Cationic Hydrogen Complexes of Rhenium. 2. Synthesis, Reactivity, and Competition Studies

D. M. Heinekey,* Catherine E. Radzewich, Mark H. Voges, and Beth M. Schomber

Contribution from the Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700

Received December 16, 1996[⊗]

Abstract: Cationic rhenium dihydrogen complexes, $[Re(H_2)(PR_3)_2(CO)_3]B(Ar')_4$ (PR_3 = PCy_3, P*i*Pr$_3$, P*i*PrPh$_2$, PPh_3; Ar′ = 3,5-$(CF_3)_2C_6H_3$), have been prepared by the protonation of $ReX(PR_3)_2(CO)_3$ (X = H, CH_3) with $[H(Et_2O)_2]B(Ar')_4$ under a hydrogen atmosphere. Deuterium is incorporated into the H_2 ligand when placed under a D_2 atmosphere and large J_{HD} values (30−33 Hz) are consistent with a dihydrogen formulation. Relaxation data indicate very short T_{1min} for these complexes. These complexes are susceptible to heterolytic cleavage of dihydrogen, and the reactivity with several bases has been investigated. Under vacuum or argon atmosphere the complexes readily lose hydrogen to form 16-electron complexes. In the solid state, $[Re(PCy_3)_2(CO)_3]B(Ar')_4$ exhibits an agostic interaction to a β C−H bond of the phosphine ligand. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $[Re(PCy_3)_2(CO)_3]B(Ar')_4$ indicate a dynamic process involving hindered rotation about the Re−P bond. Competition studies have been conducted, and the hydrogen binding affinity is higher for $[Re(H_2)(PCy_3)_2(CNtBu)_3]B(Ar')_4$ (**5**) than for $[Re(H_2)(PCy_3)_2(CO)_3]B(Ar')_4$ (**2a**). Similar experiments also find that **5** also binds hydrogen preferentially over $W(H_2)(PCy_3)_2(CO)_3$.

Introduction

Since their initial discovery by Kubas,[1] H_2 complexes of transition metals have been the subject of intensive study by several research groups.[2] Cationic dihydrogen complexes formed by protonation of neutral hydrides or by other routes are numerous. Recently, there have been several interesting reports on the synthesis and reactivity of dicationic dihydrogen complexes.[3] The effect that a net positive charge has upon the stability of dihydrogen complexes is of interest in their design and predicted reactivity. While there are reported comparisons of dihydrogen complexes within the same transition metal triad,[4,5] there are few comparisons of cationic systems to closely related neutral analogs.[6−9] Cationic systems require extra considerations. Study of cationic complexes is complicated by the requirement for polar solvents, which can act as ligands to electron-deficient metal centers. Anions can also act as potential ligands, especially if the hydrogen ligand is labile.

Since there have been numerous studies that describe the synthesis, characterization, and reactivity of $M(H_2)(PCy_3)_2(CO)_3$ (M = W, Mo, Cr),[1,10] we have chosen to investigate the group 7 cationic analogs. A previous report of $[Re(H_2)(PMe_3)_2(CO)_3]BF_4$[11] describes the low-temperature ^1H NMR spectrum of this species, but the thermal instability precluded isolation of the complex. This instability is consistent with the previous observation in our group that $[Re(H_2)(PCy_3)_2(CO)_3]BF_4$[12] also decomposes at low temperatures. We now report that the use of more weakly coordinating anions[13,14] has enabled us to *isolate* and characterize a wide range of cationic complexes of rhenium. This report details the synthesis and characterization of several cationic rhenium dihydrogen complexes of the general formula $[Re(H_2)(PR_3)_2(CO)_3]^+$. The lability of the hydrogen ligand in these complexes has also led us to investigate the formally 16-electron complexes that result from H_2 loss. A brief account of this chemistry has been previously communicated.[15] We have recently reported on a closely related series of dihydrogen complexes of the form, $[Re(H_2)(PR_3)_2(CNtBu)_3]^+$, in which the carbonyl groups have been substituted by isonitrile coligands.[16] $[ReL(PR_3)_2(CO)_3]^+$ and $[ReL(PR_3)_2(CNtBu)_3]^+$ (L = H_2, ago-

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1997.

(1) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451−452.

(2) Reviews on dihydrogen complexes: (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913−926. (b) Morris, R. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, *121*, 155−289. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95−101. (d) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120−128.

(3) (a) Heinekey, D. M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396−4399. (b) Smith, K.-T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473−9480. (c) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946−8947. (d) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261−2263. (e) Schlaf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270−2278.

(4) (a) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Am. Chem. Soc.* **1989**, *111*, 2072−2077. (b) Stefano, A.; Albertin, G.; Amendola, P.; Bordignon, E. *J. Chem. Soc., Chem. Commun.* **1989**, 229−230. (c) Amendola, P.; Antoniutti, S.; Albertin, G.; Bordignon, E. *Inorg. Chem.* **1990**, *29*, 318−324.

(5) (a) Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027−3039. (b) Bautista, M. T.; Earl, K. A.; Morris, R. H. *Inorg. Chem.* **1988**, *27*, 1126−1128. (c) Earl, K. A.; Morris, R. H.; Sawyer, J. F. *Acta Crystallogr.* **1989**, *C45*, 1137−1138. (d) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823−8827. (e) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161−171. (f) Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876−4887. (g) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 2780−3782.

(6) $[Mn(H_2)(CO)(dppe)_2]B(Ar')_4$ (dppe = $Ph_2PC_2H_4PPh_2$): King, W. A.; Luo, X.-L.; Scott, B. L.; Kubas, G. J.; Zilm, K. W. *J. Am. Chem. Soc.* **1996**, *118*, 6782−6783.

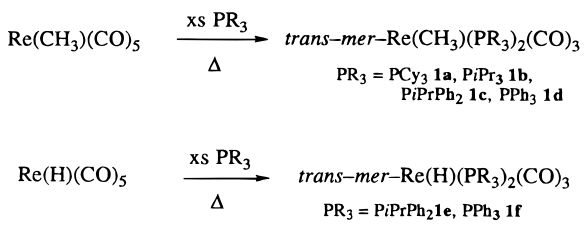
(7) $Mo(H_2)(CO)(R_2PC_2H_4PR_2)_2$: (a) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339−1341. (b) Kubas, G. J.; Ryan, R. R.; Unkefer, C. J. *J. Am. Chem. Soc.* **1987**, *109*, 8113−8115. (c) Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 569−581. (d) Zilm, K. W.; Merrill, R. A.; Kummer, M. W.; Kubas, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 7837−7839.

(8) $MnH(H_2)(R_2PC_2H_4PR_2)_2$ (R = Me, Et): Perthuisot, C.; Fan, M.; Jones, W. D. *Organometallics* **1992**, *11*, 3622−3629.

(9) $[MH(H_2)(R_2PC_2H_4PR_2)_2]^+$ (M = Fe, Ru): (a) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581−5582. (b) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780−3782. (c) Bautista, M. T.; Earl, K. A.; Morris, R. H. *Inorg. Chem.* **1988**, *27*, 1124−1126. (d) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823−8827. (e) Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876−4887.

S0002-7863(96)04322-3 CCC: $14.00

Scheme 1



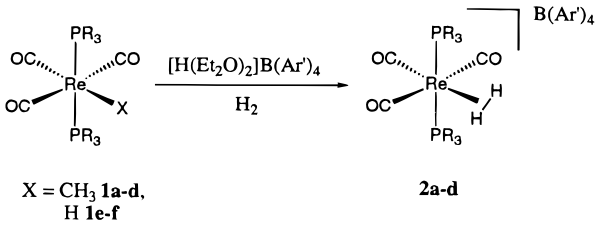
stic) react with a variety of small molecules, and the details of these experiments will be reported separately.[17]

Results

Synthesis of $Re(X)(PR_3)_2(CO)_3$ (X = H, CH_3). In the course of this work, several neutral methyl and hydride complexes of rhenium have been prepared. Compounds **1a**−**f** are generated by heating a toluene solution of $Re(H)(CO)_5$ or $Re(CH_3)(CO)_5$ with excess phosphine in a thick-walled glass vessel (Scheme 1). The solutions are heated at 110−130 °C for 40−140 h and degassed every 12 h. If the CO gas is not removed periodically, the reaction forms unidentified products. The reaction conditions are dependent upon the cone angle of the phosphine. For the largest phosphine, PCy_3, the highest temperatures (130 °C) and longest reaction times (140 h) were required. The yields for the formation of $Re(CH_3)(PCy_3)_2(CO)_3$ (**1a**) are low (50%) and can be contaminated with up to 50% of $ReH(PCy_3)_2(CO)_3$.[18] Although $ReH(PCy_3)_2(CO)_3$ is slightly more soluble in heptane, the desired product, $Re(CH_3)(PCy_3)_2(CO)_3$, can only be purified by drastically sacrificing yield. By contrast, the synthesis of $Re(CH_3)(PPh_3)_2(CO)_3$ (90% yield) requires lower reaction temperatures and shorter reaction times, and no formation of $ReH(PPh_3)_2(CO)_3$ is observed during the course of the thermolysis. Complexes **1e** and **1f** are synthesized from $ReH(CO)_5$ and PR_3 (PR_3 = P*i*PrPh$_2$, PPh_3) under similar conditions as used for their methyl analogs and are isolated in high yields. Complexes **1e** and **1f** slowly convert to the corresponding neutral chlorides over the course of several days in CD_2Cl_2 or $CDCl_3$. Alternate syntheses for complex **1f** have been previously reported.[19]

The progress of the phosphine-substitution reaction can be conveniently monitored by ^1H NMR spectroscopy. The monosubstituted phosphine compounds are typically observed as intermediates in the preparation of the disubstituted compounds. The products are isolated by removing the toluene *in vacuo* to give a sticky yellow residue. White to yellow solids are obtained by rinsing the products with several portions of pentane or by recrystallization from heptane. Table 1 lists selected ^1H NMR and IR data for complexes **1a**−**f**. The ^1H NMR spectra of the isolated complexes show a triplet for the rhenium methyl or hydride ligand due to coupling to two equivalent phosphines. The $^{31}P\{^1H\}$ NMR spectra show a single phosphorus signal for each complex. A typical $^{13}C\{^1H\}$ NMR spectrum of the carbonyl region shows two triplets from coupling to equivalent phosphine ligands. The usual pattern of the carbonyl region in the IR spectra are three bands with weak, strong, and medium intensities as the frequency decreases. All of these data are consistent with the carbonyls arranged in a meridinal configuration and trans phosphine ligands. The stereochemistry of the product was confirmed in one case by a crystal structure of $Re(CH_3)(PPh_3)_2(CO)_3$ (**1d**).[20] Although the methyl and carbonyls were disordered, the P−Re−P angle was found to be 177.5°. The facial isomer of **1d** has been previously synthesized and characterized by Bergman and Simpson.[21]

Synthesis and Characterization of $[Re(H_2)(PR_3)_2(CO)_3]B(Ar')_4$ (PR_3 = PCy_3 (2a), P*i*Pr$_3$ (2b), P*i*PrPh$_2$ (2c), PPh_3 (2d)). Protonation of complexes **1a**−**f** with $[H(Et_2O)_2]B(Ar')_4$ under a hydrogen atmosphere in CH_2Cl_2 affords the corresponding dihydrogen complex (eq 1). A broad resonance between −3



(1)

and −5 ppm is observed for each compound in the ^1H NMR spectra, with no observable phosphorus coupling. The dihydrogen resonance is typically observed at 1.5 ppm lower field than the corresponding neutral hydride in CD_2Cl_2. Table 2 lists selected ^1H NMR data for the hydride region. The complexes are thermally robust and are stable indefinitely in halogenated solvents (CD_2Cl_2, $CDCl_3$, and 1,2-difluorobenzene) under a partial H_2 atmosphere. Complexes **2a** and **2b** have been isolated as pale yellow solids in approximately 90% yield and completely characterized by spectroscopic methods. For **2c** and **2d**, the complexes are extremely reactive toward water and could not be cleanly isolated, therefore, we have only characterized them by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. No change is observed in the ^1H or $^{31}P\{^1H\}$ NMR spectra from 190 to 300 K, indicating that there is no substantial equilibrium with a dihydride structure,

(10) (a) Kubas, G. J.; Ryan, R. R. *Polyhedron* **1986**, *5*, 473−485. (b) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339−1341. (c) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294−2301. (d) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000−7009. (e) Zilm, K. W.; Merrill, R. A.; Kummer, M. W.; Kubas, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 7837−7839. (f) Eckert, J.; Kubas, G. J.; Dianoux, A. J. *J. Chem. Phys.* **1988**, *88*, 466−468. (g) Gonzalez, A. A.; Zhang, K.; Nolan S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics*, **1988**, *7*, 2429−2435. (h) Zhang, K.; Gonzalez, A. A.; Hoff, C. D. *J. Am. Chem. Soc.* **1989**, *111*, 3627−3632. (i) Gonzalez, A. A.; Hoff, C. D. *Inorg. Chem.* **1989**, *28*, 4295−4297. (j) Zhang, K.; Gonzalez, A. A.; Mukerjee, S. L.; Chou, S.-J.; Hoff, C. D.; Kubat-Martin, K. A.; Barnhart, D.; Kubas, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 9170−9176. (k) Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Kiss, G.; Hoff, C. D. *Organometallics* **1992**, *11*, 3390−3404. (l) Eckert, J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 2324−2332. (m) Van Der Sluys, L. S.; Miller, M. M.; Kubas, G. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1991**, *113*, 2513−2520. (n) Lang, R. F.; Ju. T. D.; Kiss, G.; Hoff, C. D.; Bryan, J. C.; Kubas, G. J. *J. Am. Chem. Soc.* **1994**, *116*, 7917−7918. (o) Eckert, J.; Kubas, G. J.; White, R. P. *Inorg. Chem.* **1992**, *31*, 1550−1551. (p) Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Van Der Sluys, L. S.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3855−3860. (q) Eckert, J.; Kubas, G. J. *J. Phys. Chem.* **1993**, *97*, 2378−2384. (r) Kubas, G. J. *Inorg. Synth.* **1990**, *27*, 1−8. (s) Kubas, G. J.; Nelson, J. E.; Bryan, J. C.; Eckert, J.; Wisniewski, L.; Zilm, K. *Inorg. Chem.* **1994**, *33*, 2954−2960.

(11) Gusev, D. G.; Nietlspach, D.; Eremenko, I. L.; Berke, H. *Inorg. Chem.* **1993**, *32*, 3628−3636.

(12) Heinekey, D. M.; Crocker, L. S. Unpublished observations, 1987.

(13) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920−3922.

(14) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927−942.

(15) Heinekey, D. M.; Schomber, B. M.; Radzewich, C. E. *J. Am. Chem. Soc.* **1994**, *116*, 4515−4516.

(16) Heinekey, D. M.; Voges, M. H.; Barnhart, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 10792−10802.

(17) Heinekey, D. M.; Radzewich, C. E.; Voges, M. H.; Schomber, B. M. To be submitted for publication.

(18) Walker, H. W.; Rattinger, G. B.; Belford, R. L.; Brown, T. L. *Organometallics* **1983**, *2*, 775−776.

(19) (a) Luo, X.-L.; Liu, H.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 4740−4742. (b) Jones, W. D.; Maquire, J. A. *Organometallics* **1987**, *6*, 1728−1737.

(20) Heinekey, D. M.; Voges, M. H. Unpublished reults, 1992.

(21) Simpson, R. D.; Bergman, R. G. *Organometallics* **1993**, *12*, 781−796.

Table 1. Selective ^{1}H NMR and IR Data for Compounds **1a**−**f**

compd	δ(M−CH$_3$)[a]	δ(M−H)[a]	J_{PH} (Hz)[a]	ν_{CO} (cm^{-1})[b]
Re(CH$_3$)(PCy$_3$)$_2$(CO)$_3$ (**1a**)	−0.05		6.0	N/A
Re(CH$_3$)(P*i*Pr$_3$)$_2$(CO)$_3$ (**1b**)	−0.12		5.9	2004 (w), 1902 (s), 1866 (m)
Re(CH$_3$)(P*i*PrPh$_2$)$_2$(CO)$_3$ (**1c**)	−1.12		6.6	2018 (w), 1920 (s), 1871 (m)
Re(CH$_3$)(PPh$_3$)$_2$(CO)$_3$ (**1d**)	−1.06		6.7	2018 (w), 1915 (s), 1878 (m)
Re(H)(P*i*PrPh$_2$)$_2$(CO)$_3$ (**1e**)		−5.94	18.8	2020 (w), 1919 (s)
Re(H)(PPh$_3$)$_2$(CO)$_3$ (**1f**)		−5.20	17.8	2020 (w), 1925 (s)

[a] Recorded at 298 K in C_6D_6 (**1a**, **1b**, **1e**, **1f**) and $CDCl_3$ (**1c**, **1d**). [b] Methylene chloride.

Table 2. ^{1}H NMR Data of the Hydride Region for Compounds **2a**−**d**[a]

compd	δ(HH)[b]	δ(HD)[b]	J_{HD}[c]	$\Delta\delta$[d,e]	T_{1min}[e,g]	$\Delta\nu_{1/2}$[e,k]
[Re(H$_2$)(PCy$_3$)$_2$(CO)$_3$]$^+$ (**2a**)	−4.78	−4.81	32	34	9.3[h]	49
[Re(H$_2$)(P*i*Pr$_3$)$_2$(CO)$_3$]$^+$ (**2b**)	−4.97[f]	−5.01	33	37	9.6[i]	23
[Re(H$_2$)(P*i*PrPh$_2$)$_2$(CO)$_3$]$^+$ (**2c**)	−4.26	−4.29	30	30	10.5[j]	52
[Re(H$_2$)(PPh$_3$)$_2$(CO)$_3$]$^+$ (**2d**)	−3.86	−3.89	32	30	10.3[j]	54

[a] All measurements recorded at 298 K in CD_2Cl_2 except where noted. [b] Chemical shift in ppm. [c] Coupling constant in Hz. [d] Isotope shift ($\Delta\delta$ = δ(HH) − δ(HD)) in ppb. [e] 500 MHz. [f] 200 MHz. [g] T_{1min} in ms. [h] 248 K. [i] 232 K. [j] 254 K. [k] Half-height width in Hz.

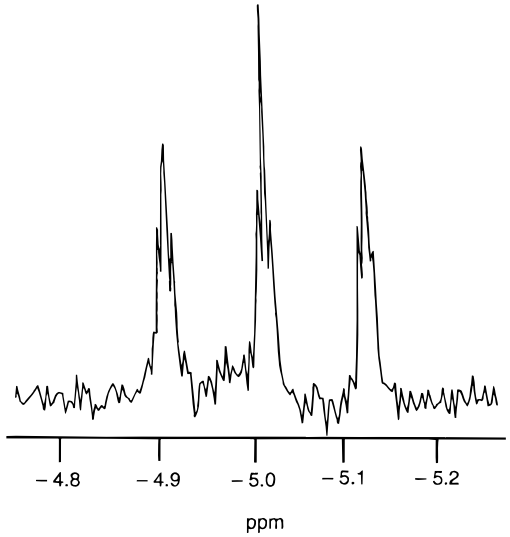


Figure 1. 200-MHz ^{1}H NMR spectrum (hydride region) of **2b**-d_1 in CD_2Cl_2. A large coupling to deuterium ($^1J_{HD}$ = 33 Hz) is observed as well as a small phosphorus coupling ($^2J_{HP}$ = 2 Hz).

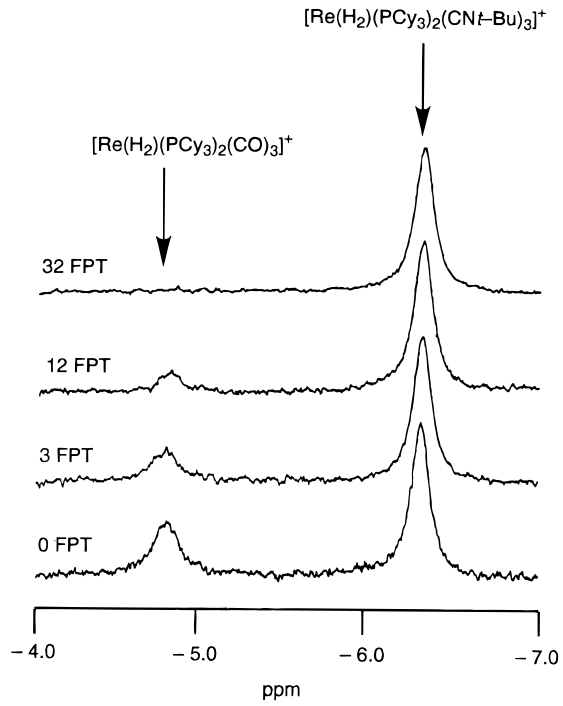


Figure 2. Partial ^{1}H NMR spectra of a solution of [Re(H$_2$)(PCy$_3$)$_2$(CO)$_3$]B(Ar′)$_4$ (**2a**) and [Re(H$_2$)(PCy$_3$)$_2$(CN*t*Bu)$_3$]B(Ar′)$_4$ (**5a**) as a function of H_2 concentration (FPT cycles).

[Re(H)$_2$(PR$_3$)$_2$(CO)$_3$]B(Ar′)$_4$. We have also observed that **2a** is formed from the addition of NaB(Ar′)$_4$ to a solution of ReCl(PCy$_3$)$_2$(CO)$_3$ in methylene chloride under an H_2 atmosphere. This reaction is quite slow and requires 24 h at room temperature to reach completion.

When [Re(H$_2$)(PR$_3$)$_2$(CO)$_3$]B(Ar′)$_4$ (**2a**−**d**) is placed under a D_2 atmosphere, loss of the H_2 ligand and formation of the D_2 isotopomer is observed. For **2a** and **2b**, isotope exchange is rapid and a distinct 1:1:1 triplet is observed with large J_{HD} values after 12 h. The line width for **2b**-d_1 is sufficiently narrow that a 2 Hz coupling from the phosphine ligands is observed. The observed ^{1}H NMR resonance of **2a**-d_1 and **2b**-d_1 is slightly upfield of the H_2 isotopomers and has a chemical shift difference of approximately 35 ppb. Isotope shifts are also observed in the ^{31}P{^{1}H} NMR spectrum, and all three isotopomers can be observed as the resonances are observed to shift to higher field as the deuterium in the H_2 ligand is increased. Isotope exchange for **2c** and **2d** is less facile and signals due to **2c**-d_1 and **2d**-d_1 were partially obscured by the presence of the residual H_2 resonance. An inversion recovery experiment (180°−τ−90°) with τ set to null the signal of the H_2 ligand reveals the resonance due to the HD ligand.

Relaxation data for **2a**−**d** were collected at 500 MHz in CD_2Cl_2 by standard inversion recovery NMR methods. Very short minimum T_1 values of 10 ± 1 ms were observed for all four dihydrogen complexes (Table 2). In contrast, the T_{1min} of the neutral complex ReH(P*i*PrPh$_2$)$_2$(CO)$_3$ (**1e**) was observed to be 325 ms.

Exposure of solid **2a**−**d** to vacuum or argon atmosphere leads to H_2 loss and a corresponding color change from pale yellow or white to orange (*vide infra*). This process is completely reversible. Similar reversible H_2 loss can be effected in solution by removal of the H_2 atmosphere and is accelerated by gentle heating. Protonation of ReH(PR$_3$)$_2$(CO)$_3$, **1e** and **1f**, under vacuum only leads to a mixture of the dihydrogen complexes, **2c** and **2d**, and the hydrogen loss products.

Reactivity of [Re(H$_2$)(PCy$_3$)$_2$(CO)$_3$]B(Ar′)$_4$ (2a) with Bases. The dihydrogen ligand is readily deprotonated by several bases. Addition of 1,8-bis(dimethylamino)naphthalene (Proton-Sponge) or 2,6-di-*tert*-butyl-4-methylpyridine to a CD_2Cl_2 solution of the dihydrogen complex leads to immediate formation of the neutral hydride, ReH(PCy$_3$)$_2$(CO)$_3$.[18] The strong base KO*t*Bu will also deprotonate the dihydrogen complex, but only over the course of several days due to its low solubility in CD_2Cl_2.

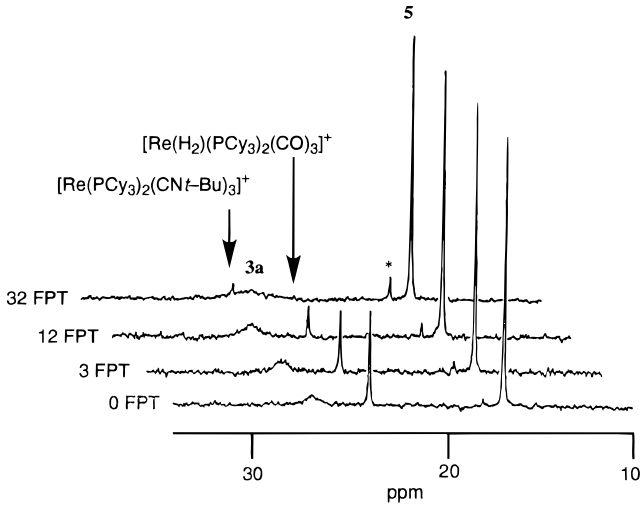


Figure 3. $^{31}P\{^1H\}$ spectra of a solution of $[Re(H_2)(PCy_3)_2(CO)_3]B(Ar')_4$ (**2a**) and $[Re(H_2)(PCy_3)_2(CNtBu)_3]B(Ar')_4$ (**5**) as a function of H_2 concentration (FPT cycles). Formation of **7** is indicated by the asterisk.

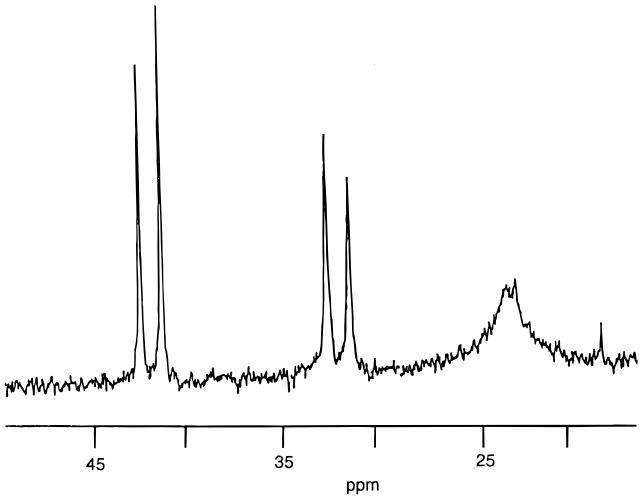
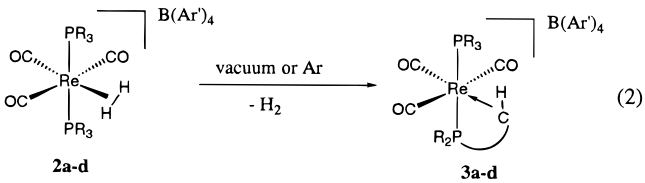


Figure 4. 81-MHz $^{31}P\{^1H\}$ NMR spectrum of $[Re(PCy_3)_2(CO)_3]B(Ar')_4$ (**3a**) at 240 K (CD_2Cl_2).

If the base is not sterically hindered, as is the case with ammonia and aniline, displacement of the H_2 ligand and coordination of the base is observed.[22] Two nitrogen bases that do not react with **2a** are pentafluoropyridine and 2,6-diisopropylaniline.

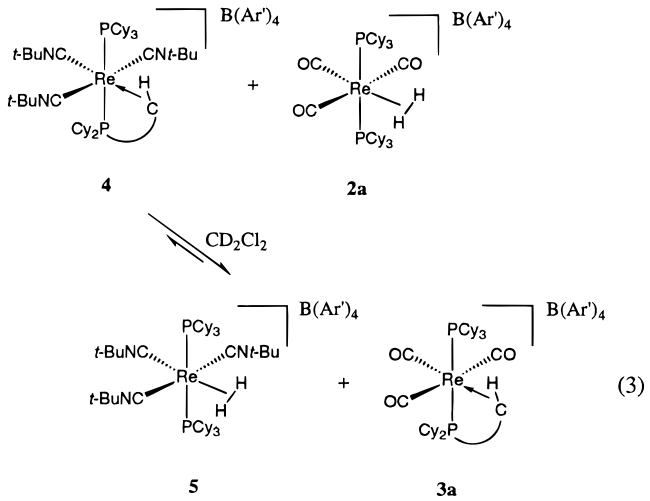
Synthesis of $[Re(PR_3)_2(CO)_3]B(Ar')_4$ (PR_3 = PCy_3 (3a), $PiPr_3$ (3b), $PiPrPh_2$ (3c), PPh_3 (3d)). When $Re(CH_3)(PR_3)_2(CO)_3$, **1a**−**d**, is reacted with $[H(Et_2O)_2]B(Ar')_4$ under vacuum, an orange solution results. Rapid methane evolution was observed. The formally ligand deficient product is also produced upon removal of H_2 from **2a**−**d** in the solid state or solution (eq 2). The compounds are thermally stable in the solid



(2)

state and in solution. **3a** and **3b** have been isolated in good yield and completely characterized by spectroscopic and analytical methods. The solid state structure of **3a** has been determined and indicates an agostic interaction with a β C−H bond of one of the cyclohexyl rings.[15] Complexes **3c** and **3d** are extremely reactive toward water and could only be characterized in solution by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra exhibit a single resonance that does not shift significantly upon changing the solvent (CD_2Cl_2, $CDCl_3$, and 1,2-difluorobenzene) or upon the removal of Et_2O. A low-temperature ^{13}C NMR spectrum in CH_2Cl_2 does not show any resonances that can be attributed to a solvent adduct. There is no evidence that the anion, $B(Ar')_4^-$, interacts with any of the cationic complexes since the ^1H and $^{13}C\{^1H\}$ NMR spectrum of the anion is invariant for all of the compounds we have studied.

Hydrogen Binding Competition Studies. The affinity of hydrogen for $[Re(PCy_3)_2(CNtBu)_3]B(Ar')_4$ (**4**) relative to the carbonyl analog, $[Re(PCy_3)_2(CO)_3]B(Ar')_4$ (**3a**), was determined by a direct competition study in CD_2Cl_2 (eq 3). Equimolar



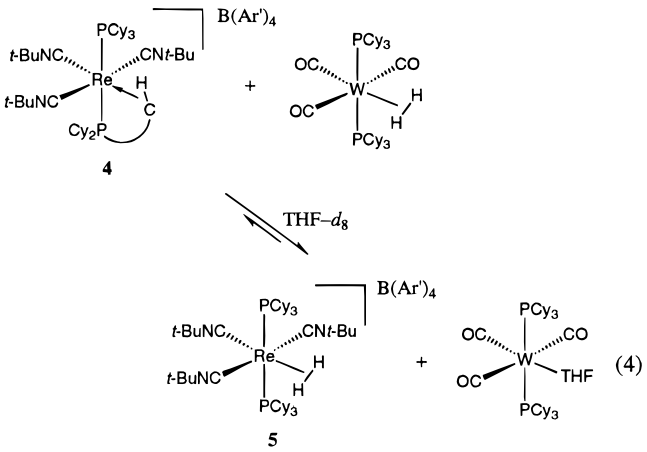
(3)

quantities of complexes **4** and **3a** were placed in a J. Young NMR tube with a Teflon valve. The solids were exposed to H_2 (760 torr) until the solid became yellow. After excess H_2 was removed at 77 K *in vacuo*, CD_2Cl_2 was vacuum transferred into the tube. The NMR tube was back-filled with argon (760 Torr) at 298 K. Figures 2 and 3 show the ^1H NMR spectra and $^{31}P\{^1H\}$ NMR spectra, respectively, of the solution at various hydrogen concentrations. The initial solution shows ^1H and $^{31}P\{^1H\}$ NMR resonances corresponding to **5**, **2a**, and **3a**. Bound hydrogen was gradually removed by repeated freeze−pump−thaw cycles. The resonances corresponding to $[Re(H_2)(PCy_3)_2(CO)_3]B(Ar')_4$ completely disappeared before any resonances corresponding to $[Re(PCy_3)_2(CNtBu)_3]B(Ar')_4$ were observed.

The bound hydrogen was removed from both **2a** and **5** by removing the solvent *in vacuo* and exposing the sample to dynamic vacuum for 15 h. Methylene chloride-d_2 was reintroduced to the NMR tube and the hydrogen concentration was slowly increased in the sample. Monitoring the progress of the reaction by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy shows that **5** grows in completely before any **2a** is detected.

A similar experiment, conducted in THF-d_8, determined the affinity of H_2 for **4** relative to the tungsten carbonyl THF complex, $W(THF)(PCy_3)_2(CO)_3$ (eq 4). Equimolar quantities of complex **4** and $W(PCy_3)_2(CO)_3$ were placed in a J. Young NMR tube with a Teflon valve. The solids were exposed to H_2 (760 Torr) until the purple color of the five-coordinate complexes was discharged. The H_2 gas was removed at 77 K and THF-d_8 was vacuum transferred to the tube. The NMR tube was back-filled with argon (760 Torr) at 298 K. The initial ^1H and $^{31}P\{^1H\}$ NMR spectra show resonances for **5**, $W(H_2)(PCy_3)_2(CO)_3$, and $W(THF)(PCy_3)_2(CO)_3$. Bound hydrogen was

(22) The products of H_2 displacement are reported separately.[17]



gradually removed by several freeze−pump−thaw cycles. The resonances corresponding to $W(H_2)(PCy_3)_2(CO)_3$ completely disappeared before any resonances corresponding to **4** were observed to grow in.

Once most of the bound hydrogen was removed from both complexes, **5** and $W(H_2)(PCy_3)_2(CO)_3$, the experiment was reversed. The hydrogen concentration was slowly increased. The ^1H and $^{31}P\{^1H\}$ NMR spectra show that **5** grows in completely, before any $W(H_2)(PCy_3)_2(CO)_3$ is detected.

Discussion

Synthesis of $Re(X)(PR_3)_2(CO)_3$ (X = H, CH_3). The thermolytic decarbonylation of $ReX(CO)_5$ (X = H, CH_3, halides) in the presence of phosphines is an often used synthetic method for generating mixed phosphine−carbonyl complexes of rhenium.[23] These include mono-, bis-, or tris-substituted products in various stereochemical configurations depending upon conditions, phosphine, and X group. We were interested in generating several bis-phosphine, tri-carbonyl complexes with bulky phosphines in a *trans-mer* configuration with methyl or hydride ligands. The synthetic route allows for generation of complexes **1a**−**f** in good yield and purity, although the more demanding conditions required for the bulkier phosphines, P*i*Pr$_3$ and PCy_3, leads to lower yields than for P*i*PrPh$_2$ and PPh_3. These complexes are convenient precursors to rhenium dihydrogen and agostic complexes.

Synthesis and Characterization of $[Re(H_2)(PR_3)_2(CO)_3]B(Ar')_4$. Protonation of complexes **1a**−**f** with $[H(Et_2O)_2]B(Ar')_4$ under a H_2 atmosphere leads to a series of cationic rhenium dihydrogen complexes. A broad peak in the hydride region of the ^1H NMR spectrum is consistent with a dihydrogen structure, and partial substitution with deuterium leads to large HD coupling values of 30−33 Hz. The ^1H NMR chemical shifts of the bound HD are slightly upfield of the corresponding H_2 resonances (30 to 37 ppb), consistent with typical intrinsic isotope shifts.[24]

The T_{1min} values of **2a**−**d** listed in Table 2 are very short and remarkably similar (9−10 ms). In order to gauge the relaxation contribution of the rhenium metal center as well as the phosphine ligands we have also investigated the T_{1min} of **1e** and **1f**. The long T_{1min} values of **1e** (325 ms) and **1f** (354 ms)[19a] are in the expected range of hydride complexes. This observation indicated the rapid relaxation in **2a**−**d** is dominated by the dipole−dipole interaction of the η^2-H_2 ligand.

Table 3. H−H Bond Lengths from T_{1min} Data in the Limit of Slow and Fast Rotation

	H−H (Å)	
compd	slow rotation	fast rotation
$[Re(H_2)(PCy_3)_2(CO)_3]^+$ (**2a**)	0.95	0.75
$[Re(H_2)(PiPr_3)_2(CO)_3]^+$ (**2b**)	0.95	0.76
$[Re(H_2)(PiPrPh_2)_2(CO)_3]^+$ (**2c**)[a,b]	0.97	0.77
$[Re(H_2)(PPh_3)_2(CO)_3]^+$ (**2d**)[a,c]	0.97	0.77

[a] Corrected for neutral hydride relaxation. [b] Measurement of the T_{1min} of $Re(H)(PiPrPh_2)_2(CO)_3$ was 325 ms at 217 K in a 500-MHz field (CD_2Cl_2) solution). [c] Measurement of the T_{1min} of $Re(H)(PPh_3)_2(CO)_3$ was taken from ref 19a and corrected to a 500-MHz field.

The T_{1min} values for the dihydrogen ligand can be used to calculate the bond distance within the limits of fast and slow rotation (Table 3).[25] An average slow rotation bond length of 0.96 Å is calculated versus the fast rotation bond length of 0.76 Å. Gusev and co-workers have recently discussed the utility of T_{1min} data in determining the H−H bond distance for dihydrogen complexes.[26] Specifically, they have addressed the difficulties in assigning "fast" or "slow" rotation corrections to calculate the H−H bond distances. They have compared several known dihydrogen complexes that have J_{HD} values greater than 25 Hz as well as reported T_{1min} data. The calculated H−H bond lengths for this series as well as complexes **2a**−**d** are best approximated by the slow-spinning data. By correcting for a fast-spinning H_2 ligand, the H−H bond lengths are on average 0.2 Å shorter, and several approach the unreasonable distance of 0.74 Å for free H_2.[27]

Recent reports from the groups of Heinekey[3a] and Morris[28] have correlated the H−H bond distances determined by solid-state NMR or neutron diffraction techniques to J_{HD} values. The J_{HD} values of complexes **2a**−**d** correspond to H−H bond distances of approximately 0.89 Å. This value is intermediate between those determined for slow and fast rotation from the T_{1min} data. Surprisingly, the H−H distance determined for $W(H_2)(PiPr_3)_2(CO)_3$ by solid-state NMR is 0.89Å.[10e,29] A recent report by Kubas and co-workers has also indicated similar H−H distances for isostructural cationic and neutral dihydrogen complexes. Solid-state NMR was used to calculate an H−H distance of 0.89 Å for $[Mn(H_2)(CO)(dppe)_2]B(Ar')_4$[6] and 0.88 Å for the analogous neutral complex $Mo(H_2)(CO)(dppe)_2$[29] (dppe = $Ph_2PC_2H_4PPh_2$).

Stability of Dihydrogen Complexes: H_2 Loss, Homolytic Cleavage, Halogenated Solvents, Anions, and Heterolytic Cleavage. Protonation of neutral hydrides is a common synthetic route to cationic dihydrogen complexes.[2] It has been

(23) (a) Hoffman, N. W.; Prokopuk, N.; Robbins, M. J.; Jones, C. M.; Doherty, N. M. *Inorg. Chem.* **1991**, *30*, 4177−4181. (b) Abel, E. W.; Wilkinson, G. *J. Chem. Soc.* **1959**, 1501−1505. (c) Abel, E. W.; Tyfield, S. P. *Can. J. Chem.* **1969**, *47*, 4627−4633. (d) Chatt, J.; Dilworth, J. R.; Gunz, H. P.; Leigh, G. J. *J. Organomet. Chem.* **1974**, *64*, 245−254. (e) Bond, A. M.; Colton, R.; McDonald, M. E. *Inorg. Chem.* **1978**, *17*, 2842−2847. (f) Reiman, R. H.; Singleton, E. *J. Organomet. Chem.* **1973**, *59*, 309−315. (g) Jolly, P. W.; Stone, F. G. A. *J. Chem. Soc.* **1965**, 5259−5261. (h) Leins, A. E.; Coville, N. J. *J. Organomet. Chem.* **1991**, *407*, 359−367. (i) Reimann, R. H.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1973**, 841−845.

(24) (a) Hamilton, D. G.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3198−3203. (b) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 4813−4821. (c) Luo, X.-L.; Michos, D.; Crabtree, R. H. *Organometallics* **1992**, *11*, 237−241. (d) Baird, G. J.; Davies, S. G.; Moon, S. D.; Simpson, S. J.; Jones, R. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1479−1486. (e) Casey, C. P.; Tanke, R. S.; Hazin, P. N.; Kemnitz, C. R.; McMahon, R. J. *Inorg. Chem.* **1992**, *31*, 5474−5479.

(25) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173−4184.

(26) Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775−6783.

(27) (a) Nageswara Rao, B. D.; Anders, L. R. *Phys. Rev.* **1965**, *140*, A112. (b) Bloyce, P. E.; Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1988**, 846−848.

(28) Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994**, *116*, 7677−7681.

(29) Zilm, K. W.; Millar, J. M. *Adv. Magn. Opt. Reson.* **1990**, *15*, 163−200.

Table 4. IR Bond Stretching Frequencies of Related Carbonyl Complexes

compd	ν_{CO} (cm^{-1}, Nujol)
$[Re(CO)_4(PPh_3)_2]^+$ (**6**)	2002
$[Re(CO)_4(PCy_3)_2]^+$ (**7**)	1983
$[Re(CO)(PCy_3)_2(CNtBu)_3]^+$ (**8**)	1900
$W(CO)_4(PCy_3)_2$	1870

observed in the $[Re(H_2)(PR_3)_2(CO)_3]^+$ system that the choice of acid to form the dihydrogen complexes is crucial to their stability. The labile dihydrogen ligands in $[Re(H_2)(PR_3)_2(CO)_3]^+$ (**2**) can be easily displaced by anionic ligands such as chloride and triflate.[17] Even BF_4^-, which is often considered an unreactive anion, led to the decomposition of **2a** at low temperature.[12] The use of the less reactive anion, $B(Ar')_4^-$, has allowed the isolation of a stable series of dihydrogen complexes, **2a**−**d**.

The nature of the ligands as well as the charge on the metal complex can be used to predict the expected backbonding to the H_2 ligand. Isonitrile ligands are expected to be better donors than carbonyls, and the donation from the alkyl phosphines should be greater than that from aryl phosphines. Neutral complexes should also be more electron rich than cationic complexes. Table 4 lists the carbonyl stretching frequencies of a series of compounds in order to demonstrate these trends.

There is now a large series of closely related cationic rhenium dihydrogen complexes which have been studied by several different research groups.[30] We have attempted to draw comparisons based on the reactivity of these complexes as summarized in Table 5. The stability toward various anions is apparently a function of the electron density at the metal center. When the carbonyl ligands of **2a** are replaced by the less π acidic isonitrile ligands, the reactivity is dramatically different. Not only is $[Re(H_2)(PCy_3)_2(CNtBu)_3]^+$ stable with a wider variety of anions, but the cationic dihydrogen complex can also be formed by chloride displacement from $ReCl(PCy_3)_2(CNtBu)_3$ by H_2.[16] Complexes with a higher phosphine-to-carbonyl ratio such as $[(triphos)Re(H_2)(CO)_2]^+$ [30c] and $[ReH_2(PR_3)_4(CO)]^+$ [30a,b] are also stable toward more nucleophillic anions such as BF_4^- and CF_3COO^-. Three of the complexes listed in Table 5 are reported to be thermally unstable and have only been investigated by low-temperature ^1H NMR spectroscopy. It is likely that the anions used in these complexes could contribute to their thermal instability.

The series of rhenium carbonyl complexes $[ReL(PR_3)_2(CO)_3]^+$ are also surprisingly stable in halogenated solvents such as methylene chloride, chloroform, and Freon-21 ($CHFCl_2$). The analogous group 6 complexes, $ML(PR_3)_2(CO)_3$ (M = W, Mo, Cr), must be studied in toluene, although it has been shown that $W(H_2)(PiPr_3)_2(CO)_3$ can briefly withstand dissolution in CD_2Cl_2 at low temperature (<−20 °C).[26] Even the rhenium isonitrile complexes $[ReL(PCy_3)_2(CNtBu)_3]^+$ are only moderately stable in halogenated solvents.[16] Both of these systems are more electron rich than the rhenium carbonyl complexes and are presumably more susceptible to oxidation. This is evidenced by the isolation and characterization of a stable Re(II) chloride complex, $[ReCl(PCy_3)_2(CNtBu)_3]^+$, which forms by decomposition of $[Re(PCy_3)_2(CNtBu)_3]^+$ in chlorinated solvents (CD_2Cl_2, $CDCl_3$, $CDFCl_2$).[16] Similarly, $W(PCy_3)_2(CO)_3$ can also be oxidized by one electron to form a neutral 17 electron halide complex, $WI(PCy_3)_2(CO)_3$.[10n]

The electron density at the metal center is not only a factor in the stability of these complexes toward anions and oxidation, but also upon the reactivity of the dihydrogen ligand. Table 5 outlines the trends of dihydrogen lability, homolytic cleavage, and heterolytic cleavage for several closely related complexes. Greater backbonding from a more electron rich metal center contributes both to a greater tendency to homolytically cleave the H_2 bond and to tighter binding to the metal center. The neutral W complexes have been observed to have an equilibrium between bound dihydrogen and dihydride, and yet the hydrogen in this system is quite labile. Contrary to this, the cationic isonitrile complex of rhenium, **5**, binds hydrogen more strongly, relative to the agostic CH bond, as determined by direct competition studies, yet there has been no evidence that oxidative addition to the dihydride complex occurs.

Certainly, there are other factors that will also affect the lability and homolytic cleavage of a dihydrogen molecule. Since these systems have been observed to interact with the phosphine through a pendant C−H bond upon loss of the dihydrogen ligand, the strength of the agostic interaction must also be considered. The strength of the agostic bond can only be measured indirectly and is presumed to be approximately 10 ± 6 kcal/mol for $W(PCy_3)_2(CO)_3$.[10g] Presumably the strength of the agostic bond for **3a** and **4** would not be significantly different from this. Another factor that will affect the oxidative addition of the dihydrogen ligand to a dihydride structure is a significant rearrangement of the metal center. This transformation results in a formal oxidation of the metal center by two electrons and a structural change from a six-coordinate, octahedral complex to a seven-coordinate complex. How these factors will affect the observed reactivity of the dihydrogen ligand is difficult to ascertain, but it is clear that there is more involved than a simple measure of electron density at the metal center.

The acidity of the dihydrogen ligand appears to fall much more within the expected trends based on electron density at the metal center. Both $W(H_2)(PCy_3)_2(CO)_3$ and **5** are only weakly acidic, and strong bases such as a copper alkoxide[10m] and KO*t*Bu,[16] respectively, are used to deprotonate the dihydrogen complexes. As expected, the dihydride complex $[ReH_2(PMePh_2)_4(CO)]^+$ is also weakly acidic and could only be deprotonated with KOH.[30b] Complexes with lower phosphine/carbonyl ratios are easily deprotonated by NEt_3 or other nitrogen bases.[30] For the reactivity of $[Re(H_2)(PCy_3)_2(CO)_3]^+$ (**2a**) with bases, we have observed three different possibilities. Sterically protected nitrogen complexes that are relatively strong bases will easily deprotonate **2a**. Less sterically demanding nitrogen bases, such as NH_3 and aniline, have been observed to displace hydrogen from **2a** to form new adducts.[17] Weaker bases, such as pentafluoropyridine and 2,6-diisopropylaniline, show no reactivity with **2a**.

Hydrogen-Binding Competition Studies. We have been interested for some time in the influence of the charge of a transition metal complex upon the binding of dihydrogen. Both $[Re(H_2)(PCy_3)_2(CO)_3]B(Ar')_4$ (**2a**) and $W(H_2)(PCy_3)_2(CO)_3$ have been demonstrated to be labile toward H_2 dissociation. Also in both instances a stable, formally unsaturated complex is generated that will re-add H_2 to form the dihydrogen complex. Very detailed studies have been conducted by Kubas, Hoff, and co-workers to determine the relative energetics of H_2 binding to $M(PR_3)_2(CO)_3$ (M = W, Mo, Cr; R = Cy, *i*Pr).[10g−l] A direct comparison between **2a** and $W(H_2)(PCy_3)_2(CO)_3$ has been hindered by the lack of a common solvent system that will allow

(30) (a) Gusev, D. G.; Nietlispach, D.; Eremenko, I. L.; Berke, H. *Inorg. Chem.* **1993**, *32*, 3628−3636. (b) Luo, X.-L.; Michos, D.; Crabtree, R. H. *Organometallics* **1992**, *11*, 237−241. (c) Bianchini, C.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R.; Vacca, A. *Organometallics* **1995**, *14*, 3203−3215.

(31) **2a** is insoluble in nonpolar solvents such as benzene, toluene, and heptane. $W(H_2)(PCy_3)_2(CO)_3$ and $W(PCy_3)_2(CO)_3$ are generally reactive with halogenated solvents except solvents such as C_7F_8, C_6F_6, and 1,2-$C_6F_2H_4$ in which they are not soluble.

Table 5. Reactivity of Related Dihydrogen Complexes

compd	H_2 lability	halogentated solvent	dihydride formation	anions
$W(H_2)(PCy_3)_2(CO)_3$[a]	labile	stable < −20 °C	equilibrium	
$[Re(H_2)(PCy_3)_2(CO)_3]^+$ (**2a**)	labile	stable	none	$B(Ar')_4^-$
$[Re(H_2)(PCy_3)_2(CNtBu)_3]^+$ (**5**)	slowly labile	stable for a few days	none	Cl^-, OTf^-, BF_4^-, $B(Ar')_4^-$
$[triphosRe(H_2)(CO)_2]^+$[b]	med. labile	stable	none	BF_4^-
$[Re(H_2)(PMe_3)_2(CO)_3]^+$[c]	thermally unstable		none	CF_3COO^-
$[Re(H_2)(PMe_3)_3(CO)_2]^+$[c]	thermally unstable		none	CF_3COO^-
$[Re(H_2)(PMePh_2)_3(CO)_2]^+$[d]	thermally unstable		equil/dihydride at higher *T*	BF_4^-
$[ReH_2(PMePh_2)_4(CO)]^+$[d]	no H_2 loss	stable	dihydride	BF_4^-
$[ReH_2(PMe_3)_4(CO)^+$[c]	no H_2 loss	stable	equil/dihydride at RT	CF_3COO^-

[a] References 1 and 10. [b] Reference 30c. [c] Reference 30a. [d] Reference 30b.

both solubility and stability to the complexes.[31] However, comparison studies to a related complex, $[Re(H_2)(PCy_3)_2(CNtBu)_3]^+$ (**5**), have become possible.

The results comparing **4** and **3a** (eq 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 the isonitrile complex (**4**). Complexes **4** and **2a** 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 eq 3. The K_{eq} is calculated to be ≥9800, which corresponds to $\Delta G°_{298} \leq -5.4$ kcal/mol. We therefore are able to conclude that, at 298 K, H_2 prefers $[Re(PCy_3)_2(CNtBu)_3]^+$ (**4**) over $[Re(PCy_3)_2(CO)_3]^+$ (**3a**) by at least 5.4 kcal/mol.

The obvious difference between the complexes is the π-acidity of their respective coligands. CO is a much better π-acid than CN*t*Bu. Since the H_2 ligand is known to act not just as a σ-donor by also as a π-acceptor, presumably it is the difference of π-bond strengths in **5** and **2a** that 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 studies between **5** and $W(H_2)(PCy_3)_2(CO)_3$ were limited to THF, the only common solvent in which all species are soluble and stable. Complex **4** has been observed to not have any significant interaction with THF[17] and $W(PCy_3)_2(CO)_3$ has been shown to weakly bind THF,[10k] allowing an *indirect* comparison of the H_2 binding ability of **4** and $W(PCy_3)_2(CO)_3$. We have observed that molecular hydrogen binds preferentially to **4**, in THF solution, and that **4** and $W(H_2)(PCy_3)_2(CO)_3$ are never detected in solution at the same time. There is a qualitative increase in H_2 binding to **5** as compared to $W(H_2)(PCy_3)_2(CO)_3$.

Synthesis and Characterization of $[Re(PR_3)_2(CO)_3]B(Ar')_4$. In the solid state, $[Re(PCy_3)_2(CO)_3]B(Ar')_4$ exhibits a distorted octahedral structure in which a β C−H bond from one of the cyclohexyl rings is interacting with the electron-deficient metal center.[15] This structure is very similar to the reported structure of the neutral tungsten analog, $W(PCy_3)_2(CO)_3$, and is consistent with the observed agostic interaction of $W(PiPr_3)_2(CO)_3$.[10c] We have synthesized several other similar compounds of the general formula $Re(PR_3)_2(CO)_3^+$, where PR_3 = P*i*Pr$_3$, P*i*PrPh$_2$, and PPh_3, that have not been structurally characterized. We were interested in investigating the nature of this agostic complex in solution by NMR spectroscopy methods. Based on our reactivity studies, this complex has been observed to react with and coordinate a wide variety of small molecules in varying strengths.[17] Reaction of the agostic species with small molecules to give 18-electron complexes is accompanied by a dramatic color change. The agostic complex in methylene chloride solution is bright orange and forms dark orange crystals in the solid state. All of the 18-electron complexes studied thus far have been observed to be pale yellow or colorless in solution and in the solid state. Similar observations were made for $[Re(PR_3)_2(CNtBu)_3]^+$ and $W(PR_3)_2(CO)_3$: both are dark purple in solution and as solids, and the 18-electron complexes are yellow or colorless.

Since the acid that we have used in synthesizing all of the cationic rhenium complexes is an etherate salt, $[H(Et_2O)_2]B(Ar')_4$, we were interested in showing that the complex is not an ether adduct, considering the moderate to strong binding observed with H_2O and THF.[17] When analytically pure $[Re(PCy_3)_2(CO)_3]B(Ar')_4$ is placed in CD_2Cl_2 there are no resonances that can be associated with diethyl ether and no change to the other proton resonances is observed. The $^{31}P\{^1H\}$ NMR chemical shift is likewise invariant in the presence or absence of ether.

We have also searched for evidence of any interaction with the solvent, which in most of our studies is methylene chloride. There have been several recent reports on coordination of methylene chloride as well as complexes that oxidatively add CH_2Cl_2 through a C−Cl bond to give chloromethyl chloride complexes. There are three reports of isolable methylene chloride complexes that have been structurally characterized,[32] as well as others that have been identified only in solution.[33] Since the structure of $[Re(PCy_3)_2(CO)_3]B(Ar')_4$ which was crystallized from CH_2Cl_2/pentane did not contain any solvent of crystallization much less a coordinated CH_2Cl_2, we were interested in looking for evidence of a solvent interaction in solution. Gladysz and co-workers have shown that an errant peak in the $^{13}C\{^1H\}$ NMR spectrum of $[Cp^*Re(NO)(PPh_3)(ClCH_2Cl)]BF_4$ is associated with a bound CH_2Cl_2 and can be distinguished from the resonance for free CH_2Cl_2.[33a] We investigated the low temperature $^{13}C\{^1H\}$ NMR spectra of $[Re(PR_3)_2(CO)_3]B(Ar')_4$ (PR_3 = PCy_3 and P*i*PrPh$_2$) in CH_2Cl_2 and did not observe any peaks that could be attributed to bound solvent. The signals due to the CO ligands are identical with those reported for the room temperature spectrum. We also find that the ^1H and ^{13}C NMR resonances due to the $B(Ar')_4$ anion are entirely independent of the nature of the cation present.

The solid-state structure of **3a** indicates an interaction between the metal center and a pendant C−H bond of a single phosphine ligand. If the inequivalent phosphine ligands could be observed by solution $^{31}P\{^1H\}$ NMR spectroscopy, a spectrum with two different doublet resonances with a large J_{PP} should result. At room temperature only one phosphorus resonance for $[Re(PR_3)_2(CO)_3]B(Ar')_4$ (**3a**−**d**) was observed. It is likely that the agostic complexes are quite fluxional and exchange occurs between the

(32) (a) 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. (b) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970−1973. (c) Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831−11843.

(33) (a) Winter, C. H.; Gladysz, J. A. *J. Organomet. Chem.* **1988**, *354*, C33−C36. (b) Beck, W.; Schloter, K. *Z. Naturforsch.* **1978**, *33B*, 1214.

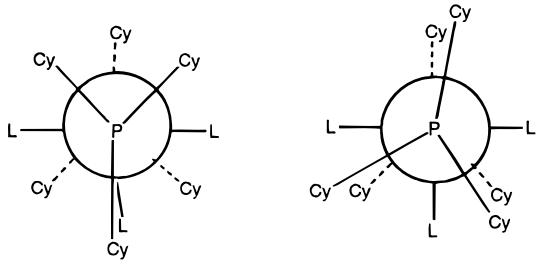
two phosphine ligands. If the limiting chemical shifts for the agostic proton and the adjacent carbon could be frozen out, the resonances would be expected to appear at higher field in the ^{1}H and ^{13}C{^{1}H} NMR than the other protons and carbons of the alkyl and aryl groups. The agostic hydrogen would have an intermediate chemical shift between the alkane CH bond and a metal hydride. No such resonances were detected in the ^{1}H and ^{13}C{^{1}H} NMR spectra at the lowest accessible temperatures. The ^{31}P{^{1}H} NMR spectra of **3b**−**d** did not show any change when cooled to the freezing point of methylene chloride.

In contrast, the ^{31}P{^{1}H} NMR spectrum for $[Re(PCy_3)_2(CO)_3]B(Ar')_4$ shows a dramatic change upon cooling. At room temperature, $[Re(PCy_3)_2(CO)_3]B(Ar')_4$ shows a single broad resonance at 27.6 ppm in CD_2Cl_2. The spectrum decoalesces at 240 K into an AB pattern and a broad resonance. The AB spectrum (δ = 42.2 and 32.1 ppm) shows a large coupling of 93 Hz, consistent with a species with inequivalent trans phosphines. The broad resonance that is observed at 24 ppm integrates as 50% of the spectrum. Our investigations of the analogous isonitrile chemistry led to similar observations for $[Re(PCy_3)_2(CNtBu)_3]^+$. The ^{31}P{^{1}H} NMR resonance at 26.4 ppm broadens when the temperature is lowered and decoalesces at 220 K into an AB pattern with a broad resonance. The AB resonances at 32.6 and 24.6 ppm show a large equivalent coupling (J_{pp} = 144 Hz) and the broad resonance at 25.5 ppm accounts for 50% of the spectrum. Decoalesence has not been observed in the ^{31}P{^{1}H} NMR spectra for $[Re(PR_3)_2(CO)_3]B(Ar')_4$ (PR_3 = P*i*Pr$_3$, P*i*PrPh$_2$, PPh$_3$) or $[Re(PPh_3)_2(CNtBu)_3]^+$.

Recent reports by Caulton and co-workers have also documented very similar observations in 5- and 6-coordinate Ru and Ir systems.[34] These complexes contain *trans* P*t*Bu$_2$Me ligands which have been observed to decoalesce into similar patterns at low temperature. Significantly, they have explained the appearance of an AB pattern as a rotational conformer in which the phosphines are still *trans* yet are inequivalent and another resonance as a conformer in which the phosphines are related by a mirror plane of symmetry. These conformers have been formed as a result of freezing out the rotation along the M−P single bond. Newman projections can show the two conformers that may account for the ^{31}P NMR spectrum in our systems. In the Ru and Ir systems the alkyl groups of the phosphine are not all the same; therefore, various rotamers are presented in which the R groups of the phosphines are eclipsed to one another. The rotamer in which the R groups are related by a plane of symmetry possesses equivalent phosphines, while the non-mirror-symmetric rotamer accounts for the inequivalent phosphines. With tricylcohexylphosphine it is necessary to consider a staggered conformation to explain the inequivalent phosphines.

A staggered orientation of the cyclohexyl groups of the phosphines would render them inequivalent as viewed in structure **A**. This would lead to the observation of two chemical shifts and large coupling between the inequivalent, mutually trans phosphines (AB pattern). Structure **B**, which shows an eclipsed pattern for the cyclohexyl groups, would have equivalent phosphines and corresponds to the broad resonance observed in the spectrum. These observations are also quite consistent with those of Kubas and co-workers for the low-temperature ^{31}P{^{1}H} NMR spectra of $M(PCy_3)_2(CO)_3$ (M = Mo, W).[35] Structures **A** and **B** have also been observed in X-ray crystal

Chart 1



Stucture A Structure B

structures. For the structures of the five-coordinate agostic complexes, $[Re(PCy_3)_2(CO)_3]B(Ar')_4$,[15] $W(PCy_3)_2(CO)_3$,[10c] and $W(PiPr_3)_2(CO)_3$,[10c] the phosphines are arranged in a staggered formation (structure **A**). For the structurally characterized six-coordinate species in this series; $ReCl(PCy_3)_2(CNtBu)_3$,[16] $[ReCl(PCy_3)_2(CNtBu)_3]OTf$,[16] $W(H_2)(PiPr_3)_2(CO)_3$,[1] and $W(OH_2)(PiPr_3)_2(CO)_3$,[10k] the alkyl groups of the phosphines are arranged in an eclipsed formation (structure **B**).

Several other complexes, $[ReL(PCy_3)_2(CNtBu)_3]^+$ (L = H_2, NH_3, C_2H_4) and $ReX(PCy_3)_2(CNtBu)_3$ (X = H, Cl, I),[16,17] have been investigated by low-temperature ^{31}P{^{1}H} NMR spectroscopy and shown to decoalesce into similar spectra. Interestingly, similar observations have not been made in the carbonyl system for $[ReL(PCy_3)_2(CO)_3]B(Ar')_4$ (L = N_2, NH_3, H_2, C_2H_4) and $ReCl(PCy_3)_2(CO)_3$.[17] Caulton and co-workers have shown that the size of the meridinal groups is a factor in the freezing out of the conformational isomers in addition to the bulkiness of the phosphines. The isonitrile ligands are considerably bulkier than the carbonyl ligands, which could explain why complexes with isonitrile coligands tend to decoalesce at higher temperatures. Also it is quite interesting that the decoalescence of the $[Re(PCy_3)_2(CO)_3]B(Ar')_4$ would occur at reasonable temperatures while it is unobserved for the 18-electron carbonyl complexes, $[ReL(PCy_3)_2(CO)_3]^+$ and $ReX(PCy_3)_2(CO)_3$, we have studied thus far in this system. This would indicate that the agostic interaction has some bearing upon increasing the barrier to rotation of the M−P bond. The reported $\Delta G^{\ddagger}_{240}$ (10.4 kcal/mol) for the decoalescence of the ^{31}P{^{1}H} NMR spectrum of $[Re(PCy_3)_2(CO)_3]B(Ar')_4$ does not directly reflect the strength of the agostic bond, as previously suggested.[15]

Conclusions

Several dihydrogen complexes have been synthesized by protonation of neutral methyl and hydride complexes of rhenium under H_2. The complexes have short H−H bonds as evidenced by the low T_{1min} values and large HD coupling constants. The thermal stability of the dihydrogen complexes as well as the agostic complexes that result from H_2 loss is attributed to the noncoordinating anion, $B(Ar')_4^-$.

Although $W(H_2)(PCy_3)_2(CO)_3$ is in equilibrium with a dihydride structure, the cationic analog $[Re(H_2)(PCy_3)_2(CO)_3]^+$ exclusively adopts the dihydrogen structure, in spite of a similar binding strength of H_2. The cationic complex is expected to backbond less to the σ^* of the dihydrogen ligand and compensates by a greater electrophillic interaction with the σ bond. Direct hydrogen binding studies between $[Re(H_2)(PCy_3)_2(CNtBu)_3]^+$ and $W(H_2)(PCy_3)_2(CO)_3$ as well as $[Re(H_2)(PCy_3)_2(CO)_3]^+$ show that the less π acidic CN*t*Bu ligands increase the H_2 binding strength by at least 4−5 kcal/mol. This effect is mainly attributed to a greater backbonding to the σ^* of the H_2 ligand.

Tricyclohexylphosphine complexes such as $[Re(L)(PCy_3)_2(CNtBu)_3]^+$ and $[Re(L)(PCy_3)_2(CO)_3]^+$ (L = agostic or other

(34) (a) Notheis, J. U.; Heyn, R. H.; Caulton, K. G. *Inorg. Chim. Acta* **1995**, *229*, 187−193. (b) Poulton, J. T.; Sigala, M. P.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1993**, *32*, 5490−5501. (c) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190−3191.

(35) Kubas, G. J. Personal communication, 1993.

ligands) exhibit complex $^{31}P\{^1H\}$ NMR spectra at low temperature as a result of hindered rotation about the Re−P bond. The bulkier isonitrile ligands contribute to a greater barrier to rotation compared to the carbonyl complexes. Similar complexes with PPh_3, P*i*PrPh$_2$, and P*i*Pr$_3$ ligands do not show hindered rotation at accessible temperatures.

Experimental Section

General Considerations. Due to the extreme air and moisture sensitivity of some of the organometallic products, manipulations were conducted with rigorous exclusion of air and water. Solid samples were handled and stored under argon in Vacuum Atmosphere or Braun inert-atmosphere boxes. Solution samples were handled by using standard vacuum line or Schlenk techniques. Chlorinated solvents were predried by distillation from P_2O_5 or CaH_2 under argon and stored under vacuum over activated silica gel (activated by heating at 320 °C under dynamic vacuum for 4 h) in glass vessels equipped with a Teflon needle valve. Hydrocarbon solvents were predried by distillation from Na/K alloy/benzophenone under argon and stored under vacuum over activated silica gel in glass vessels equipped with a Teflon needle valve. Deuterated solvents (Cambridge Isotope Labs) were dried and stored in a manner similar to their protio analogs. All solvents were subjected to 3 freeze−pump−thaw cycles and vacuum transferred immediately prior to use.

Reagent grade chemicals were used as received unless stated otherwise. $Re(CH_3)(CO)_5$ and $ReH(CO)_5$ were prepared from $Re_2(CO)_{10}$ (Strem) by using literature methods.[36,37] The synthesis and characterization of $[Re(PCy_3)_2(CNtBu)_3]^+$ (**4**), $[Re(H_2)(PCy_3)_2(CNtBu)_3]^+$ (**5**), $[Re(CO)_4(PPh_3)_2]^+$ (**6**), $[Re(CO)_4(PCy_3)_2]^+$ (**7**), and $[Re(CO)(PCy_3)_2(CNtBu)_3]^+$ (**8**) have been reported separately.[16,17] $W(PCy_3)_2(CO)_3$ was prepared by a published procedure.[10r] PCy_3 (Strem) was recrystallized from ethanol, P*i*PrPh$_2$ and PPh_3 (Aldrich) were used as received, and P*i*Pr$_3$ (Strem) was degassed and stored under argon. $[H(Et_2O)_2]B(Ar')_4$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) was prepared by the method of Brookhart.[13] Hydrogen (Airco, 99.999%) and deuterium (Cambridge, 99.8%) were used as received.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AC-200 (200.133 MHz ^1H, 81.015 MHz ^{31}P), AF-300 (300.117 MHz ^1H, 75.465 MHz ^{13}C) and WM-500 (500.136 MHz ^1H) spectrometers equipped with B-VT 1000 temperature controller modules with copper−constantan thermocouples. Temperature calibration was accomplished following the Van Geet methanol calibration method.[38] ^1H and ^{13}C NMR chemical shifts (δ) are referenced to the internal residual proton or natural abundance ^{13}C resonances of the deuterated solvent relative to TMS. $^{31}P\{^1H\}$ NMR chemical shifts (δ) are reported in parts per million relative to 85% H_3PO_4 (external standard). All NMR tube reactions were conducted in flame-sealed tubes or J. Young screw-cap tubes. T_1 measurements were performed on a Bruker WM-500 spectrometer, using a standard 180°−τ−90° inversion−recovery pulse sequence.

The ^1H and $^{13}C\{^1H\}$ resonances for $B(Ar')_4^-$ are identical with those reported for complex **2a** and have been omitted from the spectral characterization of subsequent complexes.

Infrared spectra were recorded on a Perkin Elmer 1600 series FT spectrophotometer as Nujol mulls or in solution. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and Canadian Microanalytical Service Ltd., Delta, BC.

Synthesis of Neutral Methyl and Hydride Complexes (1a−f). A thick-walled glass vessel, equipped with a Kontes valve, was charged with 20 mL of toluene, $Re(CH_3)(CO)_5$ (500 mg, 1.46 mmol) or $ReH(CO)_5$ (0.2 mL, 1.40 mmol), and 3 equiv of phosphine. The solution was cooled to −78 °C, evacuated, and warmed to room temperature and the procedure was repeated twice. The solution was heated at 130 °C for 50 to 140 h and evacuated every 12 h to remove CO gas generated during the reaction. In most cases, the toluene was removed *in vacuo* and the resulting yellow residue was washed with pentane to give a white solid. Complex **1b** was considerably more soluble and was carefully precipitated from a minimum amount of pentane at −40 °C. Further recrystallizations from pentane gave "analytically pure" solid that was free from $ReH(PiPr_3)_2(CO)_3$.

***trans-mer*-Re(CH$_3$)(PCy$_3$)$_2$(CO)$_3$ (1a)**: Yield 53%. ^1H NMR (C_6D_6) δ −0.05 (t, $^3J_{PH}$ = 6.0 Hz, 3 H, Re-C*H*$_3$); 0.9 to 2.5 (m, 66 H, PC*y*$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 10.2 (s).

***trans-mer*-Re(CH$_3$)(P*i*Pr$_3$)$_2$(CO)$_3$ (1b)**: Yield 65%. ^1H NMR (C_6D_6) δ −0.12 (t, $^3J_{PH}$ = 5.9 Hz, 3H, ReC*H*$_3$); 1.17 (dd, $^3J_{PH}$ = 12.9 Hz, $^3J_{HH}$ = 7.0 Hz, 36H, P(CH(C*H*$_3$)$_2$)$_3$); 2.31 (m, 6H, P(C*H*(CH$_3$)$_2$)$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6) δ −30.0 (t, $^2J_{PC}$ = 7.3 Hz, Re*C*H$_3$); 19.7 (s, P(CH(*C*H$_3$)$_2$)$_3$); 26.7 (t, AXX′, $J_{PC} + J_{P'C}$ = 11.4 Hz, P(*C*H(CH$_3$)$_2$)$_3$); 197.3 (t, J_{PC} = 7.2 Hz, *CO*); 203.8 (t, J_{PC} = 8.8 Hz, *CO*). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 19.9 (s). IR (cm^{-1}, Nujol, ν_{CO}): 2004 (w), 1902 (s), 1866 (m). Anal. Calcd (found): C, 43.62 (43.19); H, 7.49 (7.21).

***trans-mer*-Re(CH$_3$)(P*i*PrPh$_2$)$_2$(CO)$_3$ (1c)**: Yield 53%. ^1H NMR ($CDCl_3$) δ −1.12 (t, $^3J_{PH}$ = 6.6 Hz, 3H, ReC*H*$_3$); 1.11 (dd, $^3J_{PH}$ = 14.9 Hz, $^3J_{HH}$ = 7.0 Hz, 12H, P(CH(C*H*$_3$)$_2$)Ph$_2$); 2.91 (sept, $^3J_{HH}$ = 7.0 Hz, 2H, P(C*H*(CH$_3$)$_2$)Ph$_2$); 7.38 (m, 12H, P*i*Pr*Ph*$_2$ meta and para); 7.51 (m, 8H, P*i*Pr*Ph*$_2$ ortho). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −25.7 (t, $^2J_{PC}$ = 6.6 Hz, Re*C*H$_3$); 19.5 (s, P(CH(*C*H$_3$)$_2$)Ph$_2$); 28.9 (t, AXX′, $J_{PC} + J_{P'C}$ = 14.0 Hz, P(*C*H(CH$_3$)$_2$)Ph$_2$); 129.0 (vt, J_{PC} = 4.3 Hz, P*i*Pr*Ph*$_2$ ortho or meta); 130.6 (P*i*Pr*Ph*$_2$para); 134.4 (t, AXX′, $J_{PC} + J_{P'C}$ = 20.9 Hz, P*i*Pr*Ph*$_2$ ipso); 134.7 (vt, J_{PC} = 4.8 Hz, P*i*Pr*Ph*$_2$ ortho or meta); 197.1 (t, $^2J_{PC}$ = 6.7 Hz, *C*O trans to CH$_3$); 200.4 (t, $^2J_{PC}$ = 9.0 Hz, *C*O cis to CH$_3$). $^{31}P\{^1H\}$NMR ($CDCl_3$) δ 19.7 (s). IR (cm^{-1}, CH_2Cl_2, ν_{CO}): 2023 (w), 1916 (s), 1872 (m).

***trans-mer*-Re(CH$_3$)(PPh$_3$)$_2$(CO)$_3$ (1d)**: Yield 90%. ^1H NMR ($CDCl_3$) δ −1.06 (t, $^3J_{PH}$ = 6.7 Hz, 3H, Re-C*H*$_3$); 7.29 (m, 18H, P*Ph*$_3$ meta and para); 7.49 (m, 12H, P*Ph*$_3$ ortho). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −22.3 (t, $^2J_{PC}$ = 6.3 Hz, Re-*C*H$_3$); 128.0 (vt, J_{PC} = 4.5 Hz, P*Ph*$_3$ ortho or meta); 129.6 (s, P*Ph*$_3$ para); 133.6 (vt, J_{PC} = 5.6 Hz, P*Ph*$_3$ ortho or meta); 135.3 (t, AXX′, $J_{PC} + J_{P'C}$ = 23.2 Hz, P*Ph*$_3$ ipso); 195.4 (br,*C*O trans to CH$_3$); 199.0 (t, $^2J_{PC}$ = 9.3 Hz, *C*O cis to CH$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 16.8 (s). IR (cm^{-1}, CH_2Cl_2, ν_{CO}): 2023 (w), 1916 (s), 1872 (m).

***trans-mer*-Re(H)(P*i*PrPh$_2$)$_2$(CO)$_3$ (1e)**: Yield 75%. ^1H NMR (C_6D_6) δ −5.55 (t, $^2J_{HP}$ = 18.8 Hz, Re-*H*); 1.08 (dd, $^3J_{PH}$ = 16.2 Hz, $^3J_{HH}$ = 6.9 Hz, P(CH(C*H*$_3$)$_2$)Ph$_2$); 2.61 (m, P(C*H*(CH$_3$)$_2$Ph$_2$); 6.94 (m, P*i*Pr*Ph*$_2$ meta and para); 7.74 (m, P*i*Pr*Ph*$_2$ ortho). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 18.6 (s, P(CH(*C*H$_3$)$_2$)Ph$_2$); 29.4 (t, AXX′, $J_{PC} + J_{P'C}$ = 15.6 Hz, P(*C*H(CH$_3$)$_2$)Ph$_2$); 128.2 (s, P*i*Pr*Ph*$_2$ ortho or meta); 129.7 (s, P*i*Pr*Ph*$_2$ para); 133.3 (s, P*i*Pr*Ph*$_2$ ortho or meta); 137.0 (t, AXX′, $J_{PC} + J_{P'C}$ = 20.8 Hz, P*i*Pr*Ph*$_2$ ipso); 177.8 (m, CO trans to H); 179.1 (m, CO cis to H). $^{31}P\{^1H\}$ NMR (C_6D_6): 29.6 (s). IR (cm^{-1}, CH_2Cl_2, ν_{CO}): 2020 (w), 1919 (s).

***trans-mer*-Re(H)(PPh$_3$)$_2$(CO)$_3$ (1f)**: Yield 77%. ^1H NMR (C_6D_6) δ −4.45 (t, $^2J_{PH}$ = 17.8 Hz, Re-*H*); 7.03 (m, P*Ph*$_3$ meta and para); 7.84 (m, P*Ph*$_3$ ortho). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 22.8 (s). IR (cm^{-1}, CH_2Cl_2, ν_{CO}): 2020 (w), 1925 (s).

[*trans-mer*-Re(H$_2$)(PCy$_3$)$_2$(CO)$_3$]B(Ar′)$_4$ (2a). A small glass vessel with an 8 mm Kontes tap was charged with $Re(CH_3)(PCy_3)_2(CO)_3$ (200 mg, 0.236 mmol) and $[H(Et_2O)_2]B(Ar')_4$ (239 mg, 0.236 mmol). Methylene chloride (4 mL) was vacuum transferred to the vessel, and the solution was warmed to room temperature with stirring under an atmosphere of H_2 for 1 h. The solvent volume was reduced by half, and 8 mL of pentane was transferred to the solution. The solution was warmed to room temperature under a H_2 atmosphere, and a yellow precipitate formed immediately. After being stirred for 45 min, the solvent was removed via cannula under a H_2 flow. The solid was briefly placed under dynamic vacuum and then dried under a H_2 atmosphere. The dihydrogen complex was recovered in 73% yield (292 mg) and stored in a sealed ampule under a slight H_2 atmosphere. ^1H NMR (CD_2Cl_2) δ −4.75 (br, 2H); 1.30−1.95 (br, 60H); 2.16 (br, 6H); 7.57 (s, 4H, B(Ar′)$_4$ para); 7.73 (s, 8H, B(Ar′)$_4$ ortho). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 26.3 (s, P-δ-*C*); 27.6 (t, J_{PC} = 4.8 Hz, P-β-*C*); 30.6 (s, P-γ-*C*); 37.8 (t, J_{PC} = 12.4 Hz, P-α-*C*); 117.9 (s, B(Ar′)$_4$*p*-*C*); 125.0 (q, J_{CF} = 272 Hz, B(Ar′)$_4$ *C*F$_3$); 129.2 (q, J_{CF} = 32 Hz, B(Ar′)$_4$*m*-*C*); 135.2 (s, B(Ar′)$_4$*o*-*C*); 162.1 (q, J_{BC} = 50 Hz, B(Ar′)$_4$*i*-*C*); 189.2 (t, J_{PC} = 7.0 Hz, *C*O); 192.9 (t, J_{PC} = 5.5 Hz, *C*O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 23.9 (s). IR (cm^{-1}, CH_2Cl_2, ν_{CO}): 2069 (w), 1969 (s), 1944 (m).

[*trans-mer*-Re(H$_2$)(P*i*Pr$_3$)$_2$(CO)$_3$]B(Ar′)$_4$ (2b). A small glass vessel with an 8-mm Kontes tap was charged with $Re(CH_3)(PiPr_3)_2(CO)_3$ (75 mg, 0.124 mmol) and $[H(Et_2O)_2]B(Ar')_4$ (125 mg, 0.123 mmol).

(36) Beck, W.; Raab, K. *Inorg. Synth.* **1989**, *26*, 107−108.
(37) Urbancic, M. A.; Shapley, J. R. *Inorg. Synth.* **1989**, *26*, 77−80.
(38) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679−680.

Methylene chloride (3 mL) was vacuum transferred to the vessel, and the solution was warmed to room temperature with stirring under an atmosphere of H_2 for 10 min. The solvent volume was reduced slightly, and 3 mL of pentane was transferred to the solution. The solution was warmed to room temperature under a H_2 atmosphere and the pentane diffused slowly over an hour to form a white microcrystalline solid. The dihydrogen complex was dried under a H_2 flow and recovered in 89% yield (159 mg). ^{1}H NMR (CD_2Cl_2) δ −4.97 (br, 2H); 1.31 (m, J_{HH} = 7.0 Hz, 36H, P(CH(CH_3)$_2$)$_3$); 2.49 (m, J_{HH} = 7.0 Hz, 6H, P(CH(CH$_3$)$_2$)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 19.9 (s, P(CH(*C*H$_3$)$_2$)$_3$); 28.3 (t, J_{PC} = 13.3 Hz, P(*C*H(CH$_3$)$_2$)$_3$); 188.7 (br, *C*O); 192.0 (br, *C*O). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 32.5 (s). IR (cm^{-1}, CH_2Cl_2, ν_{CO}) 2073 (w), 1974 (s), 1950 (m).

[*trans-mer*-Re(H$_2$)(P*i*PrPh$_2$)$_2$(CO)$_3$]B(Ar′)$_4$ (2c). A screw-cap NMR tube was charged with Re(CH$_3$)(P*i*PrPh$_2$)(CO)$_3$ (10 mg, 0.013 mmol) and [H(Et$_2$O)$_2$]B(Ar′)$_4$ (13 mg, 0.013 mmol). CD_2Cl_2 (0.5 mL) was vacuum transferred to the tube. The solution was frozen, and the headspace was evacuated and replaced with an atmosphere of H_2. ^{1}H NMR (CD_2Cl_2) δ −4.26 (Re*H*$_2$); 1.17 (m, P(CH(C*H*$_3$)$_2$)Ph$_2$); 3.04 (m, P(C*H*(CH$_3$)$_2$)Ph$_2$); 7.55 and 7.73 (m, PiPr*Ph*$_2$ and B(Ar′)$_4$). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 14.7 (s).

[*trans-mer*-Re(H$_2$)(PPh$_3$)$_2$(CO)$_3$]B(Ar′)$_4$ (2d). A screw-cap NMR tube was charged with Re(CH$_3$)(PPh$_3$)$_2$(CO)$_3$ (10 mg, 0.013 mmol) and [H(Et$_2$O)$_2$]B(Ar′)$_4$ (13 mg, 0.013 mmol). CD_2Cl_2 (0.5 mL) was vacuum transferred to the tube. The solution was frozen, and the headspace was evacuated and replaced with an atmosphere of H_2. ^{1}H NMR (CD_2Cl_2) δ −3.8 (br s, Re*H*$_2$); 6.7 to 8.0 (m, P*Ph*$_3$ and B(Ar′)$_4$). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 8.1 (s).

Reactivity of [Re(H$_2$)(PCy$_3$)$_2$(CO)$_3$]B(Ar′)$_4$ (2a) with Base: Formation of ReH(PCy$_3$)$_2$(CO)$_3$. In a typical reaction, **2a** (10 mg, 0.006 mmol) with 2,6-di-*tert*-butyl-4-methylpyridine (2 mg, 0.010 mmol) was added to a sealable NMR tube attached to a 4-mm Kontes valve. Methylene chloride-d_2 (0.5 mL) was vacuum transferred to the tube and placed under H_2 (400 Torr) before sealing. The solution immediately turned colorless. ^{1}H and ^{31}P{^{1}H} NMR indicate clean formation of ReH(PCy$_3$)$_2$(CO)$_3$ in addition to the appropriate resonances due to protonated base. ^{1}H NMR (CD_2Cl_2) δ −6.66 (t, J_{PH} = 20.5 Hz, 2H); 1.1−2.1 (br, 66H). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 30.6 (s).

[*trans-mer*-Re(PCy$_3$)$_2$(CO)$_3$]B(Ar′)$_4$ (3a). A 10-mL round bottom flask was charged with Re(CH$_3$)(PCy$_3$)$_2$(CO)$_3$ (113 mg, 0.133 mmol) and [H(Et$_2$O)$_2$]B(Ar′)$_4$ (132 mg, 0.131 mmol) and attached to a swivel frit apparatus. The swivel frit was attached to a vacuum line and 3 mL of CH_2Cl_2 was vacuum transferred at −78 °C. The solution was warmed to room temperature and stirred for 15 min. The solvent was removed *in vacuo*, and the solid was placed under dynamic vacuum for 1 h. The addition and removal of CH_2Cl_2 was repeated. Methylene chloride (1 mL) was vacuum transferred to the solid followed by 3 mL of pentane. An orange crystalline solid, which formed upon mixing, was filtered and washed with 5 mL of pentane. The solid was collected in 85% yield (115 mg) and stored in a sealed ampule under vacuum. ^{1}H NMR (CD_2Cl_2) δ 1.30−1.75 (br, 60H); 2.53 (br, 6H). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 26.1 (s, P-δ-*C*); 27.8 (br, P-β-*C*); 29.7 (s, P-γ-*C*); 39.1 (t, J_{PC} = 11.0 Hz, P-α-*C*); 190.0 (t, J_{PC} = 5.5 Hz, *C*O); 198.9 (t, J_{PC} = 7.3 Hz, *C*O). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 27.2 (s). IR (cm^{-1}, Nujol, ν_{CO}) 2061 (w), 1966 (s), 1939 (m). Anal. Calcd (found): C, 50.33 (50.38); H, 4.64 (4.79).

[*trans-mer*-Re(P*i*Pr$_3$)$_2$(CO)$_3$]B(Ar′)$_4$ (3b). A 10-mL round bottom flask was charged with Re(CH$_3$)(P*i*Pr$_3$)$_2$(CO)$_3$ (71 mg, 0.117 mmol) and [H(Et$_2$O)$_2$]B(Ar′)$_4$ (132 mg, 0.131 mmol) and attached to a swivel frit apparatus. The swivel frit was attached to a vacuum line and 5 mL of CH_2Cl_2 was vacuum transferred at −78 °C. The solution was warmed to room temperature and stirred for 5 min. The solvent was removed *in vacuo*, and the solid was placed under dynamic vacuum for 30 min. The addition and removal of CH_2Cl_2 was repeated followed by drying under vacuum for 1 h. Methylene chloride (3 mL) was vacuum transferred to the solid followed by 5 mL of pentane. Orange needles were formed as the pentane diffused into the solution over 2 h at room temperature. The solid was filtered and washed with 2 × 3 mL of cold pentane. The solid was dried under vacuum for 2 h and isolated in 62% yield (106 mg). ^{1}H NMR (CD_2Cl_2) δ 1.17 (m, J_{HH} = 7.0 Hz, 36H, P(CH(C*H*$_3$)$_2$)$_3$); 2.76 (m, J_{HH} = 7.0 Hz, 6H, P(C*H*(CH$_3$)$_2$)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 18.6 (s, P(CH(*C*H$_3$)$_2$)$_3$); 29.5 (t, J_{PC} = 11 Hz, P(*C*H(CH$_3$)$_2$)$_3$); 189.8 (br, *C*O); 197.8 (t, J_{PC} = 8.0 Hz, *C*O). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 32.2 (s). IR (cm^{-1}, Nujol, ν_{CO}) 2064 (w), 1969 (s), 1950 (m). Anal. Calcd (found): C, 43.62 (43.19); H, 7.49 (7.21).

[*trans-mer*-Re(P*i*PrPh$_2$)$_2$(CO)$_3$]B(Ar′)$_4$ (3c). A sealable NMR tube was charged with Re(CH$_3$)(P*i*PrPh$_2$)$_2$(CO)$_3$ (15 mg, 0.020 mmol) and [H(Et$_2$O)$_2$]B(Ar′)$_4$ (20 mg, 0.020 mmol). A 1 mL portion of CH_2Cl_2 was vacuum transferred to the tube and removed *in vacuo* to remove excess ether from the solution. A 0.5-mL portion of CD_2Cl_2 was vacuum transferred to the tube. The sample was degassed by 3 freeze−pump−thaw cycles before sealing the tube. ^{1}H NMR (CD_2Cl_2) δ 1.17 (m, P(CH(C*H*$_3$)$_2$)Ph$_2$); 3.04 (m, P(C*H*(CH$_3$)$_2$)Ph$_2$); 7.55 and 7.73 (m, PiPr*Ph*$_2$ and B(Ar′)$_4$). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 20.9 (s).

[*trans-mer*-Re(PPh$_3$)$_2$(CO)$_3$]B(Ar′)$_4$ (3d). A sealable NMR tube was charged with Re(CH$_3$)(PPh$_3$)$_2$(CO)$_3$ (15 mg, 0.018 mmol) and [H(Et$_2$O)$_2$]B(Ar′)$_4$ (19 mg, 0.019 mmol). A 1-mL portion of CH_2Cl_2 was vacuum transferred to the tube and removed *in vacuo* to remove excess ether from the solution. A 0.5-mL portion of CD_2Cl_2 was vacuum transferred to the tube. The sample was degassed by 3 freeze−pump−thaw cycles before the tube was sealed. ^{1}H NMR (CD_2Cl_2) δ 6.7 to 8.0 (m, P*Ph*$_3$ and B(Ar′)$_4$). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 14.6 (s).

Acknowledgment. We thank the Department of Energy, Office of Basic Energy Science, for support of this research. We are grateful to Greg Kubas and Ken Caulton for helpful discussions.

JA9643228