$Fe(Bz_2DTC)_2Cl$ occurs until all of the excess ligand anion is reacted. The "induction" time of no observable product formation is quantitatively directly proportional to the salt concentration. The concentration of the Cl^- ions produced is equal to the initial concentration of the dithiocarbamate anion.

The reaction intermediate is depicted in Figure 2 as a "radical pair" consisting of a photoreduced iron(II) complex and a ligand free radical in order to emphasize the nature of the reaction pathway. However, there is no direct evidence for the participation of this radical pair. The intermediate could be depicted as the thermally equilibrated LTMCT excited state of the six-coordinate starting material or as a monodentate DTC with one uncoordinated sulfur with equal validity. In an attempt to directly observe the free radical ligand, the photoreaction was carried out in a probe of an ESR spectrometer. No organic free radical was observed in the region of $g = 2$. The absence of a signal could arise because of a short lifetime of the radical pair and the concomitant low steady state concentration. Alternatively, magnetic exchange between the free radical and the metal could also be responsible for the absence of a signal in this region. Thus, the ESR results are inconclusive. The alternatives presented above represent conceptual extremes which, in all cases, lead to the photoproduction of the five-coordinate iron(III) complex via homolytic iron–sulfur bond cleavage.

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References and Notes

(1) Camille and Henry Dreyfus Teacher–Scholar, 1974–1979.
(2) (a) A. W. Adamson and P. D. Fleischauer, "Concepts of Inorganic Photochemistry", Wiley-Interscience, New York, N.Y., 1975, Chapter 3. (b) V. Balzani and V. Canassiti, "Photochemistry of Coordination Compounds", Adademic Press, New York, N.Y., 1971, Chapter 10.
(3) D. P. Schwendiman and J. I. Zink, *J. Am. Chem. Soc.*, **98**, 1248 (1976).
(4) J. P. Fackler, Jr., A. Avdeev, and R. G. Fischer, Jr., *J. Am. Chem. Soc.*, **95**, 774 (1973).
(5) A. H. White, E. Kokot, R. Roper, H. Waterman, and R. L. Martin, *Aust. J. Chem.*, **17**, 294 (1964).
(6) A. H. Gould, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, **8**, 1837 (1969).
(7) (a) J. I. Zink, D. Schwendiman, and M. J. Incorvia, Abstracts of the 169th National Meeting of the American Chemical Society, Philadelphia, Pa. April 7–11, 1975, INOR-143; (b) D. P. Schwendiman and J. I. Zink, Abstracts of the First Chemical Congress of the North American Continent, Mexico City, Nov 30–Dec 5, 1975, INOR-99.
(8) S. Akerstrom, *Ark. Kemi*, **14**, 387 (1950)
(9) H. J. Cavell and S. Sugden, *J. Chem. Soc.*, 621 (1935).
(10) H. H. Wickman and A. M. Trozzolo, *Inorg. Chem.*, 7, 64 (1968).
(11) R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).
(12) E. A. Pasek and C. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).
(13) J. C. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, N.Y., 1966, pp 783–786.
(14) G. Kobrich and J. Liebigo, *Justus Liebigs Ann. Chem.*, **648**, 114 (1961).
(15) O. Kling, E. N. Kolaiski, and H. L. Schlafer, *Ber. Bunsenges, Phys. Chem.*, **67**, 883 (1963).
(16) L. H. Pignolet, private communication; G. L. Miessler, B. Stuk, T. P. Smith, K. W. Given, M. C. Palazzotto, and L. H. Pignolet, manuscript submitted, *Inorg. Chem.*
(17) J. I. Zink, *J. Am. Chem. Soc.*, **94**, 8039 (1972); *Inorg. Chem.*, **12**, 1018 (1973); *Mol. Photochem.*, **5**, 151 (1973); *Inorg. Chem.*, **12**, 1957 (1973); *J. Am. Chem. Soc.*, **96**, 4464 (1964).
(18) M Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 165 (1973).
(19) J. F. Endicott, G. J. Ferrandi, and J. R. Barber, *J. Phys. Chem.*, **79**, 530 (1975); J. F. Endicott, ref 2, Chapter 3.
(20) G. St. Nikolov, *Inorg. Chim. Acta*, **4**, 610 (1970).
(21) J. I. Zink, *Inorg. Chem.*, **14**, 446 (1975).
(22) N. Rosch, R. P. Messmer, and K. H. Johnson, *J. Am. Chem. Soc.*, **96**, 3855 (1974).
(23) C. F. C. Wong and A. D. Kirk, *Can. J. Chem.*, **53**, 419 (1975).
(24) F. Scandola, M. A. Scandola, and C. Bartocci, *J. Am. Chem. Soc.*, **97**, 4757 (1975).
(25) E. Wanhurst, *Q. Rev., Chem. Soc.*, **5**, 44 (1951).
(26) K. Fukai, I. T. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, **34**, 1111 (1961).
(27) D. Nonhebel and J. C. Walton, "Free Radical Chemistry", Cambridge Press, Cambridge, England, 1974.
(28) W. G. Alcock and E. Whittle, *Trans. Faraday Soc.*, **61**, 244 (1965).
(29) A. H. Shon and M. Swarc, *Proc. R. Soc. London, Ser. A*, **209**, 110 (1951).
(30) G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds", Elsevier, Amsterdam, 1972.

Spectral Properties of Organometallic Transition Metal Complexes. 2. The Solution Structure of Sodium Dicarbonyl(η^5-cyclopentadienyl)ferrate Involving Direct Sodium–Iron Ion Pairing

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Abstract: The solution spectra of $Na^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ has been recorded in ethereal solvents in the presence of varying amounts of dibenzo-18-crown-6. The resulting spectra indicate the presence of three distinct ion pairs, one of which involves a direct sodium–iron interaction, another a more normal sodium–carbonyl oxygen interaction, and a third solvent separated ion pair. The related molybdenum anion, $Na^+[(\eta^5\text{-}C_5H_5)Mo(CO)_2P(OPh)_3]^-$, exhibits only two ion pairs, a sodium–carbonyl oxygen bonded tight ion pair and the solvent separated ion pair.

There has recently been considerable interest in the solution structure of the alkali metal salts of various transition metal carbonylate anions. Extensive studies by Edgell and co-workers on the sodium tetracarbonylcobaltate were the first to illustrate the importance of ion pairing in such systems.[1–3] It was shown that an equilibrium existed between a tight ion pair involving a sodium–carbonyl oxygen interaction and a solvent separated ion pair.

$$Co^-(CO)_3C{\equiv}ONa^+S \rightleftharpoons Co^-(CO)_4 + SNa^+$$

Later studies by Pribula and Brown reported similar ion pairs existed for the sodium pentacarbonylmanganate system,[4] while Collman et al. have reported that the chemical reactivity of $Fe(CO)_4{}^{2-}2Na^+$ with alkyl halides is very dependent upon

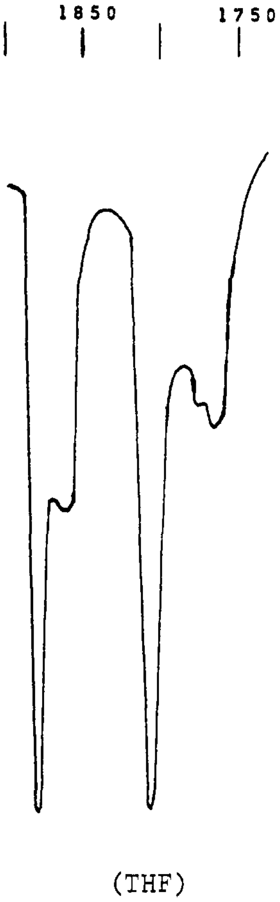


Figure 1. The $\nu(C\equiv O)$ (cm^{-1}) region of $Na^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ in THF.

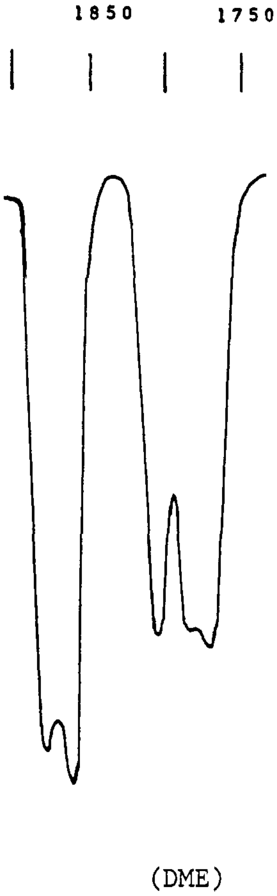
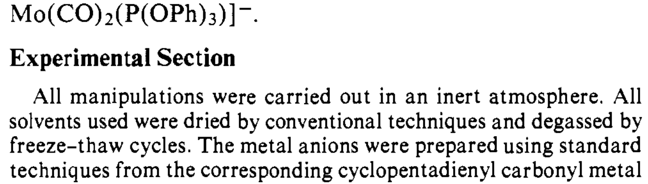


Figure 2. The $\nu(C\equiv O)$ (cm^{-1}) region of $Na^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ in DME.

the degree of ion pairing between the sodium cation and the ketonic carbonyl oxygen of an intermediate species (Fe-(CO)$_3$COR)$^-$ [5]

There appears to be little or no information concerning the solution structure of anions containing ligands other than carbon monoxide. The cyclopentadienyl carbonylate anions are among the most versatile of the transition metal anions and have been widely used to prepare many novel and significant organometallic complexes of the transition metals.[6]

We had previously observed that the nature of the product derived from the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-Na^+$ with certain alkyl chlorides was solvent dependent.[7]



$$(\eta^5\text{-}C_5H_5)Fe(CO)_2^-Na^+ + RCl \xrightarrow{\text{THF}} (\eta^5\text{-}C_5H_5)Fe(CO)_2Cl + RH$$
$$(\eta^5\text{-}C_5H_5)Fe(CO)_2^-Na^+ + RCl \xrightarrow{\text{hexane}} (\eta^5\text{-}C_5H_5)Fe(CO)_2R$$

We have thus initiated a study of the solution structure of various metal anions containing ligands other than carbon monoxide, and this present paper reports the results of such a study on the anions $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OPh)_3)]^-$.

Experimental Section

All manipulations were carried out in an inert atmosphere. All solvents used were dried by conventional techniques and degassed by freeze–thaw cycles. The metal anions were prepared using standard techniques from the corresponding cyclopentadienyl carbonyl metal dimers, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OPh)_3)]_2$,[6] which were purchased from Strem Chemicals or synthesized by literature techniques.[8] Dibenzo-18-crown-6 was purchased from Aldrich Chemicals.

Infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer using NaCl cells.

Results and Discussion

A single isolated salt of dicarbonyl(η^5-cyclopentadienyl)ferrate has been reported in the literature, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{Pm-Pm})]^+$ [Pm-Pm = tetramethyldiphosphinoethane].[9] The solid-state infrared spectrum of this complex exhibited two broad bands in the carbonyl stretching frequency region at 1858 and 1770 cm^{-1} assigned to the anion.

Our present investigation of the solution spectra of this carbonylate anion in THF yielded a significantly more complex pattern in the carbonyl region, Figure 1. When the spectrum was recorded in dimethoxyethane, DME, the same bands were present but the relative intensities were significantly altered, Figure 2. It is expected that regardless of the environment of the dicarbonyl anion, two carbonyl stretching frequencies will be observed. The data represented in Figures 1 and 2 thus indicate the presence of at least two and, considering possible overlap of bands, probably three species involving the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ anion.

The use of cyclic polyethers (crown ethers) to help in the resolution of ion pairing problems involving the alkali metal cations is now well established.[10] Gradual addition of dibenzo-18-crown-6 to the THF solution of the iron anion led to the changes in infrared pattern observed in Figure 3. This sequence of spectra reveals the gradual removal of a species, A, with carbonyl stretching frequencies at 1877 and 1806 cm^{-1}, with the corresponding growth of a large band at 1862 cm^{-1} and two smaller bands at 1770 and 1786 cm^{-1}. The band at 1862 cm^{-1} is considerably more intense than either of those associated with it at 1770 and 1786 cm^{-1} and suggests that the

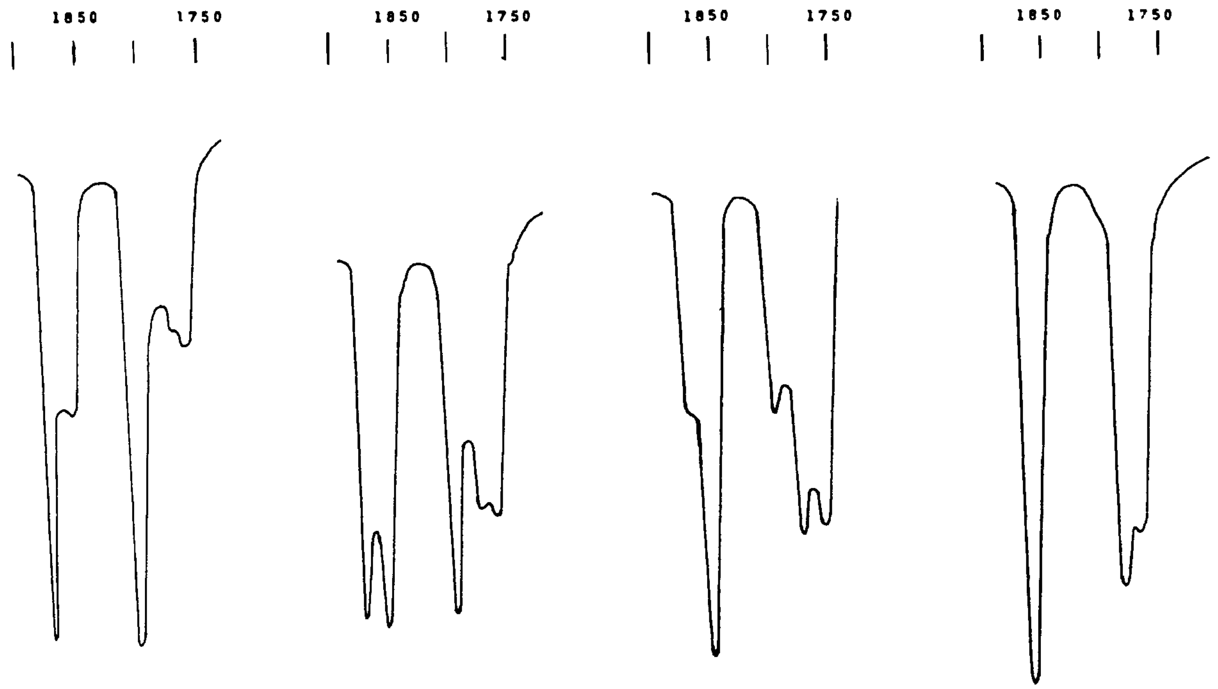


Figure 3. (Left to right) (a) $\nu(\mathrm{C{\equiv}O})$ ($\mathrm{cm^{-1}}$) region of 2.0×10^{-3} M $\mathrm{Na^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-}$ in THF; (b) 8.25×10^{-3} M in dibenzo-18-crown-6 (DBC); (c) 1.65×10^{-2} M DBC; (d) 2.1×10^{-2} M DBC. Further additions of DBC up to 6.9×10^{-2} M had no effect upon the relative intensities of the two bands at 1770 and 1786 $\mathrm{cm^{-1}}$.

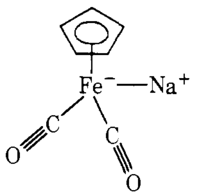
two low frequency bands represent two distinct species appearing upon crown ether addition that possess a fortuitously equivalent high frequency band, i.e., species B, $\nu(\mathrm{C{\equiv}O})$ 1862, 1770, and species C, $\nu(\mathrm{C{\equiv}O})$ 1862, 1786 $\mathrm{cm^{-1}}$. Continued addition of crown ether beyond the equivalence point (ratio crown ether:iron anion 1:1) did not alter the relative intensities of the carbonyl bands observed, the ratio $\nu(1770)/\nu(1786)$ remaining constant subsequent to the removal of species A. To confirm that the bands at 1770 and 1786 $\mathrm{cm^{-1}}$ were indeed due to two distinct anion environments we performed variable temperature infrared experiments. As the temperature is raised the ratio $\nu(1770)/\nu(1786)$ increases, and lowering the temperature causes a decrease in the ratio. Both these temperature variation effects are reversible thus proving that the bands at 1770 and 1786 $\mathrm{cm^{-1}}$ do indeed arise from two equilibrating anion species.[14]

Thus, the above studies indicate that $\mathrm{(\eta^5\text{-}C_5H_5)Fe(CO)_2{}^-Na^+}$ exists in solution as a dynamic equilibrium of three species, A, B, and C, with the following infrared spectral data: A $\nu(\mathrm{C{\equiv}O})$ 1877, 1806; B 1862, 1770; and C 1862, 1786 $\mathrm{cm^{-1}}$.

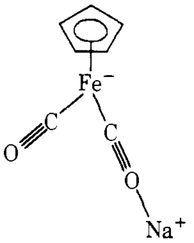
It is clear from the reduction in the abundance of A as a function of changing solvents from THF to DME, and its removal upon addition of the crown ether, that species A is some form of tight ion pair. It cannot, however, be a tight ion pair of the type observed by Edgell and also by Brown which involved the cation bonding with a terminal carbonyl oxygen. If this were the case the new species B and C formed upon removal of the cation by solvent or crown ether would exhibit at least one higher carbonyl stretching frequency upon removal of a bridging environment for the cation bound carbonyl group. Exactly the opposite is found. This decrease in stretching frequency can only be explained in terms of the cation coordinating to the anion at some other site, where, upon removal from this site, a greater amount of electron density is made available for retrodative bonding to the carbonyl groups. Two such sites exist, the metal atom itself, or the π-system of the cyclopentadienyl ligand. Studies on the protonation of ferrocene, and on the Friedel-Crafts reactions of ferrocence, indicate the initial attachment of the cation in both cases to the iron atom.[11] While there is some ambiquity about the Friedel-Crafts mechanism, there is none concerning the structure of the protonated ferrocene cation. We therefore suggest that ion pairing in this species A occurs directly to the transition metal center. Since this work was completed McVicker has reported direct magnesium-iron covalent bonding in the related system $\mathrm{Mg[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2}$. Some cleavage to ionic species involving carbonyl bridged ion pairs was observed in this study.[12] The species B and C reported in this work behave in every respect, solvent dependency, variable temperature dependency, and carbonyl stretching frequencies, as a pair of equilibrating ion pairs where B involves a tight ion pair with a cation carbonyl oxygen interaction, and C is a solvent (or crown ether) separated ion pair.[15] For example, Edgell has reported that the transformation $\mathrm{Co^-(CO)_3CONa^+S \rightarrow Co^-(CO)_4 + SNa^+}$ is exothermic, as is the transformation B → C. Further, the solvent separated ion pair would be expected to exhibit at least one carbonyl stretching frequency significantly higher than for the tight ion paired species. The other frequency could be expected to be slightly lower; however, coupling and inadequate resolution of the broad band at 1862 $\mathrm{cm^{-1}}$ could easily be responsible for our inability to observe this expected feature. The frequency at 1770 $\mathrm{cm^{-1}}$ ascribed to the bridging carbonyl is significantly higher than that observed by McVicker (1713 $\mathrm{cm^{-1}}$) for $\mathrm{[(\eta^5\text{-}C_5H_5)Fe(CO)(COMg\tfrac{1}{2})]}$, and this is probably due to the fact that the magnesium atom being dipositively charged will cause a greater shift of electrons from the iron atom into the carbonyl antibonding orbitals, thus reducing the observed frequency to a much greater extent. The shift from 1770 to 1786 is more in keeping with those observed by Edgell and Brown in their more closely related systems involving a sodium bridged carbonyl group.

Thus, the sodium dicarbonyl(η^5-cyclopentadienyl)ferrate system exists as a dynamic equilibrium of three species as outlined below.

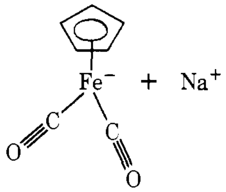
This represents the first example of the carbonylate transition metal system that ion pairs via a direct alkali metal-transition metal bond. Two major reasons for this new mode of ion pairing being observed in the present system may be proposed.



A



B

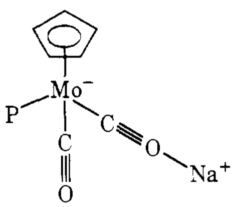


C

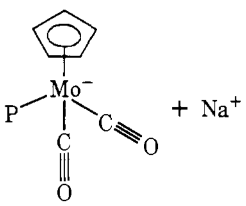
(a) In comparison to $Co(CO)_4^-$ and $Mn(CO)_5^-$, the iron anion exhibits considerably greater nucleophilicity; i.e., relative nucleophilicities are Fe:Mn:Co 7×10^7:77:1.[13] Coupling this with the fewer number of good π-accepting carbonyl ligands a greater buildup of electron density on the iron atom seems reasonable.

(b) The iron anion is nominally three coordinate. The presence of a fourth ligand, the solvated cation, may be an added factor.

Support for these ideas comes from a related infrared study we performed on $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OPh)_3)]^-Na^+$. In THF this anion exhibits two broad stretching frequencies at 1832 and 1732 cm^{-1}. Gradual addition of the crown ether removed the low frequency band at 1732 cm^{-1} as a new band appeared at 1749 cm^{-1}. The band at 1832 cm^{-1} remained essentially unchanged. This behavior exactly parallels that of two ion pairs of the type B and C, i.e.,



B′



C′

No changes were observed that indicated any molybdenum-sodium interactions. (It is significant that McVicker also failed to observe or isolate any molybdenum-magnesium bonded complexes in contrast to his results with the related iron systems.) The nucleophilicity of the Mo anion is in the range of the Co and Mn carbonylate anions, and is also already four coordinate. The molybdenum study also confirms the relative unimportance of the cyclopentadienyl ligand as a site for the interaction of the sodium cation.

Finally, it is of interest that the addition of crown ether to the iron anion does not totally remove the tight ion pair B from the system; i.e., the equilibrium $B \rightleftharpoons C$ does not lie all the way to C. There is, of course, no reason why it should. Smid and co-workers have previously shown that in low polarity solvents salt-crown ether complexes exist as a dynamic mixture of two isomeric forms, $A^-M^+C \rightleftharpoons A^-CM^+$. The equilibrium constant $[A^-CM^+]/[A^-M^+C]$ varies considerably with solvent and temperature, but is independent of anion and crown concentrations. In the present system the species B and C formed when an excess of the crown ether has been added are thus best understood in terms of crown complexed contact ion pairs (B) and crown separated ion pairs (C).

We have attempted to ascertain the enthalpy difference between the two forms via variable temperature infrared, using the two bands at 1770 and 1786 cm^{-1}. This attempt was complicated by the relatively poor resolution due to band width and closeness of the frequencies, coupled with a tendency for the iron anion to undergo slow decomposition during the long equilibration periods at elevated temperatures. However, the values all lay within the range 0.67 ± 0.15 kcal/mol which is quite significantly less than the values of around 3.0 kcal/mol obtained by Smid for various fluorenyl sodium crown ether systems in the same solvent.[10a] The enthalpy difference between crown complexed ion pairs and crown separated ion pairs will depend upon several features of the system, solvent, crown ether, anion size, and charge delocalization. The present result in THF may be taken as some measure of the greater bond strength of the sodium-carbonyl oxygen ion pairing interaction in comparison to the type of bonding that takes place between the cation and the anion in the fluorenyl tight ion pairing.

We are continuing our studies on this and various other carbonylate metal anion systems.

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References and Notes

(1) W. F. Edgell, J. Lyford IV, A. Barbetta, and C. I. Jose, *J. Am. Chem. Soc.*, **93**, 6403 (1971).
(2) W. F. Edgell and J. Lyford IV, *J. Am. Chem. Soc.*, **93**, 6407 (1971).
(3) W. F. Edgell and M. Szwarc, Ed., "Ions and Ion Pairs in Organic Reactions", Wiley, New York, N.Y., 1972, and references therein.
(4) C. D. Pribula and T. L. Brown, *J. Organomet. Chem.*, **71**, 415 (1974).
(5) J. P. Collman, J. N. Cawes, and J. I. Brauman, *J. Am. Chem. Soc.*, **94**, 5905 (1972).
(6) R. B. King, *Adv. Organomet. Chem.*, **2**, 157 (1964).
(7) K. H. Pannell and G. M. Crawford, unpublished results.
(8) R. B. King and K. H. Pannell, *Inorg. Chem.*, **7**, 2356 (1968).
(9) R. B. King, K. H. Pannell, C. A. Eggers, and L. W. Houk, *Inorg. Chem.*, **7**, 2353 (1968).
(10) (a) U. Takaki, T. E. Hogen Esch, and J. Smid, *J. Am. Chem. Soc.*, **93**, 6760 (1971); (b) *J. Phys. Chem.*, **76**, 2152 (1972).
(11) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds Vol. II. The Transition Metals", 3d ed, Methuen, London, 1968, Chapter 4.
(12) G. B. McVicker, *Inorg. Chem.*, **14**, 2087 (1975).
(13) R. E. Dessy, R. L. Pohl, and R. B. King, *J. Am. Chem. Soc.*, **88**, 5121 (1966).
(14) Addition of MeI to solutions of the anion caused removal of all these bands, and formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$, ν(CO) 2003, 1946 cm^{-1}; i.e., confirmation that *all* ν(CO) bands discussed are due to anion environments.
(15) No changes in $\nu(C{\equiv}O)$ for A, B, and C were observed upon the addition of the crown ether. The solvation of the cation by THF or crown ether insufficiently changes the anion environment in the specific ion pairs to affect the carbonyl stretching frequencies.