"I hate cynicism – it's my least-favourite quality and it doesn't lead anywhere. Nobody in life gets exactly what they thought they were going to get. But if you work really hard, and you're kind, amazing things will happen."

--Conan O'Brien, 22/01/10

University of Alberta

Dicarbenes as Bridges in Mixed-Metal Systems

by

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For my grandfather, Donald "Papas" Matheson
(1933-2009)

Abstract

The study of *hetero*bimetallic complexes (having two different metal atoms) involves combining the unique properties of each metal, which can give rise to interesting contrasts in reactivity compared to either metal alone. With two different metals incorporated into one complex, a more diverse array of reactivity patterns becomes available. In binuclear systems comprised of late, low-valent metals, the metals are most-often connected by diphosphines, ensuring metal-metal proximity during the reactions of interest. However, recently various carbene ligands ($:CR_2$) have become established as phosphine mimics with interesting electronic and steric properties. As a result, *di*carbenes are beginning to be probed as diphosphine substitutes.

Chapter 2 of this thesis explores the synthesis of heterobimetallic complexes bridged by di-*N*-heterocyclic carbenes (di-NHCs) from diimidazolium salts. The use of an "internal base strategy" (using transition metal precursors containing basic ligands to afford deprotonation of imidazolium moieties *in situ*) prevents double-deprotonation, and avoids issues which normally result in chelation. Furthermore, we establish a "pendent" ligand strategy wherein one end of the diimidazolium salt is first deprotonated by one metal (giving a metal-bound carbene), followed by deprotonation of the pendent imidazolium group by the second metal, resulting in heterobimetallic complexes of Rh, Ir, and Pd.

Chapter 3 describes our investigations into a series of new bidentate di-cyclic (alkyl)(amino)carbenes based on their monodentate counterparts. The synthesis of these species involved protocols similar to those employed for their monodentate analogues, and our efforts are described here.

Chapter 4 recounts our success in developing several unsymmetrical, hybrid dicarbenes based on both *N*-heterocyclic and mesoionic carbenes (MICs). The dicationic NHC/MIC precursors can be deprotonated one ring at a time, resulting in NHC/MIC-bridged Pd/Rh complexes, comparable to the di-NHC analogues in Chapter 2. Similarly, Chapter 5 describes our development of new di-MIC frameworks, and their incorporation into mixed metal systems (again, employing internal base and "pendent" ligand strategies).

Finally, Chapter 6 discusses our brief studies on these newly-developed complexes as "tandem catalysts", wherein the heterobimetallic complex (as opposed to two monometallic catalysts) can effect the tandem transformation of a bifunctionalized substrate in one pot through Suzuki-Miyaura coupling and catalytic hydrogenation processes.

Acknowledgements

It is hard to pinpoint and acknowledge the specific contributions from individuals throughout my studies here at the University of Alberta, because it has been a non-stop adventure from the day I landed in Edmonton. First and foremost, my supervisor Prof. Martin Cowie has been an inspirational lead-by-example role model from the day we were introduced, and I cannot thank him enough for enthusiastically welcoming me into his group. His thorough attention to detail and constructive suggestions were always encouraging and motivating (albeit numerous). Similarly, I am forever indebted to my former BSc Honours supervisor, Prof. Stephen Westcott, whose continued honest advice helped me throughout graduate school. Dr. Norman Gee is also thanked for supervising my teaching assistant duties in freshman chemistry, and for nominating me for several teaching awards during the course of my PhD. And of course, many thanks to my former students.

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emotionally) in a way few would be able to understand. They are the absolute best people I have ever met, and I consider it a huge honour to be their friends.

During the best and worst of times however, my loving family in New Brunswick was always a quick phone call or e-mail away. My mother Bea and step-father Clarence always manage to make me laugh, and are a refreshing reminder of where I come from. Additionally, weekly conversations with my father Tom about Flames hockey and music quickly became a staple to my week. But especially my brother Garrett, who is one of my best friends, and spending time with him is one thing I have missed the most. Finally, all members of the Zamora, Matheson, and LeBlanc families have constantly supported me, and I cannot thank them enough.

Of course, there are many other people who have offered their unwavering support during these last five years, but attempts to acknowledge them all and recount to you all the memories we have had would result in a document twice as large as the one you are about to read. Regardless, I would be remiss if I did not offer some form of thanks. This thesis would not have been possible without your friendship: Darren O'Donnell, John Dale, Tara Martin, Ryan Lewis, Jessie Key, Lydia Chen, Alan Martin, Chantelle Giesbrecht, Paul Lummis, Rich Burford, Greg Kaufman, Laura Zilke, Tommy Green Jr., Katie Nizio, Jesse Li, Jill Hatnean, Marie Barnes, Justin Thuss, Brittany Dever, Kyle Manchee, Leah Martin-Visscher, Adam Malcolm, Mari Shoda, Kazuki Inada, Casey Costello, Troy Montgomery, Kai Ylijoki, Teague McGinitie, Terra Bruhm, and Trina Oommen.

Cheers.

And, as always, Go Flames Go.

~Matt 

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List of Symbols, Abbreviations, and Nomenclature

–I	inductively-withdrawing
–M	mesomerically-withdrawing
{A}	decoupled-nucleus A
$\%V_{Bur}$	buried volume
‡	transition state
+I	inductively donating
+M	mesomerically donating
1D	one-dimensional
2D	two-dimensional
Å	ångström
AAC	(alky)(amino)carbene
acac	acetylacetonate
ADMET	acyclic diene metathesis
*a*NHC	abnormal *N*-heterocyclic carbene
APT	attached proton test
Ar	aryl
b.p.	boiling point
$\boldsymbol{B}_0$	external magnetic field
Bn	benzyl
br	broad
Bu	butyl

ca.	approximately
CAAC	cyclic (alkyl)(amino)carbene
cm	centimetre
COD	1,5-cyclooctadiene or η^2:η^2-1,5-cyclooctadiene in a metal complex
Cp^*	pentamethylcyclopentadienyl
CSSF	chemical shift selective filter
CuAAC	copper-catalyzed azide-alkyne cycloaddition
Cy	cyclohexyl
d	doublet
dba	dibenzylideneacetone
dcm	dichloromethane
deg.	degrees
depm	*bis*(diethylphosphino)ethane
di-$MIC_{C,C'}$	*C*,*C*′-linked di-mesoionic carbene
di-$MIC_{N,N'}$	*N*,*N*′-linked di-mesoionic carbene
Dipp	2,6-diisopropylphenyl
dmf	dimethylformamide
dmso	dimethylsulfoxide
dppe	1,2-*bis*(diphenylphosphino)ethane
dppm	*bis*(diphenylphosphino)methane
EI	electron impact
ESI	electrospray ionization
Et	ethyl

eV	electronvolt
F_1	indirectly-detected frequency (in 2D NMR)
F_2	directly-detected frequency (in 2D NMR)
FT	Fourier transform
FWHM	full width at half-maximum
g	gram
gCOSY	gradient-enhanced correlation spectroscopy
gHMBC	gradient heteronuclear multiple bond correlation
gHMQC	gradient heteronuclear multiple quantum coherence
gHSQC	gradient heteronuclear single quantum coherence
h	hour
HOMO	highest occupied molecular orbital
HRMS	high resolution mass spectrometry
Hz	hertz
Im	imidazole or imidazolyl
ipa	*iso*-propyl alcohol
^{i}Pr	*iso*-propyl
IR	infrared
iso-	isomer
K	Kelvin
$K_{a(X)}$	acid dissociation constant for substance X
$K_{b(X)}$	base dissociation constant for substance X
kg	kilogram

kJ	kilojoule
L	litre
LC/MS	liquid chromatography-mass spectrometry
LDA	lithium diisopropylamide
LUMO	lowest unoccupied molecular orbital
m	metre or multiplet
M	moles per litre
m/z	mass to charge ratio
M^+	molecular ion
Me	methyl
Mes	mesityl
meta-	1,3-
MHz	megahertz
MIC	mesoionic carbene
min	minute
mL	millilitre
mm	millimeter
mmol	millimole
mol	mole
MS	mass spectrometry
n-	normal-
n/a	not applicable
NHB^-	*N*-heterocyclic boryl anion

NHC	*N*-heterocyclic carbene
NHdi-C	*N*-heterocyclic dicarbene
NHGe	*N*-heterocyclic germylene
NHP^+	*N*-heterocyclic phosphenium cation
NHPb	*N*-heterocyclic plumbylene
NHSi	*N*-heterocyclic silylene
${}^{n}J_{A\text{-}B}$	*n*-bond A-B coupling constant
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NSHC	*N*,*S*-heterocyclic carbene
OAc (AcO)	acetate
ORTEP	Oak Ridge Thermal Ellipsoid Plot
ortho-	1,2-
OTf	triflate
para-	1,4-
Ph	phenyl
PHC	*P*-heterocyclic carbene
$pK_{a(X)}$	logarithmic reciprocal of K_a for substance X
$pK_{b(X)}$	logarithmic reciprocal of K_b for substance X
ppm	parts per million
Pr	propyl
q	quartet
RCM	ring-closing metathesis

*r*NHC	remote *N*-heterocyclic carbene
ROM	ring-opening metathesis
ROMP	ring-opening metathesis polymerization
RT	room temperature
r_w(A)	van der Waals radius of atom A
S	Siemen
s	second or singlet
t	triplet
T	Tesla
T_1	spin-lattice (longitudinal) relaxation time
$t_{1/2}$	half-life
^{t}Bu	*tert*-butyl
tert-	tertiary
TfOTf	triflic anhydride
thf	tetrahydrofuran
TMP	tetramethylpiperidide
TMS	tetramethylsilane
TOCSY	total correlation spectroscopy
TOF	time of flight
Tol	tolyl
TROESY	transverse rotating-frame Overhauser enhancement spectroscopy
Trz	triazole or triazolyl
vs.	versus

δ	partial charge or chemical shift (in ppm)
Δ	difference or heat
$\Delta G^{\ddagger}$	Gibbs energy of transition state (activation energy)
η^n-	hapticity of *n* contiguous atoms
θ	angle or Tolman cone angle
κ^n-A	ligated by atom(s) A by *n* sites
Λ	equivalent conductance
μ	micro
μ-	bridging
ν	chemical shift (in Hz)
$\nu_{A–B}$	A–B bond stretching frequency (in cm^{-1})
χ_A	Pauling electronegativity of A

Chapter 1 Introduction and Background

Section 1.1 Organometallic Chemistry – Early History

If organic chemistry is considered to be the "chemistry of carbon", then inorganic chemistry is the chemistry of all elements except carbon. However, it is somewhat naïve to view these branches of chemistry in such absolutes. The study of how organic molecules and groups (or "ligands") can interact with metal atoms constitutes a significant component of both areas, which forms a composite region known as "metal-organic chemistry",[1] more commonly referred to as *organometallic* chemistry. Although traditionally these species were required (by definition) to contain at least one metal-carbon bond,[2] the term has assumed a much broader definition in the last 20 years[3] to include organic derivatives of the metalloids, as well as systems which exhibit properties similar to those of "traditional" organometallic complexes despite the absence of metal-carbon bonds. This includes a variety of molecular metal-hydrides ($L_nM–H$), metal-alkoxides ($L_nM–OR$), as well as metal-phosphine compounds ($L_nM–PR_3$).

The first organometallic compound (dicacodyl), discovered in 1760 by Cadet de Gassicourt,[4] is somewhat unique because rather than involving a "classic" metal (such as alkali, alkaline earth, or transition metals), it was based on arsenic (characterized as $[As(CH_3)_2]_2$ sometime later by Bunsen, Figure 1-1a[5]). Arsenic occupies a position on the right of Mendeleev's Periodic Table of the Elements at the interface between classic metals and non-metals (on the staircase-shaped boundary) and is often described as a semi-metal or "metalloid" because of its intermediate physical and chemical properties (between metallic and non-metallic).[6]

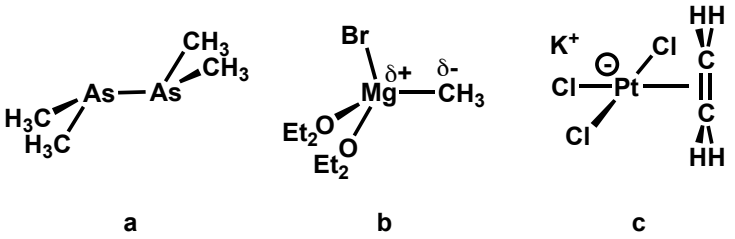


Figure 1-1. Important early organometallic complexes.

More typical organometallic compounds involve the main group metals (Groups I and II, as well as some of those from Groups XIII to XV beneath the aforementioned "staircase") which are (in general) characterized by fairly polar interactions between the metal and carbon atoms (for example, the difference in the Pauling electronegativities of carbon and the Group II alkaline earth metal magnesium ($\Delta\chi_{C,Mg}$) is 1.24). Relative to metal-nitrogen, metal-oxygen, or metal-halogen bonds, the metal-carbon bonds in these "organomain group" systems are much weaker,[7] which is reflected in their widespread use as reagents in organic synthesis. For example, stoichiometric amounts of alkyllithium[8] and magnesium-based Grignard reagents[9, 10] (Figure 1-1b) find significant use as $R_3C:^-$ delivery systems in organic chemistry, as these electropositive metals prefer a more electronegative partner, delivering an anionic alkyl group in exchange for a halide.

Transition metals on the other hand, incorporating elements from Group III to Group XII,[i] encompass a wide range of properties, from the more electropositive early transition metals ($\Delta\chi_{C,Zr}$ = 1.22) where some of the similarities with main group metals are obvious; to the very late transition metals, where in fact the electroneg-ativities of carbon and the metal are only slightly different ($\Delta\chi_{C,Pd}$ = 0.35) very much

[i] Although some definitions do not consider metals in Groups XI or XII to be transition metals.[11]

resembling elements to the right of the table such as As ($\Delta\chi_{C,As} = 0.37$). This range of properties comprises approximately 2/3 of the entire periodic table and gives rise to a wide variety of interesting reactivity.

Organo*transition* metal complexes were introduced in 1827 with the synthesis of an olefin-coordinated platinum complex (Zeise's salt, $K[PtCl_3(\eta^2\text{-}C_2H_4)]$)[12] which forced chemists in the 19th century to re-evaluate their now-considered primitive models for explaining how carbon could attach itself to metal atoms (Figure 1-1c). Although many significant developments occurred for the next hundred years, it was not until the advent of Nuclear Magnetic Resonance (NMR) spectroscopy and X-ray crystallography that these molecules could be studied more extensively, initiating a massive expansion in the area.

As the term "complex" implies, transition metal complexes are not comprised of simply a "naked" metal ion, but rely on several ligands for stabilization and protection. However, these ligands frequently do not adopt a purely-innocent position and often play as much a role in modulating the reactivity of a complex as does the transition metal itself. Traditionally, the ligands employed most often are anionic halides, and neutral phosphorus-, nitrogen-, and sulfur-containing molecules, all containing electron lone pairs on the donor atom. Despite the prevalence of these ligands in organometallic chemistry, interest in other lone pair-containing compounds such as formally neutral divalent carbon ($:CR_2$) as ligands has experienced a dramatic surge in recent years. However, the study of $:CR_2$ species (and the requirements necessary for their stabilization considering its empty p orbital and its lack of a formal "octet") dates back to 19th century organic chemistry, and an

understanding of these elusive divalent molecules is imperative to appreciating their presence in organometallic chemistry.

Section 1.2 200 Years of Ligand Design – Towards Divalent Carbon

1.2.1 Early attempts

In the early 1800s, researchers such as French chemist Jean-Baptiste Dumas set their sights on preparing the seemingly-simple methylene species ($:CH_2$). Considering that other one-carbon molecules (such as methane or carbon dioxide) were readily found in nature, it seemed reasonable to expect that a free methylene molecule was amenable to synthesis in a lab. However, attempts (through dehydration of methanol using P_4O_{10} or H_2SO_4) to generate the divalent $:CH_2$ molecule proved futile.[13]

Over the next century, a procession of chemists expended a great deal of effort trying to isolate methylene and other types of carbenes, but the general consensus had emerged that carbenes were too unstable for isolation. While carbenes played a role in many reactions as intermediates, they were identified as non-isolable transient intermediates with lifetimes of mere nanoseconds. The conclusion at the time seemed to be that the search for bottleable carbenes was a wasted pursuit.

1.2.2 Singlet vs. triplet carbenes

The inherent instability of carbenes can be partly understood by examining the relative stabilities of the two possible spin multiplicities for $:CR_2$. The nonbonding pair on carbon can adopt either a singlet (Figure 1-2a) or a diradical

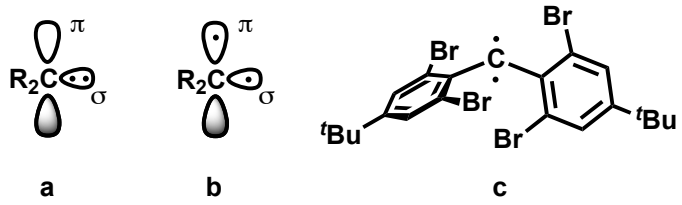


Figure 1-2. Singlet (**a**) and triplet (**b**,**c**) carbenes.

triplet (Figure 1-2b) electronic arrangement in which they occupy either the available σ orbital, or are split between both the empty σ and p_π orbitals on carbon. The energy difference between singlet and triplet states is a function both the σ-withdrawing and π-donating (*vide infra*) abilities of the substituents (R) on carbon. When the R groups are relatively electropositive (when χ of both substituents has an average value less than that of carbon – *i.e.*, $\overline{\chi}_{R,R} < 2.55$), the lower-energy σ orbital is destabilized, resulting in a σ-p_π gap smaller than (or equal to) the electron pairing energy, resulting in diradical behaviour.[14-19] Diradicals of this type are typically unstable, and undergo an energetically-favourable "diradical dimerization" process, forming $R_2C{=}CR_2$ and preventing isolation of the desired carbene. If the substituents on carbon are made sufficiently bulky, triplet carbenes become more inert,[20-23] through steric inhibition of their coupling. For example, a triplet carbene having two 2,6-dibromo-4-(*tert*-butyl)phenyl substituents (Figure 1-2c) is indefinitely stable in solution at –140 °C, or in the solid state at room temperature. However, dimerization still occurs in solution if it is not held at low temperatures ($t_{1/2}$(25 °C) = 16 s), making this carbene (and others like it) difficult to study, often requiring studies by laser flash photolysis,[24] a commonly-used "fast reaction" technique.

Replacement of H or R in carbenes :CH_2, :CHR, or :CR_2 with electron-withdrawing substituents results in stabilization of the σ orbital (*via* an increase in s character on carbon) while the p_π orbital is left relatively unchanged. As a result, the σ-p_π gap is increased and the singlet state (Figure 1-2a) now becomes more favourable.[14-19, 25] For example, when R = F (χ_F = 3.98), the singlet-triplet gap is widened to approximately 190 kJ/mol[16] and the energy of the singlet state drops to considerably low values. However, despite this stabilization of the singlet state, the issue of an unfilled p orbital on carbon continues to govern its instability.

1.2.3 Transition metal-protected carbenes

Because of the inherent instability of these species, focus was shifted to preparing "transition metal-protected" carbene complexes featuring the elusive divalent organic ligand. The characterization of [$(CO)_5W(COCH_3(Ph))$] (Figure 1-3a) in the 1960s by Ernst Otto Fischer is often cited as the starting point in this area,[26] although

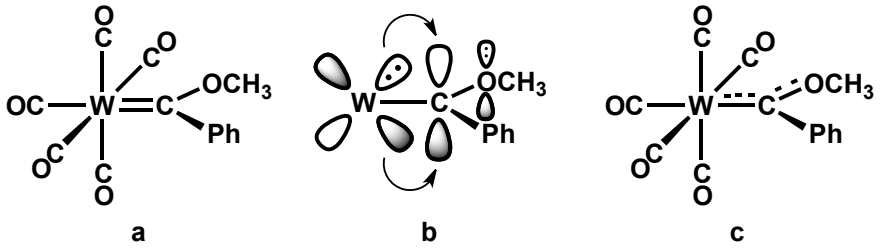
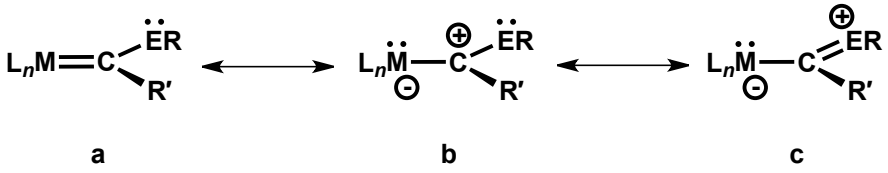


Figure 1-3. Structure and bonding in first Fischer carbene complex.

carbenoid ligands had been previously implicated. These now-dubbed "Fischer carbenes" involve replacing one of the R groups in :CR_2 with an electronegative substituent to stabilize the σ orbital (*via* inductive effects, *vide supra*). However, it was discovered that the more important aspect of these electronegative groups was that

their lone pairs of electrons are capable of π-donation into carbon's empty p orbital, allowing it to acquire a pseudo-octet (mesomeric effects). This π interaction raises the energy of the p_π orbital while the σ orbital is left unchanged.[27] Although the tungsten-carbon attachment above is represented by a double bond (W=C), this can imply that carbon's empty p orbital is populated *entirely* by metal-to-carbon π-back-bonding (Figure 1-3b), which is somewhat misleading. A more accurate depiction involves the delocalized-bonding description shown in Figure 1-3c, where in fact the lone pair on the adjacent heteroatom (oxygen) actually plays a much more significant role in stabilizing singlet carbenes, especially when detached from metal atoms (*vide infra*).

By examining the resonance forms of Fischer carbene complexes (Scheme 1-1), it is clear that both the metal (Scheme 1-1a) and the heteroatom in the α



Scheme 1-1. Resonance forms of Fischer carbene.

position (Scheme 1-1c) serve to stabilize the carbon atom in a mesomeric fashion *via* electron-donation to the electrophilic carbene centre. However, as implied above, the π-back-bonding contribution from the metal is significantly less than that of the heteroatom, as is evidenced by restricted bond rotation and bond lengths. For example, NMR studies on the analogous carbene-containing chromium complex ($[(CO)_5Cr(COCH_3(Ph))]$) indicate a high energy barrier for C–E bond rotation (Scheme 1-1, M = Cr, E = O, $\Delta G^{\ddagger}$ = 52.7 kJ/mol).[28] In fact, this value is

comparable to, for example, carboxylic acid esters (formic acid, $\Delta G^{\ddagger}$ = 52 kJ/mol)[29, 30] or amides (formamide, $\Delta G^{\ddagger}$ = 75 kJ/mol),[30, 31] which have significant C–X (X = OR, NR_2) double bond character, and supports a strong contribution from the "electrophilic carbene" resonance forms shown in Scheme 1-1b,c. Furthermore, X-ray structural studies indicate a Cr–$C_{carbene}$ bond length (2.04 Å) substantially longer than that of the *trans* Cr–CO bond (a ligand with significant π-accepting properties; Cr–CO = 1.87 Å)[32] and approaching a typical Cr–C σ bond (2.21 Å) for an alkyl ligand,[33] further suggesting that the M=C double bond resonance form in Scheme 1-1 is not the dominant contributor. Schrock carbenes on the other hand correspond to those with a triplet electronic arrangement, and generally involve early metals in higher oxidation states (Figure 1-4),[34, 35] and are mostly nucleophilic in character (with polarization of the M=C bond towards the more electronegative carbon). They are a stark contrast to Fischer carbenes, and as a result will not be discussed here.

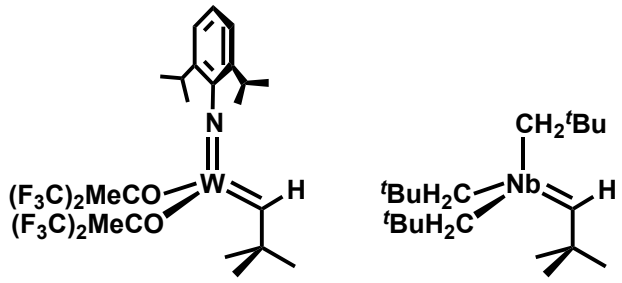
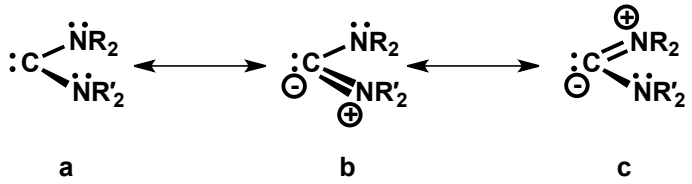


Figure 1-4. Examples of nucleophilic Schrock carbenes.

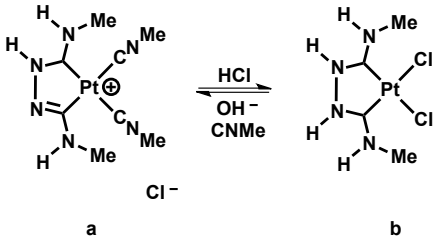
As noted above, Fischer carbenes involve replacing one of the R groups in :CR_2 with an electronegative, lone pair-containing substituent to stabilize the reactive carbene centre. However, if *both* the R groups are replaced by σ-withdrawing, π-

donating groups, this stabilization could be amplified (Scheme 1-2) to allow transition metal-protected carbenes that do not require π-back-bond stabilization, resulting in an unambiguous carbene-metal single bond. Although both –OR′ and



Scheme 1-2. Resonance forms of Fischer carbenes involving two heteroatoms.

–NR′$_2$ groups are good candidates for offering this kind of stabilization (χ_O = 3.44, χ_N = 3.04) the steric properties of –NR′$_2$ systems are more tunable, having two substituents, and as a result these systems are more-studied. One of the first discoveries in this area (although more so a fortunate stroke of serendipity) is that of Tschugajeff (Scheme 1-3),[36] whose platinum complexes were later shown to indeed be metal-protected carbenes,[37-40] which (now stabilized by *two* α-heteroatoms) involved a definite metal-carbene single bond[ii] (Pt–C$_{carbene}$ = 1.95(2) Å in Scheme 1-3a compared to 1.98(2) Å observed for Pt–C(sp^2) single bonds in other systems).



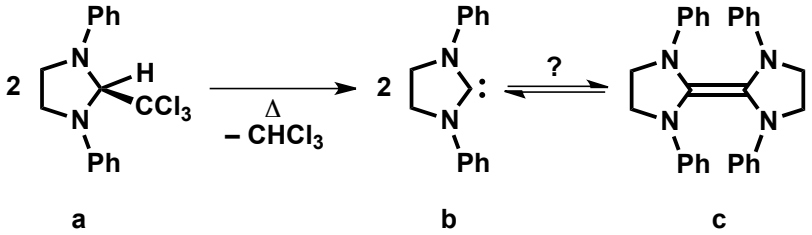
Scheme 1-3. Reversible acid/base transformation of Tschugajeff's chelating amidine carbanion/monocarbene "red salt" **a** to the chelating dicarbene "yellow salt" **b**.

[ii] In fact, Tschugajeff first synthesized these complexes *50 years earlier* in the 1920s, however had incorrectly characterized them at the time. His initial postulation of an equilibrium between two Pt(II) species $[(MeNC)_4Pt(\mu\text{-}N_2H_3)]_2[Cl]_2 + 2\ HCl \rightleftharpoons [(MeNC)_2Pt(\mu\text{-}N_2H_4)]_2[Cl]_4$ was proven incorrect upon reinvestigation of this synthesis in the 1970s after the advent of X-ray crystallography, which unambiguously proved the carbene $\rightleftharpoons$ dicarbene equilibrium, ten years after Fischer's seminal synthesis. Unfortunately, as a result, Tschugajeff is often unrecognized and forgotten in this area, although Tschugajeff carbenes are enjoying a renaissance recently.[41-45]

1.2.4 Broadening the scope – free carbenes

Although transition metal-protected carbene complexes were receiving a great deal of attention after the initial discovery of E.O. Fischer (Nobel Prize in Chemistry Lecture, 1973),[47] the only way carbenes could "compete" with other popular ancillary ligands as scaffolds in catalysis was if these divalent species could be made stable in a non-protected (or "free") *bottle-able* form. Discussions concerning closed-ring carbene variants based on nitrogen heterocycles were initiated around ten years prior by Wanzlick,[48-50] wherein the term *N*-heterocyclic carbene (or, NHC) was coined. With recent successes in delocalizing π-density over three atoms (NCN) as opposed to two, it was postulated that nitrogen atoms with phenyl substituents should provide additional delocalization, allowing for the stabilization of *free* carbenes.

Using this postulate, Wanzlick reported the α-elimination of chloroform from a phenyl-substituted imidazolidine (Scheme 1-4a), presumably forming an imidazolidin-2-ylidene carbene species (Scheme 1-4b).[51] However, he was unable to isolate (or observe) the postulated carbene, only isolating a dimeric enetetraamino species (Scheme 1-4c), which he assumed (but was unable to prove) to be in equilibrium with the desired carbene. As a result, the "Wanzlick equilibrium" had become one of the most highly-contentious issues in carbene chemistry for several



Scheme 1-4. Proposed Wanzlick equilibrium of carbenes and their respective dimers.

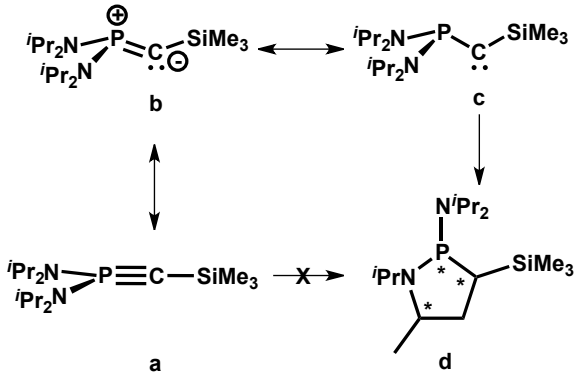
decades;[iii] D.M. Lemal was particularly opposed to Wanzlick's interpretation.[59] Possibly as a result of this controversy, interest began to grow in the area of cyclic nitrogen-based carbenes, although all initial reports failed to produce a free carbene, only metal-protected systems were isolated.[60-64]

1.2.5 Toward free carbenes

Interest in carbenes shifted briefly from nitrogen heterocycles in the late 1980s when French chemist Guy Bertrand reported the first example of a *free* (not coordinated to a metal atom) singlet carbene,[65-67] although its existence as "truly divalent carbon" was (and still is) hotly debated.[68, 69] The substance was isolated from thermolysis (250 °C) of a (phosphino)(silyl)diazomethane compound which, through the loss of N_2, resulted in a red oil having a chemical composition of $C_{16}H_{37}N_2PSi$ and was determined *via* NMR spectroscopy to have the formulation $(^{i}Pr_2N)_2PCSiMe_3$. Although the authors suggested it should be considered a divalent carbene (*i.e.*, $(^{i}Pr_2N)_2P–\ddot{C}–SiMe_3$, Scheme 1-5c) because of its tendency to form a C–H insertion product (Scheme 1-5d), it was argued to be more accurately described as a λ^5-

[iii] Wanzlick's conjecture was initially challenged because cross-over experiments, involving a mixture of two differently-substituted enetetraamines (NHC=NHC and NHC′=NHC′) did not yield any mixed-dimeric products (*i.e.*, NHC= NHC′). However, in experiments conducted 30 years later by Denk and others[52-55] (including Lemal),[56, 57] it was shown that cross-over products *can* be observed. The term "dimerization" must be used with caution, though. These enetetraamines are *not* produced by the combination of two free carbenes, but rather are the result of NHC-coordination to Lewis acid contaminants (initially minor amounts of acidic protons from imidazolium salt precursors) which catalyze a process of: carbene coordination to the Lewis acid (*i.e.*, "protonation" in this example), followed by attack of a second NHC onto the protonated carbon (which still has an empty p orbital), and finally removal ("deprotonation") of the Lewis acid by a third NHC.[58] Today, it is generally accepted that NHCs can be prevented from "dimerizing" in the presence of catalytic amounts of Lewis acid if properly designed, many stabilized indefinitely if stored under dry/moisture-free conditions. Although the relative influence of each of the following conditions is different for every carbene, dimerization can be prevented by taking into account these three NHC-stabilizing factors to some degree: Dimerization can be prevented if (1) *N*-substituents are sufficiently bulky, (2) substituents in the ring are sufficiently electron-donating, and (3) stabilization lost from a break in aromaticity is significant (if applicable).

phosphaacetylene, (*i.e.*, ($^{i}Pr_2N)_2P \equiv C–SiMe_3$, Scheme 1-5a) based on spectral data (NMR: $^{31}P\{^1H\}$, δ = –40; $^{13}C\{^1H\}$, δ = 142.75, $^1J_{C\text{-}P}$ = 159.3 Hz; $^{29}Si\{^1H\}$, δ = 19.67, $^2J_{Si\text{-}P}$ = 59.34 Hz) [iv] rather than the λ^3-phosphinocarbene proposed by Bertrand.[66, 67] Failure to crystallize this species (negating an X-ray crystal structure determination) has prolonged the dispute of whether or not it can be considered a "true" carbene.

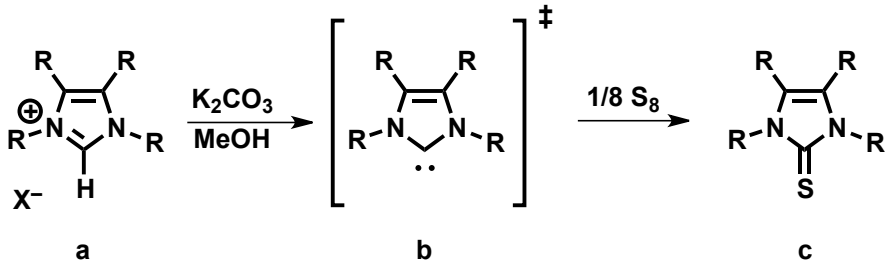


Scheme 1-5. Structure and reactivity of first proposed free carbene.

1.2.6 Free *N*-heterocyclic carbenes

In 1988, Anthony Arduengo III was investigating the use of imidazole-2-thiones (Scheme 1-6c) as cross-linking catalysts for epoxy/anhydride resin coatings while at DuPont.[71] These species seemed well-suited for these applications as they are highly nucleophilic, but not basic (in the Brønstead-Lowry sense). Typically, these species are prepared by the reaction of an imidazolium ion (Scheme 1-6a) with sulfur in the presence of methanolic potassium carbonate.[72] At the time, Arduengo had already

[iv] The low-frequency chemical shift in the $^{31}P\{^1H\}$ NMR spectrum and the large $^1J_{C\text{-}P}$ and $^2J_{Si\text{-}P}$ coupling constants suggest an increase in the number of bonds to phosphorus, and are very similar to those observed in $:P \equiv C–SiMe_3$ and other similar compounds.[70] Furthermore, the signal in the $^{13}C\{^1H\}$ NMR spectrum is characteristic of multiply-bonded carbon while the doublet in the $^{29}Si\{^1H\}$ NMR spectrum is typical for tetracoordinate silanes. However, tetravalency at silicon is consistent in all resonance forms and the chemical shift does not aid in distinguishing between the resonance forms shown in Scheme 1-5a-c.



Scheme 1-6. Proposed carbene intermediate in imidazole-2-thione catalyst synthesis.

developed a one-step synthesis to imidazolium ions (patent filed in 1990),[73] so this route seemed obvious. During the syntheses of these thiones, he noted that the reaction conditions were remarkably insensitive to air, despite the postulated intermediacy of a carbene (Scheme 1-6b). Considering the ease in production of imidazole-2-thiones (*via* this proposed carbene intermediate) in a *commercial* process, it seemed as if these divalent carbon species were much more robust than once thought.

Despite skepticism from his supervisors,[74] Arduengo successfully isolated what is often credited as the first free, isolable carbene (Figure 1-5a) in 1991 (more than 150 years after the first attempts by Jean-Baptiste Dumas) which could be unambiguously characterized due to its crystallinity (Figure 1-5b).[75] Like most breakthrough discoveries in chemistry however, the proprietor of the rights to the *first* isolable carbene is somewhat of a controversial subject.[68] In 2000, the structure

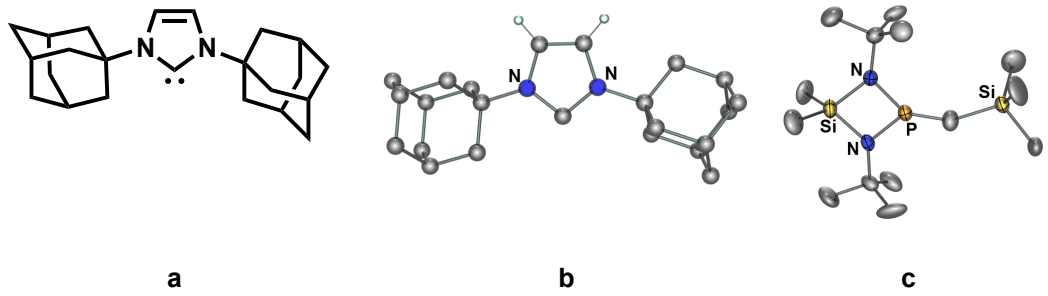


Figure 1-5. The first crystalline carbenes by Arduengo III (**a**,**b**) and Bertrand (**c**).

of another (phosphino)(silyl)carbene similar to Bertrand's original discovery was reported ($Me_2Si(N^tBu)_2PCSiMe_3$, Figure 1-5c) and was shown to have a P–C–Si bond angle which was slightly bent (152.6(3)°), implying the presence of a lone pair on carbon, and further supported Bertrand's claims that their original report ($(^iPr_2N)_2P–\ddot{C}–SiMe_3$) in the late 1980s was indeed a carbene (Scheme 1-5c).[76] However, the length of the P–C (1.532(3) Å) bond is still indicative of a double or triple bond and the NMR spectral data (almost identical to the original $(^iPr_2N)_2PCSiMe_3$ red oil) remain inconsistent with a purely divalent carbene structure. As a result, the solid state analysis in this paper suggests that both Bertrand compounds lie somewhere between a mesoionic/ylidic representation (Scheme 1-5b) and a divalent carbene (Scheme 1-5c). Regardless of who got there first, the contributions of both Bertrand and Arduengo have had a major impact in the chemistry community and spawned a new curiosity in organometallic chemistry.

Section 1.3 NHCs as Ligands in Modern Organometallic Chemistry

1.3.1 The use of NHCs as phosphine mimics

Since the isolation of a stable, "bottleable" carbene, the use of NHC ligands has risen tremendously.[v] As neutral, two-electron donors, NHCs bear an unmistakable similarity to the ubiquitous phosphine ($:PR_3$) ligands, arguably *the* most-used ligand in organometallic chemistry involving late, low-valent transition metals. The similarities between $:CR_2$ and $:PR_3$ ligands can be attributed in part to the diagonally-adjacent positions of carbon and phosphorus on the periodic table. This "diagonal

[v] A simple SciFinder® search shows an exponential increase in the number of published articles on the topic "*N*-heterocyclic carbene", from 76 reports in 2002 to 648 in 2010.

relationship" exists because descending and crossing the periodic table have opposite consequences. While moving down a row results in larger (more diffuse) outer valence orbitals, crossing from left to right leads to an increase in effective nuclear charge, inherently contracting the outer shell of the atoms involved – each outcome effectively "canceling" each other out.[77]

In addition to the similarities of the :CR_2 and :PR_3 donor atoms themselves, the electronic similarities between carbene and phosphine species are fairly obvious. Like phosphines (particularly those having alkyl substituents), NHCs have a readily available lone pair and are considered good electron donors with little π-back-bonding capabilities. However, *sterically* these two ligand types differ significantly. Whereas phosphines are often described as conical,[78] NHC ligands are more planar, having a slimmer, less sterically-hindered axis perpendicular to the NHC ring plane (Figure 1-6a). Furthermore, the directionality of the steric bulk is significantly different in both cases; whereas the R groups in phosphines are directed away from

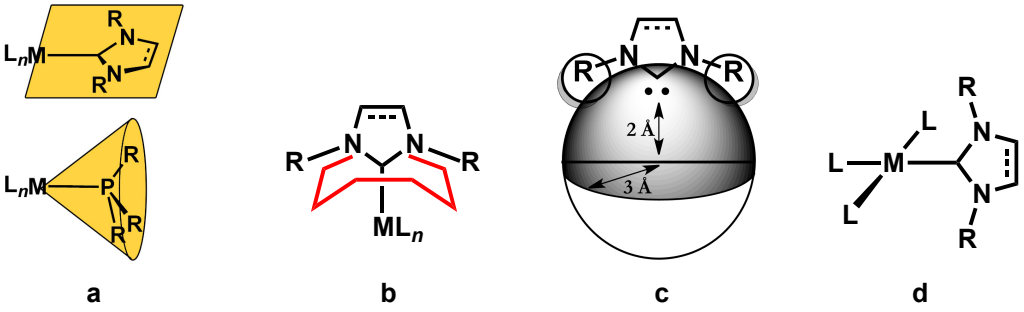


Figure 1-6. Differences in NHC steric bulk compared to phosphines and their consequences.

the metal atom, they are angled *toward* the attached metal in the case of NHCs (Figure 1-6b). The steric factors characterizing NHCs have recently been quantified by measuring the amount of spherical volume (centred on the metal) that becomes buried by overlap with atoms of various NHC ligands (Figure 1-6c)[79] – although it

can also be applied to phosphines. The term "buried volume" ($\%V_{Bur}$) has emerged as the best way to compare the steric properties of NHCs to that of phosphines, whose steric presence is frequently described by its Tolman "cone angle" (θ).[78] Despite a spherical shape used to quantify the steric bulk in NHCs, a quasi two-dimensional shape above and below the ring is evident in square-planar systems where the NHC plane is usually perpendicular to the metal coordination plane (Figure 1-6d).

Although phosphines are largely limited to middle or late transition metal complexes (with few observed with early metals), NHCs are much more widespread, being observed in cases of early[80, 81] (Figure 1-7a,b) to late[82, 83] metals (Figure 1-7c-e),

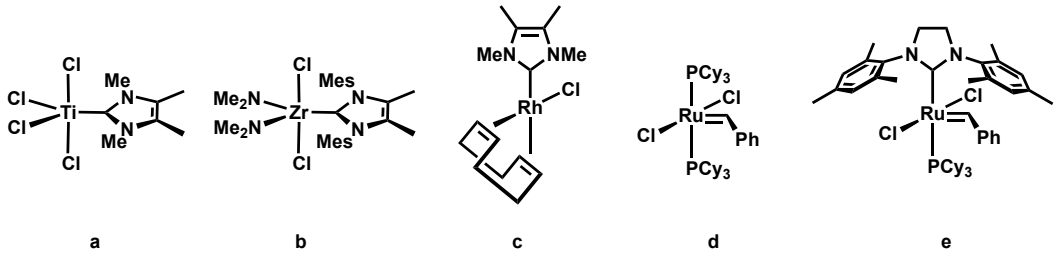


Figure 1-7. Examples of NHCs in early transition metal complexes (**a**,**b**) and as phosphine replacements in late transition metal chemistry (**c**-**e**).

the latter often being derived from their direct monophosphine analogues. However, the greater generality of carbenes makes these NHCs attractive. For example, in addition to the existence of NHC-complexes of *all* the transition metals[27, 84-88] and adducts with a large number of main-group elements[89] (including :Si=Si: and encapsulated :GeH_2 moieties),[90, 91] carbene complexes of the lanthanides,[92-94] uranium,[95-98] and of the radioactive technetium isotope ^{99r}Tc are known.[99]

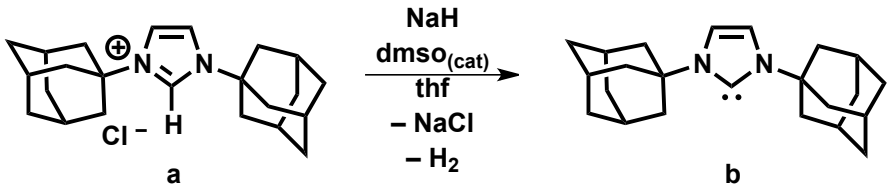
Compared to phosphorus-based ligands, carbenes tend to bind more strongly to metal centres[100] – a feature that has various implications for catalysis. For example, in transition metal-mediated catalytic processes (hydroformylation, olefin metathesis, etc.), an excess of ligand is often required, either to ensure that the metal atom does not become undersaturated (which would result in the decomposition of the catalyst), or to maintain regiochemical control of product distribution (*i.e.*, terminal vs. branched isomers) by the bulky phosphine.[101] In fact, some cases involve performing the reaction in molten PR_3 to ensure perpetual availability of stabilizing ligands.[102] However, exchanging phosphines for tighter-binding NHCs frequently avoids the need for excess ligands in catalytic reactions.

The most famous example of an NHC-based catalyst is that of Grubbs[103] in which his second generation NHC-containing metathesis catalyst (Figure 1-7e)[vi] shows a dramatic increase in activity compared to the first generation *bis*(phosphine) analogue (Figure 1-7d), and does not require an excess of ligand. Furthermore, the second generation complex (and derivatives thereof) is less air- and moisture-sensitive, and is remarkably resistant to oxidation.[104] As the robustness of carbene complexes is largely due to the presence of strong carbon-metal bonds, other types of carbon-based ligands are highly desirable. Furthermore, much success has surrounded NHCs proving themselves as excellent organocatalysts.[105-107]

[vi] The structure shown in Figure 1-7e is an archetypal example of a complex containing both a Fischer (NHC) and Schrock carbene (M=C alkylidene). In many ways, the "carbene character" of metal-alkylidene moieties is more "chemically useful" (*i.e.*, their active role in metathesis), NHCs have an important role as ancillary ligands, which is more so the topic of this thesis.

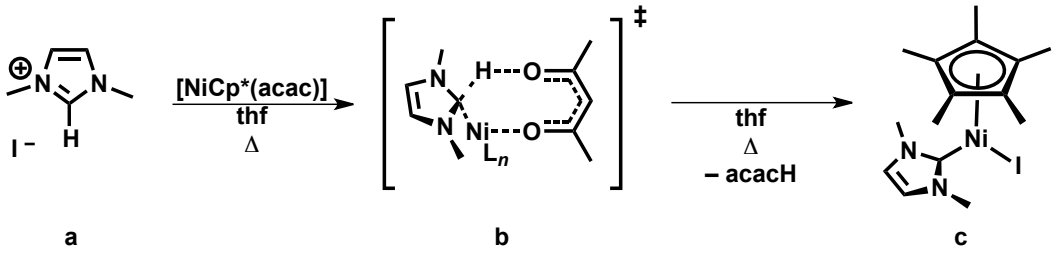
1.3.2 Methods of ligand attachment

Although early attempts to attach NHCs to metals involved the generation of a free carbene (*via* deprotonation of the corresponding imidazolium salt using strong bases such as $K[N(SiMe_3)_2]$, KO^{t}Bu, or NaH, Scheme 1-7),[75] many current synthetic techniques avoid the isolation of these species, as they decompose readily in the presence of moisture when the substituents on nitrogen are less-bulky. A method



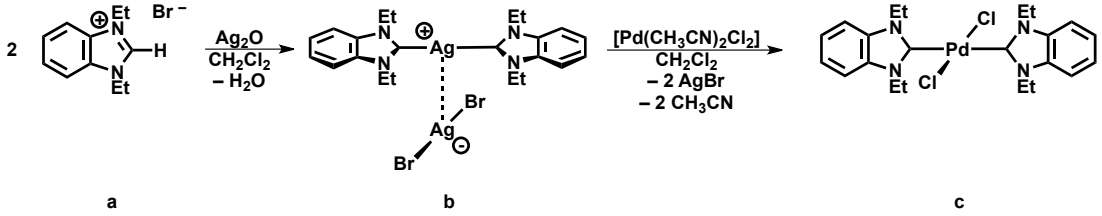
Scheme 1-7. External base deprotonation method for generating NHCs.

gaining recent popularity is the use of a basic ligand-containing metal precursor, promoting a metal-assisted deprotonation of the imidazolium salt, and the generation of the metal-carbene in a concerted fashion (Scheme 1-8).[108] One significant advantage to the use of basic ligands for the deprotonation of imidazolium salts is that the number of NHCs binding to the metal can be limited by the number of basic ligands. Certainly in the use of free carbenes, control of carbene stoichiometry can be difficult, in which the strongly-binding NHCs can displace a number of existing ligands. Perhaps the most revolutionary advancement in carbene ligand preparation is the use of Ag_2O as a transfer reagent (Scheme 1-9).[109] Although,



Scheme 1-8. Internal base deprotonation method for generating metal-NHCs.

in principle, the use of silver(I) oxide falls under the "internal base" heading mentioned above (where O^{2-} acts as a basic ligand capable of deprotonating two imidazolium ions), its distinction comes from the ability of the resulting silver *bis*(carbene) complex (Scheme 1-9b) to deliver the NHC to virtually any other metal. This delivery method (driven by the thermodynamically-favourable precipitation of



Scheme 1-9. Silver-transfer method for generating metal-NHCs.

an insoluble silver halide) is useful since the reaction can be performed at room temperature (whereas many internal base reactions require prolonged and sometimes intense heating) and the $[Ag(NHC)_2][AgX_2]$ salt precursors are usually crystalline and stable indefinitely (when stored in the absence of light).

Unfortunately, these methods also have their downfalls: The silver-transfer method (as noted) is usually quite light-sensitive and reactions must be performed over long periods of time in the absence of light, while the internal base deprotonation method is limited by the availability of appropriate metal complexes that consist of both the metal atom of interest and a ligand that is basic enough to deprotonate the imidazolium salts, which are not terribly acidic (pK_a values ranging from around 20.0 to 20.3, depending on nitrogen substituents).[110] A number of other methods exist however, such as the reduction of imidazole-2(3*H*)-thiones,[111] the heating of imidazolium-2-carboxylates to release NHCs and CO_2 *in situ*,[112] the oxidative addition of the C–H_{acid} (or a C–R) bond across a low-oxidation state,

coordinatively-unsaturated metal atom,[113] the "template-controlled" cyclization of coordinated isocyanides,[114] or using a different coinage-metal such as copper to deliver carbenes, analogous to the reactions using Ag_2O.[115]

Section 1.4 Organo-*Bi*-Metallic Chemistry

1.4.1 Motivation

With an understanding of how organic species interacted with transition metals, how these interactions influenced the reactivity of these ligated molecules, and how ancillary ligands could also influence the transformation of organic substances, organometallic complexes began to find use as catalysts in several industrial processes (as alluded to previously). In this role, the metal complex participates in the reaction to lower the reaction barrier, but is (in principle) not used up,[116] being regenerated in a subsequent step of the process, and therefore can be used to perform *numerous* transformations, limiting the amount of actual (often-costly) catalyst required. The production of acetic acid *via* the Monsanto (rhodium)[117] or Cativa (iridium) processes,[118] and acetaldehyde from ethylene using the Wacker (palladium & copper)[119, 120] process are all examples of catalysis by late transition metal complexes that have had enormous success and have been applied in industry because of the interesting ways transition metals can break and make bonds.

Despite the successes noted above and many other successes involving metal complexes,[121] a problem often facing these catalytic processes is the complete removal of the catalyst from the reaction mixture when the desired products are to be collected. As a result, in industry most catalysts used are *heterogeneous* in order to prevent catalyst leaching into the commodity produced. Furthermore,

heterogeneous systems are often more robust, allowing them to withstand the harsh conditions often needed in catalysis. For example, the Haber-Bosch process (nitrogen fixation) uses an enriched Fe or Ru catalyst over a series of steps under *very* harsh conditions of (100-300 atm; 400-550 °C).[122] Instead of dissolving both the catalyst and the reaction substrates together, liquid or gaseous substrates (or solutions thereof) can be passed over a solid metal (often porous) surface or through an array of support-bound metals or insoluble nanoparticles, allowing catalysis to occur at the phase boundary.

However, obtaining the necessary mechanistic information for rational catalyst modification and improvement is not straightforward, since such heterogeneous processes are difficult to study.[123] Examining these systems at the molecular level is often required to understand the intimate structural details in the system, as well as the bonding and reactivity involved. These heterogeneous systems are less readily tuned compared to metal complexes which can, in principle, be made with an infinite combination of ligands. By conducting *molecular* studies, a catalyst's mode of action can usually be determined, and improvements can then be incorporated in order to rationally develop new advances in the field. More specifically, molecular catalysts function as solvated molecules and can readily be studied by common spectroscopic techniques, which require dissolution of all species of interest. The use of infrared (IR) and NMR spectroscopy is of particular importance in studying environments within molecules and their behavior. Furthermore, metal surfaces can have a number of different, inequivalent active sites available, which can lead to a distribution of different (often difficult to separate)

products, requiring additional steps in product separation, while *homogeneous* catalysts (which utilize well-defined "single site" metal complexes) in principal have a single site available, limiting the number of competing reactions and thereby minimizing the distribution of products.

1.4.2 Modeling surfaces with metal complexes

Surface chemistry is coordination chemistry. If the coordinated molecules in question are organic, then the surface chemistry is organometallic chemistry.[124] Therefore studying molecular organometallic complexes should yield some valuable information on how organic molecules behave on metal surfaces. In order to model the behaviour of substrates on heterogeneous surfaces using molecules however, data cannot simply be extrapolated from monometallic organotransition metal complexes. Organic groups can adopt significantly different reactivity patterns in the presence of multiple metal atoms,[125-128] and as a result, in the late 1970s there was substantial interest in solvated higher-nuclearity clusters, which were being championed as links between classic organometallic complexes and heterogeneous metal catalysts, and therefore could serve as valuable models for catalytic processes occurring on difficult-to-study metal surfaces.[124, 129-132] The smallest multimetal system (and the one predominantly studied in the Cowie group) is the binuclear system (molecules involving two metal atoms instead of one). Although it is unreasonable to expect binuclear complexes to effectively model metal surfaces, they can, nonetheless, yield valuable information on substrate coordination and activation at surfaces and the specific role of various bridging geometries since many known ligand coordination modes occur in each.

1.4.3 Metal-metal cooperativity

The lack of unnecessary complexity in two-metal systems (compared to surfaces and even clusters) makes them ideal for establishing the intimate details of how adjacent metals can be involved in *cooperative* substrate activation.[133] This concept is one mode of metal-metal "cooperativity" and became popular outside the surface-modeling research community owing to the assumption that a bridging ligand should display reactivity different from that of a terminally bound group.[134] Once forced into close proximity, there are several instances where metals can act in a cooperative manner to activate normally inert substrates to produce new molecules not possible with monometallic analogues. Furthermore, binuclear complexes possess some of the advantages of heterogeneous systems – adjacent metals (therefore, "cooperativity") and tunability, suggesting potential application in catalysis.

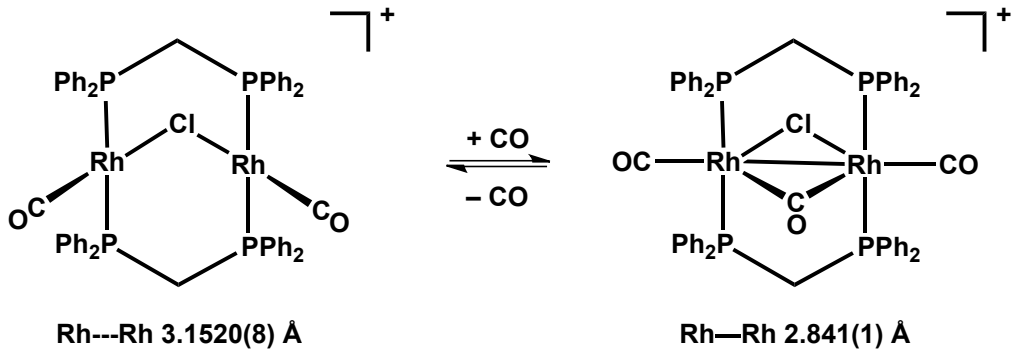
To provide a few examples, activation of the very unreactive dinitrogen molecule can occur when two metals are involved, where increased π-back-bonding from *both* metals into the ligand's π^* orbitals facilitates functionalization of this molecule.[135, 136] Also, in the activation of other normally-inert bonds, the Cowie group has demonstrated that bridging fluoroolefins are much more susceptible to C–F bond activation by F^- abstraction than fluoroolefins bound to only one metal.[137, 138]

Although homobimetallic systems (binuclear systems involving two of the same metal) can activate bonds in a cooperative manner, the observation that *different* metals catalyze the formation of different product distributions suggested that combinations of metals may lead to interesting reactivity.[139] The study of *hetero*bimetallic complexes involves combining the unique properties of different

metals, potentially giving rise to interesting contrasts in reactivity compared to either metal alone, thereby significantly extending the flexibility of the chemistry. With two different metals incorporated into one complex, a rich, more diverse array of reactivity patterns becomes available, expanding the scope of bimetallic complexes and their use in catalysis.[140] Although the concept of modeling surfaces was the driving force for this field at its inception, our primary interest now is understanding how two metals can activate simple molecules, and what properties each metal (whether identical or dissimilar) can impart on the system of interest.

1.4.4 Maintaining binuclearity

Many binuclear complexes unfortunately fragment into mononuclear species on reaction with substrates,[141-148] removing any apparent advantage of having the metals initially bound together. As a result, an appropriate bridging ligand is needed to hold the metals together, even upon cleavage of the metal-metal bond. The diphosphine ligand *bis*(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$, dppm) is commonly used as a bridging group, having two donor sites (one for each metal), an ideal bite angle, and the flexibility to bridge a wide range of metal-metal separations in the presence or absence of metal-metal bonds.[133, 149-155] This flexibility is obvious in the reaction of the dirhodium species $[Rh_2(CO)_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$,[156] containing no Rh–Rh bond, with CO gas to form the metal-metal bonded species $[Rh_2(CO)_2(\mu\text{-CO})(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ (Scheme 1-10),[157] in which the metal-metal separation contracts from 3.15 Å[158] to 2.84 Å. Diphosphines such as dppm have played a key role in late-metal binuclear complexes; not only do these soft ligands bind effectively to and stabilize the late metals, but they also act as a donor to each metal atom, functioning as an



Rh---Rh 3.1520(8) Å **Rh—Rh 2.841(1) Å**

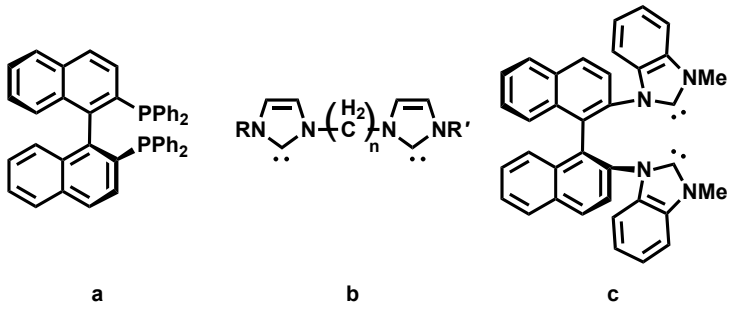
Scheme 1-10. Reversible formation of metal-metal bond in a dppm-bridged dirhodium complex.

important bridging infrastructure.

1.4.5 Di-*N*-heterocyclic carbenes as diphosphine replacements

Although our group often assesses a diphosphine's utility by its ability (or lack thereof) to bridge metal atoms (for reasons outlined in Section 1.4.4), the majority of the organometallic community uses diphosphines as *chelating* groups, often by replacing two monophosphines with a bidentate diphosphine analogue. Chelating diphosphines find significant use in catalysis for two main reasons: (1) Chelating groups lend stability to complexes owing to the chelate effect, allowing these species to better survive the harsh conditions of some catalytic reactions[159] and (2) transition metal complexes incorporating *chiral* diphosphines[vii] (Figure 1-8a) are of great industrial value in numerous enantioselective processes.[160, 161] Monodentate NHCs have, in many cases, been shown to be more strongly-attached to transition metals than phosphines and therefore routes to bidentate, di-*N*-heterocyclic carbenes (di-NHCs, Figure 1-8b, for example) found a surge in popularity at the turn of the

[vii] Although many diphosphines employed in enantioselective catalysis (such as the one shown in Figure 1-8a) are not themselves "chiral", once attached to a metal atom, they impose a spacial restriction, controlling enantioselectivity of the products. This *axial* chirality is often preferable to using two chiral monophosphines (*i.e.*, :PRR′R″) because the synthesis of chiral phosphines is much more difficult, and diphosphines also benefit from the added stability of the chelate effect.



a b c

Figure 1-8. Di-NHCs as diphosphine replacements.

millennium as chelating diphosphine replacements because of improvements observed in many catalytic reactions,[159, 162] even in asymmetric catalysis (Figure 1-8c)[163-165] – an area heavily dominated by diphosphines.[160, 161]

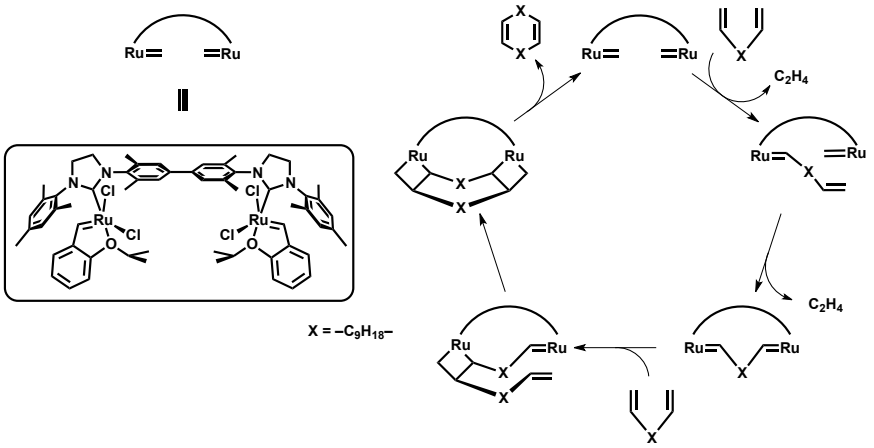
In addition to the tighter-binding and steric properties di-NHCs can offer as improvements over diphosphines, they have also experienced a surge in popularity because they can be prepared almost as easily as their monodentate counterparts (considering NHC precursors are structurally fairly simple organic molecules) by coupling two nitrogen heterocycles to an appropriate linker, shaping the backbone for di-NHCs.

1.4.6 Di-*N*-heterocyclic carbenes as bridges in binuclear chemistry

As noted earlier, the Cowie group's interest in diphosphines was as bridging groups for holding two metals in close proximity. For this reason, we viewed di-NHCs not from the perspective of potential chelating groups, but as potential bridging groups. Given the ongoing interest in using diphosphines as bridging groups and the recent resurgence of interest in NHCs, it is hardly surprising that the use of di-NHCs as bridging groups has recently increased.[166-190] However, a complication presents itself if studies are to be transferred over to di-NHCs – the ligand's preference for a

chelating vs. bridging mode. Although (entropically) a chelating arrangement should always be preferred, there are several factors dictating a di-NHC's preference for one or the other, and the desired outcome can often be reached if many of them are carefully taken into consideration. A few empirical guidelines are listed here: (1) By using bulky substituents on nitrogen (Figure 1-8b, R and R′), this can often prevent a chelating arrangement by creating too much steric repulsion at a single metal.[191] However, if the other ligands on the desired transition metal are relatively small, increasing the steric bulk on the dicarbene may not have much of an effect. (2) By using an inflexible linker, the NHC rings can be forced to point in directions that are not conducive to chelation, forcing a bridging arrangement.[189, 192] (3) Attachment *via* internal base deprotonation (see Section 1.3.2) frequently results in bridging arrangements (where a 1:1 base-to-metal ratio has been used).[193] (4) In some cases, the linker length can have a dramatic effect on bridging vs. chelating, although it is hard to predict.[172] (5) If deprotonation of the imidazolium moieties does not require heating, reaction of the free dicarbene with the metal source at lower temperature can encourage a bridging arrangement.[181]

Di-NHC-bridged complexes have been the target of many recent studies. As an archetypal example (encompassing the benefits of *both* NHCs and binuclear cooperativity), Lemcoff reported a bimetallic analogue of Grubbs's metathesis catalyst which preferentially produces cyclodimers (as double activation occurs before a new monomer can be introduced, Scheme 1-11), as opposed to oligomers normally seen with the popular monometallic complex.[194] In systems such as these, we are also interested in establishing more cases in which adjacent metals can react



Scheme 1-11. Homobinuclear ruthenium catalyst for dimer ring-closing metathesis.

with substrates with some degree of cooperativity, potentially giving rise to reactivity profiles different than what is observed when only one metal is involved.

Section 1.5 Different Carbenes

1.5.1 Modifying NHCs

Owing to the popularity of NHCs over the past twenty years, many groups have successfully altered certain aspects of the imidazole-based framework to produce interesting new types of carbenes. The standard NHC can be broken down into six different components (Figure 1-9 on the next page), all of which can be modified to generate new and exciting carbenes similar to NHCs: (1) The substituents in the backbone (R), (2) the nature of the backbone itself (E⚌E), (3) the substituents on the heteroatoms, also known as wingtips (W), (4) the donor atom itself (D̈), (5) the angle at the donor atom (θ), and (6) the heteroatoms (X) α to the donor atom.

To discuss a few examples, a common modification is substituting the backbone with different functionalities. Most frequently this is done to add an element of chirality to saturated NHCs (Figure 1-9a1),[195, 196] although more complicated

backbone-modification examples exist such as designing a system based on the structure of caffeine for biological purposes (Figure 1-9a2)[197, 198] or using a delocalized, anionic framework (Figure 1-9a3),[199, 200] to raise the ligand's frontier orbitals (although these anionic species behave more like alkyls considering, by definition, "true" carbenes are required to be neutral[100]). There are many reports involving modification of the backbone itself, ranging from simply saturated vs. unsaturated backbones, to incorporating inorganic, non-carbon groups such as a diboron-based backbone as shown in Figure 1-9b,[201, 202] or removing the backbone altogether, inherently resulting in acyclic diaminocarbenes.[203-209]

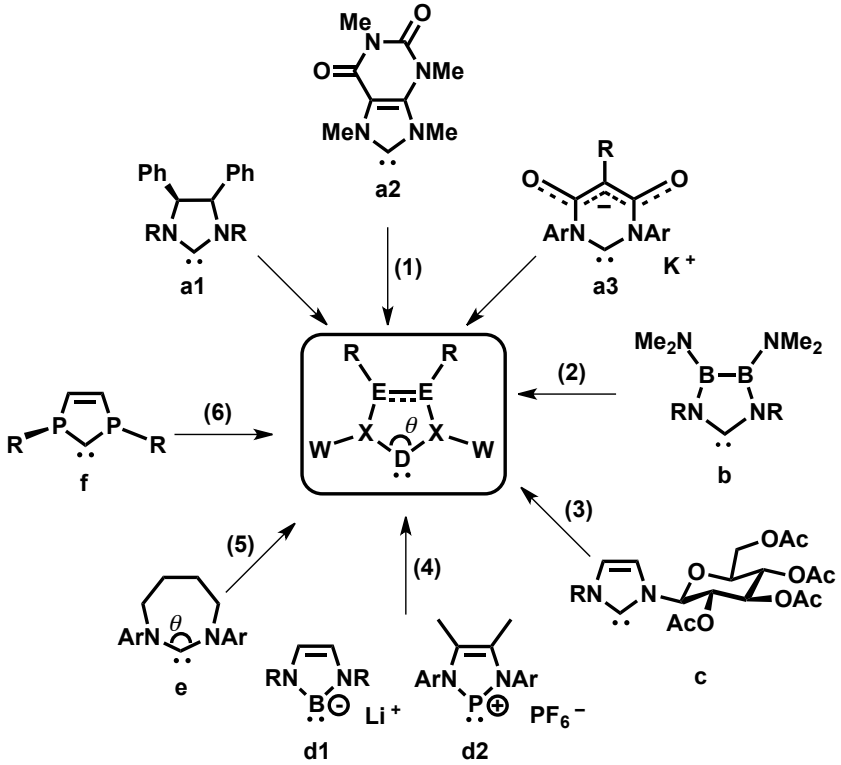


Figure 1-9. Modifying the many different components of NHCs.

The most-studied modification in NHC synthesis, however is the incorporation of different substituents (or "wingtips") on the nitrogen atoms

because replacement at this position is relatively simple from a synthetic standpoint. As a result, several different wingtips (all of which vary the NHC's $\%V_{Bur}$ values) can be incorporated into this position, ranging from simple mesityl groups (making up one of the most prevalent NHCs in modern organometallic chemistry known as "IMes")[210] to more-complicated "sugar-coated" NHCs (Figure 1-9c).[211, 212] Many groups also examine the feasibility of isolating heavier carbene congeners by modifying the donor atom, such as in NHPb, NHGe, and NHSi studies,[213-233] and even NHB^{-}s (Figure 1-9d1)[234] or NHP^{+}s (Figure 1-9d2),[214, 235-237] although (by definition) this modification transforms the NHC into a non-carbene.

There are also many instances in which the angle at the donor atom is changed, which significantly affects the s character of the lone pair-containing σ orbital,[238] as well as imposing different steric properties (Figure 1-9e).[239-244] Finally, many interesting studies focus on heteroatoms other than nitrogen in the α positions, such as replacing a nitrogen atom with sulfur (forming what are known as N*S*HCs),[245] or replacing both, such as in the phosphorus-only example shown in Figure 1-9f, known as PHCs.[246]

1.5.2 Modifying the ring framework

Although most carbenes reported (both free and attached to transition metals) involve an imidazole-based framework, there are several other types of carbenes involving a different ring makeup. Triazole-based carbenes such as "type **a**" and "type **b**" 1,2,4-triazoline-5-ylidenes (Figure 1-10a,b) are used by many groups (especially when linked to form dicarbenes),[178] as well as 1,2,3-triazol-5-ylidenes, which have become popular and known as mesoionic carbenes (MICs, Figure 1-10c).

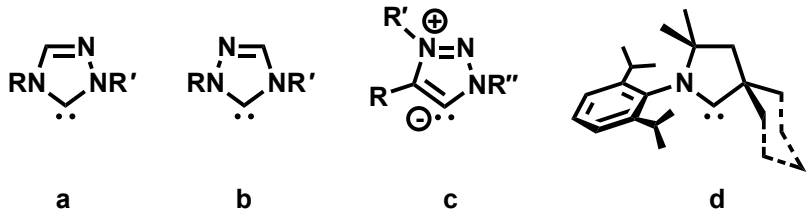


Figure 1-10. Different types of stable, free carbenes.

However, some of the most publicized advances have originated from the Bertrand group over the past six years on the development of stable, crystalline, cyclic (alkyl)(amino)carbenes (CAACs, Figure 1-10d).[247] Although only one nitrogen is adjacent to the reactive carbene moiety (offering only roughly half the electron-withdrawing inductive stabilization, and lone pair-donating mesomeric effects), the singlet-triplet gap is adequately widened and the empty p orbital on carbon is populated sufficiently to allow stabilization of these species. However, the energy gap is small enough that dimerization can still pose a problem, and a bulky substituent is required on the lone nitrogen atom, such as a 2,6-diisopropylphenyl group.

Moreover, owing to the presence of a quaternary carbon in a position α to the carbene centre, these CAACs feature a steric environment that differentiates them significantly from the previous NHCs and amplifies the *flexible* steric bulk effect when a spirocyclohexyl group is included in the structure (Figure 1-10d). Furthermore, the ring can be locked into a protective conformation by using bulky substituents on the cyclohexyl ring, preventing ring inversion. For example, placing an *iso*-propyl group on one of the β carbons in the ring locks the wingtip in a downward "protecting" orientation, wherein a boat/chair inversion would result in a highly unfavourable arrangement of the bulky group placed in an axial position.[248]

These *rigid* CAACs form a wall of protection for the attached metal atom, allowing for the possible isolation of very coordinatively-unsaturated species.[248-253]

Section 1.6 Goals of Thesis

1.6.1 Motivations

In this thesis, my interest was centred on establishing routes to dicarbene-bridged heterobinuclear complexes. Many modern monometallic catalysts have demonstrated that higher activities can be achieved when carbenes are employed as ancillary ligands.[104, 254, 255] As a result, we were interested in developing *di*-carbenes to bridge two *different* catalytic centres - a relatively unexplored area. Presumably each end of the proposed bimetallic catalysts could facilitate a different catalytic reaction, resulting in a "two-in-one" tool for synthetic chemists. The enthusiasm for this proposal stems from a few trends observed upon immersing myself into this fascinating area: (1) Most binuclear complexes are bridged by more traditional ligand sets (diphosphines, diamines, etc.) instead of dicarbenes, (2) the majority of dicarbenes were used as monometallic chelates, (3) at the time this study was initiated, any and all bridging dicarbene systems were used to bridge binuclear complexes of the *same* metal, (4) most dicarbenes reported were di-NHCs, despite the prevalence of new carbenes (MICs, NSHCs, CAACs, etc.) in the monocarbene literature, and (5) all dicarbenes were symmetric (with respect to the rings *and* the substituents), and no hybrid versions had been pursued at the time I undertook this study.

1.6.2 Establishing a strategy

For the most part, homo- and heterobimetallic complexes in the Cowie group have been bridged by two dppm ligands (and only recently have new systems been developed[193, 256]), a statement which falls in line with point (1) above. Furthermore, our group (having a focus on bimetallic systems for reasons stated in Section 1.4) had little interest in pursuing monometallic systems with chelating dicarbenes, which was already a fairly developed area, as stated in point (2). At the inception of this research, the simplest way to address point (3) and develop *hetero*binuclear dicarbene-bridged complexes was to incorporate the different metals one at a time in a stepwise fashion. Ignoring points (4) and (5) for now, a series of NHC-anchored/pendent imidazolium salts caught our attention as they appeared ideal for the stepwise incorporation of transition metal atoms to form symmetric (with respect to the dicarbene) di-NHC-bridged heterobinuclear systems. One was a zwitterionic palladium system published by the Herrmann group (Figure 1-11a);[191] the other was a system involving iridium, published by Albrecht while conducting post-doctoral research under the supervision of Robert Crabtree (Figure 1-11b).[257] Furthermore, Kyle Wells in our group had isolated a pendent intermediate in the synthesis of a di-NHC-bridged dirhodium species (Figure 1-11c, further details in Section 2.2.1),

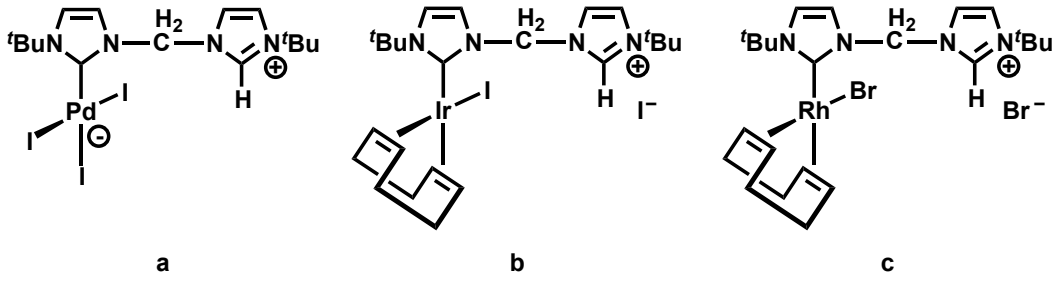


Figure 1-11. First published carbene-anchored/pendent-imidazolium complexes.

which has subsequently been published.[193] With one metal already attached, the incorporation of the second (different) metal, by deprotonation of the pendent imidazolium groups, seemed obvious. Chapter 2 focuses on our success in generating a series of Pd/Rh, Pd/Ir, and Ir/Rh mixed-metal systems using this strategy.

Re-examining the points outlined in Section 1.6.1 (point (4), in particular) we were interested in establishing new *non-imidazole* dicarbene ligands in a field crowded with NHC-based donors. During this time we became interested in the work of Guy Bertrand's group, in which they described a series of different, stable (and bottleable) carbenes, such as the CAAC and MIC systems mentioned earlier. Chapters 3 and 4 describe our efforts (some successful and others unsuccessful) in making new dicarbenes for the purposes of bridging two different metal atoms, specifically di-CAACs, and *hybrid*, *unsymmetric* NHC/MIC dicarbenes, which also corresponds to the final "motivation point" mentioned in Section 1.6.1.

With some experience in dealing with different carbenes and attaching them to metal atoms, the final synthesis-oriented chapter (Chapter 5) first focuses on organic protocols to generate a series of di-MICs, then their attachment to transition metals**.** Despite the three different sets of dicarbenes throughout this thesis however, the same pendent strategy is seen throughout to incorporate the metal atoms one at a time.

Finally, in the closing chapter (Chapter 6) we examine the catalytic ability of Pd/Rh systems in Suzuki-Miyaura cross coupling (a reaction routinely executed with palladium) and transfer hydrogenation (shown to be catalyzed by rhodium in some

cases) processes. As a result of these reactions being mechanistically distinct and orthogonal, we also examine these complexes' ability to perform *both* reactions in the same vessel, acting in a one-pot *tandem* sequence. The effect each of the different bridging dicarbenes has on the results is discussed therein.

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Chapter 2 Carbene-Anchored/Pendent-Imidazolium Species as Precursors to Di-*N*-Heterocyclic Carbene-Bridged Mixed-Metal Complexes[i]

Section 2.1 Introduction

2.1.1 *N*-heterocyclic carbenes in organometallic chemistry

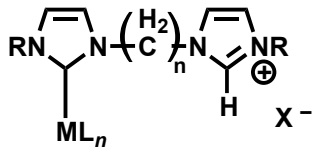
As discussed in more detail in Chapter 1, NHCs have emerged as versatile ligands in organometallic chemistry, and offer a useful alternative to the ubiquitous phosphine ligands.[1-11] Although these carbene ligands are considered to have bonding properties similar to those of trialkylphosphines[12-15] their steric properties differ significantly; whereas phosphines are often described as conical,[16] NHC ligands having an unsaturated backbone are more planar, having a slimmer, less sterically hindered axis orthogonal to the carbene ring plane. This quasi two-dimensional shape is evident in square-planar complexes of NHCs in which the NHC plane is usually perpendicular to the metal coordination plane,[17-24] although (depending on the nature of the wingtip substituents) bulky substituents can certainly add to that third dimension.

Most reports on NHC complexes involve monocarbenes,[25-28] however there are a number of reports involving di-*N*-heterocyclic carbenes (di-NHCs), in which pairs of NHC groups are linked in a number of ways, as replacements for chelating[12, 29-41] or bridging[3, 5, 12, 29-32, 34-45] diphosphines. Our group's initial study on binuclear di-NHC-bridged systems concentrated on *homo*binuclear complexes of rhodium.[46] However the group's ongoing interest in mixed-metal systems,[47-56] and their use as

[i] The work presented in this chapter has been previously reported. See: Zamora, M.T.; Ferguson, M.J.; McDonald, R.; Cowie, M. *Dalton Trans.* **2009**, 7269-7287.

mixed-metal catalysts[57-60] led us to extend our investigation to complexes in which di-NHC ligands could be used as bridging groups connecting *different* pairs of metals.

For the rational generation of mixed-metal species it appeared that stepwise incorporation of the different metals was the most straightforward strategy. A series of carbene-anchored/pendent-imidazolium salts of the type diagrammed in Figure 2-1, [6, 41, 43, 44, 46, 61-69] appeared ideal for this purpose, through deprotonation of the pendent imidazolium salt in the presence of the second metal. We therefore set out to generate a more extensive series of such pendent species and to use them as synthons for a series of dicarbene-bridged mixed-metal complexes. The results of this study, in which the first[ii] series of di-NHC-bridged heterobinuclear compounds are characterized, are reported herein.



[ML_n(^{R}C-κ^1-C(H)^{alk})][X]
alk = meth (n = 1), eth (n = 2)

Figure 2-1. Naming scheme for complexes containing pendent di-NHC ligands.

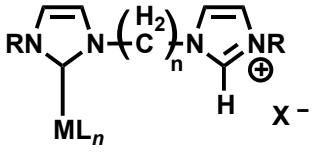
Section 2.2 Results and Compound Characterization

2.2.1 Establishing a strategy

As noted above, it appeared that di-*N*-heterocyclic carbene-bridged complexes involving two *different* metals could be accessed *via* deprotonation of a carbene-anchored/pendent-imidazolium complex, of the type shown above in Figure 2-1, in the presence of a second metal. We had already shown that such a strategy could be

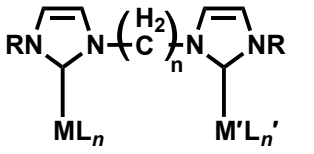
[ii] One incompletely-characterized di-NHC-bridged Rh/Ir complex was briefly described while this report was in press.[68]

employed to generate dicarbene-bridged Rh_2 complexes *via* deprotonation of the mononuclear species, [RhBr(COD)($^{t\text{Bu}}$C-κ^1-C(H)$^{\text{meth}}$)][Br] ($^{t\text{Bu}}$C-κ^1-C(H)$^{\text{meth}}$ = methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene]; see Figure 2-2b, M = Rh, L_n = COD, X = Br), by [Rh(μ-OAc)(COD)]$_2$. A number of carbene-anchored/pendent-imidazolium species of Rh,[14, 31] Ir,[14, 68-70] Pd,[71-75] Ni,[70, 76, 77] Fe,[78] and Ru[62], which seemed appropriate for generation of binuclear species, were already known and we initially sought to extend the number of these complexes of Rh and Pd to serve as potential synthons for a range of dicarbene-bridged mixed-metal complexes involving these metals.



n = 1; R = CH_3: $^{\text{Me}}$C-κ^1-C(H)$^{\text{meth}}$ (a)
n = 1; R = ^{t}Bu: $^{t\text{Bu}}$C-κ^1-C(H)$^{\text{meth}}$ (b)
n = 2; R = CH_3 $^{\text{Me}}$C-κ^1-C(H)$^{\text{eth}}$ (c)
n = 2; R = ^{t}Bu $^{t\text{Bu}}$C-κ^1-C(H)$^{\text{eth}}$ (d)

[ML_n($^{\text{R}}$C-κ^1-C(H)$^{\text{alk}}$)][X]



n = 1; R = CH_3: μ-$^{\text{Me}}$CC$^{\text{meth}}$ (a)
n = 1; R = ^{t}Bu: μ-$^{t\text{Bu}}$CC$^{\text{meth}}$ (b)
n = 2; R = CH_3: μ-$^{\text{Me}}$CC$^{\text{eth}}$ (c)
n = 2; R = ^{t}Bu: μ-$^{t\text{Bu}}$CC$^{\text{eth}}$ (d)

[ML_n(μ-$^{\text{R}}$CC$^{\text{alk}}$)M′L_n′]

Figure 2-2. Pendent ($^{\text{R}}$C-κ^1-C(H)$^{\text{alk}}$) and bridging (μ-$^{\text{R}}$CC$^{\text{alk}}$) labeling scheme.

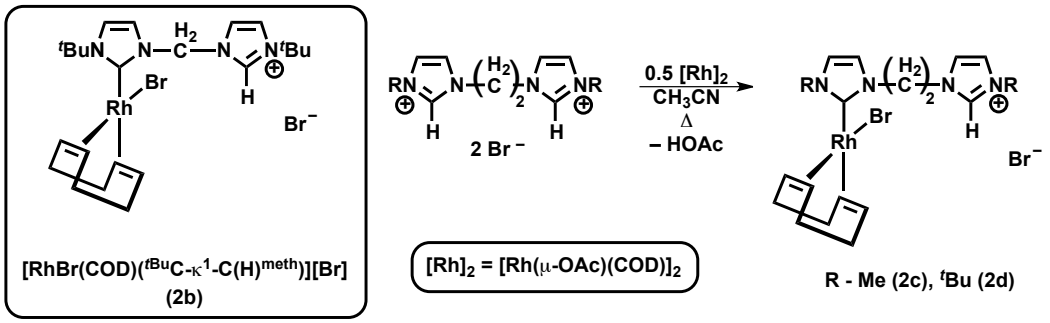
Throughout this chapter we use the abbreviations, ($^{\text{R}}$C-κ^1-C(H)$^{\text{alk}}$) for the monodentate pendent species and (μ-$^{\text{R}}$CC$^{\text{alk}}$) for bidentate dicarbene systems, as shown in Figure 2-2, which are a slight modification to the nomenclature suggested by Green, *et al.*.[43] In these abbreviations the substituent (R) on the carbene rings appears first, followed by the pendent/anchored (C-κ^1-C(H)) or dicarbene (CC) notation, and finally an abbreviation (alk = meth, eth) designating a methylene or ethylene linker between the NHC/NHC or NHC/imidazolium rings. We will

additionally use the label **a** in the numbering scheme to indicate the Me/meth combination, the label **b** to indicate ^{t}Bu/meth, the label **c** to indicate Me/eth, and **d** for the ^{t}Bu/eth combination.

2.2.2 Carbene-anchored/pendent-imidazolium complexes of Rh

Although there are a few examples in which an external base can be used to deprotonate only one end of a diimidazolium salt to generate pendent-imidazolium species, they are usually specific to diimidazolium salts terminated by bulky *N*-substituents such as ^{t}Bu and Mes[6, 44, 62, 66] and therefore limit the scope of carbene-anchored complexes possible. Most often, single deprotonation of the diimidazolium salts is carried out using complexes containing basic ligands such as acetate or methoxide groups, which serve to deprotonate these salts. This is the method used with some success in this report, and in previous reports by our group[46] and others with a variety of internal bases and NHC proligands.[14, 31, 46, 70-73, 75-77, 79-82]

In a previous study our group had shown that the acetate-bridged complex, $[Rh(\mu\text{-}OAc)(COD)]_2$, was effective in the deprotonation of a number of diimidazolium salts generating the corresponding series of di-NHC-bridged dirhodium products.[46] In one case the mononuclear carbene-anchored/pendent-imidazolium complex [RhBr(COD)($^{t\text{Bu}}$C-κ^1-C(H)$^{\text{meth}}$)][Br] (**2b**, Scheme 2-1) was



Scheme 2-1. Model complex **2b**, and the synthesis of rhodium pendent complexes **2c** and **2d**.

generated and found to be a probable intermediate in the formation of the di-NHC-bridged target. Although our initial attempts to prepare the other members of this series, namely, [RhBr(COD)L][Br] (L = ^{Me}C-κ^1-C(H)^{meth}, ^{Me}C-κ^1-C(H)^{eth}, $^{t\text{Bu}}$C-κ^1-C(H)^{eth}), from the corresponding diimidazolium salts were unsuccessful, we have subsequently been able to generate both the methyl- and *tert*-butyl-substituted *ethylene*-linked systems (**2c,d**) (Scheme 2-1) by using longer reaction times (see Section 2.4.2, Preparation of compounds). Attempts to generate the fourth member of the series, [RhBr(COD)(^{Me}C-κ^1-C(H)^{meth})][Br] (**2a**), using a similar procedure gave only a mixture of unidentified products, under a variety of conditions.

The ^{1}H NMR spectral parameters for the series of complexes (**2c** and **2d**) are closely comparable to those described for **2b**[46] and also to those of previously reported pendent complexes involving other metals.[14, 31, 62, 70-78] Complexes **2b**-**2d** show typical resonances for the coordinated COD ligands (between 1.7 and 5.7 ppm) as given in Section 2.4.2. The acidic proton of the pendent imidazolium group appears at a characteristically high-frequency (*ca.* 10 ppm) as a pseudotriplet, displaying approximately equal coupling to the pair of inequivalent olefinic protons, while these olefinic protons on the imidazolium group display mutual coupling ($^3J_{\text{H–H}}$ ≈ 2 Hz) in addition to coupling ($^4J_{\text{H-H}}$ ≈ 2 Hz) to the acidic proton and therefore also appear as pseudotriplets. The appearance of two different resonances for the *N*-bound substituents (at *ca.* 4.0 ppm for the methyl groups in **2c**; and at *ca.* 1.8 ppm for the *tert*-butyl groups in **2b,d**) is as expected for an unsymmetrical, carbene/imidazolium system, and the four separate resonances for the olefinic protons within the NHC and imidazolium rings offer further support for the pendent species (Figure 2-3).

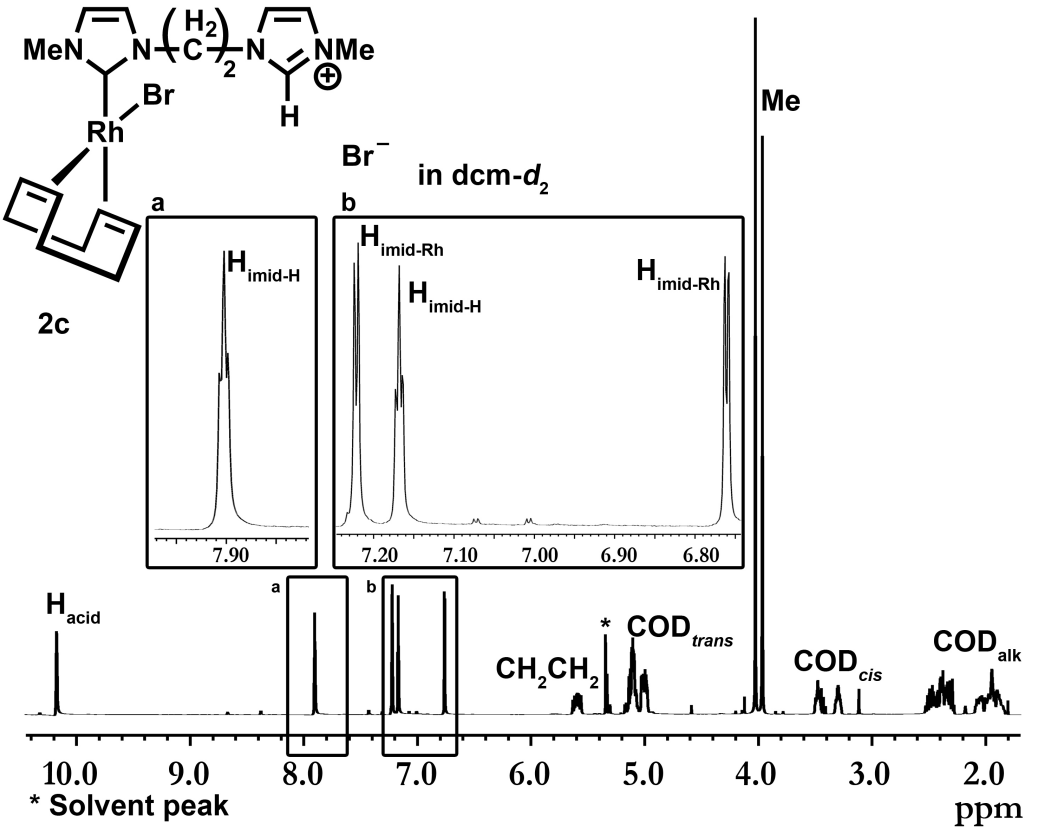


Figure 2-3. ^{1}H NMR spectrum (400 MHz) of compound **2c** in dcm-d_2, with expanded olefinic regions.

The AB pattern observed for the methylene linker in the previously-reported **2b** (rather than a singlet) suggested that the NHC unit adopts the usual orientation in which it is bound perpendicular to the square plane of the metal.[iii] In this orientation, the plane bisecting the linking CH_2 group (or CH_2CH_2 in this work) is unsymmetrical on each side, having a bromo ligand on one side and one half of the COD ligand on the other. The ^{13}C{^{1}H} NMR spectral data offer additional support for the pendent structure, displaying two different signals for the *N*-bound substituents on the carbene and imidazolium rings, and four different olefinic

[iii] With the anchored-NHC adopting an arrangement perpendicular to that of the square plane about Rh, both protons in the CH_2-linker are therefore inequivalent, having different chemical shifts (δ) in the ^{1}H NMR spectrum, and display two-bond coupling to each other ($^{2}J_{H\text{-}H}$). However, the difference in resonance frequencies ($\Delta\nu$) is sufficiently small ($\Delta\nu/^{2}J_{H\text{-}H} \approx 15$), and therefore second-order effects cause the doublets to distort, inducing a "rooftop" effect (*i.e.*, || ||).[83]

carbons. More significantly, the carbene carbon in these complexes appears at *ca.* 181.7 ppm with typical coupling to Rh[37, 46, 84-86] of approximately 50 Hz, while the protonated carbon of the imidazolium group appears as a singlet at *ca.* 122.0 ppm. This imidazolium carbon resonance appears as a doublet in the proton-*coupled* ^{13}C NMR spectrum having $^{1}J_{C\text{-}H} \approx 220$ Hz coupling to the acidic proton (as confirmed by 2D gradient heteronuclear single quantum coherence (gHSQC) and gradient heteronuclear multiple quantum coherence (gHMQC) NMR experiments).

The proposed pendent structures for complexes **2c,d** are confirmed by X-ray crystallography and their structures are shown in Figure 2-4. Consistent with the NMR spectral data, the NHC plane lies close to perpendicular to the metal coordination plane in both cases (dihedral angles = 83.2(3)° and 98.5(3)° respectively); and the Rh–$C_{carbene}$ distances are normal, suggesting a metal–carbon single bond. The Rh–C(1) and Rh–C(2) separations (2.205(3), 2.226(3) Å in **2c**;

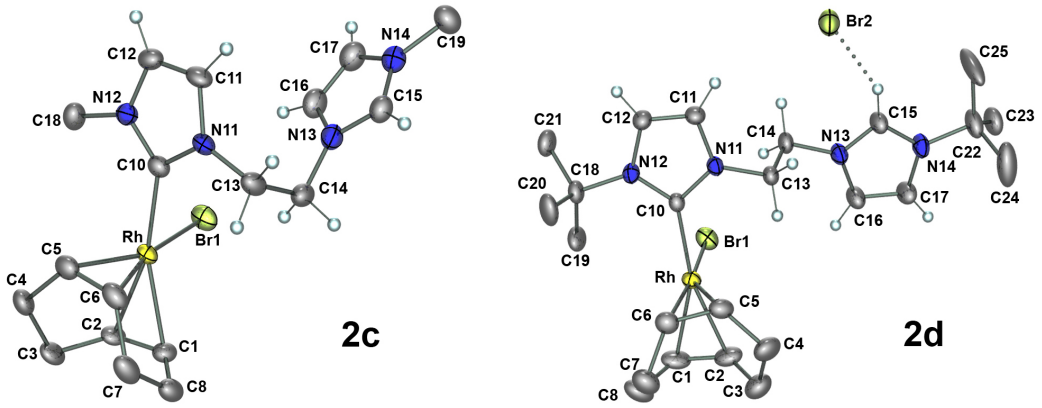
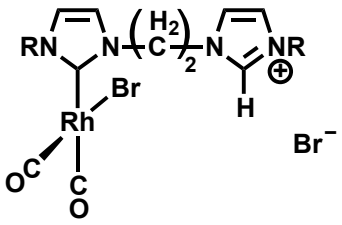


Figure 2-4. Three-dimensional representations of the complex cation of [RhBr(COD)(^{Me}C-κ^1-C(H)^{eth})][Br] (**2c**) and both the anion and cation of [RhBr(COD)(^{tBu}C-κ^1-C(H)^{eth})][Br] (**2d**) showing the numbering schemes. Thermal ellipsoids are shown at the 20% probability level. Hydrogen atoms are shown only on non-methyl carbons on the pendent carbene/imidazolium group. Relevant parameters for **2c** (distances in Å and angles in deg.): Rh–Br(1) = 2.5054(4), Rh–C(1) = 2.205(3), Rh–C(2) = 2.226(3), Rh–C(5) = 2.102(3), Rh–C(6) = 2.123(3), Rh–C(10) = 2.022(3); Br(1)–Rh–C(10)–N(12) = 83.2(3), N(11)–C(13)–C(14)–N(13) = 61.7(4). Relevant parameters for **2d** (distances in Å and angles in deg.): Rh–Br(1) = 2.5448(4), Rh–C(1) = 2.190(4), Rh–C(2) = 2.229(3), Rh–C(5) = 2.101(3), Rh–C(6) = 2.127(3), Rh–C(10) = 2.053(3); Br(1)–Rh–C(10)–N(12) = 98.5(3), N(11)–C(13)–C(14)–N(13) = –176.6(2).

2.190(4), 2.229(3) Å in **2d**) involving the olefinic moiety of the COD ligand *trans* to the NHC are longer than those of Rh–C(5) and Rh–C(6) to the other olefin moiety (2.102(3), 2.123(3) Å in **2c**; 2.101(3), 2.127(3) Å in **2b**). This difference can be rationalized either on the basis of steric repulsions between half of the COD ligand and the adjacent bromo ligand or the larger *trans*-influence of the carbene ligand.[12, 31, 35, 37] The weaker Rh–olefin interaction is paralleled by a shorter C(1)–C(2) distance (1.382(5) Å in **2c**; 1.383(6) Å in **2d**) compared to C(5)–C(6) (1.404(5) Å in **2c**; 1.403(5) Å in **2d**), consistent with less π-back-donation in this case. The major difference between the two structures involves the different torsion angles around the C_2H_4 linker as shown in Figure 2-4. These differences are presumably a consequence of packing effects and are unlikely to be of chemical significance.

The close separation (2.67 Å) between the acidic proton of the imidazolium group and the bromide counterion in **2d**, which is significantly shorter than the sum of their van der Waals radii (r_w(H) = 1.20, r_w(Br) = 1.85 Å)[87] of 3.05 Å, indicates hydrogen bonding between the two, whereas for **2c** the closest H–Br distance (3.12 Å) is typical and does not suggest such an interaction.

Although replacement of the COD ligands by CO in compounds **2c** and **2d** proceeds as expected to yield the analogous dicarbonyl complexes [RhBr(CO)$_2$(^{Me}C-κ^1-C(H)^{eth})][Br] (**3c**) and [RhBr(CO)$_2$($^{t\text{Bu}}$C-κ^1-C(H)^{eth})][Br] (**3d**), shown in Figure 2-5, CO addition to the C_1-linked complex **2b** does not proceed as expected, but instead yields a number of unidentified decomposition products. This result parallels the previously observed differences with the C_1- and C_2-linked dicarbene ligands ^{R}CC^{meth} and ^{R}CC^{eth} (R = Me, ^{t}Bu), respectively, in which the C_2-linked dicarbene-bridged complexes [RhX(COD)]$_2$(μ-^{R}CC^{eth}) underwent facile COD replacement by CO to



R = Me (3c), ^{t}Bu (3d)

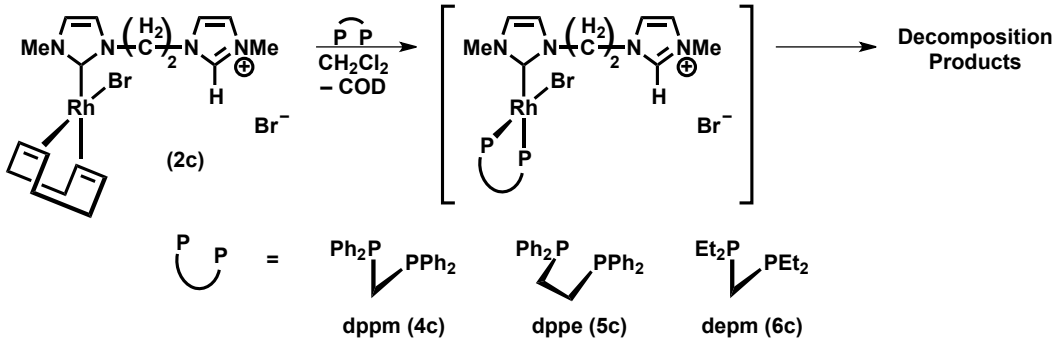
Figure 2-5. Carbonylated carbene-anchored/pendent-imidazolium rhodium complexes **3c** and **3d**.

give the anticipated products, $[RhX(CO)_2]_2(\mu\text{-}^{R}CC^{eth})$, while the related C_1-linked species $[RhBr(COD)]_2(\mu\text{-}^{R}CC^{meth})$ did not undergo simple substitution, instead yielding the unexpected mononuclear products $[RhBr(CO)(\kappa^2C^2,C^{2'}\text{-}^{R}CC^{eth})]$ together with $[Rh(\mu\text{-Br})(CO)_2]_2$,[46] through fragmentation of the dicarbene-bridged precursors.

Although single crystals of **3c**,**d** suitable for an X-ray diffraction study could not be obtained (the Br^-, BF_4^-, and OTf^- salts could only be obtained as oils), the spectral data leave little doubt about their formulations. In addition to the high-frequency pseudotriplet at *ca.* 10.1 ppm in the ^{1}H NMR spectrum for the imidazolium proton, a high-frequency peak for the carbene carbon appears as a doublet ($^1J_{C\text{-}Rh} \approx 42$ Hz) in the $^{13}C\{^1H\}$ NMR spectrum at *ca.* 172.6 ppm and together with a singlet at *ca.* 137.1 ppm, corresponding to the imidazolium carbon. Furthermore, the carbonyl stretches of **3c**,**d** appear at *ca.* 2007/2083 cm^{-1} ($\nu_{C\text{–}O(avg)}$ = 2045 cm^{-1}) and 2005/2081 cm^{-1} ($\nu_{C\text{–}O(avg)}$ = 2043 cm^{-1}), respectively in the IR spectra. Carbonyl stretching vibrations in IR spectra for $[RhX(CO)_2L]$ (and $[IrX(CO)_2L]$) complexes are used extensively for the assessment of the donor ability of phosphine and NHC ligands (L).[86, 88-93] These $\nu_{C\text{–}O(avg)}$ values indicate typical electron-donating abilities for unsaturated NHCs.[90, 91] These carbonyl carbons appear at *ca.* 186.2 ppm and 182.2 ppm in the $^{13}C\{^1H\}$ NMR spectra showing typical coupling to rhodium.

The carbonyl *trans* to the carbene displays approximately 54 Hz coupling to Rh while the carbonyl moiety *trans* to the bromide shows approximately 77 Hz coupling, as is seen in similar systems.[37] The larger $^{1}J_{\text{Rh-C}}$ and lower $\nu_{\text{C–O}(trans)}$ is consistent with this carbonyl, opposite the bromo ligand, being more strongly bound – presumably a consequence of both the lower *trans*-influence of the bromo ligand compared to the NHC group[12, 31, 35, 37] and its greater π-donor ability.

Reaction of the methyl-substituted COD complex (**2c**) with a series of diphosphine ligands generates the diphosphine-chelated products [RhBr(P⌒P)(^{Me}C-κ^1-C(H)^{eth})][Br] (**4c**-**6c**), as shown in Scheme 2-2. The ^{31}P{^{1}H} NMR spectra of



Scheme 2-2. Diphosphine-functionalized pendent rhodium complexes **4c**, **5c**, and **6c**.

these products display two sets of doublets of doublets (see Figure 2-6 for the ^{31}P{^{1}H} NMR spectrum of **4c**); both resonances display coupling to Rh (ranging from *ca.* 100 to 200 Hz) and to the other ^{31}P nucleus (30 to 100 Hz). Additionally, these peaks are located at lower frequencies when methylene-linked diphosphines (**4c**, **6c**) are used (both peaks centred about δ = –25, –21, respectively) whereas a set of peaks is observed at higher frequencies in the ethylene-linked case of **5c** (centred about δ = 65), consistent with the large deshielding reported for five-membered diphosphine rings,[94] confirming the chelating formulation above.

As observed in the parent complex **2c**, the acidic proton of the pendent imidazolium group in these pendent species appears in the high-frequency region (*ca.* 10.2 ppm) of the ^{1}H NMR spectrum. The pendent nature is also evident by the four different peaks for the olefinic protons, as well as two different peaks for the methyl

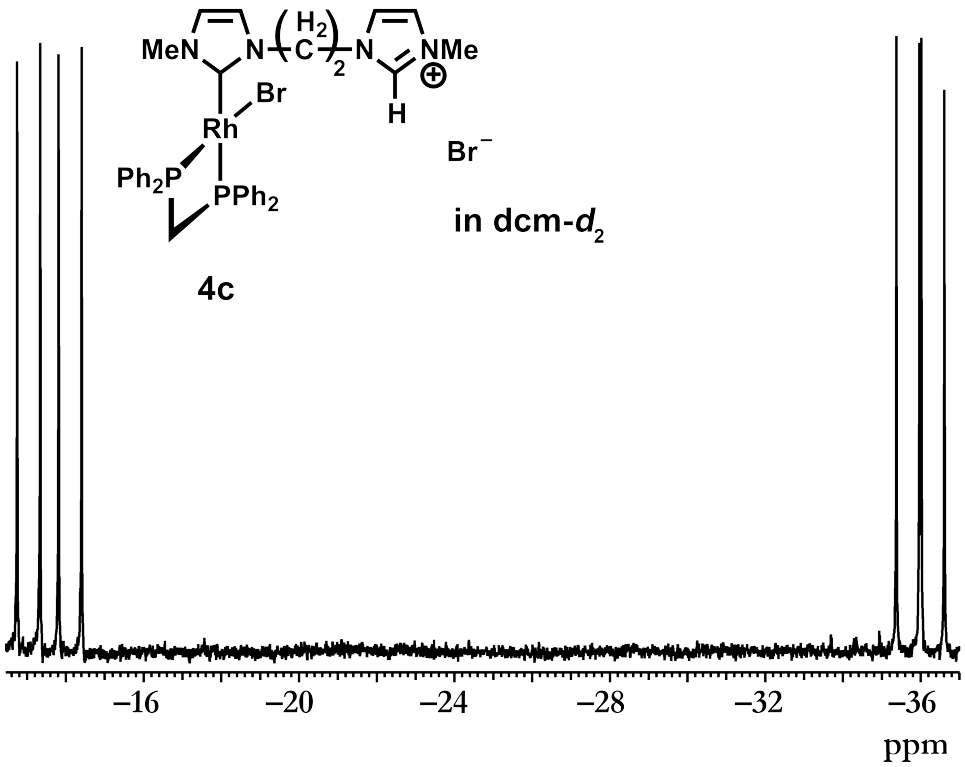


Figure 2-6. ^{31}P{^{1}H} NMR spectrum (162 MHz) of compound **4c** in dcm-d_2.

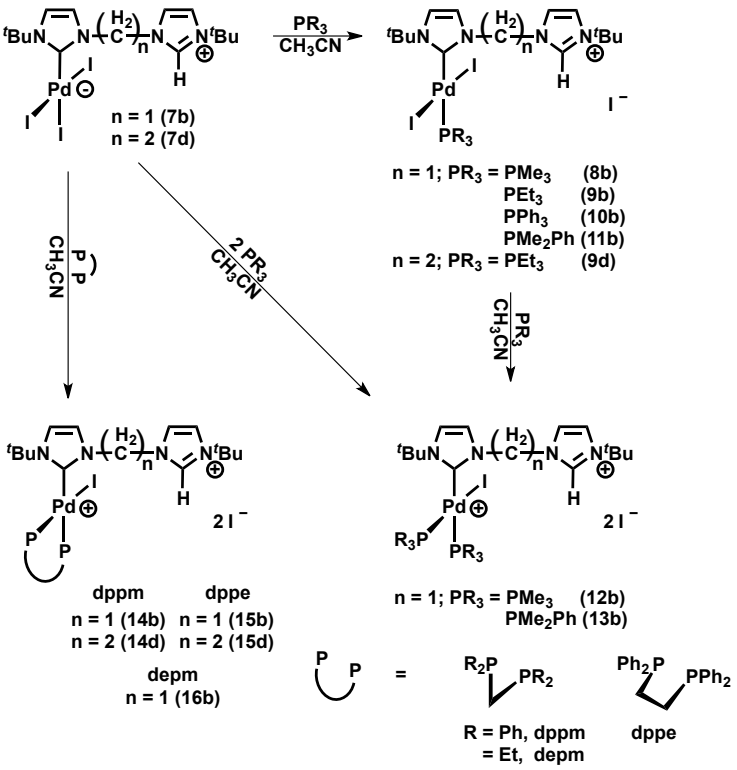
substituents in the ^{1}H NMR spectra. Surprisingly perhaps, the other *tert*-butyl-substituted COD precursors **2b**,**d** fail to react with these diphosphines, even after prolonged reflux. In addition, all complexes (**2a-d**) are inert to a number of monophosphines, even under forcing conditions.

The resulting diphosphine complexes (**4c**-**6c**) are unstable and decompose over the course of 1 h to form undesired complexes lacking the acidic proton. On the basis of ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, the resulting species most likely contain chelating diphosphine and dicarbene groups, and are unstable, decomposing

to a mixture of unidentified products over the course of 1 – 1.5 h, even in the presence of coordinating solvents such as thf or acetonitrile. These transient intermediates were not of interest, and were not characterized further.

2.2.3 Carbene-anchored/pendent-imidazolium complexes of Pd

An analogous series of carbene-anchored/pendent-imidazolium complexes of palladium can be generated by substitution of the iodo ligands in [PdI_3(^{tBu}C-κ^1-C(H)^{meth})] (**7b**),[61] by a number of mono- and diphosphine ligands as outlined in Scheme 2-3. Unlike the previously described Rh species that were unreactive to



Scheme 2-3. Synthesis of mono- and diphosphine-functionalized pendent palladium complexes.

monophosphines, the triiodide C_1-linked Pd precursor (**7b**) reacts with monophosphines in a stepwise manner yielding first the monophosphine products (**8b**-**11b**) which subsequently, in the presence of additional PR_3, result in a second

iodide substitution to give the *bis*(phosphine) species **12b** and **13b**. With a number of diphosphines, the diphosphine-substituted products (**14b**-**16b**) are produced. The analogous methyl-substituted species, [$PdI_3(^{Me}C\text{-}\kappa^1\text{-}C(H)^{meth})$] and [$PdI_3(^{Me}C\text{-}\kappa^1\text{-}C(H)^{eth})$], were not investigated since Herrmann, *et al.* have reported that only di-NHC-chelated dicarbene products [$PdX_2(\kappa^2C^2,C^{2'}\text{-}^{Me}CC^{meth})$] and [$PdX_2(\kappa^2C^2,C^{2'}\text{-}^{Me}CC^{eth})$] were obtained in such attempts.[72]

The spectral parameters for the carbene/imidazolium groups of complexes **8b**-**16b** are closely comparable to those in related pendent species which have previously been reported,[6, 41, 43, 44, 61-65, 67-69, 95] and again confirm the carbene-anchored/pendent-imidazolium formulation. The methylene protons of the C_1-linker in the pendent group show up as a singlet at $\delta \approx 6.71$ in the monophosphine complexes, reflecting the symmetry on either side of the NHC plane, whereas for the *bis*(phosphine) species (**12b**, **13b**) and the chelated diphosphine complexes (**14b**-**16b**) the protons of the methylene linker display an AB pattern, ($^2J_{H\text{-}H} \approx 14$ Hz, $\Delta\nu \approx 210$ - 300 Hz; $\Delta\nu/^2J_{H\text{-}H} \approx 18$) consistent with the lack of symmetry on either side of the carbene plane for these products (Figure 2-7 on the next page). As was observed with **4c**-**6c**, complexes **15** exhibit a similar shift to higher frequencies in their $^{31}P\{^1H\}$ NMR spectral resonances (centred at *ca.* 56 ppm) compared to the four-membered ring-containing analogues **14** and **16b** (centred at *ca.* –51 ppm and –49 ppm, respectively), consistent with the ring contribution effect[94] noted earlier. As an interesting contrast to this chelating diphosphine phenomenon, the midpoint of the two doublets in the *bis*(phosphine) complex **13b** is located at about –8 ppm. All olefinic protons, for the carbene and imidazolium moieties appear as pseudotriplets; for the imidazolium groups these olefinic protons again display mutual coupling as

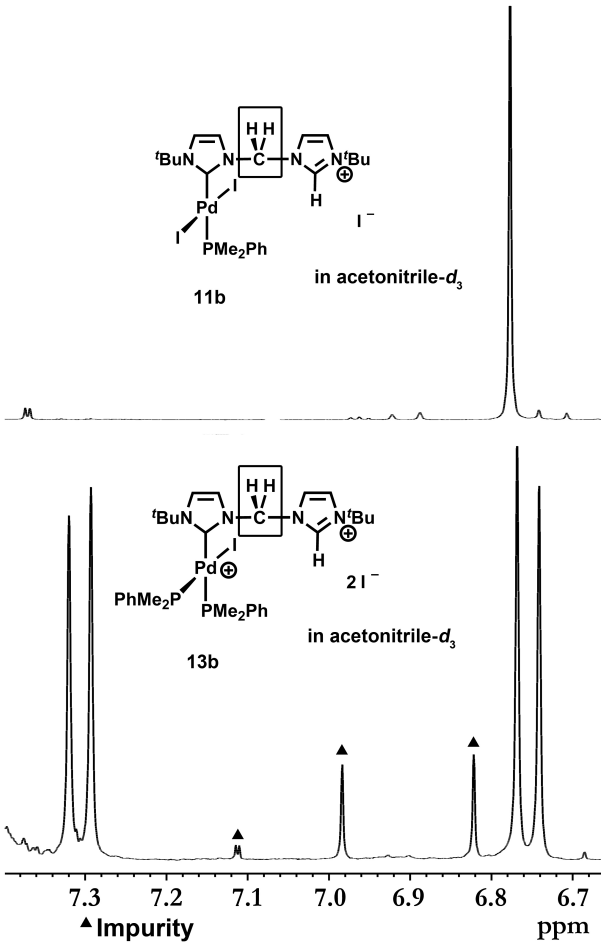


Figure 2-7. ^{1}H NMR spectra (400 MHz) of the CH_2 linker region of complexes **11b** and **13b** in acetonitrile-d_3.

well as coupling to the acidic proton, whereas for the carbene groups the olefinic protons show essentially equal coupling to each other and to the ^{31}P nucleus in the position opposite the carbene ligand (Figure 2-8). These resonances are readily differentiated by appropriate ^{1}H{^{31}P} and ^{1}H{selective ^{1}H} NMR experiments. Identification of individual ^{1}H and ^{13}C resonances is also aided by the ^{1}H nuclear Overhauser effect (NOE), gHSQC, gHMQC, and gradient heteronuclear multiple bond correlation (gHMBC) NMR experiments. Using compound **9b** as an

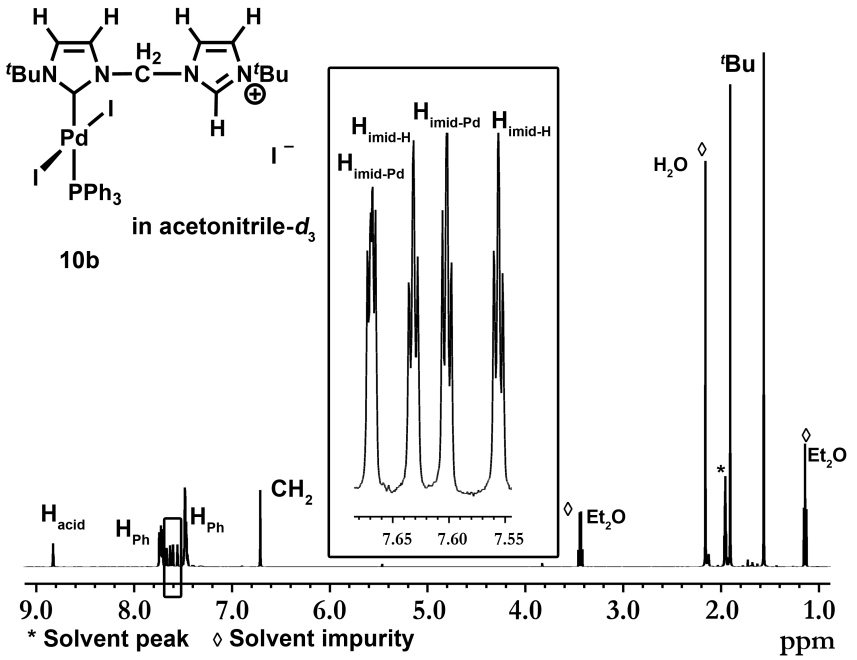


Figure 2-8. ^{1}H NMR spectrum (498 MHz) of compound **10b** in acetonitrile-d_3, with expanded olefinic region.

example (Figure 2-9), peaks representing protons in the imidazolium backbone (H6, H7) can be distinguished from those on the anchored NHC (H3, H4) by couplings to either $^1H_{acid}$ or $^{31}P_{trans}$ nuclei, as noted earlier. Both these groups can be further differentiated since the "outside" protons (H3, H7) display an NOE correlation peak (indicating proximity within ~ 3 Å) with one of the *tert*-butyl group peaks (H1, H9); whereas the "inside" protons (H4, H6) both contain cross peaks with the methylene linker protons (H5).

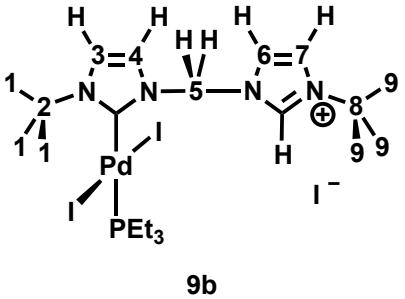


Figure 2-9. Charted image with different ^{1}H and ^{13}C environments in NHC/imidazolium backbone.

The carbene carbon in all pendent Pd complexes appears at *ca.* 160 ppm in the $^{13}C\{^{1}H\}$ NMR spectrum. In the case of the monophosphine complexes (**8b**-**11b**) this carbene resonance displays coupling ($^{2}J_{C\text{-}P} \approx 190$ Hz) to the *trans*-phosphine; while in the *bis*(phosphine) (**12b**, **13b**) or diphosphine (**14b**-**16b**) complexes, additional coupling to the *cis*-phosphorus nucleus ($^{2}J_{C\text{-}P} \approx 3$ - 7 Hz) can also be observed for all species except **16b** for which only the large *trans*-phosphine coupling is resolvable. Coupling of the pair of olefinic carbons in the carbene moiety (C3, C4) to the *trans*-phosphine can also be observed ($^{4}J_{C\text{-}P} \approx 5$ Hz) in all cases. In the proton-coupled ^{13}C NMR spectrum, the resonance for the pendent protonated carbon appears as a doublet displaying approximately 220 Hz coupling to the attached acidic proton, as noted above for the Rh species **2**.

Through this "mapping" of every proton in the complex using decoupling and NOE experiments (see above), all other peaks in the $^{13}C\{^{1}H\}$ spectrum can be similarly assigned using gHSQC, gHMQC, and gHMBC 2D gradient spectral techniques. For example, although both peaks for both *tert*-butyl methyl carbons in **9b** (C1, C9, see Figure 2-9) appear *very* close to each other in the $^{13}C\{^{1}H\}$ spectrum, they can be differentiated through gHSQC (and gHMQC) correlation peaks with their respective attached protons (H1, H9, Figure 2-10), whose peaks were unambiguously separated using NOE experiments (*vide supra*).

Although all reactions involving monophosphines were carried out with an excess of phosphine, only in the cases of PMe_3 and PMe_2Ph did I^- substitution by a second phosphine occur (Scheme 2-3). This is presumably a result of steric repulsion between the phosphine and the nearby *tert*-butyl group since the somewhat larger, yet strongly basic triethylphosphine does not substitute a second iodide ion,

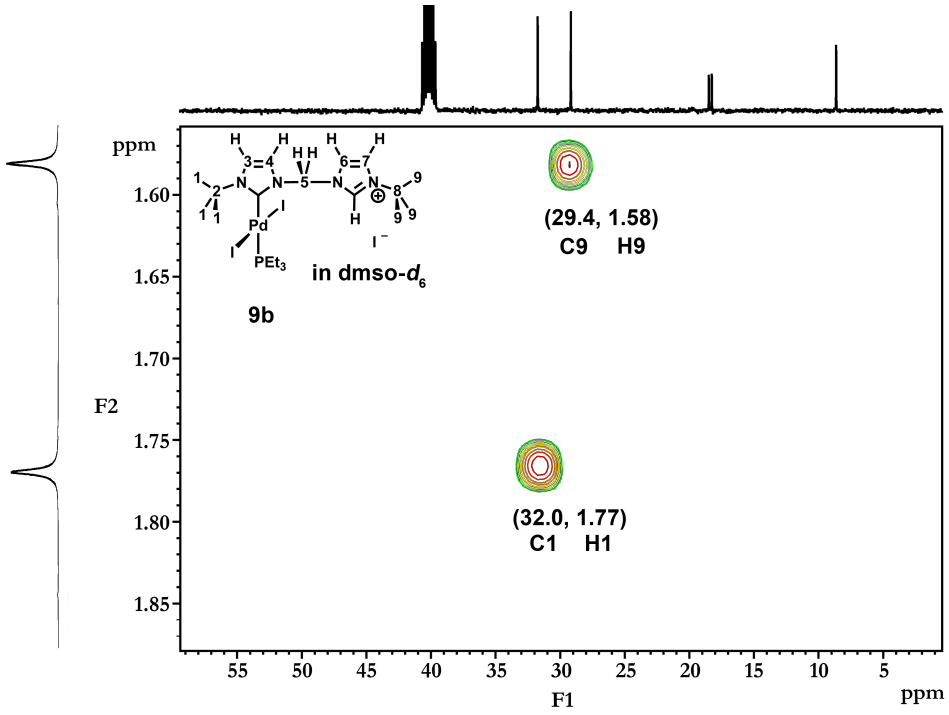


Figure 2-10. Expansion of gHSQC spectrum of compound **9b** showing ^{t}Bu correlation peaks.

even in the presence of a tenfold excess of phosphine. The only phosphines to give the double-substitution products were the two smallest studied. For the three chelating diphosphines studied, all have cone angles smaller than that of PEt_3,[16] and coordination of *both* ends of these diphosphines is additionally favoured entropically by the chelate effect.

The X-ray structure determinations for compounds **11b** and **13b**, shown in Figure 2-11, and of **16b**, shown in Figure 2-12 confirm the structural assignments determined on the basis of spectral data. In all three structures the geometry is typical of square-planar NHC complexes in which the carbene plane lies essentially perpendicular to the metal coordination plane, having a torsion angle defined by I(1), Pd, C(11), and N(11) of –93.1(3)° for **11b**; 86.1(2)° for **13b**; and –86.0(3)° for **16b**. The Pd–$C_{carbene}$ distances are also typical of such systems, suggesting a metal–carbon single bond. All three complexes display some degree of some degree of hydrogen

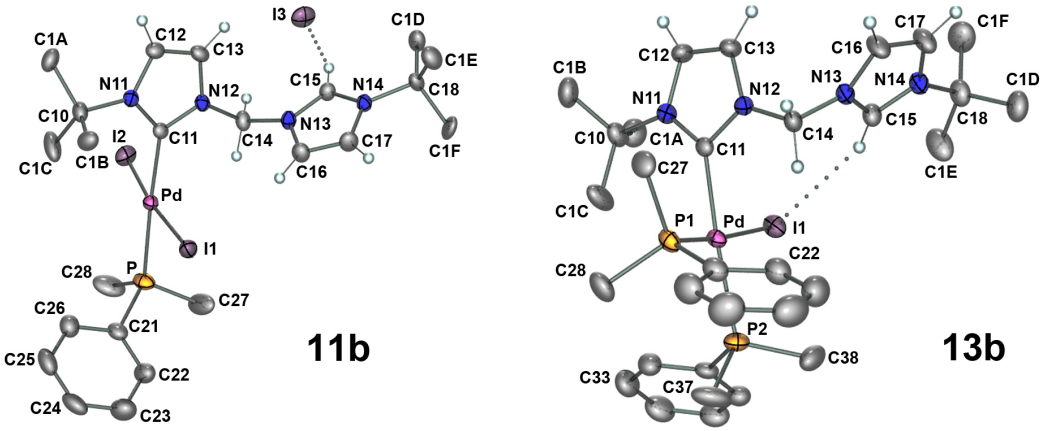


Figure 2-11. Three-dimensional representations of $[PdI_2(PMe_2Ph)(^{tBu}C\text{-}\kappa^1\text{-}C(H)^{meth})][I]$, **11b** and the dication complex $[PdI(PMe_2Ph)_2(^{tBu}C\text{-}\kappa^1\text{-}C(H)^{meth})][I]_2$, **13b** showing the numbering scheme. Thermal ellipsoids are as described in Figure 2-4. Hydrogen atoms are shown only on the pendent carbene/imidazolium group. Relevant parameters for **11b** (distances in Å and angles in deg.): Pd–C(11) = 2.049(4); N(12)–C(14)–N(13) = 110.6(3). Relevant parameters for **13b** (distances in Å and angles in deg.): Pd–C(11) = 2.052(2); N(12)–C(14)–N(13) = 111.0(2).

bonding involving the imidazolium proton and a nearby iodide ion, having H(15)–I contacts of 2.75 Å, 2.95 Å, and 2.94 Å for **11b**, **13b**, and **16b**, respectively, which are less than the sum of their van der Waals radii (r_w(H) = 1.20, r_w(I) = 1.98 Å)[87] of 3.18 Å.[87] In the case of compounds **11b** and **16b**, this hydrogen bond involves an iodide counterion, while for **13b** this is an inner-sphere interaction with the coordinated iodo ligand, forming an 8-membered pseudometallocycle (both interactions are diagrammed in Figure 2-11 and Figure 2-12). For compound **13b** an additional hydrogen bond of 2.87 Å appears between one of the outer-sphere iodide ions (I(2)) and one of the methylene hydrogens on the linker carbon C(14), while a similar interaction (I(3)–H(17) = 2.85 Å) involves a olefinic hydrogen of **16b** (not shown).

The strain within complex **16b**, resulting from diphosphine chelation to a square planar centre, is evident in the geometry within the depm group as well as in the angles about Pd. Within the diphosphine the P(1)–P(2) separation (2.691(1) Å) is much smaller than is usually observed in an unstrained depm moiety, where values

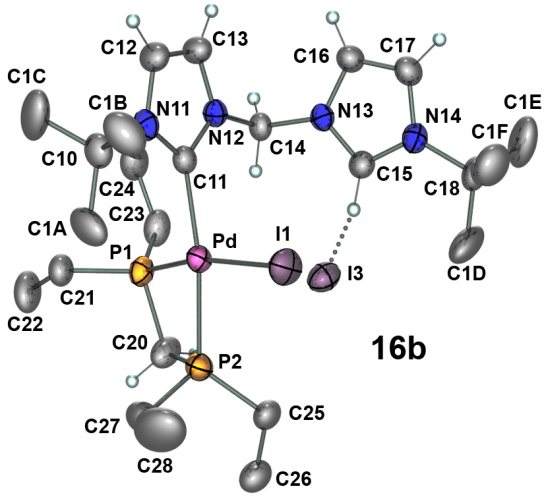


Figure 2-12. Three-dimensional representation of the cation complex [PdI(depm)($^{t\text{Bu}}$C-κ^1-C(H)^{meth})][I]$_2$, **16b** showing the numbering scheme. Thermal ellipsoids are as described in Figure 2-4. Hydrogen atoms are shown only on the pendent carbene/imidazoliaum group. Relevant parameters (distances in Å and angles in deg.): Pd–C(11) = 2.062(3); N(12)–C(14)–N(13) = 111.5(2)°, P(1)–C(20)–P(2) = 94.7(2), P(2)–Pd–C(11) = 170.58(8), I(1)–Pd–P(1) = 167.14(2).

near 3.05 Å are more typical,[46] and is accompanied by an acute P(1)–C(20)–P(2) angle (94.7(2)°) which is significantly less than the idealized 109.5°. Accompanying this strain, the P(1)–Pd–P(2) angle (72.29(3)°) is also compressed from the idealized 90°.

The C_2-linked analogue, [PdI$_3$($^{t\text{Bu}}$C-κ^1-C(H)^{eth})] (**7d**), in which the carbene is connected to the imidazolium ring by a C_2H_4 linker was also successfully prepared using a similar procedure to that used by Herrmann, *et al.* to generate [PdI$_3$($^{t\text{Bu}}$C-κ^1-C(H)^{meth})] (**7b**),[61] and a number of mono- (**9d**) and diphosphine (**14d**, **15d**) derivatives involving this C_2-linked carbene/imidazolium species have also been generated as described for the C_1-linked products (see Scheme 2-3). These species display NMR spectra very similar to those described for compounds **8b**-**11b** and **14b**-**15b**, respectively, as documented in Section 2.4.2. Interestingly, the peak corresponding to the carbene carbon in the triiodo zwitterion **7d** could not be observed in the

$^{13}C\{^{1}H\}$ NMR spectrum. This has also been reported by Herrmann, *et al.* for the C_1-linked system.[61]

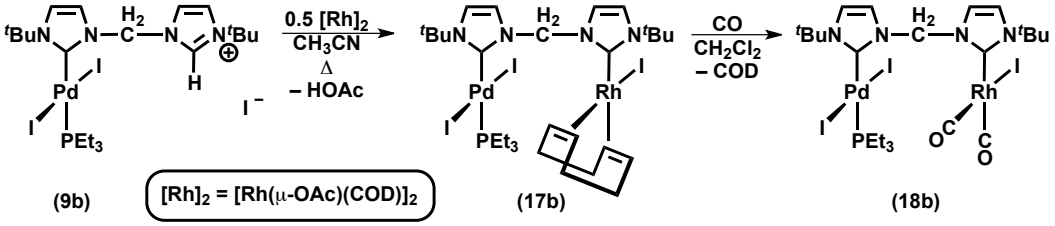
2.2.4 Mixed-metal, di-NHC-bridged heterobimetallic complexes

In our group's initial study,[46] we were able to prepare a binuclear dicarbene-bridged complex from a mononuclear, carbene-anchored/pendent-imidazolium precursor by deprotonating the pendent acidic imidazolium hydrogen of **2b** using a one-half-equivalent of $[Rh(\mu\text{-}OAc)(COD)]_2$ yielding the dirhodium target. Attempts to extend this strategy to generate mixed-metal complexes of rhodium using **2b**-**2d** as precursors and using the complexes $[Ir(\mu\text{-}OAc)(COD)]_2$, or $[Pd(OAc)_2]$, containing the basic acetate ligands, all failed. Although the ^{1}H NMR spectra indicate that deprotonation of the acidic proton on the imidazolium group has occurred (as evident from the absence of a high-frequency pseudotriplet), no evidence of a binuclear Rh/Ir or Rh/Pd product could be detected by NMR spectroscopy or high resolution mass spectrometry (HRMS).

However, using the reverse strategy, starting with carbene-anchored/pendent-imidazolium complexes of other metals and using $[Rh(\mu\text{-}OAc)(COD)]_2$ to perform the deprotonation has allowed us to successfully prepare dicarbene-bridged products of both Pd/Rh and Ir/Rh. Additionally, a number of related Pd/Ir systems can be generated by deprotonation of the pendent-imidazolium group by an *external* base in the presence of $[Ir(\mu\text{-}Cl)(COD)]_2$.

Using the first approach, the heterobimetallic Pd/Rh complex $[PdI_2(PEt_3)(\mu\text{-}^{t\text{Bu}}CC^{\text{meth}})RhI(COD)]$ (**17b**), can successfully be generated by reacting the carbene-anchored/pendent-imidazolium complex **9b** and half an equivalent of [Rh(μ-

OAc)(COD)]$_2$, as shown in Scheme 2-4. Deprotonation of the imidazolium moiety of **9b** and concomitant incorporation of Rh, yielding **17b**, is obvious in the spectral data. The high-frequency acidic proton of **9b** is conspicuously absent in the ^{1}H NMR spectrum and the olefinic protons remote from Pd no longer display coupling to this acidic proton, and now appear as doublets; whereas the olefinic protons adjacent to



Scheme 2-4. Synthesis of palladium/rhodium mixed-metal complexes **17b** and **18b**.

palladium still appear as pseudotriplets due to coupling to the *trans* phosphorus nucleus of the PEt_3 group (Figure 2-13). In addition, the loss of symmetry upon incorporation of the "RhI(COD)" moiety transforms the singlet resonance from the methylene protons of the linker in **9b** into an AB pattern in **17b**. The rhodium-coordinated COD protons display similar NMR spectral properties to those of the pendent Rh complexes noted earlier, displaying two resonance signals at *ca.* 5.2 ppm, and another set of multiplets at *ca.* 3.4 ppm, representing the protons on the olefinic moiety *trans* to the carbene and the iodide, respectively (because of the higher *trans*-influence of the NHC vs. the halide).[37] Only one multiplet from each set of resonances displays a through-space interaction (monitored *via* NOE experiments) with one of the ^{t}Bu signals, further confirming the perpendicular arrangement of the NHC ring to the Rh coordination plane.

In the $^{13}C\{^1H\}$ NMR spectra, two carbene moieties can now be observed; a doublet at δ = 160.8 ($^2J_{C\text{-}P}$ = 187.7 Hz) compares closely to that of the precursor **9b**

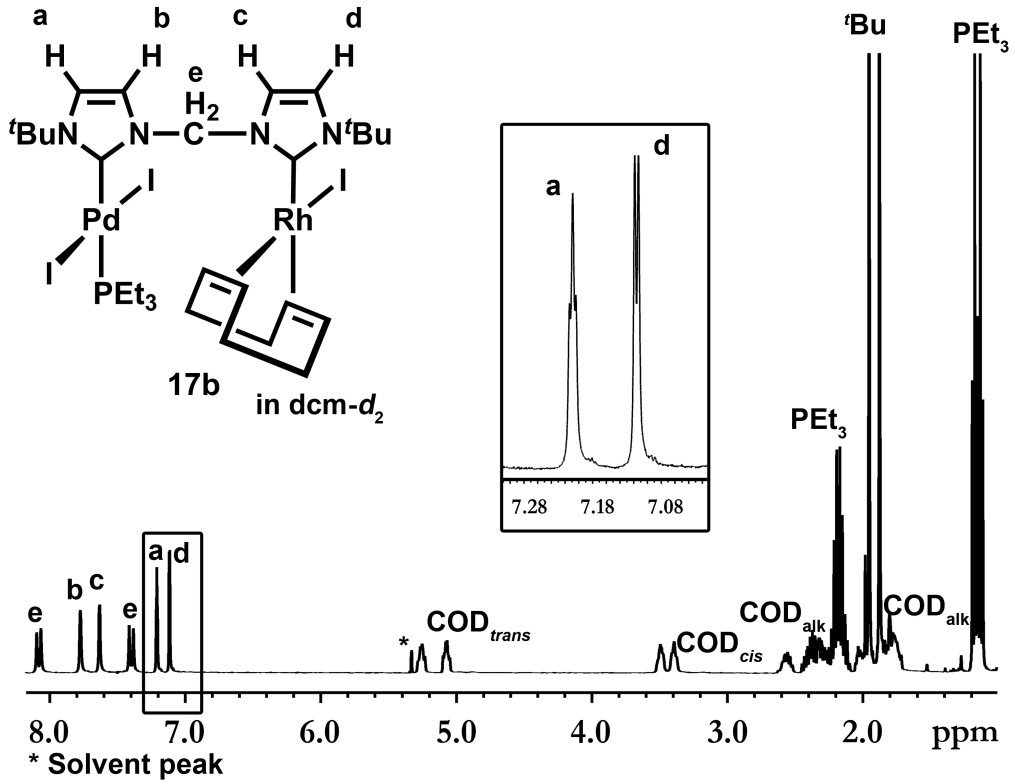


Figure 2-13. ^{1}H NMR spectrum (400 MHz) of compound **17b** in dcm-d_2, with expanded olefinic region.

(and other phosphine-containing Pd-carbenes) and again shows strong coupling to the *trans* phosphine while the other is at a significantly higher frequency (δ = 180.9) appearing in the region of other Rh-carbene species with typical coupling to Rh ($^1J_{C\text{-}Rh}$ = 49.3 Hz).[37, 46, 84-86] The remaining peaks display typical resonances for an unsymmetric di-NHC-bridging backbone, a Pd-coordinated PEt_3 ligand, and a Rh-coordinated COD ligand.

The X-ray structure determination for compound **17b**, shown in Figure 2-14 confirms the above assignment in which the two different metals are bridged by a di-NHC ligand. All parameters associated with this structure are typical of such NHC complexes. At each metal the NHC plane lies essentially perpendicular to the metal coordination plane and the metal-carbene distances are consistent with single bonds

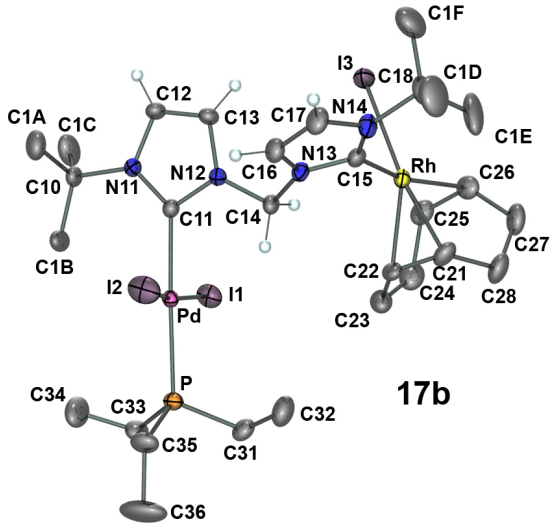


Figure 2-14. Three-dimensional representation of $[PdI_2(PEt_3)(\mu\text{-}^{t\text{Bu}}CC^{meth})RhI(COD)]$, **17b** showing the numbering scheme. Thermal ellipsoids are as described in Figure 2-4. Hydrogen atoms are shown only on the dicarbene backbone. Relevant parameters (distances in Å and angles in deg.): Pd–C(11) = 2.045(3), Rh–C(15) = 2.037(3), Rh–C(21) = 2.137(3), Rh–C(22) = 2.137(3), Rh–C(25) = 2.211(3), Rh–C(26) = 2.194(3); N(12)–C(14)–N(13) = 110.6(2), I(1)–Pd–I(2) = 170.08(1), I(1)–Pd–C(11)–N(11) = 93.3(3), I(3)–Rh–C(15)–N(14) = –91.9(3).

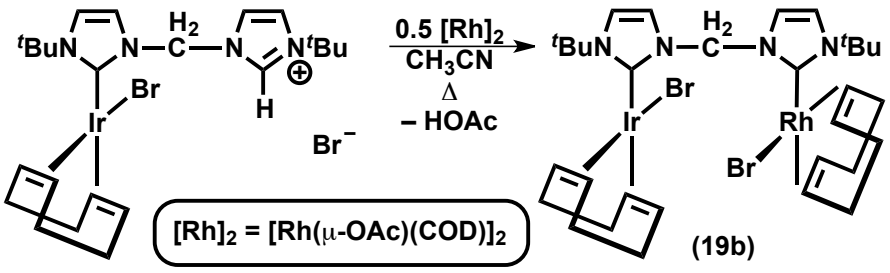
(Pd–C(11) = 2.045(3) Å, Rh–C(15) = 2.037(3) Å). The slightly longer Pd–C(11) distance may result from the larger *trans*-influence of the PEt_3 group. Consistent with such a proposal, this Pd–C(11) distance is very close to those in the phosphine compounds **11b** and **13b** (*vide infra*) and are substantially longer than the Pd-carbene distances in **7b**[61] and $[PdI_2(OAc)(^{t\text{Bu}}C\text{-}\kappa^1\text{-}C(H)^{meth})]$[61] (1.990(9) and 1.953(5) Å, respectively) in which iodo and acetate ligands, having a low *trans*-influence, are opposite the carbene. As is also typical of binuclear species bridged by only a di-NHC ligand, the dicarbene framework is twisted in such a way to allow the metal coordination planes to avoid each other. As a result the Pd–Rh separation is quite large, at 6.2054(5) Å. This skewing about the dicarbene methylene linker is shown clearly in Figure 2-14 and is evident by the dihedral angle of 71.4(1)° between the two NHC planes. Interestingly, the close contacts between part of the COD ligand

on Rh and the PEt_3 group on Pd, observed in the solid state, are also present in solution as shown by the NOE experiment noted above.

A gentle purge of carbon monoxide gas through a solution of **17b** readily results in substitution of COD and generation of the less sterically hindered carbonyl analogue $[PdI_2(PEt_3)(\mu\text{-}^{t\text{Bu}}CC^{meth})RhI(CO)_2]$ (**18b**, Scheme 2-4), as seen by the appearance of two carbonyl stretches at 2004 and 2076 cm^{-1} ($\nu_{C-O(avg)}$ = 2040 cm^{-1}) in the IR spectrum, along with two carbonyl peaks in the $^{13}C\{^1H\}$ NMR spectrum (δ = 187.2, 181.6) alongside the carbenes. The carbonyl resonances show coupling to rhodium ($^1J_{C\text{-}Rh}$ = 54.6 Hz; $^1J_{C\text{-}Rh}$ = 76.3 Hz), representing the carbonyl ligands *trans* to the carbene and iodo ligands, respectively, much as described earlier for **3c** and **3d**.

Attempts to generate di-NHC-bridged Pd/Rh complexes *via* deprotonation of the carbene-anchored/pendent-imidazolium Pd species **8**-**16** using $[Rh(\mu\text{-}OAc)(COD)]_2$ has only succeeded with **9b**, as noted above; all other attempts failed. Even the other very similar monophosphine complexes, **8b**, **9d**, **10b**, and **11b** did not generate the targeted Pd/Rh species using the conditions used to generate **17b**. In the reaction of compounds **14** and **15** (using both the C_1- and C_2-linked dicarbenes) trace amounts of the mixed-metal products could be detected by HRMS but these species were not detectable by NMR techniques.

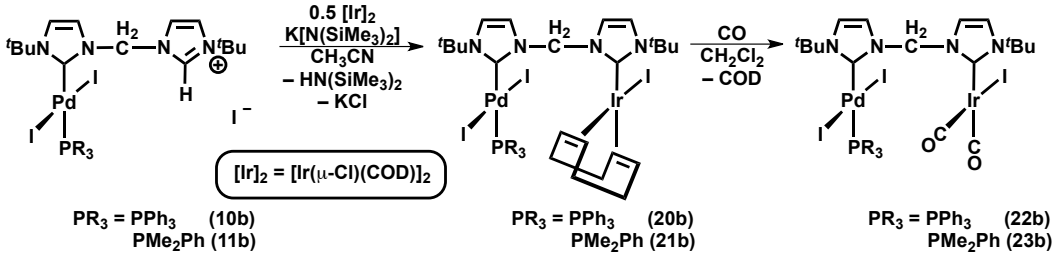
Using an identical strategy, deprotonation of the pendent imidazolium species, $[IrBr(COD)(^{t\text{Bu}}C\text{-}\kappa^1\text{-}C(H)^{meth})][Br]$ (the iodo analogue of which is known)[6] by $[Rh(\mu\text{-}OAc)(COD)]_2$ successfully yielded the mixed Ir/Rh product, $[IrBr(COD)(\mu\text{-}^{t\text{Bu}}CC^{meth})RhBr(COD)]$ (**19b**) as outlined in Scheme 2-5. The carbene carbons of the



Scheme 2-5. Synthesis of iridium/rhodium mixed-metal complex **19b**.

di-NHC groups are surprisingly close in the $^{13}C\{^1H\}$ NMR spectrum, at δ = 180.5 and 179.2, with the former being readily identified as being Rh-bound by the 50.1 Hz coupling to this metal.[37, 46, 84-86] Additionally, the appearance of two different resonances for the *N*-bound *tert*-butyl groups in the ^1H and $^{13}C\{^1H\}$ NMR spectra, combined with the absence of the high-frequency acidic proton in the ^1H NMR spectrum further support our formulation. Interestingly, reaction of **19b** with dppm or carbon monoxide did not yield the desired substituted products, but rather gave a mix of unidentified products. The instability of complex **19b** towards CO substitution parallels that of the analogous COD-substituted di-NHC-linked dirhodium complex mentioned earlier.[46]

Although the conditions employed to generate complex **17b**, using the "internal base method", failed when extended to other Pd pendent species, related mixed-metal species involving Pd can be obtained using milder conditions and an *external* base. In the presence of half an equivalent of a suitable Ir precursor, such as $[Ir(\mu\text{-}Cl)(COD)]_2$, the pendent-imidazolium arm of the monophosphine-containing **10b** and **11b** can be deprotonated using $K[N(SiMe_3)_2]$, presumably generating a transient Pd carbene-anchored/pendent-carbene intermediate which subsequently attacks the Ir dimer, forming the desired di-NHC-bridged mixed-metal species $[PdI_2(PR_3)(\mu\text{-}^{t\text{Bu}}CC^{meth})IrI(COD)]$ (PR_3 = PPh_3 (**20b**); PMe_2Ph (**21b**); Scheme 2-6).



Scheme 2-6. Synthesis of palladium/iridium mixed-metal complexes.

Although the high solubility of both complexes in most solvents did not allow us to obtain single crystals, the spectral data leave little doubt about their formulations. The carbene carbons of the di-NHC groups in the $^{13}C\{^{1}H\}$ NMR spectrum appear at *ca.* 177.9 ppm and *ca.* 168.2 ppm, with the latter being readily identified as Pd-bound by the *ca.* 212 Hz coupling to the *trans* phosphorus nucleus. As was observed in the Pd/Rh and Ir/Rh complexes, the appearance of two different resonances for the *N*-bound *tert*-butyl groups in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra combined with the absence of the high-frequency acidic proton in the ^{1}H NMR spectrum further support our formulation. Additionally, the AB pattern observed for the protons of the C_1 linker suggest the plane bisecting the linking CH_2 group is now unsymmetrical on each side, confirming the replacement of a pendent proton with an "IrBr(COD)" moiety. As a result, the methyl protons of the PMe_2Ph moiety in **21b** have become diastereotopic, giving rise to a set of two doublets in the ^{1}H NMR spectrum ($^{2}J_{H\text{-}P} \approx 10$ Hz), as well as a corresponding pair in the $^{13}C\{^{1}H\}$ NMR spectrum ($^{1}J_{C\text{-}P} \approx 33$ Hz).

A gentle purge of carbon monoxide gas through a dcm solution of both **20b** and **21b** readily results in substitution of COD generating the carbonyl analogues $[PdI_2(PPh_3)(\mu\text{-}^{t\text{Bu}}CC^{meth})IrI(CO)_2]$ (**22b**) and $[PdI_2(PMe_2Ph)(\mu\text{-}^{t\text{Bu}}CC^{meth})IrI(CO)_2]$ (**23b**), respectively, as seen by the appearance of two carbonyl stretches in the IR

spectra (1987 and 2065 cm^{-1} (**22b**); 1986 and 2065 cm^{-1} (**23b**)) along with two carbonyl resonances in the $^{13}C\{^1H\}$ NMR spectrum (δ = 169.7, 167.1 (**22b**); δ = 169.6, 167.5 (**23b**)) alongside the carbene peaks. The $\nu_{C-O(avg)}$ values (~2026 cm^{-1} for both **22b** and **23b**) indicate typical electron-donating abilities for unsaturated NHCs.[88, 91] The AB pattern resonances representing the methylene protons (previously buried under the multiplets of the aromatic region in **21b**) shift to a lower frequency in **23b** (*ca.* 6.98 ppm) upon replacement of COD by two carbonyl ligands, distancing themselves from the phenyl resonances.

Section 2.3 Discussion

Our strategy of using carbene-anchored/pendent-imidazolium complexes as precursors for di-NHC-bridged, mixed-metal complexes *via* deprotonation of the pendent imidazolium salt through an internal base route has succeeded in two cases, but has to date been surprisingly unproductive with the majority of closely related mononuclear precursors studied. On the basis of our group's successful syntheses of di-NHC-bridged complexes of dirhodium using the basic acetate ligands of $[Rh(\mu\text{-}OAc)(COD)]_2$ to deprotonate the imidazolium salts, we had anticipated that this approach should be quite general for the generation of mixed-metal analogues. However, one problem with this method appears to be the rather harsh conditions necessary for deprotonation of the imidazolium group, requiring extended reflux in acetonitrile. Even for the first deprotonation, to give the carbene-anchored/pendent-imidazolium precursors, conditions need to be carefully controlled for imidazolium deprotonation and successful incorporation of the metal. So although we have successfully generated three of four members of a series of

carbene-anchored/pendent-imidazolium precursors of Rh, the fourth member, [RhBr(COD)(^{Me}C-κ^1-C(H)^{meth})][Br] has remained elusive. It appears that successful deprotonation of the pendent imidazolium group and incorporation of the second metal, using the same strategy, is equally sensitive to reaction conditions, and is additionally plagued by the tendency of the dicarbenes to chelate rather than bridge.

The lack of success in generating the di-NHC-bridged Pd/Rh species utilizing the zwitterionic [PdI$_3$($^{t\text{Bu}}$C-κ^1-C(H)^{meth})] (**7b**) and [PdI$_3$($^{t\text{Bu}}$C-κ^1-C(H)^{eth})] (**7d**) is probably not surprising, since deprotonation of the imidazolium group by the Rh-bound acetate group leaves a three-coordinate Rh centre after carbene incorporation. Although such a three-coordinate Rh centre should be stabilized through binding of acetonitrile solvent, generation of binuclear species using this stepwise strategy has only been successful when replacement of the acetate group by a halide occurs. No free halide is available in **7b** and **7d**, and the sharing of a Pd-bound iodo ligand in a bridging arrangement may not be favourable. However, the lack of success in the case of the monophosphine (**8**-**13**) and diphosphine (**14**-**16**) complexes, in which iodo counterions are available, remains puzzling. It was expected that upon generation of the targeted Pd/Rh complex, using the diphosphine-chelated Pd complexes **14**-**16**, the diphosphine could easily unwind to bridge the metals, thereby locking the metals into close proximity. However, it appears that these systems are not well suited for the harsh conditions required for deprotonation of the weakly acidic imidazolium group. It is especially surprising that the monophosphine complexes **8**, **9d**, **10**, and **11** did not yield di-NHC-bridged Pd/Rh complexes, when the closely analogous [PdI$_2$(PEt$_3$)($^{t\text{Bu}}$C-κ^1-C(H)^{eth})][I] (**9b**) did yield the mixed-metal target.

In spite of the convenience in using a metal-coordinated base to effect the deprotonation of pendent imidazolium groups, we sought to avoid the harsh conditions noted above by using an external strong base to bring about this deprotonation under milder conditions, in the presence of a complex containing the second metal. Using this strategy, we have been able to successfully prepare the first examples of a di-NHC-bridged Pd/Ir system using potassium *bis*(trimethylsilyl)amide as an external base. Although this method generates a substantial number of unwanted byproducts (including di-NHC-chelated species), the desired products are indeed observable *via* NMR spectroscopy and can be isolated from the rest of crude mixture. Various Pd/Rh combinations (not yet accessible using [Rh(μ-OAc)(COD)]$_2$) also seem possible, although not pursued in this thesis. The importance of choice of base for deprotonating the imidazolium group in pendent imidazolium complexes has previously been noted.[68]

In any case, these strategies have been successful in generating the first unambiguously characterized examples of di-NHC-bridged heterobinuclear complexes,[68] and catalytic studies involving the Rh/Pd compound **17b** will be discussed in Chapter 6. Future work could also focus on other ways of converting the pendent imidazolium group to a metal-bound carbene, such as the use of Ag_2O in order to generate dicarbene-bridged M/Ag species as carbene-transfer agents for accessing other M/M′ combinations, or through the oxidative addition of the imidazolium C–H bond to a suitable electron-rich metal precursor (*i.e.*, Ni(COD)$_2$, Pd(PPh$_3$)$_4$, etc.).[96]

Section 2.4 Experimental Procedures

2.4.1 General comments

Deuterated solvents used for NMR experiments were freeze-pump-thaw degassed and stored under argon over type 4A molecular sieves. Reactions were performed under an inert argon atmosphere or the reactant gas using standard Schlenk techniques. Unless otherwise specified, reactions were carried out at ambient temperature. Ammonium carbonate, *tert*-butylamine, 1,5-cyclooctadiene, 1,2-dibromoethane, dibromomethane, *bis*(diphenylphosphino)methane (dppm), formaldehyde, glyoxal, 1-methylimidazole, palladium(II) acetate, potassium *bis*(trimethylsilyl)amide, triethylphosphine, triphenylphosphine, and sodium iodide were purchased from Aldrich; diammonium hexachloroiridate(III), 1,2-*bis*(diphenyl-phosphino)ethane (dppe), dimethylphenylphosphine, trimethylphosphine, and rhodium(III) chloride hydrate were purchased from Strem; potassium bromide was purchased from BDH; and sodium acetate was purchased from Fischer Scientific. All chemicals were used without further purification, with the exception of sodium acetate, which was purified by repetitive melting under dynamic vacuum before use. 1-*tert*-Butylimidazole[91] was prepared using a modified, higher-yielding procedure[97] and purified by vacuum distillation. The preparations of diimidazolium salts used in this chapter have been reported;[6, 12, 29, 98] however, a general synthetic approach has been outlined below. *Bis*(diethylphosphino)methane (depm) was prepared using published procedures and used without further purification,[99] as was *bis*(cycloocta-1,5-diene)(μ-dichloro)dirhodium ($[Rh(\mu\text{-}Cl)(COD)]_2$)[100, 101] and *bis*(cycloocta-1,5-diene)(μ-dichloro)diiridium ($[Ir(\mu\text{-}Cl)(COD)]_2$).[102] *Bis*(cycloocta-1,5-diene)(μ-diacetato)dirhodium ($[Rh(\mu\text{-}OAc)(COD)]_2$) was prepared as previously reported and

recrystallized from ethyl acetate.[103] The pendent complex methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene]bromo(η^2,η^2-cycloocta-1,5-diene)iridium(I) bromide was prepared similarly to the reported iodo analogue;[6] while methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene]triiodo-palladium(II) was prepared as previously reported.[61] The ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Varian DirectDrive 500 MHz, iNova-500, or iNova-400 spectrometer operating at 499.82, 498.12, or 399.79 MHz for ^{1}H; 125.68, 125.26, or 100.53 MHz for $^{13}C\{^{1}H\}$; and 202.33, 201.64, or 161.8 MHz for ^{31}P, respectively; or on a Varian iNova-300 operating at 299.97 MHz for ^{1}H. The ^{1}H and $^{13}C\{^{1}H\}$ chemical shifts are referenced to TMS; whereas the $^{31}P\{^{1}H\}$ chemical shifts are referenced to 85% H_3PO_4 in H_2O. The order of appearance of chemical shift assignments are based on their region in the molecule rather than increasing or decreasing frequency of their resonance. Elemental Analyses were performed by the microanalytical service within this department. Likewise, mass spectrometric analyses were performed by the departmental Mass Spectrometry Laboratory using positive ion electrospray ionization on a Micromass ZabSpec Hybrid Sector-TOF or an Agilent Technologies 6220 Accurate-mass TOF LC/MS. Infrared spectra were obtained using a Nicolet Avatar 370DGTS instrument. Carbonyl stretches reported are for non-isotopically enriched samples. Conductivity measurements on compounds **10b** and **15b** as the iodide salts were carried out on 1×10^{-3} M solutions in nitromethane using a Yellow Springs Instruments Model 31 conductivity bridge. For these species the molar conductivity of their electrolytic solutions were $\Lambda = 8.28 \times 10^{-3}$ and 1.352×10^{-2} $S \cdot m^2\ mol^{-1}$, respectively.

2.4.2 Preparation of compounds

(i) General synthetic route to diimidazolium salts (1a-d). A 500 mL round-bottom flask was charged with 100 mmol of the dibromoalkane and dissolved in 200 mL of toluene. An excess (250 mmol) of the 1-alkylimidazole was then added and the solution refluxed for 24 h. The resulting precipitate was collected by vacuum filtration and recrystallized from boiling methanol by cooling to –25 °C, whereupon colourless crystals were obtained in yields ranging from 50 to 90%. The salts were then dried *in vacuo* for several days to remove residual solvent and stored in a desiccator before use. In this chapter we use the abbreviations originally suggested by Green *et al.*,[43] with compounds **1a-d** as diprotonated versions of the respective dicarbenes $^{Me}CC^{meth}$ (**a**), $^{tBu}CC^{meth}$ (**b**), $^{Me}CC^{eth}$ (**c**), $^{tBu}CC^{eth}$ (**d**) as dibromide salts, namely 1,1′-(methylene)-3,3′-dimethyldiimidazolium-2,2′-diylidene dibromide (**1a**), 1,1′-(methylene)-3,3′-di-*tert*-butyldiimidazolium-2,2′-diylidene dibromide (**1b**), 1,1′-(1,2-ethylene)-3,3′-dimethyldiimidazolium-2,2′-diylidene dibromide (**1c**), and 1,1′-(1,2-ethylene)-3,3′-di-*tert*-butyldiimidazolium-2,2′-diylidene dibromide (**1d**). As an adaptation of these abbreviations, the carbene-anchored/pendent-imidazolium ligands are designated as $^{Me}C\text{-}\kappa^1\text{-}C(H)^{meth}$, $^{tBu}C\text{-}\kappa^1\text{-}C(H)^{meth}$, $^{Me}C\text{-}\kappa^1\text{-}C(H)^{meth}$, and $^{tBu}C\text{-}\kappa^1\text{-}C(H)^{eth}$.

(ii) Ethylene[(*N*-methyl)imidazolium][(*N*-methyl)imidazole-2-ylidene)bromo(η^2,η^2-cycloocta-1,5-diene)rhodium(I)] bromide, [RhBr(COD)-($^{Me}C\text{-}\kappa^1\text{-}C(H)^{eth}$))][Br] (2c). A 20 mL portion of acetonitrile was added to a solid mixture containing **1c** (0.422 g, 1.17 mmol) and $[Rh(\mu\text{-}OAc)(COD)]_2$ (0.301 g, 0.557 mmol). The resulting slurry was stirred for 18 h under reflux conditions and cooled

to room temperature. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of dcm. A 45 mL portion of diethyl ether was added to precipitate a white solid and the solution filtered *via* cannula. The solvent was removed under reduced pressure, giving 0.261 g (83%). ^{1}H NMR (399.79 MHz, dcm-d_2, 27.0 °C): 10.18 (br dd, 1H, $^{4}J_{H\text{-}H}$ = 1.9 Hz, $^{4}J_{H\text{-}H}$ = 1.9 Hz, NCHN); 7.90 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.9 Hz, $^{4}J_{H\text{-}H}$ = 1.9 Hz), 7.15 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.9 Hz, $^{4}J_{H\text{-}H}$ = 1.9 Hz, $NCH_{imid\text{-}H}$); 4.03 (s, 3H, $N_{imid\text{-}H}CH_3$); 7.22 (d, 1H, $^{3}J_{H\text{-}H}$ = 1.9 Hz), 6.76 (d, 1H, $^{3}J_{H\text{-}H}$ = 1.9 Hz, $NCH_{imid\text{-}Rh}$); 3.96 (s, 3H, $N_{imid\text{-}Rh}CH_3$); 5.60 (m, 1H), 5.12 (m, 2H), 4.99 (m, 1H, NCH_2CH_2N); 5.09 (m, 1H), 4.99 (m, 1H), 3.48 (m, 1H), 3.30 (m, 1H), 2.41 (m, 4H), 1.97 (m, 4H, COD). ^{13}C{^{1}H} NMR (125.68 MHz, dcm-d_2, 27.0 °C): 182.8 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 50.1 Hz, $C_{carbene}$); 124.1 (s, 1C, $NCH_{imid\text{-}Rh}$); 123.3 (s, 1C, $NCH_{imid\text{-}Rh}$); 36.9 (s, 1C, $N_{imid\text{-}Rh}CH_3$); 135.8 (s, 1C, $NCHN_{imid\text{-}H}$); 122.4 (s, 1C, $NCH_{imid\text{-}H}$); 122.3 (s, 1C, $NCH_{imid\text{-}H}$); 38.1 (s, 1C, $N_{imid\text{-}H}CH_3$); 50.0 (s, 1C), 49.6 (s, 1C, CH_2CH_2); 98.9 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 7.0 Hz), 98.5 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 7.0 Hz), 71.0 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 15.0 Hz), 69.5 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 15.0 Hz), 33.5 (s, 1C), 32.3 (s, 1C), 30.0 (s, 1C), 28.6 (s, 1C, COD). HRMS *m/z* Calcd for $C_{18}H_{27}BrN_4Rr$ ($M^+ - Br^-$): 481.0469. Found: 481.0470 ($M^+ - Br^-$). Anal Calcd for $C_{18}H_{27}Br_2N_4Rh \bullet 0.17\ CH_2Cl_2$: C, 37.85; H, 4.78; N, 9.72. Found: C, 37.63; H, 4.83; N, 9.88. The presence of 0.17 equivalents of dcm was confirmed by ^{1}H NMR spectroscopy in chloroform.

(iii) Ethylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)bromo-(η^2,η^2-cycloocta-1,5-diene)rhodium(I)] bromide, [RhBr(COD)-($^{t\text{Bu}}$C-κ^1-C(H)^{meth})][Br] (2d). The desired complex was prepared as described for **2c**, using **1d** (0.818 g, 1.88 mmol) and [Rh(μ-OAc)(COD)]$_2$ (0.507 g, 0.938 mmol) in 40 mL of acetonitrile, heated at reflux for 75 h. The crude product was purified as

described for **2c**, and isolated using 10 mL of dcm and 45 mL of diethyl ether, resulting in 0.835 g (69%) of a yellow solid. ^{1}H NMR (399.79 MHz, dcm-d_2, 27.0 °C): 9.93 (dd, 1H, $^{4}J_{H\text{-}H}$ = 2.2 Hz, $^{4}J_{H\text{-}H}$ = 2.2 Hz, NCHN); 7.98 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.2 Hz, $^{4}J_{H\text{-}H}$ = 2.2 Hz), 7.29 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.2 Hz, $^{4}J_{H\text{-}H}$ = 2.2 Hz, $NCH_{imid\text{-}H}$); 1.94 (s, 3H, $N_{imid\text{-}H}C(CH_3)_3$); 7.16 (d, 1H, $^{3}J_{H\text{-}H}$ = 2.2 Hz), 6.96 (d, 1H, $^{3}J_{H\text{-}H}$ = 2.2 Hz, $NCH_{imid\text{-}Rh}$); 1.66 (s, 3H, $N_{imid\text{-}Rh}C(CH_3)_3$); 5.66 (m, 2H), 5.31 (m, 1H), 5.04 (m, 1H, NCH_2CH_2N); 5.07 (m, 1H), 4.94 (m, 1H), 3.42 (m, 1H), 3.30 (m, 1H), 2.39 (m, 4H), 1.89 (m, 2H), 1.65 (m, 2H, COD). $^{13}C\{^{1}H\}$ NMR (100.54 MHz, dcm-d_2, 27.0 °C): 180.5 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 49.4 Hz, $C_{carbene}$); 120.0 (s, 1C, $NCH_{imid\text{-}Rh}$); 118.7 (s, 1C, $NCH_{imid\text{-}Rh}$); 59.0 (s, 1C), 32.1 (s, 3C, $N_{imid\text{-}Rh}C(CH_3)_3$); 135.8 (s, 1C, $NCHN_{imid\text{-}H}$); 122.8 (s, 1C, $NCH_{imid\text{-}H}$); 124.0 (s, 1C, $NCH_{imid\text{-}H}$); 60.4, (s, 1C), 30.0 (s, 3C, $N_{imid\text{-}H}C(CH_3)_3$); 51.6 (s, 1C), 48.9 (s, 1C, CH_2CH_2); 96.8 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 7.5 Hz), 94.1 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 6.9 Hz), 71.9 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 15.4 Hz), 70.3 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 14.1 Hz), 32.8 (s, 1C), 31.4 (s, 1C), 29.5 (s, 1C), 29.0 (s, 1C, COD). HRMS *m*/*z* Calcd for $C_{24}H_{39}BrN_4Rh$ ($M^+ - Br^-$): 565.1408. Found: 565.1410 ($M^+ - Br^-$). Anal Calcd for $C_{24}H_{39}Br_2N_4Rh$: C, 44.60; H, 6.08; N, 8.67. Found: C, 44.95; H, 6.21; N, 8.60.

(iv) Ethylene[(*N*-methyl)imidazolium][(*N*-methyl)imidazole-2-ylidene)bromodicarbonylrhodium(I)] bromide, $[RhBr(CO)_2(^{Me}C\text{-}\kappa^1\text{-}C(H)^{eth})][Br]$ (3c). A 10 mL portion of dcm was added to a flask containing **2c** (0.175 g, 0.311 mmol). A 15 min gentle purge of CO to a stirring solution yielded a more pale yellow solution. The conversion to the respective dicarbonyl complex **3c** was accompanied by the facile loss of 1,5-cyclooctadiene and was monitored to completion using ^{1}H NMR spectroscopy. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of dcm. A 30 mL

portion of diethyl ether was added to precipitate an oily pale yellow solid, which was washed with 3 × 25 mL portions of *n*-pentane before drying *in vacuo*, giving 0.157 g (85%). ^{1}H NMR (399.79 MHz, dcm-d_2, 27.0 °C): 10.11 (br dd, 1H, NCHN); 7.62 (br dd, 1H), 7.15 (br dd, 1H, $NCH_{imid\text{-}H}$); 3.98 (s, 3H, $N_{imid\text{-}H}CH_3$); 7.72 (d, 1H, $^{3}J_{H\text{-}H}$ = 1.7 Hz), 6.96 (d, 1H, $^{3}J_{H\text{-}H}$ = 1.7 Hz, $NCH_{imid\text{-}Rh}$); 3.86 (s, 3H, $N_{imid\text{-}Rh}CH_3$); 5.56 (br m, 3H), 5.33 (br m, 1H, NCH_2CH_2N). ^{13}C{^{1}H} NMR (125.68 MHz, dcm-d_2, 27.0 °C): 186.2 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 53.6 Hz), 182.1 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 76.2 Hz, CO); 173.7 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 42.6 Hz, $C_{carbene}$); 138.1 (s, 1C, NCHN); 124.2 (s, 1C), 123.6 (s, 1C), 123.4 (s, 1C), 122.7 (s, 1C, NCH); 50.3 (s, 1C), 49.6 (s, 1C, CH_2CH_2); 38.8 (s, 1C), 37.0 (s, 1C, NCH_3). IR (solution, cm^{-1}): 2083 (CO), 2007 (CO). HRMS *m*/*z* Calcd for $C_{12}H_{15}BrN_4O_2Rh$ ($M^+ - Br^-$): 428.9428. Found: 428.9427 ($M^+ - Br^-$). Compound **3c** could only be isolated as an oil so satisfactory elemental analyses could not be obtained.

(v) Ethylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)bromodicarbonylrhodium(I)] bromide, [RhBr(CO)$_2$($^{t\text{Bu}}$C-κ^1-C(H)^{eth})][Br] (3d). The desired complex was prepared as described for **3c** using **2d** (0.152 g, 0.235 mmol), and the crude product purified using 10 mL of dcm and 25 mL of diethyl ether, to precipitate an oily pale yellow solid, which was then washed with 2 × 25 mL portions of *n*-pentane before drying *in vacuo*, giving 0.104 g (87%). ^{1}H NMR (299.97 MHz, dcm-d_2, 27.0 °C): 10.01 (dd, 1H, $^{4}J_{H\text{-}H}$ = 1.8 Hz, $^{4}J_{H\text{-}H}$ = 1.8 Hz NCHN); 7.90 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.8 Hz, $^{4}J_{H\text{-}H}$ = 1.8 Hz), 7.51 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.8 Hz, $^{4}J_{H\text{-}H}$ = 1.8 Hz, $NCH_{imid\text{-}H}$); 1.94 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 7.60 (d, 1H, $^{3}J_{H\text{-}H}$ = 2.0 Hz), 7.35 (d, 1H, $^{3}J_{H\text{-}H}$ = 2.0 Hz, $NCH_{imid\text{-}Rh}$); 1.82 (s, 9H, $N_{imid\text{-}Rh}C(CH_3)_3$); 5.70 (br m, 2H), 5.31 (br m, 2H, NCH_2CH_2N). ^{13}C{^{1}H} NMR (100.54 MHz, dcm-d_2, 27.0 °C):

186.2 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 54.2 Hz), 182.3 (d, $^{1}J_{C\text{-}Rh}$ = 77.8 Hz, CO); 171.5 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 42.1 Hz, $C_{carbene}$); 136.0 (s, 1C, NCHN); 124.7 (s, 1C), 122.9 (s, 1C), 120.7 (s, 1C), 118.8 (s, 1C, NCH); 59.3 (s, 1C), 30.0 (s, 3C, $N_{imid\text{-}Rh}C(CH_3)_3$); 60.8 (s, 1C), 32.1 (s, 3C, $N_{imid\text{-}H}C(CH_3)_3$); 51.7 (s, 1C), 48.4 (s, 1C, CH_2CH_2). IR (solution, cm^{-1}): 2081 (CO), 2005 (CO). HRMS *m/z* Calcd for $C_{18}H_{27}BrN_4O_2Rh$ ($M^+ - Br^-$): 513.0367. Found: 513.0366 ($M^+ - Br^-$). Compound **3d** could only be isolated as an oil so satisfactory elemental analyses could not be obtained.

(vi) Ethylene[(*N*-methyl)imidazolium][(*N*-methyl)imidazole-2-ylidene)bromo(*bis*(diphenylphosphino)methane-κ^1*P*:κ^1*P*′)rhodium(I)] bromide, [RhBr(dppm)(^{Me}C-κ^1-C(H)^{eth})][Br] (4c). A 10 mL portion of dcm was added to a solid mixture containing **2c** (0.049 g, 0.087 mmol) and dppm (0.039 g, 0.101 mmol). The resulting solution bleached to a paler yellow immediately. ^{1}H NMR (299.97 MHz, dcm-d_2, 27.5 °C): 10.15 (br s, 1H, NCHN); 7.21 (br s, 1H), 6.79 (br, 1H, $NCH_{imid\text{-}H}$); 3.95 (s, 3H, $N_{imid\text{-}H}CH_3$); 8.04 (d, 1H, $^{3}J_{H\text{-}H}$ = 1.8 Hz), 6.79 (br s, 1H, $NCH_{imid\text{-}Rh}$); 3.91 (s, 3H, $N_{imid\text{-}Rh}CH_3$); 4.44 (m, 2H), 4.09 (m, 2H, NCH_2CH_2N); 8.04 (m, 4H), 7.34 (m, 16H, Ph); 5.88 (ddd, 1H, $^{2}J_{H\text{-}H}$ = 13.7 Hz, $^{2}J_{H\text{-}P}$ = 9.7 Hz, $^{2}J_{H\text{-}P}$ = 6.5Hz), 4.70 (ddd, 1H, $^{2}J_{H\text{-}H}$ = 13.7 Hz, $^{2}J_{H\text{-}P}$ = 3.6 Hz, $^{2}J_{H\text{-}P}$ = 3.6 Hz, PCH_2P).^{31}P{^{1}H} NMR (161.84 MHz, dcm-d_2, 27.0 °C): –13.6 (dd, 1P, $^{1}J_{P\text{-}Rh}$ = 172.8 Hz, $^{2}J_{P\text{-}P}$ = 95.9 Hz), –36.0 (dd, 1P, $^{1}J_{P\text{-}Rh}$ = 103.9 Hz, $^{2}J_{P\text{-}P}$ = 95.9 Hz, dppm). The transient nature of the product precluded the acquisition of ^{13}C{^{1}H} NMR spectra and elemental analyses.

(vii) Ethylene[(*N*-methyl)imidazolium][(*N*-methyl)imidazole-2-ylidene)bromo(1,2-*bis*(diphenylphosphino)ethane-κ^1*P*:κ^1*P*′)rhodium(I)] bromide, [RhBr(dppe)(^{Me}C-κ^1-C(H)^{eth})][Br] (5c). The desired complex was

prepared as described for **4c** using **2c** (0.087 g, 0.155 mmol) and dppe (0.062 g, 0.156 mmol). The resulting solution bleached to a paler yellow immediately. ^{1}H NMR (299.97 MHz, dcm-d_2, 27.5 °C): 10.12 (br s, 1H, NCHN); 7.92 (br s, 1H), 7.07 (br s, 1H, $NCH_{imid\text{-}H}$); 3.92 (s, 3H, $N_{imid\text{-}H}CH_3$); 6.87 (br s, 1H), 6.65 (br s, 1H, $NCH_{imid\text{-}Rh}$); 3.72 (s, 3H, $N_{imid\text{-}Rh}CH_3$); 7.98 (m, 4H, NCH_2CH_2N); 7.33 (m, 20H, Ph); 2.02 (m, 4H, PCH_2CH_2P). ^{31}P{^{1}H} NMR (161.84 MHz, dcm-d_2, 27.0 °C): 72.9 (dd, 1P, $^{1}J_{P\text{-}Rh}$ = 197.6 Hz, $^{2}J_{P\text{-}P}$ = 33.4 Hz), 57.4 (dd, 1P, $^{1}J_{P\text{-}Rh}$ = 125.3 Hz, $^{2}J_{P\text{-}P}$ = 33.4 Hz, dppe). The transient nature of the product precluded the acquisition of ^{13}C{^{1}H} NMR spectra and elemental analyses.

(viii) Ethylene[(*N*-methyl)imidazolium][(*N*-methyl)imidazole-2-ylidene)bromo(*bis*(diethylphosphino)methane-κ^{1}*P*:κ^{1}*P′*)rhodium(I)] bromide, [RhBr(depm) (^{Me}C-κ^{1}-C(H)^{eth})][Br] (6c). A 10 mL portion of dcm was added to a flask containing **2c** (0.050 g, 0.089 mmol). The resulting solution was stirred for 10 min afterwhich depm (30.2 μL, 0.134 mmol) was injected into the reaction vessel bleaching the solution to a paler yellow immediately. ^{1}H NMR (400.39 MHz, dcm-d_2, 27.0 °C): 10.29 (br s, 1H, NCHN); 7.90 (br s, 1H), 6.77 (br s, 1H, $NCH_{imid\text{-}H}$); 3.97 (s, 3H, $N_{imid\text{-}H}CH_3$); 8.16 (br s, 1H), 7.03 (br s, 1H, $NCH_{imid\text{-}Rh}$); 3.91 (s, 3H, $N_{imid\text{-}Rh}CH_3$); 5.10 (m, 4H, NCH_2CH_2N); 2.41 (m, 2H), 1.82 (m, 8H), 1.28 (m, 5H), 0.97 (m, 5H, PEt_2); 5.90 (ddd, 1H, $^{2}J_{H\text{-}H}$ = 14.2 Hz, $^{2}J_{H\text{-}P}$ = 11.9 Hz, $^{2}J_{H\text{-}P}$ = 6.9Hz), 4.89 (ddd, 1H, $^{2}J_{H\text{-}H}$ = 14.2 Hz, $^{2}J_{H\text{-}P}$ = 14.2 Hz, $^{2}J_{H\text{-}P}$ = 4.1 Hz, PCH_2P). ^{31}P{^{1}H} NMR (161.08 MHz, dcm-d_2, 27.0 °C): −11.5 (dd, 1P, $^{1}J_{P\text{-}Rh}$ = 169.1 Hz, $^{2}J_{P\text{-}P}$ = 102.7 Hz), −30.2 (dd, 1P, $^{1}J_{P\text{-}Rh}$ = 102.7 Hz, $^{2}J_{P\text{-}P}$ = 102.7 Hz, depm). The transient nature of the product precluded the acquisition of ^{13}C{^{1}H} NMR spectra, as well as and elemental analyses.

(ix) Ethylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-

ylidene)]triiodopalladium(II), [PdI_3($^{t\mathrm{Bu}}$C-κ^1-C(H)$^{\mathrm{eth}}$)] (7d). A 20 mL portion of dmso was added to a solid mixture containing **1d** (0.664 g, 1.52 mmol) and $Pd(OAc)_2$ (0.343 g, 1.53 mmol). The resulting solution was heated at 50 °C for exactly 4 h, during which time the solution bleached to a paler orange. At this point an excess of KI (19.456 g, 117.203 mmol) was added along with 8 mL dmso. The resulting dark purple solution was heated for another hour. dmso was removed overnight *in vacuo* at 50 °C to give a dark purple solid, which was then dissolved in a 60 mL portion of acetonitrile:water (50:50). The solution was heated at 80 °C for 10 min followed by the removal of the acetonitrile *in vacuo* and filtered to precipitate a dark brown solid which was washed with dcm to give the product as a brick red solid which was then recrystallized from acetonitrile, giving 0.956 g (82%). ^{1}H NMR (399.80 MHz, dmso-d_6, 26.5 °C): 9.17 (br dd, 1H, NCHN); 7.95 (br s, 1H), 7.68 (br s, 1H), 7.66 (br s, 1H), 7.31 (br s, 1H, NCH); 1.84 (s, 9H), 1.53 (s, 9H, $NC(CH_3)_3$); 4.92 (br s, 4H, NCH_2CH_2N). ^{13}C{^{1}H} NMR (125.27 MHz, dmso-d_6, 26.5 °C): $C_{carbene}$ not visible; 135.3 (s, 1C, NCHN); 123.7 (s, 1C), 123.5 (s, 1C), 123.1 (s, 1C), 121.0 (s, 1C, NCH); 60.4 (s, 1C), 32.1 (s, 3C), 59.5 (s, 1C), 29.6 (s, 3C, $NC(CH_3)_3$); 52.4 (s, 1C), 47.4 (s, 1C, NCH_2CH_2N). HRMS *m*/*z* Calcd for $C_{16}H_{27}I_2N_4Pd$ ($M^+ - I^-$): 634.9355. Found: 634.9353 ($M^+ - I^-$). Anal Calcd for $C_{16}H_{27}I_3N_4Pd$: C, 25.20; H, 3.57; N, 7.35. Found: C, 25.42; H, 3.75; N, 7.51.

(x) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]diiodotrimethylphosphinopalladium(II) iodide, [$PdI_2(PMe_3)$($^{t\mathrm{Bu}}$C-κ^1-C(H)$^{\mathrm{meth}}$)][I] (8b). A 10 mL portion of acetonitrile was added to a flask containing **7b** (0.106 g, 0.133 mmol). The resulting slurry was stirred for 10 min, afterwhich PMe_3 (14.7 μL, 0.143 mmol) was injected into the reaction vessel. The slurry

changed from dark red to a pale green solution almost instantly, and was stirred for another 10 min. The solvent was reduced to 5 mL under reduced pressure and passed through a bed of Celite *via* cannula to remove small deposits of colloidal Pd. The rest of the solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of dcm. A 20 mL portion of diethyl ether was added to precipitate a bright orange solid, which was then washed with 3 × 7 mL portions of diethyl ether and 3 × 7 mL portions of *n*-pentane before drying *in vacuo*, giving 0.084 g (72%). ^{1}H NMR (399.80 MHz, acetonitrile-d_3, 26.5 °C): 9.11 (dd, 1H, NCHN, $^{4}J_{H\text{-}H}$ = 1.7 Hz, $^{4}J_{H\text{-}H}$ = 1.7 Hz); 7.73 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.7 Hz, $^{4}J_{H\text{-}H}$ = 1.7 Hz), 7.61 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.7 Hz, $^{4}J_{H\text{-}H}$ = 1.7 Hz $NCH_{imid\text{-}H}$); 1.81 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 7.72 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.3 Hz, $^{5}J_{H\text{-}P}$ = 1.4 Hz), 7.53 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.3 Hz, $^{5}J_{H\text{-}P}$ = 2.3 Hz $NCH_{imid\text{-}Pd}$); 1.63 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 6.69 (s, 1H, NCH_2N); 1.76 (d, 9H, $^{2}J_{H\text{-}P}$ = 10.4 Hz $P(CH_3)_3$). ^{13}C{^{1}H} NMR (100.54 MHz, dmso-d_6, 26.5 °C): 163.3 (d, 1C, $^{2}J_{C\text{-}P}$ = 194.3 Hz, $C_{carbene}$); 136.6 (s, 1C, NCHN); 122.6 (s, 1C), 122.8 (s, 1C, $NCH_{imid\text{-}H}$); 124.2 (d, 1C, $^{4}J_{C\text{-}P}$ = 6.1 Hz), 123.5 (d, 1C, $^{4}J_{C\text{-}P}$ = 6.5 Hz, $NCH_{imid\text{-}Pd}$); 60.6 (s, 1C, NCH_2N); 62.6 (s, 1C), 31.9 (s, 3C, $N_{imid\text{-}H}$ $C(CH_3)_3$); 59.8 (s, 1C), 29.5 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 18.6 (d, 3C, $^{1}J_{C\text{-}P}$ = 32.2 Hz, $P(CH_3)_3$). ^{31}P{^{1}H} NMR (161.84 MHz, acetonitrile-d_3, 27.0 °C): −25.2 (s, 1P, $P(CH_3)_3$). HRMS *m*/*z* Calcd for $C_{18}H_{34}I_2N_4PPd$ ($M^+ - I^-$): 696.9640. Found: 696.9644 ($M^+ - I^-$). Repeated attempts to separate this compound from minor amounts (~ 5%) of the double-substituted **12b** failed (as observed in the ^{1}H NMR spectrum) so elemental analysis could not be obtained.

(xi) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]diiodotriethylphosphinopalladium(II) iodide, [$PdI_2(PEt_3)(^{tBu}C\text{-}\kappa^1\text{-}C(H)^{meth}$)][I] (9b). The desired complex was prepared as described for **8b**, using

7b (0.136 g, 0.182 mmol) and PEt_3 (65.7 μL, 0.441 mmol). The slurry changed from dark red to a pale green solution almost instantly, and was stirred for another 20 min. The crude product was purified as described for **8b**, and isolated using 10 mL of dcm, 20 mL of diethyl ether and 20 mL of *n*-pentane to precipitate a bright yellow solid, which was then washed with 3 × 10 mL of *n*-pentane before drying *in vacuo*, giving 0.130 g (82%). ^{1}H NMR (399.80 MHz, dmso-d_6, 26.5 °C): 9.24 (dd, 1H, NCHN, $^4J_{H\text{-}H}$ = 1.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz); 8.12 (dd, 1H, $^3J_{H\text{-}H}$ = 1.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz, ^{t}BuNC$H_{imid\text{-}H}$); 7.92 (dd, 1H, $^3J_{H\text{-}H}$ = 1.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz H_2CNC$H_{imid\text{-}H}$); 1.58 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 7.90 (dd, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $^5J_{H\text{-}P}$ = 1.9 Hz, ^{t}BuNC$H_{imid\text{-}Pd}$); 7.84 (dd, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $^5J_{H\text{-}P}$ = 1.3 Hz CH_2NC$H_{imid\text{-}Pd}$); 1.77 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 6.67 (s, 1H, NCH_2N); 2.09 (dq, 6H, $^2J_{H\text{-}P}$ = 9.5 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz), 1.07 (dt, 9H, $^3J_{H\text{-}P}$ = 16.2 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz, $P(CH_2CH_3)_3$). ^{13}C{^{1}H} NMR (125.69 MHz, dmso-d_6, 26.1 °C): 1 62.2 (d, 1C, $^2J_{C\text{-}P}$ = 185.9 Hz, $C_{carbene}$); 136.2 (s, 1C, NCHN); 121.9 (s, 1C, ^{t}BuNC$H_{imid\text{-}H}$); 122.6 (s, 1C, CH_2NC$H_{imid\text{-}H}$); 123.6 (d, 1C, $^4J_{C\text{-}P}$ = 4.7 Hz, ^{t}BuNC$H_{imid\text{-}Pd}$); 124.0 (d, 1C, $^4J_{C\text{-}P}$ = 6.3 Hz, CH_2NC$H_{imid\text{-}Pd}$); 62.8 (s, 1C, NCH_2N); 60.7 (s, 1C), 29.4 (s, 3C, $N_{imid\text{-}H}$ $C(CH_3)_3$); 60.0 (s, 1C), 32.0 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 18.8 (d, 3C, $^1J_{C\text{-}P}$ = 30.2 Hz), 9.23 (s, 3C, $P(CH_2CH_3)_3$). ^{31}P{^{1}H} NMR (161.84 MHz, acetonitrile-d_3, 27.0 °C): 10.0 (s, 1P, $P(CH_2CH_3)_3$). HRMS *m/z* Calcd for $C_{21}H_{40}I_2N_4PPd$ ($M^+ - I^-$): 739.0115. Found: 739.0109 ($M^+ - I^-$). Anal Calcd for $C_{21}H_{40}I_3N_4PPd$: C, 29.10; H, 4.65; N, 6.46. Found: C, 28.94; H, 4.70; N, 6.34.

(xii) Ethylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]diiodotriethylphosphinopalladium(II) iodide, $[PdI_2(PEt_3)(^{tBu}C\text{-}\kappa^1\text{-}C(H)^{eth})][I]$ (9d). The desired complex was prepared as described for **8b**, using **7d** (0.151 g, 0.198 mmol) and PEt_3 (58.3 μL, 0.396 mmol). The slurry changed from

dark red to a pale yellow solution almost instantly, and was stirred for another 30 min. The crude product was purified as described for **8b**, and isolated using 10 mL of dcm, 10 mL of diethyl ether and 30 mL of *n*-pentane to precipitate a bright yellow solid, which was then washed with 3 × 10 mL of *n*-pentane before drying *in vacuo*, giving 0.215 g (81%). ^{1}H NMR (399.80 MHz, dmso-d_6, 26.5 °C): 9.13 (dd, 1H, NCHN, $^{4}J_{H\text{-}H}$ = 1.5 Hz, $^{4}J_{H\text{-}H}$ = 1.5 Hz); 8.02 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.5 Hz, $^{4}J_{H\text{-}H}$ = 1.5 Hz); 7.61 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.5 Hz, $^{4}J_{H\text{-}H}$ = 1.5 Hz, $NCH_{imid\text{-}H}$); 1.77 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 7.75 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.9 Hz, $^{5}J_{H\text{-}P}$ = 1.9 Hz); 7.37 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.9 Hz, $^{5}J_{H\text{-}P}$ = 1.3 Hz, $NCH_{imid\text{-}Pd}$); 1.57 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 4.88 (m, 2H), 4.80 (m, 2H, NCH_2CH_2N); 2.08 (dq, 6H, $^{2}J_{H\text{-}P}$ = 9.4 Hz, $^{3}J_{H\text{-}H}$ = 7.7 Hz), 1.07 (dt, 9H, $^{3}J_{H\text{-}P}$ = 15.5 Hz, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $P(CH_2CH_3)_3$). $^{13}C\{^{1}H\}$ NMR (100.54 MHz, dmso-d_6, 26.5 °C): 159.5 (d, 1C, $^{2}J_{C\text{-}P}$ = 186.1 Hz, $C_{carbene}$); 135.2 (s, 1C, NCHN); 123.5 (s, 1C), 121.2 (s, 1C, $NCH_{imid\text{-}H}$); 123.0 (d, 1C, $^{4}J_{C\text{-}P}$ = 5.8 Hz), 122.7 (d, 1C, $^{4}J_{C\text{-}P}$ = 5.2 Hz, $NCH_{imid\text{-}Pd}$); 51.9 (s, 1C), 47.7 (s, 1C, NCH_2CH_2N); 60.4 (s, 1C), 29.6 (s, 3C, $N_{imid\text{-}H}C(CH_3)_3$); 59.3 (s, 1C), 32.1 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 18.6 (d, 3C, $^{1}J_{C\text{-}P}$ = 28.3 Hz), 9.20 (s, 3C, $P(CH_2CH_3)_3$). $^{31}P\{^{1}H\}$ NMR (161.84 MHz, acetonitrile-d_3, 27.0 °C): 9.3 (s, 1P, $P(CH_2CH_3)_3$). HRMS *m*/*z* Calcd for $C_{22}H_{42}I_2N_4PPd$ ($M^+ - I^-$): 753.0266. Found: 753.0266 ($M^+ - I^-$). Anal Calcd for $C_{22}H_{42}I_3N_4PPd$: C, 30.00; H, 4.81; N, 6.36. Found: C, 30.31; H, 4.88; N, 6.74.

(xiii) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]diiodotriphenylphosphinopalladium(II) iodide, $[PdI_2(PPh_3)(^{tBu}C\text{-}\kappa^1\text{-}C(H)^{meth})][I]$ (10b). A 20 mL portion of acetonitrile was added to a solid mixture of containing **7b** (0.139 g, 0.186 mmol) and PPh_3 (0.049 g, 0.153 mmol). The resulting slurry was stirred for 10 min, gradually changing from dark red to bright

orange solution. The solvent was reduced to 5 mL under reduced pressure and passed through a bed of Celite *via* cannula to remove small deposits of colloidal Pd. The rest of the solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of dcm. A 30 mL portion of diethyl ether was added to precipitate a bright orange solid, which was then washed with 3 × 7 mL portions of diethyl ether before drying *in vacuo*, giving 0.151 g (80%). ^{1}H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 8.83 (dd, 1H, $^{4}J_{H\text{-}H}$ = 1.7 Hz, $^{4}J_{H\text{-}H}$ = 1.7 Hz, NCHN); 7.63 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.7 Hz, $^{4}J_{H\text{-}H}$ = 1.7 Hz), 7.56 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.7 Hz, $^{4}J_{H\text{-}H}$ = 1.7 Hz, $NCH_{imid\text{-}H}$); 1.56 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 7.63 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.7 Hz, $^{5}J_{H\text{-}P}$ = 1.7 Hz), 7.60 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.0 Hz, $^{5}J_{H\text{-}P}$ = 1.7 Hz $NCH_{imid\text{-}Pd}$); 1.91 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 6.71 (s, 2H, NCH_2N); 7.73 (m, 6H), 7.47 (m, 9H, PPh_3). ^{13}C{^{1}H} NMR (125.69 MHz, acetonitrile-d_3, 26.5 °C): 157.5 (d, 1C, $^{2}J_{C\text{-}P}$ = 194.3 Hz, $C_{carbene}$); 135.0 (s, 1C, NCHN); 122.7 (s, 1C), 120.7 (s, 1C, $NCH_{imid\text{-}H}$), 123.7 (d, 1C, $^{4}J_{C\text{-}P}$ = 6.7 Hz), 123.2 (d, 1C, $^{4}J_{C\text{-}P}$ = 4.9 Hz, $NCH_{imid\text{-}Pd}$); 63.5 (s, 1C, NCH_2N); 61.1 (s, 1C), 28.9 (s, 3C, $N_{imid\text{-}H}$ $C(CH_3)_3$); 60.2 (s, 1C), 31.3 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 132.6 (d, 3C, $^{1}J_{C\text{-}P}$ = 45.5 Hz), 128.4 (d, 6C, $^{2}J_{C\text{-}P}$ = 10.1 Hz), 130.7 (d, 6C, $^{3}J_{C\text{-}P}$ = 2.2 Hz), 134.9 (s, 3C, PPh_3). ^{31}P{^{1}H} NMR (202.33 MHz, acetonitrile-d_3, 27.0 °C): 17.5 (s, 1P, PPh_3). HRMS *m/z* Calcd for $C_{33}H_{40}I_2N_4P_2Pd$ ($M^+ - I^-$): 883.0109. Found: 883.0116 ($M^+ - I^-$). Repeated attempts to obtain satisfactory elemental analyses were always low in the carbon analysis.

(xiv) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]diiododimethylphenylphosphinopalladium(II) iodide, [PdI$_2$(PMe$_2$Ph)($^{t\text{Bu}}$C-κ^1-C(H)^{meth})][I] (11b). The desired complex was prepared as described for **8b**, using **7b** (0.122 g, 0.164 mmol) and PMe_2Ph (20.0 μL, 0.141

mmol). The slurry changed from dark red to a pale green solution almost instantly, and was stirred for another 10 min. The crude product was purified as described for **8b**, and isolated using 10 mL of dcm and 20 mL of diethyl ether to precipitate a pale green solid, which was then washed with 2 × 5 mL portions of diethyl ether before drying *in vacuo*, giving 0.106 g (85%). ^{1}H NMR (399.80 MHz, acetonitrile-d_3, 26.5 °C): 9.21 (dd, 1H, NCHN, $^{4}J_{H\text{-}H}$ = 1.6 Hz, $^{4}J_{H\text{-}H}$ = 1.6 Hz); 7.76 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.6 Hz, $^{4}J_{H\text{-}H}$ = 1.6 Hz), 7.59 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.6 Hz, $^{4}J_{H\text{-}H}$ = 1.6 Hz $NCH_{imid\text{-}H}$); 1.59 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 7.87 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.2 Hz, $^{5}J_{H\text{-}P}$ = 1.4 Hz), 7.54 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.2 Hz, $^{5}J_{H\text{-}P}$ = 1.8 Hz $NCH_{imid\text{-}Pd}$); 1.78 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 6.78 (s, 2H, NCH_2N); 7.73 (m, 2H), 7.47 (m, 3H), 2.13 (d, 6H, $^{2}J_{H\text{-}P}$ = 10.2 Hz, $P(CH_3)_2Ph$). $^{13}C\{^{1}H\}$ NMR (125.69 MHz, dmso-d_6, 26.1 °C): 160.5 (d, 1C, $^{2}J_{C\text{-}P}$ = 197.8 Hz, $C_{carbene}$); 136.5 (s, 1C, NCHN); 122.6 (s, 1C), 121.8 (s, 1C, $NCH_{imid\text{-}H}$); 124.3 (d, 1C, $^{4}J_{C\text{-}P}$ = 4.5 Hz), 123.8 (d, 1C, $^{4}J_{C\text{-}P}$ = 5.9 Hz, $NCH_{imid\text{-}Pd}$); 62.7 (s, 1C, NCH_2N); 60.6 (s, 1C), 29.5 (s, 3C, $N_{imid\text{-}H}C(CH_3)_3$); 59.8 (s, 1C), 31.9 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 136.3 (d, 1C, $^{1}J_{C\text{-}P}$ = 44.0 Hz), 131.8 (d, 2C, $^{2}J_{C\text{-}P}$ = 10.5 Hz), 129.0 (d, 2C, $^{3}J_{C\text{-}P}$ = 9.8 Hz), 130.7 (s, 1C), 18.7 (d, 2C, $^{1}J_{C\text{-}P}$ = 32.9 Hz, $P(CH_3)_2Ph$). $^{31}P\{^{1}H\}$ NMR (161.84 MHz, acetonitrile-d_3, 27.0 °C): −16.9 (s, 1P, $P(CH_3)_2Ph$). HRMS m/z Calcd for $C_{23}H_{36}I_2N_4PPd$ ($M^+ - I^-$): 758.9796. Found: 758.9799 ($M^+ - I^-$). Anal Calcd for $C_{23}H_{36}I_3N_4PPd$: C, 31.16; H, 4.09; N, 6.32. Found: C, 31.24; H, 3.81; N, 6.39.

(xv) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]iodo*bis*(trimethylphosphino)palladium(II) diiodide, $[PdI(PMe_3)_2(^{tBu}C\text{-}\kappa^1\text{-}C(H)^{meth})][I]_2$ (12b). The desired complex was prepared as described for **8b**, using $[Pd(^{tBu}C\text{-}\kappa^1\text{-}C(H)^{meth})I_3]$ (0.143 g, 0.191 mmol) and PMe_3 (47.5 μL, 0.461 mmol). The slurry changed from dark red to a pale green solution almost

instantly, and was stirred for another 20 min. The crude product was purified as described for **8b**, and isolated using 7 mL of dcm, 20 mL of diethyl ether and 20 mL of *n*-pentane to precipitate a bright yellow solid, which was then washed with 3 × 7 mL portions of diethyl ether and 3 × 7 mL portions of *n*-pentane before drying *in vacuo*, giving 0.160 g (93%). ^{1}H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 10.27 (dd, 1H, NCHN, $^{4}J_{H\text{-}H}$ = 1.8 Hz, $^{4}J_{H\text{-}H}$ = 1.8 Hz); 7.81 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.8 Hz, $^{4}J_{H\text{-}H}$ = 1.8 Hz), 7.65 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.8 Hz, $^{4}J_{H\text{-}H}$ = 1.8 Hz $NCH_{imid\text{-}H}$); 1.80 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 8.02 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.2 Hz, $^{5}J_{H\text{-}P}$ = 1.2 Hz), 7.73 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.2 Hz, $^{5}J_{H\text{-}P}$ = 2.2 Hz $NCH_{imid\text{-}Pd}$); 1.70 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 7.22 (d, 1H, $^{2}J_{H\text{-}H}$ = 14.0 Hz), 6.78 (d, 1H, $^{2}J_{H\text{-}H}$ = 14.0 Hz, NCH_2N); 1.91 (dd, 9H, $^{2}J_{H\text{-}P}$ = 10.4 Hz, $^{4}J_{H\text{-}P}$ = 0.6 Hz), 1.60 (dd, 9H, $^{2}J_{H\text{-}P}$ = 10.9 Hz, $^{4}J_{H\text{-}P}$ = 0.7 Hz, $P(CH_3)_3$). ^{13}C{^{1}H} NMR (125.27 MHz, dmso-d_6, 26.1 °C): 165.3 (dd, 1C, $^{2}J_{C\text{-}P}$ = 158.7 Hz, $^{2}J_{C\text{-}P}$ = 6.2 Hz $C_{carbene}$); 137.1 (s, 1C, NCHN); 122.7 (s, 1C), 121.9 (s, 1C, $NCH_{imid\text{-}H}$); 124.9 (d, 1C, $^{4}J_{C\text{-}P}$ = 4.6 Hz), 124.8 (d, 1C, $^{4}J_{C\text{-}P}$ = 3.6 Hz, $NCH_{imid\text{-}Pd}$); 62.7 (s, 1C, NCH_2N); 60.9 (s, 1C), 30.9 (s, 3C, $N_{imid\text{-}H}$ $C(CH_3)_3$); 60.6 (s, 1C), 29.5 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 18.6 (d, 3C, $^{1}J_{C\text{-}P}$ = 32.3 Hz), 17.2 (dd, 3C, $^{1}J_{C\text{-}P}$ = 33.1 Hz, $^{3}J_{C\text{-}P}$ = 2.6 Hz, $P(CH_3)_3$). ^{31}P{^{1}H} NMR (201.64 MHz, acetonitrile-d_3, 27.0 °C): –11.1 (d, 1P, $^{2}J_{P\text{-}P}$ = 27.3 Hz), –19.4 (d, 1P, $^{2}J_{P\text{-}P}$ = 27.3 Hz, $P(CH_3)_3$). HRMS *m/z* Calcd for $C_{18}H_{34}I_2N_4PPd$ (M^{2+} – 2 I^-): 323.0516. Found: 323.0514 (M^{2+} – 2 I^-). Anal Calcd for $C_{21}H_{43}I_3N_4P_2Pd$: C, 28.00; H, 4.81; N, 6.22. Found: C, 27.55; H, 4.84; N, 5.86.

(xvi) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]iodo*bis*(dimethylphenylphosphino)palladium(II) diiodide, $[PdI(PMe_2Ph)_2(^{tBu}C\text{-}\kappa^1\text{-}C(H)^{meth})][I]_2$ (13b). The desired complex was prepared as described for **8b**, using **7b** (0.142 g, 0.190 mmol) and PMe_2Ph (81.5 μL, 0.570

mmol). The slurry changed from dark red to a bright yellow solution almost instantly, and was stirred for another 10 min. The crude product was purified as described for **8b**, and isolated using 10 mL of dcm, 20 mL of diethyl ether and 20 mL of *n*-pentane to precipitate a pale yellow solid, which was then washed with 3 × 10 mL portions of *n*-pentane before drying *in vacuo*, giving 0.126 g (65%). ^{1}H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 10.18 (dd, 1H, NCHN, $^{4}J_{H\text{-}H}$ = 2.0 Hz, $^{4}J_{H\text{-}H}$ = 2.0 Hz); 7.90 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.0 Hz, $^{4}J_{H\text{-}H}$ = 2.0 Hz), 7.69 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.0 Hz, $^{4}J_{H\text{-}H}$ = 2.0 Hz $NCH_{imid\text{-}H}$); 1.82 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 7.86 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.4 Hz, $^{5}J_{H\text{-}P}$ = 1.1 Hz), 7.66 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.4 Hz, $^{5}J_{H\text{-}P}$ = 2.4 Hz $NCH_{imid\text{-}Pd}$); 1.70 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 7.32 (d, 1H, $^{2}J_{H\text{-}H}$ = 13.6 Hz), 6.78 (d, 1H, $^{2}J_{H\text{-}H}$ = 13.6 Hz, NCH_2N); 2.15 (d, 3H, $^{2}J_{H\text{-}P}$ = 10.2 Hz), 2.01 (d, 3H, $^{2}J_{H\text{-}P}$ = 10.2 Hz), 1.70 (d, 3H, $^{2}J_{H\text{-}P}$ = 10.6 Hz), 1.59 (d, 3H, $^{2}J_{H\text{-}P}$ = 10.6 Hz, $P(CH_3)_2Ph$). $^{13}C\{^{1}H\}$ NMR (125.69 MHz, dmso-d_6, 26.1 °C): 162.3 (dd, 1C, $^{2}J_{C\text{-}P}$ = 161.1 Hz, $^{2}J_{C\text{-}P}$ = 7.0 Hz, $C_{carbene}$); 137.1 (s, 1C, NCHN); 122.8 (s, 1C), 121.8 (s, 1C, $NCH_{imid\text{-}H}$); 125.5 (d, 1C, $^{4}J_{C\text{-}P}$ = 5.0 Hz), 124.5 (d, 1C, $^{4}J_{C\text{-}P}$ = 4.1 Hz, $NCH_{imid\text{-}Pd}$); 62.9 (s, 1C, NCH_2N); 61.0 (s, 1C), 29.5 (s, 3C, $N_{imid\text{-}H}C(CH_3)_3$); 60.7 (s, 1C), 31.1 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 134.0 (d, 1C, $^{1}J_{C\text{-}P}$ = 48.0 Hz), 132.7 (dd, 1C, $^{1}J_{C\text{-}P}$ = 50.2 Hz, $^{3}J_{C\text{-}P}$ = 3.0 Hz), 131.6 (d, 2C, $^{2}J_{C\text{-}P}$ = 11.4 Hz), 130.1 (d, 2C, $^{2}J_{C\text{-}P}$ = 10.7 Hz), 132.0 (d, 2C, $^{3}J_{C\text{-}P}$ = 10.3 Hz), 129.3 (d, 2C, $^{3}J_{C\text{-}P}$ = 10.3 Hz), 132.4 (d, 1C, $^{4}J_{C\text{-}P}$ = 1.8 Hz), 131.3 (d, 1C, $^{4}J_{C\text{-}P}$ = 1.8 Hz), 18.6 (d, 1C, $^{1}J_{C\text{-}P}$ = 33.0 Hz), 16.8 (d, 1C, $^{1}J_{C\text{-}P}$ = 32.2 Hz), 16.0 (d, 2C, $^{1}J_{C\text{-}P}$ = 31.3 Hz, $P(CH_3)_2Ph$). $^{31}P\{^{1}H\}$ NMR (201.64 MHz, acetonitrile-d_3, 27.0 °C): –5.0 (d, 1P, $^{2}J_{P\text{-}P}$ = 25.6 Hz), –11.7 (d, 1P, $^{2}J_{P\text{-}P}$ = 25.6 Hz, $P(CH_3)_2Ph$). HRMS *m*/*z* Calcd for $C_{31}H_{47}IN_4P_2Pd$ (M^{2+} – 2 I^-): 385.0672. Found: 385.0675 (M^{2+} – 2 I^-). Anal Calcd for $C_{31}H_{47}I_3N_4P_2Pd$: C, 36.33; H, 4.62; N, 5.47. Found: C, 36.20; H, 4.92; N, 5.33.

(xvii) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)iodo(*bis*(diphenylphosphino)methane-κ^1P:κ^1P')palladium(II)] diiodide, [PdI(dppm)($^{t\text{Bu}}$C-κ^1-C(H)$^{\text{meth}}$)][I]$_2$ (14b). The desired complex was prepared as described for **10b**, using **7b** (0.114 g, 0.152 mmol) and dppm (0.059 g, 0.15 mmol). The slurry changed from dark red to a bright orange, and was stirred for another 20 min. The crude product was purified as described for **10b**, and isolated using 10 mL of dcm and 30 mL of diethyl ether to precipitate a bright orange solid, which was then washed with 3 × 7 mL portions of *n*-pentane before drying *in vacuo*, giving 0.016 g (90%). ^{1}H NMR (399.79 MHz, dmso-d_6, 26.5 °C): 9.14 (dd, 1H, $^4J_{\text{H-H}}$ = 1.6 Hz, $^4J_{\text{H-H}}$ = 1.6 Hz NCHN); 8.09 (dd, 1H, $^3J_{\text{H-H}}$ = 1.6 Hz, $^4J_{\text{H-H}}$ = 1.6 Hz), 7.84 (dd, 1H, $^3J_{\text{H-H}}$ = 1.6 Hz, $^4J_{\text{H-H}}$ = 1.6 Hz, $NCH_{\text{imid-H}}$); 1.40 (s, 9H, $N_{\text{imid-H}}C(CH_3)_3$); both $NCH_{\text{imid-Pd}}$ peaks disguised by phenyl multiplets; 1.51 (s, 9H, $N_{\text{imid-Pd}}C(CH_3)_3$); 6.76 (d, 1H, $^2J_{\text{H-H}}$ = 13.8 Hz), 6.23 (d, 1H, $^2J_{\text{H-H}}$ = 13.8 Hz NCH_2N); 8.05 (m, 6H), 7.63 (m, 8H), 7.48 (m, 1H), 7.30 (m, 3H), 7.00 (m, 2H, PPh_2); 5.44 (dm, 1H, $^2J_{\text{H-H}}$ = 16.7 Hz), 5.34 (dm, 1H, $^2J_{\text{H-H}}$ = 16.7 Hz, PCH_2P). ^{13}C{^{1}H} NMR (100.54 MHz, dmso-d_6, 26.5 °C): 164.1 (dd, 1C, $^2J_{\text{C-P}}$ = 172.2 Hz, $^2J_{\text{C-P}}$ = 2.8 Hz, C_{carbene}); 136.3 (s, 1C, NCHN); 122.5 (s, 1C), 122.2 (s, 1C, $NCH_{\text{imid-H}}$); 125.4 (d, 1C, $^4J_{\text{C-P}}$ = 4.4 Hz), 125.1 (d, 1C, $^4J_{\text{C-P}}$ = 2.9 Hz, $NCH_{\text{imid-Pd}}$); 62.2 (s, 1C, NCH_2N); 60.7 (s, 1C), 29.3 (s, 3C, $N_{\text{imid-H}}C(CH_3)_3$); 60.5 (s, 1C), 31.3 (s, 3C, $N_{\text{imid-Pd}}C(CH_3)_3$); 137.0-121.8 (24C, PPh_2); 36.8 (dd, $^1J_{\text{C-P}}$ = 27.5 Hz, $^1J_{\text{C-P}}$ = 27.5 Hz), PCH_2P). ^{31}P{^{1}H} NMR (162.08 MHz, dmso-d_6, 27.0 °C): –47.3 (d, $^2J_{\text{P-P}}$ = 77.0 Hz, 1P), –55.7 (d, $^2J_{\text{P-P}}$ = 77.0 Hz, 1P, dppm). HRMS m/z Calcd for $C_{40}H_{47}IN_4P_2Pd$ (M^{2+} – 2 I^-): 439.0672. Found: 439.0670 (M^{2+} – 2 I^-). Anal Calcd for $C_{40}H_{47}I_3N_4P_2Pd$: C, 42.41; H, 4.18; N, 4.95. Found: C, 41.99; H, 4.18; N, 5.03.

(xviii) Ethylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)iodo(*bis*(diphenylphosphino)methane-κ^1P:κ^1P')palladium(II)] diiodide, [PdI(dppm)($^{t\text{Bu}}$C-κ^1-C(H)$^{\text{eth}}$)][I]$_2$ (14d). The desired complex was prepared as described for **10b**, using **7d** (0.275 g, 0.361 mmol) and dppm (0.140 g, 0.364 mmol). The slurry changed from dark red to a bright orange, and was stirred for another 20 min. The crude product was purified as described for **10b**, and isolated using 15 mL of dcm, 30 mL of diethyl ether, and 25 mL of *n*-pentane to precipitate a bright yellow solid, which was then washed with 3 × 15 mL portions of *n*-pentane before drying *in vacuo*, giving 0.310 g (75%). ^{1}H NMR (399.80 MHz, dmso-d_6, 26.5 °C): 9.19 (br dd, 1H, $^4J_{\text{H-H}}$ = 2.1 Hz, $^4J_{\text{H-H}}$ = 2.1 Hz NCHN); 7.99 (dd, 1H, $^3J_{\text{H-H}}$ = 2.1 Hz, $^4J_{\text{H-H}}$ = 2.1 Hz), 7.45 (dd, 1H, $^3J_{\text{H-H}}$ = 2.1 Hz, $^4J_{\text{H-H}}$ = 2.1 Hz, $NCH_{\text{imid-H}}$); 1.48 (s, 9H, $N_{\text{imid-H}}C(CH_3)_3$); 7.90 (br dd, 1H, $^3J_{\text{H-H}}$ = 2.1 Hz, $^5J_{\text{H-P}}$ = 2.1 Hz), 7.56 (br dd, 1H, $^3J_{\text{H-H}}$ = 2.1 Hz, $^4J_{\text{H-H}}$ = 2.1 Hz, $NCH_{\text{imid-Pd}}$); 1.55 (s, 9H, $N_{\text{imid-Pd}}C(CH_3)_3$); 4.86 (m, 2H), 4.73 (m, 1H), 4.17 (m, 1H, NCH_2CH_2N); 7.94 (m, 6H), 7.59 (m, 9H), 7.42 (m, 5H), 7.29 (m, 3H), 7.16 (m, 2H, PPh_2); 5.36 (ddd, 1H, $^2J_{\text{H-H}}$ = 16.1 Hz, $^2J_{\text{H-P}}$ = 11.3 Hz, $^2J_{\text{H-P}}$ = 10.6 Hz), 5.12 (ddd, 1H, $^2J_{\text{H-H}}$ = 16.1 Hz, $^2J_{\text{H-P}}$ = 11.7 Hz, $^2J_{\text{H-P}}$ = 10.1 Hz, PCH_2P). ^{13}C{^{1}H} NMR (125.17 MHz, dmso-d_6, 26.1 °C): 162.2 (dd, 1C, $^2J_{\text{C-P}}$ = 173.7 Hz, $^2J_{\text{C-P}}$ = 5.9 Hz, C_{carbene}); 135.4 (s, 1C, NCHN); 123.5 (s, 1C), 121.2 (s, 1C, $NCH_{\text{imid-H}}$); 133.2 (d, 1C, $^4J_{\text{C-P}}$ = 5.2 Hz), 124.4 (d, 1C, $^4J_{\text{C-P}}$ = 4.9 Hz, $NCH_{\text{imid-Pd}}$); 51.7 (s, 1C), 47.9 (s, 1C, NCH_2CH_2N); 60.5 (s, 1C), 29.6 (s, 3C, $N_{\text{imid-H}}C(CH_3)_3$); 59.8 (s, 1C), 31.2 (s, 3C, $N_{\text{imid-Pd}}C(CH_3)_3$); 134.2-126.5 (24C, PPh_2); 37.5 (dd, $^1J_{\text{C-P}}$ = 26.7 Hz, $^1J_{\text{C-P}}$ = 26.7 Hz), PCH_2P). ^{31}P{^{1}H} NMR (161.84 MHz, dmso-d_6, 27.0 °C): –45.3 (d, $^2J_{\text{P-P}}$ = 79.6 Hz, 1P), –54.5 (d, $^2J_{\text{P-P}}$ = 79.6 Hz, 1P, dppm). HRMS m/z Calcd for $C_{41}H_{49}IN_4P_2Pd$ (M^{2+} – 2 I^-): 446.0751. Found: 446.0750 (M^{2+} – 2 I^-).

Anal Calcd for $C_{41}H_{49}I_3N_4P_2Pd$: C, 42.94; H, 4.31; N, 4.88. Found: C, 43.17; H, 4.45; N, 4.95.

(xix) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)iodo-(1,2-*bis*(diphenylphosphino)ethane-κ^1P:κ^1P')palladium(II)] diiodide, [PdI(dppe)($^{t\mathrm{Bu}}$C-κ^1-C(H)$^{\mathrm{meth}}$)][I]$_2$ (15b). The desired complex was prepared as described for **10b**, using **7b** (0.103 g, 0.138 mmol) and dppe (0.051 g, 0.13 mmol). The slurry changed from dark red to a pale green, and was stirred for another 10 min. The crude product was purified as described for **10b**, and isolated using 20 mL of dcm and 20 mL of diethyl ether to precipitate a pale green solid, which was then washed with 2 × 5 mL portions of *n*-pentane before drying *in vacuo*, giving 0.101 g (69%). ^{1}H NMR (498.12 MHz, dmso-d_6, 26.1 °C): 9.19 (dd, 1H, NCHN, $^4J_{\mathrm{H\text{-}H}}$ = 1.7 Hz, $^4J_{\mathrm{H\text{-}H}}$ = 1.7 Hz); 8.13 (dd, 1H, $^3J_{\mathrm{H\text{-}H}}$ = 1.7 Hz, $^4J_{\mathrm{H\text{-}H}}$ = 1.7 Hz), 7.79 (dd, 1H, $^3J_{\mathrm{H\text{-}H}}$ = 1.7 Hz, $^4J_{\mathrm{H\text{-}H}}$ = 1.7 Hz $\mathrm{NCH_{imid\text{-}H}}$); 1.29 (s, 9H, $\mathrm{N_{imid\text{-}H}C(CH_3)_3}$); 7.86 (dd, 1H, $^3J_{\mathrm{H\text{-}H}}$ = 2.2 Hz, $^5J_{\mathrm{H\text{-}P}}$ = 2.2 Hz), 7.72 (dd, 1H, $^3J_{\mathrm{H\text{-}H}}$ = 2.2 Hz, $^5J_{\mathrm{H\text{-}P}}$ = 1.0 Hz, $\mathrm{NCH_{imid\text{-}Pd}}$); 1.55 (s, 9H, $\mathrm{N_{imid\text{-}Pd}C(CH_3)_3}$); 6.62 (d, 1H, $^2J_{\mathrm{H\text{-}H}}$ = 14.1 Hz), 6.06 (d, 1H, $^2J_{\mathrm{H\text{-}H}}$ = 14.1 Hz, $\mathrm{NCH_2N}$); 7.95 (m, 2H), 7.87 (m, 2H), 7.69 (m, 2H), 7.59 (m, 10H), 7.41 (m, 2H) 7.23 (m, 2H, $\mathrm{PPh_2}$); 3.20 (m, 2H), 3.02 (m, 1H), 2.15 (m, 1H, $\mathrm{PCH_2CH_2P}$). ^{13}C{^{1}H} NMR (125.69 MHz, dmso-d_6, 26.1 °C): 163.8 (dd, 1C, $^2J_{\mathrm{C\text{-}P}}$ = 152.5 Hz, $^2J_{\mathrm{C\text{-}P}}$ = 5.0 Hz, $\mathrm{C_{carbene}}$); 136.4 (s, 1C, NCHN); 122.7 (s, 1C), 122.2 (s, 1C, $\mathrm{NCH_{imid\text{-}H}}$); 126.0 (d, 1C, $^4J_{\mathrm{C\text{-}P}}$ = 4.2 Hz), 123.8 (d, 1C, $^4J_{\mathrm{C\text{-}P}}$ = 3.5 Hz, $\mathrm{NCH_{imid\text{-}Pd}}$); 62.6 (s, 1C, $\mathrm{NCH_2N}$); 61.1 (s, 1C), 29.4 (s, 3C, $\mathrm{N_{imid\text{-}H}C(CH_3)_3}$); 60.0 (s, 1C), 30.7 (s, 3C, $\mathrm{N_{imid\text{-}Pd}C(CH_3)_3}$); 134.4-129.0 (24C, $\mathrm{PPh_2}$); 31.3 (dd, 1C, $^1J_{\mathrm{C\text{-}P}}$ = 33.5 Hz, $^2J_{\mathrm{C\text{-}P}}$ = 13.2 Hz), 23.8 (dd, 1C, $^1J_{\mathrm{C\text{-}P}}$ = 31.8 Hz, $^2J_{\mathrm{C\text{-}P}}$ = 12.4 Hz, $\mathrm{PCH_2CH_2P}$). ^{31}P{^{1}H} NMR (162.08 MHz, dmso-d_6, 27.0 °C): 57.8 (d, 1P, $^2J_{\mathrm{P\text{-}P}}$ = 11.5 Hz), 53.7 (d, 1P, $^2J_{\mathrm{P\text{-}P}}$ = 11.5

Hz, dppe). HRMS *m*/*z* Calcd for $C_{41}H_{49}IN_4P_2Pd$ (M^{2+} – 2 I^-): 446.0751. Found: 446.0749 (M^{2+} – 2 I^-). Anal Calcd for $C_{41}H_{49}I_3N_4P_2Pd$: C, 42.94; H, 4.31; N, 4.88. Found: C, 42.50; H, 4.53; N, 4.66.

(xx) Ethylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)iodo(1,2-*bis*(diphenylphosphino)ethane-κ^1*P*:κ^1*P′*)palladium(II)] diiodide, [PdI(dppe)($^{t\text{Bu}}$C-κ^1-C(H)$^{\text{eth}}$)][I]$_2$ (15d). The desired complex was prepared as described for **10b**, using **10d** (0.447 g, 0.586 mmol) and dppe (0.234 g, 0.587 mmol). The slurry changed from dark red to a pale green, and was stirred for another 10 min. The crude product was purified as described for **10b**, and isolated using 10 mL of dcm, 20 mL of diethyl ether, and 30 mL of *n*-pentane to precipitate a pale green solid, which was then washed with 3 × 10 mL portions of *n*-pentane before drying *in vacuo*, giving 0.453 g (67%). ^{1}H NMR (399.80 MHz, dmso-d_6, 26.5 °C): 9.41 (br dd, 1H, NCHN, $^4J_{\text{H-H}}$ = 2.3 Hz, $^4J_{\text{H-H}}$ = 2.3 Hz); 7.93 (dd, 1H, $^3J_{\text{H-H}}$ = 2.3 Hz, $^4J_{\text{H-H}}$ = 2.3 Hz), 7.50 (dd, 1H, $^3J_{\text{H-H}}$ = 2.3 Hz, $^4J_{\text{H-H}}$ = 2.3 Hz, $NCH_{\text{imid-H}}$); 1.15 (s, 9H, $N_{\text{imid-H}}C(CH_3)_3$); 7.67 (dd, 1H, $^3J_{\text{H-H}}$ = 2.1 Hz, $^5J_{\text{H-P}}$ = 2.1 Hz), 7.65 (dd, 1H, $^3J_{\text{H-H}}$ = 2.1 Hz, $^5J_{\text{H-P}}$ = 2.1 Hz, $NCH_{\text{imid-Pd}}$); 1.54 (s, 9H, $N_{\text{imid-Pd}}C(CH_3)_3$); 4.83 (m, 3H), 4.11 (m, 1H, NCH_2CH_2N); 7.94 (m, 3H), 7.82 (m, 2H), 7.55 (m, 15H), 7.39 (m, 2H), 7.21 (m, 2H, PPh_2); 3.04 (m, 3H), 1.84 (m, 1H, PCH_2CH_2P). ^{13}C{^{1}H} NMR (100.54 MHz, dmso-d_6, 26.5 °C): 162.0 (dd, 1C, $^2J_{\text{C-P}}$ = 154.0 Hz, $^2J_{\text{C-P}}$ = 4.6 Hz, C_{carbene}); 135.6 (s, 1C, NCHN); 123.9 (s, 1C), 120.9 (s, 1C, $NCH_{\text{imid-H}}$); 124.7 (d, 1C, $^4J_{\text{C-P}}$ = 4.2 Hz), 123.1 (d, 1C, $^4J_{\text{C-P}}$ = 4.2 Hz, $NCH_{\text{imid-Pd}}$); 55.6 (s, 1C), 52.4 (s, 1C, NCH_2CH_2N); 60.4 (s, 1C), 30.5 (s, 3C, $N_{\text{imid-H}}C(CH_3)_3$); 59.2 (s, 1C), 29.6 (s, 3C, $N_{\text{imid-Pd}}C(CH_3)_3$); 135.0-128.6 (24C, PPh_2); 31.4 (dd, 1C, $^1J_{\text{C-P}}$ = 33.5 Hz, $^2J_{\text{C-P}}$ = 13.0 Hz), 25.7 (dd, 1C, $^1J_{\text{C-P}}$ = 33.5 Hz, $^2J_{\text{C-P}}$ = 11.9 Hz, PCH_2CH_2P). ^{31}P{^{1}H} NMR (161.84 MHz, dmso-d_6,

27.0 °C): 57.6 (d, 1P, $^{2}J_{P\text{-}P}$ = 11.8 Hz), 52.9 (d, 1P, $^{2}J_{P\text{-}P}$ = 11.8 Hz, dppe). HRMS *m/z* Calcd for $C_{42}H_{51}IN_4P_2Pd$ (M^{2+} – 2 I^-): 453.0829. Found: 453.0833 (M^{2+} – 2 I^-). Anal Calcd for $C_{42}H_{51}I_3N_4P_2Pd$: C, 43.45; H, 4.43; N, 4.83. Found: C, 43.45; H, 4.47; N, 4.74.

(xxi) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)iodo(*bis*(diethylphosphino)methane-κ^1*P*:κ^1*P′*)palladium(II)] diiodide, [PdI(depm)($^{t\text{Bu}}$C-κ^1-C(H)^{meth})][I]$_2$ (16b). The desired complex was prepared as described for **8b**, using **7b** (0.109 g, 0.146 mmol) and depm (32.8 μL, 0.145 mmol). The slurry changed from dark red to a pale green solution almost instantly, and was stirred for another 10 min. The crude product was purified as described for **8b**, and isolated using 10 mL of dcm, and 20 mL of diethyl ether to precipitate a pale yellow solid, which was then washed with 2 × 5 mL portions of *n*-pentane before drying *in vacuo*, giving 0.125 g (92%). ^{1}H NMR (399.80 MHz, acetonitrile-d_3, 26.5 °C): 10.24 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.7 Hz, $^{4}J_{H\text{-}H}$ = 1.7 Hz NCHN); 7.78 (dd, $^{3}J_{H\text{-}H}$ = 1.7 Hz, $^{3}J_{H\text{-}H}$ = 1.7 Hz 1H), 7.63 (dd, $^{3}J_{H\text{-}H}$ = 1.7 Hz, $^{3}J_{H\text{-}H}$ = 1.7 Hz 1H, $NCH_{imid\text{-}H}$); 1.66 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 8.00 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.2 Hz, $^{5}J_{H\text{-}P}$ = 1.1 Hz), 7.65 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.1 Hz, $^{5}J_{H\text{-}P}$ = 1.1 Hz, $NCH_{imid\text{-}Pd}$); 1.77 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 7.42 (d, 1H, $^{2}J_{H\text{-}H}$ = 13.9 Hz), 6.68 (d, 1H, $^{2}J_{H\text{-}H}$ = 13.9 Hz NCH_2N); 2.89 (dm, 1H, $^{2}J_{H\text{-}P}$ = 11.4 Hz), 2.67 (m, 2H), 2.46 (m, 1H), 2.11 (m, 2H), 1.65 (m, 2H), 1.27 (dt, 3H, $^{3}J_{H\text{-}P}$ = 20.0 Hz, $^{3}J_{H\text{-}H}$ = 7.4 Hz), 1.17 (dt, 3H, $^{3}J_{H\text{-}P}$ = 18.7 Hz, $^{3}J_{H\text{-}H}$ = 7.7 Hz), 1.03 (dt, 3H, $^{3}J_{H\text{-}P}$ = 19.1 Hz, $^{3}J_{H\text{-}H}$ = 7.4 Hz), 0.88 (dt, 3H, $^{3}J_{H\text{-}P}$ = 20.0 Hz, $^{3}J_{H\text{-}H}$ = 7.4 Hz, PEt_2); 4.16 (ddd, 1H, $^{2}J_{H\text{-}H}$ = 16.6 Hz, $^{2}J_{H\text{-}P}$ = 12.4 Hz, $^{2}J_{H\text{-}P}$ = 12.4 Hz) 3.43 (ddd, 1H, $^{2}J_{H\text{-}H}$ = 16.6 Hz, $^{2}J_{H\text{-}P}$ = 10.8 Hz, $^{2}J_{H\text{-}P}$ = 9.7 Hz, PCH_2P). $^{13}C\{^{1}H\}$ NMR (125.69 MHz, dmso-d_6, 26.1 °C): 169.6 (d, 1C, $^{2}J_{C\text{-}P}$ = 158.5 Hz, $C_{carbene}$); 136.4 (s, 1C, NCHN); 122.5 (s, 1C), 122.1 (s, 1C,

$NCH_{imid\text{-}H}$); 124.4 (d, 1C, $^4J_{C\text{-}P}$ = 4.3 Hz), 124.1 (d, 1C, $^4J_{C\text{-}P}$ = 3.4 Hz, $NCH_{imid\text{-}Pd}$); 62.6 (s, 1C, NCH_2N); 60.9 (s, 1C), 29.4 (s, 3C, $N_{imid\text{-}H}C(CH_3)_3$); 61.0 (s, 1C), 31.1 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 20.8 (dd, 1C, $^1J_{C\text{-}P}$ = 13.6 Hz, $^3J_{C\text{-}P}$ = 13.6 Hz), 19.5 (d, 1C, $^1J_{C\text{-}P}$ = 22.7 Hz), 18.0 (d, 1C, $^1J_{C\text{-}P}$ = 23.4 Hz), 17.5 (dd, 1C, $^1J_{C\text{-}P}$ = 19.5 Hz, $^3J_{C\text{-}P}$ = 19.5 Hz), 9.0 (s, 1C), 8.0 (d, 1C, $^2J_{C\text{-}P}$ = 5.8 Hz), 6.8 (d, 1C, $^2J_{C\text{-}P}$ = 4.9 Hz), 6.4 (d, 1C, $^2J_{C\text{-}P}$ = 5.3 Hz, PEt_2); 27.7 (dd, 1C, $^1J_{C\text{-}P}$ = 27.2 Hz, $^1J_{C\text{-}P}$ = 27.2 Hz, PCH_2P). $^{31}P\{^1H\}$ NMR (161.84 MHz, dmso-d_6, 27.0 °C): –46.6 (d, 1P, $^2J_{P\text{-}P}$ = 81.1 Hz), –51.2 (d, 1P, $^2J_{P\text{-}P}$ = 81.1 Hz, depm). HRMS *m*/*z* Calcd for $C_{24}H_{47}IN_4P_2Pd$ (M^{2+} – 2 I^-): 343.0672. Found: 343.0675 (M^{2+} – 2 I^-). Anal Calcd for $C_{24}H_{47}I_3N_4P_2Pd$: C, 30.64; H, 5.04; N, 5.96. Found: C, 30.37; H, 5.00; N, 6.03.

(xxii) Diiodotriethylphosphinopalladium(II)-μ-(1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)iodo(η²,η²-cycloocta-1,5-diene)rhodium(I)], $[PdI_2(PEt_3)(\mu\text{-}^{t\mathrm{Bu}}CC^{\mathrm{meth}})RhI(COD)]$ (17b). A 10 mL portion of acetonitrile was added to a solid mixture containing **9b** (0.079 g, 0.091 mmol) and $[Rh(\mu\text{-}OAc)(COD)]_2$ (0.025 g, 0.046 mmol). The resulting slurry was stirred for 36 h under reflux conditions and allowed to cool to room temperature. After settling, the mother liquor was decanted to waste *via* cannula and the resulting dark green product was dissolved in 10 mL of dcm. The green solution was passed through a bed of Celite *via* cannula to remove small deposits of colloidal Pd resulting in a bright yellow solution. The solvent was then removed under reduced pressure resulting in a bright yellow powder. The crude product washed with 3 × 20 mL portions of acetone before drying *in vacuo*, giving 0.064 g (65%). ^1H NMR (399.95 MHz, dcm-d_2, 26.5 °C): 7.63 (d, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz), 7.12 (d, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $NCH_{imid\text{-}Rh}$); 1.95(s, 9H, $N_{imid\text{-}Rh}C(CH_3)_3$); 7.77 (br dd, 1H), 7.21 (dd, 1H, $^3J_{H\text{-}H}$ = 1.8 Hz, $^5J_{H\text{-}P}$ = 1.8 Hz,

$NCH_{imid\text{-}Pd}$); 1.88(s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 8.08 (d, 1H, $^2J_{H\text{-}H}$ = 13.2 Hz), 7.40 (d, 1H, $^2J_{H\text{-}H}$ = 13.2 Hz NCH_2N); 5.26 (m, 1H), 5.07 (m, 1H), 3.49 (m, 1H), 3.39 (m, 1H), 2.57 (m, 1H), 2.27 (m, 3H), 1.88 (m, 4H, COD); 2.19 (dq, 6H, $^2J_{H\text{-}P}$ = 9.5 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz), 1.15 (dt, 9H, $^3J_{H\text{-}P}$ = 16.3 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz, $P(CH_2CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.69 MHz, dcm-d_2, 26.1 °C): 180.9 (d, 1C, $^1J_{C\text{-}Rh}$ = 49.3 Hz, $C_{carbene\text{-}Rh}$); 160.8 (d, 1C, $^2J_{C\text{-}P}$ = 187.7 Hz, $C_{carbene\text{-}Pd}$); 121.4 (s, 1C), 120.7 (s, 1C, $NCH_{imid\text{-}Rh}$); 121.8 (d, 1C, $^4J_{C\text{-}P}$ = 4.1 Hz), 121.7 (d, 1C, $^4J_{C\text{-}P}$ = 6.1 Hz, $NCH_{imid\text{-}Pd}$); 66.9 (s, 1C, NCH_2N); 58.8 (s, 1C), 32.0 (s, 3C, $N_{imid\text{-}Rh}C(CH_3)_3$); 59.2 (s, 1C), 31.8 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 18.7 (d, 3C, $^1J_{C\text{-}P}$ = 28.3 Hz), 8.8 (s, 3C, $P(CH_2CH_3)_3$); 95.9 (d, 1C, $^1J_{C\text{-}Rh}$ = 7.8 Hz), 92.9 (d, 1C, $^1J_{C\text{-}Rh}$ = 7.1 Hz), 74.3 (d, 1C, $^1J_{C\text{-}Rh}$ = 15.7 Hz), 71.9 (d, 1C, $^1J_{C\text{-}Rh}$ = 14.2 Hz), 33.1 (s, 1C), 31.2 (s, 1C), 30.2 (s, 1C), 29.2 (s, 1C, COD). $^{31}P\{^1H\}$ NMR (161.84 MHz, dcm-d_2, 27.0 °C): 10.0 (s, 1P, $P(CH_2CH_3)_3$). HRMS *m/z* Calcd for $C_{29}H_{51}I_2N_4PPdRh$ ($M^+ - I^-$): 949.0025. Found: 949.0021 ($M^+ - I^-$). Anal Calcd for $C_{29}H_{51}I_3N_4PPdRh$: C, 32.35; H, 4.77; N, 5.20. Found: C, 32.68; H, 4.87; N, 5.14.

(xxiii) Diiodotriethylphosphinopalladium(II)-μ-(1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)iododicarbonylrhodium(I)], $[PdI_2(PEt_3)(\mu\text{-}^{tBu}CC^{meth})RhI(CO)_2]$ (18b). The desired complex was prepared as described for complexes **3** using **17b** (0.238 g, 0.221 mmol), and the crude product purified using 4 mL of dcm and 40 mL of diethyl ether, to precipitate a pale yellow solid at 4 °C, which was then washed with 3 × 20 mL portions of *n*-pentane before drying *in vacuo*, giving 0.215 g (85%). ^1H NMR (399.80 MHz, dcm-d_2, 50.0 °C): 7.92 (d, $^3J_{H\text{-}H}$ = 2.1 Hz, 1H), 7.30 (d, 1H, $^3J_{H\text{-}H}$ = 2.1 Hz, $NCH_{imid\text{-}Rh}$); 1.82 (s, 9H, $N_{imid\text{-}Rh}C(CH_3)_3$); 7.49 (br dd, 1H, $^3J_{H\text{-}H}$ = 2.1 Hz), 7.22 (dd, 1H, $^3J_{H\text{-}H}$ = 2.1 Hz, $^5J_{H\text{-}P}$ = 2.1 Hz, $NCH_{imid\text{-}Pd}$); 1.87 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 7.12 (d, 1H, $^2J_{H\text{-}H}$ = 13.2 Hz), 7.08 (d, 1H, $^2J_{H\text{-}H}$ = 13.2

Hz NCH_2N); 2.17 (dq, 6H, $^2J_{H\text{-}P}$ = 9.4 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz), 1.14 (dt, 9H, $^3J_{H\text{-}P}$ = 16.3 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz, $P(CH_2CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.69 MHz, dcm-d_2, 26.1 °C): 187.2 (d, 1C, $^1J_{C\text{-}Rh}$ = 54.6 Hz), 181.6 (d, 1C, $^1J_{C\text{-}Rh}$ = 76.3 Hz, CO); 171.0 (d, 1C, $^1J_{C\text{-}Rh}$ = 42.3 Hz, $C_{carbene\text{-}Rh}$); 162.2 (d, 1C, $^2J_{C\text{-}P}$ = 184.9 Hz, $C_{carbene\text{-}Pd}$); 122.0 (s, 1C), 121.8 (s, 1C, $NCH_{imid\text{-}Rh}$); 121.1 (br d, 1C), 122.0 (br d, 1C, $NCH_{imid\text{-}Pd}$); 66.4 (s, 1C, NCH_2N); 59.4 (s, 1C), 31.9 (s, 3C, $N_{imid\text{-}Rh}C(CH_3)_3$); 59.5 (s, 1C), 32.0 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 18.7 (d, 3C, $^1J_{C\text{-}P}$ = 30.3 Hz), 8.8 (s, 3C, $P(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR (161.84 MHz, dcm-d_2, 27.0 °C): 9.7 (s, 1P, $P(CH_2CH_3)_3$). IR (solution, cm^{-1}): 2076, 2004 (CO). HRMS *m*/*z* Calcd for $C_{22}H_{39}I_2N_4O_2PPdRh$ (M^+ – CO, I^-): 868.9036. Found: 868.9035 (M^+ – CO, I^-). Anal Calcd for $C_{23}H_{39}I_3N_4O_2PPdRh$: C, 26.96; H, 3.84; N, 5.47. Found: C, 27.32; H, 4.01; N, 5.64.

(xxiv) Bromo(η^2,η^2-cycloocta-1,5-diene)iridium(I)-μ-(1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)bromo(η^2,η^2-cycloocta-1,5-diene)rhodium(I)], [IrBr(COD)(μ-$^{t\text{Bu}}$CC^{meth})RhBr(COD)] (19b). A 40 mL portion of thf was added to a solid mixture containing Ir(COD)Br($^{t\text{Bu}}$C-κ^1-C(H)^{eth})][Br] (0.504 g, 0.698 mmol) and [Rh(μ-OAc)(COD)]$_2$ (0.187 g, 0.346 mmol). The resulting slurry was stirred for 2.5 h under reflux conditions. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of hot dcm and allowed to cool to room temperature, precipitating a dark orange crystalline solid. After settling, the mother liquor was decanted to waste *via* cannula and the resulting product was dried *in vacuo*, giving 0.300 g (46%). ^1H NMR (399.95 MHz, dcm-d_2, 27.0 °C): 7.89 (d, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz), 7.73 (d, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz), 7.07 (d, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz), 7.06 (d, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz, NCH_{imid}); 8.24 (d, 1H, $^2J_{H\text{-}H}$ = 11.5 Hz), 8.06 (d, 1H, $^2J_{H\text{-}H}$ = 11.5 Hz, NCH_2N); 1.97 (s, 9H), 1.89 (s, 9H,

$N_{imid}C(CH_3)_3$); 5.03 (m, 2H), 3.38 (m, 2H), 4.61 (m, 1H), 4.52 (m, 1H), 3.03 (m, 1H), 2.99 (m, 1H), 2.63 (m, 4H), 2.48 (m, 4H), 1.78 (m, 4H), 1.64 (m, 4H, COD). $^{13}C\{^1H\}$ NMR (100.58 MHz, dcm-d_2, 27.0 °C): 180.5 (d, 1C, $^1J_{C\text{-}Rh}$ = 50.1 Hz, $C_{carbene\text{-}Rh}$), 179.2 (s, 1C, $C_{carbene\text{-}Ir}$) ; 121.4 (s, 1C), 121.2 (s, 1C), 120.4 (s, 1C), 120.4 (s, 1C, NCH_{imid}); 68.0 (s, 1C, CH_2), 59.0 (s, 1C), 58.7 (s, 1C, $N_{imid}C(CH_3)_3$); 32.4 (s, 3C), 32.0 (s, 3C, $N_{imid}C(CH_3)_3$); 96.7 (d, 1C, $^1J_{C\text{-}Rh}$ = 7.3 Hz), 94.8 (d, 1C, $^1J_{C\text{-}Rh}$ = 7.0 Hz), 72.3 (d, 1C, $^1J_{C\text{-}Rh}$ = 15.7 Hz), 68.6 (d, 1C, $^1J_{C\text{-}Rh}$ = 14.0 Hz), 82.3 (s, 1C), 80.7 (s, 1C), 55.4 (s, 1C), 52.4 (s, 1C), 32.3 (s, 1C), 30.3 (s, 1C), 29.5 (s, 1C), 28.5 (s, 1C), 34.3 (s, 1C), 34.1 (s, 1C), 30.1 (s, 1C), 25.8 (s, 1C, COD). HRMS *m/z* Calcd for $C_{31}H_{48}BrN_4IrRh$ ($M^+ - Br^-$): 851.1741. Found: 851.1741 ($M^+ - Br^-$).

(xxv) Diiodotriphenylphosphinopalladium(II)-μ-(1,1′-methylene-3,3′-di*tert*-butyldiimidazoline-2,2′-diylidene)iodo(η²,η²-cycloocta-1,5-diene)iridium(I)], $[PdI_2(PPh_3)(\mu\text{-}^{t\text{Bu}}CC^{meth})IrI(COD)]$ (20b). A 5 mL portion of acetonitrile was added to **10b** (0.070 g, 0.069 mmol), and the resulting orange solution was added slowly to a 10 mL acetonitrile solution containing $K[N(SiMe_3)_2]$ (0.034 g, 0.17 mmol) and $[Ir(\mu\text{-}Cl)(COD)]_2$ (0.023 g, 0.034 mmol). The solution was stirred for 24 h, and the solvent removed under reduced pressure. The resulting solid was dissolved in 15 mL of dcm and passed through a bed of Celite *via* cannula to remove suspended white salts. The solvent was removed under reduced pressure and the product extracted with 40 mL of *n*-pentane. The solvent was removed and the deep red solid dried *in vacuo*, giving 0.014 g (15%). ^1H NMR (498.12 MHz, dcm-d_2, 26.1 °C): 7.74 (dd, 1H, $^3J_{H\text{-}H}$ = 2.4 Hz, $^5J_{H\text{-}P}$ = 1.7 Hz, $NCH_{imid\text{-}Pd}$), other $NCH_{imid\text{-}Pd}$ peak disguised by phenyl multiplets; 1.99 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); $NCH_{imid\text{-}Ir}$ peaks disguised by phenyl multiplets; 1.90 (s, 9H, $N_{imid\text{-}Ir}C(CH_3)_3$); 7.01 (d, 1H, $^2J_{H\text{-}H}$ = 11.5 Hz), 6.96 (d, 1H, $^2J_{H\text{-}}$

$_H$ = 11.5 Hz NCH_2N); 5.58 (m, 2H), 4.85 (m, 2H), 3.11-0.06 (m, 8H, COD). $^{13}C\{^1H\}$ NMR (100.54 MHz, dcm-d_2, 26.5 °C): 176.6 (s, 1C, $C_{carbene\text{-}Ir}$); 164.4 (d, 1C, $^2J_{C\text{-}P}$ = 217.1 Hz, $C_{carbene\text{-}Pd}$); 128.7 (s, 1C), 128.6 (s, 1C, $NCH_{imid\text{-}Ir}$); 128.1 (d, 1C, $^4J_{C\text{-}P}$ = 8.1 Hz), 128.0 (d, 1C, $^4J_{C\text{-}P}$ = 7.1 Hz, $NCH_{imid\text{-}Pd}$); 75.3 (s, 1C, NCH_2N); 69.6 (s, 1C), 22.5 (s, 3C, $N_{imid\text{-}Ir}C(CH_3)_3$); 67.9 (s, 1C), 14.0 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 131.0 (d, 3C, $^1J_{C\text{-}P}$ = 49.6 Hz), 132.1 (d, 6C, $^2J_{C\text{-}P}$ = 9.6 Hz), 132.0 (d, 6C, $^3J_{C\text{-}P}$ = 3.0 Hz), 135.4 (s, 3C, PPh_3); 92.2 (s, 1C), 92.0 (s, 1C), 57.0 (s, 1C), 52.7 (s, 1C), 34.8 (s, 1C), 34.3 (s, 1C), 34.2 (s, 1C), 31.7 (s, 1C, COD). $^{31}P\{^1H\}$ NMR (201.64 MHz, dcm-d_2, 27.0 °C): 28.3 (s, 1P, PPh_3). HRMS *m/z* Calcd for $C_{41}H_{51}I_2N_4PPdIr$ ($M^+ - I^-$): 1183.0600. Found: 1183.0610 ($M^+ - I^-$). Anal Calcd for $C_{41}H_{51}I_3IrN_4PPd$: C, 37.59; H, 3.92; N, 4.28. Found: C, 37.89; H, 4.12; N, 4.21.

(xxvi) Diiododimethylphenylphosphinopalladium(II)-μ-(1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)iodo(η^2,η^2-cycloocta-1,5-diene)-iridium(I)], [$PdI_2(PMe_2Ph)(\mu$-$^{tBu}CC^{meth})IrI(COD)$] (21b). The desired complex was prepared as described for **20b**, using **11b** (0.064 g, 0.072 mmol), $K[N(SiMe_3)_2]$ (0.036 g, 0.18 mmol), and $[Ir(\mu\text{-}Cl)(COD)]_2$ (0.024 g, 0.036 mmol). The crude product was purified as described for **20b**, resulting in 0.017 g (20%) of a yellow solid. ^1H NMR (498.12 MHz, dcm-d_2, 26.1 °C): 7.77 (d, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz), 7.14 (d, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $NCH_{imid\text{-}Ir}$); 1.89(s, 9H, $N_{imid\text{-}Ir}C(CH_3)_3$); 7.78 (dd, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $^5J_{H\text{-}P}$ = 1.9 Hz), 7.23 (dd, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $^5J_{H\text{-}P}$ = 1.9 Hz, $NCH_{imid\text{-}Pd}$); 1.87 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); both NCH_2N peaks disguised by phenyl multiplets; 7.88-7.16 (m, 5H), 2.16 (d, 3H, $^2J_{H\text{-}P}$ = 9.8 Hz), 2.15 (d, 3H, $^2J_{H\text{-}P}$ = 9.8 Hz, PMe_2Ph); 4.87 (m, 1H), 4.65 (m, 1H), 3.06 (m, 1H), 3.90 (m, 1H), 2.30-1.23 (m, 8H, COD). $^{13}C\{^1H\}$ NMR (125.26 MHz, dcm-d_2, 26.1 °C): 179.2 (s, 1C, $C_{carbene\text{-}Ir}$); 171.9 (d, 1C, $^2J_{C\text{-}P}$ =

207.5 Hz, $C_{carbene\text{-}Pd}$); 121.7 (s, 1C), 120.3 (s, 1C, $NCH_{imid\text{-}Ir}$); 128.9 (d, 1C, $^4J_{C\text{-}P}$ = 6.7 Hz), 121.6 (d, 1C, $^4J_{C\text{-}P}$ = 6.6 Hz, $NCH_{imid\text{-}Pd}$); 66.7 (s, 1C, NCH_2N); 59.1 (s, 1C), 32.2 (s, 3C, $N_{imid\text{-}Ir}C(CH_3)_3$); 57.3 (s, 1C), 32.0 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 136.3 (d, 1C, $^1J_{C\text{-}P}$ = 44.7 Hz), 131.3 (d, 2C, $^2J_{C\text{-}P}$ = 10.6 Hz), 128.4 (d, 2C, $^3J_{C\text{-}P}$ = 10.0 Hz), 130.1 (s, 1C), 18.8 (d, 1C, $^1J_{C\text{-}P}$ = 32.6 Hz), 18.7 (d, 1C, $^1J_{C\text{-}P}$ = 33.0 Hz, PMe_2Ph); 82.0 (s, 1C), 79.3 (s, 1C), 59.1 (s, 1C), 55.5 (s, 1C), 33.4 (s, 1C), 31.8 (s, 1C), 30.6 (s, 1C), 30.1 (s, 1C, COD). $^{31}P\{^1H\}$ NMR (201.64 MHz, dcm-d_2, 26.1 °C): 17.0 (s, 1P, PMe_2Ph). HRMS *m*/*z* Calcd for $C_{31}H_{47}I_2IrN_4PPd$ ($M^+ - I^-$): 1059.0286. Found: 1059.0276 ($M^+ - I^-$). Anal Calcd for $C_{31}H_{47}I_3IrN_4PPd$: C, 31.39; H, 3.99; N, 4.72. Found: C, 31.65; H, 4.31; N, 4.93.

(xxvii) Diiododimethylphenylphosphinopalladium(II)-μ-(1,1′-methylene-3,3′-di-*tert*-butyl-diimidazoline-2,2′-diylidene)iododicarbonyliridium(I)], $[PdI_2(PPh_3)(\mu\text{-}^{t\text{Bu}}CC^{meth})IrI(CO)_2]$ (22b). The desired complex was prepared as described for complexes **3** using **20b** (0.010 g, 0.0076 mmol), 10 mL thf, and the crude product purified by filtration after washing with 1 mL of *n*-pentane before drying *in vacuo*, giving 0.007 g (80%). ^1H NMR (498.12 MHz, dcm-d_2, 26.1 °C): $NCH_{imid\text{-}Ir}$ peaks disguised by phenyl multiplets; 1.87 (s, 9H, $N_{imid\text{-}Ir}C(CH_3)_3$); $NCH_{imid\text{-}Pd}$ peaks disguised by phenyl multiplets; 1.83 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 7.26 (d, 1H, $^2J_{H\text{-}P}$ = 16.1 Hz), 6.98 (d, 1H, $^2J_{H\text{-}P}$ = 16.1 Hz, NCH_2N); 7.77-7.31 (m, 15H, PPh_3). $^{13}C\{^1H\}$ NMR (125.26 MHz, dcm-d_2, 26.1 °C): 169.7 (s, 1C), 167.1 (s, 1C, CO); 180.1 (s, 1C, $C_{carbene\text{-}Ir}$); 164.1 (d, 1C, $^2J_{C\text{-}P}$ = 214.5 Hz, $C_{carbene\text{-}Pd}$); 128.7 (s, 1C), 128.7 (s, 1C, $NCH_{imid\text{-}Ir}$); 129.8 (d, 1C, $^4J_{C\text{-}P}$ = 9.1 Hz), 128.8 (d, 1C, $^4J_{C\text{-}P}$ = 10.3 Hz, $NCH_{imid\text{-}Pd}$); 75.3 (s, 1C, NCH_2N); 69.6 (s, 1C), 34.8 (s, 3C, $N_{imid\text{-}Ir}C(CH_3)_3$); 68.0 (s, 1C), 34.2 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 131.5 (d, 3C, $^1J_{C\text{-}P}$ = 38.7 Hz), 132.2 (d, 6C, $^2J_{C\text{-}P}$ = 9.7 Hz), 132.1

(d, 6C, $^{3}J_{C\text{-}P}$ = 3.0 Hz), 133.6 (s, 3C, PPh_3). $^{31}P\{^{1}H\}$ NMR (201.64 MHz, dcm-d_2, 26.1 °C): 28.4 (s, 1P, PPh_3). IR (solution, cm^{-1}): 2065, 1987 (CO). Anal Calcd for $C_{35}H_{39}I_3IrN_4O_2PPd$: C, 33.42; H, 3.12; N, 4.45. Found: C, 33.51; H, 3.34; N, 4.63.

(xxviii) Diiododimethylphenylphosphinopalladium(II)-μ-(1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)iododicarbonyliridium(I)], $[PdI_2(PMe_2Ph)(\mu\text{-}^{t\mathrm{Bu}}CC^{\mathrm{meth}})IrI(CO)_2]$ (23b). The desired complex was prepared as described for complexes 3 using 20b (0.015 g, 0.013 mmol), and the crude product purified by filtration after washing with 1 mL of *n*-pentane before drying *in vacuo*, giving 0.012 g (84%). ^{1}H NMR (299.97 MHz, acetonitrile-d_3, 27.5 °C): 7.73 (d, 1H, $^{3}J_{H\text{-}H}$ = 2.2 Hz), 7.45 (d, 1H, $^{3}J_{H\text{-}H}$ = 2.2 Hz, $NCH_{imid\text{-}Ir}$); 1.85 (s, 9H, $N_{imid\text{-}Ir}C(CH_3)_3$); 7.42 (dd, 1H, $^{3}J_{H\text{-}H}$ = 2.1 Hz, $^{5}J_{H\text{-}P}$ = 1.4 Hz, $NCH_{imid\text{-}Pd}$), other $NCH_{imid\text{-}Pd}$ peak disguised by phenyl multiplets; 1.81 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 7.04 (d, 1H, $^{2}J_{H\text{-}H}$ = 13.2 Hz), 6.91 (d, 2H, $^{2}J_{H\text{-}H}$ = 13.2 Hz, NCH_2N); 7.82-7.41 (m, 5H), 2.13 (d, 3H, $^{2}J_{H\text{-}P}$ = 9.8 Hz), 2.13 (d, 3H, $^{2}J_{H\text{-}P}$ = 9.8 Hz, PMe_2Ph). $^{13}C\{^{1}H\}$ NMR (125.27 MHz, acetonitrile-d_3, 26.1 °C): 169.6 (s, 1C), 167.5 (s, 1C, CO); 180.6 (s, 1C, $C_{carbene\text{-}Ir}$); 159.6 (d, 1C, $^{2}J_{C\text{-}P}$ = 194.1 Hz, $C_{carbene\text{-}Pd}$); 122.4 (s, 1C), 121.9 (s, 1C, $NCH_{imid\text{-}Ir}$); 122.6 (d, 1C, $^{4}J_{C\text{-}P}$ = 6.5 Hz), 121.5 (d, 1C, $^{4}J_{C\text{-}P}$ = 5.2 Hz, $NCH_{imid\text{-}Pd}$); 66.6 (s, 1C, NCH_2N); 59.9 (s, 1C), 31.6 (s, 3C, $N_{imid\text{-}Ir}C(CH_3)_3$); 59.4 (s, 1C), 31.4 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 136.3 (d, 1C, $^{1}J_{C\text{-}P}$ = 46.1 Hz), 131.5 (d, 2C, $^{2}J_{C\text{-}P}$ = 10.9 Hz), 128.6 (d, 2C, $^{3}J_{C\text{-}P}$ = 10.2 Hz), 130.2 (d, 1C, $^{4}J_{C\text{-}P}$ = 2.5 Hz), 18.2 (d, 1C, $^{1}J_{C\text{-}P}$ = 33.6 Hz), 17.9 (d, 1C, $^{1}J_{C\text{-}P}$ = 33.6 Hz, PMe_2Ph). $^{31}P\{^{1}H\}$ NMR (161.84 MHz, acetonitrile-d_3, 26.5 °C): –17.1 (s, 1P, PMe_2Ph). IR (solution, cm^{-1}): 2065, 1986 (CO). HRMS *m*/*z* Calcd for $C_{25}H_{35}I_2IrN_4O_2PPd$ ($M^+ - I^-$): 1006.9246. Found: 1006.9234 ($M^+ - I^-$).

2.4.3 X-ray structure determinations

(i) General considerations. All X-ray crystallography studies were carried out in the X-ray Crystallography Laboratory at the University of Alberta by either Dr. Robert McDonald or Dr. Michael J. Ferguson. Crystals were grown either from concentrated acetonitrile solutions of the compound (**11b**, **13b**), *via* slow diffusion of ether and *n*-pentane into a dcm solution of the compound (**2c**, **2d**, **17b**), or *via* slow diffusion of ether and *n*-pentane into an acetone solution of compound (**16b**). Data were collected[104] using either a Bruker SMART 1000 CCD detector/PLATFORM diffractometer with the crystals cooled to –80 °C (**2c**, **2d**) or using a Bruker APEX II detector/D8 diffractometer with the crystals cooled to –100 °C (**11b**, **13b**, **16b**, **17b**); in all case Mo Kα radiation was used. The data were corrected for absorption through use of a multiscan model (*SADABS*) (**2c**, **2d**, **11b**, **13b**) or through use of Gaussian integration (using the indexed faces and measured dimensions of the crystal (**16b**, **17b**). Structures were solved using direct methods (*SHELXS-97*[105] (**2c**, **11b**, **13b**) or *SIR97*[106] (**2d**, **17b**)) or through Patterson location of heavy atoms positions followed by structure expansion (*DIRDIF-2008*[107] (**16b**)). The program *SHELXL-97*[105] was used for structure refinements. Hydrogen atoms (including those involved in hydrogen bonds) were assigned positions on the basis of the geometries of their attached carbon atoms and were given thermal parameters 120% of their parent carbons. See Appendix III (Table III.1-1 to Table III.1-3) for a listing of crystallographic experimental data, and Appendix IV (Table IV-1) for a listing of crystallographic data.

(ii) Special refinement conditions. a) Despite crystallizing in a chiral space group ($P2_1$), the crystal of **2d** was found to be racemically twinned. This was

accommodated during refinement through use of the *SHELXL-97* [105] TWIN instruction, and the Flack parameter refined to a value of 0.364(6). b) For **13b**, a half-occupancy molecule of solvent acetonitrile was found to be disordered about the inversion centre (1/2, 0, 1/2). Distances within this molecule were constrained during refinement to be equal (within 0.01 Å) to the corresponding distances within the other (full-occupancy, non-disordered) co-crystallized solvent acetonitrile molecule: d(N(1S)–C(1S)) = d(N(2S)–C(3S)); d(C(1S)–C(2S)) = d(C(3S)–C(4S)); d(N(1S)…C(2S)) = d(N(2S)…C(4S)).

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Laboratory, Radboud University Nijmegen: Nijmegen, The Netherlands, 2008.

Chapter 3 Attempted Synthesis of Di-Cyclic (Alkyl)(Amino)Carbene Ligands

Section 3.1 Introduction

3.1.1 Different carbenes based on non-imidazole frameworks

As was mentioned in Chapter 1, flanking a carbene carbon with a pair of σ-withdrawing, π-donating groups lowers the energy of the carbene σ orbital (*i.e.*, the highest occupied molecular orbital, or "HOMO") and raises the energy of the p_π orbital (*i.e.*, the lowest unoccupied molecular orbital, or "LUMO"), resulting in a large energy difference between the two. When this energy difference is great enough (140-190 kJ/mol, depending on the system)[1, 2] the singlet carbene is favoured as is normally the case with diamino carbenes (such as NHCs). The pair of α-amino groups (Figure 3-1a) induce this kind of stabilization, in which the HOMO-LUMO gap in these singlet carbenes can be as large as 355 kJ/mol in certain cases[3] with a resting ground state as low as –5.8 eV.[4]

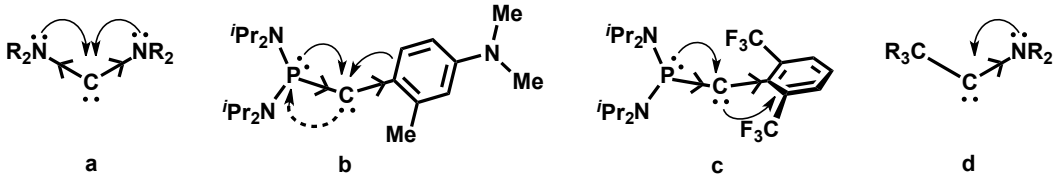


Figure 3-1. "Push/push" (**a**), "push/pull" (**b**, **c**), and "non-push/pull" (**d**) carbenes.

Of the two stabilizing interactions (σ-withdrawing or π-donating) the latter mesomeric contribution has a more significant role in inducing singlet behavior and as a result carbenes are often described on the basis of this π-directionality with respect to both substituents. For example, carbenes stabilized by mesomeric π-donation (+M) from both α-atoms (as is observed in diamino-stabilized NHCs) are

referred to as "push/push" carbenes,[5] and as noted (depending the degree of +M contribution) usually result in a singlet ground state spin multiplicity. Although a +M contribution from both α-atoms plays a large role in promoting a large HOMO-LUMO gap (and therefore inducing singlet ground-state multiplicity), the energy level of the HOMO itself dictates how strong a donor this singlet carbene will be. For example, a carbene may have a significant HOMO-LUMO gap (causing singlet ground state behaviour), but the higher the energy of the HOMO, the singlet carbene will become more reactive. In the case of NHCs, their stability is attributed to the inductively-withdrawing (–I) nature of the amino groups which decrease the energy of the σ-donating orbital to the low values noted above.[6]

In order to improve the donor capabilities of these carbenes, there has been recent interest in generating carbenes with a HOMO of higher absolute energy,[4, 7, 8] which can be done by reversing the inductive stabilization effects that impart such stability to NHCs. For example, although the (phosphino)(aryl)carbene shown in Figure 3-1b[9] involves two p_π-stabilizing (+M) groups, the less electronegative (+I) phosphino group ($\chi_P = 2.19$) *raises* the energy of the lone pair-containing HOMO. Furthermore, the aryl group is not nearly as electronegative as an amine ($\chi_N = 3.04$, $\chi_{Ar} \approx 1.74$),[10] further raising the energy of the HOMO (compared to NHCs) making this a very unstable, non-isolable carbene.[i] In Figure 3-1c, although the +I and +M effects of the phosphino group and the –I effect of the aryl group having

[i] Although it is possible for the relatively high-energy carbene lone pair to be stabilized by population of a σ^* orbital of the phosphino moiety *via* negative hyperconjugation[11, 12] (as in species **a** of Scheme 1-5 in Chapter 1, which is also a "push/pull" carbene), computational studies often confute this theory,[13] despite implicating evidence by NMR spectroscopy.[14]

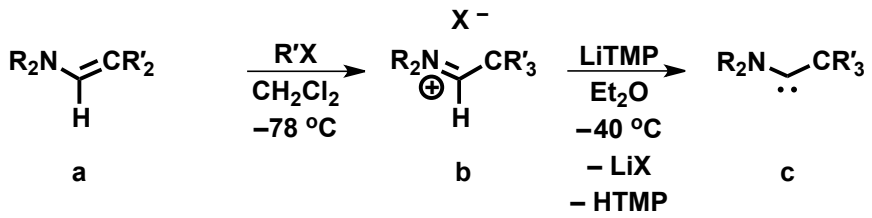
electronegative substituents influence the stability of the carbene centre to a similar degree as in Figure 3-1b, the aryl group now possesses a –M property that allows delocalization of the carbene lone pair into the ring, allowing for isolation of a free "push/pull" carbene with a relatively high-energy HOMO.[15]

"Push/push" carbenes have received considerably more attention than "push/pull" systems because of their stability, ease of synthesis, and "bottleability". In addition, the reason for the popularity of "push/push"-type diaminocarbenes in organometallic chemistry is because of their ability to bind to transition metals. As a result, NHCs have been identified as excellent ligands as discussed in the previous two chapters – they are fairly nucleophilic, but are weakly electrophilic (weak π-acceptors). In contrast, the lone pair on the carbene carbon in Figure 3-1b,c becomes less available for metal-donation given that it is possibly tied up in further bonding. This extent of multiple bond character around the carbene carbon also creates a wide valence angle at carbon, sterically concealing the carbene moiety.[16, 17]

3.1.2 (Alkyl)(amino)carbenes

In an attempt to investigate carbenes which could find a compromise between stability and binding ability, focus was diverted to systems having only one (–I, +M) group, and one "spectator" group (such as an alkyl). However, as expected, the (alkyl)(amino)carbenes (AACs, "non-push/push" type, Figure 3-1d) studied were too unstable to observe directly, and required techniques such as matrix isolation, or nanosecond time-resolved laser flash photolysis for observation and study (two commonly-used "fast reaction" techniques).[18, 19]

However, in 2004, Bertrand published the synthesis of a stable AAC by avoiding factors that prevent their synthesis, or by inhibiting common decomposition pathways.[20] For example, in the synthesis of generic AACs shown in Scheme 3-1, the greater acidity of the methyl substituents on nitrogen (R = Me) than the desired iminium proton in the cationic carbene precursor (Scheme 3-1b)[21] results in failure to obtain the targeted carbene.[ii] Furthermore, the sp^3 carbon α to the



Scheme 3-1. Generic synthesis of the first stable AAC (LiTMP = lithium tetramethylpiperidide).

carbene carbon can cause problems once the carbene is generated (Scheme 3-1c) if not properly substituted since it is known that 1,2-*H* migrations readily occur for singlet carbenes (abstraction of a proton from the adjacent sp^3 carbon by the carbene),[22] therefore only *tertiary* AACs (with a tertiary α-carbon) would be stable. By taking these factors into consideration (*i.e.*, R ≠ CH_3; CR'_3 = 3° alkyl), the first acyclic AAC was successfully isolated (R = ^{i}Pr; R′ =CH_3).[20] Without the need for a second heteroatom, "non-push/push" carbenes offer more electron density at the central carbene carbon atom (with only one inductively σ-withdrawing heteroatom in the α-position), making these AACs better donors than their diamino counterparts.

Although this AAC (^{i}Pr$_2$N–$\ddot{C}$–CMe$_3$) is stable indefinitely in the solid state, it decomposes readily in solution. In the same way that *cyclic* diaminocarbenes are more

[ii] Deprotonation of the –NCH_3 group results in an azomethine ylide (*i.e.*, $(CH_3)(CH_2^-)N^+$=C(H)CR′$_3$) instead of the desired carbene, which can undergo a number of decomposition pathways.[21]

robust than their acyclic counterparts,[6, 15, 23] cyclic (alkyl)(amino)carbenes (CAACs) have also proven to be more stable than their acyclic variants, and have received more attention. More interestingly however, manipulation of the quaternary carbon in the position α to the carbene centre can allow for steric environments that differentiate them dramatically from other carbenes reported in the literature, which can have important implications in catalysis, as will be noted later.

3.1.3 CAACs – incorporating an aspect of flexible steric bulk

As mentioned in Chapter 1, transition metal catalysts are used in many different areas of synthetic organic chemistry.[24-26] Many major advances in the field can be attributed to cyclic diaminocarbenes such as NHCs because of their ability to stabilize active catalyst intermediates. In fact, in many cases, important catalytic steps (such as reductive elimination) can be accelerated when *bulky* groups are used.[27-29] However, excessive steric hindrance can present some drawbacks when bulky organic substrates are involved in the catalytic process,[30] and a balance between the two extremes must often be achieved.

To overcome this problem, Glorius *et al.* have successfully developed NHC ligands with "flexible steric bulk" using the conformational flexibility of cyclohexyl substituents to impose steric pressure on the metal centre (Figure 3-2a1),[31] while

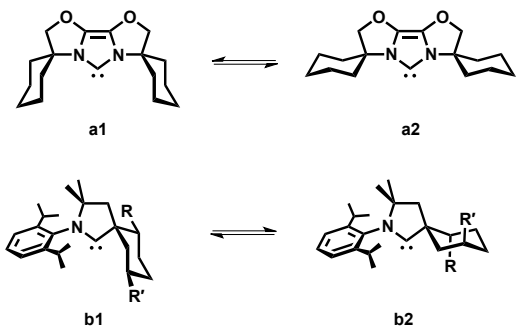


Figure 3-2. Flexible steric bulk in Glorius NHCs and Bertrand CAACs.

being flexible enough to move away from the metal in order to relieve the strain as needed (Figure 3-2a2). However, with the discoveries of Bertrand *et al.* mentioned above (the requirement of only one (–I, +M) group for carbene stabilization) the presence of a quaternary carbon atom in a position α to the carbene centre allows for modification of steric bulk *closer* to the carbene carbon and the adjacent metal centre (Figure 3-2b, "flexible CAACs", R = R′ = H). With this incorporation of a spiro-cyclohexyl group, the flexible steric bulk effect is amplified.[32] In contrast, "rigid" CAACs (Figure 3-2b, R = ^{i}Pr, R′ = Me) exemplify the rigidity and extreme steric bulk that CAACs can provide to metal centres to which they are bound. By using bulky substituents on the ring, the downward chair conformation is locked (only the conformation in Figure 3-2b1 is possible) because a chair/boat inversion to the "outward" conformation (Figure 3-2b2) would put both the *iso*-propyl and methyl groups in unfavourable axial positions. This conformation forms a "wall of protection", allowing for the isolation of compounds having unusual degrees of coordinative-unsaturation, as shown for the Pd and Rh compounds in Figure 3-3.[33]

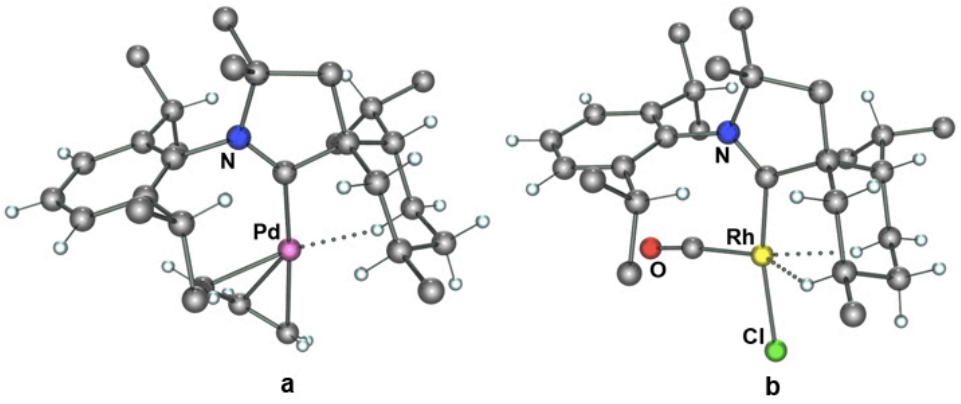
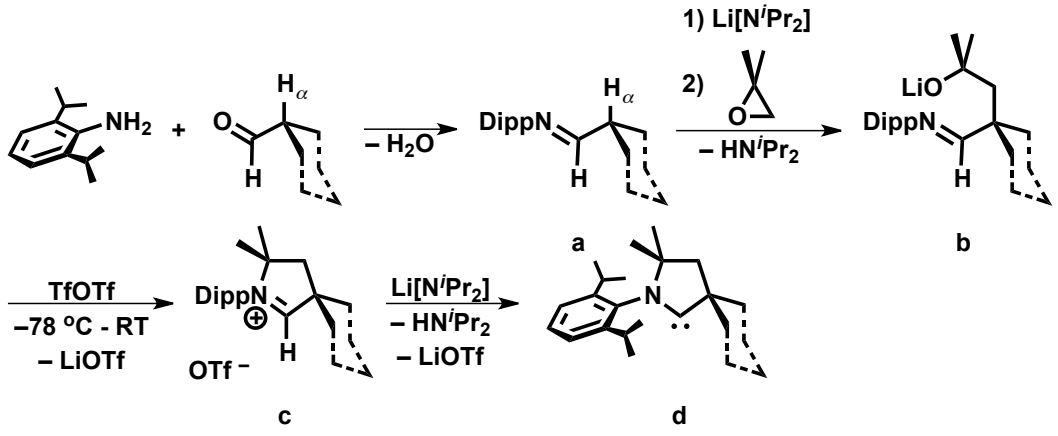


Figure 3-3. Three-dimensional representation of the cation complex [Pd(C_3H_5)(CAAC)][BF_4] (**a**) and [RhCl(CO)(CAAC)] (**b**) showing the protective downward conformation of the substituted cyclohexyl ring, and M–H agostic interactions.[34]

As a result of these exciting reports, we became interested in producing bidentate analogues of these monocarbenes for the purposes of using them as bridging units in our Pd/Rh chemistry of interest. Currently, two (slightly different) synthetic protocols are available for the synthesis of CAAC-type ligands, both of which involve building the ring framework around simple organic molecules - a primary amine ($-NH_2$) and an aldehyde featuring a secondary alkyl substituent (more specifically, containing one α-hydrogen atom ($OCH-CH_\alpha R_2$)).

3.1.4 Reported monodentate CAAC ligand syntheses

The synthesis of free (not attached to transition metals), bottleable CAAC-type ligands was first reported by Bertrand in 2005.[32] The synthesis first involves a condensation reaction between the primary amine[iii] and aldehyde starting materials, which is essentially quantitative, to yield the expected imine product (Scheme 3-2a). The imine's α-hydrogen can be deprotonated by a strong base (in this case lithium

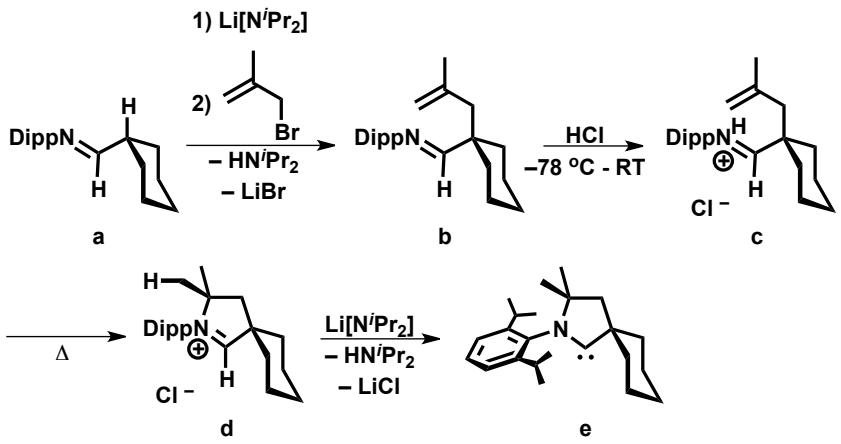


Scheme 3-2. Initial organic protocol for the synthesis of CAAC ligands.

[iii] The rationale behind the use of the bulky 2,6-diisopropylphenyl (Dipp) group on nitrogen is threefold: (1) The steric bulk prevents triplet-dimerization of the resulting carbene (with only one (–I, +M) group, the σ-p_π gap is only 189 kJ/mol),[35] (2) The amine ($DippNH_2$) is commercially available and inexpensive, and (3) the *iso*-propyl groups are conducive to the growth of good-quality single crystals for X-ray diffraction studies.

diisopropylamide, Li[N^{i}Pr$_2$], abbreviated as LDA) to afford an aza-allyl ion, which readily induces ring opening of an epoxide, yielding the corresponding lithium alkoxide (shown in Scheme 3-2b). Triflic anhydride (TfOTf) is used to exchange the LiO terminus for a TfO group, which can easily be displaced *via* attack by the imine nitrogen on the carbon atom adjacent to the triflate, effectively closing the ring to form the iminium salt (Scheme 3-2c). Subsequent deprotonation by LDA results in the desired free carbene (Scheme 3-2d) in 58% yield (with respect to the imine). Spiro-CAAC ligands can be prepared using a cyclohexyl secondary aldehyde, namely cyclohexylcarboxaldehyde (OCH–CH$_\alpha$C$_5$H$_{10}$ or OCH–Cy) while for "rigid" CAAC derivatives, (+)-*p*-menthyl-3-carboxaldehyde[36] can be used to lock the CAAC ligand in the downward (protective) conformation (Figure 3-2b, R = ^{i}Pr; R′ = CH$_3$).[32, 33, 37-42]

However, in 2007 Bertrand reported a simpler, higher-yielding synthesis involving less-costly reagents (Scheme 3-3).[37, 43] Instead of using the aza-allyl ion to ring-open an epoxide, it is used to attack a methyl-substituted propene group to afford the alkenylaldemine shown in Scheme 3-3b. Protonation at low temperature results in an alkenylaldiminium salt (Scheme 3-3c), which can be cyclized *via* the



Scheme 3-3. New and improved synthesis for CAAC ligands. In structure **d**, one of the backbone methyl protons is shown in order to indicate its location following intramolecular cyclisation.

hydroiminiumation reaction to produce the cyclic iminium salt. (Scheme 3-3d).[iv]

Our interest in making new dicarbenes to bridge mixed-metal complexes together with our interest in CAAC-type ligands led us to an investigation into the synthesis of new bidentate, di-CAAC ligand precursors based on the monodentate synthetic protocols mentioned above.

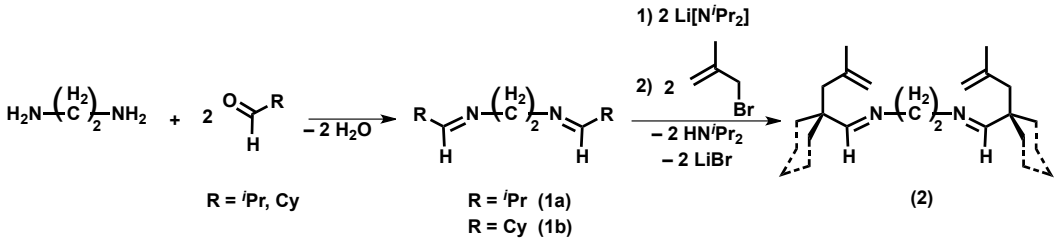
Section 3.2 Results and Compound Characterization

3.2.1 Attempted synthesis of alkyl-linked di-CAAC ligands

CAAC ligands having a wide range of steric properties are possible owing to the ready availability of functionalized aldehydes that are either commercially available, or easily synthesized. In order to attempt the synthesis of di-CAAC ligands having steric similarities to the known monocarbenes, it seemed that the obvious route was to begin with formation of a diimine (compound **1**, Scheme 3-4) from a linked-diamine (specifically, ethylenediamine)[v] using *two* equivalents of aldehyde, then to proceed using the second (higher yielding) route outlined in Bertrand's CAAC synthesis. The *iso*-propyl diimine (Scheme 3-4, R = ^{i}Pr, **1a**) had been previously reported by condensation of these two starting materials,[45] and was repeated here, along with our own similar high-yielding protocols (the reaction of ethylenediamine

[iv] It had been reported in non-CAAC cases that intramolecular transfer of a proton from an amine to an alkenyl group can occur if the amine is made sufficiently less-basic (by an attaching electron-withdrawing group).[44] Imines are certainly less-basic than amines, and therefore Bertrand *et al.* had postulated that their own rendition of Hartwig's hydroamination reaction (a "hydroiminiumation") would be an atom-economical route to cyclic iminum salts.

[v] Although each end of this diamine (RNH_2) is different than those used by Bertrand ($DippNH_2$), generation of the *free* dicarbene was not our intent, therefore inhibiting dimerization with bulky substituents was not deemed necessary. Furthermore, although we were aware that an electron-withdrawing nitrogen-substituent in Bertrand's work resulted in a higher-yielding hydro-iminiumation reaction, Hartwig's initial report involved cyclization with a more-basic amine. As a result, we anticipated that a di-CAAC *imine*-based synthesis without an electron-withdrawing substituent should proceed nonetheless. Only strongly electron-donating groups (*i.e.*, *tert*-butyl) inhibited Bertrand's hydroiminiumation synthesis.[43]



Scheme 3-4. Synthesis of ethylene-linked diimines as di-CAAC ligand precursors.

with cyclohexylcarboxaldehyde in refluxing toluene) to include a spiro-cyclohexyl functionality (Scheme 3-4, R = Cy, **1b**). The ^{1}H NMR spectral parameters confirm the formation of the diimine **1** (the ^{1}H NMR spectrum for the cyclohexyl-substituted species **1b** is shown in Figure 3-4). The disappearance of the aldehyde (δ = 9.6) and –NH_2 (δ = 0.6) proton peaks and the emergence of a new doublet at δ = 7.4 corresponding to the imine proton, showing coupling to the α-proton ($^3J_{H\text{-}H}$ = 5.0 Hz) confirm the formulation in Scheme 3-4. The coupling between these two protons can be confirmed through ^{1}H{selective ^{1}H} decoupling experiments. The

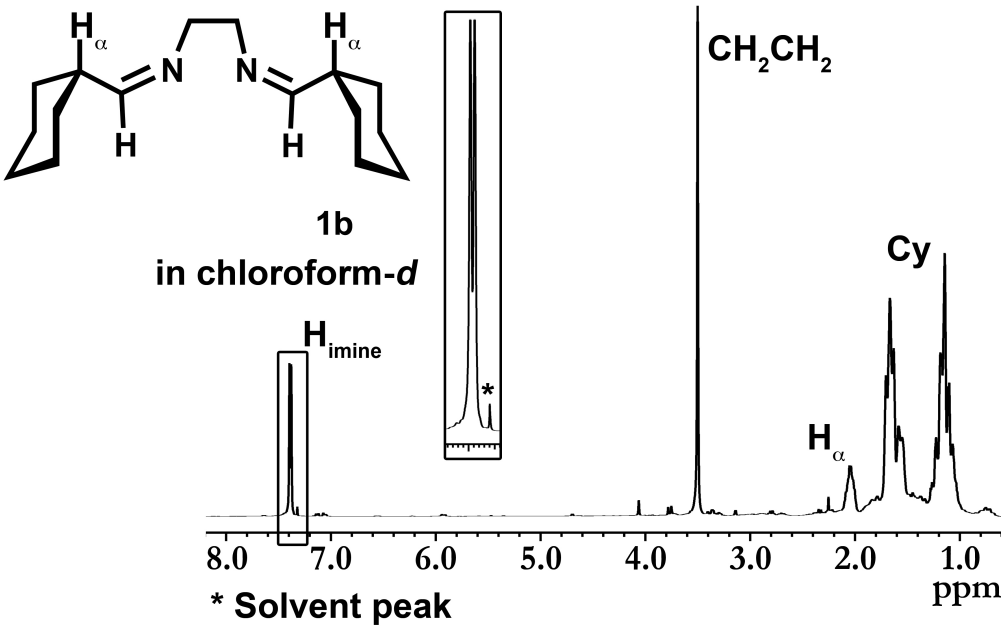


Figure 3-4. ^{1}H NMR spectrum (300 MHz) of compound **1b** in chloroform-*d*, with expanded H_{imine} region.

other peaks are typical for this species. Deprotonation of the α-proton in diimines **1** by LDA at low temperature leads to the corresponding *bis*(aza-allyl) ion which readily reacts at room temperature with 3-chloro-2-methylpropene to afford the alkenyl-substituted dialdemines **2**. The collapse of the signal at δ ≈ 7.4 in the ^{1}H NMR spectrum (the spectrum for **2b** is shown in Figure 3-5) from a doublet to a singlet (as well as the disappearance of the multiplet at δ ≈ 2.3 for the α-proton) confirm replacement by the new alkenyl fragment. All four environments in the new methylpropenyl group show up as four singlets in the ^{1}H NMR spectrum (with appropriate integrations) between δ ≈ 1.1 and δ ≈ 4.9 (one for the methylene groups, one for the methyl termina, and two peaks for the geminal olefinic protons) and interestingly display no mutual coupling (as observed in the mono-CAAC precursors),[37, 43] although the peaks are relatively broad. The peaks representing the other proton environments in the ^{1}H NMR spectrum are relatively unchanged, and are typical for these systems.

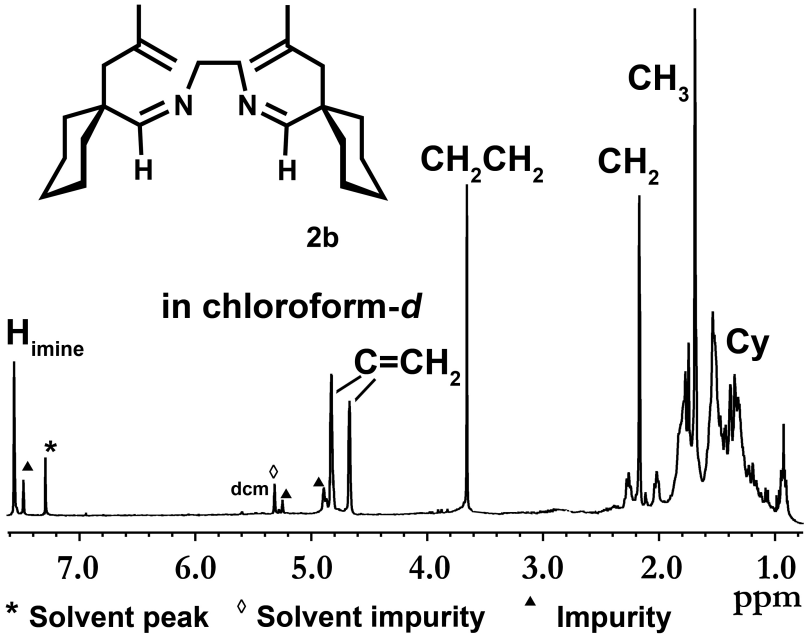
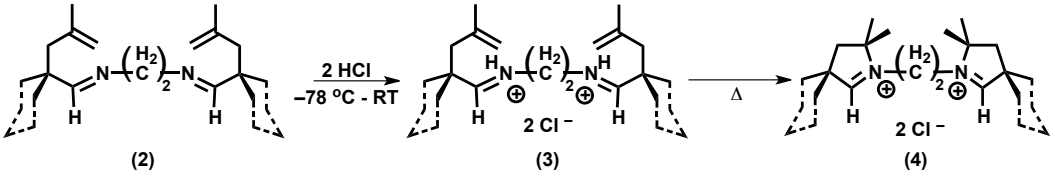


Figure 3-5. ^{1}H NMR spectrum (300 MHz) of compound **2b** in chloroform-*d*.

In the synthesis of mono-CAAC cyclic iminium salt precursors (Scheme 3-3d), the cationic species is usually prepared in one pot from the alkenylaldemine (Scheme 3-3b), skipping isolation of the acyclic alkenylaldiminium precursor (Scheme 3-3c). As a result, we sought to make our di-CAAC protio-analogues in a similar fashion, by the addition of acid to species **2** (Scheme 3-5), followed by heating at reflux. Addition of a stoichiometric amount of a 2.0 M solution of HCl in diethyl ether to a toluene solution of **2** at –78 °C resulted in the immediate formation of a white precipitate, which was subsequently heated for 24 h, after which time the volatiles were removed under vacuum to afford another white substance.



Scheme 3-5. Anticipated synthesis of ethylene-linked di-CAAC protio-precursors.

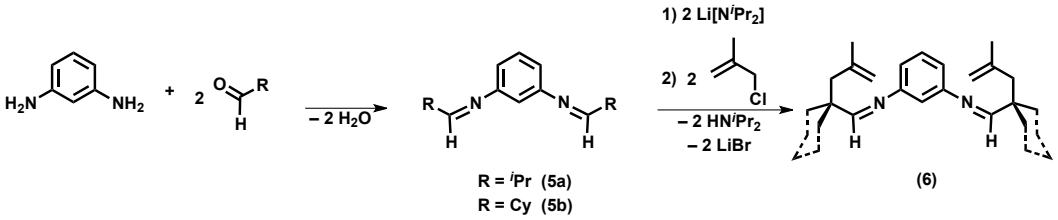
Unfortunately, this species did not show the expected high-frequency peak in the ^{1}H NMR spectrum ($\delta \approx 10$) for the acidic proton, but instead displayed a cluttered and indecipherable spectrum. Furthermore, HRMS analyses showed no evidence for the desired products (either M^+ or M^{2+}). Even attempts to isolate the acyclic species **3** (by halting the reaction after protonation) produced similar results.

3.2.2 Attempted synthesis of aryl-linked di-CAAC ligands

Since our attempts to produce alkyl-linked di-CAACs were unsuccessful, we began investigating the synthesis of analogous di-CAAC species linked by an electron-withdrawing group. Such an approach seemed reasonable since the highest-yielding mono-CAAC syntheses have involved an aryl-substituent at nitrogen,[43] and we

reasoned that an aryl-linked diamine might withdraw enough electron density from each imine to allow transfer of the proton to the pendent olefins.

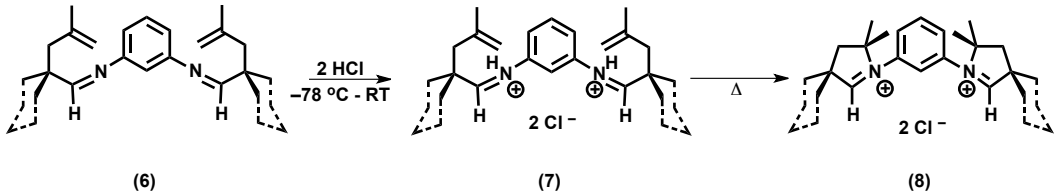
Although attempts to condense *ortho*-phenylenediamine with various secondary aldehydes failed, formation of the desired *meta*-phenylenediimine (Scheme 3-6) proved successful. Compounds involving both an *iso*-propyl- (**5a**) and



Scheme 3-6. Attempted synthesis of *meta*-substituted di-CAAC protio-precursors.

cyclohexyl-substituted α-carbon atom (**5b**) were produced in excellent yields as yellow oils. Both α-protons can be deprotonated by LDA (as was shown in the ethylene-linked attempts in Section 3.2.1) to allow aza-allyl attack on 3-chloro-2-methylpropene to produce compounds **6**. The ^{1}H and ^{13}C NMR spectral parameters are almost identical to their $–CH_2CH_2–$ analogues mentioned earlier, with the exception of the aromatic peaks in the linker.

With these diimines linked by an electron-withdrawing aromatic group, it seemed as though these systems were well set up for hydroiminiumation with HCl, as was attempted (unsuccessfully) above. The synthesis of the cyclic species **8** from **6** (without attempts to isolate species **7**, Scheme 3-7) was attempted *via* the same



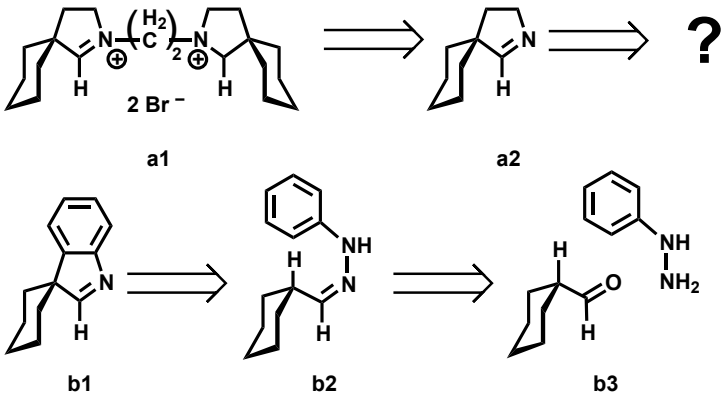
Scheme 3-7. Attempted synthesis of *meta*-substituted di-CAAC ligand precursors.

method as before – using a stoichiometric amount of a 2.0 M solution of HCl in diethyl ether to a toluene solution of **6** at –78 °C, then heating at reflux in toluene for 24 h. However, once again only a mixture of uncharacterizeable products was observed, which remained difficult to purify, even under a variety of conditions. Attempts to isolate the intermediate alkenyliminium salts (**7**) also proved futile. Furthermore, these species are dicationic, which precludes purification by column chromatography. As was the case with the ethylene-linked systems, no evidence for the desired products could be obtained from HRMS analyses.

3.2.3 Attempted synthesis of indolenine-based di-CAAC ligands

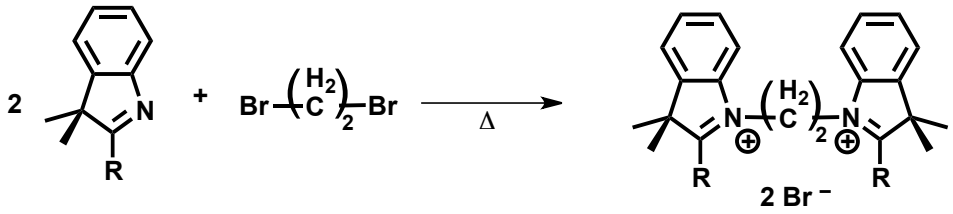
In a final attempt to make bidentate versions of the popularized CAAC ligands, we decided to attempt to build the CAAC rings individually, with subsequent coupling using an appropriate linker to make diiminium salts (Scheme 3-8a1), much like the synthesis of di-NHCs in Chapter 2, wherein we prepared imidazole rings, then coupled them with $Br(CH_2)_nBr$ (n = 1, 2) to form the diimidazolium salt precursors.

Although there have been no reports in the literature on the preparation of 3,4-dihydro-2*H*-pyrrole frameworks (Scheme 3-8a2), the preparation of similar indolenine systems (Scheme 3-8b1) is possible through the acid-catalyzed



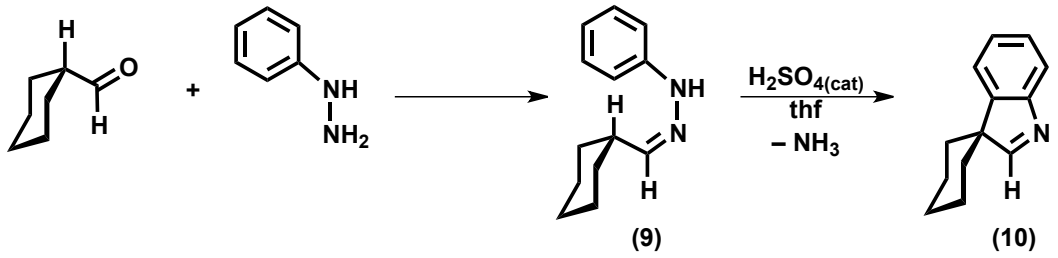
Scheme 3-8. Retrosynthetic analysis for 3,4-dihydro-2*H*-pyrrole and indolenines.

tautomerization and [3,3]-sigmatropic rearrangement of hydrazones (Scheme 3-8b2), which can easily be synthesized from their respective aldehyde and phenylhydrazine (Scheme 3-8b3). Furthermore, Mushkalo *et al.* had reported that dicationic systems similar to our target were possible through the coupling of two substituted indolenine rings (Scheme 3-9, R = CH_3).[46] Based on this finding, we believed that dicationic systems with an acidic proton (Scheme 3-9, R = H) were possible if indolines such as the one proposed in Scheme 3-8b1 were used.



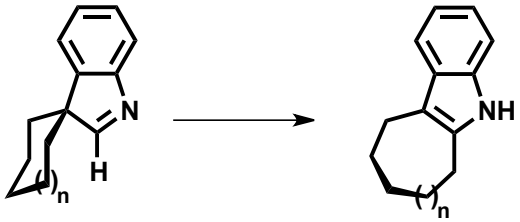
Scheme 3-9. Reported synthesis of indolium salts.

The synthesis of the indolenine species **10** had recently been reported,[47] involving condensation of the aldehyde and hydrazine precursors to form the analogous phenylhydrazone **9** (Scheme 3-10). Injection of a small amount (4 mol%) of acid catalyst initiated tautomerization and a [3,3]-sigmatropic rearrangement to afford the desired indolenine species **10** as a yellow oil.



Scheme 3-10. Synthesis of phenylhydrazone **9** and indolenine **10** from aldehyde and hydrazine.

However, indolenines have been reported to undergo indolenine-indole isomerization if not properly stabilized. For example, in the previously-mentioned report by Linnepe *et al.*, it was noted that in most cases, indolization (Scheme 3-11)



(10) (11)

Scheme 3-11. Proposed ring-expanding decomposition pathway of indolenine to indole.

of the indolenines can occur at various rates, depending on the stability of the indolenine, to form corresponding indoles **11**. In cases in which compounds **10** contained a spiro-cyclopentyl group (n = 0), this rearrangement is quite rapid, and the indolenine is often difficult to isolate. However, when a cyclohexyl or cycloheptyl group is employed (n = 1, 2), this rearrangement does *not* occur (unless under extreme forcing conditions)[vi] due to the stability of the six- and seven-membered ring. As a result, we decided to forgo attempts to synthesize dimethyl-substituted indolenine-based CAACs (considering the indolenines would surely indolize) and only examined flexible CAAC spiro-cyclohexyl systems.

Mushkalo *et al.* reported that the synthesis of their diindolium salt (Scheme 3-9) required heating in 1,2-dibromomethane (b.p. = 132.0 °C).[46] However, this temperature is higher than the reported temperature for ring expansion of **10**.[47] As a result, we instead attempted to couple these materials by heating at reflux in acetonitrile (b.p. = 82.0 °C). But, at these lower temperatures, no product was

[vi] The authors reported conversion to the indole in the case of spiro-cyclohexyl and -cycloheptyl substitution after 3 h heating at reflux in dioxane (b.p. = 101.1 °C).[47]

observed. Increasing the temperature to 132.0 °C also failed to produce the desired product; only decomposition of the starting material into some form of a ring-expanded product (containing no acidic proton) was observed.

Section 3.3 Discussion

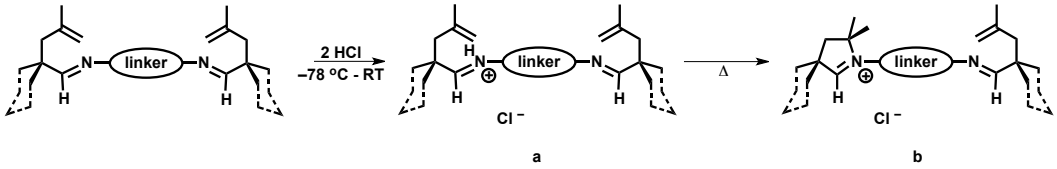
Unfortunately we were unsuccessful in our attempts to create di-CAAC ligands for use in bridging both homo- and heterobimetallic systems. Although all steps leading to protonation by HCl were not as high-yielding or as easily-purified as their reported mono-CAAC analogues, the desired diimine **2** products could still be isolated *via* slight modifications to purification methods.

However, synthesis of the dicationic carbene-precursors **4** proved to be disappointingly difficult, despite their deceiving appearance as a pristine, white, microcrystalline material. It is possible that the alkyl-substituted imines used in these attempts are too basic to allow transfer of the proton to the olefin to initiate cyclization, although aryl-substituted amines were successful in hydroamination.[44] Even in a variety of solvents, the ^{1}H NMR spectra displayed a mixture of uncharacterizeable products.

Even attempts to isolate the acyclic products **3** were ineffective. Protonation was attempted under a variety of conditions, including at various low temperatures, using a gaseous HCl purge into a low-temperature solution of the substituted diimine, as well as attempts using other strong acids. However, it appeared that all species (both alkyl- and aryl-linked) were unstable to protonation, and could not be isolated. Even attempts to produce di-CAACs using a protocol similar to the initial

reported CAAC synthesis (Scheme 3-2) produced an uncharacterizeable mixture of products without any evidence for the targeted alkoxide from epoxide ring-opening.

We also attempted the careful addition of one equivalent of hydrochloric acid (using the 2.0 M diethyl ether solution) in hopes of isolating a monocationic species (Scheme 3-12a), which could potentially be cyclized to form the mono-cyclic precursor (Scheme 3-12b), fully analogous to previous work with mono-CAACs. It



Scheme 3-12. Proposed route to CAAC-anchored/pendent alkenylaldemine precursors.

was suspected that perhaps the relatively small molecule was unable to accommodate a dicationic charge, and that isolation of a cyclic iminium salt with a pendent alkenylaldemine could potentially be attached to a transition metal (as a monocarbene) followed by formation of the second ring by protonation and subsequent heating to form a [M(CAAC)L_n/CAAC(H)][X] species, which would be well-suited as a di-CAAC-bridged heterobimetallic precursor. However, even attempts to form mono-protonated species failed. Clearly the ^{i}Pr substituents of the Dipp group plays an important role in the synthesis and stability of CAAC ligands and their precursors, which has been alluded to by Bertrand.[vii]

The final attempts to form di-CAAC precursors using spiro-indolenines were also futile. The propensity for cyclohexyl ring expansion and the high temperatures required for nucleophilic attack of the nitrogen atom on dibromomethane (and even diiodomethane) resulted in an incompatible route for di-CAAC precursors.

[vii] In conversations with Prof. Guy Bertrand and Dr. Rei Kinjo.

Section 3.4 Experimental Procedures

3.4.1 General comments

Deuterated solvents used for NMR experiments were freeze-pump-thaw degassed and stored under argon over type 4A molecular sieves. Unless otherwise specified, reactions were carried out at ambient temperature. *n*-Butyllithium (2.0 M solution in hexanes), 3-chloro-2-methylpropene, cyclohexanecarboxaldehyde, 1,2-dibromoethane, dibromomethane, diisopropylamine, 2,2-dimethyloxirane, ethylenediamine, hydrogren chloride (2.0 M in diethyl ether), isobutyraldehyde, *meta*-phenylenediamine, *ortho*-phenylenediamine, phenylhydrazine, and trifluoromethane-sulfonic anhydride were purchased from Aldrich. Type 4A molecular sieves were purchased from ACP. All chemicals were used without further purification, with the exception of ethylenediamine and cyclohexanecarboxaldehyde, which were purified by short-path vacuum distillation before use. Lithium diisopropylamide (LDA) was prepared *in situ* by the reaction of diisopropylamine with *n*-butyl lithium at –78 °C in thf. Compounds **1a**,[45] **9**,[47] and **10**[47] were prepared as reported previously. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian DirectDrive 500 MHz, iNova-500, or iNova-400 spectrometer operating at 499.82, 498.12, or 399.79 MHz for ^{1}H; 125.68, 125.26, or 100.53 MHz for ^{13}C{^{1}H}, respectively; or on a Varian iNova-300 operating at 299.97 MHz for ^{1}H. The ^{1}H and ^{13}C{^{1}H} chemical shifts are referenced to TMS. The order of appearance of chemical shift assignments are based on their region in the molecule rather than increasing or decreasing frequency of their resonance. Elemental Analyses were performed by the microanalytical service within this department. Likewise, mass spectrometric analyses were performed by the

departmental Mass Spectrometry Laboratory using positive ion electrospray ionization on an Agilent Technologies 6220 Accurate-mass TOF LC/MS.

3.4.2 Preparation of compounds

(i) N^1,N^2-*bis*(Cyclohexylmethylene)ethane-1,2-diamine, [CyCH=N]$_2$(μ-C$_2$H$_4$) (1b). A 25 mL portion of toluene was added to a flask containing cyclohexanecarboxaldehyde (8.1 mL, 67 mmol) and type 4A molecular sieves (17 g). Ethylenediamine (2.2 mL, 33 mmol) was slowly injected into the flask, resulting in a cloudy discharge above the solution. The resulting solution was stirred for 13 h under reflux conditions and cooled to room temperature. The solution was passed through a bed of Celite before the solvent was then removed under reduced pressure, giving 2.6915 g (33%) of a viscous yellow oil. ^{1}H NMR (299.97 MHz, chloroform-*d*, 27.5 °C): 10.18 (d, 2H, $^3J_{H\text{-}H}$ = 5.0 Hz, NCH); 3.50 (s, 4H, NCH_2CH_2N); 2.04 (m, 2H, CH_a); 2.03-1.00 (m, 20H, Cy). ^{13}C{^{1}H} NMR (100.54 MHz, chloroform-*d*, 26.5 °C): 170.6 (s, 2C, NCH); 61.3 (s, 2C, NCH_2CH_2N); 43.5 (s, 2C), 29.9 (s, 4C), 26.1 (s, 2C), 25.6 (s, 4C, Cy). HRMS *m*/*z* Calcd for $C_{16}H_{29}N_2$ ($M+H^+$): 249.2325. Found: 249.2322 ($M+H^+$).

(ii) N^1,N^2-*bis*(2,2,4-Trimethylpent-4-en-1-ylidene)ethane-1,2,-diamine, [(CH$_3$)$_2$C(CH$_2$C(CH$_3$)=CH$_2$)CH=N]$_2$(μ-C$_2$H$_4$) (2a). A 5 mL portion of diethyl ether was added to a flask containing diimine **1a** (0.299 g, 1.78 mmol). The solution was purged with argon gas for 10 min, at which point it was slowly added to a –78 °C solution of LDA (3.5 mmol) in 15 mL of diethyl ether *via* cannula. The mixture was allowed to warm to room temperature, and stirred for an additional 3 h, while the solution turned from colourless to yellow to dark orange. The volatiles were

then removed under reduced pressure, giving an orange foam. The foam was redissolved in 15 mL of diethyl ether and the solution was cooled to a –78 °C, to which 3-chloro-2-methyl-1-propene (0.36 mL, 3.7 mmol) was slowly injected, producing a smokey discharge above the solution. The mixture was allowed to warm to room temperature, and stirred for an additional 13 h. The volatiles were then removed under reduced pressure, and the resulting red oil was redissolved in a minimum amount of *n*-pentane (10 mL). The solution was passed through a bed of Celite, and the solvent was removed under reduced pressure, giving 0.475 g (97%) of a viscous red oil. ^{1}H NMR (498.12 MHz, chloroform-*d*, 26.1 °C): 7.31 (s, 2H, NCH); 2.19 (s, 4H, NCH_2CH_2N); 1.12 (s, 12H, $C(CH_3)_2$); 5.02 (m, 2H), 4.86 (m, 2H, $=CH_2$); 2.20 (d, 6H, $^{4}J_{H\text{-}H}$ = 2.2 Hz, CH_3); 1.86 (br s, 4H, CH_2). $^{13}C\{^{1}H\}$ NMR (100.53 MHz, chloroform-*d*, 26.5 °C): 169.7 (s, 2C, NCH); 61.8 (s, 2C, NCH_2CH_2N); 19.2 (s, 2C, $C(CH_3)_2$); 19.6 (s, 4C, $C(CH_3)_2$); 141.6 (s, 2C, $C=CH_2$); 115.9 (s, 2C, $C=CH_2$); 24.9 (s, 2C, CCH_3); 51.0 (s, 2C, CH_2).HRMS *m*/*z* Calcd for $C_{18}H_{33}N_2$ ($M+H^+$): 277.2638. Found: 277.2635 ($M+H^+$).

(iii) N^1,N^2-*bis*((1-(2-Methylallyl)cyclohexyl)methylene)ethane-1,2-diamine, $[(CH_2)_5C(CH_2C(CH_3)=CH_2)CH=N]_2(\mu\text{-}C_2H_4)$ (2b). The desired complex was prepared as described for **2a**, using **1b** (0.299 g, 1.20 mmol), LDA (2.50 mmol), and 3-chloro-2-methyl-1-propene (0.24 mL, 2.5 mmol). The crude product was purified as described for **2a**, and isolated using 15 mL of *n*-pentane, resulting in 0.368 g (86%) of a red oil. ^{1}H NMR (299.97 MHz, chloroform-*d*, 27.5 °C): 7.25 (s, 2H, NCH); 1.85 (s, 4H, NCH_2CH_2N); 1.85-1.12 (m, 12H, $C(CH_3)_2$); 4.87 (m, 2H), 4.71 (m, 2H, $=CH_2$); 2.25 (s, 6H, CH_3); 2.20 (br s, 4H, CH_2). $^{13}C\{^{1}H\}$ NMR (100.53 MHz, chloroform-*d*, 26.5 °C): 171.1 (s, 2C, NCH); 61.2 (s, 2C, NCH_2CH_2N); 28.9 (s,

4C), 27.3 (s, 4C), 26.7 (s, 4C), 21.2 (s, 2C, Cy); 140.9 (s, 2C, *C*=CH_2); 116.3 (s, 2C, C=*C*H_2); 25.6 (s, 2C, C*C*H_3); 50.9 (s, 2C, CH_2). HRMS *m*/*z* Calcd for $C_{24}H_{41}N_2$ ($M+H^+$): 357.3264. Found: 357.3259 ($M+H^+$).

(iv) Attempted synthesis of *N*^{1},*N*^{2}-*bis*(2,2,4-trimethylpent-4-en-1-ylidene)ethane-1,2-diaminium chloride, [$(CH_3)_2C(CH_2C(CH_3)=CH_2)CH=NH]_2(\mu\text{-}C_2H_4)[Cl]_2$ (3a). A 5 mL portion of *n*-pentane was added to a flask containing diimine **2a** (0.559 g, 2.02 mmol). The solution cooled to –78 °C, at which point an HCl solution (2.0 M in diethyl ether) was injected (2.6 mL, 5.2 mmol), resulting in the formation of a white precipitate. The mixture was stirred for 15 min, then slowly warmed to room temperature, at which point the mother liquor was decanted, and the white precipitate washed with 2 × 10 mL *n*-pentane, then dried under reduced pressure. The white precipitate was recrystallized in MeOH at 0 °C overnight, giving 0.524 g (74%) of a white, crystalline product. The substance was not the desired product as confirmed by spectroscopic methods. ^{1}H NMR (299.97 MHz, dmso-d_6, 27.5 °C): 8.39 (br s, 2H); 3.37 (s, 2H); 3.11 (pent, 2H, $J_{H\text{-}H}$ = 1.5 Hz). $^{13}C\{^1H\}$ NMR spectrum was not obtained.

(v) Attempted synthesis of *N*^{1},*N*^{2}-*bis*((1-(2-methylallyl)cyclohexyl)-methylene)ethane-1,2-diaminium chloride, [$(CH_2)_5C(CH_2C(CH_3)=CH_2)CH=NH]_2(\mu\text{-}C_2H_4)[Cl]_2$ (3b). Preparation of the desired complex was attempted as described for **3a**, using **2b** (0.084 g, 0.24 mmol) and HCl solution (2.0 M in diethyl ether, 2.6 mL, 5.2 mmol). Purification of the crude product was carried out as described for **3a**, and isolated as 0.030 g (30%) of a white, crystalline solid. The substance was not the desired product as confirmed by spectroscopic methods. ^{1}H NMR (299.97 MHz, dcm-d_2, 27.5 °C): 11.44 (br s, 2H); 6.02 (d, 2H,

$J_{H\text{-}H}$ = 9.3 Hz); 4.19 (d, 5H, $J_{H\text{-}H}$ = 9.3 Hz); 3.44 (s, 3H); 3.25 (t, 6, $J_{H\text{-}H}$ = 8.2 Hz); 1.95 (m, 188H). $^{13}C\{^{1}H\}$ NMR spectrum was not obtained.

(vi) First attempted synthesis of 1,1′-(ethane-1,2-diyl)*bis*(2,2,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrol-1-ium) chloride, $[(CH_3)_2C(CH_2C(CH_3)_2)CH{=}N]_2(\mu\text{-}C_2H_4)[Cl]_2$ (4a). Preparation of the desired compound was attempted as described for **3a**, using **2a** (0.100 g, 0.362 mmol) and HCl solution (2.0 M in diethyl ether, 180 μL, 0.36 mmol) in 15 mL of toluene and heated at reflux for 18 hr. Purification of the crude product was carried out as described for **3a**, and isolated as 0.043 g (34%) of a white, crystalline solid. The substance was not the desired product as confirmed by spectroscopic methods. ^{1}H NMR (498.12 MHz, dmso-d_6, 27.5 °C): 3.81 (br s, 2H); 2.51 (m, 1H); 1.25 (d, 1H, $J_{H\text{-}H}$ = 6.5 Hz); 1.02 (d, 2H, $J_{H\text{-}H}$ = 7.0 Hz). $^{13}C\{^{1}H\}$ NMR spectrum was not obtained.

(vii) Second attempted synthesis of 1,1′-(ethane-1,2-diyl)*bis*(2,2,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrol-1-ium) chloride, $[(CH_3)_2C(CH_2C(CH_3)_2)CH{=}N]_2(\mu\text{-}C_2H_4)[Cl]_2$ (4a). A 5 mL portion of diethyl ether was added to a flask containing diimine **1a** (0.300 g, 1.78 mmol). The solution was purged with argon gas for 2 min, at which point it was slowly added to a 0 °C solution of LDA (3.5 mmol) in 15 mL of diethyl ether *via* cannula. The mixture was allowed to warm to room temperature, and stirred for an additional 2.5 h, while the solution turned from colourless to dark orange. The volatiles were then removed under reduced pressure, giving an orange foam. The foam was redissolved in 15 mL of diethyl ether, to which 2,2-dimethyloxirane (0.32 mL, 3.6 mmol) was slowly injected, producing a smokey discharge above the solution. The mixture was allowed to warm to room temperature, and stirred for an additional 12 h. The solution was

then cooled to –78 °C volatiles and trifluoromethanesulfonic anhydride (0.60 mL, 3.6 mmol) was slowly injected which turned the solution a bright yellow colour instantly. The solution was allowed to warm to room temperature, and the mother liquor was decanted to waste. The crude product was washed with 3 × 10 mL diethyl ether and dried under reduced pressure. The crude mixture was redissolved in 5 mL dcm and recrystallized with diethyl ether and *n*-pentane, producing an oily yellow precipitate. The precipitate was dried under reduced pressure, which resulted in a yellow foam. The substance was not the desired product as confirmed by spectroscopic methods.

(viii) First attempted synthesis of 2,2′-ethane-1,2-diyl*bis*(3,3-dimethyl-2-azoniaspiro[4.5]dec-1-ene) dichloride, $[(CH_2)_5C(CH_2C(CH_3)_2)CH{=}N]_2(\mu\text{-}C_2H_4)[Cl]_2$ (4b). Preparation of the desired compound was attempted as described for **3a**, using **2b** (0.105 g, 0.294 mmol) and HCl solution (2.0 M in diethyl ether, 180 μL, 0.36 mmol) in 15 mL of toluene and heated at reflux for 18 hr. Purification of the crude product was carried out as described for **3a**, and isolated as 0.056 g (45%) of a white, crystalline solid. The substance was not the desired product as confirmed by spectroscopic methods. ^{1}H NMR (498.82 MHz, chloroform-*d*, 27.3 °C): 7.27 (br s, 4H); 2.99 (s, 1H); 2.80 (s, 1H); 1.50 (br s, 6H); 1.21 (m, 10H); 0.92 (m, 4H); 0.5 (br s, 20H). ^{13}C{^{1}H} NMR spectrum was not obtained.

(ix) Second attempted synthesis 2,2′-ethane-1,2-diyl*bis*(3,3-dimethyl-2-azoniaspiro[4.5]dec-1-ene) dichloride, $[(CH_3)_2C(CH_2C(CH_3)_2)CH{=}N]_2(\mu\text{-}C_2H_4)[Cl]_2$ (4b). Preparation of the desired compound was attempted as described for **4a**, using **2b** (0.422 g, 1.70 mmol), LDA (3.5 mmol), and 2,2-dimethyloxirane (0.33 mL, 3.6 mmol) in 5 mL of diethyl ether. Purification of the crude product was

carried out as described for **4a**, and isolated as a yellow foam. The substance was not the desired product as confirmed by spectroscopic methods.

(x) N^1,N^3-*bis*(2-Methylpropylidene)benzene-1,3-diamine, [^{i}PrCH=N]$_2$(μ-*m*-C$_6$H$_4$) (5a). Preparation of the desired compound was attempted as described for **2b**, using *meta*-phenylenediamine (2.372 g, 21.93 mmol), isobutyraldehyde (4.0 mL, 43.85 mmol), and type 4A molecular sieves (15 g) in 40 mL of toluene and heated at reflux for 12 hr. Purification of the crude product was carried out as described for **2b**, and isolated as 4.326 g (91%) of a yellow oil. ^{1}H NMR (299.97 MHz, chloroform-*d*, 27.0 °C): 7.36 (d, 2H, $^3J_{H\text{-}H}$ = 6.2 Hz, NCH); 7.32 (br m, 4H, Ph); 2.50 (m, 2H, CH$_\alpha$); 1.36 (br m, 6H), 1.13 (br m, 6H, ^{i}Pr). ^{13}C{^{1}H} NMR (100.54 MHz, chloroform-*d*, 26.5 °C): 163.8 (s, 2C, NCH); 147.6 (s, 2C), 140.5 (s, 1C), 123.5 (s, 2C), 120.1 (s, 1C, Ar); 29.9 (s, 2C), 12.9 (s, 2C), 8.91 (2C, ^{i}Pr). HRMS *m*/*z* Calcd for $C_{14}H_{21}N_2$ (M+H$^+$): 217.1699. Found: 217.1700 (M+H$^+$).

(xi) N^1,N^3-*bis*(cyclohexymethylene)benzene-1,3-diamine, [CyCH=N]$_2$(μ-*m*-C$_6$H$_4$) (5b). Preparation of the desired compound was attempted as described for **2b**, using *meta*-phenylenediamine (2.164 g, 20.01 mmol), cyclohexylcarboxaldehyde (5.1 mL, 42 mmol), and type 4A molecular sieves (15 g) in 40 mL of toluene and heated at reflux for 12 hr. Purification of the crude product was carried out as described for **2b**, and isolated as 4.627 g (78%) of a yellow oil. ^{1}H NMR (299.97 MHz, chloroform-*d*, 27.0 °C): 7.41 (d, 2H, $^3J_{H\text{-}H}$ = 6.0 Hz, NCH); 7.30 (br m, 4H, Ph); 2.61 (m, 2H, CH$_\alpha$); 1.90-1.12 (br m, 20H, Cy). ^{13}C{^{1}H} NMR (100.54 MHz, chloroform-*d*, 26.5 °C): 164.7 (s, 2C, NCH); 145.3 (s, 2C), 141.2 (s, 1C), 122.4 (s, 2C), 121.3 (s, 1C, Ar); 44.3 (s, 2C), 30.2 (s, 4C), 27.1 (s, 2C), 26.1 (s, 4C, Cy).

(xii) N^1,N^3-*Bis*(2,2,4-trimethylpen-4-en-1-ylidene)benzene-1,3-diamine, $[(CH_3)_2C(CH_2C(CH_3)=CH_2)CH=N]_2(\mu\text{-}m\text{-}C_6H_4)$ (6a). The desired compound was prepared as described for **2a**, using **5a** (0.309 g, 1.43 mmol), LDA (2.90 mmol), and 3-chloro-2-methyl-1-propene (0.31 mL, 3.2 mmol). The crude product was purified as described for **2a**, and isolated using 30 mL of *n*-pentane, resulting in 0.399 g (86%) of a red oil. ^{1}H NMR (299.97 MHz, chloroform-*d*, 27.0 °C): 7.24 (d, 2H, $^3J_{H\text{-}H}$ = 6.0 Hz, NCH); 7.40 (br m, 4H, Ph); 1.25 (br m, 6H), 1.13 (br m, 6H, ^{i}Pr), 4.75 (m, 2H), 4.70 (m, 2H, =CH_2); 2.31 (s, 6H, CH_3); 2.22 (br s, 4H, CH_2). ^{13}C{^{1}H} NMR (100.54 MHz, chloroform-*d*, 26.5 °C): 163.8 (s, 2C, NCH); 147.6 (s, 2C), 140.5 (s, 1C), 123.5 (s, 2C), 120.1 (s, 1C, Ar); 30.1 (s, 2C), 11.9 (s, 2C), 8.74 (s, 2C, –$C(CH_3)_2$); 141.1 (s, 2C, *C*=CH_2); 117.1 (s, 2C, C=*C*H_2); 25.6 (s, 2C, C*C*H_3); 51.3 (s, 2C, CH_2).

(xiii) N^1,N^3-*Bis*((1-(2-methylallyl)cyclohexyl)methylene)benzene-1,3-diamine, $[(CH_2)_5C(CH_2C(CH_3)=CH_2)CH=N]_2(\mu\text{-}m\text{-}C_6H_4)$ (6b). The desired compound was prepared as described for **2a**, using **5b** (0.124 g, 0.418 mmol), LDA (0.878 mmol), and 3-chloro-2-methyl-1-propene (0.11 mL, 1.1 mmol). The crude product was purified as described for **2a**, and isolated using 30 mL of *n*-pentane, resulting in 0.129 g (76%) of red/orange oil. ^{1}H NMR (299.97 MHz, chloroform-*d*, 27.0 °C): 7.34 (d, 2H, $^3J_{H\text{-}H}$ = 5.8 Hz, NCH); 7.50 (br m, 4H, Ph); 1.91-1.08 (br m, 20H, Cy); 4.74 (m, 2H), 4.77 (m, 2H, =CH_2); 2.29 (s, 6H, CH_3); 2.19 (br s, 4H, CH_2). ^{13}C{^{1}H} NMR (100.54 MHz, chloroform-*d*, 26.5 °C): 163.8 (s, 2C, NCH); 147.5 (s, 2C), 141.2 (s, 1C), 122.7 (s, 2C), 120.9 (s, 1C, Ar); 44.7 (s, 2C), 30.8 (s, 4C), 27.2 (s, 2C), 26.3 (s, 4C, Cy).; 140.7 (s, 2C, *C*=CH_2); 116.8 (s, 2C, C=*C*H_2); 25.8 (s, 2C, C*C*H_3); 50.7(s, 2C, CH_2).

(xiv) Attempted synthesis of N^1,N^3-*bis*(2,2,4-trimethylpent-4-en-1-ylidene)-benzene-1,3-diaminium chloride, $[(CH_3)_2C(CH_2C(CH_3)=CH_2)CH=NH]_2(\mu\text{-}m\text{-}C_6H_4)[Cl]_2$ (7a). Preparation of the desired compound was attempted as described for **3a**, using **6a** (0.066 g, 0.20 mmol) and HCl solution (2.0 M in diethyl ether, 0.51 mL, 1.0 mmol). Purification of the crude product was carried out as described for **3a**, and isolated as 0.061 g of a white, crystalline solid. The substance was not the desired product as confirmed by spectroscopic methods. ^{1}H NMR (299.97 MHz, dmso-d_6, 27.5 °C): 8.18-7.68 (br m), 7.54 (s), 4.63-3.80 (br s), 1.86-0.73 (br m). $^{13}C\{^1H\}$ NMR spectrum was not obtained.

(xv) Attempted synthesis of N^1,N^3-*bis*((1-(2-methylallyl)cyclohexyl)-methylene)benzene-1,3-diaminium chloride, $[(CH_2)_5C(CH_2C(CH_3)=CH_2)CH=NH]_2(\mu\text{-}m\text{-}C_6H_4)[Cl]_2$ (7b). Preparation of the desired compound was attempted as described for **3a**, using **6b** (0.235 g, 0.581 mmol) and HCl solution (2.0 M in diethyl ether, 0.6 mL, 1.2 mmol). The crude product was purified as described for **3a**, and isolated as 0.030 g of a white, crystalline solid. The substance was not the desired product as confirmed by spectroscopic methods. ^{1}H NMR (299.97 MHz, dcm-d_2, 27.5 °C): 10.56 (br s); 6.02 (br s); 1.65 (br s), 2.45-0.71 (br m) $^{13}C\{^1H\}$ NMR spectrum was not obtained.

(xvi) Attempted synthesis of $[(CH_3)_2C(CH_2C(CH_3)_2)CH=N]_2(\mu\text{-}m\text{-}C_6H_4)[Cl]_2$ (8a). Preparation of the desired compound was attempted as described for **3a**, using **6a** (0.235 g, 0.724 mmol) and HCl solution (2.0 M in diethyl ether, 1.8 mL, 3.6 mmol) in 15 mL of toluene and heated at reflux for 18 hr. Purification of the crude product was carried out as described for **3a**, and isolated as 0.154 g of a white, crystalline solid. The substance was not the desired product as confirmed by

spectroscopic methods. ^{1}H NMR (498.12 MHz, dmso-d_6, 27.5 °C): 4.35-4.12 (br s), 3.75 (br s); 2.55 (m); 1.27-0.76 (m). ^{13}C{^{1}H} NMR spectrum was not obtained.

(xvii) Attempted synthesis of [[(CH$_2$)$_5$C(CH$_2$C(CH$_3$)$_2$)CH=N]$_2$(μ-*m*-C$_6$H$_4$)[Cl]$_2$ (8b). Preparation of the desired compound was attempted as described for **3a**, using **6b** (0.325 g, 0.803 mmol) and HCl solution (2.0 M in diethyl ether, 1.0 mL, 2.0 mmol) in 15 mL of toluene and heated at reflux for 18 hr. Purification of the crude product was carried out as described for **3a**, and isolated as 0.214 g of a white, crystalline solid. The substance was not the desired product as confirmed by spectroscopic methods. ^{1}H NMR (498.12 MHz, dmso-d_6, 27.5 °C): 7.84 (m), 4.36-4.01 (br s), 2.41-0.76 (br m). ^{13}C{^{1}H} NMR spectrum was not obtained.

(xviii) Attempted synthesis of 1,1'-methylene*bis*(3-cyclohexyl-3*H*-indol-1-ium) bromide, [[(CH$_2$)$_5$C(CH$_2$C(CH$_3$)$_2$)CH=N]$_2$(μ-*m*-C$_6$H$_4$)[Cl]$_2$. A 30 mL portion of toluene was added to a flask containing indolenine **10** (0.443 g, 2.39 mmol), at which point dibromomethane (0.10 mL, 1.4 mmol) was injected. The solution was heated at reflux for 12 hours, resulting in the formation of a white precipitate. The reaction was allowed to cool to room temperature, at which point the mother liquor was decanted, and the white precipitate washed with 2 × 10 mL *n*-pentane, then dried under reduced pressure, giving 0.524 g of a white, crystalline product. The substance was not the desired product as confirmed by spectroscopic methods. ^{1}H NMR (299.97 MHz, dmso-d_6, 27.5 °C): 6.63-7.22 (m), 5.71 (s); 2.24-1.22 (m). ^{13}C{^{1}H} NMR spectrum was not obtained.

Section 3.5 References

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Chapter 4 Synthesis of Unsymmetrical Dicarbenes Based on *N*-Heterocyclic/Mesoionic Carbene Frameworks and the Use of "Pendent" Strategies for Hybrid Dicarbene-Bridged Mixed-Metal Systems

Section 4.1 Introduction

4.1.1 From metal alkylidenes to ancillary carbene ligands

As was explained in Chapter 1, carbenes are reactive organic molecules, and undoubtedly the most influential applications for these species (Nobel Prize in Chemistry, 2004)[1-3] were discovered by Grubbs[4-7] (Figure 4-1a) and Schrock[8-14] (Figure 4-1b,c). These two Nobel laureates utilized this reactivity in the form of metal-alkylidene-type carbene complexes (*i.e.*, $L_nM{=}CR_2$) that could easily catalyze [2+2] cycloadditions (*via* the $L_nM{=}CR_2$ functionality itself), which is an important reaction in directing processes such as ring-opening metathesis (polymerization) (ROM(P)), ring-closing metathesis (RCM), and acyclic diene metathesis (ADMET).[15]

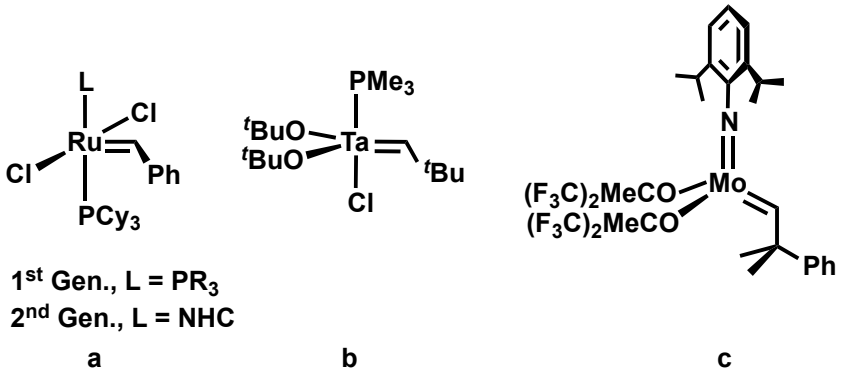

Figure 4-1. Examples of olefin metathesis catalysts incorporating $L_nM{=}CR_2$ carbene functionality.

Further indication of the reactivity of carbenes is evident in the extensive efforts over 200 years to try and stabilize them as "free", unprotected species.[16-28] Through various studies, further stabilization of $:CR_2$ systems (see Section 1.2) has

allowed for the development of certain carbenes as free "bottleable" species. As a result, they can easily be attached to a wide variety of transition metals, adopting an important role as useful *ancillary* ligands, where they can have an important influence on the catalytic activity of the attached metal (*cf.*, Grubbs's 2nd Generation catalyst).[29] For example, with the discovery of a free, isolable *N*-heterocyclic carbene (NHC) by Arduengo in 1991,[27] the use of carbene ligands has risen tremendously (especially in homogeneous catalysis),[30-33] intensifying their already well-established presence in organometallic chemistry.[15, 34, 35] The significant interest in NHCs and related species has led to several variations of this ligand, as described in Chapter 1.

However, in all cases leading up to the year 2001, imidazole-3-ylidene-based NHCs (whether free or bound to metals) invariably had its lone pair situated on the C-2 carbon (Figure 4-2a). Cases involving C-4 (Figure 4-2b, or C-5 depending on the nature of R and R′[36]) carbenes had not been considered as likely alternatives until a computational report by Sini, Eisenstein, and Crabtree[37] which indicated that free "wrong-way" C-4 carbenes should be isolable, since their lone-pair-containing HOMO lies at only slightly higher energy (–4.4 eV) relative to that of "normal" NHCs (–5.0 eV).[38]

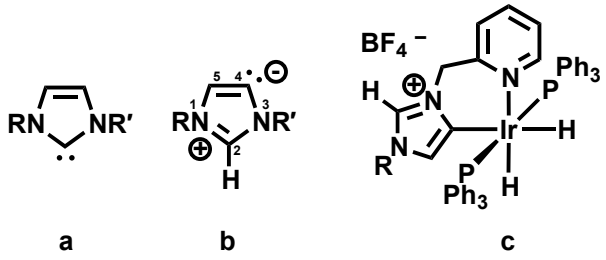

Figure 4-2. Different binding modes for NHCs.

4.1.2 "Abnormal" *N*-heterocyclic carbenes

Around the same time, Crabtree *et al.* confirmed this notion experimentally in their report of the internal base-deprotonation of a pyridine-functionalized imidazolium species at the C-5 carbon rather than the expected C-2 position (Figure 4-2c, R = ^{i}Pr, *n*-Bu).[39] Since this discovery, a number of groups have targeted these species[36, 40-49] since they exhibit impressive electron-donating properties. In addition to being adjacent to only one electron-withdrawing group, the zwitterionic character of these carbenes puts a negative charge on the carbene carbon in several relevant resonance forms (*vide infra* - Figure 4-3), making it a better donor.[36, 40]

These "wrong-way" carbenes have been referred to as NHCs as a consequence of their lineage (having very similar structural characteristics); however, since no reasonable resonance forms containing a carbene can be drawn for the free ligands without additional charges,[50, 51] they have been described as "abnormal" NHCs (*a*NHCs).[36, 38, 40, 50, 52] The fact that these compounds require mesoionic[i] resonance forms to represent the carbene character (*i.e.*, a lone pair on carbon) led Bertrand to suggest[54] that they be grouped into a category known as mesoionic carbenes (MICs).[ii]

Subsequently, Bertrand *et al.* isolated a variety of *free* MICs such as *a*NHCs (Figure 4-3a)[38], and "remote" NHCs (*r*NHCs, in which the stabilizing heteroatoms are located at positions β to the carbene as opposed to the more-common α position, Figure 4-3b1),[56-59] which are also known as bent-allenes (Figure 4-3b2).[60, 61]

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[i] Dipolar five- (or six-) membered heterocyclic compounds in which both the negative and the positive charge are delocalized, for which a totally-covalent structure cannot be written, and which cannot be represented satisfactorily by any one polar structure.[53]

[ii] MICs have several zwitterionic resonance forms which may have a larger contribution to the overall binding mode than in classical NHCs, and hence the term "carbene" needs some caution.[50, 55]

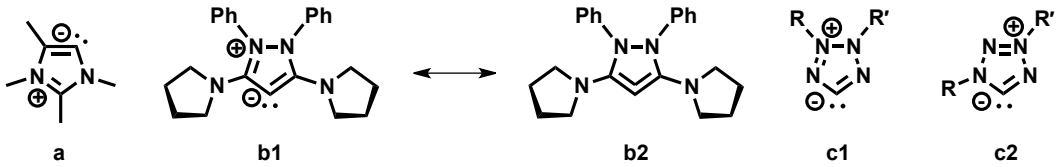


Figure 4-3. Different carbenes from the MIC family.

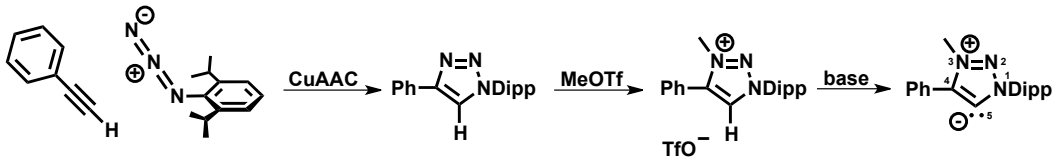
Other groups have focused on other (now-termed) MICs as well, such as 2,3-substituted tetrazol-3-ylidenes (Figure 4-3c1)[62] and 2,4-substituted tetrazol-5-ylidenes (Figure 4-3c2).[63-65]

4.1.3 Unsymmetrical dicarbenes

For reasons outlined in Chapter 1, our group is interested in studying bimetallic complexes, in many of which the two metals are different. With two different metals incorporated into one complex, a rich, more diverse array of reactivity patterns becomes available, expanding the scope of bimetallic complexes and their use in catalysis. We recently reported (in Chapter 2) success in bridging heterobimetallic complexes of the Pd/Rh combination using "normal" C-2-bound, symmetrical di-NHCs.[66] In the search for different dicarbenes to bridge our Pd/Rh systems of interest, we hoped to prepare a series of di-CAAC ligands, but were unsuccessful in our attempts as described in Chapter 3.

In a search for other dicarbenes capable of bridging two metals, we became interested in bidentate carbenes created by the coupling of two *a*NHCs (Figure 4-3a) because it seemed that their synthesis should be fairly straightforward. There already existed a few reports involving di-*a*NHCs[67-70] (one of them interestingly reporting an anchored-*a*NHC/pendent *a*NHC(H)$^+$ complex),[68] however, the harsh conditions needed to deprotonate them usually resulted in monometallic *chelates*. Around this time, Albrecht *et al.* reported the synthesis of 1,2,3-triazolium salts using the copper-

catalyzed azide-alkyne cycloaddition (CuAAC, "click" chemistry[71, 72]) and subsequent methylation, followed by internal base deprotonation (by $[Pd(OAc)_2]$) or silver-transfer to yield Pd-, Ru-, Rh-, and Ir-MICs;[55] while Bertrand *et al.* reported a similar



Scheme 4-1. Reported "click" synthesis of a 1,2,3-triazol-5-ylidene, a type of MIC.

high-yielding synthesis of a *free* MIC, as shown in Scheme 4-1.[54] Both are more-accurately described as "1,2,3-triazol-5-ylidene" carbenes, but are herein referred to as MICs for simplicity. These reports prompted us to investigate the synthesis of bridging dicarbenes incorporating MIC frameworks for our heterobimetallic Pd/Rh systems.

Although we did see value in making symmetric di-MICs[73] (see Chapter 5), we were more tempted to examine the synthesis of *unsymmetrical* dicarbenes, since only three examples were known at the time this work began.[74-76] As a result, we initiated a study on the synthesis of hybrid, unsymmetrical NHC/MIC dicarbenes (and their use as bridges in mixed-metal complexes) to further develop this area. The reports already in the literature on unsymmetrical dicarbenes ranged from comparatively simple examples of a di-NHC having different outer-nitrogen substituents (Figure 4-4a)[75] to more complicated systems[iii] involving two different types of carbenes (Figure 4-4b,c).[74, 76] On the basis of our "pendent strategy"

[iii] The homobimetallic di-Pd complex involving two 1,3-dialkylimidazol-2-ylidene/1,2,4-triazol-5-ylidene bridges (Figure 4-4b) was isolated and characterized;[74] whereas the report using an NHC/MIC framework (Figure 4-4c, analogous to our system of interest) involved deprotonation of the dicationic precursors in the presence of $[Pd_2(dba)_3]$ to generate a Suzuki-Miyaura catalyst *in situ*.[76] No dicarbene complexes were isolated or characterized.

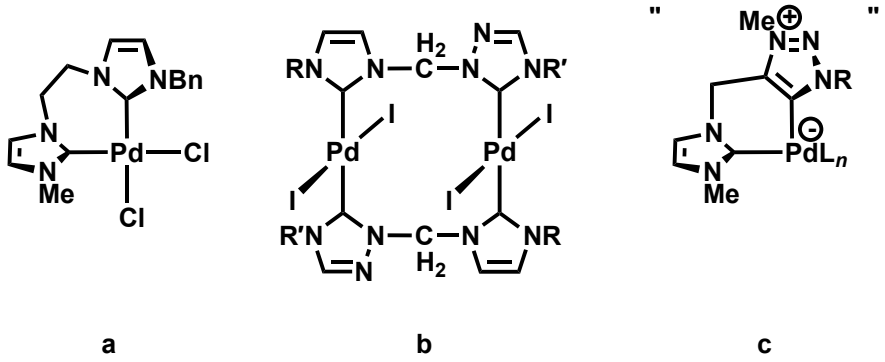
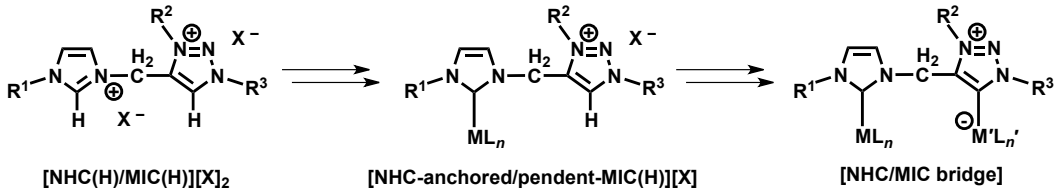


Figure 4-4. Previously-reported examples of unsymmetrical dicarbenes.

reported in Chapter 2 (and, to an extent, in Chapter 3), we anticipated that a similar strategy of incorporating the metal atoms one at a time was the most promising route to these mixed-metal NHC/MIC-bridged targets. Unlike symmetrical dicarbenes, the two different carbene precursors have different acidities, and therefore the order of metal atom incorporation dictates the nature of NHC or MIC attachment in the bridge. However, based on the acidities[77] of the two species (*vide infra*), deprotonation of the imidazolium end and accompanying attachment of the resulting NHC seemed most likely to occur first (Scheme 4-2).



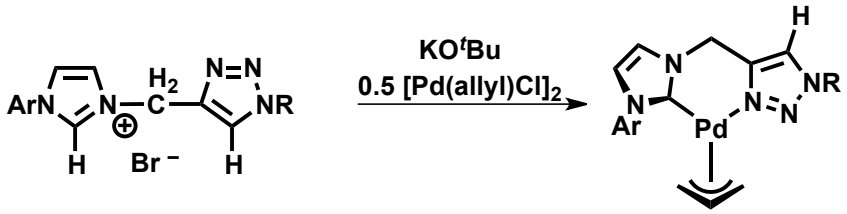
Scheme 4-2. Proposed pendent strategy for generation of dicarbene-bridged mixed-metal systems.

Section 4.2 Results and Compound Characterization

4.2.1 Establishing a strategy

As noted earlier,[54] Bertrand *et al.* had reported the synthesis of an MIC (Scheme 4-1) by coupling an aryl azide with phenylacetylene (PhC≡CH) using

"click" chemistry to form a 1,2,3-triazole,[71, 72, 78-81] followed by alkylation at N-3[iv] to generate a cationic triazolium ring, which could later be deprotonated to form the MIC. In a subsequent report by Warsink *et al.*,[86] the preparation of various triazolyl-functionalized imidazole-based NHCs (for the purpose of functionalizing a carbene with a pendent hemilabile *N*-donor, Scheme 4-3) was outlined by coupling an azide with the pendent propargyl arm (–$CH_2C\equiv CH$) of an imidazolium salt. Inspired by



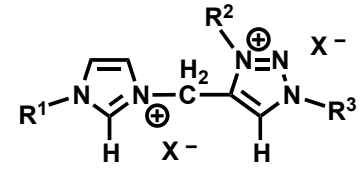
Scheme 4-3. Warsink procedure to hemilabile donor-functionalized NHC complexes of Pd.

both of these studies, we began investigating the synthesis of the desired hybrid NHC/MIC precursors by combining these two methodologies.

Throughout this chapter we use the abbreviations $[^{R1}Im(H)Trz(H)^{R2}_{R3}][X]_2$ for the $NHC(H)^+/MIC(H)^+$ dicationic dicarbene precursors, (^{R1}Im-κ^1-$Trz(H)^{R2}_{R3}$) for the monodentate NHC-anchored, pendent-triazolium $NHC/MIC(H)^+$ species, and (μ-$^{R1}ImTrz^{R2}_{R3}$) for bidentate hybrid NHC/MIC dicarbene bridges, which are a slight modification to the original nomenclature for symmetric di-NHCs used in Chapter 2 and originally suggested by Green, *et al.*,[87] as shown in Figure 4-5. In these abbreviations the imidazole substituent (R^1) on the imidazolium/NHC ring appears first, followed by either the dicationic ring (Im(H)Trz(H)), anchored-NHC/pendent-triazolium (Im-κ^1-Trz(H)), or bridging NHC/MIC (ImTrz) notation, and finally two stacked symbols designating the substituents on the triazolium/MIC ring at the N-3

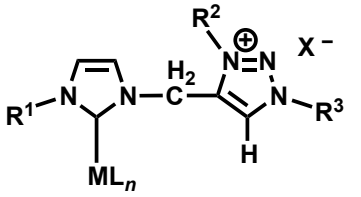
[iv] There are routes to *arylation* at N-3,[82-85] but the nature/variation of this group was not the focus of this study, and therefore methyl examples were the only ones investigated.

(R^2) and N-1 (R^3) positions. We will additionally use the label **a** in the numbering scheme to indicate the Me/Me/Bn combination, the label **b** for Me/Me/Dipp, and **d** to denote the ^{t}Bu/Me/Dipp group of substituents.



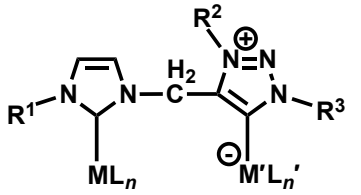
$R^1 = CH_3$; $R^2 = CH_3$; R^3 = Bn: ^{Me}Im(H)Trz(H)$^{Me}_{Bn}$ (a)
$R^1 = CH_3$; $R^2 = CH_3$; R^3 = Dipp: ^{Me}Im(H)Trz(H)$^{Me}_{Dipp}$ (b)
$R^1 = {}^t$Bu; $R^2 = CH_3$; R^3 = Dipp: ^{tBu}Im(H)Trz(H)$^{Me}_{Dipp}$ (c)

$[^{R1}\text{Im(H)Trz(H)}^{R2}_{R3}][X]_2$



$R^1 = CH_3$; $R^2 = CH_3$; R^3 = Bn: ^{Me}Im-κ^1-Trz(H)$^{Me}_{Bn}$ (a)
$R^1 = CH_3$; $R^2 = CH_3$; R^3 = Dipp: ^{Me}Im-κ^1-Trz(H)$^{Me}_{Dipp}$ (b)
$R^1 = {}^t$Bu; $R^2 = CH_3$; R^3 = Dipp: ^{tBu}Im-κ^1-Trz(H)$^{Me}_{Dipp}$ (c)

$[ML_n(^{R1}\text{Im-}\kappa^1\text{-Trz(H)}^{R2}_{R3})][X]$



$R^1 = CH_3$; $R^2 = CH_3$; R^3 = Bn: μ-^{Me}ImTrz$^{Me}_{Bn}$ (a)
$R^1 = CH_3$; $R^2 = CH_3$; R^3 = Dipp: μ-^{Me}ImTrz$^{Me}_{Dipp}$ (b)
$R^1 = {}^t$Bu; $R^2 = CH_3$; R^3 = Dipp: μ-^{tBu}ImTrz$^{Me}_{Dipp}$ (c)

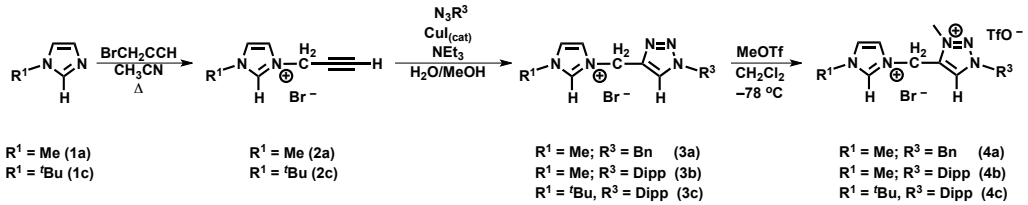
$[ML_n(\mu\text{-}^{R1}\text{ImTrz}^{R2}_{R3})M'L_n']$

Figure 4-5. Labelling scheme for free dication, pendent, and bridging systems.

4.2.2 Hybrid dicationic dicarbene precursors

As mentioned above, Warsink *et al.* reported a procedure for the syntheses of various 1,2,3-triazolyl-functionalized *N*-arylimidazolium compounds which could subsequently be transformed into several NHC complexes of Ag and Pd.[86] The NHC was functionalized with a pendent triazolyl arm to introduce a hemilabile nitrogen-donor, which would cause incipient coordinative unsaturation at the metal (because of hard-donor/soft-acceptor mismatch). From our perspective, we were

more interested in *N-alkyl* NHCs (in order to draw direct comparisons to our previous work in Chapter 2), therefore a slightly different procedure was developed. In addition, we wanted to extend the synthetic strategy to the transformation of the triazolyl moiety into a cationic triazolium species, which could be subsequently transformed into an MIC. Our developed synthesis (Scheme 4-4) produced a series of new organic compounds, and their spectral properties will be briefly discussed here.



Scheme 4-4. Synthesis of dicationic imidazolium/triazolium dicarbene precursors.

Reaction of the *N*-alkyl imidazoles (**1**)[88, 89] with propargyl bromide in refluxing acetonitrile provided the desired pendent-alkyne-functionalized imidazolium salts (**2**) in near-quantitative yields (**2a** had been prepared previously[90-92]). The products could easily be identified by their ^{1}H NMR spectra (The ^{1}H NMR spectrum for compound **2c** is shown in Figure 4-6 on the next page), in which the signal characteristic of the acidic imidazolium proton is observed as an overlapping doublet of doublets (or "pseudotriplet") at *ca.* 9.63 ppm,[v] due to equal coupling to both the imidazolium backbone protons, which also show up as doublets of doublets in the aromatic region, and can be individually distinguished using NOE NMR experiments. The propargyl substituent produces signals at *ca.* 5.35 ppm or the CH_2 moiety and *ca.* 3.35 ppm for the alkynyl proton (both showing small 4-bond mutual

[v] In acetonitrile-d_3. This peak is shifted to a significantly higher frequency (by about a full ppm) when dissolved in chlorinated solvents such as chloroform-*d* or dcm-d_2. This type of phenomenon is not uncommon in cationic carbene precursors.[93-95]

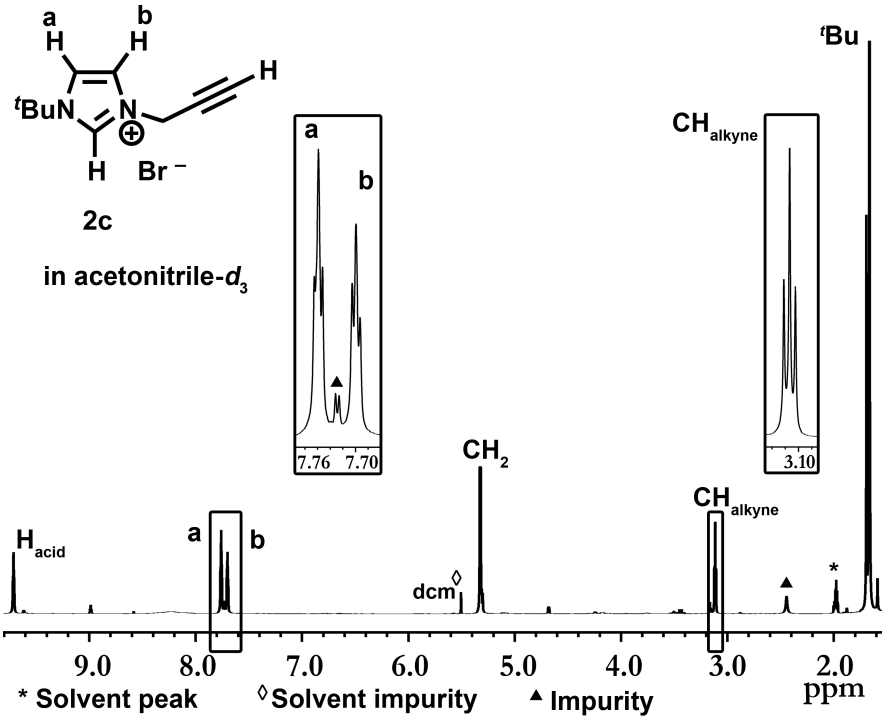


Figure 4-6. ^{1}H NMR spectrum (300 MHz) of compound **2c** in acetonitrile-d_3, with expanded olefinic and alkynyl regions.

coupling). Peaks for methyl or *tert*-butyl protons show up in the expected region of the spectrum (δ = 3.89[90-92] or δ = 1.68, respectively). In the $^{13}C\{^{1}H\}$ NMR spectra, individual peaks for all chemically inequivalent carbon nuclei (7 peaks for **2a**, 8 peaks for **2c**) are clearly evident. The assignment of two peaks (at δ = 76.0 and δ = 61.3) to each quaternary carbon (in the *tert*-butyl and the alkynyl groups) was ambiguous at first, but could be assigned using 2D gHMBC experiments through observation of (F_2, F_1) correlation peaks ($\delta_{^{1}H}$, $\delta_{^{13}C\{^{1}H\}}$) for the alkynyl group (3.13, 76.0) and for the *tert*-butyl quaternary carbon (1.68, 61.3).

The propargyl imidazolium salts **2** were then reacted with either benzyl azide (BnN_3)[96-98] or 2,6-diisopropylphenylazide ($DippN_3$)[99] in the presence of catalytic amounts of copper(I) iodide and triethylamine to form the 1,2,3-triazolyl pendent compounds (**3**). Most of the peaks in the ^{1}H NMR spectrum shift only slightly (since

their environments barely change) with the exception of the alkynyl proton – the environment for which has been transformed significantly. This proton shifts dramatically from *ca.* 3.35 ppm to *ca.* 8.41 ppm,[vi] and no longer displays coupling to the CH_2 group. This shift is consistent with the shielded environment of an alkyne proton (parallel to the magnetic field, $\boldsymbol{B}_0$) and the deshielded environment for the triazole protons (a result of the diamagnetic ring current observed in aromatic molecules).[100] Furthermore, in the cases involving the bulkier Dipp group (**3b**,**c**), the doublets representing the methyl groups of each *iso*-propyl substituent are in slightly different environments (*ca.* 1.11 ppm and *ca.* 1.08 ppm), indicating a barrier for rotation about the Ar–^{i}Pr bond. All peaks are typical for these types of systems, and display NMR spectral parameters comparable to similar systems.[76, 101-107]

The $^{13}C\{^1H\}$ NMR spectra also display typical resonances for an imidazolium/triazole system. As expected, the peaks in the imidazolium moiety change only slightly; however, there are significant shifts in the pendent arm, consistent with the transformation from an alkynyl group to a triazole ring. The terminal alkynyl carbon shifts from *ca.* 78.0 ppm to *ca.* 128.0 ppm, typical for the C–H environment of a 1,2,3-triazole,[100] and the alkynyl quaternary carbon, shifts from *ca.* 76.0 ppm to *ca.* 140.2 ppm, again as expected. The peaks corresponding to carbon atoms in the Dipp ring (**3b**,**c**) also show evidence for inhibited Ar–^{i}Pr bond rotation (two different $^i\text{Pr}_{\text{Me}}$ environments at $\delta = 24.0$ and $\delta = 24.2$, but only one $^i\text{Pr}_{\text{C–H}}$ environment, suggesting that N–Dipp rotation is not inhibited).

[vi] In acetonitrile-d_3. However, the peaks for the backbone unfortunately overlap in this solvent. Considering all peaks are more well-defined in chloroform-*d*, the NMR spectral data presented in Section 4.4.2 (Preparation of compounds) is from a sample dissolved in chloroform-*d*.

As noted earlier, Bertrand had established routes to MICs *via* alkylation[54] of a triazolyl group and subsequent deprotonation to afford the mesoionic species. Although successful methylation of the triazolyl ring at N-3 by reaction with iodomethane (CH_3I) at elevated temperatures had been reported,[41, 46, 49, 55, 76, 108, 109] we were unable to methylate our systems in this manner under a variety of conditions (others had also failed).[54, 73, 110, 111] However, the triazolyl-functionalized imidazolium salts (**3**) could be methylated using methyl trifluoromethanesulfonate (MeOTf) to afford the dicationic imidazolium/triazolium species [^{R1}Im(H)Trz(H)$^{Me}_{R3}$][Br][OTf] (**4**). At this time, we had no interest in varying this substituent (R^2), and all reports in this chapter involve a methyl group at this position.

Attempts to prepare the sterically less-bulky benzyl-substituted product **4a** did not yield the methylated product cleanly. It appears as though the benzyl group is not sufficiently bulky to afford regioselective methylation at N-3 (when using MeOTf),[vii] and results in an equal mixture of both N-2- and N-3-methylated isomers, as determined by ^{1}H NMR spectroscopy.[viii] As a result, focus was shifted to the ligands involving only a bulky N-1-group. In these systems, the Dipp substituent forces methylation solely at the N-3 position, resulting in clean production of the desired [^{Me}Im(H)Trz(H)$^{Me}_{Dipp}$][Br][OTf] (**4b**) and [(^{tBu}Im(H)Trz(H)$^{Me}_{Dipp}$][Br][OTf] (**4c**) products of the general NHC(H)$^+$/MIC(H)$^+$ formulation.

[vii] Kilpin *et al.* reported regioselective methylation at N-3 using "Meerwein's salt", Me_3OBF_4[94, 95] in the synthesis of their di-MIC precursors which contained benzyl substituents at N-1.[73] However, this methylating agent was not regioselective in our attempts. The authors mention however that various byproducts (perhaps some N-2 species) could be removed because the N-3 dications can (surprisingly) be purified by column chromatography.

[viii] Methylation using CH_3I (if applicable) is reported to be regioselective at N-3, regardless of the steric bulk of the substituent on N-1.[41, 46, 49, 76, 108, 109] Perhaps this can be attributed to the slightly higher nucleophilicity of N-3 vs. N-2, and the nonselective reactivity of MeOTf. It was postulated that heating a sample of both regioisomers would convert the N-2-methylated compounds to the N-3-products. Unfortunately, in our case, no conversion was observed.

Formation of the desired product could be monitored easily with the emergence of a new peak in the ^{1}H NMR spectrum at *ca.* 4.45 ppm, indicating methylation of the triazolyl moiety (at N-3). Once again, the other peaks in the ^{1}H NMR spectrum shift only slightly with the exception of the now-acidic triazolium proton, which moves to a higher frequency (*ca.* 8.70 ppm). Although compounds **2** and **3** all display three pseudotriplets (overlapping doublets of doublets) for the three imidazolium protons (because of identical mutual coupling between all three), only the backbone peaks appear as sharp pseudotriplets in **4b**, whereas the acidic peak is now somewhat broadened. However, by selectively decoupling at the frequency of the acidic peak at δ = 8.94, the two backbone peaks collapse into well-resolved doublets. The ^{1}H NMR spectrum of the *bis*(triflate) analogue of compound **4b** is shown in Figure 4-7. On the basis of these decoupling experiments, the two acidic

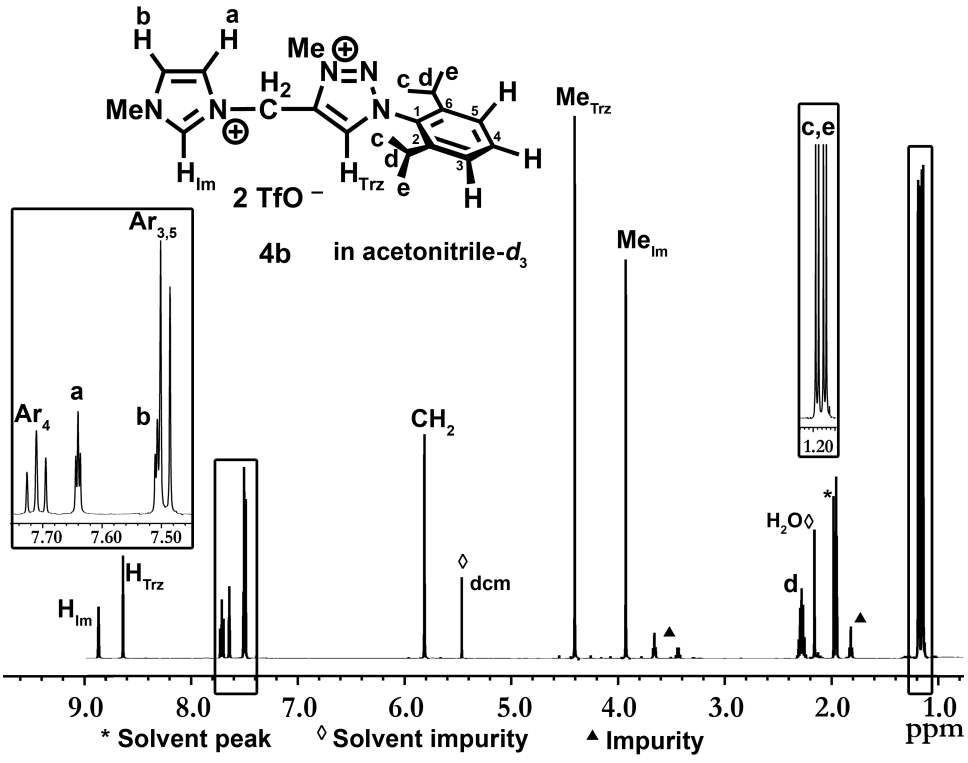


Figure 4-7. ^{1}H NMR spectrum (500 MHz) of compound **4b** in acetonitrile-d_3, with expanded olefinic/aromatic and ^{i}Pr regions

protons can be differentiated from one another, confirming that the peak at δ = 8.94 represents the imidazolium acidic proton, while the resonance at δ = 8.70 corresponds to the acid proton in the triazolium ring. To further confirm this assignment, the peak at δ = 8.94 displays an NOE correlation peak with the *N*-methyl/*tert*-butyl peak on the imidazolium ring.

The $^{13}C\{^1H\}$ NMR spectra of compounds **4** are essentially identical to those of their precursors (**3**) with the exception of the emergence of a new peak at *ca.* δ = 39.2 (for the methyl group on N-3), and a slight shift of the triazole carbons (C_{Trz}, 128.1 to 133.0 ppm) and C_{quat} (140.2 to 138.9 ppm). Once again two different $^{i}Pr_{Me}$ environments (but only one for $^{i}Pr_{C–H}$) are observed. Although the peaks for C_{Trz} and C4 in **4b** resonate at almost identical frequencies (133.2 ppm, 133.0 ppm, $\Delta\nu$ = 20 Hz), they can be differentiated with gHSQC experiments.[ix]

The X-ray structure determination for the *bis*(triflate) analogue of compound **4b**, shown in Figure 4-8,[x] confirms the structural assignments determined on the basis of spectral data. Although it was reasonably clear from the spectroscopy that methylation occurred only at the N-3 position (since the Me_{Trz} peak in the ^1H NMR spectrum displays an NOE correlation peak with the bridging methylene protons at *ca.* 5.80 ppm, while none of the ^{i}Pr peaks on the Dipp group display any interaction with this group), its N-3 attachment is unambiguously assigned with this structure

[ix] It is worth noting that the $^1J_{C-H}$ values for the peaks representing carbons attached to H_{Im}, H_{Trz}, and H_a (see Figure 4-7 for naming) are abnormally large, such that they are absent in $^{13}C\{^1H\}$ attached proton test (APT) NMR experiments (which uses a database of "normal" $^1J_{C-H}$ values to assign "up" or "down" peak intensity). Furthermore, the C–H coupling for the C_4 resonance is so large ($^1J_{C-H} \approx 210$ Hz), that it appears on the opposite phase (with CH_2/C_{quat} peaks).

[x] Note that in this and all subsequent crystallographic structures an arbitrary numbering scheme is used (and differentiated in the text with parentheses) as opposed to the standard organic numbering (naming) nomenclature.

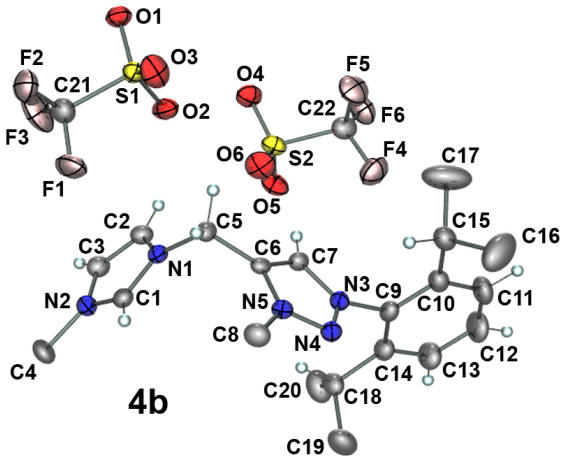


Figure 4-8. Three-dimensional representation of $[^{Me}Im(H)Trz(H)^{Me}_{Dipp}][OTf]_2$, **4b** showing the numbering scheme. Thermal ellipsoids are shown at the 20% probability level. Hydrogen atoms are shown only on non-methyl carbons. Relevant parameters (distances in Å and angles in deg.): C(2)–C(3) = 1.347(3), N(2)–C(1) = 1.323(2), N(1)–C(1) = 1.330(2), C(6)–C(7) = 1.364(2), N(5)–C(6) = 1.359(2), N(4)–N(5) = 1.321(2), N(3)–N(4) = 1.328(2), N(3)–C(7) = 1.351(2); N(1)–C(1)–N(2) = 108.5(2), N(3)–C(7)–C(6) = 106.0(2), N(4)–N(3)–C(9)–C(14) = 92.3(2).

determination (N(5) in Figure 4-8). The angles at C(1) (108.5(2)°) and C(7) (106.0(2)°) are typical for imidazolium[75] and triazolium compounds[54], which are larger than their respective metal-protected carbene (Im ≈ 104°; Trz ≈ 103°)[66, 109] and free-carbene (Im ≈ 102°; Trz ≈ 100°)[27, 54] counterparts in similar carbene systems. The protio-carbene atoms (C(1) and C(7)) are pointed in opposite directions, although rotation about the linker in solution is evident considering (for example) the protons on C(5) are chemically equivalent and show up as a singlet in the ^{1}H NMR spectrum. Similarly, the aryl ring of the Dipp group lies essentially perpendicular to the Trz(H) ring (dihedral angle N(4)–N(3)–C(9)–C(14) = 92.3(2)°), although rotation about this bond in solution is likely, as seen by the chemical equivalence of the protons on C(11) and C(13) in the ^{1}H NMR spectrum (in addition, C(11) and C(13) equivalence in the ^{13}C{^{1}H} NMR spectrum).

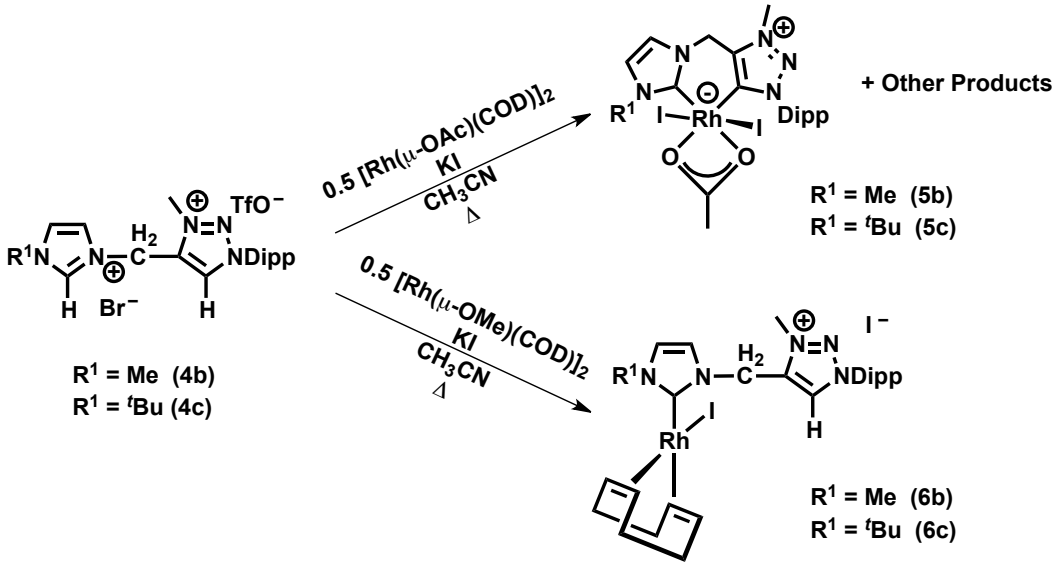
4.2.3 NHC-anchored/pendent triazolium complexes of Rh

As noted earlier, it appeared that NHC/MIC-dicarbene-bridged complexes involving two *different* metals could be accessed *via* deprotonation of a carbene-anchored/pendent-cation complex, of the type shown above in Scheme 4-2, in the presence of a second metal. We had already shown that such a strategy could be employed to generate di-NHC-bridged Rh_2,[112] Ir/Rh, and Pd/Rh complexes *via* deprotonation of mononuclear, anchored species by $[Rh(\mu\text{-}OAc)(COD)]_2$.[66] With the dicationic NHC/MIC precursors in hand (namely $[^{Me}Im(H)Trz(H)^{Me}_{Dipp}][Br][OTf]$ **4b** and $[^{tBu}Im(H)Trz(H)^{Me}_{Dipp}][Br][OTf]$ **4c**), we decided to use this acetate-containing Rh complex again to deprotonate the imidazolium half[xi] of the dicationic species **4**, in order to form the desired NHC-anchored/pendent-$MIC(H)^+$ species of Rh, which could presumably be further deprotonated by a different basic ligand-containing metal precursor ($M \neq Rh$).

However, reaction of both methyl- (**4b**) and *tert*-butyl-substituted (**4c**) complexes with half an equivalent of $[Rh(\mu\text{-}OAc)(COD)]_2$ in refluxing acetonitrile did not produce the desired NHC-$MIC(H)^+$ species, only a mixture of products, as determined by ^1H NMR spectral analysis (we were able to conclude however that *both* ends of the dication were being deprotonated, as evidenced by the disappearance of the two high-frequency acidic peaks). During purification attempts, we were successful in growing single crystals from the mixture, which allowed us to identify one product of this mixture as a chelated-NHC/MIC Rh(III) species with one OAc^-

[xi] 1,2,3-Triazol-5-ylidene-type MICs have shown to be significantly better electron donors than 1,3-dialkylimidazol-2-ylidene-type NHCs (based on lower $\nu_{C-O(trans)}$ values for MICs once attached to transition metal carbonyl complexes),[54, 55, 113] therefore it was assumed that the $MIC(H)^+$ end would be much less acidic than the $NHC(H)^+$ side. Furthermore, in our experience with carbenes, when comparing the ^1H NMR spectrum chemical shifts of two acidic pre-carbene protons, peaks which lie at higher frequencies tend to be deprotonated first (hence, more acidic).

ligand still coordinated (complexes **5b,c**, Scheme 4-5). These compounds are NHC/MIC analogues of a di-NHC species previously reported in 2002.[114]



Scheme 4-5. Reactions of dicationic species **4** with basic ligand-containing Rh precursors.

The X-ray structure determination for the compound **5b**, shown in Figure 4-9, confirms a chelate-type structure as suggested by the absence of high-frequency peaks for the acidic protons in the ^{1}H NMR spectrum.[xii] The rhodium atom has a distorted octahedral geometry with a chelated NHC/MIC group and mutually *trans* iodo ligands. The Rh–NHC (Rh–C(4) = 1.968(2) Å) and Rh–MIC (Rh–C(1) = 1.969(2) Å) bond lengths are virtually identical, and are shorter than observed in Rh(I)–NHC[66, 115] and Rh(I)–MIC cases,[55, 116] but typical for Rh(III)–carbene systems.[114] For other metals, MICs tend to have a shorter metal-MIC bond distances than analogous metal-NHC cases,[49, 66] but with an already contracted Rh-NHC bond

[xii] The amount of pure **5b** obtained was only a small quantity of crystalline material, and redissolving the sample in acetonitrile-d_3 to investigate the metal complex spectroscopically resulted only in a spectrum with a low signal-to-noise ratio, although some ^{1}H peaks could be identified. However, the initial sample (containing a mixture of species) displayed an absence of the high-frequency acidic peaks.

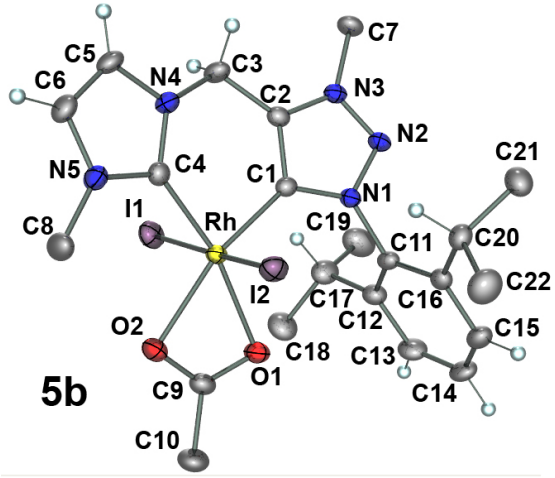


Figure 4-9. Three-dimensional representation of [$RhI_2(\kappa^2O,O'\text{-}OAc)(\kappa^2C^2,C^5\text{-}^{Me}ImTrz^{Me}_{Dipp})$], **5b** showing the numbering scheme. Thermal ellipsoids are as described in Figure 4-7. Hydrogen atoms are shown only on non-methyl carbons. Relevant parameters (distances in Å and angles in deg.): Rh–C(1) = 1.969(2), Rh–C(4) = 1.968(2), Rh–O(1) = 2.160(1), Rh–O(2) = 2.166(2); N(1)–C(1)–C(2) = 102.42(16), N(4)–C(4)–N(5) = 104.3(2), C(1)–Rh–C(4) = 87.79(8), O(1)–Rh–O(2) = 60.86(5), N(4)–C(3)–C(2) = 111.9(2), O(1)–C(9)–O(2) = 119.4(2), I(1)–Rh–I(2) = 171.778(8), N(2)–N(1)–C(11)–C(16) = 84.1(2), Rh–C(1)–C(2)–C(3) = 0.5(3), C(3)–N(4)–C(4)–Rh = 7.7(3), C(1)–Rh–O(1)–C(9) = –177.3(1), C(4)–Rh–O(2)–C(9) = 176.5(1).

(owing to the high oxidation state of Rh), a bond shorter than ~ 1.97 Å is probably unfavourable owing to crowding in this 6- coordinate species. Both Rh-acetate bonds (Rh–O(1) and Rh–O(2)) are essentially identical (2.160(1), 2.166(1) Å), suggesting no significant difference in *trans*-influence of the two carbenes.

The angles at C(4) (104.3(2)°) and C(1)[xiii] (102.4(2)°) are typical for NHC[26] and MIC complexes, which are smaller than the angles of the respective carbons in the protio-ligand (Figure 4-8) but still larger than in cases of free carbenes of these types.[27, 54] This trend of decreasing angles at carbon ($X_2C{:}\text{–}H^+ > X_2C{:}\text{–}ML_n > X_2C{:}$) is consistent with an increasing demand for s character in the lone pair-containing orbital on carbon. The highest demand (and as a result the smallest angle at carbon) occurs in free carbenes ($X_2C{:}$) wherein the lone pair (not being shared between two

[xiii] Note that C(1) in this structure refers to the MIC donor atom, and not the NHC carbene carbon, as was the case in the structure of **4b**.

atoms) it is only attracted to one nucleus, therefore it can get closer to carbon's core in an orbital with significant s character. This demand is reduced in cases where the electrons are involved in bonding, and increases with Lewis acid acceptors of increasing electronegativity.[117] The stabilizing s character on carbon is presumably aided by the withdrawal of p character from carbon by the carbene substitutents (X) into the C–X bonds.[21, 118] Again, the aryl ring of the Dipp group adopts an orientation almost perpendicular to the Trz plane (torsion angle N(2)–N(1)–C(11)–C(16) = 84.1(2)°) which, as a result, forces the *trans* iodides to bend away from the Dipp group (I(1)–Rh–I(2) = 171.778(8)°). The entire dicarbene is almost planar, deviating from planarity only slightly at the CH_2 linker (torsion angle C(3)–N(4)–C(41)–Rh = 7.7(3)°).

Since all attempts using $[Rh(\mu\text{-}OAc)(COD)]_2$ failed to generate the $[RhI(COD)(^{R1}Im\text{-}\kappa^1\text{-}Trz(H)^{Me}_{Dipp})][I]$ systems of interest, we attempted deprotonation using a complex containing a much stronger base (so that milder conditions could be used). Alkoxide anions are certainly more basic than OAc^-, and there have been a few examples of $[Rh(\mu\text{-}OMe)(COD)]_2$ functioning both as a source of Rh and a deprotonating agent.[119, 120] As a result, we tested this Rh complex's ability to deprotonate the imidazolium end of our NHC/MIC precursors (again using only one-half equivalent). With only mild heating in acetonitrile, we were able to successfully generate the desired Rh NHC/MIC(H)$^+$ species **6** (Scheme 4-5).

The ^{1}H NMR spectral parameters for the series of complexes (**6b** and **6c**) display many similarities to the NHC-anchored/pendent-imidazolium complexes of Rh, reported in Chapter 2, but also include some important differences (resulting from the triazolium arm) which were observed in complexes **4** of this chapter.

Complexes **6** show typical resonances for the CH_2 groups in the COD ligands (between ~ 1.0 and 2.6 ppm), as well as peaks for the olefinic CH groups *cis* ($\delta \approx 3.6$)[xiv] and *trans* ($\delta \approx 5.2$) to the NHC. Interestingly, both peaks for the *cis* protons overlap to form a broad singlet, whereas individual peaks can be seen for each *trans* proton.

The pendent structure of complexes **6** is easily confirmed by the presence of only one acidic (H_{Trz}) proton in the high-frequency region of the ^{1}H NMR spectrum as a sharp singlet (the ^{1}H spectrum for complex **6b** is shown below in Figure 4-10). Furthermore, the "pseudotriplets" observed for the imidazolium backbone protons have collapsed into doublets due to the absence of the $^4J_{H\text{-}H}$ coupling to the acidic proton of the precursor. The AB pattern observed for the linker CH_2 protons rather than a singlet suggests that the NHC unit adopts the usual orientation in which it is bound perpendicular to the square plane of the metal. In this orientation, the plane bisecting the linking CH_2 group is unsymmetrical on each side, having an iodo ligand on one side, and one half of the COD ligand on the other. Finally, the ^{1}H NMR spectrum implies that there is a considerable barrier to rotation about the N–Ar bond of the pendent group (in addition to the barrier for Ar–^{i}Pr rotation, as also observed in compounds **4**) since there are four separate ^{i}Pr doublets around 1.1 ppm; and two separate doublets for the protons on C3 and C5 of the aryl ring, which show coupling to the proton on C4 ($^3J_{H\text{-}H} \approx 8$ Hz), as well as small mutual coupling ($^4J_{H\text{-}H} = 1$ Hz).

[xiv] The *cis* and *trans* olefinic COD C–H peaks could be differentiated since the methyl group in **6b** displayed an NOE correlation peak with resonance for only the *cis* protons. Although correlations peaks are observed corresponding to an interaction between the *tert*-butyl protons in **6c** and *both* a) the *cis* peaks and b) one of the *trans* peaks, this is consistent with observations in Chapter 2, where the *tert*-butyl methyl groups are close (within ~ 3 Å) to both "outside" protons in the COD ligand.

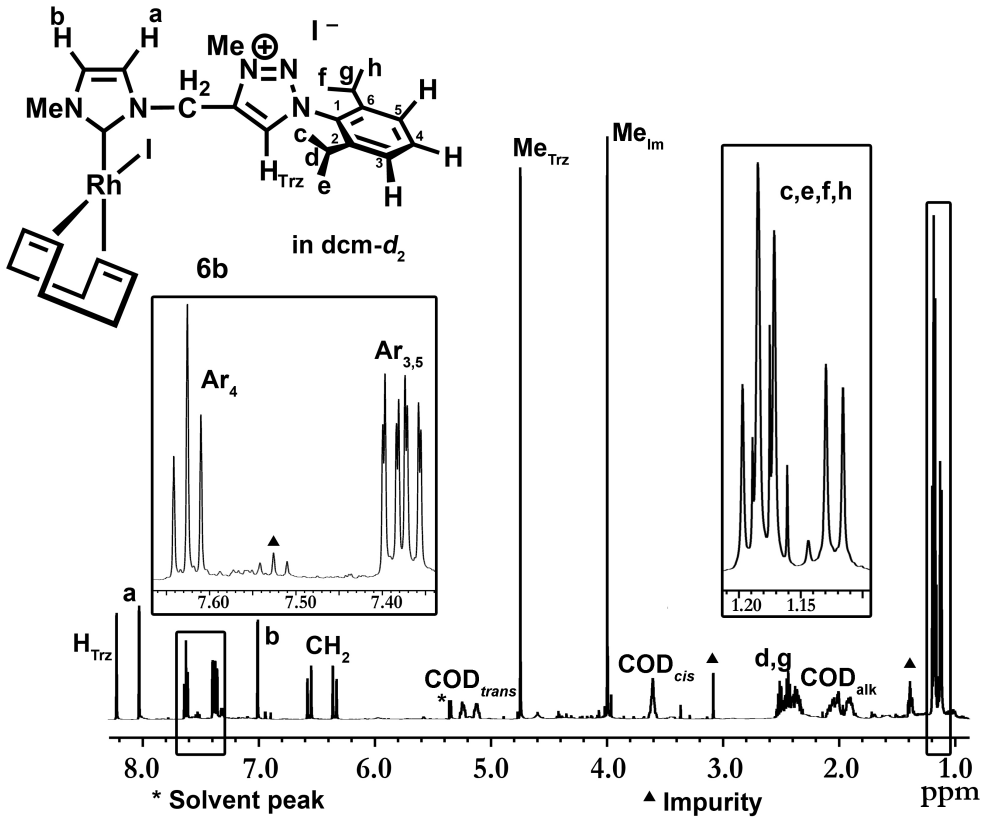


Figure 4-10. ^{1}H NMR spectrum (500 MHz) of complex **6b** in dcm-d_2, with expanded aromatic and ^{i}Pr regions.[xv]

The $^{13}C\{^1H\}$ NMR spectra for complexes **6** display peaks typical for a coordinated NHC, a pendent triazolium group, and a Rh-coordinated COD ligand. Specifically, the $C_{carbene}$ appears as a doublet ($^1J_{C\text{-}Rh}$ = 49.2 Hz) at *ca.* 185.0 ppm, whereas the rest of the peaks for the carbons in the NHC and MIC(H)$^+$ have not changed significantly from the spectra of compounds **4**. Evidence for a chelated COD ligand is also present owing to the emergence of two doublets at *ca.* 97.5 ppm

[xv] The expanded aliphatic region is somewhat complicated (see Figure 4-10) because of four different doublets (representing four different ^{i}Pr methyl environments, c,e,f,h) in a small area ($\Delta\delta \approx 0.1$ ppm or 50 Hz). Furthermore, the ^{i}Pr C–H environments (d,g) are also overlapping, and are also masked by the COD_{alkyl} peaks. However, using a chemical shift selective filter (CSSF), each individual C–H shift on C_g and C_d can be pinpointed and selectively excited. Combining this technique with a 1D-total correlation spectroscopy (1D-TOCSY) experiment, both spin systems can be separated, which results in (1) two doublets ($\Delta\delta \approx 27.7$ Hz, $^4J_{H\text{-}H}$ = 6.8 Hz) and (2) two other doublets, which overlap, appearing as a triplet ($\Delta\delta \approx 6.6$ Hz, $^4J_{H\text{-}H}$ = 6.7 Hz).

($^1J_{C\text{-}Rh}$ ≈ 6.6 Hz) representing the olefinic carbons *trans* to the NHC, as well as two doublets at *ca.* 73.0 ppm ($^1J_{C\text{-}Rh}$ ≈ 14.2 Hz) for the carbons in the *cis* position. Interestingly, as was observed in the ^{1}H NMR spectrum, the $^{13}C\{^1H\}$ NMR spectra indicate a barrier to rotation about the N–Ar bond, as well as the Ar–^{i}Pr bond, by the existence of 12 different peaks for the $C_{12}H_{17}$ Dipp group. Finally, both peaks for C4 and C_{Trz} in **6b** are extremely close together (δ = 133.3, 133.2), and could not be differentiated by 2D gHSQC or gHMQC NMR experiments (in both cases, the 2D contours were centred at δ = 133.3). In lieu of modifying acquisition parameters (digital resolution, etc.), a proton-coupled ^{13}C NMR experiment allowed for differentiation of these two peaks, because the carbon and hydrogen nuclei at

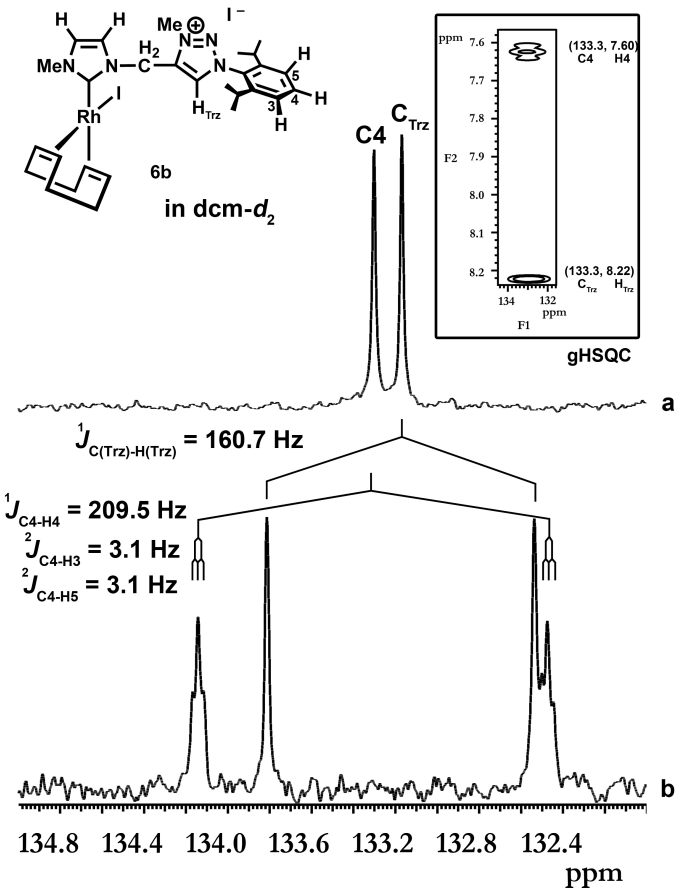
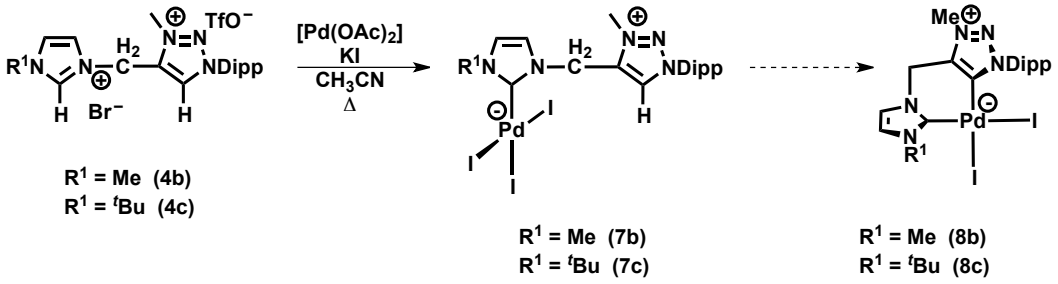


Figure 4-11. $^{13}C\{^1H\}$ (**a**) and ^{13}C (**b**) NMR spectra (101 MHz) for complex **6b** in dcm-d_2 with gHSQC inset.

position 4 display the same "abnormally large" $^{1}J_{C\text{-}H}$ behavior of its precursor **5b** (see footnote ix, page 169). This large C–H coupling ($^{1}J_{C4\text{-}H}$ = 209.5 Hz as opposed to $^{1}J_{C(Trz)\text{-}H}$ = 160.7 Hz) in addition to the obvious difference in coupling patterns (a doublet of doublet of doublets for C4 and a simple doublet for C_{Trz}) allowed us to distinguish between these two peaks, as shown above in Figure 4-11.

4.2.4 NHC-anchored/pendent triazolium complexes of Pd

An analogous series of NHC-anchored/pendent-triazolium complexes of palladium can be generated by similar procedures used to generate NHC-anchored/pendent-imidazolium complexes by Herrmann[121] and our group.[66] Reacting the dicationic NHC(H)$^{+}$/MIC(H)$^{+}$ precursors [^{Me}Im-κ^{1}-Trz(H)$^{Me}_{Dipp}$][Br][OTf] (**4b**) and [^{tBu}Im-κ^{1}-Trz(H)$^{Me}_{Dipp}$][Br][OTf] (**4c**) with the internal base-containing [Pd(OAc)$_2$] in the presence of KI in hot acetonitrile (60 °C) results in deprotonation of the imidazolium end of the dication, and formation of the zwitterionic species [PdI$_3$(^{R1}Im-κ^{1}-Trz(H)$^{Me}_{Dipp}$)] (R^{1} = Me, **7b**; ^{t}Bu, **7c** as shown in Scheme 4-6). Interestingly, the reaction does not proceed without the addition of potassium iodide. However, upon



Scheme 4-6. Synthesis of NHC-anchored/pendent-MIC(H)$^{+}$ complexes of palladium.

the addition of an excess of this halide source, the colour changes instantly (orange to dark purple). Heckenroth *et al.*[68] have shown for di-*a*NHCs that palladation (using [Pd(OAc)$_2$]) is only possible if the counteranions of the [di-*a*NHC(H)$_2$]$^{2+}$ dications

are sufficiently strongly-coordinating, such as halides (palladation of *bis*(BF_4^-) salts did not occur), presumably through the generation of the dianionic palladate $K_2[PdI_2(OAc)_2]$,[68, 121] followed by subsequent deprotonation of the dicarbene precursor. Furthermore, if a large excess of potassium iodide is not used (or if the solution is heated too long) the pendent complex will convert into an undesireable chelate species **8**, namely $[PdI_2(\kappa^2C^2,C^5\text{-}^{R1}ImTrz^{Me}_{Dipp})]$ (similar to the proposed Suzuki-Miyaura catalyst reported by Kahn,[76] Figure 4-4c). This structure is assumed based on preliminary spectroscopic evidence, but since it seemed clearly to not be a species of interest to us (no longer having a pendent proton), we have not characterized it fully.

Despite the propensity for complexes **7** to convert to these unwanted chelate species **8**, the reaction can easily be halted at the pendent stage by careful monitoring of the ^{1}H NMR spectrum. Over the course of 1-2 h under gentle heating, one of the high-frequency acidic peaks (representing the imidazolium end of species **4**) begins to disappear, while new (slightly shifted) ligand peaks emerge in the spectrum. The final pendent formulation of complexes **7** is again easily confirmed by the presence of only one acidic proton in the high-frequency region of the ^{1}H NMR spectrum as a slightly broad singlet (full width at half-maximum, FWHM ≈ 4 Hz). Furthermore, the doublets observed for the imidazolium backbone protons are also somewhat broadened (although each sharpens when the other is selectively decoupled, and show cross peaks in 2D gradient-enhanced correlation spectroscopy (gCOSY) NMR experiments). It is interesting that in these and other [PdI_3NHC-NHC(H)] complexes[66, 121] all peaks are somewhat broad (perhaps due to dynamic intramolecular rearrangement resulting from iodide exchange, etc.). Unlike the Rh pendent cases

(**6**), the peak for the CH_2 group remains as a singlet, owing to the symmetry on each side of the square plane of palladium. Again, the ^{1}H NMR spectrum implies that there is a significant energy barrier to rotation about the Ar–^{i}Pr bond since there are two separate ^{i}Pr doublets around ~ 1.1 ppm (*ca.* $\Delta\delta$ = 0.5 ppm).

The $^{13}C\{^1H\}$ NMR spectra for complexes **7** display peaks similar to the NHC/MIC(H)$^+$ group of the Rh complexes **6**. Interestingly, although no carbene peak could be observed in previous Pd triiodo NHC-anchored/pendent-carbene(H)$^+$ complexes,[66, 121] the $C_{carbene}$ peak can be observed here under special conditions (extremely concentrated sample, overnight acquisition using a cold-dual probe providing a 1500:1 ^{13}C sensitivity increase over conventional probes), which shows up as a singlet at *ca.* 161.7 ppm. Peak intensities for NHC-type carbenes are inherently weak (quaternary carbon, flanked by two quadrupolar nuclei), and perhaps the NHC-carbene ^{13}C nucleus in triiodo Pd complexes such as **7** has a particularly long spin-lattice relaxation time (T_1). Evidence for inhibited Ar–^{i}Pr bond rotation is also present (*ca.* $\Delta\delta_{^i\text{Pr}}$ = 0.80 ppm).

The X-ray structure determination for the compound **7b**, shown in Figure 4-12, confirms the pendent structure proposed on the basis of spectral data and the carbene formation *via* the NHC end. The Pd atom has a slightly distorted square-planar geometry (C(1)–Pd–I(3) = 176.3(3)°, I2–Pd–I1 = 172.68(4)°) with three coordinated iodide ligands, an anchored-NHC lying essentially perpendicular to the square plane (94.7(9)°), and pendent-MIC(H)$^+$ group. The length of the Pd–$C_{carbene}$ bond (Pd–C(1) = 1.958(1) Å) is significantly shorter than reported examples with a *trans* phosphine (Pd–$C_{carbene}$ *ca.* 2.05 Å),[66] but is similar to other Pd–C_{NHC} bonds *trans* to ligands with a low *trans*-influence (NHC–Pd(κ^2*O*,*O*′-OAc) = 1.953(5) and NHC–

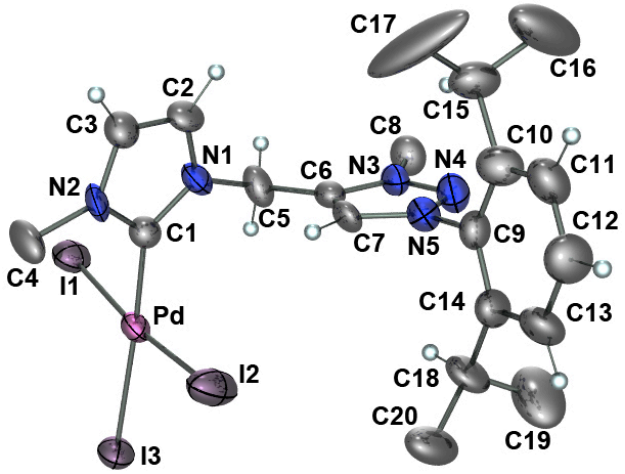


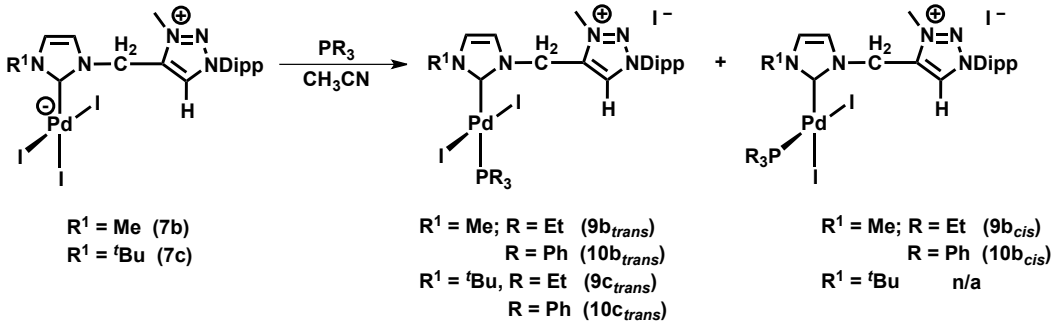
Figure 4-12. Three-dimensional representation of $[PdI_3(^{Me}Im\text{-}\kappa^1\text{-}Trz(H)^{Me}_{Dipp})]$, **7b** showing the numbering scheme. Thermal ellipsoids are as described in Figure 4-7. Hydrogen atoms are shown only on non-methyl carbons. Relevant parameters (distances in Å and angles in deg.): Pd–C(1) = 1.958(1), I(1)–Pd = 2.604(2), I(2)–Pd = 2.598(2), I(3)–Pd = 2.668(2); C(1)–Pd–I(3) = 176.3(3), I(2)–Pd–I(1) = 172.68(4), N(1)–C(1)–N(2) = 103.9(8), C(6)–C(7)–N(5) = 105.6(10), N(4)–N(5)–C(9)–C(10) = 81.1(13), I(1)–Pd–C(1)–N(2) = 94.7(9), NHC and $MIC(H)^+$ planes' dihedral angle = 84.46.

PdI = 1.990(9) Å, respectively).[121] Despite the slightly shorter metal-carbene bond, it is still considered a metal-carbon single bond since NHCs (and MICs) are not considered to possess significant π-back-bonding properties).[32, 122]

The angle at the C(1) carbon (103.9(8)°) is similar to the N–$C_{carbene}$–N angles in Chapter 2 (which range from ~ 102.8° to 105.6°),[66] and the angle at C(7) (105.6(1)°) is similar to that of the $MIC(H)^+$ moiety for **4b** (106.0(2)°) shown in Figure 4-8. Again, the aryl ring of the Dipp group adopts an orientation almost perpendicular to the Trz plane (dihedral angle N(4)–N(5)–C(9)–C(10) = 81.1(1)°). Furthermore, the planes of the NHC and $MIC(H)^+$ rings lie in almost perpendicular arrangements (dihedral angle = 84.46°).

Similar to our previous report,[66] replacement of the *trans* iodide in the zwitterionic Pd complexes with monophosphine ligands (PEt_3 and PPh_3) can be effected by adding one equivalent of phosphine to acetonitrile solutions of

complexes **7** (Scheme 4-7). Immediately upon addition, each solution changes from dark purple to bright yellow upon generation of the species [$PdI_2(PEt_3)(^{R1}Im\text{-}\kappa^1$-



Scheme 4-7. Displacement of iodo ligands by monophosphines in pendent Pd complexes.

$Trz(H)^{Me}_{Dipp})][I]$ $\mathbf{9}_{trans}$ and $[PdI_2(PPh_3)(^{R1}Im\text{-}\kappa^1\text{-}Trz(H)^{Me}_{Dipp})][I]$ $\mathbf{10}_{trans}$ from the triiodo precursor. However, for the sterically less-bulky complex **7b** (R^1 = Me), in addition to formation of $\mathbf{9b}_{trans}$ and $\mathbf{10b}_{trans}$, another isomer is also generated in which the phosphine is *cis* to the anchored NHC (R = Et, $\mathbf{9b}_{cis}$; R = Ph, $\mathbf{10b}_{cis}$). Although sterically less-favoured, this position is likely more electronically favourable owing to the high *trans*-effects of both the NHC and PR_3 ligands (disfavouring their mutually-*trans* arrangement), but is inaccessible with bulky substituents (R^1 = ^{t}Bu) on the NHC's outer nitrogen atom. In line with this hypothesis, a solution containing a mixture of both isomers can be completely converted to the *cis* products ($\mathbf{9b}_{cis}$ or $\mathbf{10b}_{cis}$) with gentle heating in acetonitrile over the course of 2 h. Owing to this facile isomerization, we were unable to isolate the pure kinetic products $\mathbf{9b}_{trans}$ and $\mathbf{10b}_{trans}$.

The existence of two products in the less-bulky anchored-NHC (R^1 = Me) is obvious from two singlets in the $^{31}P\{^1H\}$ NMR spectrum as well as roughly twice as many peaks as expected in the ^1H NMR spectrum. Although most of the peaks in the ^1H NMR spectrum for both *cis* and *trans* isomers differ only slightly, a few major differences are observed which can help to distinguish between the two. For

example, in a *cis* complex, as a consequence of the plane bisecting the linking CH_2 group rendering each side different, the protons of the methylene CH_2 linker are in significantly different environments, resulting in two doublets (or, an AB pattern) for the linker protons in the case of **9b**$_{cis}$ and **10b**$_{cis}$, showing mutual coupling; whereas both protons are represented by a singlet in all *trans* systems.

In both *cis* cases, the combination of front/back asymmetry and inhibited rotation about both Ar–^{i}Pr bonds results in the inequivalence of all nine proton environments in the Dipp substituent (as was observed in **6** where all Dipp groups became diastereotopic). As a result, the aryl region is slightly more complicated (with more coupling of inequivalent protons), as is the region for ^{i}Pr groups. The ^{1}H NMR spectrum of **10b**$_{cis}$ is shown in Figure 4-13. Finally, although both NHC backbone

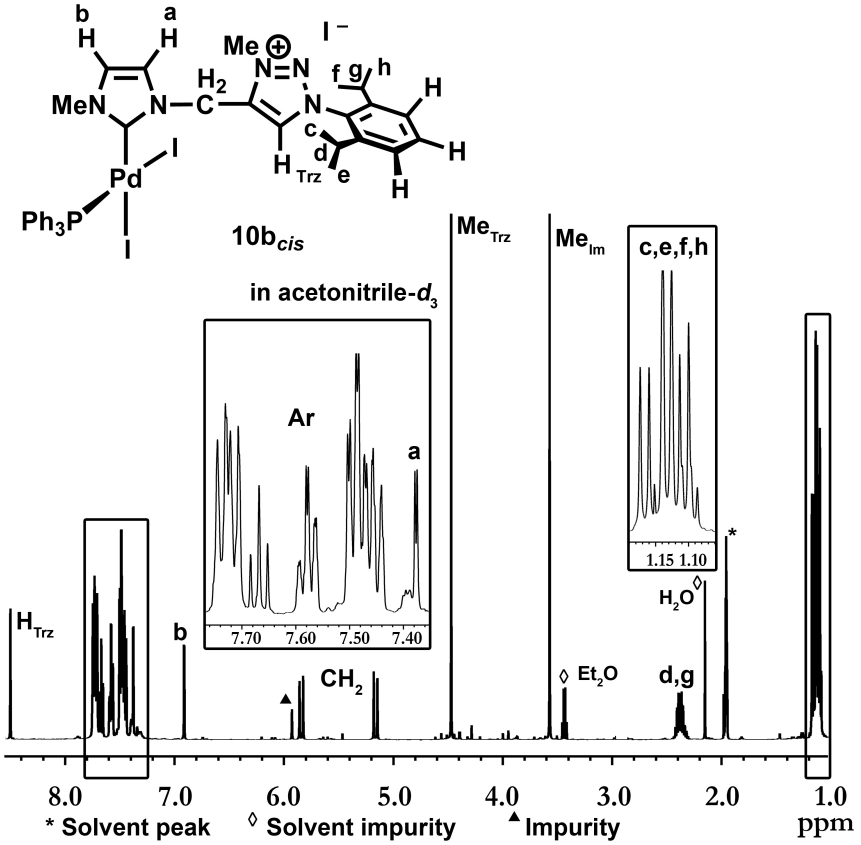


Figure 4-13. ^{1}H NMR spectrum (500 MHz) of complex **10b**$_{cis}$ in acetonitrile-d_3, with expanded olefinic/aromatic and ^{i}Pr regions.

protons exhibit mutual coupling in both cases ($^{3}J_{H\text{-}H} \approx 2.0$ Hz), only in the *trans* complexes do they show significant $^{1}H\text{-}^{31}P$ coupling ($^{5}J_{H\text{-}P} \approx 1.5$ Hz), as was observed in our previous NHC/NHC(H)$^{+}$ systems with *trans* and *cis* PR_3 groups.[66]

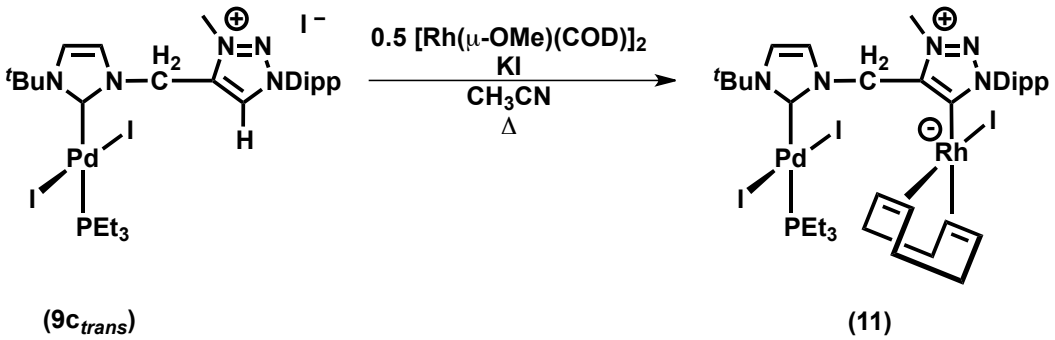
The $^{13}C\{^{1}H\}$ NMR spectra for complexes **10** display peaks similar to the NHC/MIC(H)$^{+}$ group of the zwitterionic complexes **7b**. The peak representing the carbene appears at *ca.* 165.0 ppm, as a singlet in the case of both *cis* complexes (showing no coupling to the *cis* phosphorus atom) and as a doublet for both *trans* systems ($^{2}J_{C\text{-}P} \approx 185.0$ Hz) although it is more intense and easier to observe than in the triiodo systems. In addition to the extra peaks for the carbons on the phosphine (which can easily be located with $^{13}C\{^{1}H,^{31}P\}$ experiments) there are 12 different peaks for the Dipp group.

4.2.5 Mixed-metal, NHC/MIC-bridged heterobimetallic complexes

In our previous studies, described in Chapter 2, we were able to prepare binuclear di-NHC-bridged complexes from a mononuclear, carbene-anchored/pendent-imidazolium precursor by deprotonating the pendent acidic imidazolium proton using $[Rh(\mu\text{-}OAc)(COD)]_2$ yielding the dirhodium[112] or mixed-metal targets.[66] Although our earlier attempts to deprotonate the second imidazolium moiety of the above NHC/imidazolium species using $[Pd(OAc)_2]$ failed to produce the di-NHC-bridged Rh/Pd species of interest, we decided to test whether or not $[Pd(OAc)_2]$ could facilitate deprotonation of the MIC(H)$^{+}$ arm of the Rh pendent complexes **6**. Encouragingly, Albrecht *et al.* had shown that $[Pd(OAc)_2]$ can deprotonate 1,2,3-triazolium species, although relatively harsh conditions (temperature of around 120 °C) were required.[49]

Unfortunately, these conditions proved to be too harsh for our NHC-anchored/pendent-MIC(H)$^+$ complexes of Rh, resulting in decomposition of the complex before deprotonation could occur. We instead investigated a reverse strategy, starting with the pendent complexes of palladium and attempting deprotonation of the pendent MIC(H)$^+$ groups using [Rh(μ-OMe)(COD)]$_2$, having the more basic methoxido ligands.

Attempts to deprotonate the zwitterionic Pd systems **7** failed. However this result is not surprising in light of our failure to deprotonate the triiodo systems in Chapter 2 with the di-NHC systems.[66] However, by using the *trans*-phosphine system **9c**$_{trans}$, the pendent MIC(H)$^+$ group can successfully be deprotonated by [Rh(μ-OMe)(COD)]$_2$ under mild heating to afford the desired Pd/Rh mixed-metal complex **11** (Scheme 4-8). However, complex **11** begins to decompose if the



Scheme 4-8. Synthesis of NHC/MIC-bridged Pd/Rh complexes *via* the pendent strategy.

solution is heated for prolonged periods of time, and therefore careful monitoring of the reaction progress by ^{1}H NMR spectroscopy is usually required. Unfortunately, no reaction was observed in attempts to deprotonate the PPh_3-containing pendent complex **10c**$_{trans}$ with [Rh(μ-OMe)(COD)]$_2$. Attempts to raise the temperature to force deprotonation only resulted in decomposition of the materials at temperatures above 100 °C.

Although single crystals of **11** suitable for an X-ray diffraction study have not yet been obtained (as a neutral complex, it is less-prone to crystallization by typical solvent combinations), the spectral data leave little doubt about its formulation. Formation of the bimetallic species is made fairly obvious by the disappearance of the high-frequency peak representing the acidic proton on the triazolium group. Furthermore, the obvious transformation of the methylene CH_2 peak in the ^1H NMR spectrum to an AB pattern is further indication of front-back asymmetry in the complex (due to the geometry about Rh). The olefinic peaks for the COD ligands are shifted to slightly lower frequencies compared to those in the NHC-anchored Rh pendent complexes **6** but are typical for MIC–Rh species[49] (the peak for the *cis* protons is *especially* broad). The ^1H NMR spectrum is shown in Figure 4-14.

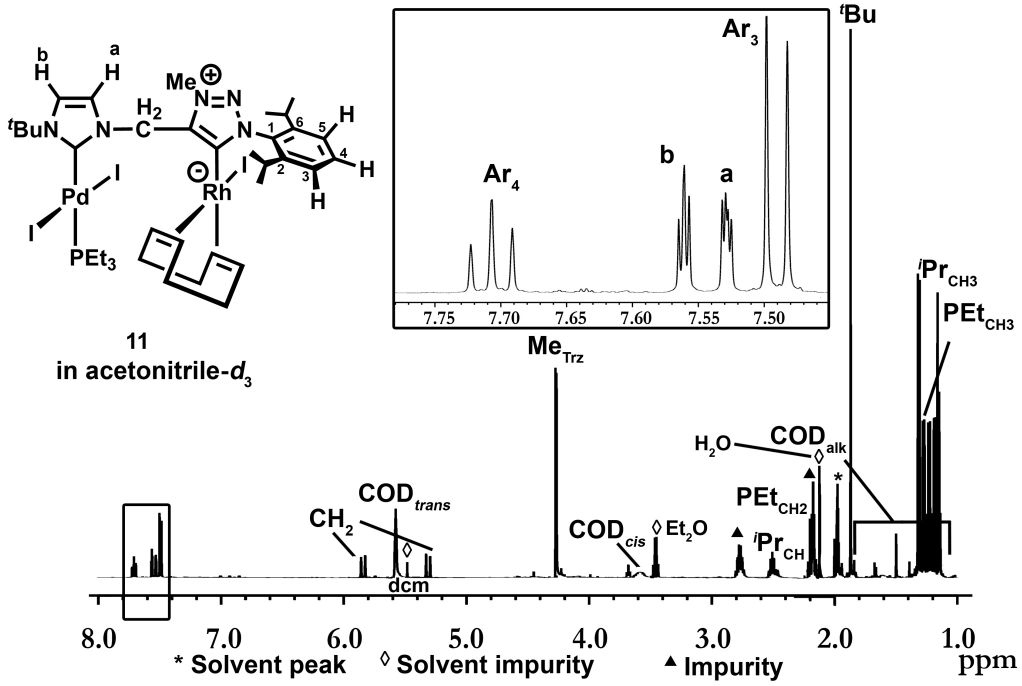


Figure 4-14. ^1H NMR spectrum (400 MHz) of complex **11** in acetonitrile-d_3 with expanded olefinic/aromatic region.

The $^{13}C\{^{1}H\}$ NMR spectrum of **11** indicates formation of a new species having two metal-carbene moieties by the emergence of two new peaks in the typical Fischer carbene region between 150 ppm and 200 ppm. Although the doublet for the Pd-bound carbene does not shift significantly, a new doublet ($^{1}J_{C\text{-}Rh}$ = 44.7 Hz) representing the Rh-bound carbene emerges at a higher frequency of δ = 173.4. This value (which is at a slightly lower frequency compared our previous Rh-NHC values above and in Chapter 2[66]) is comparable to the other Rh-MIC complex reported thus far by Albrecht *et al.*,[49] who report the carbene resonance at δ = 170.4.

Section 4.3 Discussion

In this work, we set out to design a set of hybrid dicarbenes based on linked NHC and MIC functionalities for the purposes of bridging mixed-metal (Rh/Pd) systems. We have succeeded in devising simple routes to NHC/MIC precursors based on literature precedent by functionalizing an imidazolium salt with a pendent propargyl arm, and subsequently using "click" chemistry to transform this group into a triazole. Methylation transformed the imidazole/triazole into an imidazolium/triazolium dication, which can be deprotonated to produce bidentate NHC/MICs. We were interested in unsymmetrical dicarbenes because they offer two different possibilities as bridging ligands in mixed-metal Pd/Rh systems, either as [Pd(NHC)/Rh(MIC)] or [Rh(NHC)/Pd(MIC)] systems, and the strategy of how each one can be achieved is (in principle) simply a matter of which metal is attached first *via* the more acidic end of the precursor.

As indicated, we were able to produce [Pd(NHC)/Rh(MIC)] systems by first preparing NHC-anchored/pendent-MIC(H)$^{+}$ complexes of Pd. By deprotonating

the more-acidic imidazolium end of imidazolium/triazolium dications with $[Pd(OAc)_2]$ (in the presence of KI), triiodo zwitterionic carbene-anchored/pendent-imidazolium complexes of Pd are produced, which can be further functionalized (by substitution of iodide ligands with various monophosphines). Using half an equivalent of $[Rh(\mu\text{-OMe})(COD)]_2$ as the internal base precursor,[xvi] the pendent triazolium arm of one of these functionalized pendent complexes (containing a *trans*-triethylphosphino ligand) can be deprotonated, generating the targeted heterobimetallic Pd/Rh complex.

In practice however (at least based on our limited attempts to date), the reverse strategy to prepare [Rh(NHC)/Pd(MIC)] complexes appears difficult owing to the inability of the Pd precursor used to deprotonate 1,2,3-triazolium cations under mild enough conditions. However this is a practical issue and presumably a suitable Pd compound containing ligands that are basic enough, and/or the right conditions can be found to afford this deprotonation. Certainly Albrecht *et al.* have reported that the acetate ligands in $[Pd(OAc)_2]$ to be sufficiently basic enough to afford his Pd-MIC complexes,[49, 55] albeit under conditions that are too harsh for our systems. One possibility is to substitute OAc^- by the more-basic OMe^- as this has proven to be successful in the Rh case. Even though a few Pd-OMe complexes do exist, most of them require specific ancillary ligands (such as electron-withdrawing[123, 124] or hydrotris(pyrazolyl)borate ligands,[125] for example), and many of them are unstable to disproportionation,[126] β-hydride elimination,[127] or other decomposition pathways.[126, 128]

[xvi] $[Rh(\mu\text{-OAc})(COD)]_2$ proved to be ineffective in deprotonating the less-acidic triazolium species.

A few obvious systems do seem promising however,[127, 129-132] wherein *bis*(methoxido)-bridged dimers are stabilized by simple ancillary ligands (diamines, diphosphines, etc.), although there are no reports of their use as internal base complexes in the palladium-carbene literature. Nevertheless, they will be tested in future investigations (especially in Pd-MIC work). At the outset, we did not consider hydroxide-containing internal base precursors[133-136] since deprotonation by OH^- would result in the generation of water. However, in recent experiments during this work, characterization attempts indicated a high tolerance to water (even in solution for several weeks) when dissolved in longer-shelved deuterated solvents which contained considerable amounts of adventitious H_2O. As a result, hydroxido precursors will be considered in future experiments, since their basicity is similar to that of the methoxide ion ($pK_{b(MeO^-)} = -1.5$; $pK_{b(HO^-)} = -1.75$)[137] and significantly more-basic than the acetate ion ($pK_{b(OAc^-)} = 4.75$),[137] so should be capable of deprotonating triazolium salts under mild conditions.

Using a mixed-NHC/MIC bridging framework is an interesting way to (very subtly) vary the properties of dicarbene-bridged systems, compared to di-NHCs. The mixed-metal complex reported here is a direct NHC/MIC analogue of our previously reported di-NHC-bridged Pd/Rh systems (with the exception of the Dipp substituent on the MIC). Studies, comparing our previous di-NHC-bridged Pd/Rh to this NHC/MIC-bridged system, are currently underway to examine the differences a more electron-donating MIC will have on Rh, especially in Pd/Rh tandem catalysis.[138, 139] Furthermore, work is currently in progress in examining the influence that symmetric di-MICs will have (with strong donors on *both* metals, see Chapter 5) in systems similar to the dicarbenes already mentioned. Finally, the

catalytic activity of all dicarbene-bridged Pd/Rh complexes will be investigated and compared. This follow-up will come later as work is ongoing (see Chapter 6).

Section 4.4 Experimental Procedures

4.4.1 General comments

Deuterated solvents used for NMR experiments were freeze-pump-thaw degassed and stored under argon over type 4A molecular sieves. Unless otherwise specified, reactions were carried out at ambient temperature. Potassium iodide was purchased from ACP; ammonium carbonate, *tert*-butylamine, cycloocta-1,5-diene, 2,6-diisopropylaniline, formaldehyde, glyoxal, 1-methylimidazole (**1a**), methyltrifluoromethanesulfonate, palladium(II) acetate, propargyl bromide, sodium tetrafluoroborate, triethylphosphine, triphenylphosphine were purchased from Aldrich; triethylamine was purchased from Anachemia; sodium nitrite and potassium hydroxide were purchased from Caledon Laboratory Chemicals; sodium azide was purchased from J.T. Baker Chemical Co.; copper(I) iodide and sodium acetate were purchased from Fischer Scientific.; rhodium(III) chloride hydrate was purchased from Pressure Chemical Company; and diammonium hexachloroiridate(IV) was purchased from Strem. All chemicals were used without further purification, with the exception of sodium acetate and potassium iodide, which were purified by repetitive melting under dynamic vacuum before use. Compound **1c**, was reported previously,[88] but prepared using *tert*-butylamine in a modification[xvii] to the general procedure for 1-arylimidazoles.[89] Compounds **2a**,[90-92] azidomethylbenzene (BnN_3),[96,

[xvii] It is worth noting that there exists an unfortunate typographical error in the experimental section of the report by Liu *et al.* on the synthesis of 1-arylimidazoles.[89] The quantities of amine and 30% $glyoxal_{(aq)}$ used should be in quantities of moles, not millimoles.

[98] 2-azido-1,3-diisopropylbenzene ($DippN_3$),[99,] [xviii] (cycloocta-1,5-diene)(μ-dichloro)dirhodium ($[Rh(\mu\text{-}Cl)(COD)]_2$),[140,] [141] and *bis*(cycloocta-1,5-diene)(μ-methoxido)dirhodium ($[Rh(\mu\text{-}OMe)(COD)]_2$),[142] were prepared as reported previously and *bis*(cycloocta-1,5-diene)(μ-diacetato)dirhodium ($[Rh(\mu\text{-}OAc)(COD)]_2$)[143] was prepared as previously reported and recrystallized from ethyl acetate. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a dual cold probe-equipped Varian DirectDrive 500 MHz, iNova-500, or iNova-400 spectrometer operating at 499.82, 498.12, or 399.79 MHz for ^1H; 125.68,[xix] 125.26, or 100.53 MHz for $^{13}C\{^1H\}$, respectively; or on a Varian iNova-300 operating at 299.97 MHz for ^1H. The ^1H and $^{13}C\{^1H\}$ chemical shifts are referenced to TMS, $^{19}F\{^1H\}$ chemical shifts are referenced to $CFCl_3$, and $^{31}P\{^1H\}$ chemical shifts are referenced to 85% H_3PO_4 in H_2O. The order of appearance of chemical shift assignments are based on their region in the molecule rather than increasing or decreasing frequency of their resonance. Elemental Analyses were performed by the microanalytical service within this department. Likewise, mass spectrometric analyses were performed by the departmental Mass Spectrometry Laboratory using positive ion electrospray ionization on an Agilent Technologies 6220 Accurate-mass TOF LC/MS. At the time of defense, satisfactory elemental and high-resolution mass spectrometry analyses for a few complexes were not yet obtained. Efforts are ongoing, however.

[xviii] Organic azides are potentially-explosive substances that can and will decompose with the slightest input of energy from external sources (heat, light, or pressure). Extremely high safety precautions should be exercised (*i.e.*, proper lab protection, blast shields, etc.) to prevent serious injury.

[xix] Due to the field interference caused by cationic samples **6**, smaller 3 mm tubes were required for signal lock.

4.4.2 Preparation of compounds

(i) 1-(*tert*-Butyl)-3-prop-2-yn-1-yl-1*H*-imidazol-3-ium bromide, [^{t}BuIm(H)CH$_2$C≡CH][Br] (2c). A 20 mL portion of acetonitrile was added to a flask containing 1-*tert*-butylimidazole (16.4 g, 0.132 mol). An approximately twofold excess of an 80 wt% solution (in dioxane) of propargyl bromide (37.0 mL, 0.333 mol) was slowly added to the mixture. The resulting solution was stirred for 24 h under reflux conditions and cooled to room temperature. The solvent was then removed under reduced pressure and the crude product was washed with 5 × 20 mL portions of diethyl ether before drying *in vacuo*, giving 25.7 g of a brown, sticky oil (80%). ^{1}H NMR (299.97 MHz, acetonitrile-d_3, 27.5 °C): 9.71 (dd, 1H, $^4J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz, NCHN); 7.76 (dd, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz), 7.70 (dd, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz, NCH$_{imid}$); 5.32 (d, 2H, $^4J_{H\text{-}H}$ = 2.5 Hz, CH$_2$); 3.13 (t, 1H, $^4J_{H\text{-}H}$ = 2.5 Hz, C≡CH); 1.68 (s, 9H, N^{t}Bu). ^{13}C{^{1}H} NMR (100.58 MHz, acetonitrile-d_3, –0.1 °C): 135.9 (s, 1C, NCHN); 123.0 (s, 1C), 121.2 (s, 1C, NCH$_{imid}$); 77.9 (s, 1C, C≡*C*H); 76.0 (s, 1C, *C*≡CH); 61.3 (s, 1C, N*C*(CH$_3$)$_3$); 39.8 (s, 1C, CH$_2$); 29.7 (s, 3C, NC(*C*H$_3$)$_3$). HRMS *m*/*z* Calcd for C$_{10}$H$_{15}$N$_2$ (M$^+$ – Br$^-$): 163.1230. Found: 163.1229 (M$^+$ – Br$^-$).

(ii) 1-((1-Benzyl)-1*H*-1,2,3-triazol-4-yl)methyl)-3-methyl-1*H*-imidazol-3-ium bromide, [^{Me}Im(H)Trz$_{Bn}$][Br] (3a). A 30 mL portion of MeOH:H$_2$O (50:50) was added to a flask containing **2a** (2.400 g, 1.99 mmol) and azidomethylbenzene (0.572 g, 4.30 mmol). The resulting solution was stirred for 10 min then CuI (0.096 g, 0.504 mmol) and NEt$_3$ (0.63 mL, 4.5 mmol) were quickly added, at which point the solution turned a dark green colour, and was stirred at room temperature overnight. The solution was filtered and the product was extracted with chloroform.

The solution was dried, decanted, and the solvent removed under reduced pressure, followed by washing of the crude with 5 × 20 mL portions of *n*-pentane before drying *in vacuo*, giving 0.599 g of a dark yellow oil (90%). ^{1}H NMR (299.97 MHz, chloroform-*d*, 27.5 °C): 9.97 (br dd, 1H, $^{4}J_{H\text{-}H}$ = 1.6 Hz, $^{4}J_{H\text{-}H}$ = 1.6 Hz, NCHN); 8.35 (s, 1H, H_{Trz}); 7.67 (br dd, 1H, $^{3}J_{H\text{-}H}$ = 1.6 Hz, $^{4}J_{H\text{-}H}$ = 1.6 Hz), 7.38 (br dd, 1H, $^{3}J_{H\text{-}H}$ = 1.6 Hz, $^{4}J_{H\text{-}H}$ = 1.6 Hz, NCH_{imid}); 7.33-7.21 (m, 5H, Ph); 5.72 (s, 2H, $ImCH_2Trz$); 5.46 (s, 2H, NCH_2Ph); 3.92 (s, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (125.69 MHz, chloroform-*d*, 27.7 °C): 140.3 (s, 1C, CH_2CCH); 136.9 (s, 1C, NCHN); 134.3 (s, 1C, NCH_2C_{Ar}); 129.1 (s, 2C), 128.8 (s, 1C), 128.3 (s, 2C, CH_{Ar}); 125.2 (s, 1C, CH_{Trz}); 123.4 (s, 1C), 122.7 (s, 1C, NCH_{imid}); 54.3 (s, 1C, NCH_3); 41.0 (s, 1C, NCH_2Trz); 36.8 (s, 1C, NCH_2Ph). HRMS *m*/*z* Calcd for $C_{14}H_{16}N_5$ ($M^+ - Br^-$): 254.1400. Found: 254.1399 ($M^+ - Br^-$).

(iii) 1-((1-(2,6-Diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-3-methyl-1*H*-imidazol-3-ium bromide, [^{Me}Im(H)Trz$_{Dipp}$][Br] (3b). The desired product was prepared as described for 3a, using 2a (1.27 g, 6.32 mmol), 2-azido-1,3-diisopropylbenzene (1.32 g, 6.49 mmol), CuI (0.14 g, 0.74 mmol), and NEt_3 (0.86 g, 8.5 mmol). The solution changed from red/yellow to dark green instantly, and was stirred overnight. The crude product was purified as described for **3a**, and isolated as a dark yellow powder (0.825 g, 32%). ^{1}H NMR (399.79 MHz, chloroform-*d*, 26.5 °C): 10.15 (br s, 1H, NCHN); 8.37 (s, 1H, H_{Trz}); 7.81 (br s, 1H), 7.54 (br s, 1H, NCH_{imid}); 7.40 (t, 1H, $^{3}J_{H\text{-}H}$ = 8.8 Hz), 7.18 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.8 Hz, Ar); 5.93 (s, 2H, CH_2); 4.02 (s, 3H, NCH_3); 2.02 (qq, 2H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $^{i}Pr_{CH}$); 1.01 (d, 6H, $^{3}J_{H\text{-}H}$ = 7.0 Hz), 1.00 (d, 6H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $^{i}Pr_{CH3}$). $^{13}C\{^{1}H\}$ NMR (100.54 MHz, chloroform-*d*, 26.5 °C): 145.8 (s, 2C, C ^{i}Pr); 139.9 (s, 1C, CH_2CCH); 137.0 (s, 1C,

NCHN); 132.6 (s, 1C, NC_{Ar}); 131.0 (s, 1C), 123.8 (s, 2C, CH_{Ar}); 127.8 (s, 1C, CH_{Trz}); 123.6 (s, 1C), 122.7 (s, 1C, NCH_{imid}); 44.2 (s, 1C, CH_2); 36.9 (s, 1C, NCH_3); 28.3 (s, 2C, $^{i}Pr_{CH}$); 24.1 (s, 2C), 23.9 (s, 2C, $^{i}Pr_{CH3}$). HRMS *m*/*z* Calcd for $C_{19}H_{26}N_5$ (M^+ – Br^-): 324.2183. Found: 324.2183 (M^+ – Br^-). Anal Calcd for $C_{19}H_{26}BrN_5$: C, 56.44; H, 6.48, N, 17.32. Found: C, 56.21; H, 6.47; N, 17.12.

(iv) 1-(*tert*-Butyl)-3-((1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-3-methyl-1*H*-imidazol-3-ium bromide, [$^{t\mathrm{Bu}}$Im(H)Trz$_{\mathrm{Dipp}}$][Br] (3c). The desired product was prepared as described for 3a, using 2c (2.64 g, 10.9 mmol), 2-azido-1,3-diisopropylbenzene (2.31 g, 11.4 mmol), CuI (0.10 g, 0.53 mmol), and NEt_3 (0.98 g, 9.7 mmol). The solution changed from red/yellow to dark green instantly, and was stirred overnight. The crude product was purified as described for **3a**, and isolated as a dark yellow powder (3.257 g, 67%). ^{1}H NMR (498.12 MHz, chloroform-*d*, 27.5 °C): 10.64 (br s, 1H, NCHN); 8.50 (s, 1H, H_{Trz}); 7.78 (br s, 1H), 7.49 (br s, 1H, NCH_{imid}); 7.44 (t, 1H, $^3J_{H\text{-}H}$ = 8.2 Hz), 7.23 (d, 2H, $^3J_{H\text{-}H}$ = 8.2 Hz, Ar); 6.02 (s, 2H, CH_2); 2.08 (qq, 2H, $^3J_{H\text{-}H}$ = 7.3 Hz, $^3J_{H\text{-}H}$ = 7.3 Hz, $^{i}Pr_{CH}$); 1.69 (s, 9H, N^{t}Bu); 1.07 (d, 6H, $^3J_{H\text{-}H}$ = 7.3 Hz), 1.06 (d, 6H, $^3J_{H\text{-}H}$ = 7.3 Hz, $^{i}Pr_{CH3}$). ^{13}C{^{1}H} NMR (125.69 MHz, chloroform-*d*, 26.1 °C): 145.8 (s, 2C, C ^{i}Pr); 140.2 (s, 1C, CH_2*C*CH); 135.7 (s, 1C, NCHN); 132.7 (s, 1C, NC_{Ar}); 131.0 (s, 1C), 123.9 (s, 2C, CH_{Ar}); 128.1 (s, 1C, CH_{Trz}); 122.6 (s, 1C), 119.4 (s, 1C, NCH_{imid}); 60.6 (s, 1C, N*C*$(CH_3)_3$); 44.2 (s, 1C, CH_2); 30.1 (s, 3C, NC(*C*$H_3)_3$); 28.4 (s, 2C, $^{i}Pr_{CH}$); 24.2 (s, 2C), 24.0 (s, 2C, $^{i}Pr_{CH3}$). HRMS *m*/*z* Calcd for $C_{22}H_{32}N_5$ (M^+ – Br^-): 366.2651. Found: 366.2652 (M^+ – Br^-).

(v) Attempted synthesis of 1-benzyl-3-methyl-4-((1-methyl-1*H*-imidazol-3-ium-3-yl)methyl)-1*H*-1,2,3-triazol-3-ium bromide trifluoromethanesulfonate, [^{Me}Im(H)Trz(H)$^{Me}_{Bn}$][Br][OTf] (4a). A 10 mL portion of dcm was added to a flask containing **3a** (0.400 g, 0.22 mmol). The resulting solution was stirred for 10 min cooled to –78 °C then MeOTf (25 μL, 0.23 mmol) was quickly injected, resulting in a cloudy discharge above the solution. The solution was allowed to warm to room temperature, then stirred overnight, yielding a dark red solution. The solvent was then removed under reduced pressure and the crude product was washed with 5 × 20 mL portions of *n*-pentane before drying *in vacuo*. Analysis of the crude mixture by ^{1}H NMR spectrum indicated a mixture of N-2 and N-3 methylated peaks. As a result, the species was not characterized further.

(vi) 1-(2,6-diisopropylphenyl)-3-methyl-4-((1-methyl-1*H*-imidazol-3-ium-3-yl)methyl)-1*H*-1,2,3-triazol-3-ium bromide trifluoromethanesulfonate, [^{Me}Im(H)Trz(H)$^{Me}_{Dipp}$][Br][OTf] (4b). The desired product was prepared as described for 4a, using 3b (2.04 g, 5.05 mmol) and MeOTf (0.83 mL, 7.6 mmol). The solution changed from dark green to dark red instantly, and was stirred overnight. The crude product was purified as described for **3a**, and isolated as a white powder (1.481 g, 52%). ^{1}H NMR (499.82 MHz, acetonitrile-d_3, 27.7 °C): 8.94 (br s, 1H, NCHN); 8.69 (s, 1H, H_{Trz}); 7.70 (dd, 1H, $^3J_{H\text{-}H}$ = 2.0 Hz, $^4J_{H\text{-}H}$ = 2.0 Hz), 7.54 (dd, 1H, $^3J_{H\text{-}H}$ = 2.0, $^4J_{H\text{-}H}$ = 2.0 Hz, NCH_{imid}); 7.73 (t, 1H, $^3J_{H\text{-}H}$ = 7.7 Hz), 7.51 (d, 2H, $^3J_{H\text{-}H}$ = 7.7 Hz, Ar); 5.87 (s, 2H, CH_2); 4.44 (s, 3H, Me_{Trz}); 3.95 (s, 3H, Me_{Im}); 2.31 (qq, 2H, $^3J_{H\text{-}H}$ = 6.8 Hz, $^3J_{H\text{-}H}$ = 6.8 Hz, ^{i}Pr$_{CH}$); 1.20 (d, 6H, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.16 (d, 6H, $^3J_{H\text{-}H}$ = 6.8 Hz, ^{i}Pr$_{CH3}$). ^{13}C{^{1}H} NMR (100.58 MHz, acetonitrile-d_3, 27.0 °C): 145.6 (s, 2C, C–^{i}Pr); 138.8 (s, 1C, CH_2CCH); 137.6 (s, 1C, NCHN); 130.6 (s, 1C,

NC_{Ar}); 133.2 (s, 1C), 124.8 (s, 2C, CH_{Ar}); 133.0 (s, 1C, CH_{Trz}); 124.8 (s, 1C), 122.9 (s, 1C, NCH_{imid}); 121.0 (q, 1C, $^1J_{C\text{-}F}$ = 320.3 Hz, OSO_2CF_3); 41.5 (s, 1C, CH_2); 39.2 (s, 1C, Me_{Trz}); 36.4 (s, 1C, Me_{Im}); 28.2 (s, 2C, $^i Pr_{CH}$); 23.5 (s, 2C), 22.8 (s, 2C, $^i Pr_{CH3}$). $^{19}F\{^1H\}$ NMR (468.66 MHz, acetonitrile-d_3, 27.0 °C): –79.3 (s, 3F, OSO_2CF_3). HRMS *m/z* Calcd for $C_{21}H_{29}F_3N_5O_3S$ ($M^+ - Br^-$): 488.1938. Found: 488.1936 ($M^+ - Br^-$). Anal Calcd for *bis*(triflate) salt, $C_{22}H_{29}F_6N_5O_6S_2$: C, 41.44; H, 4.58, N, 10.98. Found: C, 41.48; H, 4.37; N, 10.74.

(vii) 4-((1-(*tert*-butyl)-1*H*-imidazol-3-ium-3-yl)methyl)-1-(2,6-diisopropyl-phenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium bromide trifluoromethanesulfonate [$^{t\text{Bu}}$Im(H)Trz(H)$^{\text{Me}}_{\text{Dipp}}$][Br][OTf] (4c). The desired product was prepared as described for 4a, using 3c (3.00 g, 6.72 mmol) and MeOTf (2.2 mL, 20.1 mmol). The solution changed from dark green to dark red instantly, and was stirred overnight. The crude product was purified as described for **3a**, and isolated as a white powder (3.102 g, 76%). ^1H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 9.12 (br s, 1H, NCHN); 8.75 (s, 1H, H_{Trz}); 7.77 (br s, 1H), 7.74 (br s, 1H, NCH_{imid}); 7.71 (t, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz), 7.49 (d, 2H, $^3J_{H\text{-}H}$ = 8.1 Hz, Ar); 5.88 (s, 2H, CH_2); 4.46 (s, 3H, Me_{Trz}); 2.31 (qq, 2H, $^3J_{H\text{-}H}$ = 6.7 Hz, $^3J_{H\text{-}H}$ = 6.7 Hz, $^i Pr_{CH}$); 1.67 (s, 9H, ^{t}Bu); 1.18 (d, 6H, $^3J_{H\text{-}H}$ = 6.7 Hz), 1.15 (d, 6H, $^3J_{H\text{-}H}$ = 6.7 Hz, $^i Pr_{CH3}$). $^{13}C\{^1H\}$ NMR (125.27 MHz, acetonitrile-d_3, 26.1 °C): 145.6 (s, 2C, *C*–^{i}Pr); 138.9 (s, 1C, CH_2CCH); 135.4 (s, 1C, NCHN); 130.6 (s, 1C, NC_{Ar}); 133.1 (s, 1C), 124.8 (s, 2C, CH_{Ar}); 133.2 (s, 1C, CH_{Trz}); 123.3 (s, 1C), 121.2 (s, 1C, NCH_{imid}); 121.1 (q, 1C, $^1J_{C\text{-}F}$ = 319.4 Hz, OSO_2CF_3); 61.0 (s, 1C, $NC(CH_3)_3$); 41.5 (s, 1C, CH_2); 39.3 (s, 1C, Me_{Trz}); 28.6 (s, 3C, $NC(CH_3)_3$); 28.4 (s, 2C, $^i Pr_{CH}$); 23.5 (s, 2C), 22.9 (s, 2C, $^i Pr_{CH3}$). $^{19}F\{^1H\}$ NMR (468.66 MHz, acetonitrile-d_3, 27.0 °C): –79.2 (s, 3F, OSO_2CF_3). HRMS *m/z* Calcd

for $C_{24}H_{35}F_3N_5O_3S$ ($M^+ - Br^-$): 530.2407. Found: 530.2411 ($M^+ - Br^-$). Anal Calcd for $C_{24}H_{35}BrF_3N_5O_3S$: C, 47.21; H, 5.78, N, 11.47. Found: C, 46.99; H, 5.68; N, 11.15.

(viii) First attempted synthesis of methylene[(3-methyl-1*H*-imidazole-2-ylidene)bromo(η^2,η^2-cycloocta-1,5-diene)rhodium(I)][1-(2,6-diisopropyl-phenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium] iodide, [RhI(COD)(^{Me}Im-κ^1-Trz(H)$^{Me}_{Dipp}$)][I] (6b). A 10 mL portion of acetonitrile was added to a solid mixture containing **4b** (0.042 g, 0.074 mmol), $[Rh(\mu\text{-}OAc)(COD)]_2$ (0.021 g, 0.039 mmol), and KI (0.061 g, 0.37 mmol). The resulting slurry was stirred for 19 h under reflux conditions and cooled to room temperature. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of dcm. A 45 mL portion of diethyl ether was added to precipitate a dark red solid and the solution filtered *via* canula. The solvent was removed under reduced pressure, giving 0.0010 g of a mixture of products as determined by ^{1}H NMR (none of which appeared to be the desired product). The solution was layered with diethyl ether, and the product **5b** was crystallized in very low yield through slow mixing of the solvents. ^{1}H NMR (299.97 MHz, dcm-d_2, 27.5 °C): 7.58 (t, 1H, $^3J_{H\text{-}H}$ = 7.4 Hz), 7.36 (d, 2H, $^3J_{H\text{-}H}$ = 7.4 Hz, Ar); 7.30 (d, 1H, $^3J_{H\text{-}H}$ = 1.5 Hz), 7.17 (d, 1H, $^3J_{H\text{-}H}$ = 1.5 Hz, NCH_{imid}); 5.60 (s, 2H, CH_2); 4.25 (s, 3H, Me_{Trz}); 4.05 (s, 3H, Me_{Im}); 2.96 (qq, 2H, $^3J_{H\text{-}H}$ = 6.4 Hz, $^3J_{H\text{-}H}$ = 6.4 Hz, $^i Pr_{CH}$); 1.74 (s, 3H, OAc); 1.39 (d, 6H, $^3J_{H\text{-}H}$ = 6.4 Hz), 1.02 (d, 6H, $^3J_{H\text{-}H}$ = 6.7 Hz, $^i Pr_{CH3}$). The amount of crystalline material was insufficient to obtain a useful $^{13}C\{^1H\}$ NMR spectrum. HRMS *m*/*z* Calcd for $C_{22}H_{30}IN_5O_2Rh$ ($M^+ - I^-$): 626.0499. Found: 626.0499 ($M^+ - I^-$).

(ix) First attempted synthesis of methylene[(3-*tert*-butyl-1*H*-imidazole-2-ylidene)bromo(η^2,η^2-cycloocta-1,5-diene)rhodium(I)][1-(2,6-diisopropyl-phenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium] iodide, [RhI(COD)(^{tBu}Im-κ^1-Trz(H)$^{Me}_{Dipp}$)][I] (6c). Preparation of t**he desired product was attempted as described for 6b, using 4c (0.356 g, 0.583 mmol),** [Rh(μ-OAc)(COD)]$_2$ (0.163 g, 0.302 mmol), and KI (0.492 g, 2.96 mmol). The resulting slurry was stirred for 19 h under reflux conditions and cooled to room temperature. The crude product was purified as described for **6b**, and isolated as a black, amorphous material, giving 0.243 g of a mixture of products as determined by ^{1}H NMR spectroscopic methods (none of which were the desired product), most likely containing **5c**, analogous to **5b**.

(x) Methylene[(3-methyl-1*H*-imidazole-2-ylidene)bromo(η^2,η^2-cycloocta-1,5-diene)rhodium(I)][1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium] iodide, [RhI(COD)(^{Me}Im-κ^1-Trz(H)$^{Me}_{Dipp}$)][I] (6b). A 10 mL portion of acetonitrile was added to a solid mixture containing **4b** (0.360 g, 0.633 mmol), [Rh(μ-OMe)(COD)]$_2$ (0.155 g, 0.320 mmol), and KI (0.346 g, 2.08 mmol). The resulting solution was stirred for 4.75 h at 80 °C and cooled to room temperature. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of dcm and passed through a bed of Celite *via* cannula to remove excess KI. The rest of the solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of dcm. A 30 mL portion of diethyl ether was added to precipitate a bright yellow solid, and the mother liquor was removed *via* cannula. The resulting precipitate was then washed with 3 × 30 mL portions of diethyl ether before drying *in vacuo*, giving 0.422 g (83%). ^{1}H NMR (499.82 MHz, dcm-d_2, 27.7

°C): 8.22 (br s, 1H, H_{Trz}); 8.03 (d, 1H, $^3J_{H\text{-}H}$ = 2.0 Hz), 7.01 (d, 1H, $^3J_{H\text{-}H}$ = 2.0, NCH_{imid}); 7.63 (dd, 1H, $^3J_{H\text{-}H}$ = 8.0 Hz, $^3J_{H\text{-}H}$ = 8.0 Hz), 7.39 (dd, 1H, $^3J_{H\text{-}H}$ = 8.0 Hz, $^4J_{H\text{-}H}$ = 1.3 Hz), 7.36 (dd, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz, $^4J_{H\text{-}H}$ = 1.3 Hz, Ar); 6.56 (d, 1H, $^2J_{H\text{-}H}$ = 16.1 Hz), 6.34 (d, 1H, $^2J_{H\text{-}H}$ = 16.1 Hz, CH_2); 4.75 (s, 3H, Me_{Trz}); 4.00 (s, 3H, Me_{Im}); 2.51 (qq, 1H, $^3J_{H\text{-}H}$ = 6.7 Hz, $^3J_{H\text{-}H}$ = 6.7 Hz), 2.44 (qq, 1H, $^3J_{H\text{-}H}$ = 6.8 Hz, $^3J_{H\text{-}H}$ = 6.8 Hz, $^i Pr_{CH}$); 1.19 (d, 3H, $^3J_{H\text{-}H}$ = 6.7 Hz), 1.18 (d, 3H, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.17 (d, 3H, $^3J_{H\text{-}H}$ = 6.7 Hz), 1.12 (d, 3H, $^3J_{H\text{-}H}$ = 6.8 Hz, $^i Pr_{CH3}$); 5.24 (m, 1H), 5.12 (m, 1H), 3.60 (br m, 2H), 2.55-0.88 (m, 8H, COD). $^{13}C\{^1H\}$ NMR (100.58 MHz, dcm-d_2, 27.7 °C): 185.0 (d, 1C, $^1J_{C\text{-}Rh}$ = 49.2 Hz, $C_{carbene}$); 146.5 (s, 1C), 146.1 (s, 1C, *C*–^{i}Pr); 142.2 (s, 1C, CH_2*C*CH); 133.3 (s, 1C), 125.1 (s, 1C), 125.0 (s, 1C, CH_{Ar}); 131.1 (s, 1C, NC_{Ar}); 133.2 (s, 1C, CH_{Trz}); 124.3 (s, 1C), 122.5 (s, 1C, NCH_{imid}); 44.7 (s, 1C, CH_2); 41.1 (s, 1C, Me_{Trz}); 38.2 (s, 1C, Me_{Im}); 29.0 (s, 1C), 28.9 (s, 1C, $^i Pr_{CH}$); 25.0 (s, 1C), 24.6 (s, 1C), 24.1 (s, 1C), 24.0 (s, 1C, $^i Pr_{CH3}$); 98.3 (d, 1C, $^1J_{C\text{-}Rh}$ = 6.7 Hz), 97.1 (d, 1C, $^1J_{C\text{-}Rh}$ = 6.4 Hz), 73.4 (d, 1C, $^1J_{C\text{-}Rh}$ = 14.2 Hz), 72.8 (d, 1C, $^1J_{C\text{-}Rh}$ = 14.2 Hz), 32.8 (s, 1C), 33.6 (s, 1C), 30.1 (s, 1C), 29.7 (s, 1C, COD). HRMS *m*/*z* Calcd for $C_{28}H_{40}IN_5Rh$ ($M^+ - I^-$): 676.1378. Found: 676.1377 ($M^+ - I^-$). Anal Calcd for $C_{28}H_{40}I_2N_5Rh$: C, 41.86; H, 5.02, N, 8.72. Found: C, 41.81; H, 5.10; N, 8.66.

(xi) Methylene[(3-*tert*-butyl-1*H*-imidazole-2-ylidene)bromo(η^2,η^2-cycloocta-1,5-diene)rhodium(I)][1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium] iodide, [RhI(COD)($^{t\text{Bu}}$Im-κ^1-Trz(H)$^{\text{Me}}_{\text{Dipp}}$)][I] (6c). The desired product was prepared as described for 6b, using 4c (0.514 g, 0.842 mmol), $[Rh(\mu\text{-}OMe)(COD)]_2$ (0.201 g, 0.415 mmol), and KI (0.699 g, 4.21 mmol). The solution was heated at reflux for 12.75 h, and changed from yellow to orange. The crude product was purified as described for **6b**, and isolated as a yellow powder

(0.722 g, 87%). ^{1}H NMR (299.97 MHz, dcm-d_2, 27.5 °C): 8.15 (s, 1H, H_{Trz}); 7.63 (d, 1H, $^{3}J_{H\text{-}H}$ = 2.0 Hz), 6.50 (d, 1H, $^{3}J_{H\text{-}H}$ = 2.0, NCH_{imid}); 7.70 (dd, 1H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 7.40 (d, 1H, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 7.35 (d, 1H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, Ar); 6.60 (d, 1H, $^{2}J_{H\text{-}H}$ = 16.8 Hz), 6.35 (d, 1H, $^{2}J_{H\text{-}H}$ = 16.8 Hz, CH_2); 4.69 (s, 3H, Me_{Trz}); 2.54 (qq, 1H, $^{3}J_{H\text{-}H}$ = 6.5 Hz, $^{3}J_{H\text{-}H}$ = 6.5 Hz), 2.43 (qq, 1H, $^{3}J_{H\text{-}H}$ = 6.8 Hz, $^{3}J_{H\text{-}H}$ = 6.8 Hz, $^{i}Pr_{CH}$); 1.21 (d, 3H, $^{3}J_{H\text{-}H}$ = 6.5 Hz), 1.19 (d, 3H, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 1.18 (d, 3H, $^{3}J_{H\text{-}H}$ = 6.5 Hz), 1.10 (d, 3H, $^{3}J_{H\text{-}H}$ = 6.8 Hz, $^{i}Pr_{CH3}$); 1.80 (s, 9H, ^{t}Bu); 5.25 (m, 1H), 5.02 (m, 1H), 3.72 (br s, 2H), 2.55-1.00 (m, 8H, COD). ^{13}C{^{1}H} NMR (100.58 MHz, dcm-d_2, 27.7 °C): 182.4 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 47.8 Hz, $C_{carbene}$); 147.1 (s, 1C), 146.8 (s, 1C, *C*–^{i}Pr); 142.8 (s, 1C, CH_2*C*CH); 132.0 (s, 1C), 126.1 (s, 1C), 125.7 (s, 1C, CH_{Ar}); 132.1 (s, 1C, NC_{Ar}); 133.0 (s, 1C, CH_{Trz}); 125.2 (s, 1C), 122.3 (s, 1C, NCH_{imid}); 45.2 (s, 1C, CH_2); 41.5 (s, 1C, Me_{Trz}); 29.1 (s, 1C), 28.7 (s, 1C, $^{i}Pr_{CH}$); 61.5 (s, 1C), 29.5 (s, 3C, ^{t}Bu); 25.0 (s, 1C), 24.6 (s, 1C), 24.1 (s, 1C), 24.0 (s, 1C, $^{i}Pr_{CH3}$); 98.0 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 7.0 Hz), 97.5 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 7.1 Hz), 73.6 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 14.0 Hz), 72.7 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 14.1 Hz), 32.6 (s, 1C), 33.3 (s, 1C), 30.2 (s, 1C), 30.0 (s, 1C, COD). HRMS *m*/*z* Calcd for $C_{31}H_{46}IN_5Rh$ ($M^+ - I^-$): 718.1847. Found: 718.1845 ($M^+ - I^-$).

(xii) Methylene[(3-methyl-1*H*-imidazole-2-ylidene)triiodopalladium(II)][1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium], [PdI_3(^{Me}Im-κ^{1}-Trz(H)$^{Me}_{Dipp}$)][I] (7b). A 10 mL portion of acetonitrile was added to a solid mixture containing **4b** (0.163 g, 0.287 mmol), [$Pd(OAc)_2$] (0.070 g, 0.314 mmol), and changed colour to dark purple with the addition of KI (0.302 g, 1.82 mmol). The resulting slurry was stirred for 5 h at 80 °C in a sealed container and cooled to room temperature. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of thf. A 45 mL portion of diethyl ether was added to

precipitate a dark red solid and mother liquor was removed *via* canula. The resulting precipitate was then washed with 3 × 30 mL portions of diethyl ether before drying *in vacuo*, giving 0.105 g (44%) of a dark red powder. ^{1}H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 8.78 (br s, 1H, H_{Trz}); 7.73 (br s, 1H), 7.27 (br s, 1H, NCH_{imid}); 7.69 (t, 1H, $^{3}J_{H\text{-}H}$ = 7.9 Hz), 7.47 (d, 2H, $^{3}J_{H\text{-}H}$ = 7.9 Hz, Ar); 6.06 (s, 2H, CH_2); 4.80 (s, 3H, Me_{Trz}); 3.88 (s, 3H, Me_{Im}); 2.47 (qq, 2H, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{i}Pr_{CH}$); 1.17 (d, 6H, $^{3}J_{H\text{-}H}$ = 6.9 Hz), 1.12 (d, 6H, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{i}Pr_{CH3}$). ^{13}C{^{1}H} NMR (125.69 MHz, acetonitrile-d_3, 27.7 °C): 161.7 (s, 1C, $C_{carbene}$); 145.7 (s, 2C, *C*–^{i}Pr); 140.3 (s, 1C, CH_2*C*CH); 133.4 (s, 1C), 124.8 (s, 2C, CH_{Ar}); 130.8 (s, 1C, NC_{Ar}); 133.0 (s, 1C, CH_{Trz}); 124.7 (s, 1C), 123.1 (s, 1C, NCH_{imid}); 43.6 (s, 1C, CH_2); 40.8 (s, 1C, Me_{Trz}); 38.3 (s, 1C, Me_{Im}); 28.3 (s, 2C, $^{i}Pr_{CH}$); 23.9 (s, 2C), 23.1 (s, 2C, $^{i}Pr_{CH3}$).

(xiii) Methylene[(3-*tert*-butyl-1*H*-imidazole-2-ylidene)triiodopalladium(II)]-[1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium], [PdI_3($^{t\text{Bu}}$Im-κ^{1}-Trz(H)$^{\text{Me}}_{\text{Dipp}}$)][I] (7c). The desired product was prepared as described for 7b, using 4c (0.783 g, 1.28 mmol), $[Pd(OAc)_2]_2$ (0.289 g, 1.29 mmol), and changed colour to dark purple upon the addition of KI (1.204 g, 7.253 mmol). The solution was heated at reflux for 5 h, and allowed to cool to room temperature. The crude product was purified as described for **7b**, and isolated as a dark red powder (0.775 g, 70%). ^{1}H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 8.64 (br s, 1H, H_{Trz}); 7.23 (br s, 1H), 7.15 (br s, 1H, NCH_{imid}); 7.64 (t, 1H, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 7.41 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, Ar); 6.21 (s, 2H, CH_2); 4.81 (s, 3H, Me_{Trz}); 2.45 (qq, 2H, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{i}Pr_{CH}$); 1.23 (d, 6H, $^{3}J_{H\text{-}H}$ = 6.9 Hz), 1.10 (d, 6H, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{i}Pr_{CH3}$); 1.67 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (125.69 MHz, acetonitrile-d_3, 27.7 °C): 160.3 (s, 1C, $C_{carbene}$); 146.6 (s, 2C, *C*–^{i}Pr); 140.5 (s, 1C, CH_2*C*CH); 133.3 (s, 1C), 125.0 (s, 2C,

CH_{Ar}); 130.7 (s, 1C, NC_{Ar}); 133.2 (s, 1C, CH_{Trz}); 124.8 (s, 1C), 124.4 (s, 1C, NCH_{imid}); 44.1 (s, 1C, CH_2); 41.2 (s, 1C, Me_{Trz}); 28.1 (s, 2C, $^{i}Pr_{CH}$); 24.2 (s, 2C), 22.8 (s, 2C, $^{i}Pr_{CH3}$); 67.3 (s, 1C), 31.3 (s, 3C, ^{t}Bu).

(xiv) Methylene[(3-*tert*-butyl-1*H*-imidazole-2-ylidene)-*trans*-diiodotriethylphosphinopalladium(II)][1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium] iodide, *trans*-[$PdI_2(PEt_3)(^{t\mathrm{Bu}}Im\text{-}\kappa^1\text{-}Trz(H)^{Me}_{Dipp})$][I] (9c*trans*). A 10 mL portion of acetonitrile was added to a flask containing **7c** (0.353 g, 0.406 mmol). The resulting slurry was stirred for 10 min, afterwhich PEt_3 (101 μL, 0.686 mmol) was injected into the reaction vessel. The slurry changed from dark red to a pale yellow solution almost instantly, and was stirred for another 10 min. The solvent was reduced to 5 mL under reduced pressure and passed through a bed of Celite *via* cannula. The rest of the solvent was then removed under reduced pressure and the crude product redissolved in 5 mL of dcm. A 100 mL portion of *n*-pentane was added to precipitate a bright yellow solid, which was then washed with 3 × 30 mL portions of *n*-pentane before drying *in vacuo*, giving 0.089 g (22%). ^{1}H NMR (399.80 MHz, acetonitrile-d_3, 26.5 °C): 8.52 (s, 1H, H_{Trz}); 7.56 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.9 Hz, $^{5}J_{H\text{-}P}$ = 1.9 Hz), 7.27 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.9 Hz, $^{5}J_{H\text{-}P}$ = 1.3 Hz, NCH_{imid}); 7.71 (t, 1H, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 7.49 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, Ar); 6.07 (s, 2H, CH_2); 4.43 (s, 3H, Me_{Trz}); 2.39 (qq, 2H, $^{3}J_{H\text{-}H}$ = 6.8 Hz, $^{3}J_{H\text{-}H}$ = 6.8 Hz, $^{i}Pr_{CH}$); 1.18 (d, 3H, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 1.17 (d, 3H, $^{3}J_{H\text{-}H}$ = 6.8 Hz, $^{i}Pr_{CH3}$); 1.15 (d, 3H, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 1.15 (d, 3H, $^{3}J_{H\text{-}H}$ = 6.8 Hz, $^{i}Pr_{CH3}$); 1.87 (s, 9H, ^{t}Bu); 2.18 (dq, 6H, $^{2}J_{H\text{-}P}$ = 9.5 Hz, $^{3}J_{H\text{-}H}$ = 7.7 Hz), 1.17 (dt, 9H, $^{3}J_{H\text{-}P}$ = 16.2 Hz, $^{3}J_{H\text{-}H}$ = 7.7 Hz, PEt_3). $^{13}C\{^{1}H\}$ NMR (125.69 MHz, acetonitrile-d_3, 27.7 °C): 162.4 (d, 1C, $^{2}J_{C\text{-}P}$ = 186.7 Hz, $C_{carbene}$); 145.6 (s, 2C, *C*–^{i}Pr); 140.9 (s, 1C, CH_2CCH); 133.0 (s, 1C), 124.8 (s, 2C, CH_{Ar}); 130.7 (s, 1C, NC_{Ar}); 133.0 (s, 1C,

CH_{Trz}); 123.0 (d, 1C, $^4J_{C\text{-}P}$ = 5.8 Hz), 122.0 (d, 1C, $^4J_{C\text{-}P}$ = 4.9 Hz, NCH_{imid}); 45.6 (s, 1C, CH_2); 39.7 (s, 1C, Me_{Trz}); 28.4 (s, 2C, $^iPr_{CH}$); 59.5 (s, 1C), 31.1 (s, 3C, ^{t}Bu); 23.6 (s, 2C), 23.0 (s, 2C, $^iPr_{CH3}$); 18.4 (d, 3C, $^1J_{C\text{-}P}$ = 29.4 Hz), 8.2 (s, 3C, PEt_3). $^{31}P\{^1H\}$ NMR (161.84 MHz, acetonitrile-d_3, 27.7 °C): 8.6 (s, 1P, PEt_3). HRMS *m/z* Calcd for $C_{29}H_{49}I_2N_5PPd$ ($M^+ - I^-$): 858.0844. Found: 858.0849 ($M^+ - I^-$). Anal Calcd for triflate salt, $C_{30}H_{49}F_3I_2N_5O_3PPdS$: C, 35.75; H, 4.90, N, 6.95. Found: C, 36.01; H, 5.27; N, 6.90.

(xv) Methylene[(3-*tert*-butyl-1*H*-imidazole-2-ylidene)-*trans*-diiodo-triphenylphosphinopalladium(II)][1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium] iodide, *trans*-[$PdI_2(PPh_3)(^{tBu}Im\text{-}\kappa^1\text{-}Trz(H)^{Me}_{Dipp})$][I] ($10c_{trans}$). The desired product was prepared as described for $9c_{trans}$, using 7c (0.141 g, 0.163 mmol) and changed colour to bright yellow upon the addition of **PPh_3** (0.628 g, 0.239 mmol). The solution was stirred for 10 min, the crude product was purified as described for **$9c_{trans}$**, using thf and *n*-pentane and isolated as a bright yellow orange powder (0.??? g, ??%). ^1H NMR (399.80 MHz, acetonitrile-d_3, 26.5 °C): 8.41 (s, 1H, H_{Trz}); 7.81-7.59 (br m, 2H, NCH_{imid}); 7.69-7.07 (m, 18H, Ar); (t, 1H, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.47 (d, 1H, $^3J_{H\text{-}H}$ = 7.9 Hz, Ar_{Dipp}); 6.31 (s, 2H, CH_2); 4.18 (s, 3H, Me_{Trz}); 2.22 (br m, 2H, $^3J_{H\text{-}H}$ = 6.9 Hz, $^3J_{H\text{-}H}$ = 6.9 Hz, $^iPr_{CH}$); 1.18 (d, 3H, $^3J_{H\text{-}H}$ = 6.9 Hz), 1.09 (d, 3H, $^3J_{H\text{-}H}$ = 6.9 Hz, $^iPr_{CH3}$); 1.92 (s, 9H, ^{t}Bu). At the time of defense, satisfactory $^{13}C\{^1H\}$ NMR assignment was not yet complete. Efforts are ongoing, however.

(xvi) Methylene[(3-methyl-1*H*-imidazole-2-ylidene)-*cis*-diiodotriethyl-phosphinopalladium(II)][1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium] iodide, *cis*-[$PdI_2(PEt_3)(^{Me}Im\text{-}\kappa^1\text{-}Trz(H)^{Me}_{Dipp})$][I] ($9b_{cis}$). The desired product was prepared as described for $9c_{trans}$, using 7b (0.100 g, 0.121 mmol)

and changed colour to bright yellow upon the addition of **PEt_3** (37 μL, 6.8 mmol). The solution was stirred for 10 min, the crude product was purified as described for **$9c_{trans}$**, and isolated as a bright yellow powder (0.069 g, 60%). ^{1}H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 8.72 (s, 1H, H_{Trz}); 7.64 (d, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz), 7.23 (d, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, NCH_{imid}); 7.74 (t, 1H, $^3J_{H\text{-}H}$ = 8.4 Hz), 7.53 (d, 1H, $^3J_{H\text{-}H}$ = 8.4 Hz, Ar); 5.52 (d, 1H, $^2J_{H\text{-}H}$ = 15.9 Hz), 5.41 (d, 1H, $^2J_{H\text{-}H}$ = 15.9 Hz, CH_2); 4.24 (s, 3H, Me_{Trz}); 3.83 (s, 3H, Me_{Im}); 2.38 (qq, 1H, $^3J_{H\text{-}H}$ = 6.9 Hz, $^3J_{H\text{-}H}$ = 6.9 Hz), 2.37 (qq, 1H, $^3J_{H\text{-}H}$ = 6.8 Hz, $^3J_{H\text{-}H}$ = 6.8 Hz, ^{i}Pr$_{CH}$); 1.17 (d, 3H, $^3J_{H\text{-}H}$ = 6.9 Hz), 1.13 (d, 3H, $^3J_{H\text{-}H}$ = 6. Hz, ^{i}Pr$_{CH3}$); 1.95 (dq, 6H, $^2J_{H\text{-}P}$ = 9.2 Hz, $^3J_{H\text{-}H}$ = 8.2 Hz), 1.05 (dt, 9H, $^3J_{H\text{-}P}$ = 16.7 Hz, $^3J_{H\text{-}H}$ = 8.2 Hz, PEt_3). ^{31}P{^{1}H} NMR (161.84 MHz, acetonitrile-d_3, 27.7 °C): 18.6 (s, 1P, PEt_3). HRMS analysis only detected a chelate product, *m/z* Calcd for $C_{26}H_{42}IN_5PPd$ ($M^+ - HI_2^-$): 688.1252. Found: 688.1260 ($M^+ - I^-$). At the time of defense, satisfactory ^{13}C{^{1}H} NMR assignment was not yet complete. Efforts are ongoing, however.

(xvii) Methylene[(3-methyl-1*H*-imidazole-2-ylidene)-*cis*-diiodotriphenyl-phosphinopalladium(II)][1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium] iodide, *cis*-[$PdI_2(PPh_3)(^{Me}Im\text{-}\kappa^1\text{-}Trz(H)^{Me}_{Dipp})$][I] ($10b_{cis}$). The desired product was prepared as described for $9c_{trans}$, using 7b (0.004 g, 0.005 mmol) and changed colour to bright yellow upon the addition of **PPh_3** (0.005 g, 0.02 mmol). The solution was stirred for 10 min, then heated at 80 °C in a sealed container for 2 h. The crude product was purified as described for **$9c_{trans}$**, and isolated as a bright yellow powder (0.005 g, 90%). ^{1}H NMR (499.82 MHz, acetonitrile-d_3, 27.7 °C): 8.51 (s, 1H, H_{Trz}); 7.34 (d, 1H, $^3J_{H\text{-}H}$ = 2.0 Hz), 6.93 (d, 1H, $^3J_{H\text{-}H}$ = 2.0 Hz, NCH_{imid}); 7.69 (t, 1H, $^3J_{H\text{-}H}$ = 7.5 Hz), 7.47 (d, 2H, $^3J_{H\text{-}H}$ = 7.5 Hz, Ar_{Dipp}); 5.87 (d, 1H, $^2J_{H\text{-}H}$ = 16.3

Hz), 5.14 (d, 1H, $^{2}J_{H\text{-}H}$ = 16.3 Hz, CH_2); 4.48 (s, 3H, Me_{Trz}); 3.60 (s, 3H, Me_{Im}); 2.41 (qq, 1H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $^{3}J_{H\text{-}H}$ = 7.0 Hz), 2.36 (qq, 1H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $^{3}J_{H\text{-}H}$ = 7.0 Hz $^{i}Pr_{CH}$); 1.19 (d, 3H, $^{3}J_{H\text{-}H}$ = 7.0 Hz), 1.16 (d, 3H, $^{3}J_{H\text{-}H}$ = 7.0 Hz), 1.16 (d, 3H, $^{3}J_{H\text{-}H}$ = 7.0 Hz) 1.13 (d, 3H, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{i}Pr_{CH3}$); 7.75 (ddd, 6H, $^{3}J_{H\text{-}P}$ = 12.4 Hz, $^{3}J_{H\text{-}H}$ = 7.7 Hz, $^{4}J_{H\text{-}H}$ = 1.0 Hz), 7.60 (tdd, 3H, $^{3}J_{H\text{-}H}$ = 7.7 Hz, $^{5}J_{H\text{-}P}$ = 2.0 Hz, $^{4}J_{H\text{-}H}$ = 1.0 Hz), 7.51 (ddd, 6H, $^{3}J_{H\text{-}H}$ = 7.7 Hz, $^{3}J_{H\text{-}H}$ = 7.7 H, $^{4}J_{H\text{-}P}$ = 2.2 Hz, PPh_3). $^{13}C\{^{1}H\}$ NMR (125.69 MHz, acetonitrile-d_3, 27.7 °C): 165.5 (s, 1C, $C_{carbene}$); 145.7 (s, 1C), 145.5 (s, 1C, *C*–^{i}Pr); 140.1 (s, 1C, CH_2CCH); 133.0 (s, 1C), 124.7 (s, 1C, CH_{Ar}); 130.7 (s, 1C, $NC_{Ar\text{-}Dipp}$); 133.0 (s, 1C, CH_{Trz}); 125.4 (s, 1C), 122.4 (s, 1C, NCH_{imid}); 43.5 (s, 1C, CH_2); 40.1 (s, 1C, Me_{Trz}); 38.0 (s, 1C, Me_{Im}); 28.4 (s, 1C), 28.3 (s, 1C, $^{i}Pr_{CH}$); 23.9 (s, 1C), 23.6 (s, 1C), 23.1 (s, 1C), 22.9 (s, 1C, $^{i}Pr_{CH3}$); 131.1 (d, 3C, $^{1}J_{C\text{-}P}$ = 51.4 Hz), 134.4 (d, 6C, $^{2}J_{C\text{-}P}$ = 11.0 Hz), 128.7 (d, 6C, $^{3}J_{C\text{-}P}$ = 10.8 Hz), 131.4 (d, 3C, $^{4}J_{C\text{-}P}$ = 2.5 Hz, PPh_3). $^{31}P\{^{1}H\}$ NMR (161.84 MHz, acetonitrile-d_3, 27.7 °C): 24.1 (s, 1P, PPh_3).

(xviii) Diiodotriethylphosphinopalladium(II)-μ-[(1,1′-methylene(3-*tert*-butyl-1*H*-imidazole-2-ylidene)(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-5-ylidene)]iodo(η^2,η^2-cycloocta-1,5-diene)rhodium(I), [$PdI_2(PEt_3$(μ-$^{tBu}ImTrz^{Me}_{Dipp}$)RhI(COD)] (11). A 10 mL portion of acetonitrile was added to a solid mixture containing **9b**$_{trans}$ (0.504 g, 0.511 mmol), [Rh(μ-OMe)(COD)]$_2$ (0.135 g, 0.279 mmol), and KI (0.432 g, 2.60 mmol). The resulting solution was stirred for 1 h at 80 °C in a sealed container and cooled to room temperature. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of dcm and passed through a bed of Celite *via* cannula to remove excess KI. The rest of the solvent was then removed under reduced pressure and the crude product redissolved in 5 mL of thf. A 30 mL portion of diethyl ether was added to

precipitate a bright yellow solid, and the mother liquor was removed *via* cannula. The resulting precipitate was then washed with 3 × 30 mL portions of diethyl ether before drying *in vacuo*, giving 429 g (84%). ^{1}H NMR (399.80 MHz, acetonitrile-d_3, 26.5 °C): 7.56 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.8 Hz, $^{5}J_{H\text{-}P}$ = 1.8 Hz), 7.53 (dd, 1H, $^{3}J_{H\text{-}H}$ = 1.8 Hz, $^{5}J_{H\text{-}P}$ = 1.1 Hz, NCH_{imid}); 7.71 (t, 1H, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 7.49 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, Ar); 5.82 (d, 1H, $^{2}J_{H\text{-}H}$ = 16.0 Hz), 5.31 (d, 1H, $^{2}J_{H\text{-}H}$ = 16.0 Hz, CH_2); 4.24 (s, 3H, Me_{Trz}); 2.42 (qq, 2H, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{i}Pr_{CH}$); 1.29 (d, 6H, $^{3}J_{H\text{-}H}$ = 6.9 Hz), 1.18 (d, 6H, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{i}Pr_{CH3}$); 1.81 (s, 9H, ^{t}Bu); 2.16 (dq, 6H, $^{2}J_{H\text{-}P}$ = 9.4 Hz, $^{3}J_{H\text{-}H}$ = 7.5 Hz), 1.21 (dt, 9H, $^{3}J_{H\text{-}P}$ = 16.0 Hz, $^{3}J_{H\text{-}H}$ = 7.5 Hz, PEt_3); 5.59 (br s, 2H, $COD_{\textit{trans}}$); 3.59 (br s, 2H, $COD_{\textit{cis}}$); 1.91-1.11 (m, 8H, COD_{alk}). ^{13}C{^{1}H} NMR (125.69 MHz, acetonitrile-d_3, 27.7 °C): 173.4 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 44.7 Hz, $C_{carbene(Rh)}$); 161.6 (d, 1C, $^{2}J_{C\text{-}P}$ = 184.3 Hz, $C_{carbene(Pd)}$); 144.7 (s, 2C, *C*–^{i}Pr); 141.3 (s, 1C, CH_2CCH); 133.2 (s, 1C), 125.8 (s, 2C, CH_{Ar}); 131.3 (s, 1C, NC_{Ar}); 133.2 (s, 1C, CH_{Trz}); 123.5 (d, 1C, $^{4}J_{C\text{-}P}$ = 5.7 Hz), 122.5 (d, 1C, $^{4}J_{C\text{-}P}$ = 4.8 Hz, NCH_{imid}); 45.8 (s, 1C, CH_2); 40.1 (s, 1C, Me_{Trz}); 28.1 (s, 2C, $^{i}Pr_{CH}$); 59.3 (s, 1C), 31.0 (s, 3C, ^{t}Bu); 23.7 (s, 2C), 23.1 (s, 2C, $^{i}Pr_{CH3}$); 18.0 (d, 3C, $^{1}J_{C\text{-}P}$ = 29.0 Hz), 8.2 (s, 3C, PEt_3). ^{31}P{^{1}H} NMR (161.84 MHz, acetonitrile-d_3, 27.7 °C): 9.8 (s, 1P, PEt_3). HRMS *m*/*z* Calcd for $C_{37}H_{60}I_2N_5PPdRh$ ($M^+ - I^-$): 1068.0760. Found: 1068.0760 ($M^+ - I^-$). Anal Calcd for $C_{37}H_{60}I_3N_5PPdRh$: C, 37.16; H, 5.06, N, 5.86 Found: C, 36.94; H, 5.31; N, 5.81.

4.4.3 X-ray structure determinations

(i) General considerations. All X-ray crystallography studies were carried out in the X-ray Crystallography Laboratory at the University of Alberta by either Dr. Robert McDonald or Dr. Michael J. Ferguson. Crystals were grown from

concentrated acetonitrile solutions of the compound. Data were collected[144] using a Bruker APEX II detector/D8 diffractometer with the crystals cooled to –100 °C; in all case Mo Kα radiation was used. The data were corrected for absorption through use of Gaussian integration (using the indexed faces and measured dimensions of the crystal. Structures were solved using direct methods (*SHELXS-97*[145]). The program *SHELXL-97*[145] was used for structure refinements. Hydrogen atoms (including those involved in hydrogen bonds) were assigned positions on the basis of the geometries of their attached carbon atoms and were given thermal parameters 120% of their parent carbons. See Appendix IV (Table III.2-1) for a listing of crystallographic experimental details, and Appendix V (Table IV-2) for a listing of crystallographic data.

Section 4.5 References

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Chapter 5 The Development of Di-Mesoionic Carbene Ligands and Their Use as Bridges in Mixed-Metal Complexes of Rh and Ir

Section 5.1 Introduction

5.1.1 Mesoionic carbenes

Although Arduengo's seminal synthesis of a free *N*-Heterocyclic Carbene (NHC) in 1991[1] marked a spectacular rise in popularity for the use of carbenes as ancillary ligands,[2-20] Crabtree's report describing a "wrong-way" carbene (with a lone pair on the C-4 or C-5 carbon instead of C-2)[21] sparked an interest in *different* carbenes based on *N*-heterocycles such as abnormal (*a*NHCs)[22-25] and remote NHCs (*r*NHCs)[26-31] (see Chapter 4). Since no reasonable resonance forms containing a carbene moiety can be drawn for the free ligand without additional charges (unlike "normal" NHCs),[23, 32, 33] these carbenes were classified as "mesoionic carbenes" (or MICs)

While still in their infancy, MIC ligands have experienced a surge in popularity owing to the development of convenient routes to deprotonated "free" mesoions.[33, 34] MICs have been shown to be even stronger electron donors (and weaker π-acceptors) than NHCs, which opens up interesting perspectives for their applications.[22-25] Furthermore, the significant steric bulk required to stabilize most free carbenes is less vital in MICs because there have been no reported dimerizations of *a*NHC or *r*NHCs,[33] which suggests that the Wanzlick dimerization pathway[35] for classical carbene decomposition (see Chapter 1, Scheme 1-4) is disfavoured,[36, 37] which is not unexpected because of the negative charge located on carbon. As a

result, the scope of possible substituents is broadened significantly, making a wide variety of substituted carbenes possible.

Transition metal complexes containing MICs have been shown to be active catalysts in many different reactions, such as alcohol oxidation (Figure 5-1a),[36] hydroarylation of alkynes,[37] Suzuki-Miyaura cross-coupling (Figure 5-1b),[38-41] hydroalkoxylation of allenes (Figure 5-1c),[42] and olefin metathesis (Figure 5-1d).[34, 43] These examples illustrate the versatility of MICs, which can be generated using a wide range of different functionalities on N-1, N-3, and C-4. In all cases, these complexes exhibit catalytic activities similar to those of well-developed NHC-based systems.

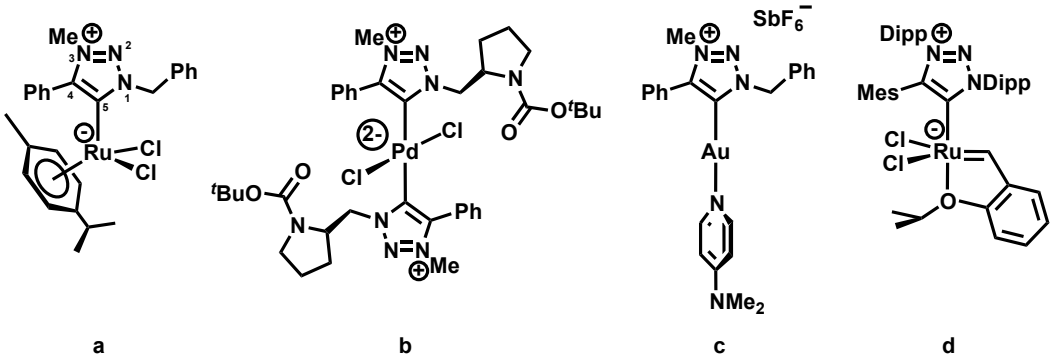
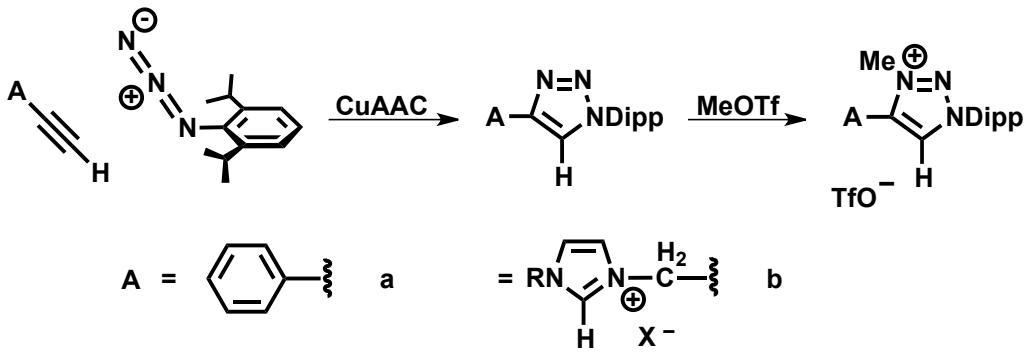


Figure 5-1. Recent examples of pre-catalysts involving 1,2,3-triazol-5-ylidene-type MIC ligands.

5.1.2 Synthesis of mesoionic carbenes

As noted in Chapter 4, Albrecht[44, 45] and Bertrand[33, 45] developed routes for the synthesis of 1,2,3-triazol-5-ylidene-based MICs through deprotonation of analogous 1,2,3-triazolium salts. The parent triazole can be prepared from the copper-catalyzed azide-alkyne cycloaddition (CuAAC, or "click" chemistry[46-48]), which is then followed by alkylation (although other routes do exist for the *arylation* at this position by the formal 1,3-dipolar cycloaddition between 1,3-diaza-2-azoniaallene salts with various

alkynes[34, 49-51]) to afford the readily-deprotonated triazolium salt (Scheme 5-1a). With a wide range of alkynes and azides available, MICs are highly tunable as is obvious from the assortment of functional groups on the pre-catalysts shown in Figure 5-1.



Scheme 5-1. Triazolium synthesis using CuAAC and methyl trifluoromethanesulfonate approach.

For reasons outlined in Chapter 1, our group focuses mainly on the study of bimetallic complexes, many of which are bridged by diphosphines such as *bis*(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$, dppm).[52] However, we recently demonstrated that dicarbenes such as di-NHCs can also effectively bridge two identical[53] or similar[54] metal atoms (Chapter 2). To expand on this work, we then investigated the use of "click" chemistry (along with a few modifications based on literature precedent[55]) to incorporate new carbenes such as MICs into our frameworks yielding a variety of unsymmetrical dicationic NHC/MIC precursors (Scheme 5-1b, as described in detail in Chapter 4), which could subsequently be doubly-deprotonated (in sequence) to provide hybrid NHC/MIC bridging units for mixed-metal complexes.

With experience in attaching a pendent $MIC(H)^+$ arm to an NHC precursor (and systematically deprotonating each end to form a bridging mixed-metal complex) we became interested in further developing this work towards incorporating *two* of

these strong-donating MICs into one bridging ligand. Surprisingly, only one bidentate di-MIC had been reported at the time this work began[42] (a second di-MIC has been published during manuscript preparation[56]). We therefore initiated a study on the synthesis of symmetric di-MICs which could be used as bridging units, or as chelating ancillary ligands (the former being of more interest to us). Similar to our methods employed in Chapters 2 and 4 (and intended in Chapter 3), we anticipated that a "pendent strategy" of deprotonating a dicationic $[\text{di-MIC}(H)_2]^{2+}$ ditriazolium species one ring at a time and introducing the metal atoms in a sequential manner would again be the most promising route to di-MIC-bridged heterobinuclear complexes.

In our previous investigations involving hybrid NHC/MICs (Chapter 4), the two different carbene precursors had different acidities, and therefore the nature of attachment (*via* NHC or MIC) was dictated by the order of metal atom incorporation into the bridge (unlike symmetrical dicarbenes). However, despite di-MICs being "symmetric", each carbene ring itself does not possess symmetry about the axis bisecting the carbene lone pair (unlike NHC rings). As a result, the method of ligand *synthesis* and the connection of the rings to the linker itself can result in different isomers.

For example, if both MIC rings are connected to the linker *via* N-1, the result is what we have labeled an *N*,*N*′-linked di-MIC (Figure 5-2a, $\text{di-MIC}_{N,N'}$), whereas connectivity *via* C-4 results in a *C*,*C*′-linkage (Figure 5-2b, $\text{di-MIC}_{C,C'}$). Of course, mixed *C*,*N*′-linked (or *N*,*C*′-linked) isomers are also possible, although they would most likely be more synthetically challenging. Regardless of connection, the impact

on the metal complex (once attached to a transition metal) would presumably be minimal (especially if $R^1 = R^3$).

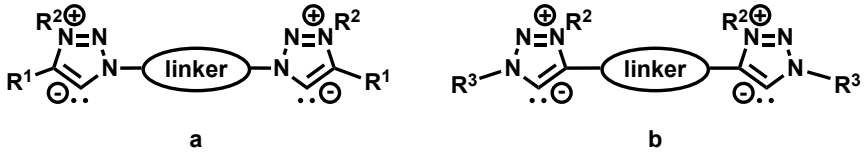


Figure 5-2. Different di-MIC isomers possible depending on N-1- (**a**) or C-4- (**b**) linkage.

Section 5.2 Results and Compound Characterization

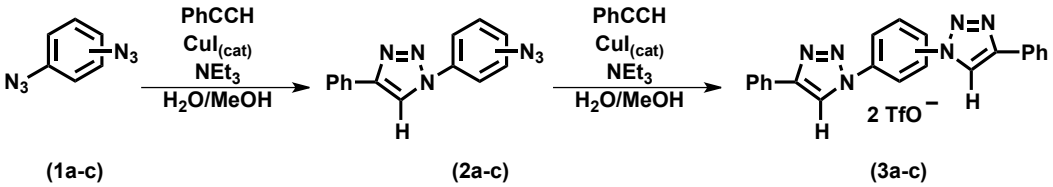
5.2.1 Establishing a strategy

With these concepts in mind, and our interest in bidentate carbenes as bridging ligands in heterobimetallic complexes, we began to investigate the synthesis of di-MICs using the CuAAC protocol mentioned above, followed by methylation to form the ditriazolium proligand. As mentioned above, both *N*,*N*′ and *C*,*C*′ isomers are possible depending on which "click" functional groups (either an azide or alkyne) are provided by the linker. For example, in order to obtain an *N*,*N*′-linked di-MIC, a diazido linker (*i.e.*, N_3–(linker)–N_3) would be required, whereas a *C*,*C*′-linked system would require a dialkyne system. Azides can be easily[i] prepared from either alkyl halides (*via* nucleophilic substitution by N_3^-)[57, 58] or from aryl amines (*via* diazotization of $ArNH_2$ to ArN_2^+, and subsequent displacement of N_2 by N_3^-),[59-64] therefore our initial plan was to begin a linking framework based on diazides (from either a dihalide or diamine), and "click" two equivalents of alkyne monomers through the CuAAC process noted above.

[i] Organic azides are explosive substances that can decompose violently with the slightest input of energy from external sources. Extremely high safety precautions should be exercised.

5.2.2 Attempted synthesis of di-MIC$_{N,N'}$ dicationic precursors

Although diazides appeared to be the easiest route to ditriazoles, we did not attempt to generate simple *alkyl*-bridged diazides (*i.e.*, N_3–$(CH_2)_n$–N_3, n = 1, 2) to form di-MICs analogous to our previously-reported di-NHCs (Chapter 2) and NHC/MICs (Chapter 4), as it is well-known that azides become dangerously shock-sensitive if a high carbon-to-nitrogen ratio is not achieved.[65] Therefore, we chose a linker of significant molecular weight (*ortho*-, *meta*-, and *para*-substituted benzene rings) to hold both azide components together (Scheme 5-2). Although this linker is significantly



Scheme 5-2. Attempted synthesis of *ortho*- (**a**), *meta*- (**b**), and *para*- (**c**) *N*,*N*′-linked ditriazoles.

different than the ones examined in Chapters 2 and 4, substituted benzene rings satisfy our criterion of allowing for metal-metal proximity (once transformed into carbenes and attached to transition metals), and therefore other differences (*i.e.*, linker shape, size, and/or electronic arrangement, etc.) were not expected to interfere with our studies.

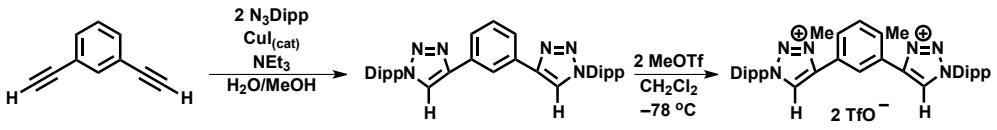
Although the diazides (**1**) could be prepared using previously-reported syntheses,[60, 62-64, 66-68] several problems arose in preparing the respective ditriazole species (**3**, Scheme 5-2). In all cases attempted, an incomplete triazole/azide product (**2**) precipitated from solution, preventing the second CuAAC reaction which is required to produce the desired product (although product **3c** had previously been reported in low yield[64]). Because of only minimal solubility in most solvents (even dmso), the NMR spectra of these triazole/azide products could not be obtained.

Addition of MeOTf to a dcm slurry of **2** produced a mixture of products. However, HRMS displayed a peak corresponding to a [triazolium–linker–N]$^+$ species in the methylated product mixture, presumably from the loss of N_2 in the instrument during electrospray ionization. Due to our lack of success in producing the *N*,*N*′-linked ditriazoles necessary to generate MIC precursors, we abandoned this pursuit in favour of the other *C*,*C*′-linked isomers mentioned above.

5.2.3 Synthesis of di-MIC$_{C,C'}$ dicationic precursors

As noted already, the synthesis of di-MIC$_{C,C'}$ systems should be possible by the reaction of a dialkyne with two equivalents of an azide. Typically, dialkynes are either notoriously expensive, or complicated to synthesize. Fortunately though, dialkyne-substituted benzene rings are relatively inexpensive, and should provide the metal-metal proximity required for our studies (as was mentioned with the diazides above). Before initiating this study however, it came to our attention that solubility issues also plagued similar *C*,*C*′-linked triazoles when organized in *ortho*- and *para*-substitution patterns,[ii] so only the *meta*-substituted *C*,*C*′-linked case was investigated.

The ditriazole (**5**) could be prepared cleanly in high yield (Scheme 5-3) from the commercially available dialkyne (**4**) and 2-azido-1,3-diisopropylbenzene (DippN$_3$) under conditions similar to the attachment of an MIC to the imidazolium group's



(4) (5) (6)

Scheme 5-3. Synthesis of di-MIC$_{C,C'}$ precursors using dialkyne route.

[ii] In conversations with Dr. Kelly J. Kilpin at a conference poster session, wherein she reported the results from her *meta*-di-MIC$_{C,C'}$-bridged di-Au complexes, which has since been published.[42]

propargyl arm in Chapter 4. Formation of **5** is obvious from the ^{1}H NMR spectrum which displays the expected pattern for a *meta*-substituted benzene ring (two triplets and a doublet of doublets of 1:1:2 intensity ratios, respectively)[69-71] and peaks typical for a Dipp-substituted triazole ring (see Chapter 4), including two doublets for the ^{i}Pr methyl groups, most likely due to inhibited Ar–^{i}Pr bond rotation. Additionally, the alkyne proton of **4** shifts dramatically from $\delta \approx 3.00$ to $\delta = 8.54$, consistent with transformation of **4** into a triazole.

The ^{13}C{^{1}H} NMR spectrum also displays typical resonances for a ditriazole bridged by a benzene ring at the 1,3-positions. The resonances corresponding to the carbons in the 6-membered rings change only slightly; however, there are significant shifts in the resonances for the alkynyl carbons of **4**, consistent with the transformation from alkynyl groups to triazole rings, shifting from ~ 80 ppm (for both) to $\delta = 127.8$ for the C–H and $\delta = 139.2$ for the quaternary connecting carbon, both of which are typical for such groups. The peaks corresponding to the carbon atoms in the Dipp ring (**3b**,**c**) also show evidence for inhibited Ar–^{i}Pr bond rotation (two different $^{i}Pr_{Me}$ environments at $\delta = 22.1$ and $\delta = 22.3$, but only one $^{i}Pr_{C-H}$ environment, suggesting that N–Dipp rotation is *not* inhibited).

With the previous observation by us that methyl trifluoromethanesulfonate (MeOTf) is not regioselective enough to afford methylation at N-3 unless a bulky group is attached to N-1, we did not attempt to prepare benzyl-substituted (–CH_2Ph, or Bn) species (although Kilpin *et al.*[42] were able to methylate N-1-benzyl-substituted compounds exclusively at N-3 using "Meerwein's salt", Me_3OBF_4[70, 72]). Upon adding MeOTf at low temperature, the bulky group directs methylation at the distal nitrogen atom, forming the desired ditriazolium salts (**6**). The ^{1}H (shown in Figure 5-3) and

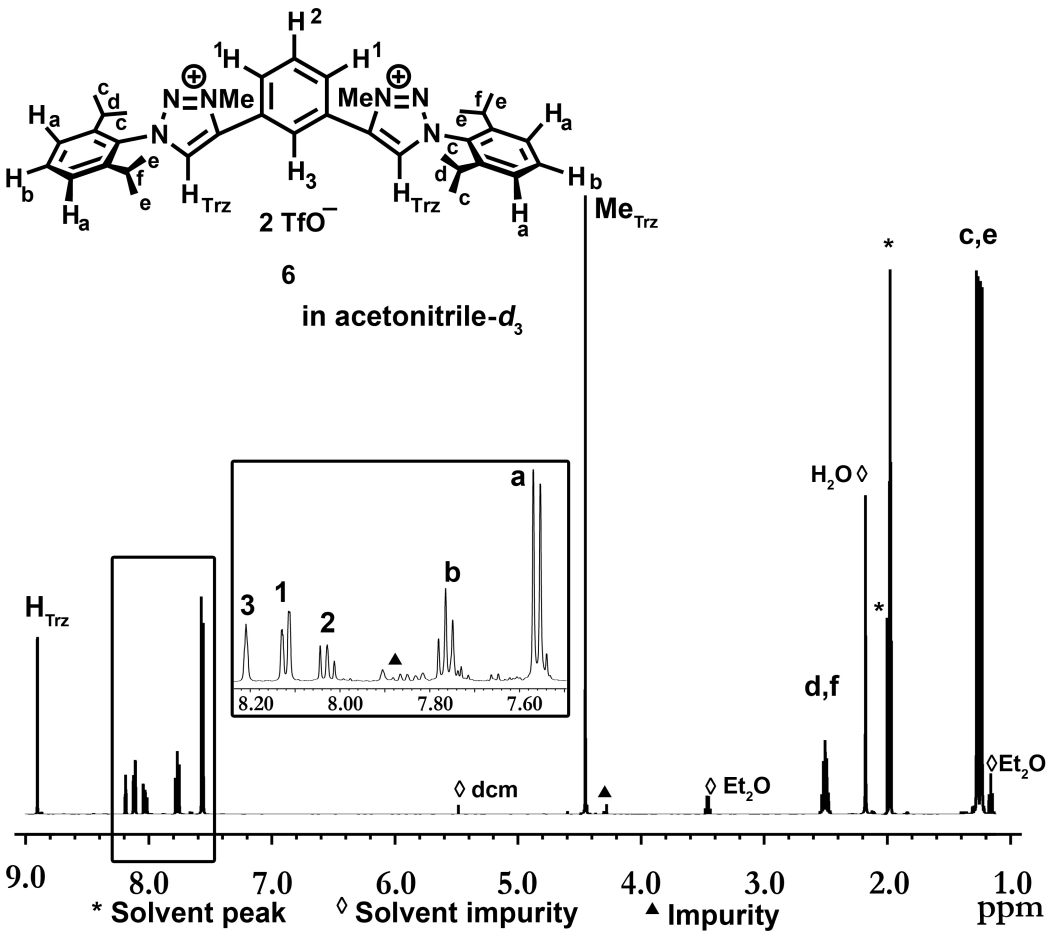


Figure 5-3. ^{1}H NMR spectrum (400 MHz) of complex **6** in acetonitrile-d_3 with expanded aromatic region.

^{13}C{^{1}H} NMR spectra are nearly identical to those of their precursors (**5**) with the exception of an additional peak (in both spectra) for the methyl group on N-3, and a slight shift for the now-acidic proton (H_{Trz}) and its attached carbon. Full proton assignment is made relatively straightforward owing to the second order "roofing effects" observed (similar to the AB patterns observed in Chapters 2 and 4) in the peaks for protons H1 and H2, as well as the two for protons Ha and Hb.

Although all di-MICs discussed in this chapter are of the *C*,*C*′-linked type (*i.e.*, di-MIC$_{C,C'}$ dicarbenes), they are herein referred to as di-MICs for simplicity. In describing metal complexes ligated by di-MICs, we use the abbreviations

[^{Dipp}Trz(H)Trz(H)][X]$_2$ for the MIC(H)$^+$/MIC(H)$^+$ dicationic dicarbene precursors, (^{Dipp}Trz-κ^1-Trz(H)) for the monodentate MIC-anchored, pendent-triazolium MIC/MIC(H)$^+$ species, and (μ-^{Dipp}Trz$_2$) for bidentate di-MIC dicarbene bridges, which are a slight modification to the original nomenclature for symmetric di-NHCs used in Chapter 2 and originally suggested by Green, *et al.*,[73] as shown in (Figure 5-4). In these abbreviations the triazole N-1 substituent (2,6-diisopropylphenyl, or Dipp in this work) on the triazolium/MIC ring appears first, followed by either the dicationic ring (Trz(H)Trz(H)), anchored-MIC/pendent-triazolium (Trz-κ^1-Trz(H)), or bridging di-MIC (Trz$_2$) notation. These abbreviations are simplified somewhat because the nature of the linker is not altered, nor are the N-1 or N-3 substituents varied in this work.

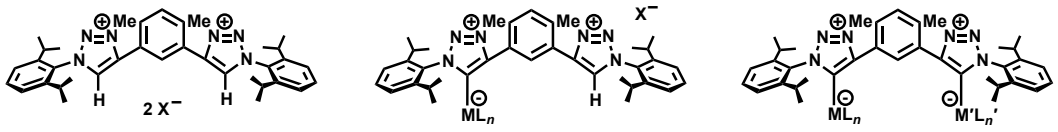


Figure 5-4. Free dication (**a**), pendent (**b**), and bridging (**c**) labeling scheme.

5.2.4 Attempted synthesis of MIC-anchored/pendent-triazolium Pd systems

Although, as described in Chapter 4, we were unable to deprotonate the MIC half of our NHC/MIC proligands using [Pd(OAc)$_2$], we thought that perhaps this system might be adequately robust to allow for high-temperature internal base deprotonation by this precursor. This proved not to be the case; even at temperatures of 100 °C (in either acetonitrile or dmso), the ^{1}H NMR spectrum of a mixture of **6**, [Pd(OAc)$_2$], and potassium iodide (KI) indicated no evidence of deprotonation, even after prolonged periods of time (24 h). Albrecht *et al.* report

that temperatures of up to 120 °C (in dmso) are required in order to effect deprotonation,[45] but heating to this temperature in our studies only resulted in decomposition, as made evident by monitoring reaction progress by ^{1}H NMR experiments.

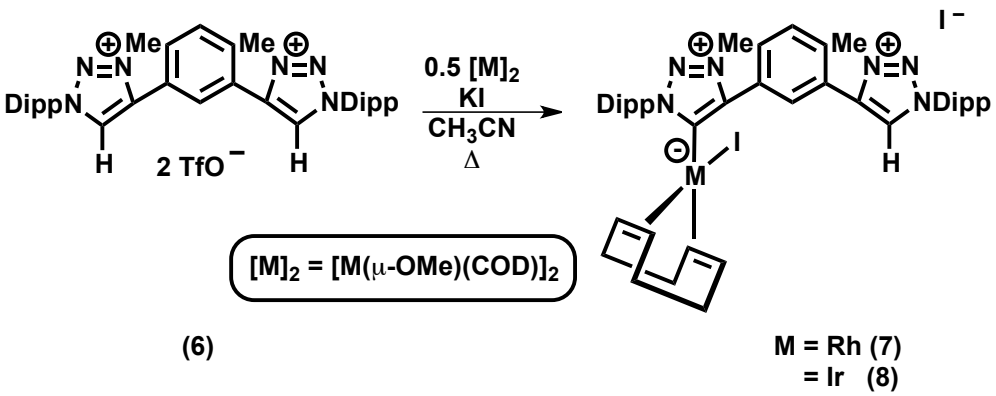
Although the generation of free dicarbenes *in situ* can often result in undesired *chelating* arrangements in the presence of transition metal precursors (in lieu of bridging), it seemed reasonable to expect that deprotonation of only *one* end of **6** using one equivalent of strong base in the presence of a Pd precursor (with labile, displaceable ligands) should effectively produce the desired MIC-anchored/pendent-triazolium Pd species of interest without risk of chelation (because only one carbene functionality would be generated). Potassium *bis*(trimethylsilylamide) ($K[N(SiMe_3)_2]$) seemed like the best choice owing to our success in deprotonating imidazolium salts to generate NHCs in Chapter 2 (see Section 2.2.4), and because potassium bases have been identified as the reagents of choice for the deprotonation of carbene precursors, as they avoid the formation of stable carbene–alkali-metal adducts that are commonly encountered when lithium bases are used.[26, 74-77]

It was anticipated that formation of a ^{Dipp}TrzTrz(H)$^{+}$ species *in situ* could facilitate displacement of weakly-coordinated ligands of a palladium precursor such as the labile acetonitrile groups in *trans*-$[PdCl_2(CH_3CN)_2]$. However, instead of displacing acetonitrile, the carbene acts as a base, deprotonating the acetonitrile ligand and resulting in a mixture of products. Protons of coordinated acetonitrile ligands have been reported to be acidic,[78-81] and this combined with the noted non-innocent nature of carbenes to behave as bases (by our group[81-83] and others[84-87])

helps to explain this result. Presumably this undesireable reaction can be avoided through the use of similarly-labile ligands on Pd which do not contain acidic protons, such as the phosphines in *trans*-$[PdCl_2(R_3P)_2]$.[88] This approach remains to be tested.

5.2.5 MIC-anchored/pendent-triazolium complexes of Rh and Ir

Although deprotonation of MIC proligands appears difficult using acetate-containing internal base precursors such as $[Pd(OAc)_2]$, deprotonation of triazolium moieties is readily achieved using $[Rh(\mu\text{-OMe})(COD)]_2$ (having a stronger methoxide base, see Chapter 4). As a consequence, we attempted to deprotonate our ditriazolium salts using half an equivalent of $[Rh(\mu\text{-OMe})(COD)]_2$ (Scheme 5-4, M = Rh). The methoxide base proved to be basic enough to easily deprotonate one half of the ditriazolium salt under mild heat (80 °C) over the course of only 1 h, yielding [RhI(COD)(^{Dipp}Trz-κ^1-Trz(H))][I], **7** in near-quantitative yield.[iii]



Scheme 5-4. Formation of MIC-anchored/pendent-triazolium complexes of Rh (**7**) and Ir (**8**).

The pendent structure of complex **7** is easily confirmed by the emergence of a new acidic (H_{Trz}) proton in the high-frequency region of the ^{1}H NMR spectrum

[iii] An excess of potassium iodide (KI) is added to the reaction in order to force an iodo product (analogous to systems in Chapters 2 and 4) rather than coordination of the dication's triflate (OTf^-) counteranion upon deprotonation and metal-carbene generation.

(shown in Figure 5-5) as a sharp singlet at δ = 9.06 as well as two singlets for the now-inequivalent N-3 methyl substituents. Although it was expected that these

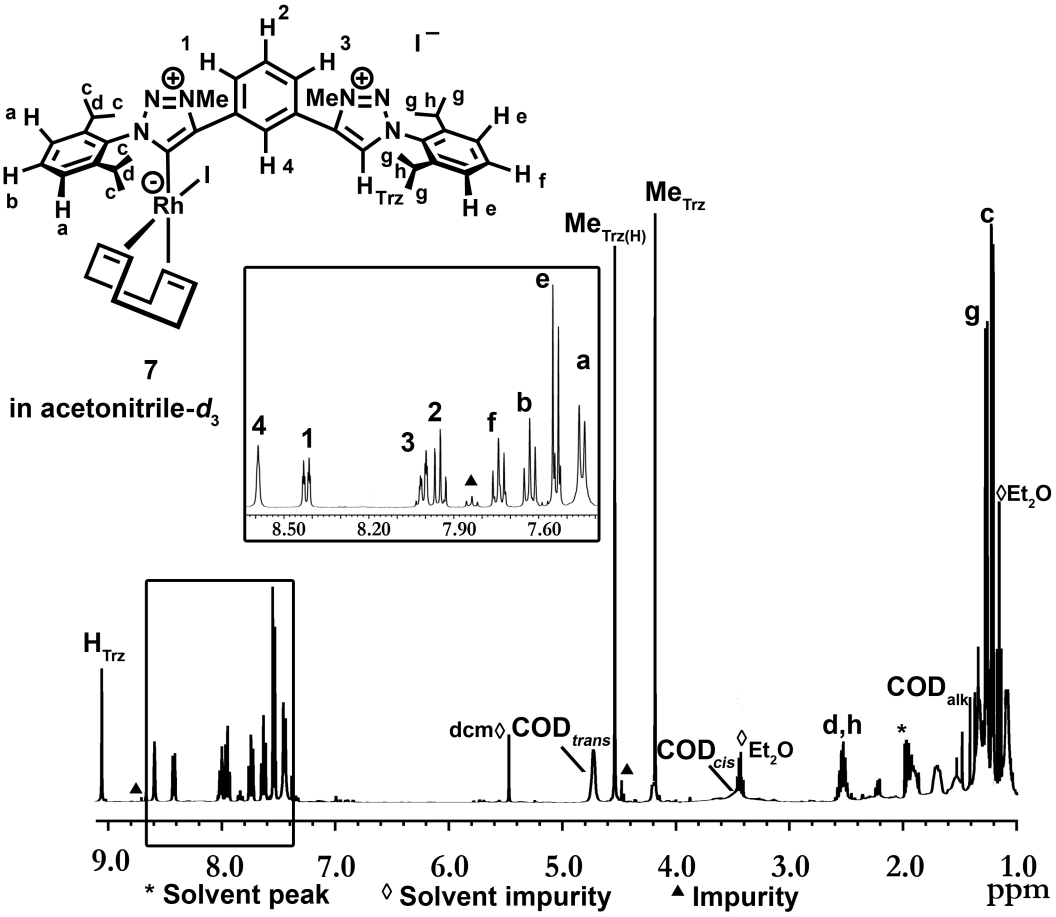


Figure 5-5. ^{1}H NMR spectrum (400 MHz) of complex **7** in acetonitrile-d_3, with expanded aromatic region.

complexes would also display evidence for inhibited rotation about the Ar–^{i}Pr bond (for both inequivalent Dipp systems), only two doublets are observed, representing the two different Trz and Trz(H)$^+$ environments, as opposed to the expected four. Two peaks representing the olefinic COD peaks appear in the spectrum at δ = 4.73 as a broad multiplet for the group *trans* to the MIC (which is at a comparatively lower frequency than COD peaks *trans* to an NHC[54]), and a broad peak at δ = 3.45 for the two protons *cis* to the carbene. It is worth noting that this *cis* peak is *significantly*

broadened (FWHM ≈ 46 Hz), and was difficult to locate (especially if the sample contains even the slightest amount of Et_2O solvent, $\delta_{CH_2} = 3.42$[89]) until an (F_2, F_1) correlation peak ($\delta_{^1H}$, $\delta_{^{13}C\{^1H\}}$) was obtained in 2D gHMQC NMR experiments confirming this location in the ^1H NMR spectrum.

With the symmetry about the aromatic linker being broken, all phenyl-linker protons are now made inequivalent and show up as four separate resonances with considerable mutual coupling. The use of 2D transverse rotating-frame Overhauser enhancement spectroscopy (TROESY) also helps to distinguish between peaks on the "acidic side" of the molecule (owing to NOE interactions with H_{Trz}) and the "coordinated side". Although there is no spectroscopic evidence to confirm that the MIC unit adopts the usual perpendicular orientation with respect to the square plane of the metal, it is presumed to bind in this manner owing to steric considerations.

The $^{13}C\{^1H\}$ NMR spectrum of **7** indicates formation of a pendent species having a rhodium-bound carbene by the emergence of a high-frequency doublet in the typical carbene region at $\delta = 171.0$ ($^1J_{C\text{-}Rh} = 46.1$ Hz). This chemical shift (as mentioned in Chapter 4[54]) is at a slightly lower frequency than for the (COD)Rh–NHC complexes[54] but comparable to the other (COD)Rh-MIC systems reported by Albrecht *et al.*,[45] and by us in Chapter 4. Several peaks crowd the high-frequency aromatic region (owing to several aromatic rings with several different environments as a result of the "left/right" asymmetry) but peak assignments are once again finalized through the use of various 2D NMR experimental techniques. Peaks for the olefinic COD carbons ($\delta = 98.8$ for *trans*, $\delta = 71.7$ for *cis*) are unusually broad and as a result, coupling to Rh cannot be resolved at room temperature. Although the ^1H NMR spectrum implied only two different ^{i}Pr methyl environments were

present in the complex, four different peaks are observed in the $^{13}C\{^{1}H\}$ NMR spectrum. This inconsistency is most likely the result of $^{13}C\{^{1}H\}$ NMR spectra inherently having better resolution (than ^{1}H) owing to a wider range of ppm values. Presumably each of the doublets in the ^{1}H NMR spectrum would separate if data were acquired at higher field strength (> 11.7 T).

The analogous Ir pendent complex (Scheme 5-4, M = Ir) can be prepared using $[Ir(\mu\text{-}OMe)(COD)]_2$ to facilitate deprotonation of the dicationic di-MIC precursor to yield [IrI(COD)(^{Dipp}Trz-κ^1-Trz(H))][I], **8**. As expected, the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are nearly identical to those of its Rh analogue. The most obvious difference is the absence of coupling in the carbene peak. Connected to a quadrupolar nucleus with a significant quadrupolar moment, the MIC carbene carbon appears as a singlet at δ = 161.2 in this case as opposed to the doublet observed in the Rh complex **7**.

Although replacement of the COD ligands by CO in compounds **7** and **8** proceeds as expected to a certain extent to yield the analogous dicarbonyl complexes [RhI(CO)$_2$(^{Dipp}Trz-κ^1-Trz(H))][I] (**9**) and [IrI(CO)$_2$(^{Dipp}Trz-κ^1-Trz(H))][I] (**10**), shown in Figure 5-6, the yields are somewhat diminished because CO addition appears to also generate an equal amount of an unidentified decomposition product. In

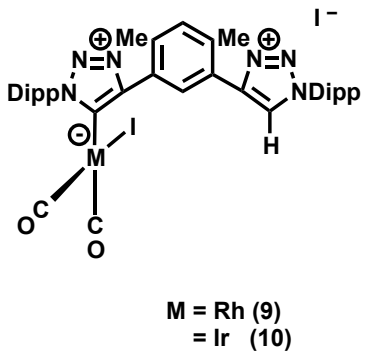
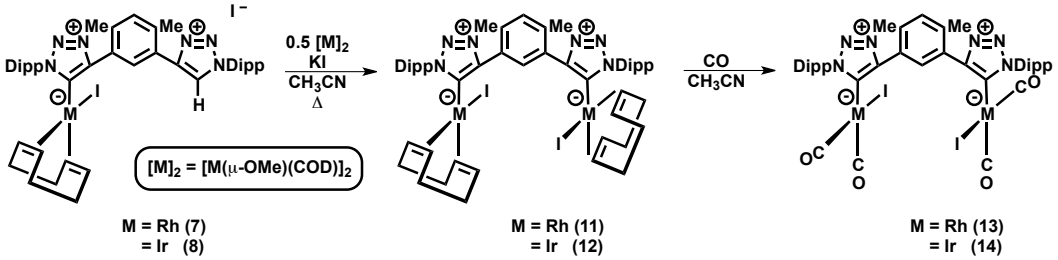


Figure 5-6. Carbonylated MIC-anchored/pendent-triazolium complexes of Rh (**9**) and Ir (**10**).

addition to the expected peaks for a carbonylated pendent complex in the ^{1}H NMR spectrum (similar to **7** and **8** without peaks for a coordinated COD ligand), a new set of peaks is present as well, clearly indicative of a more symmetric product (fewer aromatic linker peaks, only one N-3 methyl peak) which also lacks an acidic proton at high frequency. This second product could potentially be the mononuclear species [MI(CO)(κ^2C^2,$C^{2'}$-^{Dipp}Trz$_2$)], which could be forming through fragmentation of a portion of the pendent products. This chelate result parallels the previously observed issues with C_1-linked di-NHC systems in Chapter 2. Attempts are ongoing to separate the desired pendent species from the presumed neutral, chelated byproducts.

5.2.6 Di-MIC-bridged homobimetallic complexes of Rh and Ir

Both Rh (**7**) and Ir (**8**) pendent systems can be deprotonated with another half equivalent of their respective [M(μ-OMe)(COD)]$_2$ precursor to yield the expected homobimetallic di-MIC-bridged products [RhI(COD)]$_2$(μ-^{Dipp}Trz$_2$) (**11**) and [IrI(COD)]$_2$(μ-^{Dipp}Trz$_2$) (**12**) as shown in Scheme 5-5. Formation of the bimetallic



Scheme 5-5. Formation of homobimetallic di-MIC-bridged complexes of Rh (**9**, **11**) and Ir (**10**, **12**).

product is evident from the disappearance of the acidic proton H_{Trz} in the ^{1}H NMR spectra. Furthermore, both ^{1}H and ^{13}C{^{1}H} NMR spectra become less complicated owing to the symmetry of the bimetallic system (compared to the pendent species **7**

and **8**). Elemental analyses also imply a bimetallic structure rather than a chelated one. Once again, both ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra indicate a barrier to Ar–^{i}Pr rotation. As expected, these homobimetallic complexes can also be generated from the reaction of the dicationic precursor **6** with a full equivalent of [M(μ-OMe)(COD)]$_2$, in higher isolated yields than when the pendent species is isolated in workup.

Both species can be converted into their carbonylated analogues [RhI(CO)$_2$]$_2$(μ-^{Dipp}Trz$_2$) (**13**) and [IrI(CO)$_2$]$_2$(μ-^{Dipp}Trz$_2$) (**14**) from species **11** and **12** *via* a gentle purge of carbon monoxide in their respective solutions (Scheme 5-5), as monitored by ^{1}H NMR spectroscopy (the spectrum of **14** is shown in Figure 5-7). These carbonylated bimetallic species exhibit similar NMR spectra to their respective precursors, with the exception of the absence of peaks typical for olefinic and alkyl

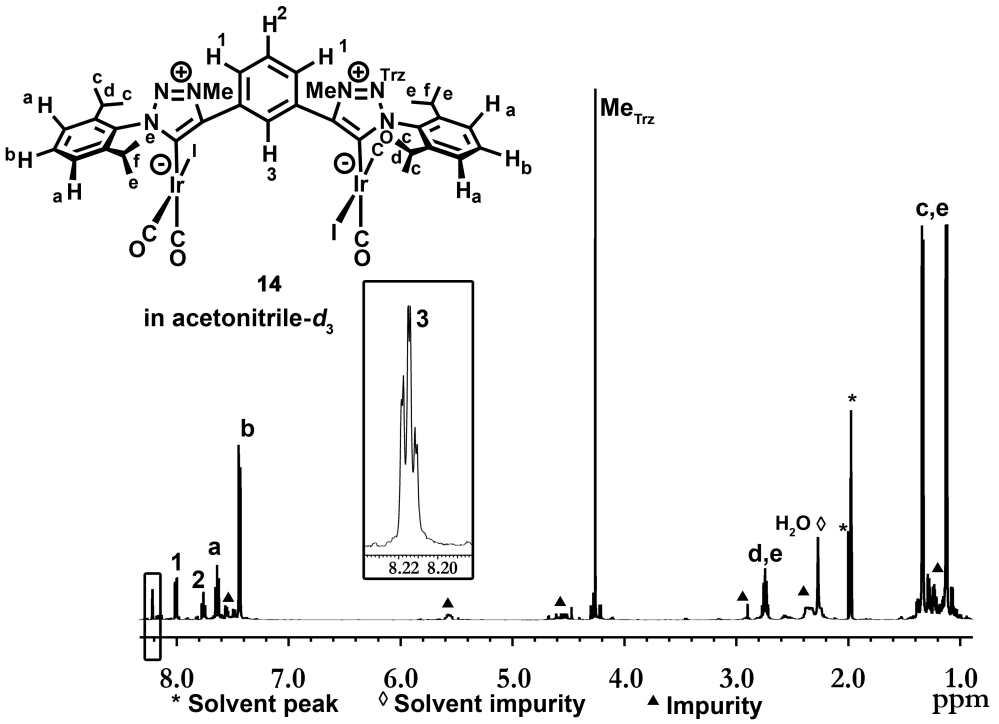


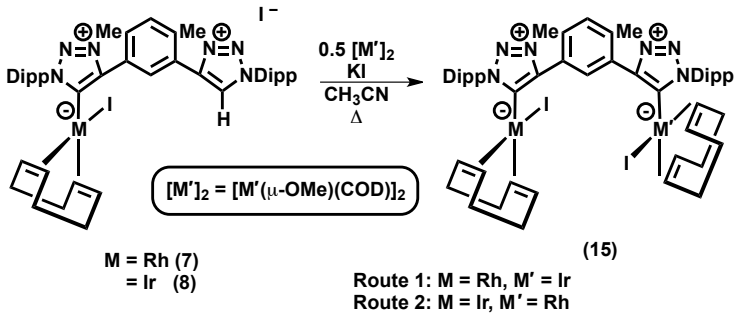
Figure 5-7. ^{1}H NMR spectrum (498 MHz) of complex **14** in acetonitrile-d_3 with expanded high-frequency region.

COD protons, and the presence of carbonyl peaks in the $^{13}C\{^{1}H\}$ NMR spectrum. It is also interesting to note that the linker of the di-Ir complex **14** exhibits a more-noticeable long-range coupling between the *para*-oriented protons H2 and H3 ($^{5}J_{H\text{-}H}$ = 0.7 Hz) than any of its precursors.

It is well-documented that bimetallic species (involving two square-planar systems) bridged by dicarbenes can either adopt *meso* (C_s) or *dl* (C_2) symmetry resulting from the hindered rotation of the M–carbene bond, wherein both iodides are either pointing in the *same* or *opposite* directions, respectively.[90-92] Although we are unable to determine which diasteromer best describes complexes **11**-**14** through spectroscopy, attempts to grow single crystals for X-ray diffraction studies are ongoing, and a structure solution would surely reveal the correct symmetry.

5.2.7 Di-MIC Heterobimetallic Rh/Ir complexes

For reasons specified in Chapter 1, our recent goal in dicarbene chemistry has been to establish routes to *hetero*bimetallic complexes through the use of our conventional "pendent strategy". Although (based on our limited attempts to date) we have been unsuccessful in generating Pd/Rh di-MIC systems analogous to those of our di-NHCs (Chapter 2) and NHC/MICs (Chapter 3), a Rh/Ir di-MIC-bridged complex (**15**, Scheme 5-6) can be generated using this "pendent strategy" through the reaction



Scheme 5-6. Formation of heterobimetallic di-MIC-bridged complexes of Rh/Ir (**15**) *via* two routes.

of half an equivalent of $[M(\mu\text{-OMe})(COD)]_2$ and a pendent complex of the other metal. Obviously two routes are possible: generation of **15** from the reaction of the Rh-containing **7** with half an equivalent of $[Ir(\mu\text{-OMe})(COD)]_2$, or a similar reaction of the Ir-containing **8** with half an equivalent of $[Rh(\mu\text{-OMe})(COD)]_2$. Although each route incorporates the metals in a different order, the symmetric nature of these di-MICs allows for the same resulting mixed-metal complex **15**. Both routes were attempted and yields are the same by both paths.

The heterobimetallic structure of complex **15** is confirmed by the disappearance of the pendent precursor's acidic proton in the ^{1}H NMR spectrum. Peaks representing groups on the "acidic" side shift slightly owing to the transformation from a pendent-triazolium group to a metal-coordinated MIC. Four different olefinic COD peaks (two for *trans*, two for *cis*) are also present, as well as a significantly-crowded aliphatic region owing to eight different aliphatic CH_2 environments of the COD ligands. The $^{13}C\{^1H\}$ spectrum contains two high-frequency peaks, representing two different carbene environments: a doublet at δ = 171.5 ($^1J_{C\text{-}Rh}$ = 46.7 Hz) representing the carbene coordinated to Rh, and a singlet at δ = 162.0 for the Ir-MIC group. The lower frequency for the carbene bound to the heavier congener is typical,[93, 94] as shown earlier in Chapter 2.[54]

Section 5.3 Discussion

With the recent increase in popularity of MIC ligands, we set out to design a set of dicarbenes of this type for the purposes of bridging mixed-metal systems, and we were able to devise simple routes to di-MIC precursors. Unlike di-NHCs, two different "attachment isomers" are possible, depending on the nature of the starting

materials. Although attempts to produce *N*,*N*′-linked di-MIC$_{N,N'}$ systems failed (through coupling of a diazide with two equivalents of alkyne), we found success in generating a *C*,*C*′-linked di-MIC$_{C,C'}$ system using an aryl-linked dialkyne and two equivalents of azide. These ditriazoles can easily be methylated with MeOTf to generate a new set of di-MIC proligands in high yield and purity.

We initially set out to design routes to Pd/Rh heterobimetallic complexes (to compare to our di-NHC and NHC/MIC species reported in Chapters 2 and 4), however we have been unable to effect deprotonation of the triazolium moieties using [Pd(OAc)$_2$]. Furthermore, we encountered problems in attempting to deprotonate one half of the ligand with an external base, owing to the acidic nature of acetonitrile ligands in *trans*-[PdCl$_2$(CH$_3$CN)$_2$]. As mentioned in Chapter 4, these are technical issues, and perhaps methoxido-containing Pd complexes can facilitate deprotonation of these weakly-acidic species, or a "free" MIC/triazolium ^{Dipp}TrzTrz(H)$^+$ species could displace the phosphine ligands in *trans*-[PdCl$_2$(R$_3$P)$_2$]. Both approaches will be attempted in order to obtain the desired di-MIC-bridged Pd/Rh target.

Conversely, both [Rh(μ-OMe)(COD)]$_2$ and [Ir(μ-OMe)(COD)]$_2$ served as excellent internal base precursors for the deprotonation of triazolium salts. Throughout much of the Rh-carbene literature, [Rh(μ-OAc)(COD)]$_2$ is frequently used as the metal's internal base precursor. However, we recommend that the aforementioned methoxido precursor be considered instead in future studies. Significantly milder conditions are required to facilitate deprotonation, and yields (in our experience) are much more favourable. Gratifyingly, the synthesis of the [Rh(μ-

OMe)(COD)]$_2$ itself is much simpler than [Rh(μ-OAc)(COD)]$_2$ and is nearly-quantitative from the ubiquitous [Rh(μ-Cl)(COD)]$_2$.[95] In addition to this species being an alternative to the OAc-deprotonation route, this methoxido species could potentially be more favourable than most silver-transfer transmetallation routes which are frequently used, as these precursors offer a much simpler protocol if the desired attachment is Rh or Ir.

Section 5.4 Experimental Procedures

5.4.1 General comments

Deuterated solvents used for NMR experiments were freeze-pump-thaw degassed and stored under argon over type 4A molecular sieves. Unless otherwise specified, reactions were carried out at ambient temperature. Potassium iodide was purchased from ACP; cycloocta-1,5-diene, 2,6-diisopropylaniline, methyltrifluoromethanesulfonate, palladium(II) acetate, sodium tetrafluoroborate, and 1,3-diethynylbenzene (**4**) were purchased from Aldrich; *ortho*-, *meta*-, and *para*-phenylenediamine were purchased from Alfa Aesar; triethylamine was purchased from Anachemia; sodium nitrite and potassium hydroxide were purchased from Caledon Laboratory Chemicals; sodium azide was purchased from J.T. Baker Chemical Co.; copper(I) iodide and were purchased from Fischer Scientific.; phenylacetylene was purchased from Lancaster; rhodium(III) chloride hydrate was purchased from Pressure Chemical Company; and diammonium hexachloroiridate(IV) was purchased from Strem. All chemicals were used without further purification, with the exception of potassium iodide, which was purified by repetitive melting under dynamic vacuum before use. *ortho*-,[67] *meta*-,[68] and *para*-

Diazidobenzene (**1a-c**)[96] have been previously reported, although all were synthesized based on the diazotization procedure.[61] 1,2-*bis*(4-Phenyl-1*H*-1,2,3-triazol-1-yl)benzene (**3c**) has previously been reported (in low yield).[64] 2-Azido-1,3-diisopropylbenzene ($DippN_3$),[61, iv] (cycloocta-1,5-diene)(μ-dichloro)dirhodium ($[Rh(\mu\text{-}Cl)(COD)]_2$),[97, 98] *bis*(cycloocta-1,5-diene)(μ-methoxido)dirhodium ($[Rh(\mu\text{-}OMe)(COD)]_2$),[95] and *bis*(cycloocta-1,5-diene)(μ-methoxido)diiridium ($[Ir(\mu\text{-}OMe)(COD)]_2$),[95] were prepared as reported previously. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a dual cold probe-equipped Varian DirectDrive 500 MHz, iNova-500, or iNova-400 spectrometer operating at 499.82, 498.12, or 399.79 MHz for ^1H; 125.68, 125.26, or 100.53 MHz for $^{13}C\{^1H\}$, respectively; or on a Varian iNova-300 operating at 299.97 MHz for ^1H. The ^1H and $^{13}C\{^1H\}$ chemical shifts are referenced to TMS, $^{19}F\{^1H\}$ chemical shifts are referenced to $CFCl_3$, and $^{31}P\{^1H\}$ chemical shifts are referenced to 85% H_3PO_4 in H_2O. The order of appearance of chemical shift assignments are based on their region in the molecule rather than increasing or decreasing frequency of their resonance. Elemental Analyses were performed by the microanalytical service within this department. Likewise, mass spectrometric analyses were performed by the departmental Mass Spectrometry Laboratory using positive ion electrospray ionization on an Agilent Technologies 6220 Accurate-mass TOF LC/MS. At the time of defense, satisfactory elemental and high-resolution mass spectrometry analyses for a few complexes were not yet obtained. Efforts are ongoing, however.

[iv] Organic azides are potentially-explosive substances that can and will decompose with the slightest input of energy from external sources (heat, light, or pressure). Extremely high safety precautions should be exercised (*i.e.*, proper lab protection, blast shields, etc.) to prevent serious injury.

5.4.2 Preparation of compounds

(i) Attempted synthesis of 1,2-*bis*(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzene (3a). A 20 mL portion of MeOH:H_2O (50:50) was added to a flask containing **1a** (0.416 g, 2.60 mmol) and phenylacetylene (0.61 mL, 5.6 mmol). The resulting solution was stirred for 5 min then CuI (0.046 g, 0.24 mmol, 9.2 mol%) and NEt_3 (0.36 mL, 2.61 mmol) were quickly added, at which point the solution turned a dark green colour, and was stirred at room temperature overnight. The solution was filtered and the product was extracted with chloroform. The solution was dried with $MgSO_4$, decanted, and the solvent removed under reduced pressure, followed by washing of the crude with 5 × 20 mL portions of *n*-pentane before drying *in vacuo*, giving 0.614 g of a dark yellow powder (90%). ^{1}H NMR (299.97 MHz, chloroform-*d*, 27.5 °C): 8.01 (s, 1H, H_{Trz}); 7.84 (m, 2H), 7.60-7.41 (m, 7H, Ar). IR (solution, cm^{-1}): 2111 (N_3, asymm.), which indicated product was the intermediate species **2a** and not the targeted complex. Attempts to convert **2a** to **3a** did not succeed, so this work was not pursued further.

(ii) Attempted synthesis of 1,3-*bis*(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzene (3b). The monotriazole product was prepared as described for 3a, using 1b (0.435 g, 2.72 mmol), phenylacetylene (0.98 mL, 5.72 mmol), CuI (0.050 g, 0.26 mmol, 9.5 mol%), and NEt_3 (0.39 mL, 2.8 mmol). The solution changed from yellow to dark green instantly, and was stirred overnight. The crude product was purified as described for **3a**, and isolated as a dark yellow powder (0.621 g, 67%). ^{1}H NMR (299.97 MHz, chloroform-*d*, 27.5 °C): 8.11 (s, 1H, H_{Trz}); 7.76 (m, 3H), 7.50-7.31 (m, 5H), 7.01 (m, 1H, Ar). IR (solution, cm^{-1}): 2107 (N_3, asymm.), which

indicated product was the intermediate species **2b** and not the targeted complex. Attempts to convert **2b** to **3b** did not succeed, so this work was not pursued further.

(iii) Attempted synthesis of 1,4-*bis*(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzene (3c). The monotriazole product was prepared as described for 3a, using 1b (0.950 g, 5.93 mmol), phenylacetylene (1.252 g, 12.25 mmol), CuI (0.548 g, 2.88 mmol, 49 mol%), and NEt_3 (1.254 g, 12.39 mmol). The solution changed from yellow to dark green instantly, and was stirred overnight. The crude product was purified as described for **3a**, and isolated as a bright yellow powder (1.477 g, 95%). ^{1}H NMR (299.97 MHz, chloroform-*d*, 27.5 °C): 8.21 (s, 1H, H_{Trz}); 7.94 (m, 2H), 7.84 (m, 2H), 7.57-7.41 (m, 3H), 7.31-7.23 (m, 2H, Ar). IR (solution, cm^{-1}): 2111 (N_3, asymm.) which indicated product was the intermediate species **2c** and not the targeted complex. Attempts to convert **2c** to **3c** did not succeed, so this work was not pursued further.

(iv) 1,3-*bis*(1-(2,6-Diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)benzene (5). The ditriazole product was prepared as described for 3a, using $DippN_3$ **(20.961 g, 103.11 mmol), 4 (5.215 g, 41.34 mmol), CuI (3.202 g, 16.81 mmol, 20 mol%), and NEt_3 (4.192 g, 41.43 mmol)**. The solution changed from yellow to dark green instantly, and was stirred for 1 h. The crude product was purified as described for **3a**, and recrystallized from dcm and pentane as a light beige powder (17.383 g, 79%). ^{1}H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 8.43 (s, 2H, H_{Trz}); 8.60 (td, 1H, $^4J_{H\text{-}H}$ = 1.8 Hz, $^5J_{H\text{-}H}$ = 0.4 Hz), 8.01 (dd, 2H, $^3J_{H\text{-}H}$ = 7.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz), 7.64 (td, 1H, $^3J_{H\text{-}H}$ = 7.8 Hz, $^5J_{H\text{-}H}$ = 0.5 Hz, Ar_{link}); 7.61 (t, 2H, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.44 (d, 4H, $^3J_{H\text{-}H}$ = 7.9 Hz, Ar_{Dipp}); 2.34 (qq, 4H, $^3J_{H\text{-}H}$ = 6.9 Hz, $^i Pr_{C\text{–}H}$); 1.19 (d, 12H, $^3J_{H\text{-}H}$ = 6.9 Hz), 1.16 (d, 12H, $^3J_{H\text{-}H}$ = 6.9 Hz, $^i Pr_{Me}$). $^{13}C\{^1H\}$ NMR (125.69 MHz, acetonitrile-d_3, 27.7

°C): 146.8 (s, 2C, Trz_{quat}); 124.1 (s, 2C, $Trz_{C–H}$); 146.1 (s, 4C, Ar_{quat}–^{i}Pr); 133.3 (s, 2C, Ar_{quat}–N); 124.0 (s, 4C), 131.1 (s, 2C, $Ar_{C–H}$); 131.6 (s, 2C, $^{link}Ar_{quat}$); 129.7 (s, 1C), 125.3 (s, 2C,$^{linker}Ar_{C–H}$); 122.7 (s, 1C, $^{link}Ar_{quat}$–$^{link}Ar_{C–H}$–$^{link}Ar_{quat}$); 28.4 (s, 4C, $^{i}Pr_{C–H}$); 23.4 (s, 4C), 23.1 (s, 4C, $^{i}Pr_{Me}$).

(v) 4,4′-(1,3-Phenylene)*bis*(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium) trifluoromethanesulfonate, [^{Dipp}Trz(H)Trz(H)][OTf]$_2$ (6). A 40 mL portion of dcm was added to a flask containing **5** (0.711 g, 1.33 mmol). The resulting solution was stirred for 10 min, cooled to –78 °C, then MeOTf (0.4 mL, 3.64 mmol) was quickly injected, resulting in a cloudy discharge above the solution. The solution was allowed to warm to room temperature, then stirred overnight, yielding a slightly darker beige solution (will be *dark* red if impure **5** is used). The solvent was then removed under reduced pressure and the crude product was washed with 5 × 20 mL portions of *n*-pentane before drying *in vacuo*, and was recrystallized from dcm and Et_2O (product will appear oily at first, but if left to stir for 1h, will form white slurry) as a *very* fine white powder (0.837 g, 73%). ^{1}H NMR (399.79 MHz, acetonitrile-d_3, 26.5 °C): 8.90 (s, 2H, H_{Trz}); 8.19 (td, 1H, $^{4}J_{H-H}$ = 1.8 Hz, $^{5}J_{H-H}$ = 0.7 Hz), 8.12 (dd, 2H, $^{3}J_{H-H}$ = 7.8 Hz, $^{4}J_{H-H}$ = 1.8 Hz), 8.03 (td, 1H, $^{3}J_{H-H}$ = 7.8 Hz, $^{5}J_{H-H}$ = 0.7 Hz, Ar_{link}); 7.77 (t, 2H, $^{3}J_{H-H}$ = 7.8 Hz), 7.56 (d, 4H, $^{3}J_{H-H}$ = 7.8 Hz, Ar_{Dipp}); 4.45 (s, 6H, N–CH_3); 2.50 (qq, 4H, $^{3}J_{H-H}$ = 6.8 Hz, $^{i}Pr_{C–H}$); 1.27 (d, 12H, $^{3}J_{H-H}$ = 6.8 Hz), 1.24 (d, 12H, $^{3}J_{H-H}$ = 6.8 Hz, $^{i}Pr_{Me}$). ^{13}C{^{1}H} NMR (125.69 MHz, acetonitrile-d_3, 27.7 °C): 142.8 (s, 2C, Trz_{quat}); 131.7 (s, 2C, $Trz_{C–H}$); 145.7 (s, 4C, Ar_{quat}–^{i}Pr); 130.8 (s, 2C, Ar_{quat}–N); 133.2 (s, 2C), 124.9 (s, 4C, $Ar_{C–H}$); 123.6 (s, 2C, $^{link}Ar_{quat}$); 131.1 (s, 1C), 133.2 (s, 2C,$^{linker}Ar_{C–H}$); 130.8 (s, 1C, $^{link}Ar_{quat}$–$^{link}Ar_{C–H}$–$^{link}Ar_{quat}$); 121.1 (q, 2C, $^{3}J_{C-F}$ = 319.9 Hz, OTf); 39.5 (s, 2C, N–CH_3), 28.4 (s, 4C, $^{i}Pr_{C–}$

$_H$); 23.6 (s, 4C), 22.9 (s, 4C, $^iPr_{Me}$). $^{19}F\{^1H\}$ NMR (376.15 MHz, acetonitrile-d_3, 26.1 °C): –79.3 (s, 2F, OTf). HRMS *m*/*z* Calcd for $C_{38}H_{46}N_6O_3S$ (M^+ – OTf^-): 711.3299. Found: 711.3293 (M^+ – OTf^-); *m*/*z* Calcd for $C_{38}H_{46}N_6$ (M^{2+} – 2 OTf^-): 281.1886. Found: 281.1889 (M^+ – 2 OTf^-). Anal Calcd for $C_{38}H_{46}F_6N_6O_6S_2$: C, 53.01; H, 5.39; N, 9.76. Found: C, 52.90; H, 5.47; N, 9.53.

(vi) Attempted synthesis of [mono((1-(2,6-diisopropylphenyl)-4-(3-(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-4-yl)phenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-5-yl)triiodopalladium(II)], [PdI_3(^{Dipp}Trz-κ^1-Trz(H))]. A 1 mL portion of acetonitrile was added to a solid mixture containing **6** (0.045 g, 0.05 mmol), [$Pd(OAc)_2$] (0.013 g, 0.06 mmol), and KI (0.093 g, 0.56 mmol). The resulting solution was stirred for 24 h at 100 °C in a sealed contained and cooled to room temperature. An aliquot was removed and the solution was confirmed to contain only starting material by spectroscopic methods. Heating to 120 °C resulted in only decomposition as observed by ^1H NMR spectroscopy.

(vii) Attempted synthesis of *trans*-[mono((1-(2,6-diisopropylphenyl)-4-(3-(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-4-yl)phenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-5-yl)acetonitriledichloropalladium(II)], *trans*-[$PdCl_2$(κ^1*N*-CH_3CN)(^{Dipp}Trz-κ^1-Trz(H))]. A 1 mL portion of thf was added to a solid mixture containing **6** (0.039 g, 0.05 mmol) and K[$N(SiMe_3)_2$] (0.011 g, 0.06 mmol). The solution was allowed to stir for 10 min and turned yellow. Spectral analysis by ^1H NMR spectrum confirmed only one end of the dication was deprotonated. A 1 mL thf solution of *trans*-[$PdCl_2(CH_3CN)_2$] was added *via* cannula, and the solution turned darker yellow. The resulting solution was stirred for 24 h at room temperature. An aliquot was removed and the solution was confirmed to

contain a mixture of uncharacterized products, including peaks representative of the dicationic starting material.

(viii) [Mono((1-(2,6-diisopropylphenyl)-4-(3-(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-4-yl)phenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-5-yl)(η^2:η^2-cycloocta-1,5-diene)iodorhodium(I)] iodide, [RhI(COD)(^{Dipp}Trz-κ^1-Trz(H))][I] (7). A 10 mL portion of acetonitrile was added to a solid mixture containing **6** (0.114 g, 0.132 mmol), $[Rh(\mu\text{-OMe})(COD)]_2$ (0.042 g, 0.086 mmol), and KI (0.105 g, 0.634 mmol). The resulting solution was stirred for 1 h at 80 °C in a sealed contained and cooled to room temperature. The solvent was then removed under reduced pressure and the crude product redissolved in 3 mL of acetonitrrile and filtered through Celite. A 45 mL portion of diethyl ether was added to precipitate a yellow solid and the mother liquor was removed *via* cannula. The precipitate was washed with 5 × 20 mL portions of *n*-pentane before drying *in vacuo*, giving 0.112 g (85%). ^{1}H NMR (399.80 MHz, acetonitrile-d_3, 26.5 °C): 9.06 (s, 1H, H_{Trz}); 8.56 (br dd, 1H, $^4J_{H\text{-}H}$ = 1.6 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz), 8.42 (ddd, 1H, $^3J_{H\text{-}H}$ = 7.7 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz), 8.01 (ddd, 1H, $^3J_{H\text{-}H}$ = 7.7 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz), 7.95 (dd, 1H, $^3J_{H\text{-}H}$ = 7.7 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz, Ar_{link}); 7.63 (t, 1H, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.45 (d, 2H, $^3J_{H\text{-}H}$ = 7.9 Hz, $Ar_{Dipp(Rh)}$); 7.74 (t, 1H, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.54 (d, 2H, $^3J_{H\text{-}H}$ = 7.9 Hz, $Ar_{Dipp(H+)}$); 4.18 (s, 3H, N–$CH_{3(Rh)}$); 4.54 (s, 3H, N–$CH_{3(H+)}$); 2.54 (qq, 2H, $^3J_{H\text{-}H}$ = 6.9 Hz), 2.52 (qq, 2H, $^3J_{H\text{-}H}$ = 6.9 Hz, ^{i}Pr$_{C\text{–}H}$); 1.21 (d, 12H, $^3J_{H\text{-}H}$ = 6.9 Hz, ^{i}Pr$_{Me(Rh)}$); 1.27 (d, 12H, $^3J_{H\text{-}H}$ = 6.9 Hz, ^{i}Pr$_{Me(H+)}$); 4.73 (br s, 2H, $COD_{C\text{–}H(\textit{trans})}$); 3.48 (br s, 2H, $COD_{C\text{–}H(\textit{cis})}$); 2.01-1.97 (m, 8H, COD_{alk}). ^{13}C{^{1}H} NMR (100.54 MHz, acetonitrile-d_3, 26.5 °C): 171.0 (d, 1C, $^1J_{C\text{-}Rh}$ = 46.1 Hz, $C_{carbene}$); 144.5 (s, 1C, $Trz_{quat(Rh)}$); 143.7 (s, 1C, $Trz_{quat(H+)}$); 131.3 (s, 1C, $Trz_{C\text{–}H}$); 146.3 (s, 2C, Ar_{quat}–^{i}Pr$_{(Rh)}$);

145.7 (s, 2C, Ar_{quat}–$^{i}Pr_{(H+)}$); 135.9 (s, 1C, Ar_{quat}–N_{Rh}); 124.0 (br s, 1C, Ar_{quat}–N_{H+}); 130.7 (s, 1C), 124.0 (s, 2C, $Ar_{C–H(Rh)}$); 133.1 (s, 1C), 124.9 (s, 2C, $Ar_{C–H(H+)}$); 131.1 (s, 1C), 130.8 (s, 1C, $^{link}Ar_{quat}$); 134.4 (s, 1C), 129.2 (s, 1C), 131.0 (s, 1C, $^{linker}Ar_{C–H}$); 132.2 (s, 1C, $^{link}Ar_{quat}$–$^{link}Ar_{C–H}$–$^{link}Ar_{quat}$); 37.9 (s, 1C, N–$CH_{3(Rh)}$); 40.3 (s, 1C, N–$CH_{3(H+)}$); 28.6 (s, 2C), 28.4 (s, 2C, $^{i}Pr_{C–H}$); 23.9 (s, 4C), 23.1 (s, 4C, $^{i}Pr_{CH3}$); 92.8 (br s, 2C, COD_{trans}); 71.7 (br s, 2C, COD_{cis}); 32.0 (br s, 1C), 29.8 (br s, 1C), 25.7 (br s, 1C), 22.7 (br s, 1C, COD_{CH2}). HRMS *m/z* Calcd for $C_{44}H_{57}IN_6Rh$ ($M^+ – I^-$): 899.2739. Found: 899.2739 ($M^+ – I^-$); Anal Calcd for $C_{44}H_{57}I_2N_6Rh$: C, 51.47; H, 5.60; N, 8.19. Found: C, 51.32; H, 5.51; N, 8.11.

(ix) [Mono((1-(2,6-diisopropylphenyl)-4-(3-(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-4-yl)phenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-5-yl)(η²:η²-cycloocta-1,5-diene)iodoiridium(I)] iodide, [IrI(COD)(^{Dipp}Trz-κ¹-Trz(H))][I] (8). The desired product was prepared as described for 7, using 6 (0.115 g, 0.134 mmol), $[Ir(\mu\text{-}OMe)(COD)]_2$ (0.056 g, 0.084 mmol), and KI (0.122 g, 0.734 mmol). The solution was heated at 80 °C in a sealed contained for 2 h and cooled to room temperature, and changed from yellow to orange. The crude product was purified as described for **7**, and isolated as an orange powder (0.121 g, 90%). ^{1}H NMR (399.80 MHz, acetonitrile-d_3, 26.5 °C): 8.99 (s, 1H, H_{Trz}); 8.61 (dd, 1H, $^4J_{H-H}$ = 1.5 Hz, $^4J_{H-H}$ = 1.5 Hz), 8.19 (ddd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.5 Hz, $^4J_{H-H}$ = 1.5 Hz), 7.96 (ddd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.5 Hz, $^4J_{H-H}$ = 1.5 Hz), 7.81 (dd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^3J_{H-H}$ = 7.6 Hz, Ar_{link}); 7.63 (t, 1H, $^3J_{H-H}$ = 8.0 Hz), 7.45 (d, 2H, $^3J_{H-H}$ = 8.0 Hz, $Ar_{Dipp(Ir)}$); 7.55 (t, 1H, $^3J_{H-H}$ = 8.0 Hz), 7.37 (d, 2H, $^3J_{H-H}$ = 8.0 Hz, $Ar_{Dipp(H+)}$); 4.16 (s, 3H, N–$CH_{3(Ir)}$); 4.61 (s, 3H, N–$CH_{3(H+)}$); 2.47 (qq, 4H, $^3J_{H-H}$ = 6.9 Hz, $^{i}Pr_{C–H}$); 1.22 (d, 12H, $^3J_{H-H}$ = 6.9 Hz, $^{i}Pr_{Me(Ir)}$); 1.29 (d, 12H, $^3J_{H-H}$ = 6.9 Hz,

$^{i}Pr_{Me(H+)}$); 4.20 (br s, 2H, $COD_{C–H(\textit{trans})}$); 3.24 (br s, 2H, $COD_{C–H(\textit{cis})}$); 1.99-0.97 (m, 8H, COD_{alk}). $^{13}C\{^{1}H\}$ NMR (100.54 MHz, acetonitrile-d_3, 26.5 °C): 161.2 (s, 1C, $C_{carbene}$); 143.4 (s, 1C, $Trz_{quat(Ir)}$); 143.5 (s, 1C, $Trz_{quat(H+)}$); 130.9 (s, 1C, $Trz_{C–H}$); 146.2 (s, 2C, Ar_{quat}–$^{i}Pr_{(Ir)}$); 145.1 (s, 2C, Ar_{quat}–$^{i}Pr_{(H+)}$); 135.8 (s, 1C, Ar_{quat}–N_{Ir}); 124.1 (br s, 1C, Ar_{quat}–N_{H+}); 131.0 (s, 1C), 124.6 (s, 2C, $Ar_{C–H(Ir)}$); 133.2 (s, 1C), 125.2 (s, 2C, $Ar_{C–H(H+)}$); 130.8 (s, 1C), 130.7 (s, 1C, $^{link}Ar_{quat}$); 134.1 (s, 1C), 129.8 (s, 1C), 131.2 (s, 1C, $^{linker}Ar_{C–H}$); 132.2 (s, 1C, $^{link}Ar_{quat}$–$^{\textit{link}}\textit{Ar}_{\textit{C–H}}$–$^{link}Ar_{quat}$); 37.6 (s, 1C, N–$CH_{3(Ir)}$); 40.2 (s, 1C, N–$CH_{3(H+)}$); 28.3 (s, 2C), 28.1 (s, 2C, $^{i}Pr_{C–H}$); 23.8 (s, 4C), 23.1 (s, 4C, $^{i}Pr_{CH3}$); 80.2 (s, 2C, $COD_{\textit{trans}}$); 52.5 (s, 2C, $COD_{\textit{cis}}$); 28.1 (s, 1C), 27.2 (s, 1C), 25.2 (s, 1C), 21.7 (s, 1C, COD_{CH2}). HRMS *m*/*z* Calcd for $C_{44}H_{57}IIrN_6$ ($M^+ – I^-$): 989.3313. Found: 989.3310 ($M^+ – I^-$); Anal Calcd for $C_{44}H_{57}I_2N_6Ir$: C, 47.35; H, 5.15; N, 7.53. Found: C, 47.55; H, 5.32; N, 7.24.

(x) [Mono((1-(2,6-diisopropylphenyl)-4-(3-(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-4-yl)phenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-5-yl)dicarbonyliodorhodium(I)] iodide, [RhI(CO)$_2$(^{Dipp}Trz-κ^1-Trz(H))][I] (9). A 10 mL portion of acetonitrile was added to a flask containing **7** (0.312 g, 0.30 mmol). A 15 min gentle purge of CO to a stirring solution yielded a more pale yellow solution. The conversion to the respective dicarbonyl complex **9** was accompanied by the facile loss of 1,5-cyclooctadiene and was monitored to completion using ^{1}H NMR spectroscopy. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of dcm. A 30 mL portion of diethyl ether was added to precipitate a yellow solid, which was washed with 5 × 25 mL portions of *n*-pentane before drying *in vacuo*, giving 0.285 g (95%), although all samples contained a considerable amount of an unknown more-symmetric product (omitted here in

spectral data). ^{1}H NMR (499.82 MHz, acetonitrile-d_3, 27.7 °C): 8.87 (s, 1H, H_{Trz}); 8.35 (br dd, 1H, $^{4}J_{H\text{-}H}$ = 1.4 Hz, $^{4}J_{H\text{-}H}$ = 1.4 Hz), 8.13 (ddd, 1H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{4}J_{H\text{-}H}$ = 1.4 Hz, $^{4}J_{H\text{-}H}$ = 1.4 Hz), 7.98 (ddd, 1H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{4}J_{H\text{-}H}$ = 1.4 Hz, $^{4}J_{H\text{-}H}$ = 1.4 Hz), 7.89 (dd, 1H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{3}J_{H\text{-}H}$ = 7.5 Hz, Ar_{link}); 7.72 (t, 1H, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 7.43 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, $Ar_{Dipp(Rh)}$); 7.63 (t, 1H, $^{3}J_{H\text{-}H}$ = 7.9 Hz), 7.52 (d, 2H, $^{3}J_{H\text{-}H}$ = 7.9 Hz, $Ar_{Dipp(H+)}$); 4.21 (s, 3H, N–$CH_{3(Rh)}$); 4.52 (s, 3H, N–$CH_{3(H+)}$); 2.52 (qq, 4H, $^{3}J_{H\text{-}H}$ = 6.9 Hz); 1.23 (d, 12H, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{i}Pr_{Me(Rh)}$); 1.19 (d, 12H, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{i}Pr_{Me(H+)}$). $^{13}C\{^{1}H\}$ NMR (100.54 MHz, acetonitrile-d_3, 26.5 °C): 162.3 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 40.1 Hz, $C_{carbene}$); 187.6 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 53.4 Hz, $CO_{\textit{trans}}$); 182.1 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 77.6 Hz, $CO_{\textit{cis}}$); 143.5 (s, 1C, $Trz_{quat(Rh)}$); 143.2 (s, 1C, $Trz_{quat(H+)}$); 133.5 (s, 1C, $Trz_{C–H}$); 147.2 (s, 2C, Ar_{quat}–$^{i}Pr_{(Rh)}$); 145.6 (s, 2C, Ar_{quat}–$^{i}Pr_{(H+)}$); 135.2 (s, 1C, Ar_{quat}–N_{Rh}); 124.1 (s, 1C, Ar_{quat}–N_{H+}); 130.5 (s, 1C), 124.1 (s, 2C, $Ar_{C–H(Rh)}$); 133.5 (s, 1C), 125.3 (s, 2C, $Ar_{C–H(H+)}$); 130.7 (s, 1C), 131.5 (s, 1C, $^{link}Ar_{quat}$); 132.1 (s, 1C), 129.3 (s, 1C), 131.2 (s, 1C, $^{linker}Ar_{C–H}$); 132.1 (s, 1C, $^{link}Ar_{quat}$–$^{\textit{link}}\textit{Ar}_{\textit{C–H}}$–$^{link}Ar_{quat}$); 39.9 (s, 1C, N–$CH_{3(Rh)}$); 41.3 (s, 1C, N–$CH_{3(H+)}$); 28.5 (s, 2C), 28.2 (s, 2C, $^{i}Pr_{C–H}$); 23.8 (s, 4C), 23.1 (s, 4C, $^{i}Pr_{CH3}$). HRMS *m/z* Calcd for $C_{38}H_{45}IN_6O_2Rh$ ($M^+ - I^-$): 847.1698. Found: 847.1689 ($M^+ - I^-$).

(xi) [Mono((1-(2,6-diisopropylphenyl)-4-(3-(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-4-yl)phenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-5-yl)dicarbonyliodoiridium(I)] iodide, [IrI(CO)$_2$(^{Dipp}Trz-κ^1-Trz(H))][I] (10). The desired product was prepared as described for 9, using 7 (0.312 g, 0.30 mmol). The solution turned a pale yellow colour after 15 min of a CO purge. The crude product was purified as described for **9**, and isolated as a yellow powder 0.285 g (95%), although all samples contained a considerable amount of an unknown

more-symmetric product (omitted here in spectral data). ^{1}H NMR (399.80 MHz, acetonitrile-d_3, 26.5 °C): 8.78 (s, 1H, H_{Trz}); 8.71 (dd, 1H, $^{4}J_{H\text{-}H}$ = 1.3 Hz, $^{4}J_{H\text{-}H}$ = 1.3 Hz), 8.13 (ddd, 1H, $^{3}J_{H\text{-}H}$ = 7.7 Hz, $^{4}J_{H\text{-}H}$ = 1.3 Hz, $^{4}J_{H\text{-}H}$ = 1.3 Hz), 7.92 (ddd, 1H, $^{3}J_{H\text{-}H}$ = 7.7 Hz, $^{4}J_{H\text{-}H}$ = 1.3 Hz, $^{4}J_{H\text{-}H}$ = 1.3 Hz), 7.81 (dd, 1H, $^{3}J_{H\text{-}H}$ = 7.7 Hz, $^{3}J_{H\text{-}H}$ = 7.7 Hz, Ar_{link}); 7.55 (t, 1H, $^{3}J_{H\text{-}H}$ = 7.8 Hz), 7.45 (d, 2H, $^{3}J_{H\text{-}H}$ = 7.8 Hz, $Ar_{Dipp(Ir)}$); 7.50 (t, 1H, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 7.35 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, $Ar_{Dipp(H+)}$); 4.11 (s, 3H, N–$CH_{3(Ir)}$); 4.65 (s, 3H, N–$CH_{3(H+)}$); 2.47 (qq, 4H, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{i}Pr_{C\text{–}H}$); 1.21 (d, 12H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $^{i}Pr_{Me(Ir)}$); 1.26 (d, 12H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $^{i}Pr_{Me(H+)}$). At the time of defense, satisfactory $^{13}C\{^{1}H\}$ NMR assignment was not yet complete. Efforts are ongoing, however.

(xii) [4,4′-(1,3-Phenylene)*bis*(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-5-yl)(η^2:η^2-cycloocta-1,5-diene)iodorhodium(I)], [RhI(COD)]$_2$(μ-^{Dipp}Trz$_2$) (11). The desired product was prepared as described for 7, using 6[v] (0.432 g, 0.502 mmol), at least *one full equivalent* of [Rh(μ-OMe)(COD)]$_2$ (0.503 g, 1.04 mmol), and KI (0.502 g, 3.02 mmol). The solution was heated at 80 °C in a sealed contained for 2 h and cooled to room temperature, at which point it turned a darker yellow colour. The crude product was purified as described for **7**, and isolated as an orange powder (0.515 g, 83%). ^{1}H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 8.51 (t, 1H, $^{4}J_{H\text{-}H}$ = 1.5 Hz, $^{4}J_{H\text{-}H}$ = 1.5 Hz), 8.42 (dd, 2H, $^{3}J_{H\text{-}H}$ = 7.6 Hz, $^{4}J_{H\text{-}H}$ = 1.5 Hz), 7.90 (t, 1H, $^{3}J_{H\text{-}H}$ = 7.6 Hz, Ar_{link}); 7.61 (t, 2H, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 7.50 (d, 4H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, $Ar_{Dipp(Rh)}$); 4.24 (s, 6H, N–$CH_{3(Rh)}$); 2.52 (qq, 4H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $^{i}Pr_{C\text{–}H}$); 1.21 (d, 12H, $^{3}J_{H\text{-}H}$ = 7.0 Hz), 1.26 (d, 12H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $^{i}Pr_{Me(Rh)}$); 4.70 (br s, 4H, $COD_{C\text{–}}$

[v] Compound **11** can also be prepared (as outlined in the body of the text) from the pendent species **7** using one half an equivalent of [Rh(μ-OMe)(COD)]$_2$ under the same conditions.

$_{H(trans)}$); 3.47 (br s, 4H, $COD_{C–H(cis)}$); 2.10-1.95 (m, 16H, COD_{alk}). $^{13}C\{^1H\}$ NMR (100.54 MHz, acetonitrile-d_3, 26.5 °C): 170.7 (d, 2C, $^1J_{C\text{-}Rh}$ = 46.5 Hz, $C_{carbene}$); 144.7 (s, 2C, $Trz_{quat(Rh)}$); 147.0 (s, 4C, Ar_{quat}–$^i Pr_{(Rh)}$); 135.1 (s, 2C, Ar_{quat}–N_{Rh}); 130.5 (s, 2C), 124.2 (s, 4C, $Ar_{C–H(Rh)}$); 131.0 (s, 2C), $^{link}Ar_{quat}$); 134.6 (s, 2C), 131.2 (s, 1C, $^{linker}Ar_{C–H}$); 132.4 (s, 1C, $^{link}Ar_{quat}$–$^{link}Ar_{C–H}$–$^{link}Ar_{quat}$); 37.9 (s, 2C, N–$CH_{3(Rh)}$); 28.5 (s, 4C, $^i Pr_{C–H}$); 23.6 (s, 4C), 23.2 (s, 4C, $^i Pr_{CH3}$); 92.6 (br s, 4C, COD_{trans}); 71.2 (br s, 4C, COD_{cis}); 32.2 (br s, 2C), 29.6 (br s, 2C), 25.6 (br s, 2C), 22.1 (br s, 2C, COD_{CH2}). Anal Calcd for $C_{52}H_{68}I_2N_6Rh_2$: C, 50.50; H, 5.54; N, 6.80. Found: C, 50.32; H, 5.14; N, 6.62.

(xiii) [4,4′-(1,3-Phenylene)*bis*(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-5-yl)(η²:η²-cycloocta-1,5-diene)iodoiridium(I)], [IrI(COD)]$_2$(μ-^{Dipp}Trz$_2$) (12). The desired product was prepared as described for 8, using 6[vi] (0.543 g, 0.631 mmol), at least *one full equivalent* of [Ir(μ-OMe)(COD)]$_2$ (0.452 g, 0.682 mmol), and KI (0.501 g, 3.01 mmol). The solution was heated at 80 °C in a sealed contained for 2 h and cooled to room temperature, at which point it turned a dark orange colour. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of acetonitrile. A 30 mL portion of diethyl ether was added to precipitate a yellow solid, which was washed with 5 × 25 mL portions of *n*-pentane before drying *in vacuo*, giving 0.480 g (76%). ^1H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 8.01 (t, 1H, $^4J_{H\text{-}H}$ = 1.3 Hz, $^4J_{H\text{-}H}$ = 1.3 Hz), 7.71 (dd, 2H, $^3J_{H\text{-}H}$ = 7.7 Hz, $^4J_{H\text{-}H}$ = 1.3 Hz), 7.43 (t, 1H, $^3J_{H\text{-}H}$ = 7.7 Hz, Ar_{link}); 7.58 (t, 2H, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.31 (d, 4H, $^3J_{H\text{-}H}$ = 7.8 Hz, $Ar_{Dipp(Ir)}$); 4.19 (s, 6H, N–$CH_{3(Ir)}$); 2.35 (qq, 4H, $^3J_{H\text{-}H}$ = 7.0 Hz, $^i Pr_{C–H}$); 1.21 (d, 12H, $^3J_{H\text{-}H}$ = 7.1 Hz), 1.24 (d, 12H, $^3J_{H\text{-}H}$ = 7.1 Hz, $^i Pr_{Me(Ir)}$);

[vi] Compound **12** can also be prepared (as outlined in the body of the text) from the pendent species **8** using one half an equivalent of [Ir(μ-OMe)(COD)]$_2$ under the same conditions.

4.23 (br s, 4H, $COD_{C–H(\textit{trans})}$); 3.15 (br s, 4H, $COD_{C–H(\textit{cis})}$); 2.15-1.92 (m, 16H, COD_{alk}). $^{13}C\{^{1}H\}$ NMR (100.54 MHz, acetonitrile-d_3, 26.5 °C): 160.3 (s, 2C, $C_{carbene}$); 143.9 (s, 2C, $Trz_{quat(Ir)}$); 146.1 (s, 4C, Ar_{quat}–$^{i}Pr_{(Ir)}$); 134.9 (s, 2C, Ar_{quat}–N_{Ir}); 129.0 (s, 2C), 125.1 (s, 4C, $Ar_{C–H(Ir)}$); 130.6 (s, 2C, $^{link}Ar_{quat}$); 134.5 (s, 2C), 131.0 (s, 1C, $^{linker}Ar_{C–H}$); 132.8 (s, 1C, $^{link}Ar_{quat}$–$^{\textit{link}}\textit{Ar}_{\textit{C–H}}$–$^{link}Ar_{quat}$); 38.2 (s, 2C, N–$CH_{3(Ir)}$); 27.9 (s, 4C, $^{i}Pr_{C–H}$); 23.8 (s, 4C), 22.9 (s, 4C, $^{i}Pr_{CH3}$); 81.6 (br s, 4C, $COD_{\textit{trans}}$); 53.6 (br s, 4C, $COD_{\textit{cis}}$); 28.5 (s, 2C), 26.7 (s, 2C), 25.1 (s, 2C), 22.0 (s, 2C, COD_{CH2}). Anal Calcd for $C_{52}H_{68}I_2Ir_2N_6$: C, 44.13; H, 4.84; N, 5.94. Found: C, 44.26; H, 5.07; N, 6.32.

(xiv) [4,4′-(1,3-Phenylene)*bis*(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-5-yl)dicarbonyliodorhodium(I)], $[RhI(CO)_2]_2(\mu\text{-}^{Dipp}Trz_2)$ (13). The desired product was prepared as described for 9, using 11 (0.356 g, 0.288 mmol). The solution turned a pale yellow colour after 15 min of a CO purge. The crude product was purified as described for **9**, and isolated as a yellow powder, giving 0.253 g (88%). ^{1}H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 8.63 (t, 1H, $^{4}J_{H-H}$ = 1.2 Hz, $^{4}J_{H-H}$ = 1.2 Hz), 8.35 (dd, 2H, $^{3}J_{H-H}$ = 7.4 Hz, $^{4}J_{H-H}$ = 1.2 Hz), 7.99 (t, 1H, $^{3}J_{H-H}$ = 7.4 Hz, Ar_{link}); 7.66 (t, 2H, $^{3}J_{H-H}$ = 7.9 Hz), 7.45 (d, 4H, $^{3}J_{H-H}$ = 7.9 Hz, $Ar_{Dipp(Rh)}$); 4.35 (s, 6H, N–$CH_{3(Rh)}$); 2.50 (qq, 4H, $^{3}J_{H-H}$ = 7.0 Hz, $^{i}Pr_{C–H}$); 1.23 (d, 12H, $^{3}J_{H-H}$ = 7.0 Hz), 1.27 (d, 12H, $^{3}J_{H-H}$ = 7.0 Hz, $^{i}Pr_{Me(Rh)}$). $^{13}C\{^{1}H\}$ NMR (100.54 MHz, acetonitrile-d_3, 26.5 °C): 160.9 (d, 2C, $^{1}J_{C\text{-}Rh}$ = 40.2 Hz, $C_{carbene}$); 188.7 (d, 2C, $^{1}J_{C\text{-}Rh}$ = 53.5 Hz, $CO_{\textit{trans}}$); 182.7 (d, 2C, $^{1}J_{C\text{-}Rh}$ = 77.9 Hz, $CO_{\textit{cis}}$); 145.0 (s, 2C, $Trz_{quat(Rh)}$); 148.3 (s, 4C, Ar_{quat}–$^{i}Pr_{(Rh)}$); 135.7 (s, 2C, Ar_{quat}–N_{Rh}); 131.2 (s, 2C), 124.1 (s, 4C, $Ar_{C–H(Rh)}$); 131.5 (s, 2C), $^{link}Ar_{quat}$); 135.9 (s, 2C), 131.9 (s, 1C, $^{linker}Ar_{C–H}$); 132.7 (s, 1C, $^{link}Ar_{quat}$–$^{\textit{link}}\textit{Ar}_{\textit{C–H}}$–$^{link}Ar_{quat}$); 39.9 (s, 2C, N–$CH_{3(Rh)}$); 27.5 (s, 4C, $^{i}Pr_{C–H}$); 23.7 (s, 4C), 23.1 (s, 4C, $^{i}Pr_{CH3}$).

HRMS *m*/*z* Calcd for $C_{40}H_{44}IN_6O_4Rh_2$ ($M^+ - I^-$): 1005.0579. Found: 1005.0575 ($M^+ - I^-$).

(xv) [4,4′-(1,3-Phenylene)*bis*(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-5-yl)dicarbonyliodoiridium(I)], $[IrI(CO)_2]_2(\mu\text{-}^{Dipp}Trz_2)$ (14). The desired product was prepared as described for **9**, using **12** (0.645 g, 0.456 mmol). The solution turned a pale yellow colour after 15 min of a CO purge. The crude product was purified as described for **9**, and isolated as a yellow powder, giving 0.401 g (67%). ^{1}H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 8.21 (td, 1H, $^4J_{H\text{-}H}$ = 1.2 Hz, $^5J_{H\text{-}H}$ = 0.7 Hz), 8.01 (dd, 2H, $^3J_{H\text{-}H}$ = 7.9 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz), 7.76 (td, 1H, $^3J_{H\text{-}H}$ = 7.9 Hz, $^5J_{H\text{-}H}$ = 0.7 Hz, Ar_{link}); 7.64 (t, 2H, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.44 (d, 4H, $^3J_{H\text{-}H}$ = 7.9 Hz, $Ar_{Dipp(Ir)}$); 4.26 (s, 6H, N–$CH_{3(Ir)}$); 2.74 (qq, 4H, $^3J_{H\text{-}H}$ = 7.0 Hz, $^iPr_{C\text{–}H}$); 1.34 (d, 12H, $^3J_{H\text{-}H}$ = 7.0 Hz), 1.12 (d, 12H, $^3J_{H\text{-}H}$ = 7.0 Hz, $^iPr_{Me(Ir)}$). At the time of defense, satisfactory $^{13}C\{^1H\}$ NMR assignment was not yet complete. Efforts are ongoing, however.

(xvi) [((1-(2,6-Diisopropylphenyl)-4-(3-(1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-5-yl)((η^2:η^2-cycloocta-1,5-diene)iodoiridium(I))phenyl)-3-methyl-1*H*-1,2,3-triazol-3-ium-5-yl)(η^2:η^2-cycloocta-1,5-diene)iodo-rhodium(I)], $[IrI(COD)(\mu\text{-}^{Dipp}Trz_2)RhI(COD)]$ (15). *Route 1*: A 10 mL portion of acetonitrile was added to a solid mixture containing **7** (0.334 g, 0.325 mmol), $[Ir(\mu\text{-}OMe)(COD)]_2$ (0.118 g, 0.178 mmol), and KI (0.297 g, 1.79 mmol). The resulting solution was stirred for 2 h at 80 °C in a sealed contained and cooled to room temperature. The solvent was then removed under reduced pressure and the crude product redissolved in 3 mL of acetonitrrile and filtered through Celite. A 45 mL portion of *n*-pentane was added to precipitate an orange solid and the mother liquor

was removed *via* cannula. The precipitate was redissolved in benzene, and another 45 mL portion of *n*-pentane was added to precipitate a bright orange solid. The precipitate was washed with 5 × 20 mL portions of *n*-pentane before drying *in vacuo*, giving 0.328 g (76%). *Route 2*: The desired product was prepared as described for Route 1, using **8** (0.573 g, 0.513 mmol), $[Rh(\mu\text{-}OMe)(COD)]_2$ (0.162 g, 0.335 mmol), and KI (0.128 g, 0.771 mmol). The resulting solution was stirred for 1 h at 80 °C in a sealed contained and cooled to room temperature. The crude product was purified as described for Route 1, and isolated as a bright orange solid, giving 0.544 g (80%). ^{1}H NMR (498.12 MHz, acetonitrile-d_3, 26.1 °C): 8.50 (dd, 1H, $^{4}J_{H\text{-}H}$ = 1.3 Hz, $^{4}J_{H\text{-}H}$ = 1.3 Hz), 8.45 (ddd, 1H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{4}J_{H\text{-}H}$ = 1.3 Hz, $^{4}J_{H\text{-}H}$ = 1.3 Hz), 8.21 (ddd, 1H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{4}J_{H\text{-}H}$ = 1.3 Hz, $^{4}J_{H\text{-}H}$ = 1.3 Hz), 7.95 (dd, 1H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{3}J_{H\text{-}H}$ = 7.5 Hz, Ar_{link}); 7.60 (t, 1H, $^{3}J_{H\text{-}H}$ = 8.0 Hz), 7.65 (t, 1H, $^{3}J_{H\text{-}H}$ = 7.9 Hz), 7.41 (d, 2H, $^{3}J_{H\text{-}H}$ = 7.9 Hz), 7.45 (d, 2H, $^{3}J_{H\text{-}H}$ = 7.9 Hz, Ar_{Dipp}); 4.18 (s, 3H), 4.13 (s, 3H, N–CH_3); 2.54 (qq, 2H, $^{3}J_{H\text{-}H}$ = 6.9 Hz), 2.48 (qq, 2H, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{i}Pr_{C\text{–}H}$); 1.23 (d, 12H, $^{3}J_{H\text{-}H}$ = 6.9 Hz); 1.21 (d, 12H, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{i}Pr_{Me}$); 4.70 (br s, 2H), 4.10 (br s, 2H, $COD_{C\text{–}H(\textit{trans})}$); 3.45 (br s, 2H), 3.20 (br s, 2H, $COD_{C\text{–}H(\textit{cis})}$); 2.03-1.98 (m, 16H, COD_{alk}). $^{13}C\{^{1}H\}$ NMR (125.69 MHz, acetonitrile-d_3, 27.7 °C): 171.0 (d, 1C, $^{1}J_{C\text{-}Rh}$ = 46.7 Hz, $C_{carbene(Rh)}$); 160.6 (s, 1C, $C_{carbene(Ir)}$); 144.5 (s, 1C), 143.1, Trz_{quat}); 146.3 (s, 2C), 145.8, Ar_{quat}–^{i}Pr); 135.9 (s, 1C), 135.7 (s, 1C, Ar_{quat}–N); 131.0 (s, 1C), 130.1 (s, 1C), 124.4 (s, 2C), 124.9 (s, 2C, $Ar_{C\text{–}H}$); 131.2 (s, 1C), 130.8 (s, 1C, $^{link}Ar_{quat}$); 134.6 (s, 1C), 133.4 (s, 1C), 131.2 (s, 1C, $^{linker}Ar_{C\text{–}H}$); 132.4 (s, 1C, $^{link}Ar_{quat}$–$^{\textit{link}}\textit{Ar}_{\textit{C–H}}$–$^{link}Ar_{quat}$); 38.5 (s, 1C), 37.4 (s, 1C, N–CH_3); 28.8 (s, 2C), 28.7 (s, 2C, $^{i}Pr_{C\text{–}H}$); 23.9 (s, 4C), 23.6 (s, 4C, $^{i}Pr_{CH3}$); 91.6 (br s, 2C), 80.1 (s, 2C, $COD_{\textit{trans}}$); 71.3 (br s, 2C), 51.6 (s, 2C, $COD_{\textit{cis}}$); 32.2

(br s, 1C), 30.2 (s, 1C), 29.7 (br s, 1C), 27.2 (s, 1C), 25.6 (s, 1C), 25.4 (br s, 1C), 22.9 (br s, 1C), 20.1 (s, 1C, COD_{CH2}).

Section 5.5 References

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Chapter 6 Dicarbene-Bridged Pd/Rh Complexes as Catalysts for Multiple Tandem Reactions

Section 6.1 Introduction

6.1.1 Transition metals and NHCs in catalysis

As mentioned in Chapter 1, Section 1.4.1, a number of organometallic complexes find use as catalysts lowering a chemical reaction's energy barrier by introducing a new reaction pathway (Figure 6-1a). These catalysts are (in principle) not used up (Figure 6-1b),[1] being regenerated in a subsequent step of the process, allowing them to be used to perform *numerous* transformations, limiting the amount of actual catalyst required. Transition metals find extensive use as catalysts in organic synthesis (Suzuki-Miyaura cross-coupling,[2] hydroformylation,[3] and olefin metathesis,[4] for example) as well as in industry (Monsanto,[5] Cativa,[6] and Wacker processes,[7, 8] etc.).

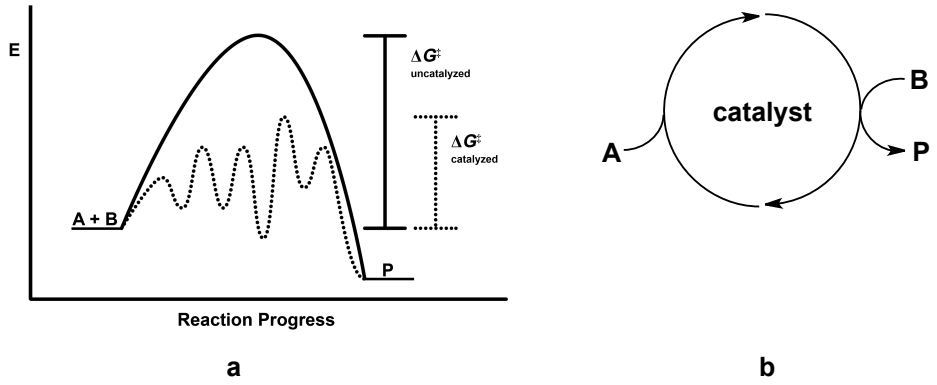
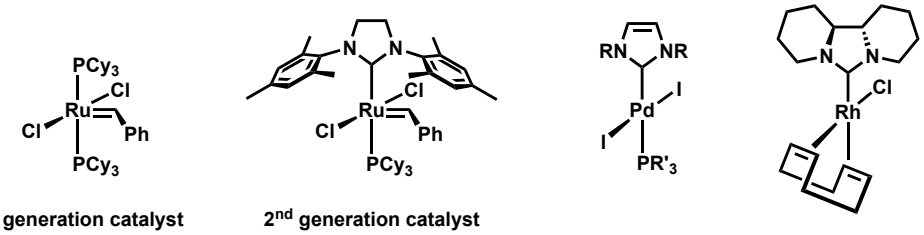


Figure 6-1. Generic energy diagram for catalyzed and uncatalyzed processes (**a**) and catalytic regeneration cycle (**b**).

In homogeneous catalysis, it is well known that the nature of ancillary ligands can have a major influence on the catalytic activity and, as mentioned throughout this thesis, NHCs have emerged as useful ligands in catalysis owing to their metal-

binding strength (compared to phosphines), and the interesting steric restrictions they can impose on the reactive catalytic centre.[9-25] Many catalysts have shown dramatic improvements in activity upon switching a common phosphine for a carbene, the most famous example being that of Grubbs, wherein substitution of a tricyclohexylphosphine (PCy_3, Figure 6-2a) for a saturated NHC in his olefin metathesis complex (Figure 6-1b) resulted in a much more active[i] and robust catalyst,[32] which is now commercially available.[33] Several others have also noted improvements in the activity in their systems when various carbenes are incorporated into the catalyst's design, such as in Pd-mediated C–C couplings (Figure 6-1c)[34] and Rh-catalyzed hydrogenation (Figure 6-1d) processes,[35] although these improvements are not just limited to NHC-type carbenes.[25, 36-50]



1st generation catalyst
5 mol % required
$t_{1/2}$ (55 °C) = 40 min
sensitive to O_2/H_2O

2nd generation catalyst
0.05 mol % required
$t_{1/2}$ (55 °C) = 6 h
stable in O_2/H_2O

a **b** **c** **d**

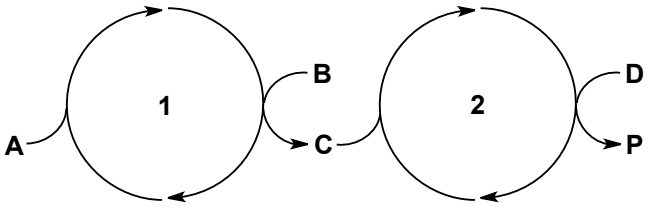
Figure 6-2. Catalysts for olefin metathesis (**a**,**b**) C–C coupling (**c**) and transfer hydrogenation (**d**).

6.1.2 Tandem catalysis

In catalysis, when the desired product requires more than one catalytic transformation, an intermediate product is usually worked up and isolated, in order

[i] Although the higher activity of Grubbs's 2nd generation catalyst (compared to the 1st) had initially been attributed an increased ability to promote phosphine dissociation (because of a higher *trans*-effect),[26-29] it has since been proven that the rate of this dissociative process is in fact *slower* with this NHC analogue.[30] The 2nd generation catalyst's higher activity is instead due to its improved selectivity for binding π-acidic olefinic substrates, and (due to an increased $\%V_{Bur}$) allows for pre-organization of the alkylidene fragment into the active conformation, allowing for efficient cyclometallation in the metathesis process.[31]

to remove the "dead" catalyst and other materials in order to prevent their interference with the second transformation. Due to the increasing demand for environmentally-benign and economical synthetic processes,[51, 52] there has been recent interest in the development of *multiple* catalytic transformations on a single bifunctionalized substrate *without* isolating the intermediate product. Among these multiple catalytic processes, those defined as "tandem" refer to coupled catalyses in which the sequential transformations of the substrate occurs *via* two (or more) mechanistically distinct processes.[52, 53] In Nature, biosynthetic systems provide many examples of tandem catalysis such as multienzymatic processes like photosynthesis.[54-57] Also known as "domino" or "cascade" processes,[ii] tandem catalysis allows reactions to be carried out in a single reaction vessel, simplifying reaction workup. Furthermore, intermediates do not need to be stable enough for isolation if they are quickly transformed by a subsequent reaction into the product. A generic scheme for the in-sequence transformation of substrate A into product P *via* two different catalytic processes is shown in Scheme 6-1.



Scheme 6-1. Generic scheme for tandem catalysis using two catalytic centres.

Tandem catalytic systems can be categorized into two groups: (1) those containing a single catalyst which performs both mechanistically-distinct reactions of the tandem process or (2) those using multiple catalysts which are added to the

[ii] By a more strict definition, "tandem" reactions differ from "domino"/"cascade" ones in that "tandem" intermediates are isolable entities.[58]

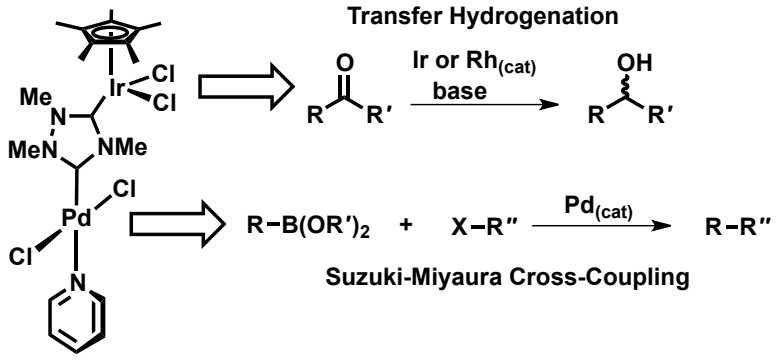
reaction medium to afford the different transformations. Each of these two possibilities has a series of advantages and disadvantages. Clearly, if a single catalyst is used, the sequence is limited to transformations for which this one catalyst is active. Alternatively, two different catalysts can be used in sequence to increase the number of possible combinations, especially if the reactions are fundamentally different in nature. This alternative clearly reduces the reaction's atom economy however, especially if the preparation of the two different catalysts is taken into account (double the amount of time, solvents, reagents, purification materials, and characterization procedures). However, if both catalytic processes can be conducted in the same pot, then the sacrifice associated with preparing two separate catalysts is somewhat balanced out.

Many different tandem processes have been established, and have been heavily reviewed.[51-53, 58] Not surprisingly, the different catalyst combinations are varied and abundant, ranging from late/early combinations (Ni/Ti for dimerization/polymerization catalyses)[59] to late/late metal combinations (Pd/Rh for allylation/Pauson-Khand catalyses),[60] as well as many others.[51-53, 58] However, recently Peris *et al.* published results wherein a *bimetallic* catalyst (as opposed to two monometallic systems) can carry out the tandem transformation of a bifunctionalized substrate in one pot.[61] As a result, we were interested to determine if our bimetallic complexes from the previous chapters could afford similar transformations.

6.1.3 Heterobimetallic tandem catalysis

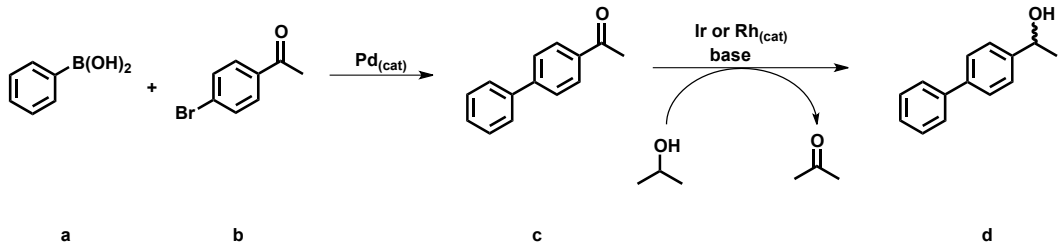
The aforementioned report by Peris *et al.* involved several heterobimetallic complexes of Pd, Rh, and Ir which are bridged by an *N*-heterocyclic dicarbene

(NHdi-C) ligand.[61] The Pd/Ir combination was of particular interest in this study because of the orthogonality of the two catalytic processes (Scheme 6-2), specifically transfer hydrogenation (by the Ir centre) and Suzuki-Miyaura cross-coupling (by Pd).



Scheme 6-2. *N*-heterocyclic dicarbene-bridged complex and each metal's role in tandem catalysis.

Using bifunctionalized substrates, this Pd/Ir complex could mediate two sequential transformations of the reagent using a single catalyst, performing two processes in tandem in one reaction vessel (Scheme 6-3).[61] Haloacetophenones (X–Ar–C(O)R) are convenient substrates for Pd and Ir/Rh processes because they contain an aryl-halide bond, for which Pd catalysts may provide a large library of transformations (such as Suzuki-Miyaura cross coupling, dehalogenation, etc.) while the Group IX metal functionality can perform certain hydrogenation processes on the C=O bond.[62-67] In their study, the palladium end effectively combines a boronic acid (Scheme 6-3a) with the aryl halide of the bifunctionalized substrate (Scheme 6-3b), and after sufficient reaction time, the cross-coupled product (Scheme 6-3c) is then hydrogenated at the ketone functionality by the Ir(III) end of the bimetallic catalyst to afford the cross-coupled alcohol (Scheme 6-3d), all in one pot, under near-identical conditions.

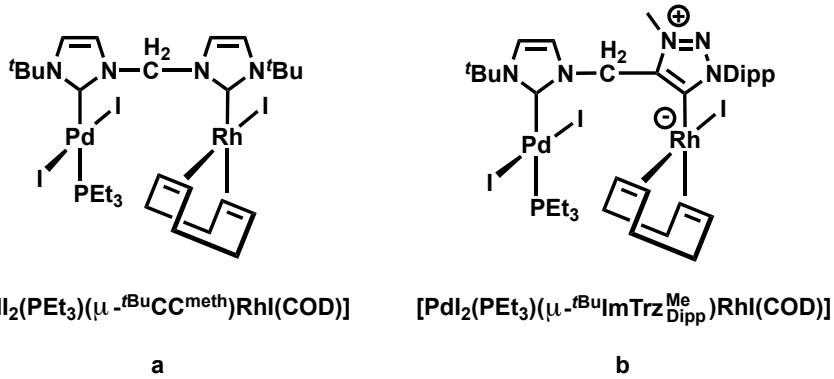


Scheme 6-3. Suzuki-Miyaura cross-coupling and transfer hydrogenation tandem catalytic processes.

More interestingly however, it was demonstrated that this tandem process had higher activity than that of a system containing equivalent Pd and Ir monomers that were analogous to the respective ends of the bimetallic system. This higher activity constitutes a clear advantage to using a bimetallic catalyst instead of two analogous monometallic species, implying some degree of metal-metal cooperativity.

6.1.4 Pd/Rh systems for tandem catalysis

Owing to this report by Peris *et al.* of a heterobimetallic system successfully displaying metal-metal cooperativity in tandem catalysis,[61] it seemed that our Pd/Rh systems from Chapters 2 and 4, specifically $[PdI_2(PEt_3)(\mu\text{-}^{tBu}CC^{meth})RhI(COD)]$ (Figure 6-3a) and $[PdI_2(PEt_3)(\mu\text{-}^{tBu}ImTrz^{Me}_{Dipp})RhI(COD)]$ (Figure 6-3b), offered an excellent opportunity to study the same tandem transformations using our own well-defined Pd and Rh precatalysts and to compare the effects of using different



$[PdI_2(PEt_3)(\mu\text{-}^{tBu}CC^{meth})RhI(COD)]$ $[PdI_2(PEt_3)(\mu\text{-}^{tBu}ImTrz^{Me}_{Dipp})RhI(COD)]$

a b

Figure 6-3. Di-NHC (**a**) and di-MIC (**b**) bridged Pd/Rh complexes as potential tandem catalysts.

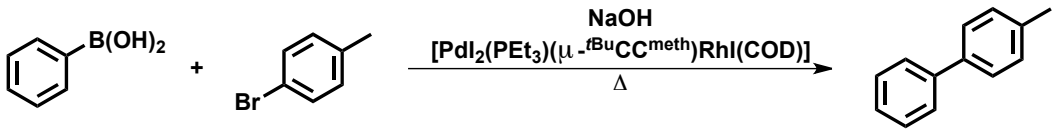
dicarbene bridges. Cross-couplings by Pd(II)[2] are well documented, as are transfer hydrogenations using Rh(I).[35, 68] As a result, we initiated a study on our Pd/Rh species[iii] and their abilities to perform sequential catalyses similar to Peris.

Section 6.2 Results and Compound Characterization

6.2.1 Suzuki-Miyaura cross-coupling ability of di-NHC Pd/Rh system

Our studies first focused on whether or not our di-NHC-bridged Pd/Rh species from Chapter 2 (Figure 6-3a) is well-suited for tandem catalysis. Before tandem reactivity can be evaluated however, each catalytic reaction must be tested individually to refine conditions for each process, and ensure compatibility between both. The Pd/Rh system was first tested for its ability to facilitate catalysis in the Suzuki-Miyaura cross-coupling of phenylboronic acid and an aryl-bromide. The Suzuki-Miyaura reaction is the coupling of an aryl or vinyl boronic acid with an aryl or vinyl halide (see above, Scheme 6-2).[2] It is a powerful cross-coupling method that allows for the synthesis of conjugated olefins, styrenes, and biphenyls. Although the most commonly used system is $[Pd(PPh_3)_4]$, other palladium sources have been used including Pd(II) pre-catalysts that are reduced to the active Pd(0) *in situ*.[69] NHC-based Suzuki catalysts are favourable because they often do not require excess stabilizing ligand (phosphines are known to form phosphonium salts or cause aryl-aryl exchange between substrate and phosphine).[70] The first reaction studied (involving phenylboronic acid and 4-bromotoluene) is shown in Scheme 6-4.

[iii] Although we set out to test both species, owing to time restrictions, we have only been able to test the di-NHC system's ability in tandem catalysis. However, studies are ongoing and results involving the NHC/MIC system will be reported at a later date.



Scheme 6-4. Suzuki-Miyaura cross-coupling of phenylboronic acid and 4-bromotoluene.

Table 6-1 summarizes our initial results in connecting two aryl groups under a few very preliminary conditions. For this reaction, a 1:1 solution of tetrahydrofuran (thf) and *iso*-propyl alcohol (ipa) was used. Although all reagents dissolve sufficiently in thf, a significant amount of ipa was added in order to ensure the reaction's compatibility with alcohol, because ipa is the hydrogen transfer reagent in the proposed tandem partner, transfer hydrogenation. Reactions proceeded to near-completion (93% conversion, entry 1) after 18 h[iv] even with low catalyst loadings (0.8 mol%). Upon decreasing both the reaction time and catalyst loading (2 h, 0.02 mol%, entry 2), the percent conversion is still relatively high. Although attempts were made to catalyze the reaction using only 0.003 mol% of catalyst, the reaction did not proceed to any appreciable degree.

Table 6-1. Suzuki-Miyaura Results at 100 °C of 4-Bromotoluene Using Pd/Rh Catalyst.

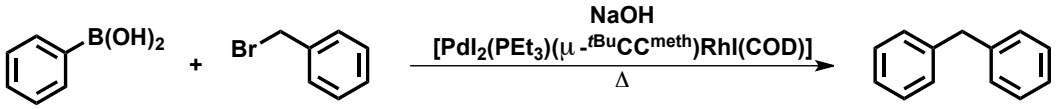
Entry	cat : $PhB(OH)_2$: BrTol: NaOH	Solvent	t_{rxn} (h)	Conv.[v] (%)	Select.[iii] (%)	TON[iii]	TOF[iii]	[Pd] (mol%)
1	1 : 142 : 126 : 198	1:1 thf/ipa	18.00	93	35	94	5	0.8
2	1 : 12,001 : 12,591 : 14,995	1:1 thf/ipa	2.00	92	1	11566	5783	0.02
3	1 : 29,981 : 31,131 : 37,622	1:1 thf/ipa	2.00	13	6	4132	2066	0.003

Although percent conversions in entries 1 and 2 were relatively high, the catalyst is unfortunately not very selective in forming the desired product (4-methyl-1,1′-biphenyl, Ph–Tol). The two other major species produced are homocoupled

[iv] Heating the reaction for 18 h was an initial estimate for time required. As made evident by the data in the rest of the table, 18 h clearly was more than enough time to allow the reaction to complete.

[v] Conversions (Conv.), selectivities (Select.), turnover numbers (TON) and frequencies (TOF) for the products determined by GC-MS analysis on samples obtained at corresponding reaction times (t_{rxn}) in column 4.

products resulting from combination of two equivalents of boronic acid (forming Ph–Ph) or the halide (forming Tol–Tol). Owing to the indiscriminate nature of the palladium end of our di-NHC catalyst, we decided to attempt coupling of phenylboronic acid with an *alkyl* bromide (Scheme 6-5), which is a more difficult cross-coupling transformation,[71] and would perhaps result in better selectivity.



Scheme 6-5. Suzuki-Miyaura cross-coupling of phenylboronic acid and benzylbromide.

Table 6-2 summarizes the representative data that we obtained using the catalyst to cross-couple phenylboronic acid with the comparatively inert alkyl halide (benzylbromide, BnBr) in the presence of sodium hydroxide. For this reaction, a variety of solvents were tested. Although dioxane and dimethylformamide (dmf) (entries 1 and 2) facilitated high conversions, thf only required 2 h heating (entry 3). The reaction was then tested in a 1:1 solution of thf and ipa (again, to test the reaction's compatibility with ipa for future tandem catalysis considerations) and similar conversions could be obtained with slightly longer heating. Using only 1.1 mol% of catalyst, 100% conversion can be achieved in only 3.5 h (entry 4). Reducing catalyst loadings lead to similar conversion values (entries 5-7), even at extremely low catalyst loadings (0.007 mol%, entry 7). Unfortunately, as observed

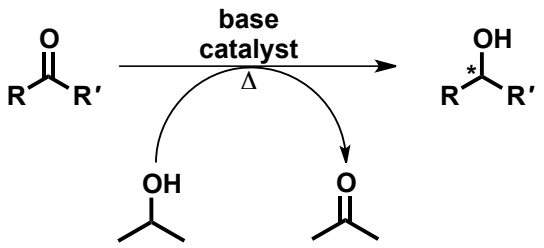
Table 6-2. Suzuki-Miyaura Results at 100 °C of Benzyl Bromide Using Pd/Rh Catalyst.

Entry	cat : $PhB(OH)_2$: BnBr: NaOH	Solvent	t_{rxn} (h)	Conv.[iii] (%)	Select.[iii] (%)	TON[iii]	TOF[iii]	[Pd] (mol%)
1	1 : 120 : 100 : 140	dioxane	66.25	87	44	87	1	1.0
2	1 : 92 : 74 : 116	dmf	17.00	98	1	73	4	1.3
3	1 : 119 : 98 : 159	thf	2.00	79	39	77	39	1.0
4	1 : 107 : 87 : 142	1:1 thf/ipa	3.50	100	40	87	44	1.1
5	1 : 1,008 : 830 : 1,211	1:1 thf/ipa	2.00	94	43	782	391	0.1
6	1 : 8,663 : 7,760 : 10,884	1:1 thf/ipa	2.00	66	34	5121	2560	0.01
7	1 : 30,511 : 13,376 : 94,223	1:1 thf/ipa	2.00	64	2	29036	14518	0.007

with 4-bromotoluene, the selectivity of the reaction is still erratic, requiring further optimization. These studies will be pursued and reported in due course.

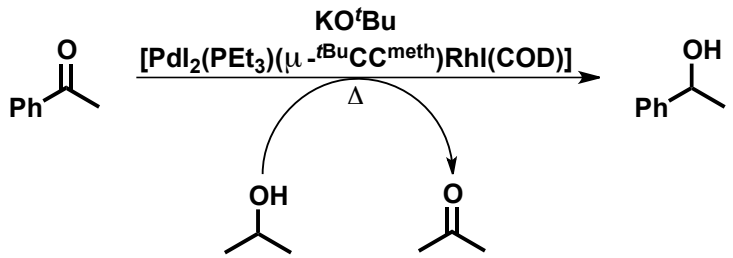
6.2.2 Transfer hydrogenation ability of di-NHC Pd/Rh system

Our next study involved examining the di-NHC-bridged Pd/Rh species to evaluate its ability to facilitate transfer hydrogenation of acetophenone using ipa as the hydrogen source *via* the Rh(I) end of the system. Transfer hydrogenation (Scheme 6-6) is the addition of dihydrogen across a molecule from a source other than gaseous H_2 (ipa is often the conventional hydrogen source because it is stable, easy to handle, non-toxic, and inexpensive[72-75]). In organic synthesis, hydrogen-transfer



Scheme 6-6. Transfer hydrogenation of ketones using ipa as the hydrogen transfer agent.

catalysts are typically based on Ru or Rh,[76] which are mainly employed for the reduction of ketones (or imines) to alcohols (or amines). The hydrogen-donor (ipa in this case), converts to a ketone (acetone) upon donation of hydrogen. Transfer hydrogenations can proceed in high enantiomeric excess when the starting material is prochiral ($R \neq R'$), and the catalyst is enantioselective. NHC-based metal complexes have recently demonstrated favourable transfer hydrogenation capability,[77] and as a result we were interested in how our catalyst could compare to known catalyses. The first hydrogenation reaction tested by us (involving transfer hydrogenation of acetophenone by ipa) is shown in Scheme 6-7.



Scheme 6-7. Transfer hydrogenation of acetophenone using ipa as the hydrogen source.

Table 6-3 summarizes the data obtained using the catalyst to facilitate transfer hydrogenation of acetophenone using ipa in the presence of base. At this time, only two different conditions have been varied: hydrogenation for 48 and 112 h. Using only 0.8 mol% of catalyst, conversion of only 44% was observed (entry 1). Although it was anticipated that this reaction could be forced to completion with more time, the longer reaction (entry 2) only resulted in slightly higher conversion. Selectivities are modest however (being somewhat better than the Suzuki-Miyaura results mentioned in Section 6.2.1), especially at longer reaction times (entry 2). Conditions clearly have to be optimized in order to improve catalytic results. These studies are ongoing and will be reported at a later date.

Table 6-3. Transfer Hydrogenation Results at 100 °C of PhC(O)Me Using Pd/Rh Catalyst.

Entry	cat : KO^{t}Bu : PhC(O)Me : ipa	Solvent	t_{rxn} (h)	Conv.[iii] (%)	Select.[iii] (%)	TON[iii]	TOF[iii]	[Pd] (mol%)
1	1 : 2 : 110 : 16,766	ipa	48.00	44	39	41	2	0.9
2	1 : 2 : 113 : 15,824	ipa	112.00	53	51	55	3	1.0

Section 6.3 Discussion

Although Peris's report[61] of an NHdi-C-bridged Pd/Ir complex's ability to facilitate the tandem transformation of a bifunctionalized substrate was an interesting account, possibly the more interesting aspect was the demonstrated higher activity than that two equivalent monometallic catalysts. As outlined in Chapter 1, Section 1.4.3, we

are interested in cases where metals, once forced into close proximity, can act in a cooperative manner to either activate normally inert substrates or promote reactivity patterns not possible with monometallic analogues. It is possible that the "other" metal in the Peris catalyst may be participating in the unexpected reaction owing to both metals' forced proximity. Or, perhaps the processes are made more efficient because of the alluded-to possibility of metal-metal cooperativity since they are in close enough proximity. Regardless, this finding was certainly of interest to us.

In discovering this report by Peris, we were interested to determine if our bimetallic complexes from the previous chapters would display similar activities in both catalytic reactions. However, these Pd/Rh system were not designed with catalysis in mind, but rather were synthetic targets containing generic Pd/Rh square-planar environments. Although no attempts were made to design a system that would have functionalities that are known to give rise to high activity in either of these reactions, our di-NHC Pd/Rh catalyst was certainly active (perhaps *too* active) in the C–C bond-forming Suzuki-Miyaura reaction. Conversions were almost 100% with both aryl and alkyl bromides, although the system lacks control based on the poor selectivities for the desired product. Although a few different conditions were varied to try and optimize the system, only NaOH was considered as the co-catalyst. The choice of base can be very important,[78] whether considering its role to form the tetracoordinate borate to effect transmetallation with palladium, or its role to induce reduction of Pd(II) to Pd(0). We have become aware that the choice of base is not a trivial one, and therefore several variations should be screened in order to perhaps achieve a higher and more desireable selectivity in both aryl- and alkyl-couplings. A better nucleophile such as KO^{t}Bu should provide better results based on literature

precedent.[79, 80] Once the individual processes are optimized, the tandem reactions will be pursued.

Although time restrictions did not allow us to pursue catalysis studies on the NHC/MIC Pd/Rh system developed in Chapter 4, we assume that its ability to catalyze the Suzuki-Miyaura reaction would not vary significantly because the environment around palladium in both systems is near-identical (*i.e.*, *trans*-$[PdI_2(NHC)(PEt_3)]$. However, considering the cooperative effects demonstrated in Peris's account,[61] perhaps a change at Rh could indeed cause variation in Suzuki results. These studies will surely be of interest.

Furthermore, once simple routes can be established to di-MIC bridged Pd/Rh complexes (recall our issues in attaching a Pd atom to an MIC in Chapter 5), this system will be of great catalytic interest because of the MIC's considerable electron-donating ability, and the effect it will have on C–C couplings. The first experiments to try (apart from ones identical to those of this report) will be to examine even more inert species such as aryl- or even alkyl chlorides, and test if the Pd half can effect this transformation owing to the proposed rich electron density on palladium.

Out initial plan for tandem catalysis was C–C coupling with Pd and transfer hydrogenation with Rh. However, based on preliminary data, perhaps the Rh end of our di-NHC precursor is not well-suited for this transformation, and other Rh(I)-based catalyses (such as alcohol carbonylation,[81] $R–B(OR')_2$ conjugate additions,[82-84] or transition metal-catalyzed hydroborations[85, 86]) should be investigated instead. Although hydrogenation catalysis by a Rh(I) centre is documented,[35, 87-89] the typical catalyst for transfer hydrogenation is Ru(II)[76] (which is isoelectronic with Rh(III), not

Rh(I)). Furthermore, the results put forth by Peris involved a more oxidized Ir(III) system.[61] It is still somewhat surprising however that our system performed so poorly considering the almost perfectly-analogous Rh monomer shown in Scheme 6-2d[35] (in addition to other similar species)[87-89] displayed impressive catalytic results. The conditions we used in our attempts were identical to Herrmann's,[35] but it is known that some degree of fine-tuning is usually required, since the choice of base and/or solvent can have a significant impact on performance.[87]

It has been noted that electron-poor ligands can often promote high activity in transfer hydrogenation,[90] and as a result, perhaps NHC-metal complexes are poor candidates in this regard. Steric pressure also plays a role in improving reactivity,[90] but perhaps this balance unfortunately is not achieved in our systems (based on *very* preliminary work done to date). Furthermore, if strongly-donating groups are detrimental to transfer hydrogenation, surely the NHC/MIC Pd/Rh species would be an even poorer catalyst. The studies presented in this chapter are preliminary results and incomplete for the time being. Further investigations are underway and will be published in due time.

Section 6.4 Experimental Procedures

6.4.1 General comments

Acetophenone, benzyl bromide, 4-bromotoluene, potassium *tert*-butoxide, and sodium hydroxide were purchased from Aldrich; and phenylboronic acid was purchased from Alfa Aesar. The di-NHC-bridged (Figure 6-3a) precatalyst used were prepared as described in Chapter 2[91] and Chapter 4. All chemicals were used without further purification. Mass spectrometric analyses were performed by the

departmental Mass Spectrometry Laboratory using positive ion electrospray ionization on an Agilent Technologies 6220 Accurate-mass TOF LC/MS.

6.4.2 General protocol for Suzuki-Miyaura cross-coupling experiments

A representative procedure for the reaction of phenylboronic acid and benzyl bromide using $[PdI_2(PEt_3)(\mu\text{-}^{t\text{Bu}}CC^{meth})RhI(COD)]$ as the precatalyst and NaOH as the co-catalyst (Table 6-2, Entry 4) is as follows: In a 50 mL Schlenk tube equipped with a stir bar, under anhydrous conditions and Ar atmosphere, $[PdI_2(PEt_3)(\mu\text{-}^{t\text{Bu}}CC^{meth})RhI(COD)]$ (0.0057g, 0.0053 mmol)[vi] was dissolved in thf:ipa (50:50) (10.0 mL) and to the resulting yellow solution a stock solution of phenylboronic acid (0.0690 g, 0.566 mmol), benzyl bromide (55 μL, 0.46 mmol) and NaOH (0.0301 g, 0.753 mmol) was added to the reaction flask *via* cannula such that the molar ratio of Pd : $PhB(OH)_2$: BnBr : NaOH = 1 : 107 : 87 : 142. The flask was then heated to 100 °C for 3.5 h while stirring. The reaction temperature was maintained at 100 °C in a sealed container throughout the course of the reaction. The reaction mixture was allowed to cool to room temperature, and the solution was collected in a vial and stored at 0 °C in the dark until the reaction mixture could be analyzed by GC-MS.

6.4.3 General protocol for transfer hydrogenation experiments

A representative procedure for the reaction of acetophenone and ipa using $[PdI_2(PEt_3)(\mu\text{-}^{t\text{Bu}}CC^{meth})RhI(COD)]$ as the precatalyst (Table 6-3, Entry 2) is as follows: In a 50 mL Schlenk tube equipped with a stir bar, under anhydrous conditions and Ar atmosphere, $[PdI_2(PEt_3)(\mu\text{-}^{t\text{Bu}}CC^{meth})RhI(COD)]$ (0.0089g, 0.0083

[vi] In cases of smaller catalyst loadings, a precise aliquot of a thf/ipa stock solution was used to inject a diluted amount of precatalyst to the reaction flask.

mmol) and acetophenone (0.11 mL, 0.94 mmol) were dissolved in thf:ipa (50:50) (20.0 mL) and to the resulting yellow solution a solution of KO^{t}Bu (0.0021 g, 0.019 mmol) was then added to the reaction flask *via* cannula such that the molar ratio of Rh : KO^{t}Bu : acetophenone : ipa = 1 : 2 : 113 : 15,824. The flask was then heated to 100 °C for 112.0 h while stirring. The reaction temperature was maintained at 100 °C in a sealed container throughout the course of the reaction. The reaction mixture was allowed to cool to room temperature, and the solution was collected in a vial and stored at 0 °C in the dark until the reaction mixture could be analyzed by GC-MS.

Section 6.5 References

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Chapter 7 Conclusions

Section 7.1 Concluding Remarks

7.1.1 Foundations for thesis objectives

In the inaugural stages of the work outlined in this dissertation, several projects in our group were, at that point, focused on developing different ligands other than the ubiquitous *bis*(diphenylphosphino)methane (dppm) infrastructure to link two metal atoms. As minor steric and electronic modifications, D. Jason Anderson and Michael Slaney were examining bridging groups similar to dppm, however containing ethyl substituents instead of phenyl groups (*bis*(di*ethyl*phosphino)methane, or depm).[1, 2] Lindsay Hounjet was exploring *ortho*-phosphinoaniline systems (based on preliminary studies by Matthias Bierenstiel, a former post-doctoral fellow) to add an element of hemilability to bridging diphosphines,[3-6] while Kyle Wells was demonstrating (based on some literature precedent[7-13]) that *N*-heterocyclic carbenes (NHCs, a type of Fischer carbene) could be linked together to form di-*N*-heterocyclic carbenes (di-NHCs), which could bridge various dirhodium complexes, much like diphosphines.[14]

Using the coordinated acetate ligands of $[Rh(\mu\text{-}OAc)(COD)]_2$ as an internal base for the deprotonation of the precursor diimidazolium salts produced *bridging* homobimetallic arrangements exclusively. The key here was that with one base/metal the deprotonation occurred stepwise *one metal at a time*. In this way the formation of chelates was avoided. Since the deprotonation was stepwise, Kyle[14] and others[15, 16] found that it could be halted halfway to produce systems wherein one end was deprotonated and the resulting carbene was anchored to the metal, while a

remaining imidazolium arm was left suspended away from the metal atom. With these reports of carbene-anchored/pendent-imidazolium complexes, and our observations that stepwise deprotonation by internal base precursors containing a 1:1 base:metal stoichiometric ratio seemed to facilitate bridging arrangements over chelating ones, we were curious as to whether routes to *hetero*bimetallic dicarbene complexes were possible, which eventually became the primary objective of this dissertation.

7.1.2 Different dicarbenes to bridge two different metals

In the introductory chapter (Chapter 1), we learn of several key figures involved in developing carbenes as ligands, extending from early work by Dumas,[17] Fischer,[18] (the often-uncredited) Tschugajeff,[19] and Wanzlick[20] to the more contemporary reports by Arduengo,[21] Bertrand,[22-25] Schrock,[26-30] Grubbs,[31-34] and Nolan.[35] With these reports, bidentate analogues (dicarbenes) began to manifest themselves in the carbene literature, finding use as linkers for bimetallic species (see Chapter 1), and sparking our interest owing to their similarity to diphosphines.

In the first experimental chapter (Chapter 2) we demonstrated the utility of both the aforementioned "pendent" and "internal base" strategies, incorporating metal atoms one at a time to produce various di-NHC-linked complexes of Pd/Rh and Rh/Ir and with some success in generating Pd/Ir systems through the use of external bases.[36] We were surprised however to observe that the strategy was somewhat unproductive in attempts to generate heterobinuclear species with the majority of closely-related mononuclear precursors studied when using $[Rh(\mu\text{-}OAc)(COD)]_2$. It was proposed that either milder conditions or a more powerful

internal base deprotonating agent would be required to expand on the scope of these strategies.

Having established that the stepwise deprotonation of di-NHC precursors by internal bases was an effective strategy for generating dicarbene-bridged mixed-metal systems, and the interest, at the time, in other varieties of NHCs, we became interested in developing *new*, original dicarbenes to link different transition metals. With the rise in popularity of cyclic (alkyl)(amino)carbenes (CAACs),[37] we first sought to generate bidentate analogues of these ligands. Although the organic synthesis was relatively straightforward in the beginning stages, we unfortunately were unsuccessful in our attempts to create di-CAAC ligands owing to puzzling technical difficulties in the final stages of diiminium (proposed di-CAAC precursors) synthesis, as well as problems in establishing routes to the coupling of two spiro-indolenines. These unsuccessful attempts are reported in Chapter 3.

Among the different sorts of non-imidazole-2-ylidene-type carbenes that we are interested in (in addition to CAACs that we had little success with) were the "abnormal"-type NHCs (or *a*NHCs), which were recategorized as mesoionic carbenes (or MICs) by Bertrand sometime later[25] owing to their delocalized charges in the free ligand. Rather than continuing to try and develop proper organic protocols for di-CAACs, we began an investigation into the preparation of hybrid dicarbene frameworks based on an NHC and these newly-developed MIC scaffolds, combining imidazole synthesis with "click" chemistry.[38, 39] In Chapter 4, the successful preparation of a small library of these unsymmetric dicarbenes was reported, which offered an interesting way to (very subtly) vary the properties of dicarbene-bridged systems, compared to di-NHCs. The different acidities of the two

different ends of the precursors provided the option for two different regioisomers depending on the order of metal incorporation. By attaching Pd first (through deprotonation of the more-acidic imidazolium moiety), we were able to generate a series of NHC-anchored/pendent-triazolium complexes of Pd analogous to those in Chapter 2. However, in trying to attach Rh to the MIC using $[Rh(\mu\text{-}OAc)(COD)]_2$, we encountered more problems owing once again to the harsh conditions required. Fortunately, we discovered that the more-basic methoxido ligand in $[Rh(\mu\text{-}OMe)(COD)]_2$ could facilitate triazolium deprotonation and MIC production, leading to an NHC/MIC-bridged Pd/Rh complex. A full paper documenting this work is in preparation.

With experience in deprotonating the triazolium arm in Chapter 4 with methoxy-based precursors to generate MIC-Rh moieties, we developed very simple routes to bidentate carbenes in Chapter 5 wherein *both* carbenes were of the MIC type. Although, in principle, two "connectivity isomers" are possible, we had difficulty in developing routes to *N*,*N*′-linked di-MICs because of solubility issues with triazole-azide intermediates. However, we successfully established synthetic methods to *C*,*C*′-linked di-MICs using dialkynes and two equivalents of azide monomer. Several MIC-anchored/pendent-triazolium species of Rh and Ir were generated (owing to the fact that Rh and Ir methoxido precursors are well-documented and easily prepared),[40, 41] which can subsequently be deprotonated to produce the second-known species bridged by a di-MIC,[42] and the first involving two different metals (results to be published in the near future). Unfortunately, the lack of success with developing di-MICs involving the Pd/Rh combination is due to the inability (in our experience) of the acetate ligands in $[Pd(OAc)_2]$ to deprotonate MIC

precursors. As a possible solution, the external base deprotonation of one half of the ditriazolium salts to generate an MIC/MIC(H)$^+$ species could potentially facilitate ligand displacement on *trans*-[$PdCl_2(R_3P)_2$]. Alternatively, investigations will also focus on preparing less-conventional methoxy-containing Pd precursors to aid in internal base deprotonation.

Finally, in Chapter 6, with a small library of heterobimetallic complexes bridged by one of three different dicarbene systems (assuming we can succeed with the di-MIC Pd/Rh system), we set out to compare the catalytic activity of our systems to that for various mono- and bimetallic species already in the literature. Specifically, we were interested in attempting to mimic reports of a well-defined Pd/Ir species, bridged by an *N*-heterocyclic dicarbene (NHdi-C), which exhibited evidence for metal-metal cooperativity in tandem catalysis.[43] Our interest was to generate a useful "two-in-one" which could potentially act as a useful catalyst for tandem organic transformations. Although one of our di-NHC species (from Chapter 2) exhibited significant activity in Suzuki-Miyaura cross-coupling catalysis (by the Pd end) with relatively inert alkylhalides even with low catalytic loadings (0.007 mol%, > 29 000 turnovers), it suffers from poor selectivity, generating many different products. Despite this impairment, the results are relatively impressive in cross-coupling, and are an exciting discovery. Once similar activities can be achieved for Rh (or a different metal), this will surely provide an interesting system for further study. Furthermore, the effect of incorporating the better electron-donating MICs will also be an interesting study.

The Rh end of the di-NHC-bridged product can facilitate transfer hydrogenation between acetophenone and *iso*-propyl alcohol, although the activity is

somewhat unimpressive (55 turnovers after 112 h). Studies to improve these values, as well as study the reactivity of the NHC/MIC-linked species from Chapter 4, are ongoing, however.

Several important findings throughout the projects outlined in this dissertation could potentially help to improve upon the problems observed in early results. For example, although $[Rh(\mu\text{-}OAc)(COD)]_2$ proved somewhat unproductive at generating a large library of Pd/Rh complexes in Chapter 2, one wonders whether some of our puzzling failures reported therein could have benefitted from the use of the methoxido-bridged dimer instead of the OAc-bridged species. $[Rh(\mu\text{-}OMe)(COD)]_2$ would undoubtedly allow for milder conditions to perhaps facilitate production of a larger library of di-NHC-bridged Pd/Rh complexes. Those with an already Pd-coordinated diphosphine would be of great interest to us, as unwinding of this group could potentially form hybrid "A-Frame" complexes, containing both μ-di-NHC and μ-diphosphine ligands, analogous to the work of Kyle Wells in Rh_2 chemistry.[14] Furthermore, NHC/MIC-linked Pd/Ir complexes (analogous to the Pd/Rh species reported in Chapter 4) should be possible owing to the ease in producing $[Ir(\mu\text{-}OMe)(COD)]_2$,[40, 41] and the noted ability of methoxy anions to deprotonate triazolium salts. The Ir moiety of these proposed Pd/Ir species could potentially allow for better transfer hydrogenation results. Finally, studies to improve these catalytic results in Chapter 6 will be explored in due course.

At the outset, at the beginning of this work, we had a number of goals in mind – to devise good routes to dicarbene-bridged, mixed-metal systems. This has been achieved clearly in Chapter 2. From then on, our project evolved slightly, examining other types of carbenes that had not been extensively studied as

*di*carbenes, where we then developped routes to those systems and (using the similar strategies), extended upon this mixed-metal aspect in Chapters 4 and 5. Following that, we began to search for potential applications of these new dicarbene-bridged, heterobimetallic species, notably in tandem catalysis, as was investigated in Chapter 6. We did not necessarily build our dicarbene frameworks with tandem catalysis in mind, but we wanted to compare our systems with ones similar to ours in the literature because it was something that was a benchmark in this area. Considering the somewhat unimpressive results of our pre-catalyst in the transfer hydrogenation of acetophenone from *iso*-propyl alcohol, perhaps replacement of Rh with a Ru system could result in an interesting Suzuki coupling/olefin metathesis tandem combination.

Section 7.2 References

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Appendices

Appendix I Co-Author Contributions and Specific Acknowledgements

APP I.1 Chapter 1 Acknowledgements

Martin Cowie assisted with revising and editing.

APP I.2 Chapter 2 Acknowledgements

Michael J. Ferguson and Robert McDonald collected all crystallographic data. Michael Slaney is acknowledged for supplying the sample of depm while Kyle Wells provided initial diimidazolium salt samples (**1a-d**). Martin Cowie supervised the project and assisted with revising and editing.

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APP I.7 Chapter 7 Acknowledgements

Martin Cowie assisted with revising and editing.

Appendix II Drying Agents for Solvents

Solvent	Drying agent	Indicator
acetone	calcium sulfate ($CaSO_4$)	cobalt(II) chloride
acetonitrile	calcium hydride (CaH_2)	N/A
benzene	sodium metal (Na)	benzophenone
dichloromethane	phosphorus pentoxide (P_2O_5)	N/A
diethyl ether	sodium metal (Na)	benzophenone
dimethylsulfoxide	type 4A molecular sieves	N/A
iso-propyl alcohol	magnesium metal (Mg)	N/A
methanol	magnesium sulfate ($MgSO_4$)	N/A
nitromethane	calcium hydride (CaH_2)	N/A
n-pentane	sodium metal (Na)	N/A
tetrahydrofuran	sodium metal (Na)	benzophenone

Appendix III Crystallographic Experimental Details

APP III.1 Chapter 2 Details

Table III.1-1. Crystallographic Experimental Details for Chapter 2, Compounds 2c and 2d.

Compound	**2c**	**2d** • $2CH_2Cl_2$
Formula	$C_{18}H_{27}Br_2N_4Rh$	$C_{26}H_{43}Br_2Cl_4N_4Rh$
Formula weight	562.17	816.17
Crystal dimensions (mm)	0.37 × 0.10 × 0.05	0.45 × 0.17 × 0.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)
Unit cell parameters		
a (Å)	23.748 (2)	8.5243 (10)
b (Å)	6.9405 (7)	13.8891 (16)
c (Å)	12.3794 (12)	14.5876 (17)
α (°)	90	90
β (°)	91.4800 (10)	101.093 (2)
γ (°)	90	90
V (Å^3)	2039.7 (3)	1694.8 (3)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.831	1.599
μ (mm^{-1})	4.764	3.199
Diffractometer	Bruker PLATFORM/SMART 1000 CCD[i]	
Radiation (λ[Å])	graphite-monochromated Mo Kα (0.71073)	
Temperature (°C)	–80	
Scan Type	ω scans (0.3°) (25 s exposures)	ω scans (0.3°) (20 s exposures)
$2\theta_{max}$ (°)	55.06	54.88
Total data collected	16813 ($-30 \le h \le 30$, $-9 \le k \le 8$, $-15 \le l \le 16$)	14567 ($-11 \le h \le 11$, $-18 \le k \le 17$, $-18 \le l \le 18$)
Independ reflns (R_{int})	4660 (0.0370)	7648 (0.0163)
Obsd reflns [$I \ge 2\sigma(I)$]	3703	7288
Restraints/params	0 / 228	0 / 335
Flack abs struct parameter	n/a	0.364(6)
Goodness-of-fit (S)[ii]	1.051	1.071
Final R indices[iii]		
R_1 [I ≥ 2σ(I)]	0.0314	0.0294
wR_2 [all data]	0.0753	0.0755
Largest diff peak, hole (e Å^{-3})	1.227, –0.331	1.989, –0.525

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

[ii] $S = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$; for **2c**, $a_0 = 0.0421$, $a_1 = 0$; for **2d**, $a_0 = 0.0504$, $a_1 = 0.2277$; for **11b**, $a_0 = 0.0310$, $a_1 = 4.1569$; for **13b**, $a_0 = 0.0281$, $a_1 = 2.5400$; for **16b**, $a_0 = 0.0380$, $a_1 = 5.5389$; for **17b**, $a_0 = 0.0143$, $a_1 = 16.7787$).

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

Table III.1-2. Crystallographic Experimental Details for Chapter 2, Compounds 11b and 13b.

Compound	**11b**	**13b** • $1.5CH_3CN$
Formula	$C_{23}H_{36}I_3N_4PPd$	$C_{34}H_{51.50}I_3N_{5.50}P_2Pd$
Formula weight	886.63	1086.35
Crystal dimensions (mm)	0.47 × 0.27 × 0.12	0.45 × 0.27 × 0.23
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Unit cell parameters		
a (Å)	9.4861 (11)	15.060 (2)
b (Å)	12.0320 (13)	13.1140 (17)
c (Å)	14.0083 (16)	22.022 (3)
α (°)	91.9746 (12)	90
β (°)	100.9332 (12)	96.159 (2)
γ (°)	103.9630 (12)	90
V (Å^3)	1518.0 (3)	4324.4 (10)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.940	1.669
μ (mm^{-1})	3.732	2.673
Diffractometer	Bruker D8/APEX II CCD[iv]	
Radiation (λ[Å])	graphite-monochromated Mo Kα (0.71073)	
Temperature (°C)	–100	
Scan Type	ω scans (0.3°) (20 s exposures)	
$2\theta_{max}$ (°)	52.80	55.00
Total data collected	11967 ($-11 \le h \le 11$, $-15 \le k \le 15$, $-17 \le l \le 17$)	36366 ($-19 \le h \le 19$, $-17 \le k \le 16$, $-28 \le l \le 28$)
Independ reflns (R_{int})	6159 (0.0148)	9905 (0.0309)
Obsd reflns [$I \ge 2\sigma(I)$]	5815	8875
Restraints/params	0 / 290	3[v] / 426
Flack abs struct parameter	n/a	n/a
Goodness-of-fit (S)[vi]	1.157	1.030
Final R indices[vii]		
R_1 [I ≥ 2σ(I)]	0.0251	0.0241
wR_2 [all data]	0.0764	0.0595
Largest diff peak, hole (e Å^{-3})	1.306, –0.697	1.093, –0.924

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

[v] The distances and angles of the inversion-disordered acetonitrile solvent molecule (N2S, C3S, C4S) were restrained to be the same as those of the ordered acetonitrile solvent molecule (N1S, C1S, C2S) by use of the *SHELXL* SAME instruction.

[vi] $S = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$; for **2c**, $a_0 = 0.0421$, $a_1 = 0$; for **2d**, $a_0 = 0.0504$, $a_1 = 0.2277$; for **11b**, $a_0 = 0.0310$, $a_1 = 4.1569$; for **13b**, $a_0 = 0.0281$, $a_1 = 2.5400$; for **16b**, $a_0 = 0.0380$, $a_1 = 5.5389$; for **17b**, $a_0 = 0.0143$, $a_1 = 16.7787$).

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

Table III.1-3. Crystallographic Experimental Details for Chapter 2, Compounds 16b and 17b.

Compound	**16b** • $(CH_3)_2CO$	**17b**
Formula	$C_{27}H_{53}I_3N_4OP_2Pd$	$C_{29}H_{51}I_3N_4PPdRh$
Formula weight	998.77	1076.72
Crystal dimensions (mm)	0.47 × 0.36 × 0.27	0.58 × 0.41 × 0.18
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)
Unit cell parameters		
a (Å)	14.2452 (6)	15.4844 (14)
b (Å)	21.1101 (8)	11.9963 (11)
c (Å)	12.9669 (5)	40.421 (4)
α (°)	90	90
β (°)	94.9031 (4)	90
γ (°)	90	90
V (Å^3)	3885.1 (3)	7508.3 (12)
Z	4	8
ρ_{calcd} (g cm^{-3})	1.708	1.905
μ (mm^{-1})	2.968	3.451
Diffractometer	Bruker D8/APEX II CCD[viii]	
Radiation (λ[Å])	graphite-monochromated Mo Kα (0.71073)	
Temperature (°C)	–100	
Scan Type	ω scans (0.3°) (20 s exposures)	ω scans (0.4°) (10 s exposures)
$2\theta_{max}$ (°)	55.00	55.04
Total data collected	33796 (–18 ≤ *h* ≤ 18, –27 ≤ *k* ≤ 27, –16 ≤ *l* ≤ 16)	59218 (–20 ≤ *h* ≤ 20, –15 ≤ *k* ≤ 15, –52 ≤ *l* ≤ 52)
Independ reflns (R_{int})	8906 (0.0162)	8629 (0.0256)
Obsd reflns [$I \geq 2\sigma(I)$]	8022	8116
Restraints/params	0/ 345	0 / 352
Flack abs struct parameter	n/a	n/a
Goodness-of-fit (*S*)[ix]	1.038	1.208
Final *R* indices[x]		
R_1 [I ≥ 2σ(I)]	0.0284	0.0250
wR_2 [all data]	0.0760	0.0560
Largest diff peak, hole (e Å^{-3})	2.290, –0.970	0.924, –0.924

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

[ix] $S = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$; for **2c**, $a_0 = 0.0421$, $a_1 = 0$; for **2d**, $a_0 = 0.0504$, $a_1 = 0.2277$; for **11b**, $a_0 = 0.0310$, $a_1 = 4.1569$; for **13b**, $a_0 = 0.0281$, $a_1 = 2.5400$; for **16b**, $a_0 = 0.0380$, $a_1 = 5.5389$; for **17b**, $a_0 = 0.0143$, $a_1 = 16.7787$).

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

APP III.2 Chapter 4 Details

Table III.2-1. Crystallographic Experimental Details for Chapter 4,[xi] Compounds 4b and 5b.

Compound	**4b**	**5b**
Formula	$C_{22}H_{29}F_6N_5O_6S_2$	$C_{22}H_{30}I_2N_5O_2Rh$
Formula weight	637.62	753.22
Crystal dimensions (mm)	0.47 × 0.44 × 0.04	0.27 × 0.25 × 0.05
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
Unit cell parameters		
a (Å)	15.5497 (7)	10.1647 (5)
b (Å)	14.4945 (7)	10.4449 (5)
c (Å)	12.9298 (6)	13.1034 (6)
α (°)	90	76.4620 (5)
β (°)	102.3006 (6)	72.6898 (5)
γ (°)	90	78.6303 (5)
V (Å^3)	2847.3 (2)	1279.03 (11)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.487	1.956
μ (mm^{-1})	0.272	3.109
Diffractometer	Bruker D8/APEX II CCD[xii]	
Radiation (λ[Å])	graphite-monochromated Mo Kα (0.71073)	
Temperature (°C)	–100	
Scan Type	ω scans (0.3°) (20 s exposures)	
$2\theta_{max}$ (°)	52.80	54.96
Total data collected	22483 ($-19 \le h \le 19$, $-18 \le k \le 18$, $-16 \le l \le 16$)	11340 ($-13 \le h \le 13$, $-13 \le k \le 13$, $-17 \le l \le 16$)
Independ reflns (R_{int})	5831 (0.0287)	5814 (0.0127)
Obsd reflns [$I \ge 2\sigma(I)$]	4762	5305
Restraints/params	0/ 372	0 / 292
Flack abs struct parameter	n/a	n/a
Goodness-of-fit (S)[xiii]	1.021	1.036
Final R indices[xiv]		
R_1 [I ≥ 2σ(I)]	0.0361	0.0172
wR_2 [all data]	0.0968	0.0436
Largest diff peak, hole (e Å^{-3})	0.322, –0.322	0.533 –0.401

[xi] At the time of defense, the structure report for complex **7b** was not yet available.

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

[xiii] $S = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$; for **2c**, $a_0 = 0.0421$, $a_1 = 0$; for **2d**, $a_0 = 0.0504$, $a_1 = 0.2277$; for **11b**, $a_0 = 0.0310$, $a_1 = 4.1569$; for **13b**, $a_0 = 0.0281$, $a_1 = 2.5400$; for **16b**, $a_0 = 0.0380$, $a_1 = 5.5389$; for **17b**, $a_0 = 0.0143$, $a_1 = 16.7787$).

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

Appendix IV Crystallographic Data

Structure reports, crystallographic information files (CIFs) and checkCIF reports for the structures discussed in Chapters 2-5 can be obtained free of charge by contacting either Dr. Robert McDonald or Dr. Michael Ferguson at the address given below and quoting the internal reference number(s) for the appropriate compound(s) provided in the following sections:

X-Ray Crystallography Laboratory (Room E3-13)
Department of Chemistry, University of Alberta
11227 Saskatchewan Drive, NW
Edmonton, AB, Canada, T6G 2G2
Tel.: 1-780-492-2485
Fax.: 1-780-492-8231
Email: bob.mcdonald@ualberta.ca
michael.ferguson@ualberta.ca

Table IV-1. Chapter 2 Crystallographic Reference Numbers

Compound	Internal Reference Number
2c	COW0808
2d	COW0804
11b	COW0835
13b	COW0833
16b	COW0828
17b	COW0844

Table IV-2. Chapter 4 Crystallographic Reference Numbers

Compound	Internal Reference Number
4b	COW1048
5b	COW1053
7b	COW1116
7b	COW1116