A Rapid Equilibrium between the Metallathiacyclopropane $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$ and Its Carbene Mercaptide Form

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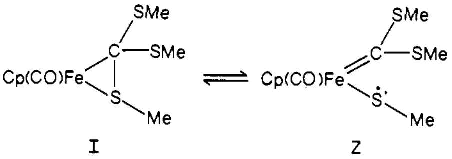
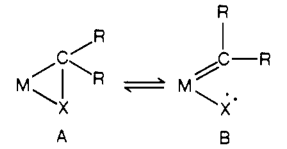
Abstract: The compound $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$ (I) was obtained by photolysis of $CpFe(CO)_2[C(SMe)_3]$ (II) and reaction of $\{CpFe(CO)(MeCN)[{=}C(SMe)_2]\}PF_6$ (III) with NaSMe. Temperature-dependent ^1H NMR studies of I suggest that it is in rapid equilibrium with a carbene mercaptide form $CpFe(CO)(SMe)[{=}C(SMe)_2]$ (Z). The existence of the carbene mercaptide form (Z) is supported by the reaction of I with 2 equiv of the phosphines PMe_3 and PMe_2Ph to give $CpFe(CO)(SMe)(PR_3)$ and the ylide $(MeS)_2C{=}PR_3$. Further support is obtained from the reaction of I with $[Me_3O]BF_4$ to give the dimethyl sulfide iron carbene complex $\{CpFe(CO)(SMe_2)[{=}C(SMe)_2]\}BF_4$.



A variety of heteroatom-containing metallacyclopropane complexes of the form A (eq 1) where X = OR, SR, NR_2, PR_2 have been reported in the literature.[1] However, there are no cases where there is direct evidence for the existence of the carbene form B in which the C–X bond is cleaved. Roper and co-workers[2] suggested that the reaction (eq 2) of $NaBH_4$ with the metallacyclopropane **1** to give **3** is promoted by the partial carbenic character of the CH_2 group as represented by resonance form **2**; however, there were no other results that would support their interesting proposal.



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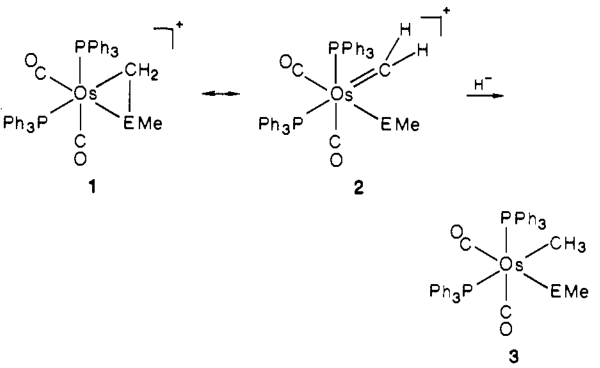

(2)

where E = S, Se, Te

We present in this paper the synthesis, characterization, and reactions of $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$ which indicate that this compound is in rapid equilibrium with the carbene mercaptide of the general type B.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of prepurified N_2 at room temperature with standard inert atmosphere and Schlenk techniques[3,4] unless otherwise stated. Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from Na/benzophenone. Hexanes, MeCN, and CH_2Cl_2 were distilled from CaH_2 under N_2.

Trimethylphosphine was prepared by the reaction of methyl Grignard reagent and triphenyl phosphite.[1h] Diphenylmethylphosphine and PMe_2Ph were obtained from Strem Chemicals and used without further purification. Triphenyl phosphite, $[Me_3O]BF_4$, and HBF_4/Et_2O were used as received from Aldrich Chemical Co. Trimethyl phosphite was distilled from sodium metal under N_2.

Infrared spectra were obtained with use of a Perkin-Elmer 681 spectrophotometer, and spectra were referenced to the 1944.0-cm^{-1} band of polystyrene. The ^1H and $^{13}C\{H\}$ NMR data were recorded on a Nicolet NT 300-MHz spectrometer with Me_4Si as the internal reference. The temperature-dependent ^1H NMR spectra were obtained on a Bruker WM 300-MHz instrument. Electron impact mass spectra (EIMS) were obtained on a Finnigan 4000 instrument. Fast atom bombardment (FAB, glycerol matrix) mass spectra were obtained on a Kratos MS-50 spectrometer.

Photochemical reactions were carried out with a 254 nm light source in a quartz Schlenk tube equipped with a cooling probe in a reactor obtained from Bradford Scientific, Inc., Marblehead, MA.

The complexes $CpFe(CO)_2[C(SMe)_3]$ (II)[5] and $\{CpFe(CO)(MeCN)[{=}C(SMe)_2]\}PF_6$ (III)[6b] were prepared according to literature methods.

Preparation of $Cp(CO)\overline{Fe[C(S}Me)(SMe)_2]$ (I). A hexanes (35 mL) solution of $CpFe(CO)_2[C(SMe)_3]$ (II) (0.12 g, 0.36 mmol) was placed in a quartz tube equipped with a water-cooled probe and purged with N_2.

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The solution was irradiated with 254-nm light for 90 min. The volume of the solution was reduced to 10 mL in vacuo and transferred onto a column of alumina (adsorption, 80–200 mesh, 1 × 15 cm). A brownish yellow-green solution, the second band, was eluted with hexane/Et_2O (5:1). The solvent was removed in vacuo giving $Cp(CO)Fe[C(SMe)(SMe)_2]$ (I) as a brownish yellow-green oil (0.080 g, 65%). Satisfactory elemental analyses could not be obtained because of the instability of the compound. Slow decomposition is observed even when the compound is stored at −20 °C under an inert atmosphere.

Synthesis of I from $\{CpFe(CO)(MeCN)[{=}C(SMe)_2]\}PF_6$ and NaSMe. Irradiation of a solution of $\{CpFe(CO)_2[{=}C(SMe)_2]\}PF_6$[6a] (0.10 g, 0.23 mmol) in MeCN (35 mL) at 254 nm for 2 h led to the formation of $\{CpFe(CO)(MeCN)[{=}C(SMe)_2]\}PF_6$,[6b] as established by the IR spectrum of the solution. After removal of the solvent in vacuo, the reddish product was extracted with THF (20 mL) and filtered through Celite on a glass frit. A THF solution of NaSMe, generated by slowly bubbling MeSH through a suspension of NaH (57% in mineral oil, 0.012 g, 0.28 mmol) in THF (20 mL) for 30 min,[5] was added to the filtrate and stirred for 60 min. The resulting solution was worked up as described in the photolytic preparation of I from II. I was obtained as an oil in 30% yield. The major impurity in I generated by this reaction was $Cp_2Fe_2(CO)_2(SMe)_2$.[7]

Reaction of $Cp(CO)Fe[C(SMe)(SMe)_2]$ and $[Me_3O]BF_4$. To a stirred solution of I (0.050 g, 0.16 mmol) dissolved in freshly distilled CH_2Cl_2 (20 mL) was added $[Me_3O]BF_4$ (0.028 g, 0.18 mmol). Stirring was continued for 45 min after which KPF_6 (~1.0 g) was added. After 1 h, the mixture was filtered through anhydrous $MgSO_4$ on a glass frit. The filtrate was layered with Et_2O (100 mL) and stored at −20 °C for 1 week. This led to the isolation of $\{CpFe(CO)(SMe_2)[{=}C(SMe)_2]\}PF_6$ (IV) (0.049 g, 74%) as dark red crystals. Anal. Calcd for $C_{11}H_{17}F_6FeOPS_3$: C, 28.59; H, 3.71; S, 20.08. Found: C, 28.57; H, 3.65; S, 20.05.

Reaction of $Cp(CO)Fe[C(SMe)(SMe)_2]$ and PMe_3. To I (0.060 g, 0.20 mmol) dissolved in freshly distilled hexane (10 mL) was added PMe_3 (0.030 g, 0.39 mmol, 40 μL). The solution was stirred for 2 h with the progress of the reaction being monitored by IR. The two bands corresponding to I were replaced by a single band at 1940 cm^{-1} (vs). The mixture was treated with 1 equiv of HBF_4/Et_2O solution. This resulted in the precipitation of a thick lavender oil. The supernatant was transferred onto a column of alumina (1 × 15 cm) and eluted with dry Et_2O. The brownish-yellow oily product $CpFe(CO)(PMe_3)(SMe)$ (V) eluted in the second band in ~45% yield. Compound V decomposes within 3 h in $CDCl_3$ solution. Owing to its instability satisfactory elemental analyses could not be obtained. However, its methylated product was characterized and analyzed as described in the following synthetic procedure. The lavender oil was extracted with CH_2Cl_2 and layered with hexanes and stored at −20 °C for 3 days. A reddish-yellow oily-solid, $[(MeS)_2CHPMe_3]BF_4$ (VII), was obtained and characterized by ^1H NMR and FAB MS (see Tables II and IV). The ylide precursor, $(MeS)_2C{=}PMe_3$ (VI), to the cationic product VII was observed prior to the addition of HBF_4 in a reaction in benzene-d_6 monitored by ^1H NMR (Table II).

As described above, I (0.060 g, 0.20 mmol) was treated with PMe_2Ph (0.12 g, 0.90 mmol, 0.13 mL). Two hours of stirring led to the formation of $CpFe(CO)(PMe_2Ph)(SMe)$ (VIII), which was also isolated by chromatography. It was characterized spectroscopically (Tables I, II, and IV) by comparison with V.

Reaction of $CpFe(CO)(SMe)(PMe_3)$ and $[Me_3O]BF_4$. To a stirred CH_2Cl_2 (20 mL) solution of V (0.045 g, 0.16 mmol) obtained from the reaction of I and PMe_3, $[Me_3O]BF_4$ (0.028 g, 0.18 mmol) was added. Stirring was continued for 10 min after which KPF_6 (~1.0 g) was added. The mixture was filtered through anhydrous $MgSO_4$ on a glass frit after 1 h. The filtrate was layered with Et_2O (100 mL) and stored at −20 °C for 3 days. The yellow powder obtained upon filtration was redissolved in acetone, layered with Et_2O, and stored at −20 °C for 1 week. Golden needle-like crystals of $[CpFe(CO)(PMe_3)(SMe_2)]PF_6$ (IX) (0.062 g, 87%) were obtained upon filtration and drying in vacuo. Anal. Calcd for $C_{11}H_{20}F_6FeOPS$: C, 30.58; H, 4.66. Found: C, 30.50; H, 4.54.

Reaction of $\{CpFe(CO)(SMe_2)[{=}C(SMe)_2]\}PF_6$ (IV) with $P(OR)_3$ (R = Ph, Me). To an acetone (10 mL) solution of IV (0.038 g, 0.082 mmol) was added $P(OPh)_3$ (92 μL, 0.47 mmol). The solution was heated to 40 °C for 6 h and the solvent was removed in vacuo. A proton NMR spectrum of the reaction mixture in acetone-d_6 indicated that $\{CpFe(CO)[P(OPh)_3][{=}C(SMe)_2]\}PF_6$ (X)[6] was the only product formed. A reaction in acetone-d_6 monitored by ^1H NMR showed that the formation of X was quantitative.

Table I. Infrared Spectra of the Complexes in Hexanes

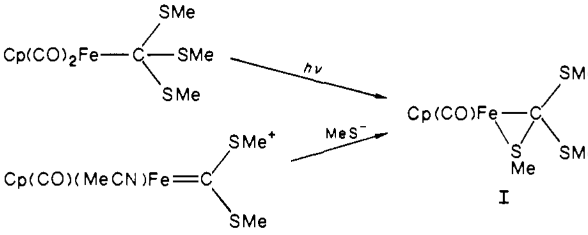
complex	$\nu(CO)$, cm^{-1}
$Cp(CO)Fe[C(SMe)(SMe)_2]$ (I)[a]	1949 (m), 1938 (s)
$Cp(CO)_2Fe[C(SMe)_3]$ (II)[b]	2025 (s), 2014 (m), 1978 (s), 1968 (m)
$\{Cp(CO)Fe(MeCN)[{=}C(SMe)_2]\}PF_6$[c] (III)	1997 (s)
$\{CpFe(CO)(SMe_2)[{=}C(SMe)_2]\}PF_6$ (IV)[d]	1985 (s)
$CpFe(CO)(PMe_3)(SMe)$ (V)	1940 (s)
$(MeS)_2C{=}PMe_3$ (VI)	
$[(MeS)_2CHPMe_3]BF_4$ (VII)	
$CpFe(CO)(PMe_2Ph)(SMe)$ (VIII)	1942 (s)
$[Cp(CO)Fe(SMe_2)(PMe_3)]PF_6$ (IX)[d]	1973 (s)
$\{CpFe(CO)[P(OPh)_3][{=}C(SMe)_2]\}PF_6$ (X)[d,e]	1985 (s)
$\{CpFe(CO)[P(OMe)_3][{=}C(SMe)_2]\}PF_6$ (XI)[d,e]	1981 (s)

[a] In CH_2Cl_2: 1924 cm^{-1}. [b] Reference 5. [c] In CH_3CN. [d] In CH_2Cl_2. [e] Reference 6.

Similarly, a reaction of IV (0.034 g, 0.074 mmol) and $P(OMe)_3$ (50 μL, 0.42 mmol) at 40 °C went to completion in 2 h. The $\{CpFe(CO)[P(OMe)_3][{=}C(SMe)_2]\}PF_6$ (XI) was formed[6] in 72% yield based on a ^1H NMR monitored reaction in acetone-d_6. There was evidence for the formation of other unidentified minor products.

Results and Discussion

Synthesis of $Cp(CO)Fe[C(SMe)(SMe)_2]$ (I). Photolysis of $CpFe(CO)_2[C(SMe)_3]$[5] in hexanes produces a brownish solution that upon chromatography gives I as a brownish yellow-green oil in 65% yield. Compound I, in which both the carbon and a sulfur are coordinated to the iron, can also be obtained but in lower yield (30%) from the reaction of $\{CpFe(CO)(MeCN)[{=}C(SMe)_2]\}PF_6$[6] and NaSMe. In the latter reaction it is not known whether SMe^- initially displaces the MeCN ligand to form the carbene mercaptide $CpFe(CO)(SMe)[{=}C(SMe)_2]$, which rapidly closes the ring to form I, or SMe^- first adds to the carbene carbon to give $CpFe(CO)(MeCN)[C(SMe)_3]$, which forms I by intramolecular displacement of the MeCN. NMR studies of the reaction show no evidence for any intermediates.



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The mass spectrum of I, which is moisture and air sensitive, shows a parent ion peak (M^+) at m/e = 302 and a base peak at m/e = 274 corresponding to $M^+ - CO$. Other fragments of the molecule such as $[C(SMe)_3]$ (m/e = 153) and CpFe (m/e = 121) are also observed. The infrared spectrum of I shows two bands (Table I), which suggests the presence of two isomers. The ambient temperature ^1H NMR spectrum (CD_2Cl_2) of I, however, displays three signals at 4.52, 2.33, and 1.90 corresponding to the Cp, the uncoordinated SMe groups, and the Fe-coordinated SMe, respectively. While isomers C and D (eq 4) are not apparent in the ambient temperature ^1H NMR spectrum, the low-temperature (−90 °C, Figure 1) spectrum shows two Cp(a,b) and six methyl signals (c–h) expected for these two isomers (eq 4). The two forms of I, which differ by the up or down position of the Fe-coordinated SMe group, are assigned to signals a, c, f, h and b, d, e, g. Although it is not possible to assign each of these sets of signals to C or D, one of them is in slight excess (52:48 ratio) as determined from integrations of the spectra. Signals g and h correspond to the Fe-coordinated SMe groups of the two forms. Four signals (c–f) are observed for the uncoordinated SMe groups because each

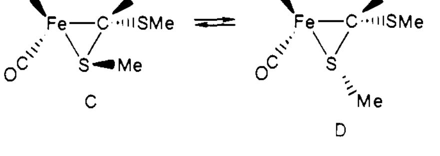

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Table II. ^1H NMR Spectra of the Complexes in C_6D_6 (δ)

complex	C_5H_5	other resonance
I	4.27	2.22 (6 H, SMe),[g] 1.38 (3 H, SMe)
II[a]	4.89	2.24 (9 H, SMe)
III[b,e]	5.03	3.23 (6 H, SMe), 2.44 (3 H, MeCN)
IV[c,f]	4.96	3.20 (6 H, SMe), 1.6–2.6 (br, SMe_2)
V	4.20 (d, J_{PH} = 1.2 Hz)	2.02 (d, J_{PH} = 1.3 Hz, 3 H, SMe), 1.01 (d, J_{PH} = 9.8 Hz, 9 H, Me)
VI		2.15 (d, J_{PH} = 1.1 Hz, 6 H, SMe), 0.94 (d, J_{PH} = 12.2 Hz, 9 H, PMe_3)
VII[c]		4.60 (d, J_{PH} = 12.9 Hz, 1 H, CH), 2.38 (6 H, SMe), 1.99 (d, J_{PH} = 13.9 Hz, 9 H, PMe_3)
VIII	4.12	2.02 (3 H, SMe), 1.46 (d, J_{PH} = 9.4 Hz, 6 H, PMe_2Ph), 7.05 (m, Ph)
IX[d]	5.25 (d, J_{PH} = 1.5 Hz)	2.50 (6 H, SMe_2), 1.72 (d, J_{PH} = 10.5 Hz, 9 H, PMe_3)
X[d]	5.20 (d, J_{PH} = 1.1 Hz)	3.07 (6 H, SMe), 7.27 (m, 15 H, $P(OPh)_3$)
XI[d]	5.22 (d, J_{PH} = 1.2 Hz)	3.19 (6 H, SMe), 3.77 (d, J_{PH} = 11.5 Hz, 9 H, $P(OMe)_3$)

[a] In CD_2Cl_2. [b] In CD_3CN. [c] In $CDCl_3$. [d] In $(CD_3)_2CO$. [e] Reference 6. [f] At 80 °C the broad SMe_2 signal becomes fairly sharp. The SMe_2 is observed as two sharp signals at −20 °C (2.40 and 1.81 ppm). [g] Resonances are singlets where not indicated otherwise.

Table III. ^{13}C NMR Spectra in C_6D_6 (δ)

complex	C_5H_5	CO	other resonances
I	79.94	216.03	70.67 [*C*$(SMe)_3$], 21.51 (Fe-coordinated SMe), 20.00 (uncoordinated SMe)
II[a]	89.66	216.18	59.72 [*C*$(SMe)_3$], 19.27 (SMe)
III[b]	85.0	216.4	321.2 [*C*$(SMe)_2$], 28.1 (SMe), 136.1 (br, CH_3*C*N), 4.2 (*C*H_3CN)
IV[c,d]	85.20	215.52	318.53 [*C*$(SMe)_2$], 28.96 (SMe), 24.12 (SMe_2), 22.62 (SMe_2)
V	82.54	220.90	16.70 (SMe), 18.52 (d, J_{PC} = 121.4 Hz, PMe_3)

[a] In CD_2Cl_2. [b] Reference 6. [c] In $CDCl_3$. [d] At −30 °C.

Table IV. Mass Spectra of the Compounds

complex	observed masses
I	302 (M^+), 274 [base peak, (M^+ − CO)], 153 [$C(SMe)_3{}^+$]
II	348 (M^+ − SMe), 153 {base peak, [$C(SMe)_3{}^+$]}
IV[a]	317 (M^+), 289 (M^+ − CO), 255 [base peak, (M^+ − SMe_2)]
V	272 (M^+), 244 [base peak, (M^+ − CO)], 197 [M^+ − (CO + SMe)]
VII[a]	183 (M^+), 167 (M^+ − CH_4), 136 (M^+ − SMe), 107 (M^+ − PMe_3)
VIII	334 (M^+), 306 (M^+ − CO), 259 [M^+ − (CO + SMe)], 138 (base peak, $PMePh_2{}^+$)
IX[a]	287 (M^+, base peak), 225 (M^+ − SMe_2), 197 [M^+ − (CO + SMe_2)]

[a] FAB MS.

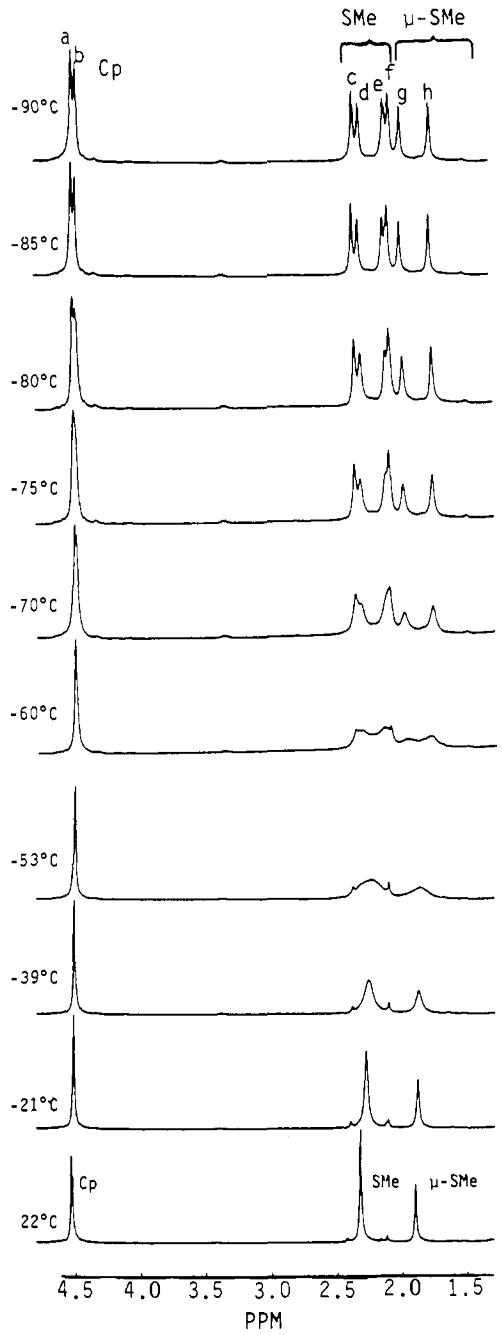

Figure 1. Variable-temperature ^1H NMR spectra of $Cp(CO)\overline{Fe[C}$-$\underline{(SMe)}(SMe)_2]$ (I) in CD_2Cl_2.

Table V. Rate Constants and Activation Parameters for the Interconversion of Isomers C and D (Eq 4) of $Cp(CO)Fe[C(SMe)(SMe)_2]$ in CD_2Cl_2[a]

T, K	*k*,[b] s^{-1}	$\Delta G^{\ddagger}$,[c] kJ mol^{-1}
198	6.85×10^1	40.9
203	1.04×10^2	41.3
213	2.0×10^2	42.0
220	3.77×10^2	42.6
234	1.02×10^3	43.7
252	2.17×10^3	45.1

[a] Concentration = 0.20 M. [b] $k = 1/\tau$. [c] $\Delta H^{\ddagger}$ = 25.4 ± 1.0 kJ mol^{-1}; $\Delta S^{\ddagger}$ = −80 ± 4 J mol^{-1} K^{-1}, where the error limits are standard deviations.

isomer has two inequivalent uncoordinated SMe groups. The four uncoordinated SMe signals become two broad signals on warming to −70 °C and become a single line at −39 °C. Also the two Cp signals, a and b, observed at 4.54 and 4.48 ppm at −90 °C coalesce to give a single line at −75 °C.

The rate of interconversion between forms C and D was calculated by simulating the broadened Fe-coordinated SMe signals at various temperatures. A two-site exchange program, based on the original work of Gutowsky and Holm[8] and run on a Nicolet 1280 computer, was used to calculate the rate (*k*) from observed line width and peak positions. A line width of 0.6 Hz was observed for the non-exchange-broadened peaks. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table V) were determined from an Eyring plot by using rate constants for the exchange process obtained at temperatures between 198 and 252 K (−75 and −21 °C).[9]

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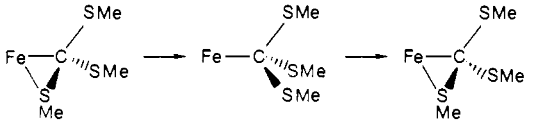
[8] Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

The rate constants for the process involving the coalescence of the Fe-coordinated SMe signals were also calculated by using the approximate expression, $\Delta G^{\ddagger} = (19.14T_c)(9.97 + \log T_c/d\upsilon)$,[9] where T_c = coalescence temperature and $d\upsilon$ = the peak separation, and found to be the same within experimental error as that found from the line-fitting procedure above. This approximate expression was also used to determine the rate constants for the processes involving the coalescence of the Cp signals (a and b in Figure 1) and the uncoordinated SMe signals (c and f, d and e, c and e, e and f, c and d, d and f). These rate constants, i.e., those for the processes involving the coalescence of the Cp, Fe-coordinated SMe, and uncoordinated SMe groups, all occur at the same rate at all temperatures (Table V) between 198 and 252 K (−75 and −21 °C). This indicates that the signals coalesce either by one process or by the less likely possibility that two processes are occurring at the same rate at all temperatures.

In order to account for the temperature-dependent NMR results, one may consider the various fluxional processes that might occur in the metallathiacyclopropane ring in I. One possible process involves initial cleavage of the Fe–S bond (eq 5) to give an intermediate in which rapid rotation around the Fe–C bond would make all of the SMe groups equivalent. Thus, one would expect the 6 SMe signals at −90 °C to coalesce to one line at 22 °C. Their observed coalescence to two lines means that this process does not explain the NMR results.



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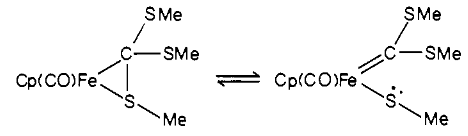
A second possible process is that involving inversion at the sulfur of the Fe-coordinated SMe group. Abel and co-workers[10] have reviewed related inversions of coordinated sulfur groups (M–$\ddot{S}$(R)R′) and noted that a number of factors contribute to the observed $\Delta G^{\ddagger}$ values that range from 20 to >90 kJ mol^{-1}. Such an inversion in I would average the Fe-coordinated SMe signals, but it would leave the uncoordinated SMe groups inequivalent. Thus, one would expect to find 3 SMe peaks at the high-temperature limit. The observed 2-peak SMe region at 22 °C means that this process does not account for the NMR results.

A third possible process is a rotation of the entire η^2-C(SMe)$_3$ unit in I about an axis through the Fe and perpendicular to the C–S bond similar to what has been suggested for (PMe$_3$)$_4$W(η^2-CH$_2$PMe$_2$)H[1h] and Cp$_2$ZrCl[η^2-CHR(SR)].[11] This rotation does not, however, make the uncoordinated SMe groups equivalent, as observed in the spectrum of I at 22 °C.

While none of the above 3 processes account for the observed coalescences, a combination of the latter two processes, inversion at the Fe-coordinated SMe and rotation of the η^2-C(SMe)$_3$ unit occurring at the same rates at all temperatures, would account for the equal rates of coalescence of the Cp, the Fe-coordinated SMe, and uncoordinated SMe signals. Although it is not possible to rigorously exclude this possibility, it is unlikely that these two quite different processes would have the same rates and activation parameters.

The mechanism that best accounts for the NMR results is that which involves cleavage of the C–S bond in isomers C and D to give the carbene mercaptide complex Z, followed by rapid rotation around the Fe–SMe bond and around the Fe=C(SMe)$_2$ bond. That rotation around the Fe=C(SMe)$_2$ bond is likely to be rapid is supported by many studies of carbene complexes,[12] particularly



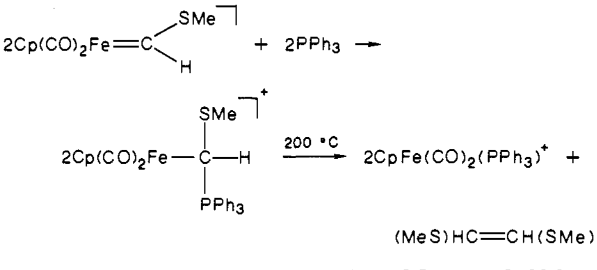
(6)

I Z

those of heteroatom carbenes. This mechanism would account for the coalescence of the two Cp peaks, the two Fe-coordinated SMe peaks, and the 4 uncoordinated SMe peaks all at the same rate.

In the ^{13}C NMR spectrum of I in C$_6$D$_6$ at ambient temperature, a distinct signal for the carbon in the η^2-*C*(SR$_3$) unit is observed at 70.67 ppm. This is characteristic of a saturated carbon and is similar to the 59.7 ppm of Cp(CO)$_2$Fe[C(SMe)$_3$] (II) and the 61.79- and 71.69-ppm signals observed for the isomers of [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)$_2$].[13] There is no evidence for a carbene carbon in form Z, which would be expected in the region 225–325 ppm, as observed for Cp(CO)$_2$Fe[=C(SMe)$_2$]$^+$,[6] Cp(CO)[P(OPh)$_3$]Fe[=CH(SMe)]$^+$,[14] and [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]$^+$.[13] Therefore, the equilibrium in eq 6 must lie far to the left and Z would be present only as a short-lived intermediate.

Reactions of Cp(CO)$\overline{\text{Fe[C(S}}$Me)(SMe)$_2$] (I). To explore the possibility that the carbene mercaptide form (Z) of I would react as a carbene, we studied reactions of I with phosphines. Phosphines are known to react with carbenes[15] and perhaps the most closely related example is that (eq 7) of Cp(CO)$_2$Fe=C(H)(SMe)$^+$ with PPh$_3$ to form Cp(CO)$_2$Fe—C(H)(SMe)(PPh$_3$)$^+$,[16] which upon heating to 200 °C releases the olefin and forms the phosphine-substituted complex.



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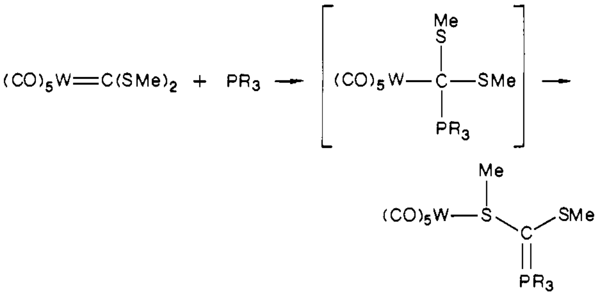
A tungsten dithiocarbene complex (CO)$_5$W=C(SMe)$_2$ also reacts with phosphines PR$_3$, presumably via a ylide intermediate.[17]



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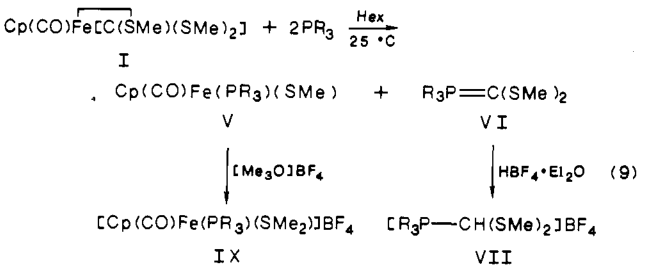
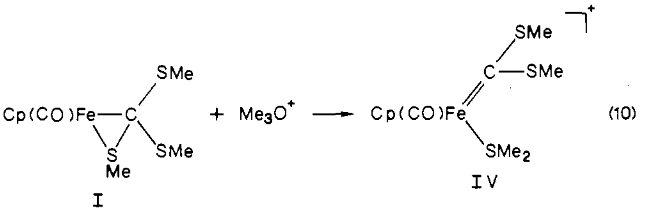
Reaction of I with nucleophilic phosphines requires 2 h and leads to the formation of V and the corresponding ylide (eq 9).



Compound V was characterized by its IR, ^{1}H and ^{13}C NMR, and MS ($PR_3 = PMe_3$). While V was too unstable for an elemental analysis, its methylated derivative, IX, was analyzed correctly. The ylide product $Me_3P{=}C(SMe)_2$ (VI) was observed in a reaction monitored by ^{1}H NMR and obtained as the tetrafluoroborate salt (VII). By analogy with reactions 7 and 8 the reaction of I with PMe_3 can be thought to occur via PMe_3 attack at the carbene carbon of the carbene mercaptide complex Z to give a $CpFe(CO)(SMe)[C(SMe)_2PMe_3]$ intermediate. Subsequent substitution of the $Me_3PC(SMe)_2$ group by a second PMe_3 results in the formation of the final products. The reaction of I with 1 equiv of phosphine does not go to completion. While **I** reacts with PMe_2Ph in the same way as PMe_3, less basic phosphines such as $PMePh_2$ do not react to an appreciable extent under the same conditions.

While compound I reacts as a carbene, presumably because of its rapid interconversion to the carbene mercaptide form Z, we sought to determine whether the SMe ligand of this form could be alkylated as has been observed for other mercaptide complexes.[18] Compound I reacts with $[Me_3O]BF_4$ in 30 min to give a reddish solution from which $\{CpFe(CO)(SMe_2)[{=}C(SMe)_2]\}PF_6$ (IV) is isolated, after anion exchange, as a dark red crystalline solid. King and Bisnette[7] reported that the reaction of $CpFe(CO)_2SMe$ with MeI proceeds rapidly (15 min) to give $CpFe(CO)_2(SMe_2)^+$. It is to be expected that a similar reaction with Me_3O^+ would be even faster. However, reaction 10 requires 30 min, presumably because the reactive form of I which is the carbene mercaptide $CpFe(SMe)(CO)[{=}C(SMe)_2]$ (Z), is present in such small concentration as a result of equilibrium 6 lying far to the left.



Compound IV was characterized by its IR, MS, and ^{1}H and ^{13}C NMR as well as elemental analysis. The coordinated dimethyl sulfide is seen as a broad signal spanning nearly 1 ppm in the ambient temperature ^{1}H NMR spectrum. On cooling to −20 °C, the methyl groups of the coordinated sulfide are observed as two sharp signals (Figure 2). At 80 °C the methyl groups are observed as a fairly sharp singlet. At low temperature the methyl groups of the sulfide are diastereotopic and as a result they occur as two singlets. At higher temperature there is a rapid inversion at the sulfur, which makes the methyl groups equivalent on the NMR time scale. A similar inversion was observed by Kuhn and Schumann[19] in the $CpFe(CO)(SMe_2)(L)^+$ complexes, where L = PPh_3, CN^-. $\Delta G^\ddagger = 54.9 \pm 0.6$ kJ mol^{-1} ($T_c = 296$) is obtained for the activation energy of the exchange process in IV[20] with use of the approximate expression previously described.[9] This compares well with the values obtained for $[CpFe(CO)(SMe_2)(PPh_3)]BF_4$, 53.7 ± 2.0 kJ mol^{-1} (T_c = 273 K), and $CpFe(CO)(SMe_2)(CN)$, 60.2 ± 3.3 kJ mol^{-1} (T_c = 286 K).[21]

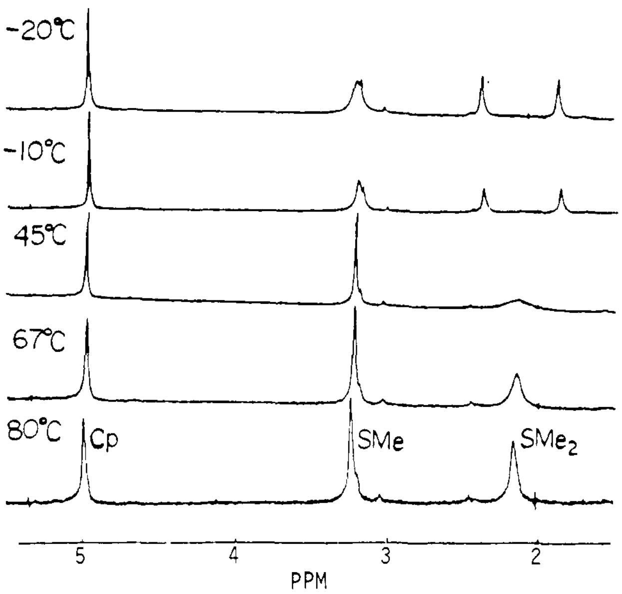


Figure 2. Temperature-dependent ^{1}H NMR spectra of $\{CpFe(CO)(SMe_2)[{=}C(SMe)_2]\}PF_6$ (IV) in $CDCl_3$.

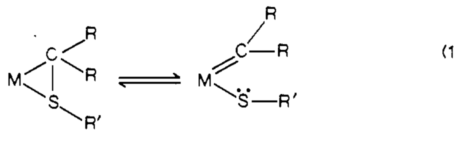
Further confirmation of the structure of compound IV was obtained from its reaction with $P(OPh)_3$ at 40 °C in acetone for 6 h to give an orange solution from which $\{CpFe(CO)[P(OPh)_3][{=}C(SMe)_2]\}PF_6$ (X) was isolated. The $P(OMe)_3$ analgoue was obtained from the reaction of IV and $P(OMe)_3$. Both of the phosphite–carbene complexes had been prepared previously[6] and identified by their characteristic spectra.

The alkylation of the SMe group in I to give $\{CpFe(CO)(SMe_2)[{=}C(SMe)_2]\}PF_6$ (IV) (eq 11) shows that I reacts as if the carbene mercaptide form of I is present in its reactions.

Conclusion

We have shown that the temperature-dependent ^{1}H NMR spectra of $\overline{Cp(CO)Fe[C}(SMe)(SMe)_2]$ are best interpreted as indicating a rapid equilibrium between the metallathiacyclopropane and the carbene mercaptide Z (eq 6). Supporting evidence for the carbene mercaptide form is found in the reactions of I with PR_3 to give free ylide and a phosphine iron complex (eq 9) and with Me_3O^+ to give the dimethyl sulfide complex $CpFe(CO)(SMe_2)[{=}C(SMe)_2]^+$ (IV) as in eq 10.

With this evidence for the carbene mercaptide form of compound I, one asks whether other complexes with similar ligands show evidence for such a form:



King and Bisnette[22] have reported the synthesis of $Cp(CO)_2\overline{M(CH_2}SMe)$ (M = Mo, W) by both photolysis and pyrolysis of $CpM(CO)_3(CH_2SMe)$. Unsuccessful attempts were also made by King and Bisnette at the synthesis of the iron analogue. A series of Ni, Pd, and Pt compounds with the general formula $(PPh_3)\overline{MCl[CH_2}SMe]$ and $(PPh_3)_2\overline{Pd(CH_2}SMe)^+$ have been

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reported.[23] In contrast to the uncoordinated SMe groups in I, the hydrogens on the carbon of the metallacyclopropane in these compounds are inequivalent at ambient temperature. There is also no evidence for a carbene mercaptide form of $\overline{\mathrm{ClPt(PPh_3)(CH_2S}}\mathrm{Me)}$. Unlike I, it reacts with $\mathrm{PPh_3}$ to displace the sulfur and give an alkyl complex $\mathrm{ClPt(PPh_3)_2[CH_2SMe]}$.[23] In addition, $\overline{\mathrm{ClPd(PPh_3)(CH_2S}}\mathrm{Me)}$ reacts with alkyl halides to give a halogen exchanged product $\overline{\mathrm{IPd(PPh_3)(CH_2S}}\mathrm{Me)}$,[24] and no alkylation of the sulfur occurs.

It is well documented in the literature[25] that α-heteroatom carbenes tend to be more stable than alkyl-, aryl-, and hydrogen-substituent carbenes because of the stabilizing effect that results from the interaction of the carbene carbon and the lone electron pairs on the heteroatoms. It is therefore understandable why the metallathiacyclopropane I in which such stabilizing groups (SMe) are present is more likely to show evidence for a carbene mercaptide form than the hydrogen-substituted analogues. Other metallathiacyclopropane complexes that are most likely to be in equilibrium with a carbene mercaptide form (eq 11) are also those where the carbene R substituents are stabilizing heteroatom groups.

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Synthesis and X-ray Crystal Structures of Ni_4 and Zn_4 Complexes of a Macrocyclic Tetranucleating Ligand

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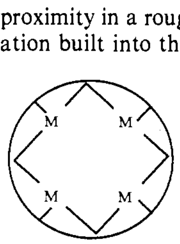
Abstract: Ni_4 and Zn_4 derivatives of the macrocyclic tetra Schiff base (LH_4) formed by condensation of two molecules of 2,6-diformyl-4-methylphenol with two molecules of 2,6-bis(aminomethyl)-4-methylphenol have been isolated. Determination of the structure of $LNi_4(CH_3CO_2)_2(OH)(CH_3O{\cdot}H{\cdot}OCH_3){\cdot}4CH_3OH$ by X-ray crystallography reveals four nickels at the corners of a rectangle with edges 2.788 (1) and 2.936 (1) Å; crystal data: monoclinic, space group *C*2/*c*, $a = 21.494$ (2) Å, $b = 8.996$ (1) Å, $c = 25.451$ (3) Å, $\beta = 93.75$ (1)°, $Z = 4$. An unusual μ_4-hydroxo group is located with its oxygen atom ca. 0.60 Å above the midpoint of the Ni_4 cluster. An unusual, strongly hydrogen bonded $CH_3O{\cdot}H{\cdot}OCH_3^-$ unit with a short O···O separation of 2.509 (7) Å bridges the "face" of the Ni_4 group on the side opposite to the μ_4-OH group, each methoxo oxygen being equally attached to two nickels. The arrangement of the macrocyclic ligand resembles a bowl with the Ni_4 group in the bottom. The $CH_3O{\cdot}H{\cdot}OCH_3^-$ unit is inside the bowl. Two acetate units bridge edges of the Ni_4 group on the outside of the bowl. A similar but less symmetrical bowl-like ligand arrangement is present in $LZn_4(CH_3CO_2)_3(OH){\cdot}2.64CH_3OH{\cdot}2.5H_2O$; crystal data: tetragonal, space group $P\bar{4}2_1c$, $a = 24.835$ (7) Å, $c = 17.172$ (4) Å, $Z = 8$. The Zn_4 group is markedly distorted from a square being no longer planar and having a short diagonal, 3.632 (7) Å, and a long diagonal, 4.742 (7) Å. A hydroxo group bridges the short diagonal with normal Zn–O bonds of length 1.97 (3) and 2.06 (3) Å, but it also interacts less strongly with the other two zincs at distances of 2.17 (2) and 2.60 (2) Å. One acetate bridges the short diagonal on the side opposite to the hydroxo group and on the inside of the bowl. A second acetate bridges an edge of the Zn_4 cluster and the third acetate is monodentate but hydrogen bonded to the hydroxo group. One zinc is intermediate between 4- and 5-coordinate, two are 5-coordinate, and the fourth is 6-coordinate.

It has been proposed that, as a result of an order–disorder-based effect related to the chelate effect, the organization provided by an appropriately designed binucleating ligand may confer unusual structural features and reactivity upon derived binuclear complexes.[1] The recently reported hydration of nitriles to carboxamides catalyzed by dipalladium complexes of binucleating ligands, which proceeds by a bimetallic pathway, provides one example of this sort of unusual reactivity.[2] Complexes in which a single ligand organizes more than two metal centers into some predetermined arrangement may similarly show unique behavior. The present report describes some initial synthetic and structural studies of complexes in which a macrocyclic ligand binds four metal centers in close proximity in a roughly square arrangement as in I. The organization built into these systems may lead to unusual behavior in a number of areas, including the following: (a) Species may be trapped at the central tetrametallic site under circumstances that would be unlikely or impossible in the absence of the order imposed by the tetranucleating ligand. The trapped



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