

2.418 Å in tris(*N,N*-di-*n*-butyldithiocarbamate)iron(III) where the Fe is said to be in equilibrium between the high-spin and low-spin ground states.⁷ The difference in bond lengths between high- and low-spin Fe³⁺ in sixfold-coordination is 0.1 Å, and they are reported as 2.4 and 2.3 Å, respectively.^{8,9} The value of the high-spin Fe³⁺-S distance in the organometallic compounds is frequently influenced by packing considerations of the large ligands, and the sixfold-coordination polyhedron is usually described as a distorted trigonal prism or as an antiprism, i.e., a distorted octahedron. None of these influences is present in this structure and the S octahedron is very regular. It appears that the 2.5-Å bond distance might also be the proper value for high-spin Fe³⁺-S. The Ba-S distances and S-S distance, with the exceptions noted previously, are as expected. Barium is in ninefold-coordination and the polyhedron is a distorted capped trigonal prism.

The density of this phase is 4.72 g/cm³ as compared to 4.14 g/cm³ for the orthorhombic Ba₃FeS₅. Increasing density is achieved by the change in coordination and near close packing of the Ba-S layers. However, size discrepancy inhibits the lateral extent of this close packing and gives rise to channels within which increased packing density is achieved by the formation of S₂ ions. It is conceivable that at even higher pressure the formation of S₃ and higher polysulfides might occur.

After the structure and stoichiometry became known, attempts were made to prepare single-phase material. Systematic experiments finally showed that the largest amount of the hexagonal phase, free of the orthorhombic polymorph,

is produced at 72 kbar and 925 ± 25 °C. The temperature stability range for this phase is very narrow and reaction temperatures outside of these limits do not yield the hexagonal phase. The best material which we prepared from a 3:1:2 mixture of BaS-Fe-S reacted for 12 h still contained Ba₂S₃. Reaction of a 9:4:6 mixture BaS-Fe-S for 5 h at 925 °C produced primarily the hexagonal phase free of Ba₂S₃ but the powder pattern contained several lines of an unknown phase.

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Supplementary Material Available: Table II listing observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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Charge Distribution and Carbonyl Site Exchange in Tricarbonyl(dienyl)iron Cations

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¹³C NMR spectroscopy has been used to study tricarbonyl(dienyl)iron cations. The ¹³C chemical shifts and MO calculations of atomic charge point to an alternation of charge along the dienyl chain with carbons 1, 3, and 5 being less electron deficient than carbons 2 and 4. This charge distribution is in accord with a simple frontier orbital picture of bonding in which the dominant bonding interaction involves electron donation from iron to an empty nonbonding molecular orbital of the dienyl cation ligand. The case for interpretation of chemical shift differences of the dienyl carbons in terms of atomic charge is discussed. Site exchange of the carbonyl ligands was studied by complete line-shape analysis of their ¹³C NMR signals over the temperature range -50 to +65 °C. The measured barrier agrees closely with that calculated for rotation of the tricarbonyliron group by the extended Hückel method. Pairwise exchange has been eliminated for a triphenylphosphine substituted cation. Carbonyl site exchange must occur via tricarbonyliron rotation or via a process which approximates Berry pseudorotation.

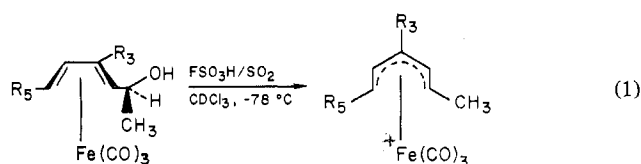
Dienyl cations exhibit the high reactivity characteristic of carbonium ions in general. They cyclize rapidly to give cyclopentenyl cations, except when steric factors intervene, and react rapidly with nucleophiles.^{2a} Yet coordination of the dienyl moiety to a transition metal such as Mn, Co, Ru, or Fe gives derivatives of considerable kinetic stability.^{2b,3} Tricarbonyl(cyclohexadienyl)iron salts survive recrystallization from water!^{2b} The nature of bonding between transition metals and cis dienyl ligands is of interest owing to this dramatic stabilization as well as its relationship to metal-ligand bonding in transition-metal π complexes in general.

Charge distribution tells much about bonding. Thus, we have investigated charge distribution in the title cations.⁴ Interpretation of ¹³C NMR chemical shifts in terms of charge

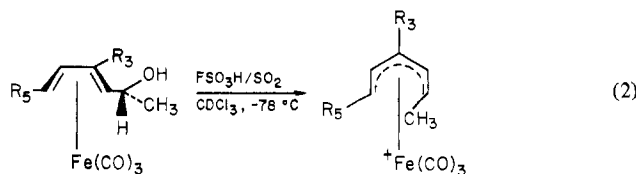
density for carbon atoms bound to transition metals has been common in the organotransition metal literature.⁵ We discuss here evidence for the validity of such an interpretation in the case of the title cations. Finally, we have studied carbonyl site exchange in the title cations and report on the mechanism and activation parameters.

¹³C NMR Spectra

Tricarbonyl(dienyl)iron cations were generated from dienol-Fe(CO)₃ complexes at low temperature in FSO₃H/SO₂/CDCl₃ mixtures. As shown previously, ψ-exo dienol-Fe(CO)₃ complexes ionize stereospecifically to give syn,syn cations (eq 1), whereas ψ-endo dienol-Fe(CO)₃ complexes give syn,anti cations (eq 2).⁶ To facilitate comparisons, data for

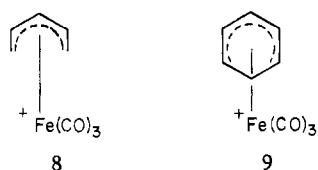


- 1, $R_3 = R_5 = H$
 2, $R_3 = H, R_5 = CH_3$
 4, $R_3 = R_5 = CH_3$
 6, $R_3 = H, R_5 = C_6H_5$



- 3, $R_3 = H, R_5 = CH_3$
 5, $R_3 = R_5 = CH_3$
 7, $R_3 = H, R_5 = C_6H_5$

cations **8** and **9** are reproduced in Table I along with data for **1**–**7**.



A spectrum of **2** labeled with 50% deuterium at C-1 and C-5 led to unambiguous assignment of the C-1 and C-5 signals in the coupled spectrum as those appearing as a broad singlet surrounded by a doublet all centered at 87.5 ppm. Assignment of the remaining signals on the basis of multiplicity in the coupled spectrum and relative intensity was unambiguous. The spectrum of **1** is also straightforward. Signals at 91.0 and 103.2 ppm are assigned to C-1 and C-2 by analogy with **2**. Assignment of the signal at 103.7 ppm to C-4 is consistent with the small (1–4 ppm) upfield shift produced by a β -methyl substituent in tricarbonyl(diene)iron complexes.⁷ The remaining doublet at 95.3 ppm is assigned to C-3, the triplet at 62.0 ppm to C-5, and the quartet to the methyl carbon. These assignments are in agreement with those made independently by Olah et al.⁸ Similar reasoning leads to complete assignments for **3**. A quartet at 20.6 ppm is assigned to the syn (C-5) methyl by analogy to **1** and **2**; thus the upfield quartet at 15.6 ppm must arise from the anti (C-1) methyl. A spectrum of this ion specifically labeled with deuterium at C-1 revealed a shift of 77.5 ppm for this carbon. The remaining signals can be assigned by analogy. The assignments for **1**–**3** were used in combination with relative signal intensities and coupled spectra to deduce reliable assignments for **4**–**7**. As discussed below, our assignments are consistent with those of others.^{8–10}

The data in Table II reveal that the chemical shifts are somewhat solvent and counterion dependent. However, this dependence is not large enough to affect our major conclusions. Rezvukhin et al.⁹ and Birch et al.¹⁰ have reported small solvent effects for tricarbonyl(cyclohexadienyl)iron cations. Our study of **5** over the temperature range -18 to -62 °C showed an average chemical shift change of only 0.2 ppm, with 0.4 ppm being the largest change observed.

The $^1J_{C-H}$ values for dienyl carbons all fall within experimental error of the range 165 ± 6 Hz, magnitudes which are consistent with sp^2 hybridization. No trends in coupling constants which offer further structural information stand out.

Table III lists effects of substituents on the chemical shifts of the dienyl carbons. These shifts exhibit a rough additivity. Thus, using shifts from **1**–**4**, **6**, and **8**, shifts can be calculated

Table I. ^{13}C Chemical Shifts and Coupling Constants^{a, b}

Compd	T, °C	C-1	C-2	C-3	C-4	C-5	CH ₃	R ₃	R ₅	CO
1	-57	91.0 (170)	103.2 (170)	95.3 (170)	103.7 (170)	62.0 (161)	20.4 (124)			197.7
2 ^c	-57	87.5 (161)	103.2 (174)	90.9 (165)	103.2 (174)	87.5 (161)	20.5 (130)		20.5 (130)	198.6
3 ^d	-51	77.5	99.0 (165)	97.5 (174)	104.7 (157)	81.9 (170)	15.6 (124)		20.6 (124)	198.1
4	-51	85.1 (165)	103.1 (165)	109.3	103.1 (165)	85.1 (165)	20.3 (128)	22.6 (130)	20.3 (128)	199.1
5	-51, -62	74.5 (165)	96.5 (165)	117.6	104.3 (165)	80.2 (174)	16.0 (124)	23.3 (132)	20.7 (128)	198.4
6	-54	87.6	102.6	89.7	94.5	88.1	20.0		^e	198.1
7	-54	77.7	98.0 ^f	96.7 ^f	97.1 ^f	82.6	16.4		^g	197.4
8 ^h		65.4 (165, 164)	104.6 (170)	98.6 (180)	104.6 (170)	65.4 (165, 164)				197.3
9 ^{h, i}		63.7 (175)	101.4 (175)	89.0 (184)	101.4 (175)	63.7 (175)	23.1 ⁱ (140)			198.4
14 ^j		68.6	96.6	115.1	99.3	77.4	16.6	23.5	20.5	205.5

^a Chemical shifts (± 0.1 ppm) in ppm downfield from Me₄Si; peaks measured relative to CDCl₃ (capillary) and converted using δ_{cap} CDCl₃ = 77.4 ppm. ^b $^1J_{C-H}$ values (± 5 Hz), measured from the coupled spectra, are given in parentheses. ^c Shifts recorded using the 1-deuterium derivative. ^d Shifts recorded using the derivative with 0.5 atom of deuterium in the 1 and 5 positions. ^e Phenyl shifts (ppm): ipso 132.9, ortho 127.1, meta 129.7, para 131.1. ^f Assignments of these three closely spaced signals are tentative; see text. ^g Phenyl shifts (ppm): ipso 127.1, ortho 127.1, meta 129.8, para 131.3. ^h Data from G. A. Olah, S. H. Yu, and G. Liang, *J. Org. Chem.*, **41**, 2383 (1976). ⁱ See also ref 9 and 10. ^j In CDCl₃; see Experimental Section. Phenyl shifts (ppm): ipso 128.4 ($\nu_{PH} = 50.0$), ortho 132.8 ($\nu_{PH} = 10.3$), meta 129.8 ($\nu_{PH} = 10.3$), para 132.6.

Table II. Solvent and Counterion Dependence of ^{13}C Chemical Shifts (ppm)

Compd	Solvent	C-1	C-2	C-3	C-4	C-5	CH_3
1-BF ₄	CH ₃ NO ₂	87.6	100.0	90.4	100.0	57.3	14.7
1-BF ₄	SO ₂	91.4	104.4	95.3	105.0	62.7	20.5
1-FSO ₃	FSO ₃ H/SO ₂	91.0	103.2	95.3	103.7	62.0	20.4
2-BF ₄	CH ₃ NO ₂	83.6	99.0	86.1	99.0	83.6	14.9
2-FSO ₃	FSO ₃ H/SO ₂	87.5	103.2	90.9	103.2	87.5	20.5

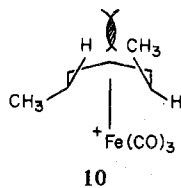
Table III. Substituent Effects on Chemical Shifts of Dienyl Carbons

Substituent	Method of estimation	Substituent effects, ppm ^a				
		C _α	C _β	C _γ	C _δ	C _ε
Syn 1-methyl	$\delta(1) - \delta(8)^b$	25.6	-1.4	-3.3	0.9	-3.4
	$\delta(2) - \delta(1)$	25.5	-0.5	-4.4	0	-3.5
Anti 1-methyl	$\delta(3) - \delta(1)$	15.5	-4.7	2.2	1.5	-9.1
	$\delta(4) - \delta(2)$	18.1	-0.1	-2.4		
3-Methyl	$\delta(5) - \delta(3)$	20.1	-2.5 (C ₂)	-3.0 (C ₁)		
			-0.4 (C ₄)	-1.7 (C ₅)		
Syn 1-phenyl	$\delta(6) - \delta(1)$	26.1	-9.2	-5.5	-0.6	-3.4

^a A positive sign signifies a downfield shift (deshielding). ^b The chemical shift of a carbon of 8 is subtracted from the shift of the corresponding carbon of 1.

for **5** and **7** with an average error of 1.2 ppm. Calculated shifts were used as the basis for assignment of the C-2-C-4 signals for **7**. Comparison of the syn 1-methyl and 3-methyl shifts to those produced by 1- and 3-methyl substituents in tricarbonyl(cyclohexadienyl)iron cations¹⁰ shows fairly close agreement. The syn 1-phenyl group causes β and γ shifts which are substantially larger than those for syn 1-methyl. It is possible that this results from conjugation (π bonding) between the phenyl and dienyl moieties and consequent changes in charge distribution and/or iron-carbon bonding. However, the observed shifts are much smaller than those for the 1-methoxy substituent for which Birch et al. have made just such a proposal in the case of tricarbonyl(cyclohexadienyl)iron cations.¹⁰ The very large α effect of methyl substitution in these ions and the corresponding cyclohexadienyl ions stands out. It is significantly larger than α -methyl effects observed for alkanes (9–10 ppm),¹¹ benzene (9 ppm),¹² isopropyl cation (10 ppm),¹³ or tricarbonyl(diene)iron complexes (16–17 ppm).⁷

Shifts for cations with anti 1-methyl substituents suggest some asymmetry in charge distribution and/or iron-carbon bonding. The large shielding effect of an anti 1-methyl at C-5 (the ϵ position) must arise from the spacial proximity of these carbons (analogous to the γ effect¹⁴). Yet in place of the expected large shielding γ effect at C-3 from the gauche anti 1-methyl a *deshielding* of 2.2 ppm is found. Furthermore, attachment of a methyl at C-3 of **3** to give **5** results in different effects at the two β carbons (C-2 and C-4) and at the two γ carbons (C-1 and C-5). The logical cause of modification of iron to dienyl bonding on introduction of an anti 1-methyl group would be relief of the anti H-anti methyl nonbonded interaction, **10**.



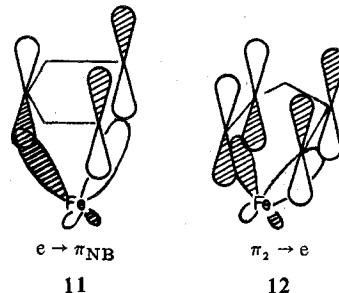
Chemical shifts of the dienyl carbons in these cations are all at higher field than that expected for sp^2 carbons, especially in cations.¹⁵ This has been interpreted as evidence for net

donation of electrons from iron to a dienyl cation ligand, in accord with the stabilizing effect of iron complexation.^{9,10} Some of the shielding must be ascribed to the well-known effect of complexation to a transition metal. For example, the 1- and 2-carbons of butadiene undergo 75 and 51 ppm upfield shifts on formation of the corresponding tricarbonyliron complex.^{7b} Yet the upfield shifts exhibited by carbons in cyclohexadienyl cations on complexation to iron are significantly larger.¹⁰ If these chemical shift changes can be interpreted in terms of changing atomic charges, a point yet to be proven, these data provide evidence for net electron donation from iron to the dienyl cation ligand. The validity of such an interpretation will be taken up below.

The chemical shifts of the para carbons of **6** and **7** allow an assessment of the electronic effect of the 1-dienyltricarbonyliron substituent. By using the correlation between $\delta(\text{C}_{\text{para}})$ values and atomic charges calculated by the CNDO/2 method, the atomic charge at the para carbon (q_{P}) of these ions and their precursors can be estimated.¹⁷ Ionization of ψ -exo dienol complex to give the syn methyl cation **6** causes a downfield shift of C_{P} from 126.6 to 131.1 ppm corresponding to a q_{P} in **6** of +0.0141 e and a $\Delta q_{\text{P}} = +0.0154$ e on ionization. The data for formation of cation **7** are nearly identical: $q_{\text{P}}(\text{7}) = +0.0147$ e, $\Delta q_{\text{P}}(\text{7}) = +0.0163$ e. The electron-withdrawing power at C_{para} (C_{P}) for the 1-dienyltricarbonyliron substituent is the same as that of $\text{NH}(\text{CH}_3)_2^+$ ($\delta(\text{C}_{\text{P}}) = 131.1$ ppm) but less than that for CF_3 ($\delta(\text{C}_{\text{P}}) = 131.7$ ppm) or CHO ($\delta(\text{C}_{\text{P}}) = 134.0$ ppm).

The salient feature of the dienyl carbon chemical shifts of these cations is alternation along the chain with C-1, C-3, and C-5 shielded more than C-2 and C-4. Every report of ^{13}C spectra of these cations has noted this pattern.^{4,8-10} Cation **2** in which all dienyl carbons are secondary (disubstituted) is a clear example with C-1, C-3, and C-5 at 87.5, 90.9, and 87.5 ppm, respectively, and C-2 and C-4 at 103.2 ppm. This pattern is clearly discernible in the shifts for **1**, **3**, **6**, and **9**; and after correction for large substituent effects (α methyl, α and β phenyl, etc.), it also stands out in the remaining cations **4**, **5**, and **7**. By contrast, in uncomplexed cyclohexadienyl cations carbons 1, 3, and 5 are the most electron deficient and are strongly deshielded with respect to carbons 2 and 4.¹⁵

Bonding in tricarbonyl(dienyl)metal complexes has been discussed by Hoffmann and Hofmann.¹⁸ The neutral "octahedral" fragment tricarbonyliron possesses a doubly occupied e (in C_{3v} symmetry) frontier orbital pair which, in effect, provides one donor and one acceptor orbital.¹⁹ The dienyl cation possesses a nonbonding LUMO of appropriate symmetry for interaction with one of the e pair on iron. Thus, the dominant (HOMO-LUMO) bonding interaction is expected to be donation from iron to the nonbonding dienyl orbital (**11**). This should be accompanied by a weaker back-donation from dienyl π_2 to the other frontier e orbital of the tricarbonyliron fragment (**12**); see Figure 1. The



consequence for a dienyl cation of coordination to a tricarbonyliron fragment should be to increase electron density at carbons 1, 3, and 5 and to decrease it at carbons 2 and 4. The chemical shift data lend credence to this simple bonding

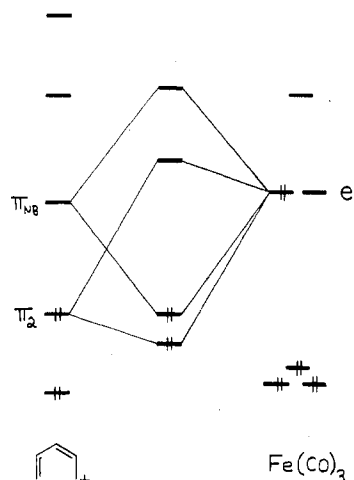


Figure 1. Frontier orbital interactions between a dienylium cation ligand and a neutral tricarbonyliron fragment (C_{3v} symmetry).

model if one assumes that they reflect atomic charge in a major way.

Molecular Orbital Calculations of Charge Distribution

Calculated charge distributions for tricarbonyl(dienyl)iron cations are listed in Figure 2. As have others, we chose the geometry of our cations to resemble that of the tricarbonyl(2-methoxycyclohexadienyl)iron cation which has been studied by x-ray diffraction.²⁰ A modest exploration of the energy surface for distortions of the tricarbonyliron fragment in **8** gave results which were in good agreement with this crystal structure. Further geometrical details and extended Hückel parameters are given in the Appendix.

Atomic charges show considerable variation owing to their dependence on method of calculation and choice of parameters. Charge iteration smooths the charge distribution but does not alter its basic features (compare calculations for **8**). The extended Hückel (EH) calculations show the expected electron transfer from the tricarbonyliron fragment to the dienylium cation ligand. For example, charge iterative EH calculation for **8** gives a total charge of +0.416 e for the dienylium carbons and +0.527 e for the tricarbonyliron fragment. The balance of the charge is on hydrogen atoms. In contrast, the INDO results predict an increase in total positive charge for the dienylium

carbons from +0.563 to +0.891 e on going from free cyclohexadienyl cation to its tricarbonyliron complex.²¹ This result does not seem reasonable on the basis of the bonding discussion above or in light of the large upfield ¹³C chemical shifts which occur on complexation.

The most striking feature of the charge distribution is the alternation of charge along the dienylium chain with carbons 1 and 5 being least positive, carbon 3 next, and carbons 2 and 4 bearing the largest positive charge. Charge alternation is independent of the method of calculation, cyclic or acyclic ligand structure, and the presence of a methyl substituent. It persisted through all the modest geometrical changes we examined. Although our calculations are too crude to give absolute atomic charges accurately, this pattern of alternating charge must be real. It can hardly be coincidental that such an alternation of atomic charges is predicted by examination of frontier orbital interactions between a dienylium cation and a neutral tricarbonyliron fragment and that the ¹³C chemical shifts show shielding decreases (C-1, C-5 > C-3 > C-2, C-4) in exactly the same order as calculated positive charge increases. The sum of evidence and theory confirms charge alternation along the dienylium chain.

Correlation between the predictions of the frontier orbital model on one hand and the all valence shell calculations and chemical shifts on the other is not perfect, however. The latter suggest that C-1 and C-5 are less positive than is C-3. In the frontier orbital model the σ to π_3 donation does not differentiate C-1 and C-5 from C-3, but the π_2 to σ donation should selectively increase the positive charge at C-1 and C-5 relative to that at C-3. Neither of the theoretical approaches taken here should be expected to provide reliable information about such details of the charge distribution.

Atomic Charge and ¹³C Chemical Shifts

The relative importance of the several factors which determine ¹³C chemical shifts of carbons which are directly bound to transition metals and how they vary with molecular structure are not known.¹⁶ Useful chemical shift structure correlations have been described, and some have succumbed to the temptation to propose electronic interpretations of such effects.¹⁶ The most widely used assumption in interpretation of ¹³C chemical shifts of transition metal bound carbons is the shielding-atomic charge correlation⁵ which has been well documented for carbon atoms in uncomplexed aromatic

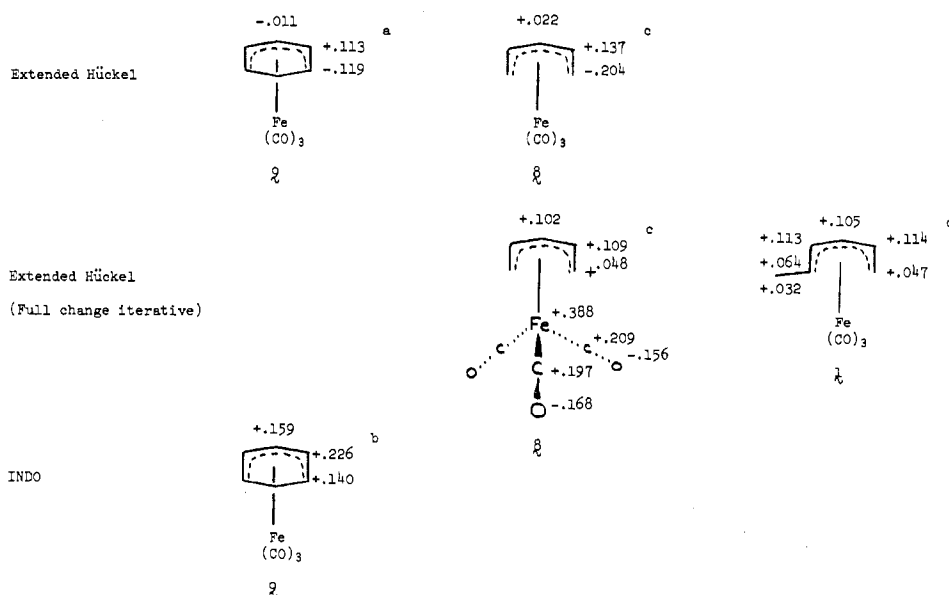


Figure 2. Calculated charge distribution in tricarbonyl(dienyl)iron cations with charges given in units of the charge on the electron: (a) R. Hoffmann and P. Hofmann, *J. Am. Chem. Soc.*, **98**, 598 (1976), charge dependence for iron only; (b) D. W. Clack, M. Monshi, and L. A. P. Kane-Maguire, *J. Organomet. Chem.*, **107**, C40 (1976); (c) this work.

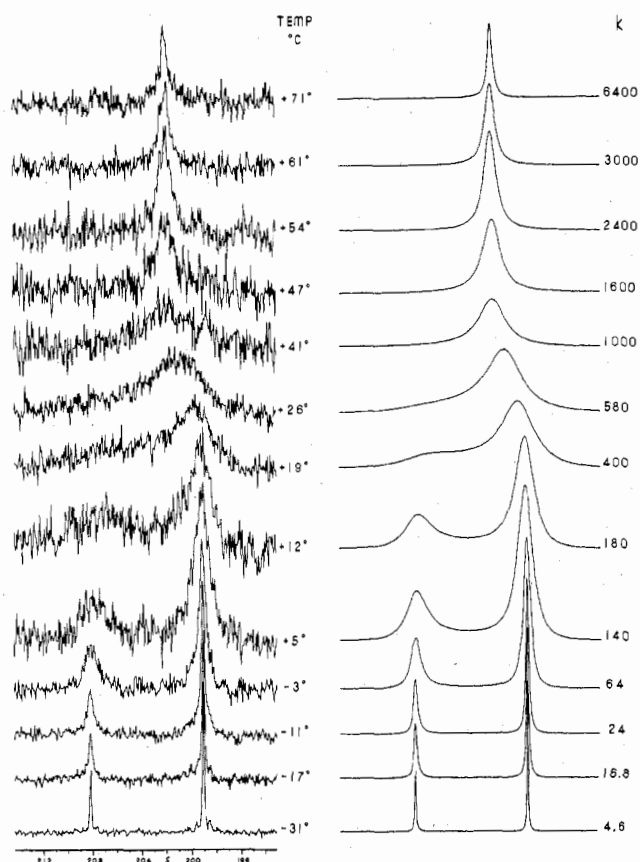


Figure 3. Observed (left) and calculated (right) line shapes for the carbonyl ^{13}C NMR signals of cation **4** in fluorosulfonic acid.

compounds,^{17,22} Olah et al.⁸ and Birch et al.,¹⁰ who also mention hybridization and energy level effects, have interpreted shifts for tricarbonyl(dienyl)iron cation in terms of atomic charge. Yet Evans and Norton have demonstrated that changes in atomic charge cannot account for changes in chemical shifts for η^5 -cyclopentadienyl and η^3 -allyl carbons.¹⁶ Can the atomic charge interpretation of the tricarbonyl(dienyl)iron cation data be valid?

Molecular orbital calculations and the frontier orbital bonding model make a strong case by themselves for the existence of charge alternation along the dienyl chain; and clearly the shielding of these carbons, after correction for α and other large substituent effects, correlates well with calculated atomic charge. Structural variables are very similar for this group of carbons. They are all attached to the same transition metal (iron) in the same oxidation state (+2). The $^1J_{\text{CH}}$ values show that hybridization is essentially constant, the small variations observed exhibiting no correlation with the site on the dienyl group. A strong case can be made that atomic charge is the major factor which determines chemical shift differences for the dienyl carbons after "correction" for major substituent effects. However, the validity of this interpretation derives from the very narrowness, in a structural sense, of the data base. Thus, significant though it is, our conclusion does not alter for the general case Evans and Norton's point that interpretation of chemical shifts for transition metal bound ^{13}C atoms in terms of atomic charge alone is invalid.

Carbonyl Site Exchange

At low temperatures tricarbonyl(dienyl)iron cations exhibit at least two distinct carbon resonances for the terminal carbonyl groups. The maximum number of three signals is frequently observed for cations which lack a plane of symmetry (e.g., **1**, **3**, and **5** but not **6** and **7**). This phenomenon has been

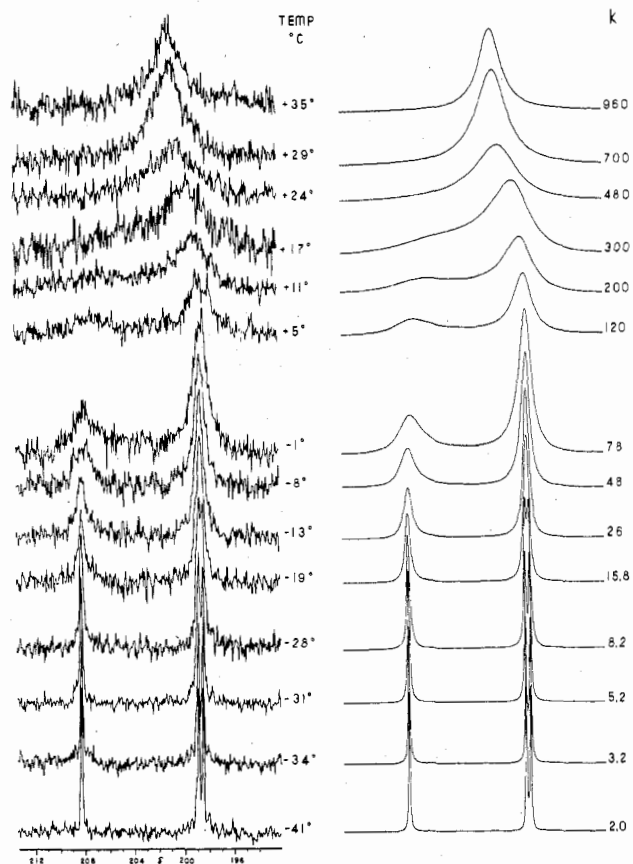
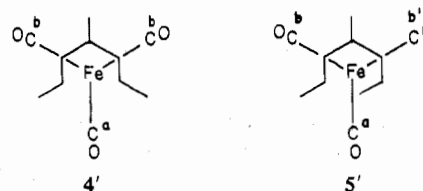


Figure 4. Observed (left) and calculated (right) line shapes for the carbonyl ^{13}C NMR signals of cation **5** in fluorosulfonic acid.

reported previously by Olah et al.⁸ and by us.⁴ This is the result of slow exchange by the carbonyl ligands between structurally distinct sites (a and b in **4'** and a, b, and b' in **5'**).



The twofold higher intensity of the upfield carbonyl signal for symmetrical cations and the two closely spaced signals for unsymmetrical cations make it clear that carbonyls in a sites exhibit signals in the range 206–208 ppm and those in b sites exhibit signals in the 197–199 ppm range.

We have recorded spectra for **4** and **5** in fluorosulfonic acid over a wide temperature range. Spectra presented in Figure 3 show that for **4** line broadening begins at ca. -30°C (243 K), and the a and b signals coalesce at $+19^\circ\text{C}$ (292 K). The fast-exchange limit was not quite achieved at our highest temperature, 71°C (344 K). For **5** (Figure 4) broadening and coalescence of the closely spaced b and b' signals occur at much lower temperatures, $T_c = -25^\circ\text{C}$ (248 K). The combined bb' signal coalesces with the a signal at $+17^\circ\text{C}$ (290 K). At the highest temperature ($+45^\circ\text{C}$ or 318 K) a broad singlet is observed. Study of **5** at higher temperatures was prevented by its substantial rate of conversion to the more stable **4**.

Selected data from a complete line-shape analysis²³ based on an $\text{Fe}(\text{CO})_3$ rotation mechanism are shown in Figures 3 and 4. Excellent fits were obtained for both cations. Data for **5** from both the b with b' and the bb' with a collapse regions clearly fall on the same straight line in a $\log k$ vs. $1/T$ plot. Activation parameters for the site-exchange process are

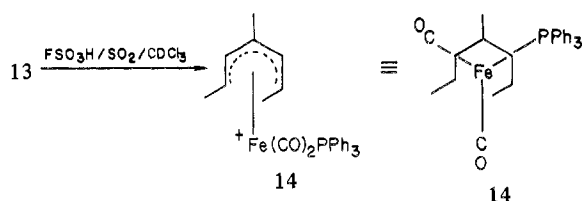
Table IV. Activation Parameters for Carbonyl Site Exchange^a

Cation	ΔH^\ddagger , kcal/mol	$\Delta G^\ddagger_{277.8}$, kcal/mol	$\Delta S^\ddagger_{277.8}$, eu
4	11.1 ± 0.2	13.6 ± 0.1	-9.0 ± 0.9
5	11.4 ± 0.1	13.6 ± 0.1	-7.7 ± 0.6
8	10.9 ^b		

^a Based on a mechanism involving rotation of the tricarbonyl fragment. ^b Calculated using an extended Hückel program: T. A. Albright, P. Hofmann, and R. Hoffmann, *J. Am. Chem. Soc.*, **99**, 7546 (1977).

presented in Table IV along with a barrier to tricarbonyliron rotation in **8** calculated using the EH method.²⁵ The calculated barrier agrees well with the observed barriers.

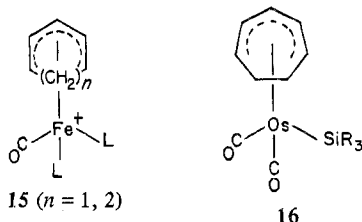
Unrestricted pairwise exchange of CO's gives a line-shape fit identical with that obtained for tricarbonyliron rotation when equal rates for all exchanges (a and b and b and b') are assumed. All other pairwise mechanisms failed to fit our line shape data. An experimental test for pairwise CO exchange was made by using ion **14** which was generated in the usual way from the corresponding ψ -endo alcohol **13**.



The two diastereotopic CO ligands of **14** (see **14'**) can be interconverted by a pairwise exchange mechanism but *cannot* be interconverted by rotation of the Fe(CO)₂PPh₃ unit. The ¹³C NMR spectrum of **13** in the CO region exhibits at -50 °C two distinct doublets at 205.5 and 215.9 ppm ($J_{PC} = 35.3$ and 16.2 Hz, respectively) which persist up to -8 °C where decomposition products began to affect the spectrum. Inasmuch as Whitesides and Budnik²⁶ have demonstrated fast site exchange in (diene)M(CO)_n(phosphite)_{3-n} (M = Mn, Re, Fe, Ru) compounds in this temperature range, it is unlikely that the triphenylphosphine ligand would slow the exchange process dramatically. Thus, we conclude that pairwise exchange of CO ligands is not operative in tricarbonyl(dienyl)iron cations and their monophosphine substitution derivatives.

The closely related diene iron complexes have been studied thoroughly. Clark and his co-workers²⁷ have reported studies of a number of (diene)Fe(CO)_n(PF₃)_{3-n} compounds. Their observations rule out pairwise exchange processes for (diene)Fe(CO)(PF₃)₂ compounds. Takats and Kruczynski²⁸ have studied dienetricarbonyliron complexes in detail. Both Clark and Takats have pointed out that the extant data permit a second mechanism which approximates a Berry pseudorotation²⁹ though the small bite size of the diene ligand may be disadvantageous in this process. A similar possibility exists for the dienyl cations we have studied. No choice between the two mechanisms, which permute the ligands in identical fashion, can be made here.

Whitesides and Budnik's study of site exchange in (diene)M(CO)_n(phosphite ester)_{3-n} complexes, e.g., **15**, gave



barriers (ΔG^\ddagger_{220}) in the 9.8–13.0 kcal/mol range, similar to

Table V. Parameters for Charge Iterative Extended Hückel Calculations

Orbital	C ^a	B ^a	A ^a	ξ_1^b
H 1s	-13.6	-27.18	-13.618	1.3
C 2s	-20.4	-11.9		1.625
C 2p	-10.6	-11.9		1.625
O 2s	-33.0	-15.2		2.275
O 2p	-16.4			2.275
Fe 4s	-7.10	-7.916	-0.911	1.575
Fe 4p	-3.71	-6.30	-0.911	0.975
Fe 3d	-9.39	-12.60	-1.71	c

^a Charge dependence parameters $H_{ii} = Aq^2 + Bq + C$. ^b Slater exponent. ^c A double- ξ function was used for the iron 3d orbital $\xi_1 = 5.35$, $\xi_2 = 1.80$, $c_1 = 0.5366$, $c_2 = 0.6678$. c_1 and c_2 are expansion coefficients in the double- ξ function.

our findings. Their more complex systems did not provide simple mechanism-dependent information; and they assumed a rotation mechanism. Stone et al. have studied site exchange in compounds **16** by ¹H NMR spectroscopy and interpreted their results in terms of a rotation mechanism as well.³⁰ Numerous studies of the closely related tricarbonyl(diene)iron complexes^{28,31} and other diene M(CO)_nL_{3-n} complexes^{27,32} have appeared. The overall mechanistic picture which has emerged from these studies is consistent with either a tricarbonyliron rotation or a Berry pseudorotation process.

Experimental Section

Preparation of NMR samples in SO₂/CDCl₃/FSO₃H solutions and instrument parameters used in obtaining their ¹³C NMR spectra were described previously.⁴ The following procedure was used to obtain carbonyl carbon line shapes over a broad temperature range. Dienol complex (400 mg) was dissolved in CDCl₃, and the solution was degassed as was the fluorosulfonic acid (1–1.5 mL) by the freeze-pump-thaw process. The acid was cooled to between -70 and -90 °C in a 10-mm NMR tube under nitrogen, and the CDCl₃ solution was added slowly to the acid solution under nitrogen. Once cold, the solutions were mixed slowly. Spectra were obtained on a Bruker HX-90 spectrometer using a pulse width of 16 μ s (45°) and a pulse repetition rate of 10 s and proton decoupling. The spectra were unaltered when a pulse repetition rate of 20 s was employed. The temperature controller was standardized using a copper-constantan thermocouple immersed in toluene in a nonspinning 10-mm sample tube in the probe with the proton decoupler power on. Chemical shifts were measured with respect to internal CDCl₃ at a value of 77.3 ppm downfield from external Me₄Si.

ψ -endo-Dicarbonyl(*trans,trans*-4-methyl-3,5-heptadien-2-ol)(triphenylphosphine)iron (**13**). ψ -endo-Tricarbonyl(*trans,trans*-4-methyl-3,5-heptadien-2-ol)iron (3.67 g, 13.8 mmol) and triphenylphosphine (3.96 g, 15.1 mmol) in THF (150 mL freshly distilled from lithium aluminum hydride under nitrogen) was irradiated through a Pyrex reaction vessel using a 275-W sunlamp. After 67 h, the color of the reaction had changed from yellow to gray. As solvent was removed under reduced pressure a copious yellow precipitate formed. This insoluble by-product (2.58 g) was removed in five fractions by filtration. The mother liquors were concentrated to a red oil which was chromatographed on silica gel using benzene eluent. After a yellow forerun and a small red band, the product eluted as a yellow band which yielded 1.0 g (14.5%) of a yellow oil which solidified on standing. Two recrystallizations from ethyl ether at -17 °C gave light yellow crystals: mp 141–142 °C; IR (CDCl₃) 3580, 1963, 1905 cm⁻¹; NMR (CS₂) τ 2.16–2.63 (m, 15 PPh₃), 5.16 (d, 1, $J_{56} = 8.5$ Hz, H-5), 6.18 (m, 1, H-2), 7.83 (d, 3, $J_{PH} = 2$ Hz, C-4-CH₃), 8.81 (d, 6, $J_{12} = 6$ Hz, $J_{67} = 6$ Hz, 1-CH₃ and 7-CH₃), 9.59 (s, broad, 1, OH), 10.10 (t, 1, $J_{23} = 6$ Hz, $J_{HP} = 6$ Hz, H-3), 10.74 (d of q, 1, $J_{56} = 8.5$ Hz, $J_{67} = 6$ Hz, H-6).

Anal. Calcd for C₂₈H₂₉O₃PFe: C, 67.21; H, 5.84; Fe, 11.6. Found: C, 67.74, 67.79; H, 5.90, 6.03; Fe, 10.89.

The same compound (**13**) was produced by sodium borohydride reduction of dicarbonyl(*trans,trans*-4-methyl-3,5-heptadien-2-ol)(triphenylphosphine)iron in methanol.

Ion **14** which was produced by treatment of **13** with FSO₃H/SO₂/CDCl₃, in contrast to other ions, remained in the upper CDCl₃ layer, the lower acid layer remaining colorless. Spectra in CDCl₃

were obtained after removal of excess acid.

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Appendix

Extended Hückel calculations were carried out using the same parameters as Hoffmann and Hofmann. Charge dependence for iron only was assumed.¹⁸ Parameters used for the full-charge iterative calculations are listed in Table V.

Geometric changes which tip the Fe(CO)₃ group so that the b-type CO's (see 4') move down away from the dienyl ligand and the a-type CO moves up toward it and a combination of the above combined with an opening of the OC_b-Fe-C_aO angle to 100° to approximate the geometry of tricarbonyl(diene)iron complexes were explored. In agreement with the extant crystal structure, these modified geometries gave higher energies. We also examined the effect of bending syn 1-hydrogens or methyl out of the dienyl plane toward iron. This stabilizes the complexes and our final calculations were carried out with syn 1-hydrogens bent 15° out of the dienyl plane and the syn 1-methyl of 1 displaced 9.5° from the dienyl plane.

Registry No. 1, 50576-99-3; 2, 46238-82-8; 3, 59685-05-1; 4, 59685-06-2; 5, 59685-07-3; 6, 66141-51-3; 7, 66141-52-4; 13, 66102-56-5; 14, 66102-57-6; ψ -endo-tricarbonyl(*trans,trans*-4-methyl-3,5-heptadien-2-ol)iron, 36006-39-0; dicarbonyl(*trans,trans*-4-methyl-3,5-heptadiene-2-one)(triphenylphosphine)iron, 66102-58-7.

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