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Dihydrogen: A Better Ligand Than Water? IR and X-ray Evidence for Aquo Coordination in $W(CO)_3(PR_3)_2(H_2O)$, Thermodynamics of H_2O versus η^2-H_2 Binding, and H_2O/D_2 Isotopic Exchange. Implications on the Biological Activation of Hydrogen

Gregory J. Kubas,*[†] Carol J. Burns,[†] Guru Rattan K. Khalsa,[‡] Lori Stepan Van Der Sluys,[†]
Gabor Kiss,[§] and Carl D. Hoff[§]

Inorganic and Structural Chemistry Group (INC-1), Los Alamos National Laboratory,
Los Alamos, New Mexico 87545, and Department of Chemistry, University of Miami,
Coral Gables, Florida 33124-0431

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Reactions of water with $M(CO)_3(PR_3)_2$ and $M(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ (M = Mo, W; R = Cy (cyclohexyl), *i*-Pr) have been studied in various organic solvents. The products contained reversibly bound H_2O, and infrared studies showed ν(OH) modes at widely varying positions. IR of ^{18}O-labeled complexes and ^1H NMR gave no evidence for hydride or hydroxide ligands, indicating that oxidative addition of water did not occur. NMR of the aquo complexes showed rapid exchange between free and coordinated water at 298 K. The aquo complex $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$ was isolated from THF and structurally characterized. A long W–O distance of 2.320 (5) Å was observed for the reversibly bound H_2O ligand, which also undergoes hydrogen-bonding interactions with both lattice THF and a CO on an adjacent molecule. Water was found to instantaneously displace the dihydrogen ligand in $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ in THF solution to give aquo complexes, but in hexane H_2 remained bound under a H_2 atmosphere. Thermodynamic measurements of the equilibrium $W(CO)_3(PR_3)_2(H_2) + H_2O \rightleftharpoons W(CO)_3(PR_3)_2(H_2O) + H_2$ in THF showed that the ΔH value for binding was 3–4 kcal/mol higher for H_2O. However, a higher entropy change related to hydrogen-bonding interactions between H_2O and solvent resulted in ΔG favoring H_2 coordination at 25 °C by 1–2 kcal/mol. Isotopic exchange of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}D_2)$ with H_2O under a D_2 atmosphere took place in THF, giving $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2O)$. Both the favored binding of H_2 versus H_2O and the latter exchange are relevant to the function of H_2-activating enzymes such as hydrogenase. Crystal data for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$: space group $P2_1/n$, $a = 13.554$ (2) Å, $b = 16.417$ (5) Å, $c = 15.059$ (4) Å, $\beta = 116.24$ (2)°, $Z = 4$.

Introduction

Activation of O–H σ bonds such as those in water and alcohols by transition-metal complexes has not been as systematically studied as that of C–H and H–H bonds. Although the number of examples of H_2O coordinated to 18e organometallic complexes has recently become greater than one might have imagined,[1] water as a ligand in such systems is still viewed as unorthodox. Neutral complexes are actually still rare, with the predominant class of aquo complexes being cationic species, most often derived from complexes with weakly coordinating anions such as BF_4:[1aa]

$$L_nM\text{–}FBF_3 + H_2O \rightarrow [L_nM\text{–}OH_2][BF_4] \quad (1)$$

In many cases, the water ligand was not intentionally introduced but derived from adventitious sources (usually moisture is scrupulously avoided). In these species, positive charge may be delocalized onto the hydrogens of H_2O.[1kk] With regard to *oxidative addition* of H_2O to form hydrido–hydroxo complexes, well-documented examples are sparse,[1q,2] and there is only *one* relevant crystallographic study.[2a,b] In view of the recent discovery of H–H σ-bond coordination,[3] it is appropriate to consider interaction of O–H σ-bonds with organometallic complexes as an area for increased study.

Over a decade ago we had found that the same group 6 transition-metal complexes $M(CO)_3(PR_3)_2$ that reversibly bind H_2[3a] also reversibly bind H_2O (and alcohols) to give "$M(CO)_3(PR_3)_2(H_2O)$" (and "$M(CO)_3(PR_3)_2(ROH)$") (M = Mo, W; R = Cy (cyclohexyl), *i*-Pr).[4] The obvious question arose as to whether the H_2O was (1) bound as a normal aquo ligand (planar or pyramidal), (2) bound in some

Table I. X-ray Data for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\bullet THF$

temp of data collecn, °C	−80
space group	$P2_1/n$
a, Å	13.554 (2)
b, Å	16.417 (5)
c, Å	15.059 (4)
β, deg	116.24 (2)
V, Å^3	3005.6 (2.7)
Z	4
fw	678.49
d(calcd), g/cm^3	1.499
μ(calcd), cm^{-1}	40.593
cryst size, mm	0.30 × 0.35 × 0.25
radiation	Mo Kα (λ = 0.709 30 Å)
scan type; range, deg	ω–2θ; 3–45
F(000)	1384
no. of rflns collected	4033
no. of unique rflns	3631
no. of rflns $F_o^2 > 3\sigma F_o^2$	2688
no. of unobsd rflns	1121
variables	299
R	0.0337
R_w	0.0498
R_{all}	0.0806
GOF	1.791
g, e^{-2}	[4.2 (9)] × 10^{-8}
p	0.04
intens stds	257; −2,10,−3; 8,−4,−1
no. of orientation stds	3
decay, %	none
min/max abs cor	0.66
2θ range for centering, deg	26–32
max Δ/σ in the final least-squares cycle	0.06
highest and lowest peaks in final diff Fourier map, e/Å^3	+0.865, −0.823

[†] Los Alamos National Laboratory.

[‡] Permanent address: Department of Chemistry, Thiel College, Greenville, PA.

[§] University of Miami.

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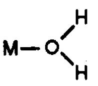
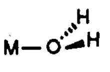
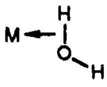
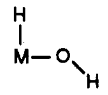
"nonclassical" fashion analogous to η^2-H_2, or (3) cleaved to hydrido–hydroxo ligands:









Independent infrared studies by both our[4a] and Ibers' research groups[5] had indicated that the PCy_3 complexes obtained from toluene solution might be more appropriately formulated as 7-coordinate $MH(OH)(CO)_3(PCy_3)_2$ resulting from oxidative addition of the H_2O. Because of inordinate difficulty in obtaining X-ray-quality crystals, molecular structures of these species have been elusive. We have now obtained suitable crystals of the W–P-*i*-Pr_3 analogue by displacement of coordinated H_2 from W$(CO)_3$(P-*i*-$Pr_3)_2(H_2)$ with H_2O in THF and report its X-ray structure and spectral data here. The H_2O appears to be bound *intact* in an overall octahedral d^6 geometry and shows unprecedented hydrogen bonding with a CO on an adjacent molecule. Although ν(OH) ranged widely in the various products of H_2O reaction with $M(CO)_3(PR_3)_2$, no clear evidence for oxidative addition has been found in these systems. In this regard, infrared studies using isotopic labeling (^{2}H and ^{18}O) were used to resolve ambiguities concerning the three possible structures/moieties that could be present: (a) M–OH_2, (b) MH(OH), and (c) hydrogen-bonded lattice H_2O.

Studies herein also compare the *binding strength of H_2O versus that of η^2-H_2 to $W(CO)_3$(P-i-$Pr_3)_2$ and isotopic exchange between H_2O and D_2*, relevant issues in the biological activation of hydrogen in enzymes such as hydrogenase and nitrogenase. The fact that H_2O–D_2 exchange can occur on $W(CO)_3$(P-*i*-$Pr_3)_2$, which contains only a *single* open coordination site, is significant and presents a mechanistic dilemma similar to that for H_2–D_2 exchange to give HD, observed even over solid $M(CO)_3(PR_3)_2$.[6] The possibility of deprotonation of η^2-H_2 by H_2O in these systems will be discussed.

Experimental Section

Syntheses and handling of the complexes were carried out under argon using Schlenk and glovebag techniques. Reagents were generally used without further purification, and solvents were distilled from Na/K alloy under argon. $H_2{}^{18}O$ (95+%) was obtained from the Mound Facility of Monsanto Research Corp., Miamisburg, OH. The complexes $M(CO)_3(PR_3)_2$,[4a,7] $M(CO)_3(PR_3)_2(H_2)$,[6,8] and $M(CO)_3(PCy_3)_2(H_2O)$[4a] (M = Mo, W; R = Cy, *i*-Pr, cyclopentyl[7b]) were prepared as previously described. Infrared spectra were recorded as Nujol mulls on Perkin-Elmer 683 and 521 instruments, as well as a Bio-Rad FTS-40 FT-IR; NMR spectra were taken on Bruker AM200 and IBM AF250 instruments. ^{2}H and ^{31}P chemical shifts were assigned relative to natural-abundance THF-*d* or toluene-*d* and H_3PO_4, respectively.

Preparation of $W(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$ and the Mo Analogue from Reaction of H_2O with $M(CO)_3(PCy_3)_2$. $W(CO)_3(PCy_3)_2$ (0.319 g, 0.385 mmol) in 4 mL of toluene was treated with 0.1 mL of H_2O under argon. After 30 min of stirring, a yellow-orange solid precipitated, which was collected on a frit, washed with 1:1 toluene–heptane saturated with H_2O, and dried *briefly* in vacuo (or under an argon stream containing water vapor). The yield was 0.30 g (88%), and elemental analysis indicated the presence of two molecules of "lattice" H_2O. Anal. Calcd for $C_{39}H_{72}O_6P_2W$: C, 53.07; H, 8.22; O, 10.88; P, 7.02. Found: C, 53.04; H, 7.92; O, 11.00; P, 7.51. The Mo analogue was prepared in an identical fashion.

Exposure of the complex to dry argon or vacuum either in the solid state or in toluene solution gave almost an immediate darkening of color toward the purple color characteristic of $W(CO)_3(PCy_3)_2$. Preparation of Nujol mull IR samples was done in an argon-filled glovebag containing a crystallization dish sprinked with water. About 1 mol of H_2O/mol of complex was released after 18 h of pumping on the solid, indicating that only partial loss of H_2O occurred.

Preparation of $W(CO)_3$(P-*i*-$Pr_3)_2(H_2O)\cdot$THF and Its Isotopomers from Reaction of H_2O with $W(CO)_3$(P-*i*-$Pr_3)_2(H_2)$ in THF. $W(CO)_3$(P-*i*-$Pr_3)_2(H_2)$ (0.50 g, 0.84 mmol) was dissolved in 2 mL of 1:1 THF–hexane in a 15-mL flask under an H_2 atmosphere, and 40 μL of H_2O was added. The yellow solution immediately became deep red, accompanied by vigorous evolution of H_2 gas. The solution was placed into a freezer in a Dewar so that it could be slowly quiescently cooled. A crystalline orange

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mass of product formed after 1 day, and the complex was collected on a frit under argon, washed with 2:1 hexane–THF, and dried *briefly* in vacuo (the H_2O ligand and lattice THF are quite labile and the complex must be stored and handled so as to avoid their loss). The yield of orange $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$ was ~ 60–70%. Infrared spectra of mull samples (prepared in a glovebag containing water and THF vapor) showed an absorption at 1051 cm^{-1} due to lattice THF (confirmed by X-ray crystallography).

The isotopomers with $H_2{}^{18}O$ and D_2O were prepared in an identical fashion, with the latter formed from $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ under a D_2 atmosphere.

Reaction of H_2O and Its Isotopes with $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ in Hexane. Preparation of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot xH_2O$. $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ (0.227 g, 0.384 mmol) was dissolved in 3 mL of hexane in a 15-mL flask under an H_2 atmosphere, and 40 μL of H_2O was added. When the yellow solution was stirred for about 30 min under H_2, no obvious color change or precipitation occurred. However, when the H_2 was replaced by argon, the color deepened to brown and a yellow-orange precipitate began to form. After further stirring and cooling in a freezer overnight, the solid was collected and dried briefly in vacuo (yield 0.194 g, 83%). The mother liquor immediately became brown and deposited deep purple $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ on exposure to vacuum or dry argon. The aquo ligand was very labile even in the solid state, and a reliable elemental analysis could not be obtained because the complex must be handled under argon containing water vapor. The presence of an unknown amount of lattice water was indicated by IR bands near 3640 cm^{-1} on analogy with the PCy_3 congener.

Preparation of $Mo(CO)_3(PCy_3)_2(H_2O)\cdot 1.5THF$. A solution–slurry of 0.5 g of $Mo(CO)_3(PCy_3)_2$ in 10 mL of THF was treated with about 0.2 mL of H_2O, giving a color change from purple to yellow-orange. Golden yellow crystals slowly formed on standing overnight and were isolated as above (yield 0.35 g, 60%). The presence of lattice THF was identified by IR bands at 1055 and 900 cm^{-1} and also by mass spectrometric analysis of the volatiles evolved upon heating a solid sample (0.160 g, 0.184 mmol) in vacuo at 85 °C on a vacuum line system. H_2O was also evolved and identified by mass spectrometry. The total volatiles evolved was measured by pressure–volume–temperature to be 0.460 mmol, giving the exact volatiles/complex ratio of 2.50 expected for the formulation $Mo(CO)_3(PCy_3)_2(H_2O)\cdot 1.5THF$. The H_2O ligand was very labile even at room temperature, and the golden crystals darkened on grinding even under an argon atmosphere containing water vapor. The IR of the resultant powdered solid in Nujol showed peaks due to the presence of minor amounts of $Mo(CO)_3(PCy_3)_2$ (formed from partial H_2O loss) at 1953, 1840, and 1812 cm^{-1}.

Preparation of $Mo(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2O)\cdot xH_2O$. The procedure was analogous to that for preparation of the PCy_3 analogue (addition of H_2O to $Mo(CO)_3(PCy_2\text{-}i\text{-}Pr)_2$), except that the solvent was 1:1 toluene–nonane. A yellow precipitate formed after stirring for several hours and was collected on a frit and dried in vacuo. The complex did not darken significantly in vacuo, indicating lower lability of the H_2O.

Reaction of H_2O with $W(CO)_3(PCy_3)_2(H_2)$ in THF–Hexane. A slurry–solution of $W(CO)_3(PCy_3)_2(H_2)$ (0.39 g) in THF–hexane under H_2 was treated with 0.13 mL of water. H_2 was evolved, and the solution became orange. Reduction of solvent volume to 2–3 mL and rapid cooling gave precipitation of dark orange microcrystals, followed by slow formation of a yellow solid. IR of the orange solid showed it to be a mixture of species. Absorptions were located similar to those reported for the yellow product "$W(CO)_3(PCy_3)_2(H_2O)$" obtained from toluene,[4a] plus peaks due to $W(CO)_3(PCy_3)_2$ and $W(CO)_4(PCy_3)_2$ resulting from H_2O dissociation and decomposition/disproportionation reactions.

Infrared Studies of Isotopic Exchange of D_2 with H_2O. A solution of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ (0.37 g, 0.62 mmol) in 2 mL of 1:1 THF–hexane was treated with 10 μL of H_2O (0.56 mmol) in a 250-mL flask under D_2. The solution was stirred for 66 h, a small amount of solvent was removed in vacuo, and 3 mL of hexane was added under argon. The flask was placed in a freezer, and the orange crystals of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_nD_{n-2}O)\cdot THF$ that formed were isolated as described above. Infrared spectroscopy showed that the product was approximately a statistical mixture of $H_nD_{n-2}O$ isotopomers. Similar experiments were carried out for shorter reaction periods and showed less deuterium incorporation into the aquo ligand.

^2H NMR Studies of Isotopic Exchange of D_2 with H_2O. A solution of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ (34 mg, 0.057 mmol) in 0.65 mL of THF containing 0.8 μL (0.009 mmol) of C_6D_6 as a reference for integration was placed into an NMR tube possessing a Teflon stopcock for facile closure. A D_2 atmosphere (~0.06 mmol of D_2) was placed over the solution in a glovebag. The ^2H NMR displayed a single resonance at δ −4.35 for the η^2-D_2 ligand and peaks at δ 3.58 and 1.72 for THF-*d* (natural abundance) and δ 7.32 for C_6D_6. H_2O (0.5 μL, 0.028 mmol) was added, evolution of D_2 gas occurred, and the resulting NMR spectrum showed a diminished intensity of the η^2-D_2 peak due to partial replacement by H_2O. The production of $H_nD_{2-n}O$ (bound plus free) was monitored with time (10–12-min intervals initially). About 1 h after addition, a singlet resonance due to the latter appeared at δ 3.05, slowly grew in intensity, and shifted to δ 2.91 over a 12-h period. The signal for the η^2-D_2 ligand diminished and broadened as protium from the H_2O replaced deuterium in the D_2 (including unbound D_2 to an extent dependent on mixing factors). The HD coupling in the HD complex formed was difficult to resolve. The final integrated intensity ratio of C_6D_6 to $H_nD_{2-n}O$ was 6.9, corresponding to incorporation of 0.008 mmol of deuterium into the water. This is about 17% of the complete statistical distribution of available deuterium, including D_2 in the head gas (21% excluding it). The experiment was not continued further because of loss of sample, but a second run using lower concentrations was carried out to completion (see Results).

An experiment similar to the above was carried out in toluene (0.7 mL) instead of THF using the same amount of D_2 complex but less H_2O (0.35 μL, 0.019 mmol). The reference was the aryl deuterons of toluene-*d* (0.015% D natural abundance). The signal for the D_2 complex was at δ −4.24, and that for the $H_nD_{2-n}O$ produced initially appeared near δ 0.60, shifting to δ 0.95 on complete scrambling. A weak peak also slowly grew in at δ 5.22. Addition of 0.3 μL of D_2O at the end of the run increased the intensity of the latter, suggesting it to be due to free water and the upfield signal to be due to coordinated water.

The reverse reaction of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2O)$ (32 mg, 0.053 mmol) with H_2 in 0.55 mL of THF was also followed by ^2H NMR. The initial spectrum showed a resonance due to D_2O at δ 3.70, shifting to δ 3.48 on addition of C_6D_6 reference (9.9 μL, 0.112 mmol) and remaining there on addition of H_2 (0.060 mmol). The initial integrated ratio of C_6D_6 to D_2O resonances was 6.1 (calculated 6.4). The latter increased with time as protium replaced deuterium in the D_2O, reaching 6.9 after 8 h (-15% of statistical incorporation), 8.2 after 55 h (40%), 10.0 after 8 days (68%), and 10.4 after 13 days (72%). The errors in these percentages are estimated to be relatively high (±20%) because of inaccuracies generated by the high integration ratios and the possible presence of adventitious water. The water resonance shifted to δ 2.79 at the end of the run.

^2H NMR Studies of Isotopic Exchange of D_2 with MeOH. The experiment and quantities were similar to that described in the first paragraph of the above section. Before addition of D_2 gas to the NMR tube, the integral ratio of C_6D_6 (standard) to the W–D_2 complex was 1.72 (~72% of the η^2-D_2 dissociated). After D_2 was added the ratio became 0.755 (37% dissociated, 63% coordinated). After addition of 1.15 μL of MeOH (0.0285 mmol; 1:2 molar ratio of MeOH to complex), the above ratio did not change appreciably (0.733), indicating that MeOH did not partially displace η^2-D_2 as H_2O did in the experiments above. After several hours, a weak resonance grew in at δ 3.02 corresponding to the position for $H_nD_{2-n}O$, and after 27 h integration indicated that the amount of D present was 0.001–0.002 mmol. After 4 days, a second resonance had begun to grow in at δ 3.20 due to MeOD (~0.005 mmol), while the first (now at δ 3.00, 0.007 mmol) had reached its maximum and remained unchanged in subsequent spectra. The exchange appeared nearly complete by 13 days (total amount of D incorporated into MeOD and adventitious $H_nD_{2-n}O$ was ~0.031 mmol).

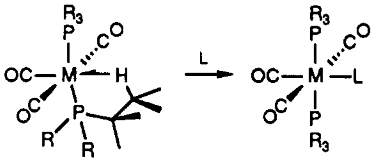
FTIR Studies of Equilibrium Constants for $W(CO)_3(PR_3)_2(H_2) + H_2O = W(CO)_3(PR_3)_2(H_2O) + H_2$. Controlled temperature/pressure measurements of the equilibria were performed in a Perkin-Elmer 1850 FTIR spectrometer using a high-pressure cell obtained from Harrick Scientific and equipped with Ge windows. Details of this cell and its loading have been reported previously.[9]

Calorimetric Measurements. Heats of reaction and solution reported here were made using either a Setaram C-80 Calvet Microcalorimeter or a Guild Isoperibol calorimeter. All enthalpies reported include corrections for any heats of solution/dilution and refer to reactions in which all species are in the solvent system stated. Procedures strictly analogous to those reported previously were used.[4b,10] Due to the highly air-sensitive nature of the reactants, larger than normal sample sizes (up to 1 g) were used in sealed ampules when using the Guild calorimeter for the complexes $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ and $W(CO)_3(PCy_3)_2$.

X-ray Crystallography of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$. An orange crystal of the complex (0.30 mm × 0.30 mm × 0.25 mm) obtained from the preparative reaction was fixed in silicon grease on a glass fiber and transferred directly to the cold stream of an Enraf-Nonius CAD-4 diffractometer. Automatic peak indexing procedures yielded a primitive monoclinic unit cell. Examination of the *h*0*l* layer revealed systematic absences unique to space group $P2_1/n$. Accurate cell parameters were determined by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 independent reflections with 2θ between 26 and 32°. The results are given in Table I along with the parameters used in data collection. The 4033 raw data were converted to structure factor amplitudes and their esd's by correcting for scan speed, background, and Lorentz–polarization effects. The tungsten was located through the use of a Patterson map, and the remaining non-hydrogen atoms were located by difference Fourier techniques. An absorption correction was then applied on the basis of a Fourier series with coefficients obtained by minimizing the sum of the squares of the residuals to calculate the absorption coefficients.[11] All non-hydrogen atoms were refined anisotropically. Subsequent difference Fourier maps revealed the hydrogen atoms on the phosphine ligands. These were placed in idealized positions but were not refined. There was evidence of secondary extinction in the low-angle, high-intensity data, and a secondary extinction correction was applied to the data. The coefficient was refined in the least-squares calculations to a value of $[4.2\ (9)] \times 10^{-8}$ e/Å^2. The final residual for 299 variables refined against the 2688 data for which $F_o^2 > 3\sigma(F_o^2)$ were $R = 0.0336$, $R_w = 0.0498$, and GOF = 1.791. The largest peak in the final difference Fourier peak had an electron density of 0.865 e/Å^3 and was associated with the tungsten atom.

Results

Reactions of $M(CO)_3(PCy_3)_2$ with H_2O. The formally 16e complexes *mer,trans*-$M(CO)_3(PR_3)_2$ (M = W, Mo) have an agostically bound C–H from an alkyl substituent (R = *i*-Pr, Cy) occupying the sixth coordination site.[4] The latter can be "displaced" by virtually any two-electron-donor ligand (L) capable of fitting into the sterically crowded site (eq 2). For L = XY, oxidative addition to give species of the type $M(X)(Y)(CO)_3(PR_3)_2$ does not readily occur here, and even H_2 binds molecularaly as η^2-H_2 (equilibrium cleavage to the dihydride $WH_2(CO)_3(PR_3)_2$ occurs to a partial extent in solution).[3b,6] However, strong acids were recently found to oxidatively add in nonaqueous media to form $WHX(CO)_3(PCy_3)_2$ (X = Cl, BF_4, triflate).[12] Thus, the question of whether H_2O binds molecularly or is cleaved to H(OH) by $M(CO)_3(PR_3)_2$ must be considered.



(2)

The addition of excess H_2O to deep purple toluene solutions of $M(CO)_3(PCy_3)_2$ (M = W, Mo) under argon and stirring of the biphasic system for 10–15 min had been found to yield a yellow precipitate of very low solubility.[4a] The products reversibly dissociated H_2O under a dry argon stream or in vacuo to reform $M(CO)_3(PCy_3)_2$, a feature characteristic of simple adduct formation. In order to avoid partial H_2O loss (as seen by rapid surface darkening), it was necessary to handle and store these and other aquo complexes under argon containing water vapor (e.g. a glovebag containing water droplets in a dish). The reversible binding, color, and low solubility of the complexes exactly paralleled that of the H_2 and N_2 analogues.[4,6] Addition of H_2O to $Cr(CO)_3(PCy_3)_2$,[14] which also contains an isostructural agostic C–H interaction, gave no color change or precipitate in toluene. This is consistent with its weaker ability to bind small molecules such as N_2 and H_2 compared to the Mo and W analogues.[4b,14]

Elemental analysis of the W complex indicated the composition to be $W(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$, assuming an aquo ligand plus two lattice H_2O molecules. IR spectra of both the Mo and W products were virtually identical and showed multiple ν(OH) signals in the range 3300–3700 cm^{-1} potentially assignable as either H_2O or hydroxo ligand or lattice H_2O, which undoubtedly was hydrogen-bonded, adding further ambiguity to the overall structural/spectroscopic problem. Attempts to grow X-ray-quality crystals of the complexes were singularly unsuccessful. Curiously, *quiescent* reactions of $M(CO)_3(PCy_3)_2$ in toluene containing immiscible droplets of excess H_2O gave solution color changes to orange but *no solid* even after several days. Solvent removal yielded primarily $M(CO)_4(PCy_3)_2$, a disproportionation product commonly found as a trace impurity in these system. Thus, solution stability may be a problem, as was evident in further crystal preparation attempts using a variety of solvents and starting materials. A homogeneous reaction in THF–hexane of H_2O with the *dihydrogen complex* $W(CO)_3(PCy_3)_2(H_2)$ as starting material gave displacement of the weakly bound H_2 ligand and an orange solution. Partial solvent removal and cooling gave a solid identified by IR to contain a mixture of $W(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$ and $W(CO)_4(PCy_3)_2$.

The reaction of $Mo(CO)_3(PCy_3)_2$ with H_2O in homogeneous THF solution rather than biphasic toluene/H_2O slowly deposited a gold-yellow product with the composition $Mo(CO)_3(PCy_3)_2(H_2O)\cdot 1.5THF$. Its ν(OH) position were much different from those of the H_2O solvates (no bands >3400 cm^{-1}), reinforcing initial speculation that the latter might contain oxidatively added H_2O. Reaction of a mixed alkylphosphine analogue, $Mo(CO)_3(PCy_2\text{-}i\text{-}Pr)_2$, with H_2O in toluene–nonane gave after several hours a fine yellow precipitate presumably of similar composition to the PCy_3 congeners formed in toluene.

Reactions of $M(CO)_3(P\text{-}i\text{-}Pr_3)_2$ and $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ with H_2O. Isolation of Crystalline $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$. In contrast to the above complexes, the products obtained for R = *i*-Pr from either hexane or THF were soluble. For the tungsten system, $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ was used as a convenient starting material and, in hexane under argon, H_2O displaced η^2-H_2 to give a yellow-orange precipitate. The aquo ligand is extremely labile and is easily displaced by N_2 to give the

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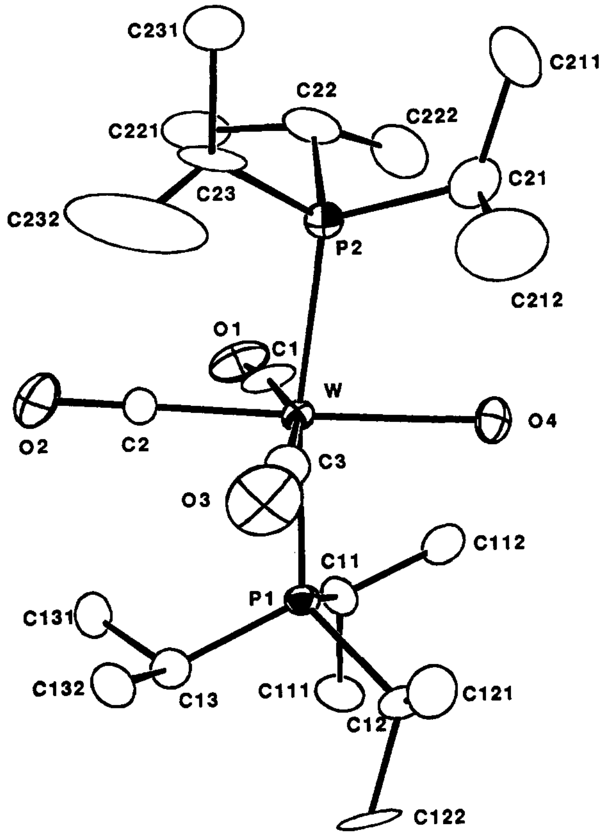

Figure 1. ORTEP drawing of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$ (50% thermal ellipsoids).

Table II. Bond Distances (Å)[a]

W-P1	2.519 (3)	C11-C112	1.54 (1)
W-P2	2.499 (3)	C12-C121	1.54 (2)
W-O4	2.320 (5)	C12-C122	1.52 (2)
W-C1	1.98 (1)	C13-C131	1.53 (1)
W-C2	1.875 (8)	C13-C132	1.53 (2)
W-C3	1.99 (1)	C21-C211	1.53 (2)
P1-C11	1.87 (1)	C21-C212	1.60 (2)
P1-C12	1.872 (9)	C22-C221	1.55 (1)
P1-C13	1.84 (1)	C22-C222	1.56 (2)
P2-C21	1.88 (1)	C23-C231	1.50 (2)
P2-C22	1.85 (1)	C23-C232	1.32 (2)
P2-C23	1.86 (1)	O51-C511	1.46 (1)
O1-C1	1.15 (1)	O51-C514	1.44 (2)
O2-C2	1.21 (1)	C512-C511	1.53 (2)
O3-C3	1.17 (1)	C512-C513	1.47 (2)
C11-C111	1.55 (2)	C514-C513	1.45 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Bond Angles (deg)[a]

P1-W-P2	171.66 (7)	W-C1-O1	170.8 (8)
P1-W-O4	86.8 (2)	W-C2-O2	178.6 (9)
P1-W-C1	85.0 (3)	W-C3-O3	171.5 (8)
P1-W-C2	95.8 (4)	P1-C11-C111	117.7 (7)
P1-W-C3	92.6 (3)	P1-C11-C112	110.9 (8)
P2-W-O4	85.3 (2)	C111-C11-C112	109.1 (8)
P2-W-C1	93.8 (4)	P1-C12-C121	113.4 (7)
P2-W-C2	92.2 (4)	P1-C12-C122	116.2 (8)
P2-W-C3	90.6 (4)	C121-C12-C122	109.0 (9)
O4-W-C1	100.3 (3)	P1-C13-C131	113.7 (7)
O4-W-C2	177.0 (4)	P1-C13-C132	111.2 (8)
O4-W-C3	94.0 (3)	C131-C13-C132	110.0 (7)
C1-W-C2	81.6 (4)	P2-C21-C211	119.5 (7)
C1-W-C3	165.4 (4)	P2-C21-C212	109.5 (9)
C2-W-C3	84.4 (4)	C211-C21-C212	112 (1)
W-P1-C11	112.4 (3)	P2-C22-C221	111.0 (9)
W-P1-C12	118.7 (4)	P2-C22-C222	110.7 (7)
W-P1-C13	115.3 (3)	C221-C22-C222	112 (1)
C11-P1-C12	102.9 (4)	P2-C23-C231	117 (1)
C11-P1-C13	101.7 (5)	P2-C23-C232	123 (1)
C12-P1-C13	103.8 (4)	C231-C23-C232	119 (1)
W-P2-C21	114.0 (4)	C511-O51-C514	110.9 (8)
W-P2-C22	116.5 (5)	C511-C512-C513	106 (1)
W-P2-C23	115.5 (6)	O51-C511-C512	105 (1)
C21-P2-C22	101.3 (6)	O51-C514-C513	107 (1)
C21-P2-C23	107.2 (7)	C512-C513-C514	110 (1)
C22-P2-C23	100.7 (5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B,[a] $Å^2$
W	0.00251 (3)	0.21848 (2)	0.19947 (2)	1.091 (8)
P1	0.0543 (2)	0.2650 (2)	0.0663 (2)	1.31 (6)
P2	−0.0699 (2)	0.1602 (2)	0.3123 (2)	1.79 (6)
O1	0.1573 (6)	0.0712 (5)	0.2207 (5)	3.3 (2)
O2	0.2172 (6)	0.2745 (5)	0.3750 (5)	2.7 (2)
O3	−0.0692 (7)	0.3953 (5)	0.2283 (6)	4.0 (2)
O4	−0.1647 (5)	0.1788 (4)	0.0726 (4)	1.8 (2)
C1	0.0930 (9)	0.1212 (6)	0.2079 (6)	2.0 (3)
C2	0.1338 (8)	0.2517 (6)	0.3061 (6)	1.5 (2)
C3	−0.0512 (8)	0.3287 (6)	0.2123 (7)	1.7 (2)
C11	0.0856 (8)	0.1779 (6)	0.0028 (7)	1.7 (2)
C12	−0.0475 (8)	0.3260 (6)	−0.0396 (7)	1.9 (3)
C13	0.1814 (8)	0.3250 (6)	0.1097 (6)	1.8 (2)
C21	−0.2235 (9)	0.1494 (8)	0.2541 (7)	3.0 (3)
C22	−0.0260 (9)	0.0556 (8)	0.3574 (8)	3.1 (3)
C23	−0.029 (1)	0.2152 (9)	0.4317 (7)	6.8 (3)
C111	0.1238 (9)	0.1982 (7)	−0.0776 (7)	2.6 (3)
C112	−0.0115 (9)	0.1182 (7)	−0.0402 (7)	2.4 (3)
C121	−0.1253 (9)	0.3771 (7)	−0.0120 (8)	2.6 (3)
C122	−0.000 (1)	0.3801 (7)	−0.0937 (8)	3.3 (3)
C131	0.2848 (8)	0.2767 (7)	0.1741 (7)	2.2 (3)
C132	0.1744 (9)	0.4018 (7)	0.1646 (7)	2.6 (3)
C211	−0.277 (1)	0.0954 (9)	0.3035 (9)	4.2 (4)
C212	−0.279 (1)	0.238 (1)	0.229 (1)	6.4 (5)
C221	0.100 (1)	0.0516 (8)	0.4228 (9)	4.1 (3)
C222	−0.065 (1)	−0.0057 (8)	0.2690 (9)	3.9 (4)
C231	−0.058 (1)	0.1770 (9)	0.5070 (8)	4.3 (3)
C232	0.014 (2)	0.289 (1)	0.448 (1)	13.8 (5)
O51	0.2549 (7)	0.4758 (5)	0.5194 (5)	3.1 (2)
C512	0.138 (1)	0.5380 (8)	0.3669 (9)	3.3 (3)
C511	0.2385 (9)	0.4829 (7)	0.4172 (7)	2.8 (3)
C514	0.1603 (9)	0.5052 (8)	0.5294 (9)	4.0 (3)
C513	0.089 (1)	0.543 (1)	0.436 (1)	10.0 (5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

known[4a] orange $[W(CO)_3(P\text{-}i\text{-}Pr_3)_2]_2(\mu\text{-}N_2)$, making elemental analysis unreliable in determining the presence of lattice H_2O.

Addition of a moderate excess of H_2O to a concentrated THF solution of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ gave instant, vigorous effervescence of H_2, even under H_2. Because of miscibility, the concentration of water in THF is much higher than that of dissolved H_2, favoring H_2O binding (see below). Addition of hexane to the deep red-orange solution, followed by slow cooling in a freezer, gave well-formed orange prismatic crystals. X-ray diffraction, IR, and NMR (see below) showed that they were $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$, containing an H_2O ligand replacing $\eta^2\text{-}H_2$. Solutions of the complex in THF did not react with NEt_3 or Proton Sponge in efforts to deprotonate the H_2O ligand.

X-ray Structure of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$. An ORTEP drawing of the molecule with atomic labels is given in Figure 1. Data collection parameters may be found in Table I. Bond distances and angles are given in Tables II and III and positional parameters in Table IV. The tungsten lies in an octahedral coordination environment formed by two mutually trans phosphine ligands, three *mer* CO groups, and oxygen of the coordinated H_2O. This overall geometry is identical with that for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)$, making possible an excellent comparison of ligand influences on bond distances and angles in this system. The angles about tungsten for the H_2O complex are actually more similar to those found in the agostic five-coordinate precursor complex[4a] than to those in the H_2 complex,[3a] which are nearly perfectly octahedral (assuming H_2 occupies one site). The addition of water to the coordination sphere of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ expands all angles about the sixth (agostic) coordination site; the C1–W–C3 angles is compressed to 165.4 (4)° from its value of 167.8 (4)° in the five-coordinate species, whie the P1–W–P2 angle opens significantly from 162.78 (7) to 171.66 (7)°. Both cis carbonyl groups are bent back from the coordinated water molcule (O4–W–C1 and O4–W–C3 are 100.3 (3) and 94.0 (3)°, respectively), while the O4–W–C2 angle is nearly linear at 177.0 (4)°. This bending does not occur in the H_2 complex.

The W–P1,2 distances are 2.519 (3) and 2.499 (3) Å, respectively. These tungsten–phosphine distances are longer than in the five-coordinate complex (2.458 (2), 2.493 (2) Å), reflecting both the higher formal coordination number and the lack of an agostic interaction between W and a phosphine alkyl group. They are similar to those in the H_2 complex (2.503 (4), 2.487 (4) Å). The tungsten–carbonyl W–C distance trans to the coordinated water molecule is 1.875 (8) Å, compared to the much longer values of 1.99 (1) and 1.98 (1) Å for the cis CO, indicative of the weak trans influence of the H_2O. These three distances are slightly longer in the agostic species and much longer (1.977 (16), 2.036 (17), and 2.025 (19) Å) in the H_2 analogue, consistent with the weak σ-donor capability of H_2 coupled with $W \rightarrow H_2$ σ* back-bonding that competes with $W \rightarrow CO$ back-bonding. As also seen in the CO IR frequencies, H_2O is clearly the superior σ-donor ligand, strengthening the W–C bonds and weakening the C–O bonds.

The W–O(water) distance is 2.320 (5) Å. For comparison purposes, there are relatively few crystallographically characterized H_2O complexes containing phosphine and carbonyl ligands of either tungsten or d^6 organometallic species. The only tungsten example is $[W(PMe_3)_4H_2(OH_2)F]F$,[1d] a tetravalent complex with a W–O distance of 2.084 (9) Å. Even when adjustment is made for the oxidation-state difference, the tungsten–water distance in $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)$ is long by comparions. The Ru–O distance in octahedral d^6 $[RuH(H_2O)(CO)_2(PPh_3)_2]BF_4\cdot EtOH$ is 2.15 (1) Å, which is also long when compared to the value of 1.99 Å predicted from the sum of covalent radii.[1n] Other reported metal–oxygen distances in "organometallic" H_2O complexes vary from 1.99 to 2.316 Å (Table VI), and thus the distance in $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)$ lies at the uppermost end of this range, consistent with the reversibility of the H_2O binding. Surprisingly long $M\text{–}OH_2$ distances (2.44–2.56 Å) are observed in complexes of the type $[TcNX_4(H_2O)]^{n-}$ (X = Cl, Br, CN; *n* = 1, 2) containing the very strong trans-influencing nitrido ligand.[15]

We were unable to locate the protons associated with the water ligand in the final difference Fourier map, precluding unambiguous structural assignment of the coordination mode. The relatively long W–O4 bond and lack of significant asymmetry in the angles about O4, however, suggest that the water is coordinated through σ donation of oxygen lone pairs and is not activated to form a hydroxyl group or a side-bonded (η^2-OH) water ligand analogous to η^2-H_2. Importantly, hydrogen-bonding interactions (discussed below) indicate that two hydrogens are attached to O4.

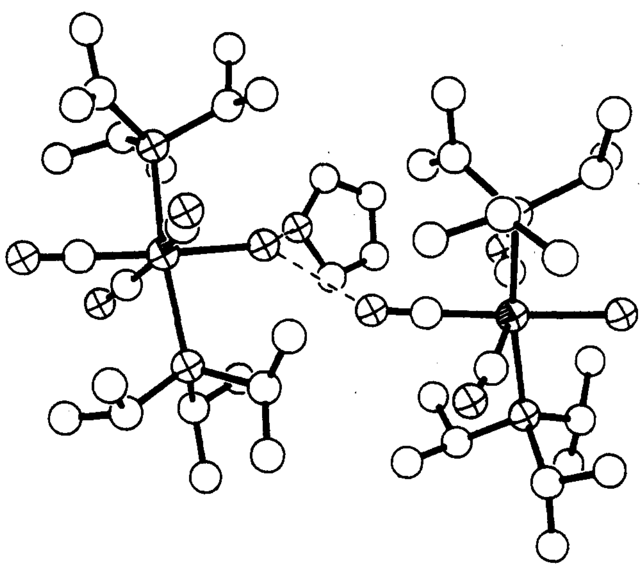

Figure 2. X-ray structure of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$, showing hydrogen-bonding interactions between H_2O, THF, and CO on an adjacent molecule, which repeat to give chainlike linkages.

Hydrogen Bonding between H_2O, THF, and CO in the Structure of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$. Two close intermolecular separations between the aquo ligand oxygen (O4) and nearby oxygen atoms are observed, as can be seen in Figure 2. The distance between O4 and the lattice THF oxygen (O51, in an adjoining asymmetric unit) is 2.739 Å (cf. 2.70 (2) Å in $[IrH_2(PPh_3)_2(THF)(H_2O)]SbF_6\cdot THF$[1f]), which is near the average O···O distance in nonsymmetrical O–H···O hydrogen bonds (2.72 Å).[16] Hydrogen bonding is quite common in aquo complexes, and several examples are known for interactions of the H_2O with oxygen-donor lattice molecules,[1e,h,in] fluoroanions (e.g. BF_4),[1b,bb,cc,ii,jj] or even both types in the same complex.[1f,o] Not so common is the interaction of O4 with O2, the *carbonyl* oxygen trans to H_2O in an adjacent molecule (O···O distance 2.792 Å). This appears to be the initial example of hydrogen bonding between H_2O and CO ligands and a rare example of any form of H-bonding involving the oxygen of metal-bound carbonyl. Although Lokshin et al.[17] claimed to be the first to report this type of phenomenon in 1986 in an IR study of the interaction of $CpMn(CO)_2(P\text{-}i\text{-}Pr_3)$ with $(CF_3)_3COH$ in liquid Xe, an earlier paper[18] gave crystallographic evidence for an intermolecular NH···OC interaction in $Mo(CO)_4$(di-2-pyridylamine). IR of complexes of the type $[CpFe(CO)_2]_2$ in hydroxylic solvents indicated H-bonding involving μ-CO.[19] Consistent with hydrogen-bonding ability, the basicity of the oxygen of carbonyl ligands has been demonstrated by Shriver, specifically in a complex related to ours, $Mo(CO)_2(PPh_3)_2$(phenanthroline).[20]

Because the hydrogens were not located, the exact geometries of the H-bonding interactions could not be as-

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Table V. Infrared Data[a] for Molybdenum and Tungsten Complexes

complex	ν(OH)	ν(CO)	δ(HOH)
$Mo(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$	3660, 3515, 3420, 3305	1933, 1806, 1710	1674
$Mo(CO)_3(PCy_3)_2(D_2O)\cdot 2D_2O$	2718, 2583, 2510, 2439	1933, 1806, 1702	1235
$W(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$	3665, 3643, 3510, 3395, 3297	1927, 1800, 1708	1677
$W(CO)_3(PCy_3)_2(D_2O)\cdot 2D_2O$	2715, 2700, 2570, 2500, 2425	1927, 1799, 1698	1238
$W(CO)_3(PCy_3)_2(H_2{}^{18}O)\cdot 2H_2{}^{18}O$	3650, 3632, 3502, 3390, 3289	1926, 1800, 1706	1672
$Mo(CO)_3(PCy_3)_2(H_2O)\cdot 1.5THF$	3390, 3285	1938, 1802, 1757	1670
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$	3450, 3210	1929, 1807, 1725	1664, 1622
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2O)\cdot THF$	2574, 2385	1931, 1808, 1725	1226[c]
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2{}^{18}O)\cdot THF$	3435, 3205	1929, 1807, 1725	1657, 1617
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot xH_2O$[b]	3648, 3630, 3352, 3298, 3214	1927, 1804, 1719	1622
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2O)\cdot xD_2O$[b]	2693, 2681, 2466, 2386	1928, 1806, 1712	1203
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2{}^{18}O)\cdot xH_2{}^{18}O$[b]	3636, 3617, 3352, 3296, 3208	1927, 1804, 1719	1617
$Mo(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot xH_2O$[b]	3635, 3390, 3330, 3220	1935, 1815, 1725	1621
$Mo(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2O)\cdot xH_2O$	3645, 3563, 3410, 3280	1923, 1804, 1750	1658, 1615

[a] Nujol mull samples, cm^{-1}. [b] From reaction in hexane solution. [c] A peak at 1240 cm^{-1} is also present but is coincident with a phosphine peak observed at 1242 cm^{-1} in the H_2O complex.

certained. The packing diagram did show that the O⋯H⋯OC linkages repeated to give an infinite chain. As was done in the structure of $[IrH_2(THF)(H_2O)(PPh_3)_2]SbF_6\cdot THF$,[1f] one might make inferences about the geometry of the bound H_2O from the O⋯O vectors in Figure 2. Assuming that the hydrogens lie along them, the $W–OH_2$ bonding appears to be pyramidal.

Infrared Studies of H_2O Complexes and Their Deuterium- and ^{18}O-Labeled Isotopomers. IR spectroscopy has been heavily relied upon for characterizing the products of H_2O reaction and determining whether or not oxidative addition to hydrido–hydroxo species occurs. IR initially indicated that the latter had occurred in the PCy_3 complexes, for which no other structural information could be obtained.[4,5] However, the structure of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$ showed that the H_2O does not split (at least in this congener) and that hydrogen bonding of lattice molecules and carbonyl oxygens to the water protons could potentially be present in all of the water complexes. Hydrogen-bonding effects could give complex IR band structures and shifts in both the ν(OH) and δ(OH) regions, especially if lattice H_2O was present in addition to coordinated H_2O. Ambiguity in frequency assignments could result, as will be discussed below. Thus, extensive use of isotopic labeling has been made to clarify assignments and obtain structural information.

The IR spectra of H_2O molecules are highly sensitive to their surroundings,[13] and the ν(OH) region of aquo complexes especially reflects this, both in our system (Table V) and in other complexes (Table VI). For coordinated H_2O, two broad OH stretches (antisymmetric and symmetric, sometimes overlapping) are expected in the region 3200–3550 cm^{-1}, along with the HOH bend near 1600 cm^{-1}.[13] Lower energy H_2O modes (<800 cm^{-1}) are likely to be obscured by extensive phosphine and M–CO modes. For *hydroxo* ligands, ν(OH) should be present at 3000–3760 cm^{-1} and δ(MOH) at 700–1200 cm^{-1} (potentially obscured).[13] Clearly there is overlap in the ν(OH) region between aquo and hydroxo ligands, but from Table VI, it appears that in organometallic systems ν(OH) generally is below 3600 cm^{-1} for $M–OH_2$ and above this for M–OH.

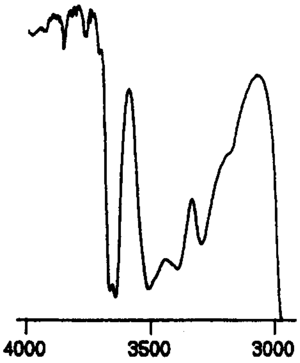


Figure 3. Nujol mull IR of $W(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$ in the ν(OH) region. Sharp weak peaks are ν(CO) overtones.

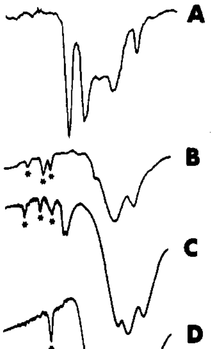


Figure 4. Nujol mull IR in the ν(OH) region of (A) $Mo(CO)_3(PCy_2\text{-}i\text{-}Pr)_2(H_2O)\cdot xH_2O$, (B) $Mo(CO)_3(PCy_3)_2(H_2O)\cdot 1.5THF$, (C) $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot xH_2O$ from hexane, and (D) $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$. Asterisks denote ν(CO) overtones.

The IR spectrum in a Nujol mull of $W(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$ showed a strong split band at 3665/3643 cm^{-1} (Figure 3, Table V), which is in the M–OH region, giving rise to the initial belief[4a,5] that the water oxidatively added to give $WH(OH)(CO)_3(PCy_3)_2\cdot 2H_2O$. This band shifted as expected on deuteration (synthesis of the complex from D_2O) to 2715/2700 cm^{-1} and also upon ^{18}O labeling to 3650/3632 cm^{-1} (bands due to coordinated or lattice H_2O would also shift in this manner). Several other broader OH stretches were present at lower frequencies (3300–3500 cm^{-1}), which were attributed to lattice H_2O modes. It should next be noted that even minor variations of phosphine and reaction solvents (but not metal) gave products with radically differing OH bands (Figure 4). None of the $P\text{-}i\text{-}Pr_3$ species exhibited strong OH IR bands higher than 3400 cm^{-1}, except for a weak band near 3640 cm^{-1} for the complexes obtained from hexane. IR of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$ revealed yet a different splitting pattern in the 3200–3500-cm^{-1} region (only two bands versus the three in the hexane-derived analogue; Figure 4). This spectral region of the other THF solvate isolated, $Mo(CO)_3(PCy_3)_2(H_2O)\cdot 1.5THF$, was much more similar to that of the latter complex than to that of the

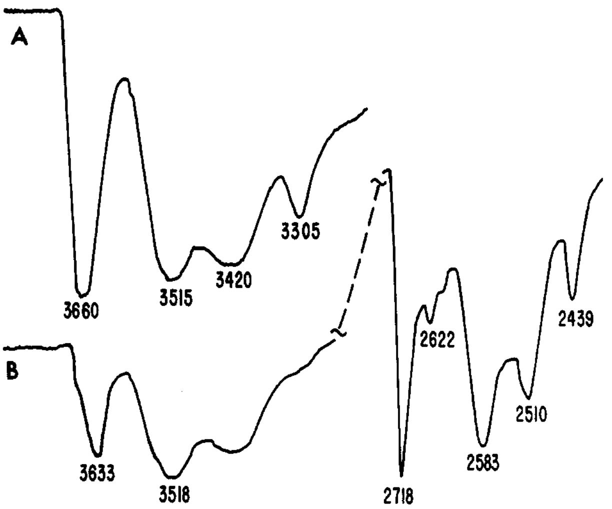


Figure 5. Nujol mull IR of (A) $Mo(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$ in the ν(OH) region and (B) $Mo(CO)_3(PCy_3)_2(D_2O)\cdot 2D_2O$ in both the ν(OD) region and the ν(OH) region (showing residual protium peaks).

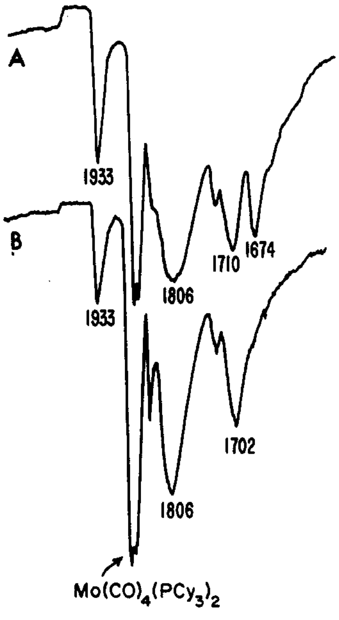
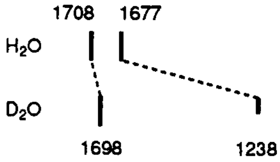


Figure 6. Nujol mull IR of (A) $Mo(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$ and (B) $Mo(CO)_3(PCy_3)_2(D_2O)\cdot 2D_2O$ in the ν(CO) and δ(HOH) regions. The peak near 1870 cm^{-1} is the extremely intense mode of the $Mo(CO)_3(PCy_3)_2$ impurity.

H_2O solvate, $Mo(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$. All of the above support the notion that *the presence of lattice H_2O and/or hydrogen-bonding interactions influences the ν(OH) region more than changes in phosphine/metal and makes IR distinction between aquo and hydroxo ligands risky if not impossible.*

Deuteration studies on $Mo(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$ as shown in Figure 5 revealed that the residual protium band at 3633 cm^{-1} had shifted to about 30 cm^{-1} lower energy than the band in the fully protium complex. This shifted band could be due to isotopically mixed species such as $Mo(CO)_3(PCy_3)_2(HDO)\cdot 2D_2O$, and the weak peak at 2622 cm^{-1} could also be due to a mixed species.

In addition to the highly variable OH frequencies, all of the complexes from the H_2O reactions displayed at least four strong bands in the 1600–1950-cm^{-1} region (Figures 6 and 7 and Table V). A ν(CO) band near 1870 cm^{-1} due to trace impurities of $M(CO)_4(PR_3)_2$ was usually also present, along with those of $[W(CO)_3(P\text{-}i\text{-}Pr_3)_2]_2(\mu\text{-}N_2)$[4a] in the case of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$ (these bands are much more intense than those for the H_2O complexes). Assignments of the bands due to the water complexes are ambiguous in this region also, especially 1600–1700 cm^{-1}, where ν(CO), ν(MH), and δ(HOH) modes are all possible. The two highest frequency bands are clearly ν(CO) and do not shift on substituting D_2O or $H_2{}^{18}O$ for H_2O reactant. The two intense, closely spaced bands at 1708 and 1677 cm^{-1} in the complex originally thought to be $WH(OH)(CO)_3(PCy_3)_2\cdot 2H_2O$ are more difficult to assign. The spectrum of the deuterium analogue shows a strong peak at 1698 cm^{-1} and a new peak at 1238 cm^{-1} which is now much weaker:



The isotopic shift ratio (1677/1238 = 1.35) is consistent with the 1238-cm^{-1} band being either ν(MD) or δ(DOD), with the 1698-cm^{-1} peak being due to ν(CO). The 1708-cm^{-1} band in the protium complex is then most likely ν(CO), which shifts down 10 cm^{-1} on deuteration, probably because of the effects of coupling with the nearby mode at 1677 cm^{-1}. The dramatic decrease in intensity of the latter when shifted to 1238 cm^{-1} on deuteration is consistent with loss of coupling to the CO band (hydrogen-bonding effects could also contribute to the ν(CO) shifts and intensity changes). In order to resolve ambiguity as to whether the band at 1677 cm^{-1} is due to a δ(HOH) bending mode or ν(MH) (if the H_2O oxidatively added), the $H_2{}^{18}O$ isotopomer was studied. This band should shift if due to δ(HOH) and not shift if due to an M–H stretch (initial experiments[4a] had showed that it did not shift; see Discussion). As a check to determine whether an ^{18}O shift should actually be resolvable for δ(HOH), the IR spectra of both the known aquo complex $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2{}^{18}O)\cdot THF$ and the $H_2{}^{18}O$ (95+%) used to synthesize it were studied using an FT-IR instrument. A 2% solution of $H_2{}^{18}O$ in 1,2-bis(2-methoxyethoxy)ethane between CaBr windows gave δ(HOH) at 1639 cm^{-1} versus 1645 cm^{-1} for a 2% solution of H_2O (ν(OH) shift: 3552, 3514 cm^{-1} to 3581, 3522 cm^{-1}). In $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2{}^{18}O)\cdot THF$, bands at 1664 and 1622 cm^{-1} shifted to 1657 and 1617 cm^{-1} in the ^{18}O species (Figure 7), confirming that they are both due to δ(HOH) and that a shift of 5 cm^{-1} is resolvable for aquo

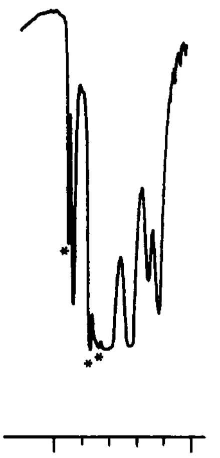


Figure 7. Nujol mull IR of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2{}^{18}O)\cdot THF$ in the ν(CO) and δ(HOH) regions. Asterisk denote peaks due to minor impurities: $[W(CO)_3(P\text{-}i\text{-}Pr_3)_2]_2(\mu\text{-}N_2)$ at 1948, 1872, and 1836 cm^{-1}1 and $W(CO)_4(P\text{-}i\text{-}Pr_3)_2$ at 1870 cm^{-1}.

Table VI. Spectroscopic Data and Metal–Oxygen Distances for Organometallic H_2O and H(OH) Complexes

H_2O complex	ν(OH)	δ(HOH)	M–O, Å	ref
$[Cp_2Ti(H_2O)_2](ClO_4)_2 \cdot 3THF$			1.99, 2.01	1i
$[Cp_2Zr(H_2O)_3](CF_3SO_3)_2 \cdot THF$	3500	1670	2.232 (7) (av)	1h
$[Cp_2Zr(C_7H_7SO_3)(H_2O)_2](C_7H_7SO_3)$	3200–3500	1670	2.232	1e
$[Cp^*ZrCl_2(\mu\text{-}OH)(H_2O)]_2$	3533,^{a} 3354	1609	2.246 (3) (av)	1g
$[Cp_2Zr(\mu\text{-}OH)_2(H_2O)_6](ClO_4)_4 \cdot 8THF$	2500–3600	1650	2.186 (av)	1e
mer-$[Cr(CO)_3(PMe_3)(CCH_3)(H_2O)]BF_4$	3435	1640		1p
$[Mo(acac)(\eta^7\text{-}C_7H_7)(H_2O)]BF_4$	3373, 3263	1640	2.202 (5)	1b
$[CpMo(CO)_3(H_2O)]BF_4$	3370			1ff
$[CpMo(CO)_2(PPh_3)(H_2O)]BF_4$	3390	1670		1x
$[CpW(CO)_3(H_2O)]AsF_6$	3480, 3435	1613		1x
$[CpW(CO)_2(PPh_3)(H_2O)]BF_4$		1645		1x
$[WH_2F(PMe_3)_4(H_2O)]F$	2750^b	1740^b	2.084 (9)	1d
$[Mn(CO)_5(H_2O)]BPh_4 \cdot nH_2O$	3386	1610		1w
cis-$[Mn(CO)_4(PPh_3)(H_2O)]BF_4$	3385			1t
mer-$[Mn(CO)_3\{P(OPh)_3\}_2(H_2O)]BF_4$	3520	1585		1m
fac-$[Re(CO)_3(tmen)(H_2O)]AsF_6$^{c}	3410	1595	2.268 (8)	1m
fac-$[Re(CO)_3(tmen)(H_2O)]BF_4$	3520	1597	2.239 (14)	1m
$[Re(CO)_5(H_2O)]AsF_6$	3400	1600	2.206 (8)	1m
$[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3]SO_4$			2.108 (11) (av)	1dd
$[RuH(CO)_2(PPh_3)_2(H_2O)]BF_4 \cdot H_2O$	3350	1620	2.15 (1)^d	1o
$[RuH(CO)(PPh_3)_3(H_2O)]BF_4 \cdot H_2O$	3500	1625		1o
$RuCl_2(CO)_3(H_2O)] \cdot diglyme$			2.105 (4)	1n
$Ru(\mu\text{-}4\text{-}F\text{-}C_6H_4CO_2)_2(CO)_5(H_2O)$	3580, 3320	1605	2.299 (6)	1k
$[CpOs(CO)_2(H_2O)]BF_4$		1645		1u
$RhCl[C_4(CF_3)_4](AsMe_3)_2(H_2O)$	3550, 3350	1580	2.243 (11)	1a
$RhCl(C_4O_2Cl_2)(PMe_2Ph)_2(H_2O)$	3550, 3350		2.280 (6)	1c
$[RhCl_2(PMe_2Ph)_3(H_2O)]PF_6$	3580, 3480	1590		1r
$RhCl_2(PPh_3)[ONN(C_6H_4Me\text{-}p)O](H_2O)$			2.202 (3)	1hh
$[Rh(PPh_3)(CO)(H_2O)]BF_4 \cdot 0.5H_2O$	3599,^{e} 3355		2.115 (5)	1bb
$[Rh(PPh_3)_2(CO)(H_2O)]CF_3SO_3$	3300		2.316 (12)	1gg
$[Rh(PP')_2(CO)(H_2O)]PF_6$^{f}			2.107 (6)	1ee
$[Rh(triphos)(C_2H_4)(H_2O)]BF_4$	3588, 3368		2.215 (5)	1ii
$[IrHCl(H_2O)(CO)(PPh_3)_2]BF_4$	3405, 3340		2.252 (7)	1l
$[IrH_2(PPh_3)_2(THF)(H_2O)]SbF_6 \cdot THF$			2.258 (8)	1f
$[IrH(bq)(PPh_3)_2(H_2O)]SbF_6$^{g}	3550		2.26 (2)	1j
$[Ir(PPh_3)_2(CO)(H_2O)]CF_3SO_3$	3373			1gg
$[Ni(C_6Cl_5)(PPhMe_2)_2(H_2O)]ClO_4$	3260	1625		1z
$[PdH(PCy_3)_2(H_2O)]BF_4$	3530, 3440	1630	2.206 (5)	1cc
$[PtCl(PBu_3)_2(H_2O)]BF_4$	3050			1s
$[Pt(C_6F_5)(PEt_3)_2(H_2O)]ClO_4$	3200–3400			1y

H(OH) complex	ν(OH)	ν(MH)	M–H, δ^h	M–OH, δ^h	ref
[*cis*-$IrH(OH)(PMe_3)_4]PF_6$	3620	2068	−11.19	−1.40	2a
$PtH(OH)(P\text{-}i\text{-}Pr_3)_2$	3600	2140	−21.4		2c
$RuH(OH)(PPh_3)_2(H_2O)$	3600^i	2100	−24.1	0.05^j	1q
$[RuH(OH)(PPh_3)_2(Me_2CO)]_2$	3600, 3580	1980	−17.7	−1.30	1q
$IrH(OH)Cl(PCy_3)_2(CH_3CN)$	3490		−24.3		2d
cis-$OSH(OH)(PMe_3)_4$			−8.0	2.73	2e
$Os_3H(OH)(CO)_{10}$	3595		−12.58		2f,g

[a] Assigned to hydroxide. [b] Hydrogen bonding to fluoride ligand and fluoride anion is present. The band at 1740 cm^{-1} is possibly due to W–H. [c] tmen = *N,N,N′,N′*-tetramethylethane-1,2-diamine. [d] For the EtOH solvate. [e] Assigned to lattice H_2O. [f] PP′ = 1,11-bis(diphenylphosphino)-3,6,9-trioxaundecane-*P,P′*. [g] bq = 7,8-benzoquinolato. [h] Proton NMR shift, ppm. [i] ν(OH) for H_2O not given. [j] For hydroxide; signal for H_2O was at 1.5 ppm.

complexes and similar to that for free H_2O. For the D_2O analogue, these bands shifted to 1226 and ~1240 cm^{-1} (partially obscured). For hexane-derived $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O) \cdot xH_2O$, an unsplit δ(HOH) mode at 1622 cm^{-1} shifted to 1617 and 1203 cm^{-1} on $H_2{}^{18}O$ and D_2O substitution, respectively.

For the complex of most interest, $W(CO)_3(PCy_3)_2(H_2O) \cdot 2H_2O$, the ambiguous 1677-$cm^{-1}$ band also shifted 5 cm^{-1} to lower energy, demonstrating that the mode here is most probably δ(HOH) and that *the water has not oxidatively added in the PCy_3 derivative.*

NMR Spectral Studies of W–H_2O Complexes and H_2O Dissociation. The ^1H NMR spectrum of crystals of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O) \cdot THF$ dissolved in dry THF-d_8 under argon at 22 °C displayed resonances at δ 1.32 (d of d, –CH_3), 2.42 (q, –C*H*), and 3.03 (broad H_2O resonance; $w_{1/2}$ = 39 Hz). $^{31}P\{^1H\}$ NMR in toluene-d_8 showed a major singlet peak at δ 41.6 with ^{183}W satellites (J_{PW} = 323 Hz) and minor peaks due to impurities. There were no observable ^1H resonances due to H or OH ligands in the region δ +11 to −48 either at 25 °C or as low as −84 °C (see Table VI for reported chemical shifts for H(OH) complexes). At 40 °C, the water resonance sharpened, moving unfield to δ 2.71, and, at 6 °C, separated into two very broad resonances at δ 3.58 and 2.87. The latter resonances narrowed and shifted to δ 4.43 and 3.01 (~1:2 ratio) at −50 °C. In order to determine if one of these peaks was due to free water (dissociated plus adventitious), 5 μL of D_2O (>5-fold excess) was added to a fresh sample of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O) \cdot THF$ in THF-d_8 displaying the resonances at δ 4.26 and 2.77. The spectrum at −30 °C showed the peak at δ 4.26 to nearly vanish, leaving a single major resonance at δ 2.95. Thus, we assign the resonance at δ 4.26 to coordinated water (replacement of protium by deuterium would greatly diminish its ^1H signal with respect to that for free water). The presence of dissociated, exchanging water indicates that an equilibrium exists in solution between the aquo complex and the agostic complex $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ (eq 3). THF is known to bind

$$\begin{tikzcd} \mathrm{W(CO)_3(P\text{-}\mathit{i}\text{-}Pr_3)_2(H_2O)} \arrow[r, shift left] & \mathrm{W(CO)_3(P\text{-}\mathit{i}\text{-}Pr_3)_2 + H_2O} \arrow[l, shift left] \arrow[d, shift left, "\mathrm{THF}"] \\ & \mathrm{W(CO)_3(P\text{-}\mathit{i}\text{-}Pr_3)_2(THF)} \arrow[u, shift left] \end{tikzcd} \qquad (3)$$

relatively weakly in these systems (see below),[4b] and some THF adduct is probably also present in equilibrium here. As a further check, a sample of 2 μL of water in THF-d_8 gave a resonance at δ 2.72 at 25 °C. The chemical shift of free water in THF is both concentration and temperature dependent; thus, this is merely an approximate value for the chemical shift of uncoordinated water in THF-d_8. In the stopped-exchange spectra of the sample containing $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)$, the resonance assigned to noncoordinated water ranged from 0.2 to 0.5 ppm upfield of the observed resonances of pure free water in THF-d_8 at the same temperatures. Reported values of chemical shifts for coordinated water in organometallic complexes range from δ 0.4 for $[RuCl(OH)(PPh_3)_2(H_2O)]_2$ in C_6D_6[1q] to δ 11.30 for $[W(PMe_3)_4H_2(OH_2)F]F$ in CD_2Cl_2.[1d]

Reaction of H_2O and $W(CO)_3[P(cyclopentyl)_3]_2$ in toluene gave a color change to gold-yellow, but attempts to isolate a solid led to decomposition to the tetracarbonyl. An NMR-tube reaction in C_6D_6 showed the appearance of signals at δ 5.70 and 5.20 presumably due to coordinated and free water.

NMR Studies of H_2O Addition to $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ To Give η^2-H_2 Substitution. In an NMR tube, 2 μL of H_2O (~0.1 mmol) was added to $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)$ (~0.2 mmol) in THF-d_8. The solution effervesced as H_2 was displaced by H_2O. The ^1H NMR (250 MHz, 25 °C) spectrum before addition showed resonances due to η^2-H_2 at δ -4.30, dihydride[6] in equilibrium at δ -3.60 (triplet), and free H_2 at δ 4.72. After addition, these diminished and a new broad resonance appeared at δ 3.83. Two more successive additions of 2 μL of water shifted the latter signal upfield to δ 3.70 and then δ 3.61. When the temperature was lowered to 2 °C, the latter separated into two very broad resonances (coalesced) at δ 4.13 and 3.30 and at -50 °C narrowed and shifted to δ 4.64 ($w_{1/2}$ = 7.8 Hz) and 3.80 (4.1 Hz). Only a very small amount of bound H_2 remained.

Addition of water as above to a solution of $W(CO)_3(PCy_3)_2(H_2)$ in THF-d_8 under argon in an NMR tube gave a color change from yellow to red, similar to the case for the P-*i*-Pr_3 analogue. At -54 °C the NMR showed two new peaks, singlets at δ 4.39 (weak) and 3.00 (strong), similar to those observed for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)$. They merged into one at δ 2.51 at 25 °C and were assigned to coordinated and free water, respectively. No evidence for a hydride or OH resonance was observed.

Qualitative Observation of Preferential H_2 over H_2O Binding on $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ in Hexane. Interestingly, if addition of H_2O to a solution of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ under an H_2 atmosphere was done in *hexane*, the aquo complex did not precipitate even after stirring for 30 min with a large excess of water present as an immiscible phase. As soon as the H_2 atmosphere was replaced by argon, the yellow solution darkened and the much less soluble yellow-orange H_2O complex began to precipitate. If this system was then exposed to *flowing* dry argon or vacuum, immediate dissociation of H_2O and precipitation of insoluble $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ as purple-black crystals occurred. H_2O recoordinated on stirring as soon as (1) the argon flow or vacuum exposure was terminated and (2) the solution and head gas became resaturated with the H_2O present as a second phase in the vessel. This demonstrates the extremely delicate nature of the water and H_2O binding and indicates that *in hexane H_2 is preferred over H_2O binding*. Undoubtedly the major factor here is mass action effects, i.e. relative concentrations of free ligand in solution. In hexane the low solubility of H_2O (~5 mM[21a]) limits its maximum concentration to the same order as that of dissolved H_2 (4.64 mM at 20 °C[21b]), as opposed to the situation in THF, where the concentration of miscible H_2O overwhelms that of H_2. The thermodynamic studies described below were performed to resolve whether dihydrogen is truly a better ligand than water here.

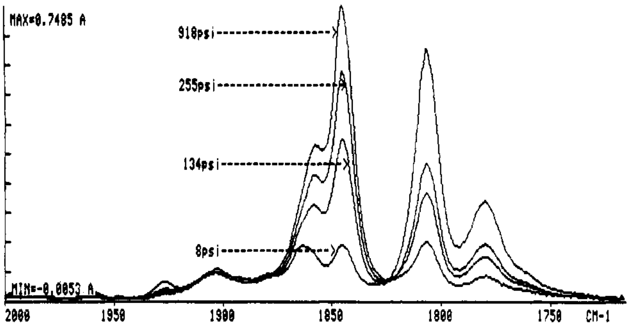


Figure 8. Variable-pressure FTIR study of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ in 1% H_2O/99% THF at 22 °C from 8 to 918 psi of H_2.

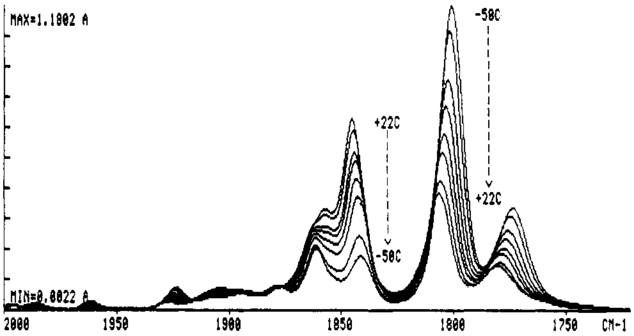


Figure 9. Variable-temperature FTIR study of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ (12.8 mM) in 1% H_2O/99% THF under 200 psi of H_2 from -50 to +22 °C. The peaks near 1850 cm^{-1} are due to the H_2 complex and decrease upon lowering the temperature. The peaks near 1800 cm^{-1} are due to the water complex and increase with decreasing temperature. A small residual peak near 1864 cm^{-1} is due to a small amount of $W(CO)_4(P\text{-}i\text{-}Pr_3)_2$ formed while the cell is loaded.

Quantitative Investigation of the Equilibrium between Dihydrogen and Water Complexes. The above observations suggested that one factor controlling whether water or hydrogen complexes formed was the relative solubilities of hydrogen and water in the solvent. The equilibrium nature of competitive binding between H_2O and H_2 was therefore investigated quantitatively in THF solution. Variable-pressure IR spectra of a solution of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ in 1% H_2O/THF are shown in Figure 8. H_2 pressures in excess of 1000 psi were needed to effect quantitative formation of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ at room temperature, as monitored by the relative intensities of the ν(CO) frequencies due to the latter and the H_2O complex. The equilibria were fully reversible and rapidly established even at low temperatures.

The equilibrium constants for displacement of dihydrogen by water were investigated at several H_2 pressures in the temperature range +25 to -70 °C. Typical

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(21) (a) Seidell, A.; Linke, W. F. *Solubilities of Inorganic and Metal-Organic Compounds*, 4th ed.; Van Nostrand: New York, 1958; Vol. 1, p 1135. (b) Gerrard, W. *Gas Solubilities Widespread Applications*; Pergamon Press: New York, 1980; p 28.

spectral data as a function of temperature are shown in Figure 9. As the temperature was lowered, the peaks due to the H_2 complex decrease and new peaks due to the H_2O complex appear. From van't Hoff plots the thermodynamic parameters shown in eq 4 were readily obtained.

$$W(CO)_3(PR_3)_2(H_2) + H_2O \rightleftharpoons W(CO)_3(PR_3)_2(H_2O) + H_2 \quad (4)$$

$$R = Cy: \ \Delta H = -2.8 \pm 0.1 \text{ kcal/mol}; \quad \Delta S = -16.5 \pm 2.0 \text{ cal/(mol K)}$$

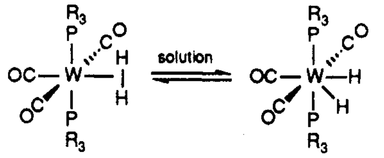
$$R = i\text{-Pr}: \ \Delta H = -4.5 \pm 0.2 \text{ kcal/mol}; \quad \Delta S = -18.8 \pm 2.0 \text{ cal/(mol K)}$$

For both phosphines, displacement of H_2 by water is exothermic by 3–4 kcal/mol. As will be discussed later, hydrogen bonding between coordinated water and solvent appears to play a role in the thermodynamics of binding of H_2O in these systems. The surprisingly high negative entropy change in eq 4 is no doubt a reflection of this. The unfavorable entropy of binding of water is largely responsible for the fact that *the equilibrium favors H_2 binding at room temperature and H_2O binding at low temperature.* ΔG_{298} for eq 4 can be calculated to be 1.1 kcal/mol for R = *i*-Pr and 2.1 kcal/mol for R = Cy, i.e. favoring the left side of the equation.

Enthalpy of Binding of H_2 by $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$. The enthalpies of binding of H_2O determined in eq 4 were relative to H_2. It was therefore of interest to determine the enthalpy of binding of H_2 to $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$. Direct measurement of the enthalpy of reaction 5 yielded ΔH =

$$W(CO)_3(P\text{-}i\text{-}Pr_3)_2 + H_2 \rightarrow W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2) \quad (5)$$

−11.2 ± 0.5 kcal/mol in toluene at 20 °C. Indirect measurement of this value based on reactions with pyridine[22] yielded a value of 10.4 ± 0.8 kcal/mol. We adopt the average value of 10.8 ± 1.0 kcal/mol for net binding of H_2 in this system. This value compares with the value of −10.0 ± 1.0 kcal/mol reported by us earlier for $W(CO)_3(PCy_3)_2$.[10] These values reflect the enthalpy for net reaction with H_2 and do not incorporate enthalpies of tautomerization between molecular hydrogen and dihydride species:



(6)

NMR studies have shown that the major species present in toluene solution is the H_2 complex and that the enthalpy of reaction 6 in the forward direction is +1.2 ± 0.6 kcal/mol for R = *i*-Pr.[3b,4b,6,23] Thus, the observed enthalpy of reaction 5 includes very little contribution (ca. 0.3 kcal/mol) from eq 6 (K_{eq} = 0.25 at 25 °C).

The calorimetric measurements described above predicted that binding of H_2 to $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ should be 0.8 ± 2.0 kcal/mol more exothermic than binding to $W(CO)_3(PCy_3)_2$. In order to test this, the equilibrium shown in eq 7 was investigated using FTIR under conditions

$$W(CO)_3(PCy_3)_2(H_2) + W(CO)_3(P\text{-}i\text{-}Pr_3)_2 \rightleftharpoons W(CO)_3(PCy_3)_2 + W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2) \quad (7)$$

where a 1:2 ratio of H_2 to total W complexes was used. Preferred binding to the *i*-Pr derivative was observed. As discussed later, the most likely explanation for the more exothermic enthalpy of binding to H_2 to $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ compared to $W(CO)_3(PCy_3)_2$ is decreased steric repulsion and lower "steric threshold"[24] for the *i*-Pr complex. It should also be pointed out that the net difference in enthalpies of binding, 0.8 ± 2.0 kcal/mol, is small compared to experimental errors.

Thermodynamics of Binding of THF: Model for an Oxygen Donor in the Absence of Secondary Hydrogen Bonding. The fact that the enthalpy of displacement of H_2 by H_2O was exothermic by 3–4 kcal/mol was surprising since the O atom donor THF was known to form complexes only at low temperature.[4b] In order to develop a benchmark for binding of oxygen donor ligands in this system, we investigated quantitatively the binding of THF to the complexes $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ and $W(CO)_3(PCy_3)_2$, as shown in eq 8. The equilibria in eq 8 were investigated

$$W(CO)_3(PR_3)_2 + THF \rightleftharpoons W(CO)_3(PR_3)_2(THF) \quad (8)$$

$$R = Cy: \ \Delta H = -8.6 \pm 0.7 \text{ kcal/mol}; \quad \Delta S = -31.0 \pm 2.5 \text{ cal/(mol K)}$$

$$R = i\text{-Pr}: \ \Delta H = -10.3 \pm 0.3 \text{ kcal/mol}; \quad \Delta S = -34.0 \pm 2.0 \text{ cal/(mol K)}$$

by FTIR spectroscopy in the temperature range +20 to −80 °C. Plots of ln *K* versus 1/*T* gave straight lines over the entire temperature range and yielded the thermodynamic data for eq 8. The entropies of binding are in keeping with statistical mechanical estimates[25] and also with data reported earlier for binding of N_2 to $Cr(CO)_3(PCy_3)_2$.[4b] The more exothermic binding of THF by the *i*-Pr congener is probably due to reduced steric repulsion for uptake of an additional ligand, as found for H_2 binding. As would be expected, the difference in enthalpies of binding of the smaller H_2 ligand (0.8 kcal/mol) was lower than that for thf (1.7 kcal/mol).

It should be pointed out that the enthalpies of binding include displacement of the agostic bond, and the differing enthalpies of binding could be due to different agostic bond strengths in the two phosphine systems. Gas-phase data[26] for binding of alkanes to the $W(CO)_5$ fragment indicate that the order of bond strength is $CH_4 \ll C_2H_6 < C_6H_{12}$. On that basis, the *i*-Pr and Cy groups might be expected to have different values for the agostic bond, since $P\text{-}i\text{-}Pr_3$ bonds with a terminal methyl and PCy_3 with a methylene group. Additional calorimetric work is in progress to clarify whether the increased enthalpy of binding of THF is due to decreased steric repulsion in $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(THF)$ or to a weaker agostic bond in $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$. However, preliminary results indicate that the gap in enthalpies for the two systems increases as the ligand size increases, supporting steric pressure as the main factor in controlling differences in complex stability for these systems.[27]

Data for enthalpies and entropies of binding of the weak ligand set THF, H_2, and H_2O can be constructed on the basis of the data obtained for reactions 4, 5, and 8. Entropies of binding of H_2 could not be determined for the W complexes, but earlier work on the analogous Cr and Mo complexes[4b] allows estimation of the entropy of binding of H_2 to be 25 ± 3.0 cal/(mol K). Combined data are shown in Table VII. For both phosphines, the bond to THF is some 8–10 kcal/mol stronger than the agostic bond.

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[22] Hoff, C. D.; Kiss, G. Unpublished results.

[23] Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Van Der Sluys, L. S.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* 1990, *112*, 3855.

[24] The idea of "steric threshold" has been widely used; see, for example: Liu, H. Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* 1990, *9*, 1758.

[25] Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

[26] Brown, C. E.; Ishikawa, Y.; Hackett, P. A.; Rayner, D. M. *J. Am. Chem. Soc.* 1990, *112*, 2530.

[27] Lang, R. L.; Kiss, G.; Hoff, C. D.; Kubas, G. J. Work in progress.

Table VII. Enthalpies and Entropies of Binding for Ligands to $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ and $W(CO)_3(PCy_3)_2$

L	$W(CO)_3(P\text{-}i\text{-}Pr_3)_2$		$W(CO)_3(PCy_3)_2$	
	ΔH^a	ΔS^b	ΔH^a	ΔS^b
agostic	0	0	0	0
THF	−10.3 ± 0.3	−34.0 ± 2.0	−8.6 ± 0.7	−31.0 ± 2.5
H_2	−10.8 ± 1.0	−25.0 ± 3.0	−10.0 ± 1.0	−25.0 ± 3.0
H_2O^c	−15.3 ± 1.2	−43.8 ± 5.0	−12.8 ± 1.1	−41.5 ± 5.0

[a] Enthalpies of reaction (kcal/mol) in toluene solution. [b] Entropies of reaction (cal/(mol K)). Value for entropy of binding of H_2 is an estimate based on measurements of the entropies of binding of H_2 for the analogous Cr and Mo complexes.[4b] [c] Values for H_2O are based on values for H_2 and measurement of the enthalpies and entropies of reaction 4 as described in the text.

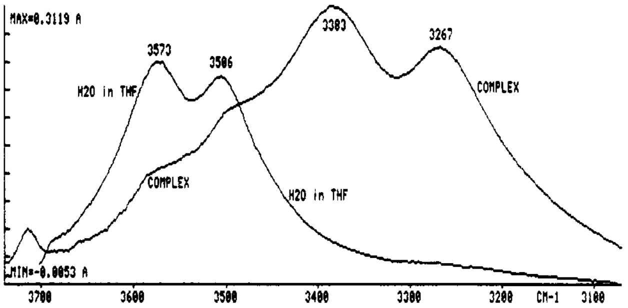

Figure 10. FT-IR spectra of H_2O in THF before and after $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ was added.

This can be compared to photoacoustic calorimetry data[28] which show that THF binds 12.4 ± 1.2 kcal/mol stronger than heptane to $Cr(CO)_5$:

$$Cr(CO)_5(\text{heptane}) + THF \rightarrow Cr(CO)_5(THF) + \text{heptane} \quad (9)$$

Differences in binding for these two types of complexes cannot be attributed to steric factors alone, since the electronic requirements of the $M(CO)_5$ and $M(CO)_3P_2$ fragments would not be expected to be the same.

Role of Hydrogen Bonding in H_2O Complex Stability. The data in Table VII show that H_2O has a more favorable enthalpy of binding of 4–5 kcal/mol than does THF. On the basis of electronic factors alone, one would expect THF to be the better donor and thus have a higher enthalpy of binding. The crystal structure of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$, which showed hydrogen bonding to be involved in the solid state, prompted us to investigated whether or not hydrogen bonding of the coordinated water was retained in solution. Hydrogen-bond strengths of up to 14 kcal/mol have been reported between rhodium alkoxide complexes and phenols[29] and thus can make considerable contributions to observed enthalpies of reaction. FTIR studies supported formulation of the complex in solution as $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdots(THF)$. As shown in Figure 10, the OH region of the FTIR of a dilute solution of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)$ in THF indicated the presence of hydrogen bonding between solvent and bound water. A spectrum of H_2O (at the same concentration as that for the spectrum of the complex) showed bands at 3573 and 3506 cm^{-1} which can be attributed to the OH stretches of H_2O associated with THF solvent. When an equimolar amount of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ is added, new bands appear at 3383 and 3267 cm^{-1}, in surprisingly good agreement with the Nujol mull spectrum of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$ in Figure 4D. Small shoulder peaks due to free water can be seen in the spectrum, indicating that there is some displacement of bound H_2O by THF.

It seems most likely to us that the source of the stability of the aquo complex relative to the THF complex derives largely from the secondary hydrogen bonding. Hydrogen-bond strengths on the order of 4–6 kcal/mol between THF and the coordinated hydrazine, diazene, and ammonia complexes $Mo(CO)_5(N_xH_y)\cdots(THF)$ have been observed on the basis of direct calorimetric measurements of heats of solution.[30] Burkey has reported H-bonding effects on the order of 5 kcal/mol for secondary interactions in similar organometallic complexes.[31] The high negative entropy of binding of H_2O to $W(CO)_3(PR_3)_2$ is also supportive of association of solvent with the water complex after it is formed. More detailed comparison of these effects and extension to studies of binding of alcohols, amines, and hydrazines is in progress.

Isotopic Exchange of H_2O and D_2 on $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$. In order to test whether isotopic exchange occurs between H_2O and H_2 on these complexes, solutions of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ under 1 atm of D_2 were stirred with a slightly deficient amount of H_2O (to avoid complete displacement of D_2). IR analysis was then performed on the isolated aquo complexes to monitor incorporation of D into the aquo ligand. The product from a 45-min reaction in hexane showed no observable D. However, longer reactions in 1:1 THF–hexane did produce, on cooling, orange crystals of an isotopomeric mixture, $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_nD_{2-n}O)\cdot THF$ (n = 0–2). From qualitative ratios of $\nu(OD)/\nu(OH)$ IR intensities, about 50% scrambling occurred after 3 days. A weak peak at 1226 cm^{-1} due to $\delta(DOD)$ of the fully deuterated isotopomer $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2O)\cdot THF$ was seen, along with comparably weak $\delta(HOH)$ bands of the fully protium species. Thus, the major species was undoubltedly the HDO complex (observation of $\delta(HOD)$ was obscured). After an 18-h reaction, weak $\nu(OD)$ peaks were observed, indicative of some exchange.

NMR-tube reactions of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ (0.05–0.1 M) and H_2O in THF or toluene under 1 atm of D_2 were also carried out, using ^2H NMR (38.40 Mhz) to monitor incorporation of D into H_2O. The closed systems contained a >4-fold excess of D as coordinated and free D_2 (~1:1 ratio) in relation to the amount of protium in the H_2O reactant. The NMR signal for the D_2 complex in THF before H_2O addition showed a singlet at δ −4.35 due to η^2-D_2 with a broad shoulder (unresolved multiplet) at ca. −3.6 ppm probably due to the dideuteride in equilibrium. A resonance for free D_2 was not observed. Some THF complex (eq 3) was probably present, as suggested by lower than calculated integration ratios of η^2-D_2 to reference compounds. The η^2-D_2 signal weakened and broadened on H_2O addition, consistent with partial displacement of D_2 ligand and exchange equilibria. Production of $H_nD_{2-n}O$ (coordinated plus free, rapidly exchanging) was shown by the appearance of a single peak near 3 ppm. The rate of D incorporation appeared to be relatively constant in this study and in similar experiments. For a ratio of H_2O to complex of 1:2, about 17–21% of statistical scrambling occurred over 12 h, depending on the amount of head gas D_2 entering into the exchange (and how much adventitious water was present). Although imprecise, this slow rate qualitatively agrees with that found in the above IR-monitored experiments.

A similar experiment using about half the concentrations of D_2 complex and water (intensities referenced to THF-*d*

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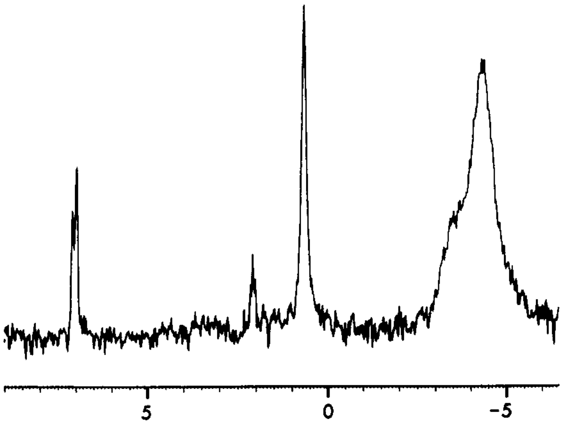

Figure 11. ^2H NMR spectrum (38.40 MHz, 25 °C) of the $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$–$H_2O$ reaction mixture in toluene under D_2 after 2 days, showing the resonance of the HDO/D_2O product at 0.65 ppm and overlapping $\eta^2\text{-}D_2/\eta^2\text{-}HD$ signals near −4 ppm. The shoulder on the latter may be due to a deuteride ligand in equilibrium.

peaks) was also carried out. The incorporation of D_2 into H_2O was unexpectedly faster here, requiring only about 3 h rather than 12 h for the same amount of exchange. The scrambling was complete in 46 h but was somewhat slower in toluene, requiring 2 days for ~43–50% scrambling and ca. 4 days for complete exchange (H_2O:complex = 1:3). The $H_nD_{2-n}O$ peak appeared at δ 0.60–0.95 (Figure 11).

The reverse experiment was also performed i.e. reaction of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2O)$ with H_2 in THF, monitored by ^2H NMR as above. The ratios of D_2O to both metal complex and H_2 were ~1:1 here, and most of the D_2O remained coordinated even after H_2 addition. Nevertheless, H/D scrambling did occur, although at an overall rate slower than that of D_2 complex plus H_2O in THF (the presence of adventitious H_2O, inefficient gas/solution mixing, and low solubility of H_2 precluded attainment of quantitative kinetic information, especially in this experiment). The "loss" of deuterium from the D_2O signal was followed and reached a plateau by 8 days at ca. 70% of the calculated protium incorporation. The factors listed above undoubtedly were responsible for a final value less than 100%. A resolvable signal for coordinated HD or D_2 was not observed at any time during the exchange process, supporting the contention that in THF H_2 does not compete favorably with H_2O for the tungsten binding site because of the much higher concentration of water than that of dissolved H_2 present here (>20-fold).

Isotopic Exchange of MeOH with $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$. An exchange experiment using MeOH in place of H_2O was conducted in THF as above. Whereas H_2O had displaced a large fraction of the bound D_2, MeOH did not not. Two resonances appeared in the OD region, the first (δ 3.02) within hours and the second (δ 3.20) after 1–4 days. After 4 days, the latter grew while the former remained unchanged in intensity, indicating that they were due to MeOD and, presumably, adventitious $H_nD_{2-n}O$, respectively. Full scrambling required >2 weeks, much slower than for the H_2O case.

Discussion

Infrared Studies as a Diagnostic of the Structure and Hydrogen-Bonding Interactions of Water Complexes. Determination of the structures and interpretation of IR spectra of the products of H_2O addition to $M(CO)_3(PR_3)_2$ has been a decidedly nontrivial problem. It was not completely resolved until a crucial isotopic-labeling experiment carried out over 10 years ago was repeated using an FT–IR instrument with higher resolution. Initial spectra of "$W(CO)_3(PCy_3)_2(H_2O)$" and its $H_2{}^{18}O$ isotopomer did not show a shift in a band then measured to be at 1674 cm^{-1},[4a] leading to speculation that this mode might be due to ν(WH) in a hydrido–hydroxo formulation. This became more doubtful when the X-ray structure of the $P\text{-}i\text{-}Pr_3$ analogue showed an aquo ligand and when IR bands near 1620 cm^{-1} analogous to the 1674-cm^{-1} band showed ^{18}O shifts of ~5 cm^{-1} resolvable by FT-IR, proving the bands to be δ(HOH). A new ^{18}O-labeling experiment for the PCy_3 species now showed a similar 5-cm^{-1} shift in the 1674-cm^{-1} peak (more accurately measured to be at 1677 cm^{-1}). Thus, all the solid complexes reported here appear to contain an unsplit aquo ligand, and NMR measurements are consistent with this in solution. The low solubility of $M(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$ precluded direct NMR studies, but NMR-tube reactions of H_2O and $W(CO)_3(PCy_3)_2(H_2)$ in THF were carried out. Hydrogen was displaced, and the spectrum of the resultant product was similar to that of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot$THF, indicating H_2O coordination is present in solution for the PCy_3 system.

Hydrogen bonding between metal-bound H_2O and "lattice" H_2O or solvent is an important factor in both IR studies and thermodynamics of H_2O binding. ν(OH) bands could undergo large unpredictable shifts, as shown in Figure 10 for H_2O hydrogen-bound to THF. The initial evidence that $W(CO)_3(PCy_3)_2(H_2O)\cdot 2H_2O$ might contain hydroxo ligand was observation of ν(OH) bands above 3600 cm^{-1}, but it is likely that these are due to hydrogen-bonded lattice water. Bands of this type (e.g. for the "free" OH of hydrogen-bonded water in $Fe(Saen)Cl\cdot H_2O$ (ν(OH) = 3620 cm^{-1} [32]) have been described to be sharp ($\nu_{1/2}$ = 20 cm^{-1}), and the high-frequency bands in the spectra of the solid PCy_3 and Mo–$PCy_2(i\text{-}Pr)$ complexes were relatively sharp ($\nu_{1/2}$ = 20–60 cm^{-1}, Figures 3–5). Also, a band at 3599 cm^{-1} was recently assigned to lattice water in $[Rh(PPh_3)_2(CO)(H_2O)]BF_4\cdot 0.5H_2O$.[1bb] Finally, it should be noted that the complexes with lattice *THF* rather than H_2O do not show bands >3600 cm^{-1} (Figure 4B,D).

Clearly, one cannot safely diagnose whether or not H_2O oxidatively adds to metal complexes using ν(OH) data alone. In the complexes here, ν(CO) data support formulation as six-coordinate aquo species because of similarity to the bands for other oxygen donor adducts of $M(CO)_3(PCy_3)_2(L)$, e.g. L = acetone, acetaldehyde.[4a] The seven-coordinate oxidative-addition product $WHCl(CO)_3(PCy_3)_2$, on the other hand, showed three closely spaced ν(CO) bands at much higher frequencies (1907, 1885, 1856 cm^{-1}).[12] The lowest energy ν(CO) band for the water complexes appeared at quite low frequency (1705–1757 cm^{-1}; cf. 1776 cm^{-1} for L = acetone) and was more variable in position than the two higher frequency modes. These effects could be the result of involvement of one of the CO ligands in hydrogen bonding similar to that found in $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot$THF. Shifts of ν(CO) to lower energy of up to 40 cm^{-1} were observed for interaction of carbonyl ligands with $(CF_3)_3COH$ in liquid xenon and CCl_4.[17]

Very little descriptive IR detail has been reported in the literature for other organometallic H_2O complexes except for positions of ν(OH) and δ(HOH). In our systems, the apparent splitting of the δ(HOH) band in $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot$THF is a matter of concern, especially since only one such band was present for $W(CO)_3(PR_3)_2(H_2O)\cdot xH_2O$ (and all other reported H_2O complexes). A possible explanation is that the hydrogen-bonding inter-

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(32) Summerton, A. P.; Diamantis, A. A.; Snow, M. R. *Inorg. Chim. Acta* **1978**, *27*, 123 and references therein.

actions with lattice THF and carbonyl ligand cause the splitting (hydrogen bonding is known to raise the value of $\delta(HOH)$[16]). However, it is puzzling that there is only one $\delta(HOH)$ signal in the H_2O solvates, which contain at least two types of H_2O (metal-bound and lattice). Hydrogen bonding may shift or eliminate these modes: a complex containing lattice water hydrogen-bonded to coordinated anions, $Re(CO)_3(bpy)(FAsF_5)\cdot H_2O$, was reported to not display $\delta(HOH)$.[1m]

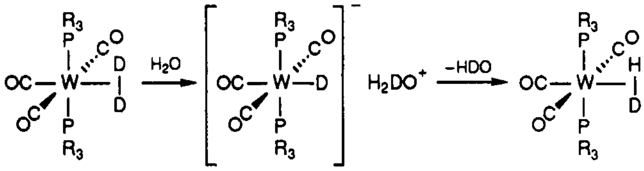
Relative Binding Abilities of H_2O and H_2, Isotopic Exchange Reactions, and Relevance to Enzymatic Reactions of Hydrogen. Thermodynamic studies of direct competitive binding indicated that H_2 is a slightly better ligand than H_2O on $W(CO)_3(PR_3)_2$. Although the enthalpy of binding favored H_2O by 3–4 kcal/mol, depending on R, an unfavorable entropic term due to hydrogen-bonding effects swung the equilibrium in favor of the H_2 complex at room temperature. It is perhaps surprising that dihydrogen, which binds nonclassically to a metal via its *bonding* pair of electrons, can even come close to the binding ability of water, which donates a *nonbonding* electron pair and is *the* classical ligand in coordination chemistry. Because H_2O is purely a σ-donor with little capability for back-bonding, one might conclude that the $M-H_2$ interaction must be enhanced by back-bonding from metal to H_2 σ^*, as supported by theoretical calculations and studies of the rotational barrier of H_2. Provided that the metal center is not exceedingly electron-poor, e.g. as in $M(CO)_5$ fragments, this back-donation thus brings η^2-H_2 out of the realm of a weak "token" ligand. Another viewpoint is that water is a poorer ligand here than might be expected, and indeed the solid-state structure of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2O)\cdot THF$ showed one of the longest known metal–OH_2 bonds. Possibly this is because H_2O is a hard donor and the organometallic tungsten center is relatively soft.

Our demonstration that H_2 can actually be favored over water for the same binding site is clearly relevant to biological activation of H_2 by enzymes such as hydrogenase and nitrogenase, where water is potentially a competing ligand. H_2 binding to $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ was preferred over H_2O in both polar and nonpolar solvents such as hexane, a situation that could be mimicked in the hydrophobic protein site known for Ni hydrogenase, which catalyzes eq 10. Agostic interactions such as shown in eq 2 or weak

$$H_2 \rightleftharpoons 2H^+ + 2e^- \qquad (10)$$

$M-OH_2$ binding may play a role in enzyme systems in preserving a lightly occupied coordination site for small-molecule activation (H_2, N_2).[33] Crabtree and others have proposed that η^2-H_2 binding possibly may occur at Mo or Ni metal centers in the enzyme systems.[34] He also found that η^2-H_2 can replace H_2O in $[IrH(L)(bq)(PR_3)_2]^+$, but only if water is removed from the system, e.g. by molecular sieves (competition experiments were not reported).[35] H_2 binding can also be preferred *over* N_2 on $M(CO)_3(PCy_3)_2$, where entropic factors again are important. H_2 is favored at higher temperatures (above −70, +28, and +46 °C for M = Cr, Mo, and W respectively) because it has a substantially lower absolute entropy than N_2.[36]

Isotopic exchange between H_2O and D_2 occurs in solutions of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ over several days, and the enzyme systems are also known to exhibit this exchange. Catalysis of H_2O/D_2 exchange has previously been demonstrated in systems which heterolytically split H_2 to metal hydride complexes[37] and in the Ir–bq system which also catalyzes ROH/D_2 exchange.[35] The latter complex contains a hydride cis to H_2O or ROH which participates in the exchange. However, in our system the *mechanism* of exchange and role of η^2-H_2 are not obvious, similar to the situation for $H_2 + D_2 \rightarrow 2HD$ exchange observed[6] on these $M(CO)_3(PR_3)_2$ systems. The bonds of two separate molecules are being broken and re-formed, but how can this occur on a metal complex with ostensibly only *one available binding site*? Formation of higher coordinate species with two weakly bound exchanging ligands is very unlikely, especially because of the steric bulk of the phosphines. With regard to mechanisms involving transient ligand dissociation, clearly the CO ligands are nonlabile in solution, the phosphines are not very labile, and HD formation was observed even on *solid* $M(CO)_3(PR_3)_2$, where ligand dissociation is even less likely (light was also excluded to prevent photochemical reaction).[6] In the case of scrambling involving water, however, the latter is of course a weak base and could function as a deprotonating agent. A mechanism involving proton removal from an η^2-H_2 ligand and readdition could occur:



This would be similar to an exchange process proposed by Collman[38] involving a Ru prophyrin system which binds η^2-H_2 and catalyzes D_2O/H_2 exchange in THF. However, their system required the presence of a strong base, KOD.[39] Our tungsten–H_2 complexes can be stoichiometrically deprotonated by strong bases (KH and CuO-*t*-Bu) but not observably by weaker ones such as Et_3N.[40] Deprotonation by H_2O could operate on an equilibrium scale, however, and this would be consistent with the observed slow rate of scrambling of D_2 with H_2O. The even slower rate of exchange observed when we use nonpolar solvents and when we start with the aquo complex and add D_2 (where the concentration of D_2 complex was low, giving fewer opportunities for deprotonation) would agree with a deprotonation mechanism. Exchange was also considerably slower between D_2 and MeOH, a poorer base than H_2O. Similar exchange experiments carried out by Crabtree on his Ir–bq system gave very much faster rates.[35b] A deprotonation mechanism similar to the above was also in-

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(33) An agostic Co--HC interaction has been recently reported to exist *even in aqueous solution* in the sterically constrained macrocyclic complex $K[Co(1,5\text{-diazacyclooctane-}N,N'\text{-diacetato})(SO_3)]\cdot 5H_2O$: Broderick, W. E.; Kanamori, K.; Willett, R. D.; Legg, J. I. *Inorg. Chem.* **1991**, *30*, 3875.

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voked to explain exchange in a sterically hindered alcohol. The dihydrogen ligand in $IrH(H_2)(bq)(PR_3)_2^+$ is more acidic than in the tungsten complex and more easily deprotonated.

It has been suggested[3c] that adventitious water mediates the enigmatic H/D scrambling observed on our dihydrogen complexes, possibly by a deprotonation mechanism similar to the above. However, the relatively slow rate (days) of D_2/H_2O exchange determined in solutions containing $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ would argue against this. Even though the $M\text{–}\eta^2\text{-}D_2 + H_2 \rightarrow M\text{–}\eta^2\text{-}HD + HD$ statistical scrambling occurs over a similar time frame (ca. 1–2 days for bulk reaction, solution or solid state), a very fast rate of D_2/H_2O reaction would be required for a trace amount of water to actively exchange with a much larger amount (up to 10 mmol) of hydrogen. Furthermore, we have found that H_2/D_2 scrambling occurs over *catalytic* amounts of *solid* $W(CO)_3(PCy_3)_2$ *thoroughly dried in vacuo*, which surely would preclude deprotonation by H_2O.[41] Additional studies of these isotopic exchange processes are planned to obtain mechanistic information.

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Supplementary Material Available: Tables of general displacement parameter expressions (U's) (2 pages). Ordering information is given on any current masthead page.

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Organometallic Oxides: Oxidation of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ with O_2 To Form *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$, *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$, and $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$

Frank Bottomley* and Jinhua Chen

Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3

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Oxidation of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ by air in $CHCl_3$ gave $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$, in an unprecedented reaction in which an oxygen atom was inserted into a C_5 ring. The previously reported complexes $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$ and $(\eta\text{-}C_5Me_5)MoCl(O)_2$ were also obtained from the oxidation. The structure of $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$ has been determined by X-ray diffraction (orthorhombic, a = 15.971 (1) Å, b = 16.825 (1) Å, c = 23.597 (1) Å, space group *Pcab*, Z = 8, R' = 0.051). The anion is a derivative of the classic $\{[Mo(O)(\mu\text{-}O)_2]_6(\mu_6\text{-}O)\}^{2-}$, in which a terminal oxygen has been replaced by $\eta\text{-}C_5Me_5$. The strong trans effect of Mo═O manifests itself across the $Mo_6(\mu_6\text{-}O)$ octahedron to the $Mo\text{–}(\eta\text{-}C_5Me_5)$ unit. Irradiation of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ in the presence of O_2 gave *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ and *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$, whose structures have been determined by X-ray diffraction. *syn*-$[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ is orthorhombic, with a = 8.581 (7) Å, b = 39.610 (6) Å, c = 56.650 (8) Å, space group *F2dd*, Z = 32, and R = 0.195. $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ is monoclinic, with a = 8.451 (8) Å, b = 28.771 (16) Å, c = 10.925 (14) Å, β = 107.2 (10)°, space group $P2_1/c$, Z = 4, and R = 0.073. These diamagnetic dinuclear compounds have long Mo—Mo distances (2.72 and 2.80 Å, respectively). Extended Hückel calculations show that there is very little Mo—Mo bonding, and the formal Mo—Mo description required by the 18-electron rule is incorrect.

Introduction

Cubanes of general formula $[(\eta\text{-}C_5R_5)M(\mu_3\text{-}A)]_4$ (M = d-block element; A = p-block element, usually from group 16) have interesting electronic and magnetic properties. In the cases where M = Mo, Fe and A = S, they may also be models for the active sites of ferridoxins and nitrogenase.[1] As part of our research into cyclopentadienylmetal oxides, we have discussed the molecular and electronic structures of $[(\eta\text{-}C_5R_5)Cr(\mu_3\text{-}O)]_4$ (R = H,[2] Me;[3] R_5 = H_4Me[4]). An extremely desirable cubane for comparison purposes would be $[(\eta\text{-}C_5R_5)Mo(\mu_3\text{-}O)]_4$. However, this molecule presents a considerable synthetic challenge. The route used to prepare $[(\eta\text{-}C_5R_5)Cr(\mu_3\text{-}O)]_4$, namely oxidation of $(\eta\text{-}C_5R_5)_2Cr$ with N_2O,[5] cannot be used for molybdenum since $(\eta\text{-}C_5R_5)_2Mo$ compounds are unknown. The routes used to prepare $[(\eta\text{-}C_5R_5)Mo(\mu_3\text{-}S)]_4$ (the reaction between $[(\eta\text{-}C_5R_5)Mo(CO)_2]_2$ and $[(\eta\text{-}C_5R_5)Mo(\mu\text{-}\eta^2\text{-}SC_3H_6S)]_2$[6] or between $[(\eta\text{-}C_5R_5)Mo(\mu\text{-}Cl)_2]_2$ and LiSH[7]) are also not available because the starting materials do not exist or because they do not react in an analogous manner when oxygen replaces sulfur.

In the absence of $(\eta\text{-}C_5R_5)_2Mo$, the carbonyl dimers $[(\eta\text{-}C_5R_5)Mo(CO)_n]_2$ (n = 2, 3) are attractive candidates for oxidation to $[(\eta\text{-}C_5R_5)Mo(\mu_3\text{-}O)]_4$. The oxidation of $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ by O_2 was first investigated by Green

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