Some Molecular Hydrogen Complexes of Iridium

Robert H. Crabtree,*‡ Maryellen Lavin,‡ and L. Bonneviot§

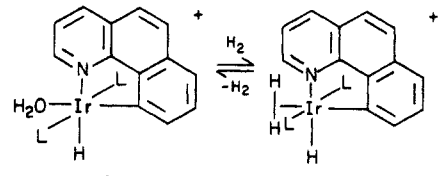
Contribution from the Departments of Chemistry and Chemical Engineering, Yale University, New Haven, Connecticut 06511. *Received January 3, 1986*

Abstract: The new molecular hydrogen complexes $[IrH(H_2)(bq)L_2]^+$ (bq = 7,8-benzoquinolinate, L = PPh_3 or PCy_3) and $[IrH_2(H_2)_2(PCy_3)_2]^+$ are described. A ^1H NMR T_1 criterion is proposed for detecting such complexes. Deprotonation of the coordinated H_2 is described. The mechanism of hydrogenolysis of d^0 alkyls is discussed and a dihydrogen complex proposed as intermediate.

The purpose of this paper is to report several new examples and a new way of detecting molecular hydrogen complexes. We also discuss their structure, bonding, spectra, and relevance to hydrogen activation. The first recognized example of a stable, isolable dihydrogen complex, $[W(H_2)(CO)_3(PR_3)_2]$,[1] together with its crystal structure by X-ray and neutron diffraction was reported in 1984. Photolysis of $Cr(CO)_6$ in an H_2-containing matrix has been shown to give species such as $[Cr(H_2)(CO)_5]$[2] which has even been shown to have a fleeting existence in alkane solution at ambient temperature. Our own complexes have also been reported in preliminary form.[3] Morris et al.[4a] have more recently characterized *trans*-$[M(H_2)H(Ph_2PCH_2CH_2PPh_2)_2]BF_4$ (M = Fe or Ru), including an X-ray structure in the iron case (H-H = 0.89 Å). They observed exchange between the (H_2) and M-H groups on the NMR time scale as we had also done.[3] In all these cases, H_2 binds in the nonclassical undissociated $M(H_2)$ form rather than in the classical dissociated MH_2 form.[4b] There is an analogy between these two binding modes for H_2 and the agostic (C-H···M) and cyclometalated (C-M-H)[5] forms known in the case of C-H binding to metal complexes.

Results and Discussion

We have previously described the cyclometalation of 7,8-benzoquinoline (bqH) in its reaction with $[Ir(cod)L_2]SbF_6$ (L = PPh_3) in moist CH_2Cl_2 at 0 °C under H_2 to give the crystallographically characterized aquo complex **1**.[6] We imagined that a precursor to **1** in this synthesis might be an Ir(V) trihydride $[IrH_3(bq)L_2]^+$ which could lose H_2 and pick up H_2O. We therefore tried to obtain it by reaction of H_2 with **1**. H_2 does indeed rapidly replace the aquo ligand in **1**, but to our surprise, rather than the expected classical trihydride we obtained the dihydrogen hydride **2**.



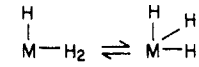
(1)

Passing N_2 through the solution rapidly reverses the equilibrium by entraining and removing the H_2 in equilibrium with the complex, and **2** reverts to the aquo complex **1**. On the other hand, chemically removing the water present by adding solid CaH_2 to the mixture shifts the equilibrium essentially completely over to the dihydrogen complex **2**. This complex is thermally stable under H_2, and the binding-release cycle can be repeated apparently without limit in solution or in the solid state.

The identity of **2** was determined by ^1H NMR methods. The H ligands exchange at room temperature, and only an averaged resonance is observed. Below 260 K two separate resonances are visible. One, at δ -2.9 and of intensity 2 is assigned to the coordinated H_2 molecule. The other at δ -15.3 and of unit intensity is assigned to the classical hydride. The value of its chemical shift, by analogy with previous work,[7] suggests that this Ir-H is trans to the nitrogen rather than the carbon of the cyclometalated bq ligand. The resonance at δ -15.2 shows a normal cis coupling of 11.4 Hz to the two equivalent PPh_3 groups at 220 K. The $Ir(H_2)$ resonance shows no resolvable coupling but remains rather broad ($\omega_{1/2}$ = 160 Hz) even at 180 K (broadening is also observed for $W(H_2)(PCy_3)_2(CO)_3$). The width of the resonance does not arise from exchange with free H_2 at 180 K but from relaxation effects (see below).

In order to distinguish between the nonclassical dihydrogen hydride formulation $M(H_2)H$ and the classical trihydride structure MH_3 for **2**, we looked at the corresponding HD complex. In the range 187-220 K we were able to see reproducible and well-resolved $^1J(H,D)$ coupling of 29.5 Hz in the form of a ca. 1:1:1 triplet in the ^1H NMR in the position we had previously identified with the dihydrogen resonance. This value is close to that reported by Kubas et al. for their HD complex (33.5 Hz). It is less than the value for free HD (43.2 Hz) but much larger than would be expected for a classical trihydride (1 Hz). Confirmatory evidence is discussed in a later section. No IR bands were observed that we could assign to the $M(H_2)$ unit. Even the terminal Ir-H vibration is weak, so they may be too weak to be seen. Raman studies were precluded by the strong luminescence of the compound at all accessible wavelengths. We were unable to obtain crystals of **2** suitable for X-ray diffraction, perhaps because the H_2 dissociates at 25 °C even in the solid state (see below).

Fluxionality of the $MH(H_2)$ Unit. At ambient temperature the $Ir(H_2)$ and IrH protons give a single resonance in the ^1H NMR. When the sample is cooled, the resonances for the IrH and $Ir(H_2)$ protons become clearly separate by 240 K; at 280 K we see coalescence. Several exchange mechanisms are possible, one is shown in eq 2. The H_2 could undergo classical "oxidative"



(2)

addition and the resulting iridium(V) trihydride, being seven-

‡Chemistry Department.
§Chemical Engineering Department.

(1) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 451-452. (b) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294-2301.
(2) Upmakis, R. R.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Wyman, R.; Simpson, A. F. *Chem. Commun.* **1985**, 27-30. Church, S. P.; Grevels, F.-W.; Herman, H.; Schaffner, K. *Chem. Commun.* **1985**, 30-32. Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374-2379.
(3) Crabtree, R. H.; Lavin, M. *Chem. Commun.* **1985**, 794-795, 1661-1662.
(4) (a) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581-5582. (b) Ashworth and Singleton[4c] had suggested this possibility for $RuH_4(PPh_3)_3$ in 1976; we have recently confirmed their hypothesis from T_1 measurements.[4d] (c) Ashworth, T. V.; Singleton, E. *Chem. Commun.* **1976**, 705. (d) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.*, in press.
(5) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395-408. (b) We do not believe that nonclassical hydrides should be called "agostic" because this term is reserved for ligated C-H bonds, and if extended to H_2, there would be no clear reason not to extend it to all three-center, two-electron bonds such as M-H-M, M-H-B, etc.
(6) Crabtree, R. H.; Holt, E. M.; Lavin, M. *Inorg. Chem.*, in preparation.
(7) Chatt, J. *J. Chem. Soc.* **1965**, 6789-6796, 7391-7405. Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994-7001.

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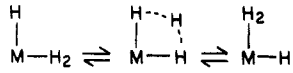
coordinate, then give rapid permutation of the hydrogens. In view of the acidic character of the H_2 ligand in this system (see below), proton transfer between the H_2 ligand and Ir–H group (eq 3) is also very reasonable. The intermediacy of a complex containing



(3)

a triangular H_3^+ ligand cannot be excluded. Line-shape analysis of the spectra has not allowed us to distinguish between the possible mechanisms because of the presence of large contributions to the line width that do not arise from fluxionality (see below), but the exchange rate is ca. 350–500 s^{-1} at 260 K.

Structures of the M(H_2) Unit. We studied the ^1H NMR spectrum of the HD complex of type **2** at 180–220 K, where both high-field resonances can be clearly seen. The chemical shift for the HD ligand did not vary significantly with temperature nor was the position significantly different from that observed for the H_2 complex. This observation provides strong evidence that the H_2 ligand is bound in a symmetrically side-on structure, rather than asymmetrically (e.g., end-on). Isotopic perturbation of resonance,[8] usually amounting to 0.1–1 ppm, would be observed in an HD complex if the proton were rapidly exchanging, by rotation of the HD ligand, between two sites that (a) differ in chemical shift and (b) show an isotope effect in the percent occupancy by H over D. The second factor relies on zero-point energy differences and therefore on differing vibrational frequencies associated with the two sites of the system. Based on our observations, an asymmetrical M–(H_2) system is an unlikely structure for **2** because it would almost certainly show isotopic perturbation of resonance. At the high-temperature limit, in contrast, isotopic perturbation is observed, as a result of the exchange between classical and nonclassical sites.

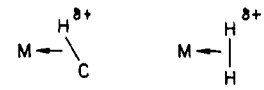
This result is consistent with the X-ray and neutron structures of $[W(H_2)(CO)_3(PCy_3)_2]$ which show that the H_2 is bound approximately side-on. Disorder problems reduced the reliability of these structures, however. The iron compound shows a similar structure by X-ray.[4a]

Cyclohexylphosphine Series. We wished to make the PCy_3 analogue of **2** to see if the coordinated H_2 molecule would be affected by the higher electron density at the metal compared to the PPh_3 case. Since the $[Ir(cod)L_2]^+$ cation does not exist in this series, we started from the pentahydride $[IrH_5L_2]$. Protonation with a noncoordinating acid such as $PhCH(SO_2CF_3)_2$ at −80 °C, followed by adding 7,8-benzoquinoline and warming to room temperature, gave the aquo complex **1** (L = PCy_3). This was spectroscopically very similar to the PPh_3 complex (values for the PPh_3 complex are given in parentheses). In particular Ir–H absorbed in the ^1H NMR at δ −15.4 (−16.1). The Ir(OH_2) resonance was obscured by PCy_3 resonances. The ν(OH) of the aquo ligand appears in the IR at 3528 and 3404 cm^{-1} (3555 cm^{-1}).

Like the PPh_3 analogue, this aquo complex reacts with H_2 to give a species we identify as $[Ir(H_2)H(bq)(PCy_3)_2]^+$. At room temperature a broad resonance is observed at ca. δ −10.34 (CD_2Cl_2). On cooling below −15 °C, two resonances are seen, one, broad, at δ −4.64 (−2.9), the other at δ −17.5 (−15.3). The latter shows a ^2J(P,H) at 215 K of 13 Hz and (in the HD complex), the dihydrogen resonance shows a ^1J(H,D) of 29 Hz. Additional confirmation that these complexes are indeed dihydrogen hydrides comes from the new T_1 method, described later.

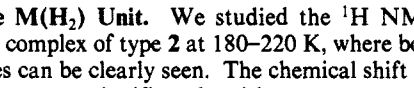
The classical dihydride $[IrH_2(bq)L_2]$ was formed in the same way we used for the PPh_3 analogue, viz., by deprotonation of the nonclassical trihydride **2** or by treatment of the aquo complex with $Li[BEt_3H]$.

Deprotonation of the Coordinated H_2 Ligand. C–H···M systems are known to be more easily deprotonated than the parent C–H groups.[4] The most likely reason is that donation from the C–H bond to the metal leaves the C–H with a partial positive charge (**3a**).



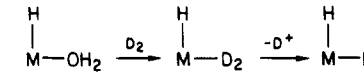
3a **3b**

A very similar bonding picture (**3b**) seems to hold for coordinated H_2. Saillard and Hoffmann[9] have commented that $\sigma(H_2) \rightarrow$ M electron transfer dominates the early stages of H_2 activation by oxidative addition. This suggests that coordinated H_2, which might be considered as an isolable intermediate on the way to oxidative addition, might also be readily deprotonated. In accord with this picture, we find that bases such as MeLi and *t*-BuLi do indeed deprotonate the complex to give the neutral dihydride **4**.



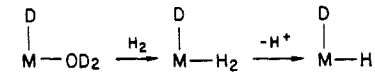
(4)

Deprotonation might have taken place directly from the nonclassical trihydride or via a classical trihydride which, if the mechanism of eq 2 were valid, would be in equilibrium with the observed nonclassical form. In order to throw some light on the mechanism, we undertook isotopic labeling experiments, shown in eq 5 and 6. It is important to note that the two hydridic sites in **4** are inequivalent and easily distinguished by ^1H NMR.



(5)

Unfortunately, there is H/D exchange between the Ir–H and Ir(H_2) groups in **2** and also between the Ir–H and H_2O groups in **1**. We were able to mitigate the effects of the first process by running the reactions at −80 °C and by bubbling H_2 (or D_2) through the aquo complexes **1** to form **2** in situ and then rapidly adding *t*-BuLi to deprotonate the intermediates. To combat the second exchange process, we started with $[IrD(D_2O)(bq)L_2]^+$ rather than $[IrD(H_2O)(bq)L_2]^+$ (eq 6).



(6)

In the reaction involving unlabeled **1** and D_2, the deprotonation product had more protium (80%) trans to the bq nitrogen than to carbon (20%). This is consistent with deprotonation of the coordinated D_2 ligand, but if a seven-coordinate classical trihydride had been formed as an intermediate, a ca. 50:50 distribution would have been expected as a result of (i) the rapid scrambling likely for such an intermediate and (ii) the similar pK_a's expected for each of the three protons. These results also rule out deprotonation of the terminal H in **2** which should give a 50:50 distribution of protium between the two sites. To make sure the observed isotopic distribution in the product was not due to a thermodynamic isotopic preference for protium being trans to N, we also looked at the complementary experiment involving $[IrD(D_2O)(bq)L_2]^+$ and H_2 followed by deprotonation. This gave more protium trans to C (60%) than to N (40%). These results are consistent with the deprotonation of the dihydrogen, rather than the terminal hydride in **2**.

The same complex **4** is also formed by the reaction of **1** with $LiBEt_3H$, in which H^- replaces H_2O in the aquo complex **1**. This material is clearly a conventional dihydride because the inequivalent (and nonexchanging) hydrides each give sharp NMR spectra and show a mutual ^2J(H,H) of 4 Hz. Such a value corresponds to a ^2J(H,D) coupling of 0.8 Hz as appropriate for a classical dihydride. The hydride resonance positions δ −10.2 and −18.3 are appropriate for IrH trans to the carbon and nitrogen atoms, respectively, of the bq ligand, and each shows a cis coupling to phosphorus.

Reprotonation of the conventional dihydride **4** to give back the dihydrogen hydride **2** is most conveniently done with PhCH-

(8) Saunders, M.; Jaffee, M. H.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2558–2562.

(9) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.

$(SO_2CF_3)_2$.[10] The reaction is rapid and quantitative.

In the labeling experiments described above, we saw that exchange takes place between H_2O and the Ir–H site. Attempts to prepare $[IrD(H_2O)(bq)L_2]^+$ always led to rapid loss of the label from the hydridic site. The addition of D_2O to the sample, however, rapidly restores D to the hydridic site. Most likely, free and coordinated H_2O are in equilibrium, and exchange between coordinated water and the hydridic site occurs subsequently. $[IrH(MeCN)(bq)L_2]^+$, a complex to which we imagine that D_2O cannot coordinate, does not exchange significantly with D_2O under the same conditions, showing that the D_2O only exchanges efficiently when coordinated. Since separate resonances are observed for the Ir–H and Ir(H_2O) protons of **1**, exchange is not rapid on the NMR time scale, but it was complete in ca. 30 min.

The most reasonable mechanism for the process is that shown below, in which proton transfer takes place between the Ir(H_2O) and Ir–H sites (eq 7) or, less efficiently, between free water and Ir–H. Rotation of the H_2 ligand then ensures the scrambling of the label.

$$\begin{array}{ccccc} H & & HD & & D \\ | & & | & & | \\ Ir-OD_2 & \rightleftharpoons & Ir-OD & \rightleftharpoons & Ir-OHD \end{array} \qquad (7)$$

Heterolytic Activation of H_2. The possibility that the H_2 in a dihydrogen complex may be readily deprotonated suggests that such complexes may be important in the heterolytic activation of hydrogen.[11] The clearest cases of heterolytic H_2 activation are those in which d^0 metal complexes are hydrogenolyzed (e.g., eq 8). Here, oxidative addition is forbidden because the metal

$$WMe_6 + PMe_3 + H_2 \rightarrow WH_6(PMe_3)_3 + MeH \qquad (8)$$

is in its highest valence state. The metal is still expected to be a Lewis acid and is not prohibited from binding H_2 as an intact molecule. This would lead to the situation shown in eq 9. The

$$\begin{array}{l} H-H^{\delta+} \\ \downarrow \\ W-Me^{\delta-} \end{array} \longrightarrow \begin{array}{l} H \\ | \\ W \end{array} + MeH \qquad (9)$$

H_2 molecule acquires $\delta+$ character by binding as an undissociated molecule. It then protonates the $\delta-$ alkyl group leading to loss of the alkane. The same mechanism could also apply to lanthanide and actinide alkyls. Previously,[11b] it had been proposed that H_2 was bound in such a way as to induce a charge separation of the $H^{\delta+}$-$H^{\delta-}$ type. Methane activation by lanthanide and actinide compounds might, by analogy, go via a transient methane complex.[11c]

Bis(dihydrogen) Dihydride Complex. As early in 1978 we had observed[12] that $IrH_5(PCy_3)_2$ (**5**) protonated readily but without H_2 evolution at −80 °C in CH_2Cl_2 containing a noncoordinating acid such as HBF_4 to give a new species, **6**, that we suspected was the "iridium(VII)" hydride $IrH_6(PCy_3)_2^+$. Treatment with base, such as NEt_3, gave back $IrH_5(PCy_3)_2$ and with MeCN gave the well-known $[IrH_2(MeCN)_2(PCy_3)_2]^+$.[13] The nature of $[IrH_6(PCy_3)_2]^+$ was never satisfactorily determined, however, and we did not report the results. The hydride resonance in the ^1H NMR was broad, and an off-resonance decoupled ^{31}P NMR experiment, to try to determine the number of hydrides present, showed only a broad and indistinct feature,[13] not the expected septet.[14] The work described in this paper led us to reexamine **6**. In this new investigation, we protonated the pentahydride with PhCH$(SO_2CF_3)_2$ in CH_2Cl_2 at −80 °C and obtained the corresponding salt of the same cationic species **6**. At room temperature the ^1H NMR showed a broad resonance at ca. δ −8.3 due to the fluxional iridium hydrides. When the mixture cooled, two features, one at δ −5.05 ($\omega_{1/2} \approx 175$ Hz) and the other at δ −15.25 ($\omega_{1/2} \approx 154$ Hz), and in an intensity ratio of ca. 2:1, were seen at 188 K. This ratio is confirmed by the fact that the original broad feature at δ −8.3 has a chemical shift which is very close to the 2:1 weighted average of the two shifts observed at 180 K. Unfortunately, **6** is more fluxional than **2**, and under HD, neither the ^2J(P,H) couplings nor the ^1J(HD) couplings are resolved even at 180 K. No low-temperature solvents other than CD_2Cl_2 proved satisfactory, not even CD_2Cl_2–$CHCl_2F$, because **6** is essentially insoluble in these media.

The width of the resonances we assign to the dihydrogen molecule suggested that the T_1 for these protons might be unusually short.[1] We therefore looked at the T_1 values[15] for **2** (L = PPh_3 and PCy_3), **5**, and **6** to see if we could obtain further information. We had already determined[15b] that T_1 values for a range of classical phosphine-substituted hydrides lie in the range 0.35 to more than 2 s. Dipole–dipole interaction with the ligand protons was proposed as the likely predominant mechanism for M–*H* relaxation. The rate of relaxation of a given proton by this mechanism depends on r^{-6} (see eq 10), where r is the distance between the proton under consideration and a neighboring proton.[15a,c] A dihydrogen complex might therefore show unusually

$$\frac{1}{T_1(DD)} = \frac{2}{5}\frac{\hbar^2\gamma_X^2\gamma_Y^2 I(I+1)}{r^6}\left(\frac{\tau_c}{1+\omega^2\tau_c^2} + \frac{4\tau_c}{1+4\omega^2\tau_c^2}\right) \qquad (10)$$

rapid relaxation in view of the very short value of r appropriate to an H_2 complex (ca. 0.8 Å). In such a system each hydrogen of the H_2 ligand would be relaxed by interaction with the other. For **2**, T_1's were measured by the inversion–recovery method at 500 MHz and −85 °C (Figure 1). While the T_1 value for the terminal Ir–H is normal (390 ms), the value for the Ir(H_2) group, 30 ms, is extremely short, implying exceptionally rapid relaxation. When the mixture warms, the T_1's begin to average as soon as the exchange time becomes less than the T_1 of a given state, while chemical shifts remain resolved longer, until the exchange times become comparable with $(\Delta\nu)^{-1}$.[15a] The PCy_3 analogue was also studied and showed T_1's of 730 ms (Ir–H) and 65 ms (Ir(H_2)), respectively. In the much more fluxional case of **6**, the T_1 values for the Ir(H_2) (48 ms) and Ir–H (73 ms) resonances are both short. Here the fluxionality is faster. These figures should be compared with the observed value of T_1 in the parent classical pentahydride **5** (780 ms). To eliminate the remote possibility that the unusual T_1 might be due to some artifact, we measured T_1 for the residual nonclassical protons of the deuterated species. The dipole–dipole contribution of nucleus X on the relaxation of nucleus Y, given in eq 10, depends on γ_X^2. In the case where X = D, relaxation of Y (=^1H) should be slower. The predicted effect is indeed observed. The relaxation time for the dihydrogen resonance of **2** lengthens to 240 ms and of **6** to 180 (Ir(H_2)) and 210 ms (Ir–H). Quantitative interpretation of these changes is hampered by the possible additional contributions to the relaxation. Nevertheless the evidence for a nonclassical structure for **6** is greatly strengthened.

The evidence points strongly to $[IrH_2(H_2)_2(PCy_3)_2]^+$ as the structure for **5**. This would make it the first nonclassical poly-

(10) Siedle, A. R. *J. Am. Chem. Soc.* **1984**, *106*, 1510–1511.
(11) (a) Brothers, P. *Prog. Inorg. Chem.* **1981**, *28*, 1–61. (b) Bell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846–1855. (c) Watson, P. L. *Ibid.* **1983**, *105*, 6491–6493.
(12) Crabtree, R. H.; Quirk, J. M., unpublished observations, 1978.
(13) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1481–1485.
(14) Mann, B. E.; Masters, C. J.; Shaw, B. L. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2195–2199.
(15) (a) Blombergen, N.; Purcell, E. M.; Pound, R. V. *Phys. Rev.* **1948**, *73*, 679–684. Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High Resolution NMR*; McGraw-Hill: New York, 1959. (b) Crabtree, R. H.; Segmuller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1984**, *24*, 1949–1950. These T_1 values were determined at 30 °C and therefore are not strictly comparable with those determined here at −80 °C. (c) The symbols in eq 10 have the following meanings: T_1(DD) = dipole–dipole contribution to relaxation; γ_X = gyromagnetic ratio of nucleus X; r = distance between the nuclei of interest. τ_c = rotational correlation time associated with the local Brownian motion; ω = Larmor frequency; I = spin of the second nucleus. In the heteronuclear case an extra factor of $^3/_2$ also enters into the right-hand side of the equation: Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University: London, 1961; Chapter 8. (d) Bloom, M. *MTP Int. Rev. Sci.: Phys. Chem., Ser. One* **1972**, *4*, 1.

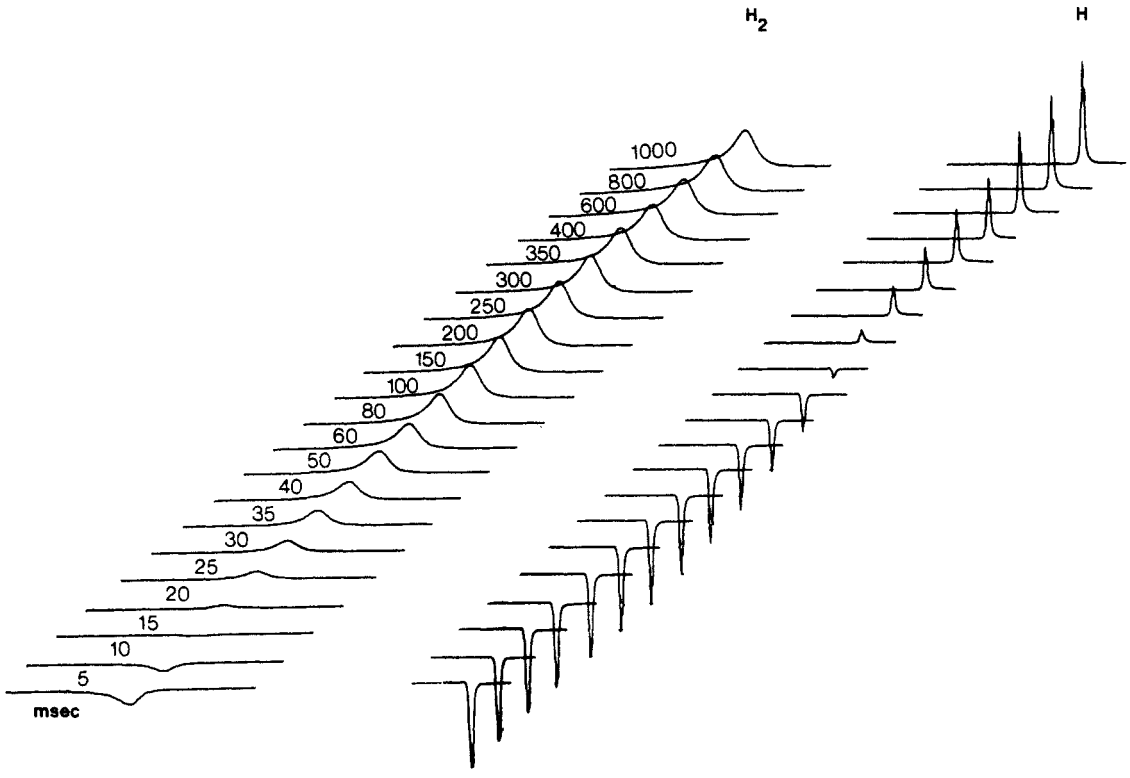
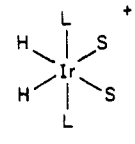


Figure 1. Inversion–recovery spectra of $[IrH(H_2)(bq)(PPh_3)_2]SbF_6$ at −85 °C and 500 MHz. Showing the low-field dihydrogen resonance (broad) and the high-field terminal hydride resonance. The dihydrogen protons clearly relax much faster than the terminal hydride. The delay times shown are in milliseconds.

(hydride)[16] complex to be characterized. We prefer the stereochemistry shown below by analogy with the many $[IrH_2S_2(PR_3)_2]^+$ complexes that are known (S = H_2O, NH_3, MeI, MeCN, $^1/_2$cod, and now H_2).



(S = H_2)

6

It is not yet clear whether, at −80 °C in CD_2Cl_2, **2** is in the extreme narrowing limit, where $\omega^2\tau_c^2 \ll 1$, or if the molecules are tumbling sufficiently slowly for $\omega^2\tau_c^2 \gg 1$, the slow-motion limit, to apply. In the latter case, eq 10 reduces to eq 11. In

$$\frac{1}{T_1(DD)} = 0.8\frac{\hbar^2\gamma_X^2\gamma_Y^2 I(I+1)}{r^6}\left(\frac{1}{\omega^2\tau_c}\right) \qquad (11)$$

the slow-motion regime, T_1 becomes proportional to the square of the magnetic field, and preliminary measurements at 250 and 500 MHz tend to support this picture. The key point is that the T_1 can depend on the solvent, the temperature, and, in principle, the magnetic field, so it is important that measurements be made under the same conditions in order to be able to compare the T_1 values obtained. Fortunately, the difference between the T_1's of classical and nonclassical hydrides is usually greater than a factor of 10, and this ratio should be preserved under different conditions. It is important to take account of such effects in interpreting any results.

The observations show that the line width of the dihydrogen resonances in our compounds is larger than can be accounted for by the short T_1 alone. This may be a result of being in the slow-motion regime, where $T_1 \neq T_2$,[15a] or there may be some further exchange process taking place. The important points are (i) that we cannot estimate T_1 simply by measuring the line width, and (ii) that nonclassical hydrides may not always have the large line widths we see here.

One circumstance under which a classical hydride might show a short apparent T_1 is if rapid exchange with free H_2 occurs. This is ruled out by a number of considerations. The appearance of the spectrum is independent of the partial pressure of free H_2 and unaffected by irradiation of the resonance of free H_2 at δ 4.54 in CD_2Cl_2 at 180 K, which can be observed when excess H_2 is present. If exchange were taking place, spin saturation transfer would be expected to alter the intensity of the bound H_2 resonance. The T_1 of the dissolved free H_2 is ~1600 ms at 180 K. This value is long probably because the H_2 is tumbling so fast compared to complexed H_2 that the dipole–dipole process becomes relatively inefficient by eq 10 (i.e., τ_c(free H_2) $\ll$ τ_c(complexed H_2)). Any exchange would therefore lengthen the apparent T_1 of the complexed H_2, not shorten it. Our measurements were made at low temperature to minimize exchange.

It is conceivable that classical and nonclassical tautomers are in rapid equilibrium in MH_2 systems, such as the ones studied here. This could lead to a short T_1 if enough of the nonclassical form were present. Since such a complex would be expected to show the reactivity of a dihydrogen complex, it is probably better to consider such systems as nonclassical until the details are worked out. In this way it should be possible to avoid the controversy that surrounds the nonclassical carbonium ion. In the cases studied here, there are both $M(H_2)$ and M–H groups in the same molecule. The observation of distinct resonances for two different types of proton at −80 °C argues that the nonclassical structures proposed above are the ground states for the systems. If the opposite were true, then the number of resonances observed in the low-temperature limit might well be different (e.g., three for a dodecahedral classical $[IrH_6L_2]^+$ with L in the B sites and three for a pentagonal bipyramidal $[IrH_3L_2(bq)]^+$).

H_2 Absorbtion Isotherms for 2. The aquo complexes **1** can easily be obtained as solids by crystallization from CH_2Cl_2 with Et_2O. Pure **2** can best be obtained as a solid by placing microcrystalline samples of **1** in vacuo (10^{-6} torr, 18 h) and then treating with dry H_2. A hydrogen absorbtion and release cycle can then be con-

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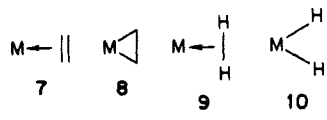
tinued without apparent limit by simply evacuating and adding H_2. The system takes only a few minutes to come to equilibrium at room temperature and much of the reaction takes place in the first few seconds. The hydrogen complex **2** is the species present under H_2, but in vacuo **1** is probably no longer present since the H_2O, unless it is tenaciously held by the crystal lattice, would be expected to be pumped away during the evacuation step. Given the pronounced tendency of these species to form C–H···Ir bridges, it is likely that, as is the case[1b] for $[W(CO)_3(PCy_3)_2]$, a C–H bond of the ligand, either PPh_3 or PCy_3, binds to the sixth site in the absence of either H_2 or H_2O. Alternatively, the sixth site may remain open; only a crystal structure would be able to distinguish for certain. We shall use the symbol Ir-□ to signify the structure of this sixth site in vacuo.

$$\text{Ir}-(\text{H}_2) = \text{Ir-}\square + \text{H}_2 \qquad (12)$$

The Langmuir isotherms of these materials show that the pressure of hydrogen needed to establish 50% loading of the material is 11.8 (L = PPh_3) and 10.3 torr (L = PCy_3). This data led directly to values of ΔG for eq 12 of −2.43 (L = PPh_3, 297 K) and −2.47 kcal/mol (PCy_3, 295 K). Carrying out these measurements at 273 and 313 K allowed us to obtain an estimate of ΔH (−3.16 kcal/mol) and ΔS (−2.3 eu) as well.

Analogies to Other Ligands. The measurements described above show that the dihydrogen ligand is held more tightly by the PCy_3 complex than by the PPh_3 species. This in turn suggests that the greater electron density at the metal in the former case may be influencing the binding by increased back-donation into the H_2 σ^* orbital. There is an interesting analogy between the binding of H_2 and of olefins to transition metals. The binding of olefins has conventionally been seen as lying between two extreme formulations shown in their valence bond representations as **7** and **8**.[17] Going from **7** to **8** involves breaking a C—C π bond and



7 **8** **9** **10**

making two M—C bonds or in MO terms as increasing the degree of M (d_π) to (C=C) π^* back-donation. Going from $M(H_2)$ to MH_2 involves a similar transformation but now involves an H–H σ bond going to two M–H bonds. It will be interesting to see how far the factors that favor **7** (e.g., strong σ acidity and low π-basicity of the metal) will also favor **9**.

There is also an analogy between the $M(H_2)$ group and the agostic C–H–M bridge. In both cases, an undissociated σ bond acts as a ligand to a transition metal. It is notable that the Ir system readily forms both H_2 complexes and agostic structures.[3] It is likely that those systems that tend to bind aliphatic C–H bonds nondissociatively will also bind H_2 in the same way.

It is not yet clear whether there will be a continuum of structures between the extremes of **9** and **10** (as is true for **7** and **8**) or whether there will be two distinct structural groups, as appears to be the case for the C–H–M system.[18] Only if the latter is true will it be possible to decide unambiguously between structures **9** and **10** by using structural criteria and the NMR method described here.

Thermodynamic Stability of $M(H_2)$ vs. MH_2. What is it about $W(H_2)(CO)_3(PCy_3)_2$, $Cr(H_2)(CO)_5$, **2**, and **6** that makes the nondissociated $M(H_2)$ form favored over the dissociated MH_2 structure? Presumably the combined bond strengths of the two M–H bonds that would be formed on dissociative binding are insufficient to compensate for the breaking of the H–H bond. One factor common to all four molecules is the presence, trans to the (H_2) ligand, of a high trans effect ligand: CO in the group 6 complexes, an aryl carbon in **2**, and hydride in **6**, all of which are known to weaken metal–ligand bonds in the trans position. All the complexes have modestly electron-withdrawing ligands or a positive charge that might be expected to favor H_2 (σ) to M (d_σ) electron donation. All are octahedral, although this may have no special significance. In the case of **2** and **6** the classical MH_2 form would be Ir(V), a rare oxidation state, but there is no reason to doubt that $IrH_5(PCy_3)_2$, for example, is an authentic classical iridium(V) polyhydride; in particular the T_1 of this compound is normal for a classical polyhydride (780 ms). Instead of H_2, the group 6 species can also bind N_2, a ligand that also requires good σ acidity but in addition requires good π donor character for the metal. We find that the Ir complexes do not bind N_2, perhaps because the π basicity of the site is too low in these cases. This suggests that σ acidity of the metal site is an important property in binding H_2 in the molecular form.

Existence of Other $M(H_2)$ Complexes. It seems likely that numerous dihydrogen complexes may well lie unrecognized in the literature. Our work suggests that the neutral and protonated forms of the well-known polyhydride complexes may repay reexamination in this connection. The existence of dihydrogen complexes also raises the interesting question of the possible existence of polyhydrides $MH_xL_y^{n+}$ for which the value of $(x + n)$ exceeds the maximum valency of the metal. It is probably more reasonable to regard these as having a lower oxidation state. For example, $IrH_2(H_2)_2L_2^+$ (**6**) is probably best regarded as Ir(III) rather than Ir(VII), an otherwise unknown oxidation state for this metal. It would also be worthwhile to reexamine hydrides which bind N_2 with loss of H_2.

Conclusion

We hope to have shown how T_1 measurements can be useful in detecting nonclassical hydrides. This is a more convenient method than neutron crystallography, and it can be applied easily to a wide range of compounds, even ones which are unstable at ambient temperatures. $M(H_2)$ structures may also be important in the interaction of metalloenzymes, notably hydrogenases, with H_2. Like **2** these also catalyse H/D exchange between H_2O and H_2.[19] We also suggest that, far from being rare, nonclassical hydrides may be widespread, especially amongst polyhydrides. They may well be involved in hydrogenolysis processes of d^0 alkyls.

Experimental Section

NMR spectra were obtained on Bruker 250- and 500-MHz instruments, and IR spectra were recorded on a Nicolet 7000 instrument. Starting materials were prepared by published procedures,[6,7] and the ligands were obtained from Aldrich Co.

(η^2-7,8-Benzoquinolinato)(η^2-dihydrogen)hydridobis(triphenylphosphine)iridium(III) Salts. Method A. To $[Ir(cod)(PPh_3)_2]SbF_6$ (433 mg, 0.41 mmol) in moist CH_2Cl_2 (20 mL) was added 7,8-benzoquinoline (73 mg, 0.41 mmol) and dihydrogen gas bubbled through the mixture at 0 °C for 30 min during which time the color changed from red to light yellow. The product was crystallized with Et_2O–heptanes and recrystallized from CH_2Cl_2/Et_2O–heptanes to give the cream-colored $[Ir(H_2O)H(bq)L_2]SbF_6$ (**1**). Yield 375 mg (88%). The complex was characterized crystallographically as well as by the usual spectral means [^{1}H NMR (reported as position in ppm (multiplicity, coupling constant in hertz, assignment)): −16.1 (t, J = 14, Ir–H), 2.54 (s, (H_2O)Ir), 7.2–7.9 (c, Ar)]. Complex **1** (20 mg) was dissolved in CD_2Cl_2 (ca. 0.5 mL), and H_2 was passed for ca. 2 min at −80 °C. The dihydrogen complex is formed in solution in equilibrium with the aquo complex **1**. Essentially complete conversion was achieved by adding a small piece of CaH_2 (1 mg) to the NMR sample to remove the adventitious water. The CaH_2 can be removed from the sample by inverting the tube before recording the NMR spectra in the normal way. ^{1}H NMR (CD_2Cl_2, −80 °C): −15.3 (t, J = 11.4, Ir–H), −2.9 (br, Ir(H_2)), 7.02–7.84 (complex, aromatic). ^{1}H NMR (CD_2Cl_2, 20 °C): −7.1 (br, IrH_3).

Method B. Complex **1** (100 mg) prepared as above was exposed to a high vacuum (10^{-6} torr) for 18 h in the solid state as a powder. When dry H_2 (1 atm) was added the sample absorbed H_2 mostly in the first few seconds, but complete reaction takes 10 min. No color change took place during this procedure.

Method C. $[IrH_2(bq)L_2]$ (20 mg, 0.021 mmol), synthesized by the method discussed below, was dissolved in PhMe (1 mL) and $PhCH(SO_2CF_3)_2$ (7.63 mg, 0.021 mmol) added at −80 °C under H_2. The ^{1}H

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NMR spectra of the product are identical with those obtained from methods A and B, except that the anion now also contains protons.

The corresponding aquo complex **1** can be fully analyzed, but the dihydrogen complex **2** loses H_2 in the solid state at 25 °C, so it cannot be analyzed.

(η^2-7,8-Benzoquinolinato)(η^2-dihydrogen)hydridobis(tricyclohexylphosphine)iridium(III) Salts. To $[IrH_5(PCy_3)_2]$ (410 mg, 0.54 mmol) in 15 mL of moist CH_2Cl_2 was added $PhCH(SO_2CF_3)_2$ (192 mg, 0.54 mmol) at -80 °C under H_2. After the solution stirred for 10 min, 7,8-benzoquinoline (97 mg, 0.54 mmol) was added, and at -80 °C Et_2O was added to crystallize the dihydrogen complex **2** (L = PCy_3) as a white solid. ^1H NMR: (-80 °C CD_2Cl_2): -4.64 (br, Ir(H_2)), -17.5 (br, Ir-H), 0.9-2.1 (c, PCy_3), 7.2-7.9 (Ar). ^1H NMR (20 °C, CD_2Cl_2): -10.34 (br, IrH_3). Carrying out the same synthetic procedure at 20 °C but with bubbling N_2 through the solution or pumping gently on it gives the corresponding aquo complex.

Bis(dihydrogen)dihydridobis(tricyclohexylphosphine)iridium(III) Salts. To $[IrH_5(PCy_3)_2]$ (20 mg, 2.64×10^{-5} mol) in CD_2Cl_2 (0.5 mL) at -80 °C was added $PhCH(SO_2CF_3)_2$ (9.4 mg, 2.6×10^{-5} mol). The resulting solution gave the following ^1H NMR spectrum. ^1H NMR (CD_2Cl_2, 188 K): -5.04 (v br, Ir(H_2)), -15.26 (br, Ir-H), 0.9-2.1 (c, PCy_3). ^1H NMR (CD_2Cl_2, 25 °C): -8.33 (v br, IrH_3). The complex was characterized by T_1 measurements described in the text.

Apparent T_1 Measurements. These were obtained by inversion-recovery at -80 °C in CD_2Cl_2 at 500 MHz with a 180°-t-90° pulse sequence. We also looked at **2** (L = PPh_3) at 250 MHz.

Isotherm Measurements. These were determined on a vacuum line by comparing the pressure change in the vessel containing the complex, on admitting a fixed volume of H_2 to the sample, compared to admitting the same volume of He. The H_2 was passed through a Pd membrane to purify it. We thank Prof. Kurt Zilm for suggesting these measurements, which were carried out in the Chemical Engineering Department with the help of Dr. L. Bonneviot.

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Kinetics of Disproportionation of Tricarbonylbis(phosphine)iron(I) Cation Radicals Probed by Double Potential Step Chronocoulometry

Michael J. Therien,[1a] Ching-Long Ni,[1b] Fred C. Anson,*[1b] Janet G. Osteryoung,[1c] and William C. Trogler*[1a]

Contribution from the Department of Chemistry, D-006, University of California, San Diego, La Jolla, California 92093, and the Division of Chemistry and Chemical Engineering, California Institute of Technology,[1d] Pasadena, California 91125. *Received September 26, 1985*

Abstract: Rates of substitution of carbon monoxide in a series of iron(I) radical complexes were measured by using double potential step chronocoulometry, a transient electrochemical technique. Carbon monoxide substitution in $Fe(CO)_3L_2^+$ (L = a phosphine) radicals proceeds solely by a second-order process that is first order in both the metal radical and the entering pyridine nucleophile. The rate of substitution depends on the basicity and size of the Lewis base, as seen in the L = PPh_3 system, where k_1 varies over 400-fold from 0.27 to 1.01×10^2 M^{-1} s^{-1}. Hammett analysis of the rate data shows that log k_1 correlates well with the σ-meta and σ-para values for nine 3- and 4-substituted pyridines. Nucleophilic attack of pyridine at $Fe(CO)_3(PCy_3)_2^+$ is 10^6 times slower than at $Fe(CO)_3(PMe_3)_2^+$, presumably because increased phosphine ligand size inhibits the associative pathway. Activation parameters further support the proposed associative mechanism: for L = PPh_3, nucleophile = pyridine, $\Delta H^\ddagger = 9.8 \pm 0.3$ kcal mol^{-1} and $\Delta S^\ddagger = -21 \pm 1$ cal mol^{-1} K^{-1}; for L = PCy_3, nucleophile= 3,4-dimethylpyridine, $\Delta H^\ddagger = 14 \pm 1.5$ kcal mol^{-1} and $\Delta S^\ddagger = -27 \pm 5$ cal mol^{-1} K^{-1}. After substitution of carbon monoxide by a nitrogen Lewis base, these complexes disproportionate via an outer-sphere electron-transfer process to yield Fe(II) and Fe(0) products. Comparison of the reactivities of $Fe(CO)_3(PPh_3)_2$ and its 17-electron analogue, $Fe(CO)_3(PPh_3)_2^+$, shows that the cation radical is about 10^9 more reactive toward pyridine than its 18-electron precursor.

Because of their role in catalytic and stoichiometric transformations,[2] there has been interest in reaction mechanisms of organometallic radicals. Studies of electrocatalysis of ligand substitution[3-6] and migratory insertion reactions,[7] of the lability of 17e species toward isomerization,[8] of radicals as oxidizing and reducing agents,[9] and of substitution labilities of stable organometallic radicals[10-13] illustrate the roles assumed by radicals in organotransition metal chemistry. Kinetic studies of simple organometallic radicals of the first transition series have been limited

(1) (a) University of California at San Diego. (b) California Institute of Technology. (c) Department of Chemistry, State University of New York, Buffalo, NY 14214. (d) Contribution No. 7297.

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