in substituted acetophenones to the value for the n,π* state in the unsubstituted molecule can be obtained. It is assumed that the $^3[n,\pi^*]$ state decays with the assistance of the strong charge-transfer singlet state (^1L_a) at 42,000 cm^{-1}, and that the $^3[\pi,\pi^*]$ state decays with the help of the nearest $^1[n,\pi^*]$ state at about 31,000 cm^{-1}.[7] The spin-orbit matrix elements are the same for both processes, and cancel out in the ratio. The result is

$$\frac{\tau_\pi}{\tau_n} = \frac{\Delta E_\pi}{f_\pi}\frac{f_n}{\Delta E_n}$$

where π and n refer to the two kinds of triplets, ΔE is the appropriate energy denominator, and the f_π and f_n are the oscillator strengths of the singlet bands. This ratio is 14 for p-methylacetophenone and is to be compared to the observed value of 28. More refined calculations would probably give improved agreement and might explain the dependence on substituent, but we feel that at this stage we can cite the values of the lifetimes as providing additional evidence for the $^3[\pi,\pi^*]$ assignments.

The somewhat rough correlation between decrease of reactivity and increase of lifetime and the near-constancy of the energy of the reacting state suggest that a factor in electronic structure must be responsible for the change in reactivity with substitution. The investigation is being continued to isolate this factor.

[7] D. S. McClure, *J. Chem. Phys.*, 20, 682 (1952); M. A. El-Sayed, *ibid.*, 38, 2834, 3032 (1963).

[8] National Science Foundation Predoctoral Fellow, 1962–1965; Esso Fellow, 1965–1966.

[9] The work is abstracted in part from the Ph.D. Thesis of S. L. Murov, submitted to the Department of Chemistry, University of Chicago.

[10] NDEA Fellow, 1966–1967.

[11] The authors wish to thank the National Science Foundation for the support of this work and Dr. A. A. Lamola of the Bell Telephone Laboratories for a copy of his preprint.

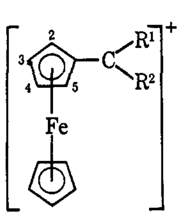
N. C. Yang, D. S. McClure, S. L. Murov[8,9]
J. J. Houser, Ruth Dusenbery[10,11]
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

Received July 31, 1967

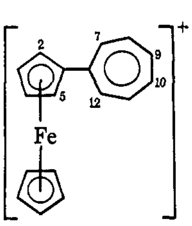
Metal π Complexes of the Sesquifulvalene and Calicene Systems[1]

Sir:

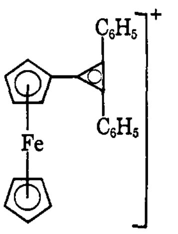
We have made use of the known stability and ready availability of tropylium,[2] diphenylcyclopropenylium,[3] and ferrocenylcarbinyl[4] cations (I) to realize the synthesis and isolation of the stable cations II and III, which are in effect iron π complexes of the sesquifulvalene and calicene systems, IV and V, respectively.



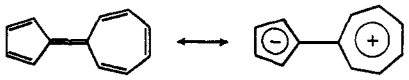
I



II



III



IV

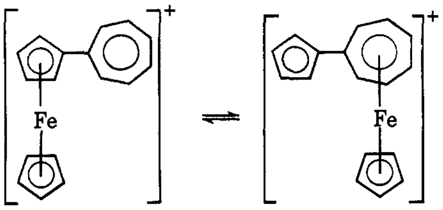
V

The green, crystalline fluoroborate salt of cation II was obtained in one step from the reaction between ferrocene and tropylium fluoroborate in acetonitrile solution. The ultraviolet spectrum (in methylene chloride solution) exhibited λ_{max} (mμ (log ε)) 332 (3.6), 404 (4.3), and 700 (3.7).

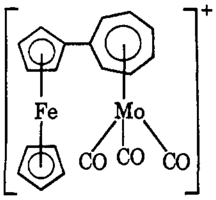
The boron trifluoride etherate catalyzed reaction between ferrocene and 3,3-dichloro-1,2-diphenylcyclopropene[5] in methylene chloride yielded the red crystalline fluoroborate salt of cation III. The ultraviolet spectrum (in methylene chloride) exhibited λ_{max} (mμ (log ε)) 250 (4.2), 307 (4.4), and 320 (4.4).

$NaBH_4$ reduction of the salts of either II or III yielded isomeric mixtures (double bond positional isomerism) of ferrocenylcycloheptatriene and ferrocenyldiphenylcyclopropene, respectively.[6]

The reported synthesis of various π-$C_5H_5MC_7H_7$ complexes[7] as well as the suggested valence tautomerism exhibited by metal π complexes of fully conjugated hydrocarbon systems[8] necessitate the consideration of the possible tautomerism IIa ⇌ IIb (or some intermediate position of the FeC_5H_5 moiety between the extreme forms IIa and IIb).



IIa IIb



VI

The apparent singlets (parts per million downfield from TMS) at δ 5.37 for the four protons[9] H_2–H_5 and at δ 8.30

---

[1] (a) Organometallic Studies. XX. (b) For part XIX see M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards *Tetrahedron Letters*, 1695 (1966).

[2] For reviews see (a) M. E. Vol'pin, *Russ. Chem. Rev.*, **29**, 129 (1960); (b) T. Nozoe in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959.

[3] R. Breslow, J. Lockhart, and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2375 (1961).

[4] For a recent review see M. Cais, *Organometal. Rev.*, **1**, 435 (1966).

[5] B. Föhlisch and P. Bürgle, *Ann.*, 701, 67 (1967).

[6] Structures were confirmed by infrared, nmr, and molecular weight (mass spectrum) measurements, and satisfactory elemental analysis results. Hydride abstraction with trityl fluoroborate from ferrocenylcycloheptatriene and ferrocenyldiphenylcyclopropene gave fluoroborate salts which were identical in every respect (ultraviolet, infrared, nmr) with the cations II and III, respectively, obtained by the direct route.

[7] For example (a) E. O. Fischer and S. Breitschaft, *Angew. Chem.*, **75**, 94 (1963); *Chem. Ber*, **96**, 2451 (1963); (b) R. B. King and M. B. Bisnette, *Inorg. Chem.*, 3, 785 (1964); (c) R. B. King, *J. Organometal. Chem.* (Amsterdam), **8**, 129 (1967).

[8] See, for example, R. Ben-Shoshan and R. Pettit, *J. Am. Chem. Soc.*, **89**, 2231 (1967), and leading references therein. See also ref 7c.

[9] The appearance of this singlet is in contrast to other α-ferrocenyl-

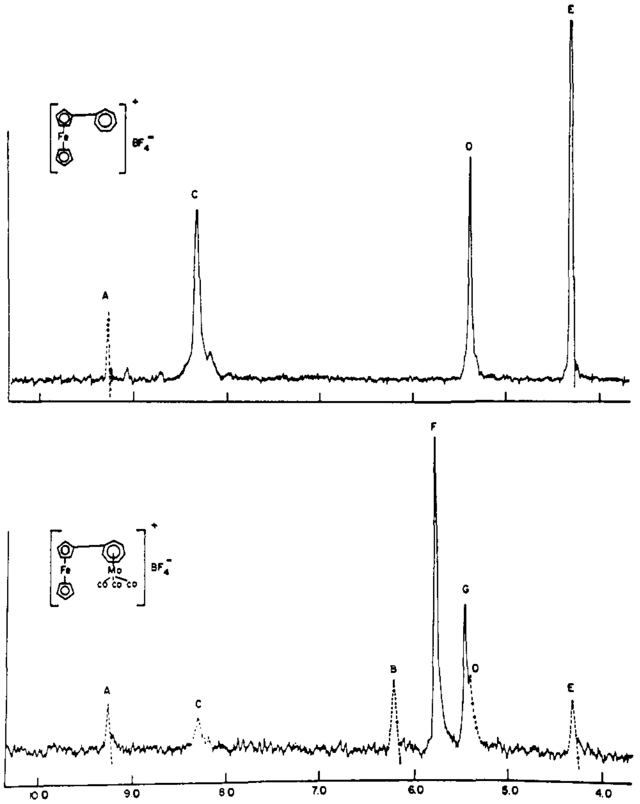


Figure 1. The nmr spectra of cations II (top) and VI (bottom) in acetonitrile. The protons belonging to the same moiety in the two structures are identified by the same letter. The dashed lines are for protons of reference compounds: A, $C_7H_7^+BF_4^-$; B, $[C_7H_7Mo(CO)_3]^+ BF_4^-$; C, tropylium protons of II; D, protons of C_5H_4 ring of II; E, protons of C_5H_5 ring of II; F, protons of C_5H_4 and C_5H_5 rings of VI; G, tropylium protons of VI (parts per million downfield from TMS) (Varian A-60).

for the six protons H_7–H_{12} in the nmr spectrum of II-BF_4^- (see Figure 1) could be interpreted as being due to the averaging out that would result from a fast (nmr time scale) tautomerism IIa $\rightleftharpoons$ IIb. The same phenomenon and the implied mutual effect (*e.g.*, aromatic ring current) between the fully conjugated π-electron system of the upper sesquifulvalene moiety and the lower unsubstituted C_5H_5 ring in II could be invoked in the explanation of the significantly higher field absorption (δ 4.30) of the C_5H_5 protons.

Since the nmr spectrum of II in the rather narrow temperature range −30° to +55° remained practically unchanged,[11] the cation VI, in which the presence of the $Mo(CO)_3$ group should prevent the "gliding" of FeC_5H_5 across the planar sesquifulvalene moiety, was prepared.[12] The nmr spectrum of VI exhibits only two apparent singlets at δ 5.74 (coalescence of the signals of protons H_2–H_5 and those of the C_5H_5 ring) and at

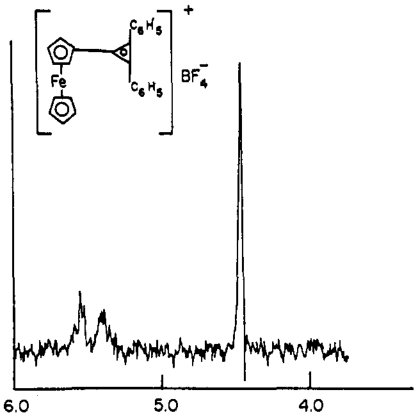


Figure 2. The nmr spectra of the C_5H_4 and C_5H_5 protons of cation III in acetonitrile (parts per million downfield from TMS) (Varian A-60).

δ 5.43 (protons H_7–H_{12}), which is not in disagreement with what might be predicted for the spectrum of the nontautomerizable[13] structure VI.

The electronic charge distribution in cations II and III as obtained from independent electron MO calculations[14] might provide a basis for an alternative, albeit oversimplified, explanation of the nmr spectra exhibited by these two cations without necessarily invoking the postulated tautomerism IIa $\rightleftharpoons$ IIb. By keeping the FeC_5H_5 moiety as in IIa (or in I, or in III) our calculations gave 3.1, 2.4, 1.4, and 1.1 for $q_2{:}q_3$ (or $q_5{:}q_4$) in I ($R^1 = R^2 = H$), I ($R^1 = H$, $R^2 = C_6H_5$), III, and IIa, respectively. This is in qualitative agreement with the observed separation[15] $\Delta\nu$ = 97, 66, 9, and ~2 cps, respectively, for the four compounds in the order given above. Furthermore, the same calculations place most of the positive charge (~88%) on the tropylium ring in IIa or on the diphenylcyclopropenyl moiety in III. This could account for the higher field absorption of the unsubstituted C_5H_5 ring in IIa (δ 4.30) and III (δ 4.46) as compared to I ($R^1 = R^2 = H$) (δ 5.15). In the latter, since most of the positive charge, as calculated, appears to reside on the Fe atom, one would expect a greater deshielding effect on the C_5H_5 ring protons (see Figure 2).

The availability of cations II and III may provide a novel and convenient route for entry into the sesquifulvalene and calicene systems. This is currently being tested in our laboratory.

carbonium ions. For example, in I ($R^1 = R^2 = H$) the two sets of protons $H_{2,5}$ and $H_{3,4}$ absorb at δ 4.62[10] and 6.20, respectively.[1b,4]

[10] (10) This number was erroneously given as δ 4.26 in ref 1b (as well as in ref 4). Similarly the first entry in Table I[1b] (and Table 4[4]) should read 97 cps instead of 118 cps.

[11] (11) Except for very slight peak half-width broadening (at 30°) of the C_7H_6 and C_5H_4 protons relative to the C_5H_5 protons.[7c] Lower temperature nmr measurements are planned.

[12] (12) Prepared by direct reaction between ferrocene and $[C_7H_7Mo(CO)_3]^+BF_4^-$ or by hydride abstraction from $C_5H_5FeC_5H_4C_7H_7Mo(CO)_3$ (the latter compound was obtained from reaction of $C_5H_5FeC_5H_4C_7H_7$ with $Mo(CO)_6$).

[13] (13) A *trans* arrangement of the FeC_5H_5 and $Mo(CO)_3$ moieties with respect to the sesquifulvalene plane in VI is probable. However, concomitant "gliding" of the two metal-containing moieties does not seem very plausible.

[14] (14) Details of several MO calculations for ferrocenes, carried out in collaboration with Professor E. Heilbronner, will be published elsewhere.

[15] (15) $\Delta\nu = \nu(H_{2,5}) - \nu(H_{3,4})$ between the centers of each pair of bands.[1b,4,10]

[16] (16) This research has been sponsored in part by the Air Force Materials Laboratory (AFSC) through the European Office of Aerospace Research (OAR), U. S. Air Force, under contract AF61(052)-752.

Michael Cais,[16] A. Eisenstadt
Department of Chemistry, Technion—Israel Institute of Technology
Haifa, Israel

Received July 18, 1967