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"Reactions of Carbon Disulfide and Carbon Dioxide Adducts
(η^5 -C₅H₅)(CO)₂Fe-CX₂⁻ with Organoiron Electrophiles"

by

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Troy, New York 12180

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Reactions of $\text{Fp-CS}_2\text{-K}^+$ (2) and $\text{Fp-CO}_2\text{-Na}^+$ (and Li^+) (1) [$\text{Fp}=(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}$] with organoiron electrophiles FpX ($\text{X}=\text{I}$, OSO_2CF_3, HgCl), $(\eta^5\text{-C}_5\text{H}_5)\text{L}(\text{CO})\text{FeI}$ [$\text{L}=\text{P}(\text{OPh})_3$, PPh_3], and $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Fe}(\text{CH}_3\text{CN})_2^+\text{PF}_6^-$ are contrasted. Treatment of the CS_2 adduct 2 with the bis-acetonitrile salt gives the $\mu(\eta^1\text{-C}:\eta^2\text{-S,S'})$ CS_2 complex Fp-C(S)S-Fe(CO)Cp (4). Reacting the CO_2 adduct 5 with the iron electrophiles Cp(L)(CO)Fe-I affords Fp_2, with only trace amounts of Fp-Fe(CO)(L)Cp (for $\text{L}=\text{PPh}_3$ and P(OPh)_3) evident. No $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ bimetallocarboxylate intermediates $\text{Fp-C(O)O-Fe(L)(CO)Cp}$ are detected. In contrast, Fp^+Na^+ upon treating with $(\eta^5\text{-C}_5\text{H}_5)\text{L}(\text{CO})\text{FeI}$ gives 1:1 mixtures of Fp_2 and Fp-Fe(CO)(L)Cp (for $\text{L}=\text{PPh}_3$ and P(OPh)_3). The bis-acetonitrile electrophile and 1 afford initially the mixed dimer $\text{Fp-Fe(CH}_3\text{CN)(CO)Cp}$, which degrades to Fp_2 at room temperature.			
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Reactions of Carbon Disulfide and Carbon Dioxide Adducts

$(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe-CX}_2^-$ with Organoiron Electrophiles

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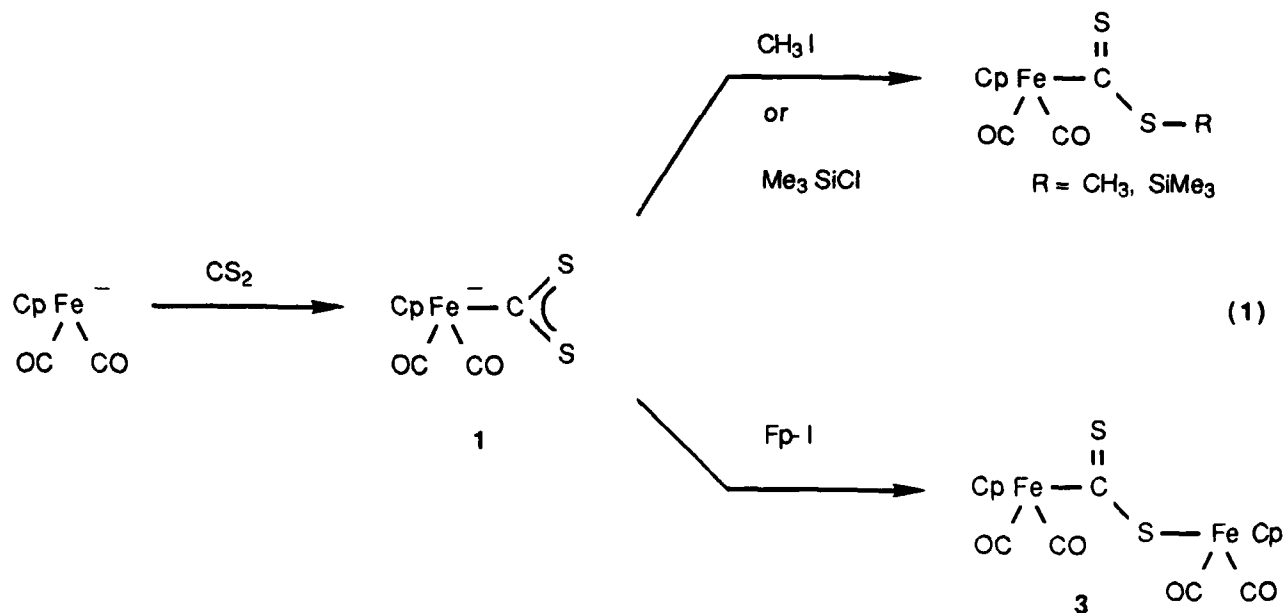
Abstract

Reactions of $\text{Fp-CS}_2^-\text{K}^+$ (1) and $\text{Fp-CO}_2^-\text{Na}^+$ (and Li^+) (2) [$\text{Fp}=(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}$] with organoiron electrophiles FpX ($\text{X}=\text{I}$, OSO_2CF_3 , HgCl), $(\eta^5\text{-C}_5\text{H}_5)\text{L}(\text{CO})\text{FeI}$ [$\text{L}=\text{P}(\text{OPh})_3$, PPh_3], and $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Fe}(\text{CH}_3\text{CN})_2^+\text{PF}_6^-$ are contrasted. Treatment of the CS_2 adduct 2 with the bis-acetonitrile salt gives the $\mu(\eta^1\text{-C}:\eta^2\text{-S,S'})$ CS_2 complex $\text{Fp-C}(\overline{\text{S}})\text{S-Fe}(\text{CO})\text{Cp}$ (4). Photolysis of the known $\mu(\eta^1\text{-C}:\eta^1\text{-S})$ CS_2 compound $\text{Fp-C}(\text{S})\text{S-Fp}$ (3) only generates traces of 3, in contrast. Reacting the CO_2 adduct 5 with the iron electrophiles $\text{Cp}(\text{L})(\text{CO})\text{Fe-I}$ affords Fp_2 , with only trace amounts of $\text{Fp-Fe}(\text{CO})(\text{L})\text{Cp}$ (for $\text{L}=\text{PPh}_3$ and $\text{P}(\text{OPh})_3$) evident. No $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ bimetallocooxylate intermediates $\text{Fp-C}(\text{O})\text{O-Fe}(\text{L})(\text{CO})\text{Cp}$ are detected. In contrast, Fp^-Na^+ upon treating with $(\eta^5\text{-C}_5\text{H}_5)\text{L}(\text{CO})\text{FeI}$ gives 1:1 mixtures of Fp_2 and $\text{Fp-Fe}(\text{CO})(\text{L})\text{Cp}$ (for $\text{L}=\text{PPh}_3$ and $\text{P}(\text{OPh})_3$). The bis-acetonitrile electrophile and 1 afford initially the mixed dimer $\text{Fp-Fe}(\text{CH}_3\text{CN})(\text{CO})\text{Cp}$, which degrades to Fp_2 at room temperature. Organic carboxylates RCO_2^-M^+ ($\text{R}=\text{Ph}$, CH_2Ph , and $t\text{-Bu}$; $\text{M}^+=\text{Li}^+$, Na^+ , K^+) do not react with $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Fe}(\text{CH}_3\text{CN})_2^+$; and photolysis of $\text{Fp}(\text{acetate})$ produces only Fp_2 , not an $(\eta^2\text{-O,O'})$ acetate complex $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{FeO}(\text{O})\text{CCH}_3$.

Introduction

Availability of analogous pairs of carbon dioxide [1] and carbon disulfide [2] transition-metal complexes permits comparing structure-bonding and chemical reactivity of these ligated heterocumulenes [3]. Such comparisons permit us to address the prevalent but questionable attitude that studying the generally more accessible CS₂ adducts affords insight into their less stable (or more labile) CO₂ congeners [4]. We are interested in one pair of (η¹-C)-bonded heterocumulene complexes, the Fe(CO)₂Cp metallodithiocarboxylates Fp-CS₂⁻ (Na⁺, K⁺) (1) [5] and metallocarboxylates Fp-CO₂⁻ (Li⁺, Na⁺) (2) [6]. Although 1 and 2 are unstable at room temperature and have not been isolated as solids, they exhibit high reactivity in solution towards electrophiles [7].

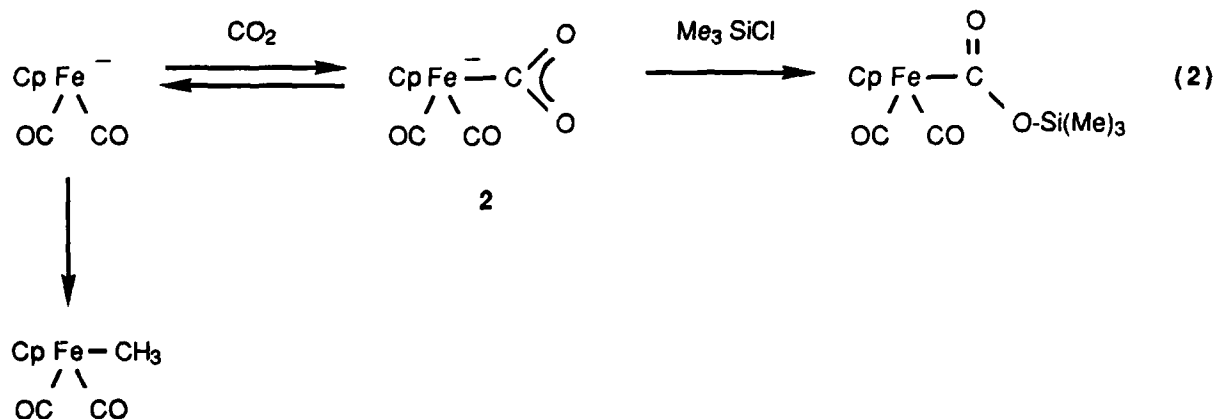
The Fp(dithiocarboxylate) anion (1) in particular readily reacts with a variety of Lewis acids. Alkylation or silylation of 1 at -20 °C gives stable dithiocarboxylate ester complexes (eq 1) [5,8]. Ellis [5] initially demonstrated that treating 1 with FpI affords the stable μ(η¹-C:η¹-S)



bis-Fp dithiocarboxylate 3 [8d,9c] in good yield. This μ-CS₂ adduct further serves as a useful

precursor to trimetallic $\mu(\eta^1\text{-C}:\eta^1\text{-S}:\eta^1\text{-S}')$ CS_2 derivatives. For example, electrophilic organoiron reagents that generate Fp^+ convert 1 into $\text{Fp-C}(\text{SFp})_2^+$ [9a]. These results appear general in that a variety of stable bimetallic and trimetallic $\mu\text{-CS}_2$ complexes derived from 1 have been characterized [9].

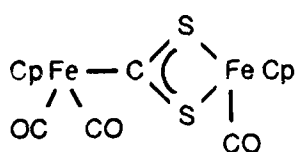
Reactions of the CO_2 complexes 2 with Lewis acids are more involved. Electrophilic methylating agents including methyl iodide and methyl triflate quantitatively convert 2 (Li^+ , Na^+ , or K^+) to Fp-CH_3 [6,10,11], a result that is consistent with these electrophiles intercepting a dissociative equilibrium between 2 and Fp^- (eq 2). Blocking this dissociation of 2 by using the



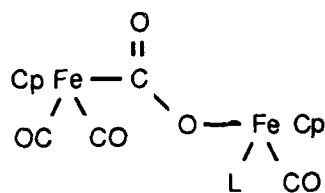
more oxophilic Mg^{+2} counterion, which evidently chelates 2 as a $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ metallo-carboxylate [$\text{Fp-C}(\text{O})\text{O}]_2\text{Mg}$], expedites methylation of 2 to selectively give its metalloester FpCO_2CH_3 in good yield [10b]. As an alternative strategy, using oxophilic trialkylsilyl chlorides efficiently traps 2 (Li^+ or Na^+) as its silylesters $\text{Fp-C}(\text{O})\text{O-SiMe}_2\text{R}$ ($\text{R}=\text{CH}_3$, *t*-Bu) [10e,12*]. The extremely robust Fp-SiMe_3 is not detected in these reactions. Results of reacting 2 with transition organometallic Lewis acids have not been reported; indeed, few bimetallic $\mu\text{-CO}_2$ adducts have been prepared [13].

In this paper we compare the reactivity of 1 and 2 towards organoiron electrophiles. These electrophiles were selected so as to contain either one or two accessible coordination sites [14]; Fp-X ($\text{X}=\text{I}$, OSO_2CF_3) and $\text{Cp}(\text{CO})\text{Fe}(\text{CH}_3\text{CN})_2^+\text{BF}_4^-$, respectively, are representative Lewis acids. Target molecules are the $\mu\text{-CS}_2$ complexes 3 [5] and 4 [9c] and the $\mu\text{-CO}_2$ metalcarboxylates 5 and 6.

* Reference numbers with asterisks indicate notes in the list of references.



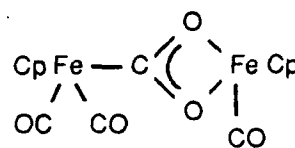
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5 (a) L = CO

(b) L = P(OPh)₃

(c) L = PPh₃



6

Experimental Section

Synthetic manipulations were performed under a nitrogen atmosphere using standard syringe-septum and Schlenk techniques or a glovebox [15]. Infrared spectra were taken as CH₂Cl₂ or THF solutions or as pressed KBr disks and were recorded on a Perkin-Elmer Model 297 spectrophotometer. The $\nu(\text{CO})$ frequencies (2200-1500 cm⁻¹) were calibrated against the polystyrene 1601 cm⁻¹ absorption; they are accurate to ± 2 cm⁻¹ below and ± 5 cm⁻¹ above 2000 cm⁻¹. NMR spectral data were obtained on a Varian Model XL-200 or a Bruker Model WP-100 spectrometer; chemical shifts (δ) are referenced to internal (CH₃)₄Si. Combustion microanalysis were done by Robertson Laboratory, Inc., Madison, NJ.

Organic reagents were obtained commercially and used as received. Dichloromethane was distilled under nitrogen from P₂O₅; anhydrous THF and diethyl ether were distilled from sodium benzophenone ketyl. Organometallic starting materials Fp₂ [16], FpCH₃ [16], FpI [16], FpHgCl [17], Fp⁻K⁺ [18], Cp(CO)Fe(CH₃CN)₂⁺PF₆⁻ [19], Cp(PPh₃)(CO)FeI [20], and Cp[P(OPh)₃](CO)FeI [21] were prepared by literature procedures and judged pure by IR and ¹H NMR spectroscopy.

Preparation of Cp(CO)₂Fe-C(S)S-Fe(CO)₂Cp (3).

The procedure of Ellis and coworkers [5] was followed. A THF solution of Cp(CO)₂Fe⁻Na⁺ (11.0 mmol, 150 mL), prepared by Na(Hg) cleavage of Fp₂ (2.00 g), was cooled to -78 °C and treated with carbon disulfide (1.5 mL, 22.8 mmol). Cp(CO)₂FeI (3.40 g, 11.2 mmol) then was added to the resulting dark red solution containing Cp(CO)₂FeCS₂⁻Na⁺ (1), and the reaction

solution was maintained at -78 °C (1 h). After warming (22 °C), the solution next was filtered through celite; the THF was evaporated; and the dark red powder was recrystallized twice from dichloromethane-heptane (-78 °C). Yield 4.58 g (97%) Fp-C(S)S-Fp (3); IR (THF) 2038, 2021, 1990(sh), 1979(br) cm^{-1} (CO); (CH_2Cl_2) 2040, 2025, 1994(sh), 1981(br) cm^{-1} (CO), 1005 cm^{-1} (CS); ^1H NMR (CDCl_3) δ 4.96 (CpFeS), 4.83 (CpFeC); ^{13}C NMR (CDCl_3) δ 298.2 (FeCS_2Fe), 214.0 and 212.6 (CO), 87.9 and 85.8 (Cp).

Preparation of $\text{Cp(CO)}_2\text{Fe-C(S)S-Fe(CO)Cp}$ (4).

In a glove box, FpK (0.496 g, 2.30 mmol) was transferred to a 250-mL side-arm flask. After removing from the glovebox, the flask was cooled (-78 °C) before adding 100 mL of THF. The orange solution turned red-orange as carbon disulfide (0.28 mL, 2.53 mmol) was added dropwise by syringe, IR spectral monitoring of the cold, dark-red solution (5 min) indicated completed conversion to $\text{FpCS}_2\text{-K}^+$ (1) [$\nu(\text{CO})$ 1998, 1944 cm^{-1}] plus varying amounts of Fp_2 (2-10%). In separate experiments, warming this solution above -20 °C exclusively affords Fp_2 ; $\{^1\text{H}\}^{13}\text{C}$ NMR spectra of 1- K^+ in THF (-78 °C): δ 308.9 (FeCS_2), 215.2 (CO), 88.0 (Cp).

The THF solution containing $\text{FpCS}_2\text{-K}^+$ (2) was treated with $\text{Cp(CO)Fe(CH}_3\text{CN)}_2\text{PF}_6^-$ (0.950 g, 2.53 mmol) and maintained at -78 °C (0.5 h). The resulting red-orange solution was warmed to room temperature before evaporating the solvent under reduced pressure and exhaustively extracting the residue with benzene (5x6 mL). Benzene was evaporated from the combined filtrates, and the resulting red solid was extracted with hexane. Flash column chromatography (silica gel, 4.5x15 cm column) of the combined red hexane extracts was used to separate the reaction mixture. Elution with 2% ethyl acetate in hexane removed faint yellow and brown bands; these afforded very small amounts of an unidentified material and Fp_2 , respectively. A final red band was eluted using 4-6% ethyl acetate in hexane; removal of solvent left 0.291 g of a red powder that was identified as Fp-C(S)S-Fe(CO)Cp (4) [9c] (31%): IR (CH_2Cl_2) 2025, 1989, 1938(br) cm^{-1} (CO); IR (KBr) 2028, 1980, 1913(br) (CO), 914, 875 cm^{-1} (CS_2); ^1H NMR (CDCl_3) δ 4.85 (Cp, FpC), 4.54 (Cp, CS_2FeCp); $\{^1\text{H}\}^{13}\text{C}$ NMR (CDCl_3) δ 306.3 (FeCS_2Fe), 218.6 (CO, CpFe(CO)), 212.2 (CO, Fp), 82.2 (Cp), 79.7 (Cp).

Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{Fe}_2\text{O}_3\text{S}_2$: C,41.82; H,2.53. Found: C,41.66; H,2.32.

Reaction of $\text{Cp}(\text{CO})_2\text{Fe-CO}_2^-\text{Na}^+$ (2) and $\text{Cp}(\text{CO})_2\text{FeI}$.

Carbon dioxide (11.2 cc, 0.50 mmol) was introduced slowly by syringe into a THF solution of Fp^-Na^+ (0.30 mmol, 4.5 mL) that was maintained at -78°C . The resulting yellow-brown solution of $\text{FpCO}_2^-\text{Na}^+$ (2) [11e] [IR after 2 min: $\nu(\text{CO})$ 2000, 1945 cm^{-1}] was treated with FpI (90 mg, 0.30 mmol). A red-brown solution was evident immediately; IR spectral monitoring within one minute of the cold solution indicated quantitative conversion to Fp_2 : $\nu(\text{CO})$ 1993, 1953, 1782 cm^{-1} . The solution was warmed to room temperature; the solvent was evaporated under reduced pressure; and the residue was extracted with 3x5 mL portions of diethyl ether. These combined ether extracts were passed through a 2 cm pad of alumina, which was further eluted with ether. The resulting purple filtrate was evaporated to leave 47 mg of purple brown crystals, for which the ^1H NMR spectrum indicated pure Fp_2 (89% yield).

Reaction of $\text{Cp}(\text{CO})_2\text{Fe-CO}_2^-\text{Li}^+$ (2) and $\text{Cp}(\text{CO})_2\text{FeOSO}_2\text{CF}_3$.

$\text{Fp}(\text{triflate})$ was prepared by adding HOSO_2CF_3 (0.29 mL, 3.25 mmol) over a 1 min period to a dichloromethane solution (30 mL) of FpCH_3 (0.625 g, 3.25 mmol). Reaction was instantaneous, as indicated by vigorous gas evolution; IR spectral monitoring was consistent with FpCH_3 quantitatively converting to $\text{FpOSO}_2\text{CF}_3$: $\nu(\text{CO})$ 2078, 2032 cm^{-1} . The product was crystallized from a mixture of dichloromethane (7 mL) and 1:1 ether-hexane (30 mL) with scratching: 629 mg of dark purple crystals that were spectroscopically identified as $\text{FpOSO}_2\text{CF}_3$ [22], ^1H NMR (CDCl_3) δ 5.04 (Cp).

$\text{Fp}(\text{triflate})$ (400 mg, 1.20 mmol) was added to a THF solution of $\text{FpCO}_2^-\text{Li}^+$ (2), which was generated by adding CO_2 (33 cc, 1.50 mmol) to FpLi (15.0 mL, 1.00 mmol) at -78°C [10c]. IR spectral analysis of the resulting cold, red-brown solution established complete conversion to Fp_2 , which was isolated after column chromatography on activity 3 alumina (168 mg, 94% yield).

Reaction of $\text{Cp}(\text{CO})_2\text{Fe-CO}_2^-\text{Fe-CO}_2^-\text{Li}^+$ (2) and $\text{Cp}(\text{CO})_2\text{FeHgCl}$.

A THF solution of Fp^-Li^+ (1.00 mmol, 15 mL) was converted to $\text{FpCO}_2^-\text{Li}^+$ (2) using CO_2

(33 cc, 1.5 mmol) at $-78\text{ }^{\circ}\text{C}$ and then was treated with FpHgCl (0.412 g, 1.00 mmol). IR spectral monitoring of the resulting orange-brown solution that immediately formed was consistent with quantitative conversion of **2** to Fp_2Hg : IR 1985, 1959, 1925 cm^{-1} . Less than 5% of Fp_2 was detected by the presence of its bridging carbonyl $\nu(\text{CO})$ at 1785 cm^{-1} . The solution was warmed to room temperature before evaporating the solvent and exhaustively extracting the residue with ether (4x6 mL). Combined extracts were concentrated to give orange-brown crystals (0.489 g) that were identified as spectroscopically pure Fp_2Hg [23] (90%): ^1H NMR (CDCl_3) δ 4.70 (Cp), vs δ 4.95 (Cp) for FpHgCl and δ 4.78 (Cp) for Fp_2 .

Reaction of $\text{Cp}(\text{CO})_2\text{Fe}-\text{CO}_2^-\text{Na}^+$ (**2**) with $\text{Cp}[\text{P}(\text{OPh})_3](\text{CO})\text{FeI}$.

A solution of Fp^-Na^+ in THF (1.00 mmol, 15.0 mL) was converted to $\text{FpCO}_2^-\text{Na}^+$ (**2**) at $-78\text{ }^{\circ}\text{C}$ and then was treated with $\text{Cp}[\text{P}(\text{OPh})_3](\text{CO})\text{FeI}$ (586 mg, 1.00 mmol). IR spectral monitoring of the cold, red-brown solution was consistent with immediate conversion of **2** to Fp_2 , as judged by the intensity of its bridging carbonyl $\nu(\text{CO})$ at 1784 cm^{-1} . A weak absorption, $\nu(\text{CO})$ 1757 cm^{-1} , was tentatively assigned to the mixed dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$, [24a] which however would be present only in low concentration (<15%). No further transformations occurred as established by IR spectral monitoring at room temperature. ^{31}P NMR spectra of the reaction mixture had major absorptions at δ 182.4 [$\text{Cp}_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$] and at δ 168.4 [$\text{Cp}[\text{P}(\text{OPh})_3](\text{CO})\text{FeI}$].

The crude reaction product was chromatographed on activity 3 alumina (neutral), eluting with 10-20% dichloromethane in hexane. Much decomposition was noted at the top of the column. A reddish purple band was eluted using 10% CH_2Cl_2 ; and a green band was removed using 15-20% CH_2Cl_2 , with no other bands detected. The first band afforded spectroscopically pure Fp_2 (101 mg, 58% yield); the second band left 141 mg of $\text{Cp}[\text{P}(\text{OPh})_3](\text{CO})\text{FeI}$ as a green solid (24% recovery): IR (THF) 1981 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.28 (m, OPh), 4.21 (s, Cp); ^{31}P NMR (CDCl_3) δ 171.8.

As a control reaction, a THF solution of Fp^-Na^+ (3.0 mL, 0.18 mmol) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated with $\text{Cp}[\text{P}(\text{OPh})_3](\text{CO})\text{FeI}$ (110 mg, 0.19 mmol). IR spectral monitoring of the cold,

red-brown solution was consistent with the presence of both Fp_2 and $\text{Cp}_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$ [24] [$\nu(\text{CO})$ 1992, 1954, 1784, 1757 cm^{-1}], although the proportion of Fp_2 to the mixed dimer increased with time: 3:2 (1 min), 1:1 (10 min), 1:1.2 (20 min at 0 °C to 1 h at 22 °C). Column chromatography of the residue on silica gel (2:1-1:1 hexane-benzene) or on activity 3 alumina (neutral) (5% ethyl acetate-hexane or 10% dichloromethane-hexane) did not adequately resolve the two red-brown bands. These were collected as one fraction, which afforded a dark red solid (58 mg) as a 1:1.2 mixture of Fp_2 and $\text{Cp}_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$: ^1H NMR (CDCl_3) δ 4.80 and 4.08 (s, Cp, mixed dimer), 4.78 (s, Cp, Fp_2).

Reaction of $\text{Cp}(\text{CO})_2\text{Fe-CO}_2^-\text{Na}^+$ (2) and $\text{Cp}(\text{CO})\text{Fe}(\text{CH}_3\text{CN})_2^+\text{PF}_6^-$.

A solution of Fp^-Na^+ in THF (1.0 mmol, 15.0 mL) was converted to a yellow-brown solution of $\text{FpCO}_2^-\text{Na}^+$ (2) at -78 °C, to which $\text{Cp}(\text{CO})\text{Fe}(\text{CH}_3\text{CN})_2^+\text{PF}_6^-$ (376 mg, 1.00 mmol) was added. The clear purple solution that resulted was examined by IR spectroscopy. Three products were immediately detected as a 2:1:1 mixture of Fp_2 [$\nu(\text{CO})$ 1993, 1952, 1785 cm^{-1}], FpH [10a,25] [$\nu(\text{CO})$ 2017, 1952 cm^{-1}], and an unidentified material [$\nu(\text{CO})$ 1993, 1952, 1756 cm^{-1}]. IR spectra of this purple solution after sitting at 22 °C (20 min) indicated only the presence of Fp_2 : its concentration had increased at the expense of the other two components. Ether extracts of the crude reaction mixture were chromatographed on alumina, from which a single red-brown band was eluted with ether. This afforded 285 mg of reddish purple crystals of spectroscopically pure Fp_2 (0.81 mmol). Considerable amounts of brown decomposition residues also were evident at the top of the column.

Results and Discussion

Reactions of FpCS_2^- (1)

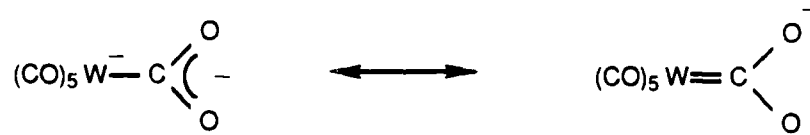
We repeated Ellis', synthesis of Fp-C(S)S-Fp (3) (eq 1) as a control for subsequent reactions of FpCS_2^- (1) and of FpCO_2^- (2) with organoiron electrophiles. As reported [6], the reaction of 1 and FpI affords the stable $\mu(\eta^1\text{-C}:\eta^1\text{-S})$ CS_2 adduct 3 in essentially quantitative yield. Table 1 contains ^{13}C NMR spectral data for 1 and 3, as well as for related CS_2^- and CO_2^- containing complexes.

Insert Table 1

The difference in chemical shifts for molecular CS₂ and CO₂ resembles the downfield trend that sp² carbons of organic thiones exhibit as compared to their carbonyl analogues. This downfield shift represents greater paramagnetic shielding for the carbon center of the CS double bond [26], a shift that also occurs for the metalloester FpC(O)OCH₃ and metallodithioester FpC(S)SCH₂Ph compounds tabulated. Data for this dithioester complex also is similar to that of FpC(S)Fp (3).

Upon coordinating Fp⁻, CO₂ and CS₂ exhibit 85 and 107 ppm downfield shifts, respectively (Table 1). The resulting (η¹-C) metallodithiocarboxylate 1 and metallo-carboxylate 2 structures are consistent with IR spectral data (which preclude other reasonable structures [7]) and with theoretical arguments (for 1 [2a]). The chemical shifts for the heterocumulene centers on 1 and 2 indicate the extent of carbon hybridization and of charge delocalization involving the heteroatoms. Corresponding dimethoxycarbene and dithiomethoxycarbene compounds [Fp-C(XCH₃)₂]⁺ (X=O, S), which have considerable charge delocalization, also display downfield shifts of their carbon centers.

The ¹³C NMR spectral data for 1 also compares with that of the anionic tungsten CO₂ adduct (CO)₅WCO₂²⁻, δ 223.4 in THF. Cooper [4a] demonstrated that NMR and IR spectral data support a superposition of the resonance structures for this adduct,

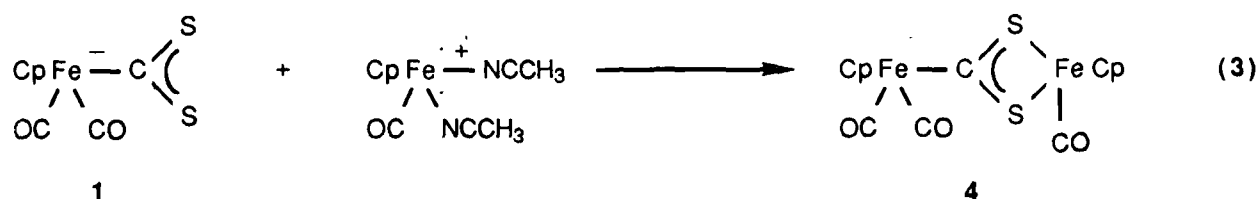


The IR spectrum resembles those of anionic pseudohalide complexes, e.g., (CO)₅WOC(O)CH₃⁻, in which the charge localizes on the W(CO)₅ moiety. The magnitude of the coupling constant J_{W-C} for the CO₂ center on (CO)₅WCO₂²⁻ indicates extensive W=C double bonding, thus favoring charge localization on the oxygens.

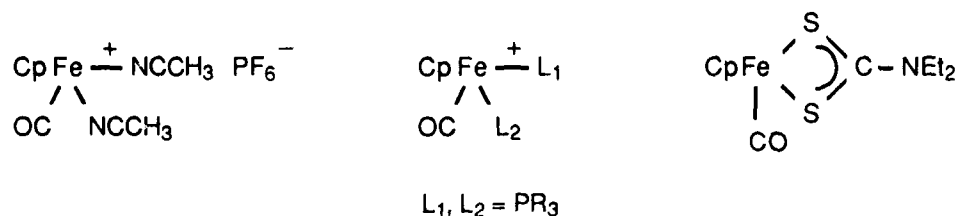
The bis-iron μ-(η¹-C:η²-S,S') CS₂ complex, Fp-C(S)S-Fe(CO)Cp (4), because of the presence of its chelating dithiocarboxylate structure, served as a synthetic objective. Busetto and

coworkers [9] demonstrated the thermodynamic stability that is associated with such chelating ligands; for example, Fp-C(S)S-Mn(CO)_5 spontaneously transforms into its chelated derivative $\text{Fp-C}(\overline{\text{S}})\text{S-Mn(CO)}_4$ [9b]. We prepared **4**, a known compound [9c], from the reaction between FpCS_2^- (**1**) and an appropriate organoiron electrophile. This methodology then would be extended to synthesizing the congeneric $\mu\text{-CO}_2$ compound **5**. (Most of the known bimetallic and trimetallic CO_2 complexes retain similar analogous chelated metallocarboxylate structures [13].)

We selected $\text{Cp(CO)Fe(CH}_3\text{CN)}_2^+\text{PF}_6^-$ [19] as the organometallic Lewis acid of choice [14] — one that bears two accessible coordination sites — to convert the CS_2 complex **1** to **4** (eq 3). In previous studies, we documented that this labile bis-acetonitrile complex readily exchanges



its ligated acetonitrile for a variety of phosphines and phosphites in dichloromethane [19b], an exchange that can be carried out stepwise in order to bind two different phosphorus-donor ligands. A particularly relevant observation [19b] is that the room-temperature reaction between $\text{Cp(CO)Fe(CH}_3\text{CN)}_2^+\text{PF}_6^-$ and $\text{Et}_2\text{NCS}_2^-\text{Na}^+$ in THF selectively affords the $(\eta^2\text{-S,S'})$ chelate $\text{Cp(CO)Fe-SC(S)NEt}_2$ (73% yield) that is uncontaminated by the $\text{Fp}(\eta^1\text{-S})$ dithiocarbamate $\text{Cp(CO)}_2\text{Fe-SC(S)NEt}_2$.



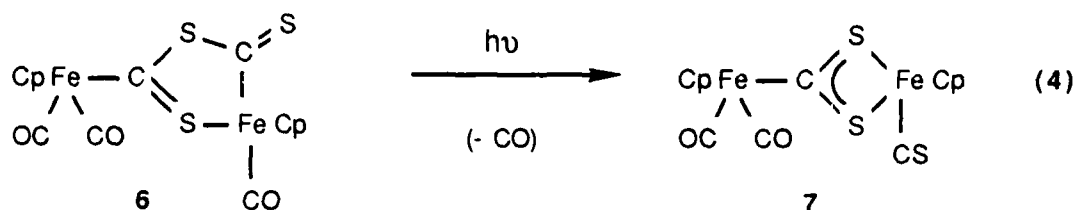
Treatment of the same labile bis-acetonitrile salt with $\text{FpCS}_2^-\text{K}^+$ (**1**) in THF (-78°C) gives the desired $\mu(\eta^1\text{-C}:\eta^2\text{-S,S'})$ dithiocarboxylate **4** in moderate yield. The actual yield corresponding to **4** isolated by column chromatography, however, varied between 21 and 45% in

six experiments.

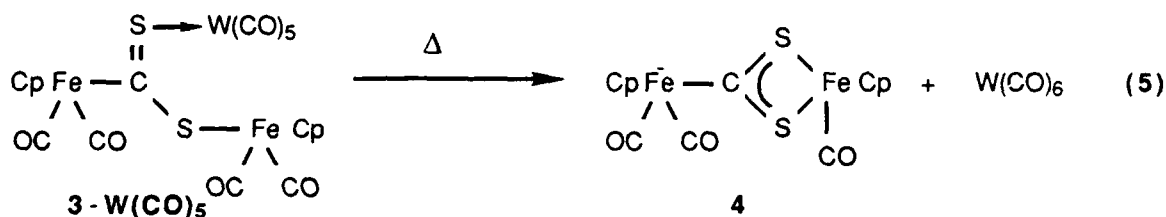
Near insolubility of the bis-acetonitrile iron reagent, particularly at lower temperatures, could account for the moderate yields observed. A sluggish reaction (eq 3), whatever the cause, expedites deleterious side reactions that are attributed to decomposition of **1** (above -20 °C) and of $\text{Cp}(\text{CO})\text{Fe}(\text{CH}_3\text{CN})_2^+ \text{PF}_6^-$ in THF. We previously noted that this bis-acetonitrile salt degrades in THF (as a suspension at room temperature) to an intermediate that has been formulated as $\text{Cp}(\text{CO})(\text{THF})\text{Fe}(\text{CH}_3\text{CN})^+$, which then rapidly decomposes to insoluble residues.[19b]

Reaction between $\text{FpCS}_2\text{-Na}^+$ (**1-Na**⁺) and $\text{Cp}(\text{CO})\text{Fe}(\text{CH}_3\text{CN})_2^+ \text{PF}_6^-$ under otherwise identical conditions affords complex mixtures. These were not adequately separated by column chromatography; ¹H NMR spectral analysis of the crude reaction mixture indicated the presence of 6-10 CpFe singlets (δ 5.2 - 4.50) of comparable intensities.

IR and ¹H NMR spectral data for the stable red solid resulting from the reaction of $\text{FpCS}_2\text{-K}^+$ (**1**) and $\text{Cp}(\text{CO})\text{Fe}(\text{CH}_3\text{CN})_2^+$ matches that previously reported for **4** [9c]. The presence of three carbonyl stretching frequencies [2025, 1989 cm^{-1} for Fp, and 1938 cm^{-1} for $\text{Cp}(\text{CO})\text{Fe}$] and of the expected [9] two thiocarboxylate $\nu(\text{CS}_2)$ absorptions [914, 875 cm^{-1}] for chelating dithiocarboxylate are particularly diagnostic. These absorptions closely correspond to similar values reported for the thiocarbonyl analogue **7** (eq 4): $\nu(\text{CO})$ 2030, 1987 cm^{-1} ; $\nu(\text{CS}_2)$ 913, 880 cm^{-1} . Our ¹³C NMR spectral data for **4** resembles that of **6** [27*] and of $[\text{FpC}(\text{SFp})\text{-(SCH}_3\text{)}]^+$ [8d], with their corresponding Fp-bound dithiocarboxylate carbons producing signals at δ 306, 329, and 315, respectively.



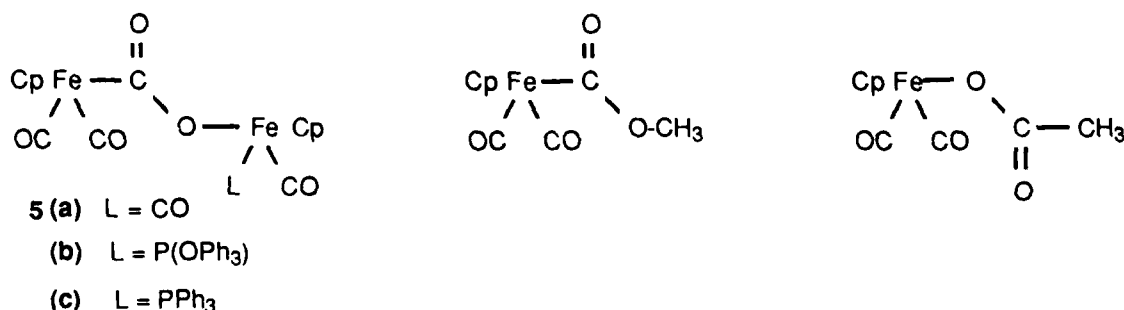
Busetto and coworkers [9c] previously obtained **4** from the thermal decomposition of the $\text{W}(\text{CO})_5$ -adduct of **3** (eq 5). Under the relatively mild conditions of this reaction (refluxing dichloromethane, 40 °C), $\text{W}(\text{CO})_5$ -**3** affords **4** in 70% yield. In contrast, thermolysis of $\text{FpC}(\text{S})\text{SFp}$ (**3**) requires refluxing octane (126 °C) before extruding CS_2 and leaving Fp_2 .



Photolysis of **3** also is reported to give **4** in 17% yield [9c]. We repeated this photolysis in benzene and in THF (+5 °C) using both a Rayonet photochemical reactor (λ 3550 Å) and a Hanovia medium-pressure mercury-vapor lamp. In all cases starting material was consumed, but isolated yields of **4** after column chromatography uniformly were less than 10%. Dimeric Fp_2 appears as the other major isolated product (less than 10% yield); other decomposition products(s) do not elute from silica gel chromatography columns.

Reactions of FpCO_2^- (2)

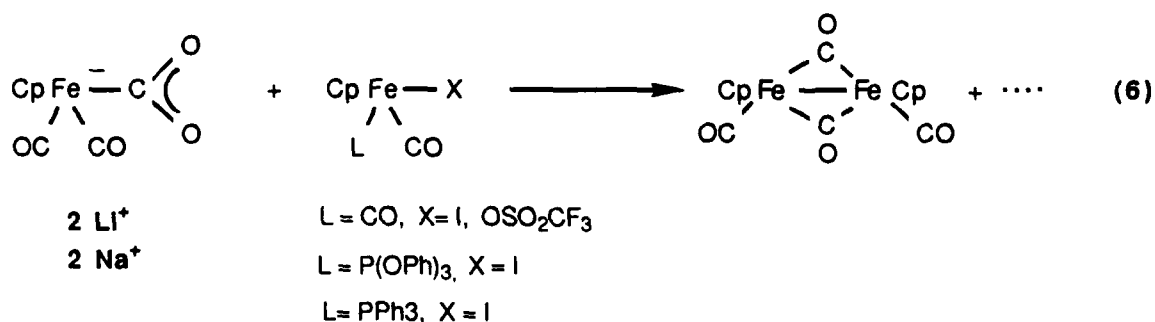
Bis-iron $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ CO_2 complexes **5a-c** offer plausible synthetic objectives in view of the thermal stability of the CS_2 congener **3**. Complex **5a** should retain $(\eta^1\text{-C})$ and $(\eta^1\text{-O})$ bonding analogous to that found in the stable methyl ester, $\text{Fp-C}(\text{O})\text{OCH}_3$ [10b], and acetate, $\text{Fp-OC}(\text{O})\text{CH}_3$ [28], complexes. These structural features will prevail only if structures **5a-c** do not



readily extrude CO_2 and leave the iron-iron dimer Fp_2 . A similar thermodynamic driving force occurs with related bimetallic ethane-1,2-diyl complexes $\text{M-CH}_2\text{CH}_2\text{-M}$, which commonly release M_2 and ethylene [29].

Fp(methylester) and Fp(acetate) complexes also serve as useful models in terms of relating their IR spectral data to that anticipated for **5a**. Since their moderately intense ester and acetate IR $\nu(\text{CO})$ absorptions appear at 1647 and 1617 cm^{-1} , respectively, we expect that **5a** would have a similar absorption in the region of 1600-1650 cm^{-1} [30*]. This IR spectral region is particularly convenient to monitor as it is devoid of terminal carbonyl absorptions (2040-1940 cm^{-1}), which typically overlap in mixtures of Fp-X compounds. The bridging carbonyl $\nu(\text{CO})$ for Fp₂ appears at 1784 cm^{-1} (THF), and similar absorptions for binuclear complexes Cp₂(CO)₃Fe₂(L) [L=P(OPh)₃, and PPh₃] [24] also anticipated byproducts in attempted syntheses of **5b,c**, appear within 1700-1750 cm^{-1} .

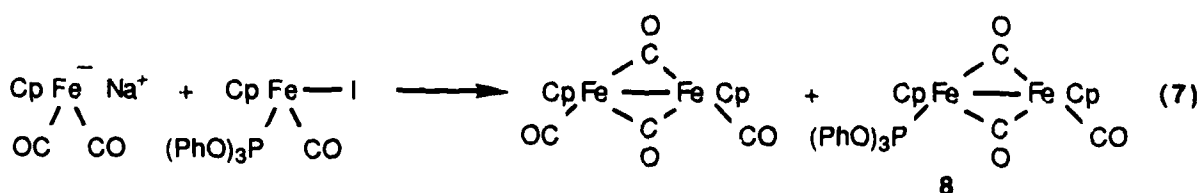
Our synthetic approach involved reacting THF solutions of FpCO₂⁻ (2-Na⁺ and 2-Li⁺) at -78 °C with the organoiron electrophiles (eq 6) and then immediately monitoring the cold solutions by IR spectroscopy, with particular attention accorded to the 1600-1650 cm^{-1} region. Initial IR data typically were recorded within 2 minutes of mixing **2** and the iron Lewis acid and at an IR cell temperature of ca. 0 °C.



Treatment of FpCO₂⁻ (2-Li⁺, 2-Na⁺) with either FpI or Fp(triflate) at -78 °C immediately and quantitatively affords Fp₂. Isolated yields of Fp₂ after column chromatography were routinely 85-95%, increasing slightly with the scale of the reaction. Attempts to use Fp(THF)⁺BF₄⁻ [33] as the organoiron electrophile were thwarted by its insolubility in THF at -78 °C. After reacting it with 2-Li⁺ (0.50 mmol scale) for 10 minutes and filtering the cold suspension, we recovered 94% of the starting Fp(THF)⁺ salt. An IR spectrum of the supernatant solution indicated quantitative conversion of 1-Li⁺ to Fp₂.

The reaction between 2-Li^+ or 2-Na^+ and $\text{Cp}[\text{P}(\text{OPh})_3](\text{CO})\text{FeI}$ likewise produces Fp_2 as the predominant organometallic species, although small amounts (10%) of the phosphite-substituted dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$ (**8**) [24a] also forms. Concentrations of this mixed dimer, estimated by IR spectral monitoring, did not change during the course of the reaction, 2 min (-78°C) to 1 h ($+22^\circ\text{C}$). ^{31}P NMR spectra of the crude reaction mixture at room temperature established the presence of this dimer as well as the starting iron-iodide complex. A typical chromatographic workup of the reaction between 2-Na^+ and $\text{Cp}[\text{P}(\text{OPh})_3](\text{CO})\text{FeI}$ delivers Fp_2 (58% yield) and starting iron iodide (24% recovery) in addition to considerable amounts of decomposition residues.

Reaction between Fp^-Na^+ and $\text{Cp}[\text{P}(\text{OPh})_3](\text{CO})\text{FeI}$ under otherwise identical conditions gives different results (eq 7). Substantial amounts of phosphite-substituted dimer **8** along with Fp_2 are evident even in the early stages of the reaction. The concentration of $\text{Cp}_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$ (**8**) increases with time at the expense of Fp_2 , so that at room temperature (1 h elapsed time) a final 1:1.2 mixture of Fp_2 to **8** prevails.



Results for the $\text{Fp}^-\text{Na}^+ / \text{Cp}[\text{P}(\text{OPh})_3](\text{CO})\text{FeI}$ reactions are complicated. A straightforward coupling of the two iron centers does not occur since approximately 50% of the reaction product is Fp_2 . Of the $\text{Cp}_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$ (**8**) that does form, at least 16% (and quite possibly more) of it derives from the Fp_2 . This mixed dimer **8** apparently doesn't result from Fp^- promoting CO displacement on Fp_2 , since treating $\text{Fp}_2 / \text{P}(\text{OPh})_3$ mixtures (1:2) with 0.10 or 1.0 molar equivalents of Fp^-Na^+ in THF (-20°C) does not give any detectable **8**. Others previously noted that Fp_2 is thermally unreactive towards phosphines and phosphites at room temperature [24].

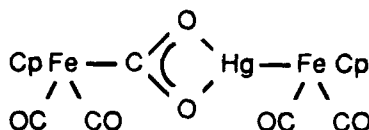
Metalloxyanion $\text{FpCO}_2^-\text{Na}^+$ (**2**) and metalate Fp^-Na^+ afford different product mixtures upon combining with $\text{Cp}[\text{P}(\text{OPh})_3](\text{CO})\text{FeI}$. The reaction involving **2** (eq 6) produces very little of $\text{Cp}_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$ (**8**) even though it is stable under the experimental conditions. Isolation

of Fp_2 as the major product is consistent with 2 interacting with the iron iodide by an electron transfer process that ultimately affords 17-electron intermediates $\text{Cp}(\text{L})(\text{CO})\text{Fe}^\cdot$ ($\text{L}=\text{CO}$, $\text{P}(\text{OPh})_3$). Others have established that these substituted odd-electron species (e.g., $\text{L}=\text{P}(\text{OPh})_3$), which remain after ligand dissociation from 19-electron intermediates $\text{Cp}(\text{L})(\text{CO})\text{FeX}^\cdot$ or $\text{Cp}(\text{L})(\text{CO})_2\text{Fe}^\cdot$ [34], preferentially give unsubstituted dimer Fp_2 [12a*,35]. The main observation is that FpCO_2^- (1) does not dissociate CO_2 and react as $\text{Fp}^\cdot$ with $\text{Cp}[\text{P}(\text{OPh})_3](\text{CO})\text{FeI}$, although further mechanistic studies clearly are needed.

This electron transfer process also could account for the Fp_2 product that results from treating $\text{FpCO}_2^-\text{Na}^+$ (2) with FpI or $\text{Fp}(\text{triflate})$. Electron transfer affords odd-electron transient species $\text{FpX}^\cdot$ and $(\text{FpCO}_2)^\cdot$ that degrade to the 17-electron $\text{Fp}^\cdot$, which dimerizes. Lee and Cooper [11b] advanced a similar mechanism to account for their observation that $\text{FpCO}_2^-\text{Li}^+$ (2) reacts with $\text{FpCO}^+\text{BF}_4^-$ to give exclusively Fp_2 .

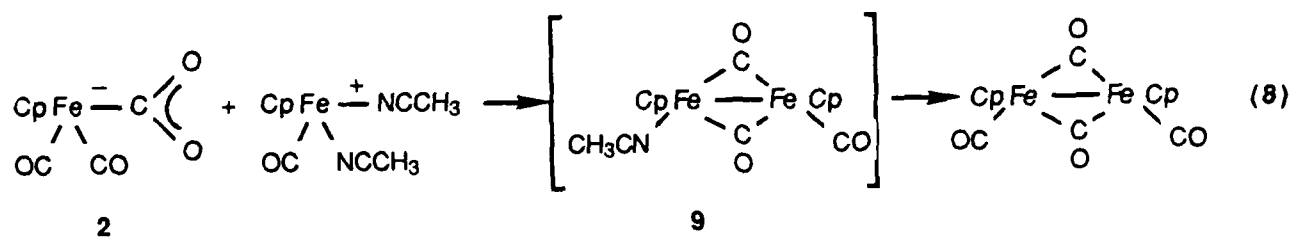
Reactions between the triphenylphosphine-substituted iron iodide, $\text{Cp}(\text{PPh}_3)(\text{CO})\text{FeI}$, and $\text{FpCO}_2^-\text{Na}^+$ (2) or Fp^-Na^+ afford results that are very similar to those observed for the phosphite-containing analogue $\text{Cp}[\text{P}(\text{OPh})_3](\text{CO})\text{FeI}$, as ascertained by IR spectral monitoring. The documented thermal instability of the mixed dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{PPh}_3)$ at room temperature [24b] precluded further analysis or workup of these reactions, however.

We examined the reaction of FpHgCl with $\text{FpCO}_2^-\text{Li}^+$ (2) in an attempt to generate an $(\eta^2\text{-O,O'})$ $\text{Fp}(\text{carboxylate})\text{-Hg(II)}$ derivative. Electrophilic FpHgCl had been used in forming metal-Hg(II) bonds to metal clusters[36] (the FpHg^+ intermediate is isolobal with H^+ , CH_3^+ , or



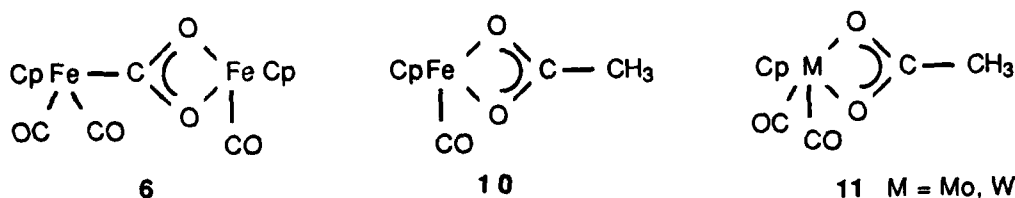
$(\text{PPh}_3)\text{Au}^+$). Our reaction, however, promptly and quantitatively generated Fp_2Hg .

Treatment of the labile bis-acetonitrile salt $\text{Cp}(\text{CO})\text{Fe}(\text{CH}_3\text{CN})_2^+\text{PF}_6^-$ with $\text{FpCO}_2^-\text{Na}^+$ (2) (eq 8) initially generates a complex mixture of Fp_2 , FpH [10b,25], and an unidentified component having a bridging carbonyl $\nu(\text{CO})$ at 1756 cm^{-1} (eq. 8). Upon warming this mixture to room temperature, only Fp_2 is evident during IR spectral monitoring (isolated yield 41%).



We formulate the unidentified component as the mono-acetonitrile adduct of Fp_2 : $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CH}_3\text{CN})$ (9). Related dimers $\text{Cp}_2\text{Fe}_2(\text{CO})_3[\text{P}(\text{OPh})_3]$ (8) and $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$ likewise exhibit lower energy bridging carbonyl $\nu(\text{CO})$ at 1757 and 1733 cm^{-1} (with respect to Fp_2 , $\nu(\text{CO})$ 1782 cm^{-1} , also in THF). Labinger [37] previously prepared 9 by photolysis of Fp_2 in acetonitrile and documented its solution instability.

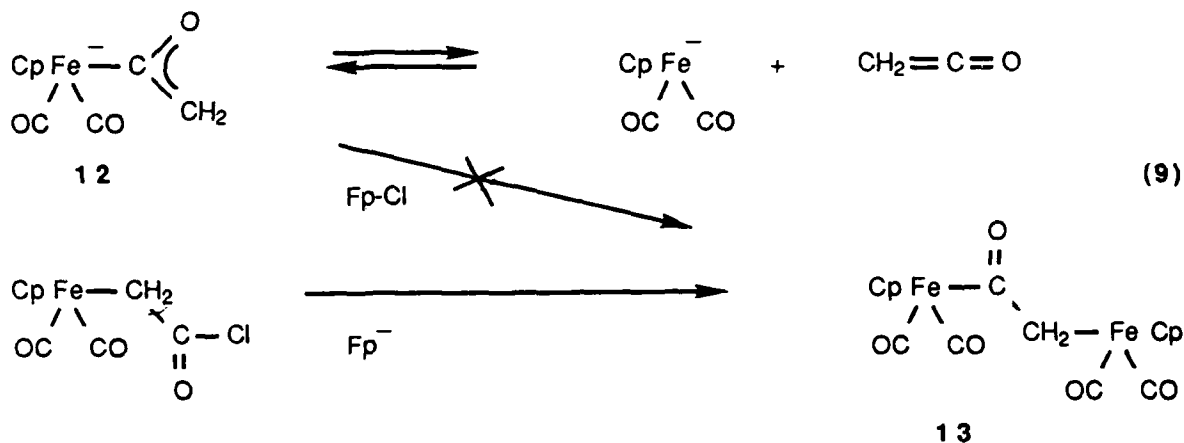
Our inability to generate the chelating bis-iron $\mu(\eta^1\text{-C}:\eta^2\text{-O,O'})$ CO_2 complex 6 raised the question: could analogous chelating organic carboxylate complexes 10 be prepared? Werner [38] reported that corresponding molybdenum and tungsten acetate chelates 11 are the stable products of warming the $(\eta^1\text{-O})$ acetates $\text{Cp}(\text{CO})_3\text{M-OC(O)CH}_3$.



We found that the bis-acetonitrile salt $\text{Cp}(\text{CO})\text{Fe}(\text{CH}_3\text{CN})_2^+ \text{PF}_6^-$ is inert to the carboxylate salts $\text{PhCO}_2^-\text{Li}^+$, $\text{Me}_3\text{CCO}_2^-\text{Li}^+$, $\text{PhCH}_2\text{CO}_2^-\text{Li}^+$ and $\text{PhCO}_2^-\text{Na}^+$ in THF solution. These carboxylates remain unchanged (IR spectral monitoring of $\nu(\text{CO}_2)$ region 1550 to 1620 cm^{-1}) as the iron-acetonitrile complex degrades (1 h, 20 °C) to insoluble residues. Attempts to prepare the chelating acetate complex 10 ($\text{R}=\text{CH}_3$) by photolysis of FpOC(O)CH_3 also failed. Irradiation (Rayonet Reactor, 3500 Å) in either benzene or THF solution (10 °C) degraded Fp acetate to Fp_2 and insoluble residues.

Reaction chemistry of FpCO_2^- (2) resembles that of the $(\eta^1\text{-C})$ ketene complex $\text{Fp}(\text{CH}_2\text{CO})^-$ (12). Helquist [39] first generated this heterocumulene adduct by deprotonating

FpCOCH_3 at low temperature, and Akitah and coworkers [31] demonstrated that **12** equilibrates with Fp^- and free ketene above -50°C . Attempts to intercept **12** with FpCl and generate $\text{FpC(O)CH}_2\text{-Fp}$ (**13**) produced only Fp_2 (eq 9). The desired μ -ketene compound **13** does form,



however, by metallating the chloroacetyl compound $\text{FpCH}_2\text{C(O)Cl}$ with Fp^- ; the resulting **13** is a thermally stable molecule that only extrudes ketene after photolysis. Our inability to generate μ - CO_2 compounds **5** and **6** likewise may not be due to their thermodynamic instability, but may indicate a need to alter the synthetic approach.

Conclusions

We did not convert the metallocarboxylate FpCO_2^- (**2**) to bimetallic CO_2 adducts FpC(O)OFp (**5a**) or Fp-C(O)O-Fe(CO)Cp (**6**) under conditions that the corresponding μ - CS_2 adducts **3** and **4**, respectively, readily form using FpCS_2^- (**2**). Either **5** or **6** could have been transient intermediates that quickly degraded, perhaps by a pathway involving odd-electron organometallic intermediates. We disfavor this explanation because there is no apparent reason why **5** and **6**, once formed, should be less stable than their CS_2 congeners or even the μ -ketene compound $\text{FpC(O)CH}_2\text{-Fp}$ (**13**) [40]. A more plausible interpretation of our results is that FpCO_2^- (**2**) reacts with the organoiron electrophiles by an alternative pathway not involving either prior dissociation of CO_2 or coupling of **2** and the metal Lewis acid.

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Table 1 ¹³ C NMR Spectral Assignments (δ)		
	δ (CDCl ₃)	Reference
O=C=O	132.0	a
S=C=S	192.5	a
$ \begin{array}{c} \text{O} \\ \parallel \\ \text{Cp Fe} - \text{C} \\ \diagup \quad \diagdown \\ \text{OC} \quad \text{CO} \quad \text{O} \\ 2 \end{array} \quad \text{Li}^+ $	217.0	b,c
$ \begin{array}{c} \text{S} \\ \parallel \\ \text{Cp Fe} - \text{C} \\ \diagup \quad \diagdown \\ \text{OC} \quad \text{CO} \quad \text{S} \\ 1 \end{array} \quad \text{K}^+ $	308.9	b,d
$ \begin{array}{c} \text{O} \\ \parallel \\ \text{Cp Fe} - \text{C} \\ \diagup \quad \diagdown \\ \text{OC} \quad \text{CO} \quad \text{O-CH}_3 \end{array} $	213.3	c
$ \begin{array}{c} \text{S} \\ \parallel \\ \text{Cp Fe} - \text{C} \\ \diagup \quad \diagdown \\ \text{OC} \quad \text{CO} \quad \text{S-CH}_2\text{Ph} \end{array} $	287.6	e
$ \begin{array}{c} \text{OCH}_3 \\ \parallel \\ \text{Cp Fe} - \text{C} \\ \diagup \quad \diagdown \\ \text{OC} \quad \text{CO} \quad \text{OCH}_3 \\ + \text{PF}_6^- \end{array} $	251.9	f
$ \begin{array}{c} \text{SCH}_3 \\ \parallel \\ \text{Cp Fe} - \text{C} \\ \diagup \quad \diagdown \\ \text{OC} \quad \text{CO} \quad \text{SCH}_3 \\ + \text{PF}_6^- \end{array} $	304.3	f
$ \begin{array}{c} \text{S} \\ \parallel \\ \text{Cp Fe} - \text{C} \\ \diagup \quad \diagdown \\ \text{OC} \quad \text{CO} \quad \text{S-Fe Cp} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{OC} \quad \text{CO} \\ 3 \end{array} $	298.2	d
$ \begin{array}{c} \text{S} \\ \parallel \\ \text{Cp Fe} - \text{C} \\ \diagup \quad \diagdown \\ \text{OC} \quad \text{CO} \quad \text{S-Fe Cp} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{OC} \quad \text{CO} \\ 4 \end{array} $	306.3	d

Table 1 (Cont.)

- a. Reference 26.
- b. Recorded in THF (-78 °C).
- c. Reference 10c.
- d. This work.
- e. This work, compound prepared according to Angelici's procedure [8c], other absorptions: δ 213.4 (CO), 137.1, 129.9, 129.3, 127.8 (Ph), 88.2 (Cp), 46.8 (CH₂).
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