30. Spectrophotometry indicated that $\mathrm{Ph_3PO}$ had no effect on the reaction. The results thus far require that MoO(sap)(DMF) quantitatively reduce $\mathrm{MoO_2(L\text{-}NS_2)}$. This point was spectrophotometrically established with use of an equimolar DMF reaction system at ambient temperature.

The foregoing results are summarized in Figure 8, which depicts spontaneous intermetal oxo-transfer reactions. In the set of complexes, MoO(sap)(DMF) (**17**) is the strongest reductant and $\mathrm{MoO_2(S_2CNEt_2)_2}$ (**19**) is the strongest oxidant. This thermodynamic series is the same as kinetic series 19, thereby showing that the activation barrier to oxo transfer is largely set by those factors which stabilize/destabilize Mo(IV) and Mo(VI). This in turn reemphasizes the beneficial effect of anionic sulfur ligands in stabilizing Mo(IV). Lastly, the reactions **17** + $^1/_2\mathrm{O_2} \rightarrow$ **13** and **18** + $^1/_2\mathrm{O_2} \rightarrow$ **15** cannot be placed precisely in the oxidative enthalpy series of Table III. However, it is clear that the first of these reactions lies below the second and that the ΔH values of both are more negative than that for the oxidation of $\mathrm{MoO(L\text{-}NS_2)(DMF)}$. The lack of reaction between **17** and 10 equiv of $\mathrm{Ph_3PO}$ in DMF for 6 h at ambient temperature suggests that $\Delta H \gtrsim -67$ kcal/mol, but slow reaction kinetics cannot be ruled out. In any case, **17** and **18**, as $\mathrm{MoO(L\text{-}NS_2)(DMF)}$ and $\mathrm{MoO(S_2CNEt_2)_2}$, should reduce $\mathrm{Me_2SO}$ to $\mathrm{Me_2S}$. This has been confirmed for the stronger reductant **17**, which is quantitatively oxidized to **13** in a system initially containing 2 equiv of $\mathrm{Me_2SO}$.

All $\mathrm{Mo^{IV}O}$ complexes in Figure 8 are now recognized to be thermodynamically competent to reduce $\mathrm{Me_2SO}$,[75] the most reductively resistant enzyme substrate for which thermodynamic data are available. The stoichiometric reduction of substrate XO by a $\mathrm{Mo^{IV}O}$ complex is, therefore, a highly necessary but not a sufficient thermodynamic criterion for a functional oxo-transferase site model. What is required for sufficiency under the oxo atom transfer hypothesis are those factors which permit at least one such atom transfer to or from substrate followed by regeneration of the original $\mathrm{Mo^{IV}O}$ or $\mathrm{Mo^{VI}O_2}$ species either by electron or oxo transfer, such that catalysis is sustained. The results presented here show that anionic sulfur ligation is a critical modulator of these factors and, as already mentioned, appears to place real or effective Mo redox potentials in a range accessible to physiological reactants.

Ongoing research on biologically related oxo-transfer reactions includes development of catalytic systems for substrate oxidation and reduction, examination of reactions in aqueous solution, and the possible role of pterins in enzymic electron transfer.

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[75] In the only other related case that has been reported, $\mathrm{[MoO(dttd)Cl]^{1-}}$ reduces $\mathrm{Me_2SO}$: Kaul, B. B.; Enemark, J. H.; Merbs, S. L.; Spence, J. T. *J. Am. Chem. Soc.* **1985**, *107*, 2885. dttd = 2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane(2−).

Molecular Hydrogen Complexes of the Transition Metals. 4. Preparation and Characterization of $\mathrm{M(CO)_3(PR_3)_2(\eta^2\text{-}H_2)}$ (M = Mo, W) and Evidence for Equilibrium Dissociation of the H–H Bond To Give $\mathrm{MH_2(CO)_3(PR_3)_2}$

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Abstract: The syntheses, properties, and spectral characterization of the first examples of molecular hydrogen complexes, $\mathrm{M(CO)_3(PR_3)_2(H_2)}$ (M = Mo, W; $\mathrm{R_3}$ = $\mathrm{Cy_3}$, i-$\mathrm{Pr_3}$, $\mathrm{Cy_2}$-i-Pr), are reported in full. All six of the expected fundamental vibrational modes for η^2-$\mathrm{H_2}$ binding, including ν(HH) at 2690 cm^{-1}, have been located. The hydrogen atoms of the $\mathrm{H_2}$ ligand, but not of the phosphines, undergo exchange with $\mathrm{D_2}$ to give HD, even in the solid state. Solid-state ^{2}H NMR of $\mathrm{W(CO)_3(P\text{-}}i\mathrm{\text{-}Pr_3)_2(D_2)}$ shows rapid rotation of the $\mathrm{D_2}$ about the metal–$\mathrm{D_2}$ axis. IR and variable-temperature ^{1}H and ^{31}P NMR of solutions of the $\mathrm{H_2}$ complexes reveal the presence of equilibrium amounts (10–30%) of a species that the data indicate is a 7-coordinate *dihydride*, $\mathrm{MH_2(CO)_3(PR_3)_2}$. The latter is presumably formed by dissociation of the H–H bond, thus completing oxidative addition of $\mathrm{H_2}$ to the metal. The dihydride is fluctional, but low-temperature NMR spectroscopy shows that both the hydride and phosphorus ligands are inequivalent. At −80 °C the T_1 value for the ^{1}H NMR signal of the $\mathrm{H_2}$ ligand is 0.004 s, almost three orders of magnitude less than that of the hydride protons (1.7 s) in $\mathrm{WH_2(CO)_3(P\text{-}}i\mathrm{\text{-}Pr_3)_2}$.

The activation of hydrogen by transition-metal complexes, e.g., oxidative addition to form hydride complexes, has been extensively studied because of its critical importance in catalytic hydrogenation.[1] The nature of the initial interaction of $\mathrm{H_2}$ with a metal center and the geometry of approach of the $\mathrm{H_2}$ molecule ("end-on" or "side-on") has long been the subject of discussion. Halpern[1a] had suggested that the bonding electrons of hydrogen could attack a vacant metal orbital, and coordination of molecular hydrogen to a metal has often been proposed and studied theoretically.[1g,2,3]

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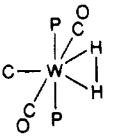
Evidence for possible intrazeolite dihydrogen complexes of Ni^+ and Pd^+ has been reported,[4] but until our work[5] a well-characterized stable molecular hydrogen complex had not been isolated. Indeed, such a complex would have been expected to have only a fleeting existence on the reaction pathway to dihydride formation. The discovery of η^2-H_2 coordination ultimately derived from cur extensive studies of SO_2 bonding to Mo(0) and W(0) complexes.[6] A key finding was a synthetic pathway to unsaturated, formally 16-electron complexes, $M(CO)_3(PCy_3)_2$, which contain agostic M···H—C interactions and readily add small molecules as a sixth ligand.[5b,7] The addition of H_2 gave complexes which reversibly coordinated the H_2 and possessed unusual infrared spectra upon comparison to that of known metal–hydride complexes.[7] This behavior suggested molecular coordination, and extensive structural and spectroscopic studies of $M(CO)_3(PCy_3)_2(H_2)$[8] and $W(CO)_3(P$-i-$Pr_3)_2(H_2)$ confirmed η^2-H_2 coordination.[5a] Single crystal neutron diffraction studies of the latter[9] provided the first structural evidence for side-on bonding, with the H_2 parallel to the P–W–P vector:



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Recent theoretical studies also have favored side-on (η^2) bonding to a metal center.[3]

The area of molecular hydrogen coordination has grown rapidly, and many new examples of dihydrogen complexes have since been reported.[10] Low-temperature infrared evidence for $M(CO)_5(H_2)$ (M = Cr,[10a–c,k] Mo,[10k] and W[10k]), $Cr(CO)_4(H_2)_2$,[10a,k] $CpMoH(CO)_2(H_2)$,[10f] $Fe(CO)(NO)_2(H_2)$,[10g] $Co(CO)_2(NO)(H_2)$,[10g] and $Pd(H_2)$[10h] has been observed. Several stable cationic complexes have been formed by protonation reactions. NMR data for $[IrH(H_2)(PPh_3)_2(C_{13}H_8N)]^+$ and $[IrH_2(H_2)_2L_2]^+$ indicate H_2 coordination,[10d,i] and $[MH(H_2)(dppe)_2]^+$ (M = Fe, Ru; dppe = (diphenylphosphino)ethane) were shown to contain η^2-H_2 coordination by X-ray crystallography (M = Fe) and NMR.[10e] $[CpRu(PPh_3)(t$-$BuNC)(H_2)]^+$ has recently been reported.[10j] We have evidence for molecular H_2 binding in another group 6 species, $Mo(CO)(dppe)_2(H_2)$,[5c] and many known polyhydrides are now being recognized to contain H_2 ligands. These complexes are very significant in that they represent incipient oxidative addition of a diatomic molecule, giving an unprecendented opportunity for study of this important class of reaction. In a preliminary communication,[5c] we reported evidence that the H–H bond in $M(CO)_3(PR_3)_2(H_2)$ indeed does *spontaneously dissociate to give equilibrium amounts of a dihydride complex*.

In this paper, the synthesis and characterization of the H_2 complexes are presented in detail, along with further evidence for equilibrium between dihydrogen and dihydride forms.

Experimental Section

General. All preparations and handling of complexes were carried out in air-free atmospheres (e.g., H_2 and/or argon). Reagent-grade solvents were used without purification. Phosphines and $Mo(CO)_3$(cycloheptatriene) were purchased from Strem Chemicals, Inc., Newburyport, MA, and $W(CO)_3$(cycloheptatriene)[11] was synthesized by literature procedure. Hydrogen (99.9% minimum purity) and deuterium were obtained in-house, and HD (98%), $P(C_6D_{11})_3{\cdot}CS_2$, and $P(i$-$C_3D_7)_3{\cdot}CS_2$ (custom-synthesis) were purchased from MSD Isotopes, Montreal, Canada. IR, NMR, and mass spectra were recorded on Perkin-Elmer 521, Varian EM-390 or Bruker AM200 and WM300, and Consolidated Electrodynamics 21-620A or Bendix MA-2 (time-of-flight) instruments, respectively. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of $M(CO)_3(PCy_3)_2(H_2)$ (M = Mo, W). A mixture of $W(CO)_3(C_7H_8)$ (2.50 g, 6.94 mmol), PCy_3 (4.0 g, 14.3 mmol), and toluene (25 mL) was stirred under hydrogen for 30 min. Precipitation of yellow microcrystalline $W(CO)_3(PCy_3)_2(H_2)$ began and was completed by addition of heptane (60 mL) and further stirring (30 min.). The product was collected on a frit, washed with H_2-saturated 2:1 heptane–toluene (25 mL), and dried in a stream of H_2 (then briefly in vacuo, followed by restoration of H_2 atmosphere). Yield: 5.06 g (88%). The Mo complex was prepared analogously except that longer (by a factor of 5) reaction periods were required to give equivalent (84%) yields. The D_2 complexes were prepared similarly. The complexes could also be prepared by H_2 addition to toluene solutions of $M(CO)_3(PCy_3)_2$[5b] and isolation as above.

The complexes are only sparingly soluble in aromatic hydrocarbons and decompose with H_2 loss in most polar solvents, including halogenated hydrocarbons. The microcrystalline solids slowly decompose in air (W slower than Mo) although X-ray size crystals are stable for hours without significant decomposition. The H_2 complexes are slightly photosensitive, slowly becoming orange on the surface in room light. Finely divided samples of the H_2 complexes quickly darken in vacuo, but the original bright yellow color returns immediately in an H_2-enriched atmosphere. Complete removal of H_2 (to form $M(CO)_3(PCy_3)_2$) by pumping is slow, however. Anal. Calcd for $C_{39}H_{68}O_3P_2Mo$: C, 63.1; H, 9.2; P, 8.3. Found: C, 62.8; H, 9.0; P, 8.0. Calcd for $C_{39}H_{68}O_3P_2W$: C, 56.4; H, 8.3; P, 7.5. Found: C, 56.9; H, 8.5; P, 7.5.

Preparation of $W(CO)_3(P$-i-$Pr_3)_2(H_2)$. A mixture of 4.757 g of $W(CO)_3(C_7H_8)$, 5.5 mL of P-i-Pr_3, and 6 mL of hexane was stirred for 4 h under a hydrogen atmosphere. A yellow microcrystalline precipitate formed, and the reaction mixture was then cooled to −20 °C in a freezer or an ice–HCl bath. The product was collected by filtration, washed with cold H_2-saturated hexane (2 × 4 mL), and dried in a stream of H_2. Yield: 4.6 g (59%).

The complex is quite soluble even in hexane. It readily decomposes in air and reacts with nitrogen to form sparingly soluble red-orange $[W(CO)_3(P$-i-$Pr_3)_2]_2(\mu$-$N_2)$.[5b]

Preparation of PCy_2-i-Pr. A solution of 10 g of PCy_2Cl in 40 mL of dry ether was slowly added from a dropping funnel to 45 mL of 2 M i-PrMgCl in a 250-mL flask at 0 °C. The mixture was heated to reflux for 7 h (thick white precipitate formed) and then stirred overnight at room temperature. Saturated aqueous NH_4Cl (50 mL) was added dropwise at 0 °C, followed by ca. 30 mL of 1 M HCl. A small amount of precipitate remained and the solution was extracted by adding 60 mL of ether, shaking the solution, and removing the settled organic phase with a syringe. The process was repeated with 80 mL of ether, and the combined extracts were dried over Na_2SO_4 and filtered. About one-half

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of the solvent was removed and heptane (50 mL) was added. A small amount of precipitate was removed by filtration, and addition of CS_2 (~5 mL) to the filtrate yielded a flocculent pink-tan precipitate of PCy_2-*i*-Pr·CS_2 (7.3 g, 54%), which was collected and washed with ether. Unlike $PCy_3 \cdot CS_2$, the latter appeared to be air- or moisture-sensitive since a sample turned into a liquid on overnight exposure to the atmosphere. The CS_2 adduct was converted to the phosphine in refluxing ethanol (150–175 mL), distilling off ca. 75 mL to remove the CS_2. The resulting colorless solution was filtered, and solvent was removed to give 5.2 mL of a colorless liquid. ^1H NMR (neat liquid, 90 MHz) δ 1.70 and 1.19 (br s, cyclohexyl), 1.03 (d of d, *J*(HH) = 6.8 Hz, ^2J(PH) = 12 Hz, isopropyl).

Preparation of $M(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2)$ (M = Mo, W). A mixture of 1.5 g (4.17 mmol) of $W(CO)_3(C_7H_8)$, 2.6 mL (ca. 9 mmol) of PCy_2-*i*-Pr, and 7 mL of hexane was stirred. Reaction took place within 10 min, and a thick precipitate formed. Toluene (5 mL) was added, the mixture was stirred overnight, and the precipitate was collected, washed with 3:1 heptane–toluene, and dried in a H_2 stream. The yield of moderately soluble, dull yellow $W(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2)$ was 2.0 g (65%). ^1H NMR (toluene-d_8, 90 MHz) δ 2.02 (br s, Cy), 1.62 (br s, Cy), 1.17 (d of d, *J*(HH) = 6.8 Hz, ^2J(PH) = 13 Hz, *i*-Pr), −3.90 (br s, H_2). The Mo analogue was prepared in a similar manner with 0.54 g of $Mo(CO)_3(C_7H_8)$, 1.2 mL of PCy_2-*i*-Pr, and 5 mL of hexane (toluene was not added). The Mo–H_2 complex partially dissociates in aromatic solvents or solvent mixtures (toluene–hexane), losing H_2 (effervescence observed) even in the presence of excess H_2 to give a rose-purple coloration characteristic of the presence of $Mo(CO)_3(PCy_2\text{-}i\text{-}Pr)_2$. When toluene–hexane solutions were cooled in a freezer for several days (H_2 atmosphere), crystalline H_2 complex did precipitate, indicating that complete dissociation does not occur. ^1H NMR (C_6D_6, 90 MHz, 35 °C) showed a weak, broad H_2 peak at −3.13 ppm, the intensity of which also indicated considerable partial dissociation. Phosphine signals similar to those for $W(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2)$ were located at 1.90, 1.60, and 1.19 ppm.

Preparation of $M(CO)_3(PR_3)_2(D_2)$ and $M(CO)_3(PR_3)_2(HD)$. The D_2 and HD complexes were generally prepared as for the H_2 complexes. The HD gas was found to contain small quantities of N_2 which resulted in formation of trace impurities of N_2 complexes.[5b] Small amounts of the H_2 and D_2 complexes also formed because of isotopic scrambling of the HD complex. Indeed, the ^1H NMR spectrum of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(HD)$ changed within 1 day, consistent with partial isotopic exchange to a mixture of H_2, HD, and D_2 complexes.

Reversible H_2 Removal To Form $M(CO)_3(PR_3)_2$. A slurry of 0.714 g (0.96 mmol) of $Mo(CO)_3(PCy_3)_2(H_2)$ in 5 mL of toluene was placed into a 25-mL flask connected to a vacuum line via a reflux condensor. The system was evacuated and opened to a manometer, and the slurry was carefully heated to reflux. The pressure in the closed system (*V* = 250 mL) rose due to evolved H_2, becoming 86 Torr within 0.5 h. Subtraction of the vapor pressure of toluene (19 Torr at 291 K) allowed calculation of the amount of H_2 evolved (0.92 mmol). The toluene solution contained deep purple $Mo(CO)_3(PCy_3)_2$. Similar experiments were carried out for the W analogue, but because of the latter's higher stability, mesitylene was used as solvent (reflux temperature ~80 °C at ~50 Torr). The complex $W(CO)_3(PCy_3)_2$ precipitated on cooling of the solution. For preparative purposes, use of toluene (or other) solvent under a partial pressure of argon (~100 Torr) speeded up H_2 removal (higher reflux temperature). The argon-H_2 was then pumped off and replaced by argon, and the process was repeated until all H_2 was removed. This general method allowed synthesis of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$, which could not be prepared by direct route.[5b] Vacuum pumping of decane solutions with Schlenk techniques also yielded the H_2-free complexes for R_3 = *i*-Pr_3 or Cy_2-*i*-Pr.[5b]

H_2–D_2 Exchange Experiments. (a) Solution. $W(CO)_3(PCy_3)_2(H_2)$ (0.19 g, 0.23 mmol) was dissolved in 45 mL of toluene under H_2. The solution was degassed by pumping in vacuo with freeze–thaw cycles, and D_2 (ca. 0.25 mmol) was added to the flask containing the partially frozen solution. The flask was closed off, and the solution was stirred overnight. Mass spectral analysis of the resulting gas mixture showed a D_2:HD:H_2 ratio of 11:3.6:1. A gas sample taken over a solution of $Mo(CO)_3(PCy_3)_2(D_2)$ in toluene (no added gases) stirred overnight showed D_2:HD:H_2 = 78:1:2, indicating that negligible exchange occurred with solvent or the cyclohexyl groups.

^1H NMR experiments (90 MHz) were also carried out. A sample of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ (0.175 g, 0.297 mmol) was dissolved in 1 mL of toluene-d_8 (dried over P_2O_5) in a tube (ca. 28 mL) on a vacuum line, and ca. 0.3 mmol of D_2 was added. This mixture was kept at 40 °C for 1 day, and a sample was syringed into an NMR tube in a glove bag. NMR showed a 1:1:1 triplet characteristic of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(HD)$ superimposed on the broad resonance due to the H_2 complex at −4.2 ppm. The signal indicated that the amount of HD complex was comparable to, if not greater than, the amount of H_2 complex. Blank experiments were also carried out to show noninvolvement of solvent and *i*-Pr groups in the exchange. Solutions of D_2 complex in toluene-d_8 and H_2 complex in toluene-d_8 were heated to 40 °C for 2 days and 60 °C for 1 day, respectively. No exchange was detected, using ^1H NMR as a diagnostic tool.

(b) Solid State. A microcrystalline sample of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ (0.775 g, 1.3 mmol) was placed into a 100-mL flask, and ~240 Torr (~1.3 mmol) of H_2 was added. The closed off flask was allowed to stand at ambient temperature for 9 days (light excluded to prevent photochemical reactions). ^1H NMR analysis of the resulting solid (dissolved in C_6D_6 under argon) showed that nearly statistical amounts of HD and H_2 complex were present. Integration of the combined HD/H_2 signals with respect to the *i*-Pr group septet resonance ($(CH_3)_2CH$) gave a ratio of 0.13 (theory: 0.165 for a mixture of H_2:HD:D_2 complexes in 1:2:1 ratio).

A mixture of $W(CO)_3(PCy_3)_2(H_2)$ (0.37 g, 0.45 mmol) and D_2 (~0.5 mmol) was allowed to stand 10 days as above. IR analysis of the solid showed a near equimixture of H_2, HD, and D_2 species based on relative intensities of $\nu_s(WX_2)$ (X_2 = H_2, HD, D_2).

Mass spectral analysis showed that solid $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ does not exchange with CH_4, even after 2 weeks.

Reaction of $W(CO)_3(PR_3)_2(H_2)$ with PR'_3. $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ (0.253 g, 0.429 mmol) and PCy_3 (0.5 g, 1.79 mmol) were reacted in toluene (5 mL) under H_2 for 2.5 days. A yellow crystalline precipitate of $W(CO)_3(PCy_3)_2(H_2)$ (0.157 g, 37% yield) formed. A similar reaction with P(*sec*-Bu)$_3$ gave no precipitate.

The reaction of $W(CO)_3(PCy_3)_2(H_2)$ (0.25 g) with a large excess of P-*i*-Pr_3 (0.6 mL) in 9 mL of toluene under H_2 gave solubilization to an orange solution within 1 min. NMR showed no peak attributable to coordinated H_2, indicating that displacement of H_2 occurred.

Reaction of $Mo(CO)_3(PCy_3)_2(H_2)$ with SO_2. A slurry of 0.141 g (0.19 mmol) of H_2 complex in 2 mL of toluene under H_2 was treated with excess SO_2 to give immediate H_2 evolution and formation of a red solution. MeOH (8 mL) was added to precipitate 0.145 g of red-orange $Mo(CO)_3(PCy_3)_2(SO_2)$[6c] (95% yield).

Photolyses of $W(CO)_3(PR_3)_2(H_2)$. A solution of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ (3.5 g) in ca. 200 mL of dry hexane was photolyzed overnight (H_2 atmosphere, 15 °C) with a 200-W Hg lamp. The solution became red, and IR of an aliquot showed ν(CO) bands due to unreacted complex and $W(CO)_4(P\text{-}i\text{-}Pr_3)_2$[5b] (major component) plus new bands at 2010, 1907, and 1888 cm^{-1}, which disappeared upon solvent removal. ^1H NMR spectra of the resulting gummy red residue in toluene-d_8 displayed several weak resonances upfield of Me_4Si, including a triplet at −2.85 ppm, a band at −4.1 ppm due to starting complex, a sharper multiplet superimposed at −4.15 ppm, and a singlet at −4.77 ppm. Integration with respect to the *i*-Pr resonances showed that the residue contained ca. 15% $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ and 5% of the −2.85-ppm species.

A similar experiment using the PCy_3 complex (3.43 g) in 350 mL of dry toluene gave new ν(CO) = 2003, 1895, 1877, and 1778 cm^{-1} after 3.5 h. Further photolysis for 2.5 h resulted in a weakening of all bands. Solvent removal gave a dark residue with solution IR bands at 1856 s ($W(CO)_4(PCy_3)_2$), 1828 w and 1778 vw cm^{-1}. ^1H NMR spectra showed no resonances other than those for PCy_3.

Solid-State ^2H NMR Experiments. Solid-state spectra of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ and $LiAlD_4$ were recorded by using an instrument[12] with a magnetic field strength of 4.7 T where the Larmor frequency is 30.5 MHz. With use of 6-μs pulses (which represent a tip angle of about 22°) and a digitizing rate of 2.5 MHz, a spectrum of the D_2 complex was obtained by averaging 194 560 free induction decays repeated every 800 ms. As described by Davis[13] and others, it is of utmost importance in a quadrupole echo experiment to (1) keep the pulse phases orthogonal and (2) keep the pulse lengths short. Our phase shift was derived from a commercial quadrature hybrid, and the phase shift measured at 30.5 MHz was less than 1°. We kept the pulse lengths as short as possible, even at the expense of not having $\pi/2$ pulses. The pulse length used is adequately short to faithfully yield the correct singularities in the spectrum, even if not the entire line shape.

High-Resolution NMR Experiments. Fourier transform ^1H and ^{31}P NMR spectra were obtained at 4.7 T on a Bruker AM-200 WB NMR spectrometer. Temperature was regulated with a Bruker VT-100 which had been calibrated with a thermocouple. ^1H spectra (200 MHz) were obtained with the following acquisition parameters: 90° pulse, 4.4 kHz sweep width, 8K data points in the FID, and 6 s recycle time. ^{31}P spectra (81 MHz) were obtained with use of the following parameters: 30° pulse, 5.4 kHz sweep width, 8K data points in the FID, and 10 s recycle time. T_1 was estimated by the inversion recovery method at 25 and −80 °C in toluene-d_8 with a standard π-τ-$\pi/2$ pulse sequence. T_1 was cal-

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(12) Fukushima, E.; Roeder, S. B. W. *Experimental Pulse NMR*; Addison-Wesley: Reading, MA, 1981; pp 361-367.

(13) Davis, J. H. *Biochim. Biophys. Acta* **1983**, *737*, 117.

Table I. IR Carbonyl Stretching Frequencies for H_2 Complexes and Equilibrium Dihydride Species

compound	ν(CO),^{a} cm^{-1}	ν(CO),^{b} cm^{-1}
$W(CO)_3(PCy_3)_2(H_2)$	1963, 1843^c	
	1958, 1840^d	1983, ~1900^{d,f}
$Mo(CO)_3(PCy_3)_2(H_2)$	1966, 1853^c	
	1960, 1842^d	1998^{d,f}
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$	1965, 1852^c	
	1969, 1856^e	1993, 1913, 1867 1828^e
$W(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2)$	1962, 1840^c	
	1960, 1842^d	1985, ~1895^{d,f}
$Mo(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2)$	1964, 1847^c	

[a] For H_2 complex; ν(CO) bands near 1865 cm^{-1} (see Figure 7) reported in ref 7 were due to $M(CO)_4(PCy_3)_2$ impurity. [b] For dihydride species in equilibrium. [c] Nujol mull. [d] Toluene solution. [e] Hexane solution. [f] Lower frequency bands obscured or not observed.

culated from an exponential fit of a plot of peak integral vs. time. The large difference in T_1 between the hydrogen complex and the hydride species allowed the hydride signals to be observed selectively. A 180-τ-90 pulse sequence was used to selectively null the hydrogen signal. τ was set to 2.8 ms (T_1 ln 2). ^{31}P-decoupled ^{1}H NMR spectra were obtained by observing the protons through the ^{1}H-decoupler coil of a standard broad-band probe and applying a low-power (0.2 W) CW radio frequency field through the observe coil. The radio frequency field was supplied by a home-built decoupler which included a synthesizer, a broad-band amplifier (Tron Tech), and a selective frequency amplifier (Henry Radio). The external synthesizer was locked to the spectrometer.

Vibrational Spectroscopy. IR samples (Nujol mulls between CsBr windows) and Raman samples (powdered solid in melting point capillaries sealed with epoxy) were prepared in a glove bag purged with argon to which was added ~10–20% hydrogen on the final fill. Solution IR cells equipped with septum stoppers were filled under hydrogen with use of syringe techniques. Raman spectra were obtained on a SPEX Model 1403 $^3/_4$-m double monochromator, using the 5682-Å line of a Kr laser (~1 mW power). Spectra were signal averaged on a Nicolet 1180E Raman data collection system.

Results and Discussion

Synthesis and Properties of $M(CO)_3(PR_3)_2(H_2)$. The complexes *mer,trans*-$M(CO)_3(PR_3)_2(H_2)$ (**1**) were initially prepared by adding hydrogen gas at 1 atm to solutions of the formally 16-electron species, $M(CO)_3(PR_3)_2$ (M = Mo, W; R = *i*-Pr, Cy).[5b,7] The distinct color change from deep purple to yellow signaled adduct formation, and for R = Cy, **1** precipitated as yellow microcrystals from toluene within minutes. Since $M(CO)_3(PR_3)_2$ contains intramolecular three-center M···H—C interactions,[5b] the H_2 essentially displaced an "agostic" C–H group. A more convenient synthesis directly from available reagents gave **1** (or the D_2 or HD isotopomers) in 60–95% yields (eq 1). The high

$$M(\eta^6\text{-cycloheptatriene})(CO)_3 + 2PR_3 \xrightarrow[\text{toluene}]{H_2} M(CO)_3(PR_3)_2(H_2) + C_7H_8 \quad (1)$$

solubility of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ necessitated the use of hexane solvent. Whether due to high solubility or instability, $Mo(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ could not be obtained as a solid, although color changes indicated H_2 coordination. As was found for syntheses of $M(CO)_3(PR_3)_2$,[5b] reaction 1 succeeded only for R = *i*-Pr, Cy, or combinations thereof. The PCy_3 complexes are sparingly soluble while those for PCy_2-*i*-Pr are moderately soluble. IR carbonyl frequencies are given in Table I; two bands are observed as for other complexes of the type *mer,trans*-$M(CO)_3(PR_3)_2L$.[5b] The H_2 complexes, like their $M(CO)_3(PR_3)_2$ precursors,[5b] generally contain small percentages of $M(CO)_4(PR_3)_2$ impurity formed by disproportionation and/or minor air-oxidation.

In all complexes, the H_2 is quite labile, and H_2-enriched atmospheres are necessary for handling and long-term storage. The stability of **1** toward H_2 loss parallels phosphine size (PCy_3 > PCy_2-*i*-Pr > P-*i*-Pr_3), with W > Mo. $Mo(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2)$ partially dissociates in aromatic solvents even in the presence of excess H_2. Bulk loss of H_2 from solid **1** is slow at 20 °C (P_{dissoc}: ~10 Torr for M = W, R = *i*-Pr and ~1 Torr for M = W, R = Cy), but the H_2 can be quantitatively removed in toluene at 25–50 °C to give $M(CO)_3(PR_3)_2$ by flushing with argon or exposure to partial vacuum. The H_2 ligand is readily displaceable by virtually any other ligand or donor solvent *sterically* capable of coordinating to $M(CO)_3(PR_3)_2$. For example, exactly as found for $W(CO)_3(PR_3)_2$,[5b] $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ reacted with primary alkyl amines to give $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(RNH_2)$ but not with secondary or tertiary amines. Presumably, steric crowding by the bulky phosphines is a limiting factor, especially for weaker ligands such as amines, THF, etc.

Reactions of H_2 Complexes; $H_2/D_2 \leftrightarrow$ HD Exchange. Facile exchange of the H_2 ligand with D_2 occurs in solution, and most interestingly, complete *equilibration of H_2, HD, and D_2 species eventually occurs for mixtures of H_2 complex and D_2 (and vice versa)*. The isotopic exchange involves neither solvent nor phosphine alkyl groups, and in fact, it takes place *even in the solid state* (20 °C, 1 atm, ca. 1–2 week). The formation of HD clearly indicates that the H–H bond is being cleaved, by an as yet unknown mechanism. Since the reaction occurs for solid–gas mixtures, transitory phosphine or CO dissociation is precluded. Isotopic scrambling also occurs within the HD complexes themselves, and NMR indicated that a solution of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(HD)$ equilibrates within days to a mixture of H_2, HD, and D_2 isotopomers. The above results are in contrast to the situation for hydrides such as $[IrH_2(CO)_2(PMePh_2)_2{}^+]$[2b] or even the molecular hydrogen complex $Cr(CO)_5(H_2)$,[10k] wherein no HD is formed. However, HD was recently reported to be formed both from $[CpRu(PPh_3)(t\text{-}BuNC)(H_2)]^+$ and D_2 in CH_2Cl_2[10j] and in thermal H_2/D_2 exchange reactions of $Cr(CO)_4(H_2)_2$ in liquid xenon at −70 °C.[10k] The latter result implies that the simultaneous coordination of two dihydrogen molecules to the same metal center facilitates exchange. Lastly, exchange of solid $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ with CH_4 does not occur.

Since the H_2 ligand is so labile, studies of reactions of **1** other than the above have been limited. Phosphine exchange does occur, and reaction of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ with excess PCy_3 for 2 days precipitates $W(CO)_3(PCy_3)_2(H_2)$ in 37% yield. Despite their bulkiness, the phosphine ligands apparently compete with the H_2 to form trisphosphine complexes, $M(CO)_3(PR_3)_x(PR'_3)_{3-x}$. Extremely crowded molecules such as $Mo(CO)_3(PCy_3)_3$ have indeed been reported to exist in equilibrium with $Mo(CO)_3(PCy_3)_2$ in the presence of large excesses of PCy_3.[14]

The H_2 complexes were found to be inactive in catalyzing hydrogenation of ethylene under mild conditions (toluene, 1 atm, 20 °C), presumably because of limited available coordination sites. Photochemical experiments directed toward attempts to cleave the H–H bond were carried out. However, photolyses of solutions of **1** (M = W; R = *i*-Pr, Cy) with unfiltered 200-W Hg lamp radiation produced large quantities of $W(CO)_4(PR_3)_2$ since dissociated CO readily displaced the H_2 ligand. ^{1}H NMR of the residues after solvent removal for R = *i*-Pr showed several weak resonances apparently due to hydridic protons. However, the low yields (<5%) of the products of interest made isolation difficult. Careful experiments with radiation at specific wavelength will be necessary to productively investigate the photochemical reactivity of the H_2 ligand. In this regard, the electronic spectrum of **1** (R = *i*-Pr) in toluene showed a band at 364 nm (ϵ = 1200), presumably related to the W–H_2 interaction since it shifted to 395 nm upon replacement of H_2 by SO_2 (spectra of $W(CO)_3(PCy_3)_2$ showed no bands in this region[5b]).

Vibrational Spectroscopic Studies. Infrared spectroscopy provided the first hint that **1** indeed contained coordinated dihydrogen rather than hydride ligands. Bands for hydride complexes generally occur in the regions 700–900 cm^{-1} (δ(MH)) and 1700–2300 cm^{-1} (ν(MH)). However, M–H bands for the Nujol mull spectra of **1** (M = W) were readily located near 1570, 950, and 465 cm^{-1} and shifted appropriately upon deuterium substitution (Figure 1). Six fundamentals (ν(HH), $\nu_a(MH_2)$, $\nu_s(MH_2)$, and three $\delta(MH_2)$) are expected for η^2-H_2 binding, and all have been observed (Table II); the above three frequencies correspond to ν_a, ν_s, and one of the δ modes, respectively.[15] The tungsten

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(14) Nolan, S. P.; Hoff, C. *J. Organomet. Chem.* **1985**, *290*, 365.

Table II. Vibrational Frequencies (cm^{-1}) for $M(CO)_3(PR_3)_2(X_2)$ Complexes[a]

	M = W; R = Cy			M = W; R = *i*-Pr			M = Mo; R = Cy		M = Mo; R_3 = Cy_2-*i*-Pr		M = W; R_3 = Cy_2-*i*-Pr	
	$X_2 = H_2$	HD	D_2	H_2	HD	D_2	H_2	D_2	H_2	D_2	H_2	D_2
$\nu(XX)$	2690[b]	2360	~1900[c]	2695[b]	2360			2180				
$\nu(MX_2)$	1575	~1350[d]	~1140[d]	1567	~1350[d]	~1140[d]		1030[d]		~1030[d]	1570	~1140[d]
$\nu_s(MX_2)$	953[e]	791	703[e]	953	793	704	885[e]	649[e]	~870[d]		937	695
$\delta(MX_2)$			442			444		429		435		447
$\delta(MX_2)$	~462[d]		319	465		312	~471[d]	325	~465[d]	325	456	325

[a] IR frequencies (Nujol mull) unless noted otherwise. In general, bands not observed were obscured. [b] Observed for perdeuteriophosphine complex. [c] Observed in Raman only. [d] Partially obscured; band positions were approximated. [e] Observed in both IR and Raman (Raman spectra of PCy_2-*i*-Pr complexes were not studied).

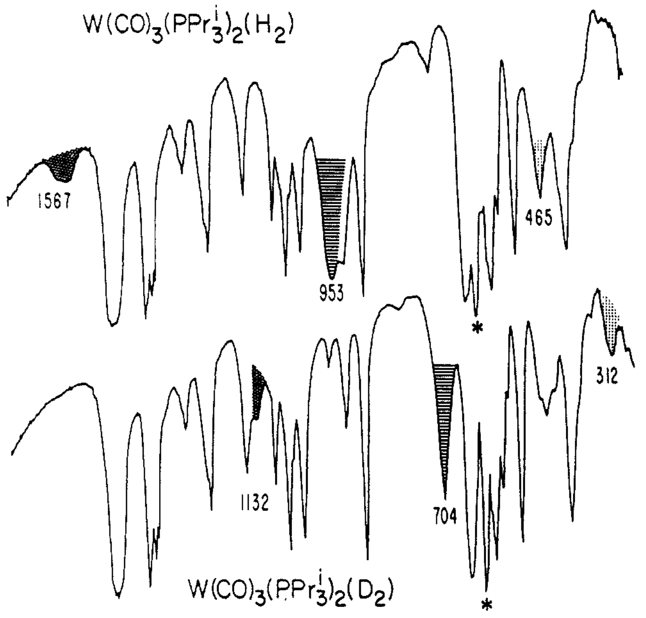

Figure 1. Nujol mull IR spectra of H_2 and D_2 complexes.

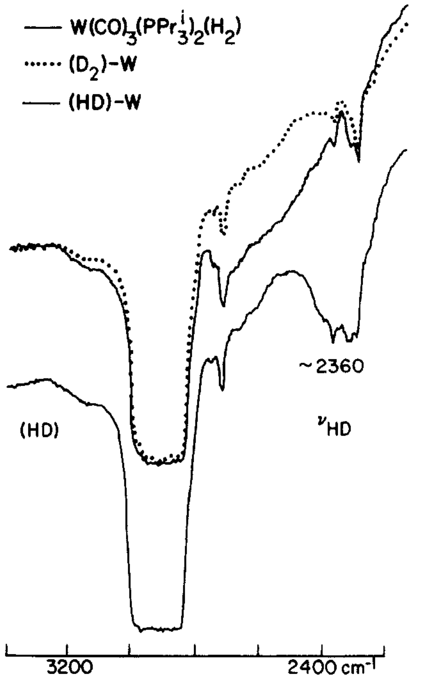

Figure 2. Nujol mull IR spectra of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(HD)$ and its isotopomers showing ν(HD). A partially obscured broad feature due to ν(HH) can also be discerned.

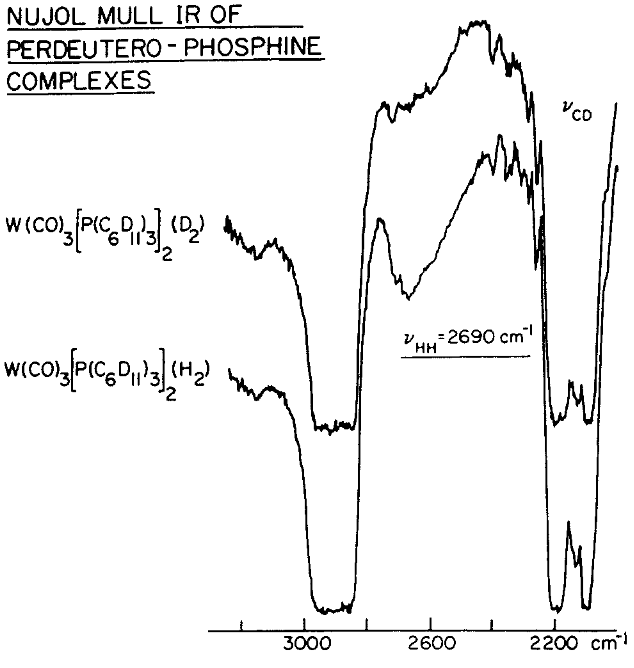

Figure 3. Nujol mull IR of $W(CO)_3[P(C_6D_{11})_3]_2(H_2)$ and D_2 species, showing ν(HH).

complexes gave more intense bands than the Mo species. The modes of most interest, ν(HH) and ν(DD), were initially not observed due to obscuration in the IR by ν(CH) and ν(CO), respectively. However, a broad, weak band at ca. 2360 cm^{-1} was located for $W(CO)_3(PR_3)_2(HD)$ and was clearly attributable to ν(HD) (Figure 2). The use of fully deuterated phosphines enabled unobscured observation of similar bands near 2690 cm^{-1} due to ν(HH) in $W(CO)_3[P(C_6D_{11})_3]_2(H_2)$ (Figure 3) and the $P(i\text{-}C_3D_7)_3$ analogue. These bands were not observed in Raman experiments, possibly because of experimental factors (low laser power (1 mW) was necessary to prevent sample decomposition and, curiously, cooling to −196 °C led to *increased* instability[16]). However, a weak, broad feature at ca. 1900 cm^{-1} was observed in the Raman of $W(CO)_3(PCy_3)_2(D_2)$ assignable to ν(DD) intensified by coupling with the nearby CO stretches. The positions of these bands are ca. 1500 cm^{-1} lower than those in the Raman spectra and induced infrared spectra of free H_2 and HD.[17] The broadness (ca. 150 cm^{-1} half-widths) indicates rotational motion of the H_2, in accord with NMR and inelastic neutron scattering evidence (see below). Similar broad bands (ν(HH) ~ 2700–3100 cm^{-1}, ν(DD) ~ 2200 cm^{-1}) have been located for liquid xenon solutions of $M(CO)_5(H_2)$ (M = Cr, Mo, W), $Fe(CO)(NO)_2(H_2)$, and $Co(CO)_2(NO)(H_2)$.[10b,g,k] ν(HH) for the Mo complex was reported[10k] to be 3080 cm^{-1}, 319 cm^{-1} higher than for $W(CO)_5(H_2)$, showing the large dependence of this mode on the metal. Thus, for $Mo(CO)_3(PCy_3)_2(H_2)$ the HH stretch is undoubtedly obscured by ν(CH) near 3000 cm^{-1}, especially since ν(DD) for the D_2 isotopomer was located near 2180 cm^{-1} as a typically broad, weak band.

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(15) An alternative description of the symmetric and antisymmetric stretching vibrations has been mentioned in a footnote in ref 10k. The motions corresponding to the lower frequency modes were not described, however.

(16) Swanson, B. I.; Kubas, G. J.; Eckert, J., manuscript in preparation.

(17) (a) Teal, G. K.; MacWood, G. E. *J. Chem. Phys.* **1935**, *3*, 760. (b) Warren, J. A.; Smith, G. R.; Guillory, W. A. *Ibid.* **1980**, *72*, 4901 and references therein.

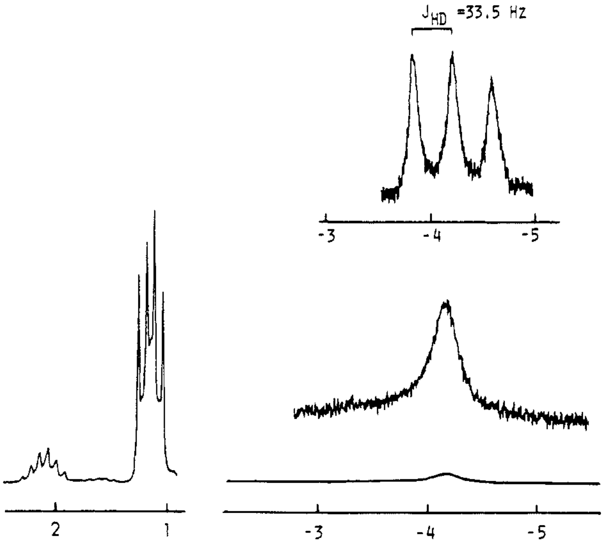

Figure 4. ^{1}H NMR (90 MHz, toluene-d_8, 35 °C) of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ (lower) and HD isotopomer (upper); Me_4Si reference.

The relatively weak, broad asymmetric $M-H_2$ stretch near 1570 cm^{-1} was not observed in the Raman nor for the Mo complexes. A strong symmetric $M-H_2$ stretch at 870–955 cm^{-1} showed clearly in both IR (Figure 1) and Raman spectra of all complexes, shifting down to 649–704 cm^{-1} for the D_2 isotopomers. Note that an entirely new set of band positions was located for the HD complexes, intermediate to those of the H_2 and D_2 species (Table II). This is further evidence for molecular binding since H–M–D species display stretching bands superimposable with a mixture of H–M–H and D–M–D species.[18]

In addition to the deformation mode near 465 cm^{-1}, a second $M-H_2$ deformation probably lies in the 600–650-cm^{-1} region. Although the latter is not directly observable, perturbations (ca. 10-cm^{-1} shifts to lower frequency) of an IR band near 625 cm^{-1} (probably an M–C–O deformation, noted by an asterisk in Figure 1) upon deuteration are evidence for a $M-H_2$ mode in this region. Furthermore, a weak IR feature at 430–450 cm^{-1} can be discerned in the spectra of $M(CO)_3(PR_3)_2(D_2)$ (Figure 1), which is not present in the spectra of the H_2 or HD complexes. This very probably is the second $\delta(MD_2)$ mode, since the calculated isotopic shift corresponds well with a $\delta(MH_2)$ mode in the region 608–636 cm^{-1}. Inelastic neutron scattering experiments[16] indicate that a third deformation mode, possibly the expected torsional mode, is present near 330 cm^{-1} in $W(CO)_3(PCy_3)_2(H_2)$. Regardless of band assignment, the important consideration is that organometallic metal hydride complexes do not exhibit bands in these low-frequency regions, lending support to the η^2-H_2 coordination geometry. It is interesting to compare our system with "ligand-free" complexes, MnH_2 and FeH_2, synthesized in low-temperature matrices by Ozin and McCaffrey, which also exhibit $\delta(MH_2)$ in the 300–400-cm^{-1} range (and $\nu(MH_2)$ at 1565–1660 cm^{-1}).[19] Despite these low values, other spectroscopic evidence indicates that these complexes are almost certainly dihydrides rather than molecular H_2 complexes.[19] In contrast, the ligand-free $Pd(H_2)$ complexes were found to contain molecular coordination and possessed $\nu(MX_2)$ (X_2 = H_2, HD, D_2) remarkably similar to $W(CO)_3(PR_3)_2(H_2)$.[10h] $Fe(CO)(NO)_2(H_2)$ and $Co(CO)_2(NO)(H_2)$ displayed these bands at somewhat lower frequencies ($\nu_a(MH_2) \sim 1350$ cm^{-1}, $\nu_a(MD_2) \sim 1000$ cm^{-1}, and $\nu_s(MH_2) \sim 870$ cm^{-1}), similar to those for $Mo(CO)_3(PCy_3)_2(H_2)$.[10g] Low-frequency deformational modes were not observed for these complexes, but a mode at 315 cm^{-1} was found for $Pd(\eta^2\text{-}H_2)$.[10h]

^{1}H NMR Studies of the H_2 Complexes. The ^{1}H NMR spectra of hydrocarbon solutions of **1** under H_2 atmosphere display PR_3 signals plus a broad resonance due to the H_2 ligand in the range −3 to −4.5 ppm (Figure 4). The δ-values (Table III) are comparable to those found for group 6 hydrides, e.g., $WH_4(PEt_3)_4$.[20] However, the H_2 signals for **1** are much broader (fwhm >24 Hz), and no coupling to ^{31}P or ^{183}W is resolved. This situation has also been observed for other reported H_2 complexes.[5c,10d,e,j] Variable-temperature studies of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ in hexane or toluene-d_8 at 90 and 200 MHz showed broadening of the line width of the H_2 signal from +60 to −85 °C. For example, the width at half-maximum increased from 15 to 40 Hz over the range +60 to −50 °C for hexane solutions (90 MHz; slightly broader in toluene). The signals for the PCy_2-i-Pr and PCy_3 analogues were even broader, with widths up to 200 Hz. The broad line widths over such a large temperature range possibly result from a combination of effects, including exchange of free and coordinated H_2, molecular motion (e.g., rotation) of the H_2 ligand (see below), and dipolar interaction between the two closely separated hydrogen atoms.

Table III. ^{1}H NMR Positions for the H_2 Ligand and for Hydrides in Equilibrium[a]

compound	T, °C	$\delta(H_2)$ [J(HD), Hz] {fwhm}[b]	$\delta(H^-)$ [J(PH), Hz] {fwhm}[b]
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$[c]	60	−4.05 s {15}	
	35	−4.24 s {24}	
	−36	−4.50 s {27}	−3.69 t [38]
	−50	−4.50 s {40}	
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$[d]	35	−4.21 s {27}	
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$[e,f]	65	−3.96 s {13}	
	54	−4.08 s {67}	
	25	−4.48 s {48}	−3.68 t [38] {29}
	−37	−4.52 s {86}	
	−71	−4.50 s	−4.93 s,[g] −2.40 s {113}
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(HD)$[e,f]	65	−4.27 s {61}	
	25	−4.55 t [34][h] {10}	−3.69 t [38] {29}
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(HD)$[d]	35	−4.24 t [34][h] {8}	
$W(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2)$[d]	35	−3.90 s {60}	−3.15 t [38] {15}[j]
	25[f]	−3.95 s {130}	−3.18 t [36] {35}[j]
$Mo(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2)$[i]	35	−3.13 s {27}	
$W(CO)_3(PCy_3)_2(H_2)$[d,f]	25	−3.85 s {200}	−3.03 s {80}[j,k]

[a] In ppm. 90 MHz unless noted. Integration of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ signals showed i-Pr/H_2 = 22 (theory: 21). [b] Full width at half half maximum. [c] In hexane. [d] In toluene-d_8. [e] In methylcyclohexane-d_{14}. [f] 200 MHz. [g] Broad, obscured by H_2 signal. [h] 1:1:1 triplet. [i] In benzene-d_6, partially dissociated. [j] Intensity ratio of H_2/hydride signals: ~70:30. [k] Signals are broad and unresolved.

The ^{1}H NMR spectrum of the monodeuterated complex $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(HD)$ provides unequivocal evidence for direct H–H bonding in the η^2-H_2 ligand. The signal at −4.2 ppm is split by spin **1** deuterium into a 1:1:1 triplet with J(HD) = 33.5 Hz (Figure 4). This value of J is an order of magnitude larger than that found for compounds containing nonbonded H and D atoms and is 77% of the value of J(HD) for HD gas, 43.2 Hz.[21] Thus, since the magnitude of the coupling constant is a good measure of the bond order here, the H–D bond is weakened on coordination. The line width of the HD resonances (Table III) is considerably less broad than that for the H_2 signal, consistent with reduced dipolar broadening. Clearly ^{1}H NMR spectroscopy of HD-substituted complexes is an excellent diagnostic for molecular hydrogen coordination, as initially reported in our communication[5a] and subsequently confirmed in $Mo(CO)(dppe)_2(HD)$[5c] and by Crabtree,[10d] Morris,[10e] and Conroy-Lewis[10j] in their complexes (J(HD) = 28.6–34 Hz). However, this criterion is inapplicable in highly fluctional H_2 complexes that also contain classical hydride

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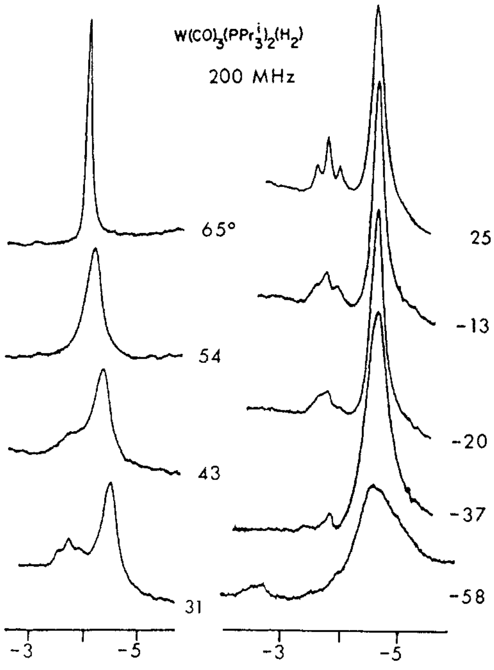
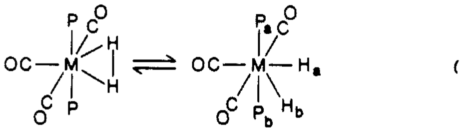


Figure 5. Variable-temperature ^1H NMR (200 MHz, methylcyclohexane-d_{14}) of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$; Me_4Si reference.

ligands,[10d,e] and Crabtree has proposed a ^1H NMR T_1 criterion.[10d,i] T_1 and other NMR measurements on $M(CO)_3(PR_3)_2(H_2)$ are discussed below.

NMR and IR Evidence for Dihydrogen ↔ Dihydride Dynamic Equilibrium. NMR and IR spectroscopy clearly show that solutions of the H_2 complexes contain an equilibrium species and that its structure is consistent with a 7-coordinate *dihydride* $MH_2(CO)_3(PR_3)_2$ produced by H–H bond cleavage:



(2)

^1H NMR spectra of the tungsten complexes display *temperature (and field) dependent secondary signals* at −2.4 to −4.9 ppm in addition to the main, broad, η^2-H_2 signal at −3.8 to −4.5 ppm (Table III). ^{31}P NMR (discussed below) also shows a second set of weaker resonances. The experimental evidence indicates that these new, minor signals are due to the equilibrium dihydride in eq 2, and their relative intensity (ca. 10–30% of the total intensity) varies depending on compound, solvent, temperature, and field. At 25 °C and 200 MHz, the ^1H NMR signal for the dihydride species (R_3 = i-Pr_3 or Cy_2-i-Pr) shows a 1:2:1 triplet pattern (Figure 5). The splitting was demonstrated to be due to ^{31}P coupling ($J(PH)$ = 38 Hz) by ^{31}P decoupling experiments (H_a and H_b, and P_a and P_b, are equivalent at 25 °C due to fluxionality; see below). This is significant because all H_2-ligand signals reported thus far *do not* show ^{31}P coupling. Furthermore, the triplet hydride resonance in the spectrum of the *HD isotopomer* (Figure 6) displays no resolvable HD coupling, which is as expected for a hydride–deuteride complex ($J(HD)$ less than 2 Hz), whereas the main signal due to the η^2-HD does show the expected large HD coupling. This (and T_1 data below) rules out formulation of the equilibrium species as an isomeric H_2 complex. At 90 MHz, the hydride signal for the i-Pr complex is barely visible as a shoulder at 35 °C (Figure 4) but becomes a resolved triplet near −30 °C, demonstrating the large field dependence of the signal. At 300 MHz and 25 °C, the hydride signal is a broad singlet. As can be seen in Figure 5, the hydride and H_2 signals at 200 MHz *coalesce* into a relatively sharp singlet near 65 °C, *indicating fast exchange between dihydride and H_2 forms in* equilibrium 2. The spectrum of the HD complex also shows similar coalescence, but the coalesced signal at 65 °C is not as sharp and the HD coupling becomes unresolvable. The dihydride is *fluctional* and multinuclear NMR spectra at the slow-exchange limit (<−80 °C) are completely consistent with formulation as $WH_2(CO)_3(PR_3)_2$, as discussed below.

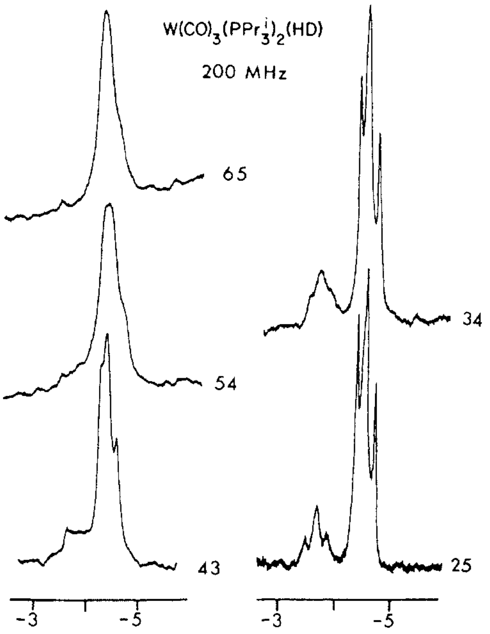


Figure 6. Variable-temperature ^1H NMR (200 MHz, methylcyclohexane-d_{14}) of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(HD)$; Me_4Si reference.

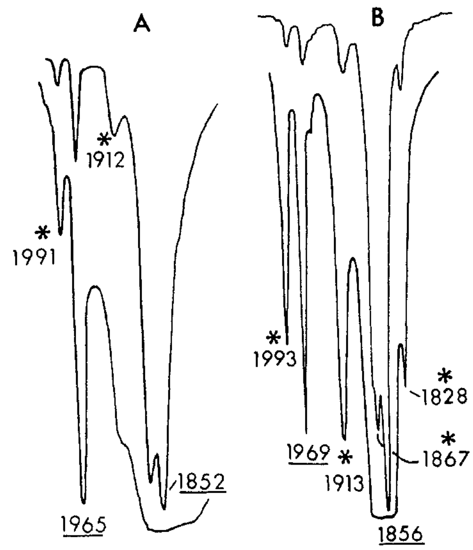


Figure 7. IR spectra of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ in the carbonyl region: (A) Nujol mull; (B) hexane solution. Underlined frequencies are due to H_2 complex and bands with asterisks are due to dihydride; band at 1870 cm^{-1} in (A) is due to a very intense mode of $W(CO)_4(P\text{-}i\text{-}Pr_3)_2$. The weak dihydride bands in (A) are due to dissolved complex ($W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ is partially soluble in Nujol).

Further evidence for equilibrium 2 includes solution IR spectra of the H_2 complexes and their HD and D_2 isotopomers. All of the complexes, including $Mo(CO)_3(PCy_3)_2(H_2)$, show additional (up to four) $\nu(CO)$ bands not present in the spectra of the solid complexes, clearly indicating that an equilibrium species (and not an impurity) is present. These bands (Figure 7; Table I), assignable to the dihydride complex, maintain their relative ratios to the two main H_2-complex bands when the H_2 complex is partially decomposed (e.g., photochemically), consistent with dynamic equilibrium behavior. The $\nu(CO)$ bands are similar to those in 7-coordinate $MoCl_2(CO)_3(PEt_3)_2$,[22] which possesses a CO-capped octahedral geometry with essentially trans phos-

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[22] Westland, A. D.; Muriithi, N. *Inorg. Chem.* **1973**, *12*, 2356.

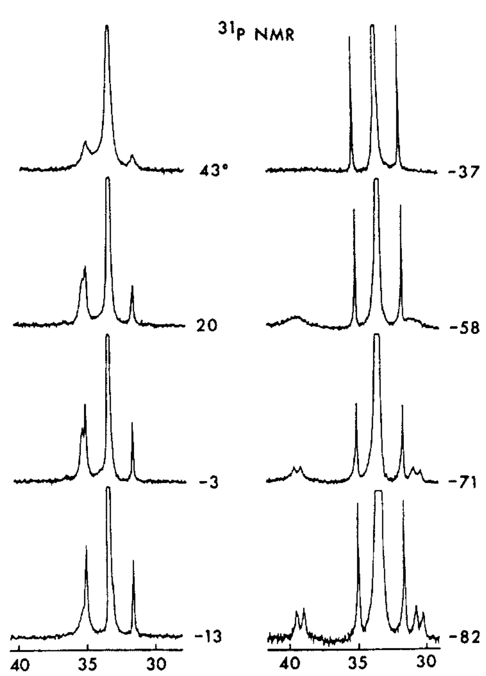

Figure 8. Variable-temperature $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-d_8) of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$, showing ^{183}W satellites (14% abundance) and hydride complex signal (ca. 11% of main signal) as a shoulder near 35 ppm (20 °C); chemical shifts are referenced to $W(CO)_4(P\text{-}i\text{-}Pr_3)_2$ impurity signal at 25.9 ppm (not shown).

phines.[23] The dihydride, $MH_2(CO)_3(PR_3)_2$, proposed in (2) may possess a similar structure, with one of the hydrides or a CO in the capping position.

^{1}H NMR T_1 Experiments. In order to further establish the existence of the η^2-H_2 complex and its equilibrium with the hydride form, the spin-lattice relaxation times (T_1) for the η^2-H_2 and hydride proton signals were determined. The ^{1}H NMR T_1 values were estimated at −80 °C in toluene-d_8 by using the inversion-recovery method[24] and are 4 ms for the η^2-H_2 protons and 1.7 s for the hydrides. As Crabtree[10d,i] has pointed out, in H_2 complexes, the dominant relaxation mechanism is the H–H dipolar interaction, and the short H–H intranuclear distance results in an extremely short T_1 (~5–20 ms). Because of the r^{-6} dependence of $1/T_1$ and the increased H–H distance, the hydride species will have a significantly longer T_1. The 425-fold difference in the T_1's observed here is larger than that reported for the Ir complexes containing both hydride and H_2 ligands[10d,i] and is consistent with the equilibrium species being a hydride. This large difference in the T_1's could be explained if the internuclear distance were increased from 0.82 Å in the η^2-H_2 complex (as determined by neutron diffraction) to 2.2–2.3 Å, which is in the range of nonbonded H··H distances in, for example, $WH_6(PPh\text{-}i\text{-}Pr_2)_3$.[25] This assumes that the relaxation is purely dipolar in both species and that the motion contributing to the spin-relaxation in each compound has a similar correlation time. At 25 °C the T_1's are nearly equal (~30 ms), consistent with exchange-averaging of the protons according to equilibrium 2. Thus, on warming the T_1's average more rapidly than do the chemical shifts, consistent with the observations of Crabtree.[10d,i]

Table IV. Multinuclear NMR Data for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$[a]

nucleus	assignment/T, °C	δ [J, Hz]
^1H[b]	P–CH	2.12 sept [6.9][c]
	CH_3	1.14 d of d [6.9][c] [13][d]
$^{31}P\{^1H\}$	25[e]	35.5 s, 33.6 s, 33.6 d [274][f,g]
	−3[j]	35.4 s, 33.4 s, 33.4 d [274][f,l]
	−82[j]	39.5 d [43],[k] 33.4 s, 33.4 d [274],[f] 30.7 d [43][k]
$^{13}C\{^1H\}$[h]	CO[i]	215.6 s
	CO	207.4 m
	P–C	28.9 s
	CH$_3$	20.3 s

[a] Toluene-d_8 solution, 25 °C. [b] 90 MHz, Me_4Si reference. [c] J(HH). [d] ^2J(PH). [e] 121.5 MHz; H_3PO_4 reference. [f] (^{31}P–^{183}W). [g] For the D_2 complex: 35.4 s, 33.4 s, 33.4 d [274]. [h] 75.5 MHz. [i] Trans to H_2. [j] 81 MHz. [k] $J(^{31}P$–$^{31}P)$. [l] Integration showed that the 35.4-ppm peak due to the dihydride is 11% of the total area.

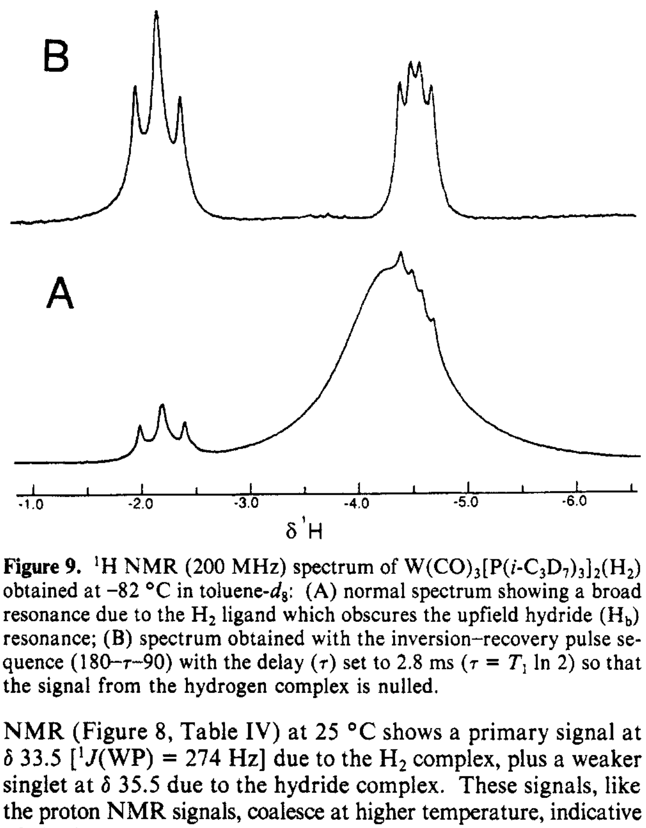

Figure 9. ^{1}H NMR (200 MHz) spectrum of $W(CO)_3[P(i\text{-}C_3D_7)_3]_2(H_2)$ obtained at −82 °C in toluene-d_8: (A) normal spectrum showing a broad resonance due to the H_2 ligand which obscures the upfield hydride (H_b) resonance; (B) spectrum obtained with the inversion-recovery pulse sequence (180–τ–90) with the delay (τ) set to 2.8 ms ($\tau = T_1 \ln 2$) so that the signal from the hydrogen complex is nulled.

^{1}H and ^{31}P NMR of the Equilibrium Dihydride Complex, $WH_2(CO)_3(P\text{-}i\text{-}Pr_3)_2$. ^{1}H and ^{31}P NMR show that $WH_2(CO)_3(P\text{-}i\text{-}Pr_3)_2$ is stereochemically nonrigid as is commonly found for 7-coordinate species, including $MoI_2(CO)_3$(As–As).[26] $^{31}P\{^1H\}$ NMR (Figure 8, Table IV) at 25 °C shows a primary signal at δ 33.5 [^1J(WP) = 274 Hz] due to the H_2 complex, plus a weaker singlet at δ 35.5 due to the hydride complex. These signals, like the proton NMR signals, coalesce at higher temperature, indicative of the interconversion between hydrogen and hydride species. Lowering the temperature to the slow-exchange limit shows that *both the hydride and phosphorus ligands in the fluxional hydride species are chemically inequivalent.* The low-temperature $^{31}P\{^1H\}$ NMR spectrum (Figure 8) contains, in addition to signals from the hydrogen complex, two signals (δ 39.5 and 30.7) which appear as doublets with ^2J(PP) = 43 Hz, showing the inequivalency of the phosphines. Likewise, the 200-MHz ^{1}H NMR of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ at 25 °C contains a minor triplet from the hydride species, which upon cooling broadens, disappears, and reappears in the slow exchange limit as separate resonances for each of the two hydride sites (Figure 5) (H_a and H_b). The spectrum at −58 °C shows one of the new peaks (H_a) at −2.4 ppm. However, the latter is broad and unresolved and furthermore the signal from H_b is obscured by the broad resonance from the hydrogen complex. Thus a second series of experiments was carried out, using $W(CO)_3[P(i\text{-}C_3D_7)_3]_2(H_2)$ (to minimize potential interference from phosphine protons in selective decoupling experiments described below) and lower temperatures. Also, toluene-d_8 instead of methylcyclohexane-d_{14} was used as solvent since the dynamic processes appeared to be slower in this medium. As can be seen in Figure 9A, two hydride signals with resolvable ^{31}P coupling were observed at −82 °C. Furthermore, the large difference in

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(25) Gregson, D.; Mason, S. A.; Howard, J. A. K.; Spencer, J. L.; Turner, D. G. *Inorg. Chem.* **1984**, *23*, 4103.

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Table V. NMR Parameters for $W(CO)_3[P(i\text{-}C_3D_7)_3]_2(H_2)$

conditions	nucleus	δ^a	fwhm, Hz	T_1, s	J, Hz
		H_2 Species			
toluene-d_6, −92 °C	H_2	−4.3	196	4×10^{-3}	
	P	33.5			$^1J(WP) = 273$
25 °C	H_2	−4.3	173	31×10^{-3}	
	P	33.6			$^1J(WP) = 274$
		Hydride Species			
−92 °C	H_a	−2.15	2.5	1.67	$^2J(H_aP_a) = 39$ $^2J(H_aP_b) = 44$
	H_b	−4.50	2.5	1.67	$^2J(H_bP_a) = 38$ $^2J(H_bP_b) = 21$
	P_a	30.8			$^2J(P_aP_b) = 43$
	P_b	39.5			
25 °C	H_a	−2.15		35×10^{-3}	$^2J(H_aP) = 40$
	H_b	−4.5			
	P	35.5			

[a] ^1H chemical shifts are reported in ppm downfield from Me_4Si and are referenced internally to the residual proton resonance from the methyl group (2.09 ppm) of toluene-d_8. ^{31}P shifts are reported in ppm downfield from external phosphoric acid.

T_1's allowed the H_2 signal to be nulled, making possible clear observation of the hydride doublets at −4.5 ppm (Figure 9B). In this experiment, an inversion–recovery pulse sequence was used and the inverted magnetization was allowed to recover until the hydrogen resonance was nulled ($t = \ln 2(T_1)$); then data were acquired after a $\pi/2$ observe pulse. During the delay ($\tau = 2.8$ ms), the hydride magnetization recovered to 99.6% of its original value so the hydride signals were observed unobscured by the H_2 signal. The NMR data are summarized in Table V. Integration of these signals showed that the equilibrium mixture in toluene-d_8 contains ~15% of the dihydride species.

^1H–^{31}P Coupling and Selective Decoupling Experiments. At −92 °C in toluene-d_8, the dihydride yielded ^1H NMR signals, observed by the inversion–recovery null method, that are well-resolved four line patterns (doublet of doublets) because of ^1H–^{31}P coupling (Figure 10A). In addition to the ^1H–^{31}P coupling, the phosphorus nuclei are homonuclear coupled so that the ^{31}P NMR signals (Figure 10D) appear as complex multiplets. The "quartet coupling pattern" at 30.8 ppm (P_a) results from equal coupling (~40 Hz) to both hydride protons and to the other phosphorus atom (P_b). P_b appears as "triplet of doublets" because one of the ^1H–^{31}P coupling constants is significantly smaller (~20 Hz) than the other two coupling interactions (~40 Hz). The coupling constants are reported in Table IV. The assignment of these complex coupling patterns was confirmed by selective heteronuclear decoupling. H_a and H_b ^1H NMR signals collapsed to the predicted doublets when the low-power CW radio frequency field was applied at the resonance frequency of P_a (Figure 10B) or P_b (Figure 10C). Selective irradiation of H_a (Figure 10E) yields a ^{31}P NMR spectrum in which P_a is a triplet coupled equally to H_b. Since the H_b–P_b and P_a–P_b coupling constants are different, P_b appears as a four-line pattern. As predicted, P_a and P_b are triplets when H_b is selectively decoupled (Figure 10F). Selective ^1H–^{31}P decoupling demonstrates that the minor signals in both the ^1H and ^{31}P spectra all result from the same equilibrium species. At −90 °C, the expected ^1H–^1H coupling (ca. 3–9 Hz) between the hydrides is absent and is probably averaged by exchange between hydride sites. The nearly equivalent coupling of H_a to both phosphine ligands is consistent with one hydride being positioned symmetrically with respect to the phosphine ligands; clearly the other hydride is asymmetrically positioned. Note that although 7-coordinate geometries other than capped octahedral may be compatible with these results, a *6-coordinate* octahedral structure (e.g., $WH_2(CO)_2(PR_3)_2$) is ruled out. The phosphines are sterically constrained to be mutually trans and thus would be chemically equivalent. A dicarbonyl dihydride produced by CO loss is also incompatible with the chemistry of the system.

Solid-State ^2H NMR of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$. In order to determine whether the H_2 ligand undergoes significant molecular motion, e.g., rotation, a deuteron quadrupole echo experiment was carried out on the D_2 isotopomer at ambient temperature. The spectrum obtained is consistent with an axially symmetric motionally averaged site for each deuteron. The full width of the quadrupole pattern (taken to be between the singularities) is 62 kHz which reduces to a quadrupole coupling constant of 124 kHz. The spin-lattice relaxation time T_1 is a fraction of a second. Both of these numbers indicate that there is significant large angle molecular motion of the D–D unit. The 62-kHz splitting is to be contrasted with a value of 120 kHz for solid polyethylene which has little or no large angle motions.[27] Also the short T_1 value is a striking demonstration of the motion since T_1 for $LiAlD_4$, which we tried as a standard compound for deuterium NMR, is about 7.5 min due to lack of large-angle motion. The only estimate on the rate of motion obtainable from the data is that it must be faster than the quadrupole splitting before averaging (ca. 130 kHz).

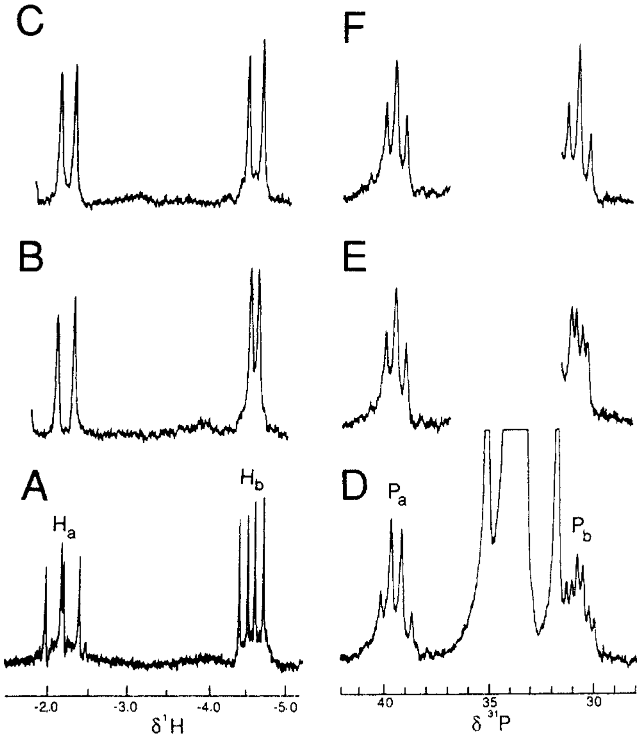

Figure 10. Selectively heteronuclear decoupled ^1H (A, B, C) and ^{31}P (D, E, F) NMR spectra of $W(CO)_3[P(i\text{-}C_3D_7)_3]_2(H_2)$ obtained at −92 °C in toluene-d_8. ^1H spectra were collected by using the inversion–recovery method to null the proton signal from the H_2 complex. The coupled ^1H (A) and ^{31}P (D) spectra each contain two multiplets from the hydride species; the multiplets are labeled H_a (−2.15 ppm), H_b (−4.5 ppm), P_a (39.5 ppm), and P_b (30.8 ppm). The ^1H–^{31}P coupling interactions were selectively decoupled by applying a CW radio frequency field at the resonance frequency of P_a (B), P_b (C), H_a (E), and H_b (F) in separate experiments.

The molecular motion of the coordinated H_2 represents another fascinating aspect of the overall, complex, dynamical problem, which in solution also includes exchange between free and coordinated H_2, reversible cleavage of the H–H bond, and fluxionality of the resulting dihydride. Rotational barriers have been determined by INS and will be the subject of future publications.[16]

Conclusions

The discovery of stable molecular hydrogen complexes was unexpected but perhaps is less startling in view of the recent advances in C–H bond activation. The H_2 complexes can be considered to be arrested oxidative addition of H_2 to give H–M–H much like "agostic" M···H–C interactions[28] can be considered to be arrested formation of H–M–C. Complexes with agostic in-

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[27] Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193 and references therein.

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teractions seem to be excellent candidates for H_2 coordination, and $M(CO)_3(PR_3)_2$, $Mo(CO)(dppe)_2$, $[IrH(PPh_3)_2(C_{13}H_8N)]^+$, and the corresponding H_2 complexes afford an unprecedented opportunity to observe both C–H and H–H coordination at a single metal center.[5b,c,10d]

The bonding of H_2 to the metal primarily involves donation of charge from the filled H_2 σ orbital into the empty σ orbital on the WL_5 fragment with some back donation into the H_2 σ^*, as shown in a theoretical post-factum study of H_2 bound to $W(CO)_3(PH_3)_2$.[3a] The calculations indeed predict stable η^2-H_2 coordination rather than oxidative addition. Clearly, a fine balance of steric and electronic factors dictates whether H_2 complexes are stable at ambient temperature or proceed to hydride complexes. Bulky ligands appear to provide steric constraints that inhibit dihydride formation, or at least stabilize the complexes ($Cr(CO)_5(H_2)$, $Fe(CO)(NO)_2(H_2)$, and $Co(CO)_2(NO)(H_2)$ are unstable at room temperature[10a–c,g]). In regard to electronic influences, it is interesting to note that for group 6 systems all of the H_2 complexes contain CO trans to the H_2 while none of the structurally characterized polyhydrides,[25,29] e.g., $MoH_2(PMe_3)_5$,[29a] contain CO or other strong acceptor ligands. The CO ligand decreases back donation into the σ^* H_2 orbital, which otherwise would lead to cleavage of the H–H bond.[3g] Experiments designed to test this influence by using ligand variations are in progress.

The discovery that solutions of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)$ and its analogues contain a significant equilibrium fraction of the dihydride form $WH_2(CO)_3(P\text{-}i\text{-}Pr_3)_2$ is extremely important for several reasons. First of all, it demonstrates that side-bonded dihydrogen complexes are indeed intermediates in "oxidative addition" of hydrogen to metals and not merely novel species. Second, the highly dynamic nature of the equilibrium shows that *hydrogen ligands can readily shift back and forth from classical* (H^-) *to nonclassical* (H_2) *in solution.* The H_2 form predominates in $M(CO)_3(PR_3)_2(H_2)$, but in other hydrogen-containing complexes, equilibria may exist that cover the entire range from classical to nonclassical. Finally, and perhaps most significantly, *these findings indicate that solid-state structures of polyhydrides, even those determined by neutron diffraction, have not been and will not always be reliable indicators of the solution structures. It is quite probable that two or more of the hydrogen ligands of many known polyhydride complexes will prove to be associated as molecular hydrogen ligands in solution, at least to an equilibrium extent.* Recent NMR and chemical evidence[30,31] points to this being true for at least two complexes shown by neutron diffraction to contain well-separated hydrides in the solid state: Cp_2NbH_3[32] and $WH_6(PPh\text{-}i\text{-}Pr_2)_3$.[25] ^1H NMR of the niobium complex displayed unusual temperature and field dependence,[30b] and the absence of diastereotopy of the hydrides in chiral $Cp'CpNbH_3$ has been accounted for[30a] by formulating the complex as $Cp'CpNbH(H_2)$. ^1H NMR T_1 measurements indicated some degree of nonclassical coordination in the tungsten complex.[31a] Complexes such as the above which readily lose H_2 by displacement by neutral donor ligands and/or possess unusually high oxidation states (based on each hydride having a −1 charge) clearly must be considered as potential H_2 complexes. Crabtree has also pointed this out, and our demonstration of the dihydrogen–dihydride equilibria greatly reinforces the viewpoint. Several other complexes, including $RuH_4(PPh_3)_3$,[2e,j] $Ru_3(CO)_8[RN{=}C(R')(R'')C{=}NR](H_2)$,[33] $[RuH_3(PR_3)_4]PF_6$,[2e] and $[IrH_2(CO)_2(PMePh_2)_2]BPh_4$,[2b] have been proposed to contain molecular hydrogen, and $IrH_4(PMe_2Ph)_3^+$ also would appear to.[34] Evidence for dynamic processes involving a *cis*-dihydride ↔ η^2-dihydrogen exchange has recently been reported for $(Cy_2P(CH_2)_nPCy_2)PtH_2$.[35] Recent NMR T_1 measurements on $MH_4(PR_3)_3$ (M = Fe, Ru) support formulation as $MH_2(H_2)(PR_3)_3$.[31] Nujol mull IR spectra[36] of $FeH_4(PR_3)_3$ were reported 15 years ago to contain inexplicable broad, weak bands near 2400 cm^{-1} which now appear to be assignable to ν(HH).[31] Thus, perhaps the truly remarkable feature of molecular H_2 binding lies in the fact that it has been unrecognized or unproven for this long a period.

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Registry No. $W(CO)_3(PCy_3)_2(H_2)$, 104198-75-6; $Mo(CO)_3(PCy_3)_2(H_2)$, 104198-76-7; $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$, 104198-77-8; $W(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2)$, 104198-78-9; $Mo(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2)$, 104198-79-0; $W(CO)_3(PCy_3)_2H_2$, 88211-53-4; $Mo(CO)_3(PCy_3)_2H_2$, 88211-52-3; $W(CO)_3(P\text{-}i\text{-}Pr_3)_2H_2$, 88211-55-6; $W(CO)_3(PCy_2\text{-}i\text{-}Pr)_2H_2$, 104198-80-3; $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$, 104198-81-4; $W(CO)_3(C_7H_8)$, 12128-81-3; $Mo(CO)_3(C_7H_8)$, 12125-77-8; $W(CO)_3(PCy_3)_2$, 73690-56-9; $Mo(CO)_3(PCy_3)_2$, 73690-53-6; $PCy_2\text{-}i\text{-}Pr$, 42758-13-4; PCy_2Cl, 16523-54-9; *i*-PrMgCl, 1068-55-9; $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$, 88211-57-8; $W(CO)_3(PCy_2\text{-}i\text{-}Pr)_2$, 100995-15-1; $Mo(CO)_3(PCy_3)_2(SO_2)$, 73682-36-7; $W(CO)_4(P\text{-i-}pr_3)_2$, 32370-65-3; $W(CO)_4(PCy_3)_2$, 38800-78-1.

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