Electronic Structure of Conformational Isomers of (η^3-Allyl)ruthenium Complexes

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The ultraviolet photoelectron spectra of conformational isomers of (η^5-cyclopentadienyl)(η^3-allyl)ruthenium carbonyl and their 2-methallyl analogues along with those of (η^5-cyclopentadienyl)ruthenium dicarbonyl chloride and *exo*-(η^5-cyclopentadienyl)(η^3-allyl)iron carbonyl for comparison have been recorded and assigned. There are notable differences in the UPS of the various conformational isomers. This work suggests that the π-allyl HOMO should be stabilized relative to the free allyl radical in these transition-metal complexes. The latter result is in contrast to some observations for bis(η^3-allyl)metal complexes from other laboratories.

Introduction

The electronic structures of conformational isomers as determined by ultraviolet photoelectron spectroscopy (UPS) are generally quite similar unless "through-space" interactions between moieties such as "lone pairs" or π orbitals are significant and different for the several conformers.[1] This paper will present evidence which suggests that such is the case for the conformers *endo*- and *exo*-(η^5-cyclopentadienyl)(η^3-allyl)ruthenium carbonyl. Although the exo isomer is thermodynamically more stable than the endo isomer, the separate conformers and their 2-methallyl analogues have been characterized[2] and were studied by UPS in the present work. The assignments of endo and exo geometry in these complexes were originally made on the basis of spectral data;[2] X-ray crystallographic data have now confirmed these assignments.[3]

There exists a certain amount of controversy concerning the interpretation of the UPS of transition-metal complexes containing the allyl ligand. The first ionization energy of the allyl radical which corresponds to removal of an electron from the π HOMO has been measured by UPS to be 8.13 eV.[4] In η^3-allyl transition-metal complexes the UPS band corresponding to ionization of the perturbed "allyl π HOMO" has been suggested to lie between 7.3 eV and ca. 9.7 eV depending upon the nature of the complex and upon the method of assignment chosen by several investigators. In this respect the UPS of the complex bis(η^3-allyl)nickel has been discussed in several works. While several theoretical studies had predicted that the "π-allyl" orbital was the HOMO for this complex,[5] Lloyd and Lynaugh[6] assigned the fourth band in the He I UPS at 9.48 eV to ionization of this ligand orbital; an analogous assignment was proposed for the UPS band at 9.73 eV for bis(η^3-allyl)palladium. Subsequently, Batich[7] used substituent-effect and band-intensity (including limited He II data) arguments for bis(η^3-2-methallyl)nickel in proposing that the band assignments for the parent complex should be revised such that the second UPS band at 8.19 eV contains the ionization process referring to the π-allyl HOMO. Very recent UPS work by Böhm and co-workers[8] on bis(η^3-allyl)nickel, bis(η^3-allyl)palladium, and bis(η^3-allyl)platinum and their 2-methyl derivatives has been interpreted to indicate that the *first* UPS band at less than 8 eV corresponds to ionization of the π-allyl HOMO. This interpretation was based upon He I/He II intensity arguments and semiempirical SCF MO calculations. It was pointed out that the in-phase linear combination of the two nonbonding allylic π orbitals for this bis complex cannot interact with metal 3d orbitals by symmetry.[8] It was suggested further that, for the bis(η^3-allyl) complexes, each allylic moiety is partially negative in charge (ca. -0.4 for each allyl fragment) causing the ionization potential for the π-allyl moiety to be lower than that (8.13 eV[4] for the allyl radical.

Green and co-workers have studied the UPS of bis(η^5-cyclopentadienyl)(η^3-allyl)niobium.[9] They assigned the second band (8.0 eV) in the UPS of this complex to ionization of the perturbed allyl π orbital. Green and Seddon[10] have recently reported the UPS of $Cr(\eta^3\text{-}C_3H_5)_3$, $Cr_2(\eta^3\text{-}C_3H_5)_4$, and $Mo_2(\eta^3\text{-}C_3H_5)_4$. The lowest nonbonding π ionization processes for these complexes were assigned in the range ca. 7.6-8.8 eV.[10] Similar assignments have been made by Hillier et al.[11,12] for $Cr(\eta^3\text{-}C_3H_5)_3$. On the other hand, work in these laboratories on the UPS of (η^3-allyl)manganese tetracarbonyl and its 2-methallyl derivative and of the η^5-cyclopentadienyl η^3-allyl dicarbonyl complexes of molybdenum and tungsten has indicated that the process corresponding to ionization of the π allyl HOMO should occur near 9 eV, at higher ionization potential than those processes corresponding to ionization of the orbitals which are predominantly metal in character.[11] Our work shows that the π HOMO of the allyl

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[1] For example, see: R. S. Brown, *J. Am. Chem. Soc.*, **99**, 6500 (1977); S. F. Nelson and J. M. Buschek, *ibid*, **95**, 2013 (1973); N. Bodor, B. H. Chen, and S. D. Worley, *J. Electron. Spectrosc. Relat. Phenom.*, 4 65 (1974).

[2] D. H. Gibson, W.-L. Hsu, A. L. Steinmetz, and B. V. Johnson, *J. Organomet. Chem.*, **208**, 89 (1981).

[3] The details of this work will be presented elsewhere.

[4] F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, **100**, 3290 (1978).

[5] D. A. Brown and A. Owens, *Inorg. Chim. Acta*, **5**, 675 (1971); A. Veillard, *J. Chem. Soc., Chem. Commun.*, 1022, 1427 (1969); M. Rohmer and A. Viellard, *ibid.*, 250 (1973).

[6] D. R. Lloyd and N. Lynaugh in "Electron Spectroscopy", D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 445.

[7] C. D. Batich, *J. Am. Chem. Soc.*, **98**, 7585 (1976).

[8] M. C. Böhm, R. Gleiter, and C. D. Batich, *Helv. Chim. Acta*, **63**, 990 (1980).

[9] J. C. Green, S. E. Jackson, and B. Higginson, *J. Chem. Soc., Dalton Trans.*, 403 (1975).

[10] J. C. Green and E. A. Seddon, *J. Organomet. Chem.*, **198**, C61 (1980).

[11] M. Berry, C. David Garner, I. H. Hillier, and A. A. McDowell, *Inorg. Chem.*, **20**, 1962 (1981).

[12] S. D. Worley, D. H. Gibson, and W.-L. Hsu, *Inorg. Chem.*, **20**, 1327 (1981).

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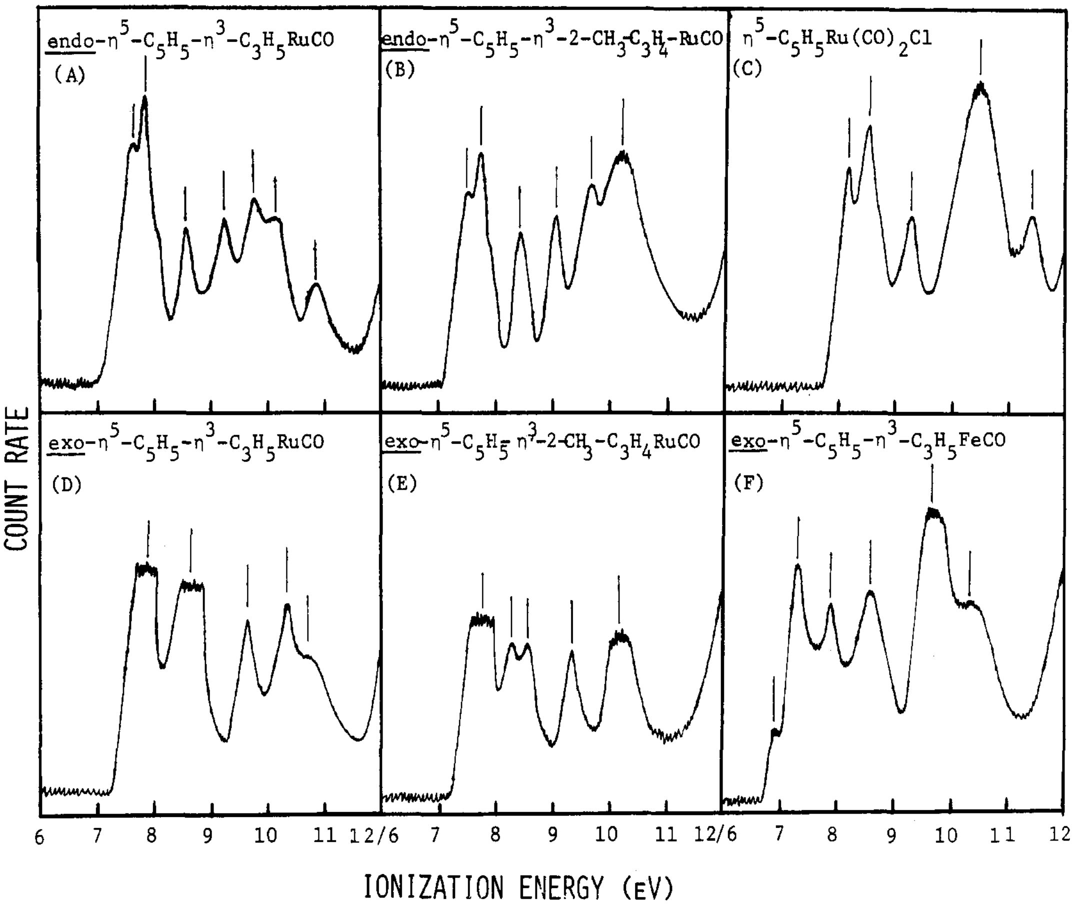

Figure 1. The UPS of several ruthenium and iron complexes. The excitation source was the He I resonance line.

Table I. Ionization Energies and Assignments[a]

compd	I_1	I_2	I_3	I_4	I_5	I_6	I_8
endo-(η^5-C_5H_5)(η^3-C_3H_5)RuCO (A)	7.65 Ru	7.85[b] Ru	8.59 Ru	9.22 C_3H_5	9.77 C_5H_5	10.17 C_5H_5	10.85 C_3H_5
endo-(η^5-C_5H_5)(η^3-2-$CH_3C_3H_4$)RuCO (B)	7.48 Ru	7.70[b] Ru	8.42 Ru	9.09 2-$CH_3C_3H_4$	9.68 C_5H_5	10.20 C_5H_5 2-$CH_3C_3H_4$	
(η^5-C_5H_5)Ru(CO)$_2$Cl (C)	8.17 Ru	8.52[b] Ru	9.26 Ru	10.46 C_5H_5, Cl	11.36 Cl		
exo-η^5-C_5H_5(η^3-C_3H_5)RuCO (D)	7.92[b] Ru	8.65[b] Ru	9.69 C_3H_5	10.29 C_5H_5	10.68 C_5H_5 C_3H_5		
exo-(η^5-C_5H_5)(η^3-2-$CH_3C_3H_4$)RuCO (E)	7.73[b] Ru	8.30 Ru	8.54 Ru	9.36 2-$CH_3C_3H_4$	10.18 C_5H_5 2-$CH_3C_3H_4$		
exo-(η^5-C_5H_5)(η^3-C_3H_5)FeCO (F)	6.90 Fe	7.28 Fe	7.87 Fe	8.58 Fe	9.64 C_3H_5 C_5H_5	10.31 C_3H_5	

[a] All values are in eV. [b] Band corresponds to two metal ionization processes.

moiety is stabilized by interaction with the metal orbitals for the complexes studied. This is in accord with extensive prior work in these laboratories concerning UPS of transition-metal complexes containing π ligands.[13-16] It should be noted that Fehlner and co-workers have studied the UPS of (η^5-cyclopentadienyl)(η^1-allyl)iron dicarbonyl also.[17] They assign a UPS band at 8.54 eV to ionization of an Fe–C σ orbital and one at 9.78 eV to ionization of the isolated π orbital, the lower bands being assigned to ionization of iron orbitals.

The current studies were undertaken in an attempt to obtain a better understanding of the UPS band assignments of η^3-allyl transition-metal complexes as well as to study the effects of conformational isomerism on the electronic structure of the complexes.

Experimental Section

The synthetic and characterization procedures employed for the ruthenium and iron complexes studied in this work have been described in detail elsewhere.[2,18]

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(13) S D. Worley, T. R. Webb, D. H. Gibson, and T.-S. Ong, *J. Organomet. Chem.* **168**, C16 (1979).

(14) S. D. Worley, T. R. Webb, D. H. Gibson, and T.-S. Ong, *J. Electron Spectrosc. Relat. Phenom.*, **18**, 189 (1980).

(15) W. E. Hill, C. H. Ward, T. R. Webb, and S. D. Worley, *Inorg. Chem.*, **18**, 2029 (1979).

(16) S. D. Worley and T. R. Webb, *J. Organomet. Chem.*, **192**, 139 (1980).

(17) B. D. Fabian, T. P. Fehlner, L. J. Hwang, and J. A. Labinger, *J. Organomet. Chem.*, **191**, 409 (1980).

(18) D. H. Gibson, W.-L. Hsu, and D.-S. Lin, *J. Organomet. Chem.*, **172**, C7 (1979).

The photoelectron spectra were obtained on a Perkin-Elmer PS-18 spectrometer. In all cases the excitation source was the He I resonance line. Argon and xenon were employed as internal calibrants, and the data presented here represent an average of several spectra for each compound.

Results and Discussion

The low ionization energy regions of the UPS of the six complexes studied in this work are shown in Figure 1. The band structures above 12 eV in the spectra were much too complex for definitive interpretation. The vertical ionization energies measured from the UPS in Figure 1 are presented in Table I. I## The band assignments to be discussed for this work are given also in Table I.

The two primary means of UPS band assignments for organometallic compounds currently being employed are molecular orbital calculations[8,19] and band-intensity arguments based upon differences between He I and He II excited spectra.[7,8,20] Although these can be useful assignment procedures and much fine work is proceeding along these lines, it is the opinion of these investigators that the technique for band assignments developed by Heilbronner and co-workers,[21] namely, the systematic study of extensive series of model compounds and substituent effects, remains the most reliable one. The latter technique will be employed in this work.

Let us consider first the UPS (Figure 1) of (η^5-cyclopentadienyl)ruthenium dicarbonyl chloride (compound C in Table I). In a prior UPS study of the iron analogue of C,[19] the first four bands at 8.00, 8.38, 8.99, and 9.90 eV were assigned to ionization of predominantly metal or metal–halogen orbitals with an intense, broad band between 10 and 11 eV corresponding to the two ring π-ionization processes (the HOMO of free cyclopentadienyl is doubly degenerate). Likewise the UPS of the *trans*-(η^5-cyclopentadienyl)iron dicarbonyl dimer has been assigned as follows: 6.95, 7.5, 7.76, 8.1, 8.68 eV, ionization of "iron 3d levels"; 9.52, 9.9 eV, ionization of C_5H_5 π orbitals.[20] In comparing diene complexes of iron and ruthenium, Green and co-workers[22] have noted that metal orbital ionizations increase from iron to ruthenium; similar increases are seen here with the iron and ruthenium halide complexes. Thus, we believe that there is little doubt that the UPS bands for C at 8.17, 8.52 (containing a shoulder on the high ionization-energy edge), and 9.26 eV correspond to ionization of the four orbitals expected to have primarily Ru character,[23] while the intense broad band centered at 10.46 eV refers to ionization of the two C_5H_5 π orbitals and possibly a Cl "lone-pair" ionization component. The remaining expected Cl "lone-pair" band clearly must be the one at 11.36 eV, although a Cl lone-pair component splitting of more than 0.5 eV does appear abnormally large. Alternatively, all Cl lone-pair ionization components could be contained under the band centered at 11.36 eV.

Replacing one carbonyl and the chlorine moiety by the η^3-allyl ligand to form ruthenium complexes A, B, D, and E (Table I, Figure 1) in all cases shifts the bands corresponding to ionization of metal orbitals to lower ionization potentials. If we consider the endo isomer A, the first four bands of the UPS for this molecule closely resemble in profile and intensity those for C. They are shifted to lower ionization potential by ca. 0.6 eV relative to the analogous bands for C.[23] Furthermore the broad double maximum at 9.77 and 10.17 eV for A logically refers to ionization of the perturbed C_5H_5 π orbitals. This leaves the bands at 9.22 and 10.85 eV to be assigned to ionization of the two perturbed allyl π orbitals. Upon methyl substitution to form endo isomer B, the expected shift to lower ionization potential is observed for all of the bands. The most dramatic shift occurs for the highest band which is now merged into the high ionization energy tail of the C_5H_5 band. This is to be expected since the lower π orbital of the allyl moiety contains maximum orbital electron density at the 2-position to which the methyl group is directly bonded. On the other hand, the π-allyl HOMO contains a node at the 2-position and is hence affected no more than are the Ru orbitals by methyl substitution.

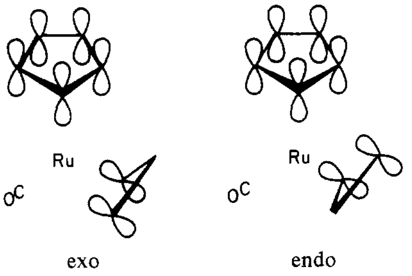

Figure 2. Through-space interactions between cyclopentadienyl and allyl π HOMO's in endo and exo isomers.

The appearances of the UPS for the exo isomers D and E are somewhat different than those for the two corresponding endo isomers discussed below. Although four predominantly metal ionization processes are evident in the UPS for D and E below 9 eV, the I_3 and I_4 bands are now substantially merged in contrast to the situation for A and B. Furthermore the π-allyl HOMO is somewhat more stable for D and E than for A and B. The cyclopentadienyl and second allyl ionization bands are not clearly resolved for the D and E isomers, such that it is difficult to predict relative stabilities for the C_5H_5 orbitals for A/D and B/E. A through-space interaction between the allyl π HOMO, which contains its orbital density at carbons 1 and 3, and the cyclopentadienyl HOMO should be more significant for the endo isomers than for the exo analogues (Figure 2). This may explain in part why the splitting between the allyl π HOMO and the C_5H_5 orbitals would be somewhat greater for A and B than for D and E as is observed in the UPS. It is impossible to assess the exact difference of this through-space interaction for the two sets of isomers because of extensive band overlapping in the UPS of D and E. Also "through-bond" interactions between the C_3H_5 and C_5H_5 moieties may be some different for the two sets of isomers, as might be inferred from the appearance of the "metal-orbital" regions of the UPS. In any case we are convinced that the UPS band corresponding to the π-allyl HOMO occurs at higher ionization energy than do all of the metal UPS bands in contrast to the apparent situation for bis(η^3-allyl)metal complexes.[7,8] The current UPS interpretations for A, B, D, and E are entirely consistent with those for the other allyl complexes studied previously in these laboratories.[12]

The interpretation of the UPS of the iron complex F is more complicated. Clearly the bands at 6.90, 7.28, and 7.87 eV can be assigned to ionization of perturbed iron orbitals.

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(19) For example, see D. L. Lichtenberger and R. F. Fenske, *J. Am. Chem. Soc.*, **98**, 50 (1976).

(20) For example, see G. Granozzi, E. Tondello, M. Bénard, and I. Fragalà. *J. Organomet. Chem.*, **194**, 83 (1980).

(21) For example, see B. Kovac, E. Heilbronner, H. Prinzbach, and K. Weidmann, *Helv. Chim. Acta*, **62**, 2841 (1979).

(22) J. C. Green, P. Powell, and J. Van Tilborg, *J. Chem. Soc., Dalton Trans.*, 1974 (1976).

(23) It has been a matter of controversy for some time with (η^5-C_5H_5)(η^3-C_3H_5)M(CO) complexes (M = Fe or Ru) whether the metal should be considered as M^{2+} or M^0 (and the ligands, therefore, as $C_5H_5^-$ and $C_3H_5^-$ or neutral radicals). In this work we have adopted the latter convention, which seems to best explain the presence of eight low-ionization-energy band components in Figure 1A. Compound C is also viewed as an Ru^0 complex.

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.

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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

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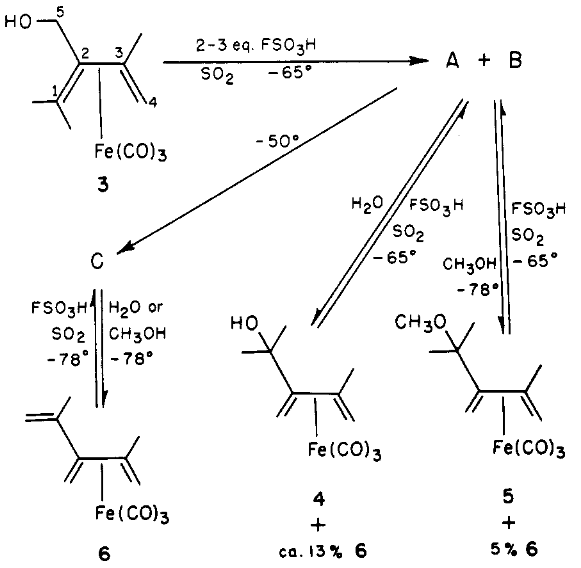
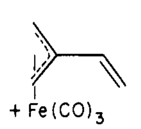
Isomeric [trimethyl(cross-conjugated dienyl)]tricarbonyliron cations A (**11a**) and B (**11b**) have been generated in SO_2 at −65 °C by using 2–3 equiv of FSO_3H or excess FSO_3H and excess 1:1 SbF_5/FSO_3H. Precursors **3–5** all produce the same equilibrium A/B mixture. These observations, and the 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.

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





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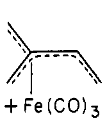

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Our previous studies of the parent cation and its isomeric 4-methyl derivatives have shown that (cross-conjugated dienyl)tricarbonyliron cations do not possess the coordinatively unsaturated η^3 structure **1** predicted by frontier orbital theory[1] 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-

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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.

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