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(14) National Institutes of Health Predoctoral Fellow, 1967–1970.
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Metalloboranes. V.[1] Carbonyl Insertion in the Formation of Icosahedral Metalloboranes

Sir:

We wish to report a new direct synthesis of quasi-icosahedral metalloboranes from the $B_{10}H_{13}^-$ ion and metal hexacarbonyls.[2] This synthesis uniquely involves incorporation of a carbon atom in the icosahedral framework by a carbonyl insertion into the $B_{10}H_{13}^-$ ion. The resulting metalloboranes comprise two classes of complexes formally derived from the $B_{10}H_{10}COH^{3-}$ ligand[3]

$$(B_{10}H_{10}COH)M(CO)_4^- \qquad B_{10}H_{10}C\underbrace{OMC}O(CO)_3^{2-}$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

with M = chromium, molybdenum, and tungsten. The class **2** ions have an unusual ether linkage between a carbonyl ligand and the icosahedral framework. Unlike other carboranes and metalloboranes,[4] all representatives of these two classes are partially degraded by base with removal of a carbon atom, not a boron atom, from the icosahedral framework to give a new set of *nido* metalloboranes, $B_{10}H_{12}M(CO)_4^{2-}$ (**3**).

Irradiation (350 nm) of tetrahydrofuran solutions of $NaB_{10}H_{13}$ and the metal hexacarbonyls (inert atmosphere) gave the $(B_{10}H_{10}COH)M(CO)_4^-$ class **1** anions[5] in 50% yield and treatment of these with sodium hydride gave quantitative yields of the yellow $B_{10}H_{10}C\underbrace{OMC}O(CO)_3^{2-}$ class **2** ions.[6]

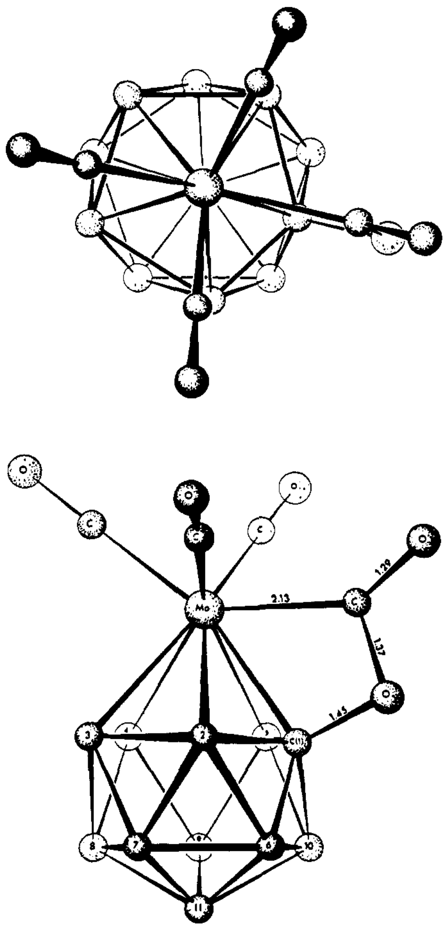

Figure 1. The bottom figure shows a side view of the $B_{10}H_{10}C\underbrace{OMoC}O(CO)_3$ class **2** dianion with the terminal hydrogen atoms omitted. The top figure shows the corresponding top view of the dianion.

$$(B_{10}H_{10}COH)M(CO)_4^- + H^- \xrightarrow{THF} H_2 + B_{10}H_{10}C\underbrace{OMC}O(CO)_3^{2-} \quad (1)$$

The structure of the class **2** boranes was established by a single-crystal X-ray analysis of the tetrabutylammonium salt of $B_{10}H_{10}C\underbrace{OMoC}O(CO)_3^{2-}$ class **2** ions from 4000 pieces of data collected on a four-circle automatic diffractometer using Mo Kα radiation. Crystals are triclinic, space group $P\bar{1}$, with a = 13.492 (6), b = 17.992 (10), c = 11.271 (8) Å, α = 104.02 (9), β = 93.63 (16), and γ = 105.78 (7)°. The observed and calculated densities for two formula units per cell are 1.12 and 1.10 g/cm³, respectively. No absorption correction was applied since the maximum μR was less than 0.1. The structure was solved by a combination of Patterson and Fourier techniques. The results are described for the least-squares refinement (R = 0.09) using the 2500 strongest reflections and a model with anisotropic thermal parameters for molybdenum and five carbonyl groups and isotropic thermal parameters for the remaining nonhydrogen atoms.

The X-ray structure (Figure 1) shows that the class **2** ions have a metal atom completing a $B_{10}C$ icosahedral

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[1] Part IV: A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 2571 (1970).

[2] Metalloboranes which are 11-atom icosahedral *fragments* have been prepared from $B_{10}H_{13}^-$: (a) N. N. Greenwood and N. F. Travers, *J. Chem. Soc., A*, 880 (1967); *Chem. Commun.*, 216 (1967); (b) F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, 7, 2073 (1968).

[3] W. H. Knoth, *J. Amer. Chem. Soc.*, **89**, 3342 (1967). The $B_{10}H_{10}COH^{3-}$ ligand was not prepared in an uncomplexed form but was obtained in the $(B_{10}H_{10}COH)_2Ni^{2-}$ ion by reaction of nitrous acid and $(B_{10}H_{10}CNH_3)_2Ni$.

[4] E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968.

[5] Sample characterization of $[(CH_3)_4N](B_{10}H_{10}COH)Mo(CO)_4$. *Anal.* Calcd: C, 25.2; H, 5.62; B, 25.2; N, 3.26; O, 18.6; Mo, 22.3; formula wt, 430.2. Found: C, 25.6; H, 5.55; B, 25.2; N, 3.29; O, 18.0; Mo, 22.4; mol wt (osmometry-CH_3CN), 211; equiv wt (titration of acid form), 395. ^{11}B nmr (32 MHz) (CH_3CN) [$B(OCH_3)_3$ = 0] 16.4 (J = 108), 23.71 (J = 124), 27.67 (J = 128 Hz), 31.38 (sh), 33.35 ppm (sh). Ir (THF) 3355 (m) (OH), 2510 (s) (B–H), 2063 (s), 1978 (s), 1950 cm⁻¹ (s) (C≡O); (Nujol) 3480 cm⁻¹ (s) (OH).

[6] Sample characterization of $[(C_4H_9)_4N]_2[B_{10}H_{10}C\underbrace{OMoC}O(CO)_3]$. *Anal.* Calcd: C, 53.0; H, 9.79; B, 12.9; O, 9.54; Mo, 11.4; formula wt, 838. Found: C, 52.6; H, 9.81; B, 14.4; O, 10.7; Mo, 11.9; mol wt (CH_3CN), 443. ^{11}B nmr (32 MHz) (CH_3CN) [$B(OCH_3)_3$ = 0] 24.70 (J = 123), 28.95 (J = 148 Hz), 31.28, 36.40 ppm. Ir (CH_3CN) 2490 (s) (B–H); 1992 (s), 1908 (s), 1883 (s) (C≡O); 1659 (>C=O); (Nujol) 2495 (B–H), 1980 (s), 1905 (s), 1875 (s) (C≡O); 1662 cm⁻¹ (>C=O).

framework. The unusual structural facet is a metal nucleus which is bonded to the carbon atom of a $-CO_2-$ group which in turn is linked through oxygen to the carbon atom in the polyhedral cage. Average bond distances are 1.97 (2) Å for Mo–C(CO), 1.16 (2) Å for C–O, 1.70 (1) Å for B–C, and 1.81 (1) Å for B–B, where the errors are based on the differences observed for chemically similar distances. The Mo–cage distances are 2.30 (1) Å for Mo–C, 2.38 (1) Å for Mo–$B_2(B_5)$, and 2.44 (1) Å for Mo–$B_3(B_4)$; shorter distances are to be expected to the more electronegative carbon atom. The Mo–CO_2–cage bonding forces the eclipsing of two carbonyls with respect to the boron atoms, but the resultant intramolecular B–C(CO) contacts of 2.89 (6) Å are not severe. The two unique $(C_4H_9)_4N^+$ ions are not disordered, but they do exhibit a considerable amount of anisotropic thermal motion.

The $-CO_2-$ linkage from C(1) to molybdenum is unique and the distances are similar to those observed in organic esters. The ester linkage is likely generated by *intra*molecular attack of an alkoxide ion formed during the reaction of class **1** ions with sodium hydride upon a coordinated carbonyl ligand. Intermolecular attack of alkyllithiums on carbonyl ligands to form coordinated "carbene" complexes is well known.[7]

The solution infrared spectra of the class **2** ions are in agreement with the X-ray structure. The terminal carbonyl bands are at lower frequencies than for the class **1** ions, consistent with the increased charge of the species, and there is a band in the ketonic carbonyl region (1660 cm^{-1} for the molybdenum complex). No hydroxyl group absorption was observed.

The class **2** ions are quantitatively converted to **1** by aqueous acid in the absence of air. This reaction involves cleavage of the ether linkage to give a simple tetracarbonyl derivative of the $B_{10}CM$ icosahedron in which there is no bonding between the carbonyl groups and the cage. All spectral data are consistent with this structural formulation. The band in the infrared spectra of the three class **1** anions attributed to OH[8] is observed in all salts and, in Nujol mulls or KBr pellets, it is sharp. In solution, the band shifts to lower frequencies and broadens. Deuteration occurs only at the OH function, and for the molybdenum complex the ratio of the OH to OD stretching frequencies is 1.2. The broad pmr resonance of the OH group appears at about τ 8 for all class **1** ions, and this resonance sharpens and shifts to lower field on addition of D_2O. The chemistry of the class **1** anions differs only in degree. The terminal carbonyl groups are relatively inert and resistant to displacement by phosphines or pyridine either under thermal or photochemical conditions. The ions are air sensitive, especially in aqueous solution, and degrade to borate. In the absence of oxygen, the class **1** ions do not react with nonoxidizing acids.

The *nido* metalloboranes of structural class **3** are formed by the action of aqueous base on either class **1** or **2** ions.[9] Addition of acid does not lead to the regeneration of class **1** or **2** ions. The $B_{10}H_{12}M(CO)_4{}^{2-}$ ions are very air sensitive, especially in acid solutions, but there is no hydrolysis in the absence of oxygen. The infrared spectrum has BH and terminal carbonyl absorptions but none attributable to hydroxyl or ketonic functions. Structurally, we believe that the class **3** ions are strictly analogous to the 11-atom icosahedral fragment metalloboranes earlier described for the $B_{10}H_{12}{}^{2-}$ complexes of metal ions derived from the group VIII and post-transition metals.[2b]

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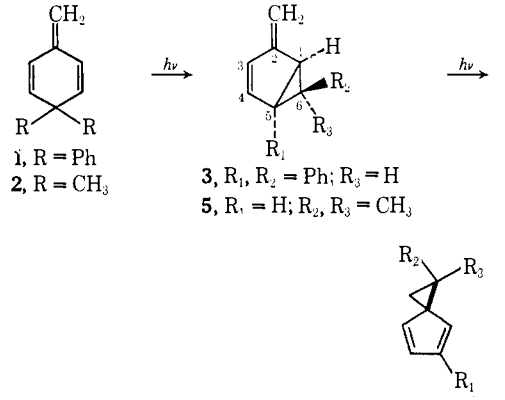
Walk Processes in Photochemical Molecular Rearrangements. A General Photochemical Transformation. Mechanistic and Exploratory Organic Photochemistry. LVII[1]

Sir:

In our description[2] of the photochemical rearrangements of 1-methylene-4,4-diphenyl-2,5-cyclohexadiene (**1**) to *trans*-5,6-diphenyl-2-methylenebicyclo[3.1.0]-3-hexene (**3**) a secondary photoproduct (**4**), shown to derive from further photolysis of product **3**, was mentioned.

We now report (1) the structure of photoproduct **4**, (2) that this product arises from a novel and general process in which a carbenoid carbon walks from one end of a butadiene moiety to the other, (3) the quantum efficiencies which are relatively independent of structure, (4) that the process proceeds only by way of the singlet-excited state, (5) the freedom of motion of the carbenoid group on the face of the π system, (6) stereochemical evidence suggesting a slither[3] mechanism, and (7) the extreme reluctance of the methylene dienone analog **2** to rearrange in contrast to acyclic di-π-methanes and cyclohexadienones.

Thus, the product of direct photolysis of *trans*-5,6-diphenyl-2-methylenebicyclo[3.1.0]-3-hexene (**3**) was shown (*vide infra*) to be 1,5-diphenylspiro[2.4]-4,6-heptadiene (**4**). Similarly, 6,6-dimethyl-2-methylenebi-



1, R = Ph
2, R = CH_3

3, R_1, R_2 = Ph; R_3 = H
5, R_1 = H; R_2, R_3 = CH_3

(1)

4a, R_1, R_3 = Ph; R_2 = H
4b, R_1, R_2 = Ph; R_3 = H
6, R_1 = H; R_2, R_3 = CH_3

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[7] E. O. Fischer and A. Maasbol, *Chem. Ber.*, **100**, 2445 (1967).

[8] A similar band was observed in spectra of the $(B_{10}H_{10}COH)_2Ni^{2-}$ ion.

[9] Sample characterization of $[(C_3H_7)_4N]_2B_{10}H_{12}Mo(CO)_4$. *Anal.* Calcd: C, 48.2; H, 9.30; N, 4.02; B, 15.5; Mo, 13.7. Found: C, 47.9; H, 9.17; N, 4.13; B, 15.3; Mo, 13.3.

[1] For paper LVI note H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, in press.

[2] H. E. Zimmerman, P. Hackett, D. Juers, and B. Schröder, *ibid.*, **89**, 5973 (1967).

[3] H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969).