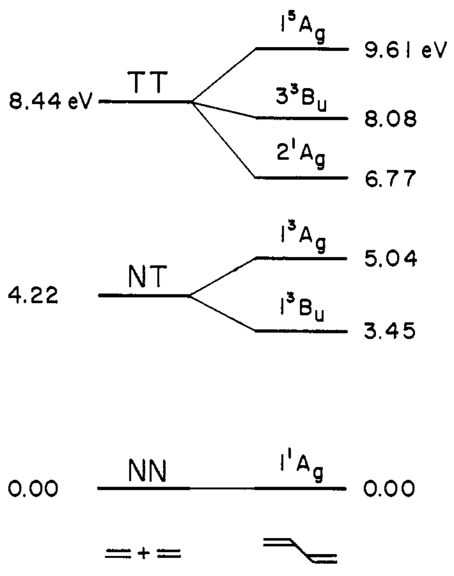

Figure 1. Correlation of computed valence states of butadiene (right) with those of two ethylene molecules (left).

Fock configuration.[12] The errors in their computed vertical excitation energies are probably quite small, as are the errors for the other valence states $1\,^3B_u$ and $1\,^3A_g$. Being essentially doubly excited states, they are not expected to make significant contributions to either the optical or the electron impact spectra of butadiene, though the 2^1A_g state may be accessible in two-photon laser spectroscopy. These states, and particularly the 2^1A_g state, may play a role in the photochemistry of butadiene. For example, the semiempirical calculations of van der Lugt and Oosterhoff[13] indicate that an excited ^1A_g state is responsible for the cyclization of butadiene to cyclobutene; this state may be identified with the 2^1A_g state.[1]

All the valence states of butadiene can easily be accounted for by a straightforward generalization of valence bond theory.[1] Using a "molecules-in-molecules" or exciton approach,[14] the ground and excited states of butadiene are described in terms of the electronic states of the two localized ethylenic subunits (Figure 1). From the two π-electron valence states of ethylene, the ground $N(\pi^2)$ and excited triplet $T(\pi\pi^*)$ states, a total of six states of butadiene can be constructed. With the two ethylenic units in the N state, the ground state of butadiene, denoted as $NN(X^1A_g)$, is obtained. Two triplet states, $NT(^3B_u)$ and $NT(^3A_g)$, are obtained if one unit is in T and the other in N. In the absence of significant stabilization effects, their average excitation energy (4.24 eV for $1\,^3A_g$ and $1\,^3B_u$ in this calculation) is just the N → T excitation energy of ethylene (calculated as 4.22 eV). With both ethylenic units in the T state, three states can be formed, $TT(^1A_g)$, $TT(^3B_u)$, and $TT(^5A_g)$. Their average excitation energy should be approximately twice the N → T energy of ethylene, *i.e.*, 8.44 eV. Correlating them with the calculated 2^1A_g, 3^3B_u, and 1^5A_g valence states of butadiene, we get $\Delta E_{av} = 8.15$ eV. The occurrence of such doubly excited states in conjugated systems is expected to be quite general.[15,16]

The diffuse π-electron states of butadiene can be constructed in a similar manner. With one ethylenic unit in the singlet $V(\pi\pi^*)$ state we obtain the $NV(^1B_u)$ and $NV(^1A_g)$ states of butadiene. In contrast to the valence states, however, the diffuse states are well represented by a single SCF configuration; delocalization is thus significant, and the simple generalized valence bond description is less appropriate for these states.

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[12] Several workers have noted the large effect of doubly excited configurations on the location of the 2^1A_g state but did not realize that the resulting 2^1A_g state is not related to the 2^1A_g state obtained in a single-excitations-only CI calculation (the latter becoming the 3^1A_g state in double-excitation CI[1]); see, *e.g.*, J. Koutecky, *J. Chem. Phys.*, **47**, 1501 (1967), and references therein. Koutecky has pointed out that this state should be reachable by double-photon excitation from the ground state.

[13] W. Th. A. M. van der Lugt and J. Oosterhoff, *J. Amer. Chem. Soc.*, 91, 6042 (1969).

[14] W. Moffitt, *J. Chem. Phys.*, **22**, 320 (1954); Y. Mori, *Bull. Chem. Soc. Jap.*, **28**, 291 (1955); R. S. Berry, *J. Chem. Phys.*, **26**, 1660 (1957).

[15] K. Schulten and M. Karplus, *Chem. Phys. Lett.*, **14**, 305 (1972), and J. Michl and J. Downing, Proceedings of the Summer Research Conference on Theoretical Chemistry, Boulder, Colo., June 1972 (to appear) have reported low-lying doubly excited states obtained in semiempirical calculations on large conjugated systems. See also J. Downing, V. Dvořák, J. Kolc, A. Manzara, and J. Michl, *Chem. Phys. Lett.*, 17, 70 (1972), and references therein.

[16] The occurrence of related states in benzene has recently been demonstrated, see P. J. Hay and I. Shavitt, to be submitted for publication.

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Received April 30, 1973

Molecular Structure of (1,7-Cyclododecadiyne)hexacarbonyldiiron. Implications on the Alkyne Disproportionation Reaction

Sir:

Addition of cyclic alkadiynes to transition metal complexes has produced some interesting intramolecular cyclization reactions in which complexed cyclobutadiene and cyclopentadiene derivatives are formed.[1,2] In particular, the reaction of 1,7-cyclododecadiyne (I) with $Fe(CO)_5$ has produced two complexes, $C_{12}H_{16}Fe_2(CO)_6$ (major product) and $C_{12}H_{16}Fe(CO)_3$ (trace). These compounds were originally formulated as II and III, respectively.[1b] We have determined the structure of the major product, (1,7-cyclododecadiyne)$Fe_2(CO)_6$, *via* X-ray diffraction techniques and have found its geometry to be not II but IV.

Crystal data for $C_{12}H_{16}Fe_2(CO)_6$: space group $P3_1$ (trigonal, no. 144);[3] $a = 9.186\ (3)$, $c = 18.604\ (6)$ Å; $V = 1359$ Å^3; ρ_{calcd} (based on $Z = 3$) = 1.61 g cm^{-3},

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[1] (a) R. B. King and C. W. Eavenson, *J. Organometal. Chem.*, **16**, P75 (1969); (b) R. B. King and I. Haiduc, *J. Amer. Chem. Soc.*, **94**, 4044 (1972); (c) R. B. King, I. Haiduc, and C. W. Eavenson, *ibid.*, **95**, 2508 (1973).

[2] R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, **92**, 6071 (1970); **94**, 3021 (1972).

[3] No attempt was made to distinguish between the two enantiomorphic space groups $P3_1$ and $P3_2$. The validity of the crystallographic results described here is in no way affected by the arbitrary selection of $P3_1$ over $P3_2$.

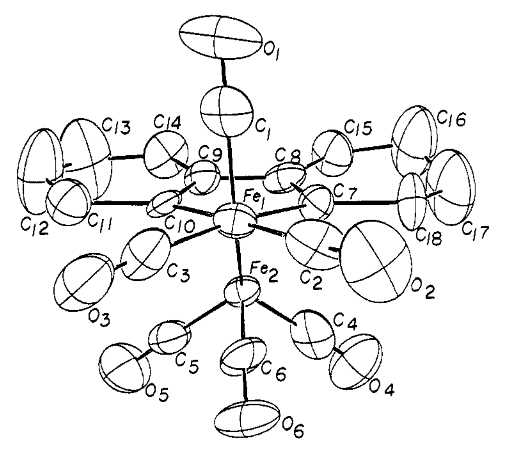
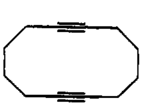
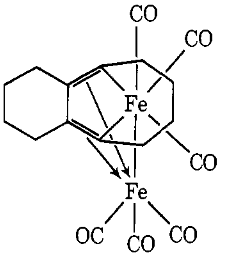


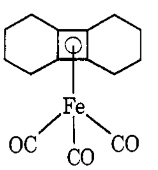
Figure 1. The molecular geometry of $(C_{12}H_{16})Fe_2(CO)_6$. Note the unusual elongation of methylene carbon atoms C_{12}, C_{13}, C_{16}, and C_{17} caused by disorder (see text).



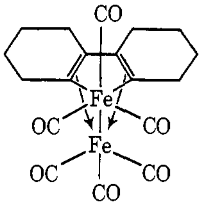
I



II



III



IV

$\rho_{obsd} = 1.57$ g cm^{-3}. Two hexants of data were collected on an automated Nonius CAD-3 diffractometer with Mo Kα radiation up to a sin θ/λ limit of 0.48 Å^{-1} and merged to give 758 nonzero reflections. The structure was solved by heavy atom methods and refined anisotropically to a final R factor of 3.8%.[4]

The geometry of the molecule is shown in Figure 1. Selected bond lengths and bond angles are listed in Table I. Copies of the final atomic parameters are available.[5]

Fe_1 is σ bonded to C_7 and C_{10} and forms part of the metallocyclic ring $Fe_1C_7C_8C_9C_{10}$. Fe_2, on the other hand, is π bonded to the four carbon atoms of the metallocycle, much as in a butadiene complex. The Fe_1–Fe_2 distance of 2.462 (3) Å lies within the bonding range. The $Fe_2(CO)_6C_4$ portion of the molecule (*i.e.*, the portion of the molecule without the eight methylene groups) closely resembles related "metallocycle + butadiene complex" linkages as found in $Fe_2(CO)_6(CH_3C{\equiv}COH)_2$,[6] $Fe_3(CO)_8(C_6H_5C{\equiv}CC_6H_5)_2$,[7] $Fe_2(CO)_4(C_6H_5C{\equiv}CC_6H_4C{\equiv}CC_6H_5)_2$,[8] and $[Rh_2Cl_2(CO)(C_2H_5C{\equiv}CC_2H_5)_2]_2$.[9] A close interaction exists between Fe_1 and C_6 (2.32 (2) Å); this causes a bending of the Fe_2–C_6–O_6 angle to 162 (3)°. This feature is shown most vividly in Figure 2. In fact, it looks very much as though it is C_6 rather than Fe_2 that fills the sixth octahedral coordination position around Fe_1. The $Fe_1 \cdots C_6$ interaction is almost strong enough to be considered bonding—this would make C_6–O_6, technically speaking, a highly asymmetrical bridging carbonyl group, a geometrical feature which has been observed in several other compounds.[6,8,10] In $Fe_2(CO)_6(CH_3C{\equiv}COH)_2$, for example, a close Fe···C interaction of 2.48 Å is coupled to a bent Fe–C–O angle of 168°,[6] while in $Fe_2(CO)_4(C_6H_5C{\equiv}CC_6H_4C{\equiv}CC_6H_5)_2$ the corresponding molecular parameters are 2.39 (2) Å and 166 (2)°.[8]

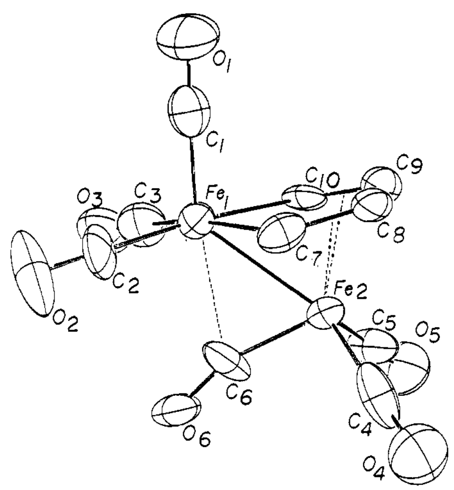


Figure 2. An alternative view of the structure of $(C_{12}H_{16})Fe_2(CO)_6$. The eight methylene groups have been left out for clarity. Note the close $Fe_1 \cdots C_6$ interaction and the curious bending of the Fe_2–C_6–O_6 angle. Also note that the C_1–$Fe_1 \cdots C_6$ angle is almost linear.

Table I. Selected Bond Distances and Angles in $(C_{12}H_{16})Fe_2(CO)_6$

	Bond Distances (Å)		
Fe_1–Fe_2	2.462 (3)	Fe_2–C_6	1.753 (21)
Fe_1–C_1	1.724 (21)	Fe_2–C_7	2.087 (14)
Fe_1–C_2	1.787 (22)	Fe_2–C_8	2.172 (12)
Fe_1–C_3	1.740 (22)	Fe_2–C_9	2.189 (13)
$Fe_1 \cdots C_6$	2.321 (19)	Fe_2–C_{10}	2.066 (12)
Fe_1–C_7	1.935 (13)	C_7–C_8	1.414 (19)
Fe_1–C_{10}	1.987 (14)	C_8–C_9	1.429 (21)
Fe_2–C_4	1.736 (25)	C_9–C_{10}	1.404 (17)
Fe_2–C_5	1.725 (25)		
	Bond Angles (in deg)		
C_1–Fe_1–Fe_2	129.0 (7)	Fe_1–Fe_2–C_4	136.1 (8)
C_1–$Fe_1 \cdots C_6$	171.8 (9)	Fe_1–Fe_2–C_5	127.6 (6)
C_2–Fe_1–C_{10}	173.0 (7)	Fe_1–Fe_2–C_6	64.3 (6)
C_3–Fe_1–C_7	167.7 (9)	Fe_2–$C_6 \cdots Fe_1$	72.8 (7)
$Fe_1 \cdots C_6$–O_6	125.1 (26)	Fe_2–C_6–O_6	161.9 (28)
Fe_1–C_7–C_8	116.5 (10)	C_7–C_8–C_9	114.4 (11)
Fe_1–C_{10}–C_9	117.1 (11)	C_8–C_9–C_{10}	110.9 (12)

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[4] Least-squares refinement was done using UCIGLS, a version o ORFLS (W. R. Busing and H. A. Levy) modified by R. J. Doedens and J. A. Ibers. All other major computations were performed using CRYM, an amalgamated set of crystallographic programs developed by R. E. Marsh's group at the California Institute of Technology.

[5] See paragraph at end of paper regarding supplementary material.

[6] A. A. Hock and O. S. Mills, *Acta Crystallogr.*, 14, 139 (1961).

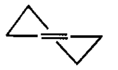
[7] R. P. Dodge and V. Schomaker, *J. Organometal. Chem.*, 3, 274 (1965).

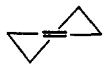
[8] E. F. Epstein and L. F. Dahl, *J. Amer. Chem. Soc.*, 92, 493 (1970).

[9] L. R. Bateman, P. M. Maitlis, and L. F. Dahl, *J. Amer. Chem. Soc.* 91, 7292 (1969).

[10] (a) D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, 11, 838 (1972); (b) M. R. Churchill and M. V. Veidis, *J. Chem. Soc. A*, 2170 (1971); (c) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *J. Amer. Chem. Soc.*, 93, 3073 (1971).

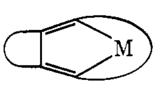
One other noticeable feature of the molecular structure is the disorder of the methylene groups. This appears in Figure 1 as unusually elongated thermal ellipsoids for the eight methylene carbons, particularly the four central ones (C_{12}, C_{13}, C_{16}, C_{17}). This effect is best explained in terms of a 1:1 statistical disorder involving a superposition of the two stable half-chair conformers Va and Vb (as in cyclohexene[11]) of each of


Va

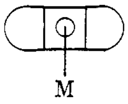

Vb

the six-membered rings. Attempts at resolving the disorder problem by using equally populated half-carbon atoms in the least-squares refinement were not entirely successful.

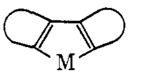
The most remarkable feature of this structure determination is the unexpected[12] finding that a gross skeletal rearrangement of the starting diyne (from a 12-membered ring to a bicyclohexenyl-type framework) has occurred upon complexation. This reaction probably occurs *via* the formation of a metallocycle of type VI first, which then rearranges to the observed type VIII metallocycle. One can speculate about the possible



VI



VII



VIII

intermediacy of a cyclobutadiene-type species VII in the VI to VIII rearrangement process. The isolation[1b] of trace amounts of III from the reaction mixture indicates that, at the very least, the formation of cyclobutadiene complexes is possible in this system. While there is ample evidence for a VI-to-VII type process from previous studies on related systems,[13] the VII-to-VIII type conversion (which may very well involve participation by the second iron atom) is, as far as we know, unknown.

Irrespective of whether VII is a true intermediate or not, our result suggests that metallocyclic intermediates may play a prominent part in the mechanism of tungsten-catalyzed alkyne disproportionation reactions[14] (eq 1) and also suggests that the $Fe(CO)_5$ system may

$$R_1C{\equiv}CR_1 + R_2C{\equiv}CR_2 \rightleftharpoons 2R_1C{\equiv}CR_2 \qquad (1)$$

in fact be one where such processes might take place. We would like to point out that other metallocycles (saturated analogs of VIII) have been implicated as intermediates in olefin disproportionation[15] and other skeletal rearrangement reactions. Very recently one such intermediate was isolated and structurally characterized.[16]

Acknowledgment. We thank Professor R. B. King of the University of Georgia for the crystals used in this work. Partial financial support was provided by the National Institutes of Health, and computer time was provided by the Computer Center of the University of Southern California. The diffractometer was purchased through a grant from the National Science Foundation.

Supplementary Material Available. A listing of the final atomic parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-5068.

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(11) F. A. L. Anet and M. Z. Haq, *J. Amer. Chem. Soc.*, **87**, 3147 (1965).

(12) The original formulation (II) for the compound was, on the basis of chemical intuition and the known spectral data, certainly the most logical choice.

(13) (a) H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, **7**, P22 (1967); (b) W. Hübel in "Organic Syntheses via Metal Carbonyls," Vol. I, I. Wender and P. Pino, Ed., Interscience-Wiley, New York, N. Y., 1968, pp 294, 330.

(14) F. Pennella, R. L. Banks, and G. C. Bailey, *Chem. Commun.*, 1548 (1968).

(15) R. H. Grubbs and T. K. Brunck, *J. Amer. Chem. Soc.*, **94**, 2538 (1972).

(16) A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Amer. Chem. Soc.*, **95**, 597 (1973).

Configurationally Isomeric Iminoxy Radicals. Intermediates in the Rearrangements of Nitrones to *O*-Alkyl Oximes[1]

Sir:

Previous investigations[2,3] of the thermal rearrangement of *N*-benzhydryl-α,α-diphenylnitrone (**1**) to benzophenone *O*-benzhydryloxime (**2**) provide evidence for a homolytic cleavage to iminoxy and benzhydryl radicals with subsequent recombination at oxygen.[4] We now report evidence which indicates that geometrically isomeric diaryliminoxy radicals (*Z*)-**4** and (*E*)-**4** undergo syn–anti isomerization five or six orders of magnitude faster than the corresponding oxime anions.

A study of the geometric course of the N to O rearrangements of syn–anti isomeric nitrones ((*Z*)-**3** and (*E*)-**3**) offered an opportunity to estimate the rates of geometric isomerization of iminoxy radicals in the absence of such potential isomerization catalysts as acids and oxidizing agents.[5]

The minimum number of processes which were anticipated for these nitrone decompositions is shown in Scheme I. Retention of configuration in product formation would be expected in the case $[(C_6H_5)_2\dot{C}H]k_d \gg k_3$ or k_4. Retention would also be anticipated if the N to O rearrangement was concerted (*i.e.*, *via* a quasi three-membered ring transition state).[6] The two *O*-

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(1) A preliminary account of this study was presented at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973, Abstract ORGN-99.

(2) E. J. Grubbs, J. A. Villarreal, J. D. McCullough, Jr., and J. S. Vincent, *J. Amer. Chem. Soc.*, **89**, 2234 (1967).

(3) J. S. Vincent and E. J. Grubbs, *ibid.*, **91**, 2022 (1969).

(4) See also D. G. Morris, *Chem. Commun.*, 221 (1971) for CIDNP evidence for caged radicals in the thermal N to O rearrangement of the nitrone derived from fluorenone oxime.

(5) See B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, **86**, 722 (1966); 123 (1968) (and references therein) for reports of the generation of mixtures of geometrically equilibrating iminoxy radicals from oxidations of isomerically pure oximes.

(6) A. C. Cope and A. C. Haven, Jr., *J. Amer. Chem. Soc.*, **72**, 4896 (1950).