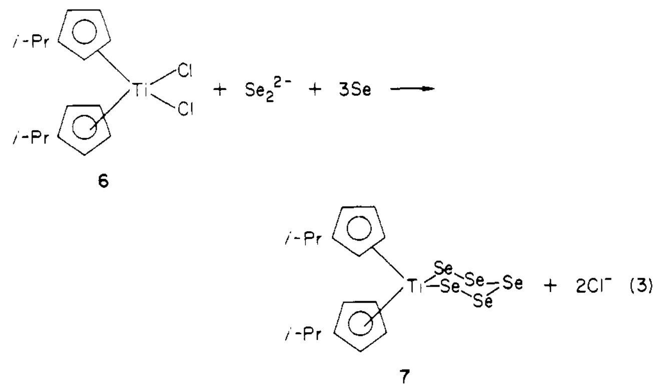
of alkyl halide in the central compartment of the cell would improve the current efficiency.[25]

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 pentaselenide 7[27] 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; Se_2^{2-}, 25778-65-8; Se^{2-}, 22541-48-6; Te, 13494-80-9; Te_2^{2-}, 62086-49-1; Te^{2-}, 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.

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Two Molecular Hydrogen Complexes: *trans*-[M(η^2-H_2)(H)($PPh_2CH_2CH_2PPh_2$)$_2$]BF_4 (M = Fe, Ru). The Crystal Structure Determination of the Iron Complex

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Recently the complexes $M(CO)_3(PR_3)_2(H_2)$ (M = Mo, W; R = Cy, *i*-Pr),[1] $Cr(CO)_5(H_2)$,[2-4] and $Cr(CO)_4(H_2)_2$[4] have been reported to contain novel η^2-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(η^2-H_2)(H)(dppe)$_2$]BF_4 (**1**) (dppe = $PPh_2CH_2CH_2PPh_2$), which is stable to H_2 loss up to 50 °C and undergoes a unique intramolecular exchange of terminal hydride with the hydrogens of the η^2-H_2 ligand.[5] The ruthenium analogue *trans*-[Ru(η^2-H_2)(H)(dppe)$_2$]BF_4 (**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 MH_2(dppe)$_2$[6] under hydrogen at 22 °C with approximately 1 equiv of HBF_4·Et_2O.[7] They can also be prepared by reaction of H_2 with monohydrides [MH(dppe)$_2$]BF_4 (see below).[8] A similar reaction using $HClO_4$ was reported to yield [FeH_3(dppe)$_2$]ClO_4 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(N_2)(dppe)$_2$]BF_4.[11] This dihydrogen adduct dissolves to give stable solutions under argon at 22 °C in THF or CH_2Cl_2 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 H_2 per Fe is rapidly evolved at 25 °C and the complexes *trans*-[FeH(L)(dppe)$_2$]BF_4[11-13] are obtained. White complex **2** loses up to 1 mol of H_2 in the solid state at 25 °C under vacuum in 10 min to give orange-yellow [RuH(dppe)$_2$]BF_4.[14] The reverse reaction with H_2 or D_2 is complete in 30 s. Reversible binding of dihydrogen by **2** is also observed in oxygen-donor solvents whereas reaction with CH_3CN and CO but not N_2 rapidly and irreversibly yields [RuH(L)(dppe)$_2$]BF_4.[13,15]

The η^2-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

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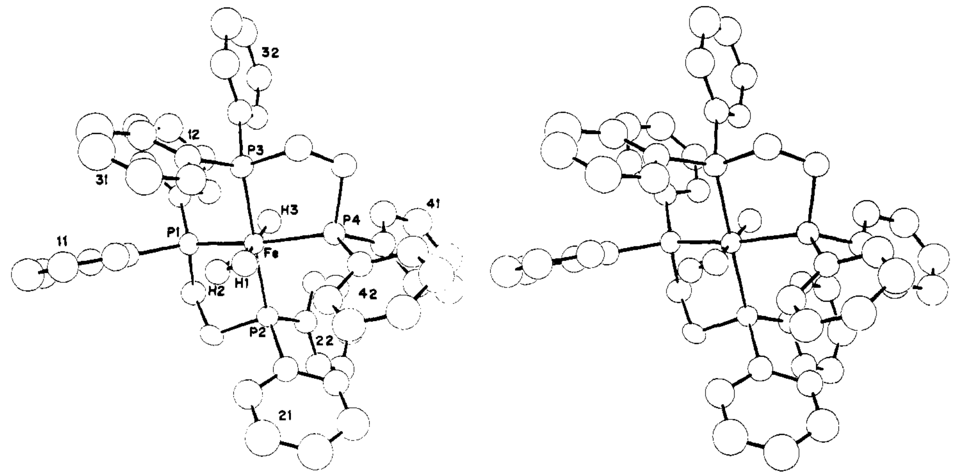

Figure 1. Stereoview of complex **1**.

separation of 0.89 (11) Å may be compared to the H_2 distance of 0.74 Å for free H_2 and of 0.75 (16) (X-ray) and 0.84 Å (neutron) in the complex $W(CO)_3(P(i\text{-}Pr)_3)_2(H_2)$.[1] The complex has distorted octahedral geometry with the η^2-H_2 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 η^2-H_2 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 $ReH_3(dppe)_2$ and $ReH_3(dppe)(PPh_3)_2$.[17]

The η^2-H_2 complexes so far reported all seem to have an octahedral geometry which is strongly favored by the formally d^6 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 d^4, seven-coordinate configurations. The $ReH(dppe)_2$ site, which does oxidatively add H_2 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, $^2J(P,H)$ = 47 Hz) or −10.0 (Ru, J = 16 Hz) and an η^2-H_2 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 η^2-H_2 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 η^2-H_2 in complexes **1**, **2**, and also $M(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ (M = Mo, W)[1] shows no resolvable coupling to phosphorus whereas the signal for the trihydride $ReH_3(dppe)_2$ does.[31] Intermolecular exchange processes are not likely. The complexes do not lose dihydrogen in this temperature range and deprotonation to give back $FeH_2(dppe)_2$ requires a strong base like hydroxide[9] or 1,8-bis(dimethylamino)naphthalene (this work).

The resonances for η^2-HD in a mixture of $[Ru(\eta^2\text{-}HD)(H)(dppe)_2]BF_4$ (δ −4.56) and $[Ru(\eta^2\text{-}HD)(D)(dppe)_2]BF_4$ (δ −4.62) generated along with the other isotopomers from the reaction of D_2 with **2** or $[RuH(dppe)_2]BF_4$ at 22 °C show, as expected for the presence of an H–D bond,[1] 1:1:1 triplets with large couplings $^1J(H,D)$ 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 simulated[32] and the activation parameters obtained: $\Delta H^{\ddagger}$ = 13.9 ± 0.7 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −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 H_2 exchange. The $^{31}P\{^1H\}$ resonance for **1** (δ 92.5) remains as a singlet to 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.

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