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photochemically active transition behaves as if it had overall a_1 symmetry it must therefore be due to an $e \leftarrow e$ transition. The assignment of actual band symmetries is complicated because not only does this transition have mixed symmetry ($a_1 + e$) but also there is considerable band overlap (Figure 7).
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$$M(CO)_5CS \xrightarrow{h\nu} M(solid) \xrightarrow{CO} M(CO)_6$$
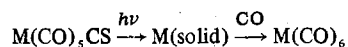
since a metal mirror was formed on the side of the Pyrex bulb during photolysis. On the other hand the solution photolysis produced no detectable increase in the amount of $Cr(CO)_6$ in the sample, and negligible ^{13}CO enrichment of the $Cr(CO)_6$.
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(29) **Note Added in Proof.** A recent general quadratic valence force field calculation on these molecules (I. S. Butler, A. Garcia-Rodriguez, K. Plowman, and C. F. Shaw III, to be published) suggests that the CO/CS coupling is *indeed* comparable to the CO/CO coupling.

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Chemistry of Metal Carbonyl Anions. 6.[1]
Preparation and Properties of Metallodithiocarboxylate Anions[2]

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Carbon disulfide reacts with highly nucleophilic carbonyl monoanions including $(\eta^5\text{-dienyl})Fe(CO)_2^-$ (dienyl = C_5H_5, C_5H_4Me, C_5Me_5), $Mn(CO)_4P(C_5H_{11})_3^-$, and $Re(CO)_5^-$ to generate a new class of organometallic compounds which may be called metallodithiocarboxylate anions. Spectral and chemical properties of these thermally unstable anions are discussed including the synthesis of methyl- and triphenylstannyl derivatives which are believed to contain monodentate metallodithiocarboxylate groups. The synthesis of the first well-characterized species containing a bridging *monodentate* metallodithiocarboxylate group, $[C_5H_5Fe(CO)_2]_2CS_2$, is described. The latter is also the first example of a metal carbonyl complex in which a carbon disulfide unit is formally inserted into a metal–metal bond.

Introduction

The ability of transition metal fragments to mimic the properties of electronically equivalent main-group moieties[3] has been utilized recently in the preparation of a variety of interesting new classes of organometallic compounds, including metalloacetylacetonates in which a 15-electron transition metal fragment plays the role of a 5-electron carbyne function[4] and Fischer type carbene complexes where a 16-electron $M(CO)_5$ unit formally replaces a 6-electron oxygen atom in an organic ester.[5] In view of the close parallels in the chemistry of metal carbonyl monoanions (containing 17-electron neutral fragments) and classical pseudohalides[3] and observations that certain of the latter species, notably N_3^- and CN^-, form 1:1 adducts with carbon disulfide,[6] we expected that carbonyl monoanions would form analogous products, MCS_2^-, which may be called metallodithiocarboxylate anions. While this work was in progress,[2] two reports on related studies appeared. The first concerned the synthesis and structure of a platinum(II) complex containing a bidentate metallodithiocarboxylate group,[7] while the second dealt with the synthesis of coordinated trithiocarbonates from the interaction of carbon

disulfide with metal carbonyl anions.[8] Previous to our work, only two reports on similar reactions have appeared in the literature. Wilkinson and co-workers synthesized a complex of stoichiometry $[(NC)_5CoSC(S)Co(CN)_5]^{6-}$, suggested to contain a unidentate metallodithiocarboxylate group, from the reaction of $Co(CN)_5^{3-}$ with CS_2.[9] However, another group formulated the same compound as $[(NC)_5CoS=C=SCo(CN)_5]^{6-}$, having a linear CS_2 unit.[10] Also, Busetto and Angelici reported that $C_5H_5Fe(CO)_2^-$ reacts with CS_2 to yield $C_5H_5Fe(CO)_2CS_2^-$ but presented no spectral or analytical proof for the existence of this anion.[11] This present study was undertaken in order to obtain spectral and chemical proof for the existence of metallodithiocarboxylate anions, to determine which factors promote the reaction of carbonyl anions with CS_2, and to investigate the possibility that these species might behave as organometallic analogues of dithiocarbamates, an extraordinarily versatile and important class of ligands.[6]

General Procedures and Materials

All operations were carried out under an atmosphere of purified nitrogen or argon, further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate, and

molecular sieves. Solutions were transferred by stainless steel cannulae and syringes; otherwise, reactions were performed by using standard Schlenk apparatus.[12] Reagent grade tetrahydrofuran was freshly distilled from the benzophenone ketyl of potassium under an argon atmosphere. Carbon disulfide was purified via an established procedure.[13] With exceptions noted below, all reagents and other solvents were obtained from commercial sources and used without further purification. The preparation of sodium–potassium alloy has been described previously.[14] Solutions of carbonylmetalate anions were generated from corresponding neutral dimers by reduction with either NaK or sodium amalgam (in the case of Re$_2$(CO)$_{10}$) as described previously.[14] 1,2,3,4,5-Pentamethylcyclopentadiene was prepared by deVries' method[15] as modified by Brintzinger.[16] The following substances were also prepared according to published procedures: [C$_5$Me$_5$Fe(CO)$_2$]$_2$,[17] [C$_5$H$_4$MeFe(CO)$_2$]$_2$,[18] C$_5$Me$_5$Fe(CO)$_2$SnPh$_3$,[17] C$_5$H$_5$Fe(CO)$_2$CH$_3$,[19] and [Mn(CO)$_4$P(C$_6$H$_{11}$)$_3$]$_2$.[20]

Ir spectra were recorded on a Perkin-Elmer 237B spectrometer. Solution spectra were obtained in sealed sodium chloride cells equipped with stainless steel Luer stopcocks to permit filling via syringe outside the glovebox with essentially complete exclusion of air. Solutions of C$_5$H$_5$Fe(CO)$_2^-$ in THF could be kept for at least 0.5 h in these cells without significant oxidation occurring. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich., by Galbraith Laboratories, and by Chemalytics, Inc., Tempe, Ariz. Melting points are uncorrected and were determined with a Buchi-Tottoli apparatus on samples sealed in capillary tubes under nitrogen. Proton NMR spectra were obtained in CDCl$_3$ and recorded on a Varian T-60 spectrometer.

(η^5-dienyl)Fe(CO)$_2$CS$_2^-$ (I). The procedures for preparing all (η^5-dienyl)Fe(CO)$_2$CS$_2^-$ complexes (dienyl = C$_5$H$_5$, C$_5$H$_4$Me, C$_5$Me$_5$) were identical and will be illustrated for η^5-C$_5$H$_4$MeFe(CO)$_2$CS$_2^-$ (I). A solution of 2.6 mmol of K$^+$C$_5$H$_4$MeFe(CO)$_2^-$, prepared by stirring 0.5 g (1.3 mmol) of [C$_5$H$_4$MeFe(CO)$_2$]$_2$ in 50 ml of tetrahydrofuran (THF) with 0.6 ml (10 mmol of K) of NaK$_{2.8}$ alloy at room temperature for 1.5 h was filtered (medium-porosity frit) and cooled to –20 °C. An infrared spectrum of this solution showed that all dimer had been converted to monoanion (see Table II). Upon addition of carbon disulfide (1.3 ml, 2.6 mmol) by syringe to the cold stirred solution, the color of the anions immediately changed from bright red (characteristic of (dienyl)Fe(CO)$_2^-$; see Table II) to dark red (characteristic of (dienyl)Fe(CO)$_2$CS$_2^-$). The infrared spectra and the thermal stability of the resulting anions are discussed later in the paper.

[Bu$_4$N][Mn(CO)$_4$P(C$_6$H$_{11}$)$_3$] (II). A solution of KMn(CO)$_5$ (7.7 mmol), prepared by NaK$_{2.8}$ reduction of Mn$_2$(CO)$_{10}$,[14] and tricyclohexylphosphine (23.1 mmol, 6.48 g, Pressure Chemical Co.) was photolyzed under partial vacuum in a borosilicate reaction vessel of about 150-ml capacity, similar to Ace Glass Model 6515, with a high-pressure Hanovia quartz mercury vapor lamp (450-W, Model 679A-36) inside a cooled quartz photochemical immersion well (Ace Glass Model 6515-25). After 4.5 h of photolysis at room temperature an infrared spectrum of the resulting deep yellow-brown solution showed practically all bands due to Mn(CO)$_5^-$ had disappeared; intense bands due to product, K[Mn(CO)$_4$P(C$_6$H$_{11}$)$_3$] (ν(CO) 1930 (s), 1811 (vs), 1772 (s) cm^{-1}), remained. To obtain a more tractable substance, the potassium salt was converted to II by stirring the above solution with 2.64 g (7.7 mmol) of [(n-C$_4$H$_9$)$_4$N][ClO$_4$] (G. F. Smith Co.) for 2 h at room temperature and then filtering (medium-porosity frit) to remove KClO$_4$. Evaporation of the solution under vacuum gave an impure salt which was recrystallized from THF–ether to give 5.30 g (47% yield based on Mn$_2$(CO)$_{10}$) of tan–light green crystalline II (ν(CO) (in THF) 1930 (s), 1801 (vs, br) cm^{-1}). Satisfactory elemental analyses of II were not obtained due to its extreme air sensitivity; however, its formulation was proven by converting II quantitatively to a new and characterizable derivative, (C$_6$H$_5$)$_3$SnMn(CO)$_4$-P(C$_6$H$_{11}$)$_3$ (light yellow crystalline substance; decomposes without melting; ν(CO) (in THF) 1943 (vs) cm^{-1}), by treatment of the salt with an equivalent of chlorotriphenylstannane in THF. Anal. Calcd for C$_{40}$H$_{48}$O$_4$MnPSn: C, 60.25; H, 6.07. Found: C, 60.17; H, 6.20. Further evidence for the correctness of the formulation for II was obtained by preparing an identical sample of II by metathesis of [Bu$_4$N][ClO$_4$] and the previously characterized Na[Mn(CO)$_4$-P(C$_6$H$_{11}$)$_3$] (ν(CO) (in THF) 1930 (s), 1813 (vs), 1760 (s) cm^{-1}), prepared by Na/Hg reduction of [Mn(CO)$_4$P(C$_6$H$_{11}$)$_3$]$_2$ in THF.[20]

Mn(CO)$_4$P(C$_6$H$_{11}$)$_3$CS$_2$SnPh$_3$ (III). An excess of carbon disulfide (0.6 ml, 10 mmol) was added by syringe to a magnetically stirred,

cold (–20 °C) solution of II (0.67 g, 1.0 mmol) in 25 ml of THF. The solution was warmed to room temperature with stirring; after 2 h, 0.38 g (1.0 mmol) of Ph$_3$SnCl in 10 ml of THF was added via syringe. Solvent was removed under vacuum, leaving a brown residue which was recrystallized from CH$_2$Cl$_2$–heptane to give a 32% yield of reddish brown microcrystalline solid formulated as III on the basis of its elemental analyses (see Table I) and infrared spectra (values are given in the Results and Discussion).

C$_5$Me$_5$Fe(CO)$_2$CS$_2$Me (IV). Carbon disulfide (0.1 ml, 1.7 mmol) was added by syringe to a cold (–20 °C) solution of K[C$_5$Me$_5$Fe(CO)$_2$] (1.4 mmol), which was prepared by reducing [C$_5$Me$_5$Fe(CO)$_2$]$_2$ (0.35 g, 0.7 mmol) with 0.50 ml of NaK$_{2.8}$ alloy at room temperature for 1.5 h in 40 ml of freshly distilled THF. After the solution was stirred for 30 min at –20 °C, methyl iodide (0.35 ml, 2.8 mmol) was added by syringe. The resulting mixture was stirred for 1 h at room temperature, filtered to remove KI, and evaporated to dryness under reduced pressure. A deep yellow-brown solution of the solid in CH$_2$Cl$_2$ (20 ml) was purified by passage through a 2-cm column of silica. Yellow brown crystals of IV were obtained by slow evaporation of the eluted CH$_2$Cl$_2$ solution (to which 5 ml of heptane was added) under partial vacuum. More crystals were obtained by cooling the resulting slurry to –50 to –60 °C. The supernatant was decanted and product was washed with two 10-ml portions of cold (–50 °C) pentane. Subsequently, it was dried under vacuum at room temperature to give 0.19 g (40% yield based on [C$_5$Me$_5$Fe(CO)$_2$]$_2$) of yellow-brown crystalline IV. Analytical data appear in Table II. The infrared spectrum of the product in the carbonyl stretch region is shown in Table II.

C$_5$Me$_5$Fe(CO)$_2$CS$_2$SnPh$_3$ (V). A cold (–20 °C) THF solution (40 ml) containing C$_5$Me$_5$Fe(CO)$_2$CS$_2^-$ (3.9 mmol) was prepared as in the synthesis of IV (vide supra). Chlorotriphenylstannane (1.5 g, 3.9 mmol) was added via syringe in 5 ml of THF. After stirring of the resulting mixture for an additional 0.5 h, it was evaporated to dryness under reduced pressure. The yellow-brown product was dissolved in CH$_2$Cl$_2$ (20 ml), passed through a short plug of silica gel (1 cm), and crystallized from the filtrate (to which 5 ml of heptane was added) by slow evaporation. Yellow crystalline V obtained in this manner was washed with pentane and dried under vacuum to give 2.25 g (86% yield based on [C$_5$Me$_5$Fe(CO)$_2$]$_2$) of analytically pure V.

C$_5$H$_4$MeFe(CO)$_2$CS$_2$SnPh$_3$ (VI). This substance was prepared by the route given for V in 35% yield as a yellow-brown analytically pure crystalline product of poor thermal stability.

C$_5$H$_5$Fe(CO)$_2$CS$_2$SnPh$_3$ (VII). Golden-brown crystals of VII (85% yield based on [C$_5$H$_5$Fe(CO)$_2$]$_2$) were obtained by the same method used for V. Difficulty was experienced in obtaining analytically pure samples of this thermally unstable substance.

[C$_5$H$_5$Fe(CO)$_2$]$_2$CS$_2$ (VIII). Carbon disulfide (0.8 ml, 14 mmol) was added to a cold (–20 °C) solution of K[C$_5$H$_5$Fe(CO)$_2$] (7.4 mmol, prepared by NaK$_{2.8}$ reduction of corresponding neutral dimer) thereby producing C$_5$H$_5$Fe(CO)$_2$CS$_2^-$. Within 10 min, 2.20 g (7.4 mmol) of solid C$_5$H$_5$Fe(CO)$_2$I was added to the cold solution with stirring. The solution rapidly changed from a deep red (characteristic of the dithiocarboxylate anion) to a bright red. After 30 min of stirring and warming to room temperature, the solution was filtered (medium-porosity frit) and evaporated under reduced pressure. The bright red crystalline product was recrystallized from CH$_2$Cl$_2$–heptane twice to give 2.88 g (91% yield based on [C$_5$H$_5$Fe(CO)$_2$]$_2$) of analytically pure product. Infrared and proton NMR spectra of this product are described later in the paper.

Results and Discussion

During routine solubility tests on salts containing carbonyl anions, we discovered that many of these underwent substantial color changes in CS$_2$. For example, [Na(diglyme)$_2$][V(CO)$_6$] or [Na(THF)$_x$][Mn(CO)$_5$] dissolved partially in CS$_2$ to give orange to deep red solutions instead of the pale yellow or nearly colorless solutions these anions give in unreactive solvents. However, in spite of the marked color changes observed, the ir spectra of the CS$_2$ or CS$_2$–THF solutions were essentially superimposable with those of the unreacted carbonyl anion for at least 1 h at room temperature. Also, addition of chlorotriphenylstannane either to slurries of V(CO)$_6^-$ and Mn(CO)$_5^-$ in CS$_2$ or to solutions of the same salts in CS$_2$–THF mixtures of various proportions stirred for at least 1 h at room temperature resulted in no reaction in the case of V(CO)$_6^-$ (which

Table I. Analytical Data and Physical Properties of Metallodithiocarboxylate Derivatives

Compd	Color	Mp, °C	% calcd			% found			Mol wt	
			C	H	S	C	H	S	Calcd	Found
Mn(CO)$_4$P(c-Hx)$_3$(CS$_2$SnPh$_3$), III	Red-brown	(Dec >70)	56.37	5.54	7.34	56.56	6.19	7.53		
Fe(CO)$_2$(C$_5$Me$_5$)(CS$_2$CH$_3$), IV	Gold-brown	103 dec	49.73	5.33	18.94	51.32	5.80	19.06	338	346^a
Fe(CO)$_2$(C$_5$Me$_5$)(CS$_2$SnPh$_3$), V	Yellow	126–128 dec	55.31	4.46	9.52	54.71	4.33	9.37	673	690^b
Fe(CO)$_2$(C$_5$H$_4$Me)(CS$_2$SnPh$_3$), VI	Gold-brown	85 dec	52.55	3.59	10.37	53.19	4.05	9.82	617	612^a
Fe(CO)$_2$(C$_5$H$_5$)(CS$_2$SnPh$_3$), VII^c	Gold-brown	(Dec >50)	51.80	3.34	10.60	52.06	3.32	11.26	603	585^a
[Fe(CO)$_2$C$_5$H$_5$]$_2$CS$_2$, VIII	Red	111–113 dec	41.90	2.34	14.89	41.74	2.34	14.76	430	440^a

^{a} Osmometry in benzene. ^{b} Osmometry in acetone. ^{c} Fe analysis: calcd, 9.30%; found, 8.58%.

Table II. Infrared Spectra of Various (η^5-dienyl)Fe(CO)$_2$ Species in the Carbonyl Stretching Frequency Region^a

Species	X = C$_5$H$_5$Fe(CO)$_2$	X = C$_5$H$_4$MeFe(CO)$_2$	X = C$_5$Me$_5$Fe(CO)$_2$
X$^-$	1865, 1788^c	1860, 1773^b	1848, 1759^b
XCS$_2^-$	2002, 1950^b	1998, 1942^b	1985, 1930^b
XCS$_2$SnPh$_3$	2035, 1989	2028, 1980	2014, 1966
XSnPh$_3$	1990, 1942	1980, 1933^d	1965, 1915^d
XCS$_2$CH$_3$	2031, 1982^b	2023, 1973^b	2011, 1961
XCH$_3$	2003, 1945	e	1988, 1936^f

^{a} All bands are sharp and strong and are of approximately equal intensity. Spectra were taken in THF except when noted. Values are in cm^{-1}. ^{b} Compound has not been isolated as a pure substance. Anions are potassium salts. ^{c} Value from ref 14; Bu$_4$N$^+$ salt. ^{d} Fluorolube mull. ^{e} Compound has not been reported in the literature. ^{f} Hexane solution; value from ref 21.

does not react with Ph$_3$SnCl under these conditions)^{22} or in nearly quantitative formation of Ph$_3$SnMn(CO)$_5$ ^{14} in the case of Mn(CO)$_5^-$. Subsequent studies have shown that Co(CO)$_4^-$ and C$_5$H$_5$M(CO)$_3^-$ (M = Cr, Mo, W) also give orange to deep red solutions in the presence of CS$_2$ but otherwise remain unchanged. Whether the color change is due to the formation of a very small equilibrium concentration of CS$_2$–anion complex, a CS$_2$–anion interaction, which is sufficiently weak to have little influence on the carbonyl stretching frequencies of the anion, or a very strongly absorbing adduct formed from an impurity in the CS$_2$ and anion is not presently known. We believe the last possibility is unlikely since purification of CS$_2$ by a variety of different techniques did not alter its apparent reactivity with these carbonyl anions. Indeed, a weak CS$_2$–anion interaction seems likely in view of the recent report that trithiocarbonate derivatives of metal carbonyls may be prepared in generally low yield (5–10%) by the reaction of carbonyl anions with an excess of CS$_2$ and subsequent treatment with an electrophile.^{8} Unfortunately, this preliminary communication failed to give a clear account of the conditions used in these reactions, so it is difficult to compare their results with ours.

In contrast to the above weakly basic and nucleophilic carbonyl anions, it was discovered that Mn(CO)$_4$P(C$_6$H$_{11}$)$_3^-$, Re(CO)$_5^-$, and various (η^5-dienyl)Fe(CO)$_2^-$ (dienyl = C$_5$H$_5$, C$_5$H$_4$Me, C$_5$Me$_5$) do undergo substantial interactions with CS$_2$ as shown by the spectral changes listed in Table II and mentioned later in the Results and Discussion. On the basis of their derivative chemistry, it is appropriate to formulate these CS$_2$–anion adducts as metallodithiocarboxylates. Individual descriptions of the chemistry and properties of this new class of organometallic compounds will now be presented.

(η^5-**dienyl)Fe(CO)$_2$CS$_2^-$ (dienyl = C$_5$H$_5$, C$_5$H$_4$Me, C$_5$Me$_5$).** These carbonyl monoanions react rapidly and quantitatively with 1 equiv of carbon disulfide in THF at –20 °C to give adducts which we formulate as (η^5-dienyl)(dicarbonyl)-ferrodithiocarboxylate anions on the basis of their derivative chemistry. Accompanying spectral changes during CS$_2$ complexation in the carbonyl stretching frequency region (shown in Table II) conclusively show that new species form which absorb in this region at substantially higher energy.

Attempts to isolate (η^5-dienyl)Fe(CO)$_2$CS$_2^-$ with a variety of large cations including Ph$_4$As$^+$, Et$_4$N$^+$, and (Ph$_3$P)$_2$N$^+$ failed to provide thermally stable products. Infrared monitoring of the decomposition of (η^5-dienyl)Fe(CO)$_2$CS$_2^-$ in THF showed that corresponding [(η^5-dienyl)Fe(CO)$_2$]$_2$ formed almost quantitatively after 1 h at room temperature;^{23} however, the ultimate fate of the "CS$_2$–" fragment in this decomposition is unknown. Exposure of (η^5-dienyl)Fe(CO)$_2$CS$_2^-$ solutions in THF to air rapidly destroys the anions to give substantial amounts of [(η^5-dienyl)Fe(CO)$_2$]$_2$, as well as moderately air-stable oxidation product(s) (for dienyl = C$_5$H$_5$, ν(CO) (in THF) is 2031 (m), 2017 (s), 1984 (vs) cm^{-1}) which decomposed when isolated from solution. It is tempting to suggest that oxidation of (η^5-dienyl)Fe(CO)$_2$CS$_2^-$ yields [(η^5-dienyl)Fe(CO)$_2$CS$_2$]$_2$ by analogy with dithiocarbamates and azidodithiocarboxylate (N$_3$CS$_2^-$) which yield thiuram disulfides^6 and "azido(carbon disulfide)" ((SCSN$_3$)$_2$)^{24} on oxidation; however, the natures of these thermally unstable oxidation products are presently unknown.

Treatment of (η^5-dienyl)Fe(CO)$_2$CS$_2^-$ with iodomethane and chlorotriphenylstannane provided metallodithiocarboxylate derivatives of varying thermal stabilities. In the case of the methyl derivatives, only η^5-C$_5$Me$_5$(CO)$_2$FeCS$_2$CH$_3$ (IV) was of sufficient thermal stability to allow characterization by elemental analysis and molecular weight determination (Table I). Proton NMR spectra of IV in CDCl$_3$ showed singlets at τ 7.40 (1) and 8.25 (5) (relative intensity) attributable to the sulfur-bound methyl protons and the cyclopentadienyl methyl protons, respectively. These values compare well with the sulfur-bound methyl proton resonance in the closely related C$_5$H$_5$(CO)$_2$FeSCS$_2$CH$_3$ (τ 7.40)^{25} and the proton resonance positions of other known η^5-C$_5$Me$_5$ groups (τ 7.66–8.38). While IV may be isolated as an analytically pure, crystalline solid, which thereby gains a measure of lattice stabilization, C$_5$H$_4$Me(CO)$_2$FeCS$_2$CH$_3$ and C$_5$H$_5$(CO)$_2$FeCS$_2$CH$_3$ are thermally unstable deep red-brown liquids and were identified only on the basis of their ir spectra in the carbonyl stretching region.^{27,28} Significantly, the physical properties of the unstable product we formulate as C$_5$H$_5$(CO)$_2$FeCS$_2$CH$_3$ are much different from those reported for the substantially more stable and crystalline trithiocarbonate species C$_5$H$_5$(CO)$_2$-FeSCS$_2$CH$_3$ (mp 104.5 °C; ν(CO) (in CCl$_4$) 2044, 2002 cm^{-1}).^{25} Mention should also be made of the steadily decreasing carbonyl stretching frequencies (Table II) in corresponding (η^5-dienyl)(CO)$_2$FeCS$_2$ derivatives as the number of methyl substituents on the cyclopentadienyl ring increases. Previous observations on similar systems are in accord with this trend which indicates that the C$_5$Me$_5$ group is a substantially better electron donor than an unsubstituted cyclopentadienyl unit. Spectra of other related (η^5-dienyl)-Fe(CO)$_2$ species are also presented in Table II for comparison, including the first reported spectra of C$_5$H$_4$MeFe(CO)$_2^-$ and C$_5$Me$_5$Fe(CO)$_2^-$ (as the potassium salts in THF).

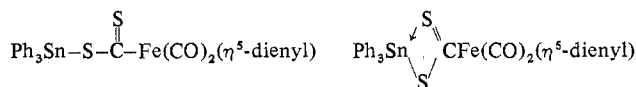Although CS$_2$ is almost invariably attacked by Lewis bases at the carbon atom, in principle, it could also react with (η-dienyl)Fe(CO)$_2^-$ to yield products containing sulfur–iron linkages of the formula (η-dienyl)(CO)$_2$FeSC$^-$=S. Reaction

of such an ion with iodomethane would yield products of structure $(\eta\text{-dienyl})(CO)_2FeSC(S)CH_3$, if rearrangements did not occur. Such S-bonded carbon disulfide compounds have been known for several years,[29] including $Mn(CO)_3$-$(Ph_2PCH_2CH_2PPh_2)(SSCH)$ containing a monodentate dithioformato group,[30] $M(CO)_4(SSCR)$ containing bidentate dithiocarboxylate groups,[31] and $C_5H_5(CO)_2Fe(SSCNMe_2)$[32] containing unidentate N,N-dimethyldithiocarbamate. On the basis of infrared and proton NMR spectra we are presently unable to absolutely eliminate the possibility that our products contain metal–sulfur rather than metal–carbon linkages. However, chemical evidence for the existence of the latter type of bonding in our products is compelling in that $C_5H_5(C$-$O)_2FeCS_2CH_3$ may be converted in high yield to the thiocarbonyl cation, $C_5H_5(CO)_2FeCS^+$.[11,33] Also, our research group has recently synthesized thermally unstable compounds of the type $(\eta\text{-dienyl})(CO)_2FeS_2CCH_3$, which should contain Fe–S linkages, from the reaction of dithioacetate ion[6] with $IFe(CO)_2(\eta\text{-dienyl})$. The chemical and physical properties of these presently incompletely characterized species are substantially different from those of the corresponding isomers in this paper and will be the subject of a future communication.[34]

Triphenylstannyl derivatives of $(\eta^5\text{-dienyl})(CO)_2FeCS_2^-$ are significantly more thermally stable than corresponding methyl compounds and have been well characterized by elemental analyses, molecular weight determinations, and ir spectroscopy. Even so, difficulty was experienced in obtaining pure samples of the unsubstituted cyclopentadienyl derivative. Although the methyl derivatives are likely to contain a unidentate MCS_2 group, i.e.

$$CH_3\text{–}S\text{–}\overset{\overset{\displaystyle S}{\|}}{C}\text{–}Fe(CO)_2(\eta^5\text{-dienyl})$$
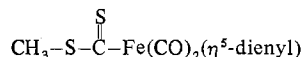
corresponding triphenylstannyl derivatives could be either uni- or bidentate, i.e.

$$Ph_3Sn\text{–}S\text{–}\overset{\overset{\displaystyle S}{\|}}{C}\text{–}Fe(CO)_2(\eta^5\text{-dienyl}) \qquad Ph_3Sn\overset{S}{\underset{S}{\diagdown}}CFe(CO)_2(\eta^5\text{-dienyl})$$

since tin has a substantial tendency to expand its valence shell. For example, tin is thought to be octahedrally coordinated in $(CH_3)_2Sn(acac)_2$.[35] To decide whether a uni- or bidentate metallodithiocarboxylate ligand is present, the carbon–sulfur stretching frequency region of these compounds was compared with that of $Ph_3SnS_2CNMe_2$[36] and $Me_3SnS_2CNMe_2$, both of which have a two-band pattern in this region which is presumed to be indicative of a unidentate dithiocarbamate group coordinated to tin.[37] In fact, the trimethyltin dithiocarbamate has been shown by x-ray structure determination to have this structural feature.[38] Also, to eliminate any vibrational absorptions due only to the Ph_3Sn and $(\eta^5\text{-die}$-$nyl)Fe(CO)_2$ groups, Nujol mull infrared spectra of $Ph_3SnFe(CO)_2(\eta^5\text{-dienyl})$ were recorded in the same region. For example, in the 1100–900 cm^{-1} region, Ph_3SnFe-$(CO)_2C_5H_5$ has the absorption pattern 1073 (s), 1021 (m), 998 (s) cm^{-1}, while twice recrystallized Ph_3SnS_2CFe-$(CO)_2C_5H_5$ absorbs at 1073 (s), 1022 (m), 1006 (s), 999 (s), 997 (s), and 967 (m) cm^{-1}. On this basis we attribute the intense bands at 1006 cm^{-1} and either 999 or 997 cm^{-1} to C–S stretching frequencies. Corresponding bands of Et_3Sn-(S_2CNEt_2)[37] occur at 1006 and 988 cm^{-1}, while those of $Ph_3SnS_2CNMe_2$[36] are at lower energy (985, 977 cm^{-1}). From these qualitative comparisons it would appear that $Ph_3SnS_2CFe(CO)_2(\eta^5\text{-dienyl})$ is best formulated as a unidentate metallodithiocarboxylate derivative. However, on this basis we cannot exclude the presence of an Fe–S linkage in these triphenylstannyl derivatives.

To gain further evidence for our formulation of the Ph_3Sn derivatives, an attempt to prepare an isomeric species, $Ph_3SnCS_2Fe(CO)_2C_5H_5$, containing an Fe–S linkage, by the reaction of "$Ph_3SnCS_2^-$" with $C_5H_5Fe(CO)_2I$ was made. Unfortunately, this approach was obviated by a rapid reaction of Ph_3SnLi with carbon disulfide even at -78 °C to generate hexaphenylditin. Carbon dioxide is also known to rapidly oxidize triphenylstannyllithium to hexaphenylditin.[39]

A significantly more thermally stable derivative of $C_5H_5Fe(CO)_2CS_2^-$ than the methyl or triphenylstannyl compounds was obtained in high yield by treating the anion with an equivalent of $C_5H_5Fe(CO)_2I$ to give $C_5H_5(CO)_2$-$FeCS_2Fe(CO)_2C_5H_5$ (VIII), which we formulate, on the basis of elemental analyses, molecular weight determination, and infrared and NMR spectra, to have the structure
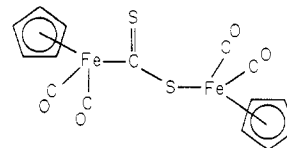
VIII

The proton NMR of VIII in $CDCl_3$ shows only two sharp singlets of equal intensity at τ 4.97 and 4.83 which are due to the slightly different chemical environments of the cyclopentadienyl groups. Equally consistent with the proposed structure of VIII is its infrared spectrum in the carbonyl stretching region which shows two sets of overlapping bands of approximately equal intensity (ν(CO) (in THF) 2037, 2018, 1982, 1972 cm^{-1}) which are attributable to the two different iron environments. Examination of the CS stretching frequency region of VIII in carbon disulfide revealed bands at 1020 (sh), 1011 (m), and 1000 (sh) cm^{-1}, due to carbon–sulfur vibrations.[40] While this information is not compelling evidence for the presence of a unidentate metallodithiocarboxylate group in VIII, we find that $Me_5C_5(CO)_2FeCS_2CH_3$, which must have a unidentate MCS_2 group, has a very similar pattern (1028 (sh), 1018 (m), 1009 (sh) cm^{-1}) in the same region due to carbon–sulfur vibrations. An alternative formulation for VIII which is also formally consistent with its proton NMR spectrum is
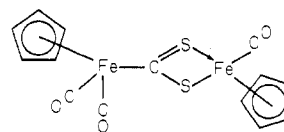
Although it has not been possible to convert VIII to such a species by thermal or photolytic means, the absence of a band in the 1960-cm^{-1} region where $C_5H_5(CO)FeS_2CSR$ absorbs[25] suggests that a bidentate MCS_2 unit is not present. Also, the cyclopentadienyl proton resonance position in the C_5H_5FeCO containing trithiocarbonate species is reported to be about τ 5.4,[25] in contrast to our values which are more consistent for two different $C_5H_5Fe(CO)_2$ units. The possibility that VIII is actually a trithiocarbonate derivative, such as similar species recently discussed in a preliminary communication,[8] is chemically unreasonable in view of the high yield (>90%) in which we obtain VIII from 1 equiv of $CS_2/2$ equiv of $C_5H_5Fe(CO)_2$ units and unlikely on the basis of the preceding data. Also, this possibility has been eliminated by showing in this laboratory that K_2CS_3 reacts with 2 equiv of $IFe(C$-$O)_2C_5H_5$ to yield entirely different products which will be reported later.[34] Surprisingly, we have been unable to prepare mixed-metal analogues of VIII by the reaction of C_5H_5-$Fe(CO)_2CS_2^-$ with other metal carbon halides such as $Mn(CO)_5Br$ and $Re(CO)_5I$. On mixing these components, extensive decomposition occurs, resulting in the formation of

$[M(CO)_5]_2$ (M = Mn, Re) and $[C_5H_5Fe(CO)_2]_2$. However, other possible routes to these species are being investigated.

Other studies with $C_5H_5Fe(CO)_2CS_2^-$ have been less fruitful thus far. Attempts to prepare thermally stable transition metal complexes of metallodithiocarboxylates of the type $M'(S_2CM)_2$ by the reactions of $C_5H_5Fe(CO)_2CS_2^-$ at −20 °C with $HgCl_2$ and $ZnCl_2$, which are known to give very stable bis(dithiocarbamates),[6] were unsuccessful. Although bright orange solids, which gave simple solution spectra in the carbonyl stretch region (ν(CO) (in THF) for "$Hg(S_2CFe(CO)_2C_5H_5)_2$" 2031 (s), 1988 (s) cm^{-1}), could be isolated at low temperatures from these reactions, the solids rapidly decomposed above 0 °C to brown material containing mainly $[C_5H_5Fe(CO)_2]_2$ and non-carbonyl-containing substances which were not characterized. Substantially more thermally stable materials have been obtained in an attempt to prepare tris chelates of these new ligands. For example, treatment of $CrCl_3\cdot3THF^{41}$ with 3 equiv of $C_5H_5Fe(CO)_2CS_2^-$ in THF at −20 °C causes the formation of a dark green-black solution which has a remarkably simple spectrum in THF (ν(CO) 2030 (s), 1980 (s) cm^{-1}). From this mixture a deep green, almost black, thermally stable solid (mp 172–173 °C dec) may be isolated in high yield which analyzes very closely for $Cr(S_2CFe(CO)_2C_5H_5)_3$. Anal. Calcd for $C_{24}H_{15}O_6CrFe_3S_6$: C, 35.53; H, 1.86; S, 23.72. Found: C, 36.00; H, 2.27; S, 22.42. However, molecular weight determinations in benzene are low (calcd 811; found 420) and attempts to purify this solvolytically unstable species have not been successful. Nevertheless, studies are continuing on novel species of this type which may have properties similar to the more thermally stable tris complexes of dithiocarbamates.[6]

$Mn(CO)_4P(C_6H_{11})_3CS_2^-$ and $Re(CO)_5CS_2^-$. Since $Mn(CO)_5^-$ gave no discernible reaction with CS_2, it was of interest to determine whether a closely related but potentially more basic anion such as $Mn(CO)_4P(C_6H_{11})_3^-$ (II) would react with CS_2. Initially, this anion was obtained by reduction of $[Mn(CO)_4P(C_6H_{11})_3]_2$ according to a procedure in the literature[20] and gave positive results (vide infra). However, our difficulty in obtaining the pure neutral precursor in high yields from costly $Mn_2(CO)_{10}$ led us to examine an alternative route which had been used previously only for the preparation of substituted anions of $M(CO)_6^-$ (M = V, Nb, Ta).[42–44] By this photochemical method we obtained the desired anion in approximately 50% yields based on $Mn_2(CO)_{10}$ and proved its formulation was correct by comparison of its spectral properties with those reported earlier for the related $Mn(CO)_4P(C_6H_5)_3^-$ [20,45] and the preparation of a triphenyltin derivative, $Ph_3SnMn(CO)_4P(C_6H_{11})_3$. This is likely to be the trans isomer in view of its single strong absorption (ν(CO) 1943 cm^{-1}) in the carbonyl stretching region. An x-ray structure determination of the related $Ph_3SnMn(CO)_4PPh_3$ has shown it to be of trans configuration.[46]

Carbon disulfide reacts slowly with II in THF. By monitoring the progress of the reaction with infrared spectra in the carbonyl stretching frequency region, it was shown that approximately 2 h is required for all of II (ν(CO) (in THF) 1930 (s), 1801 (vs, br) cm^{-1}), to be consumed. Infrared spectra of the CS_2 adduct absorb in this region at considerably higher energy (ν(CO) (in THF) 1979 (s), 1943 (m), 1899 (m, br) cm^{-1}). Attempts to isolate and characterize $(C_6H_{11})_3P(CO)_4MnCS_2^-$ were unsuccessful; however, treatment of this species with 1 equiv of Ph_3SnCl provided a 32% yield of a product of poor thermal stability which is formulated as *trans*-$Ph_3SnS_2CMn(CO)_4P(C_6H_{11})_3$ (III) on the basis of its elemental analyses and infrared spectrum (ν(CO) (in THF) 2001 (s) cm^{-1}). The carbonyl stretching frequency of III is at considerably higher energy than the corresponding value observed for $Ph_3SnMn(CO)_4P(C_6H_{11})_3$ (1943 cm^{-1}), which

is in accord with trends observed for corresponding (η^5-dienyl)$Fe(CO)_2$ systems (see Table II). The infrared spectrum of III in the carbon–sulfur stretching frequency region contains a doublet (ν(CS) (in CS_2) 1021, 996 cm^{-1}) which is attributable to an unsymmetrical MCS_2 binding to the triphenyltin group.[37] In this respect, the compound is very similar to the ferrodithiocarboxylate derivatives mentioned earlier.

In contrast to II, $Re(CO)_5^-$ reacts immediately with CS_2 at −20 °C to give an orange-brown solution (ν(CO) (in THF) 2068 (vw), 2030 (vw), 2013 (w), 1970 (s), 1908 (w) cm^{-1}), apparently free of $Re(CO)_5^-$,[47] which slowly deteriorates to $Re_2(CO)_{10}$ on standing. Treatment of this solution with chlorotriphenylstannane gives a moderately air-stable solution (ν(CO) (in THF) 2142 (w), 2118 (vw), 2071 (vw), 2033 (s), 2012 (vs), 1977 (m) cm^{-1}). Numerous attempts to isolate product from the solution failed to purify the desired species from $Ph_3SnRe(CO)_5$ [14] (ν(CO) (in THF) 2118 (m), 2069 (w), 2011 (s) cm^{-1}) which also formed in the reaction (possibly from decomposition of the desired $Ph_3SnS_2CRe(CO)_5$).

Concluding Remarks

The ability of molecular fragments containing transition metals in low formal oxidation states to act as effective Lewis Bases[48] suggested that they could play the same role in stabilizing metallodithiocarboxylates as amino or alkoxy functions do in dithiocarbamates or xanthates, respectively, in the sense that the resonance contribution

D = electronically equivalent 7- or 17-electron donor function

would play an important role in defining the electronic ground state. For a transition metal this resonance form represents metal "back-donation" which has been previously invoked to explain myriad features of organo(transition metal) complexes such as abnormally low ketonic CO stretching frequencies in acyl metal carbonyls and the M–C multiple bond orders in metal carbenes and carbonyls. Our studies indicate that transition metal groups are less effective than first-row main-group donor atoms in stabilizing such 1,1-dithiolates, since the resulting metal derivatives are much less thermally stable than corresponding dithiocarbamate or xanthate complexes. However, the relatively high thermal stability of a well-characterized platinum(II) complex containing a *bidentate* MCS_2 unit[7] suggests that a large variety of interesting compounds of this class can be synthesized and we are attempting to use the metallodithiocarboxylate anions described herein and others as a route to such species.

59654-65-8; $(C_6H_5)_3SnMn(CO)_4P(C_6H_{11})_3$, 59654-66-9; $[C_5Me_5Fe(CO)_2]_2$, 35344-11-7; $Hg(S_2CFe(CO)_2C_5H_5)_2$, 59654-68-1; $Cr(S_2CFe(CO)_2C_5H_5)_3$, 59654-67-0; $(C_6H_{11})_3P(CO)_4MnCS_2^-$, 59654-69-2; $Re(CO)_5^-$, 14971-38-1; $Re(CO)_5CS_2^-$, 59654-70-5; CS_2, 75-15-0.

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Chemistry and Electrochemistry of the Vanadium–Carbonyl System

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The chemistry and electrochemistry of the vanadium–carbonyl system are very solvent dependent. In acetone solution, electrochemical studies on the hexacarbonylvanadate(–I) anion show a reversible $V(CO)_6^-/V(CO)_6$ couple. However, chemically synthesized $V(CO)_6$ disproportionates in acetone to V^{2+} and $V(CO)_6^-$ and has no long-term stability in this or other coordinating solvents. By contrast, in dichloromethane solution, $V(CO)_6$ whether generated chemically or electrochemically, is stable and a reversible $V(CO)_6^-/V(CO)_6$ couple is observed using both $V(CO)_6^-$ and $V(CO)_6$ as the starting material. Oxidation of $V(CO)_6$ is irreversible in both solvents and the species $V(CO)_6^+$ appears to have no inherent stability under any of the conditions examined. Interesting redox reactions occur when solutions of $[V-((CH_3)_2CO)_6^{2+}][V(CO)_6^-]_2$ are diluted in dichloromethane, or alternatively when the acetone is removed under vacuum, to generate $V(CO)_6$.

Introduction

Hexacarbonylvanadium, $V(CO)_6$, is known to disproportionate in two ways on reaction with ligands. Calderazzo[1] found it reacted with arenes to give $[V(CO)_4arene^+][V(CO)_6^-]$, i.e., V^+ and V^-, but in contrast Hieber and co-workers[2,3] found that most oxygen and nitrogen donors, including common organic solvents such as acetone, gave products of the type $[VL_x^{2+}][V(CO)_6^-]_2$, i.e., V^{2+} and $2V^-$.

No detailed electrochemical studies on the vanadium-carbonyl system have been reported, although a brief mention of the reduction of $V(CO)_6$ has appeared in a recent publication.[4]

In this paper we present detailed electrochemical data on both $V(CO)_6$ and the diglyme-stabilized sodium salt of $V(CO)_6^-$ in both acetone and dichloromethane solutions. The marked differences in electrochemical behavior between the two solvents led to a study of some interesting redox reactions which occur on changing the solvent.

Experimental Section

Electrochemistry. Polarograms at a dropping mercury electrode (controlled drop time 0.5 s) and cyclic voltammograms at a platinum disk electrode were recorded with a Princeton Applied Research Corp. Model 170 electrochemistry system. A three-electrode system incorporating positive feedback circuitry to minimize the *IR* drop was