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Reactions of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSR)^+$ Bridging-Carbyne Complexes with Nucleophiles

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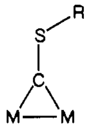
The bridging-thiocarbyne carbon in $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)^+$ (1) reacts with the nucleophiles RS^- (R = Me, Ph, and Bz) and $PhSe^-$ to give the bridging-carbene complexes $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)SR]$ (4-6) and $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)SePh]$ (7). The PhS^- and $PhSe^-$ groups in 5 and 7 migrate from the carbene carbon to an Fe with displacement of a CO group to give the carbyne complexes $Cp_2Fe_2(XPh)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)$, where X = S or Se. Treatment of the carbene complexes 4 and 5 with HBF_4 results in the removal of a RS^- group to regenerate the cationic carbyne 1 and $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSPh)^+$. The carbyne carbon in 1 is attacked by BzMgCl and BH_4^- to yield the carbene complexes $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)Bz]$ and $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)H]$. An X-ray diffraction structural investigation of this latter compound is reported. All of the bridging-carbene complexes are fluxional, and several isomers have been identified by their IR and NMR spectra. Reaction of 1 with 4-(dimethylamino)pyridine (4-DMAP) gives the CO-substituted carbyne $Cp_2Fe_2(4\text{-}DMAP)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)^+$.

Introduction

Transition-metal complexes with terminal[1-3] and bridging[4] carbyne ligands are well-known in organometallic chemistry. Although there are numerous reports concerning the preparation and reactivity of complexes with a carbyne ligand bridging two metal centers,[5-18] there are few studies of complexes with μ-carbyne ligands containing heteroatom substituents. To our knowledge, the only known dinuclear bridging-thiocarbyne complexes



are $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSR)^+$,[19] $Cp_2Fe_2(CO)_2(\mu\text{-}CS)(\mu\text{-}CSR)^+$,[20a] $Cp(CO)_2M(\mu\text{-}CSMe)Pt(PR_3)_2^+$ (where M = Mn or Re),[20b] $Cp(PMe_3)Co(\mu\text{-}CO)(\mu\text{-}CSMe)Mn(CO)Cp^+$,[20c] and $(Ph_3P)(I)Pt(\mu\text{-}SMe)(\mu\text{-}CSMe)Pt(I)(PPh_3)$.[20d] Even less is known about the reactivities of these complexes. Quick and Angelici[19] examined CO substitution reactions of the μ-thiocarbyne cations $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSR)]^+$ by phosphines, phosphites, isocyanides, and halides to give $Cp_2Fe_2(L)(CO)(\mu\text{-}CO)(\mu\text{-}CSR)^+$. We recently began to study reactions of these complexes that occur at their other reactive center, the carbyne carbon. One such reaction involved the formation of a triply bridging carbyne cluster complex from the reaction of $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]PF_6$ (1) with $Na[Co(CO)_4]$.[21] In addition, we have observed a relatively stable μ-carbyne radical, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)$, formed by reduction of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)^+$ (1).[22] Recently the reaction of 1 with CN^- to give $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)(CN)]$ was reported.[23] In this paper, we report the reactivity of the μ-thiocarbyne cations $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSR)^+$ with various other nucleophiles.

Experimental Section

General Procedure. Unless stated otherwise, all manipulations were carried out under deoxygenated N_2 in Schlenk ware at room temperature. Tetrahydrofuran (THF) and Et_2O were distilled from sodium/benzophenone. Acetonitrile, CH_2Cl_2, and hexane were stirred overnight with CaH_2 and then distilled. Acetone was dried and distilled from P_4O_{10}. All other solvents were AR grade and were stored over activated molecular sieves and purged with N_2 before use. The complexes $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]PF_6$ (1), $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSBz)]PF_6$ (2), and $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSAll)]PF_6$ (3) (All is allyl) were prepared by using a modification[24] of the method described by Quick and Angelici.[19] All other reagents were commercial products of the highest purity available and used as received. Elemental analyses were performed by Galbraith Laboratories, Inc.,

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Knoxville, TN. Decomposition points (dp) of compounds were observed on a Thomas hot-stage apparatus and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer 681 spectrophotometer and were referenced to the 1603.0 cm^{-1} band of polystyrene. Nuclear magnetic resonance (NMR) spectra (^1H and ^{13}C) were measured on either a JEOL FX-90Q or a Nicolet NT-300 spectrometer. Chemical shifts (δ) are reported in parts per million downfield from the internal reference tetramethylsilane. The shiftless relaxation reagent $Cr(acac)_3$ was added to solutions studied by ^{13}C NMR.

Preparation of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]$ (4). Excess MeSH was condensed onto NaH (0.059 g of a 57% oil dispersion, 1.4 mmol) at -80 °C. Addition of 5 mL of CH_3CN to the stirred suspension and slow warming to 0 °C formed a solution of NaSMe. Addition of 1 (0.40 g, 0.76 mmol) in 25 mL of CH_3CN gave an immediate reaction to form a purple solution which was stirred for 5 min. After the solution was warmed to room temperature, the solvent was removed under vacuum. The purple residue obtained was extracted with benzene; the resulting solution was filtered through anhydrous $MgSO_4$ and dried under vacuum. Crystallization from CH_2Cl_2 (4 mL)/hexane (20 mL) at -20 °C gave purple needles of 4 (0.26 g, 80%; dp 101.5 °C). Anal. Calcd for $C_{16}H_{16}O_3S_2Fe_2$: C, 44.48; H, 3.73; S, 14.84. Found: C, 44.16; H, 3.75; S, 15.11.

Preparation of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)SPh]$ (5). A precipitate of NaSPh was prepared by mixing PhSH (0.21 mL, 2.0 mmol) with NaH (0.080 g of a 57% oil dispersion, 1.9 mmol) in THF and removing the solvent. Addition of 1 (0.53 g, 1.0 mmol) and CH_3CN (20 mL) to the NaSPh at 0 °C immediately formed a purple solution which was stirred for 30 min. The purple residue remaining after solvent removal was worked up and crystallized following the procedure for 4, yielding purple crystals of 5 (0.37 g, 75%; dp 70 °C). Anal. Calcd for $C_{21}H_{18}O_3S_2Fe_2$: C, 51.53; H, 3.89; S, 13.76. Found: C, 51.12; H, 4.08; S, 13.87.

Preparation of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)SBz]$ (6). A THF (5-mL) solution of dibenzyl disulfide (0.020 g, 0.080 mmol) was titrated with a THF solution of sodium naphthalenide[25] (ca. 0.04 mmol/mL) to a light green end point. The solvent was evaporated to give a white residue of naphthalene and NaSBz. Addition of 1 (0.040 g, 0.080 mmol) and CH_3CN (5 mL) gave a purple solution. The color and similarity of the IR spectrum (Table I) to those of 4 and 5 supported the formulation of the product as 6.

Preparation of $Cp_2Fe_2(SePh)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)$ (8). A THF solution (20 mL) of PhSeSePh (0.16 g, 0.50 mmol) was stirred for 30 min with 5 mL of 1% w/w Na(Hg). After filtration through Celite and cooling to 0 °C, the solution was treated with 1 (0.27 g, 0.50 mmol) which gave a purple solution having ν(CO) bands at 2005 (sh), 1985 (s), 1958 (m), 1805 (sh), and 1792 (s) cm^{-1}. This color and the carbonyl bands at 1985, 1958, and 1792 cm^{-1} are consistent with the μ-carbene complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)SePh]$ (7).[22] The solvent was removed in vacuo at 0 °C leaving a brown residue which was extracted with hexane to remove PhSeSePh and $Cp_2Fe_2(CO)_3(CS)$.[26] The residue was dissolved in CH_2Cl_2 and the resulting solution was filtered through Celite and concentrated to 4 mL. Layering with hexane (20 mL) and crystallization at -20 °C gave brownish black crystals of the neutral μ-carbyne complex 8 (0.083, 32%; dp 95 °C) which are stable indefinitely at -20 °C under nitrogen. Anal. Calcd for $C_{20}H_{18}O_2SSeFe_2$: C, 46.82; H, 3.54; S, 6.25. Found: C, 46.94; H, 3.58; S, 6.25.

Preparation of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)SBz]$ (9). An CH_3CN (5 mL) solution of $NaBH_4$ (0.019 g, 0.50 mmol) and 2 (0.30 g, 0.50 mmol) was stirred for 30 min. The solvent was removed in vacuo, leaving a red residue which was extracted with CH_2Cl_2 (20 mL). The extract was filtered through Celite, concentrated to 5 mL, and layered with 20 mL of hexane. Crystals formed at room temperature; complete crystallization was achieved at -20 °C overnight, giving 0.17 g (72%) of red-violet needles of 9 (dp 102 °C). The product is stable indefinitely at -20 °C under nitrogen. Anal. Calcd for $C_{21}H_{18}O_3SFe_2$: C, 54.50; H, 3.93; S, 6.94. Found: C, 54.20; H, 3.93; S, 6.96.

Preparation of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)SMe]$ (10). Addition of 1 (0.27 g, 0.50 mmol) to a stirred solution of $NaBH_4$ (0.019 g, 0.50 mmol) in 5 mL of CH_3CN at 0 °C gave a red solution. After 30 min, the solvent was removed in vacuo and the red residue extracted with benzene; the extract was filtered through Celite and taken to dryness. Crystallization from acetone (4 mL)/hexane (16 mL) gave 0.11 g (60%) of dark red crystals (dp 100 °C), 10, which are stable indefinitely under nitrogen at -20 °C and room temperature. Anal. Calcd $C_{15}H_{14}O_3SFe_2$: C, 46.67; H, 3.66; S, 8.31. Found: C, 46.41; H, 3.73; S, 8.49. These crystals of 10 were used for the X-ray structure determination.

Preparation of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)SAll]$ (11). Stirring $NaBH_4$ (0.014 g, 0.38 mmol) with 3 (0.21 g, 0.38 mmol) in 5 mL of CH_3CN for 5 min gave a red reaction mixture. After evaporation of the solvent, the red residue was extracted with benzene; the extract was filtered through Celite and the benzene removed under vacuum. Crystallization at -20 °C from CH_2Cl_2 (4 mL)/hexane (20 mL) gave 0.112 g (76%) of a dark red powder, 11 (dp 44 °C), which was characterized spectroscopically (Tables I and II).

Preparation of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)Bz]$ (12). Addition of 1.2 mL of a 0.40 M Et_2O solution of BzMgCl[27] (0.48 mmol) to a suspension of 1 (0.25 g, 0.47 mmol) in THF (20 mL) gave an exothermic reaction which produced a brown solution and a mercaptan odor. The residue obtained from solvent evaporation was extracted with 15 mL of benzene. The extract was filtered through anhydrous $MgSO_4$ and evaporated to dryness under vacuum; the resulting residue was dissolved in a minimum of CH_2Cl_2 and loaded onto a 1.0 × 25 cm silica gel column (250–400 mesh). Elution with benzene caused two red fractions to develop. Initially, the first fraction was a discrete band, but during elution, it spread and became incorporated into the second red fraction. The combined fractions were eluted from the column with CH_2Cl_2. The red solution was taken to dryness, and the residue was dissolved in CH_2Cl_2 (4 mL). This solution was layered with hexane (20 mL) and crystallized for 3 days at -20 °C to give red needles of 12 (0.060 g, 27%; dp 90 °C). Anal. Calcd for $C_{22}H_{20}O_3SFe_2$: C, 55.46; H, 4.24; S, 6.74. Found: C, 54.64; H, 4.43; S, 6.71.

Preparation of $[Cp_2Fe_2(4\text{-}DMAP)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)]PF_6$ (13). An CH_3CN (5 mL) solution of 4-(dimethylamino)pyridine, 4-DMAP (0.33 g, 3.0 mmol), and 1 (0.27 g, 0.50 mmol) was stirred for 6 h. The solvent was removed in vacuo leaving a dark residue which was washed with 3 × 5 mL aliquots of Et_2O and dissolved in acetone (5 mL). This solution was layered with Et_2O (20 mL); crystallization at -20 °C gave 0.25 g (81%) of the black, crystalline air-stable product 13 (dp 108 °C). Anal. Calcd for $C_{21}H_{23}O_2SN_2Fe_2$: C, 40.67; H, 3.74; N, 4.52; S, 5.17. Found: C, 40.12; H, 3.72; N, 4.41; S, 5.25.

An analogous reaction of 2 with 4-DMAP gave $[Cp_2Fe_2(4\text{-}DMAP)(CO)(\mu\text{-}CO)(\mu\text{-}CSBz)]PF_6$ (14; 36% yield) which was not obtained free of impurities; it was characterized by its spectra.

Reaction of 5 with HBF_4. A CH_2Cl_2 (5 mL) solution of 5 (0.020 g, 0.040 mmol) was stirred at 0 °C with $HBF_4{\cdot}Et_2O$ (0.006 mL, 0.04 mmol) for 5 min. The red solution gave off an odor characteristic of MeSH. The solvent was removed, and the residue was washed with hexane, benzene, and ether and then dried under vacuum for 2 h. An ^1H NMR spectrum of the residue (in acetone-d_6) showed that both $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSPh)]BF_4$ (15) and the BF_4^- salt of 1 were produced in approximately a 7:1 ratio, respectively. The residue, after dissolving in acetone (0.5 mL) and layering with Et_2O (3 mL), was crystallized at 25 °C for 10 h and then at -20 °C overnight, giving (~0.010 g) red-brown crystals of 15, which was characterized by comparing its IR and ^1H NMR spectra (Tables I and II) with those of 1 and related $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSR)^+$ complexes.[19]

Preparation of $Cp_2Fe_2(SPh)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)$ (16). A CH_2Cl_2 (20 mL) solution of 5 (0.080 g, 0.16 mmol) was refluxed for 5 h giving a brown solution. The residue obtained after solvent evaporation was extracted with benzene; the extract was filtered through anhydrous $MgSO_4$ and evaporated. Crystallization of the brown-black residue from CH_2Cl_2 (3 mL)/hexane (20 mL) at -20 °C gave 0.040 g (54%) of brownish black crystals of 16 (dp 95 °C). Anal. Calcd for $C_{20}H_{18}O_2S_2Fe_2$: C, 51.53; H, 3.89; S, 13.76.

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Table I. IR Data for the Complexes

complex	solvent	IR ν(CO),[a] cm^{-1}
$[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]PF_6$ (**1**)	CH_3CN	2044 (s), 2013 (w), 1853 (m)
$[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSBz)]PF_6$ (**2**)	CH_3CN	2040 (s), 2010 (w), 1850 (m)
$[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SAll)]PF_6$ (**3**)	CH_3CN	2040 (s), 2015 (w), 1853 (m)
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]$ (**4**)	Nujol	1980 (s, b),[b] 1948 (m),[c] 1785 (s),[b] 1780 (sh)[d]
	hexane	1996 (s),[b] 1968 (s,)[b] 1960 (m),[d] 1779 (s)[c]
	CH_2Cl_2	1985 (s),[b] 1952 (m),[c] 1786 (m)[c]
	CH_3CN	1980 (s),[b] 1948 (m),[c] 1783 (m)[c]
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)SPh]$ (**5**)	CH_3CN	1985 (s),[b] 1952 (w),[c] 1786 (m)[c]
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)SBz]$ (**6**)	CH_3CN	1980 (s),[b] 1949 (m),[c] 1785 (m)[c]
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)SePh]$ (**7**)	THF	1982 (s),[b] 1952 (m),[c] 1790 (s)[c]
$Cp_2Fe_2(SePh)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)$ (**8**)	CH_3CN	1978 (s), 1800 (s)
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)SBz]$ (**9**)	hexane	1998 (s),[b] 1965 (w),[b] 1955 (w),[d] 1802 (m)[c]
	CH_2Cl_2	1985 (s),[b] 1947 (w),[b] 1780 (m)[b]
	CH_3CN	1975 (s),[b] 1938 (w),[b] 1780 (m)[b]
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)SMe]$ (**10**)	hexane	2000 (s),[b] 1968 (w),[b] 1955 (w),[d] 1805 (m)[c]
	$CDCl_3$	1989 (s),[b] 1951 (m),[c] 1780 (m)[c]
	CH_2Cl_2	1987 (s),[b] 1949 (w),[b] 1783 (m)[b]
	CH_3CN	1977 (s),[b] 1938 (w),[b] 1780 (m)[b]
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)SAll]$ (**11**)	CH_3CN	1973 (s),[b] 1937 (w),[b] 1778 (m)[b]
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)Bz]$ (**12**)	hexane	1996 (s),[b] 1964 (sh),[b] 1952 (s),[d] 1801 (m),[b] 1796 (sh)[d]
	THF	1975 (s),[b] 1950 (s),[c] 1800 (s)[c]
	CH_3CN	1977 (s),[b] 1940 (m),[b] 1782 (m)[b]
$[Cp_2Fe_2(4\text{-}DMAP)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)]PF_6$ (**13**)	CH_3CN	2000 (s), 1815 (s)
$[Cp_2Fe_2(4\text{-}DMAP)(CO)(\mu\text{-}CO)(\mu\text{-}CSBz)]PF_6$ (**14**)	CH_2Cl_2	2007 (s), 1817 (s)
$[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSPh)]BF_4$ (**15**)	CH_3CN	2049 (s), 2017 (sh), 1856 (m)
$Cp_2Fe_2(SPh)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)$ (**16**)	CH_2Cl_2	1988 (s), 1807 (s)

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. [b] Cis isomer band. [c] ν(CO) bands for cis and trans isomer are coincident. [d] Trans isomer band.

Table II. ^1H NMR for the Complexes[a]

complex	solvent	Cp	others[b]
1[c]	acetone-d_6	5.72, 5.63	3.80 (Me)
2[c]	acetone-d_6	5.75, 5.62	7.50 (m, Ph), 5.43 (CH_2)
3[c]	acetone-d_6	5.70, 5.65	6.18 (m, vinyl), 4.96 (t, CH_2, $J_{vinyl} = 7.8$ Hz)
4	CD_2Cl_2	4.89,[c] 4.90[d]	2.71,[c] 2.55 (Me),[c] 2.77 (Me)[d]
5	$CDCl_3$	4.95,[e] 4.93[f,g]	7.58 (m, Ph), 2.78,[h] 2.57,[e] 2.41[f] (Me)
8[c]	$CDCl_3$	4.84, 4.75	7.32 (m, Ph), 3.39 (Me)
9[i]	$CDCl_3$	4.53	11.43 (CH), 7.43 (m, Ph), 4.34 (CH_2)
	acetone-d_6	4.72	11.68 (CH), 7.44 (m, Ph), 4.39 (CH_2)
10[j]	acetone-d_6	4.88	11.65 (CH), 2.77 (Me)
	CD_3CN	4.84	11.57 (CH), 2.78 (Me)
	$CDCl_3$	4.77	11.47 (CH), 2.82 (Me)
11	$CDCl_3$	4.78,[d] 4.77,[d] 4.74,[c] 4.72[c]	11.61, 11.37, 11.21 (CH), 3.24 (b, vinyl), 2.11 (m, b, CH_2)
12[c]	CD_3CN	4.84	7.29 (Ph), 3.79 (CH_2), 2.81 (Me)
13[c]	acetone-d_6	5.34, 5.07	7.76 (d, py, $J_{HH} = 7.5$ Hz), 6.36 (d, py, $J_{HH} = 7.5$ Hz), 3.85 (SMe), 2.95 (NCH_3)
14[c]	acetone-d_6	5.39, 5.10	7.79 (d, py, $J_{HH} = 7.5$ Hz), 7.45 (m, Ph), 6.39 (d, py, $J_{HH} = 7.5$ Hz), 5.60 (CH_2), 2.94 (CH_3)
15[c]	acetone-d_6	5.72, 5.14	7.8 (m, Ph)
16[c]	$CDCl_3$	4.84, 4.80	3.39 (Me), 6.9–7.6 (m, Ph)

[a] Chemical shifts in δ. [b] Abbreviations: b, broad; d, doublet; m, multiplet; t, triplet. [c] Cis isomer. [d] Trans isomer. [e] *cis*-**5A**. [f] *cis*-**5B**. [g] *trans*-**5** isomer Cp resonances are coincident with cis Cp resonances. [h] *trans*-**5**. [i] *cis*-**9A**. [j] *cis*-**10A**.

Found: C, 51.12; H, 4.08; S, 13.87.

Structure Determination of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)SMe]$ (10). Relevant crystallographic data are given in Table IV. A dark red crystal of the dimensions given was glued to a glass fiber and attached to a standard goniometer head. It was then placed on a four-circle diffractometer (DATEX) controlled by an LSI-11 computer and interfaced in turn to a VAX 11/730 computer. Preliminary oscillation photographs were taken at various ϕ settings, and the approximate positions of 12 reflections were selected from these photographs and used as input to an automatic indexing program. The resulting cell dimensions and orthorhombic symmetry were confirmed by examining axial photographs.

The intensity data were corrected for Lorentz–polarization and absorption corrections. The estimated variance in each intensity was calculated by $\sigma_I^2 = C_T + C_B + (0.03C_T)^2 + (0.03C_B)^2 + (0.03I)^2$, where C_T and C_B represent the total and background count, respectively, and I is the net intensity. Computer programs used in this study are detailed in ref 28.

The positions of the iron atoms were found by the Patterson superposition technique. The positions of all other non-hydrogen atoms were obtained by successive structure factor and electron density map calculations. Hydrogen atoms were included but not refined. Positional and thermal parameters were refined initially by block-matrix least squares and subsequently by a full-matrix least-squares procedure yielding a final residual index of $R = 0.050$ and a weighted residual of $R_w = 0.058$. The final electron density difference map was featureless (≤ 0.4 e/Å^3). The atomic scattering factors used[29a] were corrected for anomalous dispersion effects in the case of iron and sulfur.[29b]

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(28) Calculations were carried out on a VAX 11/780 computer. The program BLIND (Jacobson, R. A. *J. Appl. Crystallogr.* **1976**, *9*, 115) was used for automatic indexing and Bravais lattice determination. The Patterson superposition program used is a FORTRAN modification of that described by C. R. Hubbard, M. W. Babich, and R. A. Jacobson (U.S. Department of Energy Report IS-4106, Iowa State University, Ames, IA, 1977). Structure factor calculations and least-squares refinements were done by using the block-matrix/full-matrix program ALLS (R. L. Lapp and R. A. Jacobson, U.S. Department of Energy Report IS-4708, Iowa State University, Ames, IA, 1979), Fourier series calculations were done by using the program FOUR (D. R. Powell and R. A. Jacobson, U.S. Department of Energy Report IS-4737, Iowa State University, Ames, IA, 1980), and for molecular drawings the program ORTEP (C. K. Johnson, U.S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1970) was used. An empirical absorption correction was carried out by using diffractometer ϕ-scan data and the program ABSN (B. A. Karcher, Ph.D. Dissertation, Iowa State University, 1981).

(29) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2a, pp 71–79. Hydrogen scattering factors were taken from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3176. (b) Cromer, D. T.; Liberman, D. *International Tables of X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1, pp 149–150.

Table III. ^{13}C NMR Data for the Complexes[a]

complex	solvent	Cp	R	CO	μ-CO	μ-C[b]
1[c]	CD_3CN	92.8, 92.1	38.2 (Me)	207.4	252.3	408.3
4	CD_2Cl_2	90.2,[c] 91.1[d]	25.6,[c] 24.1 (Me),[c] 26.2 (Me)[d]	210.9[c]	270.9[c]	186.9[c]
				210.4[d]	271.7[d]	189.2[d]
8[c]	CD_2Cl_2	88.9, 87.0	32.8 (Me), 135.3, 134.2, 127.1, 124.2 (Ph)	212.9	261.3	403.3
9[e]	CD_2Cl_2	86.9	46.8 (CH_2), 138.6, 128.8, 128.3, 126.6 (Ph)	210.9	272.5	163.7
10[f]	CD_2Cl_2	87.5	27.5 (Me)	211.5	272.7	169.9
13[c]	CD_3CN	90.7	36.0 (SMe), 39.3 (NCH_3), 155.1, 153.5, 108.9 (py)	210.5	267.0	407.1

[a] Chemical shifts in ppm. [b] Bridging carbene or carbyne carbon. [c] Cis isomer. [d] Trans isomer. [e] *cis*-**9A**. [f] *cis*-**10A**.

Table IV. Summary of Crystal Data for $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)(SMe)]$ (10, *cis*-10A Isomer)

formula unit	$Fe_2C_{15}H_{14}SO_3$
mol wt	386.03
space group	$P2_12_12_1$
a, Å	12.417 (2)
b, Å	17.542 (4)
c, Å	7.027 (10)
V, Å^3	1530.6 (5)
Z	4
d_{calcd}, g cm^{-3}	1.675
cryst dimens, mm	0.25 × 0.25 × 0.22
μ, cm^{-1}	20.3 (correction applied)
min, max transmissn	0.936, 0.999
λ, Å (Mo Kα)	0.709 66 (graphite monochromator)
scan mode	ω-scan
$2\theta_{max}$, deg	50
stds used	9 (no decay observed)
reflns measd	3200 (hkl, $\bar{h}\bar{k}l$)
reflns obsd ($I \geq 3\sigma_I$)	2420
unique reflns	1330
internal consistency factor[a]	0.018
R[b]	0.050
R_w[c]	0.058

[a] Residual between symmetry-related or multiply measured reflections defined as $\sum|I - \langle I\rangle|/\sum I$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma_F^2$.

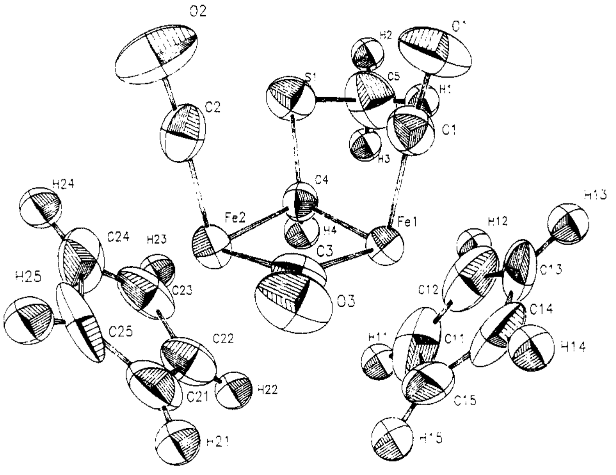


Figure 1. Perspective drawing of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)\text{-}SMe]$ (*cis*-**10A**). Thermal ellipsoids are drawn at the 50% probability level.

The final positional and thermal parameters are listed in Table V while bond lengths and bond angles are given in Table VI. An ORTEP drawing of the molecule is given in Figure 1.

Results and Discussion

Synthesis of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)(SR)]$ and $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)(SePh)]$. Mercaptides ($RS^-$) and $PhSe^-$ rapidly add to the carbyne C of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)^+$ (**1**) to generate bridging-carbene complexes (eq 1). The purple selenothiocarbene complex **7**, which has an IR spectrum (Table I) similar to **4**–**6**, was not isolated because it decomposes at 0 °C (es-

Table V. Atomic Parameters[a] for $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)SMe]$ (10, *cis*-10A Isomer)

atom	x[b]	y	z	U_{eq},[c] Å^2
Fe(1)	713 (1)	1429 (1)	3658 (2)	37.1
Fe(2)	−228 (1)	205 (1)	4486 (2)	38.1
S(1)	−1967 (2)	1511 (2)	3671 (4)	57.5
O(1)	−44 (6)	2458 (4)	6582 (12)	77.9
O(2)	−1253 (7)	625 (6)	8023 (11)	88.4
O(3)	1721 (5)	531 (4)	6629 (11)	61.8
C(1)	223 (8)	2035 (5)	5456 (15)	49.0
C(2)	−877 (7)	489 (5)	6574 (15)	48.1
C(3)	1074 (7)	678 (5)	5518 (14)	39.1
C(4)	−731 (7)	1067 (5)	2995 (13)	37.7
C(5)	−2034 (11)	2271 (7)	1945 (23)	90.1
C(11)	1280 (13)	1301 (9)	881 (16)	106.9
C(12)	984 (10)	2038 (8)	1167 (19)	90.1
C(13)	1621 (11)	2311 (7)	2536 (20)	82.6
C(14)	2308 (8)	1785 (8)	3138 (21)	81.1
C(15)	2107 (11)	1138 (7)	2138 (24)	107.1
C(21)	708 (9)	−757 (5)	3719 (20)	73.8
C(22)	130 (9)	−519 (6)	2135 (17)	65.8
C(23)	−946 (9)	−557 (6)	2528 (20)	73.0
C(24)	−1098 (9)	−804 (6)	4368 (22)	76.9
C(25)	−15 (10)	−952 (5)	5106 (20)	84.6

[a] In this and subsequent tables, estimated standard deviations are given in parentheses for the least significant digits. [b] Positional parameters × 10^4. [c] $U_{eq} = {}^1/_3\sum U_{ii} \times 10^3$.

Table VI. Selected Bond Distances and Angles for $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)SMe]$ (10, *cis*-10A Isomer)

(a) Distances (Å)

Fe(1)–C(1)	1.760 (10)	Fe(2)–C(22)	2.130 (11)
Fe(1)–C(3)	1.909 (9)	S(1)–C(4)	1.785 (9)
Fe(1)–C(4)	1.958 (9)	S(1)–C(5)	1.804 (15)
Fe(1)–C(13)	2.070 (12)	O(1)–C(1)	1.134 (12)
Fe(1)–C(12)	2.079 (14)	O(2)–C(2)	1.145 (13)
Fe(1)–C(11)	2.086 (12)	O(3)–C(3)	1.149 (11)
Fe(1)–C(15)	2.097 (15)	C(11)–C(12)	1.359 (21)
Fe(1)–C(14)	2.108 (11)	C(11)–C(15)	1.384 (21)
Fe(1)–Fe(2)	2.513 (2)	C(12)–C(13)	1.334 (19)
Fe(2)–C(2)	1.746 (10)	C(13)–C(14)	1.325 (18)
Fe(2)–C(4)	1.943 (9)	C(14)–C(15)	1.357 (20)
Fe(2)–C(3)	1.957 (8)	C(21)–C(25)	1.368 (18)
Fe(2)–C(24)	2.074 (11)	C(21)–C(22)	1.389 (17)
Fe(2)–C(25)	2.093 (9)	C(22)–C(23)	1.365 (16)
Fe(2)–C(23)	2.115 (12)	C(23)–C(24)	1.377 (20)
Fe(2)–C(21)	2.119 (10)	C(24)–C(25)	1.465 (17)

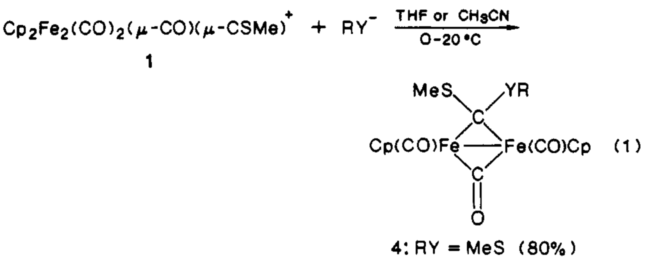
(b) Selected Bond Angles (deg)

Fe(1)–C(3)–Fe(2)	81.1 (4)	Fe(1)–C(3)–O(3)	141.6 (7)
Fe(1)–C(4)–Fe(2)	80.2 (3)	Fe(2)–C(3)–O(3)	137.3 (7)
C(3)–Fe(1)–C(4)	98.9 (4)	Fe(1)–C(1)–O(1)	175.7 (9)
C(3)–Fe(2)–C(4)	97.8 (4)	Fe(2)–C(2)–O(2)	174.0 (9)
C(4)–S(1)–C(5)	100.5 (5)	av C–C–C in Cp1	108.0 (12)
Fe(1)–C(4)–S(1)	125.7 (5)	av C–C–C in Cp2	108.0 (11)
Fe(2)–C(4)–S(1)	118.2 (5)		

(c) Selected Torsion and Interplanar Angles (deg)

Fe(1)–C(4)–S(1)–C(5)	79.6
Fe(2)–C(4)–S(1)–C(5)	178.1
Cp1–Cp2	93.5
plane 1–plane 2[a]	14.3

[a] Plane 1 is defined by Fe(1), Fe(2), and C(3) and plane 2 by Fe(1), Fe(2), and C(4).

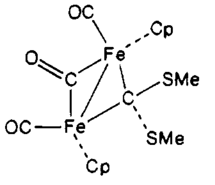


(1)

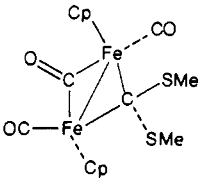
4: RY = MeS (80%)
5: RY = PhS (75%)
6: RY = BzS
7: RY = PhSe

pecially under vacuum) to give the μ-carbyne complex $Cp_2Fe_2(SePh)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)$ (**8**) and traces of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CS)$. Similarly, crystalline **5** decomposes over a period of several months at room temperature to $Cp_2Fe_2(SPh)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)$ (**16**) and insoluble products; the conversion of **5** to **16** in refluxing CH_2Cl_2 takes place within 5 h. Complexes **4** and **5** are dark purple, crystalline solids, soluble in most organic solvents and stable indefinitely under nitrogen at −20 °C.

The μ-dithiocarbene complexes exist as mixtures of isomers which could not be separated by silica gel column chromatography or fractional crystallization. The ^1H and ^{13}C spectra (Tables II and III) of **4** show the presence of a major isomer in which the Cp groups are cis to each other and the SMe groups are inequivalent and a minor isomer with trans Cp rings and equivalent SMe groups.



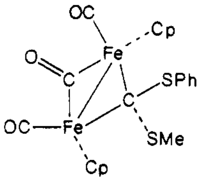
cis-**4**



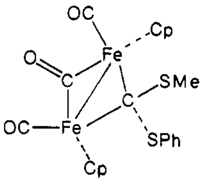
trans-**4**

In CD_2Cl_2, the cis:trans ratio is approximately 3:1, as determined by integration of the NMR peaks; this ratio does not change with time. The resonances at 186.9 (cis) and 189.2 (trans) ppm in the ^{13}C NMR spectrum have chemical shifts similar to those of the $\mu\text{-}C_{carbene}$ in other diiron μ-carbene complexes.[30] Except for the terminal carbonyl resonance in the ^{13}C spectrum, the trans isomer ^1H and ^{13}C resonances all occur downfield from those of the cis isomer.

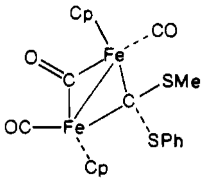
Complex **5**, because it has two different mercaptan groups bonded to the μ-carbene carbon, has three possible isomers:



cis-**5A**



cis-**5B**



trans-**5**

The relative stabilities of the isomers are expected to depend on the size of the SR substituents and minimization of their interaction with the bulky Cp ligands. Models suggest the large phenyl group will cause the following order of decreasing stability: *cis*-**5A** > *trans*-**5** > *cis*-**5B**. The ^1H NMR spectrum of **5** (at 25 °C) shows three methyl resonances at 2.78, 2.57, and 2.41 ppm indicating the presence of three isomers: their relative intensities decrease in the order 2.57 > 2.78 > 2.41. On the basis of the above steric argument, these resonances are assigned to the *cis*-**5A**, *trans*-**5**, and *cis*-**5B** isomers, respectively. As in complex **4**, the methyl resonance of the trans isomer is downfield from the cis isomers' methyl resonances. The Cp resonances for *cis*-**5A** and *cis*-**5B** are at 4.95 and 4.93 ppm, respectively; the *trans*-**5** Cp resonances apparently are coincident with the *cis*-**5** Cp resonances.

The relative abundances of the cis and trans isomers for **4** and **5** vary with solvent polarity, the cis configuration being favored in polar solvents. For example, the 1.0:2.7, cis:trans, methyl resonance ratio for **4** in benzene-d_6 becomes 2.7:1.0 in $CDCl_3$ and 5.2:1.0 in CD_3CN. While for **5** the methyl resonance ratio (*cis*-**5A** + *cis*-**5B**)/*trans*-**5** varies with solvent as follows: 1.9:1.0 ($CDCl_3$), 3.9:1.0 (CD_2Cl_2), 10:1.0 (CD_3CN). It should be noted that these ratios were observed within 10 min of preparing the solutions and did not vary with time. Similar effects were observed for $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)$ and $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)Me]$.[30]

The results discussed thus far imply the existence of a rapid cis $\rightleftarrows$ trans equilibrium. In $CDCl_3$, the equilibrium for **4** does not shift detectibly between −50 °C and 20 °C. However, the methyl resonance ratio (*cis*-**5A** + *cis*-**5B**)/*trans*-**5** for **5** in $CDCl_3$ does vary with temperature. At 0 °C the ratio is 2.2:1, while at 50 °C the ratio is 1.5:1. Equilibrium shifts toward the trans isomer with increasing temperature have been reported for other diiron μ-carbene complexes[30] such as $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)$. Resonances for the Cp and Me groups of this latter complex coalesce at 114 °C. Unfortunately, **4** rapidly decomposes to unidentified products above 80 °C, without showing any signs of coalescence; thus a quantitative comparison of the fluxionality of **4** with $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)$ is not possible. However, the rapid attainment of cis $\rightleftharpoons$ trans equilibrium by **4** in most solvents (except possibly hexane, see below) indicates that the fluxionality of **4** (and other μ-dithiocarbenes) is similar to $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)$.

As with other diiron μ-carbene complexes,[6,30] the IR spectra of the dithiocarbene and selenothiocarbene complexes show two terminal and one bridging carbonyl band (Table I). The low-energy terminal CO band at ~1950 cm^{-1} gains intensity in low polarity solvents due to an increase in the proportion of the trans isomer, whose single, terminal carbonyl band occurs at the same position as the weak band of the cis isomer. The bridging carbonyl bands of the cis and trans isomers are of similar frequency. In hexane, the terminal band (1960 cm^{-1}) of the trans isomer of **4** is strong and separated. The Nujol mull spectrum of **4** is similar to that in the hexane spectrum, which may indicate that the hexane spectrum reflects the cis:trans isomer ratio in the solid state rather than the equilibrium distribution in hexane. After refluxing **4** in hexane for 1 h, some *cis*-**4** is converted to *trans*-**4**, as evidenced by the approximately twofold increase in the relative intensity of the 1960 cm^{-1} band of the *trans*-**4** isomer. Conversion to the trans isomer does not occur (or is very slow) upon stirring **4** in hexane for 1 h at 25 °C. Thus, it would appear that the cis and trans isomers are not at equilibrium at 25 °C in hexane. The IR spectrum of **4** does not change significantly after refluxing **4** in CH_2Cl_2 for 1 h. Apparently, the isomers of **4** achieve equilibrium rapidly in CH_2Cl_2 and other solvents (C_6H_6, $CHCl_3$, CH_3CN).

Since **1** exists only as the cis isomer, complexes **4** and **5** are presumably formed initially as the cis isomers, with the trans isomers being formed by subsequent isomeriza-

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[30] (a) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417. (b) Gracey, B. P.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1985**, 1935.

tion. The Adams–Cotton[31] mechanism has been used to explain cis–trans isomerization of dinuclear metal systems with bridging ligands, including μ-carbene complexes.[30,32] This mechanism also accounts for the cis–trans isomerization of **4** as follows: The cis form of **4** first undergoes concerted bridge opening of the μ-CO and μ-C(SMe)$_2$ ligands to give a transient terminal carbene complex, which may rotate about the metal–metal bond to bring the Cp ligands trans to each other. Bridge closure then generates the trans isomer.

Further explanation is required to account for the two cis isomers of **5**, *cis*-**5A** and *cis*-**5B**. Steric arguments suggest that PhS$^-$ would attack opposite the Cp ligands of **1** to give the *cis*-**5A** configuration. The Adams–Cotton mechanism, as discussed for **4**, allows isomerization of *cis*-**5A** to *trans*-**5**. Additionally, *cis*-**5B** may form via this mechanism if the terminal carbene intermediate formed from *cis*-**5A** rotates around the Fe–C(carbene) bond to change the orientation of the SMe and SPh groups relative to the Cp ligands. This rotation is likely to be rapid,[33] although there are no direct measurements on this system.

Reactions of $Cp_2Fe_2(CO)_2(\mu$-$CO)[\mu$-$C(SMe)(SR)]$ and $Cp_2Fe_2(CO)_2(\mu$-$CO)[\mu$-$C(SMe)(SePh)]$. The reaction of **4** in CH_2Cl_2 with $HBF_4 \cdot Et_2O$ immediately gives *cis*-$Cp_2Fe_2(CO)_2(\mu$-$CO)(\mu$-$CSMe)^+$ (**1**), identified by its IR and ^1H NMR spectra as the only organometallic product.

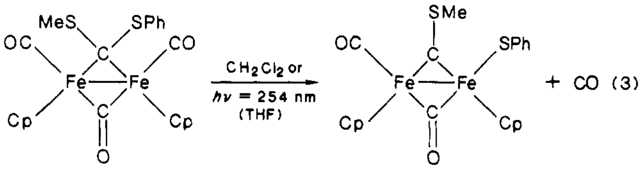
$$4 + HBF_4 \rightarrow 1 + BF_4^- + MeSH \qquad (2)$$

Although *trans*-**4** is approximately 25% abundant in CH_2Cl_2, no *trans*-**1** is produced. Either *trans*-**1** rapidly converts to *cis*-**1** or *trans*-**4** rapidly isomerizes to *cis*-**4** prior to removal of the SMe group by protonation.

Although the *cis*-**5A** isomer predominates over the *cis*-**5B** isomer in CH_3CN by a 3:1 ratio, the reaction of **5** in CH_3CN with $HBF_4 \cdot Et_2O$ gives a 50/50 mixture of $Cp_2Fe_2(CO)_2(\mu$-$CO)(\mu$-$CSPh)^+$ (**15**) and **1**. In CH_2Cl_2, all three isomers are present in significant amounts (*cis*-**5A**:*trans*-**5**:*cis*-**5B** = ca. 2.5:1:1.4), and the product ratio is 7:1 in favor of **15**. On the basis of the pK_a values[34] of MeSH (10.3) and PhSH (6.5), the MeS group might be more favorably protonated than the PhS group, which would favor the production of **15**. It is not entirely clear why the 15:1 product ratio is different in CH_2Cl_2 and in CH_3CN; it could be related to the different amounts of the various isomers of **5** present in these solvents (less *cis*-**5A** is present in CH_2Cl_2) or to different rates of protonation or isomerization.

The cyclic voltammograms of **4** and **5** have irreversible oxidation waves at 0.43 and 0.48 V, respectively. Chemical oxidation of **4** (in CH_3CN) and **5** (in CH_2Cl_2) with I_2, $C_7H_7^+$, Ph_3C^+, and Cp_2Fe^+ give immediate, clean reactions (by IR analysis) to produce $Cp_2Fe_2(CO)_2(\mu$-$CO)(\mu$-$CSMe)^+$ (**1**). An odor characteristic of CH_3SSCH_3 was produced in the oxidation of **4**, while an ^1H NMR spectrum of the products from the reaction of **5** with I_2 shows a multiplet at 7.1–7.6 ppm for PhSSPh.[35] Even though all three isomers of **5** are present in CH_2Cl_2, oxidation of **5** did not produce **15**. These oxidations of **4** and **5** may be explained as follows: (1) an electron transfer from the bridging-dithiocarbene complex to the oxidant results in the formation of a radical cation, $Cp_2Fe_2(CO)_2(\mu$-$CO)[\mu$-$C(SR)_2]^{\bullet +}$,[36] (2) subsequently an RS$^\bullet$ radical dissociates to give the μ-thiocarbyne cation product; (3) two RS$^\bullet$ radicals couple to produce the disulfide. Since the PhS$^\bullet$ radical is more stable than that of MeS$^\bullet$,[37] the oxidation of **5** should favor formation of **1** and PhSSPh, as observed. A similar mechanism was proposed for the oxidation of $Cp_2Ru_2(dppm)(\mu$-$CO)(\mu$-$CH_2)$.[7] Oxidation of this μ-carbene complex is reported to give a radical cation which then loses a hydrogen atom to give $Cp_2Ru_2(dppm)(\mu$-$CO)(\mu$-$CH)^+$.

Photolyzing or refluxing a solution of **5** causes the dithiocarbene complex to lose CO and form the brownish black μ-carbyne complex $Cp_2Fe_2(SPh)(CO)(\mu$-$CO)(\mu$-$CSMe)$ (**16**) (eq 3). The thermal reaction gives a higher yield of **16** (54% vs 20%). Photolyzing or refluxing **4** under the conditions of eq 3 results in decomposition products of an unknown nature. The analogous μ-selenocarbene complex $Cp_2Fe_2(CO)_2(\mu$-$CO)[\mu$-$C(SMe)SePh]$ (**7**) transforms at 0 °C (especially rapidly under vacuum) into the brownish black, μ-carbyne $Cp_2Fe_2(SePh)(CO)(\mu$-$CO)(\mu$-$CSMe)$ (**8**) as noted above. Solutions of **8** and **16** are moderately air-sensitive especially if warmed above 40 °C.



5 **16**

The ^1H NMR spectra of **8** and **16** (Table II) show inequivalent Cp resonances consistent with the proposed structures. The methyl resonance at 3.39 ppm for both **8** and **16** are close to the chemical shift (3.74 ppm, acetone-d_6) observed for the μ-CSMe group of the neutral μ-carbyne complex $Cp_2Fe_2(I)(CO)(\mu$-$CO)(\mu$-$CSMe)$.[24] The ^{13}C spectrum of **8** (Table III) shows an extreme downfield resonance at 403.3 ppm for the carbyne C atom; this value compares with 408.3 ppm for the corresponding C in $Cp_2Fe_2(CO)_2(\mu$-$CO)(\mu$-$CSMe)^+$ (**1**). Neutral heteronuclear μ-carbynes typically show resonances at fields lower than 400 ppm for the carbyne carbon, e.g. $[(C_6H_6)(CO)Cr(\mu$-$CO)(\mu$-CC_6H_4Me-$4)W(CO)_2Cp]$, 430.9 ppm.[38] Thus, the NMR data indicate that **8** and **16** are bridging-carbyne complexes. The transformation of the μ-carbene complex **5** to the μ-carbyne complex **16** is remarkable in the sense that **5** exists as an isomeric mixture yet it converts to only one isomer of **16**; this is presumably the isomer *cis*-$Cp_2Fe_2(SPh)(CO)(\mu$-$CO)(\mu$-$CSMe)$, in which the Cp rings are cis to each other. Although there is no experimental evidence for a cis structural assignment, all other known diiron thiocarbyne complexes have the cis Cp arrangement.[19,39]

Studies of the isomers of **5** (see above) show that they interconvert readily and are present as an equilibrium mixture during the synthesis of **16**. Examination of the ^1H NMR spectrum of **5** in $CDCl_3$ at 50 °C shows that the 2:2:1 ratio of *trans*-**5**:*cis*-**5A**:*cis*-**5B** does not change over a 2-h period as **16** grows in. This means that migration of the SPh group from the carbyne C atom probably occurs from only one isomer of **5** (perhaps *cis*-**5A**).

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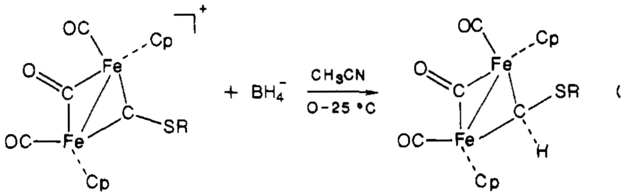
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)SR]$. Reactions of the thiocarbyne cations $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSR)^+$ (R = CH_3, Bz, All) with $NaBH_4$ result in rapid addition of H^- to the carbyne carbon to generate bridging-hydridothiocarbene complexes (eq 4). Complexes **9**, **10**, and **11** are light to dark red crystalline solids which are stable indefinitely at −20 °C under N_2 and are soluble in most common organic solvents (CH_3CN, acetone, CH_2Cl_2, $CHCl_3$, and benzene).



(4)

9: R = Bz (72%)
10: R = CH_3 (64%)
11: R = All (76%)

The IR spectrum of **9** (Table I) in polar and nonpolar solvents displays a strong, weak, medium ν(CO) band pattern (e.g., in CH_2Cl_2 at 1985 (s), 1947 (w), 1780 (m) cm^{-1}) consistent with a cis configuration (Cp ligands cis to each other). A second weak band at 1955 cm^{-1} in the IR spectrum of **9** in hexane may indicate the presence of a small amount of the trans Cp isomer. The ^1H NMR data (Table II) for **9** in $CDCl_3$ and acetone-d_6 also supports a cis configuration since the protons of the Cp ligands appear as singlets (4.53 ppm in $CDCl_3$; 4.72 ppm in acetone-d_6). Likewise, in the ^{13}C spectrum (CD_2Cl_2) only single Cp (86.9 ppm) and terminal CO (210.9 ppm) resonances are observed. The methine chemical shift ($CDCl_3$, 11.43 ppm; acetone-d_6, 11.68 ppm) is similar to that of *cis*-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)Me]$ (benzene-d_6, 11.6 ppm),[6,30] the structure of which shows the methine hydrogen syn to the cis Cp ligands.[40,41] An analogous structure, *cis*-**9A** (eq 4), is assigned to **9** since the bulky benzyl group would be on the opposite side of the carbene carbon from the Cp ligands.

In moderately polar (CH_2Cl_2) to polar (CH_3CN, acetone) solvents, the spectra of *cis*-**9A** do not change with time. In less polar solvents ($CHCl_3$, hexane) *cis*-**9A** slowly isomerizes to the other cis isomer *cis*-**9B**, where the Cp groups are still cis to each other but the methine hydrogen is syn to the CO ligands. This is seen in an ^1H NMR study of *cis*-**9A** in $CDCl_3$ (Table VII) which shows after 2 h at 45 °C new Cp and methine resonances at 4.50 and 10.57 ppm, respectively, for this new isomer. The *cis*-**9A**:*cis*-**9B** ratio is 5.8:1.0 at this point. After 4 h, resonances (Cp, 4.68, 4.63 ppm; methine H, 9.20 ppm) for a trans isomer, *trans*-**9**, are evident. The *cis*-**9A**:*cis*-**9B**:*trans*-**9** ratio is 8.7:2.2:1.0 at this stage. After 5 h, the ratio is 6.5:1.8:1.0 indicating further isomerization of *cis*-**9A** to *cis*-**9B** and *trans*-**9**. It is interesting that the *cis*-**9A**:*cis*-**9B** ratio changes from 4.0 to 3.6 during fourth and fifth hours, but the cis:trans ratio goes from 11 to 8.3. This may indicate that the *trans*-**9** isomer is more stable than the *cis*-**9B** isomer in less polar solvents. This is supported by the observed isomerization to *trans*-**9** when *cis*-**9A** is refluxed in hexane for 2 h. The IR spectrum of the refluxed solution displays an enhanced 1955 cm^{-1} ν(CO) band which may be attributed to the terminal carbonyls of *trans*-**9**. Furthermore, when the refluxed solution is evaporated to dryness under vacuum, the ^1H NMR spectrum of the residue in $CDCl_3$ shows a *cis*-**9A**:*cis*-**9B**:*trans*-**9** ratio of 5:1:1.8.

Table VII. Isomerization of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)SBz]$ (*cis*-9A) in $CDCl_3$ at 45 °C

hours	Cp (ppm)	methine[a] (ppm)	methine ratio[b]	cis:trans[c]	syn:anti[d]
0	4.53	11.43		very large	very large
2	4.53, 4.50	11.43, 10.57		very large	5.8
4	4.53, 4.50 (cis) 4.68, 4.63 (trans)	11.43, 10.57 9.20	8.7:2.2:1.0	11	4.0
5	4.53, 4.50 (cis) 4.68, 4.63 (trans)	11.43, 10.57 9.20	6.5:1.8:1.0	8.3	3.6

[a] Isomer assignment: 11.43 (*cis*-**9A**), 10.57 (*cis*-**9B**), 9.20 ppm (*trans*-**9**). [b] Ratio of *cis*-**9A**:*cis*-**9B**:*trans*-**9**. [c] Ratio of (*cis*–**9A** + *cis*-**9B**):*trans*-**9**. [d] Ratio of *cis*-**9A**:*cis*-**9B**.

The structure of **10** determined by X-ray diffraction is shown in Figure 1. Of the three possible isomers (see *cis*-**5A**, *cis*-**5B**, and *trans*-**5**), the crystals contain the *cis*-**10A** isomer with the Cp groups cis to each other and the methine hydrogen on the Cp side of the molecule which allows the more bulky SMe group to occupy the least hindered side of the carbene bridge. The bond distances and angles are nearly identical with those[40,41] of the closely related $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)Me]$.

Spectral data (Tables I and II) for **10** in moderately polar (CH_2Cl_2) to polar (MeCN) solvents also indicate a cis Cp configuration. The spectra of **10** in these solvents are invariant with time. Because the methine chemical shifts for *cis*-**9A** (acetone-d_6: 11.68 ppm) and **10** (acetone-d_6: 11.65 ppm) are similar, a configuration with the methine proton syn to the cis Cp ligands is also assigned to **10** in polar solvents; this isomer is designated *cis*-**10A** and is the same structure as found in the X-ray study.

On dissolution in less polar solvents, the IR and NMR spectra of **10** also reveal a predominately *cis*-**10A** structure. However, a weak carbonyl band at 1955 cm^{-1} and a medium intensity band at 1951 cm^{-1} in IR spectra of **10** in hexane and $CHCl_3$, respectively, may be due to partial isomerization to a trans Cp isomer, *trans*-**10**. The amount of this isomer is quite small since the ^1H NMR spectrum of a fresh $CDCl_3$ solution of **10** exhibits resonances for only a cis isomer (Cp, 4.77 ppm; methine H, 11.47 ppm; Me, 2.82 ppm).

However, the spectra of **10** in these solvents vary with time and temperature. The results of an ^1H NMR study of **10** in $CDCl_3$ are shown in Table VIII. After 1 h at 30 °C, *cis*-**10A** has partially isomerized to two other isomers. This is noted by the appearance of two new methine resonances at 10.57 and 9.18 ppm. Resolution of two equal-intensity Cp resonances at 4.80 and 4.79 ppm after 2 h at 30 °C makes it possible to assign a trans configuration, *trans*-**10**, to one of the new isomers. Since *trans*-**9** has its methine resonance at 9.20 ppm in $CDCl_3$, it is assumed that the 9.18 ppm methine resonance is associated with *trans*-**10**. The 10.57 ppm methine is thus assigned to the *cis*-**10B** isomer which would have its methine proton anti to the cis Cp ligands. The methine ratio *cis*-**10A**:*cis*-**10B**:*trans*-**10** changes significantly during the initial heating at 30 °C, going from pure *cis*-**10A** to a 15.2:2.9:1.0 ratio after 1 h and to 9.7:2.3:1.0 after 2 h. Heating at 40 °C for 1 h changes this ratio to 7.1:2.3:1.0. Additional heating at 50 °C for 1 h causes only a minor change in the

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Table VIII. Variation of the ^{1}H NMR Spectrum of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)SMe]$ (*cis*-10A) in $CDCl_3$ with Time and Temperature

°C (time)[a]	Cp (ppm)	methine[b] (ppm)	methine ratio[c]	cis:trans[d]	syn:anti[e]
0 (start)	4.77	11.47		very large	very large
30 (1 h)	4.77 (cis)[f] 4.80 (trans)[g]	11.47, 10.57 9.18	15:2.9:1.0	18	5.2
30 (2 h)	4.77 (cis)[f] 4.80, 4.79 (trans)	11.47, 10.57 9.18	9.7:2.3:1.0	13	4.2
40 (1.5 h)	4.77 (cis)[f] 4.80, 4.79 (trans)	11.47, 10.57 9.18	7.1:2.3:1.0	9.4	3.1
50 (1 h)	4.77 (cis)[f] 4.80 (trans)[g]	11.47, 10.57 9.18	7.0:2.3:1.0	9.3	3.0
0 (0.5 h)[h]	4.77 (cis)[f] 4.80, 4.79 (trans)	11.47, 10.57 9.18	8.0:2.8:1.0	11	2.9

[a] Length of time sample was at indicated temperature before spectrum was taken. [b] Methine resonance assignments: 11.47 (*cis*-**10A**), 10.57 (*cis*-**10B**), 9.18 ppm (*trans*-**10**). [c] Ratio of *cis*-**10A**:*cis*-**10B**:*trans*-**10**. [d] Ratio of (*cis*-**10A** + *cis*-**10B**):*trans*-**10**. [e] Ratio of *cis*-**10A**:*cis*-**10B**. [f] Cp resonances of *cis*-**10A** and *cis*-**10B** isomers are not resolvable. [g] Nonequivalent Cp resonances of *trans*-**10** isomer are not resolvable. [h] Spectrum taken 0.5 h after cooling from 50 to 0 °C.

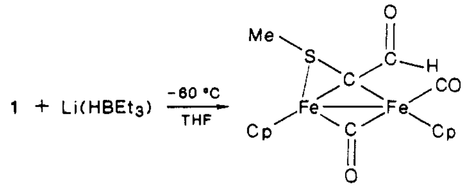
ratio to 7.0:2.3:1.0. Thus, it appears that the isomerization has reached "equilibrium" with a cis:trans ratio of 9.3 and a syn:anti ratio of 3.0. When the sample is then taken from 50 °C to 0 °C and allowed to sit for a half hour the cis:trans ratio increases to 11. The small decrease in the *cis*-**10A**:*cis*-**10B** ratio to 2.9 indicates that the shift toward the cis isomers does not substantially favor one cis isomer over the other.

The allyl complex **11** displays three methine resonances in $CDCl_3$ at 11.61, 11.37, and 11.21 ppm. Two of the three methine peaks correspond to cis isomers. Expansion of the spectrum in the Cp region reveals four signals at 4.72, 4.74, 4.77, and 4.78 ppm. The equal intensity of the latter two Cp resonances and the observation of a medium-intensity carbonyl band at 1957 cm^{-1} in the IR spectrum of **11** in $CDCl_3$ suggest that the remaining methine resonance is due to a *trans*-**11** isomer.

In most respects the solution behavior of the μ-hydridothiocarbene complexes **9** and **10** is similar to the μ-dithiocarbene complexes **4** and **5**. As with **4** and **5**, the relative abundances of the cis and trans isomers vary with solvent polarity. In polar solvents (CH_3CN and acetone) only *cis*-**9A** or *cis*-**10A** is observed. After equilibration in a less polar solvent ($CHCl_3$) both **9** and **10** will exhibit two cis isomers and a trans isomer with relative abundances of the isomers decreasing in the order: *cis*-**9A** or **10A** > *cis*-**9B** or **10B** > *trans*-**9** or **10**. Except for **4** in benzene, all of the μ-dithiocarbene complexes favor the cis isomers. Both the μ-dithiocarbenes and μ-hydridothiocarbenes favor the cis isomers at lower temperatures.

Perhaps the greatest difference between **9** and **10** and the μ-dithiocarbene complexes is in the rate of isomerization in various solvents. The μ-dithiocarbene complexes undergo rapid cis/trans isomerization (<10 min) in most solvents, while μ-hydridothiocarbene complexes isomerize rapidly in polar solvents such as CH_3CN and acetone (i.e., a mixture of *cis*-**9A**, *cis*-**9B**, and *trans*-**9** when put into these solvents gives *cis*-**9A** immediately). At ambient temperature in $CHCl_3$, **10** shows all three of its isomers only after 2–3 h while **9** requires 4–5 h. Diiron complexes, which are assumed to undergo cis/trans isomerization via the Adams–Cotton mechanism, are known to do so at different rates depending upon the nature of the bridging ligands. Qualitatively, the isomerization rates decrease in the order: $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ > $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CS)$ > $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)$ > $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$.[9,30,42] The μ-dithiocarbene complexes described in this paper isomerize at about the same rate as the carbene complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)$ whereas the μ-hydridothiocarbenes isomerize somewhat more slowly, but not as slowly as $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$.

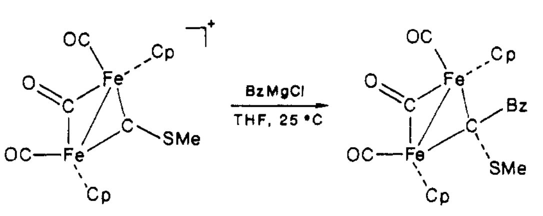
It should be noted that a reaction[23] very similar to that in eq 4 involving **1** and $Li(HBEt_3)$ at −60 °C in THF gives a quite different product (eq 5). At this point, it is not clear why the different reaction conditions lead to such different products.



(5)

Compound **9** (0.02 mmol) in 3 mL of CH_2Cl_2 reacts instantly with $HBF_4{\cdot}Et_2O$ (0.04 mmol) to give an unstable product, presumably $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)^+$ which was not isolated. However, the same reaction run in the presence of PPh_3 (0.040 mmol) gives a red solution of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)PPh_3]^+$ which was identified[6] by its IR spectrum (CH_2Cl_2: 1995 (s), 1960 (sh), 1817 (m) cm^{-1}).

$Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)CH_2Ph]$ (12). Addition of benzyl magnesium chloride to a THF suspension of **1** gives (eq 6) a 27% yield of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)Bz]$ (**12**), which is stable indefinitely under N_2 at −20 °C. The IR spectrum of **12** (in CH_3CN) exhibits terminal ν(CO) absorptions at 1977 (s) and 1940 (m) cm^{-1} and a bridging CO band at 1782 (m) cm^{-1}. The medium intensity of the terminal CO band at 1940 cm^{-1} implies the presence of some trans isomer. However, the intensity of this band is apparently an anomaly, since the ^{1}H NMR spectrum in CD_3CN shows only a single resonance (4.84 ppm) for the equivalent protons of the two Cp rings of a cis isomer. Because there are two different carbene substituents, two cis isomers are possible, analogous to isomers *cis*-**5A** and *cis*-**5B** for **5**. Molecular models of **12** show that the shorter



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$C_{carbene}$–CH_2 [1.514 (5) Å][40] and CH_2–C_{Ph} [1.515 (5) Å][38] bonds, compared to longer $C_{carbene}$–S [1.785 (9) Å] and S–CH_3 [1.804 (15) Å] bonds, make the Bz group bulkier than the SMe. Thus, one expects the cis isomer with the bulky Bz opposite the Cp rings to be more stable. This isomer is apparently sufficiently favored such that only this one isomer is observed in the ^1H NMR spectrum. A strong, low-energy terminal CO band at 1950 cm^{-1} in THF and at 1952 cm^{-1} in hexane indicates that a trans isomer of **12** is present in less polar solvents.

Other Reactions of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)^+$ (1). The methylidyne complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)^+$ forms adducts at the carbyne carbon with CO, NMe_3, and PPh_3.[6,15,18] Tri-*n*-butylphosphine reacts likewise with $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)^+$ to give $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(CH_3)P(n\text{-}Bu)_3]^+$.[6] Reactions of **1** with phosphines and phosphites give only the CO-substituted $Cp_2Fe_2(PR_3)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)^+$ complexes,[19] with no evidence, even as intermediates, for carbyne adducts. Refluxing pyridine (py) with **1** forms the unstable product $Cp_2Fe_2(py)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)^+$.[42] Even 6 equiv of the stronger nucleophile 4-(dimethylamino)pyridine (4-DMAP) with either **1** or **2** gives only the CO-substituted cations $Cp_2Fe_2(4\text{-}DMAP)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)^+$ (**13**) and $Cp_2Fe_2(4\text{-}DMAP)(CO)(\mu\text{-}CO)(\mu\text{-}CSBz)^+$ (**14**). Although these reactions take 6 and 24 h, respectively, to complete, no adduct intermediates, such as $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)(4\text{-}DMAP)]^+$, are observed. The product **13** is a black, air-stable, crystalline solid, which is obtained in excellent yield (81%). Complex **14** is a brown solid, stable indefinitely under nitrogen at −20 °C. Both **13** and **14** are soluble in polar solvents (CH_3CN, acetone) and are insoluble in hexane, benzene, and ether. The low yield (36%) for **14** may be due to a side reaction in which 4-DMAP attacks the benzyl carbon to yield the pyridinium salt 1-benzyl-4-(dimethylamino)pyridinium hexafluorophosphate and $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CS)$, which was identified as a byproduct.

Infrared data for **13** and **14** (Table I) are very similar to those of the analogous $Cp_2Fe_2(PR_3)(CO)(\mu\text{-}CO)(\mu\text{-}CSR)^+$ complexes reported previously.[19] The ^{13}C NMR spectrum of **13** shows a resonance at 407.1 ppm for the μ-carbyne carbon, which is close to that for the carbyne carbon of **1**, 408.3 ppm. In contrast, the NMe_3 adduct $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(H)NMe_3]^+$ has a ^{13}C resonance at 191.0 ppm, which is more typical of μ-carbene complexes including those (**4**, **9**, and **10**) in this paper (Table III).

In contrast to reactions of 4-DMAP, it has not been possible to isolate stable products from reactions of primary and secondary amines with **1**. However, spectroscopic studies of the reaction with $NHMe_2$ yield observations which are typical of other primary and secondary amine reactions. Bubbling $NHMe_2$ into a MeCN solution of **1** for 30 min gave a solution whose IR spectrum showed the absence of **1** but ν(CO) bands at 1972 (sh), 1938 (s), and 1770 (m) cm^{-1}. Evaporation of this solution to dryness under vacuum gave a residue whose IR spectrum showed bands for **1** and additional bands at 1938 (s) and 1768 (s) cm^{-1}. The evaporation process caused the disappearance of the 1972 cm^{-1} band and a decrease in intensity of the 1770 cm^{-1} band. We tentatively interpret these results to indicate that the initial product (1972 and 1770 cm^{-1} bands) from the reversible reaction of **1** with $NHMe_2$ is $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)(NMe_2)]$ (A) and $[Me_2NH_2]PF_6$. The structure of A is based on the similarity of its IR spectrum to other carbene complexes, e.g., **4** and **9**. This intermediate then converts to the final product (1938 (s) and 1768 (s) cm^{-1}), $Cp_2Fe_2(SMe)(CO)(\mu\text{-}CO)(\mu\text{-}CNMe_2)$ (B) by migration of the SMe from the bridging carbon to a terminal position, similar to the rearrangement of **5** to **16** (eq 3). The tentative structural assignment to B is based on the expected number (2) of ν(CO) absorptions and their positions at lower wavenumber than in **16**. The ^1H NMR spectrum of B in $CDCl_3$ shows both cis (Cp, 4.72, 4.54 ppm; NMe_2, 3.45, 3.37 ppm; SMe, 1.53 ppm) and trans (Cp, 4.69, 4.50 ppm; NMe_2, 3.24, 3.19 ppm; SMe, 1.53 ppm) isomers in an approximately 4:1 ratio. The chemical shifts for the Cp and μ-$CNMe_2$ ligands of B are upfield, as expected, compared to the ligands in *cis*-$[Cp_2Fe_2(CNMe)(CO)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]^+$ in $CDCl_3$ [5.26 and 5.20 ppm (Cp), 4.42 and 4.35 ppm (μ-$CNMe_2$)].[43] The chemical shift of the SMe resonance is similar to that observed in $CpFe(CO)_2SMe$ (1.61 ppm).[44] The neutral μ-aminocarbyne complexes B are less stable than similar cationic complexes previously prepared; the complexes $Cp_2Fe_2(L)(CO)(\mu\text{-}CO)(\mu\text{-}CNR_2)^+$ (L = CO, CNR; R = alkyl), are air-stable solids which decompose in solution,[43] while $Cp_2Fe_2(CO)(CNMe)(\mu\text{-}CNMe_2)(\mu\text{-}CSMe)^{2+}$ is reported to be an air-stable solid which apparently is stable in solution.[19,42]

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Registry No. **1**·PF_6, 76189-80-5; **1**·BF_4, 118099-47-1; **2**, 76157-30-7; **3**, 76157-32-9; *cis*-**4**, 117985-10-1; *trans*-**4**, 118099-31-3; *cis*-**5A**, 118099-32-4; *cis*-**5B**, 118099-33-5; *trans*-**5**, 118099-34-6; *cis*-**6A**, 117985-11-2; *cis*-**6B**, 118099-35-7; *trans*-**6**, 118099-36-8; *cis*-**7A**, 118099-37-9; *cis*-**7B**, 118099-38-0; *trans*-**7**, 118099-39-1; **8**, 102234-29-7; *cis*-**9A**, 117985-12-3; *cis*-**9B**, 118099-40-4; *trans*-**9**, 118099-41-5; *cis*-**10A**, 117985-13-4; *cis*-**10B**, 118099-42-6; *trans*-**10**, 118099-43-7; *cis*-**11A**, 117985-14-5; *cis*-**11B**, 118099-44-8; *trans*-**11**, 118099-45-9; *cis*-**12A**, 117985-15-6; *trans*-**12**, 118099-46-0; **13**, 117985-17-8; **14**, 117985-19-0; **15**, 117985-21-4; **16**, 102234-30-0; NaSMe, 5188-07-8; NaSPh, 930-69-8; NaSBz, 3492-64-6; PhSeSePh, 1666-13-3; BzMgCl, 6921-34-2; PhSSPh, 150-60-7.

Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atom positions (2 pages); a listing of calculated and observed structure factors (5 pages). Ordering information is given on any current masthead page.

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