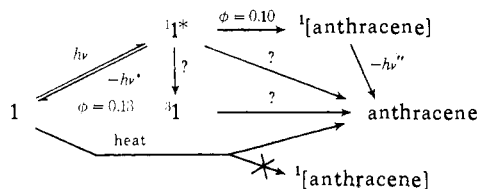


from **1** being from the singlet energy transfer from excited **1** to the anthracene present was further excluded by examining the fluorescence spectrum of a model compound, 2,3-dimethylnaphthalene, in the presence of anthracene under identical conditions. 2,3-Dimethylnaphthalene ($2.1 \times 10^{-5} M$) which has an appreciably longer fluorescence lifetime than **1** (78 nsec,⁸ 91.5 nsec⁹) exhibits no appreciable emission in the 390–440 nm region in the presence of an amount of anthracene equivalent to that present in **1** ($3.6 \times 10^{-7} M$). These observations demonstrate that the anthracene emission is derived from excited **1** and not from the small amount of anthracene present.

Using 2,3-dimethylnaphthalene fluorescence as a secondary standard, $\phi = 0.38$,⁸ the total fluorescence quantum yield of **1** was estimated to be 0.15 ± 0.02 , which is the sum of the naphthalene-like emission ($\phi = 0.13 \pm 0.02$) and the anthracene emission ($\phi = 0.024 \pm 0.004$). Since anthracene has a fluorescence quantum efficiency of 0.24 in benzene,¹⁰ our results suggest that the quantum yield of singlet excited anthracene formed in the photorearrangement of **1** is about 0.1.¹¹

Although **1** fluoresces with lower efficiency than do ordinary naphthalenes, its radiative lifetime (τ_i/ϕ_i) does not differ greatly from those of other naphthalenes.⁸ A principal mode of decay of photoexcited naphthalenes is intersystem crossing, and it is reasonable to expect that **1** will also undergo intersystem crossing but with lower efficiency. The lowest triplets (T_1) of naphthalenes are, of course, much longer lived than are the corresponding singlet states, so we expect that T_1 of **1** can also rearrange to give T_1 of anthracene. Unfortunately, neither the phosphorescence of naphthalenes nor that of anthracene is detectable in solution at room temperature, so that quantitative aspects of the observed rearrangement in the triplet manifold cannot presently be fully demonstrated. An appreciable fraction of the nonemitting anthracene formed in this rearrangement ($\phi = 0.31$) may arise *via* the triplet–triplet route mentioned, and it is probable that a much larger fraction of the anthracene formed from excited **1** is in some excited state.



Although the amount of energy available in the adiabatic conversion of **1** to anthracene may be estimated at 75–80 kcal, which is sufficient to populate the triplet state or the singlet excited state of anthracene, we have no experimental evidence that either of these two states were appreciably populated during the thermal decomposition of **1**. It has been reported that dewar benzenes decompose thermally to yield benzenes in their triplet states.¹² In spite of the fact that the conversion of **1** to

(8) Reference 7, p 110.

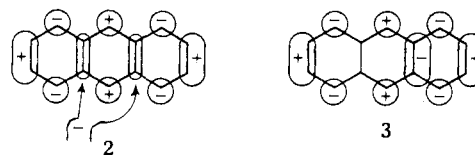
(9) J. K. McVey, unpublished result.

(10) W. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

(11) The relative intensity of the anthracene emission to the naphthalene-like emission from **1** does increase slightly upon thorough degassing; therefore, the partial contribution of T–T annihilation in the formation of S_1 of anthracene may not be excluded.

(12) P. Lechtken, R. Breslow, A. H. Schmidt, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3025 (1973).

triplet anthracene is energetically a much more favorable process, it apparently does not occur. Since the lowest antibonding orbital of anthracene (ψ_8 , **2**) is symmetrical with respect to the xz and yz planes bisecting the molecule,¹³ while the molecular orbitals in **1**, a 2,3-disubstituted naphthalene can only be symmetrical with respect to the xz plane, the adiabatic conversion of **1** to excited anthracene is not favorable because of the lack of orbital symmetry.^{13,14} The lowest antibonding orbital of **1** also lacks symmetry with respect to the yz plane. However, it is interesting to note the similarity between ψ_8 of anthracene (**2**) and the molecular orbital of **1** constructed from ψ_6 of naphthalene¹⁵ and π_1 and σ_1 of cyclobutene followed by a disrotatory ring opening (**3**). This formal similarity suggests that conversion among the excited states is allowed. The significance of such orbital correlation in the interconversion among excited molecules and related processes is being examined.



Acknowledgment. The authors wish to thank the National Institutes of Health (Grants AM-11676 and GM-20329), the National Science Foundation, and the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research, for the support of this work. The authors also wish to thank Professor K. Fukui for a stimulating discussion and Drs. J. Libman and M. Shobatake for their assistance in the laboratory.

(13) E. Heilbronner and P. A. Straub, "Hückel Molecular Orbitals," Springer-Verlag, New York, N. Y., 1966, p Z14.

(14) Dewar benzenes possess symmetries in both xz and yz planes, and the orbital correlation between dewar benzene and the B_{1u} states (S_2 or T_1) of benzene has been pointed out by D. Bryce-Smith and H. C. Loungat-Higgins, *Chem. Commun.*, 593 (1966).

(15) Reference 13, p Z10.

(16) National Science Foundation Undergraduate Research Participant, 1972.

N. C. Yang,* Richard V. Carr, Ellen Li¹⁶
Jeffrey K. McVey, Stuart A. Rice

Department of Chemistry, University of Chicago
Chicago, Illinois 60637

Received December 10, 1973

Cross-Conjugated Pentadienyliron Tricarbonyl Cations. Dominance of Frontier Orbital Interaction in Metal–Carbon Bonding

Sir:

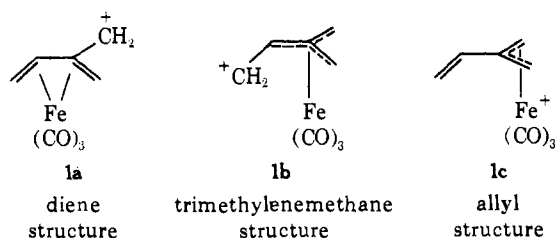
The Dewar–Chatt–Duncanson theory¹ of bonding in transition metal π -complexes has been of immense utility in understanding the structure, spectral properties, and chemical reactivity of these compounds.² Bonding is treated as charge transfer interactions of

(1) (a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, C71 (1951); (b) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(2) Its exclusive use for presentation of bonding in current general monographs on organotransition metal chemistry serves as a measure of its acceptance. Cf. (a) M. L. H. Green, "The Transition Elements, Vol. 2 of Organometallic Compounds," Methuen, London, 1968; (b) R. B. King "Transition Metal Organometallic Chemistry, An Introduction," Academic Press, New York, N. Y., 1969; (c) M. Tsutsui, M. N. Levy, A. Nakamura, M. Ichikawa, and K. Mori, "Introduction to Metal π -Complex Chemistry," Plenum Press, New York, N. Y., 1970.

occupied ligand orbitals with unoccupied metal orbitals and of occupied metal orbitals with unoccupied ligand orbitals.³ Even for relatively simple molecules a large number of symmetry-allowed interactions exists. Identification of one or two interactions which make the dominant contribution to bonding would result in a simpler, more definitive picture of metal-carbon bonding.⁴ Consider, for example, cations with odd alternate ligands such as (η -allyl)iron tricarbonyl and (η -pentadienyl)iron tricarbonyl. When these cations are formulated as complexes of a carbonium ion ligand with neutral metal moiety, electronegativity considerations and experimental observations⁵ suggest strongly that donation from metal to ligand will be the dominant mode of bonding. This should involve principally the ligand LUMO,⁶ the unoccupied nonbonding MO, of the carbonium ion, and the result is a single (two-electron) bond. A test of this simple model for metal-carbon bonding in a case where its prediction disagrees with that made on the basis of the time-honored effective atomic number (EAN) rule⁷ is described below.

Cross-conjugated pentadienyliron tricarbonyl cations could have structures **1a-c** (actual charge location not



implied). The diene and trimethylene methane structures have 36-electron configurations at iron (*i.e.*, they satisfy the EAN rule) and are supported by ample precedent.^{8,9} Allyliron tricarbonyl cations are known¹⁰ but, having a 34-electron configuration at iron, are unstable in the presence of nucleophiles which can coordinate at iron such as halide ions¹¹ and water.¹⁰ Clearly the EAN rule predicts that the structure will be **1a** or **1b**. Our model just as clearly predicts the structure will be **1c**. When cation **1** is formed by interaction of a pentadienyl cation with a neutral $\text{Fe}(\text{CO})_3$ fragment, the dominant metal-carbon bonding interaction will be that which involves donation of electrons from an occupied orbital on iron to the lowest unoccupied MO of the ligand, the nonbonding MO (ψ_3). The wave function ψ_3 has a finite amplitude only at C_1 and C_5 .¹²

(3) The latter type of interaction is sometimes referred to as back-bonding or back coordination. Cf. L. D. Pettit, *Quart. Rev., Chem. Soc.*, **25**, 1 (1971).

(4) An outstanding but rare example is the treatment by Maitlis and coworkers of bonding in olefin and acetylene complexes of Ni, Pt, and Pd: E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(5) W. R. Jackson and W. B. Jennings, *J. Chem. Soc. B*, 1221 (1969); R. E. Graf and C. P. Lillya, *J. Amer. Chem. Soc.*, **94**, 8282 (1972).

(6) Cf. K. Fukui in "Molecular Orbitals in Chemistry, Physics, and Biology," P.-O. Lowdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 513.

(7) See ref 2a, pp 2-6.

(8) Cf. R. Pettit, G. Emerson, and J. Mahler, *J. Chem. Educ.*, **40**, 175 (1963).

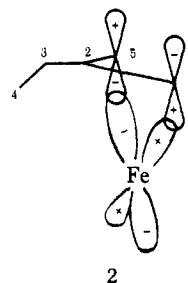
(9) Cf. K. Ehrlich and G. F. Emerson, *J. Amer. Chem. Soc.*, **94**, 2464 (1972).

(10) G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 4591 (1962).

(11) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **45**, 1927 (1962); and M. Kh. Minasyan, Yu. T. Struchkov, I. I. Knitskaya, and R. I. Avoyan, *Zh. Strukt. Khim.*, **7**, 903 (1966).

(12) E. Heilbronner and H. Straub, "Huckel Molecular Orbitals," Springer Verlag, Berlin, 1966.

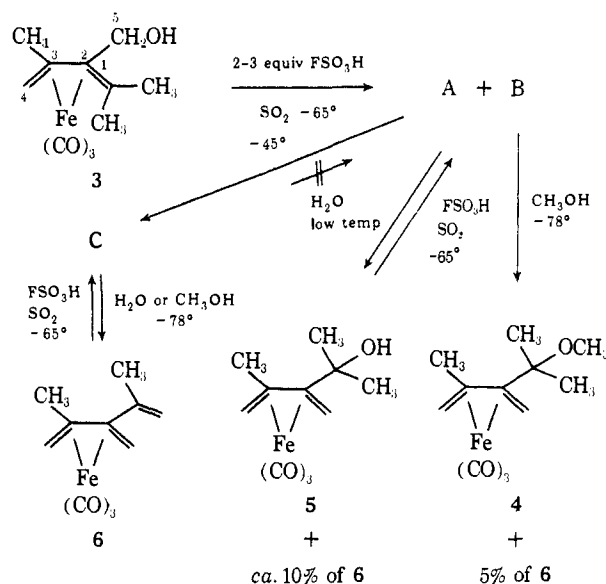
Thus, structure **1c** should be most stable because it maximizes overlap of metal orbitals with ψ_3 (2). An



ion which possess structure **1c** will be differentiated from those possessing structures **1a** or **1b** by its ability to undergo rotation about the C_2 - C_3 bond.

Chemistry of the 1,1,3-trimethyl derivative of **1** is shown in Scheme I.¹³ Spectroscopic evidence for con-

Scheme I. Chemistry of the 1,1,3-Trimethyl Derivative of Cation 1 (Drawings do not imply relative configuration of the asymmetric (diene) $\text{Fe}(\text{CO})_3$ unit)¹³

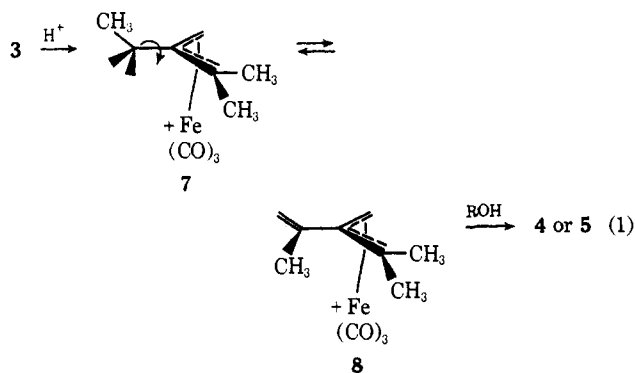


version of the original 1,1-dimethyl alcohol **3** to the isomerized 5,5-dimethyl series **4-6** is compelling. The nmr spectrum of **3** exhibits an AB pattern centered at τ 8.1 ($\Delta\nu_{\text{AB}} \approx 6$ Hz, $J_{\text{AB}} = 3$ Hz) for the C_4 hydrogens. The anti (cis) hydrogen is displaced from its customary position owing to deshielding by the anti (cis) methyl at C_1 .¹⁴ The rearranged methyl ether (**4**), which is typical in this respect, exhibited doublets at τ 9.97 ($J = 2$ Hz) and τ 10.38 ($J = 2.5$ Hz), indicative of anti (cis) hydrogens on diene ligands which bear no terminal substituents.¹⁴ Isomerization is rapid at -78° . Quenching at -78° of a solution of **3** in FSO_3H - SO_2 less than 1 min after preparation with excess -78° methanol gave only a 95:5 mixture of **4** and **6** (83% total yield). Furthermore, the nmr spectrum obtained at -65° ca. 30 sec after adding acid to a solution of **3** in SO_2 at -78° does not change with time. Isomerization requires rotation about the C_2 - C_3 bond, eq 1.

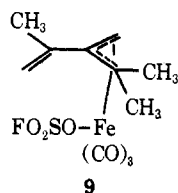
Evidence that the intermediates in the acidic solutions, **A** and **B** (see Scheme I), are in fact unipositive

(13) New compounds have been characterized by elemental analysis and nmr, ir, and (in most cases) mass spectrometry.

(14) G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, **29**, 3620 (1964).



cross-conjugated pentadienyliron tricarbonyl cations is strong. Increasing the amount of FSO_3H beyond the two equivalents necessary to produce the organometallic cation and hydronium ion caused no change in the -65° nmr spectrum. This rules out multiple protonation.¹⁵ Isomerization cannot be caused by rapid C_2-C_3 rotation in a small amount of the neutral allyl complex **9** because exactly the same chemistry and



intermediates (A, B, and C) were observed in 1:1 SbF_5-FSO_3H in $SO_2(l)$. The very low nucleophilicity of this solvent-acid system¹⁶ makes the formation of **9** highly unlikely.

The nmr spectrum of the acidic solution at -65° reveals the presence of two species A and B. They

(15) D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **91**, 6968 (1969).

(16) Cf. G. A. Olah and A. Commeyras, *J. Amer. Chem. Soc.*, **91**, 2929 (1969).

appear to be in equilibrium since the A:B ratio is independent of the precursor (**3** or **5**) and they disappear at equal rates (see below). Their nmr spectra permit assignment of structures **7** and **8** to A and B only if some chemical shift assignments untypical of simple allyliron tricarbonyl cations are made. Warming the sample to -49° in an attempt to speed their interconversion caused conversion to a new species, C, which produced olefin **6** on quenching.

Since the allyl structure, **1c**, is the only one which is consistent with rotation about the C_2-C_3 bond,^{17,18} our observations require that the energy of the allyl structure (**1c**) and that of the equilibrium structure be similar if in fact they are not the same. Thus, our model provides an insight into the chemistry of these cations which would be completely overlooked by straightforward application of the EAN rule. Broader applications will be presented in a full paper.

Acknowledgments. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work.

(17) The contribution destabilizing steric interactions involving methyl substituents in the planar conformers (**7** and **8**) make to lowering the energy barrier to rotation cannot in itself explain the isomerization. Anti (cis) methylated conjugated pentadienyliron tricarbonyl cations, which should be significantly more crowded than **7** or **8**, are configurationally stable under these conditions; Cf. T. S. Sorensen and C. R. Jablonski, *J. Organometal. Chem.* **25**, C62 (1970); C. P. Lillya and R. A. Sahatjian, *ibid.*, **25**, C67 (1970).

(18) A referee has suggested a monohapto intermediate with a σ bond between iron and C_1 or C_5 . However, simple π -allyliron carbonyl cations show no tendency to form σ -allyl isomers. Thus, syn and anti substituted cations are configurationally stable, while Faller has shown that formation of σ -allyl isomers leads to syn-anti isomerization in complexes of palladium and other metals. Cf. J. W. Faller, M. E. Thomsen, and M. J. Mattina, *J. Amer. Chem. Soc.*, **93**, 2642 (1971).

(19) Alfred P. Sloan Foundation Fellow, 1969-1971.

Benedict R. Bonazza, C. Peter Lillya*¹⁹

Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01002

Received July 13, 1973

Book Reviews

Organic Reagents in Metal Analysis. By K. BURGER (L. Eötvös University, Budapest, Hungary). Pergamon Press, Oxford. 1973. 268 pp. \$17.50.

This book is an enlarged translated version of Burger's Hungarian text which was originally published in 1969. Its appearance in English is timely. Organized in three parts, the book (i) treats the coordination chemistry of analytical reactions, (ii) reviews the application of selective reagents (organic chelates such as the oximes flavones, dithizone, β -diketones, and dithiocarbamates), and (iii) provides tabulary summaries of over 100 specific reagents, their metal specificities, general properties, and selected stability constants. A table of organic solvents has 73 entries and should be of value to both synthetic and physical chemists. The coverage of fundamentals embodies current principles of coordination chemistry. The accent is on metal-ion selectivity and sensitivity. The discussion is restricted to reagents for classical analytical methods including gravimetric, volumetric, and spectrophotometric analyses, polarography, chromatography, and ion exchange. In view of increasing interest in trace metal detection for environmental pollution control and in the identification of trace metals in biology, this book should command a respectable market.

Stephen J. Lippard, *Columbia University*

Enzyme Engineering. Edited by L. B. WINGARD. Wiley-Interscience, New York, N. Y. 1972. iv + 412 pp. \$12.50.

This book is the result of papers presented at the Engineering Foundation Conference on "Enzyme Engineering," August 9-13, 1971, Henniker, N. H., and the 64th Annual Meeting of the American Institute of Chemical Engineers, December 1, 1971, San Francisco, Calif. There were thirty-three contributors to this book, comprised of chemical engineers, biochemists, organic chemists, and microbiologists, and one might expect that the book would be disorganized and uneven, but suprisingly enough, it is very well organized and the presentations are written evenly. This is undoubtedly due to the efforts of the editor, L. B. Wingard, who must have exerted an enormous influence.

The book is concerned primarily with the development of techniques for immobilization of enzymes with retention of catalytic activity to minimize the economic problem of recovery and reuse of costly enzymes, with the result that a variety of opportunities exist for industrial, medical, and analytical applications using enzyme catalysts. In such applications, enzymes would be attached to columns and thus not be used up—a so-called "enzyme reactor."

Platforming is a well-established procedure for refining gasoline.