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Dihydrogen Complexes of Electrophilic Metal Centers: Observation of $Cr(CO)_5(H_2)$, $W(CO)_5(H_2)$ and $[Re(CO)_5(H_2)]^+$

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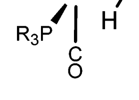
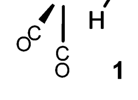
The first examples of isolable transition metal dihydrogen complexes were reported by Kubas and co-workers 20 years ago.[1] These complexes are exemplified by tungsten complexes such as $W(CO)_3(PR_3)_2(H_2)$ ($R = {}^iPr$; Cy) and their Mo analogues, which bind hydrogen relatively weakly and are prepared by displacement of an agostic interaction with H_2 gas. Subsequently, a Cr analogue was reported, which binds hydrogen more weakly.[2] Relatively weak binding of H_2 in these complexes is signaled by only slight 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 closely related class of dihydrogen complexes consists of molecules that are not isolable but have been studied in detail under matrix isolation conditions,[4] in liquid xenon,[5] or by fast spectroscopy methods.[6] For example, the prototypical molecules $M(CO)_5(H_2)$ (M = Cr, Mo, and W) have been observed in liquid Xe and in supercritical Xe, and are definitively characterized as dihydrogen complexes based on infrared spectroscopy, including studies of isotopically substituted derivatives. 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 H−H distance (d_{HH}), which is best determined by diffraction or NMR methods. Since the limited stability of these complexes precludes isolation, solution NMR spectroscopy becomes the method of choice. Hydrogen complexes with only CO as co-ligands are of fundamental interest in that these very electrophilic metal centers may bind hydrogen relatively weakly but provide substantial activation of the H−H bond toward heterolysis. These simple molecules have also been the focus of significant computational effort. The best computational results give d_{HH} of ca. 0.8 Å for $M(CO)_5(H_2)$, slightly shorter than that for the computed structures for $M(CO)_3(PH_3)_2(H_2)$, which are models for the isolable phosphine-containing complexes. In this work, we present investigations of the structure and reactivity of such complexes in conventional solvents using NMR spectroscopy, which allows for a direct experimental test of the computed structures.





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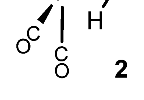

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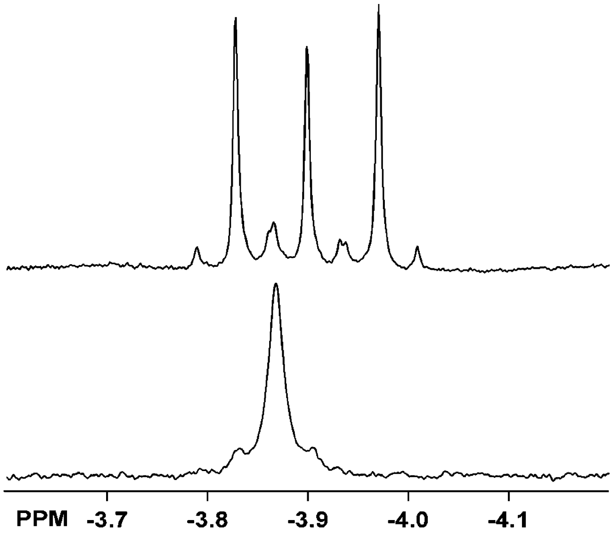

Figure 1. Partial (hydride region) ^1H NMR spectra (CD_2Cl_2, 500 MHz, 240 K) of **1** (bottom) and **1**-d_1(top).

Photolysis (Hg lamp, 195 K) of $W(CO)_6$ solutions (CD_2Cl_2, 5 mM) under 20 psi of hydrogen gas affords a thermally labile dihydrogen complex (**1**). The ^1H NMR spectrum of **1** in the hydride region is shown in Figure 1. A single resonance is observed at $\delta = -3.88$ ppm with $J_{HW} \approx 35$ Hz. Measurement of the relaxation time T_1 of this resonance at temperatures between 190 and 220 K gives values between 25 and 60 ms, respectively (500 MHz). The relaxation time was still decreasing at the lowest temperature accessible, and the maximum rate of relaxation could not be measured. Although a quantitative analysis of these data is not possible, these observations are suggestive of a dihydrogen structure for complex **1**.[7] This was confirmed by carrying out the photolysis reaction under 15 psi of HD gas, which led to the spectrum shown in Figure 1. Complex **1** is formulated as a dihydrogen complex $W(CO)_5(H_2)$.[8] The measured value of J_{HD} is 35.3 Hz, which is consistent with $d_{HH} = 0.85$ Å.[9] This coupling can be compared to the value of 34.0 Hz ($d_{HH} = 0.87$ Å) reported for $W(CO)_3(PiPr_3)_2(HD)$.[10] Measurement of d_{HH} by determination of the dipolar coupling in the bound H_2 ligand of $W(CO)_3(PCy_3)_2(H_2)$ by solid-state NMR gives a value of 0.890(6) Å.[3] The HD coupling data for complex **1** indicates that the interaction of H_2 with the metal center results in less activation of H_2 than in the original Kubas complex. Due to the narrower line width exhibited by the hydride signal in **1**-d_1, it was also possible to accurately measure $J_{HW} = 38.2$ Hz (Figure 1), which is larger than the value of $J_{HW} = 33.6$ Hz reported for $W(CO)_3(PiPr_3)_2(H_2)$.[10]

The chromium analogue $Cr(CO)_5(H_2)$ (**2**) has been similarly prepared and exhibits a single hydride resonance at $\delta = -7.45$ ppm. When the preparative reaction was carried out with HD gas, complex **2**-d_1 is obtained, with $J_{HD} = 35.8$ Hz, only slightly different from that observed in **1**-d_1.This is the largest value for J_{HD} reported to date, corresponding to $d_{HH} = 0.84$ Å, which is the shortest value of d_{HH} thus far observed for a dihydrogen complex. This observation

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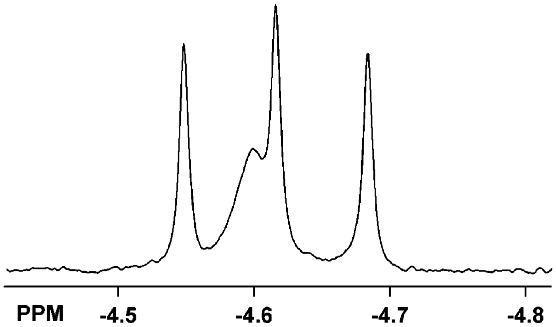

Figure 2. Partial (hydride region) ^1H NMR spectrum (fluorobenzene-d_5, 500 MHz, 260 K) of **3**-d_1. The spectrum shown was obtained using a 180$-\tau-$90 pulse sequence with $\tau = 16$ ms.

is consistent with a weak interaction of H_2 with this highly electrophilic metal center. Complex **2** had been previously prepared by photolyis of alkane solutions of $Cr(CO)_6$ under H_2 pressure and found to decay with a half-life of ca. 25 s at ambient temperature.[11]

The experimentally determined values of d_{HH} for complexes **1** and **2** can be compared to the values reported from computational studies. A study 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.[12] Using the same methodology, d_{HH} of ca. 0.79$-$0.80 Å was reported for $M(CO)_5(H_2)$, slightly shorter than the values for the phosphine complexes, as expected for less basic metal centers. The calculations seem to significantly underestimate d_{HH} in the complexes of Kubas and also in the new complexes **1** and **2**.

The bound H_2 ligand in complex **1** is significantly activated with respect to heterolytic cleavage, with deprotonation to the known[13] anion $[HW(CO)_5]^-$ by one equivalent of Et_3N or excess (10 equiv) of H_2O. As expected, complex **1** is significantly more acidic than the phosphine-containing analogues reported by Kubas and co-workers.[14]

We sought to evaluate the effect of a positive charge on the complexation of H_2, which we previously reported led to stronger hydrogen binding for cationic Re analogues of the neutral W complexes of Kubas.[15,16] Thus we examined the reaction of $Re(CO)_5Cl$ with $[Et_3Si][B(C_6F_5)_4]$[17] in fluorobenzene solution under H_2 gas. An immediate reaction occurs to give a new species **3** with a single hydride signal at $\delta = -4.60$ ppm. Complex **3** can also be generated by reaction of $Re(CO)_5H$ with excess triflic acid. A relaxation time measurement at 260 K for the hydride resonance in complex **3** gives a value of 34 ms, which diminishes slightly to 29 ms at 240 K (500 MHz). Since $T_{1(min)}$ could not be reached, it is not possible to deduce a value for d_{HH} from these data, but **3** can be formulated as the dihydrogen complex $[Re(CO)_5(H_2)][B(C_6F_5)_4]$. When the preparative reaction was carried out under HD gas, complex **3**-d_1 was obtained, with $J_{HD} = 33.9$ Hz (Figure 2).

Isolation of **3** as a solid has proven elusive due to the very high acidity of this complex (vide infra). The spectroscopic properties of complex **3** are very similar to those of the phosphine-containing complex $[cis\text{-}(CO)_4(PPh_3)Re(H_2)]^+$, previously reported by Kubas and co-workers.[18] In particular, the value for J_{HD}, and thus d_{HH}, are identical. Replacement of a PPh_3 ligand with a CO presumably leads to much reduced electron density at the metal center but does not affect d_{HH}. This confirms the crucial role of the trans CO ligand in controlling the degree of H_2 activation, as noted previously by Kubas.[19]

The acidity of complex **3** is greater than that of the neutral tungsten analogue. In contrast to complexes **1** and **2,** isotopically pure **3**-d_1 could not be cleanly prepared and invariably contained significant amounts of **3** (Figure 2). We attribute this to the greater acidity of **3** and surmise that **3** arises from **3**-d_1 by intermolecular proton (deuteron) exchange catalyzed by traces of adventitious bases such as water, as previously demonstrated for cationic dihydrogen complexes of Re.[20] This acidity was confirmed by reaction of **3** with excess Et_2O, which led to complete deprotonation to the neutral $Re(CO)_5H$.

The preparation of these simple dihydrogen complexes demonstrates that binding of hydrogen to very electrophilic metal centers leads to dramatic activation of the bound hydrogen toward heterolysis. This is despite the H$-$H distance becoming only slightly elongated in comparison to the distance in free hydrogen gas, suggesting a relatively weak interaction with the metal center. We are continuing to investigate the preparation and reactivity of σ-bond complexes of highly electrophilic metal centers.

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