theoretical and PE differences between platinum and palladium derivatives are in agreement with a higher π covalency of the former, so that π^* MOs in the latter compounds are strongly localized on halide ligands and very near in energy to n_{ip} and n_{op} lone pairs.

Acknowledgment. Thanks are expressed to the CNR (Rome) for generous financial support to this study.

Registry No. *trans*-$Pt(PEt_3)_2Cl_2$, 13965-02-1; *trans*-$Pt(PEt_3)_2Br_2$, 13985-90-5; *trans*-$Pt(PEt_3)_2I_2$, 15636-79-0.

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Dinuclear Fe, Ru, and Co Complexes with C- and S-Bonded Bridging $C(SR)_2$ Carbene Ligands

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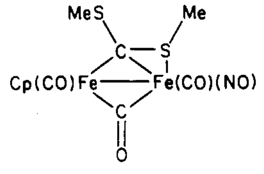
The dithiocarbene complex $Cp(CO)(MeCN)Fe{=}C(SMe)_2^+$ reacts with $Fe(CO)_3(NO)^-$ to give the dinuclear complex $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Fe(CO)(NO)$ in which the $C(SMe)_2$ ligand bridges the two metal atoms via the C atom and an S atom is also coordinated to the NO-bearing Fe:



IV

Analogously bridged complexes $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SR)_2]Fe(CO)(NO)$ are prepared from cyclic dithiocarbene complexes, $Cp(CO)(MeCN)Fe{=}\overline{CSCH_2CH_2S}^+$ and $Cp(CO)(MeCN)Fe{=}\overline{CSCH_2CH_2CH_2S}^+$, and $Fe(CO)_3(NO)^-$. Reactions with $Co(CO)_4^-$, instead of $Fe(CO)_3(NO)^-$, give the related $C(SR)_2$-bridged $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SR)_2]Co(CO)_2$ complexes. Likewise, $Cp(CO)(MeCN)Ru{=}C(SMe)_2^+$ reacts with $Co(CO)_4^-$ to yield $Cp(CO)Ru(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Co(CO)_2$. Spectroscopic studies indicate that all of the dinuclear complexes contain the unusual bridging $C(SR)_2$ ligand, as in structure IV. Reactions of IV and other $C(SR)_2$-bridged complexes with PEt_3 result in CO substitution but no displacement of the coordinated sulfur atom. The remarkable stability of the unusual bridging $C(SR)_2$ group can be understood in terms of competing π-donation by the S and metal atoms into the carbene C atom. Two-electron oxidation by $[Cp_2Fe]FeCl_4$, I_2, Ph_3C^+, and $C_7H_7^+$ of the dinuclear complexes results in metal–metal bond cleavage to yield the terminal carbene complexes $Cp(CO)_2Fe{=}C(SR)_2^+$ and $Cp(CO)_2Ru{=}C(SMe)_2^+$.

Introduction

Polynuclear transition-metal compounds containing bridging methylene (CH_2) ligands have been proposed as models for intermediates in several heterogeneously catalyzed reactions.[2] Homodinuclear metal complexes containing μ-methylene units are now known for nearly all the transition elements.[3] Polynuclear metal complexes containing a bridging carbon atom with group 15 or 16 heteroatoms such as O, S, N, or P are less well explored. Exceptions to this include compounds containing the μ-CR(OR) ligand, the chemistry of which has been amply demonstrated.[4] To date, no compounds containing bis(alkoxy)- or bis(thioalkoxy)–μ-methylene ligands have been reported. This is in contrast to terminal carbene complexes, of which several $C(OR)_2$ and $C(SR)_2$ derivatives are known.[5]

Theoretical calculations on dinuclear μ-methylene compounds imply that heteroatoms on the methylene carbon would influence the bonding in the dimetallocyclopropane ring.[6] For μ-CH_2 complexes, back-bonding from the metal pi* system into the unoccupied high-lying p_π orbital of the μ-methylene carbon atom makes a large contribution to the overall bonding. This back-bonding is also thought to be responsible for the large negative charge found on the μ-carbon atom in a Mulliken electron population analysis. The negative charge on the μ-carbon is chemically manifested in the facile reaction of these compounds with electrophiles.[3c] The presence of heteroatoms which can serve as π-donors on the carbon atom in μ-methylene compounds could result in altered patterns of reactivity. Competition for the "vacant" p_π orbital on the μ-carbon atom between the heteroatoms and the dimetal center would be expected to weaken the bonding within the dimetallocyclopropane ring.

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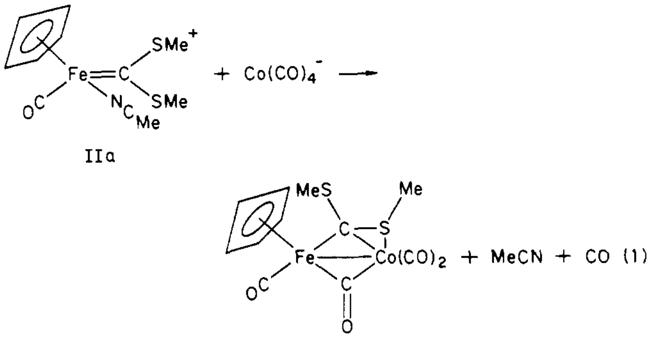
For the purpose of studying the effect of heteroatoms on the structure and reactivity of μ-methylene complexes, we have explored the synthesis of dinuclear transition-metal compounds containing μ-$C(SR)_2$ ligands. Previously[6c,7] we reported the reaction of the terminal $C(SMe)_2$ complex IIa with $Co(CO)_4^-$ to given an unusual μ-$C(SMe)_2$ dinuclear compound, III (eq 1). An



IIa

III

X-ray diffraction study[6c] of III established the presence of the bridging $C(SMe)_2$ group, which not only coordinates through the C to both metals but also binds to Co through an S atom. In order to determine whether or not this unusual structure is a regular feature of $C(SMe)_2$-bridged complexes, we have prepared a series of these complexes which are discussed in this paper.

Experimental Section

The following solvents were distilled from the indicated drying agent and stored under N_2: tetrahydrofuran (THF, sodium/benzophenone), CH_2Cl_2 (P_2O_5), Et_2O ($NaK_{2.8}$). Reagent grade MeCN, acetone, pentane, and hexane were dried over molecular sieves (4 Å) and purged with N_2 for 30 min prior to use. Piperidine was stirred over KOH, distilled, and stored over molecular sieves.

The metal carbonyl compounds $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ were sublimed prior to use. The following compounds were used as received: $Fe(CO)_5$, $Cp_2Fe_2(CO)_4$, $Mo(CO)_6$, and $P(C_2H_5)_3$. The $Cp_2Ru_2(CO)_4$ was kindly provided by Dr. Alan Steinmetz. Triphenylphosphine was recrystallized from hot methanol before use.

All manipulations were carried out in Schlenkware or similar apparatus under N_2 by using standard inert-atmosphere techniques.[8] Infrared spectra were recorded on a Perkin-Elmer 681 spectrophotometer calibrated against CO and are thought to be accurate within ±2 cm^{-1}. Proton and carbon NMR spectra were obtained on a JEOL FX-90Q spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane. The shiftless relaxation agent $Cr(acac)_3$ (~0.1 M) was added to ^{13}C samples to reduce data collection time. UV-visible spectra were recorded on a Beckman DU-8 instrument by using quartz cells of 1-cm path length. Mass spectra were obtained on a Finnigan 4000 GC-MS with an INCOS 2300 data system, GC Model 9610 with a source voltage of 20 eV. Photochemical reactions were carried out at 254 nm in a quartz Schlenk tube equipped with a cooling probe by using a reactor obtained from Bradford Scientific, Inc., Marblehead, MA. Melting points were determined with a Thomas Model 40 micro hot stage and are not corrected.

The compounds $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SCH_3)_2]Co(CO)_2$ (III),[6c] $[Cp(CO)_2Fe[C(SCH_3)_2]]PF_6$ (Ia),[9] $[Cp(CO)(NCCH_3)Fe[C(SCH_3)_2]]PF_6$ (IIa),[10] $[Cp(CO)_2Fe[\overline{CSCH_2CH_2S}]]PF_6$, (Ib), $[Cp(CO)_2Fe[\overline{CSCH_2CH_2CH_2S}]]PF_6$ (Ic),[5a] $[Fe(CO)_3NO]PPN$, and $\{Mn(CO)_2(NO)_2\}PPN$[11] were prepared by published routes.

Preparation of $[Cp(CO)(NCCH_3)Fe[\overline{CSCH_2CH_2S}]]PF_6$ (IIb). A 35-mL MeCN solution of Ib (0.15 g, 0.35 mmol) was irradiated at 254 nm for 2.5 h. During this time the bands due to Ib slowly diminished in the IR spectrum as a new band grew in at 2011 cm^{-1}. Gas evolution was apparent, and a gradual color change from bright yellow to red occurred. The solvent was removed in vacuo (1 Torr), leaving a red oil. The oil was washed several times with Et_2O. Crystallization was induced by dissolving the oil in a minimum amount of CH_2Cl_2, layering with Et_2O, and slowly cooling to −20 °C. Dark red air-stable crystals of IIb were obtained (0.11 g, 64%). IR (CH_2Cl_2): ν(CO) 2016 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.83 (s, 5 H, Cp), 3.14 (s, 4 H, SCH_2), 2.32 (s, 3 H, CH_3CN). ^{13}C NMR (CD_2Cl_2, $Cr(acac)_3$): δ 307.07 (carbene C), 214.49 (CO), 134.67 (CH_3CN), 86.13 (Cp), 46.43 (SCH_2), 4.66 (CH_3CN). Anal. Calcd for $C_{11}H_{12}ONF_6PS_2Fe$: C, 30.08; H, 2.75. Found: C 30.56; H, 2.99.

Preparation of $[Cp(CO)(NCCH_3)Fe[\overline{CSCH_2CH_2CH_2S}]]PF_6$ (IIc). This compound was prepared by the same method used for IIb. Thus, irradiation of Ic (0.12 g, 0.27 mmol) for 2.0 h afforded 0.11 g (89%) of IIc as red air-stable crystals, mp 72–73 °C. IR (CH_2Cl_2): ν(CO) 1998 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.78 (s, 5 H, Cp), 3.20 (m, 4 H, SCH_2), 2.50 (m, 2 H, CH_2), 2.31 (s, 3 H, CH_3CN). ^{13}C NMR (CD_2Cl_2, $Cr(acac)_3$): δ 300.56 (carbene C), 215.27 (CO), 134.23 ($NCCH_3$), 84.66 (Cp), 37.85 (SCH_2), 19.22 (CH_2), 4.66 ($NCCH_3$). Anal. Calcd for $C_{12}H_{14}ONF_6PS_2Fe$: C, 31.80; H, 3.11. Found: C, 31.78; H, 3.00.

Preparation of $Cp(CO)_2Ru[C(S)SCH_3]$ (Id).[12] The anion $Cp(CO)_2Ru^-$ was prepared as the sodium salt by stirring 0.80 g (1.8 mmol) of $Cp_2Ru_2(CO)_4$ in 25 mL of THF over a sodium amalgam (0.6 g Na, 15 mL Hg) for 2.5 h. The amalgam was drained from the bottom of the flask, and to the remaining muddy green solution was added 0.22 mL (0.28 g, 3.6 mmol) of CS_2. After 2 min of vigorous stirring, the solution adopted a tan color. To this solution was immediately added 0.22 mL (0.52 g, 3.6 mmol) of CH_3I. The solution was then stirred an additional 30 min, during which time the color became dark brown. At this point it became possible to handle the solution in air, and the solvent was removed by rotoevaporation. The resulting residue was extracted with three 30-mL portions of Et_2O. The combined extracts were filtered through Celite with use of a medium-porosity glass frit. The yield of the oily $Cp(CO)_2Ru[C(S)SCH_3]$ (Id) after evaporation of the solvent was 83% (0.94 g, 3.0 mmol). IR (cyclohexane): ν(CO) 2040 (s), 1990 cm^{-1} (s). IR (CH_2Cl_2): ν(CO) 2041 (s), 1988 cm^{-1} (s). ^1H NMR (CD_2Cl_2): δ 5.31 (s, 5 H, C_5H_5), 2.50 (s, 3 H, SCH_3). ^{13}C NMR (CD_2Cl_2): δ 268.8 (thioester C), 198.8 (CO), 90.6 (C_5H_5), 25.0 (CH_3).

Preparation of $[Cp(CO)_2Ru[C(SCH_3)_2]]PF_6$ (Ie). Into a rapidly stirring 50-mL CH_2Cl_2 solution containing 0.94 g (3.0 mmol) of Id, 0.24 mL (0.34 g, 3.0 mmol) of CH_3SO_3F was added dropwise and slowly via syringe. An IR spectrum of the reaction mixture after 1 h showed Id to be completely gone, and two new bands were present at 2022 (s) and 2060 (s) cm^{-1}. No visible color change had occurred. The solvent was removed in vacuo, leaving a solid brown residue. This was extracted with two 20-mL portions of Et_2O to remove traces of Id or $Cp_2Ru_2(CO)_4$ leaving behind $[Cp(CO)_2Ru[C(SCH_3)_2]]SO_3F$. The SO_3F^- anion was exchanged for PF_6^- by stirring the residue in acetone (30 mL) with 3 equiv (1.7 g, 9.0 mmol) of KPF_6 for 30 min. The solution was evacuated to dryness and the product, $[Cp(CO)_2Ru[C(SCH_3)_2]]PF_6$ (Ie), was extracted into 10 mL of CH_2Cl_2; this solution was filtered through Celite. When the CH_2Cl_2 was removed in vacuo, 0.74 g (52%, 1.6 mmol) of Ie was obtained as a brown solid. Attempts to recrystallize Ie or the SO_3F^- salt from CH_2Cl_2/Et_2O or acetone/Et_2O solutions yielded only brown air-stable oils. IR (CH_2Cl_2): ν(CO) 2066 (s), 2022 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.64 (s, 5 H, C_5H_5), 3.08 (s, 6 H, SCH_3). ^{13}C NMR (CD_2Cl_2): δ 285.3 (carbene C), 194.5 (CO), 89.7 (C_5H_5), 30.5 (SCH_3).

Preparation of $[Cp(CO)(NCCH_3)Ru[C(SCH_3)_2]]PF_6$ (IId). The preparation of this compound was similar to that used for IIa. Irradiation of a 35-mL CH_3CN solution of Ie (0.10 g, 0.21 mmol) for 2 h gave an 80% (0.080 g, 0.18 mmol) yield of IId as a red air-stable oil. IR (THF): ν(CO) 1981 (s) cm^{-1}. IR (CH_3CN): 1991 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.19 (s, 5 H, C_5H_5), 3.02 (s, 6 H SCH_3), 2.42 (s, 3 H, CH_3CN). ^{13}C NMR (CD_2Cl_2): δ 297.9 (carbene C), 199.4 (CO), 129.8 (CH_3CN), 85.3 (C_5H_5), 28.7 (SCH_3), 4.22 (CH_3CN).

Preparation of $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}\overline{CSCH_2CH_2S}]Co(CO)_2$ (VII). The procedure used here is similar to that used for III.[6c] A solution of $Na[Co(CO)_4]$ was prepared by combining $Co_2(CO)_8$ (0.059 g, 0.17 mmol) with NaOH (0.060 g, 1.5 mmol) in 10 mL of THF. This was filtered into a flask containing 0.145 g (0.33 mmol) of IIb in 10 mL of THF. After 30 min of stirring, the reaction was complete, and the solvent was removed under reduced pressure. The brown-black residue was extracted into 15 mL of Et_2O and filtered through Celite. The filtrate was evaporated to dryness, redissolved in 1 mL of CH_2Cl_2, and chromatographed on silica gel, eluting with 1:1 CH_2Cl_2/hexane. A single red band moved off the column (2 × 10 cm); this was collected and rotoevaporated to dryness, yielding 0.055 g (61%) of VII as a black solid. The solid was recrystallized from hot hexanes with minimal decomposition, yielding violet needles, mp 72–74 °C. Anal. Calcd for $C_{12}H_9O_4S_2FeCo$: C, 36.39; H, 2.29. Found: C, 36.63; H, 2.43. MS (20 eV): *m/e* 396

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Table I. IR Spectra of the Complexes in Cyclohexane (cm^{-1})[a]

complex	$\nu(\mathrm{CO})^{\mathrm{T}}$	$\nu(\mathrm{CO})^{\mathrm{B}}$	$\nu(\mathrm{NO})$
$\mathrm{Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SCH_3)_2]Co(CO)_2}$ (III)	2036 (m), 1989 (s, br)	1836 (m)	
$\mathrm{Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SCH_3)_2]Fe(CO)(NO)}$ (IV)	2003 (m), 1983 (s)	1830 (m)	1752 (s)
$\mathrm{Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}\overline{CSCH_2CH_2S}]Fe(CO)(NO)}$ (V)	2002 (m), 1985 (s)	1832 (m)	1739 (s)
$\mathrm{Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}\overline{CSCH_2CH_2CH_2S}]Fe(CO)(NO)}$ (VI)	2005 (m), 1981 (s)	1827 (m)	1739 (s)
$\mathrm{Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}\overline{CSCH_2CH_2S}]Co(CO)_2}$ (VII)	2032 (m), 1985 (s), 1973 (sh)	1831 (m)	
$\mathrm{Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}\overline{CSCH_2CH_2CH_2S}]Co(CO)_2}$ (VIII)	2032 (m), 1982 (s), 1971 (m)	1830 (m)	
$\mathrm{Cp(CO)Ru(\mu\text{-}CO)[\mu\text{-}C(SCH_3)_2]Co(CO)_2}$ (IX)	2040 (m), 1987 (s), 1983 (sh)	1841 (m)	
$\mathrm{Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SCH_3)_2]Co(CO)PEt_3}$ (X)	1978 (s), 1953 (m)	1794 (m)	
$\mathrm{Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}\overline{CSCH_2CH_2S}]Co(CO)PEt_3}$ (XI)	1976 (s), 1934 (m)	1791 (m)	
$\mathrm{Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SCH_3)_2]Fe(NO)PEt_3}$ (XII)	1970 (s)	1779 (s)	1706 (s)

[a] The superscripts T and B refer to terminal and bridging carbonyl ligands respectively.

Table II. $^{13}\mathrm{C}$ NMR Spectra of the μ-Dithiomethylene Complexes in $\mathrm{CD_2Cl_2}$ (ppm)[a]

complex	μ-CO	Fe(CO)[b]	μ-methylene carbon	Cp	other resonances
III	249.59	212.50	176.44	83.27	208.77, 201.06 ($\mathrm{Co(CO)_2}$); 30.01, 24.85 $\mathrm{(SCH_3)_2}$
IV	260.34	212.31	188.77	84.52	222.31 (Fe(CO)); 29.71, 27.54 $\mathrm{(SCH_3)_2}$
V	260.08	213.02	197.33	85.00	222.46 (Fe(CO)); 43.57, ($\mathrm{SCH_2}$); 38.99 ($\mathrm{SCH_2}$)
VI	260.08	212.84	181.90	84.66	222.20 (Fe(CO)); 40.71, 33.78 $\mathrm{(SCH_2)_2}$; 19.22 ($\mathrm{CH_2}$)
VII	249.85	213.80	185.90	84.14	208.64, 201.75 ($\mathrm{Co(CO)_2}$); 42.45, 39.50 $\mathrm{(SCH_2)_2}$
VIII	249.85	213.54	168.38	84.05	209.22, 201.50 ($\mathrm{Co(CO)_2}$); 43.23, 33.95 $\mathrm{(SCH_2)_2}$; 19.39 ($\mathrm{CH_2}$)
IX	236.23		161.71	86.18	208.36, 201.64, ($\mathrm{Co(CO)_2}$); 199.70 (Ru(CO)); 30.65, 24.24 $\mathrm{(SCH_3)_2}$
X	253.41 (d)[c]	214.67	169.73 (d)[d]	82.23	206.22 (d, Co(CO));[e] 30.49, 24.42 $\mathrm{(SCH_3)_2}$; 17.53 (d, $\mathrm{P\mathit{C}H_2CH_3}$);[f] 6.91 (s, $\mathrm{PCH_2\mathit{C}H_3}$)
XI	251.67 (br)	215.53	180.09 (d)[g]	82.84	206.60 (br, Co(CO)); 41.49, 39.24 $\mathrm{(SCH_2)_2}$; 17.70 (d, $\mathrm{P\mathit{C}H_2CH_3}$);[h] 7.08 (s, $\mathrm{PCH_2\mathit{C}H_3}$)
XII	263.12 (br)	213.45	179.22 (br)	83.01	29.10, 26.41 $\mathrm{(SCH_3)_2}$; 17.23 (d, $\mathrm{PCH_2}$);[i] 6.82 ($\mathrm{PCH_2\mathit{C}H_3}$)

[a] All resonances are singlets unless otherwise noted. Spectra were recorded at −78 °C in the presence of 0.1 M $\mathrm{Cr(acac)_3}$. [b] Refers to the carbonyl bound to the Fe coordinated to Cp. [c] $^2J_{\mathrm{PC}} = 5.86$ Hz. [d] $^2J_{\mathrm{PC}} = 17.58$ Hz. [e] $^2J_{\mathrm{PC}} = 7.81$ Hz. [f] $^1J_{\mathrm{PC}} = 21.53$ Hz. [g] $^2J_{\mathrm{PC}} = 19.48$ Hz. [h] $^1J_{\mathrm{PC}} = 21.5$ Hz. [i] $^1J_{\mathrm{PC}} = 23.48$ Hz.

($\mathrm{M^+}$). Spectroscopic data for the dinuclear μ-methylene compounds are presented in Tables I–III.

Preparation of $\mathrm{Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}\overline{CSCH_2CH_2CH_2S}]Co(CO)_2}$ (VIII). This compound was prepared in the same manner as VII. Thus, $\mathrm{Co_2(CO)_8}$ (0.023 g, 0.067 mmol) and NaOH (0.23 g, 5.7 mmol) were combined in 10 mL of THF to form $\mathrm{Na[Co(CO)_4]}$. When this suspension was filtered into a 10-mL THF solution of IIc (0.060 g, 0.13 mmol), reaction occurred, forming 0.039 g (72%) of VIII. After recrystallization from hot hexanes, violet needles were obtained. Anal. Calcd for $\mathrm{C_{13}H_{11}O_4S_2FeCo}$: C, 38.07; H, 2.70. Found: C, 37.72; H, 3.00. MS (20 eV): *m/e* 410 ($\mathrm{M^+}$).

Preparation of $\mathrm{Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SCH_3)_2]Fe(CO)(NO)}$ (IV). To a 25-mL THF solution of IIa (0.206 g, 0.47 mmol) was added 0.33 g (0.47 mmol) of $\mathrm{PPN[(CO)_3Fe(NO)]}$ against a countercurrent of $\mathrm{N_2}$. The solution very slowly turned brown over the course of 12 h. At this point the solvent was removed in vacuo. The resulting brown residue was extracted into 20 mL of $\mathrm{Et_2O}$, and the solution was filtered through Celite. Removal of the solvent in vacuo gave a black solid, which was chromatographed on silica gel (2 × 8 cm), eluting with 1:1 $\mathrm{CH_2Cl_2}$/hexane. A single red band moved off the column. Upon rotoevaporation of the solvent from the red fraction, 0.13 g (69%) of IV resulted. Violet crystals could be obtained by dissolving the solid residue in a minimum of boiling pentane and slowly cooling to −20 °C. Although stable in air for several hours, samples of IV decomposed over the course of several weeks even under an atmosphere of $\mathrm{N_2}$; mp 89–91 °C dec.

Preparation of $\mathrm{Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}\overline{CSCH_2CH_2S})Fe(CO)(NO)}$ (V). Compound V was prepared and isolated in a fashion analogous to that of IV. When 0.334 g (0.47 mmol) of $\mathrm{[Fe(CO)_3NO]PPN}$ was added to a 20-mL THF solution of IIb (0.206 g, 0.47 mmol), 0.140 g (75%) of violet crystalline V was obtained after 12 h of stirring. Like IV, compound V was observed to decompose over a period of weeks. MS (20 eV): *m/e* 395 ($\mathrm{M^+}$).

Preparation of $\mathrm{Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}\overline{CSCH_2CH_2CH_2S})Fe(CO)(NO)}$ (VI). This compound was prepared in the same manner as IV. The addition of $\mathrm{[Fe(CO)_3NO]PPN}$ (0.21 g, 0.30 mmol) to 15 mL of THF containing 0.14 g (0.30 mmol) of IIc followed by 12 h of stirring led to the formation of 0.050 g (38%) of VI. This compound slowly decomposed over a period of 2–3 weeks. Anal. Calcd for $\mathrm{C_{12}H_{11}O_4NS_2Fe_2}$: C, 35.24; H, 2.71. Found: C, 35.43; H, 2.66.

Preparation of $\mathrm{Cp(CO)Ru(\mu\text{-}CO)[\mu\text{-}C(SCH_3)_2]Co(CO)_2}$ (IX). Into a solution containing 0.150 g (0.31 mmol) of IId in 20 mL of THF was filtered a solution of $\mathrm{Na[Co(CO)_4]}$ prepared by combining 0.048 g (0.14 mmol) of $\mathrm{Co_2(CO)_8}$ and 0.12 g (3.0 mmol) of NaOH in 20 mL of THF as previously described. Upon mixing, the color slowly turned dark brown over the course of 4 h. The solvent was removed in vacuo, and the solid brown-black residue was extracted with 3 × 30 mL of hot hexane. The extracts were combined and reduced in volume to ~3 mL and then chromatographed on silica gel, eluting with 2:3 $\mathrm{CH_2Cl_2}$/hexane. A single reddish band was collected and rotoevaporated to dryness. The residue was dissolved in a minimum volume of hot hexane and slowly cooled to −20 °C. After 24 h, 0.14 g (62%) of small red crystals of IX resulted; mp 110–112 °C. Anal. Calcd for $\mathrm{C_{12}H_{11}O_4S_2RuCo}$: C, 32.51; H, 2.50. Found: C, 32.19; H, 2.52. MS (20 eV): *m/e* 443.9 ($\mathrm{M^+}$).

Table III. $^1\mathrm{H}$ NMR Spectra of the Complexes in $\mathrm{CD_2Cl_2}$ (δ)[a]

complex	$\mathrm{C_5H_5}$	other resonances
III	4.70	2.70 (3 H, $\mathrm{SCH_3}$), 2.23 (3 H, $\mathrm{SCH_3}$)
IV	4.57	2.79 (3 H, $\mathrm{SCH_3}$), 2.55 (3 H, $\mathrm{SCH_3}$)
V[b]	4.55	3.40 (m, 3 H, $\mathrm{(SCH_2)_2}$)
VI	4.55	3.17–2.92 (br (m), $\mathrm{(SCH_2)_2}$), 2.41 (m, $\mathrm{CH_2}$)[c]
VII[b]	4.69	3.59–2.89 (br (m), 4 H, $\mathrm{(SCH_2)_2}$)
VIII	4.69	2.96 (m, 4 H, $\mathrm{(SCH_2)_2}$), 2.31 (m, 2 H, $\mathrm{CH_2}$)
IX	5.16	2.57 (3 H, $\mathrm{SCH_3}$), 2.19 (3 H, $\mathrm{SCH_3}$)
X	4.58	2.76 (3 H, $\mathrm{SCH_3}$), 2.12 (3 H, $\mathrm{SCH_3}$), 1.7 (m, 6 H, $\mathrm{PCH_2}$), 1.1 (m, 9 H, $\mathrm{CH_3}$)[d]
XI	4.66	3.67–2.78 (m, 4 H, $\mathrm{SCH_2}$), 1.80 (q, 6 H, $\mathrm{PCH_2}$), 1.09 (p, 9 H, $\mathrm{CH_3}$)
XII	4.53	2.92 (3 H, $\mathrm{SCH_3}$), 2.46 (3 H, $\mathrm{SCH_3}$), 1.90 (br (m), 6 H, $\mathrm{PCH_2}$), 1.14 (m, 9 H, $\mathrm{CH_3}$)

[a] All resonances are singlets unless otherwise indicated. [b] Recorded in $\mathrm{CDCl_3}$. [c] Poor separation of peaks makes meaningful integration impossible. [d] $^3J_{\mathrm{PH}} = 13.7$ Hz; $^2J_{\mathrm{PH}} = 0.5$ Hz.

Preparation of $\mathrm{Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}\overline{CSCH_2CH_2S}]Co(CO)(PEt_3)}$ (XI). When 52 μL (0.35 mmol) of $\mathrm{PEt_3}$ was added to a $\mathrm{CH_2Cl_2}$ (20 mL) solution of VII (0.140 g, 0.35 mmol), a gradual color change from brown to amber occurred over a period of 2.5 h. The solvent was removed at reduced pressure, leaving a darkly colored solid, which was redissolved in ~1 mL of $\mathrm{CH_2Cl_2}$ and eluted through a silica gel column (2 × 15 cm) with 2:1 $\mathrm{CH_2Cl_2}$/hexane. A single amber-colored band containing XI moved off the column. This was collected and rotoevaporated to dryness. The resulting brown solid was dissolved in a minimum volume of hot

Table IV. Results of the Oxidation of μ-Dithioalkoxymethylene Complexes with 2 Equiv of $[Cp_2Fe]FeCl_4$

compd	product	% yield[a]
III	$Cp(CO)_2Fe[C(SMe)_2]^+$	75
IV	$Cp(CO)_2Fe[C(SMe)_2]^+$	73
V	$Cp(CO)_2Fe[CSCH_2CH_2S]^+$	75
VI	$Cp(CO)_2Fe[CSCH_2CH_2CH_2S]^+$	99
VII	$Cp(CO)_2Fe[CSCH_2CH_2S]^+$	87
VIII	$Cp(CO)_2Fe[CSCH_2CH_2CH_2S]^+$	93
IX	$Cp(CO)_2Ru[C(SMe)_2]^+$	80
X	$Cp(CO)_2Fe[C(SMe)_2]^+$	72
XI	$Cp(CO)_2Fe[CSCH_2CH_2S]^+$	53[b]
XII	$Cp(CO)_2Fe[C(SCH_3)_2]^+$	79

[a] Yields are determined as described in the Experimental Section. [b] The low yield in this case may be due in part to a side reaction between liberated PEt_3 and $Cp(CO)_2Fe[CSCH_2CH_2S]^+$.

heptane and slowly cooled to −20 °C. After a period of 2 days, 0.050 g (56%) of crystalline XI was obtained. Some decomposition occurred during the recrystallization process. Anal. Calcd for $C_{17}H_{24}O_3PS_2FeCo$: C, 41.99; H, 4.97. Found: C, 41.86; H, 5.22. MS (20 eV): *m/e* 486 (M^+).

Preparation of $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SCH_3)_2]Co(CO)(PEt_3)$ (X). This compound was prepared in the same fashion as XI. Thus, the addition of PEt_3 (20 μL, 0.14 mmol) to a 30-mL CH_2Cl_2 solution of III (0.052 g, 0.14 mmol) led, following recrystallization from hexane, to a 79% yield (0.052 g) of X, mp 79–80 °C. Anal. Calcd for $C_{17}H_{26}O_3S_2PFeCo$: C, 41.82; H, 5.37. Found: C, 41.57; H, 5.33. MS (20 eV): *m/e* 460 ($M^+ - CO$).

Preparation of $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SCH_3)_2]Fe(NO)(PEt_3)$ (XII). The preparation of XII was carried out in the same manner as the preparation of X. From a 12-h reaction of PEt_3 (39 μL, 0.26 mmol) with a 20-mL CH_2Cl_2 solution of IV (0.11 g, 0.26 mmol), 0.120 g (93%) of XII was isolated. Recrystallization led to small, dark brown-black cubic crystals; mp 102–104 °C. Anal. Calcd for $C_{16}H_{26}O_3NPS_2Fe_2$: C, 39.45; H, 5.38. Found: C, 39.34; H, 5.36. MS (20 eV): *m/e* 487 (M^+).

Reaction of III with I_2. When 1 equiv of I_2 (0.038 g, 0.15 mmol) was added to a 20-mL CH_2Cl_2 solution of III (0.060 g, 0.15 mmol), a rapid reaction occurred yielding a faint yellow-green solution. The IR spectrum showed that within 10 min the ν(CO) bands due to III had completely disappeared and new bands identical with those of Ia were present at 2058 (s) and 2017 (s) cm^{-1}. The solution was filtered through Celite, reduced in volume to 3 mL, layered with Et_2O, and slowly cooled to −20 °C. Gold yellow crystals, which had an ^1H NMR spectrum identical with that reported for Ia, precipitated. The yield of $Cp(CO)_2Fe[C(SCH_3)_2]^+$ was determined to be 75% by measuring the intensity of the 2058-cm^{-1} ν(CO) absorption of the reaction solution and comparing it with intensities of standard solutions of Ia.

Reactions of III, IV, X, and XII with $[Cp_2Fe]FeCl_4$. These oxidation reactions were performed by adding 2 equiv of $[Cp_2Fe]FeCl_4$ (0.052 g, 0.13 mmol) to 0.067 mmol of III, IV, X, or XII in 15 mL of CH_2Cl_2. After being stirred for 15 min, the solutions had IR spectra that showed $Cp(CO)_2Fe[C(SMe)_2]^+$ to be the only CO-containing species present. The solvent was removed under reduced pressure, and the residue was dissolved in 10.0 mL of CH_2Cl_2. As above, the yield of $Cp(CO)_2Fe[C(SMe)_2]^+$ was determined from the absorbance of the 2058-cm^{-1} band by comparison with the absorbances of standard solutions of Ia. The yields of these reactions are given in Table IV and are discussed later.

Reactions of V–VIII and XI with $[Cp_2Fe]FeCl_4$. For the same quantities of reactants and conditions as above, the yields of $Cp(CO)_2Fe[CSCH_2CH_2S]^+$ and $Cp(CO)_2Fe[CSCH_2CH_2CH_2S]^+$ from these reactions were determined by using the intensities of the ν(CO) bands of the carbene complexes, which were the only CO-containing products.

Reaction of IX with $[Cp_2Fe]FeCl_4$. As for the above reactions, $[Cp_2Fe]FeCl_4$ reacted rapidly with IX to give $Cp(CO)_2Ru[C(SMe)_2]^+$, which was identified by its IR and ^1H NMR spectra, as the only CO-containing complex. The yield (80%) of this product was established from the intensities of its ν(CO) bands.

Results and Discussion

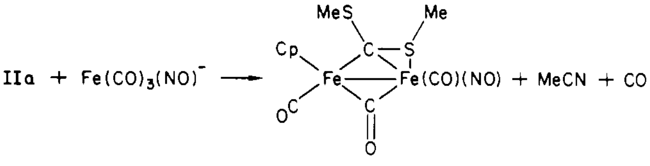
Preparation of $C(SR)_2$-Bridged Dinuclear Complexes. These complexes were prepared by reacting NCMe-substituted $C(SR)_2$ carbene complexes with $Co(CO)_4^-$ or $Fe(CO)_3NO^-$. The NCMe precursors necessary for these preparations were synthesized according to eq 2.

$$\underset{\text{Ia–c,e}}{CpM(CO)_2{=}C(SR)_2^+} + NCMe \xrightarrow{h\nu} CpM(CO)(NCMe){=}C(SR)_2^+ + CO \tag{2}$$

$$\begin{aligned}&\text{IIa: } M = Fe; {=}C(SR)_2 = {=}C(SMe)_2\\&\text{IIb: } M = Fe; {=}C(SR)_2 = {=}CSCH_2CH_2S\\&\text{IIc: } M = Fe; {=}C(SR)_2 = {=}CSCH_2CH_2CH_2S\\&\text{IId: } M = Ru; {=}C(SR)_2 = {=}C(SMe)_2\end{aligned}$$

Complex IIa was reported previously;[10] IIb and IIc were isolated in 63% and 89% yields, respectively. Compound IId was obtained only as an oil and was characterized spectroscopically.

The preparations of the $C(SR)_2$-bridged complexes were similar to that used for III (eq 1). The ease with which $Co(CO)_4^-$ reacted with IIa (eq 1) suggested the isoelectronic $Fe(CO)_3(NO)^-$ would also react. Indeed, when IIa reacts with $PPN[Fe(CO)_3NO]$ in THF at room temperature, the dinuclear dithiomethylene compound IV is obtained in 69% yield (eq 3). The IR spectrum of IV (Table I) shows a single strong band in the bridging ν(CO) region at 1830 cm^{-1}, as well as bands at 2003 and 1983 cm^{-1}, which correspond to the two terminal carbonyl ligands. The terminal NO group gives rise to a strong band at 1752 cm^{-1}. The μ-dithiomethylene carbon atom appears as a sharp singlet at 188.7 ppm in the ^{13}C NMR spectrum (Table II). The low-field region also shows a resonance at 212.3 ppm, which is in the region normally assigned to CpFe(CO) carbonyl carbons,[13] in addition to a resonance at 222.3 ppm, which is assigned to the CO ligand on the NO-bearing Fe atom. The CH_3 region of the ^1H NMR spectrum of IV (Table III) shows two peaks, as was the case for III, one shifted to slightly higher field (2.79 and 2.55 ppm). This is consistent with a structure for IV (eq 3) in which the SCH_3 groups are the inequivalent because one of the S atoms is bound to the Fe. The resonance at higher field is assigned to the S-coordinated SMe group based on observations by King and Bisnette[14] who found that the Me in the S-coordinated $MeSCH_2Mo(CO)_2Cp$ was slightly upfield (δ 1.88) as compared with the Me (δ 2.18) in $MeSCH_2Mo(CO)_3Cp$ in which the S is not coordinated to the Mo. The highest peak in the mass spectrum of IV occurs at *m/e* 397, which corresponds to the parent ion. In addition, peaks appear with masses that correspond to fragments in which one to three CO groups and an NO group have been lost from the parent. All of the spectroscopic data are in accord with a structure for IV (eq 3) in which the C atom of the $C(SMe)_2$ ligand is coordinated to both Fe atoms and the S coordinates to the NO-containing Fe atom; thus, the bridging dithiomethylene ligand bonds in the same unusual fashion found in III.



IV

(3)

It was thought that the constraint of a cyclic carbene might make sulfur coordination to the iron atom in dinuclear compounds less favorable. Such cyclic dithiomethylene-bridged derivatives were prepared by reaction of the 5- and 6-membered dithiocarbene complexes $Cp(CO)(NCMe)Fe[CSCH_2CH_2S]^+$ (IIb) and $Cp(CO)(NCMe)Fe[CSCH_2CH_2CH_2S]^+$ (IIc) with $Fe(CO)_3(NO)^-$ in a very similar manner to that in eq 3. The products, V and VI, of these reactions obtained in 69 and 75% yield, respectively, have spectral features (Tables I–III) which indicate

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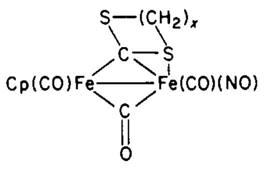


V: $x = 2$
VI: $x = 3$

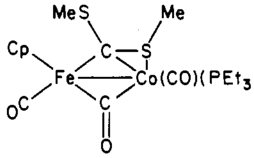
that they both have the unusual dithiomethylene-bridged structure of III and IV. The μ-carbon atom resonances of the dithiomethylene ligands appear at 197.3 ppm and 181.9 ppm, respectively. In the mass spectrum of V and VI, the highest peak (*m/e*) corresponds to the parent ion for the sulfur-coordinated structure. Peaks corresponding to fragments formed from the loss of one to three CO groups and the NO ligand are also apparent. Coordination of the sulfur to the iron atom bearing the nitrosyl ligand is supported by the observation of only a single CO carbon resonance in the Fe(NO)(CO) region of the ^{13}C NMR (222.5 and 222.2 ppm for V and VI, respectively), and the observation of a CO resonance in the CpFe(CO) region (V, 213.0 ppm; VI, 212.8 ppm). If the sulfur were not coordinated to the iron bearing the nitrosyl ligand, an additional CO carbon resonance would be expected in the region of 222 ppm; this is based on the fact that two CO resonances are observed for the $Co(CO)_2$ fragment in III. The protons in the cyclic μ-dithiomethylene ligands appear as unresolved multiplets in the ^{1}H NMR spectra of V and VI. This results because of coupling between all of these magnetically nonequivalent protons. The methylene carbons in the rings all appear as well-resolved singlets in the ^{13}C NMR spectrum (Table II).

Both IIb and IIc also react with $Na[Co(CO)_4]$ in THF at room temperature to form the corresponding dithiomethylene-bridged compounds VII and VIII. Again, the spectroscopic data indicate coordination of one of the sulfur atoms of the cyclic μ-dithiomethylene ligand to cobalt, as in III (eq 1). Both VII and VIII display ν(CO) spectra nearly identical with that of III (Table I). The shoulder observed at 1973 cm^{-1} in VII and 1971 cm^{-1} in VIII is not resolved in III, where only a single broad band is found. For both VII and VIII, the ^{13}C chemical shifts of the two CO groups bound to cobalt are very distinct from the one bound to iron (Table II), as was observed for III. The mass spectra of VII and VIII, like that for III, show the parent ion plus fragments corresponding to the loss of one to four carbonyl ligands.

The ruthenium analogue, IX, of III was prepared in 62% yield by the reaction of $Cp(CO)(NCCH_3)Ru[C(SCH_3)_2]PF_6$ (IId) with $Na[Co(CO)_4]$ in THF at room temperature. The spectral properties of $Cp(CO)Ru(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Co(CO)_2$ (IX) indicate a structure similar to that of III (eq 1). In the ^{13}C NMR spectrum of IX, the chemical shift of the μ-CO and μ-dithiomethylene carbon atoms appear at 13.4 and 14.3 ppm higher field (236.2 and 161.7 ppm, respectively) than those in the analogous Fe compound, III. This shift to higher field is expected when the first-row Fe atom is replaced by its heavier congener ruthenium. This has been observed in other μ-methylene complexes as well.[15] The ^{1}H NMR spectrum of IX exhibits a resonance at 5.16 ppm, corresponding to the protons of the Cp ligand, whereas in the iron analogues III–VIII, the Cp resonances fall in the range 4.55–4.70 ppm. The thiomethoxymethyls in IX appear at 2.57 and 2.19 ppm, at slightly higher field than in III. The highest peak (*m/e*) observed in the mass spectrum of IX corresponds to the parent ion; in addition, peaks corresponding to fragments formed from the loss of one to four carbonyl ligands are apparent. The loss of an intact μ-dithiomethylene ligand has not been observed in the mass spectrum of any of the complexes reported herein. Compound IId proved to be unreactive toward $PPN[Fe(CO)_3NO]$ in THF at room temperature.

Attempts were made to prepare μ-dithiomethylene compounds from the reactions of IIa with anions $CpFe(CO)_2^-$, $CpRu(CO)_2^-$, $CpMo(CO)_3^-$, $Mn(CO)_5^-$, and $Mn(CO)_2(NO)_2^-$. None of these reactions gave the desired product. The first four metal carbonyl anions gave variable yields of their dimers resulting from oxidation of the anions. The reaction with $Mn(CO)_2(NO)_2^-$ gave a low yield of Roussin's red methyl ester $(NO)_2Fe(\mu\text{-}SMe)_2Fe(NO)_2$.[16]

Reactions of III, IV, and VII with PEt_3. Although apparently not a general reaction,[17] displacement of the coordinated sulfur in a metallothiocyclopropane ring has been observed. Miki et al.[18] reported that in the presence of excess PPh_3 the sulfur atom bound to Pd in $MeSCH_2Pd(PPh_3)Cl$ is displaced, in an equilibrium fashion, to give the C-only-bonded ligand in $MeSCH_2Pd(PPh_3)_2Cl$. This reaction suggested that the S donor group in our μ-dithiomethylene-bridged complexes might be displaced to give methylene-bridged products in which the $C(SR)_2$ bridge was bonded to the metals only through the C atom. However, when 1 equiv of PEt_3 reacts with III, only simple displacement of a CO ligand from the Co is observed; the S of the bridging $C(SMe)_2$ group remains bonded to the Co to give X; the product is obtained in 79% yield. The IR spectrum in the ν(CO) region of X consists of two terminal bands (1978 (s), 1953 (m) cm^{-1}) and one bridging (1794 (m) cm^{-1}), all shifted to lower energy from what was observed in III. This is consistent with the replacement of a good π-acceptor CO ligand with PEt_3 having a lower π-acceptor/σ-donor ratio. No splitting of the Cp ligand by the P atom is observed in either the ^{1}H or ^{13}C NMR spectrum. Only one resonance is present in the cobalt carbonyl region of the ^{13}C NMR spectrum, a doublet, centered at 206.20 ppm (J_{PC} = 7.81 Hz). The CpFe(CO) region of the ^{13}C spectrum displays a single resonance at 214.67 ppm. The resonances corresponding to the μ-carbon atoms of the dithiomethylene and CO ligands are split into doublets by coupling to phosphorus: 169.73 ppm (J_{PC} = 17.58 Hz) and 253.13 ppm (J_{PC} = 5.86 Hz), respectively. The highest mass observed in the mass spectrum occurs at *m/e* 487, which corresponds to the molecular ion for $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SCH_3)_2]Co(CO)PEt_3$ (X). All these data are consistent with the replacement of a single CO ligand on cobalt by PEt_3. Reaction of III with a 10-fold excess of PEt_3 at room temperature does not lead to further substitution. The weaker nucleophile PPh_3 does not react with III under similar conditions.



X

The five-membered ring μ-dithiomethylene compound VII also reacts with PEt_3 via simple CO substitution to give $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}CSCH_2CH_2S]Co(CO)(PEt_3)$ (XI). Compound IV also reacts with PEt_3 with loss of the single terminal CO ligand on the iron bearing the coordinated sulfur atom, yielding $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SCH_3)_2]Fe(NO)(PEt_3)$ (XII). Thus the metallothiocyclopropane ring in these compounds appears quite robust, with loss of CO favored over opening of the 3-membered ring by S ligand displacement.

Upon substitution of a CO ligand by PEt_3 in compounds III, IV, and VII one observes a shift of the CO carbon resonances to lower field for the remaining terminal and bridging CO ligands. For example, the terminal CO on iron in III resonates at 212.50 ppm in the ^{13}C NMR spectrum. When one of the carbonyl ligands on cobalt is replaced with PEt_3, giving X, the terminal CO on iron is shifted to 214.67 ppm. This type of shift has been observed before, and, in general, CO carbon resonances shift to lower field

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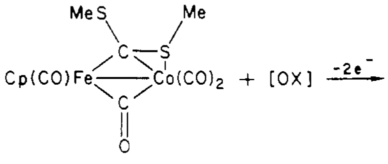
as π-back-bonding to them is increased. This chemical shift trend has also been reported for ^{13}C resonances of terminal carbene carbon atoms.[10] In contrast, the μ-dithiomethylene carbon resonances in X–XII all appear at higher field (5–10 ppm) than in the non-phosphine-substituted analogues. Knox et al.[20] have reported that upon substitution of a CO ligand in $Cp(CO)Ru(\mu\text{-}CO)[\mu\text{-}C(CH_3)_2]Ru(CO)Cp$ by PMe_2Ph to form $Cp(CO)Ru(\mu\text{-}CO)[\mu\text{-}C(CH_3)_2]Ru(PMe_2Ph)Cp$, the μ-propylidene carbon shifts from 175.8 to 167.5 ppm. This is in accord with our observations. The reason for this change in the direction of the chemical shift in μ-methylene compounds is not currently understood.

Reactions of III–XII with Oxidizing Agents. The dinuclear complex III reacts (eq 4) with 2 equiv of the oxidizing agents I_2, Br_2, $Ph_3C^+PF_6^-$, $Cp_2Fe^+FeCl_4^-$, and $C_7H_7^+BF_4^-$, in CH_2Cl_2 at room temperature under N_2 to give $CpFe(CO)_2[C(SCH_3)_2]^+$ (Ia) as the only CO-containing product. In general, no cobalt product could be isolated. However, when the reaction of III with I_2 was carried out in the presence of 2 equiv of PPh_3, the Co fragment was isolated (41%) as $ICo(CO)_2(PPh_3)_2$ and identified[19] by its IR spectrum.



III

$$Cp(CO)_2Fe{=}C(SMe)_2^+ \; + \; \text{"}Co(CO)_2^+\text{"} \qquad (4)$$

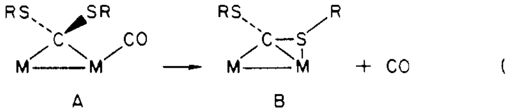
Ia

Yields of Ia were determined for a series of reactions of III with 2 equiv of several oxidizing agents at room temperature. With I_2 (2 equiv) a 91% yield of Ia was obtained after 10 min. With Br_2, a 90% yield formed within 5 min. A 95% yield of Ia was obtained after 24 h with $C_7H_7^+BF_4^-$. After only 1 min, 2 equiv of $Cp_2Fe^+FeCl_4^-$ gave a 75% yield of Ia, whereas 1 equiv gave a 46% yield. Twenty-minute reactions of III with increasing numbers of equivalents of $Ph_3C^+PF_6^-$ gave the following yields of Ia: 23% (0.5 equiv), 77% (1.5% equiv), 90% (2.0 equiv). Thus, 2 equiv of the oxidizing agent are required for reaction 4. No species other than III and Ia were observed in the $\nu(CO)$ region of the IR spectrum even when fewer than 2 equiv were used.

The two-electron oxidation of the μ-dithiomethylene compounds is a general reaction as demonstrated by the oxidation of the other binuclear complexes IV–XII with 2 equiv of $Cp_2Fe^+FeCl_4^-$ to give the cationic mononuclear terminal dithiocarbene compounds (Table IV). The yields of the terminal carbene products are generally high (>70%) and do not vary greatly with the nature of the carbene ligand or the metal (Fe, Ru, or Co).

Although it is not entirely clear how the two-electron oxidation of the bridging complexes leads to the terminal carbene products, Geiger has recently reported[3b] that a one-electron electrochemical oxidation of the μ-methylene complex $[CpMn(CO)_2]_2CH_2$ gives a radical cation in which the Mn–Mn bond is not retained. Since the HOMO in III is metal–metal bonding,[6c] perhaps the two-electron oxidation of the μ-dithiomethylene complexes proceeds similarly; initial oxidation weakens the metal–metal bond, which allows separation of the stable, cationic, mononuclear, and terminal carbene product.

Why the Unusual Bridging $C(SR)_2$ Ligand? Rather than form a dinuclear complex with a simple bridging carbene ligand (structure A in eq 5), the $C(SR)_2$ group in all of the complexes described in this paper bridges the two metals via the carbene C atom, and also one of the sulfur atoms coordinates to a metal (structure B in eq 5). Although this unusual carbene bridge (B) may arise because of a specific mechanism of formation, its remarkable stability suggests that it is thermodynamically more stable than form A. The relative instability of form A may be rationalized by considering MO calculations for the bridging carbene complexes $[CpRh(CO)]_2(\mu\text{-}CH_2)$[6a] and $[CpMn(CO)_2]_2(\mu\text{-}CH_2)$[6b]. In both studies the μ-CH_2 group was found to be a strong σ-donor and an exceptionally good π-acceptor of electron density from the metal. In μ-$C(SR)_2$ complexes with structure A, lone electron pairs on the S atoms would be expected to donate π-electron density (Figure 1) into the p orbital of the carbene carbon, thus reducing π-donation from the metals to the C p orbital and destabilizing the bonding between the metals and the carbene bridge. Apparently this decrease in stability is sufficient to favor structure B, which would be stabilized relative to structure A for the following reasons: (1) sulfur coordination in B reduces π-donation from the sulfur into the carbene C p orbital, which allows greater π-bonding from the metals; (2) the sulfur in structure B is a better electron donor than CO in A, which makes the metal more electron rich in B and therefore a better π-donor to the carbene C p orbital, thus stabilizing the bridging carbene bonding; (3) MO calculations[6c] on compound III indicate that the $C(SR)_2$ group in structure B forms strong σ- and π-bonds with the metal.



(5)

A B

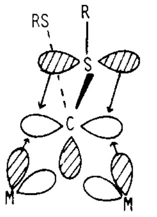


Figure 1. Bonding interactions for bridging dithiocarbene.

It should be noted that the S in complexes III–XII coordinates to the least electron rich metal, the $Co(CO)_2$ or $Fe(CO)(NO)$ group, rather than to the electron-rich $CpFe(CO)$ or $CpRu(CO)$ units. Electron richness on the metal has been observed previously[21] to shorten metal to μ-carbene distances when a strong π-acceptor CO group is replaced by a stronger electron-donating phosphine; the increased electron density provided by the sulfur on the $Co(CO)_2$ or $Fe(CO)(NO)$ group should strengthen bonding to the bridging carbene carbon in complexes III–XII.

One would expect the S lone-pair interaction to destabilize structure A in other μ-$C(SR)_2$ complexes; however, few bridging dithiocarbene complexes are known. In $Fe_3(CO)_9(\mu_3\text{-}\overline{CSCH_2CH_2S})(\mu_3\text{-}S)$[22], the carbon of the $\mu_3\text{-}\overline{CSCH_2CH_2S}$ carbene ligand bridges two Fe atoms, but one of the S atoms is coordinated to the third Fe atom, thus reducing the π-donation from that sulfur. However, the complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]$[23] has structure A, perhaps because the CpFe(CO) units are sufficiently electron rich to stabilize this form. In the related complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)(SPh)]$,[23] the SPh^- group migrates from the carbene C to an Fe to give the μ-carbyne complex $Cp_2Fe_2(CO)(SPh)(\mu\text{-}CO)(\mu\text{-}CSMe)$, perhaps an indication of the instability of form A with the μ-$C(SMe)(SPh)$ group. Similarly, the reaction of $Pt(I)(PPh_3)_2[{=}C(SMe)_2]^+I^-$ with $Pt(\mu\text{-}C_2H_4)(PPh_3)_2$,[24] which might be expected to give a Pt–Pt-bonded complex with a bridging $C(SMe)_2$ carbene, gives instead a binuclear product $(Ph_3P)(I)Pt(\mu\text{-}CSMe)(\mu\text{-}SMe)Pt(PPh_3)I$ in which one of the SMe groups has dissociated from the $C(SMe)_2$

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ligand, thereby generating a product with bridging SMe and carbyne (CSMe) groups.

If S lone-pair donation is important to the destabilization of μ-C(SR)$_2$ complexes, one might also expect O and N π-donation to destabilize complexes with μ-C(OR)$_2$ and μ-C(NR$_2$)$_2$ bridging groups; this appears to be the case. The dinuclear complex with a C(OR)$_2$ ligand, $Cp_2Fe_2(CO)[C(OMe)(O\text{-}c\text{-}Hex)](\mu\text{-}CO)_2$,[5c] has been assigned a structure in which the dioxycarbene ligand is in a terminal rather than a bridging position. Also, the di- and trinuclear complexes with dioxycarbene ligands, $Mn_2(CO)_9[C(OR)_2]$, $Re_2(CO)_9[C(OR)_2]$, $Re_2(CO)_8[C(OR)_2]_2$, $Ru_3(CO)_{10}[C(OR)_2]_2$,[25] and $Os_3(\mu_2\text{-}H)(\mu_3\text{-}CPh)(CO)_9[C(OR)_2]$,[26] have only terminal carbene groups.

The diamino carbene complexes $Cp_2Fe_2(CO)[\overline{CN(R)CH_2CH_2N}(R)](\mu\text{-}CO)_2$, where R = Me or Et,[27] have also been assigned structures in which the carbene ligand is terminal. However, the carbene ligand in the more electron-rich $Cp_2Ni_2(\mu\text{-}CO)[\mu\text{-}\overline{CN(Et)CH_2CH_2N}(Et)]$ complex is bridging.[27] Thus, in dinuclear complexes with diheteroatom carbene ligands C(YR)$_2$, where R = O, S, or NR, the carbene ligand may be simply bridging (A), bridging with a sulfur atom coordinated to a metal (B), or terminal, depending upon the electron richness of the metals and possibly steric factors. The more electron-rich metals seem to favor structure A. The variety of structures observed for these diheteroatom carbene complexes contrasts with the situation for μ-alkylidene complexes (μ-CR$_2$), where R = H or alkyl, which all have structure A.[3]

Registry No. Ia, 69532-11-2; Ib, 76136-38-4; Ic, 76136-40-8; Id, 61930-80-1; Ie, 102746-42-9; IIa, 77781-29-4; IIb, 102746-38-3; IIc, 102746-40-7; IId, 102746-45-2; III, 83043-22-5; IV, 102746-29-2; V, 102746-30-5; VI, 102746-31-6; VII, 102746-32-7; VIII, 102746-32-7; IX, 102746-33-8; X, 102746-34-9; XI, 102746-35-0; XII, 102746-36-1; $[Cp(CO)_2Ru[(C(SCH_3)_2]]SO_3F$, 102746-43-0; $Na[Co(CO)_4]$, 14878-28-5; $Cp_2Ru_2(CO)_4$, 12132-87-5; $PPN[(CO)_3Fe(NO)]$, 61003-17-6; $[Cp_2Fe]FeCl_4$, 1287-09-8; Fe, 7439-89-6; Ru, 7440-18-8; Co, 7440-48-4.

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Bidentate and Unidentate Formato Ligands in $Mo(CO)_2(PEt_3)_2(O_2CH)_2$

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Syntheses and spectroscopic properties of complexes of the type $M(CO)_2L_2(B\text{–}B)Y$ are presented [M = Mo, W; L = PEt$_3$, PPh$_3$; B–B = acetylacetonate (acac), 1,1,1,5,5,5-hexafluoroacetylacetonate (facfac), tropolonate (trop), carboxylate; Y = Cl, Br, O$_2$CR]. These products are derived from $M(CO)_3L_2X_2$ reagents (X = Cl, Br). The X-ray diffraction structure of one member of this series, $Mo(CO)_2(PEt_3)_2(OOCH)_2$ (**2**), is described. The molecule crystallizes in the monoclinic space group $P2_1/n$ with a = 12.691 (8) Å, b = 12.250 (9) Å, c = 13.813 (12) Å, β = 90.85 (6)°, and Z = 4. The structure was solved from 3410 reflections with $I > 3\sigma(I)$, with weighted and unweighted residuals of 5.4 and 4.1%, respectively. The formato ligands engage in different binding modes in the solid state. These ligands exchange unidentate and bidentate coordination modes rapidly in solution with an activation barrier too small to be readily measured by variable-temperature NMR techniques.

Introduction

Heptacoordinate carbonyl complexes of molybdenum(II) and tungsten(II) are numerous[1] in accord with effective atomic number rule expectations. In contrast to extensive studies of $M(CO)_{3-n}L_n(B\text{–}B)_2$[2] ($n$ = 0, 1) or $M(CO)_2L_2(B\text{–}B)X$[3] compounds where B–B is a monoanionic sulfur-based chelate, reports of chelating oxygen donor ligands in carbonyl complexes of Mo(II) and W(II) are less common. Early reports of such complexes include ancillary η^3-allyl ligands as in (π-allyl)$M(CO)_2(B\text{–}B)L$ (L = THF, CH_3CN, C_5H_5N),[4] (π-C_6H_6)(π-allyl)Mo(B–B),[5] and $[(\pi\text{-allyl})M(CO)_2(B\text{–}B)X]^-$,[6] where M = Mo or W, B–B = acac or O_2CR, and X = halide. More recently, Archer and co-workers[7] have reported tungsten quinolinolate (dcq) derivatives of the type $W(CO)_2L_2(dcq)Cl$, $W(CO)L_2(dcq)_2$, and $W(CO)_2L(dcq)_2$. An early example of carbyne–carbonyl coupling was promoted with acetylacetone as a reagent and resulted in $W(acac)(HOCCR)(CO)_2Cl$ products.[8] In this paper we describe the synthesis and spectroscopic properties of complexes of the type $M(CO)_2L(B\text{–}B)Y$ where M = Mo or W, L = PEt$_3$ or PPh$_3$, B–B = acac, hexafluoroacetylacetonate (facfac), tropolonate (trop), or carboxylate, and Y = halide or carboxylate.

The role of formate as a ligand has assumed increasing importance as carbon dioxide chemistry has been promulgated.[9] Of course, many carboxylate complexes have been studied and unidentate, bidentate, and bridging modes of coordination have been found for a variety of metals in a range of oxidation states.[10] Wilkinson and Lyons[11] have recently reported the dynamic solution behavior of $WH_2(PMe_3)_3(OOCH)_2$, an eight-coordinate d^2 complex with two formate ligands that exchange rapidly between unidentate and bidentate coordination modes. A similar dynamic process has been observed in six-coordinate d^6 carboxylate derivatives of Ru(II) and Os(II).[12,13] One of the compounds we have prepared is a seven-coordinate d^4 bis(formato) derivative that is fluxional on the NMR time scale. In view of recent interest in formate chemistry[9] we now report the crystal structure and

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