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Preparation of (η^5-Cyclopentadienyl)dicarbonyl[tris(organothio)methyl]iron Complexes and the Structure of $Cp(CO)_2Fe[C(SCH_3)_3]$

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The dithiocarbene complex $Cp(CO)_2Fe[C(SCH_3)_2]^+$ reacts readily with mercaptides to give the tris(organothio)methyl complexes $Cp(CO)_2Fe[C(SCH_3)_2SR]$. The bis(organothio)methyl derivative $Cp(CO)_2Fe[\overline{C(H)S(CH_2)_3S}]$ may be prepared from $Cp(CO)_2FeI$ and $Li\overline{C(H)S(CH_2)_3S}$ and is converted to the carbene complex $Cp(CO)_2Fe[\overline{CS(CH_2)_3S}]^+$, by α-hydride abstraction. Reactions of $Cp(CO)_2Fe[C(SCH_3)_2SR]$ with acid give cationic dithiocarbene complexes. The X-ray diffraction study of $Cp(CO)_2Fe[C(SCH_3)_3]$ confirms that the $C(SCH_3)_3$ ligand is σ bound to the iron with an Fe–C bond length of 2.11 Å. The IR spectrum of $Cp(CO)_2Fe[C(SCH_3)_3]$ indicates the presence of conformational isomers in solution.

Introduction

The chemistry of sulfur-stabilized organic anions has been extensively studied as they are very versatile organic synthons.[2,3] The best known examples are lithiated 1,3-dithiane derivatives, $Li(R)\overline{CS(CH_2)_3S}$, but lithiated orthothioformates, $LiC(SR)_3$, have also received much attention.[2-6] We have recently extended the scope of metalated orthothioformate chemistry to include transition-metal derivatives by the fortuitous preparation of (η^5-cyclopentadienyl)dicarbonyl[tris(methylthio)methyl]iron, $Cp(CO)_2Fe[C(SCH_3)_3]$[7] (Cp = η^5-C_5H_5). Further work now has revealed a general route to [tris(organothio)methyl]iron derivatives from $Cp(CO)_2Fe$-[dithiocarbene]$^+$ complexes. Direct preparation of these complexes from $CpFe(CO)_2X$ species and lithiated orthothioformates has not been successful. However, lithiated 1,3-dithiane does react with $CpFe(CO)_2I$ to give the corresponding iron 1,3-dithiane derivative, and this has been evaluated as a possible route to cationic iron dithiocarbene complexes. Some chemical and physical characteristics, as well as the results of an X-ray diffraction study on $Cp(CO)_2Fe[C(SCH_3)_3]$, are reported herein.

Experimental Section

General Information. Reagent grade chemicals were used without further purification, and $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ (I) was prepared as reported previously.[7] Tetrahydrofuran (THF) was distilled from $NaK_{2.8}$[8] under N_2 immediately prior to use. Infrared spectra were recorded on a Perkin-Elmer 281 spectrophotometer. Routine ^1H NMR spectra were recorded on a Perkin-Elmer Hitachi R-20B spectrometer; temperature-dependent ^1H NMR spectra were recorded on a Varian HA-100 spectrometer. Carbon-13 spectra were recorded on a JEOL FX-90Q spectrometer; $Cr(acac)_3$ (~0.1 M) was added to the solutions to reduce data collection time.[9] Tetramethylsilane (Me_4Si) was employed as the internal standard for all NMR spectra. All reactions were carried out in N_2-saturated solvents under an N_2 atmosphere.

Preparation of $Cp(CO)_2Fe[C(SCH_3)_3]$ (IIa). Sodium hydride (57% mineral oil dispersion, 0.025 g, 0.59 mmol) was dissolved in 40 mL of THF, and CH_3SH was slowly bubbled through the solution until H_2 production ceased (~0.5 h). To this, $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ (I) (0.20 g, 0.47 mmol) was added, and the reaction was stirred for 20 min at room temperature. After evaporation to dryness, the residue was extracted with Et_2O until the extracts were colorless. These were filtered and evaporated to dryness under an N_2 stream. The resulting crude product was crystallized from hexanes at −20 °C to give 0.12 g (77%) of IIa as large yellow-orange needles, mp 98–101 °C. IR (CH_2Cl_2): 2013 (s), 1964 (s) cm^{-1}. IR (hexanes): 2023 (s), 2013 (m), 1977 (s), 1968 (m) cm^{-1}. ^1H NMR (CS_2): τ 5.17 (s, C_5H_5), 7.89 (s, 3 SCH_3). ^{13}C NMR (acetone-d_6): 217.0 (s, 2 CO), 90.9 (s, C_5H_5), 60.7 (s, $C(SCH_3)_3$), 19.6 ppm (s, 3 SCH_3). Anal. Calcd for $C_{11}H_{14}FeO_2S_3$: C, 40.00; H, 4.27; S, 29.12. Found: C, 40.00; H, 4.42; S, 28.76.

Preparation of $Cp(CO)_2Fe[C(SCH_3)_2SPh]$ (IIb). Sodium hydride (57% mineral oil dispersion, 0.0205 g, 0.487 mmol) was dissolved in 40 mL of THF, and PhSH (50.0 μL, 0.487 mmol) was added. This mixture was stirred until H_2 production ceased (~20 min); then I (0.20 g, 0.47 mmol) was added. The reaction mixture immediately became dark green and then rapidly turned yellow-orange. After it was stirred 15 min, the solution was evaporated to dryness and extracted with CS_2 until the extracts were colorless. These extracts were filtered and evaporated to dryness. The crude product was crystallized by dissolving in a minimum amount of an 80:20 mixture of hexanes/Et_2O and cooling to −20 °C to give 0.13 g (70%) of IIb as dark yellow-orange crystals, mp 99–101 °C dec. IR (CH_2Cl_2): 2017 (s), 1966 (s) cm^{-1}. IR (hexanes): 2024 (s), 1978 (s) cm^{-1}. ^1H NMR (CS_2): τ 2.83 (m, C_6H_5), 5.21 (s, C_5H_5), 8.31 (s, 2 CH_3). Anal. Calcd for $C_{16}H_{16}FeO_2S_3$: C, 48.98; H, 4.11. Found: C, 48.89; H, 4.09.

Preparation of $Cp(CO)_2Fe[\overline{C(H)S(CH_2)_3S}]$ (V). Lithiated 1,3-dithiane was generated in 75 mL of THF at −78 °C from 0.395 g (3.28 mmol) of 1,3-dithiane and 2.00 mL (3.20 mmol) of butyllithium (1.6 M THF solution) by stirring the solution for 20 min. A solution of 75 mL of THF containing $Cp(CO)_2FeI$[10] (0.999 g, 3.27 mmol) was added, and the mixture was stirred at −78 °C for 15 min. Stirring continued as the mixture was allowed to come to room temperature (~2 h). After evaporation, the reaction residue was chromatographed on a Florisil column (38 × 2 cm) with CS_2/Et_2O (98:2) as the elutant. A yellow product band was followed by a maroon $[CpFe(CO)_2]_2$ band and a blue-green band, which could not be eluted. The yellow band was collected, evaporated, and crystallized from hexanes at −20 °C to give 0.53 g (55%) of V as yellow crystals, mp 104–107 °C. IR (hexanes): 2026 (s), 1979 (s) cm^{-1}. ^1H NMR (CS_2): τ 5.09 (s, C_5H_5), 5.99 (s, CH), 7.00–8.00 (m, 3 CH_2). Anal. Calcd for $C_{11}H_{12}FeO_2S_2$: C, 44.61; H, 4.08. Found: C, 44.89; H, 4.19.

Reaction of IIa with Acid. Trifluoromethanesulfonic acid (13 μL, 0.15 mmol) was added to 10 mL of Et_2O containing IIa (0.050 g, 0.15 mmol); a yellow precipitate formed instantaneously. After the reaction mixture was stirred for 15 min, the precipitate was collected and washed with Et_2O. The precipitate was crystallized from acetone with Et_2O at −20 °C to give 0.063 g (96%) of $\{Cp(CO)_2Fe[C(SCH_3)_2]\}CF_3SO_3$ (VI) as yellow crystals, mp 73–76 °C. IR (CH_2Cl_2): 2055 (s), 2014 (s) cm^{-1}. ^1H NMR (acetone-d_6): τ 4.34 (s, C_5H_5), 6.69 (s, 2 CH_3). Anal. Calcd for $C_{11}H_{11}F_3FeO_5S_3$: C,

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30.57; H, 2.57. Found: C, 30.80; H, 2.61.

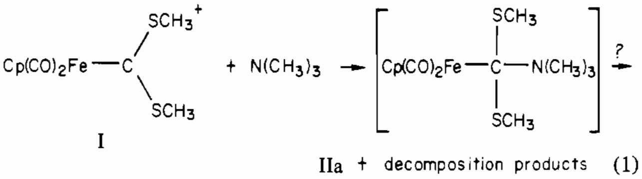
Reaction of IIb with Acid. Trifluoromethanesulfonic acid (17 μL, 0.20 mmol) was added to 15 mL of Et_2O containing IIb (0.072 g, 0.18 mmol). A yellow precipitate formed immediately and changed to a yellow oil on further stirring. After the mixture was stirred 20 min, the oil was collected and washed with Et_2O, but it could not be made to crystallize. The yield was 0.081 g (96%) of a mixture of $\{Cp(CO)_2Fe[C(SCH_3)_2]\}CF_3SO_3$ (VI) and $\{Cp(CO)_2Fe[C(SCH_3)SPh]\}CF_3SO_3$ (VII) (56 and 40% respectively, from ^{1}H NMR). IR (CH_2Cl_2): 2055 (s), 2014 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 2.24 (s, C_6H_5), 4.36 [s, C_5H_5 (VI)], 4.44 [s, C_5H_5 (VII)], 6.72 (s, CH_3).

Structural Details for IIa. A single crystal of approximately rectangular shape with dimensions of $0.2 \times 0.2 \times 0.35$ mm was chosen for X-ray diffraction studies. The observed Laue symmetry ($2/m$) indicated the monoclinic crystal system. The cell dimensions at 25 °C were $a = 11.813$ (3) Å, $b = 12.611$ (3) Å, $c = 9.736$ (2) Å and $\beta = 100.68$ (3)°, with $Z = 4$. Four octants of data ($2\theta < 45°$) were collected on a four-circle diffractometer designed and built in the Ames Laboratory[11] using graphite-monochromated Mo Kα X-rays ($\lambda = 0.71034$ Å). The 5812 measured intensities were averaged and yielded 1472 reflections that were considered observed ($I > 3\sigma_I$). Data were corrected for Lorentz-polarization effects; an absorption correction was made. The observed extinctions $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, uniquely imply space group $P2_1/n$.

The position of the iron atom was obtained from an analysis of the Patterson map. The positions of the remaining nonhydrogen atoms were found by successive structure factor and electron density map calculations. Hydrogen positions were calculated and included in subsequent structure factor calculations. The positional and anisotropic thermal parameters for the nonhydrogen atoms were refined by a block matrix and a final full-matrix least-squares procedure[12] to a final convention residual $R = 6.6\%$ and a weighted residual $R_w = 11.9\%$.

Results and Discussion

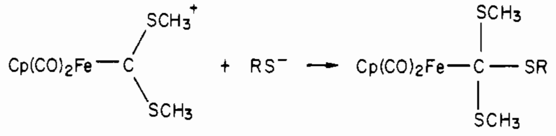
Indirect Preparation of $Cp(CO)_2Fe[C(SCH_3)_3]$ (IIa). The tris(methylthio)methyl complex $Cp(CO)_2Fe[C(SCH_3)_3]$ (IIa) was originally isolated as a side product in the reactions of the dithiocarbene complex $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ (I) with amines.[7,13] When I is reacted with other bases such as CH_3O^-, PhO^-, $PhSe^-$, and aqueous OH^-, small amounts of IIa and none of the possible product, $Cp(CO)_2Fe[C(SCH_3)_2YR]$ (Y = O, Se), may be isolated. The best yield of IIa (34%) in these indirect routes is found when trimethylamine is reacted with I. While the mechanistic nature of these syntheses of IIa is unclear, the amine reactions may be rationalized by the formation of an unstable ylide intermediate generated by nucleophilic attack at the carbene carbon of I (eq 1). Precedent for such an ylide may be found in the preparation of stable neutral ylide complexes from $(CO)_5M[carbene]$ (M = Cr, W) complexes and certain phosphines and tertiary amines.[14] No physical evidence for the proposed cationic ylide, other than the formation of a transitory bright red color in the reactions of I with amines, has been found in our system. The unstable ylide formed from I and primary and secondary amines could react intramolecularly by loss of $HSCH_3$ to give the observed cationic isocyanide and aminothiocarbene complexes.[7] This cannot occur with tertiary amines, and the unstable ylide decomposes, possibly by mercaptide transfer between two ylides or I and an ylide to give IIa in yields not to exceed the theoretical 66% value based on I. The relatively low yields of IIa and the formation of large amounts of insoluble, unidentified decomposition products in these indirect routes support this mechanistic possibility.



I

(1)

General Route to [Tris(organothio)methyl]iron Derivatives. Complex I reacts readily with mercaptides to give the corresponding tris(organothio)methyl complexes (IIa,b) in good yield (eq 2). The reaction appears to be a simple nucleophilic addition of mercaptide to the electron-deficient carbene carbon.



(2)

I

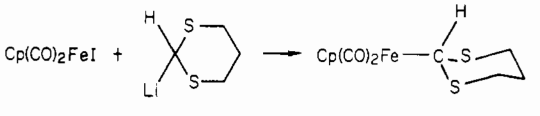
IIa,b

R = CH_3 (IIa, 77%), Ph (IIb, 70%)

The crystalline products are stable in the solid state at low temperatures (−20 °C) for several months, but at room temperature noticeable decomposition occurs within a few days, even in the absence of air. Solutions of IIa,b are not very stable at room temperature, and decomposition is evident within 1 h. Even at low temperatures (−20 °C), some decomposition occurs in the solutions after a few days.

The oxygen analogue of IIa cannot be obtained from the reaction of $\{Cp(CO)_2Fe[C(OCH_3)_2]\}PF_6$ (III)[15] and methoxide. Infrared spectra of these reaction solutions give some evidence for the formation of the iron–orthoester complex $Cp(CO)_2FeC(OCH_3)_3$ (IV), with bands appearing at 2035 and 1979 cm^{-1} (CH_2Cl_2), but attempts to isolate IV yield $Cp(CO)_2FeC(=O)OCH_3$ and $[CpFe(CO)_2]_2$ as the only identifiable organometallic products. Organic orthoesters are known to undergo hydrolysis (usually acid catalyzed) to give 1 equiv of ester and 2 equiv of alcohol.[16,17] Thus, if IV is formed, it could hydrolyze to give $Cp(CO)_2FeC(=O)OCH_3$, which is known to decompose to $[CpFe(CO)_2]_2$.[18]

Preparation of $Cp(CO)_2Fe\overline{C(H)S(CH_2)_3S}$ (V). In attempts to prepare bis- or [tris(organothio)methyl]iron complexes by the direct combination of the iron moiety and sulfur-stabilized anions, we have reacted $Cp(CO)_2FeI$[10] with $LiC(SCH_3)_3$,[4] $LiCH(SCH_3)_2$[2] and $LiCH(SPh)_2$[2] as well as $Cp(CO)_2FeCl$[10] and $Cp(CO)_2Fe(THF)^+$[19] with $LiC(SPh)_3$[4] but obtain none of the desired complexes. Lithiated 1,3-dithiane does react with $Cp(CO)_2FeI$[10] to give the [bis(organothio)methyl]iron complex V in reasonable yield (eq 3).



(3)

V (55%)

Structure of $Cp(CO)_2FeC(SCH_3)_3$ (IIa). As IIa is an unexpected product of the reaction of I and amines, an X-ray diffraction study was undertaken to confirm its formulation as a (η^5-cyclopentadienyl)dicarbonyl[tris(organothio)-

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Table I. Atomic Positional Parameters (×10^4) and Their Estimated Standard Deviations for $(C_5H_5)Fe(CO)_2C(SCH_3)_3$

atom	*x*	*y*	*z*
Fe	2789 (1)	3110 (1)	3904 (1)
S1	1355 (2)	1017 (2)	4739 (3)
S2	3853 (2)	1153 (2)	5534 (3)
S3	2349 (3)	2654 (2)	6898 (3)
O1	4659 (8)	4103 (7)	5879 (10)
O2	1063 (10)	4564 (8)	4502 (9)
C1	2537 (7)	1928 (6)	5354 (9)
C2	1708 (11)	3924 (9)	4326 (11)
C3	3891 (10)	3691 (8)	5170 (13)
C4	3714 (13)	26 (9)	6637 (13)
C5	90 (9)	1856 (11)	4445 (12)
C6	2153 (12)	1699 (12)	8193 (12)
C7	2808 (13)	1941 (9)	2364 (12)
C8	3862 (12)	2479 (11)	2590 (13)
C9	3608 (11)	3578 (9)	2257 (12)
C10	2425 (11)	3704 (8)	1827 (10)
C11	1911 (10)	2667 (9)	1905 (9)

Table II. Selected Interatomic Distances and Angles with Esd's for $(C_5H_5)Fe(CO)_2C(SCH_3)_3$

(a) Distances (Å)			
Fe–C1	2.112 (8)	Fe–C7	2.105 (11)
Fe–C2	1.747 (12)	Fe–C8	2.114 (13)
Fe–C3	1.776 (12)	Fe–C9	2.105 (12)
C2–O2	1.145 (16)	Fe–C10	2.124 (10)
C3–O1	1.156 (15)	Fe–C11	2.104 (10)
C1–S1	1.822 (9)	C7–C8	1.399 (20)
C1–S2	1.817 (9)	C8–C9	1.442 (18)
C1–S3	1.809 (9)	C9–C10	1.391 (18)
S1–C5	1.810 (12)	C10–C11	1.449 (16)
S2–C4	1.807 (12)	C11–C7	1.409 (18)
S3–C6	1.789 (14)		
(b) Angles (Deg)			
C1–Fe–C2	93.3 (4)	C1–S1–C5	104.1 (5)
C1–Fe–C3	90.2 (4)	C1–S2–C4	108.1 (6)
C2–Fe–C3	93.9 (5)	C1–S3–C6	107.2 (5)
Fe–C3–O1	172.8 (10)	C7–C8–C9	106.8 (11)
Fe–C2–O2	170.4 (10)	C8–C9–C10	109.4 (11)
Fe–C1–S1	114.8 (4)	C9–C10–C11	106.8 (10)
Fe–C1–S2	102.7 (4)	C10–C11–C7	107.8 (11)
Fe–C1–S3	104.6 (4)	C11–C7–C8	109.2 (10)

methyl]iron complex. The atomic positional parameters (Table I) and selected interatomic distances and angles (Table II) clearly show the complex to contain a tris(methylthio)methyl ligand σ bound to the $Cp(CO)_2Fe$ moiety (Figure 1).

The $Cp(CO)_2Fe$ moiety adopts the same geometry as observed in several other $Cp(CO)_2Fe$–R systems with all bond lengths and angles being in reasonable agreement with the previously determined structures.[20-24]

The most interesting part of the structure of IIa is the $Fe–C(SCH_3)_3$ moiety. The Fe–C1 σ-bond length of 2.112 Å is in good agreement with the Fe–C σ-bond lengths found for $Cp(CO)_2FeC_4H_7C_2(CN)_4$ (2.0977 Å),[24] $Cp(CO)_2FeCH_2COOH$ (2.06 Å),[20] and $Cp(CO)_2FeC_5H_5$ (2.11 Å),[21] and C1 has an approximately tetrahedral geometry (Fe–C1–S average of 107.4°). The average value of the six C–S distances of 1.809 Å is comparable to the values obtained from microwave studies of CH_3SH (1.819 Å)[25] and $(CH_3)_2S$ (1.802 Å)[26] and seems reasonable for a C–S σ bond.

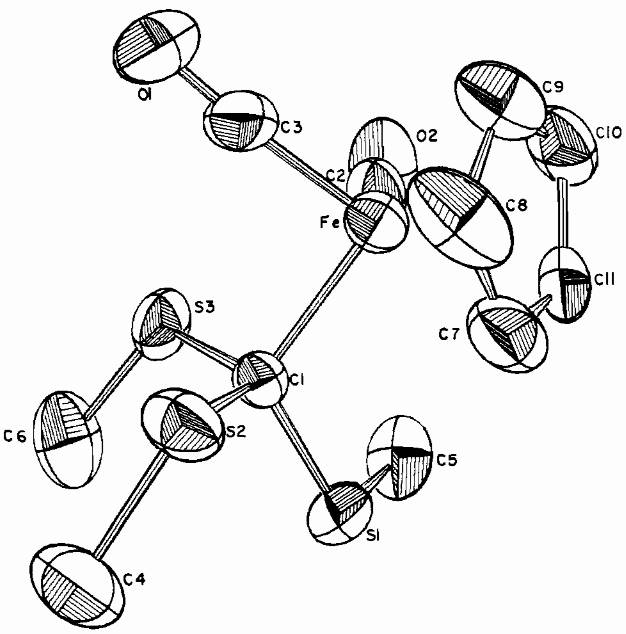

Figure 1. Structure of $Cp(CO)_2Fe[C(SCH_3)_3]$ (IIa).

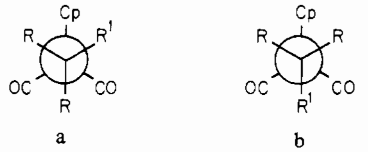

Figure 2. Newman projections of the possible conformational isomers for $Cp(CO)_2Fe[CR_2R^1]$ systems.

The three CH_3S groups of the $C(SCH_3)_3$ ligand are staggered, as expected, with respect to the Cp and CO ligands. The S2–C4 and S3–C6 bonds are nearly parallel while the S1–C5 bond is directed away from the rest of the ligand. The pseudoparallel nature of the two CH_3–S bonds is unexpected as it would not seem to be the most favored steric conformation. This conformation may be mandated by crystal packing forces and/or possible interactions of the sulfur lone pairs with the ligands on iron.

Spectra. Complex IIa displays some unusual spectral features. The IR spectrum in hexanes shows four ν(CO) absorptions at 2023 (s), 2013 (m), 1977 (s), and 1968 (m) cm^{-1} rather than the expected two bands. Similar results have been obtained for other Cp(CO)(L)Fe–R systems (L = CO, phosphorus ligands), and this has been interpreted as being the result of the presence of conformational isomers due to restricted Fe–C rotation.[27-30] However, in all these cases, conformers were detected only when the σ-bound carbon was unsymmetrically substituted (Figure 2). In $Cp(CO)_2Fe[C(SCH_3)_3]$ (IIa), the σ-bound carbon is *symmetrically* substituted and such conformational isomerization is not possible if the three mercapto groups are structurally equivalent. In the unsymmetrically substituted complexes IIb and V, where this isomerization could be expected, only two ν(CO) absorptions are observed (2024 (s) and 1978 (s) and 2026 (s) and 1979 (s) cm^{-1}, respectively, in hexanes), indicating the presence of only one conformer.

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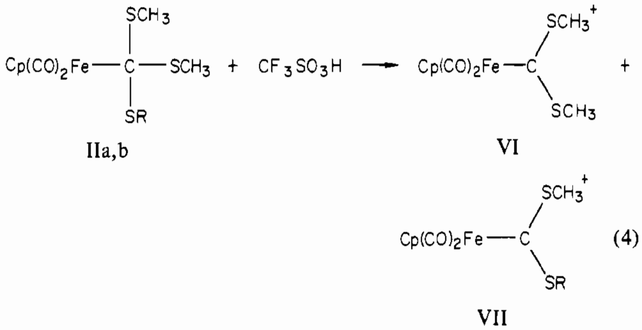
All three methyl groups of IIa are equivalent in the ambient-temperature ^{1}H NMR spectrum. However, in CS_2 at low temperature (−106 °C), two rather broad singlets at τ 7.85 (6 H) and 7.96 (3 H) for the methyls and a sharp singlet at τ 4.83 for the Cp ring appear. Lower temperature spectra could not be obtained because of sample crystallization. As the temperature is raised, the two broad singlets coalesce (−100 °C) and eventually a sharp singlet (τ 7.89) is observed for the equivalent methyl groups.

The splitting of the methyl groups at low temperature and coalescence at higher temperature may be due to restricted rotation around the Fe–C bond. The free energy of activation for this process, $\Delta G^{\ddagger} \approx 8.7$ kcal/mol, is calculated from the coalescence temperature and peak width at half-height with use of the Eyring equation.[31] This agrees reasonably well with previously observed rotational barriers for $Cp(CO)_2FeCH_3$ (2.9 kcal/mol calculated, 5.4 kcal/mol observed),[32] $Cp_3UCH(CH_3)_2$ (10.5 kcal/mol),[33] and the suggested range of 5–10 kcal/mol for such barriers.[29,34] The rotations about the C–S bonds should be less restricted than the Fe–C bond rotation as the barriers observed for CH_3SH and CH_3SCH_3 are 1.3 kcal/mol[25] and 2.1 kcal/mol,[26] respectively. Thus the low-temperature ^{1}H NMR spectrum of IIa may be described as freezing the rotation about the Fe–C bond into a staggered conformation where there is a unique mercapto group lying between two CO ligands (R^1 in Figure 2b) and two equivalent mercapto groups lying between a CO and a Cp ligand (R in Figure 2b). The resonances observed for the methyl groups in the low-temperature spectrum would then be averaged signals of the possible conformations around the C–S bonds as these rotations should be unrestricted in the temperature range studied.

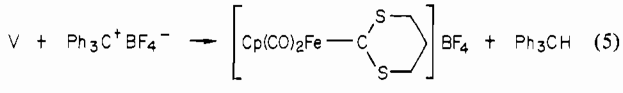
While the low-temperature ^{1}H NMR spectrum may be explained by restricted Fe–C bond rotation, it is difficult to rationalize the IR spectrum (hexanes) of IIa by the conventional conformational isomerism argument.[27-30] One possibility is that although the C–S bond rotations should be quite facile at room temperature, they may be correlated such that two of the S–CH_3 bonds are always pseudoparallel while the other S–CH_3 bond is directed away from the rest of the $C(SCH_3)_3$ ligand as observed in the solid state (Figure 1). Thus, the conformers shown in Figure 2, where R^1 is the nonparallel SCH_3 group, would exist in solution and could be interconverted by either Fe–C bond rotation or correlated rotations of the C–S bonds. Another possible explanation is that an eclipsed conformation around the Fe–C bond could have a finite lifetime on the IR time scale due to bonding interactions of the sulfur lone-pair electrons with the π^* orbitals of the CO ligands.

Reaction of the [Tris(organothio)methyl]iron Complexes with Acid. Complexes IIa,b react readily with strong acid, CF_3SO_3H, to give the triflate salts of cationic carbene complexes in almost quantitative yield by the elimination of thiol (eq 4). Complex IIa gives the bis(methylthio)carbene complex VI (previously prepared as the hexafluorophosphate salt)[7] very cleanly. Complex IIb, however, gives a mixture of VI and a new (phenylthio)(methylthio)carbene complex, VII.



R = CH_3 (VI, 96%), Ph (VII, 40%; VI, 56%)

Hydride Abstraction from $\mathrm{Cp(CO)_2Fe\overline{C(H)S(CH_2)_3S}}$ (V). Stirring complex V in CH_2Cl_2 under an N_2 atmosphere with an equivalent amount of trityl tetrafluoroborate for 12 h at room temperature leads to the formation of the new carbene complex VIII (eq 5). This product is initially obtained as an impure oil, which cannot be purified or crystallized. That the oil is predominantly VIII with some unidentified contamination may be inferred from its spectral data. The IR spectrum of the oil in CH_2Cl_2 shows two ν(CO) absorptions at 2058 (s) and 2018 (s) cm^{-1}, consistent with that observed for similar complexes.[7,13] The ^{1}H NMR (acetone-d_6) spectrum displays the expected resonances at τ 4.50 (s, C_5H_5), 6.57 (t, 2 SCH_2), and 7.45 (m, CH_2) along with unidentified phenyl, cyclopentadienyl, and aliphatic resonances. Conclusive evidence for the formation of VIII is found in the ^{13}C NMR (CD_3CN) spectrum of the oil. Major resonances occur at 283.9 (s, carbene), 210.5 (s, 2 CO), 89.1 (s, C_5H_5), 39.6 (s, 2 SCH_2), and 18.9 (s, CH_2) ppm along with minor resonances corresponding to the impurities found in the ^{1}H NMR spectrum. In addition, precedent for the reaction in eq 5 may be found in the related conversions of (η^1-1-benzocyclobutenyl)(η^5-cyclopentadienyl)dicarbonyliron,[35] (η^5-cyclopentadienyl)dicarbonyl(η^1-1-naphtho[*b*]cyclobutenyl)iron,[35] (η^5-cyclopentadienyl)dicarbonyl(η^1-methoxymethyl)iron,[36] and (η^1-cycloheptatrienyl)(η^5-cyclopentadienyl)dicarbonyliron[37] to the corresponding cationic carbene complexes by α-hydride abstraction from the σ-bound organic moiety.



VIII

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Registry No. I, 69532-11-2; IIa, 69532-55-4; IIb, 79084-52-9; V, 79084-53-0; VI, 76136-25-9; VII, 79084-54-1; VIII, 79084-55-2; $Cp(CO)_2FeI$, 12078-28-3; CH_3SH, 74-93-1; PhSH, 108-98-5; 1,3-dithiane, 505-23-7.

Supplementary Material Available: Listings of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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