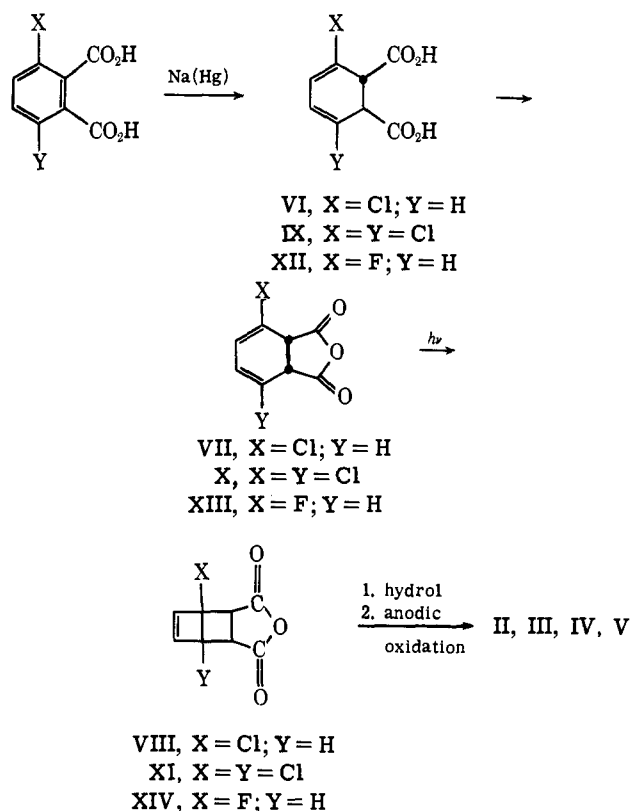zene) (V), and it rearranges even more rapidly than does compound II.

Compound II was prepared by a sequence analogous to that used by van Tamelen[3] for the preparation of IV. Thus, 3-chlorophthalic acid could be converted in 40% yield to trans-1,2-dihydro-3-chlorophthalic acid (VI), mp 152–155°, by reduction with 3% sodium

VI, X = Cl; Y = H
IX, X = Y = Cl
XII, X = F; Y = H

VII, X = Cl; Y = H
X, X = Y = Cl
XIII, X = F; Y = H

VIII, X = Cl; Y = H
XI, X = Y = Cl
XIV, X = F; Y = H

amalgam in aqueous acetic acid. This was converted to 3-chloro-cis-1,2-dihydrophthalic anhydride (VII), mp 65–67°, in 70% yield by treatment with acetic anhydride. The sublimed anhydride was converted to the tricyclic anhydride VIII, mp 134–135°, in 60–80% yield by photolysis in pentane. Anhydride VIII was converted to II by hydrolysis in aqueous pyridine and electrolytic decarboxylation at −25°, using a clean[5] platinum electrode. Since II is thermally quite unstable, it must be handled and extracted into solvents at temperatures near 0°. In a similar fashion, 3,6-dichlorophthalic acid was converted to the corresponding 3,6-dichloro-1,2-dihydrophthalic acid (IX), mp 212–214°, and this afforded the corresponding cis-anhydride X, mp 87–89°. This was also converted to the photoproduct XI, and XI was converted to III on electrolysis, although in this case no special precautions about temperatures were necessary.

The parent compound IV was prepared as described[3] by van Tamelen, except that anodic decarboxylation was performed using a potentiostat. The compound was extracted into tetradecane, and vacuum transferred into the rearrangement solvent. The very unstable fluoro(Dewar benzene) V was prepared via XII (mp 149–151°), XIII (mp 80–82°), and XIV (mp 124–125°).

It is striking that a single halogen substituent makes rearrangement of the Dewar benzene much faster,

(5) As the electrode aged, it became an effective catalyst for the isomerization of II to chlorobenzene even at −25°.

but that a second halogen more than reverses the effect.[6] A direct disrotatory[7] opening of these bicyclohexadienes to the benzenes involves an antiaromatic transition state.[8] Apparently this transition state can be markedly stabilized by unsymmetrical substitution on the two central carbons, whose electrons should be highly polarizable as the bond breaks. This is in a sense a push–pull effect in an antiaromatic transition state,[9] related to known push–pull stabilization[10] of antiaromatic compounds. An alternative description is that this substitution pattern permits easier mixing[11] of the neutral destabilized transition state with a charge-transfer state which should stabilize it.

Thus, it seems likely that in the transition state for rearrangement of the monohalo(Dewar benzenes) II or V there is appreciable polar charge separation, which is less available for the rearrangements of III or IV. Interpretation of activation parameters in solution kinetics is always hazardous, but the apparently more negative $\Delta S^{\ddagger}$ for II, compared with IV, is consistent with the greater solvation expected for the transition state of II if it is indeed more polar. The large positive entropy of activation for the rearrangement of compound III may indicate substantial solvent release as the originally polar III, with two closely aligned dipoles, rearranges through a transition state with less polarity to p-dichlorobenzene which has no macroscopic dipole moment.[12]

(6) The parameters for III are similar to those for hexamethyl(Dewar benzene).[4] Thus, the interesting difference in the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for III and IV may indicate that the parent Dewar benzene IV has a geometry available for rearrangement[7] which is of higher energy with more hindered derivatives.

(7) This is discussed in detail by R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH, Weinheim/Bergstr., West Germany, 1970, p 174.

(8) The transition state can be thought of as involving a normal cyclic delocalization of four electrons, although the extra double bond cannot be completely ignored. This transition state is to a disrotatory opening of a cyclobutene as butalene (I) is to cyclobutadiene.

(9) R. Gompper and G. Seybold in "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity" (E. D. Bergmann and B. Pullman, Ed., Israel Academy of the Sciences and Humanities, Jerusalem, Israel, 1971, p 215) describe the fast rearrangement of a probable push–pull substituted Dewar benzene reaction intermediate.

(10) See ref 9, and R. Gompper and G. Seybold, Angew. Chem., 80, 804 (1968).

(11) N. D. Epiotis, J. Amer. Chem. Soc., 94, 1924, 1935, 1941, 1946 (1972).

(12) Support of this work by the National Institutes of Health and a postdoctoral fellowship (Arthur Schmidt) from the Deutsche Forschungsgemeinschaft are gratefully acknowledged.

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The Nature of the 1:1 Adduct of Methylpentaborane(9) with Trimethylamine, $CH_3B_5H_8 \cdot N(CH_3)_3$

Sir:

The formation of the 1:1 adduct of 1-ethylpentaborane(9) and trimethylamine was reported in the literature[1] and the compound was formulated as $(CH_3)_3NH^+C_2H_5B_5H_7^-$. Detailed study of such an adduct formation was thought to yield information valuable in elucidating mechanisms of formation of the diam-

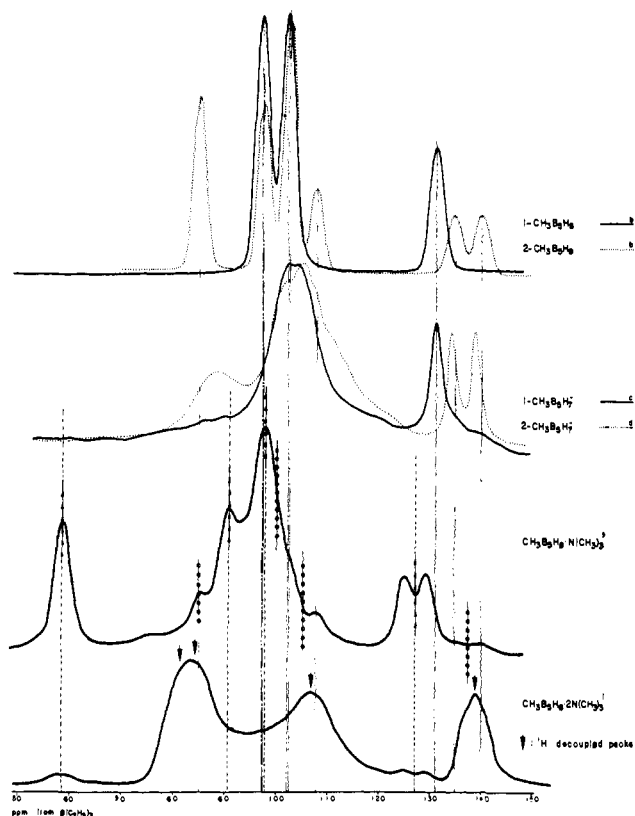(1) W. V. Hough, L. J. Edwards, and A. F. Stang, J. Amer. Chem. Soc., 85, 831 (1963).

Figure 1. ^{11}B nmr spectra of $CH_3B_5H_8 \cdot N(CH_3)_3$: (a) the spectra were recorded on a Varian XL-100-12 nmr spectrometer; (b) neat at ambient temperature; (c, d) THF solutions; prepared according to the description in ref 13; (c) at $-5°$, (d) at $15°$; (e) CH_2Cl_2 solution at ambient temperature; $(C_2H_5)_2O$ solution gave an identical spectrum; (f) CH_2Cl_2 solution at $5°$; the compound was reported in ref 7 and 8.

moniate of pentaborane(9)[2,3] and other related amine addition compounds.[4-8] Reinvestigation of the reaction of methylpentaborane(9) and trimethylamine confirmed the formation of the 1:1 adduct and revealed it not to be the salt of the $CH_3B_5H_7^-$ ion. Formulation as a molecular adduct is suggested. The results and its significant implications in speculating the mechanism of the diammoniate formation and the mechanism of the base-catalyzed apex-to-basal rearrangement of pentaborane derivatives[9-12] are reported herein.

Treatment of 1-$CH_3B_5H_8$ solution in diethyl ether with trimethylamine in 1:1 ratio gave a clear solution. If excess of the amine was used a white precipitate formed in the solution. Pumping of volatile components from such a system (first at $-80°$ and finally at room temperature), however, left a white crystalline solid

(2) G. Kodama, J. Amer. Chem. Soc., 92, 3482 (1970).
(3) G. Kodama, U. Englehardt, C. Lafrenz, and R. W. Parry, ibid., 94, 407 (1972).
(4) A. B. Burg, ibid., 79, 2129 (1957).
(5) R. T. Holzman, "Production of the Boranes and Related Research," Academic Press, New York, N. Y., 1967, pp 257–262.
(6) N. E. Miller, H. C. Miller, and E. L. Muetterties, Inorg. Chem., 3, 866 (1964).
(7) T. Onak, R. P. Drake, and I. W. Searcy, Chem. Ind. (London), 1865 (1964).
(8) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, Inorg. Chem., 6, 1465 (1967).
(9) T. Onak, J. Amer. Chem. Soc., 83, 2584 (1961).
(10) T. P. Onak, F. J. Gerhart, and R. E. Williams, ibid., 85, 1754 (1963).
(11) A. B. Burg and J. S. Sandhu, ibid., 87, 3787 (1965).
(12) T. Onak, L. B. Friedman, J. A. Hartsuck, and W. N. Lipscomb, ibid., 88, 3439 (1966).

that dissolved in diethyl ether. Composition of the solid as determined by the reaction stoichiometry was $CH_3B_5H_8 \cdot 1.06N(CH_3)_3$. The compound is unstable at room temperature and produces trimethylamine-borane slowly. The same compound could be obtained also from a methylene chloride solution. The ^{11}B nmr spectrum of the compound (Figure 1) is actually a superposition of spectra of the $CH_3B_5H_8 \cdot N(CH_3)_3$ and a small quantity of 2-$CH_3B_5H_8$. The latter was identified unequivocally by examining its proton decoupled spectrum; peaks due to 2-$CH_3B_5H_8$ were seen at lines of type i below and four peaks due to the amine adduct at lines of type ii (58.6, 90.7, 97.7, and 127.0 ppm from the $B(C_2H_5)_3$ resonance peak; 127 Hz for the separation of the doublet peaks) with an apparent intensity ratio 1:1:2:1, reading upfield.

2-Methylpentaborane(9) reacted with trimethylamine in the same manner as 1-$CH_3B_5H_8$ and the spectrum of the product *was identical with that of the adduct obtained from 1-$CH_3B_5H_8$.*

Clearly, the spectrum of $CH_3B_5H_8 \cdot N(CH_3)_3$ is unique and none of its peaks correspond to any of the peaks due to the other related compounds compared in Figure 1.

It was proposed[3] that an intermediate in the formation of the diammoniate of pentaborane(9) would be a mono-ammoniate with structure I or II. These structures
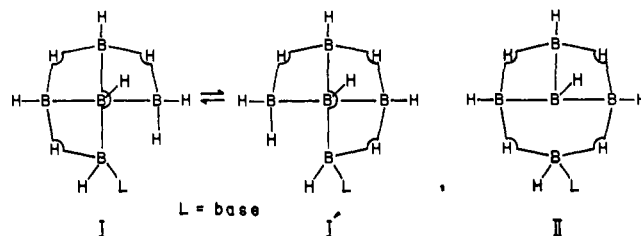

can be drawn for the adduct $CH_3B_5H_8 \cdot N(CH_3)_3$ and are consistent with the present ^{11}B nmr spectrum, provided a rapid equilibration between I and I' is assumed. It appears certain now that the reacting species in the formation of the diammoniate of pentaborane(9) is B_5H_9 and not the $B_5H_8^-$ anion which was produced first in the reaction and disappeared as the diammoniate formed.[3]

The mechanism suggested for the base-catalyzed intramolecular rearrangement of pentaboranes(9) that involves the $B_5H_8^-$ anionic species[1] now appears to be unlikely. Because the isomerization of the recently reported $CH_3B_5H_7^-$ anions[13] from the 1 isomer to the 2 isomer does not proceed as fast as the formation of $CH_3B_5H_8 \cdot N(CH_3)_3$, it is accompanied by some unidentified side reactions and no resonance peak due to these anions could ever be detected in the system of methyl-pentaborane and trimethylamine when the reaction was followed by ^{11}B nmr spectroscopy.

Formation of a base adduct of pentaboranes(9) was considered to be a possible intermediate process in the rearrangement by several investigators.[10,14] The

(13) V. T. Brice and S. G. Shore, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, INOR 57.
(14) L. B. Friedman and W. N. Lipscomb, Inorg. Chem., 5, 1752 (1966).

isolation of the adduct $CH_3B_5H_8 \cdot N(CH_3)_3$ described here provides strong support for this idea. In 1963 Onak, Gerhart, and Williams[10] proposed a structure similar to structure II for the possible intermediate. In view of the anticipated tautomerism of hydrogens[10,15] in these boron hydride structures and the lack of evidence for the positions of hydrogens in the newly isolated adduct, the two structures may be considered essentially the same at the present stage. The isomerization may be visualized as illustrated below
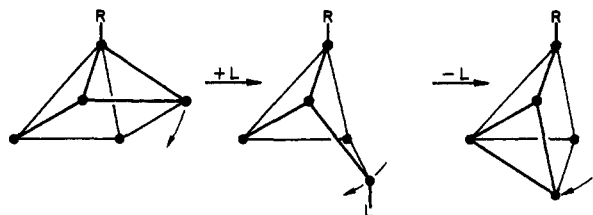
It is suggested here that the steric problem that would be introduced in going from the intermediate trigonal-bipyramid arrangement to the final structure may be relieved by rearranging the relative position of the base. Thus, the selective formation of the 2,3 isomer from $1,2\text{-}(CH_3)_2B_5H_7$[12] may be explained by the addition of the base to the basal boron atom which does not carry methyl group. The chemistry of the adduct, $CH_3\text{-}B_5H_8 \cdot N(CH_3)_3$, and the related systems will be published elsewhere upon completion of the study.

(15) (a) G. R. Eaton and W. N. Lipscomb, "Nmr Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969, p 553; (b) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961).

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Intermediates Generated in the Charge Transfer to Ligand Photochemistry of Ruthenium(II) Pyridine and Bipyridyl Complexes[1]

Sir:

It is a rather interesting contrast in gross photochemical behavior that irradiation of charge transfer to ligand (CTTL) absorption bands of $Ru(NH_3)_5py^{2+}$ should lead to extensive ligand aquation[2] while irradiation of the same type of transition in $Ru(bipy)_3{}^{2+}$ should lead to no detectable photochemistry and appreciable phosphorescent emission at room temperature in fluid solution.[3,4] In fact, the latter complex is so photochemically inert that it is an exceptionally useful triplet sensitizer.[4,5] In the present report we wish to call attention to what appears to be a new reaction pathway

(1) Partial support of this research by the National Science Foundation (Grant GP 24053) is gratefully acknowledged.
(2) P. C. Ford, D. A. Chaisson, and D. H. Stuermer, *Chem. Commun.*, 530 (1971).
(3) J. N. Demas and G. A. Crosby, *J. Mol. Spectrosc.*, **26**, 72 (1968).
(4) J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, **93**, 1800 (1971).
(5) P. Natarajan and J. F. Endicott, *ibid.*, **94**, 3635 (1972).

in the photochemistry of coordination complexes; a photochemical pathway shared by $Ru(NH_3)_5py^{2+}$ and $Ru(bipy)_3{}^{2+}$.

In the course of our studies with the triplet sensitizer, $Ru(bipy)_3{}^{2+}$, we have had occasion to flash photolyze solutions containing this species. We have observed a transient bleaching[6] of the CTTL absorption (λ_{max} 450 nm) of this substrate. The substrate absorptivity is regenerated with a pH ($1 \leq pH \leq 3$) dependent pseudo-first-order rate constant, $k_{obsd} = 0.1[H^+]^{-1} \sec^{-1}$. Very similar behavior is exhibited by $Ru(phen)_3{}^{2+}$, Fe-$(bipy)_3{}^{2+}$, and $Fe(phen)_3{}^{2+}$. The extent of the bleaching (or transient yield) and the lifetime of the bleached intermediate species do not change appreciably on replacing bipyridyl (bipy) by 1,10-o-phenanthroline (phen), but the intermediate lifetimes are about four times greater in the case of the ruthenium complexes than observed for the iron complexes. The transient produced from $Ru(bipy)_3{}^{2+}$ reacts with $Co(HEDTA)Cl^-$ to produce $Ru(bipy)_3{}^{3+}$ and presumably Co^{2+} with a second-order rate constant, $k \simeq 7 \times 10^5 \, M^{-1} \sec^{-1}$.

In order to further elucidate the nature of the observed intermediate species, we flash photolyzed some of the $Ru(NH_3)_5L^{2+}$ complexes which have been photochemically examined by Ford and coworkers.[2,7] In the cases that L = pyridine and benzonitrile we find again a transient bleaching of the characteristic CTTL absorption bands[8,9] of the ruthenium(II) complex. In each of these cases, however, the total substrate absorbance is not regenerated, consistent with some photoaquation of ligands L.[2] The variations in observed aquation parallel the pH dependencies of ϕ_L reported by Ford, *et al.*[2] In the case of $Ru(NH_3)_5py^{2+}$ we find again a pseudo-first-order, pH-dependent regeneration of substrate absorptivity, $k_{obsd} = (32 + 6.8[H^+]^{-1}) \sec^{-1}$, in the range $0 \leq pH \leq 3.5$, and for $\mu = 0.2$ ($LiClO_4$). Using published values of ϕ_{py}[2] we estimate a primary yield (extrapolated to zero time) of (0.2 ± 0.1) for bleached species. In the case of $Ru(NH_3)_5\text{-}NCC_6H_5{}^{2+}$ the transient species has a pH-independent limetime of 0.1 sec.

To accommodate the similar photochemical behavior of these several complexes requires some similar features in each of the intermediate species; thus, for example, a one-ended dissociation of bipyridyl would yield a species differing little in absorptivity from $Ru(bipy)_3{}^{2+}$,[10] cannot be extended to the case of $Ru(NH_3)_5py^{2+}$, and would not function as an electron-transfer reducing agent. There seems no viable alternative to the conclusion that the species with diminished CTTL absorptivity must contain oxidized metal centers. Since ruthenium(III) is substitution inert[11] and since the original substrate is readily regenerated, it seems evident that the radical anion (py$^-$, bipy$^-$, etc.) must remain coordinated. Thus taking $Ru(NH_3)_5py^{2+}$ as prototype for the class of compounds, a relatively simple mecha-

(6) We have made observations in several spectral regions between 600 and 300 nm; however, the substrate absorptivity is generally much too high and the transient yield too low to permit detection of the transient absorption spectrum.
(7) P. C. Ford, D. H. Stuermer, and C. P. McDonald, *J. Amer. Chem. Soc.*, **91**, 6209 (1969).
(8) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970).
(9) P. Ford, D. F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).
(10) D. M. Klassen and G. A. Crosby, *J. Chem. Phys.*, **48**, 1853 (1968).
(11) P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).