Synthesis and Characterization of a Stable Iron(II) Hydride–Thiolate Complex: $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$

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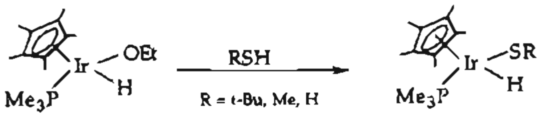
The anionic, bis(phosphite)iron hydride complex $[Et_4N][HFe(CO)_2(P(OPh)_3)_2]$ reacts with aryl disulfides to yield simple, monofunctional iron thiolate anions, $(ArS)Fe(CO)_2(P(OPh)_3)_2^-$ (Ar = Ph, Tol). Methylation of the thiolates resulted in the formation of thioether species $(ArSMe)Fe(CO)_2(P(OPh)_3)_2$, while protonation resulted in the formation of the stable thiolate–hydride complexes $(ArS)Fe(H)(CO)_2(P(OPh)_3)_2$. *cct*-$(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ was characterized by X-ray diffraction and found to be a regular octahedral complex in which the phosphite ligands are trans and the carbonyls cis, mutually trans to the hydride and benzenethiolate ligands. The hydride was located 1.41(7) Å from Fe with ∠H–Fe–S = 89(4)°. $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ crystallized in the monoclinic space group $P2_1/n$ with $a = 9.935(2)$ Å, $b = 36.185(5)$ Å, $c = 12.112(2)$ Å, $\beta = 113.42(1)°$, $V = 3995.5(0)$ Å,^{3} and $Z = 4$. $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ was protonated to form the novel thiol–hydride complex $(PhSH)Fe(H)(CO)_2(P(OPh)_3)_2^+$.

Introduction

The study of iron complexes containing hydride and thiolate ligands is of significance toward understanding the uptake of H_2 by sulfided catalysts in both enzymatic and industrial systems. The isolation of discrete $L_xM(H)(SR)$ complexes in general is complicated by the proton affinity of the sulfur site,[1–3] yielding labile thiol ligands, as well as the tendency for metal thiolate–hydrides to either eliminate H_2 in binuclear elimination[1,2] or reductively eliminate RSH from a mononuclear metal center.[1,2,4–11] Nevertheless, synthetic successes include the oxidative addition of thiols to coordinatively unsaturated organometallics,[5,6,9–18] as in the preparation of a series of ruthenium complexes of general formula *cct*-$RuH(SR)(CO)_2(PPh_3)_2$, from $Ru(CO)_2(PPh_3)_3$, eq 1.[15,16] A hydride/thiolate exchange reaction in metal dihydrides also has been used in the case of ruthenium, eq 2,[15,16] as well as with other metals.[19,20] An alkoxy hydride of iridium has been shown to react with RSH, protonating the OR^- ligand, resulting in a labile HOR, which is replaced with the RS^-, eq 3.[21]

$$Ru(CO)_2(PPh_3)_3 + RSH \rightarrow cct\text{-}Ru(H)(SR)(CO)_2(PPh_3)_2 + PPh_3 \quad (1)$$

$$Ru(H)_2(CO)_2(PPh_3)_2 + RSSR \rightarrow Ru(SR)H(CO)_2(PPh_3)_2 + RSH \quad (2)$$

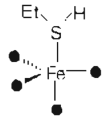


(3)

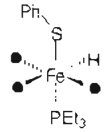
Unlike the more electron-rich Ru, examples of oxidative addition of RSH to Fe, the metal of interest in biological systems, are not available. However, eq 4 describes a protonation route

$$Fe(SPh)(CO)_3PEt_3^- + HBF_4 \xrightarrow{-78\ °C} Fe(H)(SPh)(CO)_3PEt_3 + BF_4^- \quad (4)$$

which is effective for anionic iron thiolates, leading, in the specific example shown, to a thermally unstable (decomposition at −40 °C) hydride which was characterized in solution by various spectroscopies.[2] The initial demonstration of this synthetic route of eq 4 focused on tailoring the electron densities (or proton affinities) of the thiolate sulfur and the iron center so as to control the site of protonation, resulting in complexes characterized in solution as structures **A**–**C**, where the spheres = CO.[1,2]



A



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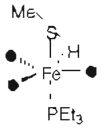

C

The anionic thiolate reagents required for eq 4 are prepared by the reaction of disulfides with electron-rich iron hydrides, in a reaction that formally converts a hydride into a proton, eqs 5

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(1) Liaw, W.-F.; Kim, C.; Darensbourg, M. Y.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989,** *111,* 3591.
(2) Darensbourg, M. Y.; Liaw, W.-F.; Riordan, C. G. *J. Am. Chem. Soc.* **1989,** *111,* 8051.
(3) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987,** *76,* 121.
(4) Shortman, C.; Richards, R. L. *J. Organomet. Chem.* **1985,** *286,* C3.
(5) Henderson, R. A.; Hughes, D. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1987,** 1115.
(6) Senoff, C. V. *Can. J. Chem.* **1970,** *48,* 2444.
(7) Gaylor, J. R.; Senoff, C. V. *Can. J. Chem.* **1972,** *50,* 1868.
(8) Gaines, T.; Roundhill, D. M. *Inorg. Chem.* **1974,** *13,* 2521.
(9) Stiddard, M. H.; Townsend, R. E. *J. Chem. Soc. A* **1970,** 2719.
(10) Stephan, D. W. *Inorg. Chem.* **1984,** *23,* 2207.
(11) Singer, H.; Wilkinson, G. *J. Chem. Soc. A* **1968,** 2516.
(12) Chatt, J.; Lloyd, J. P.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1976,** 365.
(13) Burrow, T. E.; Lazarowych, N. J.; Morris, R. H.; Lane, J.; Richards, R. L. *Polyhedron* **1989,** *8,* 1701.
(14) Lazarowych, N. J.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1987,** 1865.
(15) Lee, C.-L.; Chisholm, J.; James, B.; Nelson, P. A.; Lilga, M. A. *Inorg. Chim. Acta* **1986,** *121,* L7.
(16) Jessop, P. G.; Rettig, S. J.; Lee, C.-L.; James, B. R. *Inorg. Chem.* **1991,** *30,* 4617.
(17) Sellmann, D.; Fetz, A.; Moll, M.; Knoch, F. *Polyhedron* **1989,** *8,* 613.
(18) Darensbourg, M. Y.; Ludvig, M.; Riordan, C. G. *Inorg. Chem.* **1989,** *28,* 1630.
(19) Boyd, S. E.; Field, L. D.; Hambley, T. W.; Young, D. J. *Inorg. Chem.* **1990,** *29,* 1496.
(20) Chaudret, B.; Poiblanc, R. *Inorg. Chim. Acta* **1979,** *34,* L209.
(21) Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990,** *112,* 2022.

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Table 1. NMR (ppm) and ν(CO) Band Positions (cm^{-1}) for Solutions of $[Et_4N][XFe(CO)_2(P(OPh)_3)_2]$ (X = H, Ar) and Neutral Derivatives

complex	ν(CO)	^{1}H NMR (acetone-d_6)	^{13}C NMR (acetone-d_6)	^{31}P NMR (THF/acetone-d_6)
$[(PhS)Fe(CO)_2P_2^-]$	1928 (m), 1859 (vs)^a		220.8	173.4 (s)
$[(TolS)Fe(CO)_2P_2^-]$	1927 (m), 1858 (vs)^a		220.2	172.4 (s)
$[HFe(CO)_2P_2^-]$[22]	1928 (sh), 1911 (s), 1833 (vs)^a	−10.9 (t, J_{PH} = 57 Hz)	224.2	175.5 (d)
$(PhS)(H)Fe(CO)_2P_2$	2039 (s), 1991 (s)^a	−6.95 (t, J_{PH} = 63 Hz) (Fe–*H*)	208.9	149.5 (d)
$(TolS)(H)Fe(CO)_2P_2$	2038 (s), 1990 (s)^a	−7.02 (t, J_{PH} = 63 Hz) (Fe–*H*)	208.2	150.6 (d)
$(H)_2Fe(CO)_2P_2$[23]	2027 (s), 1986 (s)^a	−11.3 (t, J_{PH} = 62 Hz) (Fe–*H*)	209.0	175.1 (t)
$(PhSMe)Fe(CO)_2P_2$	1941 (m), 1880 (vs)^b	2.4 (S–C*H*$_3$)	219.1	171.0 (s)
$(TolSMe)Fe(CO)_2P_2$	1940 (m), 1879 (vs)^b	2.3 (S–C*H*$_3$)	218.5	170.9 (s)

^{a} THF solution at room temperature. ^{b} Hexane solution.

and 6. This ligand-based redox substitution of hydride by

$$HFe(CO)_4^- + ArSSAr \rightarrow (ArS)Fe(CO)_4^- + ArSH \qquad (5)$$

$$HFe(CO)_3PR_3^- + R'SSR' \rightarrow (R'S)Fe(CO)_3PR_3 + R'SH \qquad (6)$$

$$R = Et,\ OEt;\ R' = Ph,\ Me,\ Et$$

thiolate[1,2] is sensitive both to the disulfide and to substituents on the iron. Whereas Ph_2S_2 reacts with both $HFe(CO)_4^-$ and the more electron-rich $HFe(CO)_3PR_3^-$, dialkyl disulfides Me_2S_2 and Et_2S_2 are unreactive with $HFe(CO)_4^-$ but react with the more electron-rich phosphine or phosphite-substituted hydrides.[1,2]

In an attempt to further extend the range of iron thiolate–hydrides, as well as to prepare a thermally stable iron thiolate–hydride complex, we endeavored to prepare $[Et_4N][HFe(CO)_2(P(OPh)_3)_2]$ and $[Et_4N][(PhS)Fe(CO)_2(P(OPh)_3)_2]$.[22] Herein these results as well as the characterization of the stable complex $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ are reported. To our knowledge, this is the first iron thiolate–hydride complex whose structure has been determined by X-ray crystallography.

Experimental Section

A. Methods and Materials. All reactions, sample transfers, and sample manipulations were carried out under standard Schlenk techniques (Ar atmosphere) or in an argon atmosphere glovebox. Solvents were distilled under N_2 from the appropriate drying agents (hexane, tetrahydrofuran (THF), and toluene from Na-benzophenone; acetonitrile from P_2O_5). $Fe(CO)_2(PPh_3)_3$,[23] $[Et_4N][HFe(CO)_2(P(OPh)_3)_2]$,[22] and $[Et_4N][(PhS)Fe(CO)_2(P(OPh)_3)_2]$,[22] **1**, were prepared according to literature procedures. MeI, $[p\text{-}CH_3C_6H_4]_2S_2$, $NaBPh_4$, PhSSPh, HBF_4, CF_3SO_3D, CF_3SO_3H, DCl (35% weight solution in D_2O) (Aldrich); ^{13}CO, D_2O, acetone-d_6 (Cambridge Isotopes); and CO (Matheson) were used as received from the indicated vendor.

B. Instrumentation. Infrared spectra were obtained on an IBM IR/32 FTIR spectrometer or a Galaxy 6021 Series FTIR. ^{1}H, ^{2}H, ^{31}P, and ^{13}C NMR spectra were recorded at the appropriate frequency on a Varian XL-200. A Hewlett-Packard 8452A diode array spectrometer was used for UV–vis spectra. Gas chromatographs were taken on a Perkin-Elmer Sigma 3B GC with an OV-101 packed 6 ft × $^1/_8$ in. stainless steel column with He carrier gas and a thermal conductivity detector.

C. Preparations and Reactions. 1. Preparation of $[Et_4N][(TolS)Fe(CO)_2(P(OPh)_3)_2]$, 2. To a pale-yellow solution of the starting material $[Et_4N][Fe(H)(CO)_2(P(OPh)_3)_2]$ (0.06 g, 1.22 mmol) in 20 mL of THF cooled to 0 °C was added by cannula 5 mL of a THF solution of $[p\text{-}CH_3C_6H_4]_2S_2$ (0.30 g, 1.22 mmol). After being stirred for 1 h, the dark orange reaction mixture was concentrated to ca. 10 mL under vacuum. A 20-mL portion of hexane and diethyl ether, in a 4:1 ratio and cooled to 0 °C, was layered onto the THF solution slowly, and diffusion caused the formation of an orange semicrystalline material at the solvent interface over the course of 24 h. The supernatant was removed by cannula, and the orange solid was washed twice with 15 mL of cold (0 °C) hexane to remove *p*-methylthiophenol. The dried orange solid weighed 0.99 g, an 82% yield. It was stored cold. The thermal and air sensitivity of this complex hindered elemental analysis. Spectral parameters are found in Table 1. ^{1}H NMR (acetone-d_6): δ 7.4–7.0 (m, 30 H, $-OC_6H_5$), 6.7–6.5 (m, 4 H, $-SC_6H_4CH_3$), 1.3 (s, 3 H, $-SC_6H_4CH_3$).

2. Alkylation of $[Et_4N][(ArS)Fe(CO)_2(P(OPh)_3)_2]$ (Ar = Ph, Tol). In a typical reaction, the starting material $[Et_4N][(ArS)Fe(CO)_2(P(OPh)_3)_2]$ (0.21 mmol) was placed in a 50-mL Schlenk flask and 30 mL of THF was added to give an orange solution. The flask was placed in a 0 °C ice bath and cooled for 15 min. Iodomethane (13 μL, 0.21 mmol) was then added by syringe, and the reaction mixture was stirred for 30 min resulting in a yellow, cloudy solution. The solvent was removed in vacuo, and two 20-mL portions of hexane were added to extract the yellow product. The hexane washes were transfered by cannula to a 50-mL Schlenk flask, and solvent was removed under vacuum. The yellow oily residues were isolated in yields of ca. 88%. Spectral parameters are given in Table 1.

3. Protonation of $[Et_4N][(ArS)Fe(CO)_2(P(OPh)_3)_2]$. To an orange solution of $[Et_4N][(ArS)FeCO)_2(P(OPh)_3)_2]$ (0.20 mmol) in 30 mL of THF was injected by syringe a 44-μL (0.20 mmol) portion of $HBF_4{\cdot}Et_2O$; the solution immediately turned a paler shade of orange. The solvent was removed under vacuum, and 30 mL of toluene was added to separate the neutral product from $[Et_4N][BF_4]$. The supernatant was transferred by cannula to a 50-mL Schlenk flask and was concentrated to ca. 10 mL under vacuum. Hexane, ca. 20 mL, was layered on top of the toluene solution, and the flask was placed in a −10 °C freezer overnight. Following removal of the supernatant, the orange solid was dried under vacuum for 1 h and $(ArS)Fe(H)(CO)_2(P(OPh)_3)_2$ obtained in ca. 90% yield. Despite repeated attempts, acceptable elemental analyses were not obtained, presumably because of the thermal sensitivity of these compounds. Spectral parameters are found in Table 1.

4. Synthesis of $(PhS)Fe(D)(CO)_2(P(OPh)_3)_2$. This synthesis is identical to the protonation of $[Et_4N][(ArS)Fe(CO)_2(P(OPh)_3)_2]$, except that DCl in D_2O (16 μL, 0.18 mmol) or CF_3SO_3D (15 μL, 0.18 mmol) was used as the deuterating agent. Yield of $(PhS)Fe(D)(CO)_2(P(OPh)_3)_2$: 0.17 g, 87%. IR ($\nu$(CO), THF): 2039 (s), 1991 (s) cm^{-1}. IR (ν(FeD), THF): 1395 (vw) cm^{-1}. ^{1}H NMR (acetone-d_6): δ 7.4–6.4 (m, 35H, $-C_6H_5$). ^{2}H NMR (THF): δ −7.0 (t, J_{PD} = 9.4 Hz, 1 D, Fe*D*). ^{31}P NMR (acetonitrile-d_3): δ 151.3 (t, J_{PD} = 9.4 Hz).

5. Protonation of $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$. A 63-$\mu$L (0.72 mmol) portion of CF_3SO_3H was added by syringe to $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ (0.20 g, 0.24 mmol) in 30 mL of CH_3CN forming an orange solution. The solution was stirred for 3 h during which time the color changed to pale yellow. The solvent was removed under vacuum, and three hexane washes resulted in a yellow oil. Yield of $[(PhSH)Fe(H)(CO)_2(P(OPh)_3)_2][CF_3SO_3]$: 0.17 g, 90%. IR ($\nu$(CO), CH_3CN): 2078 (s), 2029 (s) cm^{-1}. IR (ν(SH), CH_3CN): 2267 (m) cm^{-1}. ^{1}H NMR (acetone-d_6): δ 7.4–6.4 (m, 35 H, $-C_6H_5$), 2.58 (s, 1 H, PhS*H*), −6.5 (t, J_{PH} = 60 Hz, 1 H, Fe*H*). ^{31}P NMR (acetonitrile-d_3): δ 150.0 (d, J_{PH} = 57 Hz).

6. Solvent and Ion-Pairing Studies. $[Et_4N][(PhS)Fe(CO)_2(P(OPh)_3)_2]$ (0.03 g, 0.03 mmol) was loaded into a Schlenk tube, and 2 mL of THF was added by syringe. A 2-mL portion of absolute methanol was added by syringe, and after the sample was stirred at 0 °C for 5 min, the IR solution spectrum showed bands at 1931 (m) and 1867 (s) cm^{-1}. The solvent was removed under vacuum and redissolved in THF; the resulting spectrum was identical to the original spectrum.

An equimolar amount of the $NaBPh_4$ was added to a 0.06-mmol portion of $[Et_4N][(PhS)Fe(CO)_2(P(OPh)_3)_2]$ in 2 mL of THF, resulting in the formation of a white precipitate, presumably $[Et_4N^+][BPh_4^-]$. IR spectral measurements were taken without isolation of the Na^+ salt (ν(CO), THF): 1930 (m), 1870 (s) cm^{-1}. When 2 equiv of 18-crown-6 was added to the sodium salt solution, the ν(CO) frequencies moved to the same positions as $[Et_4N][(PhS)Fe(CO)_2(P(OPh)_3)_2]$, 1928 (m) and 1859 (s) cm^{-1}.

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(22) Darensbourg, M. Y.; Wander, S. A.; Reibenspies, J. H. *Organometallics* **1992**, *11*, 3185.

(23) Brunet, J.-J.; Kindela, F. B.; LaBroue, D.; Neibecker, D. *Inorg. Chem.* **1990**, *29*, 4152.

Table 2. Crystallographic Data for $(PhS)FeH(CO)_2[P(OPh)_3]_2$

empirical formula	$C_{44}H_{36}O_8P_2SFe$
color	orange
habit	plate
cryst size	0.04 mm × 0.20 mm × 0.20 mm
space group	monoclinic, $P2_1/n$
unit cell dimens	$a = 9.935(2)$ Å
	$b = 36.185(5)$ Å
	$c = 12.112(2)$ Å
	$\beta = 113.42(1)°$
V	3995.5(0) Å^3
formula units/cell	4
fw	842.6
d(calc)	1.401 g/cm^3
abs coeff	0.472 mm^{-1}
F(000)	1744 e$^-$
temp	273 K
radiation	Cu Kα (λ = 1.541 78 Å)
R^a	5.6%
$R_w{}^a$	5.0%

^{a} Residuals: $R = \sum|F_o - F_c|/\sum F_o$; $R_w = \{[\sum w(F_o - F_c)^2]/\sum w(F_o)^2]\}^{1/2}$.

7. $[Et_4N][(PhS)Fe(CO)_2(P(OPh)_3)_2]$ + ^{13}CO. Into a Schlenk tube was loaded 66.0 mg (0.07 mmol) of $[Et_4N][(PhS)Fe(CO)_2(P(OPh)_3)_2]$ and 5 mL of THF. The flask was evacuated and backfilled with ^{13}CO. The solution was stirred at 0 °C. After 1 day of monitoring the growth of the IR peaks, the major compound had ν(CO) bands at 1911 (m) and 1868(vs) cm^{-1}, as predicted for the completely ^{13}C-enriched $[Et_4N][(PhS)Fe(^{13}CO)_2(P(OPh)_3)_2]$.

D. X-ray Structure Determination. X-ray-quality crystals of $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ were obtained from toluene/hexane. Data collection was performed on a Rigaku AFC5R X-ray diffractometer equipped with an oriented graphite monochromator. Collection parameters are listed in Table 2, while atomic coordinates and equivalent isotropic displacement parameters are in Table 3. The structure was solved by direct methods and refined using a full-matrix least-squares anisotropic refinement for all non-hydrogen atoms. The iron-bound hydrogen atom was found in a difference Fourier map. The positional parameters for the hydride were refined. Carbon-bound hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å^2.

Results and Discussion

Synthesis. The synthesis of $[Et_4N][(PhS)Fe(CO)_2(P(OPh)_3)_2]$, **1**, has been previously reported[22] and is similar to the synthesis of $[Et_4N][(TolS)Fe(CO)_2\,(P(OPh)_3)_2]$, **2**. Consistent with the assumption that the H^-/SR^- exchange reaction (via redox substitution) involves nucleophilic attack of $Fe-H^-$ on RSSR, the reaction of Tol_2S_2 with $HFe(CO)_2(P(OPh)_3)_2{}^-$ requires longer reaction times than Ph_2S_2. As indicated in Scheme 1, $[Et_4N][(ArS)Fe(CO)_2(P(OPh)_3)_2]$ salts are obtained in ~90% yields by this route. Both IR and ^1H NMR evidence show the formation of a byproduct, $H_2Fe(CO)_2(P(OPh)_3)_2$, which is presumed to be due to the protonation of the starting material $[Et_4N][HFe(CO)_2(P(OPh)_3)_2]$ by the product thiols ArSH (pK_a's ~ 8).[24]

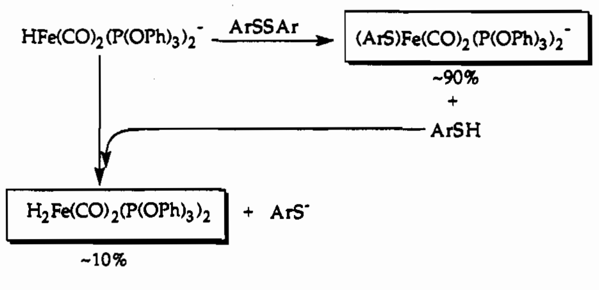
Attempts to extend the series of anionic iron thiolates by synthesizing alkane thiolato derivatives of $(RS)Fe(CO)_2(P(OPh)_3)_2{}^-$ proved unsuccessful; the disulfides R_2S_2 (R = Me, Et, *t*-Bu, Bzl) were unreactive with THF solutions of $[Et_4N][HFe(CO)_2(P(OPh)_3)_2]$. Although the crystal structure of $HFe(CO)_2(P(OPh)_3)_2{}^-$ finds the hydride to be sterically hindered,[22] the reactivity observed for Ph_2S_2 rules out steric factors as a cause for the observed lack of reactivity with alkyl disulfides. However, the Fe–H homolytic bond strength should increase concomitantly with the nucleophilicity of $Fe-H^-$ on P-donor substitution.[25] In addition, the Fe–SR bond strength is expected to weaken on P-donor substitution due to the destabilizing influence of the π-donor ability of SR^-.[26,27] These negative aspects of increasing the number of P-donors in anionic complexes evidently overwhelm the enhanced nucleophilicity of $Fe-H^-$ and inhibit the H^-SR^- exchange reaction.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $(PhS)FeH(CO)_2(P(OPh)_3)_2$

atom	x	y	z	U(eq)^{a,b}
Fe(1)	5391(1)	1276(1)	6106(1)	40(1)
S(1)	4155(2)	1231(1)	7394(2)	53(1)
P(1)	6345(2)	1780(1)	7027(2)	39(1)
P(2)	3848(3)	859(1)	5069(2)	48(1)
O(1)	7615(7)	716(2)	7332(6)	77(4)
O(2)	6379(7)	1404(2)	4177(6)	80(4)
O(3)	7706(5)	1764(1)	8315(4)	40(2)
O(4)	5477(6)	2065(1)	7511(4)	45(3)
O(5)	6911(6)	2034(1)	6207(5)	44(3)
O(6)	2121(6)	904(2)	4707(5)	50(3)
O(7)	4079(6)	456(2)	5623(5)	59(3)
O(8)	4000(6)	803(2)	3809(5)	60(3)
C(1)	6770(10)	944(2)	6896(8)	51(5)
C(2)	6029(9)	1353(2)	4949(8)	48(4)
C(3)	5883(11)	785(3)	9308(9)	69(5)
C(4)	6698(13)	726(3)	10527(11)	90(7)
C(5)	6980(12)	1008(4)	11332(10)	86(6)
C(6)	6452(11)	1346(3)	10961(9)	74(6)
C(7)	5640(10)	1410(3)	9758(8)	60(5)
C(8)	5347(9)	1130(3)	8919(8)	49(4)
C(9)	9313(10)	1314(3)	9567(8)	64(5)
C(10)	10521(11)	1087(3)	9846(9)	76(6)
C(11)	11317(11)	1085(3)	9158(10)	78(6)
C(12)	10904(10)	1309(3)	8162(9)	68(5)
C(13)	9690(9)	1534(2)	7841(7)	50(4)
C(14)	8912(8)	1532(2)	8562(7)	39(4)
C(15)	3121(10)	2185(2)	7479(8)	57(5)
C(16)	1760(10)	2341(3)	6946(9)	67(5)
C(17)	1326(11)	2522(3)	5888(9)	72(6)
C(18)	2267(11)	2539(3)	5318(9)	89(6)
C(19)	3655(10)	2379(3)	5832(8)	65(5)
C(20)	4053(8)	2202(2)	6893(7)	37(4)
C(21)	7150(9)	2607(3)	5421(8)	54(4)
C(22)	7650(10)	2967(3)	5545(9)	65(5)
C(23)	8444(11)	3112(3)	6669(10)	67(6)
C(24)	8731(10)	2895(3)	7657(9)	70(5)
C(25)	8247(10)	2534(2)	7545(9)	61(5)
C(26)	7430(9)	2398(2)	6416(8)	39(4)
C(27)	1301(11)	1392(3)	3224(9)	72(5)
C(28)	446(12)	1699(3)	2787(10)	94(7)
C(29)	−392(12)	1838(3)	3342(12)	90(7)
C(30)	−412(11)	1666(3)	4350(11)	85(7)
C(31)	450(10)	1361(3)	4802(9)	67(5)
C(32)	1315(9)	1227(3)	4258(8)	51(4)
C(33)	2923(10)	−131(3)	5284(9)	69(5)
C(34)	2020(11)	−388(3)	5476(11)	89(7)
C(35)	1334(12)	−300(3)	6212(11)	93(7)
C(36)	1522(12)	37(3)	6762(10)	92(7)
C(37)	2445(11)	298(3)	6580(8)	68(5)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. ^{b} *Estimated standard deviations are given in parentheses.*

Scheme 1



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[24] A control experiment found addition of PhSH to a THF solution of $HFe(CO)_2(P(OPh)_3)_2{}^-$ immediately yielded the dihydride $H_2Fe(CO)_2(P(OPh)_3)_2$.

[25] Kristjandottir, S. S.; Norton, J. R. Acidity of Hydrido Transition Metal Complexes in Solution. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed., VCH: Deerfield Beach, FL, 1992.

[26] Darensbourg, M. Y.; Longridge, E. L.; Payne, V. A.; Reibenspies, J. H.; Riordan, C. G.; Calabrese, J. C. *Inorg. Chem.* **1990**, *29*, 2721.

[27] Ashby, M. T. *Comments Inorg. Chem.* **1990**, *10*, 297.

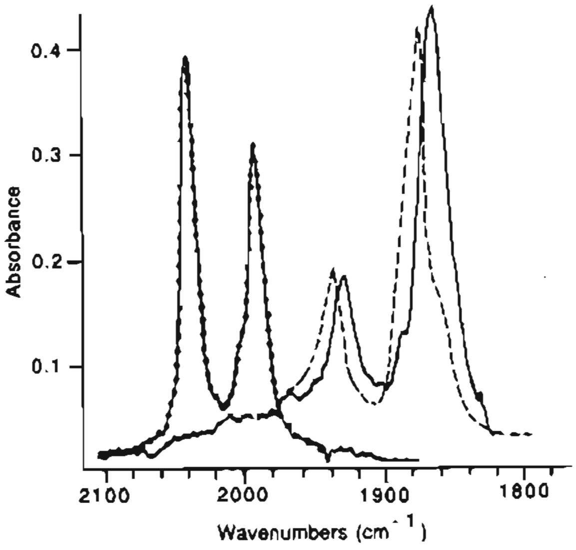
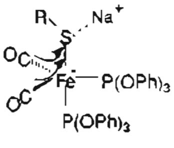


Figure 1. Overlay of IR δ(CO) spectra of [Et_4N][(PhS)Fe(CO)$_2$(P(OPh)$_3$)$_2$] (—), (PhSMe)Fe(CO)$_2$(P(OPh)$_3$)$_2$ (- - -), and (PhS)Fe(H)(CO)$_2$(P(OPh)$_3$)$_2$ (●) at 25 °C in THF.

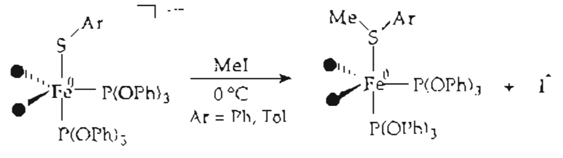
Interaction with Electrophiles. The use of cation interactions as indicators of electron density distribution in metal carbonyl anions has been well documented.[1,22,28,29] The addition of 1 equiv of $Na^+BPh_4^-$ to [Et_4N][(PhS)Fe(CO)$_2$(P(OPh$_3$)$_2$] in THF solution resulted in a shift in ν(CO) stretching frequencies from 1928 (m) and 1859 (s) cm^{-1} to 1930 (m) and 1870 (s) cm^{-1}. Upon subsequent addition of 1 equiv of 18-crown-6 ether, the spectrum reverted to the original. These results are interpreted according to structure **D**. The interaction of Na^+ at the thiolate sulfur reduces the electron-donating ability of RS^- and hence the amount of back-donation of Fe d electron density into π* CO orbitals. This pattern of shift in ν(CO) frequencies is larger than that observed on addition of $NaBPh_4$ to [PPN][(PhS)Fe(CO)$_4$],[1] consistent with greater electron density in the phosphite-substituted thiolate. A similar effect on ν(CO) shifts was seen when [Et_4N][(PhS)Fe(CO)$_2$(P(OPh$_3$)$_2$] was dissolved in a 1:1 mixture of absolute methanol and THF. The diminished electron density on the carbonyls, indicated by a shift of the ν(CO) peaks to higher frequencies (1931 (m) and 1867 (s) cm^{-1}), is consistent with H-bonding to the thiolate sulfur.



D

Reactivity. Upon addition of 1 equiv of MeI to 0 °C THF solutions of [Et_4N][(ArS)Fe (CO)$_2$(P(OPh)$_3$)$_2$], an immediate reaction occurred, precipitating bright yellow, thermally sensitive solids, which were only sparingly soluble in THF but were highly soluble in hexane. These complexes are unstable and decompose within 2 h at 0 °C in hexane solution. (Under a blanket of CO at 0 °C, quantitative formation of Fe(CO)$_3$(P(OPh)$_3$)$_2$ is observed.) A ν(CO) spectral overlay of [Et_4N][(PhS)Fe(CO)$_2$(P(OPh)$_3$)$_2$] and its methylated derivative in THF solution is shown in Figure 1, and a listing of spectral features is given in Table 1. The two-band pattern in the ν(CO) IR spectrum of **1** or **2** was maintained upon alkylation, indicating the same symmetry for reactant and product. The ^{1}H NMR spectra in acetone-d_6 at room temperature are characterized by multiplets in the aryl region, as well as singlets at ca. 2.4 ppm (S-CH_3). The ^{31}P NMR spectra in THF/acetone-d_6 at room temperature show singlets at ca. 171 ppm.

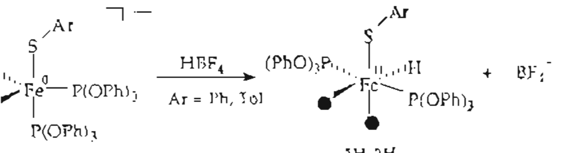
Spectroscopic parameters are consistent with alkylation at sulfur to form the thioether complexes (ArSMe)Fe(CO)$_2$(P(OPh)$_3$)$_2$ (Ar = Ph, Tol; **1Me**, **2Me**), eq 7. In comparison with the band positions of the parent anions **1** and **2**, minor shifts (~20 cm^{-1}) are observed in the ν(CO) infrared spectra of **1Me** and **2Me** indicating that the formal oxidation state of iron remains Fe(0).



(7)

1, 2 1Me, 2Me

Compounds **1** and **2** were protonated in THF solvent at 0 °C with 1 equiv of HBF_4. Weak acids, such as acetic acid, were unreactive. Moderately air-stable, orange solids were isolated and characterized at 22 °C by solution-state spectroscopies, Table 1. The ^{1}H NMR spectra were characterized by multiplets in the aryl region and triplets at ca. −7 ppm (J_{P-H} = 63 Hz), indicating formation of an Fe–H bond. The ^{31}P NMR spectra in THF/acetone-d_6 each showed a doublet at ca. 150 ppm. A ν(CO) spectral overlay of protonated **1**, or **1H**, and [Et_4N][(PhS)Fe(CO)$_2$(P(OPh)$_3$)$_2$] in THF, Figure 1, illustrates that protonation produced large shifts (~130 cm^{-1}) to more positive values in the ν(CO) IR spectrum. This indicates an oxidative addition of H^+ to iron to form an Fe(II) center in (ArS)FeH(CO)$_2$(P(OPh)$_3$)$_2$ (Ar = Ph, Tol; **1H**, **2H**), eq 8. Had protonation occurred at the sulfur to form a coordinated-thiol complex, one would have expected a small shift in the IR to higher frequency of approximately 20–30 cm^{-1}, as was seen for the alkylation reaction; vide supra.



(8)

1, 2 1H, 2H

Noteworthy are comparisons of **1H** and **2H** to the known dihydride complex $H_2Fe(CO)_2(P(OPh)_3)_2$;[23] spectral data are given in Table 1. The slightly lower ν(CO) IR bands (10 cm^{-1}) for $H_2Fe(CO)_2(P(OPh)_3)_2$ indicate that SAr^- ligands are less electron donating than is H^-. Additionally, there is a slight difference in band intensity ratio which may be due to minor geometrical differences in the overall geometry. The position of the hydride signal of $H_2Fe(CO)_2(P(OPh)_3)_2$ in the ^{1}H NMR spectrum at −11.3 ppm is upfield by approximately 4 ppm from the resonances of **1H** and **2H**, which occur at ca. −7 ppm. This major difference cannot be explained by simplistic shielding/deshielding or S-aryl ring current arguments.

Alternative approaches to the synthesis of (RS)Fe(H)(CO)$_2$(P(OPh)$_3$)$_2$ proved unsuccessful. Field's group reported the synthesis of Fe(SPh)(H)(dmpe)$_2$ and Fe(SPh)$_2$(dmpe)$_2$ from the reaction of 1 or 2 equiv of PhSH with Fe(H)$_2$(dmpe)$_2$.[19] In the case of $H_2Fe(CO)_2(P(OPh)_3)_2$, no reaction was observed after 24 h of stirring with PhSH or PhSSPh at room temperature, eq 9. Attempts at oxidative addition reactions also proved futile. Whereas $Ru(CO)_2(PPh_3)_3$ readily adds H_2S and RSH (R = Et, Ph, CH_2Ph, and *o*-, *m*-, and *p*-tolyl),[15,16] $Fe(CO)_2(P(OPh)_3)_3$ was unreactive with PhSH and BzlSH after reactions times of up to 1 week, eq 10. Photolyzing the tris(phosphite)-substituted iron complex for 30 min in THF prior to addition of thiol did not change the reactivity.

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(28) Darensbourg, M. Y.; Ash, C. E. *Adv. Organomet. Chem.* **1987**, *27*, 1.
(29) Ash, C. E.; Delord, T.; Simmons, D.; Darensbourg, M. Y. *Organometallics* **1986**, *5*, 17.

Relative Acidity of $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ and $H_2Fe(CO)_2(P(OPh)_3)_2$. The relative acidity of $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ and $H_2Fe(CO)_2(P(OPh)_3)_2$ was established by competition reactions. Since the higher frequency ν(CO) IR bands of **1H** and $H_2Fe(CO)_2(P(OPh)_3)_2$ are sharp and are separated by 10 cm^{-1}, they were used to monitor the reaction. (The lower frequency bands of **1H** and $H_2Fe(CO)_2(P(OPh)_3)_2$, at 1990 and 1987 cm^{-1}, respectively, overlap and prevent conclusive identification.) A 1:1 mixture of **1H** and $H_2Fe(CO)_2(P(OPh)_3)_2$ in THF solution reacted immediately with 1 equiv of $[Et_4N][OH]$ dissolved in MeOH. The IR spectrum showed the appearance of bands at 1929 (m) and 1860 (s) cm^{-1}, indicative of $(PhS)Fe(CO)_2(P(OPh)_3)_2^-$, along with a disappearance of the band at 2037 cm^{-1}, assigned to **1H**. The band at 2027 cm^{-1} remained unchanged, indicating unreacted $(H)_2Fe(CO)_2(P(OPh)_3)_2$. (Had $[Et_4N][HFe(CO)_2(P(OPh)_3)_2]$ been formed, bands at 1911, 1928, and 1833 cm^{-1} would have appeared.) In the reverse protonation reaction, a 1:1 molar ratio mixture of $[Et_4N][(PhS)Fe(CO)_2(P(OPh)_3)_2]$ and $[Et_4N][HFe(CO)_2(P(OPh)_3)_2]$ was placed in a THF solution containing 1 equiv of HBF_4. The appearance of an absorption at 2027 cm^{-1} in the IR spectrum of the reaction mixture showed that $H_2Fe(CO)_2(P(OPh)_3)_2$ only had formed. Both reactions indicate that $(PhS)FeH(CO)_2(P(OPh)_3)_2$ is more acidic than $H_2Fe(CO)_2(P(OPh)_3)_2$. Since the $HFe(CO)_2(P(OPh)_3)_2^-$ anion could be protonated by the weak PhSH acid ($pK_a \sim 8$),[24] while the $PhSFe(CO)_2(P(OPh)_3)_2^-$ could not be protonated by acetic acid ($pK_a \sim 5$), the acidity range is $pK_a(H_2Fe(CO)_2(P(OPh)_3)) > 8$ while the $pK_a((PhS)FeH(CO)_2(P(OPh)_3)_2) < 5$.

The relative acidity result is consistent with the electronic charge distribution as implicated from ν(CO) data both for the neutral hydrides as well as the anionic conjugate bases. Interestingly, the thermodynamic acidity of $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ and $H_2Fe(CO)_2(P(OPh)_3$ predicted by the method[30] recently developed by Morris and based on Lever's additive ligand parameter (ΣE_L)[31] is opposite that observed experimentally. Since the electrochemical parameter of the PhS^- ligand ($E_L = -0.53$) is more negative than that of the H^- ligand ($E_L = -0.4$),[31] the electron density and the basicity of the metal in the $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ complex should be greater than that of the dihydride. Thus by this analysis the thiolate hydride should have less acidic character than $H_2Fe(CO)_2(P(OPh)_3)_2$. The discrepancy with the experimental results points to the noninnocent behavior of the hydride ligand or a dependence of the electrochemical parameter of the covalently bound hydride ligand on the nature of the metal.[30]

Solid-State Structure of $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$. The molecular structure of $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ is given in Figure 2, and selected bond distances and angles are in Table 4. The complex has a nearly regular octahedral geometry with the phosphite ligands trans to each other and the carbonyl ligands cis to each other. The hydride was located trans to a carbonyl with an Fe–H distance of 1.41(7) Å and an $\angle$H–Fe–C_{trans} angle of 175(3)°. The greatest deviation from ideal octahedral geometry about Fe lies in a bending of the phosphite and *cis*-carbonyl groups toward the hydride site with $\angle$P(1)–Fe–P(2) = 163.2(1) and $\angle$S(1)–Fe–C(2) = 169.3(3). The Fe–S–C bond angle of 113.2(4)° is very close to the mean M–S–C bond angle, 110.8°, of all mononuclear thiophenylate ligand complexes crystallographically characterized.[24] There is no significant difference in the Fe–C distances of the CO trans to H and trans to PhS.

The overall geometry of the analogous structure *cct*-$Ru[S(p\text{-}C_6H_4CH_3)](H)(CO)_2(PPh_3)_2$ reported by James et al.[16] is similar to that of $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ with respect to ligand placement. The former has a more regular octahedral geometry. In both, the $\angle$H–M–S is near 90°, suggesting independent ligation of these moities (i.e., there is no tendency toward η^2-SH interaction). It is also interesting to compare the metric parameters of **1H** and the anionic trigonal bipyramidal hydride $[Et_4N][HFe(CO)_2(P(OPh)_3)_2]$.[22] The Fe–H bond distance of the anion, 1.47(1) Å, is quite similar to that of **1H**, 1.41(7) Å. The Fe–P_{av} bond length in the anionic complex was found to be 2.079(1) Å, slightly shorter than that of **1H** at 2.157(4) Å and attributable to the lower coordination number of $HFe(CO)_2(P(OPh)_3)_2^-$. The Fe–S bond length of six-coordinate **1H**, 2.343(3) Å, is slightly longer than the Fe–S bond length in five-coordinate $[PPN][(PhS)Fe(CO)_4]$, 2.332(5) Å.[1] The difference in Fe oxidation state of the two complexes would have suggested the opposite order of Fe–S bond lengths.

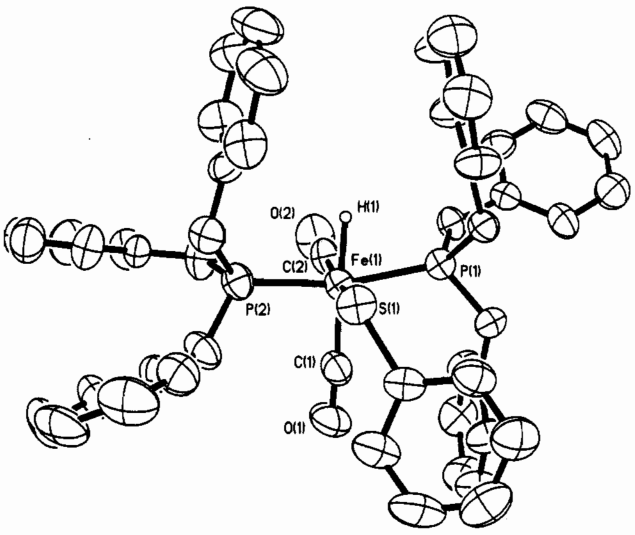

Figure 2. ORTEP representation of $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ (**1H**), showing 50% probability ellipsoids. Aryl hydrogens are omitted for clarity.

Table 4. Selected Bond Distances and Angles for $(PhS)Fe(H)(CO)_2[P(OPh)_3]_2$

(a) Bond Distances (Å)

Fe–H(1)	1.41(7)	Fe–S(1)	2.343(3)
Fe–P(1)	2.152(2)	Fe–P(2)	2.162(3)
Fe–C(1)	1.787(8)	Fe–C(2)	1.77(1)
S(1)–C(8)	1.791(8)	C(1)–O(1)	1.14(1)
C(2)–O(2)	1.13(1)		

(b) Bond Angles (deg)

H–Fe–S(1)	89(4)	H–Fe–P(2)	91(3)
H–Fe–P(1)	75(3)	H–Fe–C(2)	81(4)
C(1)–Fe–S(1)	95.1(4)	C(1)–Fe–P(1)	101.9(3)
C(1)–Fe–P(2)	93.3(3)	C(1)–Fe–C(2)	95.2(5)
P(1)–Fe–P(2)	163.2(1)	Fe–S(1)–C(8)	113.2(4)
Fe–C(1)–O(1)	175.1(8)	Fe–C(2)–O(2)	177.2(7)
C(1)–Fe–C(2)	95.2(5)	S(1)–Fe–C(2)	169.3(3)

Decomposition of Thiolate–Hydride Complexes. Although $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ is stable in THF solution under Ar at room temperature for days, upon heating to reflux, **1H** slowly decomposes over 24 h to form $Fe(CO)_3(P(OPh)_3)_2$ in a nonstoichiometric reaction. In the presence of excess $P(OPh)_3$ in refluxing THF, **1H** forms $Fe(CO)_2(P(OPh)_3)_3$ quantitatively, eq 9. This mononuclear decomposition mechanism contrasts with

$$(PhS)Fe(H)(CO)_2(P(OPh)_3)_2 + P(OPh)_3 \xrightarrow{70\,°C} PhSH + Fe(CO)_2(P(OPh)_3)_3 + \ldots \quad (9)$$

the four other known iron thiolate–hydrides of the formula $(H)(RS)Fe(CO)_3L$ (R = Et; Ph; L = PEt_3, $P(OEt)_3$), which decompose to yield H_2 and thiolato-bridged iron dimers, eq 10.[2] In view of the steric encumbrance of additional PR_3 ligands would have on such a dimer, the alternative route known for decom-

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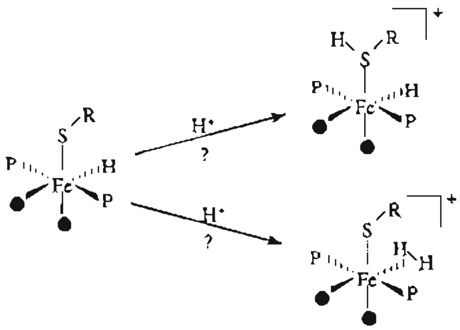
(30) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471.
(31) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.

Scheme 2



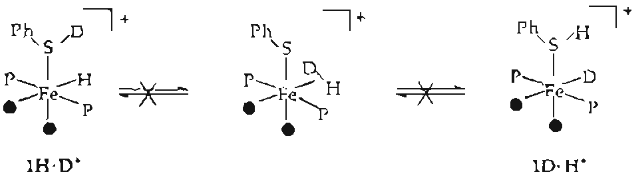
position of thiolate–hydride complexes, thiol reductive elimination, apparently becomes operative.

$$\mathrm{(H)(RS)Fe(CO)_3L} \xrightarrow[\downarrow\ \mathrm{CO}]{-40\ ^\circ\mathrm{C}} \mathrm{H_2} + (\mu\text{-RS})_2\mathrm{Fe_2(CO)_4L_2} \quad (10)$$

R = Et, Ph
L = PEt_3, $P(OEt)_3$

Protonation of 1H. Protonation of $(PhS)Fe(H)(CO)_2(P(OPh)_3)_2$ may lead to two probable products, one a formal thiol/hydride and the other a thiolate/η^2-dihydrogen complex, Scheme 2. (The likelihood of protonation at Fe^{II} resulting in an Fe^{IV} dihydride/thiolate is remote.) The reaction of an acetonitrile solution of **1H** with excess triflic acid or HBF_4 resulted in a color change from orange to pale yellow. The ν(CO) solution-state infrared spectrum of **1H·H$^+$** showed two bands at 2078 (s) and 2029 (s) cm^{-1}. (This protonation reaction was reversible, upon addition of excess Et_4NOH to **1H·H$^+$** the IR spectrum returns to the original two bands at 2039 and 1988 cm^{-1}.) The shift of ν(CO) bands to frequencies slightly higher than those of **1H** suggests the protonation is a ligand-based event. The S–H stretch of thiols is known to be weak and presumed to be in the 2500–2700 cm^{-1} range,[32] a region that is clear in the IR spectrum of **1H·H$^+$**. The ^{1}H NMR spectrum showed a triplet at δ –6.5 (Fe-*H*, J_{PH} = 60 Hz) and a singlet at δ 2.58 (assigned to S*H*), which each integrated to one proton with respect to the 35 aryl protons in the multiplet at δ 7.4–6.4. The ^{31}P NMR showed a doublet at δ 150.0 (J_{PH} = 57 Hz), little shifted from **1H**, and is presumed to indicate binding to Fe(II) splitting by a single hydrogen. The NMR evidence is consistent with protonation of the thiolate to form $(PhSH)Fe(H)(CO)_2(P(OPh)_3)_2^+$. Had an η^2-dihydrogen complex formed, one would have expected a hydride/aryl proton ratio of 1:17 in the ^{1}H NMR and a triplet in the ^{31}P NMR. The IR evidence does not provide definitive proof of the structure of **1H-+H$^+$**. In view of the fact that η^2-H_2 complexes of first-row transition metals are both rare and unstable,[33] and that thiols enjoy much greater stability, expectations lie greatly on the side of the thiol/hydride complex.

Scheme 3



Concluding Comments. A fortuitous order of proton affinity of iron and thiolate sulfur has permitted manipulation of the coordination sphere of iron, in a carbonyl/phosphite setting, producing the first example of a structurally characterized hydrido–thiolato complex of iron(II) and reasonably strong evidence of a iron(II) thiol–hydrido complex. We have established the relative order of acidity in the complexes:

$$\underset{\mathbf{1H{\cdot}H^+}}{(\mathrm{ArSH(Fe(H)(CO)_2P_2}^+} > \underset{\mathbf{1H}}{\mathrm{(ArS)Fe(H)(CO)_2P_2}} > \mathrm{H_2Fe(CO)_2P_2}$$

The steric bulk of the two phosphite ligands apparently precludes binuclear reductive elimination of H_2 from **1H** where thermal decomposition results instead in loss of ArSH. This mobility of H from iron to sulfur is not seen in **1H·H$^+$**. That is, from **1H·D$^+$**, produced upon addition of DCl to **1H**, we saw no indication of exchange of deuteride for hydride in the upfield region of the ^{2}H NMR, Scheme 3. Thus, **1H** does not perform the important H/D exchange function of acceptable biomimics of Fe-hydrogenases, a function which is assumed to require an η^2-H_2 (or in this case, η^2-HD) interaction. Such was suggested to be an intermediate in D_2/H^+ exchange examined by Sellmann et al. making use of a sulfur-rich complex of the redox-active rhodium.[34] More recently, Jessop and Morris gave evidence for intramolecular H/D exchange of a thiol proton with hydride in an iridium(III) complex.[35] Although η^2-H_2 complexes are well-known for Fe complexes ligated solely with phosphorus donors,[33,36] we suggest the proton affinity of the hydride ligand in the *carbonyl* complex of Fe(II), **1H**, in conjunction with a poor back-bonding ability of Fe(II) in the presence of CO ligands, is insufficient for formation of an η^2-H_2 complex.

Acknowledgment. The financial support of the National Science Foundation (Grant CHE-9109579) is greatly appreciated. We also wish to thank Prof. A. Clearfield for the use of the Rigaku AFC5R X-ray diffractometer.

Supplementary Material Available: Tables of bond lengths and bond angles and anisotropic displacement parameters and figures showing ORTEP and packing diagrams (6 pages). Ordering information is given on any current masthead page.

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(32) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

(33) Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993**, *93*, 913.

(34) Sellmann, D.; Kappler, J.; Moll, M. *J. Am. Chem. Soc.* **1991**, *115*, 1830.

(35) Jessop, P. G.; Morris, R. H. *Inorg. Chem.* **1993**, *32*, 2236.

(36) (a) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. (b) Bautista, M. T.; Earl, K. A.; Morris, R. H. *Inorg. Chem.* **1988**, *27*, 1124. (c) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823. (d) Riegle, J.-F.; Pelissier, M.; Eisenstein, O. *Inorg. Chem.* **1992**, *31*, 3344. (e) Baker, M. V.; Field, L. D.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 546.