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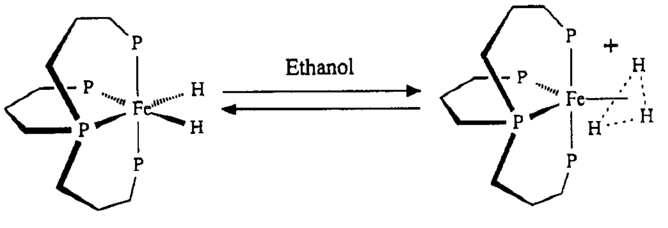
Protonation of $FeP(CH_2CH_2CH_2PMe_2)_3H_2$ with Alcohols To Form $FeP(CH_2CH_2CH_2PMe_2)_3H(\eta^2\text{-}H_2)^+$

A number of relatively stable iron complexes contain molecular hydrogen[1-4] coordinated in an η^2 fashion, and the complex $[FeH(H_2)(DPPE)_2]^+$ [DPPE = 1,2-bis(diphenylphosphino)ethane] has been characterized crystallographically.[2] In previous work, we have demonstrated that molecular hydrogen complexes of iron can be formed readily, under mild conditions, from iron dihydrides $FeH_2(PP)_2$ [PP = $R_2PCH_2CH_2PR_2$, where R = Me (PP = DMPE), Et (PP = DEPE), and *n*-Pr [PP = DPrPE)] by protonation with weak organic acids such as simple alcohols.[5]

The dihydroiron complex **1**, containing the tetradentate tripodal polyphosphine ligand $P(CH_2CH_2CH_2PMe_2)_3$, was first synthesized and characterized by Antberg, Frosin, and Dahlenberg.[6] As with other iron complexes containing bidentate alkylphosphine ligands, **1** is protonated by methanol, ethanol, or stronger acids to give a trihydride, $[Fe(H_3)(PP_3)]^+$ (**2**). In ethanol solution, **1** and **2** are in equilibrium, with **2** dominating the equilibrium at low temperature; by NMR spectroscopy, **1** is fully protonated in methanol solution. The dihydride **1** is regenerated if the alcohol solvent is removed.



1 **2**

In the ^1H NMR spectrum of $[Fe(H_3)(PP_3)]^+[Ph_4B]^-$ ($\mathbf{2}[Ph_4B]$ in acetone-d_6 solvent at room temperature,[7,8] the iron-bound hydrogens appear superficially as a three-proton quintet (δ −11.4 ppm, splitting 16 Hz, with the multiplicity due to ^{31}P coupling). The dropwise addition of CD_3OD to the sample successively exchanges the iron-bound hydrides for deuterium, and the hydride region of the phosphorus-decoupled ^1H NMR spectrum exhibits a partially superimposed singlet, a 1:1:1 triplet, and a 1:4:6:4:1 quintet for the H_3, H_2D, and HD_2 isotopomers **2**–**4**, respectively (Figure 1). The H–D coupling changes only slightly from 11.0 to 10.0 Hz from the H_2D species to the HD_2 species.

The cation formed by protonation of **1** has been reported[6] as a monohydrido species, $[FeH(PP_3)]^+$. The trihydride **2** is spectroscopically identical[8] with that previously assigned as $[FeH(PP_3)]^+$ and *the monohydride formulation is clearly incorrect.*

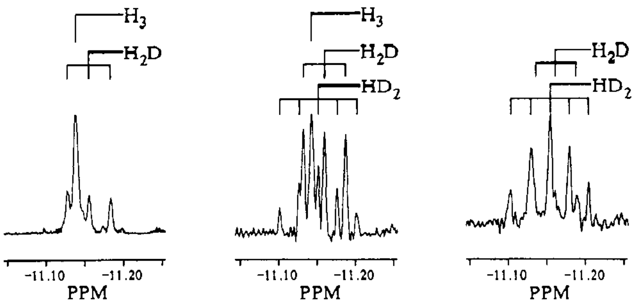


Figure 1. ^1H NMR spectra (^{31}P decoupled) of the hydride region of **2** with increasing deuteration (acetone-d_6 solvent, 298 K; left to right): (a) ca. 60%; (b) ca. 80%; (c) ca. 90%.

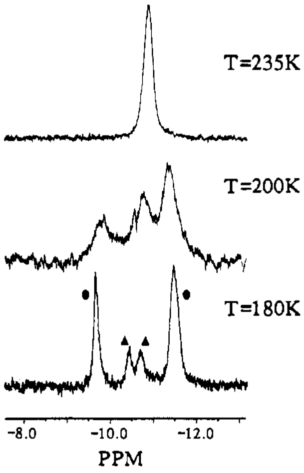


Figure 2. ^1H NMR spectra (^{31}P decoupled) of the hydride region of a mixture of **3** (▲) and **4** (●) (CH_3OH/CD_3OD solvent, at 180, 200, and 235 K).

At the lowest temperature at which the fully protonated ion, **2**, could be examined by NMR in solution (165 K), there was no evidence for freezing of the H_3 resonance into signals that could be assigned to classically bound H or η^2-bound H_2.[9] However, for the H_2D complex **3** and the HD_2 complex **4**, the rate of exchange is slowed by the isotopic substitution, and at temperatures below 180 K, the ^1H NMR resonance of the iron-bound hydrides separates into two signals each for **3** and **4** (Figure 2).[10] The two resonances at highest field (δ −10.97 and −11.70 ppm) are broadened due to coupling to ^2H but are only weakly coupled to ^{31}P whereas the resonances to lower field (δ −9.93 and −10.73 ppm) show a relatively large coupling to phosphorus and negligible coupling to ^2H. We assign the low-field resonances to hydrides of **3** and **4** and the high-field resonances to η^2-bound HD or H_2.[11] At 175 K, the measured T_1 values for both the hydride and η^2-H_2/HD protons of **3** are approximately 50 ms. However saturation-transfer experiments show that there is significant exchange between the classically bound and the η^2-bound sites so this value would reflect the dominant contribution of the characteristically short T_1 of the η^2-H_2 isotopomer to the exchange.[12] At the same temperature, the measured T_1 for the hydride of **4** is approximately 244 ms and that for the proton of

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(1) See, for example: Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124. Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Am. Chem. Soc.* **1989**, *111*, 2072.

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(7) ^{31}P NMR spectra (162.0 MHz) were referenced to external, neat, trimethyl phosphite, taken as 140.85 ppm. ^1H NMR spectra (400.1 MHz) were referenced to solvent resonances.

(8) **2** can be isolated as an air-sensitive tetraphenylborate salt by addition of sodium tetraphenylborate to a methanol solution of **1**. ^1H NMR (acetone-d_6, 300 K): δ 7.5–6.7 (20 H, m, 4 × C_6H_5B), 2.2–1.2 (18 H, m, 9 × CH_2), 1.4 (12 H, d, 6 × CH_3), −10.5 (3 H, m, Fe–H_3). $^{31}P\{^1H\}$ NMR (acetone-d_6, 300 K): δ 34.1 (1 P, dt, P_{apical}), 16.6 (3 P, br s, 3 × $P_{terminal}$); $^{31}P\{^1H\}$ NMR (acetone-d_6, 220 K): δ 33.7 (P_{apical}, dt, $J_{P-P_{terminal(ax)}}$ = 64 Hz, $J_{P-P_{terminal(eq)}}$ = 64 Hz), 20.5 (2 × $P_{terminal(ax)}$, dd, $J_{P-P_{terminal(eq)}}$ = 27 Hz); 11.6 ($P_{terminal(eq)}$, dt); ^{31}P NMR resonances of the terminal nuclei broaden and coalesce over the temperature range 220–280 K. The ^1H chemical shift is temperature dependent. $\delta(^1H)$ (CH_3OH): 180 K, −11.108 ppm; 260 K, −11.167 ppm; 300 K, −11.233 ppm.

(9) In a related system, $[Fe(H_3)(P(CH_2CH_2PPh_2)_3]^+$, Bianchini et al.[2] have observed that the broad ^1H resonance of "coordinated H_3" separated into classically bound H and η^2-H_2 resonances slightly below room temperature.

(10) $\Delta G^{\ddagger}$ for the $H/\eta^2\text{-}D_2 \rightleftarrows D/\eta^2\text{-}HD$ exchange for **4** is approximately 38 kJ/mol at 200 K.

(11) Increasing the –OH to –OD ratio in the methanol solvent systematically increases signals at −10.73 and −10.97 ppm at the expense of the signals at −9.93 and −11.7 ppm, and this indicates that the central peaks arise from the H_2D isotopomer and the outer peaks arise from HD_2 species. A further peak at about −11 ppm appears at higher H/D ratios for the H_3 species.

(12) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. Bautista, M.; Earl, K. A.; Maltby, P. A.; Moris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031.

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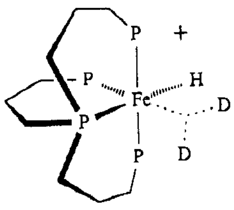
the η^2-bound HD is approximately 133 ms. Crabtree and Lavin[13] have noted that the T_1 of η^2-bound HD is significantly longer than that of the η^2-H_2 due to the smaller magnetic moment of the deuterium nucleus. Again, saturation-transfer experiments indicate that there is still significant exchange between the classically bound and η^2-bound environments at this temperature, and the measured T_1 values must have a contribution from exchange averaging.

There are two stereoisomers possible for a H/η^2-H_2 trihydride complex i.e. with the classically bonded hydride cis or trans to the apical phosphorus. Only one isomer is observed in the ^{1}H NMR spectrum of **4** at low temperature, and on the basis of ^{31}P–^{1}H coupling constants, we assign this as the stereoisomer with the hydride trans to the apical phosphorus. In the dihydride, **1**, the ^{31}P–^{1}H coupling constants uniquely define the assignment of the two iron-bound hydrides[14] with cis-^{31}P–^{1}H coupling to the terminal phosphorus atoms being relatively large (45–70 Hz) and trans-^{31}P–^{1}H coupling to the terminal phosphorus atoms being significantly smaller (ca. 30 Hz). The corresponding coupling constants to the apical phosphorus are smaller than those to the terminal nuclei by approximately 50%. The hydride in **4** exhibits three large ^{31}P couplings of ca. 56 Hz, and this locates it trans to the apical phosphorus.



4

As with other iron complexes of molecular hydrogen, the η^2-bound H_2 in **2** is substituted readily with better ligands such as halides[15] and alkane- and arenethiolate[16] to give substituted iron P_4 hydrides.

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Grants Scheme.

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(13) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661.

(14) In the dihydride **1**, the hydride located trans to the apical phosphorus exhibits a triplet splitting (60.0 Hz) to the equivalent axial ^{31}P nuclei, another relatively large coupling (47.9 Hz) to the terminal equatorial ^{31}P nucleus, and a coupling of 11.9 Hz to the apical phosphorus. In contrast, the other hydride exhibits a triplet splitting (70.9 Hz) due to the terminal diaxial ^{31}P nuclei, a coupling of 14.3 Hz to the trans terminal phosphorus and a coupling of only 33.5 Hz to the cis-apical phosphorus.

(15) Baker, M. V.; Field, L. D. *J. Organomet. Chem.* **1988**, *354*, 351–6.

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Synthesis and Characterization of $Rh_2(O_2CCH_3)_3[\{C_6H_2(OMe)_3\}_2P\{C_6H_2(OMe)_2O\}](MeOH)$ with a Novel Tridentate Ligand Derived from Tris(2,4,6-trimethoxyphenyl)phosphine

It is well-known that metal phosphine complexes are good catalyst precursors in important reactions such as hydrogenation, hydroformylation, and polymerization.[1] The investigation of bulky and labile phosphine ligands is especially interesting due to the formation of reactive coordinatively unsaturated molecules.[2] One of our recent research interests is to explore the chemistry of the unusually large and basic phosphine ligand tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) with low-valent metal centers.[3] Several other groups have reported the use of this phosphine in organic reactions[4] and in solid-state ^{31}P NMR studies.[5] The first TMPP complex that was prepared in our laboratories is $[Rh(TMPP)_2](BF_4)_2$, a novel Rh^{II} monomer possessing a chelating tridentate arrangement for the PR_3 ligand.[3a] Since both oxygen and phosphorus atoms are good donors, one may envision a variety of possible multidentate coordination modes for this ligand such as chelating tridentate (**1**), bridging bidentate (**2**), or bridging and chelating tridentate (**3**). The use of this highly flexible ligand in the series of complexes $[Rh(TMPP)_2]^{n+}$ (n = 1, 2, 3), all exhibiting some variation of structure **1** above, afforded us the rare opportunity to probe the geometrical preferences of a metal center as a function of the electronic configuration.[6] We were

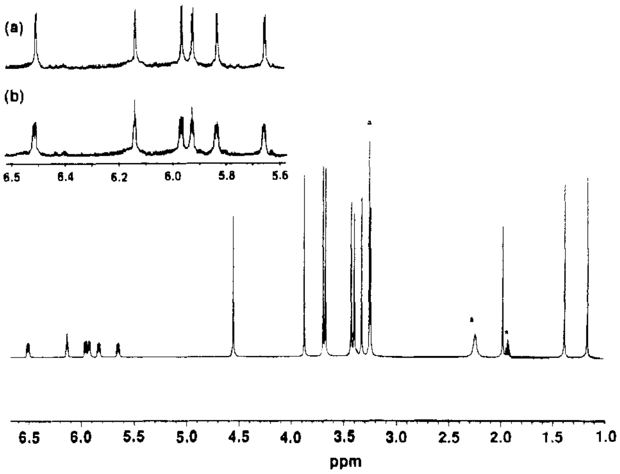

Figure 1. Room-temperature 300-MHz ^{1}H NMR spectrum of **1** in CD_3CN (peak a is methanol; an asterisk marks the CD_3CN impurity). The inset shows the metal proton region at 500 MHz with (a) phosphorus nuclei decoupled and (b) phosphorus nuclei nondecoupled.

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(1) See for example: (a) Stelzer, O. *Top. Phosphorus Chem.* **1977**, *9*, 1. (b) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (c) Nakamura, A.; Tsutsui, M. *Principles and Applications of Homogeneous Catalysis*; Wiley: New York, 1980. (d) Alyea, E. C.; Meek, D. W. *Catalytic Aspects of Metal Phosphine Complexes*; Advances in Chemistry Series 196; American Chemical Society: Washington, DC, 1982. (e) Pignolet, L. H. *Homogeneous Catalysis With Metal Phosphine Complexes*; Plenum Press: New York, 1983. (f) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986. (g) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, Part II, 2nd ed.; University Science Books: Mill Valley, CA, 1987. (h) McAuliffe, C. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Guilkard, R. D., McCleverty, J. A., Eds.; Pergammon Press: Oxford, England, 1987; Vol. 2, Chapter 14, p 989.

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(3) (a) Dunbar, K. R.; Haefner, S. C.; Pence, L. E. *J. Am. Chem. Soc.* **1989**, *111*, 5504. (b) Dunbar, K. R.; Haefner, S. C.; Burzynski, D. J. Submitted for publication in *J. Am. Chem. Soc.* (c) Dunbar, K. R.; Haefner, S. C.; Quillevéré, A. Submitted for publication in *Polyhedron*.

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