10792 *J. Am. Chem. Soc.* **1996,** *118,* 10792−10802

Rhenium Dihydrogen Complexes with Isonitrile Coligands: Novel Displacement of Chloride by Hydrogen

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Received June 12, 1996[⊗]

Abstract: The syntheses, properties, and characterization of several new complexes, $Re(CN\mathit{t}Bu)_3(PCy_3)_2H$ (**1a**), $Re(CN\mathit{t}Bu)_3(PR_3)_2Cl$ [R = Cy, Ph (**2a**, **2b**)], the 17-electron $[Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl]^+$ (**3a**), the dihydrogen complex, $[Re(CN\mathit{t}Bu)_3(PR_3)_2(H_2)]^+$ [R = Cy, Ph (**4a**, **4b**)], the coordinatively unsaturated $[Re(CN\mathit{t}Bu)_3(PCy_3)_2]^+$ (**5a**), and $[Re(CN\mathit{t}Bu)_4(PCy_3)_2]^+$ (**6a**) are reported. In addition, spectroscopic evidence for the dinitrogen complex $[Re(CN\mathit{t}Bu)_3(PCy_3)_2(N_2)]^+$ and the dihydrogen complex $[Re(CN\mathit{t}Bu)_5(H_2)]^+$ is presented. Thermodynamic parameters have been obtained for the equilibrium system, $Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl$ (**2a**) + $H_2 \rightleftharpoons [Re(CN\mathit{t}Bu)_3(PCy_3)_2(H_2)]Cl$ (**4a**). ^1H and $^{31}P\{^1H\}$ NMR studies (CD_2Cl_2) over the temperature range 286−316 K afford values of $\Delta H° = -18.0 \pm 0.7$ kcal/mol, $\Delta S° = -44 \pm 2$ eu, and $\Delta G°_{298} = -4.8 \pm 1.3$ kcal/mol for this equilibrium. The complexes **4a** and **4b** are characterized as dihydrogen complexes. Their J_{HD} (R = Cy, 30.3 Hz; R = Ph, 30.9 Hz) and $T_{1(min)}$ values of 8 ms (300 MHz) are consistent with H−H distances of *ca.* 0.80 Å. $[Re(CN\mathit{t}Bu)_5(HD)]^+$ is also characterized as a dihydrogen complex based on a J_{HD} of 33.4 Hz. This complex could not be isolated at room temperature, even with noncoordinating counteranions, due to the lability of the H_2 ligand. $[Re(PMe_3)_5HD]^+$ shows no H−D coupling and is characterized as a dihydride complex. The unsaturated complex $[Re(CN\mathit{t}Bu)_3(PCy_3)_2]^+$ (**5a**) is found to undergo a dynamic isonitrile rearrangement on the NMR time scale. ^1H NMR spin saturation transfer studies over a temperature range of 254−297 K afford the activation parameters $\Delta H^‡ = 11.4 \pm 0.8$ kcal/mol, $\Delta S^‡ = -17.6 \pm 1.6$ eu, and $\Delta G^‡_{298} = 16.6 \pm 1.2$ kcal/mol. The molecular structures of **2a** and **3a** have been determined by X-ray crystallography. **2a** shows an unusually long Re−Cl bond distance of 2.596(2) Å.

Introduction

The ability of dihydrogen to form complexes with transition metals was first recognized by Kubas and co-workers.[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. 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 noncoordinating anions such as BAr_f^- [$Ar_f = (3,5\text{-}(CF_3)_2C_6H_3)_4$].[3,4] Solvent choice is equally important, especially when polar, coordinating solvents are used. Even methylene chloride, traditionally considered to be noncoordinating, has demonstrated ligating ability.[5]

Several studies have compared the binding strength of dihydrogen to that of 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.[6] Kubas and co-workers 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).[7,8] 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.[9] Similarly, Milstein and co-workers have recently reported the ligand preferences of the sterically congested T-shaped Rh complex, $Rh[HC(CH_2CH_2P(\mathit{t}Bu)_2)_2]$, to be H_2 > N_2 > C_2H_4 > CO_2.[10]

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 described as either 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.[11] These cationic analogs of the Kubas complexes could only be prepared with the noncoordinating anion, BAr_f^-. Other anions, such as triflate ($OSO_2CF_3^-$) and chloride, 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

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.

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(5) CH_2Cl_2 complexes that have been characterized include the following: $[CpMo(CO)_3(CH_2Cl_2)]^+$ (Beck, W.; Schloter, K. *Z. Naturforsch.* **1978**, *33B*, 1214), $[Cp^*Re(NO)(PPh_3)(CH_2Cl_2)]BF_4$ (Winter, C. H.; Gladysz, J. A. *J. Organomet. Chem.* **1988**, *354*, C33−C36), $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (Newbound, T. D.; Colsmann, M. R.; Miller, M. M.; Wulfsberg, G. P.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1989**, *111*, 3762−3764), and $[Cp^*Ir(PMe_3)(CH_3)(ClCH_2Cl)]^+$ (Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970−1973).

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formation (eq 1).[12]

$$\mathrm{MCl + NaBF_4 + H_2 \rightarrow [M(H_2)]BF_4 + NaCl} \tag{1}$$

In this paper, we report the first *unaided* displacement of chloride by H$_2$ to form the novel cationic dihydrogen complex, [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(H$_2$)]Cl. This is only the second reported dihydrogen complex with isonitrile coligands.[13] By varying the ratio of phosphines and isonitriles on Re, we have further explored the suitability of isonitriles as ligands for stabilizing dihydrogen complexes.

Results

Preparation of Re(CN*t*Bu)$_3$(PR$_3$)$_2$H (1a, 1b). Re(CN*t*Bu)$_3$(PCy$_3$)$_2$H (**1a**) (Cy = cyclohexyl) was prepared in 78% yield by heating Re(PCy$_3$)$_2$H$_7$ and CN*t*Bu in toluene at 45 °C for 2 days. 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 ($J_{HP} = 20.4$). While both *fac,cis* and *mer,trans* geometry are consistent with the spectroscopic data, we favor the *mer,trans* structure based on the steric bulk of the phosphine ligands and the structures of **2a** and **3a** reported below.

The PPh$_3$ analog of **1a**, Re(CN*t*Bu)$_3$(PPh$_3$)$_2$H (**1b**), has been previously reported by Jones and Maguire.[14] They prepared **1b** by reacting Re(PPh$_3$)$_2$H$_7$ with cyclopentadiene to make Re(PPh$_3$)$_2$(η^4-C$_5$H$_6$)H$_3$, followed by ligand displacement with CN*t*Bu to give **1b**. We find that CN*t*Bu reacts directly with Re(PPh$_3$)$_2$H$_7$ to afford **1b** in 70% isolated yield.

Reaction of Re(CN*t*Bu)$_3$(PR$_3$)$_2$H with Chlorocarbons. Both **1a** and **1b** were found to react with methylene chloride-*d*$_2$ at 25 °C to give complete conversion to Re(CN*t*Bu)$_3$(PR$_3$)$_2$Cl [R = Cy (**2a**), Ph (**2b**)]. The reaction of **1a** (6 days) is slower than that of **1b** (4 h). Spectroscopic characterization by NMR indicated that **2a** and **2b** each possess two equivalent phosphine ligands and two sets of isonitrile ligands in a 2:1 ratio. When the reaction was conducted in CD$_2$Cl$_2$, and monitored by ^{1}H NMR, formation of CHD$_2$Cl was detected.

Analytically pure chloride complex **2a** was prepared and isolated by treating the hydride **1a** with excess CH$_3$Cl in methylene chloride at 25 °C for 2 h. When the reaction was conducted in CD$_2$Cl$_2$ and monitored by ^{1}H NMR, formation of CH$_4$ (as opposed to CHD$_2$Cl) 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$_3$Cl reacts more rapidly than CH$_2$Cl$_2$, CHFCl$_2$, or CHCl$_3$. In contrast to these other chlorocarbons, CH$_3$Cl does not oxidize the chloride product **2a** (*vide infra*).

Structure of Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl (2a). The identity of **2a** was further confirmed by X-ray structural determination of crystals formed at −25 °C in methylene chloride. An ORTEP diagram of **2a** (Figure 1) 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)°. Both *trans* isonitriles are bent toward the chloride. The most remarkable structural feature is the long Re−Cl bond distance, 2.596(2) Å. Information pertinent to the data collection and refinement of the structure is given in Table 1. Bond distances and angles are given in Table 2 and 3, respectively.

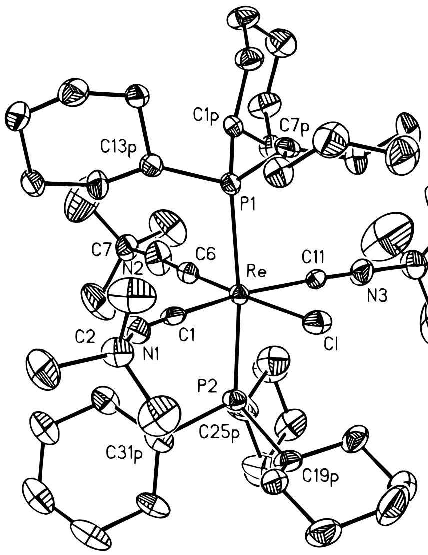
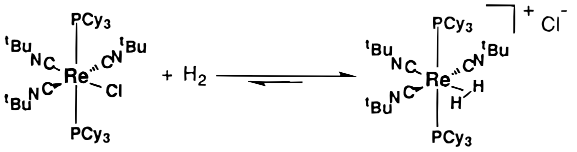


Figure 1. ORTEP projection for compound **2a**.

Reaction of Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl (2a) with Chlorocarbons. Further reaction of yellow **2a** with CH$_2$Cl$_2$, CHFCl$_2$, CHCl$_3$, or CCl$_4$ affords a pink solution. The qualitative rates vary from CCl$_4$, which reacts instantly, to CH$_2$Cl$_2$, 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$_2$ (**3a-Cl**), could be isolated from the reaction of **2a** with CH$_2$Cl$_2$. The same paramagnetic species was isolated as the triflate salt (**3a-OTf**) from the slow reaction of CD$_2$Cl$_2$ with the unsaturated complex [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]OTf (**5a-OTf**) (*vide infra*).

Structure of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl]OTf (3a-OTf). Diffraction quality crystals were grown by layering a CD$_2$Cl$_2$ solution of **3a-OTf** with diethyl ether and cooling to −20 °C. Crystallographic analysis reveals that complex **3a-OTf** has a quasioctahedral structure with a Re−Cl bond distance of 2.412(5) Å (Figure 2). Information pertinent to the data collection and refinement of the structure is given in Table 1. Bond distances and angles are given in Tables 2 and 3, respectively.

Reaction of Re(CN*t*Bu)$_3$(PR$_3$)$_2$Cl (2a) with H$_2$. **2a** reversibly reacts with H$_2$ to form the novel cationic dihydrogen complex [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(H$_2$)]Cl (**4a-Cl**) (eq 2).



2a **4a** (2)

This reaction is rapid in chlorinated solvents (CH$_2$Cl$_2$, CHCl$_3$, and CHFCl$_2$). Within seconds, the yellow solution becomes colorless. ^{1}H NMR data for **4a-Cl** show two peaks for the *tert*-butyl groups on the isonitrile ligands in a 2:1 ratio, and a broad resonance in the hydride region (δ −6.30 ppm), which integrates to two hydrogens. The ^{31}P{^{1}H} NMR spectrum shows one resonance, indicating equivalent phosphines.

Characterization of **4a-Cl** as a dihydrogen complex is based on the large H−D coupling observed ($J_{HD} = 30.3$ Hz) for the partially deuterated derivative (Figure 3). In addition, the measured T_1 for the H$_2$ ligand at the maximum rate of relaxation ($T_{1(\min)}$) is 8 ms (225 K, 300 MHz), consistent with an H−H

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Table 1. Crystal Data and Parameters for **2a** and **3a**

compound	**2a**	**3a**
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 × 0.36 × 0.38	0.5 × 0.1 × 0.15
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/m$
unit cell dimensions		
a, Å	14.270(3)	11.440(2)
b, Å	22.041(4)	17.229(3)
c, Å	18.827(4)	16.009(3)
β, deg	91.15(3)	99.67(3)
volume, Å^3	5935(3)	3110.5(16)
Z	4	2
formula wt	1197.8	1374.8
density(calc) Mg/m^3	1.341	1.468
abs coeff, mm^{-1}	2.361	2.306
F(000)	2476	1422
radiation	MoKα (λ = 0.71073 Å)	
temp, K	183	
monochromator	graphite	
2θ range, deg	2−45	2−50
scan type	ω	
scan speed	variable; 1.5 to 5.5 deg/min in ω	
scan range (ω), deg	0.80 + 0.35(tan θ)	
reflcn collected	8344	3224
independent reflcns	7703 (R_{int} = 4.22%)	3026 (R_{int} = 3.17%)
obsd reflctns	5756 ($F > 4.0\sigma(F)$)	2120 ($F > 4.0\sigma(F)$)
no. of parameters refined	560	337
R(observed data), %	4.08	4.36
R_w, %	5.84	5.46
goodness-of-fit[a]	1.16	0.99
transmission factor	0.891, 0.973	0.736, 0.792

[a] GOF = $[\sum(\text{weight}{\cdot}\text{del}^2)/(M - N)]^{1/2}$; M = observed reflections; N = parameters refined; del = $|F(\text{obs}) - F(\text{calc})|$.

Table 2. Selected Bond Distances (Å) for **2a** and **3a**

	2a	**3a**
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 3. Selected Bond Angles (deg) for **2a** and **3a**

	2a	**3a**
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)

distance of *ca.* 0.80 Å (fast rotation).[15] ^{1}H NMR spectroscopy provided no evidence for the presence of a dihydride tautomer at any temperature examined (180−300 K).

The reversibility of the reaction (eq 2) at room temperature was probed in CD_2Cl_2 by removing the dissolved hydrogen using standard freeze−pump−thaw (FPT) technique. Twenty-four FPT cycles were required to shift the ratio of **4a**:**2a** from 10:1 to 1:1. The relative concentrations of the dihydrogen product, free H_2 (corrected for 25% NMR-silent para-hydrogen),[16] and the neutral chloride complex were determined by ^{1}H and ^{31}P{^{1}H} NMR (Table 4). Apparent K_{eq} values were calculated using two models for the equilibrium.

$$K_{eq} = \frac{[\mathbf{4a}]}{[\mathbf{2a}][H_2]} \tag{3}$$

$$K_{eq} = \frac{[\mathbf{4a}]^2}{[\mathbf{2a}][H_2]} \tag{4}$$

The first model (eq 3) assumes that the dihydrogen complex, **4a**, exists as one species, a solvent-separated ion pair. Values of K_{eq} calculated this way remained constant (mean value = 2.21 × 10^3 M^{-1}; ±4%) as successive amounts of H_2 are removed from solution. The second model (eq 4) assumes that **4a** exists 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.

The temperature dependence of K_{eq} for eq 2 was determined over the temperature interval 286−316 K. The observed equilibrium constants varied from 13.6 × 10^3 M^{-1} at 286 K to

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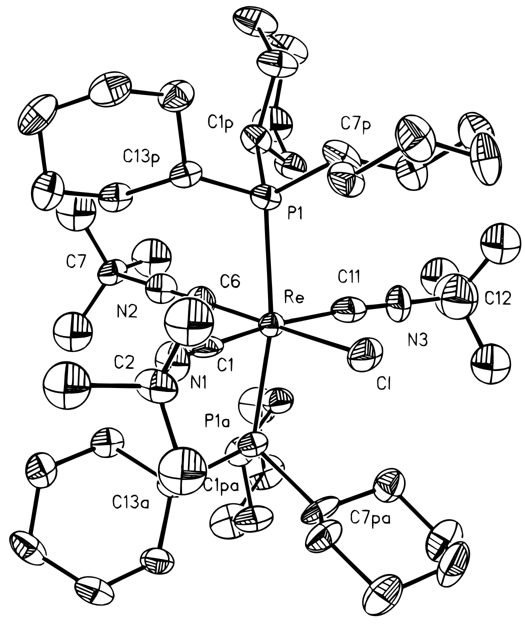


Figure 2. ORTEP projection for compound **3a**.

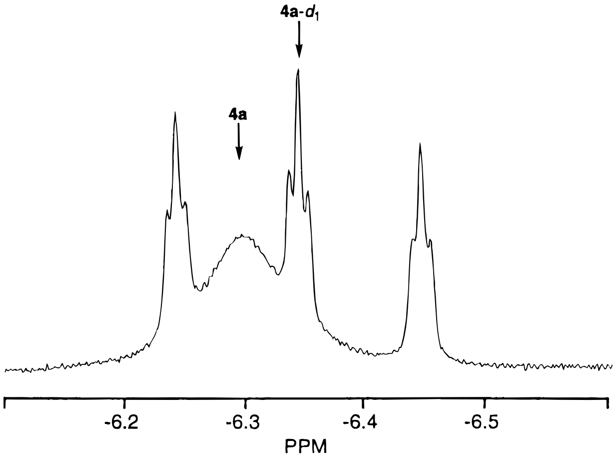


Figure 3. Partial ^1H NMR spectrum (hydride region) of a mixture of **4a** and **4a**-d_1 (300 MHz, methylene chloride-d_2, 298 K). An upfield shift of 47 pbb is observed for **4a**-d_1. **4a**-d_1 shows a large coupling to deuterium ($^1J_{HD} = 30.3$ Hz) and a much smaller coupling to the two equivalent phosphines ($^2J_{HP} \approx 2$ Hz).

Table 4. Data for the Removal of H_2 from a Solution of $[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]Cl$ (**4a-Cl**)

[**2a**], M	[H_2], M	[**4a**], 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

$4.9 \times 10^2\ M^{-1}$ at 316 K. A Van't Hoff plot is shown in Figure 4. The thermodynamic parameters for the formation of $[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]Cl$ from $Re(CN\textit{t}Bu)_3(PCy_3)_2Cl$ and H_2 are as follows: $\Delta H° = -18.0 \pm 0.7$ kcal/mol, $\Delta S° = -44 \pm 2$ eu, and $\Delta G°_{298} = -4.8 \pm 1.3$ kcal/mol.

The reaction between **2a** 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 PPh_3 complex, $Re(CN\textit{t}Bu)_3(PPh_3)_2Cl$ (**2b**).

In contrast to the complete reaction with H_2, **2a** only partially reacts with N_2 in CD_2Cl_2 to form a small equilibrium concentration of $[Re(CN\textit{t}Bu)_3(PCy_3)_2(N_2)]Cl$ (eq 5). Under N_2 pressure (500 torr), the ratio of neutral chloride to dinitrogen complex is approximately 20:1.

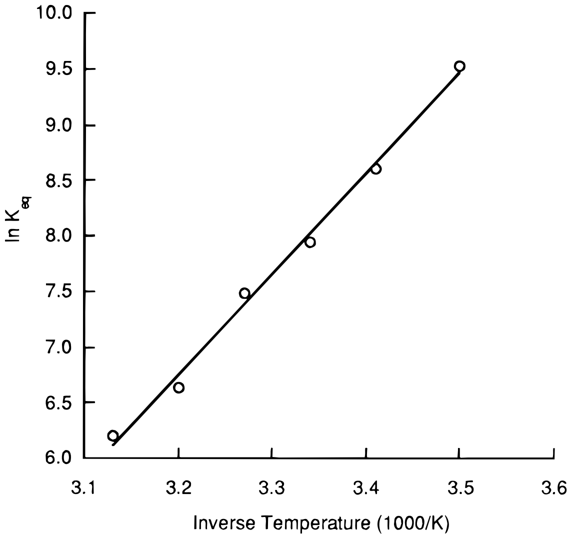
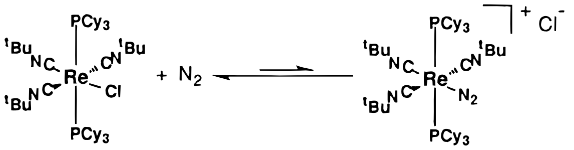


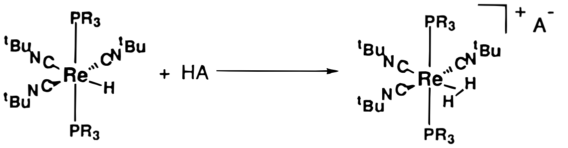
Figure 4. Plot of ln K_{eq} *vs* $1/T$ for the equilibrium $Re(CN\textit{t}Bu)_3(PCy_3)_2Cl + H_2 \rightleftharpoons Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]Cl$.



(5)

Characterization by NMR spectroscopy indicates that $[Re(CN\textit{t}Bu)_3(PCy_3)_2(N_2)]Cl$ possesses two equivalent phosphine ligands and two sets of isonitrile ligands in a 2:1 ratio. The binding mode of the N_2 ligand could not be determined. The expected region for the end-on bound N≡N stretch (2100 cm^{-1}) overlaps with the strongly−absorbing, broad isonitrile resonances. It should be noted that $\nu(C{\equiv}NR)$ for all these isonitrile complexes were consistently very broad. Similar broad and uninformative IR absorptions were reported by Maguire and Jones for the complexes $Re(CNR)_3(PPh_3)_2H$ (R = Me, Et, *i*Pr, Cy, $CH_2C(CH_3)_3$, 2,6-$Me_2C_6H_3$, and *tert*-butyl).[14]

Protonation of $Re(CN\textit{t}Bu)_3(PR_3)_2H$. The dihydrogen complexes, $[Re(CN\textit{t}Bu)_3(PCy_3)_2(H_2)]^+$ (**4a**) and $[Re(CN\textit{t}Bu)_3(PPh_3)_2(H_2)]^+$ (**4b**), were readily obtained by protonation of the corresponding neutral hydride complexes with a wide variety of acids (eq 6): HOTf ($OTf^- = OSO_2CF_3^-$), $HBF_4{\cdot}OEt_2$, and $HBAr_f{\cdot}(OEt_2)_2$.[3] **4b** exhibited similar properties to **4a** (see above), and was also characterized as a dihydrogen complex. For **4b**, the $T_{1(min)}$ was found to be 8 ms (207 K, 300 MHz). The H−D coupling of the partially deuterated complex was measured to be 30.9 Hz, slightly greater than for **4a**.



1a, 1b **4a, 4b**

(6)

In situ NMR tube preparations of **4a** or **4b** resulted in clean and complete conversion by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. This was observed to be the case even in the absence of an H_2 atmosphere.

Preparation of **4a-OTf** and **4a-BF$_4$** was readily achieved by adding HOTf or $HBF_4{\cdot}OEt_2$ to a solution of **1a** in diethyl ether. A slight deficiency of acid was used to avoid overprotonation. Both **4a** and **4b** react with strong acid, but the products have not been identified. Filtration and drying under a stream of H_2 gives **4a** in 70−90% yield.

Attempts to isolate pure **4b-BF$_4$** or **4b-BAr$_f$** by similar technique 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 and 6.81 ppm. The latter is identified as the previously reported compound $[Re(CN\mathit{t}Bu)_4(PPh_3)_2]^+$.[17]

The dihydrogen complex, $[Re(CN\mathit{t}Bu)_3(PCy_3)_2(H_2)]Cl$ (**4a-Cl**), can also be generated by the reaction of **1a** with HCl. Attempts to isolate **4a-Cl** free from solvent failed because the white precipitate that is formed loses hydrogen irreversibly in the solid state and yields the yellow chloride, **2a**.

The basicity of the neutral hydride, $Re(CN\mathit{t}Bu)_3(PCy_3)_2H$ (**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 the proton from the dihydrogen product. Other nitrogen bases such as Proton Sponge® (1,8-bis(dimethylamino)naphthalene) also failed to deprotonate **4a**. 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 equiv of methanol to a methylene chloride solution of **1a** leads to 80% protonation.

Removal of Bound H$_2$: Formation of Ligand Deficient Complex. When **4a** is prepared with a noncoordinating counteranion (OTf^-, BF_4^-, BAr_f^-), it reversibly loses H_2 in the solid state to form the "coordinatively unsaturated"[18] complex $[Re(CN\mathit{t}Bu)_3(PCy_3)_2]^+$ (**5a**). Hydrogen loss is easily monitored by inspection: **4a** is white, while **5a** is dark purple. The ^1H NMR spectrum (298 K) of **5a** shows two sets of exchange-broadened isonitrile ligands in a 2:1 ratio. $^{31}P\{^1H\}$ NMR spectroscopy indicates equivalent phosphines. ^1H and $^{31}P\{^1H\}$ NMR spectra of **5a-OTf** and **5a-BF$_4$** were identical, confirming the lack of coordination by the counteranion. Significant solvent coordination by CD_2Cl_2 or THF-d_8 also appears to be absent. Elemental analysis clearly demonstrates this for **5a** in the solid state; recrystalization of **5a-BF$_4$** from THF yields analytically pure compound. In solution, the lack of significant solvent coordination was ruled out by the very minor ^{31}P chemical shift difference ($\Delta\delta = 2.5$ ppm) observed for **5a** dissolved in the solvents CD_2Cl_2 and THF-d_8. This contrasts with a much larger chemical shift change for **5a** dissolved in the coordinating solvent CD_3CN. In this solvent, the acetonitrile adduct $[Re(CN\mathit{t}Bu)_3(PCy_3)_2(NCCD_3)]^+$ forms as evidenced by the ^{31}P chemical shift having moved 15.8 ppm upfield of **5a** dissolved in CD_2Cl_2. It is worth noting that this same species is formed when the dihydrogen complex, **4a**, is dissolved in CD_3CN, indicating that bound H_2 is readily displaced by acetonitrile.

Dynamics of $[Re(CN\mathit{t}Bu)_3(PCy_3)_2]^+$ (5a). The fluxional behavior of the isonitrile ligands was investigated by ^1H NMR spin saturation transfer techniques. Saturation of either isonitrile resonance showed spin saturation transfer to the other resonance. Rate data for this process (Scheme 1) were measured over a 43 degree temperature range. The empty box in Scheme 1 represents a vacant coordination site, which is either always present or transiently formed by the dissociation of an agostic C−H bond or a weakly coordinating solvent molecule (see Discussion). Figure 5 shows an Eyring plot for the rate constants. The activation parameters for this process were calculated as $\Delta H^\ddagger = 11.4 \pm 0.8$ kcal/mol and $\Delta S^\ddagger = -17.6 \pm 1.6$ cal/(mol·K). This corresponds to $\Delta G^\ddagger_{298} = 16.6 \pm 1.2$ kcal/mol.

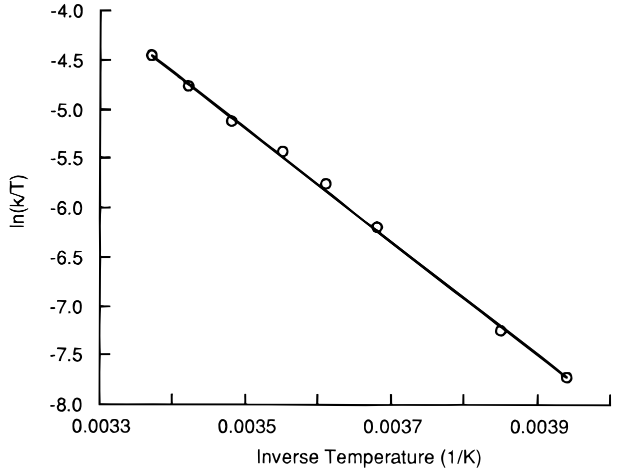
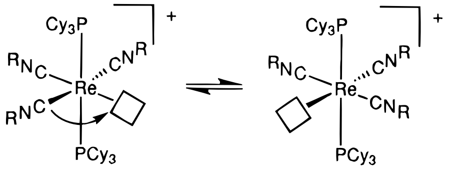


Figure 5. Plot of ln (*k/T*) *vs* 1/*T* for the isonitrile isomerization in $[Re(CN\mathit{t}Bu)_3(PCy_3)_2]^+$ (**5a**).

Scheme 1



Synthesis of $[Re(CN\mathit{t}Bu)_4(PCy_3)_2]BF_4$ (6a). Complex **6a** and the previously reported $[Re(CN\mathit{t}Bu)_4(PPh_3)_2]BF_4$ (**6b**) were observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy as minor impurities (<10%) in many of the above reactions. The identity of the previously unreported **6a** was confirmed by independent preparation. Our synthesis of **6a** follows that reported by Walton *et al.* for **6b**.[19] Reaction of $Re(CN\mathit{t}Bu)_3(PCy_3)_2H$ (**1a**) with excess CN*t*Bu in $NaBF_4$/methanol solution gives **6a** in 82% yield after 12 h. Elemental analysis confirms the empirical formula. ^1H and $^{31}P\{^1H\}$ NMR spectra respectively show a single resonance for the isonitriles and the phosphines, indicating that members of each group are equivalent.

$[Re(CN\mathit{t}Bu)_5(H_2)]BAr_f$. The reaction of $Re(CN\mathit{t}Bu)_5Cl$[20] with $NaBAr_f$ under H_2 affords solutions of the very labile H_2 complex $[Re(CN\mathit{t}Bu)_5(H_2)]BAr_f$. 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. The same material results from protonation of $Re(CN\mathit{t}Bu)_5CH_3$[20] with $HBAr_f\cdot 2Et_2O$ under an atmosphere of hydrogen. This complex could not be isolated as a solid, and decomposed over several hours in methylene chloride to afford products with no hydride ligands.

$[Re(PMe_3)_5H_2]OTf$. In contrast to the relatively electron deficient pentaisonitrile complex, we find that protonation of the electron rich $Re(PMe_3)_5H$[21] with HOTf affords the stable cationic dihydride $[Re(PMe_3)_5H_2]^+$, which has been previously reported by Green and co-workers.[22] At room temperature, the ^1H NMR spectrum (CD_2Cl_2) of $[Re(PMe_3)_5H_2]^+$ in the hydride region exhibits a sextet at $\delta = -7.55$ ppm with $J_{HP} = 28.6$ Hz.

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[17] Allison, J. D.; Wood, T. E.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 3540−3546.

[18] **5a** most likely contains an agostic interaction to a pendant C−H bond of one of the cyclohexyl rings.

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[20] Chiu, K. W.; Howard, C. G.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 803−808.

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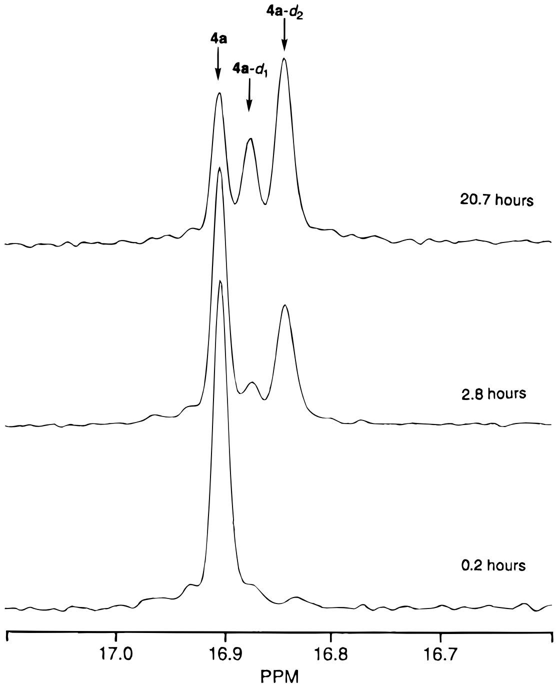


Figure 6. 81-MHz $^{31}P\{^1H\}$ NMR spectra of **4a**, **4a**-d_1, and **4a**-d_2 as a function of time for the reaction of **4a** with roughly 1 equiv of deuterium gas at 298 K.

A ^{31}P NMR spectrum with the methyl protons selectively decoupled shows a triplet, consistent with the presence of two hydride ligands. 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. The single $^{31}P\{^1H\}$ NMR resonance observed at 298 K suggests a fluxional compound. At lower temperatures the $^{31}P\{^1H\}$ NMR spectrum decoalesced into three resonances which integrated 2:2:1. The spectrum is consistent with a static seven-coordinate pentagonal bipyramidal structure with the two hydrides occupying equivalent positions in the equatorial plane.

H_2/D_2 Exchange and the Formation of HD. All three dihydrogen complexes, $[Re(CN\mathit{t}Bu)_3(PCy_3)_2(H_2)]^+$ (**4a**), $[Re(CN\mathit{t}Bu)_3(PPh_3)_2(H_2)]^+$ (**4b**), and $[Re(CN\mathit{t}Bu)_5(H_2)]^+$, 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. Qualitatively, the rate of isotope scrambling was observed to be most rapid for $[Re(CN\mathit{t}Bu)_5(H_2)]^+$.

In the case of **4a** and **4b**, it was possible to simultaneously observe all three isotopomers (**4**, **4**-d_1, and **4**-d_2) by $^{31}P\{^1H\}$ NMR and monitor the reaction of **4a** with D_2 (*ca.* 1 eq) in CD_2Cl_2 over time, as shown in Figure 6. Significantly, the peak corresponding to **4a**-d_2 was observed to grow in before the peak for **4a**-d_1.

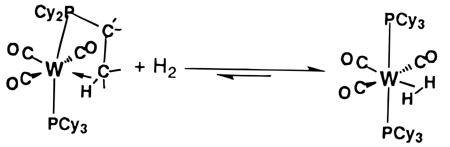
Discussion

Reaction of $Re(CN\mathit{t}Bu)_3(PCy_3)_2H$ (1a) with Chlorocarbons. The reaction of $Re(CN\mathit{t}Bu)_3(PCy_3)_2H$ (**1a**) with CCl_4, $CHCl_3$, or CH_2Cl_2 to form $Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl$ (**2a**) is a well precedented reaction for metal hydrides. The increasing reactivity as the number of Cl atoms increases also follows the previously observed trend.[23] Limited mechanistic data for these types of reactions suggest that they proceed by free radical chain mechanisms.[24] Consistent with a radical chain mechanism, the reaction of **1a** with CH_2Cl_2 shows highly variable reaction times, making it less useful for the preparation of **2a**. Extended reaction times lead to the Re^{II} decomposition product, $[Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl]Cl$ (**3a**).

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 may proceed by a different (non-radical chain) mechanism. Consistently rapid reaction times ($t_{1/2} \approx 10$ min) make this reaction preparatively the most useful.

Reaction of $Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl$ (2a) with H_2. It is surprising that H_2, which binds to a metal *via* its bonding electron pair, can displace chloride which offers both a nonbonding electron pair as well as a negative 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[2] and studies of the rotational barrier of bound H_2.[25] 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 time scale.[26] 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 ($\Delta S° = -44 \pm 2$ eu) disfavors the reaction. At higher temperatures (79 °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 co-workers for the binding of H_2 to the agostic complex, $W(CO)_3(PCy_3)_2$ (eq 7).[7]



(7)

In toluene, $\Delta H°$ was reported to be −9.9 kcal/mol, and $\Delta S°$ was estimated to be −35 eu. 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. Thus the total estimated binding strength of H_2 to the coordinatively unsaturated fragment, $W(CO)_3(PCy_3)_2$, is *ca.* 20 kcal/mol, roughly the same magnitude as $\Delta H°$ for the reaction of $Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl$ with H_2 (eq 2). This result implies that H_2 binding is much stronger in $[Re(CN\mathit{t}Bu)_3(PCy_3)_2(H_2)]^+$ (**4a**) than in $W(CO)_3(PCy_3)_2H_2$, or that part of the magnitude of $\Delta H°$ can be accounted for by differential solvation of the ionic product, **4a**, *versus* the uncharged reactants, **2a** and H_2, or both. The first possibility, that $[Re(CN\mathit{t}Bu)_3(PCy_3)_2]^+$ (**5a**) binds H_2 much more strongly than does $W(CO)_3(PCy_3)_2$, is unlikely since the corresponding dihydrogen complexes both show facile exchange of H_2 for D_2 in solution.[27] The other possibility seems more

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Table 5. Isonitrile/Phosphine *vs* Carbonyl/Phosphine Ratios and the Nature of H_2 Binding

no. of PR_3	isonitrile/phosphine complexes	type of binding	ref	carbonyl/phosphine complexes	type of binding	ref
0	$[Re(CN\mathit{t}Bu)_5(H_2)]^+$	dihydrogen	*a*			
2	$[Re(CN\mathit{t}Bu)_3(PR_3)_2(H_2)]^+$	dihydrogen	*a*	$[Re(CO)_3(PR_3)_2(H_2)\}^+$	dihydrogen	11,37
	R = Cy, Ph			R = Cy, *i*Pr, Ph, Me		
3	$[Re(CN\mathit{t}Bu)_2(PPh_3)_3H_2]^+$	dihydride	33	$[Re(CO)_2(triphos)(H_2^{)]+}$	dihydrogen	9
				$[Re(CO)_2(PMe_3)_3(H_2)]^+$	dihydrogen	38
				$[Re(CO)_2(PMe_2Ph)_3H_2]^+$	dihydride/dihydrogen	39
4	$[Re(CNR)(dppe)_2H_2]^+$	dihydride	33	$[Re(CO)(PMe_3)_4H_2]^+$	dihydride	38
	R = Me, *t*Bu, 2,6-$Me_2C_6H_3$			$[Re(CO)(PMe_2Ph)_4H_2]^+$	dihydride	39
5	$[Re(PMe_3)_5H_2]^+$	dihydride	22			

likely; in fact the exquisite solvent sensitivity of the reaction $Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl$ with H_2 (eq 2) supports this claim. While the reaction of $Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl$ with H_2 is favorable in methylene chloride ($\Delta G°_{298} = -4.8 \pm 1.4$ kcal/mol), it does not proceed to any detectable extent in THF at 298 K. Clearly differential solvation of the product, **4a**, and the starting complex, **2a**, must make a significant contribution to the thermodynamics of this reaction. Consistent with this hypothesis, the observed $\Delta S°$ (-44 ± 2 eu) is larger than the values observed for the reaction of $M(CO)_3(PCy_3)_2$ with H_2 (M = Mo, $\Delta S° = -23.8 \pm 2.1$ eu; M = Cr, $\Delta S° = -25.6 \pm 1.7$ eu).[28] This may be due to solvent ordering around the charged species.

Unlike H_2, N_2 does not displace chloride very well. Under N_2 pressure (500 Torr), less than 5% of $Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl$ is converted to $[Re(CN\mathit{t}Bu)_3(PCy_3)_2(N_2)]Cl$. The relative binding of H_2 and N_2 in this system therefore differs from that of the $M(CO)_3(PCy_3)_2$ (M = W, Mo, Cr) system which favors N_2.[28] In this regard, $[Re(CN\mathit{t}Bu)_3(PCy_3)_2]^+$ is similar to other Re^I species, including $[Re(CO)_3(PCy_3)_2]^+$,[11] $[Re(CO)_2(triphos)]^+$,[9] and the T-shaped Rh^I complex, $Rh[HC(CH_2CH_2P(\mathit{t}Bu)_2)_2]$.[10] All of these complexes bind H_2 in preference to N_2.

Structural Comparisons of $Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl$ (2a) and $[Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl]^+$ (3a). The unique reactivity of **2a** 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.[29] 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.[30] This dramatic increase in bond length, resulting from minor changes in the ligand set, is consistent with the different reactivities observed for **2a** and **2b**. The PPh_3 analog, **2b**, shows no reactivity with H_2. No structural information exists for **2b**; however, it is reasonable to predict that its Re−Cl bond length would be close to the 2.47-Å distance observed for $Re(CNMe)_3(PMePh_2)_2Cl$.

The structures of the 17 electron cation, $[Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl]^+$ (**3a**), and the 18-electron neutral chloride, $Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl$ (**2a**), provide a useful comparison between two complexes that differ only in *d*-electron count. Few such comparisons have been made in the literature of organometallic chemistry. One particularly relevant example is the structural comparison made by Salih *et al.* for *trans*-$[Re(dppe)_2Cl_2]X$ ($X^- = Cl^-, BF_4^-$) (dppe = $Ph_2PCH_2CH_2PPh_2$) with *trans*-$Re(dppe)_2Cl_2$.[31] 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 $[Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl]^+$ (**3a**) and $Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl$ (**2a**). The addition of an electron to **3a** (17-electron, d^5, Re^{II}) to form **2a** (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 sterics. For instance, the greater overall steric crowding present in complexes **2a** and **3a** *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 bond upon the one-electron reduction of **3a**.

Interestingly, two other reported monomeric Re^I complexes with long Re−Cl bonds also contain mixtures of phosphine and isonitrile coligands. They are $Re(CN\mathit{t}Bu)_2(PMe_3)_3Cl$ (Re−Cl = 2.570 Å)[21] and $Re(CNMe)(dppe)_2Cl$ (Re−Cl = 2.607 Å).[32] The reaction of these complexes with H_2 has not been reported, however, 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 co-workers[33] have prepared both $[Re(CNR)(dppe)_2H_2]^+$ (R = Me, *t*Bu, 2,6-$Me_2C_6H_3$) and $[Re(CN\mathit{t}Bu)_2(PPh_3)_3H_2]^+$ with the BF_4^- counterion (see Table 5). The large J_{HP} coupling constants of the hydrides strongly imply that these species are dihydrides and not dihydrogen complexes.[34]

$[ReL_5H_2]^+$ Complexes (L = $CN\mathit{t}Bu$, PMe_3). $[Re(CN\mathit{t}Bu)_5(H_2)]^+$ 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 16-electron cation which results from H_2 loss. $[Re(CN\mathit{t}Bu)_5(H_2)]^+$ 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)[35]

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and $[Os(NH_3)_5(H_2)]^{+2}$.[36] $[Re(CNtBu)_5(H_2)]^+$ now provides a group 7 example of this type of complex. It is interesting to note that the stability of these complexes increases 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 in solution by NMR. Of all these, the group 8 dication, $[Os(NH_3)_5(H_2)]^{+2}$, is the most stable and could be readily isolated.

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 $Re(PMe_3)_5Cl$.[20] This compound behaves as a covalent complex in nonpolar 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 react with neither H_2 nor even CO. The anticipated product from the reaction of $[Re(PMe_3)_5]Cl$ with hydrogen, $[Re(PMe_3)_5H_2]^+$, has been prepared by Green and co-workers *via* protonation of the corresponding neutral hydride.[22] We have prepared the partially deuterated analog $[Re(PMe_3)_5HD]^+$, which shows no H−D coupling. A fluxional seven coordinate dihydride structure is consistent with all of the spectoscopic observations. The observation that this complex is a dihydride and not a dihydrogen complex comes as no surprise. Not only does it fit the trends established in Table 5, 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.[6] Our results are also consistent with early work of Muetterties and co-workers for the less basic phosphite analog, $[Re(P(OMe)_3)_5H_2]^+$.[37] This complex is reported to exhibit a large hydrogen−phosphorus coupling ($J_{HP} = 20$ Hz), which is very suggestive of a dihydride structure.[33] 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 significantly ($J_{HP} = 28.6$ Hz).

Dihydrogen *vs* Dihydride Structures. As reported for the complexes $[Re(CO)_3(PR_3)_2(H_2)]^+$ (R = Cy, *i*Pr, Ph;[11] Me[38]), low-temperature NMR (180 K) of $[Re(CNtBu)_3(PR_3)_2(H_2)]^+$ (**4a** and **4b**) and $[Re(CNtBu)_5(H_2)]^+$ 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.[33] Complexes such as $[Re(CNtBu)_2(PPh_3)_3H_2]^+$ and $[Re(CNtBu)(dppe)_2H_2]^+$ 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 a *dihydrogen* structure, while those with a smaller ratio adopt the *dihydride* structure (see Table 5). Our observation that $[Re(PMe_3)_5H_2]^+$, a complex with no isonitrile coligands, is a *dihydride* also fits this trend.

Somewhat different observations have been reported for the mixed carbonyl/phosphine complexes (Table 5). 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;[11] Me[37]), 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 $[Re(CO)_2(triphos)(H_2)]^+$,[37,9] also have the *dihydrogen* structure. The exception is $[Re(CO)_2(PMe_2Ph)_3H_2]^+$,[39] 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 already been noted.[37] A satisfactory explanation remains elusive, especially since Kubas and co-workers established the opposite trend for the Mo complexes of the form $Mo(CO)(R_2PCH_2CH_2PR'_2)_2(H_2)$. Here, R and R′ were varied in a stepwise fashion between aliphatic and aromatic groups.[40] As is normally expected, aromatic R groups were found to stabilize the *dihydrogen* tautomer.

Even among the two known complexes with a carbonyl/phosphine ratio of 1:4, there is evidence for a *dihydrogen* complex. $[Re(CO)(PMe_3)_4(H_2)]^+$ can be formed at −95 °C by protonation of $Re(CO)(PMe_3)_4H$, however, it only exists as an unstable intermediate, which oxidatively adds H_2 irreversibly at temperatures greater than −30 °C.[37] The *dihydride* structure is thermodynamically preferred for both $[Re(CO)(PMe_3)_4H_2]^+$ and $[Re(CO)(PMe_2Ph)_4H_2]^+$.[39] Despite the unpredictable 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 5.

Acidity of the Dihydrogen Complexes. The acidity of $[Re(CNtBu)_3(PCy_3)_2(H_2)]^+$ (**4a**) is similar to its group 6 carbonyl analogs. While simple amines fail to deprotonate either **4a** or $W(CO)_3(PCy_3)_2(H_2)$, both can be deprotonated by stronger bases such as alkoxides.[41] 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 the mild base 2,6-di-*tert*-butylpyridine.[42] Bianchini and co-workers report that $[Re(CO)_2(triphos)(H_2)]^+$ (triphos = $MeC(CH_2PPh_2)_3$) is deprotonated by NEt_3 in methylene chloride.[9] Similarly, group 8 dicationic analogs are also more acidic than **4a**. Tilset and co-workers recently reported that $[Os(NCMe)_3(PiPr_3)_2(H_2)]^{2+}$ could be deprotonated with piperidine.[43] These observations are in agreement with the idea 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.[44 ,8] One of the most plausible mechanisms is shown in Scheme 2.

This mechanism necessitates facile H_2/D_2 exchange, a heterolytically activated dihydrogen ligand, as well as an adventi-

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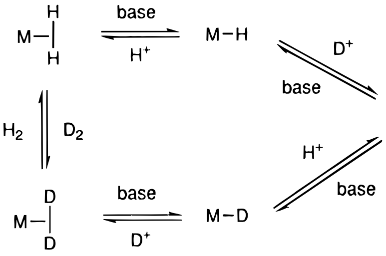
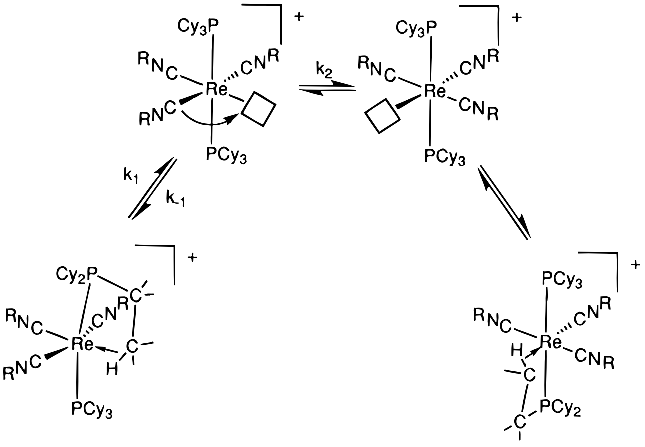
Scheme 2



Scheme 3



tious base. Complexes **4a** and **4b** provide a unique opportunity to evaluate this mechanism, since it is possible to spectroscopically resolve all three isotopomers, **4**, **4**-d_1, and **4**-d_2, by ^{31}P-{^{1}H} NMR spectroscopy (Figure 6). As long as base catalysis is slow, the mechanism predicts that when **4a** reacts with D_2, the first newly observed species should be **4a**-d_2, not **4a**-d_1. This prediction is in fact confirmed by experiment.

Structure and Dynamics of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]$^+$ (5a). Since additional ligands can be added to [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]$^+$ (**5a**), it fits the operational definition of coordinative unsaturation presented by Strauss.[45] The solution structure of **5a** 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$_3$)$_2$ and [Re(CO)$_3$(PCy$_3$)$_2$]$^+$ in the solid state.[46,11] If an agostic interaction also exists for **5a**, then the activation parameters derived for the isonitrile rearrangement (Scheme 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) implies that the agostic bond must first break in order to free the sixth coordination site. For the second step, orbital arguments suggest that the most favorable mechanism is for just a single isonitrile to move, so that an energetically unfavorable D_{3h} transition state can be avoided.[47] 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/mol) for this process approximates the Re···H–C agostic bond strength. An agostic bond strength of 11.4 ± 0.8 kcal/mol 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/mol.[7] Furthermore, results from photoacoustic calorimetry show the metal alkane bond in Mo(CO)$_5$(heptane) to be 15 ± 1 kcal/mol.[48] 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/mol can only serve as an upper limit to the strength of the agostic interaction.

Comparison of [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]$^+$ (5a) with W(CO)$_3$(PCy$_3$)$_2$. It is useful to highlight the remarkable similarities between **5a** and W(CO)$_3$(PCy$_3$)$_2$. Both complexes are purple solids and the corresponding dihydrogen complexes are lightly colored: [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(H$_2$)]$^+$ (**4a**) is white, and W(CO)$_3$(PCy$_3$)$_2$(H$_2$) is yellow. Both of these, in turn, show similar qualitative rates of H_2/D_2 exchange and isotope scrambling. Furthermore, as discussed above, they show similar acidities. Finally, it is worth noting that one electron oxidation to give stable 17-electron, d^5, halide derivatives is possible for both fragments; [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl]$^+$ (**3a**) is analogous to the neutral W$^{\text{I}}$ complex, W(CO)$_3$(P*i*Pr$_3$)$_2$I.[49] It is indeed reasonable to conclude that by exchanging the strongly π-accepting carbonyl ligands for the more weakly π-accepting isonitriles it is possible to maintain similar overall electronics by moving one group to the right on the periodic table while forming a cationic complex.

Conclusion

The Lewis-acidic rhenium complex, [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]$^+$, strongly binds dihydrogen in preference to chloride. This result is attributed, in part, to the weak Re–Cl bond in the neutral chloride. The Re–Cl bond length in Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl has been determined and compared to the corresponding Re$^{\text{II}}$ cation complex.

Complexes of the form [ReL$_5$H$_2$]$^+$ were found to adopt either the formally Re$^{\text{III}}$ dihydride structure (L = PMe$_3$) or the Re$^{\text{I}}$ 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. At least three isonitrile ligands must be present for formation of a dihydrogen structure.

The activation parameters of the isonitrile rearrangement process were determined for the complex [Re(CN*t*Bu)$_3$(PCy$_3$)$_2$]$^+$. A mechanistic hypothesis was advanced, which relates $\Delta H^\ddagger$ for this rearrangement to the strength of the Re···H–C agostic interaction.

Experimental Section

General Procedures. All reactions were performed under vacuum or argon atmosphere using standard Schlenk, drybox, 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 ^{1}H NMR experiments were conducted using a Bruker B-VT 1000 temperature control module with a copper–constantan thermocouple. Proton T_1

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studies were performed using the standard inversion recovery 180°$-\tau-$90° pulse sequence.[50] Temperature calibration was accomplished following the Van Geet methanol calibration method.[51] ^{1}H NMR spectra were referenced at all temperatures to the internal residual hydrogen signal of the deuterated solvent relative to TMS. ^{31}P{^{1}H} NMR was referenced to an external standard of 85% H_3PO_4. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, BC.

$Re(PCy_3)_2H_7$,[52] $Re(PPh_3)_2H_7$,[14] $Re(PMe_3)_5H$,[14] $Re(CN\mathit{t}Bu)_5Cl$,[20] $Re(CN\mathit{t}Bu)_5Me$,[20] and $HBAr_f{\cdot}2Et_2O$[3] 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 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%). ^{1}H NMR (CD_2Cl_2) δ 2.2$-$1.2 (br, 66H), 1.31 (s, 18H), 1.28 (s, 9H), $-$7.49 (t, $^2J_{PH} = 20.4$ Hz, 1H); ^{31}P{^{1}H} NMR (CD_2Cl_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).

$Re(CN\mathit{t}Bu)_3(PPh_3)_2H$ (1b). This preparation is more direct than the one originally reported by Jones and Maguire.[14] $Re(PPh_3)_2H_7$ (0.30 g, 0.42 mmol), *tert*-butylisonitrile (0.57 mL, 5.0 mmol), and benzene (5 mL) were stirred under Ar at 65 °C for 2 h. The product was collected on a frit in the air and washed with pentane (2 × 10 mL). Yield: 282 mg (0.29 mmol, 70%). ^{1}H NMR (C_6D_6) agrees with that reported by Jones and Maguire.[14] ^{31}P{^{1}H} NMR (C_6D_6) δ 32.7 (s).

$Re(CN\mathit{t}Bu)_3(PCy_3)_2Cl$ (2a). Method A. Dry 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 530 Torr of 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 cooled to $-$78 °C. Yellow solid precipitated and was collected on a glass frit. Yield 56 mg (0.054 mmol, 51%). **Method B.** Under an Ar atmosphere, **1a** (230 mg, 0.230 mmol) was stirred in Et_2O (20 mL). HCl in diethyl ether (1 M, 0.23 mL, 0.23 mmol) was added via syringe through a rubber septum. The solution was observed to immediately lose its yellow color and form a white precipitate. The slurry was cannula transferred onto a glass frit and filtered. During the filtration, the collected solid was observed to change color from white to yellow and then redissolve in solution (accounting for the low yield). Presumably, the white solid is **4a-Cl**. As it loses H_2, it is directly converted to **2a**, which is yellow. The collected product was washed with pentane (3 × 5 mL). Yield: 50 mg (0.011 mmol, 21%). ^{1}H NMR (CD_2Cl_2) δ 2.2$-$1.2 (br, 66H), 1.44 (s, 18H), 1.25 (s, 9H); ^{31}P{^{1}H} 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 $Re(CN\mathit{t}Bu)_3(PPh_3)_2Cl$ (2b). Methylene chloride-d_2 (0.4 mL) was vacuum transferred into a sealable NMR tube containing **2b** (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{^{1}H} NMR. The conversion of **1b** to **2b** 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. ^{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{^{1}H} NMR (CD_2Cl_2) δ 18.44 (s).

$[Re(CN\mathit{t}Bu)_3(PCy_3)_2(\eta^2\text{-}H_2)]X$ ($X^- = BF_4^-$, OTf^-) (4a-BF$_4$, 4a-OTf). For **4a-BF$_4$**, **1a** (248 mg, 0.248 mmol) was dissolved in Et_2O (20 mL). Under a counter-flow of argon, $HBF_4{\cdot}OEt_2$ (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, 83%). Complex **4a-OTf** was similarly prepared and isolated in comparable yield. Attempts to isolate **4a-Cl** were not successful. Loss of H_2 from **4a-Cl** to form the neutral chloride **2a** was observed to be irreversible in the solid state (see Method B for **2a**, above.) ^{1}H NMR and ^{31}P NMR chemical shifts of **4a** were observed to be identical, regardless of counteranion. This observation also applies to **4a-Cl** and **4a-BAr$_f$**, which were observed by NMR but not isolated. ^{1}H NMR (CD_2Cl_2) δ 2.2$-$1.2 (br, 66H), 1.41 (s, 9H), 1.37 (s, 18H), $-$6.30 (br, 2H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 16.9 (s); ^{13}C{^{1}H} NMR (CD_2Cl_2) (obtained for **4a-BAr$_f$** and **4a-BF$_4$**) δ 148.1 (t, $J_{CP} = 10$ Hz, *C*NR), 146.1 (t, $J_{CP} = 7$ Hz, *C*NR), 57.1 (s, CN*C*(CH_3)$_3$), 56.7 (s, CN*C*(CH_3)$_3$), 37.3 (br, P-α-*C*), 31.3 (s, CNC(*C*H_3)$_3$), 30.6 (s, CNC(*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*). $T_{1(\min)} = 8$ ms (225 K, 300 MHz). Anal. Calcd (found) for **4a-OTf**: C, 54.42 (53.80); H, 8.34 (7.85); N, 3.66 (3.43).

$[Re(CN\mathit{t}Bu)_3(PPh_3)_2(\eta^2\text{-}H_2)]X$ ($X^- = BF_4^-$ (4b-BF$_4$), BAr_f^-, (4b-BAr$_f$)). For **4b-BAr$_f$**, **1b** (179 mg, 0.186 mmol) was dissolved in Et_2O (80 mL) under a 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 mg. ^{1}H NMR and ^{31}P NMR show the solid to be approximately 80% **4b-BAr$_f$**. In contrast, NMR tube preparations of **4b-BAr$_f$** and **4b-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). $T_{1(\min)} = 8$ ms (207 K, 300 MHz).

$[Re(CN\mathit{t}Bu)_3(PCy_3)_2]X$ ($X^- = BF_4^-$ (5a-BF$_4$), OTf^- (5a-OTf)). Coordinated H_2 was removed from **4a-BF$_4$** or **4a-OTf** either by exposing the white solids to dynamic vacuum (24 h, 23 °C) or by simply leaving them under Ar atmosphere for 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 compound was obtained by recrystallization from THF. With exceptions made for the different anions, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR chemical shifts of **5a-BF$_4$** and **5a-OTf** were observed to be identical. ^{1}H NMR (CD_2Cl_2) δ 2.62 (broad, 6H), 2.0$-$1.2 (br, 60H), 1.59 (s, 18H), 1.20 (s, 9H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 26.4 (s); ^{13}C{^{1}H} NMR (CD_2Cl_2) (for **5a-BF$_4$**) δ 160.1 (s, *C*NR), 144.0 (s, *C*NR), 57.4 (s, CN*C*(CH_3)$_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. Calcd (found) for **5a-BF$_4$**: C, 56.54 (56.30); H, 8.65 (8.81), 3.88 (3.77).

$[Re(CN\mathit{t}Bu)_4(PCy_3)_2]BF_4$ (6a-BF$_4$). **1a** (160 mg, 0.160 mmol) was slurried overnight in a methanol solution (30 mL) containing excess *tert*-butylisonitrile (60 μL, 0.53 mmol). Slow gas evolution was observed during the first several hours. After 12 h, the solution had become pale-yellow and homogeneous. A slurry of $NaBF_4$ (220 mg) in acetone (150 mL) was added via cannula, affording a homogeneous solution 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 then washed with diethyl ether (2 × 15 mL). Yield: 168 mg (0.144 mmol, 82%). ^{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(*C*H_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).

Spectroscopic Observation of $[Re(CN\mathit{t}Bu)_3(PCy_3)_2(N_2)]Cl$. Methylene chloride-$d_2$ (0.4 mL) was vacuum transferred into a sealable NMR tube containing **2a** (4.1 mg, 4.3 × 10^{-3} mmol). The tube was pressurized with N_2 (0.5 atm) and sealed. Partial conversion (5%) to

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[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$(N$_2$)]Cl was observed by NMR. ^{1}H NMR (CD$_2$Cl$_2$) δ 2.2−1.2 (br, 66H), 1.50 (s, 18H), 1.37 (s, 9H); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 6.9 (s).

[Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl]X (X$^-$ = Cl$^-$ (3a-Cl), OTf$^-$ (3a-OTf)). These decomposition products were isolated in variable yields (10−80% yield) from the reactions of **1a**, **2a**, **4a**, **5a**, or **7a** and methylene chloride. The following two examples are representative: The reaction of **2a** 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. Anal. Calcd (found) for **3a-Cl·(CH$_2$Cl$_2$)$_3$**: C, 49.05 (49.20); H, 7.55 (7.68); N, 3.10 (3.18). The reaction of **5a-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.

Spectroscopic Observation of [Re(CN*t*Bu)$_5$(H$_2$)]BAr$_f$. Method A. Methylene chloride-d_2 (0.4 mL) was vacuum transferred into a screw-cap NMR tube containing Re(CN*t*Bu)$_5$Me (6 mg, 1×10^{-2} mmol) and excess HBAr$_f$·2Et$_2$O (6 mg, 6×10^{-3} mmol). Before closing the cap, the headspace was pressurized with H$_2$ (800 Torr). The resulting orange solution turned 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(CN*t*Bu)$_5$Cl (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 turned brown when warmed to 298 K. In both cases, ^{1}H NMR (298 K) showed a broad resonance ($\delta = -5.81$ ppm). Several CNC(C*H*$_3$)$_3$ resonances were also observed in the region between 1.3 and 1.5 ppm. These, however, could not be correlated with the upfield resonance. For Method A, additional resonances due to CH$_4$ and Et$_2$O 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 ($\delta = -5.86$ ppm; $J_{\mathrm{HD}} = 33.4$ Hz).

Method B was also carried out at lower temperatures (230 K) and monitored by ^{1}H NMR. The reaction did not proceed until a temperature of 260 K was attained, at which point deomposition products as well as [Re(CN*t*Bu)$_5$(H$_2$)]BAr$_f$ were observed to form simultaneously.

Spectroscopic Observation 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, $J_{\mathrm{HP}} = 7.3$ Hz), −7.55 (sextet, 2H, $J_{\mathrm{HP}} = 28.6$ 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$_2$ (1280 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 monodeuterated species was shifted downfield by 26 ppb relative to the diprotio complex.

Spin Saturation Transfer Experiments on 5a-BF$_4$. The sample was prepared by combining **5a-BF$_4$** (21 mg) and CD$_2$Cl$_2$ (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.[53]

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.

X-ray Structural Determination of Re(CN*t*Bu)$_3$(PCy$_3$)$_2$Cl (2a). Single crystals of **2a** 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. Diffraction measurements were made at 183 K using the Enraf Nonius low-temperature device. Twenty-five reflections in the range 32° to 38° in 2θ were found and an orientation matrix was determined providing for a well oriented monoclinic cell with a volume of 5935 Å^3. The crystals had a semiopaque appearance and were of good quality as evidenced by the reasonably narrow peaks (hwfm = 0.3° in 2θ) and agreement of the equivalents. A high χ 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 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. Hydrogen atoms were introduced by calculation using a C−H distance of 0.96 Å and fixed isotropic temperature factors. 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 (3a). Well-formed pink crystals of **3a** were grown at −20 °C by layering a CH$_2$Cl$_2$ solution with diethyl ether. A crystal of small size (0.05 × 0.10 × 0.15 mm) coated with paratone was mounted using epoxy glue. Twenty-five 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 χ reflection led to a good absorption correction. The Laue merging *R* factor for 136 reflection was 2.2%. 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 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 as much as possible the disorder. Carbons were introduced in the only mirror plane position possible and site occupancies were determined by refinement. 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. Similar attempts to resolve this were attempted, and the results are poor, probably due to the weak overall intensity ratio. Hydrogen atoms were introduced by calculation using a C−H distance of 0.96 Å and fixed isotropic temperature factors. A final *R* of 4.1% with a GOF of 1.16 was obtained.

Acknowledgment. We are grateful to the Department of Energy, Office of Basic Energy Science, for support of this research.

Supporting Information Available: Summary of X-ray analysis of **2a** and **3a**, including data collection and refinement procedures, tables of positional and thermal parameters, and bond distances and angles (25 pages). See any current masthead page for ordering and Internet access instructions.

JA961994P

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