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Photochemical Generation of Dihydrogen Complexes of Chromium and Tungsten

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Abstract: Photolysis of solutions of $M(CO)_6$ (M = Cr, W) at low temperature in the presence of hydrogen gas affords $Cr(CO)_5(H_2)$ (**1**) and $W(CO)_5(H_2)$ (**2**). Complexes **1** and **2** are characterized as dihydrogen complexes based on short T_1 values for the hydride resonances and the observation of a large HD coupling in the HD derivatives. Irradiation of a phosphine-substituted derivative $(PMe_3)Cr(CO)_5$ in the presence of hydrogen gas gave similar results. Thus *cis*-$(PMe_3)Cr(CO)_4(H_2)$ (**3**) and *trans*-$(PMe_3)Cr(CO)_4(H_2)$ (**4**) were prepared and characterized by ^{1}H and ^{31}P NMR spectroscopy. When the photolysis reactions were carried out in methylene chloride, solvent binding competitive with hydrogen binding was observed. This was not observed in less coordinating solvents such as alkanes. Subsequent displacement of solvent by H_2 leads to the dihydrogen complexes. Complexes **1** and **2** are moderately acidic, with deprotonation effected by mild bases.

Introduction

The first examples of isolable transition-metal dihydrogen complexes were reported by Kubas and co-workers over 20 years ago. These complexes are exemplified by tungsten complexes such as $W(CO)_3(PR_3)_2(H_2)$ (R = ^{i}Pr; Cy)[1] and their Mo and Cr analogues,[2] which bind hydrogen relatively weakly and are prepared by displacement of an agostic interaction with H_2 gas. Weak binding of H_2 in these complexes is consistent with moderate elongation of the H−H distance (d_{HH}) compared to H_2 gas. Values of $d_{HH} = 0.85(1)$ Å (Cr),[2] 0.87(1) Å (Mo),[3] and 0.89(1) Å (W)[3] for these complexes have been determined by solid-state NMR measurements of dipolar coupling.

A number of related species that are apparently not isolable at ambient temperature have been studied under matrix isolation conditions,[4] in liquid and supercritical xenon,[5] or by fast spectroscopy methods in alkanes.[6] The prototypical molecules $M(CO)_5(H_2)$ (M = Cr, Mo, and W) have been observed under such exotic conditions and have been characterized as dihydrogen complexes on the basis of vibrational spectroscopy. While vibrational data such as the detection in the infrared spectrum of the H−H stretching mode can confirm the presence of a dihydrogen ligand, quantitative structural information is lacking. The key structural parameter is the HH distance (d_{HH}), which is best determined by diffraction or NMR methods. For complexes that are not isolable in the solid state, solution NMR spectroscopy becomes the method of choice.

After the pioneering work of Kubas, a large number of dihydrogen complexes have been reported. A wide range of coligands have been employed, including phosphines, cyclopentadienyls, and many other ligand types. Of these diverse complexes, relatively few complexes have been reported of metal centers with a preponderance of strong π-acid ligands such as CO. Hydrogen complexes with coligands consisting largely of CO are of fundamental interest in that these very electrophilic metal centers may bind hydrogen relatively weakly but provide substantial activation of the HH bond toward heterolysis.

These relatively simple molecules may also provide experimental tests for the computational chemistry work that has led to structural predictions in cases where isolation and diffraction analysis is not possible. For example, the best computational results give d_{HH} of ca. 0.80−0.83 Å for $M(CO)_5(H_2)$, slightly shorter than the computed structures for $M(CO)_3(PH_3)_2(H_2)$, which are models for the isolable phosphine-containing complexes. Previous experimental work shows that bisphosphine moieties such as $W(CO)_3(PMe_3)_2$ form dihydride rather than dihydrogen complexes, demonstrating the importance of steric effects in the original work of Kubas and co-workers.[7]

In this work, we present investigations of the structure and reactivity of CO-rich complexes in conventional solvents using NMR spectroscopy. Coordinatively unsaturated species have been generated by photoextrusion of CO, which affords weakly solvated species. Reaction with hydrogen gas leads to hydrogen complexes, which have moderate thermal stability. With this

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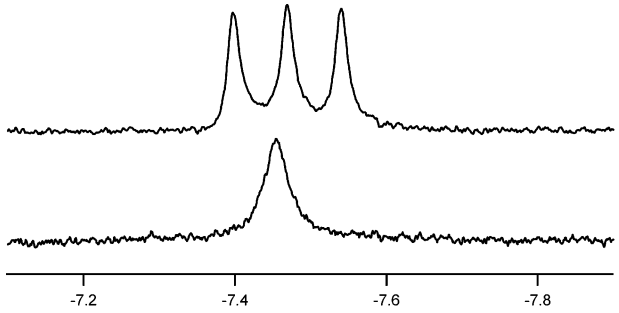
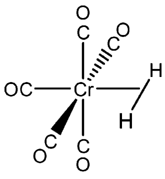


Figure 1. Partial (hydride region) ^1H NMR spectra (CD_2Cl_2, 500 MHz, 220 K) of $Cr(CO)_5(H_2)$ **1** (bottom) and $Cr(CO)_5(HD)$ **1**-d_1 (top).

methodology, we have prepared hydrogen complexes of Cr with four CO ligands and one phosphine ligand as well as complexes of Cr and W with only CO coligands. A portion of these results has been previously communicated.[8]

Results

M(CO)$_5$ Complexes (M = Cr, W) Irradiation (Hg arc lamp, Pyrex filter) of a CD_2Cl_2 solution of $Cr(CO)_6$ at 195 K under 1.5 atm of H_2 gas results in an orange solution. The ^1H NMR spectrum of the orange solution at 220 K shows only one new resonance, a broad singlet ($\nu_{1/2} = 12$ Hz) at −7.44 ppm assigned to $Cr(CO)_5(H_2)$ (**1**). When the reaction is carried out with HD gas, a new 1:1:1 triplet resonance is observed at −7.47 ppm with $^1J_{HD} = 35.8$ Hz (Figure 1). Replacement of the H_2 atmosphere over a CD_2Cl_2 solution of **1** with excess D_2 gas (1.5 atm.) resulted in the disappearance from the ^1H NMR spectrum of the resonance assigned to **1** in minutes at 240 K. This is consistent with the formation of **1**-d_2 exclusively without isotopic scrambling to form **1**-d_1. After 24 h at 195 K, **1**-d_1 was detected in solution at a very low concentration.



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The spin lattice relaxation time T_1 was measured as a function of temperature for the hydride resonance of **1** at both 500 and 750 MHz. The T_{1min} values found are 22 and 31 ms, respectively (Figure 2).

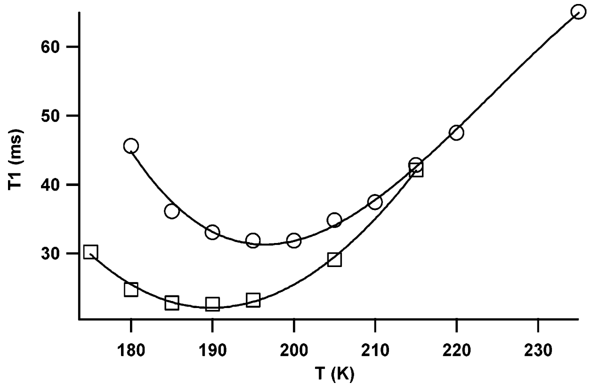

Figure 2. Relaxation time (T_1) values for complex **1** as a function of temperature at 500 MHz (□) and 750 MHz (○).

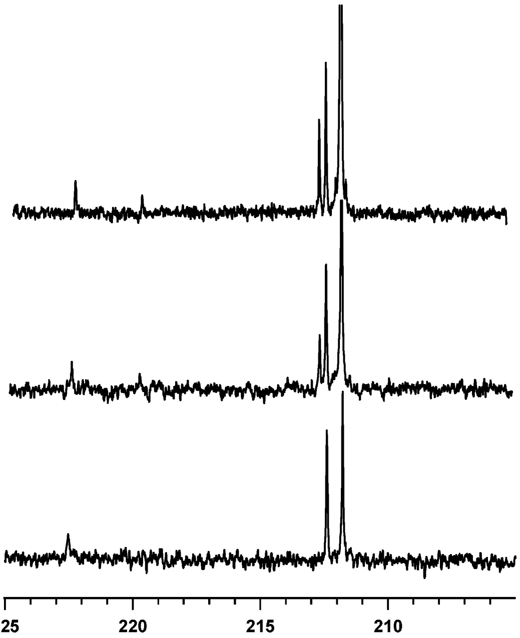

Figure 3. Partial (carbonyl region) ^{13}C NMR spectra (CD_2Cl_2, 500 MHz, 220 K) after photolysis of $Cr(CO)_6$ (bottom) and subsequent addition of $H_{2(g)}$ (middle), and ^{13}C NMR spectrum (CD_2Cl_2, 750 MHz, 210 K) after photolysis of $Cr(CO)_6$ under $H_{2(g)}$ (top). The large signal at 211.8 ppm is due to $Cr(CO)_6$.

The ^{13}C NMR signals of **1** are weak at natural abundance. Modest enrichment with ^{13}CO allows for facile ^{13}C NMR detection. Photolysis of a CD_2Cl_2 solution at 195 K of ^{13}CO-enriched $Cr(CO)_6$ under H_2 gas shows four new resonances in the carbonyl region of the ^{13}C NMR spectrum (Figure 3). These appear as two pairs with an intensity ratio of 1:4. Repeating this experiment in the absence of H_2 gave an orange solution and allowed the assignment of the resonances at 222.5 and 212.3 ppm to the solvent complex $Cr(CO)_5(CD_2Cl_2)$. Addition of hydrogen gas then leads to the formation of **1**, which was confirmed by ^1H NMR spectroscopy. The ^{13}C resonances for **1** are at 219.8 and 212.6 ppm. This solvent-coordinated species had been undetected in the ^1H NMR spectrum since the solvent contains no protons.

Photolysis of a CD_2Cl_2 solution of $W(CO)_6$ at 195 K under H_2 or HD gas results in the formation of $W(CO)_5(H_2)$ (**2**) or $W(CO)_5(HD)$ (**2**-d_1). These complexes are identified by ^1H NMR resonances at −3.88 ppm (**2**) and −3.90 ppm. (**2**-d_1) (Figure 4).

There is an upfield isotopic shift similar to that observed in **1** on deuteration of **2**. A characteristic 1:1:1 triplet is observed for **2**-d_1 with a one-bond coupling $^1J_{HD}$ of 35.3 Hz. The presence of ^{183}W ($I = {}^1/_2$, 14%) bonded to the H_2 unit produces satellites on the resonances for **2** and **2**-d_1. This one-bond coupling value $^1J_{HW}$ is measured in **2**-d_1 to be 38.2 Hz. Measurement of the T_1 for the dihydrogen resonance in **2** gives results very similar to those obtained for **1**, with T_{1min} values of 21 ms at 500 MHz and 31 ms at 750 MHz.

The photochemical generation of **1** and **2** can be carried out in other less coordinating solvents such as fluorobenzene, 1,3-diflurobenzene, toluene, *n*-pentane, and cyclopentane. For

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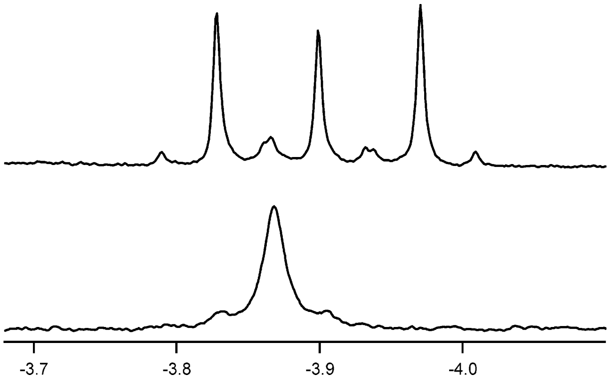

Figure 4. Partial (hydride region) ^{1}H NMR spectra (CD_2Cl_2, 500 MHz, 240K) of $W(CO)_5(H_2)$ (**2**) and $W(CO)_5(HD)$ (**2**-d_1).

example, the photolysis of a cyclopentane solution of $Cr(CO)_6$ or $W(CO)_6$ at 195 K under H_2 gas gives colorless solutions. The ^{1}H NMR spectrum of these solutions shows a broad resonance at high field assigned to complex **1** at −7.90 ppm and **2** at −4.2 ppm. The chemical shifts in this solvent are similar to those in CD_2Cl_2.

Attempts to isolate solid samples of complexes **1** and **2** were unsuccessful. Monitoring methylene chloride solutions of **1** and **2** by ^{1}H NMR spectroscopy reveals that **2** decomposes at about 250 K, while complex **1** persists up to approximately 280 K, at which temperature $Cr(CO)_6$ is formed. The Cr and W complexes are apparently more stable than the Mo analogue, since attempts to observe $Mo(CO)_5(H_2)$ by low-temperature photolysis of $Mo(CO)_6$ in the presence of hydrogen under a wide variety of conditions were not successful, even when the irradiation was carried out under 6 atm of H_2.

The chemical reactivity of complexes **1** and **2** is consistent with considerable activation of the bound H_2 ligand with respect to heterolytic cleavage. On addition of excess Et_3N at low temperature to a CD_2Cl_2 solution of **1** or **2**, clean deprotonation of the H_2 ligand is observed. The product of deprotonation of **1** is the dimeric monoanion $[(\mu\text{-H})Cr_2(CO)_{10}]^-$ identified by a characteristic hydride resonance at −19.5 ppm.[9] Deprotonation of **2** affords the monomeric anion $[W(CO)_5(H)]^-$ also identified from a characteristic ^{1}H NMR resonance.[10] The dihydrogen ligands of complexes **1** and **2** are also deprotonated upon addition of excess H_2O.

Nonphotochemical methods to synthesize **1** and **2** have been briefly explored. Heating a CD_2Cl_2 solution of $Cr(CO)_5(NMe_3)$ under H_2 at 45 °C overnight results in the formation of $[(\mu\text{-H})Cr_2(CO)_{10}][HNMe_3]$. It is believed that, after thermal amine dissociation, the solvent-bound species is able to transiently form the dihydrogen complex **1**. In the presence of the liberated amine, complex **1** is readily deprotonated. Performing the same reaction with $W(CO)_5(NMe_3)$ results in decomposition. The dihydrogen complex **2** was also synthesized chemically by treating a CD_2Cl_2 solution of $[W(CO)_5Cl][NMe_4]$ with the chloride abstracting reagent $[SiEt_3][B(C_6F_5)_4]$ under H_2 gas at low temperature. The characteristic ^{1}H NMR resonance for **2** confirmed its formation. Protonation of a solution of $[W(CO)_5H][NMe_4]$ in fluorobenzene with trifluoroacetic acid results in H_2 formation, likely through the intermediacy of **2**.

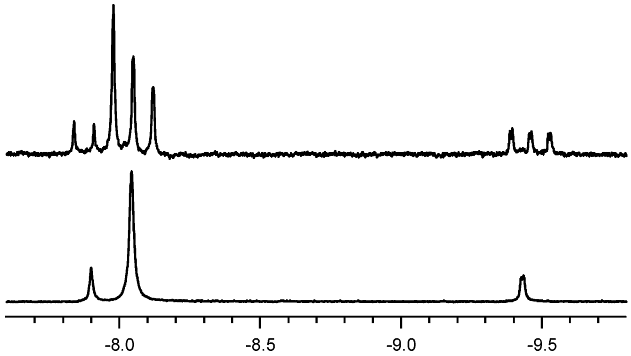

Figure 5. Partial (hydride region) ^{1}H NMR spectra (cyclopentane, 500 MHz, 220 K bottom, 240 K top) of the photolysis products of $Cr(CO)_5(PMe_3)$ under H_2 gas (bottom) and HD gas (top).

$Cr(CO)_4(PMe_3)$ Complexes. Photolysis of a cyclopentane solution of $Cr(CO)_5(PMe_3)$ at 195 K under 1 atm of H_2 gas results in three broad new resonances in the hydride region of the ^{1}H NMR spectrum at −7.90, −8.04, and −9.43 ppm (see Figure 5).

The resonance at −7.90 ppm is attributable to complex **1**, presumably arising from the photochemical dissociation of PMe_3. The other two signals are present in an approximate 4:1 ratio and both exhibit a small two-bond coupling to a single ^{31}P nucleus. Performing the reaction under HD gas results in new ^{1}H NMR resonances centered at −7.91, −8.05, and −9.45 ppm, with each one split into a 1:1:1 triplet with $^1J_{HD}$ values of 35.8 Hz (**1**) and 34.6 and 34.0 Hz. The slower relaxation in the HD isotopomers produces sharper ^{1}H NMR resonances that more readily reveal the coupling to ^{31}P. The $^2J_{HP}$ values are ~1.5 Hz in the most intense resonance at −8.05 ppm and 3.5 Hz in the other. The most intense new resonance in the ^{1}H NMR spectrum is assigned to *cis*-$Cr(CO)_4(PMe_3)(H_2)$ (**3**), arising from photochemical loss of a cis carbonyl ligand. The less intense, higher-field resonance arises from loss of the trans carbonyl ligand and is assigned to *trans*-$Cr(CO)_4(PMe_3)(H_2)$ (**4**). Stereochemistry is assigned on the basis of the magnitude of the HP couplings, where the trans coupling is larger than the cis coupling. In the ^{31}P NMR spectrum, a resonance for **3** was detected at 8.6 ppm and that for **4** is observed at 21.1 ppm. This assignment is based on the proton assignment and use of a ^{1}H−^{31}P heteronuclear multiple quantum coherence (HMQC) sequence to correlate the ^{1}H NMR resonances to the corresponding resonances in the ^{31}P NMR spectrum.

Photolysis of a CD_2Cl_2 solution of $Cr(CO)_5(PMe_3)$ at 195 K under H_2 gives a new broad hydride signal at −7.52 ppm. The preparation carried out under HD gas produces a new resonance at −7.58 ppm with $^1J_{HD} = 34.6$ Hz. These resonances are assigned to **3** and **3**-d_1, respectively. No signal for **1** or **4** is detected. The same value of $^1J_{HD}$ is observed for this resonance in cyclopentane solvent and confirms the assignment. The same small ^{31}P coupling $^2J_{HP}$ of ~1.5 Hz is also observed when HD gas is used. The ^{31}P NMR spectrum of this solution exhibits a resonance at −8.33 ppm, which is assigned to complex **3**. The relaxation time for the resonance due to bound dihydrogen in **3** was studied as a function of temperature in CD_2Cl_2. The $T_{1\text{min}}$ is found to be 18.5 ms at 500 MHz.

Discussion

$M(CO)_5(H_2)$ Complexes. The photochemical preparation of complexes **1** and **2** is well precedented in exotic solvent

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environments such as liquid xenon. We have now shown that these complexes can be prepared in conventional solvents, which allows for characterization by ^{1}H NMR spectroscopy, including the measurement of HD couplings. Using the well-established correlation between HD coupling and bond distance ($d_{HH} = 1.44-0.168\ J_{HD}$),[11] we can determine that d_{HH} is 0.84 Å in complex **1** and 0.85 Å in complex **2**. This is the shortest value for d_{HH} reported to date for neutral group 6 complexes. There is one report in the literature of a shorter value of d_{HH} in the Noyori Ru hydrogenation catalyst studied by Bergens and co-workers, where an HD coupling of 37 Hz was reported.[12]

These coupling values can be compared to the value of 34.0 Hz ($d_{HH} = 0.87$ Å) reported for $W(CO)_3(PiPr_3)_2(HD)$. This coupling was originally reported as 33.5 Hz,[13] but subsequent higher resolution data gives a value of 34.0 Hz.[14] Measurement of d_{HH} by determination of the dipolar coupling in the bound H_2 ligand in $W(CO)_3(PCy_3)_2(H_2)$ by solid-state NMR gives a value of 0.89 Å.[3] The HD coupling data for complexes **1** and **2** indicates that the interaction of H_2 with the metal center in these complexes results in slightly less bond elongation in the bound H_2 than in the original Kubas complexes. This is consistent with the lower basicity of the metal centers in the absence of phosphine ligands. Due to the narrower line width exhibited by the hydride signal in **2**-d_1, it is also possible to accurately measure $^1J_{HW} = 38.2$ Hz (Figure 1). Curiously, this coupling is greater than the value of 33.6 Hz reported for $W(CO)_3(PiPr_3)_2(H_2)$.[14]

The experimentally determined values of d_{HH} for complexes **1** and **2** can be compared to the values reported from computational studies. A comprehensive study by Lledos and co-workers[15] using DFT methods gave values for d_{HH} of ca. 0.81−0.83 Å for $M(CO)_3(PH_3)_2(H_2)$, which are computational models for the Cr, Mo, and W phosphine complexes of Kubas. Kubas has pointed out that d_{HH} is relatively insensitive to the nature of the metal.[16] A more recent study by Frenking and co-workers[17] calculates d_{HH} of ca. 0.86 Å for $W(CO)_3(PMe_3)_2(H_2)$, although this complex has been shown experimentally to be a dihydride.[7] Using the same methodology, Lledos and co-workers calculated d_{HH} of ca. 0.79−0.80 Å for $M(CO)_5(H_2)$, slightly shorter than the values for the phosphine complexes, as expected for less basic metal centers. Frenking and co-workers reported d_{HH} of ca. 0.82−0.83 Å for $M(CO)_5(H_2)$. The calculations seem to somewhat underestimate d_{HH} in the complexes of Kubas and also in complexes **1** and **2**.

An independent measure of d_{HH} in **1** and **2** is provided by measurement of the relaxation time T_1 for the dihydrogen resonance in the ^{1}H NMR spectrum. Rapid dipole−dipole relaxation results from the close proximity of the hydrogen atoms in these complexes. By use of the methodology of Halpern and co-workers,[18] values of T_{1min} can be used to calculate d_{HH}. A complication to this treatment arises when the rotation rate for the bound dihydrogen ligand is faster than the rate of molecular reorientation. Morris and Wittebort have developed a correction factor for this situation, referred to in the literature as the fast spinning correction.[19] Thus T_1 data can lead to two different values for d_{HH}, with a shorter distance arising from the fast rotation regime and a longer value resulting if the rotation of bound dihydrogen is slower than molecular reorientation. The vast majority of dihydrogen complexes reported fall in the latter category.[14]

Analysis of the T_{1min} data for **1** leads to $d_{HH} = 0.87$ Å (500 MHz) and 0.86 Å (750 MHz) with the assumption of rapid H_2 rotation. The assumption of slow H_2 rotation gives values of $d_{HH} = 1.09$ Å (500 MHz) and 1.08 Å (750 MHz). A similar analysis for complex **2** gives $d_{HH} = 0.86$ or 1.08 Å. Since the observed values of J_{HD} are only consistent with the shorter values of d_{HH}, we conclude that the dihydrogen ligand in **1** and **2** is reorienting very rapidly. This observation is consistent with vibrational spectroscopy in liquid xenon, where Poliakoff and co-workers[20] have suggested that the H_2 unit in $Cr(CO)_5(H_2)$ is essentially spinning freely on the basis of the line widths for the ν_{HH} absorptions in $Cr(CO)_5(H_2)$, $Cr(CO)_5(HD)$, and $Cr(CO)_5(D_2)$. An inverse relationship to the moment of inertia was observed.

These complexes are thus quite unusual in exhibiting very rapid H_2 rotation, which we attribute to the 4-fold symmetry of the potential energy surface corresponding to H_2 rotation. The small number of examples in the literature of dihydrogen complexes exhibiting rapid rotation share this 4-fold symmetry.[14] In contrast, the Kubas complexes with two phosphines exhibit somewhat higher barriers to H_2 rotation and values of d_{HH} derived from T_1 data do not fit to the fast rotation regime.

The short d_{HH} values exhibited by complexes **1** and **2** are consistent with a relatively weak interaction between the bound dihydrogen and the metal center. Consistent with this, exposure of solutions of **1** to D_2 leads to very rapid disappearance of the ^{1}H NMR signal. In the case of complex **1** in methylene chloride, competition between hydrogen binding and solvent binding was directly observable by ^{13}C NMR spectroscopy (Figure 2). Under 1 atm of hydrogen gas, approximately equal amounts of complex **1** and $Cr(CO)_5(CD_2Cl_2)$ are observed. Since the concentration of solvent is much greater than the concentration of H_2, this observation highlights the competence of H_2 as a ligand, clearly binding the $Cr(CO)_5$ fragment more strongly than CD_2Cl_2. The binding of methylene chloride to similar transition metal centers has been reported in a few cases; for instance, the electrophilic cationic fragments $[Re(CO)_4(PR_3)]^+$ and $[trans\text{-}Mn(CO)_3(P(O_3C_5H_9)_2]^+$ can be isolated as the CH_2Cl_2 adducts and even characterized crystallographically.[21,22] The rhenium fragment binds methylene chloride so strongly that H_2 coordination cannot be observed in this solvent. The ^{1}H NMR spectrum of $[Re(CO)_4(PR_3)(H_2)]^+$ could be obtained only in fluorobenzene.[23]

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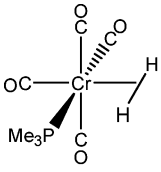
Low-temperature irradiation of $W(CO)_6$ in CD_2Cl_2 monitored by ^{13}C NMR spectroscopy leads to two new carbonyl resonances in a 4:1 ratio. The more intense resonance is at 197.1 ppm ($^1J_{CW} = 130$ Hz), while the less intense signal is at 200.5 ppm ($^1J_{CW} = 180$ Hz). These signals are assigned to the equatorial and axial carbonyl groups of $W(CO)_5(CD_2Cl_2)$. When this experiment was carried out in the presence of H_2, the formation of **2** is confirmed by ^1H NMR spectroscopy, but concentrations of **2** were insufficient for observation by ^{13}C NMR spectroscopy. This observation suggests that, like $Cr(CO)_5$, $W(CO)_5$ exhibits competitive binding of methylene chloride and hydrogen, but the hydrogen is somewhat less effective relative to the solvent in the case of tungsten.

The bound H_2 ligand in complexes **1** and **2** is significantly activated with respect to heterolytic cleavage, with deprotonation to give the known anions $[(\mu\text{-H})Cr_2(CO)_{10}]^-$ [9] and $[HW(CO)_5]^-$ [10] by Et_3N or excess of H_2O. These results are the first reported example of facile deprotonation of a *neutral* dihydrogen complex to give an anionic hydride complex. As expected, complexes **1** and **2** are significantly more acidic than the phosphine-containing analogues reported by Kubas and co-workers.[24] The acidity of **1** and **2** is comparable to that observed in cationic dihydrogen complexes,[25] confirming that the $M(CO)_5$ moiety is highly electrophilic.

Phosphine-Containing Complexes. The formation of complexes *cis*-$Cr(CO)_4(PMe_3)(H_2)$ (**3**) and *trans*-$Cr(CO)_4(PMe_3)(H_2)$ (**4**) in a 4:1 ratio suggests statistical loss of CO ligands and replacement by hydrogen. These complexes are identified as dihydrogen complexes on the basis of the large HD couplings observed in **3**-d_1 and **4**-d_1.



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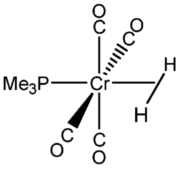

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A surprising feature of these complexes is that the HH distances in these two complexes are nearly identical, as indicated by the HD couplings of 34.6 Hz (**3**) and 34.0 Hz (**4**), corresponding to $d_{HH} = 0.86$ Å (**3**) and $d_{HH} = 0.87$ Å (**4**). This outcome is at variance with the generally accepted primacy of the nature of the trans ligand in determining the degree of activation of bound dihydrogen. Kubas[26] has summarized the extensive literature on this topic by stating that "the influence of the trans ligand on H_2 activation is generally far greater than that of the cis ligand set". Our observations suggest that complexes **1**, **3**, and **4** have quite similar values of d_{HH}. The difference between **1** and **3**, where a CO ligand is replaced with a *cis*-PMe_3, is very small, with the change in $^1J_{HD}$ and the corresponding change in d_{HH} being ~0.01 Å. More surprising is the similarity of $^1J_{HD}$ and thus d_{HH} between complexes **3** and **4**, where the change in the trans ligand from CO to PMe_3 seems to have very little effect on d_{HH}.

The $T_{1(min)}$ for the bound dihydrogen ligand in complex **3** is 18.5 ms at 500 MHz. This corresponds to $d_{HH} = 0.84$ Å (fast rotation) or $d_{HH} = 1.06$ Å (slow rotation). Only the former value agrees with the distance determined from $^1J_{HD}$. We conclude that the perturbation to 4-fold symmetry provided by one *cis*-PMe_3 ligand is not sufficient to impose a significant barrier to rapid rotation of the bound dihydrogen ligand.

Conclusions

Low-temperature photochemistry in conventional solvents allows for the facile preparation of dihydrogen complexes of CO-rich Cr and W moieties previously observed only in liquid xenon. Hydrogen binding is relatively weak but is competitive with solvent binding, allowing both the solvent complex and the dihydrogen complex to be observed. The bound dihydrogen ligand in these molecules exhibits very little bond elongation but is strongly activated toward heterolysis. In Cr complexes with one PMe_3 ligand, the HH distance is surprisingly insensitive to the nature of the ligand trans to coordinated H_2.

Experimental Section

Reagents. $M(CO)_6$ (M = Cr, Mo, W) (Aldrich) compounds were sublimed twice prior to use. CD_2Cl_2 (CIL) and 1,3-difluorobenzene (Avocado) were dried over CaH_2 and stored in glass bombs. *n*-Pentane (HPLC grade, Fischer) and cyclopentane (99+%, Aldrich) were distilled and stirred over concentrated H_2SO_4 overnight. The H_2SO_4 was replaced and the procedure was repeated until no discoloration of the H_2SO_4 was observed. The alkanes were washed with 10 × 20 mL of H_2O and dried over $MgSO_4$ before being stored over NaK alloy under vacuum. Labeled ^{13}CO was obtained from Cambridge Isotopes. Me_3NO (Aldrich) was used as received. $Cr(CO)_5(PMe_3)$ was prepared on a 50 mg scale from $Cr(CO)_5(NMe_3)$.

$Cr(CO)_5(NMe_3)$/$W(CO)_5(NMe_3)$.[27] A thick-walled glass bomb containing a Teflon-coated stir bar was charged with 0.85 mmol of $M(CO)_6$ (M = Cr, W) and 1 equiv of $ONMe_3$ in an Ar-filled glovebox. THF (15 mL) was vacuum-transferred at 77 K and the contents were warmed to room temperature. *Caution: Evolution of gas generates pressure in this reaction. Precautions should be taken to avoid overpressurizing the reaction vessel.* After stirring overnight, the solvent was evaporated under vacuum, affording a brown solid that was extracted with 2 × 10 mL of pentane. The extracts were combined and cooled to 195 K, precipitating yellow needles of $M(CO)_5(NMe_3)$. The solid was collected by filtration and stored under Ar at 250 K.

$Cr(^{13}CO)_2(CO)_4$ and $W(^{13}CO)_2(CO)_4$. A glass bomb fitted with a Teflon stopcock was charged with 200 mg of $M(CO)_6$ (M = Cr, W) in the glovebox. The bomb was pumped onto a vacuum line and evacuated briefly, and THF (10 mL) was added by vacuum transfer. The solution was subjected to irradiation at room temperature and regular freeze−pump−thaw cycles. After the last freeze−pump−thaw cycle, the bomb was backfilled with $^{13}CO_{(g)}$ (760 mmHg) and left to stand overnight. The orange solution of $M(CO)_5(THF)$ fades to colorless, re-forming $M(^{13}CO)(CO)_5$. This cycle was repeated to give additional enrichment. Isotope incorporation was confirmed by IR and NMR spectroscopy.

Photochemistry. All of the photolysis reactions were carried out at low temperature. This was achieved by directly irradiating the metal carbonyl solution contained in an NMR tube while immersed in a quartz dewar containing an alcohol/dry ice slush at 195 K. Photolysis was performed with a water-jacketed Hanovia 450 W Hg arc lamp with a Corning glass filter (no. 27) with a wavelength cutoff above 400 nm. After irradiation, the NMR tube was inserted into the precooled NMR probe for analysis. A typical procedure for complex 1 is as follows:

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An NMR tube modified to fit a Teflon stopcock was heated to 160 °C overnight and pumped into an argon-filled drybox while still hot. The tube was charged with 3 mg of $Cr(CO)_6$ and the stopcock was fitted before the tube was removed from the glovebox. The tube was pump-cycled onto a vacuum line and evacuated briefly. Approximately 0.5 mL of CD_2Cl_2 (or other solvent) was vacuum-transferred into the tube at 77 K. The sample was warmed to room temperature and backfilled with H_2 gas (~1100 mmHg) and then cooled to 195 K in the quartz dewar.

NMR Spectroscopy. NMR spectra were obtained at 500 and 750 MHz on Bruker Avance spectrometers running xwinnmr 2.6 or 3.5. Low-temperature measurements were made by cooling the probe with a stream of cold $N_{2(g)}$ from a liquid N_2 boil-off evaporator. Samples were inserted after the probe was precooled to the desired temperature. Solvent suppression of cyclopentane was accomplished by use of the DPFGSE-WATERGATE-5 sequence with a pulse sequence delay of between 300 and 125 ms. The second-order nulls under these conditions occur at ±1666 and ±4000 Hz. T_1 measurements were made with a standard inversion recovery sequence (180-τ-90). Heteronuclear correlation experiments used a proton-detected HMQC sequence with a refocusing delay set to detect the coupling of interest.

$Cr(CO)_5(H_2)$ (1). ^1H NMR (CD_2Cl_2, 220 K) $\delta = -7.44$ ppm (toluene-d_8, 200 K), $\delta = -8.83$ ppm (cyclopentane, 185 K), $\delta = -7.90$ ppm. In **1**-d_1, $^1J_{HD} = 35.8$ Hz. ^{13}C NMR (CD_2Cl_2) $\delta = 219.8$ ppm (1C, *trans*-CO), $\delta = 212.6$ ppm (4C, *cis*-CO).

$W(CO)_5(H_2)$ (2). ^1H NMR (CD_2Cl_2, 220 K) $\delta = -3.88$ ppm (toluene-d_8, 200 K) $\delta = -5.40$ ppm (cyclopentane, 185 K), $\delta = -4.2$ ppm. In **2**-d_1, $^1J_{HW} = 38.2$ Hz and $^1J_{HD} = 35.3$ Hz.

***cis*-$Cr(CO)_4(PMe_3)(H_2)$ (3).** ^1H NMR (cyclopentane, 220 K) $\delta = -8.04$ ppm ($^2J_{HP} = 1.5$ Hz). $^{31}P\{^1H\}$ NMR (cyclopentane, 220 K) $\delta = 8.6$ ppm. In **3**-d_1, $^1J_{HD} = 34.6$ Hz.

***trans*-$Cr(CO)_4(PMe_3)(H_2)$ (4).** ^1H NMR (cyclopentane, 220 K) $\delta = -9.43$ ppm ($^2J_{HP} = 3.8$ Hz). In **4**-d_1, $^1J_{HD} = 34.0$ Hz. $^{31}P\{^1H\}$ NMR (cyclopentane, 220 K) $\delta = 21.1$ ppm.

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