# Metallocarboxylate Trialkylsilyl Esters: A Means of Derivatizing the Carbon Dioxide Containing $\eta^1$-C Metallocarboxylates $Cp(CO)_2FeCO_2^-Li^+$ and $Cp(CO)_2FeCO_2^-Na^+$

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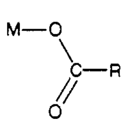
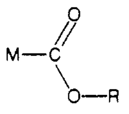
*Received August 21, 1986*

The metallocarboxylates $FpCO_2^-$ (**6**·$Li^+$,$Na^+$) are prepared by treating the requisite $Fp^-$ metalate $Li^+$ or $Na^+$ [$Fp = Cp(CO)_2Fe$] with 1.5 equiv of $CO_2$ in THF (–80 °C). These unstable $\eta^1$-C $CO_2$ adducts, characterized by IR and $^{13}C$ NMR spectroscopy for **6**·$Li^+$, react with methyl iodide or with methyl triflate to give $FpCH_3$ exclusively. This reaction course is consistent with $CH_3I$ selectively reacting with $Fp^-$, thus driving an otherwise disfavored dissociative equilibrium: **6** $\rightleftarrows$ $Fp^- + CO_2$. Trimethylsilyl chloride and *tert*-butyldimethylsilyl chloride both intercept **6**·$Li^+$ or **6**·$Na^+$ and give the corresponding metallocarboxylate trialkylsilyl ester. $FpCO_2Si(CH_3)_3$ is unstable at room temperature [decomposing to $Fp_2$, not to the stable $FpSi(CH_3)_3$], and $FpCO_2Si(CH_3)_2[C(CH_3)_3]$ is isolated as a stable, analytically pure yellow-brown gum (85% IR spectral yield, 53% isolated). No evidence for silylating $Fp^-$ was found. Use of hard oxophilic trialkylsilyl chlorides thus affords derivatives of the metallocarboxylate ligand on $FpCO_2^-$ (**6**·$Li^+$,$Na^+$).

Carbon dioxide fixation via transition organometallic complexes includes ligating the $CO_2$ as $\eta^1$-O metallocarboxylates **1** and as $\eta^1$-C metallocarboxylic acid esters **2** (i.e., alkoxycarbonyls).[1] The former evidently results



**1**



**2**

through a concerted insertion of free $CO_2$ into a metal–carbon σ-bond, as adduced by recent studies of Darensbourg and co-workers with $(CO)_5WR^-$ complexes.[2] Alternatively, electron-rich $\eta^1$-C $CO_2$ complexes (metallocarboxylates) upon reacting with an electrophilic alkylating agent may afford examples of **2**. Obtaining derivatives of an $\eta^1$-C $CO_2$ complex as C-bound metallo ester **2**, the object of the present study, has been established in only three cases.[3] One involves the metallocarboxylate $Cp(CO)_2Fe-CO_2^-$ system (eq 1).[3a]

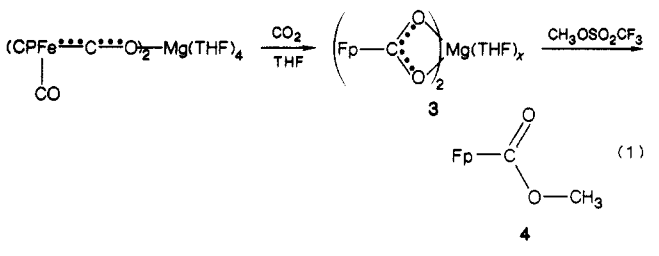
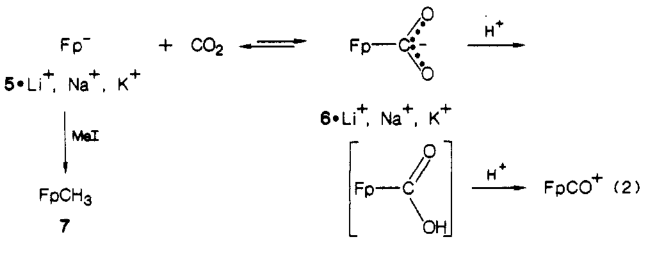


**Table I. Spectroscopic Characterization of $Cp(CO)_2FeCO_2^-$ Metallocarboxylates and Related Complexes**

| complex | IR (THF), $cm^{-1}$ | $^1H$ NMR ($CDCl_3$), δ | $^{13}C$ NMR, δ |
|---|---|---|---|
| $Fp^-Li^+$ (**5**·$Li^+$) | 1884, 1813<br>1868, 1751<br>(C≡O)[a] | | 228.4 (CO)[b]<br>76.1 (Cp) |
| $Fp^-Na^+$ (**5**·$Na^+$) | 1881, 1808<br>1864, 1770<br>(C≡O)[a] | | 226.1 (CO)[b]<br>75.2 (Cp) |
| $FpCO_2^-Li^+$ (**6**·$Li^+$) | 2000, 1938<br>(C≡O)[c] | | 217.0 (C=O)[b,f]<br>202.4 (C≡O)<br>85.4 (Cp) |
| $FpCO_2^-Na^+$ (**6**·$Na^+$) | 2000, 1945<br>(C≡O)[c] | | |
| $FpCO_2Si(CH_3)_3$ (**8**) | 2032, 1973<br>(C≡O)<br>1625 (C=O) | 4.91 (Cp)<br>0.16 ($SiCH_3$) | 214.7 (C=O)[d,f]<br>200.7 (C≡O)<br>86.8 (Cp)<br>12.1 ($CH_3$) |
| $FpCO_2Si(CH_3)_2$-$[C(CH_3)_3]$ (**10**) | 2027, 1982<br>(C≡O)<br>1627 (C=O) | 4.86 (Cp)<br>0.13 ($SiCH_3$)<br>1.72 ($C(CH_3)_3$) | 213.6 (C=O)[d]<br>200.7 (C≡O)<br>86.4 (Cp)<br>25.6 (*C*($CH_3$))<br>17.7 (C(*CH*$_3$)$_3$)<br>–4.2 ($SiCH_3$) |
| $FpCO_2CH_3$[e] (**4**) | 2030, 1976<br>(C≡O)<br>1647 (C=O) | 4.76 (Cp)<br>3.53 ($OCH_3$) | 213.3 (C=O)[d]<br>200.8 (C≡O)<br>86.0 (Cp) |

[a] These absorptions have been previously assigned[17] to Fe–alkali metal and isocarbonyl ion pairing, respectively.[19] [b] Solvent THF. [c] Lee and Cooper[8] reported 2015 and 1950 $cm^{-1}$. [d] Solvent $CDCl_3$. [e] IR and $^1H$ NMR spectral data agrees with that previously recorded. [f] Data recorded at –78 °C.

Evans and co-workers[4] first reported that $Cp(CO)_2Fe^-Na^+$ (i.e., $Fp^-Na^+$) binds $CO_2$ (eq 2) and ultimately reduces



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it to $CO_3^{2-}$. Protonating the initial $CO_2$ adduct **6**·Na$^+$ additionally provides a convenient preparation of FpCO$^+$ *via* a net two-electron reduction (by **5**·Na$^+$) of $CO_2$ to CO.[5,6] Cooper and Lee[8] rigorously established that these 1:1 adducts observed with **6**·Li$^+$,Na$^+$,K$^+$ also facilitated oxide transfer between a carboxylate oxygen and a terminal carbonyl. Their labeling studies further demonstrated that these metastable adducts **6** in THF solution decompose (giving carbonate, formate, and unidentified materials) by processes other than reductive disproportionation of $CO_2$, even in the presence of excess $CO_2$. No evidence, accordingly, is available for forming a 1:2 adduct FpC(O)OC(O)O$^-$.

Attempts[3c,4,8] at intercepting **6** with electrophilic methylating reagents ($CH_3I$, $CH_3OSO_2CF_3$, and $CH_3OSO_2F$) to yield its methyl ester **4** instead produced $FpCH_3$ (**7**) (eq 2). Evidently **6** reversibly dissociates $CO_2$, and the methylating agent drives this equilibrium by selectively scavenging Fp$^-$ (**5**) as the observed **7**. The magnesium $CO_2$ adduct **3**, in contrast, alkylates at the metallocarboxylate ligand and gives **4** (eq 1). Oxophilic Mg(II), by strongly bonding to (and possibly chelating) the carboxylate, presumably blocks $CO_2$ dissociation.[9] Results of studies with other anionic metallocarboxylates, however, evidently parallel those of **6**: organic alkylating agents preferentially trap the original metal anion, not the metallocarboxylate.[10]

We now report the use of oxophilic trialkylsilyl chlorides[11] in trapping—silylating—metallocarboxylates **6**·Li$^+$,Na$^+$ and giving fully characterized metallocarboxylate silylester derivatives. Synthetic details for preparing and reacting the 1:1 $CO_2$ adducts **6**·Li$^+$,Na$^+$ with methyl iodide, methyl triflate, trimethylsilyl chloride, and *tert*-butyldimethylsilyl chloride are documented.

## Experimental Section

All synthetic manipulations were performed under a nitrogen atmosphere by using standard syringe/septum and Schlenk-type, bench-top techniques for handling air- and moisture-sensitive organometallics.[12]

Infrared spectra were taken of $CH_2Cl_2$ and THF solutions (0.10 mmol/1.5 mL) in NaCl, lead (amalgam)-spaced (0.10 mm) solution cells and were recorded on a Perkin-Elmer Model 297 spectrophotometer. The $\nu$(CO) frequencies were calibrated against the polystyrene 1601 cm$^{-1}$ absorption; they are accurate to ±2 cm$^{-1}$ below and ±5 cm$^{-1}$ above 2000 cm$^{-1}$. IR spectra of $Fp_2$, $FpCH_3$ (**7**), $FpCO_2CH_3$ (**4**), and $FpCO_2Si(CH_3)_2(t\text{-Bu})$ (**10**) in THF solution exhibit straight-line Beer's law behavior. IR spectral monitoring of reactions was accomplished semiquantitatively (±5%) through analysis of absorptivity changes in the terminal and/or ester $\nu$(CO). Moreover, as little as 4% (yield) of **4** [$\nu$(CO) 1647 cm$^{-1}$] can be detected in the presence of excess $FpCH_3$ (**7**). Similar detectability limits apply to $Fp_2$ [$\nu$(CO) 1782 cm$^{-1}$] vs. **7** and to **10** [$\nu$(CO) 1627 cm$^{-1}$] vs. $Fp_2$ (all data in THF).

NMR spectral data were recorded in $CDCl_3$ ($^1H$, $^{13}C$) and THF ($^{13}C$) solutions, after trace amounts of insoluble residues were centrifuged. Varian Model XL-200 and IBM-WP100 instruments supplied the NMR spectra, which are reported as $\delta$ values downfield from internal $Me_4Si$. Combustion microanalyses were performed by Mic Anal, Tucson, AZ.

Organic reagents were procured commercially and used as received. Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone ketyl; methylene chloride was likewise obtained as needed from $P_2O_5$. Carbon dioxide was dried by passing through a $P_2O_5$ column. Metal carbonyl complexes $Fp_2$,[13] $FpCO_2CH_3$ (**4**),[5,14] $FpCH_3$ (**7**),[15] $FpSi(CH_3)_3$ (**9**),[16] and FpCO$^+$BF$_4^-$ [5] were prepared by literature procedures and judged pure by IR and NMR spectroscopy.

**Preparation and Methylation of $Cp(CO)_2FeCO_2^-Li^+$ (5·Li$^+$).** To a 500-mL three-neck amalgam reduction flask (fitted with an overhead stirrer) was decanted in excess 1% lithium amalgam, typically enough amalgam (70 mL) being added to just cover the Teflon stirrer blade. THF (168 mL) and $[Cp(CO)_2Fe]_2$ (1.984 g, 5.61 mmol) then were added. (The use of recrystallized iron dimer and decanted Li(Hg) minimizes the formation of "mercury dust" and other troublesome insoluble residues.) Vigorously stirring the purple solution/Li(Hg) for 2.5 h (under $N_2$) produced an orange-red supernatant of $Cp(CO)_2Fe^-Li^+$ (**5**·Li$^+$) [IR (THF) $\nu$(CO) 1884, 1868, 1813, 1751 cm$^{-1}$]. Thirty milliliters of this solution (containing 2.0 mmol of **5**·Li$^+$) was transferred by using a stainless-steel needle, cooled to −78 °C, and then treated with dry carbon dioxide (70 cm$^3$, 3.0 mmol). A 50-cm$^3$ syringe, the "plunger" wetted by THF, was used to slowly inject (over 2 min) the $CO_2$ into the gently swirled Fp$^-$Li$^+$ (**5**·Li$^+$) solution, in an otherwise closed system. After being swirled another 0.5 min, the reaction flask was revented to the $N_2$ atmosphere and pressure release bubbler.

A dark yellow-brown solution immediately resulted; its IR spectrum contained intense $\nu$(CO)s at 2000 and 1938 cm$^{-1}$, with only small amounts (5–7%) of **5**·Li$^+$ and $Fp_2$ [$\nu$(CO) 1993, 1953, 1782 cm$^{-1}$] evident. These IR spectra were promptly recorded after the cold solution was injected into a precooled cell (with cold solvent), the entire operation taking less than 2 min. Under these conditions, no IR $\nu$(OCO) carboxylate absorptions were detected within the THF IR spectral "window" (1950–1520 cm$^{-1}$). $^{13}C$ NMR spectra also were obtained quickly on the cold THF solutions of $FpCO_2^-Li^+$ (**6**·Li$^+$).

THF solutions containing **6**·Li$^+$, upon warming to room temperature, turned dark brown but did not precipitate any sediment. (After 0.75 h, however, gel formation due to polymerized THF is evident.) IR spectral monitoring indicated that $Fp_2$ and varying amounts of FpH[5] (0–25%) [$\nu$(CO) 2016, 1952 cm$^{-1}$] were the organometallic products. The FpH quantitatively converted to FpCl [$\nu$(CO) 2045, 1999 cm$^{-1}$] when $CCl_4$ was added.[18]

In a separate experiment, a cold THF solution of $FpCO_2^-Li^+$ (**6**·Li$^+$) (ca. 2.0 mmol), 2 min after adding the $CO_2$, was warmed

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(6) Ther reverse of this reaction is precedented. Hydroxide adds to FpCO$^+$ and gives the metallocarboxylic acid $FpCO_2H$,[7a] which rapidly deinserts $CO_2$ and leaves FpH (then $Fp_2$) under ambient conditions. Similar chemistry, but starting with CpCO)$(PPh_3)$FeCO$^+$, affords both the metallocarboxylic acid $Cp(PPh_3)(CO)FeCO_2H$[7b] and its stable metallocarboxylate Cp(P)(CO)FeCO$_2^-$K$^+$, all three species linked by pH-dependent equilibria.[7a]

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(9) As support for this supposition, we note that **3** (THF solution, −50 °C) is largely unreactive toward methyl iodide. Accordingly, MeI does not methylate the metallocarboxylate ligand on **3**, although it would immediately methylate any $Fp_2Mg$ that dissociated [giving FpMe (**7**)] under these conditions.

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to −50 °C and immediately treated with methyl triflate (328 mg, 2.0 mmol). IR spectral monitoring of the brown solution indicated $Fp_2$ (4–8%) and $FpCH_3$ (**7**) (>90%) [$\nu$(CO) 2004, 1974 cm$^{-1}$] are the only detected organometallic products. [Small amounts (<4%) of FpH would not have been unambiguously detected under these conditions.]

**Preparation of $Cp(CO)_2FeCO_2^-Na^+$ (5·Na$^+$).** $Fp_2$ (1.007 g, 2.84 mmol) as a THF solution (85 mL) was vigorously stirred over excess 1% Na(Hg) for 2 h, quantitatively generating a red-orange solution of $Fp^-Na^+$ (**5**·Na$^+$)[16] [$\nu$(CO) 1881, 1864, 1808, 1770 cm$^{-1}$]. An aliquot [40 mL, 2.67 mmol (**5**·Na$^+$)] of metalate solution was transferred, cooled to −78 °C, and treated with 90 cm$^3$ (4.0 mmol) of carbon dioxide in a gently swirled and closed system. IR spectral data (Table I) of the resulting dark yellow-brown solution are in accord with $FpCO_2^-Na^+$ (**6**·Na$^+$), along with small amounts (5–8%) of unreacted **5**·Na$^+$ and of $Fp_2$. These solutions, which are more unstable than observed for **6**·Li$^+$, degrade at −78 °C ($\tau_{1/2} \approx 0.5$ h) and rapidly above −20 °C ($\tau_{1/2} \approx 0.25$ h) to $Fp_2$ and variable but minor amounts of FpH. Insoluble residues, likewise, were not observed, although gel formation of the THF (its polymerization) sets in above −20 °C.

**Reaction of Trimethylsilyl Chloride and $Cp(CO)_2FeCO_2^-Li^+$ (6·Li$^+$).** $(CH_3)_3SiCl$ (217 mg, 2.0 mmol) was added to a cold (−78 °C) THF solution of $FpCO_2^-Li^+$ (**6**·Li$^+$) (ca. 2.0 mmol). IR spectral monitoring of the cold, dark brown solution within 5 min indicated that $\nu$(CO) for **6**·Li$^+$ had been replaced by terminal carbonyl and ester $\nu$(CO) (Table I) absorptions of a metallo ester species and $Fp_2$. The IR spectral yield of the resulting $FpCO_2Si(CH_3)_3$ (**8**), based on a Beer's law curve for $FpCO_2Si(CH_3)_2(t\text{-Bu})$ (**11**), is approximately 62%. Upon being warmed to room temperature, however, the in situ generated **8** degraded to 2:1 mixtures of $Fp_2$ and FpH ($\tau_{1/2}$ = 1.25 h).

The reaction was worked up by evaporating the solvent (10$^{-2}$ mm, −10 °C) and extracting the product with cold (−10 °C) pentane. Although the slightly soluble **8** was preferentially extracted, it subsequently degraded to $Fp_2$. Removal of solvent (−20 °C) left a brown gum, which by IR and NMR spectroscopy assayed as approximately 1:1 mixtures of $Fp_2$ and **8**. No $FpSi(CH_3)_3$ (**9**) was detected, although results of independent experiments indicated that by NMR and IR spectroscopy as little as a 5% yield of stable $FpSi(CH_3)_3$[16] (**9**) [$^1$H NMR ($CDCl_3$) $\delta$ 4.43; IR 1994, 1933 cm$^{-1}$] would have been detected in the presence of $Fp_2$ [($CDCl_3$) $\delta$ 4.86 (Cp)]; moreover, **9** is stable in THF. $^{13}$C and $^1$H NMR spectral data for **8** were recorded at −78 °C.

**Preparation of $FpCO_2Si(CH_3)_2[C(CH_3)_3]$ (10).** A THF solution of freshly prepared $FpCO_2^-Li^+$ (**6**·Li$^+$) (2.0 mmol/30 mL) was immediately treated with $(CH_3)_2(t\text{-Bu})SiCl$ (302 mg, 2.00 mmol) at −78 °C. IR spectral monitoring after 5 min of the darker yellow-brown solution was consistent with **6**·Li$^+$ having converted to a 4.1:1 mixture of $FpCO_2Si(CH_3)_2(t\text{-Bu})$ (**10**) and $Fp_2$; the ester and bridging carbonyl $\nu$(CO)s (1627 and 1782 cm$^{-1}$, respectively) were used in this quantification.

The solvent was evaporated (10$^{-1}$ mm, 22 °C) forming a brown gum, which was extracted with a total volume of 30 mL of pentane. Cooling to −78 °C afforded dark purple crystals of $Fp_2$; the supernatant was filtered and evaporated. Repeating the pentane extraction, cooling, and filtration removed the remaining trace amounts of $Fp_2$. Evaporating the filtrate left a yellow-brown gum (383 mg after vacuum drying 10$^{-2}$ mm/6 h) corresponding to analytically pure $FpCO_2Si(CH_3)_2(t\text{-Bu})$ (**10**) (57% yield): IR ($CH_2Cl_2$) 2037, 1982 (C≡O), 1615 cm$^{-1}$ (C=O); IR (pentane) 2038, 1984 (C≡O), 1630 cm$^{-1}$ (C=O).

Anal. Calcd for $C_{14}H_{20}O_3SiFe$: C, 50.01; H, 6.03. Found: C, 49.70; H, 5.84.

A similar reaction, but substituting $FpCO_2^-Na^+$ (**6**·Na$^+$) for **6**·Li$^+$, likewise afforded **10** in 80% spectroscopic yield and in 63% isolated yield (423 mg).

**Protonation of $FpCO_2Si(CH_3)_2[C(CH_3)_3]$ (10).** To a methylene chloride solution (15 mL) containing $FpCO_2Si(CH_3)_2[C(CH_3)_3]$ (**10**) (504 mg, 1.5 mmol) was added $HBF_4 \cdot O(CH_2CH_3)_2$ (350 mg, 2.0 mmol) with swirling. A whitish tan solid immediately settled out. The reaction (after 5 min was added to 60 mL of ether, filtered, washed with ether (40 mL), and dried in a stream of nitrogen. Reprecipitation of the light tan solid from $CH_3NO_2$ (20 mL)–ether (75 mL) afforded a 377 mg of spectroscopically pure $FpCO^+BF_4^-$ (86% yield).

## Results and Discussion

Treating red-orange THF solutions containing $Fp^-Li^+$ (**5**·Li$^+$) or $Fp^-Na^+$ (**5**·Na$^+$) (0.67 M) at −78 °C with 1.5 equiv of carbon dioxide immediately affords dark yellow-brown solutions. IR spectral monitoring indicated that this quantity of $CO_2$, added slowly by syringe, represents the optimal concentration for consuming the starting metalate **5**·Li$^+$,Na$^+$. Their terminal carbonyls $\nu$(CO), absorbing between 1885 and 1750 cm$^{-1}$,[17,19] accordingly were replaced by two intense $\nu$(CO)s at 2000 and 1940 cm$^{-1}$. $^{13}$C NMR spectra of the solutions derived from **5**·Li$^+$, recorded at −78 °C, exhibited only the absorptions noted in Table I.

These spectral data, and the formation of stable derivatives (vide infra), are consistent with the metallocarboxylate structure **6** advanced by Cooper.[8] We do not however detect carboxylate IR $\nu$(OCO) within the THF solvent absorption "window" (above 1520 cm$^{-1}$). These absorptions appear below this value and can be explained by the presence of chelating Li$^+$ or Na$^+$.[20] The related bimetallic $\mu$-($\eta^1$-C:$\eta^2$-O,O′) $CO_2$ complex Cp(NO)(CO)Re–$CO_2$–Zr(Cl)$Cp_2$, which has (Re) metallocarboxylate oxygens chelating Zr, exhibits its carboxylate $\nu$(OCO) below 1400 cm$^{-1}$, for example.[21]

$^{13}$C NMR spectrum of **6**·Li$^+$ nevertheless clearly pinpoints the carboxylate resonance at $\delta$ 217, with the $\delta$ 202 absorption assigned to the terminal carbonyl ligand. This latter assignment is consistent with those ($\delta$ 210–200) for terminal carbonyls of Fp acyl and carbamoyl compounds.[22] The metallocarboxylate esters **4**, **8**, and **10** exhibit their carboxylate $^{13}$C NMR shifts at $\delta$ 210–220 (Table I), whereas the carboxylate carbon of the O-bound acetate ligand on $FpOC(O)CH_3$ resonates at $\delta$ 212 (with the terminal carbonyl appearing at $\delta$ 180).[23]

In THF solution, **6**·Li$^+$ is much more stable than is **6**·Na$^+$, and at −78 °C solutions containing **6**·Li$^+$ are stable for at least 2 h. After these solutions are warmed to room temperature, IR spectra record $\nu$(CO) absorptions for $Fp_2$ and varying amounts of FpH growing in at the expense of those for **6**·Li$^+$ ($\tau_{1/2}$ = 0.5 h), commensurate with darkening (red-brown) of the reaction solutions. In contrast, **6**·Na$^+$ decomposes slowly even at −78 °C ($\tau_{1/2}$ = 0.5 h) and rapidly above −20 °C. Under either conditions, the amount of FpH present varied from none (i.e., $Fp_2$ is the only CpFe complex detected) to a maximum of 25% in some runs. The final solutions, moreover, remained homogeneous, as no insoluble residues formed.

The slight excess of $CO_2$ (1.5 equiv) present during our studies in part accounts for the low stability of these metallocarboxylate **6**·Li$^+$,Na$^+$, as noted also by Lee and Cooper.[8] Indeed, passing a large excess of $CO_2$ through their THF solutions (−78 °C) immediately decomposes **6**·Li$^+$,Na$^+$: the solutions darkened and solids deposited, as expected. IR spectra of the supernatant report the presence of $Fp_2$ and again variable but minor yields of FpH; identity of the latter was confirmed by degrading it to FpCl with added $CCl_4$.[5,18]

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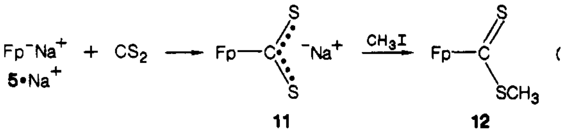
[24] Passing a large excess of $CO_2$ through a THF solution of **6**·Li$^+$ (but not **6**·Na$^+$) at −78 °C and then immediately adding excess methyl triflate (5 equiv) afforded small amounts of $FpCO_2CH_3$ (**4**). IR spectra monitoring of the brown solutions (−50 °C at room temperature) indicated the presence of **4** (10–19%, variable) and $Fp_2$ (7%), in addition to $FpCH_3$.

$$\underset{\mathbf{6}\cdot\mathrm{Li}^+}{\mathrm{FpCO_2^-Li^+}} + \mathrm{CH_3OSO_2CF_3} \rightarrow \underset{\mathbf{7}}{\mathrm{FpCH_3}} \qquad (3)$$

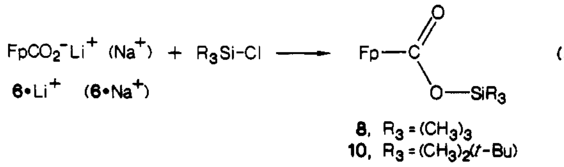
Treating either $FpCO_2^-Li^+$ (**6**·$Li^+$) or $FpCO_2^-Na^+$ (**6**·$Na^+$) with methyl triflate or with methyl iodide affords only $FpCH_3$ (**7**) (eq 3). Methylating reagents were added at −78, −40, and −20 °C, and the reactions were slowly (1 h) warmed to room temperature. IR spectral monitoring in each case indicated that the metallocarboxylate **6** quantitatively converted to $FpCH_3$ (**7**). No metallo ester $FpCO_2CH_3$ (**4**) was detected under conditions whereas little as a 5% yield easily would have been measured.

The difficulty in methylating metallo carboxylate **6** contrasts the reported reactivity of dithiocarboxylate **11**[25] (eq 4). This stable $CS_2$ adduct upon reacting with methyl iodide efficiently converts to its metallodithiocarboxylate methyl ester **12**.



(4)

Silylating $FpCO_2^-Li^+$ (**6**·$Li^+$) or $FpCO_2^-Na^+$ (**6**·$Na^+$) with trimethylsilyl chloride and *tert*-butyldimethylsilyl chloride provides an expedient method to derivatize the metallocarboxylate ligand. Both **6**·$Li^+$ and **6**·$Na^+$ immediately react with the trialkylsilyl chlorides at −78 °C to give brown solutions containing the metallocarboxylate silyl esters **8** and **10** (eq 5). IR spectra of these solutions display prominent silyl ester $\nu$(CO) at 1625 and 1627 cm$^{-1}$ that are assigned to **8** and **10**, respectively. Reactions with the *tert*-butyldimethylsilyl chloride are cleaner; **10** forms in 85% yield (IR spectral), and $Fp_2$ accounts for the remaining organometallics. Trimethylsilyl chloride and **6**·$Li^+$ or **6**·$Na^+$ afford a complex mixture, approximately 1:1 in $Fp_2$ and **8** initially, which however proved unstable.



(5)

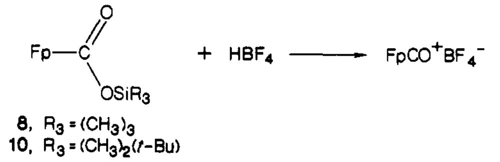
Attempts to isolate $FpCO_2Si(CH_3)_3$ (**8**) inevitably degraded it to ca. 2:1 mixtures of $Fp_2$ and FpH. Pentane extracts (kept at −20 to −10 °C) of the crude reaction products, upon evaporating the solvent (at −20 °C), left brown gums; these afforded 3:2 mixtures of **8** (45% yield) and $Fp_2$ when redissolved. The spectral data reported (Table I) for **8** were collected on these samples. Once dissolved in pentane or THF, however, **8** readily decomposes to the $Fp_2$/FpH mixtures: $\tau_{1/2}$ (22 °C) is 1.25 h.

Significantly, no Fp–$Si(CH_3)_3$[16] (**9**) was detected—either in the crude reaction mixtures or in subsequent decomposition of $FpCO_2Si(CH_3)_3$ (**8**). The stable **9** easily would have been detected in as little as 5% yield, even in the presence of excess $Fp_2$ or **8**, by using IR and $^1H$ NMR spectroscopy.

Isolating $FpCO_2Si(CH_3)_2(t\text{-Bu})$ (**10**) as a stable, analytically pure gum is, in contrast, straightforward. Both **6**-$Li^+$ and **6**·$Na^+$ afford **10** in 80% spectroscopic (IR) yield and in 57–63% isolated yield. Cooling pentane extracts (−78 °C) of the reaction precipitated $Fp_2$, the only other organoiron complex detected, and left **10** in solution. Evaporating the pentane then left **10** as a yellow-brown gum. In contrast to its trimethylsilyl analogue **8**, **10** is robust: its solutions (THF, pentane) show no measurable decomposition at room temperature (after 12 h).

Even though the two molecules are structurally and electronically similar, **10** is much more stable than **8** due to the presence of the bulky *tert*-butyl group. For example, the $^{13}C$ NMR spectral assignments for the carboxylate and terminal carbonyl centers on the metallocarboxylate silyl esters **8** and **10** match each other and those of the methyl ester **4**. Presumably the *tert*-butyl group sterically blocks access to the silicon center on **10** and precludes one or more of its decomposition pathways.

The reactivity of the trialkylsilyl metallo esters **8** and **10** resembles that of related alkoxycarbonyl complexes.[14b] In particular, treatment of **8** or **10** with acid immediately produces $FpCO^+$ (eq 6). Similar results have been noted after **8** or **10** was reacted with either $Et_3O^+PF_6^-$ or $(CH_3)_3SiOSO_2CF_3$.



(6)

## Conclusions

Reactions of the anionic $CO_2$ adduct **6** with organic electrophiles are controlled by at least two experimental parameters. (1) The extent of equilibration between **5** and **6** (eq 2) apparently depends by the oxophilicity of the cation—another example of Floriani's bifunctional $CO_2$ activation.[1g] With the Mg(II) counterion, $FpCO_2^-$ (**3**) does not dissociate $CO_2$, but it does react with methyl triflate to give the metallocarboxylate methyl ester **4** (eq 3).[3c,9] Less oxophilic $Li^+$ and $Na^+$ counterions are less effective at sequestering the metallocarboxylate ligand on **6**. Equilibrium concentrations of $Fp^-$ (**5**) thus develop and intercept methyl iodide to give $FpCH_3$ (**7**) exclusively. Equilibrium concentrations of **6**·$Li^+$ or **6**·$Na^+$ must be very low, however, since neither metalate is detected by IR and NMR spectroscopy in THF solutions containing **5**·$Li^+$,$Na^+$. (2) Metallocarboxylate oxygens on **6** react more effectively with hard alkylating reagents, from the perspective of hard–soft acid–base theory.[26] Thus, the softer methyl iodide electrophile alkylates the dithiocarboxylate **11**[25] (on S, eq 4), but not the metallocarboxylate **6**. (The relatively soft $Fp^-$ (**5**) that dissociates from **6** efficiently intercepts $CH_3I$.) The hard (oxophilic) trialkylsilyl chlorides, in contrast, selectively trap the metallocarboxylates **6**·$Li^+$,$Na^+$ and give the metallocarboxylate silyl esters **8** and **10**. We found no evidence for competitive silylation of the iron nucleophile **5**·$Li^+$,$Na^+$. Therefore, silylating $FpCO_2^-$ (**6**) represents a convenient procedure for securing derivatives of this metallocarboxylate.

**Acknowledgment.** We acknowledge the efforts of Thomas Forschner in contributing results of preliminary experiments and helpful advice. Discussions with John Cooper (Harvard University) and with Carlo Floriani (Columbia University) also were extremely helpful. This research was supported by NSF Grant CHE-8305485.

**Registry No.** **5**·$Li^+$, 33361-37-4; **5**·$Na^+$, 12152-20-4; **6**·$Li^+$, 96758-57-5; **6**·$Na^+$, 95156-02-8; **7**, 12080-06-7; **8**, 106651-35-8; **10**, 106651-36-9; FpH, 35913-82-7; $Fp_2$, 12154-95-9; $FpCO^+BF_4^-$, 12244-69-8; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_2(t\text{-Bu})SiCl$, 18162-48-6; lithium amalgam, 37352-24-2.

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