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Contribution from the Department of Chemistry,
University of Wisconsin—Madison, Madison, Wisconsin 53706

Oxidative Coupling of Mercaptide Ligands in Organometallic Thiolate Complexes

PAUL M. TREICHEL,* LAURENCE D. ROSENHEIN, and MARK S. SCHMIDT

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The one-electron oxidations of $Fe(SPh)(CO)_2(\eta\text{-}C_5R_5)$ by $NOPF_6$ (R = Me, H) or $AgPF_6$ (R = Me) produce diamagnetic complexes having the general formula $[(\eta\text{-}C_5R_5)(CO)_2Fe(\mu\text{-}PhSSPh)Fe(CO)_2(\eta\text{-}C_5R_5)](PF_6)_2$. The route to these complexes, which have bridging diphenyl disulfide ligands, probably involves loss of a nonbonding electron from the mercaptide ligand followed by coupling of the resulting ligand-centered radical species. The BF_4^- salt of the cyclopentadienyl complex may also be obtained by a reaction of $[Fe(THF)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ and PhSSPh in a 2:1 ratio. Complexes with monodentate disulfide ligands, $[Fe(RSSR)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ (R = Me, Ph), are obtained from 1:1 reactions of the disulfide and $[Fe(THF)(CO)_2(\eta\text{-}C_5H_5)]BF_4$. Oxidations of several monosubstituted $Fe(SPh)(CO)(L)(\eta\text{-}C_5R_5)$ compounds (R = H, Me; L = $PPhMe_2$, PPh_2Me, PMe_3, $P(OPh)_3$, $P(OEt)_3$) and two disubstituted compounds $Fe(SPh)(CNR)_2(\eta\text{-}C_5H_5)$ (R = $m\text{-}C_6H_4OMe$, $m\text{-}C_6H_4CF_3$) produce dark solids having stoichiometries $[Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)]PF_6$ and $[Fe(SPh)(CNR)_2(\eta\text{-}C_5H_5)]BF_4$. These compounds, as solids, have magnetic moments between 0.5 and 2.3 μ_B. Their behavior in solution is consistent with the existence of an equilibrium between paramagnetic and diamagnetic dimers. Oxidation of another disubstituted species, $Fe(SPh)(P(OPh)_3)_2(\eta\text{-}C_5H_5)$, produces $[Fe(SPh)(P(OPh)_3)_2(\eta\text{-}C_5H_5)]PF_6$, a typical low-spin iron(III) complex; this is similar to results observed previously with disubstituted phosphine complexes, $Fe(SPh)(L)_2(\eta\text{-}C_5H_5)$ (L = PMe_3, L_2 = dppe).

Introduction

Our research group and other groups have been engaged in studies on the oxidation[1-4] and reduction[5] reactions of diamagnetic 18-electron organometallic compounds during the past several years. From oxidative reactions, a number of products having 17-electron configurations were characterized.[1,4] In general, the ease of oxidation of an organometallic precursor relates to electron richness at the metal site conveyed by the presence of good donor ligands. An increased negative charge at the metal destabilizes the filled metal orbitals with the consequence that removal of the metal electron is easier to accomplish.

Similarities between oxidative chemistry observed with organometallic species and that of classical inorganic compounds can be developed. Thus, the oxidation of $FeX(dppe)(\eta\text{-}C_5H_5)$ species (X = Cl, Br, I, Me, $SnMe_3$, SPh; dppe = $Ph_2PCH_2CH_2PPh_2$) to form cationic $[FeX(dppe)(\eta\text{-}C_5H_5)]^+$ complexes[1] may be regarded as an oxidation of a low-spin d^6 iron(II) complex to a low-spin d^5 iron(III) complex.

The perspective of persons studying the redox chemistry of metal complexes usually focused on the metal as the site of oxidation. However, there are many examples in which ligand-centered redox reactions are encountered, including, notably, the complexes of 1,2-dithiolenes[6] and 2,2′-bipyridine.[7] Examples in organometallic chemistry include the oxidations of $Fe(CO)_2(L)(\eta^4\text{-}C_8H_8)$ species (L = phosphines, CO), giving products in which the hydrocarbon groups have been coupled by carbon–carbon σ-bond formation.[2] Oxidative coupling of η^1-allyl groups in $Fe(CH_2CH{=}CH_2)(CO)_2(\eta\text{-}C_5H_5)$ to form $[(\eta\text{-}C_5H_5)(CO)_2Fe(\mu\text{-}CH_2{=}CHCH_2CH_2CH{=}CH_2)Fe(CO)_2(\eta\text{-}C_5H_5)]^{2+}$ has also been reported.[3] On the basis of the standard oxidation state formalism, the iron atom has not actually changed its oxidation state in these reactions. Coupling of ligands is also encountered in the one-electron reduction of $[Rh(\eta\text{-}C_5H_5)_2]^+$ to produce $Rh_2(\eta\text{-}C_5H_5)_4$, a complex having two cyclopentadiene ligands linked via a carbon–carbon bond.[5] These examples of redox reactions appear to be related in the sense that the initial redox chemistry, the addition or subtraction of an electron, occurs at a ligand and not at the metal.

It is in the context of ligand-centered redox reactions that we report our studies of the oxidation of several iron mercaptide complexes. After completion of studies on the metal-centered oxidation of $Fe(SPh)(L)_2(\eta\text{-}C_5H_5)$ complexes (L_2 = dppe[1]; L = Me_3P[4]), to give $[Fe(SPh)(L)_2(\eta\text{-}C_5H_5)]^+$ species, we turned out attention to oxidation reactions of compounds having the formula $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$, in which L is a phosphine, phosphite, or carbon monoxide. The products of these reactions were found to contain diphenyl disulfide as a ligand bridging two metal atoms, formed by oxidation coupling of the sulfur atoms in the ligand. They are of some interest in their own right, since organometallic complexes containing disulfide ligands are quite rare.

A communication on part of this work has appeared.[8]

Experimental Section

Starting materials $[Fe(THF)(CO)_2(\eta\text{-}C_5H_5)]BF_4$,[9] $FeSPh(CO)_2(\eta\text{-}C_5H_5)$,[10] $FeI(CO)(L)(\eta\text{-}C_5H_5)$ (L = PPh_2Me,[11] $PPhMe_2$[12]), $FeI(P(OPh)_3)_2(\eta\text{-}C_5H_5)$,[13] $[Fe(CO)_2(\eta^5\text{-}C_5Me_5)]_2$,[14] PMe_3,[15] $m\text{-}MeOC_6H_4NC$, and $m\text{-}CF_3C_6H_4NC$[16] were prepared according to literature methods. The preparation of $FeI(CO)_2(\eta\text{-}C_5Me_5)$ was accomplished by the method used to prepare $FeI(CO)_2(C_5Me_4CH_2CH{=}CH_2)$.[17] Other reagents were obtained commercially and were used without further purification. Solvents, except THF, were used as obtained; prior to its use, THF was dried over sodium–benzophenone ketyl and distilled. Petroleum ether refers to the commercial solvent Skelly B, a hydrocarbon mixture (bp 60–80 °C) containing mostly hexanes.

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Table I. Spectroscopic Data

compd	ν(CO) (ν(CN)),[a] cm^{-1}	δ[b]
$Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$		
L = CO	2030, 1987[g]	
PPh_2Me	1940 vs	1.88 d (8 Hz), CH_3; 4.16 s, C_5H_5; 6.42, 6.92 m, C_6H_5
$PPhMe_2$	1937 vs	1.63 d (10 Hz), CH_3; 1.82 d (10 Hz), CH_3; 4.32 d (1 Hz), C_5H_5; 6.86, 7.42 m, C_6H_5
PMe_3	1936 vs	1.40 d (11 Hz), CH_3; 4.37 d (1 Hz), C_5H_5; 6.72, 7.18 m, C_6H_5
$P(OPh)_3$	1973 vs	4.02 d (1 Hz), C_5H_5; 6.80, 7.19 m, C_6H_5
$P(OEt)_3$	1950 vs	1.21 t (7 Hz), CH_3; 4.02 quint ($J_{P-H} = J_{H-H}$ = 7 Hz), CH_2; 4.25 s, C_5H_5; 6.80, 7.26 m, C_6H_5
$Fe(SPh)(L)_2(\eta\text{-}C_5H_5)$		
L = $m\text{-}CNC_6H_4OMe$	(2110 s, 2050 s)	3.60 s, CH_3; 4.64 s, C_5H_5; 6.4–7.4 m, C_6H_4, C_6H_5
$m\text{-}CNC_6H_4CF_3$	(2117 s, 2075 s, 2040 vs)	4.52 s, C_5H_5; 6.76–7.24 m, C_6H_4, C_6H_5
$Fe(SPh)(CO)(L)(\eta\text{-}C_5Me_5)$		
L = CO	2005 s, 1965 s[c]	1.80 s, $C_5(CH_3)_5$; 6.7–7.4 m, C_6H_5
PMe_3	1914 s[c]	1.33 d (9 Hz), PCH_3, 1.67 s, $C_5(CH_3)$; 6.65–7.3 m, C_6H_5
PPh_2Me	1916 s[c]	1.48 s, $C_5(CH_3)_5$; 1.85 d (3 Hz), PCH_3; 6.7–7.7 m, C_6H_5
$PPhMe_2$	1913 s[c]	1.48 br s, $C_5(CH_3)$ and one of the PCH_3 groups (int = 18); 1.65 d (6 Hz), the second PCH_3 group (int = 3); 6.6–7.7 m, C_6H_5
$P(OEt)_3$	1930 s[c]	1.19 t (7 Hz), CH_2CH_3; 1.68 s, $C_5(CH_3)_5$; 3.92 quint ($J_{P-H} = J_{C-H}$ = 7 Hz) CH_2CH_3; 6.7–7.7 m, C_6H_5
$[Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)]BF_4$		
L = PPh_2Me	1984 vs[d]	
$PPhMe_2$	1988 vs[d]	
PMe_3	1995 vs[d]	
$P(OPh)_3$ (PF_6 salt)	2015 vs[d]	
$P(OEt)_3$ (PF_6 salt)	2000 vs[d]	
$[Fe(SPh)(L)_2(\eta\text{-}C_5H_5)]BF_4$		
L = $m\text{-}CNC_6H_4OMe$	(2142 s, 2020 s)[d]	
$m\text{-}CNC_6H_4CF_3$	(2140 s, 2110 s, 2070 m)[d]	
$[Fe(CO)_2(\eta\text{-}C_5H_5)(\mu\text{-}Ph_2S_2)Fe(CO)_2(\eta\text{-}C_5H_5)](PF_6)_2$	2060 vs, 2025 vs[d]	5.18 s, C_5H_5; 7.88 m, C_6H_5[f]
$[Fe(CO)_2(PhSSPh)(\eta\text{-}C_5H_5)]BF_4$	2068 vs, 2025 vs	5.83 s, C_5H_5; 7.5 m, C_6H_5[e]
$[Fe(CO)_2(MeSSMe)(\eta\text{-}C_5H_5)]BF_4$	2065 vs, 2020 vs	2.80 s, 2.98 s, CH_3; 5.76 s, C_5H_5[e]
$[Fe(SPh)(CO)(L)(\eta\text{-}C_5Me_5)]PF_6$		
L = CO (dimer)	2008 s, 1980 s[c]	1.83 s, $C_5(CH_3)_5$; 7.35, 7.57 m, C_6H_5
PMe_3	1994 s[c]	
$PPhMe_2$	1990 s[c]	
PPh_2Me	1990 s[c]	

[a] Values ±1 cm^{-1}; CH_2Cl_2 solvent except as noted. [b] Resonances from internal Me_4Si; CS_2 used as a solvent except as noted. [c] $CHCl_3$. [d] KBr. [e] Acetone-d_6. [f] CD_3CN. [g] In CCl_4; see ref 21.

Infrared data were recorded on a Beckman 4230 spectrometer; NMR data were obtained on a JEOL NM-MH100 spectrometer (Table I). Melting points were determined in sealed capillaries with a Thomas-Hoover melting point apparatus. Optical absorbance measurements were made with a Cary 118 spectrophotometer, using quartz cells of various path lengths. Magnetic susceptibilities were measured at ~20 °C with a Faraday balance at several field strengths between 2 and 8 kG and extrapolated to infinite field to obtain μ_{eff}.[18] Comparison data were also obtained on several samples by using a SHE Model VTS magnetometer to check our data. Reported values are calculated on the basis of the molecular weight of the monomer, unless otherwise noted.

Identification of new compounds was accomplished via elemental analysis (Galbraith Laboratories, Knoxville, TN) or by mass spectrometric peak match (AEI MS-902 spectrometer). In the latter case, the purity of the compound was affirmed by a combination of spectroscopic (IR, NMR) and melting point data. Some molecular weight data were obtained by vapor pressure osmometry in $CHCl_3$ (Mechrolab Model 301A).

Photolyses were carried out by using a 450-W Hanovia mercury-discharge lamp contained in a water-cooled quartz immersion well.

If not otherwise described, all reactions and subsequent manipulations were carried out in a nitrogen atmosphere, primarily as a precautionary measure, since neither reactants nor products were noticeably sensitive to oxygen over short periods of time.

Preparations of $Fe(SPh)(L)(L')(\eta\text{-}C_5R_5)$ Complexes. Preparations of $Fe(SPh)(CO)(L)(\eta\text{-}C_5R_5)$ (R = H, Me) and $Fe(SPh)(L)_2(\eta\text{-}C_5H_5)$ compounds were generally accomplished by reactions of $Fe(SPh)(CO)_2(\eta\text{-}C_5R_5)$ with the ligand, L. This procedure is described in detail in the preparation of $Fe(SPh)(CO)(PPh_2Me)(\eta\text{-}C_5H_5)$, below. An alternate procedure for the preparation of the monosubstituted complexes, using the reaction of NaSPh and $FeI(CO)(L)(\eta\text{-}C_5H_5)$ is also described.

Preparation of $Fe(SPh)(CO)(PPh_2Me)(\eta\text{-}C_5H_5)$. Samples of $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$ (2.0 g, 7.0 mmol) and PPh_2Me (0.91 g, 4.6 mmol) were dissolved in 50 mL of toluene. The solution was heated at reflux for 2.5 h. After cooling, the solution was filtered. Hexane was added to the filtrate, causing the precipitation of 1.46 g of a brown powder. This was recrystallized by dissolving the solid in toluene, adding petroleum ether to the point of incipient precipitation, and chilling. The crystalline product was filtered and dried, in vacuo: 1.03 g (50%); mp 144.5–145 °C.

Anal. Calcd for $C_{25}H_{23}FePOS$: C, 65.61; H, 5.07; S, 6.99; mol wt 458. Found: C, 65.34; H, 5.02; S, 7.05; mol wt 461.

The following compounds were prepared similarly (except as noted).

$Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5H_5)$: red crystals (60%); mp 103–106 °C; mol wt (by MS peak match) calcd for $^{12}C_{15}{}^{1}H_{19}{}^{56}Fe^{16}O^{31}P^{32}S$ 334.0243, found 334.0243.

$Fe(SPh)(CO)(P(OPh)_3)(\eta\text{-}C_5H_5)$: red crystals (62%); mp 107.5–109 °C. Anal. Calcd for $C_{30}H_{20}FeO_4PS$: C, 63.39; H, 4.44, S, 5.64; mol wt 568. Found: C, 63.45; H, 4.49; S, 5.53; mol wt 530.

$Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5H_5)$. This compound was quite soluble in the designated solvents and was recrystallized from petroleum ether by cooling at −78 °C: 34%; mp 50.5–54.5 °C; mol wt calcd for $^{12}C_{18}{}^{1}H_{25}{}^{56}Fe^{16}O_4{}^{31}P^{32}S$ 424.0560, found 424.0459.

$Fe(SPh)(m\text{-}CNC_6H_4OMe)_2(\eta\text{-}C_5H_5)$. Two equivalents of ligand was used; recrystallization from CH_2Cl_2–petroleum ether gave dark red crystals: 63%; mp 81.0–83.5 °C. Anal. Calcd for $C_{27}H_{24}FeN_2O_2S$: C, 65.36; H, 4.88. Found: C, 64.81; H, 5.04.

$Fe(SPh)(m\text{-}CNC_6H_4CF_3)_2(\eta\text{-}C_5H_5)$: brown powder, recrystallized from CH_2Cl_2–petroleum ether (93%); mp 85–89 °C; mol wt calcd for $^{12}C_{27}{}^{1}H_{18}{}^{19}F_6{}^{56}Fe^{14}N_2{}^{32}S$ 572.0440, found 572.0442.

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Alternative Preparation of Fe(SPh)(CO)(PPh$_2$Me)(η-C$_5$H$_5$) and the Preparation of Fe(SPh)(CO)(PPhMe$_2$)(η-C$_5$H$_5$). This method is similar to that used to prepare Fe(SPh)(CO)$_2$(η-C$_5$H$_5$).[10] A solution of PhS$^-$ was prepared by adding 0.51 g (4.7 mmol) of PhSH to a suspension of 0.21 g (4.4 mmol) of a 50% dispersion of NaH/paraffin in 50 mL of THF. A sample of FeI(CO)(PPh$_2$Me)(η-C$_5$H$_5$) (2.0 g, 4.2 mmol) was then added, and the mixture was heated at reflux for 10.5 h. After cooling, the resulting solution was evaporated to dryness under reduced pressure. The solid residue was extracted with toluene, and this solution was filtered to remove NaI. The filtrate was concentrated to a small volume and chilled at −20 °C to give crystals of the product, 0.55g (20%).

The preparation of Fe(SPh)(CO)(PPhMe$_2$)(η-C$_5$H$_5$) was accomplished through a similar reaction: 65%; mp 110–113 °C. Anal. Calcd for C$_{20}$H$_{21}$FeOPs: C, 60.61; H, 5.35; Fe, 14.09; S, 8.09. Found: C, 60.38; H, 5.33; Fe, 14.11; S, 7.81.

Preparation of Fe(SPh)(CO)$_2$(η-C$_5$Me$_5$). Samples of [Fe(CO)$_2$(η-C$_5$Me$_5$)]$_2$ (1.5 g, 3.0 mmol) and PhSSPh (0.69 g, 3.2 mmol) were dissolved in 250 mL of toluene, and the solution was subjected to UV photolysis for 30 min. At this time, an infrared spectrum of the reaction mixture indicated complete absence of starting material; the desired product was the primary component of the solution that also contained a small amount of [Fe(SPh)(CO)(C$_5$Me$_5$)]$_2$. The solution was filtered and solvent evaporated to about 30 mL. About 70 mL of petroleum ether was added. The solution was maintained overnight at −20 °C, during which time the product precipitated. The red crystalline product was filtered and dried under vacuum. It was recrystallized in a similar manner from toluene–petroleum ether: 1.5 g (69%); mp 94–96 °C; mol wt (by MS peak match) calcd for ^{12}C$_{18}$^{1}H$_{20}$^{56}Fe^{16}O$_2$^{32}S 356.0528, found 356.0533.

The sulfido-bridged dimeric species [Fe(SPh)(CO)(η-C$_5$Me$_5$)]$_2$ in the filtrate was identified by its ν(CO) values; it was not isolated or characterized.

Two methods were used to prepare monosubstituted derivatives of Fe(SPh)(CO)$_2$(η-C$_5$Me$_5$). Examples are given below.

Preparation of Fe(SPh)(CO)(PMe$_3$)(η-C$_5$Me$_5$). A solution of 1.0 g of [Fe(CO)$_2$(η-C$_5$Me$_5$)]$_2$ (2.0 mmol), 0.46 g of PhSSPh (2.1 mmol), and 0.44 mL of PMe$_3$ (4.3 mmol) in 250 mL of toluene was subjected to photolysis for 45 min. The solution was filtered and solvent volume reduced to about 30 mL. Addition of petroleum ether followed by cooling at −20 °C produced 1.3 g (78%) of the red-purple crystalline product. This was recrystallized from the same solvent mixture: mp 123–126 °C dec; mol wt (by MS peak match) calcd for ^{12}C$_{20}$^{1}H$_{29}$^{56}Fe^{16}O^{31}P^{32}S 404.1019, found 404.1028.

Other compounds prepared by this procedure are listed below.

Fe(SPh)(CO)(PPhMe$_2$)(η-C$_5$Me$_5$): red needles (50%); mp 128–130 °C; mol wt (by MS peak match) calcd for ^{12}C$_{25}$^{1}H$_{31}$^{56}Fe^{16}O^{31}P^{32}S 466.1175, found 466.1183.

Fe(SPh)(CO)(PPh$_2$Me)(η-C$_5$Me$_5$): green solid (76%); mp 162–164 °C. Anal. Calcd for C$_{30}$H$_{33}$FeOPS: C, 68.18; H, 6.25. Found: C, 67.97; H, 6.52.

Preparation of Fe(SPh)(CO)(P(OEt)$_3$)(η-C$_5$Me$_5$). Samples of Fe(SPh)(CO)$_2$(η-C$_5$Me$_5$) (1.0 g, 2.8 mmol) and P(OEt)$_3$ (0.50 mL, 2.9 mmol) were dissolved in 250 mL of toluene. Following photolysis for 1 h, the solution was filtered and the solvent removed under vacuum. The resulting oil was placed on an alumina chromatographic column. With use of a 4:1 petroleum ether:CH$_2$Cl$_2$ solution as eluent, two bands developed. The initial yellow band (starting material) was followed by a large red band that was collected. Reduction of solvent volume (to ~25 mL) and chilling at −20 °C gave 1.16 g of the red crystalline product: 83%; mp 72–73 °C; mol wt (by MS peak match) calcd for ^{12}C$_{23}$^{1}H$_{35}$^{56}Fe^{16}O$_4$^{31}P^{32}S 494.1334, found 494.1340.

Oxidations of Fe(SPh)(L)(L′)(η-C$_5$R$_5$) Complexes. The general procedure used for these oxidations is illustrated by the example below.

Preparation of [Fe(SPh)(CO)(PPh$_2$Me)(η-C$_5$H$_5$)]BF$_4$. Samples of Fe(SPh)(CO)(PPh$_2$Me)(η-C$_5$H$_5$) (0.50 g, 1.1 mmol) and AgBF$_4$ (9.19 g, 0.97 mmol) were placed in a Schlenk tube. About 20 mL of deaerated acetone (saturated with N$_2$ by bubbling this gas through the solvent) was added. The solution turned blue immediately. After it was stirred for 10 min, the solution was filtered under positive nitrogen pressure. Ethyl ether (~50 mL) was added to the filtrate; chilling this solution at −20 °C overnight gave a dark solid. This product was filtered and immediately recrystallized from the same solvent mixture: 0.14 g (24%); mp 95.5–101 °C; μ_{eff} = 2.07 μ_{B}. Anal. Calcd for C$_{25}$H$_{23}$H$_{23}$BF$_4$FeOPS: C, 55.07; H, 4.26; S, 5.88. Found: C, 54.86; H, 4.62; S, 5.76.

Other compounds prepared by this procedure are listed below.

[Fe(SPh)(CO)(PMe$_3$)(η-C$_5$H$_5$)]BF$_4$: black microcrystals (35%): mp 142–144 °C; μ_{eff} = 0.83 μ_{B}. Anal. Calcd for C$_{16}$H$_{19}$BF$_4$FeOPS: C, 42.79; H, 4.56; S, 7.61. Found: C, 42.88; H, 4.78; S, 7.73.

[Fe(SPh)(CO)(PPhMe$_2$)(η-C$_5$H$_5$)]BF$_4$. Instead of acetone, CH$_2$Cl$_2$ was used as a solvent and for subsequent recrystallization: dark solid (85%); mp 174–176 °C; μ_{eff} = 1.61 μ_{B}. Anal. Calcd for C$_{20}$H$_{21}$BF$_4$FeOPS: C, 49.72; H, 4.39; S, 6.64. Found: C, 49.57; H, 4.42; S, 6.65.

[Fe(SPh)(CO)(P(OPh)$_3$)(η-C$_5$H$_5$)]PF$_6$. A stronger oxidizing agent, NOPF$_6$, was used. The red solution of the starting material remained red, but NO gas evolution indicated that a reaction had occurred. Recrystallization of the brick red product was carried out by using CH$_3$CN and ethyl ether; the compound is less soluble than other products in most other solvents: 67%; mp 147–149 °C; μ_{eff} = 1.61 μ_{B}. Anal. Calcd for C$_{30}$H$_{25}$F$_6$FeO$_4$P$_2$S: C, 50.50; H, 3.54; S, 4.49. Found: C, 50.58; H, 3.74; S, 4.51.

[Fe(SPh)(CO)(P(OEt)$_3$)(η-C$_5$H$_5$)]PF$_6$. A preparation similar to that for the P(OPh)$_3$ compound was used: red powder recrystallized from CH$_2$Cl$_2$–ethyl ether (32%); mp 136–138.5 °C; μ_{eff} = 0.53 μ_{B}. Anal. Calcd for C$_{18}$H$_{25}$F$_6$FeO$_4$P$_2$S: C, 37.39; H, 4.44; S, 5.63. Found: C, 38.01; H, 4.43, S, 5.18.

[Fe(CO)$_2$(η-C$_5$H$_5$)(μ-Ph$_2$S$_2$)Fe(CO)$_2$(η-C$_5$H$_5$)](PF$_6$)$_2$. This compound was prepared with NOPF$_6$ as an oxidizing agent. The solution changed color from red to yellow-orange, and NO gas was evolved. The product, an orange powder, was obtained in 70% yield. It was soluble only in CH$_3$CN and was recrystallized from mixtures of this solvent and ethyl ether. Recrystallizations had to be performed rapidly to minimize decomposition of solutions in this solvent: mp 160–165 °C; μ_{eff} = 0.35 μ_{B} (as dimer). Since a ^{1}H NMR spectrum was obtained, this compound is assumed to be diamagnetic in solution.

When the reaction of NOPF$_6$ and Fe(SPh)(CO)$_2$(η-C$_5$H$_5$) was carried out at −78 °C, the solution became intensely purple. The purple color persists at this temperature over 30 min but fades to orange-yellow upon warming. Anal. Calcd for C$_{26}$H$_{20}$F$_{12}$Fe$_2$O$_4$P$_2$S$_2$: C, 36.22; H, 2.34; S, 7.44. Found: C, 36.25; H, 2.22; S, 7.39.

An experiment was carried out in which this product was dissolved in CD$_3$CN and NMR spectra of the solution were recorded at various time intervals. The ^{1}H NMR spectrum changes over several hours from that of this compound (Table I) to a composite spectrum containing resonances for [Fe(CO)$_2$(PhSSPh)(η-C$_5$H$_5$)]PF$_6$ (vide infra) and [Fe(CO)$_2$(CD$_3$CN)(η-C$_5$H$_5$)]PF$_6$.

[Fe(SPh)(m-CNC$_6$H$_4$OMe)$_2$(η-C$_5$H$_5$)]BF$_4$. The initial red solution became an intensely purple color. The product, a dark powder, was recrystallized from CH$_2$Cl$_2$–ethyl ether: 40%; mp 81.5–83 °C; μ_{eff} = 1.40 μ_{B}. Anal. Calcd for C$_{27}$H$_{24}$BF$_4$FeN$_2$O$_2$S: C, 55.6; H, 4.18; N, 4.80. Found: C, 55.51; H, 4.29; N, 4.82.

[Fe(SPh)(m-CNC$_6$H$_4$CF$_3$)$_2$(η-C$_5$H$_5$)]BF$_4$: prepared similarly, 30% yield; mp 132–135 °C; μ_{eff} = 0.50 μ_{B}. Anal. Calcd for C$_{27}$H$_{18}$BF$_{10}$FeN$_2$S: C, 49.18; H, 2.75; N, 4.25. Found: C, 49.36; H, 2.73; N, 4.12.

[Fe(SPh)(CO)(PMe$_3$)(η-C$_5$Me$_5$)]PF$_6$: dark green crystals, prepared by using AgPF$_6$ as the oxidizing agent (47%); mp 133–135 °C; μ_{eff} = 2.28 μ_{B}. Anal. Calcd for C$_{20}$H$_{29}$F$_6$FeOP$_2$S: C, 43.72; H, 5.28. Found: C, 43.89; H, 5.18.

[Fe(SPh)(CO)(PPhMe$_2$)(η-C$_5$Me$_5$)]PF$_6$: black microcrystals (58%); mp 146–148 °C; μ_{eff} = 2.04 μ_{B}. Anal. Calcd for C$_{25}$H$_{31}$F$_6$FeOP$_2$S: C, 49.10; H, 5.07. Found: C, 49.21; H, 5.06.

[Fe(SPh)(CO)(PPh$_2$Me)(η-C$_5$Me$_5$)]PF$_6$: black crystals (65%): mp 113–116 °C dec; μ_{eff} = 2.26 μ_{B}. Anal. Calcd for C$_{30}$H$_{33}$F$_6$FeOP$_2$S: C, 53.49; H, 4.90. Found: C, 53.28; H, 4.93.

[Fe(CO)$_2$(η-C$_5$Me$_5$)(μ-Ph$_2$S$_2$)Fe(CO)$_2$(η-C$_5$Me$_5$)](PF$_6$)$_2$. This compound was prepared by using AgPF$_6$ as an oxidant (NOPF$_6$ was used for the analogous reaction of the C$_5$H$_5$ complex). The orange crystalline complex, obtained in 67% yield, darkens at 142 °C and melts at 180 °C; μ_{eff} = 0.91 μ_{B} (as dimer). A ^{1}H NMR was obtained, suggesting that in solution this compound is diamagnetic. Anal. Calcd for C$_{36}$H$_{40}$F$_{12}$Fe$_2$O$_4$P$_2$S$_2$: C, 43.11; H, 3.99. Found: C, 43.28; H, 4.05.

Preparation of [Fe(CO)$_2$(η-C$_5$H$_5$)(μ-Ph$_2$S$_2$)Fe(CO)$_2$(η-C$_5$H$_5$)](BF$_4$)$_2$ from [Fe(CO)$_2$(THF)(η-C$_5$H$_5$)]BF$_4$ and PhSSPh. A solution of [Fe(CO)$_2$(THF)(η-C$_5$H$_5$)]BF$_4$ (3.0 g, 8.9 mmol) and PhSSPh (0.66 g, 3.0 mmol) in 50 mL of CH$_2$Cl$_2$ was stirred at room temperature for 24 h. Ethyl ether was then added, causing precipitation of 0.53 g of the product (23%), which was identified by comparison of infrared and ^{1}H NMR spectra with data for the PF$_6$$^-$ complex.

Preparation of [Fe(CO)$_2$(PhSSPh)(η-C$_5$H$_5$)]BF$_4$. Equimolar amounts of [Fe(CO)$_2$(THF)(η-C$_5$H$_5$)]BF$_4$ (1.0 g, 3.0 mmol) and PhSSPh (0.65 g, 3.0 mmol) were dissolved in 50 mL of CH$_2$Cl$_2$, and the solution was stirred for 16 h. Filtration was carried out and ethyl ether added to the filtrate, precipitating the orange product, which was crystallized from the same solvent mixture: 59%; mp 150–155 °C. Anal. Calcd for C$_{19}$H$_{15}$BF$_4$FeO$_2$S$_2$: C, 47.33; H, 3.14; Fe, 11.58. Found: C, 47.04; H, 3.09; Fe, 11.58.

Preparation of [Fe(CO)$_2$(MeSSMe)(η-C$_5$H$_5$)]BF$_4$: prepared similarly, as yellow-brown plates (96%): mp 87–92 °C. Anal. Calcd for C$_9$H$_{11}$BF$_4$FeO$_2$S$_2$: C, 30.19; H, 3.10; Fe, 15.62. Found: C, 30.41; H, 3.10; Fe, 15.25.

Preparation of [Fe(SPh)(P(OPh)$_3$)$_2$(η-C$_5$H$_5$)]BF$_4$. A solution containing 2.0 g (7.0 mmol) of Fe(SPh)(CO)$_2$(η-C$_5$H$_5$) and 4.6 mL (5.4 g, 17.5 mmol) of P(OPh)$_3$ in 250 mL of toluene was subjected to UV radiation for 5 h, after which time an IR spectrum showed no ν(CO) absorption. Filtration and evaporation of the solvent produced a red oil that refused to crystallize despite repeated attempts. This oil was dissolved in acetone and treated (in one instance) with 1.36 g (7.0 mmol) of AgBF$_4$, the solution becoming blue. The solution was filtered and concentrated and ethyl ether added to cause precipitation of the black crystalline product. This was recrystallized from acetone–ethyl ether: 0.77 g (12%); mp 114–116 °C; $\mu_{\text{eff}} = 1.98$ μ_B. Anal. Calcd for C$_{47}$H$_{40}$BF$_4$FeO$_6$P$_2$S: C, 60.21; H, 4.31; S, 3.42. Found: C, 59.98; H, 4.49; S, 3.41.

An alternate method was also used to prepare this compound. A mixture of FeI(P(OPh)$_3$)$_2$(η-C$_5$H$_5$) (1.0 g, 1.2 mmol) and AgBF$_4$ (0.23 g, 1.2 mmol) in 25 mL of CH$_2$Cl$_2$ was stirred for 1 min. Then AgI was removed by filtration and PhSH (0.34 g, 3.1 mmol) added to the filtrate. After it was stirred for 15 min, the red solution was filtered and solvent partially evaporated. Ethyl ether was added and the solution chilled at −20 °C for several hours during which time a blue color developed and a black precipitate formed: 0.76 g (69%).

Attempted Oxidation of FeI(CO)$_2$(η-C$_5$H$_5$). A sample of FeI(CO)$_2$(η-C$_5$H$_5$) (2.0 g, 6.6 mmol) in 25 mL of acetone was reacted with 0.90 g (5.1 mmol) of NOPF$_6$. (This condition was similar to those used to oxidize Fe(SPh)(CO)$_2$(η-C$_5$H$_5$).) Gas evolution was seen, and the solution became red. Ethyl ether was added and the solution cooled, causing precipitation of 0.94 g (46%) of violet [Fe(CO)$_2$(η-C$_5$H$_5$)(μ-I)Fe(CO)$_2$(η-C$_5$H$_5$)]PF$_6$, mp 155–162 °C. The identity of the product was verified by comparison of ^{1}H NMR, IR, and melting point data with data on a sample of this compound prepared according to the literature method.[19]

Reduction of [Fe(CO)$_2$(η-C$_5$H$_5$)(μ-Ph$_2$S$_2$)Fe(CO)$_2$(η-C$_5$H$_5$)](PF$_6$)$_2$. A sample of this complex (2.0 g, 2.3 mmol) was dissolved in 15 mL of CH$_3$CN and the orange solution transferred to a flask containing Na/Hg, previously prepared from 0.18 g of Na and 1.0 mL of Hg. The color changed rapidly to red. After 10 min, the solution was filtered. Solvent was evaporated from the filtrate, and the solid remaining was chromatographed on Florisil. A small red band, eluted with a 1:1 petroleum ether–toluene solution, was shown by IR to contain [Fe(CO)$_2$(η-C$_5$H$_5$)]$_2$. A larger red band eluted with toluene; evaporation and recrystallization of the solid yielded 0.55 g (41%) of Fe(SPh)(CO)$_2$(η-C$_5$H$_5$).

Reduction of [Fe(CO)$_2$(PhSSPh)(η-C$_5$H$_5$)]BF$_4$ also gave Fe(SPh)(CO)$_2$(η-C$_5$H$_5$) in 57% isolated yield.

Discussion

Preparation of cyclopentadienyl(benzenethiolato)iron complexes, precursors in this study, are described by eq 1 and 2.

$$\text{Fe(SPh)(CO)}_2(\eta\text{-C}_5\text{H}_5) + \text{L} \rightarrow \text{Fe(SPh)(CO)(L)}(\eta\text{-C}_5\text{H}_5) + \text{CO} \quad (1)$$

$$\text{L} = \text{PMe}_3,\ \text{PPhMe}_2,\ \text{PPh}_2\text{Me},\ \text{P(OPh)}_3,\ \text{P(OEt)}_3$$

$$\text{Fe(SPh)(CO)}_2(\eta\text{-C}_5\text{H}_5) + 2\text{L} \rightarrow \text{Fe(SPh)(L)}_2(\eta\text{-C}_5\text{H}_5) + 2\text{CO} \quad (2)$$

$$\text{L} = m\text{-CNC}_6\text{H}_4\text{OMe},\ m\text{-CNC}_6\text{H}_4\text{CF}_3$$

Generally these reactions were carried out in toluene solution, under reflux conditions over several hours. Air-stable, red to brown crystalline products, soluble in typical organic solvents, are obtained in moderate (isolated) yields. For the monosubstituted complexes, a single ν(CO) absorption occurs in the 1900–2000-cm^{-1} range. Apart from the color, these compounds resemble known complexes of the formula FeX(CO)(L)(η-C$_5$H$_5$) (X = Cl, Br, I).

Table II. Qualitative Observations on the Equilibrium between Monomeric [Fe(SPh)(L)(L′)(η-C$_5$H$_5$)]Y and Dimeric [Fe(CO)$_2$(η-C$_5$H$_5$)(μ-PhSSPh)Fe(CO)$_2$(η-C$_5$H$_5$)]Y$_2$

complex	position of equilibrium[a]
L, L′ = CO	dimer only, at 25 °C; dimer as solid
L = CO, L′ = phosphites	monomer $\rightleftharpoons$ dimer at 25 °C[b]
L = CO, L′ = phosphines	monomer at 25 °C; monomer $\rightleftharpoons$ dimer at −78 °C[b]
L, L′ = CNR	monomer $\rightleftharpoons$ dimer at 25 °C
L, L′ = phosphite or phosphine	monomer only at 25 °C; monomer and one unpaired electron in solid

[a] In acetone solution except as noted; based on the color of solution. [b] Solids have magnetisms intermediate between zero and one unpaired electron.

An alternate preparative route to two of these complexes utilized a reaction between FeI(CO)(L)(η-C$_5$H$_5$) (L = PPh$_2$Me, PPhMe$_2$) and PhS$^-$. This route seemed to be generally satisfactory but was not extended to the synthesis of other members of this series.

The analogous preparation of (pentamethylcyclopentadienyl)benzenethiolato)iron compounds required the initial synthesis of Fe(SPh)(CO)$_2$(η-C$_5$Me$_5$). This previously unknown red crystalline compound was obtained in good yield by the reaction of [Fe(CO)$_2$(η-C$_5$Me$_5$)]$_2$ and PhSSPh under UV photolysis:

$$[\text{Fe(CO)}_2(\eta\text{-C}_5\text{Me}_5)]_2 + \text{PhSSPh} \xrightarrow{h\nu} 2\text{Fe(SPh)(CO)}_2(\eta\text{-C}_5\text{Me}_5) \quad (3)$$

The preparative method is similar to that used by King and Bisnette[20] to prepare Fe(SMe)(CO)$_2$(η-C$_5$H$_5$). Under the conditions chosen here (UV, 0.5 h, toluene), the desired species was the primary product. The sulfido-bridged dimer [Fe(SPh)(CO)(η-C$_5$Me$_5$)]$_2$ was also formed, presumably by CO loss from the monomer, but the amount was small and did not create any difficulty in the procedure. For comparison, Fe(SPh)(CO)$_2$(η-C$_5$H$_5$) has been shown to lose CO to form [Fe(SPh)(CO)(η-C$_5$H$_5$)]$_2$; photolysis for 6 h in benzene caused approximately 50% conversion to the dimer.[21] Yields of the cyclopentadienyl and pentamethylcyclopentadienyl species are comparable on a qualitative level.

It is possible to substitute one carbonyl group in Fe(SPh)(CO)$_2$(η-C$_5$Me$_5$) by a phosphine or phosphite ligand to produce the desired precursor in this study. In practice we found it simpler to carry out the photolysis of [Fe(CO)$_2$(η-C$_5$Me$_5$)]$_2$, PhSSPh, and the ligand together to produce these species. This procedure led to good yields of product while obviating the need for isolation of Fe(SPh)(CO)$_2$(η-C$_5$Me$_5$).

The pentamethylcyclopentadienyl compounds resemble their cyclopentadienyl analogues in most respects. Both possess a single strong ν(CO) absorption about 20 cm^{-1} lower than the cyclopentadienyl species, reflecting the great donor power of the η^5-C$_5$Me$_5$ ligand group.

Oxidations of the various thiolato–metal complexes were usually carried out with AgPF$_6$ or AgBF$_4$, which also furnished the counterion to the ionic product. In these procedures a distinct color change was usually observed, and silver metal precipitated from the reaction system:

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(19) Fischer, E. O.; Moser, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1965**, *20B*, 184–187.

(20) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1965**, *4*, 482–485.

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$$\mathrm{Fe(SPh)(CO)(L)(\eta\text{-}C_5R_5) + AgY \rightarrow [Fe(SPh)(CO)(L)(\eta\text{-}C_5R_5)]Y + Ag} \quad (4)$$

$R = Me$; $Y = PF_6$;

$L = CO, PMe_3, PPhMe_2, PPh_2Me, P(OEt)_3$

$R = H$; $Y = BF_4$; $L = PMe_3, PPhMe_2, PPh_2Me$

Disubstituted complexes, $Fe(SPh)(L)_2(\eta\text{-}C_5H_5)$ ($L = m\text{-}CNC_6H_4OMe$, $m\text{-}CNC_6H_4CF_3$, $P(OPh)_3$), were oxidized in a similar manner. In three instances with $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ complexes ($L = CO$, $P(OPh)_3$, $P(OEt)_3$), a stronger oxidizing agent, $NOPF_6$, was used as an oxidant. These reactions occurred with observable gas (NO) evolution:

$$\mathrm{Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5) + NOPF_6 \rightarrow [Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)]PF_6 + NO} \quad (5)$$

$L = CO, P(OEt)_3, P(OPh)_3$

The products of these oxidation reactions have been the primary focus of this project. As solids, they range in color from red to very dark blue-black. The pattern of $\nu(CO)$ absorptions for the monosubstituted species is shifted to higher frequencies, relative to values for the diamagnetic 18-electron precursor. In $[Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)]BF_4$ complexes this shift is over 40 cm^{-1} while in the pentamethylcyclopentadienyl series the shift is about 80 cm^{-1}. It is of interest to note that trends of $\nu(CO)$ frequencies in the two series $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ and $[Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)]X$ (for L = phosphines) are in the opposite order. In the neutral complexes these values decrease with increased ligand donor ability ($PPh_2Me > PPhMe_2 > PMe_3$), while in the cationic series the reverse is true ($PMe_3 > PPhMe_2 > PPh_2Me$). The same observation applies to the series of pentamethylcyclopentadienyl complexes. The shift for the two dicarbonyl species, $[Fe(SPh)(CO)_2(C_5R_5)]Y$, upon oxidation, was less: compare $\nu(CO)$ for $Fe(SPh)(CO)_2(C_5Me_5)$ at 2005 and 1965 cm^{-1} to $\nu(CO)$ in the oxidized species, 2008 and 1980 cm^{-1}.

The dicarbonyl species are orange and paramagnetic as solids ($\mu_{eff} = 0.35$ and 0.91 μ_B) but apparently are diamagnetic in solution as NMR spectra can be obtained. The other compounds listed are dark and paramagnetic, with magnetic moments between about 0.5 and 2.3 μ_B. The unusual μ_{eff} values and the differences in color between solids were the first clues to the unusual behavior of many members of this series of compounds. Further study revealed that colors of solutions of several compounds were dependent on temperature and concentration. Blue solutions of the phosphine-substituted compounds $[Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)]BF_4$ ($L = PMe_3$, $PPhMe_2$, PPh_2Me) in acetone at room temperature change to red when the solution is cooled to −78 °C. This change is reversed when the solution is warmed. Acetone solutions of the analogous phosphite complexes, $[Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)]BF_4$, are red at room temperature in higher concentration and change to blue when diluted. Several analogous d^5 low-spin (paramagnetic, $\mu_{eff} = 1.9$ μ_B) iron complexes such as $[FeX(P(OPh)_3)_2(\eta\text{-}C_5H_5)]^+$ (X = SPh, I) are known to be blue whereas red is a color typically encountered with diamagnetic 18-electron iron compounds such as the precursor species in this project. Thus, these data suggest the existence of equilibrium between a blue, paramagnetic, 17-electron monomer and a red, diamagnetic, 18-electron dimer.

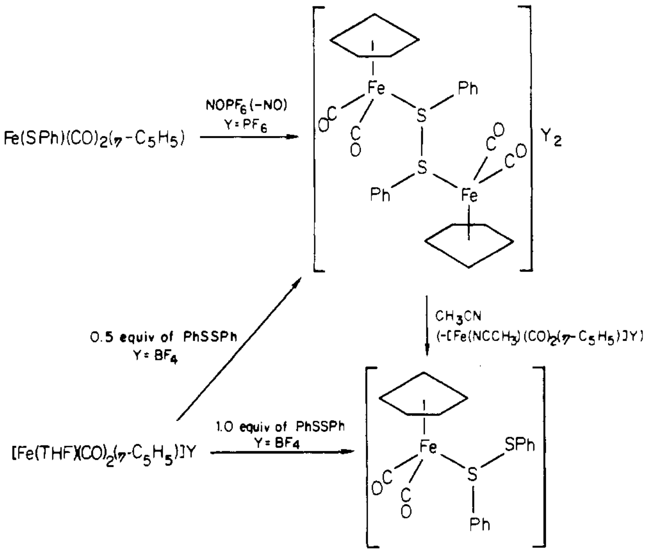
Several structures for an 18-electron diamagnetic dimer were considered. The most reasonable structure involves dimerization by formation of a sulfur–sulfur bond, giving a structure having a bridging diphenyl disulfide ligand. The structure had no obvious conceptual disadvantages on the basis of coordination geometries of the metal and ligand atoms. We rejected a dimeric structure having a metal–metal bond on the basis that this structure would require a coordination number and geometry for iron that has few precedents in organometallic chemistry. Dimerization through other ligand groups such as the $\eta\text{-}C_5R_5$ or CO groups can be ruled out by infrared and/or NMR data on the dicarbonyl complex.

Much stronger support for this structure was obtained by an independent synthesis of $[Fe(C_5H_5)(CO)_2(\mu\text{-}PhSSPh)Fe(CO)_2(\eta\text{-}C_5H_5)](BF_4)_2$ from a reaction between $[Fe(THF)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ and PhSSPh in a 2:1 molar ratio. Ample precedent is available for displacement of THF by PhSSPh, since it is well-known that the THF ligand in the starting complex is readily displaced by many different ligands.[9] Under the mild conditions for this reaction (25 °C, 24 h, CH_2Cl_2), it seems unlikely that the sulfur–sulfur bond in the disulfide would have been cleaved.

When $[Fe(THF)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ and RSSR (R = Ph, Me) are allowed to react in a 1:1 molar ratio, a product of the stoichiometry $[Fe(RSSR)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ was obtained. These complexes presumably contain a disulfide molecule as a monodentate ligand, coordinating to iron via one sulfur atom. Infrared data ($\nu(CO)$) are similar to those of other $[Fe(L)(CO)_2(\eta\text{-}C_5H_5)]^+$ complexes, and ^1H NMR data on the MeSSMe complex show two singlet methyl proton resonances, in accord with dissimilar methyl environments in this structure.

When $[Fe(\eta\text{-}C_5H_5)(CO)_2(\mu\text{-}PhSSPh)Fe(CO)_2(\eta\text{-}C_5H_5)](BF_4)_2$ is dissolved in CD_3CN, a slow reaction ensues, giving $[Fe(PhSSPh)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ and $Fe(NCCD_3)(CO)_2(\eta\text{-}C_5H_5)]BF_4$. Formation of a product with an intact disulfide ligand under mild conditions further supported the assumption that the dimer contains an intact PhSSPh ligand.

This chemistry is summarized in the following equations:



Success in isolating organometallic complexes containing organic disulfide ligands in this work is thought to be a consequence of the very mild conditions employed. Many reactions of organometallic compounds with organic disulfides have been reported in the literature previously, but in each instance cleavage of the sulfur–sulfur bond has been observed to occur and the resulting products incorporate the thiolate group as a bridging or terminal ligand. For example, reactions between $Mn_2(CO)_{10}$[22] or $MnH(CO)_5$[23] and several disulfides usually produce the dinuclear species $Mn_2(SR)_2(CO)_8$ (R = Me, Et, Bu, CF_3). In this work, such a reaction between $[Fe(CO)_2(\eta\text{-}C_5Me_5)]_2$ and PhSSPh was used to produce $Fe(SPh)(CO)_2(\eta\text{-}C_5Me_5)$. Many examples involving other metals could also be cited. Usually such reactions have been carried out

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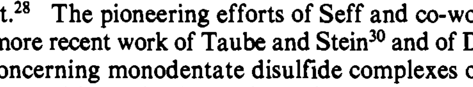
(23) Treichel, P. M.; Morris, J. H.; Stone, F. G. A. *J. Chem. Soc.* **1963**, 720–723.

at elevated temperatures or by photolysis. In contrast the oxidation and substitution reactions described in this paper were carried out at room temperature.

Complexes having bridging disulfide ligands have rarely been encountered in organometallic chemistry. The only confirmed examples of such species are several compounds of rhenium $Re_2Br_2(CO)_6(RSSR)$ (R = Me, Ph)[24] and of platinum $Pt_2X_2Me_6(MeSSMe)$ (X = Cl, Br, I);[25] in addition, disulfide bridging ligands are suspected in two other compounds.[26,27] In the rhenium and platinum species the metals are bridged by two halide ligands as well as the disulfide, so the structures are somewhat dissimilar to the compounds reported here. To our knowledge, no other examples of organometallic complexes with monodentate disulfide ligands are yet known. In the broader area of coordination chemistry, however, examples of both structural types are somewhat more abundant.[28] The pioneering efforts of Seff and co-workers[29] and the more recent work of Taube and Stein[30] and of Deutsch et al.[31] concerning monodentate disulfide complexes of nickel(II), copper(I), ruthenium(II), and cobalt(III) may be identified. There has been a recent crystal structure study on a bridging disulfide complex $Cu_2I_2(PhSSPh)$.[32] Much of the previous work was undertaken because of an interest in the effect of metals on the thiol–disulfide redox system in sulfur-containing amino acids in biological systems.

It appears that complexes with organic disulfide ligands (terminal or bridging) possess a low thermodynamic stability with respect to displacement of the ligand. Such an observation is also applicable to complexes of organic sulfides, R_2S, and probably reflects the low basicity of sulfur in these compounds. On the other hand, complexes with thiolate (RS) groups bridging two or three metals appear to be quite robust. The abundance of complexes with thiolate ligand groups is not surprising, since most reactions between metal carbonyls and disulfides have been run under conditions that seem likely to favor cleavage of the sulfur–sulfur bond of a disulfide.

The mechanism of metal-catalyzed cleavage of disulfides[33,34] is generally believed to be a two-step process, in which initial coordination of an electrophile at one sulfur atom is followed by nucleophilic attack at the second sulfur:



Metal complexes having monodentate disulfide ligands ought to be susceptible to sulfur–sulfur bond cleavage by nucleophiles, and this fact should restrict conditions under which such complexes could be prepared and isolated.

Our work suggests that metal coordination in these compounds weakens the sulfur–sulfur bond with respect to homolytic cleavage. The extent of weakening depends on the ligand environment at the metal site, as it affects the degree of electron richness at the metal. Qualitative observations are presented in Table II for the monomer–dimer equilibria for $[Fe(SPh)(L)(L')(\eta\text{-}C_5H_5)]^+$ species. The effect of L and L′ on the position of this equilibrium is striking. Although steric criteria probably contribute to these results in some way, the dominant effect seems to be electronic. It appears that a higher degree of dissociation to the paramagnetic monomer (by cleavage of the sulfur–sulfur bond) results when the better donor ligands are substituted into the coordination sphere of iron. In species with better donor ligands, the metal probably transfers electron density of the disulfide ligand into an orbital that is presumed to be antibonding with respect to the sulfur–sulfur bond.

It also seems appropriate to comment at this time on the formation of the bridged disulfide species by an oxidative process. Ordinarily in an oxidation, it is assumed that electron loss occurs from the highest occupied molecular orbital (HOMO) in a species. This implies that in the complexes $Fe(SPh)(CO)_2(\eta\text{-}C_5R_5)$, at least, the HOMO is the sulfur lone pair and not a metal-centered orbital. Loss of one electron at sulfur would lead to a radical species with the unpaired electron primarily localized at the ligand (sulfur), and dimerization via sulfur–sulfur bond formation would logically follow. The assumption that the lone-pair orbital on sulfur is the HOMO in these complexes is not unreasonable. It has been determined in a PES study and accompanying MO calculations on $MnX(CO)_5$ (X = Cl, Br, I) compounds that the HOMO in these species is a halogen lone pair.[35] It is reasonable to suppose that in $Mn(SR)(CO)_5$ (and also in $Fe(SR)(CO)_2(\eta\text{-}C_5H_5)$) the HOMO would be a ligand lone pair.

Most metal complexes are oxidized by loss of a metal electron, of course. However, redox chemistry based on ligand redox processes has well-established precedents in specific systems. The data on these complexes support the concept of ligand redox chemistry in these species.

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Registry No. $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$, 12110-44-0; $Fe(SPh)(CO)(PPh_2Me)(\eta\text{-}C_5H_5)$, 76452-69-2; $Fe(SPh)(CO)(PPhMe_2)(\eta\text{-}C_5H_5)$, 76452-70-5; $Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5H_5)$, 76452-71-6; $Fe(SPh)(CO)(P(OPh)_3)(\eta\text{-}C_5H_5)$, 76468-61-6; $Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5H_5)$, 76468-62-7; $Fe(SPh)(m\text{-}CNC_6H_4OMe)_2(\eta\text{-}C_5H_5)$, 87681-56-9; $Fe(SPh)(m\text{-}CNC_6H_4CF_3)_2(\eta\text{-}C_5H_5)$, 87681-57-0; $Fe(SPh)(CO)_2(\eta\text{-}C_5Me_5)$, 87681-58-1; $Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5Me_5)$, 87681-59-2; $Fe(SPh)(CO)(PPh_2Me)(\eta\text{-}C_5Me_5)$, 87681-60-5; $Fe(SPh)(CO)(PPhMe_2)(\eta\text{-}C_5Me_5)$, 87681-61-6; $Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5Me_5)$, 87681-62-7; $[Fe(SPh)(CO)(PPh_2Me)(\eta\text{-}C_5H_5)]BF_4$, 76452-83-0; $[Fe(SPh)(CO)(PPhMe_2)(\eta\text{-}C_5H_5)]BF_4$, 76452-84-1; $[Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5H_5)]BF_4$, 76452-85-2; $[Fe(SPh)(CO)(P(OPh)_3)(\eta\text{-}C_5H_5)]PF_6$, 76468-63-8; $[Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5H_5)]PF_6$, 76452-73-8; $[Fe(SPh)(m\text{-}CNC_6H_4OMe)_2(\eta\text{-}C_5H_5)]BF_4$, 87681-64-9; $[Fe(SPh)(m\text{-}CNC_6H_4CF_3)_2(\eta\text{-}C_5H_5)]BF_4$, 87681-66-1; $[Fe(CO)_2(\eta\text{-}C_5H_5)(\mu\text{-}Ph_2S_2)Fe(CO)_2(\eta\text{-}C_5H_5)](PF_6)_2$, 76452-65-8; $[Fe(CO)_2(PhSSPh)(\eta\text{-}C_5H_5)]BF_4$, 76452-68-1; $[Fe(CO)_2(MeSSMe)(\eta\text{-}C_5H_5)]BF_4$, 87681-68-3; $[Fe(CO)_2(\eta\text{-}C_5Me_5)(\mu\text{-}Ph_2S_2)Fe(CO)_2(\eta\text{-}C_5Me_5)](PF_6)_2$, 87681-70-7; $[Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5Me_5)]PF_6$, 87681-72-9; $[Fe(SPh)(CO)(PPhMe_2)(\eta\text{-}C_5Me_5)]PF_6$, 87681-74-1; $[Fe(SPh)(CO)(PPh_2Me)(\eta\text{-}C_5Me_5)]PF_6$, 87681-76-3; $FeI(CO)(PPh_2Me)(\eta\text{-}C_5H_5)$, 57386-76-2; $Fe(CO)_2(\eta\text{-}C_5Me_5)]_2$, 35344-11-7; $[Fe(SPh)(CO)(\eta\text{-}C_5Me_5)]_2$, 87681-77-4; $[Fe(CO)_2(PhSSPh)(\eta\text{-}C_5H_5)]PF_6$, 87681-78-5; $[Fe(CO)_2(CD_3CN)(\eta\text{-}C_5H_5)]PF_6$, 87681-80-9; $[Fe(CO)_2(THF)(\eta\text{-}C_5H_5)]BF_4$, 63313-71-3; $[Fe(SPh)(P(OPh)_3)_2(\eta\text{-}C_5H_5)]BF_4$, 87681-82-1; $FeI(P(OPh)_3)_2(\eta\text{-}C_5H_5)$, 12151-00-7; $FeI(CO)_2(\eta\text{-}C_5H_5)$, 12078-28-3; $[Fe(CO)_2(\eta\text{-}C_5H_5)(\mu\text{-}I)Fe(CO)_2(\eta\text{-}C_5H_5)]PF_6$, 12154-96-0; $[Fe(CO)_2(\eta\text{-}C_5H_5)(\mu\text{-}Ph_2S_2)Fe(CO)_2(\eta\text{-}C_5H_5)](BF_4)_2$, 76452-66-9; PhSSPh, 882-33-7.

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