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THE UNIVERSITY OF ALBERTA

MODEL COMPOUNDS IN CARBON-HYDROGEN ACTIVATION

BY

RICHARD KRENTZ ©

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled MODEL COMPOUNDS IN CARBON-HYDROGEN ACTIVATION submitted by RICHARD KRENTZ in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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External Examiner

Date 21 July 1989

TO MY WIFE CLAUDETTE, MY DAUGHTER
STEPHANIE AND
MY PARENTS

ABSTRACT

The synthesis and characterization of pyrazolylborate rhodium complexes and carborane platinum complexes have been investigated as model compounds in carbon-hydrogen bond activation.

The tris(pyrazolyl)borate complex $HB(3\text{-}PhPz)_3Rh(CO)_2$ (1) was prepared. Ultraviolet irradiation of a benzene or cyclohexane solution of 1 resulted in intramolecular C-H activation of one of the 3-PhPz groups. Reactions of the C-H activation product (7) were studied. Complex 1 and related olefin complexes demonstrated unique fluxional properties, with both bidentate and tridentate isomers present.

Bis and tris(pyrazolyl)borate ligands containing trifluoromethyl groups were prepared. With the unsymmetric pyrazole $3\text{-}CF_3\text{-}5\text{-}MePzH$ 18, a regioisomeric mixture of the bis(pyrazolyl)borate ligand $KH_2B(CF_3,MePz)_2$ 19 was obtained, but the tris(pyrazolyl)borate ligand $KHB(3\text{-}CF_3\text{-}5\text{-}MePz)_3$ 21 revealed only one regioisomer, which was demonstrated by an X-ray structure of the rhodium complex $HB(3\text{-}CF_3\text{-}MePz)_3Rh(CO)_2$ (22). A variety of ligand substitution reactions with 22 were investigated, specifically with tertiary phosphines, carbon monoxide and alkynes.

Photolysis of 22 in benzene afforded $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(C_6H_5)$ (49). A solution of 49 in toluene-d_8 underwent exchange below room temperature, and it followed first-order kinetics. The products of alkane C-H activation from 22 were not stable at room temperature.

Bis and tris(pyrazolyl)borate rhodium complexes with alkyl substituents on the pyrazole ring were prepared, specifically ethyl, isopropyl, isobutyl and tertiary butyl. Irradiation of HB(3-i-

$PrPz)_3Rh(CO)_2$ (**55**) in benzene afforded $HB(3\text{-}i\text{-}PrPz)_3Rh(CO)(H)(C_6H_5)$ (**58**), while in cyclohexane intramolecular C-H activation of the isopropyl group occurred.

Complexes of the type $(HBPz^*_3)Rh(CO)(L)$ (**79**, L = ethylene, **80**, L = CO) enriched with nitrogen-15 were prepared. Subsequent nitrogen-15 NMR studies demonstrated the hapticity of the tris(pyrazolyl)borate ligand in solution.

Carborane platinum complexes of the type [closo-3-(CO)-(L)-3,1,2-$Pt(C_2B_9H_9R'_2)$] (L = CO, PR_3, R' = H, Me) have been prepared. A variety of ligand substitution and oxidative addition reactions were carried out, but the complexes were inert with respect to C-H bond activation.

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LIST OF NUMBERED COMPOUNDS

Compound	Compound Number	Page First Cited
Chapter II		
$HB(3\text{-}PhPz)_3Rh(CO)_2$	(1)	26
$H_2B(3\text{-}PhPz)_2Rh(CO)_2$	(2)	30
$[(CO)_2Rh(3\text{-}PhPz)]_2$	(3)	36
$ClRh(CO)_2(3\text{-}PhPzH)$	(4)	39
$ClRh(CO)_2(3\text{-}PhPz)(H)B(3\text{-}PhPz)_2Rh(CO)_2$	(5)	43
$[HB(3\text{-}PhPz)_2(3\text{-}PhPzH)Rh(CO)_2]BF_4$	(6)	48
$HB(3\text{-}PhPz)_2(C_3H_2N_2\text{-}\overbracket{C_6H_4)R}h(CO)(H)$	(7)	50
$HB(3\text{-}PhPz)_2(C_3H_2N_2\text{-}\overbracket{C_6H_4)R}h(CO)(Cl)$	(8a)	53
$HB(3\text{-}PhPz)_2(C_3H_2N_2\text{-}\overbracket{C_6H_4)R}h(CO)(Br)$	(8b)	53
$HB(3\text{-}PhPz)_2(C_3H_2N_2\text{-}C_6H_4\overbracket{CH_2)R}h(CO)(CH_3)$	(9)	55
$HB(3\text{-}PhPz)_2(C_3H_2N_2\text{-}\overbracket{C_6H_4)R}h(CO)(CH_3)$	(10)	57
$HB(3\text{-}PhPz)_3\overbracket{Rh(CO)(CH_2CH_2C}H_2)$	(11)	59
$HB(3\text{-}PhPz)_3Rh(CO)(C_2H_4)$	(12)	61
$H_2B(3\text{-}PhPz)_2Rh(CO)(C_2H_4)$	(13)	62
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$KH_2B(CF_3,MePz)_2$	(19)	107
$KH_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2$	(19a)	108
$H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)_2$	(20a)	110

Chapter IV

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Chapter VI[a]

[a] *closo* and 3,1,2 terms omitted for shorthand notation.

LIST OF ABBREVIATIONS

Me	methyl
Et	ethyl
i-Pr	isopropyl
i-Bu	isobutyl
t-Bu	tertiary butyl
Cy	cyclohexyl
Ph	phenyl
Np	neopentyl
Ar	aryl
Cp	n^5-cyclopentadienyl, C_5H_5
Cp*	n^5-pentamethylcyclopentadienyl, C_5Me_5
Pz	pyrazol-1-yl, $C_3H_3N_2$
Pz*	3,5-dimethylpyrazol-1-yl, $C_5H_7N_2$
allyl	CH_2CHCH_2
acac	acetylacetonate
THF	tetrahydrofuran
DMAC	N,N-dimethylacetamide, $(CH_3)_2NC(O)CH_3$
COD	1,5-cyclooctadiene
NBD	norbornadiene
DQ	duroquinone
COE	cyclooctene
HFB	hexafluoro-2-butyne
NBS	N-bromosuccinimide
NCS	N-chlorosuccinimide
APT	attached proton test

CAPS	curve analysis program
mp	melting point
DEPT	distortionless enhanced polarization transfer
SEFT	spin-echo fourier transform
η	descriptor for hapticity
δ	chemical shifts (ppm, NMR)
NOE	nuclear overhauser effect
DMPE	1,2-bis(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$
DCPE	1,2-bis(dicyclohexylphosphino)ethane, $Cy_2PCH_2CH_2PCy_2$
PP_3	$P(CH_2CH_2PPh_2)_3$
NP_3	$N(CH_2CH_2PPh_2)_3$
NP_2	$N(SiMe_2CH_2PPh_2)_2$
TBP	trigonal bipyramidal
PH	Prentice-Hall (molecular models)
L	generalized ligand, in particular a 2e ligand
X	generalized 1e anionic ligand
m	meta
o	ortho
p	para

CHAPTER I

INTRODUCTION

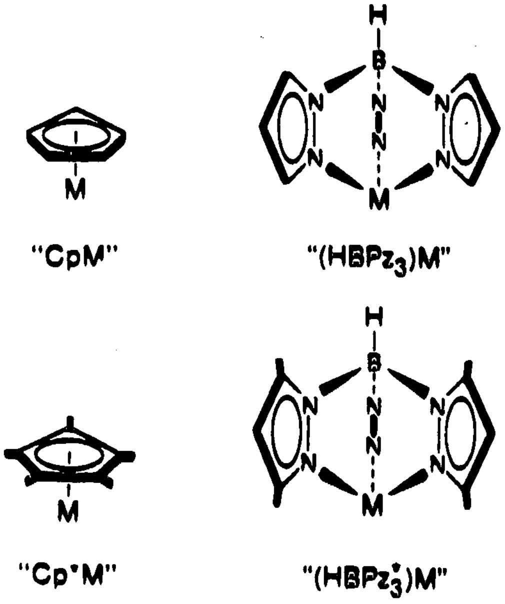
The activation of carbon-hydrogen (C-H) bonds is one of the most important areas of organometallic chemistry in the 1980's. In a recent text on organometallic chemistry,[1a] one of the historical landmarks cited was the discovery of intermolecular alkane activation in 1982. Also, the C-H bond activation reaction is embossed on the front cover design of the second edition of this text.

This Thesis describes the synthesis, characterization and reactions of model compounds for carbon-hydrogen bond activation. The first system investigates a number of tris(pyrazolyl)borate complexes of rhodium. The second type of complexes studied are platinum carborane complexes. A short discussion of the tris(pyrazolyl)borate and the carborane ligands will first be presented.

Tris(pyrazolyl)borate Ligand

The hydrotris(pyrazolyl)borate ligand was first reported by Trofimenko in 1967,[2] and is similar to the cyclopentadienide anion in its formal charge (1-) and effective occupancy of three coordination sites at the metal. Complexes with this ligand have been shown in some cases to surpass the stability and chemical diversity of their Cp analogs.[3]

The hydrotris(pyrazol-1-yl)borate anion ($HBPz_3^-$) and the hydrotris(3,5-dimethylpyrazol-1-yl)borate anion ($HBPz*_3^-$) (Pz* = 3,5 Me_2Pz) are the most widely used ligands. These have been directly compared to the cyclopentadienide anion ($C_5H_5^-$) and the pentamethylcyclopentadienide anion ($C_5Me_5^-$) respectively (eq. 1-1).

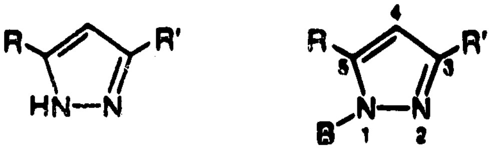


(1-1)

The above diagrams show the two tris(pyrazolyl)borate ligands bound to the metal in a tridentate manner, with C_{3v} symmetry, as two of the Pz groups are coming out of the page and the third is pointing back into the page. For convenience, the latter group is presented as a vertical "N-N", but all three Pz rings are the same <u>in this Thesis</u>.

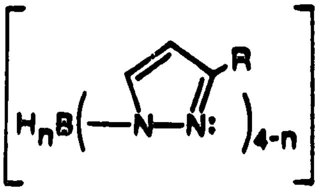
The tris(pyrazolyl)borate ligand differs from the cyclopentadienide ligand[4] in that it can commonly bind to a transition metal in either a bidentate or tridentate manner, especially for rhodium and iridium. Cotton developed a system for specifying the hapticity of a given carbocyclic ligand to a metal.[5] The hapticity is represented by a superscript after the Greek letter η or eta, which equals the number of ligand atoms bound to the metal. Hence, if Cotton's system is extended to non-carbocyclic ligands (η^2-HBPz$_3$)M represents a bidentate tris(pyrazolyl)borate metal complex, whereas (η^3-HBPz$_3$)M represents the tridentate equivalent.

Although the Cp and Cp* ligands are most commonly used in cyclopentadienyl chemistry, a number of derivatives have been prepared.[4] In the same manner, this has recently begun to occur with poly(pyrazolyl)borate ligands. As pointed out by Trofimenko,[3] there are potentially nine C-H bonds and one B-H bond in the tris(pyrazolyl)borate ligand that can be functionalized. The initial poly(pyrazolyl)borate ligands prepared involved symmetric pyrazoles, where R = R' (eq. 1-2).



(1-2)

Synthesis of a tris(pyrazolyl)borate ligand involving an unsymmetric pyrazole (R' ≠ R) was first reported by McCurdy in 1974 involving 3-MePzH (R = H, R' = Me).[6] More recently, Trofimenko has prepared his so-called second generation ligands of the type $[H_nB(3\text{-}RPz)_{4-n}]^-$ where R is a bulky group, such as Ph,[7] t-Bu[7] or i-Pr.[8]

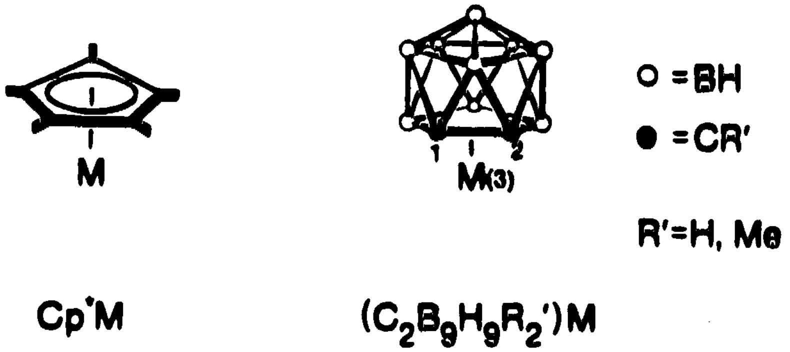


A potential problem with the use of these unsymmetric pyrazoles in the formation of poly(pyrazolyl)borate ligands is regioisomeric mixtures with the R' and R groups in both 3- and 5-positions. To date, all the literature examples are isomerically pure ligands, where the larger R or R' group occupies the 3-position. During the synthesis of these ligands, it is thought that the tetrahydridoborate ion (BH_4^-) reacts with the least sterically hindered pyrazole nitrogen.

Carborane Ligand

The synthesis of carboranes, which are boron hydride complexes containing carbon was pioneered in the early 1960's. There are a number of carboranes, but this Thesis will focus on the twelve vertex *ortho*-carborane $C_2B_{10}H_{12}$. The carborane ligand [*nido*-7,8-$C_2B_9H_9R'_2$]$^{2-}$, also referred to as the dicarbollide anion is a dinegative ligand which was prepared by Hawthorne in 1968.[9] The term *nido* refers to the fact that one vertex of the icosahedron is missing, leaving an open face to which the ligand can bind to the metal. The numbers 7 and 8 refer to the positions of the carbon atoms *in the anion only*.

The carborane anion is considered to be electronically and sterically similar to the pentamethylcyclopentadienyl anion ($C_5Me_5^-$) in transition metal complexes[10] (eq. 1-3), although the former has a formal (2-) charge, while the latter has a (1-) charge.



(1-3)

Both ligands are π-bound to a metal from an open pentagonal face. Metallacarboranes are known for a number of transition metals, and in some cases there is no known Cp analog.[11] For metallacarboranes themselves, the numbering system is slightly different (eq. 1-3). For example, in closo-3,1,2-M($C_2B_9H_9R'_2$), the 3 refers to the position of the metal and all other ligands attached to the metal, while the 1 and 2 refers to the position of the carbon atoms of the carborane cage. The term closo refers to the fact that now the metal occupies the open vertex of the carborane cage, giving a "closed" polyhedron. The numbering for the boron atoms continues from 4 to 12, but this is not pertinent to this Thesis and is not included.

Effective atomic number rule

The effective atomic number (EAN) or 18 electron (18e) rule is an effective tool for transition metal chemists to predict or rationalize the stability and reactivity of a particular complex. It originated in the 1930's and was first credited to Sidgwick and Bailey as a means to establish structures of metal carbonyl and nitrosyl compounds.[12] A transition metal itself has nine valence shell orbitals, consisting of one ns, three np and five (n-1)d orbitals. The total of 18e arises from a combination of metal valence electrons and electrons donated from the ligands surrounding the metal.

There are two conventions for counting electrons, termed the covalent and ionic models.[1] Obviously, the same results are obtained but the electrons arise formally from different sources. For the ionic model, one must consider the formal oxidation state of a metal which is obtained by removing all ligands in their closed-shell configurations. For example for the octahedral complex $Fe(CO)_4I_2$, I^- is a two-electron donor, and CO is a two-electron donor, so the metal is in the Fe(II) oxidation state, or d^6. The total electron count is (2 x 2) + (4 x 2) +

6 = 18 e. In the covalent model, I is a one-electron donor, CO is still a two-electron donor, and the metal is Fe(O) d^8, so the total electron count is (1 x 2) + (4 x 2) + 8 = 18e.

The 18e rule has many exceptions, as there are stable complexes for which the electron count is higher or lower. However, it works best for metals in low oxidation states involving high field ligands (i.e. hydrides and carbonyls.).[1] A convenient way to describe the 18e rule is by a molecular orbital description, where the atomic or molecular orbitals of the ligands and the metal are combined to make molecular orbitals of the complex.[13]

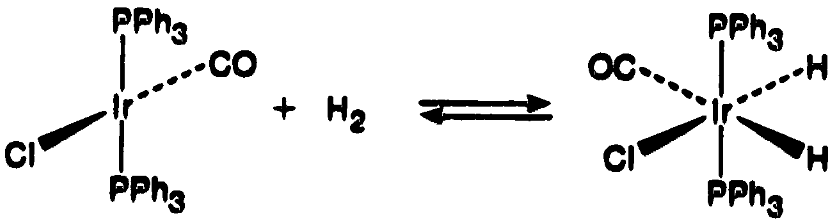
An important class of complexes do not obey the 18e rule, but only have 16e.[1] These involve the d^8 metals of Groups 8-11 and form square planar complexes. The 16e count arises from the larger energy gap between the $d_{x^2-y^2}$ orbital and the next lowest orbital for the late transition metals. Pertinent to this Thesis is the fact that Rh(I), Ir(I) and Pt(II) complexes all form predominantly 16e square planar complexes. Vaska's compound, <u>trans</u>-$ClIr(CO)(PPh_3)_2$, is such a complex. Using the ionic counting method, Cl^- is a 2e donor, as are CO and PPh_3, while the metal is Ir(I) d^8. The total electron count is (1 x 2) + (1 x 2) + (2 x 2) + 8 = 16e.

The 18e rule is useful in predicting the mechanism and reactivity of metal complexes. Two reactions frequently encountered in this Thesis are ligand substitution and oxidative addition.[1] In a ligand substitution reaction, an 18e metal carbonyl complex usually first loses a CO group (dissociating to a 16e intermediate) rather than proceeding via an associative pathway with a less stable 20e intermediate (eq. 1-4). On the other hand, a 2e donor ligand can react with a 16e complex in an associative manner, followed by loss of CO (eq. 1-5).

$$\underset{18e}{\text{M-CO}} \xrightarrow{\text{-CO}} \underset{16e}{\text{(M)}} \xrightarrow{\text{+L}} \underset{18e}{\text{M-L}} \qquad (1\text{-}4)$$

$$\underset{16e}{\text{M-CO}} \xrightarrow{\text{+L}} \underset{18e}{\left[\text{L-M-CO}\right]} \xrightarrow{\text{-CO}} \underset{16e}{\text{M-L}} \qquad (1\text{-}5)$$

The oxidative addition of a molecule X-Y to a 16e square planar complex is a common reaction. For example, Vaska's complex readily adds H_2, going from a 16e square planar to a 18e octahedral arrangement (eq. 1-6).[1]



Ir (I), d^8, 16 e Ir (III), d^6, 18e (1-6)

The oxidation state of the Ir center changes from (I) to (III), and the geometry about iridium changes from square planar to octahedral.

Carbon-hydrogen bond activation

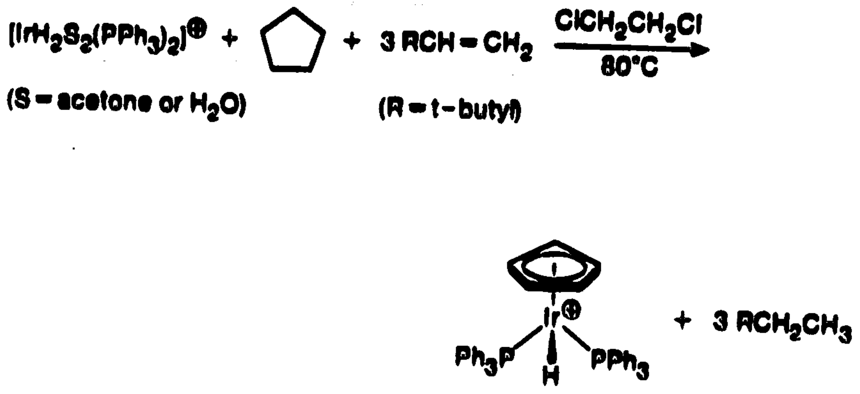
The oxidative addition of dihydrogen to Vaska's compound (eq. 1-6) was paramount among many such reactions in the 1960's. A number of other substrates, such as silanes, alkyl halides, HCl and Cl_2 were found to oxidatively add to a number of metal complexes.[1]

Interest in alkane C-H bond activation grew out of this work, and as was remarked by Halpern[14a] in 1968: "the development of successful approaches to the activation of carbon-hydrogen bonds, particularly in saturated hydrocarbons, remains to be achieved and presently constitutes one of the most important and challenging problems in this whole field [of homogeneous catalysis]".

The first examples of C-H activation occurred with orthometallation, or intramolecular activation of a C-H bond (eq. 1-7). This area has been extensively reviewed.[15]

(1-7)

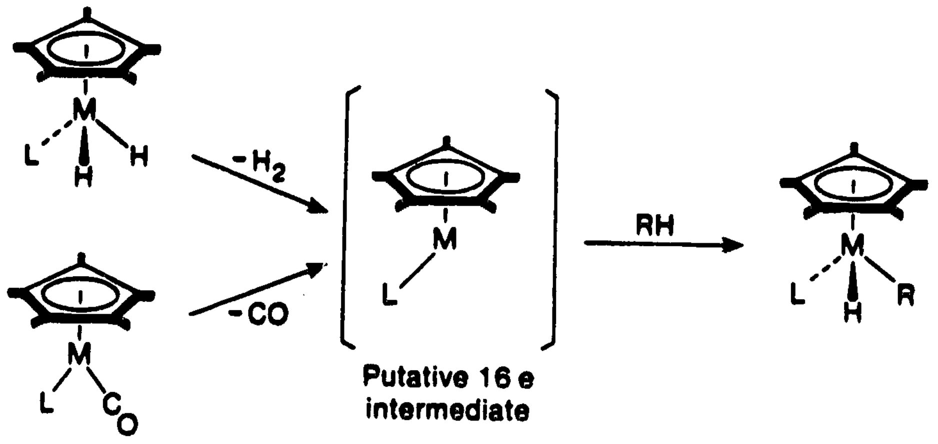
Intermolecular C-H activation was postulated to be responsible for catalytic H/D exchange of arenes and alkanes.[16] In the late 1970's, Crabtree[17] and Felkin[18] demonstrated dehydrogenation reactions of a number of alkanes which were postulated to proceed via a C-H oxidative addition reaction. For example, cyclopentane reacted with an iridium complex in the presence of a hydrogen-acceptor olefin to give a cyclopentadienyl iridium complex (eq. 1-8).[17a]



(1-8)

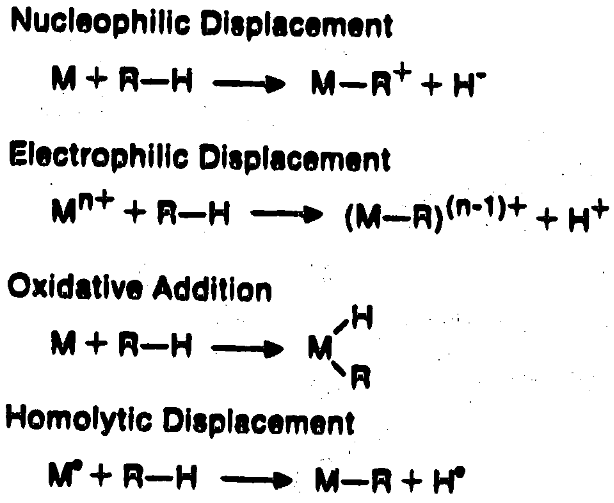
Green had earlier demonstrated thermal and photochemical arene C-H activation with Cp_2WH_2, which loses dihydrogen to give a reactive tungstenocene intermediate.[19]

The first examples of intermolecular alkane C-H activation with isolable products were provided by Bergman[20a] and Graham[21a] in 1982 with related iridium complexes. A number of arene and alkane C-H bonds were activated, with stable Ir(III) alkyl or aryl hydrides isolated (eq. 1-9, M = Ir, L = PMe_3;[20a] M = Ir, L = CO [21a]).



(1-9)

Halpern[14b] considered some of the thermodynamic and mechanistic aspects of C-H activation. He classified four main reaction types applicable to C-H activation (eq. 1-10).



(1-10)

Halpern almost immediately dismissed nucleophilic displacement and mentioned that the two most common pathways are the electrophilic displacement and oxidative addition reactions. There are now numerous examples of transition metal complexes that are capable of intermolecular C-H activation. The electrophilic displacement reaction is thought to be in operation with those systems involving lanthanides, actinides and early transition metals.[16e] On the other hand, the oxidative addition C-H activation reactions generally involve low valent late transition metal complexes. Since the initial iridium systems by Bergman and Graham, numerous other metal systems have arisen utilizing rhenium, iron, ruthenium, osmium, rhodium, iridium, palladium and platinum. Several reviews on the area of C-H activation have appeared.[16]

Table 1.I lists the transition metal complexes that have

demonstrated intermolecular C-H activation in which the primary products have been identified. Also listed is the type of C-H bond activated, the technique that was used to generate the reactive intermediate (either photochemical or thermal), the year in which the first literature report appeared and the principal author involved. The references include any subsequent work done following the initial paper.

Only those systems where the initial alkyl or aryl hydride was detected and characterized are included. This is to differentiate those systems that are thought to proceed through an alkyl or aryl hydride (Crabtree[17] and Felkin[18]) with no intermediate detected. More recently, Tanaka has demonstrated catalytic arene and alkane C-H activation using $ClRh(CO)(PMe_3)_2$; no intermediate was detected, but functionalization of the C-H bond occurred.[24]

The many interesting reactions of $Cp^*Ir(CO)_2$, especially with reference to C-H activation,[21] prompted the synthesis of other related complexes. Hawthorne and coworkers[9] have pointed out the similarity between the carborane and cyclopentadienide ligands. This prompted the synthesis of neutral carborane analogs, and because of the ligand charge difference, the use of Pt(II) in place of Ir(I) would lead to neutral platinacarborane complexes. The successful synthesis of such complexes was initially carried out, but these were inert to C-H bond activation.

At about the same time as the synthesis of the platinacarborane complexes, C.K. Ghosh[25] in this research group demonstrated the successful use of the tris(pyrazolyl)borate complex $(HBPz^*_3)Rh(CO)_2$ for C-H bond activation. This has prompted further research in related systems. With the parent complex $(HBPz^*_3)Rh(CO)_2$ either the metal, the donor ligands or lastly the tris(pyrazolyl)borate ligand can be

Table 1.I Intermolecular Carbon-Hydrogen Bond Activation

Complex	R-H	Technique[a]	Year	Principal Author	Reference
$Cp^*Ir(PMe_3)H_2$	b	$h\nu$	1982	R.G. Bergman	20
$Cp^*Ir(CO)_2$	b	$h\nu$	1982	W.A.G. Graham	21
$Cp^*Rh(PMe_3)H_2$	b	$h\nu$	1982	W.D. Jones	22
$(C_6H_6)Ru(P(i\text{-}Pr)_3)H_2$	benzene	$h\nu$	1983	H. Werner	23a
$(arene)Os(PMe_3)(C_2H_4)$	benzene	Δ	1985	H. Werner	23b
$CpRe(PMe_3)_3$	b	$h\nu$	1985	R.G. Bergman	27
$Cp^*Ir(allyl)(H)$	benzene	Δ	1985	R.G. Bergman	28
$ClIr(P(i\text{-}Pr)_3)_2$	benzene	Δ	1986	H. Werner	23c
$(DCPE)Pt(Np)(H)$[c,d]	b	Δ	1986	G.M. Whitesides	29
$HRe(PPh_3)_3L_2$	b	$h\nu$	1986	W.D. Jones	30
$(PMe_3)_4Os(Np)(H)$[d]	benzene	Δ	1986	T.C. Flood	31
$(C_6Me_6)Os(CO)H_2$	b	$h\nu$	1986	W.A.G. Graham	21d
$(DMPE)_2FeH_2$[e]	pentane	$h\nu$	1987	L.D. Field	32

continued ...

Table 1.I Continued

Complex	R-H	Technique[a]	Year	Principal Author	Reference
$(NP_2)Ir(COE)^f$	toluene	Δ	1987	M.D. Fryzuk	33
$(NP_3)Rh,^g\ (PP_3)Ir^h$	arene	Δ	1987	C. Bianchini	34
$(HBPz^*_3)Rh(CO)_2$	b	hν,Δ	1987	W.A.G. Graham	25
Cp*Ir(CO)(ArCN)	b	hν,Δ	1987	M.F. Hawthorne	35

a Method used to generate reactive intermediate; hν, photochemical; Δ, thermal.

b Both alkanes and arenes were activated.

c DCPE = $Cy_2PCH_2CH_2PCy_2$

d Np = neopentyl

e DMPE = $Me_2PCH_2CH_2PMe_2$

f NP_2 = $N(SiMe_2CH_2PPh_2)_2$

g NP_3 = $N(CH_2CH_2PPh_2)_3$

h PP_3 = $P(CH_2CH_2PPh_2)_3$

altered. Analogous iridium complexes have been prepared in this research group by Dr. J.K. Hoyano.[26] Ghosh also prepared complexes of the type $(HBPz^*_3)Rh(CO)(L)$ where L = olefin or tertiary phosphine to study the differences in reactivity from L = CO.[25a] A number of different bis and tris(pyrazolyl)borate rhodium dicarbonyl complexes were prepared in this Thesis, as well as a number of related derivatives. These were shown to successfully activate C-H bonds, but differences were observed in comparison to the parent complex $(HBPz^*_3)Rh(CO)_2$.

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CHAPTER II

PHENYL(PYRAZOLYL)BORATE RHODIUM COMPLEXES

Section 1

INTRODUCTION

Poly(pyrazol-1-yl) borate ligands of the type ($H_nB(Pz)_{4-n}^-$) (n=0,1,2) were first prepared by Trofimenko in 1967.[1a] The synthesis of the related dihydrobis(3,5-dimethylpyrazol-1-yl)borate anion ($H_2BPz*_2^-$) and the hydrotris(3,5-dimethylpyrazol-1-yl)borate anion ($HBPz*_3^-$) soon followed (Pz* = 3,5-Me_2Pz).[1b] The hydrotris(pyrazol-1-yl) borate anion ($HBPz_3^-$) is formally related to the cyclopentadienide anion ($C_5H_5^-$), in that it is a six-electron uninegative donor which formally occupies three coordination sites, and in the same manner ($HBPz*_3^-$) is related to the pentamethylcyclopentadienide anion ($C_5Me_5^-$).[2]

The class of hydrotris(pyrazol-1-yl)borate ligands differ from the cyclopentadienyl ligand in that they can be bidentate or tridentate on coordination. This would be analogous to a cyclopentadienyl ligand bonding in either a η^3-C_5H_5 or η^5-C_5H_5 manner on a metal. Of course, the latter bonding mode is most commonly observed, with a η^3-C_5H_5 intermediate postulated in some reactions or structurally characterized in a few complexes.[3]

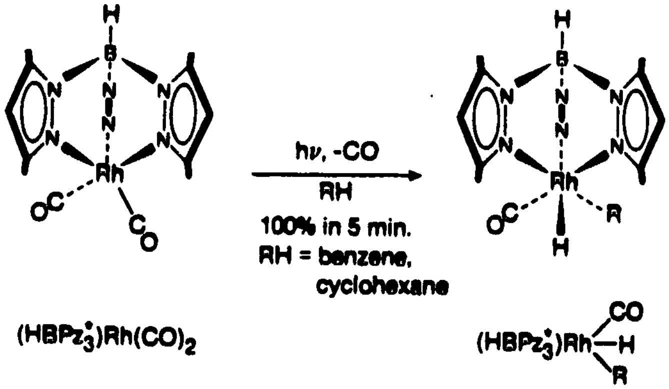
The dihydrobis(pyrazolyl)borate anions ($H_2BPz_2^-$) and ($H_2BPz*_2^-$) can be compared to the (acac$^-$) ligand, (acac is the acetylacetonate anion) in that they are four-electron uninegative donors occupying two coordination sites.[4]

Pyrazolylborate rhodium complexes containing carbonyl or olefin groups are relatively abundant in the literature.[5] Trofimenko prepared ($HBPz_3$)$Rh(C_2H_4)_2$,[6a] and found that all three Pz groups were equivalent on the NMR timescale. He proposed that the complex resembled (acac)Rh(C_2H_4)$_2$ more closely than (C_5H_5)Rh(C_2H_4)$_2$, and that some fluxional process was involved to average all three Pz ligands.

Trofimenko later prepared (HBPz*$_3$)Rh(COD) and (HBPz*$_3$)Rh(CO)$_2$ which were both fluxional by NMR spectroscopy.[6b] With the (HBPz$_3^-$) ligand, an intractable complex [(HBPz$_3$)$_2$Rh$_2$(CO)$_3$]$_n$ was obtained.[7d] More recently, Cocivera and coworkers have prepared a series of compounds of the type (BPz$_4$)Rh(diene), which were characterized by NMR spectroscopy and X-ray crystallography.[7]

In this research group, Ghosh investigated the chemistry of (HBPz*$_3$)Rh(CO)$_2$,[8a,9] first reported by Trofimenko,[6b] and later by Powell et al.[10] Ghosh and Rodgers also prepared a series of mixed carbonyl-olefin complexes of the type (HBPz*$_3$)Rh(CO)(η^2-olefin) (olefin=ethylene, propylene and cyclooctene) and studied their fluxional behaviour as well as subsequent chemistry.[8b,c,9] These latter complexes were proposed to be four-coordinate and fluxional in solution.

The first example of the use of pyrazolylborate metal complexes in carbon-hydrogen bond activation was provided by Ghosh and Graham,[8a] who used the complex (HBPz*$_3$)Rh(CO)$_2$ to efficiently activate a wide variety of C-H bonds (eq. 2-1).



(2-1)

The successful use of this complex in this research group has stimulated the synthesis of other pyrazolylborate rhodium carbonyl complexes. Trofimenko and coworkers have recently prepared so-called second generation ligands $[H_nB(3\text{-}RPz)_{4-n}]^-$, (n=0,1,2) where the R group is a bulky substituent, such as tert-butyl (t-Bu) or phenyl (Ph).[11] Due to the steric bulk of these ligands, only half sandwich transition metal complexes were formed, instead of the typical ferrocene-type sandwich analogs.

This Thesis will focus on the preparation of various tris(pyrazolyl)borate rhodium complexes with differing steric and electronic characteristics. The goal is to obtain more selective C-H activation, for example the activation of small molecules in the presence of larger solvent molecules. This Chapter describes the synthesis and characterization of complexes of the type $H_nB(3\text{-}PhPz)_{4-n}Rh(CO)_2$ (n=1,2). The formation of these complexes will be discussed and the X-ray structure of the complex with n=1 will be described.

Carbon-hydrogen bond activation of this latter complex resulted in orthometallation of a phenyl group. Reactions of this initial photoproduct will be discussed. The related olefin complexes are prepared and some reactions are presented. The tris(pyrazolyl)borate Rh(I) complexes exhibit some unique fluxional properties involving four- and five-coordinate species.

Section 2

SYNTHESIS AND PROPERTIES OF RHODIUM COMPLEXES

The synthesis of the bis and tris(pyrazolyl)borate rhodium complexes are similar to others reported previously, for example the preparation of $(HBPz^*_3)Rh(CO)_2$ by Powell et al.,[10] except that toluene is used as a solvent instead of benzene.[9] The dimer $[(CO)_2RhCl]_2$[12] was reacted with two equivalents of $KHB(3\text{-}PhPz)_3$[11] in toluene, resulting in a near quantitative yield of $HB(3\text{-}PhPz)_3Rh(CO)_2$ (1) as yellow crystals (eq. 2-2).

$$\left.\begin{array}{c}[ClRh(CO)_2]_2\\ +\\ K[HB(3\text{-}PhPz)_3]\end{array}\right\}\xrightarrow[25°C]{\text{toluene}} HB(3\text{-}PhPz)_3Rh(CO)_2 \qquad (2\text{-}2)$$

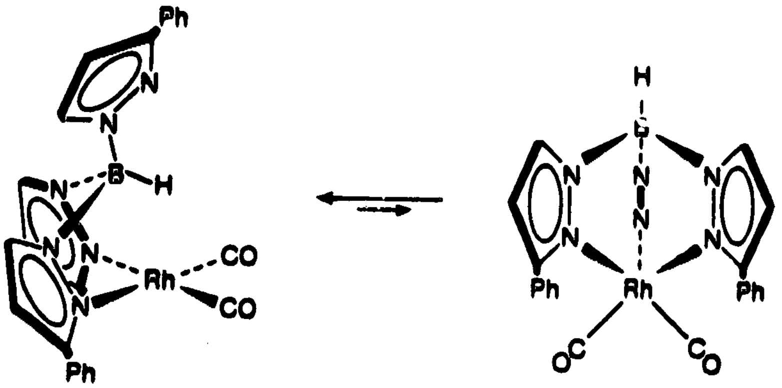
1

As observed with $(HBPz^*_3)Rh(CO)_2$, 1 does not survive chromatography on neutral alumina. However, unlike $(HBPz^*_3)Rh(CO)_2$,[9] 1 is air stable as a solid or in solution. Dicarbonyl 1 was fully characterized by elemental analysis and spectroscopic methods. The MS shows the molecular ion M^+ at m/e = 600, although it is weak (5% relative intensity). Ions at m/e = 572 (35%), 544 (44%) and 400 (100%) result from the stepwise loss of CO and a 3-PhPz group.

Nature of $HB(3\text{-}PhPz)_3Rh(CO)_2$ (1) in Solution

In solution, 1 is expected to have either a five-coordinate 18e structure η^3-$HB(3\text{-}PhPz)_3Rh(CO)_2$ 1-η^3 or a four-coordinate 16e structure η^2-$HB(3\text{-}PhPz)_3Rh(CO)_2$ 1-η^2. The infrared metal carbonyl bands of the five-coordinate form should be to lower wavenumber than the four-coordinate form, as coordination of the third basic pyrazole group will place more electron density on the metal center. This results in more backbonding to the CO antibonding orbitals, weakening the bond and lowering its stretching frequency. Of course, unless the complex exists as a mixture of the two forms the absolute IR band positions alone may not be an indication of the hapticity.

Figure II.1 shows the IR spectrum of 1 in cyclohexane with ν_{CO} bands at 2088 (s), 2079 (w), 2026 (s), 2015 (w) cm^{-1}. Assuming this spectrum demonstrate a mixture of the two isomers, 1 is predominantly 1-η^2 (2088, 2026 cm^{-1}), in equilibrium with a small amount of 1-η^3 (2079, 2015 cm^{-1}) (eq. 2-3).



(2-3)

η^2-$HB(3\text{-}PhPz)_3Rh(CO)_2$
16 electrons
1-η^2

η^3-$HB(3\text{-}PhPz)_3Rh(CO)_2$
18 electrons
1-η^3

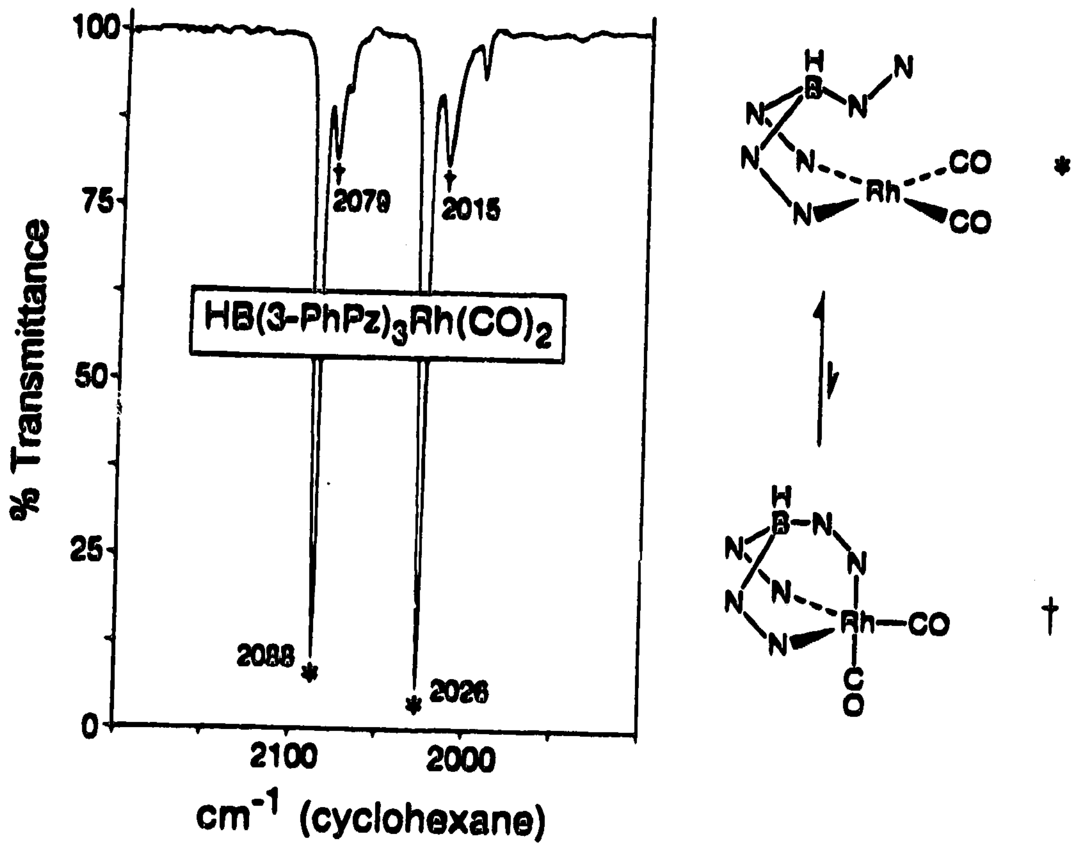


Figure II.1 Infrared Spectrum of HB(3-PhPz)$_3$Rh(CO)$_2$ (1)

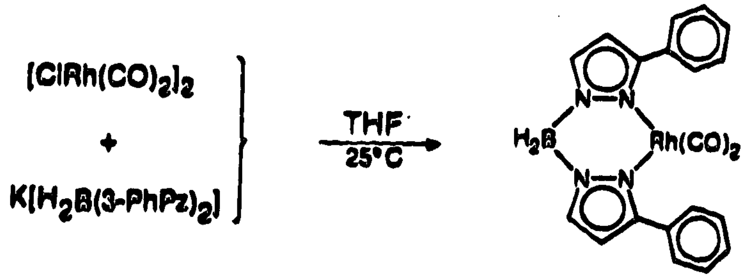
As is evident from the IR spectrum of 1, the strong higher energy bands are quite sharp while the pair of weak bands are broad. As a result of the differing band widths, the absorbance values are not directly proportional to the total area. An approximate ratio of the two forms is obtained from the relative integrated areas of the IR absorbance spectra. This was achieved using a modified procedure from Schoenberg and Anderson,[13] where the areas underneath the absorbance bands were calculated. Using two related methods one obtains an average ratio of $\eta^2:\eta^3 = 84:16\%$ in cyclohexane (see Section 6 for experimental details).

The equilibrium position of the two forms in the IR spectrum varies with solvent, with polar solvents giving more of the η^3 form. In toluene, the ratio is $\eta^2:\eta^3 = 77:23\%$, while in CH_2Cl_2 it is $\eta^2:\eta^3 = 71:29\%$.

The tris(pyrazolyl)borate complex $(HBPz^*_3)Rh(CO)_2$ was found to be entirely η^3 in hexane, with IR bands at ν_{CO} 2054, 1981 cm^{-1}.[9] This assignment was based on the assumption that the IR band positions of the η^2 form of $(HBPz^*_3)Rh(CO)_2$ should be close to those of the related bis(pyrazolyl)borate complex $(H_2BPz^*_2)Rh(CO)_2$. The IR band positions for the latter complex are considerably higher in energy, with ν_{CO} at 2079, 2013 cm^{-1}. These bands themselves are quite sharp in comparison to those of $(HBPz^*_3)Rh(CO)_2$, which is perhaps indicative of fluxional behaviour in the latter.

The predominance of the η^2 form of 1 is thought to arise from the greater steric bulk of the phenyl groups around the rhodium center, which can accommodate all three pyrazole ligands only with difficulty. The trend to more of the η^3 form in polar solvents is opposite to that found for $(HBPz^*_3)Rh(CO)_2$, which showed a small amount of the η^2 form in CH_2Cl_2.[9]

The bis(pyrazolyl)borate complex $H_2B(3\text{-}PhPz)_2Rh(CO)_2$ (**2**) was prepared in a manner similar to that of 1, but in only 33% yield (eq. 2-4).



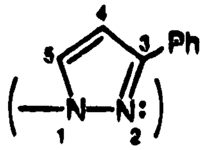
(2-4)

2

The addition of $KH_2B(3\text{-}PhPz)_2$ to the yellow THF solution of $[(CO)_2RhCl]_2$ immediately caused the solution to darken. This is a common occurrence during the preparation of most of the bis(pyrazolyl)borate complexes in this Thesis and was also observed during the preparation of $(H_2BPz^*_2)Rh(CO)_2$.[9] Trofimenko found that the bis(pyrazolyl)borate ligands were better reducing agents than the tris(pyrazolyl)borate analogs,[1] so perhaps some of the Rh(I) dimer is being reduced to rhodium metal which would decrease the yield of product. For example, many $[H_2BPz_2]^-$ derivatives of Pd(II) or Au(I) decompose as they are formed by reduction to the metal.[5b]

As discussed above, the IR bands of 2 should be close to those of η^2-$HB(3\text{-}PhPz)_3Rh(CO)_2$. The IR spectrum of 2 in cyclohexane has ν_{CO} bands at 2087, 2023 cm^{-1}, virtually the same as the η^2 form of 1 (2088, 2026 cm^{-1}). When one compares the IR spectra of 2 and $(H_2BPz^*_2)Rh(CO)_2$,[9] the ν_{CO} bands of the former are an average of 9 cm^{-1} to higher frequency, indicating that the 3-PhPz group is a weaker electron donor than the Pz* group.

The ^1H NMR spectrum of 2 shows one type of pyrazole group, as the two rings are equivalent by mirror plane symmetry. The 5-H and 4-H resonances appear as doublets at δ 7.68 (2H, $^2J_{H-H}$ = 2.2 Hz) and δ 6.47 (2H, $^2J_{H-H}$ = 2.2 Hz) respectively. The aromatic protons consist of two multiplets at δ 7.96-7.91 (4H, ortho) and δ 7.64-7.52 (6H, meta and para). The B-H protons appear as a very broad resonance from δ 5.0-2.6 (2H) caused by the large quadrupole moment of ^{11}B.



Numbering for NMR

At room temperature all the resonances in the ^1H NMR spectrum of 1 in CD_2Cl_2 are broad, indicative of fluxional behaviour. However, on cooling the sample to -30°C, three sets of 5-H and 4-H protons are observed. Figure II.2 shows the 4-H proton region, with two of the resonances in a 2:1 ratio. These are thought to correspond to the η^2 form of 1, while the third set of resonances is the η^3 form. As the latter is five-coordinate, the pyrazole groups are presumably averaged by a Berry type pseudorotation or turnstile rotation. From the integration of the 5-H and 4-H resonances of the two forms, one obtains a ratio of $\eta^2:\eta^3$ = 43:57%. It is clear that at -30°C, the kinetic

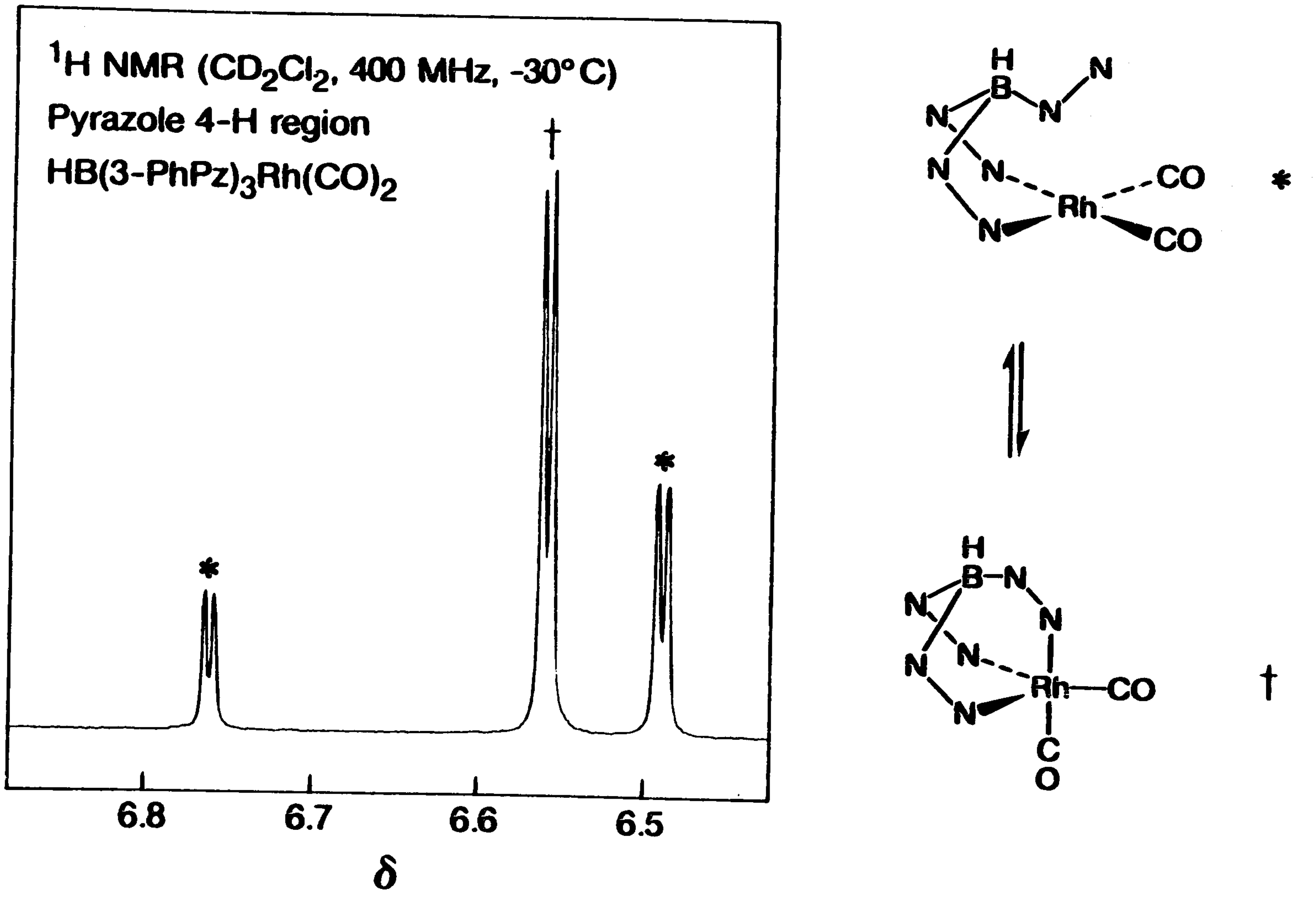


Figure II.2 ^{1}H NMR Spectrum of HB(3-PhPz)$_3$Rh(CO)$_2$ (1) at -30°C barrier for interconversion is large enough to enable both equilibrium forms to be observed by NMR.

Selective decoupling experiments of the 5-H and 4-H protons confirmed the assignment of the two forms. For example, irradiation of the 5-H doublet of the η^3 form at δ 7.80 caused the doublet at δ 6.56 to collapse to a singlet. In a qualitative spin saturation experiment at -30°C, after irradiation of the δ 7.80 doublet the difference spectrum showed a very rapid spin transfer from the η^3 to the η^2 form.

This interpretation is consistent with the ^{13}C NMR spectrum obtained using the attached proton test (APT).[14a] In CD_2Cl_2 at room temperature, the CO resonance is a sharp doublet at δ 183.68 ($^1J_{Rh-C}$ = 69 Hz), but the remaining resonances are broad. On cooling to -30°C, one observes two CO resonances as doublets in a 42:58% ratio, with the η^3 form at δ 183.52 ($^1J_{Rh-C}$ = 69 Hz) and the η^2 form at δ 183.18 ($^1J_{Rh-C}$ = 69 Hz). The remainder of the spectrum also shows three resonances for each type of carbon with similar percent ratios (Table 2.III).

The ^1H NMR spectrum of 1 in toluene-d_8 at -30°C also shows both forms, but with a ratio of $\eta^2:\eta^3$ = 69:31%. This is consistent with the trend of more of the η^2 form in less polar solvents as also observed in the IR spectra. When the NMR sample is warmed to +92°C, the ^1H NMR spectrum shows one type of pyrazole group, as the rate of isomerization is now fast on the NMR timescale. Due to the low solubility of 1 in cyclohexane-d_{12}, the low temperature ^1H NMR spectrum could not be obtained.

The above fluxional process is the first example in which a tris(pyrazolyl)borate complex demonstrates the existence of both η^2 and η^3 isomers in the low temperature limiting spectrum. In contrast, the

^1H NMR spectrum of $(HBPz^*_3)Rh(CO)_2$ shows only one type of pyrazole group down to -90°C.[9] The steric size of the tris(pyrazolyl)borate ligand in 1 must lead to a higher activation barrier for this isomerization such that it is observed on the NMR timescale.

It should be pointed out that the ratios of the two forms differ from the IR and NMR data. Table 2.I compares the IR and NMR isomer ratios obtained for 1. Of course the equilibrium constants are temperature dependent, with more of the η^3 form present at lower temperature. For the equilibrium $\eta^2 \rightleftharpoons \eta^3$ as written, one would expect $\Delta H°$ to be negative, as this corresponds to formation of the third nitrogen to rhodium bond. With the two equilibrium isomer ratios at 25°C (298K) and -30°C (243K), some simple thermodynamic parameters can be calculated.

From the data in Table 2.I, equilibrium constants can be calculated. In CH_2Cl_2 (CD_2Cl_2), $K_{298} = 29/71 = 0.41$, while $K_{243} = 57/43 = 1.33$. Using the van't Hoff equation,[15] one can calculate $\Delta H°$ to be -2.95 kcal and $\Delta S° = -11.6$ cal K^{-1}. As predicted, $\Delta H°$ is negative, and one would also expect $\Delta S°$ to be negative. The η^3 form is more ordered than the η^2 form, the latter which has a dangling pyrazole group with more degrees of freedom. In toluene (toluene-d_8), $K_{298} = 23/77 = 0.299$, while $K_{243} = 31/69 = 0.449$. The corresponding values of $\Delta H°$ and $\Delta S°$ are calculated to be -1.07 kcal and -6.0 cal K^{-1} respectively. Given the different solvents, the two sets of values are fairly close.

The same phenomenon of equilibrium between η^2 and η^3 forms is also observed with olefin complexes prepared in Section 5. Tables 2.II and 2.III present the ^1H and ^{13}C NMR data for 1 and Table 2.IV compares the NMR isomer ratios of 1 with other Rh(I) complexes.

Table 2.I IR and NMR Isomer Ratios of $HB(3\text{-}PhPz)_3Rh(CO)_2$ (1)

Technique	Solvent	Temperature	Ratio ($\eta^2:\eta^3$)
IR (weight)[a]	cyclohexane	ambient	83:17 (±1%)
IR (CAPS)[b]	cyclohexane	ambient	85:15 (RMS=4.42)[c]
IR (weight)[a]	toluene	ambient	77:23 (±1%)
IR (CAPS)[b]	toluene	ambient	77:23 (RMS=3.38)[c]
IR (weight)[a]	CH_2Cl_2	ambient	70:30 (±1%)
IR (CAPS)[b]	CH_2Cl_2	ambient	72:28 (RMS=3.94)[c]
NMR (400 MHz)	CD_2Cl_2	-30°C	43:57
NMR (400 MHz)	toluene-d_8	-30°C	69:31

(a) weight refers to method (a) in Experimental Section

(b) CAPS refers to method (b) in Experimental Section

(c) RMS = root mean square error

The solid state X-ray structure determination of 1 was carried out by Dr. R.G. Ball of this department. Details of the data collection and refinement procedure as well as tables of structural parameters, bond lengths and bond angles will be found in the Experimental Section. Two views of the structure of 1 are shown in Figures II.3 and II.4.

The geometry around the rhodium atom is square planar, with two of the three 3-PhPz groups coordinated to the rhodium center. The six-membered ring is in a boat configuration, as commonly observed for such η^2-pyrazolylborate complexes.[5] The free 3-PhPz group is formally in the equatorial position of the boat form of the six-membered ring, and definitely non-bonding with the free nitrogen N7 a long distance from the Rh center.

In some cases, the structure in solution will have a different denticity of the tris or tetrakis(pyrazolyl)borate ligand than found in the crystal structure.[5b] For example the ^{1}H NMR spectrum of $(BPz_4)Rh(COD)$ suggests that it is five-coordinate in solution, whereas the X-ray crystal structure showed it to be four-coordinate.[7] However, for complex 1, the IR and low temperature ^{1}H and ^{13}C NMR spectra are in agreement with the static structure found in the crystal.

Mechanism of $HB(3\text{-}PhPz)_3Rh(CO)_2$ Formation - Some Speculation

In the preparation of 1, a second minor product (14%) was isolated and determined to be $[(CO)_2Rh(3\text{-}PhPz)]_2$ (3), whose identity was confirmed by comparison of IR, ^{1}H NMR and mass spectra to an authentic sample of 3. Compound 3 is representative of a well known class of pyrazole-bridged dimers.[5,16] The IR spectrum in cyclohexane has the expected three ν_{CO} bands at 2089, 2076, 2023 cm^{-1}, and the MS shows the

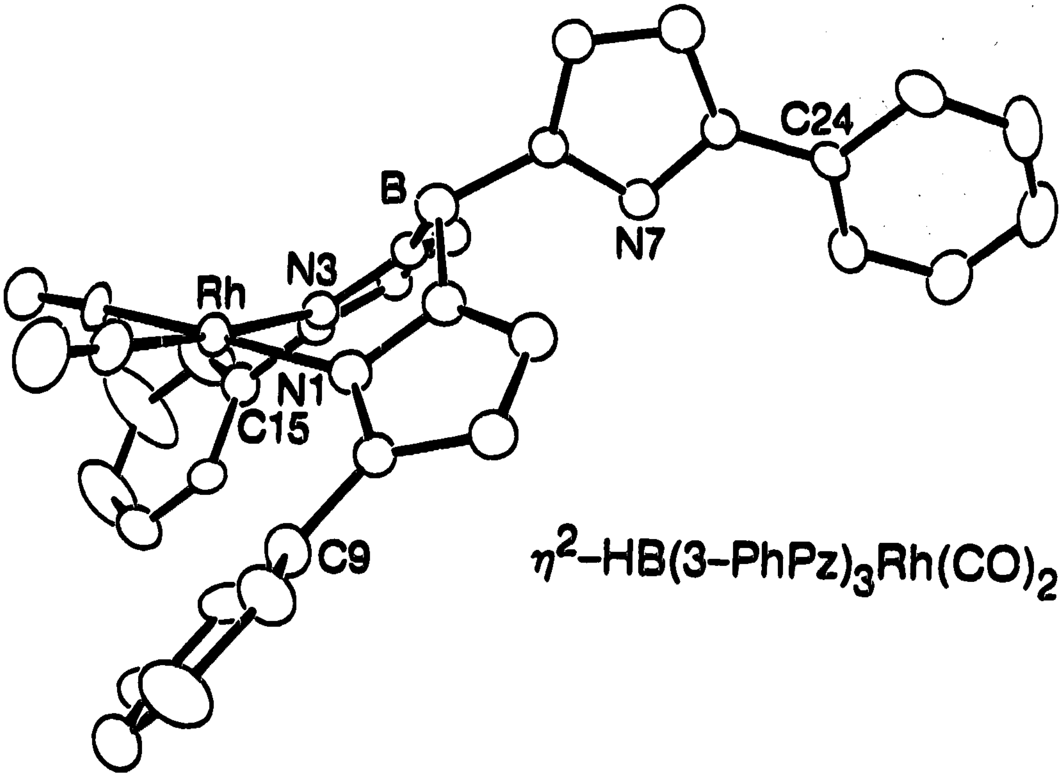


Figure II.3 Crystal Structure of HB(3-PhPz)$_3$Rh(CO)$_2$ (1)

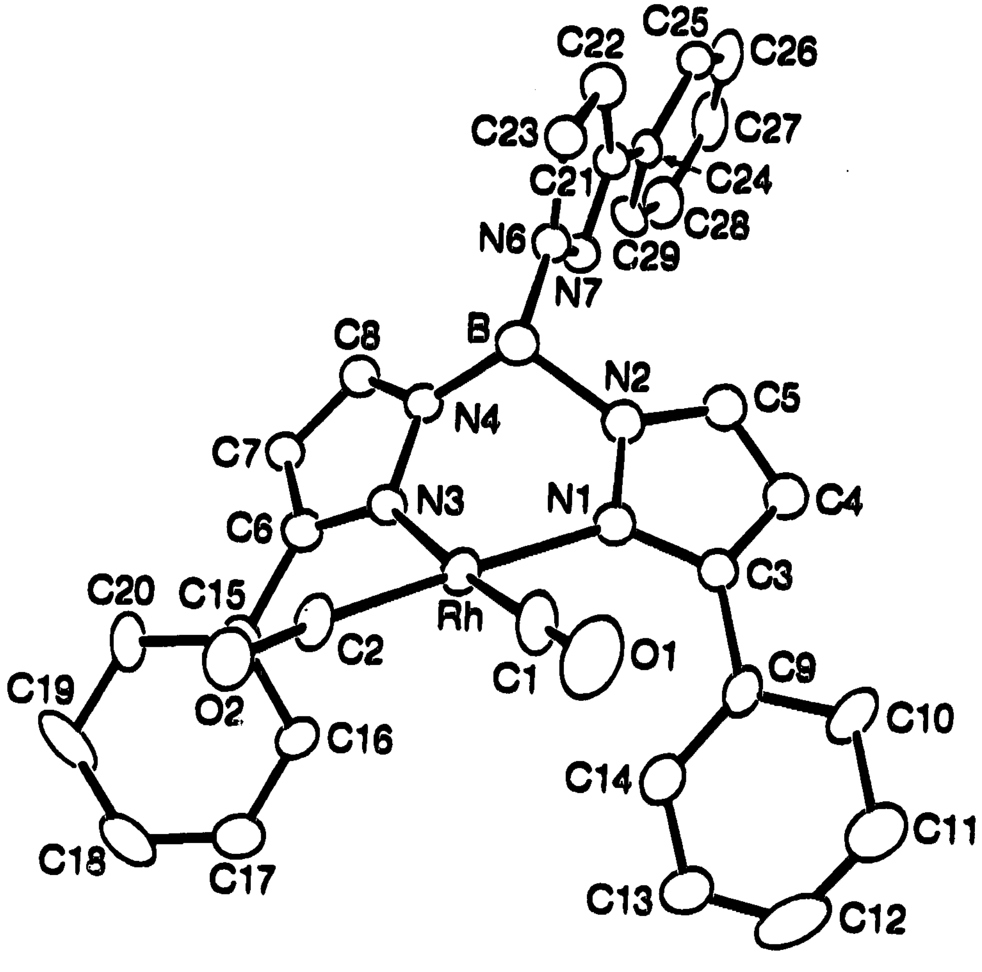
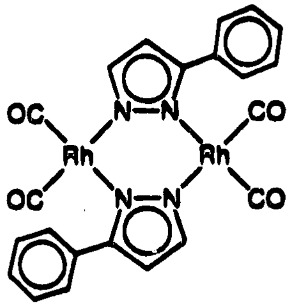
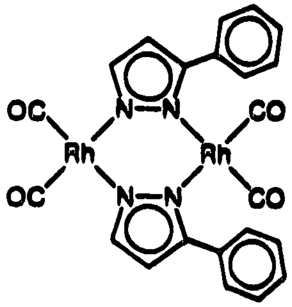


Figure II.4 Front View of Dicarbonyl (1) molecular ion M^+ at m/e=604, followed by sequential loss of four CO groups. Unlike the symmetrical dimer $[(CO)_2RhPz^*]_2$,[16] 3 can exist as a mixture of cis and trans isomers (eq. 2-5). The ^{1}H NMR spectrum shows two sets of pyrazole resonances in a ratio of 1.23:1. Based on Prentice Hall (PH) molecular models, the cis isomer 3c is sterically more crowded, so the major structure of 3 has been tentatively assigned to the trans isomer 3t.



3t



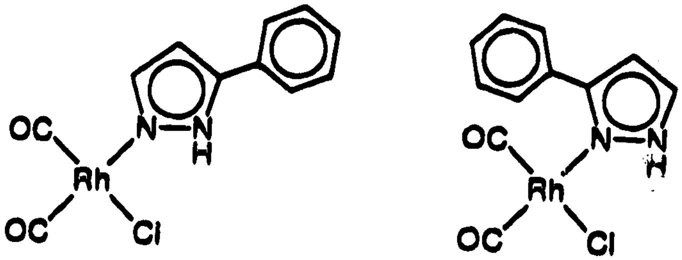
3c

(2-5)

It has been suggested by Powell and co-workers that in the preparation of $(HBPz^*_3)Rh(CO)_2$, the presence of unreacted Pz*H in $KHBPz^*_3$ results in the formation of $[(CO)_2RhPz^*]_2$.[10] However, in the salt $KHB(3\text{-}PhPz)_3$ there is no 3-PhPzH present by ^{1}H NMR. In a small scale preparation of 1, excess 3-PhPzH was added, with no increase in the amount of 3 formed.

In fact, 3-PhPzH reacts with $[(CO)_2RhCl]_2$ to give $ClRh(CO)_2(3\text{-}PhPzH)$ (4), where the chlorine bridge is split by the pyrazole nitrogen.

Compound 4 is a purplish-green solid but gives pale yellow solutions in organic solvents. It was also formed in trace amounts in the preparation of 1, where it was identified by its intense purple color and IR spectrum which in cyclohexane shows ν_{CO} at 2087, 2012 cm^{-1}. There are two possible isomeric structures for 4 (eq. 2-6).


(2-6)

Two possible isomers of 4

The ^{1}H NMR spectrum has a resonance at δ 12.34 (br, 1H), which is typical of a nitrogen-bound proton, but the 5-H and 4-H resonances are broad. This indicates a fluxional process exchanging the two nitrogen atoms.

The PzH and Pz*H analogs were prepared by Borkett and Bruce,[17a] who found a fluxional NMR process exchanging the two nitrogens between the rhodium atom. A crystal structure of the PzH complex by Stobart and coworkers[17b] showed a stacking of the square planar metal units along the z-axis, with a zig-zag chain of metal atoms.

Compound 4 is a member of the well known class of compounds of the type $ClRh(CO)_2L$ first prepared by Vallarino,[17c] where L is ammonia or an amine. These complexes exhibit a striking variety of colors in the solid state, which is thought to be due to a metal-metal interaction along the d_{z^2} axis. As Vallarino pointed out, complexes of the type $ClRh(CO)_2L$ react in a similar manner to $[(CO)_2RhCl]_2$. In fact, 4 reacts with $KHB(3\text{-}PhPz)_3$ to give 1 and 3 in the same relative amounts as found beginning with $[(CO)_2RhCl]_2$. However, reaction of 4 with NEt_3 in CH_2Cl_2 gives exclusively 3 (eq. 2-7).

This suggests that the ligand $KHB(3\text{-}PhPz)_3$ is not a strong enough base to formally remove HCl from 4 to give the dimer 3. The presence of 3 during the preparation of 1 is thought to arise from a B-N bond cleavage of the $[HB(3\text{-}PhPz)_3]^-$ ligand as suggested by Borkett and Bruce,[17a] and not from any free 3-PhPzH present.

$$\underset{\mathbf{4}}{ClRh(CO)_2(3\text{-}PhPzH)} \xrightarrow[CH_2Cl_2]{NEt_3} \underset{\mathbf{3}}{[(3\text{-}PhPz)Rh(CO)_2]_2} \qquad (2\text{-}7)$$

Section 3

REACTIONS OF $HB(3-PhPz)_3Rh(CO)_2$ (1)

Reaction with ^{13}CO

It is well known that most 18e complexes do not exchange ^{13}CO readily, while 16e square planar Rh(I), Ir(I) and Pt(II) complexes rapidly do so.[18] These latter reactions were found to proceed via an associative mechanism.[18b]

A solution of 1 in cyclohexane rapidly reacts with one atmosphere of ^{13}CO, resulting in complete exchange in about five minutes. The enriched IR spectrum shows ν_{CO} bands at 2039 (s), 2030 (w), 1980 (s), 1969 (w) cm^{-1}. The MS now shows the molecular ion M^+ at m/e = 602, with secondary ions corresponding to loss of ^{13}CO.

In contrast, the complex $(HBPz^*_3)Rh(CO)_2$, which is exclusively η^3 in hexane,[9] shows no ^{13}CO exchange in four hours. In CH_2Cl_2, where there is a small amount of the 16e η^2 form present, slow ^{13}CO exchange takes place with complete enrichment in 18 hours. However, a CH_2Cl_2 solution of the protonated complex, $[(HBPz^*_2)(Pz^*H)Rh(CO)_2](BF_4)$[8d] exchanges ^{13}CO completely in five minutes. The latter complex is exclusively in the η^2 16e form, as the proton blocks the third pyrazole group from coordination.

The major form of 1 in cyclohexane is the 16e η^2 isomer, which accounts for the rapid ^{13}CO exchange. The bis(pyrazolyl)borate complex **2**, which of course is 16e, rapidly exchanges ^{13}CO in cyclohexane with IR ν_{CO} bands at 2038, 1978 cm^{-1} after five minutes.

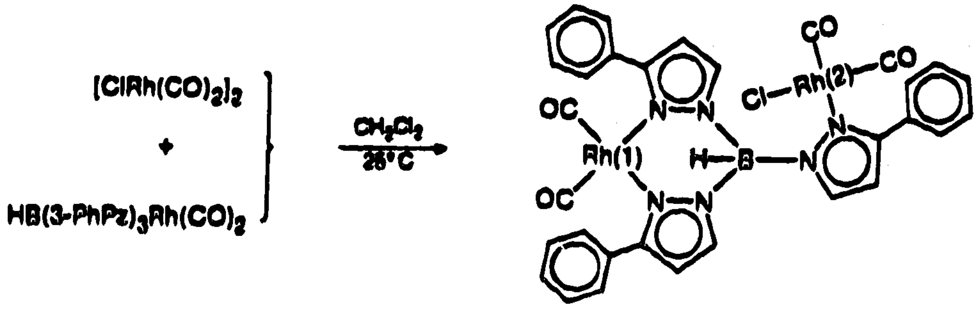
To study the intermolecular CO exchange, equal amounts of $HB(3-PhPz)_3Rh(^{12}CO)_2$ **1-12,12** and $HB(3-PhPz)_3Rh(^{13}CO)_2$ **1-13,13** were dissolved in cyclohexane. Exchange took place, with the appearance of the mixed isotopomer $\mathrm{HB(3\text{-}PhPz)_3Rh(^{12}CO)(^{13}CO)}$ **1-12,13**. An almost 1:2:1 equilibrium distribution of the isotopomers **1-12,12**:**1-12,13**:**1-13,13** was attained, but only after several days. The mixed isomer $\mathrm{HB(3\text{-}PhPz)_3Rh(^{12}CO)(^{13}CO)}$ **1-12,13** can be prepared isotopically pure (Section 5), and when it is dissolved in cyclohexane, the same equilibrium is reached, again over several days (eq. 2-8).

$$\begin{gathered}\mathrm{HB(3\text{-}PhPz)_3Rh(CO)_2} \xrightarrow[\text{cyclohexane}]{^{13}\text{CO, 5 min}} \mathrm{HB(3\text{-}PhPz)_3Rh(^{13}CO)_2} \\ \begin{matrix}\mathrm{HB(3\text{-}PhPz)_3Rh(CO)_2} \\ + \\ \mathrm{HB(3\text{-}PhPz)_3Rh(^{13}CO)_2}\end{matrix} \xrightleftharpoons[\text{several days}]{\text{cyclohexane}} \mathrm{HB(3\text{-}PhPz)_3Rh(^{12}CO)(^{13}CO)}\end{gathered} \tag{2-8}$$

Reaction with $[(CO)_2RhCl]_2$

During the preparation of **1** an intermediate is observed in the IR spectrum of the toluene solution (ν_{CO} at 2091, 2075, 2028, 1998 cm^{-1}) which forms initially but disappears as the reaction is completed. This intermediate was determined to be $\mathrm{ClRh(CO)_2(3\text{-}PhPz)(H)B(3\text{-}PhPz)_2Rh(CO)_2}$ (**5**), which was prepared by reacting two equivalents of **1** with one equivalent of $[(CO)_2RhCl]_2$ in CH_2Cl_2 (eq. 2-9).

Complex **5** was characterized by the usual methods. The MS does not show the molecular ion, but the largest fragment has m/e = 635, corresponding to $M^+\text{-}Rh(CO)_2$. The IR spectrum in CH_2Cl_2 has four ν_{CO} bands at 2093, 2079, 2031, 2004 cm^{-1}.

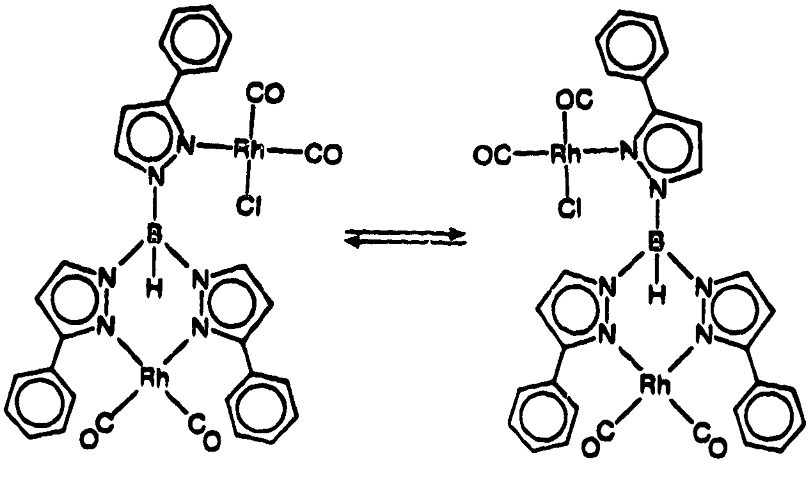


(2-9)

1

5

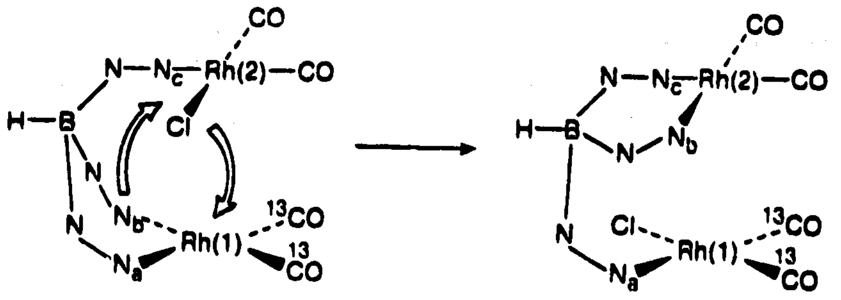
The ^{1}H NMR spectrum shows a 1:1:1 ratio of pyrazole groups, which is thought to arise from the large "ClRh(CO)$_2$" group on the free 3-PhPz group. The two bound 3-PhPz groups are then inequivalent on the NMR timescale. Decoupling experiments demonstrate that spin transfer occurs between the 5-H, 4-H or ortho protons of the pyrazole groups bound to Rh(1). This indicates that the sites are being exchanged, perhaps by a B-N bond rotation of the pyrazole bound to Rh(2) (eq. 2-10). No spin transfer is observed to the 3-PhPz group bound to Rh(2).



(2-10)

The ^{13}C APT NMR spectrum of 5 shows four doublets in the CO region, two of which are overlapping. Intuitively, one would predict that the overlapping resonances at δ 182.64 and 182.41 are the CO groups on Rh(1), while the doublets at δ 184.79 and 179.97 are the CO groups on Rh(2). Three of the four coupling constants are the same ($^1J_{Rh-C}$ = 69 Hz), while the value for the high field doublet is larger ($^1J_{Rh-C}$ = 74 Hz). This suggests that this unique CO is trans to the chloride, while the other three are trans to 3-PhPz groups.

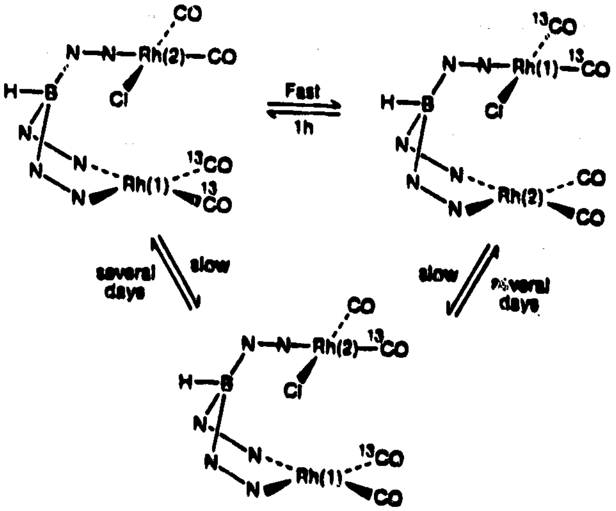
Selective ^{13}CO enrichment of 5 was used to verify these assignments. Reaction of $HB(3\text{-}PhPz)_3Rh(^{13}CO)_2$ 1-13,13 with $[(CO)_2RhCl]_2$ in CH_2Cl_2 gives $ClRh(CO)_2(3\text{-}PhPz)(H)B(3\text{-}PhPz)_2Rh(^{13}CO)_2$, with IR ν_{CO} at 2079, 2044, 2004, 1983 cm^{-1}. The original IR ν_{CO} bands at 2093, 2031 cm^{-1} are shifted to 2044, 1983 cm^{-1} respectively, indicating they are associated with Rh(1). From the ^{13}C NMR spectrum, the overlapping doublets at δ 182.64 and 182.41 are now enriched, and they appear as an AB pattern with $^2J_{C-C}$ = 7 Hz. However, a fairly rapid enrichment of the other two signals at δ 184.79 (dd, $^1J_{Rh-C}$ = 69 Hz, $^2J_{C-C}$ = 7 Hz) and δ 179.97 (dd, $^1J_{Rh-C}$ = 74 Hz, $^2J_{C-C}$ = 7 Hz) occurred, with a simultaneous transfer of both ^{13}CO groups. This is complete in one hour in the NMR spectrometer. The IR spectrum also showed scrambling of the ^{13}CO label. A postulated mechanism for intramolecular exchange is shown in eq. 2-11.



(2-11)

This involves one of the two bound pyrazole groups on Rh(1) coming off and coordinating to Rh(2). At the same time the chloride on Rh(2) must transfer to Rh(1), perhaps via a chloride bridge. If the ^{13}C NMR spectrum is run after several days, a further scrambling of the ^{13}CO label has occurred, as both Rh(1) and Rh(2) contain ^{12}CO and ^{13}CO. This is observed by the rise in the resonances which are found in the ^{13}C NMR natural abundance spectrum, where there is no C–C bond coupling.

This was further demonstrated with a spin-echo FT (SEFT) ^{13}C NMR experiment.[14b,c] The resulting spectrum is similar in appearance to an APT spectrum, and allows one to distinguish those resonances that are coupled to another similar nucleus (i.e. C–C coupling) from those that are not. In summary, there are two exchange processes occurring on two different timescales (eq. 2-12). There is a rapid process which simultaneously exchanges <u>both</u> ^{13}CO groups from Rh(1) to Rh(2), and a slower process which exchanges only one CO group at a time. The latter process may occur by a stepwise CO exchange via a carbonyl bridged intermediate.



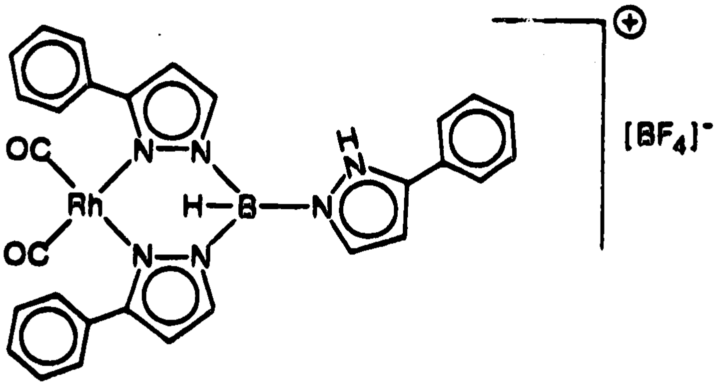
(2-12)

The other possible mechanism is intermolecular or bimolecular exchange. Both complex 5 or the partially enriched mixture of 5 above could be completely enriched with ^{13}CO to give IR ν_{CO} bands at 2044, 2030, 1985, 1959 cm^{-1}. The IR bands that were originally at 2079, 2004 cm^{-1} are now at 2030, 1959 cm^{-1}. When the completely enriched complex was mixed in equal amounts with completely unlabelled 5 in CH_2Cl_2, scrambling occurred with the same IR mixture also after one hour. This suggests that either intra or intermolecular exchange (or both) could be taking place.

The presence of 5 as a reaction intermediate in the preparation of 1 can be explained. For the preparation of 1, one equivalent of $[(CO)_2RhCl]_2$ is dissolved in toluene, and then two equivalents of the slightly soluble salt $KHB(3\text{-}PhPz)_3$ are added. As the salt slowly dissolves, 1 is formed, which is initially present with a large excess of $[(CO)_2RhCl]_2$. Complex 1 then reacts with $[(CO)_2RhCl]_2$ giving 5 (eq. 2-9). As more $KHB(3\text{-}PhPz)_3$ dissolves, it reacts with 5 to give two equivalents of 1. In a separate experiment, 5 reacts with one equivalent of $KHB(3\text{-}PhPz)_3$ to give two equivalents of 1 in 84% yield.

Reaction with HBF_4

The reaction to prepare 5 (eq. 2-9) can be considered to be that of a Lewis base $HB(3\text{-}PhPz)_3Rh(CO)_2$ 1 reacting with the known Lewis acid $[(CO)_2RhCl]_2$.[19] The free pyrazole group in 1 then behaves like 3-PhPzH, the latter reacting with $[(CO)_2RhCl]_2$ to give 4. Another more familiar Lewis acid is HBF_4, which is known to react with $(HBPz^*{}_3)Rh(CO)_2$ in CH_2Cl_2 to give $[(HBPz^*{}_2)(Pz^*H)Rh(CO)_2](BF_4)$,[8d] where the proton attacks the pyrazole nitrogen rather than the metal center. A similar reaction occurs with 1, giving $[HB(3\text{-}PhPz)_2(3\text{-}PhPzH)Rh(CO)_2](BF_4)$ (6) as colorless crystals (eq. 2-13).



(2-13)

6

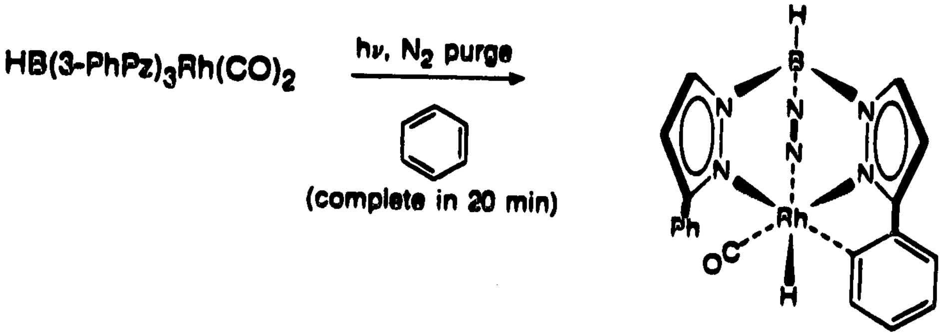
Complex 6 is slightly soluble in benzene, with the IR spectrum displaying ν_{CO} bands at 2092, 2031 cm^{-1}. The ^1H NMR spectrum exhibits a 2:1 ratio of bound and free pyrazole groups, with a resonance at δ 13.25 (br, 1H) typical of a nitrogen-bound hydrogen. Also, the 4-H resonance of the free 3-PhPz group at δ 6.79 is an apparent triplet ($J = 2.5$ Hz), with similar coupling to the 5-H and the nitrogen bound hydrogens. In comparison to complex 5, the Lewis acid on the free pyrazole nitrogen is small (a proton), so that B-N bond rotation of the free 3-PhPz group is fast on the NMR timescale.

The above protonation is reversible, as a colorless CH_2Cl_2 solution of 6 is smoothly converted back to 1 by the addition of NEt_3, giving a yellow solution. It is also of interest to compare the relative strengths of the Lewis acids. A solution of 5 in CH_2Cl_2 reacts smoothly with HBF_4 to give 6 and $[(CO)_2RhCl]_2$. The latter can be separated from 6 by hexane extraction. Hence the stronger Lewis acid HBF_4 displaces the weaker "$ClRh(CO)_2$", which dimerizes.

Section 4

C-H ACTIVATION STUDIES

Attempts at intermolecular carbon-hydrogen activation using 1 in saturated or aromatic hydrocarbons under photochemical conditions resulted in intramolecular activation of a C-H bond in the ortho position of a phenyl group. Photolysis of a pale yellow solution of 1 in benzene in a Pyrex Schlenk tube for 20 minutes with N_2 purge results in complete conversion to the orthometallated Rh(III) hydride (7) (eq. 2-14).



(2-14)

1

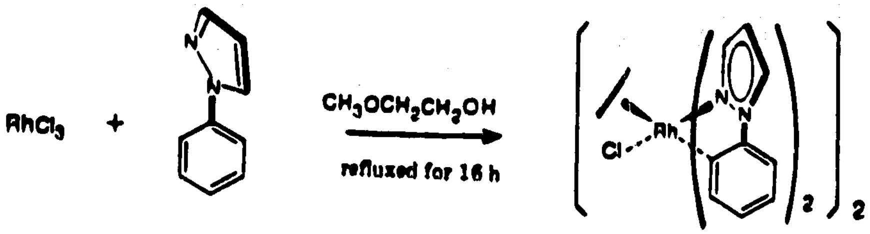
7

Although 7 is quite air sensitive in solution, it is a moderately air-stable colorless crystalline solid (as a benzene solvate) isolated in 84% yield. Unlike the aryl or alkyl hydrides prepared by Ghosh,[9] the low resolution electron impact mass spectrum showed the molecular ion M^+, as well as the loss of CO. This is a common indication of a cyclometallation reaction.[20] The IR spectrum in cyclohexane showed a single ν_{CO} at 2063 cm^{-1}, and a weak broad band at <u>ca</u>. 2104 cm^{-1} assigned as the Rh-H stretching vibration. The ^1H NMR spectrum shows a high field hydride at δ -14.51 (d, 1H, $^1J_{Rh-H}$ = 23.1 Hz). The three 5-H and three 4-H resonances are indicative of a Rh(III) octahedral geometry with three different pyrazole groups. Tables 2.V and 2.VI present the ^1H and ^{13}C NMR data for the Rh(III) complexes prepared.

The high rate of the photolysis is similar to that of the benzene activation by $(HBPz^*_3)Rh(CO)_2$, and much greater than the C-H activation by the $Cp^*Ir(CO)_2$ system. The UV-VIS spectrum of 1 in CH_2Cl_2 has two maxima at 252 ($\varepsilon = 39440$), 353 ($\varepsilon = 2440$) nm (λmax). This is similar to the UV-VIS spectrum of $(HBPz^*_3)Rh(CO)_2$ in n-hexane: 221 ($\varepsilon = 17600$), 353 ($\varepsilon = 1820$) nm (λmax), but quite different from that of $Cp^*Ir(CO)_2$ in hexane: 220 ($\varepsilon = 13000$), 290 ($\varepsilon = 5500$) nm (λmax). It is thought that the lowest energy electronic absorption at 353 nm in $(HBPz^*_3)Rh(CO)_2$ is responsible for the efficiency in near UV light.[9]

When the above photolysis was done with a H_2 purge, no dihydride was detected by IR or ^1H NMR spectroscopy, as only 7 was formed. Dihydrogen may oxidatively add but then reductively eliminate, followed by orthometallation. Although no crystallographic evidence was obtained, intramolecular activation of an ortho C-H bond is well known.[20] There are also literature examples of complexes that demonstrate both inter and intramolecular C-H activation, most notably by Jones and Werner.[21]

PH molecular models indicate that activation of only the ortho position is feasible, although the five-membered ring appears strained. Related to this work is the thermal activation of N-phenylpyrazole with $RhCl_3$, shown in eq. 2-15.[22] A similar five membered ring is formed, with a nitrogen replacing the carbon in 7.



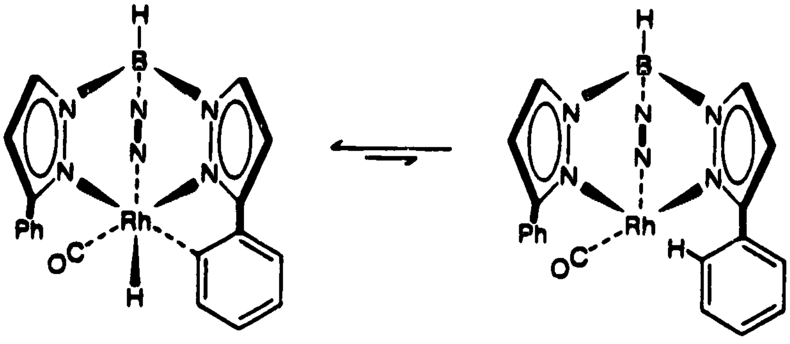
(2-15)

Reactions of $HB(3\text{-}PhPz)_2(C_3H_2N_2\text{-}\overline{C_6H_4)Rh}(CO)(H)$ (7)

Reaction with CO

Complex 7 reacts immediately with one atmosphere CO in benzene or cyclohexane to give back the parent dicarbonyl 1. The initial photolysis of 1 in benzene was done with a nitrogen gas purge, so as to sweep away free CO and minimize this rapid back reaction.

Mechanistically, this may indicate an equilibrium between 7 and the postulated 16e coordinatively unsaturated species (eq. 2-16), which would rapidly scavenge CO to form 1.



7

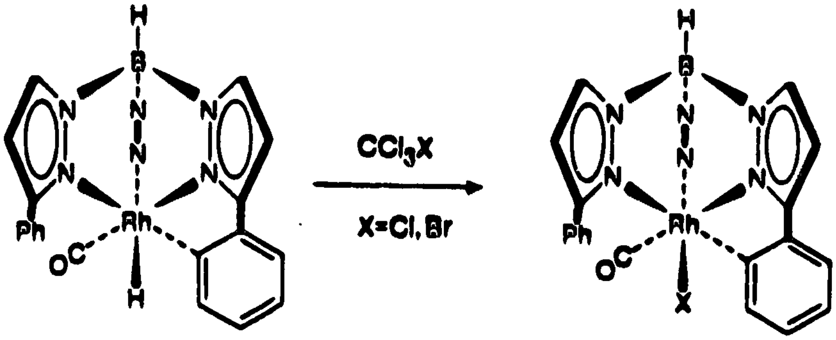
(2-16)

In contrast to 7, the reaction of $(HBPz^*_3)Rh(CO)(Ph)(H)$ with CO in hexane is slow ($t_{1/2}$ = 23 hours).[9] However, a dissociative mechanism with benzene loss was inconsistent with other kinetic results obtained.

The rate of the CO reaction was found to be directly dependent on the CO pressure, indicating an associative mechanism.[9] Neither mechanism can be ruled out in this case but the dissociative pathway may suggest a weaker rhodium carbon bond of the strained five-membered ring.

Reaction with CCl_3X (X=Cl, Br)

Complex **7** can be converted to the corresponding chloride (**8a**) or bromide (**8b**) by addition of CCl_4 or $CBrCl_3$ respectively (eq. 2-17), with the yield of the latter being much higher.



(2-17)

7

8a (X=Cl)

8b (X=Br)

The latter reaction also occurs much more rapidly, in agreement with the observation that $CBrCl_3$ is much more efficient than CCl_4 at trapping organic and organometallic radicals.[23] Both **8a** and **8b** were isolated as air-stable yellow crystalline solids. The IR spectra in cyclohexane show a ν_{CO} band at 2096 and 2090 cm^{-1} for **8a** and **8b** respectively. Figure II.5 shows the ^1H NMR spectrum of **8a** in CD_2Cl_2. The three different 5-H and 4-H resonances are consistent with a Rh(III) octahedral geometry. The ^{13}C APT NMR spectrum of **8a** has a resonance at δ 154.98 (d, $^1J_{Rh-C}$ = 25 Hz) which is the rhodium-bound phenyl carbon.

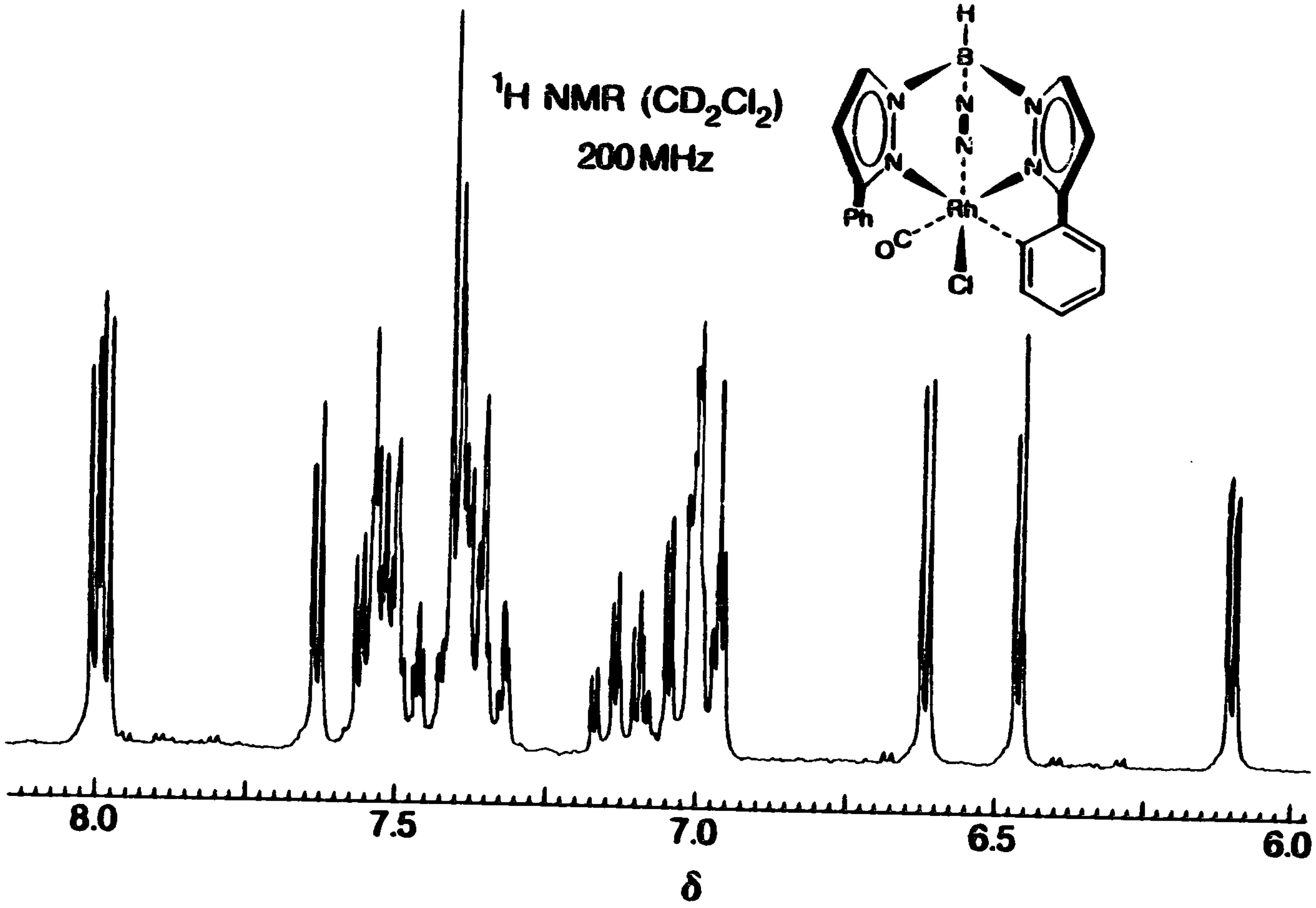
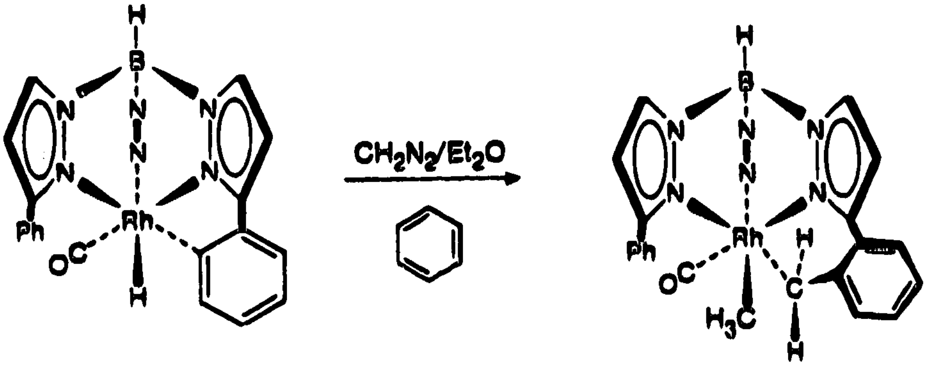


Figure II.5 ^{1}H NMR Spectrum of (8a)

Reaction with diazomethane

Reaction of **7** with excess CH_2N_2-Et_2O in benzene afforded $\mathrm{HB(3\text{-}PhPz)_2(C_3H_2N_2\text{-}C_6H_4\overline{CH_2)Rh}(CO)(CH_3)}$ (**9**), where two moles of "CH_2" have been formally added. The rhodium hydride has been converted to a rhodium methyl as expected, but a CH_2 unit is formally inserted into the Rh-C bond to give a six-membered ring (eq. 2-18).



(2-18)

7 9

The IR spectrum of 9 in cyclohexane showed a ν_{CO} band at 2042 cm^{-1}, and the MS showed the molecular ion M^+ at m/e = 600, as well as ions formed by loss of CH_3 and CO. The ^1H NMR spectrum shows three different pyrazole groups, and the diastereotopic methylene resonances appear at δ 3.40 (d of d, 1H, $^2J_{H-H}$ = 9.8 Hz, $^2J_{Rh-H}$ = 4.1 Hz) and δ 2.36 (d, 1H, $^2J_{H-H}$ = 9.8 Hz) (Figure II.6). Decoupling experiments were used to assign the coupling constants. Irradiating the resonance at δ 3.40 collapsed the resonance at δ 2.36 to a singlet, while irradiating at δ 2.36 gave a doublet at δ 3.40 ($^2J_{Rh-H}$ = 4.1 Hz). A resonance at δ -0.13 (d, 3H, $^2J_{Rh-H}$ = 2.0 Hz) is indicative of a methyl group bound to rhodium. The ^{13}C APT NMR spectrum (Table 2.VI) showed the methylene

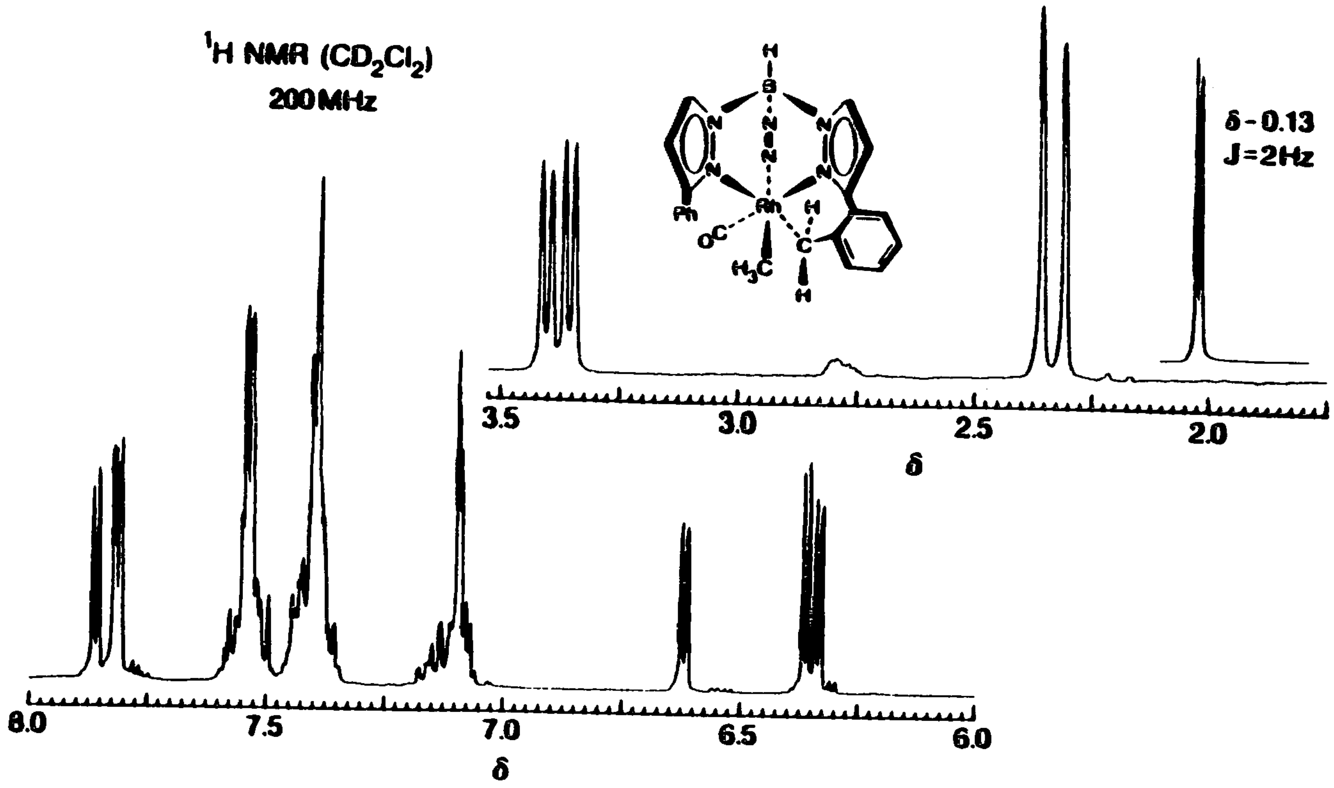
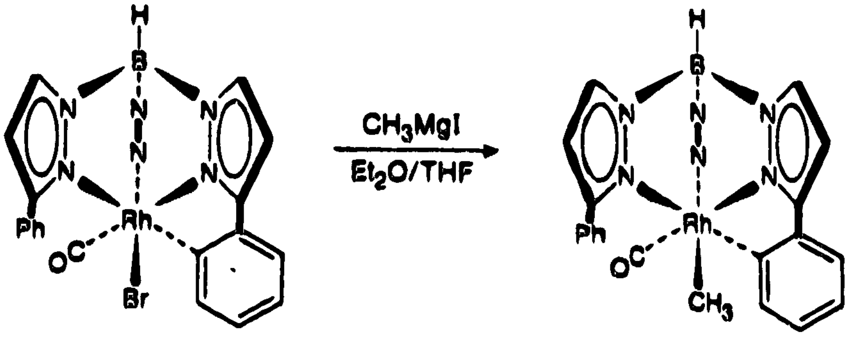


Figure II.6 ^{1}H NMR Spectrum of (9)

carbon at δ 16.39 (d, $^1J_{Rh-C}$ = 22 Hz) and the methyl carbon at δ -1.69 (d, $^1J_{Rh-C}$ = 21 Hz), and also confirmed the Rh(III) octahedral geometry.

With a slow addition of CH_2N_2 to **7**, the IR spectrum of a benzene aliquot in cyclohexane showed the presence of another product thought to be $HB(3\text{-}PhPz)_2(\overline{C_3H_2N_2\text{-}C_6H_4)Rh}(CO)(CH_3)$ (**10**) with ν_{CO} at 2052 cm^{-1}. This was confirmed by an independent synthesis of **10**, which was prepared from reaction of the bromide **8b** with MeMgI in THF (eq. 2-19).

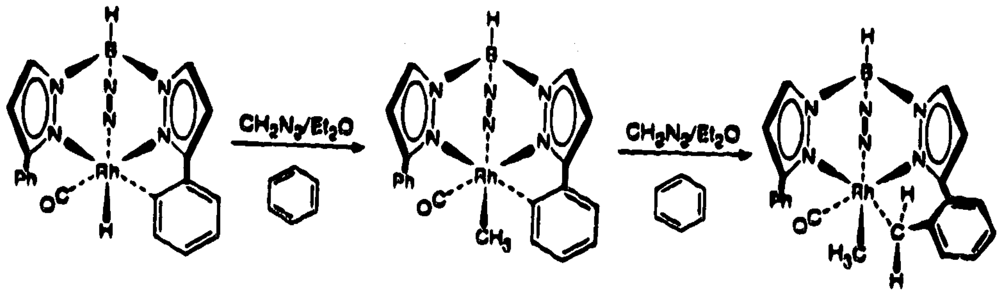


8b **10**

(2-19)

The ^1H NMR spectrum of **10** (Table 2.V) shows a rhodium bound methyl group at δ 0.25 (d, 3H, $^2J_{Rh-H}$ = 2.1 Hz) and the typical pattern of an octahedral Rh(III) complex with three different groups trans to pyrazole ligands.

When **10** is reacted with excess CH_2N_2 in benzene, **9** is isolated. This suggests that **9** is formed from **7** by stepwise addition of diazomethane, first forming **10**, which reacts with CH_2N_2 to give **9** (eq. 2-20).

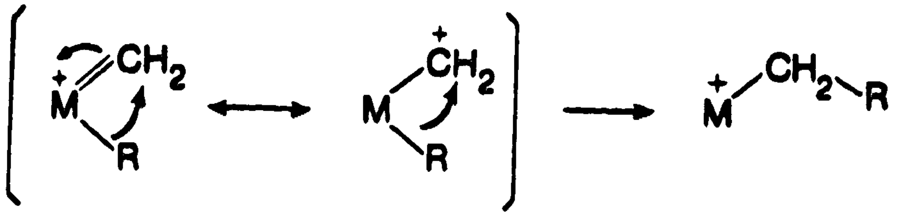


(2-20)

7 10 9

This of course does not rule out the first CH_2 insertion occurring into the ring. No evidence was found regarding the mechanism of the latter insertion, although it is interesting to note that complexes **8a** or **8b** do not react with diazomethane.

The insertion of a CH_2 unit into M-H and M-C bonds has been proposed to be involved as steps in the Fischer-Tropsch reductive polymerization of CO to form alkanes[24,25] and also the preparation of polymethylene from diazomethane in the presence of organometallic complexes.[25] The insertion of CH_2 into alkyl or aryl metal bonds has been demonstrated by several groups involving W,[25a,b] Ru[25c] or Ir[25d] complexes. No intermediate alkyl or aryl carbene complex was detected, but it is thought to be present before migration (eq. 2-21).



(2-21)

This migration reaction has been studied theoretically by both Goddard and Hoffmann.[24]

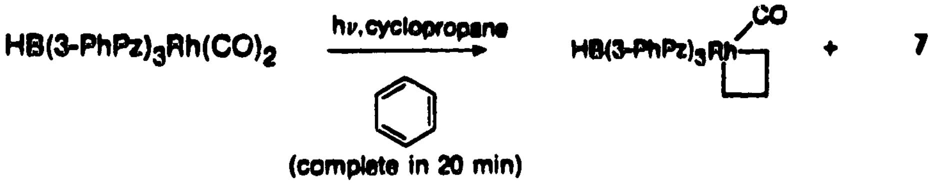
Reaction with Cyclopropane

A freshly prepared benzene solution of 7 was purged with cyclopropane for one hour, resulting in partial conversion to $HB(3\text{-}PhPz)_3\overline{Rh(CO)(CH_2CH_2CH_2})$ (11). The reaction sequence to form 11 is thought to occur via oxidation addition of cyclopropane to the 16e intermediate (eq. 2-16), giving the cyclopropyl hydride. This species was not detected as rearrangement to the rhodacyclobutane is presumed rapid.

This mechanism is based on the work of Ghosh[9] and Bergman,[26] where a cyclopropyl hydride complex observed undergoes rearrangement to the C-C inserted product. The above route is not synthetically viable, but a better method is detailed below.

Photolysis of (1) with Cyclopropane

Photolysis of 1 in benzene with a cyclopropane purge for 20 minutes resulted in consumption of 1 and a mixture of 7 and a new product, $HB(3\text{-}PhPz)_3\overline{Rh(CO)(CH_2CH_2CH_2})$ (11), the rhodacylobutane (eq. 2-22).

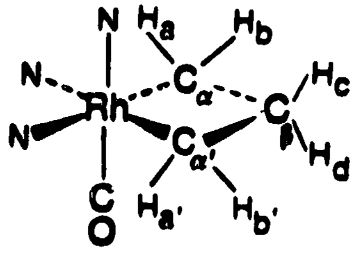


(2-22)

1 11

To the mixture was added $CBrCl_3$ which converted **7** to **8b**. A ^1H NMR spectrum of the mixture indicated a 9:1 ratio of **8b** to **11**, which shows that the photolysis still results in predominantly intramolecular C-H activation.

Better yields of **11** were obtained by continuing the photolysis for 50 minutes, where the major product by IR was now **11** with a small amount of **7**. Compound **11** could be separated by decomposition of **7** in solution in air, followed by chromatography to obtain **11** in 69% yield. The IR spectrum in cyclohexane has a ν_{CO} band at 2034 cm^{-1}. The ^1H NMR spectrum shows the expected 2:1 ratio of pyrazole resonances, and the protons of the rhodacyclobutane appear as 4 multiplets.[9] The ^{13}C APT NMR spectrum also shows a 2:1 ratio of pyrazole group carbons, with the methylene carbons at δ 31.82 (d, C_β, $^2J_{Rh-C}$=5 Hz) and δ -10.49 (d, C_α, $^1J_{Rh-C}$=13 Hz) (eq. 2-23).



(2-23)

11 (atom labelling for NMR)

The preparation of **11** is the only example of intermolecular carbon hydrogen bond activation in this system, with the driving force being the formation of the metallacycle, which is relatively stable to reductive elimination. Intermolecular C-H activation of other substrates may indeed initially occur, but could be followed by rapid reductive elimination and subsequent orthometallation.

Section 5

SYNTHESIS AND REACTIVITY OF OLEFIN COMPLEXES

There are a number of pyrazolylborate rhodium olefin complexes in the literature. Trofimenko initially prepared $(HBPz_3)Rh(C_2H_4)_2$,[6a] followed closely by $(HBPz^*_3)Rh(COD)$.[6b] More recently, Cocivera et al.[7] have prepared a series of compounds of the type $(BPz_4)Rh(diene)$, where the (diene) was bis(ethylene) $(C_2H_4)_2$, 1,5-cyclooctadiene (COD), norbornadiene (NBD) and duroquinone (DQ). By ^1H NMR spectroscopy it was suggested that the (DQ) and (COD) complexes were five-coordinate in solution, whereas the X-ray crystal structures showed that the (NBD) and (COD) complexes are four-coordinate, while the (DQ) complex is five-coordinate.

The synthesis of carbonyl-olefin complexes of the type $(HBPz^*_3)Rh(CO)(\eta^2\text{-olefin})$ (olefin = ethylene, propylene and cyclooctene) was recently reported by Ghosh and coworkers.[8b,c,9] They studied their fluxional behaviour as well as subsequent chemistry. These were determined to be four-coordinate in solution.

Synthesis of Olefin Complexes

Using methods similar to those previously reported,[8b,c,9] olefin complexes of the type $HB(3\text{-}PhPz)_3Rh(L)(olefin)$ (L = CO, C_2H_4) (olefin = C_2H_4) and (L) + (olefin) = (COD) were prepared. A freshly prepared benzene solution of **7** was purged with ethylene for 90 minutes, resulting in conversion to $HB(3\text{-}PhPz)_3Rh(CO)(C_2H_4)$ (**12**). The reaction was quantitative by IR, although other routes provided for direct synthetic access to **12**. A more rational synthesis is to react the dimer

$[(CO)(C_2H_4)RhCl]_2$[27] with two equivalents of $KHB(3\text{-}PhPz)_3$ in toluene (eq. 2-24).

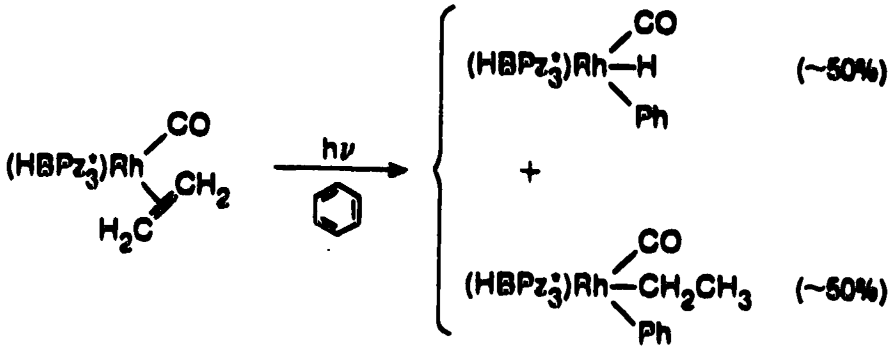
$$\left.\begin{matrix} [ClRh(CO)(C_2H_4)]_2 \\ + \\ K[HB(3\text{-}PhPz)_3] \end{matrix}\right\} \xrightarrow[25^\circ C]{toluene} \underset{\mathbf{12}}{HB(3\text{-}PhPz)_3Rh(CO)(C_2H_4)} \qquad (2\text{-}24)$$

Complex **12** is isolated in 81% yield and the IR spectrum shows a single ν_{CO} at 2030 cm^{-1} in cyclohexane. The ^1H NMR spectrum of **12** at room temperature indicates equivalence of all three pyrazole groups, and the ethylene resonance appears at δ 2.43 (d, 4H, $^2J_{Rh-H}$ = 2.2 Hz). On cooling to -90°C, one observes a 2:1 ratio of pyrazole resonances. Unlike complex **1**, **12** does not show a mixture of the η^2 and η^3 isomers at low temperature, nor a mixture of isomers in the IR spectrum. Assuming a static η^2 structure for **12**, as Ghosh postulated for $(HBPz^*{}_3)Rh(CO)(C_2H_4)$, the low temperature ^1H NMR spectrum should show three different pyrazole groups. However, as discussed by Ghosh,[9] a low energy process is thought to be involved which averages the two bound pyrazole groups. This will be discussed in full detail in Chapter IV.

The related bis(pyrazolyl)borate complex $H_2B(3\text{-}PhPz)_2Rh(CO)(C_2H_4)$ (**13**) could be prepared but not fully characterized, as it rapidly disproportionates or decomposes in solution to $H_2B(3\text{-}PhPz)_2Rh(CO)_2$ **2**. This problem was also encountered when the synthesis of $(H_2BPz^*{}_2)Rh(CO)(C_2H_4)$ was attempted.[9] However the IR spectrum of **13** in cyclohexane shows ν_{CO} at 2023 cm^{-1}, which is similar to the band of **12**, suggesting that the latter is η^2 in solution.

Complex **12** in CH_2Cl_2 reacts immediately with one atmosphere of CO to give 1. With very slow and stoichiometric addition of ^{13}CO to a cyclohexane solution of 12, the complex $HB(3\text{-}PhPz)_3Rh(CO)(^{13}CO)$ 1-12,13 can be prepared. As discussed in Section 3, a cyclohexane solution of freshly prepared 1-12,13 undergoes CO scrambling reaching an approximate 1:2:1 equilibrium distribution of 1-12,12:1-12,13:1-13,13.

When Ghosh irradiated $(HBPz^*_3)Rh(CO)(C_2H_4)$ in benzene he obtained two products in an approximate 1:1 ratio, the phenyl hydride complex $(HBPz^*_3)Rh(CO)(Ph)(H)$ and the phenyl ethyl complex $(HBPz^*_3)Rh(CO)(Ph)(Et)$[8b,9] (eq. 2-25).



(2-25)

Irradiation of a benzene solution of 12 for 20 minutes with a nitrogen purge results in intramolecular activation giving 7, with no evidence of a phenyl ethyl complex.

The related bis(ethylene) and COD complexes $HB(3\text{-}PhPz)_3Rh(C_2H_4)_2$ (14) and $HB(3\text{-}PhPz)_3Rh(COD)$ (15) are prepared in a similar manner to 12, starting with $[(C_2H_4)_2RhCl]_2$[28] and $[(COD)RhCl]_2$[29] respectively (eq. 2-26). Compound 14 was characterized by the usual methods, with the ^1H NMR spectrum being most informative. Unlike $(HBPz_3)Rh(C_2H_4)_2$, where Trofimenko observed one type of pyrazole group,[6b] the ^1H NMR spectrum of 14 at ambient temperature in CD_2Cl_2 is similar to that of 1 at -30°C, with three sets of pyrazole group resonances. Two of the three are in a

$$\left.\begin{array}{c}[ClRh(L)_2]_2 \\ + \\ K[HB(3\text{-}PhPz)_3]\end{array}\right\} \xrightarrow[25^\circ C]{toluene} HB(3\text{-}PhPz)_3Rh(L)_2 \qquad (2\text{-}26)$$

14 $L_2 = (C_2H_4)_2$
15 $L_2 = (COD)$

2:1 ratio for η^2-$HB(3\text{-}PhPz)_3Rh(C_2H_4)_2$, with the third corresponding to η^3-$HB(3\text{-}PhPz)_3Rh(C_2H_4)_2$. The ratio of the $\eta^2:\eta^3$ forms is 44:56%, which is similar to the ratio for 1 at -30°C. The ethylene protons appear at δ 2.66 (d, 8H, $^2J_{Rh-H}$ = 1.8 Hz, η^2 form) and δ 2.22 (d, 8H, $^2J_{Rh-H}$ = 1.8 Hz, η^3 form), with the same ratio by integration. The ^{13}C NMR spectrum (Table 2.III) in CD_2Cl_2 shows three resonances for each type of carbon, except for the ethylene carbons, which appear at δ 66.51 (d, $^1J_{Rh-C}$ = 12 Hz, η^3 form) and δ 65.58 (d, $^1J_{Rh-C}$ = 12 Hz, η^2 form).

When the ^1H NMR spectrum is run in toluene-d_8 at room temperature a mixture of the two isomers is again observed. However the ratio is different with values of $\eta^2:\eta^3$ = 63:37%, and in cyclohexane-d_{12} the ratio is $\eta^2:\eta^3$ = 73:27% (Table 2.II).

The ^1H NMR spectrum of **15** at room temperature in CD_2Cl_2 is similar to that of **14**, with a $\eta^2:\eta^3$ ratio of 50:50%. However, the resonances for the η^3 form are broad, and cooling to -90°C gives a 2:1 ratio of pyrazole group resonances, with the resonances of the η^2 form unchanged (Figure II.7). The relative ratio of the two isomers is also unchanged (1:1). Both a five-coordinate trigonal bipyramidal or square pyramidal ground state geometry could account for the NMR spectra, and at -90°C

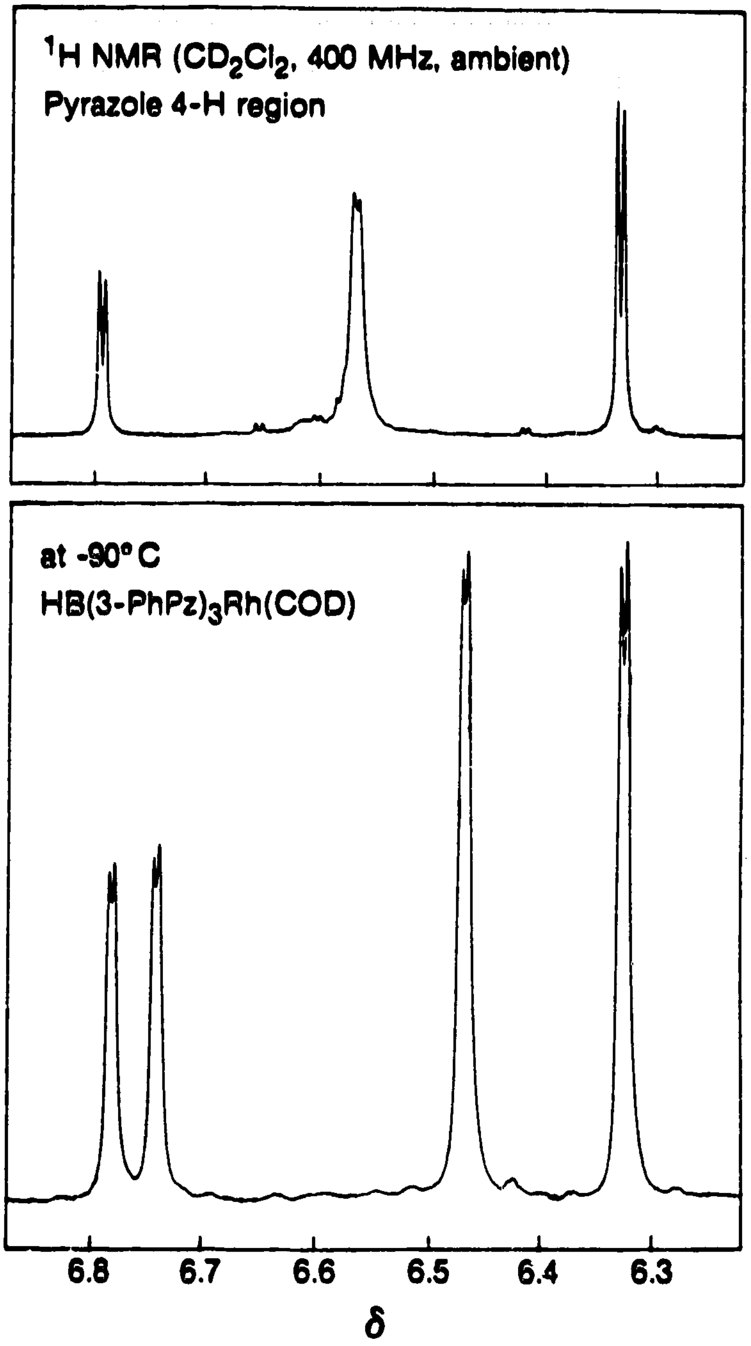


Figure II.7 ^{1}H NMR Spectrum of $HB(3\text{-}PhPz)_3Rh(COD)$ (15)

the Berry pseudorotation or turnstile rotation is slow on the NMR timescale. Changing the solvent to toluene-d_8 again gives more of the η^2 form, where the ratio of $\eta^2:\eta^3$ is 64:36%, and in cyclohexane-d_{12}, the ratio of $\eta^2:\eta^3$ is 69:31% (Table 2.II).

As demonstrated with complex **12**, both **14** and **15** react with CO in CH_2Cl_2 giving 1, although the latter reaction is slower. The exchange and displacement reactions with ^{13}CO and CO respectively provide further evidence for the η^2 16e form in solution. These results are similar to those of Lalor,[7d] who found that PPh_3 rapidly displaced ethylene from $(HBPz_3)Rh(C_2H_4)_2$ and $(BPz_4)Rh(C_2H_4)_2$. He suggested that the complexes are also four-coordinate in solution, similar to the 16e complex $(acac)Rh(C_2H_4)_2$, which also rapidly reacts with PPh_3. In contrast, the analogous reaction with the 18e complex $(C_5H_5)Rh(C_2H_4)_2$ is a high activation energy process.[30]

An interesting reaction of **15** was found. Analogous to 1, it should react with the Lewis acid $[(CO)_2RhCl]_2$ to give an adduct similar to 5. By IR spectroscopy, the appearance of 1 is observed, which suggests the $[(COD)RhCl]_2$ is also formed (eq. 2-27). Although the products could not be separated by chromatography or crystallization, the ^1H NMR spectra shows a 2:1 ratio of (**1**) to $[(COD)RhCl]_2$.

$$\begin{array}{ccc} [ClRh(CO)_2]_2 & & [ClRh(COD)]_2 \\ + & \xrightarrow{CH_2Cl_2} & + \\ HB(3\text{-}PhPz)_3Rh(COD) & & HB(3\text{-}PhPz)_3Rh(CO)_2 \\ \mathbf{15} & & \mathbf{1} \end{array} \qquad (2\text{-}27)$$

In one sense 15 reacts like the salt KHB(3-PhPz)$_3$, with the "(COD)RhCl" unit replacing potassium. However, mechanistically the sequence must involve a pyrazole group transfer from 15 to [(CO)$_2$RhCl]$_2$ with the chloride going in the opposite direction. A similar mechanism was postulated for the ^{13}CO exchange in complex 5 (eq. 2-11), although again this could be a bimolecular process. Not surprisingly, 1 does not react with [(COD)RhCl]$_2$, as the latter is not considered to be a Lewis acid, so once the exchange takes place, the resulting complex falls apart into 1 and "(COD)RhCl", which dimerizes.

Table 2.II ^1H NMR Data for HB(3-PhPz)$_3$ Rh(I) Complexes[a]

Conditions	Compound[b]	5-H[c]	4-H[c]	Aromatic[d]	Other
CD_2Cl_2 -30°C	1-η^2 (43%) 1-η^3 (57%)	7.96 (1H) 7.35 (2H) 7.80 (3H)	6.76 (1H) 6.49 (2H) 6.56 (3H)	7.95-7.88 (m, 6H) 7.63-7.27 (m, 9H)	
Toluene-d_8 -30°C	1-η^2 (69%) 1-η^3 (31%)	7.96 (1H) 7.56 (2H) 7.51 (3H)	6.79 (1H) 6.00 (2H) 6.22 (3H)	8.23-7.71 (m, 6H) 7.35-6.97 (m, 9H)	
CD_2Cl_2 ambient	12	7.81 (3H)	6.37 (3H)	7.75-7.66 (m, 6H) 7.42-7.24 (m, 9H)	2.43 (d, 4H, $^2J_{Rh-H}$=1.8 Hz)
CD_2Cl_2 -90°C	12-η^2 (100%)	7.82 (2H) 7.77 (1H)	6.43 (2H) 6.07 (1H)	7.70-7.49 (m, 6H) 7.47-7.23 (m, 9H)	2.81 (d,2H,J=8 Hz) 1.75 (d,2H,J=8 Hz)
CD_2Cl_2 ambient	14-η^2 (44%) 14-η^3 (56%)	8.13 (1H) 7.45 (2H) 7.88 (3H)	6.79 (1H) 6.36 (2H) 6.57 (3H)	8.13-7.94 (m, 6H) 7.62-7.29 (m, 9H)	2.66[e] 2.22[e]
Toluene-d_8 ambient	14-η^2 (63%) 14-η^3 (37%)	8.15 (1H) 7.67 (2H) 7.70 (3H)	6.78 (1H) 6.33 (2H) 6.01 (3H)	8.17-8.01 (m, 6H) 7.37-6.96 (m, 9H)	2.53[e] 2.20[e]
Cyclohexane-d_{12} ambient	14-η^2 (73%) 14-η^3 (27%)	7.97 (1H) 7.48 (2H) 7.68 (3H)	6.65 (1H) 6.15 (2H) 6.40 (3H)	8.10-7.90 (m, 6H) 7.50-7.10 (m, 9H)	2.59[e] 2.18[e]
CD_2Cl_2 ambient	15-η^2 (50%) 15-η^3 (50%)	8.14 (1H) 7.40 (2H) 7.82 (3H)	6.79 (1H) 6.33 (2H) 6.57 (3H)	8.16-7.94 (m, 6H) 7.62-7.25 (m, 9H)	3.88,3.35,3.28, 2.44,2.01,1.69, 1.51,1.15 (m, COD)[f]

continued ...

Table 2.II Continued

Conditions	Compound[b]	5-H[c]	4-H[c]	Aromatic[d]	Other
CD_2Cl_2	15-η^2 (50%)	8.14 (1H) 7.38 (2H)	6.78 (1H) 6.33 (2H)	8.23-7.77 (m, 6H) 7.60-7.20 (m, 9H)	3.88,3.54,3.28,3.16 2.43,2.03,1.80,1.70 1.52,1.12 (m, COD)[f]
-90°C	15-η^3 (50%)	7.96 (1H) 7.50 (2H)	6.73 (1H) 6.47 (2H)		
Toluene-d_8	15-η^2 (64%)	8.19 (1H) 7.69 (2H)	6.80 (1H) 6.03 (2H)	8.19-8.05 (m, 6H) 7.37-6.96 (m, 9H)	3.86,3.49,3.35,2.21 1.90,1.66,1.38,1.23 0.97 (m,COD)[f]
ambient	15-η^3 (36%)	7.65 (3H)	6.36 (3H)		
Cyclohexane-d_{12}	15-η^2 (69%)	7.98 (1H) 7.46 (2H)	6.67 (1H) 6.13 (2H)	8.10-7.90 (m, 6H) 7.45-7.10 (m, 9H)	3.88,3.38,3.27,2.42 1.98,1.64,1.40 1.08 (m, COD)[f]
ambient	15-η^3 (31%)	7.67 (3H)	6.40 (3H)		

(a) All spectra run at 400 MHz

(b) Percent isomer from integration of η^2 and η^3 forms

(c) (d, $^3J_{H-H}$=2.2±0.3 Hz)

(d) Aromatic protons for both isomers

(e) (d, 8H, $^2J_{Rh-H}$=1.8±0.3 Hz, ethylene groups)

(f) COD protons for both forms

Table 2.III ^{13}C APT NMR Data for HB(3-PhPz)$_3$ Rh(I) Complexes[a]

Compound[b]	3-C	5-C	C_{ipso}[c]	4-C	Aromatic[d]	Other
1-η^2 (42%)	155.92	139.11	134.23	105.21	129.53, 129.31	183.18 (d, CO, J=69 Hz)[e]
-30°C	154.20	136.49	132.90	102.40	128.53, 128.42	
	(1:2)	(1:2)	(1:2)	(2:1)	128.26, 127.48	
1-η^3 (58%)	154.95	137.55	135.55	104.60	125.64	183.52 (d, CO, J=69 Hz)[e]
14-η^2 (46%)	154.38	139.43	135.17	105.54	129.00, 128.80	65.58 (d, CH_2=CH_2, J=12 Hz)[e]
ambient	154.00	136.13	133.36	102.60	128.49, 127.99	
	(1:2)	(1:2)	(1:2)	(2:1)	127.72, 125.97	
14-η^3 (54%)	154.54	137.88	134.25	105.07	127.62, 126.11	66.51 (d, CH_2=CH_2, J=12 Hz)[e]

(a) Spectra were run in CD_2Cl_2 at 75.5 MHz.

(b) Isomer ratio an average from integration of all resonances.

(c) Phenyl carbon attached to 3-C of pyrazole ring.[31]

(d) Aromatic carbons for both isomers.

(e) $J = {}^1J_{Rh-C}$

Table 2.IV NMR Isomer Ratios for Complexes 1, 12, 14 and 15

Complex	Solvent	Temperature	Ratio (η^2:η^3)
1	toluene-d_8	-30°C	69:31
1	CD_2Cl_2	-30°C	43:57
12	CD_2Cl_2	-90°C	100:0
14	cyclohexane-d_{12}	ambient	73:27
14	toluene-d_8	ambient	63:37
14	CD_2Cl_2	ambient	44:56
15	cyclohexane-d_{12}	ambient	69:31
15	toluene-d_8	ambient	64:36
15	CD_2Cl_2	ambient	50:50
15	CD_2Cl_2	-90°C	50:50

Table 2.V ^1H NMR Data for Rh(III) Complexes[a]

Compound	5-H[b]	4-H[b]	Aromatic	Other
7	7.92	6.57	7.56-7.28 (m, 11H)	7.36 (s, 1H, 1/6C_6H_6)
	7.88	6.36	7.14-7.11 (m, 3H)	-14.51 (d, 1H, $^1J_{Rh-H}$=23.1 Hz)
	7.63	6.23		
8a	8.00	6.62	7.56-7.45 (m, 4H)	
	7.98	6.46	7.43-7.31 (m, 5H)	
	7.63	6.10	7.17-6.96 (m, 5H)	
8b	8.00	6.63	7.58-7.49 (m, 4H)	
	7.98	6.46	7.45-7.33 (m, 5H)	
	7.64	6.13	7.15-6.98 (m, 5H)	
9	7.85	6.61	7.57-7.49 (m, 5H)	3.40 (d of d, 1H, $^2J_{H-H}$=9.8 Hz,
	7.81	6.36	7.44-7.35 (m, 6H)	$^2J_{Rh-H}$=4.1 Hz), 2.36 (d, 1H, $^2J_{H-H}$=9.8 Hz),
	7.80	6.33	7.20-7.06 (m, 3H)	-0.13 (d, 3H, $^2J_{Rh-H}$=2.0 Hz)
10	7.92	6.56	7.52-7.39 (m, 1H)	
	7.87	6.38	7.37-7.27 (m, 11H)	0.25 (d, 3H, $^2J_{Rh-H}$=2.1 Hz)
	7.63	6.24	7.13-7.04 (m, 2H)	
11	7.83	6.28 (2H)	7.6-7.3 (m, 15H)	1.60 (m, 1H, H_c), 1.35 (m, 2H, H_a),
	7.77 (2H)	6.23		0.49 (m, 1H, H_d), 0.27 (m, 2H, H_b)

(a) Spectra run in CD_2Cl_2 at ambient temperature on 200 MHz instrument.

(b) (d, 1H, $^3J_{H-H}$ = 2.2±0.3 Hz).

Table 2.VI ^{13}C APT NMR Data for Rh(III) Complexes^{a}

Compound	3-C	5-C	C_{ipso}^{b}	4-C	Aromatic	Other
8a	162.12	140.34	136.49	107.96	130.81, 130.77	183.05 (d, CO, $^{1}J_{Rh-C}$=59 Hz)
	157.80	138.02	134.21	107.02	130.24, 129.84	154.98 (d, RhC, $^{1}J_{Rh-C}$=25 Hz)
	157.20	137.22	132.29	104.17	128.99, 128.55	
					128.23, 128.14	
					124.79, 124.02	
9	156.03	145.25	134.72	106.91	129.92, 129.61	191.86 (d, CO, $^{1}J_{Rh-C}$=72 Hz)
	155.87	136.51	134.65	106.39	128.77, 128.59	16.39 (d, CH_2Rh, $^{1}J_{Rh-C}$=22 Hz)
	150.32	136.41	131.18	103.14	128.49, 128.42	-1.69 (d, CH_3Rh, $^{1}J_{Rh-C}$=21 Hz)
					128.28, 127.30	
					125.07	
10	160.60	138.28	138.98	107.12	129.76, 129.61	191.42 (d, CO, $^{1}J_{Rh-C}$=68 Hz)
	156.23	138.08	134.41	104.93	128.77, 128.61	160.83 (d, RhC, $^{1}J_{Rh-C}$=29 Hz)
	155.42	136.97	134.08	103.07	128.42, 128.15	-0.85 (d, CH_3Rh, $^{1}J_{Rh-C}$=21 Hz)
					123.63, 123.50	
11	157.31	136.53	134.35	109.76	131.33, 130.22	191.40 (d, CO, $^{1}J_{Rh-C}$=79 Hz)
	156.47	135.[illegible]3	134.27	106.56	128.48, 128.43	31.82 (d, C_β, $^{2}J_{Rh-C}$=5 Hz)
	(1:2)	(1:2)	(2:1)	(1:2)		-10.49 (d, C_α, $^{1}J_{Rh-C}$=13 Hz)

(a) Spectra run in CD_2Cl_2 at ambient temperature at 75.5 MHz.
(b) Phenyl carbon attached to 3-C of pyrazole ring. (Ref. 31)

Section 6

EXPERIMENTAL

$KHB(3\text{-}PhPz)_3$ and $KH_2B(3\text{-}PhPz)_2$ were prepared according to Trofimenko et al.[11] $[(CO)_2RhCl]_2$ was prepared using the standard literature procedure.[12] $[(C_2H_4)_2RhCl]_2$ and $[(COD)RhCl]_2$ were prepared according to Cramer[28] and Crabtree[29] respectively. $[(C_2H_4)(CO)RhCl]_2$ was prepared in situ by the method of Powell and Shaw.[27] CH_2N_2 was prepared using the method of Arndt.[32] $CBrCl_3$ was used as received from Aldrich Chemical Co. ^{13}CO was purchased from Isotec Inc. and the isotopic composition is 99.7% ^{13}C, 0.3% ^{12}C, 95.8% ^{16}O, 0.2% ^{17}O and 4.0% ^{18}O.

General Techniques

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen or argon atmosphere with the use of standard Schlenk techniques. Reactions were carried out at room temperature unless otherwise stated. Linde commercial nitrogen or argon was purified by passing through a heated column (ca. 80°C) of BASF Cu-based catalyst (R3-11) to remove oxygen and a column of Mallinckrodt Aquasorb (P_2O_5 on inert base with indicator) to remove water.

Glassware was treated with KOH-Ethanol solution[33] and dried at 130°C. Solvents were scrupulously dried and distilled from appropriate drying agents[33] before storing under nitrogen. Column chromatography was performed using reagent grade solvents on either neutral alumina (CAMAG, Brockmann-Number 1) or Florisil (Baker Analysed, 60-100 Mesh) supports with a 12 x 2.5 cm column.

Unless otherwise stated, all solvents and reagents were purchased from commercial suppliers and used without purification. Sealed NMR tubes were prepared by fusing Wilmad 503-PS 7 in. NMR tubes to $B_{14/20}$ ground glass joints which were subsequently attached to Lab Glass vacuum stopcocks. All such samples were degassed by three freeze-pump-thaw cycles on a vacuum line.

^1H NMR spectra were obtained at ambient temperature unless otherwise noted on either a Bruker WH-200, a AM-300 or a WH-400 FT NMR instrument. Chemical shifts are reported in units of parts per million (ppm) (δ) downfield from tetramethylsilane (Me_4Si). ^1H NMR shifts are recorded relative to residual protiated solvent: $CHDCl_2$, 5.32; benzene-d_5, 7.15; cyclohexane-d_{11}, 1.38 and toluene-d_7, 2.09. $^{13}C\{^1H\}$ NMR spectra were recorded at 75.5 or 100.6 MHz and chemical shifts are given relative to the solvent resonance: CD_2Cl_2, 53.8. ^{19}F NMR spectra were recorded at 376.5 MHz and chemical shifts are given relative to external $CFCl_3$. $^{31}P\{^1H\}$ NMR spectra were recorded at 162.0 MHz and chemical shifts are given relative to external 85% H_3PO_4. ^{11}B NMR spectra were recorded at 64.2 MHz and chemical shifts are given relative to external $BF_3 \cdot Et_2O$. All coupling constants are reported in hertz and multiplicities assigned as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

Infrared (IR) spectra were recorded using a Nicolet MX-1 FTIR spectrometer over the range 2200-1600 cm^{-1} with 0.1 mm or 0.5 mm KCl or KBr cells. Two methods were used to determine the relative absorbance areas for those complexes displaying mixtures of isomers. Solutions were prepared in either cyclohexane, toluene or dichloromethane at concentrations of about 1 mg/ml.

For method (a), IR spectra were recorded using a Nicolet MX-1 FTIR spectrometer in linear absorbance mode. Spectra were expanded for maximum absorbance over the smallest possible wavenumber region. The relative areas were measured by weighing out the appropriate pieces of chart paper for each isomer, giving the relative ratio. This was determined for three different concentrations, which results in an average value with error limits quoted (±1%).

For method (b) IR spectra were recorded using a Nicolet 7199 FTIR spectrometer using 1 cm^{-1} resolution in linear absorbance mode. IR spectra were simulated using the Nicolet 1180 Curve Analysis Program (CAPS) (June, 1978). All simulated curves were of Lorenzian shape with no Gaussian character. The accuracy of the fit between the experimental and the calculated spectrum was described by the root-mean-square (RMS) error. (A typical RMS error for a good fit is 5%.)

Mass spectra were measured using an Associated Electronics Industries MS-12 Mass Spectrometer coupled with a Nova-3 computer employing D5-50 software. Ultraviolet-Visible spectra were recorded on a Varian DMS-100 UV/VIS spectrophotometer. Melting points were determined using a Gallenkamp capillary melting point apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory of this department.

Photochemical experiments were performed in Pyrex Schlenk tubes with a glass frit bottom which allows for a gas purge. Solutions were added with flowing gas purge connected to an oil bubbler. Samples were placed approximately 2 cm from a Hanovia 450-W medium pressure mercury lamp with a cylindrical Pyrex filter and a water-cooled quartz jacket.

Preparation of $HB(3\text{-}PhPz)_3Rh(CO)_2$ (1)

To a solution of $[(CO)_2RhCl]_2$ (435.4 mg, 1.12 mmol in 40 mL toluene) was added 1.076 g (2.24 mmol) of $KHB(3\text{-}PhPz)_3$. The cloudy yellow solution was stirred for 1 h, filtered through Celite and the solvent was removed under reduced pressure. The crude product was taken up in 40 mL CH_2Cl_2, layered with 400 mL hexane and cooled to -30°C. The first crop of crystals were collected. Two subsequent concentrations of the mother liquors gave 1 as yellow crystals (1.1470 g, 85% yield) mp 198-200°C.

The remaining mother liquor consisted of a mixture of cis and trans isomers of $[(CO)_2Rh(3\text{-}PhPz)]_2$ **3**, (91.6 mg, 14% yield), with a ratio of products 1:3 of 85:14. Compound 3 was prepared independently using a method similar to that used for $[(CO)_2RhPz^*]_2$ by Banditelli et al.[16] and the two were identical by ^1H NMR, IR and MS.

Characterization: IR (cyclohexane) 2088 (s), 2079 (w), 2026 (s), 2015 (w) cm^{-1} (ν_{CO}). MS (160°C, 70 eV) M^+ (600, 5%), M^+-CO (35%), M^+-2CO (44%), M^+-2CO-PhPz (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 7.96-7.91 (m, 6H), 7.75 (br, 3H), 7.52-7.48 (m, 9H), 6.57 (br, 3H). ^1H NMR (toluene-d_8, 200 MHz, 92°C) δ 7.95-7.75 (m, 6H), 7.61 (d, $^3J_{H-H} = 2.2$ Hz, 3H), 7.30-7.10 (m, 9H), 6.23 (d, $^3J_{H-H} = 2.2$ Hz, 3H). UV (CH_2Cl_2) 252 (ε 39,440) 353 (ε 2440) nm (λmax). Anal. Calcd for $C_{29}H_{22}BN_6O_2Rh$: C, 58.03; H, 3.69; N, 14.00. Found: C, 57.98; H, 3.69; N, 13.64.

X-Ray Structure of (1)

The X-ray crystallographic study was carried out by Dr. R.G. Ball in the Structure Determination Laboratory of this Department. This section and the tables are adapted from his report. The computer programs used in the data analysis include the Enraf-Nonius structure determination package Version 3 (1985, Delft, The Netherlands) rewritten for a Sun Microsystems computer and several locally written or modified programs.

Suitable crystals of 1 were grown from CH_2Cl_2-hexane at -30°C. A yellow air-stable needle-shaped crystal having approximate dimensions of 0.09 x 0.14 x 0.37 mm was mounted in a non-specific orientation. The automatic peak search and reflection indexing showed the crystal to be orthorhombic with systematic absences of: 0kl, l odd, h0l, l odd and hk0, h+k odd. Cell constants were obtained from the least-squares refinement of the setting angles of 23 reflections in the range $14 < 2\theta < 24$. The intensity data were collected at room temperature (23°C) using a ω-2θ scan mode. The various crystal parameters are given in Table 2.VII.

There were two reflections which were chosen as standard reflections and these were remeasured every 60 min of exposure time to check on crystal and electronic stability over the course of data collection. These reflections changed in intensity by 1.1% and 2.8% respectively over the time span of data collection, which was considered negligible. Data were corrected for Lorentz, polarization and background effects.

The structure was solved using the direct methods program MITHRIL which gave the position parameters for the Rh atom. The remaining non-hydrogen atoms were located by the usual combination of least-squares refinemenet and different Fourier synthesis.

Refinement of atomic parameters were carried out by full matrix

Table 2.VII Experimental Details

A. Crystal Data

$C_{20}H_{22}BN_6O_2Rh$; FW = 600.25

Crystal dimensions: 0.09 x 0.14 x 0.37 mm

orthorhombic space group *Pccn*

$a = 22.091\ (5)$, $b = 21.980\ (7)$, $c = 11.173\ (6)$ Å

$V = 5425$ Å^3; $Z = 8$; $D_c = 1.470$ g cm^{-3}; $\mu = 6.54$ cm^{-1}

B. Data Collection and Refinement Conditions

Radiation:	Mo K_α ($\lambda = 0.71073$ Å)
Monochromator:	incident beam, graphite crystal
Take-off angle:	3.0°
Detector aperture:	2.40 mm horiz x 4.0 mm vert
Crystal-to-detector distance:	205 mm
Scan type:	$\omega - 2\theta$
Scan rate:	10.1 - 1.8°min^{-1}
Scan width:	$0.70 + 0.35\tan(\theta)°$
Data collection 2θ limit:	55°
Data collection index range:	$h, +k, l$ for $0 < 2\theta < 24°$ h, k, l for $2\theta > 24°$
Reflections measured:	5974 unique, 1911 with $I > \sigma(I)$
Observations:variables ratio:	1911: 272
Agreement factors R_1, R_2, GOF:	0.070, 0.069, 1.41

least-squares techniques on F_o minimizing the function

$$\Sigma w (|F_o| - |F_c|)^2$$

where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes respectively, and the weighting factor w is given by

$$w = 4F_o / \sigma^2 (F_o)^2$$

All hydrogen atoms were included at their idealized calculated positions, assuming C-H and B-H distances of 0.95Å and appropriate sp^2 or sp^3 geometries. These atoms were then included in the calculations with fixed isotropic thermal parameters 1.2 times that of the attached atom and constrained to ride with this atom. The boron atom and the atoms of the pyrazole rings were refined isotropically. All other atoms were refined anisotropically.

In the final cycle 272 parameters were refined using 1911 observations having $I > \sigma(I)$. The final agreement factors were

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.070 \quad \text{and}$$

$$R_2 = (\Sigma w (|F_o| - |F_c|)^2 / \Sigma wF_o^2)^{1/2} = 0.069$$

The highest peak in the final difference Fourier has a density of 0.6(1) $eÅ^{-3}$ and is without chemical significance. The structure of 1 is depicted in Figures II.3 and II.4. Relevant bond lengths and bond angles are tabulated in Tables 2.VIII and 2.IX. Positional and thermal

Table 2.VIII Selected Interatomic Distances[a]

Atom1	Atom2	Distance	Atom1	Atom2	Distance	Atom1	Atom2	Distance
Rh	N1	2.06 (1)	N6	C23	1.36 (1)	C15	C16	1.40 (2)
Rh	N3	2.067 (8)	N6	B	1.54 (2)	C15	C20	1.38 (2)
Rh	C1	1.83 (1)	N7	C21	1.34 (1)	C16	C17	1.37 (2)
Rh	C2	1.86 (1)	C3	C4	1.40 (2)	C17	C18	1.33 (2)
O1	C1	1.15 (1)	C3	C9	1.46 (2)	C18	C19	1.41 (3)
O2	C2	1.10 (1)	C4	C5	1.36 (2)	C19	C20	1.38 (2)
N1	N2	1.37 (1)	C6	C7	1.38 (1)	C21	C22	1.38 (2)
N1	C3	1.36 (1)	C6	C15	1.45 (2)	C21	C24	1.47 (2)
N2	C5	1.36 (2)	C7	C8	1.37 (2)	C22	C23	1.34 (2)
N2	B	1.57 (2)	C9	C10	1.38 (2)	C24	C25	1.40 (2)
N3	N4	1.39 (1)	C9	C14	1.40 (2)	C24	C29	1.38 (2)
N3	C6	1.34 (1)	C10	C11	1.37 (2)	C25	C26	1.39 (2)
N4	C8	1.33 (1)	C11	C12	1.37 (3)	C26	C27	1.31 (2)
N4	B	1.52 (2)	C12	C13	1.37 (2)	C27	C28	1.41 (2)
N6	N7	1.37 (1)	C13	C14	1.34 (2)	C28	C29	1.39 (2)

[a]In angstroms. Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2.IX Selected Interatomic Angles[a]

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
N1	Rh	N3	86.3 (4)	Rh	C1	O1	178 (1)
N1	Rh	C1	91.7 (5)	Rh	C2	O2	175 (1)
N1	Rh	C2	178.5 (5)	N1	C3	C4	109 (1)
N3	Rh	C1	174.9 (5)	N1	C3	C9	121 (1)
N3	Rh	C2	94.4 (5)	C4	C3	C9	130 (1)
C1	Rh	C2	87.8 (6)	C3	C4	C5	107 (1)
Rh	N1	N2	119.6 (8)	N2	C5	C4	108 (1)
Rh	N1	C3	134.3 (9)	N3	C6	C7	110 (1)
N2	N1	C3	106 (1)	N3	C6	C15	122 (1)
N1	N2	C5	111 (1)	C7	C6	C15	129 (1)
N1	N2	B	118 (1)	C6	C7	C8	106 (1)
C5	N2	B	131 (1)	N4	C8	C7	109 (1)
Rh	N3	N4	118.8 (7)	C3	C9	C10	120 (1)
Rh	N3	C6	134.1 (9)	C3	C9	C14	121 (1)
N4	N3	C6	106.1 (8)	C10	C9	C14	119 (1)
N3	N4	C8	109.5 (9)	C9	C10	C11	118 (2)
N3	N4	B	118.9 (9)	C10	C11	C12	122 (2)
C8	N4	B	131 (1)	C11	C12	C13	119 (2)
N7	N6	C23	109.9 (9)	C12	C13	C14	121 (2)
N7	N6	B	122.0 (9)	C9	C14	C13	121 (1)
C23	N6	B	128 (1)	C6	C15	C16	122 (1)
N6	N7	C21	105.6 (8)	C6	C15	C20	120 (1)

Table 2.IX Continued

Atom1	Atom2	Atom3	Angle
C16	C15	C20	117 (1)
C15	C16	C17	120 (1)
C16	C17	C18	122 (2)
C17	C18	C19	120 (2)
C18	C19	C20	118 (2)
C15	C20	C19	122 (2)
N7	C21	C22	110 (1)
N7	C21	C24	120 (1)
C22	C21	C24	131 (1)
C21	C22	C23	107 (1)
N6	C23	C22	107 (1)
C21	C24	C25	118 (1)
C21	C24	C29	123 (1)
C25	C24	C29	119 (1)
C24	C25	C26	117 (2)
C25	C26	C27	126 (2)
C26	C27	C28	118 (2)
C27	C28	C29	119 (2)
C24	C29	C28	122 (1)
N2	B	N4	110 (1)
N2	B	N6	108 (1)
N4	B	N6	112 (1)

[a] In degrees. Numbers in parentheses are estimated standard deviations in the least significant digits.

parameters are available in the detailed report from the Structure Determination Laboratory.[34]

Preparation of $HB(3\text{-}PhPz)_3Rh(^{13}CO)_2$ (1-13,13)

A solution of 40.0 mg (0.067 mmol) 1 in 10 mL cyclohexane was treated with 1 atm ^{13}CO. After 5 min, the exchange was complete by IR spectroscopy, with a quantitative yield.

Characterization: IR (cyclohexane) 2039 (s), 2030 (w), 1980 (s), 1969 (w) cm^{-1} (ν_{CO}). MS (160°C, 70 ev) M^+ (602, 1%), M^+-^{13}CO (15%), M^+-2(^{13}CO) (18%), M^+-2(^{13}CO)-PhPz (38%), $PhPz^+$ (100%).

Preparation of $HB(3\text{-}PhPz)_3Rh(^{12}CO)(^{13}CO)$ (1-12,13)

To a solution of 102.7 mg (0.171 mmol) 12 in 25 mL cyclohexane was very slowly bubbled through 1 atm ^{13}CO. The reaction was monitored by IR spectroscopy, and the ^{13}CO addition was stopped once 12 was consumed. Solvent was removed at once in vacuo, giving a light yellow powder (96.8 mg, 94% yield).

Characterization: IR (cyclohexane) 2072 (s) with sh, 1996 (s), 1985 (w) cm^{-1} (ν_{CO}). IR (cyclohexane, after 2 weeks) 2088 (m), 2072 (s), 2039 (m), 2026 (m) 1996 (s), 1980 (m) cm^{-1} (ν_{CO}), absorbance ratio of **1-12,12:1-12,13:1-13,13** = 1:2.0:1.27. MS (190°C, 16 eV) M^+ (601, 8%), M^+-^{12}CO (33%), M^+-^{13}CO (30%), M^+-(^{12}CO)(^{13}CO) (34%), M^+-(^{12}CO)(^{13}CO)-PhPz (12%), $PhPz^+$ (100%).

Preparation of $H_2B(3\text{-}PhPz)_2Rh(CO)_2$ (2)

To a solution of $[(CO)_2RhCl]_2$ (263.0 mg, 0.677 mmol in 10 mL THF) was added 3.0 mL of a 0.2 M THF solution of $KH_2B(3\text{-}PhPz)_2$ (1.5 mmol). This gave an immediate black solution. After stirring for 1 h, the solvent was removed under reduced pressure. The yellow brown solid was taken up in 10 mL toluene and filtered through Celite giving a yellow solid after removal of solvent. Crystallization from CH_2Cl_2-hexane at -30°C gave yellow crystals (228.6 mg, 33% yield), mp darkens at 158°C, melts at 168°C.

Characterization: IR (cyclohexane) 2087, 2023 cm^{-1} (ν_{CO}). MS (130°C, 16 ev) M^{+}-CO (430, 100%), M^{+}-2CO (81%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient), δ 7.96-7.91 (m, 4H), 7.68 (d, $^3J_{H-H} = 2.2$ Hz, 2H), 7.64-7.52 (m, 6H), 6.47 (d, $^3J_{H-H} = 2.2$ Hz, 2H). UV (CH_2Cl_2) 243 (ε 25070) 354 (ε 2380) nm (λ max). Anal. Calcd for $C_{20}H_{16}BN_4O_2Rh$: C, 52.44; H, 3.52; N, 12.23. Found: C, 52.38; H, 3.45; N, 12.18.

Preparation of $[(CO)_2Rh(3\text{-}PhPz)]_2$ (3)

Following the method of Banditelli et al.[16] a solution of 45.8 mg (0.82 mmol) KOH and 139.2 mg (0.79 mmol) 3-PhPzH in 3 mL MeOH was added to 145.6 mg (0.374 mmol) $[(CO)_2RhCl]_2$ in 10 mL Et_2O, resulting in a cloudy yellow solution. After stirring for 1 h, solvent was removed. The residues were taken up in 25 mL benzene and filtered through Celite. A yellow oil resulted after removal of solvent under reduced pressure. Sublimation at 120°C/0.1 mm Hg onto a -78°C probe gave an orange solid (182.4 mg, 81% yield) mp 88-90°C.

Characterization: IR (cyclohexane) 2089, 2076, 2023 cm^{-1} (ν_{CO}). MS (150°C, 16 ev) M$^+$ (604, 100%), M$^+$-2CO (63%), M$^+$-3CO (6%), M$^+$-4CO (32%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 8.13-7.81 (m, 4H), 7.75 (d, 2H, $^3J_{H-H}$ = 2.0 Hz, major isomer), 7.67 (d, 2H, $^3J_{H-H}$ = 1.9 Hz, minor isomer), 7.63-7.29 (m, 6H), 6.57 (d, 2H, $^3J_{H-H}$ = 2.1 Hz, overlapping). Isomer ratio of 1.23:1. Anal. Calcd for $C_{22}H_{14}N_4O_4Rh_2$: C, 43.74; H, 2.34; N, 9.27. Found: C, 44.40; H, 2.46; N, 9.15.

Preparation of ClRh(CO)$_2$(3-PhPzH) (4)

To a solution of [(CO)$_2$RhCl]$_2$ (428.1 mg, 1.10 mmol) in 20 mL CH_2Cl_2 was added 318.0 mg (2.20 mmol) 3-PhPzH, giving a lemon-yellow solution. After stirring for 1 h, solvent was removed in vacuo, leaving a green-purple solid. Crystallization from CH_2Cl_2-hexane at -30°C afforded green-purple needles (653.9 mg, 88% yield) mp 129-131°C.

Characterization: IR (cyclohexane) 2087, 2012 cm^{-1} (ν_{CO}). MS (150°C, 16 eV) M$^+$ (338, 5%), M$^+$-CO (3%), M$^+$-2CO (2%), PhPz$^+$ (100%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 12.34 (br, 1H), 7.68 (s, 1H), 7.62-7.55 (m, 2H), 7.52-7.45 (m, 3H), 6.69 (s, 1H). Anal. Calcd for $C_{11}H_8N_2O_2ClRh$: C, 39.08; H, 2.38; N, 8.27. Found: C, 39.02; H, 2.42; N, 8.43.

Preparation of ClRh(CO)$_2$(3-PhPz)(H)B(3-PhPz)$_2$Rh(CO)$_2$ (5)

To a solution of 1 (65.9 mg, 0.110 mmol in 15 mL CH_2Cl_2) was added 21.4 mg (0.055 mmol) of [(CO)$_2$RhCl]$_2$. After stirring for 15 min, the solution was concentrated to a volume of 2 mL under reduced pressure, layered with 20 mL hexane and cooled to -30°C, affording yellow crystals (85.4 mg, 98% yield) mp darkens at 180°C, melts at 187-189°C.

Characterization: IR (cyclohexane) 2093, 2076, 2032, 1998 cm^{-1} (ν_{CO}). MS (180°C, 16 eV) M^+-Rh(CO)$_2$ (635, 2%), M^+-Rh(CO)$_3$ (16%), M^+-ClRh(CO)$_2$ (12%), M^+-ClRh(CO)$_3$ (100%), M^+-ClRh(CO)$_4$ (76%). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, ambient) δ 8.50 (d, 1H, $^3J_{H-H}$ = 2.2 Hz), 8.15 (d, 1H, $^3J_{H-H}$ = 2.2 Hz), 8.02 (dd, 2H, o-Ph), 7.99 (dd, 2H, o-Ph), 7.92 (dd, 2H, o-Ph), 7.60 (t, 1H, p-Ph), 7.58 (t, 1H, p-Ph), 7.56 (m, 2H, o-Ph), 7.46 (t, 1H, p-Ph), 7.44 (m, 2H, m-Ph), 7.20 (d, 1H, $^3J_{H-H}$ = 2.2 Hz), 6.685 (d, 1H, $^3J_{H-H}$ = 2.2 Hz), 6.682 (d, 1H, $^3J_{H-H}$ = 2.2 Hz), 6.50 (d, 1H, $^3J_{H-H}$ = 2.2 Hz). ^{13}C NMR (CD$_2$Cl$_2$, 75.5 MHz, ambient) δ 184.79 (d, CO, $^1J_{Rh-C}$ = 69 Hz), 182.64 (d, CO, $^1J_{Rh-C}$ = 69 Hz), 182.41 (d, CO, $^1J_{Rh-C}$ = 69 Hz), 179.97 (d, CO, $^1J_{Rh-C}$ = 74 Hz), 158.01, 157.63, 157.02 (3-C), 142.90, 140.76, 138.16 (5-C), 133.68, 133.40, 133.16 (C$_{ipso}$)[31], 130.15, 130.08, 130.04, 129.89, 129.69, 129.16, 129.05, 128.87, 128.48 (Ph-C), 106.67 (1C), 106.33 (2C) (4-C). Anal. Calcd for $C_{31}H_{22}BN_6O_4ClRh_2$: C, 46.86; H, 2.79; N, 10.58. Found: C, 46.64; H, 2.70; N, 10.32.

Reaction of (5) with KHB(3-PhPz)$_3$

To a solution of 15.4 mg (0.019 mmol) 5 in 10 mL CH$_2$Cl$_2$ was added 9.1 mg (0.019 mmol) KHB (3-PhPz)$_3$ and this was stirred for 1 h. The reaction was worked up as for 1, giving a yellow powder (19.2 mg, 84% yield) of what was identified to be 1 by IR and ^{1}H NMR spectroscopy.

Preparation of [HB(3-PhPz)$_2$(3-PhPzH)Rh(CO)$_2$](BF$_4$) (6)

To a yellow solution of 1 (222.2 mg, 0.370 mmol) in 25 mL CH$_2$Cl$_2$ was added HBF$_4$.Et$_2$O until the reaction was complete by IR spectroscopy and the solution was colorless. After concentration of the solution to

3 mL under reduced pressure 25 mL of Et_2O was added, giving a light yellow solid. This was filtered by means of a cannula, washed with 10 mL Et_2O, and dried in vacuo (235.0 mg, 92% yield) mp 157-159°C.

<u>Characterization:</u> IR (benzene) 2092, 2031 cm^{-1} (ν_{CO}). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 13.25 (br, 1H), 8.26 (d, 2H, $^3J_{H-H}$ = 2 Hz), 8.0-7.8 (m, 7H), 7.70-7.46 (m, 9H), 6.79 (t, 1H, J = 2.5 Hz), 6.69 (d, 2H, $^3J_{H-H}$ = 2.5 Hz). Anal. Calcd for $C_{29}H_{23}B_2N_6O_2F_4Rh$: C, 50.62; H, 3.37; N, 12.21. Found: C, 50.33; H, 3.30; N, 11.99.

Preparation of $HB(3\text{-}PhPz)_2(C_3H_2N_2\text{-}\overline{C_6H_4)Rh}(CO)(H)\cdot 1/6(C_6H_6)$ (7)

A solution of 1 (57.4 mg, 0.096 mmol) in 25 mL benzene was irradiated for 20 min with a N_2 purge. The initial pale yellow solution turned colorless. Solvent was removed under reduced pressure affording an off-white solid (47.5 mg, 84% yield) mp > 300°C.

<u>Characterization:</u> IR (cyclohexane) 2104 (vw) (ν_{Rh-H}), 2063 (vs) cm^{-1} (ν_{CO}). MS (210°C, 16 eV) M^+ (572, 9%), M^+-CO (5%), $PhPz^+$ (100%). Anal. Calcd for $C_{28}H_{22}BN_6ORh\cdot 1/6(C_6H_6)$: C, 59.52; H, 3.96; N, 14.36. Found: C, 59.59; H, 4.14; N, 13.92.

Preparation of $HB(3\text{-}PhPz)_2(C_3H_2N_2\text{-}\overline{C_6H_4)Rh}(CO)(Cl)$ (8a)

A solution of 1 (361.0 mg, 0.601 mmol) in benzene (35 mL) was irradiated for 20 min with a N_2 purge. Excess CCl_4 (1 mL) was added and after 1 h, solvent and excess CCl_4 were removed under reduced pressure. The resulting yellow solid was chromatographed twice on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent. Yellow crystals were obtained from CH_2Cl_2-hexane at -30°C (136.2 mg, 37% yield) mp 201-203°C.

Characterization: IR (cyclohexane) 2096 cm^{-1} (ν_{CO}). MS (200°C, 70 eV) M^+ (606, 50%), M^+-CO (78%), M^+-CO-Cl (100%). Anal. Calcd for $C_{28}H_{21}BN_6OClRh$: C, 55.43; H, 3.49; N, 13.85. Found: C, 54.97; H, 3.48; N, 13.93.

Preparation of $\mathrm{HB(3\text{-}PhPz)_2(C_3H_2N_2\text{-}\overline{C_6H_4)R}h(CO)(Br)}$ (8b)

A solution of 1 (222.3 mg, 0.370 mmol) in benzene (50 mL) was irradiated for 20 min with a N_2 purge. Excess $CBrCl_3$ (1 mL) was added and the solution immediately changed in color from pale yellow to orange. Excess solvent and $CBrCl_3$ were removed in vacuo. The residue was chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent, and yellow crystals were obtained from CH_2Cl_2-hexane at -30°C (217.1 mg, 90% yield) mp 237-239°C.

Characterization: IR (cyclohexane) 2090 cm^{-1} (ν_{CO}). MS (210°C, 70 eV) M^+ (652, 32%), M^+-CO (37%), M^+-Br (12%), M^+-CO-Br (100%). Anal. Calcd for $C_{28}H_{21}BN_6OBrRh$: C, 51.65; H, 3.25; N, 12.91. Found: C, 52.00; H, 3.43; N, 12.60.

Preparation of $\mathrm{HB(3\text{-}PhPz)_2(C_3H_2N_2\text{-}C_6H_4\overline{CH_2)R}h(CO)(CH_3)}$ (9)

A sample of 344.5 mg (0.574 mmol) of 1 was taken up in 75 mL benzene. This solution was irradiated for 20 min with a N_2 purge, and then excess CH_2N_2/Et_2O (1 mL) was added. An immediate reaction occurred and excess CH_2N_2/Et_2O and benzene were removed in vacuo. The residue was chromatographed on neutral alumina (12 x 2.5 cm) with 4:1

hexane:CH_2Cl_2 eluent. The resulting white solid was crystallized from CH_2Cl_2-hexane at -30°C giving colorless crystals (234.6 mg, 68% yield) mp darkens at 213°C, decomposes at 222-223°C.

Characterization: IR (cyclohexane) 2042 cm^{-1} (ν_{CO}). MS (190°C, 16 eV) M^+ (600, 100%), M^+-CH_3 (6%), M^+-CO (84%), M^+-CO-CH_3 (7%). Anal. Calcd for $C_{30}H_{26}BN_6ORh$: C, 60.03; H, 4.37; N, 14.00. Found: C, 60.01; H, 4.27; N, 13.85.

Preparation of $HB(3\text{-}PhPz)_2(C_3H_2N_2\text{-}\overline{C_6H_4)Rh}(CO)(CH_3)$ (10)

To a solution of **8b** (101.6 mg, 0.156 mmol in 20 mL THF) was added dropwise a solution of MeMgI in Et_2O (190.0 mg, 7.82 mmol Mg, 0.5 mL, 8.0 mmol MeI in 10 mL Et_2O). The reaction was monitored by IR spectroscopy, and when starting material had disappeared, Grignard addition was halted. Solvent was removed in vacuo, and the product was extracted with 5 x 50 mL hexane. After removing solvent, the resulting white solid was taken up in a minimum amount of CH_2Cl_2 (3 mL), layered with hexane (50 mL) and cooled to -30°C, yielding a white powder (81.9 mg, 90% yield) mp darkens at 160°C, decomposes at 169-171°C.

Characterization: IR (cyclohexane) 2052 cm^{-1} (ν_{CO}). MS (180°C, 70 eV) M^+ (586, 60%), M^+-CH_3 (2%), M^+-CO (90%), M^+-CO-CH_3 (28%), M^+-CO-PhPz (100%). Anal. Calcd for $C_{29}H_{24}BN_6ORh$: C, 59.41; H, 4.13; N, 14.33. Found: C, 59.49; H, 4.08; N, 14.10.

Preparation of $HB(3\text{-}PhPz)_3\overline{Rh(CO)(CH_2CH_2CH_2}) $ (11)

A solution of 1 (169.4 mg, 0.282 mmol) in 50 mL benzene was irradiated for 50 min with a cyclopropane gas purge, with the IR spectrum exhibiting two ν_{CO} bands at 2058 cm^{-1} 7 and 2031 cm^{-1} 11. The benzene solution was left in air overnight, whereupon 7 had decomposed. After removing benzene, the residues were chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent and solvent was removed in vacuo, giving an off-white powder (119.5 mg, 69% yield) mp darkens at 140°C.

Characterization: IR (cyclohexane) 2034 cm^{-1} (ν_{CO}). MS (180°C, 16 eV) M^+-CO (586, 10%), M^+-C_3H_6 (95%), M^+-C_3H_6-CO (100%). Anal. Calcd for $C_{31}H_{28}BN_6ORh$: C, 60.61; H, 4.59; N, 13.68. Found: C, 60.52; H, 4.67; N, 12.99.

Preparation of $HB(3\text{-}PhPz)_3Rh(CO)(C_2H_4)$ (12)

A sample of 105.1 mg (0.27 mmol) $[(C_2H_4)_2RhCl]_2$ and 105.1 mg (0.27 mmol) $[(CO)_2RhCl]_2$ were stirred together in 25 mL toluene for 0.5 h, giving approximately 0.54 mmol $[(C_2H_4)(CO)RhCl]_2$. The salt $KHB(3\text{-}PhPz)_3$ (588.8 mg, 1.08 mmol) was added, and this Indian red solution was stirred for 2 h. The solution was filtered through Celite and solvent removed under reduced pressure. The resulting orange oil was taken up in CH_2Cl_2 and chromatographed on neutral alumina (12 x 2.5 cm), eluting the product with CH_3CN. Crystallization from CH_2Cl_2-hexane at -30°C afforded yellow crystals (521.7 mg, 81% yield) mp 161-163°C.

Characterization: IR (cyclohexane) 2030 cm^{-1} (ν_{CO}). MS (200°C, 16 eV) M^+ (600, 4%), M^+-CO or C_2H_4 (41%), M^+-CO-C_2H_4 (29%), M^+-CO-C_2H_4-PhPz (11%), $PhPz^+$ (100%). Anal. Calcd for $C_{30}H_{26}BN_6ORh \cdot CH_2Cl_2$: C, 54.34; H, 4.12; N, 12.26. Found: C, 54.76, H, 4.19; N, 12.27.

Attempted Preparation of $H_2B(3\text{-}PhPz)_2Rh(CO)(C_2H_4)$ (13)

A sample of 25.6 mg (0.066 mmol) $[(C_2H_4)_2RhCl]_2$ and 25.6 mg (0.066 mmol) $[(CO)_2RhCl]_2$ were stirred together in 15 mL cyclohexane for 0.5 h, yielding approximately 0.132 mmol $[(C_2H_4)(CO)RhCl]_2$. To this solution was added 89.3 mg (0.264 mmol) of $KH_2B(3\text{-}PhPz)_2$, resulting in an immediate reaction with IR ν_{CO} at 2087 (w), 2023 (s) cm^{-1}. These band positions correspond well to **2**, except they should be of similar intensity. Hence complex **13** also has IR ν_{CO} at 2023 cm^{-1}, which is 7 cm^{-1} lower than the value for **12**. On monitoring the solution by IR spectroscopy, a conversion occurs to **2** in about an hour, either via disproportionation or decomposition.

Preparation of $HB(3\text{-}PhPz)_3Rh(C_2H_4)_2$ (14)

To a solution of $[(C_2H_4)_2RhCl]_2$ (84.3 mg, 0.217 mmol in 30 mL toluene) was added 208.3 mg (0.434 mmol) of $KHB(3\text{-}PhPz)_3$. This cloudy yellow solution was stirred for 18 h, giving an Indian red solution. This was filtered through Celite and concentrated to an orange oil. Dissolving in 30 mL hot hexane and cooling to -30°C afforded an orange solid (192.0 mg, 74% yield) mp 230-235°C.

Characterization: MS (210°C, 16 eV) M^+ (600, 31%), $M^+\text{-}PhPz\text{-}C_2H_4$ (100%), $M^+\text{-}PhPz\text{-}2(C_2H_4)$ (71%). Anal. Calcd for $C_{31}H_{30}BN_6Rh$: C, 62.02; H, 5.04; N, 14.00. Found: C, 61.90; H, 5.09; N, 14.31.

Preparation of HB(3-PhPz)$_3$Rh(COD) (15)

To a solution of [(COD)RhCl]$_2$ (100.0 mg, 0.203 mmol in 30 mL toluene) was added 194.4 mg (0.405 mmol) of KHB(3-PhPz)$_3$. This cloudy yellow solution was stirred for 18 h, filtered through Celite and solvent was removed under reduced pressure. The resultant yellow orange oil was taken up in 30 mL hexane and cooled to -30°C, which yielded a yellow precipitate. Two subsequent concentrations of the mother liquor gave yellow crystals (236.6 mg, 90% yield) mp 177-179°C.

Characterization: MS (200°C, 16 eV) M^+ (652, 100%), M^+-COD (12%), M^+-PhPz (26%). Anal. Calcd for $C_{35}H_{34}BN_6Rh$: C, 64.44; H, 5.25; N, 12.88. Found: C, 64.75; H, 5.47; N, 12.46.

Reaction of HB(3-PhPz)$_3$Rh(COD) (15) with [(CO)$_2$RhCl]$_2$

A sample of 64.7 mg (0.100 mmol) 15 and 19.2 mg (0.050 mmol) [(CO)$_2$RhCl]$_2$ were dissolved in 10 mL CH_2Cl_2. After stirring for 15 min, IR showed the disappearance of the starting material with appearance of (1). The two products could not be separated by chromatography or crystallization, but a ^{1}H NMR spectrum of the mixture showed the presence of 1 and [CODRhCl]$_2$.[29]

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33. A.J. Gordon and R.A. Ford, "The Chemist's Companion", Wiley-Interscience, New York, 1972.

34. R.G. Ball, University of Alberta, Structure Determination Laboratory, Report No. SR: 071801-12-87 (30 Sept. 1987).

CHAPTER III

SYNTHESIS OF TRIFLUOROMETHYL(PYRAZOLYL)BORATE RHODIUM COMPLEXES

Section 1

INTRODUCTION

The synthesis of the first poly(pyrazolyl)borate ligands by Trofimenko in 1967 were based on ordinary pyrazole (PzH),[1] followed by 3,5-dimethylpyrazole (Pz*H).[2] Related ligands were also prepared using various other pyrazoles,[2,3] but the extensive development of pyrazolylborate transition-metal chemistry evolved primarily from the former two systems.

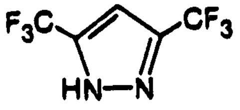
Trofimenko has demonstrated that the steric size of the groups in the 3- and 5-positions of the pyrazole ring limits the degree of substitution from tetrakis to tris to bis. With ordinary pyrazole, the tetrakis(pyrazolyl)borate ligand can be prepared,[1] but the reaction of KBH_4 with excess 3,5-Me_2PzH in a melt at 238°C stops at tris substitution giving $KHB(3,5\text{-}Me_2Pz)_3$.[2] The same degree of substitution was also observed with 3,5-Et_2PzH,[3b] but with 3,5-Ph_2PzH only the bis(pyrazolyl)borate ligand could be prepared.[3a] With 3,5-t-Bu_2PzH, not even the bis(pyrazolyl)borate ligand was formed.[3c]

The first example of the use of an unsymmetric pyrazole was with 3-MePzH.[4] Only the sterically favored ligands $[H_nB(3\text{-}MePz)_{4-n}]^-$ (n=0,1,2) were obtained, whose assignment was initially based on ^1H NMR data with final proof being a X-ray crystal structure of a metal complex.[4b] It was argued that in the transition state to form the ligand, the pyrazole approaches the boron most easily from the least hindered nitrogen, resulting in the larger group occupying the 3-position.

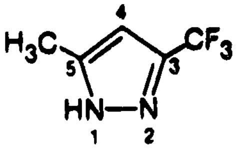
Only recently has the synthesis of new pyrazolylborate ligands been undertaken. Trofimenko et al. have prepared the so-called second generation pyrazolylborate ligands of the type $[H_nB(3\text{-}RPz)_{4-n}]^-$ (n=0,1,2) with bulky groups (Ph,[5] t-Bu,[5] and i-Pr[6]) in the 3-position of the pyrazolyl ring.

Poly(pyrazolyl)borate ligands are generally prepared by one of two routes.[7] The first involves the reaction of the tetrahydridoborate ion (BH_4^-) with excess of the appropriate pyrazole in a melt, where the degree of substitution is temperature controlled. The second method involves the reaction of one equivalent of (BH_4^-) with two equivalents of the pyrazole in anhydrous N,N-dimethylacetamide (DMAC), giving the bis(pyrazolyl)borate ligand. In some cases the tris(pyrazolyl)borate ligand can be prepared by reacting the bis(pyrazolyl)borate ligand with one equivalent of pyrazole in refluxing anisole.[5]

Preparation of complexes of the type $H_nB(3\text{-}PhPz)_{4-n}Rh(CO)_2$ (n=1,2) were described in Chapter II. However, C-H bond activation with $HB(3\text{-}PhPz)_3Rh(CO)_2$ **1** in benzene or cyclohexane resulted in intramolecular activation (or orthometallation). To further study intermolecular C-H activation, the synthesis of orthometallation-proof ligands was undertaken. Suitable candidates were pyrazoles containing a CF_3 group in the 3-position of the pyrazole ring, specifically using the known pyrazoles, 3,5-bis(trifluoromethyl)pyrazole ($3,5\text{-}(CF_3)_2PzH$)[8] and 3-trifluoromethyl-5-methylpyrazole ($3\text{-}CF_3\text{-}5\text{-}MePzH$)[9] (eq. 3-1).



$3,5\text{-}(CF_3)_2PzH$



$3\text{-}CF_3\text{-}5\text{-}MePzH$

(3-1)

This Chapter discusses the synthesis of new poly(pyrazolyl)borate ligands utilizing these pyrazoles and the subsequent preparation of Rh(I) analogs of Pz* compounds. The ligands $KH_2B(3,5-(CF_3)_2Pz)_2$, $KH_2B(3-CF_3-5-MePz)_2$ and $KHB(3-CF_3-5-MePz)_3$ were prepared by reaction of KBH_4 with the excess pyrazole in a melt at the appropriate temperature. Preparation of the bis(pyrazolyl)borate ligands was also accomplished via the solvent route in DMAC. Using the unsymmetric pyrazole $3-CF_3-5-MePzH$ results in a statistical distribution of all possible bis(pyrazolyl)borate regioisomers $KH_2B(3-CF_3-5-MePz)_2$, $KH_2B(3-CF_3-5-MePz)(3-Me-5-CF_3Pz)$ and $KH_2B(3-Me-5-CF_3Pz)_2$.

These ligands are the first known examples of pyrazolylborate ligands with CF_3 groups. The synthesis and characterization of tris(pyrazolyl)borate rhodium carbonyl and olefin complexes will be discussed, which are suitable complexes for C-H activation studies. A number of the bis(pyrazolyl)borate analogs are prepared. The IR ν_{CO} bands of the bis and the tris(pyrazolyl)borate complexes are compared to determine the hapticity of the ligand in the latter complexes. The X-ray structure of a tris(pyrazolyl)borate rhodium dicarbonyl will be presented.

Section 2

3,5-BIS(TRIFLUOROMETHYL)PYRAZOLE CHEMISTRY

$3,5-(CF_3)_2PzH$ was prepared by Trofimenko[8] who subsequently used it in the synthesis of pyrazaboles, which are boron-nitrogen heterocyclic compounds. The pyrazole has also been used to prepare rhodium and iridium pyrazole bridged dimers.[10] There are no reports in the literature of pyrazolylborate ligands with CF_3 groups on the pyrazole, except by Frauendorfer and Agrifoglio who state,[11] "The reaction of KBH_4 with 3,5-bis(trifluoromethyl)pyrazole proceeded faster than with pyrazole in a melt as well in the solvents toluene and monoglyme. In all these cases we recovered unreacted KBH_4 and disubstituted product."

The reaction of KBH_4 and excess $3,5-(CF_3)_2PzH$ in a melt at reflux gives exclusively the bis(pyrazolyl)borate ligand $KH_2B(3,5-(CF_3)_2Pz)_2$ (**16**). Excess pyrazole is sublimed off, leaving **16** as an analytically pure white solid (eq. 3-2).

(3-2)

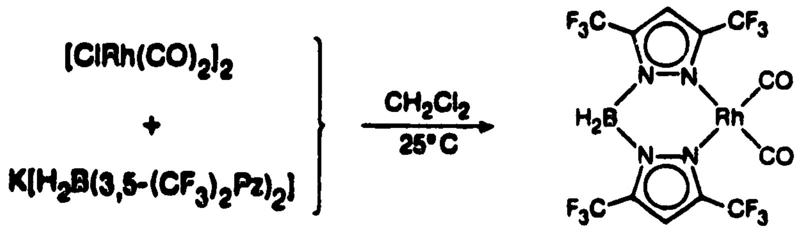
16

The ^1H NMR spectrum of **16** shows the 4-H proton as a singlet at δ 6.80, and the ^{19}F NMR spectrum shows two types of CF_3 groups, with a triplet at δ -59.57 (t, 6F, $^5J_{F-H}=3$ Hz) and a sharp singlet at δ -61.82. Further evidence in Section 3 suggests that the former resonance is the CF_3 group in the 5-position, which is a triplet due to coupling to the hydrogens on boron. This F-H coupling is confirmed when the spectrum is run with broadband proton decoupling, as the resonance at δ -59.57 collapses to a singlet.

Attempts at preparing the analogous tris(pyrazolyl)borate ligand $KHB(3,5\text{-}(CF_3)_2Pz)_3$ were not successful, and this was thought to be due to the greater steric constraints of the CF_3 group when present in both 3- and 5-positions of the pyrazole. However, it has been found that this ligand can be prepared, but it is fairly unstable.[12] Trofimenko attributes this to the acidity of the free pyrazole, making the pyrazole anion a good leaving group.

The bis(pyrazolyl)borate ligand **16** can also be prepared via the so-called solvent route using two equivalents of $3,5\text{-}(CF_3)_2PzH$ to one equivalent of KBH_4 in refluxing DMAC. It was isolated as the DMAC solvate, and reacts in the same manner as the solvent free material.

The reaction of **16** with $[(CO)_2RhCl]_2$ in CH_2Cl_2 gives $H_2B(3,5\text{-}(CF_3)_2Pz)_2Rh(CO)_2$ (**17**) in high yield (eq. 3-3).



(3-3)

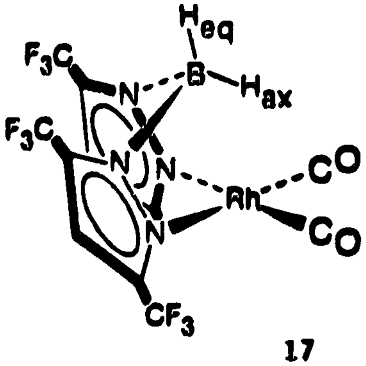
16 **17**

Unlike the synthesis of the bis(pyrazolyl)borate complex $H_2B(3\text{-}PhPz)_2Rh(CO)_2$ **2**, where the solution immediately darkened, the solution here remained yellow during the reaction. One would expect that the electron withdrawing CF_3 groups would make the ligand **16** less of a reducing agent which would account for the improved yield of **17** relative to **2**.

Also present in the reaction mixture is a small amount of the known dimer $[(CO)_2Rh(3,5\text{-}(CF_3)_2Pz)]_2$,[10a] which was identified by comparison of the IR and NMR spectra to an authentic sample. Complex **17** could be separated from this dimer by fractional crystallization and was isolated as a bright yellow air-stable solid. The IR spectrum in hexane showed two ν_{CO} bands at 2107, 2048 cm^{-1}, which are considerably higher in energy than those for $(H_2BPz^*{}_2)Rh(CO)_2$ (ν_{CO} 2079, 2013 cm^{-1}).[13]

This demonstrates that relative to a methyl group, the CF_3 group is more electron withdrawing. Complex **17** is also soluble in perfluorohexane (IR ν_{CO} at 2110, 2051 cm^{-1}), whereas $(H_2BPz^*{}_2)Rh(CO)_2$ is essentially insoluble.[14] The presence of the CF_3 groups also increases the volatility of **17** relative to the Pz* analog, as the former can be sublimed at 35°C/0.8 mm Hg. The mass spectrum was obtained at 110°C, which showed the molecular ion M^+ at m/e = 578 with secondary ions corresponding to loss of the CO groups.

The ^1H NMR spectrum shows a single resonance at δ 6.99 for the 4-H proton, and the ^{19}F NMR spectrum showed two resonances, a singlet at δ -59.95 and a doublet at δ -60.29 ($^5J_{F-H}$ = 5 Hz). The latter resonance, which is thought to correspond to the triplet in the potassium salt **16**, collapses to a singlet with broadband proton decoupling. Based on the known structures of bis and tris(pyrazolyl)borate and gallate complexes,[3c,7] the structure of 17 is not planar but is in a boat conformation, with pseudo axial (H_{ax}) and equatorial (H_{eq}) B-H groups. The 5-CF_3 group appears to couple to only one of the two hydrogens.



17

The ^{13}C NMR spectrum of 17 shows a CO carbon at δ 181.69 (d, $^1J_{Rh-C}$ = 71 Hz) and four quartets, two with a large C-F coupling for the CF_3 group (δ 119.84 and 119.13, $^1J_{C-F}$ = 270 Hz) and two with a smaller C-F coupling for the C-CF_3 carbons (δ 144.50 and 140.89, with $^2J_{C-F}$ = 39 and 43 Hz respectively). The 4-C appears as a singlet at δ 108.22.

The concept of coordination shift has been widely used in ^{31}P NMR involving phosphine ligands.[15] The 3- and 5-CF_3 groups in the ^{19}F NMR spectrum of 17 exhibit a coordination shift upon complexation relative to the free ligand 16. The 3-CF_3 group, which is at δ -61.82 in 16, shifts to -59.95 in 17, with ΔCF_3 = +1.87 ppm. On the other hand, the 5-CF_3 group has ΔCF_3 = -0.72 ppm. This positive coordination shift for the 3-CF_3 groups and a negative value for the 5-CF_3 groups is consistently observed with complexes in Sections 3 and 4.

Reactions of $H_2B(3,5-(CF_3)_2Pz)_2Rh(CO)_2$ (17)

As demonstrated in Chapter II, 16e Rh(I) complexes exchange ^{13}CO very rapidly. The reaction of a hexane solution of 17 with ^{13}CO is complete in five minutes, with the IR ν_{CO} bands for the enriched complex at 2058, 2001 cm^{-1}.

Photolysis of a benzene or cyclohexane solution of 17 for 24 hours gave no reaction. This is consistent with the observation by Ghosh that the bis(pyrazolyl)borate complex $(H_2BPz^*{}_2)Rh(CO)_2$ does not activate C-H bonds photochemically.[14]

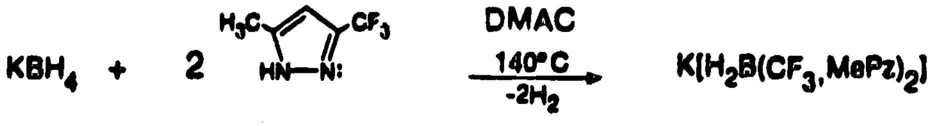
Section 3

3-TRIFLUOROMETHYL-5-METHYLPYRAZOLE CHEMISTRY

SYNTHESIS OF BIS(PYRAZOLYL)BORATE COMPLEXES

The pyrazole 3-CF_3-5-MePzH (18) has previously been prepared by several methods[9] and used to prepare mononuclear platinum[16] and dinuclear iridium complexes.[10b,c] There are no literature reports on the preparation of the corresponding poly(pyrazolyl)borate ligands. As the pyrazole itself is unsymmetric, one could possibly get regioisomeric mixtures of products. This stems from the fact that a CF_3 and a Me group are not that different in size.

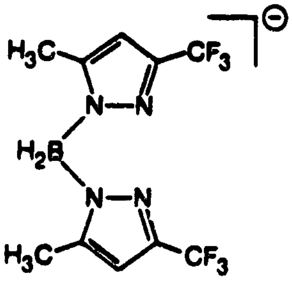
Two methods were employed for the preparation of the bis(pyrazolyl)borate ligand. Using the solution method (in DMAC), one obtains the bis(pyrazolyl)borate ligand $KH_2B(CF_3,MePz)_2$ (19), which is a mixture of the three possible regioisomers (eq. 3-4).



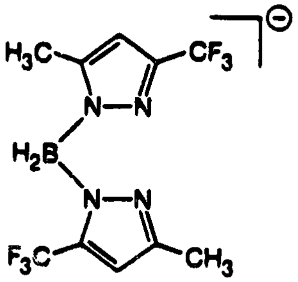
18

19

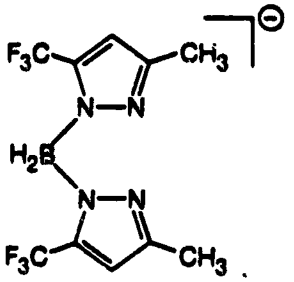
(3-4)



19a

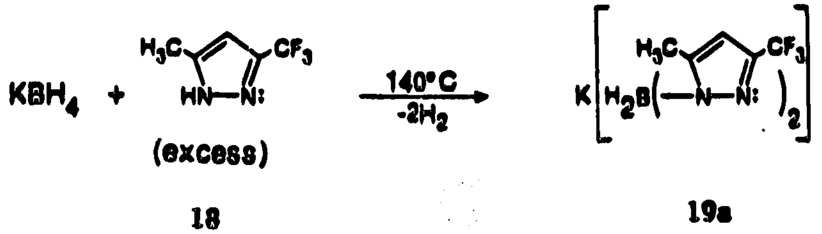


19b



19c

The unambiguous assignment of the three isomers is based on the fact that one of the three isomers can be separately prepared. The reaction of KBH_4 with excess 3-CF_3-5-MePzH at 140°C yields a white solid which melts sharply at 148-150°C (eq. 3-5).



(3-5)

The ^1H NMR spectrum displays the 4-H protons at δ 6.19 (s, 2H) and the 5-Me group at δ 2.34 (s, 6H). The ^{19}F NMR spectrum shows a single sharp resonance at δ -61.42. This and other evidence presented later suggests that this product is the sterically expected isomer $KH_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2$ (**19a**). Most of the potassium poly(pyrazolyl)borate ligands prepared in this Thesis do not give satisfactory elemental analyses. This is typical of the majority of potassium or sodium salts prepared.[1-6]

The regioisomeric mixture of **19** obtained by the solution method is also a white solid and it melts over a fairly large temperature range (95-105°C). The ^1H and ^{19}F NMR spectra of **19** show four sets of pyrazole group resonances, with one set corresponding to **19a**.

Two of the remaining three sets of resonances with similar integrals correspond to the unsymmetric isomer **19b**, as the two pyrazole groups are in different positions. The ^1H NMR spectrum shows two 4-H resonances at δ 6.27 (s, 1H) and 6.15 (s, 1H), and two 5-Me resonances at δ 2.27 (s, 3H) and 2.13 (s, 3H). Of the three remaining resonances in the ^{19}F NMR spectrum of **19**, two are of approximate equal integral corresponding to **19b**. One resonance is a broad signal at δ -58.62 assigned as the 5-CF_3 group (again broadened by coupling to the B-H protons), while the other is a sharp singlet at δ -61.44 for the 3-CF_3 group. The chemical shift of the latter signal is also close to that of isomer **19a**, where both CF_3 groups are thought to be in the 3-position.

The last set of NMR resonances is assigned to **19c**, with the ^1H NMR spectrum showing the 4-H protons at δ 6.29 (s, 2H) and the 5-Me groups at δ 2.11 (s, 6H). The ^{19}F NMR spectrum shows a broad resonance at δ -59.05, close to the 5-CF_3 signal of **19b**. When the ^{19}F NMR spectrum of **19** is ^1H decoupled, all resonances are sharp singlets.

An almost statistical product ratio for **19a**:**19b**:**19c** of 1:2:1 is observed by ^1H and ^{19}F NMR spectroscopy, indicating only a small steric preference for the CF_3 or Me groups in the 3- and 5-positions. From the integrals of the 3 isomers in the ^1H NMR spectrum, the ratio of **19a**:**19b**:**19c** is 1.3:2.9:1, indicating that the distribution is not quite statistical. The ratio of **19a**:**19c** = 1.3:1 is presumed to result from a slight steric preference.

The mixture of **19** is not surprising considering that the synthesis of the bis(trifluoromethyl)pyrazole ligand **16** has demonstrated that two CF_3 groups can "fit" close to boron. The size difference between a CF_3 and a Me group is not nearly as large as with some of the other unsymmetric pyrazoles used to prepare pyrazolylborate ligands.[4-6] What is surprising is that with excess pyrazole **18** in the melt reaction, rearrangement to the sterically favored isomer **19a** occurs. When the mixture **19** is heated with excess 3-CF_3-5-MePzH in a melt at 140°C, pure **19a** is obtained. This suggests that with the solution method one obtains a statistical or kinetic product, but reaction with excess pyrazole in a melt results in rearrangement to the thermodynamic product.

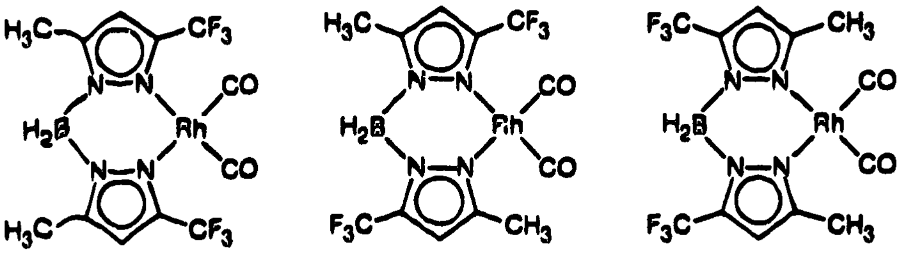
Further evidence for the assignments of the isomers in **19** arises from the rhodium complexes. Reaction of $[(CO)_2RhCl]_2$ with $KH_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2$ **19a** in CH_2Cl_2 gives $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)_2$ (**20a**) as air-stable yellow crystals in good yield (eq. 3-6).

$$\left.\begin{array}{c}[ClRh(CO)_2]_2\\ +\\ K[H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2]\end{array}\right\} \xrightarrow[25^{\circ}C]{CH_2Cl_2} H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)_2 \qquad (3\text{-}6)$$

19a **20a**

The IR spectrum in hexane shows the expected two ν_{CO} bands (with ^{13}C satellites) at 2098 (s), 2082 (vw), 2035 (s), 2004 (vw) cm^{-1}. The ^1H NMR spectrum shows only one type of pyrazole group, with the 4-H resonance at δ 6.34 (s, 2H) and the 5-Me groups at δ 2.36 (s, 6H). This indicates a mirror plane through boron and rhodium (symmetry group C_s). The ^{13}C APT NMR spectrum of **20a** shows the CO carbon at δ 183.43 (d, $^1J_{Rh-C} = 69$ Hz). The remainder of the resonances can be all uniquely assigned as demonstrated by Stobart for **18**.[16] The CF_3 carbon appears as a quartet at δ 120.92 with a large one bond C-F coupling ($^1J_{F-C} = 269$ Hz) and the pyrazole ring carbon attached to the CF_3 group is a quartet at δ 143.03 with a smaller two bond C-F coupling ($^2J_{F-C} = 38$ Hz). The pyrazole ring carbon attached to the methyl group is a singlet at δ 147.29, the 4-C is a singlet at δ 106.74 and the methyl carbon is a singlet at δ 12.79. The ^{19}F NMR spectrum shows a resonance at δ -59.62 as a singlet, with the expected positive coordination shift of ΔCF_3 = +1.84 ppm for the CF_3 groups.

The reaction of $[(CO)_2RhCl]_2$ with the regioisomeric mixture **19** yields a yellow solid (**20**). The IR spectrum in n-hexane shows three sets of dicarbonyl ν_{CO} bands at 2098 (s), 2095 (vs), 2090 (s), 2035 (s), 2030 (vs), 2026 (s) cm^{-1}. The two highest bands of each group correspond to **20a**. Complex **20a** can also be identified from the ^1H and ^{19}F NMR spectra, which allows all other resonances to be uniquely assigned, as was done for **19**. The assignments are detailed in the Experimental Section, with a product ratio for **20a**:**20b**:**20c** of 1.1:2.6:1 by ^1H NMR. The three isomers can be separated, allowing identification of the species in the original mixture (eq. 3-7).



(3-7)

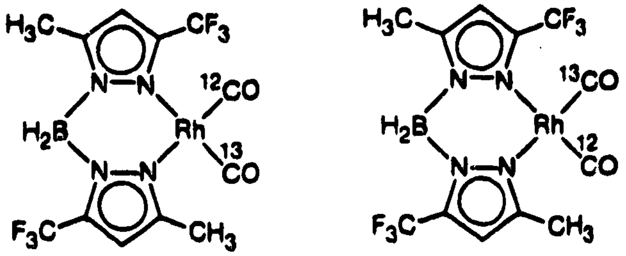
20a **20b** **20c**

When a concentrated hexane solution of the mixture **20** was cooled to -30°C only one isomer crystallized out. The IR spectrum in hexane shows that this isomer has the lowest ν_{CO} bands at 2090 (s), 2074 (vw), 2026 (s), 1996 (vw) cm^{-1}. The ^1H NMR spectrum showed one type of pyrazole group, with the 4-H proton at δ 6.39 (s, 2H) and the 5-Me groups at δ 2.45 (s, 6H).

The ^{13}C NMR spectrum of **20c** is similar to **20a**. There is a slight downfield shift of about one ppm of the CO carbon to δ 184.31 (d, $^{1}J_{Rh-C}$ = 68 Hz). This observation, along with the lower IR bands is consistent with the electronegative CF_3 groups in the 3-position in **20a** formally moving to the 5-position in **20c**. The ^{19}F NMR spectrum shows a resonance at -60.08 (ΔCF_3 = -1.03 ppm), but unlike that for **20a** it appeared as a doublet ($^{5}J_{F-H}$ = 5 Hz), which collapses on proton decoupling. This was also observed with **17** in Section 2. The spectral data is consistent with complex **20c**, the other isomer of C_s symmetry.

The remaining two isomers **20b** and **20a** can be separated by column chromatography. Complex **20a** was identical by IR and NMR spectroscopy to the pure material obtained above from **19a**.

Complex **20b** differs from **20a** and **20c** in that there is no longer a plane of symmetry through boron and rhodium (symmetry group C_1). This is evident in both the IR and NMR spectra. The IR spectrum in hexane (Figure III.1a) shows two sets of weak ^{13}C satellites for each strong ν_{CO} band at 2095 (s), 2082 (w), 2074 (w), 2030 (s), 2003 (w) and 1995 (w) cm^{-1}. The two isotopomers of the complex containing ^{13}CO are different (eq. 3-8). This has been previously demonstrated in the isomers of $CpFe(CO)_2(SiMeCl_2)$.[17]



(3-8)

20b

^{13}CO Isotopomers

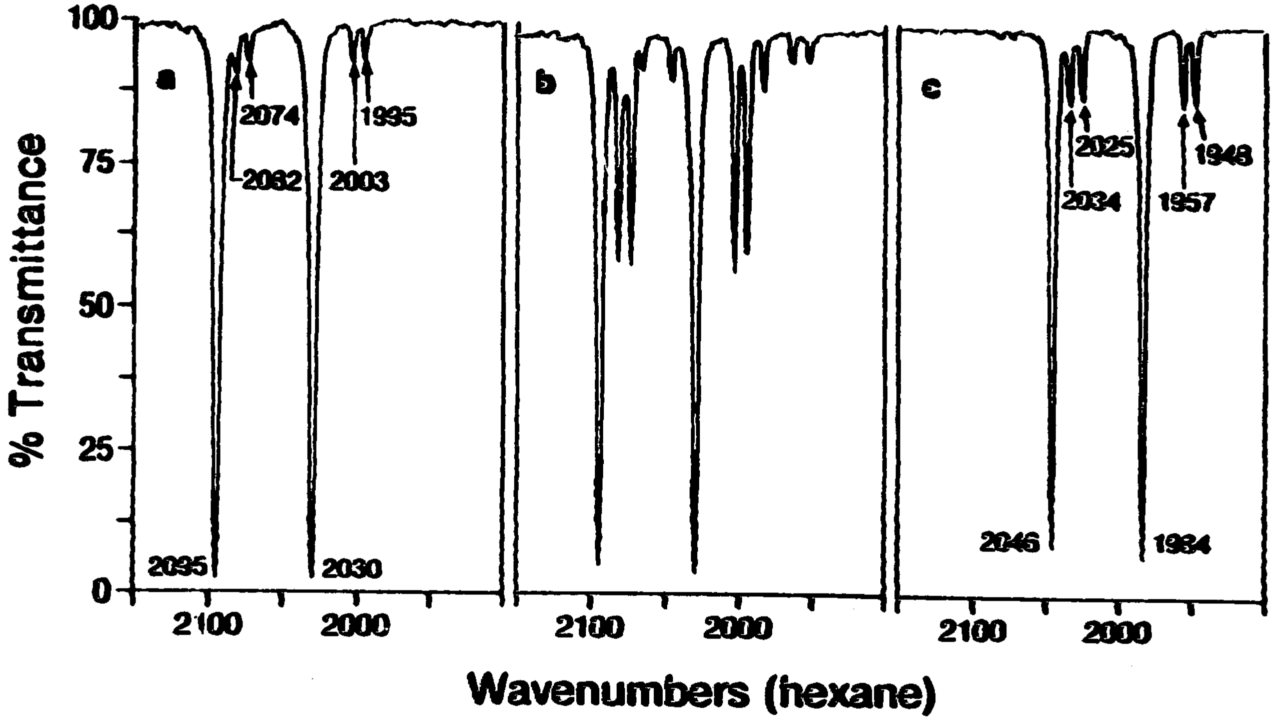


Figure III.1 Infrared Spectrum of $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)(3\text{-}Me\text{-}5\text{-}CF_3Pz)Rh(CO)_2$ (**20b**)

(a) Normal spectrum

(b) After slight ^{13}CO addition

(c) Completely ^{13}CO enriched

As expected for bis(pyrazolyl)borate rhodium dicarbonyl complexes, all three complexes **20** exchange ^{13}CO rapidly (complete in five minutes). The IR ν_{CO} bands of the enriched symmetric isomers in hexane are at 2049 (s), 2034 (w), 1989 (s), 1957 (w) cm^{-1} for **20a**, while for **20c**, they are at 2041 (s), 2026 (w), 1981 (s), 1950 (w) cm^{-1}. The weak satellites are due to the 4.0% $^{13}C^{18}O$ that is present in the ^{13}CO.

The exchange with **20b** is particularly interesting, as ^{13}CO enrichment should initially increase both sets of ^{13}C satellites. After addition of a small amount of ^{13}CO, all four ^{13}C satellites increase in intensity (Figure III.1b), and after complete enrichment, ν_{CO} 2046 (s), 2034 (w), 2025 (w), 1984 (s), 1957 (w), 1948 (w) cm^{-1}. Two sets of ^{18}O satellites are now observed in the fully enriched complex (Figure III.1c).

In regard to the IR stretching frequencies of the three isomers, one would expect that a CF_3 group at the 3-position closer to rhodium to be more electron withdrawing than one at the 5-position. This is what is observed on going from **20c** to **20b** to **20a**, as successive CF_3 groups are formally moved from the 5 to the 3-position on the pyrazole ring.

The ^1H NMR spectrum of **20b** shows two inequivalent pyrazole groups, with the 4-H protons at δ 6.37 (s, 1H) and 6.35 (s, 1H), while the two 5-Me groups are at δ 2.42 (s, 3H) and 2.34 (s, 3H). The ^{13}C NMR spectrum also shows two CO resonances. There is a doublet at δ 184.17 ($^1J_{Rh-C}$ = 70 Hz), while the other resonance is a doublet of quartets at δ 183.60 ($^1J_{Rh-C}$ = 68 Hz, $^1J_{F-C}$ = 3 Hz).

The spectrum was unchanged with proton decoupling, which indicates that this coupling is to a CF_3 group, possibly in the 3-position. The chemical shift of the low field CO carbon (doublet) is close to that of the CO carbon in **20c** (δ 184.31), while the high field resonance (doublet of quartets) is close to the CO carbon in **20a** (δ 184.43). This suggests that one CO group is coupled to the CF_3 group in the 3-position. The remainder of the spectrum is almost a composite of the ^{13}C NMR spectra of **20a** and **20c**, suggesting that one pyrazole group is bound as a 3-CF_3-5-MePz group, while the other is a 3-Me-5-CF_3Pz group.

The ^{19}F NMR of **20b** shows a singlet at δ -59.25 (3-CF_3, ΔCF_3 = +2.2 ppm) and a doublet at δ -59.97 ($^5J_{F-H}$ = 5 Hz, 5-CF_3, ΔCF_3 = -1.34 ppm). Broadband proton decoupling collapses the latter resonance to a singlet. It was of interest to attempt a selective proton decoupling experiment. At room temperature, the BH_2 resonance is a broad resonance centered at ~ 4 ppm. On cooling to -70°C, two broad but separate resonances appear at δ 3.94 (br, 1H) and δ 3.53 (br, 1H). The boat flip appears to be slow on the NMR timescale, so that the separate axial and equatorial hydrogens are observed. This phenomenon has been reported by Storr in $[Me_2GaPz_2]Rh(CO)(PPh_3)$,[18] where a single GaMe resonance was observed at room temperature. As the sample was cooled, the single resonance broadened and eventually sharpened into two GaMe resonances indicating that the inversion of the boat form was slow on the NMR timescale.

Selective proton decoupling of **20b** was performed while observing the ^{19}F NMR spectrum at -70°C. Irradiating the proton resonance at δ 3.94 caused no change in the ^{19}F NMR spectrum, but irradiating the proton resonance at δ 3.53 caused collapse of the doublet at δ -59.97 to a sharp singlet. This demonstrated that the CF_3 group in the 5-position is coupled to one of the B-H protons at room temperature, even though the B-H protons are broadened by the large quadrupole moment of ^{11}B. A similar situation exists for dimethylamine, where the N-H proton is broad in the ^{1}H NMR spectrum (^{14}N quadrupole), and yet it is coupled to the methyl group hydrogens.[19]

As expected from the ^{13}C NMR spectrum of **20b** where a C-F coupling is observed for a CO group, the ^{19}F NMR spectrum of the ^{13}CO enriched **20b** shows a doublet for the 3-CF_3 group at δ -59.25 ($^{5}J_{F-C}$ = 3 Hz), while the 5-CF_3 group is still a doublet at δ -59.97 (d, $^{5}J_{F-H}$ = 5 Hz). Broadband proton decoupling collapsed only the latter resonance to a singlet.

The three isomers have been distinguished spectroscopically. Another interesting note is the large difference in melting points between (**20a**, mp 74-76°C), (**20b**, mp 100-102°C) and (**20c**, mp 152-154°C). As observed with **17**, all three complexes **20** are soluble in perfluorohexane with IR spectra similar to those in hexane.

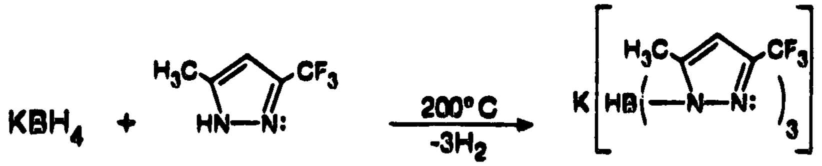
Complex **20b** is only the second example of an unsymmetric bis(pyrazolyl)borate metal complex. Frauendorfer prepared the ligand $[H_2B(Pz)(Pz^*)]^-$, as well as some metal chelate complexes of the type $[H_2B(Pz)(Pz^*)]_2M$ (M = Co, Ni, Zn).[11] The situation with **20b** is slightly different, as the ligand has the same unsymmetric pyrazole bound in the two possible orientations, whereas Frauendorfer's ligand has two different symmetric pyrazoles.

Section 4

3-TRIFLUOROMETHYL-5-METHYLPYRAZOLE CHEMISTRY

SYNTHESIS OF TRIS(PYRAZOLYL)BORATE COMPLEXES

The tris(pyrazolyl)borate ligand $KHB(3\text{-}CF_3\text{-}5\text{-}MePz)_3$ (**21**) was prepared in a similar manner to the bis(pyrazolyl)borate ligand **19a**, except that the melt temperature was increased to 200°C. The reaction is stopped when hydrogen evolution ceases, and **21** is obtained as a white solid (eq. 3-9).



18 **21**

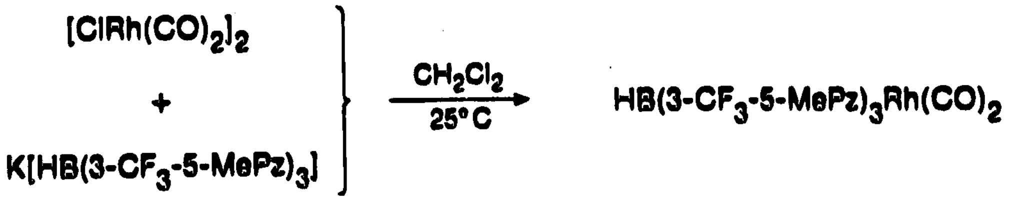
(3-9)

Prolonged heating of the initial melt at 200°C or increasing the temperature further results in a rapid decomposition, with the melt turning yellow, then brown and finally black. At this stage no material could be recovered.

Compound 21 appears to be regiospecific by NMR spectroscopy, with only one type of pyrazole group. The ^1H NMR spectrum shows the 4-H protons at δ 6.21 (s, 3H) and the 5-Me groups at δ 2.40 (s, 9H). The ^{19}F NMR spectrum in CD_2Cl_2 shows a sharp resonance at δ -61.44, which suggests that all the CF_3 groups are in the 3-position. The ligand itself appears quite volatile since a mass spectrum is obtained at 100°C, which shows the molecular ion M^+ at m/e = 498, with loss of a $3\text{-}CF_3\text{-}5\text{-}MePz$ group as the main secondary fragment.

Reaction of $[(CO)_2RhCl]_2$ with 21 gives the dicarbonyl

$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2$ (**22**) in good yield as an orange crystalline solid (eq. 3-10).



$$\left.\begin{array}{c}[ClRh(CO)_2]_2\\ +\\ K[HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3]\end{array}\right\} \xrightarrow[25°C]{CH_2Cl_2} HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2 \qquad (3\text{-}10)$$

21 **22**

Unlike $(HBPz^*_3)Rh(CO)_2$,[13] **22** is air-stable and can be chromatographed on neutral alumina but both complexes are essentially insoluble in perfluorohexane. This is in contrast to the solubility of **20** in perfluorohexane, and is somewhat surprising for **22** as it has three additional C-F bonds.

Dicarbonyl **22** was characterized by spectroscopic and analytical techniques. The ^1H NMR spectrum shows three equivalent pyrazole rings at room temperature, and the spectrum is invariant to -100°C. The ^{13}C NMR spectrum is as expected, allowing assignment of each carbon as detailed in the Experimental Section. The ^{19}F NMR spectrum shows a single resonance at δ -60.40, with again a positive coordination shift relative to **21** ($\Delta CF_3 = +1.04$ ppm).

As observed with **1**, complex **22** is a mixture of η^2 and η^3 forms in solution (eq. 3-11), as the IR spectrum in cyclohexane has four ν_{CO} bands at 2103 (s), 2090 (s), 2040 (s), 2025 (s) cm^{-1} (Figure III.2).

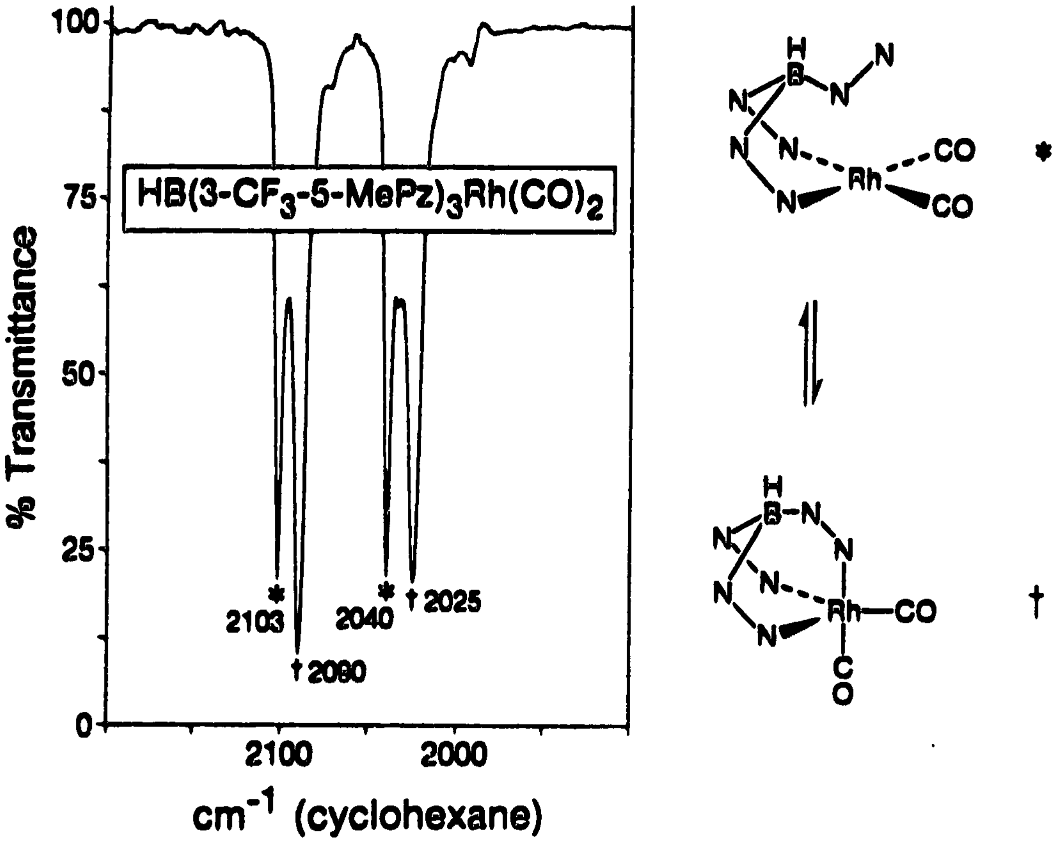
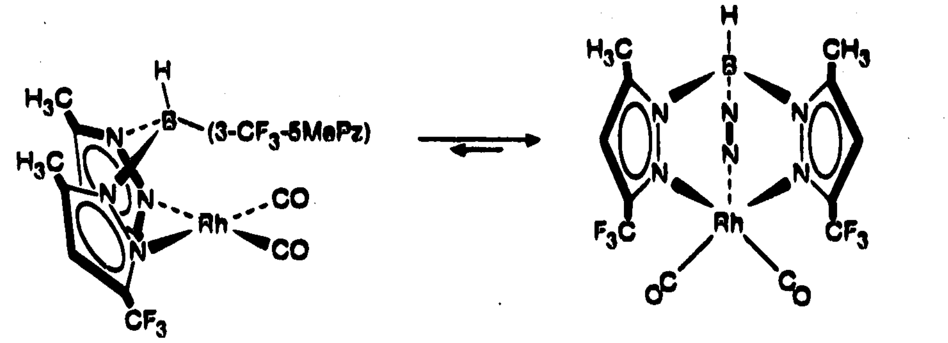


Figure III.2 Infrared Spectrum of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2$ (22)



(3-11)

η^2-HB(3-CF$_3$-5-MePz)$_3$Rh(CO)$_2$ η^3-HB(3-CF$_3$-5-MePz)$_3$Rh(CO)$_2$

However, in comparison to 1 there is significantly more of the η^3 isomer present in **22**. In hexane, the ν_{CO} bands are all one wavenumber higher at 2104 (s), 2091 (s), 2041 (s), 2026 (s) cm^{-1}. Isomer **22**-η^3 should have the lower stretching frequency, so for **22**-η^2 ν_{CO} in hexane is 2104, 2041 cm^{-1}. Comparing to the bis(pyrazolyl)borate complex **20a**, the IR spectrum in hexane shows ν_{CO} at 2098, 2035 cm^{-1}, so in fact the values for **22**-η^2 are both 6 cm^{-1} higher. Also the values for the **22**-η^3 are only 9 cm^{-1} lower than for **20a**, much smaller than the differences between the bis and tris(pyrazolyl)borate complexes in the Pz* system (25 and 28 cm^{-1} respectively).[13] Both facts are consistent with the formal replacement of a hydrogen on boron in **20a** by the more electronegative 3-CF$_3$-5-MePz group.

An approximate ratio of the two forms can again be obtained by an integration of the relative areas of the two sets of absorption bands.[20] Using the two methods described in the Experimental Section, an average ratio of η^2:η^3 = 32:68 was found in cyclohexane. As observed for 1, these ratios are solvent dependent, with a ratio of η^2:η^3 = 43:57 in toluene, while in CH_2Cl_2 the ratio is η^2:η^3 = 41:59. The trend for 1 of more η^3 form present in more polar solvents is opposite for **22**, with slightly more of the η^3 form present in toluene and CH_2Cl_2.

It is interesting to speculate as to why **22** exists as an equilibrium mixture while $(HBPz^*_3)Rh(CO)_2$ is exclusively η^3 in hexane. Both steric and electronic factors could apply, as there are larger and more electronegative CF_3 groups replacing Me groups in the 3-position of the $(HBPz^*_3)$ ligand. This would make it less likely for the rhodium center to accommodate all three pyrazole groups. The fact that **1** has a higher percentage of the η^2 form than **22** in cyclohexane (85:15) suggests that steric factors may be more important than electronic ones in determining this equilibrium position.

X-Ray Structure of (22)

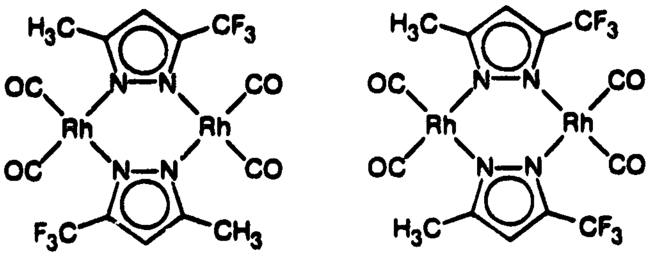
Several attempts in this research group to obtain X-ray quality crystals of $(HBPz^*_3)Rh(CO)_2$ were unsuccessful.[14] On the other hand suitable crystals of **22** could be grown, which suggests that the ligand $[HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3]^-$ imparts better crystallinity in addition to the stability mentioned previously relative to the Pz* system. The spectroscopic evidence has suggested that **22** is formulated as $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2$ and not $HB(3\text{-}Me\text{-}5\text{-}CF_3Pz)_3Rh(CO)_2$. However, direct proof of the regiospecific nature of the ligand is only obtained from the crystal structure of a complex.

The X-ray crystal structure of the dicarbonyl **22** was determined in part by Dr. R.G. Ball of this department, who collected the data set, and Professor M. Cowie who carried out the refinement. Details of the data collection and refinement procedure as well as tables of structural parameters, bond lengths and bond angles will be found in the

Experimental Section.

The structure of **22** in the solid state is shown in Figures III.3 and III.4. The regiospecificity of the ligand is as spectroscopically inferred, with the CF_3 groups in the 3-position and the methyl groups in the 5-position of the pyrazole ring. The geometry about the rhodium atom is square planar with two of the three pyrazole groups coordinated, similar to the geometry in **1**. This was not totally unexpected, as the IR spectrum of **22** shows a mixture of the η^2 and η^3 forms, although the latter is the major form. However, as discussed for the structure of **1**, the solid and solution structure need not be the same. The third pyrazole group is now in the axial position of the boat conformation, directly above the metal center, but it still appears to be nonbonding, as the Rh-N6 distance is 2.623(8) Å.

As noted in the preparation of **1** in Chapter II, during the isolation of **22**, a second minor product was isolated whose ^1H NMR, IR and mass spectra were identical to an authentic sample of $[(CO)_2Rh(3\text{-}CF_3\text{-}5\text{-}MePz)]_2$ (**23**). From the ^1H and ^{19}F NMR spectrum, both the cis **23c** and trans **23t** isomers are observed, with the sterically favored trans isomer assigned as the major product (eq. 3-12).



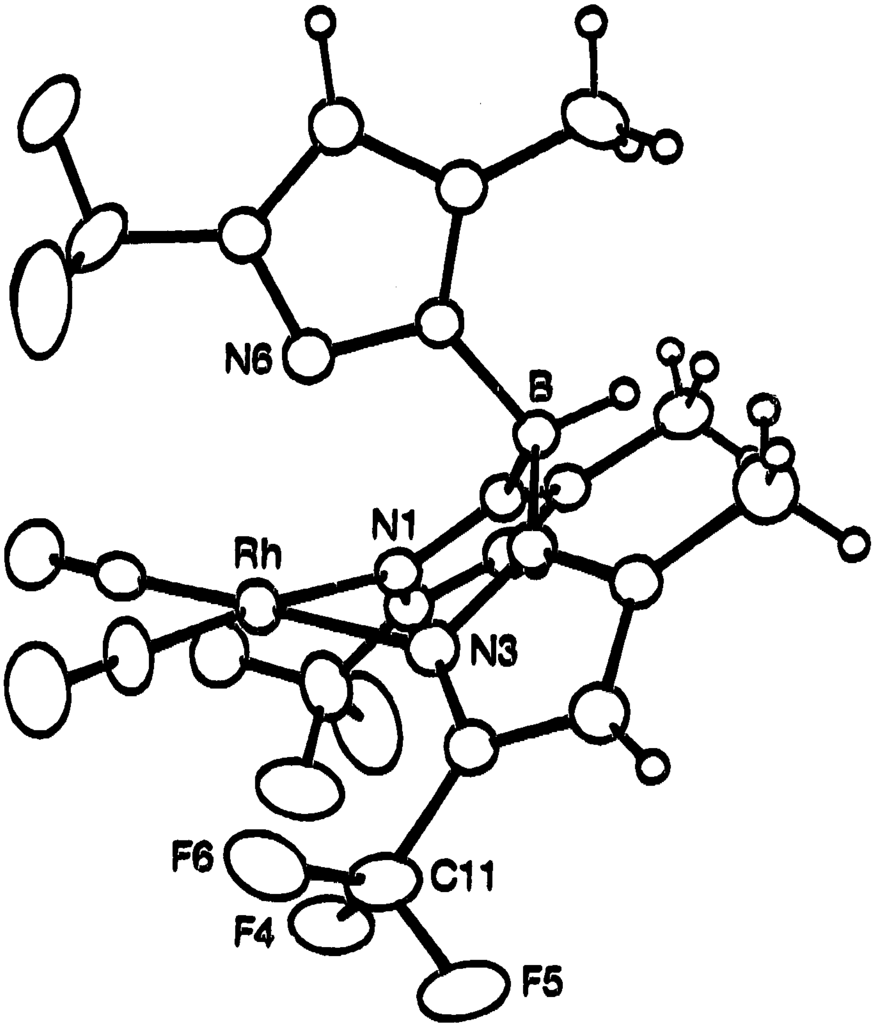
(3-12)

trans

23t

cis

23c



η^2-HB(3-CF$_3$-5-CH$_3$Pz)$_3$Rh(CO)$_2$

Figure III.3 Crystal Structure of HB(3-CF$_3$-5-MePz)$_3$Rh(CO)$_2$ (22)

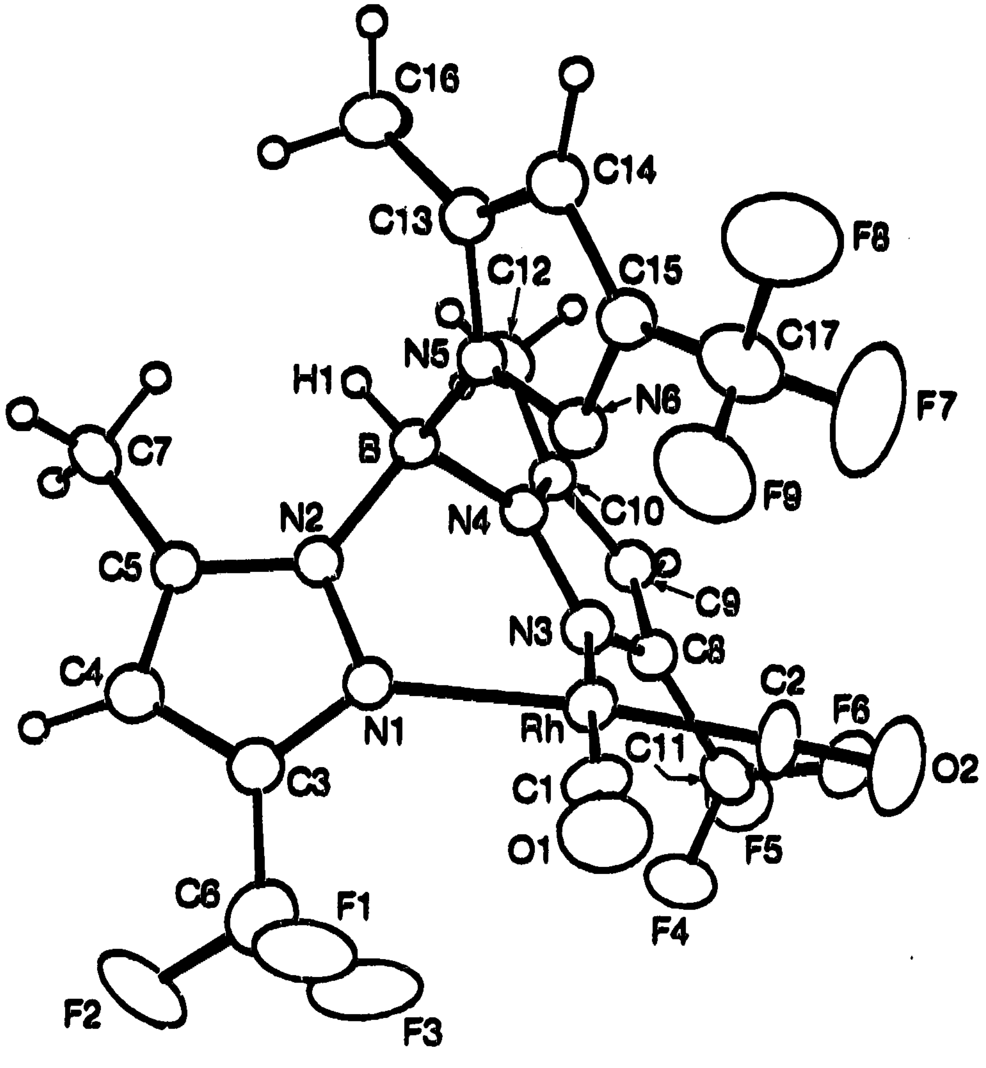


Figure III.4 Front View of Dicarbonyl (22)

The ratio of **23t**:**23c** is 1.15:1, or almost statistical. This indicates that there is a small but noticeable size difference between the CF_3 and Me groups on the pyrazole ring. It is thought that this minor product arises from B-N bond cleavage in the tris(pyrazolyl)borate ligand,[21] as once again there appears to be no free pyrazole present in **21**.

A related iridium complex, $[(COD)Ir(3\text{-}CF_3\text{-}5\text{-}MePz)]_2$ was prepared by Stobart.[10b] An X-ray crystal structure revealed disorder in terms of CF_3/CH_3 site occupancy, which suggests that a mixture of cis and trans isomers were obtained. Subsequent ^1H NMR studies revealed a 1:1 mixture of products.[10c]

Section 5

SYNTHESIS OF OLEFIN COMPLEXES

Several pyrazolylborate rhodium olefin complexes of the general type $(RBPz_3)RhL_2$ are known in the literature, where R = H, L_2 = $(C_2H_4)_2$,[22] R = Pz, L_2 = $(C_2H_4)_2$,[23] R = H, Pz = Pz*, L_2 = (COD)[24] and R=Pz, L_2 = (diene).[25] More recently, mixed carbonyl olefin complexes of the type $(HBPz^*_3)Rh(CO)(olefin)$ have been reported.[26] These complexes have been of interest firstly in studying the coordination of the poly(pyrazolyl)borate ligand (in solution and in the solid state) and secondly in thermal and photochemical carbon-hydrogen bond activation.

The synthesis and characterization of mixed carbonyl olefin complexes of the type $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(olefin)$ (olefin = ethylene, cyclooctene (COE)) is discussed, as well as the first known stable bis(pyrazolyl)borate analog, $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(COE)$. These complexes are analogs of known Pz* complexes and as such are of interest in C-H bond activation studies.

The tris(pyrazolyl)borate complexes are prepared by reacting the known dimers $[(CO)(olefin)RhCl]_2$ (olefin = C_2H_4[27] and COE[28]) with **21** in CH_2Cl_2 giving complexes of the type $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(olefin)$ (**24**) (olefin = C_2H_4) and (**25**) (olefin=COE) (eq. 3-13).

$$\left.\begin{array}{c}[ClRh(CO)(olefin)]_2\\ +\\ K[HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3]\end{array}\right\}\xrightarrow[25^{\circ}C]{CH_2Cl_2} HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(olefin) \qquad (3\text{-}13)$$

21

24 (olefin=C_2H_4)

25 (olefin=COE)

Both complexes were obtained as yellow air-stable crystals in good yields and characterized by the usual methods. As with previous tris(pyrazolyl)borate complexes, the IR and NMR spectra are useful in determining the hapticity of the ligand in solution. The IR spectra in n-hexane shows a single ν_{CO} at 2042 cm^{-1} for **24**, while **25** appears to be a mixture of η^2 and η^3 forms, with ν_{CO} at 2033 (m) and 2019 (s) cm^{-1} (η^2:η^3 ratio of 23:77% in cyclohexane). The ^1H and ^{19}F NMR spectra of **24** and **25** are very similar to that of **22** at room temperature, with one type of pyrazole group.

For **24**, the ^1H NMR spectrum at -40°C shows a 2:1 ratio of pyrazole groups resonances, as observed with complex **12**, and also by Ghosh for $(HBPz^*{}_3)Rh(CO)(C_2H_4)$ at -60°C.[13] Further cooling to -80°C only slows down the rotation of the ethylene group. Also, the ^1H and ^{19}F NMR spectra of **25** at -90°C and -50°C respectively shows a 2:1 ratio of pyrazole group resonances, indicative of the η^2 isomer. However, barring accidental degeneracies, the static η^2 structure of **24** and **25** should show three different pyrazole group resonances, as the two bound groups are different. This is not unlike the situation found for complex **12** in Chapter II and other phosphine and olefin complexes of the type $(HBPz^*{}_3)Rh(CO)(L)$ studied by Ghosh. There appears to be a low activation energy process which is thought to proceed through a trigonal bipyramidal η^3 intermediate, which averages the two pyrazole groups opposite the two different ligands. This will be discussed in detail in Chapter IV.

The bis(pyrazolyl)borate analogs of **24** and **25** were prepared in the same manner as complex **13** in Chapter II (eq. 3-14).

$$\left.\begin{array}{c}[ClRh(CO)(olefin)]_2\\ +\\ K[H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2]\end{array}\right\} \xrightarrow[25^\circ C]{Hexane} H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(olefin) \qquad (3\text{-}14)$$

19a **26** (olefin=C_2H_4)

27 (olefin=COE)

As was found for 13, $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(C_2H_4)$ (**26**) is relatively unstable in solution, and readily converts to **20a**, as monitored by IR spectroscopy. Hence complete characterization was not done, but the IR ν_{CO} band for **26** in hexane was at 2035 cm^{-1}. The IR band for the tris(pyrazolyl)borate complex **24** has a higher value (ν_{CO} at 2042 cm^{-1}), which indicates that **24** is entirely η^2 in solution.

The COE analog $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(COE)$ (**27**) was found to be fairly stable in solution and disproportionated or decomposed to **20a** in two weeks in hexane and five days in CH_2Cl_2. Complex **27** was isolated as orange crystals and the IR spectrum in hexane has a ν_{CO} band at 2020 cm^{-1}, which is close to the low energy band of **25**. Here the IR band of the η^2 form of **25** is again higher in energy (13 cm^{-1}) than that of the bis(pyrazolyl)borate complex **27**. The ^1H NMR spectrum of **27** shows only one pyrazole group, as the chemical shifts are similar. In the ^{19}F NMR spectrum, two resonances are observed as singlets at δ -59.62 and -59.63. Attempts to prepare the Pz* analog of **27**, $(H_2BPz^*{}_2)Rh(CO)(COE)$ were unsuccessful, as the complex was rapidly converted to the dicarbonyl $(H_2BPz^*{}_2)Rh(CO)_2$.[14] This further demonstrated the ability of the $3\text{-}CF_3\text{-}5\text{-}MePz$ ligand system to stabilize complexes in comparison to the Pz* analogs.

Complexes of the type $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3RhL_2$ (L_2 = $(C_2H_4)_2$, (COD) and $(allyl)_2$) can also be prepared in a straightforward manner beginning with the appropriate rhodium precursor. This demonstrates that the ligand 21, although less electron rich than $KHBPz^*_3$ still forms similar complexes as with the latter.

Reaction of $[L_2RhCl]_2$ (L_2 = $(C_2H_4)_2$,[29] (COD)[30] and $(allyl)_2$[31]) with **21** in CH_2Cl_2 results in the complexes $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(C_2H_4)_2$ (**28**), $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(COD)$ (**29**) and $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(allyl)_2$ (**30**) respectively (eq. 3-15). They were all obtained as analytical pure air-stable yellow powders.

$$\left.\begin{array}{c}[\mathrm{ClRh(L)_2}]_2\\ +\\ \mathrm{K[HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3]}\end{array}\right\} \xrightarrow[25^\circ\mathrm{C}]{\mathrm{CH_2Cl_2}} \mathrm{HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(L)_2} \qquad (3\text{-}15)$$

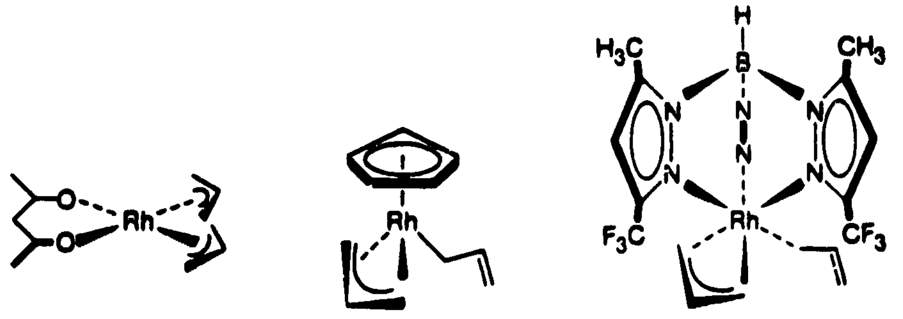
21

28 L_2 = $(C_2H_4)_2$
29 L_2 = (COD)
30 L_2 = $(allyl)_2$

The ^1H and ^{19}F NMR spectra of the bis(ethylene) complex **28** at room temperature and at -90°C showed only one type of pyrazole group and only a single ethylene resonance at δ 2.81 (d, 8H, $^2J_{Rh-H}$ = 1.8 Hz) as Trofimenko observed for $(HBPz_3)Rh(C_2H_4)_2$.[22] The Pz* analog $(HBPz^*_3)Rh(C_2H_4)_2$ has not been reported in the literature, and several attempts in this research group to prepare it pure has met with failure.[14] This again demonstrates that the ligand system in **28** imparts some extra stability relative to the Pz* system.

The COD complex 29 demonstrates some interesting variable temperature NMR spectra. At room temperature, the ^{1}H and ^{19}F NMR spectra show only one type of pyrazole group as observed with (HBPz*$_3$)Rh(COD),[24] but on cooling to -50°C the ^{1}H NMR spectrum of 29 shows a 2:1 ratio of pyrazole groups. Further cooling to -105°C now shows a 1:1:1 ratio of pyrazole resonances. If the 2:1 ratio at intermediate temperature indicates the freezing out of the η^2 form, the lowest temperature spectrum could indicate a slowing down of the B-N bond rotation of the free pyrazole group, which would make the two bound pyrazole groups inequivalent. This was shown with complex 5 in Chapter II.

Complex 30 is of interest, as both (acac)Rh(allyl)$_2$ and CpRh(allyl)$_2$ are known[31] (eq. 3-16). In the former, both allyl groups are η^3 and equivalent by ^{1}H NMR, but in the latter by necessity there must be a η^1 and a η^3 allyl group, and these are distinguishable in the ^{1}H NMR spectrum.



(3-16)

(acac)Rh(allyl)$_2$ CpRh(allyl)$_2$ HB(3-CF$_3$-5-MePz)$_3$Rh(allyl)$_2$

30

The Pz* complex $(HBPz*_3)Rh(allyl)_2$ has been prepared by Powell and coworkers.[32] Based on the ^1H NMR spectrum they proposed an octahedral Rh(III) complex with a η^1 and a η^3 allyl group. For complex 30, the ^1H and ^{19}F NMR spectra show a 2:1 ratio of pyrazole group resonances. The allyl resonances resemble those of the Cp and $(HBPz*_3)$ complexes rather than the acac analog, indicating that the allyl groups are η^1 and η^3 bound. This formulation is also consistent with 30 being an octahedral Rh(III) complex, where the 2:1 ratio of pyrazole group resonances arise from symmetry. Reactions of 30 with CO will be discussed in Chapter IV, suggesting that 30 is coordinatively saturated.

Section 6

EXPERIMENTAL

General

3,5-(Bistrifluoromethyl)pyrazole was prepared according to Trofimenko et al.[8] 3-Trifluoromethyl-5-methylpyrazole was prepared using a literature procedure,[9] with full characterization appearing below. The various rhodium starting materials were prepared using the standard literature procedures as follows: $[(C_2H_4)(CO)RhCl]_2$,[27] $[(CO)(COE)RhCl]_2$,[28] $[(C_2H_4)_2RhCl]_2$,[29] $[(COD)RhCl]_2$,[30] $[(allyl)_2RhCl]_2$,[31] and $[(CO)_2RhCl]_2$.[33] KBH_4, hexafluoroacetylacetone and trifluoroacetylacetone were used as received from Strem Chemical Company.

Preparation of $KH_2B(3,5-(CF_3)_2Pz)_2$ (16)

A mixture of 3.75 g (18.4 mmol) $3,5-(CF_3)_2PzH$ and 200 mg (3.71 mmol) of KBH_4 was refluxed for 1 h, at which time hydrogen gas evolution ceased. Excess $3,5-(CF_3)_2PzH$ was sublimed off (70°C, 0.3 mm) leaving a white solid (1.54 g, 90% yield) mp 167-169°C.

Characterization: ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.80 (s, 2H). ^{19}F NMR (CD_2Cl_2, ambient) δ -59.57 (t, $^5J_{F-H} = 3$ Hz, 6F), -61.82 (s, 6F). $^{19}F\{^1H\}$ NMR -59.57 (s, 6F), -61.82 (s, 6F). Anal. Calcd for $C_{10}H_4BN_4F_{12}K$: C, 26.22; H, 0.88; N, 12.23. Found: C, 25.80; H, 0.71; N, 12.05.

Preparation of $H_2B(3,5-(CF_3)_2Pz)_2Rh(CO)_2$ (17)

To a solution of $[(CO)_2RhCl]_2$ (204.2 mg, 0.525 mmol in 10 mL CH_2Cl_2) was added 481 mg (1.05 mmol) **16**. After stirring for 0.5 h, IR showed the reaction to be complete with bands due to the product as well as to the known dimer $[(CO)_2Rh(3,5-(CF_3)_2Pz)]_2$.[10a] A ^1H NMR spectrum at this stage showed 98.6% of **17** and only 1.4% dimer. This mixture was chromatographed on neutral alumina with CH_2Cl_2 eluent to remove KCl. After removal of solvent, the resulting yellow oil was taken up in 10 mL hexane and cooled to -78°C, whereupon pure **17** crystallized out. Repeated concentrations gave 285.3 mg (47% isolated yield) of **17**, with the mother liquor enriched in dimer but still containing **17**. They could not be further separated by chromatography or sublimination. Complex **17** was isolated as a bright yellow solid, mp 84-85°C.

Characterization: IR (n-hexane) 2107, 2048 cm^{-1} (ν_{CO}). UV (CH_2Cl_2) 258.7 (ε = 9092), 353.0 (ε = 1475) nm (λmax). MS (110°C, 70 ev) M^+ (578, 4%), M^+-CO (100%), M^+-2CO (37%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.99 (s, 2H). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, ambient) δ 181.69 (d, CO, $^1J_{Rh-C}$ = 71 Hz), 144.50 (q, C-CF_3, $^2J_{C-F}$ = 39 Hz), 140.89 (q, C-CF_3, $^2J_{C-F}$ = 43 Hz), 119.84 (q, CF_3, $^1J_{C-F}$ = 270 Hz), 119.13 (q, CF_3, $^1J_{C-F}$ = 270 Hz), 108.22 (s, C-H). ^{19}F NMR (CD_2Cl_2, ambient) δ -59.95 (s, 6F), -60.29 (d, 6F, $^5J_{F-H}$ = 5 Hz). $^{19}F\{^1H\}$ NMR -59.95 (s, 6F), -60.29 (s, 6F). Anal. Calcd for $C_{12}H_4BN_4F_{12}Rh$: C, 24.94; H, 0.70; N, 9.69. Found: C, 24.90; H, 0.70; N, 10.07.

Preparation of $3-CF_3-5-MePzH$ (18)

A sample of 18.6 mL (23.6 g, 0.153 mmol) of

1,1,1-trifluoro-2,4-pentanedione was added dropwise over 0.5h at 5°C to a solution of 10.86 g (0.184 mol) of 85% hydrazine hydrate in 230 mL 95% EtOH. After stirring for 0.5 h, solvent was removed in vacuo giving a white solid. Analysis of this crude solid showed it to be the pyrazole. Distillation of the solid at 170°C/0.10 mm Hg gave a white product, which was further sublimed onto a dry ice probe at 80°C/0.3 mm Hg (18.4 g, 80% yield) mp 84-85°C.

Characterization: MS (120°C, 70 ev) M^+ (150, 100%), M^+-F (22%), M^+-CF_3 (24%), CF_3^+ (13%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 12.22 (br, 1H), 6.34 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (CD_2Cl_2, 100.6 MHz, ambient) δ 143.27 (q, C-CF_3, $^2J_{C-F}$ = 38 Hz), 142.11 (s, C-CH_3), 122.07 (q, CF_3, $^1J_{C-F}$ = 268 Hz), 103.28 (s, CH), 10.60 (s, CH_3). ^{19}F NMR (CD_2Cl_2, ambient) δ -62.41 (s). Anal. Calcd for $C_5H_5N_2F_3$: C, 40.01; H, 3.36; N, 18.66. Found: C, 39.83; H, 3.26; N, 18.69.

Preparation of $KH_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2$ (19a)

A sample of 6.375 g (42.47 mmol) 18 and 572.8 mg (10.62 mmol) KBH_4 were heated together at 140°C until no more gas evolved (3 h). 75 mL hexane was added to the cooled melt, and with vigorous stirring, a white solid precipitated out. This was filtered and washed with 3 x 75 mL hexane and dried in vacuo (2.521 g, 68% yield) mp 148-150°C. From the combined hexane washings 2.893 g 18 was recovered after hexane was removed in vacuo.

Characterization: ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.19 (s, 2H), 2.34 (s, 6H). ^{19}F NMR (CD_2Cl_2, ambient) δ -61.42 (s). Anal. Calcd for

$C_{10}H_{10}BN_4F_6K$: C, 34.40; H, 2.88; N, 16.00. Found: C, 32.61; H, 3.13; N, 15.11.

Preparation of $KH_2B(CF_3,MePz)_2$ (19)

A sample of 2.346 g (15.63 mmol) **18** and 383 mg (7.10 mmol) KBH_4 were taken up in 40 mL DMAC and heated together at 140°C until gas evolution ceased (1 h), then further heated for 2 h. Solvent was distilled off at 140°C/10 mm Hg and the resulting oil heated in high vacuum at 140°C. The oil was taken up in 50 mL THF, stirred with Celite for 0.5 h and filtered and flash evaporated leaving a yellow oil. Stirring with hexane gave a white solid, which was filtered and washed with 3 x 75 mL hexane and dried in vacuo (1.391 g, 56% yield) mp 95-105°C.

Characterization: ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ For **19a**: 6.19 (s, 2H), 2.34 (s, 6H); **19b**: 6.27 (s, 1H), 6.15 (s, 1H), 2.27 (s, 3H), 2.13 (s, 3H); **19c**: 6.29 (s, 2H), 2.11 (s, 6H). Ratio of **19a**:**19b**:**19c** = 1.3:2.9:1. ^{19}F NMR (CD_2Cl_2, ambient) δ For **19a**: -61.46 (s, 6F); **19b**: -58.62 (br, 3F), -61.44 (s, 3F); **19c**: -59.05 (br, 6F). $^{19}F\{^1H\}$ NMR -58.62 (s, 3F), -59.05 (s, 6F). Anal. Calcd for $C_{10}H_{10}BN_4F_6K$: C, 34.40; H, 2.88; N, 16.00. Found: C, 34.37; H, 3.95; N, 14.42.

Preparation of $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)_2$ (20a)

To a solution of 133.3 mg (0.343 mmol) $[(CO)_2RhCl]_2$ in 20 mL CH_2Cl_2 was added 240.9 mg (0.688 mmol) **19a**. After stirring for 15 min, the solution was filtered through Celite, and solvent was removed in vacuo. The resulting yellow oil was chromatographed on neutral alumina

(12 x 2.5 cm) with CH_2Cl_2 eluent, and solvent was removed under reduced pressure. The resultant yellow oil crystallized on standing giving a yellow solid (258.6 mg, 80% yield) mp 74-76°C.

Characterization: IR (n-hexane) 2098 (s), 2082 (vw), 2035 (s), 2004 (vw) cm^{-1} (ν_{CO}). UV (CH_2Cl_2) 273.1 (ε = 7244), 358.5 (ε = 1243) nm (λ max). MS (160°C, 70 eV) M^+ (470, 2%), M^+-CO (100%), M^+-2CO (27%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.34 (s, 2H), 2.36 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, ambient) δ 183.43 (d, CO, $^1J_{Rh-C}$ = 69 Hz), 147.29 (s, C-CH_3), 143.03 (q, C-CF_3, $^2J_{C-F}$ = 38 Hz), 120.92 (q, CF_3, $^1J_{C-F}$ = 269 Hz), 106.74 (s, C-H), 12.79 (s, CH_3). ^{19}F NMR (CD_2Cl_2, ambient) δ -59.62 (s). Anal. Calcd for $C_{12}H_{10}BN_4O_2F_6Rh$: C, 30.67; H, 2.14; N, 11.92. Found: C, 30.72; H, 2.03; N, 12.01.

Reaction of $KH_2B(CF_3, MePz)_2$ (19) with $[(CO)_2RhCl]_2$

To a solution of 107.7 mg (0.277 mmol) $[(CO)_2RhCl]_2$ in 15 mL CH_2Cl_2 was added 193.9 mg (0.554 mmol) **19**, and the reaction was complete in 30 min. After filtering through Celite and removing solvent in vacuo, the resulting yellow oil was chromatographed on neutral alumina with CH_2Cl_2 eluent. After removing solvent, the yellow oil crystallized on standing (108.9 mg, 41% yield).

Characterization: IR (n-hexane) 2098 (s), 2095 (vs), 2090 (s), 2035 (s), 2030 (vs), 2026 (s) cm^{-1} (ν_{CO}). MS (160°C, 70 eV) M^+ (470, 3%), M^+-CO (100%), M^+-2CO (28%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ For **20a**: 6.34 (s, 2H), 2.36 (s, 6H); **20b** 6.37 (s, 1H), 6.35 (s, 1H), 2.42 (s, 3H), 2.34 (s, 3H); **20c**: 6.39 (s, 2H), 2.45 (s, 6H). Ratio of

20a:**20b**:**20c** = 1.1:2.6:1. ^{19}F NMR (CD_2Cl_2, ambient) δ For **20a**: -59.62 (s, 6F); **20b**: -59.25 (s, 3F), -59.97 (d, J_{F-H} = 5 Hz, 3F); **20c**: -60.08 (d, J_{F-H} = 5 Hz, 6F).

A hexane solution of the mixture was cooled to -30°C, and only one regioisomer came out $H_2B(3\text{-}Me\text{-}5\text{-}CF_3Pz)_2Rh(CO)_2$ (**20c**) (19.7 mg, 8% yield) mp 152-154°C.

Characterization: IR (n-hexane) 2090 (s), 2074 (vw), 2026 (s), 1996 (vw) cm^{-1} (ν_{CO}). MS (160°C, 70 eV) M^+ (470, 2%), M^+-CO (100%), M^+-2CO (26%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.39 (s, 2H), 2.45 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, ambient) δ 184.31 (d, CO, $^1J_{Rh-C}$ = 68 Hz), 151.26 (s, **C**-CH_3), 139.22 (q, **C**-CF_3, $^2J_{C-F}$ = 41 Hz), 120.06 (q, CF_3, $^1J_{C-F}$ = 269 Hz), 106.99 (s, C-H), 14.84 (s, CH_3). ^{19}F NMR (CD_2Cl_2, ambient) δ -60.08 (d, $^5J_{Rh-F}$ = 5 Hz). $^{19}F\{^1H\}$ NMR δ -60.08 (s). Anal. Calcd for $C_{12}H_{10}BN_4O_2F_6Rh$: C, 30.67; H, 2.14; N, 11.92. Found: C, 30.81; H, 2.04; N, 12.09.

The hexane mother liquor was chromatographed on neutral alumina (12 x 2.5 cm) eluting with hexane. After removing solvent in vacuo, a yellow powder was obtained, thought to be $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)(3\text{-}Me\text{-}5\text{-}CF_3Pz)Rh(CO)_2$ (**20b**) (57.7 mg, 22% yield) mp 100-102°C.

Characterization: IR (n-hexane) 2095 (s), 2082 (vw), 2074 (vw), 2030 (s), 2003 (vw), 1995 (vw) cm^{-1} (ν_{CO}). MS (160°C, 70 eV) M^+ (470, 2%), M^+-CO (100%), M^+-2CO (27%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.37 (s, 1H), 6.35 (s, 1H), 2.42 (s, 3H), 2.34 (s, 3H). ^{1}H NMR (-70°C) δ 3.94 (br, B-H, 1H), 3.53 (br, B-H, 1H). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, ambient) δ 184.17 (d, CO, $^{1}J_{Rh-C}$ = 70 Hz), 183.60 (d of q, CO, $^{1}J_{Rh-C}$ = 68 Hz, $^{5}J_{F-C}$ = 3 Hz), 151.20 (s, $C-CH_3$), 147.77 (s, $C-CH_3$), 142.96 (q, $C-CF_3$, $^{2}J_{C-F}$ = 39 Hz), 138.80 (q, $C-CF_3$, $^{2}J_{C-F}$ = 39 Hz), 120.96 (q, CF_3, $^{1}J_{C-F}$ = 269 Hz), 120.30 (q, CF_3, $^{1}J_{C-F}$ = 269 Hz), 106.86 (s, C-H), 14.62 (s, CH_3), 12.62 (s, CH_3). ^{19}F NMR (CD_2Cl_2, ambient) δ -59.25 (s, 3F), -59.97 (d, $^{5}J_{F-H}$ = 5 Hz). $^{19}F\{^{1}H\}$ NMR -59.25 (s, 3F), -59.97 (s, 3F). ^{19}F NMR (^{13}CO enriched) δ -59.25 (d, $^{5}J_{F-C}$ = 3 Hz, 3F), -59.97 (d, $^{5}J_{Rh-F}$ = 5 Hz). $^{19}F\{^{1}H\}$ NMR (ambient) δ -59.25 (d, $^{5}J_{F-C}$ = 3 Hz, 3F), -59.97 (s, 3F). $^{19}F\{^{1}H(3.53)\}$ NMR (-70°C) δ -59.25 (d, $^{5}J_{F-C}$ = 3 Hz, 3F), -59.97 (s, 3F). Anal. Calcd for $C_{12}H_{10}BN_4O_2F_6Rh$: C, 30.67; H, 2.14; N, 11.92. Found: C, 30.81; H, 2.04; N, 12.09.

Further elution of the column with CH_2Cl_2 gave the last product, identified as (**20a**) by comparison of IR, ^{1}H NMR and MS with an authentic sample (23.4 mg, 9% yield).

Preparation of $KHB(3-CF_3-5-MePz)_3$ (21)

A sample of 10.0 g (0.067 mol) **18** and 800 mg (0.0167 mol) KBH_4 were heated slowly, beginning at 80°C. At 140°C, hydrogen gas was rapidly given off, forming the bis(pyrazolyl)borate ligand **19a**. It is important to remain at this temperature until gas evolution has ceased. Gradual heating to 200°C (bath temperature) gave gas evolution which ceased after 1 h. After cooling the melt, excess **18** was sublimed off (3.85 g). A white solid was obtained by stirring the melt with hexane, which was decanted and dried in vacuo (4.46 g, 66% yield) mp 152-155°C. If heating is prolonged or the temperature is raised, the melt turns from yellow to brown to finally black, with extensive decomposition.

Characterization: MS (100°C, 16 eV) M^+ (498, 46%), M^+-3-CF_3-5-MePzH (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.21 (s, 3H), 2.40 (s, 9H). ^{19}F NMR (CD_2Cl_2, ambient) δ -61.44 (s). Anal. Calcd for $C_{15}H_{13}BN_6F_9K$: C, 36.16; H, 2.63; N, 16.87. Found: C, 34.03; H, 2.61; N, 15.37.

Preparation of $HB(3-CF_3-5-MePz)_3Rh(CO)_2$ (22)

To a solution of 383.1 mg (0.985 mmol) $[(CO)_2RhCl]_2$ in 20 mL CH_2Cl_2 was added 982 mg (1.97 mmol) **21**. After stirring for 0.5 h, the orange solution was filtered through Celite, and a concentrated CH_2Cl_2 solution was chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent, giving the crude product after solvent was removed in vacuo. Yellow crystals of **22** were obtained by layering a CH_2Cl_2 solution with hexane at -30°C (847.8 mg, 70% yield) mp 154-155°C.

Further elution of the column with CH_3CN gave 15.3 mg (2.5% yield) of $[(CO)_2Rh(3-CF_3-5-MePz)]_2$ **23**, which was identified by comparison of ^1H NMR, IR and mass spectra to an authentic sample prepared below.

Characterization: IR (cyclohexane) 2103 (s), 2090 (s), 2040 (s), 2025 (s), (hexane) 2104 (s), 2091 (s), 2041 (s), 2026 (s) cm^{-1} (ν_{CO}). MS (120°C, 16 eV) M^+ (618, 36%), M^+-CO (68%), M^+-2CO (100%). UV (CH_2Cl_2) 355.2 (ε = 1504) nm (λmax). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.44 (s, 3H), 2.40 (s, 9H). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, ambient) δ 183.40 (d, CO, $^1J_{Rh-C}$ = 69 Hz), 147.59 (s, C-CH_3), 144.15 (q, C-CF_3, $^2J_{C-F}$ = 38 Hz), 121.38 (q, CF_3, $^1J_{C-F}$ = 269 Hz), 106.62 (s, C-H), 13.12 (s, CH_3). ^{19}F NMR (CD_2Cl_2, ambient) δ -60.40 (s). Anal. Calcd for $C_{17}H_{13}BN_6O_2F_9Rh$: C, 33.04; H, 2.12; N, 13.60. Found: C, 33.45; H, 2.13; N, 13.90.

X-Ray Structure of (22)

The X-ray crystallographic study was carried out by Dr. R.G. Ball, who collected the data for the crystal, and Professor M. Cowie who performed the structure refinement.

Crystals were grown from CH_2Cl_2-hexane at -30°C. A yellow etched and rounded air-stable crystal of approximate size 0.10 x 0.13 x 0.25 mm was mounted in a non-specific orientation. The automatic peak search and reflection indexing showed the crystal to be monoclinic with systematic absences of hkl, h+k odd; and h0l, l odd. Cell constants were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $13 < 2\theta < 25°$. The intensity data were collected using a ω-2θ scan mode. The various crystal parameters are given in Table 3.I.

There were three reflections which were chosen as standard reflections and these were remeasured every 60 minutes of exposure time to check on crystal and electronic stability over the course of data collection. A linear regression analysis of these standards showed a negligible mean change in intensity of 4.8 (6.8)% over the time span of data collection.

The structure was solved using standard Patterson techniques which gave the positional parameters for the Rh atom. The remaining non-hydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier synthesis.

Refinement of atomic parameters were carried out by full matrix least-squares techniques on F_o minimizing the function

Table 3.I Experimental Details

A. Crystal Data

$C_{17}H_{13}BN_6O_2F_9Rh$ FW = 618.05

Crystal dimensions: 0.10 x 0.13 x 0.25 mm

Monoclinic space group C2/c (No. 15)

$a = 21.228(4)$, $b = 10.996(3)$, $c = 21.546(6)$ Å

$\beta = 114.96(2)°$

$V = 4560$ Å^3; $Z = 8$; $D_c = 1.800$ g cm^{-3}

B. Data Collection and Refinement Conditions

Radiation:	Mo Kα ($\lambda = 0.71073$ Å)
Monochromator:	Incident beam, graphite crystal
Take-off angle:	3.0°
Detector aperture:	2.40 mm horiz x 4.0 mm vert
Crystal-to-detector distance:	173 mm
Scan type:	ω-2θ
Scan rate:	6.7 - 1.5° min^{-1}
Scan width:	0.70 + 0.35tan(θ)°
Data collection 2θ limit:	50°
Data collection index range:	h, k, ±ℓ
Reflections measured:	4231 unique, 1860 with $I > 2\sigma(I)$
Observations: variables ratio:	1860:245
Agreement factors R_1, R_2 GOF:	0.062, 0.062, 1.476

$$\Sigma w\ (|F_o| - |F_c|)^2$$

where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes respectively, and the weighting factor w is given by

$$w = 4F_o^{\ 2} / \sigma^2(F_o)^2$$

All hydrogen atoms were included at their idealized calculated distances, assuming C-H and B-H distances of 0.95 Å and appropriate sp^2 and sp^3 geometries. These atoms were then included in the calculations with fixed isotropic thermal parameters 1.2 times that of the attached atom and constrained to ride with this atom. All hydrogen atoms were included in the structure factor calculations, but were not refined. The boron atom and the atoms of the pyrazole rings were refined isotropically. All other atoms were refined anisotropically.

In the final cycle 245 parameters were refined using 1860 observations having $I > 2\sigma(I)$. The final agreement factors were:

$$R_1 = \Sigma\ |F_o| - |F_c|\ /\ \Sigma\ |F_o| = 0.062 \quad \text{and}$$

$$R_2 = [\Sigma w\ (|F_o| - |F_c|)^2\ /\ \Sigma wF_o^{\ 2}]^{1/2} = 0.062$$

The structure of **22** is depicted in Figures III.3 and III.4. Relevant bond lengths and bond angles are tabulated in Tables 3.II and 3.III. Positional and thermal parameters are available from the University of Alberta.

Table 3.II Bond Distances in Angstroms[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Rh	N1	2.098(7)	O1	C1	1.18 (1)	N6	C15	1.34(1)
Rh	N3	2.111(7)	O2	C2	1.13 (1)	C3	C4	1.38(1)
Rh	N6	2.623(8)	N1	N2	1.373(9)	C3	C6	1.46(2)
Rh	C1	1.79 (1)	N1	C3	1.34 (1)	C4	C5	1.33(1)
Rh	C2	1.83 (1)	N2	C5	1.38 (1)	C5	C7	1.50(1)
F1	C6	1.32 (1)	N2	B	1.5[illegible] (1)	C8	C9	1.36(1)
F2	C6	1.24 (1)	N3	N4	1.362(9)	C8	C11	1.51(1)
F3	C6	1.36 (1)	N3	C8	1.35 (1)	C9	C10	1.37(1)
F4	C11	1.31 (1)	N4	C10	1.35 (1)	C10	C12	1.48(1)
F5	C11	1.35 (1)	N4	B	1.57 (1)	C13	C14	1.36(1)
F6	C11	1.32 (1)	N5	N6	1.353(8)	C13	C16	1.47(1)
F7	C17	1.31 (2)	N5	C13	1.36 (1)	C14	C15	1.38(1)
F8	C17	1.29 (1)	N5	B	1.54 (1)	C15	C17	1.48(1)
F9	C17	1.26 (2)						

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[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3.III Bond Angles in Degrees[a]

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1	Rh	N3	82.6(3)	Rh	C1	01	176.3(9)	F4	C11	F5	107 (1)
N1	Rh	C1	97.9(4)	Rh	C2	02	179 (1)	F4	C11	F6	106 (1)
N1	Rh	C2	174.9(5)	N1	C3	C4	110.4(9)	F4	C11	C8	114 (1)
N3	Rh	C1	178.8(4)	N1	C3	C6	125 (1)	F5	C11	F6	107 (1)
N3	Rh	C2	97.4(4)	C4	C3	C6	125 (1)	F5	C11	C8	110 (1)
C1	Rh	C2	82.0(5)	C3	C4	C5	107.0(9)	F6	C11	C8	113.2(9)
Rh	N1	N2	119.5(5)	N2	C5	C4	107.9(8)	N5	C13	C14	106.9(8)
Rh	N1	C3	134.9(6)	N2	C5	C7	122.0(9)	N5	C13	C16	124.1(8)
N2	N1	C3	105.7(7)	C4	C5	C7	130.1(9)	C14	C13	C16	128.9(9)
N1	N2	C5	109.0(7)	F1	C6	F2	109 (1)	C13	C14	C15	106.1(9)
N1	N2	B	123.0(7)	F1	C6	F3	97 (1)	N6	C15	C14	111.1(9)
C5	N2	B	128.1(7)	F1	C6	C3	116 (1)	N6	C15	C17	119 (1)
Rh	N3	N4	118.4(5)	F2	C6	F3	108 (2)	C14	C15	C17	130 (1)
Rh	N3	C8	135.2(6)	F2	C6	C3	115 (1)	F7	C17	F8	106 (1)
N4	N3	C8	105.1(7)	F3	C6	C3	112 (1)	F7	C17	F9	103 (1)
N3	N4	C10	109.9(7)	N3	C8	C9	111.4(8)	F7	C17	C15	114 (1)
N3	N4	B	122.5(7)	N3	C8	C11	120.8(9)	F8	C17	F9	107 (1)
C10	N4	B	127.0(7)	C9	C8	C11	128 (1)	F8	C17	C15	112 (1)
N6	N5	C13	110.9(7)	C8	C9	C10	105.9(9)	F9	C17	C15	116 (1)
N6	N5	B	118.4(7)	N4	C10	C9	107.8(8)	N2	B	N4	108.6(7)
C13	N5	B	130.6(7)	N4	C10	C12	123.3(8)	N2	B	N5	110.1(7)
N5	N6	C15	104.9(7)	C9	C10	C12	129 (1)	N4	B	N5	110.0(7)

a Numbers in parentheses are estimated standard deviations in the least significant digits.

Preparation of $[(CO)_2Rh(3\text{-}CF_3\text{-}5\text{-}MePz)]_2$ (23)

A solution of 40.5 mg (0.722 mmol) KOH and 95.0 mg (0.697 mmol) **18** in 3 mL MeOH was added to 128.4 mg (0.330 mmol) $[(CO)_2RhCl]_2$ in 9 mL Et_2O. After stirring for 1 h, solvent was removed in vacuo. The residue was taken up in 25 mL benzene and filtered through Celite. After removing solvent in vacuo, the crude product was sublimed onto a dry ice probe at 80°C/0.1 mm Hg giving a yellow powder (152.5 mg, 75% yield) mp 123-125°C.

Characterization: IR (n-hexane) 2100, 2084, 2034 cm^{-1} (ν_{CO}). MS (130°C, 16 eV) M^+ (616, 100%), M^+-CO (30%), M^+-2CO (33%), M^+-3CO (12%), M^+-4CO (22%). ^1H NMR(CD_2Cl_2, 200 MHz, ambient) δ For major isomer **23t**: 6.34 (s, 2H), 2.35 (s, 6H). For minor isomer **23c**: 6.36 (s, 2H), 2.38 (s, 6H), Ratio 1.15:1. ^{19}F NMR (CD_2Cl_2, ambient) δ -61.34 (s, **23c**), -61.52 (s, **23t**). Anal. Calcd for $C_{14}H_8N_4O_4F_6Rh_2$: C, 27.30; H, 1.31; N, 9.09. Found: C, 27.59; H, 1.41; N, 9.27.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(C_2H_4)$ (24)

A sample of 40.0 mg (0.103 mmol) $[(CO)_2RhCl]_2$ and 40.0 mg (0.103 mmol) $[(C_2H_4)_2RhCl]_2$ was taken up in 5 mL CH_2Cl_2, giving approximately (0.206 mmol) $[(CO)(C_2H_4)RhCl]_2$. A sample of 205.0 mg (0.412 mmol) **21** was added and after stirring for 1 h, this yellow solution was filtered through Celite. A concentrated CH_2Cl_2 was chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent. Yellow crystals were obtained by layering a concentrated CH_2Cl_2 solution with hexane at -30°C (212.0 mg, 83% yield) mp 188-190°C.

Characterization: IR (n-hexane) 2042 cm^{-1} (ν_{CO}). MS (150°C, 16 eV) $M^+-C_2H_4/CO$ (590, 100%), $M^+-C_2H_4-CO$ (75%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.43 (s, 3H), 3.08 (d, 4H, $^2J_{Rh-H}$ = 2.2 Hz), 2.49 (s, 9H). ^1H NMR (-80°C) δ 6.44 (s, 2H), 6.31 (s, 1H), 3.26 (d, 2H, J = 4 Hz), 2.54 (d, 2H, J = 4 Hz), 2.42 (s, 6H), 2.30 (s, 3H). ^{19}F NMR (CD_2Cl_2, ambient) δ -60.40 (s). Anal. Calcd for $C_{18}H_{17}BN_6OF_9Rh$: C, 34.98; H, 2.77; N, 13.60. Found: C, 34.77; H, 2.69; N, 13.64.

Preparation of $HB(3-CF_3-5-MePz)_3Rh(CO)(COE)$ (25)

A sample of 107.5 mg (0.277 mmol) $[(CO)_2RhCl]_2$ and 198.4 mg (0.277 mmol) $[(COE)_2RhCl]_2$ was stirred together in 20 mL CH_2Cl_2 for 0.5 h, giving approximately 0.554 mmol $[(CO)(COE)RhCl]_2$. A sample of 551.1 mg (1.11 mmol) 21 was added and the reaction stirred for 1.5 h, whereupon the solution was filtered through Celite and the solvent was removed in vacuo. The crude solid was chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent, giving a yellow solid on removal of solvent. This was taken up in CH_2Cl_2-hexane and cooled to -30°C, giving yellow crystals (539.5 mg, 69% yield) mp 149-151°C.

Characterization: IR (n-hexane) 2033 (m), 2019 (s) cm^{-1} (ν_{CO}). MS (210°C, 16 eV) M^+ (700, 1%), M^+-CO (1%), M^+-COE (96%), $M^+-CO-COE$ (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.45 (s, 3H), 4.31 (m, 2H), 2.23 (br, 9H), 2.04 (m, 2H), 1.7-1.2 (m, 10H). ^1H NMR (-95°C) δ 6.46 (s, 2H), 6.40 (s, 1H), 4.16 (m, 2H), 2.41 (s, 3H), 2.06 (s, 6H), 1.95 (m, 2H), 1.7-1.2 (m, 10H). ^{19}F NMR (CD_2Cl_2, ambient) δ -60.40 (s). Anal. Calcd for $C_{24}H_{27}BN_6OF_9Rh$: C, 41.17; H, 3.89; N, 12.00. Found: C, 41.11; H, 3.90; N, 11.85.

Attempted Preparation of $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(C_2H_4)$ (26)

A sample of 43.9 mg (0.113 mmol) $[(CO)_2RhCl]_2$ and 43.9 mg (0.113 mmol) $[(C_2H_4)_2RhCl]_2$ was taken up in 30 mL hexane, giving approximately 0.226 mmol $[(CO)(C_2H_4)RhCl]_2$. A sample of 158.2 mg (0.452 mmol) **19a** was added and after stirring for 0.5 h, this yellow solution was filtered through Celite. Attempted chromatography on neutral alumina resulted in extensive decomposition.

Characterization: IR (n-hexane) 2032 cm^{-1} (ν_{CO}). MS (150°C, 70 eV) M^+ (470, 4%), $M^+-C_2H_4/CO$ (100%), $M^+-C_2H_4-CO$ (44%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.27 (s, 2H), 3.94 (d, 4H, $^2J_{Rh-H} = 1.8$ Hz), 2.34 (s, 6H).

Preparation of $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(COE)$ (27)

A sample of 64.3 mg (0.165 mmol) $[(CO)_2RhCl]_2$ and 118.7 mg (0.165 mmol) $[(COE)_2RhCl]_2$ was stirred together in 25 mL hexane for 0.5 h giving approximately 0.33 mmol $[(CO)(COE)RhCl]_2$. A sample of 231.1 mg (0.66 mmol) **19a** was added and the reaction was monitored by IR spectroscopy. After 0.5 h, the reaction was almost complete. A further 0.5 h stirring showed the appearance of **20a**, so the solution was filtered through Celite and concentrated to 5 mL. Cooling to -30°C gave orange crystals. (218.4 mg, 60% yield). The mother liquor contained both product **27** and more **20a**, but they could not be separated. For **27**, mp 149-151°C.

Characterization: IR (n-hexane) 2020 cm^{-1} (ν_{CO}). MS (170°C, 16 eV) M^+

(552, 2%), M^+-CO (1%), M^+-COE (100%), M^+-CO-COE (12%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.25 (s, 2H), 4.64 (m, 2H), 2.58 (m, 2H), 2.34 (s, 6H), 2.0-1.3 (m, 10H). ^{19}F NMR (CD_2Cl_2, ambient) δ -59.62 (s, 3F), -59.63 (s, 3F). Anal. Calcd for $C_{19}H_{24}BN_4OF_6Rh$: C, 41.33; H, 4.38; N, 10.15. Found: C, 41.47; H, 4.53; N, 10.15.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(C_2H_4)_2$ (28)

To a solution of 70.5 mg (0.181 mmol) $[(C_2H_4)_2RhCl]_2$ in 5 mL CH_2Cl_2 was added 181.0 mg (0.363 mmol) 21. After stirring for 3 h, this yellow solution was filtered through Celite, and a concentrated CH_2Cl_2 solution was chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent, giving a yellow powder on removal of solvent. Yellow crystals were obtained by cooling a concentrated hexane solution to -78°C (60.5 mg, 27% yield) mp 117-119°C.

Characterization: MS (80°C, 16 eV) M^+-C_2H_4 (590, 62%), M^+-2(C_2H_4) (100%). UV (CH_2Cl_2) 417.3 (ε = 925) nm (λmax). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.42 (s, 3H), 2.81 (d, 8H, $^2J_{Rh-H}$ = 1.8 Hz), 2.31 (s, 9H). ^{19}F NMR (CD_2Cl_2, ambient) δ -59.87 (s). Anal. Calcd for $C_{19}H_{21}BN_6F_9Rh$: C, 36.92; H, 3.42; N, 13.60. Found: C, 36.85; H, 3.38; N, 13.45.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(COD)$ (29)

To a solution of 165.0 mg (0.335 mmol) $[(COD)RhCl]_2$ in 15 mL CH_2Cl_2 was added 337.0 mg (0.676 mmol) 21 which was stirred for 2 h. The solution was filtered through Celite and the solvent was removed in vacuo. The resulting orange oil was chromatographed on neutral alumina

(12 x 2.5 cm) with CH_2Cl_2 eluent, and solvent was removed. The resultant yellow oil was pumped in vacuo for two days, giving a yellow solid (235.7 mg, 53% yield) mp 163-165°C.

Characterization: MS (180°C, 16 eV) M^+ (670, 100%), M^+-COD (45%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.43 (s, 3H), 4.14 (br, 4H), 2.29 (s, 9H), 2.04 (br, 4H), 1.60 (m, 4H). ^1H NMR (-50°C) δ 6.52 (s, 1H), 6.40 (s, 2H), 4.30 (br, 2H), 3.81 (br, 2H), 2.43 (s, 6H), 2.35 (br, 2H) 1.92 (s, 3H), 1.80-1.30 (m, 6H). ^1H NMR (-105°C) δ 6.50 (s, 1H), 6.39 (s, 1H), 6.35 (s, 1H), 4.69 (br, 2H), 3.72 (br, 2H), 2.65 (br, 1H), 2.37 (br, 6H), 2.05 (br, 3H), 1.85 (br, 3H), 1.71-1.11 (m, 4H). Anal. Calcd for $C_{23}H_{25}BN_6F_9Rh$: C, 41.22; H, 3.76; N, 12.54. Found: C, 41.22; H, 3.80; N, 12.24.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(allyl)_2$ (30)

To a solution of 89.4 mg (0.203 mmol) $[(allyl)_2RhCl]_2$ in 10 mL CH_2Cl_2 was added 202.3 mg (0.406 mmol) 21. After stirring for 4 h, this yellow solution was filtered through Celite and solvent removed. A concentrated hexane solution (10 mL) was cooled to -30°C, giving a yellow powder (189.4 mg, 72% yield) mp 149-151°C.

Characterization: MS (170°C, 16 eV) M^+ (644, 10%), M^+-allyl (100%), M^+-2(allyl) (21%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.51 (s, 2H), 6.24 (s, 1H), 4.52 (m, 1H), 4.22 (m, 1H), 4.16 (m, 2H), 3.88 (d, 2H, J = 7.3 Hz), 3.19 (d, 2H, J = 12.0 Hz), 2.58 (s, 6H), 2.44 (s, 3H), 2.35 (d, 2H, J = 7 Hz). ^{19}F NMR (CD_2Cl_2, ambient) δ -57.06 (s, 3F), -58.34 (s, 6F). Anal. Calcd for $C_{21}H_{23}BN_6F_9Rh$: C, 39.16; H, 3.60; N, 13.05. Found: C, 39.21; H, 3.82; N, 13.00.

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CHAPTER IV

REACTIONS OF TRIFLUOROMETHYL(PYRAZOLYL)BORATE RHODIUM COMPLEXES

Section 1

INTRODUCTION

The previous Chapter has dealt with the synthesis and characterization of poly(pyrazolyl)borate rhodium complexes containing the CF_3 group on the pyrazole ring. This Chapter discusses reactions of these complexes with comparisons being made throughout to $(HBPz^*_3)Rh(CO)_2$, the complex utilized by Ghosh.[1a,b] The few studies of pyrazolylborate complexes of rhodium prior to Ghosh's investigations have focussed primarily on synthetic and structural aspects. Subsequent chemistry of these complexes had not been well developed relative to the cyclopentadienyl rhodium analogs.

This Chapter will present various ligand substitution reactions,[2] specifically with carbon monoxide, tertiary phosphines and alkynes. The reaction of tertiary phosphines with $(HBPz^*_3)Rh(CO)_2$ has been explored by Ghosh, where the substitution of CO was found to occur, giving a monophosphine complex.[1a] The analogous reaction was carried out with the dicarbonyl **22**, and with PMe_3, both mono and bis(phosphine) complexes are formed. These complexes are fluxional in solution and exhibit interesting NMR spectra which are thought to involve $\eta^2 \rightleftharpoons \eta^3$ and $\eta^1 \rightleftharpoons \eta^2$ equilibria.

With larger phosphines, such as PPh_3 and PCy_3, only the monophosphine complex is formed. The so-called low temperature fluxional process alluded to by Ghosh[1a] was found to have higher activation barriers in these phosphine complexes than in the Pz* system. For further insight into the hapticity of these complexes, a number of analogous bis(pyrazolyl)borate complexes were prepared.

There are no literature examples of pyrazolylborate rhodium alkyne complexes. Two such complexes were prepared by the displacement of COE in complex **25** by either 2-butyne or hexafluoro-2-butyne (HFB). These two complexes were spectroscopically characterized and compared to known olefin analogs.

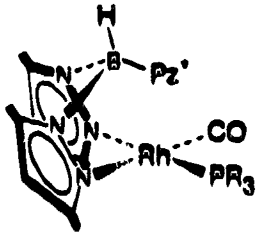
A number of products are formed by the reaction of the dicarbonyl **22** with Me_3NO in different solvents and conditions, giving substituted carbonyl complexes with nitrogen-based ligands. These exhibit similar fluxional NMR behaviour to that observed with the phosphine complexes.

The oxidative addition of "classic" reagents such as dihydrogen, silanes and methyl iodide will be discussed to determine the feasibility of C-H bond activation. C-H bond activation involving arenes and alkanes will be presented, as well as an example of the less common thermal or chemically assisted benzene activation. The first example of Me_3NO assisted activation of benzene is presented, which takes advantage of the relative electron-poor system used. Some kinetic aspects of the benzene activation and reactions of the hydridophenyl rhodium complex will be discussed, again with comparisons being made to analogous Pz* complexes.

Section 2

PHOSPHINE ADDITION REACTIONS

The addition of one equivalent of PR_3 to $(HBPz^*{}_3)Rh(CO)_2$ gives complexes of the type $(HBPz^*{}_3)Rh(CO)(PR_3)$.[1a] By comparison of the IR spectra to those of the bis(pyrazolyl)borate analogs, these complexes appear to be η^2 in solution.

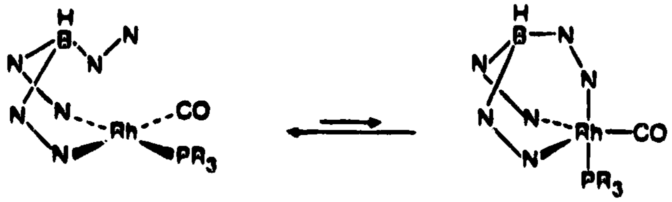


$(\eta^2\text{-}HBPz^*{}_3)Rh(CO)(PR_3)$

However, the ^1H NMR spectra show a 2:1 ratio of pyrazole group resonances at low temperature, instead of three unique groups as predicted from symmetry; this was also observed with the corresponding carbonyl-olefin complexes. When Ghosh used the phosphine PCy_3, the room temperature ^1H NMR spectrum of the complex showed a 2:1 ratio of pyrazole groups. On cooling to -80°C, the low temperature limiting spectrum was observed, with a 1:1:1 ratio of Pz* resonances.[3]

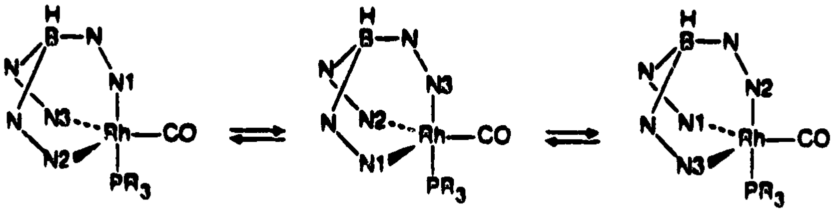
It is thought that there are two separate processes at work: a high temperature process (Figure 4-1b) which exchanges the bound and free pyrazole groups and averages all the pyrazole groups; and a low temperature process (Figure 4-1a) which averages the two bound pyrazole groups trans to different ligands in the four-coordinate structure.[1a] This latter process is thought to proceed through a five-coordinate trigonal bipyramidal intermediate, which would then give the 2:1 ratio of pyrazole resonances by averaging the two equatorial groups. As pointed out by Ghosh,[1a] it is immaterial whether the phosphine is in the axial or equatorial position, as both forms have equivalent equatorial pyrazole groups due to the plane of symmetry in the intermediate (eq. 4-1).

(a) Low temperature process



(4-1)

(b) High temperature process



When a dilute solution of one equivalent of PMe_3 is added slowly (dropwise) to a dilute solution of the dicarbonyl **22**, two products are observed by IR spectroscopy while starting material is still present. These were identified as the anticipated Pz* analog $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PMe_3)$ (**31**) and the unexpected bis(phosphine) complex $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PMe_3)_2$ (**32**) (eq. 4-2).

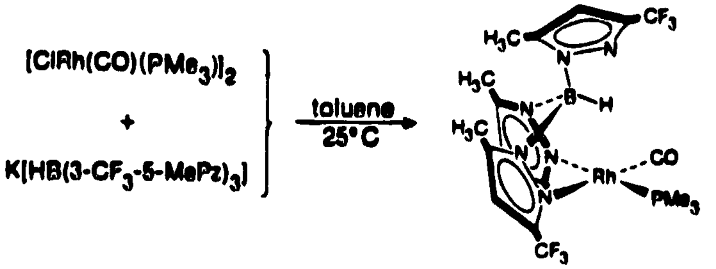
$$\mathrm{HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2} \xrightarrow[\text{Hexane}]{\mathrm{PMe_3}} \mathrm{HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PMe_3)_n} \qquad (4\text{-}2)$$

22 **31** n=1

32 n=2

Addition of another equivalent of PMe_3 reacts with **22** and **31** to give exclusively **32**. Apparently, **31** reacts more rapidly with PMe_3 than does **22** giving a substantial amount of **32**. Attempts to prepare a pure sample of **31** from the carbonyl ethylene complex **24** also gave both products.

Complex **31** can, however, be prepared pure by the reaction of $[(PMe_3)(CO)RhCl]_2$[4] with **21** (eq. 4-3).



21 **31** (4-3)

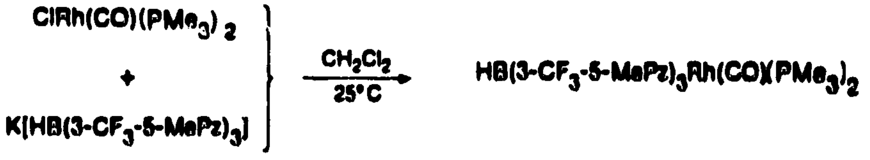
The IR spectrum of **31** in hexane shows a single ν_{CO} band at 1996 cm^{-1}, and the mass spectrum shows the molecular ion M^+ at m/e = 666.

The ^1H NMR spectrum at room temperature shows a 2:1 ratio of pyrazole group resonances, with the 4-H protons at δ 6.46 (s, 1H) and 6.37 (s, 2H) and the 5-Me groups at δ 2.46 (s, 3H) and 2.12 (s, 6H). The PMe_3 resonance appears as a doublet of doublets at δ 1.17 (9H, $^2J_{P-H}$ = 10.4 Hz, $^3J_{Rh-H}$ = 1.3 Hz). The ^{19}F NMR spectrum shows a doublet at

-60.43 (6F, J = 2 Hz) and a singlet at -60.69 (3F). The 2 Hz coupling does not disappear on broadband proton decoupling. Also, the ^{31}P NMR spectrum shows a doublet at δ 3.47 ($^{1}J_{Rh-P}$ = 152 Hz), with no smaller coupling. This implies that the 2 Hz coupling in the ^{19}F NMR spectrum is $^{4}J_{Rh-F}$.

The spectroscopic data is consistent with the η^2 isomer as observed for $(HBPz^*_3)Rh(CO)(PMe_3)$ at -40°C.[1a] However, three nonequivalent pyrazole groups should appear for **31** at low temperature. When the ^{1}H NMR spectrum was obtained at -90°C, the signal at δ 2.12 was broadened to a width of ~ 1 ppm, but the anticipated low temperature limiting spectrum was not realized.

Complex **32** can also be prepared by reacting $ClRh(CO)(PMe_3)_2$[5] with **21** (eq. 4-4).



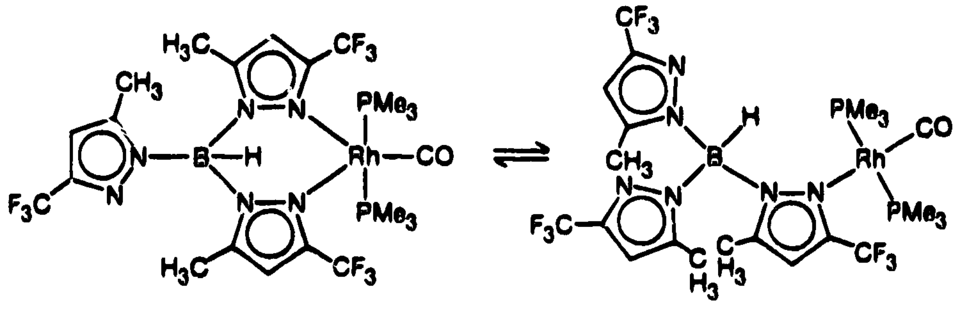
$$\left.\begin{matrix}\mathrm{ClRh(CO)(PMe_3)_2}\\ +\\ \mathrm{K[HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3]}\end{matrix}\right\} \xrightarrow[25^\circ\mathrm{C}]{\mathrm{CH_2Cl_2}} \mathrm{HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PMe_3)_2} \qquad (4\text{-}4)$$

21 **32**

The IR spectrum of **32** in hexane shows a single ν_{CO} band at 1978 cm^{-1}, and the mass spectrum shows a m/e = 714 corresponding to M^{+}-CO. The complex is fluxional on the NMR timescale as the ^{1}H NMR spectra at room temperature shows a broad resonance for the 4-H protons and a broad singlet for the 5-Me groups. The PMe_3 groups appear as a virtual triplet, with a broad central line as expected for an $AA'X_9X'_9$ spin system.[6] This portion is similar to the resonance reported for

$ClRh(CO)(PMe_3)_2$,[4] (and verified in this work) and this pattern is typical of a trans arrangement of the phosphine groups where $^2J_{P-P}$ is large.[4,7] The ^{31}P NMR spectrum shows a single phosphorus resonance at δ -9.10 with typical rhodium coupling ($^1J_{Rh-P}$ = 116 Hz).[1,8] On cooling the sample to -60°C, the ^1H NMR spectrum shows a 2:1 ratio of pyrazole group resonances as observed for **31**. Further cooling at -80°C caused broadening of the peaks but no change in the spectrum.

At least two structures for **32** are possible based on the spectroscopic data (eq. 4-5). By electron counting, **32** is presumed to be either a 18e five-coordinate complex if two of the three pyrazole groups are bound (η^2), or a 16e four-coordinate complex, with a square planar geometry, where only one pyrazole group is attached to rhodium (η^1) (eq. 4-5).



(4-5)

η^2-HB(3-CF$_3$-5-MePz)$_3$Rh(CO)(PMe$_3$)$_2$ η^1-HB(3-CF$_3$-5-MePz)$_3$Rh(CO)(PMe$_3$)$_2$

Either structure could account for the 2:1 ratio of pyrazole resonances observed at -80°C, assuming the two free pyrazole groups in the η^1 structure are equivalent. Regarding the fluxional process, it is unlikely that **32** would go through a six-coordinate 20e η^3 intermediate, so perhaps an $\eta^2 \rightleftharpoons \eta^1$ mechanism is plausible. Such a process has not been previously postulated with bis or tris(pyrazolyl)borate complexes, since prior to this work there were no known tris or tetrakis(pyrazolyl)borate RhL_3 complexes, where L is a 2e donor ligand.

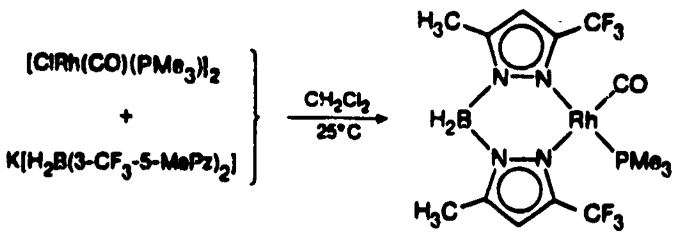
Further evidence concerning the hapticity of the tris(pyrazolyl)borate ligand in **31** and **32** can be obtained by comparing their IR spectra to those of the bis(pyrazolyl)borate analogs. Reaction of $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)_2$ **20a** with one equivalent of PMe_3 proceeds in a similar manner as with **22**, giving two products identified as $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)$ (**33**) and $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)_2$ (**34**) (eq. 4-6). Addition of another equivalent of PMe_3 gives exclusively **34**.

$$H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)_2 \xrightarrow[\text{Hexane}]{PMe_3} H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)_n \qquad (4\text{-}6)$$

20a **33** n=1

34 n=2

Complex **33** can be prepared pure in the same manner as **31**, by reacting the dimer $[(PMe_3)(CO)RhCl]_2$[4] with **19a** (eq. 4-7).

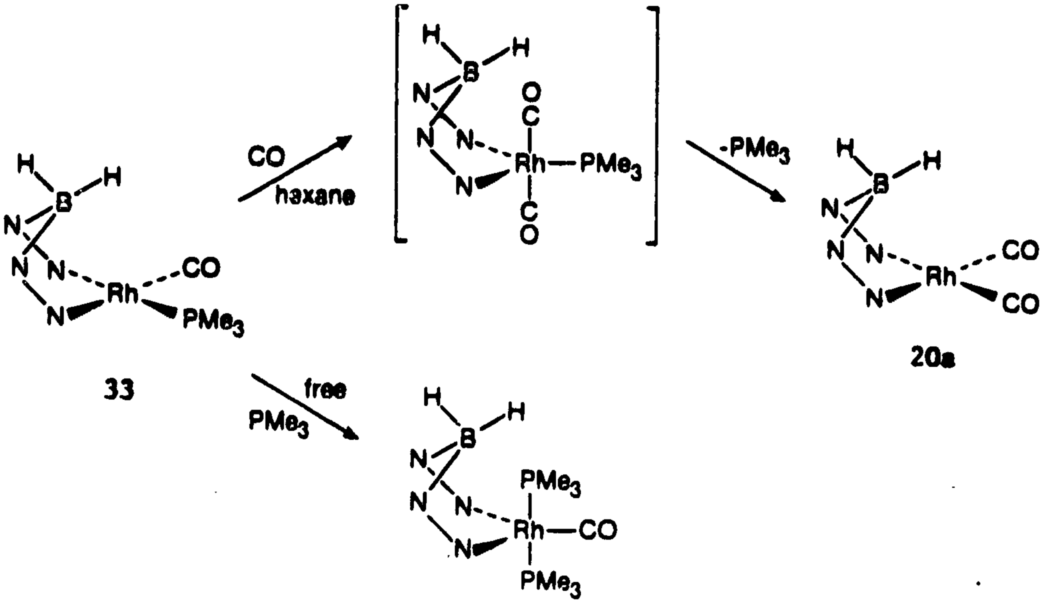


(4-7)

19a **33**

The IR spectrum of **33** in hexane has a ν_{CO} band at 1996 cm^{-1}, identical to the value for **31**, which suggests that **31** is η^2 in solution. The ^1H NMR spectrum of **33** shows two 4-H protons at δ 6.24 (s, 1H) and 6.23 (s, 1H) and the 5-Me groups at δ 2.33 (s, 3H) and 2.32 (s, 3H) as expected. The PMe_3 resonance is similar to that in **31**. The ^{19}F NMR spectrum exhibits one resonance as a singlet at δ -60.40, while the other is a doublet at δ -59.35 ($^5J_{P-F}$ = 4.6 Hz). The assignment of the coupling was confirmed by examining the ^{31}P NMR spectrum. One observes a doublet of quartets at δ 6.78, with the larger doublet coupled to rhodium ($^1J_{Rh-P}$ = 151 Hz), while the smaller quartets have couplings of 4.6 Hz. This coupling is similar to the F-C coupling of a CO and a CF_3 group in complex **20b** discussed in Chapter III.

The addition of one equivalent of PMe_3 to **33** cleanly gives **34**. When a hexane solution of **33** is purged with CO, the IR spectrum shows the appearance of dicarbonyl **20a** and the bis(phosphine) complex **34**. The following scheme is proposed to account for this reaction (eq. 4-8).



33

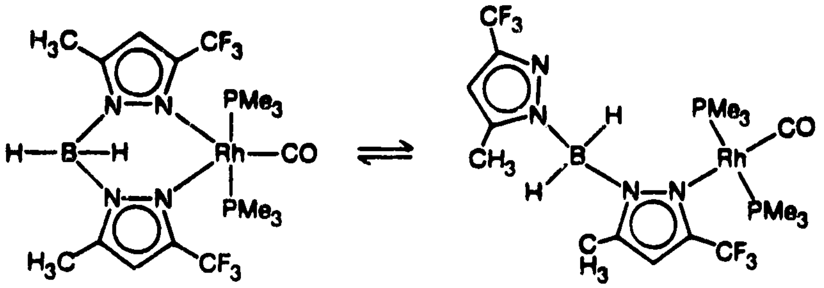
20a

34

(4-8)

The five-coordinate dicarbonyl phosphine intermediate is not unreasonable, and loss of PMe_3 would give dicarbonyl **20a**. The free PMe_3 would react with **33**, giving complex **34**.

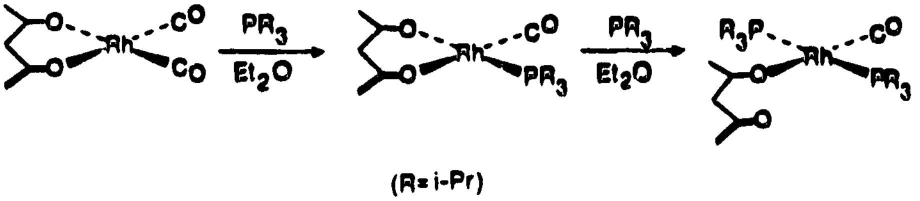
For complex **34**, the IR spectrum in hexane shows the ν_{CO} band at 1972 cm^{-1}, which is 6 cm^{-1} lower than for **32**. This suggests that the hapticity of the pyrazolylborate ligands in **32** and **34** is the same. At room temperature, the ^1H NMR spectrum shows the 4-H protons at δ 6.28 (s, 2H) and the 5-Me groups at δ 2.20 (s, 6H), as well as the typical virtual triplet for trans PMe_3 groups. On cooling the sample to -90°C, one observes two different pyrazole groups, with the 4-H protons at δ 6.36 (br, 1H) and 6.13 (br, 1H), while the 5-Me groups are at δ 2.30 (s, 3H) and 1.91 (s, 3H). The PMe_3 groups are a broad singlet at δ 1.14 (18H). This suggests that there is some fluxional process at room temperature which averages both pyrazole groups. The spectral evidence does not rule out a η^2 five-coordinate to a η^1 four-coordinate exchange process (eq. 4-9), and the low temperature NMR spectrum suggests that the η^1 isomer is present.



(4-9)

η^2-$H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)_2$ η^1-$H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)_2$

A structure based on a unidentate bis(pyrazolyl)borate cannot be ruled out. This has been recently demonstrated with the related acac ligand. Addition of one equivalent of $P(i\text{-}Pr)_3$ to $(acac)Rh(CO)_2$ gives the expected $(acac)Rh(CO)(P(i\text{-}Pr)_3)$ complex, but addition of another equivalent of $P(i\text{-}Pr)_3$ gives $(\eta^1\text{-}acac)Rh(CO)(P(i\text{-}Pr)_3)_2$, a square planar rhodium complex with a unidentate acac group and a trans phosphine arrangement (eq. 4-10).[9]



(4-10)

Although the latter complex was crystallographically characterized, the authors found that it was unstable in solution, losing $P(i\text{-}Pr)_3$ and forming $(acac)Rh(CO)(P(i\text{-}Pr)_3)$. Similarly, both bis(phosphine) complexes **32** and **34** were found to be unstable in solution, as one observes free PMe_3 and **31** and **33** respectively in the NMR and IR spectra over a few hours. To summarize, the spectral evidence suggests that in both bis(phosphine) complexes **32** and **34** the ground state structure has a η^1 tris and bis(pyrazolyl)borate ligand respectively.

The reaction of larger tertiary phosphines such as PPh_3 or PCy_3 with **22** gives exclusively $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PPh_3)$ (**35**) or $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PCy_3)$ (**36**) respectively (eq. 4-11).

$$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2 \xrightarrow[\text{Hexane}]{PR_3} HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PR_3) \qquad (4\text{-}11)$$

22

35 R=Ph

36 R=Cy

The IR ν_{CO} bands in hexane are at 2004 cm^{-1} for **35** and 1989 cm^{-1} for **36**. For **35**, the resonances of the pyrazole groups in the ^1H and ^{19}F NMR spectra at room temperature appear in a 2:1 ratio, but are broad. Cooling the sample to -60°C showed a 1:1:1 ratio of pyrazole group resonances, which sharpened further at -80°C. For **36**, the resonances of the pyrazole groups in the ^1H and ^{19}F NMR spectra at room temperature appear in a 1:1:1 ratio, with two of the three signals broad. Cooling the sample to -10°C results in the low-temperature limit. Based on the spectral data, both **35** and **36** are formulated as 16e square planar complexes, analogous to complex **31** (eq. 4-3) and those phosphine complexes prepared by Ghosh.[1a]

The barriers to both the high- and low-temperature processes are higher in complexes **31**, **35** and **36** than in the $(HBPz^*_3)Rh(CO)(PR_3)$ analogs.[1a] As previously mentioned, for the Pz* analog with PR_3=PMe_3, the room temperature ^1H NMR spectrum shows three equivalent Pz* rings, and only on cooling to -40°C is the splitting of the signals in a 2:1 ratio observed. For PR_3=PPh_3, one has to go to -105°C to obtain the same 2:1 pattern. For PR_3=PCy_3, the room temperature spectrum shows a 2:1 ratio, with the low-temperature limiting spectrum observed at -80°C. These differences could be steric in nature, since the $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3$ ligand is bulkier than the $HBPz^*_3$ ligand.

The bis(pyrazolyl)borate complex $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PPh_3)$ (37) is prepared in the same manner as 35, with the IR ν_{CO} band in hexane at 2005 cm^{-1}, suggesting that 35 is also η^2 in solution. The ^1H NMR spectrum shows two different pyrazole groups as found for the PMe_3 complex 33. As well, one CF_3 group in the ^{19}F NMR spectrum is a doublet coupled to phosphorus, while the ^{31}P NMR spectrum shows a doublet of quartets, as observed for 33. Table 4.I lists the IR ν_{CO} bands for several Rh(I) complexes in this and the previous Chapter where the Pz* analog is known. One finds that the IR ν_{CO} bands for the Pz* analogs have values that are 19-45 cm^{-1} lower than their trifluoromethyl analogs.

Addition of one equivalent PPh_3 to 31 gives a mixed bis(phosphine) derivative $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PMe_3)(PPh_3)$ (38) (eq. 4-12).

$$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PMe_3) \xrightarrow[\text{Hexane}]{PPh_3} HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PMe_3)(PPh_3) \quad (4\text{-}12)$$

31 38

The IR spectrum shows a single ν_{CO} band at 1983 cm^{-1} and the ^1H and ^{19}F NMR spectra at room temperature show three nonequivalent pyrazole groups. The PMe_3 resonance at δ 1.38 now shows additional coupling to the second phosphine (ddd, $^2J_{P-H} = 9.9$ Hz, $^4J_{P-H} = 1.8$ Hz and $^3J_{Rh-H} = 1.3$ Hz). The ^{31}P NMR spectrum shows two resonances, both as doublet of doublets with the large P-P coupling ($^2J_{P-P} = 316$ Hz) indicative of a trans geometry.[7,10] As with complex 32, the tris(pyrazolyl)borate ligand could be bound in an η^2 or η^1 manner. The spectral data is

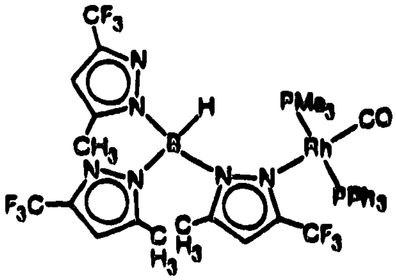
Table 4.I Comparison of ν_{CO} Bands of Rh(I) Complexes with Pz* Analogs

Compound		ν_{CO} (n-hexane) cm^{-1}		
		This Work	Pz* Analog	Difference
$H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)_2$	**(20a)**	2098, 2035	2079, 2013^c	19, 22
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2$	**(22)**	2091, 2026^a	2054, 1981^{c,d}	37, 45
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(C_2H_4)$	**(24)**	2042	2013^{c,e,f}	29
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(COE)$	**(25)**	2033^b	2000^d	33
$H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(C_2H_4)$	**(26)**	2032	2012^c	20
$H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(COE)$	**(27)**	2020	2000^g	20
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PMe_3)$	**(31)**	1996	1973^c	23
$H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)$	**(33)**	1996	1975^c	21
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PPh_3)$	**(35)**	2004	1983^c	21
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PCy_3)$	**(36)**	1989	1970^c	19
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(HFB)$	**(41)**	2086	2062^g	24

a 18e isomer of **(22)**
b 16e isomer of **(25)**
c Reference 1a
d Reference 1b
e Reference 1c
f Reference 1d
g Reference 3

inconsistent with the 18e structure as there are three inequivalent pyrazole groups instead of the 2:1 ratio observed with **32**.

Inspection of a Prentice-Hall (PH) molecular model of the η^1 form of **38** shows a sterically crowded metal center. This would present a large barrier to B-N bond rotation about the coordinated pyrazole, and the two free pyrazoles are fixed in different environments. Based on the related bis(phosphine) complexes **32** and **34**, complex **38** is thought to have the η^1 structure below.



η^1-HB(3-CF_3-5-MePz)$_3$Rh(CO)(PMe_3)(PPh_3)

Attempts to prepare the bis(pyrazolyl)borate analog of **38** yields interesting results. One equivalent of PPh_3 was added to **33** in hexane, giving an immediate reaction and a single IR ν_{CO} band at 1980 cm^{-1} which corresponds to $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)(PPh_3)$ (**39**). The ^1H NMR spectrum was complex, with several species present in solution. When the IR spectrum was subsequently rerun, additional bands had appeared at 2005, 1996 and 1972 cm^{-1}, due to the complexes **33**, **37** and **34** respectively. This could be a disproportionation reaction similar to that observed with complexes of the type $ClRh(CO)(PPh_3)(L)$ (eq. 4-13).[11]

$$ClRh(CO)(PPh_3)L \longrightarrow ClRh(CO)(PPh_3)_2 + ClRh(CO)L_2 \tag{4-13}$$

However, as observed with the bis(phosphine) complexes **32** and **34**, which lose one mole of PMe_3 readily in solution, the loss of PMe_3 or PPh_3 from **39** would give rise to **33** and **37** respectively, with free PMe_3 reacting with **33** to give complex **34** (eq. 4-14).

$$\begin{tikzcd}
H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)(PPh_3) \arrow[r, "-PMe_3"] \arrow[d, "-PPh_3"', "\mathbf{39}"] & \underset{\mathbf{37}}{H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PPh_3)} \\
\underset{\mathbf{33}}{H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)} \arrow[r, "free", "PMe_3"'] & \underset{\mathbf{34}}{H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)_2}
\end{tikzcd} \tag{4-14}$$

The complex $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PPh_3)_2$ is unlikely to form, as the reaction of **20a** with excess PPh_3 gave only the monophosphine complex **37**. Although **39** could not be obtained pure, the similar IR ν_{CO} bands of **38** (1983 cm^{-1}) and **39** (1980 cm^{-1}) suggest that both contain η^1 tris and bis(pyrazolyl)borate ligands respectively.

Section 3

OTHER LIGAND SUBSTITUTION REACTIONS

CO Reactions

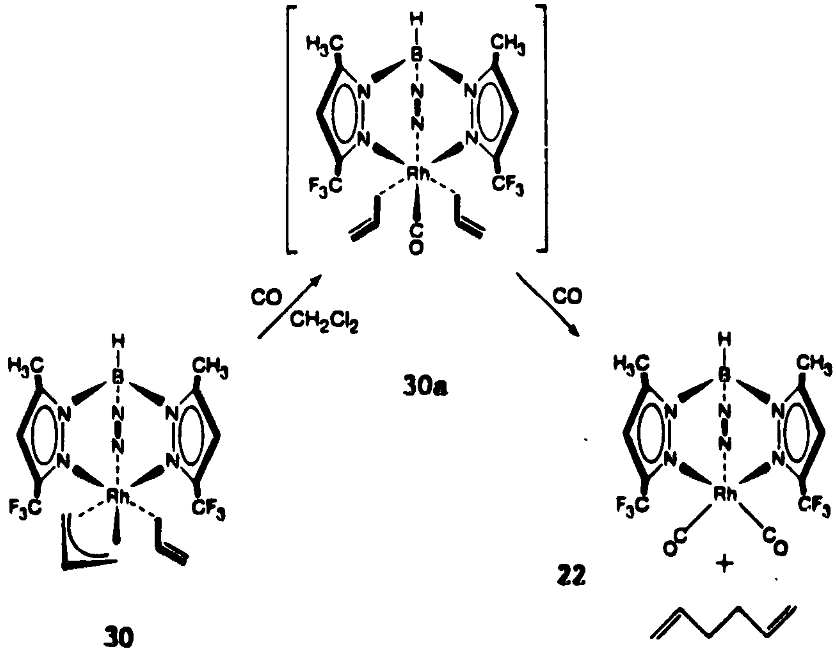
As discussed in Chapter II, CO substitution or exchange reactions with Rh(I) and Ir(I) square planar complexes are known to be rapid, involving an associative mechanism. The tris(pyrazolyl)borate rhodium complexes discussed in the previous chapter are postulated to be either equilibrium mixtures of η^2 and η^3 forms, $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2$ **22** and $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(COE)$ (**25**), or entirely η^2, $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(C_2H_4)$ **24** and $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(COD)$ (**29**). For the bis(ethylene) complex $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(C_2H_4)_2$ **28** there is no indication of the hapticity by either IR or NMR spectroscopy, whereas for $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(allyl)_2$ **30**, by analogy to $CpRh(allyl)_2$ and $(HBPz^*_3)Rh(allyl)_2$ it appears to be an η^3 18e Rh(III) complex. The relative ease of the displacement reaction with carbon monoxide may then be an indication of the hapticity of the tris(pyrazolyl)borate ligand and whether the complex is or is not coordinatively unsaturated.

Hexane solutions of the olefin complexes **24-29** all react rapidly with one atmosphere of CO resulting in complete conversion to the parent dicarbonyl **22** in five minutes. These fast CO reactions suggest an associative pathway with a 16e Rh(I) square planar species.

In contrast, the reaction of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(allyl)_2$ **30** with CO is relatively slow. When the reaction of **30** with one atmosphere CO in CH_2Cl_2 is monitored by IR spectroscopy, a single IR ν_{CO} band at 2070 cm^{-1} appears initially. Further reaction causes this intermediate (**30a**) to disappear, with the appearance of the dicarbonyl **22** after 18 hours.

The reaction can also be monitored by ^1H NMR spectroscopy. A solution of 30 in CD_2Cl_2 was kept under one atmosphere CO for 16 hours. Resonances due to 22 and 1,5-hexadiene were present. The reaction of $[(allyl)_2RhCl]_2$ with CO in benzene was rapid, with the formation of $[(CO)_2RhCl]_2$ and 1,5-hexadiene.[12]

At shorter reaction times (four or eight hours), one observes an intermediate present in the ^1H NMR spectrum with a 2:1 ratio of pyrazole group resonances and two η^1 allyl groups. This is consistent with **30a** which is present in the pathway below (eq. 4-15).



30a

30

22

(4-15)

The IR band of **30a** (2070 cm^{-1}) is consistent with a Rh(III) dialkyl species. For example, Ghosh found that for $(HBPz*_3)Rh(CO)(Me)_2$, the IR ν_{CO} band in hexane was at 2032 cm^{-1}.[1a] The IR ν_{CO} band for **30a** is then about 38 cm^{-1} higher than the dimethyl Pz* compound, which is consistent with other Rh(III) analogs presented in Section 5.

Complex **30a** does not appear to be isolable. On removing solvent and redissolving in CH_2Cl_2, the IR ν_{CO} band disappears, so perhaps **30a** loses CO to give **30**. Unlike other olefin displacements by CO, the above reaction is quite slow. There is also further evidonce that **30** is a coordinatively saturated 18e Rh(III) species and that exchange occurs only via an $\eta^3 \rightleftharpoons \eta^1$ allyl group exchange, or via an $\eta^3 \rightleftharpoons \eta^2$ pyrazolyl group exchange. Bergman postulates an $\eta^3 \rightleftharpoons \eta^1$ mechanism operative in an iridium alkyl hydride complex,[13a] and such a mechanism is also consistent with some kinetic results of CO and phosphine substitution in various systems.[13b,c]

^{13}CO Exchange Reactions

As demonstrated with $HB(3\text{-}PhPz)_3Rh(CO)_2$ **1**, the exchange of ^{13}CO with **22** is very rapid in hexane solution (complete in five minutes) with IR ν_{CO} bands at 2053 (s), 2041 (s), 1994 (s), 1979 (s) cm^{-1} for $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(^{13}CO)_2$ **22-13,13**. Even though the η^3 form is the major isomer of **22** in solution by IR spectroscopy, the $\eta^2 \rightleftharpoons \eta^3$ process facilitates ^{13}CO exchange, although the ^{13}CO exchange is thought to take place via the η^2 isomer only. On the other hand, as found for 1, the so-called intermolecular exchange is slow. When equimolar amounts of 22 and **22-13,13** are stirred together in hexane a statistical equilibrium is reached only after several days, with appearance of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(^{12}CO)(^{13}CO)$ 22-12,13.

Alkyne Reactions

Although pyrazolylborate rhodium olefin complexes are abundant, there are no reported examples of alkyne analogs. Clark prepared a series of five coordinate Pt(II) alkyne complexes of the type $(HBPz_3)Pt(Me)(alkyne)$,[14] and postulated that the alkyne was bound in an η^2 fashion. It was of interest to determine whether stable pyrazolylborate rhodium alkyne complexes could be prepared, and if so to study their structure and reactivity.

Cis-cyclooctene is a labile ligand that can be easily displaced by stronger donor groups.[15] A hexane solution of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(COE)$ **25** was found to react with 2-butyne or hexafluoro-2-butyne (HFB) resulting in complete conversion to give $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(MeC{\equiv}CMe)$ (**40**) and $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(CF_3C{\equiv}CCF_3)$ (**41**) respectively in less than an hour (eq. 4-16).

$$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(COE) \xrightarrow[\text{Hexane}]{R_3CC{\equiv}CCR_3} HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(R_3CC{\equiv}CCR_3) \quad (4\text{-}16)$$

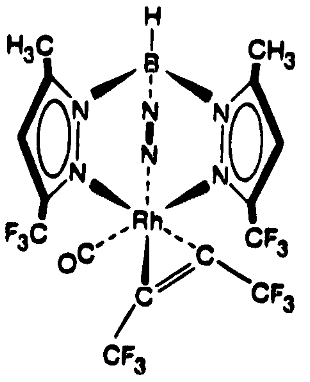
25

40 R=H

41 R=F

Complex **40** appears to be a mixture of η^2 and η^3 forms from the IR spectrum in hexane with ν_{CO} bands at 2040 (s), 2022 (w) cm^{-1}. The complex is fluxional on the ^1H NMR timescale, as the room temperature spectrum shows broad resonances corresponding to a 2:1 ratio of the pyrazole groups. The 2-butyne resonance appears as a broad singlet at δ 2.05. On cooling the sample to -95°C, all the resonances sharpen up. However, as observed with the olefin complexes in Chapter III, no low temperature limiting spectrum is obtained. From the above spectral data the low temperature form could be either the η^2 or η^3 isomer.

For complex **41** in hexane, there is a strong IR ν_{CO} band at 2086 cm^{-1}, with a weak band at 1897 cm^{-1} ($\nu_{C\equiv C}$). The band position of the terminal carbonyl is in the region of a Rh(III) complex, as discussed above for the **30a**. The ^1H NMR spectrum at room temperature shows a 2:1 ratio of pyrazole group resonances, which is unchanged at -95°C. The ^{19}F NMR spectrum shows that all the CF_3 groups on the pyrazole rings are coupled to those on HFB. The two equivalent CF_3 groups are quartets coupled to one CF_3 group of HFB, while the unique pyrazole CF_3 is a septet coupled to both HFB CF_3 groups. This latter coupling suggests that the tris(pyrazolyl)borate ligand is bound in an η^3 manner.



Postulated structure for **41**

For both complexes, the two limiting canonical forms of the alkyne linkage may resemble a Rh(I) η^2 alkyne or a Rh(III) metallacyclopropene complex (eq. 4-17).[2a]


(4-17)

As is well recognized,[2a] (p. 42) complexes containing an alkyne which is a sufficiently good acceptor (such as HFB) can be described as a metallacyclopropene. From the spectroscopic evidence, a Rh(I) alkyne complex seems reasonable for **40**, while **41** is more like a Rh(III) metallacyclopropene complex. It is also interesting to point out that the reaction of **40** with one atmosphere CO in hexane is fast, with complete conversion to dicarbonyl **22** in five minutes, while the analogous reaction with **41** is complete only after several hours.

Reactions of HB(3-CF_3-5-MePz)$_3$Rh$(CO)_2$ (22) with Trimethylamine N-oxide

A method for replacing a CO group by another ligand is by using trimethylamine N-oxide (Me_3NO). This reagent works well for CO groups with high terminal stretching frequencies, generally above 2000 cm^{-1}.[16] The nucleophilic oxygen of Me_3NO attacks the relatively electropositive carbonyl carbon, giving carbon dioxide and a trimethylamine complex, which can be replaced by a stronger donor ligand.

When one equivalent of Me_3NO is added to a solution of **22** in CH_3CN, an immediate reaction takes place with gas evolution. The acetonitrile complex $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(MeCN)$ (**42**) is formed in good yield (eq. 4-18).

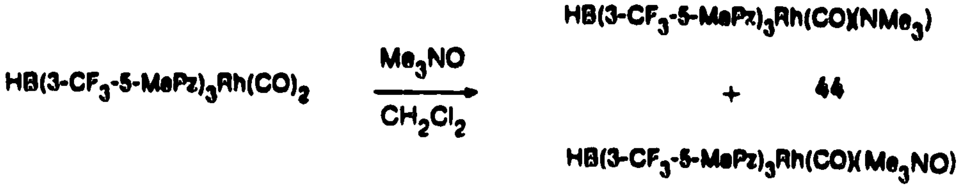
$$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2 \xrightarrow[CH_3CN]{Me_3NO} HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(CH_3CN) \qquad (4\text{-}18)$$

22 **42**

The IR spectrum in hexane shows a ν_{CO} band at 2014 cm^{-1}, and a CH_2Cl_2 or CH_3CN solution shows a weak ν_{CN} band at 2338 and 2339 cm^{-1} respectively, with the strong ν_{CO} band at 2004 and 2005 cm^{-1} respectively. The acetonitrile group can potentially bind in an end-on or side-on manner. The high ν_{CN} band in the vicinity of free CH_3CN is consistent with an end-on bound acetonitrile group,[17a] as a side-on bound nitrile would have a ν_{CN} band several hundred cm^{-1} lower. A number of rhodium and iridium side-on bound aryl nitrile complexes were recently reported.[17b]

The mass spectrum of **42** showed the molecular ion M^+ at m/e = 631, with loss of CO and MeCN. The complex is also fluxional on the ^1H NMR timescale, with a single pyrazole group resonance at room temperature, and on cooling the sample to -90°C, one observes a 2:1 ratio of pyrazole group resonances. As with the phosphine complexes, one would expect to observe a 1:1:1 ratio of pyrazole signals based on the symmetry of the η^2 form, but again the activation barrier must be quite low. The coordinated acetonitrile group is a singlet at δ 2.51, which is similar to other known end-on acetonitrile rhodium complexes.[17c]

When the addition of one equivalent of Me_3NO to **22** is carried out in CH_2Cl_2, two ν_{CO} bands appear in the IR spectrum at 1987 and 1982 cm^{-1}, but about half of the starting material still remains. The ^1H NMR spectrum shows three compounds present. There is still 45% starting dicarbonyl **22**, 39% of what is identified to be $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(NMe_3)$ (**44**), and 16% of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(ONMe_3)$ (**43**) (eq. 4-19).

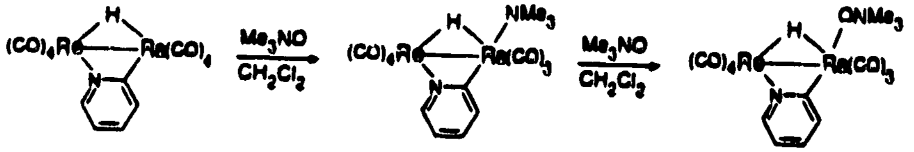


$$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2 \xrightarrow[CH_2Cl_2]{Me_3NO} \begin{array}{c} HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(NMe_3) \\ + \quad \mathbf{44} \\ HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(Me_3NO) \end{array} \qquad (4\text{-}19)$$

22 **43**

Upon addition of a second equivalent of Me_3NO, only complex **43** remains. In hexane, the IR spectrum of **43** shows a ν_{CO} band at 1982 cm^{-1}, and the MS shows the molecular ion M^+ at $m/e = 665$. The ^1H NMR spectrum shows a 2:1 ratio of pyrazole groups at room temperature, with the Me_3NO group at δ 2.72 (s, 9H). On cooling the sample to -100°C, one now observes three well separated 5-Me resonances, as found with the phosphine complexes **35** and **36**.

The product then is postulated to have an oxygen bound trimethylamine N-oxide group to rhodium. There are a few examples of other aliphatic amine oxides coordinated to a transition metal.[18] When the reaction of a rhenium carbonyl complex with Me_3NO was carried out in the CH_2Cl_2 solvent, Brown had evidence for a NMe_3 complex, and the NMe_3 ligand is displaced with more $ONMe_3$ (eq. 4-20).[18a]



(4-20)

This reaction sequence reported by Brown and coworkers is very similar to the one postulated below (eq. 4-21). In a ^1H NMR experiment, one equivalent of **22** was taken up in CD_2Cl_2 and two equivalents of Me_3NO were added. Vigorous gas evolution was noted, and the ^1H NMR spectrum showed the product **43** and one equivalent of free NMe_3 at δ 2.21 (s, 9H).

Slow dropwise addition of a CH_2Cl_2 solution of one equivalent of Me_3NO to a CH_2Cl_2 solution of **22** saturated with NMe_3 results in formation of the NMe_3 complex $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(NMe_3)$ **44**. The IR spectrum at room temperature shows a 2:1 ratio of pyrazole group resonances, with the NMe_3 group at δ 2.27 (d, 9H, $^3J_{Rh-H}$ = 1.1 Hz). On cooling the sample to -60°C, the spectrum shows three different pyrazole groups, as observed with complex **43** at -100°C. The following scheme is proposed to account for the formation of **43** and **44** from the dicarbonyl **22** (eq. 4-21).

$$\begin{tikzcd}
HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2 \arrow[r, "Me_3NO", "CH_2Cl_2"'] & HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(NMe_3) \arrow[dd, "Me_3NO"', "CH_2Cl_2"] & \\
\mathbf{22} & & \mathbf{44} \\
& HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(Me_3NO) & \\
& \mathbf{43} &
\end{tikzcd}$$

(4-21)

Brown mentions that based on IR data, Me_3NO is a good donor ligand.[18a] This is also observed in **43**, as the ν_{CO} band is lower in frequency than for the PMe_3 **31** or MeCN **42** complexes. Also, the rate of CO substitution of complexes **43** and **44** is quite different. The reaction of CO with a hexane solution of **44** is instantaneous, resulting in complete conversion to the dicarbonyl **22**. On the other hand, the analogous CO reaction with **43** requires two hours for completion.

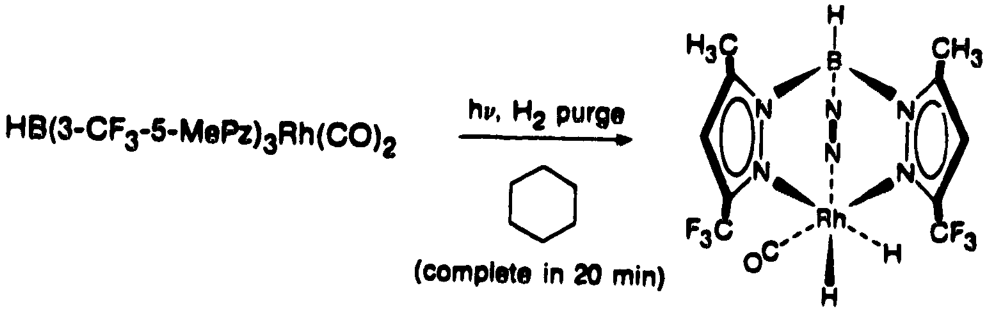
Section 4

ACTIVATION OF H-H AND Si-H BONDS

The activation of H-H and Si-H bonds by transition metal complexes can be thought of as model reactions in the study of C-H bond activation.[19]

Activation of H-H

The activation of dihydrogen with $(HBPz^*_3)Rh(CO)_2$ gave $(HBPz^*_3)Rh(CO)(H)(H)$, as demonstrated by Ghosh.[1] When a cyclohexane solution of **22** was irradiated with a dihydrogen purge for 20 minutes, the dihydride $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(H)$ (**45**) was formed, with no evidence of cyclohexane activation (eq. 4-22).



(4-22)

22 **45**

The IR spectrum in hexane showed a weak band at 2110 cm^{-1} (ν_{Rh-H}) and a strong band at 2077 cm^{-1} (ν_{CO}). The ^1H NMR spectrum showed the two sets of pyrazole resonances in a 2:1 ratio, as well as the high field hydride at δ -14.22 (d, 2H, $^1J_{Rh-H}$ = 18.8 Hz).

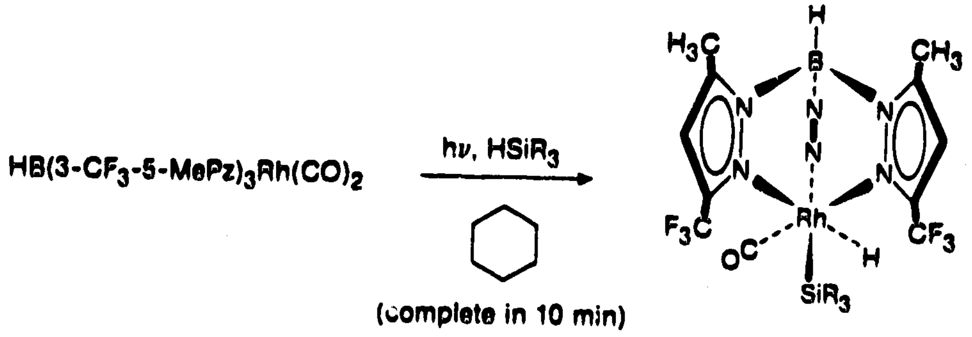
The ^{19}F NMR spectrum shows the expected two resonances of CF_3

groups in a 2:1 ratio. The two CF_3 groups trans to the hydride ligands appear as a doublet at δ -60.90 ($^4J_{Rh-F}$ = 1.5 Hz, 6F), while the remaining CF_3 group appears as a doublet at δ -61.52 ($^4J_{Rh-F}$ = 3.0 Hz, 3F). Broadband proton decoupling does not change the spectrum, so these couplings of the CF_3 groups are to the rhodium center. It is formally a four bond coupling which was also observed in the phosphine complex 31.

The reaction of diazomethane with $(HBPz^*_3)Rh(CO)(H)(H)$ gave the dimethyl complex $(HBPz^*_3)Rh(CO)(Me)(Me)$.[1a] When the same reaction was carried out with 45 no product could be isolated. The reaction is presumed to proceed through a methyl hydride intermediate, which is thought to be thermally unstable at room temperature in the CF_3,MePz system. This will be discussed further in the next Section.

Activation of Silanes

Irradiation of a cyclohexane solution of **22** containing excess trichlorosilane or trimethylsilane for 10 minutes resulted in the formation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(SiCl_3)$ (**46**) and $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(SiMe_3)$ (**47**) respectively as colorless crystalline solids (eq. 4-23).



(4-23)

R =Cl, Me

22

46 R=Cl

47 R=Me

Both complexes are air-sensitive in the solid state, but were completely characterized by analytical and spectroscopic methods. In the IR spectrum, **46** exhibited a weak band at 2160 cm^{-1} (ν_{Rh-H}) and a strong band at 2099 cm^{-1} (ν_{CO}), while the corresponding bands for **47** were at 2155 (w) and 2055 (s) cm^{-1} respectively. For complex **46**, the ^1H and ^{19}F NMR spectra show three different pyrazole resonances, as expected from the proposed octahedral structure.

The high field hydride resonance at δ −13.52 appears as a doublet of quartets (1H, $^1J_{Rh-H}$ = 14.9 Hz, $^5J_{F-H}$ = 3.5 Hz). From the ^{19}F NMR spectrum, two of the resonances are singlets at δ −57.44 and −60.84, while the third is a doublet of doublets at δ −57.30 ($^4J_{Rh-F}$ = 2.0 Hz, $^5J_{F-H}$ = 3.5 Hz). The coupling in the latter was assigned by the $^{19}F\{^1H\}$ spectrum, which now only showed a doublet ($^4J_{Rh-F}$ = 2.0 Hz).

It was found that in CH_2Cl_2 solution complex **47** rapidly converts to the dihydride **45**, so the ^1H NMR spectrum was run in cyclohexane-d_{12}.

The 4-H and 5-Me protons both appear as singlets, so the chemical shifts of the three pyrazole groups are very close. The high field hydride appears at δ -15.21 (d, 1H, ${}^{1}J_{Rh-H}$ = 20.1 Hz). Both **46** and **47** can be formed at room temperature by reaction of **25** in hexane with $HSiCl_3$ and $HSiMe_3$ respectively, which displaces COE. Both **46** and **47** do not react with the free COE, but rapidly react with CO in hexane to give the parent dicarbonyl **22**.

Common types of oxidative reactions are presented in a recent organometallic textbook by Crabtree.[2b] The oxidative addition reactions of a substrate X-Y with square planar d^8 16e Rh(I) and Ir(I) complexes is well known, giving Rh(III) or Ir(III) 18e octahedral complexes (eq. 4-24a).[2] The analogous oxidative addition to an 18e complex must be accompanied by loss of a 2e ligand to give a M(III) 18e complex (eq. 4-24b).

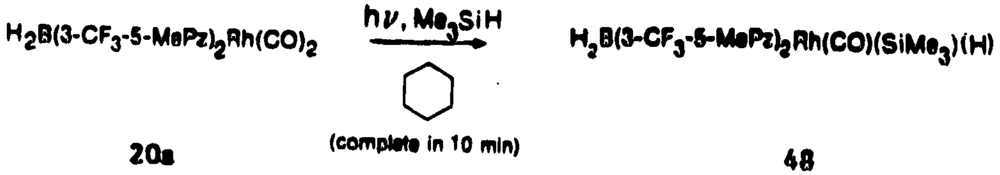
$$\underset{16e}{\mathrm{M(I)}} + \mathrm{X{-}Y} \longrightarrow \underset{18e}{\mathrm{X{-}M(III){-}Y}} \qquad (4\text{-}24a)$$

$$\underset{18e}{\mathrm{L{-}M(I)}} + \mathrm{X{-}Y} \longrightarrow \underset{18e}{\mathrm{X{-}M(III){-}Y}} + \mathrm{L} \qquad (4\text{-}24b)$$

$$\underset{16e}{\mathrm{L{-}M(I)}} + \mathrm{X{-}Y} \longrightarrow \underset{16e}{\mathrm{X{-}M(III){-}Y}} + \mathrm{L} \qquad (4\text{-}24c)$$

The oxidative addition of a molecule X-Y to a 16e square planar complex with loss of a ligand is extremely rare, as the product would be a 16e Rh(III) or Ir(III) complex (eq. 4-24c).

However, the oxidative addition of Me_3SiH to complex **20a** has been demonstrated (eq. 4-25), with loss of a CO group. Irradiation of a cyclohexane solution of **20a** with a Me_3SiH purge for 10 minutes results in complete conversion to **48**.



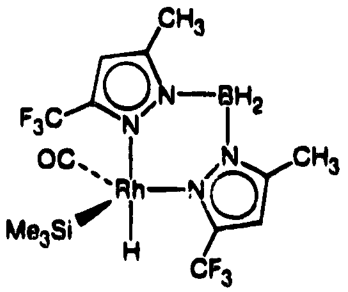
$$H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)_2 \xrightarrow[\text{(complete in 10 min)}]{h\nu,\ Me_3SiH} H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(SiMe_3)(H) \qquad (4\text{-}25)$$

20a **48**

The product **48** is unstable in solution, with **20a** reappearing. If the solvent is immediately removed, **48** is isolated as an unstable tan oil. The IR in hexane shows a weak broad band at 2120 cm^{-1} (ν_{Rh-H}) and a strong band at 2050 cm^{-1} (ν_{CO}). The latter value compares well with the more stable tris(pyrazolyl)borate analog **47** (ν_{CO} = 2055 cm^{-1}).

The ^1H and ^{19}F NMR spectra show two different pyrazole groups, with the $SiMe_3$ groups appearing at δ 0.46 (s, 9H) and the high field hydride at δ -13.80 (d, 1H, $^1J_{Rh-H}$ = 26.7 Hz). The large Rh-H coupling suggests that this is a genuine $Rh(III)(H)(SiMe_3)$ complex and not a $Rh(I)(\eta^2\text{-}HSiMe_3)$ 16e complex.

As **48** is five-coordinate, it can have a trigonal bipyramidal (TBP) or square pyramidal structure. Assuming the more common TBP geometry, both pyrazolyl groups cannot be in the equatorial plane, as they would be equivalent by symmetry. Also, the ideal bite angle for the bis(pyrazolyl)borate ligand is closer to 90° rather than 120°. The oxidative addition of silanes usually occurs in a cis manner and in TBP geometries, the more sterically demanding group occupies the equatorial position, so **48** is postulated to have the following structure.



Postulated structure for **48**

Due to the instability of **48**, a mass spectrum or a good elemental analysis could not be obtained. However, the spectroscopic data strongly supports the formulation. Complex **48** can also be prepared by reacting Me_3SiH with a hexane solution of **27**. However, on removing solvent, the more volatile Me_3SiH is removed first, leaving the less volatile COE in solution. Unlike complex **47**, **48** rapidly reacts with added COE to regenerate **27**. In a ^1H NMR experiment, reaction of **27** with a slight excess of Me_3SiH in CD_2Cl_2 gives **48** and free COE. As expected, **48** reacts instantaneously with CO in hexane solution. Also, addition of other donor ligands in order to stabilize the 16e complex resulted in reductive elimination of Me_3SiH. Other silanes react in a similar manner to Me_3SiH, but the products were less stable. No photochemical or thermal reaction of **20a** or **27** with dihydrogen was observed.

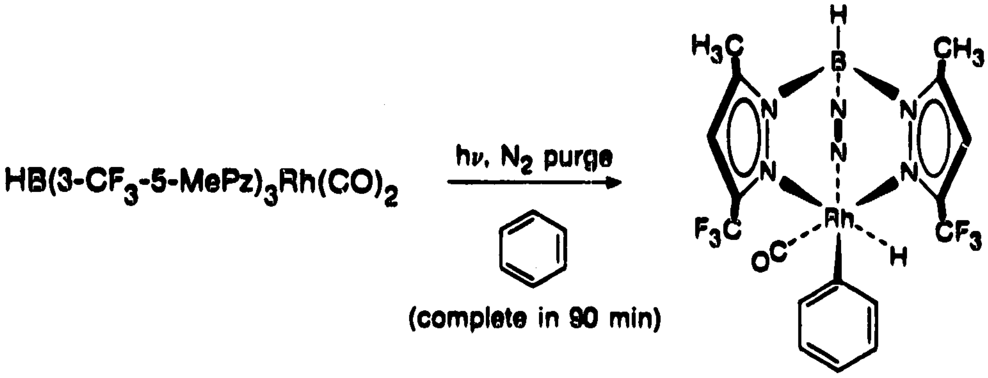
Tris(pyrazolyl)borate rhodium complexes have been shown to oxidatively add a wide variety of C-H bonds, but this has not been demonstrated with the 16e bis(pyrazolyl)borate or acac Rh(I) complexes. Under similar photolytic conditions as previously employed, no C-H activation occurred with $(H_2BPz*_2)Rh(CO)_2$[3] or $(acac)Rh(CO)_2$,[20a] the rationale being that the products would be unstable Rh(III) 16e species.

Section 5

C-H ACTIVATION STUDIES

Activation of Benzene

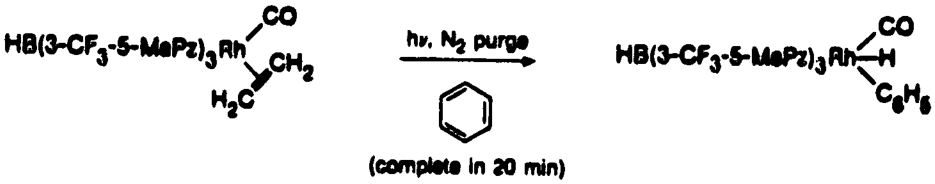
Irradiation of a benzene solution of the dicarbonyl $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2$ **22** with a nitrogen gas purge results in formation of the phenyl hydride complex $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(Ph)$ **49** (eq. 4-26). However, 90 minutes of photolysis is required for complete conversion and the yield is low.



(4-26)

22 **49**

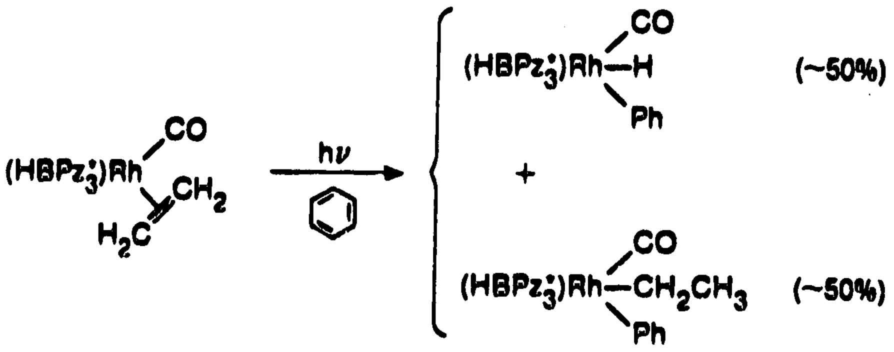
The photolysis of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(C_2H_4)$ **24** in benzene also results in formation of **49**, with the reaction complete in 20 minutes (eq. 4-27).



(4-27)

24 **49**

There is no evidence of an ethyl phenyl complex, which was observed when (HBPz*$_3$)Rh(CO)(C_2H_4) was photolysed in benzene (eq. 4-28).[1a,d]



(4-28)

Complex **49** can be isolated as an air-sensitive off-white powder. The IR spectrum in benzene shows the product at 2145 (w) cm^{-1} (ν_{Rh-H}) and 2077 (s) cm^{-1} (ν_{CO}). The analogous IR spectrum of **49** in hexane shows the product at 2145 (w) cm^{-1} (ν_{Rh-H}) and 2083 (s) cm^{-1} (ν_{CO}). There is also present another band at 2067 cm^{-1} (m), which is thought to be the hexyl hydride. This point will be further discussed later in this Section. When a few drops of benzene are added to the hexane solution, the IR band at 2067 cm^{-1} disappears. In cyclohexane, the IR spectrum shows the product **49** at 2150 (w) cm^{-1} (ν_{Rh-H}) and 2082 (s) cm^{-1} (ν_{CO}), with no evidence for the cyclohexyl hydride.

The elemental analysis and ^{1}H NMR spectrum shows the presence of one mole of benzene of crystallization. The ^{1}H NMR spectrum at room temperature shows an octahedral Rh(III) complex with three different pyrazole groups. The high field hydride is a doublet at δ -13.35 (1H, $^1J_{Rh-H}$ = 21.2 Hz). As observed for (HBPz*$_3$)Rh(CO)(H)(Ph),[1] the meta and ortho phenyl protons are broad at room temperature due to phenyl ring rotation, while the para proton is a sharp triplet. On cooling to

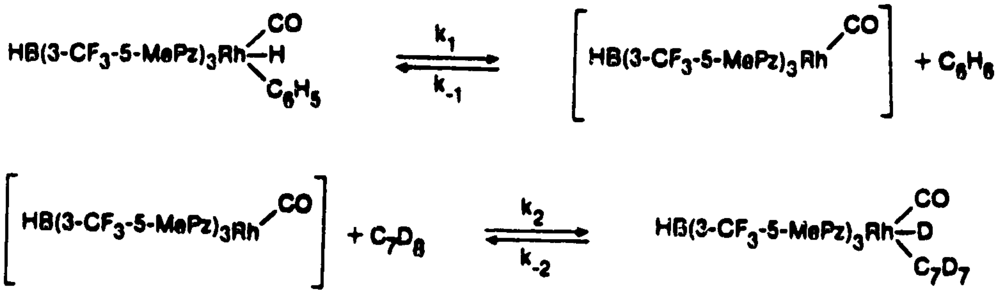
-30°C, one observes five resonances for the phenyl protons, as the phenyl ring rotation becomes slow on the NMR timescale. The ^{13}C NMR spectrum again shows three different pyrazole groups, with the rhodium bound phenyl carbon at δ 142.17 (d, $^1J_{Rh-C} = 26$ Hz). The ^{19}F NMR spectrum shows the expected three resonances at δ -59.10 (s), -60.24 (t, J = 2 Hz) and -60.51 (t, J = 2 Hz), there is one singlet and two triplets. On broadband proton decoupling, the 2 Hz coupling disappears in the latter two resonances. The coupling appears to be due to the two ortho protons of the phenyl ring, which would formally be a seven bond H-F coupling. This suggests a through space rather than a through bond interaction, as a PH molecular model of **49** shows that two CF_3 groups are in close proximity to the ortho phenyl protons.

Under comparable irradiation conditions, the rate of activation of benzene by the dicarbonyl **22** is slower than with $(HBPz^*_3)Rh(CO)_2$,[1] with the latter reaction complete in five minutes. As noted earlier, there is a substantial difference in the IR ν_{CO} bands of **22** and $(HBPz^*_3)Rh(CO)_2$, indicating that **22** is much less electron rich. The UV-Vis spectrum of **22** in CH_2Cl_2 shows a transition at $\lambda_{max} = 355.2$ nm (ε = 1504), virtually identical to that of $(HBPz^*_3)Rh(CO)_2$ in hexane (λ_{max} = 353 nm, ε = 1820). The transition at 353 nm in the latter complex is thought to account for C-H activation by visible or tungsten light. The rate of benzene activation with **22** is still much faster than with $Cp^*Ir(CO)_2$,[20b] so that these rate differences between **22** and $(HBPz^*_3)Rh(CO)_2$ are due to the electronic or steric differences of the two systems.

The rate of reaction of **24** to form **49** is slightly faster, as the ethylene group is perhaps more photochemically labile. Also, irradiation of benzene solutions of HB(3-CF_3-5-MePz)$_3$Rh(CO)(COE) **25**, HB(3-CF_3-5-MePz)$_3$Rh(CO)($CH_3C{\equiv}CCH_3$) **40** and HB(3-CF_3-5-MePz)$_3$Rh(CO)(CH_3CN) **42** resulted in complete conversion to the phenyl hydride **49** in 20 to 30 minutes.

Kinetics of C_6H_6 Exchange of (49) with C_7D_8 Solvent

Ghosh demonstrated that (HBPz*$_3$)Rh(CO)(H)(Ph) is quite stable in C_6D_6 at room temperature and does not exchange at an appreciable rate below 40°C.[1a] On the other hand, the ^1H NMR spectrum of **49** in C_6D_6 at room temperature shows rapid and complete exchange. This indicates that the activation barrier for reductive elimination for **49** is considerably lower than for (HBPz*$_3$)Rh(CO)(H)(Ph). Unfortunately, the use of C_6D_6 as a solvent is limited to temperatures above +5°C, so toluene-d_8 (C_7D_8) was used. At temperatures from -10°C to +20°C, smooth first-order reductive elimination takes place (eq. 4-29).



(4-29)

The experimental procedure for the kinetic studies in this work were the same as employed by Ghosh.[1a] The rate of reaction of **49** was followed by monitoring the rate of disappearance of the high field hydride resonance against an internal standard (hexamethyldisiloxane).

The kinetics were performed at four different temperatures in the NMR spectrometer. To determine the rate constants, least-squares plots of log(I[Rh-H]/I[int. std.]) versus time gave straight lines with rate constants k determined from the slope. Figure IV.1 shows a typical plot at -10°C. As was done with $(HBPz^*_3)Rh(CO)(H)(Ph)$, all runs were monitored for at least two to three half lives, with Table 4.II listing the rate constants.

To determine the activation parameters, an Eyring plot of the data was done (Figure IV.2), with the resulting values of $\Delta H^{\ddagger} = 19.8 \pm 1.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2.1 \pm 3.8$ eu. The parameters for $(HBPz^*_3)Rh(CO)(H)(Ph)$ are $\Delta H^{\ddagger} = 29.6 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = 12.2 \pm 2.4$ eu.[1a] This shows that $\Delta H^{\ddagger}$ for **49** is about 10 kcal mol^{-1} lower than the value for the Pz* analog, which represents a lower barrier for reductive elimination. The interpretation of the $\Delta S^{\ddagger}$ value is less obvious. The key point is that the reductive elimination in **49** is not entropically favored, as it is in the Pz* case.

Activation of Ethylene

The photolysis of a cyclohexane solution of the dicarbonyl **22** with ethylene purge resulted in a complete conversion to $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(C_2H_4)$ **24** in 150 minutes. Ghosh found that the analogous reaction with $(HBPz^*_3)Rh(CO)_2$ initially gives the vinyl hydride complex $(HBPz^*_3)Rh(CO)(H)(CH{=}CH_2)$, which isomerizes to $(HBPz^*_3)Rh(CO)(C_2H_4)$ in five minutes.[1a,21] No evidence of the vinyl hydride complex was observed in this system. When the analogous iridium ethylene complex $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Ir(CO)(C_2H_4)$ is heated at 100°C in cyclohexane, it is converted to the vinyl hydride complex $HB(3\text{-}CF_3\text{-}5\text{-}$

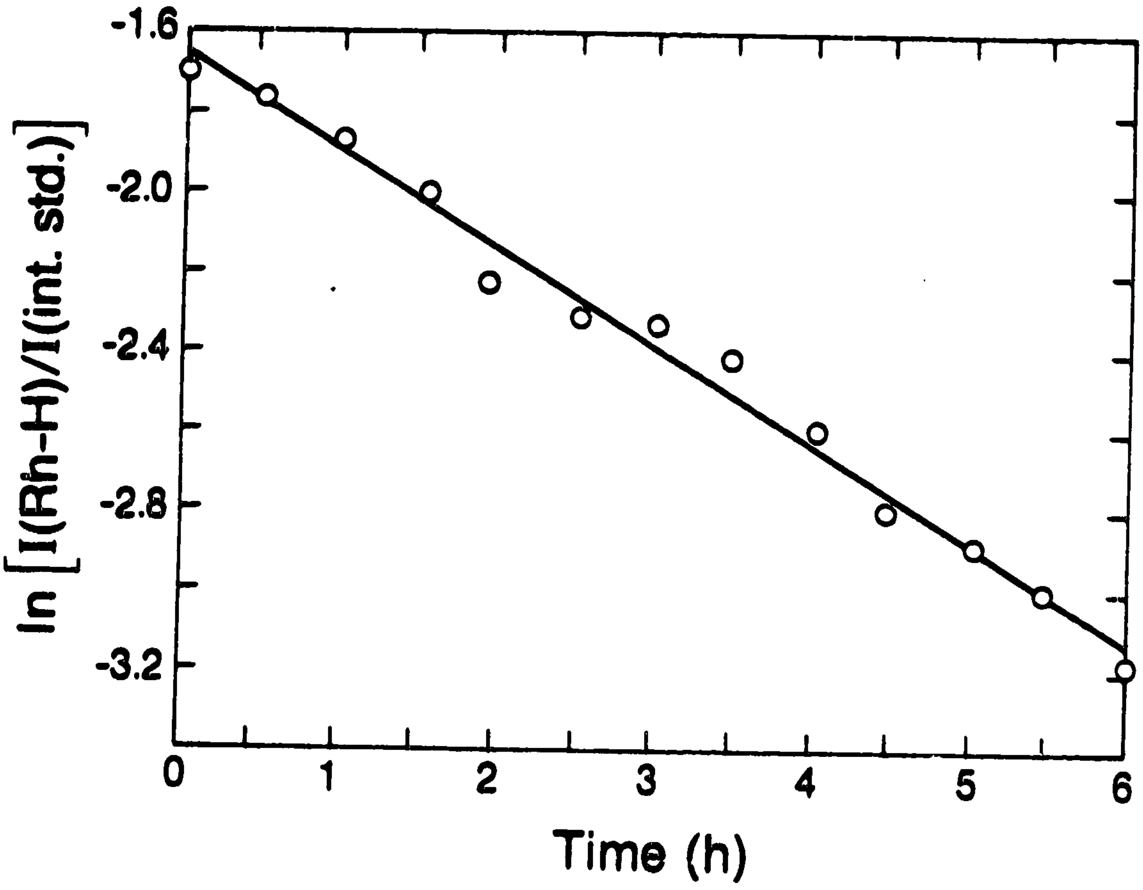


Figure IV.1 First Order Plot of Benzene Exchange Data for $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(C_6H_5)$ (**49**) in C_7D_8 at -10°C

Table 4.II Rate Constants for Exchange of Toluene-d_8 with 49

Temperature (K)	k (s^{-1})
263	$(7.10 \pm 0.30) \times 10^{-5}$
273	$(2.26 \pm 0.06) \times 10^{-4}$
283	$(1.12 \pm 0.03) \times 10^{-3}$
293	$(3.52 \pm 0.24) \times 10^{-3}$

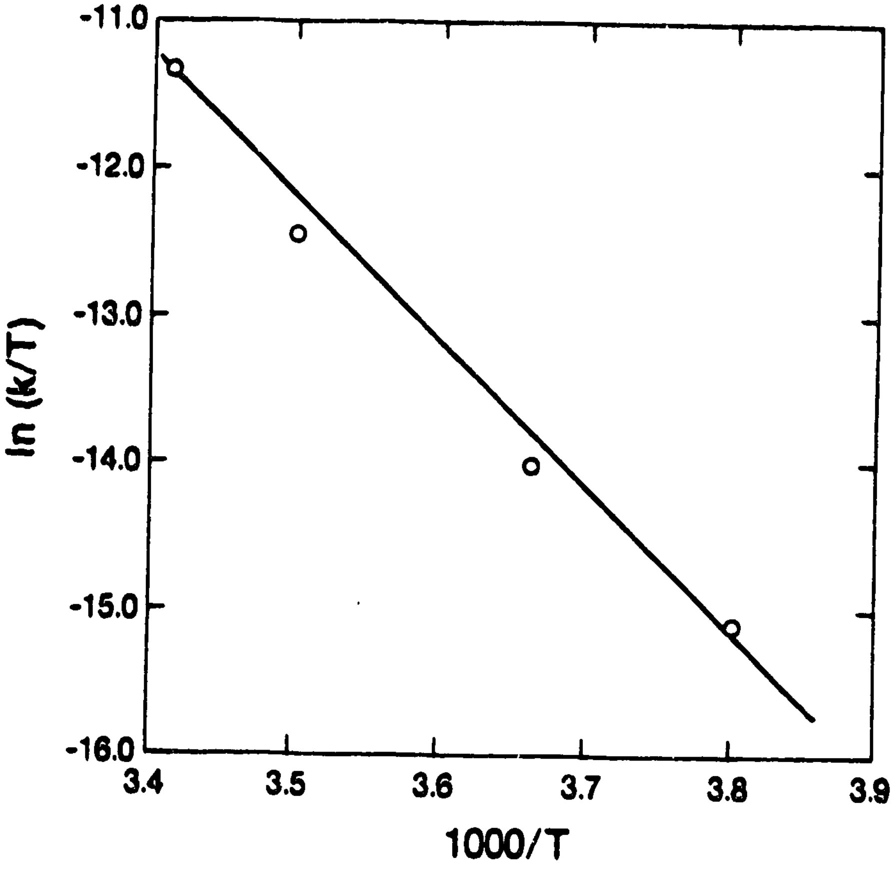
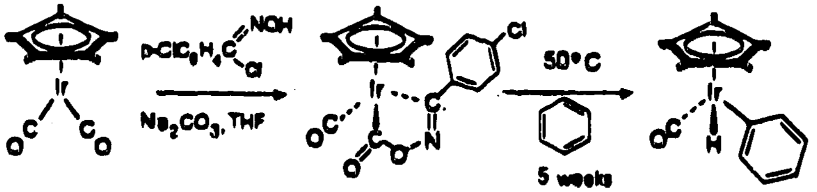


Figure IV.2 Eyring Plot for the Exchange of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(C_6H_5)$ (49) with C_7D_8

$MePz)_3Ir(CO)(H)(CH{=}CH_2)$.[21] Heating a solution of **24** in cyclohexane at 100°C for one week resulted in partial decomposition with appearance of the dicarbonyl **22** but no evidence for the vinyl hydride complex.

Thermal Activation of Benzene

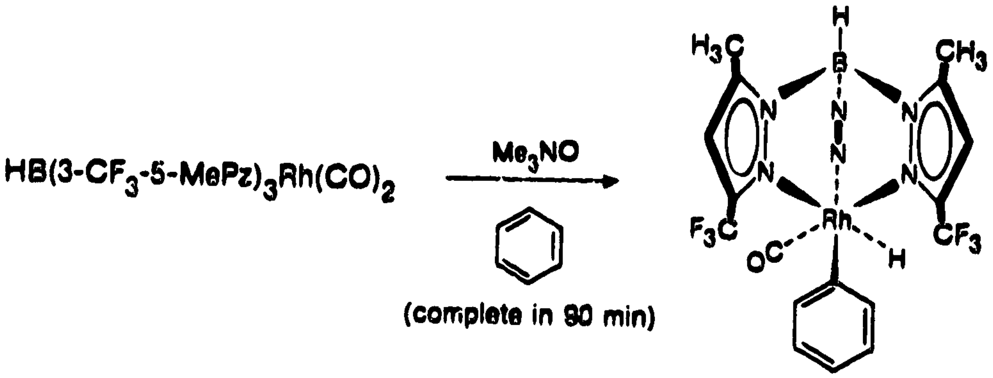
Recently, there have been several examples of "chemically assisted" C-H bond activation. Hawthorne activated C-H bonds with $Cp^*Ir(CO)_2$ using a 1,3-dipolar reagent (eq. 4-30).[22]



(4-30)

This has also been observed in this research group by Dr. C. Barrientos.[23] Ghosh demonstrated benzene activation with $(HBPz^*{}_3)Rh(CO)_2$ using another 1,3-dipolar reagent, nitrous oxide.[1a] These reagents react with a CO group on an electron-rich metal center to give CO_2 and either an aryl nitrile or nitrogen.

As demonstrated in Section 3, another method of removing CO groups is with Me_3NO, which reacts with carbonyl groups on more electron poor metal centers.[16] The reaction of a benzene solution of the dicarbonyl **22** with one equivalent of Me_3NO at 25°C results in quantitative conversion to the phenyl hydride **49** in 90 minutes (eq. 4-31).



(4-31)

22

49

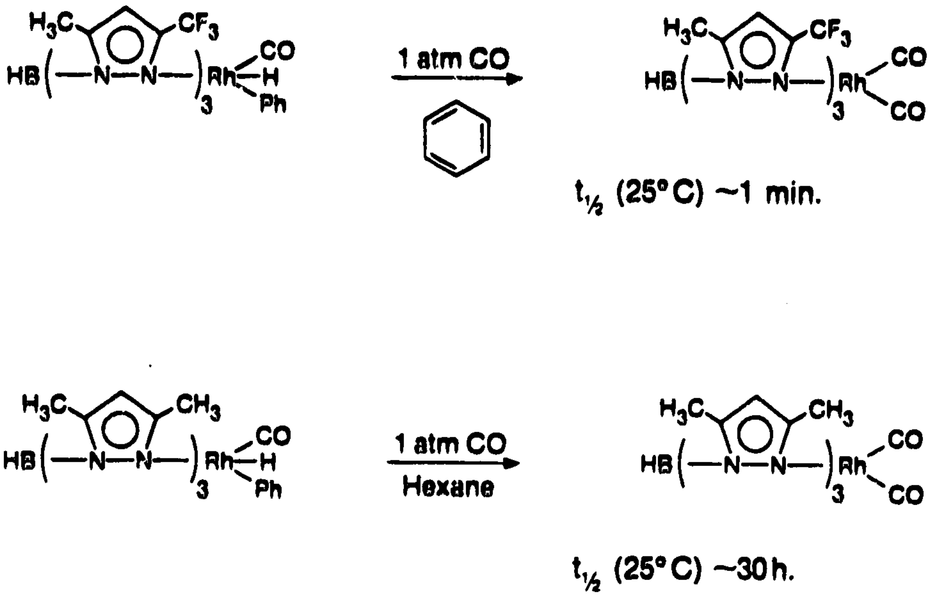
The limiting factor in the rate of the reaction is thought to be the lack of solubility of Me_3NO in benzene. An ^1H NMR experiment in C_6D_6 showed a 93% yield of 49. The spectrum also showed one equivalent of free NMe_3 present. If this solution is left overnight, the phenyl hydride is converted into $HB(3-CF_3-5-MePz)_3Rh(CO)(NMe_3)$ **44**. This is another route for the preparation of **44**. Mechanistically, it is thought that the Me_3NO removes the CO, creating a reactive intermediate which reacts with benzene, perhaps initially via an η^2 arene complex. In terms of equilibria, complex **49** must be the kinetic product in this reaction, and NMe_3 displaces benzene to give the thermodynamic product **44**, despite the huge excess of benzene.

Reactions of $HB(3-CF_3-5-MePz)_3Rh(CO)(H)(Ph)$ (49)

Reaction with CO

The reaction of complex **49** with CO in benzene is instantaneous, resulting in complete conversion to the dicarbonyl **22** in less than five minutes. This reaction could either proceed via benzene dissociation, as postulated for the toluene-d_8 exchange or by an associative reaction with CO. Based on the rate of toluene exchange at 293K = 20°C, $t_{1/2}$ = $0.693/3.52 \times 10^{-3}$ sec^{-2} = 1.98×10^{2} seconds or 3.30 minutes. This value is not inconsistent with benzene dissociation, followed by reaction with CO.

The rate of this CO reaction is in contrast to the same reaction found by Ghosh in the Pz* system (eq. 4-32).[1a]

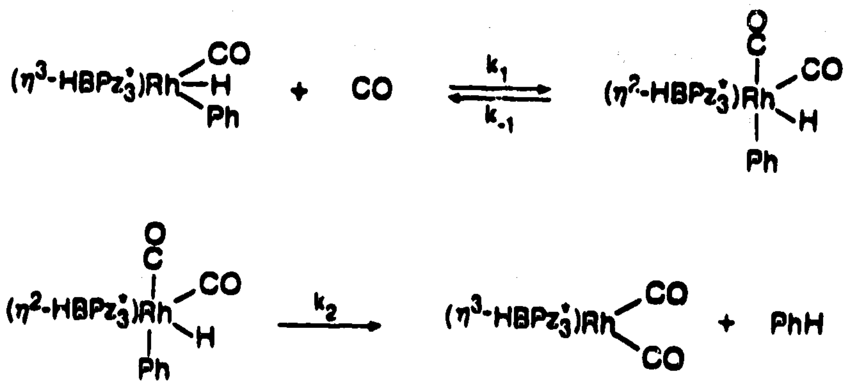


$t_{1/2}$ (25°C) ~1 min.

(4-32)

$t_{1/2}$ (25°C) ~30h.

In the latter system, a dissociative mechanism which accounts for the kinetics of C_6D_6 exchange is incompatible with the rate of CO reaction. Also, when four atmospheres of CO pressure were used, the reaction rate was faster, suggesting an associative mechanism. The following scheme was proposed (eq. 4-33).[1a]

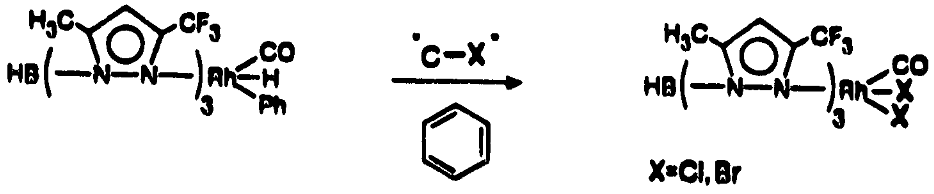


(4-33)

As pointed out by Ghosh, the rate is CO pressure dependent if k_1 is the rate determining step.[1a] Unfortunately, such a comparison is difficult here as the rate of reaction of **49** with CO is so fast, such that the pressure dependent rate information cannot be obtained. However, the same above proposed mechanism (eq. 4-33) is not incompatible for the reaction of **49** with CO. Given the fact that **22** is a mixture of η^2 and η^3 forms, the third pyrazole is less tightly bound than in $(HBPz*_3)Rh(CO)_2$, so that the weaker rhodium-nitrogen bond may be more easily broken in **49**, which would increase k_1.

Functionalization

The conversion of an aryl or alkyl hydride to the more stable chloride or bromide is a common derivatization method in C-H activation studies. For example, $(HBPz*_3)Rh(CO)(H)(Ph)$ reacts with CCl_4 to give $(HBPz*_3)Rh(CO)(Cl)(Ph)$. If the reaction is left past completion, another product forms, thought to be the dichloride $(HBPz*_3)Rh(CO)(Cl)(Cl)$, although it is too unstable to isolate.[1a] The reaction of **49** in benzene with a variety of reagents (CCl_4, CCl_3H, N-chlorosuccinimide (NCS), CBr_3H, CCl_3Br and N-bromosuccinimide (NBS)) all resulted in conversion to what is thought to be the dihalide complex $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(X)(X)$ (X = Cl, Br), which is not stable in solution (eq. 4-34).



(4-34)

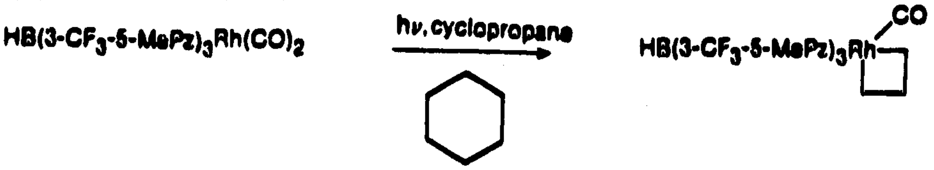
49 "C-X" = CCl_4, CCl_3H, NCS, CBr_3H, CCl_3Br, NBS

A small amount of the desired $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(X)(Ph)$ (X = Cl, Br) appears to form, but reacts further to give the dihalide.

This indicates a more reactive rhodium-phenyl bond than in the Pz* analog. There was also no reaction between **49** and excess diazomethane in benzene. The analogous reaction in the Pz* system gave the methyl-phenyl complex $(HBPz^*{}_3)Rh(CO)(Me)(Ph)$.[1a]

Reaction with C_2H_4 and C_3H_6

A benzene solution of **49** reacts slowly with excess ethylene or cyclopropane in about an hour giving **24** or the new complex $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3\overline{Rh(CO)(CH_2CH_2CH}{}_2)$ (**50**) respectively. Complex **50** can be more easily prepared by irradiating a cyclohexane solution of the dicarbonyl **22** with a cyclopropane purge for 20 minutes (eq. 4-35).

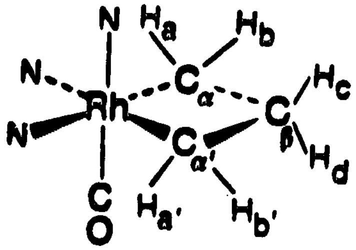


(4-35)

22 50

There is no evidence under the experimental conditions for a cyclopropyl hydride intermediate, although this is a plausible intermediate based on related systems.[24]

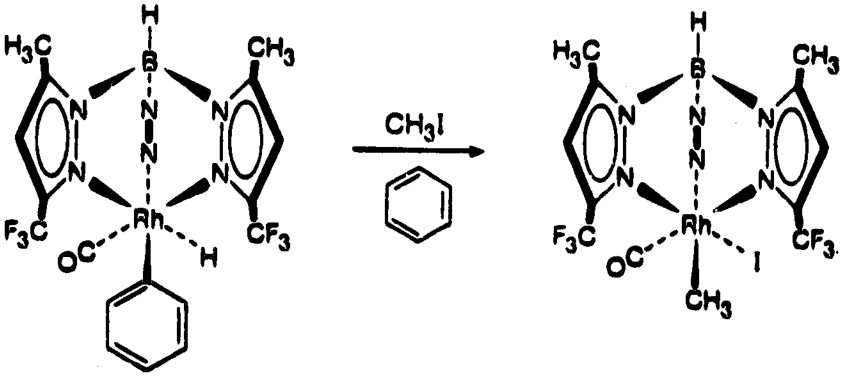
For complex **50**, there is an IR ν_{CO} band in hexane at 2056 cm^{-1} and the ^{1}H and ^{19}F NMR spectra show the expected 2:1 ratio of pyrazole groups based on the symmetry of the Rh(III) octahedral complex. The ring protons were assigned based on known analogs.[1a,24]



50 (atom labelling for NMR)

Reaction with Methyl Iodide

The oxidative addition of methyl iodide to (HBPz*$_3$)Rh(CO)$_2$ occurs in CH$_2$Cl$_2$, giving (HBPz*$_3$)Rh(CO)(I)(Me).[1a] The analogous reaction of dicarbonyl **22** with MeI in CH$_2$Cl$_2$ does not occur. It is thought the rhodium center is not nucleophilic enough to attack. However, the desired complex can be prepared by the addition of excess MeI to a benzene solution of **49**, giving HB(3-CF_3-5-MePz)$_3$Rh(CO)(I)(Me) (**51**) (eq. 4-36).



49 **51**

(4-36)

The reaction is complete in three hours. The complex has an IR ν_{CO} band in hexane at 2097 cm^{-1}. The ^1H NMR spectrum demonstrated the Rh(III) octahedral geometry, with the rhodium bound methyl group appearing as a multiplet at δ 2.08. The ^{13}C NMR spectrum shows the Rh-CH_3 at δ -1.74 (d, $^1J_{Rh-C}$ = 15 Hz), and the ^{19}F NMR spectrum shows three CF_3 groups.

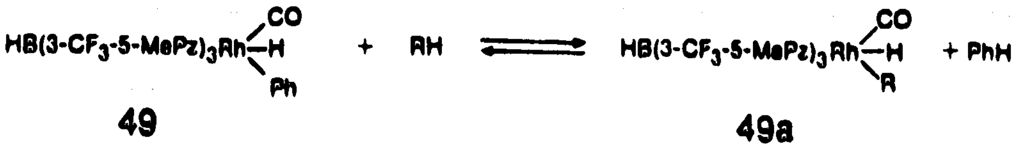
Activation of Aliphatic C-H Bonds

The activation of benzene with the dicarbonyl **22** lead to a stable Rh(III) phenyl hydride **49**. When a cyclohexane solution of the dicarbonyl **22** is irradiated, a very slow decomposition appears to occur, with no new product bands, only a precipitate forming. With the ethylene complex **24** or the COE complex **25**, a faster reaction occurred in cyclohexane, but no stable product was detected. The fact that the starting material disappears indicates a reaction, but perhaps the product is unstable at room temperature.

This was confirmed by some low temperature photolyses. Photolysis of **22** or **24** in hexane at room temperature leads to no detectable products, but the starting materials are consumed. However, when the photolysis of the more soluble COE complex $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(COE)$ **25** is performed at -30°C for 20 minutes, conversion is observed with the IR spectrum showing the product IR ν_{CO} band at 2067 cm^{-1}. In the presence of free COE in solution, **25** reappears in the IR spectrum as the solution warms up in the IR cell. However, the complex is stable at -30°C for several hours. Attempts to convert the product into a stable halo derivative also resulted in rapid formation of dihalide, as observed with the more stable phenyl hydride **49**.

The product has the same IR band position as one that is present in the IR spectrum of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(Ph)$ **49** in hexane. On this basis, the product is assigned as $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(hexyl)$ **49a**, which is apparently unstable at room temperature. Also, it was previously mentioned that the IR spectrum of the phenyl hydride in cyclohexane showed no evidence for the cyclohexyl hydride. This is consistent with Ghosh's observation that a Rh-cyclohexyl bond is weaker than a Rh-(1-hexyl) bond (primary alkyl).

The presence of the hexyl hydride $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(hexyl)$ **49a** suggests a thermal equilibrium between **49** and **49a** at room temperature (eq. 4-37).



(4-37)

$$K_{eq} = \frac{[PhH]}{[RH]} \cdot \frac{[49a]}{[49]} \qquad RH = \text{hexane}$$

From the IR spectrum of the phenyl hydride 49 in hexane, the ratio of absorbances of the 2067 and 2084 cm^{-1} band was 0.28. This would represent the molar ratio if the extinction coefficients of 49 and 49a were the same. The IR spectrum was obtained with approximately 20 mg 49 in 10 mL hexane. Accounting for 49 containing a mole of benzene solvate, [PhH] = 5.4 x 10^{-3} M, [Hexane] = 7.66 M, and thus $K_{eq} \cong 2 \times 10^{-4}$. This still indicates a high equilibrium selectivity favouring the rhodium phenyl bond over the rhodium hexyl bond in the presence of a large excess of hexane. However, the presence of hexyl hydride 49a suggests that the difference in energy of a rhodium phenyl and a rhodium hexyl bond is less here than in the Pz* system, where no hexyl hydride is observed.[1a]

Comparison of the IR band position of 49a with the Pz* analog confirms the assignment of the former species. Table 4.III lists the IR ν_{CO} bands for several of the Rh(III) complexes which are analogs of the Pz* system. There is a consistent 32-37 cm^{-1} difference between analogous complexes.

The above system appears to be very similar to that of Jones,[25] where the aryl hydride products are stable at room temperature, but the corresponding alkyl hydrides were stable only below -30°C. However, the

Table 4.III Comparison of ν_{CO} Bands of Rh(III) Complexes with Pz* Analogs

Compound		ν_{CO} (n-hexane) cm^{-1} This Work	Pz* Analog	Difference
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(H)$	**(45)**	2077	2041[a]	36
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(SiMe_3)$	**(47)**	2055	2023[b]	32
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(Ph)$	**(49)**	2083	2049[a]	34
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(hexyl)$	**(49a)**	2067	2030[a]	37
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3\overline{Rh(CO)(CH_2CH_2CH_2})$	**(50)**	2056	2024[a]	32
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(Me)(I)$	**(51)**	2097	2064[a]	33

a Reference 1a

b Reference 3

alkyl hydrides are much less stable than the Pz* analogs. This could in part be due to the electron-poor ligand in **22**, which would weaken the Rh–C bond sufficiently such that reductive elimination occurs above −30°C.

Section 6

EXPERIMENTAL

$[(CO)_2RhCl]_2$ was prepared using the standard literature procedure.[26] PMe_3, PPh_3 and $HSiCl_3$ were used as received from Strem Chemical Company. 1,5-hexadiene was obtained from Aldrich Chemical Co. $HSiMe_3$ was purchased from Petrarch Systems Inc. 2-butyne and hexafluoro-2-butyne were used as received from Columbia Organics Chemicals Co. and PCR Chemicals respectively. Anhydrous Me_3NO was dried from Aldrich $Me_3NO{\cdot}2H_2O$ by azeotropic distillation of water from toluene, followed by vacuum sublimation. $[(CO)(PMe_3)RhCl]_2$ was prepared according to Goggin and coworkers.[4] $ClRh(CO)(PMe_3)_2$ was prepared according to Poilblanc et al.[5]

Reaction of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2$ (22) with PMe_3

A sample of 128.0 mg (0.207 mmol) of 22 was taken up in 25 mL hexane. A solution of 21 µL PMe_3 (0.207 mmol) in 5 mL hexane was added dropwise over 1 h. After 1 mL of solution was added, IR showed the appearance of 2 ν_{CO} bands at 1996 cm^{-1} (31) and 1978 cm^{-1} (32). Once the addition was finished, IR still showed the presence of 22, along with approximately 1:1 of the two products. Dropwise addition of another equiv of PMe_3 gave the one band at 1978 cm^{-1}. After the solvent was removed, a light yellow solid remained 97.0 mg (0.131 mmol, 63% yield) of what was identified to be $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PMe_3)_2$ (32), mp 149-151°C.

Characterization: IR (n-hexane) 1978 cm^{-1} (ν_{CO}). MS (150°C, 16 eV), M^+-CO (714, 90%), M^+-PMe$_3$ (52%), M^+-CO-PMe$_3$ (100%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, ambient) δ 6.36-6.20 (br, 3H), 1.90 (br, 9H) 1.20 (t, 18H, $^2J_{P-H}$ = 3.8 Hz). ^{1}H NMR (-60°C) δ 6.42 (s, 1H), 6.20 (s, 2H), 1.84 (s, 3H), 1.76 (s, 6H), 1.13 (br, 18H). ^{19}F NMR (CD$_2$Cl$_2$, ambient) δ -60.40 (s). ^{31}P NMR (CD$_2$Cl$_2$, ambient) δ -9.10 (d, $^1J_{Rh-P}$ = 116 Hz). Anal. Calcd for $C_{22}H_{31}BN_6OF_9P_2Rh$: C, 35.60; H, 4.21; N, 11.32. Found: C, 36.34; H, 4.42; N, 11.20.

Alternate Preparation of HB(3-CF$_3$-5-MePz)$_3$Rh(CO)(PMe$_3$)$_2$ (32)

To a solution of ClRh(CO)(PMe$_3$)$_2$ (41.0 mg, 0.129 mmol) in 3 mL CH$_2$Cl$_2$ was added 65.0 mg (0.130 mmol) of 21. After stirring for 1 h, the solution was chromatographed on neutral alumina (12 x 2.5 cm) with CH$_2$Cl$_2$ eluent, giving a yellow oil after the solvent was removed. It was taken up in hexane and cooled to -30°C, giving a yellow crystalline solid (31.3 mg, 33% yield).

Preparation of HB(3-CF$_3$-5-MePz)$_3$Rh(CO)(PMe$_3$) (31)

To a solution of [(CO)(PMe$_3$)RhCl]$_2$ (149.0 mg, 0.307 mmol) in 10 mL toluene was added 306 mg (0.614 mmol) 21 and the reaction stirred for 1 h. The solution was filtered through Celite and the toluene was removed under reduced pressure. The solid was chromatographed on neutral alumina (12 x 2.5 cm) with CH$_2$Cl$_2$ eluent, giving a yellow solid after solvent was removed in vacuo. This was taken up in 100 mL hot hexane and cooled to -30°C, yielding yellow crystals (244.7 mg, 60% yield), mp 179-181°C.

Characterization: IR (n-hexane) 1996 cm^{-1} (ν_{CO}). MS (150°C, 70 eV) M$^+$ (666, 37%), M$^+$-CO (100%), M$^+$-PMe$_3$ (2%), M$^+$-CO-PMe$_3$ (10%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, ambient) δ 6.46 (s, 1H), 6.37 (s, 2H), 2.46 (s, 3H), 2.12 (s, 6H), 1.17 (dd, 9H, $^2J_{P-H}$ = 10.4 Hz, $^3J_{Rh-H}$ = 1.3 Hz). ^{19}F NMR (CD$_2$Cl$_2$, ambient) δ -60.43 (d, 6F, $^4J_{Rh-F}$ = 2 Hz), -60.69 (s, 3F). ^{31}P NMR (CD$_2$Cl$_2$, ambient) δ 3.47 (d, $^1J_{Rh-P}$ = 152 Hz). Anal. Calcd for $C_{19}H_{22}BN_6OF_9PRh$: C, 34.26; H, 3.33; N, 12.62. Found: C, 34.37; H, 3.43; N, 12.75.

Preparation of $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)$ (33)

To a solution of $[(CO)_2RhCl]_2$ (61.3 mg, 0.158 mmol) in 10 mL hexane was added dropwise 32 μL PMe$_3$ (0.315 mmol) in 5 mL hexane, giving an orange precipitate of $[(CO)(PMe_3)RhCl]_2$. This was concentrated to 3 mL, and cooled to -30°C. Solvent was pipetted off, giving approximately 0.158 mmol dimer. This solid was taken up in 10 mL CH$_2$Cl$_2$, 110.6 mg (0.16 mmol) of **19a** was added and the reaction stirred for 0.5 h. The solution was filtered through Celite and the solvent pumped off. The resulting solid was chromatographed on neutral alumina with CH$_2$Cl$_2$ eluent, giving a yellow solid. This was taken up in CH$_2$Cl$_2$-hexane and cooled to -30°C, affording yellow crystals (107.4 mg, 66% yield), mp 179-181°C.

Characterization: IR (n-hexane) 1996 cm^{-1} (ν_{CO}). MS (130°C, 70 eV) M$^+$ (518, 93%), M-CO$^+$ (100%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, ambient) δ 6.24 (s, 1H), 6.23 (s, 1H), 5.33 (s, 1H, 1/2CH$_2$Cl$_2$), 2.33 (s, 3H), 2.32 (s, 3H), 1.44 (dd, 9H, $^2J_{P-H}$ = 10.3 Hz, $^3J_{Rh-H}$ = 1.4 Hz). ^{19}F NMR (CD$_2$Cl$_2$, ambient) δ -59.35 (d, 3F, $^5J_{F-P}$ = 4.6 Hz), -60.40 (s, 3F). ^{31}P NMR

(CD_2Cl_2, ambient) δ 6.78 (d of q, $^1J_{Rh-P}$ = 151 Hz, $^5J_{F-P}$ = 4.6 Hz). Anal. Calcd for $C_{14}H_{19}BN_4OF_6PRh \cdot 1/2CH_2Cl_2$: C, 31.07; H, 3.60; N, 10.00. Found: C, 31.42; H, 3.68; N, 10.11.

Preparation of $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)_2$ (34)

A sample of 101.2 mg (0.215 mmol) of **20a** was taken up in 25 mL hexane. A solution of 44 μL PMe_3 (0.430 mmol) in 5 mL hexane was added dropwise over 1 h. After half of the solution was added, IR showed the appearance of 2 ν_{CO} bands at 1996 cm^{-1} **33** and 1972 cm^{-1} **34** with about half of the starting material remaining. Once the addition was complete, the IR showed one band at 1972 cm^{-1}. After the solvent was removed, a light yellow solid remained (128.1 mg, 100% yield), mp 76-82°C.

<u>Characterization</u>: IR (n-hexane) 1972 cm^{-1} (ν_{CO}). MS (150°C, 70 eV) M^+-CO (566, 75%), M^+-PMe_3 (100%), M^+-CO-PMe_3 (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.28 (s, 2H), 2.20 (s, 9H), 1.30 (t, 18H, $^2J_{P-H}$ = 3.8 Hz). ^1H NMR (-90°C) δ 6.36 (br, 1H), 6.13 (br, 1H), 2.30 (br, 3H), 1.91 (br, 3H), 1.14 (s, 18H). ^{31}P NMR (CD_2Cl_2, ambient) δ -7.71 (d, $^1J_{Rh-P}$ = 116 Hz). Anal. Calcd for $C_{17}H_{28}BN_4OF_6P_2Rh$: C, 34.37; H, 4.75; N, 9.43. Found: C, 34.51; H, 4.79; N, 9.44.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PPh_3)$ (35)

To a solution of **22** (78.7 mg, 0.127 mmol) in 10 mL hexane was slowly added 33.3 mg (0.127 mmol) PPh_3. Solvent was removed in vacuo, giving a yellow powder (100.9 mg, 93% yield), mp 183-185°C.

Characterization: IR (hexane) 2004 cm^{-1} (ν_{CO}). MS (150°C, 70 eV) M$^+$ (852, 100%), M$^+$-CO (44%), M$^+$-PPh$_3$ (1%), M$^+$-CO-PPh$_3$ (10%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, ambient) δ 7.38-7.29 (m, 15H), 6.53 (br, 1H), 6.03 (br, 2H), 2.44 (br, 3H), 2.17 (s, 6H). ^{1}H NMR (-80°C) δ 7.90 (m, 2H), 7.51 (m, 3H), 7.20 (m, 4H), 7.00 (m, 5H), 6.53 (s, 1H), 6.06 (s, 1H), 5.98 (s, 1H), 2.44 (s, 3H), 2.42 (s, 3H), 1.76 (s, 3H). ^{31}P NMR (CD$_2$Cl$_2$, ambient) δ 42.57 (d, $^1J_{Rh-P}$ = 166 Hz). Anal. Calcd for $C_{34}H_{28}BN_6OF_9PRh$: C, 47.91; H, 3.31; N, 9.86. Found: C, 47.92; H, 3.23; N, 9.75.

Preparation of HB(3-CF$_3$-5-MePz)$_3$Rh(CO)(PCy$_3$) (36)

To a solution of 22 (65.1 mg, 0.105 mmol) in 10 mL hexane was slowly added 29.3 mg (0.105 mmol) PCy$_3$. Solvent was removed in vacuo, giving a yellow oil, which on continuous pumping in vacuo afforded a yellow powder (84.0 mg, 92% yield), mp 171-173°C.

Characterization: IR (hexane) 1989 cm^{-1} (ν_{CO}). MS (150°C, 70 eV) M$^+$ (870, 78%), M$^+$-CO (62%), M$^+$-CO-3-CF$_3$-5-MePz (100%), M$^+$-PCy$_3$ (5%), M$^+$-CO-PCy$_3$ (17%). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, ambient) δ 6.49 (s, 1H), 6.39 (br, 1H), 6.27 (br, 1H), 2.55 (br, 3H), 2.39 (s, 3H), 1.70 (br, 3H), 1.90-0.8 (m, 33H). ^{1}H NMR (-10°C) δ 6.46 (s, 1H), 6.38 (s, 1H), 6.24 (s, 1H), 2.48 (s, 3H), 2.34 (s, 3H), 1.70 (s, 3H), 1.90-0.8 (m, 33H). ^{19}F NMR (CD$_2$Cl$_2$, ambient) δ -58.00 (br, 3F), -60.14 (s, 3F), -62.09 (br, 3F). ^{31}P NMR (CD$_2$Cl$_2$, ambient) δ 49.46 (d, $^1J_{Rh-P}$ = 155 Hz). Anal. Calcd for $C_{34}H_{46}BN_6OF_9PRh$: C, 46.91; H, 5.33; N, 9.65. Found: C, 47.36; H, 5.54; N, 9.13.

Preparation of $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PPh_3)$ (37)

To a solution of **20a** (94.3 mg, 0.200 mmol) in 10 mL hexane was slowly added 52.6 mg (0.200 mmol) PPh_3. After stirring for 15 min, solvent was removed, and the crude yellow solid was chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent. Recrystallization from 5 mL hexane at -30° gave orange crystals (80.6 mg, 57% yield), mp 169-171°C.

<u>Characterization:</u> IR (hexane) 2005 cm^{-1} (ν_{CO}). MS (150°C, 16 eV) M^+ (704, 100%), M^+-CO (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 7.66-7.50 (m, 6H), 7.46-7.26 (m, 9H), 6.29 (s, 1H), 5.84 (s, 1H), 2.35 (s, 3H), 2.27 (s, 3H). ^{19}F NMR (CD_2Cl_2, ambient) δ -60.03 (d, 3F, $^5J_{P-F}$ = 5 Hz), -60.23 (s, 3F). ^{31}P NMR (CD_2Cl_2, ambient) 44.93 (d of q, $^1J_{Rh-P}$ = 165 Hz, $^1J_{F-P}$ = 5 Hz). Anal. Calcd for $C_{29}H_{25}BN_4OF_6PRh$: C, 49.46; H, 3.58; N, 7.96. Found: C, 49.63; H, 3.71; N, 7.83.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PMe_3)(PPh_3)$ (38)

To a solution of 40.0 mg (0.060 mmol) **31** in 10 mL hexane was added 15.6 mg (0.060 mmol) PPh_3. After 1 h the solvent was removed, leaving a light yellow powder (40.7 mg, 73% yield), mp 139-141°C.

<u>Characterization:</u> IR (n-hexane) 1983 cm^{-1} (ν_{CO}). MS (140°C, 16 eV) M^+-CO (900, 26%), M^+-PMe_3 (4%), M^+-PPh_3 (63%), M^+-CO-PPh_3 (82%), PPh_3^+ (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 7.35-7.27 (m, 15H), 6.17 (s, 1H), 6.09 (s, 1H), 5.77 (s, 1H), 1.90 (s, 3H), 1.73 (s, 3H), 1.69 (s, 3H), 1.38 (ddd, 9H, $^2J_{P-H}$ = 9.9 Hz, $^4J_{P-H}$ = 1.8 Hz, $^3J_{Rh-H}$ = 1.3 Hz). ^{19}F NMR (CD_2Cl_2, ambient) δ -59.93 (s, 3F), -61.72 (s, 3F), -61.88

(s, 3F). ^{31}P NMR (CD_2Cl_2, ambient) δ 27.16 (dd, PPh_3, $^1J_{Rh-P}$ = 122 Hz, $^2J_{P-P}$ = 316 Hz), -5.74 (dd, PMe_3, $^1J_{Rh-P}$ = 123 Hz, $^2J_{P-P}$ = 316 Hz). Anal. Calcd for $C_{37}H_{37}BN_6OF_9P_2Rh$: C, 47.87; H, 4.02; N, 9,05. Found: C, 48.00; H, 4.00; N, 9.35.

Preparation of $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(PMe_3)(PPh_3)$ (39)

To a solution of 42.8 mg (0.083 mmol) **33** in 10 mL hexane was added 21.7 mg (0.083 mmol) PPh_3. After 30 min the solvent was removed, leaving a light yellow powder (62.8 mg). IR (n-hexane) 1983 cm^{-1} (ν_{CO}).

Reaction of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(allyl)_2$ (30) with CO in CD_2Cl_2

A sample of 24.0 mg (0.037 mmol) **30** was taken up in 0.4 mL CD_2Cl_2. The sample was pressurized with 1 atm CO for 16 h, whereupon the initial pale yellow solution had turned a lemon yellow. ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.44 (s, 3H) and 2.39 (s, 9H) for **22**; 5.82 (m, 2H), 5.06, 4.98, 4.94 (m, 4H), 2.15 (m, 4H). The three sets of multiplets were confirmed to be 1,5-hexadiene, as the spectrum was identical to that of an authentic sample (Aldrich).

At earlier reaction times (4 or 8 h), an intermediate was detected in the ^1H NMR spectrum in addition to resonances of **30**, **22** and 1,5-hexadiene. ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.58 (s, 2H), 6.22 (s, 1H), 2.66 (s, 6H), 2.48 (s, 3H), 4.70 (m, 2H), 4.20 (m, 4H), 3.26 (m, 4H).

On a IR scale reaction, about 5 mg of **30** was taken up in 5 ml CH_2Cl_2. One atm of CO was bubbled through, with the immediate appearance of a single ν_{CO} at 2070 cm^{-1}. At longer times, this band disappeared and bands due to the dicarbonyl appeared. After 18 h, IR (CH_2Cl_2) 2101 (s), 2087 (s), 2036 (s), 2020 (s) cm^{-1} (ν_{CO}), corresponding to authentic **22**.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(CH_3C{\equiv}CCH_3)$ (40)

To a solution of **25** (59.0 mg, 0.084 mmol) in 15 mL hexane was added 3 mL (excess) 2-butyne. After 40 min, the reaction was complete, so solvent was removed in vacuo, giving a white-yellow solid and an orange film. This was chromatographed on neutral alumina with CH_2Cl_2 eluent, and after the solvent was removed in vacuo, the product crystallized as fine light yellow needles from a concentrated hexane solution at -30°C (43.0 mg, 80% yield), mp 149-151°C.

Characterization: IR (n-hexane) 2040 (s), 2022 (w) cm^{-1} (ν_{CO}). MS (150°C, 16 eV) M^+ (644, 23%), M^+-CO (12%), M^+-$CH_3C{\equiv}CCH_3$ (100%), M^+-CO-$CH_3C{\equiv}CCH_3$ (45%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.47 (br, 2H), 6.31 (br, 1H), 2.47, 2.40 (br, 9H total), 2.05 (s, 6H). ^1H NMR (-95°C) 6.46 (s, 2H), 6.29 (s, 1H), 2.42 (s, 6H), 2.33 (s, 3H), 1.96 (s, 6H). ^{19}F NMR (CD_2Cl_2, ambient) δ -58.22 (br, 3F), -60.27 (br, 6F). Anal. Calcd for $C_{20}H_{19}BN_6OF_9Rh$: C, 37.29; H, 2.97; N, 13.05. Found: C, 37.42; H, 3.06; N, 13.03.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(CF_3C{\equiv}CCF_3)$ (41)

A sample of **25** (90.0 mg, 0.129 mmol) was taken up in 10 mL hexane. Hexafluoro-2-butyne was bubbled through, resulting in an almost colorless solution after 15 min. Solvent was removed in vacuo, and the residue was chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2

eluent. The product crystallized as fine colorless needles from a concentrated hexane solution at -30°C (43.0 mg, 80% yield), mp 198-200°C.

<u>Characterization</u>: IR (n-hexane) 2086 (s) (ν_{CO}), 1897 (w) ($\nu_{C\equiv C}$) cm^{-1}. MS (150°C, 16 eV) M^+ (752, 0.1%), $M\text{-}F^+$ (17%), $M\text{-}CO^+$ (4%), $M\text{-}CO\text{-}F^+$ (23%), $M^+\text{-}CF_3C\equiv CCF_3$ (90%), $M^+\text{-}CO\text{-}CF_3C\equiv CCF_3$ (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.58 (s, 2H), 6.41 (s, 1H), 2.54 (s, 6H), 2.45 (s, 3H). ^{19}F NMR (CD_2Cl_2, ambient) δ -55.91 (m, 6F, HFB), -57.69 (septet, 3F, J_{F-F} = 6.1 Hz), -60.28 (q, 6F, J_{F-F} = 8.5 Hz). Anal. Calcd for $C_{20}H_{13}BN_6F_{15}Rh$: C, 31.94; H, 1.74; N, 11.17. Found: C, 32.23; H, 1.79; N, 11.06.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(CH_3CN)$ (42)

A sample of 226.6 mg (0.367 mmol) **22** was taken up in 20 mL CH_3CN. To this yellow solution was slowly added 27.5 mg (0.367 mmol) Me_3NO. After 10 min, the solvent was removed in vacuo and the residue was chromatographed on neutral alumina with CH_2Cl_2 eluent. Crystallization from a CH_2Cl_2-hexane solution at -30°C gave 150.9 mg (65% yield) of a yellow powder, mp 155-157°C.

<u>Characterization</u>: IR (n-hexane) 2014 cm^{-1} (ν_{CO}), (CH_2Cl_2) 2338 (w) (ν_{CN}), 2004 (s) cm^{-1} (ν_{CO}), (CH_3CN) 2339 (w) (ν_{CN}), 2005 (s) cm^{-1} (ν_{CO}). MS (165°C, 16 eV) M^+ (631, 27%), $M^+\text{-}CO$ (100%), $M^+\text{-}CH_3CN$ (8%), $M^+\text{-}CO\text{-}CH_3CN$ (83%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.40 (s, 3H), 2.51 (s, 3H), 2.15 (s, 9H). ^1H NMR (-90°C) δ 6.40 (s, 2H), 6.38 (s, 1H), 2.44 (s, 3H), 2.15 (s, 3H), 2.07 (s, 6H). ^{19}F NMR (CD_2Cl_2,

ambient) δ -60.47 (br, 3F), -60.55 (br, 6F). Anal. Calcd for $C_{18}H_{16}BN_7OF_9Rh$: C, 34.26; H, 2.56; N, 15.54. Found: C, 34.39; H, 2.69; N, 15.08.

Reaction of (22) with Me_3NO in CH_2Cl_2

A sample of 86.9 mg (0.141 mmol) **22** was taken up in 10 mL CH_2Cl_2. 11 mg (0.146 mmol) Me_3NO was added and two new products appear in the IR spectrum (ν_{CO} 1987, 1982 cm^{-1}) but starting material still remains. Solvent was removed and the residues were taken up in 0.4 mL of CD_2Cl_2. The ^1H NMR spectrum showed three species in different amounts: 45% starting material **22**, 39% of what was identified to be $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(NMe_3)$ **44** and 16% of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(ONMe_3)$ **43**. Individual syntheses of the latter two complexes are detailed below.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(ONMe_3)$ (43)

To a solution of **22** (76.8 mg, 0.124 mmol) in 10 mL CH_2Cl_2 was added 18.7 mg (0.248 mmol) Me_3NO with an immediate reaction. Solvent was removed in vacuo, leaving an analytically pure yellow solid (82.9 mg, 100% yield), mp 144-146°C.

Characterization: IR (hexane) 1982 cm^{-1} (ν_{CO}). MS (150°C, 16 eV) M^+ (665, 100%), M^+-CO (41%), M^+-2Me (48%), M^+-3Me (86%), M^+-$ONMe_3$ (19%), M^+-CO-$ONMe_3$ (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.42 (br, 1H), 6.38 (br, 2H), 2.72 (s, 9H), 2.44 (s, 3H), 2.12 (s, 6H). ^1H NMR (-100°C) δ 6.38 (s, 3H), 2.63 (s, 9H), 2.45 (s, 3H), 2.36 (s, 3H), 1.58 (s, 3H). Anal. Calcd for $C_{19}H_{22}BN_7O_2F_9Rh$: C, 34.31; H, 3.33; N, 14.74. Found: C, 33.52; H, 3.33; N, 14.79.

^{1}H NMR Experiment of (43)

A sample of 22.0 mg (0.036 mmol) 22 was taken up in 0.4 mL CD_2Cl_2. 5.4 mg (0.072 mmol) Me_3NO was added with resulting vigorous gas evolution. ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.42 (br, 1H), 6.38 (br, 2H), 2.72 (s, 9H), 2.44 (s, 3H), 2.21 (s, 9H, NMe_3), 2.12 (s, 6H).

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(NMe_3)$ (44)

A sample of 90.0 mg (0.146 mmol) 22 was dissolved in 10 mL CH_2Cl_2 saturated with NMe_3. 11 mg (0.146 mmol) Me_3NO was added and the solution stirred for 90 min. Solvent was removed in vacuo, and the residues were chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent. The resulting yellow oil was taken up in 10 mL hexane and the solution cooled to -30°C, giving yellow crystals (37.0 mg, 39% yield), mp 147-149°C.

Characterization: IR (hexane) 1987 cm^{-1} (ν_{CO}). MS (160°C, 16 eV) M^+ (649, 58%), M^+-CO (92%), M^+-NMe_3 (99%), M^+-CO)-NMe_3 (100%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.41 (s, 2H), 6.34 (s, 1H), 2.44 (s, 3H), 2.27 (d, 9H, $^3J_{Rh-H}$ = 1.1 Hz), 2.18 (br, 6H). ^{1}H NMR (-60°C) δ 6.43 (s, 1H), 6.38 (s, 1H), 6.32 (s, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 2.19 (s, 9H), 1.76 (s, 3H). Anal. Calcd for $C_{19}H_{22}BN_7OF_9Rh$: C, 35.16; H, 3.42; N, 15.10. Found: C, 36.13; H, 3.41; N, 15.13.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(H)$ (45)

A sample of 205.8 mg (0.333 mmol) 22 was taken up in 50 mL cyclohexane. The solution was purged with hydrogen gas for 5 min, then irradiated for 20 min with purge. Solvent was removed in vacuo and the crude product was chromatographed on neutral alumina (12 x 2.5 cm) with 3:1 hexane:CH_2Cl_2 as the eluent. Crystallization from CH_2Cl_2-hexane layering at -30°C gave colorless crystals (157.4 mg, 80% yield), mp 233-235°C.

Characterization: IR (cyclohexane) 2110 (vw) (ν_{Rh-H}) 2077 (s) cm^{-1} (ν_{CO}). MS (180°C, 70 eV) M^+-2H (590, 53%), M^+-CO-2H (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.42 (s, 2H), 6.40 (s, 1H), 2.50 (s, 6H), 2.46 (s, 3H), -14.22 (d, 2H, $^1J_{Rh-H}$ = 19 Hz). ^{19}F and $^{19}F\{^1H\}$ NMR (CD_2Cl_2, ambient) δ -60.90 (d, 6F, $^4J_{Rh-F}$ = 1.5 Hz), -61.52 (d, 3F, $^4J_{Rh-F}$ = 3.0 Hz). Anal. Calcd for $C_{16}H_{15}BN_6OF_9Rh$: C, 32.46; H, 2.55; N, 14.19. Found: C, 32.64; H, 2.58; N, 14.05.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(SiCl_3)$ (46)

A sample of 93.7 mg (0.152 mmol) **22** was taken up in 20 mL cyclohexane. The solution was charged with 3 mL Cl_3SiH (excess), then irradiated for 10 min with N_2 purge, giving a colorless cloudy solution. Solvent was removed in vacuo, giving a light yellow solid. This was extracted with 3 x 25 mL hexane (cannular filtration), concentrated to 10 mL and cooled to -30°C, giving a white powder (101.5 mg, 92% yield), mp 131-133°C.

Characterization: IR (cyclohexane) 2160 (vw) (ν_{Rh-H}), 2099 (s) cm^{-1} (ν_{CO}). MS (200°C, 70 eV) $M\text{-}Cl^+$ (690, 1%), M^+-Cl_3SiH (88%), M^+-CO-Cl_3SiH (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.58 (s, 1H), 6.53 (s, 1H), 6.34 (s, 1H), 2.58 (s, 3H), 2.53 (s, 3H), 2.37 (s, 3H), -13.52 (d of q, 1H, $^1J_{Rh-H}$ = 14.9 Hz, $^5J_{F-H}$ = 3.5 Hz). ^{19}F NMR (CD_2Cl_2, ambient) δ -57.30 (d of d, 3F, $^5J_{F-H}$ = 3.5 Hz, $^4J_{Rh-F}$ = 2.0 Hz), -57.44, (s, 3F), -60.84 (s, 3F). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, ambient) δ -57.30 (d, 3F, $^4J_{Rh-F}$ = 2.0 Hz), -57.44 (s, 3F), -60.84 (s, 3F). Anal. Calcd for $C_{16}H_{14}BN_6OF_9SiCl_3Rh$: C, 26.49; H, 1.95; N, 11.58. Found: C, 26.70; H, 2.01; N, 11.71.

Preparation of $HB(3-CF_3-5-MePz)_3Rh(CO)(H)(SiMe_3)$ (47)

A sample of 109.4 mg (0.177 mmol) **22** was taken up in 25 mL cyclohexane. The solution was purged with Me_3SiH for 5 min, then irradiated for 10 min with purge, giving a colorless solution. Solvent was removed in vacuo, giving a tan oil, which was taken up in 5 mL hexane, then quickly removed to give an off-white solid (102.3 mg, 87% yield, mp 233-235°C.

Characterization: IR (cyclohexane) 2155 (vw) (ν_{Rh-H}), 2055 (s) cm^{-1} (ν_{CO}). MS (110°C, 16 eV) M^+ (664, 2%), M^+-Me_3SiH (100%), M^+-CO-Me_3SiH (76%). ^1H NMR (cyclohexane-d_{12}, 200 MHz, ambient) δ 6.30 (s, 3H), 2.43, 2.42 (s, 9H), 0.28 (s, 9H), -15.21 (d, 1H, $^1J_{Rh-H}$ = 20.1 Hz). Anal. Calcd for $C_{19}H_{23}BN_6OF_9SiRh$: C, 34.36; H, 3.49; N, 12.65. Found: C, 34.94; H, 3.55; N, 12.39.

Preparation of $H_2B(3-CF_3-5-MePz)_2Rh(CO)(H)(SiMe_3)$ (48)

A sample of 63.5 mg (0.135 mmol) **20a** was taken up in 25 mL cyclohexane. The solution was purged with Me_3SiH for 5 min, then irradiated for 10 min with purge, giving a colorless solution. Solvent was removed in vacuo, giving an unstable oil.

Characterization: IR (hexane) 2120 (vw) (ν_{Rh-H}), 2050 (s) cm^{-1} (ν_{CO}). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.40 (s, 1H), 6.34 (s, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 0.46 (s, 9H), -13.80 (d, 1H, $^1J_{Rh-H}$ = 26.7 Hz). ^{19}F NMR (CD_2Cl_2, ambient) δ -58.27 (s, 3F), -59.64 (s, 3F).

Preparation of $HB(3-CF_3-5-MePz)_3Rh(CO)(Ph)(H)$ (49)

A sample of 160.7 mg (0.26 mmol) of 24 was taken up in 20 mL benzene. This yellow solution was irradiated for 20 min with N_2 purge, giving a colorless solution. Benzene was removed in vacuo, giving an off-white powder as the benzene solvate (195.8 mg, 100% yield), mp 133-135°C.

Characterization: IR (cyclohexane) 2082 cm^{-1} (ν_{CO}). MS (120°C, 70 eV) $M^+-C_6H_6$ (590, 27%), $M^+-CO-C_6H_6$ (33%), $3-CF_3-5-MePz^+$ (100%). ^1H NMR (CD_2Cl_2, 400 MHz, ambient) δ 7.35 (s, 6H), 6.89 (br, 3H), 6.67 (br, 1H), 6.48 (s, 1H), 6.38 (s, 1H), 6.35 (s, 1H), 6.22 (br, 1H), 2.57 (s, 3H), 2.50 (s, 3H), 2.44 (s, 3H), -13.35 (d, 1H, $^1J_{Rh-H}$ = 21.2 Hz). ^1H NMR (-30°C) δ Phenyl Region: 7.33 (d, 1H, o-Ph), 6.99 (t, 1H, m-Ph), 6.88 (t, 1H, p-Ph), 6.65 (t, 1H, m'-Ph), 6.18 (d, 1H , o'-Ph). ^1H NMR (C_6D_6, 200 MHz, ambient) δ 7.18 (s, 12H), 5.98 (s, 1H), 5.78 (s, 1H), 5.74 (s, 1H), 1.95 (s, 3H), 1.80 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, ambient) δ 187.50 (d, $^1J_{Rh-C}$ = 70 Hz), 147.10, 146.96, 146.81 (s, $C-CH_3$), 145.13, 144.28, 144.10 (q, $C-CF_3$, $^2F_{C-F}$ = 39 Hz), 142.17 (d, $^1J_{Rh-C}$ = 26 Hz), 128.70, 127.10, 123.79 (s, Ph C), 121.20, 121.05, 120.00 (q, CF_3, $^1J_{C-F}$ = 270 Hz), 108.40, 107.45, 106.60 (s, CH), 13.40 (s, $1CH_3$), 13.08 (s,

$2CH_3$). ^{19}F NMR (CD_2Cl_2, -30°C) δ -59.10 (s), -60.24 (t, J = 2 Hz), -60.51 (t, J = 2 Hz). Anal. Calcd for $C_{22}H_{19}BN_6OF_9Rh{\cdot}C_6H_6$: C, 45.07; H, 3.38; N, 11.26. Found: C, 44.47; H, 3.41; N, 11.32.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3\overline{Rh(CO)(CH_2CH_2CH_2})$ (50)

A sample of 117.3 mg (0.190 mmol) **22** was taken up in 30 mL cyclohexane. The solution was purged with cyclopropane gas for 5 min, then irradiated for 20 min with purge. After removing solvent the crude product was chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2. Crystallization from CH_2Cl_2-hexane layering at -30°C gave light yellow crystals (51.6 mg, 43% yield), mp 209-211°C.

Characterization: IR (cyclohexane) 2055 cm^{-1} (ν_{CO}). MS (180°C, 70 eV) M^+-CO (604, 7%), $M^+-C_3H_6$ (15%), $M^+-CO-C_3H_6$ (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.56 (s, 1H), 6.39 (s, 2H), 2.87 (m, 1H, H_d), 2.68 (m, 1H, H_c), 2.48 (br, 9H), 1.90 (m, 2H, H_b), 1.65 (m, 2H, H_a). ^{19}F NMR (CD_2Cl_2, ambient) δ -56.68 (s, 3F), -60.53 (s, 6F). Anal. Calcd for $C_{19}H_{19}BN_6OF_9Rh$: C, 36.10; H, 3.03; N, 13.30. Found: C, 35.97; H, 3.00; N, 13.42.

Preparation of $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(I)(Me)$ (51)

A sample of 136.1 mg (0.220 mmol) **24** was taken up in 20 mL benzene. The solution was purged with nitrogen, then irradiated for 20 min with purge, giving a colorless solution of **49**. To this benzene solution was added 5.0 mL (11.4 g, 80.3 mmol) MeI, and reaction was complete by IR in 3 h, so solvent was removed in vacuo. The resulting orange solid was chromatographed on neutral alumina with CH_2Cl_2

eluent. 57.0 mg (36% yield) of 51 was obtained as red-orange crystals from CH_2Cl_2-hexane layering at -30°C, mp darkens at 180°C, melts at 218-220°C.

Characterization: IR (n-hexane) 2097 cm^{-1} (ν_{CO}). MS (145°C, 16 eV) M^+ (732, 11%), M^+-CH_3 (2%), $M^+-CO-CH_3$ (4%), M^+-I (8%), M^+-MeI (100%), $M^+-MeI-CO$ (68%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.52 (s, 1H), 6.44 (s, 1H), 6.40 (s, 1H), 2.46 (s, 3H), 2.45 (s, 3H), 2.40 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, ambient) δ 180.84 (d, CO, $^1J_{Rh-C}$ = 64 Hz), 148.04, 147.70, 147.01 (s, $C-CH_3$), 146.38, 145.21, 143.94 (q, $C-CF_3$, $^2J_{C-F}$ = 39.2 Hz), 121.35, 120.87, 120.84 (q, CF_3, $^1J_{C-F}$ = 270 Hz), 111.07, 109.67, 108.23 (s, C-H), 13.78 (s, 2C, CH_3), 13.06 (s, 1C, CH_3), -1.74 (d, $Rh-CH_3$, $^1J_{Rh-C}$ = 15 Hz). ^{19}F NMR (CD_2Cl_2, ambient) δ -54.70 (s, 3F), -57.02 (s, 3F), -58.90 (s, 3F). Anal. Calcd for $C_{17}H_{16}BN_6OF_9RhI$: C, 27.90; H, 2.20; N, 11.48. Found: C, 28.07; H, 2.11; N, 11.41.

Reaction of $HB(3-CF_3-5-MePz)_3Rh(CO)_2$ (22) with Me_3NO in C_6D_6

A sample of 22.0 mg (0.034 mmol) 22 was taken up in 0.4 mL C_6D_6 along with 1 µL $Me_3SiOSiMe_3$. The ^1H NMR spectrum was taken for the internal standard calibration. 2.5 mg (0.036 mmol) Me_3NO was added and the tube was sealed in vacuo. After shaking for 90 min, the ^1H NMR spectrum was run. ^1H NMR (C_6D_6, 200 MHz, ambient) δ 6.00 (s, 1H), 5.80 (s, 1H), 5.76 (s, 1H), 2.10 (s, 9H, NMe_3), 1.96 (s, 3H), 1.81 (s, 6H), 0.14 (s, $Me_3SiOSiMe_3$). The conversion was 93%.

IR Reaction

A sample of 90.0 mg (0.146 mmol) of **22** was taken up in 10 mL benzene. To this yellow solution was added 11 mg (0.146 mmol) Me_3NO, and after vigorous stirring for 90 minutes, IR shows quantitative conversion to phenyl hydride **49** (ν_{CO} = 2077 cm^{-1}). If the solution is left overnight, the IR spectrum showed disappearance of **49** and appearance of the NMe_3 complex **44**. It was isolated as detailed for the preparation of **44** by another route and identified by IR spectroscopy (12.0 mg, 13% yield).

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CHAPTER V

ALKYL(PYRAZOLYL)BORATE RHODIUM COMPLEXES

Section 1

INTRODUCTION

The successful use of the complex $(HBPz^*_3)Rh(CO)_2$ by C.K. Ghosh[1] in this research group for C-H bond activation has prompted further research into related systems. In Chapter II of this Thesis the complex $HB(3\text{-}PhPz)_3Rh(CO)_2$ **1** was used for C-H activation studies, but the proximity of the 3-Ph group to the metal center resulted in intramolecular C-H activation, or orthometallation. This problem was circumvented by using the complex $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2$ **22** in Chapters III and IV, but only the benzene C-H activation product was stable at room temperature.

One inherent problem encountered by Ghosh in C-H activation studies was the low solubility of $(HBPz^*_3)Rh(CO)_2$ in saturated hydrocarbons, typically about 1 mg/ml in cyclohexane.[1a] By increasing the size of the aliphatic groups on the pyrazole ring from Me to perhaps Et, i-Pr, i-Bu or t-Bu the solubility of the rhodium complexes in saturated hydrocarbons should increase.

The recent report of Trofimenko's so-called second generation pyrazolylborate ligands of the type $[H_nB(3\text{-}RPz)_{4-n}]^-$ (n = 0, 1, 2 and R = Ph,[2] t-Bu,[2] or i-Pr[3]) facilitated the preparation of complexes of the type $H_nB(3\text{-}RPz)_{4-n}Rh(CO)_2$ (n = 1, 2; R = t-Bu, i-Pr). The synthesis and characterization of these complexes as well as C-H activation studies will be discussed. Also, the $\eta^2{:}\eta^3$ isomer ratios and IR ν_{CO} bands of the known tris(pyrazolyl)borate rhodium dicarbonyl complexes are presented to compare the steric and electronic effects in these various systems.

Two other alkyl-pyrazoles, 3-Et-5-MePzH and 3-i-Bu-5-MePzH were prepared. However, the synthesis of the corresponding tris(pyrazolyl)borate ligands revealed regioisomeric mixtures in both cases. The subsequent rhodium (dicarbonyl) complexes were prepared, but attempts at separation of the regioisomers were unsuccessful. As a consequence, no C-H activation studies were carried out with these systems.

The synthesis of two other pyrazoles containing CF_3 groups, 3-CF_3CF_2-5-MePzH and 3-Ph-5-CF_3PzH are described, but subsequent attempts to prepare pyrazolylborate ligands were unsuccessful. Only the familiar pyrazole bridged dimers could be prepared, and these will be compared to the other such species prepared in this Thesis. This Chapter then highlights some of the problems encountered in the synthesis of new pyrazolylborate systems.

One feature of the tris and tetrakis(pyrazolyl)borate ligands is the fluxional behaviour via $\eta^2 \rightleftharpoons \eta^3$ interconversions. A possible sensitive probe to determine the hapticity of these ligands is ^{15}N NMR spectroscopy. The synthesis and subsequent ^{15}N NMR spectra of ($HBPz^*_3$) rhodium complexes enriched with ^{15}N will be explored.

Section 2

3-TERTIARYBUTYLPYRAZOLE CHEMISTRY

The so-called second generation pyrazolylborate ligands of the type $[H_nB(3\text{-}RPz)_{4-n}]^-$ (n = 0, 1, 2 and R = Ph,[2] t-Bu,[2] or i-Pr[3]) allow one to "custom-fit" a pocket about a metal center. In the preparation of cobalt half sandwich complexes of the type $HB(3\text{-}RPz)_3CoL_n$, Trofimenko and coworkers[2,3] found that for R = Ph and i-Pr, five ligands could be accommodated about the metal center. On the other hand with R = t-Bu, the complexes were always four-coordinate, prompting Trofimenko[2] to term the ligand $[HB(3\text{-}t\text{-}BuPz)_3]^-$ a "tetrahedral enforcer". A crystal structure of the thallium complex $TlHB(3\text{-}t\text{-}BuPz)_3$ was recently reported,[4a] which determined it to be monomeric, with all three pyrazole groups coordinated to thallium. This structure is quite unlike the polymeric zig-zag structures for TlCp and TlCp*, but is similar to the structure of $[TlC_2B_9H_{11}]^-$.[4a]

The dicarbonyl $HB(3\text{-}t\text{-}BuPz)_3Rh(CO)_2$ (**52**) is prepared by reacting $[(CO)_2RhCl]_2$ with $KHB(3\text{-}t\text{-}BuPz)_3$ in CH_2Cl_2 or toluene. Along with **52** a considerable amount of the dimer $[(CO)_2Rh(3\text{-}t\text{-}BuPz)]_2$ (**53**) also forms (eq. 5-1).

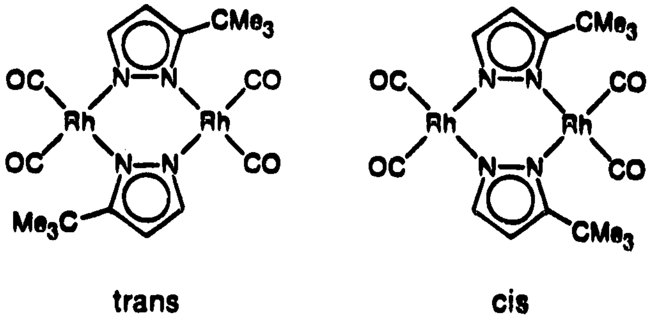
$$\left.\begin{array}{c}[ClRh(CO)_2]_2\\ +\\ K[HB(3\text{-}t\text{-}BuPz)_3]\end{array}\right\} \xrightarrow[25^{\circ}C]{toluene} HB(3\text{-}t\text{-}BuPz)_3Rh(CO)_2 + [(3\text{-}t\text{-}BuPz)Rh(CO)_2]_2 \qquad (5\text{-}1)$$

52 **53**

In previous systems in this Thesis, these two types of products could be separated by chromatography or crystallization. Unfortunately, neither technique was successful in separating 53 from 52. It was pointed out by Trofimenko that the known presence of 3-t-BuPzH in the potassium salt KHB(3-t-BuPz)$_3$ may lead to the formation of 53; he suggested using the thallium salt, which does not contain free pyrazole.[4b] However the analogous reaction of $[(CO)_2RhCl]_2$ with TlHB(3-t-Bupz)$_3$ (eq. 5-1) still produces similar amounts of 53. This suggests that its presence arises not from free 3-t-BuPzH but from B-N bond cleavage of the tris(pyrazolyl)borate ligand,[5] similar to those systems encountered in Chapters II and III.

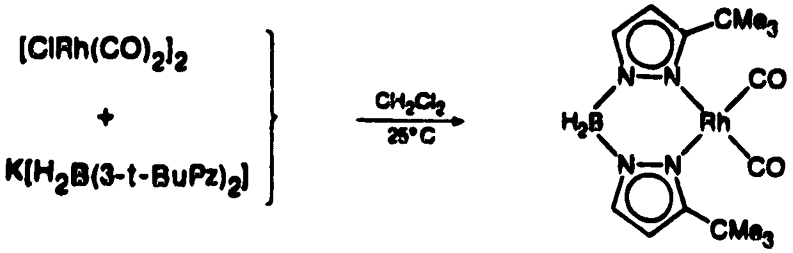
Complex 52 does not survive chromatography on Florisil, while on neutral alumina extensive decomposition occurs. This notwithstanding, small amounts of 52 can be separated from 53 for characterization. The IR spectrum of 52 in hexane shows two sharp ν_{CO} bands at 2084, 2017 cm^{-1}. The MS shows the molecular ion M^+ at m/e = 540 with ions corresponding to loss of CO and a 3-t-BuPz group. The ^1H NMR spectrum shows a 2:1 ratio of pyrazole group resonances, with the 5-H protons at δ 7.73 (d, 1H, $^3J_{H-H}$ = 2.2 Hz) and 7.28 (d, 2H, $^3J_{H-H}$ = 2.3 Hz), while the 4-H protons are at δ 6.21 (d, 1H, $^3J_{H-H}$ = 2.2 Hz) and 6.09 (d, 2H, $^3J_{H-H}$ = 2.3). The t-Bu groups appear as sharp singlets at δ 1.51 (s, 18H) and 1.35 (s, 9H). The element analysis for 52 is poor, as the complex is an unstable air-sensitive yellow oil.

The dimer 53 could be obtained pure from the above mixture by chromatography on Florisil which decomposes complex 52, and the IR, ^1H NMR and MS are identical to those of an authentic sample.[6] Complex 53 has three ν_{CO} bands in hexane at 2090, 2072, 2023 cm^{-1}, and the ^1H NMR spectrum again shows two sets of pyrazole group resonances. These are assigned as the cis and trans isomers (eq. 5-2). The trans:cis ratio of 2.37:1 is considerably larger than in **3** (Pz = 3-PhPz, 1.23:1) or **23** (Pz = $3-CF_3-5-MePz$, 1.15:1), which suggests a larger steric rather than electronic effect. Section 4 will compare and contrast a number of such unsymmetric pyrazole bridged dimers prepared in this Thesis.



(5-2)

The bis(pyrazolyl)borate analog of **52**, $H_2B(3-t-BuPz)_2Rh(CO)_2$ (**54**) was prepared (eq. 5-3).

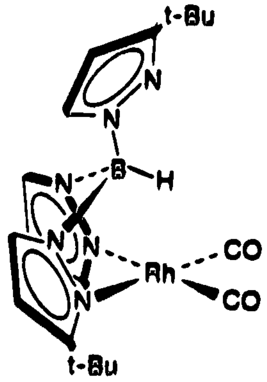


54

(5-3)

The IR ν_{CO} bands of **54** in hexane are at 2082, 2015 cm^{-1}, only 2 cm^{-1} lower than the bands for **52**. This suggests that the latter is exclusively η^2 in solution. The ^1H NMR spectrum of **54** shows one pyrazole group resonance, similar to other related complexes.

Complex **52** is the only example of a neutral tris(pyrazolyl)borate rhodium dicarbonyl species which is exclusively η^2 in solution.



52

η^2-HB(3-t-BuPz)$_3$Rh(CO)$_2$

This emphasizes the steric requirement of the ligand in **52** relative to HB(3-PhPz)$_3$Rh(CO)$_2$ **1**, where in cyclohexane one observes a η^2:η^3 ratio of 85:15%, as determined by IR spectroscopy. This further suggests that the equilibrium position of the two forms is more dependent on the size of the tris(pyrazolyl)borate ligand than on electronic factors. This will be discussed in more detail in Section 3, with comparisons made for a number of such complexes.

Attempts at C-H bond activation with **52** in aliphatic or aromatic hydrocarbons did not meet with much success. Photolyses of benzene or cyclohexane solutions of **52** led to consumption of starting material but no appearance of products containing a CO group as monitored by IR spectroscopy. One might expect to get intramolecular activation of one of the methyl groups of a t-Bu group as observed with a phenyl group in complex 1, but perhaps the size of the ligand does not allow the third pyrazole group to coordinate into an octahedral geometry. This again emphasizes the "tetrahedral enforcer" nature of the ligand $[HB(3\text{-}t\text{-}BuPz)_3]^-$. Perhaps in complex 52 this is just a case of steric overkill where access to the metal center is too restricted, even for incoming hydrocarbons.

As might be expected, since both complexes 52 and 54 are postulated as 16e square planar complexes, they should exchange ^{13}CO rapidly, as demonstrated for other tris and bis(pyrazolyl)borate rhodium dicarbonyl complexes in this Thesis. Hexane solutions of both 52 and 54 are completely enriched with one atmosphere of ^{13}CO after five minutes, with IR ν_{CO} bands at 2035, 1971 cm^{-1} and 2033, 1969 cm^{-1} respectively for the enriched species. Given the fact that large amounts of pure 52 could not be reasonably obtained, further chemistry was not done in this system.

Section 3

3-ISOPROPYLPYRAZOLE CHEMISTRY

Introduction

The unsuccessful C-H activation results with the complex HB(3-t-BuPz)$_3$Rh(CO)$_2$ **52** prompted the synthesis of other pyrazolylborate ligands with alkyl substituents. A report by Trofimenko on the pyrazolylborate ligands of intermediate steric size was recently published involving the 3-i-PrPz group. The synthesis of pyrazolylborate ligands of the type [H$_n$B(3-i-PrPz)$_{4-n}$]$^-$ (n = 0, 1, 2) as well as a number of transition metal complexes was reported.[3] This ligand system was described as a steric intermediate between the parent [H$_n$BPz$_{4-n}$]$^-$ ligands[7] and the so-called second generation bulky ligands [H$_n$B(3-RPz)$_{4-n}$]$^-$,[2] (n = 0, 1, 2, R = Ph, t-Bu) with properties lying between the two.

This Section discusses the preparation of complexes of the type H$_n$B(3-i-PrPz)$_{4-n}$Rh(CO)$_2$ (n = 1, 2) and subsequent characterization, particularly regarding the hapticity of the tris(pyrazolyl)borate ligand. C-H bond activation studies of the complex with n = 1 will be discussed.

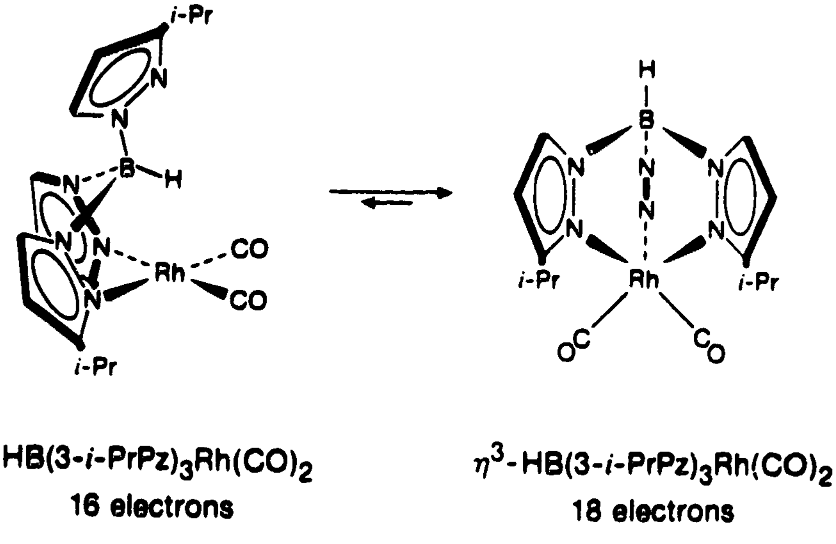
Synthesis

The dicarbonyl HB(3-i-PrPz)$_3$Rh(CO)$_2$ (55) was prepared in the same manner as other analogous complexes (eq. 5-4).

$$\left.\begin{array}{c}[ClRh(CO)_2]_2\\+\\K[HB(3\text{-}i\text{-}PrPz)_3]\end{array}\right\}\xrightarrow[25^\circ C]{CH_2Cl_2}\underset{\mathbf{55}}{HB(3\text{-}i\text{-}PrPz)_3Rh(CO)_2}\qquad(5\text{-}4)$$

Although Trofimenko reports that the salt $KHB(3\text{-}i\text{-}PrPz)_3$ contains free 3-i-PrPzH,[3] only a small amount of the familiar pyrazole bridged dimer $[(CO)_2Rh(3\text{-}i\text{-}PrPz)]_2$ (**56**) was formed. As before an authentic sample was prepared and the two were found to be identical by IR, ^1H NMR and MS.

Unlike **52**, complex **55** survives chromatography and was isolated as a yellow solid. As observed for complexes **1** and **22**, the IR spectrum of **55** in cyclohexane shows two sets of ν_{CO} bands at 2082 (s), 2058 (s, br), 2017 (s), 1987 (s, br) cm^{-1}, (Figure V.1), which arise from an equilibrium mixture of the η^2 and η^3 forms (eq. 5-5).



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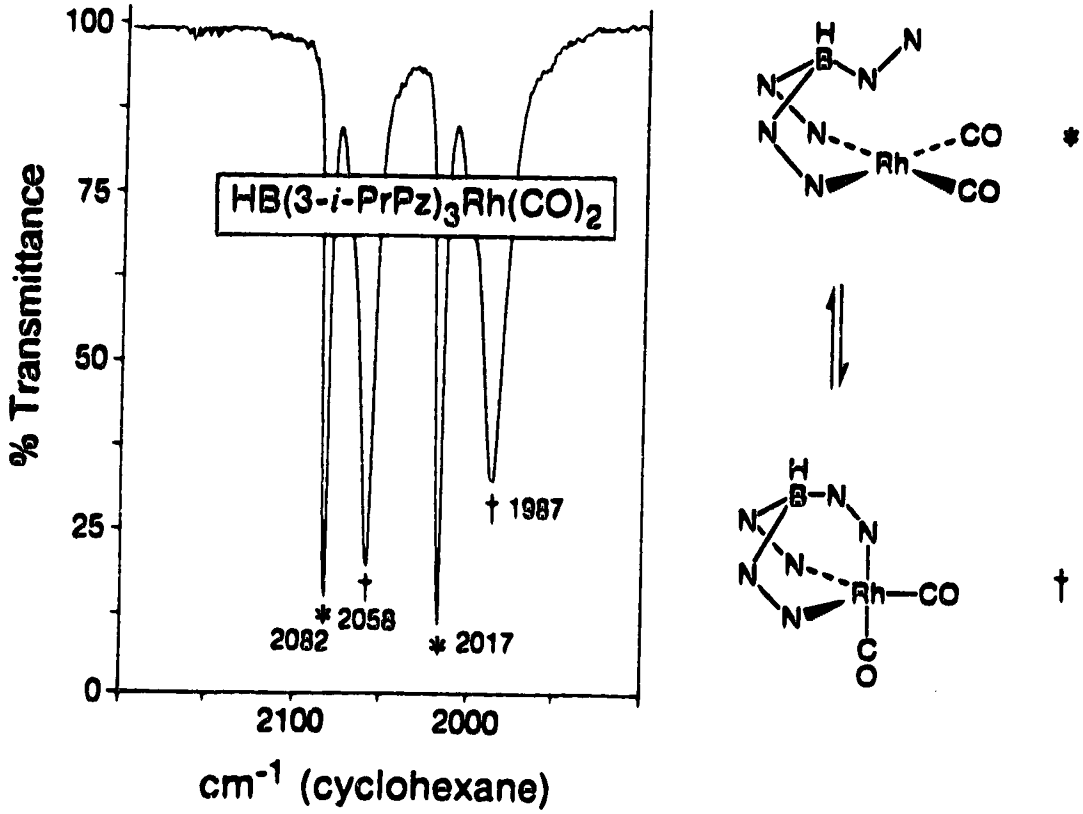


Figure V.1 Infrared Spectrum of HB(3-i-PrPz)$_3$Rh(CO)$_2$ (55)

From the combination of the two methods outlined in the General Experimental Section (Chapter II), relative ratios of the isomers can be obtained. In cyclohexane, the average ratio of $\eta^2:\eta^3$ is 35:65%, while in toluene it is 42:58% and in CH_2Cl_2 the ratio is 38:62%. As observed for **22**, the ratios in the three solvents do not follow the smooth progression observed for **1**, but the equilibrium position is still solvent dependent.

The ^1H NMR spectrum of **55** shows just one type of pyrazole group, with the 5-H and 4-H resonances at δ 7.54 (d, 3H, $^3J_{H-H}$ = 2.2 Hz) and 6.10 (d, 3H, $^3J_{H-H}$ = 2.2 Hz) respectively. For the isopropyl group, a characteristic septet for the C-H resonance is observed at δ 3.28 (3H, $^3J_{H-H}$ = 6.9 Hz), while the methyl groups are a doublet at δ 1.30 (18H, $^3J_{H-H}$ = 6.9 Hz). There is no change in the spectrum when the sample is cooled to -90°C. This was also observed with complex **22**, which shows similar $\eta^2:\eta^3$ IR ratios.

It is interesting at this point to compare and contrast the five tris(pyrazolyl)borate rhodium dicarbonyl species discussed in this Thesis, as shown in Table 5.I. The five complexes demonstrate changes in the electronic and steric properties of the tris(pyrazolyl)borate ligand which are reflected in the IR ν_{CO} bands and $\eta^2:\eta^3$ ratios respectively. These latter ratios vary from a complex that is entirely η^3 ($(HBPz^*_3)Rh(CO)_2$), to two that are mostly η^3 (approximate 2:1 ratio for **22** and **55**), to one that is mostly η^2 ($HB(3\text{-}PhPz)_3Rh(CO)_2$ **1**), and finally a complex that is entirely η^2 in solution ($HB(3\text{-}t\text{-}BuPz)_3Rh(CO)_2$ **52**).

There are several comparisons that suggest that this $\eta^2:\eta^3$ ratio is predominantly governed by steric rather than electronic factors. For

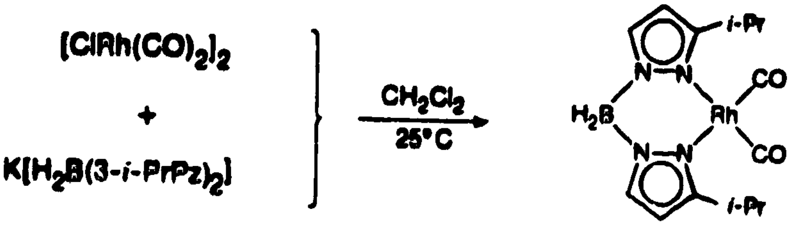
Table 5.I Isomer Ratios in Dicarbonyl(trispyrazolylborate)rhodium Complexes

Complex		ν_{CO} (cm^{-1}) Cyclohexane		
		η^2 Form	η^3 Form	$\eta^2:\eta^3$ Ratio
$(HBPz^*_3)Rh(CO)_2$		-	2054, 1980	0:100
$HB(3\text{-}PhPz)_3Rh(CO)_2$	(1)	2088, 2026	2079, 2015	85:15
$HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2$	(22)	2103, 2040	2090, 2025	32:68
$HB(3\text{-}t\text{-}BuPz)_3Rh(CO)_2$	(52)	2083, 2017	-	100:0
$HB(3\text{-}i\text{-}PrPz)_3Rh(CO)_2$	(55)	2082, 2017	2058, 1987	35:65

example, the ν_{CO} bands for the η^2 form of 52 and 55 are virtually identical, which suggests the two tris(pyrazolyl)borate ligands are similar electron donors; yet the former is entirely η^2 in solution, while for the latter the major form in solution is the η^3 isomer. Also, when comparing 22 and 55, the ν_{CO} bands for both the η^2 and η^3 isomers of the former are much higher in energy, which shows that the ligand in 22 is a poorer electron donor. However, the η^2:η^3 ratios for 22 and 55 are almost the same. If the steric effect largely governs the η^2:η^3 ratio, one could arrange the groups in the 3-position of the pyrazole ring in order of increasing size: Me < CF_3 ≈ i-Pr < Ph < t-Bu.

The steric effect in a number of phosphines was represented by Tolman using the concept of a cone angle.[8] In the same manner Trofimenko reported cone angles based on crystal structures of tris(pyrazolyl)borate complexes. He found that for $HBPz_3$ the cone angle is 184°, while $HBPz^*_3$ has a value of 224° and $HB(3\text{-}t\text{-}BuPz)_3$ has the largest value at 244°.[2a] One would expect that as the cone angle increases, the amount of η^3 form would decrease, as observed on going from $(HBPz^*_3)Rh(CO)_2$ to 52.

The analogous bis(pyrazolyl)borate complex of 55, $H_2B(3\text{-}i\text{-}PrPz)_2Rh(CO)_2$ (57) was prepared (eq. 5-6).



(5-6)

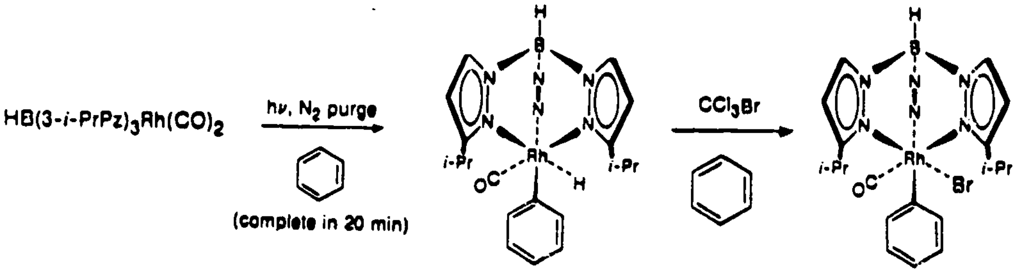
57

The IR ν_{CO} bands of **57** in hexane are at 2081, 2016 cm^{-1}, whose positions are similar to those assigned to **55**-η^2. As observed with **54**, the ^{1}H NMR spectrum of **57** shows only one type of pyrazole group.

As was demonstrated for complexes **52** and **54** in Section 2, both **55** and **57** rapidly exchange ^{13}CO (complete in five minutes in hexane) with the enriched IR spectra giving ν_{CO} bands at 2035 (s), 2011 (s, br), 1972 (s), 1941 (s, br) cm^{-1} and 2033, 1970 cm^{-1} respectively.

C-H Activation Studies

Irradiation of a benzene solution of **55** for 20 minutes resulted in the formation of the phenyl hydride complex HB(3-i-PrPz)$_3$Rh(CO)(Ph)(H) (**58**) (eq. 5-7).



(5-7)

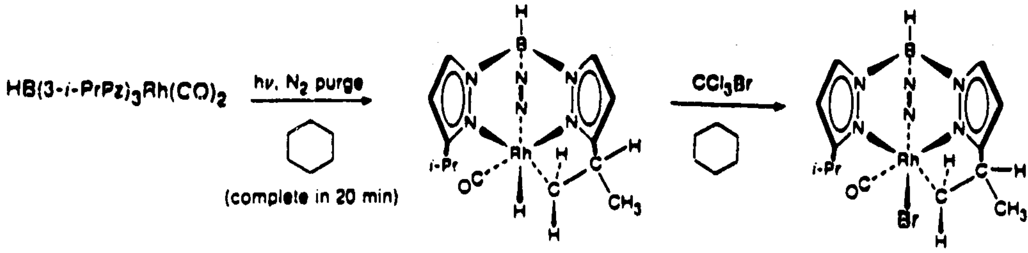
55 **58** **59**

The IR spectrum in benzene showed a weak band at 2076 cm^{-1} assigned as the Rh-H stretch and a strong band at 2048 cm^{-1} for ν_{CO}. Complex **58** was not isolated but converted to the bromide (**59**) with CBrCl$_3$ in good yield (eq. 5-7). The IR spectrum of **59** in hexane shows a ν_{CO} band at 2085 cm^{-1}, and the MS shows at weak parent ion M$^+$ at m/e = 627.

The ^{1}H NMR spectrum of **59** shows three inequivalent pyrazole groups. Three different 5-H and 4-H doublets and three C-H septets are observed. The two methyl groups on the isopropyl group are now nonequivalent by symmetry, resulting in six different doublets. It is assumed that the isopropyl group is in the least hindered position, with the C-H group pointing inward to the metal, and the two methyl groups pointing outwards. The phenyl ring is not rotating on the NMR timescale, as the five different ring protons are observed. The ^{13}C APT NMR spectrum shows the carbonyl carbon at δ 183.18 (d, $^{1}J_{Rh-C}$ = 61 Hz) and the phenyl carbon attached to rhodium at δ 143.84 (d, $^{1}J_{Rh-C}$ = 22 Hz). One also observes three carbon resonances for the 5-C, 4-C, 3-C and C-H groups, and six methyl carbons.

The irradiation of **55** in cyclohexane gives a product (**60**) with ν_{Rh-H} 2070 (w) and ν_{CO} 2031 (s) cm^{-1}. The product was found to be unstable, so the presumed hydride was converted to the bromide (**61**) with $CBrCl_3$. The IR spectrum of **61** in hexane showed a single ν_{CO} at 2068 cm^{-1}. The MS showed a molecular ion M^+ at m/e = 550, which corresponds to the product from intramolecular C-H activation.

There are two isomers possible, as one could activate the isopropyl methyl group, giving a five-membered ring, or the isopropyl C-H bond giving a four-membered ring. The former would be predicted to be favored based on a less strained ring, and in fact this structure was confirmed by ^{1}H and ^{13}C NMR spectra. Hence the C-H activation product is $HB(3\text{-}i\text{-}PrPz)_2(C_3H_2N_2CH(CH_3)\overline{CH_2)}Rh(CO)(H)$ **60**, which is converted to the bromide **61** (eq. 5-8).

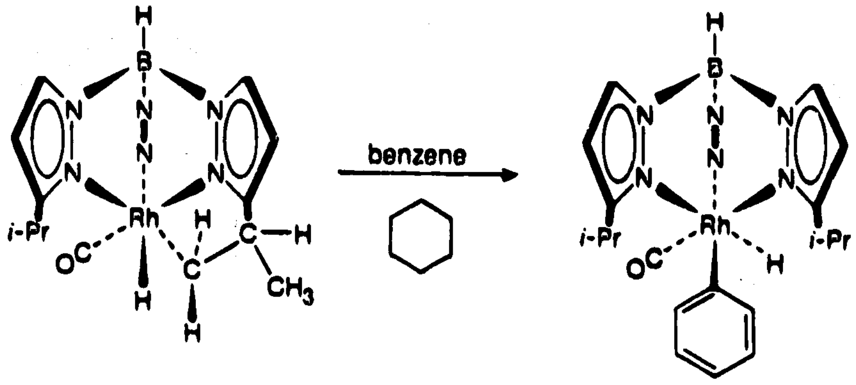


(5-8)

55 60 61

The ^1H NMR spectrum of **61** shows three 5-H and 4-H doublets, and more importantly, two septets and one multiplet for the isopropyl C-H groups. The two septets correspond to the C-H protons of the free isopropyl groups, while the multiplet arises from coupling of the C-H group to a methyl and the diastereotopic methylene groups of the metallated isopropyl group. As anticipated only five isopropyl methyl groups appear, and the diastereotopic methylene protons of the metallated group appear at δ 3.46 (m, 1H) and 2.56 (m, 1H). The ^{13}C NMR spectrum again shows the CO carbon at δ 183.53 (d, $^1J_{Rh-C}$ = 58 Hz), and sets of three resonances for the 5-C, 4-C, 3-C and C-H carbons. The metallated carbon is observed at δ 33.39 (d, $^1J_{Rh-C}$ = 18 Hz) and one now observes only five methyl carbons.

In benzene one obtains intermolecular activation with **55**, while in cyclohexane intramolecular activation results. One final experiment involves the thermal activation of benzene with **60**. A solution of **60** in cyclohexane reacts with excess benzene at room temperature with complete conversion to the phenyl hydride **58** in about one hour. This was again converted to the bromide **59** and isolated in good yield (eq. 5-9).

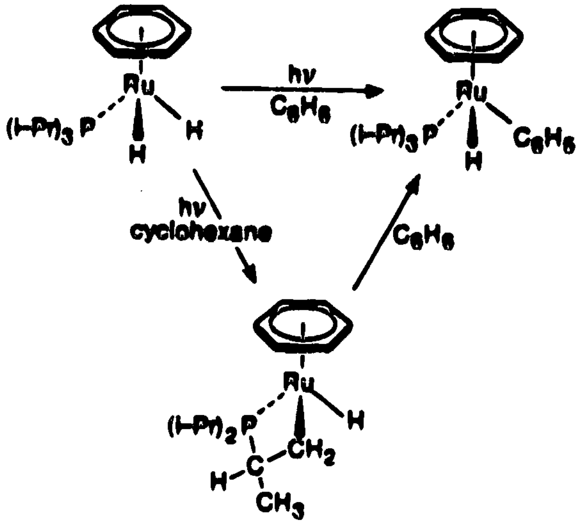


60

58

(5-9)

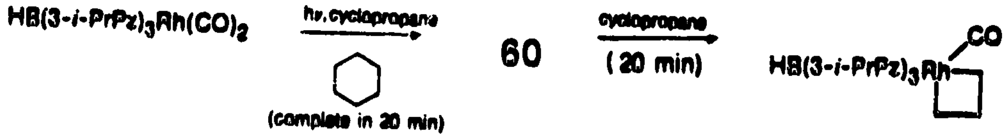
This sequence of reactions is reminiscent of Werner's work with $(C_6H_6)Ru(P(i\text{-}Pr)_3)(H)_2$ (eq. 5-10).[9]



(5-10)

Werner et al.[9] found that when the photolysis was performed in benzene, the phenyl hydride complex was obtained. When the photolysis was performed in cyclohexane, intramolecular activation of one of the i-Pr groups occurred. Subsequent reaction of the latter complex with benzene gave the phenyl hydride complex in five minutes. Of course, the metallated product in that instance contained a four-membered ring, presumably more strained than the five-membered ring in **60** and expected to react faster with benzene.

When the photolysis of **55** in cyclohexane was performed with a cyclopropane purge, a mixture of mostly **60** and $HB(3\text{-}i\text{-}PrPz)_3\overline{Rh(CO)\text{-}(CH_2CH_2CH_2)}$ (**62**) was observed after 20 minutes. If the solution was purged with cyclopropane for a further 20 minutes, **60** is completely converted to **62** (eq. 5-11), which is a stable complex which could be completely characterized.

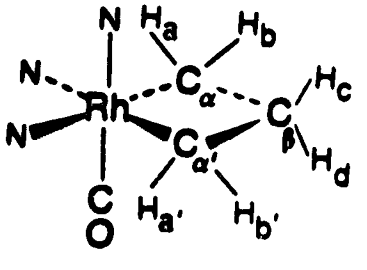


(5-11)

55 **62**

The initial product mixture is similar to that obtained from the reaction of $HB(3\text{-}PhPz)_3Rh(CO)_2$ **1** with cyclopropane. In the latter case, there was not complete conversion to the rhodacyclobutane.

The IR spectrum of **62** shows ν_{CO} at 2027 cm^{-1} and the ^1H NMR spectrum shows a 2:1 ratio of pyrazole group resonances. The assignment of the hydrogens of the metallacycle followed that used for complexes **11** and **50**.

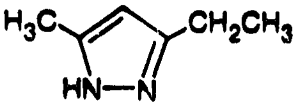


62 (atom numbering for NMR)

Section 4

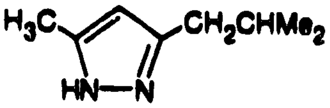
OTHER LIGAND SYSTEMS

As previously mentioned, the low solubility of (HBPz*$_3$)Rh(CO)$_2$ in saturated hydrocarbons was a problem in C-H bond activation studies. Two other pyrazoles, 3-Et-5-MePzH (**63**) and 3-i-Bu-5-MePzH (**67**) (eq. 5-12) were prepared, and these are direct extensions of Pz*H. Electronically, the subsequent pyrazolylborate ligands should be similar, but the larger alkyl groups should be more sterically demanding around the metal center.



3-Et-5-MePzH

63



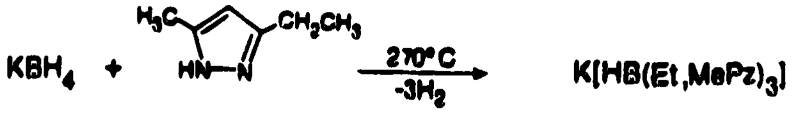
3-i-Bu-5-MePzH

67

(5-12)

3-Et-5-MePzH has been reported previously by several different routes.[10] However, spectroscopic analysis was not complete, so this is detailed in the Experimental Section. 3-Et-5-MePzH **63** was prepared by the reaction of 2,4-hexanedione with hydrazine hydrate, much like the synthesis of Pz*H.[11] It was isolated as a clear liquid after distillation. The ^{1}H NMR spectrum shows a broad resonance at δ 11.98 (1H) assigned as the N-H proton. The 4-H resonance appears at δ 5.90 (s, 1H) and the methyl group directly bound to the pyrazole ring is at δ 2.33 (s, 3H). The ethyl group consists of the typical methylene quartet (δ 2.70, 2H, $^3J_{H-H}$ = 7.8 Hz) and the methyl triplet (δ 1.28, 3H, $^3J_{H-H}$ = 7.8 Hz). Similar ^{1}H NMR spectra have been reported.[10c,d]

The synthesis of the tris(pyrazolyl)borate ligand was identical to that of KHBPz*$_3$ [12a] (eq. 5-13).



(5-13)

63 **64**

However, the ^{1}H NMR spectrum of KHB(Et,MePz)$_3$ (**64**) revealed a regioisomeric mixture, with at least four sets of pyrazole group resonances detected in a 6.5:2.2:2:1 ratio. There appears to be one major product and at least two minor isomers. With the tris(pyrazolyl)borate ligand, there are now four possible orientations of the ethyl and methyl groups in either 3- or 5-positions. Perhaps this result is not surprising in light of the fact that the complex KHB(3,5-Et$_2$Pz)$_3$ was also prepared by Trofimenko,[12b] which requires that three ethyl groups can be accommodated in the 5-position near the boron atom. The size difference between a methyl and an ethyl group is undoubtedly small, so that in the transition state for the formation of the pyrazolylborate ligand a mixture is obtained.

The subsequent rhodium dicarbonyl complex HB(Et,MePz)$_3$Rh(CO)$_2$ (**65**) was prepared (eq. 5-14), and like (HBPz*$_3$)Rh(CO)$_2$,[1a] **65** is also air-sensitive in the solid state.

$$\left.\begin{array}{c}[ClRh(CO)_2]_2\\ +\\ K[HB(Et,MePz)_3]\end{array}\right\}\xrightarrow[25^{\circ}C]{CH_2Cl_2} HB(Et,MePz)_3Rh(CO)_2 \qquad (5\text{-}14)$$

64 **65**

In contrast to $(HBPz^*_3)Rh(CO)_2$, **65** survives column chromatography, and can be separated from the ever-present rhodium dimer $[(CO)_2Rh(3\text{-}Et\text{-}5\text{-}MePz)]_2$ (**66**). Complex **65** is also much more hexane soluble than $(HBPz^*_3)Rh(CO)_2$. The IR spectrum of **65** is identical to that of $(HBPz^*_3)Rh(CO)_2$, with ν_{CO} bands at 2054 and 1980 cm^{-1} in hexane. By analogy, **65** is then entirely η^3 in solution, with no evidence for the η^2 isomer. Consistent with this observation is that complex **65** shows no ^{13}CO exchange after four hours in hexane, as previously reported for $(HBPz^*_3)Rh(CO)_2$. Since **65** appears to be entirely η^3 in solution, it was then not necessary to prepare the analogous bis(pyrazolyl)borate complex.

The ^1H NMR spectrum of **65** shows two sets of pyrazole group resonances whose intensity ratio is not indicative of a single regioisomer. The ^1H NMR spectrum of **64** shows the presence of several regioisomeric forms, but these are not all separated in the ^1H NMR spectrum of **65**. Attempts at separation of the regioisomers were unsuccessful, although a slight enrichment of one species was accomplished by fractional crystallization. Although complex **65** is analytically pure it is not isomerically pure, so no C-H activation studies were done. An obvious solution to the solubility problem in

$(HBPz^*_3)Rh(CO)_2$, without the problems present in **65** would be to prepare $HB(3,5\text{-}Et_2Pz)_3Rh(CO)_2$, as the ligand was prepared by Trofimenko. This complex was not prepared in this Thesis, but points the way to further work with these type of complexes.

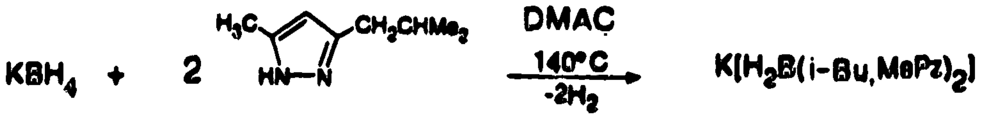
An authentic sample of **66** was prepared. It is interesting to note that the ratio of the presumed trans and cis isomers is the nearest to unity in this complex (1.09:1). This suggests a very small steric preference for a methyl or ethyl group. A comparison of such pyrazole-bridged rhodium dimers will be made later in this Section.

In the hope of preparing a tris(pyrazolyl)borate ligand where only one regioisomer is present, a pyrazole with a longer alkyl substituent was prepared. The diketone 6-methyl-2,4-heptanedione is commercially available, which would lead to 3-i-Bu-5-MePzH. There is only one report of this pyrazole in the literature, obtained from a mixture of products.[13]

The pyrazole 3-i-Bu-5-MePzH **67** (eq. 5-12) was prepared by reacting 6-methyl-2,4-heptanedione with hydrazine hydrate. It was obtained as a colorless liquid after distillation, and unlike **63**, **67** solidified at -30°C. The ^1H NMR spectrum of **67** is similar to that of **63**, except for the i-Bu rather than Et resonances. The CH_2 group appears at δ 2.48 (d, 2H, $^3J_{H-H} = 7.2$ Hz), while the methyl groups appear at δ 0.92 (d, 6H, $^3J_{H-H} = 6.6$ Hz). The C-H resonance appears as an apparent nonet from coupling to the two methylene and six methyl hydrogens at δ 1.89 (nonet, 1H, $^3J_{H-H} = 6.8$ Hz). Irradiating the methylene doublet at δ 2.48 causes the nonet to simplify to a septet, while irradiating the methyl doublet at δ 0.92 causes the nonet to collapse to a triplet.

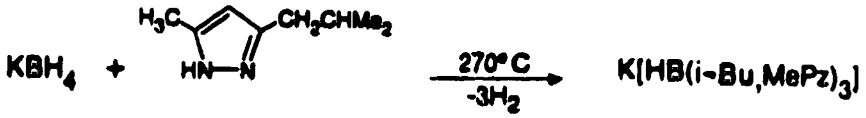
The ^{13}C APT NMR spectrum of **67** showed the 5-C and 3-C resonances at either δ 148.10 or 144.88. The 4-C resonance is at δ 103.88, while the methylene carbon is at δ 36.44. Unfortunately, the APT technique can only differentiate CH or CH_3 carbons from CH_2 or quartenary carbons, but it cannot distinguish a CH from a CH_3 group. However, the DEPT (Distortionless Enhancement Polarization Transfer) NMR technique is capable of distinguishing a CH from a CH_3 group.[14] The ^{13}C DEPT NMR spectrum of **67** determined that the C-H group was at δ 29.32, the isopropyl methyls at δ 22.55, while the single methyl group is at 12.56. The latter two assignments are based on comparison of the ^{13}C chemical shifts of the pyrazole methyl group to the Et, MePz and CF_3,MePz system, as well as the Pz* system.[1a]

The synthesis of the bis and tris(pyrazolyl)borate ligands were straightforward (eq. 5-15 and 5-16 respectively), the former prepared by the so-called solvent route.



(5-15)

67 **68**



(5-16)

67 **70**

Unfortunately, in both the bis(pyrazolyl)borate ligand KH_2B(i-Bu,MePz)$_2$ (**68**) and the tris(pyrazolyl)borate analog KHB(i-Bu,MePz)$_3$ (**70**), the ^1H NMR spectra show the presence of regioisomers. Apparently, the size difference between an i-Bu group and a Me group is still not large enough to ensure even a regioisomerically pure tris(pyrazolyl)-borate ligand. Although the isobutyl group is definitely longer than a methyl group, it can still bend away from the boron atom in the transition state and appear like a methyl group. On the other hand, with reference to the isomerically pure ligand $KHB(3\text{-}CF_3\text{-}MePz)_3$ **21**, a CF_3 group is spherically like a methyl group but larger, so that the steric effect at boron is more pronounced.

The corresponding rhodium dicarbonyl species were again prepared, the bis(pyrazolyl)borate complex $H_2B(i\text{-}Bu,MePz)_2Rh(CO)_2$ (**69**) and the tris(pyrazolyl)borate analog $HB(i\text{-}Bu,MePz)_3Rh(CO)_2$ (**71**) (eq. 5-17).

$$\left.\begin{array}{c}[ClRh(CO)_2]_2\\ +\\ K[H_nB(i\text{-}Bu,MePz)_{4\text{-}n}]\end{array}\right\}\xrightarrow[25^\circ C]{CH_2Cl_2} H_nB(i\text{-}Bu,MePz)_{4\text{-}n}Rh(CO)_2 \qquad (5\text{-}17)$$

68 n=2 **69** n=2

70 n=1 **71** n=1

The IR spectrum of **71** in hexane shows a mixture of the η^2 and η^3 forms, with ν_{CO} bands at 2079 (w), 2054 (s, br), 2014 (w), 1981 (s, br) cm^{-1}. The major species is still the η^3 form, whose bands are identical to those of $(HBPz^*{}_3)Rh(CO)_2$ and **65**. One could argue that the appearance of some η^2 form (ca. 1%) in solution is due to the greater steric bulk of the i-Bu group relative to a Me or Et group. Of course, **71** is a mixture of regioisomers, so this argument is less valid.

At this point, the question of ^{13}CO exchange rates arose. A hexane solution of **71** under one atmosphere of ^{13}CO is completely enriched after

20 hours (IR ν_{CO} bands at 2030 (w), 2004 (s), 1967 (w), 1934 (s) cm^{-1}). The small amount of the η^2 isomer of **71** present by IR is thought to have facilitated this exchange. On the other hand, $(HBPz^*_3)Rh(CO)_2$ and **65**, which show only the η^3 isomer present, show no ^{13}CO exchange after four hours. In fact, the ^{13}CO exchange of $(HBPz^*_3)Rh(CO)_2$ in CH_2Cl_2 is complete in about 18 hours, consistent with the fact that the IR spectrum in CH_2Cl_2 shows about 1% of the η^2 isomer present. Also, as expected, the bis(pyrazolyl)borate analog of **71**, complex **69**, is rapidly ^{13}CO enriched (complete in less than five minutes, with IR ν_{CO} bands at 2030, 1967 cm^{-1} in hexane).

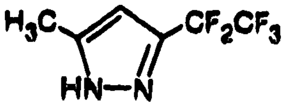
The ^1H NMR spectrum of **71** shows several pyrazole group resonances. The ^{13}C NMR spectrum of ^{13}CO enriched **71** shows three distinct CO carbons, which suggests that there are at least three regioisomers present. The remainder of the spectrum shows at least three resonances for each type of carbon.

The bis(pyrazolyl)borate complex **69** has IR ν_{CO} bands in hexane at 2079, 2012 cm^{-1}, which are very similar to the bands for **71**-η^2. The ^1H NMR spectrum shows three sets of pyrazole groups resonances, indicating the presence of regioisomers, similar to those of $H_2B(CF_3,MePz)_2Rh(CO)_2$ **20**. One might expect to observe several sets of IR bands, as with the latter complexes. However, electronically, there is not a large difference between a i-Bu and a Me group, so these bands would be superimposed.

The pyrazole-bridged dimer complex $[(CO)_2Rh(3\text{-}i\text{-}Bu\text{-}5\text{-}MePz)]_2$ (**72**) was again isolated in small amount from the preparation of **71**. Its identity was confirmed by comparison of spectral data to an authentic sample. The ratio of the trans:cis isomers now is larger than for **66**

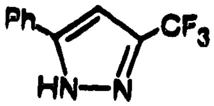
(1.80:1), which suggests a larger steric difference between an i-Bu and Me group than a Et and a Me group.

The synthesis of two other pyrazoles containing CF_3 groups were accomplished (eq. 5-18). The first, 3-CF_3CF_2-5-MePzH (**73**) was prepared by reacting the known precursor 1,1,1,2,2-pentafluoro-3,5-hexanedione[15] with hydrazine hydrate. It was obtained as a white solid in good yield. This pyrazole can be viewed as an extension of 3-CF_3-5-MePzH **18**, with the hope of increasing the fluorocarbon solubility of the tris(pyrazolyl)borate rhodium complexes without drastically changing the electron donor properties.



3-CF_3CF_2-5-MePzH

73



3-Ph-5-CF_3PzH

75

(5-18)

The ^1H NMR spectrum of **73** is very similar to that of 3-CF_3-5-MePzH **18**, and the ^{13}C NMR spectrum allows unique assignment of each resonance. Of particular interest are the resonances of the CF_3CF_2 group. The CF_3 group appears at δ 119.34 (q of t, $^1J_{F-C}$ = 285 Hz, $^2J_{F-C}$ = 39 Hz), while the CF_2 carbon is at δ 111.49 (t of q, $^1J_{F-C}$ = 252 Hz, $^2J_{F-C}$ = 39 Hz). The ^{19}F NMR spectrum shows the CF_3 group at δ -85.45 (s, 3F) and the CF_2 group at δ -113.55 (s, 2F). Although it was initially puzzling that there was no $^3J_{F-F}$ coupling, it is apparently common for a CF_3CF_2 group. In fact, for perfluorocarbons, it is generally the case that $^4J_{F-F} > {}^3J_{F-F}$, the latter couplings being less than 1 Hz.[16]

The other pyrazole 3-Ph-5-CF_3PzH (**75**) was prepared according to Nishiwaki.[17a] The Experimental Section details the complete characterization. The pyrazole has also been prepared by another method[17b] and used in the synthesis of pyrazolyl-bridged iridium dimers.[17c] This pyrazole can be considered a "hybrid" between the two systems encountered in Chapters II and III.

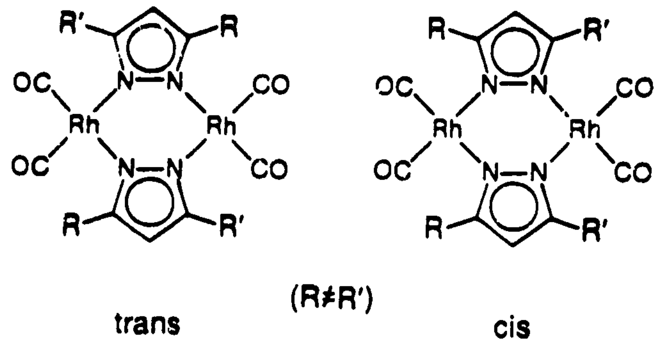
Subsequent attempts to prepare any pyrazolylborate ligands with either **73** or **75** were unsuccessful. The reaction of either pyrazole with KBH_4 resulted in a rapid coloring of the melt even at 140°C, with only unreacted pyrazole being recovered. This is similar to the decomposition that occurs if the melt reaction to prepare KHB(3-CF_3-5-MePz)$_3$ **21** is left at high temperatures for extended periods of time.

The low temperature decomposition appears to be exclusive to those pyrazoles containing CF_3 groups. The melt reactions of any of the alkylpyrazoles in this Thesis show no sign of decomposition up to 270°C. Trofimenko has pointed out that at sufficiently high temperatures, pyrazolylborates do decompose resulting in the formation of pyrazaboles and free pyrazole.[7,12] Either the subsequent pyrazolylborate ligands are simply unstable or there is some reaction of the pyrazoles with KBH_4. Even the attempt to prepare just the bis(pyrazolyl)borate ligands by the solvent route met with failure.

It is well documented that the fluorine atom of the C-F bond is susceptible to attack by nucleophilic reagents,[18a] and fluorocarbons in general are known to react with complex metal hydrides, most notably $LiAlH_4$ and $NaBH_4$, resulting in displacement of F by H and the formation of strong B-F bonds.[18b] It is therefore thought that this side reaction of KBH_4 and a CF_3 group prevents the formation of pyrazolylborate ligands.

This Chapter highlights some of the possible problems that can be encountered in the synthesis of new pyrazolylborate systems. The only rhodium complexes of the pyrazoles **73** and **75** that could be prepared are the familiar pyrazole bridged dimers $[(CO)_2Rh(3\text{-}CF_3CF_2\text{-}5\text{-}MePz)]_2$ (**74**) and $[(CO)_2Rh(3\text{-}Ph\text{-}5\text{-}CF_3Pz)]_2$ (**76**).

At this point, it is pertinent to compare all such complexes prepared in this Thesis. Table 5.II shows the IR ν_{CO} bands and the trans:cis ratio of these unsymmetric pyrazole bridge dimers. It has previously been argued that these are the cis and trans forms posible when an unsymmetric pyrazole is used. It was presumed that the major form was the trans isomer, as PH molecular models indicate more steric congestion of the larger groups in the cis positions. Hence, the ratio of the trans:cis could be taken as a measure of the steric size difference between the two groups on both 3- and 5-positions on the pyrazole ring (eq. 5-17). It should be pointed out that these dimers are not planar as shown but are in folded boat forms.



(5-17)

The work of Stobart and coworkers^{17c} with similar pyrazole-bridged iridium dimers is interesting. Complexes of the type

Table 5.II IR and NMR Data for $[(CO)_2Rh(pyrazole)]_2$ Complexes

Compound (pyrazole =)		ν_{CO} (Hexane) cm^{-1}	Trans:cis Ratio
Pz		2090, 2079, 2022	N/A
Pz*		2080, 2060, 2005[a]	N/A
3-PhPz	(3)	2090, 2077, 2023	1.23:1
3,5-$(CF_3)_2$Pz		2111, 2095, 2049	N/A
3-CF_3-5-MePz	(23)	2100, 2084, 2034	1.15:1
3-t-BuPz	(53)	2090, 2072, 2023	2.37:1
3-i-PrPz	(56)	2088, 2075, 2020	2.23:1
3-Et-5-MePz	(66)	2086, 2072, 2018	1.09:1
3-i-Bu-5-MePz	(72)	2086, 2072, 2018	1.80:1
3-CF_3CF_2-5-MePz	(74)	2101, 2083, 2034	2.49:1
3-Ph-5-CF_3Pz	(76)	2101, 2086, 2037	4.02:1

[a] Recorded in $CHCl_3$ [6]

$[(COD)Ir(pyrazole)]_2$ were prepared, and when the pyrazole was unsymmetric, either mixtures or only one of two possible isomers were obtained. For example, when the pyrazole was 3-CF_3-5-MePzH, a 1:1 ratio of cis and trans isomers was obtained. A mixture of the two products was also found with 3-MePz, but for 3-Ph-5-MePzH, only one isomer was formed. A subsequent X-ray structure showed this to be the trans isomer. Also, with the pyrazoles 3-$CF_3CF_2CF_2$-5-t-BuPz and 3-Ph-5-CF_3PzH, only one of the two isomers was found by ^1H and ^{13}C NMR studies.

Some interesting trends arise from Table 5.II to suggest that not only steric factors govern the trans:cis ratio; electronic factors also appear important. Based on the steric series found from Table 5.I, with the t-Bu group being the largest, one might expect the largest trans:cis ratio for **53**. It is one of the larger ratios, but not the largest. However, based on a steric argument for complex **3** (with Pz = 3-PhPz) the trans:cis ratio should be larger than that for **76** (Pz = 3-Ph-5-CF_3Pz), and yet the largest ratio is observed for the latter complex. This is clearly an electronic effect with the more electronegative CF_3 group in **76** replacing a hydrogen in **3**.

However, there are some comparisons that are consistent with a steric argument. For the complexes **23** (Pz = 3-CF_3-5-MePz) and **74** (Pz = 3-CF_3CF_2-5-MePz), the IR ν_{CO} bands are virtually identical, so that electronically the two pyrazoles are similar. However, the trans:cis ratio for **74** is 2.49:1, much higher than that for **23** (1.15:1), which is thus entirely a steric effect. Also, as mentioned earlier, complexes **66** (Pz = 3-Et-5-MePz) and **72** (Pz = 3-i-Bu-5-MePz) have identical ν_{CO} bands, but as expected on steric grounds, the latter complex has a large trans:cis ratio. A similar trend is observed betweeen **53** and **56**.

Section 5

NITROGEN-15 NMR STUDIES

Introduction

^1H NMR spectroscopy has been invaluable in discerning some of the dynamic processes in pyrazolylborate complexes. Unfortunately, in some cases the information obtained does not allow one to predict the hapticity of the ligand. One method used throughout this Thesis has been to compare the IR spectra of a particular tris(pyrazolyl)borate complex with its bis(pyrazolyl)borate analog, and thus infer the hapticity of the former. This has also been used by Ghosh for his Thesis work, for example, showing that $(HBPz^*_3)Rh(CO)_2$ is η^3 in solution.

A possible probe to determine the hapticity of these ligands would be ^{15}N NMR spectroscopy. The availability of high-field NMR instruments with variable frequency probes has allowed the routine study of nuclei of spin 1/2 other than the traditional ones of ^1H, ^{13}C, ^{19}F and ^{31}P studied in this Thesis.

The ^{15}N nucleus, which is present in only 0.365% natural abundance has a sensitivity of only 2% relative to ^{13}C.[19] Furthermore, the nucleus has a negative gyromagnetic ratio, which results in a long relaxation time, and proton-decoupled ^{15}N NMR has a negative Nuclear Overhauser Effect (NOE), which can diminish the intensity of the signal to zero in some cases. These drawbacks can be overcome by the addition of a paramagnetic relaxation reagent, such as $Cr(acac)_3$ to the solution.[19a] Also, the use of ^{15}N enriched samples would greatly aid the sensitivity, and spectroscopy with 95% ^{15}N enrichment is several times more sensitive than natural abundance ^{13}C.[19a] Regarding a shift reference in ^{15}N NMR spectroscopy, there is no universally accepted standard. The two most common references are external NH_3 or CH_3NO_2.[19a] However, the former reference is much more common in the recent literature and will be used in this Thesis.

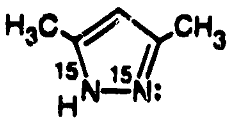
There have been a few reports of nitrogen NMR studies involving pyrazole complexes in general. The prototopic tautomerism of a series of azoles was studied by natural abundance ^{15}N NMR spectroscopy.[20a] The chemical shift of pyrazole in $CDCl_3$ was found at δ 248.0 (relative to external NH_3), while the two resonances for 1-MePz are at δ 200.9 and δ 306.5.[20a] Similar results were obtained by another group for PzH and 1-MePz.[20b] Also, for 3-MePzH, two resonances were observed at δ 247 and 242, while for 3,5-Me_2PzH, a single resonance was observed at δ 242.[20b] For 33% ^{15}N enriched pyrazole,[20c] some N-H coupling constants were reported, for example, $^3J_{H-H}$ = 3.4 Hz. For 95% enriched 1-PhPz,[20d] two ^{15}N resonances were observed at δ 198.4 and δ 280.4, with $^1J_{N-N}$ = 12.8 Hz.

A multinuclear NMR study of pyrazaboles (which are heterocyclic compounds based on the B-N-N-B-N-N ring) and pyrazolylborates reported some natural abundance ^{15}N NMR data.[21] For pyrazabole itself $[H_2B(\mu\text{-Pz})]_2$, a sharp multiplet was observed at δ 222. Although the ^1H, ^{11}B and ^{13}C NMR data were reported for $KBPz_4$, no ^{15}N NMR data was given.

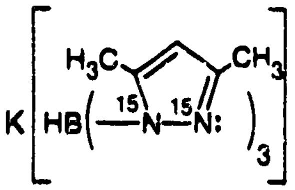
In a ^{14}N NMR study of molydenum nitrosyl complexes,[22] the authors reported that for $(HBPz^*_3)Mo(CO)_2(NO)$, the $(HBPz^*_3)$ ligand absorbs at δ -13 (relative to neat CH_3NO_2), with a line width of 850 Hz. They mention that this signal is not as easily detected as that of the nitrosyl group. There appears to be no literature work involving the synthesis and subsequent ^{15}N NMR spectra of ^{15}N enriched pyrazolylborate metal complexes. However, much work has been done with ^{15}N enriched imidazole complexes.[19a]

Synthesis of Compounds

^{15}N enriched 3,5-dimethylpyrazole (**77**) (eq. 5-20) was prepared using the procedure for natural abundance 3,5-Me_2PzH according to Wiley and Hexner,[10] beginning with 98.6% enriched ^{15}N hydrazine sulphate. The IR spectrum (Nujol) shows the expected isotopic shift to lower wavenumber of several of the vibrations. The IR spectrum in CCl_4 shows the ν_{N-H} at 3466 cm^{-1}, as compared to ν_{N-H} at 3484 cm^{-1} for natural abundance 3,5-Me_2PzH[23] (also verified in this work). The strong $\nu_{C=N}$ band at 1589 cm^{-1} in the latter is shifted to 1581 cm^{-1} in **77**. The MS shows the expected M^+ at m/e = 98 for the $^{15}N_2$ enriched sample.



77

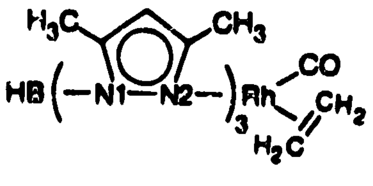


78

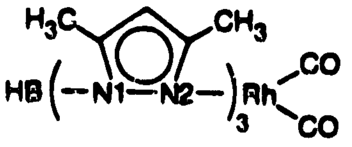
(5-20)

The ^{1}H NMR spectrum of **77** at room temperature showed the N-H resonance at δ 11.86 (br, 1H), while the 4-H proton is a triplet at δ 5.86 (1H, $^{3}J_{N-H}$ = 3 Hz) due to coupling to the two ^{15}N nuclei. The methyl resonance is a doublet at δ 2.26 (6H, $^{3}J_{N-H}$ = 2.8 Hz) coupled presumably to an adjacent ^{15}N group. On cooling to -83°C, the proton tautomerism is slow on the NMR timescale, so one now observes the N-H resonance as a doublet at δ 13.83 (1H, $^1J_{N-H}$ = 88 Hz). The coupling constant is of the same magnitude as a number of $^1J_{N-H}$ values in ^{15}N-enriched aniline derivatives.[24] The ^{13}C NMR spectrum at room temperature shows the 3-C and 5-C resonances as a broad singlet at δ 144.57, while the 4-C is a singlet at δ 104.20 and the methyl group carbons are at δ 12.28 (d, $^2J_{N-C}$ = 5 Hz).

The subsequent synthesis of $^{15}N_6$-KHBPz*$_3$ (**78**) (eq. 5-20) was similar to Trofimenko's procedure,[11] with modifications detailed in the Experimental Section for a small scale preparation. The carbonyl ethylene complex $^{15}N_6$-(HBPz*$_3$)Rh(CO)(C_2H_4) (**79**) (eq. 5-21) was prepared according to Ghosh.[1a,c,d] After chromatography to obtain **79**, a yellow band remained on top of the column. Elution with CH_3CN gave a mixture of **79** and the dicarbonyl $^{15}N_6$-(HBPz*$_3$)Rh(CO)$_2$ (**80**). A CO purge of a CH_2Cl_2 solution of this mixture converted **79** to **80** (eq. 5-21).



79



80

(5-21)

As expected the IR ν_{CO} bands of **79** and **80** are unchanged relative to the unenriched compounds[1a] at 2013 cm^{-1} and 2055, 1981 cm^{-1} in hexane respectively. The MS of both show the M$^+$ at m/e = 462 with loss of CO or C_2H_4.

^{13}C and ^{15}N NMR Spectra

The experimental details of the ^{15}N NMR spectra are found in Section 6. The ^{15}N NMR spectrum of $^{15}N_2$-3,5-Me_2PzH (77) at room temperature shows a broad resonance at δ 245. This is similar to the chemical shift reported for natural abundance Pz*H at δ 242.[20b] The broad signal is the result of the rapid proton tautomerism which averages the two nitrogens. On cooling the sample to -83°C, one observes two resonances, a singlet at δ 282.54 and a doublet at δ 207.58 ($^1J_{N-H}$ = 90 Hz), which suggests that the proton tautomerism is now slow on the NMR timescale. The doublet is then assigned as N_1 (eq. 5-20) and the coupling constant is the same as obtained in the ^{1}H NMR spectrum at -83°C. When the ^{15}N NMR spectrum is broadband proton decoupled, this doublet at δ 207.58 collapses to a sharp singlet. The chemical shifts are in the same region as found for PzH, 1-MePz and 1-PhPz.[20]

It is instructive to look first at the ^{15}N NMR spectrum of the dicarbonyl **80** (Figure V.2). As previously discussed, the ^{1}H NMR spectrum shows one type of pyrazole group down to -90°C. The ^{15}N NMR spectrum would then be a good model for more complex spectra. At -60°C, one observes the two expected resonances for the nitrogens bound to rhodium and to boron. The latter resonances are expected to be broad due to boron quadrupole broadening. A sharp triplet at δ 245.08 (J = 11 Hz) and a broad doublet at δ 223.25 (J = 11 Hz) are observed. The triplet is assigned to the N2 nitrogens bound to rhodium. The signal is thought to arise from approximate equivalent coupling of N2 to Rh and N1, that is a doublet of doublets with the coupling about the same, that is $^1J_{Rh-N2}$ = 11 Hz and $^1J_{N1-N2}$ = 11 Hz. These coupling constants are not unreasonable, as for a series of singly bent diazenido metal

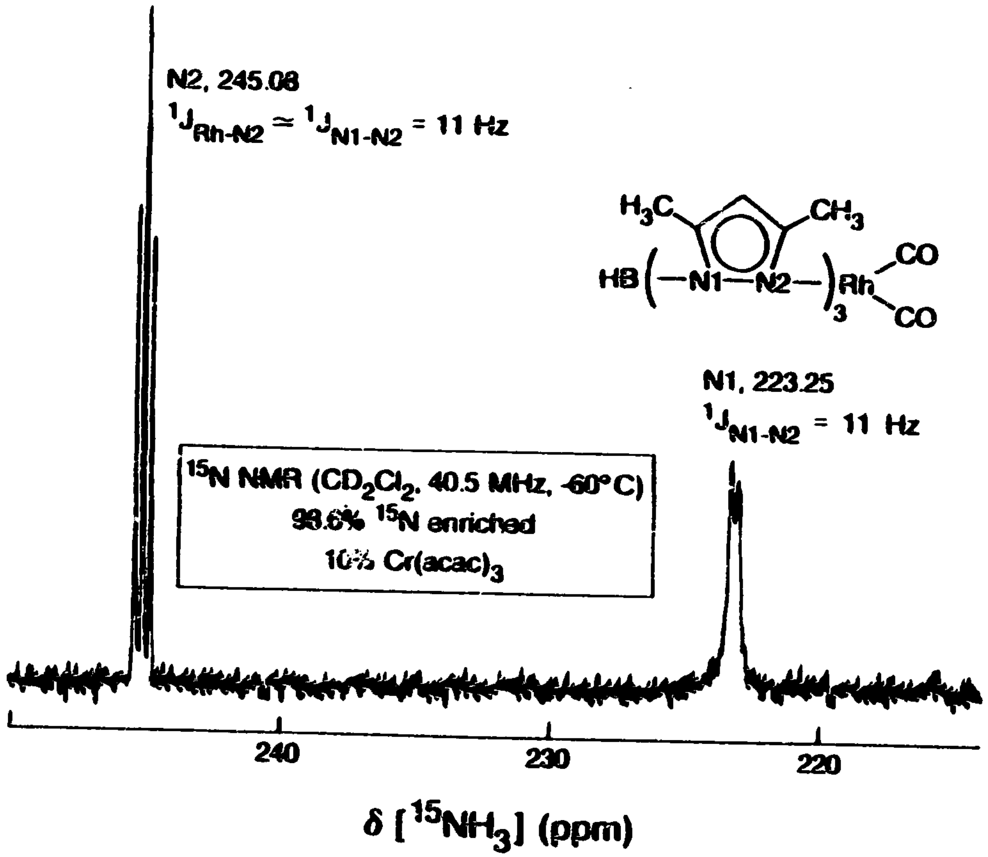


Figure V.2 ^{15}N NMR Spectrum of $^{15}N_6$-(HBPz*$_3$)Rh(CO)$_2$ (80)

complexes, ${}^1J_{N-N}$ was reported in the range 12-17 Hz.[25] Also, for 1-PhPz, ${}^1J_{N-N}$ is 12.8 Hz.[20b] The literature values of ${}^1J_{Rh-N}$ appear to be quite dependent on the geometry and the nature of the nitrogen in other complexes, with values ranging from 3-44 Hz.[19a]

Another potentially elegant method to determine the hapticity of the tris(pyrazolyl)borate ligand in these ${}^{15}N$ enriched complexes would be to obtain the ${}^{13}C$ NMR spectrum and observe N-C coupling with the CO groups. Ghosh reported that the ${}^{13}C$ NMR spectrum of $(HBPz^*_3)Rh(CO)_2$ in CD_2Cl_2 has the CO carbon at δ 189.68 (d, ${}^1J_{Rh-C} = 69.1$ Hz). Based on his presumption that the complex is entirely η^3 in solution, the ${}^{13}C$ NMR spectrum of **80** should show a doublet of quartets. This is what is observed, as the ${}^{13}C$ NMR spectrum of 70% ${}^{13}CO$ enriched **80** reveals a resonance at δ 190.35 (d of q, CO, ${}^1J_{Rh-C} = 69$ Hz, ${}^2J_{N-C} = 5$ Hz) (Figure V.3).

The remainder of the spectrum is similar to the one reported by Ghosh, except some of the resonances show additional N-C couplings. Signals at δ 150.20 (d, $J_{N-C} = 5$ Hz) and 145.21 (d, $J_{N-C} = 10$ Hz) correspond to either the 3-C or 5-C pyrazole carbons. The 4-C is at δ 106.16 (d, $J_{N-C} = 2$ Hz), while one methyl resonance is a doublet at δ 15.35 ($J_{N-C} = 6$ Hz) and the other a singlet at δ 12.80.

For the carbonyl ethylene complex **79**, Ghosh found that the ${}^1H$ NMR spectrum at room temperature showed broad resonances, indicative of fluxional behaviour. On cooling to -60°C, a 2:1 ratio of pyrazole group resonances was obtained. This evidence, along with the comparison of the IR bands of **79** and the bis(pyrazolyl)borate analog, allowed Ghosh to suggest that the tris(pyrazolyl)borate complex was η^2 in solution.

Based on the ${}^1H$ NMR spectrum at -60°C, the ${}^{15}N$ NMR spectrum of **79**

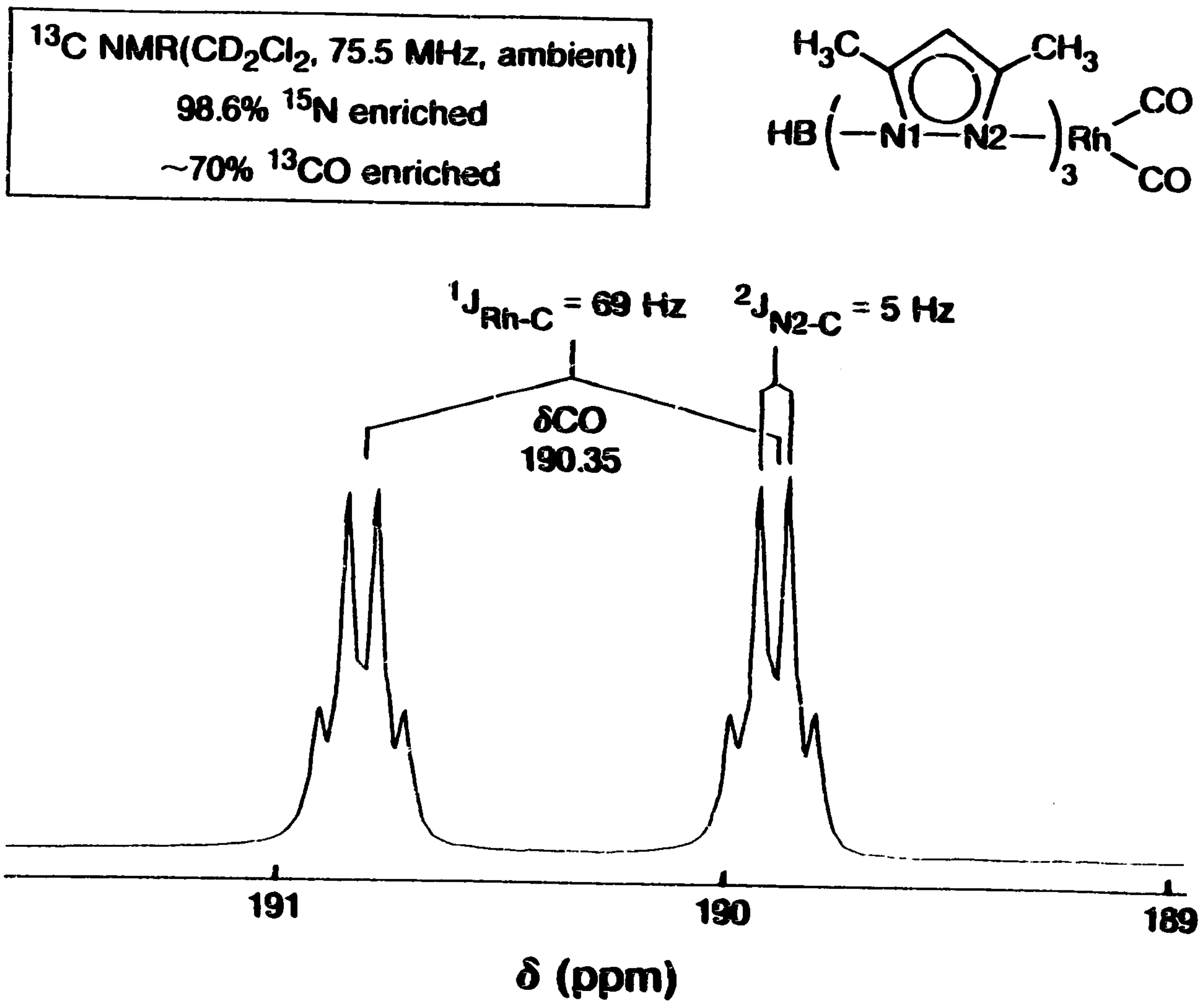


Figure V.3 ^{13}C NMR Spectrum of $^{15}N_6$-($HBPz^*_3$)$Rh(CO)_2$ (80)

at −60°C should consist of four resonances. One should be a triplet, due to the two bound N2 nitrogens coupled to Rh and N1, as observed for **80**. The other two N1 nitrogens of the bound pyrazole groups should again be a broad doublet, coupled to N2 and broadened by boron. For the uncoordinated pyrazole group, the N2 nitrogen should be a sharp doublet (coupled to N1), while N1 should be a broad doublet. One possible problem may be in the chemical shift difference of the latter two doublets. For **80**, there is a large difference between nitrogens bound to rhodium and boron, which could be interpreted as a coordination shift.

The ^{15}N NMR spectrum of **79** at −60°C in fact is almost as predicted. One has the downfield triplet at δ 248.92 (2N, $J = 12$ Hz) and a broad doublet at δ 223.20 (2N, $J = 12$ Hz) for the bound N1 and N2 nitrogens. The resonances of the uncoordinated pyrazole group appear as an AB quartet at δ 227.00, suggesting that the chemical shifts of N1 and N2 are not very different. The resonance is also closer to the N1 resonance of the bound pyrazoles, which is a good indication that the third pyrazole group is not coordinated. The AB quartet is broad, so no attempt was made to analyze it in terms of δ and J values. However, the ^{15}N NMR spectrum of **79** corroborates the other spectral evidence in suggesting that the complex is η^2 in solution.

The ^{13}C NMR spectrum of **79** again may prove to be instructive in revealing the ligand hapticity. Based on the spectrum obtained for **80**, the CO group in **79** should be a doublet of triplets, the triplets arising from coupling to the two bound pyrazoles averaged by the so-called high temperature process. A sample of 70% ^{13}CO enriched **79** was prepared by irradiating a cyclohexane solution of 70% ^{13}CO enriched complex **80** with ethylene purge for seven minutes according to Ghosh.[1a] This initially gives the vinyl hydride, which rapidly rearranges to the carbonyl ethylene complex.

The ^{13}C NMR spectrum of this sample in CD_2Cl_2 at -40° reveals an unexpected doublet of doublets for the CO group at δ 189.25 (d of d, $^1J_{Rh-C}$ = 64 Hz, J_{N-C} = 18 Hz). This suggests coupling to only one ^{15}N nucleus. Also, the N-C coupling is larger than observed in **80**, where $^2J_{N-C}$ = 5 Hz. When the same sample was run at ambient temperature, the CO resonance was a doublet of quartets, very similar to that found for **80**. This suggests a room temperature averaging of all three pyrazole groups, even though the ground state structure is the η^2 isomer. On warming the sample slowly from -40°C to room temperature, the doublet collapses to a broad resonance which sharpens up to a quartet.

There are several scenarios which can account for the ^{13}C NMR spectrum of **79** at -40°C. Firstly, this may represent the so-called low-temperature limit, where there is no exchange occurring. The 2:1 ratio of pyrazole group resonances then represent an accidental degeneracy of the two bound pyrazoles, suggesting that the carbonyl and ethylene groups are not significantly different. Some evidence for this arises from the bis(pyrazolyl)borate rhodium carbonyl olefin complexes prepared in Chapter III, $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(olefin)$, **26** (olefin = C_2H_4), **27** (olefin = COE). The ^1H NMR spectra of both these complexes show only one pyrazole group, even though no fluxional process can average the two.

On the other hand, there are a number of carbonyl olefin and carbonyl phosphine complexes prepared in this Thesis and also by Ghosh,[1a] which show a 2:1 ratio of pyrazole group resonances at low temperature. It is highly unlikely that accidental degeneracy occurs in all these systems. Also, when the low temperature limit is achieved as is the case for some of these complexes, three distinct pyrazole groups are observed.

A reasonable explanation exists based on the two-site exchange, where a nucleus (i.e. ^{13}C) is coupled to two different nuclei (i.e. cis and trans ^{15}N). At a very slow exchange limit, one would expect the ^{13}C resonance to be a doublet of doublets (ignoring ^{103}Rh coupling) with a large trans and small cis $^{2}J_{N-C}$ coupling. On increasing the exchange rate, the two inner lines of the doublets of doublets would begin the coalesce, and at an intermediate rate, one would observe a single large doublet. At the fast exchange limit for two-site exchange, the two inner lines coalesce to a single central line, giving a triplet with coupling = 1/2 (J_{trans} + J_{cis}).[26]

Thus, the doublet observed for 79 at -40°C may be only a stage of the coalescence of a doublet of doublets to a triplet. Unfortunately, the resolution of the ^{13}C NMR spectrum was insufficient to observe an intermediate triplet as the sample was warmed from -40°C to room temperature. Of course, the so-called high temperature process also comes into play, which averages all three pyrazole groups at room temperature.

Lastly, perhaps a reconsideration of earlier interpretations of the exchange processes is in order. The so-called low temperature process has been postulated to involve a trigonal bipyramidal intermediate, which exchanges the two bound pyrazole groups. It is not out of the question that this intermediate could resemble a square pyramid, as the bite angles of the tris(pyrazolyl)borate ligand are closer to 90° rather than 120°. Also, from inspection of Prentice-Hall molecular models, there is severe steric congestion of the R group in the 3-position of the axial pyrazole group with the ligand in the equatorial position.

A second possible fluxional process occurs where one pyrazole group in the square plane remains attached, while the other more labile group exchanges with the uncoordinated pyrazole. Very recent discussions within this research group of such a revised intepretation have concluded that it is equally capable of accounting for the facts known to date. It is hoped that experiments with ^{15}N labelled species subsequent to the completion of this Thesis will enable a choice to be made between the alternative interpretations.

Section 6

EXPERIMENTAL

General

$[(CO)_2RhCl]_2$ was prepared using the standard literature procedure.[27] 3-t-BuPzH[2] and 3-i-PrPzH[3] were prepared according to Trofimenko et al. $KHB(3\text{-t-BuPz})_3$ and $KH_2B(3\text{-t-BuPz})_2$ were prepared according to Trofimenko et al.[2] $KHB(3\text{-i-PrPz})_3$ and $KH_2B(3\text{-i-PrPz})_2$ were also prepared from a more recent Trofimenko effort.[3] 3-Et-5-MePzH and 3-i-Bu-5-MePzH were prepared using a procedure similar to that of 3,5-Me_2PzH.[11] 6-methyl-2,4-heptanedione and 2,4-hexanedione were used as received from Aldrich. 1,1,1,2,2 pentafluoro-3,5-hexanedione was prepared according to Park et al.,[15] with a minor modification using NaH as the base rather than NaOMe.[28]

Hydrazine-$^{15}N_2$ sulphate (98.6 atom % ^{15}N) was used as received from MSD Isotopes. $^{15}N_2$ enriched 3,5-dimethylpyrazole was prepared according to Wiley and Hexner.[11] $^{15}N_2$ enriched $KHBPz^*_3$ was prepared according to Trofimenko,[12a] with some modifications discussed below. $[(C_2H_4)_2RhCl]_2$ was prepared according to Cramer,[29] while the mixed dimer $[(CO)(C_2H_4)RhCl]_2$ was prepared according to Powell and Shaw,[30] using toluene rather than benzene as solvent. $^{15}N_6$ enriched $(HBPz^*_3)Rh(CO)(C_2H_4)$ was prepared according to Ghosh.[1a,c,d]

^{15}N NMR spectra were recorded at 40.5 MHz on a Bruker WH-400 FT spectrometer. The chemical shifts were determined with respect to external $MeNO_2$ and corrected to external ammonia at 25°C by addition of 380.2 ppm.[20a] The paramagnetic relaxation agent $Cr(acac)_3$ was added to the rhodium complexes (10% by weight), with no apparent reaction.

Preparation of HB(3-t-BuPz)$_3$Rh(CO)$_2$ (52)

A sample of 59.5 mg (0.153 mmol) [(CO)$_2$RhCl]$_2$ was taken up in 10 mL toluene. 130 mg (0.31 mmol) of KHB(3-t-BuPz)$_3$ was added, causing an immediate color change from yellow to black. After stirring for 1 h, the solution was filtered through Celite, and a concentrated hexane solution was chromatographed on neutral alumina (12 x 2.5 cm). Elution with hexane and removal of solvent gave 10.4 mg (12% yield) of a yellow oil [(CO)$_2$Rh(3-t-BuPz)]$_2$ 53 which was identified by comparison of ^{1}H NMR, IR and MS spectra to a known sample prepared by an independent method. Further elution of the column with hexane and CH$_2$Cl$_2$ gave a yellow, air sensitive oil after removal of solvent (32.7 mg, 20% yield).

Characterization: IR (n-hexane) 2084, 2017 cm^{-1} (ν_{CO}). MS (80°C, 16 eV) M$^+$ (540, 3%), M$^+$-CO (100%), M$^+$-2CO (41%), M$^+$-2CO-t-BuPz (23%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, ambient) δ 7.73 (d, 1H, $^3J_{H-H}$ = 2.2 Hz), 7.28 (d, 2H, $^3J_{H-H}$ = 2.3 Hz), 6.21 (d, 1H, $^3J_{H-H}$ = 2.2 Hz), 6.09 (d, 2H, $^3J_{H-H}$ = 2.3 Hz), 1.51 (s, 18H), 1.35 (s, 9H). Anal. Calcd for C$_{23}$H$_{34}$BN$_6$O$_2$Rh: C, 51.13; H, 6.34; N, 15.56. Found: C, 55.17; H, 7.34; N, 15.93.

Preparation of [(CO)$_2$Rh(3-t-BuPz)]$_2$ (53)

A solution of 27.0 mg (0.481 mmol) KOH and 57.6 mg (0.464 mmol) 3-t-BuPzH in 3 mL MeOH was added to 85.5 mg (0.22 mmol) [(CO)$_2$RhCl]$_2$ in 9 mL Et$_2$O. After stirring for 1 h, solvent was removed. The residues were taken up in 25 mL benzene and filtered through Celite. The dark red oil was chromatographed on neutral alumina with CH$_2$Cl$_2$ giving a yellow oil after solvent was removed (101.6 mg, 82% yield).

Characterization: IR (n-hexane) 2090, 2072, 2023 cm^{-1} (ν_{CO}). MS (160°C, 16 eV) M$^+$ (564, 89%), M$^+$-CO (17%), M$^+$-2CO (100%), M$^+$-3CO (6%), M$^+$-4CO (23%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, ambient) δ For major isomer: 7.28 (d, 2H, $^3J_{H-H}$ = 2.0 Hz), 6.00 (d, 2H, $^3J_{H-H}$ = 2.1 Hz), 1.40 (s, 18H). For minor isomer: 7.47 (d, 2H, $^3J_{H-H}$ = 2.0 Hz), 6.20 (d, 2H, $^3J_{H-H}$ = 2.1 Hz), 1.45 (s, 18H), Ratio 2.37:1. Anal. Calcd for $C_{18}H_{22}N_4O_4Rh_2$: C, 38.32; H, 3.93; N, 9.93. Found: C, 38.44; H, 3.90; N, 9.97.

Preparation of $H_2B(3\text{-}t\text{-}BuPz)_2Rh(CO)_2$ (54)

A sample of 135.7 mg (0.349 mmol) [(CO)$_2$RhCl]$_2$ was taken up in 20 mL CH$_2$Cl$_2$. 208.8 mg (0.70 mmol) of KH$_2$B(3-t-BuPz)$_2$ was added, giving a black solution and after stirring for 0.5 h, it was filtered through Celite. A concentrated CH$_2$Cl$_2$ solution was chromatographed twice on neutral alumina (12 x 2.5 cm) giving a yellow, air-sensitive oil after solvent was removed (36.1 mg, 12% yield).

Characterization: IR (n-hexane) 2082, 2015 cm^{-1} (ν_{CO}). MS (130°C, 16 eV) M$^+$-CO (390, 37%), M$^+$-2CO (50%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, ambient) δ 7.44 (d, 2H, $^3J_{H-H}$ = 2.2 Hz), 6.18 (d, 2H, $^3J_{H-H}$ = 2.3 Hz), 1.46 (s, 18H). Anal. Calcd for $C_{16}H_{24}BN_4O_2Rh$: C, 45.96; H, 5.79; N, 13.40. Found: C, 45.73; H, 5.94; N, 13.34.

Preparation of $HB(3\text{-}i\text{-}PrPz)_3Rh(CO)_2$ (55)

A sample of 338.1 mg (0.87 mmol) [(CO)$_2$RhCl]$_2$ was taken up in 25 mL CH$_2$Cl$_2$. 658.4 mg (1.74 mmol) of KHB(3-i-PrPz)$_3$ and 25 mL CH$_2$Cl$_2$ were added. After stirring for 1 h, the solution was filtered through Celite, and a concentrated hexane solution was chromatographed on neutral alumina. Elution with CH_3CN gave a yellow oil after solvent was removed in vacuo. On standing, it crystallized, giving a yellow powder (633.4 mg, 73% yield) mp 72-74°C.

Characterization: IR (n-hexane) 2083 (s), 2060 (s, br), 2018 (s), 1988 (s, br) cm^{-1} (ν_{CO}). MS (150°C, 16 eV) M^+ (498, 17%), M^+-CO (100%), M^+-2CO (79%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 7.54 (d, 3H, $^3J_{H-H}$ = 2.2 Hz), 6.10 (d, 3H, $^3J_{H-H}$ = 2.2 Hz), 3.28 (septet, 3H, $^3J_{H-H}$ = 6.9 Hz), 1.30 (d, 18H, $^3J_{H-H}$ = 6.9 Hz). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, ambient, APT) δ 187.38 (d, CO, $^1J_{Rh-C}$ = 69 Hz), 162.26 (s, 3-C), 136.83 (s, 5-C), 101.74 (s, 4-C), 29.34 (s, $CH(CH_3)_2$), 23.56 (s, CH_3). Anal. Calcd for $C_{20}H_{28}BN_6O_2Rh$: C, 48.22; H, 5.66; N, 16.87. Found: C, 48.16; H, 5.90; N, 16.63.

Preparation of $[(CO)_2Rh(3\text{-}i\text{-}PrPz)]_2$ (56)

A solution of 32.5 mg (0.579 mmol) KOH and 61.6 mg (0.559 mmol) 3-i-PrPzH in 4 mL MeOH was added to 102.0 mg (0.265 mmol) $[(CO)_2RhCl]_2$ in 10 mL Et_2O. After stirring for 1 h, solvent was removed. The residues were taken up in 25 mL benzene and filtered through Celite. The resulting dark red oil after solvent was removed was chromatographed on neutral alumina with CH_2Cl_2 and concentrated in vacuo giving a yellow oil (51.0 mg, 36% yield).

Characterization: IR (n-hexane) 2088, 2075, 2020 cm^{-1} (ν_{CO}). MS (140°C, 16 eV) M^+ (536, 100%), M^+-CO (21%), M^+-2CO (79%), M^+-3CO (5%),

M^+-4CO (15%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ For major isomer: 7.34 (d, 2H, $^3J_{H-H}$ = 2.2 Hz), 6.02 (d, 2H, $^3J_{H-H}$ = 2.2 Hz), 3.16 (septet, 2H, $^3J_{H-H}$ = 6.8 Hz), 1.22 (d, 6H, $^3J_{H-H}$ = 6.8 Hz), 1.16 (d, 6H, $^3J_{H-H}$ = 6.8 Hz). For minor isomer: 7.28 (d, 2H, $^3J_{H-H}$ = 2.2 Hz), 5.98 (d, 2H, $^3J_{H-H}$ = 2.2 Hz), 3.11 (septet, 2H, $^3J_{H-H}$ = 6.8 Hz), 1.24 (d, 6H, $^3J_{H-H}$ = 6.8 Hz), 1.20 (d, 6H, $^3J_{H-H}$ = 6.8 Hz). Ratio 2.23:1. Anal. Calcd for $C_{16}H_{18}N_4O_4Rh_2$: C, 35.84; H, 3.38; N, 10.45. Found: C, 37.22; H, 3.72; N, 10.17.

Preparation of $H_2B(3\text{-i-PrPz})_2Rh(CO)_2$ (57)

A sample of 76.9 mg (0.154 mmol) $[(CO)_2RhCl]_2$ was taken up in 10 mL CH_2Cl_2. 124.3 mg (0.46 mmol) of $KH_2B(3\text{-i-PrPz})_2$ was added, giving an instantaneous black solution. After stirring for 0.5 h, the solution was filtered through Celite, and a concentrated CH_2Cl_2 solution was chromatographed on neutral alumina (12 x 2.5 cm). Elution with CH_2Cl_2 and solvent removal gave a yellow oil (88.7 mg, 50% yield).

Characterization: IR (n-hexane) 2081, 2016 cm^{-1} (ν_{CO}). MS (120°C, 16 eV) M^+ (390, 3%), M^+-CO (96%), M^+-2CO (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 7.44 (d, 2H, $^3J_{H-H}$ = 2.2 Hz), 6.04 (d, 2H, $^3J_{H-H}$ = 2.2 Hz), 3.20 (septet, 2H, $^3J_{H-H}$ = 6.9 Hz), 1.23 (d, 12H, $^3J_{H-H}$ = 6.9 Hz). Anal. Calcd for $C_{14}H_{20}BN_4O_2Rh$: C, 43.11; H, 5.17; N, 14.36. Found: C, 42.36; H, 5.23; N, 14.03.

Preparation of $HB(3\text{-i-PrPz})_3Rh(CO)(Ph)(Br)$ (59)

A sample of 147.4 mg (0.296 mmol) 55 was taken up in 25 mL benzene and with a N_2 purge, the solution was irradiated for 20 min. HB(3-i-

PrPz)$_3$Rh(CO)(Ph)(H) (58) was detected by IR (ν_{Rh-H} = 2076 (w), ν_{CO} = 2048 (s) cm^{-1}), but the product is too unstable to isolate. 2 mL CBrCl$_3$ (excess) was added, and after 30 minutes, benzene and excess CBrCl$_3$ were removed in vacuo. The residue was chromatographed on neutral alumina (12 x 2.5 cm) with CH$_2$Cl$_2$ eluent, giving a yellow oil after solvent was removed. This was taken up in 5 mL hexane and cooled to -78°C giving yellow crystals (145.1 mg, 78% yield) mp 229-230°C.

Characterization: IR (n-hexane) 2085 cm^{-1} (ν_{CO}). MS (200°C, 70 eV) M$^+$ (627, 1%), M$^+$-Ph (3%), M$^+$-Ph-CO (3%), M$^+$-Ph-Br (96%), M$^+$-Ph-CO-Br (100%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, ambient) δ 8.02 (d, 1H, J = 8.3 Hz, o-Ph), 7.68 (d, 2H, $^3J_{H-H}$ = 2.4 Hz), 7.66 (d, 1H, $^3J_{H-H}$ = 2.5 Hz), 7.17 (t of d, 1H, J = 1.8 Hz, J = 7.5 Hz, m-Ph), 6.99 (t, 1H, J = 7.2 Hz, p-Ph), 6.84 (t of d, 1H, J = 1.8 Hz, J = 7.5 Hz, m'-Ph), 6.18 (d, 1H, $^3J_{H-H}$ = 2.3 Hz), 6.12 (d, 1H, $^3J_{H-H}$ = 2.4 Hz), 6.09 (d, 1H, $^3J_{H-H}$ = 2.5 Hz), 5.99 (d, 1H, J = 7.9 Hz, o'-Ph), 3.98 (septet, 1H, $^3J_{H-H}$ = 6.8 Hz), 2.80 (septet, 1H, $^3J_{H-H}$ = 6.7 Hz), 2.30 (septet, 1H, $^3J_{H-H}$ = 6.8 Hz), 1.29 (d, 3H, $^3J_{H-H}$ = 6.7 Hz), 1.24 (d, 3H, $^3J_{H-H}$ = 7.0 Hz), 1.04 (d, 3H, $^3J_{H-H}$ = 6.7 Hz), 0.97 (d, 3H, $^3J_{H-H}$ = 6.9 Hz), 0.70 (d, 3H, $^3J_{H-H}$ = 6.6 Hz), 0.58 (d, 3H, $^3J_{H-H}$ = 6.8 Hz). ^{13}C NMR (CD$_2$Cl$_2$, 75.5 MHz, ambient, APT) δ 183.18 (d, CO, $^3J_{Rh-C}$ = 61 Hz), 166.08, 164.67, 163.56 (s, 3-C), 143.84 (d, Rh-C, $^1J_{Rh-C}$ = 22 Hz), 141.60, 138.59 (s, Ph-C), 137.37, 136.56, 136.32 (s, 5-C), 128.66, 127.99, 124.78 (s, Ph-C), 104.29, 103.90, 102.77 (s, 4-C), 28.91, 28.51, 28.19 (s, CH(CH$_3$)$_2$), 25.59, 24.66, 24.48, 23.70, 22.77, 22.26 (s, CH$_3$). Anal. Calcd for C$_{25}$H$_{33}$BN$_6$OBrRh. (1/6C$_6$H$_{14}$): C, 48.68; H, 5.55; N, 13.10. Found: C, 48.78; H, 5.65; N, 12.96.

Preparation of $HB(3\text{-}i\text{-}PrPz)_2(C_3H_2N_2CH(CH_3)\overline{CH_2)R}h(CO)(Br)$ (61)

A sample of 157.0 mg (0.315 mmol) 55 was taken up in 25 mL cyclohexane. With a N_2 purge, the solution was irradiated for 20 min, whereupon $HB(3\text{-}i\text{-}PrPz)_2(C_3H_2N_2CH(CH_3)\overline{CH_2)R}h(CO)(H)$ (60) could be detected by IR spectroscopy (ν_{Rh-H} = 2070 (w), ν_{CO} = 2031 (s) cm^{-1}). This was not isolated but 2 mL $CBrCl_3$ (excess) was added, and after 30 min solvent was removed. The residue was chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent and solvent was removed in vacuo, giving a yellow oil. This was taken up in 5 mL hexane, and cooled -78°C giving yellow crystals (103.6 mg, 60% yield) mp 218-220°C.

<u>Characterization:</u> IR (n-hexane) 2068 cm^{-1} (ν_{CO}). MS (160°C, 16 eV) M^+ (550, 100%), M^+-CO (84%), M^+-Br (23%), M^+-CO-Br (58%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 7.73 (d, 1H, $^3J_{H-H}$ = 2.4 Hz), 7.65 (d, 1H, $^3J_{H-H}$ = 2.4 Hz), 7.43 (d, 1H, $^3J_{H-H}$ = 2.5 Hz), 6.21 (d, 1H, $^3J_{H-H}$ = 2.3 Hz), 6.08 (d, 1H, $^3J_{H-H}$ = 2.3 Hz), 5.95 (d, 1H, $^3J_{H-H}$ = 2.5 Hz), 3.80 (m, 1H, CH of intra ligand), 3.68 (septet, 1H, $^3J_{H-H}$ = 7.0 Hz), 3.46 (m, 1H, CH_2), 2.82 (septet, 1H, $^3J_{H-H}$ = 7.0 Hz), 2.56 (m, 1H, CH_2), 1.31 (d, 3H, $^3J_{H-H}$ = 7.0 Hz), 1.26 (d, 3H, $^3J_{H-H}$ = 7.0 Hz), 1.23 (d, 3H, $^3J_{H-H}$ = 7.0 Hz), 1.20 (d, 3H, $^3J_{H-H}$ = 7.0 Hz), 1.15 (d, 3H, $^3J_{H-H}$ = 7.0 Hz). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, ambient, APT) δ 186.53 (d, CO, $^1J_{Rh-C}$ = 58 Hz), 165.28, 163.70, 161.52 (s, 3-C), 138.31, 137.19, 136.97 (s, 5-C), 103.68, 102.35, 102.11 (s, 4-C), 39.05 (s, $CH(CH_3)_2$), 33.39 (d, Rh-C, $^1J_{Rh-C}$ = 18 Hz), 29.43, 28.73, 24.81, 24.43, 23.12, 22.71, 18.13 (s, two $CH(CH_3)_2$, five CH_3). Anal. Calcd for $C_{19}H_{27}BN_6OBrRh\cdot(1/6C_6H_{14})$: C, 41.56; H, 4.96; N, 15.31. Found: C, 42.39; H, 5.13; N, 14.78.

Reaction of (60) with benzene

A solution of 114.3 mg (0.229 mmol) **55** in 20 mL cyclohexane was irradiated for 20 min with a N_2 gas purge, generating **60**. 1 mL (excess) of benzene was added, and after one hour the reaction was complete with **58** present by IR spectroscopy (ν_{Rh-H} = 2077 (w), ν_{CO} = 2050 (s) cm^{-1}). A sample of 2 mL $CBrCl_3$ (excess) was added, and after 30 min solvent was removed. The bromide **59** was purified as previously described (99.1 mg, 69% yield).

Preparation of $HB(3\text{-}i\text{-}PrPz)_3\overline{Rh(CO)(CH_2CH_2CH_2})$ (62)

A solution of 90.2 mg (0.181 mmol) **55** in 20 mL cyclohexane was purged with cyclopropane for 20 min. The yellow solution was irradiated for 20 min with a cyclopropane purge, giving a colorless solution. The IR spectrum showed a mixture of mostly **60** (ν_{CO} = 2031 cm^{-1}) and some product **62** (ν_{CO} = 2026 cm^{-1}) (77:23 ratio by absorbance values). If the cyclopropane purge is continued for 20 min, only **62** is present by IR. After solvent was removed in vacuo, the residues were chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent. After removal of solvent, a tan oil remained, which on pumping in high vacuum gave a fluffy off-white solid (81.8 mg, 88% yield), mp 141-143°C (dec).

Characterization: IR (n-hexane) 2027 cm^{-1} (ν_{CO}). MS (180°C, 70 eV) $M^+-C_3H_6$ (470, 40%), $M^+-CO-C_3H_6$ (100%), $M^+-CO-C_3H_6$-3-i-PrPz (66%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 7.63 (d, 1H, $^3J_{H-H}$ = 2.2 Hz), 7.53 (d, 2H, $^3J_{H-H}$ = 2.2 Hz), 6.21 (d, 1H, $^3J_{H-H}$ = 2.4 Hz), 6.06 (d, 2H, $^3J_{H-H}$ = 2.4 Hz), 3.58 (septet, 1H, $^3J_{H-H}$ = 6.8 Hz), 3.37 (septet, 2H, $^3J_{H-H}$ = 6.8

Hz), 3.05 (m, 1H, H_c), 2.96 (m, 1H, H_d), 1.75 (m, 2H, H_a), 1.54 (m, 2H, H_b), 1.31 (d, 6H, $^3J_{H-H}$ = 6.8 Hz), 1.27 (d, 6H, $^3J_{H-H}$ = 6.8 Hz), 1.12 (d, 6H, $^3J_{H-H}$ = 6.6 Hz). Anal. Calcd for $C_{22}H_{34}BN_6O_1Rh$: C, 51.58; H, 6.69; N, 16.41. Found: C, 51.60; H, 6.65; N, 15.91.

Preparation of 3-Et-5-MePzH (63)

A sample of 4.76 g (5 mL, 0.042 mol) of 2,4-hexanedione was added dropwise over 0.5 h at 5°C to a solution of 2.21 g (0.044 mol) hydrazine hydrate in 40 mL 95% EtOH. After stirring for 1 h, solvent was removed in vacuo giving a pale yellow oil. Distillation at 77-80°C/0.1 mm Hg gave a clear liquid (3.94 g, 81% yield).

Characterization: MS (100°C, 70 eV) M^+ (110, 100%), M^+-CH_3 (96%), $M^+-CH_2CH_3$ (3%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 11.98 (br, 1H), 5.90 (s, 1H), 2.70 (q, 2H, $^3J_{H-H}$ = 7.8 Hz), 2.33 (s, 3H), 1.28 (t, 3H, $^3J_{H-H}$ = 7.8 Hz). Anal. Calcd for $C_6H_{10}N_2$: C, 65.42; H, 9.15; N, 25.43. Found: C, 65.38; H, 9.02; N, 25.24.

Preparation of KHB(Et,MePz)$_3$ (64)

A sample of 3.917 g (35.55 mmol) of freshly distilled **63** and 479.5 mg (8.89 mmol) KBH_4 were heated slowly with stirring to 270°C (fused salt bath temperature[31]) until gas evolution ceased. The melt was cooled down, and vigorous stirring with 50 mL hexane gave a white solid (1.162 g, 35% yield) mp 115-125°C.

Characterization: ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 5.78 (s, 3H), 2.61, 2.60, 2.46, 2.45 (q, 6H total, $^3J_{H-H}$ = 8 Hz), 2.19, 2.11, 2.10, 2.09 (s, 9H total), 1.15, 1.10, 1.09, 1.07 (t, 9H total, $^3J_{H-H}$ = 8 Hz). Anal. Calcd for $C_{18}H_{28}BN_6K$: C, 57.14; H, 7.46; N, 22.21. Found: C, 56.19; H, 7.51; N, 22.40.

Preparation of HB(Et,MePz)$_3$Rh(CO)$_2$ (65)

A sample of 135.3 mg (0.348 mmol) $[(CO)_2RhCl]_2$ was taken up in 15 mL CH_2Cl_2. To this solution was added 264.1 mg (0.698 mmol) of **64**. After stirring for 1 h, the yellow solution was filtered through Celite, and a concentrated hexane solution was chromatographed on neutral alumina (12 x 2.5 cm). Elution with hexane gave 15 mg (0.028 mmol) of $[(CO)_2Rh(3\text{-}Et\text{-}5\text{-}MePz)]_2$ **66** which was identified by comparison of ^1H NMR, IR and MS spectra to an authentic sample. Further elution of the column with CH_2Cl_2 followed by CH_3CN gave a yellow air-sensitive solid after solvent was removed in vacuo (204.2 mg, 59% yield) mp 162-164°C.

Characterization: IR (n-hexane) 2054, 1980 cm^{-1} (ν_{CO}). MS (150°C, 16 eV) M^+ (498, 67%), M^+-CO (100%), M^+-2CO (96%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 5.88 (s, 3H), 2.81, 2.78 (q, 6H total, $^3J_{H-H}$ = 8 Hz), 2.41, 2.36 (s, 9H total), 1.27, 1.21 (t, 9H total, $^3J_{H-H}$ = 8 Hz). Anal. Calcd for $C_{20}H_{28}BN_6O_2Rh$: C, 48.22; H, 5.66; N, 16.87. Found: C, 47.93; H, 5.63; N, 16.78.

Preparation of $[(CO)_2Rh(3\text{-}Et\text{-}5\text{-}MePz)]_2$ (66)

A solution of 37.2 mg (0.663 mmol) KOH and 70.6 mg (0.640 mmol) **63** in 3 mL MeOH was added to 117.9 mg (0.303 mmol) $[(CO)_2RhCl]_2$ in 9 mL Et_2O. After stirring for 1 h, solvent was removed. The residues were taken up in 25 mL benzene and filtered through Celite. After removing benzene, the solid was purified by sublimation onto a dry ice probe at 80°C/0.1 mm Hg giving a yellow solid (136.6 mg, 84% yield), mp 65-75°C.

Characterization: IR (n-hexane) 2086, 2072, 2018 cm^{-1} (ν_{CO}). MS (70°C, 16 eV) M^+ (536, 100%), M^+-CO (33%), M^+-2CO (36%), M^+-3CO (6%), M^+-4CO (9%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 5.89 (s, 2H, both isomers), For major isomer: 2.72 (q, 4H, $^3J_{H-H}$ = 7.7 Hz), 2.33 (s, 6H), 1.24 (t, 6H, $^3J_{H-H}$ = 7.6 Hz). For minor isomer: 2.73 (q, 4H, $^3J_{H-H}$ = 7.9 Hz), 2.31 (s, 6H), 1.27 (t, 6H, $^3J_{H-H}$ = 7.6 Hz), Ratio 1.09:1. Anal. Calcd for $C_{16}H_{18}N_4O_4Rh_2$: C, 35.84; H, 3.38; N, 10.45. Found: C, 35.97; H, 3.31; N, 10.56.

Preparation of 3-i-Bu-5-MePzH (67)

A sample of 40.15 g (0.282 mol) 6-methyl-2,4-heptanedione was added dropwise over 0.5 h at 5°C to a solution of 14.84 g (0.296 mol) hydrazine hydrate in 350 mL 95% EtOH. After stirring for 2 h, solvent was removed in vacuo giving a pale yellow oil. Distillation at 76-81°C/0.3 mm Hg gave a clear oil. This was stored under argon at -30°C, where it slowly solidified (37.35 g, 96% yield).

Characterization: MS (70°C, 16 eV) M^+ (138, 78%), M^+-CH_3 (81%), M^+-$(CH_3)_2CH$ (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 11.00 (br, 1H), 5.84 (s, 1H), 2.48 (d, 2H, $^3J_{H-H}$ = 7.2 Hz), 2.27 (s, 3H), 1.89 (nonet, 1H, $^3J_{H-H}$ = 6.8 Hz), 0.92 (d, 6H, $^3J_{H-H}$ = 6.6 Hz). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, APT, DEPT, ambient) δ 148.10, 144.88 (C_3,C_5), 103.88 (C_4), 36.44 (CH_2); 29.32 (CH), 22.55 $(CH_3)_2$, 12.56 (CH_3). Anal. Calcd for $C_8H_{14}N_2$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.60; H, 10.08; N, 19.98.

Preparation of $KH_2B(i\text{-}Bu,MePz)_2$ (68)

A sample of 3.216 g (23.27 mmol) freshly distilled **67** and 628 mg (11.27 mmol) KBH_4 were heated together in 50 mL refluxing DMAC until gas evolution ceased. Solvent was distilled off under reduced pressure (128°C/140 mm Hg), leaving a cloudy oil. This was taken up in 10 mL hexane, giving a cloudy solution which was used for the next reaction.

Preparation of $H_2B(i\text{-}Bu,MePz)_2Rh(CO)_2$ (69)

A sample of 220.4 mg (0.567 mmol) $[(CO)_2RhCl]_2$ was taken up in 20 mL hexane. To this solution was added 0.97 mL (1.134 mmol) of **68**, giving an immediate black solution. After stirring for 15 min, the solution was filtered through Celite, then chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent giving a yellow oil after solvent was removed in vacuo (235.1 mg, 46% yield).

<u>Characterization</u>: IR (n-hexane) 2079, 2012 cm^{-1} (ν_{CO}). MS (130°C, 16 eV) M^+ (446, 5%), M^+-CO (83%), M^+-2CO (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 5.80, 5.79, 5.77 (s, 2H total), 2.60-2.48 (m, 4H total), 2.36, 2.31, 2.27 (s, 6H total), 2.04, 2.02, 1.82 (m, 2H total), 0.93, 0.92, 0.87 (d, 12H total, $^3J_{H-H}$ = 7 Hz). Anal. Calcd for $C_{18}H_{28}BN_4O_2Rh$: C, 48.46; H, 6.33; N, 12.56. Found: C, 48.28; H, 6.33; N, 12.58.

Preparation of $KHB(i\text{-}Bu,MePz)_3$ (70)

A sample of 3.950 g (28.58 mmol) freshly distilled **67** and 392.3 mg

(7.27 mmol) KBH_4 were heated slowly with stirring to 270°C (fused salt bath temperature[31]) until gas evolution ceased. Excess **67** was distilled off, leaving a light yellow oil-solid. Vigorous stirring with 50 mL hexane gave an off-white solid, which was filtered and dried in vacuo (2.092 g, 62% yield) mp 152-155°C.

Characterization: MS (145°C, 16 eV) M^+ (462, 41%), M^+-i-Bu,MePzH (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 5.73 (s, 3H), 2.52 (d, J = 6.9 Hz), 2.31 (d, J = 7.1 Hz) (6H total), 2.20, 2.19, 2.11, 2.09 (s, 9H total), 1.77 (nonet, 3H), 0.89 (d, J = 6.9 Hz), 0.85 (d, J = 6.9 Hz) (18H total). Anal. Calcd for $C_{24}H_{40}BN_6K$: C, 62.32; H, 8.72; N, 18.17. Found: C, 58.47; H, 8.37; N, 17.11.

Preparation of HB(i-Bu,MePz)$_3$Rh(CO)$_2$ (71)

A sample of 316.1 mg (0.813 mmol) $[(CO)_2RhCl]_2$ was taken up in 20 mL hexane. To this solution was added 752.0 mg (1.63 mmol) of **70**. After stirring for 1 h, the yellow solution was filtered through Celite, and a concentrated hexane solution was chromatographed on neutral alumina (12 x 2.5 cm). Elution with hexane gave 15.4 mg (0.026 mmol) of $[(CO)_2Rh(3\text{-}i\text{-}Bu\text{-}5\text{-}MePz)]_2$ **72** which was identified by comparison of ^1H NMR, IR and MS spectra to an authentic sample. Further elution of the column with CH_2Cl_2 followed by CH_3CN gave a yellow oil after solvent was removed. A yellow powder was obtained as a benzene solvate (599.2 mg, 63% yield) mp 154-155°C.

Characterization: IR (n-hexane) 2079 (w), 2054 (s), 2014 (w), 1981 (s) cm^{-1} (ν_{CO}). MS (150°C, 16 eV) M^+ (582, 100%), M^+-CO (97%), M^+-2CO

(11%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 7.37 (s, 3H), 5.86, 5.84 (s, 3H total), 2.66, 2.64, 2.63 (d, 6H total, $^3J_{H-H}$ = 7 Hz), 2.40, 2.35 (s, 9H total), 2.04, 1.83 (m, 3H total), 0.96, 0.95, 0.94 (d, 18H, $^3J_{H-H}$ = 7 Hz). ^{13}C NMR (CD_2Cl_2, CO region, ^{13}CO enriched, 100.6 MHz, ambient) δ 190.55 (d, CO, $^1J_{Rh-C}$ = 69 Hz), 190.14 (d, CO, $^1J_{Rh-C}$ = 69 Hz), 189.60 (d, CO, $^1J_{Rh-C}$ = 69 Hz). (Remainder, 75.5 MHz, APT, ambient) δ 153.90, 153.67, 150.16, 149.27, 144.95, 144.62 (C_3,C_5), 106.02, 105.96, 105.57, 105.45 (C_4), 39.02, 36.51, 36.41 (CH_2), 29.42, 29.32, 29.19 (CH), 22.83, 22.76 $(CH_3)_2$, 15.70, 15.55, 13.04 (CH_3). Anal. Calcd for $C_{26}H_{40}BN_6O_2Rh.(1/2C_6H_6)$: C, 56.05; H, 6.97; N, 13.52. Found: C, 55.78; H, 7.04; N, 13.50.

Preparation of $[(CO)_2Rh(3\text{-i-Bu-5-MePz})]_2$ (72)

A solution of 41.3 mg (0.736 mmol) KOH and 98.2 mg (0.711 mmol) 67 in 3 mL MeOH was added to 130.9 mg (0.337 mmol) $[(CO)_2RhCl]_2$ in 9 mL Et_2O. After stirring for 1 h, solvent was removed. The residues were taken up in 25 mL benzene and filtered through Celite. The dark red oil obtained after removal of benzene in vacuo was chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 giving a yellow oil (88.1 mg, 44% yield).

Characterization: IR (n-hexane) 2086, 2072, 2018 cm^{-1} (ν_{CO}). MS (120°C, 16 eV) M^+ (592, 100%), M^+-CO (40%), M^+-2CO (28%), M^+-3CO (9%), M^+-4CO (9%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ For major isomer: 5.80 (s, 2H), 2.53 (d, 4H, $^3J_{H-H}$ = 7.1 Hz), 2.27 (s, 6H), 2.06 (nonet, 2H, $^3J_{H-H}$ = 7 Hz), 0.89 (d, 12H, $^3J_{H-H}$ = 6.6 Hz). For minor isomer: 5.84 (s, 2H), 2.54 (d, 4H, $^3J_{H-H}$ = 7.3 Hz), 2.32 (s, 6H), 1.98 (nonet, 2H, $^3J_{H-H}$ = 7 Hz), 0.82 (d, 12H, $^3J_{H-H}$ = 6.6 Hz), Ratio 1.80:1. Anal. Calcd for $C_{20}H_{26}N_4O_4Rh_2$: C, 40.56; H, 4.42; N, 9.46. Found: C, 40.72; H, 4.48; N, 9.49.

Preparation of 3-CF_3CF_2-5-MePzH (73)

A sample of 14.72 g (0.072 mol) 1,1,1,2,2-pentafluoro-3,5-hexanedione was added dropwise over 0.5 h at 5°C to a solution of 4.45 g (0.076 mol) hydrazine hydrate in 110 mL 95% EtOH. After stirring for 1 h, the solvent was removed in vacuo giving a crude white solid. Distillation at 170°C/0.3 mm Hg gave a clear oil, which solidified on standing. It was further purified by sublimation onto a dry ice probe at 70°C/0.3 mm Hg (9.33 g, 65% yield) mp 85-87°C.

Characterization: MS (60°C, 16 eV) M^+ (200, 100%), M^+-CF_2 (1%), M^+-CF_3 (18%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 10.76 (br, 1H), 6.36 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, ambient) δ 141.95 (s, C-CH_3), 141.72 (t, C-CF_2, $^2J_{F-C}$ = 28 Hz), 119.34 (q of t, CF_3, $^1J_{F-C}$ = 285 Hz, $^2J_{F-C}$ = 39 Hz), 111.49 (t of q, CF_2, $^1J_{F-C}$ = 252 Hz, $^2J_{F-C}$ = 39 Hz), 104.37 (s, C-H), 10.57 (s, CH_3). ^{19}F NMR (CD_2Cl_2, ambient) δ -85.45 (s, 3F, CF_3), -113.55 (s, 2F, CF_2). Anal. Calcd for $C_6H_5N_2F_5$: C, 36.01; H, 2.52; N, 14.00. Found: C, 35.51; H, 2.08; N, 14.24.

Preparation of $[(CO)_2Rh(3\text{-}CF_3CF_2\text{-}5\text{-}MePz)]_2$ (74)

A solution of 36.4 mg (0.649 mmol) KOH and 125.5 mg (0.627 mmol) 73 in 3 mL MeOH was added to 115.5 mg (0.297 mmol) $[(CO)_2RhCl]_2$ in 9 mL Et_2O. After stirring for 1 h, solvent was removed. The residues were taken up in 25 mL benzene and filtered through Celite. The product was obtained as a yellow powder after sublimation at 80°C/0.1 mm Hg onto a -78°C probe (177.3 mg, 83% yield) mp 81-83°C.

Characterization: IR (n-hexane) 2101, 2083, 2034 cm^{-1} (ν_{CO}). MS (120°C, 16 eV) M$^+$ (716, 100%), M$^+$-CO (27%), M$^+$-2CO (22%), M$^+$-3CO (6%), M$^+$-4CO (11%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 6.33 (br, 2H, not resolved), 2.39 (s, 6H, major isomer), 2.35 (s, 6H, minor isomer) Ratio 2.49:1. Anal. Calcd for $C_{16}H_8N_4O_4F_{10}Rh_2$: C, 26.84; H, 1.13; N, 7.82. Found: C, 27.55; H, 1.32; N, 7.88.

Preparation of 3-Ph-5-CF_3PzH (75)

A sample of 53.35 g (0.247 mol) of benzoyltrifluoroacetone was added slowly over 0.5 h at 5°C to a solution of 15.27 g (0.259 mol) hydrazine hydrate in 250 mL 95% EtOH. After stirring for 2 h, a thick slurry resulted and the solvent was removed in vacuo leaving a crude white solid. Distillation at 180°C/0.5 mm Hg gave a clear oil, which solidified on standing (48.47 g, 92% yield) mp 102-105°C.

Characterization: MS (120°C, 16 eV) M$^+$ (212, 66%), M$^+$-F (31%), M$^+$-CF_3 (100%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 12.45 (br, 1H), 7.61-7.41 (m, 5H), 6.76 (s, 1H). ^{19}F NMR (CD_2Cl_2, 200 MHz, ambient) δ -62.62 (s). Anal. Calcd for $C_{10}H_7N_2F_3$: C, 56.61; H, 3.33; N, 13.20. Found: C, 56.47; H, 3.17; N, 13.06.

Preparation of $[(CO)_2Rh(3\text{-}Ph\text{-}5\text{-}CF_3Pz)]_2$ (76)

A solution of 35.6 mg (0.634 mmol) KOH and 130.0 mg (0.613 mmol) 75 in 4 mL MeOH was added to 112.9 mg (0.290 mmol) $[(CO)_2RhCl]_2$ in 10 mL

Et_2O. After stirring for 1 h, solvent was removed. The residues were taken up in 25 mL benzene and filtered through Celite. Removal of benzene gave a dark red oil which was chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 giving a yellow oil upon removal of solvent, which crystallized on standing (166.3 mg, 77% yield) mp 150-153°C.

Characterization: IR (n-hexane) 2101, 2086, 2037 cm^{-1} (ν_{CO}). MS (150°C, 16 eV) M^+ (740, 100%), M^+-CO (4%), M^+-2CO (34%), M^+-3CO (8%), M^+-4CO (12%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 8.00 (m, major isomer, o-Ph), 7.90 (m, minor isomer, o-Ph), (2H total), 7.50 (m, 3H, not resolved), 6.86 (s, major isomer), 6.80 (s, minor isomer) (1H total), Ratio 4.02:1. Anal. Calcd for $C_{24}H_{12}N_4O_4F_6Rh_2$: C, 38.94; H, 1.63; N, 7.57. Found: C, 39.56; H, 1.61; N, 7.59.

Preparation of $^{15}N_2$-3,5-$(CH_3)_2$PzH (77)

The procedure of Wiley and Hexner was followed.[10] From 1.0 g (7.57 mmol) of hydrazine-$^{15}N_2$-sulphate one obtained after sublimation (50°C/0.3 mm Hg onto water-cooled probe) 635.3 mg (86% yield) of crystalline product, mp 106-109°C.

Characterization: IR (Nujol) 3186, 3127, 3100, 3022, 1653, 1588, 1420, 1301, 1148, 1122, 1014, 997, 977, 851, 780, 729, 663 cm^{-1}. IR (CCl_4) 3466 (ν_{N-H}), 3186, 3129, 3105, 3023, 2976, 2927, 2869, 1581 ($\nu_{C=N}$), 1478, 1450, 1416, 1300 cm^{-1}. MS (100°C, 70 eV) M^+ (98, 100%), M^+-H (78%), M^+-CH_3 (17%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 11.86 (br, 1H), 5.86 (t, 1H, $^3J_{N-H}$ = 3.0 Hz), 2.26 (d, 6H, $^3J_{N-H}$ = 2.8 Hz). At (-83°C, 400 MHz) 13.83 (d, 1H, $^1J_{N-H}$ = 88 Hz). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, ambient) δ 144.57 (br, C_3, C_5), 104.20 (s, C_4), 12.28 (d, CH_3, $^2J_{N-C}$ = 5 Hz). ^{15}N NMR (CD_2Cl_2, 40.5 MHz, -83°C) δ 282.54, (br, 1N), 207.58 (br. d, 1N, $^1J_{N-H}$ = 90 Hz). $^{15}N\{^1H\}$ NMR (CD_2Cl_2, 40.5 MHz, -83°C) δ 282.54, (br, 1N), 207.58 (br, 1N). Anal. Calcd for C_5H_8 (98.6% $^{15}N_2$): C, 61.21; H, 8.22; N, 28.55. Found: C, 61.21; H, 8.41; N, 28.99.

Preparation of $^{15}N_6$-KHBPz*$_3$ (78)

A modified procedure of Trofimenko was employed. A sample of 614.6 mg (6.26 mmol) **77** and 67.7 mg (1.25 mmol) KBH_4 were heated together with stirring under argon, slowly until the bath temperature reached 270°C (fused salt bath).[31] The melt was cooled under argon. Excess **77** was sublimed off (170.0 mg, 1.73 mmol), leaving 400.0 mg (93% yield) of crude **78**.

Preparation of $^{15}N_6$-(HBPz*$_3$)Rh(CO)(C_2H_4) (79)

The procedure of Ghosh was followed with minor modifications. A sample of 112.8 mg (0.29 mmol) $[(CO)_2RhCl]_2$ and 112.8 mg (0.29 mmol) $[(C_2H_4)_2RhCl]_2$ were stirred together in 50 mL toluene for 0.5 h, giving 0.58 mmol $[(CO)(C_2H_4)RhCl]_2$. To this solution was added 397.8 mg (1.16 mmol) **78**, and this was stirred in the dark for 2.5 h. Solvent was removed in vacuo, and the residues were chromatographed on neutral alumina (12 x 2.5 cm) with CH_2Cl_2 eluent. A total of 395.6 mg (74% yield) of **79** was obtained as a yellow powder. Further elution of the column with CH_3CN gave an orange band, which by IR was a mixture of **79** and $^{15}N_6$-(HBPz*$_3$)Rh(CO)$_2$ **80**. CO purge of a CH_2Cl_2 solution for 0.5 h converted the mixture to pure **80** (23.1 mg, 4% yield).

Characterization: IR (hexane) 2013 cm^{-1} (ν_{CO}). MS (160°C, 70 eV) M^+ (462, 3%), M^+-CO/C_2H_4 (100%), M^+-CO-C_2H_4 (53%). ^{13}C NMR (CD_2Cl_2, 100.6 MHz, ambient, 70% ^{13}CO enriched) δ 189.97 (d of q, $^1J_{Rh-C}$ = 64 Hz, $^2J_{N-C}$ = 6 Hz), 144.64 (br), 106.82 (br), 24.21 (d, $^1J_{Rh-C}$ = 14.4 Hz), 12.83 (br). (At -40°C) δ 189.25 (d of d, $^1J_{Rh-C}$ = 64 Hz, $^2J_{N-C}$ = 18 Hz), 152.29 (d, J_{N-C} = 5 Hz, 1C), 149.84 (d, J_{N-C} = 5 Hz, 2C), 144.58 (d, J_{N-C} = 10 Hz, 1C), 144.58 (d, J_{N-C} = 10 Hz, 1C), 144.14 (d, J_{N-C} = 10 Hz, 2C), 108.68 (s, 1C), 105.19 (s, 2C), 23.35 (d, $^1J_{Rh-C}$ = 15 Hz), 14.62 (d, J_{N-C} = 6 Hz, 2C), 13.46 (s, 1C), 12.18 (s, 3C). ^{15}N NMR (CD_2Cl_2, 40.5 MHz, -60°C) δ 248.92, (t, 2N, bound N1, $^1J_{Rh-N}$ = 12 Hz, $^1J_{N-N}$ = 12 Hz), 227.00 (AB quartet, 2N, free N1 and N2), 223.20 (br. d, 2N, bound N2, $^1J_{N-N}$ = 12 Hz). Anal. Calcd for $C_{18}H_{26}B(^{15}N_6)ORh$: C, 46.78; H, 5.67; N, 18.19. Found: 46.09; H, 5.91; N, 17.63.

Preparation of $^{15}N_6$-(HBPz*$_3$)Rh(CO)$_2$ (80)

Although small quantities of **80** can be obtained from the preparation of **79** above, a more rational route is described. Of course **80** could be prepared according to Ghosh[1] or as follows. To a solution of 45.0 mg (0.097 mmol) of **79** in 10 mL CH_2Cl_2 was bubbled through CO. After 5 min, the reaction was complete, so solvent was removed in vacuo, leaving an orange solid (43.2 mg, 96% yield).

Characterization: IR (hexane) 2054, 1981 cm^{-1} (ν_{CO}). MS (180°C, 70 eV) M^+ (462, 8%), M^+-CO (37%), M^+-2CO (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 5.82 (m, 3H), 2.38 (d, 9H, $^3J_{N-H}$ = 3.0 Hz), 2.33 (d, 9H, $^3J_{N-H}$ = 2.0 Hz). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, ambient, 70% ^{13}CO enriched) δ 190.35 (d of q, $^1J_{Rh-C}$ = 69 Hz, $^2J_{N-C}$ = 5 Hz), 150.20 (d, J_{N-C} = 5

Hz), 145.21 (d, J_{N-C} = 10 Hz), 106.16 (d, J_{N-C} = 2 Hz), 15.35 (d, J_{N-C} = 6 Hz), 12.80 (s). ^{15}N NMR (CD_2Cl_2, 40.5 MHz, -60°C) δ 245.08, (t, 3N, N1, $^{1}J_{Rh-N}$ = 11 Hz, $^{1}J_{N-N}$ = 11 Hz), 223.25 (br. d, 3N, N2, $^{1}J_{N-N}$ = 11 Hz).

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CHAPTER VI

CARBORANE PLATINUM COMPLEXES

Section 1

INTRODUCTION

The carborane anions [nido-7,8-$C_2B_9H_9R'_2$]$^{2-}$ (R' = H, Me) were first prepared by Hawthorne,[1] who prepared several transition metal derivatives and compared them to known cyclopentadienyl analogs. Both ligands are π-bound to the metal from an open pentagonal face, although the carborane anions are dinegative, while the cyclopentadienyl anion is uninegative. The carborane anion [nido-7,8-$C_2B_9H_{11}$]$^{2-}$ is considered to be electronically and sterically similar to the pentamethylcyclopentadienyl anion ($C_5Me_5^-$) ($Cp*^-$) in transition metal complexes.[2] The many interesting reactions of Cp*Ir$(CO)_2$ and related analogs have prompted the synthesis of carborane analogs. Owing to ligand charge differences, the use of Pt(II) in place of Ir(I) would lead to neutral platinacarborane complexes.

Over the last twenty years metallacarboranes have come to be known for virtually every transition metal, with many analogs to known cyclopentadienyl complexes.[3] However, very few types of platinacarboranes are known. Hawthorne and coworkers have prepared [closo-(COD)-3,1,2-Pt($C_2B_9H_{11}$)][4] (COD = 1,5-cyclooctadiene), while two other groups have prepared several derivatives of the type [closo-3,3-$(L)_2$-3,1,2-Pt($C_2B_9H_{11}$)],[5] as well as palladium and nickel analogs. These papers have dealt mainly with the structural aspects of the carborane ligands in these d^8 metal systems, but have not explored their subsequent chemistry. This Chapter deals with the synthesis, structural characterization and reactions of several platinacarboranes.

The intent of this work was to prepare complexes of the type

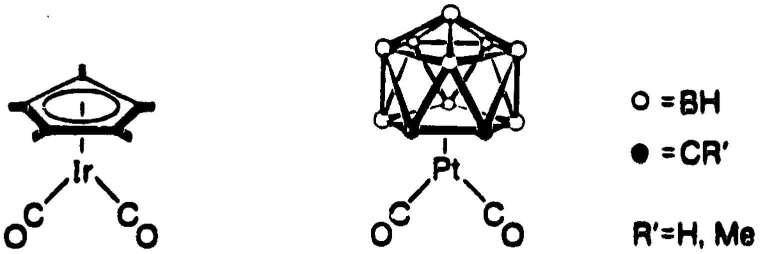
[<u>closo</u>-3-(CO)-3-(L)-3,1,2-Pt($C_2B_9H_9R'_2$)] (L = CO, PR_3, R' = H, Me) and investigate some of the reactions of these complexes which are typical of Cp*Ir$(CO)_2$. The synthesis and subsequent chemistry of these complexes will be discussed in this Chapter, including the X-ray structure of a complex.

Section 2

SYNTHESIS AND PROPERTIES OF COMPLEXES

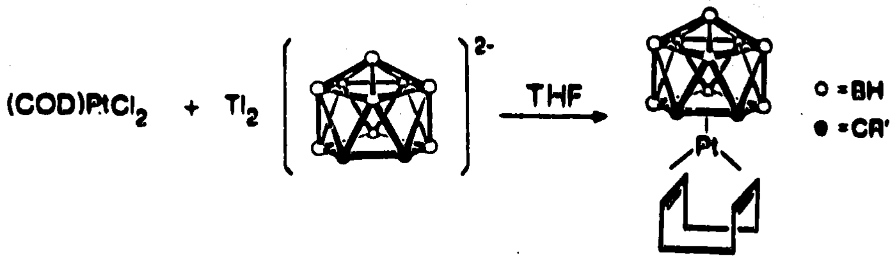
The first platinacarborane reported in the literature was [closo-(COD)-3,1,2-Pt($C_2B_9H_{11}$)] (**81**) by Hawthorne and coworkers.[4] As was mentioned in the paper, "The isolation of this platinum complex suggests that others of the general type L_2-3,1,2-Pt($C_2B_9H_{11}$) where L = a two-electron donor ligand, could be synthesized".[4]

The initial report of C-H activation with Cp*Ir(CO)$_2$[6a] in this research group has prompted the search for other such complexes. The initial target complex in this work is the platinum carborane analog, that is [closo-3,3-(CO)$_2$-3,1,2-Pt($C_2B_9H_9R'_2$)] (R' = H, Me) (eq. 6-1).



(6-1)

As Hawthorne pointed out, such complexes could be accessible from the COD complexes [closo-(COD)-3,1,2-Pt($C_2B_9H_9R'_2$)] (R' = H, Me). The COD complex **81** with R' = H has been prepared by Hawthorne[4] and the dimethyl analog is prepared by the same route. [closo-(COD)-3,1,2-Pt($C_2B_9H_9Me_2$)] (**82**) was prepared by reacting (COD)PtCl$_2$[7] and $Tl_2C_2B_9H_9Me_2$[8] in THF (eq. 6-2).



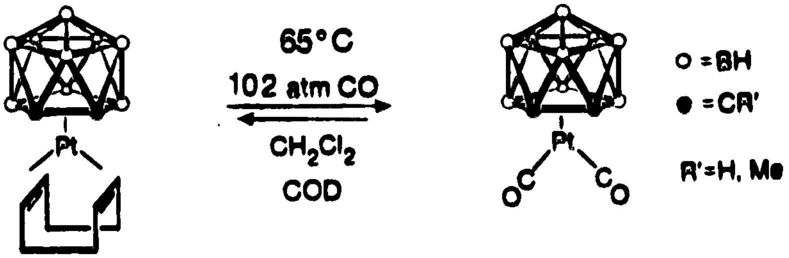
(6-2)

81 R'=H

82 R'=Me

The complex was isolated as a yellow solid, and as with Hawthorne's analog **81**, this compound did not analyze well, but was similarly characterized by ^{1}H NMR and mass spectral data.

Reaction of **82** with 1500 psi (102 atm) CO in CH_2Cl_2 at 65°C for 4 days resulted in partial converstion to the desired product [*closo*-3,3-$(CO)_2$-3,1,2-$Pt(C_2B_9H_9Me_2)$] (**83**) (eq. 6-3).



(6-3)

81 R'=H

82 R'=Me

83 R'=Me

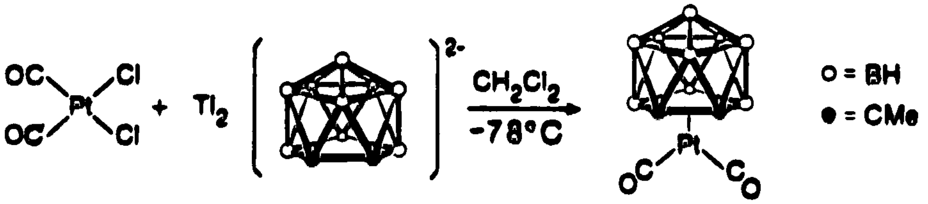
84 R'=H

The IR spectrum in hexane showed ν_{CO} at 2118 and 2079 cm^{-1}. However, the ^{1}H NMR spectrum showed only 40% of product **83** and 60% **82**. Longer reaction times and varying pressures and temperatures failed to improve the conversion. One possible problem is the reaction of the liberated COD with **83** when the CO pressure is removed to give back **82**.

In fact, when excess COD is added to the reaction mixture, the IR spectrum shows the disappearance of **83** in about one hour.

The analogous CO reaction with Hawthorne's complex [*closo*-(COD)-3,1,2-Pt($C_2B_9H_{11}$)] **81** resulted in some conversion, with IR evidence for [*closo*-3,3-$(CO)_2$-3,1,2-Pt($C_2B_9H_{11}$)] (**84**) (ν_{CO} at 2121, 2082 cm^{-1}). Unfortunately **84** appears much less stable than **83**, as removal of solvent results in decomposition. The enhanced stability of the dimethyl carborane complex **83** over **84** appears similar to the stability of some Cp* metal complexes over the Cp analogs. The dimethyl carborane ligand is slightly more electron donating, as observed by the slightly lower CO bands for **83**.

A more direct route to **83** in pure form, albeit in low yield, is by the reaction of $(CO)_2PtCl_2$[9] and $Tl_2C_2B_9H_9Me_2$ in CH_2Cl_2 under one atmosphere CO at -78°C (eq. 6-4).



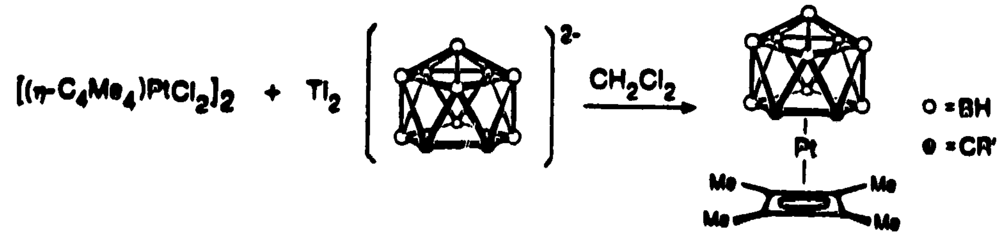
(6-4)

83

The ^1H NMR spectrum of analytically pure **83** shows a singlet at δ 2.56, and the mass spectrum shows the molecular ion M^+ at m/e = 411, with sequential loss of CO. Unfortunately, **83** is unstable even at -30°C under an inert atmosphere. The reaction of pure complex **83** and excess COD in hexane gives a good conversion to the COD complex **82** in about an hour (eq. 6-3).

A remarkable difference in the carborane platinum and Cp* iridium systems is observed. The IR spectrum of [*closo*-3,3-$(CO)_2$-3,1,2-$Pt(C_2B_9H_9Me_2)$] **83** in hexane shows ν_{CO} bands at 2118 and 2079 cm^{-1}, while for $Cp^*Ir(CO)_2$ ν_{CO} is 2020 and 1953 cm^{-1}.[10] This suggests that the carborane ligand is a much poorer electron donor than the Cp* ligand. The analogous reaction of $(CO)_2PtCl_2$ with $Tl_2C_2B_9H_{11}$ failed to give any **84**.

Other routes for the preparation of **83** and **84** were explored. Cyclobutadiene metallacarborane complexes are rare, although many mixed sandwich compounds of metallacarboranes are known.[3] Hawthorne has prepared a pair of cyclobutadienyl palladium carborane complexes, $(\eta^4-C_4Ph_4)$-3,1,2-$Pd(C_2B_9H_{11})$ and $(\eta^4-C_4Ph_4)$-3,1,2-$Pd(C_2B_9H_9Me_2)$.[11] Platinum analogs have been prepared by the reaction of $[(\eta^4-C_4Me_4)PtCl_2]_2$[12] with $Tl_2C_2B_9H_9R'_2$ (R' = H, Me) in CH_2Cl_2. Good yields of $(\eta^4-C_4Me_4)$-3,1,2-$Pt(C_2B_9H_{11})$ (**85**) and $(\eta^4-C_4Me_4)$-3,1,2-$Pt(C_2B_9H_9Me_2)$ (**86**) were obtained as air stable tan solids (eq. 6-5).



(6-5)

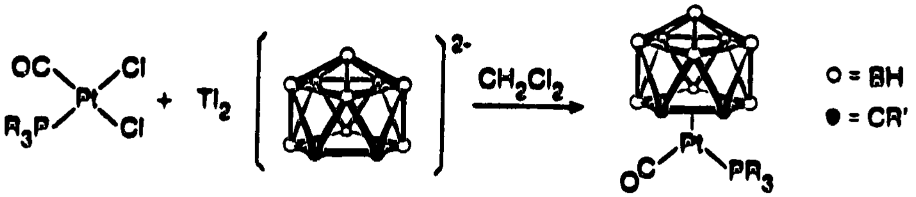
85 R'=H

86 R'=Me

For complex **86**, the ^1H NMR spectrum shows a singlet with platinum satellites at δ 2.15 (12H, $^3J_{Pt-H}$ = 22 Hz) for the C_4Me_4 group, and a singlet at δ 2.08 (6H) for the methyl groups of the carborane ligand.

Unfortunately, the complexes **85** and **86** did not react with CO under the same conditions as with the COD complexes.

The relative difficulty in obtaining large amounts of pure dicarbonyl **83**, as well as its instability prompted the search for other related complexes. A mixed phosphine carbonyl complex, that is an analog of Cp*Ir(CO)(PMe$_3$)^{13} was sought. Reaction of $Tl_2C_2B_9H_9R'_2$ (R' = H, Me), with $(PR_3)(CO)PtCl_2$^{14,15} in CH_2Cl_2 yields neutral complexes of the type [closo-3-(PR$_3$)-3-(CO)-3,1,2-Pt($C_2B_9H_9R'_2$)] (eq. 6-6).

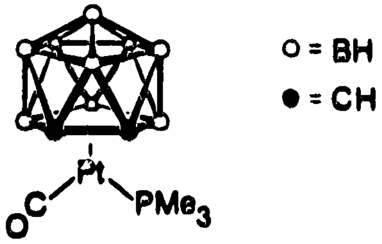


(6-6)

For R'=H,	**87** R=Me	For R'=Me,	**92** R=Me
	88 R=Et		**93** R=Et
	89 R=i-Pr		**94** R=Ph
	90 R=Ph		**95** PR$_3$=PMe$_2$Ph
	91 R=Cy		**96** R=Cy

For R' = H, the phosphines with R = Me, Et, i-Pr, Ph and Cy gave the complexes (**87**), (**88**), (**89**), (**90**) and (**91**) respectively. For R' = Me, the phosphines with R = Me, Et, Ph and Cy gave the complexes (**92**), (**93**), (**94**) and (**96**) respectively. With the phosphine PMe$_2$Ph, (**95**) was obtained. These complexes were fully characterized by ^{1}H and ^{31}P NMR, mass spectroscopy and elemental analysis. These compounds have high IR ν_{CO} bands (2057-2066 cm^{-1} in CH_2Cl_2), and the ^{31}P NMR spectra are singlets with ^{195}Pt satellites (Table 6.I). It was hoped that by increasing the size of the aliphatic R group on the phosphine or by going to the dimethylcarborane ligand (R' = Me) that the solubility of these complexes in saturated hydrocarbons would be increased. However, although the complexes are soluble in polar and aromatic solvents they are virtually insoluble in saturated hydrocarbons. They are slightly air-sensitive yellow crystalline solids, which melt without decomposition.

The characterization of a specific compound [closo-3-(PMe_3)-3-(CO)-3,1,2-Pt($C_2B_9H_{11}$)] 87 will be discussed.



87

The complex was isolated in 72% yield after chromatography. The IR spectrum shows a ν_{CO} band at 2058 cm^{-1} in CH_2Cl_2, which is considerably higher than ν_{CO} for Cp*Ir(CO)PMe_3 (1923 cm^{-1} in hexane).[13] The ^1H NMR spectrum in CD_2Cl_2 (Figure VI.I) displayed the carborane C-H protons at δ 3.65 (s, 2H) and the PMe_3 group at δ 1.94, which is a doublet with ^{195}Pt satellites (9H, $^2J_{P-H}$ = 11.5 Hz, $^3J_{Pt-H}$ = 35.8 Hz). The ^{11}B NMR spectrum is typical for a closo-3,1,2-$C_2B_9H_{11}$ cage.[16] The ^{13}C NMR spectrum (Figure VI.2) showed the CO carbon at δ 171.7, with a small phosphorus and large platinum coupling (d, $^2J_{P-C}$ = 15 Hz, $^1J_{Pt-C}$ = 1700

Table 6.I $^{31}P\{^{1}H\}$ **NMR and Infrared Spectral Data for the Complexes [<u>closo</u>-3-(L)-3-(CO)-3,1,2-Pt($C_2B_9H_9R'_2$)]**

Complex			δ(P)	$^{1}J_{(Pt-P)}$	ν_{CO} [b]
L		R'	ppm [a]	Hz	cm^{-1}
PMe_3	**(87)**	H	-22.1	3120	2058
PEt_3	**(88)**	H	19.1	3029	2055
$P(i\text{-}Pr_3)$	**(89)**	H	51.7	2942	2057
PPh_3	**(90)**	H	19.4	3112	2066
PCy_3	**(91)**	H	39.6	2909	2054
PMe_3	**(92)**	CH_3	-19.1	2974	2056
PEt_3	**(93)**	CH_3	18.3	2906	2056
PPh_3	**(94)**	CH_3	44.6	3109	2064
PMe_2Ph	**(95)**	CH_3	-10.6	2965	2059
PCy_3	**(96)**	CH_3	37.2	2802	2051

(a) All ^{31}P NMR spectra were recorded as CD_2Cl_2 solutions.

(b) Infrared spectra were recorded as CH_2Cl_2 solutions.

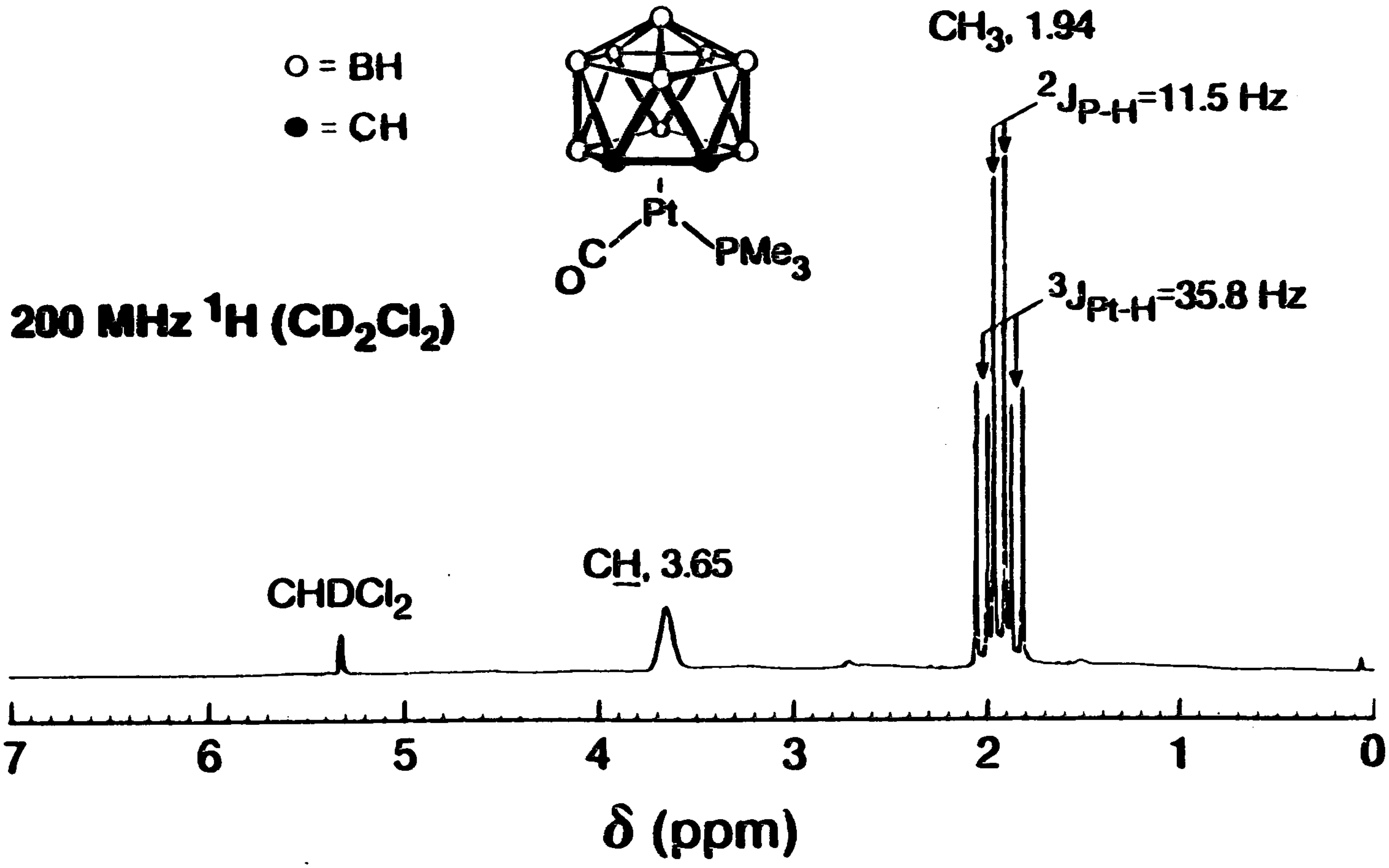


Figure VI.1 ^{1}H NMR Spectrum of [closo-3-(PMe_3)-3-(CO)-3,1,2-Pt($C_2B_9H_{11}$)] (87)

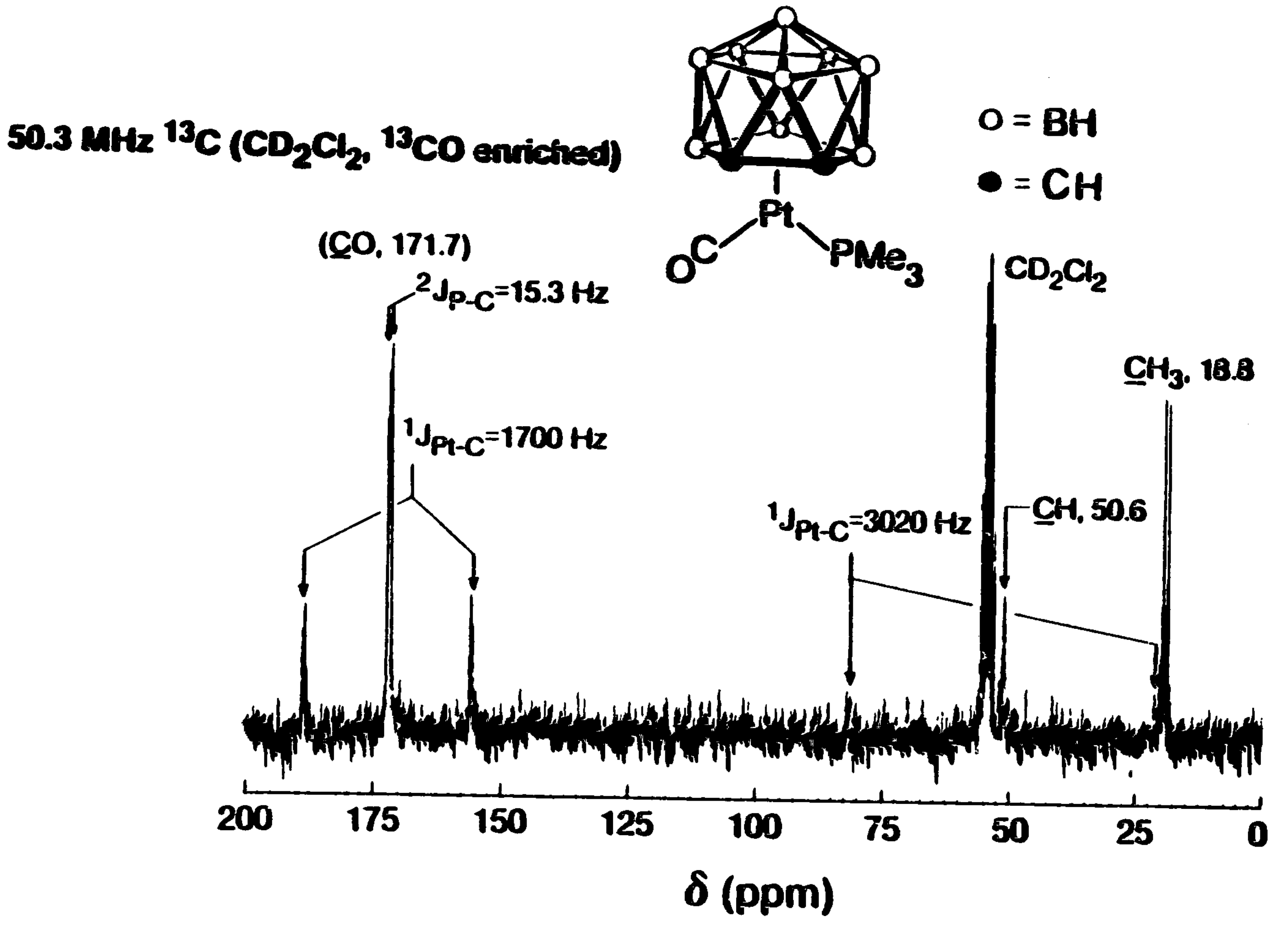


Figure VI.2 ^{13}C NMR Spectrum of [closo-3-(PMe_3)-3-(CO)-3,1,2-$Pt(C_2B_9H_{11})$] (87)

Hz, the carborane carbons at δ 50.6 (s, $^1J_{Pt-C}$ = 3020 Hz) and the carbons of the PMe_3 group at δ 18.8 (m).

X-Ray Structure of (87)

The X-ray crystal structure determination was carried out by Dr. R.G. Ball of this Department. Details of the data collection and refinement as well as tables of structural parameters, bond lengths and bond angles will be found in the Experimental Section. A perspective view of the compound is shown in Figure VI.3 with a projection of the top view shown in Figure VI.4.

The structural analysis confirms that the carborane cage and the d^8 platinum atom define a highly distorted icosahedral polyhedron. The projection in Figure VI.4 shows the so-called slipped structure and the orientation of the P-Pt-C4 fragment. The Pt atom is shifted away from C(5,6) and toward B(7,8,9), like a η^3 allyl group. This raises the question of whether the complex should be regarded as having 16 or 18e. These distortions are very similar to those reported for $3,3\text{-}(PEt_3)_2\text{-}3,1,2\text{-}Pt(C_2B_9H_{11})$.[5d]

The Pt-P bond length of 2.274(2) Å in 87 is similar to the Pt-P value of 2.2750 Å in $3,3\text{-}(PEt_3)_2\text{-}3,1,2\text{-}Pt(C_2B_9H_{11})$.[5d] As well, the Pt-C(6) and Pt-C(5) distances of 2.508(8) Å and 2.471(9) Å respectively are comparable to distances of 2.530(7) Å and 2.613(7) Å.[5d] The internal stereochemistry of the $Pt(PMe_3)(CO)$ fragment is similar to that of $3,3\text{-}(PEt_3)_2\text{-}3,1,2\text{-}Pt(C_2B_9H_{11})$, with the P-Pt-C plane parallel to the C5-C6 bond axis. The dihedral angle between the C(5,6)B(7,8,9) plane and the C4-Pt-P plane is 91.8°.

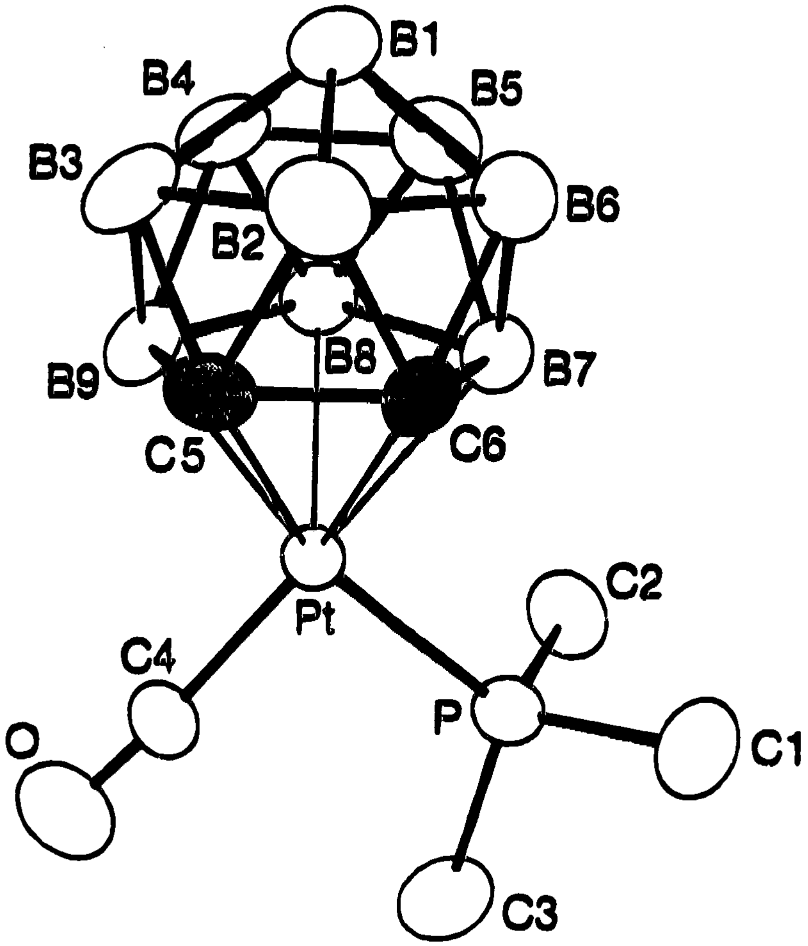


Figure VI.3 Molecular Structure of [closo-3-(PMe_3)-3-(CO)-3,1,2-$Pt(C_2B_9H_{11})$] (87)

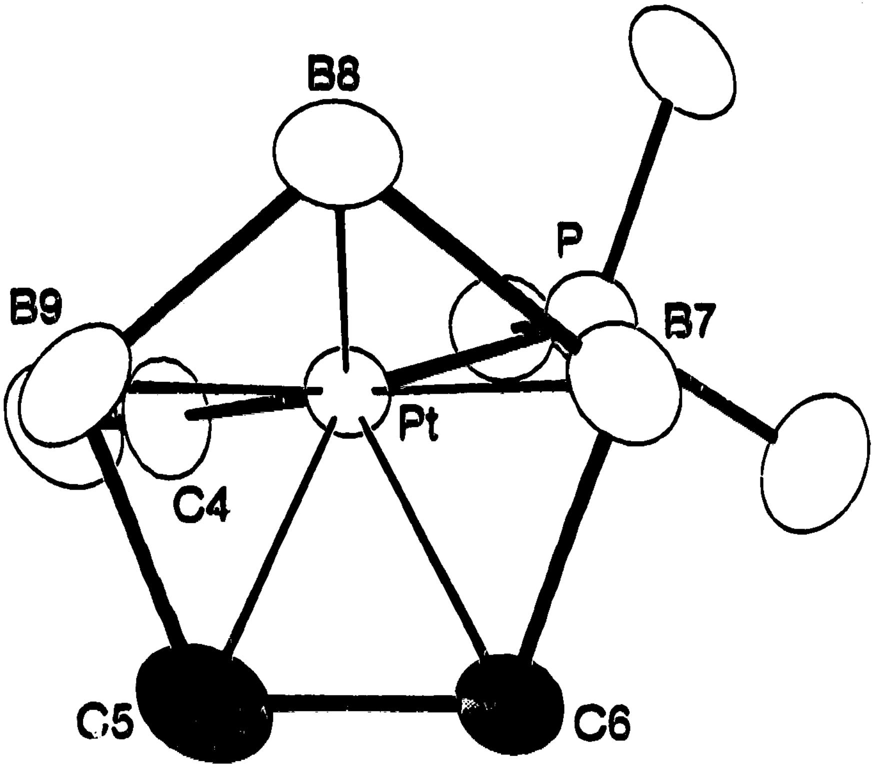


Figure VI.4 Projection View of Structure (87)

Section 3

LIGAND SUBSTITUTION REACTIONS

CO Exchange Reaction

As was mentioned in Chapter II, the rapid CO exchange reactions with square planar d^8 transition metal complexes are thought to proceed via an associative mechanism. For example, the rate of ^{14}CO exchange with $[(CO)PtCl_2]_2$ was too fast to measure.[17]

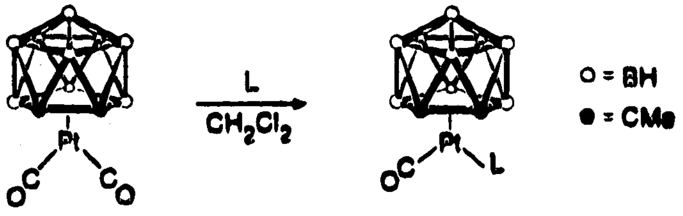
The analogy between the carborane anion [nido-7,8-$C_2B_9H_{11}$]$^{2-}$ and the pentamethylcyclopentadienyl anion (Cp^{*-}) in transition metal complexes has been recently noted.[3] Hence [closo-3,3-$(CO)_2$-3,1,2-$Pt(C_2B_9H_9Me_2)$] **83** should show reactivity similar to $Cp^*Ir(CO)_2$. The dicarbonyl **83** exchanges one atmosphere of ^{13}CO rapidly in hexane solution (complete in five min, with ν_{CO} at 2070, 2032 cm^{-1} for enriched complex). In contrast, the ^{13}CO exchange rate for $Cp^*Ir(CO)_2$ in hexane at one atmosphere CO is relatively slow ($t_{1/2}$ = two hours).[10] This suggests that there is a low activation pathway for exchange not present in the Cp* system.

The slipped structure of the carborane anion [nido-7,8-$C_2B_9H_{11}$]$^{2-}$ in complex **87** suggests a η^3-$C_2B_9H_{11}$-Pt(II) 16e complex. For the carbonyl phosphine derivative **87**, the ^{13}CO exchange reaction in CH_2Cl_2 is slower, with $t_{1/2}$ = 28 hours at one atmosphere ^{13}CO, but $t_{1/2}$ is two hours with three atmospheres of ^{13}CO. The pressure dependent rate suggests an associative mechanism for ^{13}CO exchange.

Reactions with Phosphines and Isocyanides

Dicarbonyl **83** reacts instantaneously with one equivalent of PMe_3 in

CH_2Cl_2 to give **92** (eq. 6-7).



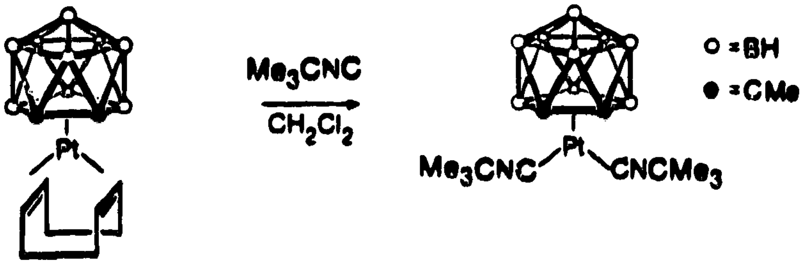
(6-7)

83

92 L=PMe_3

97 L=t-BuNC

In contrast, Cp*Ir(CO)$_2$ reacts with PMe_3 to give Cp*Ir(CO)(PMe_3) only under more forcing conditions of 70°C for 24 hours using excess ligand.[13] Complex **83** also reacts with one equivalent of Me_3CNC (t-BuNC) in CH_2Cl_2 to give [closo-3-(t-BuNC)-3-(CO)-3,1,2-Pt($C_2B_9H_9Me_2$)] **97** (eq. 6-7). The IR spectrum of **97** in CH_2Cl_2 shows ν_{NC} at 2214 cm^{-1} and ν_{CO} at 2077 cm^{-1}. The ^1H NMR spectrum shows the t-BuNC group at δ 1.59 (s, 9H). Further addition of t-BuNC to **97** gives [closo-3,3-(t-BuNC)$_2$-3,1,2-Pt($C_2B_9H_9Me_2$)] (**98**). Due to the unavailability of a larger quantity of **83**, **98** was prepared by the addition of excess t-BuNC to **82** in CH_2Cl_2 (eq. 6-8).

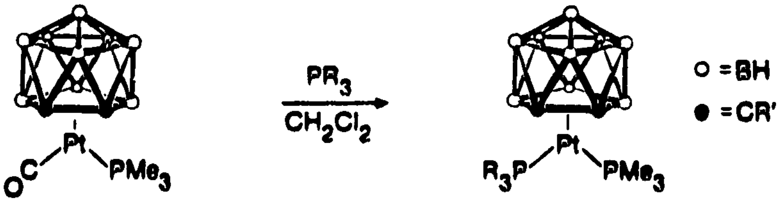


(6-8)

82 **98**

The IR spectra of the two compounds prepared by both routes were the same, with two ν_{CN} bands at 2207 and 2180 cm^{-1}. A palladium analog [closo-3,3-(t-BuNC)$_2$-3,1,2-Pd($C_2B_9H_{11}$)] has been recently reported.[5e] .

The related bis(phosphine) complexes were also prepared. Both **87** and **92** rapidly react with one equivalent of PMe_3 in CH_2Cl_2 to give [closo-3,3-(PMe_3)$_2$-3,1,2-Pt($C_2B_9H_{11}$)] (**99**) and [closo-3,3-(PMe_3)$_2$-3,1,2-Pt($C_2B_9H_9Me_2$)] (**100**) respectively (eq. 6-9).



(6-9)

87 R' = H

92 R' = Me

99 R'=H, R=Me

100 R'=Me, R=Me

102 R'=Me, R=Et

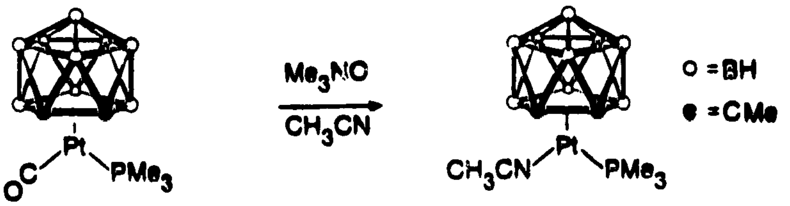
103 R'=Me, PR_3=t-BuNC

These complexes can also be prepared by Stone's method,[5a] where $(PMe_3)_2PtCl_2$[18] is reacted with $Tl_2C_2B_9H_9R'_2$ in CH_2Cl_2. Complex **99** has been reported[5e] using the second method in the Experimental Section. The addition of one equivalent of the larger PPh_3 to [closo-3-(PPh_3)-3-(CO)-3,1,2-Pt($C_2B_9H_{11}$)] **90** gives [closo-3,3-(PPh_3)$_2$-3,1,2-Pt($C_2B_9H_{11}$)] (**101**).

With the choice of suitable phosphines, mixed bis(phosphine) complexes can be obtained. For example, reaction of **92** with one equivalent of PEt_3 in CH_2Cl_2 gives [closo-3-(PMe_3)-3-(PEt_3)-3,1,2-Pt($C_2B_9H_9Me_2$)] (**102**) (eq. 6-9). A reaction related to the addition of phosphines is the reaction with isocyanides. Reaction of **92** with one equivalent of t-BuNC in CH_2Cl_2 gives [closo-3-(PMe_3)-3-(t-BuNC)-3,1,2-Pt($C_2B_9H_9Me_2$)] (**103**) (eq. 6-9). Complexes **98-103** are all air-stable yellow solids. Table 6.II presents some ^{31}P NMR and miscellaneous spectral data.

Reaction with Me_3NO

A useful criteria for the successful reaction of trimethylamine N-oxide (Me_3NO) with transition metal carbonyls is that $\nu_{CO} > 2000$ cm^{-1}.[19] Hence both dicarbonyl **83** and a mixed phosphine carbonyl **92** are suitable candidates for removing carbon monoxide chemically. Reaction of Me_3NO with the dicarbonyl **83** in a variety of solvents results in decomposition. However, reaction of **92** with one equivalent of Me_3NO in CH_3CN gives the fully characterized acetonitrile complex [closo-3-(PMe_3)-3-(CH_3CN)-3,1,2-Pt($C_2B_9H_9Me_2$)] (**104**) (eq. 6-10).



(6-10)

92 **104**

The analogous reaction in CH_2Cl_2 gave no evidence of NMe_3 or $ONMe_3$ complex as observed in Chapter IV, but only resulted in decomposition. The tris(pyrazolyl)borate rhodium acetonitrile complex HB(3-CF_3-5-MePz)$_3$Rh(CO)(CH_3CN) **42** in Chapter IV was determined from its IR spectrum

Table 6.II $^{31}P\{^{1}H\}$ **NMR and Miscellaneous Spectral Data for the Complexes** closo**-3-(PMe_3)-3-(L)-3,1,2-Pt($C_2B_9H_9R'_2$)**

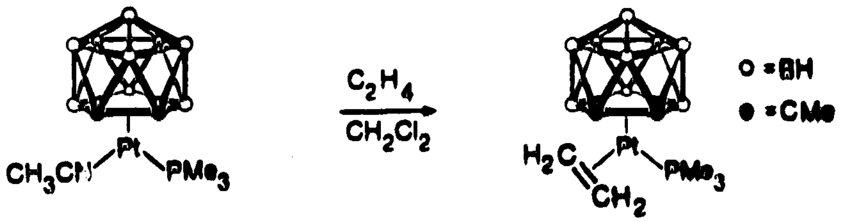
L		R'	δ(P) ppm[a]	$^{1}J_{Pt-P}$ Hz	IR[b]
PMe_3	**(99)**	H	-26.8	3379	-
PMe_3	**(100)**	CH_3	-21.0	3015	-
PEt_3	**(102)**	CH_3	16.5	3007	(PEt_3)
			-20.6	2996	(PMe_3)
t-BuNC	**(103)**	CH_3	-21.5	3088	$\nu_{NC}=2177\ cm^{-1}$
CH_3CN	**(104)**	CH_3	-16.8	3479	$\nu_{CN}=2342\ cm^{-1}$
C_2H_4	**(105)**	CH_3	-18.7	3549	$\nu_{C=C}=1511\ cm^{-1}$
$(Br)_2$	**(107)**	H	31.7	3141	-
$(Br)_2$	**(108)**	CH_3	22.6	3015	-
(H)($SiEt_3$)	**(109)**	H	-26.8	2466	$\nu_{Pt-H}=2130\ cm^{-1}$

(a) All ^{31}P NMR spectra were recorded as CD_2Cl_2 solutions.

(b) Infrared spectra were recorded as CH_2Cl_2 solutions.

to have an end-on bound acetonitrile group. In the same manner, the acetonitrile group in complex **104** could be bound to platinum in an end-on or side-on manner. These two binding modes can be distinguished by observing $\nu_{C\equiv N}$ in the IR spectrum.[20a] In fact, a weak $\nu_{C\equiv N}$ stretch is observed at 2342 cm^{-1} in CH_2Cl_2, indicative of an end-on bound CH_3CN, as represented in eq. 6-10. This IR band is very similar to other literature values of Pt(II) acetonitrile complexes.[20b,c] The ^1H NMR spectrum of **104** shows the coordinated acetonitrile at δ 2.37 (d, 3H, $^4J_{Pt-H}$ = 8.8 Hz, $^5J_{P-H}$ = 1.1 Hz). Again, this chemical shift is similar to that reported for cis-$PtCl_2(CH_3CN)(C_2H_4)$, where δ (CH_3CN) is at 2.45 ppm in CD_3CN.[20c]

Complex **104** reacts rapidly with CO in CH_3CN to give back **92** and also with ethylene in CH_2Cl_2 to give [closo-3-(PMe_3)-3-(C_2H_4)-3,1,2-$Pt(C_2B_9H_9Me_2)$] (**105**) (eq. 6-11).



104 **105**

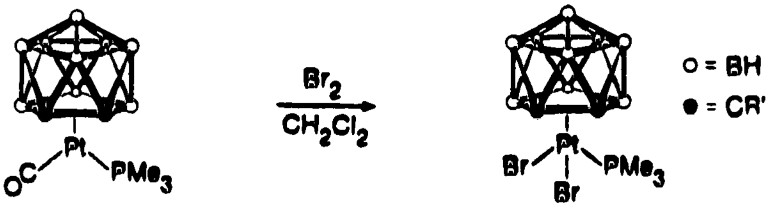
(6-11)

Complex **105** can also be prepared independently by reacting cis-$(PMe_3)(C_2H_4)PtCl_2$ (**106**) with $Tl_2C_2B_9H_9Me_2$ in CH_2Cl_2. The ethylene group in the ^1H NMR spectrum appears at δ 3.38 (d, 4H, $^2J_{Pt-H}$ = 50.9 Hz, $^3J_{P-H}$ = 2.9 Hz), which suggests that it is rapidly rotating in solution. A weak IR band appears at 1511 cm^{-1}, which has been assigned as $\nu_{C=C}$. Complex **105** also reacts rapidly with CO in CH_2Cl_2 to give back **92**.

Section 4

OXIDATIVE ADDITION STUDIES

A second reaction type explored is oxidative addition. Both Br_2 and MeI react with Cp*Ir$(CO)_2$, giving Cp*Ir(CO)Br_2[21a] and Cp*Ir(CO)(Me)(I)[21b,c] respectively. Treatment of a CH_2Cl_2 solution of **87** or **92** with one equivalent of bromine gives the dibromides [<u>closo</u>-3,3-$(Br)_2$-3,1,2-Pt$(C_2B_9H_9R'_2)$] (**107**) (R' = H) and (**108**) (R' = Me) (eq. 6-12).



(6-12)

87 R'=H

92 R'=Me

107 R'=H

108 R'=Me

These complexes are bright red crystalline solids, which are in the Pt(IV) oxidation state. In contrast to the reactions of Cp*Ir$(CO)_2$, both **87** and **92** do not oxidatively add methyl iodide and are not protonated by HBF_4 whereas Cp*Ir$(CO)_2$ is easily protonated by HBF_4.[22] This difference is indicative of the electron-poor carborane ligand on the Pt(II) metal center. There are no known examples of stable cationic metallacarborane compounds in the literature, although neutral and anionic species are abundant.[3]

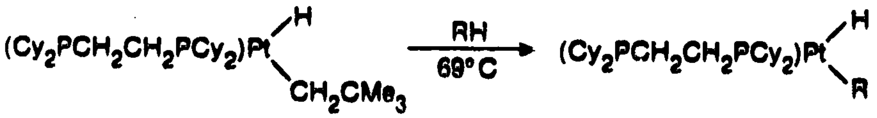
With relevance to carbon-hydrogen bond activation, Cp*Ir$(CO)_2$ activates saturated and unsaturated C-H bonds[6] and Si-H bonds[21a] photochemically whereas the photolysis of **87** or **92** in benzene under similar conditions[6b] gave no reaction. Also photolysis of complexes containing an aryl phosphine **90**, **94** and **95** in benzene showed no intramolecular C-H activation (or orthometallation). This suggests that the chances for an intermolecular process are small. Attempts to form the Pt(IV) dihydride with a H_2 purge during photolysis in benzene gave no reaction. The very low solubility of any of the complexes in saturated hydrocarbons precluded C-H activation studies in those solvents. Also, the reaction of **87** in benzene with Me_3NO resulted in decomposition, with no isolable product.

There are known examples of C-H activation with Pt(II) and Pt(IV) salts, primarily by Shilov and coworkers.[23] For example, methane is converted into methanol and methyl chloride with $[PtCl_6]^{2-}$ (eq. 6-13).

$$CH_4 + [PtCl_6]^{2-} \xrightarrow[H_2O]{90-120^\circ} (CH_3Cl, CH_3OH) + Pt(II) \qquad (6\text{-}13)$$

However, these reactions are thought to proceed by an electrophilic mechanism, and some consider that it might involve heterogeneous catalysis by platinum metal particles.

Whitesides and coworkers have recently demonstrated C-H activation via a postulated Pt(0) intermediate to give Pt(II) alkyl or aryl hydrides (eq. 6-14).[24]



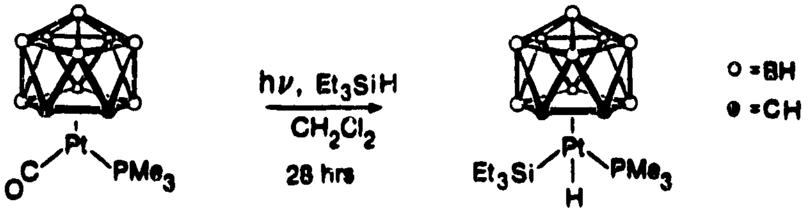
$$(Cy_2PCH_2CH_2PCy_2)Pt(H)(CH_2CMe_3) \xrightarrow[69°C]{RH} (Cy_2PCH_2CH_2PCy_2)Pt(H)(R)$$

(6-14)

The starting complex is a Pt(II) neopentyl hydride with a bulky chelating ligand. On heating, reductive elimination of neopentane occurs, generating a reactive Pt(0) intermediate which reacts with C-H bonds.

Hence, there are literature examples for C-H activation by a Pt(II) complex, although by different mechanisms. Perhaps the metal center in the platinacarboranes is too electron poor to oxidatively add a C-H bond, but not electrophilic enough to react as with Shilov's system.

A useful model for C-H activation is Si-H activation.[6a] Photolysis of a sample of **87** in the presence of excess Et_3SiH for 28 h gave a new product, assigned as the silyl hydride [<u>closo</u>-3-(Et_3Si)-3-(H)-3-(PMe_3)-3,1,2-Pt($C_2B_9H_{11}$)] (**109**) (eq. 6-15).



(6-15)

87 **109**

The IR spectrum in CH_2Cl_2 shows a weak band at 2130 cm^{-1}, assigned as the Pt-H stretch, and the MS shows the molecular ion M^+ at m/e = 520. The ^1H NMR spectrum shows two resonances at δ 1.18 (q, 6H, $^3J_{H-H}$ = 7.8 Hz) and δ 1.06 (t, 9H, $^3J_{H-H}$ = 7.8 Hz) for the Et_3Si group and a high field hydride at δ -7.85 (d, 1H, $^2J_{P-H}$ = 26 Hz, $^1J_{Pt-H}$ = 900 Hz). The reaction is general with a variety of silanes (Me_3SiH, Cl_3SiH and Ph_3SiH), but the products do not appear as stable as **109**. Reductive elimination of Et_3SiH from **109** takes place rapidly with CO in CH_2Cl_2 to give **87**.

Section 5

EXPERIMENTAL

$Tl_2C_2B_9H_{11}$ and $Tl_2C_2B_9Me_2$ were prepared using literature procedures.[8] (COD)$PtCl_2$ was prepared using the method of Clark.[7] [closo-(COD)-3,1,2-Pt($C_2B_9H_{11}$)] **81** was prepared according to Hawthorne.[4] [(η^4-C_4Me_4)$PtCl_2$)]$_2$ was prepared according to Malatesta.[12] $(CO)_2PtCl_2$ was prepared by the method of Calderazzo et al.[9]

(PMe_3)(CO)$PtCl_2$ and (PMe_2Ph)(CO)$PtCl_2$ were prepared by the methods of Goggin[14a] and Orchin[14b] respectively. Other analogous compounds (PR_3)(CO)$PtCl_2$ R=Et, i-Pr, Ph, Cy were prepared according to Clark.[15] [(PMe_3)$PtCl_2$]$_2$ and (PMe_3)Pt_2Cl_2 were prepared according to Hartley.[18] cis-Pt(PMe_3)(C_2H_4)Cl_2 **106** was prepared using a procedure similar to that of cis-Pt(PPh_3)(C_2H_4)Cl_2.[25]

Ortho-carborane was purchased from Dexsil Chemical Corporation and was used as received. PMe_3, PMe_2Ph, PEt_3, P(i-Pr)$_3$, PPh_3, PCy_3 and t-BuNC were used as received from Strem Chemical Co. Anhydrous Me_3NO was dried from Aldrich $Me_3NO.2H_2O$ by azeotropic distillation of water from toluene, followed by vacuum sublimation. Research purity ethylene (99.98%) was used as received from Matheson.

Preparation of [closo-(COD)-3,1,2-Pt($C_2B_9H_9Me_2$)] (82)

To a solutiom of (COD)$PtCl_2$ (374 mg, 1.00 mmol in 20 mL THF) was added 600 mg (1.05 mmol) $Tl_2C_2B_9H_9Me_2$. After stirring for 1.5 h, a black solution resulted. After filtering through Celite and removing the solvent, the black residue was chromatographed twice on Florisil (12 x 2.5 cm) with CH_2Cl_2 eluent, giving a yellow powder upon removal of solvent in vacuo. Recrystallization from CH_2Cl_2-hexane at -30°C gave yellow crystals (231 mg, 50% yield) mp 180°C, decomp.

Characterization: MS (105°C, 70 eV) M^+ (463, 100%), M^+-COD (18%), M^+-$C_2B_9H_9Me_2$ (29%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 5.21 (br, 4H, $^2J_{Pt-H}$ = 60 Hz), 2.60 (br, 6H), 2.47 (d, 8H, $^3J_{Pt-H}$ = 7.8 Hz). Anal. Calcd for $C_{12}H_{27}B_9Pt$: C, 31.08; H, 5.87. Found: C, 27.94; H, 5.71.

Preparation of [*closo*-3,3-$(CO)_2$-3,1,2-Pt$(C_2B_9H_9Me_2)$] (83)

A solution of $(CO)_2PtCl_2$ (254 mg, 0.79 mmol in 10 mL CH_2Cl_2) was cooled down to -78°C under 1 atm CO. To this clear solution was added 471 mg (0.83 mmol) $Tl_2C_2B_9H_9Me_2$ and the solution was slowly allowed to warm to room temperature. At -40°C, the solution darkened and the IR spectrum showed disappearance of the ν_{CO} bands of the starting material (2177, 2137 cm^{-1}) with appearance of product (2128, 2088 cm^{-1}). After warming to room temperature, the brown solution was stirred for 3 h under CO, filtered through Celite and concentrated. Chromatography twice on Florisil (12 x 2.5 cm) with CH_2Cl_2 eluent gave yellow crystals on removal of solvent in vacuo (35 mg, 11% yield) mp 128-130°C.

Characterization: IR (hexane) 2118, 2079 cm^{-1} (ν_{CO}). MS (55°C, 16 eV) M^+ (411, 15%), M^+-CO (100%), M^+-2CO (77%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.56 (s). Anal. Calcd for $C_6H_{15}B_9O_2Pt$: C, 17.51; H, 3.67. Found: C, 17.43; H, 3.61.

Attempted Preparation of [closo-3,3-$(CO)_2$-3,1,2-Pt($C_2B_9H_{11}$)] (84)

The reaction was done in the same manner as **83**, but the resulting product was much less stable. Only IR evidence for **84** was observed with ν_{CO} bands in hexane at 2121, 2082 cm^{-1}.

Reaction of COD complex 82 with CO

A sample of 482 mg (1.04 mmol) **82** was taken up in 25 mL CH_2Cl_2 in a 125 mL Parr autoclave. The solution was charged with 1500 psi CO and heated at 65°C for four days. After cooling and venting the CO, a green solution remained, with IR ν_{CO} bands at 2128, 2088 cm^{-1}. This was chromatographed twice on Florisil (12 x 2.5 cm) with CH_2Cl_2 eluent, giving 400 mg of a yellow solid. The IR spectrum in hexane showed **83** was present, but the ^1H NMR spectrum showed a mixture of 40% **83** and 60% **82**. Separation by chromatography or crystallization were unsuccessful. With different CO pressures and bath temperatures, varying amounts of **83** were obtained, but always containing **82**. The analogous reaction can be done with [closo-(COD)-3,1,2-Pt($C_2B_9H_{11}$)] **81** at 65°C, but the product **84** was much less stable and only detected by IR.

Reaction of Dicarbonyl 83 with COD

A sample of 25.0 mg (0.061 mmol) **83** was taken up in 20 mL hexane. 3 drops of COD were added, and after 1 h the reaction was complete. After removal of solvent and excess COD, a yellow solid remained. It was identified as **82** by its ^1H NMR spectrum (26.7 mg, 95% yield).

Preparation of [<u>closo</u>-(η^4-C_4Me_4)-3,1,2-Pt($C_2B_9H_{11}$)] (85)

To a sample of [(η^4-C_4Me_4)$PtCl_2$]$_2$ (37 mg, 0.05 mmol) in 5 mL CH_2Cl_2 was added 54 mg (0.1 mmol) of $Tl_2C_2B_9H_{11}$. After stirring for 6 h, the solution was filtered through Celite, concentrated and layered with hexane. On cooling to -30°C tan crystals were obtained (23.4 mg, 54% yield) mp 260-268°C.

<u>Characterization</u>: MS (135°C, 16 eV) M^+ (436, 100%), M^+-$C_2B_9H_{11}$ (72%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 3.16 (s, 2H, $^2J_{Pt-H}$ = 42.5 Hz), 2.39 (s, 12H, $^3J_{Pt-H}$ = 23.5 Hz). Anal. Calcd for $C_{10}H_{23}B_9Pt$: C, 27.57; H, 5.32. Found: C, 27.40; H, 5.27.

Preparation of [<u>closo</u>-(η^4-C_4Me_4)-3,1,2-Pt($C_2B_9H_9Me_2$)] (86)

This was isolated as light tan crystals in 57% yield using the procedure above for **85**, mp 214-216°C.

<u>Characterization</u>: MS (150°C, 70 eV) M^+ (463, 85%), M^+-$C_2B_9H_9Me_2$ (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.15 (s, 12H, $^3J_{Pt-H}$ = 22 Hz), 2.08 (s, 6H). Anal. Calcd for $C_{12}H_{27}B_9Pt$: C, 31.08; H, 5.87. Found: C, 31.07; H, 5.89.

General Preparation of [<u>closo</u>-3-(PR_3)-3-(CO)-3,1,2-Pt($C_2B_9H_9R'_2$)]

A 1 mmol equivalent of $Tl_2C_2B_9H_9R'_2$ was added to a solution of 1 mmol (PR_3)(CO)$PtCl_2$ in 10 mL CH_2Cl_2. The stirred mixture was monitored by IR spectroscopy and the reactions were generally complete in 3 h. The dark brown solution was filtered with a cannula to separate the solution from the precipitated TlCl and concentrated in vacuo. A CH_2Cl_2

extract was chromatographed on a Florisil column (12 x 2.5 cm) eluting with CH_2Cl_2. A yellow band which quickly moved down the column was collected and the solvent removed to give yellow microcrystals which were recrystallized from hexane layering of a concentrated CH_2Cl_2 solution at -30°C.

Preparation of [closo-3-(PMe_3)-3-(CO)-3,1,2-Pt($C_2B_9H_{11}$)] (87)

The complex was obtained in 72% yield using the general procedure, mp 165-168°C.

Characterization: MS (195°C, 16 eV) M^+ (431, 10%), M^+-CO (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 3.65 (s, 2H), 1.94 (d, 9H, $^2J_{P-H}$ = 11.5 Hz, $^3J_{Pt-H}$ = 35.8 Hz). ^1H NMR (C_6D_6, 200 MHz, ambient) δ 3.08 (s, 2H), 0.81 (d, 9H, $^2J_{P-H}$ = 11.4 Hz, $^3J_{Pt-H}$ = 35.8 Hz). ^{11}B NMR (CD_2Cl_2, ambient) δ 8.47 (d, $^1J_{B-H}$ = 140 Hz), -3.70, -7.00, -9.32, -11.93, -19.74, -21.53, -23.67. ^{13}C NMR (CD_2Cl_2, 50.3 MHz, ambient) δ 171.7 (d, CO, $^2J_{C-P}$ = 15 Hz, $^1J_{C-Pt}$ = 1700 Hz), 50.6 (s, carborane C, $^1J_{Pt-C}$ = 3020 Hz), 18.8 (CH_3). Anal. Calcd for $C_6H_{20}B_9OPPt$: C, 16.70; H, 4.67. Found: C, 16.59; H, 4.83.

X-Ray Structure of (87)

The X-ray crystallographic study was carried out by Dr. R.G. Ball in the Structure Determination laboratory of this Department. This section and the Tables are adapted from his report. The computer programs used in the data analysis include the Enraf-Nonius structure determination package Version 3 (1985, Delft, The Netherlands) rewritten for a Sun Microsystems computer and several locally written or modified programs.

Suitable crystals were grown from CH_2Cl_2-hexane at -30°C. A yellow air-stable crystal, with approximate dimensions of 0.23 x 0.23 x 0.37 mm was mounted in a non-specific orientation. The automatic peak search and reflection indexing showed the crystal to be orthorhombic with systematic absences of h00, h odd; 0k0, k odd; 00l, l odd. Cell constants were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $19 < 2\theta < 28°$. The intensity data were collected using a ω-2θ scan mode. The various crystal parameters are given in Table 6.III.

There were 3 reflections which were chosen as standard reflections and these were remeasured every 60 minutes of exposure time to check on crystal and electronic stability over the course of data collection. A linear regression analysis of these standards showed a negligible mean change in intensity of 1.2 (1.3)% over the time span of data collection. Data were collected for Lorentz, polarization and background effects.

The structure was solved using the direct methods program MULTAN which gave the positional parameters for the Pt atom. The remaining non-hydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier synthesis.

Refinement of atomic parameters was carried out by full matrix least-squares techniques on F_o minimizing the function

$$\Sigma w \left(|F_o| - |F_c|\right)^2$$

where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor

Table 6.III Experimental Details

formula	$C_6H_{20}B_9OPPt$
fw	431.59
crystal size/mm	0.23x0.23x0.37
appearance	yellow crystal
diffractometer	Enraf-Nonius CAD4F
radiation	Mo K_α (graphite)
wavelength/Å	0.71073
space group	$P2_12_12_1$
a/Å	11.500(2)
b/Å	12.749(3)
c/Å	10.361(2)
$V/Å^3$	1519.1
Z	4
ρ(calcd)/g cm^3	1.887
μ/cm^{-1}	94.13
scan width/deg	0.70 + 0.35 tan(θ)
scan rate/deg/min	10.1-0.9
no. of unique reflections	2120
no. of obs. reflect. $I > 3\sigma(I)$	1912
2θ max/deg	56.00
R_1	0.037
R_2	0.051
GOF	1.97

amplitudes respectively, and the weighting factor w is given by

$$w = 4\,F_o^2 / \sigma^2 (F_o^2)$$

An examination of a difference Fourier for hydrogen atoms showed very few peaks in reasonable positions. It was decided to not include any H atom contributions in the latter stages of refinement.

In the final cycle 164 parameters were refined using 1912 observations having $I > 3\sigma(I)$. The final agreement factors were:

$$R_1 = \Sigma \,||F_o| - |F_c|| \,/\, \Sigma\, |F_o| = 0.037 \text{ and}$$

$$R_2 = (\Sigma\, w\, (|F_o| - |F_c|)^2 \,/\, \Sigma\, w\, F_o^2)^{1/2} = 0.051$$

During structure refinement Roger's "eta" parameter[26] was refined to indicate if the correct polarity of the molecule was chosen. This parameter refined to a value of 0.87 which indicates that the correct enantiomorph was chosen. The highest peak in the final difference Fourier was 1.3(2) $eÅ^{-3}$, it is located near the P atom and is without chemical significance. The structure of **87** is depicted in Fig. VI.3. Relevant bond lengths and bond angles are tabulated in Tables 6.IV and 6.V. Positional and thermal parameters are available in the detailed report from the Structure Determination Laboratory.[27]

Preparation of [closo-3-(PEt_3)-3-(CO)-3,1,2-Pt($C_2B_9H_{11}$)] (88)

The complex was obtained in 32% yield using the general procedure (mp 107-109°C).

Table 6.IV Selected Interatomic Distances (Å)

from	to	dist[a]	from	to	dist[a]
Pt	P	2.274(2)	B(1)	B(5)	1.77(2)
Pt	C(4)	1.850(9)	B(1)	B(4)	1.79(2)
Pt	C(5)	2.471(9)	B(1)	B(3)	1.86(2)
Pt	C(6)	2.508(8)	B(1)	B(2)	1.75(2)
Pt	B(7)	2.24(1)	B(1)	B(6)	1.78(1)
Pt	B(8)	2.26(1)	B(2)	B(3)	1.78(2)
Pt	B(9)	2.24(1)	B(2)	B(6)	1.76(2)
P	C(1)	1.79(1)	B(3)	B(4)	1.81(1)
P	C(2)	1.83(1)	B(3)	B(9)	1.80(1)
P	C(3)	1.81(1)	B(4)	B(5)	1.73(2)
O	C(4)	1.15(1)	B(4)	B(8)	1.75(1)
C(5)	C(6)	1.56(1)	B(4)	B(9)	1.83(2)
C(5)	B(2)	1.75(1)	B(5)	B(6)	1.81(1)
C(5)	B(3)	1.65(1)	B(5)	B(7)	1.81(2)
C(5)	B(9)	1.75(1)	B(5)	B(8)	1.79(2)
C(6)	B(2)	1.73(1)	B(6)	B(7)	1.79(2)
C(6)	B(6)	1.64(1)	B(7)	B(8)	1.89(1)
C(6)	B(7)	1.74(1)	B(8)	B(9)	1.78(2)

(a) Standard deviations in parentheses.

Table 6.V Selected Interatomic Angles (deg)

from	through	to	angle[a]
P	Pt	C(4)	91.0(3)
P	Pt	C(5)	144.2(2)
P	Pt	C(6)	110.1(2)
P	Pt	B(7)	91.5(3)
P	Pt	B(8)	116.8(3)
P	Pt	B(9)	163.3(3)
C(4)	Pt	C(5)	106.1(4)
C(4)	Pt	C(6)	132.9(4)
C(4)	Pt	B(7)	175.4(4)
C(4)	Pt	B(8)	132.0(4)
C(4)	Pt	B(9)	100.2(4)
C(5)	Pt	C(6)	36.5(3)
C(5)	Pt	B(7)	69.8(4)
C(5)	Pt	B(8)	74.4(3)
C(5)	Pt	B(9)	43.4(3)
C(6)	Pt	B(7)	42.5(3)
C(6)	Pt	B(8)	75.6(3)
C(6)	Pt	B(9)	70.8(3)
B(7)	Pt	B(8)	49.6(4)
B(7)	Pt	B(9)	78.2(4)
B(8)	Pt	B(9)	46.6(4)

(a) Standard deviations in parentheses.

Characterization: MS (120°C, 16 eV) M^+ (473, 13%), M^+-CO (100%), M^+-CO-Et (8%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 3.70 (s, 2H) 2.13 (d of q, 6H, $^3J_{H-H}$ = 7.5 Hz), $^2J_{P-H}$ = 10 Hz, $^3J_{Pt-H}$ = 31 Hz), 1.22 (d of t, 9H, $^3J_{P-H}$ = 18.2 Hz, $^3J_{H-H}$ = 7.6 Hz). Anal. Calcd for $C_9H_{26}B_9OPPt$: C, 22.82; H, 5.53. Found: C, 20.64; H, 5.54.

Preparation of [closo-3-(P(i-Pr)$_3$)-3-(CO)-3,1,2-Pt($C_2B_9H_{11}$)] (89)

The complex was obtained in 25% yield using the general procedure (mp 104-106°C).

Characterization: MS (165°C, 16 eV) M^+ (515, 3%), M^+-CO (100%), M^+-CO-i-Pr (9%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 3.90 (s, 2H), 2.64 (d of septets, 3H, $^2J_{P-H}$ = 10 Hz, $^3J_{H-H}$ = 7.5 Hz) 1.37 (d of d, 18H, $^3J_{H-H}$ = 7.1 Hz, $^3J_{P-H}$ = 15.5 Hz). Anal. Calcd for $C_{12}H_{32}B_9OPPt$: C, 27.95; H, 6.25. Found: C, 26.10; H, 6.10.

Preparation of [closo-3-(PPh$_3$)-3-(CO)-3,1,2-Pt($C_2B_9E_{11}$)] (90)

The complex was obtained in 81% yield using the general procedure (mp 162-165°C).

Characterization: MS (155°C, 16 eV) M^+ (617, 8%), M^+-CO (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 7.50 (m, 15H), 3.38 (s, 2H). Anal. Calcd for $C_{21}H_{26}B_9OPPt$: C, 40.83; H, 4.24. Found: C, 38.05; H, 4.21.

Preparation of [closo-3-(PCy$_3$)-3-(CO)-3,1,2-Pt($C_2B_9H_{11}$)] (91)

The complex was obtained in 32% yield using the general procedure (mp 208-210°C).

Characterization: MS (200°C, 70 eV) M^+ (635, 1%), M^+-CO (100%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 3.86 (s, 2H), 2.40-1.22 (m, 33H). Anal. Calcd for $C_{21}H_{44}B_9OPPt$: C, 39.66; H, 6.97. Found: C, 39.07; H, 7.12.

Preparation of [closo-3-(PMe_3)-3-(CO)-3,1,2-Pt($C_2B_9H_9Me_2$)] (92)

The complex was obtained in 74% yield using the general procedure (mp 174-176°C).

Characterization: MS (95°C, 16 eV) M^+ (459, 13%), M^+-CO (100%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.39 (d, 6H, $^4J_{P-H}$ = 2.2 Hz), 1.84 (d, 9H, $^2J_{P-H}$ = 11.2 Hz, $^3J_{Pt-H}$ = 34.3 Hz). ^{11}B NMR (CD_2Cl_2, ambient) δ 12.87 (d, 1B, $^1J_{B-H}$ = 148 Hz), -1.73 (d, 2B, $^1J_{B-H}$ = 158 Hz), -5.20 (d, 2B, $^1J_{B-H}$ = 150 Hz), -8.37 (d, 2B, $^1J_{B-H}$ = 149 Hz), -17.31 (d, 2B, $^1J_{B-H}$ = 125 Hz). Anal. Calcd for $C_8H_{24}B_9OPPt$: C, 20.91; H, 5.26. Found: C, 20.87; H, 5.19.

Preparation of [closo-3-(PEt_3)-3-(CO)-3,1,2-Pt($C_2B_9H_9Me_2$)] (93)

The complex was obtained in 56% yield using the general procedure (mp 134-136°C).

Characterization: MS (95°C, 16 eV) M^+ (501, 11%), M^+-CO (100%). ^{1}H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.37 (d, 6H, $^4J_{P-H}$ = 1.9 Hz), 2.10 (d of q, 6H, $^3J_{H-H}$ = 7.5 Hz, $^2J_{P-H}$ = 10 Hz, $^3J_{Pt-H}$ = 30 Hz), 1.18 (d of t, 9H, $^3J_{P-H}$ = 17.8 Hz, $^3J_{H-H}$ = 7.5 Hz). Anal. Calcd for $C_{11}H_{30}B_9OPPt$: C, 26.33; H, 6.03. Found: C, 26.52; H, 6.01.

Preparation of [closo-3-(PPh_3)-3-(CO)-3,1,2-Pt($C_2B_9H_9Me_2$)] (94)

The complex was obtained in 47% yield using the general procedure (mp 196-198°C).

Characterization: MS (160°C, 70 eV) M^+ (645, 3%), M^+-CO (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 7.60 (m, 15H), 1.93 (d, 6H, $^4J_{P-H}$ = 2.3 Hz). Anal. Calcd for $C_{23}H_{30}B_9OPPt$: C, 42.77; H, 4.68. Found: C, 42.18; H, 4.67.

Preparation of [closo-3-(PMe_2Ph)-3-(CO)-3,1,2-Pt($C_2B_9H_9Me_2$)] (95)

The complex was obtained in 62% yield using the general procedure (mp 159-162°C).

Characterization: MS (180°C, 16 eV) M^+ (521, 7%), M^+-CO (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 7.56 (m, 5H), 2.16 (d, 6H, $^4J_{P-H}$ = 1.5 Hz), 2.13 (d, 6H, $^2J_{P-H}$ = 10.9 Hz, $^3J_{Pt-H}$ = 35.1 Hz). Anal. Calcd for $C_{13}H_{26}B_9OPPt$: C, 29.93; H, 5.02. Found: C, 29.90; H, 4.94.

Preparation of [closo-3-(PCy_3)-3-(CO)-3,1,2-Pt($C_2B_9H_9Me_2$)] (96)

The complex was obtained in 20% yield using the general procedure (mp 195-197°C).

Characterization: MS (200°C, 16 eV) M^+ (664, 5%), M^+-CO (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.35 (d, 6H, $^4J_{P-H}$ = 1.7 Hz), 2.29-1.28 (m, 33H). Anal. Calcd for $C_{23}H_{48}B_9OPPt$: C, 41.60; H, 7.29. Found: C, 41.41; H, 7.30.

Preparation of [closo-3-(t-BuNC)-3-(CO)-3,1,2-Pt($C_2B_9H_9Me_2$)] (97)

To a solution of **83** (82 mg, 0.2 mmol) in 5 mL CH_2Cl_2 was added a solution of t-BuNC (23 μL, 16.6 mg, 0.2 mmol in 2 mL CH_2Cl_2). The reaction was instantaneous and after removing the solvent under reduced pressure, the orange residue was chromatographed on Florisil (12 x 2.5 cm) with CH_2Cl_2 eluent. Hexane was layered on a concentrated CH_2Cl_2 solution at -30°C, which gave yellow-orange crystals (87 mg, 93% yield) mp 140°C (decomp).

Characterization: IR (CH_2Cl_2) 2214 cm^{-1} (ν_{NC}), 2077 cm^{-1} (ν_{CO}). MS (140°C, 70 eV) M^+ (466, 3%), M^+-CO (33%), M^+-t-BuNC (79%), M^+-t-BuNC-CO (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.41 (s, 6H), 1.59 (s, 9H). Anal. Calcd for $C_{10}H_{24}B_9NOPt$: C, 25.74; H, 5.18; N, 3.00. Found: C, 25.60; H, 5.18; N, 3.06.

Preparation of [closo-3,3-(t-BuNC)$_2$-3,1,2-Pt($C_2B_9H_9Me_2$)] (98)

To a solution of 129.2 mg (0.279 mmol) **81** in 10 mL CH_2Cl_2 was added dropwise 63 μL (46.4 mg, 0.558 mmol) of t-BuNC in 2 mL CH_2Cl_2. After the CH_2Cl_2 was removed in vacuo, the yellow solid was chromatographed on Florisil with CH_2Cl_2 eluent. Crystallization of the resulting solid from CH_2Cl_2-hexane at -30°C gave lemon yellow flakes (100 mg, 69% yield), mp 163-165°C.

Characterization: IR (CH_2Cl_2) 2207, 2180 cm^{-1} (ν_{NC}). MS (150°C, 70 eV) M^+ (521, 100%), M^+-2(t-BuNC) (50%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.23 (d, 6H, $^4J_{P-H}$ = 1.8 Hz), 1.53 (s, 9H). Anal. Calcd for

$C_{14}H_{33}B_9N_2Pt$: C, 32.23; H, 6.37; N, 5.37. Found: C, 32.48; H, 6.32; N, 5.49.

^{13}CO Reactions

One atm of ^{13}CO was bubbled through a hexane solution of **83**. The exchange was rapid (complete in 5 minutes) with IR ν_{CO} at 2070, 2032 cm^{-1}.

A slower exchange of ^{13}CO was noted for **87** in CH_2Cl_2 ($t_{1/2}$ = 28 h at 1 atm ^{13}CO, but $t_{1/2}$ = 2 h at 3 atm ^{13}CO (ν_{CO} at 2009 cm^{-1}).

Preparation of [closo-3,3-$(PMe_3)_2$-3,1,2-$Pt(C_2B_9H_{11})$] (99)

To a yellow solution of **87** in 25 mL CH_2Cl_2 (18 mg, 0.042 mmol) was added dropwise an excess PMe_3 solution (100 μL, 1.25 mmol) in 2 mL CH_2Cl_2, which immediately reacted. Solvent and excess PMe_3 were removed under reduced pressure, and crystallization from CH_2Cl_2-hexane at -30°C gave orange crystals (17 mg, 84% yield). The compound could also be prepared using Stone's method.[5a] To a solution of $(PMe_3)_2PtCl_2$ (83.6 mg, 0.2 mmol in 15 mL CH_2Cl_2) was added 113.6 mg (0.21 mmol) $Tl_2C_2B_9H_{11}$. After stirring for 19 h, a brown solution and yellow precipitate (TlCl) resulted. After filtering through a cannula, the solution was concentrated and hexane layered over. Cooling to -30°C gave a yellow solid (86 mg, 90% yield), mp 178-179°C.

Characterization: MS (145°C, 16 eV) M^+ (479, 47%), $M^+-C_2B_9H_{11}$ (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.94 (s, 2H), 1.77 (d, 18H, $^2J_{P-H}$ = 10.4 Hz, $^3J_{Pt-H}$ = 32.0 Hz). Anal. Calcd for $C_8H_{29}B_9P_2Pt$: C, 20.03; H, 6.09. Found: C, 19.51; H, 5.72.

Preparation of [closo-3,3-$(PMe_3)_2$-3,1,2-$Pt(C_2B_9H_9Me_2)$] (100)

The complex was obtained in 82 and 85% yields as a yellow-orange solid using the previous procedures for 99 (mp 160-163°C).

Characterization: MS (120°C, 16 eV) M^+ (507, 71%), $M^+-C_2B_9H_9Me_2$ (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.16 (t, 6H, $^4J_{P-H}$ = 1.1 Hz), 1.70 (d, 18H, $^2J_{P-H}$ = 10.1 Hz, $^3J_{Pt-H}$ = 29.8 Hz). Anal. Calcd for $C_{10}H_{33}B_9P_2Pt$: C, 23.66; H, 6.55. Found: C, 23.83; H, 6.48.

Preparation of [closo-3,3-$(PPh_3)_2$-3,1,2-$Pt(C_2B_9H_{11})$] (101)

The complex was obtained in 48% yield as gold-orange flakes using the procedure for 99. One equivalent of PPh_3 was added to one equivalent of 90 (mp 256-258°C).

Characterization: MS (190°C, 70 eV) M^+ (852, 10%), $M^+-C_2B_9H_{11}$ (100%), M^+-PPh_3 (6%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 7.44-7.28 (m, 30H), 2.96 (s, 2H). Anal. Calcd for $C_{38}H_{41}B_9P_2Pt$: C, 53.57; H, 4.85. Found: C, 53.24; H, 5.26.

Preparation of [closo-3-(PMe_3)-3-(PEt_3)-3,1,2-$Pt(C_2B_9H_9Me_2)$] (102)

To a yellow solution of 92 (92 mg, 0.2 mmol in 5 mL CH_2Cl_2 was added 30 μL (23.6 mg, 0.2 mmol) PEt_3, giving immediate gas evolution and an orange-yellow solution. After 0.5 h stirring, the CH_2Cl_2 was pumped off, leaving an orange solid. Recrystallization from CH_2Cl_2-hexane at -30°C gave an orange-yellow powder (93 mg, 85% yield), mp 178-180°C.

Characterization: MS (140°C, 70 eV), M^+ (550, 66%), $M^+-C_2B_9H_9Me_2$ (84%), $M^+-C_2B_9H_9Me_2-Et$ (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.17 (t, 6H, $^4J_{P-H}$ = 1.7 Hz), 1.96 (m, 6H), 1.67 (d, 9H, $^2J_{P-H}$ = 10.0 Hz, $^3J_{Pt-H}$ = 29.8 Hz), 1.14 (d of t, 9H, $^3J_{P-H}$ = 16.7 Hz, $^3J_{H-H}$ = 7.6 Hz). Anal. Calcd for $C_{13}H_{39}B_9P_2Pt$: C, 28.40; H, 7.15. Found: C, 28.35; H, 6.89.

Preparation of [*closo*-3-(PMe_3)-3-(t-BuNC)-3,1,2-Pt($C_2B_9H_9Me_2$)] (103)

To a yellow solution of **92** in 3 mL CH_2Cl_2 (46 mg, 0.1 mmol) was added dropwise a t-BuNC solution (11 μL, 0.1 mmol) in 2 mL CH_2Cl_2, giving an instantaneous reaction by IR spectroscopy. The CH_2Cl_2 was removed in vacuo, and crystallization of the resulting solid from CH_2Cl_2-hexane at -30°C gave yellow crystals (50 mg, 97% yield), mp 163-165°C.

Characterization: MS (155°C, 16 eV) M^+ (514, 60%), M^+-t-Bu (100%), M^+-t-BuNC (82%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.23 (d, 6H, $^4J_{P-H}$ = 2.2 Hz), 1.71 (d, 9H, $^2J_{P-H}$ = 11.0 Hz, $^3J_{Pt-H}$ = 33.7 Hz), 1.53 (s, 9H). Anal. Calcd for $C_{12}H_{33}B_9NPPt$: C, 28.00; H, 6.46; N, 2.72. Found: C, 27.90; H, 6.43; N, 2.51.

Preparation of [*closo*-3-(PMe_3)-3-(CH_3CN)-3,1,2-Pt($C_2B_9H_9Me_2$)] (104)

To a yellow solution of **92** (92 mg, 0.2 mmol in 10 mL CH_3CN) was added 21 mg (0.28 mmol) Me_3NO, giving immediate gas evolution and an orange solution. After 0.5 h stirring, the acetonitrile was removed under reduced pressure, leaving an orange solid. Crystallization from CH_3CN-ether gave an orange-yellow solid (31 mg, 33% yield), mp 137-139°C.

Characterization: MS (165°C, 70 eV) M^+-CH_3CN (431, 2%), M^+-CH_3CN-PMe_3 (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.37 (d, 3H, $^4J_{Pt-H}$ = 8.8 Hz, $^5J_{P-H}$ = 1.1 Hz), 2.17 (d, 6H, $^4J_{P-H}$ = 2.2 Hz), 1.56 (d, 9H, $^2J_{P-H}$ = 10.6 Hz, $^3J_{Pt-H}$ = 33.6 Hz). Anal. Calcd for $C_9H_{27}B_9NPPt$: C, 22.87; H, 5.76; N, 2.96. Found: C, 22.34; H, 5.74; N, 3.07.

Preparation of [closo-3-(PMe_3)-3-(C_2H_4)-3,1,2-Pt($C_2B_9H_9Me_2$)] (105)

To a solution of cis-Pt(PMe_3)(C_2H_4)Cl_2 (**106**) (370 mg, 1.0 mmol) in 25 mL CH_2Cl_2 was added 570 mg (1.0 mmol) $Tl_2C_2B_9H_9Me_2$. After 6 h stirring, the brown solution was filtered through Celite. Chromatography twice on Florisil (12 x 2.5 cm) with CH_2Cl_2 eluent gave a red-brown powder after solvent was removed in vacuo (176 mg, 38% yield), mp 120°C (decomp).

Characterization: MS (130°C, 70 eV) M^+ (460, 2%), M^+-$C_2B_9H_9Me_2$ (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 3.38 (d, 4H, $^2J_{Pt-H}$ = 50.9 Hz, $^3J_{P-H}$ = 2.9 Hz), 2.03 (d, 6H, $^4J_{P-H}$ = 1.9 Hz), 1.70 (d, 9H, $^2J_{P-H}$ = 11.2 Hz, $^3J_{Pt-H}$ = 34.4 Hz). Anal. Calcd for $C_9H_{28}B_9PPt$: C, 23.52; H, 6.14. Found: C, 23.03; H, 6.15.

Reactions of Acetonitrile Complex 104

A solution of **104** is taken up in CH_2Cl_2. CO is bubbled through for 15 min, and the IR spectrum shows ν_{CO} at 2056 cm^{-1}. Analysis shows the product to be the original starting material **92**.

Ethylene is bubbled through a solution of **104** in CH_2Cl_2 for 15 minutes. The product is purified as before and spectroscopic identification shows it to be **105**.

Preparation of cis-Pt(PMe$_3$)(C$_2$H$_4$)Cl$_2$ (106)

A method similar to the preparation of cis-Pt(PPh$_3$)(C$_2$H$_4$)Cl$_2$ was used. A suspension of [(PMe$_3$)PtCl$_2$]$_2$ (684 mg, 1 mmol) in 30 mL CH$_2$Cl$_2$ was pressurized with 4 atm ethylene in a thick-walled glass bottle. After stirring for 24 h, the yellow suspension changed to a colorless solution, which was filtered and concentrated to give a white solid. Recrystallization from CH$_2$Cl$_2$-ether-hexane gave a white powder (705 mg, 95% yield) mp 100°C (decomp).

Characterization: ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, ambient) δ 4.21 (br, 4H, $^2J_{Pt-H}$ = 62.6 Hz), 1.62 (d, 9H, $^2J_{P-H}$ = 11.9 Hz, $^3J_{Pt-H}$ = 29.1 Hz). ^{31}P NMR (CD$_2$Cl$_2$, ambient) δ -17.15 (s, $^1J_{Pt-P}$ = 3057 Hz). Anal. Calcd for C$_5$H$_{13}$PCl$_2$Pt: C, 16.23; H, 3.54. Found: C, 16.38; H, 3.49.

Preparation of [closo-3-(PMe$_3$)-3,3-(Br)$_2$-3,1,2-Pt(C$_2$B$_9$H$_{11}$)] (107)

To a yellow solution of 87 in 7 mL CH$_2$Cl$_2$ (73 mg, 0.169 mmol) was added dropwise a bromine solution (10 μL Br$_2$, 0.194 mmol) in 2 mL CH$_2$Cl$_2$, giving a red solution. Solvent and excess Br$_2$ were removed under reduced pressure, and recrystallization from CH$_2$Cl$_2$-hexane at -30°C gave red crystals (94 mg, 99% yield), mp 117-121°C.

Characterization: MS (130°C, 70 eV) M$^+$ (563, 4%), M$^+$-Br (100%), M$^+$-2Br (80%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, ambient) δ 5.40 (s, 2H), 2.38 (9H, d, $^2J_{P-H}$ = 12.7 Hz, $^3J_{Pt-H}$ = 36.3 Hz). Anal. Calcd for C$_5$H$_{20}$B$_9$PBr$_2$Pt: C, 10.66; H, 3.58. Found: C, 10.64, H, 3.55.

Preparation of [<u>closo</u>-3-(PMe_3)-3,3-(Br)$_2$-3,1,2-Pt($C_2B_9H_9Me_2$)] (108)

Beginning with 92, the complex was obtained in 100% yield using the procedure for 107, mp 127-130°C.

<u>Characterization</u>: MS (120°C, 70 eV) M^+ (591, 6%), M^+-Br (92%), M^+-2Br (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 2.77 (d, 6H, $^4J_{P-H} = 1.1$ Hz), 2.40 (s, 9H, $^2J_{P-H} = 12.3$ Hz, $^3J_{Pt-H} = 37.9$ Hz). Anal. Calcd for $C_7H_{24}B_9PBr_2Pt$: C, 14.22; H, 4.09. Found: C, 14.28; H, 4.06.

Preparation of [<u>closo</u>-3-(PMe_3)-3-(Et_3Si)-3-(H)-3,1,2-Pt($C_2B_9H_{11}$)] (109)

To a solution of 100.0 mg (0.232 mmol) 87 in 20 mL CH_2Cl_2 was added 1.0 mL (excess) Et_3SiH. The yellow solution was freeze-pump-thawed twice, then irradiated for 28 h. Excess Et_3SiH and CH_2Cl_2 were removed under reduced pressure, leaving an off-white solid (110.4 mg, 92% yield).

<u>Characterization</u>: IR (CH_2Cl_2) 2130 (w) cm^{-1} (ν_{Pt-H}). MS (150°C, 16 eV) M^+ (520, 23%), M^+-2Et (70%), M^+-Et_3SiH (100%). ^1H NMR (CD_2Cl_2, 200 MHz, ambient) δ 3.30 (s, 2H), 1.90 (d, 9H, $^2J_{P-H} = 11.1$ Hz, $^3J_{Pt-H} = 27.3$ Hz), 1.18 (q, 6H, $^2J_{H-H} = 7.8$ Hz), 1.06 (t, 9H, $^2J_{H-H} = 7.8$ Hz), -7.85 (d, 1H, $^2J_{P-H} = 26$ Hz, $^1J_{Pt-H} = 900$ Hz). Anal. Calcd for $C_{11}H_{36}B_9SiPPt$: C, 25.42; H, 6.98. Found: C, 25.29; H, 6.73.

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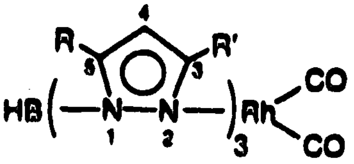
CHAPTER VII

SUMMARY AND CONCLUSIONS

The work reported in the foregoing Chapters involves the synthesis and characterization of a number of pyrazolylborate rhodium and carborane platinum complexes, which have been studied in carbon-hydrogen activation reactions. The investigations comprising this Thesis can be summarized under five major headings.

1. Synthesis of Rhodium and Platinum Dicarbonyl Complexes

A number of tris(pyrazolyl)borate rhodium dicarbonyl complexes of the general form $HB(3\text{-}R'\text{-}5\text{-}RPz)_3Rh(CO)_2$ (**1**, R' = Ph, R = H; **22**, R' = CF_3, R = CH_3; **52**, R' = t-Bu, R = H and **55**, R' = i-Pr, R = H) have been prepared (eq. 7-1).



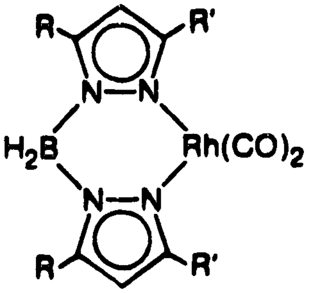
(7-1)

These are direct analogs of $(HBPz^*_3)Rh(CO)_2$ (R' = R = Me), the complex utilized by Ghosh in C-H activation studies.[1] From the IR ν_{CO} bands of the latter complex, Ghosh determined that the complex was entirely η^3 in solution. On the other hand, complexes **22** and **55** consist of mixtures of η^2:η^3 isomers in an approximate 2:1 ratio, whereas complex **1** is predominantly η^2 in solution and **52** is entirely so. These η^2:η^3 ratios appear to be governed primarily by the steric size of the R' group in the 3-position of the pyrazole ring close to rhodium. As the steric size increases from Me < CF_3 ≈ i-Pr < Ph < t-Bu, there is an increasing amount of η^2 form present in the order $(HBPz^*_3)Rh(CO)_2$ < **22** ≈ **55** < **1** < **52**.

For complex **1**, the IR and low temperature ^1H and ^{13}C NMR spectra in several solvents show both η^2 and η^3 forms present in varying amounts. The results shed new light on the question of η^2 versus η^3 coordination, and is the first example of an equilibrium where both forms were present in observable amounts which can be monitored by NMR. Based on the IR and NMR $\eta^2:\eta^3$ ratios obtained at two different temperatures, some thermodynamic parameters could be estimated in two cases. For the $\eta^2 \rightleftharpoons \eta^3$ equilibrium as written, $\Delta H° = -2.95$ kcal and $\Delta S° = -11.6$ cal K^{-1} in CH_2Cl_2, and in toluene, $\Delta H° = -1.07$ kcal and $\Delta S° = -6.0$ cal K^{-1}. These values are consistent, as ΔH° is negative, corresponding to formation of the third nitrogen to rhodium bond, and ΔS° is also negative, as the η^3 form is more ordered than the η^2 form.

It should be mentioned that two other such complexes were prepared; $HB(Et,MePz)_3Rh(CO)_2$ **65** and $HB(i\text{-}Bu,MePz)_3Rh(CO)_2$ **71**. Both the tris(pyrazolyl)borate ligands themselves were mixtures of regioisomers, where Me groups occupy both R' and R positions. The IR ν_{CO} bands of **65** and **71** in hexane are similar to those of $(HBPz*_3)Rh(CO)_2$, but **71** also shows a small amount of the η^2 isomer (estimated 1%).

For the above complexes, the bis(pyrazolyl)borate analogs $H_2B(3\text{-}R'\text{-}5\text{-}RPz)_2Rh(CO)_2$ (**2**, R' = Ph, R = H, **20a**, R' = CF_3, R = CH_3; **54**, R' = t-Bu, R = H and **57**, R' = i-Pr, R = H) have been prepared (eq. 7-2).

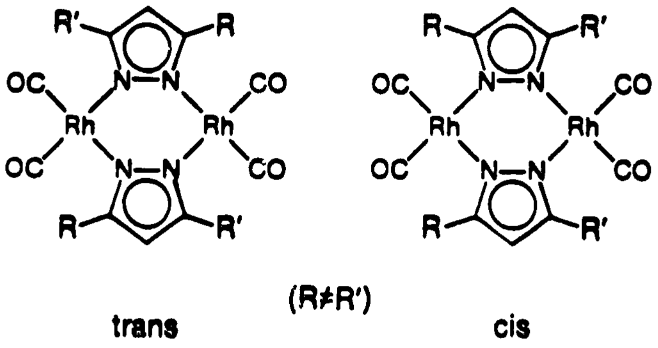


(7-2)

The hapticity of the tris(pyrazolyl)borate complexes can also be determined by comparing their IR ν_{CO} bands to those of the bis(pyrazolyl)borate analogs. For those complexes that exist as equilibrium $\eta^2:\eta^3$ mixtures, the IR ν_{CO} bands of the bis(pyrazolyl)borate complexes are very similar to those of the η^2 form present.

For complexes $H_2B(CF_3,MePz)_2Rh(CO)_2$ **20** and $H_2B(i\text{-}Bu,MePz)_2Rh(CO)_2$ **69**, mixtures of regioisomers were obtained. For the former set, the three possible isomers were separated and characterized, but this could not be accomplished with the mixture **69**. Complex $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)(3\text{-}Me\text{-}5\text{-}CF_3Pz)Rh(CO)_2$ **20b** is the first example of a bis(pyrazolyl)borate complex with an unsymmetric pyrazole bound in the two possible orientations. The bis(pyrazolyl)borate complex $H_2B(3,5\text{-}(CF_3)_2Pz)_2Rh(CO)_2$ **17** was also prepared, but the tris(pyrazolyl)borate analog was not realized.

In the reactions to prepare the tris(pyrazolyl)borate rhodium dicarbonyl complexes, a second product was isolated, so-called pyrazole bridged dimers. These are thought to arise not from free pyrazole present in the tris(pyrazolyl)borate salt, but from B-N bond cleavage in the ligand. The majority of the pyrazoles used were unsymmetric, which leads to trans and cis isomers (eq. 7-3).



(7-3)

The trans form was assigned as the major isomer, based on steric crowding of the larger R groups in the cis isomer. The trans:cis isomer ratio appears to be governed by both steric and electronic factors. Stobart has prepared related iridium dimers of the type $[(COD)Ir(pyrazole)]_2$,[2] and it was found that with unsymmetric pyrazoles, either mixtures or only one major isomer was obtained.

A platinacarborane analog of $Cp^*Ir(CO)_2$, [closo-3,3-$(CO)_2$-3,1,2-$Pt(C_2B_9H_9Me_2)$] **83** was prepared. The IR ν_{CO} bands in hexane were of higher energy than those for $Cp^*Ir(CO)_2$, indicating that the carborane ligand is a poorer electron donor than Cp*. This is the first example of a carbonyl platinacarborane complex.

2. Synthesis of Pyrazolylborate Rhodium Olefin Complexes

The synthesis of a number of bis(olefin) and mixed olefin carbonyl complexes was accomplished. With the $HB(3\text{-}PhPz)_3$ and $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3$ ligands, the carbonyl ethylene, bis(ethylene) and COD complexes were prepared.

Similar to complex **1**, the bis(ethylene) and COD complexes (**14** and **15** respectively) exhibited interesting NMR spectra, as both showed equilibrium mixtures of the η^2 and η^3 forms at room temperature. The η^2 form has the expected 2:1 ratio of pyrazole group resonances, while the η^3 form has a single resonance, where all three pyrazole groups are averaged by a pseudorotation or turnstile mechanism. On cooling the COD sample **15** to -90°C, the latter process was slowed down on the ^1H NMR timescale to give a 2:1 ratio of pyrazole group resonances arising from the five-coordinate geometry.

Ghosh prepared carbonyl olefin complexes of the type

$(HBPz^{*}_3)Rh(CO)(olefin)$ (olefin = ethylene and COE)[1] and based on comparison of the IR ν_{CO} bands of the unstable bis(pyrazolyl)borate analogs, these complexes are η^2 in solution. However, it was found that the low temperature ^1H NMR spectra showed a 2:1 ratio of pyrazole group resonances. There is thought to exist a low-temperature process which averages the two bound pyrazole groups by proceeding through a trigonal bipyramidal intermediate.

The ^1H NMR spectra of the carbonyl olefin complexes **13**, **24** and **25** all show a similar 2:1 ratio of pyrazole group resonances at low temperature. The bis(pyrazolyl)borate analogs of the carbonyl ethylene complexes **13** and **26** were also found to be unstable in solution, but the COE complex $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(COE)$ **27** was relatively stable.

The first examples of pyrazolylborate complexes enriched with ^{15}N were prepared. Efficient syntheses of ^{15}N labelled tris(dimethylpyrazol-1-yl)borato complexes $(HBPz^{*}_3)Rh(CO)(L)$ (**79**, L = ethylene, **80**, L = CO) were worked out. Subsequent ^{13}C and ^{15}N NMR studies served as a probe to establish the hapticity of the tris(pyrazolyl)borate ligand in solution, and will be important in ongoing studies of the mechanism of the fluxional processes.

3. Ligand Substitution Reactions

A number of ligand substitution reactions of the various dicarbonyl complexes were studied, specifically with carbon monoxide, tertiary phosphines and other two-electron donors.

a. Carbon monoxide

It is well established that 18e metal carbonyl complexes do not readily exchange ^{13}CO, but cyclopentadienyl complexes are thought to do so by an associative mechanism, where the Cp ring changes its hapticity from η^5 to η^3. In the same manner, a tris(pyrazolyl)borate complex which is entirely η^3 in solution (18e) would not be expected to exchange ^{13}CO, whereas one that is partially or entirely η^2 should rapidly do so. As demonstrated in this Thesis, (HBPz*$_3$)Rh(CO)$_2$, which is entirely η^3 in hexane,[1] shows no ^{13}CO exchange in hexane after four hours. In CH_2Cl_2, where a small amount of the η^2 isomer is present in the IR spectrum (estimated at 1%),[1] complete ^{13}CO exchange takes place after about 18 hours. Complexes **1**, **22**, **52** and **55**, which all show some η^2 isomer in solution, rapidly exchange ^{13}CO in about five minutes.

On the other hand, complex **65**, which is entirely η^3 in hexane, shows no ^{13}CO exchange after four hours. Complex **71**, which has about 1% of the η^2 isomer present in the IR spectrum in hexane, is completely ^{13}CO enriched after about 20 hours. As expected, all the bis(pyrazolyl)borate analogs (**2**, **17**, **20**, **54**, **57** and **69**), which by necessity are 16e species, completely exchange ^{13}CO in about five minutes.

Lastly, for the platinacarborane complex [closo-3,3-(CO)$_2$-3,1,2-Pt($C_2B_9H_9Me_2$)] **83**, rapid ^{13}CO exchange occurs. There is some question in these d^8 metallacarborane complexes regarding the slipped structure of the carborane ligand, as observed from the crystal structure of **87** and other related platinum complexes. This slipping suggests an η^3 carborane ligand, much like an η^3-Cp group, which would make the Pt complex 16e. This would account for the rapid ^{13}CO exchange relative to Cp*Ir(CO)$_2$, which exchanges ^{13}CO much more slowly ($t_{1/2}$ = two hours in hexane).[3] This is the first such chemical evidence consistent with a facile η^5-η^3 conversion.

b. Tertiary phosphines

The reactions of the bis and tris(pyrazolyl)borate complexes **22** and **20a** with PMe_3 gave both mono and bis(phosphine) complexes. These were postulated to be η^2 and η^1 isomers respectively based on the variable temperature NMR spectra. With larger phosphines, such as PPh_3 or PCy_3, only monophosphine complexes of the type $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(PR_3)$ were formed. At low temperature, the ^1H NMR spectra of these two latter complexes show a 1:1:1 ratio of pyrazole group resonances. This is the slowing down of the so-called low-temperature process responsible for averaging the two bound pyrazole groups. Both the barriers to the so-called high and low temperature processes are higher in these monophosphine complexes than in Ghosh's Pz* analogs.

The reaction of PMe_3 with the dicarbonyl **83** rapidly gives the complex [closo-3-(CO)-3-(PMe_3)-3,1,2-Pt($C_2B_9H_9Me_2$)] **92**. This is in contrast to the forcing conditions required to form Cp*Ir(CO)(PMe_3) from Cp*Ir$(CO)_2$ (excess PMe_3, 70°C, 24 hours).[4] Other carborane platinum complexes of the type [closo-3-(CO)-3-(L)-3,1,2-Pt($C_2B_9H_9R'_2$)] (L = CO, PR_3, R' = H, Me) have been prepared. These complexes also react further with tertiary phosphines to give a number of bis(phosphine) complexes.

c. Other ligand substitution reactions

Both the dicarbonyl $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)_2$ **22** and the carbonyl phosphine [closo-3-(CO)-(PMe_3)-3,1,2-Pt($C_2B_9H_9Me_2$)] **92** react with Me_3NO in CH_3CN to give the acetonitrile complexes $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3$-Rh(CO)($CH_3CN$) **42** and [closo-3-($CH_3CN$)-3-($PMe_3$)-3,1,2-Pt($C_2B_9H_9Me_2$)] **104** respectively. Based on IR and NMR spectral data, the acetonitrile ligand is bound in the more common end-on manner in both complexes.

When the reaction of **22** with Me_3NO is repeated in CH_2Cl_2, two products form, $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(NMe_3)$ **44** and $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(ONMe_3)$ **43**, and the latter complex is postulated to have a coordinated Me_3NO ligand. The reaction sequence to form these two complexes is thought to be similar to that proposed by Brown for some dinuclear rhenium complexes.[5]

The first examples of pyrazolylborate rhodium acetylene complexes were prepared in this Thesis. Displacement of the labile COE ligand in **25** by 2-butyne or hexafluoro-2-butyne resulted in complexes of the type $HB(3\text{-}CF_3\text{-}MePz)_3Rh(CO)(R_3CC{\equiv}CCR_3)$ (**40**, R = H, **41**, R = F). Complex **40** is best described as a Rh(I) acetylene complex which exists as mixtures of the η^2 and η^3 forms, while **41** appears to be best described as a Rh(III) metallacyclopropene complex, with an η^3 tris(pyrazolyl)borate ligand.

4. Carbon-Hydrogen Bond Activation

The parent complex $(HBPz^*_3)Rh(CO)_2$ utilized by Ghosh demonstrated efficient C-H bond activation of a number of alkanes and arenes. A goal of this Thesis was to prepare analogs of this complex and compare and contrast the C-H activation reactions.

Ultraviolet irradiation of a benzene or cyclohexane solution of $HB(3\text{-}PhPz)_3Rh(CO)_2$ **1** resulted in intramolecular C-H activation of one of the 3-Ph groups. The product **7** is thought to have a five-membered orthometallated ring. The reaction of **7** with CH_2N_2 resulted in a double insertion of "CH_2", giving complex **9**. The rhodium hydride has been converted to a rhodium methyl group, and formally a CH_2 group has been inserted into the five-membered ring giving a six-membered ring product.

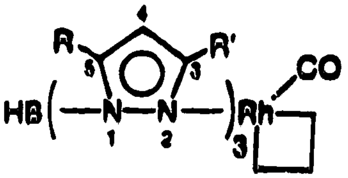
Photolysis of HB(3-CF_3-5-MePz)$_3$Rh(CO)$_2$ **22** in benzene afforded HB(3-CF_3-5-MePz)$_3$Rh(CO)(H)(C_6H_5) **49**. Complex **49** can also be formed thermally by the reaction of the dicarbonyl **22** with Me_3NO in benzene. A solution of **49** in toluene-d_8 undergoes exchange in the range of -10°C to +20°C, and it follows first-order kinetics. The enthalpy of activation $\Delta H^{\ddagger}$ is about 10 kcal mol^{-1} lower than the value for the benzene-d_6 exchange kinetics with (HBPz*$_3$)Rh(CO)(H)(C_6H_5).[1] Also, the rate of the so-called CO back reaction to give the parent dicarbonyl is quite different from that determined by Ghosh.[1]

Complex **49** reacts rapidly with one atmosphere CO in benzene ($t_{1/2}$ = five minutes) to give **22**, whereas the analogous reaction in the Pz* system is slow ($t_{1/2}$ = 23 hours in hexane). Attempts at conversion of **49** to a more stable halide derivative resulted in formation of dihalide. Also, the IR spectrum of **49** in n-hexane shows the presence of the hexyl hydride HB(3-CF_3-5-MePz)$_3$Rh(CO)(H)(hexyl) **49a**, which suggests an equilibrium between **49** and **49a**. This was not observed in the analogous Pz* system. The above reactions suggest that the rhodium phenyl bond is weaker in **49** than in the Pz* analog.

In contrast to the Pz* system, the products of alkane C-H activation from **22** were not stable at room temperature, but the hexyl hydride appears stable below -30°C. This is very reminiscent of work by Jones with Cp*Rh(PMe_3)H_2,[6] where the arene activation products are stable at room temperature, but the analogous alkane activation products are stable only below -30°C.

Irradiation of HB(3-i-PrPz)$_3$Rh(CO)$_2$ **55** in benzene afforded the phenyl hydride HB(3-i-PrPz)$_3$Rh(CO)(H)(C_6H_5) **58**, while in cyclohexane the intramolecular C-H activation product **60** is formed, which like complex **7** also is thought to have a five-membered ring. A cyclohexane solution of **60** reacts thermally with excess benzene to give the phenyl hydride **58** in about an hour. This sequence of reactions is similar to that reported by Werner with $(C_6H_6)Ru(P(i\text{-}Pr)_3)H_2$,[7] where one of the isopropyl groups of the phosphine was activated.

Although the three dicarbonyls (**1**, **22** and **55**) above give different types of C-H activation products, all three complexes react photochemically with cyclopropane to give the corresponding rhodacyclobutane complexes $HB(3\text{-}R'\text{-}5\text{-}RPz)_3\overline{Rh(CO)(CH_2CH_2CH_2})$ (**11**, R' = Ph, R = H; **50**, R' = CF_3, R = CH_3 and **62**, R' = i-Pr, R = H, eq. 7-4).



(7-4)

This reaction was also demonstrated by Ghosh with $(HBPz^*_3)Rh(CO)_2$, and this suggests that cyclopropane activation may be a good model for complexes to test C-H activation.

5. Other Oxidative Addition Reactions

One can also consider the oxidative addition of dihydrogen or silanes as model reactions for C-H activation.[8] The dicarbonyl **22** reacts photochemically with H_2 in cyclohexane giving the dihydride **45**, and also adds $HSiCl_3$ or $HSiMe_3$ to give complexes of the type $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(H)(SiR_3)$ (**46**, R = Cl, **47**, R = Me). Although the bis(pyrazolyl)borate complexes prepared in this and Ghosh's Thesis appear inert to C-H bond activation, $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)_2$ **20a** oxidatively adds $HSiMe_3$ to give an unstable 16e Rh(III) complex $H_2B(3\text{-}CF_3\text{-}5\text{-}MePz)_2Rh(CO)(H)(SiMe_3)$ **48**.

Although the platinacarborane complexes are also inert to C-H bond activation, the complex [closo-3-(PMe_3)-3-(CO)-3,1,2-Pt($C_2B_9H_{11}$)] **87** reacts with $HSiEt_3$ photochemically giving the product [closo-3-(Et_3Si)-3-(H)-3-(CO)-3,1,2-Pt($C_2B_9H_{11}$)] **109**.

The oxidative addition of bromine to complexes **87** and **92** occurs readily, giving the complexes [closo-3-(PMe_3)-3,3-$(Br)_2$-3,1,2-Pt($C_2B_9H_9R'_2$)] (**107**, R' = H, **108**, R' = Me). The oxidative addition of methyl iodide does not occur with any of the Rh(I) or Pt(II) complexes prepared in this Thesis. However, the phenyl hydride **49** reacts thermally with CH_3I giving the complex $HB(3\text{-}CF_3\text{-}5\text{-}MePz)_3Rh(CO)(I)(Me)$ **51**.

References for Chapter VII

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