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(Cross-conjugated dienyl)tricarbonyliron Cations. 2. 4-Methyl Derivatives

Benedict R. Bonazza, C. Peter Lillya,* Elaine S. Magyar, and Gary Scholes

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003.
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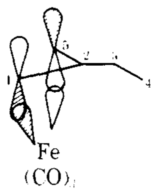
Abstract: Tricarbonyl(cross-conjugated dienyl)iron cations have been generated from precursor alcohols in strong acid solutions and studied by NMR spectroscopy in the temperature range 0 to −50 °C. The 4-*anti*-methyl cation (**11**) coordinates reversibly, but slowly, with fluorosulfonate ion to give the adduct **12**. Broadening of ^1H and ^{13}C NMR signals in the region −40 to −9 °C demonstrates rotation about the C_2–C_3 bond of **11**. The observations exclude **12** as an intermediate in the rotation process. Relief of steric strain associated with the 4-*anti*-methyl enhances the driving force for FSO_3 coordination and lowers the barrier for C_2–C_3 rotation. The 4-*syn*-methyl cation (**15**) does not give a fluorosulfonate adduct and fails to exhibit NMR signal broadening caused by C_2–C_3 rotation at temperatures below 0 °C. Neither cation coordinates with carbon monoxide. Lack of evidence of coordinative unsaturation and the substantial barrier to C_2–C_3 rotation rule out the η^3-allyl type structure predicted by the simplest (one interaction) frontier orbital model.

Introduction

A simple frontier orbital model which treats bonding in terms of dominant frontier orbital interactions enjoys considerable success when used to predict structures of metal π complexes of ligands which offer several nonequivalent coordination sites.[1] The title cations were conceived to make a severe test of a simple (one interaction) frontier orbital model. If spatial overlap for donation of electrons from an occupied frontier orbital of the $Fe(CO)_3$ fragment to the LUMO of the dienyl cation is maximized (**1**), the η^3 or "allyl" structure, **2**, will result. However, this structure can be achieved only at the expense of several other potentially important frontier orbital interactions and by sacrifice of a filled metal valence shell. The $Fe(CO)_3$ fragment possesses a degenerate pair of low-lying frontier orbitals occupied by a single electron pair.[2] Only one of these orbitals (see **1**) finds a suitable partner on the dienyl ligand in this structure. Alternatively, two coordinatively saturated structures, **3** and **4**, can be written for which η^4-diene-[3] and η^4-trimethylenemethane-[4,5] $Fe(CO)_3$ complexes offer structural precedent. The characteristics which should distinguish a cation of structure **2** from one of structures **3** or **4** are coordinative unsaturation and facile (almost free) rotation about the C_2–C_3 bond.



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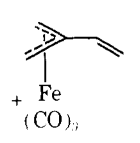

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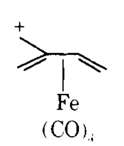
"allyl" structure



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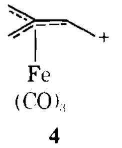
"diene" structure

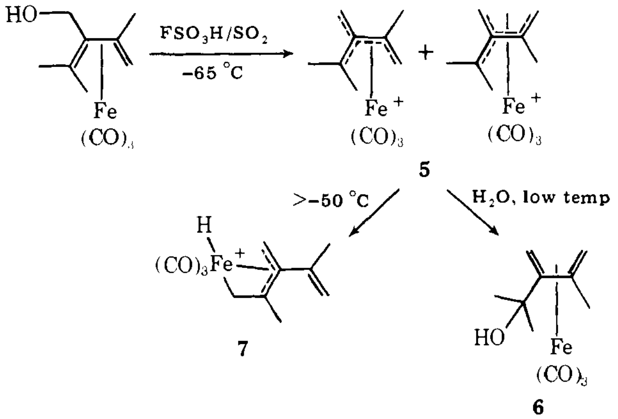


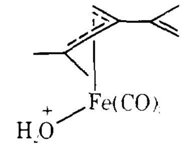
4

"trimethylenemethane" structure

Trimethyl-substituted (cross-conjugated dienyl)tricarbonyliron cations, **5**, have been generated in strong acid media, and formation of isomerized quench products (e.g., **6**) has demonstrated that C_2–C_3 rotation occurs (Scheme I).[2a] The possibility that rotation could occur during quenching owing to reversible formation of **8** led to a search for less ambiguous

Scheme I. Chemistry of the Tricarbonyl(1,1,3-trimethyl-cross-conjugated dienyl)iron Cation in Liquid Sulfur Dioxide





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evidence for structure. Evidence for coordinative unsaturation was mixed. When the temperature of the cation solution was raised above −50 °C in an attempt to study the barrier to interconversion of the proposed species **5**, irreversible formation of the C–H insertion product,[6] **7**, occurred. Ions which lacked methyl substituents at carbons 1 and 5, which would be incapable of C–H insertion, were essential, if thorough solution studies were to be carried out.

We report below the preparation and study of the 4-methyl cations. These studies clearly reveal that C_2–C_3 rotation does occur in the cations but that it is opposed by a sizable barrier.[7]

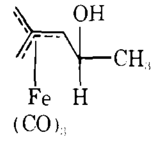
Results and Discussion

The 4-*anti*-Methyl Cation (11) and Its Fluorosulfonate Adduct (12). Sodium borohydride reduction of ketone **9**[8] produced a single epimer isolated after purification in ca. 50% yield. TLC of the crude product produced no evidence for a second epimer. The Ψ-endo[9] relative configuration, **10**, is assigned on the expectation that the borohydride reagent will approach the ketone (most stable conformation **9**) from the side opposite the large $Fe(CO)_3$ group, a phenomenon familiar in $Fe(CO)_3$ complexes of conjugated dienones.[9,10]

Treatment of an SO_2 solution of **10** with 2 equiv of FSO_3H at −78 °C gave a single species **11** (NMR at −65 °C). Warming of this solution to −40 °C caused formation of a second species, **12** (observed by NMR), which continued to form at the expense of **11** until they were in a ca. 1:1 ratio. Further temperature changes in the range −30 to −65 °C had little effect on this ratio. Addition of a large excess of FSO_3H caused complete conversion of **12** to **11**. Use of 2 equiv of 1:1 SbF_5/FSO_3H mixture in place of FSO_3H gave only **11**. These data strongly suggest initial production of a cation (**11**) which slowly comes into equilibrium with its fluorosulfonate adduct. Both in excess FSO_3H and in 1:1 SbF_5/FSO_3H the activity of FSO_3^- ion should be much lower than when a stoichiometric amount of FSO_3H is used.[11,12] This change will decrease the equilibrium concentration of a fluorosulfonate adduct.[13]

Low-temperature hydrolysis or methanolysis of $SbF_5/FSO_3H/SO_2$ solutions which contained only **11** produced moderate yields of **10** and **13**, respectively. Examination of the crude products using TLC and NMR produced no evidence for formation of epimers. The relative configuration of **13** is assigned by analogy to that of **10**. Stereospecific exo departure of water from protonated **10** would give the 4-*anti*-methyl cation **11**. The vicinal coupling $J_{3,4}$ = 9.5 Hz (see below) of **11** is consistent with a 3,4-cis configuration.[14] There is ample precedent for stereospecific exo departure of the leaving group in generation of organometallic cations.[10,15] Stereospecific exo attack by the nucleophile during quenching is almost a corollary of exo departure and also has considerable precedent.[16]

We sought to confirm stereospecific exo ionization by preparation of the Ψ-exo alcohol **17**, which is epimeric to **10**.



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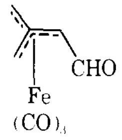

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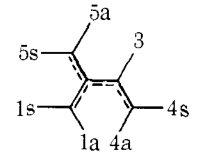
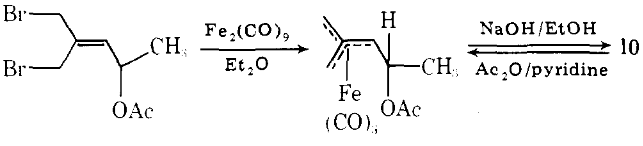
Table I. ^1H NMR Data for Species in Strong Acid/SO_2(l) at −65 °C



^1H	^1H shifts, δ ppm[a] 11	15	12
1a	3.44, d of d[b]	2.40, t	5.20, s, bd
1s	2.79, d of d	2.50, d, bd	2.94, d
3	4.87, d, bd	4.93, s, bd	5.83, d of d
4a	(2.25, d of d)[c]	~4.93, m[d]	(2.28, d of d)[c]
4s	6.28, d of q[d]	(1.80, d)[c]	~6.1, m[d]
5s	3.90, s	3.72, s	2.94, d
5a	4.82, d	4.68, d	5.20, s, bd
J_{HH}	^1H–^1H coupling constants, Hz		
J_{1a1s}	3.0	3	1.5
J_{1s3}	2.2	~1	<1
J_{1a5a}	4.2	3.3	
J_{34s}	9.5		11.5
J_{5a5s}	0	0	1.5
J_{4,CH_3}	7.5	5	6.5
J_{3,CH_3}	1.0		~1

[a] Relative to external Me_4Si. [b] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bd = broad. [c] Shifts for methyl group in parentheses. [d] Assignment confirmed by deuterium labeling.

Ionization of **17** with exo departure of the leaving group would produce the 4-*syn*-methyl ion **15**. Several methods of reduction, e.g., $THF{\cdot}BH_3$, $LiBH_4$, and others, of the ketone **9** produced only **10**. Treatment of the aldehyde **18** with methylmagnesium iodide gave **10** and two additional products with lower R_f (TLC) values which did not possess spectral properties expected for **17**. Treatment of the allylic dibromide **19** with diiron eneacarbonyl produces only the Ψ-endo acetate **20** in 57% yield. No trace of a second epimer could be detected in the crude reaction mixture. The structure of **20** was confirmed by comparison with an authentic sample produced by acetylation of **10** and by saponification to give **10**. This route, which starts with mesityl oxide (see Experimental Section), is now the best method for preparation of **10**. The strong asymmetric induction apparent in this reaction suggests a direct interaction between the polar acetoxy group and iron at some stage prior to π bonding of iron to the ligand. An attempt to equilibrate **10** and **17** in the presence of aluminum isopropoxide, 2-propanol, and a trace of acetone at 100–110 °C produced no change.



19 **20**

^1H and ^{13}C NMR data for **11** and **12** are presented in Tables I and II. Generation of **11** and **12** deuterated at position 4a (see Table I) enabled us to assign the H_3 and H_{4a} signals unambiguously. Long-range ^4J "W" coupling,[17] so characteristic of trimethylenemethane $Fe(CO)_3$ complexes, provides sufficient basis for the remaining assignments in **11**. The H_{1s} signal was assigned on the basis of its 2.2-Hz "W" coupling to H_3. The H_{1a} doublet of doublets at δ 3.44 exhibits the same 3.0 $^2J_{1a,1s}$ splitting as H_{1s}. The doublet at δ 4.82 is H_{5a}, "W" coupled to H_{1a}, while H_{5s}, which cannot exhibit "W" coupling, appears as a singlet at δ 3.90. The small ^2J values (0–3 Hz) are characteristic of 1,3-diene-,[18] trimethylenemethane-,[5] and conjugated dienyl cation-$Fe(CO)_3$[19] complexes. The value of $J_{3,4s}$ = 9.5 Hz is in accord with the 3,4-cis configuration[14] proposed above. Further, the strong deshielding (1.0–1.4 ppm)

Table II. ^{13}C NMR Data for Species in Strong Acid/SO_2(l) at −70 °C

^{13}C	^{13}C shift, δ ppm[a]		
	11	**15**[b]	**12**
1	58.5 t (165)[c]	55.4 t (165)	68.3 t (170)
2	123.4 s	108.0 s	126.9 s
3	104.2 d (165)	106.9 ?	136.8 d (157)
4	110.8 ?	121.0 d (160)[d]	134.4 d (153)
5	77.4 t (174)	77.3 t (170)	68.3 t (170)
CH_3	16.8 q	18.2 q (130)	14.2 q (124)
CO	197.7	196.2	201.1[e]
	200.6	199.0	201.6[f]
	205.8	203.0	

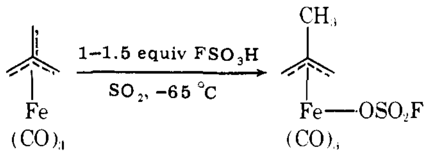
[a] Relative to Me_4Si as calibrated by internal $CDCl_3$ at 76.9 ppm. A positive shift is a downfield (from Me_4Si) shift. [b] Coupling constants ±8 Hz owing to a poor signal/noise ratio in the coupled spectrum. [c] $^1J_{^{13}C-H}$ (Hz) in parentheses, ±4 Hz. [d] Assignment confirmed by deuterium labeling. [e] Relative intensity 2. [f] Relative intensity 1.

of H_{1a} in **11** compared to **15** is an expected consequence of van der Waals deshielding by the proximal 4a-methyl.[20] Assignment of ^{13}C signals is based on signal multiplicities in the ^1H-coupled spectrum and on the spectrum of the 4a-deuterated ions.[21]

The quenching behavior of **12** was more complex than that of **11**. Methanolysis of an **11**/**12** mixture at −78 °C produced 48% of a mixture which contained **13** (76%), **16** (12%), and an unidentified methyl ether (12%). Since the **11** in the mixture produces only **13** on methanolysis, **12** must have produced substantial amounts of the other two products. Different quenching behavior is in accord with our observation that interconversion of **11** and **12** is slow.

Tables I and II present ^1H and ^{13}C NMR data for **12**. Deuterium labeling (see above) confirmed assignment of the H_3 and H_{4s} signals. The shifts of these protons (δ 5.83 and 6.1) are in accord with structure **12** in which the 3,4 double bond is uncomplexed. The remaining protons appear as two equivalent pairs which must be H_{1a}, H_{5a} and H_{1s}, H_{5s}. The lower field signal is assigned to the former pair by analogy to signals of (η^3-allyl)tricarbonyliron halides.[18] A reasonably analogous compound is (η^3-2-methylallyl)tricarbonyliron chloride, which exhibits signals at δ 4.32 and 3.27 for the syn and anti protons, respectively.[4] Lack of "W" coupling between H_{1s} and H_3 of **12** suggests that the propenyl group is rotated out of the $C_1C_2C_5$ plane, presumably to relieve steric interactions involving the 4a-methyl group. The value of $J_{3,4s}$ = 11.5 Hz is consistent with either a 3,4-cis or a 3,4-trans configuration.[14] However, the behavior of the 4-*syn*-methyl cation **15** (below), which exhibits no tendency to coodinate with fluorosulfonate ion, makes it clear that **12** has the 3,4-cis configuration.

The ^{13}C data offer compelling evidence for structure **12**. The signals were assigned easily using the ^1H-coupled spectrum (assignments for C_3 and C_4 could be reversed). The equivalence of C_1 and C_5, as seen in the ^1H spectrum, is again apparent. The C_3 and C_4 shifts show clearly that they are typical olefinic carbons, not complexed to iron.[22] Complexation would shift these signals far upfield from where they appear (cf. Table II).[23] Shifts exhibited by allyl and CO carbons of the closely analogous fluorosulfonate adduct **21** (Table III, second compound) are virtually identical with those of corresponding carbons of **12**. The correspondence between the analogous chloride adduct (Table III) and **12** is almost as close. Additional spectra reported in Table III confirm that these ^{13}C shifts are typical for η^3-allyl-$Fe(CO)_3X$ compounds.



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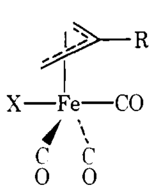
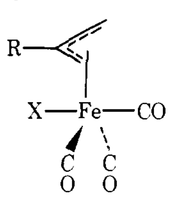
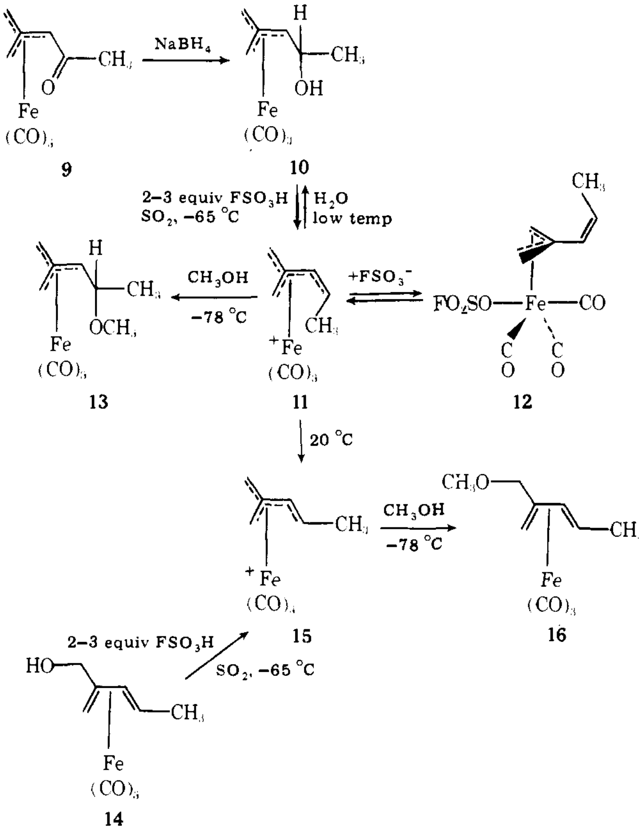
The ^1H and ^{13}C spectra of **12** provide no evidence for existence of two slowly interconverted conformational isomers such as those evident in the ^1H spectra of η^3-allyl-$Fe(CO)_3X$ (X = Cl,[25] Br,[25] I[25,26]) and the ^{13}C spectrum of the iodide (Table III). A crystal structure of the iodide[27] has revealed what is essentially a trigonal bipyramid with the allyl and two CO ligands occupying equatorial positions (**22a**, R = H; X = I). The conformational isomer has been proposed as **22b**.[25] Rossi and Hoffmann's exposition of substituent effects for pentacoordinate transition metals[28] predicts just these structures and provides the basis for predicting a geometry for **12**. We may view **12** as a d^8 complex with allyl cation (a strong π acceptor through its nonbonding HOMO[1,29]) carbonyl (π acceptor) and fluorosulfonate (σ donor) ligands.[30] The site preference for these ligands will clearly be allyl equatorial, carbonyl equatorial, and fluorosulfonate axial. Steric interaction between $X(OSO_2F)$ and R (*cis*-1-propenyl) should destabilize **22b**. Thus, **12** should possess the structure shown in Scheme II. This structure requires two ^{13}CO NMR signals at the slow exchange limit in a ca. 2:1 ratio as observed.[31] Evidence reported here (Table III) and in the literature[18,24-26] suggests that two conformers will be seen only in the absence of 2 substitution (R = H) and multiatom X groups which destabilize conformer **22b**. Slow interconversion of **22a** and **22b** is consistent with the



22a



22b



Scheme II. Chemistry of (Cross-conjugated 4-methyldienyl)tricarbonyliron Cations

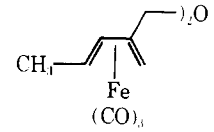
Table III. ^{13}C NMR Data for η^3-$(CH_2C(R)CH_2)Fe(CO)_3X$ Compounds

R	X	solvent	δ ^{13}C, ppm[a] ($J_{^{13}C-H}$, Hz) C$_1$	C$_2$	R	CO
CH_3	Cl	CH_2Cl_2	69.0	120.7	18.7	203.7, 205.4
CH_3	OSO_2F	SO_2/FSO_3H	69.4 t (165)[b]	124.5 s	24.3 q (128)	201.1 s, 202.5 s[c]
H	CF_3CO_2[d]	CH_2Cl_2	69.9 d of d (160, 167)	105.3 d (156)		204.4 s, 205.2 s[c]
		CF_3CO_2H[e]	70.4	107.1		204.5, 205.7
H	I	CH_2Cl_2	60.1[f] 53.1[f]	101.2[f] 107.2[f]		207.8, 208.2[c]

[a] Shifts relative to internal tetramethylsilane. [b] s = singlet, d = doublet, t = triplet, q = quartet. [c] Relative intensity 2:1. [d] $OC(=O)CF_3$ 161.4 q (37), O_2CCF_3 115.1 q (288). [e] M. Brookhart, T. H. Whitesides, and J. M. Crockett, *Inorg. Chem.*, **15**, 1550 (1976). [f] Major isomer listed first, minor isomer listed second, ratio 2:1.

sizable barrier to rotation resulting from the preference for eq$_\perp$ orientation over eq$_\parallel$ orientation exhibited by the strong π acceptor allyl ligand.[28]

The 4-*syn*-Methyl Cation (15). When solutions of the 4-*anti*-methyl cation (**11**) or of the **11**/**12** mixture were warmed above 0 °C, a new ^1H methyl NMR doublet began to grow. Fifteen minutes at 20 °C sufficed for complete conversion to a new species, **15**. Subsequent cooling to −65 °C resulted in sharpening of some ^1H NMR signals, but **11** and **12** were not re-formed. This new species could be generated in SO_2 directly from the 4-*syn*-methyl precursor **14**[32] by treatment with 2-3 equiv of FSO_3H at −78 °C. Use of excess FSO_3H or excess 1:1 SbF_5/FSO_3H at −78 °C gave solutions which exhibited the same ^1H NMR spectrum. The number of ^1H NMR signals required that only one species be present (see below). Thus, **15** can be formulated as a cation which does not coordinate with fluorosulfonate ion. The 3,4-trans configuration is indicated by facile generation at low temperature from **14** and is consistent with observed irreversible conversion of **11** to the less hindered **15** over a substantial energy barrier. Aqueous quenching of SO_2 solutions containing **15** produced complex mixtures of which the ether **23** was tentatively identified as a



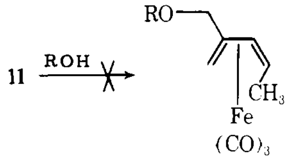
23

major component. Quenching with methanol at −78 °C produced the methyl ether **16** in high yield, adding support for formulation of the cation **15** as a 4-*syn*-methyl species. Preparation of alcohol **14** by solution of **10** in 80% H_2SO_4 followed by aqueous quenching presumably proceeds via cation **15** which produces **14** on quenching.

^1H and ^{13}C NMR data for **15** are presented in Tables I and II. Deuteration at position 4a caused collapse of the complex signal at δ 4.93 to a broadened singlet and a reduction of its relative intensity from 2 to 1. $J_{1s,3}$ was unresolved and could not be used to assign the H_{1s} signal. Nevertheless the assignments of the H_{1a}, H_{1s}, H_{5a}, and H_{5s} signals proceeded in straightforward fashion by use of W coupling, ^2J values, and analogy to **11**. Use of the C_5 deuterated alcohol **31** as precursor gave a spectrum in which the H_{1a}, H_{1s}, H_{5a}, and H_{5s} signals all appeared with diminished intensity (see below). Deuterium labeling at C_4 and use of H-coupled spectra led to unambiguous assignment of all ^{13}C signals but those for C_1 and C_5.[21] These NMR data require that only one species be present in observable amounts.

The *anti*- and *syn*-4-methyl cations, **11** and **15**, respectively, differ significantly in their coordination (and C_2–C_3 rotation, see below) properties. Cation **11** coordinates readily with the external nucleophile FSO_3^- while **15** exhibits no such coordination. We propose that fluorosulfonate coordination with **11** is not the consequence of a coordinatively unsaturated η^3 or "allyl" structure **2**, but rather is driven by the concomitant release of steric strain involving the 4a-methyl of **11**. Formation of the fluorosulfonate adduct **12** permits rotation about the C_2–C_3 bond which relieves this strain. The 4-*syn*-methyl cation **15** experiences no such driving force for coordination.[33]

Quenching Behavior. The steric effect of a 4-*anti*-methyl substituent is also evident in the quenching behavior of these cations. Ions **5** and **15**, as well as the parent cation,[33] give η^4-1,3-diene type products exclusively. This may be because 1,3-diene complexes are more stable than trimethylenemethane complexes.[5] Our conditions give products of kinetic control, which prevents a conclusion on this point. Ion **11**, as usual, is an exception giving exclusively trimethylenemethane-type products. This must be the result of the strong steric destabilization of the diene quench product **24** (and transition state) by the anti methyl group.



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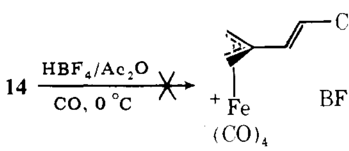
Test for Coordinative Unsaturation. Coordinative unsaturation is one of the distinguishing features of the "allyl" structure **2**, predicted by the simplest frontier orbital model. Cations of structure type **2** should give η^3-allyl-$Fe(CO)_4$ cations,[34] **25**, when generated in the presence of carbon monoxide.



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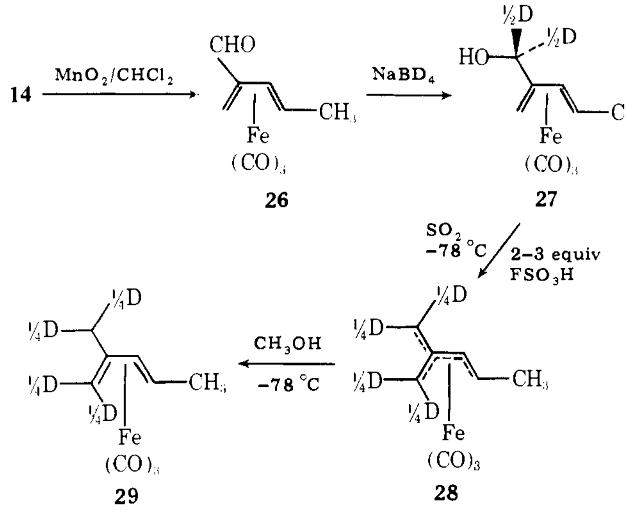
Generation of cations **11** and **15** under 1 atm of CO at 0 °C (see above)[35] or at −65 °C in SO_2 did not lead to characterizable products analogous to known stable η^3-allyl-Fe-$(CO)_4{}^+BF_4{}^-$ salts,[34,35] however.

Rotation about the C_2–C_3 Bond. As a criterion for distinguishing structure **2** from structures **3** and **4**, rotation about the C_2–C_3 bond is of vital interest. All the cations exhibit NMR spectra characteristic of the slow exchange limit at temperatures of −50 °C or below (Tables I and II). Rearrangement to **7** thwarted attempts to study the trimethyl cation, **5**, at higher temperatures.[2a,c,7] NMR spectra of the 4-*syn*-methyl cation (**15**) exhibited no temperature dependence up to −20 °C. Above this temperature spectral quality deteriorated with all lines being broadened. No selective broadening for the potentially exchanging nuclei, C_1 and C_5 and their hydrogens, could be detected. Attempts to determine spectra in neat flu-

Scheme III. Generation of the 4-*syn*-Methyl Cation from a 5-Deuterated Precursor



orosulfonic acid gave similar results. To test for rotation which was slow on the NMR time scale we generated the 4-*syn*-methyl cation with deuterium at C_5 (Scheme III). An ^1H NMR spectrum of the precursor, **27**, revealed 50% deuteration for each of the two diastereotopic hydrogens. Careful generation of the cation at −78 °C and immediate (ca. 2 min) recording of its ^1H NMR spectrum showed that the H_{1a}, H_{1s}, H_{5a}, and H_{5s} signals were all equally diminished to ca. ¾ of their normal intensity. The methanolysis product, **29**, also exhibited equal distribution of the deuterium label among the 1a, 1s, 5a, and 5s positions. Thus, while rotation is too slow to broaden these lines at temperatures under −20 °C, it is sufficiently rapid to give complete rotational equilibrium after 2 min at −65 °C.

While the fluorosulfonate adduct exhibits temperature-independent ^1H and ^{13}C NMR spectra up to ca. 0 °C, the ^1H and ^{13}C spectra of the 4-*anti*-methyl cation show the effects of C_2–C_3 rotation clearly. In the ^1H spectrum only the lines for the exchanging nuclei H_{1a}, H_{1s}, H_{5a}, and H_{5s} exhibit temperature dependence. Solutions of **11** only were prepared using 8 equiv of fluorosulfonic acid or 2 equiv of 1:1 SbF_5/FSO_3H. At −65 °C all signals were sharp. Warming to −48 °C caused perceptible broadening of the four affected lines. At −27 °C all fine structure from spin-spin coupling was lost, and at −2 °C these four lines were almost broadened into the base line. Recooling to −65 °C restored the original spectrum. The ^{13}C spectrum exhibited similar reversible selective broadening of the C_1 and C_5 signals: broadening is slight at −29 °C and pronounced at −9 °C. Further warming of these solutions caused isomerization to **15** (see above) and deterioration of spectral quality. Thus, the coalescence and fast exchange regions are inaccessible. ^1H line shapes at −31, −17, and −2 °C all gave estimates of $\Delta G^{\ddagger}$ in the range 12.8 ± 0.4 kcal/mol.[36]

When solutions which contained both **11** and **12** were warmed, **11** exhibited the same reversible line broadening while the ^1H and ^{13}C signals of **12** were completely unaffected. For example, at −9 °C the C_1 and C_5 signals of **11**, with a slow exchange separation of 18.9 ppm, were very broad, but the C_2 signals for **11** and **12**, which have only a 3.5-ppm separation, were still sharp. These important observations demonstrate unambiguously that C_2–C_3 rotation in **11** does not proceed via formation of the fluorosulfonate adduct **12**. This conclusion is in accord with the observation that conversion of **11** to **12** is a slow process. Thus, C_2–C_3 rotation is an intrinsic property of (cross-conjugated dienyl)tricarbonyliron cations.

The relatively rapid rotation in the 4-*anti*-methyl cation **11** must arise from steric destabilization of the starting "planar" conformation. Rotation in **15** is clearly opposed by a free-energy barrier which is substantially higher than the ca. 13 kcal/mol estimated for **11**.[37] Especially for this reason, but also for lack of evidence for coordinative unsaturation, the η^3-allyl structure, **2**, is untenable as the lowest energy structure for these cations.

The η^3-allyl structure must be energetically accessible, for it is just such a structure which is a transition state (or intermediate) for C_2–C_3 rotation. The rotational barrier should be a measure of the energy required to form such a coordinatively unsaturated structure. We are currently engaged in attempts to determine this barrier using the spin saturation method of Forsen and Hoffmann.[38]

Summary

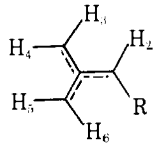
Cross-conjugated dienyltricarbonyliron cations **11** and **15** are stable in strong acid media at temperatures up to 0 °C. While the anti methyl isomer, driven by relief of steric strain, forms a fluorosulfonate adduct, the cations do not, in general, behave as coordinatively unsaturated species. Rotation about the C_2–C_3 bond occurs but is opposed by a substantial energy barrier. These observations rule out the η^3-allyl type structure (**2**) predicted by the simplest (one interaction) frontier orbital model. The properties of the parent (unsubstituted) cation are in complete accord with these conclusions and will be reported separately along with an all-valence treatment of cation structure.

Experimental Section

Infrared spectra were recorded using Perkin-Elmer 727 and Beckman IR-10 spectrometers. ^1H NMR spectra were recorded using Perkin-Elmer R-12 (60 MHz) and R-32 (90 MHz) instruments at room temperature, and Varian A-60 (60 MHz) and Perkin-Elmer R-32 (90 MHz) instruments at low temperatures. ^{13}C NMR spectra were obtained using a Bruker HX-90 spectrometer (22.63 MHz) equipped with a Nicolet Series 1080 computer and Bruker SST-100/700 variable-temperature unit. Temperatures were calibrated using a copper-constantan thermocouple potentiometer. Room temperature NMR samples were filtered through a Metricel Alpha-6 filter (pore size 0.45 μm) to remove any paramagnetic particles. Preparation of strong acid/SO_2 solutions for NMR spectroscopy has been described.[21b,39] Technical grade fluorosulfonic acid (J. T. Baker) was distilled and stored in Teflon bottles.

Dry column chromatography was carried out on 100–200 mesh silica gel (Fisher Scientific) deactivated with 10% water in Nylon tubes. After development, the columns were cut into sections, and the individual fractions were removed using 5% methanol in ether or methylene chloride. (Trimethylenemethane)tricarbonyliron was prepared from freshly distilled methallyl chloride and diiron nonacarbonyl using the procedure of Ehrlich and Emerson[5] in 18% yield.

^1H NMR signals of trimethylenemethane complexes described below are labeled as follows.



(Acetyltrimethylenemethane)tricarbonyliron (9). Modification of the reported procedure[5] by use of dichloromethane as solvent and an aqueous ammonia quench produced yields of ca. 25% of pure **9**: bp 44–45 °C (0.05 mm) (lit.[5] bp 55–59 °C (0.05 mm)); IR (CCl_4) 2070, 1990 (C≡O), 1685 cm^{-1} (C═O); NMR ($CDCl_3$) δ 3.82 (d, 1, $J_{3,6}$ = 4 Hz, H_6), 2.99 (d, 1, $J_{2,5}$ = 2 Hz, H_2), 2.41 (d, 1, $J_{2,5}$ = 2 Hz, H_5), 1.98 (d, 1, $J_{3,6}$ = 4 Hz, H_3), 1.98 (s, 3, CH_3), 1.90 (s, 1, H_4). Assignments of the H_2, H_3, H_5, and H_6 signals are different than those reported[5] and are based on the spectrum of the 2-deuterio (-$COCD_3$) derivative prepared by H-D exchange in $NaOCH_3/CH_3OD$.[40] The H_6 signal is strongly deshielded owing to the long-range anisotropic effect of the proximal carbonyl.[41]

Ψ-*endo*-(α-Hydroxyethyltrimethylenemethane)tricarbonyliron (10). Sodium borohydride reduction of **9** in methanol[5] afforded a nearly quantitative yield of reasonably pure **10.** Pure **10** was obtained using dry-column chromatography in ca. 50% yield. Infrared and NMR spectra were similar to those reported. NMR assignments were confirmed by synthesis of derivatives labeled with deuterium at the carbinol carbon (reduction of **10** with $NaBD_4$) and at the 2 and methyl positions.

4-Methyl-3-penten-2-yl Acetate. To 4-methyl-3-penten-2-ol (5 g, 0.05 mol, prepared by sodium borohydride reduction of mesityl oxide), in 20 mL of dry pyridine, acetic anhydride (10 g, 0.09 mol) was added at room temperature with stirring. After stirring overnight, the reaction mixture was poured into water from which the product was recovered by ether extraction. Washing of the combined ether extracts with 10% HCl, saturated $NaHCO_3$, and saturated NaCl, drying ($MgSO_4$), and evaporation left the product as a yellow oil. Distillation gave a colorless oil: bp 50–52 °C (15 mm); yield 86%; IR (film) 1735 cm^{-1} (C=O); NMR (neat) δ 5.60 (d of q, 1, $J_{2,3} = 9, J_{2,CH_3} = 6$ Hz, H_2), 5.15 (d, broad, 1, $J_{2,3} = 9$ Hz, H_3), 8.05 (s, 3, CH_3CO_2–), 8.30 (d, 6 H, $J = 1.5$ Hz, 4-CH_3 and 5-CH_3), 8.75 (d, 3, $J_{2,CH_3} = 6$ Hz, 1-CH_3). An NMR spectrum reported for this compound exhibits one-proton multiplets at δ 5.7–4.0 and 2.0–1.5 (under CH_3 resonances).[42] The latter is too far upfield to be consistent with either H_2 or H_3 of this structure.

Ψ-*endo*-(α-Acetoxyethyltrimethylenemethane)tricarbonyliron (20). 4-Methyl-3-penten-2-yl acetate (5 g, 0.035 mol), *N*-bromosuccinimide (12 g, 0.07 mol), and a small amount of benzoyl peroxide were heated at reflux in 100 mL of carbon tetrachloride for 3.5 h when all the *N*-bromosuccinimide had reacted. Filtration removed the succinimide, which floated on the CCl_4 surface; subsequent evaporation of solvent left the dibromide as a dark oil (11 g). Distillation gave a fraction, bp 95–110 °C (0.01 mm), which by GLC (10% SE-30, 150 °C) was mainly one compound. A second distillation afforded 6 g (57%) of 5-bromo-4-bromomethyl-3-penten-2-yl acetate in 95% purity as a colorless oil: bp 102–105 °C (0.01 mm); IR (film) 1735, 1445, 1370, 1235, and 1040 cm^{-1}; NMR (neat) δ 5.5–5.9 (m, 2, H_2 and H_3), 4.25 (AB quartet, 2, $J = 10$ Hz, CH_2Br), 4.10 (s, 2, CH_2Br), 8.0 (s, 3, CH_3CO_2–), 8.65 (d, 3, $J_{2,CH_3} = 6$ Hz, 1-CH_3).

Crude dibromide [25 g, 0.083 mol, bp 95–105 °C (0.01 mm)] was stirred at 50 °C with diiron nonacarbonyl (60.5 g, 0.167 mol) in hexane for 6 h. Filtration removed the yellow ferrous bromide precipitate, and evaporation of the filtrate left a dark residue which was purified using dry-column chromatography. Elution with benzene gave a high R_f red band (3 g) which on standing appeared to decompose to give the second component which eluted as a yellow band at R_f 0.5 (10 g). Though a satisfactory C, H, Fe analysis could not be obtained, the spectral properties of material in the yellow band, bp 60–65 °C (0.005 mm), yield 57%, show that it is **20:** IR (neat) 2075, 1990, 1740, 1460, 1375, 1240 cm^{-1}; NMR ($CDCl_3$) δ 4.40 (d of q, 1, $J_{1,2} = 10$, $J_{1,CH_3} = 6$ Hz, CHOH), 2.85 (d of d, 1, $J_{1,2} = 10, J_{2,5} = 2.5$ Hz, H_2), 2.55 (d, 1, $J_{3,6} = 4$ Hz, H_6), 2.15 (d, 1, $J_{2,5} = 2.5$ Hz, H_5), 1.98 (s, 3, CH_3CO_2–), 1.80 (s, 1, H_4), 1.75 (d, 1, $J_{3,6} = 4$ Hz, H_3), 1.40 (d, 3, $J_{1,CH_3} = 6$ Hz, CH(OAc)CH_3); mass spectrum *m/e* (rel intensity) 252 (21) $M^+ - CO$, 224 (18) $M^+ - 2CO$, 196 (100) $M^+ - 3CO$, 181 (11) $M^+ - 3CO - CH_3$, 170 (32), 154 (25), 136 (45) $M^+ - 3CO - CH_3CO_2H$, 134 (50). Absence of an *m/e* 168 fragment (252 − 3CO) establishes that *m/e* 252 is the $M^+ - CO$ fragment, not the molecular ion.

Interconversion of 10 and 20. Ψ-Endo acetate **20** (100 mg) was hydrolyzed with sodium hydroxide (500 mg) in 20 mL of 1:1 methanol–water at room temperature for 2 h. This mixture was poured into water, and the product was isolated by ether extraction. Drying ($MgSO_4$) and evaporation left Ψ-endo alcohol **10** identified by TLC, IR, and NMR.

Acetic anhydride (2.0 mL, 0.019 mol) was added to a stirred mixture of Ψ-endo alcohol **10** (100 mg, 0.42 mmol) in 2.0 mL of dry pyridine. The reaction mixture was stirred at room temperature for 5 h and poured into water. The product was isolated by ether extraction. Purification by dry-column chromatography gave Ψ-endo acetate **20** identified by TLC, IR, and NMR.

(*trans*-2-Hydroxymethyl-1,3-pentadiene)tricarbonyliron (14). Ψ-*endo*-(α-Hydroxyethyltrimethylenemethane)tricarbonyliron (**10,** 100 mg, 0.42 mmol) was dissolved in a minimum volume of chloroform and added dropwise to 2.0 mL of stirring 80% sulfuric acid at 0 °C. The resulting red solution was stirred at 0 °C for 10 min and then poured into water. The organic products were obtained as 80 mg of a yellow oil after ether extraction, washing, drying ($MgSO_4$), and evaporation of ether. Dry-column chromatography ($CHCl_3$) gave the product as a low R_f band, yellow oil: bp 85–90 °C (0.3 mm); 50 mg (50%); IR (neat) 3350, 2950, 2070, 1980 cm^{-1}; NMR ($CDCl_3$) δ 5.25 (d, 1, $J_{3,4} = 8$ Hz, H_3), 4.23 (AB quartet, 2, $J_{gem} = 13$ Hz, -CH_2OH), 2.0 (s, broad, OH), 1.74 (m, broad, 1, $H_{1\text{-syn}}$), 1.40 (d, 1, $J_{4,CH_3} = 6$ Hz, CH_3), 1.25–0.90 (m, 1, H_4), 0.31 (d, 1, $J_{1\text{-syn},1\text{-anti}} = 3$ Hz, $H_{1\text{-anti}}$); mass spectrum *m/e* 238 (M^+), 210 ($M^+ - CO$), 182 ($M^+ - 2CO$), 154 ($M^+ - 3CO$).

Anal. Calcd for $C_9H_{10}FeO_4$: C, 45.41; H, 4.23; Fe, 23.5. Found: C, 45.68; H, 4.11; Fe, 22.3.

Compound **14** was also prepared on a 1-g scale in 64% yield from Ψ-endo acetate **20** utilizing the procedure above. NMR spectra of the 4-d_1 (from deuterated **10**) and 5-d_1 (see below) derivatives are in accord with the assignment of NMR signals above.

Hydrolysis of Cation 11. From a solution of **10** (0.17 g, 0.70 mmol) and 1:1 antimony pentafluoride/fluorosulfonic acid (0.46 g, 0.18 mL, 1.4 mmol) in 2.0 mL of sulfur dioxide, the sulfur dioxide was removed at −78 °C (0.05 mm). The sample was removed from the −78 °C bath and 4 mL of water was added quickly with stirring. Additional water (10 mL) was added at room temperature, and the solution was neutralized with sodium bicarbonate. Organic products were extracted into carbon tetrachloride. The yield of **10** was 0.07 g (40%). An NMR spectrum of the product exhibited, in addition to absorptions of **10**, broad signals in the region δ 1.0–2.0.

Methanolysis of Cation 11. A solution of **11** in sulfur dioxide at −78 °C (see hydrolysis above) was quenched by addition of 3 mL of −78 °C anhydrous methanol with stirring. After 10 min at −78 °C, the solution was warmed to room temperature and 25 mL of water was added. Organic products were extracted into carbon tetrachloride, the combined extracts were washed with water and dried (molecular sieve Type 5A), and the volume was reduced to 0.5 mL. The NMR spectrum of this solution indicates that the product is 95% of one diastereomer of (α-methoxyethyltrimethylenemethane)tricarbonyliron (**13**): IR (CCl_4) 2830 (CH_3O), 2060, 1970 (C≡O), 1100 cm^{-1} (C—O—C); NMR (CCl_4, external Me_4Si) δ 3.14 (s, 3, OCH_3), 2.85 (m, 2, H_2 and CHOCH_3), 2.35 (d, 1, $J_{3,6} = 4$ Hz, H_6), 2.00 (d, broad, 1, $J_{2,5} \sim 2$ Hz, H_5), 1.65 (s, 1, H_4), 1.57 (d, 1, $J_{3,6} = 4$ Hz, H_3), 1.25 (m, 3, CCH_3). Successive additions of $Eu(fod)_3$ to the NMR sample led to resolution of the H_1–H_2 multiplet into a downfield H_1 multiplet partly obscured by the methoxy signal and an upfield H_2 doublet of doublets, $J_{1,2} = 10$, $J_{2,5} = 2$ Hz, and to simplification of the CCH_3 signal to a doublet, $J_{1,CH_3} = 5.5$ Hz. Mass spectrum: *m/e* 252 (M^+), 224 ($M^+ - CO$), 196 ($M^+ - 2CO$), 168 ($M^+ - 3CO$).

Methanolysis of an 11 + 12 Mixture. A mixture of **11** and **12** was generated by preparing a solution of **10** (0.17 g, 0.70 mmol) and fluorosulfonic acid (0.15 g, 0.09 mL, 1.5 mmol) in sulfur dioxide at −78 °C and warming to −25 °C for 10 min. Quenching at −78 °C with methanol and workup as above gave a mixture analyzed by NMR spectroscopy as 76% **13,** 12% **16,** and 12% of another methyl ether.

Methanolysis of Cation 15. Cation **15** was generated in sulfur dioxide at −78 °C from **14** and 2 equiv of fluorosulfonic acid. The ^1H NMR spectrum of this solution was that of **15.** Quenching with methanol and workup as described for methanolysis of **11** (above) gave a yellow oil which gave one spot on TLC. Spectral analysis showed that this compound was (*trans*-2-methoxymethyl-1,3-pentadiene)-tricarbonyliron (**16**): IR (CCl_4) 2830 (CH_3O), 2060, 1975 (C≡O), 1100 (C—O); NMR ($CDCl_3$) δ 5.30 (d, broad, 1, $J_{3,4} = 8$ Hz, H_3), 4.06 (s, 2, -OCH_2-), 1.76 (d of d, 1, $J_{1\text{-syn},1\text{-anti}} = 3$, $J_{1\text{-syn},3} = 1$ Hz, $H_{1\text{-syn}}$), 1.42 (d, 3, $J_{4,CH_3} = 6$ Hz, CCH_3), 1.3–0.9 (m, ca. 1, H_4), 0.31 (d, $J_{1\text{-syn},1\text{-anti}} = 3$ Hz, $H_{1\text{-anti}}$). In carbon tetrachloride the -OCH_2- signal appears as an AB quartet ($J = 12$ Hz) centered at δ 4.08. The 4-*d* derivative exhibited a broadened singlet for H_3 and a singlet for CCH_3 and gave no H_4 multiplet. Methanolysis of **31** gave a product which exhibited diminished $H_{1\text{-syn}}$, $H_{1\text{-anti}}$, and -OCH_2- NMR signals. Mass spectrum: *m/e* 252 (M^+), 224 ($M^+ - CO$), 196 ($M^+ - 2CO$), and 168 ($M^+ - 3CO$).

(*trans*-2-Formyl-1,3-pentadiene)tricarbonyliron (26). Alcohol **14** (200 mg, 0.84 mmol) was stirred in dry methylene chloride with active manganese dioxide (2.0 g, 23 mmol).[43] At 2 h time, TLC began to reveal a second product at intermediate R_f, so the reaction was stopped and the mixture filtered through Celite. Evaporation left a residue which was eluted on a dry column with methylene chloride to separate aldehyde and starting alcohol. The higher R_f component was aldehyde **26:** mp 29.5–30 °C; 70 mg (35%); IR (film) 2975, 2950, 2875, 2800, 2070, 1980, 1690 cm^{-1}; NMR ($CDCl_3$) δ 9.78 (s, 1, -CHO), 5.73 (d, broad, 1, $J_{3,4}$ = 8 Hz, H_3), 2.22 (d of d, $J_{1\text{-syn},1\text{-anti}}$ = 3, $J_{1\text{-syn},3}$ = 1.5 Hz, $H_{1\text{-syn}}$), 1.85–1.25 (m, ca. 4, complex multiplet for H_4 and apparent singlet at δ 1.53 for CCH_3), 0.46 (d, 1, $J_{1\text{-syn},1\text{-anti}}$ = 3 Hz, $H_{1\text{-anti}}$).

Anal. Calcd for $C_9H_8FeO_4$: C, 45.80; H, 3.42; Fe, 23.7. Found: C, 45.90; H, 3.37; Fe, 24.2.

(*trans*-2-Hydroxymethyl-1,3-pentadiene-*6*-d_1)tricarbonyliron (27). Aldehyde **26** (70 mg, 0.29 mmol) was dissolved in 20 mL of absolute ethanol, and sodium borodeuteride (100 mg, 2.4 mmol) was added to the stirring solution at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and at room temperature for an additional 1 h and then poured into water. The product was isolated by extraction into ether and subsequent dry-column chromatography (CH_2Cl_2): pale yellow oil, yield 60 mg (98%). An NMR spectrum exhibited a broadened -CH_2OH doublet with half the total intensity of the corresponding AB quartet exhibited by the d_0 derivative, **14.** Thus, deuterium is distributed equally between the two diastereotopic positions.

(Formyltrimethylenemethane)tricarbonyliron (18). (Hydroxymethyltrimethylenemethane)tricarbonyliron[33] (1.75 g, 0.0078 mol) was stirred at room temperature with active manganese dioxide[43] (17.5 g, 0.2 mol) for 5 h in benzene. Filtration and evaporation left crude product which was purified by dry-column chromatography (CH_2Cl_2): single yellow band, R_f 0.6. The aldehyde crystallized, 1.3 g (74%). Recrystallization from *n*-pentane at −20 °C gave waxy, yellow crystals, mp 71–71.5 °C. Sublimation at 25–30 °C (0.001 mm) raised the melting point to 75 °C: IR (CCl_4) 2100, 2020, 1670, 1150 cm^{-1}; NMR ($CDCl_3$) δ 8.96 (d, 1, J = 7.5 Hz, CHO), 3.25–3.05 [m, 2, analyzed as 3.17 (d, 1, $J_{3,6}$ = 5 Hz, H_6) and 3.15 (d of d, 1, J = 7.5, $J_{2,5}$ = 2 Hz, H_2)], 2.47 (d, 1, $J_{2,5}$ = 2 Hz, H_5), 2.38 (d, 1, $J_{3,6}$ = 5 Hz, H_3), 2.21 (s, 1, H_4); mass spectrum *m/e* (rel intensity) 222 (3) M^+, 194 (33) $M^+ - CO$, 166 (32) $M^+ - 2CO$, 138 (30) $M^+ - 3CO$, 112 (25) $Fe(CO)_2^+$, 110 (35) $M^+ - 4CO$, 84 (30) $Fe(CO)^+$, 56 (100) Fe^+.

Anal. Calcd for $C_8H_6FeO_4$: C, 43.28; H, 2.72; Fe, 25.2. Found: C, 43.17; H, 2.59; Fe, 30.0.

Treatment of **18** with methylmagnesium iodide in ether produced **10** (identified by TLC and NMR) in addition to two unidentified products.

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(33) A corollary of this proposal is that any cation which lacks substituents in positions 4a or 1a (see Table I) should show no tendency to coordinate with fluorosulfonate ion. A test of this proposal using the parent (unsubstituted) cation gave this result: Bonazza, B. R.; Lillya, C. P.; Magyar, E. S.; Scholes, G. Submitted for publication.

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