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Carbon Dioxide Complexation: Infrared Spectroscopy of Iron and Ruthenium η^5-Cyclopentadienyl Carbonyl Metallocarboxylates

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The metallocarboxylates $FpCO_2^-$ (**1**-Mg^{2+}, -Li^+, -Na^+, -K^+), $Cp^*(CO)_2FeCO_2^-K^+$ (**3**-K^+), and $Cp(CO)_2RuCO_2^-$ (**4**-Na^+, -K^+) were generated in THF at −78 °C by treating the $CpM(CO)_2^-$-Li^+, -Na^+, -K^+, or -Mg^{2+} metalate with 1.0−1.2 equiv of CO_2 (or $^{13}CO_2$). The results of studies that were carried out on Me_3SiCl trapping of **1**-Mg^{2+}, -Li^+, -Na^+, -K^+, -$^nBu_4N^+$, and -(dibenzo-18-crown-6)K^+ as $Cp(CO)_2FeC(O)OSiMe_3$ (**5**) indicated that **1**-Mg^{2+}, -Li^+, -Na^+, and -K^+ are stable at room temperature for at least 1 h, and with proper precautions their IR spectra can be obtained. The ^{13}C NMR and IR spectral υ(OCO) and υ(CO) assignments (−15 °C to room temperature) are consistent with (a) ionic or (η^1-C:η^2-O,O′) metallocarboxylate structures that are symmetrically chelated to the metallic counterion and (b) increasing charge density on the Fp moiety through the counterion sequence **1**-Mg^{2+}, -Li^+, -Na^+, and -K^+. This counterion sequence reflects an attenuation of carboxylate−counterion ion pairing that influences the (a) exchange of the ^{13}C label between the carboxylate and carbonyl ligands on $Cp(CO)_2M^{13}CO_2^-$ [$\leftrightarrow$ $Cp(CO)(^{13}CO)MCO_2^-$] and (b) reversible dissociation of carbon dioxide from these metallocarboxylates. A net effect of these coupled reactions is that $Cp(CO)_2M^{13}CO_2^-$ converts residual (unbound) $^{13}CO_2$ to unlabeled CO_2. Both of the reactions were observed only with the more reactive **1**-Na^+ and **1**-K^+, which less tightly bind their Na^+ and K^+ counterions to the carboxylate oxygens. An example of the postulated metalloanhydride intermediate $Cp(CO)M^{13}C(O)OC(O)^-$ for the carboxylate−carbonyl label exchange may have been detected for M = Ru. $Cp(CO)_2RuCO_2^-$ (**4**-Na^+) isomerized to (the tentatively assigned) $Cp(CO)Ru{-}C(O)$-$OC(O)^-$ above ∼−10 °C, which then degraded upon further warming above 0 °C to $Cp(CO)_2RuH$.

Introduction

Despite the intense interest in transition-metal carbon dioxide complexes[1] —especially those used as templates for catalytic CO_2 reduction[2] and related coordinated ligand reactions[3] —relatively few examples involving a single transition metal have been characterized. This has been ascribed to CO_2 being a poor ligand; transition-metal compounds that are sufficiently electron-rich to bind CO_2 often reduce it to carbon monoxide via reductive disproportionation[4] or oxygen atom abstraction[5] pathways. Nevertheless, two structural types of CO_2 coordination have been identified for a limited number of stable CO_2 complexes: (η^1-C) CO_2 metallocarboxylate[6] and (η^2-C,O) CO_2 side-on coordination (Chart 1).[1,7]

Metallocarboxylate complexes can be further divided into those that are cationic, neutral,[6b,c,8] or more commonly anionic. Anionic metallocarboxylates typically have varying degrees of ion pairing/chelation of alkali metal counterions.[6a,9,10] This ion

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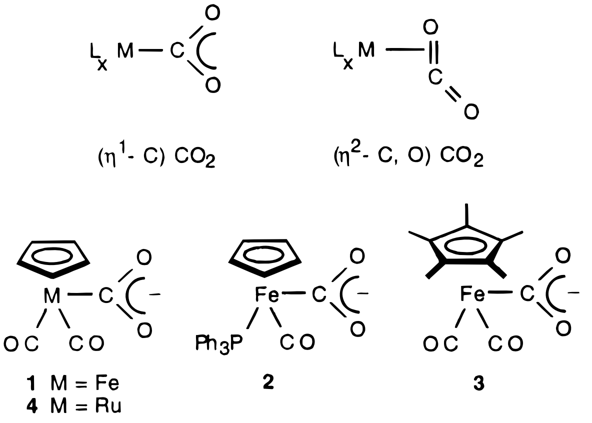
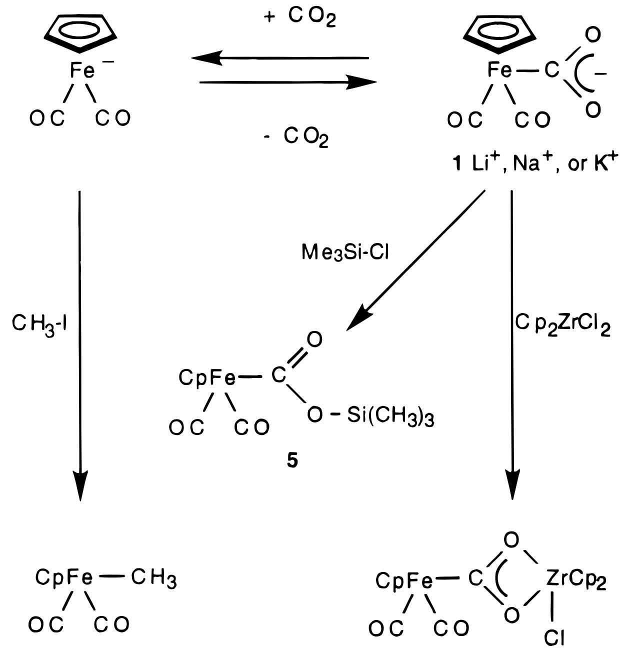
Chart 1



pairing, referred to as bifunctional CO_2 activation,[3b,6a,9a,11] stabilizes the CO_2 adduct[12] and potentially influences subsequent chemical reactivity. Alkali or alkaline earth metal counterions accordingly promote metal alkyl−CO_2 insertion[11b] and catalytic electrochemical CO_2 reduction by Fe(0) porphyrins.[11c] Further stabilization of metallocarboxylates also occurs through hydrogen bonding that typically involves water.[6c,8b,9b,c] The water originates through the use of pH-dependent equilibria involving carbonyl−(η^1-C)metallocarboxylate−metallocarboxylic acid ligands[1,12] to synthesize the ligated CO_2 of many metallocarboxylates[8c,9b−d,10g−j].

Infrared (IR) spectroscopy has proved to be especially useful for distinguishing between metallocarboxylate and side-on CO_2 coordination and for characterizing metallocarboxylate chelation to alkali or alkaline earth metal counterions.[13] This IR spectral characterization of metallocarboxylates came from spectral correlations involving absorptions for ligated organic carboxylate RCO_2^- M^+, $\Delta\upsilon(CO_2) = [\upsilon(CO_2)_{asym} - \upsilon(CO_2)_{sym}]$.[14]

Scheme 1. Reactions of Electrophiles with $Cp(CO)_2FeCO_2^-$ (1-Li^+, -Na^+, -K^+)



The most extensively documented metallocarboxylate complexes correspond to two series of CpFe-containing CO_2 adducts $Cp(CO)_2FeCO_2^-$ (**1**) and $Cp(PPh_3)(CO)FeCO_2^-$ (**2**) with Li^+, Na^+, K^+, or Mg^{2+} counterions.[3a,10] The stable phosphine-containing metallocarboxylates **2**, which have been isolated, are synthesized by adding OH^- to cationic carbonyl salts $Cp(PPh_3)(CO)FeCO^+$; whereas the less stable Fp adducts **1** usually are generated at lower temperatures and under anhydrous conditions by adding CO_2 to the nucleophilic metalate $Cp(CO)_2Fe^-$ (i.e., Fp^-) in tetrahydrofuran (THF).[15] In a recent report, however, Gibson and co-workers extended the basic hydrolysis of cationic carbonyl salts to generating transient **1**-K^+ from $FpCO^+$ and intercepting it with Ph_3SnCl as $FpCO_2SnPh_3$.[16]

These two series of iron CO_2 adducts undergo similar chemical reactions. Treatment of **2**-K^+ with MeI, Ph_3SnCl, or $Re(CO)_4(PPh_3)(FBF_3)$ afforded stable metalloester derivatives $Cp(PPh_3)(CO)FeCO_2R$; similar reactions between **1** and silyl chlorides or zirconocene dichloride yielded the metalloester derivatives depicted in Scheme 1. Attempts to trap **1** with MeI or Ph_3SnCl, however, extruded CO_2 and left FpR and Fp_2. Gibson and co-workers demonstrated that the reaction between **1**-K^+ and Ph_3SnCl in fact provides $FpCO_2SnPh_3$, but this metallotin ester readily decarboxylates in THF.[16] The difference in reactivity of **1** toward MeI or Me_3SiCl has been rationalized by the presence of a (previously) undetected equilibrium between **1** and the corresponding metalate Fp^-. Although the hard or more oxophilic electrophiles preferentially react at the carboxylate oxygens, the softer MeI intercepts the Fp^- and drives the equilibrium.[17] Alkylation of **1** to give $FpCO_2Me$

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(15) Other metallocarboxylates that were synthesized by directly complexing CO_2 to a metalate nucleophile: $Cp(CO)_2RuCO_2^-$ (**4**) Na^+,[10l,m] $Cp^*(CO)_2FeCO_2^-$ (**3**) K^+,[10k] $(CO)_5WCO_2^{-2}$ $2Li^+$,[4b] and a few others.[6a,b,8a,b,9a,11a]

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nevertheless occurred with methyl triflate and **1**-Mg^{2+}, presumably because of tighter binding between the chelating magnesium cation and the metallocarboxylate.[10c]

Recent advances in indirectly characterizing **1** as its metalloester derivatives overshadowed the conflicting reports concerning its IR spectral characterization and even its solution thermal stability. Originally prepared by Evans and coworkers,[10a] FpCO$_2$Na (**1**-Na$^+$) was generated at room temperature by treating THF solutions of FpNa with excess CO$_2$. Under these conditions, **1**-Na$^+$ promptly degraded to Fp$_2$. In benchmark studies, Lee and Cooper[10d] established that in cold THF solutions 1 equiv of CO$_2$ transforms Fp$^-$ to the metallocarboxylates **1**, which apparently decreased in solution stability: Li$^+$ > Na$^+$ > K$^+$ > *n*-Bu$_4$N$^+$. In particular, **1**-Li$^+$ exhibited a solution half-life of 4 h at room temperature, during which Fp$_2$ plus formate and carbonate salts accumulated. By using ^{13}C- and ^{18}O- labeled CO$_2$ to generate labeled **1**-Li$^+$ and MeI to trap it (as FpCH$_3$ with labeled CO ligands), Lee and Cooper also demonstrated reversible metallocarboxylate-to-carbonyl ligand oxygen atom interchange, *vide infra*. Of particular relevance to the present work are the solution IR spectral data that were attributed to **1**-Li$^+$, -Na$^+$, -K$^+$, and -*n*-Bu$_4$N$^+$.

Our experience with **1** has resulted in somewhat different conclusions. Although it is relatively straightforward to generate FpCO$_2^-$ (**1** Mg^{2+}, -Li$^+$, -Na$^+$, -K$^+$) in THF at low temperatures and trap it as a variety of metalloester derivatives, often in near-quantitative spectroscopic yields, **1** proved extremely difficult to characterize by IR spectroscopy. Whether Fp$^-$ was converted to **1** by bubbling excess CO$_2$ or by transferring 1 equiv of CO$_2$ by syringe or vacuum line techniques made little difference.[10b,c,e,f,k−m] We gradually have come to appreciate that **1** generated in the reaction vessel will only correspond to the sample in the solution IR cell when extreme precautions are undertaken. For example, the perception of solution stability ordered as follows, **1**-Mg^{2+} > -Li$^+$ > -Na$^+$ > -K$^+$ > -*n*-Bu$_4$N$^+$,[3a,10d] is inaccurate; any inherent thermal stability differences are insignificant compared to their sensitivity toward the usual solution transfer and IR spectroscopic recording procedure.

For the present study, we adopted two procedures to characterize the Fp series of CO$_2$ adducts. First, the amount of **1** present in the reaction flask was assayed at a specified temperature after trapping it with Me$_3$SiCl as FpCO$_2$Si(CH$_3$)$_3$ (**5**).[10e] Second, variable-temperature IR spectral data were acquired for FpCO$_2^-$ (**1**-Mg^{2+}, -Li$^+$, -Na$^+$, -K$^+$), as well as for Cp*(CO)$_2$FeCO$_2$K (**3**-K$^+$)[10k] and Cp(CO)$_2$RuCO$_2^-$ (**4**-Na$^+$, -K$^+$).[10l,m] Analogous ^{13}CO$_2$ adducts were examined in order to assign the IR carboxylate ν(OCO) bands, and low-temperature ^{13}C NMR spectra of **1**-Mg^{2+} and -Li$^+$ also were recorded. Two other objectives of this study were to relate this spectral data with (1) the extent of carboxylate−carbonyl label shuttle [for Cp(CO)$_2$M^{13}CO$_2^-$ ⇔ Cp(CO)(^{13}CO)MCO$_2^-$][10d] and (2) the presence of reversible CO$_2$ binding for these metallocarboxylates.

Experimental Section

Materials. Synthetic manipulations were performed in a nitrogen atmosphere using a combination of standard Schlenk line, glovebox, and vacuum line procedures.[17] Infrared spectra of the carbonyl ν(CO) and carboxylate ν(OCO) frequency region (2200−1200 cm^{-1}) were recorded on a Perkin-Elmer Model 1600 spectrophotometer; ^{13}C{^{1}H} NMR spectra were obtained on Varian Models XL-200 and Unity-500 spectrometers. The apparatus and vacuum line procedure for treating THF solutions of the metalates Cp(CO)$_2$M$^-$ (M = Fe, Ru) and Cp*(CO)$_2$Fe$^-$ K$^+$ with 1.0 equiv of CO$_2$ or of 99% C^{13}-labeled CO$_2$ (−78 °C) have been described.[10k−m] Standard procedures were used in reducing THF solutions of [CpFe(CO)$_2$]$_2$, [Cp*Fe(CO)$_2$]$_2$, and [CpRu(CO)$_2$]$_2$ to their carbonyl metalates[10,18,19] [Cp(CO)Fe═C═O]$_2$Mg(THF)$_4$ [with Mg(Hg)], ν(CO) 1915 (m), 1882 (vs), 1850 (m), 1713 (vs) cm^{-1};[19a] FpLi/Cp(CO)Fe$^-$═C═O−Li$^+$ [with Li(Hg)], ν(CO) 1883 (s), 1867 (s), 1811 (s), 1787 (w), 1749 (s) cm^{-1};[10e] FpNa [sonication with excess Na], ν(CO) 1881 (s), 1864 (m), 1809 (s), 1771 (m) cm^{-1};[10b] FpK [with KH-*sec*-Bu$_3$ (isolated)], ν(CO) 1869, 1793, 1774 cm^{-1};[19b] Cp*(CO)$_2$FeK (sonication with K), ν(CO) 1844, 1756 cm^{-1};[10k,19c,d] Cp(CO)$_2$RuNa [sonication with Na], ν(CO) 1904, 1823 cm^{-1};[10l] and Cp(CO)$_2$RuK [sonication with K], ν(CO) 1894, 1810, 1786 (sh) cm^{-1}.[19e] IR spectra of these extremely air and moisture sensitive metalates routinely exhibited the presence of only negligible concentrations of their hydrides, Cp(CO)$_2$MH and Cp*(CO)$_2$FeH, or dimer precursors, [CpM(CO)$_2$]$_2$ and [Cp*Fe(CO)$_2$]$_2$.

Fp(*n*-Bu$_4$N)[20] was generated by treating a THF solution of FpNa (0.033 M, 15 mL) with *n*-Bu$_4$NBF$_4$ (161 mg, 0.49 mmol). The solution was stirred for 10 min as the NaBF$_4$ settled and left Fp(*n*-Bu$_4$N) as a cherry-red solution [ν(CO) 1863, 1789 cm^{-1}]. Fp(dibenzo-18-crown-6)K was generated as a red solution, ν(CO) 1862, 1789 cm^{-1}, by treating a THF solution of FpK with 1.2 equiv of the vacuum-dried crown ether for 30 min.

Low-Temperature IR Flow Cell. A recently cleaned and reassembled IR solution cell with NaCl plates, Luer ports, and a 0.1-mm Teflon spacer was fitted with an insulated 38-cm length of Teflon tubing (1.5-mm i.d.) that attached to a three-way Teflon valve (Rainin Model 45-1102). Rainin polypropylene low-pressure and Luer fittings were used for connections with this tubing, which was insulated with glass wool and wrapped with 0.25-in. Tygon tubing. A three-way T-fitting and valve (Rainin Model P-173) that was inserted into this tubing 6 cm from the IR cell also was fitted to the thermocouple probe (type K) of a Digi-sense Model 8528-40 digital thermometer. This thermometer was used to continuously monitor the temperature of the solution as it entered the cell.

The second port of the three-way Teflon valve was connected to a 20-cm length of insulated Teflon tubing that had a 6-in. 18-gauge sampling needle attached to the other end. This sampling needle was used to transfer either cold solvent or reaction mixture into the flow cell. The third port of the three-way valve also was fitted with a Teflon tube; solvent was introduced through this tube in order to flush suspended **1** or solid degradation residues from either the cell or the sampling needle. The outlet from the cell consisted of a 15-cm Teflon tube, connected to the cell by a Luer fitting, that transferred cell effluent to a waste container.

Operation of the low-temperature flow cell first entailed precooling the cell to −25 °C with cold THF. A 200-mL round-bottom flask containing 100 mL of dry, degassed THF and sealed with a rubber septum was attached to a nitrogen line and cooled to −78 °C. The septum was pierced by the 18-gauge sampling needle with its attached Teflon tube, and nitrogen pressure was used to control the flow of cold THF through the cell (10−11 mL/min). An IR spectrum of the cold THF was obtained and saved for subtraction from the sample spectrum.

The needle then was quickly switched from the solvent flask to the sample flask (by insertion through a septum and stopcock on the the side arm) and the cold (−78 °C) sample solution was forced through the IR cell. IR spectra were recorded (typically one transient) as the temperature was monitored between −8 and −15 °C. Once the low-

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temperature IR spectrum was obtained, the sample flow was stopped and additional IR spectra were recorded over a few minutes as the cell warmed to room temperature. Excellent quality IR spectra were obtained over the region of interest (2400−1100 cm^{-1}), except for the 25-cm^{-1} area centered at 1455 cm^{-1} for the intense solvent absorption.

Preparation of $Cp(CO)_2FeC(O)OSi(CH_3)_3$ (5). A 100-mL Schlenk flask containing a magnetric stirring bar and FpK (864 mg, 4.0 mmol) in 50 mL of THF was attached to a vacuum line and frozen (−178 °C). CO_2 (4.0 mmol) was deposited, and the reaction was warmed to −78 °C. Within 8 min, the vigorously stirred cherry-red solution turned yellowish brown; after 30 min, trimethylsilyl chloride (0.52 mL, 4.1 mmol) was added, and the reaction was warmed to room temperature. The resulting red-brown solution was evaporated; the red-brown gum was extracted with hexane (20 mL); and the filtrates (medium sintered-glass frit) were evaporated to a red-brown gum (791 mg) that was identified as **5**[10e] (yield 67%): IR (THF) 2030, 1975 (C≡O), 1627 (C═O), 1250 (C−O) cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.19 (Cp), 0.29 ($SiMe_3$); ^{13}C NMR (C_6D_6) δ 214.7 (C≡O), 199.9 (C═O), 86.3 (Cp), 0.52 ($SiMe_3$). Anal. Calcd for $C_{11}H_{14}O_4SiFe$: C, 44.91; H, 4.80. Observed: C, 45.21; H, 5.33.

Assay of $Cp(CO)_2FeCO_2^-$ (1) via Yields of $Cp(CO)_2FeC(O)OSi(CH_3)_3$ (5). A 50-mL Schlenk flask containing a 0.033 M THF solution of FpK (10 mL) and a magnetric stirring bar was attached to a vacuum line and subjected to three freeze−pump−thaw cycles. The frozen FpK (−178 °C) was treated with 0.35 mmol of CO_2 and warmed to −78 °C (30 min). The resulting thick yellowish tan suspension was treated with trimethylsilyl chloride (43 μL, 0.34 mmol), producing a clear reddish brown solution. The IR spectrum of the cold solution indicated essentially quantitative conversion to **5**, with only a trace of Fp_2 evident.

In related experiments, 10-mL aliquots of 0.033 M THF solutions of Fp^- as its Mg^{+2}, Li^+, Na^+, K^+, and n-Bu_4N^+ salts were treated similarly with 1 equiv of CO_2 (−178 to −78°C). In these reactions, the resulting suspensions containing $FpCO_2^-$ (**1**) were maintained at 22 °C (measured) for either 5 min or 2 h before the 1 equiv of Me_3SiCl was added. Concentrations of **5** were estimated by quantitative IR spectroscopy (Table 1), with an observed reproducibility of absorbancy values of ±10%.

Preparation of Metallocarboxylate Solutions for IR Spectral Studies. A THF solution of a metalate $Cp(CO)_2M^-$ (M = Fe, Ru) or $Cp^*(CO)_2FeK$ (0.50 mmol in 15 mL) was transferred to a 50-mL round-bottom flask that was equipped with a rubber septum on its side arm, a magnetic stir bar, and an adapter for connecting it to the vacuum line. The metalate solution was sampled via syringe needle inserted through the septum and stopcock on the the side arm, and an IR spectrum was recorded. Then the solution was treated with 1.0 equiv of CO_2 or of 99% C^{13}-labeled CO_2 as previously described[10k−m] and stirred at −78 °C for 30 min. Nitrogen was introduced into the flask; the reaction flask (maintained at −78 °C) then was removed from the vacuum line and attached to a nitrogen manifold.

A similar procedure was followed in preparing metallocarboxylate solutions for low-temperature ^{13}C NMR spectral studies, except that a 10-mm NMR tube fitted with a J. Wiley-Young valve also served as the reaction vessel. The NMR tube containing the THF metalate solution (0.50 mmol in 5 mL) was attached to the vacuum line and 1.0 equiv of 99% labeled $^{13}CO_2$ was transferred. After warming to −78 °C, the NMR tube and attached valve was removed from the vacuum line and gently swirled (at −78 °C) before it was inserted into the precooled NMR probe.

Results and Discussion

Derivitization of $Cp(CO)_2FeCO_2^-$ (1) as Its Silyl Ester $Cp(CO)_2FeC(O)OSiMe_3$ (5). Treatment of Fp^- with CO_2 followed by addition of Me_3SiCl efficiently derivatized the metallocarboxylate **1** as its more stable silyl ester **5**. A particularly efficient preparation of **5** involved treating **1**-K^+, which was generated and maintained at −78 °C in THF, with 1 equiv of trimethylsilyl chloride. Under these conditions, the initial thick yellowish tan suspension of **1**-K^+ afforded a clear reddish brown solution, and this showed no further changes after reaching room temperature. Its IR spectrum (Figure 2D) then indicated nearly quantitative conversion to **5**, which was isolated analytically pure in 67% yield as a red-brown gum that contained only a trace of Fp_2.[21] In contrast to the facile decarboxylation of $FpCO_2SnR_3$ (R = Me, Ph) in THF to yield $FpSnR_3$,[16] the Fp silyl ester **5** appears to be stable in THF solution at room temperature. Attempts to crystallize **5** from pentane at low temperatures or otherwise purify it inevitably increased the amount of Fp_2.

Table 1. Thermal Stability of $FpCO_2^-$ (1): Results of Trapping Experiments with Trimethylsilyl Chloride at Room Temperature

metallocarboxylate **1** treated with Me_3SiCl	yield (%) $FpCO_2SiMe_3$ (5): **1** at 22 °C for 5 min	yield (%) $FpCO_2SiMe_3$ (5): **1** at 22 °C for 2 h
$(FpCO_2)_2Mg$		74
$FpCO_2Li$	85	65
$FpCO_2Na$	55	54
$FpCO_2K$	77	69
$FpCO_2(n\text{-}Bu_4N)$	43	

We previously reported generating **5** from **1**-Li^+, although it degraded to Fp_2 upon attempted isolation. In contrast, its much more stable *tert*-butyldimethylsilyl ester analog $FpC(O)OSiMe_2(t\text{-}Bu)$ was isolated and fully characterized.[10e] The η^1-O or nonchelating silyl ester structure for **5** is consistent with the presence of its IR acyl υ(C═O) at 1627 cm^{-1}, analogous to the acyl υ(C═O) 1647-cm^{-1} absorption of $Cp(CO)_2FeC(O)OCH_3$. NMR spectra of the isolated **5**, although important for establishing its purity, are not useful for probing the chelating vs nonchelating interactions of the metallocarboxylate ligand. ^{13}C NMR spectral assignments of the terminal and acyl carbonyl groups (δ 213.3 and 199.9, respectively, in C_6D_6), for example, are comparable to those of $FpC(O)OCH_3$ (δ 213.3, 200.8) and $FpC(O)OSiMe_2(t\text{-}Bu)$ (δ 213.6, 200.7) ($CDCl_3$)[10e], which are η^1-C:η^1-O metalloesters, as well as those of $FpC(O)OSnPh_3$ (δ 213.3, 209.8)[16] and $FpCO_2Zr(Cl)Cp_2$ (δ 213.9, 206.2) ($CDCl_3$ and C_6D_6),[10l] which are η^1-C:η^2-O,O′ metalloesters.

Since the trapping of **1** by Me_3SiCl occurs rapidly and in high yield, we used this reaction to quantify the amount of CO_2 adduct **1** that was present in solution as a function of solution temperature, residence time, and choice of counterion for $FpCO_2^-$ (**1**). Solutions containing **1** were warmed to room temperature either for 5 min or for 2 h before treatment with 1 equiv of Me_3SiCl. Concentrations of the resulting **5** were measured by IR spectroscopy (Table 1). Figure 1E illustrates the IR spectrum for the Me_3SiCl trapping of **1**-Li^+ after 5 min at room temperature. Most reactions produced trace quantities to 10% Fp_2 [υ(CO) 1992, 1951, 1781 cm^{-1}] as the only detectable organoiron byproduct, although Me_3SiCl trapping of **1**-Na^+ also left variable amounts of FpH[22] [υ(CO) 2011, 1950 cm^{-1}]. The iron silyl complex $FpSiMe_3$[23] [υ(CO) 1988, 1932 cm^{-1}], however, was conspicuously absent from all reactions.[21]

From these results we conclude that (1) $FpCO_2^-$ (**1**) has limited solution stability at room temperature and (2) the choice from among the counterions Mg^{+2} through K^+ has relatively little effect on its thermal stability. Indeed, all four metal cations stabilize **1** to the extent that after sitting for 2 h at room tem-

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[21] Similar results were observed for the metalation of **1**-K^+ by Cp_2ZrCl_2. Near-quantitative yields of the $\mu(\eta^1$-C:η^2-O,O′) CO_2 complex $FpCO_2Zr(Cl)Cp_2$[10l] but not $FpZr(Cl)Cp_2$ were observed. Pinkes, J . R.; Steffey, B. D.; Vites, J. C.; Cutler, A. R. *Organometallics* **1994**, *13*, 21.

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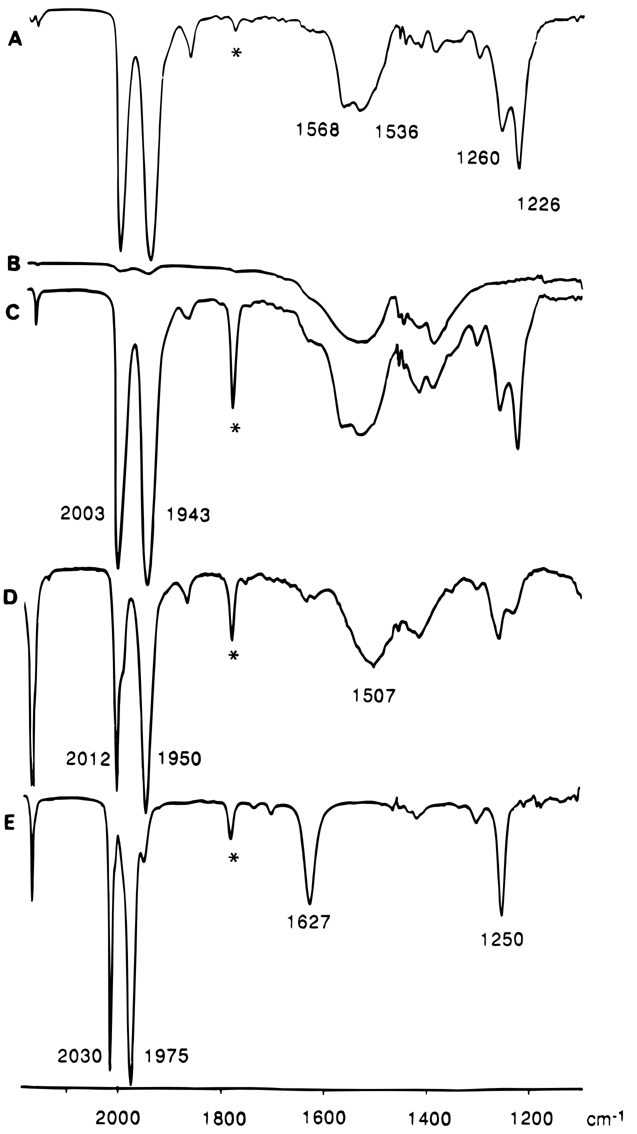


Figure 1. Infrared spectra of $FpCO_2^-Li^+$ (**1**-Li^+). (A) Solution of **1**-Li^+ (0.033 M in THF), prepared at −78 °C and maintained at room temperature for 5 min. (B) Decomposition residues deposited by **1**-Li^+ on cell windows (results of eight experimental runs; THF in cell). (C) **1**-Li^+ after 2 h at room temperature. (D) Spurious run in which **1**-Li^+ decomposed (to FpH) due to handling problems. (E) Treatment of **1**-Li^+ (A) with Me_3SiCl. (∗) $[CpFe(CO)_2]_2$.

perature, treatment with Me_3SiCl provided 54−74% yields of **5**. Of the four bimetallocarboxylates examined, **1**-Na^+ reproducibly incurred the unusually low yields of **5**, which we attribute to its lower solution stability than observed with either the Li^+ or K^+ counterions. When the *n*-Bu_4N^+ counterion was used, the resulting **1**-*n*-Bu_4N^+ proved to be the least stable. We obtained the lowest yields of **5** upon treatment with Me_3SiCl, and we were unable to detect **1**-*n*-Bu_4N^+ by IR spectral monitoring using procedures outlined in the following section.

IR Spectral Studies of $Cp(CO)_2FeCO_2M$ (1) and $Cp(CO)_2Fe^{13}CO_2M$ [1(^{13}C)]. In initial studies, IR spectra of aliquots of **1** were irreproducible; IR spectral monitoring of some experimental runs indicated that **1** immediately degraded to FpH, as opposed to slowly decomposing to Fp_2. The THF solutions of **1** were generated using 0.033 M Fp^- and 1.0−1.2 equiv of CO_2 at −78 °C, and aliquots were removed at room temperature for recording their IR spectra. Results obtained with **1**-Li^+ are typical: for most of these reactions, we observed the slow degradation of **1**-Li^+ at room temperature to Fp_2 ($\tau_{1/2} = \sim 6$ h); whereas some experimental runs occasioned immediate decomposition (**1**-Li^+ was not detected) at or below room temperature to yield FpH.

Chart 2

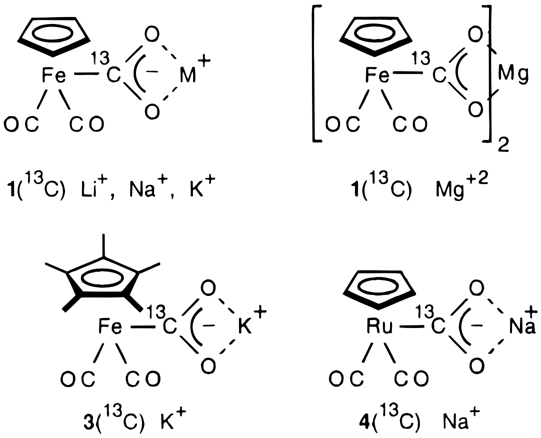


Figure 1 compares IR spectra of **1**-Li^+ that were recorded under different conditions. Scans A and C are for samples that were removed after 5 min and 2 h at room temperature, respectively. They differ by the slight increase of Fp_2 and the growth of broad bands between 1600−1480 (υ_{max} 1530 cm $^{-1}$) and 1460−1320 cm $^{-1}$ (υ_{max} 1390 cm $^{-1}$). These broad bands correspond to unidentified decomposition residues that were evident as a white coating on the IR cell. An IR spectrum, scan B, of this coating was recorded independently with an IR cell that had been used for eight experimental runs with **1** and flushed again with THF. IR spectrum E depicts the **5** that results from treating **1**-Li^+, which sat at room temperature for 5 min (cf. Table 1), with Me_3SiCl. IR spectral scan D, on the other hand, is an example of the occasionally observed immediate decomposition of **1**-Li^+ to FpH and our decomposition residues.

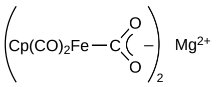
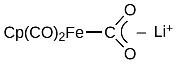
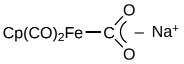
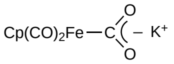
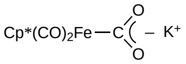
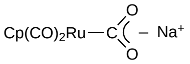
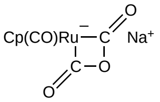
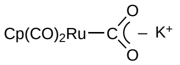
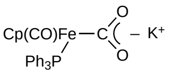
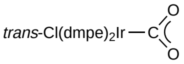
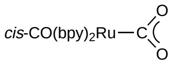
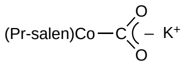
We ascribe the immediate degradation of **1** to FpH in some experimental runs to the extreme sensitivity of its solutions toward contamination during transfer to the IR cell or during acquisition of its spectrum in the cell. In some experimental runs, the degradation of **1** resulted from hairline cracks in the cell. Interestingly, the acquisition of IR spectra of the extremely air and moisture sensitive metalates Fp^-, which routinely had negligible Fp_2 or FpH present, did not guarantee that IR spectra of **1** subsequently would be obtained. It is worth noting that **1** Mg^+ appeared to be less prone toward the immediate solution degradation to FpH than when Li^+, Na^+, or K^+ counterions were used.

The best expedient was to use a freshly cleaned and reassembled cell each day. It made no difference whether lead amalgam or Teflon spacers were used between the sodium chloride plates of the solution cell. Only by taking this precaution were we able to reproducibly get IR spectra of **1**.

The resulting IR spectral data for $FpCO_2^-$ (**1**-Mg^{2+}, -Li^+, -Na^+, -K^+), as well as that for $Cp^*(CO)_2FeCO_2K$ (**3**-K^+) and $Cp(CO)_2RuCO_2^-$ (**4**-Na^+, -K^+) are summarized in Table 2. Terminal carbonyl υ(CO) bands are reported only for the unlabeled metallocarboxylates; those for 99% labeled $Cp(CO)_2M^{13}CO_2^-$ (Chart 2) absorb at essentially identical frequencies. The carboxylate absorptions (1600−1100 cm^{-1}) are assigned on the basis of isotopic frequency shifts that were observed for the $^{12}CO_2$ vs $^{13}CO_2$ adducts.

These isotopic frequency shifts are illustrated in Figure 2 for the IR spectra of $FpCO_2K$ (**1**-K^+), scan B, and $Fp^{13}CO_2K$ (**1**(^{13}C)-K^+), scan C. The higher frequency pair of carboxylate bands of **1**-K^+ and **1**(^{13}C)-K^+ correspond to $\upsilon(OCO)_{asym}$ and the lower frequency pair to $\upsilon(OCO)_{sym}$. We do not discern the

Table 2. Infrared Spectral Data of Metallocarboxylates

entry no.	metallocarboxylate[a]	ν(CO)	$\nu(OCO)_{asym}$	$\nu(OCO)_{sym}$	$\Delta\nu(OCO)$[b]	$\nu(O^{13}CO)_{asym}$	$\nu(O^{13}CO)_{sym}$
1	 **1**-Mg^{2+}	2011 1950	1541 (br)	1265 1240	301	1509 (br)	1247 1221
2	 **1**-Li^+	2002 1942	1571 (br) 1530 (br)	1261 1227	323 (344)	1529 1494	1243 1212
3	 **1**-Na^+	1998 1935	1536 (br)	1262 1231	305	1490 (br)	1244 1216
4	 **1**-K^+	1991 1907	1543 1525	1258 1224	310 (319)	1501 1486	1238 1211
5	 **3**-K^+	1973 1907	1520 (br)	1261 1226 (br)	294	1480 (br)	1238 1202 (br)
6	 **4**-Na^+	2015 1938	1569 1527	1327 1253	295 (316)	1483 (br)	1290 1228
7	 **5**	1923 (br)	1526	1321 1246	280	1484 (br)	nd[h]
8	 **4**-K^+	2003 1913	1546 1525	1243 (br)	303		
9[d]	 **2**-K^+	1893 1885 (sh)	1480 1438 (br)	1204 (br)	276		
10[e]			1550	1230	320	1515	1220
11[f]		1911	1428	1242	186	1407	1213
12[g]			1650	1280 1215	370 435	1610	1250 1192

[a] Metallocarboxylates were generated at −78 °C in THF by treating the Mg^{2+}, Li^+, Na^+, or K^+ metalate $Cp(CO)_2M^-$ with 1.0 to 1.2 equiv of CO_2 or $^{13}CO_2$ (99% label); metalate was not detected thereafter. IR spectra were recorded between −15 and 22 °C; terminal carbonyl ν(CO) assignments for $Cp(CO)_2M^{13}CO_2^-$ are identical to those of its unlabeled 1:1 CO_2 adduct. [b] $\Delta\nu(OCO) = [\nu(OCO)_{asym} - \nu(OCO)_{sym}]$, using average of the two $\nu(OCO)_{asym}$ absorptions (or the single broad $\nu(OCO)_{asym}$ absorption) and the lower frequency $\nu(OCO)_{sym}$ band. $[\Delta\nu(OCO)]$ refers to maximum possible separation of ν(OCO) values. [c] Observed for $Cp(CO)_2M^{13}CO_2^-$. [d] Reference 10h, KBr data. [e] Reference 8a, Nujol data. [f] Reference 6c, KBr data. [g] Reference 6a, Nujol data. [h] Not detected.

$\delta(OCO)_{asym}$ deformation that should appear near the latter stretching frequencies.[13] Also of interest are values for the carboxylate peak separations, $\Delta\nu(OCO) = [\nu(OCO)_{asym} - \nu(OCO)_{sym}]$, which correlate with the mode of carboxylate O,O′ bonding. We observed a maximum $\Delta\nu$(OCO) value of 319 cm^{-1} with **1**-K^+ that is consistent with an ionic or (η^1-C:η^2-O,O′) metallocarboxylate structure.[14] These symmetrically chelated metallocarboxylates typically have $\Delta\nu$(OCO) values of <400 cm^{-1} (cf. entries 10−12, Table 2), whereas $\Delta\nu$(OCO) values for (η^2-C,O) CO_2 adducts are >500 cm^{-1}.

IR spectra for the metallocarboxylates in this study resemble those of **1**-K^+, although the $\nu(OCO)_{asym}$ absorptions appeared either as two resolved peaks or as a broad band. Nevertheless, the carboxylate IR absorptions for these (unlabeled) metallocarboxylates fall into the regions, $\nu(OCO)_{asym}$ (1580−1520 cm^{-1}) and $\nu(OCO)_{sym}$ (1330−1220 cm^{-1}), and the $\Delta\nu$(OCO) values fall within 290−340 cm^{-1}. The $\Delta\nu$(OCO) values in Table 2 were calculated as the separation from the average of the two $\nu(OCO)_{asym}$ absorptions (or more commonly, a single broad $\nu(OCO)_{asym}$ absorption) to the lower frequency $\nu(OCO)_{sym}$ band.

The appearance of these IR spectra for **1** remained unchanged between −15 °C and room temperature. By using the low-temperature flow cell described in the Experimental Section, we recorded IR spectra of **1** and related metallocarboxylates in THF between −8 and −15 °C. This IR cell was precooled by passing cold THF before small volumes of the cold metallocarboxylate reaction mixture were forced through the same precooled transfer tubing into the cell. IR spectra were run at the limiting low temperature and then as the sample warmed to room temperature.

The ∼−15 °C low-temperature limit for recording solution IR spectra of these metallocarboxylates is due to the increased viscosity of the suspensions of **1** at lower temperatures, especially with the K^+ counterion. Attempts to alleviate this problem by switching to 2-methyltetrahydrofuran, 1,2-dimethox-

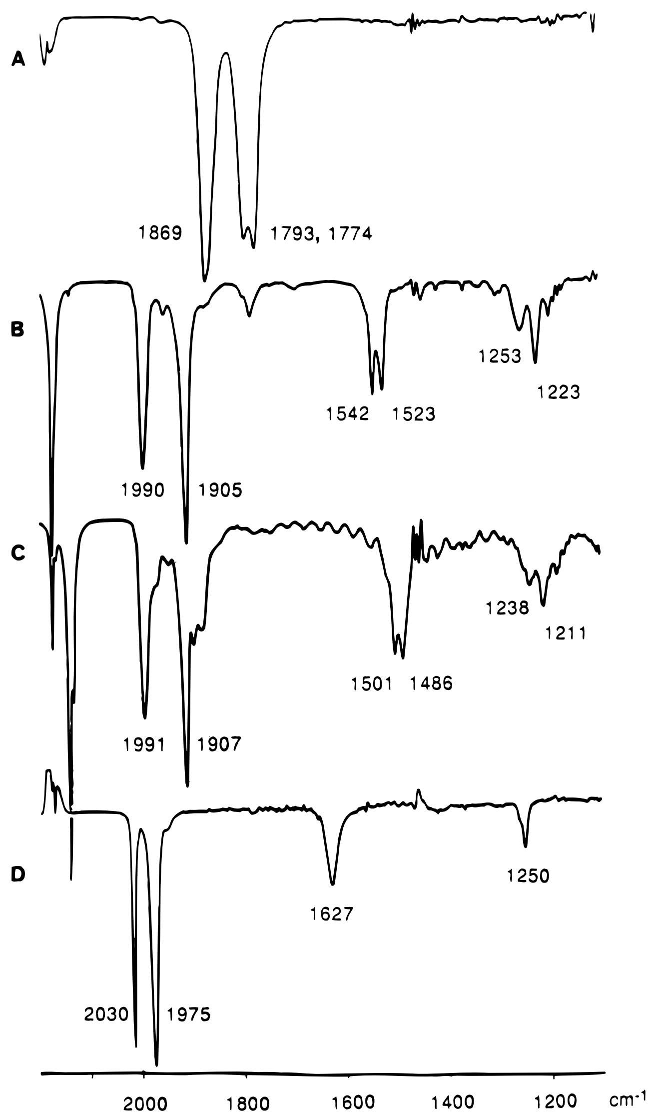


Figure 2. Infrared spectra of $FpCO_2^-K^+$ ($\mathbf{1}$-K^+) in low-temperature flow cell. (A) Starting Fp^-K^+ (0.50 mmol in 15 mL of THF). (B) $FpCO_2^-$ ($\mathbf{1}$-K^+), result of adding 1.2 equiv of CO_2 (−78 °C). Cell at −10 °C; weak ν(CO) bands at 1992 and 1950 cm^{-1} correspond to $[Cp(CO)_2Fe]_2$. (C) $Fp^{13}CO_2^-$ [$\mathbf{1}$(^{13}C)-K^+], result of adding 1.2 equiv of $^{13}CO_2$ (−78 °C); cell at −16 °C. (D) Treatment of $\mathbf{1}$-K^+ with Me_3SiCl at −78 °C.

yethane, or dimethoxymethane as solvents were unsuccessful due to solubility limitations and the presence of intense solvent absorptions in the 2000−1100-cm^{-1} region.

The design of this low-temperature flow cell, particularly the cell spacing and the diameter of the entrance needle and Teflon tubing, optimizes the balance between the need for a faster solution throughput for the cell (hence lower temperatures) and a thinner cell path length (for better solvent subtraction). With a 0.5 mm cell spacer, IR spectra of these metallocarboxylates were recorded down to −40 °C, but only in the carbonyl υ(CO) region (the solvent cutoff is below 1500 cm^{-1}). It is worth noting that this same temperature minimum can be reached even with the 0.1-mm cell spacer when determining IR spectra of the moisture-sensitive metalates, e.g., Fp^-Na^+, which are not viscous.

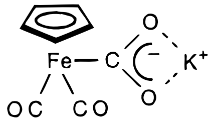
In ascertaining a counterion dependency on the physical and chemical properties of these metallocarboxylates, we compared the IR spectral data for $\mathbf{1}$-Mg^{2+}, -Li^+, -Na^+, and -K^+. Their $\Delta\upsilon$(OCO) values exhibit no discernible trend; those for Mg^{+2}, Na^+, and K^+ vary from 301 to 310 cm^{-1} and the Li^+ value is 323 cm^{-1}. The only related IR data, that of Floriani and co-workers for $Co(Pr\text{-}salen)CO_2^-$ (Li^+, Na^+, K^+, or Cs^+),[6a] similarly elicits no obvious trend. Their $\Delta\upsilon$(OCO) values varied from 405 to 455 cm^{-1} (Na^+ is the highest). The relative insensitivity of metallocarboxylate $\Delta\upsilon$(OCO) values is consistent with an ionic formulation, even though magnitudes of these $\Delta\upsilon$(OCO) values exceed the ~200 cm^{-1} that is associated with organic carboxylate salts.[14]

The IR terminal carbonyl υ(CO) absorptions for $\mathbf{1}$, however, uniformly decrease as the cation size increases: $\upsilon(CO)_{asym}$ and $\upsilon(CO)_{sym}$ drop 20 and 43 cm^{-1}, respectively, through the counterion sequence Mg^{+2}, -Li^+, -Na^+, and -K^+. Their iron centers evidently become progressively more electron-rich, perhaps as the degree of tight ion pairing or covalency[18b,c] involving the carboxylate ligand diminishes from Mg^{+2} to K^+.

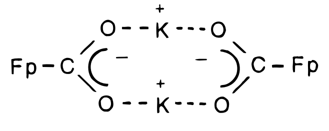
Two issues concerning the IR spectral data of $\mathbf{1}$ need to be addressed, the number of metallocarboxylate IR υ(OCO) bands that we observed and a discrepancy between the present IR spectral data and that previously reported. Our observation of two sets of metallocarboxylate υ(OCO) bands is (a) independent of counterion, (b) independent of temperature (−15 to +22 °C), (c) independent of using 1 equiv of or excess of CO_2, (d) consistent with results of labeling studies using $^{13}CO_2$, (e) consistent with results of derivatizing the metallocarboxylate ligand as its Fp silyl ester $\mathbf{5}$ in moderate to high yields, and (f) reproducible once proper precautions are taken.

Although only one set of metallocarboxylate υ(OCO) bands is expected,[13] multiple υ(OCO) bands are prevalent for a number of well-characterized metallocarboxylates such as (Pr-salen)-$CoCO_2^-$ (with Li^+, Na^+, K^+; cf. entry 12, Table 2) and $Cp(PPh_3)(CO)FeCO_2^-$ ($\mathbf{2}$) (with Li^+, K^+; cf. entry 9, Table 2). An X-ray structure determination of the former cobalt carboxylate, moreover, verified the presence of two different carboxylate ligand to K^+ bonding modes. In a study to be published,[24] we demonstrated that the more tractable rhenium carboxylates Cp*-$(CO)(NO)ReCO_2M$ (M = Li, Na) also exhibit two sets of IR υ(OCO) bands in THF: M = Li, $\upsilon(OCO)_{asym}$ (1514, 1484 cm^{-1}), $\upsilon(OCO)_{sym}$ (1332, 1257 cm^{-1}); M = Na, $\upsilon(OCO)_{asym}$ (1490, br, cm^{-1}), $\upsilon(OCO)_{sym}$ (1320, 1248 cm^{-1}). These rhenium CO_2 adducts were generated by deprotonation of Cp*-$(CO)(NO)ReCO_2H$ with LiH or NaH at 0 °C.

We speculate that isomeric mixtures of $\mathbf{1}$, differing in the $FpCO_2^-$/metal cation association, account for the two sets of IR υ(OCO) bands. The presence of the illustrated isomers of $\mathbf{1}$-K^+ with chelating and bridging K^+, for example, could justify the two sets of υ(OCO) bands and one set of terminal carbonyl υ(CO) absorptions (the latter due to imperceptible differences in the charge density on the Fp moiety for a given metal counterion). Nevertheless, the appearance of two sets of IR υ(OCO) bands for $\mathbf{1}$ and the relative insensitivity of their positions to the choice of counterion [in contrast to the carbonyl υ(CO) bands] is counterintuitive. Further studies clearly are required with other anionic metallocarboxylates in order to clarify the counterion dependency on both the number and positions of the carboxylate IR υ(OCO) bands.



1K+



1K+ dimer

The remaining issue concerns the discrepancy between the present IR spectral data and that of Cooper and co-workers[10d]

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(24) DiBiase Cavanaugh, M.; Tetrick, S. M.; Masi, C. J.; Cutler, A. R., manuscript submitted.

for **1**. They reported that **1**-Li^+, -Na^+, -K^+, and -*n*-Bu_4N^+ in THF exhibited the same IR terminal carbonyl υ(CO) absorptions (2015, 1950 cm^{-1}) and that **1**-Li^+ has a broad $\upsilon(OCO)_{asym}$ absorption at 1510 cm^{-1} (1480 cm^{-1} with $^{13}CO_2$). Our IR spectral data for **1** [and **1**(^{13}C); Table 2], in contrast, features carbonyl absorptions in which $\upsilon(CO)_{asym}$ drops from 2011 to 1991 cm^{-1} and $\upsilon(CO)_{sym}$ ranges from 1950 to 1907 cm^{-1} through the counterion sequence Mg^{+2}, -Li^+, -Na^+, and -K^+, respectively. In addition, our metallocarboxylate $\upsilon(OCO)_{asym}$ absorptions reproducibly varied from 1525 to 1541 cm^{-1} (verified with $^{13}CO_2$). We submit that Cooper's IR spectral data[10d] correspond to FpH plus the decomposition residues, as we present in Figure 1D. This suggestion by no means impugns the results of their labeling studies. They undoubtedly worked with **1** but did not appreciate the exceptional difficulty of recording their IR spectra, an observation that admittedly took us several years to adequately resolve.

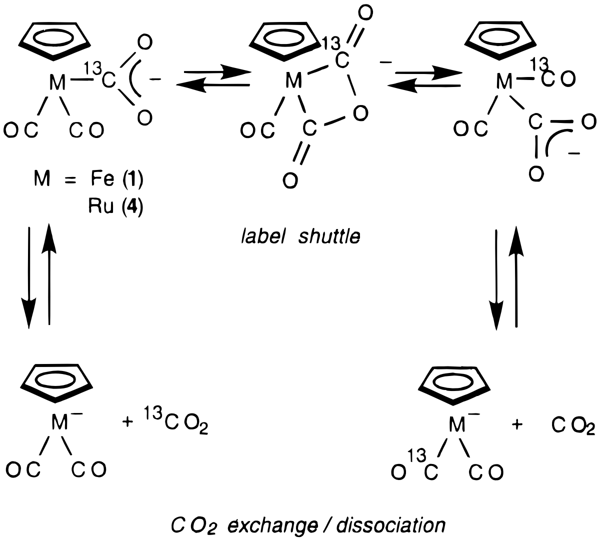
One outcome of this work is that the choice from among the Mg^{2+}, -Li^+, -Na^+, and -K^+ counterions has relatively little effect on the THF solution stability of **1**. Nevertheless, the presence of a metal counterion, as opposed to *n*-Bu_4N^+ or $K^{\bullet +}$ crown ether, stabilizes **1**. Previous observations by Cooper[10d] and by us[3a] regarding a qualitative solution stability of **1** with respect to choice of counterion, $Mg^{+2} > Li^+ > Na^+ > K^+ > n\text{-}Bu_4N^+$, must be revised. The difficulty of reproducibly collecting their IR spectral data obscured any solution stability differences. Apparently **1**-*n*-Bu_4N^+ remains the least stable: we were unable to detect it. The results of our Me_3SiCl trapping experiments thus are consistent with the following stability order, $Mg^{+2} \approx Li^+ \approx Na^+ \approx K^+ > n\text{-}Bu_4N^+$.

We now add qualitative judgments concerning the relative thermal stabilities of $Cp^*(CO)_2FeCO_2K$ (**3**-K^+) and $Cp(CO)_2RuCO_2^-$ (**4**-Na^+, -K^+). Thus **3**-K^+ proved to be more thermally sensitive; its dark orange THF solutions immediately turned red above −20 °C as **3**-K^+ rapidly degraded to *FpH. The ruthenium CO_2 adducts **4**-Na^+ and **4**-K^+, on the other hand, appeared to exhibit stability comparable to that of **1**, although warming THF solutions of **4** to room temperature (10 min) cleanly produced $Cp(CO)_2RuH$ [υ(CO) 2021, 1958 cm^{-1}] as the final species.

CO_2/$^{13}CO_2$ Dissociation Exchange and the Carboxylate−Carbonyl ^{13}C Label Shuttle $Cp(CO)_2FeCO_2M$ (1) and $Cp(CO)_2Fe^{13}CO_2M$ [1(^{13}C)]. In addition to facilitating the assignment of the metallocarboxylate IR $\upsilon(OCO)_{asym}$/$\upsilon(OCO)_{sym}$ absorptions, the ^{13}C-labeled metallocarboxylates $Cp(CO)_2M^{13}CO_2^-$ proved to be useful for studying reversible CO_2 binding and the interchange of carboxylate and carbonyl ligand sites (Scheme 2). The coupling of a label shuttle between carboxylate and carbonyl ligand sites, which interconverts $Cp(CO)_2M^{13}CO_2^-$ and $Cp(CO)(^{13}CO)MCO_2^-$,[10d] with reversible carbon dioxide coordination transformed remaining uncoordinated $^{13}CO_2$ to CO_2.

These studies were carried out by warming THF solutions of ^{13}C-labeled metallocarboxylates to room temperature and monitoring the changes in the concentrations of unligated $^{13}CO_2$. (Typically 1.0−1.2 equiv of CO_2 per metalate were used in quantitatively forming the metallocarboxylate.) The transformation of this unligated $^{13}CO_2$ to free CO_2 commensurate with the buildup of ^{13}C label in a terminal carbonyl ligand was monitored by variable-temperature IR and ^{13}C NMR spectroscopy. The facility of the $^{13}CO_2$/CO_2 and carboxylate−carbonyl label exchanges depended on the choice of both the iron or ruthenium metallocarboxylate moiety and the counterion.

Scheme 2. Postulated Metalloanhydride Pathway for Carboxylate-Carbonyl Exchange and CO_2 Label Exchange



With **1**(^{13}C)-K^+, for example, the IR spectra of the solutions (−20 to −5 °C) were consistent with the appearance of unlabeled CO_2 (2336 cm^{-1}) along with residual $^{13}CO_2$ (2270 cm^{-1}). Significantly, unlabeled CO_2 accumulated before **1**(^{13}C)-K^+ started degrading. Although we did not definitively identify the requisite $Cp(^{13}CO)(CO)FeCO_2K$, its anticipated IR υ(CO) peaks (~1975 and 1877 cm^{-1})[25] were evident as shoulders on the broad υ(CO) bands. The carboxylate υ(OCO) absorptions appeared as broad bands that conformed to the υ(OCO) and $\upsilon(O^{13}CO)$ assignments (Table 2). Solutions of **1**(^{13}C)-Na^+ upon warming above −15 °C likewise gave mixtures of CO_2 and $^{13}CO_2$.

The labeled Cp*Fe metallocarboxylate **3**(^{13}C)-K^+ was more reactive. Its THF solutions immediately converted any residual $^{13}CO_2$ to unlabeled CO_2 and approached a 1:1 mixture of these gases. Solutions of **3**(^{13}C)-K^+ above −20 °C invariably contained substantial concentrations of unlabeled CO_2, which also started to build up prior to the decomposition of **3**(^{13}C)-K^+.

The presence of lithium and magnesium counterions for **1** hindered the conversion of $^{13}CO_2$ to CO_2. IR spectra of **1**(^{13}C)-Li^+ and **1**(^{13}C)-Mg^{2+} thus indicated the absence of either unlabeled CO_2 or incorporation of label into the terminal carbonyls below −15 °C. Between −15 °C and room temperature, only **1**(^{13}C)-Li^+ underwent carboxylate−carbonyl (label) exchange. Reversible CO_2 dissociation, as detected by build up of unlabeled CO_2 at the expense of free $^{13}CO_2$, however, was not evident at room temperature (0.5 h).

^{13}C NMR spectra of **1**(^{13}C)-Li^+ in THF between −80 and −50 °C retained only one intense resonance for the carboxylate carbon (202.32 ppm) and weak absorptions for the terminal carbonyls (216.51 ppm) and the Cp moiety (85.42 ppm). Warming these solutions and holding at −20 °C (20 min) noticeably broadened the carboxylate carbon resonance and increased the intensity of the carbonyl absorption. Our previously reported ^{13}C NMR spectral assignments for the carboxylate and terminal carbonyl carbons on unlabeled **1**-Li^+ in THF therefore must be reversed to δ 202.4 and 217.0, respectively.[10e] ^{13}C NMR spectra of **1**(^{13}C)-Mg^{+2} under comparable conditions were inconsistent with any detectable carboxylate−carbonyl

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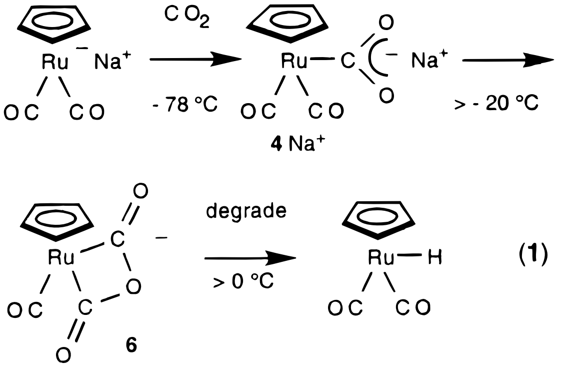
(25) (a) Alexander, J. J.; Wojcicki, A. J. *Inorg. Chem.* **1973**, *12*, 74. Alexander, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 1729. (b) Fettes, D. J.; Narayanaswamy, R.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2311. Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans.* **1985**, 1365. (c) Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602. (d) Bodnar, T. C.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926.

exchange (resonances: 210.01, 216.11, and 86.16 ppm, assigned as above) even after slowly (30 min) warming to room temperature.

Results of IR spectral studies on the unlabeled and ^{13}C-labeled ruthenium systems **4**-Na$^+$ and Cp(CO)$_2$Ru^{13}CO$_2$Na [**4**(^{13}C)-Na$^+$] proved to be especially informative on the coupling of the carboxylate−carbonyl label exchange and reversible carbon dioxide binding (Scheme 2). IR spectra of **4**-Na$^+$ as the solution slowly warmed appear in Figure 3. Spectrum A shows the starting metalate Cp(CO)$_2$RuNa; scan B corresponds to the initially formed **4**-Na$^+$ that entered the cell at −15 °C. Upon sitting in the cell, **4**-Na$^+$ transformed first to mixtures of **4**-Na$^+$ plus an intermediate that we tentatively formulate as the metalloanhydride Cp(CO)RuC(O)OC(O)Na (**6**) (scan C), then to mixtures of **6** and Cp(CO)$_2$RuH (eq 1). IR spectral scans D



(1)

and E monitor the degradation of **6** to Cp(CO)$_2$RuH as a 5 °C solution was warmed to room temperature over 4 min. Similar experimental runs starting with ^{13}CO$_2$ produced detectable metalloanhydride Cp(CO)Ru^{13}C(O)OC(O)Na [**6**(^{13}C)] (Table 2) and then 1:1 mixtures of Cp(CO)$_2$RuH and Cp(^{13}CO)(CO)RuH[10m] and of CO$_2$ and ^{13}CO$_2$ at 20 °C.

Our formulation of the metalloanhydride intermediate **6** must be regarded as tentative since it was assigned solely on the basis of its IR spectrum, i.e., the presence of one terminal carbonyl v(CO) band at 1923 cm^{-1} plus lower energy v(CO)$_{\mathrm{asym}}$ and v(CO)$_{\mathrm{sym}}$ bands (1526, 1246 cm^{-1}) that may be appropriate for an anionic metalloanhydride. Several attempts at recording ^{13}C NMR spectra between −78 and −10 °C afforded only broad, unresolved absorptions in the δ 160−200 carbonyl region and several Cp resonances. Similar metalloheterocycles previously had been reported by Fehlhammer and co-workers as a result of adding heterocumulenes to Fp$^-$, e.g., Cp(CO)FeC(O)NRC(=NR)Na.[26]

Observations on the thermal degradation of the ruthenium ^{13}C-labeled metallocarboxylate Cp(CO)$_2$Ru^{13}CO$_2$Na [**4** (^{13}C)-Na$^+$] and its putative metalloanhydride tautomer **6**(^{13}C) are consistent with the intermediacy of similar metalloanhydrides for the iron and ruthenium metallocarboxylates in this study (Scheme 2). These metalloanhydrides presumably mediate the reversible interchange of the ^{13}C label between the carboxylate and carbonyl ligands.

The reactions between the Na$^+$ and K$^+$ metallates Cp(CO)$_2$M$^-$ and ^{13}CO$_2$ yielded unlabeled CO$_2$. Initially produced Cp(CO)$_2$M^{13}CO$_2$$^-$ underwent label interchange giving Cp(^{13}CO)(CO)MCO$_2$$^-$, which in the presence of Na$^+$ and K$^+$ counterions reversibly dissociated unlabeled CO$_2$. Reversible dissociation entails the resulting metalate Cp(^{13}CO)(CO)Ru$^-$ preferentially associating ^{13}CO$_2$ from the initial pool of residual (unbound) ^{13}CO$_2$. Concentrations of unlabeled CO$_2$ therefore accumulated at the expense of residual ^{13}CO$_2$. This reversible ligation of carbon dioxide to the metalate accounts for the production of unlabeled CO$_2$ [from **1**(^{13}C)-K$^+$ and **3**(^{13}C)-K$^+$] before the metallcarboxylate degrades.

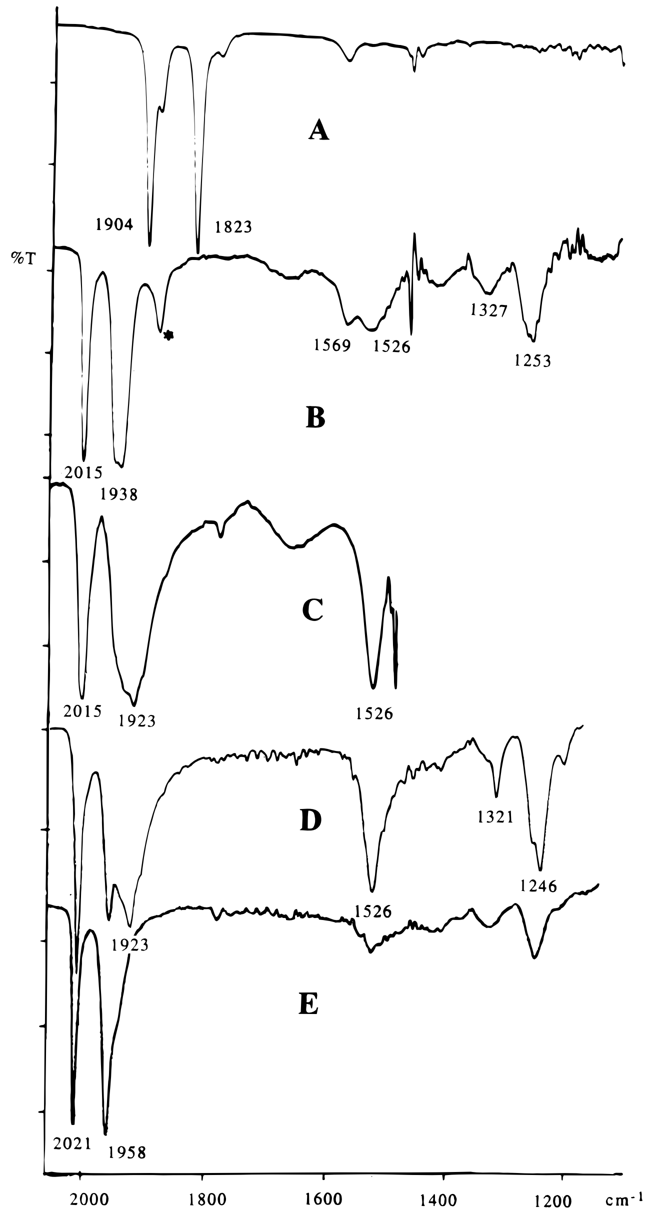


Figure 3. Infrared spectra of Cp(CO)$_2$RuCO$_2$$^-Na^+$ (**4**-Na$^+$) in low-temperature flow cell. (A) Starting Cp(CO)$_2$Ru$^-$ Na$^+$ (0.50 mmol in 15 mL of THF). (B) Cp(CO)$_2$Ru−CO$_2$$^-$ (**4**-Na$^+$), result of adding 1 equiv of CO$_2$ (−78 °C); cell at −18 °C. $*$, impurity. (C) **4**-Na$^+$ and Cp(CO)RuC(O)OC(O)$^-$Na$^+$ (**6**); cell (0.50 mm spacer) at −9 °C. (D) **6**-Na$^+$ and Cp(CO)$_2$RuH; cell at +5 °C. (E) Solution in (D) was warmed to room temperature over 4 min.

Lee and Cooper first reported the carboxylate−carbonyl label shuttle for **1**(^{13}C)-Li$^+$ and postulated the metalloanhydride intermediate.[10d] In their experiments, label exchange began at −20 °C (6% after 1 h) and was rapid at 2 °C (43% after 1 h). [They quantitated Cp(^{13}CO)(CO)FeCH$_3$ that formed after quenching the reactions with MeI.] We also observed sluggish label shuttle for **1**(^{13}C)-Li$^+$ between −20 °C and room temperature. Similar label shuttling between carboxylate and terminal carbonyl sites has been observed for [Cp(CO)$_2$Fe=C(^{17}O)O−WCp$_2$]$^+$,[27] Cp(CO)$_2$M^{13}CO$_2$Zr(Cl)Cp$_2$ (M = Fe,[21]

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[26] (a) Fehlhammer, W. P.; Christian, G.; Mayr, A. J. *J. Organomet. Chem.* **1980**, *199*, 87. (b) Fehlhammer, W. P.; Hirschmann, P.; Mayr, A. J. *J. Organomet. Chem.* **1982**, *224*, 153. (c) See also: Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1989**, *111*, 7424.

Ru[10m]), and Cp*(CO)$_2$Fe^{13}CO$_2$SnMe$_3$.[10k] Metalloanhydride species (cf. Scheme 2) were proposed as intermediates.

Conclusions

The (η^1-C) CO$_2$ adducts FpCO$_2^-$ (**1**-Mg^{2+}, -Li$^+$, -Na$^+$, -K$^+$), Cp*(CO)$_2$FeCO$_2$K (**3** K$^+$), and Cp(CO)$_2$RuCO$_2^-$ (**4** Na$^+$, K$^+$) were generated at −78 °C in THF by treating the CpM(CO)$_2^-$ Li$^+$, Na$^+$, K$^+$, or Mg^{+2} metalates with 1.0−1.2 equiv of CO$_2$ (or ^{13}CO$_2$). A surprising development was the initial difficulty encountered in reproducibly recording solution IR spectra of these metallocarboxylates, which proved to be independent of any intrinsic instability of **1**. The results of studies that were carried out on Me$_3$SiCl trapping of **1**-Mg^{2+}, -Li$^+$, -Na$^+$, -K$^+$, -*n*-Bu$_4$N$^+$, and -(dibenzo-18-crown-6)K$^+$ as Cp(CO)$_2$FeC(O)OSiMe$_3$ (**5**) indicated that **1**-Mg^{2+}, -Li$^+$, -Na$^+$, and -K$^+$ are stable at room temperature for at least 1 h, and with proper precautions, their IR spectra can be obtained. The υ(OCO) assignments, confirmed by isotope shifts for 99% labeled Fp^{13}CO$_2^-$ [**1**(^{13}C)], are consistent with an ionic or (η^1-C:η^2-O,O′) metallocarboxylate. A decrease in the IR terminal carbonyl υ(CO) absorptions for **1** through the counterion sequence Mg^{+2}, -Li$^+$, -Na$^+$, and -K$^+$ is consistent with increasing charge density on the Fp moiety due to attenuation of carboxylate−counterion ion pairing.

Results of variable-temperature (−15 °C to room temperature) IR and ^{13}C NMR spectral studies were consistent with Cp(CO)$_2$M^{13}CO$_2^-$ gradually transforming exogenous ^{13}CO$_2$ to unlabeled CO$_2$. This results from two coupled reactions: (a) exchange of the ^{13}C label between the carboxylate and carbonyl ligands and (b) reversible dissociation of carbon dioxide from the metallocarboxylates. The initial ^{13}C label shuttle interconverted Cp(CO)$_2$M^{13}CO$_2^-$ and Cp(^{13}CO)(CO)MCO$_2^-$ via the proposed metalloanhydride intermediates Cp(CO)M^{13}C(O)OC(O)$^-$ (the ruthenium example may have been detected). Then Cp(^{13}CO)(CO)MCO$_2^-$ dissociated unlabeled CO$_2$ and exchanged it for residual ^{13}CO$_2$.

The facility with which the labeled metallocarboxylates Cp(CO)$_2$M^{13}CO$_2^-$ exchanged the ^{13}C label between the carboxylate and carbonyl ligands and reversibly dissociated carbon dioxide depended on the choice of the counterion. Thus, **1**-Li$^+$ and especially **1**-Mg^{2+} were much less labile toward the first step and were unreactive toward CO$_2$ dissociation. These observations are consistent with tight binding of the counterions to the carboxylate oxygens, commensurate with localization of the negative charge on the carboxylate oxygens. Hence, their IR spectra exhibit high υ(CO) values. On the other hand, **1**-Na$^+$ and **1**-K$^+$ delocalized more of the negative charge onto the Fp moiety [exhibiting lower υ(CO) values] due to their Na$^+$ and K$^+$ counterions being less tightly bound to the carboxylate oxygens. Thus **1**-Na$^+$ and **1**-K$^+$ were more reactive than **1**-Mg^{2+} and **1**-Li$^+$ toward label shuttle and exchange.

Acknowledgment. We thank Drs. Jose Vites and Bruce Landrum of this laboratory for sharing preliminary observations. Incisive comments by the reviewers are gratefully appreciated. Support from the National Science Foundation, Grant CHE-8305484, is acknowledged.

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(27) Pilato, R. S.; Housmekerides, C. E.; Jernakoff, P.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2333.