However, the fourth band at 8.58 eV for F appears broader and more intense than does the corresponding band for exo ruthenium complexes D and E. Thus the π allyl HOMO ionization process may lie under this band centered at 8.58 eV, or it may lie under the leading edge of the extremely intense band centered at 9.64 eV, which undoubtedly contains one or more C_5H_5 components. The I_6 band at 10.31 eV for F must correspond to ionization of the most stable π-allyl orbital as well as a second C_5H_5 component. Given that it is only ca. 0.4 eV lower in ionization energy than the corresponding band for its ruthenium analogue (D), we believe that the π allyl HOMO ionization band is most probably contained beneath the leading edge of the 9.64 eV band.

In conclusion, it is apparent that UPS may be used to detect subtle differences in the electronic structures of conformational isomers of transition-metal complexes. Furthermore, we believe that the allyl π HOMO in transition-metal complexes containing a single η^3-allyl moiety will be stabilized relative to free allyl in contrast to the destabilization noted in a recently published report concerning bis(η^3-allyl)metal complexes.[8] We realize, however, that the two types of complexes may be quite different electronically, due to the presence of the second allyl group in the bis complexes, such that both interpretations may well be correct.

Acknowledgment. S.D.W. gratefully acknowledges the financial support of the Research Corp. for the UPS portion of this work. D.H.G. gratefully acknowledges the financial support by the Graduate Research Council of the University of Louisville.

Registry No. A, 77983-17-6; B, 77933-78-9; C, 32611-12-4; D, 77983-18-7; E, 78037-33-9; F, 52326-25-7.

(Cross-conjugated dienyl)tricarbonyliron Cations. 4. Trimethyl Derivatives

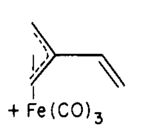
Benedict R. Bonazza, C. Peter Lillya,* and Gary Scholes

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

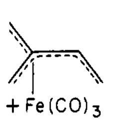
Received June 25, 1981

Isomeric [trimethyl(cross-conjugated dienyl)]tricarbonyliron cations A (**11a**) and B (**11b**) have been generated in SO_2 at −65 °C by using 2–3 equiv of FSO_3H or excess FSO_3H and excess 1:1 SbF_5/FSO_3H. Precursors **3**–**5** all produce the same equilibrium A/B mixture. These observations, and the isomerization which attends generation of A and B from **3** followed by immediate methonolysis at low temperature to give mainly **5**, require facile isomerization about the C_2–C_3 bond at low temperature. At temperatures up to −40 °C no NMR line broadening owing to rotation is observed. Warming of the A/B mixture to −50 °C causes conversion to a σ,π-allyl complex of structure **7a** or **7b**. Generation of the cations under short lifetime conditions by solvolysis in 80% aqueous acetone gives nearly complete (95%) isomerization. Cations A and B fail to give detectable fluorosulfonate, halide, or CO adducts, possibly owing to an increase in steric crowding attendant to adduct formation. Isomerization to the (conjugated dienyl)tricarbonyliron cation **10** resulted when **3** was treated with HBF_4 under 1 atm of CO at 0 °C. These observations are in accord with our earlier deduction that (cross-conjugated dienyl)tricarbonyliron cations do not possess the coordinatively unsaturated structure **1** predicted by a one-interaction frontier orbital model but that they can achieve such a structure at the cost of a modest amount of energy.

Our previous studies of the parent cation and its isomeric 4-methyl derivatives have shown that (cross-conjugated dienyl)tricarbonyliron cations do not possess the coordinatively unsaturated η^3 structure **1** predicted by frontier orbital theory[1] but that they can achieve it at the cost of a modest amount of energy.[2,3] ^1H and ^{13}C NMR data are in best accord with the η^4 structure **2** with substantial charge delocalization.[3] We report below our observations of trimethyl derivatives of these cations.[4] This system was designed to make rotation about the C_2–C_3 bond, a consequence of formation of structure **1**, manifest as isomerization. These ions exhibit more complex chem-

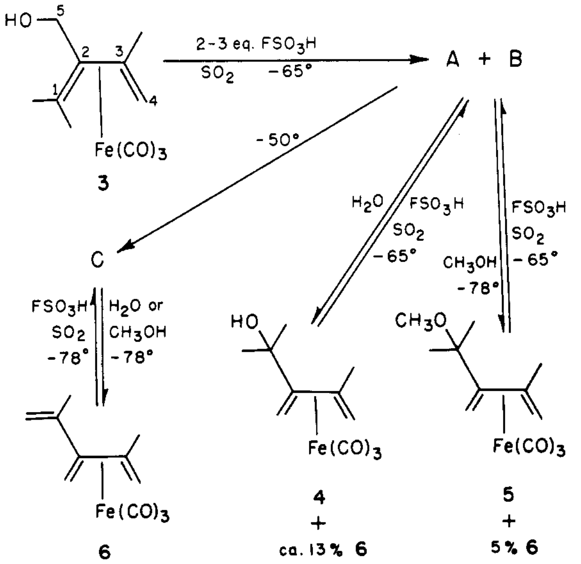


1



2

Scheme I. Generation and Quench of (Cross-conjugated dienyl)tricarbonyliron Cations



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(1) Lillya, C. P. In "Stereodynamics of Molecular Systems"; Sarma, R. H., Ed.; Pergamon Press: New York, 1979; p 209.

(2) Bonazza, B. R.; Lillya, C. P.; Magyar, E. S.; Scholes, G. *J. Am. Chem. Soc.* **1979**, *101*, 4100.

(3) Dobosh, P. A.; Lillya, C. P.; Magyar, E. S.; Scholes, G. *Inorg. Chem.* **1980**, *19*, 228.

(4) Preliminary communication: Bonazza, B. R.; Lillya, C. P. *J. Am. Chem. Soc.* **1974**, *96*, 2298.

ical behavior than their predecessors; several new rearrangements are reported. Nevertheless, their properties are in accord with our earlier conclusions about electronic structure.

Results

The readily available alcohol complex **3** was chosen as our first precursor for a cross-conjugated cation complex (see Experimental Section for details on synthesis). The chemistry observed when ions were generated and quenched at low temperatures is depicted in Scheme I. Treatment (under nitrogen) of a yellow −65 °C solution of **3** in SO_2 with 2–3 equiv of cold FSO_3H produced a clear red-brown solution. Cooling of this solution to −78 °C (Dry Ice/acetone bath), addition of excess water, and subsequent gradual warming to 0 °C to allow the ice to melt and quenching to occur produced one major product, **4**. Quenching with an aqueous bicarbonate solution gave the same result. Addition of −78 °C methanol to the −78 °C red-brown solution caused the color to change back to the original yellow at −78 °C. Workup produced an 83% yield of crude product demonstrated to be a mixture of only two compounds: **5** (95%) and **6** (5%). Within the limits imposed by experimental method, quench products did not depend on the age of the red-brown acidic solution. Low-temperature methanolysis performed immediately after mixing, all at −78 °C, gave the same mixture of **5** and **6**. The time from addition of the first FSO_3H to mixing of the methanol quench solution was less than 30 s. Treatment of cold SO_2 solutions of **4** or **5** with FSO_3H generated red-brown solutions which were, according to ^1H NMR, identical with that generated from **3**. Even when the methyl region was scanned immediately (≤1 min) after ion generation, the results were independent of precursor.

Spectroscopic evidence for rearrangement of the original 1,1-dimethyl alcohol, **3** (see Scheme I for numbering), to compounds of the 5,5-dimethyl series **4–6** is compelling. The highest field ^1H NMR signals of **3** are an AB pattern centered at δ 1.9 ($\Delta\nu_{AB} \approx 6$ Hz, $J_{AB} = 3$ Hz) for the hydrogens at C_4. The anti (cis) hydrogen is deshielded, owing to its nonbonded interaction with the anti methyl at C_1.[5,6] Methyl ether **5**, which is typical of **4–6** in this regard, exhibited doublets at δ 0.03 ($J = 2$ Hz) and δ −0.38 ($J = 2.5$ Hz). These high-field signals are characteristic of anti hydrogens on diene ligands which bear no terminal substituents.[6] The remaining spectral and analytical data confirm the structures shown for **4–6** (see Experimental Section).

Warming of the red-brown acidic solution to temperatures in excess of −50 °C for several minutes followed by quenching at −78 °C with either water or methanol gave a new quench product, **6**, in high yield. The same compound was subsequently shown to be identical with the minor product of hydrolysis or methanolysis of the original red-brown solution. The triene structure **8** is uniquely consistent with the spectral properties and elemental composition of this compound.

The ^1H NMR spectrum (see Figure 1) of the original red-brown solution exhibits signals that are consistent with the presence of two species, A and B. Integration of what are clearly methyl singlets gives a ratio of 2 parts of A to 1 part of B. Treatment of cold SO_2 solutions of **3** with excess FSO_3H or with excess 1:1 SbF_5/FSO_3H gave red-brown solutions of A and B in the same 2:1 ratio, and quenching gave the same products described above. Addition of potassium fluorosulfonate to a solution of A and B caused no observable change. However, it could not be demonstrated that significant amounts of $KFSO_3$ dissolved. Treatment of **3** with excess 98% H_2SO_4 at 0 °C caused some gas evolution and formation of a brown solution. Subsequent aqueous quenching gave triene complex **6**. Spectral data do not permit unambiguous assignment of structures to A and B and will be dealt with in the Discussion.

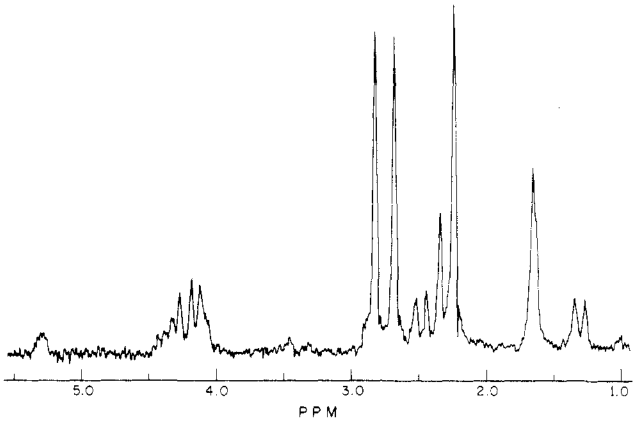
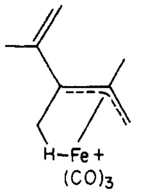
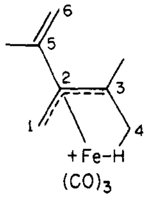


Figure 1. 60-MHz ^1H NMR spectrum of species A and B generated by treatment of **3** in SO_2(l) with 2 equiv of fluorosulfonic acid at −65 °C. The spectrum was recorded at −68 °C.

Warming to −50 or −40 °C caused formation of a new species, C, at the expense of A and B, which maintain their 2:1 ratio as they disappear. Subsequent cooling to −78 °C had no effect on the ^1H NMR spectrum of this solution. The ^1H and ^{13}C NMR spectra (see Experimental Section) of species C are consistent with either of the structures[7] **7a** or **7b** (data tabulated in Experimental Section). Characteristic signals are the highly shielded σ-bound carbon 4.1-ppm upfield from Me_4Si[8] and the signal for the proton bound to iron at δ −14.1.[7] Work of Ittel et al. with protonated (diene)iron triphosphites and triphosphines has proven the bridged, Fe–H–C, structure.[9]



7a



7b

The cations were generated at 45 °C under short lifetime conditions by solvolysis of the 3,5-dinitrobenzoate ester of **3** in 80% aqueous acetone (v/v) buffered with an equivalent amount of sodium 3,5-dinitrobenzoate. The ^1H NMR spectrum of **3-ODNB** shows clearly that it has the unrearranged 1,1-dimethyl structure. Careful analysis of the solvolysis product mixture by thin-layer chromatog-

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[5] Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; Pergamon Press: London, 1969; p 71.

[6] Emerson, G. F.; Mahler, J. E.; Kochhar, R.; Pettit, R. *J. Org. Chem.* **1964**, *29*, 3620.

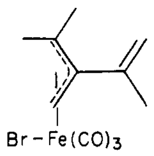
[7] Brookhart, M.; Harris, D. L. *Inorg. Chem.* **1974**, *13*, 1540. Whitesides, T. H.; Arhart, R. W. *Ibid.* **1975**, *14*, 209.

[8] Brookhart, M.; Whitesides, T. H.; Crockett, J. M. *Inorg. Chem.* **1976**, *15*, 1550. Olah, G. A.; Liang, G.; Yu, S. H. *J. Org. Chem.* **1976**, *41*, 2227.

[9] Ittel, S. D.; Van-Catledge, F. A.; Tolman, C. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 1317. Williams, J. M.; Brown, R. K.; Schultz, A. J.; Stucky, G. D.; Ittel, S. D. *Ibid.* **1978**, *100*, 7407. Williams, J. M.; Brown, R. K.; Schultz, A. J.; Stucky, G. D.; Harlow, R. L.; Ittel, S. D. *Ibid.* **1980**, *102*, 981. Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *Ibid.* **1979**, *101*, 6905.

raphy and by ^1H NMR spectroscopy revealed a composition of 90% **4**, 5% **3**, and 5% **6**. In a control experiment unrearranged alcohol **3** was heated at 45–50 °C in 80% aqueous acetone with an equivalent amount of 3,5-dinitrobenzoic acid for 67 h. TLC monitoring of the reaction mixture showed no change.

Several attempts to trap a coordinatively unsaturated ion, e.g., **1**, failed. Treatment of a SO_2 solution of **3** with excess HBr at −78 °C produced no evidence for formation of the (η^3-allyl)tricarbonyliron bromide, **10**.[10] Treatment of **3** with HBF_4 in trifluoroacetic acid in the presence of 1 atm of carbon monoxide was designed to produce the (η^3-allyl)iron tetracarbonyl salt **11**.[11] However, only the rearrangement product **10**, identified by its IR and NMR spectra, was isolated.[12]



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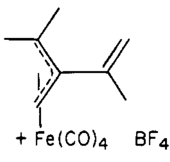

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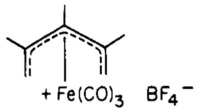
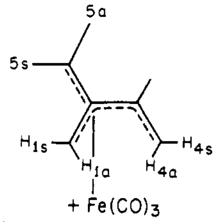


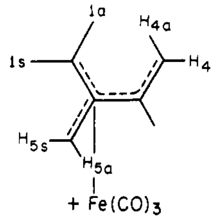
10

Discussion

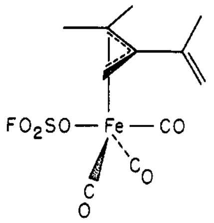
Possible structures for A and B which enjoy some precedent are the isomeric cations **11a** and **11b**, fluorosulfonate adduct(s) **12**, σ,π-allyl species,[7] and η^3-allyl cations which possess an additional interaction between a proximate hydrogen and the iron atom, like **7a** and **7b**, as a means of giving iron a stable 18-electron configuration.[9] The latter have been described as protonation products of (diene)(tris(trialkyl phosphito)iron compounds and exhibit an ^1H NMR signal at ca. δ −15 for the highly shielded iron coordinated proton. Absence of any signals for unusually shielded protons in the spectra of A and B eliminate this type of structure. σ,π-Allyl cations also exhibit high-field proton signals[7,8] and are thereby eliminated.



11a



11b



12

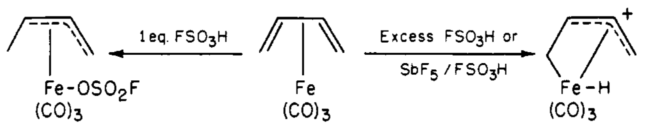
Table I. ^1H NMR Assignments for A and B

H or CH_3	species A (**11a**) obsd	species A (**11a**) expected[c]	species B (**11b**) obsd	species B (**11b**) expected[c]
1s	2.50 (d, 5.0)	3.1^d (d, 3)	1.70 (s)	
1a	1.35 (d, 5.0)	2.0 (d, 3)	1.70 (s)	
3	2.30 (s)		2.40 (s)	
4s	4.28 (d, 3)	4.5 (d, 1)	4.10 (d, 3)	4.1 (d, 1)
4a	4.17 (d, 3)	3.6 (d, 1)	4.42 (d, 3)	4.6^e (d, 1)
5a	2.87 (s)		unresolved[f]	4.3^d (s)
5s	2.72 (s)		5.26 (s)[g]	5.2^d (s)

chem shifts (δ)[a] and signal multiplicity (J, Hz)[b]

[a] Relative to internal tetramethylsilane in liquid sulfur dioxide at −65 °C. [b] s = singlet and d = doublet. [c] Expected shifts are estimated from the shifts for the unsubstituted, the 4-*syn*-methyl, and the 4-*anti*-methyl analogues. [d] Includes a downfield increment of 0.6 ppm for the van der Waals effect of a proximate methyl. This increment estimated from shifts in (η^3-allyl)$Fe(CO)_4$ cations reported by: Gibson, D. H.; Vonnahme, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 5090. Gibson, D. H.; Erwin, D. K. *J. Organomet. Chem.* **1975**, *86*, C31. [e] Includes a downfield increment of 1.0 ppm for the van der Waals effect of the 1a-methyl: Bonazza, B. R.; Lillya, C. P.; Magyar, E. S.; Scholes, G. *J. Am. Chem. Soc.* **1979**, *101*, 4100. [f] An excess in the total integral for the δ 4.0–4.5 region of ca. 0.5 H for **11b** suggests H_{5a} is hidden in this multiplet. [g] $J_{5a,5s} = 0$ in cations **17a–c**, thus a singlet is expected.

The possibility that either A or B is a fluorosulfonate adduct, **12**, is eliminated by our observation that the A to B ratio does not change as the acid is changed from 2–3 equiv of FSO_3H to excess FSO_3H or to excess 1:1 FSO_3H/SbF_5. Both of these changes should reduce the activity of fluorosulfonate ion in solution[13] and consequently reduce the equilibrium concentration of a fluorosulfonate adduct as they do in the case of the 4s-methyl cation **16c**.[2] The possibility that both A and B are fluorosulfonate adducts, even in 1:1 FSO_3H/SbF_5, seems remote. For example, 1 equiv of FSO_3H gives an adduct, **13**, with (butadiene)$Fe(CO)_3$, but excess FSO_3H and FSO_3H/SbF_5 give the fluorosulfonate-free ion **14**.[7,8,14] In addition, steric crowding will strongly oppose an increase in the coordination number of iron from four to five (see below). The isomeric (cross-conjugated dienyl)tricarbonyliron cations **11a** and **11b** are left as the best structures for A and B.



13 14

Table I presents the best set of assignments for the ^1H NMR signals observed for A and B. Expected values are derived from firmly established shifts for the parent cation (**17a**) and its 4-methyl derivatives (**17b,c**).[2,3] The NMR data are consistent with those for structure **11a** for the

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(10) Impastato, F. J.; Ihrman, K. G. *J. Am. Chem. Soc.* **1961**, *83*, 3726. Murdoch, H. D.; Weiss, E. *Helv. Chim. Acta* **1962**, *45*, 1927. Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 4591. Plowman, R. A.; Stone, F. G. A. *Z. Naturforsch, B: Anorg. Chem., Org. Chem. Biochem., Biophys., Biol.* **1962**, *17*, 575.

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

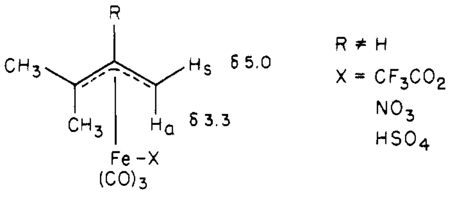
(12) (Conjugated dienyl)tricarbonyliron cations with the unstable trans configuration rearrange via intramolecular hydride shifts: Jablonski, C. R.; Sorensen, T. S. *Can. J. Chem.* **1974**, *52*, 2085.

(13) Cf. Gillespie, R. J.; Peel, T. E. *Adv. Phys. Org. Chem.* **1971**, *9*, 1. Lillya, C. P.; Sahatjian, R. A. *Inorg. Chem.* **1972**, *11*, 889.

(14) Young, D. A. T.; Holmes, J. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1969**, *91*, 6968 and reinterpreted in ref 16.

major isomer and those for **11b** for the minor isomer. ^{13}C NMR spectra of A and B which we have obtained were of such poor quality as to defy analysis.

The ^{1}H data are not in good agreement with the fluorosulfonate adduct structure **12**. Extant measurements on (η^3-allyl)tricarbonyliron–oxyanion adducts lead to expectation of the chemical shifts shown in **15**.[15] The value for

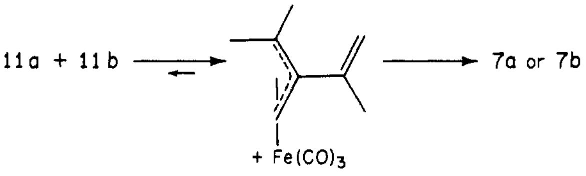


15

H_{1s} includes a downfield increment of 0.6 ppm for the van der Waals effect[5] of the proximate methyl group estimated from data on (η^3-allyl)tetracarbonyliron cations.[16] The one-proton doublets observed at δ 1.35 and 2.50 are far upfield from these. Furthermore, the 5-Hz value of $J_{1s,1a}$ is inconsistent with the value of <1 Hz expected for **15**[15,16] (or **12**) but is close to the values of this coupling constant we have observed for the related ions **17a–c** (2.7, 3.0, and 3.0 Hz).[2,3]

Next we address the questions of C_2–C_3 rotation and coordinative unsaturation which would be characteristic of bonding like that depicted in **1**. The rearrangements we have observed require such rotation. In low-temperature methonolysis, nucleophilic attack on the major species **11a** leads to the major quench product **6**. Material balance requires that **11b** also give a substantial quantity of **6**. Thus, rapid C_2–C_3 rotation is required. Generation of the cations under short lifetime conditions during solvolysis also demonstrates rapid rotation. An inherent ambiguity complicates interpretation of these data, however. Reversible nucleophilic attack at iron would give an adduct like **12** with an essential single C_2–C_3 bond. Thus, behavior in nonnucleophilic media are more likely to reflect intrinsic properties of the cations themselves. Cation generation at −65 °C using excess 1:1 SbF_5/FSO_3H gives after only 1 min and, probably more rapidly, the same equilibrium mixture regardless of precursor (**3–5**). This same **11a**/**11b** ratio is maintained as they are converted to **7** at −50 to −40 °C. These observations require facile rotation, though it is not rapid enough to cause NMR line broadening. Formation of fluorosulfonate adduct **12** is highly unlikely under these conditions. In the related case of the 4a-methyl cation, **17c**, which is in *slow* equilibrium with its fluorosulfonate adduct, we have proven that C_2–C_3 rotation is an intrinsic property of the free cation.[2]

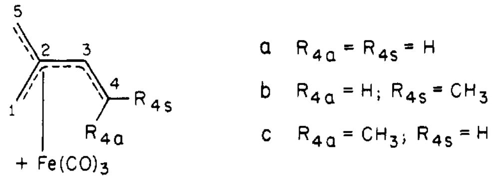
Evidence for coordinative unsaturation is present. The simple analogues of structure **1**, (η^3-allyl)tricarbonyliron cations, have never been observed,[18] but their coordinatively saturated halide, fluorosulfonate, trifluoroacetate, carbon monoxide, and other adducts are well-known.[7-11] Cations **11a,b** show no tendency to form adducts, but this may be the result of adduct destabilization owing to steric



16

crowding. Insertion of iron into a C–H bond to give a cation like **7** is a reaction which is characteristic of the coordinatively unsaturated (η^3-allyl)tricarbonyliron cations.[7,8] This behavior is not inconsistent with our conclusions reached during study of the cations **17a–c**, that the structures are of type **2** but that type **1** structures are easily formed. Formation of **7** would proceed via **16**.

From a comparison of the key properties of **11a,b** with those of (cross-conjugated dienyl)tricarbonyliron cations we have reported on previously, **17a–c**, the factors which determine differences in behavior and the electronic nature of Fe–C bonding emerge clearly.



17

Of the five cations, only **17c** forms an observable fluorosulfonate adduct when treated with 2–3 equiv of FSO_3H in SO_2 at −65 °C. Concomitant rotation of the *cis*-propenyl group ($C_3C_4R_{4a}$) out of the $C_1C_2C_5$ plane away from iron relieves the H_{1a}–4a-methyl steric interaction and provides driving force for adduct formation. **17a** and **17b** lack the 4-*anti*-methyl substituent and fail to give adducts. In cations **11a,b** steric factors strongly oppose adduct formation which increases the coordination number of iron. The pentacoordinate adduct is depicted (**12**) in the eq$_\perp$ conformation favored by electronic factors.[19] All of the above cations fail to form observable halide or CO adducts. Thus, adduct formation occurs only in the special case of **17c** in which relief of steric strain makes it especially favorable. Cations **11a,b** do undergo intramolecular C–H insertion to give **7**. This reaction is not possible for **17a–c**. Taken together, these observations are not consistent with the highly electrophilic character expected of a coordinatively unsaturated cation like **1**.

Cations **11a,b** exhibit no line broadening in their ^{1}H NMR spectrum owing to interconversion by rotation about the C_2–C_3 bond. Formation of **7** prevents the search for this effect at temperatures above −35 °C. Cations **17a,b** have been studied at temperatures up to −20 and 0 °C, respectively, and exhibit no ^{1}H or ^{13}C NMR line broadening attributable to C_2–C_3 rotation. Only **17c** exhibits such effects. Conversion to **17b** prevented its study above 0 °C, but estimates based on line-shape measurements in the −2 to −31 °C range gave a $\Delta G^\ddagger$ value for C_2–C_3 rotation of 13 kcal/mol. Relief of the H_{1a}–4-*anti*-methyl interaction during rotation must be responsible for the anomalous behavior of **17c**. Thus, the barrier to rotation, and probably the energy difference between structures **2** and **1** for sterically unperturbed cations, is larger than 13 kcal/mol. This is inconsistent with a structure like **1**.

The conclusion of this series of investigations is that the simple frontier orbital theory can provide useful insight

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(18) Species originally assigned this structure (cf. Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 4591) must be reformulated as (η^3-allyl)Fe(CO)$_4$ cations in light of subsequent investigations.[11]

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into metal–carbon bonding in transition-metal π complexes. The energetic accessibility of structure 1 to (cross-conjugated dienyl)tricarbonyl cations despite its coordinative unsaturation is testimony to that fact. However, a model which focuses on one or two donor–acceptor interactions alone must be applied with care and a clear understanding of what is being ignored. In the case of the species studied here, maximization of overlap for the HOMO–LUMO interaction to give structure 1 is accomplished only at the sacrifice of several other important interactions[3] and does not give the correct ground-state structure.

Experimental Section

General Data. Infrared spectra were recorded by using Perkin-Elmer 727 and Beckman IR 10 instruments, and NMR spectra were obtained by using Varian A-60 (ambient and low temperature) and Perkin-Elmer R-12 (ambient temperature) spectrometers. NMR samples in $CDCl_3$ and CCl_4 were filtered (Metricel-alfa 6) immediately before their spectra were recorded. Preparation of samples in SO_2(l)/strong acid has been described.[20] 3-Methyl-2-(1-methylethenyl)-2-buten-1-ol was donated by E.I. du Pont de Nemours and Co. Technical grade FSO_3H was purchased from J.T. Baker Chemical Co. and was distilled and stored in Teflon bottles. Reagent grade antimony pentafluoride was purchased from Ozark Mahoning Co. Dry-column chromatography was carried out in Nylon columns using silica gel deactivated by addition of 10% water. Bands were cut from the developed columns, and the products were recovered by washing with 5% methanol in ether. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

(3-Methyl-2-(1-methylethenyl)-2-buten-1-ol)tricarbonyliron (3). (3-Methyl-2-(1-methylethenyl)-2-buten-1-ol[21a] (12.6 g, 0.10 mol) and diiron enneacarbonyl (80.0 g, 0.22 mol) were stirred in the dark and under nitrogen at reflux in 430 mL ether for 22 h. Filtration of the reaction mixture and evaporation of ether left a yellow-green oil which was purified by using dry-column chromatography ($CHCl_3$). A green $Fe_3(CO)_{12}$ band was followed by a large yellow band: 17.45 g (66%); mp 91–95 °C. Recrystallization from Skelly Solve-F gave yellow crystals: mp 94–96 °C; IR (CCl_4) 3635 (OH), 2040, 1965 ($C{\equiv}O$), 1065 cm^{-1} (CO); NMR (CCl_4) δ 4.70 (m, 2, CH_2OH), 3.44 and 3.33 (two d, 2, J = 3.0 Hz, $=CH_2$), 2.33 (s, 3, 3-CH_3), 1.71 (s, 3, *syn*-CH_3), 1.13 (s, 3, *anti*-CH_3); mass spectrum, *m/e* 266 (M^+), 238 ($M^+ - CO$), 210 ($M^+ - 2CO$), 182 ($M - 3CO$).

Anal. Calcd for $C_{11}H_{14}FeO_4$: C, 49.66; H, 5.30; Fe, 20.99. Found: C, 49.82; H, 5.44; Fe, 20.8.

Methanolysis of A and B. A red-brown solution of A and B in 30 mL of SO_2(l) was prepared at −78 °C from **5** (3.0 g, 0.011 mol) and FSO_3H (1.94 mL, 3.38 g, 0.034 mol). Addition of 20 mL of −78 °C methanol changed the color to light yellow. SO_2 was allowed to evaporate as the solution warmed, and the residue was treated with 200 mL of water. Organic products were isolated by chloroform extraction, giving 2.61 g (83%) of crude product shown to be 95% **5** and 5% **6** by NMR spectroscopy. Dry-column chromatography afforded 1.21 g (38%) of methyl ether **5** as a yellow oil: IR (CCl_4) 2845 (CH_3O), 2055, 1965 ($C{\equiv}O$), 1065 (CO); NMR (CCl_4) δ 3.29 (s, 3, OCH_3), 2.26 (s, 3, 3-CH_3), 1.76 (d, 1, J = 3 Hz, H_{syn}), 1.60 (d, 1, J = 2 Hz, H'_{syn}), 1.53 and 1.39 (two s, 6, $C(CH_3)OCH_3$), 0.03 (d, 1, J = 2 Hz, H'_{anti}), −0.38 (d, 1, J = 3 Hz, H_{anti}); mass spectrum, *m/e* 280 (M^+), 252 ($M^+ - CO$), 224 ($M^+ - 2CO$), 196 ($M^+ - 3CO$).

Anal. Calcd for $C_{12}H_{16}FeO_4$: C, 51.46; H, 5.76; Fe, 19.94. Found: C, 51.63; H, 5.67; Fe, 19.5.

Hydrolysis of A and B. A solution of A and B in 20 mL of SO_2(l) was prepared at −78 °C from **5** (2.23 g, 0.008 mol) and FSO_3H (2.51 g, 1.45 mL, 0.025 mol). After 10 min, most of the SO_2 was removed under vacuum and 20 mL of ice water was added cautiously with stirring to the sample while it remained in an acetone/Dry Ice bath. The mixture was then allowed to warm and was neutralized with sodium bicarbonate, and the organic products were isolated by extraction into CCl_4. The crude product was a yellow oil which NMR analysis showed to be 86% **6** and 14% **8**. Dry-column chromatography (C_6H_6) gave alcohol **4** (the low R_f band) as a cloudy yellow oil which was purified by evaporative distillation at 94–100 °C (4 torr): 1.04 g (48%), yellow oil; IR (CCl_4) 3620, 3520 (OH), 2080, 1980 ($C{\equiv}O$), 1110 cm^{-1} (CO); NMR (CCl_4) δ 2.38 (s, 3, 3-CH_3), 1.89 (d, 1, J = 3 Hz, H_{syn}), 1.68 (d, 1, J = 2 Hz, H'_{syn}), 1.68 and 1.40 (two s, 6, $C(CH_3)OH$), 1.20 (s, 1, OH), 0.12 (d, 1, J = 2 Hz, H'_{anti}), −0.25 (d, 1, J = 3 Hz, H_{anti}); mass spectrum, *m/e* 266 (M^+), 238 ($M^+ - CO$), 210 ($M^+ - 2CO$), 182 ($M^+ - 3CO$).

Anal. Calcd for $C_{11}H_{14}FeO_4$: C, 49.66; H, 5.30; Fe, 20.99. Found: C, 49.21; H, 5.26; Fe, 21.3.

Generation of C. When a solution of A and B in SO_2(l) was warmed to −45 °C, signals for C replaced those of A and B over the course of ca. 10 min. Recooling to −65 °C caused no further change. A solution which exhibited an identical spectrum could be obtained by treatment of triene complex **6** with FSO_3H at −78 °C. NMR data (see numbering on formula **7b**) are consistent with either structure **7a** or structure **7b**. ^1H NMR (SO_2, external Me_4Si, −50 °C): δ 6.08 (br s, 1, H_6), 5.93 (s, 1, $H_{6'}$), 3.57 (d, J = 4 Hz, $H_{1\text{-}syn}$), 2.57 (s, 3, C_3-CH_3), 2.38 (d, 3, J = 1 Hz, C_5-CH_3), 1.46 (d, 1, J = 4 Hz, $H_{1\text{-}anti}$), 0.92 (br, 1, FeCH), −0.92 (br, 1, FeCH′), −14.1 (br, ca. 1, FeH). ^{13}C NMR (SO_2, −50 °C, internal $CDCl_3$ corrected to Me_4Si): δ 137.1 (s, C_5), 123.1 (t, C_6), 114.2 (s, C_2), 101.2 (t or s, C_3), 51.1 (probable t, C_1), 22.3 and 19.0 (two q, CH_3's), −4.1 (?, $FeCH_2C_3$) plus $C{\equiv}O$ signals at 201.3, 199.4, 195.6 ppm.

Methanolysis and Hydrolysis of C. A solution of A and B, prepared in 30 mL of SO_2 from **5** (2.57 g, 0.010 mol), was allowed to warm until SO_2 began to boil (ca. −20 °C) and then was added slowly with stirring to 80 mL of ice water and 20 mL of methylene chloride. Organic products were isolated by extraction into methylene chloride. Evaporation of methylene chloride left (1–3,7-η^4-2,4-dimethyl-3-methylidene-1,4-pentadiene)tricarbonyliron (**6**), 1.71 g (72%), shown to be pure by NMR and TLC analysis.[21b] Evaporative distillation at 55–65 °C (0.2 torr) gave 1.55 g (69%) of a yellow oil: IR (CCl_4) 3100, 3070 ($=CH$), 2060, 1970 ($C{\equiv}O$), 910 cm^{-1} ($=CH_2$); NMR (CCl_4) δ 5.22 and 5.12 (two m, 2, $=CH_2$), 2.17 (s, 3, 2-CH_3), 2.04 (d, 3, J = 1 Hz, 4-CH_3), 1.65 [apparent t, 2, analyzed as 1.67 (d, 1, J = 2.1 Hz, H_{syn}) and 1.63 (d, 1, J = 3.0 Hz, H'_{syn})], 0.10 (d, 1, J = 2.1 Hz, H_{anti}), 0.00 (d, 1, J = 3.0 Hz, H'_{anti}); mass spectrum, *m/e* 248 (M^+), 220 ($M^+ - CO$), 192 ($M^+ - 2CO$), 164 ($M^+ - 3CO$).

Anal. Calcd for $C_{11}H_{12}FeO_3$: C, 53.26; H, 4.88; Fe, 22.51. Found: C, 52.90; H, 4.81; Fe, 22.2.

Compound **6** was also the sole product of methanolysis of C at −78 °C.

(3-Methyl-2-(1-methylethenyl)-2-buten-1-yl 3,5-dinitrobenzoate)tricarbonyliron (3-ODNB). Alcohol **3** (2.52 g, 0.009 mol) was esterified by using 3,5-dinitrobenzoic anhydride[22] (11.3 g, 0.028 mol) according to the procedure of Kuhn and Lillya[23] to give an orange oil. Crystallization from ether gave **5-ODNB** as yellow crystals: 2.37 g (57%); mp 85–86 °C (uncorrected); IR (CCl_4) 3080, 2060, 1985, 1970, 1730, 1620, 1540 cm^{-1}; NMR ($CDCl_3$) δ 9.23 (m, 3, ArH), 5.60 and 5.36 (two d of AB system, 2, J = 12.5 Hz, $-CH_2O$), 2.32 (s, 3, 3-CH_3), 1.87 (d, 1, J = 3.3 Hz, $H_{4\text{-}anti}$), 1.72 (s, 4, *syn*-CH_3 and $H_{4\text{-}syn}$), 1.11 (s, 3, *anti*-CH_3).

Anal. Calcd for $C_{18}H_{16}N_2FeO_9$: C, 46.97; H, 3.51. Found: C, 47.01; H, 3.74.

Solvolysis of 3-ODNB. Sodium 3,5-dinitrobenzoate (0.053 g, 0.23 mmol) and **3-ODNB** (0.100 g, 0.217 mmol) were heated in a mixture of 8 mL of acetone and 2 mL of water at 45–50 °C in a stoppered flask under nitrogen and protected from light. After 143 h, TLC (silica gel/benzene) showed almost no **3-ODNB**. The solvolysis mixture was poured into 100 mL of 5% aqueous sodium bicarbonate, and the organic products were isolated by extraction into methylene chloride. The crude product was a yellow oil which

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(21) (a) Blume, R. C. U.S. Patents 3 806 551, 1974, and 3 860 669, 1975, assigned to E.I. du Pont de Nemours and Co.; *Chem. Abstr.* **1975**, *81*, P3344; **1975**, *82*, P172295. (b) Reflux of alcohol **3** in benzene with catalytic *p*-toluenesulfonic acid gives **6** in excellent yield and purity. Personal communication from Professor Thomas A. Albright.

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Organometallics **1982,** *1,* 142-148

NMR analysis showed to be 90% **4**, 5% **3**, and 5% **6**. To determine the stability of **3** under solvolysis conditions, we heated **3** (0.028 g, 0.10 mmol), 3,5-dinitrobenzoic acid (0.022 g, 0.10 mmol), 1.0 mL of water, and 4.0 mL of acetone at 45–50 °C. Comparison of a sample with drawn after 72 h with one withdrawn prior to heating by TLC (silica gel/benzene) showed that no change had occurred.

Reaction of 3 with H_2SO_4 and HBr. Alcohol **3** dissolved in cold 98% H_2SO_4 with some gas evolution to give a brown solution. This solution was poured immediately into an ice-water mixture and the mixture extracted with ether. Washing, drying ($MgSO_4$), and evaporation of the ether layer left a yellow oil whose IR and NMR spectra were identical with those of **6**. Treatment of **3** in SO_2 at −78 °C with excess HBr gave a black solution from which no organic products could be isolated.

(2,3,4-Trimethylpentadienyl)tricarbonyliron Fluoroborate (10). Alcohol **5** (500 mg) was added to a solution of trifluoroacetic anhydride (14 g) and 48% fluoroboric acid (2.5 g), and the mixture was stirred at room temperature under an atmosphere of carbon monoxide for 3 h. This mixture was poured into cold ether to precipitate the product as a pale yellow solid: 190 mg (25%); mp 260 °C; IR (CH_3NO_2) 3675, 2125, 2080, 1060 cm^{-1}; NMR (acetone-d_6) δ 3.85 (d, 2, $J_{\mathrm{syn,anti}} = 3$ Hz, $H_{1\text{-syn}}$), 2.80 (s, 3, 3-CH_3), 2.60 (s, 6, 2-CH_3), 1.4 (br, 2, $H_{1\text{-anti}}$); NMR (SO_2 at −20 °C) δ 3.58 (br, 2, $H_{1\text{-syn}}$), 2.68 (br s, 3, 3-CH_3), 2.53 (br s, 6, 2-CH_3), 8.37 (br, 2, $H_{1\text{-anti}}$). Further purification of this material was not possible, and hydrolysis and methanolysis gave no identifiable products. Lower reaction temperatures gave the same product in lower yield. A perchlorate salt, IR [(CH_3NO_2) 3675, 2125, 2075, 2050, and 1050 cm^{-1}] and NMR spectra identical with those of **10**, was prepared in 56% yield by dropwise addition of 60% $HClO_4$ in acetic anhydride to a stirred solution of **3** in acetic anhydride at 0 °C.

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Registry No. 3, 52472-512; **3-ODNB**, 78782-43-1; **4**, 52472-54-5; **5**, 52472-53-4; **6**, 52472-52-3; **7**, 78782-44-2; **8**, 78791-21-6; **10**, 78791-23-8; **11**, 78791-24-9; diiron enneocarbonyl, 15321-51-4; 3-methyl-2-(1-methylethenyl)-2-buten-1-ol, 52385-60-1; (2,3,4-trimethylpentadienyl)tricarbonyliron perchlorate, 78791-25-0.

Improved Synthesis of Seven-Coordinate Molybdenum(II) and Tungsten(II) Isocyanide Complexes. Dealkylation of Coordinated *tert*-Butyl Isocyanide[1,2]

Christen M. Giandomenico, Lawrence H. Hanau, and Stephen J. Lippard*

Department of Chemistry, Columbia University, New York, New York 10027

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A general, high-yield synthesis of seven-coordinate cations $[M(CNR)_6X]^+$, $[Mo(CNR')_6I]^+$, and $[M(CNR)_7]^{2+}$, where M = Mo, W; R = alkyl; R′ = aryl; X = Cl, I, CN, has been developed. The synthetic procedure includes the oxidation of the appropriate $M(CNR)_3(CO)_3$ species with a mild reagent, followed by displacement of carbon monoxide with isocyanide. The oxidant $PhICl_2$ was found to be especially convenient in this procedure. This method can be used to prepare 1–20 g of crystalline products in good yields. Mixed halo–carbonyl–isocyanide products $(CO)_yX_z^{(2-z)+}$, $x + y + z = 7$, may also be obtained by this synthetic route. A novel dealkylation reaction of a coordinated *t*-BuNC ligand occurs when heptakis(*tert*-butyl isocyanide)molybdenum(II) or -tungsten(II) is refluxed in ethanol. The products are the cyanohexakis(*tert*-butyl isocyanide)metal(II) cations.

During studies of the reductive coupling[2,3] of alkyl isocyanide ligands in seven-coordinate molybdenum(II) and tungsten(II) complexes, we found it desirable to develop improved syntheses of compounds having the general formulas $[M(CNR)_6X]^+$ [4,5] and $[M(CNR)_7]^{2+}$ [5-9] (M = Mo, W; R = alkyl, aryl; X = halide) which have been known for a number of years. These compounds have been prepared by a variety of methods, including reductive alkylation[4,5] of molybdenum(IV) cyanide complexes, chemical oxidation[5,10] of metal(0) carbonyl or isocyanide complexes followed by displacement of the carbonyl ligands by isocyanide, and photochemical[11] oxidation of metal(0) isocyanide complexes in $CHCl_3$. Recently reported syntheses[7-9] of $[M(CNR)_7]^{2+}$ and $M(CNR)_5X_2$ (X = $CF_3CO_2^-$, Cl^-) involve cleavage of the quadruply bonded Mo_2^{4+} core by alkyl isocyanide.

This paper describes high-yield preparations of the desired compounds through oxidation of $M(CNR)_x(CO)_{6-x}$ ($1 \leq x \leq 3$; R = alkyl, aryl; M = Mo, W) with mild oxidants such as $PhICl_2$ and I_2 followed by displacement of the carbon monoxide ligand with isocyanide. Conditions have been developed so that either the $[M(CNR)_6X]^+$ or the $[M(CNR)_7]^{2+}$ complexes may be prepared. These reactions require inexpensive starting materials, can be conducted on a large (1–20 g) scale, and produce good to excellent quantities of isolated crystalline product. The procedure

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[1] Part 14 of a continuing series on higher coordinate cyanide and isocyanide complexes. For part 13, see ref 2.

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