Ion-Pairing Thermodynamics for $(\eta^5\text{-pentadienyl})Fe(CO)_2^-$ (Pentadienyl = MeCp, C_5Me_5, C_5Ph_5, C_9H_7) and X-ray Crystal Structure of $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2][PPN]$

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The pentadienyl complexes $[(\eta^5\text{-pentadienyl})Fe(CO)_2][Na]$ (pentadienyl = MeCp, C_5Me_5, C_5Ph_5, C_9H_7) have been prepared in THF from the corresponding dimers $[(\eta^5\text{-pentadienyl})Fe(CO)_2]_2$ and $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2Br$. The exact composition of the ion pairs that exist in THF solution was explored as a function of temperature by FT-IR spectroscopy. The sodium metalates bearing the pentadienyl ligands MeCp, C_5Me_5, and C_9H_7 show the presence of two species that involve carbonyl oxygen−sodium and iron−sodium contact ion pairs in THF. In contrast, the pentaphenylcyclopentadienyl complex $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2][Na]$ reveals the existence of solvent-separated ion pairs and carbonyl oxygen−sodium contact ion pairs. The absence of iron−sodium contact ion pairs in $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2][Na]$ is attributed to a steric shielding of the iron center by the ancillary phenyl groups. The temperature-dependent behavior of these sodium metalates was explored by variable-temperature FT-IR measurements, and the equilibrium constants for the observed ion-pairing equilibria have been used to determine values for ΔH and ΔS. The X-ray structure of $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2][PPN]$ is reported. The reactivity of $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]^-$ with CO_2 was investigated, and only in the case of the lithium salt was the carboxylate complex $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2(CO_2)]^-$ observed by IR spectroscopy.

Introduction

Numerous cyclopentadienyliron compounds have been employed in the construction of complex organic molecules by serving as masked synthons and as chiral auxiliaries in asymmetric syntheses.[1,2] While these reactions constitute the majority of interest in this genre of compound because of their demonstrated practical utility, the reactivity of $[(\eta^5\text{-Cp})Fe(CO)_2]^-$ and related Fp-derived [Fp = $(\eta^5\text{-Cp})Fe(CO)_2$] carbonylmetalates has also attracted considerable interest in the area of CO_2 fixation chemistry.[3] The use of CO_2 as a feedstock in the production of C_1-derived commodity chemicals through homogeneous transition-metal catalysis remains a global priority, given the present day concern over motor vehicle and power plant emissions of CO_2 and the resulting manifestations of the greenhouse effect on the planet's climate.[4]

The literature abounds with reports on the coordination of CO_2 by the carbonylmetalates $[(\eta^5\text{-pentadienyl})Fe(CO)_2]^-$ (pentadienyl = Cp, MeCp, C_5Me_5, indenyl) and the functionalization chemistry of the resulting metallocarboxylate;[5−8] however, no data exist on the synthesis and reactivity of the corresponding anionic

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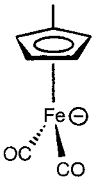
pentaphenylcyclopentadienyl analogue [(η^5-C_5Ph_5)Fe-$(CO)_2$]$^-$.[9] Moreover, with the exception of the parent cyclopentadienyl compound [(η^5-Cp)Fe$(CO)_2$]$^-$,[10] the ion-pairing phenomena exhibited by the other cyclopendienyl derivatives in this family are not well-documented,[11] despite the fact that ion pairing plays a critical role in the stabilization of the metallocarboxylates that are obtained from the reaction of these iron anions with CO_2.[6e,12,13] Herein we report our data on the temperature-dependent IR behavior of the compounds [(η^5-pentadienyl)Fe$(CO)_2$][Na] (pentadienyl = MeCp, C_5Me_5, C_5Ph_5, C_9H_7) in THF solution and the thermodynamics for the various ion pairs present in THF solution. The X-ray crystal structure of [(η^5-C_5Ph_5)-Fe$(CO)_2$][PPN] has been determined, and the reactivity of [(η^5-C_5Ph_5)Fe$(CO)_2$]$^-$ with CO_2 was investigated and found to afford the carboxylate complex [(η^5-C_5Ph_5)Fe-$(CO)_2(CO_2)$]$^-$ when lithium was employed as the gegencation.



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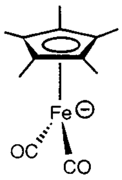

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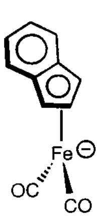

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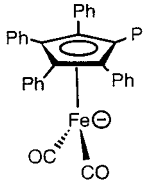

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Results and Discussion

I. IR Spectral Data for [(η^5-pentadienyl)Fe$(CO)_2$]-[Na]. With the exception of the anionic C_5Ph_5 derivative, whose solution chemistry has only been examined with respect to the 17-electron radical,[9] the other three carbonylmetalates have been prepared via the amalgam route or from the direct reaction of the corresponding Fe_2 dimer with an alkali-metal reducing agent. Despite the widespread use of the compounds [(η^5-pentadienyl)-Fe$(CO)_2$][Na] (pentadienyl = MeCp, C_5Me_5, C_9H_7) in a variety of reactions,,[6d,e,14,15] no detailed information has been published regarding the IR spectral data for these anions. Accordingly, we reduced each of the dimeric [(η^5-pentadienyl)Fe$(CO)_2$]$_2$ compounds with sodium amalgam in THF solution and recorded the IR spectra of the resulting [(η^5-pentadienyl)Fe$(CO)_2$][Na]. These reactions proceed without complications, provided moisture and oxygen are rigorously excluded, and only in the case of the highly substituted compounds [(η^5-C_5Me_5)Fe$(CO)_2$]$_2$ and [(η^5-C_5Ph_5)Fe$(CO)_2$]$_2$ is the reduction found to occur slowly (up to several hours). Qualitatively, the pentaphenyl iron complex affords the expected carbonylmetalate more slowly than the pentamethyl derivative. Use of (η^5-C_5Ph_5)Fe$(CO)_2$Br in place of the parent dimer also furnishes [(η^5-C_5Ph_5)Fe$(CO)_2$][Na] without any noticeable complications.

The IR data for each of the carbonylmetalates are reported in Table 1. Relative to the starting dimeric compound or (η^5-C_5Ph_5)Fe$(CO)_2$Br the product carbonylmetalate exhibits a low-energy shifting of the CO stretching bands consistent with an increased electron density at the iron center. The anionic pentadienyl compounds [(η^5-MeCp)Fe$(CO)_2$][Na] ([**1**][Na]), [(η^5-C_5Me_5)Fe$(CO)_2$][Na] ([**2**][Na]), and [(η^5-C_9H_7)Fe$(CO)_2$][Na] ([**3**][Na]) reveal significantly more complicated IR spectra, as a result of the contact ion pairing (CIP) between the sodium gegencation and the iron center and a CO ligand.[16] Here there are two symmetric and two antisymmetric CO stretches present in THF solution at room temperature due to the coordination of the sodium gegencation with the iron center and one of the CO ligands. For example, in [(η^5-MeCp)Fe$(CO)_2$][Na] the iron−sodium CIPs exhibit two ν(CO) bands observed at 1878 and 1806 cm^{-1}, while the sodium−carbonyl oxygen CIPs reveal ν(CO) bands at 1860 and 1768 cm^{-1}. These CO groups in both ion pairs are readily ascribed to the symmetric and antisymmetric CO stretching modes, on the basis of group theoretical considerations.[17] Equation 1 depicts the equilibrium that exists for this carbonylmetalate in THF solution. Unlike the parent cyclopentadienyliron anion [(η^5-Cp)Fe$(CO)_2$][Na], which displays an equilibrating mixture of the above two CIPs and solvent-separated ion pairs (SSIP),[10] the presence of a single methyl substituent in [**2**][Na] appears to be electron donating enough to render the formation of SSIPs thermodynamically unfavorable. The absence of SSIPs in [(η^5-MeCp)Fe$(CO)_2$]$^-$ was verified by the addition of excess HMPA to a THF solution containing [(η^5-MeCp)Fe$(CO)_2$][Na]. The aforementioned ν(CO) bands

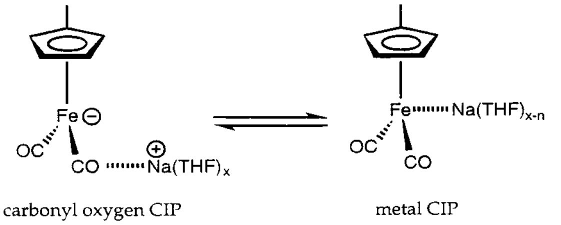

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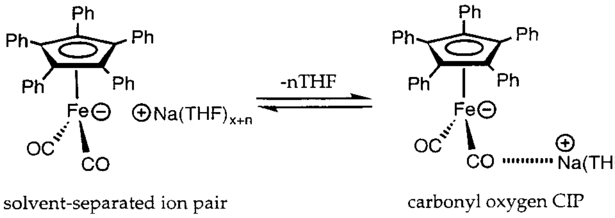
Table 1. IR Data for the Carbonyl Bands in [(η^5-pentadienyl)Fe(CO)$_2$][Na] and [(η^5-pentadienyl)Fe(CO)$_2$][Na(HMPA)$_x$][a]

[(η^5-MeCp)Fe(CO)$_2$][Na]	1878, 1806 1860, 1768
[(η^5-MeCp)Fe(CO)$_2$][Na(HMPA)$_x$]	1862, 1790
[(η^5-C$_5$Me$_5$)Fe(CO)$_2$][Na]	1860, 1791 1847, 1756
[(η^5-C$_5$Me$_5$)Fe(CO)$_2$][Na(HMPA)$_x$]	1847, 1778
[(η^5-C$_9$H$_7$)Fe(CO)$_2$][Na]	1882, 1816 1866, 1780
[(η^5-C$_9$H$_7$)Fe(CO)$_2$][Na(HMPA)$_x$]	1862, 1790
[(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][Na]	1867, 1804 1867, 1790
[(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][Na(HMPA)$_x$]	1872, 1807

[a] All spectra were recorded in THF solution at room temperature, and the quoted data are in cm^{-1}.

were replaced by ν(CO) bands at 1862 and 1790 cm^{-1}, in keeping with the trend observed in other carbonylmetalate anions when HMPA disrupts the ion-pairing equilibria extant in solution.[16a,18] The compounds [(η^5-C$_5$Me$_5$)Fe(CO)$_2$][Na] and [(η^5-C$_9$H$_7$)Fe(CO)$_2$][Na] display both types of CIPs in THF as [(η^5-MeCp)Fe(CO)$_2$][Na], and upon the addition of excess HMPA the exclusive formation of SSIPs is found.

The anionic compound [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][Na] ([**4**][Na]) reveals slightly different IR behavior relative to the above carbonylmetalates. The IR spectrum of [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][Na] in THF at room temperature exhibits two ν(CO) bands at 1867 and 1790 cm^{-1} that are assigned to the symmetric and antisymmetric CO stretching modes of the carbonyl oxygen CIP, in addition to a small ν(CO) band at 1804 cm^{-1}. The absence of two symmetric ν(CO) bands in [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][Na] allows us to rule out the presence of an iron−sodium CIP (vide infra) and suggests that the major species in solution is either the carbonyl oxygen CIP or the SSIP.[19] The exact nature of this particular ion pair was demonstrated by the frequency response of the CO bands to added HMPA (excess), which afforded new ν(CO) bands at 1872 and 1807 cm^{-1}. The fact the antisymmetric ν(CO) band moved ca. 20 cm^{-1} to higher frequency is fully consistent with the conversion of the carbonyl oxygen CIP to the SSIP. Equation 2 depicts the pertinent ion-pairing equilibrium for [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][Na] in THF. Independent verification of the SSIP was further shown by the IR spectrum of [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][PPN], which displayed ν(CO) bands at 1872 and 1806 cm^{-1}, in excellent agreement with the SSIP data obtained from the addition of HMPA to [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][Na].



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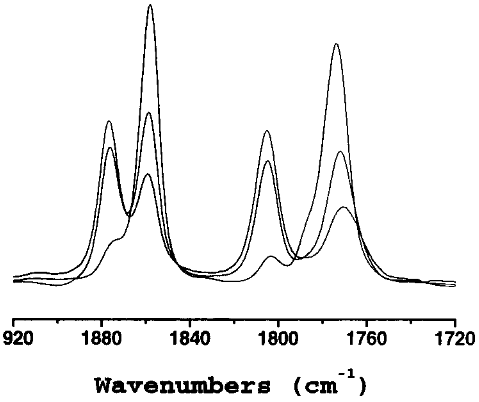

Figure 1. Selected IR spectra of [(η^5-MeCp)Fe(CO)$_2$][Na] in THF as a function of temperature (−70, −25, 0 °C). All absorbances are relative to a common scale.

Table 2. Equilibrium Parameters for the Conversion of the Carbonylmetalates [1−3][Na] from Carbonyl Oxygen−Sodium CIPs into Iron−Sodium CIPs[a]

1000/T, K^{-1}	ln K_{eq}[b]	1000/T, K^{-1}	ln K_{eq}[b]
	[(η^5-MeCp)Fe(CO)$_2$][Na] ([**1**][Na])[c]		
4.93	3.51	3.80	0.15
4.69	2.53	3.66	0.51
4.48	1.66	3.53	0.78
4.29	1.08	3.41	1.00
4.12	0.67		
	[(η^5-C$_5$Me$_5$)Fe(CO)$_2$][Na] ([**2**][Na])[d]		
4.93	1.90	3.66	0.04
4.48	1.31	3.37	0.33
3.95	0.40		
	[(η^5-C$_9$H$_7$)Fe(CO)$_2$][Na] ([**3**][Na])[e]		
3.88	3.08	3.55	1.59
3.80	2.53	3.47	1.28
3.77	2.29	3.36	0.82
3.66	2.12	3.30	0.68

[a] From ca. 10^{-2} M solutions of [**1**−**3**][Na] in THF by following the changes in the area of the antisymmetric carbonyl bands. [b] Defined as [iron−sodium CIPs]/[carbonyl oxygen−sodium CIPs]. [c] $\Delta H = 5.7 \pm 0.1$ kcal/mol; $\Delta S = 22 \pm 1$ eu. [d] $\Delta H = 3.0 \pm 0.2$ kcal/mol; $\Delta S = 11 \pm 1$ eu. [e] $\Delta H = 7.9 \pm 0.2$ kcal/mol; $\Delta S = 24 \pm 1$ eu.

II. Ion-Pairing Thermodynamics in [(η^5-pentadienyl)Fe(CO)$_2$][Na]. The temperature-dependent behavior of the various carbonylmetalates was explored by VT-IR spectroscopy. Figure 1 shows selected IR spectra and the effect of temperature on the equilibrium involving the two CIPs of [**1**][Na] in THF. Lowering the temperature from room temperature to −70 °C leads to a shift in the equilibrium defined in eq 1 and an increased concentration of the carbonyl oxygen−sodium CIP. Compounds [**2**][Na] and [**3**][Na] exhibit similar behavior as a function of temperature. All IR spectra are fully reproducible and have been examined by repeated temperature cycling over a wide range of temperatures. Band-area measurements on the overlapping antisymmetric carbonyl stretching bands permit the calculation of the equilibrium constant defined by eq 1 for compounds **1**−**3**. The resulting K_{eq} values (Table 2) were obtained by making the assumption that the area from each deconvoluted band was proportional to the relative amount of each CIP present in solution. Figure 2 shows the van't Hoff plot for these data, from which the values of ΔH and ΔS have been computed from the slope of the straight line and the intercept, respectively.

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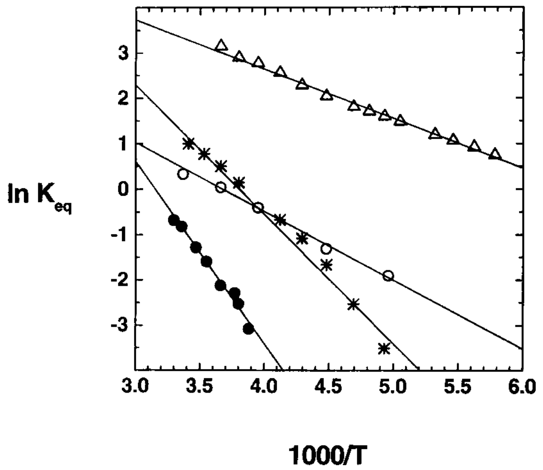

Figure 2. Plots of ln K_{eq} versus T^{-1} for the ion-pair equilibria defined by eqs 1 and 2 in THF: (*) [(η^5-MeCp)-Fe(CO)$_2$][Na]; (○) [(η^5-C$_5$Me$_5$)Fe(CO)$_2$][Na]; (●) [(η^5-C$_9$H$_9$)-Fe(CO)$_2$][Na]; (△) [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][Na].

The anionic compounds [**1**−**3**][Na] display similar temperature-dependent processes, and as the temperature is lowered, the carbonyl oxygen−sodium CIP becomes the dominant ion pair in solution. Higher temperatures lead to a shift in the equilibrium represented by eq 1 and to the iron−sodium CIP, in keeping with the increased importance of the $T\Delta S$ term in the van't Hoff expression. While ion-pairing phenomena have been demonstrated in many carbonylmetalates, no theory exists that can accurately predict the types of ion pairs that might occur in solution and the effect that temperature has on a given equilibrium. The subtle balance between the electrostatic potential for sodium cation solvation by the various ion pairs available and the THF solvent molecules, coupled with steric interactions between the solvated gegencation and the ancillary ligands associated with the carbonylmetalate, serve to define the ion-pairing chemistry observed in solution. Qualitatively, the observed equilibrium for [**1**−**3**][Na] could be explained by considering the number of THF solvent molecules bound to the sodium gegencation. If there were a higher coordination number of THF molecules to the sodium gegencation in the carbonyl oxygen−sodium CIP rather than the iron−sodium CIP, the effect of temperature on the K_{eq} would appear to be reasonable. Increased temperatures would favor the release of at least one THF molecule into solution and allow for the partially solvated [Na(THF)$_{x-n}$]$^+$ gegencation to further penetrate the coordination sphere of the carbonylmetalate all the way to the iron center.

The perphenylated derivative [**4**][Na] shows reversible temperature-dependent IR behavior, as defined by eq 2. The presence of the phenyl groups is sufficient to change the nature of ion pairs in THF relative to compounds [**1**−**3**][Na]. The dominant form of [**4**][Na] in THF from room temperature (ca. 97%) to 173 K (ca. 68%) corresponds to the carbonyl oxygen−sodium CIP. Lowering the temperature leads to the increased formation of SSIPs of [**4**][Na]. Figure 3 shows the spectral changes as a function of temperature, while the appropriate van't Hoff data may be found in Figure 2 and Table 3. It is interesting that the ion-pairing equilibrium here is different from that found for [**1**−**3**][Na], which undoubtedly has its origin in the presence of the five phenyl groups, which are sterically more demanding than the substituents on the other cyclopentadienyl rings. The attachment of five phenyl groups to the cyclopentadienyl ring in [**4**][Na] is sure to disrupt and, in this case, completely eliminate the possibility of a direct iron−sodium CIP. The close intermolecular contacts that exist between the ortho hydrogens on the phenyl rings and the iron atom (ca. 3.15 Å) shield the iron center from the sodium cation. The phenyl-derived steric bias in [**4**][Na] retards the formation of metal CIPs, leading to the exclusive generation of SSIPs and carbonyl oxygen−sodium CIPs.

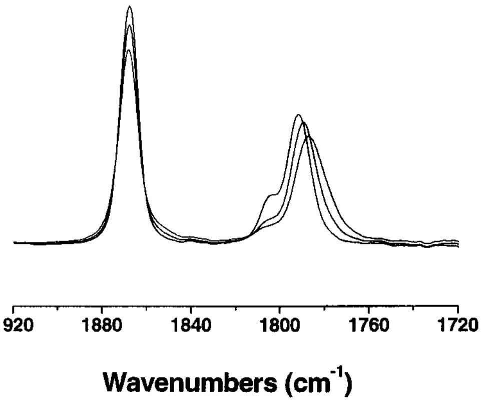

Figure 3. Selected IR spectra of [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][Na] in THF as a function of temperature (−70, −30, 0 °C). All absorbances are relative to a common scale.

Table 3. Equilibrium Parameters for the Conversion of the Carbonylmetalate [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][Na] ([4][Na])[a] from SSIPs into Carbonyl Oxygen−Sodium CIPs[b]

1000/T, K^{-1}	ln K_{eq}[c]	1000/T, K^{-1}	ln K_{eq}[c]
5.78	0.74	4.69	1.80
5.62	0.92	4.48	2.04
5.46	1.06	4.29	2.28
5.32	1.19	4.12	2.56
5.05	1.48	3.95	2.77
4.93	1.59	3.80	2.90
4.81	1.70	3.66	3.15

[a] $\Delta H = 2.2 \pm 0.3$ kcal/mol; $\Delta S = 14 \pm 0.1$ eu. [b] From ca. 10^{-2} M solutions of [**4**][Na] in THF by following the changes in the area of the antisymmetric carbonyl bands. [b] Defined as [carbonyl oxygen−sodium CIPs]/[SSIPs].

III. X-ray Diffraction Structure of [(η^5-C$_5$Ph$_5$)-Fe(CO)$_2$][PPN]. The structure of [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$]-[PPN] was determined by single-crystal X-ray diffraction analysis in order to establish the structure and the disposition of the ancillary phenyl groups in [**4**]$^-$. Single crystals of [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][PPN] were grown from THF/hexane, and [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][PPN] was found to exist in the unit cell with no unusually short inter- or intramolecular contacts. The X-ray data collection and processing parameters for [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$][PPN] are given in Table 4 with selected bond distances and angles listed in Table 5.

Figure 4 shows the molecular structure of [(η^5-C$_5$Ph$_5$)-Fe(CO)$_2$][PPN]. The bond lengths and angles found for the ancillary pentadienyl ligand in [(η^5-C$_5$Ph$_5$)Fe(CO)$_2$]$^-$ are in keeping with those values found for the isoelectronic molecule (η^5-C$_5$Ph$_5$)Co(CO)$_2$[20] and other structur-

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Table 4. X-ray Crystallographic Data and Processing Parameters for [(η^5-C_5Ph_5)Fe(CO)$_2$][PPN]

space group	$P3_2$, trigonal
a, Å	13.3229(6)
c, Å	33.356(2)
V, Å^3	5127.5(5)
mol formula	$C_{73}H_{55}FeNO_2P_2$
fw	1095.97
formula units per cell (Z)	3
ρ, g cm^{-3}	1.065
λ(Mo Kα), Å	0.710 73
μ, cm^{-1}	3.08
collecn range, deg	$4.0 \le 2\theta \le 48.0$
total no. of data collcd	18482
no. of indep data, $I > 3\sigma(I)$	10086
R	0.0590
R_w	0.1492
GOF	1.10
weights	$[0.04F^2 + (\sigma F)^2]^{-1}$

Table 5. Selected Bond Distances (Å) and Angles (deg) in [(η^5-C_5Ph_5)Fe(CO)$_2$][PPN]^a

Bond Distances			
Fe−C(1)	2.106(5)	Fe−C(2)	2.133(4)
Fe−C(3)	2.121(5)	Fe−C(4)	2.097(5)
Fe−C(5)	2.085(5)	Fe−C(6)	1.714(6)
Fe−C(7)	1.715(6)	Fe−centroid	1.715(3)
O(1)−C(6)	1.182(7)	O(2)−C(7)	1.186(7)
C(1)−C(2)	1.446(6)	C(1)−C(5)	1.447(7)
C(2)−C(3)	1.420(7)	C(3)−C(4)	1.453(6)
C(4)−C(5)	1.439(7)		
Bond Angles			
C(6)−Fe−C(7)	88.0(3)	O(1)−C(6)−Fe	178.0(5)
O(2)−C(7)−Fe	178.6(5)	P(2)−N(1)−P(1)	147.2(3)

^{a} Numbers in parentheses are estimated standard deviations in the least significant digit.

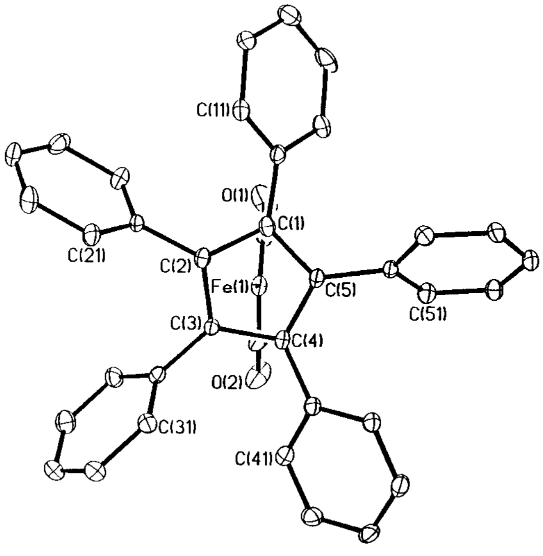


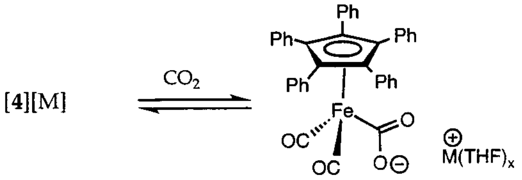
Figure 4. ORTEP drawing of the non-hydrogen atoms of [(η^5-C_5Ph_5)Fe(CO)$_2$][PPN] showing the thermal ellipsoids at the 50% probability level. The PPN gegencation has been omitted for clarity.

ally characterized compounds possessing an η^5-C_5Ph_5 ligand.[21] The five phenyl groups orient themselves in a paddlewheel fashion about the cyclopentadienyl ligand, and the phenyl ring torsion angles range from 37.7 to 61.8°, with an average torsion angle of 53.4°. This value agrees well with the 55.8° average angle found for the canted phenyl groups in (η^5-C_5Ph_5)Co(CO)$_2$.[20] The Fe−centroid distance of 1.715(3) Å is in excellent agreement with the 1.70(1) Å distance reported for (η^5-C_5Ph_5)Co(CO)$_2$ and suggests that no unusual intramolecular interactions exist in the carbonylmetalate [**4**]$^-$.

The Fe−CO bond distances and bond angles fall within normal ranges relative to other organometallic iron complexes.[22] The OC−Fe−CO bond angle of 88.0(3)° in [**4**][PPN] is similar to the value of 89.5(5)° reported for (η^5-C_5Ph_5)Co(CO)$_2$ and is not unreasonable when compared with the calculated solution OC−Fe−CO bond angle of ca. 96°.[23] The ca. 8° increase in this angle in solution may reflect a repositioning of the phenyl groups about the iron center, allowing for an opening in the OC−Fe−CO bond angle.

IV. CO$_2$ Reactivity with [(η^5-C_5Ph_5)Fe(CO)$_2$]$^-$. Since the carbonylmetalates [**1**−**3**]$^-$ have been shown to react with CO$_2$ to afford the corresponding metallocarboxylates [(η^5-pentadienyl)Fe(CO)$_2$(CO$_2$)]$^-$, we wished to explore the reactivity of [(η^5-C_5Ph_5)Fe(CO)$_2$]$^-$ with CO$_2$, because the phenyl groups could significantly alter the stability of the metallocarboxylate product. Treatment of [(η^5-C_5Ph_5)Fe(CO)$_2$][Na] in THF with CO$_2$ at −78 °C did not lead to any noticeable spectral changes when examined by low-temperature IR spectroscopy. This lack of reactivity between [(η^5-C_5Ph_5)Fe(CO)$_2$]$^-$ and CO$_2$ was a bit surprising, as it is accepted that the anionic compounds [(η^5-pentadienyl)Fe(CO)$_2$]$^-$ generate [(η^5-pentadienyl)Fe(CO)$_2$(CO$_2$)]$^-$ rapidly at low temperatures in the presence of added CO$_2$. We next prepared the potassium and lithium salts of [(η^5-C_5Ph_5)Fe(CO)$_2$]$^-$, as it is known that the stability of the metallocarboxylate of this genre of compound is sensitive to the nature of the gegencation. The anion of [(η^5-C_5Ph_5)Fe(CO)$_2$][K],[24] which was prepared by potassium amalgam reduction of (η^5-C_5Ph_5)Fe(CO)$_2$Br, also showed no reactivity with CO$_2$ at −78 °C. Apart from a trace amout of (η^5-C_5Ph_5)Fe(CO)$_2$H, only [**4**][K] was observed in solution −78 °C. Spectroscopic monitoring showed that the warmup of [**4**][Na] and [**4**][K] in the presence of CO$_2$ gradually led to (η^5-C_5Ph_5)Fe(CO)$_2$H without any sign of the expected metallocarboxylate ion.

We did observe an instantaneous reaction between [(η^5-C_5Ph_5)Fe(CO)$_2$][Li] and CO$_2$ (excess) to yield the expected metallocarboxylate ion [(η^5-C_5Ph_5)Fe(CO)$_2$(CO$_2$)][Li] (eq 3). [**4**][Li] exists in solution as a mixture of carbonyl oxygen−lithium CIPs and SSIPs. In the reaction of [**4**][Li] with CO$_2$ the IR bands belonging to



(3)

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[24] Carbonyl bands indicative of the ion pairs depicted in eq 2 were observed at 1867, 1805, and 1789 cm^{-1}.

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[**4**][Li] at 1870, 1802, and 1765 cm^{-1} are replaced with new ν(CO) bands at 1994 and 1936 cm^{-1}. The IR data for $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2(CO_2)][Li]$ compare favorably to the carbonyl bands reported for $[(\eta^5\text{-Cp})Fe(CO)_2(CO_2)]$-[Li] at 2002 and 1942 cm^{-1}. Allowing solutions of $[(\eta^5\text{-Cp})Fe(CO)_2(CO_2)][Li]$ to warm to room temperature leads to the known hydride complex $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2H$, as verified by IR and ^1H NMR spectroscopy. Decomposition of $[(\eta^5\text{-Cp})Fe(CO)_2(CO_2)][Li]$ via the formal homolytic cleavage of the Fe$-CO_2$ bond would furnish the metallo radical $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2^{\bullet}$, which would be free to react with THF by hydrogen abstraction to furnish the iron hyride as the major end product.

The tight binding of the lithium cation with the carboxylate oxygens accounts for the stabilization of the metallocarboxylate ion. The sodium and potassium cations are not expected to bind to the carboxylate oxygens as strongly as the lithium gegencation, and the unfavorable equilibrium for $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2(CO_2)]^-$ would facilitate the reversible dissociation of CO_2 from $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2(CO_2)]^-$ to re-form [**4**]$^-$. Proof of the importance of the lithium gegencation in helping stabilize the metallocarboxylate product was demonstrated by adding $LiPF_6$ to a solution containing $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2][Na]$ with CO_2. Immediate CO_2 coordination was confirmed by low-temperature IR spectroscopy upon the addition of the lithium salt. Moreover, we have also established that SSIPs of [**4**]$^-$ do not afford a stable metallocarboxylate compound. Both [**4**][PPN] and solutions of [**4**][K] containing 18-crown-6 showed no sign of CO_2 complexation. These data taken collectively demonstrate that the presence of the lithium gegencation is required for the stabilization of the metallocarboxylate $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2(CO_2)]^-$. While spectroscpically observed in the case of the lithium salt, the metallocarboxylate ion $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2(CO_2)]^-$ is most likely a precursor to the iron hydride when THF solutions of the sodium and potassium salts of [**4**]$^-$ are warmed to room temperature.

Conclusions

The temperature-dependent behavior of several anionic iron pentadienyl compounds in THF has been studied by VT IR spectroscopy. The nature of the ion pairs has been established, and the equilibrium constants have been determined and the values of ΔH and ΔS reported. The reactivity of $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]^-$ with CO_2 was examined and found to give a metallocarboxylate product with lithium as the gengencation. Our data support the importance of tight ion binding between the carboxylate oxgyens and the cation in controlling the stability of the resulting metallocarboxylate complex. The metallocarboxylate $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2(CO_2)]^-$ is thermally unstable and furnishes $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2H$ at ambient temperatures.

Experimental Section

General Procedures. The $Fe(CO)_5$ used in all syntheses was purchased from Pressure Chemical Co. and was used without further purification. $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2Br$ was prepared by a known procedure utilizing C_5Ph_5H,[25] while all $[(\eta^5\text{-pentadienyl})Fe(CO)_2]_2$ complexes were synthesized by following the basic procedure of Pauson.[26] THF was distilled from sodium/benzophenone under argon and was handled and stored under inert atmosphere using Schlenk techniques.[27] The combustion analysis was performed by Atlantic Microlab, Norcross, GA.

Routine infrared spectra were recorded on a Nicolet 20 SXB FT-IR spectrometer in 0.1 mm NaCl cells. The variable-temperature IR spectra were recorded on the same spectrometer with a Specac Model P/N 21.000 variable-temperature cell equipped with inner and outer CaF_2 windows. The coolant was either dry ice/acetone or pentane/liquid nitrogen, and the reported cell temperatures, taken to be accurate to ±1 °C, were determined by a copper$-$constantan thermocouple.

Preparation of $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2][PPN]$. A 0.20 g amount (0.31 mmol) of $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2Br$ dissolved in 15 mL of THF was transferred via cannula to a Schlenk flask containing excess dilute sodium amalgam. The orange solution immediately turned olive green with the concomitant formation of the solid dinuclear compound $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]_2$. Stirring was continued for ca. 1 h, at which time IR analysis revealed only the presence of the carbonylmetalate [**4**][Na]. The deep red solution was next transferred to a vessel containing solid [PPN][Cl] (excess) and stirred for an additional 30 min. The solution was filtered and then layered with an equal amount of hexane. The resulting crystals were subsequently isolated to yield 0.18 g (53%) of dark red $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2][PPN]$. IR (THF): ν(CO) 1872 (vs, symm), 1806 (s, asymm) cm^{-1}. Anal. Calcd for $C_{73}H_{55}FeNO_2P_2$: C, 79.93; H, 5.02. Found: C, 78.98; H, 5.74.

X-ray Diffraction Structure of $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2]$-[PPN]. Single crystals of $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2][PPN]$ suitable for X-ray diffraction analysis were grown from a THF solution containing $[(\eta^5\text{-}C_5Ph_5)Fe(CO)_2][PPN]$ that had been layered with hexane. A red crystal of dimensions 0.40 × 0.30 × 0.20 mm^3 was selected and found to belong to the trigonal crystal system. Systematic absences in the diffraction data and Laue diffraction symmetry limited the possible space groups to $P3_1$ and $P3_2$. The Flack parameter indicated that the latter option was correct. An empirical correction for absorption (SADABS) was applied to the data. The crystal structure was solved by direct methods, completed from difference Fourier maps, and refined with anisotropic thermal parameters for all non-hydrogen atoms. Refinement converged at $R = 0.0590$ and $R_w = 0.1492$ for 10 086 unique reflections with $I > 3\sigma(I)$. All computations used SHELXTL 5.1 (NT) software (G. Sheldrick, Bruker AXS, Madison, WI).

Band-Shape Analysis. Given that antisymmetric CO stretching bands in all of the $[(\eta^5\text{-pentadienyl})Fe(CO)_2][Na]$ compounds exhibit significant overlap, the IR band shapes of these CO bands were calculated by using a numerical procedure in order to determine the ratio of their areas, as previously described,[28] or by employing the commercially available program PeakFit.

Thermodynamic Evaluation of the Ion-Pairing Equilibrium in $[(\eta^5\text{-pentadienyl})Fe(CO)_2][Na]$. THF solutions of ca. 10^{-2} M of each carbonylmetalate were examined over a wide range of temperatures in order to establish the composition of ion pairs present in solution. From the areas associated with each antisymmetric CO stretching band, the equilibrium constants were calculated as defined by eq 1 for compounds [**1**$-$**3**][Na] and eq 2 for [**4**][Na]. The thermodynamic parameters were obtained by plotting ln K_{eq} vs T^{-1}, from which the slope and intercept gave ΔH and ΔS, respectively. The error

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limits associated with the enthalpy and entropy values were calculated by using the available least-squares regression program.

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Supporting Information Available: Listings giving crystallographic data, bond distances, bond angles, and atomic and thermal parameters of [(η^5-C_5Ph_5)Fe(CO)$_2$][PPN]. This material is available free of charge via the Internet at http://pubs.acs.org.

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