Mössbauer Spectroscopy of Tricarbonylferrole-Iron Tricarbonyl Derivatives. The Resolution of Two Slightly Nonequivalent Iron Atoms

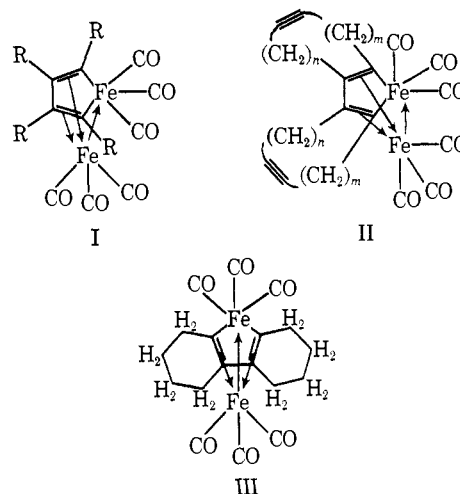R. H. Herber,[1] R. B. King,*[2] and M. N. Ackermann[3]

*Contribution from the School of Chemistry, Rutgers University,
New Brunswick, New Jersey 08903, Department of Chemistry,
University of Georgia, Athens, Georgia 30602, and Department of Chemistry,
Oberlin College, Oberlin, Ohio 44074. Received March 7, 1974*

Abstract: The two nonequivalent iron atoms in several tricarbonylferrole-iron tricarbonyl derivatives (see structures I, II, and III in text) could be resolved in Mössbauer spectra taken in glassy *n*-butylbenzene matrices at 85 ± 3°K even in cases where they could not be resolved in solid state Mössbauer spectra at the same temperature. The doublet with a quadrupole splitting in the range 1.22–1.26 mm/sec can be assigned to the iron atom of the iron tricarbonyl group bonded to all four carbon atoms of the ferrole ring whereas the other doublet at a less positive isomer shift with a quadrupole splitting in the range 0.94–1.02 mm/sec can be assigned to the iron atom in the ferrole ring. The implications of this work in connection with the resolution of two only slightly nonequivalent iron atoms by Mössbauer spectroscopy are discussed.

Since the earliest application of ^{57}Fe Mössbauer effect spectroscopy to the study of cyclopentadienyliron derivatives,[4-6] this technique has become a major spectroscopic tool for the elucidation of bonding and structure in a wide range of organoiron compounds[7,8] and can frequently be used to great advantage for the characterization of such species containing two or more distinct iron atoms.[8] In addition, Mössbauer spectroscopy is a useful technique for comparing molecular structures in neat solid covalent crystals with those in inert solvents where crystalline stacking forces may be presumed to have a negligible effect. The potential value of Mössbauer spectroscopy for such problems is particularly great when the metal atoms are only slightly nonequivalent making spectroscopic techniques not directly measuring the metal atom (*e.g.*, infrared ν(CO) frequencies in metal carbonyls) too insensitive to provide the necessary differentiation.

An extensive series of bimetallic iron carbonyls in which the two iron atoms are known by X-ray crystallography[9] to be slightly nonequivalent are the tricarbonylferrole–iron tricarbonyl derivatives I,[10] II,[11] and III.[12,13] None of the reported spectroscopic studies on such compounds provides a direct differentia-

tion of the two nonequivalent iron atoms in these structures. It was felt that Mössbauer spectroscopy might provide a means for differentiating these two nonequivalent iron atoms and thus the study reported in this paper was undertaken. The results obtained provide some general insight into problems associated with the resolution of two only slightly nonequivalent metal atoms by Mössbauer spectroscopy.

I   II

III

Experimental Section

The ^{57}Fe Mössbauer spectra were obtained in standard transmission geometry, using a constant acceleration spectrometer of the type described earlier.[14] The spectrometer was calibrated using National Bureau of Standards SRM 1541, 0.85 mil 99.99% metallic iron as previously described.[15] All isomer shifts reported in this paper are with reference to the center of a room temperature metallic iron absorber spectrum. The neat solid absorbers were ground to minimize crystal orientation line asymmetry effects and sandwiched between pieces of iron-free aluminum foil prior to

(1) Rutgers University.
(2) University of Georgia.
(3) Oberlin College.
(4) (a) R. H. Herber, H. A. Stöckler, and G. K. Wertheim, paper presented at the 140th Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, abstracts paper 17, p 9T: (b) G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, 38, 2106 (1963).
(5) U. Zahn, P. Kienle, and H. Eicher, *Z. Phys.*, 166, 220 (1962).
(6) L. M. Epstein, *J. Chem. Phys.*, 36, 2731 (1962).
(7) For a recent review of this field, see R. H. Herber in "Mössbauer Spectroscopy and its Applications," Proceedings of a Panel, I.A.E.A., Vienna, 1972, and references therein.
(8) (a) N. N. Greenwood and T. C. Gibb, "Molecular Spectroscopy," Chapman and Hall, London, 1971; (b) V. I. Gol'danskii and R. H. Herber, Ed., "Chemical Applications of Mössbauer Spectroscopy," Academic Press, New York, N. Y., 1968.
(9) A. A. Hock and O. S. Mills, *Acta Crystallogr.*, 14, 139 (1961).
(10) (a) G. N. Schrauzer, *J. Amer. Chem. Soc.*, 81, 5307 (1959); (b) W. Hübel and E. H. Braye, *J. Inorg. Nucl. Chem.*, 10, 250 (1959).
(11) R. B. King and M. N. Ackermann, *J. Organometal. Chem.*, 60, C57 (1973).
(12) R. B. King, I. Haiduc, and C. W. Eavenson, *J. Amer. Chem. Soc.*, 95, 2508 (1973).
(13) H. B. Chin and R. Bau, *J. Amer. Chem. Soc.*, 95, 5068 (1973).

(14) R. L. Cohen, P. G. McMullin, and G. K. Wertheim, *Rev. Sci. Instrum.*, 34, 671 (1963). See also G. M. Calvius and E. Kankeleit, ref 7; Y. Hazony and R. H. Herber in "Physical Methods of Chemistry," Vol. I, Part III, A. Weissberger and B. W. Rossiter, Ed., Wiley-Interscience, New York, N. Y., 1972.
(15) J. J. Spijkerman, J. R. deVoe, and J. C. Travis, *Nat. Bur. Stand. (U. S.), Spec. Publ.*, 260–20 (1970); R. H. Herber in "Mössbauer Effect Methodology," Vol. 6, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1971.

Table I. ^{57}Fe Mössbauer Data for Tricarbonylferrole-Iron Tricarbonyl and Related Model Compounds[a]

Compound (absorber)	Structure[d]	Matrix[e]	Temp, °K	IS[a,b] (mm/sec)	QS[a,b] (mm/sec)	Γ+[a,b] (mm/sec)	Γ-[a,b] (mm/sec)	R[c] (I+/I-)
		(a) Tricarbonylferrole-Iron Tricarbonyl Derivatives						
Me4C4Fe2(CO)6	I, R = CH3	Neat	85.5	-0.010	1.157	0.592	0.560	1.29
Et4C4Fe2(CO)6	I, R = C2H5	Neat	87	-0.006	1.163	0.587	0.623	1.28
		0.36 M BuPh	83.5	A, +0.020	1.257	0.263	0.296	0.98
				B, -0.055	1.019	0.237		
Ph4C4Fe2(CO)6	I, R = C6H5	Neat	86	-0.001	1.152	0.474	0.510	0.87
		0.13 M BuPh	82	+0.023	1.098	0.369	0.270	1.06
(C12H16)2Fe2(CO)6	II, m = 4; n = 4	Neat	84	+0.005	1.126	0.536	0.346	1.39
		0.14 M BuPh	83.5	A, +0.039	1.241	0.251	0.331	0.92
				B, -0.078	1.007	0.243		
(C13H18)2Fe2(CO)6	II, m = 4; n = 5	Neat	85.5	-0.003	1.139	0.415	0.320	1.12
(C14H20)2Fe2(CO)6	II, m = 5; n = 5	Neat	86.5	-0.009	1.122	0.532	0.520	1.06
(C14H20)2Fe2(CO)6	II, m = 4; n = 6	Neat	86.5	-0.009	1.140	0.576	0.598	1.05
(C15H22)2Fe2(CO)6	II, m = 5; n = 6	Neat	84	-0.012	1.108	0.515	0.504	1.01
C12H16Fe2(CO)6	III	Neat	82	A, +0.088	1.226	0.318	0.381	1.06
				B, -0.053	0.945	0.359		
		0.23 M BuPh	83	A, +0.047	1.219	0.293	0.273	1.00
				B, -0.087	0.951	0.236		
		(b) Related Model Compounds						
C4H4Fe(CO)3	IV, R = H	Neat[f]	78	+0.02	1.54			
		50:50 (v/v) BuPh	86	+0.014	1.487	0.381	0.391	0.98
Ph4C4Fe(CO)3	IV, R = C6H5	Neat	82	-0.056	1.516	0.249	0.358	0.91
C8H6Fe(CO)3	V	Neat	83.5	+0.062	1.659	0.340	0.356	0.84
		1.64 M BuPh	83.5	+0.060	1.703	0.322	0.357	0.97
C8H8Fe(CO)3	VI	Neat	82	+0.082	1.186	0.339	0.322	1.40
		0.82 M BuPh	84	+0.101	1.178	0.299	0.317	0.97
C6H8Fe(CO)3	VIII	50:50 (v/v) BuPh	82.5	+0.020	1.394	0.332	0.340	0.99
C4H4Fe2(CO)6	VII	Neat	82	+0.038	0.965	0.384	0.444	0.98
		BuPh	82	+0.057	0.966	0.286	0.308	0.99

[a] Estimated errors of the IS and QS data are ±0.015 mm/sec. The estimated errors take into account that the IS and QS parameters involve estimates of the positions of two resonance maxima in each case. [b] The parameters in this table are reported to one more significant figure than is justified by the estimated experimental errors. The line width parameters are calculated from the Lorentzian fitting program and have estimated errors of ±0.005 mm/sec. [c] Estimated error: ±0.01. [d] These structures are given in the text. In the structures, II, of the compounds (C13H18)2Fe2(CO)6, (C14H20)2Fe2(CO)6, and (C15H22)2Fe2(CO)6 containing methylene chains of unequal length (i.e., m = 4, n = 5, and 6; m = 5, n = 6) there are ambiguities concerning the positions of these unequal methylene chains in structure II, but these ambiguities do not affect any of the conclusions in this paper. [e] BuPh = n-butylbenzene. [f] Data from R. Grubbs, R. Breslow, R. Herber, and S. J. Lippard, J. Amer. Chem. Soc., 89, 6864 (1967); Γ+, Γ-, and R are not given in this paper.

mounting in the liquid nitrogen cooled dewar. Sample temperatures were monitored with calibrated thermocouples and were constant to ±2° over the data acquisition time interval. Data reduction of the Mössbauer results was carried out using a least-squares matrix inversion program[16] suitably modified to run on the Rutgers IBM 360/67 computer. In this program the effect magnitude, line width, and line position are treated as independent variables in a five-step iterative procedure. The results obtained under these conditions consisted of a two resonance maximum fit with one line (the line lying at positive velocities with respect to the spectrum centroid) generally showing a considerably larger line width than the other. Moreover, as expected, such spectra show area ratios (i.e., the ratio of the area under the more positive velocity peak to that under the more negative velocity peak) which are very significantly different from unity, sometimes by as large as a factor of 1.5 or greater. Attempts to fit such spectra to three or four Lorentzian maxima were generally unsuccessful and did not lead to unique solutions for the required parameters.

In order to minimize crystal orientation caused asymmetries (i.e., in order to allow the specification of equal intensities of the resonance effect magnitude for each pair of the four components of the Mössbauer spectrum) as well as to reduce line width problems associated with excessive sample thicknesses, Mössbauer spectra were also obtained on frozen solutions of the sample compounds in n-butylbenzene as discussed below. This solvent was chosen since it is expected to be noncoordinating with respect to the solutes in question and since it has an exceptionally high temperature dependence of the viscosity.[17] This latter property, which amounts to a change in excess of 47 orders of magnitude in the viscosity co-efficient between room temperature and 78°K, is especially desirable in the context of the present study, since it may be safely assumed that on (rapid) cooling of the solutions diffusional processes are greatly slowed down that the growth of microcrystallite solute domains is effectively prevented. Hence, the frozen glassy matrix is assumed to consist of isolated solute molecules in an inert matrix of solvent molecules, randomly oriented with respect to the solute and with the optical axis of the spectrometer. Under these conditions the intensity ratio of the two components of the quadrupole split doublet should be independent of crystal orientation (texture) effects.[18] Making the assumption that any vibrational anisotropy of the iron atom (Gol'danskii-Karyagin effect)[19] is negligible at ~80°K in these compounds, the computer fit can be constrained by initial estimates of equal line widths and intensities of the two components of a given doublet. The very small departure of the R values listed in Table I from unity reflect the probably adequacy of this assumption for n-butylbenzene solutions of the samples. A more rigorous test of this assumption would require a complete ^{57}Fe Mössbauer effect study over a temperature range in order to determine that R is, in fact, not a temperature dependent quantity, as implied by the above. This analysis does not require equal f factors (recoil-free fraction) for the two distinct iron atoms although this is probably the case to a very good approximation in these molecular solids.

An additional advantage to the use of the frozen solution technique is that thickness broadening effects, which are commonly encountered in trying to prepare adequate polycrystalline absorbers, are minimized, thus leading to a narrowing of the resonance lines and a concomitant increase in the resolution of the spectral parameters.

(16) Developed by R. P. Bell, Boston University; modified by J. Fischer and M. F. Leahy, Rutgers University.

(17) A. C. Ling and J. E. Willard, J. Phys. Chem., 72, 1918, 3349 (1968).

(18) H. D. Pfannes and U. Gonser, Appl. Phys., 1, 93 (1973).

(19) For a discussion of this effect and original references, see pp 74–76 of ref 8; V. I. Gol'danskii and E. F. Makarov, ref 8b, pp 102–107; R. H. Herber and S. C. Chandra, J. Chem. Phys., 54, 1847 (1971).

Mössbauer spectra obtained on such samples were analyzed by the computer in terms of three resonance maxima, a, b, and c, in which a and b are the positive velocity components of two distinct quadrupole doublets and c is the resonance maximum resulting from the fortuitous superposition of the negative velocity components of the same two doublets.

Such an analysis leads to unique solutions for the isomer shifts (IS) and quadrupole splittings (QS) as well as to reasonable and internally self-consistent values for the line widths and area ratios of the two distinct iron sites. In the tricarbonylferrole–iron tricarbonyl derivative, III, where two distinct iron resonances could be resolved even for the neat solid, no major differences (i.e., larger than ±0.025 mm/sec) were observed in the IS and QS values of the neat solid compared to the frozen solution data at the same temperature. Whether the small differences in the IS parameter which are observed are due to specific chemical effects (e.g., the relaxation of crystal stacking forces) was not explored further due to the small magnitude of the differences observed for the neat solid and solution spectra. In any case, our observations suggest that there are no major structural differences between the entities present in the neat covalent crystalline solids and the species present in their respective solutions and hence that the structural implications deduced from solution spectroscopic techniques (infrared and nmr methods) can be directly correlated with the results obtained from X-ray diffraction studies on single crystals of the neat solid.

Preparation of Compounds. The tricarbonylferrole–iron tricarbonyl derivatives I (R = CH_3, C_2H_5, and C_6H_5) and II ($m = 4$, $n = 4, 5$, and 6; $m = 5$, $n = 5$ and 6) were prepared from benzalacetonetricarbonyliron and the appropriate alkyne or macrocyclic alkadiyne, respectively.[11] The tricarbonylferrole–iron tricarbonyl derivative III was prepared from $Fe_3(CO)_{12}$ and 1,7-cyclododecadiyne by Professor Ionel Haiduc while at the University of Georgia. Cyclobutadienetricarbonyliron (IV, R = H) and benzocyclobutadienetricarbonyliron (V) were prepared by Professor Avi Efraty of Rutgers University using published procedures.[20] The cyclooctatetraenetricarbonyliron (VI)[21] was provided by M. K. Landsberg. Butatrienehexacarbonyldiiron (VII),[22] 1,3-cyclohexadienetricarbonyliron(VIII),[23] and tetraphenylcyclobutadienetricarbonyliron (IV, R = C_6H_5)[24] were prepared by the cited published procedures.
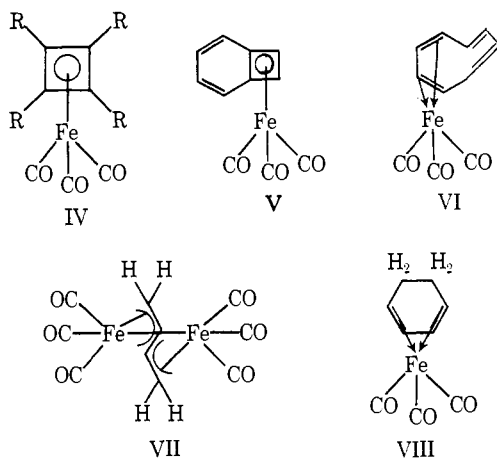
Results and Discussion

The numerical parameters extracted from the Mössbauer spectra at liquid nitrogen temperature for the tricarbonylferrole–iron tricarbonyl complexes as well as for a number of model compounds are summarized in Table I. A typical [57]Fe Mössbauer spectrum is shown in Figure 1. All of the compounds examined have isomer shifts (IS) lying within ±0.1 mm/sec of that of metallic iron at room temperature in accord

(20) G. F. Emerson, L. Watts, and R. Pettit, J. Amer. Chem. Soc., 87, 131 (1965).

(21) (a) T. A. Manuel and F. G. A. Stone, J. Amer. Chem. Soc., 82, 366 (1960); (b) R. B. King, Organometal. Syn., 1, 126 (1965).

(22) A. Nakamura, P. J. Kim, and N. Hagihara, J. Organometal. Chem., 3, 7 (1965); R. B. King, J. Amer. Chem. Soc., 88, 2075 (1966).

(23) R. B. King, Organometal. Syn., 1, 129 (1965).

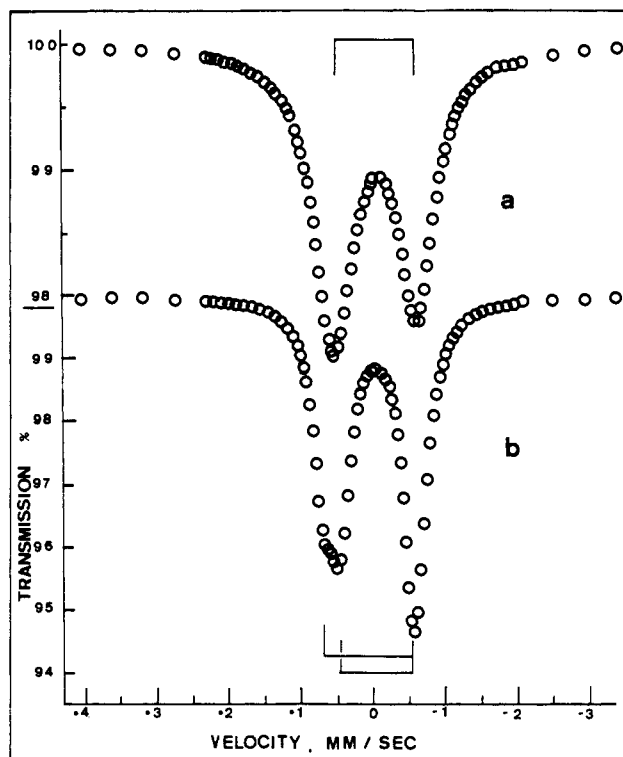(24) P. L. Maitlis and M. L. Games, J. Amer. Chem. Soc., 85, 1887 (1963).

Figure 1. [57]Fe Mössbauer spectra of $(C_2H_5)_4C_4Fe(CO)_6$ (I, R = C_2H_5). (a) Spectrum of the neat solid at 87°K. The average line width of the two resonance maxima is 0.605 mm/sec and the intensity ratio of the two components is 1.28. (b) Spectrum of an 0.38 M solution in n-butylbenzene at 83.5°K. Using the assumptions discussed in the text, the computer fit to a four-line spectrum results in an average line width of 0.265 mm/sec and an average intensity ratio of 0.98. The assignments of the doublet components are indicated above and below the two curves, respectively.

with their formulations as low spin iron complexes in which the metal atom has an 18-electron valence shell configuration. The quadrupole splittings (QS) observed for diene–iron tricarbonyl derivatives containing a single $Fe(CO)_3$ group lie in the range 1.18–1.70 mm/sec with the magnitude of this parameter decreasing with increasing ring size. The QS of 1.39 mm/sec of cyclohexadienetricarbonyliron (VIII) can be taken as representative of the value associated with a typical diene–$Fe(CO)_3$ system.

Butatrienehexacarbonyldiiron (VII) has been shown[25] to have a structure containing two equivalent $Fe(CO)_3$ groups. The magnitudes of the line widths (Γ_+, Γ_-) and the intensity ratio R of 1.0 in the Mössbauer spectrum of VII are consistent with the identity of the two $Fe(CO)_3$ groups and thus can be taken as representative of the values of these parameters to be expected for a diiron hexacarbonyl derivative in which the two $Fe(CO)_3$ groups are structurally identical. The QS of 0.97 mm/sec for VII is essentially identical for the neat solid and the frozen solution in glassy n-butylbenzene suggesting that the structure of VII is identical in solution and in the crystalline state. Furthermore, our present measurements of 0.97 ± 0.02 mm/sec for the QS of VII are in good agreement with the value of 0.98 mm/sec determined several years ago[26] for this same compound.

(25) D. Bright and O. S. Mills, J. Chem. Soc., Dalton Trans., 2465 (1972).

(26) R. B. King, L. M. Epstein, and E. W. Gowling, J. Inorg. Nucl. Chem., 32, 441 (1970).

A strikingly different observation can be made for the tricarbonylferrole–iron tricarbonyl derivatives I, II, and III listed in Table I. Although at first glance the Mössbauer spectra of these compounds at liquid nitrogen temperature appear to be those of a simple quadrupole split doublet, the wide (0.5 to 0.7 mm/sec) and unequal line widths, as well as the marked departure of the intensity ratios R from unity, suggest that these compounds contain two distinct iron atoms implying structural nonequivalence of the two $Fe(CO)_3$ groups similar to the inferences drawn by Emerson, Mahler, Petit, and Collins[27] in their study of the unsubstituted tricarbonylferrole–iron tricarbonyl (I, R = H) and in contrast to the analysis of the Mössbauer spectrum of $C_{29}H_{20}Fe_2(CO)_6$ reported by Greatrex, Greenwood, and Pauson[28] in which both $Fe(CO)_3$ groups were found to be equivalent.

Using the frozen solution technique as discussed in detail in the Experimental Section, the Mössbauer spectra of the tricarbonylferrole–iron tricarbonyl derivatives in glassy n-butylbenzene matrices could be fit to two pairs of quadrupole split doublet spectra in which initially the line width and effect magnitude of the two partially resolved components were given equal values, while the total area under the third resonance maximum observed in the spectrum (presumed to arise from a fortuitous overlap of the two negative velocity components of the two doublets) was initially set to the sum of the other two (positive velocity) components. In a subsequent fit, the results of the initial calculation were used as initial estimates and the intensities and line widths of the two (partially resolved) peaks were allowed to vary as free parameters. The results of this analysis are listed in Table I for the tricarbonylferrole–iron tricarbonyl derivatives I (R = C_2H_5), II (m = 4, n = 4), and III. For the other tricarbonylferrole–iron tricarbonyl derivatives, either the solubility in n-butylbenzene was too low to give satisfactory spectra or the overlap of both doublet spectra prevented the resolution of the two individual doublets. In the special type of tricyclic tricarbonylferrole–iron derivative III where the two iron Mössbauer resonances could be resolved even in the neat solid spectrum, the Mössbauer parameters observed for the neat solid and for the n-butylbenzene solution are in good agreement except, as expected, for the intensity ratio R for the reasons noted above. From this observation on the Mössbauer spectrum of III, the crystalline stacking forces can be inferred to be insignificant in determining the bond angles and distances in tricarbonylferrole–iron tricarbonyl derivatives, and the structural integrity in these compounds is maintained when the pure solid is dissolved in a glassy matrix. Attempts to fit the other neat solid spectra to more than two resonance peaks were unsuccessful.

For this analysis the two iron atoms in the tricarbonylferrole–iron tricarbonyl complexes are readily distinguishable in terms of the two doublets observed in the Mössbauer spectra, since these spectra consist of one doublet A with a QS in the range 1.22–1.26 mm/sec and a second doublet B with a QS in the range 0.94–1.02 mm/sec. The doublet A has a slightly more

positive IS than the doublet B, although this isomer shift difference is small (less than 0.15 mm/sec).

If the iron tricarbonyl complexes IV (R = H and C_6H_5), VI, and VIII are used as model compounds for an $Fe(CO)_3$ group in a diene–iron tricarbonyl type of system as discussed above, a QS of 1.2–1.4 mm/sec can be inferred to be typical for such an $Fe(CO)_3$ group. The data summarized in Table I indicate that in the tricarbonylferrole–iron tricarbonyl derivatives the average QS for doublet A is 1.24 ± 0.04 mm/sec whereas the average QS for doublet B is 0.98 ± 0.06 mm/sec. This indicates that doublet A can be assigned to the π-bonded $Fe(CO)_3$ group (i.e., the one bonded to four carbon atoms as in diene–iron tricarbonyl complexes) and doublet B can be assigned to the σ-bonded $Fe(CO)_3$ group (i.e., the one in the ferrole ring and bonded to only two carbon atoms). This assignment is also consistent with the more positive isomer shift found for doublet A relative to doublet B, since the σ-bonded $Fe(CO)_3$ group, by virtue of the two carbon–metal σ-bonds, is expected to have a greater s electron density at the metal nucleus compared with the π-bonded $Fe(CO)_3$ group and hence a less positive isomer shift.

This analysis of the tricarbonylferrole–iron tricarbonyl Mössbauer spectra supports the analysis of the data for $[(C_6H_5)_2C_2]_2COFe_2(CO)_6$ suggested by Greatrex, Greenwood, and Pauson[28] in which the isomer shift is -0.011 ± 0.010 (recalculated for metallic iron as reference) and the quadrupole splitting is 0.995 ± 0.010 mm/sec with a line width (Γ) of 0.31 ± 0.02 mm/sec. These authors have inferred from their data analysis that the compound $[(C_6H_5)_2C_2]_2COFe_2(CO)_6$ has structure IX (R = C_6H_5) in which both $Fe(CO)_3$

IX
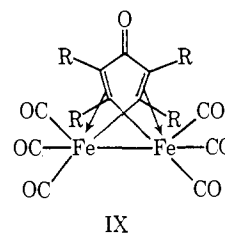
groups are structurally equivalent. Our interpretation of the Mössbauer spectra of the tricarbonylferrole–iron tricarbonyl derivatives I, II, and III in which the two $Fe(CO)_3$ groups are structurally nonequivalent confirms the essential validity of the reported[28] interpretation of the Mössbauer spectrum of IX.

In the present study it has been shown that the careful analysis of ^{57}Fe Mössbauer effect spectra obtained on frozen glassy solution matrices of organometallic iron compounds can lead to the resolution of two slightly nonequivalent iron atoms which cannot be resolved by normal Mössbauer spectra of the neat solids alone. Such spectra are useful not only because the isomer shift, quadrupole splitting, and vibrational anisotropy parameters calculated for the two distinct iron atoms can be related to other structural features but also because they increase the sensitivity of the Mössbauer technique to distinguish nearly similar iron nuclei in soluble polymetallic iron compounds. Furthermore, the observation of Mössbauer spectra of neat solids which show what appears to be only a (broadened) doublet cannot be taken as conclusive evidence for the identity of the two Mössbauer atoms. That such spectra must be interpreted with considerable caution is

(27) G. F. Emerson, J. E. Mahler, R. Pettit, and R. Collins, *J. Amer. Chem. Soc.*, **86**, 3590 (1964).
(28) R. Greatrex, N. N. Greenwood, and P. L. Pauson, *J. Organometal. Chem.*, **13**, 533 (1968).

well demonstrated by the results of the present investigation.

π Groups in Ion Pair Bonding. The Effect of the Cation on the Structural and Spectroscopic Properties of Fluorenyl Ion Pairs

R. Zerger, W. Rhine, and G. D. Stucky*

Contribution from the School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801. Received February 9, 1974

Abstract: The synthesis and isolation of the 1:1 complexes of fluorenyllithium with pentamethyldiethylenetriamine and hexamethylphosphoramide, the 1:1 complex of fluorenylpotassium with tetramethylethylenediamine, the 1:2 complex of fluorenyllithium with tetrahydrofuran, and the unsolvated fluorenyltetra(n-propyl)ammonium salt are described. The visible absorption spectra of these compounds were examined in order to determine the effects of solvation number and cation position on the 340–380 nm band in the fluorenyl carbanion. A comparison of the solid state and solution spectra is given. In addition, the molecular and crystal structure of fluorenylpotassium tetramethylethylenediamine (FlK–TMEDA), $C_{13}H_9K(N_2C_6H_{16})$, was determined from single-crystal X-ray data (2785 reflections) measured on a four-circle Picker X-ray diffractometer equipped with a graphite monochromator. The crystal system is monoclinic with $a = 10,000$ (6) Å, $b = 17.425$ (12) Å, $c = 11.080$ (8) Å, and $\beta = 108.71$ (3)°, four molecules of $C_{13}H_9K(N_2C_6H_{16})$ per unit cell, and $\rho_{calcd} = 1.164$ g cm^{-3}. Least-squares refinement gave a final agreement factor of $R_w = 0.044$ and $R = 0.043$. The tetramethylethylenediamine group is not bidentate but instead bridges two potassium atoms. Each potassium atom is associated with two nitrogen atoms and two fluorenyl groups with a potassium ring plane distance of 3.052 (1) and 2.972 (1) Å. The nitrogen–potassium–nitrogen atom angle is 90.4 (1)°. The geometry of the fluorenyl carbanion agrees well with that predicted by simple molecular orbital calculations.

It is now generally accepted that many of the solution properties of unsaturated alkali metal organometallic compounds can be interpreted in terms of two distinct species which may coexist in a rapid equilibrium.[1]

$$R^-M^+ + nS \rightleftharpoons R^-\|M^+ \tag{1}$$

(S = solvent molecule of solvation)

The distinguishing feature of the two ion pairs, R^-M^+ and $R^-\|M^+$ is presumably a change in the degree of solvation of M^+.

Some information as to what one might expect for the coordination of the metal to the delocalized carbanion for species such as R^-M^+ was recently reported in a series of studies on the solid state molecular structures of disolvated lithium complexes: benzyl-,[2] fluorenyl-,[3] and triphenylmethyllithium.[4] It was noted that the detailed molecular structures of these solvated ion pairs could not be predicted solely by electrostatic considera-

tions but that they were consistent with some directed covalent interaction involving the formation of a three-center bond between an unoccupied lithium orbital and the highest occupied molecular orbital of the carbanion. It was also suggested that, for these carbanions, the position of an alkali metal with respect to the carbanion could be expected to be dependent on the degree of solvation and atomic number of the metal; e.g., a position directly over the five-membered ring of the fluorenyl carbanion was predicted for the heavier alkali metals or for trisolvated lithium. This could result in the possibility of solution equilibria for fluorenyllithium of the form

$$S_2LiF + S \rightleftharpoons S_3LiFl \tag{2}$$

$$S_3LiF + S \rightleftharpoons S_4Li^+ Fl^- \tag{3}$$
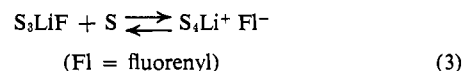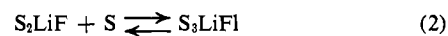
(Fl = fluorenyl) (3)

In the eq 2, the position of the lithium atom with respect to the fluorenyl group may be altered as indicated above.

The nature of the cation-coordinated base interaction is also of importance in understanding the properties of ion pairs. For example, the physical properties of the very important N,N,N',N'-tetramethylethylenediamine

(1) See, for example, T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **87**, 669 (1965); **88**, 307, 318 (1966).
(2) S. P. Patterman, I. L. Karle, and G. D. Stucky, *J. Amer. Chem. Soc.*, **92**, 1150 (1970).
(3) J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, **94**, 7339 (1972).
(4) J. J. Brooks and G. D. Stucky, *J. Amer. Chem. Soc.*, **94**, 7333 (1972).