independent ligands, like $(CO)_4FeHSiPh_3$, are significantly smaller at about 20 Hz.[21] The J_{Si-H} of the $CpMn(CO)_2HSiR_3$ complexes are intermediate between that of a covalently bonded Si–H and a nonbonded Si–H. These intermediate coupling values have been cited as evidence for some amount of Si–H bonding interaction being retained in these complexes. Alternatively, calculations of NMR coupling constants have shown that nonbonding contacts between atoms that are closer than van der Waals distances will dominate the value of the coupling constant between the atoms.[57,58] The distance between the silicon and hydrogen atoms in this complex is 1.8 Å, which is shorter than the van der Waals distance of 3.1 Å for neutral atoms. We attribute the intermediate value of the coupling constant in $CpMn(CO)_2HSiCl_3$ to nonbonded NMR coupling. This coupling is a consequence of the inherently narrow angle between the d_{yz} and d_{z^2} metal hybrids, which holds the Si and H atoms in close proximity, and not to the presence of a weak bond between the Si and the H.

Conclusions

The results on this Si–H addition to the metal differ from the results of C–H interaction with the metal in (cyclohexenyl)-manganese tricarbonyl. The photoelectron information on the cyclohexenyl complex did not give measurable interaction of the C–H σ^* orbital with the metal center. The Si–H σ^* is naturally lower in energy than the C–H σ^* allowing more effective interaction of the Si–H σ^* with the filled metal orbitals. The Cl substituents on the Si also aid in this interaction because of the electronegativity of Cl. The net result is that both the σ and σ^* levels collapse in $CpMn(CO)_2HSiCl_3$ to give Mn–H and Mn–Si bonds. In (cyclohexenyl)manganese tricarbonyl, the donation of the σ C–H electrons to the empty metal LUMO's was the major interaction. In $CpMn(CO)_2HSiCl_3$, although the latter interaction is always present, the interaction of the metal HOMO with the Si–H σ^* plays a more important role.

With these two complexes we have now observed the effects of strong interaction with the metal center (the Si–H case) and weak interaction with the metal center (the C–H case). It remains to be seen if molecules in the intermediate regions of interaction can be characterized so that the crossover between the two limits can be understood. Molecules of the form $CpM(CO)(L)HSiR_3$ offer the possibility of characterizing a wide range of electron donating and accepting abilities of the metal complex and the Si–H bond. Molecules have been prepared for observing the effects of different R substituents (F, Cl, alkyl, phenyl), different ligands L (CO, PPh_3, PMe_3, CNR), different methylated cyclopentadienyls, and different metals. It appears possible to tune the extent of interaction and electron donation/acceptance between the metal and the silane. Photoelectron spectroscopy is important to characterization of the actual electron distribution and bonding in these complexes.

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Thiolate, Thioether, and Thiol Derivatives of Iron(0) Carbonyls

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Abstract: A new series of anionic complexes of iron tetracarbonyl monofunctionalized with the ligand $[RS^-]$, $[RSFe(CO)_4^-]$ (R = Ph, Et, Me, H), have been synthesized and characterized. The compound $[PPN][PhSFe(CO)_4]$ was formed in the reaction of $[PPN][HFe(CO)_4]$ and PhSSPh. The $[PhSFe(CO)_4^-]$ anion was characterized by X-ray diffraction as its $[PPN^+]$ salt and found to be a typical trigonal-bipyramidal complex in which the phenylthiolate ligand occupies an axial position with a Fe–S bond distance of 2.332 (5) Å and $\angle$Fe–S–C(Ph) = 111.3 (6)°. The salt crystallized in the orthorhombic space group $Pbc2_1$, with $a = 9.529$ (4) Å, $b = 21.493$ (9) Å, $c = 20.185$ (9) Å, $V = 4134$ (3) Å^3, and $Z = 2$. Other members of the series of complexes, $[RSFe(CO)_4^-]$, were best obtained by ligand exchange of $[RS^-]$ and the labile thioether complex $(PhSMe)Fe(CO)_4$. The latter was produced from the low-temperature alkylation of the $[PhSFe(CO)_4^-]$. Protonation of the thiolates (R = Ph, Et, Me, H) ultimately leads to formation of H_2 and $Fe_2(\mu\text{-}SR)_2(CO)_6$; however, the intermediate thiol, $(RSH)Fe(CO)_4$, could be observed at −78 to −40 °C for R = Et, Me. The PhSH and HSH derivatives were unstable even at −78 °C.

Advances in the understanding of reaction pathways at a metal–ligand site, particularly those of hydride and hydrogen atom transfer from hydridometalcarbonyl anions,[1] have suggested analogous reactivity approaches to other $M–X^-$ functionalities. Accessible for investigation is a wide range of functionalities in the series $XM(CO)_5^-$; where M = Cr, Mo, and W and X may be H^-, all the halides, pseudohalides, carbon donor ligands, oxygen donor ligands such as O_2CR^-, OR^-, or OAr^-, and sulfur donor ligands such as SR^- or SAr^-. However, for the analogous $XFe(CO)_4^-$ complexes, X is limited to the well-known hydride derivative,[2] C donor ligands,[3] and cyanide.[4] Derivatives of anionic oxygen donor ligands are unknown as are all halides with the possible exception of iodide.[5] Simple thiolate derivatives had been proposed as intermediates in reactions of thioketones with $HFe(CO)_4^-$, prepared in situ from $Fe(CO)_5$ and KOH;[6] however, there

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was no characterization of them until this work.

Recently, we noted that certain anionic hydrides provided synthetic entry to simple, monofunctional MSR^- complexes. Herein, the synthesis and characterization of one such series, $RSFe(CO)_4^-$ (R = Ph, Me, Et, H), is described along with preliminary reactivity/mechanism studies of the $FeSR^-$ functionality. Several new thioether complexes, $(RSR')Fe(CO)_4$, and thiols, $(RSH)Fe(CO)_4$, were prepared by the low-temperature alkylation and protonation, respectively, of the $RSFe(CO)_4^-$ anions.

Experimental Section

A. Methods and Materials. All reactions, sample transfers, and sample manipulations were carried out under standard Schlenk techniques (N_2 atmosphere) and/or in an argon atmosphere glovebox. All solvents were distilled under N_2 from appropriate drying agents (hexane and tetrahydrofuran (THF), from Na-benzophenone; diethyl ether, from lithium aluminum hydride; methanol, from Mg-iodine; acetonitrile, from CaH_2/P_2O_5) and then stored in dried, N_2-filled flasks over activated 4A molecular sieves. A nitrogen purge was used on these solvents prior to use, and transfers to the reaction vessels were via stainless steel cannula under a positive N_2 pressure. The reagents, $[Et_4N][SH]$ (Alfa Chemical Co.), PhSSPh, $Fe(CO)_5$, $W(CO)_6$, HSEt, NaSMe, and MeI (Aldrich Chemical Co.), were used as received.

B. Instrumentation. Infrared spectra were recorded on an IBM FTIR/32 spectrometer using 0.1-mm sealed CaF_2 solution cells. ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian XL 200 spectrometer. Cyclic voltammetric measurements were performed on a BAS-100A electrochemical analyzer, using Pt as the working electrode, SCE as the reference electrode, and 0.1 M $[n\text{-}Bu_4N][PF_6]$ as the supporting electrolyte. Gas chromatography was carried out on a Perkin-Elmer recorder Model LCI-100. Analyses made use of either a flame ionizing detector (FID) or a thermal conductivity detector (TCD); helium was the carrier gas. Columns used for analysis were purchased from Alltech and were used as follows: hydrogen gas on Carbosphere, 80/100 mesh, 6 ft × 1/8 in. stainless steel tubing; thioethers, OV-17 on Chromosorb W-HP, 80/100 mesh, 6 ft × 1/8 in. stainless steel tubing.

C. Preparation of $[PPN][RSFe(CO)_4]$. 1. $[PPN][PhSFe(CO)_4]$. The starting material $[PPN][HFe(CO)_4]$,[2] 0.707 g (1 mmol), was placed in a 100-mL Schlenk flask with 0.218 g (1 mmol) of diphenyl disulfide. A total of 40 mL of dried THF was added to give an orange-red solution. The reaction mixture was stirred for 30 min after which the solution was concentrated to 10 mL under vacuum. Hexane or diether ether was slowly added to precipitate an orange solid. The mother liquor was removed via cannula, and the solid was washed twice with hexane. The dried orange-red solid weighed 0.775 g, a 96% yield. Anal. Calcd for $C_{46}H_{35}O_4NP_2SFe$ (Galbraith Labs): C, 67.74; H, 4.33. Found: C, 67.02; H, 4.33. Spectroscopic characterization includes the following. IR (ν(CO), THF): 2016 m, 1910 vs cm^{-1}. ^1H NMR (acetone-d_6): 7.5 d, 6.95 t, 6.74 t ppm. ^{13}C NMR (acetone-d_6): 219.69 (CO), 132 (Ph) ppm. The phenylthiol product, PhSH, was identified by its strong S-H stretching frequencies at 2525 cm^{-1} and by gas chromatography.

2. $[PPN][RSFe(CO)_4]$ (R = Et, Me, H). The compound (MeSPh)-$Fe(CO)_4$ (0.500 mmol; isolated from hexane and dried under vacuum at 0 °C; see the Experimental Section, section E, for details), was dissolved in CH_3CN at 0 °C. To this solution was added 0.5 mmol of [PPN][SR], prepared by the reaction of NaSR and PPNCl in CH_3CN and filtered to remove NaCl, and the solution was stirred overnight. Solvent was removed under vacuum, the orange-brown residue was washed with hexane, and THF solvent was added to extract the product. Upon addition of hexane, orange-brown semisolids develop for R = Et, Me. For R = H, a green oil separates on addition of hexane. Despite repeated washings with hexane and recrystallization, satisfactory elemental analysis could not be obtained. The yields were typically 80%. Spectroscopic parameters, IR and ^1H and ^{13}C NMR, are found in Table IV.

D. Reactions of $[PPN][PhSFe(CO)_4]$. 1. Addition of ^{13}CO. Into a 50-mL Schlenk flask was loaded 81.5 mg (0.1 mmol) of $[PPN][PhSFe(CO)_4]$ and a 15-mL portion of THF. The flask was evacuated and back-filled with ^{13}CO. The solution was stirred at room temperature. After 6 days of monitoring the growth of the new peaks by IR, the major compound had ν(CO) bands at 1970 m and 1867 vs, as predicted for the completely ^{13}C enriched $[PPN][PhSFe(^{13}CO)_4]$.

2. Reaction with Acid. A 81.5-mg (0.1-mmol) portion of $[PPN][PhSFe(CO)_4]$ was loaded into a 50-mL Schlenk flask and dissolved in 10 mL of THF. Dry HCl gas (prepared simultaneously in another flask from the addition of concentrated H_2SO_4 to NaCl) was slowly bubbled into the THF solution. Gas chromatograph analysis of a sample of the gases over the solution showed the presence of H_2. The reaction was monitored immediately by IR to confirm the presence of $[PhSFe(CO)_3]_2$: ν(CO) 2076 m, 2040 vs, 2001 s, 1988 sh.[7] The reaction mixture was filtered to separate the white precipitate of [PPN][Cl] and, upon removal of solvent from the filtrate, $[PhSFe(CO)_3]_2$, was obtained as a red solid.

3. Reaction with Alkyl Halides. This is described in section E below.

4. Addition of $[NO][PF_6]$. Equimolar amounts of $[PPN][PhSFe(CO)_4]$ (0.1 mmol, 81.5 mg) and $NOPF_6$ (0.1 mmol, 17.5 mg) were dissolved in THF at -78 °C and stirred for 20 min. A red-brown solution and a white precipitate were formed. The reaction mixture was warmed to room temperature. The iron-sulfur dimers, $[PhSFe(CO)_3]_2$ and $[PhSFe(NO)_2]_2$,[8] are formed. IR (ν(NO); THF): 1757 s, 1784 s cm^{-1} for $[PhSFe(NO)_2]_2$. IR (ν(CO); THF): 2076 m, 2040 vs, 2001 s, 1988 sh cm^{-1} for $[PhSFe(CO)_3]_2$.

5. Solvent and Ion-Pairing Studies. $[PPN][PhSFe(CO)_4]$ (81.5 mg, 0.1 mmol) was loaded into a 50-mL Schlenk flask, and 15 mL of absolute methanol was added by syringe. After the reaction mixture was stirred at room temperature for 5 min, the IR solution spectrum displayed bands at 2026 m and 1921 s cm^{-1}. The solvent was removed under vacuum and redissolved in THF; the resulting spectrum was identical with the original THF spectrum.

Equimolar amounts of $[PPN][PhSFe(CO)_4]$ and $NaBPh_4$ were dissolved in THF and stirred for 15 min. The solution was filtered to remove the white precipitate $[PPN][BPh_4]$. Only the cation-exchanged product, $[Na][PhSFe(CO)_4]$, was observed. IR (ν(CO); THF): 2018 m, 1913 vs, 1887 sh cm^{-1}. When 18-crown-6 ether was added to this solution, the ν(CO) frequencies moved to the same positions as $[PPN][PhSFe(CO)_4]$, 2016 m and 1910 vs cm^{-1}. The same results of this study were obtained when a 10-fold excess of $NaBPh_4$ was used. Addition of $NaBPh_4$ to $[PPN][EtSFe(CO)_4]$ resulted in decomposition, with the major organometallic product being $[EtSFe(CO)_3]_2$.[7]

E. Preparation of $(RS'R)Fe(CO)_4$. 1. $(MeSPh)Fe(CO)_4$. A 32-μL (0.5-mmol) portion of MeI was added to 407.5 mg (0.5 mmol) $[PPN][PhSFe(CO)_4]$ in 20 mL of THF at 0 °C. The solution was stirred for 15 min, and a white precipitate of PPNI settles out. The THF solvent was removed under vacuum, and the orange residue was extracted with hexane at 0 °C. Upon removal of hexane in vacuo, a red-orange oil was obtained. Attempts that were made to obtain this material as a solid were unsuccessful. Since solutions exhibited thermal sensitivity, they were kept at 0 °C at all times. IR (ν(CO); hexane): 2057 m, 1979 s, 1956 vs, 1946 vs cm^{-1}. IR (ν(CO); THF): 2054 m, 1969 m, 1946 vs cm^{-1}. ^1H NMR: 2.24 (CH_3), 7.42 ppm (Ph). Since the alkylation of $[PPN][PhSFe(CO)_4]$ by MeI was spectroscopically quantitative, quantities of (MeSPh)Fe-$(CO)_4$ used in subsequent syntheses were based on the amount of $[PPN][PhSFe(CO)_4]$ used in its preparation.

2. $(n\text{-}BuSEt)Fe(CO)_4$. Equimolar amounts of $[PPN][EtSFe(CO)_4]$ and 1-bromobutane (or iodobutane) were dissolved in THF at room temperature and stirred for 2 h (30 min). The reaction mixture was filtered to remove [PPN][Br] and dried under vacuum. An orange-brown semioil solid, soluble in hexane as well as polar organic solvents, $(n\text{-}BuSEt)Fe(CO)_4$ was obtained. IR (ν(CO); THF): 2051 m, 1968 m, 1942 vs cm^{-1}. IR (ν(CO); hexane): 2055 m, 1976 m, 1952 s, 1941 s cm^{-1}. ^{13}C NMR (C_6D_6): 214.8 ppm (CO). ^1H NMR (C_6D_6): 3.38-3.48 ppm ($-CH_2SCH_2$), 0.78 ppm ($-SCH_2CH_3$), 1.95-2.04 ppm ($-CH_2CH_2CH_2S-$), 0.70 ppm ($CH_3(CH_2)_3S-$).

F. Reactions of $[PPN][EtSFe(CO)_4]$. Addition of HBF_4. A 76.7-mg (0.1-mmol) portion of $[PPN][EtSFe(CO)_4]$ was loaded into a 50-mL Schlenk flask and dissolved in 10 mL of THF at -78 °C. A 23-μL portion (0.1-mmol) of $Et_2O{\cdot}HBF_4$ solution was syringed into the flask. The reaction mixture was stirred for 2 min and monitored immediately. IR (ν(CO); THF): 2053 m, 1966 m, 1944 vs cm^{-1}. IR (ν(SH)): 2363 cm^{-1}. The ^1H NMR (d_8-THF) was assigned as follows: CH_3, 1.37 ppm (t); $-CH_2-$, 2.71 ppm (complex m); SH, 2.47 ppm. Upon warming to room temperature, the dimer, $[EtSFe(CO)_3]_2$,[7] was formed. IR (ν(CO); THF): 2072 m, 2033 vs, 1922 s, 1984 sh cm^{-1}.

G. Crystallographic Characterization of $[PPN][Fe(CO)_4SPh]$. Table I contains data relating to this structural study. Orange crystals of $[PPN][Fe(CO)_4SPh]$ were mounted on glass fibers with epoxy cement. The unit cell parameters were obtained from the least-squares fit of the angular settings of 25 reflections (21° ≤ 2θ ≤ 24°). Systematic absences and photographic work determined either of the orthorhombic space groups *Pbcm* of *Pbc*2_1 (nonstandard *Pca*2_1). The latter, noncentrosym-

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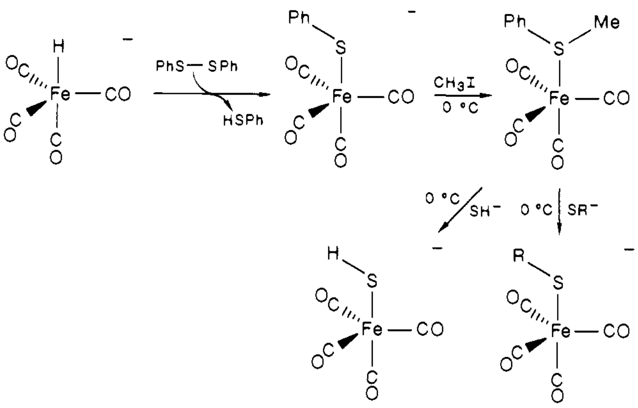
Table I. Crystallographic Data for [PPN][Fe(CO)$_4$SPh]

(a) Crystal Data	
formula	$C_{46}H_{35}NO_4P_2SFe$
cryst syst	orthorhombic
space grp	*Pbc*2$_1$
a, Å	9.529 (4)
b, Å	21.493 (9)
c, Å	20.185 (9)
V, Å^3	4134 (3)
Z	2
D(calc)	1.311
temp, °C	22
cryst dimen, nm	0.42 × 0.36 × 0.36
μ(Mo Kα), cm^{-1}	5.30
(b) Data Collection	
diffractometer	Nicolet R3m/μ
radiatn	Mo Kα
wavelength, Å	λ = 0.71073
scan limits, deg	$4 \leq 2\theta \leq 50$
scan method	Wyckoff
rflns collected	4121
data collected	$+h,+k,+l$
indpdt rflns	3762
obs rflns, $3\sigma(F_o)$	1757
decay, %	<1
(c) Refinement	
R(*F*), %	7.09
R(w*F*), %	7.57
Δ/σ	0.042
Δ(<<rrho), e Å^{-3}	0.45
N_o/N_v	7.20
GOF	1.411

Scheme I



metric alternative proved correct; it was first suggested by the distribution of *E* values and confirmed by the absence of mirror-plane symmetry. No correction for absorption was required (T_{max}/T_{min} = 1.09).

The structure was solved by direct methods. The phenyl rings of the PPN cation were constrained to rigid, planar hexagons, and the associated carbon atoms were refined isotropically. Hydrogen atom contributions were incorporated as idealized contributions (*d*(CH) = 0.96 Å).

All computations used SHELXTL (5.1) software (G. Sheldrick, Nicolet XRD, Madison, WI). Atomic coordinates are given in Table II and selected bond distances and angles in Table III.

Results and Discussion

Syntheses. In contrast to [HW(CO)$_5^-$], which will form the thiolate–tungsten carbonylate[9] by either of the routes described by eq 1 and 2, [HFe(CO)$_4^-$] does not react with PhSH and was prepared by reacting [HFe(CO)$_4^-$] with Ph$_2$S$_2$ in THF in a 1:1 ratio (Scheme I).

$$[HW(CO)_5^-] + PhSH \rightarrow [PhSW(CO)_5^-] + H_2 \quad (1)$$

$$[HW(CO)_5^-] + Ph_2S_2 \rightarrow [PhSW(CO)_5^-] + PhSH \quad (2)$$

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for [PPN][Fe(CO)$_4$(SPh)]

	x	*y*	*z*	*U*^{a}
Fe	698 (2)	9200 (1)	9637	69 (1)*
P(1)	6859 (4)	8648 (2)	2444 (2)	52 (1)*
P(2)	6791 (4)	7551 (2)	1545 (2)	48 (1)*
S	2885 (5)	9621 (2)	9376 (2)	82 (2)*
N	6799 (12)	8241 (4)	1796 (5)	53 (4)*
C(1)	3121 (18)	10141 (7)	10637 (8)	76 (6)*
C(2)	3862 (29)	10329 (8)	11207 (11)	113 (10)*
C(3)	5334 (26)	10297 (8)	11162 (10)	98 (9)*
C(4)	5962 (23)	10079 (9)	10582 (11)	118 (10)*
C(5)	5132 (24)	9877 (8)	10099 (9)	87 (8)*
C(6)	3751 (20)	9880 (7)	10083 (8)	70 (7)*
C(7)	34 (21)	9956 (10)	9536 (9)	84 (7)*
O(7)	−450 (18)	10449 (6)	9472 (8)	140 (8)*
C(8)	965 (21)	8658 (9)	8948 (11)	97 (8)*
O(8)	1155 (19)	8346 (6)	8525 (8)	146 (8)*
C(9)	−962 (23)	8927 (9)	9807 (9)	91 (9)*
O(9)	−2068 (13)	8753 (7)	9925 (8)	137 (7)*
C(10)	1443 (20)	8893 (8)	10404 (10)	79 (8)*
O(10)	1829 (20)	8716 (7)	10878 (7)	132 (8)*
C(11)	6914 (8)	7890 (5)	3551 (5)	70 (4)
C(12)	7575	7573	4068	74 (4)
C(13)	9003	7664	4186	85 (5)
C(14)	9770	8071	3788	107 (6)
C(15)	9110	8388	3272	89 (5)
C(16)	7682	8298	3153	59 (4)
C(21)	8054 (10)	9796 (5)	2721 (4)	83 (5)
C(22)	8889	10310	2569	94 (6)
C(23)	9553	10348	1955	79 (5)
C(24)	9382	9872	1491	84 (5)
C(25)	8546	9359	1643	65 (4)
C(26)	7882	9321	2257	47 (3)
C(31)	4920 (9)	9120 (5)	3342 (4)	66 (4)
C(32)	3598	9341	3523	80 (5)
C(33)	2503	9338	3064	86 (5)
C(34)	2731	9114	2424	99 (6)
C(35)	4053	8893	2244	78 (5)
C(36)	5147	8898	2702	59 (4)
C(41)	7185 (9)	6607 (5)	2464 (5)	79 (5)
C(42)	6705	6199	2951	104 (6)
C(43)	5279	6174	3104	105 (6)
C(44)	4332	6558	2771	134 (8)
C(45)	4813	6966	2283	94 (6)
C(46)	6239	6990	2130	53 (4)
C(51)	5229 (10)	6924 (3)	600 (5)	62 (4)
C(52)	4385	6892	36	88 (5)
C(53)	3967	7437	−283	74 (4)
C(54)	4394	8014	−39	73 (4)
C(55)	5238	8046	524	58 (4)
C(56)	5656	7501	844	48 (3)
C(61)	8740 (13)	6812 (6)	862 (7)	113 (7)
C(62)	10110	6613	739	126 (7)
C(63)	11233	6901	1060	138 (9)
C(54)	10986	7386	1503	156 (9)
C(65)	9617	7585	1626	147 (9)
C(66)	8494	7298	1305	68 (4)

^{a}Values with asterisks are equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U$_{ij}$ tensor.

Table III. Selected Bond Distances and Angles for [PPN][Fe(CO)$_4$SPh]

(a) Bond Distances (Å)			
Fe-S	2.332 (5)	P(2)-N	1.57 (1)
Fe-C(7)	1.76 (2)	S-C(6)	1.74 (2)
Fe-C(8)	1.83 (2)	C(7)-O(7)	1.16 (3)
Fe-C(9)	1.72 (2)	C(8)-O(8)	1.10 (3)
Fe-C(10)	1.83 (2)	C(9)-O(9)	1.14 (3)
P(1)-N	1.57 (1)	C(10)-O(10)	1.09 (3)
(b) Bond Angles (deg)			
Fe-S-C(16)	111.3 (6)	C(7)-Fe-C(8)	123.4 (9)
S-Fe-C(7)	86.4 (7)	C(7)-Fe-C(9)	90.4 (9)
S-Fe-C(8)	87.2 (6)	C(7)-Fe-C(10)	124.9 (8)
S-Fe-C(9)	176.6 (7)	C(8)-Fe-C(9)	93.5 (9)
S-Fe-C(10)	89.1 (6)	C(8)-Fe-C(10)	111.1 (9)
P(1)-N-P(2)	142.6 (7)	C(9)-Fe-C(10)	93.7 (9)

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Table IV. Spectroscopic and Electrochemical Parameters for Salts of $RSFe(CO)_4^-$

	^1H (acetone-d_6), ppm	^{13}C (CO) (acetone-d_6), ppm	IR ν(CO) (acetone-d_6), ppm	E_p, V
$[Et_4N][HSFe(CO)_4]$	-4.08	220.0	2014 w, 1906 vs	-0.057
$[PPN][PhSFe(CO)_4]$	7.5 (d), 6.95 (t), 6.74 (t)	219.7 ^{13}C (Ph) 132	2016 m, 1910 vs	+0.070
$[PPN][MeSFe(CO)_4]$	1.78 (s)	220.8	2007 m, 1899 vs	-0.068
$[PPN][EtSFe(CO)_4]$	1.16 (t), 2.19 (q)	220.8 $^{13}C(-CH_2-)$ 28.6 $^{13}C(-CH_3)$ 19.7	2007 m, 1899 vs	-0.066
$[PPN][HFe(CO)_4]^a$	-8.68 (s)	223.3	1998 m, 1905 m, 1876 s	+0.20

[a] Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. L. C. *Inorg. Chem.* **1978**, *17*, 3286.

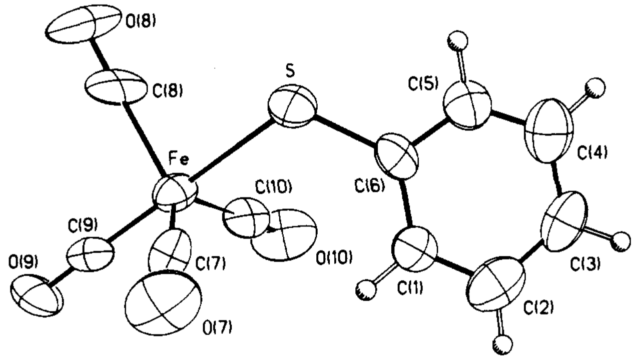

Figure 1. Thermal ellipsoid plot of $PhSFe(CO)_4^-$ anion with numbering scheme.

Addition of MeSSMe to a solution of $[PPN][HFe(CO)_4]$ yielded $MeSFe(CO)_4^-$ only after weeks at 22 °C. A better synthetic route utilized the following procedure: alkylation of $[PhSFe(CO)_4^-]$ by MeI at 0 °C led to a neutral compound, $(MeSPh)Fe(CO)_4$, vide infra. The lability of the thioether ligand permitted ligand displacement by $[SR^-]$ (R = H, Me, Et) at 0 °C overnight (Scheme I). The $[PPN][RSFe(CO)_4]$ salts are indefinitely stable solids in the absence of air at room temperature. In THF solution $[PPN][PhSFe(CO)_4]$ or $[PPN][EtSFe(CO)_4]$ are stable to prolonged (at least 24 h) periods at 65 °C in THF. The $[Et_4N][HSFe(CO)_4]$ is thermally unstable at 22 °C decomposing to insoluble solids in CH_3CN, over the period of 1 day.

Description of $[PPN][PhSFe(CO)_4]$ Molecular Structure. Appropriate crystallographic data are found in Tables I–III. The PPN^+ cation is bent with an $\angle P-N-P = 142.6\ (2)°$. The anion $[PhSFe(CO)_4^-]$ has an almost regular trigonal-bipyramidal coordination geometry, with the sulfur atom of the phenyl thiolate ligand occupying an axial site on the coordination sphere of iron (Figure 1). As given in Table III, the greatest deviation from expected TBP angles is in the equatorial plane where one C(eq)–Fe–C(eq) closes to 111.1 (9)° and the other two open to 123.4 (9)° and 124.9 (8)°. A view of the anion along the S–Fe–C(9)–O(9) axis shows the phenyl group oriented so as to bisect the larger C(7)–Fe–C(10) (124.9°) angle. The dihedral angle defined by the intersection of the plane containing the phenyl ring and that containing Fe–S–C(6) is 30.5°. The Fe–S–C(6) bond angle of 111.3 (6)° indicates a tetrahedral disposition of electron pairs about the sulfur atom.

The Fe–S distance of 2.332 (5) Å in $PhSFe(CO)_4^-$ is, interestingly, the same as that in $Fe(SPh)_4^{2-}$ (average Fe–S of 2.353 (9) Å),[10] as well as in the iron(III) cluster, $Fe_3S_4(SPh)_4^{3-}$, 2.332 (14) Å,[11a] but significantly longer than the average Fe–S in the well-known cubic cluster, $Fe_4S_4(SPh)_4^{2-}$, 2.263 (3) Å.[11b] For the organometallic, $CpFe(CO)_2SEt$, the Fe–S distance of 2.296 (2) Å reflects both a higher charge on Fe and the better electron-donating ability of the EtS ligand.[12] The neutral thioether complex $(c\text{-}1,3\text{-}C_4H_8S_2)Fe(CO)_4$ provides an appropriate comparison for the zero-oxidation state of Fe.[13] Again the complex is regular TBP with the dithiane ligand in the axial position. That study found little significant difference between the Fe–CO(ax) and the Fe–CO(eq) distances (in ours, there is none), and the average Fe–C distances are, within experimental error, almost identical for the two complexes, 1.78 Å. Interestingly, the Fe–S distance of 2.288 (2) Å is significantly shorter than in the anionic complex reported here. Finally, we note the comparison between $PhSFe(CO)_4^-$ and $HFe(CO)_4^-$.[2] Whereas the thiolate derivative is a regular TBP, the hydride derivative shows distortion in the direction of a hydrogen face-capped tetrahedron. The Fe–C distances are in $HFe(CO)_4^-$, on the average (1.74 (2) Å), shorter than observed for $PhSFe(CO)_4^-$, indicating a better dispersal of charge over the carbonyl groups for the hydride derivative.

Physical Properties. The series of compounds, $[RSFe(CO)_4^-]$, were characterized by IR, ^1H NMR, ^{13}C NMR (Table IV), and cyclic voltammetry. Assuming that the solid-state structure of the anion $[PhSFe(CO)_4^-]$ is preserved in solution, an idealized local C_{3v} symmetry would be predicted for the $Fe(CO)_4$ unit. The ν(CO) infrared spectrum of this compound in fact showed only two carbonyl bands, 2016 m and 1910 vs cm^{-1} in THF. The former is assigned to the (primarily axial CO) A_1^2 vibration and the latter assumed to be a composite of (primarily equatorial) A_1^1 and E vibrational modes.[14]

The ^{13}C NMR spectra show one signal in the CO region, indicating that the $[RSFe(CO)_4^-]$ (R = Ph, Et, Me, H) anions are fluxional, scrambling equatorial and axial carbonyl ligands even at −80 °C. This is not surprising in view of the extremely low barrier for carbonyl scrambling in $Fe(CO)_5$ and its derivatives, such as $Fe(CO)_4L$ ($L = PR_3, H^-$).[15]

The IR spectra for all anions had the same pattern but differed slightly in position. The shift of IR ν(CO) frequencies to lower numbers for the series R = Ph, H, Me, Et, (E mode: 1910 vs, 1906 vs, 1899 vs, 1899 vs cm^{-1}, respectively) and the shift of ^{13}C NMR resonances downfield (219.7, 220.0, 220.8, 220.8 ppm, respectively) indicate a trend of increasing electronic donation of the $[RS^-]$ ligand to the iron carbonyls. In comparison, the H^- ligand of $[PPN][HFe(CO)_4]$ is even more electron-donating (IR ν(CO): 1876 vs cm^{-1}. ^{13}C NMR: 223.3 ppm.) and fits at the end of the series.

electron-donating ability: $PhS^- < HS^- < MeS^- < EtS^- < H^-$

Electrochemistry. The characteristic features of the cyclic voltammograms of $[RSFe(CO)_4^-]$ are irreversible oxidation waves around 0.0 V. For R = H, Me, and Et, the E_p values are around −0.06 V in THF solution; for R = Ph, the electron is less accessible, E_p = +0.07 V. The irreversibility is ascribed to the rapid loss of CO from the $RSFe(CO)_4^{\cdot}$ radical, ultimately resulting in formation of the dimers, $[RSFe(CO)_3]_2$ whose complex oxidation

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(10) Coucouvanis, D.; Swenson, D.; Baeziger, N. C.; Murphy, C.; Holah, D. G.; Sfarnas, N.; Simopoulos, A.; Kostikas, A. *J. Am. Chem. Soc.* **1981**, *103*, 3350.

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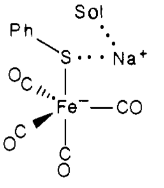
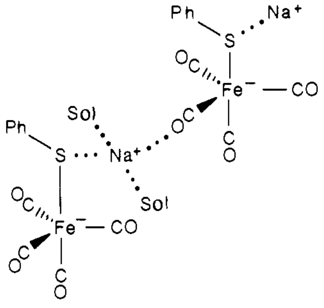
and reduction waves are observed at $E > +1.0$ and $E < -1.5$, respectively.[16] In contrast the $HFe(CO)_4^-$ anion as its PPN^+ salt in THF has an oxidation wave at $E_p = +0.20$ V, again indicating a less available electron, consistent with the conclusion from spectroscopic data that electron density is more delocalized over the $Fe(CO)_4$ in the hydride derivative.

Interaction with Electrophiles. The interaction of Na^+ with the $[PhSFe(CO)_4^-]$ anion was probed by ν(CO) IR spectroscopy in THF solution. The ν(CO) stretching frequencies 2016 m and 1910 s for $[PPN][PhSFe(CO)_4]$ changed to 2018 m, 1913 s, and 1887 sh with contact interaction of Na^+. This contact ion pairing could be removed upon addition of 18-crown-6 ether. The resulting spectrum is identical with that of $[PPN][PhSFe(CO)_4]$, indicating that there is no permanent change in the anion's configuration with change in counterion. This pattern of the shift in ν(CO) frequencies is very similar, although less dramatic, to that observed on addition of $NaBPh_4$ to $[PPN][HFe(CO)_4]$ forming $[Na][HFe(CO)_4]$.[17] The interpretation of the infrared data in that case is that there was a site-selective interaction of the Na^+ at the equatorial carbonyl oxygen. Interestingly, although the perturbation of ν(CO) IR spectrum upon addition of Na^+ was greater for $HFe(CO)_4^-$ than for $PhSFe(CO)_4^-$, only *1* equiv of $NaBPh_4$ was required to achieve maximum spectral charge for the latter; 4 equiv were required for the former. We interpret this result as indicative of a greater binding of Na^+ either by chelation, structure A, or by two anions, B, similar to the observed solid-state structure of $Na[HSW(CO)_5]$.[18]



A



B

When $[PPN][PhSFe(CO)_4]$ was dissolved in absolute methanol, the IR spectrum indicated diminished electron density on the carbonyls by a definite shift of the ν(CO) peaks to higher frequencies: 2026 m and 1921 s cm^{-1}. The interpretation here is that MeOH hydrogen bonds to the thiolate sulfur, reducing its electron-donating activity with a concomitant loss in Fe → CO π-back-bonding.

Chemical Reactivity. The nucleophilicity of $[PPN][PhSFe(CO)_4]$ is evident in reactions with electrophiles such as RX and Brønsted acids. The $[PhSFe(CO)_4^-]$ reacts readily with alkyl iodides at 0 °C but is unreactive with RBr or RCl at room temperature. In contrast the $[EtSFe(CO)_4^-]$ is reactive with RI at 0 °C and with RBr and $PhCH_2Cl$ at room temperature.

Within 5 min at 0 °C $[PhSFe(CO)_4^-]$ reacted with MeI to yield a product whose spectroscopic properties are consistent with alkylation at sulfur (eq 3). For example, the $(PhSMe)Fe(CO)_4$

$$R'X + [PPN][RSFe(CO)_4] \rightarrow (R'SR)Fe(CO)_4 + [PPN][X] \quad (3)$$

complex showed four carbonyl stretching bands, 2057 m, 1979 s, 1956 vs, 1946 vs cm^{-1} in hexane, which could be rationalized in terms of the asymmetry introduced by the thioether ligand, that is, C_s symmetry obtained. Analogous thioether complexes of Fe(0), (1,3-dithiane)carbonyliron,[13,19] and (1,3-dithia-5-cycloheptene)tetracarbonyliron,[20] have almost identical ν(CO) IR spectra, both in pattern and in ν(CO) position.

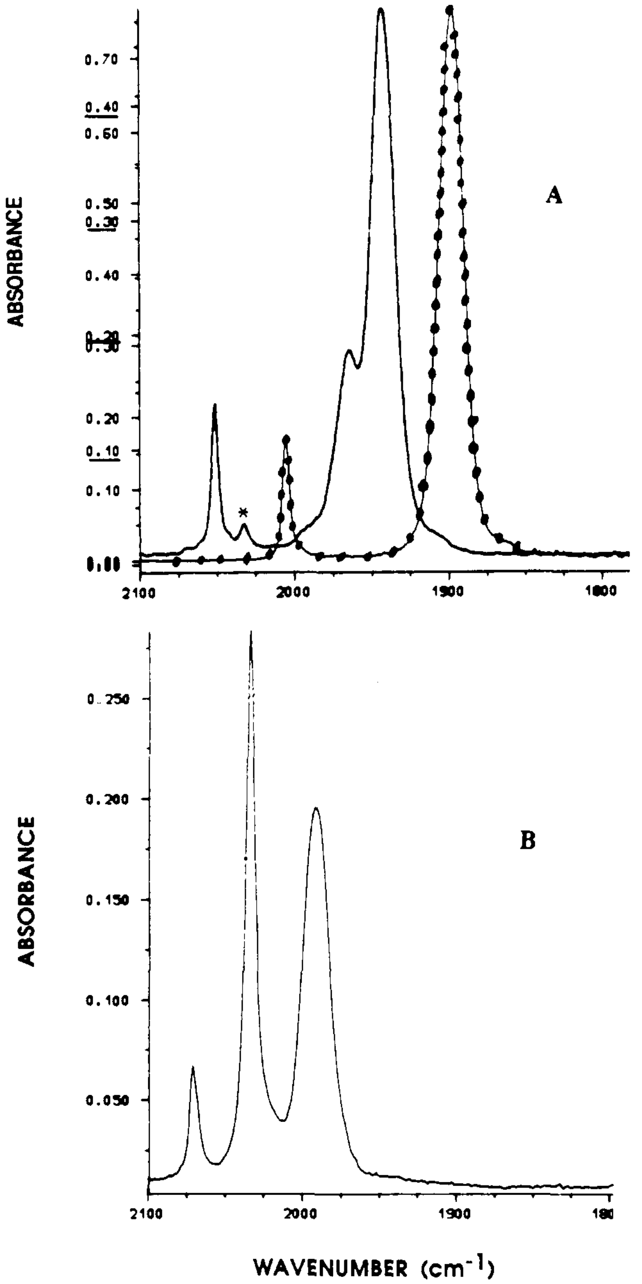


Figure 2. (a) IR ν(CO) spectrum of $[PPN][EtSFe(CO)_4]$ (●—●) and product of protonation, $(EtSH)Fe(CO)_4$ (—), at −50 °C in THF. An asterisk denotes major peak of dimeric $Fe_2(CO)_6(\mu\text{-SEt})_2$). (b) IR ν(CO) spectrum of same solution when warmed to 22 °C, $Fe_2(CO)_6(\mu\text{-SEt})_2$. The absorbance scale for the neutral species is underlined.

The thioether complex $(MeSPh)Fe(CO)_4$ could be isolated only as an oil even at low temperatures. Either neat or in solution, it decomposed at $T > 0$ °C, yielding the free thioether and $Fe(CO)_5$ (less than stoichiometric) as organometallic product. The *n*-butyl derivative, $(n\text{-BuSPh})Fe(CO)_4$, is, in contrast, stable in THF solution for at least 1 h at 20 °C. The $(n\text{-BuSEt})Fe(CO)_4$ derivative, also prepared by the analogous reaction of *n*-BuBr and $[EtSFe(CO)_4^-]$, displays little decomposition overnight in THF at room temperature. The relative order of stability toward thioether loss of the new iron(0) complexes is as follows: $(n\text{-BuSEt})Fe(CO)_4 > (n\text{-BuSPh})Fe(CO)_4 > (MeSPh)Fe(CO)_4$.

The ultimate reaction of the thiolate derivative and Brønsted acids (HBF_4 in ether or gaseous HCl) was oxidation/reduction

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to yield $[RSFe(CO)_3]_2$ and H_2 (eq 6). Attempts to observe an intermediate in the protonation were not successful for R = Ph; the sole product observed was $[PhSFe(CO)_3]_2$ even at −78 °C. However, as Figure 2 indicates, the low-temperature ν(CO) IR spectrum of $[EtSFe(CO)_4^-]$ in THF cleanly converts to a neutral species on addition of HBF_4 (IR (ν(CO); THF): 2053 m, 1965 m, 1944 s cm^{-1}), which on warming to room temperature converts to the dimer.[21] The intermediate neutral species could also be prepared in CH_3CN and extracted into hexane (IR (ν(CO); hexane): 2059 m, 1980 m, 1957 s, 1949 s cm^{-1}). The latter two bands are presumed to be due to a splitting of the E band under pseudo C_{3v} symmetry of the $Fe(CO)_4$ fragment.[14] The ^1H NMR (THF-d_8) was consistent with the presence of ligated CH_3CH_2SH with an *SH* resonance at 2.47 ppm. Unligated Et*SH* appears at 1.67 ppm in THF-d_8. A band at 2363 cm^{-1} in the IR (THF solution) was assigned to the ν(SH); the S–H stretch of free EtSH in THF is at 2555 cm^{-1}. Upon addition of Et_3N to the THF solution of the neutral intermediate, the starting anion, $EtSFe(CO)_4^-$, was obtained. Subsequent protonation with HBF_4 led once again to a neutral species of identical spectral properties.

Thus, the evidence is convincing that the unstable neutral species resulting from protonation of $EtSFe(CO)_4^-$ is the thiol derivative, $(EtSH)Fe(CO)_4$ (eq 4), rather than, for example, a sulfur-coupled product as was observed in the oxidation of SR ligands in d^6 Fe^{II} complexes, $CpFe(CO)_2SPh$: $[CpFe(CO)_2(\mu\text{-}PhSSPh)Fe(CO)_2Cp]$. A similar intermediate would explain the production of dimer and H_2 on addition of PhSH to the labile ligand complex $(MeSPh)Fe(CO)_4$ (eq 5). The presence of an unstable intermediate $(PhSH)Fe(CO)_4$ was previously suggested in the reaction of $H_2Fe(CO)_4$ with PhSH, yielding $[PhSFe(CO)_2]_2$.[23] Our work is the first report of spectroscopic evidence of a thiol iron tetracarbonyl species, and few other organometallic and coordination complex thiols have been characterized.[24]

$$\begin{aligned} &[PPN][EtSFe(CO)_4] + HBF_4 \xrightarrow[THF]{-78\ °C} \\ &\qquad (EtSH)Fe(CO)_4 + [PPN][BF_4] \\ &\qquad\qquad \Big\downarrow {\scriptstyle 22\ °C} \\ &\qquad [EtSFe(CO)_3]_2 + H_2 + 2CO \end{aligned} \quad (4)$$

$$(MeSPh)Fe(CO)_4 + \text{excess } PhSH \xrightarrow[MeSPh]{22\ °C} H_2 + [PhSFe(CO)_3]_2 + 2CO \quad (5)$$

Other Oxidations. Similar to $HFe(CO)_4^-$,[25] the $[PPN][PhSFe(CO)_4]$ salt reacted on time of mixing with $Co_2(CO)_8$ to yield cleanly $[PPN][Co(CO)_4]$ [IR (ν(CO)): 1887 cm^{-1}] (eq 6).

$$2[PPN][PhSFe(CO)_4] + Co_2(CO)_8 \xrightarrow{\text{rapid}} [PhSFe(CO)_3]_2 + 2[PPN][Co(CO)_4] + 2CO \quad (6)$$

Since the SPh^- anion as its PPN^+ salt also reduces $Co_2(CO)_8$ to $Co(CO)_4^-$ immediately, we cannot determine whether $PhSFe(CO)_4^-$ is more or less reactive toward electron transfer than SPh^-.

Reactions of the stronger oxidant $[NO][PF_6]$ with $[PPN][PhSFe(CO)_4]$ at −78 °C yielded the red solid $[PhSFe(CO)_3]_2$ as well as, in approximately equal quantities, a dark brown solid whose IR and NMR suggested formulation as the well-known $[PhSFe(NO)_2]_2$ (eq 7).[8] Since NO is known to exchange with CO of the dimeric $[PhSFe(CO)_3]_2$ complex,[7] it is possible that this product resulted from CO/NO exchange following an initial reduction of NO^+ to NO.[8]

$$[PPN][PhSFe(CO)_4] + NOPF_6 \rightarrow [PhSFe(CO)_3]_2 + [PhSFe(NO)_2]_2 + [PPN][PF_6] \quad (7)$$

Ligand Exchange. The SEt^- ligand could be replaced by SPh^- only in the presence of Na^+. In the absence of the alkali cation, $[PPN][EtSFe(CO)_4]$ was stable in the presence of 1 equiv of [PPN][SPh] over the course of 2 days in THF. In its presence, thiolate ligand exchange occurred within 10 min, yielding NaSEt as an insoluble precipitate in THF.

The reaction of $[PPN][EtSFe(CO)_4]$ and PhSH in THF solution at room temperature for 2 days resulted in the generation of $[PPN][PhSFe(CO)_4]$, which was characterized by IR and the EtSH identified by GC. This SR^- ligand substitution reaction is expected to be driven both by the formation of the weaker acid (eq 8) (pK_a (DMSO): PhSH = 10.3; PrSH = 17.05)[11,26] as well as the formation of an Fe–S bond that is *probably* stronger in the product than in the reactant.[27,28] A hydrogen-bonded intermediate $PhSH\cdots S(Et)Fe(CO)_4^-$, as suggested by the MeOH effect on IR spectra of $RSFe(CO)_4^-$ and analogous alkoxide structures,[29] most reasonably accounts for the reaction pathway.

$$[PPN][EtSFe(CO)_4] + PhSH \rightarrow [PPN][PhSFe(CO)_4] + EtSH \quad (8)$$

A THF solution of $[PPN][PhSFe(CO)_4]$ was stable under 1 atm of ^{13}CO at room temperature for at least 6 days. At the end of this time, the major product was the completely enriched $[PPN][PhSFe(^{13}CO)_4]$. As in the case of $[PPN][HFe(CO)_4]$, the carbon monoxide atmosphere did not displace the anionic $[RS^-]$ or $[H^-]$ ligand but instead exchanged with the more labile carbonyl ligands.[30] In contrast, the neutral ligand MeSPh was displaced $(MeSPh)Fe(CO)_4$ by 1 atm of CO at 0 °C with a reaction half-life of 40 h (eq 9). This result suggests that the Fe–S bond is considerably weaker in $(MeSPh)Fe(CO)_4$ than in $[PhSFe(CO)_4^-]$.

$$(MeSPh)Fe(CO)_4 + CO \xrightarrow{0\ °C} Fe(CO)_5 + MeSPh \quad (9)$$

Similarly, the thioether group is removed in the reaction of $(MeSPh)Fe(CO)_4$ with $[HW(CO)_5^-]$. The slow reaction was determined by IR to be complete after 4 days. Four products were separated by consecutive solvent washes and identified by their characteristic ν(CO) frequencies. Two of the products, $[HFe(CO)_4^-]$ and $[HFe(CO)_4W(CO)_5^-]$,[31] were the result of a transfer of the hydride from the tungsten to the iron. The $W(CO)_6$ and $[(\mu\text{-}H)W_2(CO)_{10}^-]$ products are rationalized by the capture of $W(CO)_5$ by CO (produced by some decomposition) and $HW(CO)_5^-$, respectively. There was no evidence of attack on the

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[27] The statement that the Fe–SPh bond is *probably* stronger than the Fe–SEt bond is based on thermochemical studies of $M^{IV}SR$ complexes (M = W, Mo), which clearly show this trend.[28] The transferability of this result to Fe(0) complexes is not without question.

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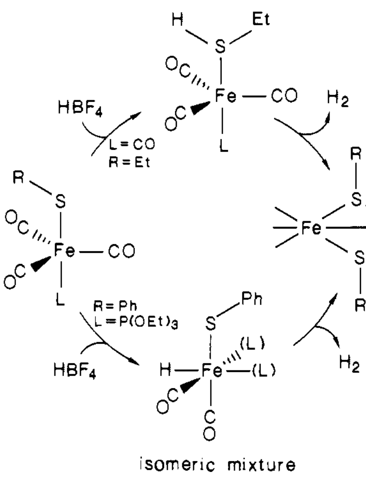
Scheme II



thioether S–C bonds by the hydride.[32]

Comments and Conclusions

The structure of $PhSFe(CO)_4^-$ is the first containing an iron(0) phenylthiolate functionality. The Fe–S bond length and ∠Fe–S–C(Ph) suggest little difference from the PhS–Fe bonding in $Fe(SPh)_4^{2-}$ or some higher valent iron–sulfur clusters. This study showed $PhSFe(CO)_4^-$ to be a convenient starting material for synthesis of acyclic thioether complexes and the further utility of the thioether complexes as labile ligand reservoirs for $[Fe(CO)_4]$. The study also provided direct evidence for $(RSH)Fe(CO)_4$, a species that was earlier proposed as an intermediate in the production of H_2 from RSH in the presence of iron carbonyls.[23] Noncyclized thioether complexes of Fe(0), $(RSR')Fe(CO)_4$, or thiols, $(RSH)Fe(CO)_4$, have not been reported until this work.

The isolation of $RSFe(CO)_4^-$ anions is important as the series provides an avenue for examining the $FeSR^-$ as an isolated chemical entity. The inaugural reactivity studies described above imply that electrophilic attact on the sulfur site as well as electron transfer is an accessible reaction pathways. The latter results in Fe–Fe coupled products rather than S–S coupling. In this connection, the similarity between the HFe^- and the $RSFe^-$ functionalities is notable. An additional reaction pathway, readily demonstrated for $HFe(CO)_4^-$ and $HFe(CO)_3PR_3^-$, is iron-site nucleophilicity,[1] resulting in the conversion of d^8 (TBP) Fe(0) to the favored configuration of d^6 (Oh) Fe(II). Thus, protonation of $HFe(CO)_4^-$ yields the dihydride, $H_2Fe(CO)_4$,[23] and acylation reactions of $HFe(CO)_4^-$ most likely proceed by oxidative addition yielding $RC(O)Fe(H)(CO)_4$ prior to the reductive elimination of RC(O)H.[33] Clearly from IR ν(CO) data, the RS^- ligands are less electron-donating to $Fe(CO)_4$ than is H^-, and the lone pairs of electrons in ligated SR^- are available for further reactivity.[34,35] Nevertheless, attempts to promote reactivity at the Fe site by preparing a more electron-rich center have been promising. Preliminary spectroscopic data[36,37] suggest that protonation of the phosphite-substituted complex, *trans*-$PhSFe(CO)_3P(OEt)_3^-$, generates the oxidative addition $Fe^{II}H$ product rather than the neutral thiol (Scheme II). Further studies of this presumed hydridoiron thiolate are underway.

Finally it is notable that the H^- and SR^- ligands are among the few which form stable $XFe(CO)_4^-$ anions. In this study the reducing equivalents of FeH^- generated $FeSR^-$ from an oxidized form of $(SR)^-$, R_2S_2.[38] These interconvertibilities, similar stabilities, and manifold reaction pathways lend credence to the contention that H and SR are compatible ligands, perhaps even as proposed in the biological setting $Fe_4S_4(SR)_3H^{-x}$.[39]

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Registry No. PhSSPh, 882-33-7; $[PPN][PhSFe(CO)_4]$, 119435-51-7; $[PPN][HFe(CO)_4]$, 56791-54-9; $[PPN][EtSFe(CO)_4]$, 119435-53-9; $[PPN][MeSFe(CO)_4]$, 119435-55-1; $[PPN][HSFe(CO)_4]$, 119435-57-3; $(MeSPh)Fe(CO)_4$, 119435-58-4; [PPN][SEt], 119414-78-7; [PPN][SMe], 119414-79-8; [PPN][SH], 119435-49-3; NaSEt, 811-51-8; NaSMe, 5188-07-8; NaSH, 16721-80-5; PPNCl, 21050-13-5; $[PPN][PhSFe(^{13}CO)_4]$, 119435-60-8; $[PhSFe(CO)_3]_2$, 15634-63-6; $[PhSFe(NO)_2]_2$, 20959-77-7; $[EtSFe(CO)_3]_2$, 15634-62-5; $(n\text{-}BuSEt)Fe(CO)_4$, 119435-61-9; 1-bromobutane, 109-65-9.

Supplementary Material Available: Tables of bond lengths (Table 2S), bond angles (Table 3S), anisotropic thermal parameters (Table 4S), and H atom coordinates and isotropic thermal parameters (Table 5S) (4 pages); listing of observed and calculated structure factors (Table 1S) (11 pages). Ordering information is given on any current masthead page.

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[36] *trans*-$[PPN][PhSFe(CO)_3P(OEt)_3]$ was obtained as an orange-brown solid at 0 °C from the reaction of $[PPN][HFe(CO)_3P(OEt)_3]$[37] and PhSSPh. The IR spectrum suggested an anionic TBP structure with SPh and $P(OEt)_3$ ligands trans to each other. IR (ν(CO); THF): 1957 vw, 1865 vs. ^{13}C NMR (acetone-*d*): 219.9 ppm (d, J_{C-P} = 36 Hz). Protonation of $[PPN][PhSFe(CO)_3P(OEt)_3]$ at −78 °C in THF or acetone by HBF_4 yielded a neutral product whose IR and NMR spectra were significantly different from that of the $(PhSH)Fe(CO)_4$. The ν(CO) bands (2077 m, 2019 sh, 2012 vs cm^{-1} in THF at −78 °C) are indicative of an Fe(II) rather than Fe(0) species. The ^1H NMR (acetone-d_6, −78 to −40 °C) spectrum showed three hydride signals at −7.22 ppm with J_{H-P} = 67 Hz; −7.36, J_{H-P} = 57 Hz; and −7.47, J_{H-P} = 57 Hz. At this point we cannot determine whether different orientations of the PhS ligand or different isomeric forms account for the multiple hydride signals.

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