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Cationic Hydrogen Complexes of Rhenium

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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] Many workers have observed that formal positive charge on the metal center (frequently to give a d^6 octahedral configuration) promotes H_2 binding. In fact, of the approximately 200 reported H_2 complexes, fully one-half are cationic. However, no comparisons have so far been made between directly analogous neutral and cationic H_2 complexes. In particular, it would be interesting to compare the properties of the isolable Kubas complexes $M(H_2)(PR_3)_2(CO)_3$ (M = W, Mo) with those of isostructural and isoelectronic cationic Re(I) derivatives. A recent report[3] gave evidence for a trimethylphosphine complex, $[Re(H_2)(PMe_3)_2(CO)_3]BF_4$, but spectroscopic and structural data on this compound are incomplete due to its thermal instability. We now report the synthesis and characterization of *isolable* cationic hydrogen complexes $[Re(H_2)(PR_3)_2(CO)_3]^+$ and related compounds and compare their properties to those of the neutral Mo and W analogs.[4]

Under an atmosphere of hydrogen, protonation of *mer,trans*-$Re(CH_3)(PR_3)_2(CO)_3$ (PR_3 = PCy_3, P-*i*-Pr_3, PPh_3)[5] with $H(Et_2O)_2B(Ar')_4$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$)[6] affords [*mer,trans*-$Re(H_2)(PR_3)_2(CO)_3]B(Ar')_4$ (PR_3 = PCy_3 (**1a**), P-*i*-Pr_3 (**1b**), PPh_3 (**1c**)) with loss of methane. Complexes **1a** and **1b** are isolated as white or pale yellow microcrystalline solids from H_2-saturated CH_2Cl_2/pentane in 70–90% yield.[7] The H_2 ligand is moderately labile[8] in these complexes (vide infra); thus storage under an H_2-enriched atmosphere is necessary. Complexes **1a–c** are soluble in a variety of halogenated hydrocarbon solvents (CH_2Cl_2, $CHCl_3$, 1,2-difluorobenzene), but insoluble in aromatic and aliphatic hydrocarbons. In contrast to the thermal instability of $[Re(H_2)(PMe_3)_2(CO)_3]BF_4$[3] and $[Re(H_2)(PCy_3)_2(CO)_3]BF_4$,[9] solutions of **1a–c** (under H_2) are stable at room temperature for weeks. We attribute the thermal stability of **1a–c** to the low reactivity of the tetraarylborate counterion.

Formulation of **1a–c** as dihydrogen complexes is based primarily on spectroscopic data. The ^1H NMR spectrum (CD_2Cl_2) of each complex exhibits a single broad resonance in the hydride region (−3 to −5 ppm). A T_1 determination (300 MHz) for the dihydrogen resonance gives a minimum value of 3 ms at 206 K for **1a** and a value of 4 ms at 201 K for **1b**.[10] In the HD complexes (vide infra), $^1J_{H-D}$ values of 32 Hz (**1a**), 33 Hz (**1b**), and 32 Hz (**1c**) are obtained. Coupling to ^{31}P is also observed for the HD isotopomer of **1b**, with $^2J_{H-P}$ = 2 Hz.

Variable temperature NMR studies of **1a–c** give no evidence of the classical dihydride complex $[Re(H)_2(PR_3)_2(CO)_3]B(Ar')_4$ in the temperature range −80 to 24 °C. This contrasts with the observations of Kubas, who noted the presence of the dihydride species $W(H)_2(PR_3)_2(CO)_3$ in equilibrium with the dihydrogen complex $W(H_2)(PR_3)_2(CO)_3$.[11] The reluctance of **1** to undergo formal oxidative addition to give a dihydride complex is consistent with the lower electron density at the cationic rhenium center.

Facile exchange of the H_2 ligand with D_2 occurs in solution for **1a–c**. Of greater interest is the equally facile equilibration of H_2 and D_2 with the HD isotopomer. This isotopic scrambling is significantly faster than that reported by Kubas and co-workers for $W(H_2)(PR_3)_2(CO)_3$ in solution.[12] Analysis of a solution of **1b**-H_2 placed under D_2 (1 atm) by ^1H NMR spectroscopy reveals detectable amounts of the HD complex within 30 min (statistical amounts of the HD and H_2 complexes are present after 12 h). Control experiments reveal that neither the solvent nor phosphine ligand plays a role in the H/D exchange process observed in **1b**. Water was rigorously excluded from the solutions, but the possibility of very small amounts of adventitious water acting as a *catalytic* base in the deprotonation of bound H_2 has not been ruled out.

Loss of H_2 from **1a–c** gives the formally 16-electron complexes [*mer,trans*-$Re(PR_3)_2(CO)_3]B(Ar')_4$ (**2a–c**). Although H_2 can be removed quantitatively from **1b** in solution at 40 °C, we find that a more convenient route to **2** is via direct protonation of $(PR_3)_2(CO)_3ReCH_3$ in vacuo. Isolation of orange **2a** and **2b** is achieved in 85–90% yield from CH_2Cl_2/pentane.[13] These complexes are stable indefinitely in the solid state and for weeks in solution (CH_2Cl_2 or 1,2-difluorobenzene). The structure of **2a** in the solid state has been determined by X-ray crystallography.[14] An agostic interaction between the electron-deficient rhenium center and a C–H bond of the pendant cyclohexyl group is clearly present (see Figure 1). The distance between the rhenium center and the agostic carbon atom is 2.89(5) Å. There is a slight distortion of the bond angles from idealized octahedral

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(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) For recent reviews on dihydrogen complexes, see: (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913–926. (b) Morris, J. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, *121*, 155–289.

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

(4) A preliminary report of this work was given at the 106th National Meeting of the American Chemical Society, Chicago, IL, 1993. Abstract IN-249.

(5) These compounds were prepared in 40–90% yield by reaction of $(CO)_5ReCH_3$ and excess phosphine in toluene at 110–130 °C for ca. 100 h, with periodic removal of CO. Spectral and analytical data were unremarkable. An isomer of one complex, *fac,cis*-$Re(CH_3)(PPh_3)_2(CO)_3$, has been reported: Simpson, R. D.; Bergman, R. G. *Organometallics* **1993**, *12*, 781–796.

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

(7) Characterization of the dihydrogen complexes. **1a**: ^1H NMR (CD_2Cl_2) δ 7.73 (s, 8 H), 7.57 (s, 4 H), 2.16 (br, 6 H), 1.95–1.30 (br, 60 H), −4.75 (br, 2 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ + 23.9 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 192.9 (t, J_{PC} = 5.5 Hz, *C*O), 189.2 (t, J_{PC} = 7.0 Hz, *C*O), 162.1 (q, J_{BC} = 50 Hz, *i*-*C*), 135.2 (s, *o*-*C*), 129.2 (q, J_{CF} = 32 Hz, *m*-*C*), 125.0 (q, J_{CF} = 272 Hz, CF_3), 117.9 (s, *p*-*C*), 37.8 (t, J_{PC} = 12.4 Hz, P-α-*C*), 30.6 (s, P-γ-*C*), 27.6 (t, J_{PC} = 4.8 Hz, P-β-*C*), 26.3 (s, P-δ-*C*); IR (cm^{-1}; CH_2Cl_2, ν_{CO}) 2069 (w), 1969 (s), 1944 (m). Note: All of the rhenium cations were obtained as the $B(Ar')_4$ salts, and in every case the ^1H and ^{13}C NMR data for the anion were identical to those reported above for complex **1a**. These data have been omitted from subsequent complexes. **1b**: ^1H NMR (CD_2Cl_2) δ 2.49 (m, J_{HH} = 7.0 Hz, 6 H), 1.31 (m, J_{HH} = 7.0 Hz, 36 H), −4.97 (br, 2 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ, 32.5 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 192.0 (br, *C*O), 188.7 (br, *C*O), 28.3 (t, J_{PC} = 13.3 Hz, P[*C*$HMe_2]_3$), 19.9 (s, $P[CH(CH_3)_2]_3$); IR (cm^{-1}, CH_2Cl_2, ν_{CO}) 2073 (w), 1974 (s), 1950 (m). **1c**: ^1H NMR ($CDCl_3$) δ 7.9–7.2 (br), −3.91 (br, 2 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ + 7.6 (br).

(8) Dissolution of **1a** in CD_2Cl_2 in vacuo at 297 K leads to a **1a**:**2a** ratio (equilibrium) of 57:43. This result indicates that hydrogen binding in **1a** is comparable to that in the neutral tungsten analog.

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(10) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173–4184. Luo, X. L.; Howard, J. A. K.; Crabtree, R. H. *Magn. Reson. Chem.* **1991**, *29*, S89–S93. Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1991**, *30*, 3116–3118.

(11) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000–7009.

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(13) Spectroscopic and elemental analysis data for **2** are as follows. **2a**: ^1H NMR (CD_2Cl_2) δ 2.53 (br, 6 H), 1.75–1.30 (br, 60 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ + 27.2 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 198.9 (*t*, J_{PC} = 7.3 Hz, *C*O), 190.0 (t, J_{PC} = 5.5 Hz, *C*O), 39.1 (t, J_{PC} = 11.0 Hz, P-α-*C*), 29.7 (s, P-γ-*C*), 27.8 (br, P-β-*C*), 26.1 (s, P-δ-*C*); IR (cm^{-1}, Nujol, ν_{CO}) 2061 (w), 1966 (s), 1939 (m). Anal. Calcd (found) for $C_{71}H_{78}BF_{24}O_3P_2Re$: C, 50.33 (50.38); H, 4.64 (4.79). **2b**: ^1H NMR (CD_2Cl_2) δ 2.76 (m, J_{HH} = 7.0 Hz, 6 H), 1.17 (m, J_{HH} = 7.0 Hz, 36 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ + 32.2 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 197.8 (t, J_{PC} = 8.0 Hz, *C*O), 189.8 (br, *C*O), 29.5 (t, J_{PC} = 11 Hz, P[*C*$HMe_2]_3$), 18.6 (s, $P[CH(CH_3)_2]_3$); IR (cm^{-1}, Nujol, ν_{CO}) 2064 (w), 1969 (s), 1950 (m). Anal. Calcd (found) for $C_{53}H_{56}BF_{24}O_3P_2Re$: C, 43.78 (43.62); H, 3.74 (3.72). **2c**: ^1H NMR ($CDCl_3$) δ 7.9–7.2 (m); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ + 17.0 (br).

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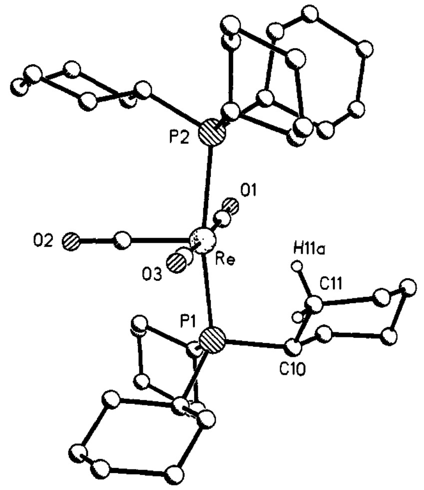

Figure 1. PLUTO projection for complex **2a**. Relevant bond angles (deg) are as follows: P(1)–Re–P(2) = 167.5(3), C(1)–Re–C(3) = 174.1(13), C(1)–Re–C(2) = 92.2(13), P(1)–Re–C(2) = 95.4(10), P(2)–Re–C(2) = 94.6(9), P–Re–C_{ipso}(average) = 115, Re–P(1)–C(10) = 97.6(10).

geometry about the rhenium, consistent with this agostic interaction. The structure of **2a** in the solid state is very similar to that of the neutral tungsten analog $W(CO)_3(PCy_3)_2$ reported by Kubas and co-workers.[15] In contrast, it differs substantially from the structure of the neutral 17-electron complex $Re(CO)_3(PCy_3)_2$, which exhibits a square pyramidal structure with no evidence of an agostic interaction.[16]

Since the cationic rhenium center in **2a–c** is presumably more electrophilic than the neutral tungsten center in the Kubas complexes, we sought to confirm the presence of the agostic C–H bond in solution. Examination of the $^{31}P\{^1H\}$ NMR spectrum of **2a** reveals a single resonance at ambient temperature. At lower temperatures, the signal broadens substantially. Decoalescence was observed at 240 K. An AB spectrum results (δ_A = 42.2 ppm; δ_B = 32.1 ppm) with J_{P-P} = 93 Hz.[17] The low-temperature spectrum indicates a structure with two inequivalent phosphine ligands in a *trans* disposition, presumably corresponding to the observed solid-state structure. We attribute the observation of a single resonance at higher temperatures to a dynamic process in which the agostic C–H interaction is interchanged from one of the phosphine ligands to the other. Line-shape analysis of the ^{31}P NMR spectra indicates that $\Delta G^{\ddagger}_{240}$ = 10.4 kcal mol^{-1} for this rearrangement process. The activation energy for this rearrangement presumably reflects the strength of the agostic interaction. No evidence of a similar phosphine inequivalence has been reported for the neutral tungsten or molybdenum analogs, so we conclude that the agostic interaction in the cationic rhenium complexes is stronger than in the neutral tungsten and molybdenum species. The strength of the agostic interaction is apparently also dependent on the nature of the organic moiety in the phosphine ligand. In the case of complex **2b** (R = *i*-Pr) and **2c** R = Ph), ^{31}P NMR spectra give only a single resonance at all accessible temperatures, indicative of a very rapid dynamic process which renders the two phosphine ligands equivalent on the NMR time scale.

The unsaturated compounds **2** react with a variety of small donor molecules in addition to H_2. For example, both CO and MeCN bind irreversibly to give the coordinatively saturated compounds $[Re(L)(PR_3)_2(CO)_3]B(Ar')_4$ (L = CO, MeCN). These two ligands also displace H_2 from **1**, even under 1 atm of H_2. Reaction with dioxygen is also irreversible, producing $[Re(PR_3)_2(CO)_4]B(Ar')_4$ as the only diamagnetic product in ca. 60% yield. More sterically demanding ligands bind either reversibly or not at all; for example, neither diethyl ether nor THF forms an isolable complex with **2**. Surprisingly, N_2 is a comparatively poor ligand in this system. Under 0.8 atm of N_2, ^1H and $^{31}P\{^1H\}$ spectra (297 K) reveal that only ca. 0.5 equiv of dinitrogen adduct is formed from **2a,b**. ^1H and $^{31}P\{^1H\}$ spectra also reveal that H_2 complexation is highly favored over N_2 complexation at 297 K. This contrasts with the results of Kubas, who reports that N_2 coordination is favored over H_2 for both $W(PR_3)_2(CO)_3$ and $Mo(PR_3)_2(CO)_3$ at ambient temperature.[18] As was reported for the tungsten and molybdenum analogs, dinitrogen coordination to **2** is apparently favored enthalpically over H_2 coordination; thus NMR spectra indicate increased concentrations of the N_2 adduct at lower temperatures.[19]

The affinity of **2a–c** for water appears to vary with the identity of the phosphine coligands. NMR evidence reveals that **2a,b** bind H_2O reversibly and competitively with H_2. For complex **2c**, however, H_2O complexation is irreversible to give $[Re(OH_2)(PPh_3)_2(CO)_3]B(Ar')_4$.[20]

We are continuing to explore the coordination chemistry of these very reactive, coordinatively unsaturated cationic complexes. In particular, we note that the synthetic methods employed here can in principle be extended to sterically undemanding phosphine coligands, providing access to a wider range of complexes than is possible in the tungsten and molybdenum chemistry.

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Supplementary Material Available: Summary of X-ray analysis of **2a**, including data collection and refinement procedures, tables of positional and thermal parameters, and bond distances and angles (10 pages); tables of observed and calculated structure factors (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) The structure of **2a** was determined by X-ray crystallography using a crystal that measured 0.2 × 0.25 × 0.3 mm. Diffraction measurements were made at 183 K in a stream of dry nitrogen on an Enraf-Nonius CAD4 difractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Monoclinic symmetry (space group $P2_1/n$) was indicated based on the systematic absences. The cell parameters are a = 15.421(3) Å, b = 13.955(3) Å, c = 34.556(7) Å, β = 91.50(3)°, V = 7434(3) Å^3 (Z = 4; density of 1.514 g/cm^3). There were 6535 unique reflections collected, with $2\theta \leq 24°$; of those reflections, 4179 with $I \geq \sigma(I)$ were adjudged observed. The structure was solved by locating the position of the rhenium atom using the Patterson function. Full-matrix least squares refinement (isotropic) of the non-hydrogen atoms was carried out, and the hydrogen atoms were input at their calculated locations (riding model, fixed isotropic U). Final R = 0.12.

(15) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294–2301.

(16) Heinekey, D. M.; Crocker, L. S.; Schulte, G. K. *J. Am. Chem. Soc.* **1989**, *111*, 405–406.

(17) An additional broad resonance at 24 ppm is also evident in the low-temperature ^{31}P NMR spectrum. This signal broadens and coalesces with the AB pattern. Low-temperature ^1H and ^{13}C NMR spectra exhibit no evidence for coordinated methylene chloride, and the signal is present at the same chemical shift regardless of solvent (CD_2Cl_2; $CDCl_3$; *o*-difluorobenzene). The $^{31}P\{^1H\}$ NMR resonance for trace amounts of $[Re(OH_2)(PCy_3)_2(CO)_3]B(Ar')_4$ is distinct from the broad resonance at 24 ppm over the temperature range 295–208 K. The ^1H NMR spectra of analytically pure **2a** show no traces of diethyl ether.

(18) Gonzalez, A. A.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Khalsa, G. R.; Kubas, G. J. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990; Chapter 9.

(19) Data for N_2 complexes. $[Re(N_2)(PCy_3)_2(CO)_3]^+$: ^1H NMR (CD_2Cl_2, 235 K) δ 2.7–1.1 (br); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 235 K) δ + 17.0 (s). $[Re(N_2)(P\text{-}i\text{-}Pr_3)_2(CO)_3]^+$: ^1H NMR (CD_2Cl_2, 235 K) δ 2.54 (m, J_{HH} = 7.0 Hz, 6 H), 1.31 (m, J_{HH} = 7.0 Hz, 36 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 250 K) δ + 25.1 (s). Efforts to obtain high-pressure IR spectra of the N_2 complexes are in progress.

(20) In the ^1H NMR spectra of the water complexes $[Re(H_2O)(PR_3)_2(CO)_3]^+$, resonances for bound water have been identified at widely variable chemical shifts. For R = Cy or *i*-Pr, the bound water signal is at 4.0 ppm, while for R = Ph, the corresponding resonance is at 1.4 ppm (t, J_{P-H} = 2 Hz). In no case is there any evidence for oxidative addition to give a hydroxy–hydride complex.