evaluation of substituent effects on titanacyclobutene

reactivity. For the first time in propargyltitanium chemistry, competitive radical attack at the metal centre was observed during central carbon alkylation of a *tert*-butyl substituted η^3-propargyltitanium complex, likely due to isomerisation to an η^1-propargyltitanium complex.

Chapter 3: Insertion of Isonitriles and Demetallation of Titanacyclobutene Complexes

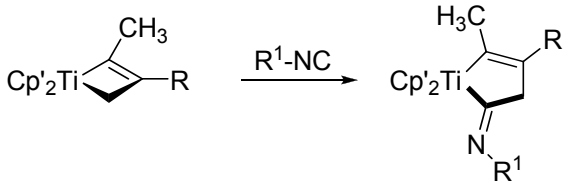
3.1 Introduction

Titanacyclobutene complexes react with a range of reagents bearing polar multiple bonds.[68] Insertion of small molecules rapidly enhances complexity of the molecule by introducing new functional groups, increasing the potential synthetic utility of downstream decomplexed organic material. Developing new reactions in this area is clearly desirable and worthy of continued investigation.

Titanacyclobutene complexes react with carbon monoxide to provide acyl titanacyclopentene complexes arising from selective insertion into the sp^3-hybridized Ti-C bond.[28] Carbonyl-containing compounds insert into both the vinylic and alkyl Ti-C bonds, resulting in the formation of homoallylic alcohols[35] and conjugated dienes.[36,37] Reactions with nitriles also potentially lead to two different products, from apparent insertion into both Ti-C bonds; the double insertion products have been converted into substituted pyridines upon treatment with acid.[35,36,95,159] Additionally, homoallylic hydroxylamines have been prepared from insertion reactions involving organonitroso compounds followed by hydrolysis.[30] A detailed description of these reactions is presented in the introduction (Chapter 1).

Reactions between titanacyclobutene complexes and various isonitriles have been investigated. The first such reaction was reported by Grubbs as part of a competition experiment with carbon monoxide, although only one iminoacyl complex was reported and further transformations were not investigated (refer to Equation **1.7**).[28] In research completed by Whitby *et al*, monocyclic α-methylene titanacyclobutene complexes react with two equivalents of isonitrile to produce allenylketenimines (the intermediate formed from insertion of one equivalent of isonitrile reacts faster than the initial titanacyclobutene complex. Refer to Equation **1.8**.) The authors report the isolation of the initial insertion product for only one complex, from a bicyclic titanacyclobutene (refer to Scheme **1.3**); subsequent reaction with ^{t}BuOH then HCl resulted in the formation of a conjugated amide. The yield was not specified and no experimental details were provided.[31]

Preliminary studies were initiated previously in the Stryker group, with a handful of iminoacyl titanacyclopentene complexes synthesized and characterized, however demetallation was not achieved (Equation **3.1**).[29] That work, focussed primarily on Cp* and ^{t}BuCp titanacyclobutene complexes, indicated that 2-methyltitanacyclobutenes provided the best results for insertion of isonitriles, although no other α-substituted titanium iminoacyl complexes were prepared.[29] Only titanium iminoacyl complexes prepared from 2,6-dimethylphenyl isonitrile and *tert*-butyl isonitrile were characterized and it was noted that less hindered isonitriles produce a mixture of unidentified products. Indeed, most reports of isonitrile insertion to Group IV transition metal-alkyl complexes involve sterically bulky isonitriles, with ^{t}BuNC the most prevalent reagent used.



Equation **3.1**

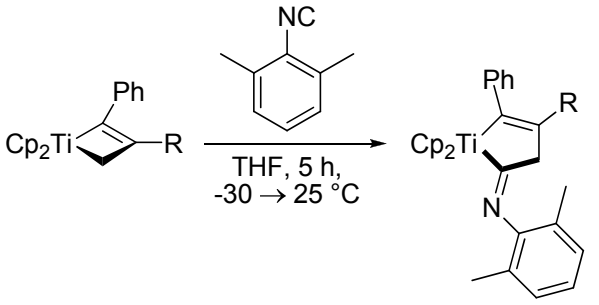
Cp'	R	R^1	Yield
Cp*	^{i}Pr	2,6-dimethylphenyl	88 %
Cp*	TMS-CH_2	2,6-dimethylphenyl	85 %
^{t}BuCp	Bn	2,6-dimethylphenyl	87 %
Cp	Bn	2,6-dimethylphenyl	84 %
Cp	^{i}Pr	2,6-dimethylphenyl	81 %
^{t}BuCp	Bn	^{t}Bu	84 %
Cp	Bn	^{t}Bu	88 %

3.2 Results and Discussion:

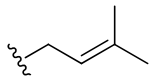
Synthesis of iminoacycl titanacyclopentene complexes

With new bis(cyclopentadienyl)titanacyclobutene complexes now available for study, isonitrile insertion into the Ti-C bonds was investigated more thoroughly. 2-Phenyltitanacyclobutene complexes were treated with one equivalent of bulky 2,6-dimethylphenyl isonitrile in dry THF at -30 °C and stirred at room temperature for 5

hours to afford iminoacyl titanacyclopentene complexes **39** and **40** (Equation **3.2**). Once the solvent was removed, the product was extracted into hexanes and filtered through Celite before cooling to -30 °C for crystallization. The dark red solid that precipitated out of solution was spectroscopically clean but not of sufficient quality for X-ray crystal analysis.



Equation **3.2**

18 **39**: R =  , 57 %

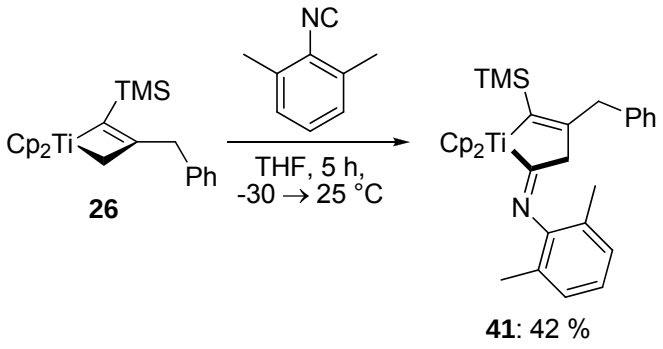
19 **40**: R = 2-methylallyl, 49 %

Both of these iminoacyl titanacyclopentene complexes bore spectroscopic signatures consistent with those already reported. For complex **39**, two downfield carbon signals at 232.9 and 190.7 ppm are assigned to the α-iminoacyl and α-alkenyl carbon, respectively. The β-alkenyl carbon resonance is observed at 127.4 ppm. The sp^3-hybridized ring carbon has a markedly upfield chemical shift of 45.6 ppm and the attached hydrogens are observed as a singlet at 2.71 ppm. The aromatic proton resonances fall between 7.11 and 6.73 ppm. An IR absorption at 1550 cm^{-1} is assigned to the C=N stretch of the iminoacyl moiety.

HMQC was used to identify the majority of the ^{13}C NMR signals for iminoacyl complex **39**. HMBC correlations were observed between the titanacyclopentene ring hydrogens (2.71 ppm) and the other ring carbons (232.9, 190.7, 127.4 ppm). The side-chain methylene hydrogens (2.32 ppm) correlated to the alkenyl ring carbons (190.7, 127.4 ppm) but not the iminoacyl carbon. Complex **40** bore similar resonances and complete NMR data is provided in the experimental section.

A single α-trimethylsilyl iminoacyl titanacyclopentene was also prepared in 42 % yield by insertion of 2,6-dimethylphenyl isonitrile (Equation **3.3**). Complex **41** had two

downfield ^{13}C resonances at 233.0 and 208.2 ppm for the iminoacyl and α-alkenyl ring carbons, respectively. The latter carbon's downfield shift, much like in the titanacyclobutene complex, can be attributed to negative $\pi_{C=C} \rightarrow \sigma^*_{Si-C}$ hyperconjugation and β-carbon effects. The sp^3-hybridized ring carbon appears at 48.2 ppm, whereas the β-alkenyl ring carbon is found at 139.1 ppm. The olefinic ring carbons are significantly downfield of the same carbons in the α-phenyl complexes, which was also noted for the original titanacyclobutene complexes. A peak at 1598 cm^{-1} in the IR spectrum is assigned to the C=N stretch of complex **41**.



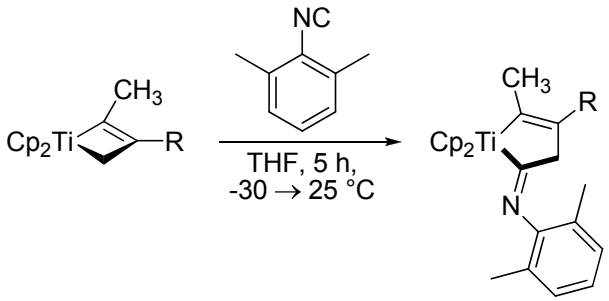
26 **41**: 42 %

Equation **3.3**

Methyl-substituted iminoacyl titanacyclopentene complexes **42** and **43** were previously prepared by Qui but not rigourously purified (Equation **3.4**), with no combustion analysis data reported.[29] Following the same procedure as already described, the synthesis was repeated and the products recrystallized from hexanes. The compounds were spectroscopically identical to those already prepared and analytically pure. As with the other iminoacyl complexes synthesized, reported yields are for recrystallized product, however the mother liquor still contained significant quantities of product as well.

The C=N stretching frequency can be used to determine whether the bonding mode of the iminoacyl fragment is η^1 or η^2, although it has been noted that infrared absorption is not an ideal parameter for assigning the bonding mode.[207] Lower stretching frequencies typically indicate an η^1-bonding mode, however for two similar iminoacyl molybdenum complexes this does not hold as $\nu(\eta^1\text{-C=N}) > \nu(\eta^2\text{-C=N})$.[208] A series of early transition metal η^2-iminoacyl complexes show stretching frequencies in the range of 1520 – 1590 cm^{-1}.[209] Another parameter used to identify the bonding mode is the ^{13}C NMR shift of the iminoacyl carbon. For the same series of early transition metal η^2-

iminoacyl complexes, the iminoacyl carbon was observed between 230 – 265 ppm[209] and between 195 – 268 ppm for iminoacyl transition metal complexes in general.[207] The pertinent IR and ^{13}C NMR data of the five iminoacyl complexes prepared are summarized in Table **3.1**. Based on comparison to known complexes, the IR data suggest that these iminoacyl titanium complexes are bonding in an η^2-mode. ^{13}C NMR data also indicates an η^2-bonding mode, although the iminoacyl carbons are at the lower threshold of the known η^2-iminoacyl complexes.



22
21

42: R = ^{i}Pr, 58 %
43: R = Bn, 55 %

Equation **3.4**

Table **3.1**: Selected C=N spectroscopic properties of iminoacyl titanacyclopentenes

Complex	**39**	**40**	**41**	**42**	**43**
ν (C=N) (cm^{-1})	1550	1575	1598	1565[a]	1577[a]
C=N (δ)	232.9	232.9	233.0	234.2	234.4

a) Reference 29

Where possible, the iminoacyl titanacyclopentene complexes were crystallized or precipitated from a cold hexanes solution. Spectroscopically clean material was obtained although diffractable crystals were not. However, during the initial investigation by Qui, a solid state structure was acquired for complex **42** bearing a β-isopropyl substituent.[29] This strongly indicated an η^1-bonding mode based on a typical C=N bond length of 1.283 Å and a long Ti-N distance of 3.16 Å (*cf* Ti-C bond lengths of 2.16 and 2.21 Å). Of course, an iminoacyl complex bonding in an η^2 fashion would be expected to have a longer C-N bond length and a shorter Ti-N distance. Considering the uncertainty associated with determining the bonding mode from spectroscopic measurements, it is

probably reasonable to assume that this solid state structure provides a more accurate indication of the bonding in this series.

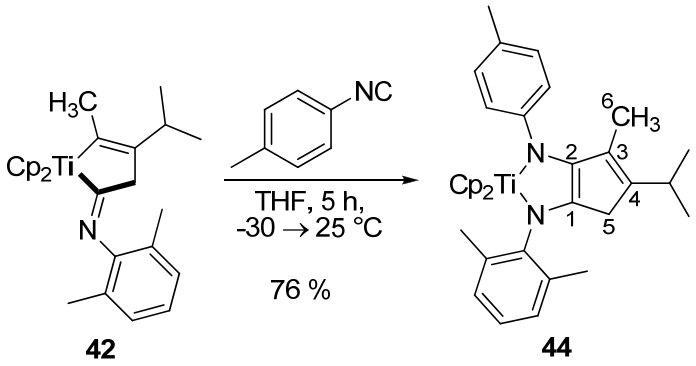
Treatment of titanacyclobutene complexes with one equivalent of *p*-tolyl isonitrile resulted in the formation of multiple unidentified products. Numerous signals in the 6.2 – 5.0 ppm region of the ^{1}H NMR spectrum indicated that at least three major species were present, and purification by fractional crystallization was unsuccessful. Considering the examples known in the literature and Qui's previous investigation, these results are not surprising. Competitive insertion into the vinylic Ti-C bond, or incorporation of more than one molecule of less bulky *p*-tolyl isonitrile into the titanacyclobutene complex, likely accounts for the additional by-products (*vide infra*).

Synthesis of titanium-diamidate complexes

Having established the synthesis of iminoacyl titanacyclopentenes, decomplexation strategies to yield organic products were explored. With knowledge of Whitby's sparse report of formation of allenylketenimines from α-methylene titanacyclobutene complexes by insertion and demetallation with two equivalents of isonitrile,[31] iminoacyl titanacyclopentene **42** was treated with one equivalent of *p*-tolyl isonitrile in THF. After extraction into hexanes and removal of solvent, a dark red (nearly black) oil was obtained. The product appeared clean by NMR spectroscopy, but displayed no ^{13}C resonances downfield of 153.5 ppm. Six inequivalent methyl groups were indicated, as well as inequivalent ring methylene hydrogens at 2.67 and 2.07 ppm (which correlated to the same carbon at 31.6 ppm), were observed. Based on a comprehensive two-dimensional spectroscopic analysis to determine atom connectivity, as well as a similar structure obtained from double isonitrile insertion in the titanacyclobutane series,[210-212] the product was identified with confidence as bicyclic cyclopentadiene **44** (Equation **3.5**).

The absence of ^{13}C signals downfield of 154 ppm indicates that there are no vinylic Ti-C or C=N bonds present. Complex **44** exhibits downfield resonances of 153.5 and 152.0 ppm for the *ipso*-xylene carbon and *ipso*-tolyl carbon, respectively. A third downfield signal at 152.8 ppm is assigned to C4 of the cyclopentadiene ring (see Equation **3.5** for atom labelling). The other cyclopentadiene ring carbons are observed at

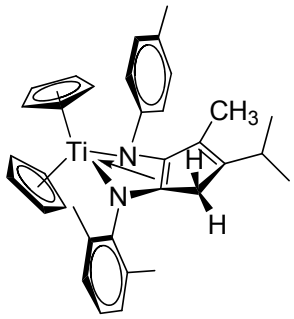
135.4, 133.1, and 130.23 for the olefinic carbons and 31.6 ppm for the sp^3 carbon. The exocyclic methyl carbon is the furthest upfield signal at 12.2 ppm. Every carbon in the molecule is inequivalent on the NMR time scale, including the arene rings. Of course, this makes the aromatic hydrogens inequivalent as well, and the aromatic region of the ^1H NMR spectrum is spread from 7.06 – 6.56 ppm. Interestingly, the Cp rings are also inequivalent, appearing as two singlets at 5.49 and 5.42 ppm by ^1H NMR and 109.5 and 105.1 ppm by ^{13}C NMR spectroscopy. The dissymmetry in the NMR spectra suggests that there is restricted rotation of the aromatic rings and that the titanium-containing ring is not planar, possibly coordinating in a puckered η^4-bonding mode (Figure **3.1**). A similar structure has been identified by single crystal X-ray analysis of the product obtained from the reaction between a titanacyclobutane complex and three equivalents of *tert*-butyl isonitrile.[212]



42 **44**

Equation **3.5**

Figure **3.1**: Perspective drawing of titanium diamidate **44**



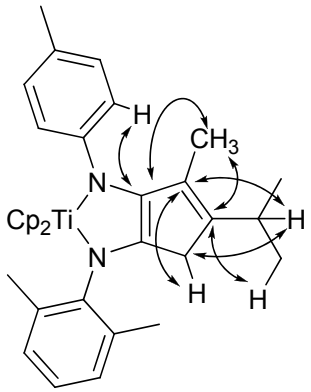
The key HMQC and HMBC correlations are summarized in Table **3.2**; identification of specific cyclopentadiene ring carbon signals was possible using this 2D

NMR data. C1 and C2 could be assigned because the methylene ring hydrogens on C5 do not correlate to C2 using the typical HMBC parameters, and because the exocyclic methyl group hydrogens correlate to C2 but not C1. The correlation between the isopropyl methyl groups and C4 allows for the differentiation of C3 from the downfield C4. An unexpected correlation from the aromatic protons between 6.91 – 6.89 ppm and the C2 carbon at 133.1 ppm is attributed to a long-range four-bond coupling of an *o*-tolyl hydrogen (as opposed to five-bond coupling from a *m*-xylyl hydrogen), providing evidence for the identified regioisomer (Figure **3.2**).

Table **3.2**: Selected 2D correlations for titanium diamidate **44**

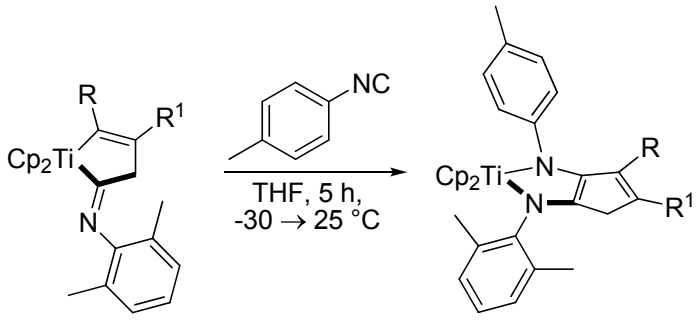
^{1}H NMR	HMQC	HMBC
δ 2.75 (C*H*)	δ 27.6	δ 152.8 (C4), 130.23 (C3), 31.6 (C5), 22.7, 22.0 (^{i}Pr-*C*H$_3$)
δ 2.67, 2.07 (C^5*H*$_2$)	δ 31.6	δ 152.8 (C4), 135.4 (C1), 130.23 (C3)
δ 1.43(C^6*H*$_3$)	δ 12.2	δ 152.8 (C4), 133.1 (C2), 130.23 (C3)
δ 0.83, 0.78 (^{i}Pr-C*H*$_3$)	δ 22.7, 22.0	δ 152.8 (C4), 27.6 (*C*H), 22.0/22.7 (^{i}Pr-C*H*$_3$)

Figure **3.2**: Selected 3- and 4-bond HMBC correlations for titanium diamidate **44**



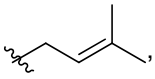
Two additional titanium diamidates, complexes **45** and **46**, were prepared by analogous insertion of *p*-tolyl isonitrile (Equation **3.6**). These compounds were also obtained as dark red or near-black oils. Spectroscopically, the complexes show no symmetry and restricted rotation about the nitrogen-bonded aromatic rings. These

structural features are manifest as inequivalent Cp rings, inequivalent cyclopentadiene sp^3-hybridized ring hydrogens, and distinct carbon signals for each nitrogen-bonded aromatic ring. Characteristic and comparative NMR signals are included in Table **3.3**.



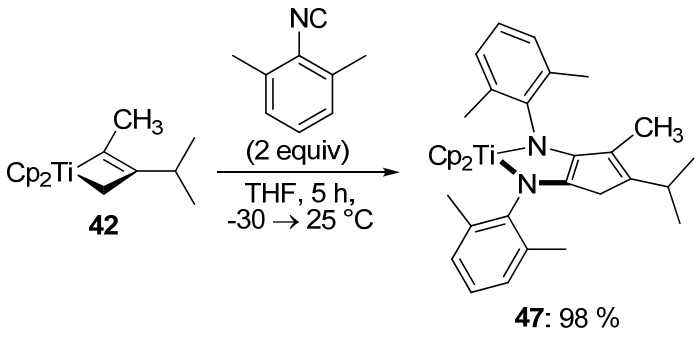
Equation **3.6**

43 **45**: R = CH_3, R^1 = Bn, 96 %

39 **46**: R = Ph, R^1 =  , 72 %

Iminoacyl titanacyclopentene complex **42** was also treated with one equivalent of 2,6-dimethylphenyl isonitrile to produce a dark red oil. However, many of the signals appeared broad in the ^{1}H NMR spectrum, in particular a peak in the alkyl region from 2.50 – 2.20 ppm that integrated to 14 hydrogens. The complex was synthesized again directly from the titanacyclobutene complex and two equivalents of isonitrile in 98 % yield (Equation **3.7**), and the ^{1}H NMR spectrum of this material was identical. The complex was redissolved in toluene-d_8 and heated in the spectrometer probe to 70 °C, at which point the ^{1}H NMR signals sharpened somewhat: the Cp rings were observed as one singlet at 5.49 ppm, the cyclopentadiene ring hydrogens appeared between 2.55 – 2.48 ppm, and the four sets of benzylic hydrogens were observed as one broad singlet from 2.25 – 2.16 ppm. The sample was then cooled to -40 °C and characterized fully at that temperature where the dissymmetry of the complex was apparent. As expected by comparison with the other titanium-diamidates characterized, inequivalent Cp rings and benzylic methyl groups are observed. Characteristic ^{1}H and ^{13}C NMR signals of the four titanium-diamidates prepared are tabulated in Table **3.3**, demonstrating the closely analogous spectroscopic signatures.

Presumably the isonitrile inserts into the vinylic Ti-C bond to produce an intermediate bis(iminoacyl)titanacyclohexene, which undergoes reductive ring-closing to afford the products that are isolated (Equation **3.8**).

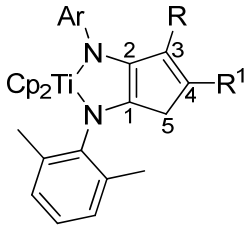


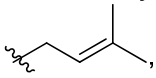
42

47: 98 %

Equation **3.7**

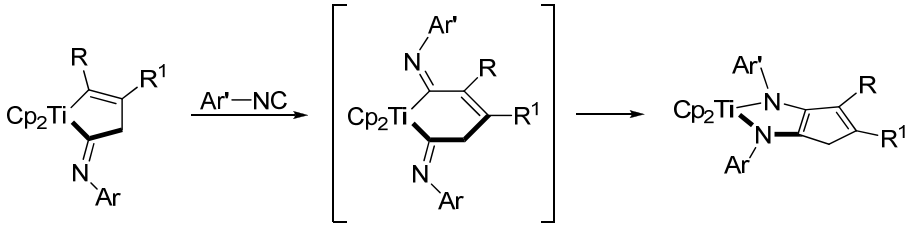
Table **3.3**: Characteristic chemical shifts of titanium diamidate complexes



44: R = CH_3, R^1 = ^{i}Pr, Ar = *p*-Tol
45: R = CH_3, R^1 = Bn, Ar = *p*-Tol
47: R = CH_3, R^1 = ^{i}Pr, Ar = Xyl
46: R = Ph, R^1 =  , Ar = *p*-Tol

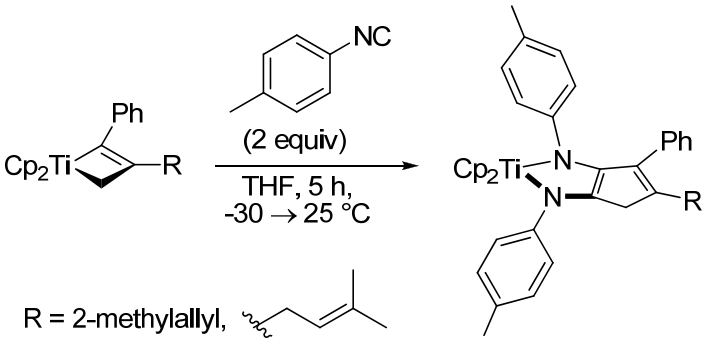
Complex:	**44**	**45**[a]	**47**[b]	**46**
C1	135.4	136.7	132.4	135.6
C2	133.1	132.5	131.4	133.2
C3	130.23	132.8	133.0	136.7
C4	152.8	145.0	151.6	147.8
C5	31.6	36.0	32.9	36.1
C^5H_2	2.67, 2.07	2.59, 2.03	2.84, 2.24	2.95, 2.34
CH_3	12.2	12.6	11.9	-
CH_3	1.43	1.55	1.28	-
Cp	109.5, 105.1	109.6, 105.2	111.5, 107.7	109.7, 105.0
Cp*H*	5.49, 5.42	5.50, 5.42	5.60, 5.45	5.68, 5.52
ipso-Xyl	153.5	153.3	153.5	153.6
ipso-Ar	152.0	151.9	153.2	150.9

a) C1 and C2 are not unambiguously identified; b) **47** characterized in tol-d_8 at -40 °C; **44**, **45**, **46** characterized in C_6D_6 at 27 °C



Equation **3.8**

2-Phenyltitanacyclobutene complexes incorporated two equivalents of *p*-tolyl isonitrile (Equation **3.9**); however, characterization of the expected titanium-diamidate products was not conclusive. The complexes did not dissolve completely in C_6D_6 and remained quite viscous. By NMR spectroscopy, the material appeared clean and exhibited signals similar to the other titanium-diamidates synthesized. However, the sp^3 carbon and hydrogens on the cyclopentadiene ring were not visible and no otherwise unaccounted-for 2D NMR correlations were observed. A consistent explanation for these perplexing results has yet to be found.



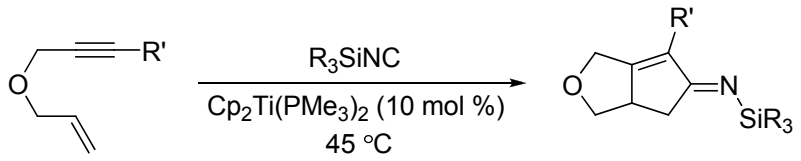
Equation **3.9**

Demetallation

Productive or hydrolytic decomplexation of the cyclic titanium-diamidates was not successful, although only preliminary studies were conducted. Nitrous oxide (N_2O), introduced at -78 °C to THF solutions containing titanium-diamidates **44** and **45** and removed five hours later at 25 °C under vacuum with other volatiles, did not produce a reaction. No change was noted while heating to 80 °C in the presence of Me_2SiCl_2 either. Exposure to protic acids, methanol, or water produced multiple products that were not further separated or characterized. Treatment with triphosgene and transmetallation using dichlorophenylborane[213,214] may, however, be promising avenues, as each of these

reactions produces one major species in solution. With a more thorough investigation, removal of the titanium portion should be achievable. Liberating the diamidate fragment would afford an unsymmetrical chelating ligand bearing disparate olefinic groups that could be functionalized further, a compound that could be of interest in asymmetric chemical applications, as well as for other purposes.

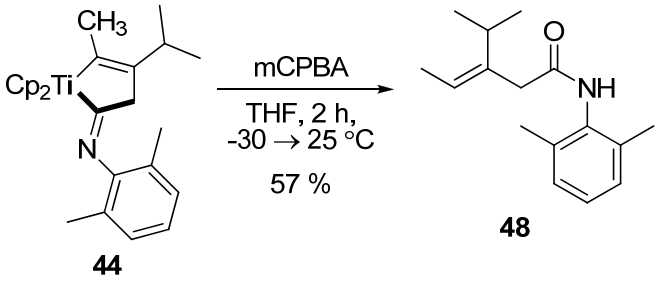
Demetallation of the iminoacyl titanacyclopentene complexes was still sought, with particular interest in developing a strategy for inducing reductive elimination, producing synthetically interesting cyclobutenimines. Several strategies known to promote reductive elimination for other systems failed to succeed here. In reactions catalytic in "titanocene", intermediate iminoacyl titanacyclohexenes reductively eliminate under the reaction conditions, either spontaneously or promoted by isonitrile (Equation **3.10**).[215-217] Reductive elimination from iminoacyl zirconacyclohexenes is also part of a catalytic cycle.[218] The new iminoacyl titanacyclopentene complexes slowly decomposed when heated to 80 °C in C_6D_6 for multiple days, with no evidence of coherent product. Only slow decomposition was noted when iminoacyl titanacyclopentenes were combined with diphenylacetylene and heated at 75 °C.



Equation **3.10**

Only paramagnetic material was recovered when iminoacyl titanacyclopentenes were treated with Cp_2FePF_6, which has been used to promote reductive elimination by oxidation of various metals.[219,220] Iodine is known to react with an iminoacyl zirconacyclohexene to liberate organic product following reductive elimination.[221] Iodine[222] and bromine[76] also react with titanacyclobutanes to release organic material (cyclopropanes and dibromoalkanes, respectively), although only a complex mixture of products was obtained upon treatment of the iminoacyl titanacyclopentenes with these reagents. Multiple, unidentified products were also observed from reactions with $PhBCl_2$ and protic sources (gaseous HCl, H_2O, 2,4,6-trimethylpyridinium chloride). No reaction occurred with nitrous oxide.

Knowing that titanium is quite oxophilic and readily reacts with oxygen-containing species, the use of *m*-chloroperbenzoic acid (mCPBA) was investigated. Iminoacyl titanacyclopentene **44** was thus treated with one equivalent of mCPBA in THF at -30 °C, providing acyclic organic amide **48** in 57 % yield following purification by chromatography through silica (Equation **3.11**). Upon addition of mCPBA, the solution colour changed from dark red to light yellow within 20 seconds, though the reaction was stirred for an additional 2 hours. A basic aqueous workup with $NaHCO_3$ was identified as the best conditions for removal of the unidentified titanium by-products and sodium benzoate once the reaction was complete; this does not interfere with the amide functionality.

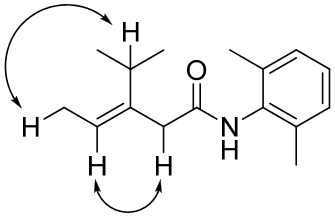


44 **48**

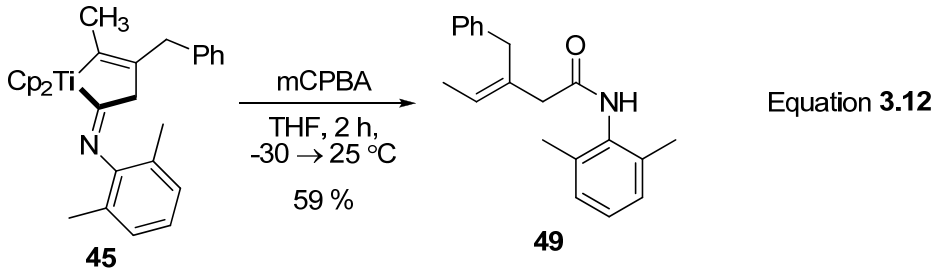
Equation **3.11**

Although formation of the carbonyl was unexpected, HRMS data demanded the presence of oxygen. Additionally, the IR spectrum showed a broad absorption at 3249 and two strong absorptions at 1704 and 1656 cm^{-1}, consistent with aromatic amide stretching frequencies. The 1D and 2D NMR data was used to identify the atom connectivity in the new amide. A TROESY experiment was conducted to determine the orientation of the double bond; two correlations confirmed that it was the *Z* isomer (Figure **3.3**). NOE correlations exist between the vinylic hydrogen and the α-methylene hydrogens (δ 5.58 ↔ δ 3.13), and between the allylic methyl hydrogens and the isopropyl methine hydrogen (δ 1.77 ↔ δ 3.01). Additionally, correlations expected for the *E* isomer, namely between the vinylic hydrogen and the isopropyl group or the methyl and α-methylene hydrogens, were not observed. Whitby also obtained an amide by treating an iminoacyl titanacyclopentene complex successively with ^{t}BuOH and HCl, however no experimental details were reported.[31]

Figure **3.3**: NOE correlations indicative of the *Z* isomer for amide **48**



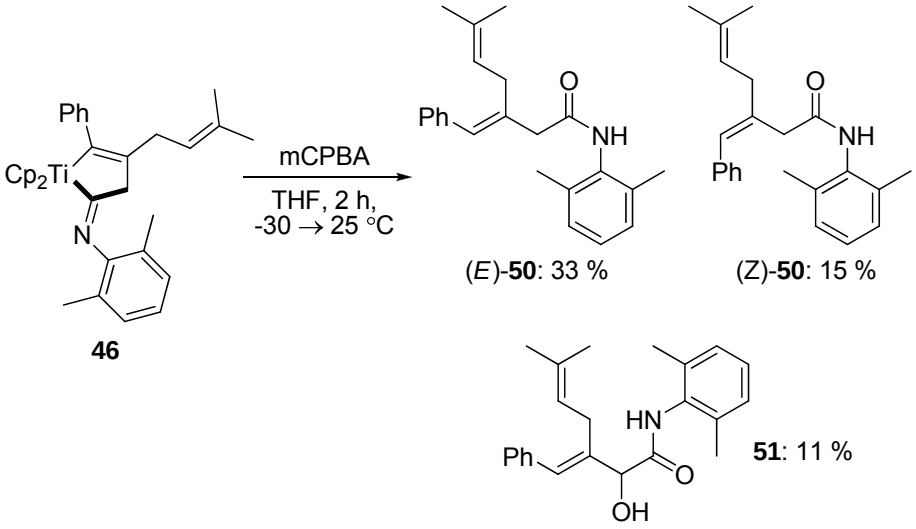
Two more iminoacyl titanacyclopentene complexes were oxidatively demetallated with mCPBA by the same procedure. Pentenamide **49** was obtained in 59 % yield following chromatography through silica. The C=O stretch and N-H stretch of the amide occurs at 1654 and 3260 cm^{-1}, respectively. The NMR spectra are fully consistent with the assigned structure. A TROESY experiment was used to determine the stereochemistry of the double bond: NOE correlations between the vinylic hydrogen and α-methylene hydrogens (δ 5.79 ↔ δ 3.08) and between the benzylic hydrogens and the allylic methyl group (δ 3.61 ↔ δ 1.90) confirm that no isomerisation of the olefin is induced by the oxidation.



Equation **3.12**

One α-phenyl iminoacyl titanacyclopentene complex was also demetallated using mCPBA. Two amide products **50** were obtained: the expected *E* diastereomer in 33 % yield, accompanied by the *Z* diastereomer in 15 % yield. 1D and 2D NMR data are fully consistent with the assigned structures. The major *E* isomer displays NOE correlations between the vinylic hydrogen and α-methylene hydrogens (δ 6.67 ↔ δ 3.33) as well as between the *ortho* phenyl hydrogens and doubly allylic methylene hydrogens (δ 7.32-7.27 ↔ δ 3.16). Conversely, the *Z* diastereomer exhibits NOE correlations between the *ortho* phenyl hydrogens and α-methylene hydrogens (δ 7.39-7.37 ↔ δ 3.45), and between the vinylic hydrogen and doubly allylic methylene hydrogens (δ 6.67 ↔ δ 3.10).

Isomerization of the double bond may be promoted by acid after demetallation, or possibly under the mild work-up conditions.



Equation **3.13**

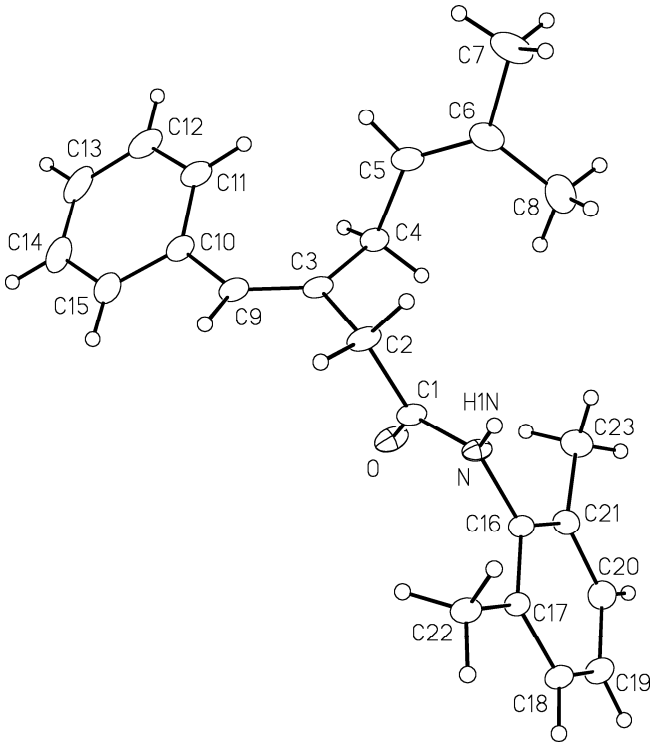


Figure **3.4**: Perspective view of (3*E*)-3-benzylidene-*N*-(2,6-dimethylphenyl)-6-methyl-hept-5-enamide **50**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. $R_1 = 0.0477$, R*(w)* = 0.1402.

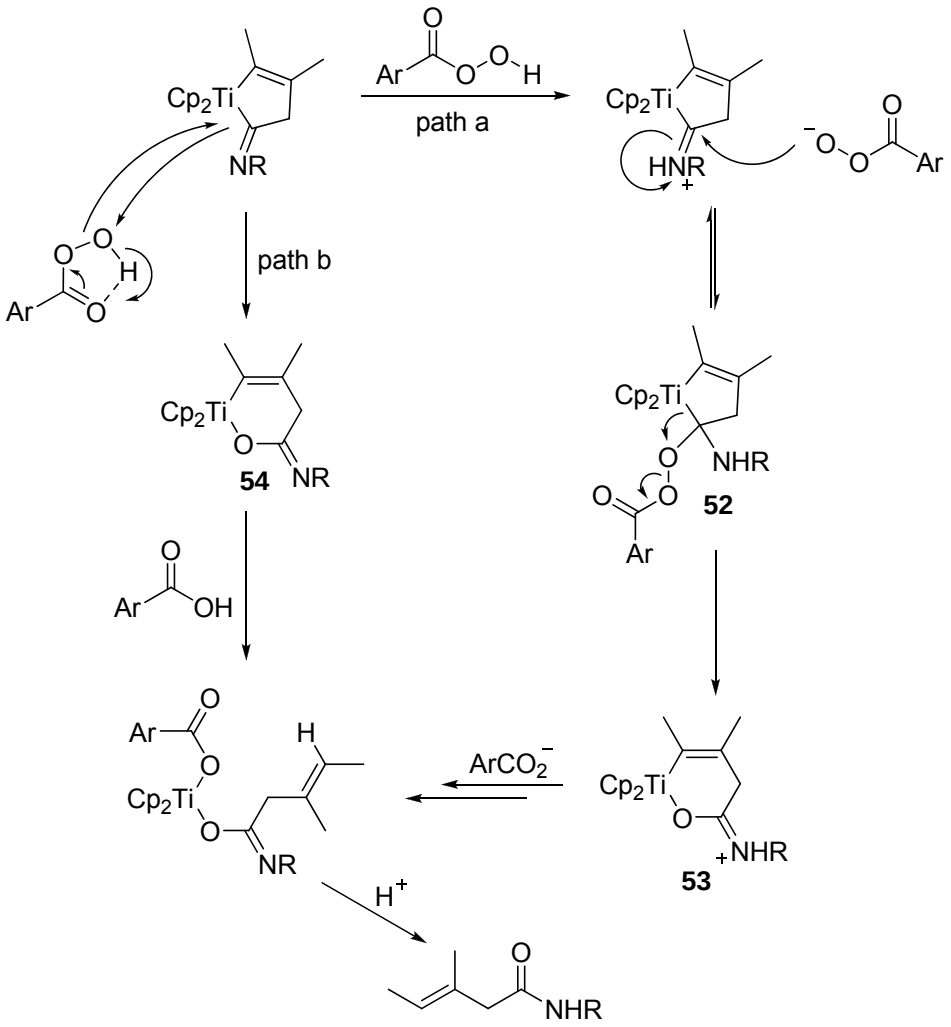
A third product, α-hydroxylamide **51** was also recovered from the oxidation, albeit in only 11 % yield (Equation **3.13**). HRMS data indicated a molecular formula of $C_{23}H_{27}NO_2$, one more oxygen atom than the isolated amides. Stretches of the O-H and N-H bonds are visible in the IR spectrum as a single broad absorption centred at 3347 cm^{-1} with a higher frequency hump, while the C=O stretch is observed at 1662 cm^{-1}. There was some question as to the location of the hydroxyl group; an isomeric structure containing a benzylic alcohol and a conjugated amide was also considered. However, the structure of **51** was confirmed based on 2D NMR correlations: the proton α to the carbonyl at 4.88 ppm showed long-range HMBC couplings to the carbonyl and neighbouring olefinic carbons (170.5, 140.9, and 130.1 ppm), while the benzylidene hydrogen at 6.85 ppm correlated to carbons in the phenyl ring (136.7 and 129.1 ppm) and not to the carbonyl carbon. To identify the stereochemistry of the styrene fragment, the benzylidene hydrogen at 6.85 ppm was irradiated; based on a 7 % NOE correlation to the α-carbonyl hydrogens, the α-hydroxylamide was identified as the *E* isomer.

The mCPBA used for these reactions was not purified, so *m*-chlorobenzoic acid and water were still present as well. As a control experiment, iminoacyl titanacyclopentene complex **44** was also treated with benzoic acid, a weaker acid than the chlorinated analogue. Analysis of the crude product mixture indicated that amide product was present, also the *Z*-isomer, but less than half of that found for reactions with mCPBA. Treatment with solid DABCO·$2H_2O_2$[223] complex (*vide infra* – Chapters 5 and 6) produced at least three compounds, none of which were formed from mCPBA.

Because the mechanism of amide formation from iminoacyl titanacyclopentene oxidation was not investigated, it is impractical to make a confident proposal in that regard. However, considering the modes of action known for oxidation with peracids, it is reasonable to illustrate two feasible possibilities (Scheme **3.1**). One potential route is based upon the mechanism of the Baeyer-Villager[172,224] oxidation: in "path a", protonation of the imine followed by nucleophilic addition of the perbenzoate to the iminoacyl carbon forms Criegee-like intermediate **52**. Ring expansion with concomitant loss of benzoate provides cationic titanium-alkoxide **53**, which could easily be converted to an amide by acid-base chemistry. Alternatively, in a mechanism similar to the epoxidation of olefins[172,225,226] (Scheme **3.1**, path b), the oxidation of the Ti-C bond may

occur through a concerted mechanism to give cyclic titanium-alkoxide **54**. Protonation of the vinylic Ti-C bond and hydrolysis would also give an amide. However, protonation of the vinylic Ti-C bond may be the first step in the reaction, after which oxidation of the iminoacyl carbon could still occur by either route described. Of course, *m*-chlorobenzoic acid and water are also present and presumably participate in the acid-base aspects of the transformation.

Scheme **3.1**: Possible mechanisms for amide formation



3.3 Conclusion

While direct reductive elimination from iminoacyl titanacyclopentene complexes could not be achieved, two new organic reactions have been developed. In the presence of a second equivalent of isonitrile, bicyclic titanium-diamidates are formed and may prove important provided the reaction can be optimized and demetallation accomplished. Conversely, acyclic organic amides were obtained by oxidation with mCPBA. One avenue that could be explored for cyclobutenimine formation is a late transition metal-mediated reaction, similar to a Kumada-Coriu[227-230] cross-coupling concept, as late transition metals such as nickel are more likely to undergo reductive elimination.

Chapter 4: Preparation of Boracyclobutenes by Transmetallation

4.1 Introduction

Boracyclobutene synthesis was targeted to investigate potential uses as novel boron synthons for organic synthetic methodology. Derivatization of organoboranes is well established as a means of introducing new functional groups to organic molecules;[231-233] the pervasiveness of organoborane methodology is rooted in low toxicity, ease of use, and commonly efficient oxidative, substitutive, and catalytic transformations. Three additional structural features of boracyclobutenes that make them uniquely multifunctional and of particular interest: the vinylic and allylic carbon-boron bonds, and small-angle strain. That boracyclobutene chemistry is largely unexplored provides added incentive for investigation.

Catalytic transition metal cross-coupling of alkenylboranes with organic halides and triflates is an effective means of forming carbon-carbon bonds.[234] Allylboration of aldehydes and ketones produces a new carbon-carbon bond as well, while leaving olefin and alcohol functional groups on the new homoallylic alcohol for further elaboration.[235-237] Generating and utilizing boracyclobutenes in these types of reaction could potentially lead to the rapid formation of complex molecules from simple building blocks.

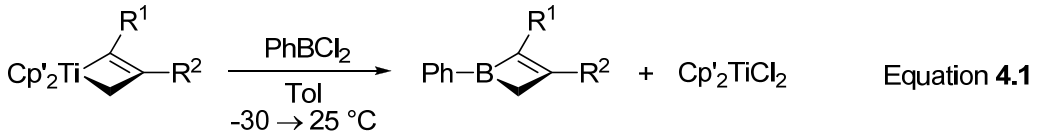
Small-angle strain, or what is commonly referred to as ring strain, arises from structural configurations that require bond angles to be smaller than what normal orbital overlap would dictate and is only present in three- and four-membered rings.[238] For a given ring/molecule, it is defined as the amount of energy above a hypothetical strain-free molecule, the energy of which typically cannot be definitively determined; of course, this may lead to controversy where different methods of estimation are used.[239] Determinations have been made based on computational analyses,[240] and heats of combustion have been used to order the amount of strain present in different sized cyclic hydrocarbons.[241] By any means of reckoning, small rings that experience small-angle strain have a lower activation energy barrier to overcome for a given reaction than a comparable acyclic or low-strain cyclic molecule, which is manifest as a higher degree of reactivity, as observed for cyclopropanes and cyclobutanes.[242,243]

The small-angle strain of a boracyclobutene has not been calculated, however recent computational results indicate that unsubstituted cyclobutene has a small-angle strain energy of 30.2 kcal/mol, whereas for 1,2-dimethylcyclobutene it is 21.5 kcal/mol.[239] The lower energy predicted for the disubstituted molecule is attributed to the so-called corset effect, where ring opening would cause additional unfavourable steric interactions between the substituents. Assuming boracyclobutenes are comparable to cyclobutenes, an estimated small-angle strain of 17 – 26 kcal/mol is reasonable. Therefore, much like small cyclic hydrocarbons and epoxides, it was expected that reactions inaccessible to acyclic boranes may be discovered by using boracyclobutenes.

While boracyclobutenes have fascinating potential, actual knowledge is currently limited by restrictive synthetic strategies and unstudied reactivity potential. As presented in detail in the introduction, a few boracyclobutenes have been prepared by [2 + 2] cycloaddition of boraalkenes and alkynes, and by 1,3-addition of dianions to boron halides. Boraalkenes are, for the most part, prepared by pyrolysis and are both thermodynamically and kinetically unstable under typical conditions. Nucleophilic 1,3-addition results in products containing the boracyclobutene structural motif embedded in benzene and naphthalene rings, reducing their utility in desired applications as synthons. A new and more general synthetic route, while still expected to have limitations of its own, would be useful, particularly if it can avoid the use of artificially large substituents and generation of highly transient intermediates.

Preparation of titanacyclobutene complexes by central carbon addition of η^3-propargyltitanium intermediates has been, and continues to be, researched by the Stryker group. While various applications have been developed to obtain functionalized organic material from titanacyclobutene complexes, new directions are always of interest. Considering the known transmetallation chemistry of Group IV metallacycles (refer to Chapter 1), including titanacyclobutene complexes, it seemed reasonable to explore this avenue further with regard to the synthesis of boracyclobutenes. Not only would this represent a new and potentially general synthetic route to an uncommon class of compound, it would also present an electronically and sterically different manifold for the organic moiety from which new transformations might be developed.

Prior to this report, two boracyclobutenes were prepared by the reaction of titanacyclobutene complexes with dichlorophenylborane (Equation **4.1**), although at that time analytically pure material could not be isolated and the characterizations were incomplete; the principal known difficulty involved separating the boracyclobutene from the Cp'_2TiCl_2 co-product.[29,95] However, the generality of the transmetallation process also remained in question. While not of particular importance at this developmental stage, the co-generation of Cp'_2TiCl_2 is conceptually expedient, since it is a primary material for synthesizing titanacyclobutene complexes.



Equation **4.1**

Cp*: $R^1 = p\text{-}C_6H_4OMe$, R^2 = Bn
Cp: R^1 = Ph, $R^2 = {}^iPr$

Due to the rarity and absence of spectroscopic and analytical data for the target molecules, thorough characterization was especially important. Some NMR spectroscopic features characteristic of organoboranes are pertinent to further discussion. ^{11}B is the isotope most commonly used for NMR analysis, which is 80.4 % abundant and has spin 3/2. The chemical shift of a boron atom is quite useful for identifying its bonding environment; sp^2-hybridized trivalent boron maintains chemical shifts downfield of tetracoordinate boron. Of course, the nature of the boron substituents plays a large role in the observed chemical shift: the vacant p orbital on boron readily accepts electron donation from adjacent non-bonding electron pairs or π-bonds. Trialkylboranes typically show chemical shifts between 80 and 90 ppm relative to $BF_3{\cdot}OEt_2$. Aryl, alkene, and alkyne substituents result in an upfield shift to as low as 50 ppm (BPh_3 has a chemical shift of 68.0 ppm and trivinylborane is 56.4 ppm).[244] For comparison, tetracoordinate borate anions are upfield of 5 ppm, and amine-complexed tetracoordinate neutral trialkylboranes are upfield of 10 ppm.

The expected splitting pattern for a nucleus of spin ½ attached to boron is a 1 : 1 : 1 : 1 quartet. Instead, what is typically observed is a broad signal or no signal at all (*i.e.* broadened over several ppm to an extent that it is unobservable). To overcome this

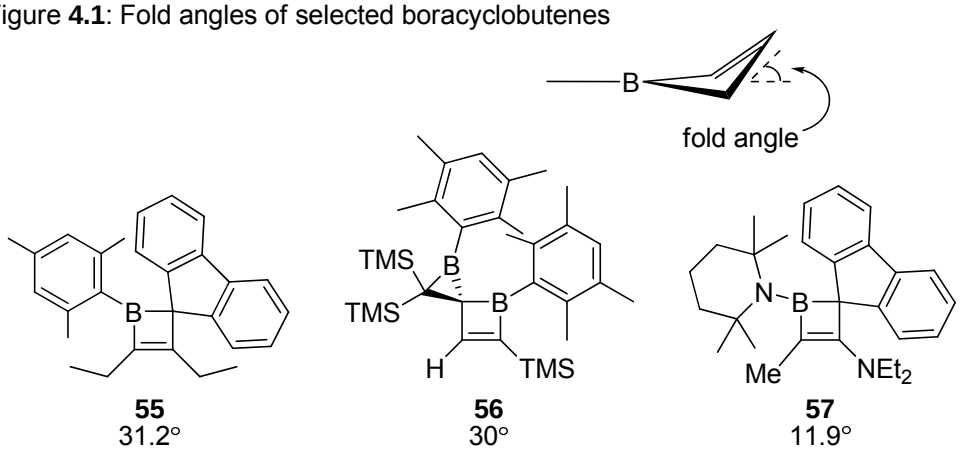
coupling effect, NMR analyses of organoboranes are often conducted at other than ambient temperature. Cooling an NMR sample increases the viscosity of the solvent, which induces faster relaxation and interconversion between the different ^{11}B spin states (through energy transfer from the molecule to the solvent) such that nearby atoms experience a time-averaged environment.[245,246] When this rate of relaxation is fast enough (it must be greater than the boron-carbon coupling constant, J_{BC}), the quartet lines merge and a sharp singlet is observed; it is said that the ^{11}B has become "self-decoupled" from ^{13}C.[247] Conversely, warming a sample decreases the quadrupolar relaxation rate (a lower viscosity solvent causes faster molecular tumbling and slower spin relaxation), resulting in a broader resonance, or, as the B-C coupling is resolved, the expected 1 : 1 : 1 : 1 quartet.[246] However, this does not account for the overall averaging of signals that occurs at elevated temperatures, which makes the observed spectrum a combination of the average NMR parameters of each individual species present.[247] Thus, if restricted rotation or multiple conformations of a given molecule arise at low temperature, the averaging that transpires in the fast-exchange regime may provide signals with improved resolution. The most common practice is to cool the NMR sample for better resolution, however the temperature dependent variables are difficult to predict. Alternatively, many compounds are simply reported with data collected at the standard temperature (~ 25 °C), with the understanding that carbon signals for nuclei attached to boron are generally not observed. Considering the relative novelty of the targeted class of compound, that option is not available. Most of the new boracyclobutenes reported herein were spectroscopically characterized at both 27 °C and 60 – 80 °C, with the higher temperature consistently providing the expected signals and correlations with good resolution.

Ab initio Hartree-Fock calculations predict an optimized non-planar structure for boracyclobutenes with a fold angle of 28°.[248] Based on an analysis of the electron density calculated for a hypothetical unsubstituted boracyclobutene, the majority of the electron density is centred around the olefinic carbons, however some delocalization of the π-electrons from the olefin to the empty p orbital on boron occurs; by comparison, the isoelectronic cyclobutenyl cation is considered to have greater delocalization.[248]

Solid state structures, available for a handful of highly-substituted boracyclobutenes, exhibit varying degrees of folding in the four-membered ring.

Molecules containing electron-deficient boron atoms appear to have strong 1,3-transannular interactions with the β-ring carbon. Boracyclobutenes **55**[140] and **56**[141] bearing aromatic substituents have fold angles of 31.2° and 30°, respectively (Figure **4.1**). Conversely, boracyclobutene **57** with an electron-releasing nitrogen substituent on boron has a fold angle of only 11.9°.[151] Based on the limited information, it is reasonable to postulate that donation of electron density from the lone pair of electrons on nitrogen to the empty p orbital on boron decreases electron deficiency and, consequently, the extent of 1,3-bonding interactions with the olefinic π bond.

Figure **4.1**: Fold angles of selected boracyclobutenes



55
31.2°

56
30°

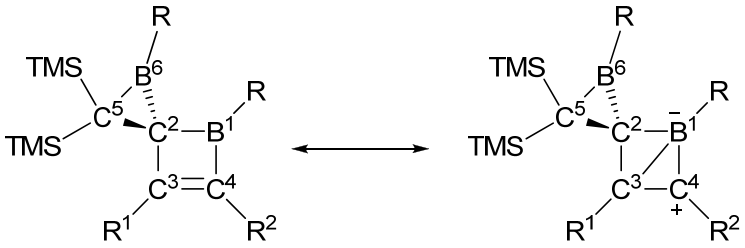
57
11.9°

NMR data for spiro-diboracyclobutenes support the contention of a 1,3-bonding interaction (Table **4.1**). The boracyclobutene boron (δ = 32 – 45 ppm) is shielded relative to a trialkylborane (δ ~ 80 ppm) and close to the expected range for a tetracoordinate boron atom. The neighbouring olefinic carbon is deshielded (δ = 164 – 195 ppm), whereas the β-carbon is relatively shielded (δ = 135 – 168 ppm). Additionally, the β-carbon signal appears broadened at room temperature, indicative of coupling with boron.[150] The zwitterionic resonance structure shown with Table **4.1** illustrates the contribution of the bonding interaction between the β-carbon and boron.[68]

2-Borolenes (4,5-dihydroboroles, 2-boracyclopentenes, *i.e.* **58** in Figure **4.2**) exhibit less-exceptional NMR characteristics that more closely resemble those observed for unstrained alkenylboranes. For a series of 2-borolenes unsubstituted except at boron, C2 is in the range 131.6 – 140.0 ppm whereas C3 is downfield between 162.0 – 178.7 ppm. Both C2 and C5 are broadened due to quadrupolar coupling with boron. The NMR

signals for 2-borolene **58** are shown in Figure **4.2**; the α-alkenyl carbon is upfield of the β-alkenyl carbon by 37 ppm and the boron signal appears at 73.9 ppm.[249,250] In acyclic alkenylboranes, the α-alkenyl carbon signal is also upfield of the β-alkenyl carbon signal.[251] This common trend can be explained by $\pi_{C=C} \rightarrow p_B$ electron donation (Figure **4.3**), which deshields the β-alkenyl carbon, as well as an electropositive boron atom bonded to the α-carbon. Note that this is opposite to that observed for the series of spiro-diboracyclobutenes.

Table **4.1**: ^{11}B and ^{13}C NMR spectroscopic data for spiro-diboracyclobutenes



R	R^1	R^2	$\delta(^{11}B^1)$	$\delta(^{11}B^6)$	$\delta(^{13}C^3)$	$\delta(^{13}C^4)$	$\delta(^{13}C^2)$	$\delta(^{13}C^5)$
Dur	Me	Me	-	-	155.8	164.5	51.2	24.6
Dur	Et	Et	-	-	162.7	166.2	47.9	24.8
Dur	$SnMe_3$	3,5-(^{t}Bu)$_2$-C_6H_3	-	-	167.8	179.6	55.7	28.7
Dur	H	TMS	32	69	154.3	176.1	53.1	24.7
^{t}Bu	H	TMS	45	80	153.3	185.7	53.6	29.4
^{t}Bu	Me	Me	34.5	83	143.2	185.5	53.6	27.7
^{t}Bu	H	^{t}Bu	40	81	135.1	195	56.5	27.9
^{t}Bu	Ph	Ph	-	-	137.1-144.8	180.1	56.2	27.0

Figure **4.2**: NMR signals for 2-borolene **58**

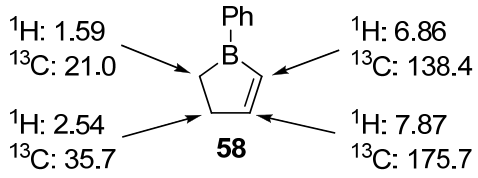
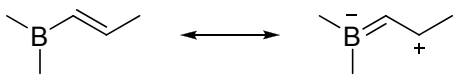


Figure **4.3**: $\pi_{C=C} \rightarrow p_B$ canonical resonance structure

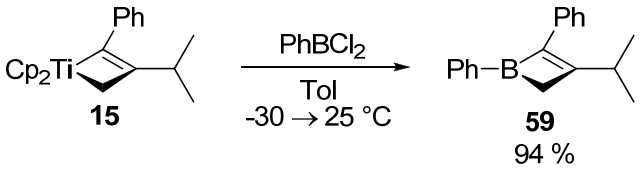


4.2 Results and Discussion

A number of factors influence the transmetallation of titanacyclobutenes, but the results diverge markedly for complexes bearing different α-olefinic (C2) substituents. As such, this discussion is divided based on that observation.

2-Phenylboracyclobutenes: Synthesis and Optimization

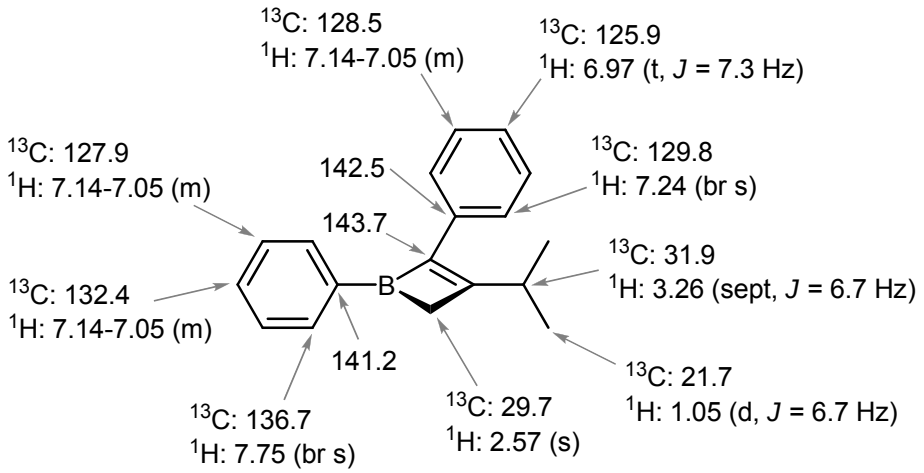
Boracyclobutene **59** was prepared from the analogous titanacyclobutene complex by treatment with a toluene solution of dichlorophenylborane at -30 °C under a rigourously inert atmosphere (Equation **4.2**). As the reaction warmed to room temperature, the solution colour changed from dark red to the lighter red colour of soluble Cp_2TiCl_2, which typically occurs within 4 hours. Work-up entailed sequential removal of volatiles *in vacuo*, trituration of the boracyclobutene into hexanes, filtration through Celite, and removal of solvents again. This provided the target molecule as an analytically pure amorphous yellow powder in excellent yield.



Equation **4.2**

Using ^{11}B NMR spectroscopy, the only observable signal for **59** is a broad singlet at 78.0 ppm, which falls within the range expected for a trialkylborane. If the alkenyl and phenyl substituents are taken into account, 78.0 ppm may be somewhat downfield of the predicted chemical shift value. By means of ^{1}H NMR spectroscopy at 27 °C in C_6D_6, the furthest downfield signal appears as a broad singlet at 7.75 ppm, which is assigned to the *ortho* protons of the phenyl ring attached to electrophilic boron, with the observed broadening probably due to restricted rotation (three-bond quadrupolar broadening seems less likely, particularly because the *o*-phenyl carbons are not broadened). A slightly broadened resonance at 7.24 ppm is assigned to the C2 phenyl *ortho* protons, with the remaining aromatic proton signals observed between 7.14 – 6.97 ppm. The ring methylene protons are observed as a singlet at 2.57 ppm and the isopropyl methine proton as a septet at 3.26 ppm. Figure **4.4** illustrates the respective assignments.

Figure **4.4**: ^{1}H and ^{13}C NMR signals for boracyclobutene **59** at 27 °C in C_6D_6

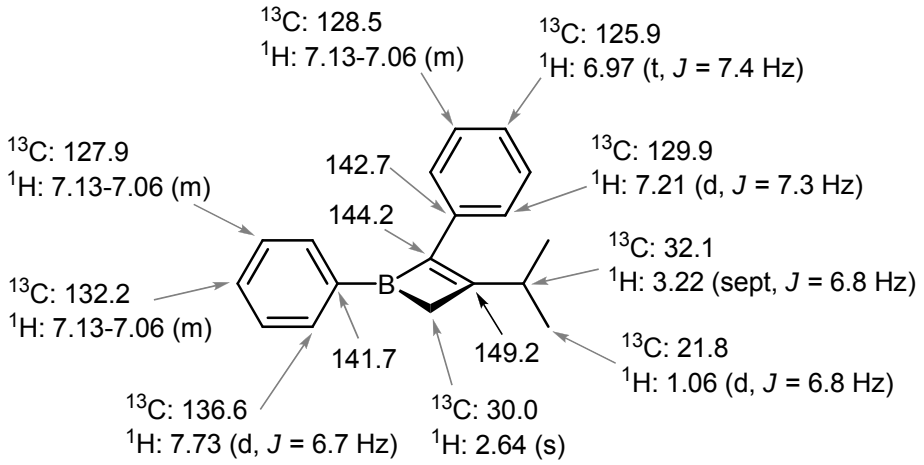


The furthest downfield signal in the ^{13}C NMR spectrum obtained at 27 ºC appears at 143.7 ppm, assigned to olefinic carbon C2 based on HMBC data (*vide infra*). C4, the sp^3-hybridized ring carbon of boracyclobutene **59**, is observed at 29.7 ppm, a chemical shift that expectedly falls between the sp^3-hybridized carbons (C4 and C5) in 2-borolene **58** (refer to Section 4.1). As a result of quadrupolar coupling, the carbons directly bonded to boron appear broadened; additionally, the C3 olefinic carbon is *not* observed at 27 °C, which suggests that there may be significant bonding interactions between boron and C3, as previously proposed.[248] The *ipso*-phenyl carbons are observed at 142.5 ppm and 141.2 ppm for the C2 phenyl and B1 substituents, respectively; other aromatic carbon resonances fall between 136.7 and 125.9 ppm, in the expected region. Resonances from the isopropyl substituent are observed at 31.9 ppm and 21.7 ppm for the methine and methyl carbons, respectively. These assignments are shown in Figure **4.4**.

2D NMR spectroscopic techniques were used to confirm the assignments, although some of the expected correlations were not observed. COSY correlations were used primarily to assign the aromatic protons of each phenyl substituent, in particular the *ortho* and *para* protons of the C2 phenyl ring (δ 7.24 ↔ δ 6.97 ppm). HMQC and HMBC correlations differentiated the aromatic carbons, and confirmed the assignments for the methylene hydrogens and carbon. The key HMBC correlation occurs between the methylene ring protons at 2.57 ppm and a signal at 143.7 ppm, assigned to the C2 α-olefinic carbon. Many other correlations were not observed at 27 °C.

At a temperature between 40 and 60 °C, free rotation of the phenyl substituent on boron is attained, which is evident by the sharpening of the *ortho* proton signals. At 80 °C, the ^{1}H NMR spectrum of boracyclobutene **59** displays each set of *ortho* phenyl protons as a doublet instead of as a broad singlet. Otherwise, the spectrum is similar to that obtained at 27 °C, with minor changes in the observed chemical shifts. At 80 °C, the ^{13}C NMR spectrum has improved resolution and all of the carbon signals are observable. Other than slight shifts in the previously observed resonances (< 1 ppm) and sharper peaks, a new broad signal is present at 149.2 ppm that is assigned to C3. Figure **4.5** illustrates the assignments.

Figure **4.5**: ^{1}H and ^{13}C NMR signals for boracyclobutene **59** at 80 °C in C_6D_6



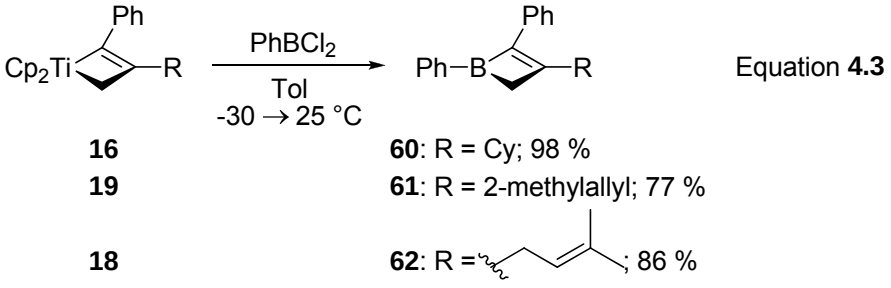
Complete assignment of signals to specific ring carbons was possible using the improved 2D NMR data obtained at 80 °C; pertinent data is summarized in Table **4.2**. Two HMBC correlations were particularly helpful in making assignments: the correlation between the isopropyl methyl hydrogens and 149.2 ppm (C3) and the correlation between the *ortho* C2-phenyl hydrogens and 144.2 ppm (C2). Long-range HMBC correlations (*i.e.* > 3 bonds; see Table **4.2**: C^4H_2 to *o*-Ph, δ 2.64 ↔ δ 129.9) were noted, and were frequently observed for other boracyclobutenes and titanacyclobutene complexes. Due to the presence of extended conjugation, long-range coupling is not a surprising occurrence.

Table **4.2**: 2D NMR correlations for boracyclobutene **59** at 80 °C[a]

^{1}H NMR	HMQC	HMBC
δ 7.21 (*o*-Ph*H*)	δ 129.9	δ 144.2 (C2), 129.9 (*o*-Ph), 125.9 (*p*-Ph)
δ 3.22 (C*H*)	δ 32.1	δ 149.2 (C3), 144.2 (C2), 30.0 (*C*H$_2$), 21.8 (*C*H$_3$)
δ 2.64 (C^4*H*$_2$)	δ 30.0	δ 149.2 (C3), 144.2 (C2), 141.7 (*ipso*-Ph), 129.9 (*o*-Ph)
δ 1.06 (C*H*$_3$)	δ 21.8	δ 149.2 (C3), 32.1 (*C*H), 21.8

a) C_6D_6, ^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz

Following the same procedure used for the preparation of **59**, several other 2-phenylboracyclobutenes were synthesized in good to excellent yield (Equation **4.3**). Analytical samples were prepared by precipitation from hexanes at -30 °C, but material of greater than 95 % purity was easily obtained during the initial separation from Cp_2TiCl_2 by-product by extraction into hexanes. Crystalline material was never isolated despite numerous attempts in that regard. Unexpectedly, the 2-phenyltitanacyclobutene complex bearing a benzyl substituent at C3 (*i.e.* Equation **4.3**, R = Bn) reacted too slowly to obtain pure material; while the reaction proceeded cleanly over two days, longer reaction times resulted in formation of undesired by-products (possibly phenylboronic acid derivatives based on an observation of broad ^{1}H NMR signals downfield of 8 ppm), despite performing the reaction under a rigourously inert atmosphere.



Equation **4.3**

2-Phenylboracyclobutenes **60** – **62** exhibited closely analogous NMR characteristics to those observed for boracyclobutene **59**, specifically: one of the carbon signals is not observed at 27 °C but is visible as a broad downfield resonance between 140 and 150 ppm at 80 °C; many of the expected HMQC and HMBC correlations are absent at 27 °C but observable at 80 °C; and broadened peaks are observed for both sets

of *ortho*-phenyl hydrogens. Table **4.3** contains the representative 1D NMR data for this set of four boracyclobutenes. Detailed correlational NMR analyses were performed, similar to those presented above, providing data fully consistent with the assigned structures.

Table **4.3**: 1D NMR data at 27 °C and *(80 °C)*[a] for 1,2-diphenylboracyclobutenes[b]

Boracyclobutene:	**59**	**60**	**61**	**62**
C3 substitutent:	^{i}Pr	Cy	2-methylallyl	3-methylbut-2-enyl
CH_2	2.57 *(2.64)*	2.63 *(2.64)*	2.85 *(2.86)*	2.86 *(2.89)*
C2	143.7 *(144.2)*	144.2 *(144.6)*	140.1 *(141.2)*	141.2 *(141.4)*
C3	n.o. *(149.2)*	n.o. *(148.6)*	146.8 *(147.5)*	n.o. *(145.2)*
C4	29.7 *(30.0)*	31.4 *(31.8)*	34.8 *(35.0)*	35.7 *(35.7)*
ipso-Ph	142.5 *(142.7)*	142.5 *(142.8)*	142.1 *(142.4)*	144.6 *(144.0)*
B-*ipso*-Ph	141.2 *(141.7)*	141.2 *(141.6)*	n.o. *(140.8)*	143.0 *(142.9)*
B	78.0	80.4	75.5	71.3

a) bracketed and italicized data collected at 80 °C;
b) C_6D_6, ^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz; n.o. = not observed

It is not clear why C3 in **61** is observable at 27 °C but the B1 *ipso*-phenyl carbon is not, whereas the opposite is true for the other three 2-phenylboracyclobutenes. Otherwise, the assignments are consistent within the series and 2D NMR analysis supports the above formulations. The β-olefinic carbon is found downfield of the α-olefinic carbon in all cases, albeit not by a substantial amount (~ 4 – 6 ppm). This correlates to the trend observed for 2-borolenes and acyclic alkenylboranes, however for those compounds, the difference in chemical shift is typically much larger. As previously noted in a series of spiro-diboracyclobutene complexes (refer to Table **4.1**), there is also

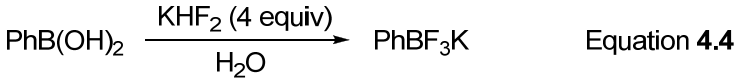
broadening of the β-carbon signal due to coupling with boron. Based on the ^{13}C NMR data of the 1,2-diphenylboracyclobutenes prepared by this transmetallation, there appears to be weaker 1,3-bonding character than observed in Berndt's spiro-diboracyclobutenes.

There are several additional technical notes with respect to optimization of this methodology: reactions conducted on small scale (< 100 mg) were cleaner, however pure material was also obtained from reactions using 1 g of titanacyclobutene complex provided a 1 – 2 mL hexanes wash is included in the work-up immediately before trituration. For additional purification, 2-phenylboracyclobutenes can be precipitated at -30 °C as amorphous powders in high yield from saturated hexanes solution. Due to low solubility in hexanes (~ 0.1 M), extraction is time consuming but progress can be roughly monitored by the deepness of colour. Reactions initiated at -30 °C or below and allowed to warm to room temperature by atmospheric convection are ideal. Undesired side reactions occur if $PhBCl_2$ is added at room temperature, and the reaction does not go to completion if maintained at -30 °C; further temperature-related optimization was not conducted. Toluene was identified as the most effective solvent from a limited selection; ethers and nitriles[252] react with $PhBCl_2$ while use of hexanes produced slightly impure material. Reduction of the Cp_2TiCl_2 co-product to $[Cp_2TiCl]_2$ by using aluminum foil in the presence of the boracyclobutene was explored as a work-up procedure, but degradation of the desired product occurs as well.

Dichlorophenylborane, the transmetallation reagent used to this point, is very sensitive, decomposing rapidly in air. It is also the only readily available dichloroborane. However, potassium alkyl- and aryltrifluoroborate salts are quite stable, easy to prepare, and can be purchased inexpensively. These salts have found uses primarily in transition metal-catalyzed cross-coupling reactions and for *in situ* generation of difluoroboranes.[253-255] With an eye towards expanding the reaction scope while simplifying the methodology, potassium phenyltrifluoroborate was investigated for applicability in the titanium-to-boron transmetallation process. The compound was synthesized easily from phenylboronic acid and potassium hydrogen fluoride (KHF_2) by a literature procedure (Equation **4.4**).[256]

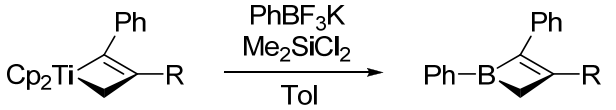
No reaction occurs between $PhBF_3K$ and titanacyclobutene complexes when heated at 110 °C for several days in toluene. Thus, a means of generating

difluorophenylborane from $PhBF_3K$ *in situ* was sought. In addition to formation at temperatures in excess of 250 °C, difluorophenylborane can be generated in the presence of various additives.[253,254,257] Of the reagents tested (LiCl, LiBr, LiI, TMS-Cl, $BF_3{\cdot}OEt_2$), dichlorodimethylsilane (Me_2SiCl_2) produced the best results for transmetallation. Five equivalents or more of Me_2SiCl_2 were generally used because reactions did not consistently go to completion with smaller amounts. Presumably, Me_2SiCl_2 works like TMS-Cl as a fluorophile that assists B-F bond heterolysis to generate $PhBF_2$,[257] although $PhBF_3K$ reacts with $SiCl_4$ to form $PhBCl_2$, promoting exchange as well as fluoride abstraction.[258,259]



Equation **4.4**

Boracyclobutenes are obtained upon heating 2-phenyltitanacyclobutene complexes with $PhBF_3K$ and Me_2SiCl_2 in sealed bombs at 80 °C for 12 hours (Equation **4.5**). The solution changes slowly to a green-red colour with concomitant formation of predominantly red crystals, identified as a mixture of Cp_2TiX_2 complexes (X = F, Cl). Small amounts of green crystals, presumably $[Cp_2TiX]_2$, are also formed. Removal of solvent followed by extraction into hexanes afforded pure boracyclobutene **59** in 60 % yield; ^1H and ^{13}C NMR data are identical to that prepared from $PhBCl_2$, however the yield is substantially lower (*cf.*, 94 %).



Equation **4.5**

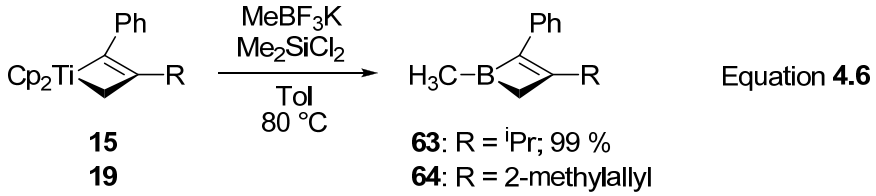
15
16
19

59: R = ^{i}Pr; 60 %
60: R = Cy; 55 %
61: R = 2-methylallyl; 48 %

Yields of boracyclobutenes **60** and **61** were also diminished in reactions using the $PhBF_3K$ protocol (Equation **4.5**). The decrease in effectiveness may result from the higher reaction temperatures or the less efficient Ti/B exchanges mediated by fluoride compared to chloride. Reactions do not proceed at 25 °C, probably due to an inherently

high energy barrier to $PhBF_2$ formation, although low solubility of the salts in toluene may also be a factor. To improve the solubility of the potassium salt, 18-crown-6 ether was added to the reaction mixture prior to heating. NMR spectroscopy of the crude material from this reaction indicated that no boracyclobutene forms; signals downfield of 8 ppm were noted in the ^{1}H NMR spectrum, which are often indicative of *ortho*-phenyl protons of phenylboronic acid derivatives (*i.e.* $PhBF_2$ likely reacted with the crown ether). Tetraalkyl ammonium salts are more soluble than potassium complexes, so $PhBF_3{\cdot}NBu_4$ was prepared;[260] the use of this reagent leads only to decomposition of titanacyclobutene complexes without formation of boracyclobutene.

Because anhydrous conditions are required regardless of the boron transmetallating reagent, the most useful feature of the RBF_3K salts is that they are easily prepared in anhydrous form from boronic acids or esters. This makes potassium aryl- and alkyltrifluoroborate salts ideal for investigating the range of organic boron substituents for which transmetallation occurs, despite the lower yields obtained. Potassium methyltrifluoroborate, purchased from Aldrich, transmetallates readily with 2-phenyltitanacyclobutenes in the presence of Me_2SiCl_2 (Equation **4.6**). Following the typical work-up protocol, analytically pure boracyclobutene **63** was obtained in 99 % yield. Boracyclobutene **64** was isolated as a red oil that could not be separated from the titanocene by-product by precipitation: the impure mixture was characterized spectroscopically, with HRMS (electron impact) used to determine the composition of the product.



Equation **4.6**

Pertinent NMR data for 1-methylboracyclobutenes **63** and **64** are summarized in Table **4.4**. ^{1}H NMR spectroscopy of complex **63** displays a broad singlet at 2.70 ppm for the C4 methylene, essentially the same chemical shift as for the analogous 1,2-diphenylboracyclobutene. Signals for the methyl substituent on boron are shifted

upfield due to the electropositive boron atom. C2 is not observed at 27 °C but appears as a broad peak at 134.9 ppm at 60 °C. The signals for C3 and C4 are observed at 157.8 ppm and 42.4 ppm, respectively, the latter of which is also broadened. ^{11}B NMR exhibited a single broad peak at 78.1 ppm, within the range observed for 1,2-diphenylboracyclobutenes. Boracyclobutene **64** has similar chemical shifts for ^{1}H, ^{13}C and ^{11}B NMR. In comparison to 1,2-diphenylboracyclobutenes, carbons C3 and C4 are shifted downfield for 1-methyl-2-phenylboracyclobutenes, while C2 is relatively upfield; this may be indicative of increased resonance delocalization from the olefinic π-bond to the empty boron p-orbital, decreased 1,3-bonding interactions due to a stronger inductively electron-releasing methyl-substituent, or a combination of both effects.

Table **4.4**: 1D NMR data for 1-methyl-2-phenylboracyclobutenes at 27 °C[a]

Boracyclobutene:	**63**	**64**
C3 substituent:	^{i}Pr	2-methylallyl
B-CH_2	2.70	2.87
B-CH_3	0.75	0.72
C2	134.9[b]	140.6
C3	157.8	151.1
C4	42.4	43.8
ipso-Ph	146.0	145.7
B-*C*H$_3$	13.7	13.6
B	78.1	76.5

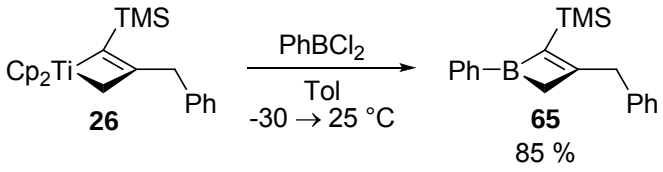
a) C_6D_6, ^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz. b) 60 °C

Potassium isopropyltrifluoroborate does not react with 2-phenyltitanacyclobutene complexes under the standard conditions, and longer reaction times at higher temperatures resulted only in decomposition. The same is observed for reactions with potassium mesityltrifluoroborate, which was prepared by literature procedure.[261] Both of these boron substituents are larger than those that do successfully transmetallate, so the reaction appears to be limited by sterically hindered boranes.

2-(Trimethylsilyl)boracyclobutenes and 2-tert-butylboracyclobutenes: Synthesis and Optimization

The next series of titanacyclobutene complexes investigated bore 2-trimethylsilyl substituents; successful transmetallation of this series would increase the scope and generality of the reaction. However, significant steric and electronic differences exist between the two types of complexes: 2-(trimethylsilyl)titanacyclobutenes are sterically more hindered at C2, while the TMS substituent is electron donating.

2-(Trimethylsilyl)titanacyclobutene complexes undergo transmetallation, albeit with concomitant formation of unidentified by-products. Boracyclobutene **65** is obtained as a green oil by transmetallation of the corresponding titanacyclobutene complex with one equivalent of $PhBCl_2$ at -30 °C in toluene (Equation **4.7**). As before, once toluene was removed under vacuum, the crude material was triturated into hexanes and filtered through Celite. Cooling of this concentrated hexanes solution to -30 °C causes precipitation of a small amount of fine green powder, identified as $[Cp_2TiCl]_2$ by combustion analysis; however, the majority of the titanium by-product is isolated as red crystals of Cp_2TiCl_2. Boracyclobutene **65** is significantly more soluble in hexanes than any of the 1,2-diphenylboracyclobutenes, and even the most concentrated solutions failed to crystallize or precipitate the product.



Equation **4.7**

Despite repeated precipitation cycles, ^{1}H NMR spectroscopy provides evidence of persistent impurities, with resonances largely in the aromatic region and upfield of 0.5 ppm. The same ratio of product and impurities is reproducibly obtained, but the impurities could not be identified. Using hexamethylbenzene as an internal NMR standard, the solid material was determined to be approximately 76 % boracyclobutene **65** by weight, equalling a chemical yield of 85 %. Due to the green colour of the isolated oil, slightly broadened NMR signals noted for some of the impurity resonances, and the otherwise relatively clean NMR spectra, a Ti(III) species is likely present.

^{1}H NMR spectroscopy of impure **65** provided some interesting data. The TMS hydrogens are detected at 0.28 ppm, as expected, but the benzylic protons are inequivalent and appear as mutually coupled doublets at 4.26 and 3.59 ppm, with coupling constants of 14.6 – 14.7 Hz. The C4 hydrogens are also observed as individual doublets at 2.57 and 2.43 ppm, with coupling constants of 18.7 – 18.8 Hz, respectively. Note that for the initial titanacyclobutene complex, two singlets are observed for each set of corresponding hydrogens. The inequivalency within the two sets of protons could be caused by a number of factors: restricted rotation of a substituent; a tetrahedral boron atom from coordination with another species in solution; or a slow boracyclobutene ring inversion. When heated to 90 °C, neither set broadens nor coalesces, which renders restricted rotation an unlikely explanation. It also points away from a slow ring inversion on the NMR timescale, unless, as is possible, there is a very strong 1,3-bonding interaction in 2-(trimethylsilyl)boracyclobutenes.

Using ^{13}C NMR spectroscopy, the ring carbons of 2-(trimethylsilyl)boracyclobutene **65** are observed at 145.8 153.4, and 39.8 ppm for C2, C3, and C4, respectively. These chemical shifts are 1 – 10 ppm downfield of those observed for 1,2-diphenylboracyclobutenes, which is a smaller difference than noted for the analogous titanacyclobutene complexes (8 – 25 ppm). One possible explanation is that decreased shielding of the ring carbons is a result of increased electron donation from the olefinic carbons to the empty p-orbital on boron; this could be assisted by hyperconjugative stabilization of the partial build-up of positive charge at C3 with the adjacent C-Si bond (direct hyperconjugation to the empty p-orbital on boron is not likely, since the orbitals in question are not oriented for optimal overlap). However, decreased shielding may also be attributable to negative $\pi_{C=C} \rightarrow \sigma^*_{Si-C}$ hyperconjugation[199] and, for C2, β-carbon effects.[200]

A COSY correlation between 4.26 ppm and 7.48 ppm was used to distinguish between the C4 hydrogens and the benzylic hydrogens (in addition to the difference in chemical shift and HMBC data). HMQC data were used to assign the majority of the carbon signals, and each set of inequivalent protons correlated to a single carbon. HMBC correlations of the benzylic hydrogens and C4 hydrogens were used to identify the olefinic ring carbons, C2 and C3. However, it was the HMBC correlation between the

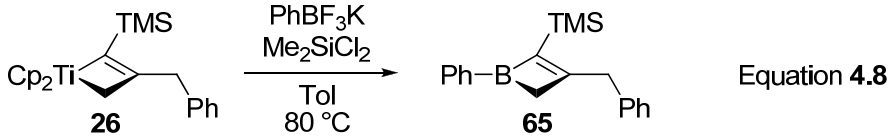
TMS hydrogens and 145.8 ppm that was most instructive for assigning C2. The 2D NMR data is summarized in Table **4.5**. In contrast to the majority of 2-phenylboracyclobutenes, complete characterization of **65** was possible at 27 °C.

Table **4.5**: HMQC and HMBC data for boracyclobutene **65**[a]

^{1}H NMR	HMQC	HMBC correlations
δ 4.26/3.59 (CH_2-Ph)	δ 47.6	δ 153.4 (C3), 145.8 (C2), 140.9 (*ipso*-Ph), 129.5 (*o*-Ph), 39.8 (C4)
δ 2.57/2.43 (C$^4H_2$)	δ 39.8	δ 153.4 (C3), 145.8 (C2)
δ 0.28 (TMS)	δ 1.6	δ 145.8 (C2), 1.6 (TMS)

a) 27 °C, C_6D_6, ^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz.

Using the previously described protocol, transmetallation of a 2-(trimethylsilyl)titanacyclobutene complex was also achieved by using $PhBF_3K$ in the presence of Me_2SiCl_2 at 80 °C (Equation **4.8**). A green oil was isolated in low yield, while ^{1}H and ^{13}C NMR analysis proved that undesired side reactions were occurring to a greater extent under these conditions; $PhBCl_2$ was selected as the better reagent for transmetallation in this case.

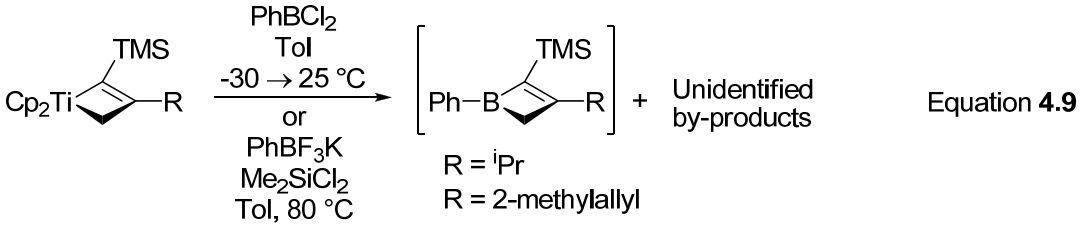


Equation **4.8**

All attempts to separate the persistent impurities from boracyclobutene **65**, prepared by either protocol, were to no avail. The ratio of boracyclobutene to impurity remained unchanged through successive extractions and over numerous reactions. Consequently, some control experiments were conducted to explore the possibility of a desilylation side-reaction. 2-(Trimethylsilyl)titanacyclobutene complexes do not react rapidly with potassium phenyltrifluoroborate, although a small amount of decomposition occurs in toluene solution over multiple days at 80 °C. Likewise, 2-(trimethylsilyl)boracyclobutene **65** does not react with $PhBF_3K$ and Me_2SiCl_2. At room temperature, trimethylvinylsilane does not react with $PhBCl_2$, Cp_2TiCl_2, $[Cp_2TiCl]_2$, or

any combination of the reagents, although slow decomposition does occur at 45 °C. Despite inconclusive results from the control experiments, the presence of a reactive halide species in solution may be incompatible with a silane-containing material. However, the simplest explanation is that significant steric bulk in the C2-substituent is detrimental to transmetallation.

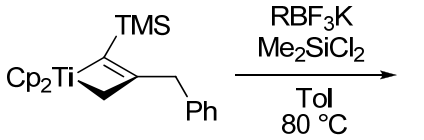
Other 2-(trimethylsilyl)titanacyclobutene complexes gave even poorer results. Titanacyclobutene complexes bearing β-isopropyl and β-methylallyl substituents underwent transmetallation too slowly to be effective (Equation **4.9**). For both complexes, ^{1}H NMR analysis clearly exhibited signals from boracyclobutene and unreacted titanacyclobutene, however the reaction could not be coaxed to completion before significant decomposition of the boracyclobutene occurred. This was mildly surprising since 2-(trimethylsilyl)boracyclobutene **65** demonstrated no tendency to decompose upon storage for long periods under an inert atmosphere, even in solution. It is noteworthy that, while transmetallation is not clean and products are not isolated, these boracyclobutenes also show diastereotopic C4 hydrogens, inequivalent on the NMR time scale.



Equation **4.9**

The use of other boron transmetallation reagents failed to produce boracyclobutenes from 2-(trimethylsilyl)titanacyclobutene complexes as well. $MesBF_3K$, $^{i}PrBF_3K$, and $MeBF_3K$, in the presence of Me_2SiCl_2, do not react with any of the 2-(trimethylsilyl)titanacyclobutene complexes studied (Equation **4.10**). Starting material is recovered in near quantitative yield under the standard conditions, while extended reaction times simply lead to slow decomposition. Consequently, the only 2-(trimethylsilyl)boracyclobutene characterized was **65**, albeit in impure form. The easiest explanation for this limitation is that sterically hindered C2 substituents inhibit the transmetallation, promoting unidentified reaction pathways. Alternatively, trimethylsilyl

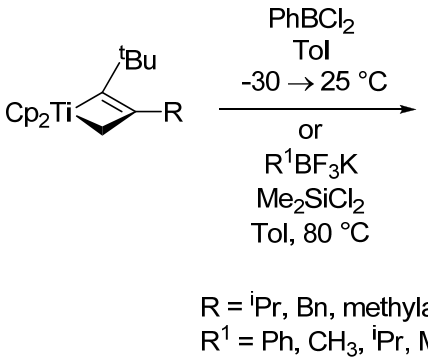
groups stabilize anionic character at the α-position;[262] perhaps this effect decreases the weakly nucleophilic character at C2 of 2-(trimethylsilyl)titanacyclobutene complexes, making them less conducive to transmetallation. If this is true, however, then an inexplicable exception is found in the substantially clean synthesis of boracyclobutene **65**.



No reaction

Equation **4.10**

2-*Tert*-butyltitanacyclobutene complexes were also subjected to the standard transmetallation conditions. There was particular interest in comparing these substrates to the 2-(trimethylsilyl)titanacyclobutene complexes. Surprisingly, not a single reaction provided any evidence for the production of boracyclobutene. Three 2-*tert*-butyltitanacyclobutene complexes bearing different C3-substituents were treated under five sets of transmetallation conditions, all to no avail (Equation **4.11**). This set of titanacyclobutene complexes was not investigated further.



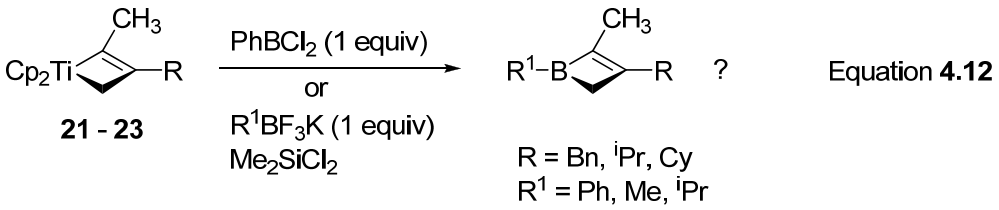
No boracyclobutene

Equation **4.11**

2-Methylboracyclobutenes: Synthesis and Optimization

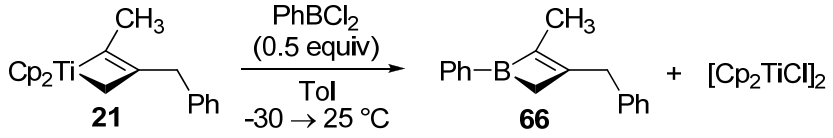
2-Methyltitanacyclobutene complexes, the final class of titanacyclobutenes studied, react differently to boron transmetallation than the other sets of substrates. Using the standard protocol, for example, titanacyclobutene complex **21** reacts with one

equivalent of $PhBCl_2$ to produce a complex mixture of products that could not be unambiguously identified, with similar results obtained from the use of $PhBF_3K$. In fact, all of the transmetallation reactions conducted using a 1 : 1 ratio of titanacyclobutene complex and boron reagent led to the formation of multiple products (Equation **4.12**).



Equation **4.12**

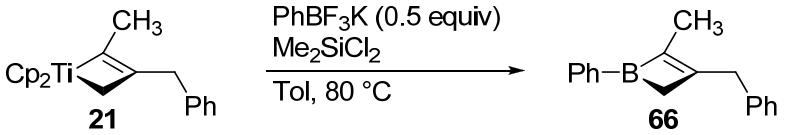
However, careful scrutiny of the ^1H NMR data from the crude product mixtures obtained from these transmetallation reactions suggested that the desired products may be present. To determine if the formation of the undesired by-products were occurring catalytically or stoichiometrically, titanacyclobutene complex **21** was treated with less than one equivalent of the boron reagent. Remarkably, the ^1H NMR spectrum of the crude product appeared cleaner while showing no sign of unreacted starting material. Following optimization of a sort, it was determined that the addition of *half* an equivalent of $PhBCl_2$ results in the formation of the spectroscopically cleanest material (Equation **4.13**). Trituration of the crude product with hexanes provided boracyclobutene **66** as an impure green oil. The green solid remaining from the transmetallation and trituration was recrystallized and identified as $[Cp_2TiCl]_2$ by X-ray crystal diffraction, not Cp_2TiCl_2, which was isolated from the transmetallation reactions of 2-phenyltitanacyclobutene complexes.



Equation **4.13**

This new information was applied to the same reaction, but using $PhBF_3K$ and Me_2SiCl_2 at 80 °C (Equation **4.14**). The boracyclobutene product from this reaction was

identical, with a slight decrease in the number and intensity of spurious signals in the NMR spectra of this material (< 5 %).



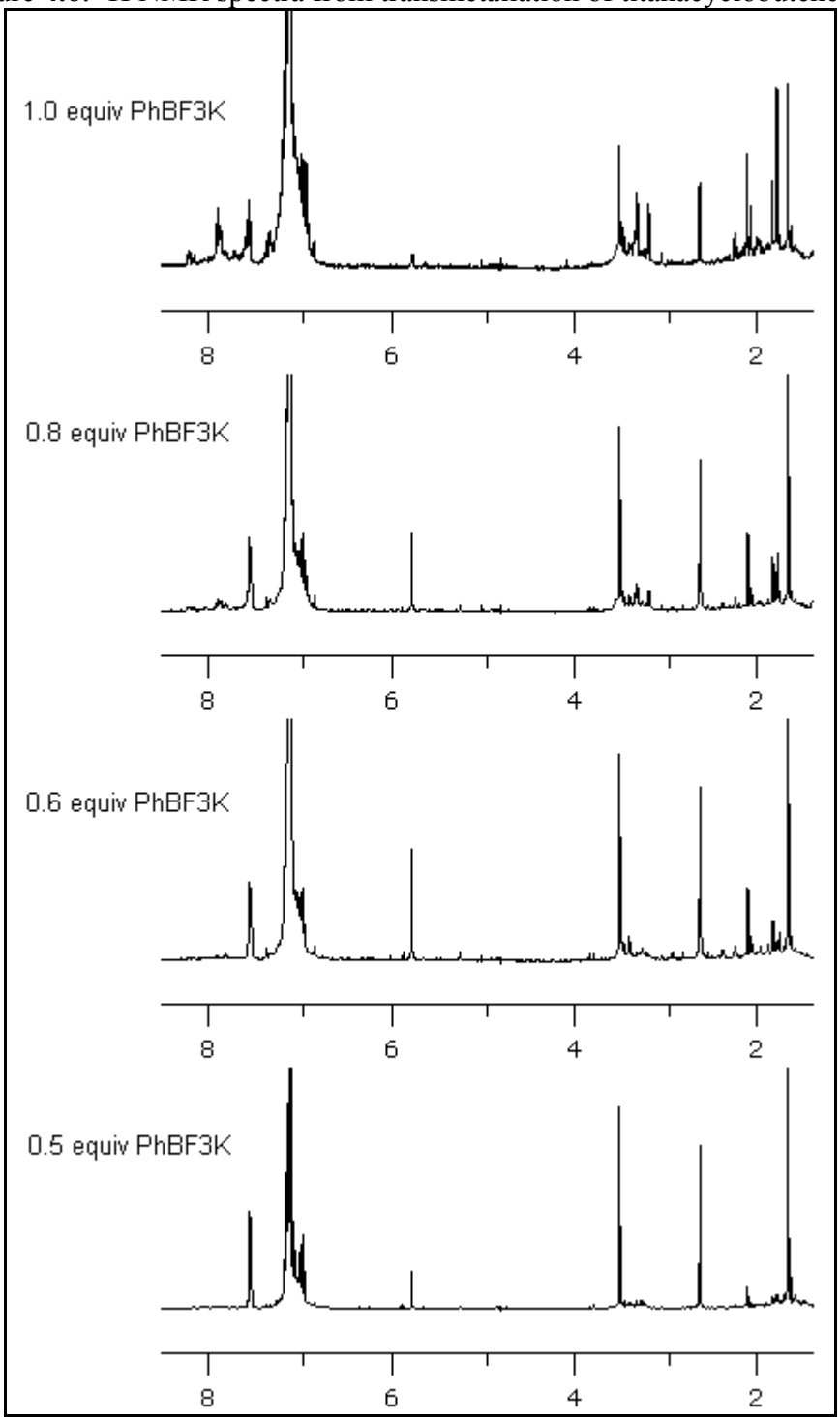
Equation **4.14**

Using a series of ^{1}H NMR spectra, Figure **4.6** illustrates the impact that varying the quantity of the boron transmetallation reagent has on the crude reaction mixture. The experiments were conducted on titanacyclobutene complex **21** with varying amounts of $PhBF_3K$ and Me_2SiCl_2 at 80 °C (*i.e.* Equation **4.14**). Using one equivalent of $PhBF_3K$, multiple undesired signals are evident, with some signals appearing quite broad. Treatment with just 0.8 equivalents of $PhBF_3K$ significantly decreases the proportion of observable by-products, as indicated by diminished signals around 7.9 ppm and between 3.5 – 1.5 ppm. The bottom spectrum in Figure **4.6**, which arises from the reaction using 0.5 equivalents of $PhBF_3K$, is the cleanest and contains minimal impurities. Reactions performed with less than 0.5 equivalents of $PhBF_3K$ returned unreacted starting material as well as the desired boracyclobutene products.

The molar quantity of isolated material from either preparative route was greater than that calculated for a quantitative transformation based on boron ("205 %" with $PhBCl_2$; "150 %" with $PhBF_3K/Me_2SiCl_2$). Using an internal hexamethylbenzene standard, the ^{1}H NMR spectrum of the crude product from the $PhBF_3K/Me_2SiCl_2$ protocol (Equation **4.14**) indicated that the material was only 44 % boracyclobutene, equalling a chemical yield of 66 %. Crystallization of boracyclobutene **66** was attempted multiple times, however concentrated cooled pentane or hexanes solutions precipitated only small amounts of $[Cp_2TiCl]_2$. The persistent green colour of the boracyclobutene oil suggested that paramagnetic Ti(III) species were still present, however the relatively sharp signals in the NMR spectra indicated that this accounted for only a small fraction of the total quantity. Reagents expected to oxidize Ti(III) complexes to spectroscopically observable Ti(IV) complexes, including BnCl, ^{i}PrI, and allyl chloride, produced no observable change by ^{1}H NMR spectroscopy. Treatment with $PbCl_2$ for the same

purpose[263] induced decomposition of the product mixture, as did inclusion of $PbCl_2$ during the reaction.

Figure **4.6**: ^{1}H NMR spectra from transmetallation of titanacyclobutene **21**[a]



a) 27 °C, C_6D_6, 300 MHz.

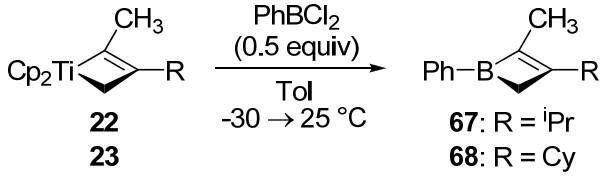
Other than the minor titanium impurity, other organic products could also be present. The optimized reaction conditions require two equivalents of 2-methyltitanacyclobutene complex for each equivalent of the boron reagent, so the organic fragment from half of the titanacyclobutene starting material remains unaccounted for. Integration of the aromatic region in the ^{1}H NMR spectrum was somewhat greater than expected, although the alkyl region was relatively clean. These NMR data are surprising, particularly if any organic by-products are present, as the spectra suggest conversion to purely aromatic compounds. Individual fractions from the initial extraction of boracyclobutene **66** were essentially identical in composition, indicating that the products could not be separated by differential solubility. Further purification, unfortunately, could not be achieved and characterization was conducted as is.

The ^{1}H NMR spectrum of the impure boracyclobutene **66** displays the characteristic downfield peaks for the *ortho*-protons of the B1-phenyl, while the other aromatic protons are overlapping with signals from the unidentified impurities and C_6D_5H. The benzylic hydrogens and C4 hydrogens are observed as typical singlets at 3.52 ppm and 2.63 ppm, respectively, and the C2-methyl substituent appears as a singlet at 1.66 ppm. Using ^{13}C NMR spectroscopy, C3 is again the furthest downfield resonance at 145.7 ppm. C2 is not observed directly at 27 °C, however HMBC correlations indicate it has a chemical shift of 130.2 ppm; at 70 °C C2 is observed as a broad peak at 130.0 ppm. The C4 resonance is broad (42.2 ppm) and the exocyclic methyl carbon appears as a sharp peak at 18.2 ppm. By means of ^{11}B NMR spectroscopy, the boron atom appears as an intense broad peak at 78.5 ppm, with a pendant small hump centred at 86.0 ppm (~ 5 %).

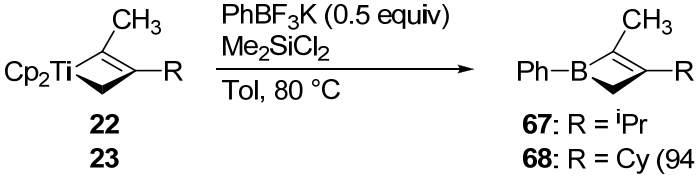
2D NMR experiments were again used to identify specific resonances. The exocyclic methyl hydrogens exhibit COSY correlations to the benzylic hydrogens at 3.52 ppm and to the C4 hydrogens at 2.63 ppm. HMQC spectroscopy provided the expected correlations. Both the exocyclic methyl group and C4 hydrogens exhibit HMBC correlations to 145.7 and 130.2 ppm, for C3 and C2, respectively; the benzylic hydrogens only correlate to C3. These data were collected at 27 °C and verified with NMR

experiments conducted at 70 °C. These data unequivocally confirm the formation of the anticipated boracyclobutene in this transmetallation.

Using half an equivalent of either $PhBCl_2$ or $PhBF_3K/Me_2SiCl_2$, 2-methylboracyclobutenes **67** and **68** were prepared and isolated as non-viscous liquids (Equations **4.15** and **4.16**). These compounds provided cleaner NMR spectra with fewer observable impurities, particularly in the case of β-isopropylboracyclobutene **67**, which may be related to the volatility of the by-products formed. Discouragingly, greater-than-quantitative yields were still obtained and purification by crystallization was not possible. In general, reactions using $PhBF_3K$ consistently appeared cleaner than those using $PhBCl_2$, and the former reagent is preferred for transmetallation of 2-methyltitanacyclobutene complexes.



Equation **4.15**



Equation **4.16**

Pertinent NMR data for 2-methyl-1-phenylboracyclobutenes is collected in Table **4.6**. Chemical shift values are consistent within the series and were confirmed individually by 2D NMR experiments. For the three compounds, C3 is consistently downfield of C2 by 15 – 22 ppm. The same relative ordering is typical of alkenylboranes in general[251] and the other boracyclobutenes synthesized by the transmetallation methodology. However, it is interesting to note that for the analogous 2-phenylboracyclobutenes, the difference in chemical shift is much smaller, between 4 – 6 ppm. More data are necessary to confirm a general trend, but this suggests that electron withdrawing substituents on boron increase the strength of 1,3-bonding interaction between the boron and C3.

Electron impact HRMS was used to confirm the molecular composition of the 2-methylboracyclobutenes. Interestingly, for heavier boracyclobutenes **66** and **68**, ions that correspond to twice the mass of the titanacyclobutene organic moiety were noted. Thus, for β-benzylboracyclobutene complex **66** (ring portion = $C_{11}H_{12}$), an ion of mass 288.18812 is observed, which corresponds to a $C_{22}H_{24}$ species within 1.1 ppm of the calculated mass. Analogously, an ion of mass 272.24992 (1.7 ppm from that calculated for $C_{20}H_{32}$) is observed from impure boracyclobutene **68** (ring portion $C_{10}H_{16}$). Analysis of unexpected mass spectral fragments is tenuous at best, however these ions are heavier than the molecular mass of the boracyclobutenes analyzed and appear in a relatively unpopulated area of the mass spectrum, which lends more credence to their assignments. Therefore, the organic material "lost" from the second equivalent of titanacyclobutene complex may be dimerizing, possibly by homocoupling of two radicals. The data from the lighter boracyclobutenes are less reliable, due to greater deviation from calculated values and the presence of additional fragments of similar mass.

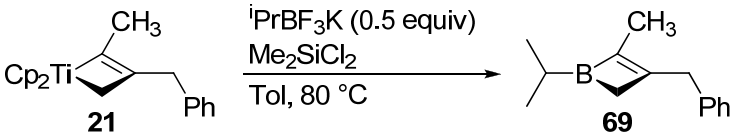
Table **4.6**: NMR data for 2-methyl-1-phenylboracyclobutenes[a]

Complex:	**66**	**67**	**68**
C3 Substituent:	Bn	^{i}Pr	Cy
C^4H_2	2.63	2.46	2.62
CH_3	1.66	1.79	1.80
C2	130.0[b]	128.7	128.0
C3	145.7	149.9	149.9
C4	42.2	33.5	37.0
C=C-CH_3	18.2	16.4	16.5
B-*ipso*-Ph	141.4[b]	140.6	140.9
B	78.2	69.0	76.0

a) 27 °C, C_6D_6, 400 MHz. b) Values obtained at 70 °C

1-Isopropylboracyclobutene **69** was prepared by treating the analogous titanacyclobutene complex with potassium isopropyltrifluoroborate in the presence of Me_2SiCl_2 (Equation **4.17**). Similar to the previous transmetallations of

2-methyltitanacyclobutene complexes, the use of half an equivalent of $^{i}PrBF_3K$ produced the cleanest ^{1}H and ^{13}C NMR spectra. After work-up however, greater than quantitative material balance was again obtained (106 % calculated based on B). The extraneous material could be neither identified nor separated despite numerous attempts.



Equation **4.17**

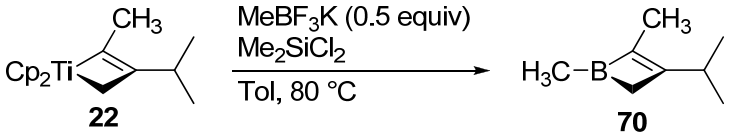
1-Isopropylboracyclobutene **69** was characterized in a similar fashion to those noted previously. In the ^{13}C NMR spectrum collected at 27 ºC, the ring carbons are observed at 131.2, 143.8, and 40.9 ppm for C2, C3, and C4, respectively. As expected, the olefinic carbons C2 and C3 are upfield of the 2-phenyl- and 2-(trimethylsilyl)boracyclobutenes; the former substituent is electron-withdrawing, whereas the latter TMS substituent is sterically bulky and causes β-carbon compression.

COSY data gives the expected correlations, including that from the exocyclic methyl group to both the benzylic hydrogens and the C4 ring hydrogens. HMQC signals were readily observable at 27 °C, in contrast to other boracyclobutenes. The olefinic ring carbons were assigned based on previously observed trends and an HMBC correlation between the benzylic hydrogens and C3 at 143.8 ppm; no correlation to C2 (131.2 ppm) is noted. High resolution mass spectrometry confirms the presence of boracyclobutene **69** in the impure mixture.

1-Methylboracyclobutene **70** was prepared from titanacyclobutene complex **22** and potassium methyltrifluoroborate by the same experimental protocol, with half an equivalent of $MeBF_3K$ producing the cleanest results (Equation **4.18**). However, in this reaction mixture, many unassigned aliphatic signals are evident by ^{1}H and ^{13}C NMR spectroscopy and boracyclobutene **70** is formed in only 20 % yield according to integration against an internal standard.

A broad singlet at 3.46 ppm is assigned to the C4 ring hydrogens of boracyclobutene **70**, further downfield than for any other boracyclobutenes reported. The

exocyclic C2-methyl group appears as a typical singlet at 1.41 ppm, whereas the methyl substituent on boron is observed as an upfield singlet at 0.81 ppm.



Equation **4.18**

The ^{13}C NMR data for **70**, collected at 80 °C for improved resolution, differ significantly from that of other boracyclobutenes, although it is unclear if this is caused by the presence of, and interaction with, the by-products or is inherent to the molecule. The signals for the two olefinic carbons are observed at 163.1 and 91.7 ppm; these values are further downfield and upfield, respectively, than noted for any other boracyclobutenes. Additionally, due to conflicting observations, it is difficult to assign the signals to specific carbons. In other boracyclobutenes prepared, C3 is broadened and upfield of C2, so the signal at 91.7 ppm is presumably C3. However, HMBC correlations between the isopropyl methyl groups and 163.1 ppm, and between the B1-methyl substituent and 91.7 ppm, suggest instead that the 163.1 ppm resonance is C3, whereas C2 appears at 91.7 ppm (Table **4.7**). Only one 1-methylboracyclobutene complex was prepared and characterized (in the presence of impurities); therefore, it is not possible to ascertain the validity of these tentative assignments.

Table **4.7**: HMQC and HMBC data of boracyclobutene **70**[a]

^{1}H NMR	HMQC	HMBC correlations
δ 3.38 (B-CH_2)	δ 66.2	δ 163.1, 91.7, 33.5 (C*H*)
δ 2.46 (C*H*)	n.o.[b]	δ 163.1, 66.2 (C4), 21.6 (CH(CH_3)$_2$)
δ 1.38 (B-C-CH$_3$)	δ 15.8	δ 163.1, 91.7
δ 0.87 (CH(CH_3)$_2$)	δ 21.3	δ 163.1, 33.5 (CH), 21.3
δ 0.74 (B-CH$_3$)	δ 8.9	δ 91.7

a) C_6D_6, 80 °C, 400 MHz; b) n.o. = HMQC correlation not observed, ^{13}C NMR: δ = 33.5.

All of the boracyclobutenes are substantially more air-sensitive than titanacyclobutene complexes and decompose rapidly upon brief exposure, which was

quite evident while performing typical characterization procedures. Whereas NMR data for titanacyclobutene complexes can be collected overnight in a standard NMR tube with the cap sealed by Parafilm, the same minimal precautions for boracyclobutene samples results in up to 30 % decomposition as judged by NMR data. Therefore, all NMR experiments requiring more than 30 minutes were conducted in a screw-cap Teflon-sealed NMR tube. Air-oxidation appears to largely result in formation of cyclic boroxines such as $(PhBO)_3$, which were tentatively identified by ^1H NMR signals downfield of 7.85 ppm.[264] Phenylboroxine was also commonly observed in the mass spectral analysis of boracyclobutenes bearing a phenyl substituent on boron, and was presumably formed in the extremely short interval between exposure to air and insertion into the spectrometer probe. In general, HRMS data were difficult to obtain and frequently required numerous analyses to identify the molecular ion. Samples for elemental analysis were particularly prone to oxidation due to the relatively lengthy time exposed to air prior to combustion; technicians reported that the mass of samples increased during weighing. Unfortunately, except for three 2-phenylboracyclobutenes, the combustion analysis data for boracyclobutenes prepared in this investigation analyze low, in large part attributable to competitive oxidation.

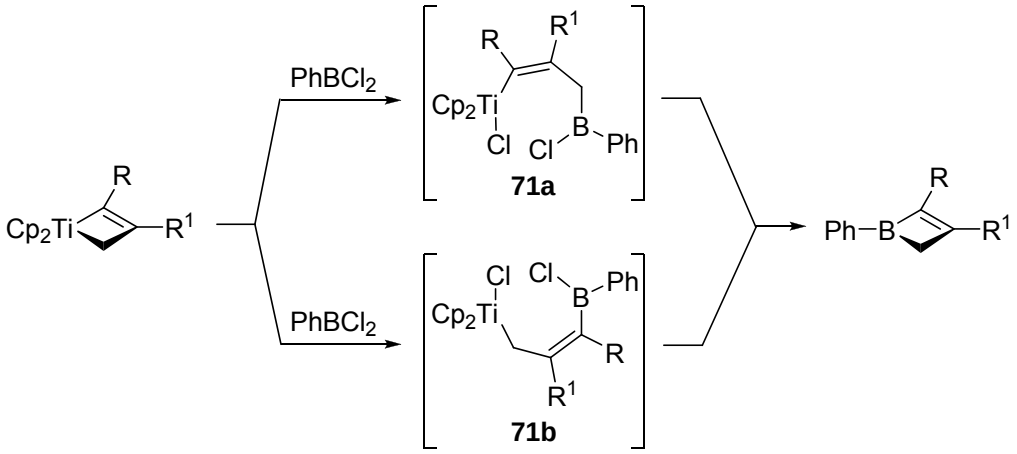
Mechanistic Implications

The reason this transmetallation from titanium to boron proceeds can be viewed in a number of ways. As discussed in Section 1.4, this transmetallation is thermodynamically favoured because the carbon ligands are transferred to the more electronegative metal (B, Pauling EN = 2.0) whereas the less electronegative metal (Ti, Pauling EN = 1.5) forms bonds with the halide ligands. Thus, the result is that the most electronegative atoms in the system, the halides, become bound to the most electropositive atom, titanium. Considered using a bond strength analysis, the Ti-Cl and B-C bonds in the products are stronger than the B-Cl and Ti-C bonds in the starting materials. Additionally, from a kinetic standpoint, the products formed are not sufficiently nucleophilic, nor electrophilic, to effect the reverse transformation.

While the mechanism of the transmetallation of titanacyclobutene complexes with boron dihalides has not been thoroughly studied, it is useful to consider likely

intermediates to formulate an explanation for the varying results. A concerted reaction is unlikely, considering the structure of the titanacyclobutene complexes and the required orientation for approach of the incoming dihaloborane. So assuming a step-wise mechanism, the initial transmetallation reaction can occur by, presumably, nucleophilic addition of either the alkyl or vinylic Ti-C bond to the electrophilic borane. This would lead to intermediates **71a** or **71b**, depicted in Scheme **4.1**; both intermediates are illustrated as acyclic, however it is possible that there is a weak B-Cl bonding interaction (i.e. Ti-$Cl^{+}\cdots B^{-}$). For either bimetallic intermediate, a second transmetallation event would then produce boracyclobutene product and Cp_2TiCl_2. For the transfer of the organic ligand, σ-bond metathesis is possible (*i.e.* a closed S_E2 transition state), although precedent also exists for an insertion mechanism that has been established for the reaction between dimethylzirconocene and borane[61] (refer to Equation **1.38**).

Scheme **4.1**: Potential transmetallation intermediates



For reference, it is reasonable to draw parallels to the established insertion chemistry of titanacyclobutene complexes, as presented in Section 1.1. To recapitulate, some reagents insert into one or the other Ti-C bond, however some reagents, such as ketones and aldehydes, react competitively at both sites. For the most part, bulky substituents on the titanacyclobutene ring, particularly at the vinylic C2 position, favour insertion into the alkyl Ti-C4 bond. Conversely, less sterically demanding methyl and alkyl substituents favour insertion into the vinylic Ti-C2 bond. The influence of the C2 substituent is balanced by the size of the incoming reactant: bulky electrophiles favour

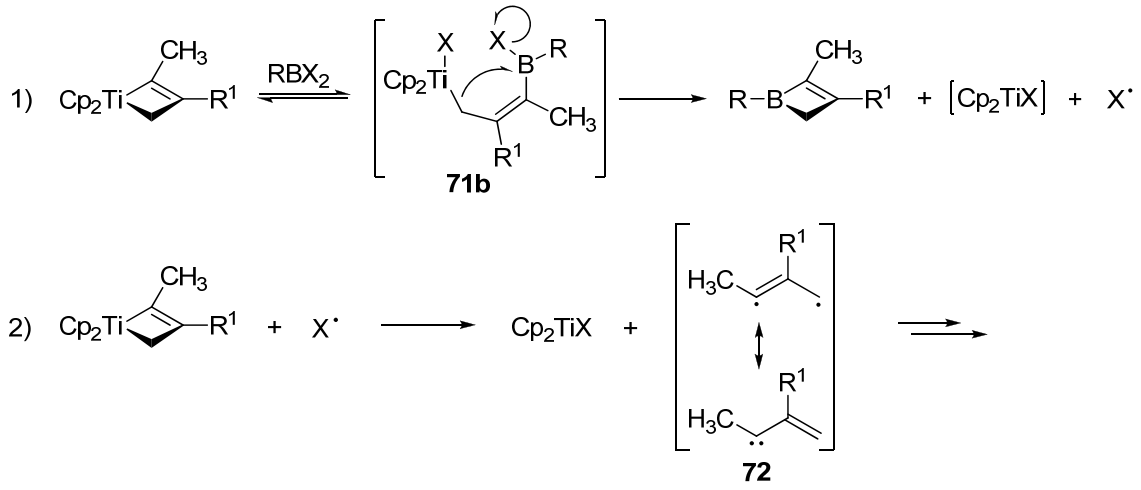
reaction at the alkyl Ti-C4 bond, whereas less bulky reagents can insert into the vinylic Ti-C2 bond of titanacyclobutene complexes. Depending on the initial site of attack, divergent products are obtained.

A superficial evaluation finds similar observations for the transmetallation of titanacyclobutene complexes with dihaloboranes. Titanacyclobutene complexes bearing bulkier C2 substituents, such as Ph and TMS, undergo the expected transmetallation smoothly. Less bulky 2-methyltitanacyclobutene complexes produce mixed results, with an as yet unknown decomposition pathway. If the reaction bears any resemblance to known insertion chemistry, then one would propose that the initial site of attack is different for hindered and unhindered titanacyclobutene complexes. Specifically, 2-phenyltitanacyclobutene complexes initially react with incoming RBX_2 at the sterically more open sp^3-hybrized carbon, generating alkenyltitanium intermediate **71a** (Scheme **4.1**, R = Ph), from which further transmetallation proceeds to boracyclobutene. On the other hand, 2-methyltitanacyclobutene complexes bearing a smaller substituent at C2 may react preferentially on the vinyl side, forming allylic titanium intermediate **71b** (Scheme **4.1**, R = CH_3). Subsequent reactions from intermediates **71a** and **71b** could be where the transmetallation reactions diverge.

Further into the speculative realm, reasonable proposals can be made regarding the decomposition pathways from 2-methyltitanacyclobutene complexes and intermediate **71b**. However, any proposal must account for formation of $[Cp_2TiCl]_2$ and the very odd requirement for only half an equivalent of the boron reagent. From control experiments, boracyclobutenes do not react with Cp_2TiCl_2 or $[Cp_2TiCl]_2$ and the titanacyclobutene complexes do not spontaneously decompose at 80 °C. However, titanacyclobutene complexes do react with Cp_2TiCl_2 at 50 °C in C_6D_6. After 15 hours, approximately 20 %, 5 %, and 0 % decomposition was noted for 2-methyl, 2-phenyl, and 2-(trimethylsilyl)titanacyclobutene complexes, respectively; after 48 hours, approximately 40 % of the 2-methyltitanacyclobutene remained. Considering the slow decomposition process and low reaction temperatures used for the reactions with $PhBCl_2$, it is unlikely that Cp_2TiCl_2-promoted degradation is responsible for non-productive pathways.

Boracyclobutene product is still observed in reactions using a full equivalent of RBX_2 and it is the major product in all substoichiometric reactions, so it seems improbable that the boracyclobutene participates in decomposition once formed. Instead, it appears more likely that titanacyclobutene complexes react unfavourably with an intermediate generated during transmetallation. Allyltitanium(IV) complexes are known to undergo homolytic Ti-C bond scission;[265] if η^1-intermediate **71b** is formed, homolysis of the Ti-C bond may be faster than transmetallation. Thus, rapid radical cyclization and subsequent loss of a highly reactive halogen radical could produce boracyclobutene, as well as $[Cp_2TiX]$ (Scheme **4.2**). Halogen radical could then react with another titanacyclobutene complex, which if Ti-C bond homolysis occurred again, would produce $[Cp_2TiX]$ and allylic radical **72**. Any radical species formed could abstract hydrogen radical from solvent or couple with other radicals in solution; if two **72** radicals homocouple, the product would correspond to the ions observed by HRMS. Alternatively, a slight modification of this proposal is that a titanacyclobutene complex abstracts halogen radical from intermediate **71b**, and consequently expels the organic fragment. Isolation of $[Cp_2TiCl]_2$ supports contention for a radical process, as no reducing agent strong enough to react with Cp_2TiCl_2 is present; this proposal also explains the 2 : 1 ratio of reactants. However, it must be noted that the near-absence of Cp_2TiX_2 is remarkable if halogen radical is formed during the reaction.

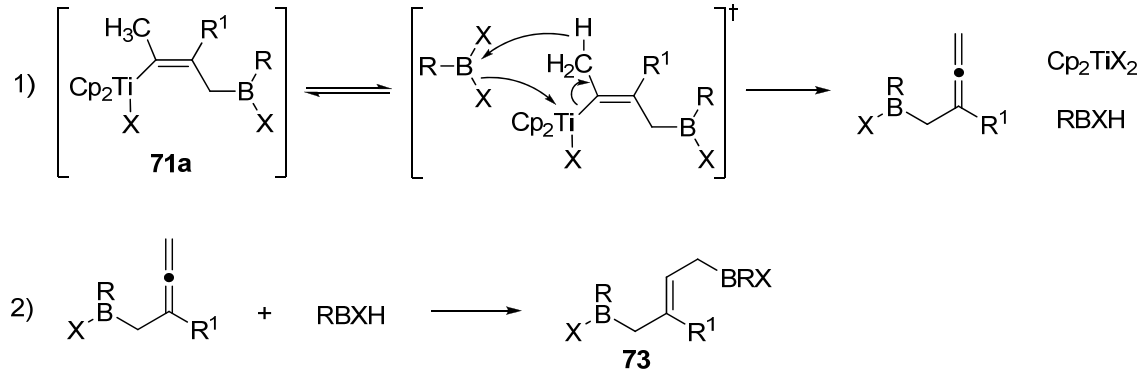
Scheme **4.2**: Proposed transmetallation mechanism for α-methyltitanacyclobutene complexes



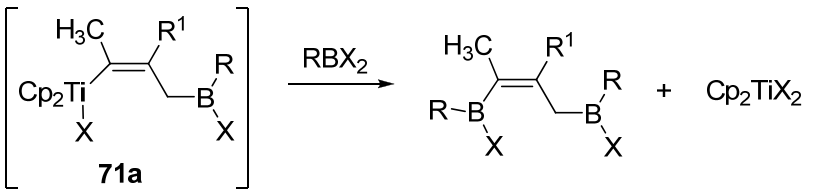
Several other explanations should be considered as well. Regardless of the initial site of transmetallation, the reaction may be slower for 2-methyltitanacyclobutene complexes, resulting in reactions not known for phenyl-substituted analogues. This would be unexpected, as the methyl-substituted complexes are more electron-rich; however, there are also fewer steric constraints with the smaller substituent.

The initial 2-methyltitanacyclobutene complexes display no tendency to undergo β-hydride elimination, however vinylic titanium intermediate **71a** is expected to be more susceptible to β-hydride elimination due to the increased conformational mobility in the system upon ring opening/expansion. Alternatively, β-hydride elimination may be promoted by Lewis acidic dihaloboranes. In one potential scenario (Scheme **4.3**), intermediate **71a** is converted to an allene with concomitant formation of Cp_2TiX_2 and RBXH; presumably hydroboration of the allene would then occur, possibly providing diborane **73**. This could also occur in a stepwise fashion.

Scheme **4.3**



A diborane would also be obtained if 2-methyltitanacyclobutene complexes transmetallate with two equivalents of RBX_2 (Equation **4.19**).

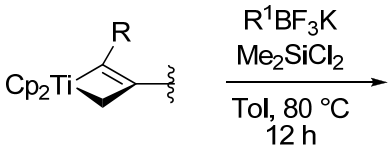


Equation **4.19**

However, these potential decomposition routes seem unlikely because the observations clearly indicate that the results are influenced by the amount of RBX_2 reagent (*i.e.* exactly half an equivalent of RBX_2 gives the best results). β-Hydride elimination from a titanium intermediate, if it occurs, would be expected with half an equivalent of dihaloborane as well. Intermolecular transmetallation of intermediate **71a** or **71b** would also occur with fewer equivalents of RBX_2, albeit to a smaller extent if the concentration is consequently lowered, and is not observed with the other α-substituents. Additionally, these explanations do not account for the formation of $[Cp_2TiX]_2$. While results from the transmetallation of 2-methyltitanacyclobutene complexes have not been adequately explained, it is probably not coincidental that the analogous phosphorous transmetallation to 2-methylphosphacyclobutenes has not been reported either, despite research in that area.[49]

Limitations to the Transmetallation Process

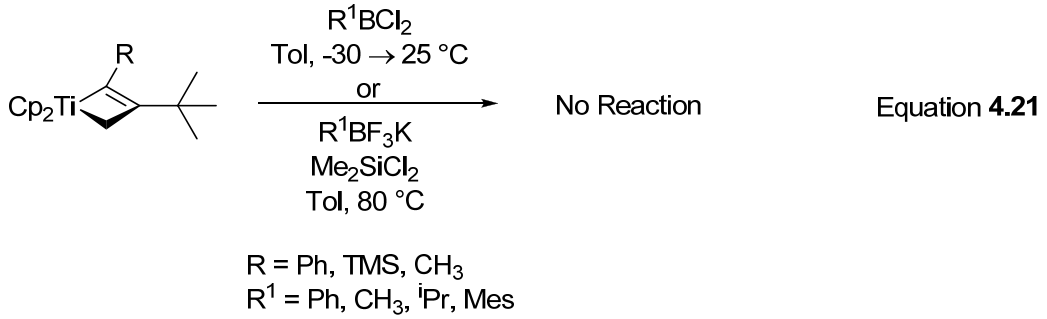
A trend was noted while evaluating the success of various boron reagents for transmetallation reactions of the titanacyclobutene complexes studied. $PhBCl_2/PhBF_2$ was the most general reagent used, which mediated the desired transformation on titanacyclobutene complexes bearing three different α-substituents. $MeBF_2$ reacted with titanacyclobutene complexes bearing α-phenyl and α-methyl substituents, whereas $^{i}PrBF_2$ only reacted with the latter complexes. $MesBF_2$, the bulkiest reagent investigated, did not participate in any transmetallation reaction. It is quite apparent that a balance must be achieved between the sizes of the boron reagent and titanacyclobutene α-substituents in working transmetallation reactions. This is summarized in Equation **4.20**, showing the reactions that did not meet with success.



Equation **4.20**

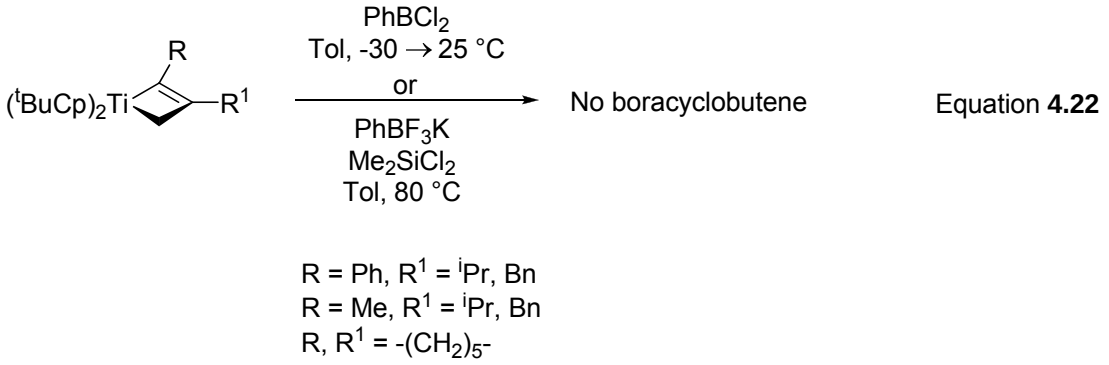
R = CH_3; R^1 = Mes
R = Ph; R^1 = Mes, ^{i}Pr
R = TMS; R^1 = Mes, ^{i}Pr, CH_3
R = ^{t}Bu; R^1 = Mes, ^{i}Pr, CH_3, Ph

In addition to titanium- and boron-substituent steric factors, titanacyclobutene complexes bearing *tert*-butyl substituents at the C3 ring position also fail to transmetallate. Starting material is recovered when using the normal conditions and slow degradation takes place over extended reaction periods at 80 °C or 110 °C (Equation **4.21**). For 2-phenyl and 2-methyltitanacyclobutene complexes, a small amount of boracyclobutene may form under forcing conditions, but decomposition is the major process.



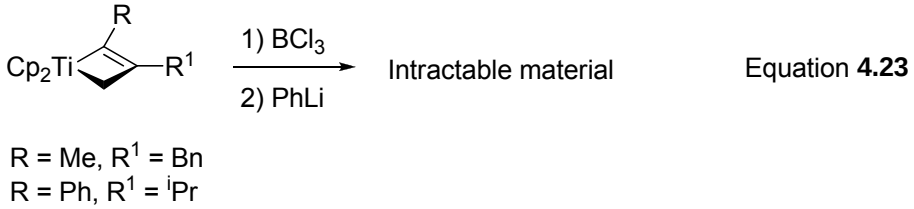
Equation **4.21**

Titanacyclobutene complexes bearing ^{t}BuCp ancillary ligands failed to produce any boracyclobutene product upon treatment with $PhBCl_2$ (Equation **4.22**). Every reaction, regardless of the substitution pattern of the ring, resulted in the formation of a green solution that provided only broadened signals in the ^{1}H NMR spectrum. The process that leads to paramagnetic material is not known. As already noted, transmetallation of a bis(pentamethylcyclopentadienyl)titanacyclobutene complex has been reported (refer to Equation **4.1**).[29]



Equation **4.22**

Several other boron reagents were evaluated unsuccessfully in this transmetallation process. Phenylboronic acid and phenylboronic pinacol ester do not react with titanacyclobutene complexes at 75 °C over 16 hours; continued heating leads only to slow decomposition. Synthesis of the unknown phenylboronic oxalyl ester was attempted from both phenylboronic acid and dichlorophenylborane, but this compound could not be prepared. Reactions with BCl_3 resulted in the formation of multiple species by NMR spectroscopy, and it could not be determined if the mixture contained the desired product. Thus, titanacyclobutene complexes were treated with BCl_3 and then, *in situ*, with PhLi (Equation **4.23**). Whereas 1-phenylboracyclobutenes were expected, none of the observed NMR signals coincided with the desired products. B-chlorocatecholborane ($C_6H_4O_2B$-Cl) was investigated as a means for generating acyclic diboranes,[57] by treatment of titanacyclobutene complexes with both one and two equivalents, but multiple uncharacterized products were formed. Synthesis of free $PhBF_2$ by halide exchange between $NaBF_4$ and $PhBCl_2$ did not proceed as described;[266] this preparation has not been applied by others in the literature and may be flawed.



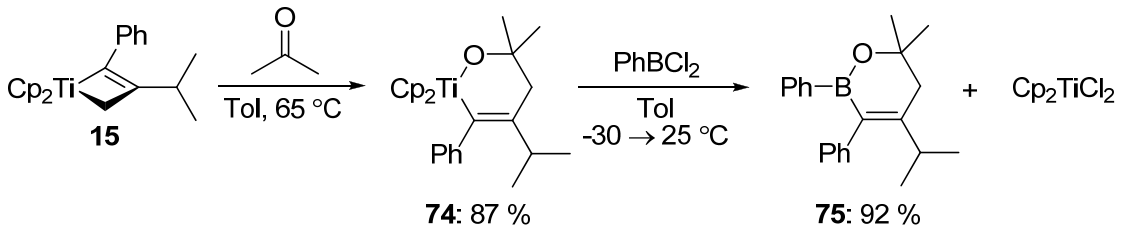
Equation **4.23**

Transmetallation of a 2-oxatitanocenecyclohex-5-ene complex

One indirect derivatization of titanacyclobutene complexes was researched. It has been established that, for appropriately substituted titanacyclobutene complexes, insertion of aldehydes and ketones occurs into the alkyl Ti-C bond to yield 2-oxatitanocenecyclohex-5-enes (refer to Section 1.1).[35] Generating boracyclic material from these expanded complexes could also lead to some interesting developments. This direction has some precedent with phosphorous transmetallations using $PhPCl_2$ following carbonyl insertion, however, only two products were reported in 7 % and an unspecified yield.[267] Thus, titanacyclobutene **15** was treated with acetone and heated for 14 hours in

a sealed bomb at 65 °C, cleanly producing oxatitanacycle **74** (Scheme **4.4**). ^{1}H and ^{13}C NMR spectra were similar to those of other complexes in this structural class.[35]

Scheme **4.4**



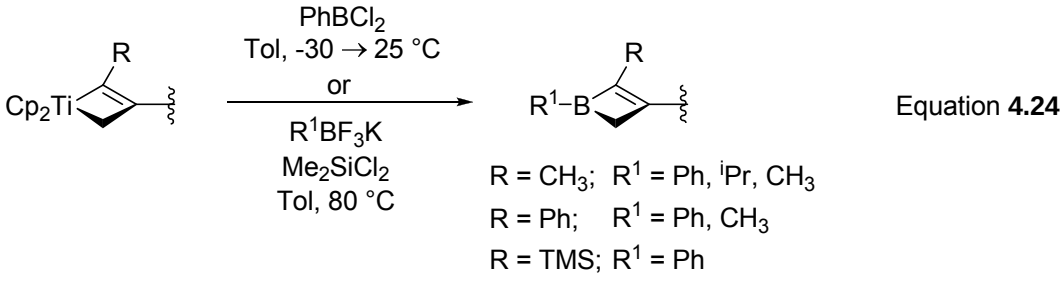
Upon treatment of 2-oxatitanocenecyclohex-5-ene **74** with $PhBCl_2$ in toluene, cyclic borinic ester **75** and Cp_2TiCl_2 were formed in excellent yield, along with a minor impurity comprising less than 10 % (Scheme **4.4**). The standard transmetallation work-up removed Cp_2TiCl_2 but retained the unidentified by-product. Crystallization/precipitation of the orange oil was unsuccessful, so the product was characterized as is. Pure material may be accessible by chromatographic separation, although hydrolysis of the B-C bonds could be a problem. Interestingly, while far from a definitive determination, the fact that a titanium oxide transmetallates with a chloroborane reagent suggests that boronic acid derivatives will not be suitable for transmetallation of organometallic titanacycles (i.e. a strong driving force will be necessary to transfer a B-O bond).

By means of ^{11}B NMR spectroscopy, the boron atom of **75** is observed as a broad signal centred at 37.9 ppm. The allylic protons at C5 are observed as a singlet at 2.10 ppm, and the remaining substituent signals are as expected. The furthest downfield signal in the ^{13}C NMR spectrum is 159.2 ppm, which is assigned to the β-alkenyl carbon. The α-alkenyl carbon is observed as a broad upfield signal at 135.8 ppm; these data follow the general spectroscopic trend for alkenylboranes. Resonances for the remaining ring carbons are found at 72.5 and 37.6 ppm for the ether and allylic carbons, respectively. The assignments are based largely on HMBC correlations and chemical shift values. In particular, while both sets of allylic protons correlate to the alkenyl carbons, the isopropyl methyl groups only correlate to the β-alkenyl carbon at 159.2 ppm.

No other cyclic borinic esters were prepared in this manner. 2-(Trimethylsilyl)titanacyclobutene complexes are mostly unreactive toward benzaldehyde or acetone over multiple days at 65 °C. 2-Methyltitanacyclobutene complexes are known to insert carbonyl compounds largely at the vinylic Ti-C bond to give diene products;[35] a terminal diene was obtained upon treatment of complex **22** with acetone. There is no reason to believe that boron transmetallation of 2-oxatitanocenecyclohex-5-ene complexes could not be extended further, although obtaining enantiopure material will be a challenge for insertion complexes derived from aldehydes.

4.3 Conclusion

In summary, the first extended series of boracyclobutene products has been prepared from the analogous titanacyclobutene complexes by transmetallation using aryl- and alkylboron dihalides (Equation **4.24**). 2-Phenyltitanacyclobutene complexes are by far the most successful substrates for the transmetallation studied, from which boracyclobutenes can be generated as pure substances in high yield. Only one boracyclobutene bearing an α-TMS group was obtained, but it could not be isolated in analytically pure form. Reactions involving 2-methyltitanacyclobutenes require additional study to elucidate decomposition pathway(s) in order to overcome current limitations; however, boracyclobutenes can be formed provided one equivalent of the titanacyclobutene complex is sacrificed. ^{13}C NMR spectroscopic data indicate that 1,2-diphenylboracyclobutenes exhibit pronounced 1,3-bonding interactions, whereas in other boracyclobutenes this interaction is diminished. While the transmetallation methodology requires improvement, it does afford a more general synthetic route to these compounds of interest than any previously described.



Equation **4.24**

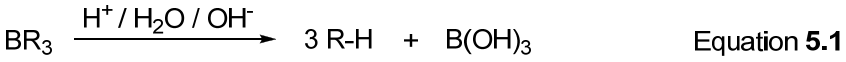
Chapter 5: Derivatization of Boracyclobutenes

5.1 Introduction

With the elucidation of a general protocol for boracyclobutene synthesis by transmetallation, investigation of the reactivity of these compounds became the primary research focus. Due to the relative lack of information on the boracyclobutene structural class, elementary transformations were targeted in order to establish a foundation prior to more complex studies. While numerous reactions involving organoboranes are known, three features unique to boracyclobutenes were of particular interest for exploitation: the vinylic and allylic carbon-boron frameworks, and small-angle strain. It was anticipated that functionalization of boracyclobutenes with common organoborane chemistry would produce novel and fascinating results.

Derivatization of organoboranes with a wide range of reagents is well established.[231-233,268,269] While an exhaustive review of the extensive literature is beyond the scope of this dissertation, background for the reactions studied, and in some cases unexpectedly encountered, is warranted.

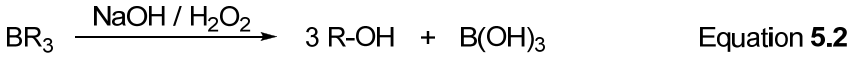
Protodeboronation is the term used for protonolysis of a carbon-boron bond; it is known to occur in acidic,[270] basic,[271] and neutral media, and the reaction has been thoroughly studied by Kuivila, *et al*., in a series of early papers. The products formed are unfunctionalized alkanes and boric acid or its derivatives (Equation **5.1**). While typically observed as a minor and undesired side reaction for alkylboranes, protodeboronation was identified as a major process for boroles (boracyclopenta-2,4-dienes) in acidic, neutral, and basic media.[158]



Equation **5.1**

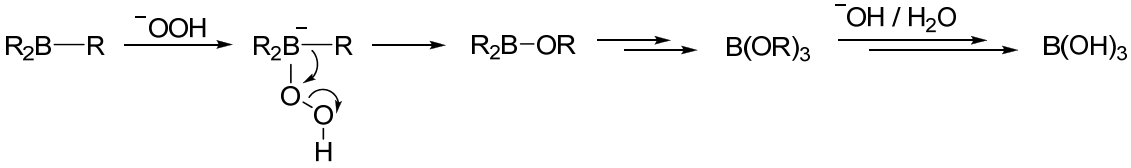
Oxidation is one of the most common transformations applied to organoboranes,[272-275] resulting in the conversion of alkylboranes to alcohols and alkenylboranes to aldehydes and ketones (boric acid or its derivatives are formed from the boron fragment, however this is typically not the product of interest). Oxidation

occurs with retention of configuration at carbon, making it an ideal process when coupled with selective hydroboration for enantioselective syntheses. The most prevalent oxidation protocol uses alkaline hydrogen peroxide, although several other reagents also affect oxidation of a B-C bond (Equation **5.2**). Mechanistically, coordination of hydrogen peroxidate to boron occurs in the first step, producing a tetracoordinate borate anion. Carbon migration from boron to oxygen, with consequent loss of hydroxide, affords a borinic ester. Once all of the B-C bonds have been oxidized, the boric ester that is formed is readily hydrolyzed in aqueous conditions (Scheme **5.1**).

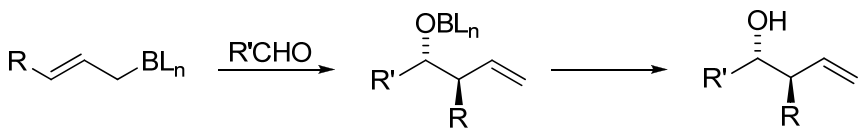


Equation **5.2**

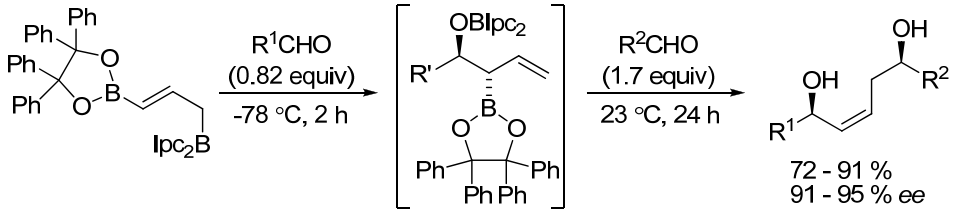
Scheme **5.1**



Allylboration of aldehydes is an efficient method for stereoselective carbon-carbon bond formation, resulting in the production of homoallylic alcohols with two new stereocentres (Equation **5.3**).[276] Due to high selectivity, excellent generality and functional group tolerance, and dense packing of functionality in the product, allylboration has earned prominence in enantioselective syntheses. In a fascinating modification, double allylboration has been achieved by use of a boryl-substituted allylborane (Equation **5.4**). Allylboration of an aldehyde occurs at low temperature for the reactive dialkylallylborane to produce a less reactive allylboronic ester; warming of the reaction solution in the presence of a second aldehyde results in a second allylboration and formation of a 1,5-diol bearing a *cis* double bond in high enantioselectivity following work-up.[277]



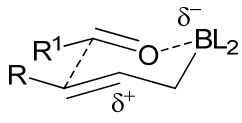
Equation **5.3**



Equation **5.4**

Mechanistically, allylboration proceeds through a six-membered chair-like transition state, leading to high selectivity (Figure **5.1**).[278] Orientation of the majority or largest substituents in a pseudo-equatorial position is favoured, which ensures confident predictions regarding the configuration of the new stereocentres formed. Note that in Equation **5.4**, the bulky tetraphenyl glycol-derived boronic ester forces the substituent into an axial position in the transition state, leading to the production of *syn* diols. The transition state, which involves concentration of positive charge at the β-carbon, is stabilized by hyperconjugation from the electron-rich B-C bond. The reaction is primarily assisted by activation of the carbonyl moiety,[279] which is apparent in the relative rates of allylboration by different allylboranes; more electrophilic allyldialkylboranes react faster than boronic amide and ester derivatives.[280]

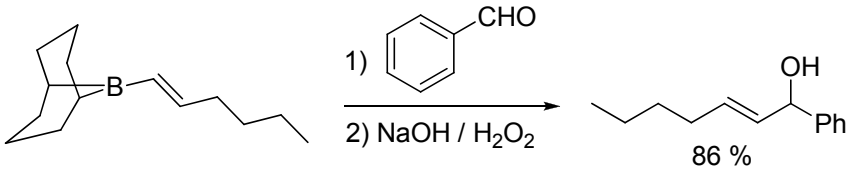
Figure **5.1**: Chair-like transition state for allylboration



Several asymmetric allylboranes have been developed for stereoselective allylboration of aldehydes, including bis(isopinocampheyl)[281] and bis(isocaranyl)[282] allylborane derivatives, tartrate[283,284] and ethylenetartramide[285,286] allylboronates, and bis(sulfonamide)allylboranes,[287,288] to name a few. More recently, the development of Lewis acid-catalyzed allylboration reactions has received accolades, an improvement with the significant advantage of avoiding the stoichiometric use of chiral reagents.[235,289]

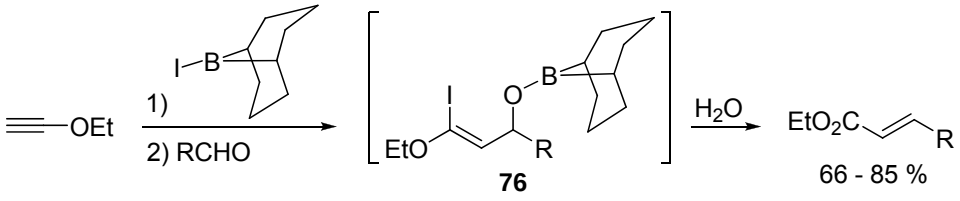
Other than allylboranes, nucleophilic addition to carbonyl groups by neutral organoboranes is rare, the result of a strong, weakly-polarized C-B bond. Nucleophilic 1,2-addition of an organoborane to an aldehyde was first reported in 1977. B-alkenyl-9-

borabicyclo[3.3.1]nonane (B-alkenyl-9-BBN) compounds, formed by hydroboration of terminal alkynes, react with aldehydes by addition to the carbonyl carbon (Equation **5.5**).[290]



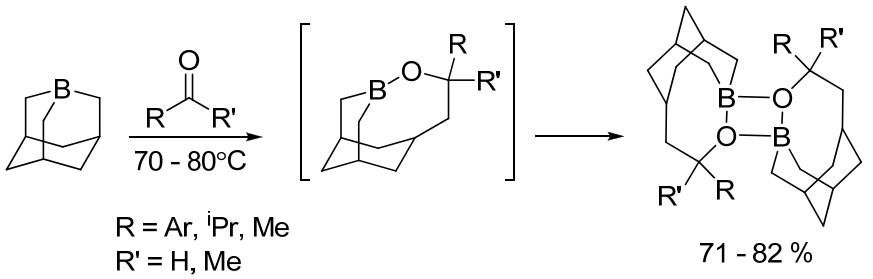
Equation **5.5**

Ethoxyacetylene, upon treatment with first B-iodo-9-borabicyclo[3.3.1]nonane (B-I-9-BBN) then an aldehyde, forms trans-α,β-unsaturated esters with high diastereoselectivity (Equation **5.6**).[291] While reactive intermediates were not characterized, the authors propose that an alkenylborane, formed by addition to the triple bond, reacts with aldehyde to afford allylic borinic ester **76**; conjugate addition of H_2O and elimination of the borinate fragment and iodide would yield the esters that are isolated. Aryl- and alkenylboronates have also been reported to act as nucleophiles with N-acyliminium ion precursors in the presence of a BF_3-etherate.[292]



Equation **5.6**

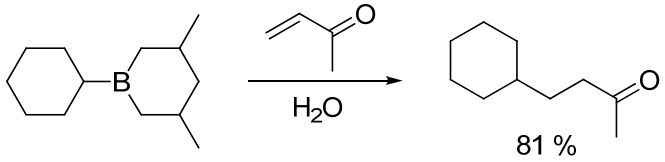
Nucleophilic 1,2-addition of alkyl B-C bonds has also been reported, although this is even less common. Due to a significant degree of strain caused by deviation from a planar geometry at boron, 1-boradamantane undergoes ring expansion in the presence of aldehydes and ketones between 70 – 80 °C (Equation **5.7**).[293] 1-Boradamantane readily forms adducts because of the imposed pseudo-tetrahedral geometry, complexing ethyl acetate and ethers, weak Lewis bases that typically do not produce adducts with trialkylboranes.[294]



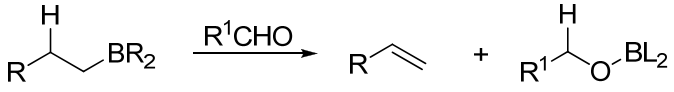
Equation **5.7**

Other reports of sp^3-hybridized carbon-migration from alkylboranes are from anionic borate complexes or through radical-promoted processes. 1,2-Migration from anionic borate complexes is well-studied.[295-300] Radicals generated from trialkylboranes by the reaction with oxygen add to formaldehyde, however this is not formally a migration.[301,302] Chlorodialkylboranes and dichloroalkylboranes also transfer organic substituents in the presence of oxygen.[303,304] β-Hydroxyaldehydes and -ketones are alkylated by organoboranes, presumably through a six-membered cyclic intermediate, although radical species were implicated in this mechanism as well.[305]

Upon reaction with α,β-unsaturated aldehydes and ketones, alkylboranes undergo 1,4-addition, producing alkylated saturated carbonyl compounds[306,307] by a free radical mechanism (Equation **5.8**).[308] Selective transfer of a specific alkyl group from a trialkylborane bearing different alkyl substituents was problematic until six- and seven-membered boracycles were utilized. Additionally, under forcing conditions in the absence of oxygen, trialkylboranes can reduce aldehydes and ketones by formation of an intermediate borohydride through β-hydrogen elimination, producing an olefinic by-product and alcohol (Equation **5.9**).[309,310]



Equation **5.8**



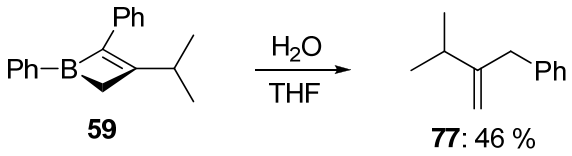
Equation **5.9**

5.2 Results and Discussion

General reactivity

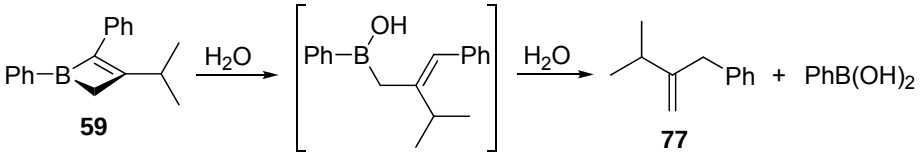
1,2,3-Substituted boracyclobutenes prepared by the transmetallation methodology were exposed to a variety of conditions to determine potential pathways for further transformations. Boracyclobutenes are indefinitely stable in THF, diethyl ether, toluene, hexanes, pentane, and benzene, although rapid degradation was observed in acetonitrile. A solution of boracyclobutene was treated with pure oxygen gas at -78 °C; analysis of the crude reaction mixture indicated no starting material and a multitude of products. As expected, the boracyclobutenes could not be purified by chromatography through silica or Grade III neutral alumina; only decomposed material was recovered.

Alkylboranes readily oxidize in air but are typically stable in water.[199] In contrast, boracyclobutene **59** reacts to form olefin **77** as the major product upon treatment with water deoxygenated by a steady stream of argon for 30 minutes (Equation **5.10**). ^{1}H NMR analysis of the crude mixture indicates that at least three other compounds are present by identification of characteristic isopropyl group signals, but in significantly lower quantities. Olefin **77** was isolated in an unoptimized yield of 46 % and displayed identical spectroscopic data to those previously reported.[311] Treatment of boracyclobutene **59** with dry and degassed methanol also afforded olefin **77** along with other minor species. The mechanism of formation is unknown, however protonation of the vinylic B-C bond is likely the first step. From the allylborane intermediate thus formed, direct E_2' elimination would produce the observed olefin (Equation **5.11**); prior coordination of a Lewis base with boron would assist this elimination process. Products arising from protodeboronation are not surprising, because this was also noted during studies of boroles.[158]



59 **77**: 46 %

Equation **5.10**



Equation **5.11**

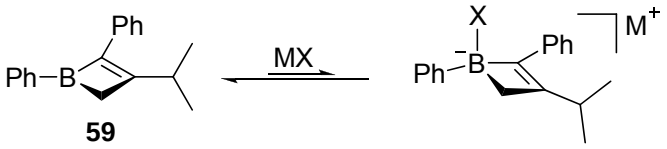
Coordination complexes and Lewis acidity

Despite extensive efforts to obtain crystalline material for solid-state structure determination, boracyclobutenes were isolated only as amorphous powders or oils. Considering the electron deficiency at boron and the rich chemistry of boron coordination complexes,[312,313] addition of neutral amines[314-317] and salts[139,318] was explored as an avenue for generating simple boracyclobutene derivatives that may be more crystalline. The targeted tetrahedral anionic borates and neutral boranes may also be less prone to decomposition while maintaining a range of exploitable reactivity. Additionally, if boracyclobutene derivatives are accessible by complexation with a cyanide salt, trialkylcyanoborates have been explored thoroughly, and alkyl migration transformations would be within reach.[319-327]

A series of salt additives were stirred with 2-phenylboracyclobutene **59** in THF for 12 hours, after which time solvent was removed and the crude material taken up in C_6D_6 for NMR analysis (Equation **5.12**). There was no apparent reaction with KCN and Bu_4NCl, whereas treatment with NaI and KF resulted in partial conversion (< 5 %) to a species exhibiting signals with the same coupling pattern shifted slightly upfield by 0.2 – 0.6 ppm. Bu_4NI produced similar results, although the new species was 15 – 20 % of the mixture. Crystallization was unsuccessful and it remains unknown whether the change to benzene for NMR analysis influenced the observed product distributions. Two sources of soluble cyanide, Bu_4NCN and KCN in combination with 18-Crown-6, resulted in decomposition of boracyclobutene **59**. In the presence of NaOMe and LiO^tBu, two alkoxide salts that may be necessary for metal-mediated cross-coupling reactions, no reaction was observed.

Similar experiments were conducted on 2-(trimethylsilyl)boracyclobutene **65**. Exposure to LiBr, LiI, and NaOMe in THF did not produce a noticeable reaction. Conversely, when dissolved in THF and stirred for 12 hours in the presence of LiO^tBu, complete decomposition of boracyclobutene **65** was noted. Treatment of

2-methylboracyclobutene **66** with NaOMe also resulted in degradation. Decomposition of boracyclobutenes in the presence of alkoxide salts is unexpected, however, it is not clear if the minor impurities in the starting material play a role in these observations.

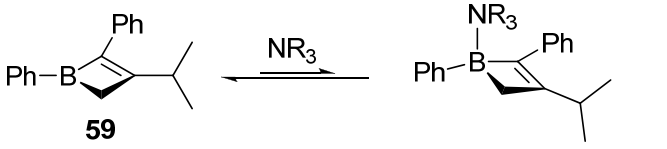


59

Equation **5.12**

MX = KCN, NaI, KF, Bu_4NCl,
Bu_4NI, Bu_4CN, KCN/18-C-6,
NaOMe, LiO^tBu

Neutral amine complexation was somewhat more promising as a pathway to coordination complexes. 2,6-Dimethylpyridine, DMAP, DABCO, imidazole, and *n*-butylamine were separately stirred with boracyclobutene **59** in THF, then analyzed by ^1H NMR in C_6D_6 (Equation **5.13**) 2,6-Dimethylpyridine did not form a stable complex with boracyclobutene **59**, although approximately 5 % was converted to a new species bearing otherwise identical signals shifted upfield from those of the starting material. DMAP, DABCO, imidazole, and *n*-butylamine produced soluble species exhibiting only broadened upfield signals. While the data is ambiguous, this was interpreted as formation of weak coordination complexes, whereas amines typically coordinate strongly with trialkylboranes. Formation of crystals suitable for X-ray diffraction analysis, the intended goal, was not successful, either from saturated solutions at low temperature or by slow evaporation of solvent at room temperature.



59

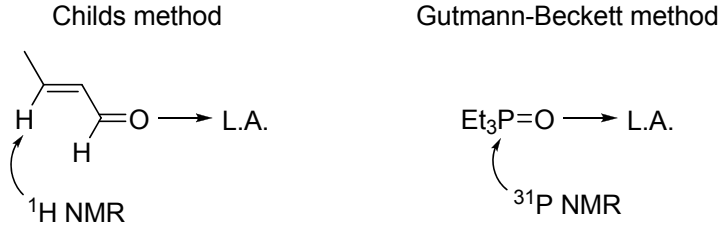
Equation **5.13**

NR_3 = DMAP, 2,6-dimethylpyridine,
DABCO, imidazole, $BuNH_2$

At this point, it became a question of how Lewis acidic these boracyclobutenes are, both as a means to explain the poor coordination results and to gain a better

understanding of the fundamental properties of this strained synthon. Several techniques have been used to quantify Lewis acidity, including chemical reactivity,[328] thermodynamic data,[329,330] and UV, IR, and NMR spectroscopic data. The convenience of NMR spectroscopic techniques has made this mode of analysis the most common. The Childs method, which measures the relative downfield shift of protons in crotonaldehyde upon complexation with various Lewis acids was developed first; the effect on H3 of the aldehyde is linear and a larger shift indicates a stronger acid (Figure **5.2**).[331] In a similar vein, the Gutmann-Beckett method measures ^{31}P NMR of triethylphosphine oxide in the presence of a Lewis acid, with larger downfield shifts also signifying a stronger acid (Figure **5.2**).[332] This is an adaptation by Beckett of Gutmann's classic Acceptor Number scale for solvents, which also uses $Et_3P{=}O$.[333] Relative Lewis acidity scales have also been derived by spectroscopic means from ethyl acetate (IR),[334] fluorenone (IR, UV, NMR),[335] pyridine (NMR),[336] and heptanal (NMR, IR)[337] complexes, as well as others. The Childs and Gutmann-Beckett methods are the most popular.

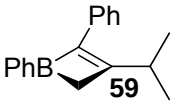
Figure **5.2**: NMR determination of relative Lewis acidity



Because aldehydes react with boracyclobutenes (*vide infra*), the Gutmann-Beckett method was chosen to determine the Lewis acidity relative to other boron compounds. In contrast to the original experiment, in which a 1 : 1 ratio was used, a recent adaptation that calls for a 3 : 1 ratio of Lewis acid to $Et_3P{=}O$ was applied, which ensures that the oxide is fully complexed.[338] Data was collected at 27 °C in C_6D_6 and at constant volume and compared to free $Et_3P{=}O$, which resonates at 46.8 ppm (Table **5.1**). Only a small downfield shift of 4.4 ppm was noted for the ^{31}P signal of $Et_3P{=}O$ when complexed to boracyclobutene **59**. For comparison, this is close to the values found for two very weak Lewis acids: trimethylborate and triethylborane, with downfield shifts of 1.3 and 5.1

ppm, respectively. In contrast, complexation with triphenylborane produces a downfield shift of 25.7 ppm, whereas phenylboronic acid causes a shift of 16.4 ppm. Clearly, the Gutmann-Beckett method indicates that boracyclobutene **59** is but a weak Lewis acid. This data could be corroborated by another method, possibly by measuring the change in chemical shift of the *para* carbon of pyridine upon coordination.[336]

Table **5.1**: ^{31}P NMR data of Lewis acid-base adducts with $Et_3P{=}O$

	^{31}P NMR (ppm)[a]	$\Delta\delta$ (ppm)
$Et_3P{=}O$	46.8	-
$B(OMe)_3$	48.1	1.3
Et_3B	51.9	5.1
$PhB(OH)_2$	63.2	16.4
Ph_3B	72.5	25.7
 **59**	51.2	4.4

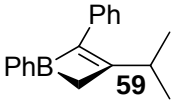
a) 3:1 B:P, 27 °C, C_6D_6

These results are not particularly surprising in light of the minimal or absent coordination to amines and anions, however a cursory evaluation of the substituents and structure would have predicted greater Lewis acidity than observed. The electron-withdrawing effect of phenyl and vinylic substituents should increase Lewis acidity beyond that of trialkylboranes. Additionally, release of small-angle strain by transitioning from tri-coordinate sp^2-hybridized boron to an sp^3-hybridized atom in the Lewis adduct was anticipated.[339] Indirectly, this data may corroborate the argument for strong 1,3-interactions in some boracyclobutenes, which would involve partial filling of the "empty" p orbital on boron while decreasing the susceptibility to external coordination; a computational investigation may provide significant information about this interaction.

^{11}B NMR spectroscopy of organoboranes is not useful for measuring Lewis acidity because the acid-base complexes typically exhibit variable upfield chemical shifts and signals broadened by chemical exchange.[332] Largely for interest's sake, these values

were obtained for boracyclobutene **59** and triethylborane in 1 : 1 and approximately 1 : 2 ratios with an excess of $Et_3P{=}O$ (Table **5.2**). Complexation is clearly evident by an upfield shift of the ^{11}B signals, albeit not into the range typically observed for neutral tetra-coordinate boranes, which generally resonate upfield of ~ 5 ppm. For comparison, the ^{11}B NMR signal of a 1 : 1 adduct of tris(pentafluorophenyl)borane and $Et_3P{=}O$ is reported at -2.8 ppm.[340]

Table **5.2**: ^{11}B NMR data of Lewis acid-base adducts with $Et_3P{=}O$

	ratio (B : P)	^{11}B NMR (ppm)[a]	^{11}B NMR (ppm) uncomplexed
Et_3B	1 : 1	72.5	86.7
	1 : 2	61.9	
 **59**	1 : 1	59.1	70.0
	1 : 2.3	52.9	
$B(C_6F_5)_3$[b]	1 : 1	-2.8	63

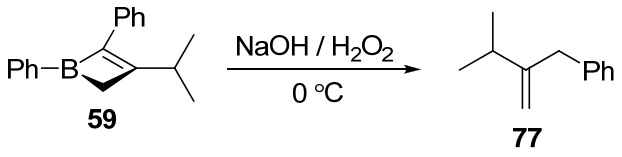
a) 27 °C, C_6D_6; b) Reference 337

Oxidation

Proof of structure by single-step derivatization was sought as a means to corroborate the spectroscopic characterization of the boracyclobutenes (Chapter 4). Oxidation, with the consequent appending of alcohol or carbonyl groups to the organic framework, is typically an efficient process that occurs with retention of configuration at carbon.[232] A variety of reagents have been discovered for this purpose, including alkaline H_2O_2,[341,342] trialkylamine N-oxides such as Me_3NO,[343,344] perbenzoic acids such as mCPBA,[345,346] $MoO_5{\cdot}py{\cdot}HMPA$ (MoOPH),[347] sodium perborate ($NaBO_3{\cdot}4H_2O$),[348] and sodium percarbonate ($2Na_2CO_3{\cdot}3H_2O_2$),[349] among others.

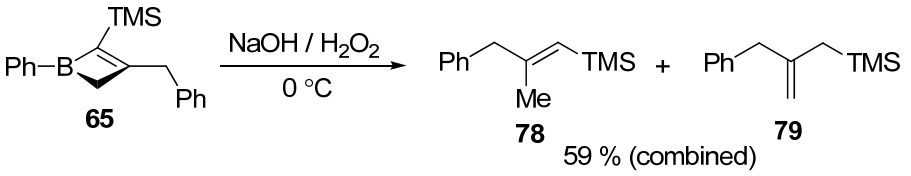
The most common oxidation protocol uses aqueous NaOH / H_2O_2. Thus, boracyclobutene **59** was added to a solution of 2 M NaOH at 0 °C, after which 30 % H_2O_2 was added dropwise (Equation **5.14**). Analysis of the crude mixture by ^1H NMR showed that the major product from this reaction was olefin **77**, the same product from simple protolytic hydrolysis, with several other compounds also present. The reaction

was repeated, adding boracyclobutene to an aqueous solution of both NaOH and H_2O_2, but returned the same result. Protodeboronation was also noted as the major process when boroles were treated with basic, neutral, and acidic aqueous solutions.[158]



59 **77** Equation **5.14**

2-(Trimethylsilyl)boracyclobutene **65** was also treated with NaOH and H_2O_2 at 0 °C (Equation **5.15**). The crude material was chromatographed through silica, eluting with hexanes to afford inseparable alkenylsilane **78** and terminal olefin **79** in a 1.3 : 1 ratio and a combined 59 % yield. The alkenylsilane **78** is the product expected from direct double protodeboronation, whereas olefin **79** appears to arise from protodeboronation at the vinylic B-C bond followed by E_2' elimination. The expected β-hydroxy acylsilane product was not observed under these conditions.

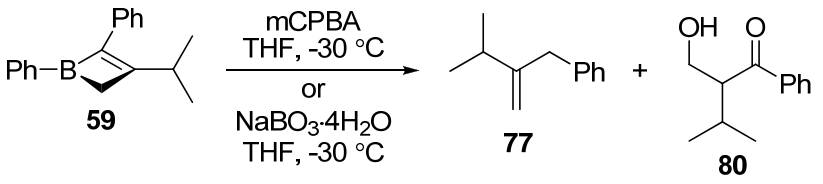


65 **78** **79** 59 % (combined) Equation **5.15**

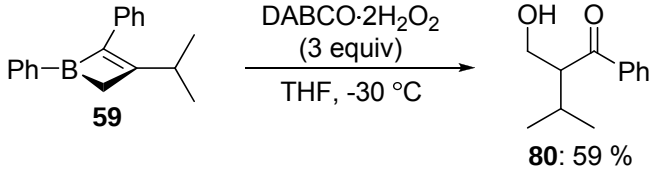
Single-step derivatization to the expected oxidation product was thus elusive. Treatment of boracyclobutene **59** with unpurified mCPBA (containing ~ 20 % *m*-chlorobenzoic acid) or sodium perborate also gave olefin **77** as the major product (~ 50 % of crude), as well as a small amount (~ 20 % of crude) of the desired β-hydroxy ketone **80** (Equation **5.16**). Using ^{1}H NMR spectroscopy, an approximate determination of the product distribution was possible by comparison to spectroscopic signals from phenol, which is a by-product from oxidation. While phenol is not a perfect internal standard (oxidation of the Ph-B bond may not go to completion or the phenol produced may react in some manner), the relative integration of characteristic resonances provides useful information.

By this point, it was quite apparent that protodeboronation of boracyclobutenes is the major reaction in the presence of trace water and protic sources, so a "dry" source of

hydrogen peroxide was prepared. The DABCO·2H_2O_2 complex is a solid that has been applied in other non-aqueous oxidations.[223] The material was synthesized by addition of DABCO to an aqueous solution of 30 % H_2O_2; drying under Schlenk vacuum (~ 0.05 torr) afforded a predominantly dry white powder that was easy to handle. (Note: typical safety precautions for peroxides should be taken; refer to experimental section for more information.) Under an inert atmosphere, boracyclobutene **59** was added to a suspension of three equivalents of DABCO·2H_2O_2 in THF at -30 °C (Equation **5.17**). Over 20 seconds, the solution lost its yellow colour to leave a milky white suspension; subsequent basic work-up with saturated $NaHCO_3$ solution and chromatographic purification through silica afforded β-hydroxy ketone **80** in moderate but acceptable yield, unaccompanied by olefinic by-product.

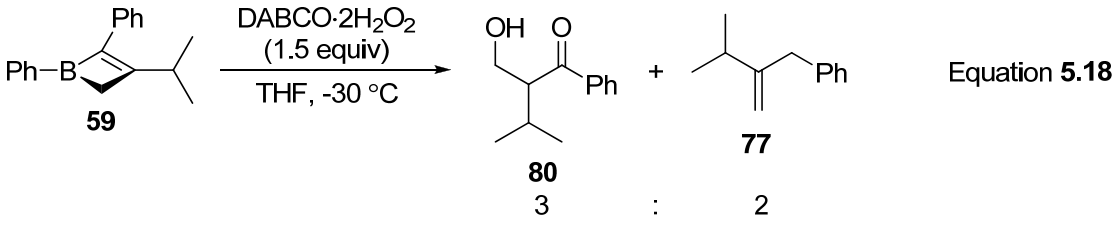


Equation **5.16**

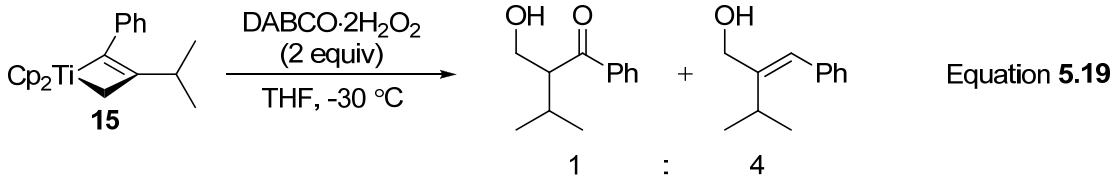


Equation **5.17**

Addition of dehydrated 4 Å molecular sieves to the reaction mixture produced a small quantity of olefin **77**, which arises from protodeboronation, as well as β-hydroxy ketone **80**. Oxidation of 1,2-diphenylboracyclobutene **59** with 1.5 equivalents of DABCO·2H_2O_2 (i.e. 1 : 1 ratio of H_2O_2 and C-B bonds) gave a 3 : 2 mixture of β-hydroxy ketone **80** and olefin **77** (Equation **5.18**); further optimization was not explored. For comparison, titanacyclobutene **15** reacts cleanly with DABCO·2H_2O_2 to give β-hydroxy ketone **80** and an allylic alcohol[350] in a 1 : 4 ratio, which was determined by ^{1}H NMR analysis of the crude material (Equation **5.19**). Me_3NO, despite preliminary observations to the contrary, also cleanly oxidizes boracyclobutene **59** to β-hydroxy ketone **80**.



Equation **5.18**

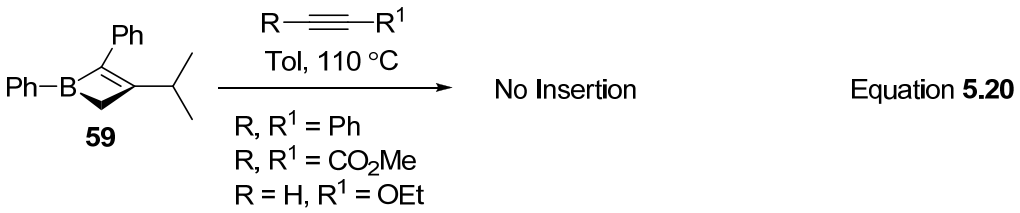


Equation **5.19**

Treatment of 2-methyl- and 2-(trimethylsilyl)boracyclobutenes with DABCO·$2H_2O_2$ or Me_3NO was less productive. Only small amounts of the desired oxidation products are obtained; analysis of the crude reaction mixtures indicate yields of less than 30 % in comparison to phenol. This is especially disappointing since these particular boracyclobutenes were the most in need of structural confirmation.

Reactions with alkynes

Based on the ring expansion reactions observed upon treatment of spiro-diboracyclobutenes with excess alkyne, as reported by Berndt, *et al*. (refer to Section 1.3), boracyclobutene **59** was heated with DMAD, diphenylacetylene, and ethoxyacetylene, respectively, in toluene at 110 °C (Equation **5.20**). The solution containing DMAD suffered slow decomposition over 12 hours, whereas quantitative recovery of starting material was obtained from the other two solutions. These results suggest that cycloreversion, whether by ring opening to a bora-diene or by extrusion of alkyne, is an unfavourable process.

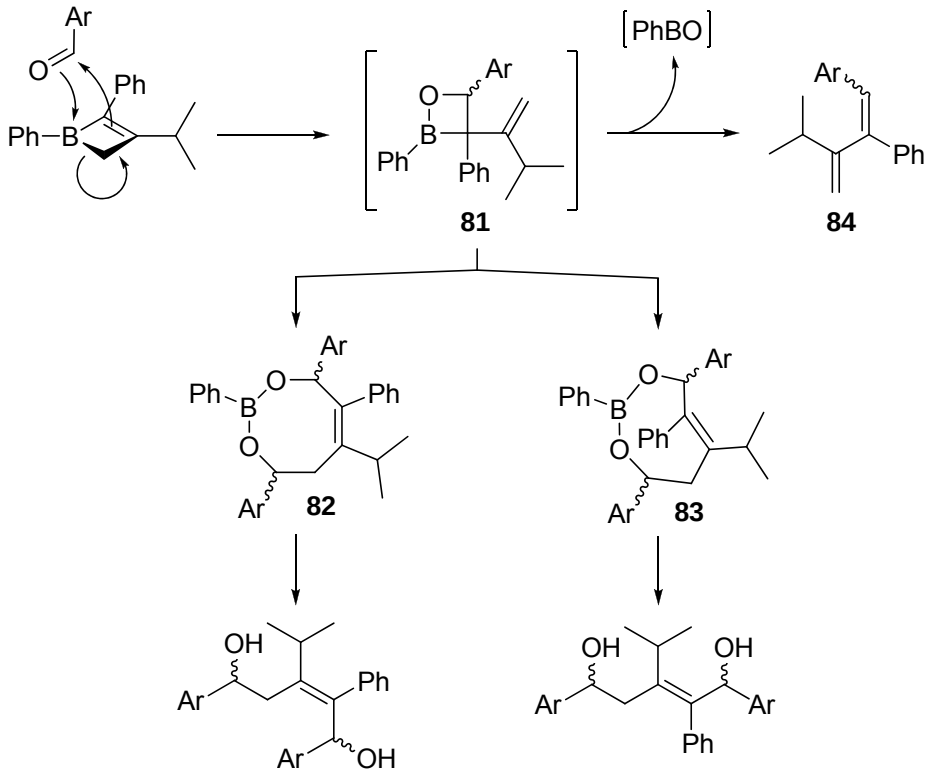


Equation **5.20**

Reactions with aldehydes

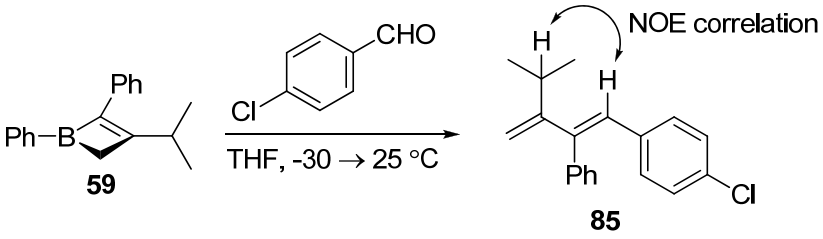
Among the highest potential transformations targeted for investigation of boracyclobutene reactivity is that with aldehydes. Due to the presence of an allylborane moiety embedded in the boracyclobutene, it was anticipated that carbon-carbon bond formation could be realized by allylboration of compounds containing polar carbon-heteroatom bonds, particularly carbonyls. Conceptually, the first allylboration would produce a four-membered cyclic borinic ester **81** featuring a pendant allyl moiety (Scheme **5.2**). This allylborane could potentially undergo a second allylboration to produce one of two eight-membered[351] cyclic boronic esters **82** and **83**; simple hydrolysis would afford a diol with two stereocentres in a 1,5-relationship separated by an olefin, potentially in a selective manner (Scheme **5.2**). Alternatively, the initial cyclic borinic ester **81** could also eliminate [PhBO] to yield a butadiene (**84**).

Scheme **5.2**:



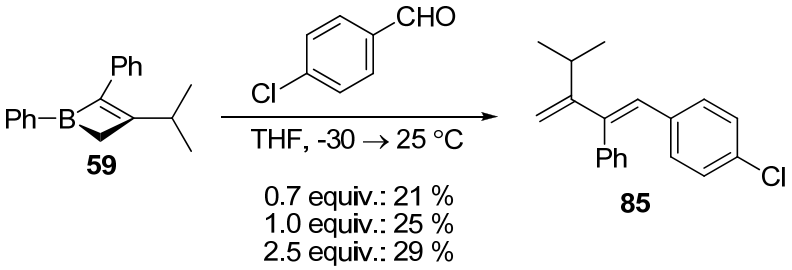
Thus, under a nitrogen atmosphere, boracyclobutene **59** was treated with benzaldehyde, p-chlorobenzaldehyde, and p-anisaldehyde, respectively, and the crude

product isolated by an aqueous wash. The latter two electrophiles were chosen largely for the presence of easily identifiable analytical signatures: *p*-chlorobenzaldehyde for characteristic ions from mass spectral analysis and *p*-anisaldehyde for characteristic O-CH_3 signals using ^1H and ^{13}C NMR spectroscopy. Early small-scale reactions with aromatic aldehydes yielded mixtures of products, containing three major components. The first compound isolated was butadiene **85**, albeit in only 25 % yield after chromatography through silica (Equation **5.21**); standard 1D and 2D NMR techniques were used for characterization, with HMBC proving most effective for determining the connectivity. Using a TROESY experiment, an NOE correlation was noted between the isopropyl methine proton and the sp^2-hybridized proton of the tri-substituted olefin, confirming the *Z* stereochemistry in the product (Equation **5.21**).



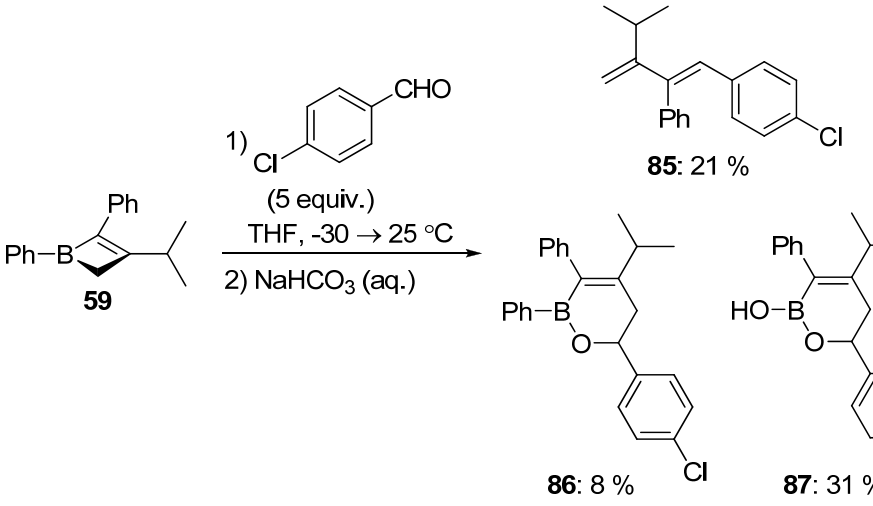
Equation **5.21**

The molar ratio of aldehyde was varied to determine the effect on product distribution; however, the impact was minimal. Compared to using a substoichiometric amount (0.7 equivalents), an excess of 2.5 equivalents of *p*-chlorobenzaldehyde increased the isolated yield of butadiene **85** only 8 % (Equation **5.22**). Additionally, the ratios of the other two major unidentified products did not change significantly based on ^1H NMR analysis of the crude material, although the formation of minor by-products was further attenuated.



Equation **5.22**

Different work-up conditions, including extractions with 2 M HCl, saturated NH_4Cl solution, H_2O, saturated $NaHCO_3$ solution, 2 M NaOH, and direct addition onto silica were tested using crude material from reactions between various boracyclobutenes and aldehydes. Based on ^1H NMR analysis following work-up, saturated $NaHCO_3$ was identified as the best quenching reagent because it induced the least decomposition of the three major components and removed phenol from the crude mixture, although the differences between the acidic, neutral, and basic conditions were minimal. Unfortunately, an oxidative work-up was not considered at this point in our investigation. A handful of experiments were conducted at -78 °C and using toluene as solvent; however, it appeared that additional by-products were formed and these modifications were not probed further. Therefore, boracyclobutene **59** was treated with five equivalents of *p*-chlorobenzaldehyde at -30 °C and stirred at 25 °C for 2 hours, after which the solution was diluted with ether and extracted with saturated $NaHCO_3$ (Equation **5.23**). Chromatography through silica yielded three products: butadiene **85** in 21 % yield, 2,3-diphenyl-1,2-oxaborin **86** in 8 % yield, and 2-hydroxy-1,2-oxaborin **87** in 31 % yield. The two oxaborin products arise from an uncommon 1,2-nucleophilic addition of the sp^3-hybridized C-B bond to the aldehyde.

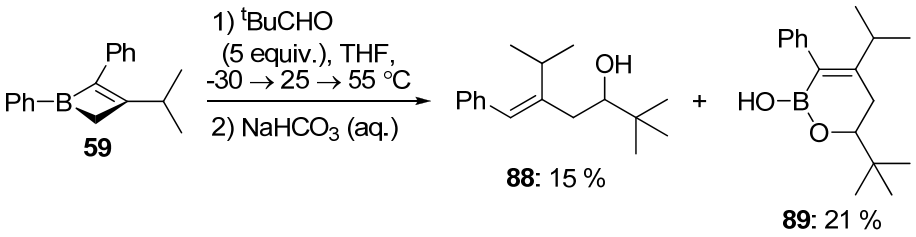


Equation **5.23**

2-Hydroxy-1,2-oxaborin **87** was characterized by 1D and 2D NMR spectroscopy, with corroboration of the molecular composition attained by HRMS. IR spectroscopy

indicates a characteristic broad peak at 3433 cm^{-1} for the O-H stretch, although it is a weak absorption. This can be explained in part by formation of a boronic anhydride (i.e. an oxygen-bridged dimer) with loss of water, which was also observed by HRMS. Unfortunately, this sample decomposed before variable temperature NMR spectroscopy could be used to identify the sp^2-hybridized carbon attached to boron, the signal for which suffers from broadening due to quadrupolar coupling to boron. ^{11}B NMR spectroscopy shows a single signal at 29.7 ppm, similar to chemical shifts of boronic acids and esters. Diphenyl-1,2-oxaborin **86** was not clean when isolated due to competitive decomposition on silica, however, the identification was based on IR, HRMS, and ^1H NMR spectroscopy; the latter technique afforded nearly identical coupling patterns as the more stable 2-hydroxy analogue **87**. In general, 1,2-oxaborins are not stable to hydrolytic conditions,[352] and decomposition partially accounts for the low isolated yields.

Upon review of the ^1H NMR data from the reactions of boracyclobutenes and aromatic aldehydes, it appears that competition between reactions occurring at the alkyl and vinylic B-C bonds is a consistent phenomenon. Bulky, aliphatic pivalaldehyde was thus selected for comparison to the aromatic aldehydes previously studied. Analysis of initial reactions and purification trials indicated that two major species were produced, however the presence of an additional non-polar compound that decomposed on silica was also noted. Consequently, it was determined that heating the reaction afforded a cleaner product distribution. Therefore, boracyclobutene **59** was treated with five equivalents of pivalaldehyde at -30 °C, stirred for two hours at 25 °C, then heated at 55 °C for 2 hours. The crude material was quenched with aqueous $NaHCO_3$ and chromatographed through silica to afford homoallylic alcohol **88** in 15 % yield and 2-hydroxy-1,2-oxaborin **89** in 21 % yield (Equation **5.24**); both products clearly arise from a reaction at the alkyl B-C bond. Presumably, subsequent protodeboronation of the vinylic B-C bond in 2-hydroxy-1,2-oxaborin **89** followed by hydrolysis yields the homoallylic alcohol. From this reaction, the 2,3-diphenyl-1,2-oxaborin was not isolated, however this may have decomposed on silica to the observed hydroxy derivative.



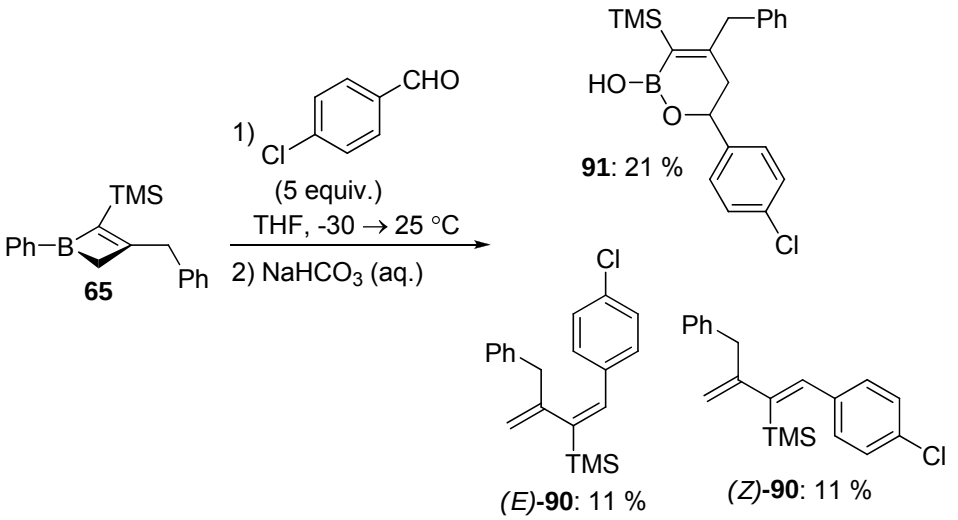
Equation **5.24**

Homoallylic alcohol **88** was characterized by ^{1}H and ^{13}C NMR spectroscopy, as well as 2D NMR data. Chemical ionization of the sample was necessary to observe the molecular ion because electron impact induced elimination of H_2O. 2-Hydroxy-1,2-oxaborin **89** is spectroscopically similar to that derived with *p*-chlorobenzaldehyde. In an effort to identify the α-alkenyl carbon bonded to boron, variable temperature ^{13}C NMR spectroscopy was performed; remarkably, the alkenyl carbon was not observed at either -60 °C or 60 °C. HMBC experiments conducted with normal parameters also failed to identify the multiple bond correlations to the α-alkenyl carbon, either at 27 °C or 60 °C. It was not until an extended HMBC experiment was conducted that the three-bond correlations to the allylic protons were visible. Upon re-analysis of the ^{13}C NMR spectrum, a broad peak at 128.4 ppm is barely apparent underneath two sp^2-hybrized carbon signals. In similar and recently published 2-hydroxy-1,2-oxaborin compounds, the α-alkenyl carbon resonance is not reported.[353] HRMS does identify the expected molecular ion, as well as that of the boronic anhydride.

In a final experiment, 2-(trimethylsilyl)boracyclobutene **65** was treated with five equivalents of *p*-chlorobenzaldehyde at -30 °C (Equation **5.25**). After two hours, the solution was extracted with aqueous $NaHCO_3$, dried, and chromatographed through silica to yield *E*-butadiene **90** and *Z*-butadiene **90** in equal amounts, along with 2-hydroxy-1,2-oxaborin **91**. The latter compound was collected simultaneously with phenol and not purified further due to poor stability, however this compound displayed similar ^{1}H and ^{13}C NMR characteristics to those prepared previously. 2D NMR techniques were used to confirm the atom connectivity.

In the three reactions between aldehydes and boracyclobutenes reported here, the recovery of products is poor due to concomitant decomposition; this was evident when almost pure 1,2-oxaborin products were chromatographed for a second time to remove minor impurities, forming substantial quantities of protodeboronated material in the

process. Additionally, TLC analysis of crude reaction material and chromatographed fractions indicated decomposition on silica. It is anticipated that the reaction yields might be improved by oxidative derivatization of the 1,2-oxaborin compounds; the standard protocol using NaOH / H_2O_2 should be suitable in the absence of a strained boracyclobutene ring, although non-aqueous conditions may offer the best results. Once a work-up procedure is optimized, it should be relatively straightforward to assess the favoured reaction site for boracyclobutenes with various aldehydes, in a manner analogous to that reported for titanacyclobutene complexes.[37]



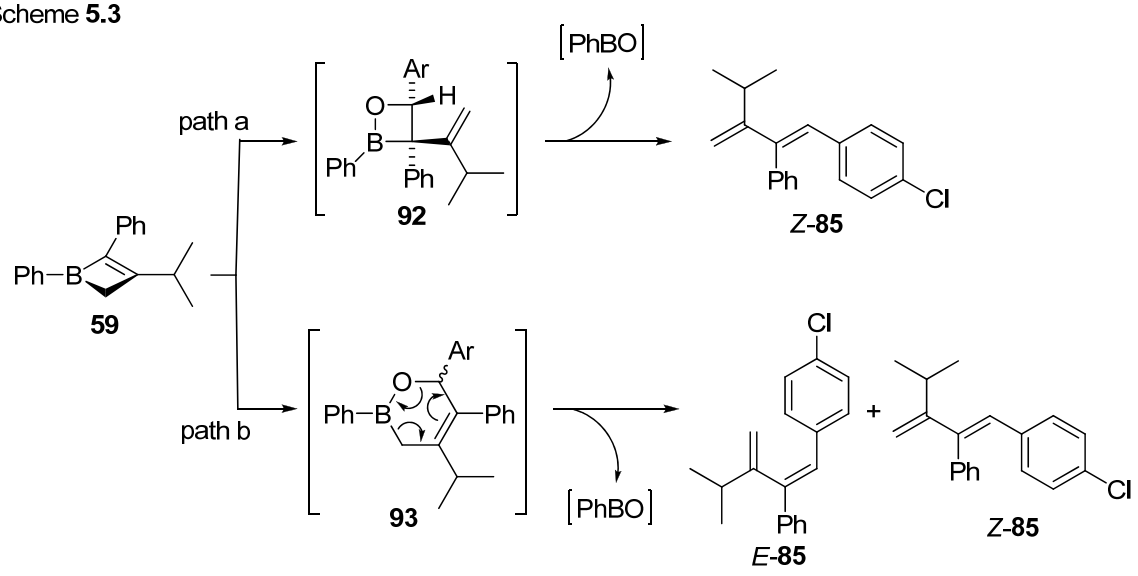
Equation **5.25**

Current information indicates that, because the less stable oxaboranes arising from insertion into the alkyl B-C bond are isolated in higher yield, 1,2-nucleophilic addition of an alkyl C-B bond in boracyclobutenes is favoured over the other process (*vide infra*). As discussed in the introduction (Section 5.1), migration of an sp^3-hybridized carbon substituent on boron to a carbonyl carbon is rare. Indeed, the only such process found in the literature that does not involve radical chemistry is for 1-boradamantane (refer to Equation **5.7**).[293] Whereas that ring expansion is driven by release of hybridization strain caused by enforcing a non-planar geometry at tri-coordinate boron, the observed insertion reactions between boracyclobutenes and aldehydes is driven by release of small-angle strain. However, due to the weak Lewis acidity of the 1,2,3-substituted boracyclobutenes, significant activation of the carbonyl is unlikely, as opposed to that expected for 1-boradamantane.[294] Alternatively, the observed products may arise from

intermediate boracycles formed by migration of the allylic ring hydrogens, although this seems unlikely because no isomerization was noted when the initial boracyclobutenes are characterized at 80 °C.

Referring back to Equation **5.23** for the reaction between *p*-chlorobenzaldehyde and 1,2-diphenylboracyclobutene **59**, two mechanistic possibilities exist for the formation of *Z*-butadiene **85**. Based on our original assumption that allylboration would predominate, the intermediate cyclic four-membered borinic ester **92** could undergo *syn*-elimination of [PhBO] to afford a butadiene (due to the presence of a B-O bond in the intermediate, an intermolecular *anti*-elimination seems unlikely). To minimize steric interactions, the smallest substituent, hydrogen, would be expected to be *syn* to the branched vinylic substituent. If this is true, *Z*-butadiene **85** with *cis* aromatic groups would be the anticipated product, which is the isomer isolated (Scheme **5.3**, path a). A review of the literature indicates that only one isolable four-membered borinic ester has been reported; the complex in question is a tetracoordinate borate bearing bulky and electron-withdrawing substituents.[354] Considering this information, it is not surprising that the presence of neutral borinic ester intermediate **92** is not observed.

Scheme **5.3**



Alternatively, insertion of aldehyde into the vinylic B-C bond is also conceivable, producing 1,2-oxaborin intermediate **93**; subsequent cycloreversion and extrusion of [PhBO] would lead to butadiene **85** as well (Scheme **5.3**, path b). However, in this case a

mixture of *E*- and *Z*-butadienes might be anticipated from the lack of stereocontrol in the original insertion. Therefore, diene formation by allylboration seems the most reasonable mechanistic proposal at this early stage. Unfortunately, evidence for either proposed borinic ester intermediate is lacking.

In addition to the alkyl insertion product, 2-(trimethylsilyl)boracyclobutene **65** gives both the *E*- and *Z*-butadiene isomers **90** upon treatment with *p*-chlorobenzaldehyde. It is possible that this reaction is mechanistically different from that obtained from 2-phenylboracyclobutene **59** and that the insertion occurs into the vinylic B-C bond. Alternatively, *E/Z*-isomerization of the sterically crowded silyl-substituted butadiene may be more facile, and occurs during the work-up and/or purification.

Treatment with DMSO and N_2O

Two other polar reagents were explored for potential insertion reaction with boracyclobutenes. It was envisioned that DMSO could oxygenate the B-C bond while expelling labile dimethylsulfide. Upon treatment with an excess of DMSO at room temperature, 2-phenylboracyclobutene **59** produces multiple products and gives incomplete conversion; subsequent heating at 75 °C forces complete conversion, but the reaction is not clean. 2-Methylboracyclobutene **66** decomposes completely when treated at room temperature with DMSO, whereas 2-(trimethylsilyl)boracyclobutene **65** is unchanged in the presence of DMSO, even at elevated temperatures.

Similarly, nitrous oxide (N_2O) was also explored as an atom-transfer reagent for insertion of oxygen, producing only nitrogen gas as a by-product. While the three boracyclobutenes studied (**59**, **66**, and **65** bearing Ph, Me, and TMS 2-substituents, respectively) do react upon exposure to nitrous oxide from -50 °C to 25 °C, the reactions do not yield any identifiable material among the complex crude mixtures produced.

5.3 Conclusion

Protodeboronation appears to be the preferred reaction route in the presence of protic sources. Protodeboronation of boracyclobutenes is observed using any wet oxidation reagent, however the expected oxidation products, β-hydroxy ketones, are accessible using a dry DABCO·$2H_2O_2$ complex. The boracyclobutenes studied displayed

weak Lewis acidity, failing to form stable coordination complexes with salts and amines; weak Lewis acidity was confirmed by a Gutmann-Beckett determination using $Et_3P{=}O$. In reactions with aldehydes, two productive pathways have been identified: likely through an allylboration mechanism, butadienes are formed; alternatively, an uncommon 1,2-nucleophilic addition of the alkyl boron-carbon bond to the carbonyl group was also observed, producing synthetically interesting oxaborin intermediates.

Investigations into boracyclobutene reactivity were initially hindered by the high susceptibility to decomposition and by non-convergent reaction pathways, leading to the formation of small quantities of multiple products. Preliminary observations suggest that while boracyclobutenes are conceptually interesting for applications as unique synthons, the very features that are so enticing for derivatization make this research difficult to conduct. However, having now laid a foundation for the transmetallative preparation of boracyclobutenes and subsequent reactivity pathways, chemistry in this area is primed for the rapid development of substantial applications.

Future Boracyclobutene Research

The preparation of 2-phenylboracyclobutenes from the analogous titanacyclobutene complexes proceeds smoothly. However, titanacyclobutenes bearing 2-trimethylsilyl and 2-methyl substituents afford poorer results, with concomitant formation of unidentified by-products. To improve the scope of the transmetallation reaction, conditions must be found that tolerate a broader range of titanacyclobutene substrates; to accomplish this, determining the decomposition pathway(s) may be necessary. It is possible that adapting the titanacyclobutene ancillary ligand set will effect the necessary changes, however modification of the substituent on the dihaloorganoborane is more facile, and it could potentially impact the reactivity of the boracyclobutene products as well. In particular, the use of dihaloaminoboranes would install a nitrogen substituent on boron, which would increase electron density at boron and, consequently, the boracyclobutene ring, possibly attenuating the reactivity with nucleophiles to a more controllable level.

The reactions observed with aldehydes are highly interesting. As already noted, 1,2-migration of organoborane carbon substituents to carbonyls is very uncommon. Therefore, this reactivity should be probed with a range of ketones and aldehydes so that, in conjunction with an oxidative work-up, the relative alkyl- versus vinyl-side selectivity can be determined. This investigation should also study reactions with other polar multiple bonds, such as nitriles and imines, as well as small molecules known to undergo migratory insertion.

The applicability of boracyclobutenes in transition metal-catalyzed cross-coupling processes is also an area that should be explored. Selective functionalization of a carbon-boron bond with late metals, and coupling with a reactive carbon atom, would conceivably produce more complex organoborane intermediates that could be further elaborated by a different process, i.e. a one-pot sequential difunctionalization of boracyclobutenes. However, while extremely interesting intermediates and products can be envisioned, controlling selectivity in the presence of transition metals will be challenging.

Chapter 6: Experimental Details

Reagents and Methods:

All manipulations of air sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in an mBraun Labmaster 100 drybox equipped with a -35 → -29 °C freezer. Toluene, benzene, hexanes, THF, pentane, and diethyl ether were distilled under a nitrogen atmosphere either from sodium (toluene), sodium benzophenone ketyl (THF, diethyl ether, benzene), or potassium benzophenone ketyl (hexanes, pentane). Dichloromethane and acetonitrile were distilled from calcium hydride and degassed by a series of freeze-pump-thaw cycles. Where appropriate, a high vacuum line (< 10^{-5} torr) was used to remove volatile material from products. Cylindrical medium-walled Pyrex vessels equipped with Teflon vacuum stopcocks are referred to as glass bombs. Unless stated otherwise, all reactions were conducted under an inert atmosphere. Samples for elemental analysis were prepared in the drybox in pre-weighed tin foil and stored in nitrogen-filled one-dram vials sealed with Parafilm until immediately prior to analysis. Samples for mass spectrometric analysis were prepared in the drybox in glass tubes that were then sealed with a septum; these were transported and stored under a nitrogen atmosphere in a test tube sealed with a septum until immediately prior to analysis. NMR experiments were conducted in a standard NMR tube with a plastic cap wrapped with Parafilm or in a valved NMR tube equipped with a sealable Teflon screw-cap. Flash column chromatographic separations were performed using Silicycle flash silica gel (40 – 63 μm).

Instrumentation:

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian DirectDrive (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometer, one of two Varian Inova 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometers, a Varian Mercury 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer, or a Varian Inova (^{1}H, 300 MHz) spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to external tetramethylsilane by using residual protiated solvent resonances for internal reference. Unless stated otherwise, NMR experiments were conducted at 27 °C. High-resolution electron impact mass spectra were obtained by the

Mass Spectrometry Facility on a Kratos MS-50G spectrometer with an ionization energy of 70 eV and GC-MS was performed on an Agilent Technologies 7890 GC with a 5975C electron impact MS detector. Elemental analyses were performed by the Analytical and Instrumentation Laboratory with a Carlos Erba Instruments CHSN-O EA1108 Elemental Analyzer. IR spectra were recorded on a Nicolet Magna IR 750 spectrophotometer equipped with a Nic-Phan FTIR Microscope in the same Laboratory. X-Ray structural data were collected on a Bruker Platform diffractometer with a SMART 1000 CCD area detector at -80 °C. Data collection, structural solutions, and further refinements were performed by Dr. Robert McDonald and Dr. Michael J. Ferguson of the X-Ray Crystallography Laboratory. The position of hydrogen atoms in ORTEP diagrams are derived from the idealized hybridization geometry of the attached atom. All Laboratories and Facilities used are in the University of Alberta Department of Chemistry.

An internal hexamethylbenzene standard was used in some cases to estimate the percent by weight of some identifiable species. ^{1}H NMR data were obtained on 20 – 30 mg of sample and 3 – 6 mg of hexamethylbenzene in C_6D_6 at 27 °C, which was used to calculate weight percentage. The values obtained should be accurate to within the limits of such a measurement (ca. ± 5 %).

Materials:

All commercial materials were purified prior to use by distillation or crystallization where appropriate. mCPBA (77 % maximum purity) was purchased from Aldrich and used without further purification. The following compounds were prepared and purified by literature procedures: $[Cp_2TiCl]_2$,[184] 3-phenyl-2-propynol,[355] 3-trimethylsilyl-2-propynol,[198] 4,4-dimethyl-2-pentynol,[356] $MesBF_3K$,[261] $PhBF_3K$,[256] and $PhBF_3NBu_4$.[260] Celite was dried in a vacuum oven at 80 °C prior to use.

DABCO·$2H_2O_2$ was prepared by literature procedure,[223] by addition of DABCO to an aqueous solution of H_2O_2 at 0 °C. The reaction is exothermic and it is important to maintain a temperature of 0 °C for at least 30 minutes. On two occasions the product was isolated by filtration prior to completion, which resulted in continued heat generation. Degradation in water was not noted, so longer periods at 0 °C should not be harmful. Solid DABCO·$2H_2O_2$ was stored at -30 °C and transferred with a plastic spatula.

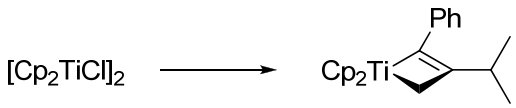
General procedure for conversion of propargyl alcohols to propargyl bromides:[194] To a solution of Br_2 (0.97 equivalents) in CH_2Cl_2 (25 volumes) at -78 °C was added neat PPh_3 (0.98 equivalents) and imidazole (1 equivalent). The suspension was warmed towards room temperature until all solid dissolved, then re-cooled to -78 °C where propargyl alcohol (1 equivalent) was added in CH_2Cl_2 (3 volumes). Once the reaction was complete by TLC analysis, 90 % of the solvent was removed under vacuum before pouring the remaining solution into hexanes (25 volumes). Removal of $Ph_3P{=}O$ by filtration and concentration under vacuum gave crude propargyl bromide, which was purified by chromatography through silica with hexanes as eluent. Spectra of isolated propargyl bromides were identical to published data.

Samarium diiodide was prepared according to a modified published procedure.[193] To a cold (-78 °C) stirred suspension (500 mL) of samarium metal (46.01 g, 0.306 moles) was added a THF solution of iodine (76.14 g, 0.300 moles in 500 mL THF). After addition was complete, the mixture was stirred for 5 days at room temperature before filtering through Celite, extracting the remaining solid into THF until the fractions were no longer a deep blue colour. Solvent was removed *in vacuo* to obtain solid $SmI_2{\cdot}x$THF. The molecular weight was determined by titration of a THF solution of SmI_2 with iodine (0.1 M in THF) to a yellow endpoint. Reactions using solid $SmI_2{\cdot}x$THF behaved identically to those using a 0.1 M solution of SmI_2.

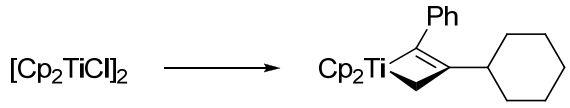
$^{i}PrBF_3K$ was prepared according to a modified published procedure.[256] To a cold stirred solution of $B(OMe)_3$ (1.5 g, 14.4 mmol) in ether (-78 °C, 25 mL) was slowly added a solution of $^{i}PrMgCl$ (1.8 M ether solution from Aldrich, concentration not verified, 9.6 mL, 17.3 mmol). The reaction was stirred at 25 °C for 16 hours, then a saturated aqueous solution of KHF_2 (4.51 g in approximately 10 mL H_2O, 57.7 mmol) was added and stirred for 10 minutes. Volatiles were removed under vacuum, after which azeotropic distillation with toluene (2 x 10 mL) was performed to remove remaining water. The white solid was triturated with acetone (2 x 10 mL at 25 °C, 2 x 5 mL at 55 °C) and the organic extracts combined. Acetone was removed by boiling until the solution became slightly cloudy, at which point it was cooled to -10 °C to crystallize $^{i}PrBF_3K$. Filtration yielded white crystalline solid in low yield (0.43 g, 20 %). Spectra were identical to the published data.[357]

A note on the labelling format: NMR signals are assigned to the italicized atoms, which are identified at the end of the bracketed descriptive data. These labels are meant only to indicate the atoms that produce the signal, and in no way suggest the connectivity through which coupling occurs.

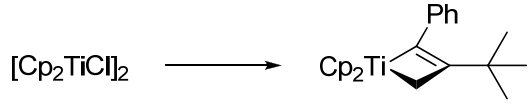
Procedures:



1,1-Bis(cyclopentadienyl)-3-isopropyl-2-phenyltitanacyclobutene (15): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (1.000 g, 2.34 mmol) and $SmI_2 \cdot 3.8THF$ (9.555 g, 14.05 mmol SmI_2) in dry THF (70 mL) was added a cold (-30 °C) solution of 1-bromo-3-phenyl-2-propyne (914 mg, 4.68 mmol) and 2-iodopropane (796 mg, 4.68 mmol) in dry THF (10 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (1.284 g, 82 % yield) as an analytically pure red crystalline solid. Spectra were identical to those previously reported.[95] **^{1}H NMR** (400 MHz, C_6D_6) δ 7.25 (app tt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.7 Hz, 2H, *m*-Ph*H*); 7.01 (tt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, *p*-Ph*H*); 6.96-6.93 (m, 2H, *o*-Ph*H*); 5.59 (s, 10H, Cp*H*); 3.21 (s, 2H, CH_2); 2.66 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*); 0.87 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 210.2 (Ti-*C*=C); 148.9 (*ipso*-Ph); 128.5 (*m*-Ph); 124.9 (*o*-Ph); 124.1 (*p*-Ph); 111.5 (Cp); 99.7 (Ti-C=*C*); 68.9 (*C*H_2); 27.6 (*C*H); 21.3 (*C*H_3). **HMQC** (400 MHz, C_6D_6) δ 7.25 ↔ δ 128.5; δ 7.01 ↔ δ 124.1; δ 6.96-6.93 ↔ δ 124.9; δ 5.59 ↔ δ 111.5; δ 3.21 ↔ δ 68.9; δ 2.66 ↔ δ 27.6; δ 0.87 ↔ δ 21.3. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 6.96-6.93 ↔ δ 210.2, 124.9, 124.1; δ 3.21 ↔ δ 210.2, 148.9, 99.7, 27.6; δ 2.66 ↔ δ 210.2, 99.7, 68.9, 21.3; δ 0.87 ↔ δ 99.7, 27.6, 21.3. **Anal**. Calcd. for $C_{22}H_{24}Ti$: C, 78.57, H, 7.19. Found: C, 78.23, H, 6.99.

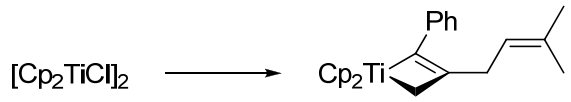


1,1-Bis(cyclopentadienyl)-3-cyclohexyl-2-phenyltitanacyclobutene (16): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (491 mg, 1.15 mmol) and $SmI_2 \cdot 3.8THF$ (680 g/mol, 4.690 g, 6.90 mmol SmI_2) in dry THF (30 mL) was added a cold (-30 °C) solution of 1-bromo-3-phenyl-2-propyne (448 mg, 2.30 mmol) and iodocyclohexane (483 mg, 2.30 mmol) in dry THF (5 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (691 mg, 80 % yield) as an analytically pure red solid. Diffractable crystals were obtained from hexanes solution by slow evaporation at 25 °C; refer to Appendix 1 for additional X-Ray analysis information. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.25 (app tt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.7 Hz, 2H, *m*-Ph*H*); 7.00 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, *p*-Ph*H*); 6.98-6.94 (m, 2H, *o*-Ph*H*); 5.60 (s, 10H, Cp*H*); 3.27 (s, 2H, Ti-CH_2); 2.35 (m, 1H, C=C-C*H*); 1.66-1.62 (m, 2H, Cy*H*); 1.55-1.53 (m, 1H, Cy*H*); 1.36-1.30 (m, 4H, Cy*H*); 1.12-1.06 (m, 3H, Cy*H*). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 210.7 (Ti-*C*=C); 148.9 (*ipso*-Ph); 128.5 (*m*-Ph); 124.9 (*o*-Ph); 124.1 (*p*-Ph); 111.5 (Cp); 99.3 (Ti-C=*C*); 71.1 (Ti-*C*H_2); 38.6 (C=C-*C*H); 32.0 (Cy); 26.9 (Cy); 26.7 (4-Cy). **HMQC** (400 MHz, C_6D_6) δ 7.25 ↔ δ 128.5; δ 7.00 ↔ δ 124.1; δ 6.98-6.94 ↔ δ 124.9; δ 5.60 ↔ δ 111.5; δ 3.27 ↔ δ 71.1; δ 2.35 ↔ δ 38.6; δ 1.66-1.62 ↔ δ 26.9; δ 1.36-1.30 ↔ δ 32.0; δ 1.12-1.06 ↔ δ 26.7. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 3.27 ↔ δ 210.7, 148.9, 124.9, 99.3, 38.6; δ 2.35 ↔ δ 32.0. **Anal**. Calcd. for $C_{25}H_{28}Ti$: C, 79.78, H, 7.50. Found: C, 79.52, H, 7.46.



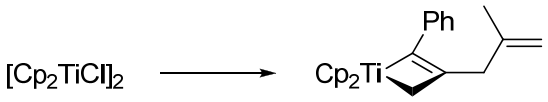
1,1-Bis(cyclopentadienyl)-2-phenyl-3-*tert*-butyltitanacyclobutene (17): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (50 mg, 0.12 mmol) and $SmI_2 \cdot 3.8THF$ (680 g/mol, 478 mg, 0.70 mmol SmI_2) in dry THF (4 mL) was added a cold (-30 °C) solution of 1-bromo-3-phenyl-2-propyne (46 mg, 0.23 mmol) and 2-iodo-2-methylpropane (43 mg, 0.23 mmol) in dry THF (1 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was

removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (63 mg, 76 % yield) as an analytically pure red crystalline solid. Diffractable crystals were obtained from hexanes solution by slow evaporation at 25 °C; refer to Appendix 1 for additional X-Ray analysis information. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.19-7.14 (m, 2H, *m*-Ph*H*); 6.93-6.88 (m, 3H, *o*- and *p*-Ph*H*); 5.60 (s, 10H, Cp*H*); 3.25 (s, 2H, CH_2); 0.98 (s, 9H, CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 204.7 (Ti-*C*=C); 151.1 (*ipso*-Ph); 128.3 (*m*-Ph); 123.9 (*o*-Ph); 122.9 (*p*-Ph); 112.5 (Cp); 101.3 (Ti-C=*C*); 72.1 (*C*H_2); 36.6 (*C*CH_3); 31.0 (*C*H_3). **HMQC** (400 MHz, C_6D_6) δ 5.60 ↔ δ 112.5; δ 3.25 ↔ δ 72.1; δ 0.98 ↔ δ 31.0. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 3.25 ↔ δ 204.7, 101.3; δ 0.98 ↔ δ 101.3, 36.6, 31.0. **Anal**. Calcd. for $C_{23}H_{26}Ti$: C, 78.86, H, 7.48. Found: C, 78.69, H, 7.47.



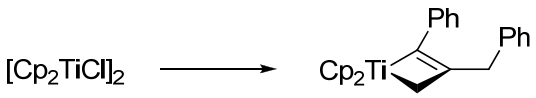
1,1-Bis(cyclopentadienyl)-3-(1,1-dimethyl-1-propenyl)-2-phenyltitanacyclobutene (18): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (1.000 g, 2.34 mmol) and SmI_2·3.8THF (680 g/mol, 9.555 g, 14.05 mmol SmI_2) in dry THF (70 mL) was added a cold (-30 °C) solution of 1-bromo-3-phenyl-2-propyne (914 mg, 4.68 mmol) in dry THF (5 mL). After 30 minutes of stirring at 25 °C, the mixture was cooled to -30 °C and 4-bromo-2-methyl-2-butene (698 mg, 4.68 mmol) was added in dry THF (5 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (1.273 g, 75 % yield) as a spectroscopically clean dark red oil. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.26 (br t, $^3J_{HH}$ = 6.8 Hz, 2H, *m*-Ph*H*); 7.05-7.00 (m, 3H, *o*- and *p*-Ph*H*); 5.60 (s, 10H, Cp*H*); 5.23 (br t, $^3J_{HH}$ = 6.3 Hz, 1H, C=C*H*); 3.39 (s, 2H, Ti-CH_2); 2.80 (d, $^3J_{HH}$ = 6.9 Hz, 2H, C=C-CH_2); 1.70 (s, 3H, CH_3); 1.54 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 210.5 (Ti-*C*=C); 148.1 (*ipso*-Ph); 131.9 (C=*C*$(CH_3)_2$); 128.5 (*m*-Ph); 125.5 (*o*-Ph); 124.5 (*p*-Ph); 122.9 (C=*C*H); 111.4 (Cp); 95.8 (Ti-C=*C*); 77.6 (Ti-*C*H_2); 30.1 (C=C-*C*H_2); 26.1 (*C*H_3); 18.2 (*C*H_3). **HMQC** (400 MHz, C_6D_6) δ 7.26 ↔ δ

128.5; δ 7.05-7.00 ↔ δ 125.5; δ 5.60 ↔ δ 111.4; δ 5.23 ↔ δ 122.9; δ 3.39 ↔ δ 77.6; δ 2.80 ↔ δ 30.1; δ 1.70 ↔ δ 26.1; δ 1.54 ↔ δ 18.2. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 5.23 ↔ δ 30.1, 26.1, 18.2; δ 3.39 ↔ δ 210.5, 125.5, 95.8, 30.1; δ 2.80 ↔ δ 210.5, 131.9, 122.9, 95.8, 77.6; δ 1.70 ↔ δ 131.9, 122.9, 18.2; δ 1.54 ↔ δ 131.9, 122.9, 26.1. **Anal**. Calcd. for $C_{24}H_{26}Ti$: C, 79.56, H, 7.23. Found: C, 78.66, H, 6.59. **HRMS** Calcd. *m/z* for $C_{24}H_{26}Ti$: 362.15140. Found: 362.15104.

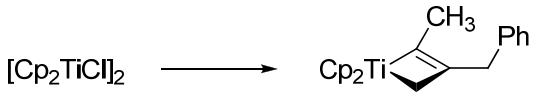


1,1-Bis(cyclopentadienyl)-3-(2-methylallyl)-2-phenyltitanacyclobutene (19): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (1.000 g, 2.34 mmol) and SmI_2·3.8THF (680 g/mol, 9.555 g, 14.05 mmol SmI_2) in dry THF (70 mL) was added a cold (-30 °C) solution of 1-bromo-3-phenyl-2-propyne (914 mg, 4.68 mmol) in dry THF (5 mL). After 30 minutes of stirring at 25 °C, the mixture was cooled to -30 °C and 2-methylallyl chloride (424 mg, 4.68 mmol) was added in dry THF (5 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (1.372 g, 84 % yield) as an analytically pure red crystalline solid. Diffractable crystals were obtained from hexanes solution by slow evaporation at 25 °C; refer to Appendix 1 for additional X-Ray analysis information. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.25 (app tt, $^3J_{HH}$ = 7.5 Hz, other *J* too small to identify, 2H, *m*-Ph*H*); 7.02 (tt, $^3J_{HH}$ = 7.4 Hz, other *J* too small to identify, 1H, *p*-Ph*H*); 6.98-6.95 (m, 2H, *o*-Ph*H*); 5.60 (s, 10H, Cp*H*); 4.87-4.86 (m, 1H,C=CH_2); 4.81-4.79 (m, 1H,C=CH_2); 3.26 (s, 2H, Ti-CH_2); 2.67 (s, 2H, C=C-CH_2); 1.54 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 211.3 (Ti-*C*=C); 148.1 (*ipso*-Ph); 144.5 (C=*C*-CH_3); 128.5 (*m*-Ph); 125.2 (*o*-Ph); 124.4 (*p*-Ph); 112.0 (C=*C*H_2); 111.6 (Cp); 95.1 (Ti-C=*C*); 76.1 (Ti-*C*H_2); 39.5 (C=C-*C*H_2); 22.9 (*C*H_3). **HMQC** (400 MHz, C_6D_6) δ 7.25 ↔ δ 128.5; δ 7.02 ↔ δ 124.4; δ 6.98-6.95 ↔ δ 125.2; δ 5.60 ↔ δ 111.6; δ 4.87-4.86 ↔ δ 112.0; δ 4.81-4.79 ↔ δ 112.0; δ 3.26 ↔ δ 76.1; δ 2.67 ↔ δ 39.5; δ 1.54 ↔ δ 22.9. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 4.87-

4.86 ↔ δ 39.5, 22.9; δ 4.81-4.79 ↔ δ 39.5, 22.9; δ 3.26 ↔ δ 211.3, 148.1, 95.1, 39.5; δ 2.67 ↔ δ 211.3, 144.5, 112.0, 95.1, 76.1, 22.9; δ 1.54 ↔ δ 144.3, 112.0, 39.5. **Anal**. Calcd. for $C_{23}H_{24}Ti$: C, 79.31, H, 6.95. Found: C, 79.71, H, 7.09.

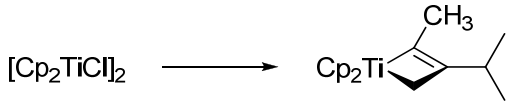


1,1-Bis(cyclopentadienyl)-3-benzyl-2-phenyltitanacyclobutene (20): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (100 mg, 0.23 mmol) and SmI_2·2.8THF (607 g/mol, 853 mg, 1.41 mmol SmI_2) in dry THF (4 mL) was added a cold (-30 °C) solution of 1-bromo-3-phenyl-2-propyne (91 mg, 0.47 mmol) and benzyl chloride (54 μL, 0.47 mmol) in dry THF (1 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (134.4 mg, 75 % yield) as a spectroscopically clean solid. Recrystallization from saturated pentane solution at -30 °C afforded an analytically pure red crystalline solid. Spectra were identical to those previously reported.[29] **^{1}H NMR** (400 MHz, C_6D_6) δ 7.29 (t, $^3J_{HH}$ = 7.6 Hz, 2H); 7.21-7.09 (m, 4H); 7.09-7.02 (m, 4H); 5.54 (s, 10H, Cp*H*); 3.25 (s, 2H, Ph-CH_2); 3.13 (s, 2H, Ti-CH_2). **COSY** (400 MHz, C_6D_6) δ 7.15 ↔ δ 3.25. **Anal**. Calcd. for $C_{26}H_{24}Ti$: C, 81.25, H, 6.29. Found: C, 81.29, H, 6.50.

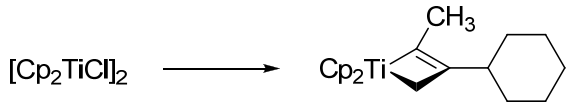


1,1-Bis(cyclopentadienyl)-3-benzyl-2-methyltitanacyclobutene (21): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (1.000 g, 2.34 mmol) and SmI_2·3.8THF (680 g/mol, 9.554 g, 14.05 mmol SmI_2) in dry THF (70 mL) was added a cold (-30 °C) solution of 1-bromo-2-butyne (623 mg, 4.68 mmol) and benzyl chloride (593 mg, 4.68 mmol) in dry THF (10 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (1.173 g, 78 % yield) as a spectroscopically clean red oil. Spectra were identical to those previously reported.[97] **^{1}H NMR** (400 MHz, C_6D_6) δ 7.21-7.17 (m, 2H, *m*-Ph*H*); 7.11-7.05 (m, 3H,

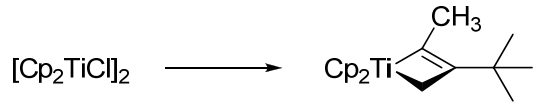
o- and *p*-Ph*H*); 5.43 (s, 10H, Cp*H*); 3.23 (s, 2H, PhCH_2); 3.05 (q, $^5J_{HH}$ = 2.0 Hz, 2H, Ti-CH_2); 2.23 (t, $^5J_{HH}$ = 2.0 Hz, 3H, CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 211.2 (Ti-*C*=C); 141.1 (*ipso*-Ph); 129.4 (*o*-Ph); 128.4 (*m*-Ph); 125.9 (*p*-Ph); 110.4 (Cp); 91.0 (Ti-C=*C*); 75.7 (Ti-*C*H_2); 34.8 (Ph*C*H_2); 22.0 (*C*H_3). **COSY** (400 MHz, C_6D_6, selected correlation only) δ 7.11-7.05 ↔ δ 3.23. **HMQC** (400 MHz, C_6D_6) δ 7.21 ↔ δ 128.4; δ 7.11-7.05 ↔ δ 125.9; δ 5.43 ↔ δ 110.4; δ 3.23 ↔ δ 34.8; δ 3.05 ↔ δ 75.7; δ 2.23 ↔ δ 22.0. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 3.23 ↔ δ 211.2, 141.1, 129.4, 91.0, 75.7; δ 3.05 ↔ δ 211.2, 91.0; δ 2.23 ↔ δ 211.2, 91.0. **Anal**. Calcd. for $C_{21}H_{22}Ti$: C, 78.27, H, 6.88. Found: C, 76.81, H, 6.83. **HRMS** Calcd. for $C_{21}H_{22}Ti$: 322.1201. Found: 322.1199.



1,1-Bis(cyclopentadienyl)-3-isopropyl-2-methyltitanacyclobutene (22): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (1.000 g, 2.34 mmol) and SmI_2·2.8THF (607 g/mol, 8.529 g, 14.05 mmol SmI_2) in dry THF (70 mL) was added a cold (-30 °C) solution of 1-bromo-2-butyne (623 mg, 4.68 mmol) and 2-iodopropane (796 mg, 4.68 mmol) in dry THF (10 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (102 mg, 79 % yield) as a spectroscopically clean red oil. Spectra were identical to those previously reported.[97] **^{1}H NMR** (400 MHz, C_6D_6) δ 5.49 (s, 10H, Cp*H*); 3.10 (q, $^5J_{HH}$ = 2.0 Hz, 2H, Ti-CH_2); 2.74 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*); 2.10 (t, $^5J_{HH}$ = 2.1 Hz, 3H, Ti-C-CH_3); 0.89 (d, $^3J_{HH}$ = 6.8 Hz, 6H, C(CH_3)$_2$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 211.8 (Ti-*C*=C); 110.3 (Cp); 94.3 (Ti-C=*C*); 69.1 (*C*H_2); 24.9 (*C*H); 21.4 (Ti-C-*C*H_3); 20.8 (C(*C*H_3)$_2$). **HMQC** (400 MHz, C_6D_6) δ 5.49 ↔ δ 110.3; δ 3.10 ↔ δ 69.1; δ 2.10 ↔ δ 21.4; δ 0.89 ↔ δ 20.8. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 3.10 ↔ δ 211.8, 94.3, 24.9; δ 2.74 ↔ δ 211.8, 94.3, 69.1, 20.8; δ 2.10 ↔ δ 211.8, 94.3; δ 0.89 ↔ δ 94.3, 24.9, 20.8. **Anal**. Calcd. for $C_{17}H_{22}Ti$: C, 74.46, H, 8.09. Found: C, 73.02, H, 8.00. **HRMS** Calcd. for $C_{17}H_{22}Ti$: 274.12009. Found: 274.11979.

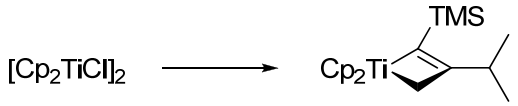


1,1-Bis(cyclopentadienyl)-3-cyclohexyl-2-methyltitanacyclobutene (23): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (100 mg, 0.23 mmol) and $SmI_2 \cdot 3.8THF$ (680 g/mol, 956 mg, 1.41 mmol SmI_2) in dry THF (6 mL) was added a cold (-30 °C) solution of 1-bromo-2-butyne (62 mg, 0.47 mmol) and iodocyclohexane (98 mg, 0.47 mmol) in dry THF (1 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (102 mg, 70 % yield) as a spectroscopically clean red oil. **^{1}H NMR** (400 MHz, C_6D_6) δ 5.51 (s, 10H, Cp*H*); 3.14 (q, $^5J_{HH}$ = 2.1 Hz, 2H, Ti-C*H*$_2$); 2.40 (m, 1H, C=C-C*H*); 2.13 (t, $^5J_{HH}$ = 2.1 Hz, 3H, C*H*$_3$); 1.80-1.74 (m, 2H, Cy*H*); 1.71-1.64 (m, 1H, Cy*H*); 1.39-1.15 (m, 7H, Cy*H*). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 212.7 (Ti-*C*=C); 110.3 (Cp); 93.8 (Ti-C=*C*); 71.2 (Ti-*C*H$_2$); 36.2 (C=C-*C*H); 31.4 (Cy); 27.4 (Cy); 26.8 (4-Cy); 21.5 (*C*H$_3$). **HMQC** (400 MHz, C_6D_6) δ 5.51 ↔ δ 110.3; δ 3.14 ↔ δ 71.2; δ 2.40 ↔ δ 36.2; δ 2.13 ↔ δ 21.5; δ 1.80-1.74 ↔ δ 27.4; δ 1.39-1.15 ↔ δ 31.4. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 3.14 ↔ δ 212.7, 93.8, 36.2; δ 2.40 ↔ δ 212.7, 93.8, 71.2, 31.4; δ 2.13 ↔ δ 212.7, 93.8, 71.2, 36.2. **Anal**. Calcd. for $C_{20}H_{26}Ti$: C, 76.43, H, 8.34. Found: C, 75.98, H, 8.51. **HRMS** Calcd. for $C_{20}H_{26}Ti$: 314.15140. Found: 314.15229.

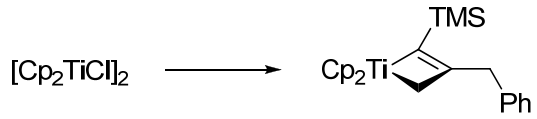


1,1-Bis(cyclopentadienyl)-2-methyl-3-*tert*-butyltitanacyclobutene (24): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (100 mg, 0.23 mmol) and $SmI_2 \cdot 3.8THF$ (680 g/mol, 956 mg, 1.41 mmol SmI_2) in dry THF (7 mL) was added a cold (-30 °C) solution of 1-bromo-2-butyne (62 mg, 0.47 mmol) and 2-iodo-2-methylpropane (86 mg, 0.47 mmol) in dry THF (1 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (106 mg, 79 % yield) as a spectroscopically clean red oil. **^{1}H NMR**

(400 MHz, C_6D_6) δ 5.55 (s, 10H, Cp*H*); 3.09 (q, $^5J_{HH}$ = 2.0 Hz, 2H, CH_2); 2.16 (t, $^5J_{HH}$ = 2.0 Hz, 3H, Ti-C-CH_3); 1.09 (s, 9H, C(CH_3)$_3$). **^{13}C NMR** (100 MHz, C_6D_6) δ 205.9 (Ti-*C*=C); 111.2 (Cp); 97.6 (Ti-C=*C*); 72.6 (*C*H_2); 35.1 (*C*(CH$_3$)$_3$); 30.3 (C(*C*H$_3$)$_3$); 23.0 (Ti-C-*C*H$_3$). **Anal**. Calcd. for $C_{18}H_{24}Ti$: C, 75.00, H, 8.39. Found: C, 74.29, H, 8.43. **HRMS** Calcd. for $C_{18}H_{24}Ti$: 288.13574. Found: 288.13576.

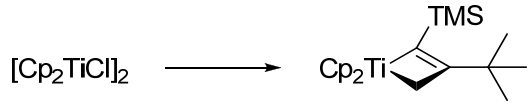


1,1-Bis(cyclopentadienyl)-3-isopropyl-2-(trimethylsilyl)titanacyclobutene (25): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (100 mg, 0.23 mmol) and SmI_2·3.8THF (680 g/mol, 956 mg, 1.41 mmol SmI_2) in dry THF (6 mL) was added a cold (-30 °C) solution of 1-bromo-3-trimethylsilyl-2-propyne (90 mg, 0.47 mmol) and 2-iodopropane (80 mg, 0.47 mmol) in dry THF (1 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (115 mg, 74 % yield) as a spectroscopically clean red oil. **^{1}H NMR** (400 MHz, C_6D_6) δ 5.52 (s, 10H, Cp*H*); 3.23 (s, 2H, CH_2); 2.67 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*); 0.91 (d, $^3J_{HH}$ = 6.6 Hz, 6H, C(CH_3)$_2$); 0.17 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 221.0 (Ti-*C*=C); 117.5 (Ti-C=*C*); 110.6 (Cp); 73.2 (*C*H_2); 33.2 (*C*H); 21.0 (C(*C*H$_3$)$_2$); 1.7 (Si(*C*H$_3$)$_3$). **HMQC** (400 MHz, C_6D_6) δ 5.52 ↔ δ 110.6; δ 3.23 ↔ δ 73.2; δ 2.67 ↔ δ 33.2; δ 0.91 ↔ δ 21.0; δ 0.17 ↔ δ 1.7. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 3.23 ↔ δ 221.0, 117.5, 33.2; δ 2.67 ↔ δ 21.0; δ 0.91 ↔ δ 117.5, 33.2; δ 0.17 ↔ δ 221.0, 1.7. **Anal**. Calcd. for $C_{19}H_{28}SiTi$: C, 68.66, H, 8.49. Found: C, 67.45, H, 8.17. **HRMS** Calcd. for $C_{19}H_{28}SiTi$: 332.14398. Found: 332.14350.



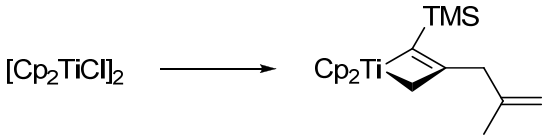
1,1-Bis(cyclopentadienyl)-3-benzyl-2-(trimethylsilyl)titanacyclobutene (26): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (500 mg, 1.17 mmol) and SmI_2·3.8THF (680 g/mol, 4.777 g, 7.03 mmol SmI_2) in dry THF (30 mL) was added a cold (-30 °C) solution

of 1-bromo-3-trimethylsilyl-2-propyne (448 mg, 2.34 mmol) and benzyl chloride (296 mg, 2.34 mmol) in dry THF (5 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (624 mg, 70 % yield) as an analytically pure dark red oil. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.23-7.18 (m, 2H, *m*-Ph*H*); 7.15-7.12 (m, 2H, *o*-Ph*H*); 7.08 (tt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, *p*-Ph*H*); 5.49 (s, 10H, Cp*H*); 3.33 (s, 2H, PhCH_2); 3.13 (s, 2H, Ti-CH_2); 0.24 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 220.9 (Ti-*C*=C); 140.5 (*ipso*-Ph); 129.6 (*o*-Ph); 128.5 (*m*-Ph); 126.2 (*p*-Ph); 112.7 (Ti-C=*C*); 110.7 (Cp); 81.1 (Ti-*C*H$_2$); 41.8 (Ph*C*H$_2$); 2.0 (Si(*C*H$_3$)$_3$). **COSY** (400 MHz, C_6D_6, selected correlation only) δ 7.15 ↔ δ 3.33. **HMQC** (400 MHz, C_6D_6) δ 7.23-7.18 ↔ δ 128.5; δ 7.08 ↔ δ 126.2; δ 5.49 ↔ δ 110.7; δ 3.33 ↔ δ 41.8; δ 3.13 ↔ δ 81.1; δ 0.24 ↔ δ 2.0. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 7.15-7.12 ↔ δ 41.8; δ 3.33 ↔ δ 220.9, 140.5, 112.7; δ 3.13 ↔ δ 220.9, 112.7, 41.8; δ 0.24 ↔ δ 220.9, 2.0. **Anal**. Calcd. for $C_{23}H_{28}SiTi$: C, 72.62, H, 7.42. Found: C, 72.93, H, 7.42.

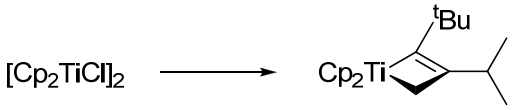


1,1-Bis(cyclopentadienyl)-3-*tert*-butyl-2-(trimethylsilyl)titanacyclobutene (27): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (100 mg, 0.23 mmol) and SmI_2·3.8THF (680 g/mol, 956 mg, 1.41 mmol SmI_2) in dry THF (7 mL) was added a cold (-30 °C) solution of 1-bromo-3-trimethylsilyl-2-propyne (90 mg, 0.47 mmol) and 2-iodo-2-methylpropane (86 mg, 0.47 mmol) in dry THF (1 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (120 mg, 74 % yield) as a spectroscopically clean red solid. Crystallization from a saturated cold hexanes solution was unsuccessful. **^{1}H NMR** (400 MHz, C_6D_6) δ 5.56 (s, 10H, Cp*H*); 3.49 (s, 2H, CH_2), 1.04 (s, 9H, C(CH_3)$_3$), 0.22 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 213.8 (Ti-*C*=C); 121.4 (Ti-C=*C*); 111.2 (Cp); 82.0 (Ti-*C*H$_2$); 37.2 (*C*(CH$_3$)$_3$); 31.0

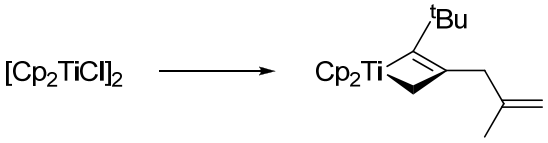
(C(CH_3)$_3$); 4.0 (Si(CH_3)$_3$). **HMQC** (400 MHz, C_6D_6) δ 5.56 ↔ δ 111.2; δ 3.49 ↔ δ 82.0; δ 1.04 ↔ δ 31.0; δ 0.22 ↔ δ 4.0. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 3.49 ↔ δ 213.8, 121.4, 37.2; δ 1.04 ↔ δ 121.4, 37.2, 31.0; δ 0.22 ↔ δ 213.8, 4.0. **Anal**. Calcd. for $C_{20}H_{30}SiTi$: C, 69.34, H, 8.73. Found: C, 67.53, H, 8.59. **HRMS** Calcd. for $C_{20}H_{30}SiTi$: 346.15964. Found: 346.15971.



1,1-Bis(cyclopentadienyl)-3-(2-methylallyl)-2-(trimethylsilyl)titanacyclobutene (28): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (30 mg, 0.070 mmol) and SmI_2·2.8THF (607 g/mol, 256 mg, 0.42 mmol SmI_2) in dry THF (2 mL) was added a cold (-30 °C) solution of 1-bromo-3-trimethylsilyl-2-propyne (27 mg, 0.14 mmol) and 2-methylallyl chloride (13 mg, 0.14 mmol) in dry THF (1 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (39 mg, 81 % yield) as a spectroscopically clean red oil. **^{1}H NMR** (400 MHz, C_6D_6) δ 5.54 (s, 10H, Cp*H*); 4.89 (br s, 1H, C=CH_2); 4.80 (br s, 1H, C=CH_2); 3.31 (s, 2H, Ti-CH_2); 2.75 (s, 2H, C=C-CH_2); 1.57 (s, 3H, CH_3); 0.17 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 222.3 (Ti-*C*=C); 144.1 (*C*=CH$_2$); 112.5 (C=*C*H$_2$); 111.9 (Ti-C=*C*); 110.7 (Cp); 81.5 (Ti-*C*H$_2$); 44.1 (C=C-*C*H$_2$); 22.8 (*C*H$_3$); 1.9 (Si(*C*H$_3$)). **HMQC** (400 MHz, C_6D_6) δ 5.54 ↔ δ 110.7; δ 4.89 ↔ δ 112.5; δ 4.80 ↔ δ 112.5; δ 3.31 ↔ δ 81.5; δ 2.75 ↔ δ 44.1; δ 1.57 ↔ δ 22.8; δ 0.17 ↔ δ 1.9. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 4.89 ↔ δ 22.8; δ 4.80 ↔ δ 44.1; δ 3.31 ↔ δ 222.3, 111.9, 44.1; δ 2.75 ↔ δ 222.3, 144.1, 112.5, 111.9, 81.5, 22.8; δ 1.57 ↔ δ 144.1, 112.5, 111.9, 44.1; δ 0.17 ↔ δ 222.3, 1.9. **Anal**. Calcd. for $C_{20}H_{28}SiTi$: C, 69.75, H, 8.19. Found: C, 68.62, H, 8.20. **HRMS** Calcd. for $C_{20}H_{28}SiTi$: 344.14397. Found: 344.14351.

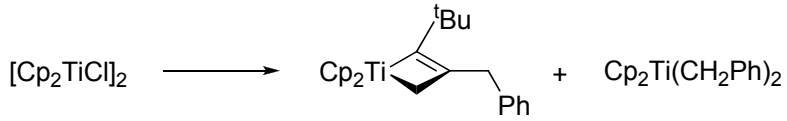


1,1-Bis(cyclopentadienyl)-3-isopropyl-2-*tert*-butyltitanacyclobutene (31): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (100 mg, 0.23 mmol) and $SmI_2 \cdot 3.8THF$ (680 g/mol, 956 mg, 1.41 mmol SmI_2) in dry THF (4 mL) was added a cold (-30 °C) solution of 1-bromo-4,4-dimethyl-2-pentyne (82 mg, 0.47 mmol) and 2-iodopropane (80 mg, 0.47 mmol) in dry THF (1 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the titanacyclobutene (113 mg, 76 % yield) as a spectroscopically clean red oil. **^{1}H NMR** (400 MHz, C_6D_6) δ 5.59 (s, 10H, Cp*H*); 3.29 (s, 2H, Ti-CH_2); 2.97 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*); 1.12 (s, 9H, C(CH_3)$_3$); 0.88 (d, $^3J_{HH}$ = 6.7 Hz, 6H, HC(CH_3)$_2$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 221.7 (Ti-*C*=C); 110.2 (Cp); 95.8 (Ti-C=*C*); 74.6 (Ti-*C*H_2); 38.9 (*C*(CH_3)$_3$); 32.2 (C(*C*H_3)$_3$); 27.2 (*C*H); 20.7 (HC(*C*H_3)$_2$). **HMQC** (400 MHz, C_6D_6) δ 5.59 ↔ δ 110.2; δ 3.29 ↔ δ 74.6; δ 2.97 ↔ δ 27.2; δ 1.12 ↔ δ 32.3; δ 0.88 ↔ δ 20.7. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 3.29 ↔ δ 221.7, 95.8, 32.2, 27.2; δ 2.97 ↔ δ 74.6, 20.7; δ 1.12 ↔ δ 221.7, 38.9, 32.2; δ 0.88 ↔ δ 95.8, 27.2, 20.7. **Anal**. Calcd. for $C_{20}H_{28}Ti$: C, 75.94, H, 8.92. Found: C, 75.52, H, 8.47. **HRMS** Calcd. for $C_{20}H_{28}Ti$: 316.16705. Found: 316.16740.



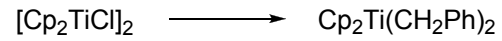
1,1-Bis(cyclopentadienyl)-3-(2-methylallyl)-2-*tert*-butyltitanacyclobutene (32): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (30 mg, 0.07 mmol) and $SmI_2 \cdot 2.8THF$ (607 g/mol, 256 mg, 0.42 mmol SmI_2) in dry THF (2 mL) was added a cold (-30 °C) solution of 1-bromo-4,4-dimethyl-2-pentyne (25 mg, 0.14 mmol). After 30 minutes of stirring at 25 °C, the mixture was cooled to -30 °C and methyallyl chloride (13 mg, 0.14 mmol) in dry THF (1 mL) was added. The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the

titanacyclobutene (40 mg, 87 % yield) as a spectroscopically clean red oil. **^{1}H NMR** (400 MHz, C_6D_6) δ 5.60 (s, 10H, Cp*H*); 4.88 (br s, 1H, C=C*H*$_2$); 4.74 (br s, 1H, C=C*H*$_2$); 3.32 (s, 2H, Ti-C*H*$_2$); 2.73 (s, 2H, C=C-C*H*$_2$); 1.58 (s, 3H, C=C-C*H*$_3$); 1.11 (s, 9H, C(C*H*$_3$)$_3$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 223.0 (Ti-*C*=C); 144.5 (*C*=CH$_2$); 111.8 (C=*C*H$_2$); 110.0 (Cp); 90.2 (Ti-C=*C*); 83.0 (Ti-*C*H$_2$); 39.1 (C=C-*C*H$_2$); 38.6 (*C*(CH$_3$)$_3$); 32.1 (C(*C*H$_3$)$_3$); 22.8 (C=C-*C*H$_3$). **HMQC** (400 MHz, C_6D_6) δ 5.60 ↔ δ 110.0; δ 4.88 ↔ δ 111.8; δ 4.74 ↔ δ 111.8; δ 3.32 ↔ δ 83.0; δ 2.73 ↔ δ 39.1; δ 1.58 ↔ δ 22.8; δ 1.11 ↔ δ 32.1. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 4.88 ↔ δ 39.1, 22.8; δ 4.74 ↔ δ 39.1, 22.8; δ 3.32 ↔ δ 223.0, 90.2, 39.1, 38.6, 32.1; δ 2.73 ↔ δ 223.0, 144.5, 111.8, 90.2, 83.0, 22.8; δ 1.58 ↔ δ 144.5, 111.8, 39.1; δ 1.11 ↔ δ 223.0, 38.6, 32.1. **Anal**. Calcd. for $C_{21}H_{28}Ti$: C, 76.82, H, 8.60. Found: C, 74.13, H, 8.12. **HRMS** Calcd. for $C_{21}H_{28}Ti$: 328.16705. Found: 328.16686.

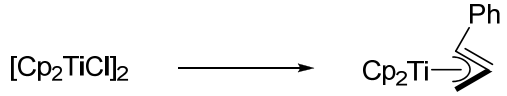


1,1-Bis(cyclopentadienyl)-3-benzyl-2-*tert*-butyltitanacyclobutene (33): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (50 mg, 0.12 mmol) and SmI_2·2.8THF (607 g/mol, 427 mg, 0.70 mmol SmI_2) in dry THF (3 mL) was added a cold (-30 °C) solution of 1-bromo-4,4-dimethyl-2-pentyne (41 mg, 0.23 mmol) and benzyl chloride (27 μL, 0.23 mmol) in dry THF (1 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the desired titanacyclobutene and 1,1-bis(cyclopentadienyl)-1,1-bis(benzyl)titanium **34** as an inseparable mixture in a 1:0.12 ratio as determined by ^{1}H NMR spectroscopy (78 mg, red oil). Varying the time at which benzyl chloride was added to the reaction mixture had no effect on the product distribution. 1,1-Bis(benzyl)-1,1-bis(cyclopentadienyl)titanium **34** was independently synthesized to verify the identity of the impurity (*vide infra*). **^{1}H NMR** (400 MHz, C_6D_6) δ 7.21 (t, $^3J_{HH}$ = 7.4 Hz, 2H, *m*-Ph*H*); 7.13-7.07 (m, 3H, Ph*H*); 5.57 (s, 10H, Cp*H*); 3.31 (s, 2H, Ph-C*H*$_2$); 3.12 (s, 2H, Ti-C*H*$_2$); 1.19 (s, 9H, C(C*H*$_3$)$_3$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC) δ 222.1 (Ti-*C*=C); 141.5 (*ipso*-Ph); 129.5 (*o*-Ph); 128.4 (*m*-Ph); 126.0 (*p*-Ph); 110.3 (Cp); 91.3 (Ti-C=*C*); 83.1 (Ti-

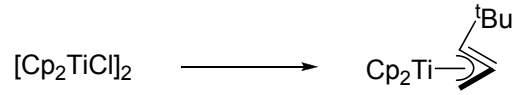
CH_2); 38.8 ($C(CH_3)_3$); 37.1 (Ph-CH_2); 32.6 (CH_3). **HMQC** (400 MHz, C_6D_6) δ 7.21 ↔ δ 128.4; δ 7.13-7.07 ↔ δ 129.5; δ 5.57 ↔ δ 110.3; δ 3.31 ↔ δ 37.1; δ 3.12 ↔ δ 83.1; δ 1.19 ↔ δ 32.6. **HRMS** Calcd. for $C_{24}H_{28}Ti$: 364.16705. Found: 364.16697.



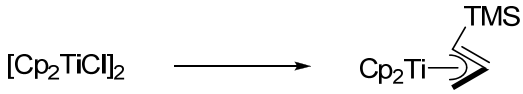
1,1-Bis(cyclopentadienyl)-1,1-bis(benzyl)titanium (34): To a cold (-30 °C) suspension of $[Cp_2TiCl]_2$ (10 mg, 0.023 mmol) and SmI_2·2.8THF (607 g/mol, 85 mg, 0.14 mmol SmI_2) in dry THF (2 mL) was added a cold (-30 °C) solution of benzyl chloride (11 μL, 0.094 mmol) in dry THF (1 mL). The solution was then stirred for 12 hours at 25 °C. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble SmX_3. Concentration under vacuum yielded the product (15 mg, 89 % yield) as a spectroscopically pure red oil. The ^{1}H NMR was identical to that already published.[201] **^{1}H NMR** (400 MHz, C_6D_6) δ 7.21 (t, $^3J_{HH}$ = 7.7 Hz, 4H, *m*-Ph*H*); 6.93 (t, $^3J_{HH}$ = 7.4 Hz, 2H, *p*-Ph*H*); 6.82 (d, $^3J_{HH}$ = 7.2 Hz, 4H, *o*-Ph*H*); 5.54 (s, 10H, Cp*H*); 1.88 (s, 4H, Ph-CH_2). **^{13}C NMR** (100 MHz, C_6D_6) δ 153.9; 126.3; 121.9; 115.3; 73.7; (one C under C_6D_5H).



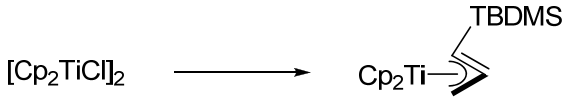
Bis(cyclopentadienyl)(η^3-1-phenylpropargyl)titanium (35): To a cold (-30 °C) solution of $[Cp_2TiCl]_2$ (30 mg, 0.070 mmol) and SmI_2·xTHF (171 mg, 607 g/mol, 0.28 mmol) in dry THF (4 mL) was added a solution of phenylpropargyl bromide (27 mg, 0.14 mmol) in THF (1 mL). The reaction mixture was then stirred at 25 °C for 3 hours. Solvent was removed *in vacuo*, then the residue was extracted into hexanes and filtered through Celite. Evaporation of solvent from the filtrate provided the propargyltitanium product as a green oil in moderate yield (23 mg, 57 %). **IR** (THF solution, 1 mm cell) 3083 (m), 3029 (m), 2959 (m), 2927 (m), 1925 (s), 1709 (w), 1592 (s), 1570 (m), 1488 (s), 1442 (s), 1277 (w), 1062 (s), 1012 (s), 897 (w), 790 (s), 760 (s).



Bis(cyclopentadienyl)(η^3-1-*tert*-butylpropargyl)titanium (36): To a cold (-30 °C) solution of $[Cp_2TiCl]_2$ (30 mg, 0.070 mmol) and SmI_2·xTHF (191 mg, 680 g/mol, 0.28 mmol) in dry THF (4 mL) was added a solution of phenylpropargyl bromide (25 mg, 0.14 mmol) in THF (1 mL). The reaction mixture was then stirred at 25 °C for 3 hours. Solvent was removed *in vacuo*, then the residue was extracted into hexanes and filtered through Celite. Evaporation of solvent from the filtrate provided the propargyltitanium product as a green oil in good yield (31 mg, 81 %). **IR** (THF solution, 1 mm cell) 3104 (w), 3036 (w), 2964 (s), 2925 (m), 2899 (m), 2862 (m), 1954 (w), 1923 (m), 1752 (w), 1578 (w), 1473 (m), 1457 (m), 1442 (m), 1358 (s), 1269 (s), 1143 (m), 1014 (s), 789 (s).

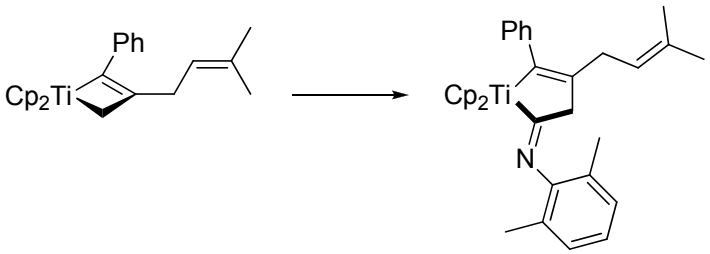


Bis(cyclopentadienyl)(η^3-1-(trimethylsilyl)propargyl)titanium (37): To a cold (-30 °C) solution of $[Cp_2TiCl]_2$ (30 mg, 0.070 mmol) and SmI_2·xTHF (171 mg, 607 g/mol, 0.28 mmol) in dry THF (4 mL) was added a solution of (trimethylsilyl)propargyl bromide (27 mg, 0.14 mmol) in THF (1 mL). The reaction mixture was then stirred at 25 °C for 30 hours. Solvent was removed *in vacuo*, then the residue was extracted into hexanes and filtered through Celite. Evaporation of solvent from the filtrate provided the propargyltitanium product as a green oil in good yield (36 mg, 88 %). **IR** (THF solution, 1 mm cell) 3107 (w), 2959 (s), 2893 (w), 1948 (s), 1933 (s), 1442 (w), 1408 (w), 1244 (s), 1146 (s), 1124 (w), 1016 (s), 836 (s), 789 (s), 760 (s).



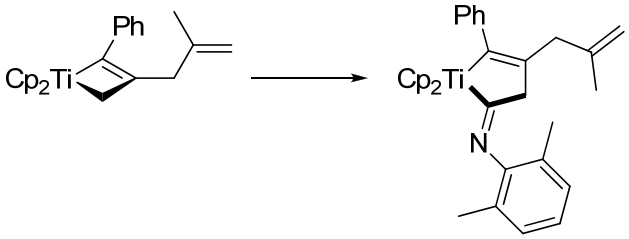
Bis(cyclopentadienyl)(η^3-1-*tert*-butyldimethylsilylpropargyl)titanium (38): To a cold (-30 °C) solution of $[Cp_2TiCl]_2$ (30 mg, 0.070 mmol) and SmI_2·xTHF (171 mg, 607 g/mol, 0.28 mmol) in dry THF (4 mL) was added a solution of *tert*-butyldimethylsilylpropargyl bromide (33 mg, 0.14 mmol) in THF (1 mL). The reaction mixture was then stirred at 25 °C for 30 hours. Solvent was removed *in vacuo*, then the

residue was extracted into hexanes and filtered through Celite. Evaporation of solvent from the filtrate provided the propargyltitanium product as a green oil in good yield (44 mg, 95 %). **IR** (THF solution, 1 mm cell) 3108 (w), 2953 (s), 2928 (s), 2885 (m), 2857 (s), 1947 (m), 1932 (m), 1716 (w), 1471 (w), 1463 (w), 1249 (s), 1089 (m), 1016 (m), 802 (s), 774 (s).



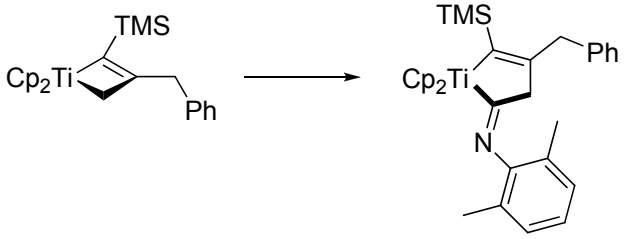
1,1-Bis(cyclopentadienyl)-2-(2,6-dimethylphenylimino)-4-(3-methylbut-2-enyl)-5-phenyltitanacyclopent-4-ene (39): To a cold (-30 °C) solution of **18** (300 mg, 0.83 mmol) in dry THF (9 mL) was added a solution of 2,6-dimethylphenyl isocyanide (109 mg, 0.83 mmol) in THF (1 mL), and the resulting solution stirred for 5 hours at 25 °C. The solvent was removed *in vacuo* and the residue was extracted with a solution of 10 % toluene and 90 % hexanes. The extracts were filtered through Celite then cooled to -30 °C for recrystallization. Filtration provided an analytically pure dark brown solid (234 mg, 57 %). **IR** (solid, FTIR microscope) 1550 cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.11 (d, $^3J_{HH}$ = 7.4 Hz, 2H, *o*-Ph*H*); 7.02 (d, $^3J_{HH}$ = 7.4 Hz, 2H, *m*-Xyl*H*); 6.91 (tt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, *p*-Ph*H*); 6.87 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Xyl*H*); 6.73 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, *m*-Ph*H*); 6.11 (s, 10H, Cp*H*); 5.05 (tt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, C=C*H*); 2.71 (s, 2H, Ti-C(N)-CH_2); 2.32 (d, $^3J_{HH}$ = 7.4 Hz, 2H, C=C-CH_2); 2.26 (s, 6H, Xyl-CH_3); 1.58 (s, 3H, C=C-CH_3); 1.20 (s, 3H, C=C-CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 232.9 (Ti-*C*=N); 190.7 (Ti-*C*=C); 152.5 (*ipso*-Xyl); 148.3 (*ipso*-Ph); 131.2 (C=*C*$(CH_3)_2$); 128.3 (*m*-Xyl); 128.1 (*o*-Ph); 127.4 (Ti-C=*C*); 126.6 (*m*-Ph); 124.8 (*o*-Xyl); 123.7 (*p*-Ph); 123.1 ($(CH_3)_2$C=*C*H); 121.8 (*p*-Xyl); 115.7 (Cp); 45.6 (Ti-C(=N)-*C*H_2); 33.1 (C=C(H)-*C*H_2); 25.7 (C=C-*C*H_3); 18.9 (Xyl-*C*H_3); 17.6 (C=C-*C*H_3). **COSY** (400 MHz, C_6D_6) δ 7.11 ↔ δ 6.91, 6.73; δ 7.02 ↔ δ 6.87, 2.26; δ 6.91 ↔ δ 7.11, 6.73; δ 6.87 ↔ δ 7.02; δ 6.73 ↔ δ 7.11, 6.91; δ 5.05 ↔ δ 2.32, 1.58, 1.20; δ 2.71 ↔ δ 2.32; δ 2.32 ↔ δ 5.05, 2.71, 1.58, 1.20; δ 2.26 ↔ δ 7.02; δ

1.58 ↔ δ 5.05, 2.32, 1.20; δ 1.20 ↔ δ 5.05, 2.32, 1.58. **HMQC** (400 MHz, C_6D_6) δ 7.02 ↔ δ 128.3; δ 6.91 ↔ δ 123.7; δ 6.87 ↔ δ 121.8; δ 6.73 ↔ δ 126.6; δ 6.11 ↔ δ 115.7; δ 5.05 ↔ δ 123.1; δ 2.71 ↔ δ 45.6; δ 2.32 ↔ δ 33.1; δ 2.26 ↔ δ 18.9; δ 1.58 ↔ δ 25.7; δ 1.20 ↔ δ 17.6. **HMBC** (400 MHz, C_6D_6) δ 7.11 ↔ δ 148.3, 128.1; δ 7.02 ↔ δ 152.5, 128.3, 18.9; δ 6.91 ↔ δ 128.1, 126.6; δ 6.87 ↔ δ 128.3, 124.8; δ 6.73 ↔ δ 190.7, 126.6, 123.7; δ 6.11 ↔ δ 115.7; δ 2.71 ↔ δ 232.9, 190.7, 152.5, 127.4, 33.1; δ 2.32 ↔ δ 190.7, 131.2, 127.4, 123.1, 45.6; δ 2.26 ↔ δ 152.5, 128.3, 124.8; δ 1.58 ↔ δ 131.2, 123.1, 17.6; δ 1.20 ↔ δ 131.2, 123.1, 25.7. **Anal**. Calcd. for $C_{33}H_{35}NTi$: C, 80.31, H, 7.15, N, 2.84. Found: C, 80.12, H, 7.40, N, 2.84.



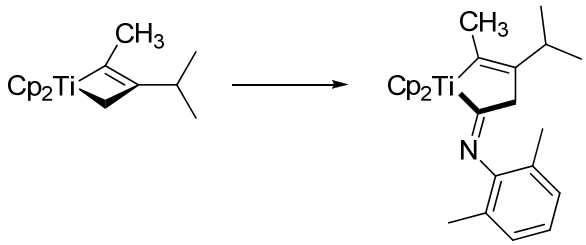
1,1-Bis(cyclopentadienyl)-2-(2,6-dimethylphenylimino)-4-(2-methylallyl)-5-phenyltitanacyclopent-4-ene (40): To a cold (-30 °C) solution of **19** (100 mg, 0.29 mmol) in dry THF (4 mL) was added a solution of 2,6-dimethylphenyl isocyanide (38 mg, 0.29 mmol) in THF (1 mL), and the resulting solution stirred for 5 hours at 25 °C. The solvent was removed *in vacuo* and the residue was extracted with a solution of 10 % toluene and 90 % hexanes. The extracts were filtered through Celite then cooled to -30 °C for recrystallization. Filtration provided a spectroscopically clean dark brown solid (67 mg, 49 %). **IR** (solid, FTIR microscope) 1575 cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.07 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-Ph*H*); 6.98 (d, $^3J_{HH}$ = 7.3 Hz, 2H, *m*-Xyl*H*); 6.87 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Ph*H*); 6.82 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Xyl*H*); 6.72-6.70 (m, 2H, *o*-Ph*H*); 6.12 (s, 10H, Cp*H*); 4.65 (s, 1H, C=CH_2); 4.61 (s, 1H, C=CH_2); 2.70 (s, 2H, Ti-C(=N)-CH_2); 2.24 (s, 8H, H_2C=C-CH_2 and Xyl-CH_3); 1.40 (s, 3H, C=C-CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 232.9 (Ti-*C*=N); 192.8 (Ti-*C*=C); 152.3 (*ipso*-Xyl); 147.9 (*ipso*-Ph); 144.7 (*C*=CH_2); 128.5 (*m*-Xyl); 128.0 (*m*-Ph); 126.22 (*o*-Ph or Ti-C=*C*); 126.20 (*o*-Ph or Ti-C=*C*); 124.7 (*o*-Xyl); 123.8 (*p*-Ph); 121.8 (*p*-Xyl); 115.7 (Cp); 110.8 (C=*C*H_2); 46.6 (Ti-C(=N)-*C*H_2); 42.0 (H_2C=C-*C*H_2); 22.8 (H_2C=C-

CH_3); 19.0 (Xyl-*C*H_3). **COSY** (400 MHz, C_6D_6) δ 7.07 ↔ δ 6.87, 6.72-6.70; δ 6.98 ↔ δ 6.82, 2.24; δ 6.87 ↔ δ 7.07; δ 6.82 ↔ δ 6.98; δ 6.72-6.70 ↔ δ 7.07; δ 6.12 ↔ δ 6.12; δ 4.65 ↔ δ 4.61, 1.40; δ 4.61 ↔ δ 4.65, 2.24; δ 2.70 ↔ δ 2.24; δ 2.24 ↔ δ 6.98, 4.61, 2.70, 1.40; δ 1.40 ↔ δ 4.65, 2.24. **HMQC** (400 MHz, C_6D_6) δ 7.07 ↔ δ 128.0; δ 6.98 ↔ δ 128.5; δ 6.87 ↔ δ 123.8; δ 6.82 ↔ δ 121.8; δ 6.72-6.70 ↔ δ 126.22 or 126.20; δ 6.12 ↔ δ 115.7; δ 4.65 ↔ δ 110.8; δ 4.61 ↔ δ 110.8; δ 2.70 ↔ δ 46.6; δ 2.24 ↔ δ 42.0, 19.0; δ 1.40 ↔ δ 22.8. **HMBC** (400 MHz, C_6D_6) δ 7.07 ↔ δ 147.9, 128.0; δ 6.98 ↔ δ 152.3, 128.5, 19.0; δ 6.87 ↔ δ 126.22 or 126.20; δ 6.82 ↔ δ 124.7; δ 6.72-6.70 ↔ δ 192.8, 123.8; δ 4.65 ↔ δ 42.0, 22.8; δ 4.61 ↔ δ 42.0, 22.8; δ 2.70 ↔ δ 232.9, 192.8, 126.22 or 126.20, 42.0; δ 2.24 ↔ δ 192.8, 152.3, 144.7, 128.5, 124.7, 110.8, 46.6, 22.8; δ 1.40 ↔ δ 144.7, 110.8, 42.0. **Anal**. Calcd. for $C_{32}H_{33}NTi$: C, 80.16, H, 6.94, N, 2.92. Found: C, 77.37, H, 6.67, N, 2.72. **HRMS** Calcd. for $C_{32}H_{32}NTi$ $(M-H)^+$: 478.20142. Found: 478.20120.

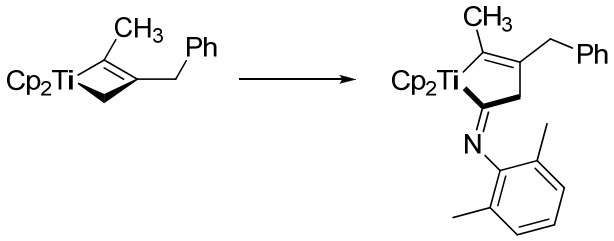


1,1-Bis(cyclopentadienyl)-2-(2,6-dimethylphenylimino)-4-benzyl-5-(trimethylsilyl)titanacyclopent-4-ene (41): To a cold (-30 °C) solution of **26** (100 mg, 0.26 mmol) in dry THF (4 mL) was added a solution of 2,6-dimethylphenyl isocyanide (34 mg, 0.26 mmol) in THF (1 mL), and the resulting solution stirred for 5 hours at 25 °C. The solvent was removed *in vacuo* and the residue was extracted with a solution of 10 % toluene and 90 % hexanes. The extracts were filtered through Celite then cooled to -30 °C for recrystallization. Filtration provided an analytically pure dark brown solid (57 mg, 42 %). **IR** (solid, FTIR microscope) 1598 cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.09-7.06 (m, 2H, *m*-Ph*H*); 7.02-6.97 (m, 3H, *p*- and *o*-Ph*H*); 6.82 (d, $^3J_{HH}$ = 7.4 Hz, 2H, *m*-Xyl*H*); 6.69 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Xyl*H*); 6.17 (s, 10H, Cp*H*); 2.92 (s, 2H, Ph-CH_2); 2.39 (s, 2H, Ti-C(=N)-CH_2); 2.05 (s, 6H, Xyl-CH_3); -0.13 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 233.0 (Ti-*C*=N);

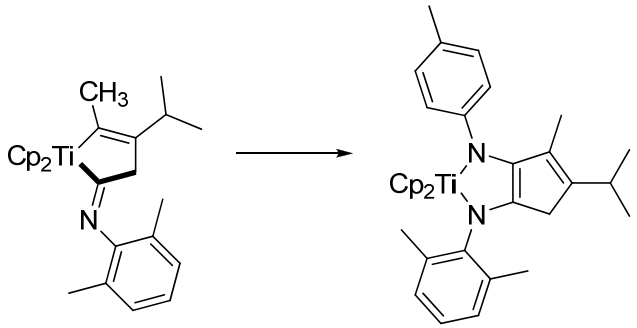
208.2 (Ti-*C*=C); 152.0 (*ipso*-Xyl); 140.6 (*ipso*-Ph); 139.1 (Ti-C=*C*); 128.6 (*m*-Ph); 128.4 (*o*-Ph); 128.3 (*m*-Xyl); 125.9 (*p*-Ph); 124.5 (*o*-Xyl); 121.6 (*p*-Xyl); 115.1 (Cp); 48.2 (Ti-C(=N)-*C*H_2); 45.0 (Ph-*C*H_2); 18.5 (Xyl-*C*H_3); 2.3 (Si(*C*H_3)$_3$). **COSY** (400 MHz, C_6D_6) δ 7.09-7.06 ↔ δ 7.02-6.97; δ 7.02-6.97 ↔ δ 7.09-7.06, 2.92; δ 6.82 ↔ δ 6.69, 2.05; δ 6.69 ↔ δ 6.82; δ 6.17 ↔ δ 6.17; δ 2.92 ↔ δ 7.02-6.97, 2.39; δ 2.39 ↔ δ 2.92; δ 2.05 ↔ δ 6.82; δ -0.13 ↔ δ -0.13. **HMQC** (400 MHz, C_6D_6) δ 7.09-7.06 ↔ δ 128.6; δ 7.02-6.97 ↔ δ 128.4; δ 6.82 ↔ δ 128.3; δ 6.69 ↔ δ 121.6; δ 6.17 ↔ δ 115.1; δ 2.92 ↔ δ 45.0; δ 2.39 ↔ δ 48.2; δ 2.05 ↔ δ 18.5; δ -0.13 ↔ δ 2.3. **HMBC** (400 MHz, C_6D_6) δ 7.09-7.06 ↔ δ 140.6, 128.6, 128.4; δ 7.02-6.97 ↔ δ 128.6, 125.9; δ 6.82 ↔ δ 152.0, 128.3, 18.5; δ 6.69 ↔ δ 124.5; δ 2.92 ↔ δ 208.2, 140.6, 128.4, 139.1, 48.2; δ 2.39 ↔ δ 233.0, 208.2, 139.1; δ 2.05 ↔ δ 152.0, 128.3, 124.5; δ -0.13 ↔ δ 208.2, 2.3. **Anal**. Calcd. for $C_{32}H_{37}NSiTi$: C, 75.13, H, 7.29, N, 2.74. Found: C, 75.47, H, 7.38, N, 3.11. **HRMS** Calcd. for $C_{32}H_{37}NSiTi$: 511.21747. Found: 511.21766.



1,1-Bis(cyclopentadienyl)-2-(2,6-dimethylphenylimino)-4-isopropyl-5-methyltitanacyclopent-4-ene (42): To a cold (-30 °C) solution of **22** (283 mg, 1.04 mmol) in dry THF (9 mL) was added a solution of 2,6-dimethylphenyl isocyanide (135 mg, 1.04 mmol) in THF (1 mL), and the resulting solution stirred for 5 hours at 25 °C. The solvent was removed *in vacuo* and the residue was extracted with a solution of 10 % toluene and 90 % hexanes. The extracts were filtered through Celite then cooled to -30 °C for recrystallization. Filtration provided an analytically pure dark brown solid (243 mg, 58 %). ^{1}H NMR spectrum was identical to that previously reported.[29] **^{1}H NMR** (400 MHz, C_6D_6) δ 7.02 (d, $^3J_{HH}$ = 7.4 Hz, 2H); 6.89 (t, $^3J_{HH}$ = 7.4 Hz, 1H); 6.09 (s, 10H); 2.60 (q, $^5J_{HH}$ = 1.8 Hz, 2H); 2.38 (sept, $^3J_{HH}$ = 6.8 Hz, 1H); 2.26 (s, 6H); 0.75 (t, $^5J_{HH}$ = 1.8 Hz, 3H); 0.72 (d, $^3J_{HH}$ = 6.8 Hz, 6H). **Anal**. Calcd. for $C_{26}H_{31}NTi$: C, 77.03, H, 7.71, N, 3.46. Found: C, 76.84, H, 7.84, N, 3.43.



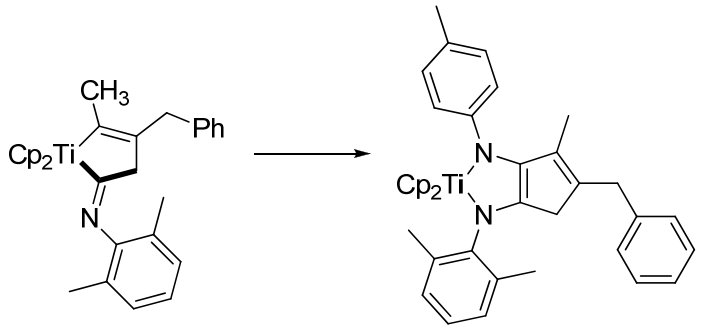
1,1-Bis(cyclopentadienyl)-2-(2,6-dimethylphenylimino)-4-benzyl-5-methyltitanacyclopent-4-ene (43): To a cold (-30 °C) solution of **21** (300 mg, 0.93 mmol) in dry THF (9 mL) was added a solution of 2,6-dimethylphenyl isocyanide (122 mg, 0.93 mmol) in THF (1 mL), and the resulting solution stirred for 5 hours at 25 °C. The solvent was removed *in vacuo* and the residue was extracted with a solution of 10 % toluene and 90 % hexanes. The extracts were filtered through Celite then cooled to -30 °C for recrystallization. Filtration provided an analytically pure dark brown solid (234 mg, 55 %). ^{1}H NMR spectrum was identical to that previously reported.[29] **^{1}H NMR** (400 MHz, C_6D_6) δ 7.18 (m, 2H); 7.03 (m, 3H); 6.88 (m, 2H); 6.82 (m, 1H); 6.09 (s, 10H); 2.92 (s, 2H); 2.54 (q, $^{5}J_{HH}$ = 1.8 Hz, 2H); 2.14 (s, 6H); 0.88 (t, $^{5}J_{HH}$ = 1.8 Hz, 3H). **Anal**. Calcd. for $C_{30}H_{31}NTi$: C, 79.46, H, 6.89, N, 3.09. Found: C, 79.43, H, 7.06, N, 3.06.



Bis(cyclopentadienyl)titanium-N-(2,6-dimethylphenyl)-N'-(4-methylphenyl)-3-methyl-4-(propan-2-yl)cyclopenta-1,3-diene-1,2-diamide (44): To a cold (-30 °C) solution of **42** (29 mg, 0.071 mmol) in dry THF (2 mL) was added a solution of 4-methylphenyl isocyanide (8 mg, 0.071 mmol) in 1 mL THF, and the resulting solution stirred for 5 hours at 25 °C before removing solvent *in vacuo*. The residue was extracted with hexanes and filtered through Celite. Removal of solvent under vacuum provided a spectroscopically clean dark brown oil (28 mg, 76 %). **IR** (solid, FTIR microscope) 3016 (w), 2957 (m), 2921 (m), 2868 (m), 2732 (w), 1643 (w), 1604 (w), 1590 (w), 1502 (s),

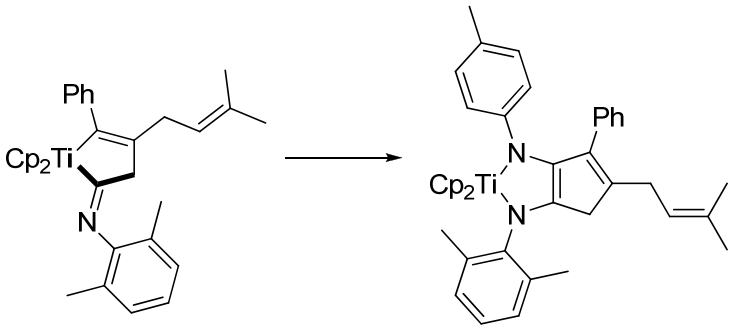
1464 (s), 1416 (s), 1387 (m), 1359 (w), 1302 (m), 1264 (m), 1212 (m) cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.06-7.05 (m, 2H, *o*-Tol*H*, *m*-Xyl*H*); 6.97 (d, $^3J_{HH}$ = 6.5 Hz, 1H, *p*-Xyl*H*); 6.91-6.89 (m, 2H, *o*-Tol*H*, *m*-Xyl*H*); 6.76 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, *m*-Tol*H*); 6.56 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.3 Hz, 1H, *m*-Tol*H*); 5.49 (s, 5H, Cp*H*); 5.42 (s, 5H, Cp*H*); 2.75 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, *H*C$(CH_3)_2$); 2.67 (app dd, $^2J_{HH}$ = 22.4 Hz, $^5J_{HH}$ = 1.8 Hz, 1H, CH_2); 2.30 (s, 3H, Xyl-CH_3); 2.21 (s, 3H, Tol-CH_3); 2.07 (app dd, $^2J_{HH}$ = 22.4 Hz, $^5J_{HH}$ = 2.0 Hz, 1H, CH_2); 1.78 (s, 3H, Xyl-CH_3); 1.43 (t, $^5J_{HH}$ = 2.0 Hz, 3H, C=C-CH_3); 0.83 (d, $^3J_{HH}$ = 6.8 Hz, 3H, HC(CH_3)$_2$); 0.78 (d, $^3J_{HH}$ = 6.8 Hz, 3H, HC(CH_3)$_2$). **^{13}C NMR** (100 MHz, APT, C_6D_6, assignments confirmed by HMQC and HMBC) δ 153.5 (p, *ipso*-Xyl); 152.8 (p, *C*=C-CH_3); 152.0 (p, *ipso*-Tol); 135.4 (p, CH_2-*C*(N)=C); 133.1 (p, CH_2-C(N)=*C*(N)); 132.9 (p, *o*-Xyl); 130.9 (p, *o*-Xyl); 130.23 (p, C=*C*-CH_3); 130.16 (p, *p*-Tol); 129.6 (a, *m*-Xyl); 129.14 (a, *m*-Xyl or *o*-Tol); 129.10 (a, *m*-Xyl or *o*-Tol); 128.8 (a, *o*-Tol); 123.9 (a, *p*-Xyl); 122.8 (a, *m*-Tol); 122.1 (a, *m*-Tol); 109.5 (a, Cp); 105.1 (a, Cp); 31.6 (p, *C*H_2); 27.6 (a, *C*H); 22.7 (a, C(*C*H_3)$_2$); 22.0 (a, C(*C*H_3)$_2$); 21.1 (a, Xyl-*C*H_3); 20.7 (a, Tol-*C*H_3); 18.6 (a, Xyl-*C*H_3); 12.2 (a, C=C-*C*H_3). **COSY** (400 MHz, C6D6) δ 7.06-7.05 ↔ δ 6.97, 6.91-6.89, 6.56, 2.30, 2.21, 1.78; δ 6.97 ↔ δ 7.06-7.05, 6.91-6.89, 2.30, 1.78; δ 6.91-6.89 ↔ δ 7.06-7.05, 6.97, 6.76, 2.21, 1.78; δ 6.76 ↔ δ 6.91-6.89, 6.56, 2.21; δ 6.56 ↔ δ 7.06-7.05, 6.76, 2.21; δ 2.75 ↔ δ 0.83, 0.78; δ 2.67 ↔ δ 2.07, 1.43; δ 2.30 ↔ δ 7.06-7.05; δ 2.21 ↔ δ 7.06-7.05, 6.91-6.89; δ 2.07 ↔ δ 2.67, 1.43; δ 1.78 ↔ δ 6.97; δ 1.43 ↔ δ 2.67, 2.07; δ 0.83 ↔ δ 2.75, 0.78; δ 0.78 ↔ δ 2.75, 0.83. **HMQC** (400 MHz, C_6D_6) δ 7.06-7.05 ↔ δ 128.8; δ 6.97 ↔ δ 123.9; δ 6.91-6.89 ↔ δ 129.14 or 129.10; δ 6.76 ↔ δ 122.8; δ 6.56 ↔ δ 122.1; δ 5.49 ↔ δ 109.5; δ 5.42 ↔ δ 105.1; δ 2.75 ↔ δ 27.6; δ 2.67 ↔ δ 31.6; δ 2.30 ↔ δ 21.1; δ 2.21 ↔ δ 20.7; δ 2.07 ↔ δ 31.6; δ 1.78 ↔ δ 18.6; δ 1.43 ↔ δ 12.2; δ 0.83 ↔ δ 22.7; δ 0.78 ↔ δ 22.0. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 7.06-7.05 ↔ δ 153.5, 152.0, 129.6, 128.8, 21.1, 20.7; δ 6.97 ↔ δ 153.5, 129.6, 129.1, 18.6; δ 6.91-6.89 ↔ δ 152.0, 133.1, 130.16, 21.1, 20.7; δ 6.76 ↔ δ 130.16, 122.1; δ 6.56 ↔ δ 130.16, 122.8; δ 2.75 ↔ δ 152.8, 130.23, 31.6, 22.7, 22.0; δ 2.67 ↔ δ 152.8, 135.4, 130.23; δ 2.30 ↔ δ 153.5, 129.6; δ 2.21 ↔ δ 130.16, 129.10; δ 2.07 ↔ δ 152.8, 135.4, 130.23; δ 1.78 ↔ δ 153.5, 132.9, 129.6; δ 1.43 ↔ δ 152.8, 133.1, 130.23; δ 0.83 ↔ δ 152.8, 27.6, 22.0; δ 0.78 ↔ δ

152.8, 27.6, 22.7. **Anal**. Calcd. for $C_{34}H_{38}N_2Ti$: C, 78.15, H, 7.33, N, 5.36. Found: C, 78.53, H, 7.91, N, 5.40. **HRMS** Calcd. for $C_{34}H_{38}N_2Ti$: 522.25145. Found: 522.25309.



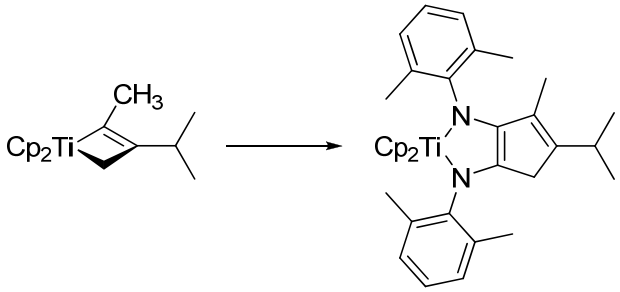
Bis(cyclopentadienyl)titanium-N-(2,6-dimethylphenyl)-N'-(4-methylphenyl)-4-benzyl-3-methyl-cyclopenta-1,3-diene-1,2-diamide (45): To a cold (-30 °C) solution of **43** (50 mg, 0.11 mmol) in dry THF (2 mL) was added a solution of 4-methylphenyl isocyanide (13 mg, 0.11 mmol) in THF (1 mL), and the resulting solution stirred for 5 hours at 25 °C before removing solvent *in vacuo*. The residue was extracted with hexanes and filtered through Celite. Removal of solvent under vacuum provided a spectroscopically clean dark brown oil (61 mg, 96 %). **IR** (solid, FTIR microscope) 3024 (m), 2957 (m), 2919 (m), 2870 (m), 1603 (m), 1502 (s), 1466 (s), 1418 (s), 1383 (m), 1357 (w), 1264 (s), 1218 (w) cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.11-7.06 (m, 3H, Ar*H*); 7.05-6.87 (m, 7H, Ar*H*); 6.81 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.3 Hz, 1H, Tol*H*); 6.60 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.3 Hz, 1H, Tol*H*); 5.50 (s, 5H, Cp*H*); 5.42 (s, 5H, Cp*H*); 3.61 (d, $^2J_{HH}$ = 15.2 Hz, 1H, Ph-CH_2); 3.35 (d, $^2J_{HH}$ = 15.2 Hz, 1H, Ph-CH_2); 2.59 (app dd, $^2J_{HH}$ = 22.3 Hz, $^5J_{HH}$ = 1.8 Hz, 1H, C=C(N)-CH_2); 2.25 (s, 3H, Tol-CH_3); 2.15 (s, 3H, Xyl-CH_3); 2.03 (app dd, $^2J_{HH}$ = 22.4 Hz, $^5J_{HH}$ = 2.0 Hz, 1H, C=C(N)-CH_2); 1.78 (s, 3H, Xyl-CH_3); 1.55 (t, $^5J_{HH}$ = 1.9 Hz, 3H, C=C-CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 153.3 (p, *ipso*-Xyl); 151.9 (p, *ipso*-Tol); 145.0 (p, *C*=C-CH_3); 141.2 (p, *ipso*-Ph); 136.7 (p, N-C=*C*-N); 132.9 (p, *o*-Xyl); 132.8 (p, C=*C*-CH_3); 132.5 (p, N-C=*C*-N); 131.0 (p, *p*-Tol); 130.2 (p, *o*-Xyl); 129.5 (a, *m*-Xyl); 129.2 (a, Tol); 129.0 (a, Ar); 128.9 (a, Tol); 128.7 (a, *o*- or *m*-Ph); 128.4 (a, *o*- or *m*-Ph); 126.2 (a, Ar); 123.9 (a, Ar); 122.8 (a, Tol); 122.2 (a, Tol); 109.6 (a, Cp); 105.2 (a, Cp); 36.0 (p, C=C(N)-*C*H_2); 35.5 (p, Ph-*C*H_2); 21.0 (a, Xyl-*C*H_3); 20.7 (a, Tol-*C*H_3); 18.6 (a, Xyl-*C*H_3); 12.6 (C=C-*C*H_3). **COSY** (400 MHz, C_6D_6, selected correlations only) δ 7.11-7.06

↔ δ 7.05-6.87, 6.60; δ 7.05-6.87 ↔ δ 7.11-7.06; δ 6.81 ↔ δ 7.05-6.87, 6.60; δ 6.60 ↔ δ 7.11-7.06, 6.81; δ 3.61 ↔ δ 3.35; δ 3.35 ↔ δ 3.61; δ 2.59 ↔ δ 2.03, 1.55; δ 2.03 ↔ δ 2.59, 1.55; δ 1.55 ↔ δ 2.59, 2.03. **HMQC** (400 MHz, C_6D_6) δ 7.05-6.87 ↔ δ 129.5, 128.7, 126.2, 123.9; δ 6.60 ↔ δ 122.2; δ 5.50 ↔ δ 109.6; δ 5.42 ↔ δ 105.2; δ 2.25 ↔ δ 20.7; δ 2.15 ↔ δ 21.0; δ 1.78 ↔ δ 18.6; δ 1.55 ↔ δ 12.6. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 7.11-7.06 ↔ δ 151.9, 141.2, 129.0, 20.7; δ 7.05-6.87 ↔ δ 153.3, 151.9, 132.9, 131.0, 129.5, 126.2, 36.0; δ 6.81 ↔ δ 131.0, 128.9; δ 6.60 ↔ δ 131.0, 122.8; δ 3.61 ↔ δ 145.0, 141.2, 132.8, 128.7, 36.0; δ 3.35 ↔ δ 145.0, 141.2, 132.8, 128.7, 36.0; δ 2.25 ↔ δ 131.0, 129.2; δ 2.15 ↔ δ 153.3, 130.2; δ 1.78 ↔ δ 153.3, 132.9, 129.5; δ 1.55 ↔ δ 145.0, 132.8. **Anal**. Calcd. for $C_{38}H_{38}N_2Ti$: C, 79.99, H, 6.71, N, 4.91. Found: C, 80.53, H, 7.27, 4.41. **HRMS** Calcd. for $C_{38}H_{38}N_2Ti$: 570.25145. Found: 570.25225.



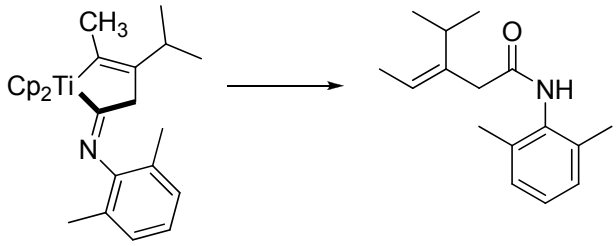
Bis(cyclopentadienyl)titanium-N-(2,6-dimethylphenyl)-N'-(4-methylphenyl)-3-phenyl-4-(3-methyl-but-2-enyl)cyclopenta-1,3-diene-1,2-diamide (46): To a cold (-30 °C) solution of **39** (50 mg, 0.10 mmol) in dry THF (2 mL) was added a solution of 4-methylphenyl isocyanide (12 mg, 0.10 mmol) in THF (1 mL), and the resulting solution stirred for 5 hours at 25 °C before removing solvent *in vacuo*. The residue was extracted with hexanes and filtered through Celite. Removal of solvent under vacuum provided a spectroscopically clean dark brown oil (45 mg, 72 %). **IR** (solid, FTIR microscope) 3012 (m), 2968 (m), 2731 (w), 1606 (m), 1589 (m), 1568 (w), 1503 (s), 1466 (s), 1445 (s), 1406 (s), 1385 (m), 1313 (m), 1262 (s), 1210 (s) cm^{-1}. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.11-7.08 (m, 2H, *o*-Ph*H*); 7.06 (d, $^3J_{HH}$ = 7.3 Hz, 1H, Ar*H*); 6.99-6.85 (m, 6H, Ar*H*); 6.53-6.46 (m, 2H, Ar*H*); 6.41 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, Tol*H*); 5.68 (s, 5H, Cp*H*); 5.52 (s, 5H, Cp*H*); 5.19 (app tt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, C=C*H*); 3.17 (d, $^3J_{HH}$ =

6.5 Hz, 2H, C=C(H)-CH_2); 2.95 (d, $^2J_{HH}$ = 22.7 Hz, 1H, C=C(N)-CH_2); 2.34 (d, $^2J_{HH}$ = 23.0 Hz, 1H, C=C(N)-CH_2); 2.31 (s, 3H, Xyl-CH_3); 2.07 (s, 3H, Tol-CH_3); 1.83 (s, 3H, Xyl-CH_3); 1.51 (s, 3H, C=C-CH_3); 1.36 (s, 3H, C=C-CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 153.6 (p, *ipso*-Xyl); 150.9 (p, *ipso*-Tol); 147.8 (p, Ph-C=*C*); 136.7 (p, Ph-*C*=C); 135.9 (p, *ipso*-Ph); 135.6 (p, CH_2-*C*-N); 133.2 (p, CH_2-C=*C*-N); 132.9 (p, *o*-Xyl); 132.3 (p, *C*=CH); 130.3 (p, *o*-Xyl); 130.2 (p, *p*-Tol); 129.7 (a, Ar); 129.2 (a, *m*-Xyl); 128.9 (a, *o*-Ph); 128.3 (a, Tol); 128.2 (a, Ar); 127.5 (a, Ar); 126.0 (a, Ph); 124.0 (a, Ar); 122.94 (a, C=*C*H or Tol); 122.92 (a, C=*C*H or Tol); 121.9 (a, Ar); 109.7 (a, Cp); 105.0 (a, Cp); 36.1 (p, C=C(N)-*C*H_2); 29.2 (p, C=C(H)-*C*H_2); 25.5 (a, C=C-*C*H_3); 21.0 (a, Xyl-*C*H_3); 20.6 (a, Tol-*C*H_3); 18.7 (a, Xyl-*C*H_3); 17.6 (C=C-*C*H_3). **COSY** (400 MHz, C_6D_6, selected correlations only) δ 5.19 ↔ δ 3.17, 1.51, 1.36; δ 3.17 ↔ δ 5.19, 1.51, 1.36; δ 2.95 ↔ δ 2.34; δ 2.34 ↔ δ 2.95. **HMQC** (400 MHz, C_6D_6) δ 7.11-7.08 ↔ δ 128.9; δ 6.99-6.85 ↔ δ 128.3, 126.0, 124.0; δ 6.53-6.46 ↔ δ 128.2, 122.94 or 122.92; δ 6.41 ↔ δ 121.9; δ 5.68 ↔ δ 105.0; δ 5.52 ↔ δ 109.7; δ 5.19 ↔ δ 122.94 or 122.92; δ 3.17 ↔ δ 29.2; δ 2.31 ↔ δ 21.0; δ 2.07 ↔ δ 20.6; δ 1.83 ↔ δ 18.7; δ 1.51 ↔ δ 25.5; δ 1.36 ↔ δ 17.6. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 7.11-7.08 ↔ δ 136.7, 128.9, 126.0; δ 7.06 ↔ δ 153.6; δ 6.99-6.85 ↔ δ 153.6, 150.9, 135.9, 132.9, 129.7, 129.2, 128.2, 20.6, 18.7; δ 6.53-6.46 ↔ δ 150.9; δ 6.41 ↔ δ 130.2, 122.94 or 122.92; δ 5.68 ↔ δ 105.0; δ 5.52 ↔ δ 109.7; δ 3.17 ↔ δ 147.8, 136.7, 132.3, 122.94 or 122.92, 36.1; δ 2.95 ↔ δ 147.8, 136.7; δ 2.34 ↔ δ 147.8, 136.7, 135.6; δ 2.31 ↔ δ 153.6, 130.3; δ 2.07 ↔ δ 130.2, 128.3; δ 1.83 ↔ δ 153.6, 132.9, 129.2; δ 1.51 ↔ δ 132.3, 122.9, 17.6; δ 1.36 ↔ δ 132.3, 122.9, 25.5. **Anal**. Calcd. for $C_{41}H_{42}N_2Ti$: C, 80.64, H, 6.93, N, 4.59. Found: C, 81.19, H, 8.07, 4.26. **HRMS** Calcd. for $C_{41}H_{42}N_2Ti$: 610.28275. Found: 610.28180.



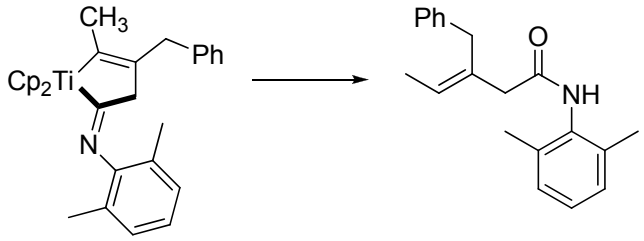
Bis(cyclopentadienyl)titanium-N,N'-bis(2,6-dimethylphenyl)-3-methyl-4-(propan-2-yl)cyclopenta-1,3-diene-1,2-diamide (47): To cold 2,6-dimethylphenyl isonitrile in an NMR tube was added a dry 0.5 mL toluene-d_8 solution of **42** (10 mg, 0.025 mmol) at -30 °C. Variable temperature NMR experiments were carried out 24 hours later. Removal of solvent provided an analytically pure dark red oil (13 mg, 98 %). **IR** (solid, FTIR microscope) 3059 (w), 3008 (w), 2956 (m), 2915 (m), 2864 (w), 2147 (w), 1591 (m), 1444 (s), 1412 (s), 1389 (s), 1350 (w), 1317 (w), 1291 (w), 1258 (w), 1229 (s), 1206 (s) cm^{-1}. **^{1}H NMR** (500 MHz, Tol-d_8, 27 °C) δ 7.04-7.02 (m, 2H, *m*-Xyl*H*); 7.00-6.97 (m, 2H, *m*-Xyl*H*); 6.91 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Xyl*H*); 6.88 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Xyl*H*); 5.57-5.46 (br s, 10H, Cp*H*); 2.80 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *H*C(CH_3)$_2$); 2.50-2.20 (br s, 14H, Xyl-CH_3, CH_2); 1.26 (t, $^5J_{HH}$ = 2.1 Hz, 3H, C=C-CH_3); 0.90 (br d, $^3J_{HH}$ = 6.0 Hz, 6H, HC(CH_3)$_2$). **^{1}H NMR** (500 MHz, Tol-d_8, -40 °C) δ 7.11-7.09 (m, 1H, *m*-Xyl*H*); 7.06-7.04 (m, 1H, *m*-Xyl*H*); 7.01-6.93 (m, 4H, *m*- and *p*-Xyl*H*); 5.60 (s, 5H, Cp*H*); 5.45 (s, 5H, Cp*H*); 2.84 (d, $^2J_{HH}$ = 23.0 Hz, 1H, CH_2); 2.75 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, *H*C(CH_3)$_2$); 2.45 (s, 3H, Xyl-CH_3); 2.43 (s, 3H, Xyl-CH_3); 2.24 (d, $^2J_{HH}$ = 22.0 Hz, 1H, CH_2); 2.18 (s, 3H, Xyl-CH_3); 2.10 (s, 3H, Xyl-CH_3); 1.28 (s, 3H, C=C-CH_3); 0.89 (d, $^3J_{HH}$ = 6.8 Hz, 3H, HC(CH_3)$_2$); 0.84 (d, $^3J_{HH}$ = 6.7 Hz, 3H, HC(CH_3)$_2$). **^{1}H NMR** (500 MHz, Tol-d_8, 70 °C) δ 6.96 (d, $^3J_{HH}$ = 7.2 Hz, 2H, m-XylH); 6.92 (d, $^3J_{HH}$ = 7.3 Hz, 2H, m-XylH); 6.84 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Xyl*H*); 6.80 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Xyl*H*); 5.49 (s, 10H, Cp*H*); 2.78 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, *H*C(CH_3)$_2$); 2.55-2.48 (br s, 2H, CH_2); 2.25-2.16 (br s, 12H, Xyl-CH_3); 1.21 (t, $^5J_{HH}$ = 2.1 Hz, 3H, C=C-CH_3); 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 6H, HC(CH_3)$_2$). **^{13}C NMR** (125 MHz, Tol-d_8, APT, -40 °C, assignments confirmed by HMQC and HMBC) δ 153.5 (p, *ipso*-Xyl); 153.2 (p, *ipso*-Xyl); 151.6 (p, *C*=C-CH_3); 133.9 (p, *o*-Xyl); 133.3 (p, *o*-Xyl); 133.0 (p, C=*C*-CH_3); 132.4 (p, CH_2-*C*(N)=C); 131.54 (a, *m*-Xyl); 131.50 (p, *o*-Xyl); 131.4 (p, CH_2-C=*C*(N)); 131.1 (p, *o*-Xyl); 131.0 (a, *m*-Xyl); 130.8 (a, *m*-Xyl); 129.5 (a, *m*-Xyl); 124.6 (a, *p*-Xyl); 124.1 (a, *p*-Xyl); 111.5 (a,

Cp); 107.7 (a, Cp); 32.9 (p, *C*H_2); 28.4 (a, *C*H); 23.66 (a, Xyl-*C*H_3); 23.62 (a, HC(*C*H_3)$_2$); 23.4 (a, HC(*C*H_3)$_2$); 23.2 (a, Xyl-*C*H_3); 22.7 (a, Xyl-*C*H_3); 22.2 (a, Xyl-*C*H_3); 11.9 (a, C=C-*C*H_3). **COSY** (500 MHz, Tol-d_8, -40 °C) δ 7.11-7.09 ↔ δ 7.06-7.04, 7.01-6.93; δ 7.06-7.04 ↔ δ 7.11-7.09, 7.01-6.93; δ 7.01-6.93 ↔ δ 7.11-7.09, 7.06-7.04; δ 2.84 ↔ δ 2.24, 1.28; δ 2.75 ↔ δ 0.89, 0.84; δ 2.24 ↔ δ 2.84, 1.28; δ 1.28 ↔ δ 2.84, 2.24; δ 0.89 ↔ δ 2.75, 0.84; δ 0.84 ↔ δ 2.75, 0.89. **HSQC** (500 MHz, Tol-d_8, -40 °C) δ 7.11-7.09 ↔ δ 131.0; δ 7.06-7.04 ↔ δ 130.8; δ 7.01-6.93 ↔ δ 129.6, 124.6, 124.1; δ 5.60 ↔ δ 111.5; δ 5.45 ↔ δ 107.7; δ 2.84 ↔ δ 32.9; δ 2.75 ↔ δ 28.4; δ 2.45 ↔ δ 23.66; δ 2.43 ↔ δ 22.2; δ 2.24 ↔ δ 32.9; δ 2.18 ↔ δ 23.2; δ 2.10 ↔ δ 22.7; δ 1.28 ↔ δ 11.9; δ 0.89 ↔ δ 23.62; δ 0.84 ↔ δ 23.4. **HMBC** (500 MHz, Tol-d_8, -40 °C, selected correlations only) δ 7.11-7.09 ↔ δ 153.5; δ 7.06-7.04 ↔ δ 153.5, 131.5, 126.4; δ 7.01-6.93 ↔ δ 153.2, 133.9, 133.3, 131.5, 131.1; δ 2.84 ↔ δ 151.6, 132.4; δ 2.75 ↔ δ 151.6, 133.0, 32.9, 23.62, 23.4; δ 2.45 ↔ δ 153.2, 131.1; δ 2.43 ↔ δ 153.5, 131.50; δ 2.24 ↔ δ 151.6; δ 2.18 ↔ δ 153.5, 133.9, 130.8; δ 2.10 ↔ δ 153.2, 133.3, 129.6; δ 1.28 ↔ δ 151.6, 133.0, 131.4; δ 0.89 ↔ δ 151.6, 28.4, 23.4; δ 0.84 ↔ δ 151.6, 28.4, 23.62. **Anal**. Calcd. for $C_{35}H_{40}N_2Ti$: C, 78.34, H, 7.51, N, 5.22. Found: C, 78.43, H, 7.59, N, 5.28. **HRMS** Calcd. for $C_{35}H_{40}N_2Ti$: 536.26710. Found: 536.26738.



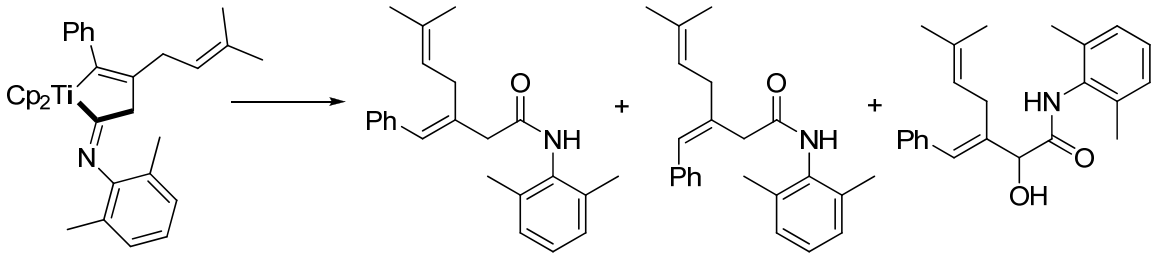
(*Z*)-N-(2,6-dimethylphenyl)-3-isopropyl-pent-3-enamide (48): To a cold (-30 °C) solution of **44** (50 mg, 0.12 mmol) in THF (3 mL) was added a cold 1 mL THF solution of mCPBA (~ 70 % by weight, 30 mg, 0.12 mmol). The solution changed from dark brown to yellow immediately. After 2 hours of stirring, 5 mL of sat. $NaHCO_3$ solution was added and stirred for 5 minutes. After extracting three times with 10 mL ether, the combined extracts were washed with brine solution before drying over $MgSO_4$ and removing solvent under vacuum. The crude solid was chromatographed through silica, eluting with hexanes:ethyl acetate, to provide a spectroscopically clean white solid (17

mg, 57 %). **IR** (solid, FTIR microscope) 3249 (m), 3071 (w), 2962 (s), 2924 (s), 2872 (m), 1704 (s), 1656 (s), 1596 (s), 1575 (m), 1520 (s), 1474 (s), 1430 (s), 1415 (m), 1303 (m), 1263 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.26 (br s, 1H, N*H*); 7.12-7.06 (m, 3H, Xyl*H*); 5.58 (q, $^3J_{HH}$ = 6.9 Hz, 1H, C=C*H*); 3.13 (s, 2H, CH_2); 3.01 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *H*C(CH_3)$_2$); 2.24 (s, 6H, Xyl-CH_3); 1.77 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C=C-CH_3); 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 6H, HC(CH_3)$_2$). **^{13}C NMR** (100 MHz, $CDCl_3$, assignments confirmed by HMQC and HMBC) δ 170.1 (p, *C*=O); 141.7 (p, *C*=CH); 135.4 (p, *o*-Xyl); 134.3 (p, *ipso*-Xyl); 128.5 (a, *m*-Xyl); 127.4 (a, *p*-Xyl); 124.8 (a, C=*C*H); 41.1 (p, *C*H_2); 28.9 (a, H*C*(CH_3)$_2$); 21.1 (a, HC(*C*H_3)$_2$); 18.9 (a, Xyl-*C*H_3); 13.4 (a, C=C-*C*H_3). **COSY** (400 MHz, $CDCl_3$) δ 7.12-7.06 ↔ δ 2.24; δ 5.58 ↔ δ 3.13, 1.77; δ 3.13 ↔ δ 5.58, 1.77; δ 3.01 ↔ δ 1.11; δ 2.24 ↔ δ 7.12-7.06; δ 1.77 ↔ δ 5.58, 3.13; δ 1.11 ↔ δ 3.01. **HMQC** (400 MHz, $CDCl_3$) δ 7.12-7.06 ↔ δ 128.5, 127.4; δ 5.58 ↔ δ 124.8; δ 3.13 ↔ δ 41.1; δ 3.01 ↔ δ 28.9; δ 2.24 ↔ δ 18.9; δ 1.77 ↔ δ 13.4; δ 1.11 ↔ δ 21.1. **HMBC** (400 MHz, $CDCl_3$) δ 7.12-7.06 ↔ δ 135.4, 134.3; δ 5.58 ↔ δ 41.1, 28.9, 13.4; δ 3.13 ↔ δ 170.1, 141.7, 124.8, 28.9; δ 3.01 ↔ δ 124.8, 21.1; δ 2.24 ↔ δ 135.4, 128.5; δ 1.77 ↔ δ 141.7, 124.8; δ 1.11 ↔ δ 141.7, 28.9, 21.1. **TROESY** (400 MHz, $CDCl_3$, selected correlations only) δ 5.58 ↔ δ 3.13; δ 3.01 ↔ δ 1.77. **Anal**. Calcd. for $C_{16}H_{23}NO$: C, 78.32, H, 9.45, N, 5.71. Found: C, 77.20, H, 9.43, N, 5.23. **HRMS** Calcd. for $C_{16}H_{23}NO$: 245.17796. Found: 245.17814.



(*E*)-N-(2,6-dimethylphenyl)-3-benzyl-pent-3-enamide (49): To a cold (-30 °C) solution of **45** (50 mg, 0.11 mmol) in THF (3 mL) was added a cold 1 mL THF solution of mCPBA (~ 70 % by weight, 27 mg, 0.11 mmol). The solution changed from dark brown to light red immediately. After 2 hours of stirring, 5 mL of sat. $NaHCO_3$ solution was added and stirred for 5 minutes. After extracting three times with 10 mL ether, the combined extracts were washed with brine solution before drying over $MgSO_4$ and

removing solvent under vacuum. The crude solid was chromatographed through silica, eluting with hexanes:ethyl acetate, to provide an analytically pure white solid (19 mg, 59 %). **IR** (solid, FTIR microscope) 3260 (s), 3115 (w), 3061 (w), 3023 (m), 2958 (m), 2924 (m), 2859 (m), 1654 (s), 1599 (m), 1519 (s), 1494 (m), 1474 (m), 1463 (m), 1451 (m), 1402 (m), 1345 (m), 1294 (w), 1276 (w), 1240 (w), 1213 (m), 1184 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H, *o*-Ph*H*); 7.26-7.21 (m, 3H, *m*- and *p*-Ph*H*); 7.14-7.07 (m, 3H, Xyl*H*); 6.97-6.93 (br s, 1H, N*H*); 5.79 (q, $^3J_{HH}$ = 6.8 Hz, 1H, C=C*H*); 3.61 (s, 2H, Ph-CH_2); 3.08 (s, 2H, C(O)CH_2); 2.22 (s, 6H, Xyl-CH_3); 1.90 (d, $^3J_{HH}$ = 6.7 Hz, 3H, C=C-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$, assignments confirmed by HMQC and HMBC) δ 169.5 (p, *C*=O); 139.2 (p, *ipso*-Ph); 135.5 (p, *o*-Xyl); 134.6 (p, *ipso*-Xyl); 134.1 (p, HC=*C*); 128.95 (a, *o*- or *m*-Ph); 128.90 (a, *o*- or *m*-Ph); 128.5 (a, *m*-Xyl); 127.5 (a, *p*-Xyl); 126.6 (a, *p*-Ph); 126.5 (a, C=*C*H); 45.0 (p, C(O)*C*H_2); 36.1 (p, Ph-*C*H_2); 18.7 (a, Xyl-*C*H_3); 14.3 (a, C=C-*C*H_3). **COSY** (400 MHz, $CDCl_3$) δ 7.35-7.30 ↔ δ 7.26-7.21; δ 7.26-7.21 ↔ δ 7.35-7.30, 3.61; δ 7.14-7.07 ↔ δ 2.22; δ 5.79 ↔ δ 3.61, 3.08, 1.90; δ 3.61 ↔ δ 7.26-7.21, 1.90; δ 3.08 ↔ δ 1.90; δ 2.22 ↔ δ 7.14-7.07; δ 1.90 ↔ δ 5.79, 3.61, 3.08. **HMQC** (400 MHz, $CDCl_3$) δ 7.35-7.30 ↔ δ 128.95 or 128.90; δ 7.26-7.21 ↔ δ 128.95 or 128.90, 126.6; δ 7.14-7.07 ↔ δ 128.5, 127.5; δ 5.79 ↔ δ 126.5; δ 3.61 ↔ δ 36.2; δ 3.08 ↔ δ 45.0; δ 2.22 ↔ δ 18.7; δ 1.90 ↔ δ 14.3. **HMBC** (400 MHz, $CDCl_3$, selected correlations only) δ 7.35-7.30 ↔ δ 139.2, 128.95, 128.90; δ 7.26-7.21 ↔ δ 126.6, 36.6; δ 7.14-7.07 ↔ δ 134.6, 128.5, 127.5; δ 5.79 ↔ δ 45.0, 36.2, 14.3; δ 3.61 ↔ δ 139.2, 134.1, 128.95 or 128.90, 126.5, 45.0; δ 3.08 ↔ δ 169.5, 134.1, 126.6, 36.2; δ 2.22 ↔ δ 134.6, 128.5; δ 1.90 ↔ δ 134.1, 126.5. **TROESY** (400 MHz, $CDCl_3$, selected correlations only) δ 5.79 ↔ δ 3.08; δ 3.61 ↔ δ 1.90. **Anal**. Calcd. for $C_{20}H_{23}NO$: C, 81.87, H, 7.90, N, 4.77. Found: C, 81.47, H, 7.96, N, 4.55. **HRMS** Calcd. for $C_{20}H_{23}NO$: 293.17796. Found: 293.17799.



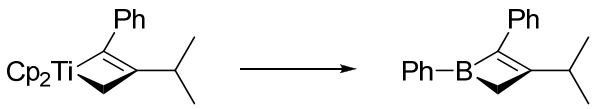
(*E*)- and (*Z*)-3-benzylidene-6-methyl-N-(2,6-dimethylphenyl)hept-5-enamide (50) and (*E*)-3-benzylidene-2-hydroxy-6-methyl-N-(2,6-dimethylphenyl)hept-5-enamide (51): To a cold (-30 °C) solution of **46** (100 mg, 0.20 mmol) in THF (3 mL) was added a cold 1 mL THF solution of mCPBA (~ 70 % by weight, 50 mg, 0.20 mmol). The solution changed from dark brown to light red immediately. After 2 hours of stirring, 5 mL of sat. $NaHCO_3$ solution was added and stirred for 5 minutes. After extracting three times with 10 mL ether, the combined extracts were washed with brine solution before drying over $MgSO_4$ and removing solvent under vacuum. The crude solid was chromatographed through silica, eluting with hexanes:ethyl acetate, to provide three major components. The minor *Z*-diastereomer (brown powder, 10 mg, 15 %) eluted prior to the major *E*-diastereomer (brown powder, 22 mg, 33 %). α-Hydroxyamide **51** (brown oil, 8 mg, 11 %) eluted last. ***(E)*-50**: Refer to Appendix 1 for X-Ray analysis information. **IR** (solid, FTIR microscope) 3262 (s), 3022 (m), 2960 (s), 2928 (s), 2854 (m), 1652 (s), 1594 (m), 1519 (s), 1466 (s), 1445 (s), 1401 (s), 1376 (s), 1340 (s), 1296 (w), 1277 (w), 1261 (w), 1222 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.37 (m, 2H, *m*-Ph*H*); 7.32-7.27 (m, 3H, *o*- and *p*-Ph*H*); 7.19-7.17 (br s, 1H, N*H*); 7.13-7.08 (m, 3H, Xyl*H*); 6.67 (s, 1H, C=C(Ph)*H*); 5.24 (t of sept, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, C=C*H*-CH_2); 3.33 (s, 2H, C(O)-CH_2); 3.16 (d, $^3J_{HH}$ = 6.5 Hz, 2H, C=CH-CH_2); 2.27 (s, 6H, Xyl-CH_3); 1.77 (s, 3H, C=C-CH_3); 1.67 (s, 3H, C=C-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$, APT, assignments confirmed by HMQC and HMBC) δ 169.1 (p, *C*=O); 137.6 (p, Ph-C=*C*); 137.2 (p, *ipso*-Ph); 135.5 (p, *ipso*-Xyl); 135.0 (p, HC=*C*-CH_3); 134.1 (p, *o*-Xyl); 130.9 (p, Ph-*C*=C); 128.9 (a, *o*-Ph); 128.6 (a, *m*-Ph); 128.5 (a, *m*-Xyl); 127.6 (a, *p*-Ph); 127.2 (a, *p*-Xyl); 121.0 (a, CH_3-C=*C*H); 45.7 (p, *C*H_2-C=O); 30.9 (p, C=C(H)-*C*H_2); 26.1 (a, C=C-*C*H_3); 18.8 (a, Xyl-*C*H_3); 18.3 (a, C=C-*C*H_3). **COSY** (400 MHz, $CDCl_3$) δ 7.41-7.37 ↔ δ 7.32-7.27; δ 7.32-7.27 ↔ δ 7.41-7.37, 6.67; δ 7.13-7.08 ↔ δ 2.27; δ 6.67 ↔ δ 7.32-7.27, 3.33, 3.16; δ 5.24 ↔ δ 3.16, 1.77, 1.67; δ 3.33 ↔ δ 6.67; δ 3.16 ↔ δ 6.67, 5.24, 1.77,

1.67; δ 2.27 ↔ δ 7.13-7.08; δ 1.77 ↔ δ 5.24, 3.16, 1.67; δ 1.67 ↔ δ 5.24, 3.16, 1.77. **HMQC** (400 MHz, $CDCl_3$) δ 7.41-7.37 ↔ δ 128.6; δ 7.32-7.27 ↔ δ 128.9; δ 7.13-7.08 ↔ δ 128.5; δ 6.67 ↔ δ 130.9; δ 5.24 ↔ δ 121.0; δ 3.33 ↔ δ 45.7; δ 3.16 ↔ δ 30.9; δ 2.27 ↔ δ 18.8; δ 1.77 ↔ δ 26.1; δ 1.67 ↔ δ 18.3. **HMBC** (400 MHz, $CDCl_3$, selected correlations only) δ 7.41-7.37 ↔ δ 137.2, 128.6; δ 7.32-7.27 ↔ δ 130.9, 127.6; δ 7.13-7.08 ↔ δ 135.5, 128.5; δ 6.67 ↔ δ 128.9, 45.7, 30.9; δ 3.33 ↔ δ 169.1, 137.6, 130.9, 30.9; δ 3.16 ↔ δ 137.6, 135.0, 130.9, 121.0, 45.7; δ 2.27 ↔ δ 135.5, 128.5; δ 1.77 ↔ δ 135.0, 121.0, 18.3; δ 1.67 ↔ δ 135.0, 121.0, 26.1. **TROESY** (400 MHz, $CDCl_3$, selected correlations only) δ 6.67 ↔ δ 3.33; δ 7.32-7.27 ↔ δ 3.16. **Anal**. Calcd. for $C_{23}H_{27}NO$: C, 82.84, H, 8.16, 4.20. Found: C, 81.13, H, 7.97, N, 3.90. **HRMS** Calcd. for $C_{23}H_{27}NO$: 333.20926. Found: 333.20929.

***(Z)*-50**: **IR** (solid, FTIR microscope) 3245 (m), 3056 (w), 3024 (m), 2968 (m), 2922 (m), 2856 (w), 1651 (s), 1599 (w), 1521 (s), 1494 (m), 1478 (m), 1445 (m), 1376 (m), 1337 (w), 1266 (w), 1227 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.37 (m, 2H, *o*-Ph*H*); 7.31-7.26 (m, 3H, *m*- and *p*-Ph*H*); 7.13-7.05 (m, 3H, Xyl*H*); 6.99-6.97 (br s, 1H, N*H*); 6.67 (s, 1H, C=C(Ph)*H*); 5.31 (t of sept, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, C=C*H*-CH_2); 3.45 (s, 2H, C(O)-CH_2); 3.10 (d, $^3J_{HH}$ = 7.7 Hz, 2H, C=CH-CH_2); 2.17 (s, 6H, Xyl-CH_3); 1.81 (s, 3H, C=C-CH_3); 1.74 (s, 3H, C=C-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$, APT, assignments confirmed by HMQC and HMBC) δ 168.6 (p, *C*=O); 137.4 (p, *ipso*-Ph); 136.4 (p, Ph-C=*C*); 135.7 (p, HC=*C*-CH_3); 135.3 (p, *ipso*-Xyl); 134.0 (p, *o*-Xyl); 129.9 (p, Ph-*C*=C); 128.8 (a, *o*-Ph); 128.7 (a, *m*-Ph); 128.5 (a, *m*-Xyl); 127.6 (a, *p*-Ph); 127.3 (a, *p*-Xyl); 121.0 (a, CH_3-C=*C*H); 39.7 (p, *C*H_2-C=O); 37.6 (p, C=C(H)-*C*H_2); 26.1 (a, C=C-*C*H_3); 18.7 (a, Xyl-*C*H_3); 18.2 (a, C=C-*C*H_3). **COSY** (400 MHz, $CDCl_3$) δ 7.39-7.37 ↔ δ 7.31-7.26; δ 7.31-7.26 ↔ δ 7.39-7.37; δ 7.13-7.05 ↔ δ 2.17; δ 6.67 ↔ δ 3.45, 3.10; δ 5.31 ↔ δ 3.10, 1.81, 1.74; δ 3.45 ↔ δ 6.67; δ 3.10 ↔ δ 6.67, 5.31, 1.81, 1.74; δ 2.17 ↔ δ 7.13-7.05; δ 1.81 ↔ δ 5.31, 3.10, 1.74; δ 1.74 ↔ δ 5.31, 3.10, 1.81. **HMQC** (400 MHz, $CDCl_3$) δ 7.39-7.37 ↔ δ 128.8; δ 7.13-7.05 ↔ δ 128.5; δ 6.67 ↔ δ 129.9; δ 3.45 ↔ δ 39.7; δ 3.10 ↔ δ 37.6; δ 2.17 ↔ δ 18.7; δ 1.81 ↔ δ 26.1; δ 1.74 ↔ δ 18.2. **HMBC** (400 MHz, $CDCl_3$, selected correlations only) δ 7.39-7.37 ↔ δ 137.4; δ 7.13-7.06 ↔ δ 135.7, 134.0, 128.5; δ 6.67 ↔ δ 128.8, 39.7, 37.6; δ 3.45 ↔ δ 168.6, 136.4, 129.9, 37.6; δ 3.10 ↔ δ 136.4, 129.9, 121.0; δ 2.17 ↔ δ 135.3, 128.5; δ 1.81 ↔ δ 135.7, 121.0, 18.2; δ 1.74

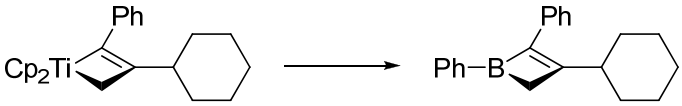
↔ δ 135.7, 121.0, 26.1. **TROESY** (400 MHz, $CDCl_3$, selected correlations only) δ 7.39-7.37 ↔ δ 3.45; δ 6.67 ↔ δ 3.10. **HRMS** Calcd. for $C_{23}H_{27}NO$: 333.20926. Found: 333.20919.

α-Hydroxyamide **51**: **IR** (solid, FTIR microscope) 3347 (m, br), 3057 (w), 3025 (w), 2966 (m), 2924 (m), 2856 (w), 1662 (s), 1594 (w), 1503 (s), 1446 (m), 1376 (m), 1266 (m), 1221 (w), 1128 (w), 1096 (w), 1074 (w) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (br s, 1H, NH), 7.41-7.30 (m, 5H, Ph*H*); 7.15-7.08 (m, 3H, Xyl*H*); 6.85 (s, 1H, C=C(Ph)*H*); 5.28 (app t, $^3J_{HH}$ = 7.0 Hz, 1H, C=C*H*-CH_2); 4.88 (s, 1H, *H*C-OH), 3.53 (s, 1H, O*H*); 3.28 (dd, $^2J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, C=CH-C*H*$_2$); 3.10 (dd, $^2J_{HH}$ = 15.3 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, C=CH-C*H*$_2$); 2.26 (s, 6H, Xyl-C*H*$_3$); 1.73 (s, 3H, C=C-C*H*$_3$); 1.67 (s, 3H, C=C-C*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$, APT, assignments confirmed by HMQC and HMBC) δ 170.5 (p, *C*=O); 140.9 (p, Ph-C=*C*); 136.7 (p, *ipso*-Ph); 135.4 (p, *o*-Xyl); 134.4 (p, HC=*C*-CH_3); 133.3 (p, *ipso*-Xyl); 130.1 (a, Ph-*C*=C); 129.1 (a, *o*-Ph); 128.61 (a, *m*-Ph or *m*-Xyl); 128.60 (a, *m*-Ph or *m*-Xyl); 127.7 (a, *p*-Xyl); 127.5 (a, *p*-Ph); 121.9 (a, CH_3-C=*C*H); 77.2 (a, *C*-OH); 28.0 (p, *C*H_2); 26.0 (a, C=C-*C*H_3); 18.7 (a, Xyl-*C*H_3); 18.2 (a, C=C-*C*H_3). **COSY** (400 MHz, $CDCl_3$) δ 7.15-7.08 ↔ δ 2.26; δ 6.85 ↔ δ 4.88; δ 5.28 ↔ δ 3.28, 3.10, 1.73, 1.67; δ 4.88 ↔ δ 6.85, 3.53; δ 3.53 ↔ δ 4.88; δ 3.28 ↔ δ 5.28, 3.10, 1.73; δ 3.10 ↔ δ 5.28, 3.28, 1.73; δ 2.26 ↔ δ 7.15-7.08; δ 1.73 ↔ δ 5.28, 3.28, 3.10, 1.67; δ 1.67 ↔ δ 5.28, 1.73. **HMQC** (400 MHz, $CDCl_3$) δ 7.41-7.30 ↔ δ 129.1-127.5; δ 7.15-7.08 ↔ δ 129.1-127.5; δ 6.85 ↔ δ 130.1; δ 2.26 ↔ δ 18.7; δ 1.73 ↔ δ 26.0; δ 1.67 ↔ δ 18.2. **HMBC** (300 MHz, $CDCl_3$) δ 7.41-7.30 ↔ δ 136.7, 128.61 or 128.60, 127.5; δ 7.15-7.08 ↔ δ 135.4, 133.3, 18.7; δ 6.85 ↔ δ 140.9, 136.7, 129.1, 121.9, 77.2, 28.0; δ 5.28 ↔ δ 26.0, 18.2; δ 4.88 ↔ δ 170.5, 140.9, 130.1, 28.0; δ 3.28 ↔ δ 140.9, 134.4, 130.1, 121.9, 77.2; δ 3.10 ↔ δ 140.9, 134.4, 130.1, 121.9, 77.2; δ 2.26 ↔ δ 135.4, 133.3, 128.61 or 128.60; δ 1.73 ↔ δ 134.4, 121.9, 18.2; δ 1.67 ↔ δ 134.4, 121.9, 26.0. **NOE** (400 MHz, $CDCl_3$) δ 6.85 ↔ δ 4.88 (7 %). **HRMS** Calcd. for $C_{23}H_{27}NO_2$: 349.20419. Found: 349.20405.



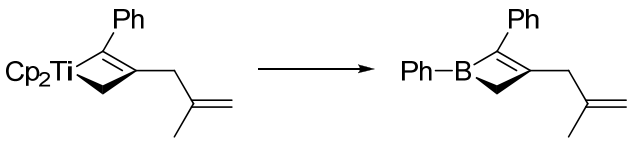
3-Isopropyl-1,2-diphenylboracyclobutene (59): To a cold toluene (-30 °C, 10 mL) solution of titanacyclobutene **15** (302 mg, 0.90 mmol) was added a cold toluene (-30 °C, 2 mL) solution of dichlorophenylborane (150 mg, 0.94 mmol). The solution was allowed to warm to 25 °C over a 12 hour period. During that time the solution changed from dark red to light red and red crystals of Cp_2TiCl_2 formed. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble Cp_2TiCl_2. Concentration under vacuum yielded the boracyclobutene (208 mg, 94 % yield) as an analytically pure amorphous yellow powder. *Alternate procedure:* A suspension of titanacyclobutene **15** (100 mg, 0.30 mmol), potassium phenyltrifluoroborate (55 mg, 0.30 mmol), and dichlorodimethylsilane (200 mg, 1.55 mmol) in dry toluene (5 mL) was heated at 80 °C for 12 hours in a sealed glass bomb. The solution changed from red to dark green during this time. The solution was cooled to room temperature, and then the solvent removed *in vacuo*. The residue was triturated with dry hexanes then filtered through Celite to separate from insoluble titanium by-products. Concentration under vacuum yielded the boracyclobutene (44 mg, 60 % yield). **^{1}H NMR** (400 MHz, C_6D_6, 27 °C) δ 7.75 (br s, 2H, B-*o*-Ph*H*); 7.24 (br s, 2H, *o*-Ph*H*); 7.14-7.05 (m, 5H, B-*m,p*-Ph*H*, *m*-Ph*H*); 6.97 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *p*-Ph*H*); 3.26 (sept, $^3J_{HH}$ = 6.7 Hz, 1H, *H*C(CH$_3$)$_2$); 2.57 (s, 2H, B-C*H*$_2$); 1.05 (d, $^3J_{HH}$ = 6.7 Hz, 6H, HC(C*H*$_3$)$_2$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC, 27 °C) δ 143.7 (B-*C*=C); 142.5 (*ipso*-Ph); 141.2 (B-*ipso*-Ph); 136.7 (br, B-*o*-Ph); 132.4 (B-*p*-Ph); 129.8 (*o*-Ph); 128.5 (*m*-Ph); 127.9 (B-*m*-Ph); 125.9 (*p*-Ph); 31.9 (H*C*(CH$_3$)$_2$); 29.7 (B-*C*H$_2$); 21.7 (*C*H$_3$); B-C=*C* resonance not observed at 27 °C. **COSY** (400 MHz, C_6D_6, 27 °C) δ 7.75 ↔ δ 7.14-7.05; δ 7.24 ↔ δ 7.14-7.05, 6.97; δ 7.14-7.05 ↔ δ 7.75, 7.24, 6.97; δ 6.97 ↔ δ 7.24, 7.14-7.05; δ 3.26 ↔ δ 1.05; δ 1.05 ↔ δ 3.26. **HMQC** (400 MHz, C_6D_6, 27 °C) δ 7.14-7.05 ↔ δ 132.4; δ 6.97 ↔ δ 125.9; δ 2.57 ↔ δ 29.7; δ 1.05 ↔ δ 21.7. **HMBC** (400 MHz, C_6D_6, 27 °C) δ 7.14-7.05 ↔ δ 142.5, 128.5, 127.9; δ 6.97 ↔ δ 129.8; δ 3.26 ↔ δ 29.7, 21.7; δ 2.57 ↔ δ 143.7, 31.9; δ 1.05 ↔ δ 31.9, 21.7. **^{1}H NMR** (400 MHz, C_6D_6, 80 °C) δ 7.73 (d, $^3J_{HH}$ = 6.7 Hz, 2H, B-*o*-Ph*H*); 7.21 (d, $^3J_{HH}$ = 7.3 Hz, 2H, *o*-Ph*H*); 7.13-7.06 (m, 5H, B-*m,p*-Ph*H*, *m*-Ph*H*); 6.97 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Ph*H*);

3.22 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, *H*C(CH$_3$)$_2$); 2.64 (s, 2H, B-C*H*$_2$); 1.06 (d, $^3J_{HH}$ = 6.8 Hz, 6H, HC(C*H*$_3$)$_2$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC, 80 °C) δ 149.2 (br, B-C=*C*); 144.2 (B-*C*=C); 142.7 (*ipso*-Ph); 141.7 (B-*ipso*-Ph); 136.6 (B-*o*-Ph); 132.2 (B-*p*-Ph); 129.9 (*o*-Ph); 128.5 (*m*-Ph); 127.9 (B-*m*-Ph); 125.9 (*p*-Ph); 32.1 (H*C*(CH$_3$)$_2$); 30.0 (B-*C*H$_2$); 21.8 (*C*H$_3$). **HMQC** (400 MHz, C_6D_6, 80 °C) δ 7.73 ↔ δ 136.6; δ 7.21 ↔ δ 129.9; δ 7.13-7.06 ↔ δ 132.2, 128.5; δ 6.97 ↔ δ 125.9; δ 3.22 ↔ δ 32.1; δ 2.64 ↔ δ 30.0; δ 1.06 ↔ δ 21.8. **HMBC** (400 MHz, C_6D_6, 80 °C) δ 7.73 ↔ δ 141.7, 136.6, 132.2, 127.9; δ 7.21 ↔ δ 144.2, 129.9, 125.9; δ 7.13-7.06 ↔ δ 142.7, 141.7, 136.6, 128.5, 127.9; δ 6.97 ↔ δ 129.9; δ 3.22 ↔ δ 149.2, 144.2, 30.0, 21.8; δ 2.64 ↔ δ 149.2, 144.2, 141.7, 129.9; δ 1.06 ↔ δ 149.2, 32.1, 21.8. **^{11}B NMR** (128 MHz, C_6D_6, 27 °C) δ 78.0 (br). **Anal**. Calcd. for $C_{18}H_{19}B$: C, 87.83, H, 7.78. Found: C, 87.77, H, 7.84.



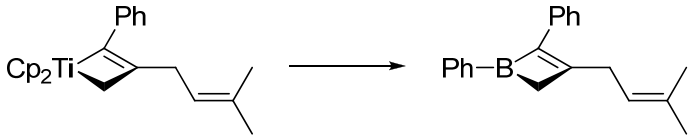
3-Cyclohexyl-1,2-diphenylboracyclobutene (60): To a cold toluene (-30 °C, 10 mL) solution of titanacyclobutene **16** (300 mg, 0.80 mmol) was added a cold toluene (-30 °C, 2 mL) solution of dichlorophenylborane (133 mg, 0.84 mmol). The solution was allowed to warm to 25 °C over a 12 hour period. During that time the solution changed from dark red to light red and red crystals of Cp_2TiCl_2 formed. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble Cp_2TiCl_2. Concentration under vacuum yielded the boracyclobutene (225 mg, 98 % yield) as an analytically pure amorphous yellow powder. *Alternate procedure:* A suspension of titanacyclobutene **16** (100 mg, 0.27 mmol), potassium phenyltrifluoroborate (49 mg, 0.27 mmol), and dichlorodimethylsilane (200 mg, 1.55 mmol) in dry toluene (5 mL) was heated at 80 °C for 12 hours in a sealed glass bomb. The solution changed from red to dark green during this time. The solution was cooled to room temperature, and then the solvent removed *in vacuo*. The residue was triturated with dry hexanes then filtered through Celite to separate from insoluble titanium by-products. Concentration under vacuum yielded the boracyclobutene (42 mg, 55 % yield). **^{1}H NMR** (400 MHz, C_6D_6, 27 °C) δ 7.79 (br s, 2H, B-*o*-Ph*H*); 7.24 (br s, 2H, *o*-Ph*H*);

7.16-7.08 (m, 5H); 6.96 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *p*-Ph*H*); 2.93 (tt, $^3J_{HH}$ = 11.8, 3.1 Hz, 1H, C=C-C*H*); 2.63 (s, 2H, B-CH_2); 1.80 (br d, $^3J_{HH}$ = 11.6 Hz, 2H, 2-Cy*H*); 1.67 (br d, 12.5 Hz, 2H, Cy*H*); 1.57-1.39 (m, 3H, Cy*H*); 1.24-1.01 (m, 3H, Cy*H*). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC, 27 °C) δ 144.2 (B-*C*=C); 142.5 (br, *ipso*-Ph); 141.2 (B-*ipso*-Ph); 136.8 (br, B-*o*-Ph); 132.5 (B-*p*-Ph); 129.8 (*o*-Ph); 128.5 (*m*-Ph); 127.9 (B-*m*-Ph); 126.0 (*p*-Ph); 43.2 (C=C-*C*H); 32.2 (2-Cy); 31.4 (B-*C*H_2); 26.51 (3-Cy); 26.46 (4-Cy); B-C=*C* resonance not observed at 27 °C. **COSY** (400 MHz, C_6D_6, 27 °C) δ 7.79 ↔ δ 7.16-7.08; δ 7.24 ↔ δ 7.16-7.08, 6.96; δ 7.16-7.08 ↔ δ 7.79, 7.24, 6.96; δ 6.96 ↔ δ 7.24, 7.16-7.08; δ 2.93 ↔ δ 1.80, 1.57-1.39; δ 1.80 ↔ δ 2.93, 1.67, 1.57-1.39, 1.24-1.01; δ 1.67 ↔ δ 1.80, 1.57-1.39, 1.24-1.01; δ 1.57-1.39 ↔ δ 2.93, 1.80, 1.67, 1.24-1.01; δ 1.24-1.01 ↔ δ 1.80, 1.67, 1.57-1.39. **HMQC** (400 MHz, C_6D_6, 27 °C) δ 7.16-7.08 ↔ δ 132.5; δ 6.96 ↔ δ 126.0; δ 2.93 ↔ δ 43.2; δ 2.63 ↔ δ 31.4; δ 1.80 ↔ δ 32.2; δ 1.67 ↔ δ 26.5; δ 1.57-1.39 ↔ δ 26.5; δ 1.24-1.01 ↔ δ 26.5. **HMBC** (400 MHz, C_6D_6, 27 °C) δ 7.16-7.08 ↔ δ 142.5; δ 6.96 ↔ δ 142.5, 129.8; δ 2.93 ↔ δ 144.2, 32.2; δ 2.63 ↔ δ 144.2, 141.2, 43.2; δ 1.80 ↔ δ 32.2, 26.5; δ 1.67 ↔ δ 43.2; 32.2; 26.5; δ 1.57-1.39 ↔ δ 32.2, 26.5; δ 1.24-1.01 ↔ δ 26.5. **^{1}H NMR** (400 MHz, C_6D_6, 80 °C) δ 7.71 (d, $^3J_{HH}$ = 6.3 Hz, 2H, B-*o*-Ph*H*); 7.16 (d, $^3J_{HH}$ = 7.3 Hz, 2H, *o*-Ph*H*); 7.09-7.01 (m, 5H); 6.92 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *p*-Ph*H*); 2.84 (t, $^3J_{HH}$ = 11.8, 1H, C=C-C*H*); 2.64 (s, 2H, B-CH_2); 1.74 (d, $^3J_{HH}$ = 12.1 Hz, 2H, 2-Cy*H*); 1.62 (d, 11.9 Hz, 2H, Cy*H*); 1.53-1.38 (m, 3H, Cy*H*); 1.18-0.99 (m, 3H, Cy*H*). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC, 80 °C) δ 148.6 (br, B-C=*C*); 144.6 (B-*C*=C); 142.8 (*ipso*-Ph); 141.6 (B-*ipso*-Ph); 136.8 (B-*o*-Ph); 132.3 (B-*p*-Ph); 129.9 (*o*-Ph); 128.4 (*m*-Ph); 127.8 (B-*m*-Ph); 125.9 (*p*-Ph); 43.6 (C=C-*C*H); 32.4 (2-Cy); 31.8 (B-*C*H_2); 26.7 (3-Cy); 26.6 (4-Cy). **HMQC** (400 MHz, C_6D_6, 80 °C) δ 7.71 ↔ δ 136.8; δ 7.16 ↔ δ 129.9; δ 7.09-7.01 ↔ δ 132.2, 128.4; δ 6.92 ↔ δ 125.9; δ 2.84 ↔ δ 43.6; δ 2.64 ↔ δ 31.8; δ 1.74 ↔ δ 32.4; δ 1.62 ↔ δ 26.7 or 26.6; δ 1.53-1.38 ↔ δ 32.4, 26.7 or 26.6; δ 1.18-0.99 ↔ δ 26.7 or 26.6. **HMBC** (400 MHz, C_6D_6, 80 °C) δ 7.71 ↔ δ 136.8, 132.3; δ 7.16 ↔ δ 144.6, 129.9, 125.9; δ 7.09-7.01 ↔ δ 142.8, 128.4; δ 6.92 ↔ δ 129.9; δ 2.64 ↔ δ 148.6, 144.6, 43.6; δ 1.80 ↔ δ 43.6, 26.7 or 26.6; δ 1.62 ↔ δ 43.6, 26.7 or 26.6; δ 1.53-1.38 ↔ δ 26.7 or 26.6; δ 1.18-0.99 ↔ δ 26.7 or 26.6. **^{11}B NMR** (128 MHz, C_6D_6, 27 °C) δ 80.4 (br). **Anal**. Calcd. for $C_{21}H_{23}B$: C, 88.12, H, 8.10. Found: C, 88.17, H, 8.30.



3-(2-Methylallyl)-1,2-diphenylboracyclobutene (61): To a cold toluene (-30 °C, 10 mL) solution of titanacyclobutene **19** (300 mg, 0.86 mmol) was added a cold toluene (-30 °C, 2 mL) solution of dichlorophenylborane (144 mg, 0.90 mmol). The solution was allowed to warm to 25 °C over a 12 hour period. During that time the solution changed from dark red to brown. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble Cp_2TiCl_2. Concentration under vacuum yielded the boracyclobutene (161.2 mg, 77 % yield) as a spectroscopically clean amorphous brown solid. *Alternate procedure:* A suspension of titanacyclobutene **19** (100 mg, 0.29 mmol), potassium phenyltrifluoroborate (52 mg, 0.29 mmol), and dichlorodimethylsilane (200 mg, 1.55 mmol) in dry toluene (5 mL) was heated at 80 °C for 12 hours in a sealed glass bomb. The solution changed from red to dark green during this time. The solution was cooled to room temperature, and then the solvent removed *in vacuo*. The residue was triturated with dry hexanes then filtered through Celite to separate from insoluble titanium-containing by-products. Concentration under vacuum yielded the boracyclobutene (36 mg, 48 % yield). **^{1}H NMR** (400 MHz, C_6D_6, 27 °C) δ 7.86 (br d, $^3J_{HH}$ = 5.0 Hz, 2H, B-*o*-Ph*H*); 7.27 (d, $^3J_{HH}$ = 7.4 Hz, 2H, *o*-Ph*H*); 7.16-7.11 (m, 3H, B-*m*-Ph*H* and B-*p*-Ph*H*); 7.08 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-Ph*H*); 6.94 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Ph*H*); 5.06 (br s, 1H, C=CH_2); 5.00 (br s, 1H, C=CH_2); 3.15 (s, 2H, C=C-CH_2); 2.85 (s, 2H, B-CH_2); 1.72 (s, 3H, C=C-CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC, 27 °C) δ 146.8 (B-C=*C*); 144.5 (H_2C=*C*-CH_3); 142.1 (*ipso*-Ph); 140.1 (br, B-*C*=C); 136.4 (B-*o*-Ph); 132.4 (B-*p*-Ph); 129.4 (*o*-Ph); 128.5 (*m*-Ph); 128.1 (B-*m*-Ph); 126.0 (*p*-Ph); 112.5 (C=*C*H_2); 44.7 (H_2C=C-*C*H_2); 34.8 (br, B-*C*H_2); 22.9 (*C*H_3); B-*ipso*-Ph not observed at 27 °C. **COSY** (400 MHz, C_6D_6, 27 °C) δ 7.86 ↔ δ 7.16-7.11; δ 7.27 ↔ δ 7.08, 6.94; δ 7.16-7.11 ↔ δ 7.86; δ 7.08 ↔ δ 7.27, 6.94; δ 5.06 ↔ δ 3.15, 1.72; δ 5.00 ↔ δ 3.15, 1.72; δ 3.15 ↔ δ 5.06, 5.00, 1.72; δ 1.72 ↔ δ 5.06, 5.00, 3.15. **HMQC** (400 MHz, C_6D_6, 27 °C) δ 7.86 ↔ δ 136.4; δ 7.27 ↔ δ 129.4; δ 7.16-7.11 ↔ δ 132.4; δ 7.08 ↔ δ 128.5; δ 6.94 ↔ δ 126.0; δ 5.06 ↔ δ 112.5; δ 5.00 ↔ δ 112.5; δ 3.15 ↔ δ 44.7; δ 2.85 ↔ δ 34.8; δ 1.72 ↔ δ 22.9.

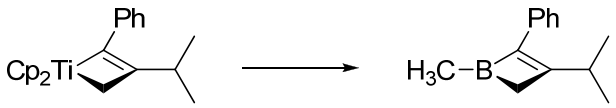
HMBC (400 MHz, C_6D_6, 27 °C) δ 7.86 ↔ δ 132.4, 128.1; δ 7.27 ↔ δ 146.8, 129.4, 126.0; δ 7.08 ↔ δ 142.1, 128.5; δ 5.06 ↔ δ 144.5, 44.7, 22.9; δ 5.00 ↔ δ 144.5, 44.7, 22.9; δ 3.15 ↔ δ 146.8, 144.5, 140.1, 112.5, 34.8, 22.9; δ 2.85 ↔ δ 146.8, 140.1, 129.4, 44.7; δ 1.72 ↔ δ 144.5, 112.5, 44.7. **^{1}H NMR** (400 MHz, C_6D_6, 80 °C) δ 7.79 (m, 2H, B-*o*-Ph*H*); 7.20 (m, 2H, *o*-Ph*H*); 7.14-7.09 (m, 3H, B-*m/p*-Ph*H*); 7.06 (t, $^3J_{HH}$ = 7.8 Hz, 2H, *m*-Ph*H*); 6.93 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Ph*H*); 4.99 (s, 1H, C=CH_2); 4.94 (s, 1H, C=CH_2); 3.11 (s, 2H, C=C-CH_2); 2.86 (s, 2H, B-CH_2); 1.71 (s, 3H, C=C-CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC, 80 °C) δ 147.5 (br, B-C=*C*); 144.6 (H_2C=*C*-CH_3); 142.4 (*ipso*-Ph); 141.2 (br, B-*C*=C); 140.8 (br, B-*ipso*-Ph); 136.3 (B-*o*-Ph); 132.2 (B-*p*-Ph); 129.7 (*o*-Ph); 128.6 (*m*-Ph); 128.3 (B-*m*-Ph); 126.1 (*p*-Ph); 112.7 (C=*C*H_2); 45.1 (C=C-*C*H_2); 35.0 (B-*C*H_2); 22.9 (*C*H_3). **HMQC** (400 MHz, C_6D_6, 80 °C) δ 7.79 ↔ δ 136.3; δ 7.20 ↔ δ 129.7; δ 7.14-7.09 ↔ δ 132.2, 128.3; δ 7.06 ↔ δ 128.6; δ 6.93 ↔ δ 126.1; δ 4.99 ↔ δ 112.7; δ 4.94 ↔ δ 112.7; δ 3.11 ↔ δ 45.1; δ 2.86 ↔ δ 35.0; δ 1.71 ↔ δ 22.9. **HMBC** (400 MHz, C_6D_6, 80 °C) δ 7.79 ↔ δ 140.8, 136.3, 132.2, 128.3; δ 7.20 ↔ δ 147.5, 142.4, 129.7, 126.1; δ 7.14-7.09 ↔ δ 140.8, 136.3, 128.3; δ 7.06 ↔ δ 142.4, 128.6, 126.1; δ 6.93 ↔ δ 142.4, 129.7, 128.6; δ 4.99 ↔ δ 144.6, 45.1, 22.9; δ 4.94 ↔ δ 144.6, 45.1, 22.9; δ 3.11 ↔ δ 147.5, 144.6, 141.2, 112.7, 35.0, 22.9; δ 2.86 ↔ δ 147.5, 141.2, 129.7, 45.1; δ 1.71 ↔ δ 144.6, 112.7, 45.1. **^{11}B NMR** (128 MHz, C_6D_6) δ 75.5 (br). **Anal**. Calcd. for $C_{19}H_{19}B$: C, 88.39, H, 7.42. Found: C, 87.26, H, 7.51. **HRMS** Calcd. for $C_{19}H_{19}B$: 258.15798. Found: 258.15841.



3-(3,3-Dimethyl-2-propenyl)-1,2-diphenylboracyclobutene (62): To a cold toluene (-30 °C, 10 mL) solution of titanacyclobutene **18** (300 mg, 0.83 mmol) was added a cold toluene (-30 °C, 2 mL) solution of dichlorophenylborane (138 mg, 0.87 mmol) in dry toluene (2 mL). The solution was allowed to warm to 25 °C over a 12 hour period. During that time the solution changed from dark red to brown. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble Cp_2TiCl_2. Concentration under vacuum yielded the boracyclobutene (195

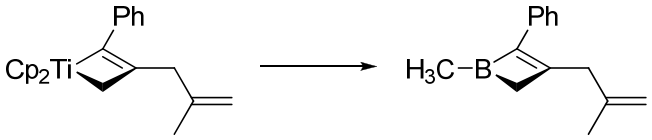
mg, 86 % yield) as a spectroscopically clean amorphous brown solid. **^{1}H NMR** (400 MHz, C_6D_6, 27 °C) δ 7.79 (br s, 2H, B-*o*-Ph*H*); 7.28 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H, *o*-Ph*H*); 7.14-7.05 (m, 5H, *m*-Ph*H*, B-*m,p*-Ph*H*); 6.95 (t, $^{3}J_{HH}$ = 7.1 Hz, 1H, *p*-Ph*H*); 5.37 (t, $^{3}J_{HH}$ = 6.5 Hz, 1H, C=C-*H*); 3.19 (d, $^{3}J_{HH}$ = 6.7 Hz, 2H, C=C(H)-CH_2); 2.86 (s, 2H, B-CH_2); 1.60 (s, 3H, C=C-CH_3); 1.48 (s, 3H, C=C-CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC, 27 °C) δ 144.6 (*ipso*-Ph); 143.0 (B-*ipso*-Ph); 141.2 (B-*C*=C); 136.1 (B-*o*-Ph); 133.0 (C=*C*$(CH_3)_2$); 132.1 (B-*p*-Ph); 130.1 (*o*-Ph); 128.5 (*m*-Ph); 128.0 (B-*m*-Ph); 125.9 (*p*-Ph); 123.3 (C=*C*-H); 36.0 (C=C-*C*H_2); 35.7 (B-*C*H_2); 25.9 (C=C-*C*H_3); 18.0 (C=C-*C*H_3); B-C=*C* not observed at 27 °C. **COSY** (400 MHz, C_6D_6, 27 °C) δ 7.79 ↔ δ 7.14-7.05; δ 7.28 ↔ δ 7.14-7.05, 6.95; δ 7.14-7.05 ↔ δ 7.79, 7.28, 6.95; δ 6.95 ↔ δ 7.28, 7.14-7.05; δ 5.37 ↔ δ 3.19, 1.60, 1.48; δ 1.60 ↔ δ 5.37, 3.19, 1.48; δ 1.48 ↔ δ 5.37, 3.19, 1.60. **HMQC** (400 MHz, C_6D_6, 27 °C) δ 7.79 ↔ δ 136.1; δ 7.28 ↔ δ 130.1; δ 7.14-7.05 ↔ δ 132.1, 128.5, 128.0; δ 6.95 ↔ δ 125.9; δ 5.37 ↔ δ 123.3; δ 3.19 ↔ δ 36.0; δ 2.86 ↔ δ 35.7; δ 1.60 ↔ δ 25.9; δ 1.48 ↔ δ 18.0. **HMBC** (400 MHz, C_6D_6, 27 °C) δ 7.79 ↔ δ 136.1, 132.0; δ 7.28 ↔ δ 144.6, 130.1, 125.9; δ 7.14-7.05 ↔ δ 143.0, 141.2?__, 136.1, 128.5; δ 6.95 ↔ δ 130.1; δ 5.37 ↔ δ 25.9, 18.0; δ 3.19 ↔ δ 144.6, 133.0, 123.3, 35.7; δ 2.86 ↔ δ 144.6, 36.0; δ 1.60 ↔ δ 133.0, 123.3, 18.0; δ 1.48 ↔ δ 133.0, 123.3, 25.9. **^{1}H NMR** (400 MHz, C_6D_6, 80 °C) δ 7.76-7.73 (m, 2H, B-*o*-Ph*H*); 7.23 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, *o*-Ph*H*); 7.13-7.06 (m, 5H, *m*-Ph*H*, B-*m,p*-Ph*H*); 6.95 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H, *p*-Ph*H*); 5.36 (t, $^{3}J_{HH}$ = 7.1 Hz, 1H, C=C-*H*); 3.15 (d, $^{3}J_{HH}$ = 7.1 Hz, 2H, C=C-CH_2); 2.89 (s, 2H, B-CH_2); 1.60 (s, 3H, C=C-CH_3); 1.47 (s, 3H, C=C-CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC, 80 °C) δ 145.2 (br, B-C=*C*); 144.9 (br, *ipso*-Ph); 142.9 (B-*ipso*-Ph); 141.4 (B-*C*=C); 135.7 (B-*o*-Ph); 132.6 (C=*C*$(CH_3)_2$); 131.6 (B-*p*-Ph); 129.9 (*o*-Ph); 128.2 (*m*-Ph); 127.6 (B-*m*-Ph); 125.6 (*p*-Ph); 123.1 (C=*C*-H); 35.9 (C=C(H)-*C*H_2); 35.7 (B-*C*H_2); 25.5 (C=C-*C*H_3); 17.7 (C=C-*C*H_3). **HMQC** (400 MHz, C_6D_6, 80 °C) δ 7.76-7.73 ↔ δ 135.7; δ 7.23 ↔ δ 129.9; δ 7.13-7.06 ↔ δ 131.6, 128.2, 127.6; δ 6.95 ↔ δ 125.6; δ 5.36 ↔ δ 123.1; δ 3.15 ↔ δ 35.9; δ 2.89 ↔ δ 35.7; δ 1.60 ↔ δ 25.5; δ 1.47 ↔ δ 17.7. **HMBC** (400 MHz, C_6D_6, 80 °C) δ 7.76-7.73 ↔ δ 135.7, 131.6, 127.6; δ 7.23 ↔ δ 144.9, 129.9, 125.6; δ 7.13-7.06 ↔ δ 142.9, 135.7, 128.2; δ 6.95 ↔ δ 129.9; δ 5.36 ↔ δ 35.9, 25.9, 18.0; δ 3.15 ↔ δ 145.2, 132.6, 123.1, 35.7; δ 2.89 ↔ δ 145.2, 141.4, 129.9, 35.9; δ 1.60 ↔ δ 132.6, 123.1, 17.7; δ

1.47 ↔ δ 132.6, 123.1, 25.5. **^{11}B NMR** (128 MHz, C_6D_6, 27 °C) δ 71.3 (br). **Anal**. Calcd. for $C_{20}H_{21}B$: C, 88.25, H, 7.78. Found: C, 78.94, H, 6.96. **HRMS** Calcd. for $C_{20}H_{21}B$: 272.17363. Molecular ion not observed. Calcd. for $C_{20}H_{21}BO$: 288.16855. Found: 288.16933.



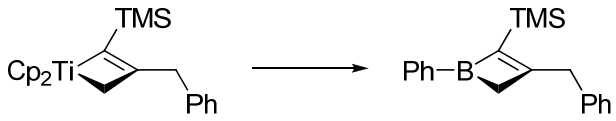
3-Isopropyl-1-methyl-2-phenylboracyclobutene (63): A suspension of titanacyclobutene **15** (100 mg, 0.30 mmol), potassium methyltrifluoroborate (38 mg, 0.31 mmol), and dichlorodimethylsilane (200 mg, 1.55 mmol) in dry toluene (10 mL) was heated at 80 °C for 12 hours in a sealed glass bomb, during which time the solution changed from red to dark green. The solution was cooled to room temperature, and then the solvent removed *in vacuo*. The residue was triturated with dry hexanes then filtered through Celite to separate from insoluble titanium by-products. Concentration under vacuum yielded the boracyclobutene (54 mg, 99 % yield) as an analytically pure red oil. **^{1}H NMR** (400 MHz, C_6D_6, 27 °C) δ 7.22 (t, $^{3}J_{HH}$ = 7.1 Hz, 2H, *m*-Ph*H*); 7.12-7.10 (m, 2H, *o*-Ph*H*); 7.07 (tt, $^{3}J_{HH}$ = 7.2 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1H, *p*-Ph*H*); 2.78 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, *H*C(CH$_3$)$_2$); 2.70 (br s, 2H, B-C*H*$_2$); 0.88 (d, $^{3}J_{HH}$ = 6.8 Hz, 1H, HC(C*H*$_3$)$_2$); 0.75 (s, 3H, B-C*H*$_3$). **^{13}C NMR** (100 MHz, C_6D_6, 27 °C, assignments confirmed by HMQC and HMBC) δ 157.8 (B-C=*C*); 146.0 (*ipso*-Ph); 129.2 (*m*-Ph); 128.5 (*o*-Ph); 125.4 (*p*-Ph); 42.4 (br, B-C*H*$_2$); 33.4 (H*C*(CH$_3$)$_2$); 21.2 (HC(*C*H$_3$)$_2$); 13.7 (B-*C*H$_3$). **COSY** (400 MHz, C_6D_6, 27 °C, selected correlations only) δ 0.88 ↔ δ 2.78; δ 0.75 ↔ δ 2.70. **HMQC** (400 MHz, C_6D_6, 27 °C) δ 7.22 ↔ δ 129.2; δ 0.88 ↔ δ 21.2; δ 0.75 ↔ δ 13.7. **HMBC** (400 MHz, C_6D_6, 27 °C) δ 7.22 ↔ δ 146.0, 128.5; δ 7.12-7.10 ↔ δ 125.4; δ 7.07 ↔ δ 129.2; δ 2.78 ↔ δ 157.8, 21.2; δ 2.70 ↔ δ 157.8, 33.4; δ 0.88 ↔ δ 157.8, 33.4, 21.2. **^{1}H NMR** (400 MHz, C_6D_6, 60 °C) δ 7.15 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, *m*-Ph*H*); 7.05-6.98 (m, 3H, *o/p*-Ph*H*); 2.72 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, *H*C(CH$_3$)$_2$); 2.68 (s, 2H, B-C*H*$_2$); 0.84 (d, $^{3}J_{HH}$ = 6.8 Hz, 1H, HC(C*H*$_3$)$_2$); 0.68 (s, 3H, B-C*H*$_3$). **^{13}C NMR** (100 MHz, C_6D_6, 60 °C, assignments confirmed by HSQC and HMBC) δ 157.6 (B-C=*C*); 145.9 (*ipso*-Ph); 134.9 (br, B-*C*=C); 129.3 (*m*-Ph); 128.5 (*o*-Ph); 125.5 (*p*-Ph); 42.7 (br, B-C*H*$_2$); 33.4 (H*C*(CH$_3$)$_2$); 21.0 (HC(*C*H$_3$)$_2$); 13.5 (B-*C*H$_3$). **HSQC** (400 MHz, C_6D_6, 60 °C) δ 7.15 ↔

δ 129.3; δ 7.05-6.98 ↔ δ 128.5, 125.5; δ 2.72 ↔ δ 33.4; δ 2.68 ↔ δ 42.7; δ 0.84 ↔ δ 21.0; δ 0.68 ↔ δ 13.5. **HMBC** (400 MHz, C_6D_6, 60 °C) δ 7.15 ↔ δ 145.9, 128.5; δ 7.05-6.98 ↔ δ 134.9, 129.3, 125.5; δ 2.72 ↔ δ 157.6, 42.7, 21.0; δ 2.68 ↔ δ 157.6, 134.9, 33.4, 13.5; δ 0.84 ↔ δ 157.6, 33.4, 21.0; δ 0.68 ↔ δ 134.7, 42.7. **^{11}B NMR** (128 MHz, C_6D_6, 27 °C) δ 78.1 (br). **Anal**. Calcd. for $C_{13}H_{17}B$: C, 84.82, H, 9.31. Found: C, 84.74, H, 8.94. **HRMS** Calcd. for $C_{13}H_{17}B$: 184.14233. Found: 184.14195.



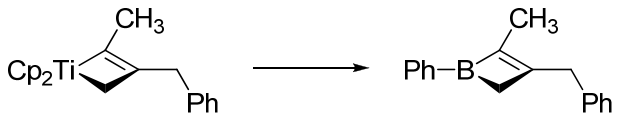
3-(2-Methylallyl)-1-methyl-2-phenylboracyclobutene (64): A suspension of titanacyclobutene **19** (200 mg, 0.57 mmol), potassium methyltrifluoroborate (74 mg, 0.60 mmol), and dichlorodimethylsilane (240 mg, 1.86 mmol) in dry toluene (10 mL) was heated at 80 °C for 12 hours in a sealed glass bomb, during which time the solution changed from red to dark green. The solution was cooled to room temperature, and then the solvent removed *in vacuo*. The residue was triturated with dry hexanes then filtered through Celite to separate from insoluble titanium by-products. Concentration under vacuum yielded the boracyclobutene as a red oil contaminated with unidentified by-products (124 mg, "110 % yield"). **^{1}H NMR** (400 MHz, C_6D_6) δ 7.22-7.15 (m, 2H, Ph*H*); 7.10-7.05 (m, 3H, Ph*H*); 4.85(s, 1H, C=CH_2); 4.83 (s, 1H, C=CH_2); 2.87 (s, 2H, B-CH_2); 2.81 (s, 2H, H_2C=C-CH_2); 1.55 (s, 3H, C=C-CH_3); 0.72 (s, 3H, B-CH_3). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 151.1 (B-C=*C*); 145.7 (*ipso*-Ph); 143.7 (C=*C*-CH_3); 140.6 (br, B-*C*=C); 129.1 (Ph); 128.5 (Ph); 125.7 (*p*-Ph); 113.0 (C=*C*H_2); 46.6 (H_2C=C-*C*H_2); 43.8 (br, B-*C*H_2); 23.1 (H_2C=C-*C*H_3); 13.6 (B-*C*H_3). **COSY** (400 MHz, C_6D_6) δ 7.22-7.15 ↔ δ 7.10-7.05; δ 7.10-7.05 ↔ δ 7.22-7.15; δ 4.85 ↔ δ 4.83, 2.81, 1.55; δ 4.83 ↔ δ 4.85, 2.81, 1.55; δ 2.87 ↔ δ 0.72; δ 2.81 ↔ δ 4.85, 4.83, 1.55; δ 1.55 ↔ δ 4.85, 4.83, 2.81; δ 0.72 ↔ δ 2.87. **HMQC** (400 MHz, C_6D_6) δ 7.22-7.15 ↔ δ 129.1; δ 7.10-7.05 ↔ δ 128.5; δ 4.85 ↔ δ 113.0; δ 4.83 ↔ δ 113.0; δ 2.87 ↔ δ 43.8; δ 2.81 ↔ δ 46.6; δ 1.55 ↔ δ 23.1; δ 0.72 ↔ δ 13.6. **HMBC** (400 MHz, C_6D_6) δ 7.22-7.15 ↔ δ 145.7, 128.5; δ 7.10-7.05 ↔ δ 140.6, 129.1, 125.7; δ 4.85 ↔ δ 46.6, 23.1; δ 4.83 ↔ δ 46.6, 23.1; δ 2.87 ↔ δ 151.1, 140.6, 46.6; δ 2.81 ↔ δ 151.1, 143.7,

140.6, 113.0, 43.8, 23.1; δ 1.55 ↔ δ 143.7, 113.0, 46.6; δ 0.72 ↔ δ 140.6, 43.8. **^{11}B NMR** (128 MHz, C_6D_6) δ 76.5 (br). **Anal**. Calcd. for $C_{14}H_{17}B$: C, 85.75, H, 8.74. Found: C, 83.14, H, 8.21. **HRMS** Calcd. for $C_{14}H_{17}B$: 196.14233. Found: 196.14251.



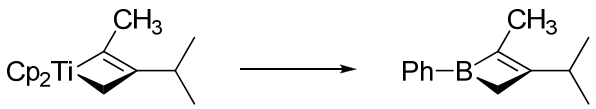
3-Benzyl-1-phenyl-2-(trimethylsilyl)boracyclobutene (65): To a cold toluene (-30 °C, 9 mL) solution of titanacyclobutene **26** (394 mg, 1.03 mmol) was added a cold toluene (-30 °C, 2 mL) solution of dichlorophenylborane (173 mg, 1.09 mmol). The solution was allowed to warm to 25 °C over a 12 hour period, during which time the solution changed from dark red to dark green with formation of red crystals. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble Cp_2TiCl_2. Concentration under vacuum yielded the impure boracyclobutene as a dark green oil that solidified slowly (337 mg, "112 % yield", 76 % boracyclobutene by weight by ^{1}H NMR internal hexamethylbenzene standard, approximate chemical yield is 85 %). *Alternate procedure:* A suspension of titanacyclobutene **26** (100 mg, 0.26 mmol), potassium phenyltrifluoroborate (48 mg, 0.26 mmol), and dichlorodimethylsilane (200 mg, 1.55 mmol) in dry toluene (5 mL) was heated at 80 °C for 12 hours in a sealed glass bomb. The solution changed from red to dark green during this time. The solution was cooled to room temperature, and then the solvent removed *in vacuo*. The residue was triturated with dry hexanes then filtered through Celite to separate from insoluble titanium, KF, and KCl by-products. Concentration under vacuum yielded the impure boracyclobutene as a dark green oil (34 mg, 45 % yield). Spectroscopically, the same contaminant(s) were present, however in a greater amount; the use of $PhBCl_2$ is preferable. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.63 (d, $^3J_{HH}$ = 7.3 Hz, 2H, B-*o*-Ph*H*); 7.48 (d, $^3J_{HH}$ = 7.3 Hz, 2H, CH_2-*o*-Ph*H*); 7.28 (t, $^3J_{HH}$ = 7.7 Hz, 2H, CH_2-*m*-Ph*H*); 7.13-7.08 (m, 2H, B-*p*-Ph*H*, CH_2-*p*-Ph*H*); 7.05 (t, $^3J_{HH}$ = 7.2 Hz, 2H, B-*m*-Ph*H*); 4.26 (d, $^2J_{HH}$ = 14.7 Hz, 1H, Ph-CH_2); 3.59 (d, $^2J_{HH}$ = 14.6 Hz, 1H, Ph-CH_2); 2.57 (d, $^2J_{HH}$ = 18.7 Hz, 1H, B-CH_2); 2.43 (d, $^2J_{HH}$ = 18.8 Hz, 1H, B-CH_2); 0.28 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 153.4 (B-C=*C*); 145.8 (br, B-*C*=C); 140.9 (CH_2-*ipso*-Ph); 139.9 (br, B-*ipso*-

Ph); 135.8 (B-*o*-Ph); 132.6 (B-*p*-Ph); 131.8 (CH_2-*p*-Ph); 129.5 (CH_2-*m*-Ph); 129.1 (B-*m*-Ph); 126.6 (CH_2-*o*-Ph); 47.6 (Ph-*C*H_2); 39.8 (B-*C*H_2); 1.6 (Si(*C*H_3)$_3$). **COSY** (400 MHz, C_6D_6) δ 7.63 ↔ δ 7.05; δ 7.48 ↔ δ 7.28, 7.13-7.08, 4.26; δ 4.26 ↔ δ 7.48, 3.59; δ 3.59 ↔ δ 4.26; δ 2.57 ↔ δ 2.43; δ 2.43 ↔ δ 2.57. **HMQC** (400 MHz, C_6D_6) δ 7.63 ↔ δ 135.8; δ 7.28 ↔ δ 129.5; δ 7.13-7.08 ↔ δ 132.6; δ 7.05 ↔ δ 129.1; δ 4.26 ↔ δ 47.6; δ 3.59 ↔ δ 47.6; δ 2.57 ↔ δ 39.8; δ 2.43 ↔ δ 39.8; δ 0.28 ↔ δ 1.6. **HMBC** (400 MHz, C_6D_6) δ 7.63 ↔ δ 135.8, 132.6; δ 7.48 ↔ δ 129.5, 126.6; δ 7.28 ↔ δ 140.9, 129.5; δ 7.13-7.08 ↔ δ 135.8, 129.5; δ 7.05 ↔ δ 139.9, 129.1; δ 4.26 ↔ δ 153.4, 140.9, 129.5, 39.8; δ 3.59 ↔ δ 153.4, 145.8, 140.9, 129.5; δ 2.57 ↔ δ 153.4, 145.8; δ 2.43 ↔ δ 153.4, 145.8; δ 0.28 ↔ δ 145.8, 1.6. **^{11}B NMR** (128 MHz, C_6D_6) δ 72.2 (br). **HRMS** Calcd. for $C_{19}H_{23}BSi$: 290.16621. Molecular ion not observed; M(100): 73.04740.



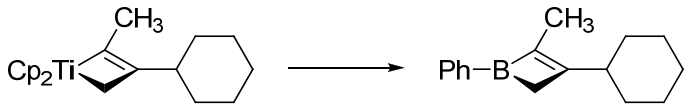
3-Benzyl-2-methyl-1-phenylboracyclobutene (66): A suspension of titanacyclobutene **21** (400 mg, 1.24 mmol), potassium phenyltrifluoroborate (114 mg, 0.62 mmol), and dichlorodimethylsilane (320 mg, 2.48 mmol) in dry toluene (17 mL) was heated at 80 °C for 12 hours in a sealed glass bomb, during which time the solution changed from red to dark green. The solution was cooled to room temperature, and then the solvent removed *in vacuo*. The residue was triturated with dry hexanes then filtered through Celite to separate from insoluble titanium by-products. Cooling the hexanes solution to -30 °C caused precipitation of additional Ti(III) by-product (10 mg). Filtration and concentration under vacuum yielded the impure boracyclobutene as a green oil (216 mg, "150 % yield", ^{1}H NMR spectroscopy with internal hexamethylbenzene standard indicated boracyclobutene is 44 % by weight, approximate chemical yield is 66 %). *Alternate procedure:* To a cold (-30 °C) solution of titanacyclobutene **21** (100 mg, 0.31 mmol) in dry toluene (5 mL) was added a cold (-30 °C) solution of dichlorophenylborane (20 μL, 0.16 mmol) in dry toluene (1 mL). The solution was allowed to warm to 25 °C over a 12 hour period. During that time the solution changed from dark red to green. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble green Ti(III) by-products. Cooling the hexanes

solution to -30 °C caused precipitation of additional green solid (9 mg). Filtration and concentration under vacuum yielded the boracyclobutene with impurities as a green oil (58 mg, "205 % yield"). The green solid was crystallized and identified as $[Cp_2TiCl]_2$ with the same cell parameters as previously reported.[358] **^{1}H NMR** (400 MHz, C_6D_6, 27 °C) δ 7.61-7.59 (m, 2H, B-*o*-Ph*H*); 7.21-7.00 (m, 8H, B-*m/p*-Ph*H*, Ph*H*); 3.52 (s, 2H, C*H*$_2$-Ph); 2.63 (s, 2H, B-C*H*$_2$); 1.66 (s, 3H, C*H*$_3$). **^{13}C NMR** (100 MHz, C_6D_6, 27 °C, assignments confirmed by HMQC and HMBC) δ 145.7 (B-C=*C*); 140.6 (CH_2-*ipso*-Ph); 135.1 (B-*o*-Ph); 131.7 (Ar); 130.2 (indirectly observed by HMBC, B-*C*=C); 129.5 (Ar); 129.4 (Ar); 128.8 (Ar); 128.6 (Ar); 126.3 (Ar); 42.2 (br, B-*C*H$_2$); 42.0 (*C*H$_2$-Ph); 18.2 (*C*H$_3$). **COSY** (400 MHz, C_6D_6, 27 °C) δ 7.61-7.59 ↔ δ 7.21-7.16; δ 7.21-7.16 ↔ δ 7.61-7.59, 3.52 δ 3.52 ↔ δ 7.21-7.16, 1.66; δ 2.63 ↔ δ 1.66; δ 1.66 ↔ δ 3.52, 2.63. **HMQC** (400 MHz, C_6D_6, 27 °C) δ 7.61-7.59 ↔ δ 135.1; δ 7.21-7.00 ↔ δ 131.7, 129.5, 128.8, 126.3; δ 3.52 ↔ δ 42.0; δ 2.63 ↔ δ 42.2; δ 1.66 ↔ δ 18.2. **HMBC** (400 MHz, C_6D_6, 27 °C) δ 7.61-7.59 ↔ δ 135.1, 131.7; δ 7.21-7.00↔ δ 140.6, 129.5, 126.3; δ 3.52 ↔ δ 145.7, 140.6, 129.5, 42.2; δ 2.63 ↔ δ 145.7, 130.2, 42.0; δ 1.66 ↔ δ 145.7, 130.2. **^{1}H NMR** (400 MHz, C_6D_6, 70 °C) δ 7.54-7.52 (m, 2H, B-*o*-Ph*H*); 7.16-7.00 (m, 7H, B-*m/p*-Ph*H*, *m/o*-Ph*H*); 6.98 (t, $^3J_{HH}$ = 7.1 Hz, 1H, CH_2-*p*-Ph); 3.48 (s, 2H, C*H*$_2$-Ph); 2.63 (s, 2H, B-C*H*$_2$); 1.63 (s, 3H, C*H*$_3$). **^{13}C NMR** (100 MHz, C_6D_6, 70 °C, assignments confirmed by HMQC and HMBC) δ 144.9 (B-C=*C*); 141.4 (br, B-*ipso*-Ph); 140.5 (*ipso*-Ph); 134.8 (B-*o*-Ph); 131.3 (B-*p*-Ph); 130.0 (br, B-*C*=C); 129.3 (*o*-Ph); 128.5 (*m*-Ph); 127.7 (B-*m*-Ph); 126.0 (*p*-Ph); 42.5 (br, B-*C*H$_2$); 41.9 (*C*H$_2$-Ph); 17.8 (*C*H$_3$). **COSY** (400 MHz, C_6D_6, 70 °C) δ 7.54-7.52 ↔ δ 7.16-7.00; δ 7.16-7.00 ↔ δ 7.54-7.52, 6.98, 3.48; δ 6.98 ↔ δ 7.16-7.00; δ 3.48 ↔ δ 7.16-7.00, 2.63, 1.63; δ 2.63 ↔ δ 3.48, 1.63; δ 1.63 ↔ δ 3.48, 2.63. **HMQC** (400 MHz, C_6D_6, 70 °C) δ 7.54-7.52 ↔ δ 134.8; δ 7.16-7.00 ↔ δ 131.3, 129.3; δ 6.98 ↔ δ 126.0; δ 3.48 ↔ δ 41.9; δ 2.63 ↔ δ 42.5; δ 1.63 ↔ δ 17.8. **HMBC** (400 MHz, C_6D_6, 70 °C) δ 7.54-7.52 ↔ δ 141.4, 134.8, 131.3, 127.7; δ 7.16-7.00↔ δ 140.5, 134.8, 129.3, 126.0, 41.9; δ 6.98 ↔ δ 129.3; δ 3.48 ↔ δ 144.9, 140.5, 129.3, 42.5; δ 2.63 ↔ δ 144.9, 130.0, 41.9; δ 1.63 ↔ δ 144.9, 130.0. **^{11}B NMR** (128 MHz, C_6D_6, 27 °C) δ 78.2. **Anal**. Calcd. for $C_{17}H_{17}B$: C, 87.96, H, 7.38. Found: C, 83.06, H, 7.67. **HRMS** Calcd. for $C_{17}H_{17}B$: 232.14233. Found: 232.14306.



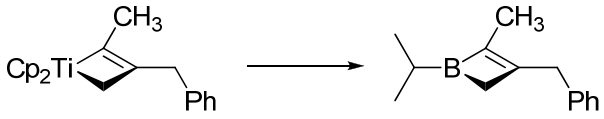
3-Isopropyl-2-methyl-1-phenylboracyclobutene (67): A suspension of titanacyclobutene **22** (300 mg, 1.09 mmol), potassium phenyltrifluoroborate (50 mg, 0.55 mmol), and dichlorodimethylsilane (300 mg, 2.32 mmol) in dry toluene (15 mL) was heated at 80 °C for 12 hours in a sealed glass bomb, during which time the solution changed from red to dark green. The solution was cooled to room temperature, and then the solvent removed *in vacuo*. The residue was triturated with dry hexanes then filtered through Celite to separate from insoluble titanium by-products. Cooling the hexanes solution to -30 °C caused precipitation of additional green solid (21 mg). Filtration and concentration under vacuum yielded the impure boracyclobutene as a green oil (152 mg, "150 % yield". *Alternate procedure:* To a cold (-30 °C) solution of titanacyclobutene **22** (50 mg, 0.18 mmol) in dry toluene (5 mL) was added a cold (-30 °C) solution of dichlorophenylborane (12 μL, 0.091 mmol) in dry toluene (1 mL). The solution was allowed to warm to 25 °C over a 12 hour period. During that time the solution changed from dark red to green. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble green Ti(III) by-products. Cooling the hexanes solution to -30 °C caused precipitation of additional green solid (~3 mg). Filtration and concentration under vacuum yielded the impure boracyclobutene (24 mg, "143 % yield"). **^{1}H NMR** (400 MHz, C_6D_6) δ 7.80 (m, 2H, *o*-Ph*H*); 7.25-7.19 (m, 3H, *m*- and *p*-Ph*H*); 3.11 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, *H*C(CH$_3$)$_2$); 2.46 (s, 2H, B-C*H*$_2$); 1.79 (s, 3H, C=C-C*H*$_3$); 1.03 (d, $^{3}J_{HH}$ = 6.7 Hz, 6H, HC(C*H*$_3$)$_2$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 149.9 (B-C=*C*); 140.6 (br, *ipso*-Ph); 135.9 (*o*-Ph); 132.2 (*p*-Ph); 128.7 (br, B-*C*=C); 128.2 (*m*-Ph); 33.5 (br, B-*C*H$_2$); 30.3 (H*C*(CH$_3$)$_2$); 21.2 (HC(*C*H$_3$)$_2$); 16.4 (C=C-*C*H$_3$). **COSY** (400 MHz, C_6D_6) δ 7.80 ↔ δ 7.25-7.19; δ 7.25-7.19 ↔ δ 7.80; δ 3.11 ↔ δ 1.03; δ 2.46 ↔ δ 1.79; δ 1.79 ↔ δ 2.46; δ 1.03 ↔ δ 3.11. **HMQC** (400 MHz, C_6D_6) δ 7.80 ↔ δ 135.9; δ 7.25-7.19 ↔ δ 132.2, 128.2; δ 3.11 ↔ δ 30.3; δ 2.46 ↔ δ 33.5; δ 1.79 ↔ δ 16.4; δ 1.03 ↔ δ 21.2. **HMBC** (400 MHz, C_6D_6) δ 7.80 ↔ δ 140.6, 135.9, 132.2; δ 7.25-7.19 ↔ δ 140.6, 135.9; δ 3.11 ↔ δ 149.9, 128.7, 33.5, 21.2; δ 2.46 ↔ δ 149.9, 128.7, 30.3; δ 1.79 ↔ δ 149.9, 128.7; δ 1.03

↔ δ 149.9, 30.3, 21.2. **^{11}B NMR** (128 MHz, C_6D_6) δ 69.0 (br). **HRMS** Calcd. for $C_{13}H_{17}B$: 184.14233. Found: 184.14236.



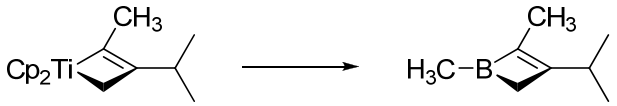
3-Cyclohexyl-2-methyl-3-phenylboracyclobutene (68): A suspension of titanacyclobutene **23** (55 mg, 0.18 mmol), potassium phenyltrifluoroborate (16 mg, 0.09 mmol), and dichlorodimethylsilane (140 mg, 1.10 mmol) in dry toluene (5 mL) was heated at 80 °C for 12 hours in a sealed glass bomb, during which time the solution changed from red to orange. The solution was cooled to room temperature, and then the solvent removed *in vacuo*. The residue was triturated with dry hexanes then filtered through Celite to separate from insoluble titanium by-products. Cooling the hexanes solution to -30 °C caused precipitation of additional green solid (4 mg). Filtration and concentration under vacuum yielded the boracyclobutene (37 mg, 94 % yield) as a yellow oil. *Alternate procedure:* To a cold (-30 °C) solution of titanacyclobutene **23** (20 mg, 0.064 mmol) in dry toluene (3 mL) was added a cold (-30 °C) solution of dichlorophenylborane (4 μL, 0.032 mmol) in dry toluene (1 mL). The solution was allowed to warm to 25 °C over a 12 hour period. During that time the solution changed from dark red to green. Solvent was removed *in vacuo* and the residue triturated with dry hexanes, then filtered through Celite to separate from insoluble green Ti(III) by-products. Concentration under vacuum yielded the impure boracyclobutene as a green oil (13 mg, "182 % yield"). **^{1}H NMR** (400 MHz, C_6D_6, 27 °C) δ7.86-7.82 (m, 2H, *o*-Ph*H*); 7.26-7.22 (m, 3H, *m*- and *p*-Ph*H*); 2.80-2.73 (m, 1H, C=C-C*H*); 2.62 (s, 2H, B-CH_2); 1.82-1.58 (m, 4H, Cy*H*); 1.80 (s, 3H, B-C-CH_3); 1.41-1.20 (m, 6H, Cy*H*). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC, 27 °C) δ 149.9 (B-C=*C*); 140.9 (*ipso*-Ph); 135.8 (*o*-Ph); 132.1 (*p*-Ph); 128.2 (*m*-Ph); 128.0 (br, B-*C*=C); 38.1 (C=C-*C*H); 37.0 (br, B-*C*H_2); 31.7 (Cy); 27.1 (Cy); 26.7 (4-Cy); 16.5 (B-C-*C*H_3). **COSY** (400 MHz, C_6D_6, 27 °C) δ 7.86-7.82 ↔ δ 7.26-7.22; δ 2.80-2.73 ↔ δ 1.82-1.58, 1.41-1.20; δ 2.62 ↔ δ 1.80; δ 1.82-1.58 ↔ δ 2.80-2.73, 1.41-1.20; δ 1.80 ↔ δ 2.62; δ 1.41-1.20 ↔ δ 2.80-2.73, 1.82-1.58. **HMQC** (400 MHz, C_6D_6, 27 °C) δ 7.86-7.82 ↔ δ 135.8; δ 7.26-7.22 ↔ δ 132.1, 128.2; δ 2.80-2.73 ↔ δ 38.1; δ 1.80 ↔ δ 16.5; δ 1.82-1.58, 1.41-

1.20 ↔ δ 31.7, 27.1, 26.7. **HMBC** (400 MHz, C_6D_6, 27 °C) δ 7.86-7.82 ↔ δ 140.9, 135.8, 132.1; δ 7.26-7.22 ↔ δ 140.9, 135.8; δ 1.80 ↔ δ 149.9, 128.0. **^{1}H NMR** (400 MHz, C_6D_6, 80 °C) δ7.79-7.76 (m, 2H, *o*-Ph*H*); 7.24-7.20 (m, 3H, *m*,*p*-Ph*H*); 2.80-2.71 (m, 1H, C=C-C*H*); 2.69 (s, 2H, B-CH_2); 1.80-1.57 (m, 4H, Cy*H*); 1.77 (s, 3H, B-C-CH_3); 1.41-1.12 (m, 6H, Cy*H*). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMBC, 80 °C) δ 150.0 (B-C=*C*); 141.4 (*ipso*-Ph); 135.5 (*o*-Ph); 131.8 (*p*-Ph); 128.1 (*m*-Ph); 125.6 (br, B-*C*=C); 42.4 (C=C-*C*H); 39.0 (br, B-*C*H_2); 31.9 (Cy); 27.2 (Cy); 26.8 (4-Cy); 16.5 (B-C-*C*H_3). **HMBC** (400 MHz, C_6D_6, 80 °C) δ 7.79-7.76 ↔ δ 131.8; δ 7.24-7.20 ↔ δ 131.8; δ 2.69 ↔ δ 150.0, 125.6, 42.4; δ 1.77 ↔ δ 150.0, 125.6, 42.4. **^{11}B NMR** (128 MHz, C_6D_6, 27 °C) δ 76.0 (br). **HRMS** Calcd. for $C_{16}H_{21}B$: 224.17363. Found: 224.17377.



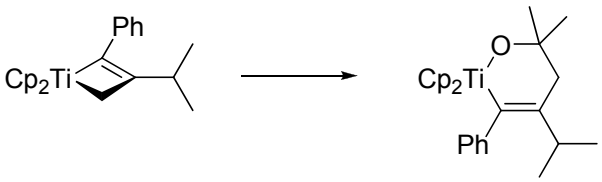
3-Benzyl-1-isopropyl-2-methylboracyclobutene (69): A suspension of titanacyclobutene **21** (271 mg, 0.84 mmol), potassium isopropyltrifluoroborate (112 mg, 0.88 mmol), and dichlorodimethylsilane (270 mg, 2.09 mmol) in dry toluene (5 mL) was heated at 80 °C for 12 hours in a sealed glass bomb, during which time the solution changed from red to dark green. The solution was cooled to room temperature, and then the solvent removed *in vacuo*. The residue was triturated with dry hexanes then filtered through Celite to separate from insoluble titanium by-products. Cooling the hexanes solution to -30 °C caused precipitation of additional green solid (~7 mg). Filtration and concentration under vacuum yielded the boracyclobutene with impurities as a green oil (176 mg, "106 % yield"). **^{1}H NMR** (400 MHz, C_6D_6) δ 7.16-7.10 (m, 4H, *o*- and *m*-Ph*H*); 7.08-7.04 (m, 1H, *p*-Ph*H*); 3.38 (s, 2H, Ph-CH_2); 2.20 (s, 2H, B-CH_2); 1.59 (s, 3H, CH_3); 1.40 (sept, $^3J_{HH}$ = 7.2 Hz, 1H, *H*C$(CH_3)_2$); 0.88 (d, $^3J_{HH}$ = 7.3 Hz, 6H, HC(C$H_3)_2$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 143.8 (B-C=*C*); 140.5 (*ipso*-Ph); 131.2 (br, B-*C*=C); 129.4 (*o*-Ph); 128.7 (*m*-Ph); 126.2 (*p*-Ph); 41.8 (Ph-*C*H_2); 40.9 (br, B-*C*H_2); 23.9 (br, B-*C*H); 18.8 (HC(*C*$H_3)_2$); 16.4 (C=C-*C*H_3). **COSY** (400 MHz, C_6D_6) δ 7.16-7.10 ↔ δ 3.38; δ 3.38 ↔ δ 7.16-7.10, 1.59; δ 2.20 ↔ δ 1.59; δ 1.59 ↔ δ 3.38, 2.20; δ 0.88 ↔ δ 1.40. **HMQC** (400 MHz, C_6D_6) δ 7.16-7.10 ↔ δ

129.4; δ 7.08-7.04 ↔ δ 126.2; δ 3.38 ↔ δ 41.8; δ 2.20 ↔ δ 40.9; δ 1.59 ↔ δ 16.4; δ 0.88 ↔ δ 18.8. **HMBC** (400 MHz, C_6D_6) δ 7.16-7.10 ↔ δ 140.5, 129.4, 126.2; δ 7.08-7.04 ↔ δ 129.4; δ 3.38 ↔ δ 143.8, 140.5, 129.4, 40.9; δ 2.20 ↔ δ 143.8, 131.2, 41.8; δ 1.40 ↔ δ 18.8; δ 0.88 ↔ δ 23.9, 18.8. **^{11}B NMR** (128 MHz, C_6D_6) δ 82.2 (br). **Anal**. Calcd. for $C_{14}H_{19}B$: C, 84.88, H, 9.67. Found: C, 82.17, H, 8.76. **HRMS** Calcd. for $C_{14}H_{19}B$: 198.15798. Found: 198.15832.

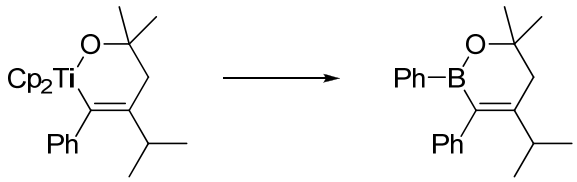


3-Isopropyl-1,2-dimethylboracyclobutene (70): A suspension of titanacyclobutene **22** (100 mg, 0.36 mmol), potassium methyltrifluoroborate (22 mg, 0.18 mmol), and dichlorodimethylsilane (100 mg, 0.77 mmol) in dry toluene (10 mL) was heated at 80 °C for 12 hours in a sealed glass bomb, during which time the solution changed from red to dark green. The solution was cooled to room temperature, and then the solvent removed *in vacuo*. The residue was triturated with dry hexanes then filtered through Celite to separate from insoluble titanium by-products. Concentration under vacuum yielded the boracyclobutene with impurities as a green oil (26 mg, "117 % yield", ^{1}H NMR spectroscopy with internal hexamethylbenzene standard indicated boracyclobutene is 27 % by weight, approximate chemical yield is 20 %). **^{1}H NMR** (400 MHz, C_6D_6, 27 °C) δ 3.46 (s, 2H, B-CH_2); 2.48 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, HC(CH$_3$)$_2$); 1.41 (s, 3H, C=C-CH_3); 0.91 (d, $^3J_{HH}$ = 6.8 Hz, 6H, HC(CH_3)$_2$); 0.81 (s, 3H, B-CH_3). **^{13}C NMR** (100 MHz, C_6D_6, 27 °C, assignments confirmed by HMQC and HMBC) δ 163.3 (B-C=C or B-C=C); 33.5 (HC(CH$_3$)$_2$); 66.0 (br, B-CH$_2$); 21.5 (HC(CH$_3$)$_2$); 15.7 (C=C-CH$_3$); 9.0 (br, B-CH$_3$); One olefinic carbon not observed at 27 °C. **COSY** (400 MHz, C_6D_6, 27 °C) δ 3.46 ↔ δ 1.41, 0.81; δ 2.48 ↔ δ 0.91; δ 1.41 ↔ δ 3.46; δ 0.91 ↔ δ 2.48; δ 0.81 ↔ δ 3.46. **HMQC** (400 MHz, C_6D_6, 27 °C) δ 2.48 ↔ δ 33.5; δ 1.41 ↔ δ 15.7; δ 0.91 ↔ δ 21.5; δ 0.81 ↔ δ 9.0. **HMBC** (400 MHz, C_6D_6, 27 °C) δ 3.46 ↔ δ 163.3, 33.5; δ 2.48 ↔ δ 163.3, 21.5; δ 1.41 ↔ δ 163.3; δ 0.91 ↔ δ 163.3, 33.5, 21.5. **^{1}H NMR** (400 MHz, C_6D_6, 80 °C) δ 3.38 (s, 2H, B-CH_2); 2.46 (sept, $^3J_{HH}$ = 6.7 Hz, 1H, HC(CH$_3$)$_2$); 1.38 (s, 3H, C=C-CH_3); 0.87 (d, $^3J_{HH}$ = 6.8 Hz, 6H, HC(CH_3)$_2$); 0.74 (s, 3H, B-CH_3). **^{13}C NMR** (100 MHz, C_6D_6, 80 °C, assignments confirmed by HMQC and HMBC) δ 163.1 (B-C=C); 66.0 (br, B-CH$_2$); 33.5

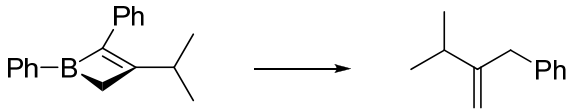
(H*C*(CH_3)$_2$); 21.6 (HC(*C*H_3)$_2$); 15.8 (C=C-*C*H_3); 8.9 (br, B-*C*H_3). B-*C*=C not observed, identified by HMBC correlations at δ 91.7. **HMQC** (400 MHz, C_6D_6, 80 °C) δ 3.38 ↔ δ 66.0; δ 1.38 ↔ δ 15.8; δ 0.87 ↔ δ 21.3; δ 0.74 ↔ δ 8.9. **HMBC** (400 MHz, C_6D_6, 80 °C) δ 3.38 ↔ δ 163.1, 91.7, 33.5; δ 2.46 ↔ δ 163.1, 66.0, 21.6; δ 1.38 ↔ δ 163.1, 91.7; δ 0.87 ↔ δ 163.1, 33.5, 21.6; δ 0.74 ↔ δ 91.7. **^{11}B NMR** (128 MHz, C_6D_6, 27 °C) δ 82.2 (br). **HRMS** Calcd. for $C_{14}H_{19}B$: 198.15797. Found: 198.15798.



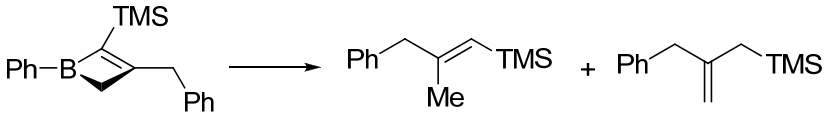
3,3-Dimethyl-5-isopropyl-6-phenyl-2-oxa-titanocenecyclohex-5-ene (74): A dry toluene solution (3 mL) of titanacyclobutene **15** (162 mg, 0.48 mmol) and acetone (35 μL, 0.48 mmol) was heated at 65 °C for 14 hours in a sealed glass bomb, then solvent was removed *in vacuo*. The crude solid was washed with pentane (3 mL) then product was extracted into THF and passed through Celite. Concentration under vacuum provided analytically pure titanacycle as an amorphous orange powder (165 mg, 87 %). **^{1}H NMR** (400 MHz, C_6D_6) δ 7.24 (t, $^3J_{HH}$ = 7.4 Hz, 2H, *m*-Ph*H*); 7.02-6.96 (m, 3H, *o/p*-Ph*H*); 5.72 (s, 10H, Cp*H*); 2.64 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*); 2.24 (s, 2H, CH_2); 1.14 (s, 6H, OC(CH_3)$_2$); 0.89 (d, $^3J_{HH}$ = 6.8 Hz, 6H, HC(CH_3)$_2$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 185.6 (Ti-*C*=C); 154.5 (*ipso*-Ph); 135.8 (Ti-C=*C*); 128.2 (*m*-Ph); 126.3 (*o*-Ph); 123.2 (*p*-Ph); 113.6 (Cp); 88.1 (O-*C*); 48.4 (*C*H_2); 33.1 (H*C*(CH_3)$_2$); 28.6 (OC(*C*H_3)$_2$); 21.7 (HC(*C*H_3)$_2$). **COSY** (400 MHz, C_6D_6) δ 7.24 ↔ δ 7.02-6.96; δ 7.02-6.96 ↔ δ 7.24; δ 2.64 ↔ δ 0.89; δ 2.24 ↔ δ 1.14; δ 1.14 ↔ δ 2.24; δ 0.89 ↔ δ 2.64. **HMQC** (400 MHz, C_6D_6) δ 7.24 ↔ δ 128.2; δ 7.02-6.96 ↔ δ 126.3; δ 5.72 ↔ δ 113.6; δ 2.64 ↔ δ 33.1; δ 2.24 ↔ δ 48.4; δ 1.14 ↔ δ 28.6; δ 0.89 ↔ δ 21.7. **HMBC** (400 MHz, C_6D_6) δ 7.24 ↔ δ 154.5, 128.2, 123.2; δ 7.02-6.96 ↔ δ 185.6, 126.3, 123.2; δ 5.72 ↔ δ 113.6; δ 2.64 ↔ δ 135.8, 48.4, 21.7; δ 2.24 ↔ δ 185.6, 135.8, 126.3, 88.1, 33.1, 28.6; δ 1.14 ↔ δ 88.4, 48.4, 28.6; δ 0.89 ↔ δ 135.8, 33.1, 21.7. **Anal**. Calcd. for $C_{25}H_{30}OTi$: C, 76.14, H, 7.67. Found: C, 75.99, H, 7.72.



6,6-dimethyl-5-hydro-4-isopropyl-2,3-phenyl-2H-1,2-oxaborin (75): To cold toluene solution (-30 °C, 5 mL) of titanacycle **74** (235 mg, 0.59 mmol) was added a cold toluene (2 mL) solution of $PhBCl_2$ (104 mg, 0.65 mmol). The solution was allowed to warm to 25 °C over a 12 hour period, after which time it was concentrated under vacuum. The product was extracted into hexanes then passed through a short plug of Celite. Concentration under vacuum yielded the boracycle as an orange oil with a small amount of unidentified impurity (167 mg, 92 % yield, single impurity is approximately 7 % by ^{1}H NMR spectral integration). Recrystallization from hexanes or pentane was not successful. Red solid by-product from transmetallation was identified as Cp_2TiCl_2 (136 mg, 92 %). **^{1}H NMR** (400 MHz, C_6D_6) δ 7.75-7.72 (m, 2H, B-*o*-Ph*H*); 7.21-7.16 (m, 2H, Ph*H*); 7.13-7.08 (m, 4H, Ph*H*); 7.06-7.03 (m, 2H, o-Ph*H*); 2.95 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, *H*C(CH_3)$_2$); 2.10 (s, 2H, CH_2); 1.37 (s, 6H, OC(CH_3)$_2$); 0.73 (d, $^3J_{HH}$ = 6.7 Hz, 6H, HC(CH_3)$_2$). **^{13}C NMR** (100 MHz, C_6D_6, assignments confirmed by HMQC and HMBC) δ 159.2 (B-C=*C*); 143.6 (*ipso*-Ph); 135.8 (br, B-*C*=C); 135.7 (B-*o*-Ph); 130.4 (B-*p*-Ph); 129.4 (*o*-Ph); 128.5 (*m*-Ph); 127.4 (B-*m*-Ph); 125.9 (*p*-Ph); 72.5 (O-*C*); 37.6 (*C*H_2); 30.5 (H*C*(CH_3)$_2$); 28.8 (OC(*C*H_3)$_2$); 19.6 (HC(*C*H_3)$_2$). **COSY** (400 MHz, C_6D_6) δ 7.75-7.72 ↔ δ 7.13-7.08; δ 7.21-7.16 ↔ δ 7.13-7.08, 7.06-7.03; δ 7.13-7.08 ↔ δ 7.21-7.16; δ 7.06-7.03 ↔ δ 7.21-7.16; δ 2.95 ↔ δ 2.10, 0.73; δ 2.10 ↔ δ 2.95, 1.37; δ 1.37 ↔ δ 2.10; δ 0.73 ↔ δ 2.95. **HMQC** (400 MHz, C_6D_6) δ 7.75-7.72 ↔ δ 135.7; δ 7.21-7.16 ↔ δ 128.5; δ 7.13-7.08 ↔ δ 130.4, 127.4; δ 7.06-7.03 ↔ δ 129.4; δ 2.10 ↔ δ 37.6; δ 1.37 ↔ δ 28.8; δ 0.73 ↔ δ 19.6. **HMBC** (400 MHz, C_6D_6) δ 7.75-7.72 ↔ δ 135.7, 130.4; δ 7.21-7.16 ↔ δ 143.6, 128.5; δ 7.13-7.08 ↔ δ 129.4; δ 7.06-7.03 ↔ δ 129.4, 125.9; δ 2.95 ↔ δ 159.2, 135.8, 37.6, 19.6; δ 2.10 ↔ δ 159.2, 135.8, 129.4, 72.5, 30.5; δ 1.37 ↔ δ 72.5, 37.6, 28.8; δ 0.73 ↔ δ 159.2, 30.5, 19.6. **^{11}B NMR** (128 MHz, C_6D_6) δ 37.9 (br). **HRMS** Calcd. for $C_{21}H_{25}BO$: 304.19985. Found: 304.19929. Cp_2TiCl_2: **^{1}H NMR** (400 MHz, C_6D_6) δ 5.92 (s, 10H, Cp*H*). **Anal**. Calcd. for $C_{10}H_{10}TiCl_2$: C, 48.24, H, 4.05. Found: C, 48.36, H, 4.06.



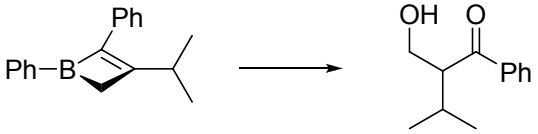
2-benzyl-3-methylbutene (77): A chilled solution (0 °C) of boracyclobutene **59** (50 mg, 0.20 mmol) in THF (3 mL) was added to stirred cold deoxygenated water (0 °C, 2 mL, bubbled argon through it for 30 minutes prior to use). After 15 minutes, the product was extracted into ether (3 x 8 mL) and separated from water. The combined organic extracts were washed with saturated brine solution (5 mL) then dried over $MgSO_4$. Filtration and concentration under vacuum afforded the crude product mixture. Purification by chromatography through silica with hexanes eluent provided the olefin as a colourless oil (15 mg, 46 %). This olefin is also readily formed from other protic sources. Spectral data is identical to that previously reported.[311] **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30-7.15 (m, 5H, Ph*H*); 4.85 (s, 1H, C=CH_2); 4.63 (s, 1H, C=CH_2); 3.39 (s, 2H, CH_2-Ph); 2.20 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, *H*C$(CH_3)_2$); 1.03 (d, $^3J_{HH}$ = 6.7 Hz, 6H, HC(C$H_3)_2$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 140.1, 129.1, 128.2, 125.9, 109.0, 41.6, 33.0, 21.9. **HRMS** Calcd. for $C_{12}H_{16}$: 160.12520. Found: 160.12536.



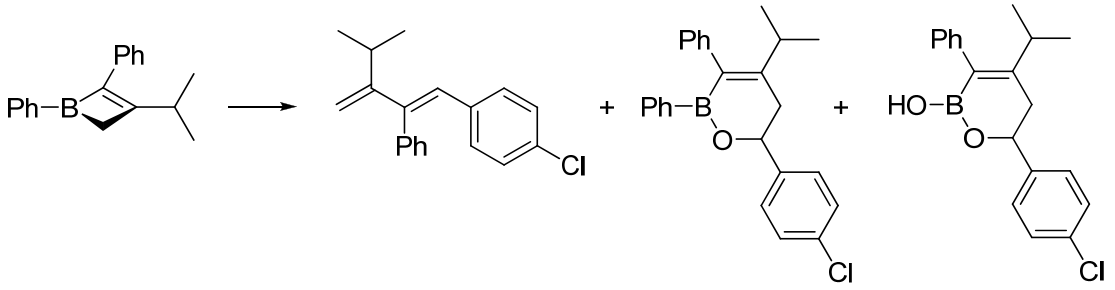
(*E*)-2-Methyl-3-phenyl-1-(trimethylsilyl)propene (78) and 2-benzyl-3-(trimethylsilyl)propene (79): A chilled solution (0 °C) of boracyclobutene **65** (50 mg, 0.17 mmol) in THF (3 mL) was added to stirred cold deoxygenated water (0 °C, 2 mL, bubbled argon through it for 30 minutes prior to use). After 15 minutes, product was extracted into ether (3 x 8 mL) and separated from water. The combined organic extracts were washed with saturated brine solution (5 mL) then dried over $MgSO_4$. Filtration and concentration under vacuum afforded the crude product mixture. Purification by chromatography through silica with hexanes eluent afforded inseparable alkenylsilane **78** and olefin **79** in a 1.3 : 1 ratio as a colourless oil (21 mg, 59 % combined). Spectral data for alkenylsilane **78**[359] and olefin **79**[360] are identical to those previously reported. **IR** (film cast, FTIR microscope) 3063 (w), 3028 (w), 2955 (s), 2925 (s), 2855 (m), 1618 (w), 1601 (w), 1494 (w), 1453 (w), 1376 (w), 1248 (s), 1157 (w) cm^{-1}. **(*E*)-78: ^{1}H NMR** (300

MHz, $CDCl_3$) δ 7.38-7.16 (m, 5H, Ph*H*); 5.28 (s, 1H, C=C*H*); 3.39 (s, 2H, CH_2-Ph); 1.73 (s, 3H, CH_3); 0.11 (s, 9H, Si(CH_3)$_3$).

79: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.16 (m, 5H, Ph*H*); 4.62 (s, 1H, C=CH_2); 4.58 (s, 1H, C=CH_2); 3.28 (s, 2H, CH_2-Ph); 1.51 (s, 2H, CH_2-TMS); 0.06 (s, 9H, Si(CH_3)$_3$). **HRMS** Calcd. for $C_{13}H_{20}Si$: 204.13343. Found: 204.13332.



3-Hydroxy-2-isopropyl-1-phenyl-1-propanone (80): To a stirred cold THF (-30 °C, 4 mL) suspension of DABCO·2H_2O_2 (110 mg, 0.61 mmol) was added a cold THF (-30 °C, 2 mL) solution of boracyclobutene **59** (50 mg, 0.20 mmol). The solution changed from yellow to colourless within 30 seconds. After 2 hours, the suspension was removed from the drybox and 5 mL saturated $NaHCO_3$ solution was added. The mixture was extracted with ether (3 x 8 mL) and the combined organic extracts were washed with saturated brine solution then dried over $MgSO_4$. Filtration and removal of solvents under vacuum provided the crude material. Chromatography through silica with dichloromethane eluent afforded the β-hydroxy ketone as a pale yellow oil (23 mg, 59 %). Spectral data are identical to that previously reported.[361] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.95 (m, 2H, *o*-Ph*H*); 7.59 (tt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, *p*-Ph*H*); 7.51-7.46 (m, 2H, *m*-Ph*H*); 4.08 (dd, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 7.4 Hz, 1H, CH_2-OH); 3.84 (dd, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 3.4 Hz, 1H, CH_2-OH); 3.48 (dt, $^3J_{HH}$ = 11.0, 3.3 Hz, 1H, *H*C-C=O); 2.22 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, *H*C(CH_3)$_2$); 1.95 (br s, 1H, O*H*); 0.97 (d, $^3J_{HH}$ = 6.9 Hz, 3H, HC(CH_3)$_2$); 0.96 (d, $^3J_{HH}$ = 6.9 Hz, 3H, HC(CH_3)$_2$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.3, 137.8, 133.3, 128.7, 128.4, 61.3, 54.1, 28.6, 21.4, 19.7. **HRMS** Calcd. for $C_{12}H_{16}O_2$: 192.11503. Found: 192.11489.



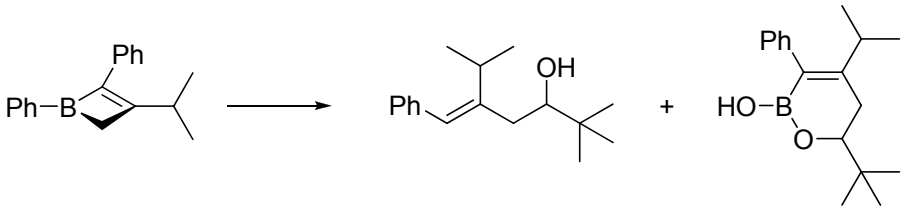
***(Z)*-1-(4-chlorophenyl)-3-isopropyl-2-phenylbutadiene (85)**, **6-(4-chlorophenyl)-2,3-diphenyl-5,6-dihydro-4-isopropyl-2H-1,2-oxaborin (86)**, and **6-(4-chlorophenyl)-5,6-dihydro-2-hydroxy-4-isopropyl-3-phenyl-2H-1,2-oxaborin (87):** To a stirred cold THF solution (-30 °C, 4 mL) of boracyclobutene **59** (50 mg, 0.20 mmol) was added a cold THF solution (-30 °C, 1 mL) of p-chlorobenzaldehyde (143 mg, 1.0 mmol). After 2 hours stirring at room temperature, 4 mL of saturated $NaHCO_3$ solution was added. The product was extracted into ether (3 x 8 mL), and the combined organic extracts were washed with saturated brine solution and dried over $MgSO_4$. Filtration and removal of solvents provided the crude material. Chromatographic separation was achieved by gradient elution through silica (starting with 100 % hexanes and increasing the dichloromethane content by 10 % every 10 mL) to afford *(Z)*-butadiene **85** as a colourless oil (100 % hexanes, 12 mg, 21 %), 2,3-diphenyl-1,2-oxaborin **86** as a colourless oil (~ 60 : 40 hexanes/dichloromethane, 6 mg, 8 %), and 2-hydroxy-1,2-oxaborin **87** as a colourless oil (~ 40 : 60 hexanes/dichloromethane, 21 mg, 31 %). **85**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 3H, *m/p*-Ph*H*); 7.14-7.10 (m, 2H, *o*-Ph*H*); 7.07-7.02 (m, 2H, *m*- or *o*-Ar*H*); 6.85-6.80 (m, 2H, *m*- or *o*-Ar*H*); 6.64 (s, 1H, C=C*H*); 5.06 (s, 1H, C=CH_2); 4.95 (s, 1H, C=CH_2); 2.52 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *H*C$(CH_3)_2$); 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 6H, HC(C$H_3)_2$). **^{13}C NMR** (100 MHz, $CDCl_3$, assignments confirmed by HMQC and HMBC) δ 157.7 (*C*=CH_2); 145.0 (C=*C*-Ph); 139.6 (*ipso*-Ar); 135.9 (*ipso*-Ar); 132.0 (*C*-Cl); 130.7 (*o*- or *m*-Ar); 129.7 (*o*- or *m*-Ar); 128.5 (*o*- or *m*-Ar); 128.0 (*o*- or *m*-Ar); 127.2 (*p*-Ph); 125.1 (C=*C*H); 112.4 (C=*C*H_2); 30.0 (H*C*$(CH_3)_2$); 22.1 (HC(*C*$H_3)_2$). **COSY** (400 MHz, C_6D_6) δ 7.32-7.26 ↔ δ 7.14-7.10; δ 7.14-7.10 ↔ δ 7.32-7.26; δ 7.07-7.02 ↔ δ 6.85-6.80; δ 6.85-6.80 ↔ δ 7.07-7.02; δ 5.06 ↔ δ 4.95; δ 4.95 ↔ δ 5.06; δ 2.52 ↔ δ 1.10;δ 1.10 ↔ δ 2.52. **HMQC** (400 MHz, C_6D_6) δ 7.32-7.26 ↔ δ 128.5; δ 7.14-7.10 ↔ δ 129.7; δ 7.07-7.02 ↔ δ 128.0; δ 6.85-6.80 ↔ δ 130.7; δ 6.64 ↔ δ 125.1; δ 5.06 ↔ δ 112.4; δ 4.95 ↔ δ 112.4; δ 1.10 ↔ δ 22.1. **HMBC** (400 MHz, C_6D_6) δ 7.32-7.26 ↔ δ

139.6, 130.7; δ 7.14-7.10 ↔ δ 145.0, 129.7; δ 7.07-7.02 ↔ δ 135.9, 132.0, 128.5; δ 6.85-6.80 ↔ δ 132.0, 128.5, 125.1; δ 6.64 ↔ δ 157.7, 145.0, 139.6, 135.9, 130.7; δ 5.06 ↔ δ 145.0, 30.0, 22.1; δ 4.95 ↔ δ 157.7, 145.0, 30.0, 22.1; δ 2.52 ↔ δ 157.7, 112.4, 22.1; δ 1.10 ↔ δ 157.7, 22.1. **TROESY** (400 MHz, C_6D_6, selected correlations only) δ 6.64 ↔ δ 2.52. **HRMS** Calcd. for $C_{19}H_{19}Cl$: 282.11752. Found: 282.11726.

86: **IR** (film cast, FTIR microscope) 3431 (br, w), 3210 (m), 3078 (w), 3055 (w), 3025 (w), 2962 (s), 2927 (s), 2871 (m), 1669 (w), 1601 (m), 1540 (w), 1491 (s), 1440 (s), 1364 (s), 1348 (s), 1318 (s), 1266 (m), 1091 (s), 1027 (m), 1013 (s), 827 (w), 761 (w), 700 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H, *o*-ArH); 7.43-7.27 (m, 8H, Ar*H*); 7.18-7.10 (m, 2H, *m*-Ar*H*); 7.09-7.05 (m, 2H, *o*-Ar*H*); 5.25 (dd, $^3J_{HH}$ = 11.9, 3.8 Hz, 1H, O-C*H*); 2.94 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, *H*C(CH_3)$_2$); 2.66 (dd, $^2J_{HH}$ = 16.9 Hz, $^3J_{HH}$ = 4.0 Hz, 1H, C=C-CH_2); 2.47 (dd, $^2J_{HH}$ = 16.9 Hz, $^3J_{HH}$ = 12.1 Hz, 1H, C=C-CH_2); 0.99 (d, $^3J_{HH}$ = 6.7 Hz, 3H, HC(CH_3)$_3$); 0.96 (d, $^3J_{HH}$ = 6.7 Hz, 3H, HC(CH_3)$_3$). **COSY** (400 MHz, C_6D_6) δ 5.25 ↔ δ 2.66, 2.47; δ 2.94 ↔ δ 0.99, 0.96; δ 2.66 ↔ δ 5.25, 2.47; δ 2.47 ↔ δ 5.25, 2.66; δ 0.99 ↔ δ 2.94, 0.96; δ 0.96 ↔ δ 2.94, 0.99. **HRMS** Calcd. for $C_{25}H_{24}BClO$: 386.16087. Found: 386.16070.

87: **IR** (film cast, FTIR microscope) 3433 (br, m), 3054 (w), 3026 (w), 2964 (s), 2931 (m), 2871 (m), 1610 (m), 1492 (s), 1380 (s), 1320 (s), 1289 (s), 1229 (m), 1202 (m), 1090 (s), 1014 (m), 889 (w), 825 (m), 760 (m), 738 (m), 702 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.37 (m, 6H, *o/m*-Ph*H*, *o*-Ar*H*); 7.31-7.26 (m, 1H, *p*-Ph*H*); 7.14-7.10 (m, 2H, *m*-Ar*H*); 5.19 (dd, $^3J_{HH}$ = 11.5, 4.0 Hz, 1H, O-C*H*); 4.16 (s, 1H, O*H*); 2.84 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*(CH_3)$_2$); 2.57 (dd, $^2J_{HH}$ = 17.0 Hz, $^3J_{HH}$ = 4.0 Hz, 1H, C=C-CH_2); 2.44 (dd, $^2J_{HH}$ = 17.1 Hz, $^3J_{HH}$ = 11.5 Hz, 1H, C=C-CH_2); 1.04 (d, $^3J_{HH}$ = 6.8 Hz, 3H, HC(CH_3)$_2$); 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 3H, HC(CH_3)$_2$). **^{13}C NMR** (100 MHz, $CDCl_3$, assignments confirmed by HMQC and HMBC) δ 161.9 (B-C=*C*), 141.4 (*ipso*-Ar), 140.1 (*ipso*-Ph), 133.2 (*C*-Cl), 128.54 (*o*- or *m*-Ar), 128.50 (*o*- or *m*-Ar), 128.4 (*o*- or *m*-Ar), 127.1 (*o*- or *m*-Ar), 126.2 (*p*-PhH), 75.0 (O-*C*), 34.8 (C=C-*C*H_2), 30.9 (H*C*(CH_3)$_2$), 21.1 (HC(*C*H_3)$_2$), 19.7 (HC(*C*H_3)$_2$). B-*C*=C carbon not observed. **COSY** (400 MHz, C_6D_6) δ 7.45-7.37 ↔ δ 7.31-7.26, 7.14-7.10, 5.19; δ 7.31-7.26 ↔ δ 7.45-7.37, 7.14-7.10; δ 7.14-7.10 ↔ δ 7.45-7.37, 7.31-7.26; δ 5.19 ↔ δ 7.45-7.37, 2.57, 2.44; δ 2.84 ↔ δ 1.04. 0.88; δ 2.57 ↔ δ 5.19, 2.44; δ 2.44 ↔ δ 5.19, 2.57; δ 1.04 ↔ δ 2.84, 0.88; δ 0.88 ↔ δ 2.84, 1.04.

HMQC (400 MHz, C_6D_6) δ 7.45-7.37 ↔ δ 128.54 or 128.50 or 128.4, 127.1; δ 7.31-7.26 ↔ δ 126.2; δ 7.14-7.10 ↔ δ 128.54 or 128.50 or 128.4; δ 5.19 ↔ δ 75.0; δ 2.84 ↔ δ 30.9; δ 2.57 ↔ δ 34.8; δ 2.44 ↔ δ 34.8; δ 1.04 ↔ δ 21.1; δ 0.88 ↔ δ 19.7. **HMBC** (400 MHz, C_6D_6) δ 7.45-7.37 ↔ δ 141.4, 140.1, 133.2, 128.54 or 128.50 or 128.4, 75.0; δ 7.31-7.26 ↔ δ 128.54 or 128.50 or 128.4; δ 7.14-7.10 ↔ δ 128.54 or 128.50 or 128.4; δ 2.84 ↔ δ 161.9, 34.8, 21.1, 19.7; δ 2.57 ↔ δ 161.9, 141.4, 75.0; δ 2.44 ↔ δ 161.9, 141.4, 75.0; δ 1.04 ↔ δ 161.9, 30.9, 19.7; δ 0.88 ↔ δ 161.9, 30.9, 21.1. **^{11}B NMR** (128 MHz, C_6D_6) δ 29.7. **HRMS** Calcd. for $C_{19}H_{20}BClO_2$: 326.12449. Found: 326.12482. **87**-Anhydride Calcd. for $C_{38}H_{38}O_3B_2Cl_2$: 634.23841. Found: 634.23816.

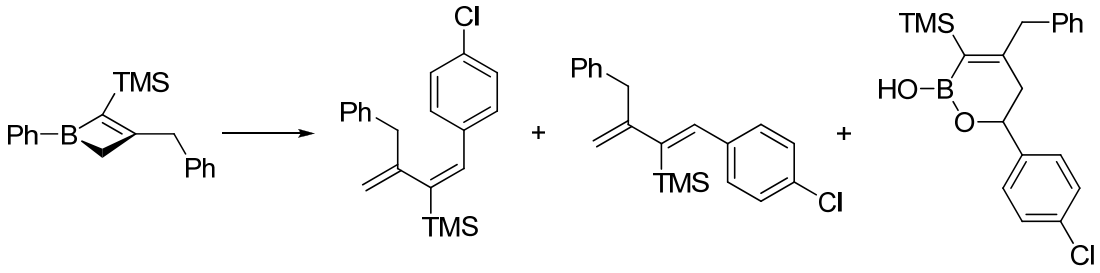


***(Z)*-5-benzylidene-2,2,6-trimethyl-heptan-3-ol (88)** and **5,6-dihydro-2-hydroxy-4-isopropyl-3-phenyl-6-tertbutyl-2H-1,2-oxaborin (89):** To a stirred cold THF solution (-30 °C, 4 mL) of boracyclobutene **59** (66 mg, 0.27 mmol) was added a cold THF solution (-30 °C, 1 mL) of pivalaldehyde (115 mg, 1.34 mmol). After 2 hours stirring at room temperature under nitrogen, the solution was heated to 55 °C for 2 hours, after which time 4 mL of saturated $NaHCO_3$ solution was added. The product was extracted into ether (3 x 8 mL), and the combined organic extracts were washed with saturated brine solution and dried over $MgSO_4$. Filtration and removal of solvents provided the crude material. Chromatographic separation was achieved by gradient elution through silica (starting with 100 % hexanes and increasing the dichloromethane content by 10 % every 10 mL) to afford heptan-3-ol **88** as a colourless oil (~ 1 : 1 hexanes/dichloromethane, 10 mg, 15 %) and 5,6-dihydro-1,2-oxaborin **89** as a colourless oil (~ 30 : 70 hexanes/dichloromethane, 15 mg, 21 %). **88**: **IR** (film cast, FTIR microscope) 3498 (s), 3055 (w), 3023 (w), 2959 (s), 2870 (m), 1599 (w), 1479 (w), 1467 (m), 1362 (m), 1270 (w), 1072 (m), 1009 (m), 917 (w), 832 (w), 754 (m), 699 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2H, *m*-Ph*H*); 7.24-7.19 (m, 3H, *o/p*-Ph*H*); 6.39 (s, 1H, C=C*H*); 3.50 (d, $^3J_{HH}$ = 10.0 Hz, 1H, O-C*H*); 3.14 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, *H*C$(CH_3)_2$); 2.52 (d,

$^{2}J_{HH}$ = 14.4 Hz, 1H, C=C-CH_2); 2.00 (dd, $^{2}J_{HH}$ = 14.5 Hz, $^{3}J_{HH}$ = 10.9 Hz, 1H, C=C-CH_2); 1.91 (s, 1H, OH); 1.08 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, HC(CH_3)$_2$); 1.04 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, HC(CH_3)$_2$); 1.00 (s, 9H, C(CH_3)$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$, assignments confirmed by HMQC and HMBC) δ 146.1 (C=*C*-CH$_2$); 138.2 (*ipso*-Ph); 129.0 (*o*-Ph); 128.4 (*m*-Ph); 127.0 (*C*=C-CH$_2$) 126.5 (*p*-Ph); 35.2 (*C*(CH$_3$)$_3$); 34.0 (C=C-*C*H$_2$); 29.7 (H*C*(CH$_3$)$_2$); 26.1 (C(*C*H$_3$)$_3$); 21.9 (HC(*C*H$_3$)$_2$); 21.7 (HC(*C*H$_3$)$_2$). **COSY** (400 MHz, C_6D_6) δ 7.35-7.32 ↔ δ 7.24-7.19; δ 7.24-7.19 ↔ δ 7.33, 6.39; δ 6.39 ↔ δ 7.24-7.19, 2.52, 2.00; δ 3.50 ↔ δ 2.52, 2.00; δ 3.14 ↔ δ 1.08, 1.04; δ 2.52 ↔ δ 6.39, 3.50, 2.00; δ 2.00 ↔ δ 6.39, 3.50, 2.52; δ 1.08 ↔ δ 3.14, 1.04; δ 1.04 ↔ δ 3.14, 1.08. **HMQC** (400 MHz, C_6D_6) δ 7.35-7.32 ↔ δ 128.4; δ 7.24-7.19 ↔ δ 129.0, 126.5; δ 6.39 ↔ δ 127.0; δ 3.50 ↔ δ 77.3; δ 3.14 ↔ δ 29.7; δ 2.52 ↔ δ 34.0; δ 2.00 ↔ δ 34.0; δ 1.08 ↔ δ 21.9; δ 1.04 ↔ δ 21.7; δ 1.00 ↔ δ 26.1. **HMBC** (400 MHz, C_6D_6) δ 7.35-7.32 ↔ δ 138.2, 128.4; δ 7.24-7.19 ↔ δ 129.0, 127.0; δ 6.39 ↔ δ 146.1, 138.2, 129.0, 128.4, 34.0, 29.7; δ 3.50 ↔ δ 26.1; δ 3.14 ↔ δ 146.1, 127.0, 34.0, 21.9, 21.7; δ 2.52 ↔ δ 146.1, 127.0; δ 2.00 ↔ δ 146.1, 127.0, 77.3, 29.6; δ 1.08 ↔ δ 146.1, 29.7, 21.7; δ 1.04 ↔ δ 146.1, 29.7, 21.9; δ 1.00 ↔ δ 77.3, 35.2, 26.1. **^{11}B NMR** (128 MHz, C_6D_6) ^{11}B atom not present. **HRMS** (EI) Calcd. for $C_{17}H_{26}O$: 246.19837. Molecular ion not observed. Calcd. for $C_{17}H_{24}$: 228.18781. Found: 228.18719. **HRMS** (CI) Calcd. For $C_{17}H_{26}ONa$: 269.18759. Found: 269.18766.

89: **IR** (film cast, FTIR microscope) 3633 (w), 3500 (br, w), 3078 (w), 3055 (w), 3018 (w), 2960 (s), 2869 (m), 1611 (m), 1480 (m), 1464 (m), 1390 (s), 1370 (s), 1324 (w), 1302 (s), 1228 (m), 1207 (m), 1104 (m), 1094 (w), 1071 (w), 1051 (w), 1021 (w), 916 (w), 875 (w), 757 (m), 700 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 2H, *m*-Ph*H*); 7.27-7.20 (m, 1H, *p*-Ph*H*); 7.08-7.04 (m, 2H, *o*-Ph*H*); 3.89 (s, 1H, OH); 3.73 (dd, $^{3}J_{HH}$ = 12.3, 3.6 Hz, 1H, O-C*H*); 2.80 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, *H*C(CH$_3$)$_2$); 2.29 (dd, $^{2}J_{HH}$ = 16.8 Hz, $^{3}J_{HH}$ = 3.6 Hz, 1H, C=C-CH_2); 2.16 (dd, $^{2}J_{HH}$ = 16.8 Hz, $^{3}J_{HH}$ = 12.4 Hz, 1H, C=C-CH_2); 1.00 (s, 9H, C(CH_3)$_3$); 0.97 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, HC(CH_3)$_2$); 0.94 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, HC(CH_3)$_2$). **^{13}C NMR** (100 MHz, $CDCl_3$, assignments confirmed by HMQC and HMBC) δ 162.7 (B-C=*C*); 140.7 (*ipso*-Ph); 128.44 (*o*- or *m*-Ph); 128.43 (*o*- or *m*-Ph); 128.4 (br, B-*C*=C); 125.9 (*p*-Ph); 81.3 (O-*C*); 34.5 (*C*(CH$_3$)$_3$); 31.1 (H*C*(CH$_3$)$_2$); 26.3 (C=C-*C*H$_2$); 25.8 (C(*C*H$_3$)$_3$); 21.3 (HC(*C*H$_3$)$_2$); 19.8 (HC(*C*H$_3$)$_2$).

COSY (400 MHz, C_6D_6) δ 7.38-7.32 ↔ δ 7.27-7.20, 7.08-7.04; δ 7.27-7.20 ↔ δ 7.38-7.32, 7.08-7.04; δ 7.08-7.04 ↔ δ 7.38-7.32, 7.27-7.20; δ 3.73 ↔ δ 2.29, 2.16; δ 2.80 ↔ δ 0.97, 0.94; δ 2.29 ↔ δ 3.73, 2.16; δ 2.16 ↔ δ 3.73, 2.29; δ 0.97 ↔ δ 2.80, 0.94; δ 0.94 ↔ δ 2.80, 0.97. **HMQC** (400 MHz, C_6D_6) δ 7.38-7.32 ↔ δ 128.44 or 128.43; δ 7.27-7.20 ↔ δ 125.9; δ 7.08-7.04 ↔ δ 128.44 or 128.43; δ 3.73 ↔ δ 81.3; δ 2.80 ↔ δ 31.1; δ 2.29 ↔ δ 26.3; δ 2.16 ↔ δ 26.3; δ 1.00 ↔ δ 25.8; δ 0.97 ↔ δ 19.8; δ 0.94 ↔ δ 21.3. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 7.38-7.32 ↔ δ 140.7, 128.44, 128.43; δ 7.27-7.20 ↔ δ 128.44, 128.43; δ 7.08-7.04 ↔ δ 128.44, 128.43, 125.9; δ 3.73 ↔ δ 162.7, 34.5, 26.3, 25.9; δ 2.80 ↔ δ 162.7, 128.4, 26.3, 21.3, 19.8; δ 2.29 ↔ δ 162.7, 140.7, 128.4, 81.3, 34.5, 31.1; δ 2.16 ↔ δ 162.7, 140.7, 128.4, 81.3, 34.5, 31.1; δ 1.00 ↔ δ 81.3, 34.5, 25.8; δ 0.97 ↔ δ 162.7, 31.1, 21.3; δ 0.94 ↔ δ 162.7, 31.1, 19.8. **^{11}B NMR** (128 MHz, C_6D_6) δ 27.3. **HRMS** Calcd. for $C_{17}H_{25}BO_2$: 272.19476. Found: 272.19391. **89**-Anhydride Calcd. for $C_{34}H_{48}O_3B_2$: 526.37896. Found: 526.38352.



***(E)*-3-benzyl-1-(4-chlorophenyl)-2-(trimethylsilyl)butadiene (90)**, ***(Z)*-3-benzyl-1-(4-chlorophenyl)-2-(trimethylsilyl)butadiene (90)**, and **4-benzyl-6-(4-chlorophenyl)-5,6-dihydro-2-hydroxy-3-trimethylsilyl-2H-1,2-oxaborin (91):** To a stirred cold THF solution (-30 °C, 4 mL) of boracyclobutene **65** (62 mg, 0.21 mmol) was added a cold THF solution (-30 °C, 1 mL) of p-chlorobenzaldehyde (150 mg, 1.07 mmol). After 2 hours stirring at room temperature, the reaction vessel was removed from the drybox and 4 mL of saturated $NaHCO_3$ solution was added. The product was extracted into ether (3 x 8 mL), and the combined organic extracts were washed with saturated brine solution and dried over $MgSO_4$. Filtration and removal of solvents provided the crude material. Chromatographic separation was achieved by gradient elution through silica (started with 100 % hexanes and increased the dichloromethane content by 10 % every 10 mL) to afford ***(E)*-90** as a colourless oil (100 % hexanes, 6 mg, 11 %), ***(Z)*-90** as a colourless oil

(100 % hexanes, 6 mg, 11 %), and 2-hydroxy-1,2-oxaborin **91** as an impure brown oil (~ 20 : 80 hexanes/dichloromethane, 17 mg, 21 %, ~ 5 : 1 ratio of product to phenol by ^{1}H NMR analysis). Yields were calculated based on 76 % boracyclobutene by weight, which was determined with a ^{1}H NMR internal standard. ***(E)*-90**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H, Ar*H*); 7.31-7.24 (m, 4H, Ar*H*); 7.23-7.17 (m, 1H, *p*-Ph*H*); 7.09-7.05 (m, 2H, Ar*H*); 6.61 (s, 1H, *H*C=C-TMS); 4.80 (s, 1H, C=CH_2); 4.65 (s, 1H, C=CH_2); 3.21 (s, 2H, Ph-CH_2); 0.12 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.0; 149.0; 140.5; 138.4; 136.5; 133.0; 130.1; 129.7; 128.26; 128.21; 126.2; 111.8; 42.2; -1.5. **HRMS** Calcd. for $C_{20}H_{23}ClSi$: 326.12576. Found: 326.12610.

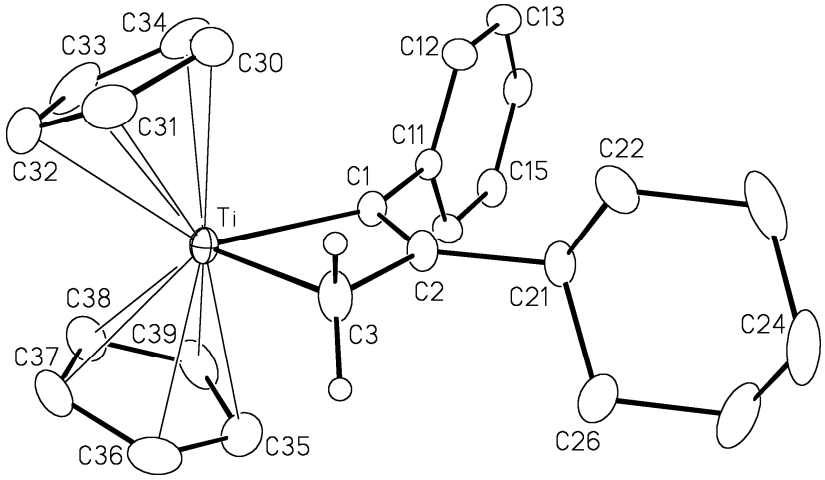
***(Z)*-90**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H, *m*-Ph*H*); 7.30-7.27 (m, 2H, *m*-Ar*H*); 7.27-7.23 (m, 3H, *o/p*-Ph*H*); 7.13-7.09 (m, 2H, *o*-Ar*H*); 6.98 (s, 1H, *H*C=C-TMS); 4.82 (s, 1H, C=CH_2); 4.75 (s, 1H, C=CH_2); 3.52 (s, 2H, Ph-CH_2); 0.02 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$, assignments confirmed by HMQC and HMBC) δ 154.1 (*C*=CH_2); 148.5 (C=*C*-TMS); 141.8 (C=*C*H); 139.1 (*ipso*-Ph); 138.4 (*ipso*-Ar); 132.9 (*C*-Cl); 129.9 (*o*-Ar); 129.6 (*o*-Ph); 128.3 (*m*-Ph); 128.0 (*m*-Ar); 126.2 (*p*-Ph); 111.0 (C=*C*H_2); 44.1 (Ph-*C*H_2); 0.7 (Si(*C*H_3)$_3$). **HMQC** (400 MHz, C_6D_6) δ 7.36-7.31 ↔ δ 128.3; δ 7.30-7.27 ↔ δ 128.0; δ 7.27-7.23 ↔ δ 129.6, 126.2; δ 7.13-7.09 ↔ δ 129.9; δ 6.98 ↔ δ 141.8; δ 4.82 ↔ δ 111.0; δ 4.75 ↔ δ 111.0; δ 3.52 ↔ δ 44.1; δ 0.02 ↔ δ 0.7. **HMBC** (400 MHz, C_6D_6) δ 7.36-7.31 ↔ δ 139.1, 128.3; δ 7.30-7.27 ↔ δ 138.4, 132.9, 128.0; δ 7.27-7.23 ↔ δ 129.6, 126.2, 44.1; δ 7.13-7.09 ↔ δ 141.8, 132.9, 129.9, 128.0; δ 6.98 ↔ δ 154.1, 148.5, 138.4, 129.9; δ 4.82 ↔ δ 154.1, 148.5, 44.1; δ 4.75 ↔ δ 148.5, 44.1; δ 3.52 ↔ δ 154.1, 148.5, 139.1, 129.6, 111.0; δ 0.02 ↔ δ 148.5, 0.7. **TROESY** (400 MHz, C_6D_6, selected correlations only) δ 7.27-7.23 ↔ δ 4.75, 3.52; δ 6.98 ↔ δ 4.82, 3.52; δ 4.82 ↔ δ 6.98, 4.75; δ 4.75 ↔ δ 4.82, 3.52; δ 3.52 ↔ δ 6.98, 4.75, 0.02; δ 0.02 ↔ δ 7.13-7.09, 4.82, 3.52. **HRMS** Calcd. for $C_{20}H_{23}ClSi$: 326.12576. Found: 326.12575.

91: **IR** (film cast, FTIR microscope) 3397 (m), 3063 (w), 3027 (w), 2952 (m), 2894 (m), 1717 (w), 1572 (m), 1493 (s), 1452 (w), 1369 (s), 1353 (s), 1308 (s), 1248 (s), 1090 (m), 1014 (m), 841 (s), 759 (m), 700 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.08 (m, 9H, Ph*H* and Ar*H*); 4.93 (dd, $^3J_{HH}$ = 10.2, 4.9 Hz, 1H, O-C*H*); 4.15 (s, 1H, B-O*H*); 3.72 (s, 2H, Ph-CH_2); 2.24-2.18 (m, 2H, C=C-CH_2); 0.29 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$, APT, assignments confirmed by HMQC and HMBC) δ 168.5 (p, B-C=*C*);

141.1 (p, *ipso*-Ar); 138.3 (p, *ipso*-Ph); 133.1 (p, *C*-Cl); 129.64 (a, *o*-Ph); 129.63 (br, B-*C*=C); 129.1 (a, Ar); 128.7 (a, Ar); 128.6 (a, Ar); 128.4 (a, Ar); 128.3 (a, Ar); 127.1 (a, *o*-Ar); 126.7 (a, Ar); 126.4 (a, Ar); 74.3 (a, O-*C*); 45.2 (p, Ph-*C*H_2); 42.1 (p, C=C-*C*H_2); 1.5 (a, Si(*C*H_3)$_3$). Note: three ^{13}C signals between 129.1 – 126.4 are assigned to **91**, other signals from impurity. **COSY** (400 MHz, C_6D_6) δ 7.31-7.08 ↔ δ 3.72; δ 4.93 ↔ δ 2.24-2.18; δ 3.72 ↔ δ 7.31-7.08; δ 2.24-2.18 ↔ δ 4.93. **HMQC** (400 MHz, C_6D_6) δ 7.31-7.08 ↔ δ 129.64-126.4; δ 4.93 ↔ δ 74.3; δ 3.72 ↔ δ 45.2; δ 2.24-2.18 ↔ δ 42.1; δ 0.29 ↔ δ 1.5. **HMBC** (400 MHz, C_6D_6, selected correlations only) δ 7.31-7.08 ↔ δ 141.1, 138.3, 133.1, 129.64-126.4; δ 4.93 ↔ δ 127.1; δ 4.15 ↔ δ 129.63; δ 3.72 ↔ δ 168.5, 138.3, 129.64 and/or 129.63, 42.1; δ 2.24-2.18 ↔ δ 168.5, 141.1, 129.63, 74.3, 45.2; δ 0.29 ↔ δ 129.63, 1.5. **^{11}B NMR** (128 MHz, C_6D_6) δ 27.3. **HRMS** Calcd. for $C_{20}H_{24}BClO_2Si$: 370.13271. Molecular ion not observed. Calcd. for $C_{19}H_{21}BClO_2Si$: 355.10925. Found: 355.10955.

Appendix 1: Crystallographic Data

Selected crystallographic data for **1,1-Bis(cyclopentadienyl)-3-cyclohexyl-2-phenyl-titanacyclobutene (16).** Additional information (including structure factors, etc.) can be obtained directly from Dr. Robert McDonald or Dr. Michael Ferguson at the X-Ray Crystallography Laboratory, University of Alberta, Department of Chemistry, Edmonton AB T6G 2G2 Canada. Request report # JMS0807.



Perspective view of one of the two crystallographically-independent molecules of [$Cp_2Ti(PhC{=}C(Cy)CH_2$], **16**, showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atoms bonded to C3 are shown with arbitrarily small thermal parameters; all other hydrogens are not shown.

Crystallographic Experimental Details for Titanacyclobutene **16**

A. Crystal Data

formula	$C_{25}H_{28}Ti$
formula weight	376.37
crystal dimensions (mm)	0.61 × 0.58 × 0.17
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters[a]	
a (Å)	7.9825 (8)
b (Å)	14.1635 (14)
c (Å)	19.1861 (19)

α (deg)	109.6839 (13)
β (deg)	97.5399 (14)
γ (deg)	93.8787 (14)
V (Å^3)	2010.2 (3)
Z	4
ρ_{calcd} (g cm^{-3})	1.244
μ (mm^{-1})	0.431

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	55.04
total data collected	17749 (-10 ≤ h ≤ 10, -18 ≤ k ≤ 18, -24 ≤ l ≤ 24)
independent reflections	9166 (R_{int} = 0.0170)
number of observed reflections (*NO*)	7358 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson search/structure expansion (*DIRDIF99*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9304–0.7791
data/restraints/parameters	9166 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 469
goodness-of-fit (S)[e]	1.068 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0411
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.1119
largest difference peak and hole	0.467 and –0.246 e Å^{-3}

[a]Obtained from least-squares refinement of 4982 reflections with 4.54° < 2θ < 54.82°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

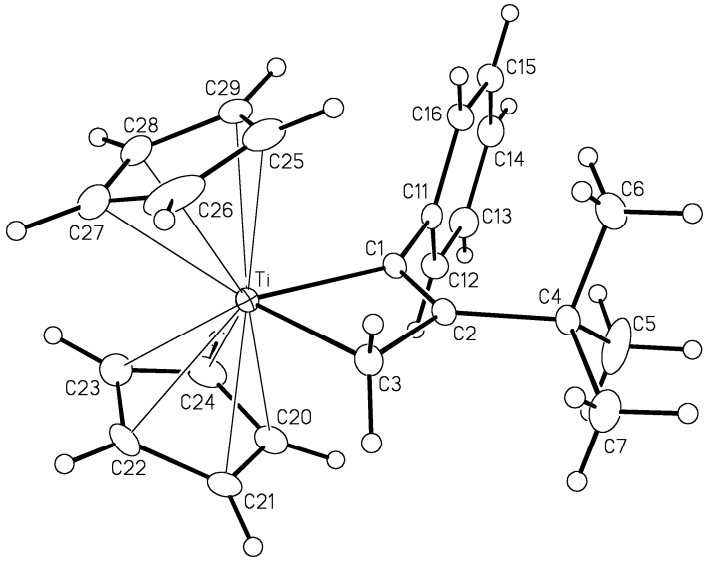
[c]Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Israel, R.; Gould, R. O.; Smits, J. M. M. (1999). The *DIRDIF-99* program system. Crystallography Laboratory, University of Nijmegen, The Netherlands.

[d]Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0568P)^2 + 0.5273P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Selected crystallographic data for **1,1-Bis(cyclopentadienyl)-2-phenyl-3-*tert*-butyl-titanacyclobutene (17).** Additional information (including structure factors, etc.) can be obtained directly from Dr. Robert McDonald or Dr. Michael Ferguson at the X-Ray Crystallography Laboratory, University of Alberta, Department of Chemistry, Edmonton AB T6G 2G2 Canada. Request report # JMS0733.



Perspective view of the [$Cp_2Ti(PhC{=}C^tBuCH_2)$] molecule, **17**, showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

Crystallographic Experimental Details for Titanacyclobutene **17**

A. Crystal Data

formula	$C_{23}H_{26}Ti$
formula weight	350.34
crystal dimensions (mm)	0.49 × 0.35 × 0.22
crystal system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
unit cell parameters[a]	
a (Å)	8.3561 (8)
b (Å)	12.3950 (12)
c (Å)	17.8827 (17)
V (Å^3)	1852.2 (3)
Z	4

ρ_{calcd} (g cm^{-3})	1.256
μ (mm^{-1})	0.462

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	54.96
total data collected	15641 ($-10 \le h \le 10$, $-16 \le k \le 16$, $-23 \le l \le 23$)
independent reflections	4242 (R_{int} = 0.0224)
number of observed reflections (*NO*)	4070 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SIR*97[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[d])
absorption correction method	multi-scan (*SADABS*)
range of transmission factors	0.9051–0.8052
data/restraints/parameters	4242 [$F_o^2 \ge -3\sigma(F_o^2)$] / 0 / 217
Flack absolute structure parameter[e]	0.008(19)
goodness-of-fit (*S*)[f]	1.055 [$F_o^2 \ge -3\sigma(F_o^2)$]
final *R* indices[g]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0307
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0830
largest difference peak and hole	0.260 and –0.179 e Å^{-3}

[a]Obtained from least-squares refinement of 5859 reflections with $4.56° < 2\theta < 54.74°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115–119.

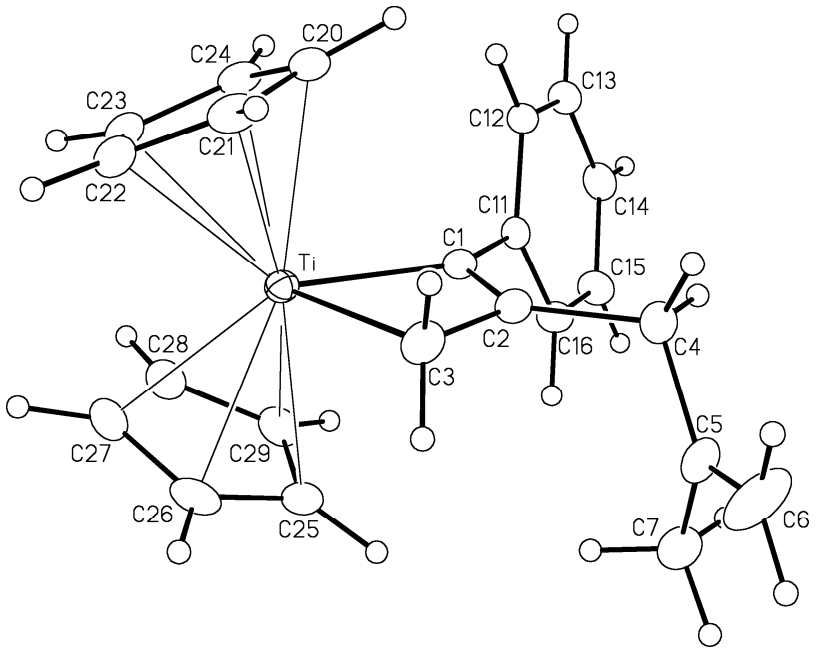
[d]Sheldrick, G. M. *SHELXL-97*. Program for crystal structure determination. University of Göttingen, Germany, 1997.

[e]Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881; Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908–915; Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, *33*, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration.

[f]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0504P)^2 + 0.3418P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Selected crystallographic data for **1,1-Bis(cyclopentadienyl)-3-(2-methallyl)-2-phenyl-titanacyclobutene (19).** Additional information (including structure factors, etc.) can be obtained directly from Dr. Robert McDonald or Dr. Michael Ferguson at the X-Ray Crystallography Laboratory, University of Alberta, Department of Chemistry, Edmonton AB T6G 2G2 Canada. Request report # JMS0746.



Perspective view of one of the two crystallographically independent [$Cp_2Ti\{PhC{=}C(CH_2CMeCH_2)CH_2\}$] molecules, **19**, showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

Crystallographic Experimental Details for Titanacyclobutene **19**

A. Crystal Data

formula	$C_{23}H_{24}Ti$
formula weight	348.32
crystal dimensions (mm)	0.43 × 0.18 × 0.15
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])

unit cell parameters[a]	
a (Å)	13.7922 (12)
b (Å)	16.3279 (15)
c (Å)	17.0364 (15)
β (deg)	107.6410 (10)
V (Å^3)	3656.1 (6)
Z	8
ρ_{calcd} (g cm^{-3})	1.266
μ (mm^{-1})	0.468

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	54.98
total data collected	29870 ($-17 \le h \le 17$, $-21 \le k \le 21$, $-22 \le l \le 22$)
independent reflections	8345 (R_{int} = 0.0354)
number of observed reflections (*NO*)	6402 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SIR*97[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[d])
absorption correction method	multi-scan (*SADABS*)
range of transmission factors	0.9331–0.8241
data/restraints/parameters	8345 [$F_o^2 \ge -3\sigma(F_o^2)$] / 0 / 433
goodness-of-fit (S)[e]	1.040 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0434
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.1158
largest difference peak and hole	0.376 and –0.211 e Å^{-3}

[a]Obtained from least-squares refinement of 5366 reflections with $4.54° < 2\theta < 54.76°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

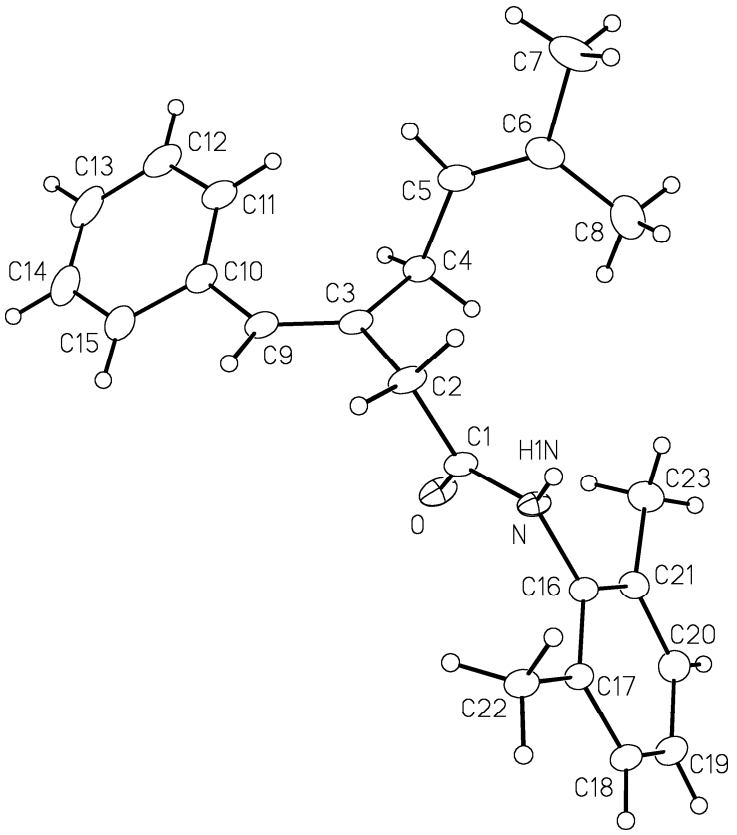
[c]Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115–119.

[d]Sheldrick, G. M. *SHELXL-97*. Program for crystal structure determination. University of Göttingen, Germany, 1997.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0560P)^2 + 1.3645P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Selected crystallographic data for **(3*E*)-3-Benzylidene-*N*-(2,6-dimethylphenyl)-6-methylhept-5-enamide (50).** Additional information (including structure factors, etc.) can be obtained directly from Dr. Robert McDonald or Dr. Michael Ferguson at the X-Ray Crystallography Laboratory, University of Alberta, Department of Chemistry, Edmonton AB T6G 2G2 Canada. Request report # JMS0746.



Perspective view of the (3*E*)-3-benzylidene-*N*-(2,6-dimethylphenyl)-6-methylhept-5-enamide molecule, *(E)*-**50**, showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

Crystallographic Experimental Details for molecule **50**

A. Crystal Data

formula	$C_{23}H_{27}NO$
formula weight	333.46
crystal dimensions (mm)	0.42 × 0.24 × 0.21
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)

unit cell parameters[a]	
a (Å)	4.8015 (4)
b (Å)	14.6009 (13)
c (Å)	14.7061 (13)
α (deg)	110.6353 (10)
β (deg)	91.9089 (10)
γ (deg)	93.7043 (11)
V (Å^3)	961.09 (14)
Z	2
ρ_{calcd} (g cm^{-3})	1.152
μ (mm^{-1})	0.069

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	54.98
total data collected	8441 ($-6 \le h \le 6$, $-18 \le k \le 18$, $-18 \le l \le 19$)
independent reflections	4350 (R_{int} = 0.0154)
number of observed reflections (*NO*)	3329 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–97*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[c])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9856–0.9713
data/restraints/parameters	4350 [$F_o^2 \ge -3\sigma(F_o^2)$] / 0 / 230
goodness-of-fit (S)[d]	1.066 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[e]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0477
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.1402
largest difference peak and hole	0.608 and –0.206 e Å^{-3}

[a]Obtained from least-squares refinement of 4395 reflections with $4.90° < 2\theta < 54.34°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

[d]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0642P)^2 + 0.2359P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[e]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

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