

Kubas Complexes Revisited: Novel Dihydride Complexes of Tungsten

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Received August 4, 2001

A large number of transition metal dihydrogen complexes have been reported since the seminal work of Kubas and co-workers.¹ The vast majority of known complexes contain d⁶ metals, and there are several examples of neutral complexes of the Cr group and cationic complexes of the Mn triad which have a mixture of simple monodentate phosphines and CO ligands.² In these prototypical dihydrogen complexes, there are a number of cases where both 6-coordinate dihydrogen and 7-coordinate dihydride structures are reported to exist in dynamic equilibrium, indicating a delicate energetic balance between two quite different structures. For example, NMR observations establish that the dihydrogen complex (PCy₃)₂W(CO)₃(H₂) is in equilibrium with the 7-coordinate dihydride complex (PCy₃)₂W(CO)₃H₂, with the dihydrogen form predominant. Neutral complexes of Cr and Mo have a stronger preference for the dihydrogen form. Due to limitations in synthetic methodology, only bulky phosphines have been explored as co-ligands. The carbonyl/phosphine ratio is apparently an important determinant of structure, with phosphine-rich ligand sets leading only to dihydride complexes such as (PMe₃)₅WH₂.³

In contrast, the well-characterized cationic Mn⁴⁺ and Re⁵⁺ analogues such as [(PCy₃)₂Mn(CO)₃(H₂)]⁺ and [(PPh₃)₂Re(CO)₃(H₂)]⁺ are entirely dihydrogen complexes. In the cationic manifold, a wider range of phosphine ligands has been explored. For example, the unstable complex [(PMe₃)₂Re(CO)₃(H₂)]⁺ has been generated by low-temperature protonation of the corresponding neutral hydride. This complex is assigned a dihydrogen structure based on the observation of a large H–D coupling.⁶

We now report our photochemical preparation of several new hydrides of tungsten. While the complexes have not been isolated, NMR spectroscopy allows definitive assignment of the structures of these molecules as dihydride complexes.

Photolysis (Hg lamp, 195 K, Ar purge, 20 min) of solutions (toluene-*d*₈, 5 mM) of *cis*-(PMe₃)₂W(CO)₄⁷ affords a yellow solution. Treatment with H₂ gas at 195 K in the absence of light affords a new hydride species, formulated as the dihydride (PMe₃)₂W(CO)₃H₂ (**1**). Complex **1** is stable in solution at room temperature under an atmosphere of H₂, but could not be isolated due to rapid decomposition if the hydrogen atmosphere is removed.⁸ The ¹H NMR spectrum of **1** at 320 K exhibits a well resolved triplet at –5.37 ppm (²J_{P–H} = 36.5 Hz). In the ¹H{³¹P} spectrum, a single resonance was observed with appropriate

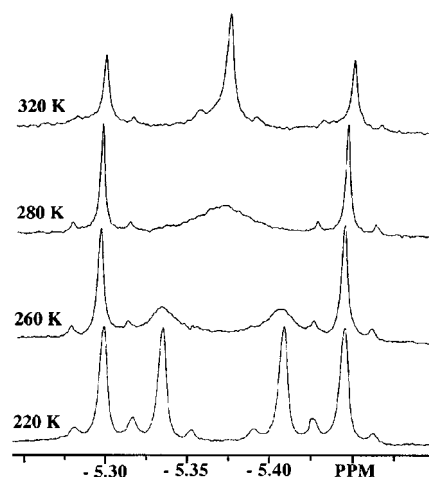
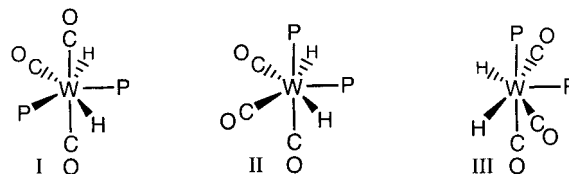


Figure 1. Partial (hydride region) ¹H NMR spectra (toluene-*d*₈) of complex **1** at various temperatures.

satellites due to coupling to a single ¹⁸³W nucleus (*I* = 1/2, 14%, ¹J_{H–W} = 18 Hz⁹). Lowering the observation temperature leads to selective line broadening and ultimately to a doublet of doublets (see Figure 1). No further changes were observed at lower temperatures. The ³¹P NMR spectrum of **1** at 220 K exhibits two resonances at δ –24.9 and –29.5 ppm (²J_{P–P} = 120 Hz). The low-temperature ¹H NMR spectrum is modeled by computer simulation as a H₂P_AP_B spin system, with equivalent hydride ligands (²J_{P–H} = 54.6 Hz, 18.4 Hz). Formulation of **1** as a dihydride species is confirmed by carrying out the preparative reaction with HD gas. Appropriate resonances for 1-*d*₁ were observed, with no measurable H–D coupling.

Low-temperature NMR spectroscopy indicates that the structures of the dihydride form of the Kubas complexes such as (PCy₃)₂W(CO)₃H₂ and (PiPr₃)₂W(CO)₃H₂ have inequivalent hydride and phosphine ligands, but the exact structure remains experimentally inaccessible.¹⁰ Several computational studies have been carried out on these molecules with increasingly sophisticated methodologies,¹¹ with recent results from DFT calculations providing good agreement with experiment for the dihydride/dihydrogen energy differences.¹² Steric factors were approximately accounted for in these computations by restricting the search for possible structures to those with P–W–P angles greater than or equal to 120°. The approximately pentagonal bipyramidal structure favored by Tomàs and Lledós¹¹ for the Kubas dihydride is depicted below as structure **I**.



All computational studies reported to date on these molecules use the computationally expedient ligand “PH₃” and thus do not

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(7) Preparation of the precursor complex *cis*-(PMe₃)₂W(CO)₄: Mathieu, R.; Lenzi, M.; Poilblanc, R. *Inorg. Chem.* **1970**, *9*, 2030–2034.

(8) Attempts to concentrate solutions of **1** in a stream of H₂ also led to decomposition.

(9) The magnitude of ¹J_{W–H} does not allow a distinction between dihydride and dihydrogen structures. For the dihydrogen complex (PiPr₃)₂W(CO)₃(H₂), ¹J_{W–H} = 34 Hz has been reported, which is much larger than the W–H coupling observed in the dihydride **1**. (Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775–6783.)

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explicitly take into account steric factors resulting from the use of bulky phosphine ligands. In the preparation of **1**, it was our intention to address the steric issue by employing PMe_3 , a prototypical phosphine ligand of modest steric demand with electronic properties very similar to that of $\text{P}(\text{iPr})_3$ and PCy_3 . We anticipated that the dihydrogen/dihydride ratio might be slightly shifted. Surprisingly, our results indicate that the structure of **1** is a dihydride, indicating a reversal of the relative stability of the dihydrogen and dihydride forms. Additionally, complex **1** cannot have the structure **I** calculated for the Kubas dihydride, since the hydride ligands in **1** are chemically equivalent. Thus we propose the possible structures depicted above as **II** and **III** for complex **1**, which are consistent with our NMR observations. The different structural outcome for complex **1** versus the Kubas complexes with bulky phosphine ligands is intuitively reasonable in that structure **I** avoids a cis arrangement of the phosphine ligands. Electronic stabilization of **II/III** versus **I** may plausibly arise from the lack of CO ligands trans to each other.

With the dihydride structure for complex **1** established, we investigated the replacement of one PMe_3 ligand with CO in the expectation that the dihydrogen/dihydride ratio would be shifted in favor of the dihydrogen structure. Low-temperature photolysis (30 min) of $(\text{PMe}_3)\text{W}(\text{CO})_5$ ¹³ followed by reaction with H_2 gas as above affords a single new hydride-containing species **2** as indicated by a resonance at -2.04 ppm ($J_{\text{H-W}} = 12$ Hz). When the experiment was carried out with HD gas, no H–D coupling was observed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** exhibits a single resonance at -27.3 ppm, which was unaffected when selective decoupling of the methyl region only was employed. The appearance of these spectra was independent of temperature between 200 and 300 K. The lack of coupling between the bound phosphine ligand and the hydride ligands is somewhat surprising, but may arise from a dynamic process as noted above for complex **1**. Complex **2** presumably has a lower barrier to rearrangement and may have two H–P couplings of comparable magnitude and opposite sign. The lack of H–D coupling is consistent with formulation of **2** as a dihydride complex. Solutions of complex **2** are stable in the absence of light under an atmosphere of H_2 , but the compound could not be isolated.

In an effort to ensure the formation of a dihydrogen complex by using a less electron rich metal center, low-temperature photolysis of $\text{W}(\text{CO})_6$ in toluene- d_8 was undertaken with the objective of preparing the dihydrogen complex $\text{W}(\text{CO})_5(\text{H}_2)$ which has been previously reported in low-temperature matrix isolation experiments and in liquid Xe solvent.¹⁴ Treatment with H_2 gas after photolysis at 195 K (30 min) affords a new hydride species (**3**) with a single resonance at -3.06 ppm ($J_{\text{H-W}} = 16$ Hz), shifting to -3.01 ppm when HD gas is used. The line width of the hydride signal in **3-*d*₁** is only 4 Hz, but no H–D coupling is observed, suggesting formulation of **3** as a dihydride, $\text{W}(\text{CO})_5\text{H}_2$. This result is quite surprising, since computational studies have predicted that the dihydrogen complex $\text{W}(\text{CO})_5(\text{H}_2)$ is more stable than the dihydride form $\text{W}(\text{CO})_5\text{H}_2$ by ca. 14 kcal/mol.¹²

Extension of this investigation to complexes with chelating phosphine ligands gives a very different outcome. Thus low-temperature photolysis (45 min) of $(\text{dmpe})\text{W}(\text{CO})_4$, followed by treatment with hydrogen as above affords a single hydride species with a complex NMR resonance at -4.11 ppm (Figure 2a). The

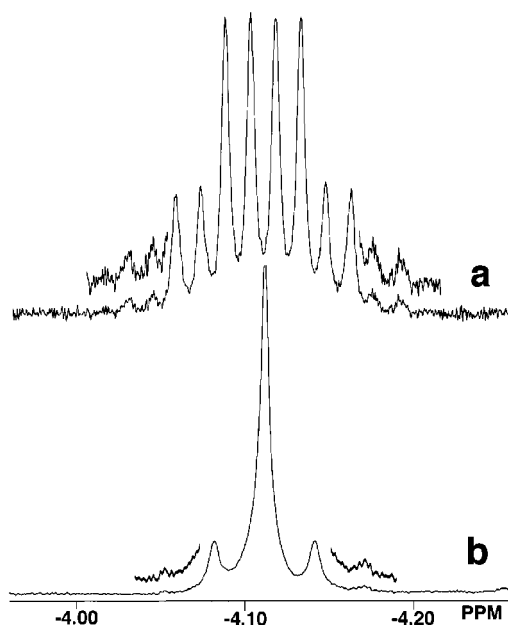
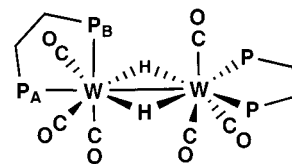


Figure 2. (a) Partial (hydride region) ^1H NMR spectrum (toluene- d_8 , 298 K) of **4**. Inset at $2\times$ intensity. (b) $^1\text{H}\{^{31}\text{P}\}$ spectrum, inset at $3\times$ intensity to show weak outer lines due to tungsten satellites ($^{183}\text{W}_2$ isotopomer).

$^1\text{H}\{^{31}\text{P}\}$ spectrum exhibits a single resonance, with tungsten satellites consistent with a dimeric species ($J_{\text{H-W}} = 28$ Hz).¹⁵

The ^1H NMR spectrum was successfully simulated as a $\text{H}_2\text{P}_A\text{P}_B(\text{P}_X)_2$ spin system, which is consistent with the ABX_2 pattern of resonances observed in the ^{31}P NMR spectrum. The ^1H NMR spectrum of **4** is independent of temperature (200–300 K). A possible structure for **4** is shown below. We surmise that the dimeric structure of **4** results from the more open coordination sphere around the central tungsten atom resulting from the constraints of the chelating dmpe ligand.



In none of the above examples was the expected outcome (a dihydrogen complex) obtained. These results suggest that all five coordinate tungsten(0) complexes react with hydrogen to give dihydride, not dihydrogen complexes, unless steric factors mitigate against the formation of a seven-coordinate complex. In the pioneering work of Kubas and co-workers, the steric demands of the phosphine ligands apparently disfavor the formation of a 7-coordinate species, which led to the initial discovery of H_2 coordination. Our work suggests that further computational studies of molecules of this type are warranted, with due attention to the crucial role of steric factors.

Acknowledgment. This research was supported by the NSF.

JA016766W

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(15) When the preparation of **4** was carried out with HD, the same ^1H NMR spectrum results, with an upfield shift of 50 ppb. No H–D coupling was observed. Treatment of solutions of **4** with D_2 leads to rapid disappearance of the hydride resonance, with release of H_2 and formation of HD.