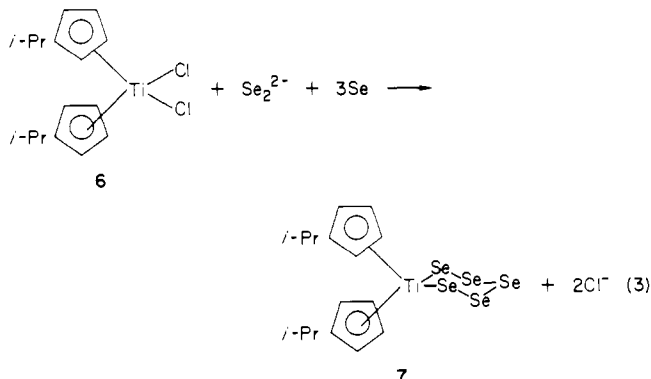


of alkyl halide in the central compartment of the cell would improve the current efficiency.²⁵

Electrochemical reduction of Se and Te with ultrasound can provide an elegant technique to prepare organotransition-metal chalcogenides. An example corresponds to electrolysis no. 5 of Table I. The formation of the pentaselenide⁷²⁷ corresponds to the overall process (3).



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Registry No. 1, 84019-98-7; 2, 1482-82-2; 3, 20727-11-1; 4, 1842-38-2; 5, 62654-03-9; 6, 12130-65-3; 7, 97732-75-7; Se, 7782-49-2; Se₂²⁻, 25778-65-8; Se²⁻, 22541-48-6; Te, 13494-80-9; Te₂²⁻, 62086-49-1; Te²⁻, 22541-49-7; *p*-cyanobenzyl chloride, 874-86-2; benzyl chloride, 100-44-7.

(25) The influence of the nature of the supporting electrolyte has not been investigated. However, it may be suggested that use of alkali salts would modified the current efficiency. Furthermore, as suggested by a reviewer, use of a cation-exchange membrane such as Nafion should prevent the loss of anions and thus improve the yields of alkylated products.

(26) Sullivan, M. F.; Little, W. F. *J. Organomet. Chem.* **1967**, *8*, 277.

(27) Data for compound 7. Anal. Calcd for C₁₆H₂₂Se₅Ti: C, 29.25; H, 3.37; Se, 60.09; Ti, 7.21. Found: C, 29.38; H, 3.40; Se, 60.07; Ti, 7.40. ¹H NMR (benzene-*d*₆) δ 5.84 (t, 2 H), 5.59 (s, 4 H), 5.45 (t, 2 H), 2.97 (hp, 1 H), 2.58 (hp, 1 H), 1.02 (d, 6 H, ³J = 6.8 Hz), 0.83 (d, 6 H, ³J = 6.8 Hz).

Two Molecular Hydrogen Complexes: *trans*-[M(η²-H₂)(H)(PPh₂CH₂CH₂PPh₂)₂]BF₄ (M = Fe, Ru). The Crystal Structure Determination of the Iron Complex

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Recently the complexes M(CO)₃(PR₃)₂(H₂) (M = Mo, W; R = Cy, *i*-Pr),¹ Cr(CO)₅(H₂)₂²⁻⁴ and Cr(CO)₄(H₂)₂⁴ have been reported to contain novel η²-dihydrogen ligands which retain an H-H bond. Hydrogen is readily lost from these complexes and only the tricyclohexylphosphine molybdenum complex^{1b} and the two tungsten complexes are isolable. By contrast we report here

the discovery of the complex *trans*-[Fe(η²-H₂)(H)(dppe)₂]BF₄ (**1**) (dppe = PPh₂CH₂CH₂PPh₂), which is stable to H₂ loss up to 50 °C and undergoes a unique intramolecular exchange of terminal hydride with the hydrogens of the η²-H₂ ligand.⁵ The ruthenium analogue *trans*-[Ru(η²-H₂)(H)(dppe)₂]BF₄ (**2**) contains a more labile dihydrogen ligand.

The title complexes are prepared by reaction of a THF or benzene solution of the corresponding dihydride complexes MH₂(dppe)₂⁶ under hydrogen at 22 °C with approximately 1 equiv of HBF₄·Et₂O.⁷ They can also be prepared by reaction of H₂ with monohydrides [MH(dppe)₂]BF₄ (see below).⁸ A similar reaction using HClO₄ was reported to yield [FeH₃(dppe)]ClO₄ although no physical properties of the complex were reported.⁹ Reactions with weaker acids give monohydride complexes.¹⁰

Complex **1** is a pale yellow solid that must be stored under hydrogen or argon since it reacts slowly with nitrogen to give *trans*-[FeH(N₂)(dppe)₂]BF₄.¹¹ This dihydrogen adduct dissolves to give stable solutions under argon at 22 °C in THF or CH₂Cl₂ but THF solutions slowly evolve hydrogen when heated under vacuum to 66 °C (*t*_{1/2} ~ 2.5 h). In the presence of the more strongly coordinating ligands acetonitrile or carbon monoxide (L) 1 mol of H₂ per Fe is rapidly evolved at 25 °C and the complexes *trans*-[FeH(L)(dppe)₂]BF₄¹¹⁻¹³ are obtained. White complex **2** loses up to 1 mol of H₂ in the solid state at 25 °C under vacuum in 10 min to give orange-yellow [RuH(dppe)₂]BF₄.¹⁴ The reverse reaction with H₂ or D₂ is complete in 30 s. Reversible binding of dihydrogen by **2** is also observed in oxygen-donor solvents whereas reaction with CH₃CN and CO but not N₂ rapidly and irreversibly yields [RuH(L)(dppe)₂]BF₄.^{13,15}

The η²-dihydrogen ligand in **1** is symmetrically coordinated with Fe-H distances of 1.53 (8) and 1.55 (7) Å, slightly longer than the terminal Fe-H distance of 1.28 (8) Å (Figure 1).¹⁶ The H-H

(5) The report of a molecular hydrogen complex of iridium, [IrH(H₂)-(PPh₃)₂(C₁₃H₈N)]⁺, with similar properties to **1** appeared after the submission of our paper: Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794-795.

(6) (a) Peet, W. G.; Gerlach, D. H. *Inorg. Synth.* **1974**, *15*, 38-42. (b) Peticci, P.; Vitulli, G.; Poarzio, W.; Zocchi, M. *Inorg. Chim. Acta.* **1979**, *37*, L521-L522.

(7) Dr. Steven D. Ittel at E.I. Du Pont de Nemours & Co. prepared the iron complex with the stoichiometry of **1** in 1977 in unpublished work (recent personal communication from S. D. Ittel).

(8) Giannoccaro, P.; Sacco, A.; Ittel, S. D.; Cushing, M. A., Jr. *Inorg. Synth.* **1977**, *17*, 69-72.

(9) Giannoccaro, P.; Rossi, M.; Sacco, A. *Coord. Chem. Rev.* **1972**, *8*, 77-79.

(10) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H.; Howells, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 1510-1511.

(11) Azizian, H.; Morris, R. H. *Inorg. Chem.* **1983**, *6*-9.

(12) Mori, G.; Takashima, Y. *Chem. Lett.* **1979**, 425-428.

(13) Morris, R. H.; Shiralian, M.; Zubkowski, J. D., unpublished results.

(14) [RuH(dppe)₂]BF₄: Ir (Nujol) 1949 cm⁻¹ (Ru-H); δ (³¹P vs. 85% H₃PO₄, acetone-*d*₆) 63.1.

(15) Smith, G.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1203-1208.

(16) (a) Orange crystals of **1** obtained from THF solution were sealed in 0.2-0.3 mm Lindemann capillaries under Ar. Diffractometer: Enraf-Nonius CAD4. Radiation: graphite monochromatized Mo Kα (λ = 0.710 69 Å). Crystal data: [Fe(H₂)(H)(dppe)₂]BF₄(THF)₂(Et₂O), dimensions 0.2 × 0.26 × 0.26 mm, monoclinic, space group P2₁/n, *a* = 14.871 (3) Å, *b* = 12.773 (3) Å, *c* = 32.205 (8) Å, β = 103.23 (2)°, *U* = 5950 (5) Å³, and *D*_c = 1.29 g cm⁻³ for *Z* = 4. 11275 Data in the quadrants *h,k,±l* with 2θ < 48° collected. Systematically absent and zero *F*_{obsd} data rejected (2275) and 815 symmetry-equivalent data averaged (*R*_{merge}(*F*) = 0.057) to give data set of 7858 reflections. Patterson, least-squares, and Fourier solution. Hydrogen atoms bonded to iron located in Δ*F* Fourier and successfully refined.^{16b} Current residuals *R* = 0.0791 (*R*_w = 0.0836) for 4346 observed (*I* > 3σ(*I*)) reflections. The asymmetric unit of the complex contains the Fe cation, a BF₄⁻ anion disordered over two orientations, two molecules of THF solvent, and one of diethyl ether which is disordered over three or more orientations. Other selected bond lengths: Fe-P1 2.235 (3), Fe-P2 2.247 (3), Fe-P3 2.243 (3), Fe-P4 2.231 (2), average B-F 1.30 (3) Å. (b) It is common to locate hydrogens bonded to 3d metals using X-ray techniques. Other iron-hydrides: McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* **1977**, *99*, 6243-6249. Smith, M. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 2388-2389. Ghilardi, C. A.; Innocenti, P.; Midollini, S.; Orlandini, A. *J. Chem. Soc., Dalton Trans.* **1985**, 605-609. Guggenberger, L. J.; Titus, D. D.; Flood, M. T.; Marsh, R. E.; Orio, A. A.; Gray, H. B. *J. Am. Chem. Soc.* **1972**, *94*, 1135-1143. Huffman, J. C.; Wells, N. J.; Caulton, K. G. *J. Crystallogr. Spectrosc. Res.* **1984**, *14*, 581-587.

(1) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451-452. (b) Kubas, G. J. *J. Chem. Soc., Chem. Commun.* **1980**, 61-62.

(2) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27-30.

(3) Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1985**, 30-32.

(4) Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374-2379.

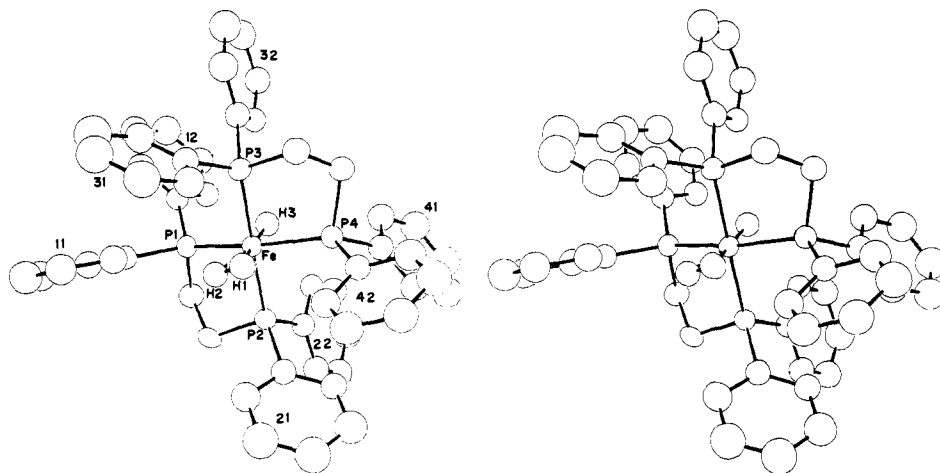


Figure 1. Stereoview of complex 1.

separation of 0.89 (11) Å may be compared to the H₂ distance of 0.74 Å for free H₂ and of 0.75 (16) (X-ray) and 0.84 Å (neutron) in the complex W(CO)₃(P(*i*-Pr)₃)₂(H₂).¹ The complex has distorted octahedral geometry with the η²-H₂ ligand occupying one vertex. The only significant distortion (>5° deviation) of angles in the octahedron is found in the angle P1-Fe-P4 of 163.0 (1)° which can be explained by a bending of these Fe-P bonds away from the H atoms of the η²-H₂ ligand with which they are coplanar and toward the smaller terminal hydride ligand. Trans P-Fe-P angles in **1** (163.0 (1)°, 178.7 (1)°) are much closer to 180° than corresponding P-Re-P angles in the pentagonal bipyramidal trihydrides ReH₃(dppe)₂ and ReH₃(dppe)(PPh₃)₂.¹⁷

The η²-H₂ complexes so far reported all seem to have an octahedral geometry which is strongly favored by the formally d⁶ configuration (Cr(0), Mo(0), W(0), Fe(II), Ru(II)). In addition the complexes are not very electron rich and so are inhibited for electronic (and possibly steric) reasons from oxidative addition reactions to form d⁴, seven-coordinate configurations. The ReH(dppe)₂ site, which does oxidatively add H₂ and C-H bonds,¹⁸ oxidizes at ~1 V more negative potential than FeH(dppe)₂⁺ which does not activate C-H bonds.¹⁹ More electron-rich iron-group hydrides are very reactive C-H bond activators.²⁰⁻²⁹

The ¹H NMR spectra of **1** and **2** in acetone-*d*₆ are comparable at temperatures below -20 °C. Each shows a terminal hydride resonance as a sharp quintet at δ -12.9 (Fe, ²*J*(P,H) = 47 Hz) or -10.0 (Ru, *J* = 16 Hz) and an η²-H₂ resonance as a broad singlet at δ -8.0 (Fe) or -4.6 (Ru) which begins to broaden further below -60 °C. This broadening may be due to a slowing of the rotation of the η²-H₂ ligand on the square face of a square pyramid defined by the four phosphorus atoms and apical hydride. The no-exchange spectrum has not yet been obtained.³⁰ This resonance

associated with η²-H₂ in complexes **1**, **2**, and also M(CO)₃(PR₃)₂(η²-H₂) (M = Mo, W)¹ shows no resolvable coupling to phosphorus whereas the signal for the trihydride ReH₃(dppe)₂ does.³¹ Intermolecular exchange processes are not likely. The complexes do not lose dihydrogen in this temperature range and deprotonation to give back FeH₂(dppe)₂ requires a strong base like hydroxide⁹ or 1,8-bis(dimethylamino)naphthalene (this work).

The resonances for η²-HD in a mixture of [Ru(η²-HD)(H)(dppe)₂]BF₄ (δ -4.56) and [Ru(η²-HD)(D)(dppe)₂]BF₄ (δ -4.62) generated along with the other isotopomers from the reaction of D₂ with **2** or [RuH(dppe)₂]BF₄ at 22 °C show, as expected for the presence of an H-D bond,¹ 1:1:1 triplets with large couplings ¹*J*(H,D) of 32 Hz. Only a broad singlet is observed for the corresponding iron complexes at 22 °C.

The iron complex displays a second fluxional process at temperatures above -20 °C where the unique hydride undergoes exchange with the two equivalent hydrogens. Coalescence of the resonances to a broad singlet at δ -9.4 occurs at 50 °C. The spectra have been accurately simulated³² and the activation parameters obtained: Δ*H*[‡] = 13.9 ± 0.7 kcal mol⁻¹, Δ*S*[‡] = -1 ± 3 eu, and rate = 400 s⁻¹ at 303 K. The mechanism of this rearrangement is under further study. The spectra for complex **2** above 25 °C are broadened by intermolecular H₂ exchange. The ³¹P{¹H} resonance for **1** (δ 92.5) remains as a singlet at low temperatures; **2** also gives a singlet at δ 68.6.

A careful study of the IR spectra of **1** and **2** and their deuterated analogues reveals only weak modes due to the terminal M-H stretches at 1919 (Fe) and 1961 cm⁻¹ (Ru). Further studies involving other diphosphine analogues of **1** and **2** are in progress.

Note Added in Proof. We recently learned of the study of complex **2** by Ashworth and Singleton where it was postulated, without spectral evidence, that the H-H bond might not be ruptured.³³

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Supplementary Material Available: Preparation and spectra of complexes **1** and **2** and tables of positional and thermal parameters and interatomic distances and angles (12 pages). Ordering information is given on any current masthead page.

(17) (a) Albano, V. G.; Bellon, P. *J. Organomet. Chem.* **1972**, *37*, 151-157. (b) Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G. *Adv. Chem. Ser.* **1978**, *167*, 73-92.

(18) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379-384.

(19) Chatt, J.; Kan, C. T.; Leigh, G. J.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2032-2038.

(20) Chaudret, B. *J. Organomet. Chem.* **1984**, *268*, C33-C37.

(21) Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1985**, *284*, 73-93.

(22) Werner, H.; Roder, K. *J. Organomet. Chem.* **1985**, *281*, C38-C42.

(23) Kletzin, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 873-874.

(24) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *209*, C60-C64.

(25) Morris, R. H.; Shiralian, M. *J. Organomet. Chem.* **1984**, *260*, C47-C51.

(26) Karsch, H. K. *Chem. Ber.* **1984**, *117*, 3123-3133.

(27) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742-1751.

(28) Graimann, C. E.; Green, M. L. H. *J. Organomet. Chem.* **1984**, *275*, C12-C14.

(29) Bennett, M. A.; Huang, T.; Latten, J. L. *J. Organomet. Chem.* **1984**, *272*, 189-205.

(30) Estimates for this rearrangement of **1**: Coalescence temperature 180 ± 10 K; Δ*v* ~ 160 ± 80 Hz; Δ*G*[‡] = 8.3 ± 0.7 kcal.

(31) Ginsberg, A. P.; Tully, M. E. *J. Am. Chem. Soc.* **1973**, *95*, 4749-4751.

(32) Howe, J. J.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1970**, *92*, 7342-7348. Bushweller, C. H.; Letenare, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Whalon, M. R.; Fleischman, S. H. Quantum Chemistry Program Exchange, No. 466, DNMR-4.

(33) Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 705-706.