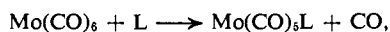


proceed by way of an SN1 mechanism. These investigations were carried out at relatively low phosphine concentrations (less than 0.025 *M*). At higher concentrations (greater than 0.050 *M*) of the phosphine, L, we have found that the rate of the reaction



depends on the concentration of L (Figure 1) and obeys the following rate law.

$$\text{rate} = k_1[\text{Mo(CO)}_6] + k_2[\text{Mo(CO)}_6][\text{L}]$$

These reactions were carried out in a syringe immersed in a constant-temperature oil bath. Solutions of Mo(CO)_6 and L in decalin solvent were sampled periodically through the long syringe needle which had been bent up above the surface of the oil bath. There was no gas phase above the reaction solution in the syringe, thus avoiding any problems due to the sublimation of Mo(CO)_6 at these temperatures.

The two terms in the rate expression suggest that the reaction proceeds by two mechanisms. The first-order term, k_1 , indicates an SN1 mechanism in which the rate-determining step is the dissociation of a CO group from Mo(CO)_6 . This is the term that was observed by Werner.¹ Our value of k_1 ($6.22 \times 10^{-5} \text{ sec}^{-1}$) at 97.8° is in good agreement with that reported by him ($6.01 \times 10^{-5} \text{ sec}^{-1}$), obtained in refluxing *n*-decane-cyclohexane solvent. The enthalpy and entropy of activation for the first-order process are 31.7 kcal/mole and 6.7 eu, respectively. The positive ΔS^* is consistent with a dissociative mechanism. Within experimental error, the enthalpy of activation is the same as that ($E_a = 30.8 \text{ kcal/mole}$) reported for the exchange of ^{14}CO with Mo(CO)_6 in the gas phase by an SN1 mechanism.²

The second-order term suggests an SN2 pathway in which the phosphine, L, attacks the complex to form a seven-coordinated activated complex or intermediate. It is not possible, however, to rule out an attack at the carbonyl carbon, with a subsequent rearrangement. This latter mechanism has been suggested for the reactions of Mn(CO)_6^+ and Re(CO)_6^+ with alkoxide ions.³ At 112.0°, the second-order rate constants increase with the nature of L in the following order: $\text{P(OC}_6\text{H}_5)_3$, $1.43 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1} < \text{P(C}_6\text{H}_5)_3$, $1.77 \times 10^{-4} < \text{P(OCH}_2)_3\text{CC}_2\text{H}_5$, $3.56 \times 10^{-4} < \text{P(OC}_2\text{H}_5)_3$, $6.69 \times 10^{-4} < \text{P}(n\text{-C}_4\text{H}_9)_3$, 20.5×10^{-4} . The activation parameters for the second-order portion of the reaction of Mo(CO)_6 with $\text{P}(n\text{-C}_4\text{H}_9)_3$ are $\Delta H^* = 21.7 \text{ kcal/mole}$ and $\Delta S^* = -14.9 \text{ eu}$. The negative ΔS^* is also consistent with an SN2 mechanism.⁴

The unusual feature of these reactions is that they indicate that octahedral complexes of transition metals can, in fact, undergo substitution reactions by way of an SN2 mechanism. Since the vast majority of octahedral complexes are known to undergo ligand substitution via an SN1 mechanism,⁵ there has been some question as to the correctness of an assignment of an SN2 mechanism to some fairly complicated systems.⁶ Reasons why octahedral complexes of transition metals would

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(3) T. Kruck and M. Noack, *Chem. Ber.*, **97**, 1693 (1964).

(4) H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, **88**, 1657 (1966).

(5) R. G. Pearson, D. N. Edgington, and F. Basolo, *ibid.*, **84**, 3233 (1962).

(6) D. W. Margerum and L. P. Morgenthaler, *ibid.*, **84**, 706 (1962).

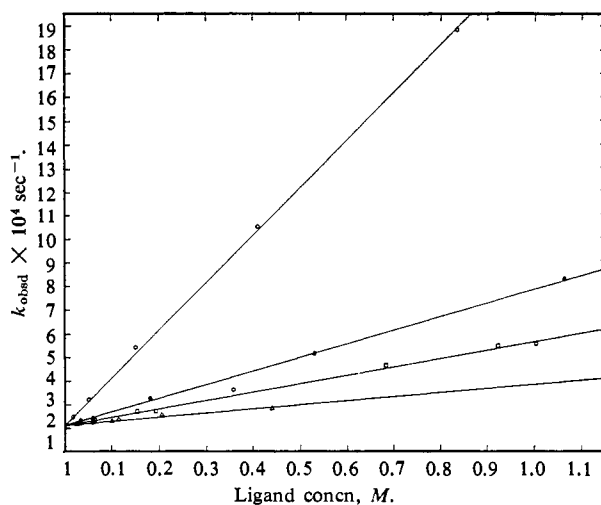


Figure 1. Plots of k_{obsd} vs. ligand concentrations for the reaction of Mo(CO)_6 in decalin at 112.0° with $\text{P}(n\text{-C}_4\text{H}_9)_3$, \circ ; $\text{P(OC}_2\text{H}_5)_3$, \bullet ; $\text{P(OCH}_2)_3\text{CC}_2\text{H}_5$, \square ; and $\text{P(C}_6\text{H}_5)_3$, \triangle ($[\text{Mo(CO)}_6] = 6 \times 10^{-4} \text{ M}$).

not be expected to participate in an SN2 mechanism have been discussed in terms of steric crowding and electronic configurations.⁵ The present Mo(CO)_6 system, however, offers the most straightforward evidence for ligand attack on an octahedral complex. The possibility that Mo(CO)_6 is able to undergo nucleophilic attack at a rate which is comparable to the rate of dissociation of a CO group suggests that the rates of substitution reactions of other complexes containing relatively large second- and third-row transition metal atoms might also exhibit ligand dependences. Examples are the closely related $\text{Mo(CO)}_4(\text{dipy})$ and $\text{W(CO)}_4(\text{dipy})$.⁷

Since the ΔH^* of the second-order path is significantly less than that of the first-order path, it appears that the primary reason why the SN1 mechanism is so common for octahedral complexes is not the lower activation energy but instead the rather large positive entropy of activation associated with this mechanism as compared to the negative entropy of activation involved in the SN2 process.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(7) J. R. Graham and R. J. Angelici, *ibid.*, **87**, 5590 (1965).

Robert J. Angelici, James R. Graham
Department of Chemistry, Iowa State University
Ames, Iowa 50010
Received June 1, 1966

Structure of $\text{B}_{20}\text{H}_{16}(\text{NCCH}_3)_2 \cdot \text{CH}_3\text{CN}$

Sir:

Reaction of the new boron hydride,^{1,2} $\text{B}_{20}\text{H}_{16}$, with ligands occurs^{1,2} without loss of hydrogen and usually

(1) (a) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 12; (b) L. B. Friedman, R. D. Dobrott, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 3505 (1963); (c) R. D. Dobrott, L. B. Friedman, and W. N. Lipscomb, *J. Chem. Phys.*, **40**, 866 (1964).

(2) (a) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3506 (1963); (b) N. E. Miller, H. C. Miller, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1690 (1964).

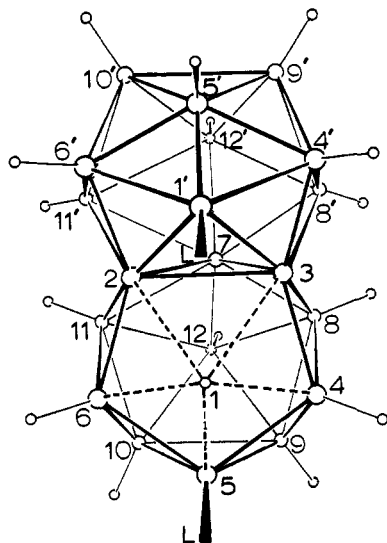


Figure 1a. The structure of $B_{20}H_{16}(NCCH_3)_2$. L is CH_3CN . Molecular symmetry is very nearly C_2 with the C and N atoms of the two CH_3CN groups lying in the mirror plane. H₁ appears to be closest to B₅, but primarily associated with B₅, B₄, and B₆ (see footnote 5).

yields adducts containing two molecules of the electron-pair donor. It has been assumed^{2b} that the B_{20} arrangement of the parent $B_{20}H_{16}$ molecule is retained in these adducts and that the ligands are probably *trans*. Our X-ray diffraction results show that when the ligand is acetonitrile a rather remarkable rearrangement has taken place, yielding a new type of boron framework attached to the two ligands.

Reaction of $B_{20}H_{16}$ with acetonitrile proceeds smoothly with no evolution of hydrogen. Single crystals have unit cell parameters $a = 12.55 \pm 0.02$, $b = 10.70 \pm 0.02$, $c = 16.12 \pm 0.01$ Å, and $\beta = 99^\circ 40' \pm 10'$ and are in the space group $P2_1/c$. An experimental crystal density of 1.11 g cm^{-3} gives the empirical formula $B_{20}H_{16}(CH_3CN)_3$ with four molecules per unit cell ($M_{\text{calcd}} = 356$, $M_{\text{exptl}} = 357 \pm 3$). Diffraction maxima were measured with a proportional counter on a Buerger automated X-ray diffractometer. The structure was solved by reiterative application of Sayre's equation³ using the multiple solution computer program of Long.⁴ In the correct solution all 364 reflections with $|E| \geq 1.5$ had been phased in nine passes through the data, which gave the consistency index

$$C = \langle |E_H \sum_K E_K E_{H-K}| \rangle / \langle |E_H \sum_K |E_K| |E_{H-K}| \rangle = 0.61$$

Only one other solution required as few as nine passes to phase the 364 reflections, but its index was $C = 0.42$. An E map computed from the 364 signs revealed all 29 B, C, and N atoms unambiguously. Refinement has been carried out using 1495 observed reflections to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.070$, assuming isotropic thermal parameters for H and anisotropic thermal parameters for B, C, and N. All 16 H atoms bonded to the B cage have been located directly in electron density maps from which B, C, and N atoms were subtracted.

The structure (Figure 1a), to be compared with that for $B_{20}H_{16}$ (Figure 1b), indicates that one of the three

(3) D. Sayre, *Acta Cryst.*, **5**, 60 (1952).

(4) R. E. Long, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," Ph.D. Thesis (Part III), UCLA, 1965.

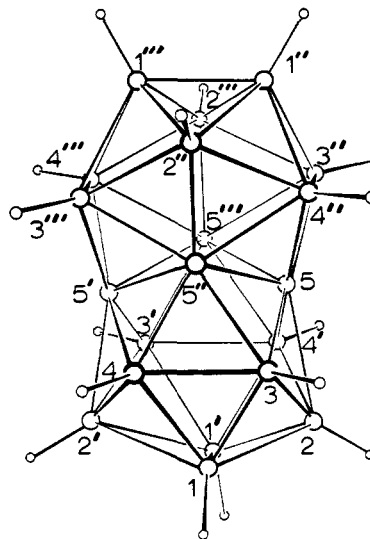


Figure 1b. $B_{20}H_{16}$

acetonitrile units of the crystalline material is isolated from the $B_{20}H_{16}(NCCH_3)_2$ molecule, which has two very nearly linear acetonitrile ligands attached in terminal positions to B atoms. The B-atom rearrangement has yielded a B_{12} icosahedron which shares a triangular face with a B_{11} icosahedral fragment. A single bridge H atom occupies the open pentagonal face of the B_{11} fragment (Figure 1a).⁵ If we replace conceptually^{1a} the ligands by H^- , the corresponding boron hydride ion is predicted to be $B_{20}H_{18}^{-2}$, different, of course, from the known⁶ ion of this formula. Insertion of a BH unit in place of the bridging H^- would give a completed polyhedron of the formula $B_{21}H_{18}^-$.

The similarity between the appropriate part of $B_{20}H_{16}^-(NCCH_3)_2$ and the $B_9C_2H_{12}^-$ ion⁷ leads us to propose that boron hydrides composed of icosahedra sharing a triangular face be generally called polyicosahedralboranes, and that the compound $B_{20}H_{16}(NCCH_3)_2$ be named as an ollyl^{7a} derivative of the unknown diicosahedral ion, $B_{21}H_{18}^-$, described above. We therefore suggest the name (1)-1',5-bisacetonitrileollyldiicosahedralborane for $B_{20}H_{16}(NCCH_3)_2$.

Further studies are under way to see if this rearrangement is general among ligand derivatives of $B_{20}H_{16}$. Possibly an intermediate can be isolated, for molecular orbital studies⁸ indicate that the belt B atoms unattached to H in $B_{20}H_{16}$ are the most positively charged ($B_5 = +0.36$) of those in this molecule ($B_1 = B_2 = -0.11$, $B_3 = B_4 = -0.05$) and hence probably most susceptible to nucleophilic attack, if steric and other effects permit.

(5) This bridge H atom appeared in two successive difference electron density maps. Final distances are: $B_2-H_1 = 2.07$; $B_3-H_1 = 2.28$; $B_4-H_1 = 2.08$; $B_5-H_1 = 1.38$; $B_6-H_1 = 1.56$ (all ± 0.06 Å). Assuming C_2 symmetry, $B_2-H_1 = B_3-H_1 = 2.18 \pm 0.14$ Å; $B_4-H_1 = B_5-H_1 = 1.82 \pm 0.37$ Å. These values indicate that H₁ is nearer the B₅ end of the face and that the major uncertainty regarding the position of H₁ is its coordinate in the B₂-B₅ direction. Possibly H₁ is statistically disordered, forming both B₄-H₁-B₅ and B₅-H₁-B₅ bridges.

(6) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S. A.*, **48**, 729 (1962).

(7) (a) M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, **87**, 3987 (1965); (b) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *ibid.*, **87**, 3988 (1965); (c) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *ibid.*, **87**, 1818 (1965); (d) R. A. Wiesboeck and M. F. Hawthorne, *ibid.*, **86**, 1642 (1964); (e) F. P. Olsen and M. F. Hawthorne, *Inorg. Chem.*, **4**, 1839 (1965).

(8) F. P. Boer, Ph.D. Thesis, Harvard University, 1965.

Although not necessarily unique, a mechanism combining least motion with the cubeoctahedron mechanism^{1a} yields a very simple account of the rearrangement: (a) let the first CH₃CN add at B_{5''}, (b) form a B₅-B_{5'} bond, (c) apply the dsd mechanism^{1a,9} to the faces 5' 4 2' 3', 5''' 3' 1' 4', 5 3 2 4', and 1 2 1' 2', (d) break B₄-B_{5''}, B₃-B_{5''}, and B₃-B₄, (e) move H₁ into the open bridging position, and (f) add the second CH₃CN to B₁. Of course, we cannot be sure at which stage the second CH₃CN is added, but the other steps are built around the generally accepted mechanism^{1a} for the rearrangement of *o*-B₁₀C₂H₁₂ to *m*-B₁₀C₂H₁₂.

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(9) W. N. Lipscomb, *Science*, in press.

John H. Enemark, Lawrence B. Friedman
Jean A. Hartsuck, William N. Lipscomb
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138
Received May 27, 1966

Studies of Stereoisomerism by Photoionization Mass Spectrometry. Fragmentation of *cis*- and *trans*-4-*t*-Butylcyclohexanols

Sir:

It has been suggested¹ that the process of water elimination from alcohols which occurs in the mass spectrometer shows some slight stereospecific dependence insofar that for several epimeric pairs of alcohols it has been observed that the one having the most sterically hindered hydroxyl function generally exhibits the lower intensity molecular ion (M) and the higher intensity (M - H₂O) peak. We now report a mass spectrometric investigation of the *cis* (I) and *trans* (II) isomers of 4-*t*-butylcyclohexanol² which reveals an unexpectedly large steric dependence for water elimination and which, furthermore, at first sight appears to contravene the generalization outlined above for this process.

Our initial study of these compounds utilized a conventional electron impact ionization source,³ and under these conditions our results were irreproducible and inconclusive. In view of recent studies⁴ it seemed highly probable that this was the result of spurious processes caused by the hot filament together with the attendant high temperature of the ion chamber (200°). Accordingly, we repeated our measurements using a modification⁵ of a recently developed photoionization

(1) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 145.

(2) These compounds were prepared according to the method of S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955). In the following discussion roman numerals I-V refer to the parent compounds whereas Ia, etc., refer to the corresponding positive ions. After completion of the mass spectral measurements thin layer chromatography showed a single spot for each sample, and comparison with authentic material showed that the samples had not been inadvertently interchanged.

(3) An A.E.I. M.S.9 high-resolution mass spectrometer was used throughout this study.

(4) C. E. Brion *Anal. Chem.*, **37**, 1706 (1965).

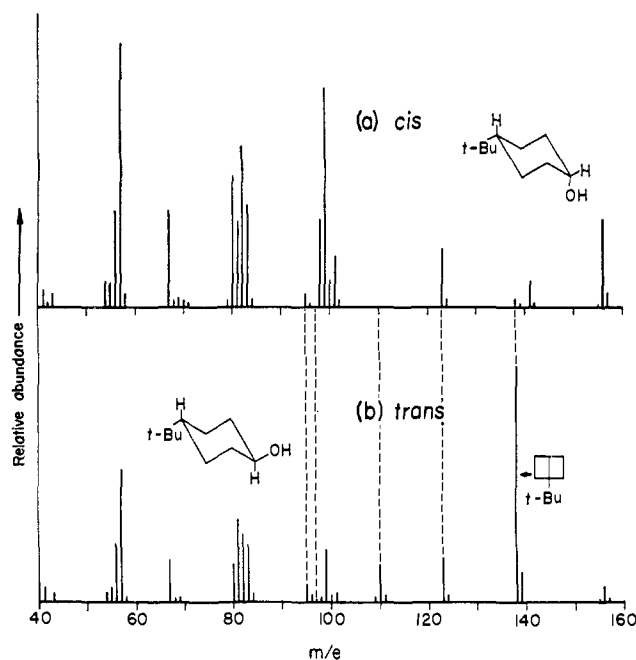


Figure 1. 4-*t*-Butylcyclohexanols; helium light source (II), 25°.

source⁴ which operates at any desired temperature at or above room temperature. The spectra obtained were quantitatively reproducible and are shown in Figure 1. The higher mass peaks in the photoionization mass spectrum are much more intense than their electron impact counterparts. It has already been shown⁴ that this is due, at least in part, to thermal effects. It is also clear that there is a most significant difference between the fragmentation patterns of the two isomers, particularly in the high mass region of the spectrum. If we assume that the molecular ions Ia and IIa adopt the same conformations in the gas phase as are believed⁶ to be preferred for I and II in solution, then the *cis* isomer (I) would have the hydroxyl function in the more sterically hindered position (axial) and should thus eliminate water more readily¹ than the *trans* isomer (II). In fact the reverse is observed, with the relative (M - H₂O) peak abundances being (M - H₂O)_{trans}:(M - H₂O)_{cis} = 38:1. There is also a significant difference in the ratio of parent ion abundance with M_{trans}:M_{cis} = 1:5. A simple rationale of these findings, together with other characteristics of the spectra, can be given if we abandon the above conformational hypothesis. Previous studies^{7,8} of the fragmentation of cyclohexanol have shown that water elimination occurs preferentially (83%) *via* 1,4 and 1,3 elimination processes and furthermore have led to the suggestion⁸ that 1,4 elimination will occur preferentially when the substituents to be eliminated from these positions have a *trans* relationship.

(5) Details of the improved light source will be published later. Radiation of 584 Å (21.2 eV) was used and the samples were introduced at room temperature.

(6) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(7) H. Budzikiewicz, C. Djerassi, and D. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 42.

(8) C. G. MacDonald, T. S. Shannon, and G. Sugowdz, *Tetrahedron Letters*, 807 (1963).