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Reactions of carbon disulfide and carbon dioxide adducts $(\eta\text{-}C_5H_5)(CO)_2Fe\text{–}CX_2^-$ with organoiron electrophiles

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Abstract

Reactions of $FpCS_2^-K^+$ (**1**) and $FpCO_2^-Na^+$ (and Li^+) (**2**) ($Fp = (\eta^5\text{-}C_5H_5)(CO)_2Fe$) with organoiron electrophiles FpX (X = I, OSO_2CF_3, HgCl), $(\eta^5\text{-}C_5H_5)L(CO)FeI$ (L = $P(OPh_3)$, PPh_3), and $(\eta^5\text{-}C_5H_5)(CO)Fe(CH_3CN)_2^+PF_6^-$ are contrasted. Treatment of the CS_2 adduct **1** with the bis-acetonitrile salt gives the $\mu(\eta^1\text{-}C:\eta^2\text{-}S,S')\text{-}CS_2$ complex $FpC(\overline{S)S}Fe(CO)Cp$, (**4**). Photolysis of the known $\mu(\eta^1\text{-}C:\eta^1\text{-}S)\text{-}CS_2$ compound FpC(S)SFp (**3**) only generates traces of **4**, in contrast. Treating the CO_2 adduct **2** with the iron electrophiles Cp(L)(CO)FeI affords Fp_2, with only trace amounts of FpFe(CO)(L)Cp (for L = PPh_3 and $P(OPh)_3$) evident. No $\mu(\eta^1\text{-}C:C\eta^1\text{-}O)$ bimetallocarboxylate intermediates FpC(O)OFe(L)(CO)Cp are detected. In contrast, Fp^-Na^+ upon treatment with $(\eta^5\text{-}C_5H_5)L(CO)FeI$ gives 1/1 mixtures of Fp_2 and FpFe(CO)(L)Cp (for L = PPh_3 and $P(OPh)_3$). The bis-acetonitrile electrophile and **2** afford initially the mixed dimer $FpFe(CH_3CN)(CO)$-Cp, which degrades to Fp_2 at room temperature. Organic carboxylates $RCO_2^-M^+$ (R = Ph, CH_2Ph, and t-Bu; $M^+ = Li^+$, Na^+, K^+) do not react with $(\eta^5\text{-}C_5H_5)(CO)Fe(CH_3CN)_2^+$; and photolysis of Fp(acetate) produces only Fp_2, not an $(\eta^2\text{-}O,O')$ acetate complex $(\eta^5\text{-}C_5H_5)(CO)Fe\overline{OC(O)}CH_3$.

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 CS_2 adducts affords insight into their less stable (or more labile) CO_2 congeners [4*]. We are interested in one pair of $(\eta^1\text{-}C)$-bonded heterocumulene complexes, the $Fe(CO)_2Cp$ metallodithiocarboxylates $FpCS_2^-$ (Na^+,K^+) (**1**) [5] and metallocar-

* Reference number with asterisk indicates note in the list of references.

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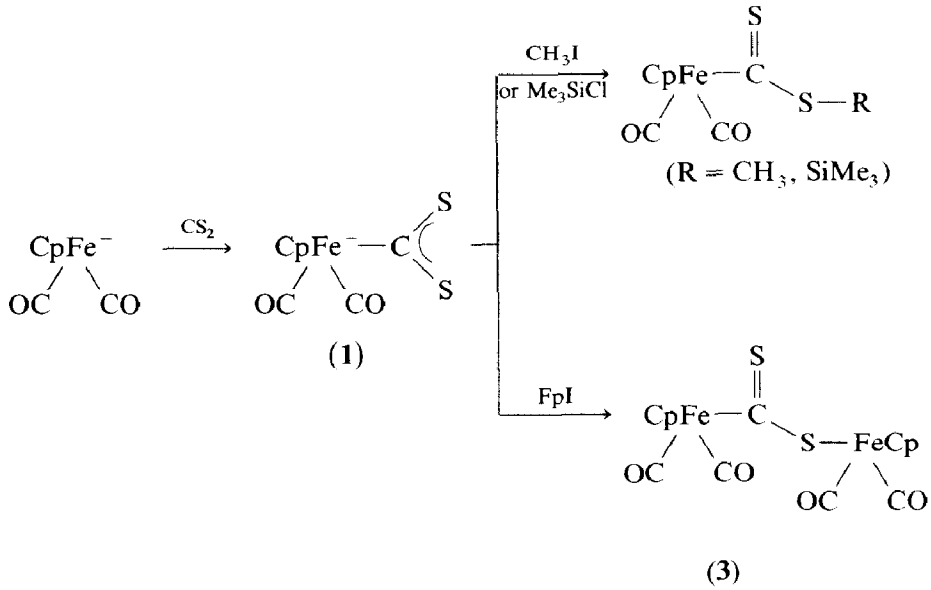
boxylates $FpCO_2^-(Li^+,Na^-)$ (**2**) [6] ($Fp = (\eta^5\text{-}C_5H_5)(CO)_2Fe$). Although **1** and **2** are unstable at room temperature and have not been isolated as solids, both exhibit high reactivity in solution towards electrophiles [7].

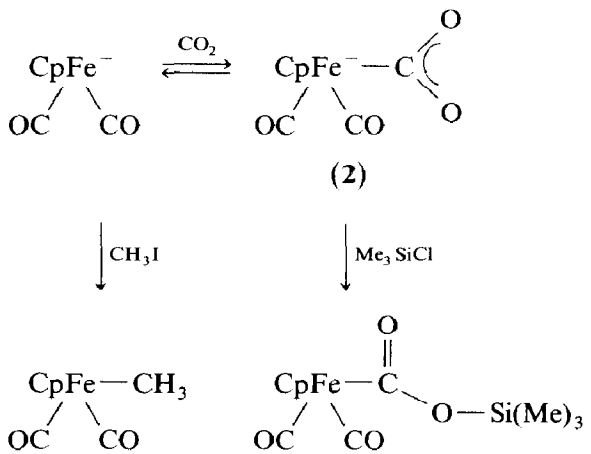
The Fp(dithiocarboxylate) anion (**1**) in particular readily reacts with a variety of Lewis acids. Alkylation or silation of **1** at −20 °C gives stable dithiocarboxylate ester complexes (eq. 1) [5,8]. Ellis [5] initially demonstrated that treating **1** with FpI



(1)

affords the stable $\mu(\eta^1\text{-C}:\eta^1\text{-S})$ bis-Fp-dithiocarboxylate **3** [8d,9c] in good yield. This μ-CS_2 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 $FpC(SFp)_2^+$ [9a]. These results appear general in that a variety of stable bimetallic and trimetallic μ-CS_2 complexes derived from **1** have been characterized [9].

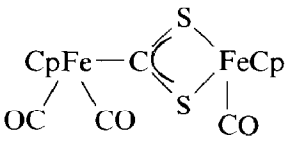
Reactions of the CO_2 complexes **2** with Lewis acids are more involved. Electrophilic methylating agents including methyl iodide and methyl triflate quantitatively convert **2** (Li^+, Na^+, or K^+) to $FpCH_3$ [6,10,11], a result that is consistent with these electrophiles intercepting a dissociative equilibrium between **2** and Fp^- (eq. 2).



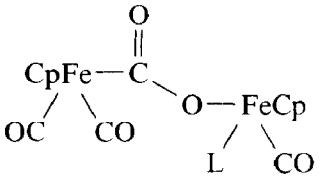
(2)

Blocking this dissociation of **2** by using the more oxophilic Mg^{2+} counterion, which evidently chelates **2** as a $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ metallocarboxylate $[FpC(\overline{O)O]_2}Mg]$, 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 $FpC(O)OSiMe_2R$ ($R = CH_3$, t-Bu) [10c,12*]. The extremely robust $FpSiMe_3$ is not detected in these reactions. Results of treating **2** with transition organometallic Lewis acids have not been reported; indeed, few bimetallic μ-CO_2 adducts have been prepared [13*].

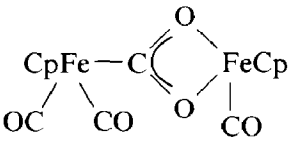
In this paper we compare the reactivity of **1** and **2** towards organoiron electrophiles. These electrophiles were selected so as to contain either one or two accessible coordination sites [14]; FpX (X = I, OSO_2CF_3) and $Cp(CO)Fe(CH_3CN)_2^+BF_4^-$, respectively, are representative Lewis acids. Target molecules are the μ-CS_2 complexes **3** [5] and **4** [9c] and the μ-CO_2 metallocarboxylates **5** and **6**.



(**4**)



(**5a**: L = CO;
5b: L = $P(OPh_3)$;
5c: L = PPh_3)



(**6**)

Experimental

Synthetic manipulations were performed under a nitrogen atmosphere using standard syringe-septum and Schlenk techniques or a glovebox [15]. Infrared spectra were taken of CH_2Cl_2 or THF solutions or of pressed KBr disks and were recorded on a Perkin–Elmer Model 297 spectrophotometer. The ν(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}. MR spectral data were obtained on a Varian Model XL-200 or a Bruker Model WP 100 spectrometer; chemical shifts (δ) are referenced to internal $(CH_3)_4Si$. Combustion microanalyses were done by Robertson Laboratory, Inc., Madison, NJ.

Organic reagents were obtained commercially and used as received. Dichloromethane was distilled under nitrogen from P_2O_5; anhydrous THF and diethyl ether were distilled from sodium benzophenone ketyl. Organometallic starting materials Fp_2 [16], $FpCH_3$ [16], FpI [16], FpHgCl [17], Fp^-K^+ [18], $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$ [19], $Cp(PPh_3)(CO)FeI$ [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 Fp_2 (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 $Cp(CO)_2FeCS_2^-Na^+$ (**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%) FpC(S)SFp (**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 $Cp(CO)_2Fe$-C($\overline{S)S}$-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 $FpCS_2^-K^+$ (**1**) (ν(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, $\{^1H\}^{13}C$ NMR spectra of **1**-K^+ in THF ($-78°C$): δ 308.9 ($FeCS_2$), 215.2 (CO), 88.0 (Cp).

The THF solution containing $FpCS_2^-K^+$ (**1**) was treated with $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$ (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 (5 × 6 ml). Benzene was evaporated from the combined filtrates, and the resulting red solid was extracted with hexane. Flash column chromatography (silica gel, 4.5 × 15 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 FpC($\overline{S)S}$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); $\{^1H\}^{13}C$ NMR ($CDCl_3$) δ 306.3 ($FeCS_2Fe$), 218.6 (CO, CpFe(CO)), 212.2 (CO, Fp), 82.2 (Cp), 79.7 (Cp).

Anal. Found: C, 41.66; H, 2.32. $C_{14}H_{10}Fe_2O_3S_2$ calcd.: C, 41.82, H, 2.53%.

Reaction between $FpCS_2^-Na^+$ (**1**-Na^+) and $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$ 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.

Reaction of $Cp(CO)_2FeCO_2^-Na^+$ (2) and $Cp(CO)_2FeI$

Carbon dioxide (12.0 ml, 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 $FpCO_2^-Na^+$ (**2**) [11e] (IR after 2 min: ν(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 quantitatively conversion to Fp_2: ν(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 3 × 5 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 ^{1}H NMR spectrum indicated pure Fp_2 (89% yield).

Reaction of $Cp(CO)_2FeCO_2^-Li^+$ (2) and $Cp(CO)_2FeOSO_2CF_3$

Fp(triflate) was prepared by adding $HOSO_2CF_3$ (0.29 ml, 3.25 mmol) over a 1min 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 $FpOSO_2CF_3$: ν(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 $FpOSO_2CF_3$ [22] ^{1}H NMR ($CDCl_3$) δ 5.04 (Cp).

Fp(triflate) (400 mg, 1.20 mmol) was added to a THF solution of $FpCO_2^-Li^+$ (**2**), which was generated by adding CO_2 (33 ml, 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 $Cp(CO)_2FeCO_2^-Li^+$ (2) and $Cp(CO)_2FeHgCl$

A THF solution of Fp^-Li^+ (1.00 mmol, 15 ml) was converted to $FpCO_2^-Li^+$ (**2**) using CO_2 (33 ml, 1.5 mmol) at −78°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 ν(CO) at 1785 cm^{-1}. The solution was warmed to room temperature before evaporating the solvent and exhaustively extracting the residue with ether (4 × 6 ml). Combined extracts were concentrated to give orange-brown crystals (0.489 g) that were identified as spectroscopically pure Fp_2Hg [23] (90%): ^{1}H NMR ($CDCl_3$) δ 4.70 (Cp), vs. δ 4.95 (Cp) for FpHgCl and δ 4.78 (Cp) for Fp_2.

Reaction of $Cp(CO)_2FeCO_2^-Na^+$ (2) with $Cp[P(OPh)_3](CO)FeI$

A solution of Fp^-Na^+ in THF (1.00 mmol, 15.0 ml) was converted into $FpCO_2^-Na^+$ (**2**) at −78°C and then treated with $Cp(PCOPh)_3(CO)FeI$ (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 ν(CO) at 1784 cm^{-1}. A weak absorption, ν(CO) 1757 cm^{-1}, was tentatively assigned to the mixed dimer $Cp_2Fe_2(CO)_3[P(OPh)_3]$ [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 {$Cp_2Fe_2(CO)_3[P(OPh)_3]$} and at δ 168.4 {$Cp[P(OPh)_3](CO)FeI$}.

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 $Cp[P(OPh)_3](CO)FeI$ 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 $-78°C$ and treated with $Cp[P(OPh)_3](CO)FeI$ (110 mg, 0.19 mmol). IR spectral monitoring of the cold, red-brown solution was consistent with the presence of both Fp_2 and $Cp_2Fe_2(CO)_3[P(OPh)_3]$ [24] (ν(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 to 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 $Cp_2Fe_2(CO)_3[P(OPh)_3]$: ^1H NMR ($CDCl_3$) δ 4.80 and 4.08 (s, Cp, mixed dimer), 4.78 (s, Cp, Fp_2).

Reaction of $Cp(CO)_2FeCO_2^-Na^+$ (2) and $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$

A solution of Fp^-Na^+ in THF (1.0 mmol, 15.0 ml) was converted to a yellow-brown solution of $FpCO_2^-Na^+$ (**2**) at $-78°C$, to which $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$ (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 (ν(CO) 1993, 1952, 1785 cm^{-1}), FpH [10a,25] (ν(CO) 2017, 1952 cm^{-1}), and an unidentified material (ν(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)

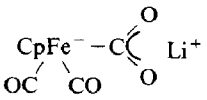
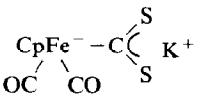
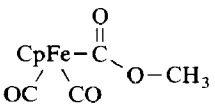
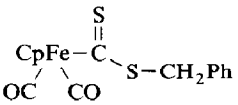
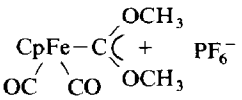
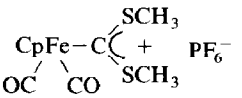
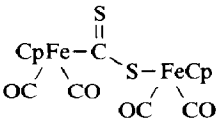
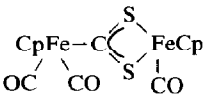
We repeated Ellis' synthesis of FpC(S)SFp (**3**) (eq. 1) as a control for subsequent reactions of $FpCS_2^-$ (**1**) and of $FpCO_2^-$ (**2**) with organoiron electrophiles. As reported [5], the reaction of **1** and FpI affords the stable $\mu(\eta^1\text{-C}:\eta^1\text{-S})$ CS_2 adduct **3** in 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.

The difference in chemical shifts for molecular CS_2 and CO_2 resembles the downfield trend that sp^2 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 $FpC(O)OCH_3$ and metallodithioester $FpC(S)SCH_2Ph$ compounds tabulated. Data for this dithio-ester complex also are similar to that of FpC(S)SFp (**3**).

Upon coordinating Fp^-, CO_2 and CS_2 exhibit 70 and 116 ppm downfield shifts, respectively (Table 1). The resulting (η^1-C) metallodithiocarboxylate **1** and metallocarboxylate **2** structures are consistent with IR spectral data (which preclude other reasonable structures [7]) and with theoretical arguments (for **1** [2a]). The chemical

Table 1

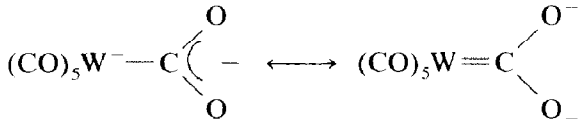
^{13}C NMR spectral assignments (δ)

	δ ($CDCl_3$)	Reference
O=C=O	132.0	[26]
S=C=S	192.5	[26]
 (2)	217.0	[10c] [a]
 (1)	308.9	this work [a]
	213.3	[10c]
	287.6	this work [b]
	251.9	[40*]
	304.3	[40*]
 (3)	298.2	this work
 (4)	306.3	this work

[a] Recorded in THF (−78°C). [b] 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 (CH_2).

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 $[FpC(XCH_3)_2]^+$ (X = O, S), which have considerable charge delocalization, also display downfield shifts of their carbon centers.

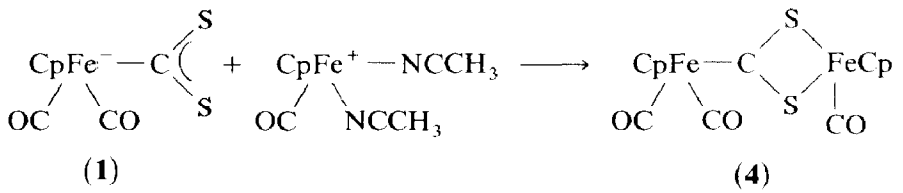
The ^{13}C NMR spectral data for **1** also compares with that of the anionic tungsten CO_2 adduct $(CO)_5WCO_2^{2-}$, δ 223.4 in THF. Cooper [4a] demonstrated that NMR and IR spectral data support a superposition of the resonance structures for this adduct:



The IR spectrum resembles those of anionic pseudohalide complexes, e.g., $(CO)_5WOC(O)CH_3^-$, in which the charge localizes on the $W(CO)_5$ moiety. The magnitude of the coupling constant $J(W-C)$ for the CO_2 center on $(CO)_5WCO_2^{2-}$ indicates extensive W=C double bonding, thus favoring charge localization on the oxygens.

The bis-iron μ-(η^1-C : η^2-S,S′) CS_2 complex, $FpC(\overline{S)SFe}(CO)Cp$ (**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, $FpC(S)SMn(CO)_5$ spontaneously transforms into its chelated derivative $FpC(\overline{S)SMn}(CO)_4$ [9b]. We prepared **4**, a known compound [9c] vide infra, from the reaction between $FpCS_2^-$ (**1**) and an appropriate organoiron electrophile. This methodology then would be extended to synthesizing the congeneric μ-CO_2 compound **5**. (Most of the known bimetallic and trimetallic CO_2 complexes retain analogous chelated metallocarboxylate structures [13*].)

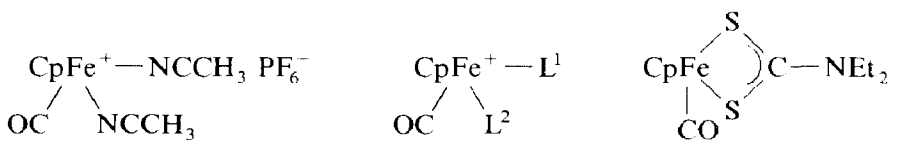
We selected $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$ [19] as the organometallic Lewis acid of choice [14], one that bears two accessible coordination sites, to convert the CS_2 complex **1** to **4** (eq. 3). In previous studies, we documented that this labile bis-acetonitrile complex readily exchanges its ligated acetonitrile for a variety of



(3)

(**1**) (**4**)

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 $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$ and $Et_2NCS_2^-Na^+$ in THF selectively affords the (η^2-S,S′) chelate $Cp(CO)\overline{FeSC(S)}NEt_2$ (73% yield) that is uncontaminated by the Fp (η^1-S) dithiocarbamate $Cp(CO)_2FeSC(S)NEt_2$.



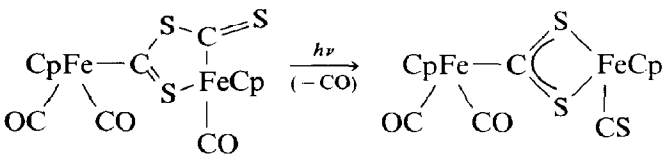
$(L^1, L^2 = PR_3)$

Treatment of the same labile bis-acetonitrile salt with $FpCS_2^-K^+$ (**1**) in THF (−78°C) gives the desired μ(η^1-C : η^2-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 $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$ 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 $Cp(CO)(THF)Fe(CH_3CN)^+$,which then rapidly decomposes to insoluble residues [19b].

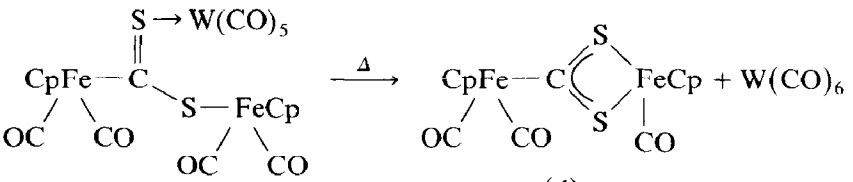
IR and ^1H NMR spectral data for the stable red solid resulting from the reaction of $FpCS_2^-K^+$ (**1**) and $Cp(CO)Fe(CH_3CN)_2^+$ matches that previously reported for **4** [9c]. The presence of three carbonyl stretching frequencies (2025, 1989 cm^{-1} for Fp, and 1938 cm^{-1} for Cp(CO)Fe) and of the expected [9] two thiocarboxylate $\nu(CS_2)$ 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): ν(CO) 2030, 1987 cm^{-1}; $\nu(CS_2)$ 913, 880 cm^{-1}. Our ^{13}C NMR spectral data for **4** resembles that of **6** [27*] and of $[FpC(SFp)(SCH_3)]^+$ [8d], with their corresponding Fp-bound dithiocarboxylate carbons producing signals at δ 306, 329, and 315, respectively.



(4)

(**6**) (**7**)

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

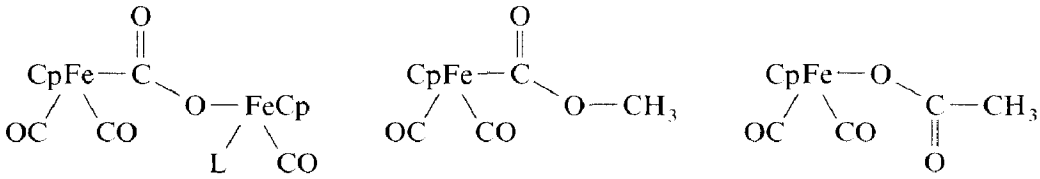


(**3**-$W(CO)_5$) (**4**)

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 do not elute from silica gel chromatography columns.

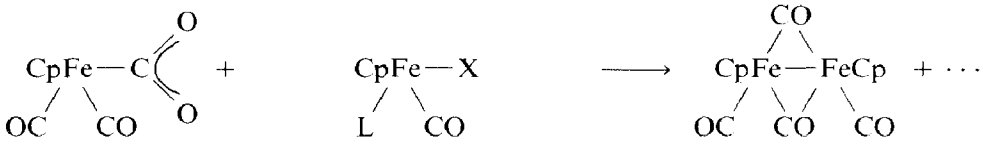
Reactions of $FpCO_2^-$ (2)

Bis-iron $\mu(\eta^1\text{-C}:\eta^1\text{-O})CO_2$ complexes **5a**–**5c** offer plausible synthetic objectives in view of the thermal stability of the CS_2 congener **3**. Complex **5a** should retain (η^1-C) and (η^1-O) bonding analogous to that found in the stable methyl ester, $Fp(C(O)OCH_3$ [10b], and acetate, $FpOC(O)CH_3$ [28], complexes.



(**5a**: L = CO,
5b: L = $P(OPh_3)$,
5c: L = PPh_3)

Our synthetic approach involves treating THF solutions of $FpCO_2^-$ (**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 [29*]. Initial IR data typically were recorded within 2 min of mixing **2** and the iron Lewis acid and at an IR cell temperature of ca. 0°C.



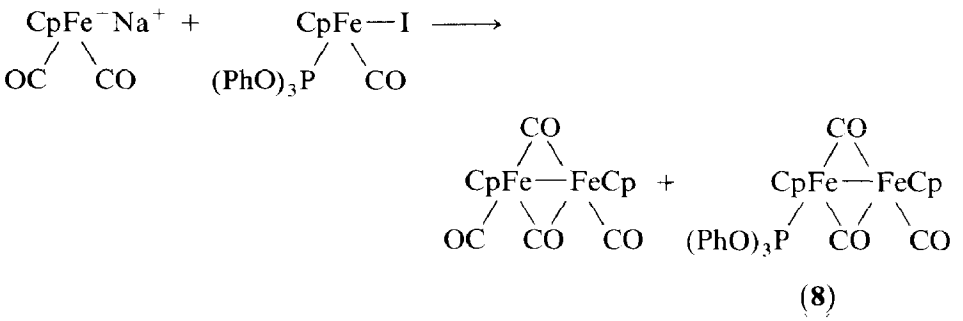
(**2**-Li^+, **2**-Na^+) (L = CO, X = I, OSO_2CF_3; L = $P(OPh)_3$, X = I; L = PPh_3, X = I)

(6)

Treatment of $FpCO_2^-$ (**2**-Li^+, **2**-Na^+) with either FpI or Fp(triflate) at −78°C immediately and quantitatively affords Fp_2. Attempts to use $Fp(THF)^+BF_4^-$ [32] as the organoiron electrophile were thwarted by its insolubility in THF at −78°C. After treatment 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 Fp_2. The iron-mercury electrophile FpHgCl [33] also readily reacts with $FpCO_2^-Li^+$ (**2**), but Fp_2Hg immediately and quantitatively forms in preference to an $Fp(\eta^2\text{-OO}')$(carboxylate)-Hg^{II} derivative.

The reaction between **2**-Li^+ or **2**-Na^+ and $Cp[P(OPh)_3](CO)FeI$ likewise produces Fp_2 as the predominant organometallic species, although small amounts (10%) of the phosphite-substituted dimer $Cp_2Fe_2(CO)_3[P(OPh)_3]$ (**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°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.

Reaction between Fp^-Na^+ and $Cp[P(OPh)_3](CO)FeI$ 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 $Cp_2Fe_2(CO)_3[P(OPh)_3]$ (**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.



(7)

(**8**)

A straightforward coupling of the two iron centers does not occur upon treating Fp^-Na^+ with $Cp[P(OPh)_3](CO)FeI$ (eq. 7), since approximately 50% of the reaction product is Fp_2. Of the $Cp_2Fe_2(CO)_3[P(OPh)_3]$ (**8**) that does form, at least 16% (and quite possible 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 $Fp_2/P(OPh)_3$ 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].

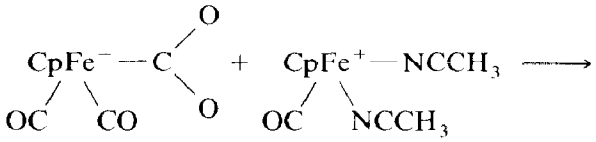
Treating metallocarboxylate $FpCO_2^-Na^+$ (**2**) with $Cp[P(OPh)_3](CO)FeI$ (eq. 6) produces very little $Cp_2Fe_2(CO)_3[P(OPh)_3]$ (**8**) even though it is stable under the experimental conditions. Isolation of Fp_2 as the major product is consistent with **2** interacting with the iron iodide by an electron-transfer process that ultimately affords 17-electron intermediates $Cp(L)(CO)Fe\cdot$ ($L = CO$, $P(OPh)_3$). Others have established that these substituted odd-electron species (e.g., $L = P(OPh)_3$), which remain after ligand dissociation from 19-electron intermediates $Cp(L)(CO)FeX^{\cdot-}$ or $Cp(L)(CO)_2Fe^\cdot$ [34], preferentially give unsubstituted dimer Fp_2 [12a*,35]. The main observation is that $FpCO_2^-$ (**1**) does not dissociate CO_2 and reacts as Fp^- with $Cp[P(OPh)_3](CO)FeI$, although further mechanistic studies clearly are needed.

This electron transfer process also accounts for the Fp_2 product that results from treating $FpCO_2^-Na^+$ (**2**) with FpI or Fp(triflate). Electron transfer affords odd-electron transient species $FpX^{\cdot-}$ and $(FpCO_2)^\cdot$ that degrade to the 17-electron $Fp^\cdot$, which dimerizes. Lee and Cooper [11b] advanced a similar mechanism to account for their observation that $FpCO_2^-Li^+$ (**2**) reacts with $FpCO^+BF_4^-$ to give exclusively Fp_2.

Reactions between the triphenylphosphine-substituted iron iodide, $Cp(PPh_3)(CO)FeI$, and $FpCO_2^-Na^+$ (**2**) or Fp^-Na^+ afford results that are very similar to those observed for the phosphite-containing analogue $Cp[P(OPh)_3](CO)FeI$, as ascertained by IR spectral monitoring. The documented thermal instability of the mixed dimer $Cp_2Fe_2(CO)_3(PPh_3)$ at room temperature [24b] precluded further analysis or workup of these reactions, however.

Treatment of the labile bis-acetonitrile salt $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$ with $FpCO_2^-Na^+$ (**2**) (eq. 8) initially generates a complex mixture of Fp_2, FpH [10b,25],

and a new component having a bridging carbonyl ν(CO) 1756 cm^{-1} (eq. 8). Upon warming this mixture to room temperature, only Fp_2 is evident during IR spectral monitoring (isolated yield 41%).



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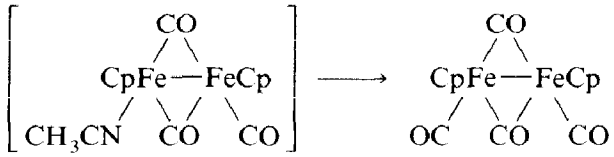
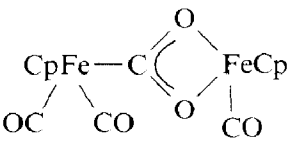


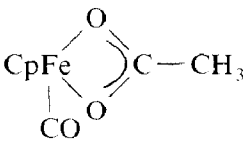
(9)

We formulate the new component as the mono-acetonitrile adduct of Fp_2: $Cp_2Fe_2(CO)_3(CH_3CN)$ (**9**). Related dimers $Cp_2Fe_2(CO)_3[P(OPh)_3]$ (**8**) and $Cp_2Fe_2(CO)_3PPh_3$ likewise exhibit lower energy bridging carbonyl ν(CO) at 1757 and 1733 cm^{-1} (with respect to Fp_2, ν(CO) 1782 cm^{-1}, also in THF). Labinger [36] previously prepared **9** by photolysis of Fp_2 in acetonitrile and documented its solution instability.

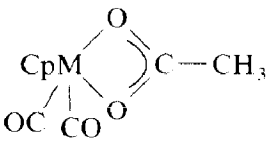
Our inability to generate the chelating bis-iron $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$-$CO_2$ complex **6** raised the question: could analogous chelating organic carboxylate complexes **10** be prepared? Werner [37] reported that corresponding molybdenum and tungsten acetate chelates **11** are the stable products of warming the (η^1-O)acetates $Cp(CO)_3MOC(O)CH_3$.



(6)



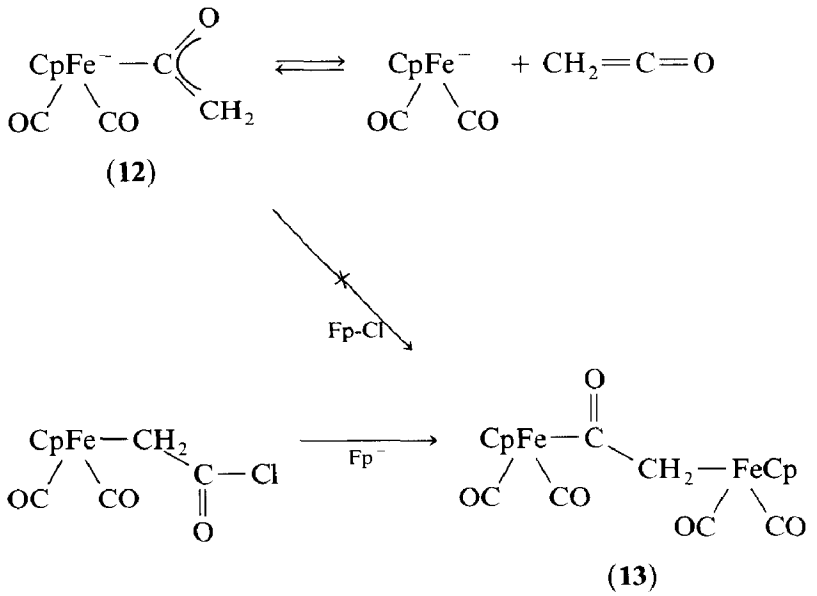
(10)



(**11**: M = Mo, W)

We found that the bis-acetonitrile salt $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$ is inert to the carboxylate salts $PhCO_2^-Li^+$, $Me_3CCO_2^-Li^+$, $PhCH_2CO_2^-Li^+$ and $PhCO_2^-Na^+$ in THF solution. These carboxylates remain unchanged (IR spectral monitoring of $\nu(CO_2)$ 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** (R = 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 (η^1-C) ketene complex $Fp(CH_2CO)^-$ (**12**). Helquist [38] first generated this heterocumulene adduct by deprotonating $FpCOCH_3$ at low temperature, and Akitah and coworkers [30] demonstrated that **12** equilibrates with Fp^- and free ketene above −50 °C. Attempts to intercept **12** with FpCl and generate $FpC(O)CH_2$-Fp (**13**) produced only Fp_2 (eq. 9). The desired μ-ketene compound **13** does form, however, by metallating



(9)

the chloroacetyl compound $FpCH_2C(O)Cl$ 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 FpC(O)OFe(CO)Cp (**6**) under conditions that the corresponding μ-CS_2 adducts **3** and **4**, respectively, readily form using $FpCS_2^-$ (**1**). 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 $FpC(O)CH_2Fp$ (**13**) [39*]. 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.

Acknowledgment

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