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Synthesis and Characterization of Iron Metallocarboxylates

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The synthesis and characterization of hydrated metallocarboxylate anion salts $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-M^+\cdot xH_2O$ (M = Li, Na, K) and $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)COO^-K^+\cdot xH_2O$ together with the anhydrous analogues $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-M^+$ (M = Li, K) and $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)COO^-K^+$ are reported. Comparisons of the reactions of these salts toward equimolar amounts of acids or methylating agents show that there is competitive cleavage of the carboxylate C–O and O–M bonds. The more oxophilic cations promote C–O bond cleavage; the more electron-donating pentamethylcyclopentadienyl ligand also promotes C–O bond cleavage when compared to the cyclopentadienyl-substituted compound. Hydration appears to strengthen the O–M bond slightly. Reactions of the potassium salts with an electrophilic cation $Mn(CO)_5(PPh_3)^+BF_4^-$ result in oxide transfer whereas reactions of the same metallocarboxylates with Ph_3SnCl yield bimetallic CO_2-bridged complexes. The anhydrous salts are more thermally stable than the hydrates. All of the metallocarboxylate salts bind CO_2 strongly; decomposition occurs as a result of hydrolysis to the corresponding metallocarboxylic acids.

Introduction

Interest in metallocarboxylic acids and their conjugate bases derives from their proposed intermediacy in metal carbonyl catalyzed water gas shift (WGS) reactions.[1] Also, the anions serve as models for catalytic intermediates in CO_2 fixation processes.[2] While it has been possible to prepare some of the metallocarboxylate anions by direct carbonation of a metal anion[3] or by deprotonation of a metallocarboxylic acid,[4] few have been isolated and fully characterized; crystallographic data are available for only one such compound.[5]

A number of years ago, Pettit and co-workers[4a] reported the preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$ and several of its derivatives, including one described as the "potassium salt" of the acid. Neither the preparation nor the characterization of this latter product was described; thus it is not known whether the compound was generated in aqueous media. The apparent stability of this compound toward CO_2 loss was remarkable in view of the ready reversibility of CO_2 binding to alkali-metal salts of $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$.[3a,d,f,g] We report herein the preparation, isolation, characterization, and derivatization of both hydrated and anhydrous forms of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-K^+$ and other related alkali-metal salts[6] as well as the hydrated and anhydrous forms of $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)COO^-K^+$.

Results and Discussion

Synthesis of the Hydrated and Anhydrous Metallocarboxylate Anions. The hydrated ions, **2a–c** and **5** (see Table I) were prepared by addition of an excess of the alkali-metal hydroxide to the corresponding metal carbonyl cations, **1a,b** and **4**, in aqueous acetone, as illustrated in eq 1 for **2a**.

$$\underset{\textbf{1b}}{(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)^+BF_4^-} \xrightarrow[\text{acetone/water}]{\text{KOH}} \underset{\textbf{2a}}{(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-K^+\cdot 3H_2O} \quad (1)$$

The metallocarboxylate salt precipitates from this medium in each case. All products were collected and dried under vacuum at low temperature before use. Potassium salt **2a** is a shiny dark orange solid; the others are yellow-orange. All are air-sensitive and should be handled by Schlenk techniques or in an inert-atmosphere glovebox. The compounds are labile in solution in organic solvents at ambient temperature (see below); however, at low temperatures, spectral data can be obtained and some chemical reactions can be performed without deterioration of the anions. The compounds should be stored (as solids) below −20 °C and under nitrogen; **2a–c** can be stored in this way for several weeks, **5** deteriorates significantly after 3–4 days.

Anions **2a** and **5** were treated with potassium tri-*sec*-butylborohydride to effect their dehydration; compound **2b** was treated with the corresponding lithium compound. The reactions were heterogeneous and were conducted at −30 °C so that the carboxylates suffered no decomposition. The byproduct MOH precipitated as a gel onto the walls of the flask; the slurry containing the anhydrous carboxylate could be poured away from it readily and the product collected by filtration. The products **3a,b** and **6** are somewhat lighter in color than their precursors; all are more stable in the solid state than the corresponding hydrates. When exposed to the air, the anhydrous salts quickly absorb water and return to the hydrated form; prolonged exposure to water causes hydrolysis and subsequent decomposition. Again the salts should be stored under nitrogen and below −20 °C; all can be kept for several weeks without deterioration.

Characterization and Derivatization of the Metallocarboxylate Anions. The salts have been characterized primarily by spectral methods and conversion, in the case of the potassium salts, to the corresponding tri-

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[5] Gambarotta, S.; Arena, F.; Floriani, C.; Zanuzzi, P. F. *J. Am. Chem. Soc.* 1982, *104*, 5082.

[6] Preliminary accounts of some of this work have been published: (a) Gibson, D. H.; Ong, T.-S. *J. Am. Chem. Soc.* 1987, *109*, 7191. (b) Gibson, D. H.; Ong, T.-S. in *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: New York, 1988; p 210–214.

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Table I. Selected IR (DRIFTS) Spectra of Metallocarboxylates

compd	$\nu_{(-OH)}$, cm^{-1}	terminal carbonyl and other characteristic absorptions, 2000–1000 cm^{-1}	
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$	3200–2600 (w, m)	1928 (s)	1575 (w), 1561 (vs), 1484 (mw), 1438 (m), 1122 (vs)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-K^+\cdot xH_2O$ (**2a**)	3700–2700 (w, centered at 3370)	1885 (s), 1877 (sh, s)	1480 (s), 1434 (vs, br), 1211 (s)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-Li^+\cdot xH_2O$ (**2b**)	3638 (w), 3291 (vw, br)	1912 (s), 1899 (sh, s)	1479 (m), 1435 (s), 1243 (m, br)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-Na^+\cdot xH_2O$ (**2c**)	3700–2730 (w, centered at 3471)	1912 (s), 1895 (s)	1457 (s), 1434 (m), 1224 (m, br)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-K^+$ (**3a**)		1893 (s), 1885 (sh, s)	1480 (s), 1438 (s, br), 1204 (s, br)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-Li^+$ (**3b**)		1918 (s), 1901 (m, sh)	1480 (s), 1452 (vs), 1219 (m, br)
$(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)COO^-K^+\cdot xH_2O^a$ (**5**)	3500–2800 (s, br, centered at 3150)	1910 (m, sh), 1870 (s)	1395 (m, br), 1203 (m)
same^b		1869 (s), 1860 (s)	1434 (m), 1373 (m)
$(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)COO^-K^{+a}$ (**6**)		1835 (s, br)	1390 (m, br), 1208 (m)
same^b		1822 (s)	1434 (m), 1371 (m)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOCH_3$ (**7a**)		1937 (s)	1594 (s), 1484 (m), 1436 (ms), 1094 (s)
$(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)COOCH_3{}^c$ (**7b**)		1923 (vs)	1606 (m), 1435 (mw), 1380 (w), 1019 (m)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOSnPh_3$ (**8a**)		1952 (s)	1480 (m), 1432 (s), 1174 (m, br)
$(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)COOSnPh_3$ (**8b**)		1924 (m), 1917 (s)	1480 (m), 1432 (s), 1139 (m, br)

^{a}KBr disc. ^{b}Flurolube mull. ^{c}Solution in tetrachloroethylene.

Table II. Selected ^{13}C NMR Spectra of Metallocarboxylates

compd	solvent/temp, °C	chemical shift of carbonyl and carboxylate ligands,^{a} ppm (J_{PC}, Hz)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}COOH$	THF-d_8/−35	220.90 (d, 30.6) 214.10 (d, 34.6)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}COO^-K^+\cdot xH_2O$ (**2a**)	THF-d_8/−30 18-crown-6 added	221.32 (d, 28.1) 221.06 (d, 27.8)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}COO^-K^+$ (**3a**)	THF-d_8/−30 18-crown-6 added	221.31 (d, 27.9) 221.06 (d, 27.9)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}COO^-Li^+\cdot xH_2O$ (**2b**)	THF-d_8/−35	221.98 (d, 34.2) 217.93 (d, 26.9)
same	THF-d_8/−35 12-crown-4 added	221.61 (d, 36.1) 216.49 (m)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}COO^-Li^+$ (**3b**)	THF-d_8/40	222.17 (d, 34.3) 218.07 (d, 23.6)
$(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)\text{-}COO^-K^+\cdot xH_2O$ (**5**)	THF-d_8/−24	224.05 (d, 32.0) 220.26 (d, 28.2)
same	THF-d_8/−20 18-crown-6 added	224.03 (d, 33.6) 212.17 (d, 27.4)
$(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)\text{-}COO^-K^+$ (**6**)	THF-d_8/−24	224.95 (d, 32.7) 216.51 (d, 27.1)
same	THF-d_8/−20 18-crown-6 added	223.28 (d, 27.2) 223.04 (d, 27.9)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}COOSnPh_3$ (**8a**)	THF-d_8/20	228.16 (d, 31.5) 220.11 (d, 29.4)
$(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)\text{-}COOSnPh_3$ (**8b**)	C_6D_6/65	232.22 (d, 28.8) 220.08 (d, 27.4)
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}COOCH_3$ (**7a**)	THF-d_8/−30	220.81 (d, 29.8) 212.18 (d, 36.0)
$(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)\text{-}COOCH_3$ (**7b**)	THF-d_8/36	222.94 (d, 27.6) 217.22 (d, 34.2)

^{a}The values are relative to tetramethylsilane.

phenyltin derivatives. Elemental analysis was performed on compound **2a**; the results are in agreement with its formulation as a trihydrate (^1H NMR data, in THF-d_8, show the coordinated water). The extent of hydration with **2b**,**c** and **5** is not known precisely, but appears to be similar to that of **2a**. Except for **2a**, the degradation of the metallo carboxylate anions at room temperature prevented us from obtaining elemental analyses.

The major infrared spectral bands observed by the DRIFTS method for the metallocarboxylates are summarized in Table I. Compounds **5** and **6** are unstable under DRIFTS conditions, even with a nitrogen purge of the spectrometer; spectra of these compounds were obtained from KBr disks and Flurolube mulls. The hydrated salts show one or more weak, broad bands centered at about 3400 cm^{-1}, which are assigned to ν_{OH} of the coordinated water molecules. Comparisons of the DRIFTS spectra of the metallocarboxylates with cyclopentadienyl ligands show two bands in the region 1400–1500 cm^{-1}, one centered at 1471 ± 13 cm^{-1} and the other at 1442 ± 10 cm^{-1}. Also, all of these show a medium to strong band in the 1000–1250-cm^{-1} region. The metallocarboxylate anions and the tin complex in this series are distinguished by having a more intense band at 1442 ± 10 cm^{-1} than the others and in having the low-frequency band at much higher wavenumbers (1174–1243 cm^{-1}). A chelating mode of bonding of the carboxylate oxygens to the tin atom in **8a** has been established from X-ray data (see below). The bimetallic rhenium/tin carboxylate prepared by Gladysz[4c] shows strong bands at 1395 and 1188 cm^{-1}, and crystallographic data indicate nearly equal bonding of both carboxylate oxygens to the tin atom. Similarly, the rhenium metallocarboxylate anions show bands at 1420 ± 15 and 1244 ± 5 cm^{-1}; these were assigned to the ν_{asym} and ν_{sym} of the chelated carboxylate ligand. The analogous bands in the cyclopentadienyl iron metallocarboxylate anions and tin complexes appear to be those at 1442 ± 10 and 1209 ± 35 cm^{-1}, respectively. Together with the absence of bands near 1580 cm^{-1}, which the acid and esters exhibit, we believe this provides good support for a bonding mode involving chelation of the carboxylate group in the anions to the alkali-metal counterion.[7] We were unable to obtain DRIFTS spectra of compounds **5** and **6**; spectra of these compounds in KBr disks show a single broad absorption near 1400 cm^{-1} and a low-frequency band at 1205 ± 3 cm^{-1}. The spectra are clearly similar to those of the other anions, and we suggest chelated carboxylate oxygens for these also; clear assignment of the ν_{asym} cannot be made, but the low-frequency band is assigned as ν_{sym}. Comparisons of ester **7b** with tin compound **8b** in this series suggest that the ν_{asym} and ν_{sym} bands for the chelated carboxylate are at 1432 and 1139 cm^{-1} for **8b** (closely related to 1432 and 1174 cm^{-1} in **8a**). All of the metallocarboxylate anions show lowered ν_{CO} for the terminal carbonyl ligands as compared to the covalent compounds; these are centered at about 1900 cm^{-1} in **2a–c** and **3a**,**b** but are lowered below

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[7] (a) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227. (b) Deacon, G. B.; Huber, F.; Phillips, R. J. *Inorg. Chim. Acta* **1985**, *104*, 41.

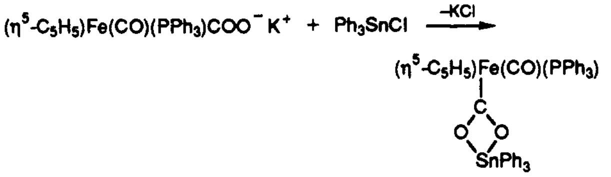
1870 cm^{-1} in **5** and **6** due to the enhanced electron-donating characteristics of the pentamethylcyclopentadienyl ligand.

The ^{13}C NMR data (carboxyl and carbonyl bands only) for the metallocarboxylate anions, in THF-d_8, are summarized in Table II; the spectra of some have also been recorded in acetone-d_6/D$_2$O (see Experimental Section). The resonance positions of both of these types of ligands are well below 200 ppm. The intensities of the resonances are approximately the same, and each is a doublet due to coupling with a single phosphorus ligand. We have used ion-specific crown ethers in several cases, not only to enhance the solubility of some of the salts but also to probe for chemical shift differences that might help in assigning the two resonances. Spectra of **2a** with and without 18-crown-6 could be obtained in acetone-d_6/D$_2$O, only, for solubility reasons. Comparing the spectral data, one sees that the lowest field resonance changes very little while the other low field resonance moves upfield by about 2 ppm. Similar behavior is seen with the lithium salt **2b** when spectra with and without 12-crown-4 in either solvent are compared; however, the chemical shift difference is not as great as with **2a**. Compound **5** shows the largest shift difference (8 ppm). Compound **6** is the only anhydrous salt for which we were able to obtain carbon spectra with and without the crown ether (because of solubility limitations). Addition of the crown ether alters the chemical shift positions of both these low-field resonances but moves the higher field one most; interestingly, this resonance is moved to *lower* field by addition of the crown.

We conclude from these data that it is the higher of the two low-field resonances, in all cases, which should be assigned to the carboxylate carbon; this one is closer to the alkali-metal center and should be the one most affected by coordination changes at that metal center prompted by the crown ether. Interestingly, water does not seem to have a similar effect. Comparison of **2a** with **3a**, both with added crown ether, shows the two to be nearly identical. Compounds **2b** and **3b** are closely similar also. Note that the spectrum of **3b** was recorded at +40 °C; compound **2b** would not have been stable in solution at this temperature.

We are not yet able to assign the carbonyl and carboxylate resonances to the metallocarboxylic acid or to either of the esters. However, in comparing the carbon spectral data of the tin compounds **8a,b** with that from the precursor potassium salts, we find some parallels with previous work that allow tentative assignments to be made. The bimetallic rhenium/tin complex prepared by Gladysz[4c] has the bridging carboxyl group as the lowest field carbon resonance. In comparison to the potassium salt of the rhenium carboxylate, this carbon shifts about 15 ppm downfield after coordination to tin. Similarly, one of the low-field carbons in **8a,b** has shifted dramatically downfield in comparison to the corresponding potassium salts. We suggest that these are the carboxyl carbons in each case. Note that the spectrum of tin derivative **8b** was obtained at +65 °C. The ambient-temperature spectrum of this compound in THF is quite complicated, but began to simplify as the probe temperature was increased; changing to benzene allowed a higher temperature to be obtained and afforded a clean spectrum. Apparently, there is restricted rotation, particularly with regard to the phenyl carbons, which is overcome with the increase in temperature.

X-ray-quality crystals could not be obtained from any of the metallocarboxylate anions, so we have chosen to prepare derivatives of some of them to complete the characterization process. Reaction of each of the potassium salts with triphenyltin chloride allows a crystalline derivative of the metallocarboxylate anion to be prepared that can be fully characterized by spectral data, elemental analysis, and in the case of compound **8a**, X-ray crystallographic analysis. The reaction products in each case are bimetallic complexes with bridging carbon dioxide ligands; the sequence with **3a** is shown:



(2)

8a

As noted previously by Gladysz,[4c] O–Sn bond lengths in triaryltin derivatives of organic carboxylates differ by 0.7–0.8 Å. The O–Sn bond distances in **8a** differ by much less (2.123 and 2.342 Å), indicating bidentate binding of the carboxylate ligand to the tin atom.[8] The tin derivative of the rhenium carboxylate reported by Gladysz[4c] also displays a chelated carboxylate ligand. The η^1 coordination of the carboxylate carbon to the iron atom, which is evident in **8a**, suggests that there is similar coordination of this carbon center to iron in the metallo carboxylate anions as well. Conversions of the anions to the corresponding methyl esters by reactions with methyl iodide (see discussion below) also provide support for this coordination mode.

Reactions of the Metallocarboxylate Anions with Electrophiles. Efforts have been made to probe for differences in the behavior of the metallocarboxylate anions toward strong electrophiles. Bearing in mind that there are significant differences in the solubility of the pentamethylcyclopentadienyl and cyclopentadienyl complexes (complexes **2a–c** are slightly soluble in acetone/water, while **5** is very soluble; complexes **2a–c** and **3a,b** are sparingly soluble in CH$_3$CN, but **5** and **6** are soluble), it is still possible to draw some qualitative conclusions about their comparative reactions with protonic acids and methylating agents. These results are tabulated in Table III; except with CH$_3$I, reactions between each anion and 1 equiv of the electrophile are recorded.

The hydrated complexes **2a–c** all give the corresponding metallocarboxylic acid when treated with HCl in acetone/water. With HBF$_4$ in acetone/water or ether, mixtures of acid and cation are obtained with **2a–c**, except with **2b** in ether, which gives cation only. A control experiment involving (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)COOH and LiBF$_4$ in ether showed 25% cleavage of the acid to the cation after 2 h at 0 °C (the conditions of the experiment with **2b**); thus, some small amount of metallocarboxylic acid may have been formed in the reaction with **2b** also. There is considerable degradation of **2a–c** in HBF$_4$/acetone/water. In the more polar solvent CH$_3$CN, reactions with HBF$_4$ yield the cation only (these observations do not result from simple ionization of the initially formed metallocarboxylic acid in this solvent). Compound **5** behaves differently, giving cation only from the reaction with HCl, a mixture of acid and cation with HBF$_4$ in acetone/water and cation only with HBF$_4$ in CH$_3$CN. The results can be rationalized, fairly well, in terms of the strength of the acid reagent and differences in strengths of the carboxylate C–O and O–M bonds among these compounds. With the complexes **2a–c**, the most vulnerable site is the O–M bond, but use of the stronger HBF$_4$ allows C–O bond breaking to occur with this becoming predominant in

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[8] A full account of this work has been published elsewhere: Gibson, D. H.; Richardson, J. F.; Ong, T.-S. *Acta Crystallogr.* **1991**, *C47*, 259.

Table III. Reactions of Metallocarboxylates with Electrophiles[a]

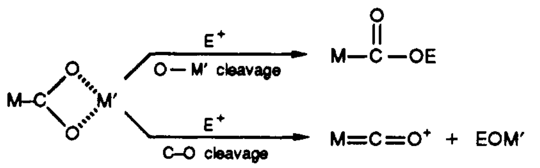
	electrophiles					
carboxylate	HCl/H_2O/ acetone	HBF_4/H_2O/ acetone	HBF_4/ether	HBF_4/CH_3CN	CH_3I/CH_3CN	$(CH_3)_3O^+/CH_3CN$
2a	acid (74)	acid (34)	acid (37)		ester (92)	ester (81)
		cation (19)	cation (42)	cation (90)		cation (7)
2b	acid (81)	acid (22)			ester (11)	ester (50)[b]
		cation (41)	cation (71)	cation (83)	cation (69)	cation (23)[b]
2c	acid (71)	acid (31)	acid (36)		ester (15)	ester (43)
		cation (37)	cation (53)	cation (87)	cation (71)	cation (49)
5	cation (86)	acid (72)			ester (77)	ester (38)[b]
		cation (21)		cation (92)[b]		cation (43)[b]
3a			acid (40)	acid (57)	ester (92)	ester (80)
			cation (41)	cation (17)		
3b						ester (61)[b]
			cation (94)	cation (65)	cation (69)	cation (26)[b]
6					ester (77)	ester (33)[b]
				cation (91)[b]		cation (45)[b]

[a] Product yields (%) are shown in parentheses. [b] Reaction conducted in CD_3CN.

CH_3CN. Also, the oxophilic lithium and sodium counterions in **2b,c** increase the difficulty in cleaving the O–M bond as compared to the corresponding potassium salt. With **5**, the most vulnerable site is the carboxylate C–O bond, since HCl cleavage gives cation only; stronger acid media gives progressively more O–M bond breaking. Comparisons of the reactions of **3a** with those of **3b** again show the ability of lithium ion to strengthen the O–M bond relative to the C–O bond; also, HBF_4 in CH_3CN is better able to cleave the O–M bond than the same acid in ether. Hydration appears to strengthen the O–M bond, since there is less cleavage at this site with **2a** than with **3a** or with **2b** as compared to **3b**. No differences can be detected between the hydrated and anhydrous salts **5** and **6**; unfortunately, these compounds are unstable toward ether.

Reactions of the salts toward two methylating agents, CH_3I and $(CH_3)_3O^+BF_4^-$, have also been compared. The interpretation of the results of the reaction with CH_3I, which requires prolonged reaction times and temperatures higher than the ones with the oxonium ion, is further complicated by the ability of lithium and sodium salts to cleave the product esters (see Experimental Section). Under the short times and low temperatures allowed with the oxonium ion, this secondary reaction does not compete. Here, again, the lithium and sodium counterions are observed to strengthen the O–M bond as compared to the corresponding potassium salts. The more electrophilic oxonium ion is better able to promote cleavage of the C–O bond in **2a–c** and **3a,b** when compared to CH_3I. Also, the oxonium ion is better able to promote O–M bond breaking than HBF_4 in the same solvent (CH_3CN) with all of the salts.

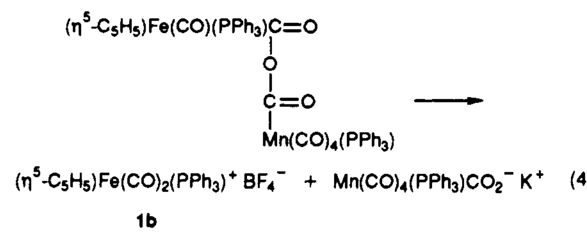
The overall picture which emerges is one of competitive cleavage of the C–O and O–M bonds in the metallocarboxylate anions, as shown in eq 3. A highly oxophilic counterion can play a major role in promoting C–O bond cleavage instead of O–M cleavage in these complexes. Furthermore, a highly electron-donating ligand, such as pentamethylcyclopentadienyl, would be expected to enhance the contribution of the carbene form of the metallocarboxylate and, therefore, to strengthen the O–M bond and direct the electrophilic cleavage toward the carboxylate C–O bond. Whether the salt is hydrated or not appears less significant, as long as the reactions are conducted at low enough temperatures to suppress hydrolysis of the hydrated salts in solution, but there is some evidence to suggest that the O–M bond is somewhat stronger in the hydrated form. The competition between O–M and C–O bond breaking in these complexes again underscores the fundamental differences between the metallocarboxylate anions and the corresponding salts of organic carboxylic acids, which react with electrophiles at the O–M bond exclusively.



(3)

It is possible to rationalize some previous observations on other metallocarboxylate anions in reactions with electrophiles through consideration of the factors discussed above. Thus, Cooper[3e] obtained $W(CO)_6$ as the principal product from reactions of $Li_2W(CO)_5(CO_2)$ with electrophiles such as trifluoroacetic acid and methyl triflate. The metal carbonyl would result from C–O bond breaking in the carboxylate anion; such cleavage would be promoted by the lithium ion and by the dianionic nature of the tungsten carboxylate, which should have enhanced carbene character in the metal to carboxylate carbon bond. The metallocarboxylate reacts with excess CO_2 to liberate $W(CO)_6$ and lithium carbonate. This reaction has been proposed to occur through nucleophilic addition of a carboxylate oxygen to the weakly electrophilic carbon of CO_2. However, since the anion cannot be alkylated by methyl triflate it seems more likely that reaction with CO_2 also occurs at the carboxylate C–O bond. Similarly, it has been observed[3a] that $(\eta^5\text{-}C_5H_5)Fe(CO)_2CO_2^-Na^+$ reacts further with CO_2 and yields sodium carbonate and the iron carbonyl dimer.

The capacity of some metallocarboxylate anions to serve as oxygen-transfer agents toward certain types of electrophiles has been described previously.[3] In order to probe the behavior of the present systems in this regard, we chose the electrophilic manganese cation, $Mn(CO)_5(PPh_3)^+BF_4^-$. Based on the earlier work, a possible course for our reactions can be illustrated for compound **3a**:



(4)

If oxygen transfer did occur, it was thought that the stability of the manganese carboxylate would be determinative in establishing the final products. Whether C–O or O–M bond cleavage in the original carboxylate occurred, the manganese carboxylate should result from oxygen transfer.

The first carboxylate to be examined was **2a**. The reaction was conducted at −40 °C in order to minimize hydrolysis of **2a** in CH_3CN. After 30 min, an IR spectrum of the solution showed that **2a** and the manganese cation were no longer present. New carbonyl bands appeared which could be assigned, in part, to cation **1b**; the others suggested the presence of a metal carbonyl anion. Excess methyl iodide was added to the mixture and the carbonyl bands due to the anion disappeared and were replaced by others at higher frequency. The reaction products were isolated and identified as **1b** (91% yield) and $CH_3Mn(CO)_4(PPh_3)$ (86% yield). The formation of the latter product can be rationalized as resulting from decarboxylation of the expected intermediate manganese carboxylate followed by alkylation of the resulting manganese carbonyl anion. The reactions of the other iron carboxylate anions toward the manganese cation, followed by CH_3I, are nearly the same; the methyl complex is obtained in uniformly high yields (80–100%) in all cases. The iron cation is obtained in high yields (83–97%) in each case except in the reaction of **6**. In this case, only a 38% yield of cation **4** was obtained together with a 21% yield of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2I$; the latter product is more easily rationalized as resulting from radical intermediates than from the ionic pathway formulated above. Clearly, there is a reaction path available to the anhydrous salt, **6**, that is not available to the corresponding hydrate, **5**.

Reactions between **2a** and a phosphite-containing iron cation have been reported by us previously.[9] In these, the target cation is converted to a phosphonate complex as a result of oxygen transfer followed by an internal displacement reaction. Also formed in the reaction, however, are significant amounts of the iron dimer, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, a product which suggests that a radical pathway may be involved in these reactions also.[10]

Reactions of all four potassium salts (**2a**, **3a**, **5**, **6**) with Ph_3SnCl have been examined, as indicated above, in order to derivatize the complexes and to facilitate their characterization. The reaction products are CO_2-bridged bimetallic compounds and the yields are quite high (83–99%). In these reactions, the O–M bond is broken in the carboxylates exclusively.

Thermolyses of the Metallocarboxylates. The other metallocarboxylate salts that have been reported have shown varying degrees of thermal stability and differ widely with regard to the reversibility of CO_2 binding. Thus, the lithium, sodium, and potassium salts of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CO_2^-$ lose CO_2 readily,[3a,d] but the magnesium salt is much more stable.[3f] Alkali-metal salts of the cobalt salen complex studied by Floriani[5] lose CO_2 when pumped under vacuum. The lithium salt of the cyclopentadienyl rhenium complex studied by Sutton[4b] loses CO_2 in solution, but the corresponding pentamethylcyclopentadienyl complex does not. Salts of the rhenium complex studied by Gladysz,[4c] which have both cyclopentadienyl and phosphine ligands, appear to be relatively stable. Also, $Li_2W(CO)_5(CO_2)$ showed stability toward CO_2 loss.[3b,e] Highly electron rich metal centers, then, do stabilize the metallocarboxylate anions toward loss of the carbon dioxide ligand. Furthermore, a very acidic metal center, as with the magnesium salt prepared by Cutler, can further assist the stabilization.

Thermal decompositions of **2a–c** take place readily in dry organic solvents at ambient temperatures. In order to have direct comparisons, thermolyses were done of all three in THF-d_8 in the glovebox. In all cases, the carboxylate turned dark green upon contact with the solvent. After standing for a period of time, the solutions were analyzed by ^1H NMR spectroscopy. All three showed mixtures of two iron dimers, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(PPh_3)$. There was considerable degradation of **2a**; the reaction is cleaner with the other two, with product yields totaling about 70%. The phosphine-containing dimer is dark green and is known to decompose in solution to the other dimer.[11] Since these two dimers are produced, rapidly, from thermolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$,[6b] we believe that **2a–c** suffer hydrolysis upon dissolution and subsequent decomposition of the resulting metallo carboxylic acid. In the solid state, **2a** decomposes, after 4 days at 50 °C, to the same dimers. The product yields are low and about the same as the reaction in solution. Compound **5** degrades extensively in solution at room temperature, producing only a small amount of $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$. The anhydrous compounds are more stable toward thermolysis; for example, the thermolysis of **3b** was still incomplete after 3 days at room temperature in THF. The decomposition products from **3a,b** were the same as those from the hydrated salts, presumably as a result of hydrolysis by adventitious water. In the solid state, after 4 days at 50 °C, **3b** became pale green, but an IR spectrum indicated that the solid was still predominantly the metallocarboxylate anion. Compound **6** decomposed completely only after 10 days at 50 °C. As with the other electron-rich metallocarboxylate anions, this series of compounds also binds CO_2 strongly.

The nature of the "potassium salt" of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$ reported by Pettit[4a] remains obscure; its reported stability, at 100 °C in DMF, clearly makes it different from the compounds we have studied. We do know that when isolated compound **2a** is mixed with water at room temperature it quickly changes color; after recovery and drying under vacuum, this material has spectral properties that are different from **2a**: ν_{CO} at 1940 (s) and 1610 (m) cm^{-1}. Reaction of this product with methanol gave ester **7a** and reaction with excess HCl afforded $(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)^+Cl^-$. Treatment of the product with excess KOH in acetone/water converted it back to **2a** in part, but the reaction was accompanied by some decomposition also. We have been unable to get satisfactory NMR spectral data on the compound. The results of the chemical reactions and the IR spectral data for the compound are consistent with its formulation as an anhydride, $(\eta^5\text{-}C_5H_5)(PPh_3)(CO)FeC(O)O(O)CFe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)$. Possibly this is the "potassium salt" isolated by the Pettit group.

Thermolyses of the tin complexes **8a,b** do not extrude CO_2 smoothly in the manner shown by Gladysz[4c] for the rhenium/tin complex. Extensive degradation of **8a** was observed after heating at 50 °C for several days; the only organometallic product was a small amount of ferrocene. Alternatively, **8b** was stable to thermolysis under these conditions.

Experimental Section

General Data. Reactions and manipulations were conducted

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[9] Gibson, D. H.; Ong, T.-S.; Ye, M.; Franco, J. O.; Owens, K. *Organometallics* **1988**, *7*, 2569.

[10] Gibson, D. H.; Ong, T.-S. Unpublished results.

[11] Haines, R. J.; du Preez, A. L. *Inorg. Chem.* **1969**, *8*, 1459.

under prepurified N_2 by means of standard Schlenk tube techniques or a Vacuum Atmospheres glovebox (with Dri-train). Glassware was oven- or flame-dried before use. Solvents were distilled from drying agents under nitrogen as follows: sodium benzophenone ketyl for diethyl ether and tetrahydrofuran (THF); P_2O_5 for CH_2Cl_2, CH_3CN, pentane, hexane, and CH_3I; CaH_2 for CH_3OH. Reagent grade acetone and chloroform were used as received. Spectral data were obtained on the following instruments: ^{1}H NMR, Varian XL-300 and EM-390; ^{13}C and ^{31}P NMR, Varian XL-300; IR, Nicolet SX-170 FT-IR and Perkin-Elmer 599B. NMR chemical shifts are referenced to tetramethylsilane. $AgBF_4$, pentamethylcyclopentadiene, ferrocene, triphenylphosphine, chlorotriphenyltin, potassium and lithium tri-*sec*-butylborohydride, $HBF_4 \cdot Me_2O$, $(CH_3)_3O^+BF_4^-$, THF-d_8, CD_2Cl_2, acetone-d_6, and D_2O were obtained from Aldrich and used directly. CD_3CN was distilled over P_2O_5. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was obtained from Pressure Chemical Co. and used directly. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(PPh_3)^+BF_4^-$ (4).[12] In the glovebox, $(\eta^5\text{-}C_5Me_5)Fe(CO)_2I$ (2.00 g, 5.35 mmol) was dissolved in 60 mL of anhydrous ether and this solution was added dropwise to a slurry of $AgBF_4$ (1.30 g, 6.68 mmol) in ether. The solvent was then evaporated to dryness to give a dark purple solid. The solid was triturated with 30 mL of CH_2Cl_2 and filtered; PPh_3 (1.40 g, 5.35 mmol) was added to the filtrate, and the mixture was refluxed for 30 min. Solvent was then evaporated, and the crude product was recrystallized from CH_2Cl_2/ether; yield 2.80 g (88%).

IR ν_{CO} (CH_2Cl_2): 2034 (w), 1983 (w) cm^{-1}. ^{1}H NMR (acetone-d_6): δ 7.64 (br), 7.53 (br), 1.75 (s). ^{13}C NMR (acetone-d_6): δ 213.81 (d, J_{PC} = 22.9 Hz), 133.56 (d, J_{PC} = 10.5 Hz), 132.43 (d, J_{PC} = 2.5 Hz), 131.18 (d, J_{PC} = 49.0 Hz), 129.87 (d, J_{PC} = 10.2 Hz), 101.22 (s), 9.24 (s). ^{31}P NMR (CD_3CN): δ 64.50 (vs external H_3PO_4).

Preparation of Hydrated Metallocarboxylate Salts. A. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-K^+\cdot xH_2O$ (2a). KOH (1.50 g, 22.72 mmol) was dissolved in 40 mL each of H_2O and acetone. Cation $(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)^+I^-$ (**1a**)[13] (6.00 g, 10.60 mmol) was added in portions during 5 min to give a dark orange solution, which became slightly cloudy during the addition. The mixture was quickly filtered and the filtrate then chilled, under nitrogen, overnight at –5 °C to effect complete precipitation of the product. Dark orange crystals were collected under nitrogen on the frit of a low-temperature crystallizer[14] with the cooling bath temperature maintained at 0 °C. The product was then dried, under vacuum, at 0 °C for 3 h. The salt was washed, in the same vessel at 0 °C, with approximately 3 × 50 mL of anhydrous ether (until the filtrate became colorless). The product was then dried, in vacuo, at 0 °C for a further 2 h (yield 4.66 g, 83%); the product had a melting point of 57–60 °C dec. The orange solid was transferred, under nitrogen, to a Schlenk vessel for storage at –20 °C.

Anal. Calcd for $C_{25}H_{26}FeKO_6P[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}COO^-K^+\cdot 3H_2O]$: C, 54.76; H, 4.78; P, 5.65. Found: C, 54.30; H, 4.83; P, 5.54. IR ν_{CO}: (Nujol) 1875 (s, br) cm^{-1}; (neat, DRIFTS) 3700–2700 (w, centered at 3370), 1885 (s), 1877 (sh, s), 1500–1425 (s, br) (most prominent bands at 1480 and 1434), 1230–1180 (s, br) (centered at 1211) cm^{-1}. ^{1}H NMR: (1:1 acetone-d_6/D_2O, 20 °C) δ 7.39 (m), 7.24 (m), 4.33 (s); (THF-d_8, –30 °C, 18-crown-6 added) δ 7.57 (m), 7.38 (s), 4.37 (s), 3.58 (s, 18-crown-6), 3.05 (s, br, H_2O). ^{13}C NMR: (1:1 acetone-d_6/D_2O, 20 °C) δ 221.67 (d, J_{PC} = 34.8 Hz), 220.34 (d, J_{PC} = 27.1 Hz), 138.08 (d, J_{PC} = 41.5 Hz), 133.48 (d, J_{PC} = 9.8 Hz), 129.81 (s), 128.15 (d, J_{PC} = 8.8 Hz), 84.86 (s); (1:1 acetone-d_6/D_2O, 20 °C, 18-crown-6 added) δ 221.42 (d, J_{PC} = 34.3 Hz), 218.43 (d, J_{PC} = 27.0 Hz), 138.06 (d, J_{PC} = 40.1 Hz), 133.32 (d, J_{PC} = 6.1 Hz), 129.55 (s), 127.93 (d, J_{PC} = 6.4 Hz), 84.68 (s), 69.89 (s, 18-crown-6); (THF-d_8, –30 °C, 18-crown-6 added) δ 221.32 (d, J_{PC} = 28.1 Hz), 221.06 (d, J_{PC} = 27.8 Hz), 139.42 (d, J_{PC} = 42.8 Hz), 133.95 (d, J_{PC} = 10.2 Hz), 130.19 (s), 128.72 (d, J_{PC} = 9.5 Hz), 81.01 (s), 71.40 (s, 18-crown-6).

B. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-Li^+\cdot xH_2O$ (2b). In the manner described above for **2a**, $LiOH\cdot H_2O$ (0.30 g, 7.15 mmol) was dissolved in 10 mL each of H_2O and acetone followed by cation **1a** (2.00 g, 3.50 mmol). The mixture was filtered under nitrogen and then chilled overnight at –5 °C to effect precipitation of the salt. The product was collected, as above, at 0 °C and then dried, under vacuum, at 0 °C. The salt was washed, in the same vessel at 0 °C, with 3 × 50 mL of anhydrous ether (until the filtrate became colorless). The yellow-orange crystals were then dried again, in vacuo, at 0 °C (yield 1.30 g, 77%); the product had a melting point of 65–68 °C dec. The yellow-orange crystals were transferred under nitrogen to a Schlenk vessel for storage at –20 °C.

IR ν_{CO}: (Nujol) 1901 (m, sh), 1888 (s, br) cm^{-1}; (neat, DRIFTS) 3638 (w), 3291 (vw, br), 1912 (s), 1899 (sh, s), 1479 (m), 1435 (s), 1275–1215 (m, br) (centered at 1243) cm^{-1}. ^{1}H NMR: (2:1 acetone-d_6/D_2O, 20 °C) δ 7.43 (m), 7.27 (m), 4.35 (s); (THF-d_8, –35 °C) δ 7.65 (s, br), 7.31 (s, br), 4.48 (s), 4.24 (s, br, H_2O); integration showed 2 mol of water/mol of the carboxylate. ^{13}C NMR: (2:1 acetone-d_6/D_2O, 20 °C) δ 221.56 (d, J_{PC} = 34.5 Hz), 219.87 (d, J_{PC} = 26.5 Hz), 138.23 (d, J_{PC} = 41.3 Hz), 133.52 (d, J_{PC} = 9.4 Hz), 129.74 (s), 128.12 (d, J_{PC} = 9.2 Hz), 84.85 (s); (2:1 acetone-d_6/H_2O, 20 °C, 12-crown-4 added) δ 221.62 (d, J_{PC} = 35.8 Hz), 218.71 (d, J_{PC} = 27.6 Hz), 138.56 (d, J_{PC} = 40.9 Hz), 133.68 (d, J_{PC} = 8.9 Hz), 129.71 (s), 128.16 (d, J_{PC} = 9.4 Hz), 84.94 (s), 70.24 (s, 12-crown-4); (THF-d_8, –35 °C) δ 221.98 (d, J_{PC} = 34.2 Hz), 217.93 (d, J_{PC} = 26.9 Hz), 139.67 (d, J_{PC} = 39.6 Hz), 134.53 (s, br), 129.76 (s), 128.45 (d, J_{PC} = 7.6 Hz), 85.58 (s); (THF-d_8, –35 °C, 12-crown-4 added) δ 221.61 (d, J_{PC} = 36.1 Hz), 216.49 (m), 138.96 (d, J_{PC} = 46.5 Hz), 134.42 (d, J_{PC} = 11.3 Hz), 130.07 (s), 128.57 (d, J_{PC} = 8.8 Hz), 85.52 (s), 71.50 (s, 12-crown-4).

C. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COO^-Na^+\cdot xH_2O$ (2c). In the same manner, NaOH (0.60 g, 14.70 mmol) was dissolved in 20 mL each of H_2O and acetone followed by cation **1a** (4.00 g, 7.00 mmol). After filtration, the solution was allowed to stand overnight at –5 °C. Yellow-orange crystals precipitated, which were collected under nitrogen, as above, at 0 °C. The product was then dried, under vacuum, at 0 °C. The salt was washed, in the same vessel at 0 °C, with approximately 3 × 50 mL of anhydrous ether (until the filtrate was colorless) and then dried again under vacuum at 0 °C; yield 2.75 g (percentage yield not calculated; extent of hydration not known).

IR ν_{CO}: (Nujol) 1910 (s, br) cm^{-1}; (neat, DRIFTS) 3700–2730 (vw, centered at 3471), 1912 (s), 1895 (s), 1488–1430 (m-s, br) (most prominent bands at 1457 and 1434), 1242–1205 (m, br) (centered at 1224) cm^{-1}. ^{1}H NMR: (2:1 acetone-d_6/D_2O, 16 °C) δ 7.42 (br), 7.28 (br), 4.44 (br); (2:1 acetone-d_6/D_2O, 16 °C, 15-crown-5 added) δ 7.45 (s, br), 7.28 (s, br), 4.37 (s), 3.60 (s, 15-crown-5). ^{13}C NMR: (2:1 acetone-d_6/D_2O, 16 °C) δ 221.47 (d, J_{PC} = 34.2 Hz), 219.56 (d, J_{PC} = 28.1 Hz), 138.26 (d, J_{PC} = 41.5 Hz), 133.53 (d, J_{PC} = 8.8 Hz), 129.77 (s), 128.14 (d, J_{PC} = 8.6 Hz), 84.86 (s); (2:1 acetone-d_6/D_2O, 16 °C, 15-crown-5 added) δ 221.51 (d, J_{PC} = 35.3 Hz), 218.02 (d, J_{PC} = 24.4 Hz), 138.27 (d, J_{PC} = 41.0 Hz), 133.54 (d, J_{PC} = 9.8 Hz), 129.66 (s), 128.07 (d, J_{PC} = 9.4 Hz), 84.83 (s), 68.80 (s, 15-crown-5).

D. $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)COO^-K^+\cdot xH_2O$ (5). Cation **4** (1.00 g, 1.68 mmol) was dissolved in 6 mL of acetone and cooled to 0 °C. KOH (0.47 g, 6.71 mmol) was dissolved in 6 mL of H_2O, and the resulting solution was cooled to 0 °C and added to the solution of **4**. This mixture was filtered, and the filtrate was chilled at –5 °C for 6 h. After this time, a yellow-orange solid precipitated, which was collected on the frit of a low-temperature crystallizer[14] maintained at 0 °C and then dried in vacuo at 0 °C to give 0.85 g of **5** (percentage yield not calculated; extent of hydration not known); the product had a melting point of 74–79 °C dec.

IR ν_{CO}: (Nujol) 3390 (w, br), 1850 (m, br) cm^{-1}; (KBr) 3500–2800 (s, br, centered at 3150), 1910 (m, sh), 1870 (s, br), 1430–1360 (m, br, centered at 1395 cm^{-1}), 1203 (m) cm^{-1}; (Flurolube) 1890 (m), 1869 (s), 1860 (s), 1434–1373 (m, br, most prominant bands at

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(12) The ^{1}H and ^{13}C NMR data obtained for this compound are closely similar to that reported previously for the PF_6 salt: Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094. However, the IR data in that previous report are those for the tricarbonyl cation (ν_{CO} 2130, 2078 cm^{-1}: Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1982**, *226*, C52) not the triphenylphosphine-substituted one. For comparison, note that $(\eta^5\text{-}C_5H_5)Fe(CO)_3{}^+PF_6^-$ has ν_{CO} at 2130 and 2080 cm^{-1} (Roman, E.; Astruc, D. *Inorg. Chem.* **1979**, *18*, 3284) while $(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)^+BF_4^-$ shows ν_{CO} at 2050 and 2010 cm^{-1} (see ref 15).

(13) Treichel, P. M.; Shubkin, R. L.; Barnett, K. W.; Reichard, D. *Inorg. Chem.* **1966**, *5*, 1177.

(14) Gibson, D. H.; Hsu, W.-L. *Inorg. Chim. Acta* **1982**, *59*, 93.

1434 and 1373) cm^{-1}. ^{1}H NMR: (THF-d_8, −24 °C) δ 7.34 (m), 1.54 (s); no resonance for coordinated water could be identified. ^{13}C NMR: (THF-d_8, −24 °C) δ 224.05 (d, J_{PC} = 32.0 Hz), 220.26 (d, J_{PC} = 28.2 Hz), 93.58 (s), 10.43 (s). The phenyl region (δ 128–137) was very complicated. ^{13}C NMR: (THF-d_8, −20 °C, 18-crown-6 added) δ 224.03 (d, J_{PC} = 33.6 Hz), 212.17 (d, J_{PC} = 27.4 Hz), 93.29 (s), 10.59 (s). The phenyl region (δ 127–143) was very complicated.

Preparation of Anhydrous Metallocarboxylate Salts. A. (η^5-C_5H_5)Fe(CO)(PPh_3)COO^-K^+ (3a). In the glovebox, KB(*sec*-butyl)$_3$H in ether (27.00 mL, 6.00 g, 27.00 mmol) was diluted with 150 mL of pentane and the solution cooled to −30 °C. **2a** (3.50 g, 6.60 mmol) was added, and the slurry was warmed to −10 °C and stirred for 4 h. After this time, the dispersed solid became a fine powder with a gelatinous precipitate sticking on the walls of the flask. An IR spectrum of a sample of the powder in Nujol showed no absorption at 3200–3500 cm^{-1}. This orange product was collected, then washed by stirring it in pentane (2 × 150 mL) at −30 °C. After washing, the product was then collected and dried under vacuum (yield 3.00 g, 92%; mp 89–93 °C dec).

IR ν_{CO}: (Nujol) 1870 (s, br) cm^{-1}; (neat, DRIFTS) 1893 (s), 1885 (sh, s), 1500–1386 (m-s, br) (most prominent bands at 1480 and 1438 (s)), 1204 (s, br) cm^{-1}. ^{1}H NMR: (THF-d_8, −30 °C, 18-crown-6 added) δ 7.56 (m), 7.37 (s), 4.37 (s), 3.58 (s, 18-crown-6). ^{13}C NMR: (THF-d_8, −30 °C, 18-crown-6 added) δ 221.31 (d, J_{PC} = 27.9 Hz), 221.06 (d, J_{PC} = 27.9 Hz), 139.43 (d, J_{PC} = 42.7 Hz), 133.96 (d, J_{PC} = 10.3 Hz), 130.19 (s), 128.72 (d, J_{PC} = 9.6 Hz), 81.01 (s).

B. (η^5-C_5H_5)Fe(CO)(PPh_3)COO^-Li^+ (3b). In the glovebox, LiB(*sec*-butyl)$_3$H in THF (24.00 mL, 4.56 g, 24.00 mmol) was evaporated to dryness. The resulting white solid was dissolved in 150 mL of pentane, and the solution was then cooled to −30 °C. **2b** (3.33 g, 6.95 mmol) was added in small portions into the solution and clumped in this process. The mass dispersed to a fine powder with a gelatinous precipitate sticking on the walls of the flask after stirring at −30 °C for 2 h. After an additional 2 h, an IR spectrum of a sample of the fine powder in Nujol showed no absorption at 3200–3500 cm^{-1}. This pale orange product was collected and then washed by stirring it in pentane (2 × 150 mL) at −30 °C; it was then dried under vacuum (mp 65–70 °C dec; yield 3.08 g, 96%).

IR ν_{CO}: (Nujol) 1900 (s, br) cm^{-1}; (neat, DRIFTS) 1918 (s), 1901 (m, sh), 1480 (s), 1452 (vs), 1270–1185 (m, br) (centered at 1219) cm^{-1}. ^{1}H NMR: (THF-d_8, 40 °C) δ 7.66 (br), 7.26 (br), 4.45 (s). ^{13}C NMR: (THF-d_8, 40 °C) δ 222.17 (d, J_{PC} = 34.3 Hz), 218.07 (d, J_{PC} = 23.6 Hz), 139.88 (d, J_{PC} = 39.7 Hz), 134.64 (d, J_{PC} = 9.9 Hz), 129.54 (s), 128.33 (d, J_{PC} = 9.3 Hz), 85.52 (s).

C. (η^5-C_5Me_5)Fe(CO)(PPh_3)COO^-K^+ (6). In the glovebox, KB(*sec*-butyl)$_3$H in ether (6.68 mL, 1.49 g, 6.68 mmol) was evaporated to dryness and 200 mL of pentane was then added followed by chilling the mixture to −10 °C. Solid **5** (1.00 g, 1.67 mmol) was added, and the slurry was stirred at this temperature for 6 h. After this time, an IR spectrum of a sample of this solid in Nujol showed no ν_{OH} absorption at 3600–2500 cm^{-1}. The orange product was collected by filtration, leaving a gelatinous precipitate sticking on the walls of the flask. This orange product was then washed by stirring it in 2 × 200 of mL pentane at −20 °C. After washing, the product was collected and then rinsed with 100 mL of cold pentane; after drying in vacuo (yield 1.01 g, 89%), the product had a melting poing of 85–91 °C dec.

IR ν_{CO}: (Nujol) 1808 (s) cm^{-1}; (KBr) 1835 (s, br), 1410–1370 (m, br; centered at 1390), 1208 (m) cm^{-1}; (Flurolube) 1822 (s), 1457–1371 (m, most prominent bands at 1434 and 1371) cm^{-1}. ^{1}H NMR: (THF-d_8, −20 °C, 18-crown-6 added) δ 7.63 (br), 7.32 (br), 1.57 (s). ^{13}C NMR: (THF-d_8, −20 °C) δ 226.44 (d, J_{PC} = 36.9 Hz), 214.97 (d, J_{PC} = 26.0 Hz), 93.33 (s), 10.53 (s), the phenyl region (δ 127–137) was very complicated; (THF-d_8, −20 °C, 18-crown-6 added) δ 223.28 (d, J_{PC} = 26.4 Hz), 223.04 (d, J_{PC} = 27.2 Hz), 138.80 (d, J_{PC} = 39.1 Hz), 134.24 (d, J_{PC} = 10.5 Hz), 129.83 (s), 128.47 (d, J_{PC} = 9.0 Hz), 91.18 (s), 10.91 (s).

Reactions of 2a. (a) With 1 Equiv of HCl. Compound **2a** (0.300 g, 0.566 mmol) was added to 20 mL of 1:1 acetone/H_2O containing 50 μL of 12 M HCl (0.58 mmol) cooled to 0 °C. The solution was stirred at 0 °C for 2 h. After this time, a yellow solid began to precipitate. The mixture was then chilled at −5 °C overnight to effect complete precipitation. The yellow product was then collected and dried, in vacuo. The spectral properties of the product were identical with those of an authentic sample of (η^5-C_5H_5)Fe(CO)(PPh_3)COOH;[6b] the yield was 0.190 g, 74%. IR ν_{CO}: (Nujol) 1930 (s), 1575 (m), 1565 (s) cm^{-1} (lit.[4a] 1930, 1565 cm^{-1}); (neat, DRIFTS) 1928 (s), 1575 (w), 1561 (vs), 1484 (mw), 1438 (m), 1122 (vs) cm^{-1}. ^{1}H NMR: (THF-d_8, −35 °C) δ 7.40 (m), 4.48 (s), 9.01 (s, br, COOH); (THF-d_8, −60 °C) δ 7.42 (m), 4.50 (s), 9.36 (s, br, COOH). ^{13}C NMR: (THF-d_8, −35 °C) δ 220.90 (d, J_{PC} = 30.6 Hz), 214.10 (d, J_{PC} = 34.6 Hz), 137.76 (d, J_{PC} = 43.4 Hz), 134.36 (d, J_{PC} = 8.6 Hz), 130.46 (s), 128.71 (d, J_{PC} = 9.3 Hz), 85.44 (s).

(b) With 1 Equiv of $HBF_4 \cdot Me_2O$ in Aqueous Acetone. $HBF_4 \cdot Me_2O$ (49 μL, 0.076 g, 0.566 mmol) was dissolved in 20 mL of 1:1 acetone/H_2O, and the solution was cooled to 0 °C. Compound **2a** (0.300 g, 0.566 mmol) was then added to the solution, which was stirred for 2 h at 0 °C. The mixture was then chilled at −5 °C overnight to effect precipitation. The yellow product was then collected and dried, in vacuo. The mixture consisted of (η^5-C_5H_5)Fe$(CO)_2$(PPh_3)$^+BF_4^-$ (**1b**) [IR ν_{CO} (Nujol) 2055 (s) and 2010 (s) cm^{-1}; lit.[15] ν_{CO} (KBr) 2069 (vs) and 2033 (vs) cm^{-1}] and (η^5-C_5H_5)Fe(CO)(PPh_3)COOH in a ratio of approximately 1:2, as evidenced by the IR spectrum of the mixture. CH_2Cl_2 was added to the solid to dissolve acid and **1b** and the mixture filtered. The filtrate was left standing at room temperature for 2 h to decompose the acid. After this time, the mixture was filtered and the filtrate was concentrated; the addition of ether precipitated cation **1b** (yield 0.056 g, 19%). Cation **1b** is not a decomposition product of the acid. The yield of acid, as calculated from an IR spectrum of the mixture, was 34% (0.089 g).

(c) With 1 Equiv of $HBF_4 \cdot Me_2O$ in Ether. In the glovebox, **2a** (0.300 g, 0.566 mmol) was slurried in 30 mL of ether that was chilled to 0 °C. $HBF_4 \cdot Me_2O$ (49 μL, 0.076 g, 0.566 mmol) was then added, and the mixture was stirred for 2 h at 0 °C. The crude product was collected; an IR spectrum of the yellow solid showed bands for **1b** and (η^5-C_5H_5)Fe(CO)(PPh_3)COOH with the cation predominant. CH_2Cl_2 was added to dissolve the acid and **1b** and the mixture filtered. The filtrate was left standing at room temperature for 2 h to decompose the acid. After this time, the mixture was filtered and the filtrate was concentrated; the addition of ether precipitated cation **1b** (yield 0.126 g, 42%). The yield of the acid, as calculated by an IR spectrum of the mixture, was 37% (0.095 g).

(d) With 1 Equiv of $HBF_4 \cdot Me_2O$ in CH_3CN. In the glovebox, **2a** (0.400 g, 0.730 mmol) was slurried in 25 mL of CH_3CN that was cooled to −30 °C. $HBF_4 \cdot Me_2O$ (63 μL, 0.098 g, 0.732 mmol) was added, and the mixture was stirred for 30 min at −30 °C, then warmed to −10 °C, and stirred for an additional 5 min. After this time, an IR spectrum of the solution showed bands for cation **1b** only. The reaction mixture was then filtered, and the filtrate was evaporated to dryness. The residue was redissolved in CH_2Cl_2 and then concentrated; the addition of ether precipitated 0.346 g (90%) of cation **1b**.

(e) With Mn$(CO)_5$(PPh_3)$^+BF_4^-$ Followed by CH_3I. Mn$(CO)_5$(PPh_3)$^+BF_4^-$ (0.500 g, 0.920 mmol) was dissolved in 20 mL of CH_3CN and the solution chilled to −40 °C. This solution was poured onto **2a** (0.460 g, 0.868 mmol), and the mixture was maintained at −40 °C, with stirring, for 30 min. After this time, the mixture became dark yellow; an IR spectrum indicated that reaction was complete. Cold CH_3I (5 mL, excess) in 10 mL of CH_3CN was then added, and the mixture became light yellow. Stirring was continued for 2 h, and then the reaction mixture was allowed to warm to room temperature; solvent was evaporated to give a yellow solid. The crude product was triturated with 3 × 30 mL of anhydrous ether; concentrating this solution followed by adding hexane and chilling to 0 °C gave 0.330 g (86%) of a yellow solid, which was identified as Mn$(CO)_4$(PPh_3)CH_3: IR ν_{CO} (hexane) 2060 (m), 1981 (s, br), 1967 (vs), 1935 (s) cm^{-1}; ^{1}H NMR (CS_2) δ 7.5 (s, 15 H), −0.61 (d, J_{PH} = 7.4 Hz, 3 H) [lit.:[16] IR ν_{CO} (hexane) 2055 (w), 1983 (m), 1969 (s), 1939 (m) cm^{-1}; ^{1}H NMR (CS_2) δ 7.33, −0.59 (d, J = 7.6 Hz)]. The ether-insoluble residue was triturated with 3 × 30 mL of CH_2Cl_2; the extracts were concentrated and hexane added to precipitate the product whose

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[15] Davison, A.; Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3172.

[16] Kraihanzel, C. S.; Maples, P. K. *Inorg. Chem.* **1968**, *7*, 1806.

spectral properties were identical with those of authentic **1b** (yield 0.414 g, 91%).

(f) With CH_3I. CH_3I (7 mL, excess) was dissolved in 20 mL of CH_3CN and the solution chilled to −40 °C. This solution was then poured onto **2a** (0.300 g, 0.566 mmol), with stirring. Stirring was continued at −40 °C for 30 min. The mixture was then warmed to 10 °C and stirred for an additional 2 h. The resulting cloudy yellow mixture was evaporated to dryness, and the yellow solid was triturated with 3 × 30 mL of 3:1 hexane/CH_2Cl_2. The extracts were dried, concentrated, and cooled to −20 °C to precipitate 0.244 g (92%) of ester **7a**.[4a] IR ν_{CO}: (Nujol) 1930 (s), 1590 (m) cm^{-1}; (neat, DRIFTS) 1937 (s), 1594 (s), 1484 (m), 1436 (ms), 1094 (s) cm^{-1}; (THF) 1940 (s), 1610 (mw) cm^{-1} [lit.[4a] IR ν_{CO}: (C_6H_6, CS_2, or $CDCl_3$) 1935, 1605 cm^{-1}]. ^1H NMR: (THF-d_8, −30 °C) δ 7.51 (m), 7.40 (m), 4.48 (d, J_{PH} = 1.26 Hz), 2.87 (s). ^{13}C NMR: (THF-d_8, −30 °C) δ 220.81 (d, J_{PC} = 29.8 Hz), 212.18 (d, J_{PC} = 36.0 Hz), 137.38 (d, J_{PC} = 43.9 Hz), 134.30 (d, J_{PC} = 9.9 Hz), 130.59 (d, J_{PC} = 1.7 Hz), 128.76 (d, J_{PC} = 9.4 Hz), 85.53 (s), 50.29 (s).

(g) With $(CH_3)_3O^+BF_4^-$. In the glovebox, **2a** (0.340 g, 0.641 mmol) was slurried in 30 mL of CH_3CN that was chilled to −30 °C. $(CH_3)_3O^+BF_4^-$ (0.095 g, 0.642 mmol) was added and stirring was continued for 30 min. After this time, an IR spectrum of the solution indicated that reaction was complete. The mixture was filtered, and the filtrate was evaporated to dryness. Trituration of the yellow solid with 2 × 30 mL of 1:2 CH_2Cl_2/hexane followed by concentration and chilling at −20 °C, gave **7a** (yield 0.244 g, 81%). The residue was dissolved in 30 mL of CH_2Cl_2; after filtration and concentration, this solution was poured into 20 mL of cold hexane to give 0.023 g (7%) of cation **1b**.

(h) With H_2O. Compound **2a** (0.50 g, 0.91 mmol) was added to 40 mL of water at room temperature; the orange solid turned greenish yellow upon addition. The solid was collected by filtration, washed with water, and dried under vacuum to give 0.21 of product (still greenish yellow). The IR spectrum (Nujol) of this product showed ν_{CO} at 1940 (s) and 1610 (m) cm^{-1}. A small sample of this product was dissolved in CH_3OH and allowed to stand for 3 h then the solution was evaporated to dryness. Recrystallization of the residue from CH_2Cl_2/hexane afforded **7a** as the only product. Reaction of a small sample of the unknown product described above with excess aqueous HCl at 0 °C afforded $(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)^+Cl^-$[15] as the only product. Treatment of a sample of the unknown compound with excess KOH in aqueous acetone dissolved most of the solid, but also gave some decomposition to an intractable black solid. Evaporation of the solution to dryness afforded **2a** as the only product.

(i) With Ph_3SnCl. **2a** (1.000 g, 1.886 mmol) was slurried in 75 mL of THF chilled to −78 °C. Ph_3SnCl (0.780 g, 2.020 mmol) was then added, and the mixture was warmed to −10 °C, stirred for 30 min (until it turned yellow), then chilled to −30 °C, and filtered. The filtrate was warmed to −5 °C, and the solvent was evaporated, in vacuo, to give a yellow solid. The crude product was recrystallized from CH_2Cl_2/pentane (1:1, v/v) and afforded a yellow solid, identified as $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOSnPh_3$, mp 110–112 °C dec; yield 1.510 g (99%).

Anal. Calcd for $C_{43}H_{35}FeO_3PSn$: C, 64.14; H, 4.38; P, 3.85; Sn, 14.74. Found: C, 63.80; H, 4.51; P, 3.29; Sn, 14.10. IR ν_{CO}: (CH_2Cl_2) 1941 (s, br) cm^{-1}; (Nujol) 1941 (s) cm^{-1}; (neat, DRIFTS) 1952 (s), 1480 (w), 1432 (s), 1495–1137 (m, br) (centered at 1174) cm^{-1}. ^1H NMR: (THF-d_8, −30 °C) δ 7.52 (m, br), 7.30 (m, br), 4.56 (s). ^{13}C NMR: (THF-d_8, 20 °C) δ 228.16 (d, J_{PC} = 31.5 Hz), 220.11 (d, J_{PC} = 29.4 Hz), 143.86 (s), 137.74 (t, J = 47.6 Hz), 137.11 (d, J_{PC} = 44.1 Hz), 134.20 (d, J_{PC} = 9.9 Hz), 130.53 (s), 129.28 (s), 128.71 (d, J_{PC} = 9.8 Hz), 128.71 (t, J = 59.3 Hz), 85.70 (s).

A sample of **8a** was sealed in a glass tube, in vacuo, and heated at 50 °C for 10 days. After this time, the solid had turned completely brownish gray while orange crystals were deposited (sublimed) at the top of the tube. The powder showed no carbonyl absorption in the IR spectrum and was not identified. The orange crystals had a mp and spectral properties that were identical with those of an authentic sample of ferrocene.

(j) Thermolyses of 2a. (1) In Solution. Compound **2a** (0.053 g, 0.100 mmol) was added to 0.75 mL of THF-d_8 at room temperature; the orange solid turned green upon contact. The mixture was then filtered into an NMR tube containing ferrocene as an internal standard. The ^1H NMR spectrum indicated that the decomposition was complete within a few minutes (the cyclopentadienyl peak of **2a** was absent), but it showed broad resonances due to precipitated solids. After standing for 3 h at 18 °C, the sample tube was inverted and centrifuged; the new ^1H NMR spectrum showed sharp resonances at δ 4.87 [$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$], δ 4.50 and 4.25 [$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$],[11] and δ 4.12 (ferrocene) in a ratio of 1:4:9.86, respectively. The yields of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$ were calculated as 6% and 22%, respectively.

(2) In the Solid State. Compound **2a** (0.040 g, 0.075 mmol) was sealed in a glass tube, in vacuo, and heated at 50 °C for 4 days. After this time, the sample was very dark green; it was then dissolved in 0.75 mL of THF-d_8, and the solution was filtered into an NMR tube containing ferrocene as an internal standard. The ^1H NMR spectrum showed resonances at δ 4.87 [$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$], δ 4.50 and 4.25 [$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$], and δ 4.12 (ferrocene) in a ratio of 1:4.78:17.94, respectively. The yields of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$ were calculated as 5% and 23%, respectively.

Reactions of 2b. (a) With 1 Equiv of HCl. In the manner described above for **2a**, 0.300 g (0.625 mmol) of **2b** was treated with 55 μL of 12 M HCl (0.66 mmol) in 20 mL of 1:1 acetone/H_2O at 0 °C for 3 h. Workup in the manner previously described afforded 0.230 g (81%) of a product whose properties were identical with those of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$ described above.

(b) With 1 Equiv of $HBF_4{\cdot}Me_2O$ in Aqueous Acetone. In the manner described above for **2a**, $HBF_4{\cdot}Me_2O$ (54 μL, 0.084 g, 0.627 mmol), dissolved in 30 mL of 1:1 acetone/H_2O, was treated with **2b** (0.301 g, 0.627 mmol) at 0 °C and stirred for 2 h. The yellow product was then collected and dried, in vacuo. The mixture consisted of **1b** and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$ in a ratio of approximately 2:1, as evidenced by the IR spectrum. Workup in the manner previously described afforded 0.134 g (41%) of **1b**. The yield of acid, as calculated from an IR spectrum of the mixture, was 22% (0.064 g).

(c) With 1 Equiv of $HBF_4{\cdot}Me_2O$ in Ether. In the glovebox, compound **2b** (0.359 g, 0.748 mmol) was slurried in 40 mL of ether that was chilled to 0 °C. $HBF_4{\cdot}Me_2O$ (65 μL, 0.101 g, 0.754 mmol) was then added, and the mixture was stirred for 2 h. After this time, the mixture had become pale yellow. An IR sample of the yellow solid showed bands at 2050 (s) and 1993 (s) cm^{-1}. The crude pale yellow product was collected and then triturated with 2 × 30 mL of CH_2Cl_2; the combined extracts were filtered, concentrated, and then 30 mL of ether was added; a pale yellow precipitate of cation **1b** was obtained; yield 0.279 g (71%).

(d) With 1 Equiv of $HBF_4{\cdot}Me_2O$ in CH_3CN. In the glovebox, in the manner described above for **2a**, $HBF_4{\cdot}Me_2O$ (50 μL, 0.078 g, 0.580 mmol) was added to a slurry of **2b** (0.268 g, 0.558 mmol) in 25 mL of CH_3CN that was cooled to −30 °C. The mixture was stirred for 5 min, then warmed to −10 °C, and stirred for an additional 40 min. An IR spectrum of the solution showed bands for cation **1b** only. Workup in the manner previously described afforded 0.235 g (83%) of cation **1b**.

(e) With CH_3I. CH_3I (5 mL, excess) was added to 20 mL of CH_3CN and the solution chilled to −40 °C. Compound **2b** (0.302 g, 0.629 mmol) was added, and the mixture was then warmed to 0 °C and allowed to stir for 3 h. After this time, the mixture became homogeneous and light orange; an IR spectrum showed the presence of **1a** and a small amount of **7a**. The reaction mixture was warmed to room temperature and the solvent removed on a rotary evaporator. Trituration of the residue with 2:1 hexane/CH_2Cl_2 mixture gave only a small amount of **7a**. Trituration of the residue with 3 × 30 mL of CH_2Cl_2 followed by concentrating this solution and then adding hexane gave 0.284 g of a yellow precipitate; the ^1H NMR spectrum showed a mixture of **1a** and **7a** in an 8:1 ratio. The yields of the two compounds were calculated as 69% and 11%, respectively.

(f) With $(CH_3)_3O^+BF_4^-$. In the glovebox, **2b** (0.050 g, 0.104 mmol) was slurried in 4 mL of CD_3CN that was chilled to −20 °C. $(CH_3)_3O^+BF_4^-$ (0.016 g, 0.108 mmol) was dissolved in 1 mL of CD_3CN, and the solution was added to the slurry followed by stirring for 30 min. After this time, an IR spectrum showed bands for ester **7a** as the major product and cation **1b**. The mixture was filtered and 0.005 g (0.027 mmol) of ferrocene was added as an internal standard. The ^1H NMR of it at −16 °C showed cation **1b** and ester **7a** in a ratio of 1:2.21. The yields of cation **1b** and ester **7a** were calculated as 23% and 50%, respectively.

(g) With $Mn(CO)_5(PPh_3)^+BF_4^-$ Followed by CH_3I. In the manner described above for **2a**, 0.500 g (0.920 mmol) of $Mn(CO)_5(PPh_3)^+BF_4^-$ was treated with 0.425 g (0.885 mmol) of **2b** and then treated with excess of CH_3I (5 mL). Workup, in the manner described for **2a**, afforded 0.395 g (100%) of $Mn(CO)_4(PPh_3)CH_3$ and 0.452 g (97%) of **1b**.

(h) Thermolysis of 2b. Compound **2b** (0.034 g, 0.071 mmol) was added to 0.5 mL of THF-d_8 at room temperature in an NMR tube that contained ferrocene as an internal standard. The sample tube was inverted and centrifuged to precipitate solids in the cap of the tube. As **2b** dissolved, it gave a dark green mixture in 2 min. The ^1H NMR spectrum showed resonances at δ 4.87 $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$, δ 4.50 and 4.25 $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3]$, and δ 4.12 (ferrocene) in a ratio of 1:2.16:3.12, respectively. The yields of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$ were calculated as 23% and 49%, respectively.

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$ with $LiBF_4$. The acid (0.274 g, 0.601 mmol) was slurried in 10 mL of ether that was chilled to 0 °C. $LiBF_4$ (0.056 g, 0.597 mmol) was then added, and stirring was continued for 2 h at 0 °C. After this time, an IR spectrum of the solid showed a mixture of cation **1b** and the metallo carboxylic acid (1:3, respectively).

Reactions of 2c. In the following experiments, the yields were calculated on the assumption that the compound has two molecules of coordinated water.

(a) With 1 Equiv of HCl. In the manner described above for **2a**, 0.300 g (0.584 mmol) of **2c** was treated with 54 μL of 12 M HCl (0.65 mmol) in 20 mL of 1:1 acetone/H_2O at 0 °C for 5 h. Workup in the manner previously described afforded 0.190 g (71%) of a product whose properties were identical with those of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$ described above.

(b) With 1 Equiv of $HBF_4 \cdot Me_2O$ in Aqueous Acetone. In the manner described above for **2a**, $HBF_4 \cdot Me_2O$ (50 μL, 0.078 g, 0.583 mmol), dissolved in 20 mL of 1:1 acetone/H_2O, was treated with **2c** (0.300 g, 0.583 mmol) at 0 °C, and the mixture was stirred for 2 h. The yellow product was then collected and dried, in vacuo. The mixture consisted of approximately equal amounts of **1b** and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$, as evidenced by an IR spectrum of the product. Workup in the manner previously described afforded 0.112 g (37%) of **1b**. The yield of acid, as calculated from an IR spectrum of the mixture, was 31% (0.082 g).

(c) With 1 Equiv of $HBF_4 \cdot Me_2O$ in Ether. In the glovebox, in the manner described above for **2a**, $HBF_4 \cdot Me_2O$ (50 μL, 0.078 g, 0.584 mmol) was added to a slurry of **2c** (0.300 g, 0.584 mmol) in 30 mL of ether that was chilled to 0 °C, and the mixture was stirred for 2 h. An IR spectrum of the yellow solid showed bands for **1b** and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$ with the cation predominant. Workup in the manner previously described afforded 0.164 g (53%) of cation **1b**. The yield of acid, as calculated from the IR spectrum of the mixture, was 36% (0.097 g).

(d) With 1 Equiv of $HBF_4 \cdot Me_2O$ in CH_3CN. In the glovebox, in the manner described above for **2a**, $HBF_4 \cdot Me_2O$ (71 μL, 0.110 g, 0.823 mmol) was added to a slurry of **2c** (0.400 g, 0.778 mmol) in 25 mL of CH_3CN that was cooled to −30 °C. The mixture was stirred for 30 min, then warmed to −10 °C, and stirred for an additional 30 min. After this time, an IR spectrum of the solution showed bands for cation **1b** only. Workup in the manner previously described afforded 0.344 g (87%) of cation **1b**.

(e) With CH_3I. CH_3I (5 mL, excess) in 20 mL of CH_3CN was chilled to −40 °C and then poured onto **2c** (0.311 g, 0.605 mmol). Stirring was continued for 1 h; the mixture was then warmed to room temperature and stirred for an additional 1 h. The solvent was then evaporated, and the residue was triturated with 2 × 30 mL of 2:1 hexane/CH_2Cl_2. This solution was then concentrated and chilled at −20 °C to give a yellow precipitate, identified as ester **7a** (yield 0.043 g, 15%). The residue from above was then triturated with 2 × 30 mL of CH_2Cl_2. Concentrating this solution followed by pouring it into 30 mL of cold hexane gave 0.260 g (71%) of **1a**.

(f) With $Mn(CO)_5(PPh_3)^+BF_4^-$ Followed by CH_3I. In the manner described above for **2a**, 0.306 g (0.562 mmol) of $Mn(CO)_5(PPh_3)^+BF_4^-$ was treated with 0.270 g (0.525 mmol) of **2c** and then treated with excess of CH_3I (5 mL). Workup in the manner previously described afforded 0.239 g (96%) of $Mn(CO)_4(PPh_3)CH_3$ and 0.280 g (95%) of **1b**.

(g) With $(CH_3)_3O^+BF_4^-$. In the glovebox, $(CH_3)_3O^+BF_4^-$ (0.093 g, 0.630 mmol) in 20 mL of CH_3CN was chilled to −40 °C and then poured onto **2c** (0.301 g, 0.585 mmol), which was also chilled to −40 °C. The mixture was then warmed to −20 °C and stirred for 1 h; it became bright yellow during this time. An IR spectrum of the solution showed bands for **7a** and **1b** in a ratio of 1:1. The mixture was warmed to room temperature, and the solvent evaporated. The residue was triturated with 3 × 30 mL of 1:2 CH_2Cl_2/hexane; the extracts were concentrated and then chilled at −20 °C to give a yellow solid identified as ester **7a** (yield 0.118 g, 43%). The insoluble residue was triturated with 30 mL of CH_2Cl_2. Concentrating this solution followed by pouring it into 20 mL of cold hexane resulted in a yellow precipitate of **1b** (yield 0.151 g, 49%).

(h) Thermolysis of 2c. In the glovebox, compound **2c** (0.031 g, 0.061 mmol) was dissolved in 0.5 mL of THF-d_8 at room temperature in an NMR tube that contained ferrocene as an internal standard. As **2c** dissolved, it gave a dark green mixture in 2 min. The sample tube was inverted and centrifuged to precipitate solids in the cap of the tube. The ^1H NMR spectrum showed resonances at δ 4.87 $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$, δ 4.50 and 4.25 $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3]$, and δ 4.12 (ferrocene) in the ratio of 1:2.05:5.63, respectively. The yields of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$ were calculated as 22% and 49%, respectively.

Reactions of 5. In the following experiments, the yields were calculated on the assumption that the compound has two molecules of coordinated water.

(a) With 1 Equiv of HCl. Compound **5** (0.100 g, 0.167 mmol) was added to 6 mL of 1:1 acetone/H_2O containing 16 μL of 12 M HCl (0.19 mmol) at 0 °C and stirred at this temperature for 1 h. An IR spectrum of this cloudy yellow solution showed bands for the cation, $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(PPh_3)^+$, only. The solvent was then evaporated, and the yellow residue was dried under vacuum. CH_2Cl_2 (5 mL) was added to this residue and the mixture was filtered. The amount of insoluble material separated was 0.018 g. The filtrate was evaporated to dryness to give 0.085 g (86% yield) of product whose spectral properties were closely similar to those of cation **4** (see above); it is identified as $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(PPh_3)^+Cl^-$ (IR ν_{CO}: (CH_2Cl_2) 2036 (s) 1987 (s) cm^{-1}).

(b) With 1 Equiv of $HBF_4 \cdot Me_2O$ in Aqueous Acetone. $HBF_4 \cdot Me_2O$ (33 μL, 0.052 g, 0.388 mmol) was dissolved in 8 mL of 1:1 acetone/H_2O, and the solution was cooled to 0 °C. Compound **5** (0.220 g, 0.388 mmol) was added in portions during 10 min, and the solution was stirred for an additional 20 min. After this time, the IR indicated that reaction was complete and a yellow precipitate had formed. The reaction mixture was then evaporated to dryness (crude yield 0.228 g). An IR analyses of this residue in Nujol showed the presence of cation **4** and a second, predominant compound identified from spectral data as $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)COOH$. IR ν_{CO}: (Nujol) 1913 (s), 1563 (w) cm^{-1}. ^1H NMR: (THF-d_8, −35 °C) δ 7.34 (m, br), 1.28 (s); the hydroxyl proton was not observed. ^{13}C NMR: (THF-d_8, −35 °C): δ 223.21 (d, J_{PC} = 27.1 Hz), 221.03 (d, J_{PC} = 33.0 Hz), 134.52 (d, J_{PC} = 19.5 Hz), 129.59 (s), 129.35 (d, J_{PC} = 7.0 Hz), 93.61 (s), 9.91 (s); the quaternary carbon of the phenyl group was not observed. The crude product was then dissolved in 15 mL of CH_2Cl_2; $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)COOH$ immediately decomposed to form dimer $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$, as indicated by the IR spectrum. After filtration, the filtrate was concentrated followed by the addition of ether to precipitate the cation **4** (yield 0.045 g, 21%). The insoluble residue amounted to 0.044 g. The yield of the acid, $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)COOH$, was determined, by difference, as 0.139 g (72%).

(c) With 1 Equiv of $HBF_4 \cdot Me_2O$ in CD_3CN. In the glovebox, compound **5** (0.034 g, 0.057 mmol) was slurried in 1 mL of CD_3CN at −30 °C. $HBF_4 \cdot Me_2O$ (5 μL, 7.63 mg, 0.057 mmol) in 0.3 mL of CD_3CN was added dropwise during about 5 min, and the resulting solution became yellow quickly. An IR spectrum of the solution showed that only cation was present. The reaction mixture was then filtered and 0.010 g of ferrocene was added as an internal standard for the ^1H NMR spectrum. The spectrum showed that cation **4** was the only product; the yield of **4** was 0.031 g (92%).

(d) With $Mn(CO)_5(PPh_3)^+BF_4^-$ Followed by CH_3I. $Mn(CO)_5(PPh_3)^+BF_4^-$ (1.45 g, 2.26 mmol) in 30 mL of CH_3CN was chilled to −30 °C in the glovebox. Compound **5** (1.36 g, 2.26 mmol) was then added, in portions, during 20 min. The mixture was allowed to stir for an additional 5 min at −30 °C. After this time, the mixture became yellow-orange. CH_3I (3 mL, excess) was then added; after 5 min, the reaction mixture was allowed to warm to room temperature and then the solvent was evaporated. The residue was triturated with 100 mL of hexane; concentrating these extracts followed by chilling to −20 °C gave 0.73 g of a yellow solid. The filtrate was evaporated and then triturated with ether; concentration of these extracts then chilling to −20 °C gave an additional 0.24 g of $Mn(CO)_4(PPh_3)CH_3$ for a total of 0.97 g (80% yield). The insoluble residue was triturated with 60 mL of CH_2Cl_2; the extracts were concentrated and ether added to precipitate the product, which was identical with authentic **4** (yield 1.12 g, 83%).

(e) With CH_3I. Compound **5** (0.40 g, 0.67 mmol) was slurried in 30 mL of CH_3CN, and the slurry was chilled to −40 °C. CH_3I (1.5 mL, excess) was added, and the mixture was warmed to −10 °C and stirred for 20 min. The mixture was then filtered and the filtrate evaporated to dryness at −5 °C in vacuo to give a yellow powder, which was identified as ester **7b** (yield 0.28 g, 77%). Compound **7b** is labile in solution and could not be obtained in analytically pure form; it has the following spectral properties. IR ν_{CO}: (THF) 1918 (s), 1606 (m) cm^{-1}; (C_2Cl_4) 1923 (vs), 1606 (m), 1435 (mw), 1380 (w), 1019 (m) cm^{-1}. ^1H NMR: (THF-d_8, 36 °C) δ 7.30 (m, br), 7.59 (m, br), 3.01 (s), 1.51 (s). ^{13}C NMR: (THF-d_8, 36 °C) δ 222.94 (d, J_{PC} = 27.6 Hz), 217.22 (d, J_{PC} = 34.2 Hz), 134.87 (d, J_{PC} = 8.5 Hz), 134.53 (d, J_{PC} = 20.1 Hz), 130.09 (s), 128.35 (d, J_{PC} = 9.1 Hz), 93.94 (s), 50.73 (s), 9.91 (s). ^{31}P NMR: (CD_3CN) δ 76.99 (vs external H_3PO_4).

(f) With 1 Equiv of $(CH_3)_3O^+BF_4^-$ in CD_3CN. In the glovebox, compound **5** (0.047 g, 0.078 mmol) was slurried in 3.5 mL of CD_3CN at −30 °C. $(CH_3)_3O^+BF_4^-$ (0.012 g, 0.081 mmol) in 0.5 mL of CD_3CN was added dropwise, and the resulting solution changed from orange to yellow. The cold solution was quickly filtered, and 0.4 mL of the solution was placed in an NMR tube together with 0.004 g of triphenylphosphine as an internal standard. The ^1H NMR spectrum (at −16 °C) showed only the resonances of cation **4** and ester **7b**, but the pentamethylcyclopentadienyl groups in the resonances of the two compounds overlapped badly. The ^{31}P NMR spectrum was then recorded and the product yields calculated accordingly: cation **4** (δ 64.50), yield = 43%; ester **7b** (δ 76.99), yield = 38%. Triphenylphosphine oxide was also present as a product (δ 27.64, yield = 16%); this product was evident in spectra of aliquots of the product mixture before triphenylphosphine was added.

(g) With Ph_3SnCl. Ph_3SnCl (0.36 g, 0.90 mmol) in 30 mL of THF was chilled to −70 °C. Compound **5** (0.54 g, 0.90 mmol) was added to the solution. The mixture was then warmed to −20 °C and stirred for 3 h; after this time, it became a yellow solution containing a small amount of a white precipitate. The mixture was then filtered at −40 °C and the filtrate evaporated to dryness at −5 °C, in vacuo, to give a yellow solid. This residue was washed with pentane and dried. Recrystallization from CH_2Cl_2/pentane gave **8b** as a yellow solid (yield 0.65 g, 83%); mp 144–145 °C.

Anal. Calcd for $C_{48}H_{45}FeO_3PSn$: C, 65.86; H, 5.18; P, 3.54. Found: C, 65.75; H, 5.17; P, 3.99. IR ν_{CO}: (THF) 1923 (s), 1630 (w) cm^{-1}; (neat, DRIFTS) 1924 (m), 1917 (s), 1480 (m), 1432 (s), 1186–1120 (m, br) (centered at 1139) cm^{-1}. ^1H NMR: (THF-d_8) δ 7.55 (m), 7.28 (m), 1.41 (s). ^{13}C NMR: (C_6D_6, 65 °C) δ 232.22 (d, J_{PC} = 28.8 Hz), 220.08 (d, J_{PC} = 27.4 Hz), 128.9 (d, J_{PC} = 9.8 Hz), 129.6 (s), 134.3 (d, J_{PC} = 9.1 Hz), 136.7 (d, J_{PC} = 34.0 Hz), 128.9 (t, J = 7.0 Hz), 128.4 (s), 137.8 (t, J = 23.0 Hz), 143.8 (s), 93.8 (s), 9.9 (s). The phenyl region of the ambient-temperature ^{13}C spectrum is complicated by restricted rotation (see Results and Discussion).

A sample of **8b** was sealed in a glass tube, in vacuo, and heated at 50 °C for 12 days. This compound did not decompose after this time, as indicated by the IR spectrum.

Reactions of 3a. (a) With 1 Equiv of $HBF_4 \cdot Me_2O$ in Ether. In the glovebox, in the manner described above for **2a**, $HBF_4 \cdot Me_2O$ (75 μL, 0.116 g, 0.867 mmol) was added to a slurry of **3a** (0.425 g, 0.860 mmol) in 30 mL of ether that was chilled to 0 °C, and the mixture was stirred for 10 h. After this time, an IR spectrum showed that reaction was complete. The crude yellow product was collected and dried in vacuo. The product consisted of approximately equal amounts of **1b** and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$ as evidenced by an IR spectrum of the mixture. Workup in the manner previously described afforded 0.185 g (41%) of cation **1b**. The estimated yield of acid, as calculated from the IR spectrum of the mixture, was 40% (0.158 g).

(b) With 1 Equiv of $HBF_4 \cdot Me_2O$ in CH_3CN. In the glovebox, **3a** (0.495 g, 1.002 mmol) was slurried in 25 mL of CH_3CN that was cooled to −30 °C. $HBF_4 \cdot Me_2O$ (87 μL, 0.135 g, 1.008 mmol) was added, and the mixture was stirred for 30 min at −30 °C, then warmed to −10 °C, and stirred for an additional 5 min. An IR spectrum of the solution indicated bands for cation **1b** as the major product. The reaction mixture was then filtered, and the filtrate was evaporated to dryness. At this time, an IR spectrum of the residue in Nujol showed the presence of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$ as the major product together with cation **1b**, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$, and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. The residue was triturated with ether to give 0.076 of a mixture of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in a ratio of approximately 1:1 (from the IR analysis). The ether-insoluble portion was dissolved in CH_2Cl_2 and left standing at room temperature for 2 h in order to decompose the acid. The mixture was filtered, and the filtrate was concentrated; the addition of ether precipitated cation **1b** (0.090 g, 17% yield). The yield of the acid, as calculated from the IR spectrum of the mixture, was 57% (0.261 g).

(c) With CH_3I. CH_3I (6 mL, excess) in 25 mL of CH_3CN was chilled to −20 °C in the glovebox. Compound **3a** (0.487 g, 0.803 mmol) was added, and the slurry was stirred for 30 min at this temperature. After this time, an IR spectrum indicated that the carboxylate had been consumed; ester **7a** was the only product evident. The mixture was filtered, and the filtrate was evaporated to dryness, in vacuo. The crude product was recrystallized from 3:1 hexane/CH_2Cl_2 to give a yellow powder whose spectral properties were identical with those of authentic **7a** (0.427 g, 92%) (see above).

(d) With $(CH_3)_3O^+BF_4^-$. In the glovebox, **3a** (0.467 g, 0.828 mmol) was slurried in 30 mL of CH_3CN that was chilled to −30 °C. $(CH_3)_3O^+BF_4^-$ (0.123 g, 0.832 mmol) in 5 mL of CH_3CN was added slowly, and stirring was continued for 30 min. After this time, an IR spectrum of the solution indicated that reaction was complete; ester **7a** was the only product evident. The mixture was filtered, and the filtrate was evaporated to dryness. Trituration of the yellow solid with 30 mL of 1:2 CH_2Cl_2/hexane followed by filtration, concentration, and chilling at −20 °C gave **7a** (yield 0.312 g, 80%).

(e) With $Mn(CO)_5(PPh_3)^+BF_4^-$ Followed by CH_3I. In the manner described above for **2a**, 0.300 g (0.551 mmol) of $Mn(CO)_5(PPh_3)^+BF_4^-$ was treated with 0.277 g (0.457 mmol) of **3a**, in the glovebox, and then treated with excess of CH_3I (6 mL) and stirred for 1 h and 15 min. Workup in the manner previously described afforded 0.235 g (94%) of $Mn(CO)_4(PPh_3)CH_3$ and 0.285 g (97%) of **1b**.

(f) With Ph_3SnCl. Compound **3a** (0.553 g, 0.912 mmol) was slurried in 50 mL of THF chilled to −40 °C in the glovebox. Ph_3SnCl (0.455 g, 1.121 mmol) was added, and the mixture was warmed to −10 °C and stirred for 30 min. The resulting yellow mixture was cooled to −30 °C and filtered; the filtrate was warmed to −5 °C, and then the solvent was evaporated to dryness, in vacuo. The crude product was stirred with 100 mL of pentane, and the yellow solid was collected by filtration and then recrystallized from CH_2Cl_2/pentane (1:1, v/v) to give a yellow solid (yield 0.732 g, 97%) whose spectral properties were identical with those described above for **8a**.

(g) Thermolyses of 3a. (1) In Solution. In the glovebox, compound **3a** (0.043 g, 0.087 mmol) was dissolved in 0.5 mL of THF-d_8 in an NMR tube that contained ferrocene as an internal standard. As **3a** dissolved, it gave a dark green mixture during about 30 min. The sample tube was inverted and centrifuged to collect the solids in the tube cap. The ^1H NMR spectrum showed resonances at δ 4.50 and 4.25 [$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$], δ 4.35 (compound **3a**), and δ 4.12 (ferrocene); the ratio of these was 1:1.74:2.73, respectively. The yields of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$ and **3a** were calculated as 24% and 43%, respectively. The sample tube was left standing at room temperature for 36 h. After this time, the ^1H NMR spectrum of the sample showed that $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ was now one of the decomposition products. The percentages of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$, and compound **3a** were 2%, 33%, and 16%, respectively. After the sample tube was left standing at room temperature for a total of 3 days, the decomposition was still incomplete but broadening of the NMR spectral lines prevented a determination of the composition of the sample.

(2) In the Solid State. A sample of **3a** was sealed in a glass tube, in vacuo, and heated at 50 °C for 4 days. After this time, it became light green. An IR spectrum of this product indicated that it was still primarily **3a**.

Reactions of 3b. (a) With 1 Equiv of $HBF_4 \cdot Me_2O$ In Ether. In the glovebox, compound **3b** (0.300 g, 0.649 mmol) was slurried in 30 mL of diethyl ether cooled to 0 °C. $HBF_4 \cdot Me_2O$ (0.087 g, 56 μL, 0.650 mmol) was then added and the slurry was allowed to stir at 0 °C for 12 h. After this time, an IR spectrum of the yellow solid showed no absorption for **3b**. The yellow product was collected by filtration and then extracted with 2 × 20 mL of CH_2Cl_2. The solution was concentrated, and hexane was added to give a yellow precipitate (yield 0.320 g, 94%) whose spectral properties were identical with those of cation **1b**.

(b) With 1 Equiv of $HBF_4 \cdot Me_2O$ in CH_3CN. In the glovebox, **3b** (0.300 g, 0.649 mmol) was slurried in 25 mL of CH_3CN that was cooled to −30 °C. $HBF_4 \cdot Me_2O$ (56 μL, 0.087 g, 0.650 mmol) was added, and the mixture was stirred for 30 min, then warmed to −10 °C, and stirred for an additional 1 h. The reaction remained incomplete; the temperature was raised to 0 °C, and stirring continued for an additional 20 min to complete the reaction. The mixture was filtered, and the filtrate was evaporated to dryness. An IR analysis of the residue in Nujol showed bands for cation **1b** only. The residue was then redissolved in CH_2Cl_2 and then concentrated; the addition of ether precipitated cation **1b** (yield 0.223 g, 65%).

(c) With CH_3I. In the glovebox, compound **3b** (0.300 g, 0.649 mmol) was slurried in 20 mL of CH_3CN chilled to −20 °C. CH_3I (5 mL, excess) was added slowly and the mixture was then warmed to 0 °C and stirred for 4 h. After this time, the mixture became a yellow slurry. An IR spectrum of the solid in Nujol indicated the presence of **1b** only. The yellow product was then collected by filtration. The crude product was then triturated with 2 × 30 mL of CH_2Cl_2; the solution was concentrated and hexane added to give a yellow precipitate (yield 0.254 g, 69%) whose spectral properties were identical with those of authentic **1b**.

(d) With $(CH_3)_3O^+BF_4^-$. In the glovebox, **3b** (0.050 g, 0.180 mmol) was slurried in 4 mL of CD_3CN that was chilled to −20 °C. $(CH_3)_3O^+BF_4^-$ (0.016 g, 0.108 mmol) was dissolved in 1 mL of CD_3CN, the solution was added to the slurry, and the mixture was stirred for 30 min. After this time, an IR spectrum of the solution showed bands for ester **7a** as the major product and a small amount of cation **1b**. The mixture was filtered, and 0.006 g (0.032 mmol) of ferrocene was added as internal standard. The ^1H NMR spectrum of it at −16 °C showed cation **1b** and ester **7a** in a ratio of 1:2.33. The yields of **1b** and **7a** were calculated as 26% and 61%, respectively.

(e) Thermolysis of 3b. In the glovebox, compound **3b** (0.042 g, 0.091 mmol) was dissolved in 0.5 mL of THF-d_8 in an NMR tube that contained ferrocene as an internal standard. As **3b** dissolved, it gave a light green mixture during about 30 min. The sample tube was inverted and centrifuged to precipitate solids in the tube cap. The ^1H NMR spectrum showed resonances at δ 4.87 [$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$], δ 4.50 and 4.25 [$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$], δ 4.35 (compound **3b**), and δ 4.12 (ferrocene); the ratio was 1:8.92:2.38:19.48, respectively. The percentages of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$, and **3b** were calculated as 3%, 26%, and 7%, respectively. The sample tube was left standing at room temperature for 18 h and then centrifuged again and the ^1H NMR spectrum recorded. The yields of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$ were 9% and 13%, respectively.

Reactions of 6. (a) With 1 Equiv of $HBF_4 \cdot Me_2O$ in CD_3CN. In the glovebox, compound **6** (0.031 g, 0.055 mmol) was slurried in 1.2 mL of CD_3CN at −30 °C. $HBF_4 \cdot Me_2O$ (5 μL, 7.84 mg, 0.059 mmol) in 0.3 mL of CD_3CN was added dropwise during about 5 min, and the resulting solution became yellow. An IR spectrum of the solution showed the presence of cation **4** as the major product and a small amount of an unidentified compound (ν_{CO} at 1923 cm^{-1}). The cold solution was quickly filtered, and 0.008 g of ferrocene was added as an internal standard. Both the ^1H NMR and ^{31}P NMR (δ 64.50 vs external H_3PO_4) spectra of the sample taken at −16 °C showed the cation **4** as the only product. The yield of cation **4** was calculated as 91% (0.030 g).

(b) With CH_3I. In the glovebox, compound **6** (0.18 g, 0.32 mmol) was added to 30 mL of CH_3CN cooled to −40 °C. CH_3I (1.5 mL, excess) was added to this slurry, which was then warmed to −10 °C and stirred for 20 min. The mixture was then filtered and the filtrate evaporated to dryness at −5 °C in vacuo to give ester **7b** (yield 0.13 g, 77%) as the only organometallic product.

(c) With 1 Equiv of $(CH_3)_3O^+BF_4^-$ in CD_3CN. In the glovebox, compound **6** (0.045 g, 0.080 mmol) was slurried in 1.5 mL of CD_3CN at −30 °C. $(CH_3)_3O^+BF_4^-$ (0.012 g, 0.081 mmol) in 0.50 mL of CD_3CN was added dropwise, and the color of the solution changed from light orange to yellow. The cold solution was filtered, and 0.032 g of triphenylphosphine was added as an internal standard. A 0.5-mL aliquot of the sample was used, and the ^{31}P NMR spectrum was recorded at −16 °C. The yields of each product were then calculated on the basis of the standard: cation **4**, 45%; ester **7b**, 33%.

(d) With $Mn(CO)_5(PPh_3)^+BF_4^-$ Followed by CH_3I. $Mn(CO)_5(PPh_3)^+BF_4^-$ (1.28 g, 2.00 mmol) in 30 mL of CH_3CN was chilled to −30 °C in the glovebox. Compound **6** (1.12 g, 2.00 mmol) was then added, in portions, during 15 min followed by CH_3I (3 mL, excess) in 10 mL of CH_3CN. Stirring was continued for 15 min, then the mixture was allowed to warm to room temperature, and solvent was evaporated to dryness. The residue was triturated with 100 mL of hexane; the extracts were concentrated to a small volume and then chilled to −20 °C to give 0.65 g of $Mn(CO)_4(PPh_3)CH_3$. The insoluble residue was triturated with 50 mL of CH_2Cl_2; the extract was concentrated, and ether was added to precipitate the product, which was collected and identified as compound **4** (yield 0.45 g, 38%). The filtrate was evaporated to dryness and the residue dissolved in CH_2Cl_2 and then chromatographed on Florisil using hexane/CH_2Cl_2 (75:25 v/v) to obtain 0.26 g of $Mn(CO)_4(PPh_3)CH_3$ (total yield 84%); further elution with hexane/CH_2Cl_2 (60:40 v/v) gave 0.16 g (21%) of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2I$ [IR ν_{CO}: (CH_2Cl_2) 2020 (vs) and 1965 (vs) cm^{-1} (lit.:[17] ν_{CO} (cyclohexane) 2017 (vs) and 1980 (vs) cm^{-1})].

(e) With Ph_3SnCl. In the manner described for **5**, 0.50 g (0.886 mmol) of **6** was treated with 0.54 g (1.401 mmol) of Ph_3SnCl in the glovebox. Workup in the manner previously described afforded 0.56 g (70%) of a product whose properties were identical with those of **8b** described above.

Reaction of 7a with 1 Equiv of LiI. (1) At Room Temperature. Compound **7a** (0.102 g, 0.217 mmol) was dissolved in 30 mL of CH_3CN; LiI (0.029 g, 0.217 mmol) was added, and the slurry was stirred for 15 min. After this time, an IR spectrum of the solution showed bands for **1a** only. Solvent was evaporated, and the yellow residue was triturated with 2 × 30 mL of CH_2Cl_2; the combined extracts were concentrated and then poured into 30 mL of cold hexane; a yellow powder precipitated whose spectral properties were identical with those of authentic **1a**; yield 0.110 g, 91%.

(2) At 0 °C. Compound **7a** (0.145 g, 0.308 mmol) was dissolved in 25 mL of CH_3CN that was cooled to −30 °C. LiI (0.042 g, 0.314 mmol) was added, and the slurry was stirred for 15 min. An IR spectrum of the solution portion showed that there was no reaction at this temperature. The reaction mixture was then warmed to 0 °C and stirred for 3 h. After this time, an IR spectrum of the solution showed bands for **1a** and **7a**, with **1a** predominant. The reaction mixture was then filtered, and the filtrate was evaporated to dryness. Triturating the yellow residue with 30 mL of 2:1 hexane/CH_2Cl_2 followed by concentration and chilling at −20 °C gave **7a** (0.024 g, 17%). The residue was dissolved in 30 mL of CH_2Cl_2; after filtration and concentration, ether was added to precipitate cation **1a** (yield 0.130 g, 75%).

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