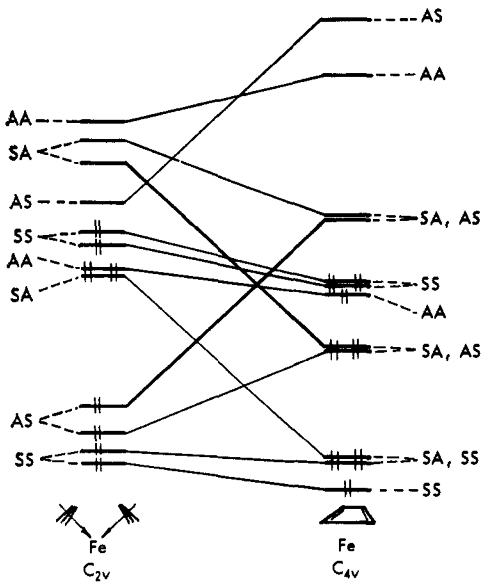
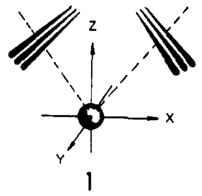


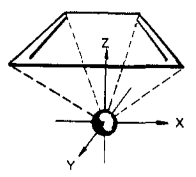
Figure 1. Correlation diagram.

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 ($\overline{SA}$ and $\overline{AS}$) 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.



1



2

Acknowledgments. We are grateful to Dr. D. H. Dugre for helpful comments and suggestions.

Frank D. Mango, J. H. Schachtschneider
Shell Development Company
Emeryville, California
Received November 1, 1968

---

[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).

[9] G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).

[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 ^1H 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)].

---

[1] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 879 (1968).

[2] M. F. Hawthorne and T. A. George, *ibid.*, **89**, 7114 (1967).

[3] M. F. Hawthorne and A. D. Pitts, *ibid.*, **89**, 7115 (1967).

[4] T. A. George and M. F. Hawthorne, *ibid.*, **90**, 1661 (1968).

[5] S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, **20**, 1205 (1968).

[6] T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2**, 1097 (1963).

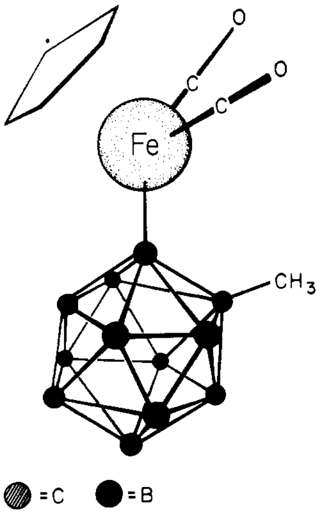


Figure 1. Proposed structure of 1-(π-C_5H_5)Fe$(CO)_2$-2-(CH_3)-(σ-1,2-$B_{10}C_2H_{10}$) (I). H atoms of BH units not shown.

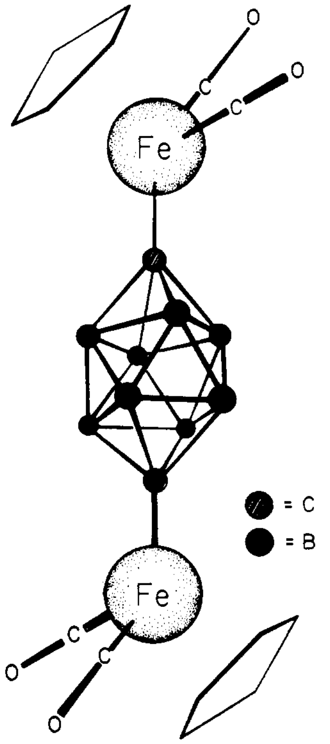


Figure 2. Proposed structure of 1,10-[(π-C_5H_5)Fe$(CO)_2$]$_2$-1,10-(σ-$B_8C_2H_8$) (II). H atoms of BH units not shown.

Reaction of 1,10-$B_8C_2H_{10}$[7] with 2 moles of *n*-butyllithium gives 1,10-Li_2-$B_8C_2H_8$.[8] Treatment of this dianion with (π-C_5H_5)Fe$(CO)_2$I in diethyl ether solvent gave a 71% yield of dark yellow crystalline 1,10-[(π-C_5H_5)Fe$(CO)_2$]$_2$-1,10-(σ-$B_8C_2H_8$) (II). Purification of II was achieved by column chromatography using silica gel and 20% benzene–hexane as the eluent followed by recrystallization from benzene–heptane (mp 203.0–204.0°). *Anal.* Calcd for $B_8C_{16}H_{18}Fe_2O_4$: B, 18.31; C, 40.68; H, 3.81; Fe, 23.65. Found: B, 18.82; C, 40.53; H, 3.88; Fe, 24.67. The parent peak in the mass spectrum calculated for the $(^{11}B_8{}^{12}C_{16}{}^{1}H_{18}{}^{56}Fe_2{}^{16}O_4)^+$ ion: *m/e* 474 (found 474).

The proposed structure of II is presented in Figure 2. The 60-Mcps ^1H nmr spectrum consisted of a sharp singlet at τ 5.0 (relative to TMS) which was assigned to the cyclopentadienyl protons. Infrared absorptions in the carbonyl stretching region of II gave two bands observed at 2038 (s) and 1991 (s) cm^{-1}. The electronic spectrum of II was determined in cyclohexane solution [λ_{max} mμ (ϵ): 290 sh (12,500) and 360 (2200)].

Preliminary evidence suggests that similar σ-bonded manganese complexes can be prepared Further work is in progress and will be reported elsewhere.

Acknowledgment. This research was supported in part by the Office of Naval Research.

James C. Smart, Philip M. Garrett
M. Frederick Hawthorne
Department of Chemistry, The University of California
Riverside, California 92502

Received October 25, 1968

---

[7] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 869 (1968).

[8] Unpublished results.

Photodifluoramination of Allene. A Novel Substitution Pathway[1]

Sir:

Continuing our study of the photochemistry of tetrafluorohydrazine,[2] we irradiated (2537 Å, room temperature) mixtures of allene and N_2F_4 in the gas phase. Two types of carbon-containing products were isolated (70% yield), one resulting from an addition process with the elements of NF_3 added to the allenic substrate ($C_3H_4NF_3$) and the other product arising from a substitution process where an NF_2 moiety has replaced a hydrogen atom ($C_3H_3NF_2$). The data collected in Table I show the addition and substitution products to be, respectively, 3-difluoramino-2-fluoropropene (I) and 3-difluoraminopropyne (II).[3]

Formation of these compounds was not unexpected since previous work[4] indicated that photolysis of N_2F_4 leads to atomic fluorine which may add to a carbon–carbon double bond or abstract hydrogen atoms from alkanes.

Compound II thus appeared to arise simply by allenic hydrogen abstraction followed by combination of NF_2 with the resulting delocalized propargyl radical.[5,6]

---

[1] We gratefully acknowledge support of this work by National Science Foundation Grant GP 8083.

[2] C. L. Bumgardner, E. L. Lawton, and H. Carmichael, *Chem. Commun.*, 1079 (1968).

[3] These products differ from those obtained in the thermal reaction of allene and N_2F_4; see G. N. Sausen and A. L. Logathetis, *J. Org. Chem.*, **32**, 2261 (1967). The thermal process at 25° is negligibly slow relative to the photochemical reaction.

[4] (a) C. L. Bumgardner, *Tetrahedron Lett.*, 3683 (1964); (b) C. L. Bumgardner and E. L. Lawton, *ibid.*, 3059 (1968).

[5] Allene does not isomerize to propyne under the reaction conditions. Photolysis of N_2F_4 with propyne also affords II as well as 1,1-difluoro-2-(N-fluorimino)propane, but no I.

[6] Photochlorination of allene with *t*-butyl hypochlorite gives propargyl chloride: M. C. Caserio and R. E. Pratt, *Tetrahedron Lett.*, 91 (1967).