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Synthesis and Electrochemical Behavior of a Group of Thiolato-Bridged Iron Carbonyl Complexes

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Four complexes of the formula $[Fe(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4$ (L = PMe_3, PMe_2Ph, PEt_2Ph, PPh_3) have been prepared by reactions of the known complexes $Fe_2(\mu\text{-}SMe)_2(CO)_4(L)_2$ with $[Me_2SSMe]BF_4$, the latter reagent functioning as a MeS^+ donor. Solution ^1H NMR and IR data indicate that these reactions give a single isomeric form relative to placement of the phosphine ligands. Variable-temperature (−80 to +60 °C) NMR data on $[Fe(\mu\text{-}SMe)_3(CO)_4(PMe_2Ph)_2]BF_4$ show changes in chemical shifts of the thiolate and phosphine protons; at lower temperatures this is due to restricted rotation about the metal–phosphorus bond, while at higher temperature there is inversion at the bridging sulfur. In a solution a slow conversion of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4$ to $[Fe_2(\mu\text{-}SMe)_3(CO)_3(L)_3]BF_4$ and $[Fe_2(\mu\text{-}SMe)_3(CO)_2(L)_4]BF_4$ occurs. According to cyclic voltammetry these compounds undergo two sequential oxidations. Potentials for these oxidations varied predictably with the nature of L and the degree of substitution. The products of oxidation were not isolated.

Introduction

A cationic iron–thiolate complex with the formula $[Fe_2(\mu\text{-}SMe)_3(CO)_6]^+$ had been found as the unexpected product from oxidation of $Fe_2(\mu\text{-}SMe)_2(CO)_6$ by $NOPF_6$ or $(CF_3)_2C_2S_2$.[1] More recently, the synthesis of this compound was accomplished by the reaction of $Fe_2(\mu\text{-}SMe)_2(CO)_6$ with $[Me_2SSMe]BF_4$.[2] In this designed synthesis, the latter reagent is a MeS^+ donor, a common mode of reaction for this species.[3] Mechanistically, it is assumed that this reaction occurs by attack of the incoming nucleophile, the metal complex, at the sulfur atom of the MeS group with concurrent displacement of Me_2S. Other examples of the use of $[Me_2SSMe]BF_4$ as MeS^+ donor in organometallic syntheses have been reported from our research group.[4]

Our research group[5] and others,[6] have also reported the syntheses and chemistry of the compounds $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$ (R = Me, Bu^t, Ph). The methyl complex is isoelectronic and isostructural with $[Fe_2(\mu\text{-}SMe)_3(CO)_6]^+$. Notably, the manganese anion was found to undergo two one-electron oxidations in cyclic voltammetric studies, and it was assumed that oxidation to a cation $[Mn_2(\mu\text{-}SR)_3(CO)_6]^+$ was accompanied by the formation of a metal–metal bond between the two manganese centers.[7]

The work referenced above[2,6,7] led into the study reported here. We undertook to synthesize and study the complexes $[Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4$ (L = phosphines), derivatives of $[Fe(\mu\text{-}SMe)_3(CO)_6]BF_4$ in which two carbonyl groups have been replaced by phosphines. Phosphines are better electron donors than CO, a fact that should lead to the increased electron richness at the metal centers and favor oxidative chemistry in these complexes.

Experimental Section

Standard procedures for purification of solvents were followed. All manipulations were carried out under an inert atmosphere (N_2), and this work was carried out in a good hood. Syntheses of $[Me_2SSMe]BF_4$[8] and $Fe_2(\mu\text{-}SMe)_2(CO)_4(L)_2$ (L = PMe_3, PMe_2Ph, PEt_2Ph, PPh_3)[9] were carried out according to published procedures; for the metal complexes, it was first necessary to prepare $Fe_2(\mu\text{-}SMe)_2(CO)_6$ from $Fe_3(CO)_{12}$ and CH_3SH.[10]

Infrared spectra were recorded on a Beckman 4230 spectrometer using CH_2Cl_2 solutions. Nuclear magnetic resonance spectra (^1H NMR) were obtained with Bruker WP 200 and AM-500 spectrometers using CD_2Cl_2 solutions of these compounds; ^{31}P NMR (^1H decoupled) spectra were run on a Bruker AM-500 spectrometer and chemical shifts referenced to H_3PO_4. Elemental analyses were provided by Galbraith Laboratories, Knoxville, TN.

Electrochemical measurements were made by using a Princeton Applied Research (EG&G Princeton Applied Research, Princeton, NJ) Model 175 generator and a Model 173 three-electrode potentiostat equipped with a Model 176 current-to-voltage converter. Solution resistance was compensated by using the positive feedback resistance compensation circuit of the Model 176 current–voltage converter. Calculations of solution resistance and the use of ferrocene as a standard for verifying adequate compensation have been previously discussed.[11,12] The voltammetric data were collected by using two different data acquisition schemes. In the first, data were recorded on a Nicolet Model 4094 digital oscilloscope and transferred to an IBM Model 9000 computer for analysis. In the second, a Nicolet Explorer 111A oscilloscope was used to record the data which were then transferred to an IBM AT computer. Background voltammograms were obtained in separate experiments with solvent and supporting electrolyte and these were subtracted from the raw data to provide background-corrected voltammograms. All data reported in this paper have been corrected in this way.

The cell for voltammetry was of standard design[11] and included inlet ports for the working electrode, counter electrode (platinum

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wire), and reference electrode probe. The working electrode was a platinum disk (diameter = 0.25 cm) sealed in soft glass that was polished on a polishing wheel with 0.3-μm alumina followed by 0.05-μm alumina. The electrode was then rinsed in a sonicating bath with triply distilled water and further rinsed with the electrochemical solvent. The reference electrode was an aqueous saturated calomel electrode (SCE), and the closure of the probe tip was a cracked-glass seal. The stability of the SCE was verified by frequent measurement of the reversible half-wave potential for the ferrocene 0/+ couple, which has a value of +0.39 V vs SCE in acetonitrile. The solution temperature was ambient (22 ± 2 °C).

General Procedure for the Syntheses of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4$. A 1.0-mmol sample of the complex $Fe_2(\mu\text{-}SMe)_2(CO)_4(L)_2$ was dissolved in 75 mL of CH_2Cl_2; then 1.0 mmol of solid $[Me_2SSMe]BF_4$ was added. The mixture was stirred at ambient temperature for approximately 2 h; periodically the progress of the reaction was monitored by recording the infrared spectrum of a small sample withdrawn from the solution by a syringe. A rapid change in the color of solution, from deep red to a paler orange, was observed. When the reaction was judged by infrared spectroscopy to be complete, the solvent was evaporated in vacuo. The residue was extracted with a minimal amount of CH_2Cl_2 and after filtration, diethyl either was layered on top of this solution. Cooling at −20 °C led to precipitation of the product. Repeated crystallizations from CH_2Cl_2/Et_2O were usually required to get an analytically pure material. The solid products were separated by filtration and dried in vacuo.

$[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_3)_2]BF_4$: bright orange, yield 38%, mp 170–173 °C. Anal. Calcd: C, 25.85; H, 4.51; S, 15.92. Found: C, 26.09; H, 4.70; S, 15.64. IR: ν(CO) 2035, 2020, 1983 cm^{-1}. ^{1}H NMR, δ: (20 °C) 1.50 (d, int 18, J_{PH} = 10.3 Hz), 2.37 (t, J_{PH} = 3.60 Hz), 2.42 (s), 2.47 (s, int 3 for each resonance); (−40 °C) 1.43 (d, J_{PH} = 10.7 Hz, 18 H, PMe_3), 2.34 (t, J_{PH} = 3.5 Hz, 3 H, SMe, trans to PMe_3), 2.37 (s, 3 H, SMe, cis to PMe_3), 2.44 (s, 3 H, SMe, cis to PMe_3). ^{31}P NMR (CD_2Cl_2, 500 MHz, relative to 85% H_3PO_4), δ: (20 °C) 20.88 (s, int 100), 52.76 (s, int 3). ^{31}P NMR (CD_3CN, 500 MHz, relative to 85% H_3PO_4), δ: (20 °C) 21.81 (s); (−40 °C) 22.66 (s).

$[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_2Ph)_2]BF_4$: orange solid, yield 30%, mp 144–146 °C. Anal. Calcd: C, 37.38; H, 4.28; S, 13.17. Found: C, 37.60; H, 4.27; S, 13.20. IR: ν(CO) 2035, 2020, 1985 cm^{-1}. ^{1}H NMR, δ: (20 °C) 1.76 (d, int 12, J_{PH} = 10.12 H), 2.07 (s, int 3), 2.26 (int 3) overlapping 2.26 (t, int 3, J_{PH} = 3.53 Hz), 7.38 (m, int 4), 7.53 (m, int 6); (−40 °C) 1.68 (d, J_{PH} = 10.6 Hz, 6 H, PMe), 1.72 (d, J_{PH} = 10.2 Hz, 6 H, PMe), 1.72 (s, 3 H, SMe, cis to $PhMe_2$), 2.18 (t, J_{PH} = 3.6 Hz, 3 H, SMe, trans to $PPhMe_2$), 2.24 (s, 3 H, SMe, cis to $PPhMe_2$). ^{31}P NMR (CD_2Cl_2, 500 MHz, relative to 85% H_3PO_4), δ: (20 °C) 26.12 (s), 49.22. ^{31}P NMR (CD_3CN, 500 MHz, relative to 85% H_3PO_4), δ: (20 °C) 27.09 (s), 50.28 (s); (−40 °C) 27.22 (s).

$[Fe_2(\mu\text{-}SMe)_3(CO)_4(PPh_3)_2]BF_4$: orange, yield 15%, mp 166–168 °C. Anal. Calcd: C, 52.90; H, 4.03; S, 9.85. Found: C, 49.24, H, 4.21; S, 9.45. IR: ν(CO) 2038, 2025, 1983 cm^{-1}. The ^{1}H NMR spectrum of this compound was complicated by the resonances of an impurity, which may also be the cause of the poor carbon analysis.

$[Fe_2(\mu\text{-}SMe)_3(CO)_4(PEt_2Ph)_2]BF_4$: orange, yield 84%, mp 140–143 °C. Anal. Calcd: C, 41.3; H, 5.01; S, 12.3. Found: C, 40.31; H, 5.00; S, 11.99. IR: ν(CO) 2035, 2020, 1983 cm^{-1}. ^{1}H NMR, δ: 1.10 (septet, int 12, J_{av} = 7.45 Hz), 1.72 (s, int 3), 2.16 (m, int 14), 7.30 (m, int 4), 7.55 (m, int 6). The complicated ^{1}H NMR spectrum for this species was not easily interpreted; this led us to record the spectrum of this compound at 500 MHz; vide infra.

Variable-Temperature ^{1}H NMR Spectrum for $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_2Ph)_2]BF_4$. An ^{1}H NMR spectrum of this compound at 500 MHz reproduced the data given above. Besides the phenyl proton multiplet, one observes a singlet (δ 2.233) overlapping the low-field line of a triplet (δ 2.226, J = 3.59 Hz) and a singlet (V 1.982) for the SCH_3 groups. The resonance for the $P(CH_3)_2$ protons is better resolved as a pair of doublets, this pattern arising since the methyl protons are diastereotopic. Analyses of this pattern gives parameters for $(CH_3)_a$ (δ 1.737, J = 10.35 Hz) and for $(CH_3)_b$ (δ 1.741, J = 10.09 Hz). Figure 1 reproduces this spectrum, which also contains a multiplet due to residual protons in the solvent, CD_3CN, and very small impurity peaks.

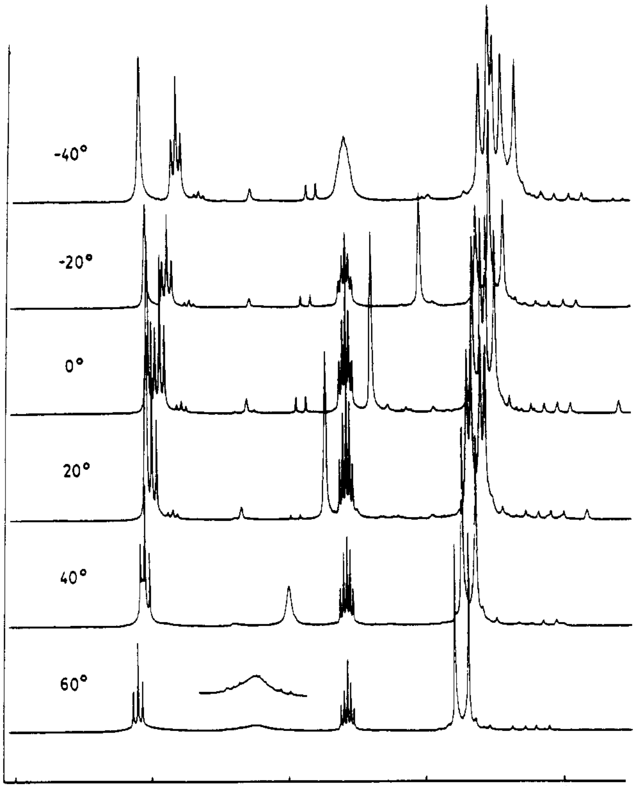

Figure 1. Temperature dependence of the 500-MHz ^{1}H NMR spectrum of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_2Ph)_2]BF_4$ in CD_3CN.

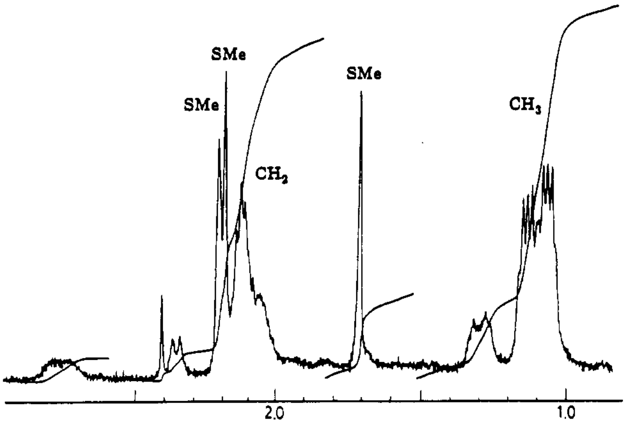

Figure 2. Alkyl region of the 500-MHz ^{1}H NMR spectrum of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PEt_2Ph)_2]BF_4$ in CD_2Cl_2.

Dramatic changes in the spectrum of this compound occur as the temperature is lowered to −40 °C. The triplet originally overlapping one singlet separates and moves upfield, the other singlet moves upfield by a larger extent and has become coincident with the resonances for the $P(CH_3)_2$ protons, and the $P(CH_3)_2$ resonances shift upfield and the appearance is altered dramatically (Figure 1). Spectra at intermediate temperatures show a progressive shift of the resonances in the directions given.

The choice of solvent (CD_3CN) limits going to lower temperatures. However, we have recorded further data in CD_2Cl_2, down to −80 °C. The data for the higher temperatures reproduce the CD_3CN data with small variations in chemical shifts and lower resolution. At −80 °C, the resonances have broadened slightly but are otherwise similar to those given in the −40 °C spectrum above.

500-MHz ^{1}H NMR Spectrum of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PEt_2Ph)_2]BF_4$. The complete spectrum for this compound contains resonances for the phenyl protons between δ 7.4 and 8.1

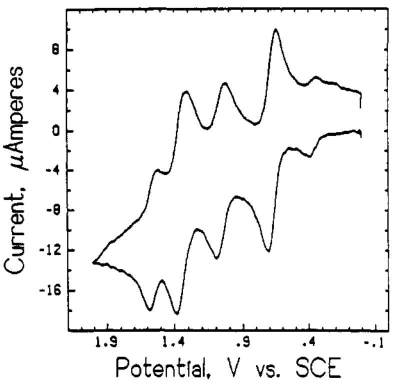

Figure 3. Cyclic voltammogram for 1.0 mM $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PEt_2Ph)_2]BF_4$ in 1.0 M TBAP/acetonitrile at 0.2 V/s.

Table I. Cyclic Voltammetric Data[a]

$[Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4$

L	$E_{1/2}(B^+/B^{2+})$[b]	ΔE_p[c]	$E_{1/2}(B^{2+}/B^{3+})$	ΔE_p[c]
PMe_3	1.001	64	2.510	80
PMe_2Ph	2.040	64	1.537	64
PEt_2Ph	2.050	64	1.550	56
PPh_3	1.812	85	1.641	95

$[Fe_2(\mu\text{-}SMe)_3(CO)_3(L)_3]BF_4$

L	$E_{1/2}(A^+/A^{2+})$[b]	ΔE_p[c]	$E_{1/2}(A^{2+}/A)$	ΔE_p[c]
PMe_3	0.628	64	1.297	88
PMe_2Ph	0.667	56	1.337	64
PEt_2Ph	0.669	72	1.342	72
PPh_3	1.812	75	1.468	95

$[Fe_2(\mu\text{-}SMe)_3(CO)_2(L)_4]BF_4$

L	$E_{1/2}(C^+/C^{2+})$[b]	ΔE_p[c]	$E_{1/2}(C^{2+}/C^{3+})$	ΔE_p[c]
PMe_3	0.34 v	56	obscured	

[a] 0.10 M TBAP in acetonitrile. Platinum-disk working electrode. Scan rate: 0.2 V/s. [b] V vs SCE. Reversible half-wave potential taken as the mean of the anodic and cathodic peak potentials. [c] mV. Anodic peak potential minus cathodic peak potential.

and a series of resonances between δ 1.0 and 2.5 for the remaining protons in this molecule. An expansion of this latter region is given in Figure 2.

The protons in the methyl group of the phosphine ($P\text{-}CH_2CH_3$) appear as two five-line 1:2:2:2:1 patterns centered at about δ 1.1. Two patterns arise because the ethyl groups are diastereotropic due to the SMe orientations. The 1:2:2:2:1 doublet arises from coupling to the methylene protons (8 Hz) and the phosphorus atom (J_{PH} = 15 Hz). The methylene protons of this ligand are seen as a broad, undecipherable multiplet at about δ 2.1. There are three resonances at δ 2.21, 2.19, and 1.72, assignable to SCH_3 protons.

Several additional resonances in this spectrum at lower intensity (notably the ones at δ 1.2 and 2.35) arise from a second species in solution; an 88:12 ratio of these two species can be determined on the basis of intensities of the phosphine methyl groups. Most likely, it is a compound having other than two phosphines (vide infra).

Electrochemistry on $[Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4$ Species. It will be useful to summarize the results of electrochemical studies at this point, since these data provide a rationale for additional synthetic studies to be described next.

In our initial investigations on these compounds, cyclic voltammograms were obtained, having two sets of oxidation/reduction processes. Figure 3 portrays a typical result for the compound $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PPhEt_2)_2]BF_4$. One set of oxidation/reduction peaks ($E_{1/2}$ = 0.669 V, 1.342 V) had peak currents different from the second set ($E_{1/2}$ = 1.050 V, 1.550 V). Cyclic voltammograms on the other three compounds in this study, compounds that differed only by the phosphine ligand, showed the same behavior although with different ratios of currents. The numerical values of $E_{1/2}$ and ΔE_p for the four compounds are given in Table I. Different peak currents argue persuasively for the presence of two different species in solution at different concentrations.

An understanding of this situation came about when we discovered that the relative peak currents of the pairs of oxidation peaks changed over time. Knowing this, it was easy to design an experiment that involved freshly prepared solutions, something that had not been closely attended to in the initial studies. Such solutions showed only two of the four oxidation steps. We were able to conclude from this that the second compound was derived from the first on standing in solution. We then set out to identify the second compound and then determine the parameters influencing its formation. As will be noted below, the second products were found to have the formula $[Fe_2(\mu\text{-}SMe)_3(CO)_3(L)_3]BF_4$. Later we realized that another oxidation peak at lower potential (in Figure 3, $E_{1/2}$ = 0.34 V) previously assumed to be spurious on the basis of very low peak current and nonreproducibility from one experiment to the next, was due to small amounts of still a third compound $[Fe_2(\mu\text{-}SMe)_3(CO)_2(L)_4]BF_4$.

The experiments that follow were designed to determine how $[Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4$ species underwent these ligand redistributions to form $[Fe_2(\mu\text{-}SMe)_3(CO)_{6-x}(L)_x]BF_4$ (x = 3, 4) and to characterize the new species.

Reaction of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_3)_2]BF_4$ and PMe_3. A solution of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_3)_2]BF_4$ (0.360 g, 0.596 mmol) in 40 mL of CH_3CN was treated with 0.25 mL (3.3 mmol) of PMe_3 and stirred at ambient temperature for 16 h. The solution was treated with an additional 0.25 mL (3.30 mmol) of PMe_3 and gently heated for 24 h. The deep red solution showed new IR absorptions at 2025 (s), 1998 (s), 1975 (s), 1940 (vs), and 1868 (m) cm^{-1}. The solvent was removed on a rotary evaporator; chromatography of the oily residue on alumina gave a pale yellow band (eluting with 10% ether in hexane) and a deep red band (eluting with 5% methanol/CH_2Cl_2).

The first fraction was concentrated under nitrogen to precipitate 0.024 g of waxy orange solid, mp 108–110 °C, identified by IR and ^1H NMR as $Fe_2(CO)_4(PMe_3)_2(SMe)_2$.[9] IR ($CH_2Cl_2$): ν(CO) 1998s, 1940s cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz), δ: 1.82 (s, 6 H, SMe), 1.56 (t, J_{PH} = 4.2 Hz, 18 H, PMe_3). ^1H NMR (acetone-d_6, 200 MHz) δ: 1.76 (s, 6 H, SMe), 1.59 (t, J_{PH} = 4.2 Hz, 18 H, PMe_3).

The second fraction was concentrated to a deep red oil with a rotary evaporator. Crystallization of this residue from CH_2Cl_2/ether yielded 0.135 g of a red powder that was shown by ^1H NMR and cyclic voltammetry to be a mixture of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_3)_2]BF_4$ (starting material, identified in data below as B), 65% $[Fe_2(\mu\text{-}SMe)_3(CO)_3(PMe_3)_3]BF_4$ (A), and 25% $[Fe_2(\mu\text{-}SMe)_3(CO)_2(PMe_3)_4]BF_4$ (C) (approximate ratio of B, A, and C: 7:68:25). IR of mixture (CH_2Cl_2): ν(CO) 2025 (vs), 1975 (s), 1940 (vs) cm^{-1}. IR (KBr): ν(CO) 2025 (s), 1975, 1930 (s), 1905 (m) cm^{-1}; $\nu(BF_4)$ 1100 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz), δ: A (71% of mixture) 1.38 (d, J_{PH} = 7.4 Hz, 9 H, PMe_3), 1.43 (d, J_{PH} = 8.5 Hz, 9 H, PMe_3), 1.47 (d, J_{PH} = 11.1 Hz, 9 H, PMe_3), 2.25 (t, J_{PH} = 3.6 Hz, 3 H, SMe), 2.28 (s, 3 H, SMe), 2.31 (d, J_{PH} = 2.5 Hz, 3 H, SMe); B (6% of mixture, data given above); C (23% of mixture) 1.38 (d, J_{PH} = 7.4 Hz, 36 H, PMe_3), 2.15 (broad s, 6 H, SMe), 220 (s, 3 H, SMe). ^{31}P NMR (CD_3CN, 500 MHz), δ: A (66% of mixture) 17.59 (dd, J_{PP} = 6.3, 46.0 Hz), 19.18 (dd, J_{PP} = 18.8, 46.1 Hz), 21.31 (dd, J_{PP} = 6.6, 19.1 Hz); B (7% of mixture, data given above); C (28% of mixture) 17.62 (s). $E_{1/2}$ = 0.40 V (25% of mixture, C), 0.67 V (67% of mixture, A), 0.98 V (33% of mixture, B and C), 1.26 V (67% of mixture, A), 1.51 V (8% of mixture, B).

Attempts to further separate these three compounds to get analytically pure samples were unsuccessful.

Reaction of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_2Ph)_2]BF_4$ and H_2O. A solution of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PPhMe_2)_2]BF_4$ (0.194 g, 0.269 mmol in 15 mL of CH_3CN was treated with 1 mL of distilled water and heated at reflux for 15 h. The color of the solution changed from pale orange to red. The solvent was removed on a rotary evaporator and chromatography (alumina/20% ether/CH_2Cl_2) of the residue yielded a single red band. The fraction was concentrated to give 0.040 g of intractable red tar. ^1H and ^{31}P NMR spectra and cyclic voltammetry indicated that the tar was 10% $Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_2Ph)_2]BF_4$ and 90% $[Fe_2(\mu\text{-}SMe)_3(CO)_3(PMe_2Ph)_3]BF_4$.

Alternatively, a sample of $[Fe_2(\mu\text{-}SMe)_3(CO)_3(PMe_2Ph)_3]BF_4$ was prepared by treating $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_2Ph)_2]BF_4$ (0.476 g, 0.653 mmol) in 30 mL of CH_3CN with $PPhMe_2$ (0.15 mL, 1.1

mmol). The solution was heated at reflux for 5.5 h and was worked up as previously described. The product was an intractable red tar that was characterized by IR and ^{1}H NMR as a 1:9 mixture of starting material and $[Fe_2(\mu\text{-}SMe)_3(CO)_3(PMe_2Ph)_3]BF_4$.

Results

Synthesis. The complexes, $[Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4$, were prepared by the following reaction:

$$Fe_2(\mu\text{-}SMe)_2(CO)_4(L)_2 + [Me_2SSMe]BF_4 \rightarrow [Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4 + Me_2S \quad (1)$$

$$L = PMe_3,\ PMe_2Ph,\ PEt_2Ph,\ PPh_3$$

Yields of purified products were around 30% except for the compound with L = PEt_2Ph, for which an 84% yield was obtained. It is likely that the low yields reflect losses of product during purification; infrared spectra of crude mixtures indicated a complete reaction to a single carbonyl-containing product, and there were no insoluble residues characteristic of decomposition. The orange crystalline complexes appeared stable and unreactive toward oxygen and moisture over at least moderate periods of time. However, ligand redistribution reactions are found to occur in solution (vide infra).

The phosphine ligands in the starting materials, $[Fe_2(\mu\text{-}SMe)_2(CO)_4(L)_2]$, are trans to the metal–metal bond. Infrared spectra of these species contain three ν(CO) absorptions. A similar pattern of ν(CO) absorptions is seen for the products, $[Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4$, shifted to a higher frequency, as expected due to the positive charge on the complex. The similarity between this absorption pattern and the pattern of ν(CO) absorptions in the starting materials suggests that the overall molecular geometry is not greatly perturbed by the addition of a SMe^+ group. The best assumption is that the SMe group from $[Me_2SSMe]BF_4$ ends up in a position trans to the phosphines. Other work in our labs supports this assumption; we have found in reactions between $Fe_2(\mu\text{-}SR)_2(CO)_4(L)_2]$ (R = Me) and $[Me_2SSMe]BF_4$ that the added SMe group is always trans to the phosphines.[13]

These examples further develop the use of $[Me_2SSMe]BF_4$ in organometallic synthesis. Prior use has been made of this reagent for the synthesis of other metal thiolate complexes and also for the synthesis of metal complexes of organic disulfides.[2,4] A reaction mechanism involving attack of a nucleophile at the MeS group in $[Me_2SSMe]BF_4$ with displacement of Me_2S is generally postulated. In the present context, it is interesting that the electron pair between the two metals is the nucleophilic center in this reaction.

The ^{1}H NMR spectra of both the crude and purified products indicated that single isomers formed in these reactions. These spectra contained three resonances of equal intensity for protons of the methyl thiolate groups. Two of the resonances are singlets, while the third is a triplet, the multiplicity arising by virtue of coupling to the phosphorus nuclei in trans positions. Protons of the phosphines give rise to predictable resonances, assuming the two ligands are in chemically equivalent environments.

The ^{31}P NMR (hydrogen decoupled) spectra for several compounds were run and showed only one singlet resonance indicating that one species is present and there is equivalence of the phosphine ligands.

In the course of this investigation we carried out a variable-temperature ^{1}H NMR study on two of these compounds. For $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_3)_2]BF_4$, the study revealed nothing unusual; the only variation involved small chemical shift changes. However, there were striking changes in the ^{1}H NMR spectrum of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_2Ph)_2]BF_4$. Spectra for this compound from −40 to +60 °C are portrayed in Figure 1.

At temperatures above +20 °C, the two singlet SCH_3 resonances are seen to broaden, indicative of an exchange process. It was not possible to reach a temperature at which these resonances coalesced to a single resonance due to decomposition of the sample. However, a similar pattern of behavior has been reported in the literature for $Fe_2(\mu\text{-}SMe)_2(CO)_6$,[10] and for this species, a process involving inversion of configuration at sulfur is assumed responsible for this change in the spectrum. The similarity to data presented here argues for the occurrence of a similar process.

As the CD_3CN solution of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(PMe_2Ph)_2]BF_4$ is cooled from +20 to −40 °C, the positions of the SCH_3 resonances change position, the triplet moving upfield, by a small extent (0.05 ppm), and the upfield singlet moving upfield, by a substantially greater amount (about 0.5 ppm). The diastereotopic protons in the methyl groups of the phosphine ligand are also shifted somewhat, causing a substantial change in the appearance of this pattern. The freezing point of CD_3CN restricts this study to a minimum temperature of −40 °C. Switching to CD_2Cl_2 as solvent allows spectra to be obtained down to about −80 °C. The spectra from room temperature down to −40 °C duplicated the spectra in CD_3CN but with lower resolution; the approximately 4-Hz half-width of the resonances caused the triplet pattern for SCH_3 and the small chemical shift difference in the diastereomeric $P(CH_3)_2$ protons not to be resolved. Between −40 and −80 °C, the chemical shifts of the SCH_3 protons changed only slightly; otherwise the spectrum was unchanged.

These changes probably result from rotation of the phosphines around the phosphorus–metal bond. The position of the phenyl ring will presumably have considerable influence on the chemical shifts of the SCH_3 protons in its vicinity. Over the range of temperatures studied, the relative populations of various conformations could be altered sufficiently to cause the observed shifts in the SCH_3 resonances.

We noted earlier the apparent stability and unreactivity of these compounds as solids. However, they undergo quite remarkable chemical transformations in solution. This first became known during an investigation into the electrochemistry of these compounds. Initial cyclic voltammetry studies revealed the presence of two different compounds. While freshly prepared solutions showed only two oxidation processes ($B^+ \rightarrow B^{2+}$ and $B^{2+} \rightarrow B^{3+}$), as expected for these complexes, solutions that had stood for some time showed the presence of two compounds. By monitoring the cyclic voltammetry over a period of time, we could follow the formation of a second compound, as seen by oxidation peaks. These oxidations occurred at lower potential; i.e., the new compound is easier to oxidize.

A series of attempts to isolate and identify the new compounds ensued. The definitive result was obtained

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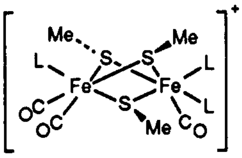
when we found that the new compounds were formed in a reaction of $[Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4$ and an additional ligand. Furthermore in this reaction a third species was also detected. The reaction (CH_3CN solution at reflux, 24 h) was

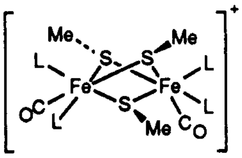
$$[Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2]BF_4 + L \rightarrow [Fe_2(\mu\text{-}SMe)_3(CO)_3(L)_3]BF_4 + [Fe_2(\mu\text{-}SMe)_3(CO)_2(L)_4]BF_4 + CO$$

Carbonyl displacement by a ligand is a reasonable and expected reaction in this situation, so the new species, predictably, have the formulas $[Fe_2(\mu\text{-}SMe)_3(CO)_{4-n}(L)_{2+n}]BF_4$ ($n = 1, 2$).

Unfortunately, the mixtures of products along with starting materials proved very difficult to separate, so that analytically pure products were not obtained. However, ^1H NMR data provided unequivocal characterizations. For example, the ^1H NMR spectrum of $[Fe_2(\mu\text{-}SMe)_3(CO)_3(PMe_3)_3]BF_4$ consisted of three doublets for the three chemically different phosphines, plus a singlet, doublet, and triplet for the three SCH_3 groups. The multiplicity of these latter resonances result from coupling to zero, one, and two phosphines located trans to the methyl group. The $^{31}P\{^1H\}$ NMR spectrum was also in accord with this formulation, since it contained three resonances that were doublets of doublets, the splitting due to ^{31}P–^{31}P couplings. These spectra uniquely fit the structure



The ^1H and ^{31}P NMR spectra of the third compound $[Fe_2(\mu\text{-}SMe)_3(CO)_2(PMe_3)_4]BF_4$ showed only one type of phosphine. The ^1H NMR spectrum contained one doublet for the phosphine methyl protons, along with two SCH_3 resonances in a 2:1 intensity ratio. The ^{31}P NMR spectrum was a singlet. These data uniquely identify this species as



Knowing the identities of these compounds allows comment on their formation in the electrochemical experiments. Several factors seem to be in evidence. The first is that the presence of water seems to promote this reaction. Water can be present, of course, from the calomel reference electrode. Second, most of the original electrochemical runs were on solutions that had been made up some time earlier and stored for periods up to several days. Control experiments indicated that this is sufficient time for some ligand redistribution to take place. Finally, electrochemical oxidation would presumably give product species that are quite labile, so that free phosphine would likely be generated in these solutions. In this context, note that oxidation products of isoelectronic $[Mn_2(\mu\text{-}SMe)_3(CO)_6]^-$ were found to rapidly decompose. Further we tried, without success, to isolate the products of oxidation of these compounds. All efforts gave only products of decomposition. Decomposition of an oxidation product means that free phosphine is expected to be present in these solutions. The presence of free phosphine also promotes this process.

It is appropriate to add a brief comment on the electrochemistry. The oxidation potential data, given in tabular form (Table I) show predictable trends. A trend in $E_{1/2}$ values is seen on the basis of the nature of the phosphine. This small variation is predictable on the basis of donor ability of the phosphines $PMe_3 > PEt_2Ph$ or $PMe_2Ph > PPh_3$. Increasing the numbers of phosphines makes it easier to oxidize the complex, again as predicted since phosphines are better electron donors than CO.

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Synthesis and Molecular Structure of a Molybdenum Difluorocarbene Complex, $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3(CF_2)]OSO_2CF_3$

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Treatment of $(\eta^5\text{-}C_5R_5)Mo(CO)_3CF_3$ (R = H, Me (**3**)) with Me_3SiOTf in benzene solution at ambient temperature results in precipitation of the corresponding carbene triflate salts $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CF_2)]OTf$ (**1**) and $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3(CF_2)]OTf$ (**4**) in high yield. The solid-state structures of **4** and its trifluoromethyl precursor **3** have been determined. In addition to being the first example of a structurally characterized group VI dihalocarbene complex, the observed lateral orientation of the planar CF_2 carbene moiety with respect to the basal plane in **4** is unprecedented for $CpML_3$(carbene) systems. Crystal data for **3**: orthorhombic, $P2_1cn$, with $a = 9.208$ (1) Å, $b = 9.822$ (1) Å, $c = 17.176$ (2) Å, $V = 1553.4$ (3) Å^3, $Z = 4$, $R_F = 2.49\%$, and $R_{wF} = 3.52\%$. Crystal data for **4**: tetragonal, $P4_2/mbc$, with $a = 17.895$ (2) Å, $c = 12.040$ (2) Å, $V = 3855.5$ (10) Å^3, $Z = 8$, $R_F = 3.86\%$, and $R_{wF} = 3.78\%$.

Introduction

Transition-metal dihalocarbene complexes constitute an unusual subclass of carbene compounds which may exhibit either electrophilic reactivity, as observed for classic heteroatom-substituted "Fischer-type" systems, or nucleophilic reactivity that is normally associated with "Schrock-type" alkylidenes.[1] In addition to addressing

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