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(Cross-conjugated dienyl)tricarbonyliron Cations. 3. The Parent Cation

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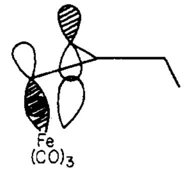
The parent (unsubstituted) (cross-conjugated dienyl)Fe(CO)$_3$ cation, **10**, has been generated and studied in FSO$_3$H/SO$_2$(l) at −20 to −65 °C. The dienyl ligand of this cation lacks the anti methyl substituent which we propose modifies the behavior of cation **5a** through steric effects. Cation **10**, like **5s**, behaves as a coordinatively saturated species and possesses a substantial (>13 kcal/mol) barrier to rotation about its C$_2$–C$_3$ bond. These properties eliminate the η^3 structure, **2**, predicted for these cations by a simplified (one-interaction) frontier-orbital model. The structure must be η^4, **3**, **4**, or a structure which lies on the **3**–**4** interconversion pathway. An extended Hückel treatment predicted similar energies for structures **2**–**4**. No single geometry allows good bonding partners for all the frontier orbitals.

(Cross-conjugated dienyl)tricarbonyliron cations were conceived as a severe test of a simplified (one-interaction) frontier-orbital model for bonding in transition-metal π complexes.[2,3] If bonding in these cations is dominated by donation from the Fe(CO)$_3$ HOMO to the unoccupied nonbonding LUMO of the dienyl cation ligand, maximization of spacial overlap for this interaction (**1**) will lead to structure **2**.



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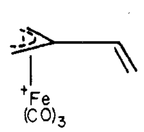
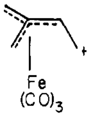


2

Structure **2** would be achieved only at the expense of a filled valence shell for iron. Alternative structures **3** and **4** which are coordinatively saturated can be envisaged. Structure **3** is analogous to (trimethylenemethane)tricarbonyliron complexes[4] while **4** finds a close analogue in (conjugated diene)tricarbonyliron complexes.[5] Thus, existence of structure **2** would be impressive evidence for domination of metal–carbon bonding by the single interaction **1**.



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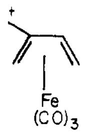
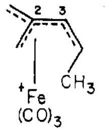
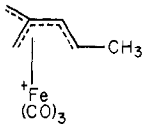


4

Cations **5a** and **5s** have been generated and studied in So$_2$/FSO$_3$H.[3] They differ significantly in their response to tests for coordinative unsaturation and ability to rotate about the C$_2$–C$_3$ bond, properties which should distinguish **2** from **3** and **4**. We have ascribed these differences to perturbation of properties intrinsic to the cations owing to steric effects associated with the anti methyl substituent in **5a**. We have now synthesized the parent (unsubstituted) cation **10**. Since it lacks the anti methyl, it should exhibit properties similar to those of **5s**. We report on these properties below.[6]

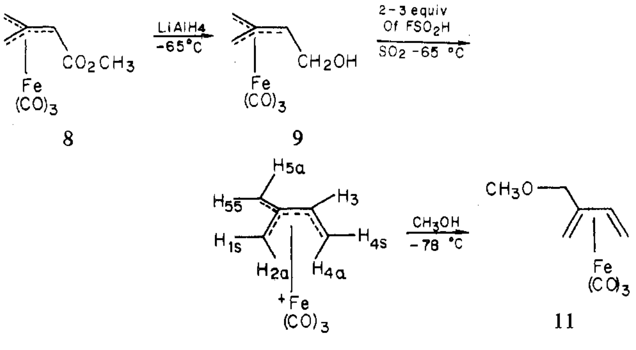


5a



5s

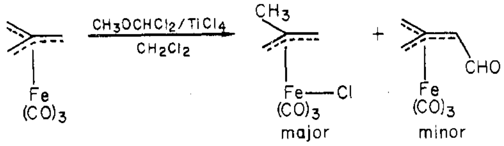
Scheme I



10 11

Results

((Hydroxymethyl)trimethylenemethane)tricarbonyliron (**9**) was sought as a precursor to cation **10**. Attempts to prepare the aldehyde **6** by direct formylation[7] of (trimethylenemethane)tricarbonyliron were unsuccessful. Use of the CH$_3$OCHCl$_2$/TiCl$_4$ reagent[7,8] gave 10% of impure aldehyde, identified by NMR, IR, and mass spectral comparisons with an authentic sample;[3] but the major product was (2-methallyl)tricarbonyliron chloride.[4a] Use of AlCl$_3$ and BF$_3$·OEt$_2$ catalysts gave even poorer results, and the triethyl orthoformate/BF$_3$·OEt$_2$ reagent[9] did not react with the trimethylenemethane complex. A successful synthesis of the desired precursor (**9**) is shown in Scheme I. Ehrlich and Emerson[4b] reported that lithium aluminum hydride reduction of the ester **8** resulted in extensive destruction of the π complex. However, when the reduction was carried out at −65 °C, alcohol **9** was produced in 79% yield.



7 6

Treatment of a solution of **9** in SO$_2$ with 2–3 equiv of FSO$_3$H at −65 °C produced cation **10**. Use of excess FSO$_3$H gave the same result. Methanolysis of **10** at −78 °C gave the

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(1) (a) Mt. Holyoke College. (b) University of Massachusetts.
(2) Bonazza, B. R.; Lillya, C. P. *J. Am. Chem. Soc.* **1974**, *96*, 2298.
(3) Bonazza, B. R.; Lillya, C. P.; Magyar, E. L.; Scholes, G. *J. Am. Chem. Soc.* **1979**, *101*, 4100.
(4) (a) Emerson, G. F.; Ehrlich, K.; Giering, W. P.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1966**, *88*, 3172. (b) Ehrlich, K.; Emerson, G. F. *Ibid.* **1972**, *94*, 2464.
(5) Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1958**, 642, 646. Mills, O. S.; Robinson, G. *Acta Crystallogr.* **1963**, *16*, 758.
(6) Presented in part: Bonazza, B. R.; Lillya, C. P.; Maygar, E. S.; Scholes, G. "Abstracts of Papers", 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 29–Sept 3, 1976; American Chemical Society: Washington, D.C., 1976; INOR 109.
(7) Graf, R. E.; Lillya, C. P. *J. Organomet. Chem.* **1976**, *122*, 377.
(8) Rieche, A.; Gross, H.; Höft, E. *Org. Synth.* **1967**, *47*, 1.
(9) Cf.: Gross, H.; Rieche, A.; Matthey, G. *Chem. Ber.* **1963**, *96*, 308; Treibe, W. *Tetrahedron Lett.* **1967**, 4707.

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Table I. ^{1}H NMR Data for (Cross-conjugated dienyl)tricarbonyliron Cations in $FSO_3H/SO_2(l)$ at −65 °C

	chem shift,[a] δ		
H	**5a**[b]	**5s**[b]	**10**[c]
1a	3.44	2.40	2.00 d of d
1s	2.79	2.50	2.25 d of d
3	4.87	4.93	5.00 four d
4a		4.93	3.60 d of d
4s	6.28		4.10 d of d
5a	4.82	4.68	4.50 d
5s	3.90	3.72	3.63 s
	coupling const, Hz		
J	**5a**[b]	**5s**[b]	**10**
1a,1s	3.0	3	2.7
1a,5a	4.2	3.3	3.3
1s,3	2.2	~1	1.5
3,4a			13
3,4s	9.5		7.5
4a,4s			1.3
5a,5s	0	0	0

[a] Ppm relative to external Me_4Si, recorded at 90 MHz. [b] From ref 3. [c] s = singlet; d = doublet.

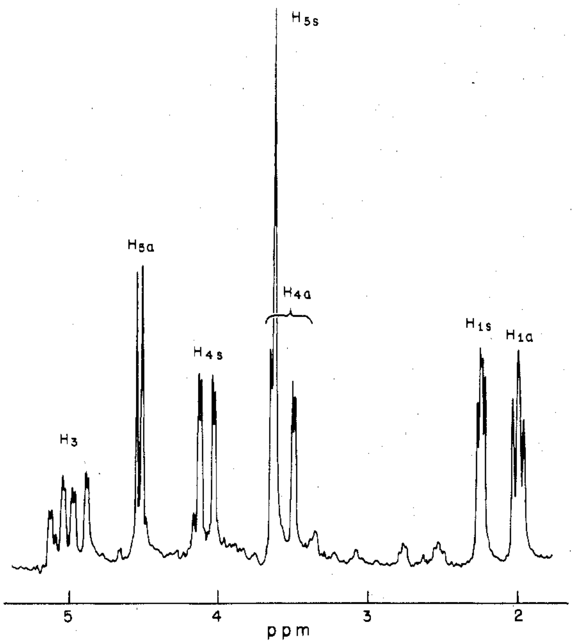


Figure 1. 90-MHz ^{1}H NMR spectrum of cation **10** in $FSO_3H/SO_2(l)$ at −65 °C, ppm downfield from external Me_4Si. The apparent triplet at 2.00 ppm, assigned to H_{1a}, was resolved into a doublet of doublets when the horizontal scale was expanded.

Table II. ^{13}C NMR Data for (Cross-conjugated dienyl)tricarbonyliron Cations in $FSO_3H/SO_2(l)$ at −65 °C

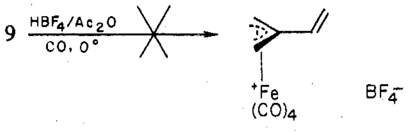
	^{13}C shift,[a] δ		
C	**5a**[b]	**5s**[b]	**10**[c–e]
1	58.5	55.4	56.7 t (166)
2	123.4	108.0	110.0 s
3	104.2	106.9	113.0 d (158)
4	110.8	121.0	90.0 t (170)
5	77.4	77.3	79.4 t (170)

[a] Ppm relative to internal Me_4Si as calibrated by internal $CDCl_3$ at 70.9 ppm. A positive shift is a downfield (from Me_4Si) shift. [b] From ref 3. [c] s = singlet, d = doublet, and t = triplet. [d] Numbers in parentheses are $^1J_{C-H}$ values in Hz (±8 Hz). [e] ^{13}CO signals at 196.6, 199.4, and 203.4 ppm. **5a** and **5s** exhibit similar signals.[3]

2-(methoxymethyl)butadiene complex **11** as the only product. ^{1}H NMR data for cations **5a**, **5s**, and **10** are presented in Table I. The spectrum of cation **10** shown in Figure 1 exhibits a resolved signal for each of its seven protons. Chemical shifts and coupling constants are similar to those exhibited by the monomethyl cations **5a** and **5s**, including substantial long-range "W" couplings.[3] The "quartet" of doublets (J = 13, 7.5, 1.5 Hz) at δ 5.00 must be H_3 coupled strongly to H_{4a} at δ 3.60 (trans coupling) and H_{4s} at δ 4.10 (cis coupling). "W" coupling of H_3 to H_{1s} allows assignment of the latter as the doublet of doublets (J = 2.7, 1.5 Hz) at δ 2.25. The ^2J coupling $J_{1a,1s}$ is characteristically small.[2-4] In fact $J_{5a,5s}$ = 0, and, since H_{5s} cannot exhibit "W" coupling, it can be confidently assigned as the only singlet in the spectrum at δ 3.63. This same proton appears as a characteristic singlet in the spectra of cations **5a** and **5s** also. H_{5a} can then be assigned as the doublet at δ 4.50 "W" coupled ($J_{1a,5a}$ = 3.3 Hz) to H_{1a} which appears at δ 2.00 as the required doublet of doublets (J = 3.3, 2.7 Hz). The above assignments agree well with those for **5a** and **5s** which have been confirmed by using deuterium labeling. Chemical shifts and coupling constants for the three cations are similar with the expected exceptions of H_{1a} of **5a** which is deshielded by the proximal anti 4-methyl group and H_{4a} and H_{4s} which are deshielded in **5a** and **5s** owing to the presence of an α-methyl.

^{13}C NMR data for the cations are presented in Table II. Assignment of the C_2 and C_3 signals of **10** using $^1J_{C-H}$ coupling was unambiguous. The remaining three signals, which are triplets in the ^{1}H-coupled spectrum, were assigned by analogy with assignments for **5a** and **5s** (see Table II). The lowest field signal at 90 ppm was assigned to C_4. It is more strongly shielded than C_4 of **5a** and **5s** owing to the absence of an α-methyl group. The remaining signals appear at chemical shifts which are virtually identical with those assigned as C_1 and C_5 of **5a** and **5s**. The most shielded carbon was assigned as C_1 because it is expected to interact more strongly with the iron atom than is C_5[10] and because estimates of charge distribution predict significantly higher electron density at C_1 (see below).

In search of properties which should distinguish structure **2** from **3** and **4**, we looked for NMR temperature dependence. No changes in the ^{1}H and ^{13}C spectra were observed up to −20 °C. Above this temperature spectral quality deteriorated, and all lines were broadened. No selective reversible broadening of lines for the nuclei which C_2–C_3 rotation would interconvert, C_1 and C_5 and their hydrogens, could be detected. In a test for coordinative unsaturation, **10** was generated under 1 atm of CO by using conditions employed by Whitesides et al. for preparation of stable (η^3-allyl)tricarbonyliron cations.[11] No isolable products were observed, and the terminal CO stretching region of IR spectra of crude reaction products gave no evidence for formation of **12**.



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Discussion

Our previous investigation of the monomethyl cations **5a** and **5s** revealed some significant differences in their properties.[3] Although, like **10**, neither formed an adduct with carbon monoxide, **5a** was slowly converted to its fluorosulfonate adduct **13** when generated in SO_2 at −65 °C. The syn methyl cation

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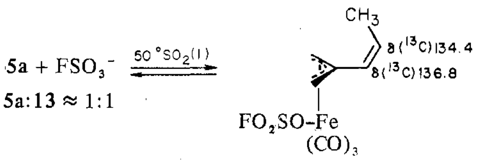
(10) Large upfield shifts of sp^2 carbons on complexation to transition metals are common. Cf.: Evans, J.; Norton, J. R. *Inorg. Chem.* **1974**, *13*, 3043.

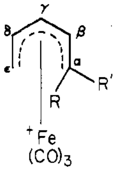
(11) Whitesides, T. H.; Arhart, R. W.; Slaven, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 5792. See also: Gibson, D. H.; Vonnahme, R. L. *Ibid.* **1972**, *94*, 5090; *Chem. Commun.* **1972**, 102.



13

5s gave no detectable fluorosulfonate adduct. The anti methyl cation **5a** undergoes rotation about its C_2–C_3 bond over a ca. 13 kcal/mol barrier. The rotation process does *not* involve formation of **13**. In contrast, **5s** exhibits no NMR temperature dependence up to −20 °C and must possess a significantly higher barrier to C_2–C_3 rotation. We have proposed that the fluorosulfonate adduct formation from **5a** is driven by relief of steric strain caused by the anti methyl and that the low barrier to C_2–C_3 rotation exhibited by this ion is caused by the same driving force. If this is so, the parent ion **10** should behave like **5s**, not like **5a**, because it lacks an anti methyl substituent.

The observed properties of **10** are in complete accord with this expectation. It shows no tendency to form a fluorosulfonate adduct, and its ^{1}H and ^{13}C NMR spectra exhibit no temperature dependence up to −20 °C. Comparison of NMR data for cations **5a**, **5s**, and **10** reveals close similarities and supports the idea that metal–dienyl bonding is similar for all three. The C_1 and C_5 signals span ranges of only 2.9 and 2.1 ppm, respectively, and all exhibit three nonequivalent carbonyl signals at −65 °C. Carbons 2 and 4 (see below) of **5a** are exceptions which may be caused by geometric (and bonding) adjustments to relieve steric crowding associated with the anti methyl group. This factor has already been identified as the cause of unusual chemical and physical behavior of **5a**.[3] We have reported shifts produced by introduction of terminal anti (R) and syn (R′) methyls in (conjugated dienyl)tricarbonyliron cations (**14**).[12,13] Shifts at C_1, C_3, and C_4 show strong similarities to these. For example, the effect of an α-methyl is unusually large and about 10 ppm larger for introduction of a syn methyl in both types of cation. The C_2 signal which is γ to the methyl substituent is the exception. Introduction of syn and anti methyls in **14** induced shifts of 3–4 ppm upfield and 2.2 ppm downfield, respectively. The corresponding shifts in the cross-conjugated cations are 2.0 ppm upfield and 13.4 ppm downfield. It is possible this large downfield shift reflects some adjustment in the metal–ligand interaction in response to the steric stain in cation **5a**.



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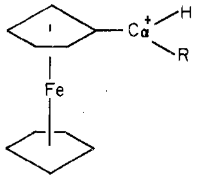
The NMR data carry some strong structural implications. First the η^3-allyl structure **2** can be eliminated because carbons 3 and 4 are too strongly shielded to be uncomplexed olefinic carbons such as those of the fluorosulfonate adduct **13**.[3] The choice between structures **3** and **4** is more difficult. We favor the former principally because relatively greater shielding of C_5 than of C_4 is in accord with a structure in which C_5 is π bonded to iron.[10] The rest of our NMR data is most consistent with an η^4-trimethylenemethane structure (**3**). In this structure C_4 is analogous to C_α of the ferrocenylmethyl cations (**15**) and (cyclobutadienylmethyl)tricarbonylmethyl cations (**16**). These carbons are attached to delocalized systems which are π bonded to iron atoms but are themselves too distant from the iron atom[14] to permit strong direct bonding. Chemical shifts for C_α and attached hydrogens in **15** and **16** are shown in Table III. The shifts of C_4 in (dienyl)tricarbonyliron cations **5s** and **10** are within 2 ppm of the C_α shifts in the corresponding ferrocenyl cations **15** (R = CH_3) and **15** (R = H), respectively, and are 13–14 ppm upfield of the C_α shifts for the corresponding complexed cyclobutadienylmethyl cations. Stronger shielding of C_4 in cation **5a** (ca. 8 ppm upfield of C_α in **15** (R = CH_3)) may be caused by perturbations of iron–carbon bonding caused by steric crowding of the anti methyl (see above).[3] Chemical shifts of the C_4 hydrogens of **5s** and **10** appear 1.5–2 ppm upfield of their counterparts in **15** and **16** but are downfield from similar hydrogens on iron-coordinated terminal carbons of conjugated (η^5-dienyl)tricarbonyliron cations (**14**)[15] and neutral (η^4-diene)tricarbonyliron complexes.[16] The large H_{syn}–H_{anti} chemical shift difference of ca. 1.5 ppm so characteristic of the latter compounds is not exhibited by cation **10**. The shifts of C_2 in **5s** and **10** are close to those observed for the central carbons of a series of (trimethylenemethane)tricarbonyliron complexes (103–107 ppm),[17] while C_3 appears far downfield of its counterparts in either η^4-diene[18] or η^4-trimethylenemethane[17] models. Thus the NMR data, especially those for ^{13}C, favor a structure like **3**.

Table III. Chemical Shifts in (Ferrocenylmethyl)- and (Cyclobutadienylmethyl)tricarbonyliron Cations

cation	δ_{H_α}[a]	δ_{C_α}[a]
15, R = H	5.75[b]	88.6,[e] 87.8[f]
15, R = CH_3	6.89,[c] 7.03[b]	119.5,[e] 117.9[f]
16, R = H	5.09[d]	104.5[g]
16, R = CH_3	6.19[d]	133.8[g]

[a] Ppm downfield from external Me_4Si; solvent H_2SO_4 unless specified. [b] Cais, M.; Dannenberg, J. J.; Eisenstadt, A.; Levenberg, M. I.; Richards, J. H. *Tetrahedron Lett.* **1966**, 1695. [c] Horspool, W. M.; Sutherland, R. G. *Chem. Commun.* **1967**, 786. [d] Fitzpatrick, J. D.; Watts, L.; Pettit, R. *Tetrahedron Lett.* **1966**, 1299. [e] Braun, S.; Abram, T. S.; Watts, W. E. *J. Organomet. Chem.* **1975**, *97*, 429. Relative to internal Me_4Si, in CF_3CO_2H. [f] Olah, G. A.; Liang, G. *J. Org. Chem.* **1975**, *40*, 1849. [g] Eschbach, G. S.; Seyferth, D.; Reeves, P. C. *J. Organomet. Chem.* **1976**, *104*, 363.



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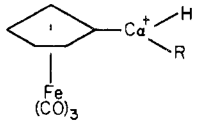

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It is clear that (cross-conjugated dienyl)tricarbonyliron cations, in the absence of perturbing steric effects, exhibit no evidence for coordinative unsaturation and possess significant barriers ($\Delta G > 13$ kcal/mol) to rotation about their C_2–C_3 bonds. These properties show that they do not possess the η^3 structure (**2**) but rather should be represented as **3** or **4** with

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(12) Dobosh, P. A.; Gresham, D. G.; Lillya, C. P.; Magyar, E. S. *Inorg. Chem.* **1976**, *15*, 2311. Dobosh, P. A.; Gresham, D. G.; Kowalski, D. J.; Lillya, C. P.; Magyar, E. S. *Ibid.* **1978**, *17*, 1775.

(13) For similar shifts in (cyclohexadienyl)tricarbonyliron cations see: Birch, A. J; Westerman, P. W.; Pearson, A. J. *Aust. J. Chem.* **1976**, *29*, 1671.

(14) Cais, M.; Dani, S.; Herbstein, F. H.; Kapon, M. *J. Am. Chem. Soc.* **1978**, *100*, 5554. Sime, R. L.; Sime, R. J. *Ibid.* **1974**, *96*, 892. Davis, R. E.; Simpson, H. D.; Grice, N.; Pettit, R. *Ibid.* **1971**, *93*, 6688.

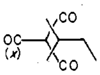
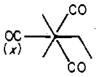
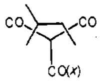
(15) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 3955. Mahler, J. E.; Gibson, D. H.; Pettit, R. *Ibid.* **1963**, *85*, 3959.

(16) Emerson, G. F.; Mahler, J. E.; Kochaar, R.; Pettit, R. *J. Org. Chem.* **1964**, *29*, 3620.

(17) Magyar, E. S.; Lillya, C. P. *J. Organomet. Chem.* **1976**, *116*, 99.

(18) Pearson, A. J. *Aust. J. Chem.* **1976**, *29*, 1679. Magyar, E. S., unpublished observations in this laboratory.

Table IV. Relative Extended Hückel Energies for (Cross-conjugated dienyl)tricarbonyliron Cations

	rel energy,[a] eV		
			
iron parameters	2	3	4
b	0.672	0	1.542
c	0.602	0	1.242
d	0.673	0	1.274

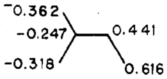
[a] The CO ligand on the x axis in the drawings is designated by (x). [b] Albright, T. A.; Hoffmann, R. *Chem Ber.* **1978**, *111*, 1578. [c] Hoffmann, R.; Hoffmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598. [d] Dobosh, P. A.; Gresham, D. G.; Kowalski, D. J.; Lillya, C. P.; Magyar, E. S. *Inorg. Chem.* **1978**, *17*, 1775.

NMR data favoring the former. A simplified frontier orbital model which considers one interaction only gives an inadequate account of the metal–ligand interaction. An all-valence-electron treatment is presented below.

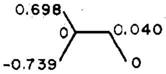
Extended Hückel Calculations

Results of extended Hückel calculations for structures **2**–**4** are presented in Table IV. The relative energies are little affected by the choice of parameters. An octahedral $Fe(CO)_3$ fragment[19] with its C_3 axis perpendicular to a planar C_5H_7 ligand was used in this initial survey. Conformations of the $Fe(CO)_3$ group about its C_3 axis were chosen to maximize the expected bonding interactions as described by Albright, Hofmann, and Hoffmann.[19f] These are the same conformations found in simple $M(CO)_3$ complexes of η^3-allyl,[20] η^4-trimethylenemethane,[21] and η^4-diene ligands[5] and should be close to optimum for structures **2**–**4**. Other relaxations (see below) will lower the calculated energies of all three structures but should not affect our overall conclusion that all three structures lie close in energy.

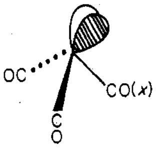
A fragment-orbital analysis revealed the principal factors involved in the energy differences. The important interacting fragment orbitals are the π HOMO and LUMO of the cross-conjugated dienyl ligand, ϕ_2 and ϕ_3, and the degenerate HOMO and LUMO of the $Fe(CO)_3$ fragment, xz and yz.[19] (The CO ligand on the x axis is designated by (x). See Table III.) The lowest dienyl π orbital, ϕ_1, does not mix in a major way with any $Fe(CO)_3$ orbitals.



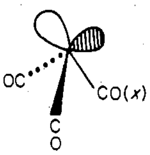
ϕ_2



ϕ_3



yz



xz

In the η^4-diene structure (**4**) the principal bonding interaction is, as expected, that between ϕ_2 and yz (see Figure 2). It is a relatively weak interaction because it includes repulsion between the occupied $Fe(CO)_3$ e and ϕ_2 orbitals and because the lobes of yz are polarized[19d,f] toward the open side of the diene away from ϕ_2. The next three orbitals are mainly the a_1 and e of the $Fe(CO)_3$ fragment. The highest occupied orbital is mainly ϕ_3, which fails to find a partner with which it can overlap efficiently. Bonding in (butadiene)tricarbonyliron has been analyzed recently by Albright, Hoffmann, and Hofmann.[22] Their result shows some similarities to that above. Overlap for the ϕ_2–yz bonding interaction can be improved and that for the repulsive interaction decreased by bending the outside hydrogens at the diene termini down toward iron and the inside terminal hydrogens up away from iron. This effectively rehybridizes the p orbitals at the diene termini so that they point more directly at yz.[23] In fact, a structure in which the affected C–H bonds make angles of 15 and 45°, respectively, with the dienyl plane is more stable than the trimethylenemethane structure.[24] Bonding overlap can be improved further by tipping the $Fe(CO)_3$ group so that the CO(x) ligand and the lobes of the yz orbital tip up toward the dienyl ligand.[23] These changes lead to a geometry which is close to that determined experimentally for (η^4-diene)tricarbonyliron complexes.[25]

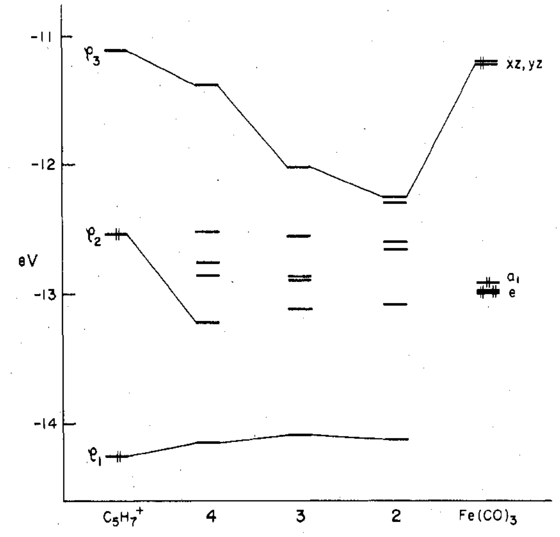


Figure 2. High-lying occupied molecular orbitals for cation **10** as a function of geometry. Energies are from extended Hückel calculations.

When the η^4-diene structure converts to the trimethylenemethane structure (**3**), mixing of ϕ_2 and the $Fe(CO)_3$ a_1 and e orbitals increases, but the net change from **4** is small (Figure 2). Stabilization of **3** derives from a strong ϕ_3–yz interaction. Polarization of yz toward CO(x) increases overlap for this interaction. A further change to the η^3-allyl geometry (**2**) leads to a stronger ϕ_3–yz interaction owing to increased overlap. However, an even larger increase in repulsive interactions between the occupied dienyl orbitals, ϕ_1 and ϕ_2, and the $Fe(CO)_3$ a_1 and e orbitals ensues. This a_1 and e set has been discussed by Albright, Hofmann, and Hoffmann.[19f,26] When the z and C_3 axes are coincident, the e pair is principally d_{xy} and $d_{x^2-y^2}$ with some d_{xz} and d_{yz}. The set of three orbitals, a_1 (which is mainly d_{z^2}) + e, can be treated as a set of three

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(19) Orbitals of the $M(CO)_3$ fragment have been discussed by: (a) Burdett, J. K. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1599. (b) Whitesides, T. H.; Lichtenberger, D. L.; Budnik, R. A. *Inorg. Chem.* **1975**, *14*, 68. (c) Elian, M.; Hoffmann, R. *Ibid.* **1975**, *14*, 1058. (d) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Ibid.* **1976**, *15*, 1148. (e) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50. (f) Albright, T. A.; Hofmann, P.; Hoffmann, R. *Ibid.* **1977**, *99*, 7546.

(20) Seip, R. *Acta Chem. Scand.* **1972**, *26*, 1966. Cann, K.; Riley, P. E.; Davis, R. E.; Pettit, R. *Inorg. Chem.* **1978**, *17*, 1421.

(21) Churchill, M. R.; Gold, K. *Inorg. Chem.* **1969**, *8*, 401. Churchill, M. R.; DeBoer, B. G. *Ibid.* **1973**, *12*, 525.

(22) Albright, T. A.; Hoffmann, R.; Hofmann, P. *Chem. Ber.* **1978**, *111*, 1591.

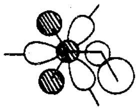
(23) This has been observed for extended Hückel calculations on (butadiene)tricarbonyliron: Dobosh, P. A.; Lillya, C. P., unpublished work.

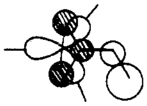
(24) Additional stabilization derives from relief of van der Waals repulsion between the two anti (inside) hydrogens.

(25) Cotton, F. A.; Day, V. W.; Frenz, B. A.; Hardcastle, K. I.; Troup, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 4522. Cotton, F. A.; Troup, J. M. *J. Organomet. Chem.* **1974**, *77*, 369.

(26) Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7736.

equivalent hybrids which eclipse the CO ligands when viewed down the C_3 axis and, as the result of a small amount of mixing with p orbitals, point slightly away from the CO ligands and toward the C_5H_7 ligand. Overlap of this occupied set of hybrids with the occupied ϕ_2 orbital increases as the trimethylene structure **17** is converted to the η^3-allyl structure **18**.[27] It can be predicted that geometrical modifications similar to those discussed for the η^4-diene structure above will also stabilize the η^3-allyl structure.


17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The picture which emerges is one in which different structures possess similar energies. No single geometry provides good bonding partners for all the frontier orbitals. Geometry optimization may lead to η^4-diene and η^3-allyl structures separated by a less stable trimethylenemethane structure. In any case, the barriers to interconversion of these structures are expected to be small. The results are entirely consistent with our observations which require a most stable structure like **3** (or **4**), preventing equilibration of C_1 and C_5, with structure **2**, which allows C_1–C_5 equilibration, easily accessible over a barrier of 10–20 kcal/mol.

Estimates of total carbon atom charges give higher electron density at C_1 than at C_5 for all three structures. This has been used as a partial basis for assignment of the C_1 and C_5 NMR signals (see above).

Summary

The properties of the unsubstituted (cross-conjugated dienyl)tricarbonyliron cation **10** are identical with those of the syn 4-methyl derivative **5s**. This supports the view that the unusual properties of the anti 4-methyl derivative, **5a**, namely coordination with FSO_3^- and rapid rotation about the C_2–C_3 bond, are caused by steric strain associated with the anti 4-methyl group. Thus these cations cannot have the η^3-allyl structure (**2**) predicted by the simplest, one-interaction, frontier-orbital model. NMR data, especially for ^{13}C, favor the trimethylenemethane type structure (**3**). Extended Hückel calculations show that all three possible structures, **2**–**4**, lie close in energy and reveal the important factors in stabilization of each.

Experimental Section

Infrared spectra were recorded by using Perkin-Elmer 727 and Beckman IR-10 spectrometers while ^1H NMR spectra were recorded by using a Varian A-60 and Perkin-Elmer R-12 and R-32 spectrometers. ^{13}C NMR spectra were obtained by using a Bruker HX-90 spectrometer (22.63 MHz) equipped with a Nicolet Series 1080 computer and Bruker SST-100/700 variable-temperature unit. Preparation of NMR samples in FSO_3H/SO_2 has been described.[12]

((Hydroxymethyl)trimethylenemethane)tricarbonyliron (9). ((Carbomethoxy)trimethylenemethane)tricarbonyliron (**8**)[4b] (4.0 g, 0.016 mol) in 100 mL of degassed anhydrous ether was treated at −60 to −65 °C with lithium aluminum hydride (1.2 g, 0.031 mol) added in portions to the stirring reaction mixture. The resulting brown solution was stirred at ca. −65 °C for 30 min when 20 mL of cold ethyl acetate was added. Slow warming to −20 °C was followed by dropwise addition of 10% aqueous ammonium chloride. Inorganic salts were removed by filtration, the burgundy-colored ether layer was separated, and the aqueous layer was further extracted with ether. Drying ($MgSO_4$) and evaporation of the combined extracts left a dark residue which was purified by dry-column chromatography (CH_2Cl_2). The product appeared as a red band, preceded by smaller green and orange bands; yield 2.8 g (79%). Cooling at 4 °C caused crystallization: mp 45–46 °C; IR (film) 3350, 2075, 1980, 1470, 1000 cm^{-1}; NMR[28] ($CDCl_3$) δ 3.9–3.5 (m, 2, CH_2O) and 3.5–2.9 (m, 1, H_2) [a three-proton ABC-type spectrum], 2.54 (d, 1, $J_{3,6}$ = 4.5 Hz, H_6), 2.20 (d, 1, $J_{2,5}$ = 2 Hz, H_5), 2.00 (s, 1, OH), 1.89 (s, 1, H_4), 1.82 (d, 1, $J_{3,5}$ = 4.5 Hz, H_3); mass spectrum [*m/e* (relative intensity) assignment] 224 (3) M^+, 207 (2) M^+ − OH, 196 (34) M^+ − CO, 168 (30) M^+ − 2CO, 140 (67) M^+ − 3CO or $Fe(CO)_3$, 122 (43) M^+ − 3CO − H_2O, 114 (59), 112 (28) $Fe(CO)_2$, 84 (43) M^+ − $Fe(CO)_3$ or Fe(CO), 56 (100) Fe^+.

Table V. Extended Hückel Parameters

orbital	H_{ii}, eV	ζ
H 1s	−13.6	1.3
C 2s	−21.4	1.625
C 2p	−11.4	1.625
O 2s	−32.3	2.275
O 2p	−14.8	2.275
Fe 4s[a]	−9.1	1.9
Fe 4p[a]	−5.32	1.9
Fe 3d[a]	−12.6	5.35 [0.5505][d] + 2.00 [0.6260][d]
Fe 4s[b]	−10.76	1.575
Fe 4p[b]	−6.19	0.975
Fe 3d[b]	−13.5	5.35 [0.53659][d] + 1.8 [0.66779][d]
Fe 4s[c]	−10.05	1.575
Fe 4p[c]	−6.25	0.975
Fe 3d[c]	−14.4	5.35 [0.53659][d] + 1.8 [0.66779][d]

[a] Parameters for iron from: Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1578. [b] Parameters for iron from: Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598. [c] Parameters for iron obtained from a charge-iterative calculation on the (conjugated dienyl)tricarbonyliron cation: Dobosh, P. A.; Gresham, D. G.; Kowalski, D. J.; Magyar, E. S. *Inorg. Chem.* **1978**, *17*, 1775. [d] Numbers in parentheses are expansion coefficients for double-ζ 3d orbitals.

Anal. Calcd for $C_8H_8FeO_4$: C, 42.89; H, 3.60; Fe, 24.93. Found: C, 43.16; H, 3.75; Fe, 24.85.

Methanolysis of Cation 10. Cation **10** was generated in sulfur dioxide from **9** (70 mg) and fluorosulfonic acid at −78 °C. Quenching with excess methanol at −78 °C gave **11** as a yellow oil: IR (film) 2850, 2060, 1970, 1120 cm^{-1}; NMR[28] ($CDCl_3$) δ 5.52 (t, broad, 1, *J*(apparent) ≈ 9 Hz), 4.15 (s, 2, CH_2O), 3.49 (s, 1, OCH_3), 1.89 (d of d, 1, $J_{1s,1a}$ = 3 Hz, $J_{1s,3}$ = 1.5 Hz, H_{1s}), 1.74 (d of d, 1, $J_{3,4s}$ = 7 Hz, $J_{4s,4a}$ = 2.5 Hz, H_{4s}), 0.3–0.05 [m, 2, analyzed as 0.29 (d, 1, *J* = 3 Hz, H_{1a}) and 0.21 (d of d, $J_{3,4a}$ = 12 Hz, $J_{4s,4a}$ = 2.5 Hz, H_{4a})]. In carbon tetrachloride the CH_2O protons appeared as an AB quartet (*J* = 11 Hz).

Appendix

Extended Hückel calculations were carried out by using the parameters shown in Table V. The modified formula for off-diagonal matrix elements proposed to reduce counter-intuitive orbital mixing[29] was employed.

$$H_{ij} = [k - (k - 1)\Delta^2](S_{ij}/2)[(1 + \Delta)H_{ii} + (1 - \Delta)H_{jj}]$$

$$\Delta = (H_{ii} - H_{jj})/(H_{ii} + H_{jj})$$

An octahedral fragment $Fe(CO)_3$[19d] was placed with its C_3 axis normal to a planar cross-conjugated dienyl ligand and the iron atom 1.585 Å out of the dienyl plane.

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Registry No. 8, 36620-14-1; **9**, 71374-98-6; **10**, 71700-00-0; **11**, 71700-01-1.

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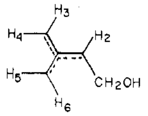
[27] With the use of the separate a_1 and e orbitals[14f] strong repulsions are seen to increase from one ($1a_1$–ϕ_2) in structure **3** to two ($1a_1$–ϕ_2 and $1e_s$–ϕ_2) in **2**.

[28] Numbering of hydrogens is as indicated in i:



i

[29] Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.