Of the conceivable intermediates involved in the photoisomerization of **1** to **2**, the enolate **15** is favored over the enol **16**. If **16** were the intermediate, it would be protonated more readily at C$_4$ (giving **1**) than at C$_6$ (giving **2**),[13] and thus the equilibrium $\mathbf{1} \rightleftarrows \mathbf{16}$ would be present. However, this possibility can be excluded on grounds of the fact that when irradiation of the 4β-deuterated **13** was stopped after the reaction had proceeded more than 50%, the D content of recovered starting material was unchanged. Intermediate **17**, similar to that encountered in transoid dienes,[14] is also conceivable. Studies are being continued to characterize the intermediate and to clarify the excited species of this photochemical reaction.

(13) H. J. Ringold and S. K. Malhotra, *Tetrahedron Letters*, 669 (1962); S. K. Malhotra and H. J. Ringold, *J. Am. Chem. Soc.*, **85**, 1538 (1963); 87, 3228 (1965).

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Molecular Orbital Symmetry Restrictions on Transition Metal Catalyzed Bis(acetylene)–Cyclobutadiene Interconversion

Sir:

The concerted fusion of two olefins to a cyclobutane ring is a symmetry-forbidden process.[1] We have recently proposed that transformations of this kind can be rendered allowed by an appropriate transition metal system through a unique catalytic process in which the metal and fusing olefin ligands exchange electron pairs as the reaction proceeds across the reaction coordinate.[2] Highly selective and unusually facile transition metal catalyzed valence isomerizations[3] support this hypothesis, and a new catalytic process—olefin metathesis[4]—involving the smooth disproportionation of olefins through interchanging alkylidene groups has been interpreted in terms of this mechanism. The ease with which simple olefins undergo transformations in these catalytic processes is not paralleled in acetylene chemistry. Transition metal catalyzed π-bond fusion of acetylene ligands to the cyclobutadiene ligand would seem to be a relatively low-energy process due to the comparative stability[5] of the cyclobutadiene ligand. The metal-catalyzed concerted cycloaddition would, conceivably, be assisted by the ligand-to-metal π bonding generated along the reaction coordinate with incipient cyclobutadiene formation. An examination of the molecular orbital symmetry conservation aspects of this transformation, however, reveals that such is not the case. Unlike the simple olefin transformation, the concerted transition metal catalyzed interconversion of bis(acetylene) (C$_{2v}$) and cyclobutadiene (C$_{4v}$) is not a ground-state process.

The ligand orbitals in both the bis(acetylene)metal complex **1** (C$_{2v}$) and cyclobutadienemetal complex **2** (C$_{4v}$) can be treated as two sets, one (Ω) containing orbitals positioned parallel to the *X* axis (*e.g.*, the p$_x$ orbitals) and the other ($\bar{\Omega}$) parallel to the *Z* axis (*e.g.*, p$_z$ orbitals) (molecular orbitals in $\bar{\Omega}$ are denoted with a bar, —). The elements of symmetry for the concerted transformation $\mathbf{1} \rightarrow \mathbf{2}$ are the *ZY* and *ZX* planes. The π-orbital combinations in Ω for **1** are described relative to these elements SS (a$_1$) and AS (b$_2$) (where A = antisymmetric to *ZY* and S = symmetric to *ZX*) and the π* combinations SA (b$_1$) and AA (a$_2$); the corresponding orbitals in $\bar{\Omega}$ are similarly described $\overline{\text{SS}}$, $\overline{\text{AS}}$, $\overline{\text{SA}}$, and $\overline{\text{AA}}$. In **2**, the π combinations are $\overline{\text{SS}}$ (a), $\overline{\text{AS}}$ (e), $\overline{\text{SA}}$ (e), and $\overline{\text{AA}}$ (b); the σ bonds are SS and SA. Metal complex molecular orbitals are constructed from combinations of metal atomic orbitals of the appropriate symmetry with the members of both sets.

The concerted fusion of the Ω–π bonds in **1** to the σ bonds in **2** necessarily effects an exchange of electron pairs between the transforming ligands and the metal.[2] An electron pair moves from the metal d$_{yz}$ orbital into the incipient cyclobutadiene SA σ orbital, while a pair of ligand electrons passes from the AS π combination into the metal d$_{zx}$ orbital. This process can be envisaged as proceeding smoothly across the reaction coordinate. The net result of metal-catalyzed cycloaddition is the relocation of an electron pair from one metal d orbital to another, *i.e.*, from d$_{yz}$ to d$_{zx}$ in $\mathbf{1} \rightarrow \mathbf{2}$.

The second set ($\bar{\Omega}$) of π bonds in **1** interacts negatively with the metal as it undergoes electronic relocalization across the reaction coordinate. The populated $\overline{\text{AS}}$ π combination interacts with the growing electron density in the metal d$_{zx}$ while the unoccupied $\overline{\text{SA}}$ π* combination interacts with the diminishing density in the metal d$_{yz}$. Metal-assisted cycloaddition of the Ω–π bonds, therefore, imparts an electronic ordering on the metal which is essentially antibonding with respect to the $\bar{\Omega}$–π bonds. The result is a crossing of bonding and antibonding molecular orbitals across the reaction coordinate. In **1**, the $\overline{\text{AS}}$ π combination is populated and correlates with the π $\overline{\text{AS}}$ (e) orbital in **2**. AS, also populated in **1**, is consequently correlated with the ligand-to-metal antibonding combination of that symmetry. The $\overline{\text{SA}}$ π orbital in **2** (e) is similarly correlated with an unoccupied π* combination in **1**.

The correlation diagram in Figure 1[6] was constructed from extended Hückel[7] molecular orbital calculations

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(1) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

(2) F. D. Mango and J. H. Schachtschneider, *ibid.*, **89**, 2483 (1967).

(3) H. Hogeveen and H. C. Volger, *ibid.*, **89**, 2486 (1967); *Chem. Commun.*, 1133 (1967).

(4) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Am. Chem. Soc.*, **90**, 4133 (1968).

(5) (a) H. C. Longuet-Higgens and L. E. Orgel, *J. Chem. Soc.*, 1956 (1959); (b) see also W. Hubel in "Organic Synthesis via Metal Carbonyls," Vol. I, I. Wender and P. Pino, Ed., Interscience Publishers, New York, N. Y., 1968.

(6) Figure 1 contains only those molecular orbitals critical to the ligand transformation. Since the molecular orbitals listed are actually mixtures of orbitals of the two sets and metal atomic orbitals of the same symmetry, clear set assignments cannot always be made and have not been attempted in the diagram. Symmetry assignments were made for all the molecular orbitals in the two models. The number of occupied orbitals of the various symmetry classifications for 1 are six SS, four AS, two SA, and two AA; for 2, six SS, three AS, three SA, and two AA.

(7) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

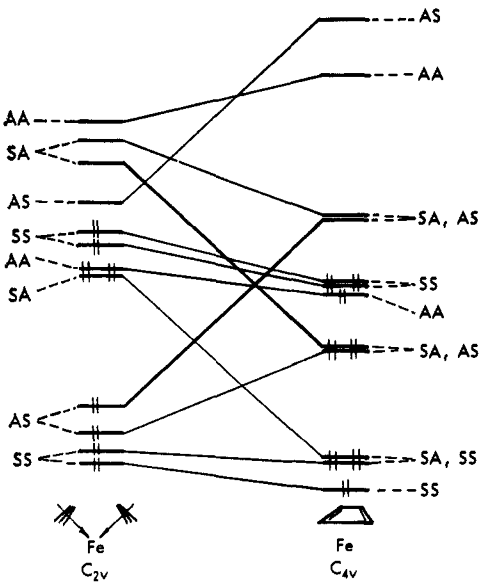
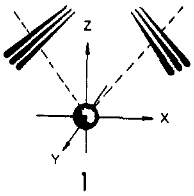


Figure 1. Correlation diagram.

carried out on bis(acetylene)iron and cyclobutadieneiron. The crossing AS ($b_2 \rightarrow e$) and SA ($b_1 \rightarrow e$) orbitals in Figure 1 (indicated with heavy lines) are the corresponding π and π^* combinations discussed above. Clearly, the normal cyclobutadiene-to-metal bonding associated with the population of the two cyclobutadiene e orbitals ($\overline{\text{SA}}$ and $\overline{\text{AS}}$) is not realized with π-bond fusion of adjacent acetylene ligands. The orbital pattern described precludes the concerted interconversion of bis(acetylene) and cyclobutadiene ligands as a ground-state process.[8] Although this pattern will change upon attachment of different ligand systems on the metal, the qualitative description should remain relatively unaltered. Extended Hückel molecular orbital calculations were also carried out on bis(acetylene)-tricarbonyliron and tricarbonylcyclobutadieneiron, a stable cyclobutadiene complex.[9] The correlation diagram described by the symmetry-assigned molecular orbitals was qualitatively the same as that shown for the naked metal (Figure 1).

These results suggest that the concerted π-bond fusion of transition metal bound acetylenes to a cyclobutadiene ligand is, necessarily, a high-energy process relative to the analogous olefin conversion. In a ground-state configuration, fusing acetylene ligands enjoy little of the metal-to-ligand π bonding associated with the incipient formation of cyclobutadiene. Cylcobutadiene-metal complexes have been obtained from reactions of the corresponding acetylene with metal complexes.[5b,10] The above results would suggest that if these are ground-state transformations, they are either stepwise processes or involve the catalytic action of two metal centers. These results further indicate that ligand transformations proceeding on metals are not free of molecular orbital symmetry conservation restraints.



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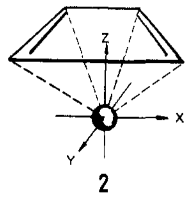

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[8] The symmetry restrictions noted here are associated with the limitations of a single metal. They are lifted with the interaction of two metals sharing opposite faces of a bis(acetylene) plane (at the apices of a C_{2h} complex).

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[10] W. Hubel and E. H. Brayl, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959); A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **34**, 452 (1961).

Novel σ-Bonded Transition Metal Carborane Complexes

Sir:

Numerous π-bonded transition metal complexes with $B_9C_2H_{11}^{2-}$, $B_7C_2H_9^{2-}$, and $B_6C_2H_8^{2-}$ dianion ligands have recently been reported.[1-4] Bresadola, Rigo, and Turco[5] have recently reported platinum(II) complexes with 1,2- and 1,7-$B_{10}C_2H_{12}$. We now wish to report the first examples of σ-bonded transition metal complexes of 1,10-$B_8C_2H_{10}$ carboranes and an additional transition metal complex of the $B_{10}C_2H_{12}$ carborane series.

Reaction of 1-(CH_3)-1,2-$B_{10}C_2H_{11}$ with 1 mole of *n*-butyllithium produces the lithium salt[6] of the 1-(CH_3)-1,2-$B_{10}C_2H_{10}^-$ ion. Treatment of this anion with π-(C_5H_5)Fe(CO)$_2$I in 1,2-dimethoxyethane solvent gave a 47% yield of dark yellow crystalline 1-[(π-C_5H_5)Fe-(CO)$_2$]-2-(CH_3)-(σ-1,2-$B_{10}C_2H_{10}$) (I). Purification of I was accomplished by column chromatography using silica gel and 50% benzene-hexane as the eluent followed by high-vacuum sublimation at 130° to a −80° cold finger (mp 144.0–145.0°). *Anal.* Calcd for $B_{10}C_{10}H_{18}FeO_2$: B, 32.35; C, 35.94; H, 5.39; Fe, 16.71. Found: B, 32.60; C, 35.62; H, 5.53; Fe, 16.90. The parent peak in the mass spectrum calculated for the $({}^{11}B_{10}{}^{12}C_{10}{}^{1}H_{18}{}^{56}Fe{}^{16}O_2)^+$ ion: *m/e* 336 (found, 336).

The proposed structure of I is presented in Figure 1. The 60-Mcps ^{1}H nmr spectrum of I exhibited two sharp singlets at τ 8.0 and 5.1 (relative to tetramethylsilane, TMS) of relative areas 3 and 5, respectively. The resonance at τ 8.0 was assigned to the C-methyl protons and the resonance at τ 5.1 was assigned to the cyclopentadienyl protons. Infrared absorptions in the carbonyl stretching region of I gave four bands observed at 2041 (s), 2046 (m), 2000 (m), and 1993 (m) cm^{-1}. The electronic spectrum of I was determined in cyclohexane solution [λ_{max} mμ (ϵ): 259 sh (9400), 290 sh (3200), and 367 (740)].

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