*Journal of Organometallic Chemistry*, 402 (1991) 233–248
Elsevier Sequoia S.A., Lausanne
JOM 21427

# The synthesis of new thiolato bridged-iron carbonyl complexes

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(Received June 6th, 1990)

## Abstract

The reagent $[Me_2SSMe]BF_4$ has been shown to function as $MeS^+$ donor in organometallic synthesis. Here we report reactions of this species and also reactions of the related species $[Me_2SSR]BF_4$ (R = Ph, tol) with $Fe_2(\mu\text{-}X)(\mu\text{-}Y)(CO)_4(L)_2$ (X, Y = SMe, SPh, Stol, $PMe_2$; L = $PMe_3$, $PPhMe_2$, $PPh_2Me$) to give $[Fe_2(\mu\text{-}X)(\mu\text{-}Y)(\mu\text{-}SR)(CO)_4(L)_2]BF_4$. This is the first use of the reagents, $[Me_2SSR]BF_4$ (R = Ph, tol), as $SR^+$ donors in organometallic synthesis. The regiospecific addition of the $SR^+$ group trans to the phosphine ligands in the precursor was exploited in the synthesis of isomeric species with the formula $[Fe_2(\mu\text{-}SMe)_2(\mu\text{-}SPh)(CO)_4(PMe_3)_2]BF_4$. The $^1H$ NMR spectra of certain products with bridging SPh and Stol groups indicated the presence of two species, assumed to be conformers differing by the orientation of the organic group. Steric factors are thought to control this structure feature. Reactions between $[Me_2SSMe]BF_4$ and either *e,e*- or *a,e*-$Fe_2(\mu\text{-}SMe)_2(CO)_6$ (separable conformers that differ by the orientation of the methyl groups) result in formation of $[Fe_2(\mu\text{-}SMe)_3(CO)_6]BF_4$. From both reactions, only the more symmetric conformer ($C_3$ symmetry) can be isolated. An $^1H$ NMR study indicated that the reaction proceeded through an intermediate, possibly $[(CO)_3(SMe)Fe(\mu\text{-}SMe)_2Fe(NCMe)(CO)_3]BF_4$. A single-crystal X-ray diffraction study of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PPhMe_2)_2]BF_4$ is reported. Crystal data: space group $P2_1/c$; $a = 14.032$ (6) Å, $b = 11.935$ (5) Å, $c = 18.494$ (6) Å, $\beta = 101.58$ (6)°, $V = 3034$ (2) $Å^3$, $D_{calc} = 1.594$ g/cm$^3$, $Z = 4$, $R = 0.0970$, $R_w = 0.0482$ for 2458 independent reflections with $F \geqslant 4\sigma(F)$ and $2\theta \leqslant 55.0°$.

## Introduction

In the last several years, our group has used the reagent $[Me_2SSMe]BF_4$ for synthesis of organometallic thiolate complexes. Initial experiments showed that nucleophilic metal carbonyl anions react with these species to give metal carbonyl thiolate complexes [1]. The use of $[Me_2SSMe]BF_4$ in the synthesis of metal complexes with organo-disulfide (RSSR) ligands was reported in a second paper [2]. In both examples the organometallic precursor displaced $Me_2S$, a good leaving group, from the organosulfur reagent.

A proposed mechanism for these reactions, involving nucleophilic attack by an organometallic precursor on $[Me_2SSMe]BF_4$, provided a good basis to extend this work. The dinuclear complexes, $Fe_2(\mu\text{-}SMe)_2(CO)_4(L)_2$ (L = $PMe_3$, $PPhMe_2$,

0022-328X/91/$03.50

$PPh_2Me$, $PPh_3$) are protonated in strong acid [3]. Knowing this led us to attempt a reaction between $Fe_2(\mu\text{-}SMe)_2(CO)_6$ and $[Me_2SSMe]BF_4$. This planned synthesis gave $[Fe_2(\mu\text{-}SMe)_3(CO)_6]BF_4$, a known complex previously made by another route [4], in 44% yield, eq. 1 [5]. Subsequently, reactions of the organosulfur reagent with several phosphine derivatives of the diiron carbonyl thiolate species were carried out, eq. 2 [6].

$$Fe_2(\mu\text{-}SMe)_2(CO)_6 + [MeSSMe_2]BF_4 \rightarrow [Fe_2(\mu\text{-}SMe)_3(CO)_6]BF_4 + Me_2S \qquad (1)$$

$$Fe_2(\mu\text{-}SMe)_2(CO)_4(L)_2 + [MeSSMe_2]BF_4 \rightarrow [Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4 + Me_2S \qquad (2)$$

($L = PPh_3$, $PPhMe_2$, $PPhEt_2$, or $PMe_3$)

Reactions of $[Me_2SSMe]BF_4$ with other compounds with metal–metal bonds were a logical next step. These reactions were found to be applicable for preparations of mono-metallic compounds with terminal thiolate groups even when the organometallic precursors were not notably nucleophilic. For example, the reaction of $[CpW(CO)_3]_2$ with $[Me_2SSMe]BF_4$ gives $CpW(CO)_3SMe$ and $[CpW(CO)_3SMe_2]BF_4$. This reaction, similar to oxidative cleavage of the metal–metal bond, can also be interpreted mechanistically to involve initial nucleophilic attack by the dinuclear metal complex on $[Me_2SSMe]BF_4$ [7].

The work described in this paper extends earlier work [5,6] on diiron carbonyl thiolate species. Basically, there were two goals. The first was to develop the related reagents, of the general formula $[Me_2SSR]BF_4$, that might be useful as donors of $RS^+$ with organic substituent groups other than methyl. This being established, the second goal to develop specific routes to isomeric species differing by the positions of the organic group of bridging thiolates, became viable. We report on the success of both endeavors in this paper.

## Experimental

The following compounds were prepared by literature methods: $PMe_3$ [8], $PPhMe_2$ [9], $PPh_2Me$ [9], $PPh(OMe)_2$ [10], $PPh_2OMe$ [11], $Fe_3(CO)_{12}$ [12], $Fe_2(\mu\text{-}SBu^t)_2(CO)_6$ [13], $Fe_2(\mu\text{-}SMe)_2(CO)_4(L)_2$ ($L = CO$ [14], $PMe_3$ [15]), $Fe_2(\mu\text{-}SMe)(\mu\text{-}SPh)(CO)_6$ [16], $Fe_2(\mu\text{-}SPh)_2(CO)_4(PMe_3)_2$ [17], $Fe_2(\mu\text{-}PMe_2)_2(CO)_6$ [18], $[Me_2SSMe]BF_4$ [19], and $[Me_2SSPh]BF_4$ [20]. Samples of $[Me_2SStol]BF_4$ was prepared analogously to $[Me_2SSPh]BF_4$. Other starting materials were commercial samples. Solvents were dried by standard methods and distilled prior to use. Glassware was oven dried prior to use. All reactions were performed under dry $N_2$. Infrared spectra were recorded on a Mattson Polaris FT-IR or a Beckman Model 4230 spectrophotometer. $^1H$ NMR were obtained on an IBM-WP-200 spectrometer. Melting points were obtained on a Thomas-Hoover apparatus. Some new compounds were characterized by mass match measurement. Accurate parent peak data were obtained using a Kratos MS-80 mass spectrometer with a heated (solids) inlet and electron impact (EI) ionization. When the compound was not amenable to mass spectral characterization, elemental analyses were obtained (Galbraith Laboratories, Knoxville, TN). Some of the species analyzed retained solvent and, when so, the presence of solvent in the sample was confirmed by NMR data.

### *New iron dimers with two bridging ligands*

*$Fe_2(\mu\text{-}SCD_3)_2(CO)_6$.* The cost of deuterated reagents led us to seek the most efficient method of synthesis, and we chose the one by Seyferth et al. to prepare the undeuterated analogue [21]. A solution of $Fe_2(\mu\text{-}S_2)(CO)_6$ (0.938 g, 2.73 mmol) in 30 mL of THF was cooled at −78 °C and 5.4 mL of 1 *M* (approx. 5.4. mmol) $LiBEt_3H$ in ether was added. The color of the solution changed from red to dark green. After 0.5 mL of $CD_3I$ was added at −78 °C, the solution was allowed to slowly warm to ambient temperature. The color changed to deep red. Solvent was removed on a rotary evaporator and chromatography (alumina/hexane) of the residue gave a single red band. The solution was concentrated and crystallization from heptane at −78 °C gave 0.882 g (85%) of red powder, m.p. 60–61 °C. MS: $m/e = 379.8674$. $C_8D_6Fe_2O_6S_2$ calc.: 379.8681. IR ($CH_2Cl_2$): $\nu$(CO) 2070m, 2035s, 1990s $cm^{-1}$ (lit.: *a,e* 2085s, 2050vs, 2000vs; *e,e* 2075s, 2040vs, 2000vs, 1995sh $cm^{-1}$ [14]).

*$Fe_2(\mu\text{-}Stol)_2(CO)_6$.* A procedure analogous to that of Kettle and Orgel [22] was used to prepare this complex. A solution of $Fe_3(CO)_{12}$ (4.02 g, 7.95 mmol) and *p*-thiocresol (5.69 g, 45.9 mmol) in 30 mL of benzene was heated at reflux for two hours. The red solution was filtered through a 2.5 cm pad of filter cell and the filtrate evaporated to an oil on a rotary evaporator. Purification of the product by chromatography (alumina/hexane) and crystallization from hexane gave 3.61 g (86%) of the product, a red powder, m.p. 105 °C. MS: $m/e = 525.8939$. $C_{20}H_{14}Fe_2O_6S_2$ calc.: 525.8930. IR($CH_2Cl_2$): $\nu$(CO) 2065s, 2030s, 1995s $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 2.21 (s, 6H, tolyl methyl), 6.96 (d, $J = 8.1$ Hz, 4H, tol), 7.14 (d, $J = 8.0$ Hz, 2H, tol), 7.16 (d, $J = 8.3$ Hz, 2H, tol).

*$Fe_2(\mu\text{-}SBu^t)_2(CO)_4(PMe_3)_2$* A solution of $Fe_2(\mu\text{-}SBu^t)_2(CO)_6$ (0.510 g, 1.12 mmol) in 25 mL of toluene was treated with 0.50 mL (6.6 mmol) of $PMe_3$ and heated at reflux for 5 hours. The solvent was removed on a rotary evaporator and chromatography (silica/$CH_2Cl_2$) of the residue gave a single red band. The solution was concentrated and the residue crystallized from hexane to give 0.428 g (69%) of air-sensitive red powder, m.p. 122–124 °C. IR ($CH_2Cl_2$): $\nu$(CO) 1978vs, 1933ms, 1905s $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 1.38 (s, 18H, $SBu^t$), 1.27 (d, $J(PH) = 14.8$ Hz, 18H, $PMe_3$).

The following complexes were prepared by an analogous procedure to the above:

*$Fe_2(\mu\text{-}SBu^t)_2(CO)_4(PPhMe_2)_2$.* 47%, dark red crystals, m.p. 148–149 °C. MS: $m/e = 566$ ($M^+ - 4CO$). IR($CH_2Cl_2$): $\nu$(CO) 1980vs, 1935m, 1910s $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 0.95 (s, 9H, $SBu^t$, *a,e* isomer), 1.08 (s, 9H, $SBu^t$, *e,e* isomer), 1.29 (s, 9H, $SBu^t$, *a,e* isomer), 1.79 (d, $J = 8$ Hz, 12H, PMe, *a,e* isomer), 1.83 (d, $J = 8.5$ Hz, 12H, *e,e* isomer), 7.4 (m, 6 H, PPh, *a,e* and *e,e* isomers), 7.53 (m, 4H, PPh, *a,e* and *e,e* isomers). The ratio of *a,e* to *e,e* was 1 : 3.

*$Fe_2(\mu\text{-}SCD_3)_2(CO)_4(PMe_3)_2$.* 26%, black crystals, m.p. 109–110 °C. IR ($CDCl_3$): $\nu$(CO) 1982s, 1940s, 1912s $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 1.52 (d, $J(PH) = 13.3$ Hz), 1.50 (d, $J(PH) = 6$ Hz).

*$Fe_2(\mu\text{-}SMe)(\mu\text{-}SPh)(CO)_4(PMe_3)_2$.* 76%, dark red crystals, m.p. 89–92 °C. MS: $m/e = 531.9255$. $C_{14}H_{17}Fe_2O_4PS_2$ calc.: 531.94455. IR ($CDCl_3$): $\nu$(CO) 1987s, 1945s, 1917s $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 1.42 (d, $J(PH) = 8.8$ Hz, 18H, $PMe_3$ minor isomer), 1.58 (d, $J(PH) = 7$ Hz, 18H, $PMe_3$ major isomer), 1.88 (s, 3H, SMe major isomer), 1.96 (s, 3H, SMe minor isomer), 7.08 (m, 3H, SPh both isomers), 7.34 (m, 2 H, SPh both isomers). The ratio of isomers was 1 : 1.3.

*$Fe_2(\mu\text{-}Stol)_2(CO)_4(PPhMe_2)_2$.* 80%, black platelets, m.p. 137 °C. Anal. Found: C, 54.36; H, 4.62. $C_{34}H_{36}Fe_2O_4P_2S_2$ calc.: C, 54.71; H, 4.86%. IR ($CH_2Cl_2$): $\nu$(CO) 2050w, 1980s, 1938s, 1912s, 1890sh cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 1.67 (d, $J$(PH) = 8.6 Hz, PMe, minor isomer), 1.77 (d, $J$(PH) = 8.5 Hz, PMe, minor isomer), 1.95 (d, $J$(PH) = 8 Hz, PMe, major isomer), 2.16 (s, tolyl methyl, major isomer), 2.21 (s, tolyl methyl, minor isomer), 6.61–7.25 (m, overlapping $A_2B_2$ patterns for 3 different tolyl groups), 7.36–7.43 (m, 6 H, PPh), 7.57–7.64 (m, 4 H, PPh). The ratio of isomers was 1 : 2.5. The minor isomer has *a,e* conformation: this structure leads to two doublets for the diastereotopic $PMe_2$ protons.

*$Fe_2(\mu\text{-}Stol)_2(CO)_4(PPh_2Me)_2$.* 62%, purple powder, m.p. 192 °C. Anal. Found: C, 60.02; H, 4.71. $C_{44}H_{40}Fe_2O_4P_2S_2$ calc.: C, 60.69; H, 4.63%. IR ($CH_2Cl_2$): $\nu$(CO) 2045w, 1999sh, 1983s, 1937s, 1918s cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 1.95 (d, $J$(PH) = 10 Hz, PMe minor isomer), 2.12 (s, tolyl methyl, major isomer), 2.14 (s, tolyl methyl, minor isomer), 2.22 (s, tolyl methyl, major isomer), 2.24 (d, $J$ = 8 Hz, PMe minor isomer), 6.38 (d, $J$ = 8 Hz, tol), 6.58 (d, $J$ = 8 Hz, tol), 6.67–7.02 (m, tol), 7.28–7.45 (m, 12 H, PPh), 7.52–7.80 (m, 8 H, PPh). The ratio of isomers was 1 : 1.75. The minor isomer has the *a,e* conformation.

*$Fe_2(\mu\text{-}Stol)_2(CO)_4(P\{OMe\}_3)_2$.* 86%, red powder, m.p. 158–159 °C. IR ($CH_2Cl_2$): $\nu$(CO) 2005s, 1968s, 1943s, 1920m cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 2.20 (s, 3H, tolyl methyl, *a,e* isomer), 2.22 (s, 3H, tolyl methyl, a,e isomer), 2.24 (s, 6H, tolyl methyl, *e,e* isomer), 3.68 (d, $J$(PH) = 11.3 Hz, 18H, POMe, *a,e* isomer), 3.83 (t, $J$(PH) = 5.5 Hz, 18H, POMe, *e,e* isomer), 6.91 (q, $J$ = 8.6 Hz, tol), 7.32 (q, $J$ = 7.1 Hz, tol). The ratio of isomers was 1 : 1.5.

### *New triply bridged complexes prepared using $[Me_2SSMe]BF_4$*

*$[Fe_2(\mu\text{-}PMe_2)_2(\mu\text{-}SMe)(CO)_6]BF_4$.* A solution of $Fe_2(\mu\text{-}PMe_2)_2(CO)_6$ (0.207 g, 0.516 mmol) and $[Me_2SSMe]BF_4$ (0.229 g, 0.117 mmol) in 20 mL of $CH_2Cl_2$ was stirred for 3 hours at ambient temperature. The solution immediately turned dark red and the color continued to deepen during this time. The solution was filtered and the filtrate concentrated. Crystallization of the residue from ether at −15 °C gave 0.180 g (65%) of pale orange powder, m.p. 133–134 °C. Anal. Found: C, 24.52; H, 3.29. $C_{11}H_{15}BF_4Fe_2O_6P_2S$ calc.: C, 24.66; H, 2.82%. IR ($CH_2Cl_2$): $\nu$(CO) 2090s, 2035s, 1985m cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 1.86 (dd, $J$(PH) = 10.2 Hz, 30.3 Hz, 3H, PMe), 2.16 (dd, $J$(PH) = 9.5 Hz, 30.3 Hz, 6H, PMe), 2.24 (s, 3H, SMe), 2.35 (dd, $J$(PH) = 5.3 Hz, 10.3 Hz, 3H, PMe).

The following complexes were prepared by a similar procedure to the above:

*$[Fe_2(\mu\text{-}SCD_3)_2(\mu\text{-}SCH_3)(CO)_4(PMe_3)_2]BF_4$.* 27%, orange powder. IR ($CH_2Cl_2$): $\nu$(CO) 2042s, 2030s, 1990s cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 1.52 (d, $J$(PH) = 10.3 Hz, 18H, $PMe_3$), 2.37 (t, $J$(PH) = 3.6 Hz, 3H, SMe).

*$[Fe_2(\mu\text{-}SMe)_2(\mu\text{-}SPh)(CO)_4(PMe_3)_2]BF_4$* (from $Fe_2(\mu\text{-}SMe)(\mu\text{-}SPh)(CO)_4(PMe_3)_2$ and $[Me_2SSMe]BF_4$). 53%, orange powder, m.p. 119–122 °C. IR ($CH_2Cl_2$): $\nu$(CO) 2045m, 2030s, 1992s cm$^{-1}$. $^1$H NMR ($CD_3CN$): $\delta$ 1.47 (d, $J$(PH) = 10.4 Hz, $PMe_3$ major isomer), 1.56 (d, $J$(PH) = 11.3 Hz, $PMe_3$ minor isomer), 2.06 (br s, SMe minor isomer); 2.30 (br s, SMe major isomer) 2.47 (s, SMe, minor isomer), 2.56 (s, SMe, major isomer), 7.41 (m, 3H, major and minor isomers), 7.85 (m, 2H, minor isomer), 8.05 (m, 2H, major isomer). The ratio of the isomers was 4 : 1. The line width of the SMe groups *trans* to the phosphine was sufficient to obscure the triplet pattern.

*$[Fe_2(\mu\text{-}Stol)_2(\mu\text{-}SMe)(CO)_4(PMe_3)_2]BF_4$*. 6%, red powder, m.p. 138 °C. Anal. Found: C, 37.59; H, 4.56. $C_{25}H_{35}BF_4Fe_2O_4P_2S_3 \cdot 0.8CH_2Cl_2$ calc.: C, 37.60; H, 4.48%. IR($CH_2Cl_2$): $\nu$(CO) 2030m, 2015s, 1985m cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 1.58 (d, $J$(PH) = 10.3 Hz, 18H, PMe), 1.94 (t, $J$(PH) = 3.4 Hz, 3H, SMe), 2.35 (s, 6H, tolyl methyl), 7.16–7.23 (m, 4H, tol), 7.63 (d, $J$ = 7.9 Hz, 2H, tol), 7.86 (d, $J$ = 8.2 Hz, 2H, tol).

*$[Fe_2(\mu\text{-}Stol)_2(\mu\text{-}SMe)(CO)_4(PPhMe_2)_2]BF_4$*. 9%, orange crystals, m.p. 109 °C. Anal. Found: C, 45.07; H, 4.20. $C_{35}H_{39}BF_4Fe_2O_4P_2S_3 \cdot CH_2Cl_2$ calc.: C, 44.80; H, 4.28%. IR ($CH_2Cl_2$): $\nu$(CO) 2025m, 2010s, 1983m cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 1.77 (t, $J$(PH) = 3.6 Hz, 3H, SMe), 1.84 (d, $J$(PH) = 10 Hz, 6H, PMe), 1.92 (d, $J$(PH) = 10 Hz, 6H, PMe), 2.28 (s, 3H, tolyl methyl), 2.33 (s, 3H, tolyl methyl), 7.01 (d, $J$ = 8 Hz, 2H, tol), 7.11 (d, $J$ = 8.1 Hz, 2H, tol), 7.22 (d, $J$ = 6 Hz, 2H, tol), 7.24–7.49 m, 10H, PPh), 7.67 (d, $J$ = 8 Hz, 2H, tol).

*New triply thiolato bridged-iron carbonyl complexes prepared using $[Me_2SSPh]BF_4$ or $[Me_2SStol]BF_4$*

The reactions using these sulfur reagents were conducted in an analogous fashion to the reactions previously described to give the following products:

*$[Fe_2(\mu\text{-}SBu^t)_2(\mu\text{-}SPh)(CO)_6]BF_4$*. 4%, m.p. 141°C (dec.). IR ($CH_2Cl_2$): $\nu$(CO) 2120w, 2100vs, 2080m, 2020w, 1980w cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 1.72 (s, 9H, SBu$^t$), 1.75 (s, 9H, SBu$^t$), 7.5 (m, 3H, SPh), 8.05 (m, 2H, SPh).

*$[Fe_2(\mu\text{-}SMe)_2(\mu\text{-}SPh)(CO)_6]BF_4$*. 57%, light orange flakes, m.p. 145 °C (dec.). Anal. Found: C, 29.40; H, 1.92. $C_{14}H_{11}BF_4Fe_2O_6S_3$ calc.: C, 29.48; H, 1.95%. IR ($CH_2Cl_2$): $\nu$(CO) 2110s, 2065s cm$^{-1}$. $^1$H NMR ($CD_3CN$): $\delta$ 2.28 (s, 3H, SMe), 2.51 (s, 3H, SMe), 7.48 (m, 3H, SPh), 7.97 (dd, $J$ = 1.1 Hz, 8.2 Hz; 2 H, SPh).

*$[Fe_2(\mu\text{-}SMe)_2(\mu\text{-}Stol)(CO)_6]BF_4$*. 74%, light orange powder, m.p. 165 °C (dec.). Anal. Found: C, 30.77; H, 2.28. $C_{15}H_{13}BF_4Fe_2O_6S_3$ calc.: C, 30.85; H, 2.24%. IR ($CH_2Cl_2$): $\nu$(CO) 2125 m, 2105 s, 2065 s cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 2.32(s, 3H, SMe), 2.39 (s, 3H, tolyl methyl), 2.56 (s, 3H, SMe), 7.26 (d, $J$ = 8.1 Hz, 2H, tolyl), 7.83 (d, $J$ = 8.3 Hz, 2H, tolyl).

*$[Fe_2(\mu\text{-}SMe)_2(\mu\text{-}SPh)(CO)_4(PMe_3)_2]BF_4$* (from $Fe_2(\mu\text{-}SMe)_2(CO)_4(PMe_3)_2$ and $[Me_2SSPh]BF_4$). 50%, red-orange powder, m.p. 157–160 °C. Anal. Found: C, 31.13; H, 4.41. $C_{18}H_{29}BF_4Fe_2O_4P_2S_3$ calc.: C, 32.46; H, 4.39%. IR ($CH_2Cl_2$): $\nu$(CO) 2045m, 2035s, 1980s cm$^{-1}$. $^1$H NMR ($CD_3CN$): $\delta$ 1.52 (d, $J$(PH) = 11 Hz, 18H, $PMe_3$), 2.35 (br s, 6H, SMe), 7.37 (m, 3H, SPh), 7.89 (m, 2h, SPh).

*$[Fe_2(\mu\text{-}SMe)_2(\mu\text{-}Stol)(CO)_4(PMe_3)_2]BF_4$*. 43%, orange flakes, m.p. 144–145 °C. Anal. Found: C, 31.67; H, 4.81. $C_{19}H_{31}BF_4Fe_2O_4P_2S_3$ calc.: C, 33.56; H, 4.59%. IR ($CH_2Cl_2$): $\nu$(CO) 2045m, 2030s, 1990s cm$^{-1}$. $^1$H NMR (acetone-$d_6$): $\delta$ 1.63 (d, $J$(PH) = 11 Hz, minor isomer, $PMe_3$), 1.69 (d, $J$(PH) = 11 Hz, major isomer, $PMe_3$), 2.32 (s, 3H, major isomer), 2.45 (s, 6H, major and minor isomers), 2.50 (s, 3H, minor isomer), 2.60 (s, 3H, minor isomer), 7.23 (d, $J$ = 7.9 Hz), 7.84 (d, $J$ = 7.9 Hz). The ratio of isomers was 4 : 1.

*$[Fe_2(\mu\text{-}SMe)(\mu\text{-}SPh)_2(CO)_4(PMe_3)_2]BF_4$* (from $Fe_2(\mu\text{-}SMe)(\mu\text{-}SPh)(CO)_4(PMe_3)_2$ and $[Me_2SSPh]BF_4$). 34%, orange flakes, m.p. 161–162 °C. Anal. Found: C, 35.46; H, 4.30. $C_{23}H_{31}BF_4Fe_2O_4P_2S_3$ calc.: C, 37.94; H, 4.29%. IR ($CH_2Cl_2$): $\nu$(CO) 2050m, 2035s, 1995s cm$^{-1}$. $^1$H NMR ($CD_3CN$): $\delta$ 1.52 (d, $J$(PH) = 11 Hz, 18H, $PMe_3$, major isomer), 1.73 (d, $J$(PH) = 9.9 Hz, 18H, $PMe_3$, minor isomer), 2.38 (s, 3H, SMe), 7.35 (m, 7H), 7.91 (m, 3H). The ratio of isomers was 3 : 1.

*$[Fe_2(\mu\text{-}SPh)_3(CO)_4(PMe_3)_2]BF_4$.* 49%, red powder, m.p. 151–152 °C. Anal. Found: C, 40.79; H, 4.21. $C_{28}H_{33}BF_4Fe_2O_4P_2S_3$ calc.: C, 42.56; H, 4.21%. IR ($CH_2Cl_2$): $\nu$(CO) 2045m, 2030s, 1990s $cm^{-1}$. $^1H$ NMR (acetone-$d_6$): $\delta$ 1.72 (d, $J$(PH) = 11 Hz, 18H, $PMe_3$), 7.36 (m, 10H, SPh), 7.90 (m, 2H, SPh), 8.0 2(m, 3H, SPh).

### *Reactions between $Fe_2(\mu\text{-}SMe)_2(CO)_6$ and $[Me_2SSMe]BF_4$ monitored by $^1H$ NMR and IR*

*e,e-$Fe_2(\mu\text{-}SMe)_2(CO)_6$ and $[Me_2SSMe]BF_4$.* An NMR tube was charged with solid *e,e*-$Fe_2(\mu\text{-}SMe)_2(CO)_6$ (0.020 g, 0.054 mmol), and $[Me_2SSMe]BF_4$ (0.008 g, 0.04 mmol), and evacuated. The tube was cooled in liquid $N_2$, charged with 0.3 mL of $CD_3CN$, and sealed under vacuum. The tube was thawed just prior to insertion into the NMR probe and spectra were recorded for 105 minutes at 7 minute intervals.

The initial spectrum (approximately 5 minutes after warming) gave peaks assignable to *e,e*-$Fe_2(\mu\text{-}SMe)_2(CO)_6$($\delta$ 2.08), $[Fe_2(\mu\text{-}SMe)_3(CO)_6]BF_4$ ($\delta$ 3.20), and $[Me_2SS\mathit{Me}]BF_4$ ($\delta$ 2.85). A single peak that continuously shifted upfield from $\delta$ 2.54 to $\delta$ 2.05 was assigned to $Me_2S$ and $[\mathit{Me}_2SSMe]BF_4$; since there is a rapid transfer of $SMe^+$ between the two species the position varies as the ratio of these reagents changes. Two peaks belonging to a transient species were observed to grow in at $\delta$ 3.17 and $\delta$ 2.15 (relative intensity of these two peaks is 1 : 2 respectively). The ratio of the intermediate to the product was 2 : 1 after 20 minutes of reaction time. The concentration of the intermediate remained constant and the concentration of the product continued to grow. The ratio of intermediate to product was 3 : 2 after 105 minutes. A spectrum measured after 12 hours showed that the intermediate was totally absent in the reaction mixture.

A reaction between *a,e*-$Fe_2(\mu\text{-}SMe)_2(CO)_6$ and $[Me_2SSMe]BF_4$ carried out with similar experimental conditions gave the same results (with minor rate differences).

The peak at $\delta$ 2.15 was absent in the reaction between $Fe_2(\mu\text{-}\mu SCD_3)_2(CO)_6$ and $[Me_2SSMe]BF_4$, but the peak at $\delta$ 3.17 continued to be present. Thus the peak at $\delta$ 2.15 can be assigned to SMe groups which originate in the precursor, $Fe_2(\mu\text{-}SMe)_2(CO)_6$, and the peak at $\delta$ 3.17 must be from $[Me_2SSMe]BF_4$.

The reaction between $Fe_2(\mu\text{-}SMe)_2(CO)_6$ and $[Me_2SSMe]BF_4$ was also monitored by IR in $CH_3CN$. The spectrum was dominated by the absorptions from $Fe_2(\mu\text{-}SMe)_2(CO)_6$ at 2070, 2035, and 1990 $cm^{-1}$ and from $[Fe_2(\mu\text{-}SMe)_3(CO)_6]BF_4$ at 2105 and 2065 $cm^{-1}$. Three new absorptions were observed to grow in at 2145, 2122, and 2090 $cm^{-1}$. Presumably these new absorptions belong to the intermediate species observed in the NMR experiments.

### *Attempted thermal isomerization of $[Fe_2(\mu\text{-}SCD_3)_2(\mu\text{-}SCH_3)(CO)_4(PMe_3)_2]BF_4$*

An NMR tube was charged with $[Fe_2(\mu\text{-}SCD_3)_2(\mu\text{-}SCH_3)(CO)_4(PMe_3)_2]BF_4$ (0.010 g, 0.016 mmol), evacuated, and cooled in liquid $N_2$. $CD_2Cl_2$ (1 g) was distilled into the tube and the tube was then sealed under vacuum. The tube was thawed, wrapped with aluminium foil, and stored at ambient temperature. No change in the spectrum was observed over a period of five days.

### *X-Ray diffraction study of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PPhMe_2)_2]BF_4$*

A sample of $Fe_2(\mu\text{-}SMe)_3(CO)_4(PPhMe_2)_2]BF_4$ was prepared as previously described [6]. A crystal suitable for diffraction was grown by slow diffusion of diethyl

Table 1

Crystal structure of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PPhMe_2)_2]BF_4$

| | |
|---|---|
| *Data collection* | |
| Diffractometer used | Syntex *P*1 |
| Radiation | Mo-$K_\alpha$ ($\lambda$ = 0.71073 Å) |
| Temperature (K) | 223 |
| Monochromator | highly oriented graphite crystal |
| $2\theta$ range | 3.0 to 55.0° |
| Scan type | Wyckoff |
| Scan speed | 4.00°/min in $\omega$ |
| Scan range ($\omega$) | 0.80° |
| Background measurement | Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time |
| Standard reflections | 3 measured every 100 reflections |
| Index ranges | $-15 \leqslant h \leqslant 18$, $-4 \leqslant k \leqslant 15$, $-24 \leqslant l \leqslant 23$ |
| Reflections collected | 7569 |
| Independent reflections | 6952 ($R_{int}$ = 2.44%) |
| Observed reflections | 2458 ($F > 4.0\sigma(F)$) |
| Absorption correction | face-indexed numerical |
| min./max. transmission | 0.9520/0.9769 |
| *Solution and refinement* | |
| System used | Siemens SHELXTL PLUS (MicroVAX II) |
| Solution | direct methods |
| Refinement method | full-matrix least-squares |
| Quantity minimized | $\Sigma w(F_o - F_c)$ |
| Hydrogen atoms | riding model, fixed isotropic $U$ |
| Weighting scheme | $w^{-1} = \sigma^2(F)$ |
| Final $R$ indices (obs. data) | $R$ = 9.70%, $wR$ = 4.82% |
| Goodness-of-fit | 1.95 |
| Largest and mean $\Delta/\sigma$ | 0.415, 0.010 (for $BF_4$)<br>0.035, 0.003 (for cation) |
| Data-to-parameter ratio | 7.2 : 1 |
| Largest difference peak | 1.11 e Å$^{-3}$ |
| Largest difference hole | −0.80 e Å$^{-3}$ |
| *Crystal data* | |
| Empirical formula | $C_{23}H_{31}BF_4Fe_2P_2S_3$ |
| Color; habit | red prism |
| Crystal size (mm) | 0.22 × 0.24 × 0.45 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions $a$ | 14.032(6) Å |
| $b$ | 11.935(5) Å |
| $c$ | 18.494(6) Å |
| $\beta$ | 101.58(6)° |
| Volume | 3034(2) Å$^3$ |
| $Z$ | 4 |
| Formula weight | 728.1 |
| Density (calc.) | 1.594 Mg/m$^3$ |
| Absorption coefficient | 1.310 mm$^{-1}$ |
| F(000) | 1488 |

ether into a $CH_2Cl_2$ solution of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PPhMe_2)_2]BF_4$ at −20 °C. A red crystal measuring 0.22 × 0.24 × 0.45 mm was selected and mounted on a glass fiber with epoxy cement. Details of data acquisition, solution and refinement, and crystal data are summarized in Table 1. Atomic coordinates and isotropic displace-

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PPhMe_2)_2]BF_4$

| | *x* | *y* | *z* | $U_{eq}$ [a] |
|---|---|---|---|---|
| Fe(1) | 3135(2) | 2155(2) | 1303(1) | 35(1) |
| Fe(2) | 3570(2) | 4599(2) | 1766(1) | 36(1) |
| S(1) | 4576(3) | 3036(3) | 1872(2) | 37(1) |
| C(1) | 5446(8) | 3134(10) | 1287(6) | 43(6) |
| S(2) | 2742(3) | 3816(3) | 666(2) | 40(1) |
| C(2) | 3348(10) | 4022(10) | −118(6) | 57(7) |
| S(3) | 2570(3) | 3276(3) | 2161(2) | 35(1) |
| C(3) | 3116(9) | 2791(10) | 3079(6) | 49(6) |
| P(4) | 1632(3) | 1446(3) | 843(2) | 40(2) |
| C(4) | 3443(10) | 987(11) | 1909(7) | 37(6) |
| O(4) | 3668(7) | 252(8) | 2301(5) | 62(5) |
| C(5) | 3632(13) | 1536(12) | 584(8) | 51(7) |
| O(5) | 3971(9) | 1212(9) | 116(5) | 60(5) |
| C(6) | 1412(9) | 61(10) | 1179(7) | 55(7) |
| C(7) | 609(8) | 2247(10) | 1048(7) | 55(6) |
| C(8) | 1330(10) | 1325(12) | −159(7) | 39(6) |
| C(9) | 1374(10) | 287(13) | −512(9) | 58(7) |
| C(10) | 1136(12) | 193(14) | −1266(9) | 62(8) |
| C(11) | 826(11) | 1130(16) | −1674(8) | 61(8) |
| C(12) | 809(11) | 2138(15) | −1351(9) | 62(8) |
| C(13) | 1044(10) | 2274(13) | −587(8) | 59(7) |
| P(5) | 2440(3) | 5985(3) | 1601(2) | 43(2) |
| C(14) | 4062(11) | 5034(11) | 2683(7) | 44(6) |
| O(14) | 4351(8) | 5291(8) | 3274(5) | 58(4) |
| C(15) | 4404(12) | 5378(12) | 1345(9) | 54(8) |
| O(15) | 4935(8) | 5867(9) | 1098(7) | 69(6) |
| C(16) | 2364(11) | 6792(11) | 2418(7) | 77(8) |
| C(17) | 1195(8) | 5577(10) | 1239(8) | 69(7) |
| C(18) | 2717(9) | 6990(11) | 940(7) | 35(6) |
| C(19) | 2310(12) | 6927(11) | 183(7) | 55(7) |
| C(20) | 2659(13) | 7630(12) | −312(8) | 60(8) |
| C(21) | 3362(13) | 8408(12) | −58(10) | 67(9) |
| C(22) | 3749(13) | 8480(12) | 677(9) | 56(8) |
| C(23) | 3434(11) | 7791(13) | 1181(8) | 55(7) |
| B | 1311(13) | 5345(15) | 8347(10) | 74(7) |
| F(1A) | 1084(19) | 5178(21) | 9031(11) | 77(2) |
| F(2A) | 574(18) | 4742(18) | 7834(11) | 77(2) |
| F(3A) | 1189(19) | 6454(14) | 8133(13) | 77(2) |
| F(4A) | 2179(15) | 4983(24) | 8260(11) | 77(2) |
| F(1B) | 2329(11) | 5579(22) | 8417(10) | 77(2) |
| F(2B) | 815(15) | 6348(15) | 8236(12) | 77(2) |
| F(3B) | 1235(19) | 4930(19) | 9034(11) | 77(2) |
| F(4B) | 1017(18) | 4576(15) | 7818(10) | 77(2) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 3

Selected bond lengths (Å) and angles (°) for $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PPhMe_2)_2]BF_4$

| | | | |
|---|---|---|---|
| *a. bond lengths (Å)* | | | |
| Fe(1)–S(1) | 2.334(4) | Fe(1)–S(2) | 2.314(4) |
| Fe(1)–S(3) | 2.333(4) | Fe(1)–P(4) | 2.273(4) |
| Fe(1)–C(4) | 1.788(13) | Fe(1)–C(5) | 1.781(17) |
| Fe(2)–S(1) | 2.324(4) | Fe(2)–S(2) | 2.326(4) |
| Fe(2)–S(3) | 2.325(4) | Fe(2)–P(5) | 2.269(5) |
| Fe(2)–C(14) | 1.775(13) | Fe(2)–C(15) | 1.790(18) |
| S(1)–C(1) | 1.791(13) | S(2)–C(2) | 1.838(14) |
| S(3)–C(3) | 1.813(11) | P(4)–C(6) | 1.814(13) |
| P(4)–C(7) | 1.826(13) | P(4)–C(8) | 1.821(13) |
| P(5)–C(16) | 1.814(14) | P(5)–C(17) | 1.808(12) |
| P(5)–C(18) | 1.809(15) | | |
| *b. angles (°)* | | | |
| S(1)–Fe(1)–S(2) | 86.6(1) | S(1)–Fe(1)–S(3) | 79.4(1) |
| S(2)–Fe(1)–S(3) | 77.1(1) | S(1)–Fe(1)–P(4) | 172.4(2) |
| S(2)–Fe(1)–P(4) | 91.2(1) | S(3)–Fe(1)–P(4) | 92.9(2) |
| S(1)–Fe(1)–C(4) | 89.4(4) | S(2)–Fe(1)–C(4) | 171.9(5) |
| S(3)–Fe(1)–C(4) | 95.3(5) | P(4)–Fe(1)–C(4) | 91.9(4) |
| S(1)–Fe(1)–C(5) | 95.2(6) | S(2)–Fe(1)–C(5) | 93.7(5) |
| S(3)–Fe(1)–C(5) | 169.5(5) | P(4)–Fe(1)–C(5) | 92.2(6) |
| C(4)–Fe(1)–C(5) | 93.6(7) | S(1)–Fe(2)–S(2) | 86.5(1) |
| S(1)–Fe(2)–S(3) | 79.8(1) | S(2)–Fe(2)–S(3) | 77.0(1) |
| S(1)–Fe(2)–P(5) | 173.1(2) | S(2)–Fe(2)–P(5) | 87.8(1) |
| S(3)–Fe(2)–P(5) | 95.0(2) | S(1)–Fe(2)–C(14) | 92.3(5) |
| S(2)–Fe(2)–C(14) | 169.3(5) | S(3)–Fe(2)–C(14) | 92.4(5) |
| P(5)–Fe(2)–C(14) | 92.5(5) | S(1)–Fe(2)–C(15) | 90.8(5) |
| S(2)–Fe(2)–C(15) | 94.8(5) | S(3)–Fe(2)–C(15) | 167.8(5) |
| P(5)–Fe(2)–C(15) | 93.6(5) | C(14)–Fe(2)–C(15) | 95.8(7) |
| Fe(1)–S(1)–Fe(2) | 82.4(1) | Fe(1)–S(2)–Fe(2) | 82.7(1) |
| Fe(1)–S(3)–Fe(2) | 82.4(1) | Fe(1)–S(1)–C(1) | 113.0(4) |
| Fe(2)–S(1)–C(1) | 111.8(4) | Fe(1)–S(2)–C(2) | 114.5(4) |
| Fe(2)–S(2)–C(2) | 114.0(4) | Fe(1)–S(3)–C(3) | 108.5(4) |
| Fe(2)–S(3)–C(3) | 110.1(4) | | |

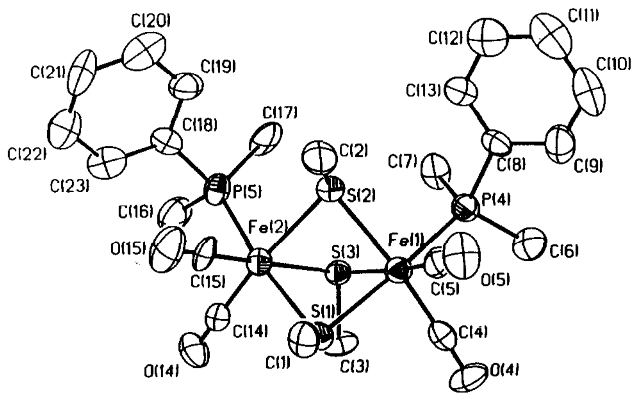


Fig. 1. Molecular structure of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PPhMe_2)_2]BF_4$, showing the atomic labeling scheme (50% probability thermal ellipsoids). The $BF_4^-$ anion and the hydrogen atoms have been removed for clarity.

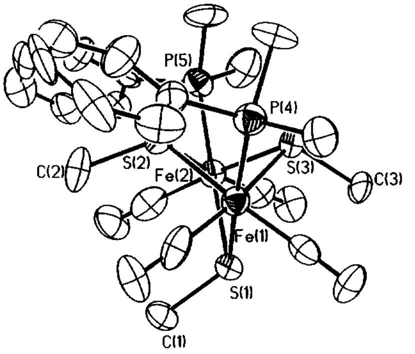


Fig. 2. Molecular structure of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PPhMe_2)_2]BF_4$ (axial view). The $BF_4^-$ anion and the hydrogen atoms have been removed for clarity.

ment coefficients are contained in Table 2. Selected bond lengths and bond angles are presented in table 3. ORTEP drawings of the molecule are presented in Figures 1 and 2. The $BF_4^-$ ion was omitted for clarity. Full tables of bond distances and bond angles, atomic coordinates, isotropic displacement coefficients, anisotropic displacement parameters and hydrogen-atom coordinates (calc.), observed and calculated structure factors are available from the authors upon request.

## Discussion

Previous work in our laboratories established that $[Me_2SSMe]BF_4$ is a useful reagent for syntheses of organometallic complexes having thiolate ligands [1,2,5–7]. Formally, these reagents donate a $MeS^+$ in reactions with nucleophilic metal complexes. A procedure using a $MeS^+$ donor complements the long-established procedures for syntheses of metal thiolate complexes using thiolate anions ($RS^-$), thiols (RSH), and disulfides (RSSR). Whereas $RS^+$ is electrophilic, the thiolate anions ($RS^-$) are nucleophiles. One may reasonably expect radical reactions, that is, participation of $RS\cdot$, in many reactions involving organic disulfides.

Studies presented in this paper reflect our ongoing interest in dinuclear metal complexes containing three bridging thiolate ligands. Earlier, we prepared complexes $[Mn_2(\mu\text{-}SR)_3(CO)_6]^-$ (R = Me, Bu$^t$, Ph, $CF_3$) and studied their chemistry [23]. The cationic complexes, $[Fe_2(\mu\text{-}SR)_3(CO)_6]^+$, are isoelectronic analogues to the manganese species; the methyl complex, $[Fe_2(\mu\text{-}SMe)_3(CO)_6]^+$, had been prepared some time ago by a non-standard procedure [4]. Recently, however, our group showed that complexes of this type are better prepared by rational synthesis from $Fe_2(\mu\text{-}SMe)_2(CO)_6$ and $[Me_2SSMe]BF_4$ [5]. The metal–metal bond in related organometallic precursors was known to protonate [3], so its reaction with the electrophilic thiolate reagent was anticipated.

The synthesis of $[Fe_2(\mu\text{-}PMe_2)_2(\mu\text{-}SMe)(CO)_6]BF_4$ reported here is a noteworthy extension of this work. The pale orange complex was prepared by reaction of $Fe_2(\mu\text{-}PMe_2)_2(CO)_6$ and excess $[Me_2SSMe]BF_4$ in $CH_2Cl_2$, and isolated in 65% yield.

Substitution of carbonyl groups by phosphines enhances the basicity of a metal complex. Thus it was not surprising to find that $Fe_2(\mu\text{-}SMe)_2(CO)_4(L)_2$ (L =

phosphine) complexes react with $[Me_2SSMe]BF_4$ to give related species containing the $Fe_2(\mu\text{-}SMe)_3$ structural unit [6].

Until now, $[Me_2SSMe]BF_4$ has been the only reagent of this type used in organometallic syntheses. The usefulness of this kind of procedure would be enhanced if synthetic reagents with different organic substituent groups could be developed. This paper reports initial steps toward this goal. The reagents $[Me_2SSPh]BF_4$ and $[Me_2SStol]BF_4$ were prepared by the following reactions, eq. 3:

$$Me_2S + RSCl + AgBF_4 \rightarrow [Me_2SSR]BF_4 + AgCl \qquad (R = Ph, tol) \qquad (3)$$

In this work, these reagents were shown to react with several $Fe_2(\mu\text{-}SR)_2(CO)_4(L)_2$ (L = CO, $PR_3$) species in a way analogous to $[Me_2SSMe]BF_4$:

$$Fe_2(\mu\text{-}SR')_2(CO)_4(L)_2 + [Me_2SSR]BF_4 \rightarrow [Fe_2(\mu\text{-}SR')_2(\mu\text{-}SR)(CO)_4(L)_2]BF_4 + Me_2S \qquad (4)$$

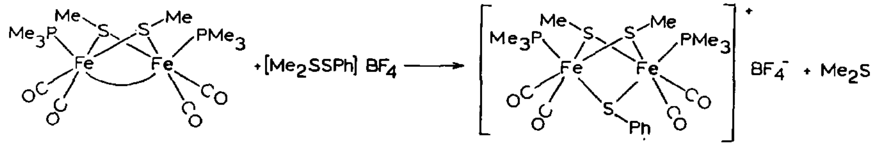
| R′ | R | L |
|---|---|---|
| $Bu^t$ | Ph | CO |
| Me | Ph, tol | CO |
| Me | Ph, tol | $PMe_3$ |
| Me, Ph | Ph | $PMe_3$ |
| Ph | Ph | $PMe_3$ |

These reactions were carried out in $CH_2Cl_2$ using an excess of $[Me_2SSR]BF_4$. The reactions occurred over several hours, as judged by the color change (the red color became red orange) and by following the appearance of $\nu(CO)$ absorptions for the product and the disappearance of $\nu(CO)$ absorptions for the reactant. The organometallic products were isolated as pale orange to red orange solids; yields were sometimes low because the complexes did not crystallize well.

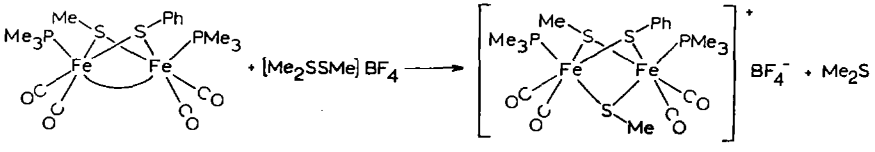
In previous studies using $[Me_2SSMe]BF_4$ it was found that $SMe^+$ addition occurred regiospecifically to the metal–metal bond in the organometallic precursor. Regiospecificity in reactions between $Fe_2(\mu\text{-}SMe)_2(CO)_4(PMe_3)_2$ and $[Me_2SSR]BF_4$ (R = Ph, tol) was ascertained from NMR spectra. Resonances for the thiolate methyl groups in the precursor and in the product are singlets, indicating their location *trans* to carbonyl groups. Had an SMe group been *trans* to two phosphines, the resonance would have been a 1 : 2 : 1 triplet.

With the use of $[Me_2SSR]BF_4$ (R = Ph, tol) as an $SR^+$ donor being established and the regiospecificity of the reactions of these species being known, it was now possible to design syntheses for isomeric complexes which differ by the location of thiolate substituent groups. Chemistry carried out in this study to illustrate this is shown in eqs. 5 and 6 below.

The isomeric species were clearly differentiated by NMR spectra. For example $[Fe_2(\mu\text{-}SMe)_2(\mu\text{-}SPh)(CO)_4(PMe_3)_2]BF_4$ (prepared from $Fe_2(\mu\text{-}SMe)_2(CO)_4(PMe_3)_2$ and $[Me_2SSPh]BF_4$), shows a broad singlet in the $^1H$ NMR for both SMe groups with fortuitous magnetic equivalence of these groups. The spectrum of $[Fe_2(\mu\text{-}SMe)_2(\mu\text{-}SPh)(CO)_4(PMe_3)_2]BF_4$ prepared from $Fe_2(\mu\text{-}SMe)(\mu\text{-}SPh)(CO)_4(PMe_3)_2$ and $[Me_2SSMe]BF_4$, is more complicated. There are two isomers in the ratio of 4 : 1 and each of the SMe groups has a unique chemical shift. There are two sharp SMe



(5)



(6)

singlets at 2.47 (minor isomer) and 2.56 (major isomer). In addition, there are peaks at $\delta$ 2.06 (minor isomer) and 2.30 (major isomer) that are singlets with a line width broad enough to obscure the expected coupling to phosphorus. The existence of isomers is discussed below.

Although regiospecificity of $SR^+$ addition to $Fe_2(\mu\text{-}SR')_2(CO)_4(L)_2$ was established through judicious choice of organic substituent groups, we thought that it would be appropriate to verify this with the simplest case situation, with the compounds having only methyl groups (R = R′ = Me). Accordingly we prepared $Fe_2(\mu\text{-}SCD_3)_2(CO)_4(PMe_3)_2$ as a precursor and reacted the species with $[Me_2SSMe]BF_4$. Only one product, $[Fe_2(\mu\text{-}SCD_3)_2(\mu\text{-}SCH_3)(CO)_4(PMe_3)_2]BF_4$, was detected and this contained a triplet resonance at $\delta$ 2.37 for the thiomethyl group protons. A further experiment with this product detected no rearrangement of thiomethyl groups in this species in solution over a 5 day period at room temperature, indicating a lack of ligand lability in this species.

We have been interested in molecular structures of various $[Fe_2(\mu\text{-}SR)_3(CO)_4(L)_2]^+$ species, particularly with respect to the orientation of the thiolate substituents. Not surprisingly, in the all-carbonyl species the higher symmetry ($C_3$) isomer is favored. The $^1H$ NMR spectrum indicates a single type of substituent group, and there has been a crystal structure study on one species [4]. Likely, this structure is preferred to minimize the steric interaction between the substituent groups. For the compounds with two phosphine ligands, the $^1H$ NMR data are not informative as to the structure vis-a-vis the thiolate group orientation; there are four possible structures, and in each the three substituent groups are in different environments.

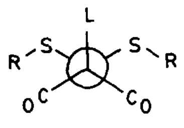
The conformation of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_3)_2]BF_4$ was determined by a single-crystal X-ray diffraction study. The coordination geometry about each iron is essentially that of a distorted octahedron. The iron–iron distance of 3.07 Å is longer that the iron–iron bond distance of 2.518 Å found in $Fe_2(\mu\text{-}SMe)_2(CO)_4(PMe_3)_2$ [24], and comparable to the iron–iron bond lengths found in $[Fe_2(\mu\text{-}SMe)_3(CO)_6]^+$, 3.062Å, [4] and in $Fe_2(\mu\text{-}SMe)_2(\mu\text{-}SO_2)(CO)_4(PMe_3)_2$, 3.117 Å [25]. Distances between the two iron centers greater than 3.0 Å indicated the absence of an iron–iron bond in these species.

In the iron–sulfur core, the bridging thiolate ligands assume a configuration with the methyl groups on S(2) and S(3) *anti* to one another. A similar *anti* (*e*,*e*) configuration was observed in $Fe_2(\mu\text{-}SMe)_2(CO)_4(PMe_3)_2$ [24], presumably to minimize steric interactions between the methyl thiolate groups and the trimethylphosphines. The $Fe_2S_3$ core is distorted as a consequence of the presence of the phosphines. The angle between the Fe(1)–S(1)–Fe(2) plane and the Fe(1)–S(2)–Fe(2) plane is 131.7°, significantly larger than the 120° angle predicted for the idealized structure. The angle between the Fe(1)–S(1)–Fe(2) plane and the Fe(1)–S(3)–Fe(2) plane is 116.5°, only slightly smaller than 120°. The remaining angle between the Fe(1)–S(2)–Fe(2) plane and the Fe(1)–S(3)–Fe(2) plane is 111.8°. The bulk of the distortion occurs in moving S(2) closer to S(3), and is presumably to minimize steric interactions between the *syn* methyl groups on S(1) and S(2).

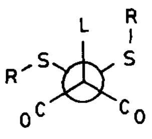
The mean iron–sulfur bond distance of 2.326 Å is only slightly longer than the 2.305 Å found in $[Fe_2(\mu\text{-}SMe)_3(CO)_6]^+$. Slightly shorter mean iron–sulfur bond lengths in $Fe_2(\mu\text{-}SMe)_2(CO)_4(PMe_3)_2$ (2.273 Å) and $Fe_2(\mu\text{-}SEt)_2(CO)_6$ (2.259 Å) are noted. The mean iron–sulfur bond distance in $Fe_2(\mu\text{-}SMe)_2(\mu\text{-}SO_2)(CO)_4(PMe_3)_2$ is longer at 2.356 Å. While all bond lengths are within the realm of single bonds, the oxidative addition of $SR^+$ appears to be associated with a lengthening of the iron–sulfur bond distance. There are no significant differences in the iron–sulfur bond lengths between the methyl thiolate groups *trans* to carbon monoxide and the methyl thiolate group *trans* to the dimethylphenylphosphine ligands.

The dimethylphenylphosphine ligands were not remarkable except for the orientation to the phenyl rings. As may best be seen in Fig. 2, both phenyl rings were oriented near S(2). The advantages of this orientation are probably to minimize steric interactions between the phenyl ring and the methyl group on S(2).

This structure for $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PPhMe_2)_2]BF_4$ is presumably the result of a balance in the steric interactions between the thiolate substituent groups and the large phosphines and between thiolate groups with each other. A significant phosphine–thiolate steric interaction is anticipated based on earlier studies of the species $Fe_2(\mu\text{-}SR)_2(CO)_4(L)_2$; for these species the *e*,*e* (*e* = equatorial, *a* = axial) isomer is known to be favored definitively over the *a*,*e* isomer [24]. A Newman-type projection along the metal–metal axis of the molecule allows a clear focus on the orientation of the substituents.



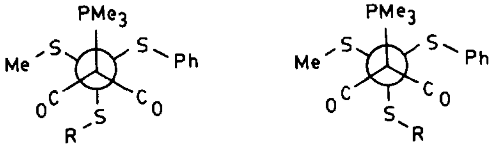
e,e



a, e

The $^1H$ NMR spectra of the two compounds derived by $RS^+$ (R = Me, Ph) addition to $Fe_2(\mu\text{-}SMe)(\mu\text{-}SPh)(CO)_4(PMe_3)_2$ indicated the presence of two isomeric species. There are several possible explanations; the one that we favor, based on possible orientations of the added $RS^+$ group, assumes the general structure defined by the crystallographic study. It seems logical to assume that there will be little preference to the orientation of the added $RS^+$ group, and that the molecule assumes the two conformations illustrated below. While on the subject of conformers, we report that several of the precursors in this study, $Fe_2(\mu\text{-}SR)(\mu\text{-}SR')(CO)_4(L)_2$ (R = Ph, R′ = Me; L = $PMe_3$; R = R′ = tol, L = $PMe_3$, $PPhMe_2$,

$PPh_2Me$) also occur as two different conformers. For example, $Fe_2(\mu$-$Stol)_2(CO)_4(PPhMe_2)_2$ had two isomers in the ratio of 1:2.7 by $^1H$ NMR. Presumably, the major species is the e,e isomer, because this isomer would have the least steric interaction between the thiolate and phosphine moieties. Two isomers were also observed for $Fe_2(\mu$-$SMe)(\mu$-$SPh)(CO)_4(PMe_3)_2$ and $Fe_2(\mu$-$Stol)_2(CO)_4(PPh_2Me)_2$. As a general observation, we note that these are all complexes containing bridging aryl thiolate groups. Presumably the conformers differ with respect to orientation of the SPh and Stol groups.



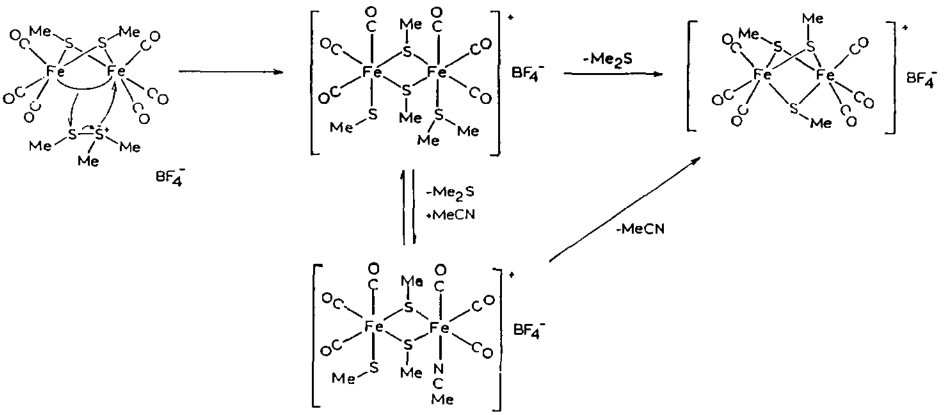
R = Me, Ph

Our interest in thiolate group conformations led to one additional study. Both the *e,e* and *a,e* isomers of $Fe_2(\mu$-$SMe)_2(CO)_6$ are separable [14] so we decided to look at the reaction between each with $[Me_2SSMe]BF_4$, monitoring the reaction in a sealed NMR tube. In both cases the reaction proceeded over the course of several hours with the disappearance of $Fe_2(\mu$-$SMe)_2(CO)_6$ and the eventual formation of a single conformer, the known $C_3$ symmetry species, $[Fe_2(\mu$-$SMe)_3(CO)_6]BF_4$.

It had been our expectation in carrying out reactions of *a,e* and *e,e* $Fe_2(\mu$-$SMe)_2(CO)_6$ with $[MeSSMe_2]BF_4$ that a second conformer of $[Fe_2(\mu$-$SMe)_3(CO)_6]^+$ might be detected and perhaps even isolated. Indeed, while monitoring these reactions using $^1H$ NMR, an intermediate species was detected. This species had singlet resonances at $\delta$ 3.14 and $\delta$ 2.16 with relative intensities 1:2. Deuterium labeling of the starting material showed that the resonance at $\delta$ 3.14 originated with the $[MeSSMe_2]BF_4$. In addition, $Me_2S$ was formed in this system. During the course of the reaction, the resonance associated with the protons of the dimethylsulfide portion of the organosulfur reagent ($[MeSSMe_2]BF_4$) moved upfield from $\delta$ 2.54 to $\delta$ 2.05. This is accounted for by rapid exchange of the $SMe^+$ group in $[MeSSMe_2]BF_4$ with free $Me_2S$ resulting in the averaging of the methyl group magnetic environments. We had previously shown that this exchange process occurs [26].

These NMR data did not support the presence of a second conformer of the product, however. The $\delta$ 3.14 resonance is too far downfield to be an SMe group bridging two metals. Reference to data given in this paper and elsewhere will confirm that the protons in a bridging SMe group are expected to be near $\delta$ 2.0. The $\delta$ 3.14 peak is much more in line with a terminal SMe group, i.e., an SMe group bonded to a single metal.

Scheme 1 gives a possible mechanism for this reaction and suggests a structure for this intermediate. The initial step proposed here involves addition of $[Me_2SSMe]BF_4$ to the metal–metal bond, in much the same way that halogens add to the metal–metal bonded species. To free $Me_2S$ into the system it must be assumed that this species is displaced rapidly by the solvent ($CD_3CN$); or, we could assume that solvent rather than $Me_2S$ is incorporated directly in the initial step. This intermediate could then be converted to the final product in a slower second step when coordinated $Me_2S$ or $CD_3CN$ is displaced by the lone pair of the added thiolate ligand.



Scheme 1. Postulated mechanism for the reaction between $Fe_2(\mu\text{-}SMe)_2(CO)_6$ and $[Me_2SSMe]BF_4$ in acetonitrile.

Halogen-like behavior of $[Me_2SSMe]BF_4$ has already been observed with several metal–metal bonded species. For example, $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$ and $[Me_2SSMe]BF_4$ react to form $W(SMe)(CO)_3(\eta^5\text{-}C_5H_5)$ and $[W(SMe_2)(CO)_3(\eta^5\text{-}C_5H_5)]BF_4$; similar reactions are noted for other metal–metal bonded species with this precursor [7].

We observe in passing that the halogens are also known to react with $Fe_2(\mu\text{-}SR)_2(CO)_4(L)_2$ with insertion of $X^+$ into a position bridging two metals [27]. Also, we note that the mechanism of halogen reactions with metal–metal bonds has not been fully defined with radical, polar ($X^{\delta+}\text{–}X^{\delta-}$), and four-center reactions having been postulated to occur under various conditions. The reactions reported here bear a striking similarity to the polar reactions of the halogens.

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