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Cationic Dihydrogen Complexes of Rhenium with Isonitrile Coligands

by

Mark Huggins Voges

A dissertation submitted in partial fulfillment
of the requirements for the degree of

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(Chairperson of Supervisory Committee)

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Abstract

Cationic Dihydrogen Complexes of Rhenium with Isonitrile Coligands

by Mark Huggins Voges

Chairperson of the Supervisory Committee: Professor Dennis Michael Heinekey
Department of Chemistry

Abstract: The syntheses, characterizations, and reactivities of the following new complexes are reported: $\mathrm{Re(CN\textit{t}Bu)_3(PR_3)_2X}$ (R = Cy, X = H, F, Cl, Br, I; R = Ph, X = H, Cl), $\mathrm{[Re(CN\textit{t}Bu)_3(PR_3)_2L]^+}$ (R = Cy, L = $\mathrm{H_2}$, agostic H–C, CN*t*Bu, $\mathrm{N_2}$, $\mathrm{O_2}$, $\mathrm{PMe_3}$, $\mathrm{NH_3}$, CO, $\mathrm{C_2H_4}$; R = Ph, L = $\mathrm{H_2}$, agostic H–C, $\mathrm{N_2}$), $\mathrm{[Re(CN\textit{t}Bu)_3(PR_3)_2Cl]^+}$ (R = Cy, Ph), $\mathrm{[Re(CN\textit{t}Bu)_5(H_2)]^+}$. Thermodynamic parameters have been obtained for the novel equilibrium, $\mathrm{Re(CN\textit{t}Bu)_3(PCy_3)_2Cl + H_2 \rightleftharpoons [Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]Cl}$. ^{1}H and ^{31}P{^{1}H} NMR studies ($\mathrm{CD_2Cl_2}$) over the temperature range 286–316 K afford values of $\Delta H^\circ = -18.0 \pm 0.7$ kcal/mol, $\Delta S^\circ = -44.0 \pm 2.2$ e.u., and $\Delta G^\circ_{298} = -4.8 \pm 1.3$ kcal/mol. The complexes $\mathrm{[Re(CN\textit{t}Bu)_3(PR_3)_2(H_2)]^+}$ (R = Cy, Ph) are characterized as dihydrogen complexes. Their J_{HD} (R = Cy, 30.3 Hz; R = Ph, 30.9 Hz) and $T_{1(\mathrm{min})}$ values of 8 msec (300 MHz) are consistent with H-H distances of *ca.* 0.80 Å. Direct competition studies found the strength of the metal dihydrogen bond in $\mathrm{[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]^+}$ to be stronger than those in $\mathrm{[Re(CO)_3(PCy_3)_2(H_2)]^+}$ and $\mathrm{W(CO)_3(PCy_3)_2(H_2)}$. $\mathrm{[Re(CN\textit{t}Bu)_5(HD)]^+}$ is also characterized as a dihydrogen complex based on a J_{HD} of 33.4 Hz. The agostic complex $\mathrm{[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+}$ is found to undergo a dynamic isonitrile rearrangement on the NMR time-scale. ^{1}H NMR spin saturation transfer studies over a temperature range of 255–298 K afford the activation parameters: $\Delta H^\ddagger = 11.4 \pm 0.8$ kcal/mol, $\Delta S^\ddagger = -17.6 \pm 1.6$ e.u., and $\Delta G^\ddagger_{298} = 16.6 \pm 1.2$ kcal/mol. The molecular structures of $\mathrm{[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]^+}$, $\mathrm{Re(CN\textit{t}Bu)_3(PCy_3)_2Cl}$, and $\mathrm{[Re(CN\textit{t}Bu)_3(PCy_3)_2Cl]^+}$ have been determined by X-ray crystallography. $\mathrm{Re(CN\textit{t}Bu)_3(PCy_3)_2Cl}$ shows an unusually long Re–Cl bond distance of 2.596(2) Å.

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ABBREVIATIONS AND SYMBOLS

A	conjugate base of generic Brønsted-Lowry acid HA
Å	Angstrom, 10^{-10} meters
AB pattern	two doublets that couple to one another
atm	atmosphere
BAr_f	$B(3,5-(CF_3)_2C_6H_3)_4$
br	broad
Bu	butyl
cm^{-1}	wavenumber
Cp	cyclopentadienyl
Cp^*	pentamethylcyclopentadienyl
Cy	cyclohexyl
Cyp	cyclopentyl
δ	ppm relative to reference
d	doublet
D	deuterium, also ^2H
$\Delta G^\ddagger$	free energy of activation
ΔG°	free energy of reaction (subscript # denotes temperature in K)
$\Delta H^\ddagger$	enthalpy of activation
ΔH°	enthalpy of reaction

$\Delta S^\ddagger$	entropy of activation
ΔS°	entropy of reaction
dippe	1,2-bis(diisopropylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
eq	equation or equivalent
Et	ethyl
FPT	freeze-pump-thaw cycle
g	gram
GOF	goodness of fit (X-ray cystallography)
Gomberg's Dimer	1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene
HA	generic Brønsted-Lowry acid
η	hapticity
HOTf	triflic acid, ($HOSO_2CF_3$)
h	hours
Hz	Hertz (sec^{-1})
*i*Pr	isopropyl
IR	infrared
J	coupling constant, subscripts denote which atoms are coupling
k	rate constant
K	degrees Kelvin
kcal	kilocalories

K_{eq}	equilibrium constant
L	two electron donor ligand. or liter
LT	low temperature
M	transition metal, or moles/liter
(m)	medium (IR spectroscopy)
Me	methyl
µL	microliter, 10^{-6} liters
mg	milligram
MHz	megahertz, 10^{6} Hertz
mL	milliliter, 10^{-3} liters
mmol	millimole, 10^{-3} moles
mol	mole
ν	bond stretch (IR spectroscopy)
$\nu_{1/2}$	line width at half height
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge Thermal Ellipsoid Parameters
OTf	triflate, (OSO_2CF_3)
Ph	phenyl
ppb	parts per billion
ppm	parts per million
py	pyridine

R	alkyl group
q	quartet
s	singlet
(s)	strong (IR spectroscopy)
(sh)	shoulder (IR spectroscopy)
T	temperature
t	triplet
T_1	spin-lattice relaxation time
*t*Bu	tertiary-butyl
T_c	temperature of coalescence
terpy	terpyridine
THF	tetrahydrofuran
TMS	tetramethylsilane
torr	1/760 atmosphere
triflate	$OSO_2CF_3^-$, also OTf^-
triphos	$MeC(CH_2PPh_2)_3$
(w)	weak (IR spectroscopy)
X	anionic two electron donor ligand

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CHAPTER 1

Isonitrile Dihydrogen Complexes and Competition Studies.

Introduction

The ability of dihydrogen to form complexes with transition metals was first recognized by Kubas and coworkers.[1] While the first isolable tungsten dihydrogen compounds were quite labile with respect to H_2 loss, subsequent work has demonstrated that quite strong binding of H_2 is possible.[2] Particularly robust H_2 complexes are frequently formed when the metal carries a positive charge.[3] Isolation of such complexes requires a careful choice of counterion and solvent. Anions of low nucleophilicity are preferred and considerable effort has been expended on the development of truly non–coordinating anions such as BAr_f^-.[4,5] Solvent choice is equally important, especially when polar, coordinating solvents are used. Even methylene chloride, traditionally considered to be non-coordinating, has demonstrated ligating ability.[6]

Our goal was to synthesize dihydrogen complexes containing isonitrile coligands. Complexes with isonitrile coligands were underrepresented relative to their preponderance in other areas of areas of organometallic chemistry. Of the 300+ dihydrogen complexes known, only one contains an isonitrile ligand. Simpson and Conroy-Lewis reported $[CpRu(CN\textit{t}Bu)(PPh_3)(H_2)]PF_6$ in 1986.[7]

In particular we have chosen to study dihydrogen complexes of the form $[Re(CN\textit{t}Bu)_3(PR_3)_2(H_2)]^+$. These are analogous to the Kubas complexes $W(CO)_3(PR_3)_2(H_2)$ (R = Cy, *i*Pr, Cyp), which have been intensively investigated from almost every conceivable angle. Comparison to these complexes provides an almost continual point of reference. Likewise, the initial investigation of the carbonyl analogs, $[Re(CO)_3(PCy_3)_2(H_2)]^+$ reported by Heinekey *et al.*,[8] provides another possibility for fruitful comparisons, in this case between isonitrile and carbonyl complexes.

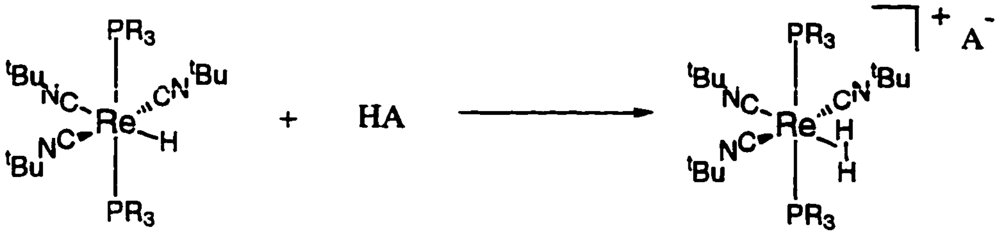
This chapter describes the synthesis, characterization, and reactivity of the dihydrogen complexes $[Re(CN\mathit{t}Bu)_3(PR_3)_2(H_2)]^+$ (R = Ph, Cy). Two direct competition studies, the first of their kind, compare the H_2 binding affinities of three dihydrogen complexes to one another.

Results

Preparation of $Re(CN\mathit{t}Bu)_3(PR_3)_2H$ (1a, 1b). $Re(CN\mathit{t}Bu)_3(PCy_3)_2H$ (**1a**), was prepared by heating $Re(PCy_3)_2H_7$ and $CN\mathit{t}Bu$ in toluene at 45 °C for 2 days. Complex **1a** was isolated as a yellow solid in 78% yield. NMR data indicate that **1a** possesses two sets of isonitrile ligands in a 2:1 ratio and one hydride ligand showing coupling to two equivalent phosphines (J_{HP} = 20.4 Hz). The IR spectrum showed a single broad band at 1928 cm^{-1} which was assigned to $\nu(C{\equiv}N)$. No bands attributable to $\nu(Re\text{-}H)$ were observed; presumably these were obscured by the $C{\equiv}N$ stretching frequency.[9]

The PPh_3 analog of **1a**, $Re(CN\mathit{t}Bu)_3(PPh_3)_2H$ (**1b**), has been previously reported by Jones and Maguire.[10] They prepared **1b** by reacting $Re(PPh_3)_2H_7$ with cyclopentadiene to make $Re(PPh_3)_2(\eta^4\text{-}C_5H_6)H_3$, followed by ligand displacement with $CN\mathit{t}Bu$ to make **1b**. We found that $CN\mathit{t}Bu$ reacts directly with $Re(PPh_3)_2H_7$ to give **1b** in 70% isolated yield.

Protonation of $Re(CN\mathit{t}Bu)_3(PR_3)_2H$. The dihydrogen complexes, $[Re(CN\mathit{t}Bu)_3(PCy_3)_2(H_2)]^+$ (**2a**) and $[Re(CN\mathit{t}Bu)_3(PPh_3)_2(H_2)]^+$ (**2b**), were readily obtained by protonation of the corresponding neutral hydride complexes with a wide variety of acids (eq 1.1): HOTf, $HBF_4{\cdot}OEt_2$, and $HBAr_{f}{\cdot}(OEt_2)_2$.[4]



1a, 1b **2a, 2b**

Equation 1.1

Upon the addition of acid, the yellow solution immediately becomes colorless. The ^{1}H NMR spectrum of either **2a** or **2b** shows two resonances for the *tert*-butyl groups on the isonitrile ligands in a 1:2 ratio, and a broad resonance in the hydride region (**2a** δ -6.30, **2b** δ -5.56), which integrates to two hydrogens. The ^{31}P{^{1}H} NMR spectrum shows one resonance, indicating equivalent phosphines. The IR spectrum of **2a** showed several broad bands between 2120 and 2020 cm^{-1} which were assigned to ν(C≡N). No bands attributable to any of the six (Re-(H_2)) vibration modes were observed.[2d]

Characterization of **2a** as a dihydrogen complex is based on the large H-D coupling observed (J_{HD} = 30.3 Hz) for the partially deuterated derivative (Figure 1.1). In addition, the measured T_1 for the H_2 ligand at the maximum rate of relaxation ($T_{1(min)}$) is 8 msec (225 K, 300 MHz) (Figure B.1), consistent with an H-H distance of *ca.* 0.80 Å (fast rotation).[11] ^{1}H NMR spectroscopy provided no evidence for the presence of a dihydride tautomer at any temperature examined (160–300 K). **2b** exhibited similar properties to **2a**, and was also characterized as a dihydrogen complex. For **2b**, the $T_{1(min)}$ was found to be 8 msec (207 K, 300 MHz) (Figure B.2). The H-D coupling of the partially deuterated complex was measured to be 30.9 Hz, slightly greater than for **2a**.

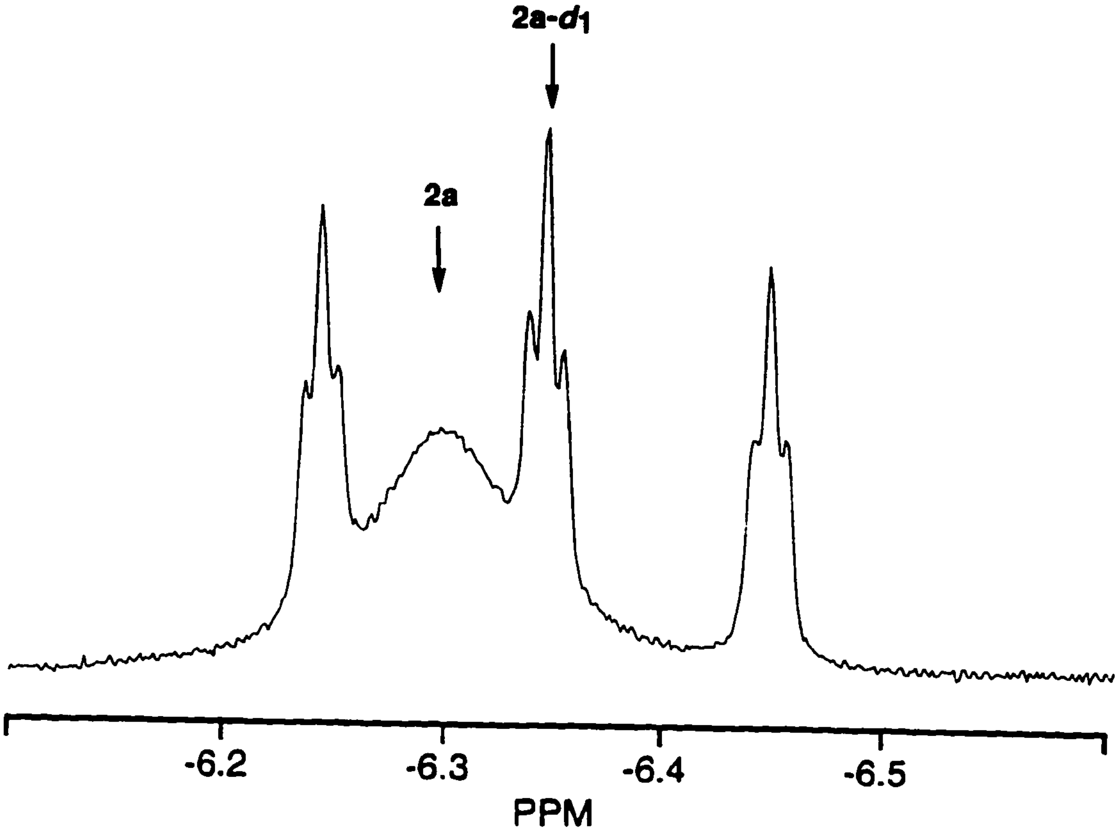


Figure 1.1 Partial ^1H NMR spectrum (hydride region) of a mixture of **2a** and **2a**-d_1 (300 MHz, methylene chloride-d_2, 298 K). An upfield shift of 50 pbb is observed for **2a**-d_1. **2a**-d_1 shows a large coupling to deuterium ($^1J_{HD}$ = 30.3 Hz) and a much smaller coupling to the two equivalent phosphines ($^2J_{HP} \approx 2$ Hz).

In situ NMR tube preparations of **2a** or **2b** resulted in clean and complete conversion, as observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. This was the case even in the absence of an H_2 atmosphere.

Preparation of **2a-OTF**, **2a-BF$_4$** and **2a-BAr$_f$** was readily achieved by adding HOTf, $HBF_4{\cdot}OEt_2$, or $HBAr_f(OEt_2)_2$ to a solution of **1a** in diethyl ether. A slight deficiency of acid was used to avoid overprotonation. Both **2a** and **2b** react with strong acid, but the products have not been identified. Filtration and drying under a stream of H_2 gives **2a** in 65–90% yield.

Attempts to isolate pure **2b-BF$_4$** or **2b-BAr$_f$** by similar techniques failed to yield product in greater than 80% purity as determined by NMR. The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) shows two minor impurities at 16.4 ppm and 6.81 ppm. The latter is identified as the previously reported compound $[Re(CN\textit{t}Bu)_4(PPh_3)_2]^+$.[12]

The dihydrogen complex, $[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]Cl$ (**2a-Cl**), can also be generated by the reaction of **1a** with HCl. Attempts to isolate **2a-Cl** free from solvent failed because the white precipitate that is formed loses hydrogen irreversibly in the solid state and yields the yellow chloride, $Re(CN\textit{t}Bu)_3(PCy_3)_2Cl$ (**5a**) (chapter 2).

The basicity of the neutral hydride, $Re(CN\textit{t}Bu)_3(PCy_3)_2H$ (**1a**), was further probed by reacting this complex with weaker acids. Reaction of **1a** with $[HNEt_3]Cl$ in methylene chloride gave complete protonation. In agreement with this observation, simple amines, even in 10-fold excess, failed to remove a proton from the dihydrogen product. Other nitrogen bases such as 1,8-bis(dimethylamino)naphthalene (Proton Sponge®) also failed to deprotonate **2a**. Complete deprotonation was ultimately achieved using excess NaOMe or KO*t*Bu. The high basicity of **1a** is further demonstrated by the observation that the addition of 5 equivalents of methanol to a methylene chloride solution of **1a** leads to 80% protonation.

X-ray Structure of 2a-BAr$_f$. Slow cooling of a methylene chloride solution (-20 °C) of **2a-BAr$_f$** resulted in the formation of colorless diffraction-quality crystals. A large consistent data set was collected, but the structure did not refine. A final R of 13.6% (R_w = 20.73%) with a GOF of 4.4 was obtained. There are a number of non-positive-definite atoms, which indicates that the absorption correction may not have been effective.

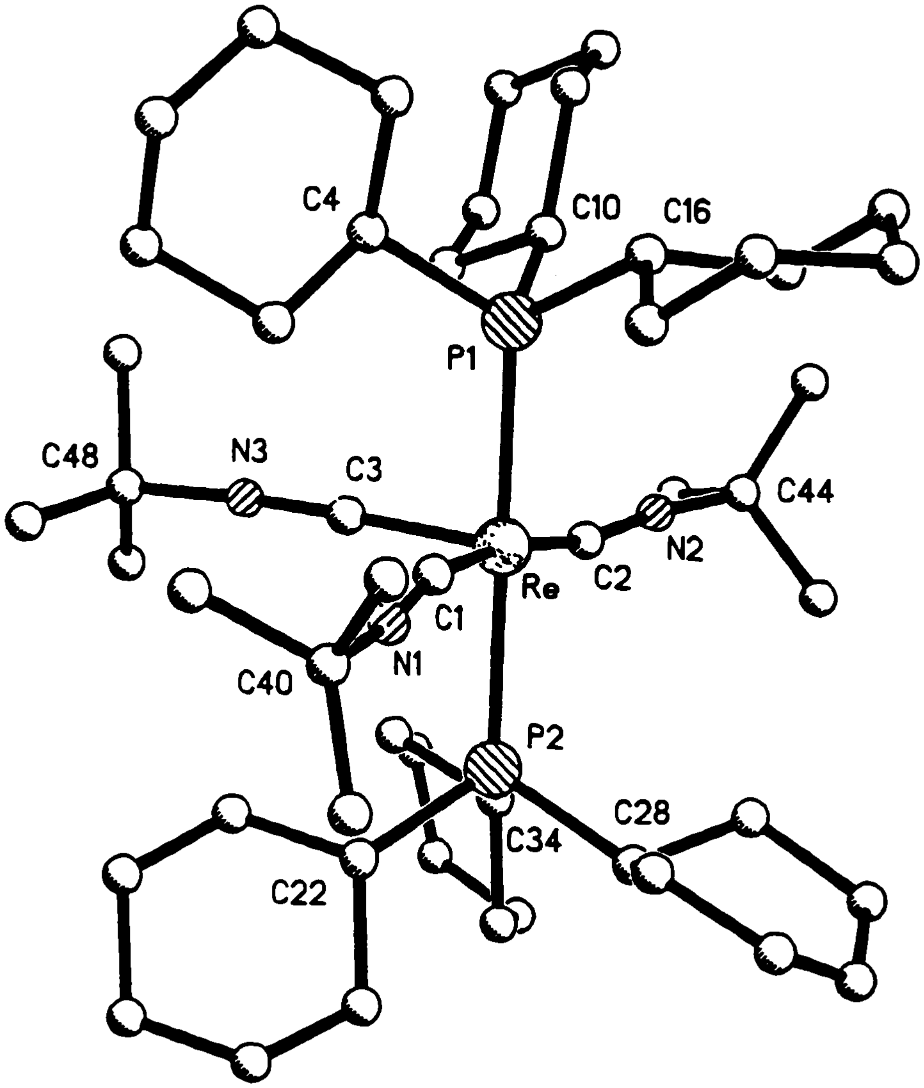


Figure 1.2 PLUTO projection of complex **2a**.

Table 1.1 Select Bond Distances (Å) for **2a**

Re-P(1)	2.429(5)
Re-P(2)	2.449(5)
Re-C(1)	1.962(16)
Re-C(2)	1.971(18)
Re-C(3)	1.892(14)
P(1)-C(4)	1.891(17)
P(1)-C(10)	1.892(18)
P(1)-C(16)	1.853(16)
P(2)-C(22)	1.880(17)
P(2)-C(28)	1.872(16)
P(2)-C(34)	1.847(24)
C(1)-N(1)	1.217(25)
N(1)-C(40)	1.436(31)
C(2)-N(2)	1.250(27)
N(2)-C(44)	1.449(33)
C(3)-N(3)	1.270(18)
N(3)-C(48)	1.487(20)

Table 1.2 Select Bond Angles (deg) for **2a**

P(1)-Re-P(2)	178.6(2)
P(1)-Re-C(1)	89.5(5)
P(2)-Re-C(1)	91.7(5)
P(1)-Re-C(2)	96.1(5)
P(2)-Re-C(2)	82.7(5)
C(1)-Re-C(2)	170.8(7)
P(1)-Re-C(3)	85.9(5)
P(2)-Re-C(3)	93.5(5)
C(1)-Re-C(3)	94.0(6)
C(2)-Re-C(3)	93.6(7)
Re-P(1)-C(4)	119.5(5)
Re-P(1)-C(10)	114.3(6)
Re-P(1)-C(16)	117.0(5)
Re-P(2)-C(22)	114.0(6)
Re-P(2)-C(28)	114.3(6)
Re-P(2)-C(34)	115.5(7)
Re-C(1)-N(1)	165.5(15)
C(1)-N(1)-C(40)	171.9(19)
Re-C(2)-N(2)	161.6(15)
C(2)-N(2)-C(44)	172.7(16)
Re-C(3)-N(3)	177.7(14)
C(3)-N(3)-C(48)	174.9(16)

The quality of the solution is such that only the basic geometry can be determined with any certainty. A PLUTO diagram of **2a-BAr$_f$** (Figure 1.2) shows an octahedral geometry with a *mer,trans* arrangement of the ligands. Bond distances and angles are given in Table 1.1 and 1.2, respectively; however, a detailed analysis of these is not encouraged. Information pertinent to the data collection and refinement of the structure is given in Table 1.4.

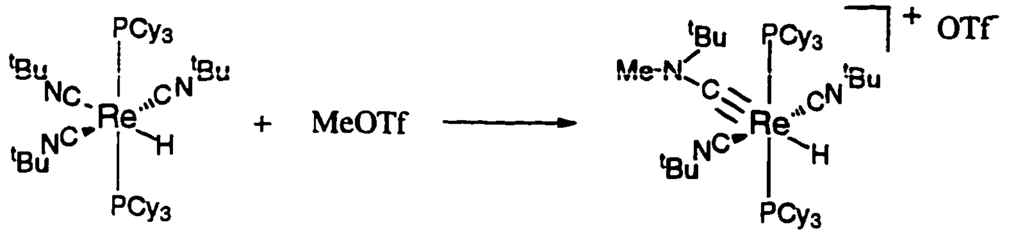
Removal of bound H_2: Formation of an Agostic Complex. When **2a** is prepared with a non-coordinating counteranion (OTf^-, BF_4^-, BAr_f^-), it reversibly loses H_2 in the solid state to form the "coordinatively unsaturated"[13] complex $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ (**3a**). Hydrogen loss is easily monitored by inspection: **2a** is white, while **3a** is dark purple. The ^1H NMR spectrum (298 K) of **3a** shows two sets of exchange-broadened isonitrile ligands in a 2:1 ratio. $^{31}P\{^1H\}$ NMR spectroscopy indicates equivalent phosphines. The IR spectrum of **3a** showed one broad band at 2024 cm^{-1}, with a shoulder at 2073 cm^{-1}; these were assigned to $\nu(C{\equiv}N)$. No absorption is observed that could be assigned to an agostic Re···H–C interaction. However, such absorptions are expected to be weak, and accordingly are not reliable criteria for an agostic interaction.[14]

For $[Re(CN\textit{t}Bu)_3(PPh_3)_2(H_2)]^+$ (**2b-BF$_4$**, **2b-BAr$_f$**), the H_2 loss products analogous to **3a** have not been characterized (but see reaction of **1b** with $(CPh_3)BAr_f$ below). Exposing the white solid to dynamic vacuum for 12 h does not result in a color change. Dissolution of this sample in CD_2Cl_2 and subsequent analysis by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy reveals that as much as 70% of the total signal intensity is accounted for by the dihydrogen complex, **2b**. Other products identified by NMR include $[Re(CN\textit{t}Bu)_4(PPh_3)_2]BF_4$ (**4b**) and $[\textit{mer}\text{-}Re(CN\textit{t}Bu)_3(PPh_3)_3]^+$. Complex **4b** has been reported previously.[15] It is characterized by a single resonance for the isonitrile ligands (δ

0.95) in the ^{1}H NMR spectrum,[16] and a single resonance (δ 16.4) in the $^{31}P\{^{1}H\}$ NMR spectrum. $[Re(CN\textit{t}Bu)_3(PPh_3)_3]^+$ is characterized by two isonitrile resonances of intensity 2:1 in the ^{1}H NMR spectrum, and two phosphine resonances of intensity 2:1 in the $^{31}P\{^{1}H\}$ NMR spectrum. The upfield resonance of intensity two is a doublet, and the downfield resonances is a triplet. Coupling constants are equal (J_{PP} = 15 Hz) and correspond to the appropriate magnitude for a *cis*-J_{PP}.[17]

Synthesis of $[Re(CN\textit{t}Bu)_4(PCy_3)_2]BF_4$ (4a). The complex, **4a**, and the previously reported $[Re(CN\textit{t}Bu)_4(PPh_3)_2]BF_4$ **(4b)**[12] were observed by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy as minor impurities (< 10%) in many of the above reactions. The identity of the previously unreported **4a** was confirmed by independent preparation. Reaction of $Re(CN\textit{t}Bu)_3(PPh_3)_2H$ **(1a)** with excess CN*t*Bu in $NaBF_4$/methanol solution gives **4a** in 82% yield after 12 h. Elemental analysis confirms the empirical formula. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra respectively show a single resonance for the isonitriles and the phosphines, indicating that members of each group are equivalent. The IR spectrum of **4a** showed one broad band at 2022 cm^{-1}, with a shoulder at 2064 cm^{-1}; these were assigned to $\nu(C{\equiv}N)$.

Reaction of 1a with Electrophiles other than Protons. Complex **1a** readily reacts with MeOTf and $SiMe_3OTf$ to yield a mixture of products. The reaction of **1a** with MeOTf in diethyl ether yielded a purple precipitate. The $^{31}P\{^{1}H\}$ NMR spectrum of the dissolved solid showed the following product distribution: **3a** (69%), a new species (23%), **2a** (6.5%), and **4a** (1.5%). The new species is consistent with an aminocarbyne complex formed by electrophilic attack at the nitrogen of the *trans* isonitrile (eq. 1.2).



Equation 1.2

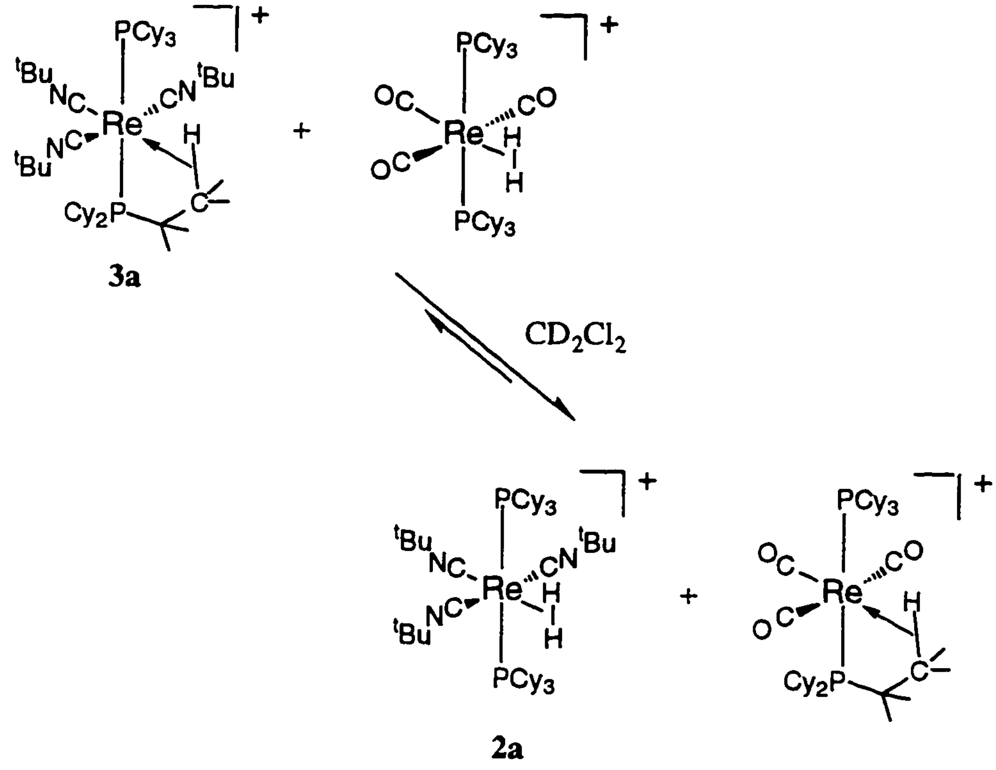
The ^{1}H NMR spectrum of $[Re(CNtBu)_2(CN(Me)tBu)(PCy_3)_2]^+$ exhibits a triplet (δ -4.87, J_{HP} = 23 Hz), two singlets, one for each of the *tert*-butyl groups, in a 2:1 ratio (δ 1.46 and 1.30, respectively), and a singlet assigned to the methyl group attached directly to the nitrogen (δ 2.82). The $^{31}P\{^{1}H\}$ NMR spectrum shows one peak (δ 21.29) consistent with equivalent phosphines. This product showed similar solubility properties to **2a** and **3a**. Attempts to isolate it were not successful.

The addition of Me_3SiOTf to a solution of **1a** with in CD_2Cl_2 lead to an immediate change in color from yellow to purple. The $^{31}P\{^{1}H\}$ NMR spectrum showed the following product distribution: new species (61%), **3a** (17%), with other impurities including, **2a** and **4a**, accounting for the balance. The formation of Me_3SiH was also observed. The new species is also consistent with an aminocarbyne complex. The ^{1}H NMR spectrum of the putative $[Re(CNtBu)_2(CN(SiMe_3)tBu)(PCy_3)_2]^+$ exhibits a triplet (δ -5.66, J_{HP} = 26.3 Hz), two singlets, one for each of the *tert*-butyl groups, in a 2:1 ratio (δ 1.45, 1.33, respectively). A singlet of appropriate intensity is tentatively assigned to the nitrogen-bound trimethylsilyl group (δ 0.06). The $^{31}P\{^{1}H\}$ NMR spectrum shows one peak (δ 16.6) consistent with equivalent phosphines.

The addition of excess $(CPh_3)BAr_f$ to a solution of **1a** in CD_2Cl_2 lead to an immediate change in color from yellow to rust brown. Complex **2a** (80%) and **3a** (20%) are the only products detected by $^{31}P\{^{1}H\}$ NMR spectroscopy. The ^{1}H NMR spectrum indicated that Gomberg's dimer and the 17-electron complex $[Re(CNtBu)_3(PCy_3)_2Cl]^+$

(**9a**, see chapter 2) are also formed in significant quantities. Triphenylmethane was not detected. This contrasts with the reaction of **1b** with $(CPh_3)BAr_f$ which forms primarily triphenyl-methane. Very little Gomberg's dimer, **2b**, and $[Re(CN\textit{t}Bu)_3(PPh_3)_2Cl]^+$, are detected by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The major product is consistent with the otherwise elusive $[Re(CN\textit{t}Bu)_3(PPh_3)_2]^+$ (**3b**). The ^1H NMR spectrum exhibits two broad singlets ($\nu_{1/2} = 7$ Hz), one for each of the *tert*-butyl groups, in a 1:2 ratio (δ 1.11, 1.03, respectively). The $^{31}P\{^1H\}$ NMR spectrum shows one peak (δ 23.5) consistent with equivalent phosphines. This species is observed to decompose in CD_2Cl_2 over several days to form **4b**, $[Re(CN\textit{t}Bu)_3(PPh_3)_3]^+$, as well as other unidentified products.

Hydrogen Binding Competition Studies.[18] The affinity of hydrogen for $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ relative to the carbonyl analog, $[Re(CO)_3(PCy_3)_2]^+$, was determined by a direct competition study in CD_2Cl_2 (eq 1.3).



Equation 1.3

Complex **3a-BAr$_f$** and [Re(CO)$_3$(PCy$_3$)$_2$]BAr$_f$ (1 equivalent) were both placed in a screwcap NMR tube. The solids were exposed to H$_2$ (1 atm) till they lost their color. After removing excess H$_2$ at 77 K *in vacuo*, methylene chloride-*d*$_2$ was vacuum transferred into the tube. The headspace was back-filled with argon (1.1 atm) at 298 K. Figures 1.3 and 1.4 show the ^{31}P{^{1}H} NMR spectra and ^{1}H NMR spectra, respectively, of the solution at various hydrogen concentrations. The initial solution shows ^{1}H and ^{31}P{^{1}H} NMR resonances corresponding to **2a**, [Re(CO)$_3$(PCy$_3$)$_2$(H$_2$)]$^+$, and [Re(CO)$_3$(PCy$_3$)$_2$]$^+$. Bound hydrogen was gradually removed by freeze-pump-thaw technique. Significantly, the resonances corresponding to [Re(CO)$_3$(PCy$_3$)$_2$(H$_2$)]$^+$ completely disappeared before any resonances corresponding to **3a** were observed to grow in.

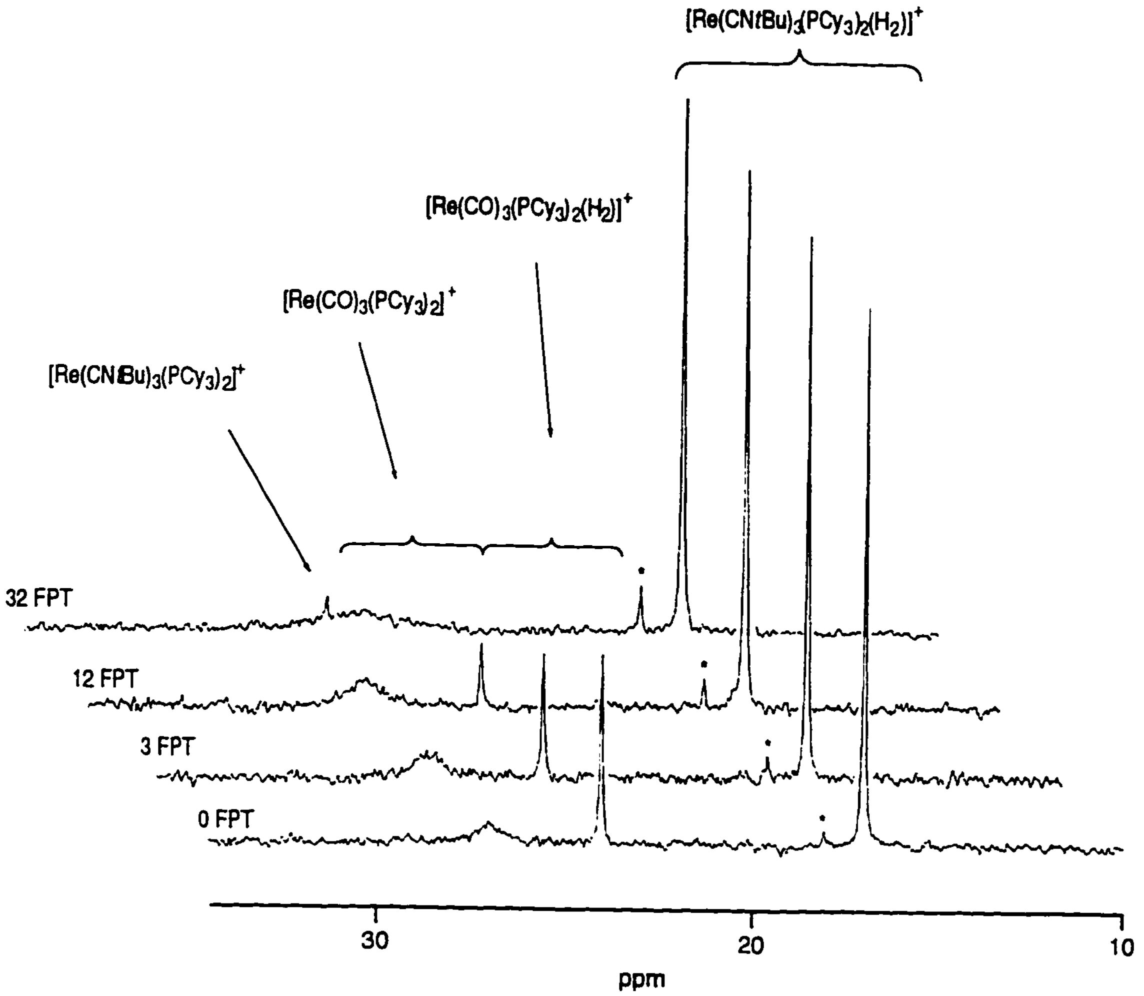


Figure 1.3 $^{31}P\{^{1}H\}$ NMR spectra of a solution of $[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]^+$ (**2a**) and $[Re(CO)_3(PCy_3)_2(H_2)]^+$ as a function of H_2 concentration (FPT cycles). (* corresponds to the decomposition product $[Re(CO)_4(PCy_3)_2]^+$)

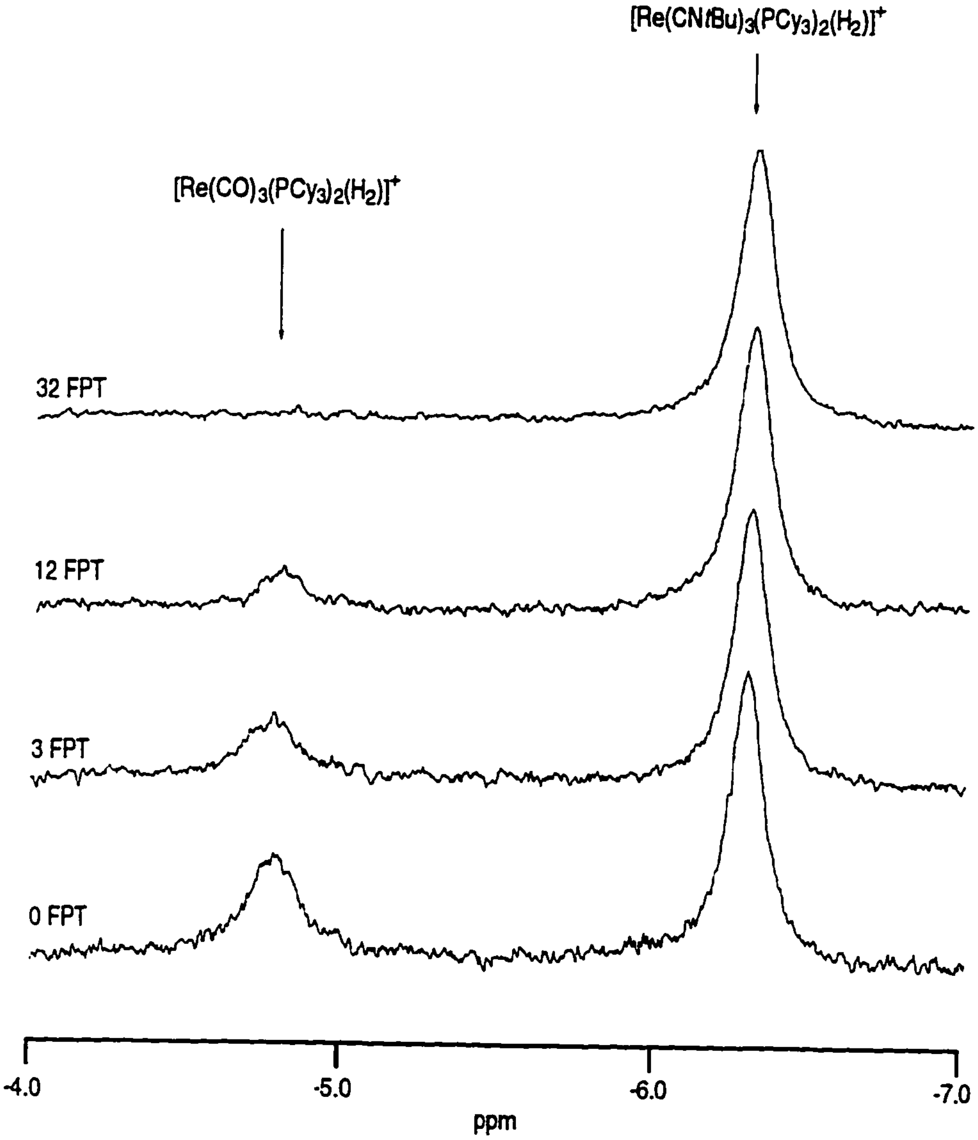
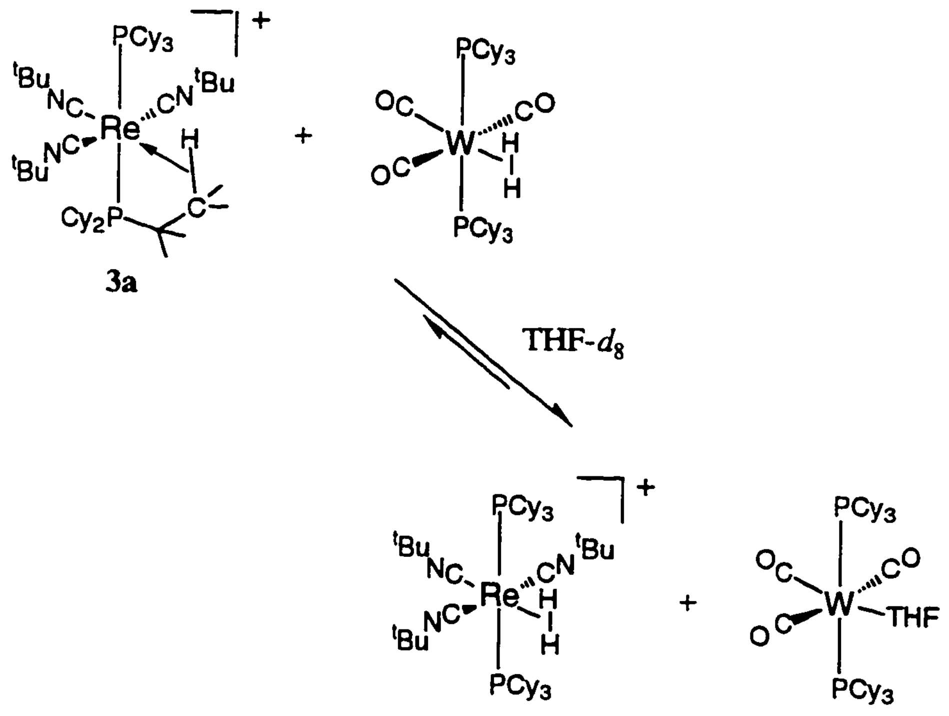


Figure 1.4 Partial ^{1}H NMR spectra of a solution of $[Re(CNtBu)_3(PCy_3)_2(H_2)]^+$ **(2a)** and $[Re(CO)_3(PCy_3)_2(H_2)]^+$ as a function of H_2 concentration (FPT cycles).

Once most of the bound hydrogen was removed from both **2a** and $[Re(CO)_3(PCy_3)_2(H_2)]^+$, the experiment was reversed. The hydrogen concentration was slowly increased. The ^1H and $^{31}P\{^1H\}$ NMR spectra show that **2a** grows in completely, before $[Re(CO)_3(PCy_3)_2(H_2)]^+$ is detected.

A similar experiment, conducted in THF-d_8, determined the affinity of H_2 for $[Re(CN\mathit{t}Bu)_3(PCy_3)_2]^+$ relative to the tungsten carbonyl THF complex, $W(CO)_3(PCy_3)_2(THF)$ (eq 1.4).



3a

2a

Equation 1.4

Complex **3a** and $W(CO)_3(PCy_3)_2$ (1 equivalent) were both placed in a screwcap NMR tube. The solids were exposed to H_2 (1 atm) till they lost their dark color. Unbound H_2 was removed at 77 K before THF-d_8 was vacuum transferred into the tube. The headspace was back-filled with argon (1.1 atm) at 298 K. The initial solution is dark purple[19] and shows ^1H and $^{31}P\{^1H\}$ NMR resonances corresponding to **2a**, $W(CO)_3(PCy_3)_2(H_2)$,[20] and $W(CO)_3(PCy_3)_2(THF)$. Bound hydrogen was gradually removed by several freeze-pump-thaw cycles. Significantly, the resonances corresponding to $W(CO)_3(PCy_3)_2(H_2)$ completely disappeared before any resonances corresponding to **3a** were observed to grow in.

Once most of the bound hydrogen was removed from both complexes, **2a** and $W(CO)_3(PCy_3)_2(H_2)$, the experiment was reversed. The hydrogen concentration was slowly increased. The ^1H and $^{31}P\{^1H\}$ NMR spectra show that **2a** grows in completely, before any $W(CO)_3(PCy_3)_2(H_2)$ is detected.

H_2/D_2 Exchange and the Formation of HD. Both dihydrogen complexes, $[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]^+$ (**2a**) and $[Re(CN\textit{t}Bu)_3(PPh_3)_2(H_2)]^+$ (**2b**), were observed to incorporate D_2 into the dihydrogen site when placed under D_2 gas. They also rapidly scramble the isotopes to form both free and bound HD. The ^1H NMR isotope shifts for the dihydrogen protons of **2a**-d_1 and **2b**-d_1 were upfield of **2a** and **2b** by 50 ppb. In addition, **2a** and **2b**, upon incorporating deuterium into the dihydrogen site, display an isotope shift in the protons of the isonitrile ligand *trans* to the dihydrogen ligand. This six-bond isotopic shift is downfield by *ca.* 8 ppb for **2** → **2**-d_2. The shift for **2** → **2**-d_1 was too small to resolve. The isonitrile ligands *cis* to the dihydrogen ligand are not observed to shift upon isotopic substitution at the dihydrogen ligand.

In the case of **2a** and **2b**, it was possible to simultaneously observe all three isotopomers (**2**, **2**-d_1, and **2**-d_2) by $^{31}P\{^1H\}$ NMR spectroscopy. For the incorporation of one deuterium into **2a** and **2b**, the upfield isotope shifts are 30 and 39 ppb, respectively. The incorporation of a second deuterium results in an additional upfield isotope shift of 30 ppb for both **2a** and **2b**. Significantly, when the reaction of **2** (either

2a or **2b**) with D_2 (*ca.* 1 eq) in CD_2Cl_2 was monitored over time (Figure 1.5), the peak corresponding to **2**-d_2 was usually observed to grow in before the peak for **2**-d_1.

The reverse reaction, the reaction of **2a**-d_2 with H_2, has also been monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Consistent with the above experiment, the peak corresponding to **2a** was observed to grow in before that corresponding to **2a**-d_1.

Statistically one would expect the final product distribution for the reaction of **2** with one equivalent of H_2 to be 1:2:1 for **2**:**2**-d_1:**2**-d_2. In these reactions of **2a**, ***but not*** **2b**, the formation of the d_1 species was often observed to slow down over time, and eventually stop before the expected product distribution was achieved.

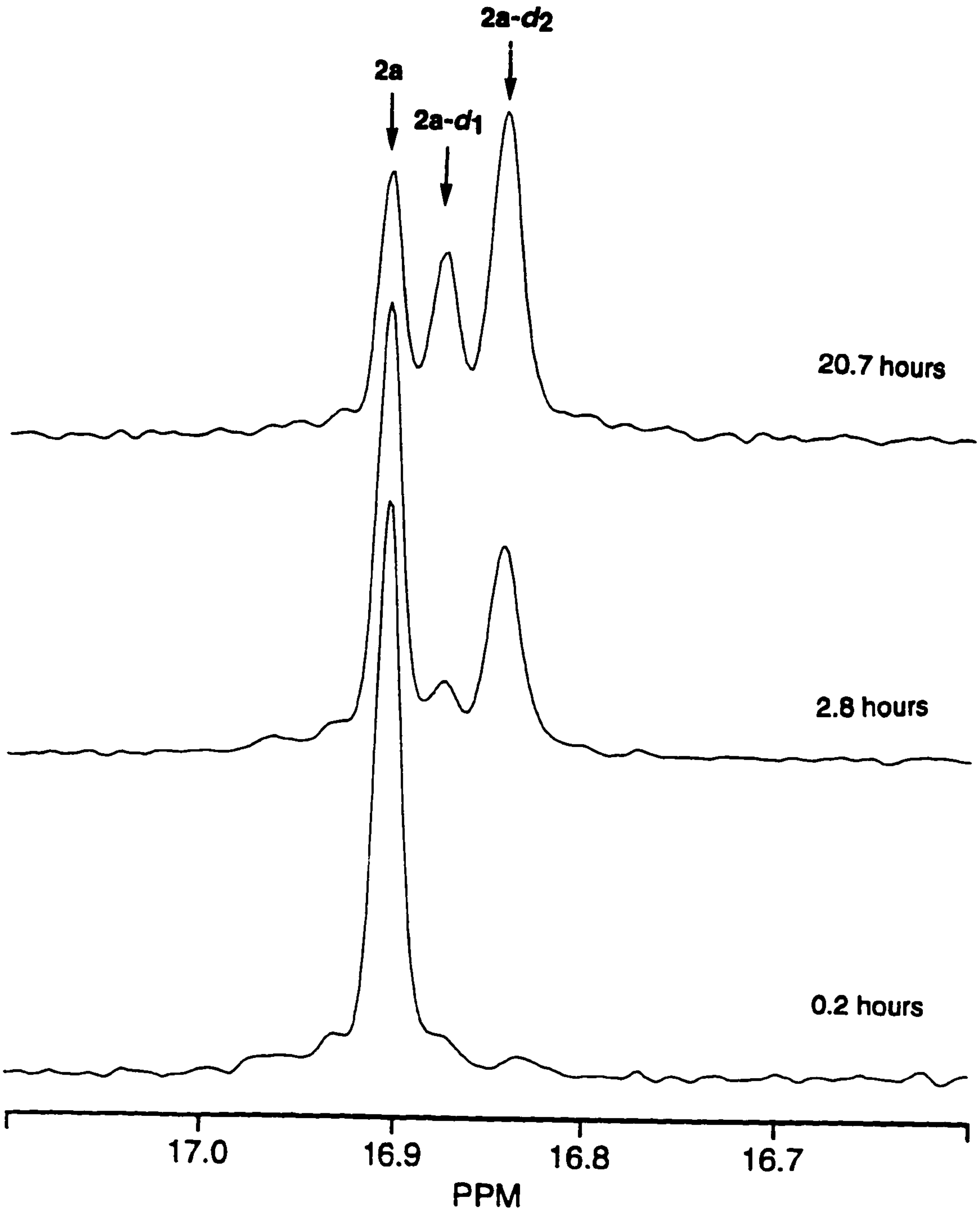


Figure 1.5 81-MHz $^{31}P\{^1H\}$ NMR spectra of **2a**, **2a**-d_1, and **2a**-d_2 as a function of time for the reaction of **2a** with roughly one equivalent of deuterium gas at 298 K.

Discussion

Formation of the Dihydrogen Complex. Protonation of neutral hydrides is the most commonly employed strategy to synthesize dihydrogen complexes.[2] Still, the protonation of $Re(CNtBu)_3(PR_3)_2H$ (**1a**, **1b**) to give the dihydrogen complex, $[Re(CNtBu)_3(PR_3)_2(H_2)]^+$ (**2a**, **2b**) was not entirely expected. With isonitrile coligands, the potential for protonation at the nitrogen of the coordinated isonitrile is great, especially in cases where the ν(C≡N) frequency is low (< 2000 cm^{-1}).[21,22] This situation certainly applies to **1a** (1928 cm^{-1}) and **1b** (1995, 1900 cm^{-1}). Low C≡N stretching frequencies are diagnostic of considerable metal to ligand ($d \rightarrow \pi^*$) backbonding leading to relatively electron rich isonitrile ligands. Protonation at the isonitrile ligands leads to amino-carbyne complexes, of which there are many examples.[23] A particularly relevant example to this chemistry is the reaction, $Re(CNtBu)_3(PMe_3)_2Cl + HBF_4{\cdot}OEt_2 \longrightarrow [Re(CNtBu)_2(CN(H)tBu)(PMe_3)_2Cl]BF_4$ reported by Wilkinson *et al.*.[24] Switching the X group from Cl to H is all that is required to change the site of protonation from the isonitrile nitrogen to the Re–H bond. Simpson and Conroy-Lewis also observed that protonation of a complex containing both a hydride and an isonitrile ligand, $CpRu(CNtBu)(PPh_3)H$, yields a dihydrogen compound, $[CpRu(CNtBu)(PPh_3)(H_2)]^+$.[7] Even when no M–H bond is present, protonation at the isonitrile is not always observed. $Fe(CNtBu)_5$ is reported to protonate at the metal center to yield $[Fe(CNtBu)_5H]^+$.[25] Walton and coworkers have reported a system in which protonation of a complex containing both hydride and isonitrile ligands, $Re(CNtBu)(PPh_3)_3H_3$, in acetonitrile, leads to the formation of an amino carbyne complex, $[Re(CN(H)tBu)(NCMe)(PPh_3)_3H_2]^{2+}$.[22] This result does not necessarily imply that the isonitrile ligands are more basic than the Re–H bonds in this system. Initial protonation may still be occurring at the metal hydrogen bond.

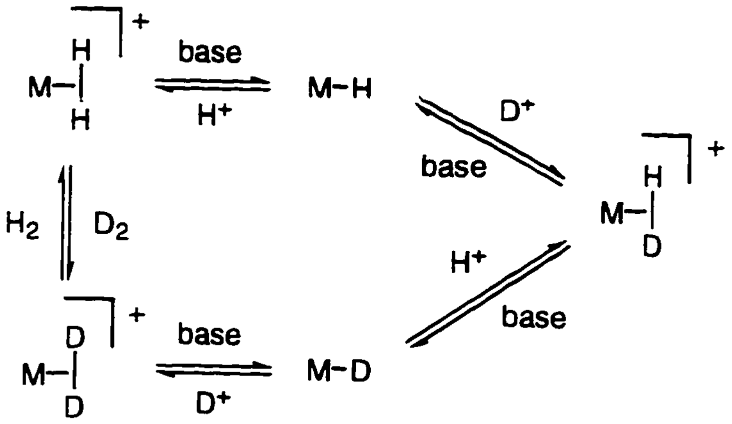
For electrophiles other than protons (MeOTf, Me_3SiOTf), attack at the isonitrile nitrogen of $Re(CN\textit{t}Bu)_3(PCy_3)_2H$ (**1a**) is observed. The product distribution correlates well with the size of the electrophile. The reaction of **1a** with the smallest electrophile, H^+, yields **2a** exclusively. For the reaction of **1a** with a larger electrophile, Me^+, the product of M–H bond attack, **3a** (69%), is no longer exclusively formed. The other primary product is the aminocarbyne, $[Re(CN\textit{t}Bu)_2(CN(Me)\textit{t}Bu)(PCy_3)_2]^+$, which accounts for 23% of the yield. With an even larger electrophile, Me_3Si^+, the formation of the M–H bond attack product is further disfavored. Complex **3a** now only accounts for 17% of the product, while the aminocarbyne, $[Re(CN\textit{t}Bu)_2(CN(SiMe_3)\textit{t}Bu)(PCy_3)_2]^+$, accounts for 61%. For Me^+, Me_3Si^+, and possibly for H^+,[26] the product distribution is most likely under kinetic control. Formation of either CH_4 or Me_3SiH is no doubt irreversible. It seems plausible then, that while the most basic site in **1a** is most likely the M–H bond, larger electrophiles may not be able to attack there on account of the sterically demanding PCy_3 ligands (cone angle = 170°).[27]

Trityl cation is known to act both as a hydride abstracting agent and a one-electron oxidant.[28] With **1a** and **1b**, it displays both types of reactivity. The reaction of **1a** with $(CPh_3)BAr_f$ is most consistent with one-electron oxidation, especially since CPh_3H was not detected, and **3b** was not the primary rhenium product. The formation of both **2a** and **3a** is most consistent with an oxidatively-induced proton-transfer reaction of the type first reported by Ryan, Tilset, and Parker.[29] Under ideal conditions, this type of reaction should yield **2a** and **3a** in a 1:1 ratio. Presumably further oxidation of either **2a** or **3a** by excess $(CPh_3)BAr_f$ or solvent yields the observed 17-electron $[Re(CN\textit{t}Bu)_3(PCy_3)_2Cl]^+$ (**9a**, see chapter 2).

In contrast, the reaction of $(CPh_3)BAr_f$ with **1b** forms primarily $CHPh_3$ and a species believed to be $[Re(CN\textit{t}Bu)_3(PPh_3)_2]^+$ (**3b**). These products are most consistent with CPh_3^+ abstracting H^- from **1b**. The broad isonitrile resonances observed for **3b** in the ^1H NMR spectrum are evidence for a dynamic ligand set. Presumably the unique isonitrile exchanges with the two equivalent isonitriles. Such an isonitrile rearrangement was clearly observed and studied for the analogous complex, **3a** (chapter 3). The difference in reactivity between **1a** and **1b** towards trityl cation is consistent with **1b** containing less basic phosphines, and therefore being more difficult to oxidize. It is also consistent with **1a** containing more sterically demanding PCy_3 ligands which are expected to hinder hydride abstraction, but not outer-sphere electron transfer.

Acidity of the Dihydrogen Complex (2a). The acidity of $[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]^+$ (**2a**) is similar to its Group 6 carbonyl analogs. While simple amines fail to deprotonate either **2a** or $W(CO)_3(PCy_3)_2(H_2)$, both can be deprotonated by stronger bases such as alkoxides.[30] However, when carbonyls are substituted for isonitriles on Re, the complex becomes more acidic. For instance, the direct carbonyl analog, $[Re(CO)_3(PCy_3)_2(H_2)]^+$, can be deprotonated by 2,6-di-*tert*-butylpyridine.[31] Bianchini and coworkers report that $[Re(CO)_2(triphos)(H_2)]^+$ is deprotonated by NEt_3 in methylene chloride.[32] Similarly, group 8 dicationic analogs are also more acidic than **2a**. For example, Tilset and coworkers recently reported that $[Os(NCMe)_3(P\textit{i}Pr_3)_2(H_2)]^{2+}$ could be deprotonated with piperidine.[33] These observations are in agreement with the basic understanding that cationic dihydrogen complexes are more acidic than neutral ones, and that complexes with the more electron withdrawing set of coligands (carbonyl > isonitrile > acetonitrile) are also more acidic.

Isotope Exchange Reactions. There has been much speculation on the mechanism by which metal-(H_2) complexes react with D_2 to form the metal-(HD) isotopomer.[34,35] One of the most plausible mechanisms is shown in Scheme 1.



Scheme 1

This mechanism necessitates facile H_2/D_2 exchange, a heterolytically activated dihydrogen ligand, as well as the presence of base. Complexes **2a** and **2b** provide a unique opportunity to evaluate this mechanism, since it is possible to spectroscopically resolve all three isotopomers, **2**, **2**-d_1, and **2**-d_2, by ^{31}P NMR (Figure 1.5). As long as base catalysis is slow, the mechanism predicts that when **2** reacts with D_2, the first newly observed species should be **2**-d_2, not **2**-d_1. The reactions of either **2a** or **2b** with D_2 represent the first reported example where the d_1 species usually grows in first. Presumably this is caused by these dihydrogen complexes being weak acids (*vide supra*). Since the quantity of adventitious base may vary from sample to sample, it not surprising that the d_1 species is not always the first to grow in.

Statistically one would expect the final product distribution for the reaction of **2** with one equivalent of D_2 to be 1:2:1 for **2**:**2**-d_1:**2**-d_2. In the reaction of **2a** *but not* **2b** with H_2, the formation of **2a**-d_1 often stopped completely before the expected product distribution was achieved. One possible explanation, consistent with the proposed mechanism, is that the base catalyst responsible for the atom exchange is decomposing. The neutral hydride **1a** is a reasonable base-catalyst candidate that would also be subject to decomposition under the reaction conditions. **1a** reacts with H_2 in methylene chloride to give $[Re(CNtBu)_3(PCy_3)_2(H_2)]Cl$ **(2a-Cl)** (see chapter 2). This reaction occurs on the same time scale as H/D exchange, and would effectively create a complex that was no longer a competent base catalyst. For the PPh_3 system, the reaction of **1b** with methylene chloride yields $Re(CNtBu)_3(PPh_3)_2Cl$, which does not react with H_2, but is presumably still a competent enough base to effect H/D exchange.

Water has also been considered a possible adventitious base for H/D exchange reactions;[8,35] however, considering that **2a** has a pK_a corresponding to that of an alcohol (*vide supra*), this is not considered very likely for either **2a** or **2b**.

The agostic complex. Agostic interactions are convincingly demonstrated for $[Re(CO)_3(PCy_3)_2]^+$,[8] $W(CO)_3(PCy_3)_2$,[36] and $W(CO)_3(PiPr_3)_2$[36] in the solid state. The distances from the metal center to the carbon involved in the M···H–C interaction vary from 2.89, 2.94, and 3.03 Å, respectively. Based on its similar ligand set, $[Re(CNtBu)_3(PCy_3)_2]^+$ **(3a)** is also considered to be an agostic complex. The ^1H and $^{31}P\{^1H\}$ NMR spectra of **3a-OTf**, **3a-BF$_4$**, and **3a-BAr$_f$** were identical, confirming the lack of coordination by the counteranion. Significant solvent coordination by methylene chloride or THF also appears to be absent. Elemental analysis clearly demonstrates this for **3a** in the solid state; recrystalization of **3a-BF$_4$** from THF yields analytically pure compound. In solution, the lack of significant solvent coordination is ruled out by the very minor ^{31}P-chemical shift difference ($\Delta\delta = 0.4$) observed for **3a** dissolved in the solvents, CD_2Cl_2 and THF-d_8 (Table C.2). This contrasts with a much larger chemical shift change for **3a** dissolved in the coordinating solvent CD_3CN. In this solvent, the acetonitrile adduct $[Re(CNtBu)_3(PCy_3)_2(NCCD_3)]^+$ forms as evidenced both by the color change from purple to yellow, as well as by the ^{31}P-chemical shift having moved 19.6 ppm upfield of **3a** dissolved in THF. It is worth noting that this same species is formed when the dihydrogen complex, **2a**, is dissolved in CD_3CN, indicating that bound H_2 is readily displaced by acetonitrile.

This contrasts with the observations by Heinekey and Radzewich for $[Re(CO)_3(PCy_3)_2]^+$. In this system, the $^{31}P\{^1H\}$ NMR resonance shifts considerably more ($\Delta\delta = 6.6$) upon changing the solvent from CD_2Cl_2 to THF-d_8. Consistent with the chemical shift change, the colors of the solutions are also different.[37] $[Re(CO)_3(PCy_3)_2]^+$ is an orange solid and makes an orange solution in methylene chloride. When dissolved in THF-d_8, however, the color changes to pale yellow, strongly implying that it should now be formulated as $[Re(CO)_3(PCy_3)_2(THF)]^+$.

Competition Study 1. Of the many reported dihydrogen complexes, only a small number also yield a stable coordinatively unsaturated complex. In some cases, this is caused by molecular hydrogen binding so strongly that the presumably severe conditions required to remove it would lead to decomposition for reasons other than H_2 loss. For example, the dicationic complex, $[Os(bpy)(PPh_3)_2(CO)(H_2)]^{2+}$, reported by Heinekey and Luther,[3] did not exchange with D_2 over a period of months in CD_2Cl_2 solution. The tight binding of H_2 is consistent with the long H-H bond distance (1.05 Å, determined by the $T_{1(min)}$ method).[11] The H–H distances for **2a** and **2b** (0.80 Å both, $T_{1(min)}$ method) are considerably shorter, and the H_2 ligand is considerably less tightly bound. For the Os example, it is therefore not known whether a coordinatively unsaturated 16-electron complex is viable, or not. We have conducted competition studies comparing the H_2 binding affinity of $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ with two complexes in which both the dihydrogen complex and the agostic complex are stable. $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ has a higher affinity for H_2 than $[Re(CO)_3(PCy_3)_2]^+$ in CD_2Cl_2, and $W(CO)_3(PCy_3)_2$ in THF-d_8.

The results comparing **3a** and $[Re(CO)_3(PCy_3)_2]^+$ (eq 1.3) are unambiguous, since there is no indication that either of the agostic complexes are solvated by methylene chloride. Molecular hydrogen clearly binds preferentially to **3a**.[38] Complex **3a** and $[Re(CO)_3(PCy_3)_2(H_2)]^+$ are never detected in solution at the same time. Assuming a minimum detection limit of 1% for the ^1H and $^{31}P\{^1H\}$ NMR spectra, a lower limit for the equilibrium constant can be calculated for the reaction shown in equation 1.3. The *Keq* is calculated to be ≥ 9,800, which corresponds to $\Delta G^\circ_{298} \leq -5.4$ kcal/mole. We therefore are able to conclude that, at 298 K, H_2 prefers $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ to $[Re(CO)_3(PCy_3)_2]^+$ by at least 5.4 kcal/mole.

The obvious difference between the complexes is the π-acidity of their respective coligands. CO is a much better π-acid than CNR.[39] Since the H_2 ligand is known to act not just as a σ-donor but also as a π-acceptor,[2,40,41] presumably the difference of its π-bond strengths in **2a** and $[Re(CO)_3(PCy_3)_2(H_2)]^+$ is accounting for these observations. In the presence of the less π-acidic CN*t*Bu coligands, there is much more accessible π-electron density for donation into the σ* orbital of the H_2 ligand. This can only be expected to strengthen its overall binding to the metal center.

Competition Study 2. Observations have been made which strongly suggest that $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ binds H_2 more strongly than $W(CO)_3(PCy_3)_2$. At 298 K, the ^1H NMR resonances of $W(CO)_3(PCy_3)_2(H_2)$ and free H_2 exhibit broadening due to exchange, both in THF-d_8[42] and toluene-d_8 (T ≥ -15 °C),[43] which indicates that the W complex is significantly labile towards H_2 loss. **2a** and free H_2 do not exhibit exchange broadening in the ^1H NMR spectrum (CD_2Cl_2 or THF-d_8), even at higher temperatures (40° C).[44] These observations are consistent with the qualitative conclusion that **3a** binds H_2 more strongly than $W(CO)_3(PCy_3)_2$. We had a great desire to obtain some direct evidence for this, and to possibly quantify the difference.

Determining an appropriate solvent for this study was a challenge. $W(CO)_3(PCy_3)_2$ binds THF and reacts with methylene chloride.[36] Furthermore, **3a** is not soluble in non-polar solvents. A direct competition study between **3a** and $W(CO)_3(PCy_3)_2$ was therefore not possible. However, since the thermodynamic parameters for the reaction $W(CO)_3(PCy_3)_2 + THF \rightleftharpoons W(CO)_3(PCy_3)_2THF$ in toluene are known ($\Delta H^\circ = -8.6 \pm 0.7$ kcal, $\Delta S^\circ = -31.0 \pm 2.5$ e.u., $\Delta G^\circ_{298} = 0.64 \pm 1.4$ kcal/mol),[35] we were able to *indirectly* compare the H_2 binding ability of **3a** and $W(CO)_3(PCy_3)_2$ by *directly* comparing the H_2 binding abilities of **3a** and $W(CO)_3(PCy_3)_2THF$. (At 298 K, in 40 M THF, the majority of $W(CO)_3(PCy_3)_2$ is properly considered to be the THF adduct. Since $K_{eq} = 0.34\ M^{-1}$, the ratio $W(CO)_3(PCy_3)_2(THF){:}W(CO)_3(PCy_3)_2$ is 13.6:1. At these high concentrations of THF, the [THF] stays approximately constant and can be included into the equilibrium constant. The equilibrium constant for $W(CO)_3(PCy_3)_2 \rightleftharpoons W(CO)_3(PCy_3)_2(THF)$ in THF is 13.6, which corresponds to a $\Delta G^\circ_{298} = -1.55 \pm 1.4$ kcal/mol) Since **3a** and $W(CO)_3(PCy_3)_2(H_2)$ were never observed to be simultaneously detectable, we can set a lower limit on the equilibrium constant for the reaction shown in eq 1.4. (Assuming a detection limit of 1%, K_{eq} is calculated to be $\geq 9{,}800$, which corresponds to $\Delta G^\circ_{298} \leq -5.4$ kcal/mole.) By adding equations 1.5 and 1.6 shown in Table 1.3 we can get the upper limit for the free energy change of the reaction we are interested in, namely equation 1.7.

Table 1.3 Thermodynamic Parameters for the Reaction of **3a** with W(H_2).

	$\Delta G°_{298}$	eq
3a + W(H_2) $\rightleftharpoons$ **2a** + W(THF)	≤ -5.4	(1.5)
+ W(THF) $\rightleftharpoons$ W	1.55	(1.6)
3a + W(H_2) $\rightleftharpoons$ **2a** + W	≤ -3.9	(1.7)

W = $W(CO)_3(PCy_3)_2$, W(H_2) = $W(CO)_3(PCy_3)_2(H_2)$, W(THF) = $W(CO)_3(PCy_3)_2$(THF)

We are now able to directly compare the H_2 binding affinity of $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ with $W(CO)_3(PCy_3)_2$. We find that, at 298 K, H_2 prefers $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ to $W(CO)_3(PCy_3)_2$ by at least 3.9 kcal/mole. Presumably, the entropy change for the reaction $W(CO)_3(PCy_3)_2(H_2) + [Re(CN\textit{t}Bu)_3(PCy_3)_2]^+ \rightleftharpoons W(CO)_3(PCy_3)_2 + [Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]^+$ is approximately zero. It is therefore reasonable to assert that that H_2 binds stronger to $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ than to $W(CO)_3(PCy_3)_2$ by 3.9 kcal/mole.

Experimental Section

General procedures: All reactions were performed under vacuum or argon atmosphere using standard Schlenk, dry-box, and high-vacuum techniques. The solvents pentane, heptane, tetrahydrofuran, toluene, and diethyl ether were distilled from Na/K and benzophenone under oxygen- and water-free N_2 (deoxygenated over BASF R3-11 CuO catalyst and dried by passing through a column of P_2O_5). Methylene chloride was distilled from P_2O_5. All deuterated solvents were obtained from Cambridge Isotope Laboratories. Tetrahydrofuran-d_8, toluene-d_8, and benzene-d_6 were dried over benzophenone ketyl in an evacuated vessel. Acetonitrile-d_3, chloroform-d_1, and methylene chloride-d_2 were dried and stored over calcium hydride in an evacuated vessel.

All other reagents were obtained from commercial sources and used without further purification.

Infrared spectra were obtained on a Perkin Elmer 1600 Series FTIR. Mass spectra were obtained on a Kratos Profile sector instrument. NMR spectra were obtained using a Bruker AC-200, AF-300, or WM-500 spectrometer. All NMR tube reactions were conducted in flame sealed tubes or J. Young® screw-cap tubes. Variable temperature ^1H NMR experiments were conducted using a Bruker B-VT 1000 temperature control module with a copper-constantan thermocouple. Proton T_1 studies were performed using the standard inversion recovery 180°-τ-90° pulse sequence.[45] Temperature calibration was accomplished following the Van Geet methanol calibration method.[46] ^1H NMR spectra were referenced at all temperatures to the internal residual hydrogen signal of the deuterated solvent relative to TMS. $^{31}P\{^1H\}$ NMR was referenced to an external standard of 85% H_3PO_4.

Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, BC.

$Re(PCy_3)_2H_7$,[47] $Re(PPh_3)_2H_7$,[10] $[Re(CO)_3(PCy_3)_2]BAr_f$,[8] $W(CO)_3(PCy_3)_2$,[48] $HBAr_f{\cdot}2Et_2O$[4], and $(CPh_3)BAr_f$[49] were prepared by reported procedures.

$Re(CN\mathit{t}Bu)_3(PCy_3)_2H$ (1a). $Re(PCy_3)_2H_7$ (4.86 g, 6.44 mmol), CN*t*Bu (3.2 mL, 28 mmol), and toluene (200 mL) were stirred under Ar atmosphere for 48 h at 45 °C. The solution turned deep dark red, and maintained this color throughout the reaction. The deep red color is attributed to using less than completely pure $Re(PCy_3)_2H_7$. Upon addition of pentane and subsequent filtration, a rust colored impurity of unknown identity was removed. The solvents were removed under vacuum. The remaining oily solid was triturated and washed with acetone resulting in a yellow slurry. Upon filtration, yellow microcrystals were collected on a frit and washed with acetone (3 × 10 mL). Yield: 5.01 g (5.02 mmol, 78%). IR (Nujol) ν(C≡N) 1928 (m, br) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 2.2–1.2 (br, 66H), 1.31 (s, 18H), 1.28 (s, 9H), -7.49 (t, J_{PH} = 20.4 Hz, 1H); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 28.5 (s); ^{13}C{^{1}H} NMR (toluene-d$_8$) δ 173.9 (br t, *C*NR), 166.8 (t, J_{CP} = 10 Hz, *C*NR), 54.1 (s, CN*C*(CH$_3$)$_3$), 53.6 (s, CN*C*(CH$_3$)$_3$), 38.1 (br, P-α-*C*), 32.0 (s, CNC(*C*H$_3$)$_3$), 31.9 (s, CNC(*C*H$_3$)$_3$) 30.3 (s, P-γ-*C*), 28.6 (t, J_{PC} = 4 Hz, P-β-*C*), 27.9 (s, P-δ-*C*). Anal. Calcd (found): C, 61.41 (61.07); H, 9.50 (9.13); N, 4.21 (4.12).

Re(CN*t*Bu)$_3$(PPh$_3$)$_2$H (1b). This preparation is more direct than the one originally reported by Jones and Maguire.[10] Re(PPh$_3$)$_2$H$_7$ (0.30 g, 0.42 mmol), *tert*-butyl-isonitrile (0.57 mL, 5.0 mmol), and benzene (5 mL) were stirred under Ar at 65 °C for 2 hours. The product was collected on a frit under air, washed with pentane (2 × 10 mL), and stored in the dry-box. Yield: 282 mg (0.29 mmol, 70%). IR (Nujol) ν(C$\equiv$N) 1995 (m, br) cm^{-1}, 1900 (m, br); ^{1}H NMR (C$_6$D$_6$) agrees with that reported by Jones and Maguire.[10] ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 32.7 (s).

[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(η^2-H$_2$)]X (X$^-$ = BF$_4^-$, OTf$^-$, BAr$_f^-$) (2a). For **2a-BF$_4$**, **1a** (248 mg, 0.248 mmol) was dissolved in Et$_2$O (20 mL). Under a counter-flow of argon, HBF$_4$·OEt$_2$ (42 µL, 0.29 mmol) was added via Teflon tubing attached to a gas-tight syringe. A white precipitate immediately formed. The slurry was cannula-transferred onto a glass frit and filtered. The collected product was washed with diethyl ether (3 × 5 mL), and dried under a stream of hydrogen. Yield: 222 mg (0.205 mmol, 82.6%). Preparation of **2a-OTF** was achieved by analogous technique, and isolated in similar yield. For **2a-BAr$_f$** (which has a higher solubility in diethyl ether), Re(CN*t*Bu)$_3$(PCy$_3$)$_2$H (127 mg, 0.127 mmol) and HBAr$_f$·(OEt$_2$)$_2$ (123 mg, 0.121 mmol) were combined as solids and then dissolved in 5 mL diethyl ether. This resulted in a yellow slurry, which turned white after 1 h of stirring at room temperature. The slurry was cannula-transferred onto a glass frit, filtered, but not washed. Yield: 149 mg (8.03 × 10^{-2} mmol, 66.4%). Attempted preparation of **2a-Cl** was not possible. Loss of H$_2$ from

2a-Cl to form the neutral chloride, **2a**, was observed to be irreversible in the solid state. ^{1}H NMR and ^{31}P NMR chemical shifts of **2a** were observed to be identical, regardless of counteranion. This observation also applies to **2a-Cl**, and **2a-BAr$_f$**, which were observed by NMR, but not isolated. IR (Nujol) $\nu(C{\equiv}N)$ 2120 (w), 2073.1 (sh), 2023 (m) cm^{-1}; IR (CH_2Cl_2) $\nu(C{\equiv}N)$ 2124.8 (w), 2076 (m), 2030 (m); ^{1}H NMR (CD_2Cl_2) δ 2.2–1.2 (br, 66H), 1.41 (s, 9H), 1.37 (s, 18H), -6.30 (br, 2H); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) δ 16.9 (s); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) (obtained for **2a-BAr$_f$** and **2a-BF$_4$**) δ 148.1 (t, J_{CP} = 10 Hz, *C*NR), 146.1 (t, J_{CP} = 7 Hz, *C*NR), 57.1 (s, $CN\mathit{C}(CH_3)_3$), 56.7 (s, $CN\mathit{C}(CH_3)_3$), 37.3 (br, P-α-*C*), 31.3 (s, $CNC(\mathit{C}H_3)_3$), 30.6 (s, $CNC(\mathit{C}H_3)_3$) 30.2 (s, P-γ-*C*), 27.8 (t, J_{PC} = 4 Hz, P-β-*C*), 27.0 (s, P-δ-*C*). $T_{1(min)}$ = 8 msec (225 K, 300 MHz). Anal. for **2a-OTf**, Calcd (found): C, 54.42 (53.80); H, 8.34 (7.85); N, 3.66 (3.43).

$[Re(CN\mathit{t}Bu)_3(PPh_3)_2(\eta^2\text{-}H_2)]X$ (X^- = BF_4^-, BAr_f^-) (2b). For **2b-BAr$_f$**, **1b** (179 mg, 0.186 mmol) was dissolved in Et_2O (80 mL) under an H_2 atmosphere. A clear yellow solution was observed to form. $HBAr_f{\cdot}(OEt_2)_2$ (12.6 mg, 1.24×10^{-2} mmol) was separately dissolved in Et_2O (3 mL). The acid solution was transferred via Teflon cannula to the first solution under vigorous stirring. The yellow solution was observed to lose color. After reducing the solution to 4 mL under vacuum, pentane (20 mL) was added causing a white precipitate to form. The slurry was cannula-transferred onto a glass frit and filtered. An off-white solid was collected. The product was washed with pentane (3 × 10 mL) and dried under a stream of H_2. Yield: 173.5 mg. ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR show the solid to be approximately 80% **2b-BAr$_f$**. In contrast, NMR tube preparations of **2b-BAr$_f$** and **2b-BF$_4$** were clean and quantitative. ^{1}H NMR (cation portion) (CD_2Cl_2) δ 7.42 (br, 30H), 0.94 (s, 9H), 0.82 (s, 18H), -5.56 (br, 2H); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) δ 18.7 (s). $T_{1(min)}$ = 8 msec (207 K, 300 MHz).

[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]X (X$^-$ = BF$_4^-$, OTf$^-$, BAr$_f^-$) (3a). Coordinated H_2 was removed from **2a** by either exposing the white solids to dynamic vacuum (24 h, 23 °C), or by simply leaving them under Ar atmosphere in the dry-box (2 weeks). Removal of H_2 was monitored by observing the solids change color from white to dark purple. This reaction was observed to be quantitative, and it was not accompanied by any decomposition. Analytically pure **3a-BF$_4$** was obtained by recrystalization from THF. IR (Nujol) ν(C≡N) 2070 (sh), 2019 (m) cm^{-1}; IR (CH_2Cl_2) 2073 (m), 2024 (m) cm^{-1}. With exceptions made for the different anions, ^{1}H NMR, ^{13}C NMR, and ^{31}P{^{1}H} NMR chemical shifts of **3a-BF$_4$**, **3a-OTf**, and **3a-BAr$_f$** were observed to be identical. ^{1}H NMR (CD_2Cl_2) δ 2.62 (broad, 6H), 2.0–1.2 (br, 60H), 1.59 (s, 18H), 1.20 (s, 9H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 26.4 (s); ^{13}C{^{1}H} NMR (CD_2Cl_2) (for **3a-BF$_4$**) δ 160.1 (s, *C*NR), 57.4 (s, CN*C*(CH$_3$)$_3$), 39.2 (t, J_{PC} = 11 Hz P-α-*C*), 31.9 (s, CNC(*C*H$_3$)$_3$), 31.6 (s, CNC(*C*H$_3$)$_3$), 29.9 (s, P-γ-*C*), 27.9 (t, J_{PC} = 5 Hz, P-β-*C*), 26.6 (s, P-δ-*C*). Anal. for **3a-BF$_4$**, Calcd (found): C, 56.54 (56.30); H, 8.65 (8.81); N, 3.88 (3.77).

[Re(CN*t*Bu)$_4$(PCy$_3$)$_2$]BF$_4$ (4a-BF$_4$). **1a** (160 mg, 0.160 mmol) was slurried overnight in a methanol solution (30 mL) containing excess *tert*-butyl isonitrile (60 μL, 0.53 mmol). Slow bubble formation was observed during the first several hours. After 12 h, the solution had become pale-yellow and homogeneous. To this, a slurry of $NaBF_4$ (220 mg) in acetone (150 mL) was added via cannula. Everything dissolved upon stirring. The solvent was removed under vacuum, and the product was extracted with CH_2Cl_2 (2 × 25 mL) resulting in a yellow solution. Upon addition of diethyl ether (100 mL), a white precipitate formed. The precipitate was collected by filtration, and was washed with diethyl ether (2 × 15 mL). Yield: 168 mg (0.144 mmol, 82%). IR (Nujol) ν(C≡N) 2064 (sh), 2022 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.28 (broad virtual triplet, J_{HP} = 12 Hz, 6H), 2.0–1.3 (br, 60H), 1.46 (s, 36H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 5.6 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 149.0 (t, J_{CP} = 8 Hz, *C*NR), 56.8 (s, CN*C*(CH$_3$)$_3$), 37.2 (t,

J_{PC} = 10 Hz, P-α-*C*), 31.2 (s, CNC(CH_3)$_3$), 29.8 (s, P-γ-*C*), 27.7 (t, J_{PC} = 4 Hz, P-β-*C*), 26.9 (s, P-δ-*C*). Anal. Calcd (found): C, 57.66 (57.12); H, 8.82 (8.58); N, 4.80 (4.70).

X-ray Structure Determination of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(H$_2$)]BAr$_f$. Well-formed mostly colorless (pink surface coating) crystals of **2a-BAr$_f$** were grown at -20 °C from CH_2Cl_2. A crystal of small size (0.4 × 0.4 × 0.2 mm) coated with paratone was mounted using epoxy glue. Diffraction measurements were made at 183 K. The data was collected for a triclinic cell. There was no indication that the crystal would not provide adequate data. The density and the occupancy indicates that the choice of space group is probably correct. The number of data is large, and the peaks are fairly strong and well shaped. A high–chi reflection led to a poor absorption correction. The decay was normal. The data to parameter ratio was 10.3:1. The Laue merging R factor for the equivalent reflection was a poor 5%. The decay was less than 1%. Reduction of the data was carried out using XCAD4 and all further work was performed using the PC version of Siemen's SHELX PLUS PC.

The structure was solved primarily from difference maps with refinement on the Re obtained from the direct methods procedure. However, the structure did not refine. A final R of 13.6% with a GOF of 4.4 was obtained. The weighing scheme required a correction of 0.002. There are a number of non-positive-definite atoms, which indicates that the absorption correction may not have worked. An attempt was made to check this correction by sending out the data for external correction. This resulted in no improvements. A number of steps were taken to check the data but it appears either there was some problem in the crystal that was not indicated by the preliminary data collection steps or something led to an inconsistent data set.

The gross structure is most likely correct.

Table 1.4 Crystal Data and Parameters for **2a**.

Compound	**2a**
Molecular Formula	$[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]$ $BAr_f^- \cdot CH_2Cl_2$
Empirical Formula	$C_{84}H_{109}BCl_2F_{24}N_3P_2Re$
Color; Habit	Clear Plate
Crystal Size (mm)	0.4 × 0.4 × 0.2
Crystal System	Triclinic
Space Group	$P\bar{1}$
Unit Cell Dimensions	$\underline{a}$ = 13.007(2) Å $\underline{b}$ = 16.860(3) Å $\underline{c}$ = 21.010(3) Å α = 97.69(2)° β = 99.67(3)° γ = 93.19(2)°
Volume	4505.1(11) $Å^3$
Z	2
Formula weight	1946.4
Density(calc.)	1.435 Mg/m^3
Absorption Coefficient	1.536 mm^{-1}
F(000)	1960
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	183
Monochromator	graphite
2θ Range	2 to 50°
Scan Type	$2\theta-\theta$
Scan Speed	variable; 1.5 to 5.5°/min. in ω
Scan Range (ω)	0.80 + 0.35(tanθ)°
Reflections Collected	12399
Independent Reflections	11770 (R_{int} = 14.61%)
Observed Reflections	10202 ($F > 4.0\sigma(F)$)
# of Parameters Refined	994
R (observed data)	13.37%
R_w	20.73%
Goodness-of-fit	4.37

NOTES TO CHAPTER 1

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NMR spectrum. The resonance for free H_2, presumably having broadened into the baseline, was reproducibly undetectable.

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CHAPTER 2

The Displacement of Coordinated Halide by Hydrogen.

Introduction

The reactivity of metal chloride complexes is often determined by the stability of their M–Cl bond towards dissociation. The investigation of steric and electronic factors which can labilize these bonds is of importance in developing an understanding of the reactivity of such complexes, particularly in catalysis where vacant coordination sites are necessary for the activation of a substrate by the metal center.

Several studies have compared the binding strength of dihydrogen to other neutral ligands. In many cases, the binding of H_2 was found to be competitive with N_2 binding. In fact, Morris has shown that the $\nu(N{\equiv}N)$ of dinitrogen complexes can be used to predict the stability of the corresponding dihydrogen complex.[1] Kubas and coworkers have shown that H_2 is also competitive with N_2 and H_2O for binding to $M(CO)_3(PR_3)_2$ (M = Mo, W; R = Cy, *i*Pr).[2,3] Bianchini has reported that $[Re(CO)_2(triphos)]^+$ [triphos = $MeC(CH_2PPh_2)_3$] shows the following preference for ligands: $CO > CH_3CN > HC{\equiv}CR > H_2 > C{-}H$ (agostic) $> N_2$.[4] Similarly, Milstein and coworkers have recently reported the ligand preferences of the sterically congested T-shaped Rh complex, $Rh[HC(CH_2CH_2P(tBu)_2)_2]$, to be: $H_2 > N_2 > C_2H_4 > CO_2$.[5]

To the best of our knowledge, no binding studies have found H_2 to show binding affinity comparable to that of an anionic ligand. Cationic dihydrogen compounds are either described as stable to a given counterion, or unstable. For example, the dihydrogen complexes, $[Re(CO)_3(PR_3)_2(H_2)]^+$ (R = Cy, *i*Pr, Ph), have been recently reported.[6] These cationic analogs of the Kubas system could only be prepared with the non-coordinating anion, BAr_f^-. Other anions, such as triflate ($OSO_2CF_3^-$), were found to displace hydrogen and bind irreversibly.

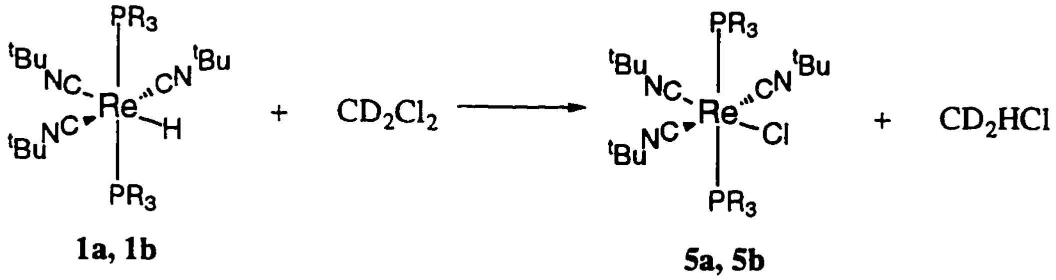
Typically, molecular hydrogen has been considered a weaker ligand than chloride, especially when coordinated to cationic metal fragments. Several metal dihydrogen complexes have been made from metal chloride starting materials. These examples, however, have all required the driving force of salt formation (eq 2.1).[7]

$$MCl + NaBF_4 + H_2 \longrightarrow [M(H_2)]BF_4 + NaCl \qquad (2.1)$$

In this chapter, I report the first *unaided* displacement of halide, by H_2, from a neutral metal halide, $Re(CN\mathit{t}Bu)_3(PCy_3)_2X$ ($X = F^-, Cl^-, Br^-, I^-$), to form a cationic dihydrogen complex, $[Re(CN\mathit{t}Bu)_3(PCy_3)_2(H_2)]^+$ (**2a**).

Results

Reaction of $Re(CN\mathit{t}Bu)_3(PR_3)_2H$ with Halocarbons. Both **1a** and **1b** were found to react with methylene chloride-d_2 at 25 °C to give complete conversion to $Re(CN\mathit{t}Bu)_3(PR_3)_2Cl$ [R = Cy (**5a**); R = Ph (**5b**)] (eq 2.2). In the case of **1a**, the conversion is accompanied by broadening of the ^1H and $^{31}P\{^1H\}$ NMR resonances of **1a**. The reaction of **1a** (6 days) is slower than **1b** (4 hrs). Spectroscopic characterization by NMR indicate that **5a** and **5b** each possess two equivalent phosphine ligands and two sets of isonitrile ligands in a 2:1 ratio. The IR spectrum of **5a** shows three broad bands between 2097 and 1919 cm^{-1}; these were assigned to ν(C≡N). When the reactions were conducted in CD_2Cl_2, and monitored by ^1H NMR, formation of CHD_2Cl was detected.



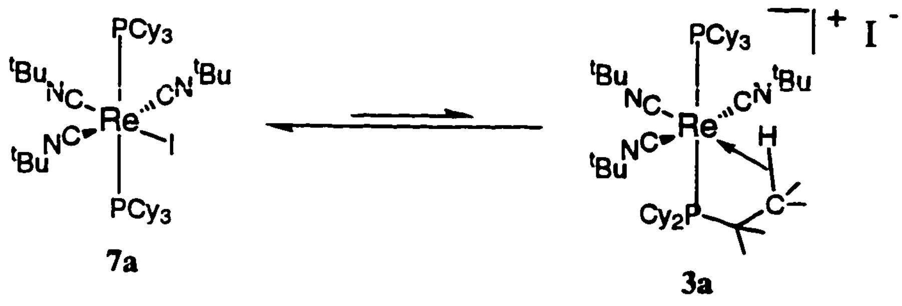
Equation 2.2 Hydrogenolysis of CD_2Cl_2 by **1a**, **1b**.

The reaction (eq 2.2), as well as the spectral broadening of **1a** in methylene chloride-*d*$_2$, could be inhibited by the presence of a strong base such as NaOMe or KO*t*Bu.

Analytically pure chloride complex, **5a**, was prepared and isolated by treating the hydride **1a** with excess CH_3Cl in methylene chloride at 25 °C for 2 h. When the reaction was conducted in CD_2Cl_2, and monitored by ^{1}H NMR, formation of CH_4 (as opposed to CHD_2Cl) was detected. Two other chlorocarbons, $CDCl_3$ and $CDFCl_2$, were also found to effect this transformation. In each case, formation of the product carbon species, containing one less chlorine atom and one additional hydrogen ($CHDCl_2$ and CHDFCl respectively), was detected. CH_3Cl reacts more rapidly than CH_2Cl_2, $CHFCl_2$, or $CHCl_3$. Furthermore, unlike these others, it doesn't oxidize the chloride product **5a** (*vide infra*).

NMR tube reactions show that $Re(CNtBu)_3(PCy_3)_2H$ (**1a**) also reacts with CH_3Br and CH_3I in methylene chloride-*d*$_2$ to make $Re(CNtBu)_3(PCy_3)_2Br$ (**6a**) and $Re(CNtBu)_3(PCy_3)_2I$ (**7a**), respectively. In both cases, the concomitant formation of methane was also observed by ^{1}H NMR spectroscopy. The bromide complex, **6a**, exhibits a single ^{31}P NMR resonance (δ 5.0) and two ^{1}H NMR resonances in a two to one ratio (δ 1.44, 1.26) corresponding to the *tert*-butyl groups of isonitrile coligands. These spectra are consistent with an octahedral *mer, trans* geometry.

The iodide complex, **7a**, is observed to partially dissociate in methylene chloride-*d*$_2$ (eq 2.3) to give a brown solution.



Equation 2.3

The $^{31}P\{^{1}H\}$ NMR spectrum (298 K) reveals two resonances broadened by exchange. The minor resonance (15%) corresponds to the chemical shift of the agostic complex, **3a**, (δ 26.4 ppm); the major resonance (δ -0.1 ppm, 85%) is attributed to **7a**. The ^{1}H NMR spectrum exhibits two exchange averaged isonitrile resonances (δ 1.46, 1.29) in a 2:1 ratio.

The relative intensities of the $^{31}P\{^{1}H\}$ NMR resonances of **7a** and **3a** were the same for two different total concentrations of **7a** and **3a**, suggesting that $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+[I]^-$ (**3a-I**) exists as a solvent separated ion pair in methylene chloride.[8] The equilibrium expression shown below (eq 2.4) was therefore used to calculate K_{eq}.

$$K_{eq} = \frac{[\mathbf{3a}]}{[\mathbf{7a}]} \qquad 2.4$$

K_{eq} was found to be essentially invariant over the temperature interval 227–309 K. A Van't Hoff plot is shown in Figure 2.1. The thermodynamic parameters for the formation of $[Re(CN\textit{t}Bu)_3(PCy_3)_2]I$ (**3a-I**) from $Re(CN\textit{t}Bu)_3(PCy_3)_2I$ (**7a**) are as follows: $\Delta H^\circ = -0.1 \pm 0.5$ kcal/mol, $\Delta S^\circ = -3.9 \pm 1.4$ e.u., and $\Delta G^\circ_{298} = 1.1 \pm 0.9$ kcal/mol.

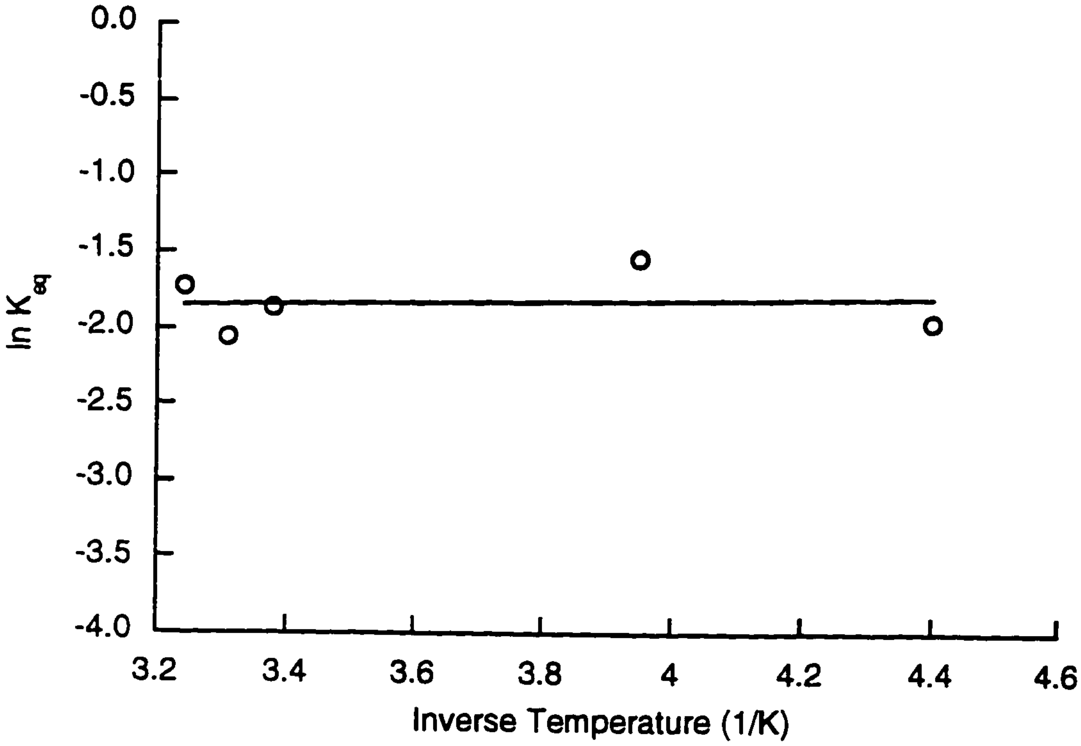


Figure 2.1 ln K_{eq} *vs.* 1/T for the equilibrium Re(CN*t*Bu)$_3$(PCy$_3$)$_2$I $\rightleftharpoons$ Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(H$_2$)]I.

Over time, in CD$_2$Cl$_2$, additional broadening is observed for the ^{1}H and ^{31}P{^{1}H} NMR resonances attributed to **6a** and **7a**. Like the similar broadening observed for **1a** and **5a**, this observation is consistent with a rapid self-exchange reaction between Re(CN*t*Bu)$_3$(PCy$_3$)$_2$X (X = H, Cl, Br, I) and minor amounts of the one-electron oxidized species [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$X]$^+$.

Reaction of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]$^+$ (3a) with F$^-$. The reaction of **3a-BF$_4$** with [Bu$_4$N]F·hydrate in methylene chloride-*d*$_2$ leads to a yellow solution. The NMR spectra exhibit a new species with a doublet ^{31}P NMR resonance (δ 15.0, J_{PF} = 24 Hz) and two ^{1}H NMR resonances in a two to one ratio (δ 1.44, 1.17) corresponding to the *tert*-butyl groups of the isonitrile coligands. These spectra are consistent with either Re(CN*t*Bu)$_3$(PCy$_3$)$_2$F (**8a**) or Re(CN*t*Bu)$_3$(PCy$_3$)$_2$F·H$_2$O. When the solution was placed under H_2 (1015 torr), it loses its yellow color and quantitative formation of the dihydrogen complex is indicated by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

Structure of Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl (5a). Complex **5a** was further characterized by X-ray structural determination of crystals formed at -25 °C in methylene chloride. An ORTEP diagram of **5a** (Figure 2.2) shows an octahedral disposition of the ligands in a *mer,trans* geometry. Both phosphines are bent away from the chloride and one of the *trans* isonitriles, *i.e.* into the quadrant defined by the two other isonitriles. The P–Re–P angle is 173.2(1)°. This distortion results in considerable bending of the isonitrile ligand *cis* to the chloride (∠C(1)N(1)C(2) = 153.6°). This angle is 22° more acute than that of the chemically equivalent isonitrile, also *cis* to the chloride (∠C(11)N(3)C(12) = 175.5°) (see Figure 2.3). Both *trans* isonitriles are bent towards the chloride. The most remarkable structural feature is the long Re–Cl bond distance, 2.596(2) Å. Bond distances and angles are given in Table 2.1 and 2.2, respectively. Information pertinent to the data collection and refinement of the structure is given in Table 2.4.

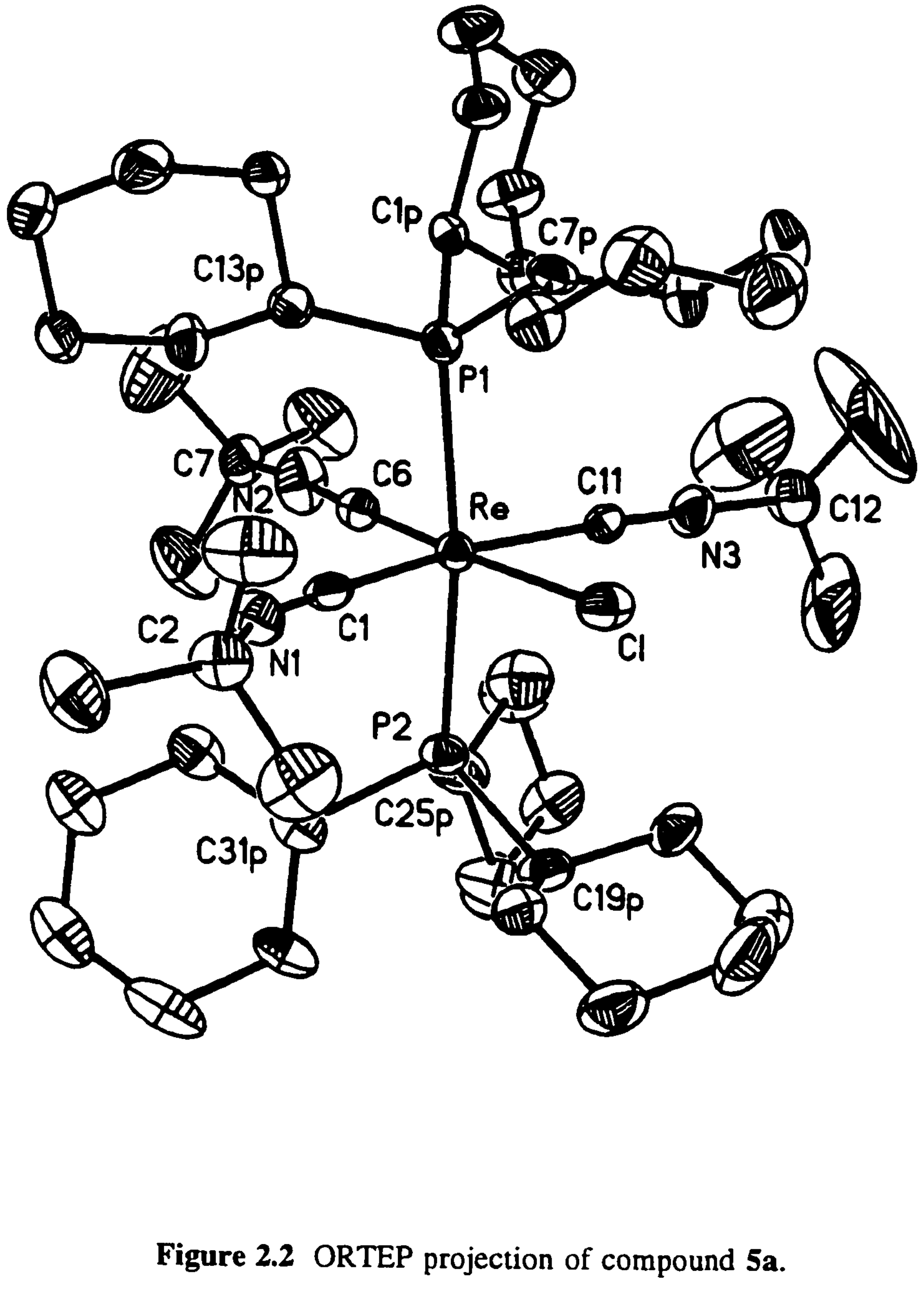


Figure 2.2 ORTEP projection of compound 5a.

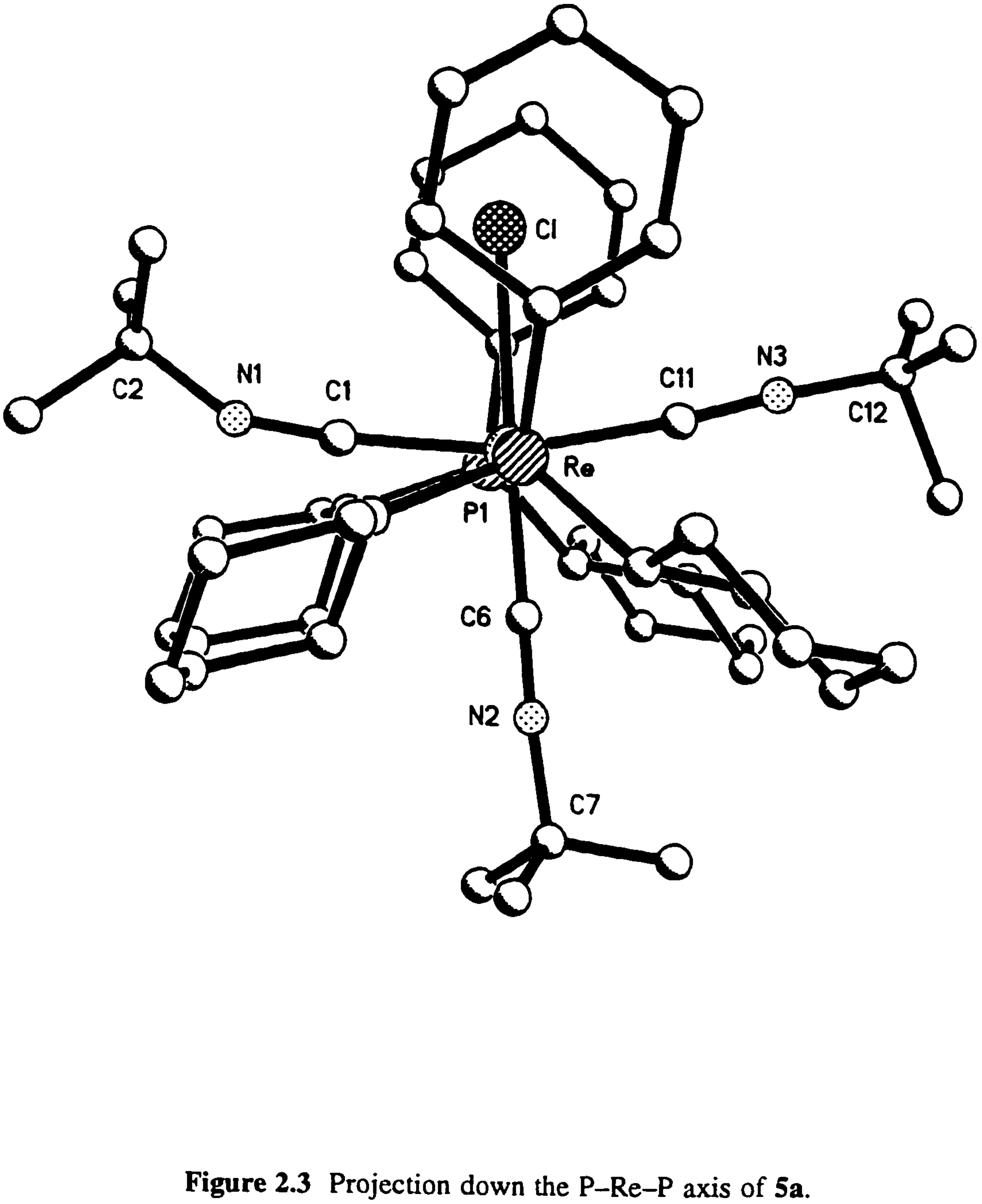


Figure 2.3 Projection down the P–Re–P axis of **5a**.

Reaction of Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl (5a) with Chlorocarbons. As was observed for **1a**, ^{1}H and ^{31}P{^{1}H} NMR resonances of **5a** in chlorinated solvents (CD_2Cl_2, $CDCl_3$, $CDFCl_2$) are observed to broaden over time.[9] Further reaction of **5a** in these solvents (and also in CCl_4) causes the solution to change color from yellow to pink. The qualitative rates vary from CCl_4, which reacts instantly, to CH_2Cl_2, which requires several days before the reaction is apparent. Broad, temperature-dependent resonances, suggesting a paramagnetic species, are observed to grow in when the reaction is monitored by ^{1}H NMR. Pink solid, shown by elemental analysis to be consistent with the 17-electron [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl]Cl·3CH$_2$Cl$_2$ (**9a-Cl**), could be isolated from the reaction of **5a** with CH_2Cl_2. The IR spectrum of **9a-Cl** shows three broad bands between 2133 and 2038 cm^{-1}; these were assigned to ν(C≡N). The same paramagnetic species was isolated as the triflate salt (**9a-OTf**) from the slow reaction of CD_2Cl_2 with the unsaturated complex [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]OTf (**3a-OTf**).

The PPh$_3$ complexes, **2b** and **5b**, also slowly decompose in CD_2Cl_2 to give similarly broad, temperature dependent resonances. The proposed product is [Re(CN*t*Bu)$_3$(PPh$_3$)$_2$Cl]$^+$ (**9b**), however, no attempts have been made to isolate or characterize it.

Structure of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl]OTf (9a-OTf). Diffraction quality crystals of **9a-OTf** were grown by layering a CD_2Cl_2 solution with diethyl ether and cooling to -20 °C. Crystallographic analysis reveals that complex **9a-OTf** has a quasi-octahedral structure with a Re-Cl bond distance of 2.412(5) Å (Figure 2.4). As was seen for **5a**, both phosphines are bent away from the chloride and one of the *trans* isonitriles, *i.e.* into the quadrant defined by the two other isonitriles. This distortion also results in considerable bending of an isonitrile ligand *cis* to the chloride. In this case, it was less severe (∠C(1)N(1)C(2) = 160.1(18)°). This angle is still 19° more acute than that of the chemically equivalent isonitrile, also *cis* to the chloride (∠C(11)N(3)C(12) = 179.4°) (Figure 2.5). Both *trans* isonitriles are bent towards the chloride (∠C(1)ReC(11) = 168.8(8)°). Bond distances and angles are given in Tables 2.1 and 2.2, respectively. Information pertinent to the data collection and refinement of the structure is given in Table 2.4.

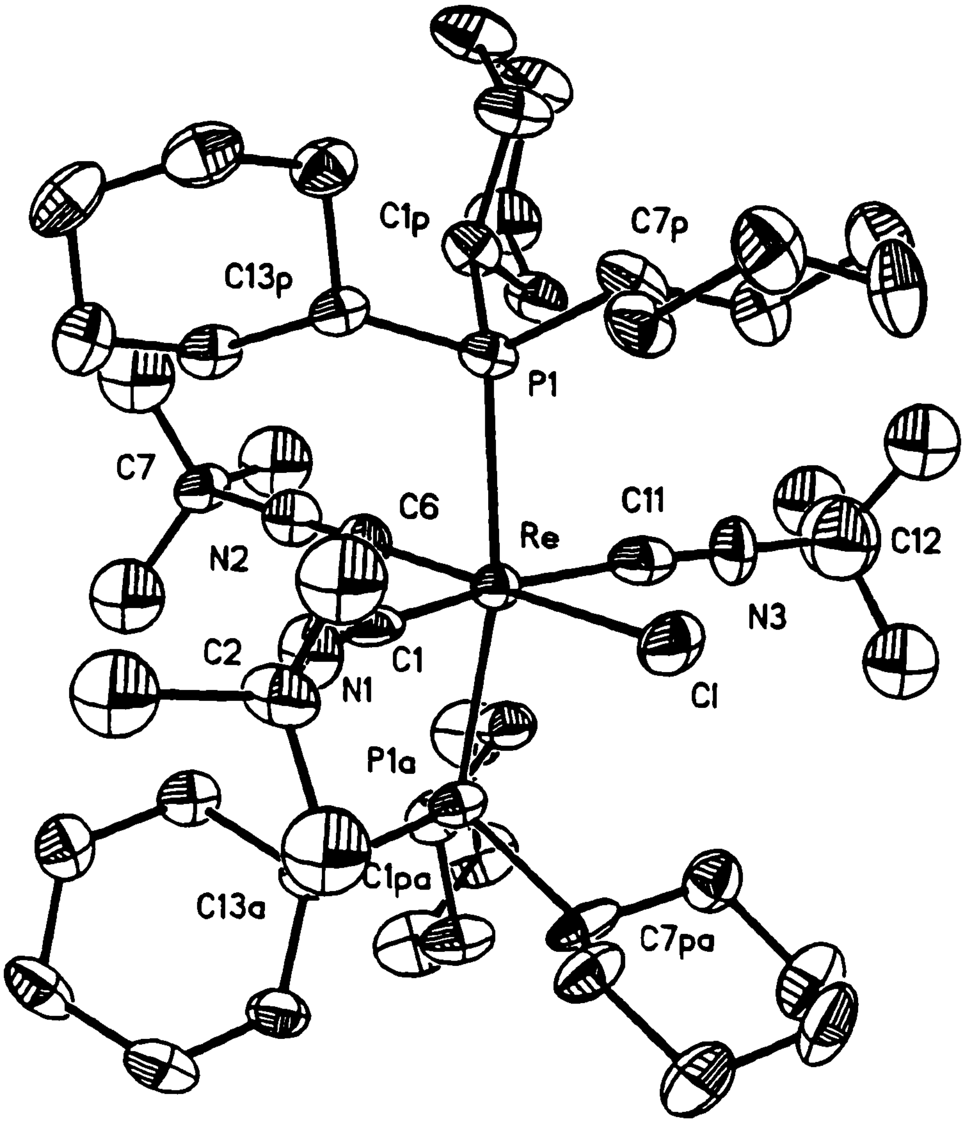


Figure 2.4 ORTEP projection for compound **9a**.

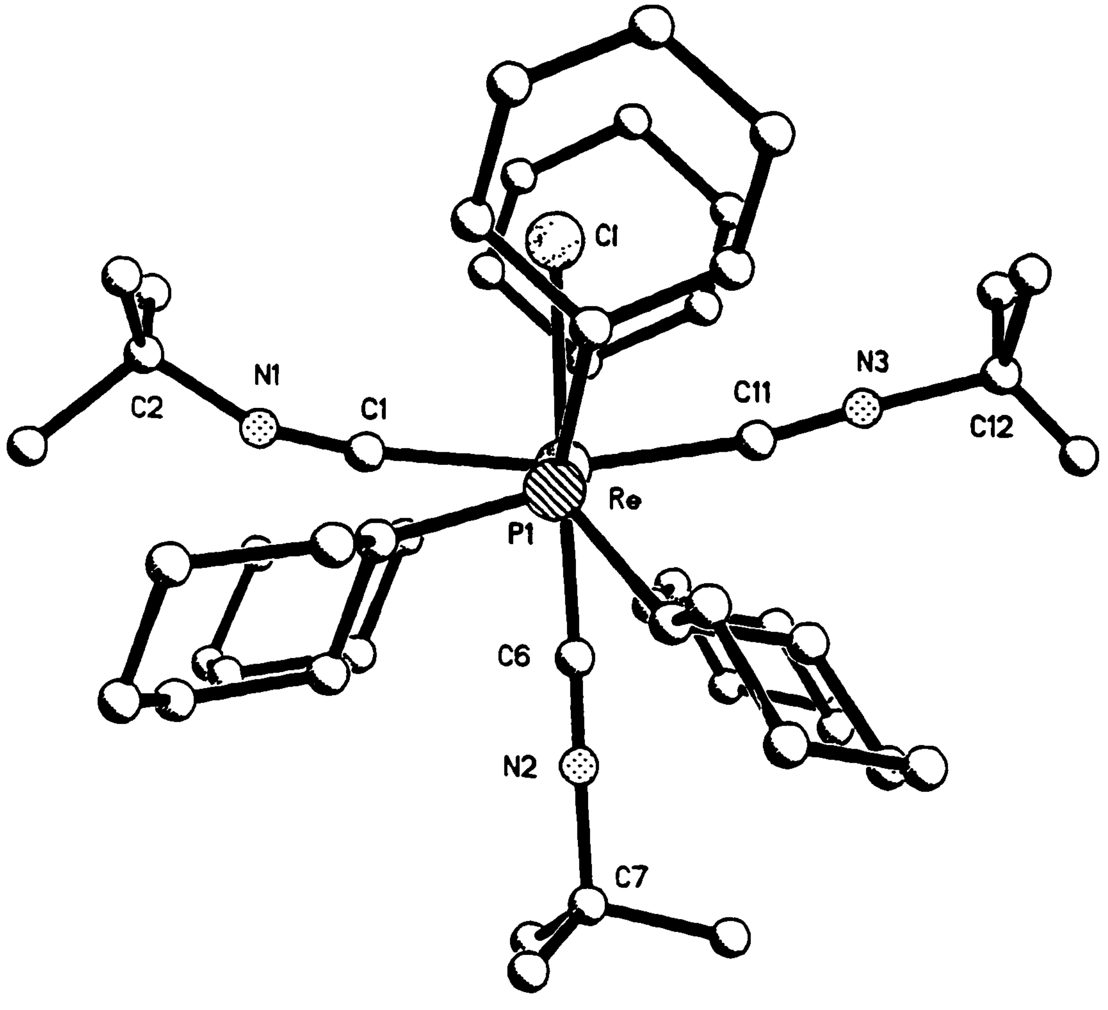


Figure 2.5 Projection down the P–Re–P axis of **9a**.

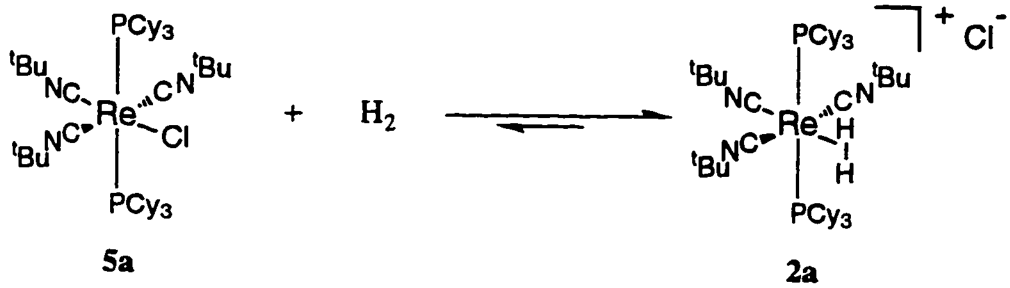
Table 2.1 Select Bond Distances (Å) for **5a** and **9a**

	5a	**9a**
Re–Cl	2.596(2)	2.412(5)
Re–P1	2.449(2)	2.486(3)
Re–P2	2.450(2)	
Re–C1	1.974(8)	2.08(3)
Re–C6	1.927(8)	2.03(3)
Re–C11	2.003(8)	2.04(3)
C1–N1	1.19(1)	1.14(3)
C6–N2	1.18(1)	1.13(3)
C11–N3	1.17(1)	1.16(3)
N1–C2	1.46(1)	1.47(3)
N1–C7	1.43(1)	1.43(2)
N1–C12	1.44(1)	1.42(3)

Table 2.2 Select Bond Angles (deg.) for **5a** and **9a**

	5a	**9a**
P1–Re–Cl	92.4(1)	95.6(1)
P2–Re–Cl	93.0(1)	
Cl–Re–C(6)	177.5(2)	178.6(6)
Cl–Re–C(1)	82.7(2)	82.3(5)
Cl–Re–C(11)	83.2(2)	83.5(6)
P1–Re–P2	173.2(1)	
P1–Re–C(1)	88.3(2)	88.5(1)
P1–Re–C(6)	86.4(2)	84.5(1)
P1–Re–C(11)	92.5(2)	92.8(1)
P2–Re–C(1)	88.4(2)	
P2–Re–C(6)	88.3(2)	
P2–Re–C(11)	92.1(2)	
C(1)–Re–C(11)	165.9(3)	165.8(8)
Re–C(1)–N(1)	173.5(7)	173.1(17)
Re–C(6)–N(2)	177.9(7)	178.8(11)
Re–C(11)–N(3)	175.4(6)	173.0(18)
C(1)–N(1)–C(2)	153.6(7)	160.1(18)
C(6)–N(2)–C(7)	172.6(8)	179.4(15)
C(11)–N(3)–C(12)	175.5(8)	180.0(2.4)

Reaction of Re(CN*t*Bu)$_3$(PR$_3$)$_2$Cl (5a) with H$_2$. **5a** reversibly reacts with H$_2$ to form the novel cationic dihydrogen complex [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(H$_2$)]Cl (**2a-Cl**) (eq 2.5).



5a **2a**

Equation 2.5 Hydrogen and **5a** in equilibrium with **2a**.

This reaction is rapid in chlorinated solvents (CH_2Cl_2, $CHCl_3$, and $CHFCl_2$). Within seconds, the yellow solution becomes colorless. ^{1}H and ^{31}P{^{1}H} NMR spectra for **2a-Cl** are identical to **2a-X** where X$^-$ is BF_4^-, OTf$^-$, or BAr$_f^-$.

The reversibility of the reaction (eq 2.5) at room temperature was probed in CD_2Cl_2 by removing the dissolved hydrogen using standard freeze–pump–thaw (FPT) technique (figure 2.6).

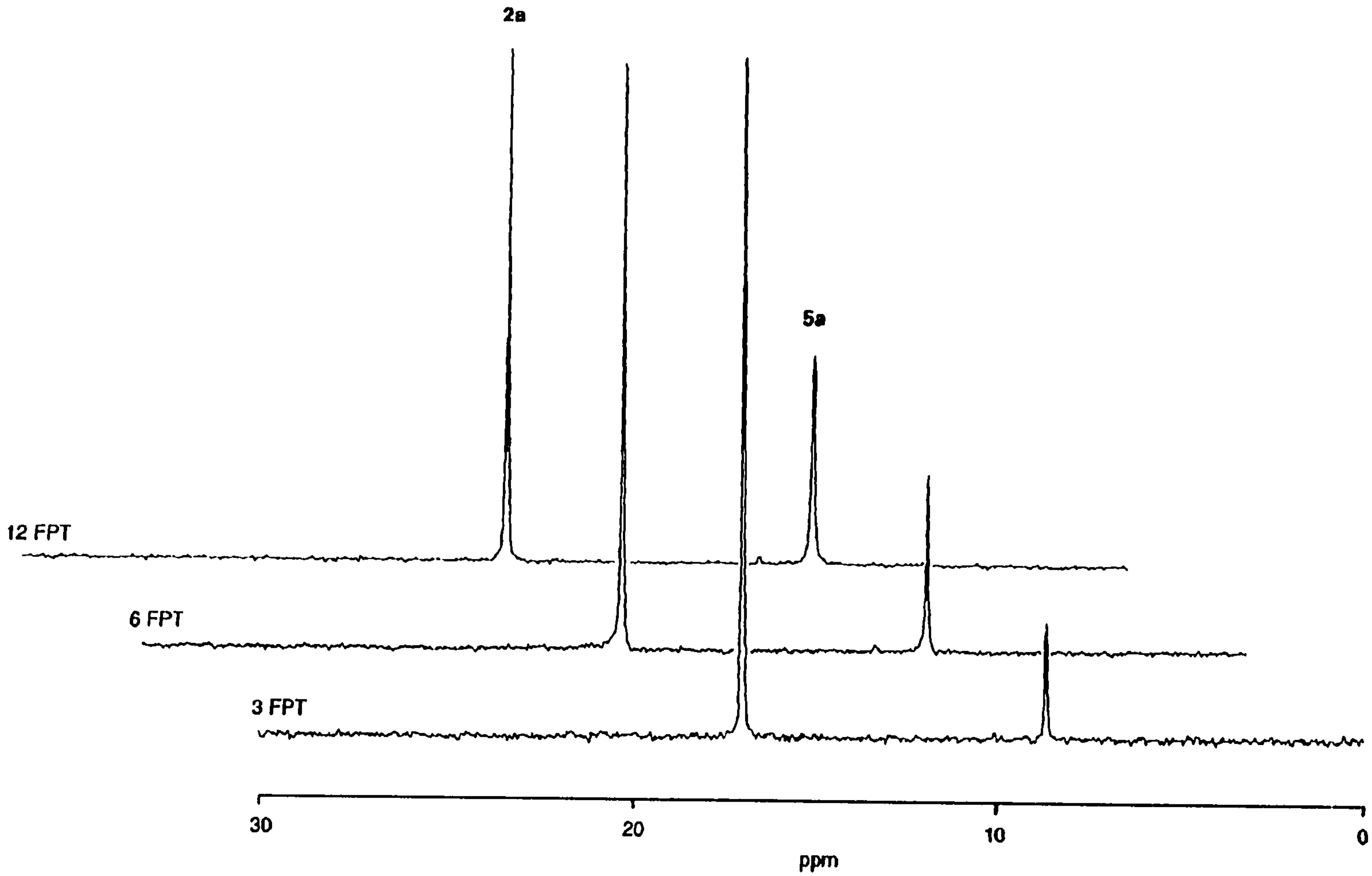


Figure 2.6 Relative peak intensities of **2a** and **5a** as a function of H_2 concentration (FPT cycles) by $^{31}P\{^1H\}$ NMR

24 FPT cycles were required to shift the ratio of **2a**:**5a** from 10:1 to 1:1. The relative concentrations of the dihydrogen product, free H_2 (corrected for 25% NMR-silent para-hydrogen),[10] and the neutral chloride complex were determined by ^1H and $^{31}P\{^1H\}$ NMR (Table 2.3). Apparent K_{eq} values were calculated using two models for the equilibrium.

$$K_{eq} = \frac{[\mathbf{2a}]}{[\mathbf{5a}][\mathrm{H_2}]} \qquad (2.6)$$

$$K_{eq} = \frac{[\mathbf{2a}]^2}{[\mathbf{5a}][\mathrm{H_2}]} \qquad (2.7)$$

The first model (eq 2.6) assumes that the dihydrogen complex, **2a**, exists as one species, a solvent-separated ion pair. Values of K_{eq} calculated this way remains constant (mean value = 2.21×10^3 M^{-1}; ± 4%) as successive amounts of H_2 are removed from solution. The second model (eq 2.7) assumes that **2a** exist as free ions. Values of K_{eq} calculated using this model steadily decrease as the concentration of H_2 is reduced. We have therefore adopted the solvent-separated ion pair model as the correct expression for the equilibrium constant.

Table 2.3 Data for the removal of H_2 from a solution of **2a-Cl**.

[**5a**] M	[H_2] M	[**2a**] M	K_{eq} (free ion)	K_{eq} (ion pair) M^{-1}
0.39×10^{-2}	2.45×10^{-3}	2.11×10^{-2}	46.6	2.21×10^3
0.66×10^{-2}	1.23×10^{-3}	1.84×10^{-2}	41.7	2.27×10^3
1.02×10^{-2}	0.68×10^{-3}	1.48×10^{-2}	31.6	2.13×10^3
1.23×10^{-2}	0.46×10^{-3}	1.27×10^{-2}	28.5	2.24×10^3
1.45×10^{-2}	0.33×10^{-3}	1.05×10^{-2}	23.0	2.19×10^3

The temperature dependence of K_{eq} for equation 2.5 was determined over the temperature interval 286–316 K. The observed equilibrium constants varied from 13.6×10^3 M^{-1} at 285 K to 4.9×10^2 M^{-1} at 319 K. A Van't Hoff plot is shown in Figure 2.7. The thermodynamic parameters for the formation of $[Re(CN\mathit{t}Bu)_3(PCy_3)_2(H_2)]Cl$ from

Re(CN*t*Bu)3(PCy3)2Cl and H2 are as follows: $\Delta H^\circ = -18.0 \pm 0.7$ kcal/mol, $\Delta S^\circ = -44.0 \pm 2.2$ e.u., and $\Delta G^\circ_{298\text{ K}} = -4.8 \pm 1.3$ kcal/mol.

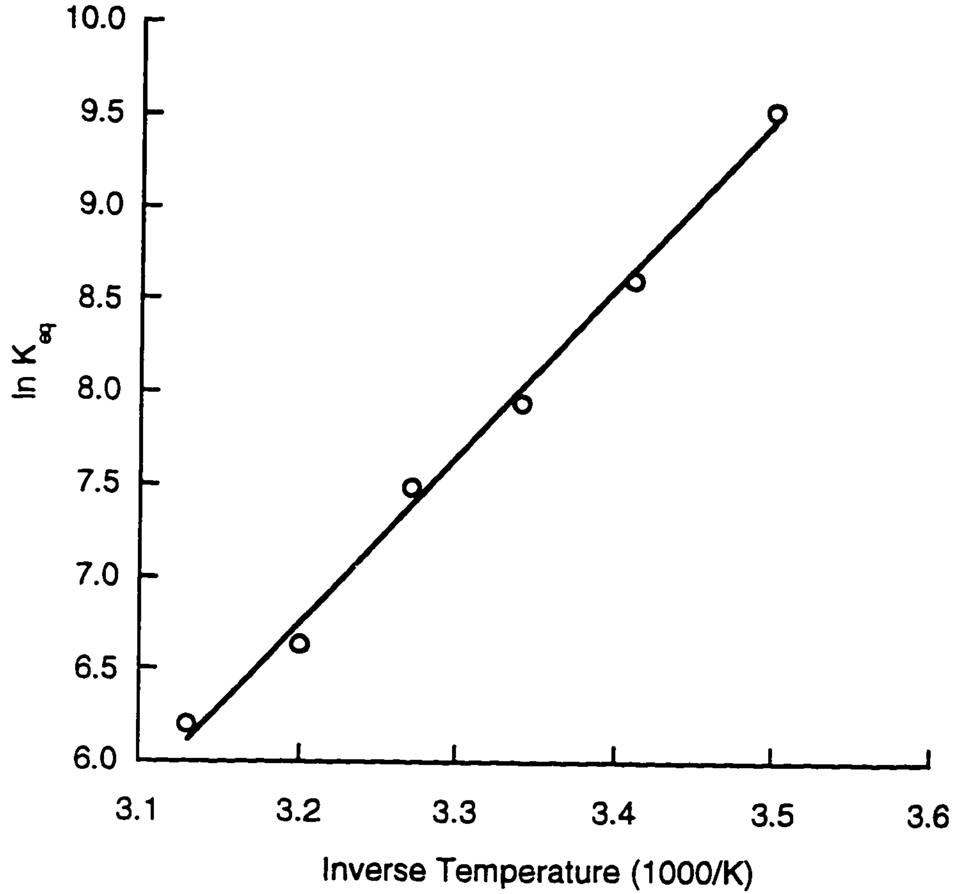
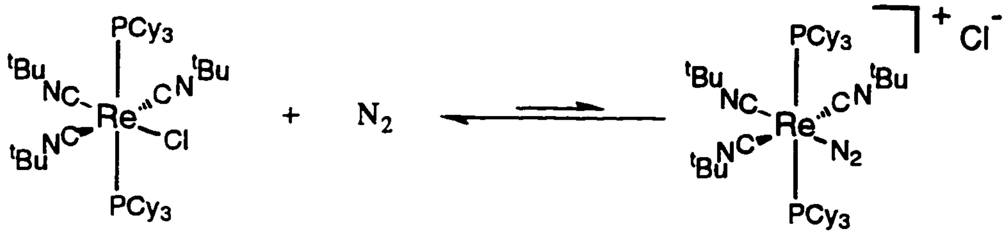


Figure 2.7 ln K_{eq} *vs.* 1/T for the equilibrium $Re(CN\textit{t}Bu)_3(PCy_3)_2Cl + H_2 \rightleftharpoons [Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]Cl$.

The reaction between **5a** and H_2 was found to be highly sensitive to the nature of the solvent and phosphine coligands. The reaction is favorable in chlorinated solvents, but does not occur in THF. Also, chloride displacement by hydrogen does not occur in the PPh3 complex, $Re(CN\textit{t}Bu)_3(PPh_3)_2Cl$ (**5b**).

Reactions of 5a and 3a with N_2. In contrast to the complete reaction with H_2, **5a** only partially reacts with N_2 in CD_2Cl_2 to form a small equilibrium concentration of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(N$_2$)]Cl (**10a**) (eq 2.8). Under N$_2$ pressure (500 torr), the ratio of neutral chloride to dinitrogen complex is approximately 20:1. The lack of a convenient NMR handle for N$_2$, as well as the lack of solubility data for N$_2$ in dichloromethane,[11] prevented the determination of an equilibrium constant.



5a **10a**

Equation 2.8

Unlike the above reaction (eq. 2.8), **10a** could be synthesized quantitatively from the reaction of **3a** with N$_2$. Placing a solution of **3a** under N$_2$ results in the solution changing from purple to colorless. Characterization by NMR spectroscopy indicates that [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(N$_2$)]$^+$ possesses two equivalent phosphine ligands and two sets of isonitrile ligands in a 2:1 ratio (Table C.2). The IR of **10a** showed three broad bands between 2125 and 2031 cm^{-1} which were assigned to ν(C≡NR).

Discussion

Reaction of Re(CN*t*Bu)$_3$(PCy$_3$)$_2$H (1a) with Chlorocarbons. The reaction of Re(CN*t*Bu)$_3$(PCy$_3$)$_2$H (**1a**) with CCl$_4$, CHCl$_3$, or CH$_2$Cl$_2$ to form Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl (**5a**) is a well precedented type of reaction for metal hydrides.[12] The increasing reactivity as the number of Cl atoms increases also follows the previously observed trend. Limited mechanistic investigations of these types of reactions, suggest that they proceed by free radical chain mechanisms.[13] Consistent with a radical chain mechanism, the reaction of **1a** with CH$_2$Cl$_2$ shows highly variable reaction times. Other observations, however, suggest that it may be proceeding by an electron-transfer mechanism, or possibly an electron-transfer-initiated radical-chain mechanism. It has been established that one-electron oxidation of a metal hydride leads to a very acidic species—one with a pKa *ca.* 18 units below that of the unoxidized species.[14] The inhibition of the reaction of **1a** with methylene chloride by base is consistent with the inactivation of such an intermediate by deprotonation. For the preparation of **5a**, none of these reactions had much utility. This is especially the case since extended reaction times lead to the Re^{II} decomposition product, $[Re(CN\textit{t}Bu)_3(PCy_3)_2Cl]Cl$ (**9a**).

The reaction of **1a** with CH_3Cl is the exception to the above reactivity trend. Even though it contains one less chlorine than CH_2Cl_2, it reacts more rapidly. In fact, **1a** reacts preferentially with CH_3Cl in methylene chloride. This suggests that this reaction proceeds by a different (non-radical chain) mechanism, possibly with the M–H bond acting as a nucleophile. Nucleophilic behavior by M–H bonds is well established.[15] Consistently rapid reaction times ($t_{1/2} \approx 10$ min) make this reaction preparatively the most useful.

Oxidation of $Re(CN\textit{t}Bu)_3(PCy_3)_2X$ (X = H, Cl, Br, I) by Chlorocarbons. The mechanism by which the paramagnetic complex, **9a**, is formed from the reaction of either $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ (**3a**) or $Re(CN\textit{t}Bu)_3(PCy_3)_2Cl$ (**5a**) with chlorinated solvents is not understood. The possibilities include outer-sphere one-electron transfer from the complex to the solvent, or an inner-sphere mechanism involving Cl atom abstraction by the coordinatively unsaturated complex **3a**. For the latter mechanism, in the case of **5a**, chloride loss would presumably have to occur first in order to create a vacant coordination site. This has been shown to be facile, however, so this mechanism cannot be ruled out. Pombeiro and coworkers have reported that the electron-rich Re^I complex $[NBu_4][\textit{trans}\text{-}Re(CN)_2(dppe)_2]$ is unstable in methylene chloride and gets oxidized to the red, Re^{II} complex *trans*-$Re(CN)_2(dppe)_2$.[16] The color similarity between this product and **9a** should be noted. Importantly, unlike **9a**, this product contains no chloride ligands. Oxidation by chlorine atom abstraction therefore appears to be a very unlikely mechanism in this case. Additional evidence that formation of **9a** doesn't occur by an inner-sphere electron transfer mechanism, is the observation that the ^{1}H and $^{31}P\{^{1}H\}$ NMR resonances of $Re(CN\textit{t}Bu)_3(PCy_3)_2H$ (**1a**), $Re(CN\textit{t}Bu)_3(PCy_3)_2Cl$ (**5a**), $Re(CN\textit{t}Bu)_3(PCy_3)_2Br$ (**6a**), and $Re(CN\textit{t}Bu)_3(PCy_3)_2I$ (**7a**) all broaden over time in methylene chloride-d_2. This broadening is most consistent with the formation of small quantities of the one-electron oxidized species which then undergoes a rapid self-exchange reaction with the unoxidized parent compound (eq. 2.9).

$$\mathrm{ReX} + [\mathrm{ReX}]^{+} \rightleftharpoons [\mathrm{ReX}]^{+} + \mathrm{ReX} \tag{2.9}$$

$$(\mathrm{X} = \mathrm{H, Cl, Br, I})$$

NMR line broadening is commonly observed for self-exchange reactions, and can be used to determine the rate constants of these reactions.[17] No such attempts have been made in this system.

Structural Comparisons of $Re(CN\textit{t}Bu)_3(PCy_3)_2Cl$ (5a) and $[Re(CN\textit{t}Bu)_3(PCy_3)_2Cl]^{+}$ (9a). The unique reactivity of **5a** is consistent with its unusual structure. The Re–Cl bond length, 2.596(2) Å, is one of the longest reported for a non-bridging Re^{I}–Cl bond.[18] It exceeds the Re–Cl bond length reported by Warner and Lippard for an analogous complex, $Re(CNMe)_3(PMePh_2)_2Cl$ (Re–Cl = 2.47(2) Å), by more than 0.1 Å.[19] This dramatic increase in bond length, resulting from minor changes in the ligand set, is consistent with the different reactivities observed for **5a** and **5b**. The PPh_3 analog, **5b**, shows no reactivity with H_2. No structural information exists for **5b**, however, it is reasonable to predict that its Re–Cl bond length would be close to the 2.47 Å distance observed for $Re(CNMe)_3(PMePh_2)_2Cl$.

[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl]OTf (**9a**) belongs to a small group of mononuclear Re^{II} complexes which have been structurally characterized.[20] Of these, [Re(terpy)(PPh$_3$)$_2$Cl]OTf, reported by Harman and coworkers, is most similar in structure to **9a**.[21] The Re–Cl bond lengths were also found to be similar, 2.404(3) Å for [Re(terpy)(PPh$_3$)$_2$Cl]$^+$, and 2.412(5) Å for **9a**. An analogous, stable, 17-electron, d^5, halide derivative has also been reported and structurally characterized by Kubas and coworkers.[22] The neutral W^I complex, W(CO)$_3$(P*i*Pr$_3$)$_2$I, is formed from the reaction of W(CO)$_3$(PCy$_3$)$_2$ with I$_2$. A similar reaction was attempted with the 16-electron complex [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]$^+$ (**3a**) and Cl$_2$ in CD$_2$Cl$_2$. This reaction eventually leads to **9a**, but not markedly faster than when Cl$_2$ was absent. Nor was there any indication that Cl$_2$ oxidatively added to a single metal center to give a Re^{III} complex. Such a complex is expected to be stable. Lippard and coworkers have structurally characterized [Re(CN*t*Bu)$_3$(PMePh$_2$)$_2$Cl$_2$]SbF$_6$.[23] This product was synthesized by adding excess *tert*-butyl isonitrile to Re(PMePh$_2$)$_3$Cl$_3$ and exchanging the anion.

The structures of the 17 electron cation, [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl]$^+$ (**9a**), and the 18-electron neutral chloride, Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl (**5a**), provide a useful comparison between two complexes that differ only in *d*–electron count. Few such comparisons have been made in the literature. One particularly relevant example is the comparison made by Salih *et al.* for *trans*-[Re(dppe)$_2$Cl$_2$]X (X$^-$ = Cl$^-$, BF$_4^-$) with *trans*-Re(dppe)$_2$Cl$_2$.[24] In this case, a 16-electron, d^4, Re^{III} complex is compared with a 17-electron, d^5, Re^{II} complex. They found that the Re–Cl distances *increase* by 0.1 Å and the average M–P distance *decreases* by 0.08 Å upon reduction of Re^{III} to Re^{II}. Similar overall trends are observed in the complexes, [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl]$^+$ (**9a**) and Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl (**5a**). The addition of an electron to **9a** (17-electron, d^5, Re^{II}) to form **5a** (18-electron, d^6, Re^I), also results in an *increase* in the Re–Cl distance and a *decrease* in the Re–P distances. However, the *increase* in the Re–Cl distance (0.18 Å) is much greater in this case, while the *decrease* in the average Re–P distance (0.04 Å) is smaller. The differences between the two sets of complexes can be attributed to several factors, including the differences in the oxidation states being compared (Re^{II}, Re^{I} *vs.* Re^{III}, Re^{II}), the differences in coligands, and the differences in steric demand of the ligands. For instance, the greater overall steric crowding present in complexes **5a** and **9a** *versus* $Re(dppe)_2Cl_2$ and $[Re(dppe)_2Cl_2]^+$ may both exacerbate the lengthening of the Re–Cl bond, and impede the shortening of the Re–P upon the one-electron reduction of **9a**. Metal chloride bond lengths do not always change when the oxidation state of the metal changes. The Mo–Cl bond length in [*trans*-$Mo(dppe)_2Cl_2]^+$ only increases by 0.02 Å upon the addition of an electron (d^3 to d^4).[24]

The interpretation of isonitrile bending angles (∠CNC) should be approached with caution. Their origin results as often from steric effects as it does from electronic effects. Pombeiro and coworkers have compared the crystal structures of $Re(CNMe)(dppe)_2Cl$ and $Re(CN\textit{t}Bu)(dppe)_2Cl$.[16,25] The CNC angle of the methyl isonitrile complex and the *tert*-butyl isonitrile complex are 139.4(10)° and 174.0(9)°, respectively. Both complexes should be electronically identical, yet their CNC angles are dramatically different. Presumably steric effects lead to this discrepancy. For both **5a** and **9a**, the most bent isonitriles are not the ones *trans* to the π-basic chlorides, as would be expected. This too presumably arises from steric effects. However, the average ∠CNC of **5a** (167.2°) is less than that of **9a** (173.2°), which confirms the expectation that the oxidized complex should have less electron density with which to π-bond. Consistent with the structural information, the C≡N stretching frequencies of **5a** are lower than those of **9a** by *ca.* 100 cm^{-1}.

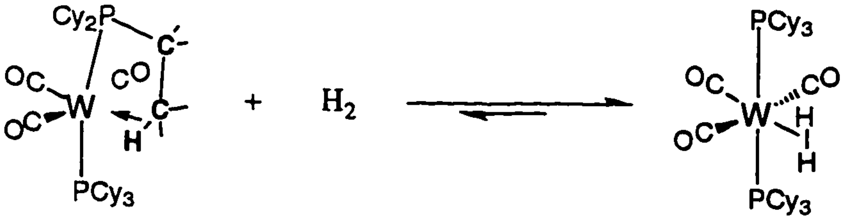
Two other structurally characterized Re^I complexes have been reported with unusually long Re–Cl bond lengths. Interestingly, both contain mixtures of phosphine and isonitrile coligands: $Re(CN\textit{t}Bu)_2(PMe_3)_3Cl$ (Re–Cl = 2.570 Å)[26] and $Re(CNMe)(dppe)_2Cl$ (Re–Cl = 2.607 Å).[16] Attempts to react either of these with H_2 have not been reported. Re–Cl bond length arguments lead us to predict that these compounds will readily react with hydrogen. The products, however, would not likely be dihydrogen complexes. Walton and coworkers have prepared both $[Re(CNR)(dppe)_2H_2]^+$ (R = Me, *t*Bu, 2,6-$Me_2C_6H_3$) and $[Re(CN\textit{t}Bu)_2(PPh_3)_3H_2]^+$ with the BF_4^- counterion (see Table 4).[27] The large J_{HP} constants of the hydrides strongly imply that these are dihydrides and not dihydrogen complexes.[28,29]

Re–Cl distances in Re^I carbonyl phosphine analogs are universally shorter: 2.487 (15) Å for $Re(CO)_3(PEt_3)_2Cl$, 2.501 (3) Å for *cis*-$Re(CO)_4(PEt_3)Cl$, 2.515 (2) Å $Re(CO)_5Cl$.[30] Consistent with the shortened distances, the chloride ligands are less easily dissociated. Hoffman, Doherty, and coworkers have studied the complex $Re(CO)_3(PPh_3)_2Cl$ and found it to possess relatively low lability.[31]

Thermodynamic Considerations for the Halide Displacement Reactions. It is surprising that H_2, which binds to a metal *via* its bonding electron pair, can displace chloride which offers both a non-bonding electron pair as well as an anionic charge complementary to that of the cationic metal center. It is necessary to consider both the factors which make the M–H_2 interaction stronger than expected, and those which weaken the M–Cl interaction. One clear distinction is that dihydrogen acts as a π-acid, while chloride behaves as a π-base. On a d^6 metal center, with all π-symmetry orbitals filled, binding of a π-acid ligand would clearly be favored. Indeed, the ability of the empty H_2 σ^* orbital to accept electron density from a filled metal π orbital is well supported by theoretical calculations[32] and studies of the rotational barrier of bound H_2.[33]

These include recent studies of d^2-complexes in which it has been possible to block the rotation of bound H_2 on the NMR timescale.[34] Our studies (in CD_2Cl_2) of the relative binding strengths of H_2 and Cl^- indicate that H_2 binding is strongly enthalpically favored, $\Delta H° = -18.0 \pm 0.7$ kcal/mol. However, an unfavorable entropic term ($\Delta S° = -44.0 \pm 2.2$ e.u.) disfavors the reaction. At higher temperatures (135 °C and above), the free energy of reaction is predicted to become positive.

It is useful to compare these thermodynamic parameters with those determined by Hoff and coworkers for the binding of H_2 to the agostic complex, $W(CO)_3(PCy_3)_2$ (eq 2.10).[2]



Equation 2.10

In toluene, $\Delta H°$ was reported to be -9.9 kcal/mol, and $\Delta S°$ was estimated to be -35 e.u.. It should be pointed out that the relatively low $\Delta H°$ includes displacement of the agostic interaction which is assumed to contribute *ca.* 10 kcal/mol.[2] Thus the total estimated binding strength of H_2 to the truly coordinatively unsaturated fragment, $W(CO)_3(PCy_3)_2$, is *ca.* 20 kcal/mol, close to the same magnitude as $\Delta H°$ for the reaction of $Re(CN\textit{t}Bu)_3(PCy_3)_2Cl$ (**5a**) with H_2. In this case, however, H_2 is displacing a chloride from **5a**, which is only a stable complex because chloride binds more strongly than the agostic interaction in **3a**.[35] Taken together, this comparison suggests that H_2 binding is stronger in $[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]^+$ (**2a**) than in $W(CO)_3(PCy_3)_2H_2$. Indeed, a direct competition between the two showed that H_2 binding in **2a** is more favorable by at least 3.9 kcal/mol (chapter 1).

While a strong affinity for H_2 at least partially explains the relatively large $\Delta H°$ of the reaction (eq 2.5), it does not explain the unusually large negative entropy change ($\Delta S°$ = -44.0 ± 2.2 e.u.), which is considerably larger than that reported for the reactions of $M(CO)_3(PCy_3)_2$ with H_2 in toluene (M = Mo, $\Delta S°$ = -23.8 ± 2.1 e.u.; M = Cr, $\Delta S°$ = -25.6 ± 1.7 e.u.).[36] Differential solvation of the ionic product, **2a**, *versus* the uncharged reactants, most likely contributes to both the $\Delta H°$ and the $\Delta S°$ of this reaction. The thermodynamic parameters determined for the partial dissociation of $Re(CN\textit{t}Bu)_3(PCy_3)_2I$ (**7a**) into the solvent separated ion-pair, $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+I^-$, in CD_2Cl_2 ($\Delta H°$ = -0.1 ± 0.5 kcal/mol, $\Delta S°$ = -3.9 ± 1.4 e.u.), illustrates that forming an ionic species in methylene chloride is not entropically favorable. The ordering of the solvent dipoles around the charged species most likely accounts for this. In the case of **5a**, formation of an ionic species is expected to be even more entropically disfavored, since the more localized charge of chloride compared with iodide is expected to lead to an even higher degree of solvent ordering.[37]

While solvation entropy disfavors the ionization reaction, the solvation enthalpy most likely favors it. This is certainly the case for the reaction, $Re(CN\textit{t}Bu)_3(PCy_3)_2I \rightleftharpoons [Re(CN\textit{t}Bu)_3(PCy_3)_2]I$, since the heterolytic BDE of Re–I must be overcome in order for the overall reaction to have an observed enthalpy change of zero.[38] Likewise a more negative ΔH_{solv} for the product, **2a**, compared with the starting compounds, **5a** and H_2, most likely contributes to the overall $\Delta H°$ observed in the reaction: **5a** + $H_2 \rightleftharpoons$ **2a**.

The exquisite solvent sensitivity of the reaction between **5a** and H_2 supports the above suggestion that differential solvation is contributing to the thermodynamics of the reaction. While the reaction of **5a** with H_2 is favorable in methylene chloride ($\Delta G°_{298}$ = -4.8 ± 1.3 kcal/mol), it does not proceed to any detectable extent in THF. This observation can be rationalized by comparing the different dielectric constants of the two solvents. Methylene chloride's dielectric constant ($\varepsilon = 9.08$, 20 °C) is greater than that of THF ($\varepsilon = 7.6$, 20 °C).[39] Since the dielectric constant is the factor by which the electrostatic interaction between two charges is reduced by a medium, methylene chloride's higher dielectric constant is consistent with it being better suited to solvate a charged species. Still, this small difference is unlikely to account for a $\Delta\Delta G^\circ \geq 5$ kcal/mol. No doubt to structure of the solvent also plays a role. THF is particularly well suited to solvating small cations. In this case of **2a-Cl** the cation is large, and the anion is small.

The Other Halides (F^-, Br^-, I^-). The *in situ* generated complexes, $Re(CN\textit{t}Bu)_3(PCy_3)_2Br$ (**6a**) and $Re(CN\textit{t}Bu)_3(PCy_3)_2I$ (**7a**), both react quantitatively with H_2 to give the dihydrogen complex. An equilibrium constant could not be determined for either of these, even at very low H_2 concentrations. This indicates that Br^-, and I^- are both less strongly bound than Cl^-. Since I^- is clearly the weakest—it partially dissociates in the absence of ligand(*vide supra*)—the ligand binding potentials of the halides to $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ in methylene chloride are as follows: $Cl^- > Br^- > I^-$.

The results obtained for the fluoride complex, **8a**, should be regarded cautiously. Since **8a** was formed using a hydrated salt, the solution is not water-free. The NMR spectra obtained may therefore correspond to a hydrogen-bonded complex. This possibility should be considered seriously because another doublet (δ 15.6, $J = 34$ Hz) was frequently observed as a minor impurity in the $^{31}P\{^1H\}$ NMR spectra of "dry" solutions of **3a-BF₄** in CD_2Cl_2. The doublet was *not* observed for either **3a-OTf** or **3a-BAr$_f$**. Since it occurs within a ppm of the chemical shift given for **8a**, and since its coupling constant is larger (34 *vs.* 24 Hz), this impurity may in fact be $Re(CN\textit{t}Bu)_3(PCy_3)_2F$. The J_{PF} coupling constants of two related complexes do *not* help resolve this. $Re(CO)_3(PPh_3)_2F$ has J_{PF} = 35 Hz,[31] while $Re(CNMe)(dppe)_2F$ has J_{PF} = 23.4 Hz.[16]

The apparent observation that the reaction of **8a** with H_2 is quantitative, and therefore more favorable, than the reaction of $Re(CNtBu)_3(PCy_3)_2Cl$ with H_2 should also be treated cautiously. The water molecules that are known to be present in solution would certainly be involved in hydrogen bonding interactions with a dissociated fluoride. Hydrogen bonding can make considerable contribution to the energetics of a reaction.[3,40] The reaction of **8a** with H_2 may therefore be less favorable than that of **5a** with H_2, which would be in keeping with the trend established for the other halides. This need not be the case, however; other studies comparing the lability of the M–F complexes with M–Cl complexes have found the fluorides to be more labile.[31,41] The isolation of water-free **8a** and the investigation of its reactions in rigorously water-free solvent is needed in order to resolve these uncertainties. A reasonable synthetic route to water-free **8a** is the reaction of **3a-OTf** with TAS-F $[(Me_2N)_3S^+(Me_3SiF_2)^-]$. The reaction of **1a** with CH_3F may also work, but CH_3F is prohibitively expensive.

The Nitrogen Complex. Unlike H_2, N_2 does not displace chloride very well. Under N_2 pressure (500 torr), less than 5% of $Re(CNtBu)_3(PCy_3)_2Cl$ is converted to $[Re(CNtBu)_3(PCy_3)_2(N_2)]Cl$ (**10a-Cl**). The relative binding of H_2 and N_2 in this system therefore differs from the $M(CO)_3(PCy_3)_2$ (M = W, Mo, Cr) system which favors N_2 over H_2.[36] For $W(CO)_3(PCy_3)_2$, the binding of N_2 was enthalpically favored ($\Delta\Delta H$ = -4.4 kcal/mol) and entropically disfavored ($\Delta\Delta S$ = -13.8 e.u.). The difference in entropy change was accounted for by the greater total entropy at 298 K of N_2 (45.8 e.u.) relative to H_2 (31.2 e.u.).[42] N_2 loses more entropy upon binding because its mass and moment of inertia are greater than those of H_2. This difference in entropy change ($\Delta\Delta S$)

would be expected to remain constant for different metal fragments. In fact, it was found to vary only slightly among the analogous complexes of the Group 6 triad.

With regard to N_2 *vs.* H_2 binding, $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ is similar to other Re^I species, including $[Re(CO)_3(PCy_3)_2]^+$,[6] $[Re(CO)_2(triphos)]^+$,[4] as well as the T-shaped Rh^I complex, $Rh[HC(CH_2CH_2P(\textit{t}Bu)_2)_2]$.[5] All of these complexes bind H_2 in preference to N_2.

It was not possible to determine the binding mode of the N_2 ligand. The IR spectrum of **10a** showed three broad bands between 2125 and 2031 cm^{-1} which were assigned to $\nu(C{\equiv}NR)$. No band attributable to $\nu(N{\equiv}N)$ was detected. This band is expected to resonate in the range 2150–2060 cm^{-1} for an end-on bound N_2 ligand binding at a known dihydrogen coordination site.[1] Presumably, it was obscured by the isonitrile stretching frequencies. Mononuclear end-on bound N_2 adducts are reported by Kubas and coworkers for the products of $M(CO)_3(PCy_3)_2$ (M = Mo, W) with N_2. They are able to observe the $\nu(N{\equiv}N)$ bands at 2159 cm^{-1} and 2120 cm^{-1} for tungsten and molybdenum, respectively.[43] However, for the N_2 adduct formed with $W(CO)_3(P\textit{i}Pr_3)_2$, Kubas and coworkers don't detect a $\nu(N{\equiv}N)$ in the IR spectrum. Raman spectral evidence and the reports of similar complexes leads them to propose a dinuclear formulation containing an μ-N_2 bridging ligand.[44] Since **10a** contains the bulkier PCy_3 ligands like the former complexes, it seems most likely that **10a** is also ligated by an end-on bound dinitrogen ligand.

Conclusion

The halide substitution reactions to form dihydrogen complexes represent an unprecedented example of unaided displacement of bound halide by H_2. All previous examples have required the driving force of salt formation (NaCl) (eq 2.1).[7] For the well studied chloride reaction, this result is attributed to the unusually long Re–Cl bond length in **5a**, as well as the strong binding of H_2 in **2a**.

Experimental

For the general procedures, see the experimental section in chapter 1.

$Re(CN\textit{t}Bu)_3(PCy_3)_2Cl$ (5a). Method A. Rigorously dried CH_2Cl_2 (5 mL) was vacuum transferred into a 20 mL reaction flask containing **1a** (107 mg, 0.107 mmol). The flask was pressurized with *ca.* 400 torr CH_3Cl. The reactants were stirred at room temperature for 2 h. The initially formed canary yellow solution was observed to darken to gold during the course of the reaction. The solution was concentrated and then cooled to -78 °C. Yellow solid precipitated and was collected on a glass frit. Yield 56 mg (5.4×10^{-2} mmol, 51% yield). **Method B.** Under an Ar atmosphere, **1a** (230 mg, 0.230 mmol) was stirred in Et_2O (20 mL). HCl in diethyl ether (1 M, 0.23 mL, 0.23 mmol) was added via syringe through a rubber septum. The solution was observed to immediately lose its yellow color and form a white precipitate. The slurry was cannula-transferred onto a glass frit and filtered. During the filtration, the collected solid was observed to change color from white to yellow and then redissolve in solution (accounting for the low yield). Presumably, the white solid is **2a-Cl**. As it loses H_2, it is directly converted to **5a**, which is yellow. The collected product was washed with pentane (3 × 5 mL). Yield: 50 mg (1.1×10^{-2} mmol, 21% yield). **Method C.** CD_2Cl_2 (0.4 mL) was vacuum transferred into a sealable NMR tube containing **1a** (12.6 mg, 1.26×10^{-2} mmol). The tube was sealed under vacuum, and the reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The conversion of **1a** to **5a** with concomitant formation of CD_2HCl was observed to proceed cleanly over six days. The color of the solution changed from canary yellow to gold. Cooling the solution (-30° C) resulted in the formation of diffraction quality crystals (see below). IR (Nujol) $\nu(C{\equiv}N)$

2097 (w), 1976 (m, br), 1919 (m, br) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.2 -1.2 (br, 66H), 1.44 (s, 18H), 1.25 (s, 9H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 8.6 (s). Anal. Calcd (found): C, 59.36 (59.08); H, 9.08 (9.15); N, 4.07 (4.05).

Reaction of 1b with CD_2Cl_2: Formation of Re(CN*t*Bu)$_3$(PPh$_3$)$_2$Cl (5b). Methylene chloride-*d*$_2$ (0.4 mL) was vacuum transferred into a sealable NMR tube containing **5b** (4.1 mg, 4.3 × 10^{-3} mmol). The tube was sealed under vacuum, and the reaction was monitored by ^{1}H NMR and $^{31}P\{^1H\}$ NMR. The conversion of **1b** to **5b** was observed to go cleanly to completion over 2.5 h at 23 °C. Concomitant formation of CD_2HCl was also observed by ^{1}H NMR. NMR for **5b**: ^{1}H NMR (CD_2Cl_2) δ 7.77 (br, 12H), 7.30 (br, 18H), 0.95 (s, 18H), 0.71 (s, 9H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 18.4 (s).

Spectroscopic observation of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(N$_2$)]Cl (10a). Methylene chloride-*d*$_2$ (0.4 mL) was vacuum transferred into a sealable NMR tube containing **5a** (4.1 mg, 4.3 × 10^{-3} mmol). The tube was pressurized with N_2 (0.5 atm) and sealed. Partial conversion (5%) to [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(N$_2$)]Cl was observed by NMR. ^{1}H NMR (CD_2Cl_2) δ 2.2 -1.2 (br, 66H), 1.50 (s, 18H), 1.37 (s, 9H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 6.9 (s).

[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(N$_2$)]X (X = BF$_4$, BAr$_f$) (10a-BF$_4$, 10a-BAr$_f$). (Observation of **10a-Cl** is described in chapter 3). The following preparation and characterization apply equally to **10a-BF$_4$** and **10a-BAr$_f$**, except as noted. **3a** was placed in a reaction flask. After evacuation of the Ar atmosphere, N_2 (1.1 atm) was inserted. Conversion of the purple starting material to the white product was slow (8 h) and easily reversible. Reducing the N_2 pressure below 0.3 atm caused immediate darkening of the solid. Dissolution of the solid in methylene chloride under N_2 (0.5 atm) resulted in a clear colorless solution. IR of **10a-BAr$_f$** (CH_2Cl_2) ν(C≡N) 2125 (w), 2074 (m), 2031 (m), ν(CF_3) 1223–1127 (br) cm^{-1}, (no bands attributable to ν(N≡N) were observed); ^{1}H and $^{31}P\{^1H\}$ NMR spectra are identical with those reported above.

Analysis of **10a-BF$_4$** showed loss of nitrogen and reaction with oxygen. It solved for [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(O$_2$)]$^+$ (**11a-BF$_4$**, chapter 3): Calcd (found): C, 54.92 (55.15); H, 8.41 (8.20); N, 3.77 (3.83).

[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl]X (X$^-$ = Cl$^-$, OTf$^-$) (9a-Cl, 9a-OTf). These decomposition products were isolated in variable yields (10–80% yield) from the reactions of **1a**, **2a**, **3a**, **5a**, or **10a** with methylene chloride. The following two examples are representative: The reaction of **5a** with methylene chloride was observed to be slow ($t_{1/2} \approx$ 1 week) and produce a pink solution. ^{1}H NMR spectra show very broad temperature-dependent peaks. Upon addition of diethyl ether, a pink solid was precipitated and isolated. IR (Nujol) ν(C≡N) 2132.9 (w), 2084 (m), 2038 (sh) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$) δ 10.5 (br), 0.0 (br), -2.9 (br). Anal. Calcd for **9a-Cl·(CH$_2$Cl$_2$)$_3$** (found): C, 49.05 (49.20); H, 7.55 (7.68); N, 3.10 (3.18). The reaction of **3a-OTf** with methylene chloride was also observed to be slow and produce a pink solution with identical NMR chemical shifts. Layering the solution with diethyl ether resulted in the growth of small pink diffraction quality crystals.

X-ray Structural Determination of Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl (5a). Single crystals of **5a** were grown at -20 °C from methylene chloride solutions. A crystal of suitable size (0.34 × 0.36 × 0.38 mm) coated with paratone was mounted using epoxy glue. 25 reflections in the range 32° to 38° in 2θ were found and an orientation matrix was determined providing for a well oriented cell with a volume of 5935 Å^3. The crystals had a semi-opaque appearance and were of good quality as evidenced by the reasonably narrow peaks and agreement of the equivalents. The data was collected for a monoclinic cell. A high chi reflection was scanned to provide for an absorption correction. The decay was negligible. The data to parameter ratio was 10.3/1. Reduction of the data was carried out using XCAD4 and all further work was carried out using the Siemens version of SHELX. The Laue merging R factor was a good 2% for 474 reflections with a density of 1.33 for 4 molecules in the unit cell, based on the assumption of a unique molecule.

The structure was solved by direct methods and determined from the difference map thus obtained. Two methylene chloride solvent molecules were located, although they suffered from disorder. The solution contains a model of this disorder that provided for the best fit of all data. All atoms except the hydrogens were refined anisotropically, and a final R of 4.1% with a GOF of 1.16 was obtained. The weighting scheme required a correction of 0.002.

X-ray Structural Determination of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl]OTf (9a): Well-formed pink crystals of **9a** were grown at -20 °C by layering a CH_2Cl_2 solution with diethyl ether. Diffraction measurements were made at 183 K. 25 reflections in the range 20° to 30° in 2θ were found and an orientation matrix was determined. The monoclinic space group was assigned as $P2_1/m$. A high–chi reflection led to a good absorption correction. The Laue merging R factor for 136 reflection was 2.2%. The decay was less than 1%.

The structure was solved by locating the position of the rhenium atom using the Patterson function. A final R of 4.3% with a GOF of 1 was obtained. The weighting scheme required a correction of 0.002.

The *tert*-butyl groups were disordered in the mirror plane of the cell and standard techniques were used to resolve this as much as possible. Carbons were introduced in the only mirror plane position possible and site occupancies were determined. Due to symmetry, it was not feasible to use distance fixing techniques and attempts to approximate this failed. The methyl carbons were refined with a common temperature factor. The anion was also disordered and disordered atoms were introduced from a difference map and occupancies determined. Two methylene chlorides were present and badly disordered.

Table 2.4 Crystal Data and Parameters for **5a** and **9a**.

Compound	**5a**	**9a**
Molecular Formula	$Re(CN\textit{t}Bu)_3(PCy_3)_2Cl \cdot 2CH_2Cl_2$	$[Re(CN\textit{t}Bu)_3(PCy_3)_2Cl]SO_3CF_3 \cdot 2CH_2Cl_2$
Empirical Formula	$C_{53}H_{97}Cl_5N_3P_2Re$	$C_{56}H_{97}Cl_5F_3N_3O_3P_2ReS$
Color; Habit	Clear Yellow Blocks	Clear Pink Plate
Crystal Size (mm)	0.34 × .36 × .38	0.5 × 0.1 × 0.15
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/m$
Unit Cell Dimensions	$\underline{a}$ = 14.270(3) Å $\underline{b}$ = 22.041(4) Å $\underline{c}$ = 18.827(4) Å β = 91.15(3)°	$\underline{a}$ = 11.440(2) Å $\underline{b}$ = 17.229(3) Å $\underline{c}$ = 16.009(3) Å β = 99.67(3)°
Volume	5935(3) $Å^3$	3110.5(16) $Å^3$
Z	4	2
Formula weight	1197.8	1374.8
Density(calc.)	1.341 Mg/m^3	1.468 Mg/m^3
Absorption Coefficient	2.361 mm^{-1}	2.306 mm^{-1}
F(000)	2476	1422
Radiation	MoKα (λ = 0.71073 Å)	
Temperature (K)	183	
Monochromator	graphite	
2θ Range	2 to 45°	2 to 50°
Scan Type	ω	
Scan Speed	variable; 1.5 to 5.5°/min. in ω	
Scan Range (ω)	0.80 + 0.35(tanθ)°	
Reflections Collected	8344	3224
Independent Reflections	7703 (R_{int} = 4.22%)	3026 (R_{int} = 3.17%)
Observed Reflections	5756 (F > 4.0σ(F))	2120 (F > 4.0σ(F))
# of Parameters Refined	560	337
R (observed data)	4.08%	4.36%
R_w	5.84%	5.46%
Goodness-of-fit	1.16	0.99

NOTES TO CHAPTER 2

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CHAPTER 3

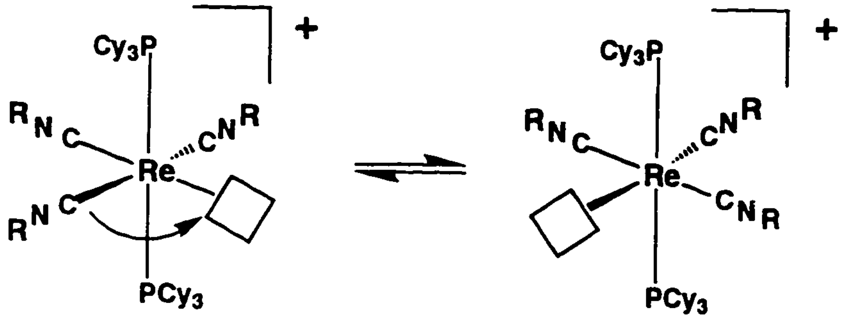
Dynamics and Reactivity of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]$^+$.

Introduction

This chapter explores the dynamic properties of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]$^+$ (**3a**) and its various adducts, as studied by line shape analysis and spin-saturation transfer techniques. Low temperature ^{31}P{^{1}H} NMR studies of **3a** are compared with those of [Re(CO)$_3$(PR$_3$)$_2$]$^+$ (R = Ph, *i*Pr, Cy), and W(CO)$_3$(PR$_3$)$_2$ (R = *i*Pr, Cy). A considerable reinterpretation of the low temperature ^{31}P{^{1}H} NMR spectrum of [Re(CO)$_3$(PCy$_3$)$_2$]$^+$ is offered.[1] The unique reactivity of **3a** towards O_2, PMe$_3$, NH$_3$, CO, C_2H_4, and H_2O is also explored.

Results

Dynamics of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]$^+$ (3a). The ^{1}H NMR spectrum indicated fluxional behavior for the isonitrile ligands in **3a**. The resonances corresponding to the isonitrile ligands were observed to broaden and coalesce as the temperature was raised from 298 to 328 K. These observations are consistent with the dynamic process indicated in Scheme 3.1.



Scheme 3.1 Isonitrile rearrangement.

The empty box in scheme 3.1 represents a vacant coordination site, which is believed to form transiently upon the dissociation of an agostic interaction. While it should be possible to obtain the rate constants for this process from line shape analysis, the interfering resonances of the cyclohexyl protons made this impractical. The equilibrium spin-saturation transfer technique became the method of choice. Indeed, it was observed that saturation of either isonitrile resonance showed spin-saturation transfer to the other one. Rate constants were obtained over a 43 °C temperature range by standard analysis for a two-site exchange process.[2] Figure 3.1 shows the resulting Eyring plot. The derived activation parameters are as follows: $\Delta H^{\ddagger} = 11.4 \pm 0.8$ kcal/mol, $\Delta S^{\ddagger} = -17.6 \pm 1.6$ cal/mol·K. This corresponds to $\Delta G^{\ddagger}_{298} = 16.6 \pm 1.2$ kcal/mol.

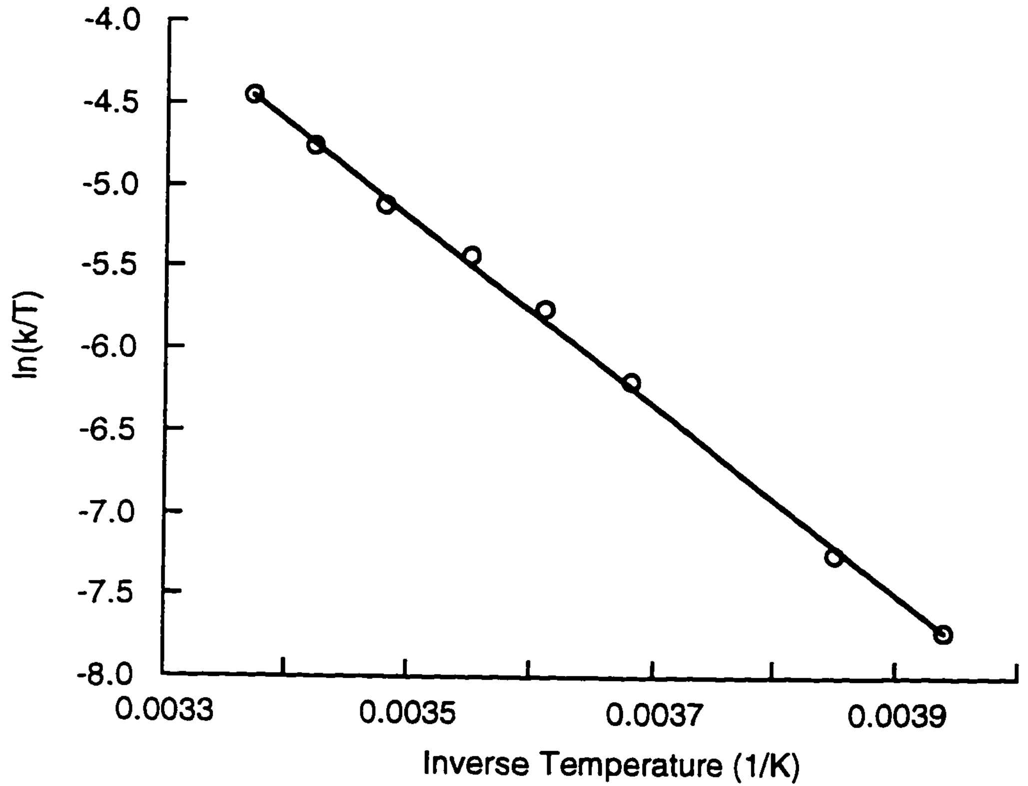
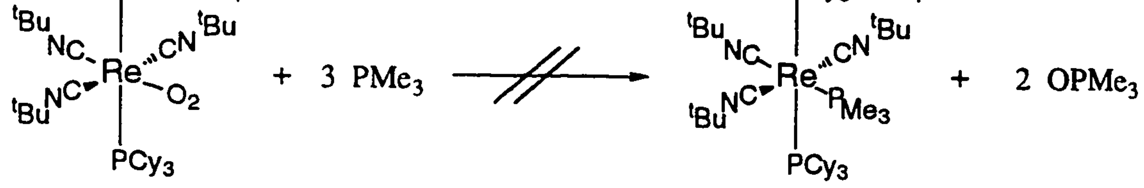


Figure 3.1 ln (*k*/T) *vs.* 1/T for the isonitrile isomerization in $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$.

Reaction of 3a with O_2. The complex, **3a**, was found to react with O_2 (1 atm) both in solution and in the solid state. Both reactions are rapid and result in the solution/solid changing from purple to colorless. The NMR spectrum (CD_2Cl_2) of either the product formed in solution or of the dissolved solid product shows that the quantitative conversion to a new species has taken place. The product exhibits a single ^{31}P NMR resonance (δ 1.1 ppm) and two ^1H NMR resonances in a 1:2 ratio (δ 1.59, 1.41 ppm) corresponding to the *tert*-butyl groups of isonitrile coligands. These spectra are consistent with an octahedral *mer, trans* geometry.

The sixth ligand is believed to be O_2, either in the η^1 superoxo, the η^2 superoxo, or in the η^2 peroxo binding mode. The elemental analysis is consistent with the dioxygen complex, $[Re(CN\textit{t}Bu)_3(PCy_3)_2(O_2)]^+$ (**11a**). The IR spectrum of **11a** in methylene chloride solution or as a Nujol mull did not show any bands assignable to ν(O–O) between 950–800 cm^{-1}, characteristic of η^2-peroxo ligand.[3] The region between 1200–1050 cm^{-1}, characteristic of η^1-superoxo ligand,[3] was alternately obscured by either of the two different counterions employed, BAr_f^- and BF_4^-. Three broad bands between 2193 and 2030 cm^{-1} were assigned to ν(C≡N). Another band, at 1712 cm^{-1}, is only observed for IR spectra of **11a** taken in methylene-chloride. This band has not been assigned.

An attempt was made to react **11a** with three equivalents of PMe_3 in order to further confirm the number of oxygens associated with each metal center (eq 3.1). The formation of two equivalents of $OPMe_3$ and one equivalent of $[Re(CN\textit{t}Bu)_3(PCy_3)_2(PMe_3)]^+$ (**12a**) (*vide infra*) would offer reasonable proof that there are two oxygens per metal center.



11a **12a**

Equation 3.1

Neither of these anticipated products was observed after 4 h (298 K). The instability of **11a** in methylene chloride (*vide infra*) made it impossible to conduct the reaction over longer periods or at elevated temperatures. The lack of solubility of **11a** in THF precluded the use of this alternative solvent.

Complex **11a** only shows moderate stability in CD_2Cl_2, and decomposes with an approximate half-life of 2 hours to form several products, the most conspicuous being an unidentified complex with a $^{31}P\{^1H\}$ NMR resonance at -3.7 ppm. This compound could not be identified as it too decomposes in methylene chloride ($t_{1/2} \approx 4$ h). Those decomposition products which could be identified include, $[Re(CNtBu)_4(PCy_3)_2]^+$ (**4a**), $[Re(CNtBu)_3(PCy_3)_2Cl]^+$ (**9a**), *tert*-butyl isocyanate, and $OPCy_3$.

The reversibility of this reaction was probed in the solid state by exposing the product to dynamic vacuum for 15 h at 25 °C. After only a slight yellowing of the solid was observed, the temperature was increased to 100 °C. At this temperature, the solid rapidly turned brown after 1 h. After 12 h, it had formed a black congealed tar at the bottom of the tube. It should be noted that **3a**, the anticipated product (should the reaction be reversible), is stable to these conditions.

The dioxygen complex, $[Re(CNtBu)_3(PCy_3)_2(O_2)]^+$ (**11a**), could also be formed by combining either $[Re(CNtBu)_3(PCy_3)_2(H_2)]^+$ (**2a**), or $[Re(CNtBu)_3(PCy_3)_2(N_2)]^+$ (**10a**) with O_2. Both reactions were also found to be irreversible. Pressurizing a solution of $[Re(CNtBu)_3(PCy_3)_2(O_2)]^+$ (**11a**) with H_2 (1 atm) resulted in no back reaction (298 K). Neither **2a** nor **10a** react as rapidly with O_2 as the agostic complex, **3a**. For both **2a** and **10a**, detectable amounts of starting material could still be observed by ^1H and $^{31}P\{^1H\}$ NMR after 30 min of reaction.

Reaction of 3a with PMe$_3$. It was possible to generate [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(PMe$_3$)]$^+$ (**12a**) from the direct reaction of the agostic complex, **3a**, with PMe$_3$ in methylene chloride-*d*$_2$. PMe$_3$ also displaces H$_2$ from **2a** to form **12a**. Complex **12a** was characterized in solution by ^{1}H NMR and ^{31}P{^{1}H} NMR. The ^{31}P{^{1}H} NMR spectrum shows two multiplets, a doublet of intensity two (δ -4.0) and a triplet of intensity one (δ -54.6). The coupling constants are of equal magnitude (J_{PP} = 15 Hz). A 15 Hz coupling constant is consistent with *cis* coordination of the PMe$_3$ ligand relative to the PCy$_3$ ligands.[4] The ^{1}H NMR spectrum exhibits a doublet (δ 1.56, J_{HP} = 7 Hz), for the methyl groups of the PMe$_3$ ligand, and the *tert*-butyl groups of the isonitrile ligands show up in the expected 1:2 ratio (Table C.2).

Reaction of 3a with NH$_3$. Pressurizing **3a** (solid or solution) with NH$_3$ (0.9 atm) results in an immediate color change, purple to yellow. Elemental analysis of the solid product is consistent with [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(NH$_3$)]$^+$ (**13a**). The ^{31}P{^{1}H} NMR spectrum shows a single resonance indicating equivalent phosphines. The ^{1}H NMR spectrum of **13a** shows two singlets (Table C.2) in a 2:1 ratio corresponding to the *tert*-butyl isonitrile ligands. The resonance corresponding to the protons of the bound NH$_3$ ligand (δ 2.35) could not initially be assigned from the ^{1}H NMR spectrum, due to overlap with the protons of the cyclohexyl groups. Its position was determined from the ^{2}H NMR spectrum (CH$_2$Cl$_2$) of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(ND$_3$)]$^+$ (**13a**-*d*$_3$) which exhibited one peak (δ 2.3) in addition to the resonance for unbound ND$_3$ and solvent (Figure 3.2).

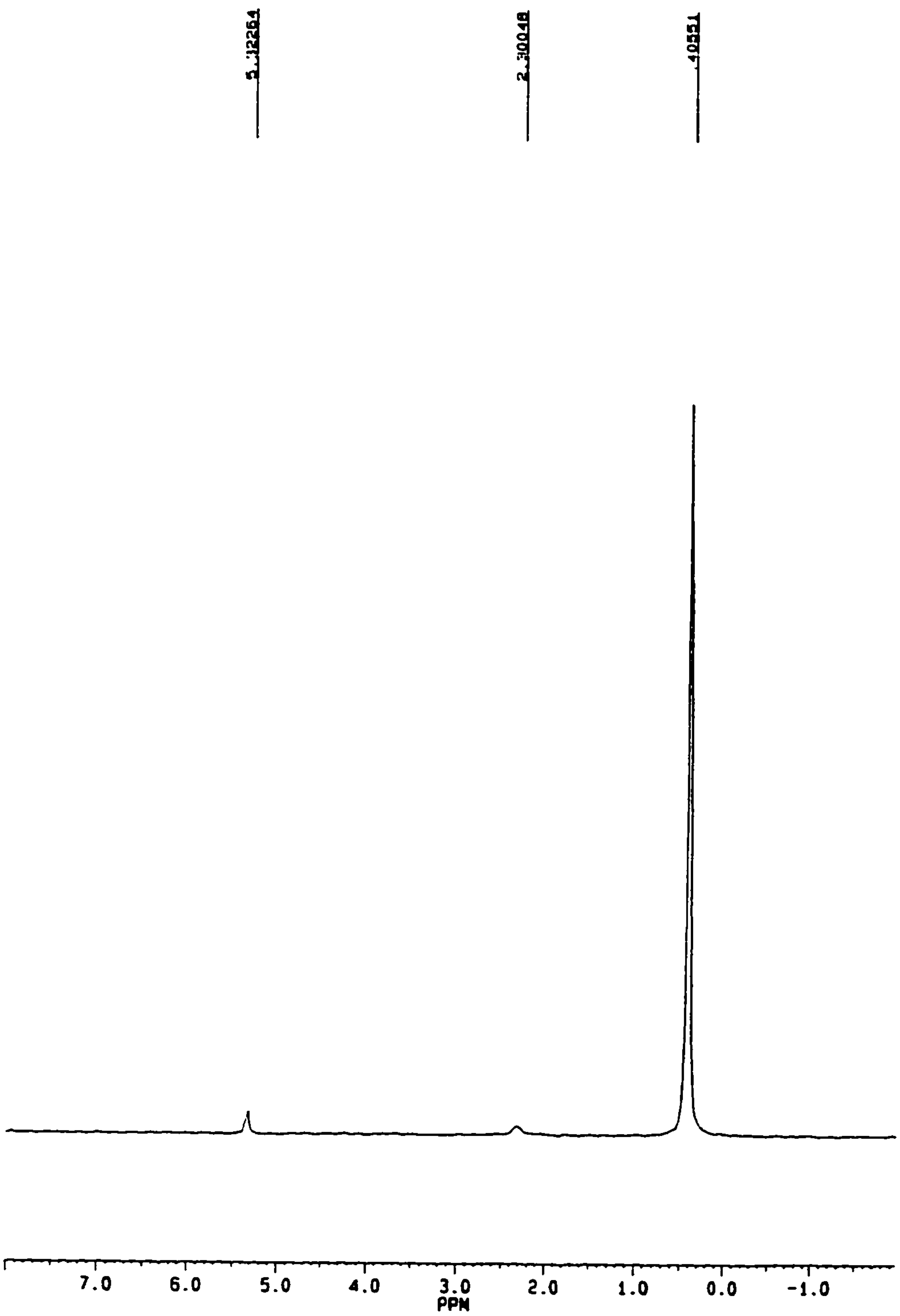
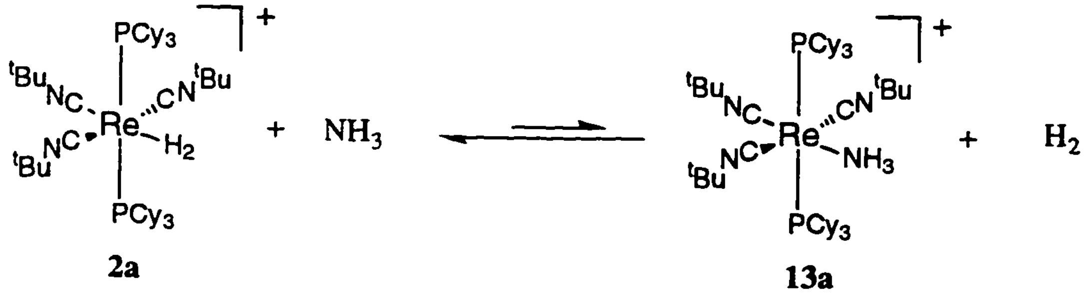


Figure 3.2 ^{2}H NMR spectrum (298 K) showing the resonances of free (δ 0.41) and coordinated ammonia-d_3 (δ 2.30) as well as solvent (δ 5.32).

$[Re(CN\textit{t}Bu)_3(PCy_3)_2(NH_3)]^+$ (**13a**) is also formed by pressurizing a solution of the dihydrogen complex (**2a**) in CD_2Cl_2 with NH_3 (1.1 atm) (eq 3.2). Within seconds the solution is observed to change from colorless to pale yellow. ^1H and $^{31}P\{^1H\}$ NMR spectra indicate that not all of the bound H_2 is displaced by NH_3, suggesting that binding of H_2 and NH_3 is competitive. The reversibility of the reaction was probed by briefly exposing the solution to dynamic vacuum, and then pressurizing the headspace with H_2 (1.1 atm). The relative concentrations of the species in equation 3.2 were observed to shift back towards **2a** and NH_3.



Equation 3.2

By pressurizing a solution of **3a** with roughly equal amounts of H_2 and NH_3 (600 torr each), it was possible to observe all species, **2a**, **13a**, free H_2, and NH_3 simultaneously, by ^1H NMR spectroscopy. The equilibrium constant was calculated from the relative concentrations using the expression:

$$K_{eq} = \frac{[\mathbf{13a}][H_2]}{[\mathbf{2a}][NH_3]} \qquad (3.3)$$

The temperature dependence of K_{eq} (eq 3.3) was determined over the temperature interval 224–297 K. The calculated equilibrium constants varied only slightly from 8.5×10^{-3} (224 K) to 7.8×10^{-3} (297 K). A Van't Hoff plot is shown in Figure 3.3. The thermodynamic parameters for the formation of $[Re(CN\textit{t}Bu)_3(PCy_3)_2(NH_3)]^+$ and H_2

from $[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]^+$ and NH_3 are as follows: $\Delta H^\circ = -0.4 \pm 0.2$ kcal/mol, $\Delta S^\circ = -11.3 \pm 0.6$ e.u., and $\Delta G^\circ_{298} = 2.9 \pm 0.4$ kcal/mol.

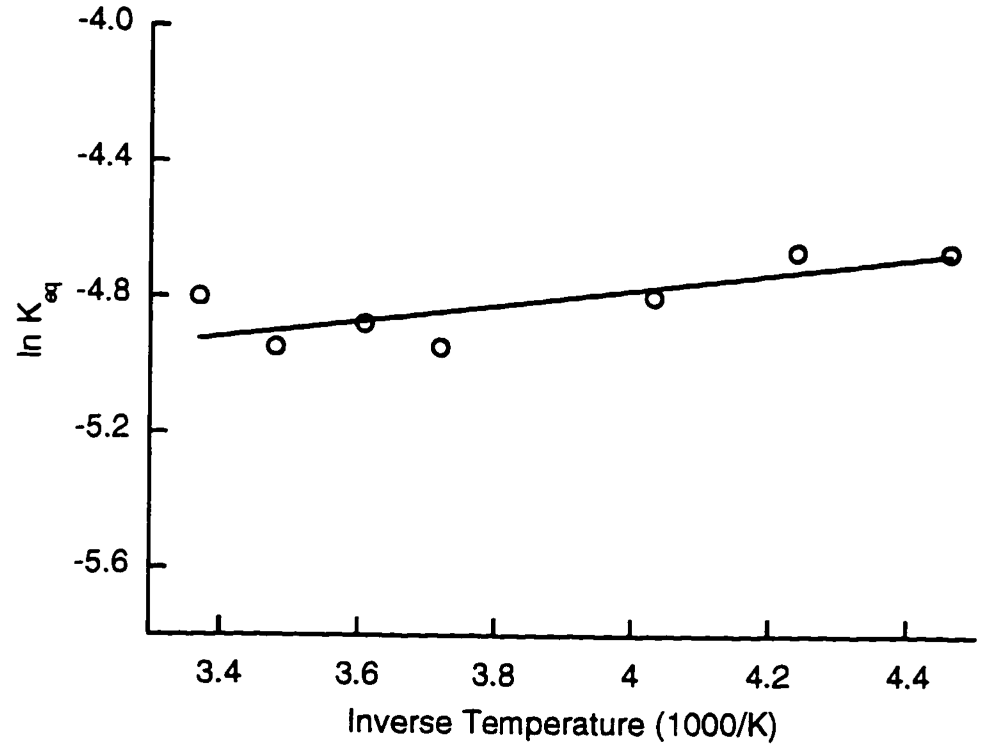
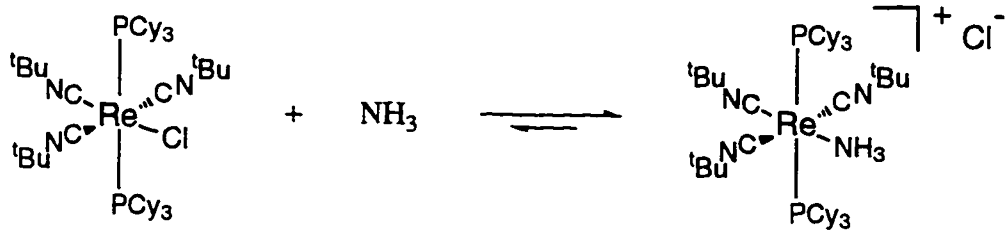


Figure 3.3 ln (K_{eq}) *vs.* 1/T for the equilibrium, **2a** + NH_3 $\rightleftharpoons$ **13a** + H_2.

The reaction of $Re(CN\textit{t}Bu)_3(PCy_3)_2Cl$ (**5a**) with ammonia also leads to an observable chemical equilibrium (eq 3.4).



5a

13a

Equation 3.4

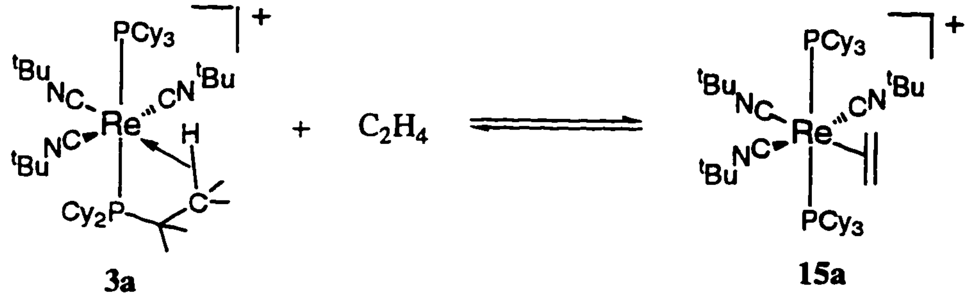
The equilibrium constant (eq 3.5) for this reaction was determined from the relative concentrations of **5a**, free ammonia, and **13a**, as determined by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.

$$K_{eq} = \frac{[\mathbf{13a}]}{[\mathbf{5a}][\mathrm{NH_3}]} \qquad 3.5$$

At 298 K, K_{eq} equals 31 M^{-1}, which corresponds to $\Delta G°_{298} = -2.0 \pm 0.2$ kcal/mol.

Reaction with CO. The dihydrogen complex $[Re(CN\mathit{t}Bu)_3(PCy_3)_2(H_2)]BF_4$ **2a-BF$_4$** is observed to react irreversibly with carbon monoxide in methylene chloride-d_2. The reaction of **3a** with CO showed the characteristic loss of purple color signaling adduct formation. The product exhibited a single ^{31}P{^{1}H} NMR resonance (δ 11.1) and two ^{1}H NMR resonances in a 2:1 ratio (δ 1.47, 1.46) corresponding to the *tert*-butyl groups of the isonitrile ligands. The ^{13}C{^{1}H} NMR spectrum showed a downfield triplet of low intensity (δ 199.0, J_{CP} = 6 Hz). Taken together these spectra are consistent with [*mer,trans*-$Re(CN\mathit{t}Bu)_3(PCy_3)_2(CO)]BF_4$ (**14a**). The IR spectrum of **14a** showed four bands of medium intensity in the range 2150–2045 cm^{-1} which were assigned to ν(C≡N). A strong band at 1900 cm^{-1} was assigned to ν(C≡O).

Reaction with Ethylene. Placing ethylene (130 torr) over a solution of $[Re(CN\mathit{t}Bu)_3(PCy_3)_2]BF_4$ (**3a-BF$_4$**) in methylene chloride-d_2 did not cause the characteristic loss of purple color indicative of adduct formation, at least not at ambient temperature. However, upon cooling to -78 °C, the solution did become colorless. This was observed to happen reversibly. Heating the solution back to 25 °C changed the color back to purple. Similar loss of color upon cooling is not observed in the absence of ethylene. As the temperatures is lowered below 0 °C, ^{1}H and ^{31}P{^{1}H} NMR data indicate that a new species, consistent with $[Re(CN\textit{t}Bu)_3(PCy_3)_2(C_2H_4)]^+$ (**15a**), is in equilibrium with **3a** (eq 3.6).



Equation 3.6

At 256 K, complex **15a** exhibits a single ^{31}P NMR resonance (δ -3.9) and two ^1H NMR resonances in a 2:1 ratio (δ 1.52, 1.29) corresponding to the *tert*-butyl groups of isonitrile ligands. The resonance corresponding to the bound ethylene (δ 2.2) is broad and could not initially be assigned from the ^1H NMR spectrum. Its position was determined from the ^2H NMR spectrum (CH_2Cl_2, 256 K) of $[Re(CN\textit{t}Bu)_3(PCy_3)_2(C_2D_4)]^+$ (**15a**-d_4) which exhibited one broad peak (δ 2.3) in addition to the resonance for unbound C_2D_4. From the relative concentrations of **3a**, free ethylene, and **15a**, as determined by ^1H NMR spectroscopy, the equilibrium constant for the reaction (eq 3.6) was determined from equation 3.7.

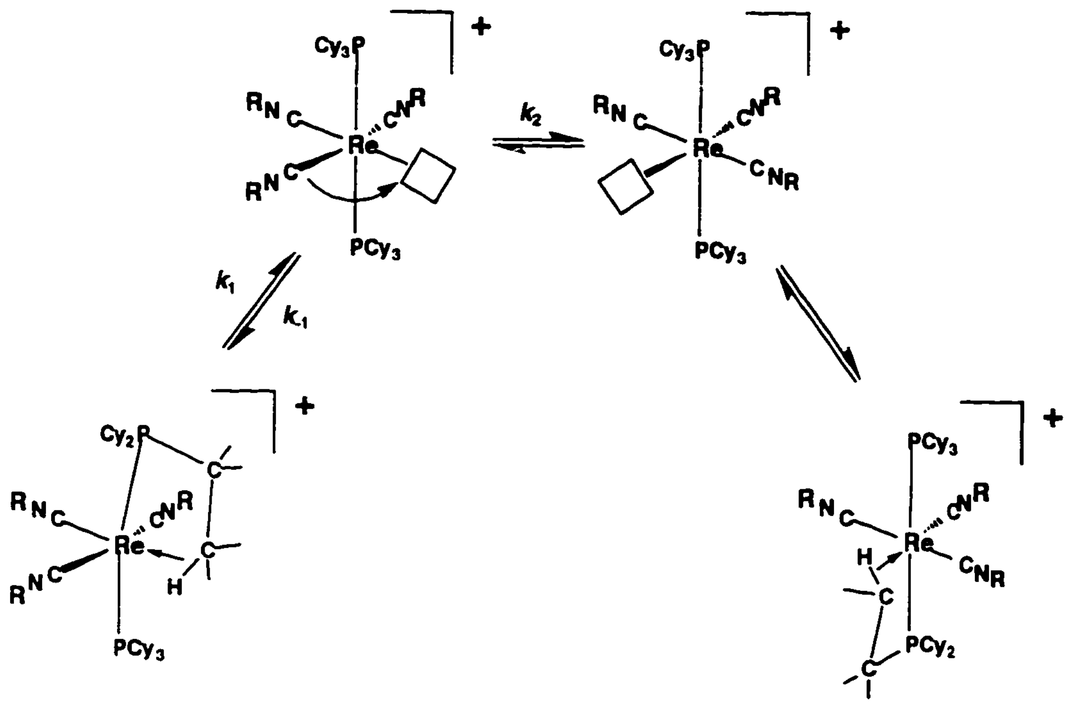
$$K_{eq} = \frac{[\mathbf{15a}]}{[\mathbf{3a}][C_2H_4]} \qquad 3.7$$

At 261 K, where the concentrations of **3a** and **15a** were approximately equal, K_{eq} is calculated to be 24 M^{-1}. This corresponds to $\Delta G^\circ_{261} = -1.6$ kcal/mol.

Attempted Reaction of 3a with H_2O. Even in a biphasic CD_2Cl_2/H_2O mixture , **3a-BF$_4$** does not react with water. Both the color and ^1H and $^{31}P\{^1H\}$ NMR spectra remain unchanged.

Discussion

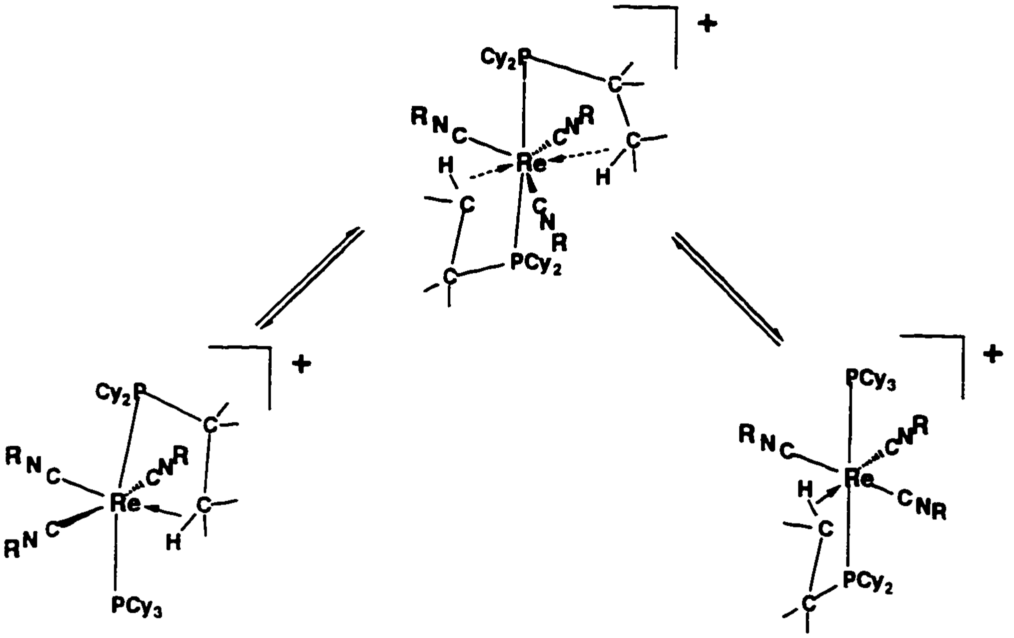
Structure and Dynamics of $[Re(CNtBu)_3(PCy_3)_2]^+$ (3a). Since additional ligands can be added to $[Re(CNtBu)_3(PCy_3)_2]^+$ (**3a**), it fits the operational definition of coordinative unsaturation presented by Strauss.[5] The solution structure of **3a** possesses either weak solvent coordination, a vacant coordination site, or an agostic interaction. Agostic interactions have been convincingly demonstrated for both $W(CO)_3(PCy_3)_2$[6] and $[Re(CO)_3(PCy_3)_2]^+$[1] in the solid state. If an agostic interaction also exists for **3a**, then the activation parameters derived for the isonitrile rearrangement (Scheme 3.1) provide some insight into the strength of this interaction. In order for an isonitrile to change its position, we can consider both dissociative and associative mechanisms. A dissociative mechanism (Scheme 3.2), implies that the agostic bond must first break in order to open up the sixth coordination site. For the second step, orbital arguments suggest that the most favorable mechanism is for a single isonitrile to move, so that an energetically unfavorable D_{3h} transition state can be avoided.[7] If the pre-equilibrium dissociation of the agostic bond (k_1) is rate limiting, then the activation enthalpy ($\Delta H^\ddagger = 11.4 \pm 0.8$ kcal/mole) for this process approximates the strength of the Re$\cdots$H–C interaction.



Scheme 3.2 Isonitrile rearrangement by dissociative mechanism.

An agostic bond strength of 11.4 ± 0.8 kcal/mole is in fact reasonable. Hoff has estimated the strength of the agostic interaction in $W(CO)_3(PCy_3)_2$ to be 10 ± 6 kcal/mole.[8] Furthermore, results from photoacoustic calorimetry show that the strength of the metal alkane bond in $Mo(CO)_5$(heptane) is 15 ± 1 kcal/mole.[9] Since the rate limiting step (k_1 or k_2) for the proposed dissociative mechanism is not known, the value of 11.4 ± 0.8 kcal/mole can only serve as an upper limit to the strength of the agostic bond.

It is also useful to consider an associative mechanism for this rearrangement. In fact the rather large, negative entropy of activation ($\Delta S^{\ddagger}$ = -17.6 ± 1.6 e.u.) is consistent with a well-ordered transition-state in which considerable bond formation has occurred (Scheme 3.3).



Scheme 3.3 Isonitrile rearrangement by associative mechanism.

While an associative mechanism seems unlikely for such a sterically-crowded complex, Hoff and coworkers have found evidence for partial formation of a W···H-C agostic bond in the transition-state for the dissociation of pyridine from the similarly crowded complex, $W(CO)_3(PCy_3)_2(py)$.[10] Until more definitive results are available, both associative and dissociative mechanisms must be considered as viable possibilities for this rearrangement.

LT ^{31}P NMR Studies. It was thought that a low temperature $^{31}P\{^1H\}$ NMR study of **3a** would help resolve some of the issues raised by the spin-saturation-transfer study. The phosphines of **3a** are predicted to be inequivalent on the grounds that one of them is binding to the metal *via* one of its H–C bonds, while the other one isn't. At 298 K, the $^{31}P\{^1H\}$ NMR peak corresponding to **3a** is a singlet, presumably because the on–off rate of the agostic interaction is fast on the NMR time-scale. At sufficiently low temperatures, it should be possible to stop this exchange. A study of this kind has been previously attempted for the carbonyl analog, $[Re(CO)_3(PCy_3)_2]^+$.[1] The $^{31}P\{^1H\}$ NMR resonance for this complex is also a singlet at ambient temperature. At lower temperatures however it decoalesces (T_c = 240 K)reversibly into an AB pattern (J_{PP} = 93 Hz) and a broad peak. The signal intensity of the AB pattern and the broad peak are approximately equal. Interpretation of the spectrum was possible by ignoring the broad peak, and assuming that the AB pattern corresponded to the frozen out agostic complex. From the frequency difference of the two chemical shifts, the free energy of activation was calculated at the temperature of coalescence ($\Delta G^{\ddagger}_{240}$ = 10.4 kcal/mol). This was said to reflect the strength of the agostic interaction. Significantly, of the three carbonyl complexes, $[Re(CO)_3(PR_3)_2]^+$ (R = Cy, *i*Pr, Ph), only the $^{31}P\{^1H\}$ NMR resonance of the PCy_3 complex decoalesces at lower temperatures. All the others remain as singlets, and show no sign of broadening even at the lowest accessible temperature (*ca.* 176 K). It remained to be explained why the agostic interaction of the PCy_3 compound should be so much stronger.

Very similar observations have now been made for $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ (**3a**). The $^{31}P\{^1H\}$ NMR resonance of this complex also decoalesces (T_c = 220 K) into an AB pattern (J_{PP} = 142 Hz) and a broad resonance, which accounts for approximate 50% of the signal intensity.[11] The differences involve the placement of the broad peak. In the present case, it resonates between the two AB doublets. For the carbonyl system, it resonates outside of, and upfield, of the AB pattern. Needless to say, the appearance of the broad peak, now for the second time, suggested that a more critical evaluation was warranted.

The problematic issue is that the broad peak indicates that another species of comparable energy is in equilibrium with the AB system. The AB system, in turn, is believed to correspond to the frozen-out agostic complex. It is not immediately obvious what sort of species would correspond to the broad peak. The idea that this species might be the truly unsaturated, 16 electron complex (*i.e.* no agostic interactions at all), was not acceptable in light of the evidence that an agostic interaction should be worth approximately 10 kcal/mol of binding energy.[8,9] Alternative explanations were sought. One possibility that was considered is that the broad peak might correspond to another agostic complex of a slightly different structure. In both the crystal structures of $[Re(CO)_3(PCy_3)_2]^+$ and $W(CO)_3(PCy_3)_2$, the apparent agostic interactions are between the metal and a H–C bond of one of the β-carbons.[6,1] Counting the hydrogen, a five-membered ring is thereby formed. An agostic interaction from the metal to the H–C bond of one of the γ-carbons to from a six-membered ring could also be imagined. Precedent for this possibility is provided by some kinetic studies by Caulton and coworkers.[12] They found that the reaction of $Re(PCy_3)_2H_7$ with C_6D_6 leads to deuterium incorporation into the cyclohexyl rings of the phosphine ligands. Presumably this is occurring through a transiently formed cyclometallated complex. Significantly, they report that deuterium incorporates faster into the hydrogens of the γ-carbons than the β-carbons. A stable agostic interaction to a γ-carbon is therefore quite plausible.

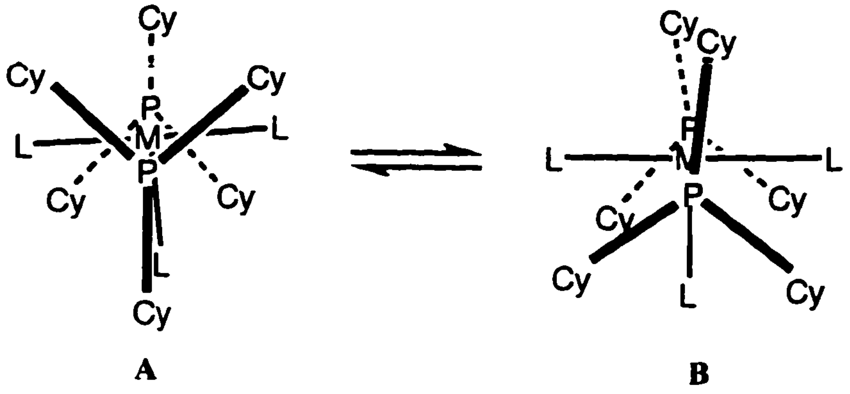
The approach taken to investigate this possibility was to attempt $^{31}P\{^1H\}$ NMR studies of complex **3a** at even lower temperatures. The idea was to decoalesce the broad peak into what was predicted to be another separate AB pattern and thereby freeze out the hypothetical Re···H–γC interaction. By either conducting the experiment in supercooled methylene chloride-d_2 solutions, or using the solvent $CDFCl_2$, it was possible to acquire $^{31}P\{^1H\}$ NMR spectra in the range 140–160 K. These spectra show that at lower temperatures, the broad peak does decoalesce and that another AB pattern ($J_{PP} \approx 150$ Hz) does emerge. However, along with this AB pattern, there is yet another broad singlet peak that decoalesces with it. This fractal-like behavior was most perplexing. The study did. however, lead to an important observation.

It was observed that not only did the $^{31}P\{^1H\}$ NMR resonance of **3a** decoalesce at low temperatures but so did the $^{31}P\{^1H\}$ NMR resonance of the dihydrogen complex, $[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]^+$ (**2a**). (There was some **2a** present in the sample.) The $^{31}P\{^1H\}$ NMR resonance (singlet at 298 K) for **2a** decoalesces ($T_c \approx 190$ K) into two broad peaks in an approximately 40:60 ratio (T ≈160 K).[13] Line shape analysis for the ^{31}P NMR spectrum indicates that $\Delta G^{\ddagger}_{190} \approx 8$ kcal/mol. (It might be argued that all peaks would be described as broad at these low temperatures, but this was not observed to be the case. Another minor impurity present in the sample was the tetra isonitrile complex, **4a**, which definitely remained much sharper ($\nu_{1/2} = 15$ Hz) at these temperatures (160 K) than any of the peaks associated with either **2a** or **3a**.) The decoalescence of the $^{31}P\{^1H\}$ NMR resonance of **2a** presented us with a new puzzle—a less complicated one, it was hoped.

The initially favored explanation was that complex **2a** did not possess 100% dihydrogen structure, but in fact existed as an equilibrium between *dihydrogen* and *dihydride* tautomers. Such dynamic equilibria have been seen in solution for several complexes.[14] The studies most relevant to **2a** are those by Kubas and coworkers for $W(CO)_3(PR_3)_2(H_2)$ (R = *i*Pr, Cyp, Cy).[14c-e] Both species are observed as *separate* resonances by ^1H and $^{31}P\{^1H\}$ NMR at 298 K. Where R = *i*Pr, ^{31}P NMR spin saturation transfer studies afford the thermodynamic parameters for the dihydrogen to dihydride exchange process: $\Delta H^{\ddagger} = 10.1 \pm 1.8$ kcal/mole, $\Delta S^{\ddagger} = -19.9 \pm 6.0$ e.u., $\Delta G^{\ddagger}_{298} = 16.6 \pm 0.2$ kcal/mole.[14e] These values are considerably greater than those observed for the exchange process observed in **2a** ($\Delta G^{\ddagger}_{190} \approx 8$ kcal/mol), indicating that either dihydride/dihydrogen interconversion is remarkably more rapid for **2a**, or that the observed exchange process corresponds to an entirely different rearrangement.[15]

Several important observations lead us to suspect the latter. The initially most startling observation was that the $^{31}P\{^{1}H\}$ NMR resonance of Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl (**5a**) also decoalesces upon cooling the sample. Like **3a**, the spectrum of **5a** displays an AB pattern and a broad peak. Since **5a** is a straight forward octahedral complex without agostic interactions or dihydrogen ligands, it was difficult to rationalize these observations in a similar manner. More observations (mine and others) soon followed, which are summarized with the earlier ones as follows: The $^{31}P\{^{1}H\}$ NMR resonances of Re(CN*t*Bu)$_3$(PCy$_3$)$_2$X (X = H, Cl, I), [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$L]$^+$ (L = agostic, H$_2$,[16] NH$_3$, C$_2$H$_4$), [Re(CO)$_3$(PCy$_3$)$_2$]$^+$,[1] and W(CO)$_3$(PCy$_3$)$_2$[17] *all* decoalesce into a pair of AB doublets and a broad singlet upon cooling. The $^{31}P\{^{1}H\}$ NMR resonances of [Re(CN*t*Bu)$_4$(PCy$_3$)$_2$]$^+$ (**4a**), [Re(CN*t*Bu)$_3$(PPh$_3$)$_2$(H$_2$)]$^+$ (**2b**), [Re(CO)$_3$(PR$_3$)$_2$]$^+$ (R = Ph, *i*Pr),[1] and W(CO)$_3$(P*i*Pr$_3$)$_2$[17] *do not* decoalesce upon cooling. A pattern had formed that could not be denied.

These observations are consistent with the freezing out of the two rotational conformers depicted below (Scheme 3.4). In both cases the sixth coordination site is left unfilled to represent a ligand of type X, L, or H–C (agostic).



Scheme 3.4 Isomerization between two rotomers as viewed down the P–M–P axis.

In structure **A** the cyclohexyl groups of one phosphine are staggered with respect to the cyclohexyl groups of the other phosphine. When rotation of the phosphorus rotor is slow on the NMR time scale they are inequivalent, since there is no symmetry element which relates them. The phosphines should therefore resonate at different chemical shifts and show large equivalent couplings.[4] Rotomer **A** therefore corresponds to the AB pattern. In rotomer **B**, the cyclohexyl groups of the phosphines are eclipsed with respect to one another. Regardless of whether rotation of the phosphorus rotor is fast or slow on the NMR time-scale, these phosphines will be equivalent since they are related by a mirror plane. Structure **B** is therefore consistent with the broad singlet observed alongside the AB doublets. Interestingly, X-ray crystal structures of **1a**, **2a**, **5a**, and **9a** all correspond best to geometry **B** (see especially Figures 2.3 and 2.5). Since our arguments suggest that structure **A** should have a similar energy to that of **B**, the lack of structural evidence for **A** may be attributed to less favorable crystal packing interactions, or slower crystal growth rates.

In the case where all four ligands in the meridinal plane are equivalent, *i.e.* for $[Re(CN\textit{t}Bu)_4(PCy_3)_2]^+$ (**4a**), the phosphines are equivalent for both geometries . In **A** the phosphines are related by a C_2-rotation axis; in **B** they are related by a plane of symmetry. The potential therefore exists for the $^{31}P\{^1H\}$ NMR resonance of **4a** to decoalesce into two singlets at low temperatures. The observation of one singlet isn't surprising, however. With equivalent ligands in the meridinal plane, there would be no energetic preference for geometry **B**, in which the two cyclohexyl groups eclipse the same L. The geometry that is most likely adopted is **A**. The observation that the $^{31}P\{^1H\}$ NMR resonances of the PPh_3 and $P\mathit{i}Pr_3$ analogs do not decoalesce when cooled below 200 K is consistent with PPh_3 and $P\mathit{i}Pr_3$ having smaller cone angles than PCy_3.[18]

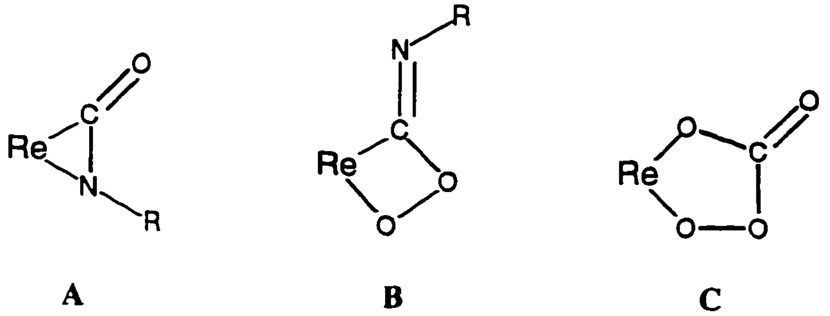
It should be noted that the interpretation presented is consistent with *all* the observations for these complexes, and represents a considerable revision of the previously reported interpretation.[1] Caulton *et al.* have also observed hindered rotation about the M–P single bonds in $RuHX(CO)(P\mathit{t}Bu_2Me)_2$ and $IrHCl_2(P\mathit{t}Bu_2Me)_2$.[19] Both of these complexes also contain very sterically demanding phosphines and exhibit LT $^{31}P\{^1H\}$ NMR spectra which are remarkably similar to those described above.

The rotation of the phosphorus rotor about the M–P single bond in **3a**, and the isonitrile rearrangement (*vide supra*), are distinct dynamic processes. ^1H NMR spectra of **3a** at 298 K clearly show two isonitrile peaks in a 2:1 ratio, indicating inequivalent isonitriles. The peaks are somewhat broadened by exchange, especially on the lower field instruments. Warming the solution causes the peaks to broaden further and eventually *coalesce* ($T_c \approx 320$ K). This exchange process corresponds to the isonitrile rearrangement studied by spin-saturation transfer technique. Cooling the solution below 298 K also causes the isonitrile peaks to broaden and *decoalesce* ($T_c \approx 210$ K) to give two sets of unequal singlets in the predicted ratio.[20] This spectrum presumably corresponds to the slow exchange region for the conformational isomerization between **A** and **B** (Scheme 3.4), which is entirely distinct from the isonitrile site exchange.

By rotating the phosphine which is not chelating to the metal *via* an agostic interaction, interchange between conformers **A** and **B** can take place without the agostic bond breaking. If one assumes that the agostic bond can form without perturbing the chemical shift of the phosphine (an admittedly difficult, but possibly accurate, position to take), the energetics of the conformational isomerism seen in these systems between rotomers **A** and **B** will have little bearing on the strength of the agostic bond. One is then lead to conclude that, of the two dynamic processes, the isonitrile rearrangement has the greater bearing on the energetics of the agostic interaction.

Dioxygen Complex. Three other coordinatively unsaturated complexes have been reported to bind dioxygen at an established dihydrogen binding site. These are $[RuH(dippe)_2]^+$,[21] $[Cp^*Ru(dppe)]^+$,[22] and $OsHCl(CO)(P\mathit{i}Pr_3)_2$.[23] All of these show reversible binding of H_2 but *irreversible* binding of O_2. Our observations for the reaction of $[Re(CN\mathit{t}Bu)_3(PCy_3)_2]^+$ (**3a**) with oxygen and hydrogen conform to this trend. $[Re(CN\mathit{t}Bu)_3(PCy_3)_2(H_2)]^+$ (**2a**) readily loses H_2 to give **3a**, but the dioxygen complex, **11a**, does not lose O_2, even under forcing conditions. This is not the case for all dioxygen complexes. Both hemoglobin and Vaska's complex react reversibly with O_2.[24] Vaska's complex also reacts reversibly with H_2, but the product has dihydride, not dihydrogen, structure.

The identified decomposition products of **11a** in methylene chloride include *tert*-butyl isocyanate, $P(O)Cy_3$, and $[Re(CN\mathit{t}Bu)_4(PCy_3)_2]^+$ (**4a**). The formation of $[Re(CN\mathit{t}Bu)_4(PCy_3)_2]^+$ (**4a**) is not unexpected. Previous work in our group has shown that $[Re(CO)_3(PCy_3)_2]^+$ reacts with oxygen to give $[Re(CO)_4(PCy_3)_2]^+$ in *ca.* 60% yield.[1] No intermediates were detected. The high recovered yield accounts for all the CO, and rules out the possibility of oxidation of CO to CO_2. The oxidization of phosphines and isonitriles by dioxygen complexes has been reported.[25] The majority of these reactions are believed to occur intramolecularly. A mechanism for the formation of the decomposition products of **11a** is not known, however, the band observed at 1712 cm^{-1} might provide a clue. Since this band is only observed in IR spectra of **11a** in methylene chloride, and not in the solid state, it may correspond to a decomposition product. Three possibilities are considered in Scheme 3.5.



Scheme 3.5

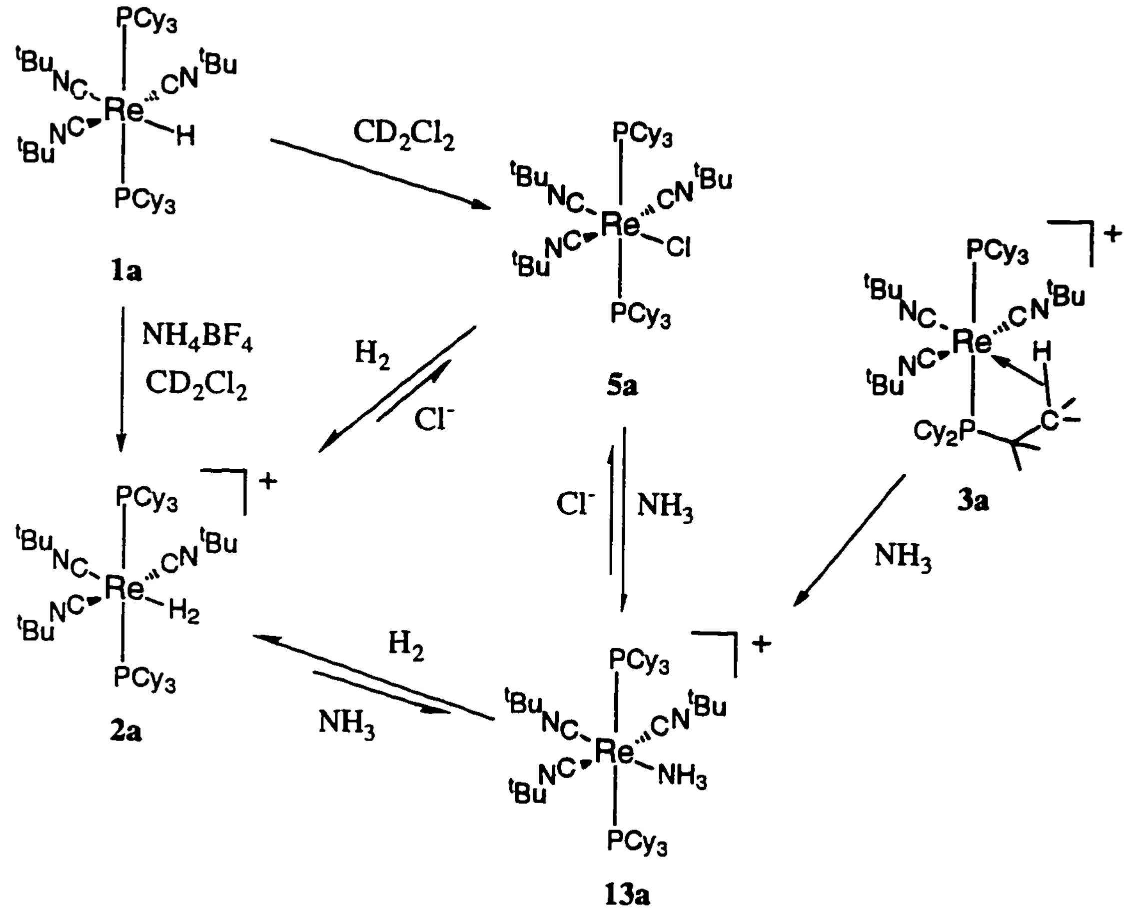
Structure **A** shows a coordinated isocyanate, which could be formed by cleavage of the O–O bond and insertion of an oxygen into the isonitrile. Coordinated isocyanates with this structure are known for rhenium. The complex Re(dppe)$_2$(η^2-N(O)CMe)Cl has been reported with a ν(C=O) frequency at 1835 cm^{-1}.[26] A peroxoformate structure analogous to **B** has been proposed for a carbonyl system.[27] The peroxycarbonate (structure **C**) is a product frequently observed when a dioxygen complex reacts with CO$_2$.[25] Since the IR investigations of **11a** in methylene chloride were not conducted in a CO$_2$ free environment, structure **C** cannot be ruled out. Further studies of **11a** and its decomposition in methylene chloride are necessary to resolve these uncertainties. A structural investigation is most desirable.

Reaction with H$_2$O. The lack of affinity of **3a** for ligands coordinating through an oxygen atom, with the exception of O$_2$, extends from THF to less sterically demanding ligands such as H$_2$O. The observations are in contrast to the [Re(CO)$_3$(PR$_3$)$_2$]$^+$ (R = Cy, *i*Pr, Ph) which were found to bind both THF and H$_2$O.[1,28]

In fact, for R = Ph binding of water was observed to be so strong that it was deemed irreversible. Kubas and coworkers have reported that H_2O competes favorably with H_2 at the complexes $W(CO)_3(PR_3)_2$ (R = Cy, *i*Pr).[29] For the reaction $W(CO)_3(PCy_3)_2(H_2)$ + $H_2O \rightleftharpoons W(CO)_3(PCy_3)_2(H_2O) + H_2$, the reaction was enthalpically favored, ΔH° = -2.8 ± 0.1 kcal/mole, and entropically disfavored ΔS° = -16.5 ± 2.0 cal/mol·K. We find that these observations are further evidence that **3a** is not a strong σ Lewis acid, but relies heavily on its π basicity for ligand binding.

The PMe_3 Complex. Both $[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]^+$ (**2a**) and $[Re(CN\textit{t}Bu)_3(PCy_3)_2]^+$ (**3a**) readily react with PMe_3 to form $[Re(CN\textit{t}Bu)_3(PCy_3)_2(PMe_3)]^+$ (**12a**). Complex **3a** may also react with slightly larger phosphines, but this reaction was not attempted. Kubas and coworkers report that $P(OMe)_3$, $P(OPh)_3$, PPh_2Me, and P-*n*-Bu_3 will displace coordinated H_2 and bind irreversibly with $W(CO)_3(PCy_3)_2$.[6] They have also shown, using PCy_3-*d*33 that, while $W(CO)_3(PCy_3)_2$ will not bind PCy_3, it will exchange bound phosphine for free phosphine. Hoff and coworkers have shown that equilibrium amounts of $Mo(CO)_3(PCy_3)_3$ can be formed in the presence of excess PCy_3.[30]

Formation of the amine complex. Complex **13a** could be formed in several ways: by the direct solid/gas reaction of **3a** with NH_3, the solution phase reaction of **3a** and NH_3, the chloride displacement reaction of **5a** with NH_3, and the hydrogen displacement reaction of **2a** with NH_3. These paths, as well as all the observed interconversions, are summarized in Scheme 3.6.



Scheme 3.6

The thermodynamic parameters obtained for the equilibrium **2a** + NH_3 $\rightleftharpoons$ **13a**+ H_2 (Table 4) indicate that the position of the equilibrium is primarily determined by entropy. The difference in entropy can be accounted for by the larger mass and moment of inertia of NH_3 compared to H_2. Similar arguments have been used to explain why the ΔS° of N_2 coordination was lower than that of H_2 in the $W(CO)_3(PR_3)_2$ complexes.[31]

The reaction enthalpy is close to zero suggesting that both ligands bind equally strong to **3a**. However, this isn't necessarily true, since the enthalpy of solvation in CD_2Cl_2 is probably more negative for NH_3, since it has a dipole, than it is for H_2, which does not.

The thermodynamic parameters obtained for the reaction of **2a** with NH_3, coupled with those obtained for the reaction of **5a** with H_2, allow us to calculate the values for the reaction of **5a** with NH_3: $\Delta H^\circ = -18.4 \pm 0.9$ kcal/mol, $\Delta S^\circ = -55.3 \pm 2.8$ e.u., and $\Delta G^\circ_{298} = -1.9 \pm 1.7$ kcal/mol. Table 3 illustrates this explicitly.

Table 3 Calculation of Thermodynamic Parameters for the Reaction of **5a** with NH_3.

	ΔH°	ΔS°	ΔG°_{298}
5a + H_2 $\rightleftharpoons$ **2a**	-18.0	-44.0	-4.8
+ **2a** + NH_3 $\rightleftharpoons$ **13a** + H_2	-0.4	-11.3	2.9
5a + NH_3 $\rightleftharpoons$ **13a**	-18.4	-55.3	-1.9

The reaction **5a** + NH_3 $\rightleftharpoons$ **13a** is calculated to be exergonic ($\Delta G^\circ_{298} = -1.9 \pm 1.7$ kcal/mol) which could be confirmed experimentally. The measured value, $\Delta G^\circ_{298} = -2.0 \pm 0.2$ kcal/mol, agrees remarkably well.

Kubas and coworkers have reported that primary amines will displace H_2 on $M(CO)_3(PR_3)_2$ (M = Mo, W), but that secondary and tertiary amines won't.[14d] They have also reported the complex $Mo(CO)_3(PCy_3)_2(NH_3)$, and indicated that ammonia binds irreversibly.[6] Hoff *et al.* have studied the reaction $W(CO)_3(PCy_3)_2(H_2)$ + pyridine $\longrightarrow$ $W(CO)_3(PCy_3)_2$ + H_2 by solution calorimetry. They determined an enthalpy of reaction of -9.5 ± 0.5 kcal/mole. Nitrogen bases clearly bind more strongly to the group 6 carbonyl analogs than they do to **3a**.

Ethylene Complex. The ethylene complexes reported by Kubas, $M(CO)_3(PCy_3)_2(C_2H_4)$ (M = Mo, W) can be observed spectroscopically at ambient temperature, and can be isolated as solids.[32] While they bind reversibly, they are clearly more stable than our ethylene complex, $[Re(CN\textit{t}Bu)_3(PCy_3)_2(C_2H_4)]^+$ (**15a**), which can only be observed below 0 °C. Similarly weak binding of ethylene was observed by Milstein *et al.* for the complex $Rh[HC(CH_2CH_2P(t\text{Bu})_2)_2(C_2H_4)]$.[33]

Conclusion

It is useful to highlight the similarities between **3a** and $W(CO)_3(PCy_3)_2$. Both complexes are purple solids, suggesting similar orbital energies. The corresponding dihydrogen complexes are lightly colored: $[Re(CNt\text{Bu})_3(PCy_3)_2(H_2)]^+$ (**2a**) is white, and $W(CO)_3(PCy_3)_2(H_2)$ is yellow. Furthermore, they show similar acidities. Formal one-electron oxidation of each gives the stable 17-electron, d^5, halide derivative (compare $[Re(CNt\text{Bu})_3(PCy_3)_2Cl]^+$ (**9a**) with $W(CO)_3(Pi\text{Pr}_3)_2I$).[34] In addition, they exhibit similar LT $^{31}P\{^1H\}$ NMR spectra.

There are profound differences, however. By exchanging the strongly π-accepting carbonyl ligands for the more weakly π-accepting isonitriles, $[Re(CNt\text{Bu})_3(PCy_3)_2]^+$ is a weaker σ-Lewis acid and more π-basic despite being a cationic complex. This difference has considerable effect on the reactivity displayed by the complex. Complex **3a** binds H_2, a ligand for which π-bonding is a significant component, more strongly than $W(CO)_3(PCy_3)_2$ (by at least 6 kcal/mole). However it binds σ-donor ligands such as nitrogen bases, THF, and H_2O much more weakly.

Experimental

General procedures and the preparation of complex **3a** are described in the experimental section of chapter 2.

Spin Saturation Transfer Experiments on 3a-BF$_4$. The sample was prepared by combining **3a-BF$_4$** (21 mg) and CD_2Cl_2 (0.4 mL) in a flame-sealed 5-mm NMR tube. T_1's for the isonitrile resonances were determined at each temperature (255–

298 K) by the 180°-τ-90° pulse sequence. Decoupler power was adjusted so that complete saturation of the irradiated peak was observed after irradiating for at least five T_1's. The extent of saturation transfer was ascertained by examining difference spectra resulting from subtraction of data collected with and without saturation at the upfield isonitrile resonance. Rates of exchange were calculated as previously outlined for a two-site exchange process.[2]

An Eyring plot of ln (k_{obs}/T) *vs.* $1/T$ was constructed. A best-fit line drawn from a least squares analysis of the data provided the enthalpy and entropy of activation from the slope and the intercept, respectively. Uncertainties in the activation enthalpy and entropy were calculated from the uncertainties in the slope and intercept of the best-fit line.

[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(O$_2$)]X (X = BF$_4$, BAr$_f$) (11a-BF$_4$, 11a-BAr$_f$). The following preparation and characterization apply equally to **11a-BF$_4$** and **11a-BAr$_f$**, except as noted. **3a** was placed in a reaction flask. After evacuation of the Ar atmosphere, oxygen (1 atm) was inserted. The rate of conversion of the purple starting material to the white product was observed to be variable (between 1–20 m). The reaction was irreversible. Exposure of **11a-BF$_4$** to dynamic vacuum for 12 h resulted in a slight yellowing of the solid, but no hint of purple color. Heating **11a-BF$_4$** at 90 °C under dynamic vacuum for another 12 h resulted in the formation of a brown tar. The IR of **11a** were reproducibly different in Nujol *vs* CH_2Cl_2. In neither case were bands attributable to ν(O–O) observed. IR of **11a-BF$_4$** (Nujol) ν(C≡N) 2093 (m), 2071 (m), 2030 (m), ν(BF_4^-) 1052 (br) cm^{-1}; IR of **11a-BAr$_f$** (CH_2Cl_2) 2094 (m), 2076 (m) 2028 (m), ν(unknown) 1712 (m), ν(CF_3) 1223–1127 (br) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.2 -1.2 (br, 66H), 1.59 (s, 9H), 1.41 (s, 18H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 1.1 (s). Anal. Calcd (found): C, 54.92 (53.67); H, 8.41 (8.20); N, 3.77 (3.68). **11a** was observed to be thermally unstable both in methylene chloride ($t_{1/2} \approx 2$ h) and in the solid state ($t_{1/2} \approx 1$

month). The white solid is observed to turn yellow and then brown. Decomposition products observed by ^1H and $^{31}P\{^1H\}$ NMR (CD_2Cl_2) include an unidentified transient peak in the $^{31}P\{^1H\}$ NMR spectrum (δ -3.7). Identifiable decomposition products are **4a**, $P(O)Cy_3$, and *t*BuNCO.

[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(NH$_3$)]X (X = Cl, BF$_4$) (13a-Cl, 13a-BF$_4$). **3a-BF$_4$** was placed in a reaction flask. After evacuation of the Ar atmosphere, NH_3 (0.5 atm) was inserted. Conversion of the purple starting material to the pale yellow product was observed to be immediate. ^1H and $^{31}P\{^1H\}$ NMR spectra of the dissolved product showed clean conversion to a single new species: ^1H NMR (CD_2Cl_2) δ 2.35 (s, N*H*$_3$), 2.2 -1.2 (br, 66H), 1.47 (s, 18H), 1.29 (s, 9H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 9.6 (s). Anal. Calcd. (found): C, 55.67 (54.80); H, 8.80 (8.82); N, 5.09 (5.06). **13a-Cl** was generated in CD_2Cl_2 (0.4 mL) by the reaction of **5a** (4 mg, 4×10^{-3} mmol) with excess NH_3 (1.1 atm). ^1H and $^{31}P\{^1H\}$ NMR spectra of **13a-Cl** were indistinguishable from **13a-BF$_4$**.

[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(ND$_3$)]Cl (13a-Cl-*d*$_3$). The experimental procedure was identical to that described above for **13a-Cl** except for the use of ND_3, in place of NH_3, and CH_2Cl_2, in place of CD_2Cl_2. ^2H NMR (CH_2Cl_2) δ 2.3 (s, N*D*$_3$).

[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(CO)]BF$_4$ (14a-BF$_4$). Freshly hydrogenated **2a-BF$_4$** (6.2 mg, 5.7×10^{-3} mmol) was combined with CD_2Cl_2 (0.4 mL) and CO (130 torr) in a 5 mm NMR tube. The reaction was observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy to generate H_2, and yield a new complex. After 4 h, the reaction was complete. ^1H NMR (CD_2Cl_2) δ 2.2 -1.2 (br, 66H), 1.47 (s, 18H), 1.45 (s, 9H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 11.1 (s); $^{13}C\{^1H\}$NMR (CD_2Cl_2) δ 199.0 (t, $J_{CP} = 6$ Hz, *C*O), 143.4 (t, $J_{CP} = 7$ Hz, *C*NR), 141.7 (s, *C*NR), 58.3 (s, CN*C*(CH$_3$)$_3$), 57.5 (s, CN*C*(CH$_3$)$_3$), 36.8 (br, P-α-*C*), 31.2 (s, CNC(*C*H$_3$)$_3$), 30.2 (s, CNC(*C*H$_3$)$_3$), 30.1 (s, P-γ-*C*), 27.8 (t, $J_{PC} = 5$ Hz, P-β-*C*), 26.6 (s, P-δ-*C*). Evaporation of the **14a-BF$_4$**

solution on an agate mortar lead to the following IR bands: (Nujol) ν(C≡N) 2145 (w), 2109 (m), 2074 (m), 2045 (m), ν(C≡O) 1900 (s), ν(BF_4^-) 1054 (br) cm^{-1}.

[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(C_2H_4)]BF_4 (15a-BF_4). **3a-BF_4** (6.0 mg, 5.5 × 10^{-3} mmol) was combined with CD_2Cl_2 (0.4 mL) under C_2H_4 (130 torr). Neither visual inspection (the color remained purple), nor ^1H and $^{31}P\{^1H\}$ NMR spectra indicated any reaction at 25 °C. Cooling the solution to -78 °C, however caused the solution to become colorless. This was observed to happen reversibly: heating the solution back to 25 °C changed the color back to purple. ^1H NMR (256 K, CD_2Cl_2) δ 2.22 (br, C_2H_4), 2.1–1.2 (br, 66H), 1.52 (s, 18H), 1.29 (s, 9H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ -3.9 (s).

[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(C_2D_4)]BAr$_f$ (15a-BAr$_f$-d_4). The experimental procedure was similar to that described above for **15a-BF_4**. C_2D_4 was used in place of C_2H_4, CH_2Cl_2 was used in place of CD_2Cl_2, and a different counter-ion was used. ^2H NMR (256 K, CH_2Cl_2) δ 2.3 (s, C_2D_4).

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CHAPTER 4

Studies of H_2 Complexes with Identical Coligands.

Introduction

Kubas concludes that hydrogen coordination to metals, "... can be best described as an equilibrium system between two tautomeric forms, with the electronics at the metal controlling where the equilibrium lies."[1] We are able to vary the electronics at Re, by changing the isonitrile/phosphine coligand ratio. In doing so, we are also able to further explore the suitability of isonitriles as ligands for stabilizing dihydrogen complexes.

In this chapter we report the characterization of $[Re(CN\textit{t}Bu)_5(H_2)]^+$. There are very few examples of six-coordinate dihydrogen complexes containing five identical coligands. Group 6 complexes of the type $M(CO)_5(H_2)$ (M = Cr, Mo, W) are all very unstable and could only be studied by IR in low temperature Ar matrices.[2] The other known examples are the Group 8 pentaamine analogs reported by Taube *et al.*,[3] $[Os(NH_3)_5(H_2)]^{2+}$ and $[Os(NH_3)_5(H_2)]^{3+}$. The dication version was found to be stable and could be isolated readily.

Results

$[Re(CN\textit{t}Bu)_5(H_2)]BAr_f$. The reaction of $Re(CN\textit{t}Bu)_5Cl$[4] with $NaBAr_f$ under H_2 affords solutions of the very labile H_2 complex $[Re(CN\textit{t}Bu)_5(H_2)]BAr_f$. The ^1H NMR spectrum in CD_2Cl_2 exhibits a broad resonance at δ -5.81 ppm. Upon exposure to D_2, a well resolved 1:1:1 triplet was observed with J_{HD} = 33.4 Hz (Figure 4). The same material results from protonation of $Re(CN\textit{t}Bu)_5CH_3$[4] with $HBAr_f{\cdot}2Et_2O$ under an atmosphere of hydrogen. This complex was not isolated; it decomposed over several hours in methylene chloride to afford products with no hydride ligands.

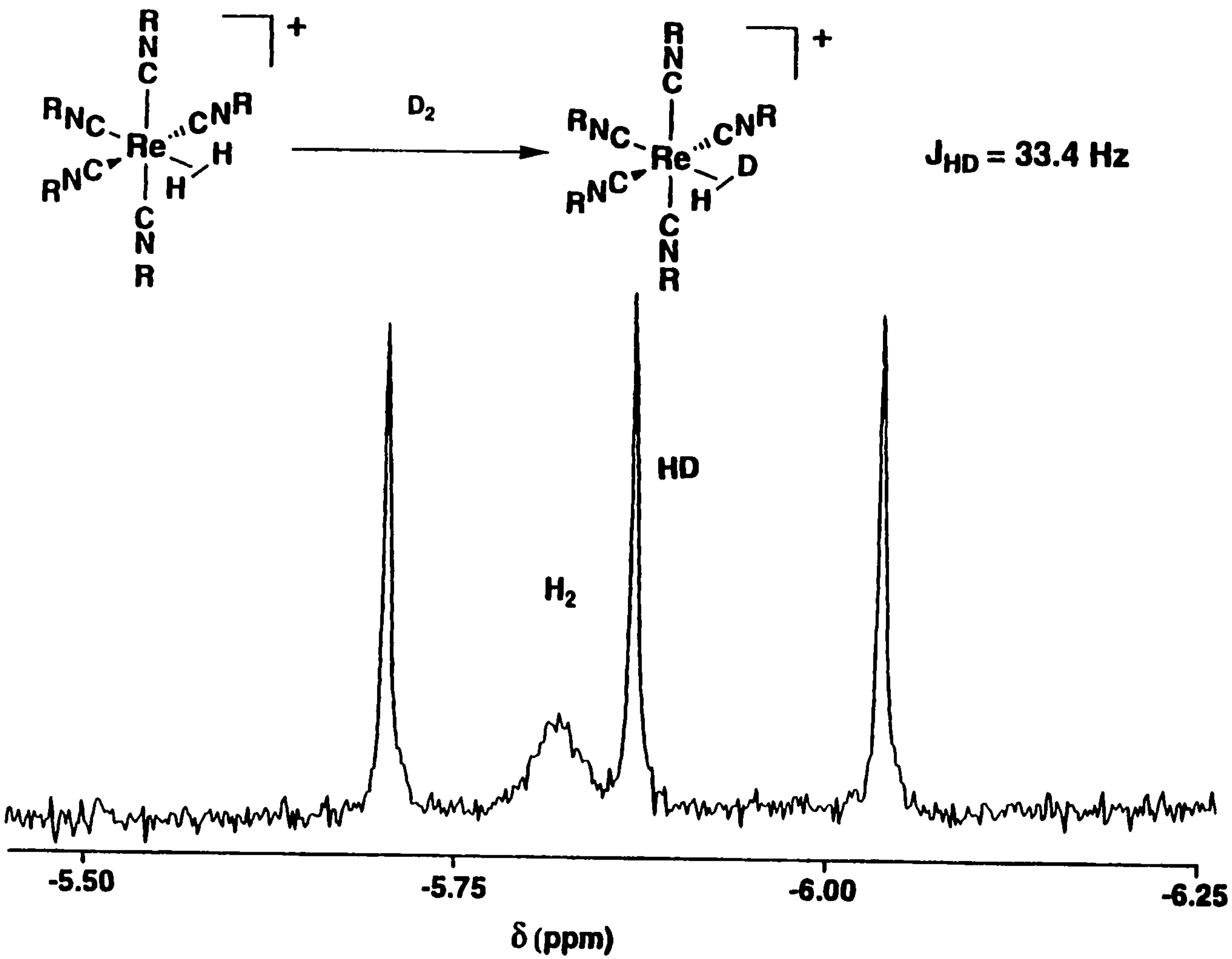
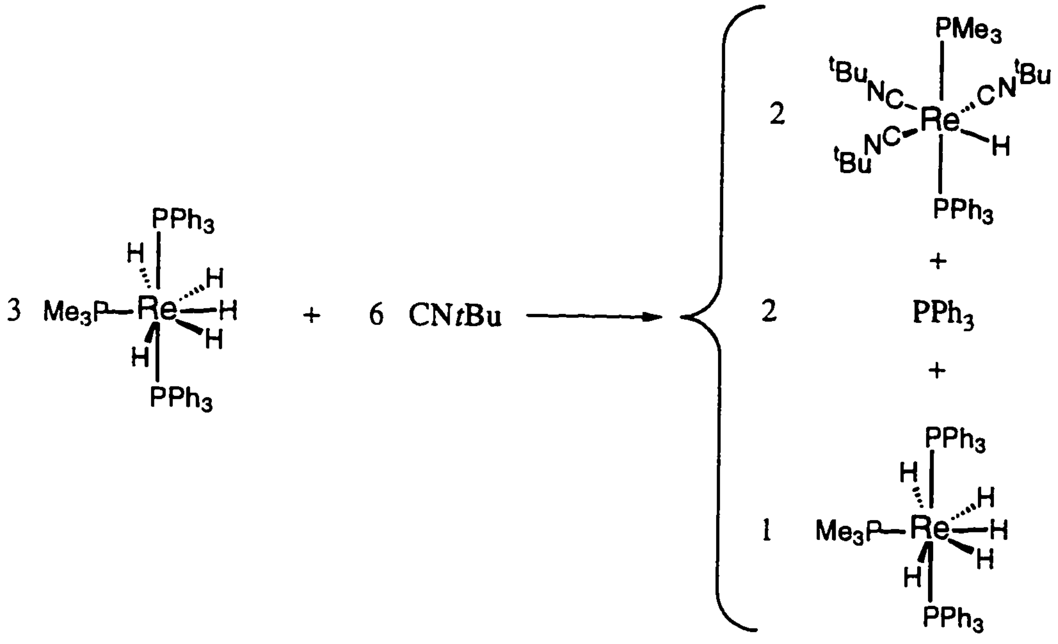


Figure 4 Partial ^{1}H NMR spectrum (hydride region) of a mixture of $[\mathrm{Re(CN}t\mathrm{Bu)_5(H_2)]^+}$ and $[\mathrm{Re(CN}t\mathrm{Bu)_5(HD)]^+}$ (200 MHz, methylene chloride-d_2, 298 K). $[\mathrm{Re(CN}t\mathrm{Bu)_5(HD)]^+}$ displays an upfield shift of 50 pbb and a large coupling to deuterium ($J_{\mathrm{HD}} = 33.4$ Hz).

Preparation of $Re(PMe_3)_5H$, $Re(PPh_3)_2(PMe_3)H_5$, and $Re(CN\textit{t}Bu)_3(PMe_3)(PPh_3)H$. $Re(PMe_3)_5H$ was prepared from the reaction of $Re(PPh_3)_2(\eta^4\text{-}C_5H_6)H_3$ and excess PMe_3, as reported by Jones and Maguire.[5] Since compounds of the type $Re(CN\textit{t}Bu)_3(PR_3)_2H$ (R = Ph, Cy) could be prepared from the reaction of *tert*-butyl isonitrile with either $Re(PPh_3)_2H_7$ or $Re(PPh_3)_2(\eta^4\text{-}C_5H_6)H_3$ (chapter 1), an attempt was made to synthesize $Re(PMe_3)_5H$ directly from the reaction of $Re(PPh_3)_2H_7$ with PMe_3 at 40 °C. Instead, this reaction lead to the formation of the previously unreported complex $Re(PPh_3)_2(PMe_3)H_5$ in 78% yield.

$Re(PPh_3)_2(PMe_3)H_5$ was characterized by elemental analysis and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. While this compound did not react with additional trimethyl phosphine, it did react with three equivalents of *tert*-butyl isonitrile in C_6D_6 at 80 °C in a sealed NMR tube (eq 4).



Equation 4

Analysis of the reaction solution after 2 days by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy showed three species, Re(CN*t*Bu)$_3$(PMe$_3$)(PPh$_3$)H, triphenylphosphine, and Re(PPh$_3$)$_2$(PMe$_3$)H$_5$ in a 2:2:1 ratio.

The new compound, Re(CN*t*Bu)$_3$(PMe$_3$)(PPh$_3$)H exhibits two isonitrile resonances in the ^{1}H NMR spectrum. The 1:2 intensity ratio is consistent with a meridinal geometry at the metal center. The hydride region shows a doublet of doublets of intensity one, indicating coupling to two inequivalent phosphines. The ^{31}P{^{1}H} NMR spectrum shows two doublets of equal intensity. The large coupling constant (J_{PP} = 160 Hz) is consistent with a *trans* geometry for the coordinated phosphines.[6]

[Re(PMe$_3$)$_5$H$_2$]OTf. Consistent with the report by Green and coworkers,[7] we find that protonation of the electron rich Re(PMe$_3$)$_5$H[8] affords the stable cationic dihydride [Re(PMe$_3$)$_5$H$_2$]$^+$. At room temperature, the ^{1}H NMR spectrum (CD$_2$Cl$_2$) of [Re(PMe$_3$)$_5$H$_2$]$^+$ in the hydride region exhibits a sextet. The ^{31}P{^{1}H} NMR (298 K) spectrum shows a single resonance suggesting a fluxional ligand set. This much had been reported by Green and coworkers.

A ^{31}P NMR spectrum with the phosphine protons selectively decoupled shows a triplet, consistent with the presence of two hydride ligands. At lower temperatures, the ^{31}P{^{1}H} NMR spectrum decoalesced into three resonances which integrated 2:2:1. The hydride resonance in the ^{1}H NMR spectrum remained a sextet down to the lowest accessible temperatures (172 K). This complex exhibits no evidence for bound dihydrogen, and appears to be entirely a dihydride complex. Low temperature (195 K) protonation studies also provided no evidence for the initial formation of a dihydrogen complex as a kinetic product. Exchange with D$_2$ gas does not occur. A partially deuterated sample was prepared by addition of D^+ to the neutral hydride. No H-D coupling was observed.

Discussion

$[Re(CNtBu)_5H_2]^+$. $[Re(CNtBu)_5(H_2)]^+$ is one of the few known dihydrogen complexes not containing a phosphine ligand. It may be relatively unstable in solution due to the lack of a pendant C-H bond to form an agostic interaction in the formally sixteen electron cation which results from H_2 loss. $[Re(CNtBu)_5(H_2)]^+$ nicely fills a gap between analogous group 6 and group 8 compounds. There are d^6-dihydrogen complexes in both of these groups in which all the coligands are identical: $M(CO)_5(H_2)$ (M = Cr, Mo, W)[2] and $[Os(NH_3)_5(H_2)]^{+2}$.[3] $[Re(CNtBu)_5(H_2)]^+$ now provides a Group 7 example of this type of complex. It is interesting to note that the stability of these complexes increase from group 6 to group 8. $M(CO)_5(H_2)$ complexes are very unstable and could only be studied at low temperature in argon or hydrocarbon matrices. $[Re(CNtBu)_5(H_2)]^+$ is more stable and could be observed at ambient temperature by solution NMR spectroscopy. Of all these, the group 8 dication, $[Os(NH_3)_5(H_2)]^{2+}$, is the most stable and can be readily isolated. Presumably, the Os compound binds H_2 most strongly because of its highly electron-rich nature,[9] coupled with a reluctance to oxidatively add the H_2 to form a 7-coordinate complex. The conclusion is reached that the ligand set, *not* the charge of the complex, is the more important of the two in determining the strength of the metal dihydrogen interaction. The ligand set which leads to the most π-basic complex is expected to lead to the strongest metal dihydrogen bond. However, since very π-basic complexes have a great tendency to oxidatively add H_2, to form a *dihydride* structure, this assertion is difficult to test.

$Re(PPh_3)_2(PMe_3)H_5$ and $Re(CNtBu)_3(PMe_3)(PPh_3)H$. Reactions of the type $Re(PPh_3)_2H_7 + L \longrightarrow Re(PPh_3)_2LH_5$, where L is a neutral donor ligand, have been reported before.[10] In this case ($L = PMe_3$), the product has not been reported. Similar compounds include $Re(PPh_3)_3H_5$ and $Re(PPh_3)_2(PEt_2Ph)H_5$, reported by Chatt and Coffey, as well as $Re(PMe_2Ph)_3H_5$ and $Re(PMePh_2)_3H_5$, reported by Geoffroy and Roberts.[11] Koeztle and coworkers have studied $Re(PMePh_2)_3H_5$ by neutron diffraction; a dodecahedral geometry was determined.[12]

The lack of thermal reactivity of complexes $Re(PR_3)_3H_5$ towards additional non-π-acidic neutral ligands is well documented.[10,11] With π-acid ligands, however, these complexes are more reactive. Freni and coworkers reported that the reaction of $Re(PPh_3)_3H_5$ with CO (200 atm, 120 °C) yields $Re(CO)_3(PPh_3)_2H$.[13] Our observations show that $Re(PPh_3)_2(PMe_3)H_5$ will react with three equivalents of CN*t*Bu to give $Re(CNtBu)_3(PMe_3)(PPh_3)H$ under considerably milder conditions (80 °C, 2 days). PPh_3 is lost in preference to PMe_3; none of the PMe_3-loss product, $Re(CNtBu)_3(PPh_3)_2H$ (**1b**), is detected. The preference for loss of PPh_3 could either be kinetic, *i.e.* it might be easier to lose a phosphine *trans* to another phosphine, or thermodynamic, *i.e.* $Re(CNtBu)_3(PMe_3)(PPh_3)H$ is more stable than **1b**. No attempts have been made to resolve this; however, Caulton and coworkers have shown that the $Re(PR_3)_2H_7$ complex with the most basic phosphines is the most stable. $Re(PPh_3)_2H_7$ reacts with PCy_3 to yield $Re(PCy_3)_2H_7$.[14]

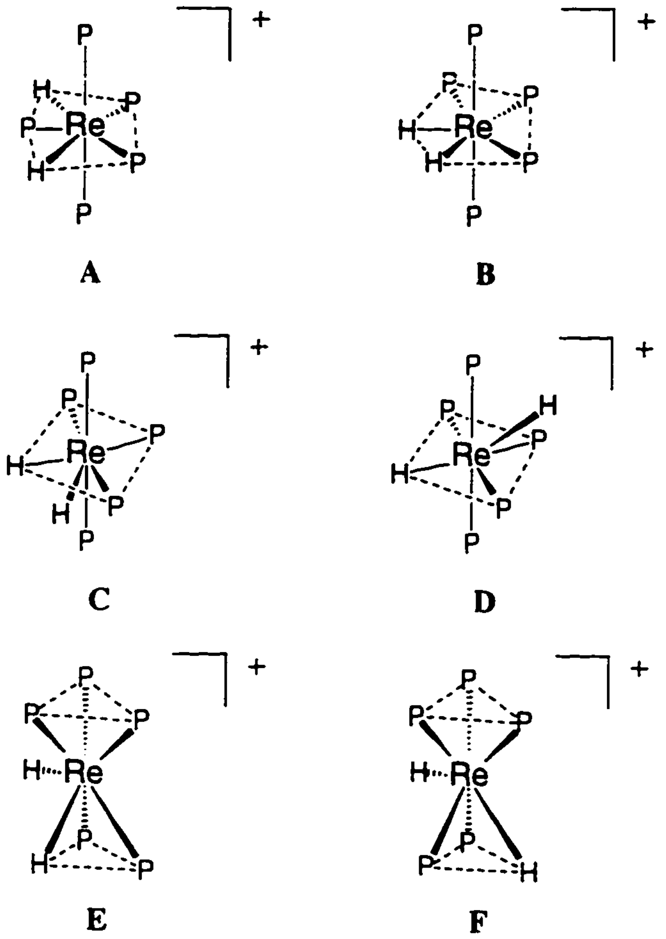
The reaction $Re(PPh_3)_2(PMe_3)H_5 + 3\ CNtBu \longrightarrow Re(CNtBu)_3(PMe_3)(PPh_3)H + PMe_3$ provides a clean convenient route to Re isonitrile complexes with two different phosphines. It may have general utility for basic phosphines other than PMe_3.

$[Re(PMe_3)_5H_2]^+$. As the metal center becomes more electron rich and less Lewis acidic, σ and π-donating ligands generally bind less strongly. In a few cases, it has been shown that ligands such as chloride can be labilized to the point where dissociation occurs even in the absence of a competing ligand. Wilkinson has shown this to be the case for $Re(PMe_3)_5Cl$.[8] This compound behaves as a covalent complex in non-polar solvents, but ionizes in ethanol to give the chloride-dissociated complex, $[Re(PMe_3)_5]Cl$. The ionized form reacts with N_2 to give the dinitrogen complex $[Re(PMe_3)_5N_2]Cl$. Surprisingly, $[Re(PMe_3)_5]Cl$ was reported to neither react with H_2, nor even CO. Green and coworkers have shown that the anticipated product from the reaction of $[Re(PMe_3)_5]Cl$ with hydrogen, $[Re(PMe_3)_5H_2]^+$, can be prepared through an indirect approach.[7] Our deuterium incorporation studies of $[Re(PMe_3)_5H_2]^+$ are most consistent with this complex having a dihydride structure. Not only does it fit the trends established in Table 4, but the $\nu(N{\equiv}N)$ for $[Re(PMe_3)_5N_2]Cl$ (2030 cm^{-1}) falls into the range where the corresponding dihydrogen analog is predicted to oxidatively add to form a dihydride.[15] Our results are also consistent with early work of Muetterties and coworkers for the less basic phosphite analog, $[Re(P(OMe)_3)_5H_2]^+$.[16] This complex is reported to exhibit a large hydrogen-phosphorus coupling ($J_{HP} = 20$ Hz), which is indicative of a dihydride structure.[17,18] The use of the more electron donating PMe_3 ligands can only be expected to further stabilize the dihydride structure. In fact, the coupling constant does increase ($J_{HP} = 28.6$ Hz).

Our attempts to find evidence by ^1H NMR for the initial formation of a dihydrogen compound upon protonating $Re(PMe_3)_5H$ at low temperature (195 K) were not successful. Protonation remained fast at this temperature, and no intermediates *en route* to the *dihydride* product were detected. The formation of a dihydrogen complex as the kinetic product is expected based on observations in other systems. Chinn and Heinekey have shown that protonation of $Cp'RuL_2H$ ($Cp' = Cp, Cp^*$; L = a variety of monodentate and bidentate phosphine ligands) at 195 K affords exclusively the dihydrogen complexes

$[Cp'RuL_2(H_2)]^+$.[19] Upon warming to 222 K, intramolecular isomerization occurs to give variable amounts (as a function of L) of the transoid dihydride tautomer in equilibrium with dihydrogen tautomer. More directly relevant to the Re system, Berke and coworkers have shown that low temperature protonation (-95 °C) of $Re(CO)(PMe_3)_4H$ forms the dihydrogen complex $[Re(CO)(PMe_3)_4(H_2)]^+$, which only exists as an unstable intermediate and oxidatively adds H_2 irreversibly at temperatures greater than -30 °C.[7,20]

The stereochemical non-rigidity of $[Re(PMe_3)_5(H_2)]^+$ is not unexpected. It is a general observation for seven-coordinate complexes due to facile intramolecular rearrangements.[21] A notable exception are the complexes $ReH_2(EPh_3)(CO)(PMe_2Ph)_3$ (E = Si, Sn), reported by Crabtree and coworkers.[18] These displayed distortions from the standard seven-coordinate polyhedra and were stereochemically rigid. Cooling $[Re(PMe_3)_5(H_2)]^+$ to 172 K succeeds in freezing out the rearrangements of the phosphines on the NMR time scale, but not the hydrides. The low temperature (172 K) $^{31}P\{^1H\}$ NMR spectrum (three broad peaks in a 2:2:1 ratio) and ^1H NMR spectrum (binomial sextet) constrains the structural possibilities for $[Re(PMe_3)_5(H_2)]^+$. Scheme 4 shows the limiting seven-coordinate geometries, pentagonal bipyramidal (**A** and **B**), capped-octahedral (**C** and **D**), and capped trigonal prismatic (**E** and **F**).



A B

C D

E F

Scheme 4

In structures **A** and **B**, the pentagonal girdle consists of two hydrides and three phosphines; two equatorial phosphines form one chemically equivalent pair; two axial phosphines form another; one of the equatorial phosphines remains unique. The $^{31}P\{^1H\}$ NMR spectrum at 172 K is consistent with either **A** or **B**. It is also consistent with structures **E** and **F**. The other limiting 7 coordinate geometry is capped-octahedral. This geometry (structures **C** and **D**) would also show two pairs of chemically equivalent phosphines and one unique phosphine when the hydrides are frozen out. At 172 K, however the hydrides remain fluxional as evidenced by a single resonance displaying equivalent coupling to each of the five phosphines. In this situation four of the phosphines should be equivalent. Since this is not observed, the capped-octahedral geometries (**C** and **D**) can be ruled out. Of the four remaining possible geometries, structure A is preferred, since that is the geometry adopted by $Mo(PMe_3)_5H_2$, which has been crystallographically characterized.[22]

Dihydrogen *vs.* Dihydride Structures. As reported for the complexes $[Re(CO)_3(PR_3)_2(H_2)]^+$ (R = Cy, *i*Pr, Ph;[23] Me[20]), low temperature NMR (-90 °C) of $[Re(CN\textit{t}Bu)_3(PR_3)_2(H_2)]^+$ (**2a** and **2b**) and $[Re(CN\textit{t}Bu)_5(H_2)]^+$ provided no evidence for the presence of a dihydride tautomer. These observations are in contrast to the report of Walton and Moehring, who studied closely related complexes with two isonitrile and three phosphine ligands, as well as complexes with one isonitrile and four phosphines.[24] Complexes such as $[Re(CN\textit{t}Bu)_2(PPh_3)_3H_2]^+$ and $[Re(CN\textit{t}Bu)(dppe)_2H_2]^+$ were found to be *dihydrides*. This empirical evidence clearly shows that Re^I cationic complexes with an isonitrile/phosphine ratio greater than or equal to 3:2 have *dihydrogen* structure, while those with a smaller ratio have *dihydride* structure (see Table 4). The observation that $[Re(PMe_3)_5H_2]^+$, a complex with no isonitrile coligands, is a *dihydride*, also fits this trend.[7]

Somewhat different observations have been reported for the mixed carbonyl/phosphine complexes (Table 4). Like the isonitrile/phosphine complexes above, complexes with carbonyl/phosphine ratios of 3:2, $[Re(CO)_3(PR_3)_2(H_2)]^+$ (R = Cy, *i*Pr, Ph;[23] Me[20]) were also found to have the *dihydrogen* structure. However, the majority of the reported complexes with a carbonyl/phosphine ratios of 2:3, $[Re(CO)_2(PMe_3)_3(H_2)]^+$ and $[Re(CO)_2(triphos)(H_2)]^+$,[20,25] also have the *dihydrogen* structure. The exception is $[Re(CO)_2(PMe_2Ph)_3H_2]^+$,[26] which exists as a mixture of the *dihydrogen* and *dihydride* tautomers. The unexpected observation that PMe_3, the most basic of the phosphines, stabilizes the non-classical tautomer for complexes of the type $[Re(CO)_2(PR_3)_3(H_2)]^+$ has previously been noted.[20] A satisfactory explanation remains elusive, especially since the opposite trend is usually observed. For instance, Kubas and coworkers varied R and R' on $Mo(CO)(R_2PCH_2CH_2PR'_2)_2(H_2)$ in a stepwise fashion between aliphatic and aromatic groups. As is expected, aromatic R groups were found to stabilize the *dihydrogen* tautomer.[27] Heinekey and Chinn have also varied the R groups in the complexes $[Cp'Ru(PR_3)_2(H_2)]^+$ (Cp' = Cp, Cp*) and found that the less basic phosphines favor the *dihydrogen* tautomer.[19] Similarly, Crabtree and coworkers have varied the para-substituent (X) on the complexes $ReH_5(H_2)\{P(C_6H_4X)_3\}$ and found that $T_{1(\mathrm{min})}$ values (*i.e.* H–H distances) decrease as the electron-withdrawing capability of X increases.[28] The observation that $[Re(CO)_2(PMe_3)_3(H_2)]^+$ has a 100% *dihydrogen* geometry and that $[Re(CO)_2(PMe_2Ph)_3(H_2)]^+$ does not, remains an unexplained anomaly.

Even among the two known complexes with a carbonyl/phosphine ratio of 1:4, there is evidence for a *dihydrogen* complex, *cf.* $[Re(CO)(PMe_3)_4(H_2)]^+$. This, however, was shown to be the kinetic product formed at -95 °C by protonation of $Re(CO)(PMe_3)_4H$ (see above).[7,20] The *dihydride* structure is thermodynamically preferred for both $[Re(CO)(PMe_3)_4H_2]^+$ and $[Re(CO)(PMe_2Ph)_4H_2]^+$.[26] Despite the at times incongruous dependence on the nature of PR_3, it is apparent that substitution of CN*t*Bu with the more π-acidic CO ligands shifts the ligand mix required for oxidative addition of H_2. An isonitrile/phosphine ratio of at least 3:2 is needed to favor the *dihydrogen* structure, while a lower ratio usually suffices when the coligand combination is carbonyl/phosphine. These trends are summarized in Table 4.

Table 4. Effect of Isonitrile/Phosphine vs. Carbonyl/Phosphine Ratio on the Nature of H_2 Binding.

# of PR_3	isonitrile/phosphine complexes	type of binding	ref.	carbonyl/ phosphine complexes	type of binding	ref.
0	$[Re(CNtBu)_5(H_2)]^+$	dihydrogen	*			
2	$[Re(CNtBu)_3(PR_3)_2(H_2)]^+$ R = Cy, Ph	dihydrogen	*	$[Re(CO)_3(PR_3)_2(H_2)]^+$ R = Cy, *i*Pr, Ph, Me	dihydrogen	23,20
3	$[Re(CNtBu)_2(PPh_3)_3H_2]^+$	dihydride	24	$[Re(CO)_2(triphos)(H_2)]^+$	dihydrogen	25
				$[Re(CO)_2(PMe_3)_3(H_2)]^+$	dihydrogen	20
				$[Re(CO)_2(PMe_2Ph)_3H_2]^+$	dihydrogen/dihydride	26
4	$[Re(CNR)(dppe)_2H_2]^+$ R = Me, *t*Bu, 2,6-$Me_2C_6H_3$	dihydride	24	$[Re(CO)(PMe_3)_4H_2]^+$	dihydride	7,20
				$[Re(CO)(PMe_2Ph)_4H_2]^+$	dihydride	26
5	$[Re(PMe_3)_5H_2]^+$	dihydride	7,*			

(* indicates this work)

Conclusion

Complexes of the form $[ReL_5H_2]^+$ were found to adopt either the formally Re^{III} dihydride structure (L = PMe_3), or the Re^I dihydrogen structure (L = CN*t*Bu). More basic ligands (phosphines) favor the dihydride structure, while π-acid ligands such as CO and CNR favor the dihydrogen structure. By comparing Re cation complexes with different ratios of isonitrile to phosphine coligands, the conclusion is reached that at least three isonitrile ligands must be present for formation of a dihydrogen structure.

A cationic dihydrogen complex of Re with five phosphorus based coligands remains elusive. An unexplored possibility is the use of π-acidic PF_3 coligands. The complex $Re(PF_3)_5H$ has been reported.[29]

Experimental

For general procedures see the experimental section in chapter 2.

$Re(PMe_3)_5H$[5], $Re(CNtBu)_5Cl$[4], and $Re(CNtBu)_5Me$[23] were prepared by reported procedures.

Spectroscopic observation of $[Re(CNtBu)_5(H_2)]BAr_f$. Method A. Methylene chloride-d_2 (0.4 mL) was vacuum transferred into a screw-cap NMR tube containing $Re(CNtBu)_5Me$ (6 mg, 1×10^{-2} mmol) and excess $HBAr_f \cdot 2Et_2O$ (6 mg, 6×10^{-3} mmol). Before closing the cap, the headspace was pressurized with H_2 (800 torr). The resulting orange solution was observed to change to brown when warmed to 298 K. **Method B.** Methylene chloride-d_2 (0.4 mL) was vacuum transferred into a screw-cap NMR tube containing $Re(CNtBu)_5Cl$ (8.3 mg, 1.3×10^{-2} mmol) and $NaBAr_f$ (12 mg, 1.3×10^{-3} mmol). Before closing the cap, the headspace was pressurized with H_2 (800 torr). The resulting yellow solution was observed to change to brown when warmed to 298 K. In both cases, ^1H-NMR (298 K) showed a broad resonance ($\delta = -5.81$ ppm). Several

$CNC(CH_3)_3$ resonances were also observed in the region between 1.3–1.5 ppm. These, however, could not be correlated with the upfield resonance. For Method A, the additional resonances due to CH_4 and Et_2O could also be observed. When the H_2 gas in the headspace of either of these solutions (Method A or B) was removed and replaced with D_2, rapid H/D atom exchange resulted. A sharp 1:1:1 triplet was observed in the hydride region (δ = -5.86 ppm; J_{HD} = 33.4 Hz).

Method B was also conducted at lower temperatures (230 K) and monitored by ^1H NMR. The reaction was not observed to proceed till a temperature of 260K was attained, at which point decomposition products as well $[Re(CNtBu)_5(H_2)]BAr_f$ were observed to form simultaneously.

$Re(PPh_3)_2(PMe_3)H_5$. $Re(PPh_3)_2H_7$ (380 mg, 0.529 mmol) and PMe_3 (550 µL, 5.3 mmol) were combined with benzene (2 mL) in a Kontes flask under Ar. The resulting slurry was heated for 2 days during which time it became an orange solution. Solvent and excess PMe_3 were removed *in vacuo*. The resulting off-white solid was washed with diethyl ether (50 mL) and collected on a glass frit. Yield: 327 mg (0.413 mmol, 78.1%). ^1H NMR (C_6D_6) δ 7.9 (br, 12H), 7.0 (br, 18H), 1.0 (d, J_{HP} = 8 Hz, 9H), -5.38 (td, J_{HP} = 20 Hz, J_{HP} = 17 Hz, 5H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 40.7 (s, 2P), -39.7 (1P). Anal. Calcd (found): C, 59.15 (58.26); H, 5.60 (5.47).

Reaction of $Re(PPh_3)_2(PMe_3)H_5$ with CN*t*Bu. $Re(PPh_3)_2(PMe_3)H_5$ (17.9 mg, 2.26×10^{-2} mmol) was combined with CN*t*Bu (5 µL, 4.4×10^{-2}) in C_6D_6 (0.4 mL). The reaction mixture formed an undissolved slurry that showed not initial reaction by ^1H and $^{31}P\{^1H\}$ NMR. Everything was observed dissolved after the mixture was heated overnight at 40 °C. ^1H and $^{31}P\{^1H\}$ NMR spectra still indicated no reaction. Further heating at 80 °C for 2 days resulted in a fully dissolved yellow solution. The ^1H and $^{31}P\{^1H\}$ NMR spectra indicated free PPh_3, unreacted $Re(PPh_3)_2(PMe_3)H_5$, the absence of free CN*t*Bu, as well as a new compound formulated as

Re(CN*t*Bu)$_3$(PMe$_3$)(PPh$_3$)H: ^{1}H NMR (C$_6$D$_6$) δ 7.9 (t br, 6H), 7.4 (br, 3H), 7.1 (br, 6H), 1.88 (dd, J_{HP} = 8 Hz, J_{HP} = 1 Hz, 9H), 1.17 (9H), 0.95 (18 H), -5.38 (dd, J_{HP} = 16 Hz, J_{HP} = 25 Hz, 1H); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 32.9 (d, J_{PP} = 160 Hz, 1P), -38.9 (J_{PP} = 160 Hz, 1P).

Spectroscopic studies of [Re(PMe$_3$)$_5$H$_2$]OTf. Methylene chloride-*d*$_2$ (0.4 mL) was vacuum transferred into a screw-cap NMR tube containing Re(PMe)$_5$H (12.5 mg, 2.2 × 10^{-2} mmol). HOTf (1–2 µL, *ca.* 2 × 10^{-2} mmol) was added *via* syringe under a blanket of argon. The solution was observed to change from yellow/orange to pale yellow. The conversion is clean and quantitative by ^{1}H and ^{31}P{^{1}H} NMR. The product shows no signs of decomposition in solution. ^{1}H NMR (CD$_2$Cl$_2$; 298 K) δ 1.66 (d, 45H, J_{HP} = 7.3 Hz), -7.55 (sextet, 2H, J_{HP} = 28.6 Hz); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$; 298 K) δ -45.5 (s); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$; 172 K) δ -31.5 (s, 1P), -46.1 (s, 2P), -48.3 (s, 2P). Reaction of the product solution with D$_2$ (1,280 torr) was not detected after 1 week.

Preparation of [Re(PMe$_3$)$_5$HD]OTf was achieved by the reaction of Re(PMe)$_5$H with DOTf following the above procedure. The initial product ratio ([Re(PMe$_3$)$_5$H$_2$]$^+$:[Re(PMe$_3$)$_5$HD]$^+$) observed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy was 3.44:1. The hydride resonance of the mono-deuterated species was shifted downfield by 26 ppb relative to the fully protio complex.

NOTES TO CHAPTER 4

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APPENDIX A

Table A.1 Positional Parameters (× 10^5) and Equivalent Isotropic Displacement Coefficients ($Å^2$ × 10^4) for **2a-BAr$_f$**

atom	*x*	*y*	*z*	U(eq)
Re	9783(4)	22987(4)	27827(3)	133(2)
P(1)	-934(31)	30683(27)	34552(23)	174(12)
P(2)	20384(33)	15360(29)	20822(25)	220(12)
C(1)	12165(119)	15793(88)	34415(76)	173(19)
N(1)	14968(107)	10518(117)	37547(85)	483(19)
C(40)	17269(150)	4691(133)	41846(110)	539(19)
C(41)	18686(178)	8527(147)	48454(129)	692(30)
C(42)	26496(163)	521(138)	40678(110)	564(20)
C(43)	7643(185)	398(196)	43489(219)	4413(20)
C(2)	9834(128)	30376(102)	21312(79)	242(19)
N(2)	10149(112)	36671(110)	18787(107)	591(19)
C(44)	11940(123)	43978(139)	16050(123)	664(19)
C(45)	9956(156)	51331(106)	20475(104)	425(19)
C(46)	4551(150)	42772(128)	9279(99)	448(19)
C(47)	22913(131)	43956(153)	14482(129)	703(19)
C(3)	-2842(111)	17285(94)	23621(69)	145(18)
N(3)	-11187(99)	13463(80)	20583(67)	191(18)
C(48)	-20533(118)	8315(127)	17156(103)	398(19)
C(49)	-21081(161)	852(129)	19710(144)	754(20)
C(50)	-19632(149)	6885(137)	10248(93)	482(19)
C(51)	-29548(138)	13573(136)	18683(148)	917(20)
C(4)	-11381(113)	25267(97)	38110(79)	176(19)
C(5)	-14680(117)	29642(107)	44307(80)	225(19)
C(6)	-24093(124)	24938(112)	45947(93)	302(19)
C(7)	-21966(141)	15860(102)	46485(92)	327(19)
C(8)	-18932(134)	12075(156)	40633(118)	719(19)
C(9)	-9278(119)	16470(117)	38599(101)	372(19)
C(10)	-8331(112)	38398(103)	30402(89)	236(19)
C(11)	-14469(126)	44518(108)	34619(91)	295(19)
C(12)	-18756(123)	50220(99)	30563(91)	265(19)
C(13)	-25893(131)	46022(120)	23895(105)	416(19)
C(14)	-20356(130)	40426(110)	20300(89)	301(19)
C(15)	-15269(114)	34079(96)	24132(74)	174(19)
C(16)	5933(111)	37272(98)	41874(89)	232(19)
C(17)	12712(122)	44637(106)	40632(83)	263(19)
C(18)	17457(137)	49436(114)	46573(102)	388(19)
C(19)	23949(133)	44808(120)	51354(88)	361(19)
C(20)	17883(127)	37448(110)	52394(87)	296(19)
C(21)	13239(133)	32201(112)	46297(102)	423(19)
C(22)	19684(119)	4294(97)	21294(86)	218(19)
C(23)	27812(143)	-762(111)	18142(108)	402(19)
C(24)	26802(138)	-9001(126)	20092(132)	577(19)
C(25)	16354(140)	-13208(113)	17437(102)	398(19)
C(26)	8303(168)	-8383(131)	20197(173)	1038(20)
C(27)	8856(136)	67(106)	18628(120)	432(19)
C(28)	34745(118)	17996(120)	23040(95)	336(19)
C(29)	37529(127)	26646(103)	22274(107)	338(19)

Table A.1 (continued)

atom	*x*	*y*	*z*	U(eq)
C(30)	49431(132)	28664(123)	23678(110)	436(19)
C(31)	55048(256)	23080(208)	27784(182)	1538(32)
C(32)	50674(133)	18827(110)	31462(102)	350(19)
C(33)	39105(114)	16461(112)	29685(87)	271(19)
C(34)	18230(136)	16903(137)	12206(110)	486(19)
C(35)	24868(146)	12941(129)	7579(89)	410(19)
C(36)	22518(170)	16120(183)	1227(130)	980(20)
C(37)	12130(183)	14929(164)	-1885(114)	732(20)
C(38)	5104(156)	17466(128)	2024(96)	456(19)
C(39)	6466(145)	14957(149)	8795(99)	532(19)
B	49701(132)	31489(112)	80071(93)	192(19)
C(1B)	43537(114)	38756(95)	84551(79)	177(19)
C(2B)	47966(118)	46338(102)	86479(83)	224(19)
C(3B)	43586(119)	51817(106)	90493(86)	256(19)
C(4B)	34185(128)	49827(104)	92798(87)	271(19)
C(5B)	29723(126)	41881(111)	90405(87)	269(19)
C(6B)	34226(116)	36774(100)	86753(79)	195(19)
C(7B)	48603(124)	59987(109)	92893(90)	286(19)
C(8B)	19441(148)	39829(125)	92459(104)	416(19)
F(1)	48334(142)	62870(118)	99122(99)	326(27)
F(1A)	59141(180)	59757(154)	94407(135)	578(30)
F(2)	41676(170)	66546(144)	91787(119)	480(30)
F(2A)	44215(210)	65312(180)	89416(154)	768(31)
F(3)	57416(185)	61443(156)	91135(137)	588(30)
F(3A)	51501(263)	61240(236)	87022(216)	1514(32)
F(4)	11461(179)	39304(159)	86980(130)	602(30)
F(4A)	12679(254)	32844(236)	86916(206)	1398(32)
F(5)	16935(201)	31810(173)	91002(157)	722(31)
F(5A)	19315(170)	33398(145)	95006(128)	524(29)
F(6)	15701(161)	44842(136)	96207(119)	470(29)
F(6A)	13042(177)	44878(151)	91370(133)	588(30)
C(9B)	55957(117)	27258(99)	85657(82)	204(19)
C(10B)	65733(120)	30708(106)	88765(84)	245(19)
C(11B)	71105(112)	27797(105)	94215(82)	228(19)
C(12B)	67208(132)	21074(116)	96315(94)	336(19)
C(13B)	57358(119)	17599(100)	93303(81)	208(19)
C(14B)	51851(129)	20652(113)	88069(96)	319(19)
C(15B)	81480(130)	31627(108)	97309(82)	274(19)
C(16B)	53112(143)	10225(121)	95560(103)	398(19)
F(7)	89175(114)	29721(94)	94013(78)	110(24)
F(7A)	82747(211)	33276(190)	104624(161)	875(31)
F(8)	83897(213)	39243(187)	95762(162)	853(31)
F(8A)	81540(128)	39758(106)	98307(88)	184(26)
F(9)	84940(140)	28678(119)	102702(97)	1024(29)
F(10)	45243(160)	6576(134)	91593(112)	387(29)
F(10A)	60168(151)	5742(129)	97585(107)	356(28)
F(11)	50201(152)	12289(129)	101693(106)	402(28)
F(11A)	48926(292)	3079(278)	87145(260)	2459(33)
F(12)	58848(195)	3245(170)	94746(145)	687(31)

Table A.1 (continued)

atom	*x*	*y*	*z*	U(eq)
F(12A)	42793(173)	8576(148)	93537(124)	482(30)
C(17B)	41179(114)	24987(100)	75137(82)	211(19)
C(18B)	30669(128)	26266(113)	72647(90)	305(19)
C(19B)	24438(120)	20544(109)	68598(91)	268(19)
C(20B)	28015(134)	13094(115)	66293(98)	357(19)
C(21B)	38437(135)	11787(120)	68227(105)	397(19)
C(22B)	44759(119)	17730(105)	72863(85)	241(19)
C(23B)	42518(143)	4613(127)	66679(111)	451(19)
C(24B)	13709(142)	21779(117)	66494(101)	381(19)
F(13)	40524(132)	-1186(110)	70539(91)	258(27)
F(13A)	52550(205)	4596(177)	68216(147)	715(31)
F(14)	38176(164)	802(143)	59235(105)	1095(31)
F(15)	52771(146)	4737(124)	65517(98)	284(28)
F(15A)	38336(172)	285(146)	61369(110)	366(29)
F(16)	6976(200)	16379(177)	67497(152)	747(31)
F(16A)	9343(171)	18812(146)	60494(123)	519(30)
F(17)	11695(155)	29647(131)	66044(112)	374(29)
F(17A)	7018(160)	19774(139)	70546(117)	440(29)
F(18)	11692(212)	22628(187)	59749(159)	847(31)
F(18A)	10244(183)	29130(156)	69008(136)	593(30)
C(25B)	56622(128)	35305(109)	75552(92)	284(19)
C(26B)	65516(106)	31377(94)	73757(81)	160(18)
C(27B)	70691(123)	33572(105)	68913(86)	255(19)
C(28B)	67736(134)	39891(113)	65456(96)	339(19)
C(29B)	58636(116)	43709(98)	67088(84)	212(19)
C(30B)	53346(107)	41328(89)	71730(78)	143(18)
C(31B)	80049(144)	29543(127)	67594(102)	406(19)
C(32B)	55427(142)	49878(119)	63269(107)	407(19)
F(19)	77120(187)	22319(162)	62996(136)	607(30)
F(19A)	78002(179)	21732(154)	66157(129)	550(30)
F(20)	84326(153)	32038(128)	62597(107)	339(28)
F(20A)	86945(182)	34443(155)	65008(131)	547(30)
F(21)	87004(116)	29196(95)	72795(77)	122(25)
F(21A)	78066(294)	28461(283)	61579(262)	2428(33)
F(22)	55054(121)	47805(101)	56738(83)	162(25)
F(22A)	45454(164)	51091(136)	63054(112)	362(29)
F(23)	61802(94)	56800(77)	64982(64)	536(24)
F(24)	46149(128)	53390(105)	65120(84)	753(28)
C(1S)	47188(226)	25087(195)	56467(167)	1158(32)
Cl(1A)	53738(142)	16150(118)	55252(100)	986
Cl(1B)	50689(140)	13706(117)	51698(97)	986
Cl(2A)	45420(139)	30283(117)	51264(98)	986
Cl(2B)	42899(137)	27174(115)	47195(98)	986

Table A.2 Positional Parameters ($\times 10^5$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^4$) for **5a**

atom	*x*	*y*	*z*	U (eq)
Re	21934(2)	5250(1)	25747(1)	194(1)
Cl	37838(13)	10552(9)	23473(11)	316(6)
C(1)	26074(50)	5871(33)	35788(41)	248(25)
N(1)	29294(49)	6599(29)	41632(36)	348(24)
C(2)	36499(55)	8647(38)	46699(41)	329(28)
C(11)	20780(46)	5585(33)	15134(41)	215(24)
N(3)	20739(46)	5901(32)	8953(37)	370(26)
C(12)	20182(81)	5905(50)	1310(46)	585(40)
C(13)	9629(111)	3802(85)	-173(75)	1538(106)
C(14)	25266(98)	898(67)	-1640(53)	1028(65)
C(15)	20589(189)	11746(76)	-1447(72)	2786(218)
C(3)	36374(69)	15455(43)	46907(52)	587(37)
C(4)	45874(66)	6221(49)	44184(53)	609(40)
C(5)	34209(78)	6013(47)	53886(47)	585(39)
C(6)	9904(55)	1490(33)	27079(35)	234(25)
C(7)	-6246(52)	-3867(39)	28413(43)	341(28)
N(2)	2425(47)	-627(36)	27908(37)	432(27)
C(8)	-10678(76)	-4177(51)	21151(57)	684(43)
C(9)	-12502(76)	-232(63)	33367(67)	887(55)
C(10)	-4277(73)	-10117(47)	31282(58)	673(42)
P(1)	13805(13)	14951(9)	27130(10)	222(6)
C(1P)	1831(50)	15734(35)	22734(36)	253(23)
C(2P)	-1533(57)	22245(36)	21533(43)	365(29)
C(3P)	-11730(57)	22410(42)	18714(44)	422(31)
C(4P)	-12697(62)	18724(42)	11850(47)	463(32)
C(5P)	-9531(58)	12364(41)	13114(48)	438(31)
C(6P)	645(52)	12126(37)	15867(39)	309(26)
C(7P)	19714(53)	22151(33)	24463(38)	271(25)
C(8P)	28118(54)	23786(37)	29291(42)	345(27)
C(9P)	32718(66)	29606(41)	26822(50)	491(34)
C(10P)	35890(70)	29017(48)	19140(55)	613(40)
C(11P)	27557(68)	27560(41)	14261(48)	505(35)
C(12P)	22716(58)	21729(38)	16667(42)	380(29)
C(13P)	11297(52)	16532(34)	36709(37)	268(24)
C(14P)	5542(56)	11420(36)	40115(38)	313(26)
C(15P)	5617(64)	12263(36)	48266(41)	379(29)
C(16P)	1889(63)	18376(39)	50401(44)	426(30)
C(17P)	7173(60)	23457(38)	46600(41)	395(29)
C(18P)	6966(53)	22597(33)	38762(36)	274(25)
P(2)	28868(13)	-4913(9)	25459(10)	258(6)
C(19P)	41171(57)	-5853(37)	22553(42)	341(28)
C(20P)	42476(58)	-3082(41)	15140(42)	394(29)
C(21P)	52652(72)	-3622(54)	12761(52)	646(42)
C(22P)	59234(68)	-644(59)	17956(54)	684(44)
C(23P)	58268(61)	-3783(47)	25267(51)	507(35)
C(24P)	48341(55)	-3117(39)	27995(42)	357(28)
C(25P)	22206(70)	-10913(40)	20096(48)	480(34)

Table A.2 (continued)

atom	*x*	*y*	*z*	U (eq)
C(26P)	16181(68)	-8562(45)	14228(51)	530(36)
C(27P)	10375(63)	-13521(41)	10787(52)	505(34)
C(28P)	16377(64)	-18733(45)	8181(50)	519(35)
C(29P)	21892(83)	-21150(46)	13895(55)	675(43)
C(30P)	28283(71)	-16167(41)	17394(53)	580(36)
C(31P)	29576(56)	-8466(36)	34481(42)	321(27)
C(32P)	34304(60)	-14736(36)	35007(46)	401(29)
C(33P)	35657(72)	-16733(43)	42840(52)	567(37)
C(34P)	26697(71)	-16591(42)	46819(51)	535(36)
C(35P)	21913(64)	-10283(40)	46179(46)	458(32)
C(36P)	20329(55)	-8559(39)	38410(43)	360(29)
C(1S)	41009(124)	67031(84)	20563(97)	1308(59)
Cl(1A)	31750(35)	61981(24)	17298(28)	1416(17)
Cl(2A)	37974(70)	69716(47)	27729(56)	1406(33)
Cl(2B)	44804(58)	71829(37)	14473(44)	1103(25)
C(2S)	50094(155)	63717(106)	43071(123)	661(61)
Cl(4A)	39604(63)	62322(43)	45551(54)	1188(28)
Cl(4B)	38326(107)	64581(68)	40814(87)	2072(59)
Cl(5A)	54596(63)	69602(44)	49459(50)	1038(25)
Cl(5B)	52238(264)	68237(161)	47299(205)	4620(225)

Table A.3 Positional Parameters ($\times 10^5$) and Equivalent Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^4$) for **9a-OTf**

atom	*x*	*y*	*z*	U(eq)
Re	-15304(7)	75000	-26863(5)	243(3)
Cl	6066(38)	75000	-24982(34)	468(19)
C(1)	-13831(153)	75000	-39557(146)	348(75)
N(1)	-11658(130)	75000	-46197(102)	392(62)
C(2)	-4800(164)	75000	-53120(110)	396(72)
C(11)	-12571(166)	75000	-13902(148)	401(80)
N(3)	-9510(137)	75000	-6520(111)	474(67)
C(12)	-6285(256)	75000	3008(198)	1227(175)
C(13)	-13889(297)	75000	7339(210)	700(5998)
C(13A)	-489(982)	75000	2372(730)	700(5998)
C(14)	2337(181)	82506(121)	4784(128)	700(5998)
C(14A)	-19906(496)	80071(372)	6313(387)	700(5998)
C(3)	1661(186)	67505(121)	-52820(136)	700(5998)
C(3A)	-5814(563)	67380(369)	-58147(407)	700(5998)
C(4)	-13556(253)	75000	-61758(180)	700(5998)
C(4A)	9827(728)	75000	-47647(568)	700(5998)
C(6)	-33081(195)	75000	-28055(109)	352(76)
C(7)	-56190(142)	75000	-29812(126)	339(71)
N(2)	-43191(140)	75000	-28912(91)	359(62)
C(8)	-59142(263)	75000	-20844(188)	700(5998)
C(8A)	-57336(756)	75000	-40976(572)	700(5998)
C(9)	-60953(185)	67766(126)	-34216(141)	700(5998)
C(9A)	-59944(574)	67826(386)	-28799(425)	700(5998)
P(1)	-17475(26)	60635(17)	-27652(21)	280(11)
C(1P)	-28876(106)	56180(68)	-21954(76)	339(45)
C(2P)	-27083(111)	47574(67)	-19953(91)	456(53)
C(3P)	-37970(123)	44107(79)	-17010(89)	562(59)
C(4P)	-40245(121)	48232(73)	-8934(86)	512(57)
C(5P)	-41181(122)	57049(79)	-10298(92)	544(58)
C(6P)	-30778(107)	60448(69)	-13693(76)	392(49)
C(7P)	-3845(95)	54820(74)	-23949(78)	382(49)
C(8P)	5385(102)	55331(74)	-29965(87)	428(50)
C(9P)	15888(109)	50140(89)	-26513(81)	526(56)
C(10P)	21224(119)	52554(97)	-17579(90)	656(66)
C(11P)	12161(123)	51758(91)	-11650(94)	659(64)
C(12P)	1611(108)	56818(76)	-14891(77)	421(51)
C(13P)	-21968(94)	57362(62)	-38796(73)	277(43)
C(14P)	-33690(93)	60935(69)	-43190(76)	333(47)
C(15P)	-35976(103)	59336(74)	-52760(75)	386(49)
C(16P)	-35378(110)	50846(75)	-54889(82)	457(54)
C(17P)	-23942(115)	47357(74)	-50302(79)	469(55)
C(18P)	-22217(109)	48719(66)	-40771(75)	372(49)
O(1S)	25625(119)	75000	19816(81)	613(57)
S(1S)	20362(47)	75000	27241(32)	458(20)
O(2S)	14117(83)	82058(54)	28623(66)	721(44)
F(1)	39358(99)	68910(68)	35327(85)	1301(60)
F(2)	29366(204)	75000	43116(99)	1792(125)

Table A.3 (continued)

atom	*x*	*y*	*z*	U(eq)
C(1F)	32342(268)	75000	35248(180)	926(137)
O(1H)	48745(121)	75000	2986(81)	500
C(1H)	25621(169)	75000	-7128(126)	500
C(2H)	35749(344)	75000	1663(257)	500
C(3H)	51800(375)	75000	6414(257)	500
C(4H)	28033(234)	69080(156)	-3597(170)	500
C(1C)	58452(340)	75000	25088(247)	500
Cl(1C)	65981(519)	66537(295)	22682(235)	500
Cl(2C)	64093(219)	67340(149)	19149(160)	500
Cl(3C)	65899(485)	67065(273)	23938(244)	500
C(1CA)	53999(417)	73967(498)	16206(300)	500

APPENDIX B

T_1 Studies of 2a and 2b

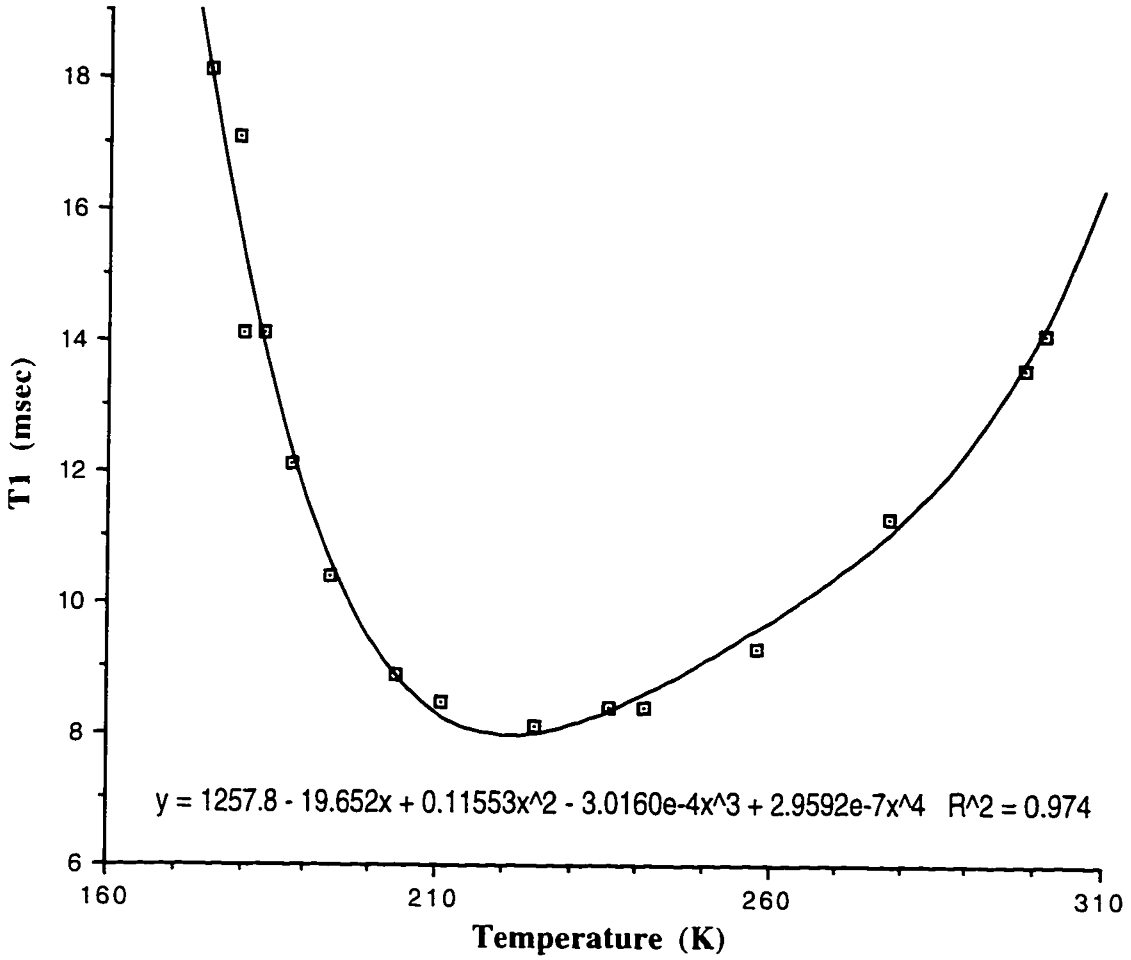

Figure B.1 Lattice relaxation time (T_1) of the dihydrogen ligand of $[\mathrm{Re(CN}t\mathrm{Bu)_3(PCy_3)_2(H_2)]^+}$ (**2a**) as a function of temperature at 300 MHz.

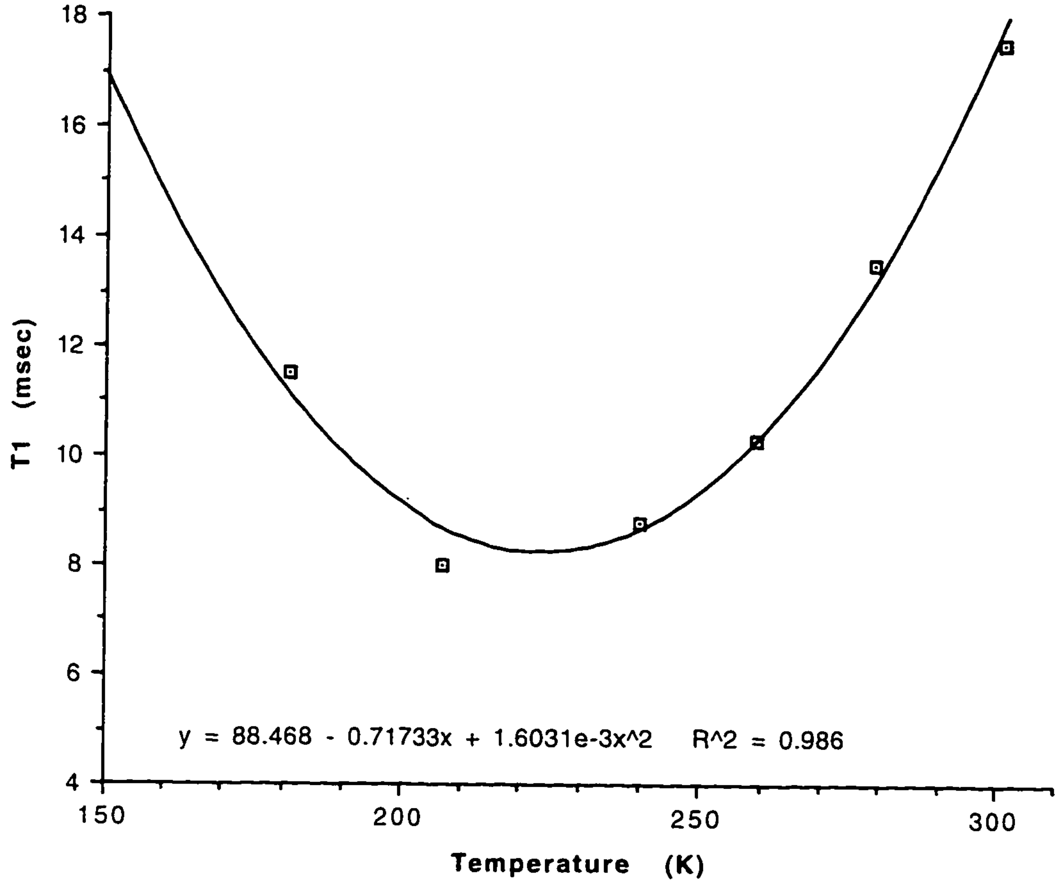

Figure B.2 Lattice relaxation time (T_1) of the dihydrogen ligand of $[Re(CN\textit{t}Bu)_3(PPh_3)_2(H_2)]^+$ (**2b**) as a function of temperature at 300 MHz.

APPENDIX C

Collected Tables of ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR Chemical Shifts and Coupling Constants

Table C.1 ^1H and $^{31}P\{^1H\}$ NMR chemical shifts (ppm) and coupling constants (Hz) for PPh_3 complexes. (298 K in CD_2Cl_2, unless specified otherwise.)

Compound		$^{31}P\{^1H\}$ NMR	^1H NMR isonitrile peaks	^1H NMR other
$Re(CN\mathit{t}Bu)_3(PPh_3)_2H$	**1b**	30.4	0.90, 0.70 (1:2)	-5.96 t J_{HP} = 17
(C_6D_6) →		32.7	0.95, 0.71 (1:2)	-5.09 t J_{HP} = 17
$[Re(CN\mathit{t}Bu)_3(PPh_3)_2(H_2)]^+$	**2b**	18.7	0.94, 0.82 (1:2)	-5.56
(C_6D_6) →		18.8	0.63, 0.51 (1:2)	-5.51
$[Re(CN\mathit{t}Bu)_3(PCy_3)_2]^+$	**3b**	23.5	1.11, 1.03 (1:2)	
$[Re(CN\mathit{t}Bu)_4(PPh_3)_2]^+$	**4b**	16.4	0.95	
(C_6D_6) →		16.3	0.72	
$Re(CN\mathit{t}Bu)_3(PPh_3)_2Cl$	**5b**	18.4	0.98, 0.72 (2:1)	
$[Re(CN\mathit{t}Bu)_3(PPh_3)_2(N_2)]^+$	**10b**	17.3	1.21, 0.98 (1:2)	
$[Re(CN\mathit{t}Bu)_3(PPh_3)_3]^+$		11.6, 9.6 d,t (2:1) J_{PP} = 15	0.90, 0.62 (2:1)	

Table C.2 ^1H and $^{31}P\{^1H\}$ NMR chemical shifts (ppm) and coupling constants (Hz) for PCy_3 complexes. (298 K in CD_2Cl_2, unless specified otherwise).

Compound		$^{31}P\{^1H\}$ NMR	^1H NMR isonitrile peaks	^1H NMR other
$Re(CNtBu)_3(PCy_3)_2H$	**1a**	28.5	1.31, 1.28 (2:1)	-7.48 t $J_{HP} = 20$
$(THF\text{-}d_8) \rightarrow$		29.3	1.35, 1.31 (2:1)	-7.45 t $J_{HP} = 20$
$(C_6D_6) \rightarrow$		29.3	1.40, 1.32 (1:2)	-7.18 t $J_{HP} = 20$
$[Re(CNtBu)_3(PCy_3)_2(H_2)]^+$	**2a**	16.9	1.41, 1.37 (1:2)	-6.30
$(THF\text{-}d_8) \rightarrow$		17.2	1.47, 1.44 (1:2)	-6.17
$[Re(CNtBu)_3(PCy_3)_2]^+$	**3a**	26.4	1.59, 1.20 (2:1)	
$(THF\text{-}d_8) \rightarrow$		26.8	1.62, 1.26 (2:1)	
$[Re(CNtBu)_4(PCy_3)_2]^+$	**4a**	5.6	1.47	
$Re(CNtBu)_3(PCy_3)_2Cl$	**5a**	8.6	1.44, 1.25 (2:1)	
$(THF\text{-}d_8) \rightarrow$		9.2	1.47, 1.28 (2:1)	
$Re(CNtBu)_3(PCy_3)_2Br$	**6a**	5.0	1.44, 1.26 (2:1)	
$Re(CNtBu)_3(PCy_3)_2I$	**7a**	-0.1 (85%)	1.46, 1.29 (2:1)	
		26.4 (15%)	(av. of **7a** & **3a**)	
$Re(CNtBu)_3(PCy_3)_2F\cdot H_2O$	**8a**	15.9 d	1.46, 1.17 (2:1)	
(see discussion in chap. 2)		$J_{PF} = 24$		
$[Re(CNtBu)_3(PCy_3)_2(N_2)]^+$	**10a**	6.9	1.50, 1.37 (2:1)	
$[Re(CNtBu)_3(PCy_3)_2(O_2)]^+$	**11a**	1.1	1.59, 1.41 (1:2)	
$[Re(CNtBu)_3(PCy_3)_2(PMe_3)]^+$	**12a**	-4.0, -54.6	1.49, 1.46 (1:2)	1.56 d
		d,t (2:1)		$J_{HP} = 7$ Hz
		$J_{PP} = 15$		$P(CH_3)_3$
$[Re(CNtBu)_3(PCy_3)_2(NH_3)]^+$	**13a**	9.6	1.47, 1.29 (2:1)	2.35 (NH_3)
$[Re(CNtBu)_3(PCy_3)_2(CO)]^+$	**14a**	11.1	1.47, 1.45 (2:1)	
$[Re(CNtBu)_3(PCy_3)_2(C_2H_4)]^+$	**15a**			
(256 K) →		-3.9	1.52, 1.29 (2:1)	2.22 br (C_2H_4)
$[Re(CNtBu)_3(PCy_3)_2(NCCD_3)]^+$				
$(CD_3CN) \rightarrow$		7.3	1.22, 0.92 (1:2)	

Table C.3 ^{13}C NMR (298 K) chemical shifts (δ) and coupling constants (Hz) of isontrile ligands of PCy_3 complexes.

Compound		solvent	C_a	C_b	C_c	CO
$Re(CN\mathit{t}Bu)_3(PCy_3)_2H$	**1a**	C_7D_8	166.8 t (J_{CP} = 10) 2	54.1 2	31.9 2	
			173.9 t br 1	53.6 1	32.0 1	
$[Re(CN\mathit{t}Bu)_3(PCy_3)_2(H_2)]^+$	**2a**	CD_2Cl_2	146.1 t (J_{CP} = 7) 2	56.7 2	31.3 2	
			148.2 t (J_{CP} = 10) 1	57.1 1	30.6 1	
$[Re(CN\mathit{t}Bu)_3(PCy_3)_2]^+$	**3a**	CD_2Cl_2	160.1 br	57.4	31.6 br 2	
					31.9 br 1	
		THF-d_8	160.2 br	58.2	31.5 br 2	
					32.1 br 1	
$[Re(CN\mathit{t}Bu)_4(PCy_3)_2]^+$	**4a**	CD_2Cl_2	149.0 t (J_{CP} = 8)	56.8	31.2	
$[Re(CN\mathit{t}Bu)_3(PCy_3)_2(CO)]^+$	**14a**	CD_2Cl_2	143.4 t (J_{CP} = 7) 2	57.5 2	31.2 2	199.0 t
			141.7 br 1	58.3 1	30.2 1	(J_{CP} = 6)

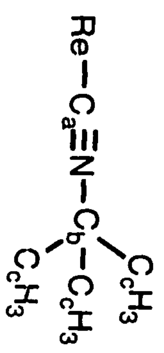

Table C.4 ^{13}C NMR (298 K) chemical shifts (δ) and coupling constants (Hz) of cyclohexyl groups of PCy_3 complexes.

Compound		solvent	P-α-C	P-β-C	P-δ-C	P-γ-C
$Re(CNtBu)_3(PCy_3)_2H$	**1a**	C_7D_8	38.1 br	28.6 t (J_{CP} = 4)	30.3	27.9
$[Re(CNtBu)_3(PCy_3)_2(H_2)]^+$	**2a**	CD_2Cl_2	37.3 br	27.8 t (J_{CP} = 4)	30.2 br	27.0
$[Re(CNtBu)_3(PCy_3)_2]^+$	**3a**	CD_2Cl_2	39.2 t (J_{CP} = 11)	27.9 t (J_{CP} = 5)	29.9	26.6
		THF-d_8	39.7 br	28.4	30.6	27.2
$[Re(CNtBu)_4(PCy_3)_2]^+$	**4a**	CD_2Cl_2	37.2 t (J_{CP} = 10)	27.7 t (J_{CP} = 4)	29.8	26.9
$[Re(CNtBu)_3(PCy_3)_2(CO)]^+$	**14a**	CD_2Cl_2	36.8 br	27.8 t (J_{CP} = 5)	30.1	26.6

Mark Huggins Voges was born Mark Stefan Voges on September 8, 1969 in New York City, New York. His interest in chemistry developed strongly while attending Mr. Saltman's very stimulating chemistry class at Bronxville High School. He graduated from there in June of 1987. He then attended Bowdoin College in Brunswick, Maine. In his junior year, he spent a semester studying biochemistry and the humanities at the Albert Ludwig Universität in Freiburg, Germany. In June 1991, he graduated from Bowdoin College with a double major in Chemistry and German. His pursuit of chemistry continued at the University of Washington. In July of 1996, he earned a Doctor of Philosophy in Inorganic Chemistry. He has accepted a postdoctoral position in Professor Mats Tilset's research group at the University of Oslo. He and his wife, Katherine, look forward to enjoying themselves in Norway and wherever they may live afterwards.