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Highly Electrophilic $[Re(CO)_4(PR_3)]^+$ Center Binds Et_2O and CH_2Cl_2 and Heterolytically Activates H_2

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The activation of H_2 by transition-metal complexes is an important step in many chemical processes, and the study of η^2-H_2 complexes has provided valuable insight into the activation of H−X (X = H, Si, C) bonds in general.[1] Metal−H_2 binding is governed by both σ-donation from H_2 to metal and π-back-bonding from metal to H_2. The relative strengths of each bonding component has been quantified theoretically and is dependent on the electronic nature of the ancillary ligands.[1g−i] We are currently interested in synthesizing new *extremely* electrophilic cationic systems containing mainly π-acceptor ligands that enhance σ-donation from H_2 to metal at the expense of back-donation. Such species increase the acidity of coordinated H_2 and potentially other σ-ligands such as alkanes, thus promoting heterolytic activation via known deprotonation pathways.[1b−d,2] Although many organometallic Lewis acid fragments are known,[3] complexes containing only one donor ligand and *four* electron-withdrawing carbonyls that bind H_2 at or near ambient temperature are unknown. In this paper, we report such a cationic Re fragment, $[Re(CO)_4(PR_3)][BAr_f]$, that binds and heterolytically activates H_2, as well as coordinates weak bases.

Protonation of the Re(I) methyl complexes [*cis*-$Re(Me)(CO)_4(PR_3)$] (R = Ph (**1a**),[4] Cy (cyclohexyl, **1b**)[5]) with $[H(OEt_2)_2][BAr_f]$[6] ($BAr_f = B[3,5\text{-}C_6H_3(CF_3)_2]_4^-$) in Et_2O proceed with the elimination of methane to afford [*cis*-$Re(CO)_4(PR_3)(OEt_2)][BAr_f]$ (R = Ph, 98% yield (**2a**); Cy, 89% yield (**2b**)).[7] These complexes form even in CH_2Cl_2 (crystallize on hexane addition) where the acid is the ether source and are soluble in halogenated solvents such as CH_2Cl_2 and C_6H_5F. Although some Et_2O complexes have been characterized spectroscopically such as [*trans*-$Pt(H)(P^iPr_3)_2(OEt_2)][BAr_f]$ and $[CpRe(NO)(PPh_3)(OEt_2)][BF_4]$,[8] few have been characterized crystallographically (none for Re). X-ray analysis of **2a** showed Et_2O in an octahedral position cis to PPh_3 and no unusual contacts with the BAr_f anion (Figure 1).[9] The Re−O distance is 2.254(11) Å, and the ether C−O−C angle is 113.9(13)°, typical of other M−OEt_2 structures.[10]

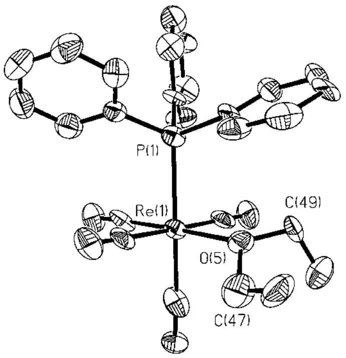

Figure 1. ORTEP of **2a** with 50% probability ellipsoids: Re(1)−P(1), 2.504(2) Å; C(49)−O(5)−Re(1), 119.3(9)°; C(47)−O(5)−Re(1), 116.7(9)°.

The Et_2O in **2** is bound strongly in the solid, and the ratio of BAr_f/OEt_2 did not decrease after exposing the complexes to vacuum for 12 h. For **2a** in CD_2Cl_2 at −73 °C, resonances at 3.53 (q) and 0.98 (t) ppm in the ^1H NMR spectrum are assigned to the CH_2 and CH_3 groups of coordinated Et_2O (resonances for free Et_2O at this temperature are 3.34 (q) and 1.08 (t)).[8a] Upon warming the CD_2Cl_2 solution of **2a** to room temperature, dissociation and exchange of the Et_2O was observed. However, the Et_2O could not be completely removed by recrystallization from CH_2Cl_2/hexanes, and decomposition products formed upon prolonged dissolution in CH_2Cl_2. The bound Et_2O was easily displaced in CH_2Cl_2 solution by more basic ligands such as H_2O or THF.[11]

To obtain the ether-free derivatives of **2**, methyl abstraction from **1** was carried out by reaction with $[Ph_3C][BAr_f]$[12] in CH_2Cl_2 solution. However, instead of producing coordinatively unsaturated or agostic complexes, the CH_2Cl_2 adducts [*cis*-$Re(CO)_4(PR_3)(CH_2Cl_2)][BAr_f]$ (R = Ph, 81% yield, (**3a**); Cy, 80% yield, (**3b**))[13] were formed. They are moderately air stable in solid and solution, although the coordinated CH_2Cl_2 is quickly replaced by adventitious water. CH_2Cl_2 solutions decompose at room temperature within days to form chloride-bridged dimers {[*cis*-$Re(CO)_4(PR_3)]_2(\mu\text{-}Cl)\}\{BAr_f\}$.[14] The fact that the Et_2O and CH_2Cl_2 complexes are isolable is attributed to the strong electrophilicity of the $[Re(CO)_4(PR_3)]^+$ fragment. This is in direct contrast to Heinekey's analogous bis-phosphine complexes, [*mer*-$Re(CO)_3(PR_3)_2][BAr_f]$, which are isolated as the *agostic* compounds in CH_2Cl_2.[15] Furthermore, the importance of a noninteracting counterion is reflected by the existence of anion-coordinated derivatives *cis*-$Re(CO)_4(PPh_3)(FBF_3)$ and *cis*-$Re(CO)_4(PPh_3)(OTeF_5)$.[16]

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[1] Reviews: (a) Schneider, J. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1068. (b) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (c) Morris, R. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1992**, *32*, 789. (e) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. See also: (f) Butts, M. D.; Kubas, G. J.; Luo, X.-L.; Bryan J. C. *Inorg. Chem.* **1997**, *36*, 3341. (g) Li, J.; Dickson, R. M.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 11482. (h) Li, J.; Ziegler, T. *Organometallics* **1996**, *15*, 3844. (i) Dapprich, S.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 354.

[2] (a) Rocchini, E.; Mezzetti, A.; Rugger, H.; Burckhardt, U.; Gramlich, V.; Zotto, A. D.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711. (b) For a review of heterolytic H_2 activation, see: Brothers, P. J. *Prog. Inorg. Chem.* **1981**, *28*, 1.

[3] See, for example: Beck, W.; Sunkel, K. *Chem. Rev.* **1988**, *88*, 1405.

[4] McKinney, R. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3066.

[5] [*cis*-$Re(CO)_4(PCy_3)Cl$] was isolated from the reaction of $Re(CO)_5Cl$ and 1 equiv of PCy_3 in refluxing $CHCl_3$. Recrystallization from cyclohexane gave white microcrystals (85%) used to prepare **1b** as a white solid (48%) by reaction with MeLi in Et_2O and chromatography (SiO_2/hexanes).

[6] Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

[7] Data for **2a**: IR (cm^{-1}, Nujol, ν_{CO}) 2118 (m), 2035 (s), 2010 (s), 1988 (s); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −73 °C) δ 16.2; Anal. Calcd for $C_{58}H_{37}BF_{24}O_5PRe$: C, 46.51; H, 2.49. Found: C, 46.40; H, 2.36.

[8] (a) Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831. (b) Agbossou, S. K.; Fernández, J. M.; Gladysz, J. A. *Inorg. Chem.* **1990**, *29*, 476.

[9] Crystal data for **2a**: monoclinic, $P2_1/c$, $a = 12.567(3)$ Å, $b = 25.370(4)$ Å, $c = 18.999(3)$ Å, $\beta = 105.28(2)°$, $V = 5843(2)$ Å^3, $Z = 4$, R1 = 0.0700 and wR2 = 0.1313, GOF = 0.981, colorless plates from Et_2O/hexane.

[10] (a) Yi, C. S.; Wodka, D.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 2. (b) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436. (c) Solari, E.; Musso, F.; Gallo, E.; Floriani, C.; R, N.; Chiese-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 2265.

[11] Addition of hexanes to a CH_2Cl_2 solution of **2a** and 5 equiv of THF provided [*cis*-$Re(CO)_4(PPh_3)(THF)][BAr_f]$ in 91% yield.

[12] Bahr, S. R.; Boudjouk *J. Org. Chem.* **1992**, *57*, 5545. Ph_3CCl was used in place of $Ph_3C(OTf)$.

[13] Data for **3a**: IR (cm^{-1}, Nujol, ν_{CO}) 2122 (m), 2051, 2041, 2033, 2019, 2008, 1987 (s, overlapping); ^1H NMR (CD_2Cl_2) δ 5.33 (s, 2H, CH_2Cl_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 11.1; Anal. Calcd for $C_{55}H_{29}BCl_2F_{24}PO_4Re$: C, 43.79; H, 1.94. Found: C, 44.15; H, 1.75.

[14] Identified by crystallography as the major components from CH_2Cl_2/hexanes solutions of **3a** or **3b** after 2 weeks at −30 °C. Manuscript in preparation.

[15] Heinekey, D. M.; Radzewich, C. E.; Voges, M. H.; Schomber, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 4172.

[16] (a) Cheng, T. Y.; Bullock, R. M.*Organometallics* **1995**, *14*, 4031. (b) Beck, W.; Schweiger, M. *Z. Anorg. Allg. Chem.* **1991**, *595*, 203. (c) Brewer, S. T.; Buggey, L. A.; Holloway, J. H.; Hope, E. G. *J. Chem. Soc., Dalton Trans.* **1995**, 2941.

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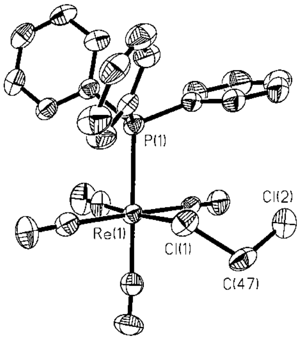

Figure 2. ORTEP of **3a** with 50% probability ellipsoids: Re(1)−P(1), 2.500(2) Å; Cl(1)−C(47), 1.817(6) Å; Cl(2)−C(47), 1.716(6) Å; Re(1)−Cl(1)−C(47), 112.1(2)°; Cl(1)−C(47)−Cl(2), 112.0(3)°.

The bound CH_2Cl_2 in **3** exchanges rapidly on the NMR time scale in CD_2Cl_2 solution at room temperature and is not distinguishable from free CH_2Cl_2. However, the coordinated CH_2Cl_2 is readily observed in the $^{13}C\{^1H\}$ NMR spectra in CH_2Cl_2 solution at −90 °C as singlets at 66.36 ppm for **3a** and 67.62 ppm for **3b**. These peaks are shifted downfield from that of free CH_2Cl_2 (54.00 ppm) at this temperature and are not present in the ^{13}C NMR spectra at room temperature. In the proton-coupled ^{13}C NMR spectra, the peaks at 66.36 and 66.62 ppm split into triplets with $J_{CH} = 184.3$ and 186.5 Hz for **3a** and **3b**, respectively, confirming that these peaks are indeed due to coordinated dichloromethane ($J_{CH} = 179.3$ Hz for free CH_2Cl_2 at −90 °C). These peaks are absent in the analogous NMR experiments performed in CD_2Cl_2 at −90 °C as a result of peak broadening from deuterium coupling. The observations in the ^{13}C NMR spectra are analogous to those reported for $[CpRe(NO)(PPh_3)(CH_2Cl_2)][BF_4]$.[17]

Although dichloromethane has been traditionally thought of as a noncoordinating solvent, the isolation of stable CH_2Cl_2 complexes has been a recurring theme in recent literature,[8a,17,18] particularly for extremely electron-deficient cationic metal centers with low-interacting anions. From crystallographic evidence, CH_2Cl_2 coordinates either monodentate, as in $[Cp^*Ir(PMe_3)(CH_3)(CH_2Cl_2)][BAr_f]$[18c] and [*trans*-$PtH(P^iPr_3)_2(CH_2Cl_2)][BAr_f]$,[8a] or bidentate, as in $[RuH(CO)(P^tBu_2Me)_2(CH_2Cl_2)][BAr_f]$.[18a] To verify the coordination mode in **3a**, an X-ray structure was determined (Figure 2),[19] and the CH_2Cl_2 is monodentate. The M−Cl distance is 2.546(2) Å, somewhat longer than that reported for η^1-CH_2Cl_2 complexes of Ir (2.462(3) Å)[18c] and Pt (2.489(4) Å).[8a] The Re−Cl distances in related Re(I) and Re(II) chloride complexes, $[ReCl(CN^tBu)_3(PCy_3)_2]^n$, are 2.596(2) and 2.412(5) Å for $n = 0, 1$.[20] The C−Cl bond length of the Re-bound chloride is slightly longer than that of the noncoordinated chloride. The Re−C distance for CO trans to CH_2Cl_2 (1.887(6) Å) is significantly shorter than that for CO trans to PPh_3 (1.966(6) Å).

Despite the lability of CH_2Cl_2 in **3** in CD_2Cl_2 solution, no peaks attributable to the expected η^2-H_2 complexes were observed in ^1H NMR spectra taken at −80 to 20 °C on these solutions under H_2. Similarly, no evidence for N_2 binding was seen at 20 °C. However, when solutions of **3** in noncoordinating C_6D_5F were placed under 3 atm of H_2, broad resonances integrating to two protons were observed in ^1H NMR spectra (20 °C) at −4.69 ppm for [*cis*-$Re(CO)_4(PPh_3)(H_2)][BAr_f]$ (**4a**) and −5.12 ppm for the PCy_3 analogue (**4b**). The resonance for free H_2 was broad at 25 °C for both complexes, indicating exchange with coordinated H_2. The addition of H_2 was completely reversible. Complex **4** could not be isolated due to loss of H_2 and decomposition in C_6H_5F solutions. To verify that these resonances were due to H_2 rather than dihydride ligands, **3** was reacted with HD in C_6D_5F, and J_{HD} values of the resulting upfield triplets were measured to be 33.9 and 33.8 Hz for **4a** and **4b**, respectively. The high J_{HD} observed for these complexes is consistent with those observed in other electrophilic cationic $M(H_2)$ systems[21] and suggests a short H−H distance (0.87 Å calculated from J_{HD}[22]) and a bonding picture in which the metal−H_2 σ-interaction is enhanced relative to back-bonding.[1f,21a,b]

Electrophilic transition metals have been shown to greatly raise the acidity of η^2-coordinated H_2.[1b,c,2] The pK_a values of H_2 complexes have been measured over a range of approximately −3 to +17 for monocationic complexes, and as low as −6 for dicationic Ru, Os,[2a] and Fe[21b] complexes. In nearly all cases, however, such highly acidic H_2 ligands are generated by protonation of a hydride ligand with a strong acid rather than from H_2 *gas* as for **4**, a crucial distinction. Although the ^1H NMR signals for η^2-H_2 were not observed in CD_2Cl_2 solutions of **4**, heterolytic activation of H_2 was evident in CH_2Cl_2 by protonation of free diisopropyl ether. When $^iPr_2O$ (4−10 equiv) was added to CD_2Cl_2 solutions of **3** and placed under H_2 atmosphere, complete conversion to the hydride-bridged dimers $\{[$*cis*-$Re(CO)_4(PR_3)]_2(\mu$-$H)\}\{BAr_f\}$[23] was observed. This suggests that **3** is in equilibrium with **4** in CH_2Cl_2 solutions, but the exchange is too fast on the NMR time scale to observe the $M(H_2)$ resonances. Similar deprotonation of $[Cp^*Re(CO)(NO)(H_2)][BF_4]$ with Et_2O gives a hydride-bridged dimer.[24] Unfortunately, the protonation of Et_2O with **3** could not be utilized as an estimation of the acidity in this study due to ether coordination to form **2**. The pK_a of $^iPr_2OH^+$ has not been reported, but the pK_a's of Et_2OH^+ and Me_2OH^+ in aqueous sulfuric acid are −2.4 and −2.5, respectively.[25] Thus, if the pK_a of $^iPr_2OH^+$ is −2.0 to −2.4, the pK_a of **4** can be estimated to be −2, although it is likely to be higher because the coproduct is a hydride-bridged *dimer*.[26] In this regard also, $[Re(H_2)(CO)_3(PCy_3)]^+$ is moderately acidic but does not protonate ethers.[15]

In summary, the [*cis*-$Re(CO)_4(PR_3)(L)][BAr_f]$ system represent the first structurally characterized Re diethyl ether and CH_2Cl_2 complexes and the first H_2 adduct of the simple $M(CO)_4(PR_3)$ fragment. The heterolytic activation of H_2 is particularly interesting in that it may be applicable to reactions in which ionic hydrogenation of hindered substrates from a metal catalyst and H_2 is desired. Preliminary evidence shows that heterolytic cleavage of R_3Si−H bonds also occurs.

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Supporting Information Available: Synthetic, spectroscopic, analytical, and X-ray data for **2a** and **3a** (30 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(17) Fernandez, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207.

(18) (a) Huang, D.; Huffman, J. C.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 7398. (b) Forniés, J.; Martínez, F.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **1996**, *15*, 1813. (c) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. (d) Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 2349.

(19) Crystal data for **3a**: triclinic, $P\bar{1}$, $a = 12.030(9)$ Å, $b = 15.012(5)$ Å, $c = 17.515(6)$ Å, $\alpha = 70.84(1)°$, $\beta = 72.44(1)°$, $\gamma = 80.53(1)°$, $V = 2841(3)$ Å^3, $Z = 2$, R1 = 0.0331 and wR2 = 0.0791, GOF(F^2) = 1.215. Methylene hydrogens were fixed in ideal geometry with C−H = 0.97 Å.

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

(21) (a) King, W. A.; Luo, X.-L.; Scott, B. L.; Kubas, G. J.; Zilm, K. W. *J. Am. Chem. Soc.* **1996**, *118*, 6782. (b) Forde, C. E.; Landau, S. E.; Morris, R. H. *J. Chem. Soc., Dalton Trans.* **1997**, 1663. (c) Albertin, G.; Antoniutti, S.; Bettiol, M.; Bordignon, E.; Busatto, F. *Organometallics* **1997**, *16*, 4959.

(22) Luther, T. A.; Heinekey, D. M. *Inorg. Chem.* **1998**, *37*, 127.

(23) Identified by an upfield triplet in the ^1H NMR (CD_2Cl_2) spectrum (−15.6, $J_{HP} = 10.7$, PPh_3; −17.6, $J_{HP} = 8.0$, PCy_3). Authentic samples were prepared from 1:1 [*cis*-$ReH(CO)_4(PR_3)]$ and [*cis*-$Re(CO)_4(PR_3)(OEt_2)][BAr_f]$ in CH_2Cl_2, and their synthesis and X-ray structures will be reported elsewhere.

(24) Chinn, M. S.; Heinekey, M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824.

(25) Perdoncin, G.; Scorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983.

(26) As pointed out by a reviewer, irreversible formation of the dimer provides a driving force so that even if the H_2 complex has a pK_a of 1 or higher, it would still be deprotonated by a base that has a conjugate acid form with a pK_a of −2. Thus, a more conservative estimate of the pK_a is 1 to −2.