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Iron–Tin Carbon Dioxide Complexes (η^5-C_5Me_5)$(CO)_2Fe$–CO_2SnR_3 (R = Me, Ph): Observations Pertaining to Unsymmetrical Metallocarboxylates and Carboxylate–Carbonyl ^{13}C-Label Exchange

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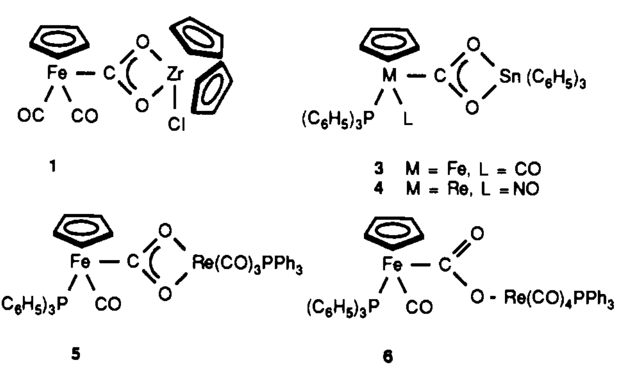
Treatment of $Cp(CO)_2Fe$–$CO_2^-K^+$ with R_3SnCl (R = Me, Ph) in THF (−78 °C) gave $Cp(CO)_2Fe$–SnR_3, which was attributed to preferred dissociation of the starting metallocarboxylate to $Cp(CO)_2Fe^-K^+$. (Abbreviations: Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5.) The more nucleophilic $Cp^*(CO)_2Fe$–$CO_2^-K^+$ was trapped by Ph_3SnCl as the thermally stable iron–tin carboxylate $Cp^*(CO)_2Fe$–CO_2SnPh_3 (**8**). ^{13}C-labeled product $Cp^*(CO)_2Fe$–$^{13}CO_2SnPh_3$ also was obtained in excess of 90% yield. Similar trapping experiments using Me_3SnCl gave $Cp^*(CO)_2Fe$–CO_2SnMe_3 (**9**) and (using $^{13}CO_2$) $Cp^*(CO)_2Fe$–$^{13}CO_2SnMe_3$. Both slowly decarboxylated at room temperature to $Cp^*(CO)_2$-Fe–$SnMe_3$. A competing (slower) carboxylate–carbonyl label exchange also was documented for $Cp^*(CO)_2Fe$–$^{13}CO_2SnMe_3$ transforming to $Cp^*(^{13}CO)(CO)Fe$–CO_2SnMe_3 and then to $Cp^*(^{13}CO)(CO)Fe$–$SnMe_3$. IR $\upsilon(CO_2)$ bands for **8** and **9** were assigned only after comparing spectra for $Cp^*(CO)_2Fe$–CO_2SnR_3, $Cp^*(CO)_2Fe$–$^{13}CO_2$-SnR_3, and $Cp^*(CO)_2Fe$–SnR_3. This data was consistent with a chelating $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ structure for **8** and an *unsymmetric* or metalloester $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ bonding for the more reactive/labile **9**.

Introduction

The hetereobimetallic $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ carbon dioxide complex $Cp(CO)_2Fe$–CO_2–$Zr(Cl)Cp_2$ (**1**) (Cp = η^5-C_5H_5) has been obtained either from the reaction between the metallocarboxylate $Cp(CO)_2Fe$–CO_2^- (**2a**) and Cp_2ZrCl_2[1] or from the insertion of CO_2 into the Fe–Zr bond of $Cp(CO)_2Fe$–$Zr(Cl)Cp_2$.[2] Structure assignment of **1** (Chart 1)and related bimetallocarboxylates[3] in the absence of X-ray crystallography studies rests on interpretation of infrared (IR) spectral data of the carboxylate $\upsilon(CO_2)$ bands. Provided that these $\upsilon_{asym}(CO_2)$ and $\upsilon_{sym}(CO_2)$ bands can be identified, it should be possible to deduce whether a bimetallocarboxylate retains a chelating $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ or a nonchelating $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ metalloester structure.[4]

Related tin–metallocarboxylates such as $Cp(CO)(PPh_3)Fe$–CO_2SnPh_3 (**3**)[5] and $Cp(NO)(PPh_3)Re$–CO_2SnPh_3 (**4**)[6] are of interest as derivatives of their unstable anionic metallocarboxylates and as structural models for hetereobimetallic carbon dioxide complexes. Results of X-ray structure determinations of **3** and **4** indicate chelating $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ structures. The iron CO_2 adduct $Cp(CO)(PPh_3)Fe$–CO_2^- also has been derivatized by Gibson's group as its Fe–Re bimetallocarboxylates, chelating $Cp(CO)(PPh_3)Fe$–$CO_2Re(PPh_3)(CO)_3$ (**5**), and nonchelating $Cp(CO)(PPh_3)Fe$–$CO_2Re(Ph_3)(CO)_4$ (**6**).[7] In contrast, analogous derivatives of $Cp(CO)_2Fe$–CO_2^- (**2a**), perhaps the most extensively documented metallocarboxylate,[8,9] are limited to its silyl or methyl metalloesters [e.g., $Cp(CO)_2Fe$–$C({=}O)OSiR_3$; SiR_3 = $SiMe_2{}^tBu$, $SiMe_3$ (**7**)][8] that retain nonchelating $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ structures.[9]

Chart 1



1

3 M = Fe, L = CO
4 M = Re, L = NO

5

6

The impetus for the present study was to synthesize $Cp(CO)_2$-Fe–CO_2SnR_3 complexes in order to compare their IR carboxylate $\upsilon(CO_2)$ data with that reported for **3** and for **1**. We were surprised to find that treatment of the anionic iron CO_2 complex **2a** with triphenyltin chloride does not afford $Cp(CO)_2Fe$–CO_2SnPh_3 (**3**). Switching to the more electron-rich permethylcyclopentadienyl ligand (Cp*) and $Cp^*(CO)_2Fe$–CO_2^- (**2b**),[10] however, afforded a stable iron–tin carboxylate $Cp^*(CO)_2Fe$–CO_2–$SnPh_3$ (**8**). Its trimethyltin analog $Cp^*(CO)_2Fe$–CO_2SnMe_3 (**9**), also reported in this study, decarboxylates[11] at room temperature. Special attention was directed toward studying these Fe–Sn carboxylates with ^{13}C-labeled CO_2 ligands in order to assign their IR $\upsilon(CO_2)$ bands and also to follow the facile carboxylate–carbonyl label shift that occurs for **9** but not **8**.

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Experimental Section

Synthetic manipulations were performed using a combination of standard Schlenk line, glovebox, and vacuum line[12] procedures. Infrared spectra of the carbonyl ν(CO) and carboxylate $\nu(CO_2)$ frequency region (2200–1200 cm^{-1}) were recorded of solutions on a Perkin-Elmer Model 1610 spectrophotometer. ^1H and $^{13}C\{^1H\}$ NMR spectral data were obtained in C_6D_6 using Varian Models XL-200 and Unity-500 spectrometers. NMR shifts were measured relative to solvent C_6D_6 absorptions, using the residual ^1H NMR resonance (δ 7.15) and the ^{13}C NMR C_6D_6 triplet (δ 128.0). Combustion microanalyses were done by Quantitative Technologies, Inc., Whitehouse, NJ.

Organic and inorganic reagents were obtained commercially and used as received; THF and hexane were distilled from sodium benzophenone ketyl. Further drying of the carbon dioxide, Matheson "bone dry" grade, entailed passage through a 1 cm × 1 m glass column that was packed with a 25% P_2O_5 powder dispersion on activated silica gel (70–200 mesh) containing 1% Congo Red indicator. Before using, carbon dioxide and 99% ^{13}C-labeled CO_2 were frozen (-196 °C) and pumped on to remove noncondensable materials. The iron carbonyl dimers $[Cp^*(CO)_2Fe]_2$[10] and $[Cp(CO)_2Fe]_2$[13] as well as $Cp(CO)_2FeK$[14] were prepared by literature procedures and judged pure by IR and ^1H NMR spectroscopy. Authentic samples and spectral data for $Cp^*(CO)_2FeH$[10b,15] were available for comparison.

Synthesis of (η^5-C_5Me_5)(CO)$_2$Fe–CO_2SnPh_3 (8). An oven-dried, 30-mL centrifuge tube was charged with $[Cp^*Fe(CO)_2]_2$ (247 mg, 0.50 mmol), potassium (150 mg), and 10 mL of THF, sealed with a rubber septum, and sonicated[16] in an ultrasonic cleaning bath for 1.0 h. The initially dark purple solution turned dark red; an IR spectrum of the centrifugate was consistent with $Cp^*(CO)_2Fe^-K^+$,[10b,17] ν(CO) 1844, 1757 cm^{-1}. The presence of small amounts of $Cp^*(CO)_2FeH$, ν(CO) 1993, 1932 cm^{-1}, was avoided by prior flushing of the IR cell with the $Cp^*(CO)_2Fe^-K^+$ solution (0.5 mL) in order to remove traces of adsorbed water.

The supernatant solution was filtered and transferred to a 100-mL round-bottom flask that was attached to a high-vacuum line. Three freeze–pump–thaw cycles were carried out on the solution before it was frozen (–196 °C) and the CO_2 (24 mL, 1.0 mmol) was condensed. The reaction flask then was isolated from the vacuum line and warmed to –78 °C with vigorous stirring (30 min). Nitrogen was admitted before an IR spectrum of the dark red-brown $Cp^*(CO)_2Fe–CO_2^-K^+$ (**2b**) solution was obtained, ν(CO) 1974, 1904 cm^{-1}. A solution of Ph_3SnCl (385 mg, 1.0 mmol) in 15 mL of THF immediately was added (at –78 °C) via syringe, and the red-orange solution was stirred for 20 min. An IR spectrum then showed ν(CO) bands that corresponded only to $Cp^*(CO)_2Fe–CO_2SnPh_3$ (**8**), ν(CO) 2013, 1961 cm^{-1}. The THF was evaporated, and the orange-red residue was extracted with 100 mL of hexane and filtered. Removal of the solvent left 590 mg of an orange-brown gummy solid, which was identified as $Cp^*(CO)_2Fe–CO_2SnPh_3$ (**8**) (92% yield). Anal. Calcd for $C_{31}H_{30}O_4FeSn$: C, 58.08; H, 4.72. Found: C, 58.25; H, 4.83.

Synthesis of (η^5-C_5Me_5)(CO)$_2$Fe–$SnPh_3$ (10). To a stirred THF solution containing $Cp^*(CO)_2Fe^-K^+$ (1.0 mmol, 10 mL) was added a second solution containing Ph_3SnCl (385 mg, 1.0 mmol) in 15 mL of THF. An infrared spectrum of the dark reddish brown solution after stirring for 10 min was consistent with quantitative formation of $Cp^*(CO)_2Fe–SnPh_3$ (**10**),[18] ν(CO) 1974, 1925 cm^{-1}. Evaporation of solvent left an orange-brown solid which was extracted with 100 mL of hexane and filtered. The resulting orange solution yielded 560 mg of analytically pure **10** as a light brown solid (94% yield), mp 168–171 °C dec. Anal. Calcd for $C_{30}H_{30}O_2FeSn$: C, 60.35; H, 5.06. Found: C, 60.53; H, 5.08.

Preparation of (η^5-C_5Me_5)(CO)$_2$Fe–CO_2SnMe_3 (9). A THF solution containing $Cp^*(CO)_2Fe–CO_2^-K^+$ (**2b**) (1.0 mmol, 10 mL) was generated and warmed to –78 °C before nitrogen was admitted. To this was added a THF solution (15 mL) of $(CH_3)_3SnCl$ (199 mg, 1.0 mmol), and the red-orange solution was stirred vigorously for 20 min. An IR spectrum of the cold, red solution was consistent with $Cp^*Fe(CO)_2CO_2Sn(CH_3)_3$ (**8**) as the major product. The THF was evaporated (0–5 °C), and the orange-red residue was extracted with 100 mL of hexane and filtered. Removal of solvent under vacuum left 350 mg of orange-red gummy residue; its ^1H NMR spectra were consistent with a mixture consisting of $Cp^*(CO)_2Fe–CO_2Sn(CH_3)_3$ (**9**) (60%), $Cp^*(CO)_2Fe–Sn(CH_3)_3$ (**11**) (30%), and $[Cp^*Fe(CO)_2]_2$ (10%). Attempts to procure analytically pure samples of **9** were frustrated by the presence of moderate amounts (10–20%) of **11**.

Synthesis of (η^5-C_5Me_5)(CO)$_2$Fe–Sn(CH$_3$)$_3$ (11). Dimeric $[Cp^*Fe(CO)_2]_2$ (247 mg, 0.50 mmol) in 10 mL of THF was reduced to $Cp^*(CO)_2Fe^-K^+$ with potassium (150 mg) before it was treated with a second solution of $(CH_3)_3SnCl$ (199 mg, 1.0 mmol) in 15 mL of THF. After 10 min, IR spectral monitoring established quantitative conversion to $Cp^*Fe(CO)_2Sn(CH_3)_3$ (**11**). The dark red-brown solution was stripped under vacuum at room temperature, and the brown residue was extracted with 100 mL of hexane and filtered. Evaporation of the resulting clear yellow filtrate afforded 370 mg of $Cp^*Fe(CO)_2Sn(CH_3)_3$ (**11**) (90% yield) as a bright yellow solid, mp 84–86 °C. Anal. Calcd for $C_{15}H_{24}O_2FeSn$: C, 43.85; H, 5.89. Found: C, 44.21; H, 5.75.

Preparation of (η^5-C_5Me_5)(CO)$_2$Fe–$^{13}CO_2SnMe_3$ (9a) and (η^5-C_5Me_5)(CO)(^{13}CO) Fe–CO_2SnMe_3 (9b). One equivalent of $^{13}CO_2$ (24 mL, 1.0 mmol) was condensed to a frozen solution (–196 °C) of $Cp^*(CO)_2Fe^-K^+$ in THF (1.0 mmol, 10 mL), and the reaction flask, isolated from the vacuum line, was kept at –78 °C with vigorous stirring for 30 min. Nitrogen was admitted to the $Cp^*(CO)_2Fe^{13}CO_2^-K^+$ (**2b**) solution; then a solution of $(CH_3)_3SnCl$ (199 mg, 1.0 mmol) in 15 mL of THF was added by syringe. The orange solution was stirred for 20 min before an IR spectrum of the cold solution indicated the presence of $Cp^*(CO)_2Fe–^{13}CO_2SnMe_3$ (**9a**) and $Cp^*(CO)_2Fe–SnMe_3$ (**11**) (5:1 ratio) as the major products. Trace concentrations of both $Cp^*(CO)(^{13}CO)Fe–CO_2SnMe_3$ (**9b**) and $Cp^*(CO)(^{13}CO)Fe–SnMe_3$ (**11a**) also were observed. The THF solution was evaporated, and the orange residue was extracted with 100 mL of hexane and filtered. The filtrate was evaporated, and IR and NMR spectra of the remaining brownish solid were consistent with a 1.2:1.5:1.5:1.0 mixture of **9a**/**11**/$Cp^*(CO)(^{13}CO)Fe–CO_2SnMe_3$ (**9b**)/$Cp^*(CO)(^{13}CO)Fe–SnMe_3$ (**11a**). After sitting for another 4 h, the residue, 400 mg of orange-yellow crystals, was characterized as a 3:1 mixture of $Cp^*(CO)_2Fe–SnMe_3$ (**11**) and $Cp^*(CO)(^{13}CO)Fe–SnMe_3$ (**11a**) (97% yield).

Reaction of (η^5-C_5H_5)(CO)$_2$Fe–$CO_2^-K^+$ (2a) with Ph_3SnCl. Solid $Cp(CO)_2Fe^-K^+$ (218 mg, 1.0 mmol) was dissolved in 10 mL of THF, and the dark orange solution was degassed on a high-vacuum line by applying three freeze–pump–thaw cycles. Dried CO_2 (24 mL, 1.0 mmol) then was condensed into the reaction flask (–196 °C) from a gas storage bulb. The reaction flask then was isolated from the vacuum line before the reaction mixture was warmed to –78 °C and stirred for 30 min. Nitrogen was admitted to the flask, and an IR spectrum of the cold orange-brown solution confirmed that all of the $Cp(CO)_2Fe^-K^+$, ν(CO) 1870, 1781 cm^{-1}, had transformed to $Cp(CO)_2Fe–CO_2^-K^+$ (**2a**), ν(CO) 1974, 1904 cm^{-1}.

Ph_3SnCl (385 mg, 1.0 mmol) in 15 mL of THF immediately was added via syringe to the $Cp(CO)_2Fe–CO_2^-K^+$ (**2a**) solution. The red-orange solution was stirred for 20 min (at –78 °C) before an IR spectrum was recorded. It was consistent with $Cp(CO)_2Fe–SnPh_3$[19] as the only organoiron product, ν(CO) 1992, 1942 cm^{-1}. THF was removed from the reaction mixture under vacuum, the resulting reddish brown solid residue was extracted with 100 mL of hexane and filtered, and the hexane was evaporated from the red filtrate. This left 440 mg of a fluffy, light tan solid, which was identified as spectroscopically pure $Cp(CO)_2Fe–SnPh_3$, 83% yield, by IR and ^1H NMR spectroscopy.[19] Its spectral data matched that of an authentic sample of this iron–tin complex.

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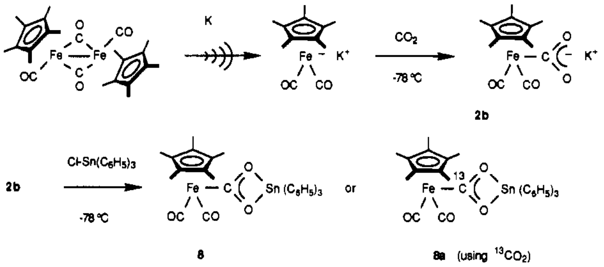
Table 1. Spectroscopic Characterization of (η^5-C_5Me_5)Fe$(CO)_2$ Complexes

IR ν(CO), cm^{-1}	^{1}H NMR (C_6D_6), ppm	^{13}C{^{1}H} NMR (C_6D_6), ppm
	Cp*$(CO)_2$Fe–CO_2SnPh_3 (**8**)	
2018, 1966[a]	7.97 (m, 2H, Ph) 7.20 (m, 3H, Ph) 1.40 (s, Cp*)	218.05 (CO_2) 215.71 (CO) 142.21 (ipso-Ph) 96.90 (ipso-Cp*) 9.46 (Me–Cp*)
	Cp*$(CO)_2$Fe–$^{13}CO_2SnPh_3$ (**8a**)	
2018, 1966[a]		
	Cp*$(CO)_2$Fe–$SnPh_3$ (**10**)	
1978, 1929[a]	7.96 (m, 2H, Ph) 7.27 (m, 3H, Ph) 1.39 (s, Cp*)	217.62 (CO) 145.43 (ipso-Ph) 94.46 (ipso-Cp*) 9.97 (Me–Cp*)
	Cp*$(CO)_2$Fe–CO_2SnMe_3 (**9**)	
2006, 1951[b]	1.53 (s, CH_3Sn) 0.40 (s, Cp*)	216.52 (CO_2) 211.90 (CO) 96.72 (ipso-Cp*) 9.58 (Me–Cp*) –2.26 (CH_3Sn)
	Cp*$(CO)_2$Fe–$^{13}CO_2SnMe_3$ (**9a**)	
2005, 1951[b]		
	Cp*(CO)(^{13}CO)Fe–CO_2SnMe_3 (**9b**)	
1991, 1918[b]		
	Cp*$(CO)_2$Fe–$SnMe_3$ (**11**)	
1967, 1917[b]	1.50 (s, CH_3Sn) 0.52 (s, Cp*) 1.29 (br s, 15H, Si*Et*)	217.45 (CO) 93.70 (ipso-Cp*) 10.14 (Me–Cp*) –5.42 (CH_3Sn)
	Cp*(CO)(^{13}CO)Fe–$SnMe_3$ (**11a**)	
1952, 1886[b]		

[a] CCl_4. [b] THF.

Results and Discussion

We generated the new metallocarboxylate Cp*$(CO)_2$Fe–$CO_2^-K^+$ (**2b**) by essentially the same procedure that was used for its (η^5-C_5H_5)Fe analog **2a**.[1,9] Sonication of a THF solution of $[Cp^*Fe(CO)_2]_2$ and potassium metal in a standard ultrasonic cleaning bath[16] conveniently produced the starting iron metalate Cp*$(CO)_2$FeK.[10b,17] When treated with 1 equiv of CO_2 at –78 °C, Cp*$(CO)_2$FeK quantitatively transformed to its CO_2 adduct **2b** (eq 1).[20b] This was characterized as its stable Fe–Sn metallocarboxylates Cp*$(CO)_2$Fe–CO_2SnPh_3 (**8**) and (η^5-C_5Me_5)$(CO)_2$Fe–$^{13}CO_2SnPh_3$ (**8a**) (starting with 99% ^{13}C-labeled CO_2). Both were isolated in over 90% yields as stable, resinous orange-brown materials; spectral data for these fully characterized Fe–Sn carboxylates are summarized in Table 1.



(1)

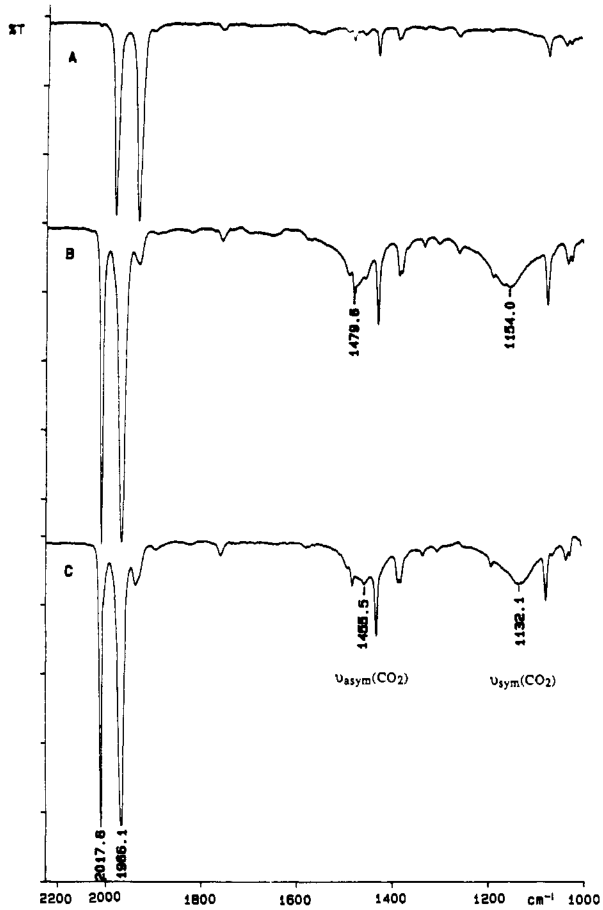


Figure 1. Infrared spectra in carbon tetrachloride solution of (a) (η^5-C_5Me_5)$(CO)_2$Fe–$SnPh_3$ (**10**), (b) (η^5-C_5Me_5)$(CO)_2$Fe–CO_2SnPh_3 (**8**), and (c) (η^5-C_5Me_5)$(CO)_2$Fe–$^{13}CO_2SnPh_3$ (**8a**).

The presence of the ^{13}C-label on **8a** allowed us to assign the absorptions for the carbonyl and carboxylate carbons in the ^{13}C NMR spectrum at δ 215.7 and 218.0, respectively. The latter absorption only appeared very intense. The small separation between the carbonyl and carboxylate ^{13}C NMR spectral absorptions for several metalloester derivatives (e.g., Cp(CO)(L)Fe–CO_2R, L = CO, PPh_3)[5,8] had precluded their unambiguous assignment.

In order to do further studies on **8** and **8a**, we required spectral data for Cp*$(CO)_2$Fe–$SnPh_3$ (**10**). This known[18] Fe–Sn complex was synthesized in 94% yield from the reaction between Cp*$(CO)_2Fe^-K^+$ and Ph_3SnCl; the resulting stable, light brown solid was fully characterized. Its IR and ^{13}C NMR spectral data readily distinguish between **8** and **10** (Table 1).

The superposition of IR spectra for Cp*$(CO)_2$Fe–$SnPh_3$ (**10**), Cp*$(CO)_2$Fe–CO_2SnPh_3 (**8**), and Cp*$(CO)_2$Fe–$^{13}CO_2SnPh_3$ (**8a**), Figure 1 (CCl_4 solution), greatly facilitated assigning the carboxylate $\upsilon(CO_2)$ bands. All three complexes exhibit weak-to-moderate intensity absorptions at 1479, 1430 (1427 for **10**), 1385 (weak doublet), 1074 (1068 for **10**), and 1031 cm^{-1} (weak doublet) that represent fingerprint absorptions for the Cp*Fe/$SnPh_3$ moieties. The lower energy $\upsilon_{sym}(CO_2)$ bands for **8** and **8a** were assigned to the broad, low-intensity absorptions centered at 1154 and 1132 cm^{-1}, respectively. Due to interference by the fingerprint absorptions, the $\upsilon_{asym}(CO_2)$ bands were identified by contrasting the relative peak intensities of the spectra in the 1460–1430-cm^{-1} region (Figure 1). The $\upsilon_{asym}(CO_2)$ band for **8** thus overlaps a weak-intensity fingerprint absorption at 1480 cm^{-1}, whereas the same band for **8a** comes at 1456 cm^{-1}.

The carboxylate IR absorptions of **8** resemble those of Cp(CO)(PPh_3)Fe–CO_2SnPh_3 (**3**) and Cp*(CO)(PPh_3)Fe–CO_2SnPh_3,[5] both in terms of band energies (Table 2) and their broad

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[20] (a) Pinkes, J. R.; Chiulli, R. J.; Steffey, B. D.; Cutler, A. R. Manuscript in preparation. (b) Interpretation of IR and ^{13}C NMR spectral data for Cp$(CO)_2$Fe–CO_2^- and Cp*$(CO)_2$Fe–CO_2^- is complicated by the presence of equilibria that link these metallocarboxylates with carboxylate-carbonyl ligand interchange, metalloanhydrides Cp(CO)Fe[(C=O)$_2$O]$^-$, and reversible CO_2 association. Results of studies on equilibria involving metalate/metallocarboxylate/metalloanhydride complexes will be reported in due course.

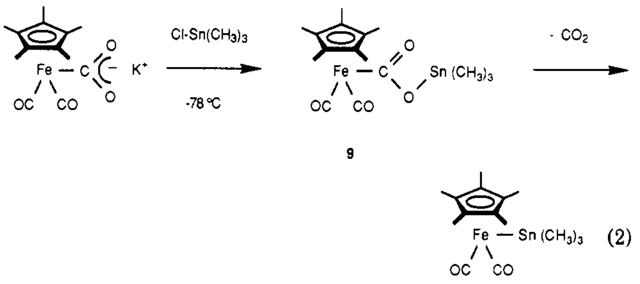
Table 2. Metallocarboxylate Infrared Spectral $\nu(CO_2)$ Bands

metallocarboxylate[a]	$\nu_{asym}(CO_2)$, cm^{-1}	$\nu_{sym}(CO_2)$, cm^{-1}	ref
$Cp^*(CO)_2Fe{-}CO_2SnPh_3$ (**8**)	1480	1154	*a*
$Cp^*(CO)_2Fe{-}^{13}CO_2SnPh_3$ (**8a**)	1456	1132	*a*
$Cp^*(CO)_2Fe{-}CO_2SnMe_3$ (**9**)	1540	1123	*b*
$Cp^*(CO)_2Fe{-}^{13}CO_2SnMe_3$ (**9a**)	1494	1103	*b*
$Cp(CO)(PPh_3)Fe{-}CO_2SnPh_3$ (**3**)[f]	1480	1174	*c*
$Cp^*(CO)(PPh_3)Fe{-}CO_2SnPh_3$	1480	1139	*c*
$Cp(NO)(PPh_3)Re{-}CO_2SnPh_3$ (**4**)[f]	1395	1188	*d*
$Cp(NO)(PPh_3)Re{-}CO_2SnMe_3$	1456	1158	*d*
$Cp(NO)(PPh_3)Re{-}C({=}O)OGePh_3$	1545	1048	*d*
$Cp(CO)(PPh_3)Fe{-}CO_2Re(Ph_3)(CO)_3$ (**5**)	1435	1247	*e*
$Cp(CO)(PPh_3)Fe{-}CO_2Re(Ph_3)(CO)_4$ (**6**)	1505	1135	*e*

[a] This work, recorded in CCl_4 solution. Sum of label frequency shifts,[25] $\Delta\nu = 46\ cm^{-1}$. [b] This work, recorded in THF solution. $\Delta\nu = 66\ cm^{-1}$. [c] Reference 5, recorded as thin film. The high and low of the three $\nu(CO_2)$ band frequencies reported: the middle value of $1432\ cm^{-1}$ apparently corresponds to a phenyl bending mode; cf. Figure 1. [d] Reference 6, recorded as thin film. [e] Reference 7, recorded as thin film. [f] Structure assignments by X-ray crystallography: chelating $\mu(\eta^1\text{-}C{:}\eta^2\text{-}O,O')$.

band shapes. Since **3** retains a (crystallographically determined) chelating $\mu(\eta^1\text{-}C{:}\eta^2\text{-}O,O')$ CO_2 ligand,[5] we assign a metallocarboxylate structure similar to that of **8**. Supporting evidence for this metallocarboxylate assignment for **8** is the absence of an IR $\upsilon(CO_2)_{asym}$ absorption above $1500\ cm^{-1}$ that would indicate a nonchelating $\mu(\eta^1\text{-}C{:}\eta^1\text{-}O)$ Fe–Sn carboxylate.[4] Analogous iron metalloester species $Cp(CO)(L)Fe{-}C(O)OCH_3$ or $Cp^*(CO)(L)Fe{-}C(O)OCH_3$ (L = CO, PPh_3)[5] and $Cp(CO)_2Fe{-}C(O)OSiMe_3$,[8] for example, show medium-intensity $\upsilon(CO_2)_{asym}$ absorptions over $1600\ cm^{-1}$.

Attempts to prepare the analogous trimethyltin–iron carboxylate $Cp^*(CO)_2Fe{-}CO_2SnMe_3$ (**9**) were partially successful. Treatment of $Cp^*(CO)_2Fe{-}CO_2^-K^+$ (**2b**) with Me_3SnCl at −78 °C formed **9** (eq 2), but it cleanly degraded to its Fe–Sn derivative $Cp^*(CO)_2Fe{-}SnMe_3$ (**11**) upon working up the reaction or even allowing it to sit at room temperature for several hours. Although **9** was characterized by IR and ^{13}C NMR spectroscopy (Table 1), we did not obtain an analytically pure sample. The fully characterized Fe–Sn compound **11**, a stable yellow solid, was independently synthesized in 90% yield from the reaction of $Cp^*(CO)_2Fe^-K^+$ and Me_3SnCl.



9

(2)

11

IR spectral data for $Cp^*(CO)_2Fe{-}CO_2SnMe_3$ (**9**) are especially diagnostic. Carboxylate $\upsilon(CO_2)$ bands for **9** and $Cp^*(CO)_2Fe{-}^{13}CO_2SnMe_3$ (**9a**) in THF solutions were assigned unambigiously (Table 1) using the procedure outlined for $Cp^*(CO)_2Fe{-}CO_2SnPh_3$ (**8**). Although these spectra lack the complicating phenyl ring bending modes in the fingerprint region, the $\upsilon(CO_2)$ bands nevertheless appeared broad and very weak. Particularly noteworthy is the presence of the higher energy $\upsilon_{asym}(CO_2)$ band for **9** at $1540\ cm^{-1}$, which is consistent with a nonchelating $\mu(\eta^1\text{-}C{:}\eta^1\text{-}O)$ carboxylate structure.[4] Similar metalloester structures have been identified for $Cp(NO)(PPh_3)Re{-}C({=}O)OGePh_3$ and $Cp(CO)(PPh_3)Fe{-}C({=}O)ORe(Ph_3)(CO)_4$ (**6**) [cf. $\upsilon_{asym}(CO_2)$ values in Table 2].

A reviewer thoughtfully suggested that ionization of **9** to an ion-pair structure $Cp^*(CO)_2Fe{-}CO_2^-{\cdot}SnMe_3^+$ could precede CO_2 extrusion. Decarboxylation thus would transform $Cp^*(CO)_2Fe{-}CO_2^-$ to $Cp^*(CO)_2Fe^-$; the resulting $Cp^*(CO)_2Fe^-{\cdot}SnMe_3^+$ then would convert to $Cp^*(CO)_2Fe{-}SnMe_3$ (**11**). A similar decarboxylation step intervenes in the reaction of $Cp(CO)_2Fe{-}CO_2^-\ K^+$ (**2a**) and methyl iodide to give $Cp(CO)_2Fe{-}CH_3$.[9a] In this reaction, decarboxylation of **2a** (an equilibrium process[20]) thus gives the metalate $Cp(CO)_2Fe^-K^+$, which preferentially intercepts the methyl iodide. These two decarboxylation steps differ, however, in that **9** first must ionize to the requisite metallocarboxylate.

We disfavor the proposed decarboxylation pathway involving ionization of **9** for two reasons. First, precedent lacks for ionization of covalent metalloesters, $L_xM{-}CO_2R$, to metallocarboxylates, $L_xM{-}CO_2^-\ R^+$, as opposed to their frequently observed dissociation to carbonyl salts, $L_xM{-}CO^+\ OR^-$.[21] Second, we note that immediately adding 1 equiv of methyl iodide to **9** at −78 °C and warming to room temperature does not alter its degradation to **11**. Neither $Cp^*(CO)_2FeMe$[10] nor $Cp^*(CO)_2Fe{-}CO_2Me$ was detected. These two observations obviously do not preclude ionization of **9** to a *tight* ion pair $Cp^*(CO)_2Fe{-}CO_2^-{\cdot}SnMe_3^+$ that decarboxylates and converts to the observed $Cp^*(CO)_2Fe{-}SnMe_3$ (**11**).

The decarboxylation study of **9** was extended to its ^{13}C-labeled isomer $Cp^*(CO)_2Fe{-}^{13}CO_2SnMe_3$ (**9a**). THF solutions containing 80–90% **9a** were generated using $Cp^*(CO)_2Fe{-}^{13}CO_2^-K^+$; the balance of the $Cp^*(CO)_2Fe$ moiety was accounted for by IR and ^{13}C NMR spectroscopy as unlabeled $Cp^*(CO)_2Fe{-}SnMe_3$ (**11**) and at most a trace of $[Cp^*Fe(CO)_2]_2$. Over several hours at room temperature, **9a** degraded to a 3:1 mixture of $Cp^*(CO)_2Fe{-}SnMe_3$ (**11**) and $Cp^*(CO)(^{13}CO)Fe{-}SnMe_3$ (**11a**) in 97% yield. The latter iron–tin complex **11a** was identified by its intense ^{13}C NMR carbonyl resonance and by its IR spectrum. The shift in its IR $\upsilon_{asym}(CO)$ and $\upsilon_{sym}(CO)$ bands to lower energies by 15 and $31\ cm^{-1}$, respectively, resembles the $\upsilon(CO)$ band shifts for the similarly labeled alkyl complexes $(\eta^5\text{-dienyl})Fe(^{13}CO)(CO)R$ (η^5-dienyl = Cp and Cp*).[22]

Spectral monitoring of the decarboxylation of **9a** to **11** and **11a** further revealed the intermediacy of $Cp^*(CO)(^{13}CO)Fe{-}CO_2SnMe_3$ (**9b**). IR spectra of this reaction mixture were resolved into six of the eight expected carbonyl $\upsilon(CO)$ bands for **9a**, **9b**, **11**, and **11a**. Overlap occurred at $1952\ cm^{-1}$, $\upsilon_{sym}(CO)$ and $\upsilon_{asym}(CO)$ bands for **9a** and **11a**, respectively, and at $1918\ cm^{-1}$, $\upsilon_{sym}(CO)$ and $\upsilon_{asym}(CO)$ bands for **11** and **9b**, respectively. (Of these four complexes, only **9b** did not have both IR $\upsilon(CO)$ bands independently assigned.) Results of both IR and ^{13}C NMR spectral monitoring of this reaction also were consistent with coupling the carboxylate–carbonyl label shift, **9a** to **9b**, with the appearance of **11a**. The intense ^{13}C NMR carboxylate resonance of **9a** (δ 216.5) accordingly decreased concurrent with growth of the carbonyl absorptions for initially **9b** (δ 211.9) and then **11a** (δ 217.5).

This carboxylate–carbonyl label exchange requires transferring the ^{13}C-label from the ligated $^{13}CO_2$ on **9a** to a carbonyl group on **9b**. A plausible pathway (eq 3) entails **9a** equilibrating with **9b** via a metalloanhydride intermediate. Similar metalloanhydride intermediates have been proposed for label shuttling between carboxylate and terminal carbonyl sites on $Cp(CO)_2Fe{-}^{13}CO_2^-Li^+$ or $Cp(CO)_2Fe{-}C^{18}O_2^-Li^+$,[23a] $[Cp(CO)_2Fe{=}C(^{17}O)O{-}WCp_2]^+$,[23b] and $Cp(CO)_2M{-}^{13}CO_2{-}Zr(Cl)Cp_2$ (M = Fe,[2] Ru[1b]).

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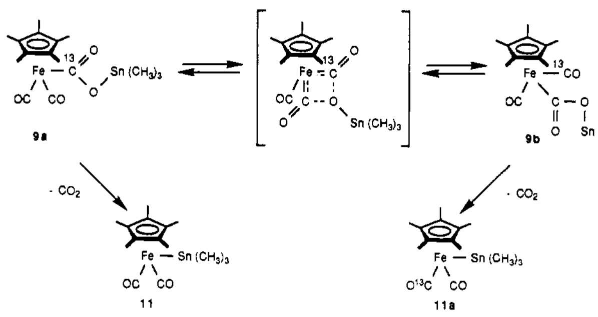
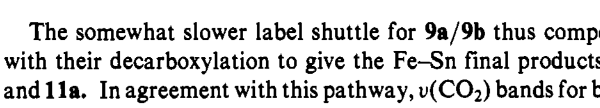


(3)

The somewhat slower label shuttle for **9a**/**9b** thus competes with their decarboxylation to give the Fe–Sn final products **11** and **11a**. In agreement with this pathway, $\upsilon(CO_2)$ bands for both free CO_2 and $^{13}CO_2$ at 2336 and 2270 cm^{-1}, respectively, were observed.

The room-temperature decarboxylation of the Fe–Sn bimetallocarboxylate compounds **9a** and **9b** to their Fe–Sn derivatives **11** and **11a** occurs under milder conditions than those reported by Gladysz for $Cp(CO)(PPh_3)Re–CO_2SnPh_3$ (**4**) (>140 °C).[6] All of these decarboxylation examples contrast with our previous results pertaining to hetereobimetallic carboxylate complexes such as $Cp(CO)_2Fe–CO_2–Zr(Cl)Cp_2$ (**1**),[1,2] which thermally degrades to its zirconocene μ-oxide and free carbon monoxide. Unfortunately, CO_2 extrusion from **9** is not reversible; neither the Fe–Sn complex $Cp^*(CO)_2Fe–SnPh_3$ (**10**) nor $Cp^*(CO)_2Fe–SnMe_3$ (**11**) in THF added carbon dioxide at 70 psig.

Related studies involving reactions between $(\eta^5-C_5H_5)(CO)_2Fe–CO_2^-K^+$ (**2a**) and tin chlorides R_3SnCl (R = Ph, Me) gave different results. Treatment of **2a**, also a CO_2-derived metallocarboxylate, with triphenyltin chloride afforded only the well-known[19] iron–tin complex $Cp(CO)_2Fe–SnPh_3$ (eq 4). If significant concentrations of the anticipated Fe–Sn carboxylate $Cp(CO)_2Fe–CO_2SnPh_3$ had formed, then it would have been detected in IR spectra of the reaction mixtures at lower temperatures. Using a similar IR spectral monitoring approach, we had characterized metallocarboxylates such as **2a** that rapidly degrade above –60 °C.[1,20a]



(4)

Repeating the same reaction sequence using $^{13}CO_2$ also produced only $Cp(CO)_2Fe–SnPh_3$. We detected neither $Cp(CO)_2Fe–^{13}CO_2SnPh_3$ nor $Cp(CO)(^{13}CO)Fe–SnPh_3$ during ^{13}C NMR and IR spectral monitoring of this reaction. The absence of $Cp(CO)(^{13}CO)Fe–SnPh_3$ precludes the transience of a labile $Cp(CO)_2Fe–^{13}CO_2SnPh_3$ that competitively shuttled its ^{13}C label as it lost carbon dioxide. Conceivably, $Cp(CO)_2Fe–^{13}CO_2SnPh_3$ could form at low temperatures and decarboxylate before it can scramble the label. The independence of these competing reactions was established via the chemistry that is summarized in eq 3, although $Cp^*(CO)_2Fe–^{13}CO_2SnMe_3$ (**9a**) transformed to $Cp^*(CO)(^{13}CO)Fe–CO_2SnMe_3$ (**9b**) more rapidly than it decarboxylated to $Cp^*(CO)_2Fe–SnMe_3$ (**11**).

Results of several exploratory experiments also are germane to our attempts at generating $Cp(CO)_2Fe–CO_2SnPh_3$. Substituting lithium and magnesium metallocarboxylates $Cp(CO)_2Fe–CO_2Li$ and $[Cp(CO)_2Fe–CO_2]_2Mg$ for **2a**[8,9] in its reactions with Ph_3SnCl likewise gave only $(\eta^5-C_5H_5)(CO)_2Fe–SnPh_3$, as deduced from IR spectral monitoring. Trimethyltin chloride also transformed **2a** directly to the known $Cp(CO)_2Fe–Sn(CH_3)_3$,[24] which we prepared independently for comparison of spectral data.

These reactions between the metallocarboxylate **2a** and the tin chlorides R_3SnCl (R = Ph, Me) can be accounted for by two plausible mechanisms. (1) Undetected tin metalloester intermediates, $Cp(CO)_2Fe–CO_2SnR_3$, could form and promptly decarboxylate. (2) The metallocarboxylate **2a** is not sufficiently nucleophilic to react with Ph_3SnCl or $(CH_3)_3SnCl$; therefore, the tin chloride intercepts the dissociative equilibrium between **2a** and the metalate $Cp(CO)_2Fe^-K^+$ and selectively provides $Cp(CO)_2Fe–SnR_3$.

We favor the second pathway for two reasons. First, this pathway is essentially the same that we established for the reaction of **2a** and methyl iodide to give $Cp(CO)_2Fe–CH_3$.[9a] (We have since demonstrated via labeling studies that **2a** reversibly binds its CO_2, although free $Cp(CO)_2Fe^-K^+$ was not detected.[20]) The more oxophilic trimethylsilyl chloride, in contrast, traps **2a** as its metalloester $Cp(CO)_2Fe–C(=O)OSiMe_3$ (**7**).[8] Second, it is unlikely that the two series of Fe–Sn metallocarboxylates $Cp^*(CO)_2Fe–CO_2SnR_3$ (**8**/**9**) and $Cp(CO)_2Fe–CO_2SnR_3$ should so differ in thermodynamic stability that only the former **8** can be isolated, whereas the latter (e.g., R = Ph) cannot be detected even at lower temperatures.

Conclusions

In order to assign chelating and nonchelating carboxylate structures to the iron–tin metallocarboxylates $Cp^*(CO)_2Fe–CO_2SnR_3$, we had to identify their IR $\upsilon(CO_2)$ bands. These bands, however, appeared in the fingerprint region as broad, featureless absorptions, irrespective of whether the data were collected for KBr disks, fluorolube mulls, or in solution. Identifying these bands required comparing this IR spectral data with that of at least one of the model systems, either $Cp^*(CO)_2Fe–^{13}CO_2SnR_3$ or $Cp^*(CO)_2Fe–SnR_3$. Our assignments of chelating and nonchelating carboxylate structures to $Cp^*(CO)_2Fe–CO_2SnPh_3$ (**8**) and $Cp^*(CO)_2Fe–CO_2SnMe_3$ (**9**), respectively, then correlate with the presence of a $\upsilon(CO_2)_{asym}$ band above 1500 cm^{-1} for chelating metallocarboxylates, consistent with IR spectral data for the related complexes listed in Table 2.

Three limitations to interpreting this IR data immediately became apparent. First, the presence of broad and diffuse IR spectral $\upsilon(CO_2)$ bands for **8**, **8a**, **9**, and **9a** precluded a more detailed analysis.[25] Second, our assignments of chelating and nonchelating carboxylate structures for **8** and **9**, respectively, do not account for the possibility of varying degrees of ***unsymmetric*** η^2-O,O′ carboxylate–Sn bonding. Structures for unsymmetrically chelated organic carboxylate ligands to metal systems have been reported.[26]

The third limitation is that the usual IR spectral correlation involving carboxylate peak separations,[4] $\Delta\upsilon(CO_2) = [\upsilon(CO_2)_{asym} - \upsilon(CO_2)_{sym}]$, does not apply to Sn–metallocarboxylates. This rule-of-thumb has been used in discerning the bonding of organic carboxylate ligands to metal systems: symmetrical chelating or (η^2-O) carboxylate ligands have $\Delta\upsilon(CO_2)$ values less than 100 cm^{-1}. Of the eight Sn–metallocarboxylates listed in Table 2, all but **9** and **9a** exhibit $\Delta\upsilon(CO_2)$ values between 207 and 341 cm^{-1}. X-ray structure determinations of **3**[5] and **4**[6] confirmed chelating $\mu(\eta^1$-C:η^2-O,O′) structures, even though these complexes have $\Delta\upsilon(CO_2)$ values of 207 and 306 cm^{-1}, respectively. The iron–

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trimethyltin carboxylates **9** and **9a** have higher $\Delta\nu(CO_2)$ = 417 and 391 cm^{-1} that agree with their $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ metalloester formulation.

An intriguing result of this work is an emerging structure/reactivity correlation involving the Fe–Sn carboxylates Cp*(CO)$_2$Fe–CO$_2$SnPh$_3$ (**8**) and Cp*(CO)$_2$Fe–CO$_2$SnMe$_3$ (**9**). The triphenyltin–Fe carboxylates **8** and **8a**, which retain chelating $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ structures, are surprisingly nonreactive; Cp*(CO)$_2$Fe–^{13}CO$_2$SnPh$_3$ (**8a**) neither shuttles its ^{13}C label nor decarboxylates at room temperature. In contrast, the trimethyltin–Fe carboxylates **9** and **9a** favor nonchelating $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ CO$_2$ ligands and, accordingly, are quite reactive. Thus Cp*(CO)$_2$Fe–^{13}CO$_2$SnMe$_3$ (**9a**) and Cp*(CO)(^{13}CO)Fe–CO$_2$SnMe$_3$ (**9b**) competitively interconvert as they decarboxylate to their Fe–Sn derivatives Cp*(CO)$_2$Fe–SnMe$_3$ (**11**) and Cp*(CO)(^{13}CO)Fe–SnMe$_3$ (**11a**). Future studies will further elaborate the relationship between symmetrical vs unsymmetric $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ bimetallocarboxylate structure and reactivity.

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