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THE UNIVERSITY OF ALBERTA

TRISPYRAZOLYL TRANSITION METAL COMPLEXES

BY

LIANGBING GAN

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE
STUDIES AND RESEARCH IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

SPRING 1990

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a Thesis entitled TRISPYRAZOLYL TRANSITION METAL COMPLEXES submitted by LIANGBING GAN in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

Supervisor

R G Cavell

R S Brown

D G Dalla Lana

External Examiner

Date 24 October 1989

TO MY PARENTS

ABSTRACT

Trispyrazolyl rhenium and rhodium complexes have been synthesized, and their reactivity has been investigated.

The structure of $HBPz^{*}{}_3Re(CO)_3$ **1** has been determined by a single crystal X-ray diffraction study. Irradiation of **1** in THF afforded the useful intermediate $HBPz^{*}{}_3Re(CO)_2(THF)$ **3** from which complexes $HBPz^{*}{}_3Re(CO)_2L$ ($L = PMe_3, PPh_3, N_2$) are available. An unusual reaction of **3** with CCl_4 gave the stable 17-electron radical $HBPz^{*}{}_3Re(CO)_2Cl$ **8** and the 16-electron $HBPz^{*}{}_3Re(CO)Cl_2$. Sodium sand reduced **8** to the anion $[HBPz^{*}{}_3Re(CO)_2Cl]^-$, the X-ray structure of which has been determined as the PPN^+ salt. Other 17-electron radicals $HBPz^{*}{}_3Re(CO)_2X$ (X = Br, I, OMe, OEt) have been prepared. Oxidation of **3** using NO^+ gave the radical cation $[HBPz^{*}{}_3Re(CO)_2(THF)]BF_4$. The ability of the bulky ligand $[HBPz^{*}{}_3]^-$ to stabilize these 16- and 17-electron complexes is remarkable.

Trispyrazolylborate rhodium complexes have been shown to activate C-H bonds. Irradiation of $HBPz^{*}{}_3Rh(CO)(PMe_3)$ in benzene produced $HBPz^{*}{}_3Rh(CO)(H)(Ph)$ and $HBPz^{*}{}_3Rh(H)(Ph)(PMe_3)$ **46** in a ratio of 3:7. Pure **46** resulted when $HBPz^{*}{}_3Rh(C_2H_4)(PMe_3)$ was irradiated or heated (dark, 101°C) in a benzene solution. Complex **46** reacted with H_2O to form the novel hydroxy derivative $HBPz^{*}{}_3Rh(OH)(Ph)(PMe_3)$ **50**. For the exchange reaction of **46** with C_6D_6, $\Delta H^{\neq}$ is equal to 24.9 ± 0.4 Kcal mol^{-1}, and $\Delta S^{\neq}$ is equal to -10.3 ± 1.1 cal K^{-1} mol^{-1}.

The acetylacetonate derivative $AcacRh(CO)L$ ($L = CO, PEt_3, PCy_3, PPh_3$) was used to prepare complexes with the general formula

$[HCPz^*{}_3Rh(CO)L]BF_4$. All these cationic complexes activate C-H bonds when irradiated in benzene solutions.

Some prelimilary results on the coordination chemistry of imidazolylmethanol ligands have been obtained. Several trisimidazolyl methanol complexes of molybdenum and manganese were prepared.

ACKNOWLEDGEMENTS

The author expresses sincere appreciation and gratitude to:

Dr. W.A.G. Graham for his expert guidance, encouragement throughout the course of this work.

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LIST OF ABBREVIATIONS

Acac	acetylacetonate anion
COD	cyclooctadiene
COE	cyclooctene
Cleland Reagent	dithiothreitol
Cp	cyclopentadienyl
Cp^*	pentamethylcyclopentadienyl
Cy	cyclohexyl
dmpe	$Me_2PCH_2CH_2PMe_2$
ESR	electron spin resonance
Hacac	acetylacetone
$HBPz_3$	hydrotris(pyrazol-1-yl)borato
$HBPz^*_3$	hydrotris(3,5-dimethylpyrazol-1-yl)borato
$HCPz_3$	tris(pyrazol-1-yl)methane
$HCPz^*_3$	tris(3,5-dimethylpyrazol-1-yl)methane
$HOCIm'_3$	tris(1-methylimidazol-2-yl)methanol
$HOCIm^*_3$	tris(1,4,5-trimethylimidazol-2-yl)methanol
Hz	hertz, sec^{-1}
IR	infrared
MS	mass spectrum
NBL	norbornylene
NBS	N-bromosuccinimide
NMR	nuclear magnetic resonance
PPN^+	$[(Ph_3P)_2N]^+$
UV	ultraviolet
μ	linear absorption coefficient (in the description of crystal data)
μ_B	magnetic moment in Bohr magneton
χ	magnetic susceptibility

LIST OF NAMED COMPLEXES

Compound Formula	Compound Number	Page Number First cited
$HBPz^{*}_{3}Re(CO)_3$	1	30
$(CH_3O)_2BPz^{*}_{2}Re(CO)_3(CH_3OH)$	2	30
$HBPz^{*}_{3}Re(CO)_2(THF)$	3	31
$HBPz^{*}_{3}Re(CO)_2(PMe_3)$	4	31
$HBPz^{*}_{3}Re(CO)_2(PPh_3)$	5	32
$HBPz^{*}_{3}Re(CO)_2(N_2)$	6	33
$[HBPz^{*}_{3}Re(O)_3]_n$	7	34
$HBPz^{*}_{3}Re(CO)_2(Cl)$	8	56
$HBPz^{*}_{3}Re(CO)(Cl)_2$	9	58
$PPN[HBPz^{*}_{3}Re(CO)_2(Cl)]$	10	57
$HBPz^{*}_{3}Re(CO)(NO)(Cl)$	11	59
$HBPz^{*}_{2}(4\text{-}Cl\text{-}Pz^{*})Re(CO)(Cl)_2$	12	60
$HBPz^{*}(4\text{-}Cl\text{-}Pz^{*})_2Re(CO)(Cl)_2$	13	60
$HBPz^{*}_{3}Re(CO)_2(Br)$	14	60
$HBPz^{*}_{3}Re(CO)(Br)_2$	15	60
$PPN[HBPz^{*}_{2}(4\text{-}Br\text{-}Pz^{*})Re(CO)_2(Br)]$	16	61
$PPN[HBPz^{*}(4\text{-}Br\text{-}Pz^{*})_2Re(CO)_2(Br)]$	17	61
$HBPz^{*}_{3}Re(CO)_2(I)$	18	62
$[HBPz^{*}_{3}Re(CO)_2(THF)]BF_4$	19	63
$[HBPz^{*}_{3}Re(CO)_2(NO)]BF_4$	20	64
$HBPz^{*}_{3}Re(CO)_2(OMe)$	21	65
$HBPz^{*}_{3}Re(CO)_2(OEt)$	22	65

continued

Compound Formula	Compound Number	Page Number First cited
$HBPz^{*}{}_3Re(CO)_2(OCH_2CH_2OH)$	23	66
$HBPz^{*}{}_3Re(CO)(NO)(COOH)$	24	66
$HBPz^{*}{}_3Re(CO)(NO)(CH_3)$	25	67
$[HCPz^{*}{}_3Rh(CO)_2]BF_4$	26	102
$\{[HCPz^{*}{}_2(HPz^{*})]Rh(CO)_2\}(BF_4)_2$	27	103
$[HCPz^{*}{}_3Rh(CO)(Br)_2]BF_4$	28	104
$[HCPz^{*}{}_3Rh(CO)(CH_3)(I)]BF_4$	29	104
$[HCPz^{*}{}_3Rh(CO)(PPh_3)]BF_4$	30	105
$[HCPz^{*}{}_3Rh(CO)(PEt_3)]BF_4$	31	106
$[HCPz^{*}{}_3Rh(Ph)(H)(PEt_3)]BF_4$	31 A	111
$[HCPz^{*}{}_3Rh(H)_2(PEt_3)]BF_4$	31 B	111
$[HCPz^{*}{}_3Rh(CO)(PCy_3)]BF_4$	32	106
$[HCPz^{*}{}_3Rh(CO)(COE)]BF_4$	33	107
$[HCPz^{*}{}_3Rh(CO)(Ph)(H)]BF_4$	34	107
$[HCPz^{*}{}_3Rh(CO)(H)_2]BF_4$	35	110
$[HCPz^{*}{}_3Rh(CO)(Ph)(Cl)]BF_4$	36	108
$[HCPz^{*}{}_3Rh(CO)(C_2H_4)]BF_4$	37	109
$\{HCPz^{*}{}_3Rh[(C_6H_4)P(C_6H_5)_2](H)\}BF_4$	38	110
$[HCPz_3Rh(CO)_2]BF_4$	39	112
$[(HCPz_3Rh)_2(CO)_3](BF_4)_2$	40	112
$[HCPz_3Rh(C_2H_4)_2]BF_4$	41	113
$[HCPz_3Rh(C_2H_4)(PPh_3)]BF_4$	42	113
$HCPz^{*}{}_3Rh(Cl)_3$	43	114

continued

Compound Formula	Compound Number	Page Number First cited
$\mathrm{(EtO)CPz_3Rh(Cl)_3}$	44	114
$\mathrm{HBPz^*_3Rh(C_2H_4)(PMe_3)}$	45	139
$\mathrm{HBPz^*_3Rh(Ph)(H)(PMe_3)}$	46	140
$\mathrm{HBPz^*_3Rh(C_6D_5)(D)(PMe_3)}$	47	141
$\mathrm{HBPz^*_3Rh(Ph)(Br)(PMe_3)}$	48	141
$\mathrm{HB(4\text{-}Br\text{-}Pz^*)_3Rh(Ph)(Br)(PMe_3)}$	49	142
$\mathrm{HBPz^*_3Rh(Ph)(OH)(PMe_3)}$	50	142
$\mathrm{HBPz^*_3Rh(H)_2(PMe_3)}$	51	144
$\mathrm{HBPz^*_3Rh(CO)(NBL)}$	52	144
$\mathrm{HBPz^*_3Rh(CO)(PMe_3)}$	53	139
$\mathrm{HBPz^*_3Rh(CO)(PEt_3)}$	54	139
$\mathrm{HBPz^*_3Rh(Ph)(H)(PEt_3)}$	54 A	145
$\mathrm{HBPz^*_3Rh(CO)(PCy_3)}$	55	139
$\mathrm{[im'_2CO]Re(CO)_3Br}$	56	170
$\mathrm{[HOCIm'_3Mo(CO)_3]_n}$	57	170
$\mathrm{[HOCIm'_3Mo(CO)_2(NO)]BF_4}$	58	171
$\mathrm{[HOCIm^*_3Mo(CO)_3]_n}$	59	172
$\mathrm{[HOCIm^*_3Mo(CO)_2(NO)]BF_4}$	60	172
$\mathrm{[Im^*C(OH)Im^*_2Mo(CO)_2(NO)]BF_4}$	60 A	172
$\mathrm{[HOCIm'_3Mn(CO)_3]PF_6}$	61	173
$\mathrm{[HOCIm^*_3Mn(CO)_3]PF_6}$	62	173
$\mathrm{[(MeO)_2BIm']_2}$	63	175
$\mathrm{Re(CO)_3(HIm')_2Br}$	64	175
$\mathrm{[(MeO)_2BIm'_2]Rh(CO)_2}$	65	175

CHAPTER ONE

INTRODUCTION

This Thesis describes the syntheses of transition-metal complexes having polydentate nitrogen donor ligands. Since most contain at least one metal to carbon bond, they are by definition organometallic complexes. The two main and separate themes of the work to be described are the reactivity of these complexes in carbon-hydrogen (C-H) activation, and the ability of the ligands to stabilize complexes which have other than the 18-electron closed shell electronic configuration.

In this introductory Chapter, some basic principles of transition-metal organometallic chemistry and the current state of C-H activation will be briefly reviewed.

SECTION I

EIGHTEEN-ELECTRON FORMALISM

Most transition-metal complexes contain 18 valence electrons, a statement known as the 18-electron Rule or Effective Atomic Number Rule or the Inert Gas Formalism. It was first proposed by Sidgwick in 1934.[1] A theoretical treatment was given by Craig and Doggett in 1963.[2] Later, Mitchell and Parish provided a helpful qualitative explanation for this rule.[3]

The reasons why this formalism works can be seen in terms of a molecular orbital description of a typical octahedral complex. A transition-metal has nine valence orbitals: five nd orbitals (where n

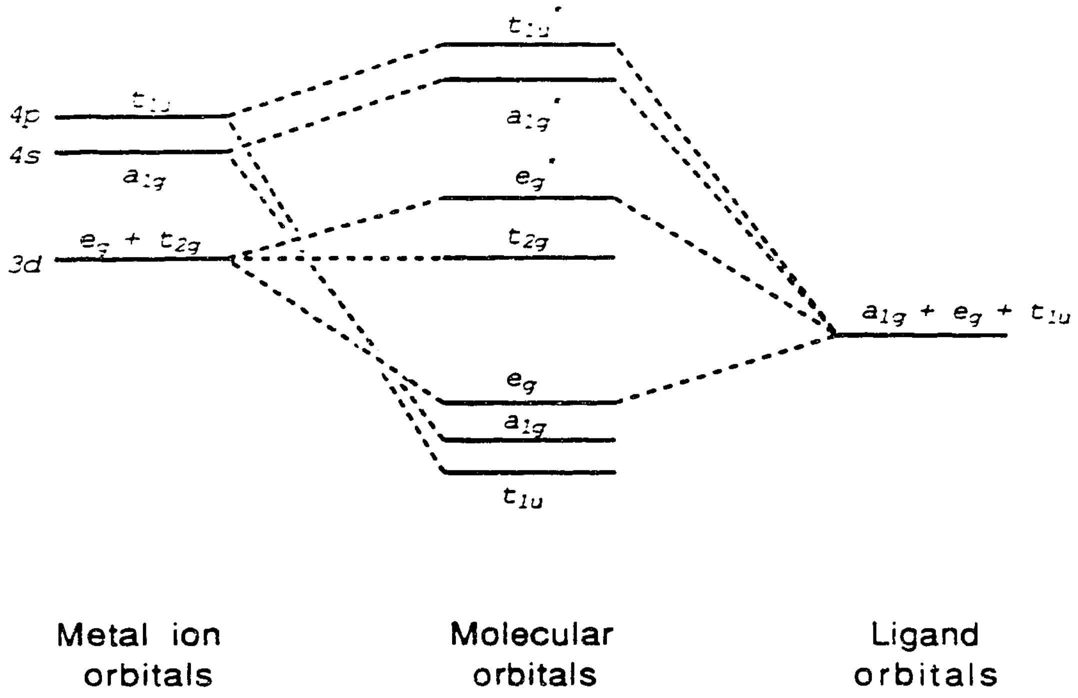
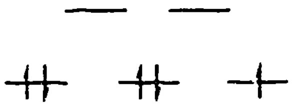


Figure I-1 Molecular Orbital Energy Diagram for Octahedral ML_6 Complex is the principal quantum number), three (n+1)p orbitals, and one (n+1)s orbital. In an octahedral environment, as shown in Figure I-1,[3,4] the nd orbitals split into orbitals of t_{2g} and e_g symmetries, the (n+1)p orbitals have t_{1u} symmetry, and the (n+1)s orbital has a_{1g} symmetry. The six σ-bonding ligands give rise to ligand orbitals of e_g, t_{1u}, and a_{1g} symmetries. Metal and ligand orbitals of proper symmetry then interact to give bonding (lower in energy than the isolated metal or ligand orbitals) and antibonding (higher in energy then the isolated metal or ligand orbitals) molecular orbitals. Thus there are six bonding and six antibonding molecular orbitals. The metal nd orbitals of t_{2g} symmetry have no corresponding ligand orbitals with which they can interact; they therefore remain as nonbonding orbitals of t_{2g} symmetry.

In an octahedral transition-metal complex, the six bonding orbitals are always occupied and accommodate 12 electrons, which may be considered as being donated by the ligands. A maximum of six electrons, which may be considered as being donated by the metal atom, can be accommodated in the three nonbonding orbitals. The e_g^* orbitals are antibonding, and not occupied. Hence the total number of electrons is 18, which is what the Eighteen-electron Rule refers to.

If the three nonbonding orbitals are partially occupied, a complex containing fewer than 18 valence electrons results. Thus, a 17-electron complex results from the occupation of the nonbonding t_{2g} orbitals by five electrons. For example, $HBPz^*{}_3Re(CO)_2Cl$, described later in this Thesis, is a 17-electron complex since the formal oxidation state of rhenium is +2 and there are only five d-electrons from Re(II) available to populate the t_2 orbitals.



$HBPz^*_3Re(CO)_2Cl$ **8**
Re(II), d^5

Another common type of complexe is the square planar ML_4 compounds. These complexes usually consists of a d^8 metal center and have a total of 16 valence electrons. Many of the Rh(I) (d^8) complexes are square planar with 16 valence electrons such as $AcacRh(CO)_2$.[5]

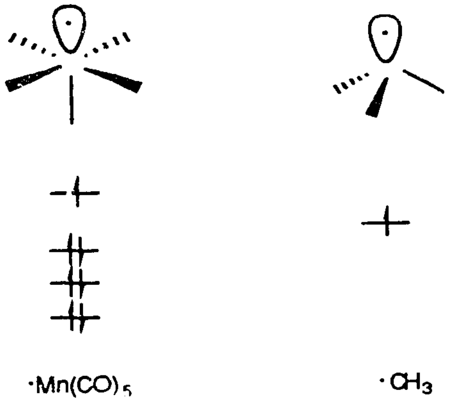
Complexes having more than or fewer than 18 valence electrons are known. Chu and Hoffmann[6] have pointed out that all these complexes actually obey the spirit of the 18-electron rule: all their bonding and nonbonding orbitals are occupied and all of their antibonding molecular orbitals are empty.

SECTION II

ISOLOBAL ANALOGY

Two fragments are isolobal if "the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar -- not identical, but similar".[7] The frontier orbitals are the higher occupied and lower unoccupied molecular orbitals.

The figure below shows the frontier orbitals of $\cdot Mn(CO)_5$ and $\cdot CH_3$. Both fragments consist of a single a_1 orbital with a single electron. The similarity of the two can also be demonstrated from their chemical behavior. $\cdot CH_3$ dimerizes to ethane, $\cdot Mn(CO)_5$ dimerizes to $Mn_2(CO)_{10}$. The two radicals can even be co-dimerized to give $(CO)_5Mn(CH_3)$.



Addition of one electron to both fragments should give two anionic isolobal species, $Mn(CO)_5^-$ and CH_3^-. Similarly, removal of one electron from both fragments should give two isolobal cationic species, $Mn(CO)_5^+$ and CH_3^+.

Examination of their frontier orbitals shows that CH_2 is isolobal to $Fe(CO)_4$; CH is isolobal to $Mn(CO)_4$ and C is isolobal to $Fe(CO)_3$. Similar examination of the frontier orbitals of cyclopentadienyl ligand Cp^- reveals that it is isolobal with $HBPz_3^-$ and three mutually cis carbonyl ligands. So $CpRe(CO)_3$ is isolobal to $HBPz_3Re(CO)_3$ and

$$\mathrm{CpRe(CO)_3} \underset{\smile}{\longleftrightarrow} \mathrm{HBPz_3Re(CO)_3} \underset{\smile}{\longleftrightarrow} \mathrm{Re(CO)_5Br}$$

$(CO)_5ReBr$ (the "two-headed arrow with half an orbital below" represents an isolobal relationship). Table I-1 [8] shows some examples of metal fragments which are isolobal with each of the fundamentally different one-carbon hydrocarbon fragments: CH_3, CH_2, CH and C. Note that the addition or subtraction of a proton from the one-carbon fragments does not change the number of electrons in frontier orbitals and makes no important change in their symmetry properties, and thus produces a hydrocarbon fragment isolobal with the original one.

The term "isoelectronic" has been frequently used, which means "having the same structure and the same number of valence electrons, but differing by exchange of one or two nuclei with those of adjacent elements in the periodic table".[8] For example, $[V(CO)_6]^-$, $Cr(CO)_6$ and $[Mn(CO)_6]^+$ form an isoelectronic series. $HBPz^*{}_3Re(CO)_3$ is considered as isoelectronic with $[HBPz^*{}_3Mo(CO)_3]^-$ despite the fact that the

Table I-1 Isolobal Relationships Among Organic and Inorganic Fragments.[8]

Neutral hydrcarbon fragments	CH_4	CH_3	CH_2	CH	C
Charged hydrocarbon fragments related by ± H^+	CH_3^-	CH_2^-	CH^- CH_3^+	CH_2^+	CH^+
Common isolobal inorganic fragments containing metals of the first transition series	$Cr(CO)_6$ $Fe(CO)_5$ $Ni(CO)_4$	$Mn(CO)_5$ $CpFe(CO)_2$ $Co(CO)_4$	$Cr(CO)_5$ $Fe(CO)_4$ CpCo(CO) $Ni(CO)_3$ CpCu $Ni(CO)_2$	$CpCr(CO)_2$ $Mn(CO)_4$ CpFe(CO) $Co(CO)_3$ CpNi	$Cr(CO)_4$ CpMn(CO) $Fe(CO)_3$ CpCo

metals involved belong to different rows of the periodic table. Two isoelectronic species are necessarily isolobal.

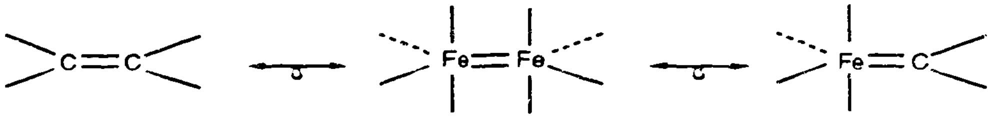
Many organometallic complexes are related to each other and to organic molecules by isolobal substitution. The previously mentioned dinuclear $Mn_2(CO)_{10}$ is isolobal to CH_3CH_3. The trinuclear $[Mn_3(CO)_{14}]^-$ must then be related to $CH_3CH_2CH_3$ since CH_2 is isolobal to $Mn(CO)_4^-$.

$$Mn_2(CO)_{12} \underset{\sigma}{\longleftrightarrow} CH_3CH_3$$

$$[Mn(CO)_4]^- \underset{\sigma}{\longleftrightarrow} CH_2$$

$$[Mn_3(CO)_{14}]^- \underset{\sigma}{\longleftrightarrow} CH_3CH_2CH_3$$

Molecules with double, triple bonds and ring structure can be related similarly.[7] For example:

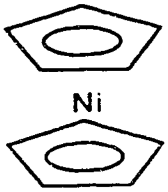


SECTION III

PARAMAGNETIC TRANSITION-METAL COMPLEXES

In Chapter III a series of 17- and 16-electron complexes which are paramagnetic will be described. This section provides a discussion of some general properties of paramagnetic transition-metal complexes.

Complexes having unpaired electrons are paramagnetic. Most commonly there is an odd number of valence electrons, but complexes with even number of electrons can also be paramagnetic. $HBPz^{*}{}_3Re(CO)_2(Cl)$ **8** and $HBPz^{*}{}_3Re(CO)_2(OMe)$ **21** are 17-electron complexes, and they are paramagnetic. $HBPz^{*}{}_3Re(CO)(Cl)_2$ **9** is a 16-electron complex and is also paramagnetic. As another example, the 20-electron complex nickelocene, Cp_2Ni, is paramagnetic despite having an even number of electrons.



The NMR spectra of paramagnetic complexes are different from those of diamagnetic ones. The NMR spectra of paramagnetic complexes are usually broad and difficult to detect, and the resonances are shifted compared to those of the diamagnetic analogues.

ESR spectra are complementary to NMR spectra. Complexes with broad NMR resonances usually give sharp ESR spectra, and complexes with sharp NMR spectra usually give broad ESR spectra. It is unusual that one can perform NMR and ESR experiments on the same compound at the same temperature.[9a]

In general, complexes with triply degenerate (T) ground states give sharp NMR and broad ESR spectra. These include octahedral complexes having the following configurations: d^1, d^2, low spin d^4, low spin d^5, high spin d^6, and high spin d^7. When large distortions from octahedral geommetry exist in the complex, the T state is split and the NMR spectrum often becomes broader and the ESR spectrum becomes sharper. Tetrahedral complexes with T ground states also give sharp NMR spectra. Systems having particularly broad NMR and sharp ESR lines include those complexes with octahedral d^3, high spin d^5 and d^9 configurations.[9a]

Determination of the magnetic susceptibility

There are several methods available for the measurement of magnetic susceptibility.[9] The Evans' NMR method,[10] employed in this work, will be discussed in detail. In this method, a solution of the paramagnetic complex containing an internal standard is added to the outer of two concentric tubes, a normal NMR tube and a capillary. A solution of the same internal standard, dissolved in the same solvent with the same concentration, is placed in the inner of the two concentric tubes, or vice versa. Two separate NMR lines corresponding to the standard will be observed with the line from the paramagnetic solution lying at higher frequency. The mass susceptibility, χ_g, of the dissolved substance is given by the expression:

$$\chi_g = \frac{3\Delta\upsilon}{2\pi\upsilon m} + \chi_o + \frac{\chi_o(d_o - d_s)}{m} \qquad \text{1-1}$$

where $\Delta\upsilon$ is the frequency separation between the two lines in Hz, υ is the frequency at which the proton resonances are being studied, m is the mass in grams of substance per mL of solution, χ_o is the mass susceptibility of the solvent, d_o is the density of the solvent, and d_s is the density of the solution. The importance of correcting the density change with temperature in temperature dependent studies has been pointed out.[9b] Multiplying χ_g by the molecular weight produces a molar susceptibility, χ

$$\chi_g \times MW = \chi\ (cm^3 mole^{-1})$$

The measured value χ is the net magnetism, which is the sum of the paramagnetic, χ_{para} and diamagnetic, χ_{dia}, contributions.[9]

$$\chi = \chi_{para} + \chi_{dia} \qquad \text{1-2}$$

To obtain the paramagnetic susceptibility, the diamagnetic susceptibility must be subtracted from the net susceptibilty. Pascal's constants in Table II-1 [9] are used in this work to calculate χ_{dia}.

In describing the magnetic properties of transition-metal complexes, it is common to employ the quantity called the effective magnetic moment, μ_{eff}. It is defined as follows:[9a]

$$\mu_{eff} = 2.828(\chi_{para}T)^{0.5} \text{ (units of Bohr Magneton, } \mu_B) \qquad \text{I-3}$$

where χ_{para} is the paramagnetic molar susceptibility, and T is the absolute temperature. This equation holds for substances that obey the Curie Law $\chi' = C/T$ where C is a constant. In practice, it is found that for many compounds the temperature variation of the susceptibility is expressed not by the Curie Law but by the Curie-Weiss Law:

$$\chi'_{para} = \frac{C}{T - \theta}$$

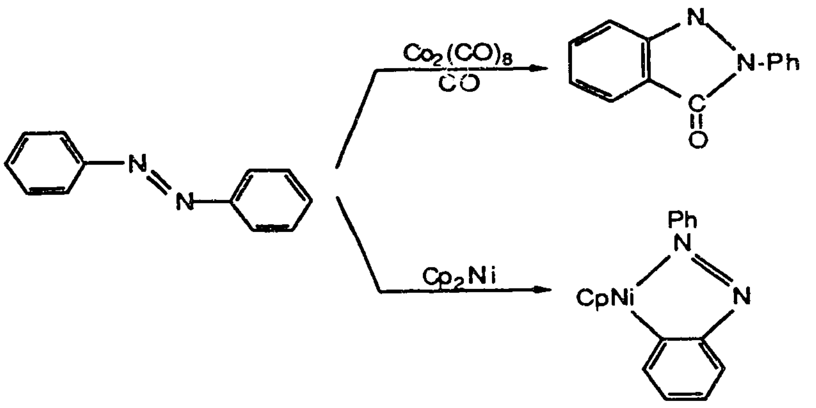
where θ is also a constant. Often θ is not known (unless the temperature dependence of χ_{para} is measured), and equation I-3 is used to calculate the moment.[9a]

SECTION IV

CARBON-HYDROGEN ACTIVATION

The activation of carbon-hydrogen bonds, as remarked 21 years ago by Halpern,[11e] is one of the most important and challenging problems in the field of homogeneous catalysis. Progress in the area has been extensively reviewed.[11]

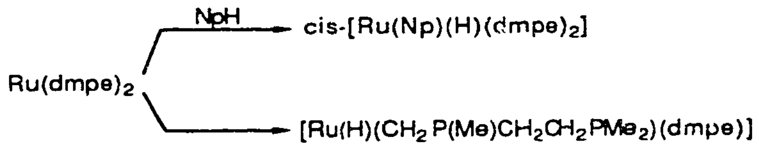
Following the recognition of "oxidative addition",[12] interest in alkane activation grew among organometallic chemists. The first example of oxidative addition of C-H bonds was provided by the so-called orthometallation or cyclometallation reactions.[13] The catalytic synthesis of indazolones from azobenzene and CO using $Co_2(CO)_8$[14] (I-4) is an early example (1960) that must involve arene C-H bonds cleavage. The first isolated cyclometallation product is from the reaction of Cp_2Ni with azobenzene (I-5), reported by Kleiman and Dubeck in 1963.[15]



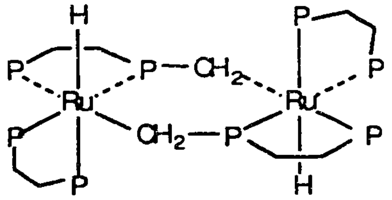
I-4

I-5

In the study of Ru(dmpe)$_2$,[16] Chatt and Davidson found not only that this complex spontaneously cyclometallates at the phosphorus methyl groups but also that the system reacts with free naphthalene to give cis-[Ru(Np)(H)(dmpe)$_2$] (Np = 2-naphthyl).

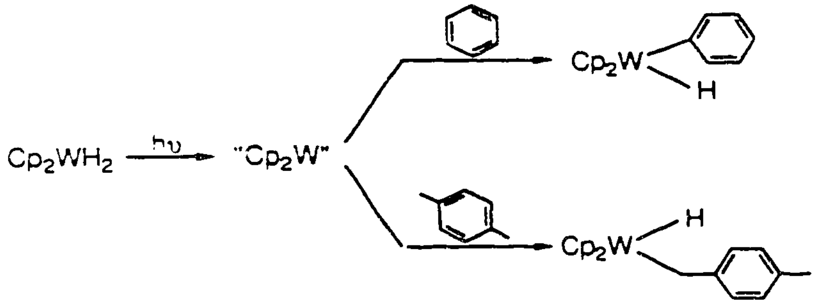


A crystallographic re-examination, by Cotton and co-workers,[17] showed that the cyclometallated form "Ru(dmpe)$_2$" is in fact a dimer of the type shown below:

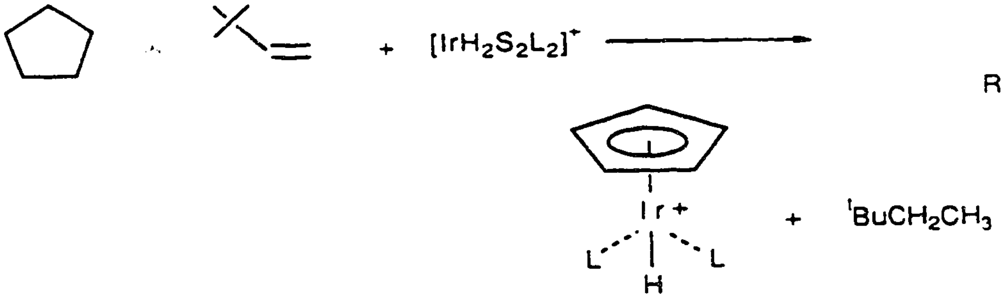


Other examples of homogeneous intermolecular activation of C-H bonds are depicted in Figure I-2[18, 19, 20, 39, 40]

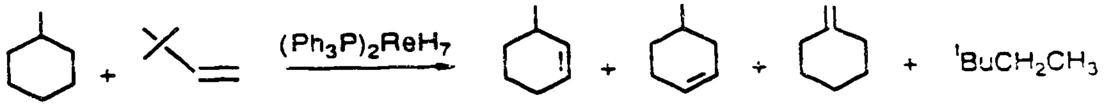
The first direct observation of alkane C-H bonds activation was reported in 1982 by Bergman and Janowicz[21a] and Graham and Hoyano.[22a] This was particularly significant because it allowed the critical first step in alkane activation to be studied in detail.



Ref. 18

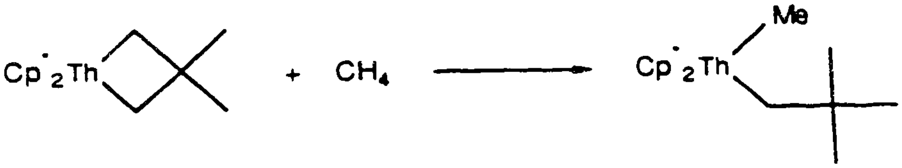


Ref. 19

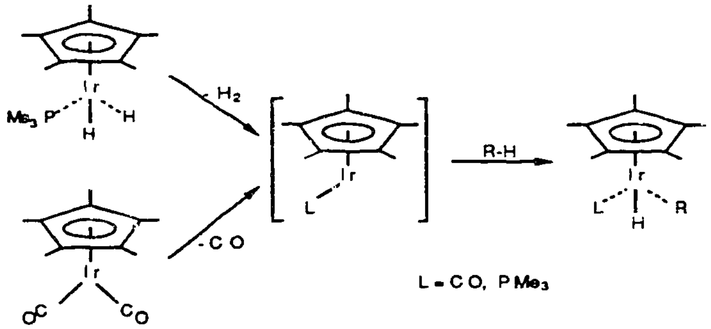


Ref. 20

$Cp^{*}_{2}Lu(CH_3) + {}^{13}CH_4 \longrightarrow Cp^{*}_{2}Lu({}^{13}CH_3) + CH_4$ Ref. 39



Ref. 40



Among the most important alkane activation reactions is the activation of methane, which was reported by Graham et al. for the first time to form a characterizable oxidatively added product.[22b] This reaction was shown to occur at 12 K in a CH_4 matrix,[22c] demonstrating the low kinetic barrier to alkane activation in this system.

Since these studies first appeared, numerous other systems have been reported utilizing transition-metals such as rhenium, iron, ruthenium, osmium, rhodium, palladium and platinum. Table I-3[38] lists intermolecular C-H activation systems in which the initial alkyl or aryl hydride products have been identified.

Halpern considered some of the thermodynamic and mechanistic aspects of C-H activation.[11d] He classified the activation of saturated molecules into five main reaction types.

Table I-2 Intermolecular Carbon-Hydrogen Bond Activation

(Taken from reference 38 with permission; some references have been added)

Complex	R-H	Technique[a]	Year	Principal Author	Reference
$Cp^*Ir(PMe_3)H_2$	b	$h\nu$	1982	R.G. Bergman	21
$Cp^*Ir(CO)_2$	b	$h\nu$	1982	W.A.G. Graham	22
$Cp^*Rh(PMe_3)H_2$	b	$h\nu$	1982	W.D. Jones	23
$(C_6H_6)Ru(P(i\text{-}Pr)_3)H_2$	benzene	$h\nu$	1983	H. Werner	24a
$(arene)Os(PMe_3)(C_2H_4)$	benzene	Δ	1985	H. Werner	24b
$CpRe(PMe_3)_3$	b	$h\nu$	1985	R.G. Bergman	25
$Cp^*Ir(allyl)(H)$	benzene	Δ	1985	R.G. Bergman	26
$ClIr(P(i\text{-}Pr)_3)_2$	benzene	Δ	1986	H. Werner	24c
$(DCPE)Pt(Np)(H)^{c,d}$	b	Δ	1986	G.M. Whitesides	27
$HRe(PPh_3)_3L_2$	b	$h\nu$	1986	W.D. Jones	28
$(PMe_3)_4Os(Np)(H)^d$	benzene	Δ	1986	T.C. Flood	29
$(C_6Me_6)Os(CO)H_2$	b	$h\nu$	1986	W.A.G. Graham	22d
$(dmpe)_2FeH_2^e$	pentane	$h\nu$	1987	L.D. Field	30
$(NP_2)Ir(COE)^f$	toluene	Δ	1987	M.D. Fryzuk	31
$(NP_3)Rh,^g (PP_3)Ir^h$	arene	Δ	1987	C. Bianchini	32

continued ......

1. Electrophilic Displacement

$$M^{n} + X\text{-}Y \longrightarrow M^{n}\text{-}X^{-} + Y^{+}$$

2. One-Center Oxidative Addition

$$M^{n} + X\text{-}Y \longrightarrow M^{(n+2)}(X^{-})(Y^{-})$$

3. Two-Center Oxidative Addition

$$2M^{n}\ (\text{or } M^{n}_{2}) + X\text{-}Y \longrightarrow M^{(n+1)}X^{-} + M^{(n+1)}Y^{-}$$

4. Homolytic Displacement

$$M^{n} + X\text{-}Y \longrightarrow M^{(n+1)}X^{-} + Y^{\cdot}$$

5. Nucleophilic Displacement

$$M^{n} + X\text{-}Y \longrightarrow M^{(n+2)}X^{-} + Y^{-}$$

Of these mechanisms, only the first three are thought to be applicable to C-H activation. Nucleophilic displacement requires a good anionic leaving group such as halide and, thus, is not expected (nor found) in the activation of C-H bonds. Homolytic displacement is expected only in special circumstances because it is thermodynamically highly unfavorable due to the weakness of M-H and M-R bonds.

A rare example has very recently been reported,[42] in which activation of methane has been achieved through a metalloradical species.

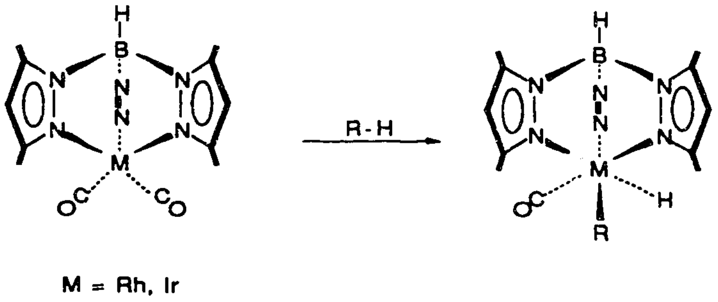
$$2\,(\text{TMP})\text{Rh}\cdot + CH_4 \rightleftharpoons (\text{TMP})\text{Rh-H} + (\text{TMP})\text{Rh-}CH_3$$

TMP = Tetramesitylporphyrin

There are many examples of C-H activation via oxidative addition and electrophilic displacement. Most systems listed in Table I-3 involve oxidative addition. Electrophilic displacement is considered by Halpern to be the most promising approach to the activation of alkanes. A recent example of this type is the activation of methane by palladium(II).[41]

$$CH_4 + Pd(O_2CMe)_2 \xrightarrow[80^{\circ}C]{CF_3COOH} CF_3CO_2CH_3 + CF_3CO_2H + Pd(0)$$

Many of the original systems involve either cyclopentadienyl (Cp^-) or pentamethylcyclopentadienyl (Cp^{*-}) ligands. A remarkable new C-H activation system, developed recently in this group, is comprised of the pyrazolylborate complexes $HBPz^*{}_3M(CO)_2$ (M = Rh, Ir).[33] This new system activates both arene and alkane C-H bonds with great efficiency and selectivity. The activation of methane has been achieved under relatively mild conditions and in better yields than previously reported systems.



It is the interest of this Thesis to further explore trispyrazolyl transition-metal complexes in the field of C-H activation.

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CHAPTER TWO

MOLECULAR STRUCTURE AND SOME REACTIONS OF $HBPz^{*}{}_{3}Re(CO)_{3}$ (Pz^{*}=3,5-dimethylpyrazol-1-yl)

SECTION I

INTRODUCTION

Following Trofimenko's first report, pyrazolylborate transition-metal chemistry has been developed extensively.[1] Dicarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl)borato]rhodium was reported recently to photochemically activate C-H bonds with great efficiency.[2] It has been shown[3] that there are strong similarities between the complex chemistry of the trispyrazolylborate anion and that of cyclopentadienyl (Cp^-) or pentamethylcyclopentadienyl (Cp^{*-}) anion. Bergman and co-workers have observed C-H activation by cyclopentadienyl and pentamethylcyclopentadienylrhenium complexes.[4] Thus, it was of interest to investigate the analogous tricarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl)borato]rhenium complex $HBPz_3^*Re(CO)_3$ (Pz^*=3,5-dimethylpyrazol-1-yl) **1**. This Chapter describes the molecular structure of **1** and its photochemistry resulting in the formation of $HBPz_3^*Re(CO)_2L$ (L = THF, N_2, PMe_3, PPh_3) and $[HBPz_3^*Re(O)_3]_n$.

SECTION II

EXPERIMENTAL

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Most of the compounds prepared in this work do show oxygen sensitivity, particularly in solution, however, all can be handled in air for brief periods.

Solvents were distilled under nitrogen from the following drying agents: hexane from Na/K; THF from potassium/benzophenone; CH_2Cl_2 from P_2O_5.

$[Re(CO)_4Br]_2$ was prepared by a literature method.[5] All other reagents were purchased from commercial suppliers and used as received.

Infrared spectra were recorded using a Nicolet MX-1 FT Spectrometer in 0.5 mm KBr cells. Raman Spectra were obtained with a Beckman Model 700 Laser Spectrometer (Krypton Laser operating at 6471 Å). Mass spectra were measured using an Associated Electronics Industries MS-12 Mass Spectrometer coupled with a Nova-3 computer employing D5-50 software. Unless otherwise noted, all NMR spectra were recorded at ambient temperature using Bruker WH-200, AM-300 and WH-400 FT NMR instruments. Microanalyses were performed by the Microanalytical Laboratory of this Department.

Photolyses were generally carried out in a quartz vessel with a gas purge. A Hanovia 450-W medium pressure mercury lamp was used as the light source.

Tricarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl)borato] rhenium(I) (1)

Freshly prepared $[Re(CO)_4Br]_2$ (0.52 g, 0.69 mmol) in THF (15 mL) was stirred with $KHBPz^*_3$ (0.52 g, 1.55 mmol) for 24 h. The mixture was then filtered and the solvent was evaporated on a rotary evaporator with water-aspirated vacuum. The residue was washed with methanol (3 x 10 mL) to give a white solid. The solid was dissolved in CH_2Cl_2 (3 x 15 mL) and filtered. Evaporation of the filtrate gave the desired product as a white solid (0.65 g, 83%).

Characterization: IR (hexane) 2020 (s), 1909 (vs) cm^{-1}, υ(CO). MS, 170°C/16ev (m/e, rel.int.): M^+(568, 100), M^+-CO(540, 18), M^+-2CO(512, 24), M^+-3CO(484, 34). ^1H NMR (CD_2Cl_2): δ 2.36 (s, 9H), 2.45 (s, 9H), 5.89 (s, 3H). Anal. Calcd for $C_{18}H_{22}N_6BO_3Re$: C 38.09, H 3.88, N 14.81. Found: C 37.90, H 3.93, N 14.24.

Tricarbonyl[dimethoxybis(3,5-dimethylpyrazol-1-yl)borato] (methanol)rhenium(I) (2)

A white precipitate deposited from the above methanol extract on standing at room temperature for 3 days. The supernatant liquid was syringed from the solid which was then washed with minimum amounts of CH_2Cl_2 and dried in vacuum (yields variable, but always less than 15%).

Characterization: IR (CH_2Cl_2) 2023 (m), 1908 (s), 1897 (s) cm^{-1}, υ(CO); MS, 115°C/70ev (m/e, rel.int.): M^+(566, 44), M^+-OCH_3(535, 24),

BP^+(base peak, 378, 100). ^{1}H NMR (CD_2Cl_2): δ 2.16 (s, 3H), 2.22 (s, 3H), 2.30 (s, 3H), 2.52 (s, 3H), 3.20 (s, 3H), 3.51 (s, 3H), 3.76 (s, 3H), 5.86 (s, 1H), 5.89 (s, 1H), 9.9 (br, 1H). Anal. Calcd for $C_{16}H_{24}N_4BO_6Re$: C 33.92, H 4.24, N 9.89. Found: C 33.67, H 4.22, N 10.00.

Dicarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl)borato](THF) rhenium(I) (3)

Compound **1** (300 mg, 0.53 mmol) in freshly distilled THF (200 mL) was photolyzed for 20 min with a H_2 purge. IR (CO bands) showed complete conversion of **1** and formation of the THF derivative **3**. Pure **3** was not isolated and it was used as its THF solution in further reactions.

For best results, the THF solution was placed in a tube with a side arm to allow H_2 to purge through, and the mercury lamp fitted with a water-cooled jacket was submerged into the solution.

Characterization: IR (THF): 1896 (s), 1810 (s) cm^{-1}, υ(CO).

Dicarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl)borato] (trimethylphosphine)rhenium(I) (4)

To a fresh THF solution of **3** (50 mL, an aliquot of 185 mL THF solution of **3** generated from 220 mg, 0.39 mmol of **1**), trimethylphosphine (0.15 mL, 1.45 mmol) was added. The solution was stirred until IR υ(CO) showed complete disappearance of **3**. THF was removed on a rotary evaporator and the residue was placed on a Florisil column (1 x 20 cm, 60-100 mesh), eluting with CH_2Cl_2. Recrystallization from hexane gave white needles of the desired product (30 mg, 46% based on **1**).

Characterization: IR (CH_2Cl_2) 1911 (s), 1823 (s) cm^{-1}, υ(CO). MS, 150°C/16ev (m/e, rel.int.): M^+(616, 100), M^+-CO(588, 2), M^+-2CO(560, 14), M^+-2CO-PMe_3(484, 12). ^1H NMR (CD_2Cl_2): δ 1.52 (d, 8Hz, 9H), 2.24 (s, 3H), 2.36 (s, 6H), 2.42 (s, 3H), 2.46 (s, 6H), 5.76 (s, 1H), 5.88 (s, 2H). Anal. Calcd for $C_{20}H_{31}N_6O_2PBRe$: C 38.96, H 5.03, N 13.64. Found: C 38.82, H 5.05, N 13.43.

Dicarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl)borato]-(triphenylphosphine)rhenium(I) (5)

To a fresh THF solution of **3** (50 mL, an aliquot of 185 mL THF solution of **3** generated from 220 mg, 0.39 mmol of **1**), was added PPh_3(150 mg, 0.57 mmol). THF was removed under reduced pressure and the residue was dissolved in benzene (20 mL). The solution was then stirred until IR υ(CO) showed complete disappearance of **3**. Benzene was removed on a rotary evaporator and the residue was placed on a Florisil column (1 x 20 cm, 60-100 mesh), eluting with CH_2Cl_2. Recrystallization from CH_2Cl_2/hexane (1:1) gave colourless crystals of the desired product. Drying in vacuum changed the crystals to pink (34 mg, 40% based on **1**).

Characterization: IR (CH_2Cl_2) 1910 (s), 1827 (s) cm^{-1}, υ(CO). MS, 150°C/70ev (m/e, rel.int.): M^+(802, 100), M^+-CO(774, 9), M^+-2CO(746, 2). ^{1}H NMR (CD_2Cl_2): δ 1.59 (s, 6H), 2.25 (s, 3H), 2.38 (s, 6H), 2.59 (s, 3H), 5.50 (s, 2H), 5.78 (s, 1H), 7.2 (br, 15H). Anal. Calcd for $C_{35}H_{37}N_6O_2PBRe$: C 52.37, H 4.61, N 10.47. Found: C 51.94, H 4.72, N 10.81.

Dicarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl)borato](dinitrogen)rhenium(I) (6)

A fresh THF solution of **3** (50 mL, an aliquot of 185 mL THF solution generated from 220 mg, 0.39 mmol of **1**) was pressurized to 1500 psi using U.S.P. grade nitrogen (Linde-Union Carbide) in a Parr bomb and stirred for 5 days at room temperature. An IR υ(CO) spectrum showed 5% **3** unreacted. THF was removed on a rotary evaporator and the residue was placed on a Florisil column (1 x 20 cm, 60-100 mesh), eluting with CH_2Cl_2/hexane (1:1). Recrystallization from CH_2Cl_2/hexane (1:1) gave the dinitrogen product as a white solid (22 mg, 51% based on **1**).

Characterization: IR (hexane) 2129 (m) cm^{-1}, υ(N_2); 1947 (s), 1884 (s) cm^{-1}, υ(CO). MS, 240°C/70ev (m/e, rel.int.): M^+(568, 12), M^+-N_2 or CO(540, 36), M^+-N_2-2CO(484, 100). ^{1}H NMR (CD_2Cl_2): δ 2.35 (s, 3H), 2.38 (s, 6H), 2.40 (s, 3H), 2.48 (s, 6H), 5.84 (s, 1H), 5.92 (s, 2H). Anal. Calcd for $C_{17}H_{22}N_8O_2BRe$: C 35.92, H 3.87, N 19.72. Found: C 36.52, H 4.01, N 19.36.

[Hydrotris(3,5-dimethylpyrazol-1-yl)borato]trioxorhenium(VII) (7)

Compound **1** (100 mg, 0.18 mmol) in cyclohexene (100 mL) was irradiated with N_2 purge until IR υ(CO) showed complete disappearance of **1**. The supernatant was syringed from the solid which was then washed with acetone and CH_2Cl_2. Drying in vacuum gave the desired product as a white solid (60 mg, 64%).

Characterization: IR (KBr) 1070 (s), 908 (vs) cm^{-1}, υ(Re=O). Raman: 1068 cm^{-1}, υ(Re=O). MS, 160°C/16ev (m/e, rel.int.): M^+(532, 100); Isotope pattern (m/e, rel.int.): 533 (Found: 16; Calcd: 19); 532 (100; 100); 531 (32; 34); 530 (59; 58); 529 (12; 14). Anal. Calcd for $C_{15}H_{22}N_6O_3BRe$: C 33.83, H 4.14, N 15.79. Found: C 33.37, H 4.17, N 15.44.

C-H and Si-H activation attempts

Photolysis of **1** in benzene or refluxing a benzene solution of **3** resulted in loss of the starting material, but no new bands in IR spectra in the 1600-2200 cm^{-1} region were observed.

Photolysis of **1** in cyclohexane with excess Ph_3SiH resulted in a decrease of **1**, but there were no new bands in IR spectra in the 1600-2200 cm^{-1} region.

X-ray Structure of 1

The X-ray crystallographic study was carried out by Dr.R.G.Ball of 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 Microsystem computer and several locally written or modified programs.

A suitable crystal was obtained from CH_2Cl_2/hexane, having approximate dimensions of 0.19 x 0.18 x 0.47 mm, was mounted in a non-specific orientation on an Enraf-Nonius CAD4 automated diffractometer.

The structure was solved using a three-dimensional Patterson synthesis which gave the positional parameters for the Re 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 using full-matrix least-squares techniques on $\underline{Fo}$ minimizing the function

$$\Sigma w(|\underline{Fo}|-|\underline{Fc}|)^2$$

where $|\underline{Fo}|$ and $|\underline{Fc}|$ are the observed and calculated structure factor amplitudes respectively, and the weighting factor w is given by

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

The neutral atom scattering factors were calculated from the analytical expression for the scattering curves. The $\underline{f}'$ and $\underline{f}''$ components of anomalous dispersion were included in the calculations for all non-hydrogen atoms.

All hydrogen atoms were included in the calculations at their 'ideal' positions (C-H and B-H of 0.95 A). These positions were confirmed with a difference Fourier calculation which clearly showed most of these H atoms. The H atoms were assigned fixed isotropic thermal parameters 1.2 times those of the attached atoms. The positional parameters were constrained to 'ride' with those of the connected atom during least-squares refinement.

In the final cycle 262 parameters were refined using 3688 observations having $I>3\sigma(I)$. The final agreement factors were

$$R_1 = \Sigma||\underline{Fo}|-|\underline{Fc}||/\Sigma|\underline{Fo}| = 0.025, \text{ and}$$

$$R_2 = (\Sigma w(|\underline{Fo}|-|\underline{Fc}|)^2/\Sigma w\underline{Fo}^2)^{0.5} = 0.035$$

The largest shift in any of the parameters was 0.2 times its estimated standard deviation and the error in an observation of unit weight was 1.27 e. An analysis of R_2 in terms of $\underline{Fo}$, $\lambda^{-1}\sin\theta$, and various combinations of Miller indices showed no unusual trends. The highest peak in the final difference Fourier was 0.6(1) eA^{-3}.

Crystal Data

$C_{18}H_{22}BN_6O_3Re$

F.W. = 567.43

Crystal dimensions: 0.19 x 0.18 x 0.47 mm

Monoclinic space group $P2_1/c$

a = 7.995 (1)   b = 14.076 (2)   c = 18.877 (3) A

$\beta = 97.27(2)^{\circ}$

V = 2107 A^3 Z = 4

Dc = 1.789 gm/cm^3 $\mu = 58.74\ cm^{-1}$

Data Collection and Refinement Conditions

Radiation:	Mo Kα (λ = 0.71073 Å)
Monochromator:	Incident beam, graphite crystal
Take-off angle:	3.0 deg
Detector aperture:	2.40 mm horizontal 4.0 mm vertical
Crystal-to-detector distance:	205 mm
Scan type:	ω-2θ
Scan rate:	10.1 - 1.5 deg/min
Scan width:	0.66 + 0.35tan(θ) deg
Data collection 2θ limit:	55.00 deg
Data collection index range:	h, k, ±l
Reflections measured:	5031 unique 3688 with $I>3\sigma(I)$
Observations:variables ratio:	3688:262
Agreement factors R_1, R_2, GOF:	0.025, 0.035, 1.27
Corrections applied:	Absorption correction

Table of Bond Distances in Angstroms II-1

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Re	N1	2.179(4)	N5	N6	1.390(5)
Re	N3	2.168(3)	N5	C17	1.343(6)
Re	N5	2.168(3)	N6	C14	1.348(5)
Re	C1	1.904(5)	N6	B	1.535(6)
Re	C2	1.925(5)	C4	C5	1.442(8)
Re	C3	1.904(5)	C4	C6	1.405(8)
O1	C1	1.148(6)	C6	C7	1.329(8)
O2	C2	1.139(5)	C7	C8	1.538(9)
O3	C3	1.143(6)	C9	C10	1.438(6)
N1	N2	1.377(6)	C9	C11	1.386(7)
N1	C7	1.346(6)	C11	C12	1.399(7)
N2	C4	1.352(6)	C12	C13	1.452(7)
N2	B	1.544(6)	C14	C15	1.477(7)
N3	N4	1.393(5)	C14	C16	1.350(7)
N3	C12	1.346(5)	C16	C17	1.426(7)
N4	C9	1.353(5)	C17	C18	1.484(7)
N4	B	1.536(6)			

Numbers in parentheses are estimated standard deviations in the least significant digit

Dihedral Angles between Planes II-2

Plane No	Plane No	Dihedral Angle in Deg.
1	2	0.8
1	3	0.5
1	4	0.9
2	3	0.3
2	4	0.6
3	4	0.6

Table of Weighted Least-Squares Planes II-3

The equations of the plane is of the form: AxX + BxY + CxZ - D = 0 where A,B,C & D are constants and X,Y, & Z are crystallographic coordinates

Plane No	A	B	C	D	
1	1.1846	1.7255	-18.7296	-2.1209	
Atoms in Plane	X	Y	z	Distance	Esd
C8	-.4129	0.2375	0.1090	0.0000	0.0000
C13	0.3134	0.4452	0.1741	0.0000	0.0000
C18	0.2460	-0.0002	0.1288	0.0000	0.0000
Other Atoms					
Re	0.0484	0.2353	0.1323	0.107	
B	0.0625	0.2643	-0.0395	3.391	

Plane No	A	B	C	D	
2	1.2975	1.7489	-18.7176	-0.6173	
Atoms in Plane	X	Y	Z	Distanc	Esd
N1	-0.1571	0.2504	0.0455	0.0000	0.0000
N3	0.1699	0.3457	0.0771	0.0000	0.0000
N5	0.1488	0.1420	0.0566	0.0000	0.0000
Other Atoms					
Re	0.0484	0.2353	0.1323	-1.384	
B	0.0625	0.2643	-0.0395	1.900	

Plane No	A	B	C	D	
3	1.2578	1.7409	-18.7222	0.7441	
Atoms in Plane	X	Y	Z	Distance	Esd
N2	-0.1222	0.2604	-0.0237	0.0000	0.0000
N4	0.1506	0.3475	0.0027	0.0000	0.0000
N6	0.1495	0.1711	-0.0138	0.0000	0.0000
Other Atoms					
Re	0.0484	0.2353	0.1323	-2.750	
B	0.0625	0.2643	-0.0395	0.535	

Plane No	A	B	C	D	
4	1.2640	1.8907	-18.6955	2.8952	
Atoms in Plane	X	Y	Z	Distance	Esd
C5	-0.2732	0.2772	-0.1453	0.0000	0.0000
C10	0.2177	0.4524	-0.0944	0.0000	0.0000
C15	0.2441	0.1160	-0.1266	0.0000	0.0000
Other Atoms					
Re	0.0484	0.2353	0.1323	-4.862	
B	0.0625	0.2643	-0.0395	-1.577	

Table of Bond Angles in Degrees II-4

Atom1	Atom2	Atom3	Angle
N1	Re	N3	84.8(1)
N1	Re	N5	82.5(1)
N1	Re	C1	93.9(2)
N1	Re	C2	94.1(2)
N1	Re	C3	176.4(2)
N3	Re	N5	83.8(1)
N3	Re	C1	178.7(2)
N3	Re	C2	93.0(2)
N3	Re	C3	95.0(2)
N5	Re	C1	96.1(2)
N5	Re	C2	175.5(2)
N5	Re	C3	93.9(2)
C1	Re	C2	87.1(2)
C1	Re	C3	86.2(2)
C2	Re	C3	89.5(2)
N5	N6	C14	109.9(3)
N5	N6	B	119.9(3)
C14	N6	B	130.1(4)
Re	C1	O1	175.5(5)
Re	C2	O2	178.3(4)
Re	C3	O3	176.5(5)
N2	C4	C5	123.8(5)
N2	C4	C6	105.5(5)
C5	C4	C6	130.7(5)
C4	C6	C7	107.6(4)
N1	C7	C6	111.1(5)
N1	C7	C8	120.4(5)
C6	C7	C8	128.5(5)
N4	C9	C10	124.0(5)
N4	C9	C11	106.8(4)
Re	N1	N2	119.9(3)
Re	N1	C7	134.5(4)
N2	N1	C7	105.5(4)
N1	N2	C4	110.3(4)
N1	N2	B	120.0(3)
C4	N2	B	129.7(4)
Re	N3	N4	119.9(2)
Re	N3	C12	133.1(3)
N4	N3	C12	106.8(3)
N3	N4	C9	110.0(4)
N3	N4	B	119.6(3)
C9	N4	B	130.3(4)
Re	N5	N6	119.8(2)
Re	N5	C17	133.8(3)
N6	N5	C17	106.3(4)
C10	C9	C11	129.1(5)
C9	C11	C12	107.5(4)
N3	C12	C11	108.8(4)
N3	C12	C13	123.9(4)
C11	C12	C13	127.3(4)
N6	C14	C15	122.1(4)
N6	C14	C16	108.5(4)
C15	C14	C16	129.3(4)
C14	C16	C17	106.6(4)
N5	C17	C16	108.6(4)
N5	C17	C18	123.4(5)
C16	C17	C18	127.9(4)
N2	B	N4	108.3(4)
N2	B	N6	108.3(4)
N4	B	N6	109.1(3)

Numbers in parentheses are estimated standard deviation in the least significant digit

SECTION III

RESULTS AND DISCUSSION

A Preparation of $HBPz^{*}{}_3Re(CO)_3$ (1)

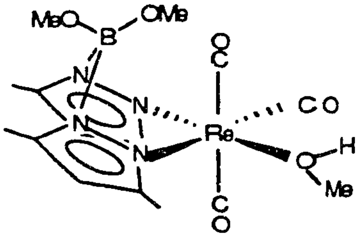
Compound **1** was first prepared by McCleverty and co-workers by treatment of $[Re(CO)_4Cl]_2$ with $KHBPz^{*}{}_3$, where $(HPz^{*})_2Re(Cl)(CO)_3$ was isolated as a by-product.[6] The authors suggested that some rhenium species catalyzed the decomposition of $KHBPz^{*}{}_3$ into pyrazolyl fragments. Replacing $[Re(CO)_4Cl]_2$ with the bromo analogue $[Re(CO)_4Br]_2$, we obtained a better yield (80% vs 60% from $[Re(CO)_4Cl]_2$). There is also a difference in the by-product.

$$[Re(CO)_4Br]_2 + 2KHBPz^{*}{}_3 \xrightarrow[2,\ CH_3OH]{1,\ THF} \qquad (II\text{-}1)$$

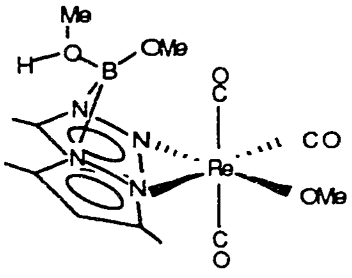
$$\underset{\mathbf{1}}{HBPz^{*}{}_3Re(CO)_3} + \underset{\mathbf{2}}{(MeO)_2BPz^{*}{}_2Re(CO)_3}$$

While Cl is still bonded to Re in $(HPz^{*})_2Re(Cl)(CO)_3$ when $[Re(CO)_4Cl]_2$ was used, there is no Br in $(CH_3O)_2BPz^{*}{}_2Re(CO)_3(CH_3OH)$ **2** in the above reaction. The CH_3O groups of **2** must originate from methanol used to wash the major product **1**. $KHBPz^{*}{}_3$ normally contains small amounts of $KH_2BPz^{*}{}_2$. When a sublimed sample of $KHBPz^{*}{}_3$ was used, a better yield of **1** (>90%) was obtained, but one can not rule out the possibility that the fragment $BPz^{*}{}_2$ in **2** results from the decomposition of $HBPz^{*}{}_3{}^{-}$.

There is an alternative structure for **2** as shown below. Structure **A** and **B** would be tautomers. IR and NMR alone can not establish the true identity of **2**. Both **A** and **B** would have the same IR $\nu(CO)$ pattern of mer-isomers and their ^1H NMR should show seven distinct methyl-proton resonances, as was observed. The boat form of $(CH_3O)_2BPz^*_2$ was assumed here in the light of structures determined for other bispyrazolylborate metal complexes.[1b] Structure **B** is nevertheless less likely since the reaction between the plausible precursor $H_2BPz^*_2{}^-$ or $H_2BPz^*_2Re(CO)_3(THF)$ and CH_3OH should form $(CH_3O)_2BPz^*_2{}^-$ or $(CH_3O)_2BPz^*_2Re(CO)_3(THF)$.



A



B

B Irradiation of 1 in THF

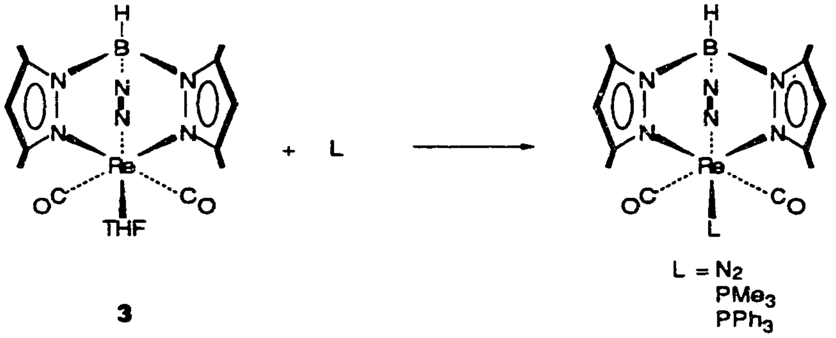
Irradiation of **1** in THF with a H_2 purge gave rise to a clean and relatively fast reaction. The major product is $HBPz^*_3Re(CO)_2(THF)$ **3**. The dihydride complex $HBPz^*_3Re(CO)_2(H)_2$ may have formed in the process but it was never detected. Using cyclohexane or benzene instead of THF as the solvent only resulted in the disappearance of **1**. Irradiation of **1** in THF always results in a yellow solution. The colour of this solution is hardly attributable to **3** alone since **3** is only pale yellow. It has proven to be extremely difficult to identify the species or species responsible for the yellow colour. When a N_2 purge was used, the reaction was much slower and more decomposition occurred, and once again the solution turned intense yellow after irradiation. The N_2 purge also brought about some $HBPz^*{}_3Re(CO)_2(N_2)$ **6** (see below) as a by-product. The trioxo-complex $[HBPz^*{}_3Re(O)_3]_n$ **7** was found occasionally as a precipitate from the solution. This compound will be discussed in detail in a later section.

In the preparation of $CpRe(CO)_2THF$ and $Cp^*Re(CO)_2THF$,[7] trace amounts of dinuclear complexes were formed. We did not observe any analogous complex here. The steric demand of $HBPz^*{}_3{}^-$ is substantially different from that of Cp^- and Cp^{*-}. Cp^- and Cp^{*-} are planar, but $HBPz^*{}_3{}^-$ is more like an umbrella and the Re atom is about 0.1 A inside the face of this umbrella as we see in the crystal structure of **1** (below). Any dinuclear species would require the two $HBPz^*{}_3{}^-$ facing each other rather closely and thus causing considerable steric crowding.

Pure **3** was not isolated. It was generated in situ and used as its THF solution for most purposes. Storage under argon for a few days led to a darker solution but no noticeable change occurred in the IR spectrum ($\nu(CO)$). The CO stretching bands of **3** in THF appear at 1896, 1810 cm^{-1}.

C Reactions of $HBPz^*{}_3Re(CO)_2(THF)$ 3

As expected, both PMe_3 and PPh_3 replace THF in **3** readily, forming $HBPz^*{}_3Re(CO)_2(PMe_3)$ **4** and $HBPz^*{}_3Re(CO)_2(PPh_3)$ **5** respectively. Their IR in the ν(CO) region are typical for this kind of dicarbonyl complex, stretching bands at 1911, 1823 cm^{-1} for **4** and 1910, 1827 cm^{-1} for **5**.



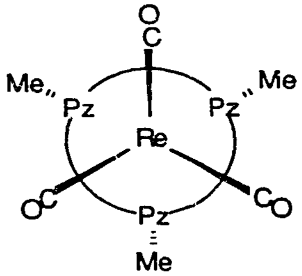
(II-2)

The ^1H NMR spectra of these complexes show a 2:1:2:1 pattern for the six methyl groups and a 2:1 pattern for the 4-H's of the pyrazolylborate ligand. These are consistent with an octahedral geometry around the rhenium center. The reaction was carried out under argon since nitrogen reacts with **3** to form $HBPz^*{}_3Re(CO)_2(N_2)$ **6**.

When a solution of **3** in THF was pressurized with N_2, the dinitrogen complex $HBPz^*{}_3Re(CO)_2(N_2)$ **6** was obtained. Small amounts of $[HBPz^*{}_3Re(O)_3]_n$ **7** also formed in this reaction presumably as a result of O_2 impurity in N_2.[7b] The infrared stretching band at 2129 cm^{-1} indicative of the N_2 ligand.

All attempts to produce $HBPz^*{}_3Re(CO)_2XY$ type complexes failed. No reaction occurred between **3** and Ph_3SiH. Br_2 and CH_3I react with **3** to give $HBPz^*{}_3Re(CO)_2L$ (L = Br,I) radicals.[8] McCleverty and co-workers found that bromination of **1** resulted only in the replacement of the 4-H on pyrazolyl rings and the three CO groups remained unchanged.[6]

The figure below shows a view of **1** along its C_3 axis. Re is about 0.1 Å inside the 3-methyl-carbon-plane (see crystal structure below).



With three methyl groups projecting out from the pyrazole 3-positions, only the staggered conformation is possible. Formation of any $HBPz^*{}_3Re(CO)_2XY$ type complex would require two of the four $(CO)_2XY$ groups sharing one slot, which is not favorable sterically. It has been suggested that $HBPz_3^-$ ligand hybridizes the metal orbitals into an octahedral array much more effectively than does Cp^-.[9] The same should be true for $HBPz^*{}_3^-$ and Cp^{*-}. Thus both steric and electronic effects favour $HBPz^*{}_3ReL_3$ not $HBPz^*{}_3ReL_4$ type complexes.

In the case of unsubstituted pyrazolylborate complexes $HBPz_3ML_n$, there is less crowding around the metal center. $HBPz_3Mo(CO)_3Br$ has been reported as a 3:4 or four-legged piano-stool structure.[9a] Storr et al. have shown that $MeGaPz_3Mo(CO)_3(CuPPh_3)$ adopts a 3:3:1 or capped octahedral structure.[10] The 3:3:1 structure represents a minimum in the potential energy surface for analogous $CpML_4$ complexes whose global minimum (ground state) is always the 3:4 structure according to the calculation of Kubacek et al.[11] Whether $HBPz^*{}_3Re(CO)_2XY$ can be prepared and adopt a 3:3:1 structure remains to be seen.

We have not been able to activate C-H bonds with **1** or **3** which was our original goal. Oxidative addition of H_2 or Br_2 to **1** or **3** has not been achieved here either.

D Formation of $[HBPz^*{}_3Re(O)_3]_n$ 7

The trioxo complex **7** was observed in several reactions as mentioned above. The best method of preparing it is via photolysis of **1** in commercial cyclohexene (MCB). Peroxide impurities in the solvent are considered to be the active species. It is well known that cyclohexene reacts with O_2 in the air to form peroxides. Shaking the solvent with KI produced I_2. This positive KI test of the commercial sample supports the presence of such impurities. Peroxides have been used to prepare other oxo-complexes in the literature. H_2O_2, for example, was employed to prepare the $Cp^*Re(O)_3$ from $Cp^*Re(CO)_3$.[12]

It is somewhat surprising that **7** is insoluble in any of the common solvents such as hexane, benzene, CH_2Cl_2, acetone and methanol. The analogous mononuclear $Cp^*Re(O)_3$ was reported to be rather soluble and can even be chromatographed.[13] Perhaps **7** is better described as $[HBPz^*{}_3Re(O)_3]_n$. The MS of **7** (Figure II-1) showed a strong peak at 532 (100% rel.int.) corresponding to the mononuclear $HBPz^*{}_3Re(O)_3$, but this peak could easily come from the fragmentation of $[HBPz^*{}_3Re(O)_3]_n$

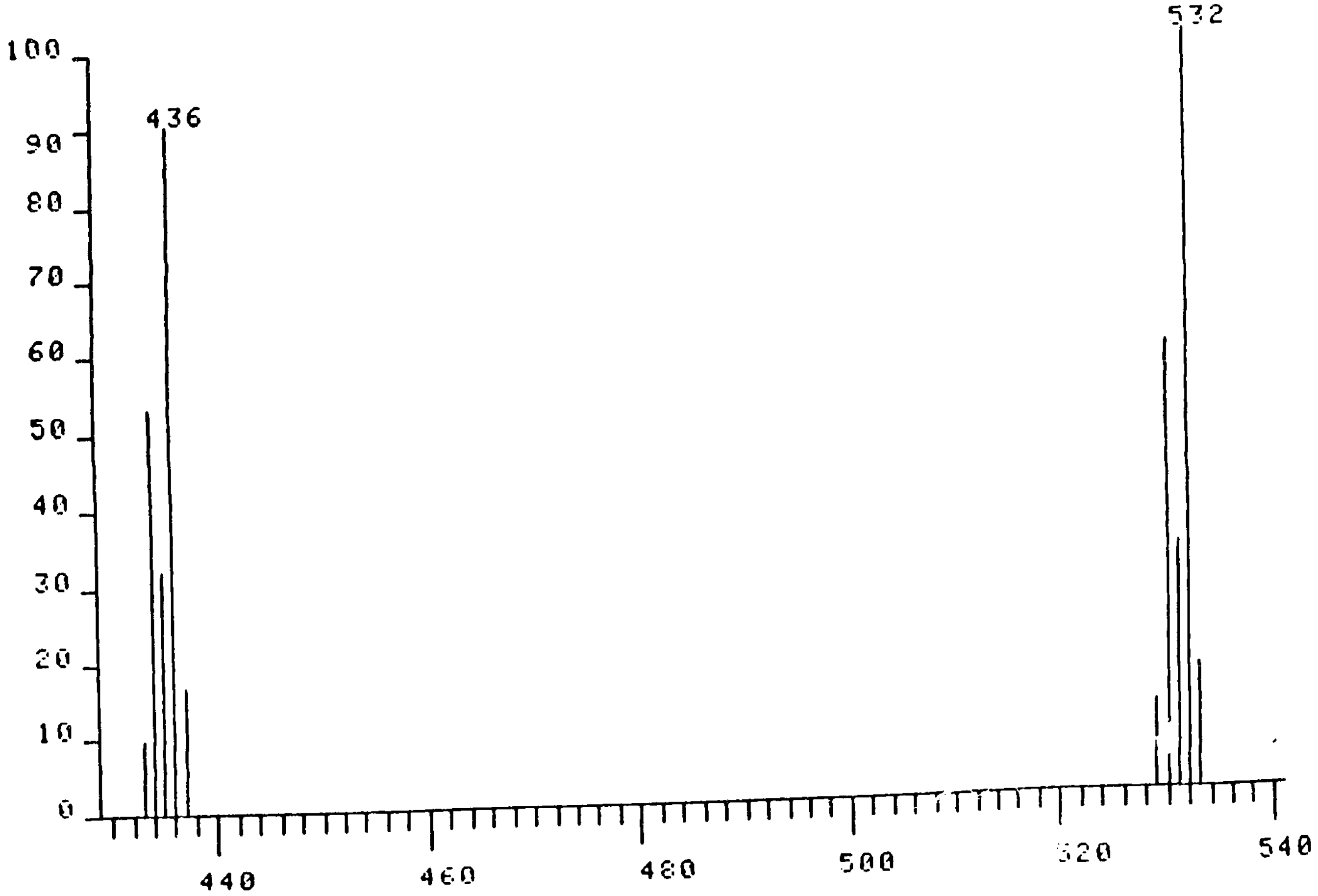


Figure II-1 Mass Spectrum of $[HBPz^{*}{}_{3}Re(O)_{3}]$ 7 under the conditions. The isotope pattern observed is in good agreement with that calculated for $HBPz^*{}_3Re(O)_3$.

E Molecular Structure of 1

The structure of **1** is shown in Figure II-2. The three CO groups and three pyrazole N atoms form a slightly distorted octahedron, and the Re atom occupies the center of this octahedron. Although $HBPz^*{}_3^-$ acts as a bidentate ligand in some cases,[1b,14] it is definitely tridentate here, which is in good agreement with the spectroscopic data (IR and ^1H NMR) and the 18-electron requirement.

Selected bond angles and distances are listed in Tables II-1 & II-4. The three N_n-Re-$C_{n'}$ angles (175.5(2), n=5, n'=2; 176.7(2), n=1, n'=3; 178.7(2)°, n=3, n'=1) in **1** are virtually the same as those in the isolobal $HBPz^*{}_3Mo(CO)_3^-$ complex (175.5(5), 176.8(3), 178.4(3)°).[15] The M-C-O (M=Re,Mo) angles in the two molecules (175.5(5), 176.5(5) & 178.3(4)° in **1**; 175.5(7), 176.0(7) & 178.4(6)° in $HBPz^*{}_3Mo(CO)_3^-$) are also very close. The Re-N_{avg} distance in **1** is 2.174(6) Å. This is close to Re-N_{avg} (2.18(4) Å) in $PhPPz^*{}_2Re(CO)_3Br$[16] and slightly longer than that found in $Re_2O_3Cl_4(HPz^*)_4$ (2.109(12) Å),[17] reflecting the electron deficiency of the oxorhenium(V) compared to the Re(I) in **1**.

Table II-3 lists the distances of Re and B atoms from various planes. The dihedral angles between these planes are listed in Table II-2. All the angles are less than 1 deg. Thus the planes are essentially parallel to each other. An important feature of the

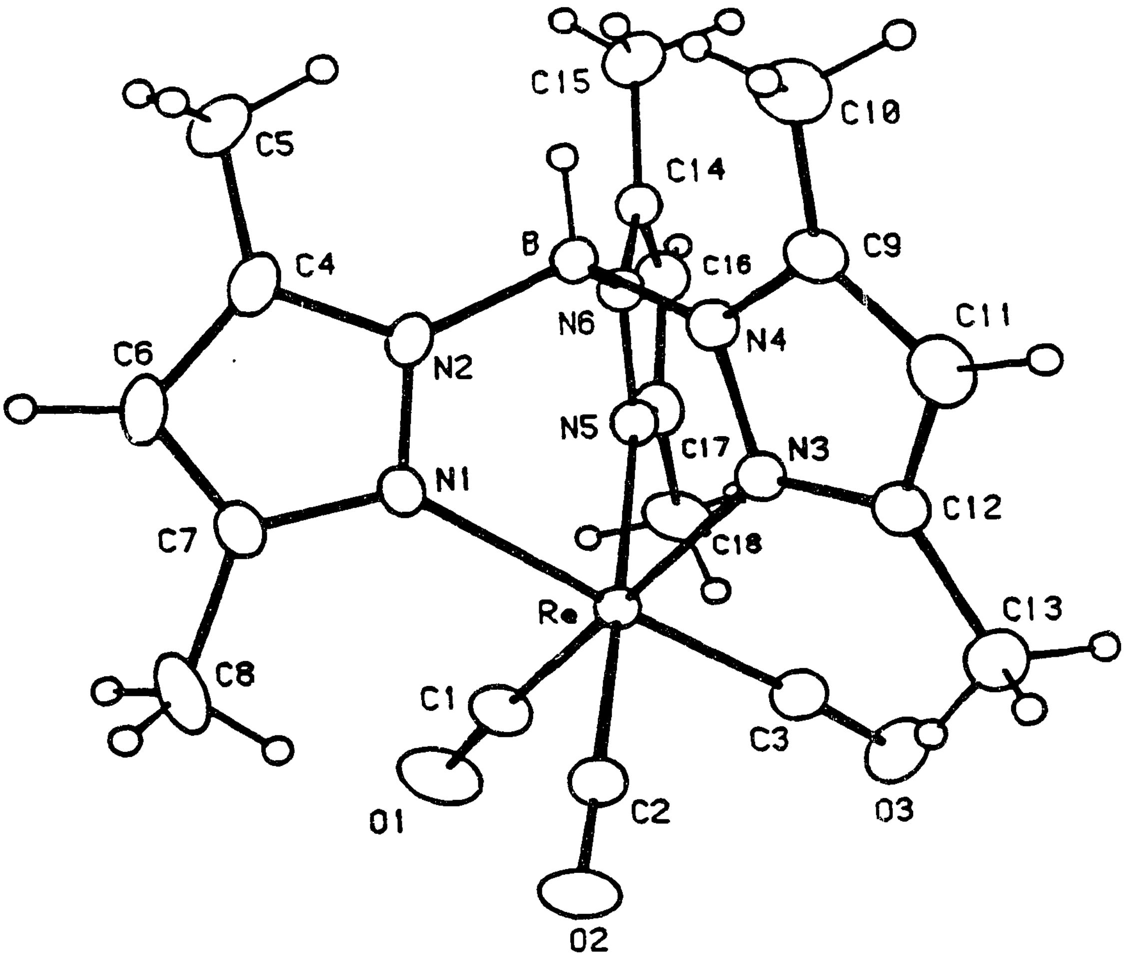


Figure II-2 Molecular Structure of $HBPz^*{}_3Re(CO)_3$ 1 structure is that the Re atom is 0.1 Å above the 3-methyl-carbon-plane (plane No 1) or 0.1 Å inside the symmetrical pocket formed by the 3-methyl substituents. This feature distinguishes $HBPz^*{}_3^-$ from Cp^{*-} and explains some of the reactivity differences between their complexes.

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CHAPTER THREE

NEW CHEMISTRY OF
HYDROTRIS(3,5-DIMETHYLPYRAZOL-1-YL)RHENIUM

SECTION I

INTRODUCTION

Pyrazolylborate complexes of many transition-metals have been reported. Surprisingly, few such rhenium complexes are known.[1] Chapter II described the preparation of $HBPz^{*}{}_3Re(CO)_2(THF)$ **3** from $HBPz^{*}{}_3Re(CO)_3$ **1**, and showed that complexes $HBPz^{*}{}_3Re(CO)_2L'$ ($L'=PMe_3$, PPh_3, and N_2) are readily available from the reaction of **3** with the corresponding ligand L'.[2] Following this work, the chemistry of **3** with other reagents was investigated. Unlike the analogous pentamethylcyclopentadienylrhenium complex $Cp^{*}Re(CO)_2(THF)$, **3** formed stable radicals when treated with a variety of reagents. The topic of metal-centered 17-electron radicals has been reviewed recently,[3] and several such rhenium radicals are known.[4] However examples of rhenium-centered radicals remain relatively rare, and no pyrazolylborate rhenium radicals have ever been reported.

This Chapter describes the formation of 17-electron complexes $HBPz^{*}{}_3Re(CO)_2L$ (L=Cl, Br, I, OMe, OEt, OCH_2CH_2OH), $[HBPz^{*}{}_3Re(CO)_2(THF)]^{+}$ and the 16-electron complex $HBPz^{*}{}_3Re(CO)(Cl)_2$. The reduction of $HBPz^{*}{}_3Re(CO)_2(Cl)$ to $[HBPz^{*}{}_3Re(CO)_2(Cl)]^{-}$ **10** and the crystal structure of **10** as its PPN^{+} salt are also reported.

SECTION II

EXPERIMENTAL

All reactions were carried out under argon using standard Schlenk techniques. UV-Visible spectra were recorded at room temperature on a Varian DMS-100 spectrophotometer. $HBPz^*_3Re(CO)_2(THF)$ was prepared as in Chapter II.

Dicarbonylchloro[hydrotris(3,5-dimethylpyrazol-1-yl)borato]rhenium(II) 8

Method A Excess CCl_4 (4 mL, 41.5 mmol) was added to a THF solution of **3** generated from $HBPz^*_3Re(CO)_3$ (**1**, 1.2 g, 2.11 mmol) in 200 mL THF. After stirring overnight, IR showed 95% conversion of 3. THF was removed on a rotary evaporator and the residue was placed on a Florisil column (2 x 20 cm, 60-100 mesh) prepared in hexane. Hexane first eluted trace amounts of **1**. CH_2Cl_2/hexane (1:1) then eluted an orange band of **8** (0.8 g, 65% based on **1**). Next, CH_2Cl_2/hexane (2:1) eluted a yellow band from which $HBPz^*_3Re(CO)(Cl)_2$ **9** was obtained (yield was variable, but always less than 5%).

Characterization: IR (CH_2Cl_2) 1995 (s), 1876 (s) cm^{-1}, υ(CO). MS, 145°C/16ev (m/e, rel.int.): M^+(575, 81), M^+-CO(547, 80), M^+-2CO(519, 100). Anal. Calcd for $C_{17}H_{22}N_6O_2BClRe$: C 35.48, H 3.83, N 14.61. Found: C 35.41, H 3.81, N 14.57. Solution magnetic moment (CD_2Cl_2): 2.20 μ_B.

Method B A mixture of $[HBPz^*{}_3Re(CO)_2(THF)]BF_4$ **19** (see below, 21 mg, 0.030 mmol) and PPNCl (20 mg, 0.035 mmol) was dissolved in CH_2Cl_2 (15 mL) at room temperature. Stirring for 1.5 h gave complete conversion of **19** to **8** as indicated by IR. The product was purified as above and characterized by IR and MS (16 mg, 81%).

Method C Complex **1** (20 mg, 0.035 mmol) in cyclohexene (25 mL) was irradiated for 45 min with H_2 purge. Use of a Pyrex cut-off filter gave a cleaner result. IR showed an estimated 30% conversion of **1** to presumably $HBPz^*{}_3Re(CO)_2(\eta^2\text{-}C_6H_{10})$ (υ(CO) 1993, 1876 cm^{-1}). CCl_4 (4 mL, 41.5 mmol) was then added to the solution. Stirring for 15 min gave 100% conversion of the presumed $HBPz^*{}_3Re(CO)_2(\eta^2\text{-}C_6H_{10})$ to **8** (by IR). Complex **8** was isolated as above and characterized by IR and MS.

Bis(triphenylphosphine)iminiumdicarbonylchloro[hydrotris(3,5-dimethylpyrazol-1-yl)borato]rhenium(0) 10

Complex **8** (0.16 g, 0.28 mmol) in THF (30 mL) was stirred with sodium sand (ca. 100 mg, 4.35 mmol). The solution turned from yellow to colourless in a few minutes and showed υ (CO) at 1875, 1781 cm^{-1}. PPNCl (0.178 g, 0.31 mmol) was then added. After stirring for 15 min, the volume of the solution was reduced to 10 mL under vacuum. Addition of hexane gave a yellow precipitate, which was twice dissolved in THF and precipitated with hexane. Yellow crystals of 10 were obtained from CH_2Cl_2/hexane (0.242 g, 78%).

Sodium borohydride ($NaBH_4$) can also be used as the reducing reagent.

Characterization: IR (CH_2Cl_2) 1872 (s), 1780 (s) cm^{-1}, υ(CO). Negative FAB in Cleland (m/e, rel.int.): M^- (575, 25), $(Cleland-1)^-$ (153, 100). ^1H NMR (CD_2Cl_2): δ 2.47 (s, 6.67H, due to overlap), 2.60 (s, 4.67H, due to overlap), 2.72 (s, 6.67H, due to overlap), 5.70 (s, 2H), 5.79 (s, 2H), 7.6 (m, 30H). Anal. Calcd for $C_{53}H_{52}N_7O_2BClP_2Re$: C 57.17, H 4.67, N 8.81. Found: C 57.11, H 4.64, N 8.82.

Carbonyldichloro[hydrotris(3,5-dimethylpyrazol-1-yl)borato]rhenium(III) 9

Method A See the preparation of **8** (*method A*) in which **9** was isolated as a by-product.

Characterization: IR (CH_2Cl_2) 1928 cm^{-1}, υ(CO). MS, 140°C/70ev (m/e, rel.int.): M^+(582, 5.2), M^+-CO(554, 100), M^+-CO-Cl(519, 4). ^1H NMR (CD_2Cl_2): δ 4.92 (s, 2H), 5.59 (s, 3H), 6.68 (s, 6H), 7.32 (s, 6H), 7.42 (s, 1H), 8.69 (s, 3H). Anal. Calcd for $C_{16}H_{22}N_6OBCl_2Re$: C 32.99, H 3.78, N 14.43. Found: C 32.38, H 3.80, N 14.31. Solution magnetic moment: 0.88 μ_B.

Method B A sample of $NOBF_4$ (18 mg, 0.15 mmol) was added to complex **8** (90 mg, 0.16 mmol) in CH_3NO_2 (20 mL). The solution turned black in a few minutes and showed υ(CO) at 2060, 1949 cm^{-1}; the latter species could be converted back to **8** by $NaBH_4$ as demonstrated in an independent experiment. Excess PPNCl (200 mg, 0.35 mmol) was then added to the solution. Stirring overnight gave **9** as the only product by IR. Solvent was removed under vacuum and the residue was placed on a Florisil column (1 x 20 cm, 60-100 mesh). Eluting with CH_2Cl_2/hexane (1:1) gave the product as a yellow solid (67 mg, 74%).

Carbonylchloro[hydrotris(3,5-dimethylpyrazol-1-yl)borato]nitrosylrhenium(I) 11

Complex **8** (0.25 g, 0.43 mmol) in THF (25 mL) was reacted with $NOBF_4$ (0.051 g, 0.44 mmol) at -78^{0}C. The solution was slowly warmed to room temperature and stirred at room temperature for 20 min. More $NOBF_4$ (0.05 g, 0.43 mmol) was then added. Stirring overnight gave 80% conversion of **8**. The solvent was removed under vacuum and the residue was placed on a Florisil column (1 x 20 cm, 60-100 mesh). Eluting with CH_2Cl_2/hexane (1:1) gave the product as an orange solid (0.15 g, 60%).

Characterization: IR (CH_2Cl_2) 1989 (s) cm^{-1}, υ(CO); 1741 (m) cm^{-1}, υ(NO). MS, 150°C/70ev (m/e, rel.int.): M^+(577, 17), M^+-CO(549, 100), M^+-CO-NO(519, 78). ^{1}H NMR (CD_2Cl_2): δ 2.35 (s, 3H), 2.40 (s, 3H), 2.41 (s, 6H), 2.58 (s, 3H), 2.60 (s, 3H), 5.86 (s, 1H), 5.96 (s, 2H). Anal. Calcd for $C_{16}H_{22}N_7BClO_2Re$: C 33.28, H 3.81, N 16.98. Found: C 33.38, H 3.85, N 16.69.

Photolysis of 8 in CH_2Cl_2/CCl_4

Complex **8** (35 mg, 0.06 mmol) in CH_2Cl_2/CCl_4 (1:1, 25 mL) was irradiated with a H_2 purge for 25 min. IR showed complete conversion of **8**. The solvent was removed under vacuum and the residue was placed on a Florisil column (1 x 20 cm, 60-100 mesh). Eluting with CH_2Cl_2/hexane (1:1) gave the product as a yellow solid, which contained both $HBPz^*_2(4\text{-}Cl\text{-}Pz^*)Re(CO)(Cl)_2$ **12** and $HBPz^*(4\text{-}Cl\text{-}Pz^*)_2Re(CO)(Cl)_2$ **13** (1:1 ratio).

Characterization: IR (CH_2Cl_2) 1928 cm^{-1}, ν(CO). MS, 155°C/16ev (m/e, rel.int.): M^+-CO of **13**(623, 18), M^+-CO of **12**(589, 43), BP^+(base peak, 554, 100). Anal. Calcd for **12** and **13** in 1:1 ratio $C_{16}H_{20.5}N_6BOCl_{3.5}Re$: C 30.33, H 3.47, N 13.26. Found: C 30.94, H 3.71, N 13.92. Solution magnetic moment: 4.69 μ_B.

Bromodicarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl) borato]rhenium(II) 14 and Dibromocarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl)borato]rhenium(III) 15

Method A Excess CBr_4 (1.3 g, 3.9 mmol) was added to a THF solution of **3** generated from $HBPz^*_3Re(CO)_3$ (**1**,1.23 g, 2.17 mmol) in 200 mL THF. After stirring overnight, IR showed complete consumption of **3**. THF was removed on a rotary evaporator and the residue was placed on a Florisil column (2 x 20 cm, 60-100 mesh) prepared in hexane. Hexane first eluted trace amounts of **1**. CH_2Cl_2/hexane (1:1) then eluted **14** as an orange solid (0.6 g, 45% based on **1**). Next,

CH_2Cl_2/hexane (2:1) eluted a yellow band from which $HBPz^*{}_3Re(CO)(Br)_2$ **15** was obtained (yield is variable, but always less than 5%).

Characterizaton of **14**: IR (CH_2Cl_2) 1994 (s), 1877 (s) cm^{-1}, υ(CO). MS, 140^0/16ev (m/e, rel.int.): M^+(619, 96), M^+-CO(591, 56), M^+-2CO(563, 100). Anal. Calcd for $C_{17}H_{22}N_6O_2BBrRe$: C 32.90, H 3.55, N 13.55. Found: C 32.69, H 3.69, N 13.44. Solution magnetic moment (CD_2Cl_2): 2.37 μ_B.

Characterizaton of **15**: IR (cyclohexane) 1931 (s) cm^{-1}, υ(CO). MS, 150^0/16ev (m/e, rel.int.): M^+(672, 15), M^+-CO(644, 100), M^+-CO-Br(563, 100). ^1H NMR (CD_2Cl_2): δ 4.70 (s, 2H), 5.96 (s, 3H), 6.98 (s, 6H), 7.51 (s, 1H), 7.82 (s, 6H), 9.98 (s, 3H).

Method B for **14** A mixture of $[HBPz^*{}_3Re(CO)_2(THF)]BF_4$ **19** (see below, 20 mg, 0.029 mmol) and Et_4NBr (25 mg, 0.12 mmol) was dissolved in CH_2Cl_2 (15 mL) at room temperature. Stirring for 1.5 h gave complete conversion of **19** to **14** as indicated by IR. The product was purified as above and characterized by IR and MS (15 mg, 75%).

Preparation of $PPN[HBPz^*{}_2(4\text{-}Br\text{-}Pz^*)Re(CO)_2(Br)]$ 16 and $PPN[HBPz^*(4\text{-}Br\text{-}Pz^*)_2Re(CO)_2(Br)]$ 17

To a solution of **3** in THF, Br_2 was added dropwise until IR showed complete disappearance of **3**. The solution was then stirred for 30 min. At this stage IR showed υ (CO) at 1991, 1873 cm^{-1}. Excess $NaBH_4$ was added and the solution was stirred until complete disappearance of the band at 1991, 1873 cm^{-1} occurred. Metathesis with PPNCl gave a mixture of PPN[$HBPz^*_2$(4-Br-Pz*)Re$(CO)_2$(Br)] **16** and PPN[HBPz*(4-Br-Pz*$)_2$Re$(CO)_2$(Br)] **17** (1:1 ratio), which was purified by recrystallization from THF/hexane.

Characterization: IR (CH_2Cl_2) 1877 (s), 1787 (s) cm^{-1}, υ(CO). ^1H NMR (CD_2Cl_2): δ 2.40 (m, 20.4H, due to overlap), 2.65 (m, 15.6H, due to overlap), 5.66 (s, 1H), 5.72 (s, 1H), 5.77 (s, 1H), 7.6 (br. 30H). Anal. Calcd for **16** and **17** in 1:1 ratio $C_{16}H_{20.5}N_6BO_2Br_{3.5}Re$: C 49.85, H 3.96, N 7.68. Found: C 49.44, H 4.07, N 7.23.

Dicarbonyliodo[hydrotris(3,5-dimethylpyrazol-1-yl)borato]rhenium(II) 18

Method A Excess MeI (4 mL, 64.3 mmol) was added to a THF solution of **3** (50 mL, an aliquot of a THF solution of **3** generated from 220 mg, 0.39 mmol $HBPz^*_3Re(CO)_3$ **1** in 185 mL THF). After stirring for 3 days, IR showed complete conversion of **3**. THF was removed on a rotary evaporator and the residue was placed on a Florisil column (1 x 20 cm, 60-100 mesh) prepared in hexane. Hexane first eluted trace amount of **1**. CH_2Cl_2/hexane (1:1) then eluted **18** as a dark purple solid (45 mg, 57% based on **1**).

Characterization: IR (CH_2Cl_2) 1988 (s), 1876 (s) cm^{-1}, υ(CO). MS, 150^0/70ev (m/e, rel.int.): M^+(667, 69), M^+-CO(639, 22), M^+-2CO(611, 100). Anal. Calcd for $C_{17}H_{22}N_6O_2BIRe$: C 30.58, H 3.30, N 12.59. Found: C 30.50, H 3.30, N 13.60. Solution magnetic moment (CD_2Cl_2): 2.34 μ_B.

Method B A mixture of $[HBPz^*_3Re(CO)_2(THF)]BF_4$ **19** (see below, 25 mg, 0.036 mmol) and Bu_4NI (37 mg, 0.10 mmol) was dissolved in CH_3NO_2 (15 mL) at room temperature. Stirring for 2 h gave complete conversion of **19** by IR. The product was purified as above and characterized by IR and MS (<10% yield).

Dicarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl) borato](THF)rhenium(II)tetrafluroborate 19

Complex **3** in THF (generated from 43.3 mg, 0.076 mmol of **1** in 150 mL THF) was reacted with $NOBF_4$ (8 mg, 0.068 mmol) at -78^0C. An argon purge with a rate of one bubble per second was passed through the solution to remove NO gas formed in the reaction. The solution was slowly warmed to room temperature (over 8 h), and stirring was continued for 2 days to give a red solution. The volume of the solution was reduced to 20 mL. Addition of hexane gave a red precipitate, which was twice dissolved in THF and precipitated with hexane in the same manner (45 mg, 85%).

The above scale was good for avoiding side reactions. If a larger scale (>1.0 g) was employed, or if the solution was warmed up too quickly, complex $[HBPz^*_3Re(CO)_2(NO)]BF_4$ **20** (see below) formed as a by-product.

Characterization: IR (THF) 2004 (s), 1904 (s) cm^{-1}, $\upsilon(CO)$. FAB in Cleland (m/e, rel.int.): M^+(612, 67), M^+-THF(540, 100), M^+-THF-CO(512, 27), M^+-THF-2CO(484, 88). Anal. Calcd for $C_{21}H_{30}N_6O_3B_2F_4Re$: C

36.11, H 4.30, N 12.04. Found: C 35.79, H 4.35, N 12.47. Solution magnetic moment (CD_2Cl_2): 2.21 μ_B.

Dicarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl)borato]nitrosylrhenium(I)tetrafluoroborate 20

Method A Complex **3** in THF (generated from 300 mg, 0.53 mmol of **1** in 200 mL THF) was treated with $NOBF_4$ (55.7 mg, 0.48 mmol) at -78^{0}C. The reaction was carried out in a pop-bottle capped under argon (not nitrogen). The solution was slowly warmed to room temperature (over 8 h), and stirring was continued for 2 days to give a yellow solution with copious yellow precipitate. The volume of the solution was reduced to 50 mL and the solution was syringed from the precipitate, which was washed with THF (3 x 10 mL) (0.272 g, 70%).

Characterization: IR (CH_2Cl_2) 2106 (s), 2043 (s) cm^{-1}, ν(CO); 1806 (m) cm^{-1}, ν(NO). FAB in "Cleland Reagent" (m/e, rel.int.): M^+(570, 100). ^1H NMR (CD_2Cl_2): δ 2.41 (s, 3H), 2.46 (s, 6H), 2.49 (s, 6H), 2.51 s, 3H), 6.07 (s, 1H), 6.13 (s, 2H). Anal. Calcd for **20**$\cdot CH_2Cl_2$ $C_{18}H_{24}N_7B_2O_3F_4Cl_2Re$: C 29.16, H 3.24, N 13.23. Found: C 28.87, H 3.28, N 13.15.

Method B NO gas was bubbled through a THF solution of **19**, and the reaction was followed by IR. Excess NO should be avoided to prevent side reactions.

This reaction was carried out on a small exploratory scale without isolation of the product **20**.

Dicarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl) boratolmethoxorhenium(II) 21

Method A Complex **19** (19 mg, 0.027 mmol) in MeOH (12 mL) was treated with excess aqueous KOH solution (0.25 mL, 4 M). After stirring for 10 min, the solvent was removed on a rotary evaporator and the residue was extracted with hexane (3 x 15 mL). Removal of hexane gave the product as a greenish solid (15 mg, 84%).

Characterization: IR (hexane) 1966 (s), 1863 (s) cm^{-1}, υ(CO). MS, $105^0C/70ev$ (m/e, rel.int.): M^+(571, 41), M^+-CO(543, 36), M^+-2CO(515, 100). Anal. Calcd for $C_{18}H_{25}N_6O_3BRe$: C 37.83, H 4.38, N 14.71. Found: C 38.54, H 4.55, N 14.37. Solution magnetic moment (C_6D_6): 2.17 μ_B.

Method B Complex **3** (20 mg, 0.029 mmol, from removal of THF under vacuum) was dissolved in MeOH (15 mL), KOH (100 mg, 1.79 mmol) was then added. Stirring overnight gave complete conversion of **3**. The product **21** was purified by recrystallization from hexane, and characterized by IR and MS.

Dicarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl) borato]ethoxorhenium(II) 22

Excess aqueous KOH solution (0.25 mL, 4 M) was added to complex **19** (20 mg, 0.029 mmol) in EtOH (12 mL). After stirring for 10 min, the solvent was removed on a rotary evaporator and the residue was extracted with hexane (3 x 20 mL). Removal of hexane gave the product as a greenish solid (12 mg, 68%).

Characterizaton: IR (hexane) 1966 (s), 1862 (s) cm^{-1}, υ(CO). MS, 140^{0}C/16ev (m/e, rel.int.): M^{+}(585, 98), M^{+}-CO(557, 68), BP^{+}(base-peak, 485, 100). Anal. Calcd for $C_{19}H_{27}N_6O_3BRe$: C 38.97, H 4.62, N 14.36. Found: C 38.92, H 4.71, N 14.55. Solution magnetic moment (C_6D_6): 2.20 μ_B.

Dicarbonyl[hydrotris(3,5-dimethylpyrazol-1-yl)borato](2-hydroxyethoxo)rhenium(II) 23

Complex **19** (30 mg, 0.043 mmol) in $HOCH_2CH_2OH$ (20 mL) was treated with excess aqueous KOH solution (0.50 mL, 4 M). After stirring for 2 h, water (15 mL) was added. Extracting the solution with hexane (3 x 10 mL) gave the product as a green-yellow solid (12 mg, 42%).

Characterizaton: IR (hexane) 1970 (s), 1866 (s) cm^{-1}, υ(CO). MS, 210^{0}C/16ev (m/e, rel.int.): M^{+}-33(568, 100), M^{+}-33-CO(540, 22). Anal. Calcd for $C_{19}H_{27}N_6O_4BRe$: C 37.94, H 4.49, N 13.98. Found: C 39.09, H 4.87, N 13.70. Solution magnetic moment (C_6D_6): 2.38 μ

Carbonyl(hydroxycarbonyl)[hydrotris(3,5-dimethylpyrazol-1-yl)borato]nitrosylrhenium(I) 24

Complex **20** (56 mg, 0.085 mmol) in acetone (20 mL) was treated with H_2O (5 mL) and NEt_3 (1.5 mL, 10.8 mmol). After stirring for 2 h, the solution was filtered and the precipitate was washed with acetone (3 x 10 mL) to give the product as a light orange solid (36 mg, 81%).

Characterization: IR (CH_2Cl_2) 1991 (s), 1634 (m) cm^{-1}, ν(CO); 1743 (s) cm^{-1}, ν(NO). MS, 185°C/70ev (m/e, rel.int.): M^+(587, 37), M^+-OH(570, 20), M^+-OH-CO(542, 48), BP^+(base peak, 531, 100). ^{1}H NMR (CD_2Cl_2): δ 2.28 (s, 3H), 2.31 (s, 3H), 2.32 (s, 3H), 2.36 (s, 3H), 2.38 (s, 3H), 2.40 (s, 3H), 5.84 (s, 1H), 5.94 (s, 2H), 7.4 (br. 1H). Anal. Calcd for $C_{17}H_{23}N_7O_4BRe$: C 34.75, H 3.92, N 16.70. Found: C 34.71, H 4.01 N 16.62.

Carbonyl[hydrotris(3,5-dimethylpyrazol-1-yl)borato]-methylnitrosylrhenium(I) 25

A mixture of complex **20** (29.3 mg, 0.045 mmol) and $NaBH_4$ (7.6 mg, 0.20 mmol) in THF (20 mL) was stirred for 45 min. THF was removed on a rotary evaporator and the residue was placed on a Florisil column (1 x 20 cm, 60-100 mesh) prepared in hexane. CH_2Cl_2 eluted the product as a pink solid (19 mg, 86%).

Characterization: IR (CH_2Cl_2) 1953 (s) cm^{-1}, ν(CO); 1707 (s) cm^{-1}, ν(NO). MS, 160°C/16ev (m/e, rel.int.): M^+(557, 40), M^+-CH_2(543, 98), M^+-CO(529, 100). ^{1}H NMR (CD_2Cl_2): δ 0.83 (s, 3H), 2.33 (s, 3H), 2.37 (s, 3H), 2.41 (s, 3H), 2.43 (s, 3H), 2.44 (s, 6H), 5.8 (s, 1H), 5.92 (s, 1H), 5.95 (s, 1H). Anal. Calcd for $C_{17}H_{25}N_7O_2BRe$: C 36.69, H 4.53, N 17.62. Found: C 36.04, H 4.34, N 17.00.

Determination of magnetic moments

The solution magnetic moment was determined by the Evans method,[5] mploying a 5-mm coaxial tube and using cyclohexane in CD_2Cl_2 or C_6D_6 as the reference signal. To illustrate the application of this method, the calculation of μ_{eff} for $HBPz^*{}_3Re(CO)_2(Cl)$ **8** is shown below. Table III-2 lists the results for all the paramagnetic complexes.

On the 400 MHz FT NMR instrument, two resonance lines of the reference cyclohexane at 562.887 and 357.086 Hz were observed at 23°C for a sample of complex **8** (50.8 mg) in 0.8 mL CD_2Cl_2 (containing less than 1% cyclohexane as reference signal). Thus $m = 6.35\times10^{-2}$ g/mL and $\Delta\upsilon$ = 562.887-357.086 = 205.801 Hz. The mass susceptibility of CD_2Cl_2 (χ_o) is calculated from Pascal's constants (Table II-1, assume $\chi_H = \chi_D$):

$$2 \times H = 2 \times (-2.93) \times 10^{-6} = -5.86 \times 10^{-6}\ cm^3mole^{-1}$$

$$2 \times Cl = 2 \times (-20.1) \times 10^{-6} = -40.2 \times 10^{-6}\ cm^3mole^{-1}$$

$$1 \times C = -6.0 \times 10^{-6}\ cm^3mole^{-1}$$

$$\chi_o = (-5.86 - 40.2 - 6.0) \times 10^{-6}\ cm^3mole^{-1}$$

$$= -52.06 \times 10^{-6}\ cm^3mole^{-1}$$

$$\chi_g = (-52.06 \times 10^{-6}) / 87 = -0.61 \times 10^{-6}\ cm^3g^{-1}$$

Substituting the above values into eq (I-1), and neglecting the last term because the solution is dilute, gives:

$$\chi_g = \frac{3x205.801}{2x3.14x400x10^6x6.35x10^{-2}} - 0.61x10^{-6}$$

$$= 3.26x10^{-6}\ (cm^3g^{-1})$$

$$= 575 \times 3.26x10^{-6}$$

$$\chi = 1874.8x10^{-6}\ (cm^3mole^{-1})$$

Table III-1 **Pascal's Constants ($\times 10^{-6}$ cm^3 mole^{-1})**

Atoms				Bonds	
Atom	χ	Atom	χ	Bond	χ
H	-2.93	F	-6.3	C=C	+5.5
B	-7	Cl	-20.1	C≡C	+0.8
C	-6.00	Br	-30.6	C=N	+8.2
C (aromatic)	-6.24	I	-44.6	C≡N	+0.8
N	-5.57	Mg^{2+}	-5	N=N	+1.8
N (aromatic)	-4.61	Zn^{2+}	-15	N=O	+1.7
N (monamide)	-1.54	Pb^{2+}	-32.0	C=O	+6.3
N (diamide, imide)	-2.11	Ca^{2+}	-10.4		
O (alcohol, ether)	-4.61	Fe^{2+}	-12.8		
O (carbonyl)	+1.72	Cu^{2+}	-12.8		
O_2 (carboxylate)	-7.95	Co^{2+}	-12.8		
S	-15.0	Ni^{2+}	-12.8		
P	-26.3				

The diamagnetic susceptibility (χ_{dia}) of complex **8** is calculated from Pascal's constants in the same way as that of CD_2Cl_2, and is found to be -164.1×10^{-6} cm^{3}mole^{-1}.

Therefore $\chi_{para} = \chi - \chi_{dia}$

$$= 1874.8 \times 10^{-6} - (-164.1 \times 10^{-6})$$

$$= 2038.9 \times 10^{-6}\ \text{cm}^3\text{mole}^{-1}$$

Finally, substituting the above value into eqn (I-3) gives

$$\mu_{eff} = 2.828 \times (2038.9 \times 10^{-6} \times 296)^{-0.5}$$

$$= 2.20\ \mu_B$$

Table III-2 Magnetic Moments of Paramagnetic Complexes [a]

Complex	Mass (mg)	Volume (mL)	$\Delta\upsilon$ (Hz)	χ_{dia} (x 10^{-6}) (cm^3mole^{-1})	Field (x 10^6 Hz)	μ (μ_B)
$HBPz^*_3Re(CO)_2Cl$ **8**	50.8	0.80 [b]	205.8	-164.1	400	2.20
$HBPz^*_3Re(CO)_2Br$ **14**	68.9	0.97 [b]	123.5	-174.6	200	2.37
$HBPz^*_3Re(CO)_2I$ **18**	144.5	0.85 [b]	271	-188.6	200	2.34
$HBPz^*_3Re(CO)Cl_2$ **9**	7.8	0.50 [b]	110.7	-186.2	200	0.88
$[HBPz^*_3Re(CO)_2(THF)]BF_4$ **19**	22.7	0.50 [d]	118.5	-228.3	400	2.21
$HBPz^*_3Re(CO)_2(OMe)$ **21**	10.6	0.50 [c]	48.2	-163.4	300	2.17
$HBPz^*_3Re(CO)_2(OEt)$ **22**	9.3	0.50 [c]	56.4	-175.3	400	2.20
$HBPz^*_3Re(CO)_2(OCH_2CH_2OH)$ **23**	7.2	0.50 [c]	37.1	-179.9	300	2.38
Mixture **12 + 13**	4.9	0.75 [b]	42	-222 [e]	200	4.69

[a] All spectra were recorded at 296K.

[b] In CD_2Cl_2, χ -0.61 x 10^{-6} cm^3mole^{-1}.

[c] In C_6D_6, χ -0.43 x 10^{-6} cm^3mole^{-1}.

[d] In CD_3CN, χ -0.49 x 10^{-6} cm^3mole^{-1}.

[e] Calculated as the average of 12 and 13.

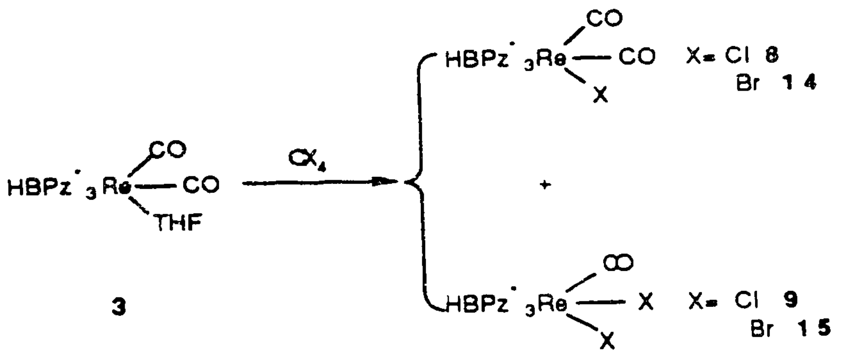
SECTION III

RESULTS AND DISCUSSION

A Preparation of HBPz*$_3$Re(CO)$_2$X (X=Cl, Br, I) and HBPz*$_3$Re(CO)(X)$_2$ (X=Cl, Br)

These paramagnetic complexes were first encountered in the ^{1}H NMR study of HBPz*$_3$Re(CO)$_2$(THF) **3**. A sample of **3** in CD_2Cl_2 was observed to change from yellow to orange over several days. Both IR and MS suggested the formation of HBPz*$_3$Re(CO)$_2$(Cl) **8**. It has been shown that HBPz*$_3^-$ stabilizes [illegible] complexes such as HBPz*$_3$Mo(O)(Cl)$_2$[9] and HBPz*$_3$[illegible] The special steric demand of HBPz*$_3^-$ is considered to be a major factor. The cone angles of CpMo, RBPz$_3$Mo and HBPz*$_3$Fe are 100^0, 180^0 and 225^0 respectively.[6]

The reaction of **3** with CCl_4 afforded both **8** and HBPz*$_3$Re(CO)(Cl)$_2$ **9**. Similarly, the reaction of **3** with CBr_4 afforded HBPz*$_3$Re(CO)$_2$(Br) **14** and HBPz*$_3$Re(CO)(Br)$_2$ **15**. Complex **14** can also



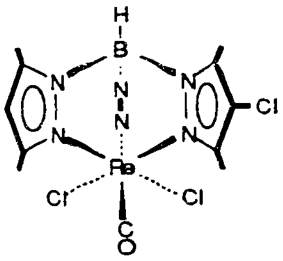
3

(III-1)

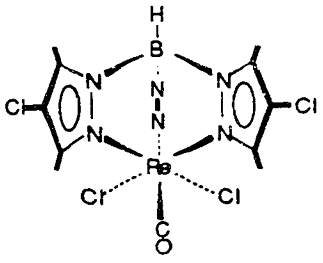
be prepared from the reaction of **3** with CH_3Br. None of the expected $HBPz^*{}_3Re(CO)_2(CH_3)(Br)$ was observed in this reaction. The iodo-derivative $HBPz^*{}_3Re(CO)_2(I)$ **18** was prepared from the reaction of **3** with CH_3I. Alternatively, all the 17-electron radicals can be prepared from $[HBPz^*{}_3Re(CO)_2(THF)]^+$ **19** as shown in Scheme III-1.

The presumed intermediate $HBPz^*{}_3Re(CO)_2(\eta^2\text{-}C_6H_{10})$ (C_6H_{10} = cyclohexene) has similar reactivity to **3** and reacts with CCl_4 to form **8**. But because of its poor yield (30% from $HBPz^*{}_3Re(CO)_3$ **1**), $HBPz^*{}_3Re(CO)_2(\eta^2\text{-}C_6H_{10})$ is not a preferred precursor.

Irradiation of **8** in CH_2Cl_2/CCl_4 afforded a mixture of $HBPz^*{}_2(4\text{-}Cl\text{-}Pz^*)Re(CO)(Cl)_2$ **12** and $HBPz^*(4\text{-}Cl\text{-}Pz^*)_2Re(CO)(Cl)_2$ **13**. In addition to the expected replacement of one CO group, the 4-protons of Pz^* were also replaced by Cl. Another example of such pyrazole ring halogenation was observed in the reaction between **3** and Br_2. These products were identified as the reduced forms $[HBPz^*{}_2(4\text{-}Br\text{-}Pz^*)Re(CO)_2(Br)]^-$ **16** and $[HBPz^*(4\text{-}Br\text{-}Pz^*)_2Re(CO)_2(Br)]^-$ **17**. **16** and **17** formed in an approximate 1:1 ratio as determined by the integration of 4-protons in the ^1H NMR spectrum. Cases of partial and



12



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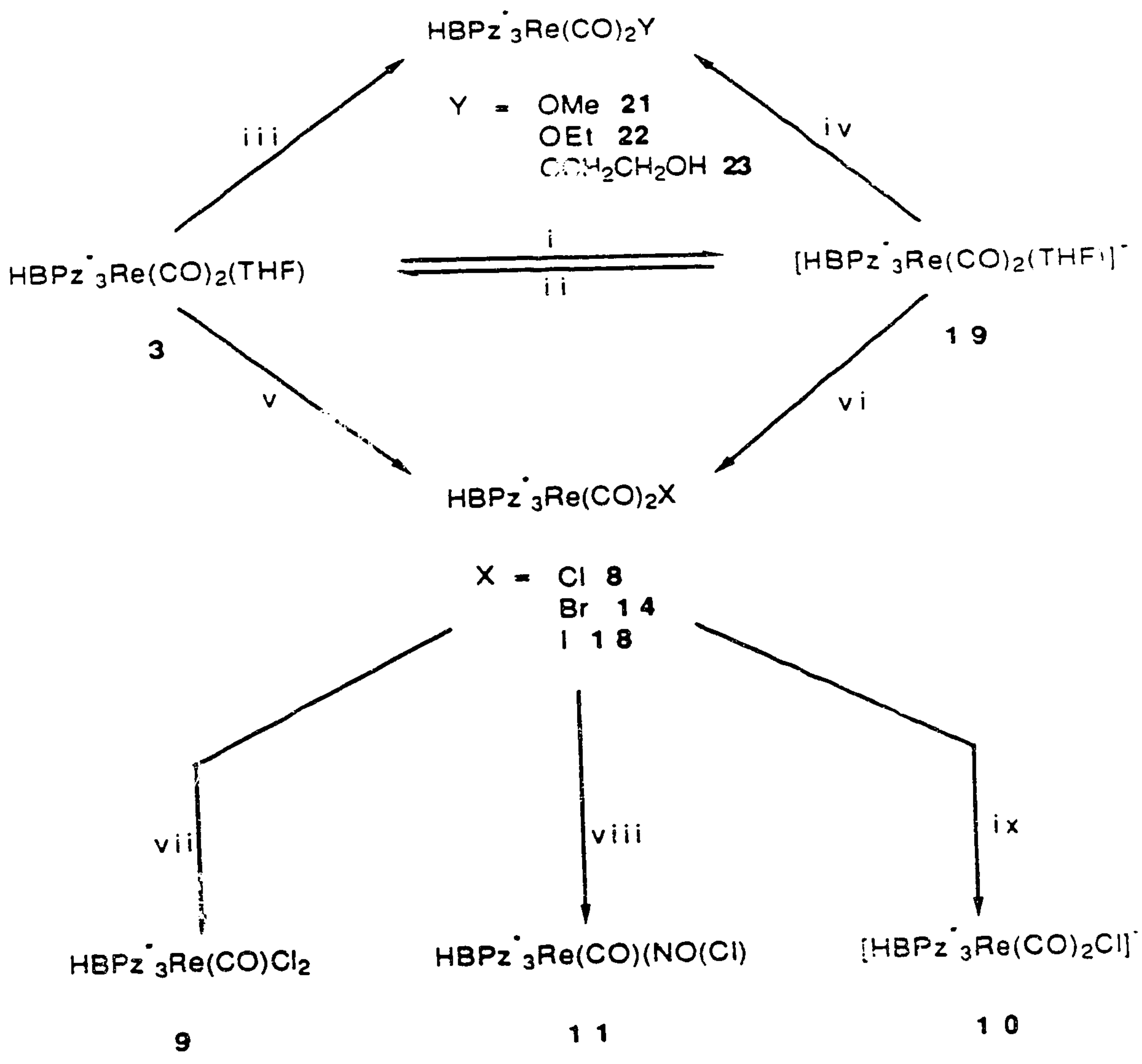


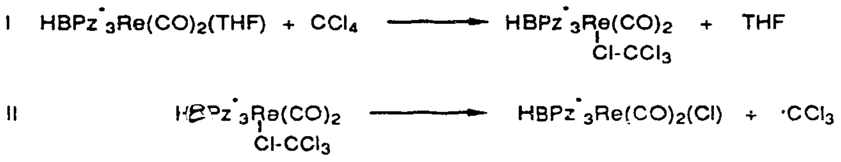
Scheme III-1

i NOBF$_4$, Ar purge ii NaBH$_4$, H$_2$O iii MeOH iv HY+KOH(aq) v MeBr, X = Br; MeI, X = I vi PPNCl, X = Cl; Et$_4$NBr, X = Br; Bu$_4$NI, X = I vii 1.NOBF$_4$ 2.PPNCl in CH$_3$NO$_2$ viii 2eq NOBF$_2$ in THF ix Na sand complete pyrazole halogenation at the 4-positions have been reported before. For example, chlorination of $HBPz^{*}{}_3Mo(CO)_2(NO)$ afforded $HB(4\text{-}Cl\text{-}Pz^{*})_3Mo(NO)(Cl)_2$.[7]

B Mechanistic considerations

Carbon tetrachloride is known to react with $Cp^{*}Ir(CO)_2$ to produce $Cp^{*}Ir(CO)(Cl)_2$ [15] and $CBrCl_3$ was used to prepare $HBPz^{*}{}_3Rh(CO)(Br)_2$ from $HBPz^{*}{}_3Rh(CO)_2$.[16] The formation of 17-electron **8** and 16-electron **9** is unusual. There are two plausible routes, A and B, for the reaction between **3** and CCl_4. Route A does not account for the formation of the 16-electron species. A similar sequence appears likely in the reactions between **3** and CH_3X (X=Br, I) where no 16-electron complexes were isolated. Examples of halocarbon binding to transition-metals are known.[8]

Route A



$$\text{I}\quad HBPz^{*}{}_3Re(CO)_2(THF) + CCl_4 \longrightarrow HBPz^{*}{}_3\underset{\text{Cl-CCl}_3}{\underset{|}{Re}}(CO)_2 + THF$$

$$\text{II}\quad HBPz^{*}{}_3\underset{\text{Cl-CCl}_3}{\underset{|}{Re}}(CO)_2 \longrightarrow HBPz^{*}{}_3Re(CO)_2(Cl) + \cdot CCl_3$$

Route B

$$\text{I}\quad HBPz^{*}{}_3Re(CO)_2(THF) + CCl_4 \longrightarrow [HBPz^{*}{}_3Re(CO)_2(THF)]^{+} + CCl_4^{\cdot -}$$

$$\text{II}\quad CCl_4^{\cdot -} \longrightarrow Cl^{-} + \cdot CCl_3$$

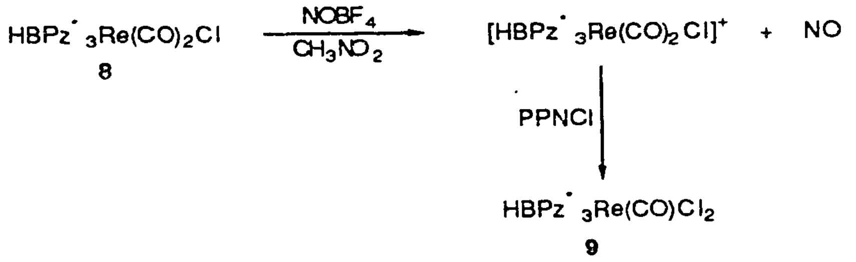
$$\text{III}\quad [HBPz^{*}{}_3Re(CO)_2(THF)]^{+} + Cl^{-} \longrightarrow HBPz^{*}{}_3Re(CO)_2(Cl) + THF$$

$$\text{IV} \quad HBPz^*{}_3Re(CO)_2(Cl) + CCl_4 \longrightarrow [HBPz^*{}_3Re(CO)_2(Cl)]^+ + CCl_4^{\cdot -}$$

$$\text{V} \quad CCl_4^{\cdot -} \longrightarrow Cl^- + \cdot CCl_3$$

$$\text{VI} \quad [HBPz^*{}_3Re(CO)_2(Cl)]^+ + Cl^- \longrightarrow HBPz^*{}_3Re(CO)(Cl)_2 + CO$$

Step III of route B was confirmed directly by treating the isolated $[HBPz^*{}_3Re(CO)_2(THF)]^+$ **19** with PPNCl in THF. Steps IV-VI are parallel to I-III except the starting complexes are different. Step I starts with **3** and Step IV starts with **8**. Step VI was confirmed indirectly from the preparation method B of **9**. In this method, NO^+



$$\begin{tikzcd} \underset{\mathbf{8}}{HBPz^*{}_3Re(CO)_2Cl} \arrow[r, "NOBF_4", "CH_3NO_2"'] & {[HBPz^*{}_3Re(CO)_2Cl]^+} + NO \arrow[d, "PPNCl"'] \\ & \underset{\mathbf{9}}{HBPz^*{}_3Re(CO)Cl_2} \end{tikzcd}$$

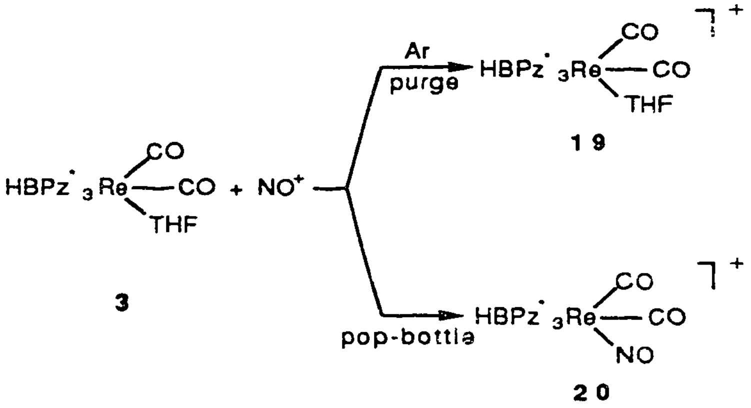
(III-2)

first oxidizes **8** into $[HBPz^*{}_3Re(CO)_2(Cl)]^+$ (suggested by IR ν(CO) (CH_3NO_2) at 2060, 1949 cm^{-1}), PPNCl then reacts with this intermediate to form **9**. Unfortunately this intermediate was not fully characterized as it is very unstable.

Preparation method B of **9** mentioned above was carried out in CH_3NO_2. Changing the solvent to THF afforded a completely different result. Instead of any radical species, the diamagnetic $HBPz^*{}_3Re(CO)(NO)(Cl)$ **11** was formed (Scheme I). The maximum conversion of **8** was 80% even though 2eq of $NOBF_4$ was used.

C Reactions of 3 with $NOBF_4$

Complex **3** reacts with $NOBF_4$ to give either $[HBPz^*_3Re(CO)_2(NO)]BF_4$ **20** or $[HBPz^*_3Re(CO)_2(THF)]BF_4$ **19** depending on the experimental conditions. In a closed system **20** formed; and in an open system with an inert gas purge, **19** formed. The selectivity was good (>90%) in small scale (ca. 43 mg) reactions.



(III-3)

While **20** is scarcely soluble in THF, **19** is fairly soluble. This solubility difference provides a handy means of separating the two compounds. Both **19** and **20** are air-stable and can be stored for weeks without noticeable decomposition.

Bubbling NO gas through a solution of **19** in THF produces **20** (Scheme III-1), which suggests that 20 probably formed according to the following two steps in the above reaction. A similar mechanism has been proposed for the formation of CpRe(CO)(NO)(COPh) from $[CpRe(CO)_2(COPh)]^-$ and $AgBF_4$/NO.[4e]

$$HBPz^{*}_{3}Re(CO)_2(THF) + NO^{+} \longrightarrow [HBPz^{*}_{3}Re(CO)_2(THF)]^{+} + NO$$

$$[HBPz^{*}_{3}Re(CO)_2(THF)]^{+} + NO \longrightarrow [HBPz^{*}_{3}Re(CO)_2(NO)]^{+} + THF$$

Step I is a simple redox reaction. NO^+ obtains one electron from **3** to produce **19** and NO gas. The NO gas formed here can be removed from the system with a flow of inert gas. Thus in an open system the reaction stops at Step I and affords **19**. In a closed flask, like the pop-bottle used in this work, NO remains in the system and Step II becomes possible, producing **20**. NO is formally a radical and can act as a one-electron or three-electron donor. In Step II, NO probably first couples with **19** and acts as a one-electron donor to form a diamagnetic intermediate which then loses THF to give **20**. NO is considered as a three-electron donor in the diamagnetic 20..

D Preparation of $HBPz^*_3Re(CO)_2(OR)$ (R=Me 21, Et 22, CH_2CH_2OH 23)

The three alkoxide derivatives were prepared analogously from **19** (Scheme I). They are all greenish air-stable complexes. The methoxide derivative **21** was also observed from a methanol solution of the neutral intermediate **3**. Stirring the solution in air accelerates the formation of **21**. It is reasonable to suggest that O_2 in the air oxidizes the intermediate $HBPz^*_3Re$[illegible]$_2$(MeOH) to 21. Unfortunately this presumed intermediate could [illegible]e identified.

Complex **23** was intended as a precursor to a 16-electron complex $HBPz^*{}_3Re(CO)(\eta^2-OCH_2CH_2O)$. However both irradiation of **23** and reaction with NO^+/OH^- resulted in decomposition. Ring formation with the dianion of ethanediol has been observed in $HBPz^*{}_3Mo(O)(\eta^2-OCH_2CH_2O)$.[9] In marked contrast, only $HBPz^*{}_3Mo(NO)(I)(OCH_2CH_2OH)$ and $HBPz^*{}_3Mo(NO)(OCH_2CH_2OH)_2$ were reported.[10]

E Reactions of 20

Extensive research has been carried out on the $Cp^*Re(CO)(NO)$ system. A stepwise reduction of coordinated carbon monoxide was achieved from the reduction of $Cp^*Re(CO)_2(NO)BF_4$ by $NaBH_4$ in THF/H_2O.[11] In the present work, two complexes of this type were prepared, $HBPz^*{}_3Re(CO)(NO)(COOH)$ **24** and $HBPz^*{}_3Re(CO)(NO)(CH_3)$ **25**.

Table III-3 shows $\upsilon(CO)$ bands of some $HBPz^*{}_3Re$ complexes along with their Cp^*Re analogues. In the first three sets of complexes, the average wave numbers of $\upsilon(CO)$ are higher for Cp^{*-} than those for $HBPz^*{}_3{}^-$, and in the last two, the trend is reversed. Differences up to 12 and 26 cm^{-1} can be seen for υ (CO) and $\upsilon(NO)$, respectively.

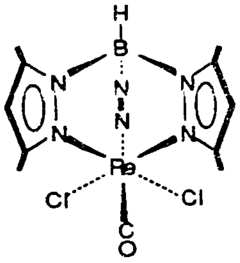
Table III-3 Comparison of IR Data Between $HBPz^{*}{}_{3}Re$ and $Cp^{*}Re$ Derivatives

	$L = HBPz^{*}{}_{3}^{-}$	$L = Cp^{*-e}$
$LRe(CO)3$	2021(s), 1909 (vs)^{a}, ν (CO)	2017 (s), 1925 (vs)^{a}, ν (CO)
$LRe(CO)_2THF$	1896(s), 1810(s)^{b}, ν (CO)	1894(s), 1823(s)^{b}, ν (CO)
$LRe(CO)_2(N_2)$	1947(s), 1884(s)^{c}, ν (CO) 2129(m), ν (N_2);	1953(s), 1901(s)^{c}, ν (CO) 2124(m), ν (N_2);
$LRe(CO)_2(NO)^{+}$	2106(s), 2043(s)^{d}, ν (CO) 1806(m), ν (NO)	2092(s), 2036(s)^{d}, ν (CO) 1794(m), ν (NO)
$LRe(CO)(NO)(CH_3)$	1958(s)^{c}, ν (CO) 1718(m), ν (NO)	1949(s)^{c}, ν (CO) 1692(m), ν (NO)
$LRe(CO)(NO)(COOH)$	1991(s), 1634(m)^{d}, ν (CO) 1743(m), ν (NO)	

a, cyclohexane; b, THF; c, hexane; d, CH_2Cl_2; e, references 10, 18, 19 and 20.

F Spectroscopic studies of the paramagnetic complexes

All 17-electron complexes showed very broad resonances in their ^1H NMR spectra. However, the 16-electron complex **9** showed sharp resonances for all the protons (Figure III-1). The 4-protons of the $HBPz^*_3{}^-$ ligand normally appear around 5.8 ppm and the methyl protons appear in the 1-4 ppm region in a diamagnetic complex. Compared to these chemical shifts, two of the 4-protons of $HBPz^*_3{}^-$ in **9** were shifted upfield and all the other protons were shifted downfield. The four methyl resonances integrate as 1:2:2:1 and the two 4-proton resonances integrate as 2:1. The analogous dibromo derivative **15** showed the same pattern in its ^1H NMR spectrum. These integral ratios are consistent with the structure below:



9

The values of the solution magnetic moments at room temperature are shown in Table III-2. They were determined by the Evans method. All the magnetic moment values for 17-electron radicals are larger than the spin-only value 1.73 μ_B for one unpaired electron, indicating the possibility of an equilibrium between electronic states.

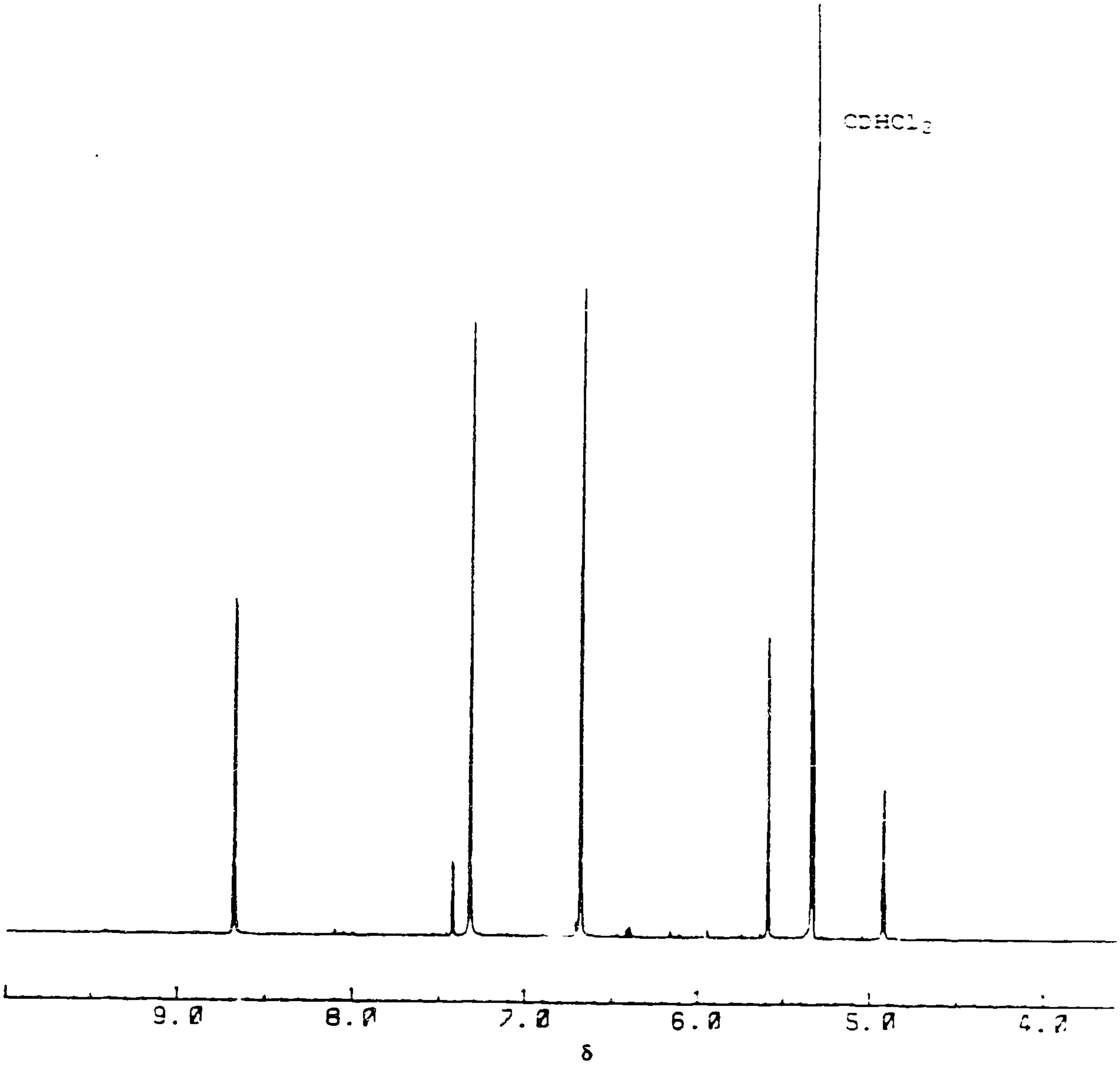


Figure III-1 ^{1}H NMR Spectrum of HBPz$^*{}_3$Re(CO)Cl$_2$ **9**

Table III-4 IR, Magnetic and UV-Visible Data of $HBPz^{*}{}_3Re$ Derivatives

Compound	I. R. (CH_2Cl_2, cm^{-1})	μ_{eff} (μ_B)	UV-Visible λ (nm)	ε
$PPN[HBPz^{*}{}_3Re(CO)_2(Cl)]$ **10**	1872(s), 1780(s)		267	13300 [f]
$HBPz^{*}{}_3Re(CO)_2(Cl)$ **8**	1994(s), 1876(s)	2.20 [c]	330 388	6028 [f] 4845
$HBPz^{*}{}_3Re(CO)_2(Br)$ **14**	1994(s), 1877(s)	2.37 [c]	291 430	4940 [f] 6400
$HBPz^{*}{}_3Re(CO)_2(I)$ **18**	1988(s), 1876(s)	2.34 [c]	300 576	6280 [f] 4650
$HBPz^{*}{}_3Re(CO)(Cl)_2$ **9**	1928	0.88 [c]	366	8230 [f]
$[HBPz^{*}{}_3Re(CO)_2(THF)]^{+}$ **19**	2004(s), 1904(s)[a]	2.21 [d]	390 440	3020 [a] 2160
$HBPz^{*}{}_3Re(CO)_2(OMe)$ **21**	1966(s), 1863(s)[b]	2.17 [e]	340 404	4446 [b] 3002
$HBPz^{*}{}_3Re(CO)_2(OEt)$ **22**	1966(s), 1862(s)[b]	2.20 [e]	332 410	3253 [b] 2305
$HBPz^{*}{}_3Re(CO)_2(OCH_2CH_2OH)$ **23**	1970(s), 1866(s)[b]	2.38 [e]	336 406	5685 [b] 3907

a, THF; b, hexane; c, CD_2Cl_2; d, CD_3CN; e, C_6D_6; f, CH_2Cl_2

In complex **9**, Re(III) is d^4 and the total number of electrons is sixteen. The small magnetic moment exibited by **9** could reflect the existence of high-spin and low-spin cross-over with the low-spin state predominant in this 16-electron complex. In contrast, the mixture of **12** and **13** is strongly paramagnetic and exhibits a magnetic moment of 4.64 μ_B, close to the spin-only value 4.90 μ_B for four unpaired electrons. Thus the high-spin state seems to be predominant in this mixture. For the closely related 16-electron complex $HBPz_3Re(PPh_3)Cl_2$,[22] no ^1H NMR spectrum was reported and its magnetic moment was determined as 2.1 μ_B.

The UV-Visible absorption spectra showed two bands for all the 17-electron complexes and one band for the 16-electron **9** and 18-electron **10**. All the dicarbonyl species show two CO stretching bands in the 1600-2200 cm^{-1} region. The cationic **19** exibits $\upsilon(CO)$ at 2004, 1904 cm^{-1}, which are about 100 cm^{-1} higher than its neutral precursor **3** ($\upsilon(CO)$ in THF, 1896, 1810 cm^{-1}).

G Preparation and molecular structure of $PPN[HBPz^*{}_3Re(CO)_2(Cl)]$ 10

Complex **8** was reduced by sodium sand in THF. Metathesis with PPNCl gave **10**. PPNCl was used so that Cl^- could depress the cleavage of Re-Cl bond. The CO stretchings of **10** appear at 1872, 1780 cm^{-1} in CH_2Cl_2, which are about 100 cm^{-1} lower than the neutral complex **8** (1995, 1876 cm^{-1}, υ (CO) in CH_2Cl_2). This is the same difference observed between the neutral **3** and cationic **19**. The ^1H NMR of **10** exhibits five resonances for the pyrazolylborate ligand. The three 4-Hs are as expected with a 2:1 ratio. The methyl groups, however, are not in the expected 2:1:2:1 pattern. There are only three resonances due to the six methyl groups. Perhaps accidental overlap occurs for the methyl groups. Accidental overlap of the methyl groups is also assumed for **11**, **16**, **17** and **25**, where less than expected distinct resonances were observed.

The structure of **10** was confirmed by an X-ray diffraction analysis carried out by Dr. R.G. Ball in the Structure Determination Laboratory in this Department.[21] Figure III-2 shows the structure of the ion pair PPN-[$HBPz^*{}_3Re(CO)_2(Cl)$] **10**. Clearly there is no interaction between the two ions. Figures III-3 and III-4 show different views of [$HBPz^*{}_3Re(CO)_2(Cl)$]$^-$. The anion is disordered with respect to the Cl atom and one of the CO groups. To model this disorder, two half-occupancy CO groups and two half-occupancy Cl groups were included in fixed positions on Re atom. In spite of the disorder, respectable R_1 and R_2 values were obtained, 0.051 and 0.058 respectively.

E Conclusion

The hydrotris(3,5-dimethylpyrazol-1-yl)borate ligand $HBPz^*{}_3{}^-$ stabilizes unusual complexes. Prior to this work, the 17-electron complexes $HBPz^*{}_3Mo(CO)_3$[12] and $HBPz_3Mo(CO)_3$[13] had been reported. Now some 17- and 16-electron rhenium complexes have been prepared by using this ligand. However none of the $HBPz^*{}_3Re(CO)_2(X)(Y)$ type complexes was prepared. Perhaps too much strain would be involved in a $HBPz^*{}_3Re(CO)_2(X)(Y)$ type complex if it adopts a piano-stool or 3:4 structure. The theoretically allowed capped-octahedral or 3:3:1 structure[14] was reported by Storr and co-workers for $MeGaPz_3Mo(CO)_3(CuPPh_3)$.[17] The steric demand of $HBPz^*{}_3{}^-$ plays a vital role in the chemistry of its complexes, and the ability of $HBPz^*{}_3{}^-$ to stabilize 17- and 16-electron complexes is remarkable.

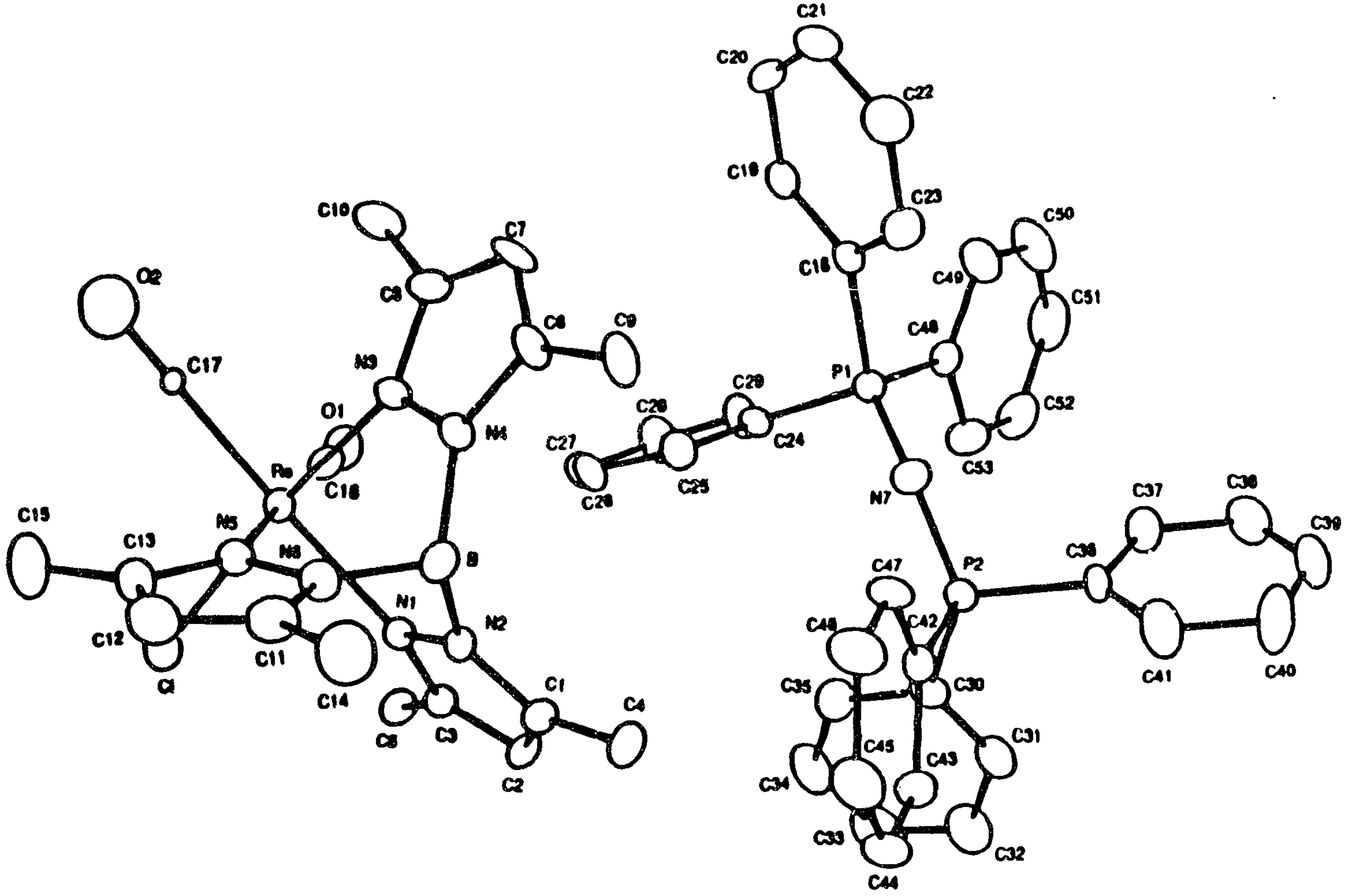


Figure III-2 Molecular Structure of PPN[HBPz*$_3$Re(CO)$_2$Cl] 10

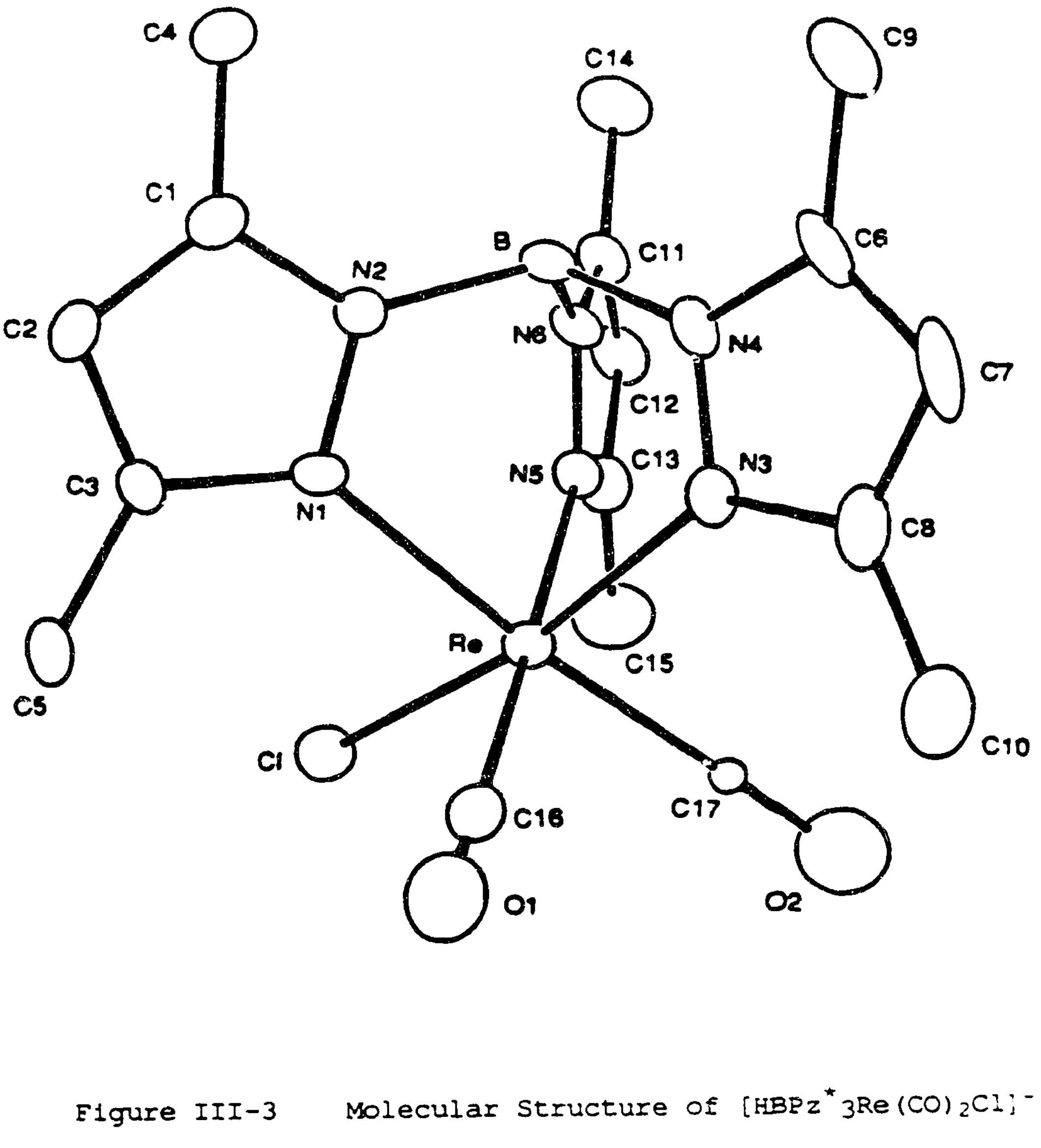


Figure III-3 Molecular Structure of $[HBPz^*_3Re(CO)_2Cl]^-$

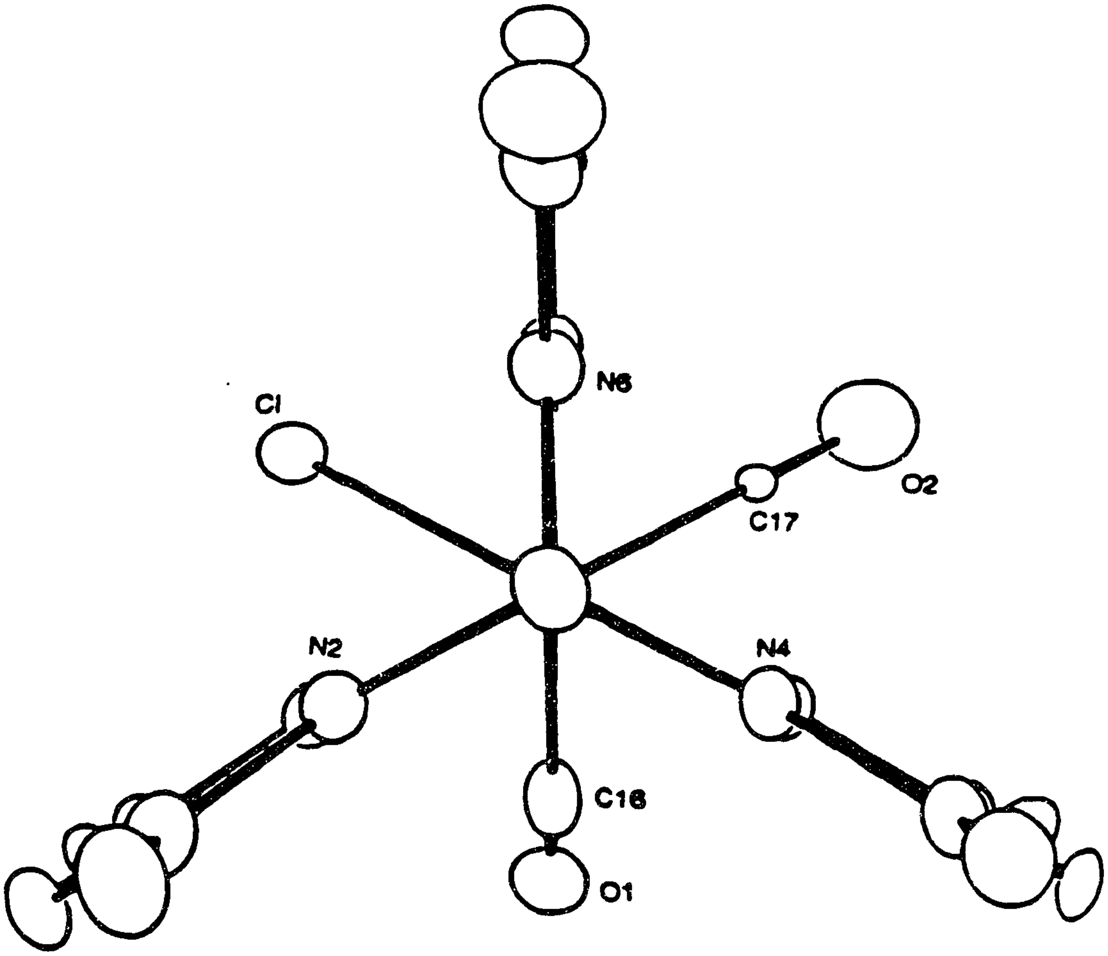


Figure III-4 Structure of $[\mathrm{HBPz^*_3Re(CO)_2Cl}]^-$, viewed approximately along the pseudo threefold axis

Crystal Data

$C_{53}H_{52}BClN_7O_2P_2Re$

F.W. = 1113.46

Crystal dimensions: 0.16 x 0.21 x 0.23 mm

Triclinic space group P-1

a = 15.896 (5)   b = 16.422 (3)   c = 9.847 (3) A

α = 95.05 (2) β = 96.55 (2) γ = 84.24 (2)°

V = 2533 A^3 Z = 2

Dc = 1.460 gm/cm^3 μ = 25.91 cm^{-1}

Data Collection and Refinement Conditions

Radiation:	Mo Kα (λ = 0.71073 A)
Monochromator:	Incident beam, graphite crystal
Take-off angle:	3.0 deg
Detector aperture:	2.40 mm horizontal 4.0 mm vertical
Crystal-to-detector distance:	205 mm
Scan type:	ω-2θ
Scan rate:	10.1 - 2.2 deg/min
Scan width:	0.80 + 0.35tan(θ) deg
Data collection 2θ limit:	55.00 deg
Data collection index range:	h, ±k, ±l
Reflections measured:	10152 unique 7228 with I>3σ(I)
Observations:variables ratio:	7228:577
Agreement factors R_1, R_2, GOF:	0.051, 0.058, 1.60
Corrections applied:	Absorption correction

Table III-5 Bond Distances in Angstrom

Atom1	Atom2	Distance	Atom1	Atom2	Distance	Atom1	Atom2	Distance
Re	C1	2.42	N5	N6	1.377 (7)	C28	C29	1.37 (1)
Re	C1'	2.32	N5	C13	1.339 (8)	C30	C31	1.37 (1)
Re	N1	2.194 (5)	N6	C11	1.361 (8)	C30	C35	1.38 (1)
Re	N3	2.157 (5)	N6	B	1.52 (1)	C31	C32	1.37 (1)
Re	N5	2.181 (5)	C1	C2	1.373 (9)	C32	C33	1.36 (2)
Re	C16	2.01 (1)	C1	C4	1.479 (9)	C33	C34	1.36 (2)
Re	C17'	2.00	C2	C3	1.368 (8)	C34	C35	1.37 (1)
Re	C17	2.00	C3	C5	1.458 (8)	C36	C37	1.36 (1)
P1	N7	1.573 (6)	C6	C7	1.35 (1)	C36	C41	1.37 (1)
P1	C18	1.793 (6)	C6	C9	1.48 (1)	C37	C38	1.38 (1)
P1	C24	1.795 (7)	C7	C8	1.38 (1)	C38	C39	1.35 (1)
P1	C48	1.791 (7)	C8	C10	1.47 (1)	C39	C40	1.36 (2)
P2	N7	1.563 (6)	C11	C12	1.34 (1)	C40	C41	1.40 (1)
P2	C30	1.792 (7)	C11	C14	1.46 (1)	C42	C43	1.388 (9)
P2	C36	1.805 (6)	C12	C13	1.38 (1)	C42	C47	1.370 (9)
P2	C42	1.791 (7)	C13	C15	1.46 (1)	C43	C44	1.36 (1)
O1	C16	0.874 (9)	C18	C19	1.384 (9)	C44	C45	1.34 (1)
O2	C17	1.20	C18	C23	1.386 (9)	C45	C46	1.36 (1)
O2'	C17'	1.20	C19	C20	1.37 (1)	C46	C47	1.39 (1)

Table III-5 Bond Distances in Angstrom (continued)

N1	N2	1.376 (6)	C20	C21	1.34 (1)	C48	C49	1.36 (1)
N1	C3	1.359 (7)	C21	C22	1.36 (1)	C48	C53	1.40 (1)
N2	C1	1.362 (8)	C22	C23	1.37 (1)	C49	C50	1.39 (1)
N2	B	1.537 (9)	C24	C25	1.376 (9)	C50	C51	1.33 (1)
N3	N4	1.376 (7)	C24	C29	1.369 (9)	C51	C52	1.36 (1)
N3	C8	1.367 (9)	C25	C26	1.38 (1)	C52	C53	1.37 (1)
N4	C6	1.350 (8)	C26	C27	1.36 (1)			
N4	B	1.534 (9)	C27	C28	1.38 (1)			

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

Table III-6 Bond Angles in Degree

Atom1	Atom2	Atom3	Angle
C1	Re	C1′	93.08
C1	Re	N1	89.6 (1)
C1	Re	N3	170.0 (1)
C1	Re	N5	88.6 (1)
C1	Re	C16	94.9 (3)
C1	Re	C17	94.46
C1′	Re	N1	176.0 (1)
C1′	Re	N3	93.4 (1)
C1′	Re	N5	92.7 (1)
C1′	Re	C16	90.5 (2)
C1′	Re	C17′	92.92
N1	Re	N3	83.5 (2)
N1	Re	N5	84.5 (2)
N1	Re	C16	92.2 (3)
N1	Re	C17′	89.8 (1)
N1	Re	C17	173.9 (1)
N3	Re	N5	83.5 (2)
N3	Re	C16	92.7 (3)
N3	Re	C17′	170.3 (1)
N3	Re	C17	91.8 (1)
N5	Re	C16	175.2 (3)
N5	Re	C17′	88.9 (1)
N5	Re	C17	91.1 (1)
N1	N2	B	119.4 (3)
C1	N2	B	130.1 (5)
Re	N3	N4	120.6 (4)
Re	N3	C8	134.4 (5)
N4	N3	C8	104.8 (6)
N3	N4	C6	109.9 (6)
N3	N4	B	118.8 (5)
C6	N4	B	131.2 (6)
Re	N5	N6	118.6 (4)
Re	N5	C13	134.5 (5)
N6	N5	C13	106.9 (5)
N5	N6	C11	108.5 (6)
N5	N6	B	120.7 (5)
C11	N6	B	130.7 (6)
P1	N7	P2	150.2 (4)
N2	C1	C2	106.7 (5)
N2	C1	C4	122.6 (6)
C2	C1	C4	130.7 (6)
C1	C2	C3	107.8 (5)
N1	C3	C2	109.5 (5)
N1	C3	C5	120.4 (3)
C2	C3	C5	130.1 (6)
N4	C6	C7	108.7 (7)

Table III-6 Bond Angles in Degree (continued)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C16	Re	C17'	94.6 (3)	N4	C6	C9	123.2 (8)
C16	Re	C17	92.0 (2)	C7	C6	C9	128.1 (8)
C17'	Re	C17	94.31	C6	C7	C8	106.5 (6)
Re	C1	O2'	178.70	N3	C8	C7	110.1 (7)
O2'	C1	C17'	177.06	N3	C8	C10	120.3 (7)
Re	C1'	O2	170.03	C7	C8	C10	129.4 (8)
O2	C1'	C17	161.90	N6	C11	C12	108.0 (6)
N7	P1	C18	108.4 (3)	N6	C11	C14	122.7 (8)
N7	P1	C24	113.6 (3)	C12	C11	C14	129.3 (7)
N7	P1	C48	113.9 (3)	C11	C12	C13	107.5 (6)
C18	P1	C24	105.5 (3)	N5	C13	C12	109.0 (7)
C18	P1	C48	108.6 (3)	N5	C13	C15	121.8 (6)
C24	P1	C48	106.4 (3)	C12	C13	C15	129.2 (7)
N7	P2	C30	115.1 (3)	Re	C16	O1	177. (1)
N7	P2	C36	111.2 (3)	Re	C17'	C1	178.01
N7	P2	C42	109.5 (3)	Re	C17'	O2'	180.00
C30	P2	C36	108.2 (3)	Re	C17	C1'	169.75
C30	P2	C42	105.8 (3)	Re	C17	O2	180.00
C36	P2	C42	106.6 (3)	P1	C18	C19	122.1 (5)
Re	N1	N2	119.3 (4)	P1	C18	C23	120.1 (5)
Re	N1	C3	134.2 (4)	C19	C18	C23	117.8 (6)
N2	N1	C3	106.0 (5)	C18	C19	C20	120.3 (7)
N1	N2	C1	109.9 (5)	C19	C20	C21	121.0 (7)

Table III-5 Bond Angles in Degree (continued)

Atom1	Atom2	Atom3	Angle
C20	C21	C22	120.1 (7)
C21	C22	C23	120.4 (7)
C18	C23	C22	120.3 (7)
P1	C24	C25	117.8 (5)
P1	C24	C29	123.9 (5)
C25	C24	C29	118.2 (6)
C24	C25	C26	120.6 (6)
C25	C26	C27	120.9 (7)
C26	C27	C28	118.8 (7)
C27	C28	C29	120.1 (7)
C24	C29	C28	121.3 (7)
P2	C30	C31	122.9 (6)
P2	C30	C35	119.3 (6)
C31	C30	C35	117.7 (7)
C30	C31	C32	122.1 (8)
C31	C32	C33	118.1 (9)
C32	C33	C34	122.1 (9)
C33	C34	C35	118.6 (9)
C30	C35	C34	121.3 (8)
P2	C36	C37	119.6 (6)
P2	C36	C41	122.2 (6)
C37	C36	C41	118.2 (7)
C36	C37	C38	122.2 (8)
C37	C38	C39	118.9 (9)
C38	C39	C40	121.2 (9)
C39	C40	C41	119.1 (9)
C36	C41	C40	120.3 (9)
P2	C42	C43	121.4 (5)
P2	C42	C47	119.4 (5)
C43	C42	C47	119.1 (6)
C42	C43	C44	120.4 (6)
C43	C44	C45	120.7 (7)
C44	C45	C46	120.2 (7)
C45	C46	C47	120.4 (7)
C42	C47	C46	119.1 (6)
P1	C48	C49	122.0 (6)
P1	C48	C53	120.3 (6)
C49	C48	C53	117.7 (7)
C48	C49	C50	120.7 (8)
C49	C50	C51	120.1 (9)
C50	C51	C52	121.4 (8)
C51	C52	C53	119.2 (8)
C48	C53	C52	120.9 (8)
N2	B	N4	108.1 (5)
N2	B	N6	110.0 (5)
N4	B	N6	109.8 (5)

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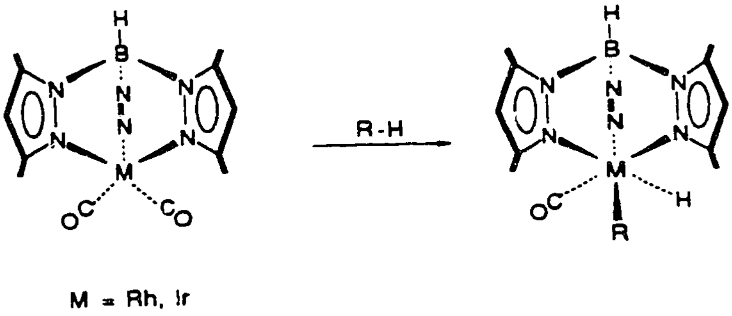
CHAPTER FOUR

SYNTHESIS OF AND C-H ACTIVATION BY TRIS(3,5-DIMETHYLPYRAZOL-1-YL)METHANERHODIUM COMPLEXES

SECTION I

INTRODUCTION

Following the first report of C-H activation by a tris(pyrazol-1-yl)borate rhodium complex,[1] several related papers have appeared.[2] These pyrazolylborate transition-metal complexes provide a highly efficient and selective system in C-H activation.



(IV-1)

Tris(3,5-dimethylpyrazol-1-yl)methane $HCPz^*_3$ is isoelectronic to $HBPz^*_3{}^-$. However, the coordination behavior of the neutral ligand $HCPz^*_3$ has not been studied as extensively as that of $HBPz^*_3{}^-$.[3] As an extension of the successful C-H activation by the pyrazolylborate system, the possibility of C-H activation by tris(pyrazol-1-yl)methane rhodium complexes was investigated. It has been noted that the cationic fragment $\{[N(CH_2CH_2PPh_2)_3]Rh\}^+$, generated from $[N(CH_2CH_2PPh_2)_3]Rh(H)$, activates C-H bonds.[4]

This Chapter describes the preparation of $[HCPz^*_3Rh(CO)L]^+$ (L = CO, PEt_3, PPh_3, COE and C_2H_4), and the activation of arene C-H bonds by these complexes.

SECTION II

EXPERIMENTAL

General

$[Rh(CO)_2Cl]_2$,[5] $AcacRh(CO)_2$[6a], $AcacRh(C_2H_4)_2$[6b], $HCPz_3$[7] and $HCPz^*_3$[8] were prepared by literature methods.

Dicarbonyl[tris(3,5-dimethylpyrazol-1-yl)methane]rhodium(I) tetrafluoroborate 26

To a solution of $AcacRh(CO)_2$ (52.1 mg, 0.20 mmol) and $HCPz^*_3$ (64.8 mg, 0.22 mmol) in CH_2Cl_2 (25 mL), $HBF_4 \cdot Et_2O$ was added dropwise. The reaction was followed by IR. Excess $HBF_4 \cdot Et_2O$ should be avoided to prevent side reactions. After all the $AcacRh(CO)_2$ had been converted, hexane was added to give crude **26** as a yellow precipitate. Complex 26 was purified by twice dissolving the crude product in CH_2Cl_2 and precipitating with hexane (81.6 mg, 75%).

Characterization: IR (CH_2Cl_2) 2098 (w), 2078 (s), 2036 (w), 2010 (vs) cm^{-1}, ν(CO). ^1H NMR (CD_2Cl_2): δ 2.56 (s, 9H), 2.45 (s, 9H), 6.14 (s, 3H), 7.93 (s, 1H); there was no change down to -100^0C. Anal. Calcd for $C_{18}H_{22}N_6O_2BF_4Rh$: C 39.69, H 4.04, N 15.44. Found: C 39.77, H 4.12, N 15.50.

Reaction between $[Rh(CO)_2Cl]_2$ and $HCPz^*_3$

A solution of $[Rh(CO)_2Cl]_2$ (40 mg, 0.10 mmol) and $HCPz^*_3$ (25 mg, 0.08 mmol) in CH_2Cl_2 (20 mL) was stirred overnight. The IR spectrum then showed CO stretching bands at 2090 (m), 2079 (s), 2070 (s), 2035 (w), 2019 (br. m), 1992 (s) and 1862 (w)cm^{-1}. Separation or further identification of the products was not attempted.

Protonation of 26

To a CH_2Cl_2 solution of **26**, $HBF_4 \cdot Et_2O$ was added dropwise. IR showed complete conversion of **26** to a new species, presumably $[\{HCPz^*_2(HPz^*)\}Rh(CO)_2](BF_4)_2$ **27** with ν(CO) at 2110, 2050 cm^{-1}. Complex **27** could be converted back to **26** by addition of $HCPz^*_3$. An attempt at isolation of **27** failed because of its instability.

Reaction of 26 with NEt_3

A solution of **26** (20 mg, 0.036 mmol) in acetone (15 mL) was reacted with NEt_3 (1 mL, 1.2 mmol) and H_2O (0.5 mL). The reaction was complete in a few minutes as indicated by IR. Evaporation of the organic layer and hexane extraction of the residue gave a bright yellow solid, which was characterized as the known $[Rh(CO)_2Pz^*]_2$.

Characterization: IR (hexa [illegible] 2086 (s), 2072 (s), 2018 (s) cm^{-1}, ν(CO). ^1H NMR (CD_2Cl_2): δ 5.85 [illegible] 2H), 2.30 (s, 12H). MS, 180^oC/16ev (m/e, rel.int.): M^+(508, 11), M^+-CO(480, 3.4), M^+-2CO(452, 4.3), M^+-3CO(424, 1.7), M^+-4CO(396, 3.3), BP^+(base peak, 202, 100).

Carbonyldibromo[tris(3,5-dimethylpyrazol-1-yl)methane]rhodium(III)tetrafluoroborate 28

A solution of Br_2 in CH_2Cl_2 was added dropwise to **26** (20 mg, 0.036 mmol) in CH_2Cl_2 (15 mL) until IR showed complete disappearance of **26**. The solution changed from yellow to orange when the reaction was complete. Removal of CH_2Cl_2 gave the product as an orange solid (24 mg, 100%).

Exposure of **28** to wet CH_2Cl_2 caused the appearance of a broad IR band at 2060 cm^{-1} in the 1600-2200 cm^{-1} region. These new species was not isolated or further identified.

Characterization: IR (CH_2Cl_2) 2132 cm^{-1}, υ(CO). ^1H NMR (CD_2Cl_2): δ 2.67 (s, 6H), 2.73 (s, 6H), 2.75 (s, 3H), 2.85 (s, 3H), 6.25 (s, 2H), 6.28 (s, 1H), 8.11 (s, 1H). Anal. Calcd for **28**·CH_2Cl_2, $C_{18}H_{24}N_6Br_2OCl_2RhBF_4$: C 28.42, H 3.18, N 11.05. Found: C 28.29, H 3.22, N 11.40.

Carbonyliodomethyl[tris(3,5-dimethylpyrazol-1-yl)methane]rhodium(III)tetrafluoroborate 29

Iodomethane (2 mL, 32 mmol) was added to a THF (15 mL) solution of **26** (20 mg, 0.036 mmol). The solution was stirred at room temperature for 16 h. IR showed complete disappearance of **26**. THF was emoved under vacuum and the residue was recrystallized from H_2Cl_2/hexane to give the product as an orange solid (2[illegible].1 mg, 85%).

Characterization: IR (CH_2Cl_2) 2086 cm^{-1}, υ(CO). ^1H NMR (CD_2Cl_2): 2.10 (d, 2Hz, 3H), 2.43 (s, 3H), 2.58 (s, 3H), 2.66 (s, 6H), 2.69 (s, 3H), 2.72 (s, 3H), 6.16 (s, 1H), 6.21 (s, 1H), 6.22 (s, 1H), 7.99 (s, 1H). Anal. Calcd for $C_{18}H_{25}N_6OIBF_4Rh$: C 32.85, H 3.83, N 12.77. Found: C 32.97, H 4.11, N 12.78.

Carbonyltriphenylphosphinetris(3,5-dimethylpyrazol-1-yl) methanerhodium(I)tetrafluoroborate 30

A solution of AcacRh$(CO)_2$ (40 mg, 0.155 mmol) was stirred with PPh_3 (40.6 mg, 0.155 mmol) in CH_2Cl_2 (25 mL), evolving CO gas instantaneously. The product AcacRh(CO)(PPh_3) showed υ(CO) at 1977 cm^{-1}. $HCPz^*_3$ (46.3 mg, 0.155 mmol) was then added. Complete conversion of AcacRh(CO)(PPh_3) to **30** was obtained with the addition of 1 eq $HBF_4 \cdot Et_2O$ (monitored by IR). The pure product was obtained by twice dissolving the crude product in CH_2Cl_2 and precipitating with hexane as a green-yellow solid (106 mg, 88%).

Characterization: IR (CH_2Cl_2) 1999 cm^{-1}, υ(CO). ^1H NMR (CD_2Cl_2): δ 1.84 (s, 9H), 2.29 (s, 9H), 6.00 (s, 3H), 7.4 (m, 15H), 7.80 (s, 1H). At -76^{0}C: δ 1.25 (s, 6H), 2.06 (s, 6H), 2.48 (s, 6H), 5.84 (s, 2H), 6.24 (s, 1H), 7.3 (m, 15H), 7.76 (s, 1H). Anal. Calcd for **30**$\cdot$0.5 CH_2Cl_2, $C_{35.5}H_{38}N_6POClRhBF_4$: C 51.91, H 4.63, N 10.24. Found: C 51.49, H 4.71, N 10.09.

Carbonyltriethylphosphinetris(3,5-dimethylpyrazol-1-yl)methanerhodium(I)tetrafluoroborate 31

This complex was prepared according to the same procedure as above. The pure product was obtained by twice dissolving the crude product in CH_2Cl_2 and precipitating with benzene as a pale yellow solid (>80% yield).

Characterization: IR (CH_2Cl_2) 1991 cm^{-1}, υ(CO). ^1H NMR (CD_2Cl_2): δ 1.0 (d of t, 17Hz, 7Hz, 9H), 1.63 (q of d, 6H), 2.3 (b, 18H), 6.18 (s, 3H), 7.70 (s, 1H). At -36^{0}C: δ 0.93 (d of t, 17Hz, 7Hz, 9H), 1.56 (q of d, 6H), 2.04 (s, 6H), 2.23 (s, 6H), 2.43 (s, 3H), 2.45 (s, 3H), 6.09 (s, 2H), 6.22 (s, 1H), 7.65 (s, 1H). Anal. Calcd for $C_{23}H_{37}N_6OPBF_4Rh$: C 43.55, H 5.88, N 13.25. Found: C 42.69, H 5.97, N 13.44.

Carbonyltricyclohexylphosphinetris(3,5-dimethylpyrazol-1-yl)methanerhodium(I)tetrafluoroborate 32

This complex was prepared according to the same procedure as 30. The pure product was obtained by twice dissolving the crude product in CH_2Cl_2 and precipitating with hexane as a green-yellow solid (>80% yield).

Characterization: IR (CH_2Cl_2) 1986 cm^{-1}, υ(CO). ^1H NMR (CD_2Cl_2): δ 1.3 (m, 15H), 1.85 (b, 18H), 2.10 (s, 6H), 2.29 (s, 6H), 2.44 (s, 3H), 2.51 (s, 3H), 6.11 (s, 2H), 6.25 (s, 1H), 7.58 (s, 1H). At -60^{0}C: δ 0.7-2.0 (m, 33H), 1.59 (s, 3H), 2.08 (s, 3H), 2.36 (s, 3H), 2.40 (s, 3H), 2.47 (s, 6H), 6.03 (s, 1H), 6.10 (s, 1H), 6.22 (s, 1H), 7.52 (s, 1H). Anal. Calcd for $C_{35}H_{55}N_6OPBF_4Rh$: C 52.78, H 6.96, N 10.55. Found: C 51.71, H 6.77, N 10.21.

Carbonylcyclooctene[tris(3,5-dimethylpyrazol-1-yl)methane] rhodium(I)tetrafluoroborate 33

A solution of complex **26** (192.8 mg, 0.35 mmol) in CH_2Cl_2/COE (10/35 mL) was stirred at room temperature for 4 days. A N_2 purge with a rate of one bubble per second was passed above the solution to remove CO formed in the reaction. The IR showed 90% conversion of **26** to **33**. Hexane was added to the solution to give a mixture of **26** and **33** (1:8 ratio by ^1H NMR) as a yellow solid. Separation of the two was not achieved and the mixture was used as the source of **33** in further reactions.

Characterization: IR (CH_2Cl_2) 2017 cm^{-1}, υ(CO). ^1H NMR (CD_2Cl_2): δ 1.5-1.9 (m, 10H), 2.0 (d, 2H), 2.44 (s, 9H), 2.58 (s, 9H), 4.22 (d, 2H), 6.10 (s, 3H), 7.84 (s, 1H). Anal. Calcd for $C_{25}H_{36}N_6OBF_4Rh$: C 47.94, H 5.79, N 13.42. Found: C 46.63, H 5.67, N 13.53; Calcd for 1:8 mixture of **26** and **33**: C 47.02, H 5.60, N 13.64.

Photolysis of 26 in benzene

A solution of **26** (20 mg, 0.036 mmol) in CH_2Cl_2/benzene (1:25 ratio, 20 mL) was irradiated for 8 min with N_2 purge. The IR spectrum showed complete disappearance of **26** and ^1H NMR showed that the products contained both $[HCPz^*{}_3Rh(CO)(Ph)(H)]^+$ **34** and $[HCPz^*{}_3Rh(CO)(H)_2]^+$ **35** in a 97:3 ratio by ^1H NMR.

Characterization of **34**: IR (benzene) 2063 cm^{-1}, ν(CO). ^1H NMR (CD_2Cl_2): δ 1.63 (s, 3H), 2.06 (s, 3H), 2.38 (s, 3H), 2.64 (s, 3H), 2.67 (s, 3H), 2.72 (s, 3H), 6.05 (s, 1H), 6.12 (s, 1H), 6.20 (s, 1H), 7.0 (b, 5H), 8.06 (s, 1H), -12.71 (d, 21Hz, 1H). At -60^{0}C: δ 6.53 (d, 7.5Hz, 1H), 6.85 (t of d, 7Hz, 1H), 7.02 (q of d, 7.5Hz, 2H), 7.45 (d, 7.0Hz, 1H), no significant change to other H's.

Carbonylchlorophenyl[tris(3,5-dimethylpyrazol-1-yl)methane]rhodium(III)tetrafluoroborate 36

A sample of **26** (201.9 mg, 0.37 mmol) in CH_2Cl_2/benzene (1:25 ratio, 100 mL) was irradiated for 45 min with a N_2 purge. CCl_4 (3 mL, 31 mmol) was then added and the resulting solution was stirred for 1 h. **36** deposited from the solution slowly as a yellow solid. Filtering the solution and adding pentane to the mother liquor gave a second crop of **36**. The combined solid was twice dissolved in CH_2Cl_2 and precipitated with hexane (190 mg, 82%).

Characterization: IR (CH_2Cl_2) 2110 cm^{-1}, ν(CO). ^1H NMR (CD_2Cl_2): δ 1.84 (s, 3H), 1.85 (s, 3H), 2.63 (s, 3H), 2.71 (s, 3H), 2.74 (s, 3H), 2.77 (s, 3H), 6.14 (s, 1H), 6.22 (s, 2.5H, due to overlap), 6.26 (s, 0.5H, due to overlap), 6.94 (t of d, 7.2Hz, 2.0Hz, 1H), 7.12 (t of d, 1H), 7.24 (t of d, 1H), 7.77 (d of d, 7.7Hz, 1H), 8.16 (s, 1H). Anal. Calcd for **36**·0.5 C_6H_6, $C_{26}H_{30}N_6ClORhBF_4$ C 46.77, H 4.53, N 12.59. Found: C 47.19, H 4.64, N 12.66.

Carbonylethylene[tris(3,5-dimethylpyrazol-1-yl)methane]rhodium(I)tetrafluoroborate 37

Method A A solution of complex **26** (88.7 mg, 0.16 mmol) was irradiated in CH_2Cl_2/benzene (1:25 ratio, 100 mL) as above for 20 min. Solvent was removed under vacuum and the residue was dissolved in CH_2Cl_2 (10 mL). The solution was pressurized to 900 psi ethylene and stirred at room temperature for 42 h. The pure product was obtained by twice dissolving the crude product in CH_2Cl_2 and precipitating with hexane as a greenish solid (41 mg, 46%).

Characterization: IR (CH_2Cl_2) 2032 cm^{-1}, ν(CO). ^{1}H NMR (CD_2Cl_2): δ 2.40 (s, 9H), 2.60 (s, 9H), 3.15 (b, 4H), 6.10 (s, 3H), 7.87 (s, 1H). At -16^{0}C: δ 3.4 (d, 8Hz, 2H), 2.74 (d, 8Hz, 2H), assigned to C_2H_4, no significant change to other H's. At -56^{0}C: δ 2.22 (s, 3H), 2.42 (s, 6H), 2.50 (s, 3H), 2.55 (s, 6H), 2.72 (d, 8Hz, 2H), 3.34 (d of d, 2H), 5.90 (s, 1H), 6.17 (s, 2H), 7.76 (s, 1H). Anal. Calcd for $C_{19}H_{26}N_6OBF_4Rh$: C 41.94, H 4.82, N 15.44. Found: C 41.61, H 4.82, N 15.27.

Method B A solution of complex **33** (20 mg, 0.036 mmol) in CH_2Cl_2 (5 mL) was pressurized to 900 psi ethylene and stirred for 2 days at room temperature. The IR spectrum showed complete conversion of **33** to **37**. The product was purified as above and identified by comparing IR and ^{1}H NMR spectra with those from above.

Carbonyldihydrido[tris(3,5-dimethylpyrazol-1-yl)methane] rhodium(III)tetrafluoroborate 35

A sample of **26** (15 mg, 0.028 mmol) in CH_2Cl_2/benzene (1:25 ratio, 30 mL) was irradiated for 8 min with a N_2 purge. Solvent was removed under vacuum and the residue was dissolved in CH_2Cl_2 (2 mL), which was then pressurized to 800 psi H_2 and stirred for 22 h. IR showed complete conversion of **34** to **35**.

Characterization: IR (CH_2Cl_2) 2067 cm^{-1}, ν(CO). ^1H NMR (CD_2Cl_2): δ 2.29 (s, 3H), 2.32 (s, 6H), 2.62 (s, 3H), 2.64 (s, 6H), 6.12 (s, 1H), 6.14 (s, 2H), 7.98 (s, 1H), -13.80 (d, 19Hz, 2H). Elemental analysis was not obtained because of its low stability.

Photolysis of 30 in THF

A sample of **30** (77.8 g, 0.1 mmol) in THF (30 mL) was irradiated for 23 min with N_2 purge. IR showed complete disappearance of **30**. Adding hexane to the solution and recrystallizing the precipitate from CH_2Cl_2/hexane gave the product $[HCPz^*{}_3Rh\{(C_6H_4)P(C_6H_5)_2\}(H)]BF_4$ **38** as an off-white solid (62 mg, 80%).

Characterization: ^1H NMR (CD_2Cl_2): δ 0.72 (s, 3H), 1.82 (s, 3H), 2.58 (s, 3H), 2.66 (s, 3H), 2.68 (s, 3H), 2.70 (s, 3H), 5.83 (s, 1H), 6.08 (s, 1H), 6.22 (s, 1H), 7.1-7.8 (m, 14H), 7.98 (s, 1H), -14.93 (d of d, 21Hz, 31Hz, 1H). Anal. Calcd for $C_{33}H_{36}N_6PBF_4Rh$: C 54.42, H 4.97, N 11.20. Found: C 53.59, H 5.14, N 10.64.

Photolysis of 30 in benzene

A sample of **30** (20 mg, 0.025 mmol) in CH_2Cl_2/benzene (1:25 ratio, 25 mL) was irradiated for 12 min with N_2 purge. Removal of solvent under vacuum gave a mixture of **38** and a new species $[HCPz^*{}_3Rh(H)(Ph)(PPh_3)]BF_4$ [or $[HCPz^*{}_3Rh(H)_2(PPh_3)]BF_4$ **30 A**] in a 97:3 ratio, which was detected by ^1H NMR spectrometry.

Characterization: ^1H NMR of **30 A** (CD_2Cl_2): δ -16.26 (t, 12Hz), other resonances were not resolved.

Photolysis of 31 in benzene

A sample of **31** (20 mg, 0.033 mmol) in CH_2Cl_2/benzene (1:25 ratio, 25 mL) was irradiated for 12 min with N_2 purge. Removal of solvent under vacuum gave a mixture of **34, 31 A** and **31 B,** which were detected by the ^1H NMR spectrum.

Characterization: ^1H NMR (CD_2Cl_2): δ -12.70 (d, 21Hz), -16.33 (d of d, 25Hz, 33Hz), -17.00 (t, 26Hz) in an integral ratio of 6:22:11. others resonances were not resolved.

Photolysis of 37 in benzene

A sample of **37** (20 mg, 0.036 mmol) in CH_2Cl_2/benzene (1:25 ratio, 25 mL) was irradiated for 12 min with N_2 purge. Removal of solvent under vacuum gave **34,** which was identified by ^1H NMR spectrum.

Dicarbonyl[tris(pyrazol-1-yl)methane]rhodium(I) tetrafluoroborate 39

To a solution of AcacRh(CO)$_2$ (40.0 mg, 0.16 mmol) and HCPz$_3$ (33.3 mg, 0.17 mmol) in CH$_2$Cl$_2$ (20 mL), HBF$_4$·Et$_2$O was added dropwise until IR showed complete disappearance of AcacRh(CO)$_2$. The reaction was preferably carried out under CO atmosphere instead of Ar since 39 loses CO readily to form **40** as a white precipitate. The clear yellow solution was syringed from the precipitate **40** (see below), and hexane was added to it to give a yellow solid **39**, which was twice dissolved in CH$_2$Cl$_2$ and precipitated with hexane in the same manner.

Characterization: IR (CH$_2$Cl$_2$) 2104 (w), 2088 (s), 2045 (w), 2023 (vs) cm^{-1}, υ(CO). ^{1}H NMR (CD$_2$Cl$_2$): δ 6.51 (t, 2.5Hz, 3H), 7.89 (d, 2.1Hz, 3H), 8.38 (d of d, 0.7Hz, 2.2Hz, 3H), 9.39 (s, 1H). Anal. Calcd for $C_{12}H_{10}N_6O_2BF_4Rh$: C 31.34, H 2.19, N 18.27. Found: C 31.42, H 2.13, N 18.26.

(μ-tricarbonyl)bis(trispyrazol-1-ylmethane)dirhodium(I) bis(tetrafluoroborate) 40

The white precipitate from above was washed with CH$_2$Cl$_2$ (3 x 10 mL) and dried.

Complex **40** is insoluble in CH$_2$Cl$_2$, CH$_3$OH and acetone.

Characterization: IR (CCl$_4$ supension) 1858 (b), υ(CO). Anal.Calcd for $C_{23}H_{20}N_{12}O_3B_2F_8Rh_2$: C 30.97, H 2.26, N 18.84. Found: C 30.28, H 2.30, N 18.45.

Bisethylene[tris(pyrazol-1-yl)methane]rhodium(I) tetrafluoroborate **41**

One equivalent of $HBF_4 \cdot Et_2O$ was added to a solution of $AcacRh(C_2H_4)_2$ (61.3 mg, 0.237 mmol) and $HCPz_3$ (50.9 mg, 0.238 mmol) in CH_2Cl_2 (25 mL). After stirring for 1 h, the volume of the solution was reduced under vacuum (10 mL). Crude **41** was precipitated by the addition of hexane, which was then twice dissolved in CH_2Cl_2 and precipitated with hexane to give **41** as a pale yellow solid (87.1 mg, 82%).

Characterization: ^1H NMR (CD_2Cl_2): δ 2.73 (d, 1.7Hz, 8H), 6.48 (t, 2.5Hz, 3H), 7.94 (d, 2.2Hz, 3H), 8.35 (d, 2.7Hz, 3H), 9.27 (s, 1H). At -80^0C: 2.22 (d, 10.7Hz, 2H), 2.89 (d, 10.5Hz, 2H), assigned to C_2H_4, no significant change to other H's. Anal. Calcd for $C_{14}H_{18}N_6BF_4Rh$: C 36.55, H 3.94, N 18.27. Found: C 36.26, H 3.84, N 18.10.

Ethylenetriphenylphosphine[tris(pyrazol-1-yl)methane]rhodium (I)tetrafluoroborate **42**

A sample of $AcacRh(C_2H_4)_2$ (100 mg, 0.39 mmol) was stirred with PPh_3 (83 mg, 0.32 mmol) in CH_2Cl_2 (20 mL) for 30 min. $HCPz_3$ (83 mg, 0.41 mmol) was then added, followed by 1 eq $HBF_4 \cdot Et_2O$. After stirring for 1 h, the volume of the solution was reduced under vacuum (10 mL). Crude **42** was precipitated by the addition of hexane, which was then twice dissolved in CH_2Cl_2 and precipitated with hexane to give **42** as a pale yellow solid (226 mg, 85%).

Characterization: ^1H NMR (CD_2Cl_2): δ 1.8 (m, 2H), 2.3 (m, 2H), 6.28 (s, 3H), 7.3 (m, 18H), 8.38 (d, 3Hz, 3H), 9.30 (s, 1H). Anal.Calcd for **42**·0.5 CH_2Cl_2, $C_{30.5}H_{30}N_6ClPRhBF_4$: C 49.72, H 4.10, N 11.41. Found: C 49.84, H 4.35, N 11.23.

Trichloro[tris(3,5-dimethylpyrazol-1-yl)methane]rhodium(III) 43

A mixture of $RhCl_3 \cdot xH_2O$ (76.3 mg, 0.29 mmol) and $HCPz^*_3$ (86.4 mg, 0.29 mmol) was refluxed for 4 h in absolute ethanol (20 mL). EtOH was syringed from the solid, which was washed with THF (2 x 10 mL) and hexane (2 x 5 mL). Drying in vacuum gave the product as a reddish solid. Complex **43** is not soluble in CH_2Cl_2 and acetone.

Characterization: Anal. Calcd for $C_{16}H_{22}N_6Cl_3Rh$: C 37.86, H 4.37, N 16.55. Found: C 37.63, H 4.50, N 15.80.

Trichloro(ethoxytrispyrazol-1-ylmethane)rhodium(III) 44

A mixture of $RhCl_3 \cdot xH_2O$ (92.3 mg, 0.35 mmol) and $HCPz_3$ (75.0 mg, 0.37 mmol) was refluxed for 4 h in absolute ethanol (20 mL). EtOH was syringed from the solid, which was washed with THF (2 x 10 mL) and hexane (2 x 5 mL). Drying in vacuum gave the product as a pale yellow solid. Complex **44** is not soluble in CH_2Cl_2 and acetone.

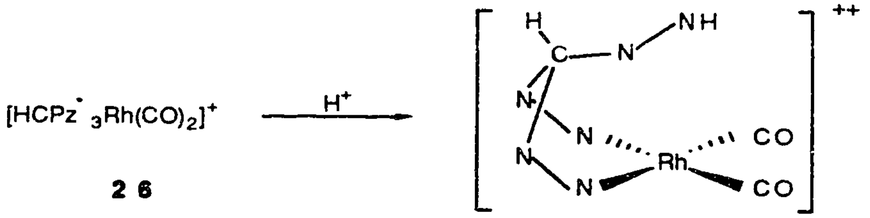
Characterization: Anal. Calcd for $C_{12}H_{14}N_6Cl_3ORh$: C 30.83, H 3.02, N 17.97. Found: C 31.25, H 3.02, N 17.83.

SECTION III

RESULTS AND DISCUSSION

A Preparation of $[HCPz^*{}_3Rh(CO)_2]BF_4$ 26

The anionic $HBPz^*{}_3^-$ reacts with $[Rh(CO)_2Cl]_2$ cleanly to form $HBPz^*{}_3Rh(CO)_2$.[9] In contrast, the reaction between the neutral $HCPz^*{}_3$ and $[Rh(CO)_2Cl]_2$ gave a very complex result, and no CO bands were attributable to $[HCPz^*{}_3Rh(CO)_2]^+$ **26**. As an alternative $AcacRh(CO)_2$ was employed to prepare **26**. Addition of acid to a mixture of $AcacRh(CO)_2$ and $HCPz^*{}_3$ released HAcac and gave **26** as the only detected product. The reaction was instantaneous, making IR monitoring both effective and efficient. Excess acid should be avoided since protonation of **26** occurs as follows:



26 **27**

(IV-2)

In the protonation of $HBPz^*{}_3Rh(CO)_2$,[10] it was shown that the incoming proton attacks the pyrazole nitrogen rather than rhodium. The same pattern is assumed here. Prior to this work, $AcacRh(CO)_2$ has been used by L. A. Oro and co-workers to prepare some bispyrazolylmethane rhodium complexes such as $[H_2CPz^*{}_2Rh(CO)_2]ClO_4$.[11]

As an intended precursor to **26**, $HCPz^*_3RhCl_3$ was prepared from refluxing $RhCl_3 \cdot xH_2O$ and $HCPz^*_3$ in EtOH. Its intermediacy has not been tested because of the success of using $AcacRh(CO)_2$. Worth mentioning here is the reaction between the unsubstituted pyrazole ligand $HCPz_3$ and $RhCl_3 \cdot xH_2O$ in EtOH, where $EtOCPz_3RhCl_3$ was isolated. This indicates that the C-H bond of $H-CPz_3$ was cleaved and replaced by a $EtO-CPz_3$ bond. Such a reaction is formally "alkane alcoholysis".

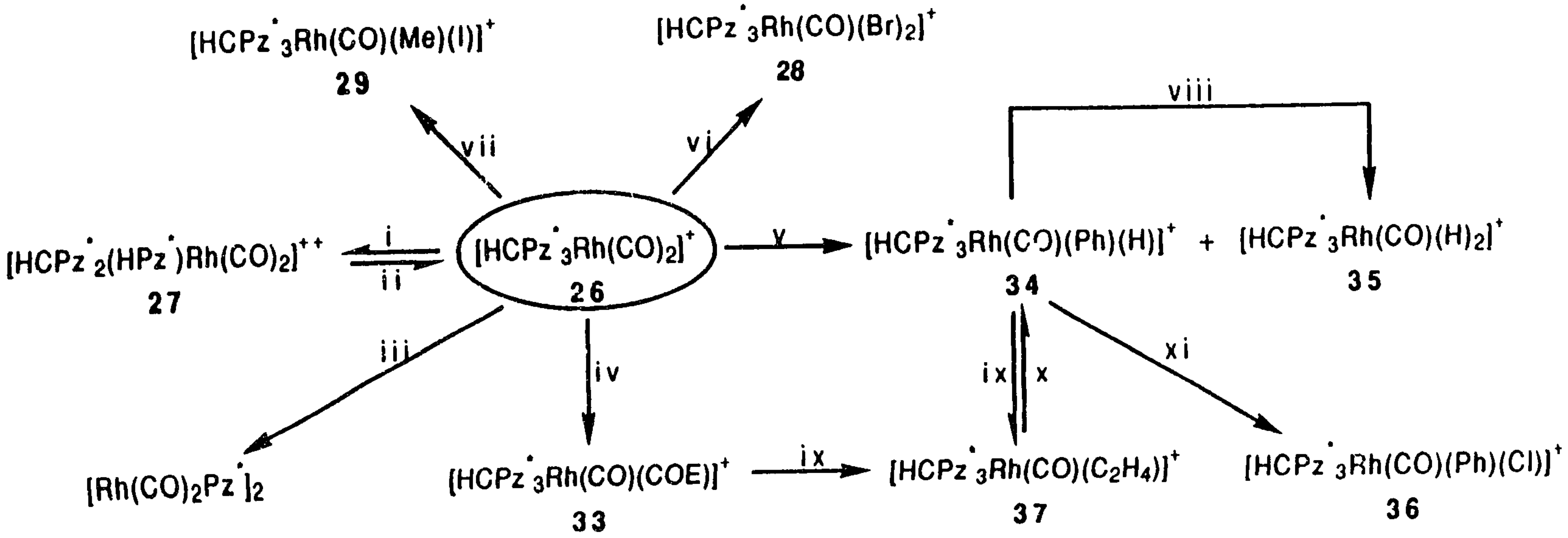
$$R_3C\text{-}H \quad + \quad R'H \xrightarrow[\text{Alcoholysis}]{\text{Alkane}} R_3C\text{-}OR' \quad + \quad H_2 \qquad \text{(IV-3)}$$

$$R_3Si\text{-}H \quad + \quad R'H \xrightarrow[\text{Alcoholysis}]{\text{Silane}} R_3Si\text{-}OR' \quad + \quad H_2 \qquad \text{(IV-4)}$$

In the reaction of $HCPz^*_3$ with $RhCl_3 \cdot xH_2O$, the same process is probably sterically unfavorable, thus not observed. The related silane alcoholysis (eq IV-4) is well known, and its catalysis by an iridium complex has very recently been reported.[12]

B Reactions of 26 with CH_3I, Br_2 and Et_3N

Both CH_3I and Br_2 add oxidatively to **26** forming Rh(III) complexes (Scheme IV-1). The methyliodo derivative **29** is air-stable, but the dibromo- derivative **28** seems to be moisture sensitive. Exposing **28** to wet CH_2Cl_2 produced a new IR band at 2060 (very broad) cm^{-1}, which has not been assigned.



Scheme IV-1

i HBF_4-Et_2O ii $HCPz^{*}_{3}$ iii NEt_3/H_2O iv COE/CH_2Cl_2 v C_6H_6/CH_2Cl_2, $h\nu$
vi Br_2 vii MeI viii H_2, 900 psi ix C_2H_4 x C_6H_6, $h\nu$ xi CCl_4

The ^1H NMR spectra of **28** and **29** are as expected for an octahedral geometry around rhodium. **29** exhibits three sets of pyrazole resonances and **28** exhibits two with a ratio of 2:1.

In an attempt to prepare a neutral pyrazolylmethane rhodium complex, **26** was treated with Et_3N and H_2O. Instead of any neutral species, decomposition occurred and the known pyrazolyl bridged dimer $[Rh(CO)_2Pz^*]_2$[9a] formed (Scheme IV-1). Degradation of $HCPz^*_3$ by base appears to be common, and decomposition of other complexes were also observed when treated with base.

C Preparation of $[HCPz^*_3Rh(CO)(L)]^+$ (L = PEt_3, PPh_3, PCy_3, C_2H_4 and COE)

The three phosphine complexes were prepared according to the same procedure as that of **26** starting from the corresponding $AcacRh(CO)(PR_3)$ (R = Et, Ph and Cy). All three compounds are more soluble in organic solvents than **26** and are moderately air-stable.

$$\mathrm{AcacRh(CO)(L)} + \mathrm{HCPz^*_3} \xrightarrow[\text{-Hacac}]{H^+} [\mathrm{HCPz^*_3Rh(CO)(L)}]^+ \qquad \text{(IV-5)}$$

$$L = \begin{array}{ll} CO & COE \\ PPh_3 & C_2H_4 \\ PEt_3 & \\ PCy_3 & \end{array}$$

Stirring **26** at room temperature in CH_2Cl_2/COE led to the replacement of one CO group and the formation of **33**. The reaction was very slow and 100% conversion of **26** was not achieved. Pressurizing 33 with ethylene afforded the ethylene derivative $[HCPz^*{}_3Rh(CO)(C_2H_4)]^+$ **37**. Complex **37** also formed from the reaction of $[HCPz^*{}_3Rh(CO)(Ph)(H)]^+$ **34** with ethylene (Scheme IV-1). No ethylrhodium product from an insertion reaction was detected.

D Spectroscopic studies of $[HCPz^*{}_3Rh(CO)(L)]^+$ (L = CO, PR_3, COE and C_2H_4)

In this group[13], a detailed spectroscopic study has been carried out on the neutral $HBPz^*{}_3Rh(CO)(L)$ (L = CO, PR_3) system. It has been well established that $HBPz^*{}_3Rh(CO)_2$ exists as both the 18- and 16-electron forms in CH_2Cl_2 (eq IV-6) and the equilibrium lies far to the left where $HBPz^*{}_3{}^-$ acts as a tridentate ligand (η^3-).

$$\eta^3\text{-}HBPz^*{}_3Rh(CO)_2 \rightleftharpoons \eta^2\text{-}HBPz^*{}_3Rh(CO)_2 \qquad (IV\text{-}6)$$

The $HBPz^*{}_3Rh(CO)(PR_3)$ complexes, on the other hand, exist only as the 16-electron form in which $HBPz^*{}_3{}^-$ is bidentate (η^2-). Solution IR spectra using the related bispyrazolylborates $H_2BPz^*{}_2Rh(CO)(PR_3)$ for comparison strongly support this η^2- only formulation.

Table IV-1 lists CO stretching frequencies of $[HCPz^*{}_3Rh(CO)(L)]^+$ along with those of the analogous $HBPz^*{}_3Rh(CO)(L)$ complexes. All the values for $[HCPz^*{}_3Rh(CO)(L)]^+$ complexes are higher than those for $HBPz^*{}_3Rh(CO)(L)$, indicating rhodium is more electron rich in the latter. The CO stretching bands of **26** (Figure IV-1) exhibit a very

Table IV-1 Comparison of υ(CO) between $HBPz^*_3Rh$, $HCPz^*_3Rh$ and $HCPz_3Rh$ Derivatives

	υ(CO) $(CH_2Cl_2)^a$		
	L = $HCPz^*_3$	L = $HBPz^*_3$	L = $HCPz_3$
$LRh(CO)_2$	2098(w), 2036(w) 2078(s), 2010(s)	2080(w)^b, 2012(w)^b 2058(s), 1982(s)	2104(w), 2045(w) 2088(s), 2023(s)
$LRh(CO)(PPh_3)$	1999	1977	
$LRh(CO)(PEt_3)$	1991	1961	
$LRh(CO)(PCy_3)$	1986	1965	
LRh(CO)(COE)	2017	2001^c	
$LRh(CO)(C_2H_4)$	2032	2013^c	

a w = weak; s = strong

b shoulder

c in hexane

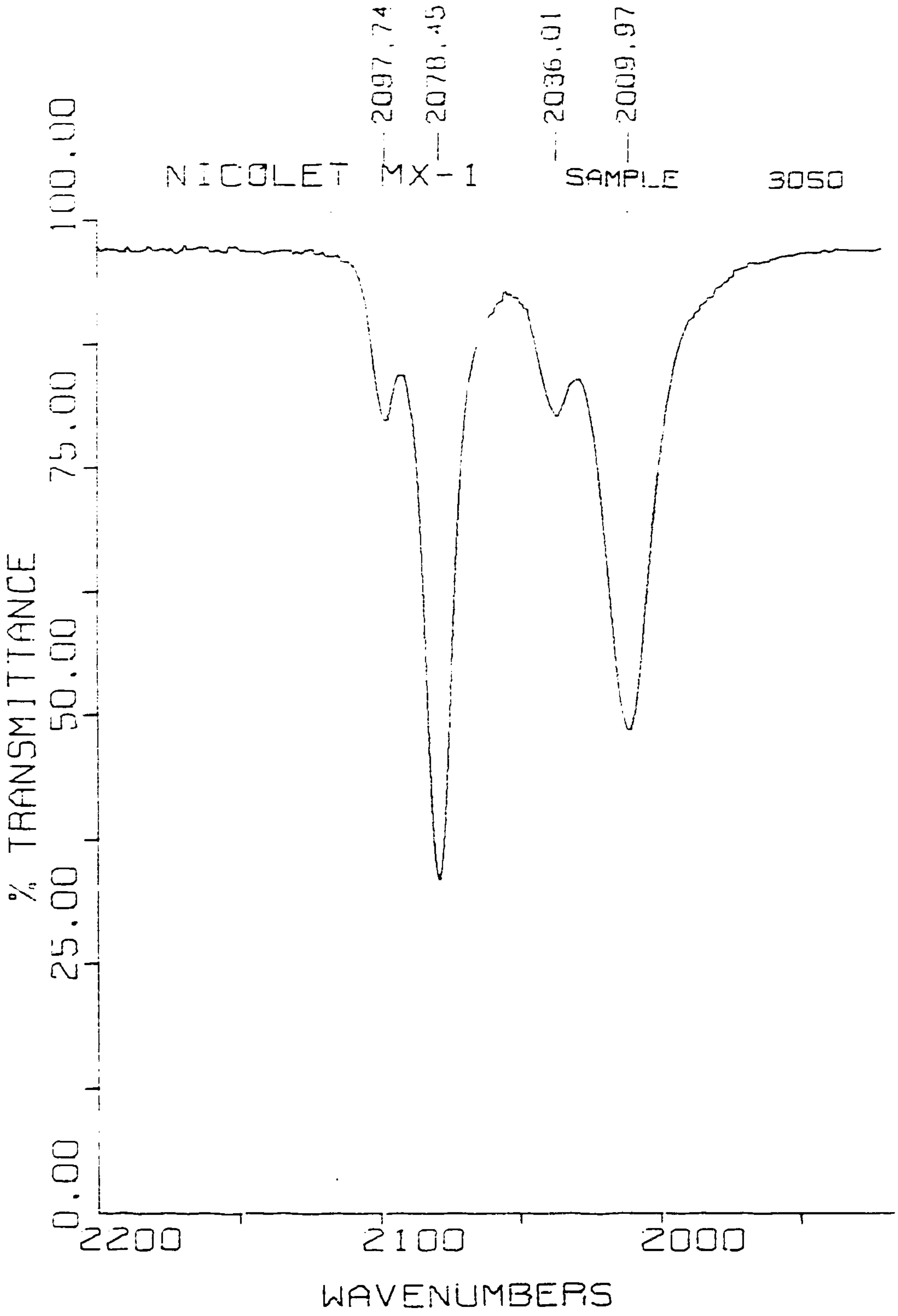
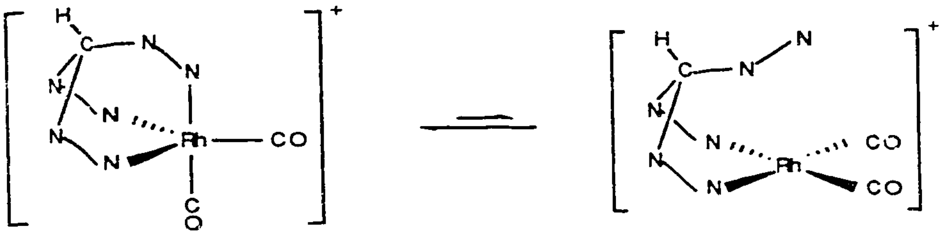


Figure IV-1 ν(CO) of [HCPz$^*{}_3$Rh(CO)$_2$]BF$_4$ in CH$_2$Cl$_2$

similar pattern to that of $HBPz^{*}_3Rh(CO)_2$. Thus it is reasonable to assume the same equilibrium exists for **26** in CH_2Cl_2 solution:



(IV-7)

The bis(3,5-dimethylpyrazol-1-yl)methane rhodium complex $[H_2CPz^{*}_2Rh(CO)_2]ClO_4$[11] shows CO bands at 2100, 2035 cm^{-1} (Nujol mull), which are very close to those of the above 16-electron form. The ^1H NMR spectrum of **26** was not useful in studying the above equilibrium. It showed all the three pyrazole rings to be equivalent both at room temperature and down to -100^0C. Presumably the above interconversion of 16- and 18-electron forms is too rapid for NMR to show both separately as was the case in the analogous $HBPz^{*}_3Rh(CO)_2$.[13] Remarkably, NMR did show the two forms for $HB(3\text{-}PhPz)_3Rh(CO)_2$ according to Krentz's work.[14]

Unlike the dicarbonyl **26**, the IR spectra of $[HCPz^{*}_3Rh(CO)(L)]^+$ (L = PEt_3, PPh_3, PCy_3 and C_2H_4) show a single CO stretching band likely due to the 16-electron species $[\eta^2\text{-}HCPz^{*}_3Rh(CO)(L)]^+$ by comparison to the well-established $HBPz^{*}_3Rh(CO)(L)$ complexes. The ^1H NMR spectra of **30**, **31** and **37** are similar. They showed one type of pyrazole at room temperature and two types with a 2:1 ratio at lower temperatures (Figure IV-2). The more bulky PCy_3 derivative **32** showed a somewhat different pattern with two types of pyrazoles at room temperature and three types at lower temperatures (Figure IV-3). The interconversions shown in Scheme IV-2 provide a plausible explanation for this ^1H NMR behavior, but other mechanisms cannot be ruled out at this stage. A similar mechanism has been proposed to explain the ^1H NMR behavior of $HBPz^*{}_3Rh(CO)(PR_3)$ complexes.[13]

For **30**, **31** and **37**, all the 16- and 18-electron interconversions are rapid on the NMR time scale at room temperature, averaging all three pyrazoles. At lower temperatures, only the first two processes are active, averaging the two pyrazoles bonded to rhodium. Thus a 2:1 ratio of pyrazole proton resonances is observed. The 18-electron intermediate is perhaps very short lived and not observed in ^1H NMR, which is in accord with a single $\nu(CO)$ band in the IR spectrum. For the more bulky PCy_3 derivative **32**, there is likely more crowding around the rhodium center and as a consequence the energy barriers are greater for all the processes. Thus only the first two processes are active at room temperature. At lower temperatures, all the processes are effectively "stopped" and all the three pyrazoles exhibit proton resonances at different chemical shifts.

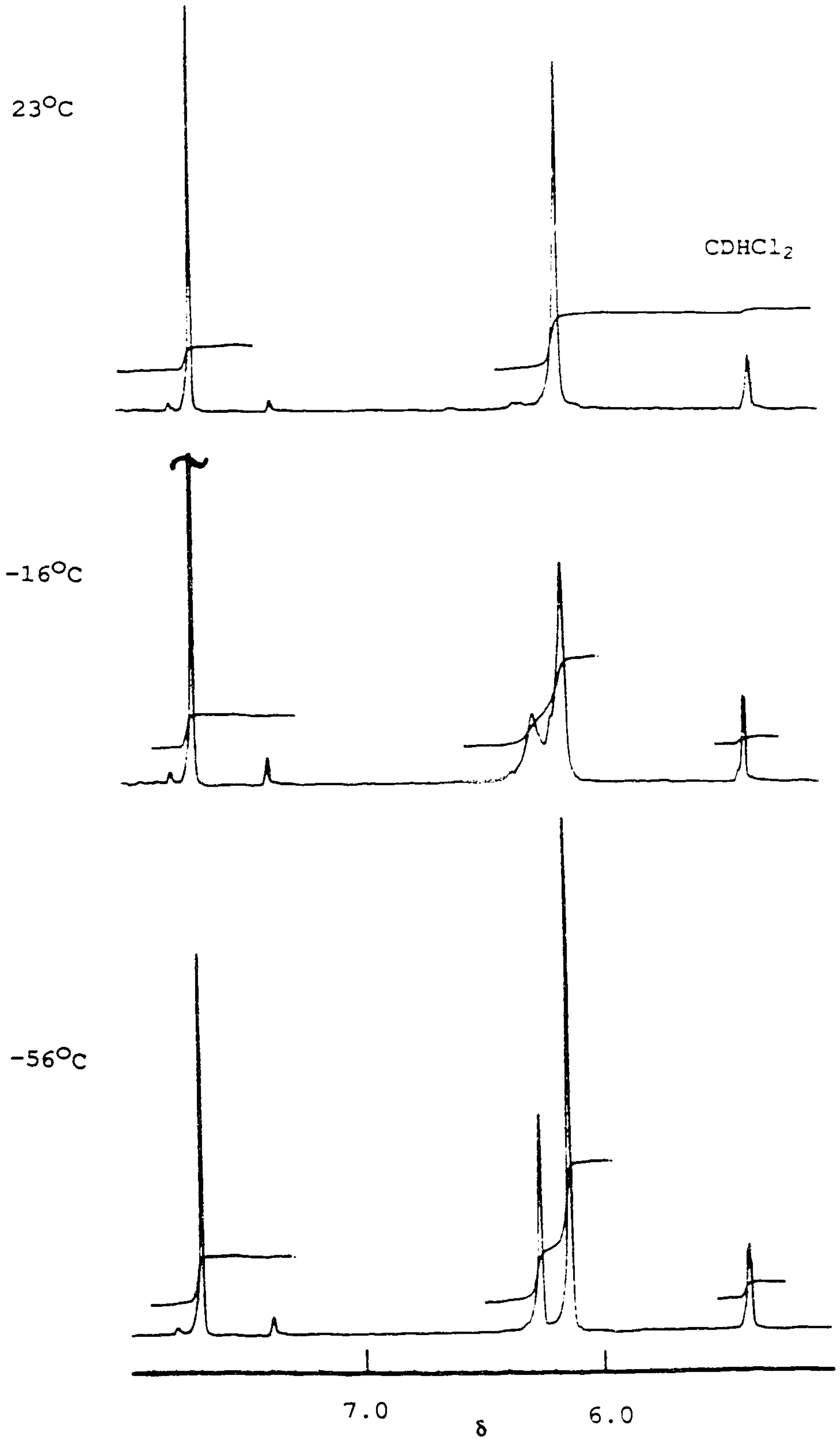


Figure IV-2 VT ^{1}H NMR Spectra of [HCPz$^*{}_3$Rh(CO)(PEt$_3$)]BF$_4$ in the δ5.0 to 8.0 region

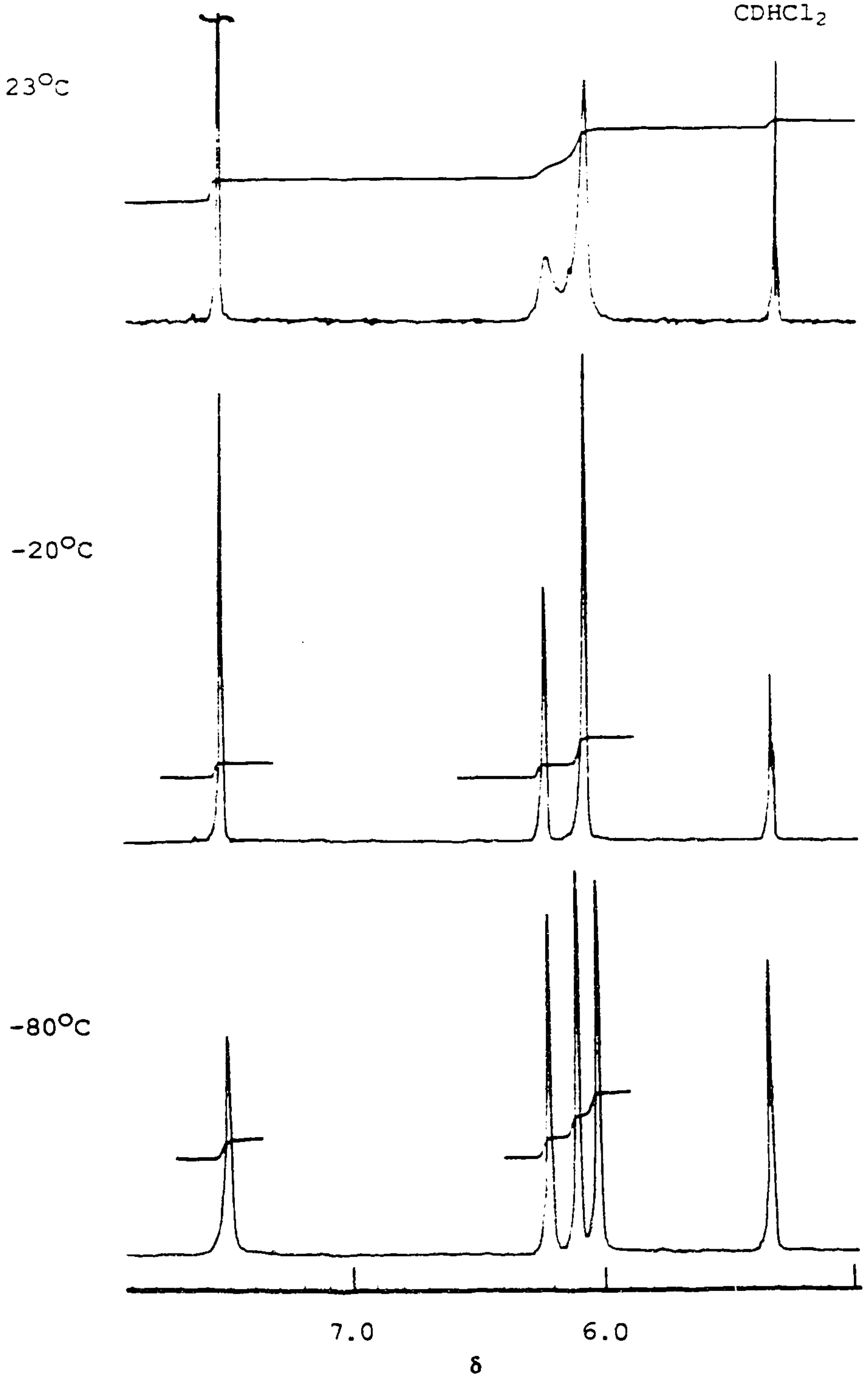
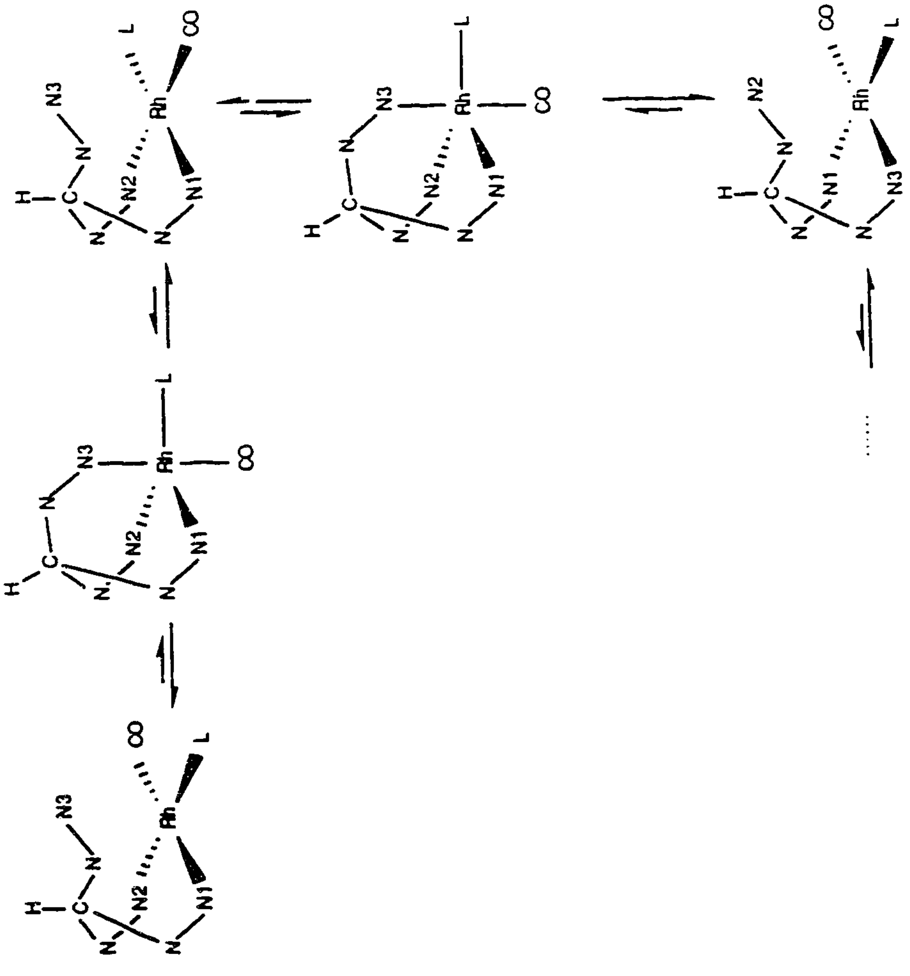


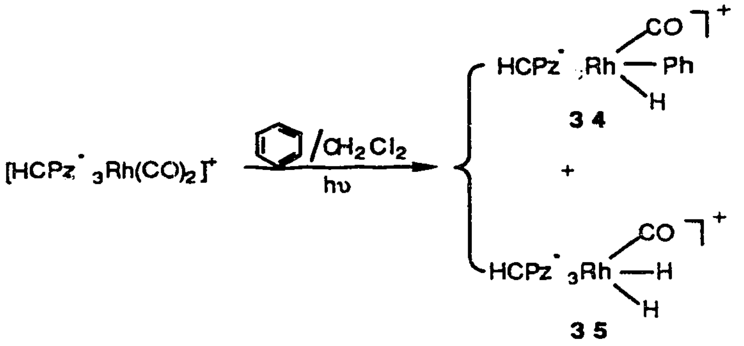
Figure IV-3 VT ^{1}H NMR Spectra of [HCPz$^{*}_{3}$Rh(CO)(PCy$_3$)]BF$_4$ in the δ5.0 to 8.0 region



Scheme IV-2

E Activation of arene C-H bonds by 26

Irradiation of **26** in benzene yielded both **34** and **35** in ca. 97:3 ratio by ^1H NMR. Addition of small amount of CH_2Cl_2 improves the solubility of **26** in benzene, but too much CH_2Cl_2 tends to slow down the reaction. A ratio of 1:25 (v/v) between CH_2Cl_2 and benzene was usually employed.



(IV-8)

The phenylhydridorhodium complex **34** shows three distinct pyrazoles in its ^1H NMR spectrum. The hydrido proton appears at -13.8 ppm as a doublet (J_{Rh-H} = 18Hz), indicative of a Rh-H bond. The phenyl protons appear as a broad singlet at room temperature as rotation about the Rh-Ph bond is vast(Figure IV-4). Four separate multiplets with a ratio of 1:1:2:1 were observed on cooling to -60^{0}C (Figure IV-5).

Treating **34** with CCl_4 produced the chlorophenyl derivative **36** (Scheme IV-1). Complex **36** showed five separate multiplets with a ratio of 1:1:1:1:1 for the phenyl protons at room temperature. The

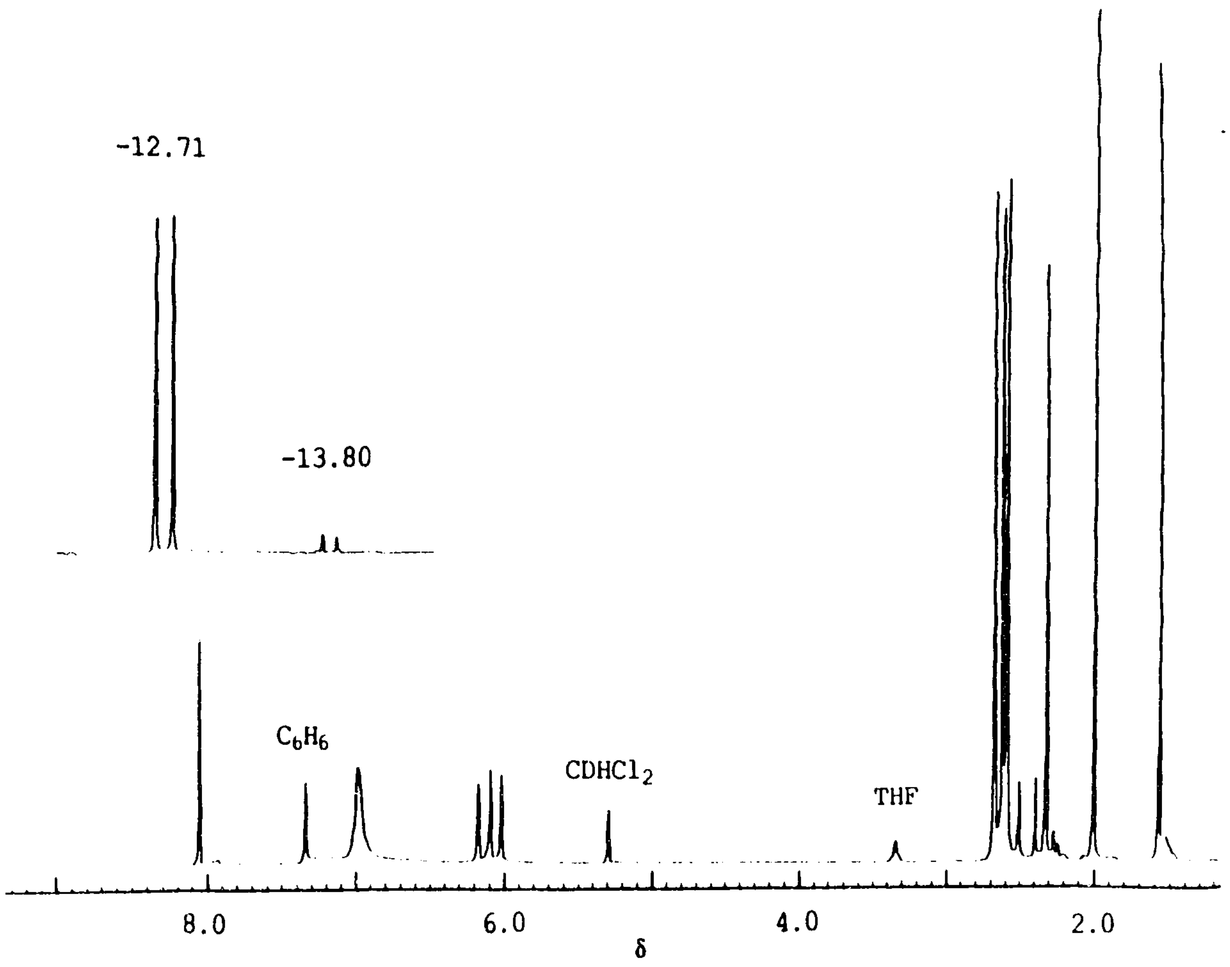


Figure IV-4 ^{1}H NMR Spectrum of [HCPz$^*{}_3$Rh(CO)(H)(Ph)]BF$_4$ at room temperature

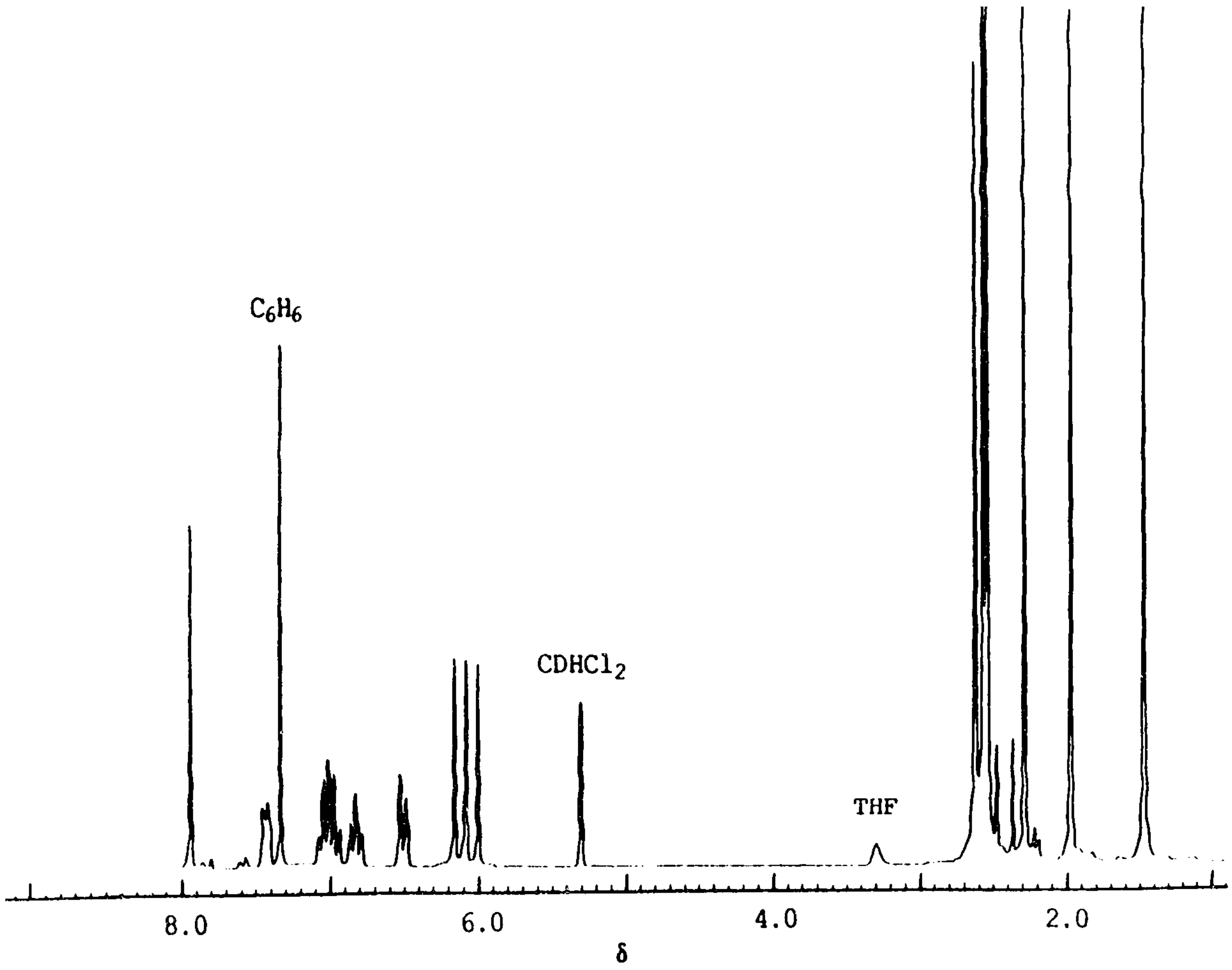


Figure IV-5 ^1H NMR Spectrum of $[HCPz^*{}_3Rh(CO)(H)(Ph)]BF_4$ at $-60^{\circ}C$

barrier for Rh-Ph rotation, as expected, is higher in **36** than that in **34**. The same trend has been observed for other systems.[1,15]

The formation of the dihydride **35** is puzzling. The analogous reaction of $HBPz^*{}_3Rh(CO)_2$ gave only the phenylhydride species. Other systems[16] including the cationic $[P(CH_2CH_2PPh_2)_3Rh]^+$ fragment[4] activate benzene C-H bonds but do not form dihydrido complexes in the process.

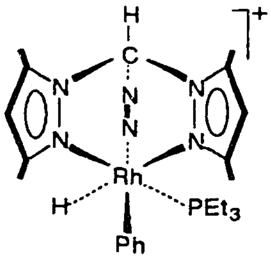
Pressurizing a mixture of **34** and **35** with H_2 brought about complete conversion of **34** to **35** (Scheme IV-1). The ^1H NMR spectrum of **35** shows a 2:1 ratio for the three pyrazole resonances, in accord with a mirror plane in the molecule.

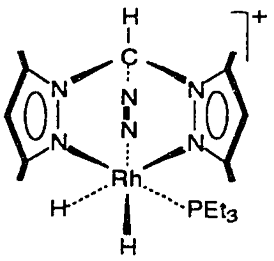
F Activation of arene C-H bonds by $[HCPz^*{}_3Rh(CO)(L)]BF_4$ L = PEt_3, PPh_3 and C_2H_4)

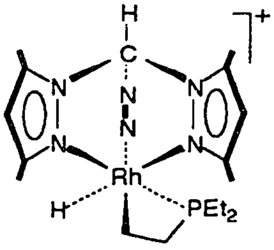
Photolysis of **31** in benzene gave at least three products as indicated from the hydride region of the ^1H NMR spectrum. Besides the known phenylhydrido **34**, **31 A** and **31 B** were

$$\underset{\mathbf{31}}{[HCPz^*{}_3Rh(CO)(PEt_3)]^+} \longrightarrow \mathbf{34} + \mathbf{31A} + \mathbf{31B} \qquad (IV\text{-}9)$$

also observed. **34** corresponds to the loss of PEt_3. **31 A** or **31 B** may correspond to the loss of CO as indicated by the presence of phosphine coupling to the hydride resonance, and could be formulated as $[HCPz^*{}_3Rh(H)(Ph)(PEt_3)]^+$. The third species is probably a dihydride or a cyclometalated compound (structures below). Separation of the a cyclometalated compound (structures below). Separation of the products was not practical because their ionic character ruled out column chromatography and recrystallization failed.





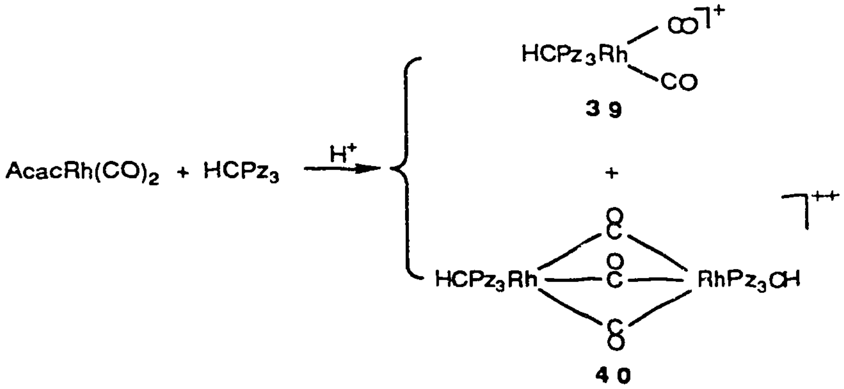


The PPh_3 derivative **30** is different from **31** in that photolysis cleaved the Rh-CO bond exclusively. No ν(CO) band was detected from the photolysis solution of **30**. When THF was used as the solvent, only the orthometallated product **38** formed. But a second product **30 A** was detected in ca. 3% yield when benzene was used as the solvent. It has not been identified, but is probably a phenylhydridorhodium complex $[HCPz^*{}_3Rh(H)(Ph)(PPh_3)]BF_4$ or the dihydride $[HCPz^*{}_3Rh(H)_2(PPh_3)]BF_4$.

Irradiation of **37** in benzene yielded **34** cleanly (Scheme IV-1). No other hydrido species were observed. $HBPz^*{}_3Rh(CO)(C_2H_4)$ was reported to form the ethylene inserted product $HBPz^*{}_3Rh(CO)(Et)(Ph)$ in addition to $HBPz^*{}_3Rh(CO)(H)(Ph)$ when irradiated in benzene. Apparently the same insertion did not occur with **37**.

G Trispyrazolylmethanerhodium(I) complexes

An analogous method was used for the preparation of unsubstituted pyrazolylmethane complexes $[HCPz_3Rh(L)(L')]BF_4$. Unlike the 3,5-dimethylpyrazolylmethane ligand $HCPz^*_3$, the reaction between $HCPz_3$ and $AcacRh(CO)_2$ afforded a dinuclear product **40** besides the expected **39** (eq IV-10).



(IV-10)

The formation of **40** is probably a result of both steric and electronic factors. $HCPz_3$ is less electron donating than $HCPz^*_3$. Thus its Rh-CO bond in **39** should be weaker than that in **26**, and should more easily dissociate to form a monocarbonyl intermediate $[HCPz_3Rh(CO)]^+$; this intermediate could then combine with another molecule of **39** to form **40**. With no methyl groups, $HCPz_3$ does not impose any steric crowding on **40**. The methyl substituted $HCPz^*_3$ would introduce considerable crowding into an analogous dimer $[(HCPz^*_3Rh)_2(CO)_3]^{2+}$.

The ν(CO) bands in the IR spectrum of **39** appear about 10 cm^{-1} higher than those of **26** (Table IV-1), reflecting the weaker electron donating ability of $HCPz_3$ compared to $HCPz^*_3$. As in the case of **26** and $HBPz^*_3Rh(CO)_2$, **39** shows two sets of carbonyl stretching bands. A similar 16- and 18-electron equilibrium must exist here as well.

The bispyrazolylmethanerhodium cation $[H_2CPz_2Rh(CO)_2]^+$ [11] showed ν(CO) at 2100, 2040 cm^{-1}, close to the 16-electron species above.

While this work was in progress, Oro and co-workers reported the preparation of $[HCPz_3Rh(COD)]ClO_4$[17] and $[(HCPz_3Rh)_2(CO)_3](BF_4)_2$,[18] which is numbered as **40** in this work. The pyrazolylmethane dimer **40** is very similar to the pyrazolylgallate $[(MeGaPz_3)Rh_2(CO)_3]$[19] and the pyrazolylborate $[(HBPz_3)Rh_2(CO)_3]$[20] complexes.

The ethylene derivatives **41** and **42** were prepared from $AcacRh(C_2H_4)_2$ and $AcacRh(C_2H_4)(PPh_3)$ respectively. Both **41** and **42** are pale yellow moderately air-stable solids.

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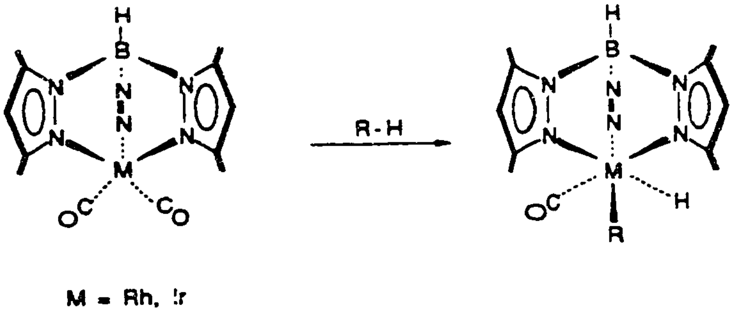
CHAPTER FIVE

C-H ACTIVATION BY TRIS(3,5-DIMETHYLPYRAZOL-1-YL) BORATOPHOSPHINERHODIUM COMPLEXES

SECTION I

INTRODUCTION

Extensive research has been carried out on pyrazolylborate transition-metal chemistry. Recently, $HBPz^*_3M(CO)_2$ (M = Rh, Ir) has been shown to activate C-H bonds with high efficiency and selectivity.[1]



Prompted by these successful results, monophosphine analogs of the above dicarbonyl complexes were investigated. Compared to a CO group, PR_3 (R = alkyl) is a better electron donor and more sterically demanding. Both of these two factors should stabilize the C-H inserted M(III) products in this system. The phosphine ligand should also enhance the solubility of the complex in the hydrocarbon to be activated. This Chapter describes the activation of benzene C-H bonds by $HBPz^*_3Rh(L)(L')$ (L = CO, L' = PMe_3, PEt_3, PCy_3; L = C_2H_4, L' = PMe_3) and the kinetic study of benzene reductive elimination from $HBPz^*_3Rh(H)(Ph)(PMe_3)$ **46** in C_6D_6. The novel formation of $HBPz^*_3Rh(OH)(Ph)(PMe_3)$ from **46** and H_2O is also reported.

SECTION II

EXPERIMENTAL

General

$[Rh(C_2H_4)_2Cl]_2$,[2] $HBPz^*{}_3Rh(CO)(PR_3)$ (R = Me,[3] Cy[5]) were prepared by literature methods. $HBPz^*{}_3Rh(CO)(PEt_3)$ was prepared by the same procedure as $HBPz^*{}_3Rh(CO)(PR_3)$. A Hanovia 450-W medium pressure mercury lamp, fitted with a Pyrex filter and a water-cooled jacket, was used as the light source and samples were placed approximately 2 cm from the lamp in photolysis reactions.

Ethylenetrimethylphosphine[tris(3,5-dimethylpyrazol-1-yl)borato]rhodium(I) 45

To a solution of $[Rh(C_2H_4)_2Cl]_2$ (196.9 mg, 0.51 mmol) in toluene (50 mL), PMe_3 (104.7μL, 1.01 mmol) was added, and the resulting mixture was stirred for 5 h. $KHBPz^*{}_3$ (358 mg, 1.07 mmol) was then added. After stirring overnight, the solvent was removed under vacuum and the residue was extracted with hexane (2 x 20 mL). The hexane extracts were evaporated to give a yellowish solid which was extracted again with fresh hexane (15 + 5 mL). Removal of the solvent gave crude product as a pale yellow solid. Pure **45** was obtained by cooling a concentrated solution to -40^0C and syringing the solution from the precipitate **45** at the same temperature (149 mg, 58%).

Characterization: MS, 170°C/16ev (m/e, rel.int.): $M^+-C_2H_4$(476, 100), $M^+-C_2H_4-PMe_3$(400, 17). ^1H NMR (CD_2Cl_2): δ 0.90 (d, 10Hz, 9H), 2.05 (s, 3H), 2.14 (s, 3H), 2.42 (s, 6H), 2.47 (s, 6H), 5.38 (s, 1H), 5.86(s, 2H), C_2H_4 proton resonances were very broad and not observed; At -40°C: δ 1.48 (m, 2H), 2.58 (m, 2H) due to C_2H_4, no significant change to other protons down to -60°C. Anal. Calcd for $C_{20}H_{35}N_6PBRh$: C 47.64, H 7.00, N 16.67. Found: C 47.34, H 6.86, N 16.81.

Hydridophenyltrimethylphosphine[hydrotris(3,5-dimethylpyrazol-1-yl)borato]rhodium(III) 46

A solution of **45** (20 mg, 0.04 mmol) in benzene (20 mL) was irradiated for 12 min. A N_2 purge was maintained during the irradiation. Removal of solvent gave **46** as a yellowish solid.

Characterization: MS, 160°C/70ev (m/e, rel.int.): M^+-H(553, 2), $M^+-C_6H_6$(476, 43), $M^+-C_6H_6-PMe_3$(400, 14), BP^+(base peak, 78, 100). ^1H NMR (CD_2Cl_2): δ 1.35 (s, 3H), 1.47 (dd, 1Hz, 9Hz, 9H), 2.02 (s, 3H), 2.33 (s, 3H), 2.35 (s, 3H), 2.40 (s, 3H), 2.51 (s, 3H), 5.56 (s, 1H), 5.79(s, 1H), 5.87 (s, 1H), 6.5-6.9 (m, 4H), 7.45 (d, 8Hz, 1H), -17.40 (dd, 25Hz, 30Hz, 1H); In C_6D_6: δ 1.1 (d, 9Hz, 9H), 1.72 (s, 3H), 2.02 (s, 3H), 2.10 (s, 3H), 2.18 (s, 3H), 2.24 (s, 3H), 2.35 (s, 3H), 5.47 (s, 1H), 5.67(s, 1H), 5.87 (s, 1H), 6.83 (t of d, 1H), 7.01 (t of d, 1H), 7.13 (m, 1H), 7.23 (d, 1H), 7.67 (d, 1H), -16.89 (dd, 24Hz, 30Hz, 1H).

Thermolysis of 45 in benzene-d_6

A solution of **45** (10 mg, 0.02 mmol) in d_6-benzene (0.6 mL) in an NMR tube was freeze-pump-thaw degassed three times, then sealed under vacuum. Irradiating for 14 min or heating the solution at 101°C in the dark afforded 100% conversion of **46** to HBPz$^*{}_3$Rh(D)(C_6D_5)(PMe_3) **47** which was detected by ^{1}H NMR and shown to have the same chemical shifts as those of **46** for all the pyrazole protons. The half-life $t_{0.5}$ of the thermal reaction is about 30 h.

Bromo(phenyl)(trimethylphosphine)[hydrotris(3,5-dimethylpyrazol-1-yl)borato]rhodium(III) 48

A solution of **45** (20 mg, 0.04 mmol) in benzene (20 mL) was irradiated for 12 min while purging with N_2. NBS (7.1 mg, 0.04 mmol) was then added, and the solution was stirred for 8 h. Solvent was removed under vacuum and the residue was extracted with hexane (3 x 15 mL). The hexane extracts were combined and evaporated to give crude product as yellow solid. Pure product was obtained by recrystallization from hexane as yellow crystals.

Characterization: MS, 240°C/70ev (m/e, rel.int.): M^+(633, 0.6), M^+-C_6H_5-Br(476, 100). ^{1}H NMR (C_6D_6): δ 1.15 (d, 10Hz, 9H), 1.49 (s, 3H), 2.07 (s, 3H), 2.12 (s, 3H), 2.16 (s, 3H), 2.27 (s, 3H), 2.74 (s, 3H), 5.48 (s, 1H), 5.54(s, 1H), 5.69 (s, 1H), 6.58 (m, 2H), 7.00 (t, 1H), 7.17 (t, 1H), 8.17 (d, 1H). Anal. Calcd for $C_{24}H_{36}N_6PBrBRh$: C 45.53, H 5.73, N 13.27. Found: C 46.13, H 5.78, N 13.25.

Bromo(phenyl)(trimethylphosphine)[hydrotris(4-bromo-3,5-dimethylpyrazol-1-yl)borato]rhodium(III) 49

A solution of **45** (20 mg, 0.04 mmol) in benzene (20 mL) was irradiated for 12 min with a N_2 purge. NBS (42.1 mg, 0.24 mmol) was then added, and the mixture was stirred for one week. Solvent was removed under vacuum and the residue was extracted with hexane (3 x 20 mL). The product was purified as above as yellow crystals.

Characterization: MS, 270°C/18ev (m/e, rel.int.): M^+(870, 0.6), BP^+(base peak, 78, 100). ^1H NMR (CD_2Cl_2): δ 1.51 (d, 10Hz, 9H), 1.61 (s, 6H), 2.39 (s, 3H), 2.50 (s, 6H), 2.65 (s, 3H), 6.30 (d, 1H), 6.67 (t of d, 1H), 6.92 (t of d, 1H), 7.05 (t of d, 1H), 7.71 (d, 1H); In C_6D_6: δ 0.98 (d, 10Hz, 9H), 1.55 (s, 3H), 1.97 (s, 3H), 2.07 (s, 3H), 2.10 (s, 3H), 2.16 (s, 3H), 2.77 (s, 3H), 6.43 (d, 1H), 6.55 (t of d, 1H), 6.92 (t fo d, 1H), 7.10 (t of d, 1H), 9.97 (d, 1H); Anal. Calcd for $C_{24}H_{33}N_6PBr_4BRh$: C 33.14, H 3.82, N 9.66. Found: C 32.92, H 3.77, N 9.69.

Hydroxo(phenyl)(trimethylphosphine)[hydrotris(3,5-dimethylpyrazol-1-yl)borato]rhodium(III) 50

A solution of **45** (40 mg, 0.08 mmol) in benzene (25 mL) was irradiated for 14 min with N_2 purge. H_2O (1 mL, 56 mmol) was then added. After stirring for 10 days, solvent was removed under vacuum and the residue was extracted with hexane (3 x 10 mL). The volume of the combined hexane extracts was reduced under vacuum to 10 mL. Cooling the concentrated hexane solution to -78^{0}C afforded some white precipitate, which has not been identified. The solution was then filtered at -78^{0}C and the filtrate was evaporated to give crude **50** as a yellowish solid. Pure **50** was obtained as a white solid by cooling a hexane solution of the crude **50** to -78^{0}C and syringing the solution from the precipitate **50** at the same temperature.

Hexane could also be used as the solvent in the reaction with H_2O.

Characterization: MS, 155^{o}C/16ev (m/e, rel.int.): M^+(570, 0.4), M^+-H_2O(552, 7), M^+-94(476, 7), BP^+(base peak, 84, 100). ^{1}H NMR (CD_2Cl_2): δ 1.34 (s, 3H), 1.43 (d, 10Hz, 9H), 1.75 (s, 3H), 2.35 (s, 3H), 2.44 (s, 3H), 2.45 (s, 3H), 2.53 (s, 3H), 5.60 (s, 1H), 5.78(s, 1H), 5.82 (s, 1H), 6.54 (d, 1H), 6.68 (t of d, 1H), 6.88 (t of t, 1H), 7.50 (t of d, 1H), 7.40 (d, 1H), -3.24 (1H, broad at room temperature, sharp at -20^{0}C, disappears upon addition of D_2O); in C_6D_6: δ 1.10 (d, 10Hz, 9H), 1.68 (s, 3H), 1.70 (s, 3H), 2.10 (s, 3H), 2.22 (s, 3H), 2.27 (s, 3H), 2.61 (s, 3H), 5.43 (s, 1H), 5.63(s, 1H), 5.72 (s, 1H), 6.84 (t of d, 1H), 6.98 (d, 1H), 7.07 (t, 1H), 7.28 (t of d, 1H), 7.83 (d, 1H), the OH proton was not detected at room temperature and low temperatures were not accessible because of the melting point of benzene-d_6 (ca. 7^{o}C); Anal. Calcd for $C_{24}H_{37}N_6POBRh$: C 50.55, H 6.54, N 14.74. Found: C 50.60, H 6.53, N 14.47.

Dihydridotrimethylphosphine[hydrotris(3,5-dimethylpyrazol-1-yl)borato]rhodium(III) 51

Complex **45** (40 mg, 0.08 mmol) in CH_2Cl_2 was pressurized to 2000 psi H_2. Stirring the solution for four days at room temperature gave complete conversion of **45** to **51** as indicated by ^1H NMR. Recrystallizing from hexane gave the product as a white solid.

Characterization: MS, 155°C/16ev (m/e, rel.int.): M^+-2H(476, 100), M^+-2H-PMe_3(400, 42). ^1H NMR (C_6D_6): δ 1.21 (d, 9Hz, 9H), 2.16 (s, 3H), 2.27 (s, 6H), 2.33 (s, 6H), 2.45 (s, 3H), 5.53 (s, 1H), 5.77 (s, 2H), -17.07 (dd, 21Hz, 36Hz, 2H).

Carbonyl(norbornylene)trimethylphosphine[hydrotris(3,5-dimethylpyrazol-1-yl)borato]rhodium(III) 52

Complex $HBPz^*{}_3Rh(CO)_2$ (60 mg, 0.132 mmol) in hexane/NBL (25 mL/3 g) was irradiated for 11 min with N_2 purge. IR showed υ(CO) at 2030 cm^{-1}, due to $HBPz^*{}_3Rh(H)(C_6H_{13})(CO)$ according to Ghosh's work.[3] After stirring for 1 h, a new band at 1996 cm^{-1} had formed and the 2030 cm^{-1} band had disappeared. Solvent was removed under vacuum and the residue was placed on a neutral alumina column (1 x 20 cm) eluting with CH_2Cl_2. Recrystallizing from CH_2Cl_2/hexane gave the product as a yellow solid.

Characterization: IR (hexane) 1996 cm^{-1}, υ(CO); MS, 150°C/16ev (m/e, rel.int.): M^+(522, 1), M^+-NBL(428, 100), M^+-NBL-CO(400, 51). ^1H

NMR (CD_2Cl_2): δ 0.83 (d, 11Hz, 1H), 1.26 (m, 3H), 1.67 (d, 8Hz, 2H), 2.35 (s, 18H), 2.77 (s, 2H), 3.73 (d, 3Hz, 2H), 5.79 (s, 3H). At -80^{0}C: 0.75 (d, 11Hz, 1H), 1.16 (m, 3H), 1.58 (d, 7Hz, 2H), 2.15 (s, 3H), 2.19 (s, 3H), 2.32 (s, 6H), 2.35 (s, 6H), 2.69 (b, 2H), 3.59 (b, 2H), 5.56 (s, 1H), 5.90 (s, 2H). Anal. Calcd for $C_{23}H_{32}N_6BORh$: C 52.90, H 6.18, N 16.09. Found: C 53.11, H 6.16, N 15.83.

Photolysis of 52 in benzene

A solution of **52** (10 mg, 0.02 mmol) in benzene (15 mL) was irradiated with N_2 purge. The reaction was followed by IR at four-minute intervals for 12 min, which showed $HBPz^*{}_3Rh(H)(Ph)(CO)$ as the only product; no transient carbonyl species were observed.

Photolysis of $HBPz^*{}_3Rh(CO)(PMe_3)$ 53

A solution of **53** (20 mg, 0.04 mmol) in benzene (20 mL) was irradiated for 1 h in a sealed tube. Solvent was removed under vacuum and the residue was dissolved in CD_2Cl_2 (0.6 mL) for ^1H NMR spectroscopy, which showed both **46** and $HBPz^*{}_3Rh(H)(Ph)(CO)$ (68:32 ratio) were present.

Photolysis of $HBPz^*{}_3Rh(CO)(PEt_3)$ 54

A solution of **54** (20 mg, 0.037 mmol) in benzene (20 mL) was irradiated for 38 min with N_2 purge. Solvent was removed under vacuum and the residue was dissolved in CD_2Cl_2 (0.6 mL) for ^1H NMR spectroscopy, which showed both $HBPz^*{}_3Rh(H)(Ph)(PEt_3)$ **54 A** and $HBPz^*{}_3Rh(H)(Ph)(CO)$ (61:39 ratio) were present.

Characterization: ^1H NMR of **54 A** (CD_2Cl_2): δ-16.97 ("apparent triplet", 25Hz), other resonances were not resolved.

Photolysis of $HBPz^*{}_3Rh(CO)(PCy_3)$ 55

A solution of **55** (20 mg, 0.037 mmol) in benzene (20 mL) was irradiated for 40 min with N_2 purge. Solvent was removed under vacuum and the residue was dissolved in CD_2Cl_2 (0.6 mL) for ^1H NMR spectroscopy, which showed $HBPz^*{}_3Rh(H)(Ph)(CO)$, **55 A, 55 B** and **55 C** were present.

Characterization: ^1H NMR of $HBPz^*{}_3Rh(H)(Ph)(CO)$, **55 A, 55 B** and **55 C** (CD_2Cl_2): δ -12.35 (d, 22Hz), -16.15 (q, 21Hz, 22Hz), -17.20 (q, 20Hz, 24Hz), -19.40 (q, 22Hz, 30Hz) in an integral ratio of 17:7:5:13. Other proton resonances were not resolved.

Reductive elimination of C_6H_6 from 46 in C_6D_6

A sample of **46** in benzene (6 mL, an aliquot of a solution generated from 44 mg (0.087 mmol) of **45** in 30 mL benzene) was evaporated and the residue was dissolved in C_6D_6 (0.55 mL). The sample was placed in an NMR tube and freeze-pump-thaw degassed three times before sealing under vacuum. The NMR tube was then immersed in a Laude K6 temperature bath and heated at the required temperature.

The disappearance rate of **46** was monitored by following the integral change of the Rh-H resonance at δ -16.89 using the pyrazolyl methyl resonance at δ1.72 as a standard. Duplicate runs were obtained for each different temperature from 64°C to 104°C at an increment of 10°, giving a total of ten runs. All ^{1}H NMR spectra were recorded at room temperature (the rate of arene exchange at room temperature is negligible compared to that at the bath temperatures).

SECTION III

RESULTS AND DISCUSSION

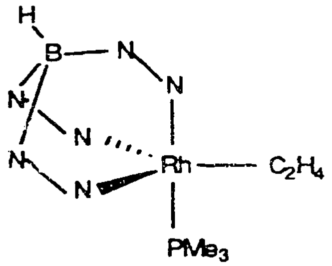
A Preparation of 45, 51 and 52

The ethylene derivative $HBPz^*{}_3Rh(CH_2CH_2)(PMe_3)$ **45** was prepared analogously to $CpRh(C_2H_4)(PMe_3)$.[4] $[Rh(C_2H_4)_2Cl]_2$ was stirred with two moles of PMe_3 in toluene to give $[Rh(C_2H_4)(PMe_3)Cl]_2$, which was then treated with $KHBPz^*{}_3$. **45** was purified by recrystallization from hexane. Decomposition occurred when **45** was placed on a Florisil column.

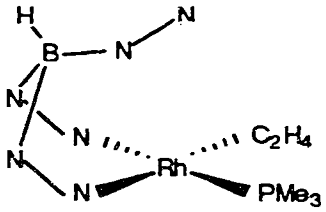
45

V-1

The ^1H NMR of **45** showed two sets of pyrazole resonances in a 2:1 ratio at room temperature. The ethylene protons are fluxional and appear very broad. Two separate multiplets were observed for the four ethylene protons at -40^0C. No significant change occurred for pyrazole protons down to -60^0C. This is consistent with a static 18-electron trigonal bypyramidal structure for **45**.



In view of the $HBPz^*_3Rh(CO)(PR_3)$ complexes studied by Ghosh,[3,5] an alternative structure (below) for **45** is possible.



The rhodium atom in this structure is four-coordinate with an η^2-$HBPz^*_3$ ligand. The complex is fluxional between -60°C and room temperature such that only two pyrazolyl signals are observed by NMR rather than the three expected. In the complex $HBPz^*_3Rh(CH_2CH_2)(CO)$,[3] all three Pz^* groups were NMR equivalent at 25°C, but showed a 2:1 pattern at -60°C. The complexes $HBPz^*_3Rh(CO)(PR_3)$[3,5] showed one Pz^* signal, 2:1 Pz^* signals, or 1:1:1 Pz^* signals depending on PR_3 and temperature. IR evidence suggested that both of these carbonyl derivatives were four-coordinate, 16e, and that they had an η^2-$HBPz^*_3$ ligand.

The nature of **45** in solution remains to be determined, since the NMR evidence is consistent with either η^2 or η^3 bonding modes for the $HBPz^*_3$ ligand. The invaluable evidence provided by a carbonyl ligand through its IR absorption is lacking in **45**.

$$\underset{\textbf{45}}{HBPz^*{}_3Rh(C_2H_4)(PMe_3)} \xrightarrow[2000\ psi]{H_2} \underset{\textbf{51}}{HBPz^*{}_3Rh(H)_2(PMe_3)} \qquad V\text{-}2$$

Pressurizing **45** with H_2 yielded $HBPz^*{}_3Rh(H)_2(PMe_3)$ **51**. No other products were detected in this reaction. Although the analogous $Cp^*Rh(H)_2(PMe_3)$ is described as extremely air-sensitive,[7] **51** is moderately air-stable. The MS of **51** showed M^+-2H as the major peak. The ^1H NMR spectrum of **51** showed two sets of pyrazole resonances in a 2:1 ratio and a high field doublet of doublets at -17.05 ppm due to hydrido protons, consistent with an octahedral geometry around the rhodium center.

Complex $HBPz^*{}_3Rh(NBL)(PMe_3)$ **52** was prepared by irradiating **45** with excess NBL in hexane solution. The intermediate $HBPz^*{}_3Rh(H)(C_6H_{13})(CO)$[3] was observed even though a large excess of NBL is present. The conversion of $HBPz^*{}_3Rh(H)(C_6H_{13})(CO)$ to **52** was monitored by IR and was complete in 1 h.

$$\begin{tikzcd}
\underset{\textbf{45}}{HBPz^*{}_3Rh(C_2H_4)(PMe_3)} \arrow[r, "NBL/Hexane"] & HBPz^*{}_3Rh(H)(C_6H_{13})(PMe_3) \arrow[d, "+NBL"', "-C_6H_{14}"] & \\
& \underset{\textbf{52}}{HBPz^*{}_3Rh(NBL)(PMe_3)} & V\text{-}3
\end{tikzcd}$$

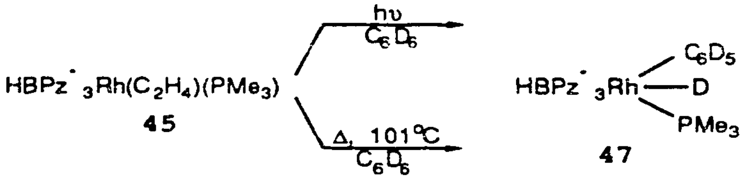
Complex **52** showed the same ^1H NMR pattern as that of $HBPz^*{}_3Rh(C_2H_4)(CO)$.[3] All six methyl groups appear at the same chemical shift at room temperature and in a 2:2:1:1 ratio at [illegible] temperatures. The MS of **52** showed a very weak molecular ion peak.

B Formation of 46 and 47

Irradiation of **45** in benzene resulted in rapid formation of $HBPz^*{}_3Rh(H)(Ph)(PMe_3)$ **46**. The solution changed from yellow to colourless upon completion of the reaction. The ^1H NMR spectrum of **46** exhibits three sets of pyrazole resonances and a high field quartet at -16.89 ppm, indicative of a doublet Rh-H resonance coupled to phosphorus. The five phenyl protons appear as two multiplets in a 1:4 ratio in CD_2Cl_2, but five separate multiplets were observed in C_6D_6. This is attributed to a Rh-Ph rotation which is slow on the NMR time scale, making the two sides of the ring different. Changing CD_2Cl_2 to C_6D_6 also caused a large shift of one methyl group, which appears at 1.35 ppm in CD_2Cl_2 and 1.72 ppm in C_6D_6. The rotation barrier for the [illegible] bond in **46** is apparently greater than that in the analogous [illegible]$Pz^*{}_3Rh(H)(Ph)(CO)$, for which the five phenyl proton signals are sharp and separated only at -20°C.

When the above irradiation was carried out in C_6D_6, complex **47** formed. The ^1H NMR spectra of **47** and **46** are superimposable in the 1.0-5.8 ppm region (protons in $HBPz^*{}_3$). **47** was also prepared by heating a C_6D_6 solution of **45** at 101°C in dark. The half-life of this thermal reaction is ca. 30 h. The analogous complexes

$HBPz^{*}{}_3Rh(CO)(\eta^2$-olefin) have been reported to activate benzene thermally.[12]

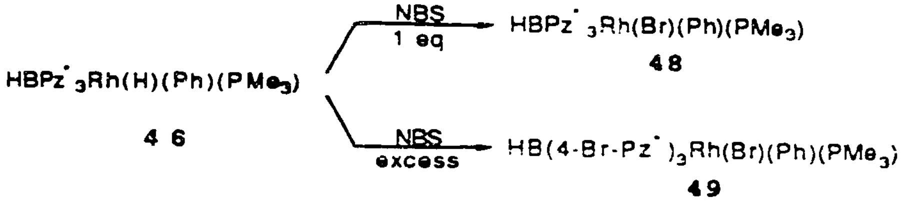


V-4

Both reactions leading to **47** were carried out in sealed NMR tubes and followed by ^1H NMR. The conversion of **45** to **47** is quantitative. No other products were detected. Recently $HBPz^{*}{}_3Rh(C_2H_4)(CO)$ has been reported to form both $HBPz^{*}{}_3Rh(H)(Ph)(CO)$ and $HBPz^{*}{}_3Rh(Et)(Ph)(CO)$ when irradiated in benzene.[6] There is definitely no ethylene inserted product here.

C **Reactions of 46**

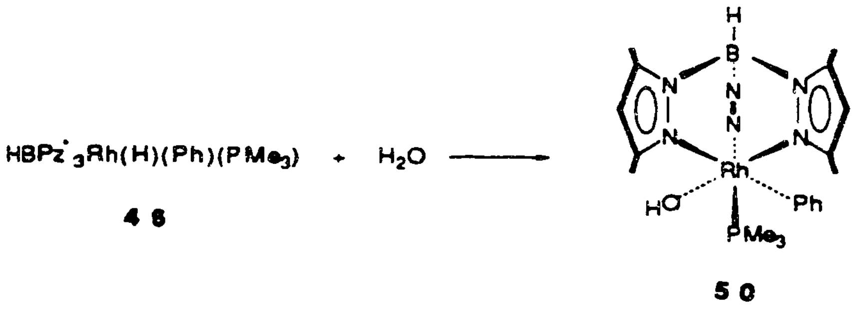
The reaction between **46** and CCl_4 is very slow (a few days), and ^1H NMR showed more than one product formed. NBS reacts with one equivalent **46** to form $HBPz^{*}{}_3Rh(Br)(Ph)(PMe_3)$ **48**. Stirring excess NBS with **46** for one week resulted in complete bromination of the pyrazole 4-positions and formation of $HB(4\text{-}Br\text{-}Pz^{*})_3Rh(Br)(Ph)(PMe_3)$ **49**. Species presumed to be partially brominated at the 4-positions were observed after stirring for two days. The pyrazolyl ring halogenation has been observed before by McCleverty and co-workers for rhenium and molybdenum complexes.[13]



V-5

The ^1H NMR of **49** exhibits only two sets of pyrazole methyl resonances in a 2:1:2:1 ratio in CD_2Cl_2 instead of the expected three. Accidental overlap must have occurred. Three sets of pyrazolyl methyl resonances were observed in C_6D_6. There are no resonances attributable to 4-H's of the pyrazole rings, in accord with complete bromination of the 4-positions. The ^1H NMR of **48** in C_6D_6 exhibits a similar pattern for the methyl groups, but the three singlets of 4-H's clearly indicates no bromination in this case. The phenyl protons of both complexes appear as five separate multiplets at room temperature.

Addition of H_2O to a benzene or hexane solution of **46** yielded $HBPz^*{}_3Rh(OH)(Ph)(PMe_3)$ **50** slowly. On an 80 mg scale, 50% conversion was observed by ^1H NMR in 10 days. Besides **50**, there is another

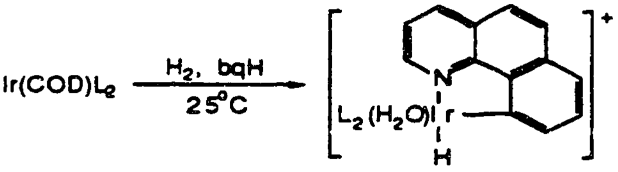


V-6

product formed in this reacton. It is a white solid and showed no sharp ^1H NMR resonances. Its identity has not been established.

The ^1H NMR of **50** (Figure V-1) exhibits three sets of pyrazole resonances and five separate multiplets for the phenyl protons. Changing CD_2Cl_2 to C_6D_6 caused a large shift of one methyl group, which appears at 1.34 ppm in CD_2Cl_2 and 1.68 ppm in C_6D_6. The same phenomenon was observed for **46** as discussed earlier. The OH proton appears broad at room temperature, and as a sharp singlet at lower temperatures. Addition of one drop of D_2O caused the disappearance of this resonance, which is characteristic of OH groups. The MS of **50** (Figure V-2) showed a weak molecular ion peak at 570. The peak at 476 is attributable to $M^+-C_6H_5OH$, i.e., elimination of phenol.

The reaction of **46** with H_2O is unusual. Most metal hydrides decompose when exposed to moisture. A few metal hydrides are stable in H_2O and some are strongly acidic in H_2O.[8] Recently Crabtree and co-workers reported an aqua hydride $[(bq)Ir(H)(H_2O)(PPh_3)_2]SbF_6$



bqH = 7,8-benzoquinoline; L = PPh_3

(bq = 7,8-benzoquinolato) which resulted from benzoquinoline cyclometallation.[9] Unlike the reaction with **46**, H_2O does not attack the Ir-H bond, but instead coordinates to the metal.

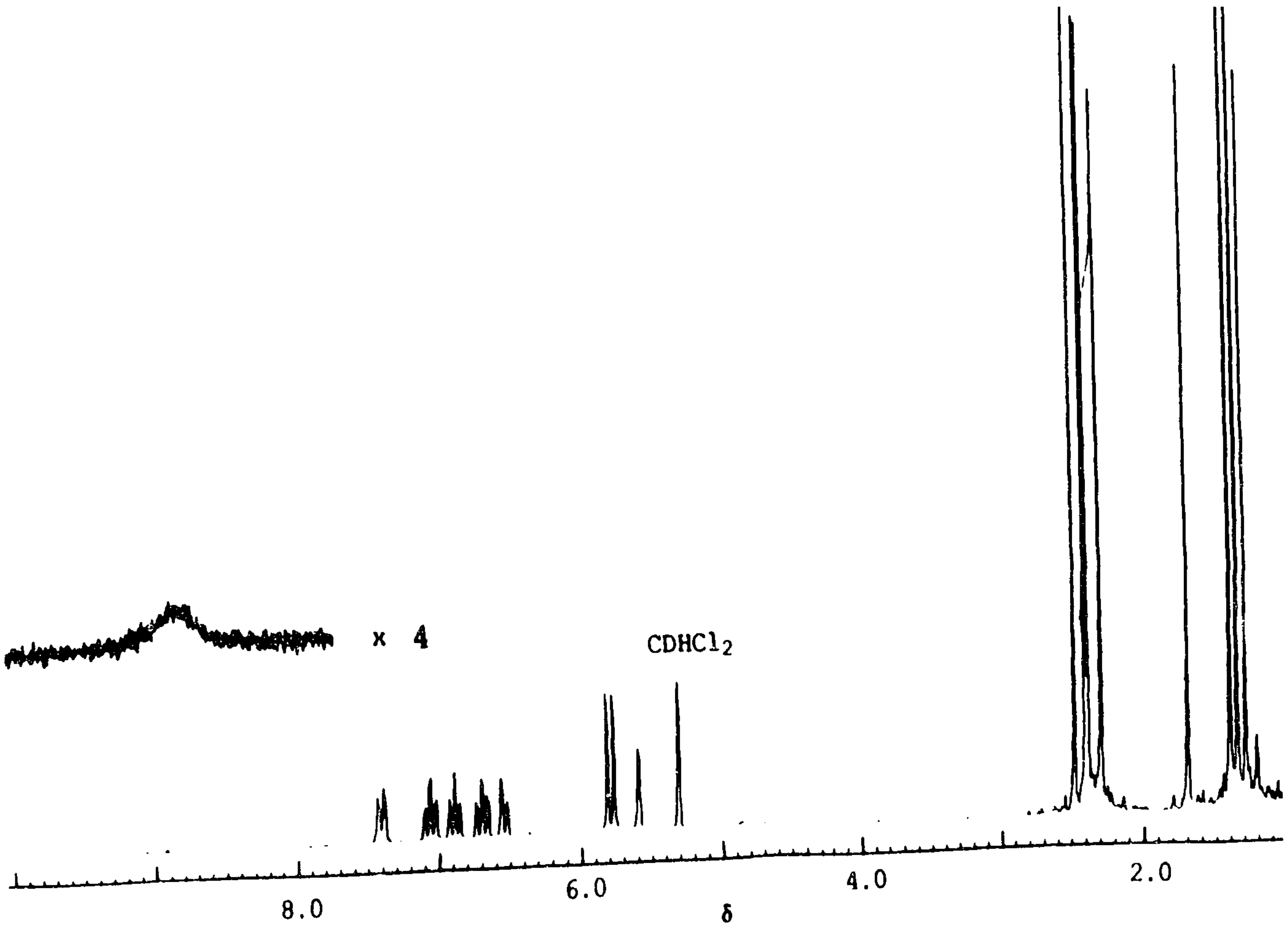


Figure V-1A ^{1}H NMR Spectrum of HBPz'$_3$Rh(OH)(Ph)(PMe$_3$) **50**
at Room Temperature

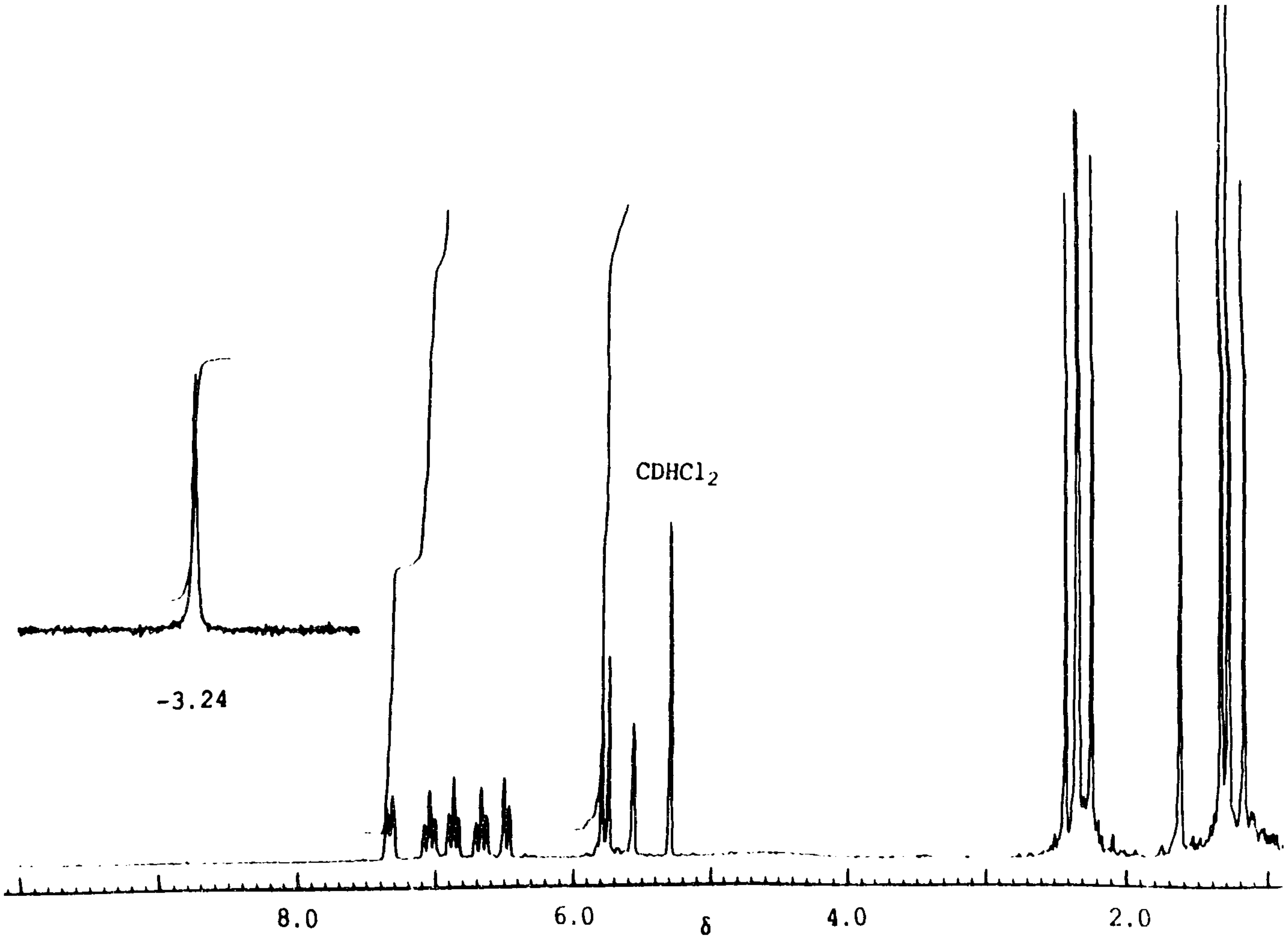


Figure V-1B ^1H NMR Spectrum of HBPz$^*_3$Rh(OH)(Ph)(PMe$_3$) **50** at -60°C

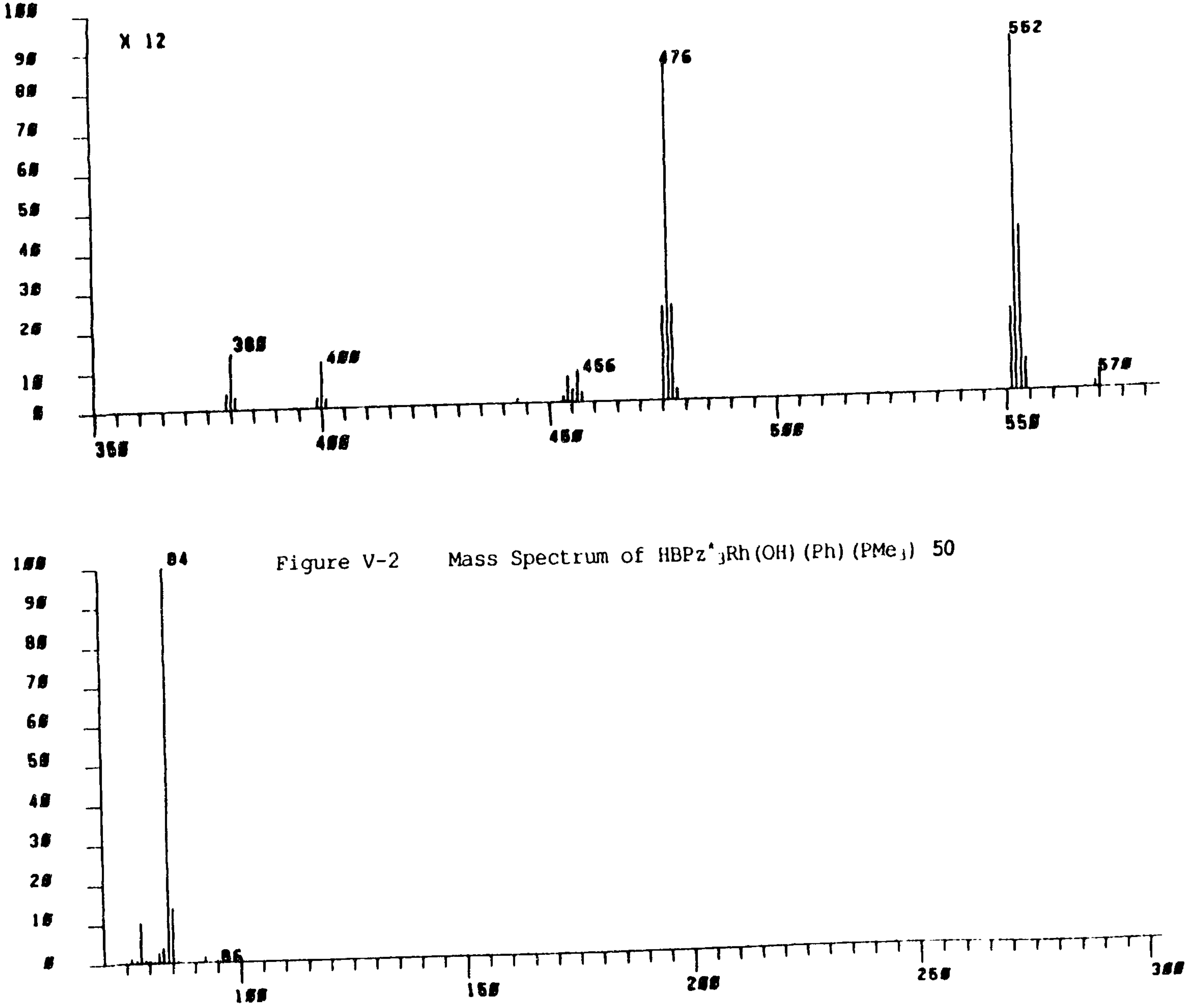
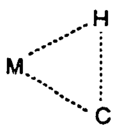


Figure V-2 Mass Spectrum of HBPz'$_3$Rh(OH)(Ph)(PMe$_3$) 50

D Benzene exchange reaction

Complex **46** in C_6D_6 was heated over a 40°C temperature range. The conversion rate of **46** to **47** was monitored by following the integral change of the hydride resonance against the methyl resonance at 1.72 ppm, which appears at the same chemical shift in **46** and **47**. Table V-1 lists the rate constants at different temperatures over a 40°C range. These rate constants are obtained by plotting logarithmic ratios of hydride resonance/methyl resonance versus time. A typical first-order plot is shown in Figure V-3. The activation parameters are obtained from the Eyring plot of the data in Table V-1 (Figure V-4). They are $\Delta H^{\neq} = 24.9 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\neq} = -10.3 \pm 1.1$ cal $K^{-1}mol^{-1}$.

Jones and Feher reported the activation parameters for the exchange of $Cp^*Rh(PMe_3)(H)(Ph)$ with C_6D_6 to be $\Delta H^{\neq} = 30.5 \pm 0.8$ kcal mol^{-1}, $\Delta S^{\neq} = 14.5 \pm 2.5$ cal $K^{-1}mol^{-1}$.[7b] Ghosh's work on $HBPz^*{}_3Rh(H)(Ph)(CO)$ shows $\Delta H^{\neq} = 29.6 \pm 0.8$ kcal mol^{-1}, $\Delta S^{\neq} = 12.2 \pm 2.4$ cal $K^{-1}mol^{-1}$.[3] The values of both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are virtually the same in the two systems. The positive $\Delta S^{\neq}$ value is surprising, according to the authors, since the transition state for reductive elimination presumably involves a highly ordered 3-center



transition state. Negative or slightly positive $\Delta S^{\neq}$ values have been found for other reductive elimination reactions.[10]

Table V-1 Rate Constants of Benzene Reductive Elimination from 46 in C_6D_6

Temperature (^oC)	K (S^{-1})	R^a
64	2.803×10^{-6}	0.988
	2.685×10^{-6}	0.982
74	8.400×10^{-6}	0.987
	7.188×10^{-6}	0.990
84	2.443×10^{-5}	0.994
	2.103×10^{-5}	0.999
94	6.628×10^{-5}	0.993
	6.137×10^{-5}	0.993
104	1.471×10^{-4}	0.995
	1.602×10^{-4}	0.997

[a] correlation coefficient

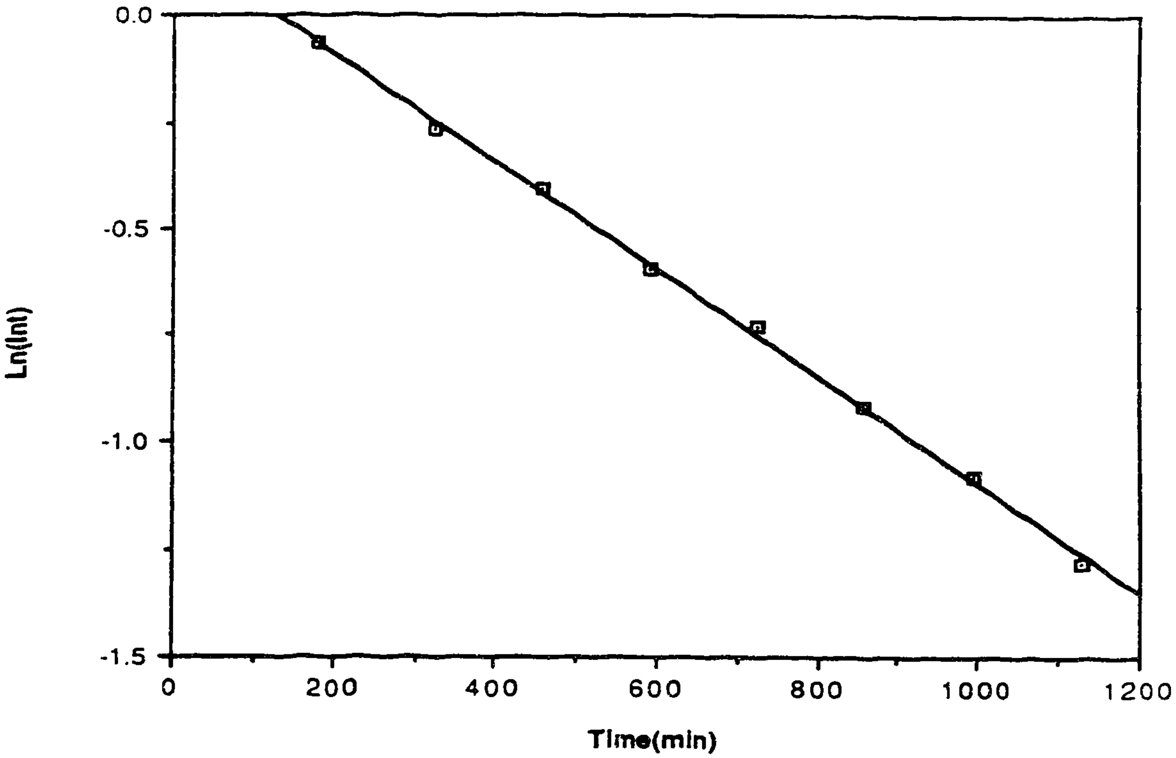


Figure V-3 First Order Plot of Benzene Exchange Data for $HBPz^*{}_3Rh(H)(Ph)(PMe_3)$ **46** with C_6D_6 at 80°C

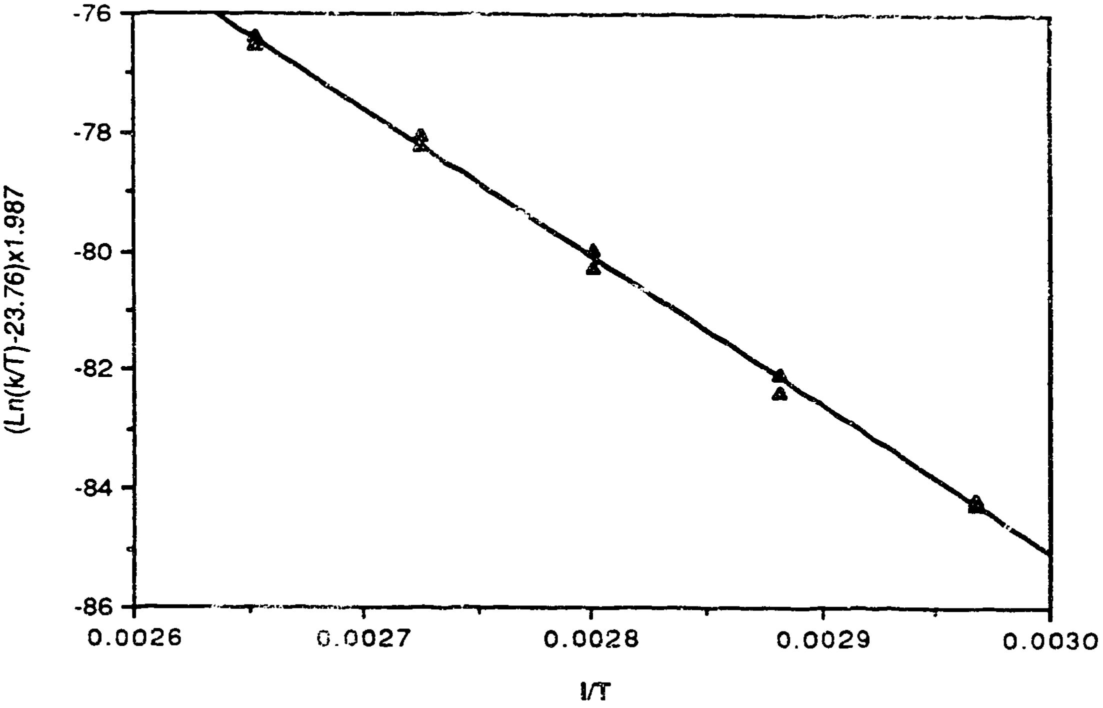
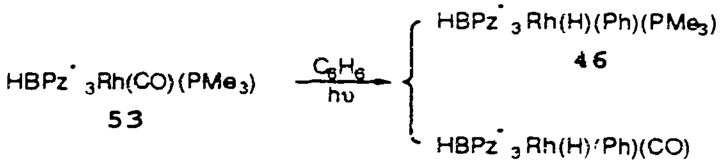


Figure V-4 Eyring Plot of Benzene Exchange Data for $HBPz^{*}_3Rh(H)(Ph)(PMe_3)$ **46** with C_6D_6

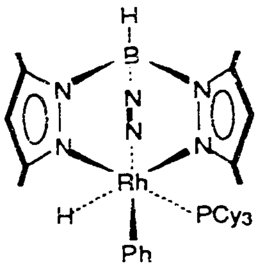
E Photolysis of HBPz$^*{}_3$Rh(CO)(L) in benzene (L = PMe$_3$, PEt$_3$, PCy$_3$ and NBL)

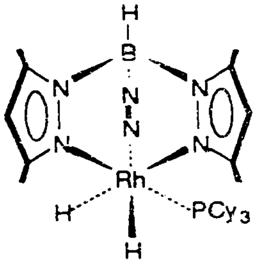
Irradiation of the carbonyl phosphine derivatives in benzene gives more than one product. In the case of HBPz$^*{}_3$Rh(CO)(PMe$_3$) **53**, both **46** and HBPz$^*{}_3$Rh(H)(Ph)(CO) are produced as indicated by comparison of the ^{1}H NMR spectrum to those of authentic samples.

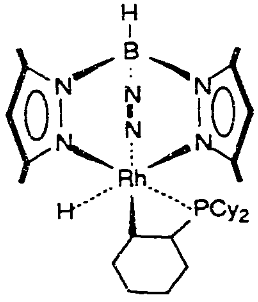


This indicates that both Rh-CO and Rh-PMe$_3$ bonds are cleaved by the irradiation source employed. The triethylphosphine complex HBPz$^*{}_3$Rh(CO)(PEt$_3$) **54** shows a similar result with a 61:39 ratio for the two products HBPz$^*{}_3$Rh(H)(Ph)(PEt$_3$) **54 A** (not completely characterized) and HBPz$^*{}_3$Rh(H)(Ph)(CO). Prior to this work, Ghosh had observed the same type of mixture in the irradiation of HBPz$^*{}_3$Rh(CO)(PPhMe$_2$) in benzene.^{3}

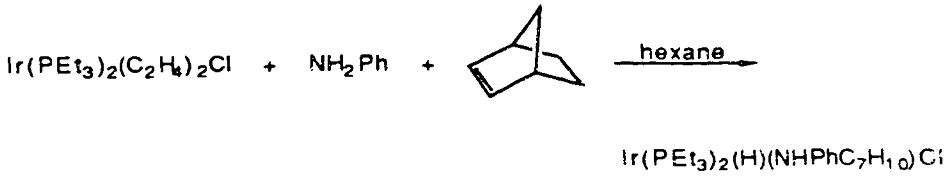
The bulky tricyclohexyl derivative HBPz$^*{}_3$Rh(CO)(PCy$_3$) **55** is different from other phosphine derivatives in that at least four products are produced judging from the hydride resonances of the ^{1}H NMR spectrum. One of them is a doublet, attributable to HBPz$^*{}_3$Rh(H)(Ph)(CO). The other three resonances are all quartets, coupled to both rhodium and phosphorus. Separation of these products has not been achieved. Some speculative structures are drawn below.







Milstein and co-workers recently reported Ir(I)-catalyzed norbornylene insertion into a N-H bond.[11]



In the light of this result and the combination of benzene activation with ethylene insertion by $HBPz^*{}_3Rh(CO)(C_2H_4)$,[6] $HBPz^*{}_3Rh(CO)(NBL)$ **52** was prepared and the possibility of norbornylene insertion into an arene C-H bond was investigated. The result is negative. No insertion products were detected. Irradiation of **52** resulted in only the loss of NBL and formation of $HBPz^*{}_3Rh(H)(Ph)(CO)$.

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CHAPTER SIX

TRANSITION-METAL COMPLEXES OF IMIDAZOL-2-YL TRIDENTATE LIGANDS

SECTION ONE

INTRODUCTION

A variety of trisimidazolylmethanol ligands have been prepared.[1] The zinc(II) complexes of the trisubstituted methanols have been employed as models for the enzyme carbonic anhydrase by Brown and co-workers,[2] and the copper(I) complex has been noted as a model for the carbonyl derivative of Hemocyanin.[3] The complex binding constants of $(N\text{-}MeIm)_3COH$ to metals such as Cu^{2+}, Zn^{2+} and Co^{2+} have been reported by Breslow and co-workers.[1a]

In Chapter IV the preparation of some pyrazolylmethane rhodium complexes was described, and $[HCPz^*_3Rh(CO)_2]BF_4$ **26** has been shown to activate benzene C-H bonds. Trisimidazolylmethanol ligands are analogous to trispyrazolylmethane in that both are neutral tridentate ligands and have three five membered rings. Similar coordination behavior between the two ligands is therefore expected. This Chapter presents some *preliminary* results on the coordination chemistry of trisimidazolylmethanol ligands. This includes the syntheses of several Mo and Mn carbonyl complexes of both $HOCIm'_3$ (Im' = 1-methylimidazol-2-yl) and $HOCIm^*_3$ (Im^*_3 = 1,4,5-trimethylimidazol-2-yl).

An objective in this part of the work was to prepare imidazolyl analogs of the pyrazolylborates such as $KHBIm'_3$. This was not realized, but some of the unsuccessful reactions are described.

SECTION II

EXPERIMENTAL

General

1,4,5-trimethylimidazole (HIm*),[5] HOCIm'$_3$[1a], Re(CO)$_5$Br[6] [Re(CO)$_4$Br]$_2$[7] and [Rh(CO)$_2$Cl]$_2$[8] were prepared according to literature methods. All other reagents were used as received.

Tris(1-methylimidazol-2-yl)methanol, HOCIm'$_3$

To a solution of 1-methylimidazole (2.2 g, 26.8 mmol) in ether (40 mL) at [illegible] was added n-butyllithium in hexane (2.4 M, 11 mL, 26.4 mmol [illegible] the resulting mixture was stirred for 1 h. Diethylcarbonate (0.925 g, 7.8 mmol) was then added. The solution was warmed to 10°C over 2.5 h, followed by addition of H_2O. The product was isolated by continuous extraction with ethylcarbonate and crystallization from benzene as a white solid (644 mg, 30%).

Characterization: MS, 100°C/70ev (m/e, rel.int.): M^+(272, 95), M^+-81(191, 100). ^1H NMR (D_2O): δ 3.42 (s, 9H), 6.96 (d, 1.2Hz, 3H), 7.20 (d, 1.2Hz, 3H). Anal. Calcd for $C_{13}H_{16}N_6O$: C 57.34, H 5.92, N 30.86. Found: C 57.08, H 5.82, N 30.85.

Bis(1-methylimidazol-2-yl)ketone, O=CIm'$_2$

The same procedure as above was followed, except each reagent was increased by a factor of 3. Compound Im'$_2$CO was purified by recrystallization from benzene/hexane.

Characterization: MS, 100°C/70ev (m/e, rel.int.): M$^+$(190, 100). ^{1}H NMR (D_2O): δ 3.92 (s, 6H), 7.20 (d, 2H), 7.38 (d, 2H). Anal. Calcd for $C_9H_{10}ON_4$: C 56.83, H 5.30, N 29.46. Found: C 56.48, H 5.41, N 29.52.

Tris(1,4,5-trimethylimidazol-2-yl)methanol

To a solution of 1,4,5-trimethylimidazole (1.82 g, 16.5 mmol) in ether (40 mL) at -60°C, was added n-butyllithium in hexane (2.4 M, 6.88 mL, 16.5 mmol), and the reaction mixture was stirred for 2 h. Diethylcarbonate (0.65 g, 5.5 mmol) was then added. Stirring was continued for 30 min at -60°C and 1 h at room temperature. The reaction was quenched by addition of H_2O. The product was isolated by continuous extraction with ethylcarbonate and crystallization from benzene/hexane as a white solid (1.2 g, 60%).

Characterization: MS, 100°C/70ev (m/e, rel.int.): M$^+$(356, 52), M$^+$-126(230, 100). ^{1}H NMR (CD_2Cl_2): δ 2.08 (s, 9H), 2.09 (s, 9H), 3.17 (s, 9H), 6.10 (s, 1H). Anal. Calcd for $C_{19}H_{28}N_6O$:
C 64.02, H 7.92, N 23.58. Found: C 63.15, H 7.90, N 23.39. Note: difficulty was experienced in getting duplicate analyses due to the moisture sensitivity of the compound.

Bromo[bis(1-methylimidazol-2-yl)ketone]tricarbonylrhenium (I) 56

A mixture of $Re(CO)_5Br$ (0.196 g, 0.48 mmoL) and $HOCIm'_3$ (0.131 g, 0.48 mmol) in THF (15 mL) was stirred for 12 h. Solvent was removed under vacuum and the residue was placed on a Florisil column (1 x 12 cm). Eluting with CH_2Cl_2/CH_3OH (10:1) gave two yellow bands, which were collected separately. Evaporation of the second fraction gave **56** as a yellow solid.

Characterization of the second fraction (**56**): IR (CH_2Cl_2) 2023, 1917, 1895 cm^{-1}, υ(CO). MS, 200°C/16ev (m/e, rel.int.): M^+(540, 100), M^+-CO(512, 37), M^+-2CO(484, 36), M^+-3CO(456, 23). ^1H NMR (CD_2Cl_2): δ 4.13 (s, 6H), 7.24 (d, 1.5Hz, 2H), 7.62 (d, 1.5Hz, 2H). Anal. Calcd for $C_{12}H_{10}N_4O_3ReBr$: C 26.67, H 1.87, N 10.37. Found: C 26.23, H 1.88, N 10.55.

Evaporation of the first fraction gave a yellow solid **56 A** with υ(CO) (CH_2Cl_2) at 2022, 1910, 1881 cm^{-1}. Crystallization of **56 A** from CH_2Cl_2/hexane resulted in complete conversion of **56 A** to **56** (see discussion).

Tricarbonyl[tris(1-methylimidazol-2-yl)methanol]molybdenum 57

A solution of $Mo(CO)_6$ (0.54 g, 2.05 mmol) and $HOCIm'_3$ (0.556 g, 2.04 mmol) in CH_3CN (20 mL) was heated at 70°C for 3.5 h. Two υ(CO) bands at 1895 (s), 1760 (vs) cm^{-1} gradually appeared, then disappeared along with the formation of some precipitate. The solution was syringed from the precipitate, which was then washed with THF and dried under vacuum to give complex **57** as a greenish solid (0.38 g, 41%).

Characterization: IR (Nujol mull) 1891, 1773, 1682 cm^{-1}, ν(CO). Anal. Calcd for $C_{16}H_{16}N_6O_4Mo$: C 42.49, H 3.57, N 18.58. Found: C 42.14, H 3.63, N 18.62.

Dicarbonylnitrosyl[tris(1-methylimidazol-2-yl)methanol]molybdenumtetrafluoroborate 58

To a solution of $HOCIm'_3Mo(CO)_3$ (0.11 g, 0.24 mmol) in CH_3NO_2 (15 mL), $NOBF_4$ (0.028 g, 0.26 mmol) was added, and the solution was stirred overnight. Solvent was removed under vacuum. The residue was dissolved in CH_3CN, filtered and the filtrate was evaporated to give crude solid **58**. Crystallization of the crude product from CH_2Cl_2/hexane gave **58** as orange crystals.

Characterization: IR (CH_2Cl_2) 2024, 1935 cm^{-1}, ν(CO); 1669 cm^{-1}, ν(NO). ^1H NMR (CD_3CN): δ 4.03 (s, 3H), 4.08 (s, 6H), 5.98 (s, 1H), 6.96 (d, 1.5Hz, 1H), 7.05 (d, 1.5Hz, 2H), 7.06(d, 1.5Hz, 1H), 7.29 (d, 1.5Hz, 2H). Anal. Calcd for $C_{15}H_{16}N_7O_4MoBF_4$: C 33.30, H 2.98, N 18.12. Found: C 33.07, H 2.94, N 18.03.

Tricarbonyl[tris(1,4,5-trimethylimidazol-2-yl)methanol] molybdenum 59

A mixture of $Mo(CO)_6$ (0.30 g, 1.14 mmol) and $HOCIm^*_3$ (0.407 g, 1.14 mmol) in CH_3CN (20 mL) was heated at 70°C for 3.5 h. Two υ(CO) bands at 1892 (s), 1757 (vs) cm^{-1} gradually appeared, then disappeared along with the formation of some precipitate. The solution was syringed from the precipitate, which was then washed with THF and dried under vacuum to give complex **59** as a pale yellow solid (0.24 g, 39%).

Characterization: IR (Nujol mull) 1887, 1772, 1755, 1733, 1719 cm^{-1}, υ(CO). Anal. Calcd for $C_{22}H_{28}N_6O_4Mo$: C 49.26, H 5.26, N 15.67. Found: C 49.51, H 5.32, N 16.10.

Reaction of 59 with $NOBF_4$

To a solution of $HOCIm^*_3Mo(CO)_3$ (0.175 g, 0.33 mmol) in CH_3NO_2 (15 mL), $NOBF_4$ (0.035 g, 0.33 mmol) was added, and the solution was stirred overnight. Solvent was removed under vacuum. Crystallization of the residue from CH_2Cl_2/hexane gave a mixture of $[HOCIm^*_3Mo(CO)_2(NO)]BF_4$ **60** and $[Im^*C(OH)Im^*_2Mo(CO)_2(NO)]BF_4$ **60 A** (see discussion) as yellow crystals (0.10 g, 49%).

Characterization of the mixture: IR (CH_2Cl_2) 2020, 1929 cm^{-1}, υ(CO); 1663, 1616 cm^{-1}, υ(NO). ^1H NMR (CD_2Cl_2), **60** (or **60 A**): δ 2.02 (br, 9H), 2.14 (d, 0.7Hz, 3H), 2.17 (d, 0.7Hz, 6H), 3.76 (s, 3H), 3.80 (s, 6H), 6.20 (s, 1H); **60 A** (or **60**): 2.12 (d, 0.7Hz, 9H), 2.26

(d, 0.7Hz, 3H), 2.28 (d, 0.7Hz, 6H), 3.88 (s, 3H), 3.92 (s, 6H), 6.60 (s, 1H); the ratio between **60** (or **60 A**) and **60 A** (or **60**): 30:70. Anal. Calcd for $C_{21}H_{28}N_7O_4MoBF_4$: C 40.34, H 4.51, N 15.68. Found: C 40.34, H 4.42, N 15.61.

Tricarbonyl[tris(1-methylimidazol-2-yl)methanol] manganesehexafluorophosphate 61

A mixture of $Mn(CO)_5Br$ (2.144 g, 7.8 mmol) and $HOCIm'_3$ (2.12 g, 7.8 mmol) in CH_3CN (20 mL) was heated at 70°C until IR showed complete disappearance of $Mn(CO)_5Br$. The reaction mixture was then poured into H_2O (40 mL) containing excess $NaPF_6$. The resulting precipitate was filtered and washed with minimum amount of CH_2Cl_2 to give complex **61** as a pale yellow solid (3.6 g, 83%).

Characterization: IR (CH_2Cl_2) 2038, 1935 cm^{-1}, ν(CO). Positive FAB in Cleland (rel. int.): M^+(411, 100). ^1H NMR (CD_3CN): δ 3.95 (s, 9H), 6.02 (s, 1H), 6.97 (d, 3H), 7.34 (d, 3H). Anal. Calcd for $C_{16}H_{16}N_6O_4MnPF_6$: C 34.55, H 2.90, N 15.11. Found: C 34.65, H 2.95, N 15.11.

Tricarbonyl[tris(1,4,5-trimethylimidazol-2-yl)methanol] manganesehexafluorophosphate 62

A solution of $Mn(CO)_5Br$ (0.348 g, 1.27 mmol) and $HOCIm^*_3$ (0.45 g, 1.26 mmol) in CH_3CN (20 mL) was heated at 70°C for 20 min. The reaction mixture was then poured into H_2O (40 mL) containing excess

$NaPF_6$. The resulting precipitate was filtered and crystalized from CH_2Cl_2/Hexane to give complex **62** as a yellow solid (0.61 g, 75%).

Characterization: IR (CH_2Cl_2) 2031, 1926 cm^{-1}, υ(CO). Positive FAB in Glycerol (rel. int.): M^+(495, 24), BP^+(base peak, 93, 100). ^1H NMR (CD_2Cl_2): δ 2.15 (s, 9H), 2.39 (s, 9h), 3.90 (s, 9H), 5.21 (s, 1H). Anal. Calcd for $C_{22}H_{28}N_6O_4MnPF_6$: C 41.26, H 4.41, N 13.12. Found: C 41.54, H 4.67, N 12.49.

Reaction of $NaBH_4$ with 1-methylimidazole

A mixture of 1-methylimidazole (6.8 g, 82.8 mmol) and $NaBH_4$ (0.94 g, 24.9 mmol) in THF (50 mL) was refluxed overnight, then filtered. The filtrate was cooled to and maintained at -20°C for 18 h, yielding $[HIm'_3Na]BH_4$ as white crystalline solid .

Characterization: ^1H NMR (THF-d^8): δ -0.4 (quartet, 40Hz, 3.2H; septet, 12Hz, 0.8H), 3.65 (s, 9H), 6.86 (s, 3H), 6.91 (s, 3H), 7.40 (s, 3H). Anal. Calcd for $C_{12}H_{22}N_6NaB$: C 50.72, H 7.80, N 29.58. Found: C 49.13, H 7.54, N 29.11.

In a separate experiment under similar conditions, $[HIm'_2Na]BH_4$ was isolated as suggested by its analysis instead of $[HIm'_3Na]BH_4$.

Characterization of $[HIm'_2Na]BH_4$: Anal. Calcd for $C_8H_{16}N_4NaB$: C 47.56, H 7.98, N 27.73. Found: C 47.77, H 7.59, N 27.87. ^1H NMR spectrum was not available due to insufficient sample.

Formation of $[(CH_3O)_2BIm']_2$ 63

To a solution of 1-methylimidazole (1.8 g, 22 mmol) in THF (20 mL) at -40°C, LiBu in hexane (2.6 M, 8.44 mL, 22 mmol) was added via syringe. The mixture was stirred for 20 min. Neat $B(OCH_3)_3$ (2.80 mL, 23.8 mmol) was then added dropwise. After stirring for 18 h, the solution was filtered, and the filtrate was evaporated under vacuum. The residue was dissolved in a minimum amount of CH_2Cl_2/hexane (1:1), from which $[(CH_3O)_2BIm']_2$ **63** slowly deposited as a white solid.

Characterization: ^1H NMR (CD_2Cl_2): δ 2.90 (s, 12H), 3.92 (s, 6H), 7.01 (d, 1.6Hz, 2H), 7.18 (d, 1.6Hz, 2H). Anal. Calcd for $C_{12}H_{22}N_4B_2O_4$: C 46.80, H 7.20, N 18.19. Found: C 47.08, H 7.20, N 18.19. Determination of molecular weight by osmometry in CH_2Br_2: 319 (Calcd for $[(CH_3O)_2BIm']_2$: 308).

Reaction of lithium(1-methylimidazol-2-ate) with $B(OCH_3)_3$

To a solution of 1-methylimidazole (5.15 g, 62.7 mmol) in THF (50 mL) at -60°C, LiBu in hexane (2.39 M, 26.24 mL, 62.7 mmol) was added via syringe. The mixture was stirred for 2 h at -60°C, then 30 min at room temperature. $B(OCH_3)_3$ (2.38 mL, 20.2 mmol) in THF (25 mL) was added to the mixture dropwise at -60°C. Stirring was continued at -60°C for three days and at room temperature for another three days. The clear solution was syringed from the precipitate (presumably CH_3OLi as suggested by its ^1H NMR spectrum), and treated with hexane to give some white precipitate. The solid was then twice dissolved in THF and precipitated with hexane.

Characterization: ^{1}H NMR (D_2O): δ 3.33 (s, LiOMe), 3.68 (s, 3H), 6.96 (s, 1H), 7.08 (s, 1H).

Formation of $Re(CO)_3(HIm')_2Br$ 64

To a solution of $[Re(CO)_4Br]_2$ (40 mg, 0.05 mmol) in Et_2O, excess amount of the white solid from above was added. The mixture was stirred until IR showed complete disappearance of $[Re(CO)_4Br]_2$. Solvent was removed under vacuum, and the residue was placed on a Florisil column eluting with CH_2Cl_2/CH_3OH (9:1). Removal of solvent gave complex **64** as a yellow solid.

Characterization: IR (CH_2Cl_2) 2021, 1910, 1881 cm^{-1}, υ(CO). MS, 170°C/16ev (m/e, rel.int.): M^+(514, 0.2), BP^+(82, 100). ^{1}H NMR (CD_2Cl_2): δ 3.70 (s, 6H), 6.80 (t, 2H), 7.20 (t, 2H), 8.0 (b, 2H). Anal. Calcd for $C_{11}H_{12}N_4O_3ReBr$: C 25.69, H 2.35, N 10.89. Found: C 25.68, H 2.33, N 10.89.

Preparation of $[(CH_3O)_2BIm'_2]Rh(CO)_2$ 65

To a solution of $[Rh(CO)_2Cl]_2$ (10 mg, 0.026 mmol) in toluene (20 mL) was added excess amount of the white solid (the same solid as used for the preparation of complex **64**). IR showed complete disappearance of $[Rh(CO)_2Cl]_2$ instantly, and formation of new υ(CO) bands at 2074, 2051 cm^{-1} (both with a higher wave number shoulder) and 2001 cm^{-1}. After stirring overnight, the solution turned colourless and only two υ(CO) bands remained at 2073, 2002 cm^{-1}. The solution was filtered and the filtrate was evaporated to give a yellow solid. Crystallization of the yellow solid from hexane gave **65** as a moderately air-stable solid.

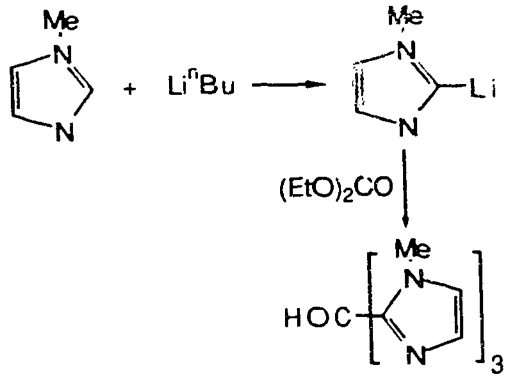
Characterization: IR (hexane) 2074, 2005 cm^{-1}, υ(CO). MS, 100^{o}C/70ev (m/e, rel.int.): M^{+}(394, 36), M^{+}-CO(366, 32), M^{+}-OMe(363, 40), BP^{+}(base peak, 308, 100). ^{1}H NMR (CD_2Cl_2): δ 2.65 (s, 3H), 2.66 (s, 3H), 3.80 (s, 6H), 6.82 (d, 1.5Hz, 2H), 6.98 (d, 1.5Hz, 2H). Anal. Calcd for $C_{12}H_{16}N_4O_4RhB$: C 36.58, H 4.09, N 14.22. Found: C 36.50, H 4.21, N 13.30.

SECTION III

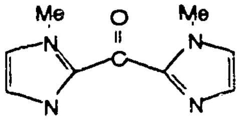
RESULTS AND DISCUSSION

A Synthesis of tris(imidazol-2-yl)methanol ligands

Tris(1-methylimidazol-2-yl)methanol was prepared according to the method reported by Breslow and co-workers.[1a] 1-methylimidazole was metallated at C-2 with n-butyllithium, which was then treated with diethylcarbonate to give HOCIm'$_3$.



In scales of 2.2 g 1-methylimidazole, HOCIm'$_3$ is the only isolated product. When the scale was increased by a factor of 3 (6.6 g 1-methylimidazole), bis(1-methylimidazol-2-yl)ketone Im'$_2$CO was produced.



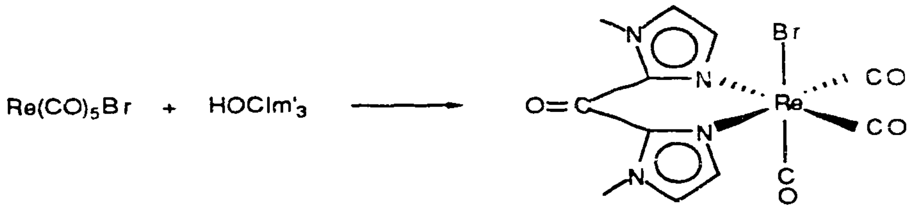
Recently Lippard et al[9] reported an improved method of preparing Im'$_2$CO, in which 0.157 mol (12.9 g) 1-methylimidazole was lithiated, and treated with 0.05 mol diethylcarbonate. There is no trisubstituted product reported even though a 3:1 ratio of LiIm' and (EtO)$_2$CO was used. So large scales seem to favour the formation of Im'$_2$CO.

The trimethyl substituted HOCIm$^*_3$ was prepared by the same procedure. Unlike HOCIm'$_3$, HOCIm$^*_3$ appears very moisture sensitive. Exposure of HOCIm$^*_3$ to air results in rapid liquification.

B Reactions of HOCIm'$_3$ and HOCIm$^*_3$

(a) Reactions with M(CO)$_5$Br (M = Re, Mn)

Stirring Re(CO)$_5$Br with one equivalent of HOCIm'$_3$ brought about the degradation of HOCIm'$_3$. Only the bis(imidazol-2-yl)ketone derivative (Im'$_2$CO)Re(CO)$_3$Br **56** was obtained. Two complexes are isolated initially by chromatography with ν(CO) at 2023, 1917, 1895 cm^{-1} (due to **56**) and 2022, 1910, 1881 cm^{-1} respectively. Crystallization of the second species caused its isomerization to complex **56**, but the fully characterized complex Re(CO)$_3$(HIm')$_2$Br **64** exhibits the same ν(CO) bands as this second species, i.e., 2022, 1910, 1881 cm^{-1}. Further evidence is needed to clarify this result.

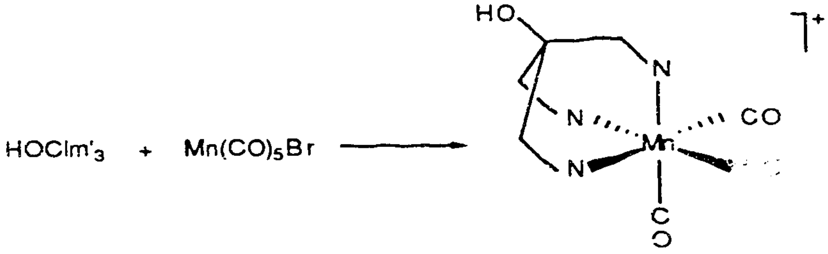


VI-2

56

The ^{1}H NMR spectrum of complex **56** shows a single methyl resonance and two resonances with an AB pattern for the 4,5- ring protons, reflecting the presence of a mirror plane in the molecule. This suggests that **56** has the structure shown in eqn VI-2. The MS shows a molecular ion peak at 540 and consecutive losses of three CO groups.

Treating Mn(CO)$_5$Br with HOCIm'$_3$ or HOCIm$^*_3$, followed by metathesis with NaPF$_6$ gave the salts [HOCIm'$_3$Mn(CO)$_3$]PF$_6$ **61** and [HOCIm$^*_3$Mn(CO)$_3$]PF$_6$ **62**, respectively.



VI-3

61

The ^{1}H NMR spectra of both **61** and **62** show one type of imidazole resonance and OH proton at 6.02 and 5.21 ppm respectively. The CO stretching frequencies of **61** (Table VI-1) are higher than those of **62**, reflecting the electron donating effect of additional methyl groups on the imidazole rings. A comparison of ν(CO) of **61** and

Table VI-1
Infrared CO Stretching Bands of Mo and Mn Complexes[a]

	L			
	$HOCIm'_3$	$HOCIm^*_3$	$HCPz_3$ [10]	$HCPz^*_3$ [10]
$LMo(CO)_3$	1981, 1773 1682 [b]	1887, 1772, 1755, 1773, 1719 [b]	1882, 1765 [b]	1900, 1760 [b]
$[LMo(CO)_2(NO)]^+$	2024, 1935 1669	2020, 1929 1663, 1616	2037, 1953 1691	2031, 1945 1686
$[LMn(CO)_3]^+$	2038, 1935	2031, 1926	2059, 1961	

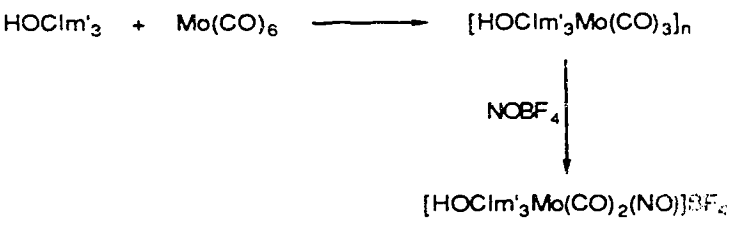
[a] In CH_2Cl_2 except as note.

[b] Nujol mull.

$[HCPz_3Mn(CO)_3]PF_6$ reveals once again that $HOCIm'_3$ is more electron donating than $HCPz_3$.

(b) Reactions with $Mo(CO)_6$

The reactions of $Mo(CO)_6$ with $HOCIm'_3$ and $HOCIm^*_3$ are similar to those with $HCPz_3$.[10] A rather insoluble solid of empirical formula $HOCIm'_3Mo(CO)_3$ or $HOCIm^*_3Mo(CO)_3$ was formed when $Mo(CO)_6$ was reacted with one equivalent of $HOCIm'_3$ or $HOCIm^*_3$. Their insolubility suggests "polymeric" structures, as in the case of trispyrazolylmethane derivatives $HCPz_3M(CO)_3$ (M = Cr, Mo, W).[10]

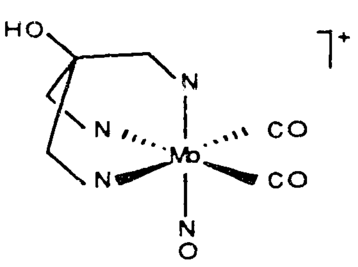


58

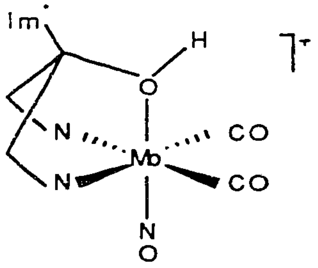
VI-A

The "polymeric" $HOCIm'_3Mo(CO)_3$ reacts readily with $NOBF_4$ to give $[HOCIm'_3Mo(CO)_2(NO)]BF_4$ **58**. The ^1H NMR spectrum of **58** shows two types of imidazole resonances in a 2:1 ratio and the OH proton at 5.89 ppm. The CO and NO stretching frequencies of **58** (Table VI-1) are lower than those of the pyrazolylmethane analogs, indicating $HOCIm'_3$ is more electron donating than $HCPz_3$.

The insoluble $HOCIm^*_3Mo(CO)_3$ reacts with $NOBF_4$ forming $[HOCIm^*_3Mo(CO)_2(NO)]BF_4$ **60** and $[Im^*C(OH)Im^*_2Mo(CO)_2(NO)]BF_4$ **60 A**.



60



60 A

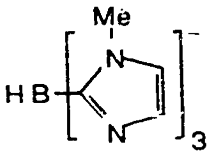
The presence of two isomers is evident from the ^{1}H NMR spectrum, which showed more than two types of imidazole resonances as would be expected for a single isomer. While two NO stretching bands are observed, only one set of CO bands are observed for the mixture of **60** and **60 A** It is possible that the NO group is trans to the O atom in **60 A** and the interchange of the ligand trans to NO does not affect ν(CO) significantly.

The coordination of O atom of OH in the place of an imidazole N atom or pyridyl N atom has been reported before in [HOCIm'$_3$Hg(Me)]NO$_3$[4] and [(HOCPy$_3$)$_2$Ru]$^{2+}$ (Py = 2-pyridyl).[11]

C Attempted synthesis of poly(imidazol-2-yl)borates

Both polypyrazolylborates and polypyrazolylalkanes are known. However only polyimidazolylalkanes are known. To the writer's knowledge, no polyimidazolylborates have been reported in the literature.

To synthesize the tris(1-methylimidazol-2-yl)borate HBIm'$_3^-$



ligand, the reaction between 1 mol $NaBH_4$ and 3 mol 1-methylimidazole was first investigated. It was hoped that the 2-H of the imidazole ring would be acidic enough to neutralize the BH_4^-. This did not occur, however, under the condition of refluxing the mixture in THF overnight. The only product isolated was $(HIm')_3NaBH_4$ and $(HIm')_2NaBH_4$.

The ^1H NMR of $(HIm')_3NaBH_4$ is worth mentioning. There are three imidazole ring proton resonances, indicating that the 2-H of the ring remains unsubstituted. The integral ratios between the BH_4^- proton resonance and that of HIm' suggest that the sodium atom is coordinated to three HIm'. The BH_4^- anion appears as a quartet and a septet coupled to ^{11}B (I = 3/2) and ^{10}B (I = 3), respectively (Figure VI-1). The integral ratio of the two multiplets, 80:20, is in good agreement with the relative natural abundance of the two isotopes of boron (^{11}B:^{10}B = 80.4:19.6).

As an alternative approach to the target ligand $HBIm'_3^-$, 1-methylimidazole was reacted with LiBu to give lithium 1-methylimidazol-2-ate LiIm', which was then treated with $B(OMe)_3$. Complex $[(MeO)_2BIm']_2$ **63** was isolated when LiIm' was treated with one mole of $B(OMe)_3$.

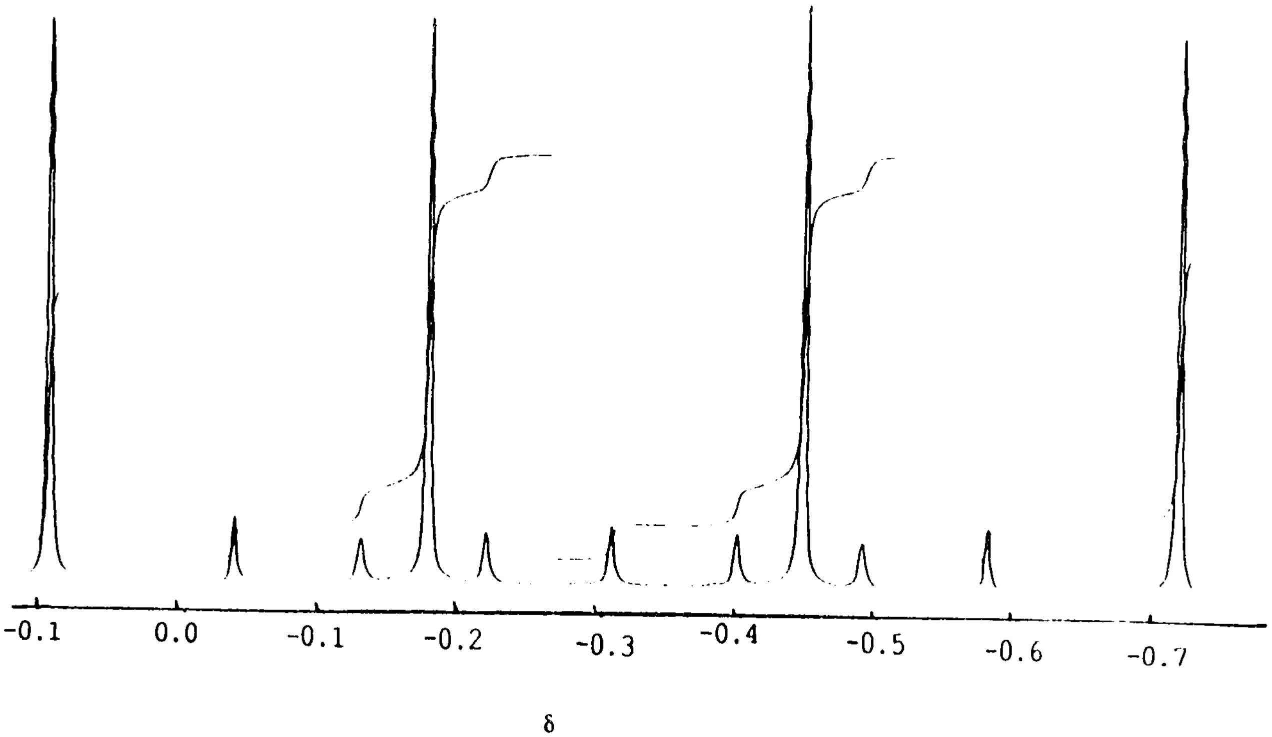
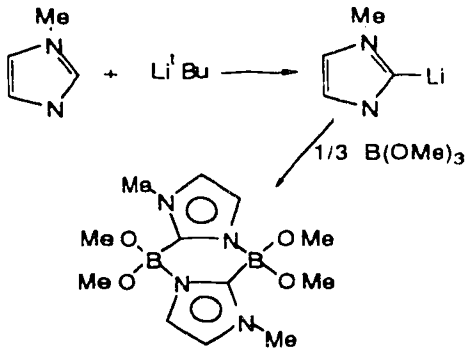
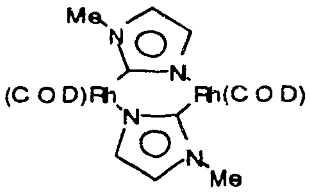


Figure VI-1 ^{1}H NMR Spectrum of BH_4^- in [Na{HIm')$_3$]BH$_4$



The ^{1}H NMR spectrum of **63** shows one type of imidazole resonances. The two imidazole ring proton resonances exhibit a AB pattern. The absence of a third ring proton resonance is indicative of the substitution of the 2-H. The formulation of a dimer is indicated by a solution molecular weight measurement.

An interesting rhodium dimer [Rh(COD)Im']$_2$ has been reported,

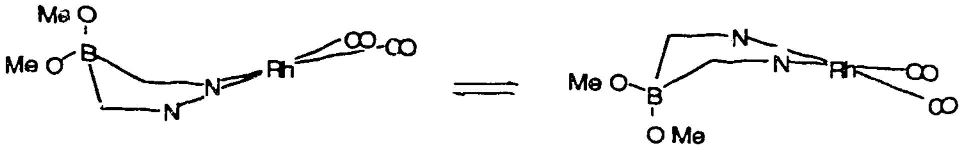


which was prepared by the reaction of (COD)Rh(HIm')Cl and CH_3Li.[12] The two imidazole rings bridge the two rhodium atoms in the same manner as that in complex **63**.

Treating one mole B(OMe)$_3$ with three moles LiIm' gave a white solid. It is thought that this white solid is a mixture of LiOMe and Li(MeO)BIm'$_3$ and/or Li(MeO)$_2$BIm'$_2$. Separation of the mixture has proven to be difficult and has not been achieved. The ^{1}H NMR spectrum shows two imidazole ring proton resonances, suggesting the substitution of the third.

The assumption that the white solid contained Li(MeO)BIm'$_3$ and/or Li(MeO)$_2$BIm'$_2$ is partially verified through the preparation of [(MeO)$_2$BIm'$_2$]Rh(CO)$_2$ **65**. The rhodium dimer [Rh(CO)$_2$Cl]$_2$ reacts with an excess of the above white solid, yielding complex **65**. The reaction is relatively clean; no other υ(CO) bands were observed when the reaction was complete.

The ^{1}H NMR spectrum of complex **65** (Figure VI-2) exhibits resonances due to one type of imidazole, two ring proton resonances with a AB pattern and a single resonance due to the three methyl protons. The two methoxo groups appear at slightly different chemical shifts. This small difference is perhaps a result of slow conformational interchange on the NMR time scale, and only the static structure is observed.



The mass spectrum (Figure VI-3) shows the molecular ion peak at 394 and losses of CO and OMe groups, consistent with the formula (MeO)$_2$BIm'$_2$Rh(CO)$_2$. The υ(CO) bands of **65** appear at 2074, 2005 cm^{-1} (Figure VI-4). These values are lower than those of $H_2BPz^*{}_2Rh(CO)_2$ (2079, 2013 cm^{-1}),^{14} indicating that (MeO)$_2$BIm'$_2{}^-$ is more electron donating than $H_2BPz^*{}_2{}^-$.

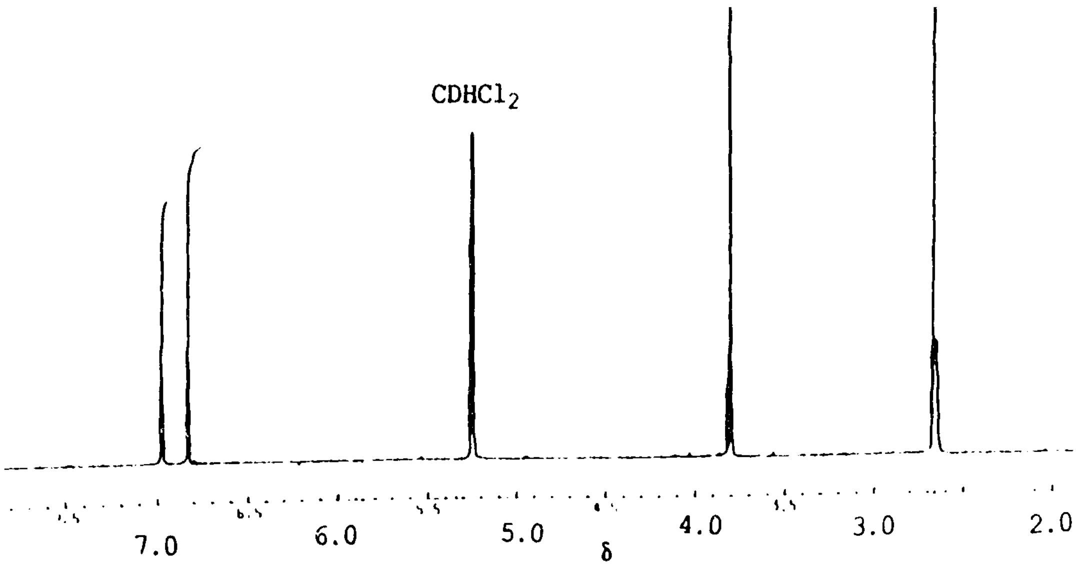


Figure VI-2 ^{1}H NMR Spectrum of $[(MeO)_2BIm'_2]Rh(CO)_2$ **65** at Room Temperature

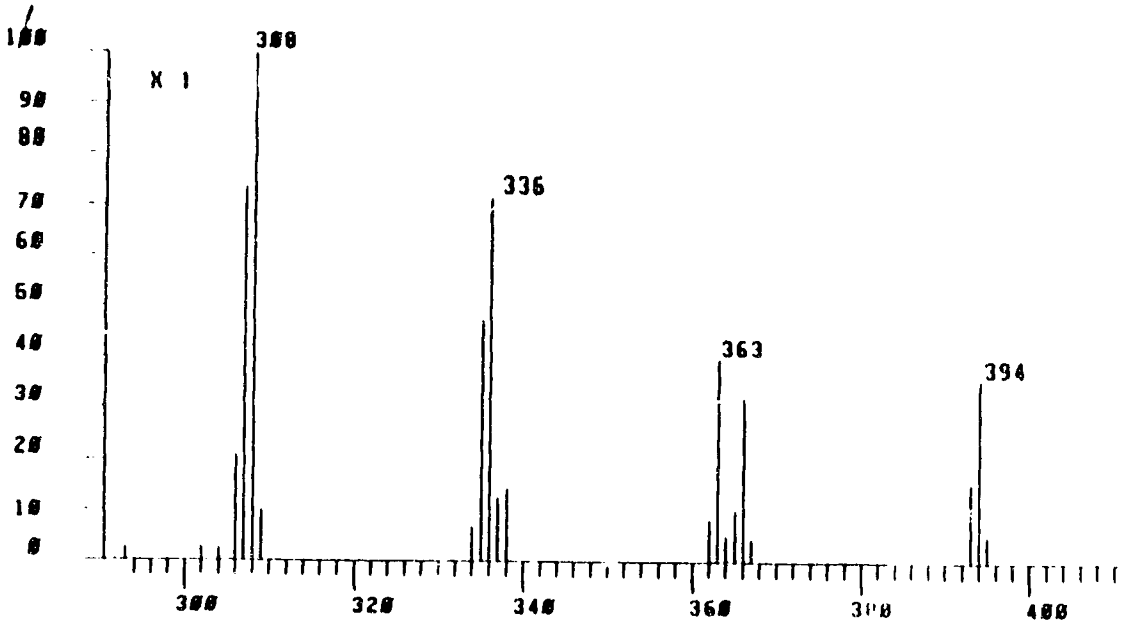


Figure VI-3 Mass Spectrum of [(MeO)$_2$BIm'$_2$]Rh(CO)$_2$ 65

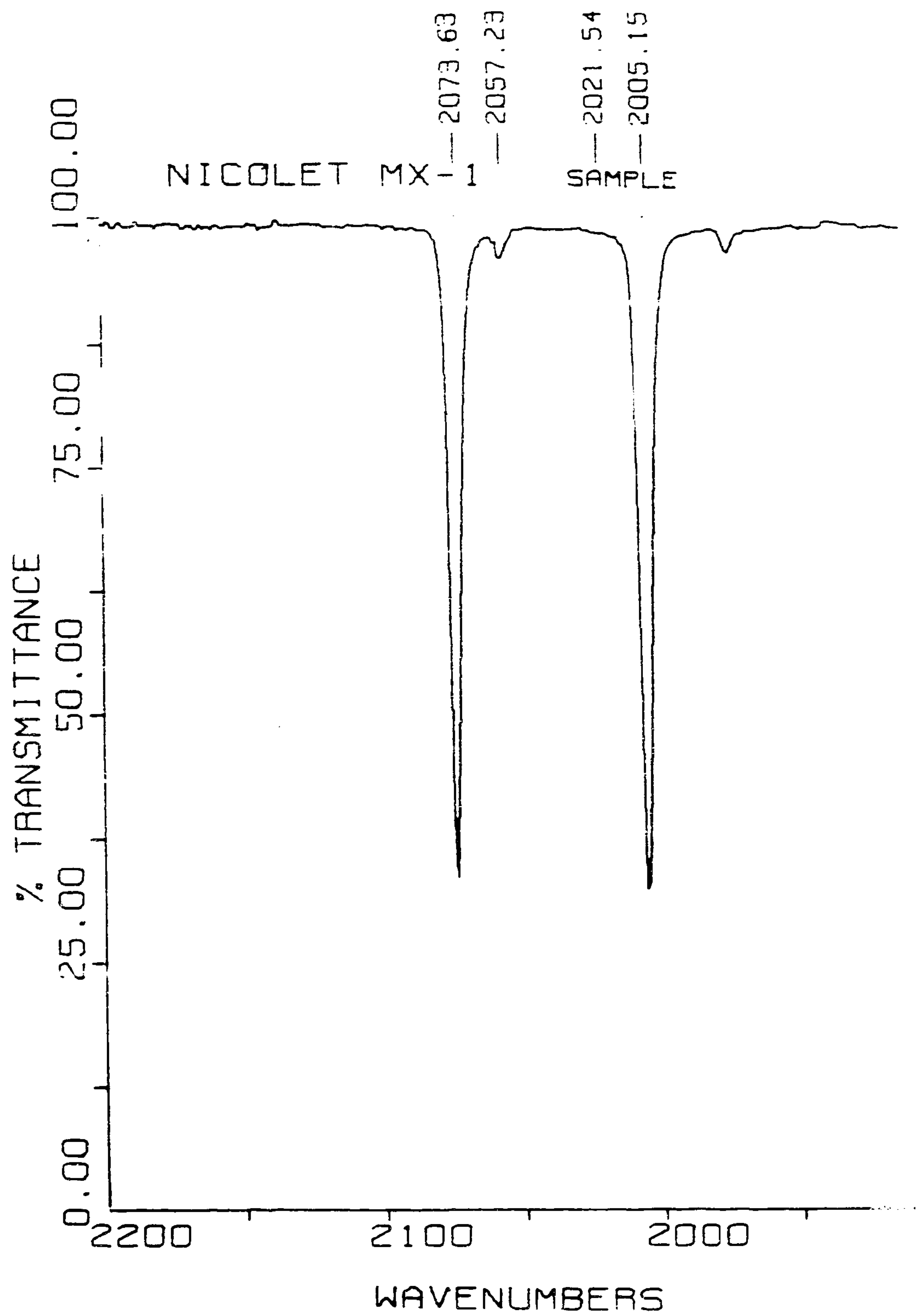


Figure VI-4 IR Spectrum of $[(MeO)_2BIm'_2]Rh(CO)_2$ **65**

Somewhat contrary to the assumption of the white solid containing $Li(MeO)BIm'_3$ and/or $Li(MeO)_2BIm'_2$, complex $Re(CO)_3(HIm')_2Br$ **64** was isolated from the reaction of $[Re(CO)_4Br]_2$ with the white solid. The presence of three ring proton resonances in the ^1H NMR spectrum of **64** indicates that unsubstituted 1-methylimidazole is present. Perhaps degradation of the ligand occurred in this reaction. Rhenium species have been noted to catalyze the decomposition of pyrazolylborate ligands.[13] As discussed earlier, degradation of $HOCIm'_3$ is thought to take place in the preparation of complex **56**.

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CHAPTER SEVEN

SUMMARY AND CONCLUSIONS

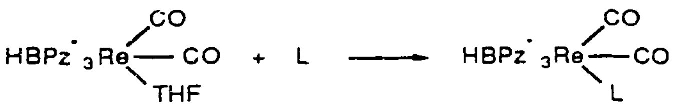
A number of pyrazolyl tridentate transition-metal complexes have been prepared, and their reactivity in C-H activation has been investigated. The rhodium complexes activated C-H bonds efficiently. The rhenium complexes, however, did not show any activity in C-H activation, and instead provided some rare examples of 17- and 16-electron radical compounds. The work described in this Thesis is summarized below according to the tridentate ligands: $HBPz^{*}{}_3{}^{-}$ and $HCPz^{*}{}_3$.

1. Trispyrazolylborate complexes

A Rhenium

The rhenium tricarbonyl complex, $HBPz^{*}{}_3Re(CO)_3$ **1**, was first reported by McCleverty and co-workers in 1979.[1] It was prepared by treating $[Re(CO)_4Cl]_2$ with $KHBPz^{*}{}_3$. In the light of the successful C-H activation by $HBPz^{*}{}_3M(CO)_2$ (M = Rh, Ir),[2] it was of interest to investigate the reactivity of **1** in C-H activation.

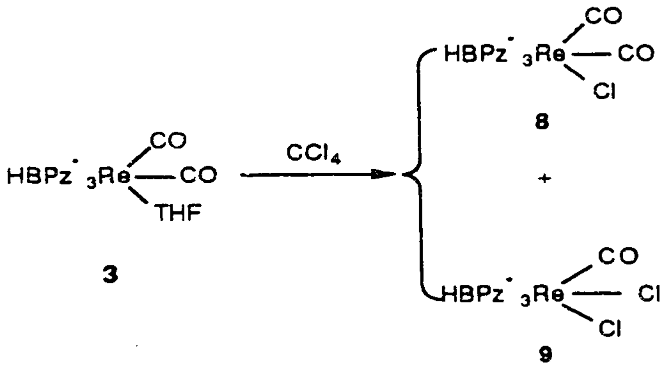
Photolysis of **1** in benzene gave no detectable products, resulting in only the decomposition of **1**. The THF derivative $HBPz^{*}{}_3Re(THF)(CO)_2$ **3** was prepared from the photolysis of **1** in THF with a gas purge. Hydrogen purge is preferred over nitrogen since the latter gave a poor yield of **3** and formed the by-product $HBPz^{*}{}_3Re(CO)_2(N_2)$ **6**. Complex **6** and the phosphine derivatives **4** and **5** are readily available from **3** (eq VII-1).



L = PMe_3 **4**
PPh_3 **5**
N_2 **6**

(VII-1)

An unusual reaction of **3** with CCl_4 afforded the 17-electron complex $HBPz^{*}{}_3Re(CO)_2(Cl)$ **8** and the 16-electron complex $HBPz^{*}{}_3Re(CO)(Cl)_2$ **9**.



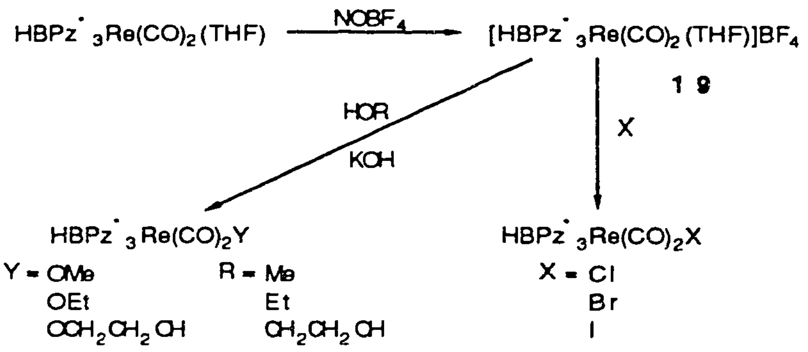
(VII-2)

Complex **9** was isolated as a minor product in the above reaction (<5%). It can be prepared from **8** as follows:

$$HBPz^{*}{}_3Re(CO)_2Cl \xrightarrow[CH_3NO_2]{NOBF_4} \xrightarrow{PPNCl} HBPz^{*}{}_3Re(CO)Cl_2 \qquad (VII\text{-}3)$$

8 **9**

Another route to the 17-electron radical **8** involved the cationic radical **19** (eq VII-4).



(VII-4)

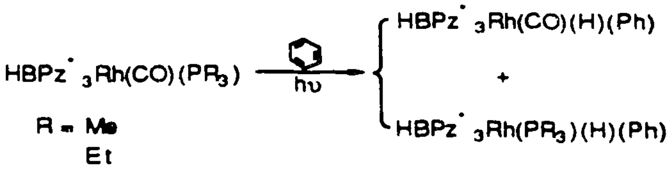
Complex **19** is a useful precursor in the syntheses of other neutral 17-electron radicals such as $HBPz^*{}_3Re(CO)_2(OR)$ (R = Me, Et, CH_2CH_2OH) (eq VII-4).

All 17-electron complexes are paramagnetic and exhibit magnetic moments, μ_{eff}, close to the spin-only value 1.73 μ_B for one unpaired electron. Two X-ray molecular structures were obtained in this work. One is that of complex **1**; the other is that of $PPN[HBPz^*{}_3Re(CO)_2Cl]$ **10** which was prepared by the reduction of **9** with sodium sand.

B Rhodium

Much of the previous C-H activation work was done on the dicarbonyl system $HBPz^*{}_3M(CO)_2$ (M = Rh, Ir).[2] In this work the reactivity of several monophosphine derivatives was investigated.

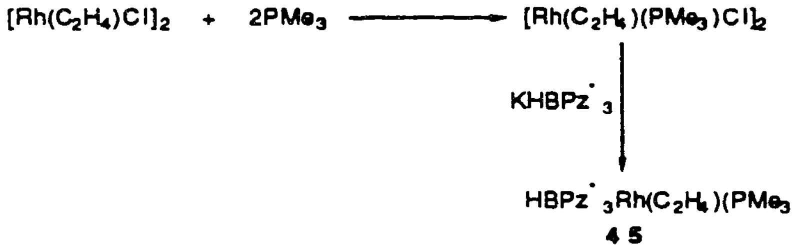
Photolyses of the carbonylphosphine derivatives, $HBPz^*{}_3Rh(CO)(PMe_3)$ and $HBPz^*{}_3Rh(CO)(PEt_3)$, in benzene gave two products (eq VII-5).



(VII-5)

The tricyclohexylphophine derivative $HBPz^*{}_3Rh(CO)(PCy_3)$ gave a more complicated result in that at least four products were formed judging from the hydride region of the ^1H NMR spectrum. Perhaps the bulky cyclohexyl ring was activated. Separation of the products was not achieved and they are not identified.

To avoid a mixture in the photolysis reaction, complex $HBPz^*{}_3Rh(C_2H_4)(PMe_3)$ **45** was prepared (eq VII-6).



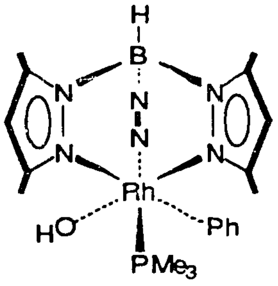
(VII-6)

Photolysis of **45** in benzene, as hoped, gave only $HBPz^*{}_3Rh(H)(Ph)(PMe_3)$ **46**. Treating **46** with 1 equivalent NBS yielded $HBPz^*{}_3Rh(Br)(Ph)(PMe_3)$. If an excess amount of NBS was used, bromination of the pyrazole 4-positions took place, giving $HB(4\text{-}Br\text{-}Pz^*)_3Rh(Br)(Ph)(PMe_3)$.

The reaction of **46** with H_2O afforded the novel hydroxy derivative $HBPz^*{}_3Rh(OH)(Ph)(PMe_3)$ **50** (eq VII-7).

$HBPz^{*}_{3}Rh(H)(Ph)(PMe_3) + H_2O \longrightarrow$ (VII-7)

46



50

A kinetic study has been carried out on the following reaction:

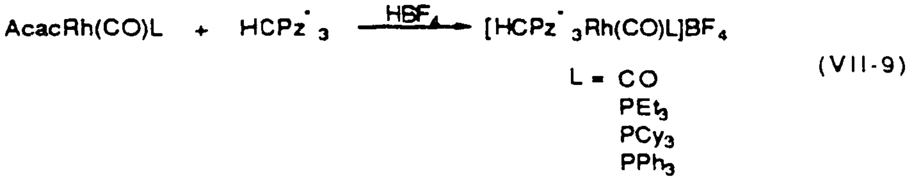
$$HBPz^{*}_{3}Rh(H)(Ph)(PMe_3) + C_6D_6 \longrightarrow HBPz^{*}_{3}Rh(D)(C_6D_5)(PMe_3) + C_6H_6 \quad (VII\text{-}8)$$

The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were determined as 24.9 ± 0.4 kcal mol^{-1} and -10.3 ± 1.1 cal $K^{-1}mol^{-1}$ respectively. The $\Delta S^{\neq}$ is negative here, opposite to the value reported for similar systems, but like that for other reductive eliminations. The same exchange reaction of $HBPz^{*}_{3}Rh(CO)(H)(Ph)$ and $Cp^{*}Rh(H)(Ph)(PMe_3)$ exhibit $\Delta S^{\neq}$ as 12.2 ± 2.4 cal $K^{-1}mol^{-1}$ and 14.59 ± 2.5 cal $K^{-1}mol^{-1}$ respectively.[2a,3]

2. Trispyrazolylmethane complexes

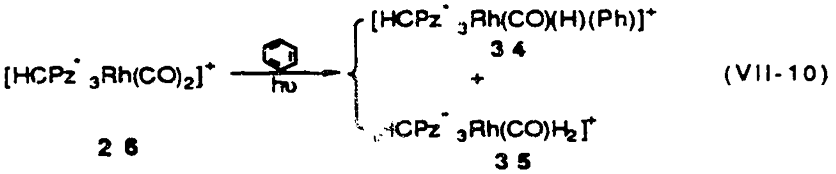
The neutral tris(3,5-dimethylpyrazol-1-yl)methane ligand $HCPz^{*}_{3}$ is isoelectronic and isosteric to the anionic ligand $HBPz^{*}_{3}{}^{-}$, but the coordination chemistry of $HCPz^{*}_{3}$ has not been studied as extensively as that of $HBPz^{*}_{3}{}^{-}$. In Chapter IV, a series of trispyrazolylmethane rhodium complexes were described and some of them were shown to activate benzene C-H bonds.

The acetylacetone derivative AcacRh(CO)L (L = CO, PEt$_3$, PCy$_3$, PPh$_3$) was used as the rhodium source in the preparation of complexes with the general formula [HCPz$^*_3$Rh(CO)L]BF$_4$ as follows:



$$\mathrm{AcacRh(CO)L} + \mathrm{HCPz^*_3} \xrightarrow{\mathrm{HBF_4}} \mathrm{[HCPz^*_3Rh(CO)L]BF_4} \qquad \mathrm{L} = \mathrm{CO},\ \mathrm{PEt_3},\ \mathrm{PCy_3},\ \mathrm{PPh_3} \qquad \text{(VII-9)}$$

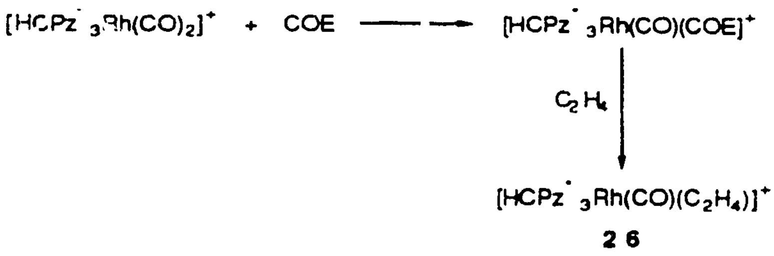
All these complexes activated benzene C-H bonds when irradiated in a benzene solution. The dicarbonyl **26** gave one major product [HCPz$^*_3$Rh(H)(Ph)(CO)]BF$_4$ **34** with small amounts of the dihydride [HCPz$^*_3$Rh(H)$_2$(CO)]BF$_4$ **35**.



$$\underset{\mathbf{26}}{\mathrm{[HCPz^*_3Rh(CO)_2]^+}} \xrightarrow[h\nu]{} \left\{ \begin{array}{c} \mathrm{[HCPz^*_3Rh(CO)(H)(Ph)]^+} \\ \mathbf{34} \\ + \\ \mathrm{[HCPz^*_3Rh(CO)H_2]^+} \\ \mathbf{35} \end{array} \right. \qquad \text{(VII-10)}$$

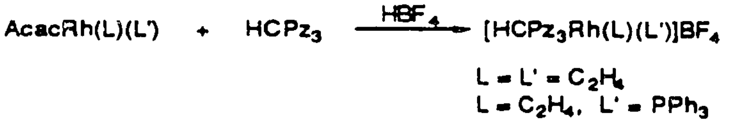
Complex **34** reacted with CCl$_4$ to give the chloro derivative [HCPz$^*_3$Rh(Cl)(Ph)(CO)]BF$_4$ **36**, which has been fully characterized. The dihydride species **35** is rather unstable and the yield is only about 3% from the above reaction. A larger amount of **35** was obtained by pressurizing a mixture of **34** and **35** with H$_2$.

Two olefin complexes were prepared in this system, [HCPz$^*_3$Rh(CO)(COE)]BF$_4$ **33** and [Rh(CO)(C$_2$H$_4$)]BF$_4$ **37** (eq VII-11). Photolyses of both in benzene gave **34** as the only product.



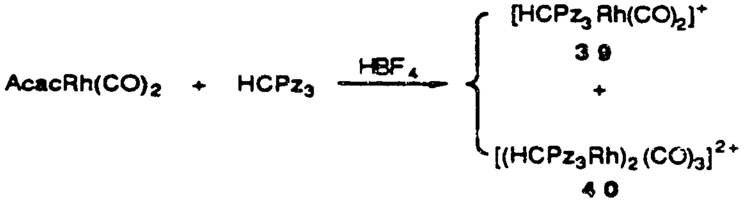
(VII-11)

Several rhodium complexes of $HCPz_3$ were prepared similarly to those of $HCPz^*_3$.



(VII-12)

In the synthesis of the dicarbonyl complex **39**, a dinuclear by-product **40** was isolated, which has been very recently reported by Oro and co-workers.[4]



(VII-13)

3. The coordination chemistry of imidazolyl multidentate ligands.

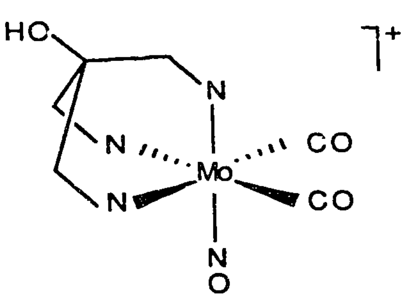
There are strong similarities between the trisimidazolylmethanol ligands, $HOCIm'_3$ and $HOCIm^*_3$, and trispyrazolylmethane ligands.

Treating 1 mol $HOCIm'_3$ with 1 mol $Mo(CO)_6$ produces a "polymeric" solid $[HOCIm'_3Mo(CO)_3]_n$ **57**. Complex **57** reacted readily with $NOBF_4$ to give the monomeric salt **58**.

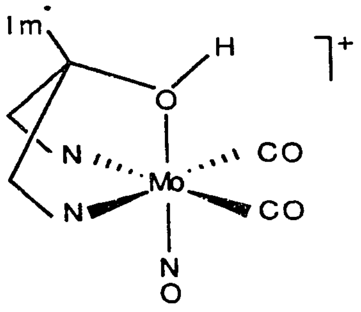
$$\begin{tikzcd} Mo(CO)_6 + HOCIm'_3 \arrow[r] & {[HOCIm'_3Mo(CO)_3]_n} \arrow[d, "NOBF_4"'] \\ & {[HOCIm'_3Mo(CO)_2(NO)]BF_4} \end{tikzcd} \qquad (VII\text{-}14)$$

58

The trimethylimidazolylmethanol derivative behaved slightly differently from that of $HOIm'_3$ in that two isomers, **60** and **60 A**, were formed in the reaction of $[HOCIm^*_3Mo(CO)_3]_n$ **59** with $NOBF_4$.

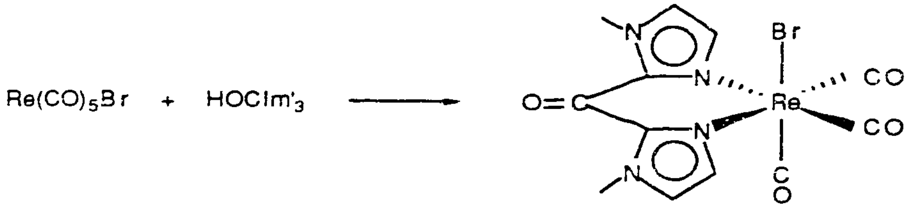


60



60 A

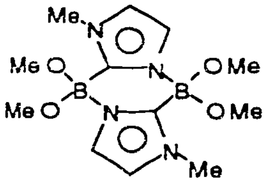
The reaction of $HOIm'_3$ or $HOIm^*_3$ with $Mn(CO)_5Br$ gave $[HOCIm'_3Mn(CO)_3]^+$ or $[HOCIm^*_3Mn(CO)_3]^+$. However the analogous reaction of rhenium caused the degradation of the ligand, and $[Im'_2CO]Re(CO)_3Br$ was formed (eq VII-15).



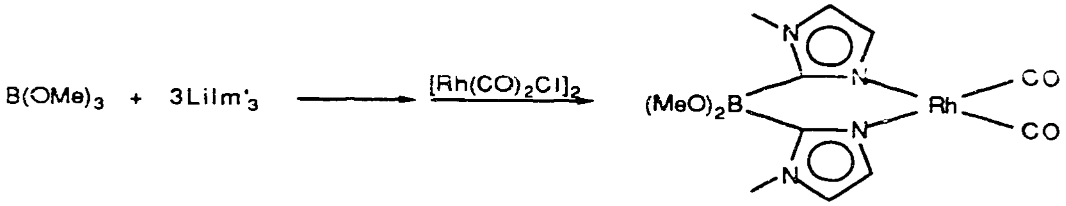
(VII-15)

56

Attempts to prepare trisimidazolylborate ligands failed. Nevertheless some interesting results were obtained. Trimethylborate reacted with 1 mol LiIm' to give an imidazole bridged dimer.



Treating 3 mol LiIm' with 1 mol $B(OMe)_3$ produced a white solid, which reacted with $[Rh(CO)_2Cl]_2$ to give $[(MeO)_2BIm'_2]Rh(CO)_2$ **65**. This suggested that the white solid contained $Li[(MeO)_2BIm'_2]$.



(VII-16)

65

The same reaction of the white solid with $[Re(CO)_4Br]_2$, however, gave only $Re(CO)_3(HIm')_2Br$. Perhaps rhenium brought about the degradation of imidazolylborate as it does to pyrazolylborates.[1,5]

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