

Acidic Dicationic Iron(II) Dihydrogen Complexes and Compounds Related by H₂ Substitution

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Received July 23, 1999

[*trans*-Fe(H₂)(CO)(dppe)₂]²⁺ (**3**) (dppe = 1,2-bis(diphenylphosphino)ethane) was generated by protonation of [*trans*-FeH(CO)(dppe)₂]⁺ in CD₂Cl₂. [*trans*-Fe(H₂)(CO)(depe)₂]²⁺ (**6**) (depe = 1,2-bis(diethylphosphino)ethane) was generated by the treatment of [*trans*-FeCl(CO)(depe)₂]⁺ in CD₂Cl₂ with AgSbF₆ under 1 atm of H₂. Complex **3** is more acidic than trifluoromethanesulfonic acid (HOTf) in CD₂Cl₂, while **6** is suspected to be less acidic than [Et₂OH]⁺. **3**[OTf]₂ is stable to H₂ loss under reduced pressure for several hours, an indication of strong three-center (Fe–H₂), two-electron σ -bonding. Both complexes **3** and **6** undergo H₂ substitution reactions. There is evidence of the formation of [*trans*-Fe(H₂O)(CO)(dppe)₂]²⁺ and [*trans*-Fe(OTf)(CO)(dppe)₂]⁺, although these complexes could not be isolated. [*trans*-FeY(CO)(depe)₂]⁺Y complexes (Y[−] = [BF₄][−], **7**[BF₄]; Y[−] = [OTf][−], **8**[OTf]) were isolated from the corresponding reactions of [*trans*-FeH(CO)(depe)₂]⁺Y with [Et₂OH][BF₄] or HOTf. **7**[BF₄] was structurally characterized by single-crystal X-ray diffraction. Attempts to grow crystals of **8**[OTf] yielded salts containing the complex [*trans*-Fe(H₂O)(CO)(depe)₂]²⁺ (**9**), which were structurally characterized by single-crystal X-ray diffraction. Coordination of [BF₄][−] in **7**[BF₄] was demonstrated, by variable-temperature ³¹P{¹H} NMR spectroscopy, to be dynamic. Dissolving **7**[BF₄] in methanol results in nucleophilic substitution at B to yield the new complex [*trans*-FeF(CO)(depe)₂]⁺ (**10**). An attempt to grow crystals of **10**[BF₄] from the reaction mixture resulted in crystals of [H₂(depe)][BF₄], which were structurally characterized by single-crystal X-ray diffraction.

Introduction

In η^2 -H₂ complexes metal–H₂ bonding has both σ and π components. The relative strength and importance of the two bonding interactions has been a topic of considerable discussion in the past, with emphasis being put on the importance of the π component.^{1,2} However, this work³ and the recent work of others⁴ on the synthesis of electron-deficient dicationic dihydrogen complexes, thought to possess little potential for metal–H₂ π -bonding, indicate that the stability of dihydrogen complexes with respect to elimination of H₂ is highly dependent on the strength of the metal–H₂ σ interaction.

One of us previously proposed that for any d⁶ octahedral metal complex with dinitrogen trans to a π acid ligand and having $E^\circ(d^5/d^6)$ greater than or equal to 1 V, the corresponding dihydrogen complex would be thermally unstable with respect to H₂ elimination.² This report deals with the synthesis, characterization, and reactivity of two dicationic dihydrogen complexes of iron: [Fe(H₂)(CO)(dppe)₂]²⁺ and [Fe(H₂)(CO)(depe)₂]²⁺. These complexes, on the basis of ligand additivity principles, are expected to have dinitrogen analogues with E° values much greater than 1 V, and yet these complexes are remarkably stable with respect to elimination of H₂.

A number of dicationic dihydrogen complexes have been reported recently including the highly acidic complexes [Os(H₂)(CO)(dppp)₂]²⁺ and [Fe(H₂)(CNH)(dppe)₂]²⁺.³ [Os(H₂)-

(NH₃)₅]²⁺, although dicationic, is not appreciably acidic compared to most other dicationic dihydrogen complexes.⁶ The comparatively high pK_a of [Os(H₂)(NH₃)₅]²⁺ is relevant to this study as it relates to the favorable formation of the new aqua complexes [Fe(H₂O)(CO)(dppe)₂]²⁺ and [Fe(H₂O)(CO)(depe)₂]²⁺. The strong σ -donor ligands H₂O and NH₃ are highly polarizable and thus stabilize electron-deficient metal centers.

Dicationic dihydrogen complexes tend to be highly acidic and are often susceptible to H₂ ligand substitution reactions. For this reason the counteranions chosen for these dihydrogen complexes are critical since many of these complexes cannot exist in the presence of even very weakly nucleophilic anions such as [BF₄][−] and [OTf][−].

Also relevant to this study was the nature of the ancillary ligand set and the effects of its variation on the stability and reactivity of the complexes. Both of these new dicationic iron dihydrogen complexes have a {(R₂PCH₂CH₂PR₂)₂(CO)} (R = Ph, Et) ancillary ligand set. In terms of electronics dppe (R = Ph) is much less donating than depe (R = Et), where the E_L parameters for these bidentate ligands are 0.72 V (2 × 0.36 V) and 0.58 V (2 × 0.29 V), respectively.⁷ However, depe is much less sterically bulky than dppe, where the cone angles about P for these ligands are approximately 122° (PEt₃) and 136° (PMePh₂), respectively.⁸ The effects of these electronic and steric disparities will be discussed.

Many of the known cationic dihydrogen complexes are highly acidic. The generation of these highly acidic dihydrogen

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Table 1. Crystal Structure Data Acquisition and Solution Details

	9[OTf] ₂ ·H ₂ O	{9[OTf] ₂ }{[(OTf) ₂ Ag] ₂ (μ-depe)}	7[BF ₄]
empirical formula	C ₂₃ H ₅₂ F ₆ FeO ₉ P ₄ S ₂	C ₅₈ H ₁₂₄ Ag ₂ F ₁₈ Fe ₂ O ₂₂ P ₁₀ S ₆	C ₂₁ H ₄₈ B ₂ F ₈ FeOP ₄
fw	830.50	2345.32	669.95
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>Cc</i>	<i>P2(1)/c</i>	<i>P2₁/m</i>
<i>a</i> /Å	21.5801(5)	16.6339(6)	10.270(2)
<i>b</i> /Å	10.3554(2)	14.7060(5)	15.014(3)
<i>c</i> /Å	20.1249(5)	19.0563(6)	39.908(8)
<i>β</i> /deg	118.318(1)	94.328(2)	96.23(3)
<i>V</i> /Å ³	3959.1(2)	4648.2(3)	6117(2)
<i>Z</i>	4	2	8
<i>d</i> _{calc} /(Mg m ⁻³)	1.393	1.676	1.455
<i>μ</i> (Mo Kα)/mm ⁻¹	0.717	1.126	0.766
<i>T</i> /K	200.0(1)	100.0(1)	173.0(1)
R1 ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0566	0.0361	0.0608
wR2 ^a (all data)	0.1682	0.1013	0.1560

$$^a R1 = \sum(F_o - F_c)/\sum(F_o), \quad ^b wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}.$$

complexes by the treatment of some precursor complex with molecular hydrogen therefore has potential application where strong acids are required. The in situ generation of these acids from molecular H₂ has obvious advantages including handling and storage.

Experimental Section

General Procedures. Unless otherwise stated, all manipulations and reactions were carried out under an atmosphere of prepurified argon or nitrogen (both gases were suitable) using standard Schlenk and glovebox techniques. Unless otherwise stated, all solvents were thoroughly dried over the appropriate drying agents and made free of nitrogen and oxygen by distillation under argon. THF, Et₂O, toluene, and hexanes were refluxed over sodium wire with benzophenone indicator. CH₂Cl₂ was refluxed over calcium hydride. ³PrOH, EtOH, and MeOH were refluxed over iodine-activated magnesium turnings. Acetone was refluxed over anhydrous CaSO₄. CD₂Cl₂, acetone-*d*₆, and CDCl₃ were obtained from Cambridge Isotopes Laboratories. These deuterated solvents were degassed by freeze-pump-thaw (three cycles) and dried by storing over molecular sieves (3A, beads, 8–12 mesh, Aldrich Chemical Co.).

¹H, ³¹P, and ¹⁹F NMR spectra were acquired on a Varian Gemini 300 MHz spectrometer operating at 300 MHz for ¹H, 121 MHz for ³¹P, and 282 MHz for ¹⁹F. ²H NMR spectra were acquired on a Varian Unity 400 MHz instrument operating at 61 MHz for ²H. These instruments were used to acquire spectra in deuterated and nondeuterated solvents. For the acquisition of ¹H NMR spectra of samples in nondeuterated solvents, the following criteria were essential: deactivation of deuterium locking (set IN = N on Gemini instruments), minimization of pulse width (set PW = 0.3 on Gemini instruments), minimization of gain (set GAIN = 0 on Gemini instruments). For good-quality spectra a double-precision Fourier transform (set MATH = D on Gemini instruments) and high sample concentration were desirable. The acquisition of ³¹P and ¹⁹F NMR spectra for samples in nondeuterated solvents required only the deactivation of deuterium locking. ¹H NMR spectra were indirectly referenced to TMS via solvent peaks. ³¹P and ¹⁹F NMR spectra were referenced to external 85% H₃PO₄ and external CFCl₃, respectively. *T*₁ measurements were made using the inversion recovery method.

Infrared spectra were acquired on a Nicolet Magna-IR spectrometer 550 or a Perkin-Elmer Paragon 500 FT-IR spectrometer.

Single-crystal X-ray diffraction data were collected using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A combination of 1° φ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.⁹ The structures were solved and refined using the SHELXTL/PC V5.1 package.¹⁰

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Table 2. Selected Bond Lengths

	bond length/Å		
	9[OTf] ₂ ·H ₂ O	{9[OTf] ₂ }{[(OTf) ₂ Ag] ₂ (μ-depe)}	7[BF ₄]
Fe(1)–P(1)	2.291(2)	2.2940(9)	2.285(3)
Fe(1)–P(2)	2.285(2)	2.2917(9)	2.299(3)
Fe(1)–P(3)	2.303(2)	2.2770(9)	2.287(3)
Fe(1)–P(4)	2.301(2)	2.2730(9)	2.302(3)
Fe(1)–C(1)	1.719(7)	1.722(4)	1.71(1)
Fe(1)–O(2)	2.051(5)	2.037(2)	
Fe(1)–F(4)			2.081(6)

Table 3. Selected Bond Angles^a

	angle/deg		
	9[OTf] ₂ ·H ₂ O	{9[OTf] ₂ }{[(OTf) ₂ Ag] ₂ (μ-depe)}	7[BF ₄]
C(1)–Fe(1)–O(2)	178.3(2)	177.8(1)	175.8(4)
C(1)–Fe(1)–P(2)	88.8(2)	89.4(1)	93.1(4)
O(2)–Fe(1)–P(2)	90.3(2)	90.38(7)	90.8(2)
C(1)–Fe(1)–P(1)	89.0(2)	90.9(1)	88.2(4)
O(2)–Fe(1)–P(1)	89.5(1)	86.94(7)	90.5(2)
P(2)–Fe(1)–P(1)	86.30(6)	86.02(3)	83.8(1)
C(1)–Fe(1)–P(4)	90.2(2)	89.9(1)	87.7(3)
O(2)–Fe(1)–P(4)	90.7(1)	90.36(7)	88.5(2)
P(2)–Fe(1)–P(4)	178.65(7)	179.00(4)	178.4(1)
P(1)–Fe(1)–P(4)	94.57(7)	94.70(3)	97.6(1)
C(1)–Fe(1)–P(3)	91.4(2)	91.2(1)	93.8(4)
O(2)–Fe(1)–P(3)	90.2(2)	90.99(7)	87.7(2)
P(2)–Fe(1)–P(3)	94.23(7)	94.02(3)	94.0(1)
P(1)–Fe(1)–P(3)	179.39(7)	177.93(4)	177.1(1)
P(4)–Fe(1)–P(3)	84.90(6)	85.29(3)	84.6(1)

^a For 7[BF₄], substitute F(4) for O(2).

Refinement was by full-matrix least-squares on *F*² using all data (negative intensities included). Hydrogen atoms were included in calculated positions, except for the hydride atoms, which were refined with isotropic thermal parameters. Structure solution and refinement details are listed in Table 1. Selected bond lengths are given in Table 2, and selected bond angles are listed in Table 3. The bond lengths and angles listed for [Fe(BF₄)(CO)(depe)₂][BF₄] are for one of four similar formula units.

The following compounds were prepared by literature methods: FeHCl(dppe)₂,¹¹ FeHCl(depe)₂,¹² [FeCl(CO)(depe)₂]Cl,¹³ AgBF₄, AgOTf, AgSbF₆, HBF₄·Et₂O, HOTf, and DOTf were obtained from Aldrich Chemical Co. The silver salts were heated at 100 °C under

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reduced pressure for several hours before use. dppe was obtained from Digital Specialty Chemicals. depe was obtained from Strem. N₂ gas (grade 4.8), Ar gas (grade 5.0), CO gas (C.P. grade) and H₂ gas (grade 4.0) were obtained from BOC Gases, Canada. D₂ gas (C.P. grade) was obtained from Matheson Gas Products, Canada.

Preparation of [FeCl(CO)(depe)₂]Cl. This compound was prepared by the literature method of Bellerby, Mays, and Sears.¹³ No NMR spectroscopic data have been published for this compound, so it is presented here. ¹H NMR (CDCl₃): δ 2.40 (m, 4H, backbone CH₂): 2.15 (m, 8H, ethyl CH₂), 2.01 (m, 8H, ethyl CH₂), 1.82 (m, 4H, backbone CH₂), 1.33 (m, 12H, CH₃), 1.27 (m, 12H, CH₃). ³¹P{¹H} NMR (CDCl₃): δ 66.7 (s). IR (CH₂Cl₂, cm⁻¹): 1932 (CO).

Preparation of [FeH(CO)(depe)₂][BF₄] (1[BF₄]). This method is similar to that reported by Bancroft for the preparation of [FeH(CO)(depe)₂][BPh₄].¹⁴ A mixture of acetone (20 mL), FeHCl(depe)₂ (1.273 g, 2.521 mmol), and NaBF₄ (0.920 g, 8.38 mmol) was stirred for 12 h under 1 atm of CO. The solvent was removed under vacuum, and the residue was extracted with CH₂Cl₂ (20 mL). The solids were filtered off, washed with CH₂Cl₂ (2 × 1.5 mL), and discarded. The combined filtrate and washings were reduced in volume under reduced pressure to 5 mL, and Et₂O (25 mL) was slowly added with stirring to precipitate the yellow product. The product was collected by filtration, washed with Et₂O (3 × 3 mL), and dried under vacuum. Yield: 63%. ¹H NMR (CDCl₃): δ 2.01 (m, 8H, ethyl CH₂), 1.84 (m, 4H, backbone CH₂), 1.78 (m, 8H, ethyl CH₂), 1.46 (m, 4H, backbone CH₂), 1.23 (m, 12H, CH₃), 1.10 (m, 12H, CH₃), -10.99 (qi, ²J(HP) = 47 Hz, 1H, FeH). ³¹P{¹H} NMR (CDCl₃): δ 86.1 (s). IR (Nujol, cm⁻¹): 1918 (CO).

Preparation of [FeH(CO)(depe)₂][OTf] (1[OTf]). The procedure for the preparation of [FeH(CO)(depe)₂][BF₄] was followed, substituting NaOTf (1.435 g, 8.34 mmol) for NaBF₄. Quantities of other reagents used: acetone (20 mL), FeHCl(depe)₂ (1.552 g, 2.825 mmol). Yield: 64%. ¹H NMR (CDCl₃): δ: 2.01 (m, 8H, ethyl CH₂), 1.84 (m, 4H, backbone CH₂), 1.78 (m, 8H, ethyl CH₂), 1.46 (m, 4H, backbone CH₂), 1.23 (m, 12H, CH₃), 1.10 (m, 12H, CH₃), -10.99 (qi, ²J(HP) = 47 Hz, 1H, FeH). ³¹P{¹H} NMR (CDCl₃): δ 86.1 (s). IR (Nujol, cm⁻¹): 1918 (CO).

Preparation of [FeH(CO)(dppe)₂][OTf] (2[OTf]). The procedure outlined for the preparation of [FeH(CO)(depe)₂][BF₄] was followed, substituting NaOTf (1.435 g, 8.34 mmol) for NaBF₄ and FeHCl(dppe)₂ (1.055 g, 1.130 mmol) for FeHCl(depe)₂. Quantities of other reagents used: acetone (20 mL). The product was purified by reprecipitation by slow addition of Et₂O to a CH₂Cl₂ solution of the salt. Yield 70%. ¹H NMR (CDCl₃): δ 7.41–7.06 (m, 40H, phenyl H), 2.41 (m, 4H, backbone CH₂), 2.16 (m, 4H, backbone CH₂), -7.74 (qi, ²J(HP) = 47.1 Hz, 1H, FeH). ³¹P{¹H} NMR (CDCl₃): δ 84.8 (s). IR (Nujol, cm⁻¹): 1947 (CO).

Observation of [Fe(H₂)(CO)(dppe)₂][OTf]₂ (3[OTf]₂). HOTf (0.045 g, 0.30 mmol) was added to a solution of [FeH(CO)(dppe)₂][OTf] (0.030 g, 0.029 mmol) in CD₂Cl₂ (0.65 mL) or CDCl₃ (0.65 mL). Some gas evolution was observed. Isolation of the product was not attempted. ¹H NMR (CDCl₃): δ 7.56, 7.40, 7.26, 6.62 (multiplets, 40H, phenyl H), 2.99 (m, 4H, CH₂), 2.58 (m, 4H, CH₂), -6.67 (br s, 2H, FeH). ¹H NMR (CD₂Cl₂): δ -6.8 (br s, 2H, FeH). T₁ data (300 MHz): 0.013 s at 273 K, 0.011 s at 248 K, 0.011 s at 223 K, 0.023 s at 198 K. η²-H₂ T₁(min) = 0.011 ± 0.001 s (235 K, 300 MHz, CD₂Cl₂). T₁(min) was found by fitting observed data to a general equation.¹⁵ ³¹P{¹H} NMR (CD₂Cl₂): δ 67.4 (s). ³¹P{¹H} NMR (CDCl₃): δ 68.1 (s). IR (CH₂Cl₂, cm⁻¹): 2006 (CO).

Testing the Stability of [Fe(H₂)(CO)(dppe)₂][OTf]₂. A solution of [Fe(H₂)(CO)(dppe)₂][OTf]₂ (prepared as previously outlined) was exposed to partial vacuum for a period of 2 h. The solvent had evaporated off within 15 min, and the excess HOTf had evaporated off within the first hour. The orange solid residue remaining was dissolved in CH₂Cl₂ and examined by ¹H and ³¹P{¹H} NMR spectroscopy. The ¹H NMR spectrum exhibited no η²-H₂ resonance; however, an intense upfield resonance was observed for [FeH(CO)(dppe)₂]⁺. The

³¹P{¹H} NMR spectrum exhibited a major resonance for [FeH(CO)(dppe)₂]⁺ and much less intense resonances for [Fe(H₂O)(CO)(dppe)₂]²⁺ and [Fe(OTf)(CO)(dppe)₂]⁺ (approximately 5% each).

Observation of [Fe(HD)(CO)(dppe)₂][OTf]₂. A solution of [FeH(CO)(dppe)₂][OTf] (0.032 g, 0.031 mmol) in CD₂Cl₂ (0.65 mL) was treated with DOTf (0.056 g, 0.37 mmol). Some gas evolution was observed. Isolation of the product was not attempted. ¹H NMR (CD₂Cl₂): δ -6.82 (t of qi, ¹J(HD) = 33.11 ± 0.05 Hz, ²J(HP) = 3.3 Hz, 1H, FeH). ³¹P{¹H} NMR (CD₂Cl₂): δ 67.4 (s).

Reaction of [Fe(H₂)(CO)(dppe)₂][OTf]₂ with D₂. HOTf (0.042 g, 0.280 mmol) was added to a solution of [FeH(CO)(dppe)₂][OTf] (0.026 g, 0.025 mmol) in CD₂Cl₂ (0.65 mL). The solution was cooled to approximately -130 °C (ethanol cooled to freezing point with liquid N₂), evacuated, and filled with 1 atm of D₂ gas. The tube and contents were shaken on reaching room temperature and immediately before NMR examination. The ²H NMR spectrum exhibited a resonance at 11.33 ppm, which is attributed to DOTf, in addition to the intense CD₂Cl₂ resonance.

Preparation of [Fe(BF₄)(CO)(depe)₂][BF₄] (7[BF₄]). A solution of HBF₄·Et₂O in Et₂O (1.732 g, 85% by mass, 9.09 mmol) was added to a solution of [FeH(CO)(depe)₂][BF₄] (0.410 g, 0.702 mmol) in CH₂Cl₂ (10 mL). The resulting solution was stirred for 3 h, after which time 50 mL of Et₂O was added with stirring to precipitate an orange, pasty solid. The pale yellow liquor was decanted off and discarded. The residue was dissolved in CH₂Cl₂ (5 mL) and carefully layered with Et₂O (20 mL) in a test tube with an inner diameter of 2 cm. Slow diffusion afforded large orange-brown crystals, which were collected by filtration, washed with Et₂O (3 × 1.5 mL), and dried under vacuum. Yield: 64%. ¹H NMR (CDCl₃): δ 2.4–1.9 (m, 24H, CH₂), 1.34 (m, 24H, CH₃). ³¹P{¹H} NMR (CDCl₃): δ 67.8 (qi, ²J(FP) = 5.2 Hz). ³¹P{¹H} NMR (CH₂Cl₂, 293 K): δ 67.7 (qi, ²J(FP) = 5.2 Hz). ³¹P{¹H} NMR (CH₂Cl₂, 223 K): δ 68.3 (d, ²J(FP) = 20.2 Hz). ¹⁹F NMR (CDCl₃): δ -147.6 (br s, 4F, coordinated [BF₄]⁻), -152.3 (br s, 4F, free [BF₄]⁻). IR (Nujol, cm⁻¹): 1944 (CO). IR (CH₂Cl₂, cm⁻¹): 1944.4 (CO). Anal. Calcd for C₂₁H₄₈B₂F₈FeOP₄: C, 37.64; H, 7.24. Found: C, 37.26; H, 7.61.

A crystal of [Fe(BF₄)(CO)(depe)₂][BF₄] was grown by slow vapor diffusion of Et₂O into a CH₂Cl₂ solution of this salt. The crystal was analyzed by single-crystal X-ray diffraction.

Observation of [FeF(CO)(depe)₂][BF₄] (10[BF₄]). [Fe(BF₄)(CO)(depe)₂][BF₄] (0.015 g, 0.022 mmol) was dissolved in CD₃OD (0.65 mL) and analyzed by ¹H and ³¹P{¹H} NMR spectroscopy. Attempts to isolate this salt by precipitation were unsuccessful as the product was always contaminated with [Fe(BF₄)(CO)(depe)₂][BF₄]. Slow diffusion (several weeks) of Et₂O into a MeOH solution of [Fe(BF₄)(CO)(depe)₂][BF₄] resulted in the crystallization of [H₂(depe)₂][BF₄]₂ as evidenced by a single-crystal X-ray diffraction structural determination. ¹H NMR (CD₃OD): δ 2.4–1.7 (m, 24H, CH₂), 1.31 (m, 12H, CH₃), 1.23 (m, 12H, CH₃). ³¹P{¹H} NMR (CD₃OD): δ 72.8 (d, ²J(FP) = 28.8 Hz). ¹⁹F NMR (CD₃OD): δ -152.7 (s, 4F, free [BF₄]⁻), -156.2 (s, 1F, FeF).

Observation of [Fe(H₂)(CO)(depe)₂][SbF₆]₂ (6[SbF₆]₂). CD₂Cl₂ (0.65 mL) was distilled under partial static vacuum into an NMR tube containing a mixture of [FeCl(CO)(depe)₂]Cl (0.021 g, 0.037 mmol) and AgSbF₆ (0.032 g, 0.093 mmol). The tube was filled with 1 atm of H₂, and the contents were vigorously shaken several times over 1 h. No attempt was made to isolate the product. ¹H NMR (CD₂Cl₂): δ 1.8–2.5 (m, 24H, CH₂), 1.26 (m, 24H, CH₃), -9.82 (br s, 2H, FeH). T₁ data (300 MHz): 0.014 s at 260 K, 0.012 s at 248 K, 0.010 s at 236 K, 0.011 s at 229 K. η²-H₂ T₁(min) = 0.010 ± 0.001 s (225 K, 300 MHz, CD₂Cl₂). T₁(min) was found by fitting observed data to a general equation.¹⁵ ³¹P{¹H} NMR (CD₂Cl₂): δ 69.5 (s). IR (CH₂Cl₂, cm⁻¹): 1996 (CO).

Preparation of [Fe(OTf)(CO)(depe)₂][OTf] (8[OTf]). [FeH(CO)(depe)₂][OTf] (0.895 g, 1.38 mmol) was dissolved in 2 mL of CH₂Cl₂, and HOTf (0.425 g, 2.83 mmol) was slowly added with stirring. Addition of the acid resulted in vigorous gas evolution and darkening of the solution (turned from yellow to intense orange). This solution was stirred for 16 h to ensure complete reaction, and then it was filtered through Celite. Et₂O (15 mL) was slowly added to the filtrate with stirring and the yellow product eventually oiled out. This mixture was

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stirred for another 12 h, during which time the oil had changed to a yellow powder. The solid was collected by filtration, washed with 5 × 3 mL of Et₂O, and dried under vacuum. To ensure that the product was free of water and HOTf, it was recrystallized by vapor diffusion of Et₂O into an EtOH solution of the salt, and the crystals obtained were heated for 2 days at 100 °C while being exposed to vacuum. Yield: 93%. ¹H NMR (CDCl₃): δ 2.29 (m, 8H, CH₂), 2.13 (m, 8H, CH₂), 2.02 (m, 8H, CH₂), 1.31 (m, 24H, CH₃). ³¹P{¹H} NMR (CDCl₃): δ 65.0 (s). ¹⁹F{¹H} NMR (CDCl₃): δ -77.7 (s, 3F, coordinated [OTf]⁻), -78.4 (s, 3F, free [OTf]⁻). IR (Nujol, cm⁻¹): 1949, 1940 (CO). IR (CH₂Cl₂, cm⁻¹): 1943 (CO). Anal. Calcd for C₂₃H₄₈F₆FeO₇P₄S₂: C, 34.77; H, 6.10. Found: C, 34.61; H, 6.21.

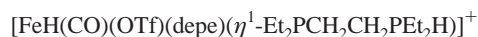
Repeated attempts to grow crystals of [Fe(OTf)(CO)(depe)₂][OTf] for X-ray structural determination were unsuccessful.

Observation of [Fe(H₂O)(CO)(depe)₂][OTf]₂ (9[OTf]₂). [Fe(OTf)(CO)(depe)₂][OTf] (0.015 g, 0.019 mmol) was dissolved in acetone-*d*₆ (0.65 mL), and distilled, degassed H₂O (0.117 g, 6.49 mmol) was added to the resulting solution. ¹H NMR (acetone-*d*₆): δ 4.58 (br s, 2H, H₂O), 2.46–2.24 (m, 24H, CH₂), 1.41 (m, 24H, CH₃). ³¹P{¹H} NMR (acetone-*d*₆): δ 67.8 (s). ³¹P{¹H} NMR (CDCl₃): δ 66.5 (s). ¹⁹F{¹H} NMR (CDCl₃): δ -78.6 (s).

Crystals of 9[OTf]₂ could not be grown from the reaction mixtures. However, a crystal of [Fe(H₂O)(CO)(depe)₂][OTf]₂·H₂O was grown by slow vapor diffusion of Et₂O into an EtOH (apparently wet) solution of [Fe(OTf)(CO)(depe)₂][OTf]. The crystal was analyzed by single-crystal X-ray diffraction.

Observation of {[Fe(H₂O)(CO)(depe)₂][OTf]₂}{(OTf)₂Ag₂(μ-depe)}. A mixture of CH₂Cl₂ (10 mL), AgOTf (0.465 g, 1.46 mmol), and [FeCl(CO)(depe)₂]Cl (0.224 g, 0.395 mmol) was stirred for 12 h, after which time the excess AgOTf and precipitated AgCl were removed by filtration. The yellow filtrate was concentrated under reduced pressure to 5 mL, and Et₂O (25 mL) was added to precipitate the yellow product. The product was collected by filtration, washed with Et₂O (3 × 3 mL), and dried under vacuum. The isolated product was expected to be [Fe(OTf)(CO)(depe)₂][OTf], and its CDCl₃ solution ³¹P{¹H} NMR spectrum exhibited only a resonance at 65.0 ppm. However, a single crystal of {[Fe(H₂O)(CO)(depe)₂][OTf]₂}{(OTf)₂Ag₂(μ-depe)} was obtained by diffusion of Et₂O into a CH₂Cl₂ solution of the product isolated from this reaction. The crystal was analyzed by X-ray diffraction.

Reaction of [Fe(H₂O)(CO)(depe)₂][SbF₆]₂ with D₂. A CD₂Cl₂ solution of [Fe(H₂O)(CO)(depe)₂][SbF₆]₂ was prepared as described above except that 1 equiv of NaOTf was added to facilitate H⁺/D⁺ exchange. The mixture was cooled to approximately -130 °C (ethanol cooled to freezing with liquid N₂), evacuated, and filled with 1 atm of D₂ gas. The tube was shaken prior to NMR spectroscopic examination. ¹J(HD) for [Fe(HD)(CO)(depe)₂][SbF₆]₂ was estimated from the ¹H NMR spectrum to be 33 ± 1 Hz. [*trans*-FeD(CO)(depe)₂]⁺ was observed by ³¹P{¹H} NMR spectroscopy as a triplet at 86.0 ppm with a ²J(DP) of 9.8 Hz, in addition to [FeH(CO)(depe)₂]⁺ (85.9 ppm) and [Fe(η²-L)(CO)(depe)₂]²⁺ (L = H₂, HD, D₂; broad resonance at 69.5 ppm). A multiplet pattern was observed at -10.46 ppm in the ¹H NMR spectrum. This pattern appeared to be a doublet of doublet of doublets with approximate ²J(HP) values of 33, 26, and 20 Hz. The splittings may all be assumed to be ³¹P couplings since no other hydride resonance was observed for this complex. This complex is believed to be



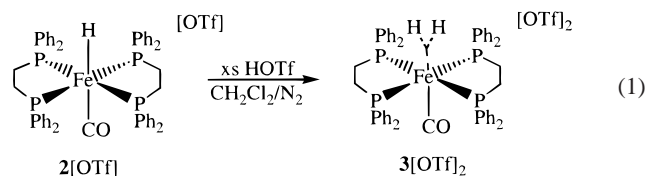
Results and Discussion

Synthesis of the Monohydride Complexes. [FeH(CO)(depe)₂][BF₄] (**1**[BF₄]), [FeH(CO)(depe)₂][OTf] (**1**[OTf]), and [FeH(CO)(dppe)₂][OTf] (**2**[OTf]) were prepared in yields of 63%, 64%, and 70%, respectively, by exposing acetone solutions of the corresponding FeHCl(pp)₂ (pp = bidentate diphosphine ligand) complexes to CO in the presence of NaBF₄ or NaOTf. Caution must be exercised when FeHCl(depe)₂ is prepared for use in the preparation of salts of **1** since any unreacted FeCl₂(depe)₂ will react with CO to produce salts of [FeCl(CO)-

(depe)₂]⁺. **2**[OTf] may also be contaminated if the FeHCl(dppe)₂ used in its preparation is contaminated with paramagnetic FeCl₂(dppe), which reacts with CO to produce diamagnetic isomers of FeCl₂(CO)₂(dppe).¹⁶ The cations **1** and **2** were each assigned a trans configuration on the basis of the upfield quintet in their ¹H NMR spectra and singlet in their ³¹P{¹H} NMR spectra. These yellow salts are air-stable in the solid state and when dissolved in acetone, CH₂Cl₂, and CHCl₃.

Observation of [Fe(H₂O)(CO)(dppe)₂][OTf]₂. The synthesis of dihydrogen complexes is usually achieved via two general routes: coordination of H₂ or protonation of a classical hydride ligand. In the case of [Fe(H₂O)(CO)(dppe)₂]²⁺ only the second of these two routes was employed since a suitable precursor for the H₂-coordination method, such as [FeX(CO)(dppe)₂]⁺ (X = halide), was unavailable. [FeCl(CO)(dppe)₂][FeCl₄] has been reported in the literature.¹⁷ However, due to the poor yields cited and paramagnetic nature of the anion, the generation of [Fe(H₂O)(CO)(dppe)₂]²⁺ using this precursor was not attempted.

The complete protonation of **2** (eq 1) required at least 10 equiv of HOTf to generate the new dihydrogen complex [*trans*-Fe(H₂O)(CO)(dppe)₂]²⁺ (**3**). The aqueous pK_a of HOTf has been



estimated⁵ at approximately -5, indicating a pK_a of less than -5 for **3**. The related and very acidic complex [*trans*-Os(H₂O)(CO)(dppp)₂]²⁺ has been reported to have an estimated pK_a of -6.⁵

The ³¹P{¹H} NMR spectrum for a yellow-orange CH₂Cl₂ solution of **3**[OTf]₂ consists of a singlet at 67.4 ppm, indicating a trans configuration about iron in **3**. Preparations of **3** must be done in the absence of nucleophiles and bases including H₂O.

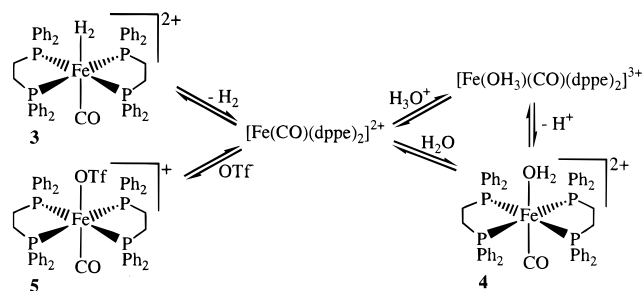
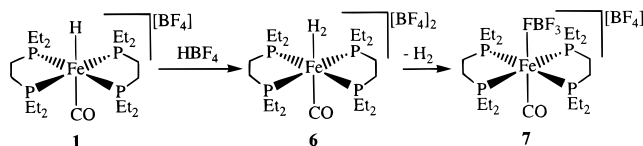
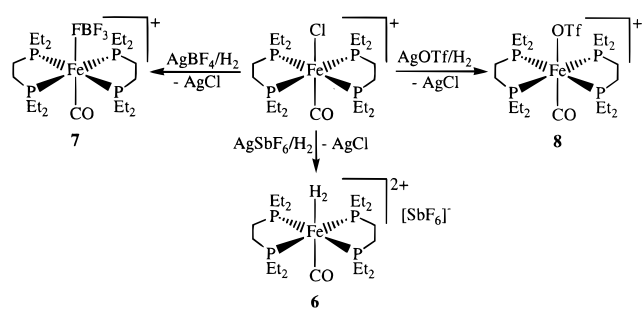
For the preparation of **3**[OTf]₂ the reaction conditions are extremely acidic and result in the gradual decomposition of the complex as evidenced by the appearance of a ³¹P{¹H} NMR resonance at 10.9 ppm, which is attributed to protonated dppe. Two additional species have been observed as singlets at 60.6 and 59.7 ppm in ³¹P{¹H} NMR spectra for preparations of **3**[OTf]₂ in CH₂Cl₂. These complexes could not be isolated but have been identified as [*trans*-Fe(H₂O)(CO)(dppe)₂]²⁺ (**4**) and [*trans*-Fe(OTf)(CO)(dppe)₂]⁺ (**5**), respectively, on the basis of the observation that the addition of H₂O to these reaction mixtures results in, among other things, a reduction of the intensity of the signal at 59.7 ppm, while the signal at 60.6 ppm increases in intensity. The replacement of H₂ in **3** by H₂O is consistent with the findings of Kubas, where in a related study of tungsten complexes W(CO)₃(PR₃)₂ (R = alkyl), H₂O was found to displace H₂ at room temperature.¹⁸ A ¹H NMR signal for coordinated H₂O in **4** could not be assigned definitively, although there were several resonances near 3 ppm which were possible candidates (in [Os(H₂O)(H₂O)(dppe)₂]²⁺ a ¹H NMR resonance for coordinated H₂O appears at 3.2 ppm¹⁹). These

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Scheme 1. Reactions of $[\text{Fe}(\text{H}_2)(\text{CO})(\text{dppe})_2][\text{OTf}]_2$ **Scheme 2.** Displacement of H_2 by $[\text{BF}_4]^-$ in $[\text{Fe}(\text{H}_2)(\text{CO})(\text{depe})_2][\text{BF}_4]$ **Scheme 3.** Reactions of $[\text{FeCl}(\text{CO})(\text{depe})_2]^+$ 

reactions are summarized in Scheme 1 and are assumed, without direct evidence, to proceed via the unobserved intermediate $[\text{Fe}(\text{CO})(\text{dppe})_2]^+$. The pathway to complex **4** involving the unprecedented intermediate complex $[\text{Fe}(\text{OH}_3)(\text{CO})(\text{dppe})_2]^{3+}$ may or may not operate and is suggested as a possibility only due to the fact that the concentration of H_2O in these highly acidic reaction mixtures is expected to be negligible.

Synthesis of $[\text{Fe}(\text{H}_2)(\text{CO})(\text{depe})_2][\text{SbF}_6]_2$ and Related Complexes. Monohydride complex **1** is not a practical precursor for the synthesis of the new dihydrogen complex $[\text{trans-Fe}(\text{H}_2)(\text{CO})(\text{depe})_2]^{2+}$ (**6**) since a sufficiently strong acid with a weakly coordinating conjugate base is not commercially available. This predicament is exemplified by failed attempts to prepare **6** by the protonation of **1** using excess $[\text{HOEt}_2][\text{BF}_4]$ or HOTf . These experiments resulted in the quantitative conversion to $[\text{trans-Fe}(\text{BF}_4)(\text{CO})(\text{depe})_2]^+$ (**7**) or $[\text{trans-Fe}(\text{OTf})(\text{CO})(\text{depe})_2]^+$ (**8**), respectively. **6** has been observed as a low-concentration transient species by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy in the reaction of **1** with $[\text{HOEt}_2][\text{BF}_4]$ (Scheme 2). The generation of **7** via the protonation of **1** required the addition of only 1 equiv of $[\text{Et}_2\text{OH}][\text{BF}_4]$, and on the basis of the vigorous gas evolution in this reaction, complex **6** is likely significantly less acidic than $[\text{HOEt}_2]^+$. **2** is unchanged in the presence of excess $[\text{HOEt}_2][\text{BF}_4]$, which demonstrates that **3** is much more acidic than **6**.

The new dihydrogen complex **6** may be generated by the H_2 -coordination method since $[\text{FeCl}(\text{CO})(\text{depe})_2]\text{Cl}$, a convenient precursor, is easily prepared in high yield by the treatment of $\text{FeCl}_2(\text{depe})_2$ with CO in methanol.¹³ This precursor, when treated with AgSbF_6 under 1 atm of H_2 in CD_2Cl_2 , affords yellow-orange solutions of $[\text{6}][\text{SbF}_6]_2$. As in the preparation of $[\text{3}][\text{OTf}]_2$, the preparation of $[\text{6}][\text{SbF}_6]_2$ must be done in the absence

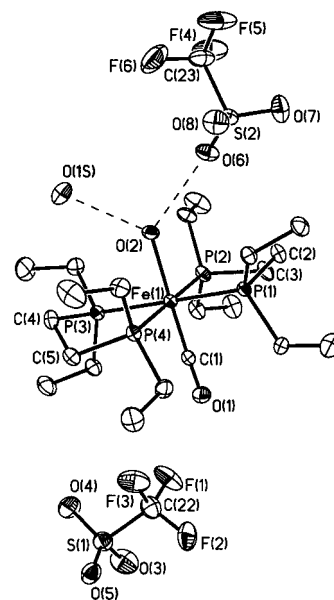


Figure 1. Structure of $[\text{Fe}(\text{OH}_2)(\text{CO})(\text{depe})_2][\text{OTf}]_2 \cdot \text{H}_2\text{O}$. Carbon atom labels and hydrogen atoms have been omitted for clarity.

of nucleophiles and bases. No reaction was observed when $\text{Na}[\text{B}(\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2)_4]$ was used instead of AgSbF_6 . The use of AgBF_4 and AgOTf salts instead of AgSbF_6 resulted in the generation (Scheme 3) of **7** and **8**, respectively, which again demonstrates the necessity to minimize the donor properties of the anions. Complexes **6**, **7**, and **8** are trans according to their singlet $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. **7** and **8** generated from $[\text{FeCl}(\text{CO})(\text{depe})_2]\text{Cl}$ are contaminated with the corresponding CH_2Cl_2 -soluble silver salts, which makes the halide abstraction method undesirable and unsuitable for the preparation of pure $[\text{7}][\text{BF}_4]$ - and $[\text{8}][\text{OTf}]$. All future references to $[\text{7}][\text{BF}_4]$ and $[\text{8}][\text{OTf}]$, unless otherwise stated, will be to those prepared via the protonation of $[\text{Fe}(\text{H}(\text{CO})(\text{depe})_2)]^+$.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra for CH_2Cl_2 solutions of $[\text{7}][\text{BF}_4]$ and $[\text{8}][\text{OTf}]$ often reveal the presence of an impurity in the form of a singlet at 66.4 ppm (CH_2Cl_2) or 66.5 ppm (CHCl_3). This impurity has been identified as $[\text{trans-Fe}(\text{H}_2\text{O})(\text{CO})(\text{depe})_2]^{2+}$ (**9**) on the basis of the fact that the addition of a large excess of water to solutions of $[\text{8}][\text{OTf}]$ results in the quantitative conversion of **8** to the impurity.

Attempts to grow crystals of $[\text{8}][\text{OTf}]$ have afforded only crystals of $[\text{9}][\text{OTf}]_2 \cdot \text{H}_2\text{O}$ (Figure 1). This is peculiar given that the solutions from which the crystals were grown were prepared using dry solvents and appeared to be free of $[\text{9}][\text{OTf}]_2$ according to $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. These observations indicate that $[\text{9}][\text{OTf}]_2$ is much less soluble than $[\text{8}][\text{OTf}]$ in the recrystallization solvents used (EtOH, acetone, and CH_2Cl_2). Complex **9** is octahedral, with CO trans to H_2O . The observed Fe–P bond lengths are between 2.28 and 2.30 Å, which is typical for octahedral bis(depe) complexes of iron.^{20–23} According to a 1989 review of the Cambridge Crystallographic Database (to which all subsequent bond length comparisons will be made, unless otherwise stated), the observed Fe–CO bond length of 1.719(7) Å and Fe–OH₂ bond length of 2.051(5) Å are both

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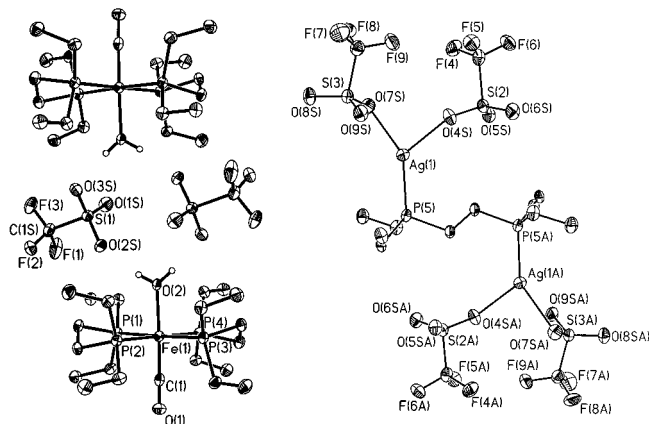


Figure 2. (a, left) Structure of the $\{[\text{Fe}(\text{H}_2\text{O})(\text{CO})(\text{depe})_2][\text{OTf}]\}^{2+}$ cation (depe hydrogen atoms and carbon atom labels have been omitted for clarity). (b, right) Structure of the $\{[\text{Ag}(\text{OTf})_2]_2(\mu\text{-depe})\}^{2-}$ anion.

typical.²⁴ The carbonyl C–O bond length is also typical at 1.165(9) Å. There is a hydrogen-bonding interaction between the protons of the aqua ligand and a counterion. The hydrogen atoms of the water ligand were not located or refined. The shortest observed FeO \cdots OSO₂CF₃ distance is 2.721(7) Å. There is also 1 equiv of noncoordinated water, O(1S), in the lattice which may be hydrogen-bonded to the aqua ligand and/or a triflate counterion.

As mentioned earlier, salts of **7** and **8** prepared using AgBF₄ and AgOTf, respectively, are contaminated with the CH₂Cl₂-soluble silver reagents. This became apparent when a crystal was grown from the product obtained by the reaction of [FeCl(CO)(depe)₂]Cl with AgOTf. The cation of this salt was found to be an unusual hydrogen-bonded dimer of two $[\text{trans}\text{-Fe}(\text{H}_2\text{O})(\text{CO})(\text{depe})_2][\text{OTf}]^+$ ($9[\text{OTf}]^+$) units (Figure 2a), while the anion is $\{[\text{Ag}(\text{OTf})_2]_2(\mu\text{-depe})\}^{2-}$ (Figure 2b). All of the bond lengths for the cation, except for the Fe–P bonds, are equal within experimental error to the corresponding bond lengths previously stated for $9[\text{OTf}]_2\cdot\text{H}_2\text{O}$. The hydrogen atoms of the aqua ligand were located roughly in the O(2S)–O(2)–O(3SA) plane and then refined isotropically. The aqua O–H bond lengths are 0.81(3) and 0.82(3) Å, while the OH \cdots OS hydrogen-bond distances are 1.90(3) and 1.87(3) Å. The CH₂Cl₂ solution of the isolated amorphous product exhibited a ³¹P{¹H} NMR spectrum identical to that of **8**[OTf] isolated from the reaction of HOTf and **1**[OTf]. Thus, the product isolated from the reaction of [FeCl(CO)(depe)₂]Cl and AgOTf, may be **8**[OTf] contaminated with AgOTf or it may be $8_2\{[(\text{OTf})_2\text{Ag}]_2(\mu\text{-depe})\}$. No ³¹P{¹H} resonance was observed for the anion, but this could be attributed to labile Ag–P bonds. The use of an excess of the silver salt reagent is necessary since water impurities in this reagent may be only partially removed by heating under vacuum.

Interpretation of ¹J(HD) of the HD Ligands and T₁(min) of the H₂ Ligands. The generation of $[\text{Fe}(\text{HD})(\text{CO})(\text{dppe})_2]^{2+}$ (**3-d**) was effected by the substitution of DOTf for HOTf in the procedure for the preparation of **3**[OTf]₂. $[\text{Fe}(\text{HD})(\text{CO})(\text{depe})_2]^{2+}$ (**6-d**) was not prepared directly but was generated in situ by the treatment of **6**[SbF₆]₂ with D₂ gas. A linear correlation between $d(\text{HH})$ for an $\eta^2\text{-H}_2$ complex and ¹J(HD) for the corresponding HD isotopomer allows one to calculate $d(\text{HH})$ from ¹J(HD). The observed ¹J(HD) values for **3-d** and **6-d** are 33.11 ± 0.05 and 33 ± 1 Hz, respectively, both of which

correspond to $d(\text{HH})$ values of 0.87 Å. A rather peculiar and consistent observation is that, in general, ¹J(HD) is between 32 and 34 Hz for complexes with HD trans to CO, regardless of the other ligands involved.^{25,26a} It appears that the magnetic and structural features of a dihydrogen ligand which is trans to CO are insensitive to changes in the remaining ligands. This is consistent with the fact that the observed $T_1(\text{min})$ values for complexes **3** and **6** are 0.011 ± 0.001 s (235 K, 300 MHz, CD₂Cl₂) and 0.010 ± 0.001 s (225 K, 300 MHz, CD₂Cl₂), which are equal within experimental error. Similarly in the related complexes $[\text{trans}\text{-Mn}(\text{H}_2)(\text{CO})\text{L}_2][\text{BAR}^f_4]$, L = dppe, depe, the H–H distances are equal within experimental error.²⁶

The fact that changes in the P₄ ligand set confer changes in the electronic properties of the metal is apparent by the differences in the pK_a and IR $\nu(\text{CO})$ values for complexes **3** and **6**. On the basis of reaction conditions necessary for the generation of complexes **3** and **6**, it appears that **3** (dppe complex) is more acidic than **6** (depe complex). This is as would be expected given that depe is more basic than dppe. The observed IR $\nu(\text{CO})$ values (CH₂Cl₂) for complexes **3** and **6** are 2006 and 1996 cm⁻¹, respectively, which indicates greater π -back-bonding in **6** than in **3**.

For fast rotation of H₂ (relative to the spectrometer frequency), the observed $T_1(\text{min})$ values correspond to $d(\text{HH})$ values of 0.84 and 0.83 Å for complexes **3** and **6**, respectively; for restricted motions these distances become 1.06 and 1.04 Å. The reasonable agreement between $d(\text{HH})$ from ¹J(HD) and $T_1(\text{min})$ for fast-spinning H₂ ligands is evidence that in these complexes the H₂ ligands have a high rotational frequency relative to the spectrometer frequency. Furthermore, the fast spinning of H₂ in **3** and **6** is additional evidence of the poor π -base character of the $[\text{Fe}(\text{CO})(\text{pp})_2]^{2+}$ moieties.

Importance of Metal–H₂ σ -Bonding for Stability of $\eta^2\text{-H}_2$ Complexes. The relative importance of the metal–H₂ σ and π bonds, in terms of the stability of $\eta^2\text{-H}_2$ complexes with respect to the elimination of H₂, is not well understood. The synthesis of **3**, **6**, and other electron-deficient dihydrogen complexes has shed light on the matter. $[\text{Fe}(\text{CO})(\text{pp})_2]^{2+}$ moieties are poor π -bases, and as such, Fe–H₂ bonding in the corresponding H₂ complexes is primarily σ in character. In the series of isoelectronic complexes $[\text{trans}\text{-M}(\text{H}_2)(\text{CO})(\text{dppe})_2]^{n+}$ (M = Mo,^{27,28} $n = 0$; M = Mn,²⁶ $n = 1$; M = Fe, $n = 2$, this work) only the iron complex (**3**) is stable with respect to H₂ loss under dinitrogen or argon atmospheres.³ In fact **3** eliminates H₂ only very slowly under vacuum, which may simply be a consequence of the displacement of H₂ by the counterion. It is possible that the small degree of metal-to-H₂ π -back-bonding in $[\text{Fe}(\text{H}_2)(\text{CO})(\text{dppe})_2]^{2+}$ is accompanied by a very strong three-center, two-electron metal–H₂ σ -bond, the net result of which is surprising thermal stability. These findings are consistent with previous findings where cationic complexes $[\text{Re}(\text{CO})_3(\text{PR}_3)_2]^+$ were at least as effective at binding H₂ as the isoelectronic neutral complexes $\text{W}(\text{CO})_3(\text{PR}_3)_2$ (R = Cy, ⁱPr).²⁹

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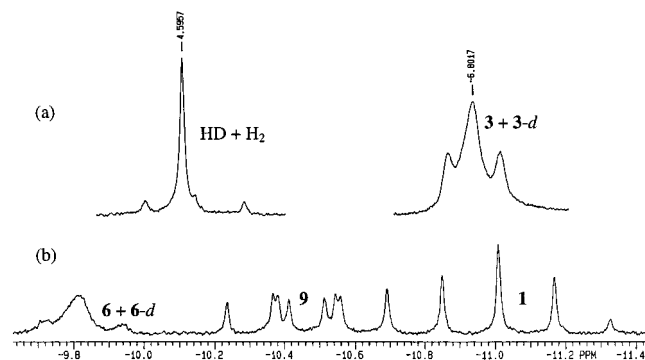
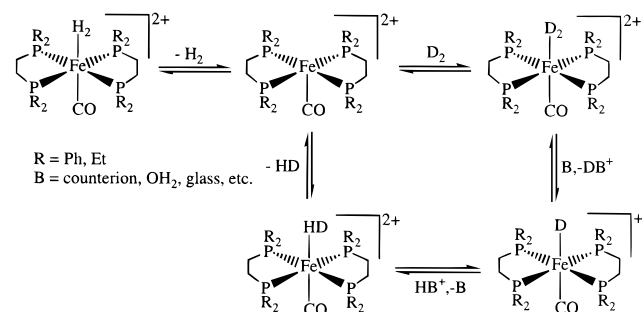


Figure 3. Selected regions of ^1H NMR spectra for the reactions of D_2 with (a) $[\text{Fe}(\text{H}_2)(\text{CO})(\text{dppe})_2]^{2+}$ and (b) $[\text{Fe}(\text{H}_2)(\text{CO})(\text{depe})_2]^{2+}$.

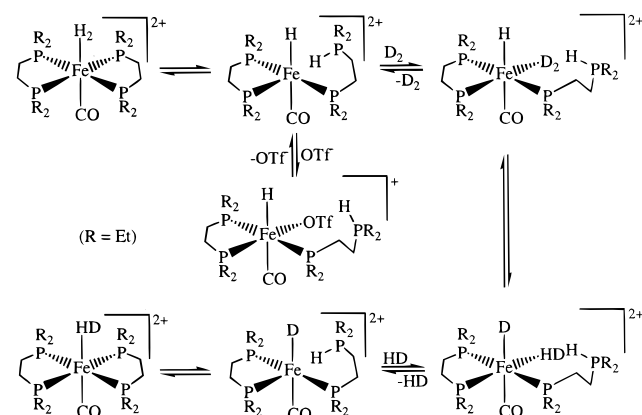
Scheme 4. H_2/D_2 Dissociation Mechanism of H/D Scrambling



H_2/D_2 Exchange and H/D Scrambling. Exposure of CH_2Cl_2 solutions of **3** and **6** to D_2 results in scrambling of H and D. In these experiments the ^1H NMR resonances for the HD complexes have been observed in addition to resonances for free H_2 and HD (Figure 3). In the dppe case ^2H NMR spectroscopy revealed the presence of a substantial amount of DOTf, which is a testament to the low pK_a of complex **3**. Although $3[\text{OTf}]_2$ and $6[\text{SbF}_6]_2$ are thermally stable with respect to H_2 elimination, these experiments demonstrate that H_2 coordination in **3** and **6** may be reversible. One possible mechanism for the observed H/D scrambling is outlined in Scheme 4. This pathway is likely a dissociative one in which the elimination of H_2 yields a low-concentration transient species, possibly stabilized by a C–H bond or solvent Cl, which binds D_2 . The D_2 isotopomers thus produced are, like **3** and **6**, very acidic and may to some extent deuterate anions, glass, etc. The conjugate base deuteride complexes are protonated in the reverse processes to yield HD complexes. Finally, replacement of HD by H_2 or D_2 yields free HD.

A second possible mechanism is illustrated in Scheme 5. In this process the highly acidic H_2 ligand protonates an Fe–P bond and chelate ring-opening results. The resulting 16-electron species (not observed) may be stabilized by some agostic interaction with the newly formed P–H bond or by a C–H bond. The vacant coordination site allows for coordination of D_2 and scrambling of H and D among the classical hydride and dihydrogen ligands. Protonation of the classical deuteride ligand by the dangling protonated phosphine and coordination of the phosphine follow dissociation of HD. Evidence for this mechanism was the appearance of an eight-line multiplet (approximate J values of 33, 26, and 20 Hz) centered at -10.46 ppm in the ^1H NMR spectrum for the reaction of **6** with D_2 , in which NaOTf was added as a proton/deuteron shuttle. This pattern can be assigned to the complex $[\text{FeH}(\text{CO})(\text{OTf})(\eta^2\text{-depe})(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2\text{H})]^+$, which can be accounted for by the

Scheme 5. Intramolecular Proton-Transfer Mechanism of H/D Scrambling



mechanism proposed. A mechanism similar to that in Scheme 5 has been established for H_2 replacement in $[\text{FeH}(\text{H}_2)(\text{dppe})_2]^+$.³⁰

Kinetics versus Thermodynamics in H_2 Coordination. It is clear that the binding of $[\text{BF}_4]^-$ and $[\text{OTf}]^-$ is thermodynamically favored over H_2 in the case of $[\text{Fe}(\text{CO})(\text{depe})_2]^{2+}$. However, the situation with the dppe analogue is more complicated. One would expect, given the greater electron-deficient nature of the dppe moiety, that $[\text{BF}_4]^-$ and $[\text{OTf}]^-$ coordination would be favored over H_2 coordination for **3** as is the case for **6**. However, **3** is reasonably stable in the presence of $[\text{OTf}]^-$, which cannot be said of **6**. The most likely explanation for the persistence of $3[\text{OTf}]_2$ in solution is kinetic, where replacement of H_2 by $[\text{OTf}]^-$ is possible and favorable but rather slow due to the steric bulk of dppe. Exposure of $3[\text{OTf}]_2$ to vacuum for several hours does not result in loss of H_2 . However, heating a toluene solution of $3[\text{OTf}]_2$ with excess HOTf does result in replacement of H_2 by $[\text{OTf}]^-$ as evidenced by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Unlike $[\text{BF}_4]^-$ and $[\text{OTf}]^-$, SbF_6^- exhibits no propensity to displace H_2 in **6**. This is most probably due to electronic effects since SbF_6^- is much less nucleophilic than $[\text{BF}_4]^-$ and $[\text{OTf}]^-$. Sterics are probably not a factor in the coordination of SbF_6^- to the $[\text{Fe}(\text{CO})(\text{depe})_2]^{2+}$ moiety since Sb–F bond distances of 1.8 Å in SbF_6^- would put this ligand far removed from the ethyl substituents of the depe ligands, assuming an Fe–F–Sb angle greater than 160° like that observed for the Fe–F–B angle in **7**.

Solution NMR and X-ray Structure of $[\text{Fe}(\text{BF}_4)(\text{CO})(\text{depe})_2][\text{BF}_4]$. In solution at room temperature the coordinated $[\text{BF}_4]^-$ of $[\text{Fe}(\text{BF}_4)(\text{CO})(\text{depe})_2]^+$ is highly fluxional. Evidence of the nonstatic nature of the $[\text{BF}_4]^-$ coordination is the spectroscopic equivalence of the fluorides for this ligand, which gives rise to a quintet in the room-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** $[\text{BF}_4]$. This contrasts with the spectrum at -50°C , which consists of a doublet with ^{31}P coupling to only the coordinated F of $[\text{BF}_4]^-$ (Figure 4). Related variable-temperature ^{31}P NMR spectra were observed for the complex $\text{cis-W}(\text{CO})_3(\text{NO})(\text{PMe}_3)(\text{PF}_5)$, and an intramolecular anion exchange mechanism was deduced.³¹

Figure 5 depicts the structure of the cation of one of four distinct formula units in the unit cell of **7** $[\text{BF}_4]$. The bonding in the other three cations is similar. A particularly noteworthy

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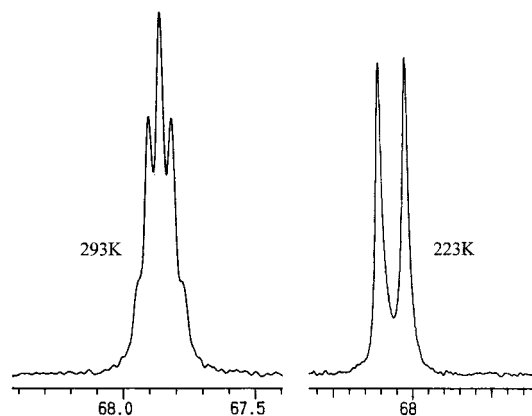
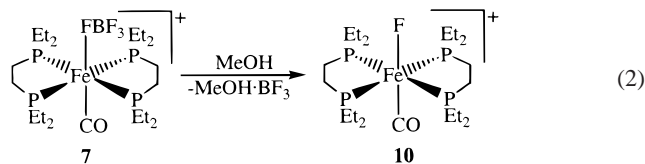


Figure 4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{Fe}(\text{BF}_4)(\text{CO})(\text{depe})_2][\text{BF}_4]$ in CH_2Cl_2 .

structural feature of **7** is the disparity between terminal and bridging B–F distances (Table 4). In **7** the average bridging B–F distance is 1.47 Å, while the average terminal B–F bond length is 1.35 Å. The longer average bridging B–F distance illustrates the pronounced electron-withdrawing effect of the metal on the ligand. The average bridging B–F bond length for **7** is greater than the typical value of 1.37(4) Å, while the average terminal B–F bond length for **7** is comparable to the corresponding typical value of 1.33(6) Å. This complex contains a rare $\text{Fe}^{\text{II}}-(\mu\text{-F})$ bond. The Fe–F distance of 2.081(6) Å is comparable to the ones previously observed.³² The Fe–P bond lengths all lie between 2.28 and 2.32 Å, which is typical for octahedral bis(depe) complexes of iron. The Fe–CO bond lengths range from 1.71 to 1.76 Å (typical). The observed carbonyl C–O bond lengths range from 1.12(1) to 1.18(1) Å, which is not unusual.

Electrophilic Activation of $[\text{BF}_4]^-$ in $[\text{Fe}(\text{BF}_4)(\text{CO})(\text{depe})_2]^+$. The structural distortion of $[\text{BF}_4]^-$ upon coordination to the electron-deficient $[\text{Fe}(\text{CO})(\text{depe})_2]^{2+}$ moiety is consistent with the observed reactivity of **7**. Treatment of **7** with methanol quickly and quantitatively affords a species which has been identified as $[\text{trans-Fe}(\text{CO})(\text{depe})_2]^+$ (**10**) on the basis of its doublet $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. This reaction likely proceeds via an $\text{S}_{\text{N}}2$ mechanism (eq 2). Although there are previous



examples³³ of fluoride abstraction from $[\text{BF}_4]^-$, this is the first reported example in which a tetrafluoroborate complex is an observable and isolable intermediate.

The reaction illustrated in eq 2 above is apparently reversible since the precipitation of **10** $[\text{BF}_4]$ by the addition of Et_2O to a sample of **7** $[\text{BF}_4]$ dissolved in CH_2Cl_2 or MeOH yields a product which is highly contaminated with **7** $[\text{BF}_4]$. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these reaction mixtures exhibit no resonance for **7** $[\text{BF}_4]$. Attempts to grow a single crystal of **10** $[\text{BF}_4]$ were unsuccessful. Over many weeks slow vapor diffusion of Et_2O into a sample of **7** $[\text{BF}_4]$ dissolved in MeOH resulted in the crystallization of the colorless salt $[\text{Et}_2\text{HPCH}_2\text{CH}_2\text{PHEt}_2][\text{BF}_4]$.

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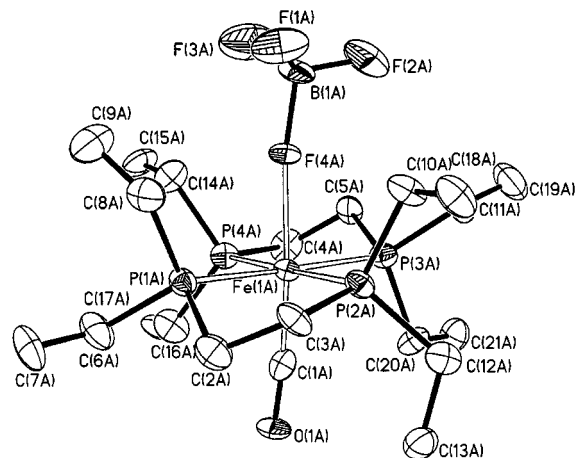


Figure 5. Structure of the $[\text{Fe}(\text{BF}_4)(\text{CO})(\text{depe})_2][\text{BF}_4]$ subunit A cation.

Table 4. Coordinated $[\text{BF}_4]^-$ B–F Bond Lengths for $[\text{Fe}(\text{BF}_4)(\text{CO})(\text{depe})_2][\text{BF}_4]$

subunit	bridging B–F bond length/Å	terminal B–F bond length/Å
A	1.47(1)	1.38(1), 1.30(2), 1.33(2)
B	1.46(1)	1.38(1), 1.32(1), 1.40(1)
C	1.46(1)	1.36(2), 1.33(2), 1.39(1)
D	1.48(2)	1.37(1), 1.31(2), 1.36(1)

The most noteworthy feature of this structure is the fairly strong H(1P)–F(1) hydrogen bond, which is characterized by a bond length of 2.46 Å. This compound evidently arises through the slow decomposition of some complex in solution since no $^{31}\text{P}\{^1\text{H}\}$ NMR resonance for this species has been observed for freshly prepared samples of **7** $[\text{BF}_4]$ in MeOH. MeOH is not sufficiently acidic to protonate depe. However, $\text{MeOH}\cdot\text{BF}_3$, a byproduct of this reaction, should be quite acidic. It is likely that over time $\text{MeOH}\cdot\text{BF}_3$ or $[\text{MeOH}_2]^+$ (if $\text{MeOH}\cdot\text{BF}_3$ is more acidic than $[\text{MeOH}_2]^+$) protonates the Fe–P bonds, eventually resulting in the formation of the species observed. This may be facilitated by a cis labilizing effect of the F^- ligand.

Conclusions

$[\text{trans-Fe}(\text{H}_2)(\text{CO})(\text{dppe})_2][\text{OTf}]_2$ (**3** $[\text{OTf}]_2$) was generated by the reaction of $[\text{trans-FeH}(\text{CO})(\text{dppe})_2][\text{OTf}]$ with HOTf. $[\text{trans-Fe}(\text{H}_2)(\text{CO})(\text{depe})_2][\text{SbF}_6]_2$ (**6** $[\text{SbF}_6]_2$) was generated by the reaction of AgSbF_6 with $[\text{FeCl}(\text{CO})(\text{depe})_2]\text{Cl}$ in the presence of molecular H_2 . Neither of these salts has been isolated. **3** is more acidic than HOTf, and **6** is less acidic than $[\text{HOEt}_2]^+$ and much less acidic than **3**. $\nu(\text{CO})$ of **3** is greater than that of **6**. The relative acidities and $\nu(\text{CO})$ values of **3** and **6** are consistent with the greater basicity of depe as compared to dppe. **3** is stable with respect to H_2 loss even when exposed to reduced pressure for several hours, but under the extremely acidic conditions required to produce **3**, this complex slowly decomposes. **3** is much less reactive to nucleophiles than **6**. This relative reactivity is contrary to the relative electronic deficiencies of the iron centers in these complexes but may be attributed to the greater steric hindrance of reactions for **3** compared to **6**.

Changing the phosphine ligands from depe to dppe has a great effect on the reactivity, $\text{p}K_{\text{a}}$, and π -back-bonding but has little effect on the structural (H–H distance) and magnetic properties ($^2J(\text{HD})$, T_1) of the $\eta^2\text{-H}_2$ ligands. This is generally the case for complexes with H_2 trans to CO. The H_2 ligands in **3** and **6** rotate about the Fe– H_2 bond axis much faster than 300 MHz, which is consistent with the poor π -base character of iron in these complexes.

The great stability of the dicationic complex **3** with respect to H₂ loss indicates that the increase in metal–H₂ σ -bond strength more than compensates for the reduced π -back-bonding when compared to the analogous neutral Mo⁰ and monocationic Mn^I complexes.

Complexes **3** and **6** facilitate H/D scrambling between molecular H₂ and D₂. There is evidence for a chelate ring-opening mechanism for **6**. The rapid formation of [*trans*-Fe(OTf)(CO)(depe)₂]⁺ (**8**) and [*trans*-Fe(BF₄)(CO)(depe)₂]⁺ (**7**) via the protonation of [FeH(CO)(depe)₂]⁺ with HOTf and HBF₄, respectively, strongly indicates an H₂-dissociation mechanism, at least for **6**.

There is NMR evidence for the formation of [*trans*-Fe(H₂O)(CO)(dppe)₂]⁺ (**4**) and [*trans*-Fe(OTf)(CO)(dppe)₂]⁺ (**5**) in reaction mixtures of **3**; however, these complexes could not be isolated. Complexes **7**, **8**, and [*trans*-Fe(H₂O)(CO)(depe)₂]²⁺ (**9**) have been observed and characterized by NMR (**7**, **8**, **9**) and IR (**7**, **8**) spectroscopy and single-crystal X-ray diffraction (**7**, **9**). The [BF₄]⁻ ligand of **7** is highly fluxional at room temperature. This dynamic behavior contrasts with the observed activation and reactivity of the [BF₄]⁻ ligand, which undergoes nucleophilic substitution reactions with water and some alcohols

to afford the complex [*trans*-FeF(CO)(depe)₂]⁺ (**10**). In the presence of the acidic byproduct MeOH·BF₃, **10** slowly decomposes in methanol solution to yield [HEt₂PCH₂CH₂PEt₂H]-[BF₄]₂, which has been structurally characterized by single-crystal X-ray diffraction. While we have observed the coordination of the anions [OTf]⁻ and [BF₄]⁻ in this work, we have not observed solvent complexes of the type [Fe(ClCH₂Cl)(L)₂(CO)]²⁺ (cf. the electrophilic cations [Re(CO)₄(PR₃)(ClCH₂Cl)]-[BAR^f]³⁴).

Acknowledgment. This research was funded by an NSERC research grant to R.H.M. and NSERC and OGS scholarships to S.E.L.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **7**[BF₄], **9**[OTf]₂·H₂O, {**9**[OTf]₂}{(OTf)₂Ag}₂(μ -depe)}, and [HEt₂PCH₂CH₂PEt₂H]-[BF₄]₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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