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Reaction of $Co(CO)_4^-$ with a Bridging Carbyne Complex, $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]PF_6$. Crystal and Molecular Structures of $Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$ and $Cp_2Fe_2Co(CO)_2(PPh_3)(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$

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Reaction of $Na[Co(CO)_4]$ with $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]PF_6$, **1a**, under UV photolysis gives a high yield of $Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu\text{-}CSMe)$, **2a**. A single-crystal X-ray diffraction study of **2a** shows that it crystallizes in the monoclinic cell $P2_1/c$ with $a = 7.057$ (1) Å, $b = 14.767$ (2) Å, $c = 17.674$ (3) Å, and $\beta = 99.86$ (3)° and four molecules per unit cell. The structure was refined to $R = 0.044$ and $R_w = 0.051$ for the 2942 observed reflections with $I(\text{obsd}) \geq 3\sigma I$. The cluster has an L-shaped triangular structure, but there is no Co–Fe bond on one edge of the triangle. The CSMe group bonds through the carbyne carbon to all three metals, and in addition, the sulfur coordinates to the cobalt atom. Compound **2a** reacts with phosphines (PPh_3, PEt_3, PCy_3, $PHPh_2$, $PMePh_2$, $Ph_2PCH_2PPh_2$) to substitute a CO on cobalt. A single-crystal X-ray diffraction study of the PPh_3 derivative $Cp_2Fe_2Co(CO)_2(PPh_3)(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, **3a**, shows that it crystallizes in the monoclinic cell $P2_1/n$ with $a = 13.388$ (3) Å, $b = 23.188$ (6) Å, $c = 10.126$ (2) Å, and $\beta = 100.11$ (2)° and four molecules per unit cell. The structure was refined to $R = 0.067$ and $R_w = 0.068$ for the 2127 observed reflections with $I(\text{obsd}) \geq 3\sigma I$. Compound **3a** has the same basic structure as **2a** except that a CO on Co is substituted by PPh_3. Compound **2a** reacts with $HBF_4\cdot Et_2O$ and with oxidants (Ag^+, Ph_3C^+, I_2, $NOPF_6$) to yield **1a**. IR and ^1H NMR spectra of the complexes are also reported and discussed.

Introduction

Heteronuclear bridging carbynes MM′ (μ-CR) are known to react with metal fragments to give trinuclear carbynes, MM′M″(μ_3-CR).[1,2] Nucleophilic attack on heteronuclear carbyne cations MM′(μ-CR)$^+$ gives variable yields (4–90%) of bridging carbene products MM′[μ-CR(Nuc)],[3,4] where Nuc = H^-, Me^-, MeO^-, EtO^-, $t\text{-BuC}{\equiv}C^-$, $C_6H_4Me\text{-}4^-$, and $SC_6H_4Me\text{-}4^-$. These (μ-CR) reactivities appear to be influenced by the metal, the electron-donating ability of the auxilliary ligands, and the type of nucleophile. The product may be the expected carbene MM′[μ-CR(Nuc)] or an acylcarbene, MM′{μ-CR[C(O)Nuc]}.

Homonuclear bridging carbyne cations $M_2(\mu\text{-}CR)^+$ show variable reactivity which depends largely on the R substituent. Thus, the methylidyne complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)^+$ reacts with CO, NMe_3, PR_3, and RO^- to form the corresponding adducts and μ-carbenes.[5,6] In addition, this complex will undergo 1,2 addition to alkenes to give alkylidyne complexes.[7] These alkylidyne complexes react with hydrides to give bridging hydridoalkyl carbenes.[6,8] However, bases (HCO_3^-, NEt_3, MeLi) deprotonate the α-carbon of the alkylidyne to give μ-vinylidene or μ-alkenylidene complexes.[9,10]

In this article, we report the synthesis and reactivity of a new μ_3-carbyne-bridged complex $Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, **2a**, formed from the reaction of $Co(CO)_4^-$ with the bridging thiocarbyne cation $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)^+$, **1a**. This represents a new type of reactivity for a bridging carbyne.

Experimental Section

General Procedures. Preparation and crystallization of complexes were carried out by using Schlenk-tube techniques under a dry, oxygen-free nitrogen atmosphere (BASF catalyst). Methylene chloride (CH_2Cl_2) and hexane were dried over CaH_2 and distilled under N_2. Tetrahydrofuran (THF) was distilled under N_2 in the presence of sodium benzophenone ketyl. Benzene was dried over 4-Å molecular sieves and purged with nitrogen prior to use. Reactions were carried out at room temperature unless stated otherwise. Products were crystallized by using a layering technique, whereby the compound dissolved in CH_2Cl_2 (3–10 mL) was layered with hexane (15–50 mL) and allowed to sit at room temperature or cooled.

Infrared spectra were recorded with a Perkin-Elmer 681 spectrophotometer. The ν(CO) frequencies were calibrated against the 1603 cm^{-1} band of polystyrene. ^1H, $^{13}C\{H\}$ and $^{31}P\{H\}$ measurements were made with a JEOL FX-90Q, Nicolet NT-300, or Bruker WM-300 spectrometer. ^1H and ^{13}C chemical shifts were referenced relative to the internal standard Me_4Si, ^{31}P shifts were referenced relative to the external standard 85% H_3PO_4. All positive shifts are downfield of the standards. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Decomposition points (uncorrected) were determined in air on a Thomas hot stage apparatus.

Ultraviolet photolysis experiments were conducted by using a water-jacketed quartz immersion reactor with a solution volume of 125 mL. A 100-W medium-pressure mercury arc lamp was the photon source.

The complexes $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]PF_6$, **1a** and $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSCH_2Ph)]PF_6$, **1b**, were prepared from

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Table I. Infrared[a] and ^1H NMR[b] Spectra of the Complexes

complex	IR ν(CO), cm^{-1}	^1H NMR Cp	Me	other[c]
$Cp_2Fe_2Co(CO)_5(CSMe)$, **2a**	2023 (s), 1981 (s), 1951 (w) 1818 (s), 1781 (w)	4.83 4.42	2.75	
$Cp_2Fe_2Co(CO)_5(CSCH_2Ph)$, **2b**	2024 (s), 1982 (s), 1950 (w) 1820 (s), 1752 (w)	4.92 4.50		7.54 (m, Ph) CH_2[d]
$Cp_2FeCo(CO)_4(PPh_3)(CSMe)$, **3a**	1980 (s), 1930 (w) 1798 (s), 1760 (w)	4.87 3.97	2.80	7.56 (m, Ph)
$Cp_2Fe_2Co(CO)_4(PEt_3)(CSMe)$, **3b**	1976 (s), 1926 (w) 1796 (s), 1760 (w)	4.85 4.38	2.77	1.68 (b, PCH_2) 1.11 (b, $PCCH_3$)
$Cp_2Fe_2Co(CO)_4(PCy_3)(CSMe)$, **3c**	1977 (s), 1928 (w) 1793 (s), 1753 (w)	4.92[e] 4.50	2.83	1.26 (b, Cy)
$Cp_2Fe_2Co(CO)_4(PHPh_2)(CSMe)$, **3d**	1982 (s), 1937 (w) 1803 (s), 1762 (w)	4.86 4.24	2.78	7.41 (m, Ph) PH[f]
$Cp_2Fe_2Co(CO)_4(PMePh_2)(CSMe)$, **3e**	1979 (s), 1928 (w) 1796 (s), 1755 (w)	4.79 3.98	2.87	1.97 (d, PMe, J_{PH} = 6.5)
$Cp_2Fe_2Co(CO)_3(dppm)(CSMe)$, **3f**	1937 (s), 1760 (s) 1720 (w)	4.48 4.39	2.85	1.76 (b, CH_2) 7.13 (m, Ph)

[a] CH_2Cl_2 solution. s = strong, m = medium, and w = weak. [b] $CDCl_3$ solution. Chemical shifts in δ and coupling constants in Hz. [c] b = broad, d = doublet, m = multiplet, and all undesignated resonances are singlets. [d] No CH_2 resonance observed, but integration suggests it lies under the Cp resonances. [e] Seven equivalents of PCy_3 added to the sample. [f] No PH observed, possibly lies under Ph resonances.

$Cp_2Fe_2(CO)_3CS$[11] by using the previously described procedures.[12] The phosphines PEt_3 and $PMePh_2$ were fractionally distilled and stored under N_2. All other reagents were used without further purification.

Syntheses of Complexes. $Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 2a. A solution of $Na[Co(CO)_4]$ was prepared in situ by combining $Co_2(CO)_8$ (0.45 g, 1.3 mmol) with finely ground NaOH (4.50 g, 113 mmol) in THF (25 mL).[13] After the mixture was shaken for 30 min, the brown color of $Co_2(CO)_8$ disappeared. The resulting suspension was filtered through Celite into the photolysis tube containing **1a** (1.0 g, 1.9 mmol) and 100 mL of THF. The resulting reddish-brown solution was photolyzed with stirring until the 2050 cm^{-1} band of the carbyne starting material disappeared (~6 h). The residue, after solvent removal under vacuum, was extracted with benzene. The extract was filtered through anhydrous $MgSO_4$ and evaporated to dryness to give a brownish-purple residue which was crystallized from CH_2Cl_2 (10 mL) and hexane (50 mL) at -20 °C. The brownish-purple crystals obtained were collected, washed with hexane, and vacuum dried; yield 0.76 g (80%). An analytical sample was recrystallized from the same solvents: decomp pt 60 °C; ^{13}C NMR (CD_2Cl_2, -60 °C) δ 322.0 (s, μ_3-C), 262.1 (s, μ-CO), 252.1 (s, br, μ-CO), 211.3 (s, CO), 207.7 (s, br, CO), 201.7 (s, br, CO), 86.57 (s, Cp), 86.31 (s, Cp), 36.63 (s, Me). Anal. Calcd for $C_{17}H_{13}O_5SCoFe_2$: C, 40.84; H, 2.62; S, 6.41. Found: C, 40.76; H, 2.50; S, 6.32.

$Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu_3\text{-}CSCH_2Ph)$, 2b. Following the procedure for **2a**, the reaction between **1b** (0.30 g, 0.50 mmol) and $Na[Co(CO)_4]$ ($Co_2(CO)_8$, 0.12 g, 0.35 mmol; NaOH, 1.2 g, 30 mmol) required 12 h of photolysis at 12 °C. After the solution was evaporated to dryness, the residue was dissolved in a minimum of benzene and chromatographed on a 2 × 16 cm silica gel (230–400 mesh) column. Elution with benzene removed $Cp_2Fe_2(CO)_3CS$ and other side products. The product **2b** was then eluted as a brown band with 1:1 CH_2Cl_2 benzene. Evaporation and crystallization from CH_2Cl_2 (4 mL)/hexane (20 mL) at -20 °C gave brownish-purple crystals: yield 0.80 g (28%); decomp at 65 °C. Anal. Calcd for $C_{23}H_{17}O_5SCoFe_2$: C, 47.96; H, 2.97. Found: C, 47.59; H, 3.37.

$Cp_2Fe_2Co(CO)_2(PPh_3)(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 3a. A solution of **2a** (0.25 g, 0.50 mmol) and PPh_3 (0.92 g, 3.5 mmol) in 10 mL of CH_2Cl_2 was stirred for 9 h, filtered through anhydrous $MgSO_4$, and concentrated under vacuum to 5 mL. Layering with hexane (25 mL) and allowing the solution to stand at room temperature for 24 h gave black rhombohedral crystals. The crystals were washed three times with hexane and vacuum dried: yield 0.34 g (93%); decomp pt 108 °C; ^{13}C NMR (CD_2Cl_2, taken in the presence of 7 equiv of PPh_3) δ 317.7 (d, μ_3-C, J_{PC} = 15.9 Hz), 262.2 (s, μ-CO), 253.7 (s, br, μ-CO), 212.4 (s, CO), 205.8 (s, br, CO), 127–138 (PPh_3), 85.82 (s, Cp), 85.34 (s, Cp), 35.79 (s, Me). Anal. Calcd for $C_{34}H_{28}O_4PSCoFe_2$: C, 55.61; H, 3.84; S, 4.37. Found: C, 55.85; H, 3.86; S, 4.60.

$Cp_2Fe_2Co(CO)_2(PEt_3)(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 3b. With use of the procedure for **3a**, **2a** (0.20 g, 0.40 mmol) and PEt_3 (0.070 mL, 0.47 mmol), stirred for $1^1/_2$ h, gave, after crystallization from CH_2Cl_2 (3 mL)/hexane (20 mL) at -20 °C, grayish-black crystals: yield 0.16 g (68%); decomp at 95 °C. Anal. Calcd for $C_{22}H_{28}O_4PSCoFe_2$: C, 44.78; H, 4.78; S, 5.43. Found: C, 44.77; H, 4.80; S, 5.71.

$Cp_2Fe_2Co(CO)_2(PCy_3)(\mu\text{-}CO)_2(\mu_3\text{-}CMe)$, 3c. With use of the procedure for **3a**, **2a** (0.20 g, 0.40 mmol) and PCy_3 (0.78 g, 2.8 mmol), stirred for 12 h and crystallized at -20 °C, gave small black crystals: yield 0.16 g (54%); decomp pt 95 °C. This compound was identified by its IR and NMR spectra (Table I).

$Cp_2Fe_2Co(CO)_2(PHPh_2)(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 3d. As in **3c**, **2a** (0.20 g, 0.40 mmol) and $PHPh_2$ (0.30 mL, 1.7 mmol), stirred for 5 h, gave black crystals: yield 0.17 g (63%); decomp pt 90 °C. Anal. Calcd for $C_{28}H_{24}O_4PSCoFe_2$: C, 51.10; H, 3.68; S, 4.87. Found: C, 50.12; H, 3.69; S, 5.16.

$Cp_2Fe_2Co(CO)_2(PMePh_2)(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 3e. As in **3c**, **2a** (0.05 g, 0.1 mmol) and $PMePh_2$ (0.14 g, 0.70 mmol) gave black crystals. This product was identified from its IR and NMR spectra (Table I).

$Cp_2Fe_2Co(CO)(Ph_2PCH_2PPh_2)(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 3f. A solution of **2a** (0.20 g, 0.40 mmol) and $Ph_2PCH_2PPh_2$ (dppm, 0.31 g, 0.81 mmol) was stirred in 15 mL of CH_2Cl_2 for 45 h. The brown-black residue obtained after solvent evaporation was extracted three times with hexane to remove dppm, redissolved in CH_2Cl_2, filtered through anhydrous $MgSO_4$, and concentrated to 4 mL. Layering with hexane (25 mL) and cooling to -20 °C gave a crystalline product contaminated with free dppm. Crushing this product, extracting three times with hexane, and recrystallizing from CH_2Cl_2 (4 mL)/hexane (25 mL) at -20 °C gave black crystals which were washed three times with hexane and vacuum dried: yield 0.19 g (57%); decomp pt 90 °C; $^{31}P\{H\}$ NMR (CD_2Cl_2) δ 72.95 (d, J_{PP} = 81.4 Hz), 46.45 (m, br). Anal. Calcd for $C_{40}H_{35}O_3P_2SCoFe_2$: C, 58.00; H, 4.26; S, 3.87. Found: C, 57.53; H, 4.29; S, 4.32.

X-ray Crystallographic Analysis. A brownish-purple needle crystal of **2a** was mounted on a glass fiber and positioned on a standard goniometer head. Preliminary ω-oscillation photographs gave 12 independent reflections which were input into the automatic indexing program (BLIND).[14] The resulting reduced-cell scalars indicated monoclinic symmetry. Unit cell parameters were determined by a least-squares refinement utilizing the tuned 2θ values ($23° \leq 2\theta \leq 36°$) of 23 independent reflections. From the systematic extinctions of $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$), the space group was determined to be $P2_1/c$. Crystallographic data are given in Table II.

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Table II. Crystallographic Data

	2a	3a
empirical formula	$C_{17}H_{13}O_5SCoFe_2$	$C_{34}H_{28}O_4PSCoFe_2$
f wt.	499.95	734.24
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	7.057 (1)	13.388 (3)
b, Å	14.767 (2)	23.188 (6)
c, Å	17.674 (4)	10.126 (2)
β, deg	99.86 (3)	100.11 (2)
V, Å^3	1814.7 (4)	3095.0 (2)
Z	4	4
cryst size, mm	0.1 × 0.12 × 0.4	0.18 × 0.28 × 0.28
cryst color	brownish-purple	black
μ(Mo Kα), cm^{-1}	29.01^a	16.54^b
ρ_{calcd}, g/cm^3	1.83	1.58
ρ_{obsd}, g/cm^3	1.74	1.59
temp, °C	25	25
radiation	Mo Kα (λ = 0.71034 Å)	Mo Kα (λ = 0.71069 Å)
scan type	ω scan	ω scan
diffractometer	AL^{15}	Syntex $P2_1$
monochromator	graphite	graphite
standard reflctn(s)	3, measured every 75 reflctns^c	1, measured every 100 reflectns^c
reflctns measd	hkl, $\bar{h}\bar{k}l$; 2 octants	hkl, $\bar{h}\bar{k}l$, $\bar{h}k\bar{l}$, $h\bar{k}\bar{l}$; 4 octants
reflectns collected	3779 collected, 2942 observed ($I > 3\sigma_I$)	8902 collected, 2127 observed ($I > 3\sigma_I$)
max 2 θ, deg	50	50
min 2θ, deg	0	4
R^d	0.044	0.067
$R_w{}^d$	0.051	0.068

[a] A phi scan showed significant intensity variations; no absorption correction applied. [b] Absorption correction was applied via an empirical absorption correction technique. [c] No decay correction was applied. [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$; $w = 1/\sigma(F)^2$.

The estimated error in each intensity was calculated by $\sigma(I)^2 = C_T + K_tC_B + (0.03C_T)^2 + (0.03C_B)^2$, where C_T, K_t, and C_B represent the total count, counting time factor, and background count, respectively, and the factor 0.03 represents an estimate of the nonstatistical errors. The estimated standard deviations in the structure factors (F) were calculated by the finite difference method.[16] Equivalent reflections were averaged yielding 2304 unique observed reflections.

The positions of the cobalt and iron atoms were determined by Harker vector analysis of a three-dimensional Patterson map. All remaining non-hydrogen atoms were found by successive electron density map calculations.[17] The positional and anisotropic thermal parameters for the non-hydrogen atoms were refined by a combination of block-matrix/full-matrix least-squares calculations.[18] The positional parameters for the Cp hydrogens were refined by using fixed isotropic temperature factors. The final difference map was featureless. The scattering factors were those from ref 19 and were modified for the real and imaginary parts of anomalous dispersion.[20]

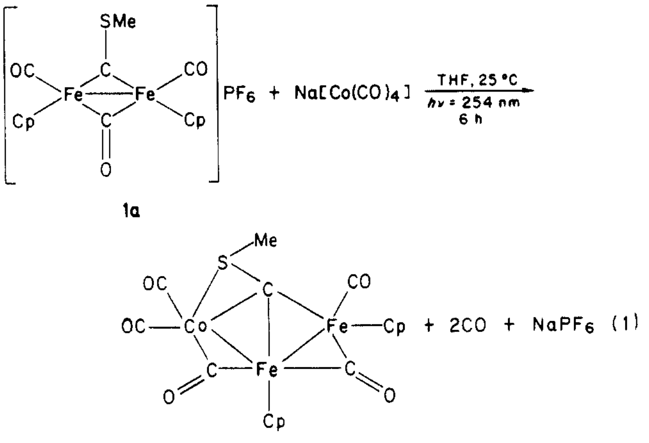
A black rhombohedral crystal of **3a** was mounted and indexed as for **2a**. The resulting reduced cell scalars indicated monoclinic symmetry. Unit cell parameters were determined for 20 independent reflections (17° ≤ 2θ ≤ 31°). Systematic extinctions of $0k0$ ($k = 2n$) and $h0l$ ($h + l = 2n$) determined the space group to be $P2_1/n$.

The estimated errors in the intensities and standard deviations in the structure factors were calculated as for **2a**. Equivalent reflections were averaged yielding 1088 independent observed reflections in the range 4° ≤ 2θ ≤ 50°.

The five heavy atoms were determined by using an automatic Harker analysis program (ORGES) from a superposition map.[21] All remaining non-hydrogen atoms were found by successive electron density map calculations.[17] The positional and anisotropic thermal parameters for the non-hydrogen atoms were refined by the methods used for **2a**. However, the atoms C2, C5, C8–C16, C21, C26, C28–C30, and C35 could not be anisotropically refined. (The rapid decrease in intensity as a function of (sin θ)/λ and the relatively low observation to parameter ratio also indicate that such anisotropic refinement is not warranted.)

Results and Discussion

Preparation of $Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 2a. Reaction of the bridging thiocarbyne complex **1a** with excess $Na[Co(CO)_4]$ in THF under ultraviolet photolysis gives an 80% yield of the unusual bridging carbyne complex **2a** (eq 1). The product is an air-stable brownish-purple solid, soluble in most organic solvents, forming brown solutions which are photostable but susceptible to air oxidation. The IR spectrum of **2a** shows bands characteristic of terminal (2023, 1981, and 1951 cm^{-1}) and bridging (1818 and 1781 cm^{-1}) CO groups. The ^{1}H spectrum exhibits three resonances with relative intensities of 5:5:3 with chemical shifts assignable to the cyclopentadienyl and CSMe ligands. The ^{13}C spectrum shows resonances for a methyl group (36.63 ppm), two Cp ligands (86.31 and 86.57 ppm), three terminal carbonyls (201.7, 207.7, and 211.3 ppm), two bridging carbonyls (252.1 and 262.1 ppm), and a triply bridging carbyne carbon (322.0 ppm). The resonances at 201.7, 207.7, and 252.1 ppm are carbonyl ligands coordinated to cobalt since they are broadened by the cobalt quadrupole. The chemical shift of the carbyne carbon is similar to those observed for other μ_3-carbyne complexes: $CpFe_3(CO)_6(\mu\text{-}CO)_2(\mu_3\text{-}CMe)$, 333.0 ppm;[22] $Fe_3(CO)_9(\mu_3\text{-}OMe)(\mu_3\text{-}CMe)$, 334.0 ppm.[23] Although these spectral data are consistent with the observed unsymmetrical structure, they do not exclude other similar structures; for that reason the X-ray diffraction study described elsewhere in this paper was undertaken.



1a

2b

(1)

The photolytic preparation of **2a** according to eq 1 is free of side products. When performed under thermal conditions (25–81 °C), the reaction gives low yields (<12%) of **2a** for the following reasons: (1) a competing reaction occurs to give $Cp_2Fe_2(CO)_3CS$ and an unknown cobalt

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product; (2) higher temperatures also decompose the desired product **2a**; (3) the mixtures obtained under thermal conditions require chromatographic separation with loss of product.

Addition of a THF solution of Na[Co(CO)$_4$] to **1a** greatly increases the solubility of the carbyne salt in THF, and the color of the reaction mixture changes from orange to brownish-purple. The color change might be attributed to a charge-transfer absorption between the ion pair [Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CSMe)]$^+$[Co(CO)$_4$]$^-$.[24] However, the expected IR absorptions for the Co(CO)$_4^-$ anions[25] resulting from such an interaction were absent; the IR spectrum of the reaction mixture shows no change from that of the starting materials. Since the carbyne C atom of **1a** is attacked by other nucleophiles to form μ-carbene complexes Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(SMe)(Nuc)],[26] one might expect the weakly nucleophilic[25] Co(CO)$_4^-$ to attack the carbyne to give the μ-carbene intermediate Cp$_2$Fe$_2$(CO)$_2$(μ-CO){μ-C(SMe)[Co(CO)$_4$]}. However, characteristic IR bands for this type of product {e.g., Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(SMe)$_2$] has carbonyl bands at 1985 (s), 1952 (m), and 1786 (s) cm^{-1}}[26] or any other intermediate were absent during the reaction.

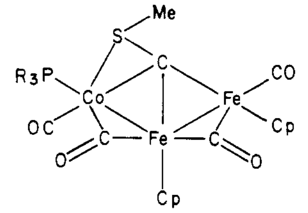
Recently, photoreactions (λ = 366–505 nm; in THF at 25 °C) of Cp$_2$Fe$_2$(CO)$_2$(μ-CO)$_2$ with phosphines (PR$_3$) to give Cp$_2$Fe$_2$(PR$_3$)(CO)(μ-CO)$_2$ products were proposed to go through the intermediate Cp(CO)Fe(μ-CO)Fe(CO)$_2$Cp, which contains a single bridging CO ligand and no Fe–Fe bond.[27] This intermediate, after reacting with a phosphine, loses CO rapidly to give the observed product. The similarity between the experimental conditions for the photoinduced substitution reactions of Cp$_2$Fe$_2$(CO)$_2$(μ-CO)$_2$ and the synthesis of **2a** in eq 1 suggests that **1a** may form photolytically the intermediate species Cp(CO)Fe(μ-CSMe)Fe(CO)$_2$Cp$^+$ prior to reacting with Co(CO)$_4^-$. Because μ-carbyne complexes, of the type Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-R$^+$), have higher activation energies for cis/trans isomerization than Cp$_2$Fe$_2$(CO)$_2$(μ-CO)$_2$,[28] and the fact that **1a** shows no evidence for this type of isomerization up to 90 °C,[26] suggest that the thiocarbyne ligand would favor the bridging position in this intermediate more than a carbonyl ligand. Nucleophilic attack by Co(CO)$_4^-$ at the unsaturated Fe atom of Cp(CO)Fe(μ-CSMe)Fe(CO)$_2$Cp$^+$ would give a trinuclear intermediate which might rapidly lose two CO groups to yield **2a**. While this mechanism is attractive, others cannot be eliminated.

Preparation of Cp$_2$Fe$_2$Co(CO)$_3$(μ-CO)$_2$(μ_3-CSCH$_2$Ph), 2b. Compound **2b** under the conditions of eq 1 is formed in low yields (<13%) due to the facile formation of Cp$_2$Fe$_2$(CO)$_3$CS. At 12 °C, higher yields (28%) are obtained. Under thermal conditions Cp$_2$Fe$_2$(CO)$_3$CS is essentially the only product.

Product **2b** is a brownish-purple solid which has a shelf life under a nitrogen atmosphere of less than 1 month. The similarity of its IR and ^{1}H NMR spectra (Table I) to those of **2a** establish it as having the same basic structure.

Reaction of 2a with Phosphines. The reaction of **2a** in CH$_2$Cl$_2$ with a variety of phosphines, as shown in eq 2, results in the formation of black crystalline complexes. Excess phosphine is necessary in most cases to drive the

$$\mathrm{Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu_3\text{-}CSMe) + PR_3 \xrightarrow[1.5-12\ h]{room\ temp,\ CH_2Cl_2}}$$



(2)

3a, PR$_3$ = 7 equiv of PPh$_3$ (93%)
b, PR$_3$ = 1 equiv of PEt$_3$ (68%)
c, PR$_3$ = 7 equiv of PCy$_3$ (54%)
d, PR$_3$ = 4 equiv of PHPh$_2$ (63%)
e, PR$_3$ = 7 equiv of PMePh$_2$

reaction to completion. Because of the presumed strain in the Co–S–C$_{\text{carbyne}}$ triangle of **2a** (see structure of **2a** below), it was anticipated that a product resulting from phosphine displacement of the SMe group bonded to the Co would be obtained; an X-ray diffraction study (vide infra) of **3a** shows instead that a CO group was replaced by the phosphine. The crystalline products are stable indefinitely under N$_2$ at −20 °C. In solution (CH$_2$Cl$_2$) under a N$_2$ atmosphere, all the complexes except **3b** are unstable, decomposing to **2a**. Apparently, **3a,c–e** decompose by phosphine dissociation giving an unsaturated species which scavenges free CO liberated by some decomposition of **3a**. Solutions of **3a**, **3d**, and **3e** are of approximately equal stability, in that their IR and ^{1}H NMR are obtainable with little or no excess phosphine being present. The IR spectrum of a solution of **3a** reverts after 20 h to a spectrum that is similar to that obtained from an equimolar mixture of PPh$_3$ and **2a**. Solutions of **3b** show only slight reversion to **2a** after 5 h. The greater stability of **3b** compared to **3a** may be due to the higher basicity of PEt$_3$ compared to PPh$_3$.[29] Steric factors may also affect the stability of the phosphine-substituted complexes. In the crystal structure (Figure 2) of **3a** the Co–P–C(18) angle is ~5° smaller than the other two Co–P–C angles while the Fe(1)–Co–P angle is 10° larger than the Fe(1)–Co–C(7) angle in **2a**. Although these differences are small, they do indicate some steric strain in the phosphine complexes. This is most evident for the PCy$_3$ derivative **3c**; the IR spectrum of a solution of **3c** reverts within 7 h to a spectrum similar to an equimolar mixture of PCy$_3$ and **2a**. Because of its instability the ^{1}H of NMR of **3c** can only be obtained in the presence of 7 equiv of PCy$_3$.

The IR and ^{1}H NMR data for **3a–e** are given in Table I. The chemical shift of one Cp resonance is essentially the same in **2a** and **3a**; the other Cp resonance in **3a** is 0.45 ppm upfield from that in **2a**. The crystal structure of **3a** (Figure 2) shows a phenyl ring of the PPh$_3$ ligand sitting orthogonal to the Cp ring of Fe(1). This phenyl orientation is probably favored for steric reasons and may result in diamagnetic anisotropic shielding causing an upfield shift of the Cp resonance. Upfield shifts of 0.18 and 0.44 ppm are also observed for the PHPh$_2$ and PMePh$_2$ derivatives **3d** and **3e**, respectively. The smaller upfield for the PHPh$_2$ complex is probably due to the lower steric requirements of this ligand[29] which may not require the Ph and Cp rings to spend as much time being orthogonal to each other.

The ^{13}C spectrum of **3a** shows one sharp (212.4 ppm) and one broad (205.8 ppm) resonance which may be assigned to the single terminal CO ligands on the Fe and Co, respectively; the Co–CO resonance is broadened by the Co quadrupole. In addition, two bridging carbonyls at 253.7 ppm, Fe(μ-CO)Co, and 262.2 ppm, Fe(μ-CO)Fe, and a

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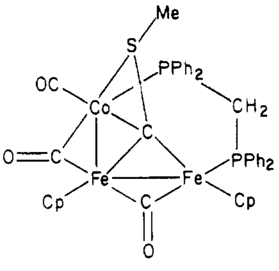
Table III. Atomic Coordinates[a] and Average Temperature Factors[b] for $Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 2a

atom[c]	x	y	z	U_{av}, Å^2
Co	2497 (1)	1156.2 (6)	3460.3 (5)	33
Fe1	2702 (1)	2142.5 (6)	4621.0 (5)	32
Fe2	2444 (1)	1490.5 (6)	8739.7 (5)	35
S	−573 (2)	1746 (1)	3142.6 (9)	36
O1	4483 (10)	1153 (5)	2153 (4)	94
O2	5257 (8)	3230 (4)	2745 (3)	73
O3	5937 (7)	3397 (3)	4917 (3)	57
O4	6176 (7)	1118 (3)	4457 (3)	57
O5	2119 (10)	−792 (4)	3690 (4)	78
C1	1443 (8)	2332 (4)	3597 (4)	35
C2	9075 (10)	2156 (5)	2147 (4)	47
C3	3664 (11)	1192 (5)	2644 (4)	53
C4	4141 (9)	3315 (4)	3146 (4)	44
C5	4457 (10)	3086 (4)	4602 (4)	40
C6	4607 (9)	1368 (4)	4262 (4)	40
C7	2251 (11)	−56 (5)	3622 (4)	47
C8	177 (12)	4205 (5)	4131 (6)	62
C9	−149 (12)	4217 (5)	3341 (6)	60
C10	1417 (13)	4652 (5)	3103 (5)	61
C11	2695 (13)	4936 (5)	3771 (6)	61
C12	1925 (13)	4656 (5)	4400 (6)	66
C13	1800 (14)	2648 (6)	5608 (5)	65
C14	3332 (13)	2029 (7)	5817 (4)	60
C15	2703 (13)	1201 (7)	5504 (5)	63
C16	798 (12)	1292 (6)	5116 (5)	55
C17	223 (11)	2184 (6)	5184 (4)	52

[a] Values are 10^4. The numbers in parentheses are the estimated standard deviations in the last significant digits. [b] Values are 10^3. U_{av} = average of U_{11}, U_{22}, and U_{33}. [c] Atoms are labeled in agreement with Figure 1.

resonance at 317.7 ppm due to the μ_3-C ligand were observed. The high field μ-CO resonance is broad so that P coupling could not be resolved. The chemical shift of the carbyne carbon is shifted upfield by 4.3 ppm compared to the parent complex **2a**. In addition, this resonance occurs as a doublet, J_{PC} = 15.9 Hz, which is in the range observed for other μ_3-carbynes: $[FePtW(Cp)(CO)_5(PMe_2Ph)_2(\mu\text{-}CO)(\mu_3\text{-}CC_6H_4Me\text{-}4)]$, J_{PC} = 27.0 Hz; $[FePtW(Cp)(CO)_6(PMePh_2)(\mu_3\text{-}CC_6H_4Me\text{-}4)]$, J_{PC} = 7.0 Hz.[1]

Two equivalents of dppm react with **2a** to give a 57% yield of $Cp_2Fe_2Co(CO)(\mu\text{-}CO)_2(dppm)(\mu_3\text{-}CSMe)$, **3f**. The IR spectrum shows evidence for one terminal (1937 cm^{-1}) and two bridging (1760 and 1720 cm^{-1}) CO ligands. The $^{31}P\{H\}$ spectrum has a broad resonance at 46.45 ppm and a sharp doublet at 72.95 ppm (J_{PP} = 81.4 Hz) indicating phosphine substitution at Co and Fe, respectively.[30,31a,b] In comparison, the ^{31}P resonance for free dppm is at −23.6 ppm.[32]



3f

A possible structure for **3f** is shown. This structure assumes that the metal core remains intact with the dppm ligand bridging the Co–Fe(2) distance of ~3.5 Å (Table III). The ability of dppm to coordinate to two widely separated metals is demonstrated by "A-frame" complexes: e.g., $Pd_2(dppm)_2(\mu\text{-}SO_2)Cl_2$ (Pd–Pd = 3.38 (4) Å),[33a–c] Although the Co–Fe(2) distance in **3f** is ~0.12 Å longer, an intraligand P–P distance of 3.429 Å has been observed in the complex $Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(dppm)_2^+$.[34]

The IR spectrum of the dppm reaction after 11 h shows carbonyl bands at 1980 (s), 1937 (w), 1795 (s), and 1760 (w) cm^{-1} which are similar to the monodentate products **3a–e**. This would indicate initial coordination of one end of the dppm ligand to cobalt. An additional 35 h is needed to convert from this intermediate to **3f**. With a large excess of dppm the reaction gives the intermediate product within an hour, but formation of the final product still requires an additional 24 h of stirring. The solid product is stable under nitrogen for less than 2 months at room temperature. Solutions of **3f** do not revert to a monodentate form or to **2a** over several hours at room temperature. However, they are sensitive to heat and oxygen.

In a qualitative experiment, $Ph_2PCH_2CH_2PPh_2$(dppe) reacts with **2a** to give a product with carbonyl bands at 1980 (s), 1930 (w), 1795 (s), and 1755 (w) cm^{-1} corresponding to coordination of one end of the dppe ligand to cobalt. No further reaction occurs to give a product similar to **3f**. Either the "bite" of this ligand is unsatisfactory for bridging between the Co and Fe(2) atoms or dppe forms a dimeric species by substituting a carbonyl on cobalt of two **2a** molecules.

The reaction of **2a** in CH_2Cl_2 with excess NEt_3, $NHEt_2$, NH_2-*n*-Bu, pyridine, 4-(dimethylamino)pyridine, $SbPh_3$, $AsPh_3$, CO, H_2, Me_2S, $SPPh_3$, $ONMe_3$, PhS^-, I^-, N_3^-, NO_2^-, MeI, PhC≡CH, cyclohexene, fumaronitrile, and CS_2 showed no reaction at room temperature after 1 h. Both CN^- and *t*-BuNC gave products whose IR spectra were similar to those of the **3a–e** products but they could not be isolated.

Addition of $HBF_4 \cdot Et_2O$ to **2a**, **3a**, or **3b** gives **1a** as the only stable carbonyl-containing product. Dark colored products were also observed which readily decomposed to insoluble material. The bidentate complex **3f** reacts with $HBF_4 \cdot Et_2O$ to give a product with carbonyl bonds at 1990 (s) and 1815 (s) cm^{-1}. Since these bands are similar to those observed for phosphine derivatives of **1a**,[12] this product is most probably $[Cp_2Fe_2(CO)(\eta^1\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CSMe)]BF_4$. Surprisingly, CH_3SO_3F does not react with **2a**.

Oxidation of **2a** in CH_2Cl_2 with Ag^+, Ph_3C^+, I_2, or $NOPF_6$ gives within 10 min **1a**; with $NOPF_6$ (2 equiv) the yield of **1a** is >90%. A stable cobalt product containing carbonyl ligands was not observed. Oxidation with I_2 in the presence of excess PPh_3,did not trap the expected $Co(CO)_2^+$ product as $ICo(CO)_2(PPh_3)_2$.[35] Chemical oxidation (Ag^+, halogens) of μ_3-carbyne clusters of cobalt $\{[(CO)_{9-n}(X)_nCo(\mu_3\text{-}CMe)]$; X = phosphine; n = 1–3$\}$ also yields unstable cobalt products.[36,37] In a similar reaction, $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}$

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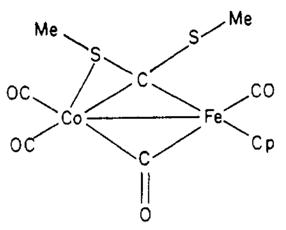
$C(SMe)_2]Co(CO)_2$, **4**, which contains a bridging carbene



4

that also coordinates to cobalt through sulfur, reacts with oxidants to give the stable terminal carbene complex $CpFe(CO)_2[C(SMe)_2]^+$. In this case, the $Co(CO)_2^+$ product was trapped as $ICo(CO)_2(PPh_3)_2$ when the I_2 oxidation was performed in the presence of excess PPh_3.[35,38]

Molecular Structures of $Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 2a, and $Cp_2Fe_2Co(CO)_2(PPh_3)(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 3a. The atom labeling scheme and molecular geometry of the bridged thiocarbyne complexes **2a** and **3a** are shown in Figures 1 and 2, respectively. Atomic coordinates for **2a** and **3a** are given in Tables III and IV, respectively. Selected bond lengths and angles of both compounds are compared in Tables V and VI. Since the structures are similar and the bond distances and angles are more precise for **2a**, this discussion will focus mainly on the unsubstituted complex **2a**.

The crystallographically determined structure of **2a** has a trinuclear core that is approximately "L" shaped with a Co–Fe(1)–Fe(2) angle of 88.38°; there is no metal–metal bond between Co and Fe(2) (3.511 (1) Å). The bridging thiocarbyne ligand bonds to all three metals through the carbyne carbon and in addition coordinates to cobalt through the sulfur atom. A similar type of coordination was observed for the μ_3-COMe ligand in the complex $Fe_4(CO)_{12}(\mu\text{-}H)(\mu_3\text{-}COMe)$.[39] The "open" triangular structure observed for **2a** is unusual for μ_3-carbyne complexes in that most complexes of this type have a "closed" structure with metal–metal bonds between the three metal atoms.[40a,b] Other "open" triangular μ_3-carbyne complexes include $[(CO)_3Fe]_3(\mu_3\text{-}CMe)(\mu_3\text{-}OMe)$,[23] **5**, and the Pt and W complexes derived from $L_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)W(CO)_2Cp$ (L = CO or phosphine) such as $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2(Cp)]$.[41a,b]

Complex **5** is, to our knowledge, the only other triply bridging carbyne complex with an "open" triangular cluster of first-row transition metals. This complex has an Fe(1)–Fe(2)–Fe(3) angle of 76.7° and an Fe(1)–Fe(3) distance of 3.059 (4) Å. The Fe(1)–Fe(2) distance 2.537 (1) Å in **2a** is longer than either Fe–Fe distance (2.472 (3) and 2.459 (3) Å) in **5**. However, it is similar to the corresponding distances in *cis*-$Cp_2Fe_2(\mu\text{-}CO)_2(CO)_2$, 2.531 (2) Å,[42] and $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8Cp]$, 2.538 (2) Å.[40b] The Fe(1)–Co distance 2.500 (1) Å is the same as in **4**, 2.502 (1) Å,[38] but is shorter than in the carbonyl-bridged complex $(CO)_3Co(\mu\text{-}CO)_2Fe(CO)Cp$, 2.545 (1) Å.[43]

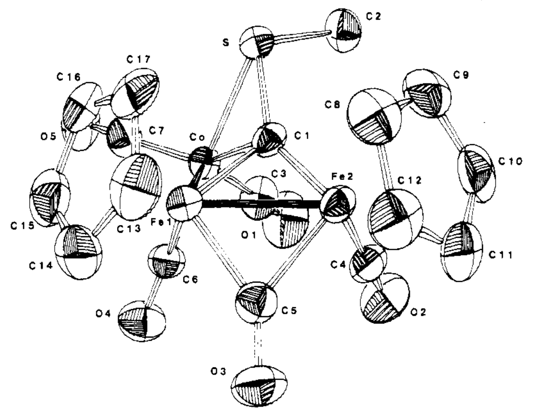


Figure 1. ORTEP drawing of $Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, **2a**.

Table IV. Atomic Coordinates[a] and Temperature Factors for $Cp_2Fe_2Co(CO)_2(PPh_3)(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 3a

atom[b]	x	y	z	U,[c] Å^2
Co	2725 (3)	1254 (2)	1093 (3)	49
Fe1	1862 (3)	2219 (2)	696 (4)	64
Fe2	2653 (3)	2299 (2)	−1406 (4)	70
S	1629 (6)	992 (3)	−869 (6)	65
P	2305 (6)	556 (3)	2481 (7)	56
O1	4811 (15)	976 (10)	1309 (20)	134
O2	4817 (15)	1974 (10)	−607 (18)	131
O3	3266 (16)	3178 (8)	640 (18)	115
O4	3411 (15)	2117 (8)	3062 (16)	98
C1	2213 (20)	1647 (9)	−482 (22)	55
C2	2409 (22)	649 (12)	−2024 (26)	85 (10)
C3	3945 (23)	1086 (11)	1140 (27)	90
C4	3995 (21)	2103 (11)	−880 (22)	73
C5	2794 (20)	2735 (11)	285 (24)	70 (8)
C6	2918 (22)	1917 (11)	2039 (21)	75
C8	1730 (22)	2128 (13)	−3337 (26)	92 (10)
C9	2739 (21)	2273 (17)	−3415 (26)	86 (10)
C10	2948 (21)	2874 (12)	−2897 (25)	84 (10)
C11	2054 (21)	3049 (12)	−2528 (26)	81 (9)
C12	1296 (22)	2581 (12)	−2782 (27)	92 (10)
C13	698 (20)	2829 (12)	271 (25)	84 (10)
C14	1123 (23)	2864 (13)	1666 (28)	99 (11)
C15	975 (24)	2316 (14)	2232 (29)	109 (11)
C16	415 (23)	1964 (12)	1244 (27)	94 (11)
C17	265 (21)	2292 (14)	17 (30)	106
C18	3147 (17)	452 (10)	4075 (20)	48
C19	2300 (20)	−172 (11)	1725 (20)	66
C20	1032 (18)	611 (10)	2987 (22)	49
C21	3101 (22)	−125 (11)	4721 (26)	84 (10)
C22	3814 (21)	−175 (11)	5971 (26)	74
C23	4422 (19)	240 (11)	6597 (23)	69
C24	4454 (20)	794 (11)	5976 (23)	70
C25	3803 (20)	882 (11)	4713 (22)	63
C26	1554 (21)	−597 (12)	1973 (26)	81 (10)
C27	1638 (24)	−1149 (12)	1478 (25)	96
C28	2373 (20)	−1277 (12)	780 (25)	80 (9)
C29	3068 (21)	−885 (11)	544 (26)	81 (9)
C30	3051 (20)	−313 (11)	956 (24)	67 (9)
C31	1001 (20)	774 (11)	4346 (25)	81
C32	−77 (19)	846 (11)	4566 (24)	75
C33	−923 (22)	767 (13)	3567 (30)	103
C34	−829 (22)	602 (11)	2297 (27)	85
C35	205 (20)	544 (11)	1963 (25)	67 (8)

[a] Values are $\times 10^4$. The numbers in parentheses are the estimated standard deviations in the last significant digits. [b] Atoms are labeled in agreement with Figure 2. [c] Values are $\times 10^3$. Atoms refined isotropically have the estimated standard deviations in parentheses. For all other atoms U = average of U_{11}, U_{22}, and U_{33}.

The dihedral angle formed by the planes Fe(1)–C(1)–Fe(2) and Fe(1)–C(5)–Fe(2) is 150.8°. This compares with 164° found between the two Fe(μ-CO)Fe planes in *cis*-$Cp_2Fe_2(\mu\text{-}CO)_2(CO)_2$.[42] The planes Co–C(1)–Fe(1) and Co–C(6)–Fe(1) make a dihedral angle of 140.9°. This

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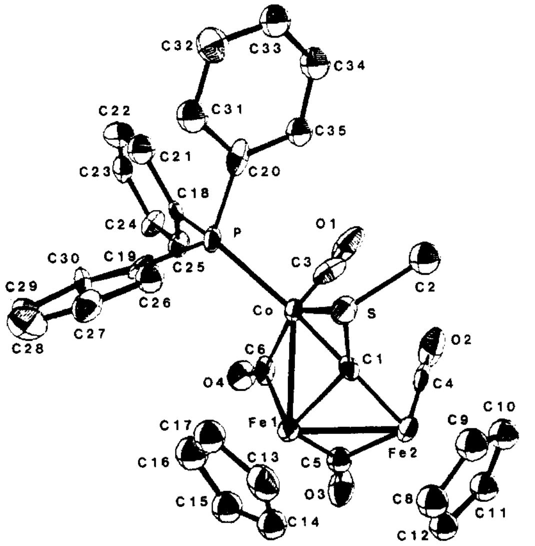

Figure 2. ORTEP drawing of $Cp_2Fe_2Co(CO)_2(PPh_3)(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, **3a**.

Table V. Selected Bond Distances[a] for $Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 2a, and $Cp_2Fe_2Co(CO)_2(PPh_3)(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 3a

	length, Å	
type[b]	**2a**	**3a**
Co–Fe1	2.500 (1)	2.518 (5)
Co–Fe2	3.511 (1)	3.493 (5)
Fe1–Fe2	2.537 (1)	2.545 (5)
Co–C1	1.921 (6)	1.86 (2)
Fe1–C1	1.895 (6)	1.90 (2)
Fe2–C1	1.877 (6)	1.92 (2)
Co–S	2.313 (2)	2.334 (8)
C1–S	1.740 (6)	1.72 (2)
C2–S	1.837 (7)	1.88 (3)
Co–C3	1.780 (8)	1.67 (3)
Co–C6	1.897 (7)	1.80 (2)
Co–C7	1.826 (7)	
Fe1–C5	1.867 (7)	1.83 (3)
Fe1–C6	1.951 (7)	1.91 (3)
Fe2–C4	1.746 (7)	1.84 (3)
Fe2–C5	1.998 (7)	1.97 (3)
C3–O1	1.124 (10)	1.17 (4)
C4–O2	1.153 (9)	1.13 (4)
C5–O3	1.189 (8)	1.23 (3)
C6–O4	1.162 (8)	1.22 (3)
C7–O5	1.098 (9)	
Co–P		2.278 (8)
P–C18		1.82 (2)
P–C19		1.85 (3)
P–C20		1.87 (2)
Fe1–C13	2.094 (9)	2.09 (3)
Fe1–C14	2.091 (8)	2.13 (3)
Fe1–C15	2.090 (9)	2.13 (3)
Fe1–C16	2.133 (8)	2.19 (3)
Fe1–C17	2.156 (8)	2.13 (3)
Fe2–C8	2.114 (9)	2.19 (3)
Fe2–C9	2.120 (8)	2.16 (3)
Fe2–C10	2.088 (8)	2.06 (3)
Fe2–C11	2.114 (7)	2.10 (3)
Fe2–C12	2.123 (9)	2.15 (3)
O4–C25		3.31 (3)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digits. [b] Atoms are labeled in agreement with Figures 1 and 2.

Table VI. Selected Bond Angles[a] for $Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 2a, and $Cp_2Fe_2Co(CO)_2(PPh_3)(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$, 3a

	angle, deg	
type[b]	**2a**	**3a**
Co–Fe1–Fe2	88.38 (4)	87.2 (2)
Co–C1–Fe1	81.8 (2)	84.2 (9)
Co–C1–Fe2	135.2 (3)	135 (1)
Fe1–C1–Fe2	84.5 (3)	83.5 (9)
Co–C1–S	78.2 (2)	81.2 (9)
S–C1–Fe1	125.4 (3)	127 (1)
S–C1–Fe2	141.5 (4)	138 (1)
C1–S–C2	104.1(3)	104 (1)
Co–S–C2	108.9 (2)	108 (1)
C3–Co–C7	103.0 (3)	
Fe1–Co–S	84.27 (6)	83.9 (2)
Co–C3–O1	174.3 (7)	173 (2)
Co–C7–O5	177.1 (7)	
Co–C6–O4	139.0 (6)	141 (2)
Fe1–C6–O4	139.8 (6)	133 (2)
Fe1–C5–O3	144.3 (6)	145 (2)
Fe2–C5–O3	133.6 (5)	131 (2)
Fe2–C4–O2	176.7 (6)	177 (2)
C1–Co–Fe1	48.6 (2)	48.5 (7)
C1–Fe1–Co	49.5 (2)	47.3 (7)
C1–Fe1–Fe2	47.4 (2)	48.7 (7)
C1–Fe2–Fe1	48.0 (2)	47.8 (7)
C1–Co–S	47.4 (2)	46.8 (7)
Co–S–C1	54.4 (2)	52.0 (8)
C1–Co–C7	144.8 (3)	
C1–Co–P		141.6 (8)
Fe1–Fe2–C4	104.7 (2)	
Fe1–Co–C3	132.7 (3)	129.1 (9)
Fe1–Co–C7	115.9 (2)	
Fe1–Co–P		125.1 (3)
C3–Co–P		99.4 (9)
Co–P–C18		112.1 (8)
Co–P–C19		117.5 (8)
Co–P–C20		117.1 (8)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digits. [b] Atoms are labeled in agreement with Figures 1 and 2.

compares with dihedral angles between the $Fe(\mu\text{-}CO)Co$ planes found in $(CO)_3Co(\mu\text{-}CO)_2Fe(CO)Cp$ (143.5°)[43] and $(\pi\text{-}C_9H_7)(CO)Fe(\mu\text{-}CO)_2Co(CO)_3$ (148.0°).[44] Relative to the metal-to-bridge-carbon distances in *cis*-$Cp_2Fe_2(\mu\text{-}CO)_2(CO)_2$[42] and $Co_2(CO)_8$,[45] the Co–(μ-CO) distance is reduced slightly from 1.92 (1) to 1.897 (7) Å, while the Fe(1)–(μ-CO) distance has lengthened from 1.917 (4) to 1.951 (7) Å. Likewise, the μ-CO between the iron atoms is shifted toward Fe(1); Fe(1)–(μ-CO) = 1.867 (7) Å; Fe(2)–(μ-CO) = 1.998 (7) Å.

The geometry about the bridging carbyne carbon is unusual in that it lies only 0.724 Å off the metal plane, substantially less than the 1.25 Å observed for the "closed" metal triangular carbyne complex $(CO)_9Co_3(\mu_3\text{-}CMe)$.[46] Relative to the metal triangle, μ_3-C sits approximately over the midpoint of the line between Co and Fe(2). A similar geometry was observed for the μ_3-nitride complex $Mo_3(\mu_3\text{-}N)(O)(CO)_4Cp_3$.[47] The atoms Co, S, C(1), and Fe(2) are nearly coplanar; the sum of the angles around C(1) to S, Co, and Fe(2) are 354.8° with C(1) being only 0.220 Å out of the S, Co, Fe(2) plane toward the Fe(1) atom. The Fe(1)–C(1) and Fe(2)–C(1) distances, 1.895 (6) and 1.877 (6) Å, are slightly shorter than the CpFe–(μ_3-CMe) distances in $[CpFe_3(CO)_6(\mu\text{-}CO)_2(\mu_3\text{-}CMe)]$, 1.902 (3) Å.[22] The Co–C(1) distance, 1.921 (6) Å, compares with $(CO)_3Co$–(μ_3-C) distances found in the following bridging carbyne complexes with "closed" triangular metal cores: $[CpCo_2W(CO)_8(\mu_3\text{-}CC_6H_4Me\text{-}4)]$, 1.953 (6) Å,[29] $[CpCo_2Mo(CO)_8(\mu_3\text{-}CPh)]$, 1.933 (5) Å,[48] and

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$[(C_5Me_5)_2Co(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CMe)]$, 1.932 (6) Å.[49] The Co–C(1) distance is slightly longer than the Co–[μ-C-$(SMe)_2$] distance in 4, 1.916 (2) Å.[38]

The Co–C(1)–Fe(1) and Fe(1)–C(1)–Fe(2) angles of 81.8° and 84.5°, respectively, are in the range observed for closed μ_3-carbyne complexes.[30,40b] The plane defined by Co–C(1)–Fe(1) makes a dihedral angle of 128.9° with the Co–C(1)–S plane. The Co–C(1)–S triangle has a C–S distance of 1.740 (6) Å, substantially shorter than the C(2)–S distance 1.837 (7) Å and shorter than that observed in 4, 1.789 (2) Å.[38] It is much less than the C–S single bonds in ethylene sulfide, 1.819 (1) Å, and tetrahydrothiophene, 1.839 (1) Å.[50] It is slightly shorter than C(sp^2)–S bonds (1.75–1.78 Å)[51,52] but longer than the C–S distance in thiophene, 1.718 (5) Å.[53] Thus it would appear that the C–S bond in **2a** has some double-bond character. Molecular orbital calculations[38] on 4 suggest that the Co–C–S triangle is stabilized by σ bonding from p orbitals on carbon and sulfur and back-donation from cobalt d orbitals into the π^* orbital located mainly on these two atoms. The bonding in the Co–C(1)–S triangle of **2a** is probably very similar. The stability of this triangle in both **2a** and 4 may account for their reactions with phosphines, which lead to the replacement of a CO group on the Co rather than displacement of the coordinated sulfur (eq 2 and ref 38).

As can be seen in Figures 1 and 2 the basic geometries of **2a** and **3a** are very similar. The greater electron density provided by PPh_3 substitution causes shortening of the Co–CO bonds (Co–C(3) = 1.67 (3) Å; Co–C(6) = 1.80 (2) Å in **3a** vs. 1.780 (8) and 1.897 (7) Å, respectively, in **2a**). In addition, the Co–C(1) distance is ~0.06 Å shorter in **3a** possibly as a result of greater d–π^* back-bonding into the C–SMe fragment. As a consequence, the Fe(2)–C(1) distance is ~0.04 Å longer. The greater steric requirements of PPh_3 as compared with CO are probably responsible for the Fe(1)–Co–P angle (125.1°) being larger than the Fe(1)–Co–C(7) angle (115.9°) in **2a**.

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Registry No. **1a**, 76189-80-5; **1b**, 76157-30-7; **2a**, 96211-43-7; **2b**, 96211-44-8; **3a**, 96211-45-9; **3b**, 96211-46-0; 3 (PR_3 = dppe), 96211-52-8; **3c**, 96211-47-1; **3d**, 96211-48-2; **3e**, 96211-49-3; **3f**, 96211-50-6; 3f (PR_3 = dppm), 96211-51-7; dppe, 1663-45-2; Na[$Co(CO)_4$], 14878-28-5; $Co_2(CO)_8$, 10210-68-1; $Cp_2Fe_2(CO)_3CS$, 67113-80-8; [$Cp_2Fe_2(CO)(\eta'\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CSMe)$]$BF_4$, 96227-22-4; PPh_3, 603-35-0; PEt_3, 554-70-1; PCy_3, 2622-14-2; $PHPh_2$, 829-85-6; $PMePh_2$, 1486-28-8; $Ph_2PCH_2PPh_2$, 2071-20-7.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

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New Difunctional Phosphine–Borane Species as Ligands for Organometallic Compounds

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Convenient high yield syntheses have been developed for the molecules $(CH_3)_3PBH_2P(CH_3)_2{=}X$, where X = O (**1**) and X = S (**4**). $(CH_3)_3PBH_2Br$ can be treated with K[$P(CH_3)_2O$] or K[$(CH_3)_2PS$] to give **1** or **4**, respectively. Routes via the intermediates [$(CH_3)_3PBH_2P(CH_3)_2Cl$]Cl, **2**, [$(CH_3)_3PBH_2P(CH_3)_2OCH_3$]Cl, **3**, or [$(CH_3)_3PBH_2P(CH_3)_2NHCH_3$]Cl, **5**, are possible but offer no advantages. However, the conversion of **1** into **4** using P_2S_5 is an acceptable alternative preparation for **4** (45% yield). An imine $(CH_3)_3PBH_2P(CH_3)_2{=}NCH_3$, **6**, was generated from **5** with $n\text{-}C_4H_9Li$ but could not be separated from LiCl. **1** and **4** are easily metalated at one of the $P(CH_3)_3$ methyl groups to yield products for which the formula Li[$CH_2(CH_3)_2PBH_2P(CH_3)_2{=}X$], where X = O (**7**) and X = S (**9**) is proposed. These reagents afford spirobicyclic complexes with $BeCl_2$ (**8** from **1** via **7**) and $ZnCl_2$ or $CdCl_2$ (**10** and **11**, respectively, from **4** via **9**). All materials were characterized by elemental analyses and spectral data.

Introduction

The stability of metal-to-carbon σ-bonds in organometallic compounds is a function of the nature of the substituents attached to the metal center and the organic ligands. Among the large variety of possible combinations, organic ligands bearing a positively charged onium center proved to be one of the most efficient systems to yield unusual bond characteristics. These unusual properties result from electronic, steric, and mechanistic effects associated with the electronegativity and the bulkiness of the ligand and its stability toward classical reductive elimination. The most thoroughly studied systems are the organometallic derivatives of the ylides of phosphorus and sulfur, as summarized in a number of review articles in the recent literature.[1–3] It has been pointed out previously[4]

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