aquation,[6] while retention of configuration generally occurs in thermal paths.[11,12] Thus, *trans*-$Cr(en)_2Cl_2^+$ photoaquates chloride, yet at least 70% of the product is *cis*-$Cr(en)_2(H_2O)Cl^{2+}$,[13] and the photoproducts of several *trans*-$Cr(NH_3)_4XY$ ions, where the acido groups X and/or Y are the only ones to be aquated, are exclusively cis.[14] Furthermore, stereomobility may well be a necessary condition for photosubstitution to occur; *trans*-$Cr(cyclam)Cl_2^+$, in which rigidity is imposed by the cyclam[15] ring is, in fact, photoinert.[16] These findings suggest that the NH_3 photoreleased in thiocyanatopentaamminechromium(III), and in the other $Cr(NH_3)_5X^{2+}$ systems, is indeed most probably the one in trans position to the acido group. The present results eliminate an apparent exception and it now appears that a uniform photoaquation mechanism applies to chromium(III) ammines and, moreover, one which requires stereomobility, that is, trans → cis isomerization, for its occurrence.

Registry No. $[Cr(NH_3)_5(NCS)](ClO_4)_2$, 22478-28-0; *cis*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$, 38781-21-4; *trans*-$[Cr(NH_3)_4(H_2O)(NCS)](ClO_4)_2$, 38781-22-5.

Acknowledgment. The National Research Council of Italy (CNR) is acknowledged for financial support through Contract No. 71,01553,03.

(13) A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, 49, 1524 (1971).

(14) P. Riccieri and E. Zinato, *Proc. Int. Conf. Coord. Chem.*, 14, 252 (1972).

(15) Cyclam = 1,4,8,11-tetraazacyclotetradecane.

(16) C. Kutal and A. W. Adamson, *J. Amer. Chem. Soc.*, 93, 5581 (1971).

Contribution from the Department of Chemistry,
Tufts University, Medford, Massachusetts 02155

Direct Synthesis of Dialkyl Sulfide Derivatives of Dodecahydrododecaborate(2−), $B_{12}H_{12}^{2-}$

Joel Wright and Alexander Kaczmarczyk*

Received November 27, 1972

A number of Lewis bases react with the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions under acidic conditions, and the reaction can formally be treated as a displacement of a hydride ion by the base, as shown in eq 1. A neutral base reduces the charge

$$B_{12}H_{12}^{2-} + L + H^+ \rightarrow B_{12}H_{11}L^- + H_2 \qquad (1)$$

of the polyhedral system by one unit; an anion will leave it intact. The investigators who first explored these reactions[1,2] found that water inhibited and high proton concentration promoted the substitution. Some protonated form of the polyhedral ions was assumed to be a key reaction intermediate in these reactions.[1] We have been interested for some time in the effects of ionic charge on the chemical properties of functional groups attached to the polyhedral cage. Several types of substituents capable of reducing the charge on the polyhedron are known, but many of them are quite reactive and interfere with subsequent substitutions at other boron sites. Since we have found the $-SR_2^+$ group to be the most satisfactory because of its inertness, we decided to look for high-yield syntheses of dialkyl sulfide derivatives of polyhedral boranes. A satisfactory method has been published for the synthesis of dimethyl sulfide derivatives of the $B_{10}H_{10}^{2-}$ ion.[3] However, the simple one-step reaction with methyl sulfoxide fails to proceed under similar conditions with the $B_{12}H_{12}^{2-}$ ion.[3] Multiplicity of steps and low overall yields make the three methods reported for the synthesis of $B_{12}H_{11}SR_2^-$ derivatives quite unsatisfactory. The oldest method starts with diborane and an alkyl sulfide as the base in the cage-condensation reaction.[4] Alkylation of $B_{12}H_{11}SH^{2-}$, which is made from $B_{12}H_{12}^{2-}$ and H_2S,[5] or of $B_{12}H_{11}SR^{2-}$, which is made from $B_{12}H_{12}^{2-}$ and alkyl disulfides,[5] will also yield the desired products.

Results and Discussion

The reaction of $B_{10}H_{10}^{2-}$ with aqueous acidic methyl sulfoxide results in the elimination of water and the formation of a boron–sulfur bond, in contrast with similar reactions involving sulfones where the sequence of bonds is boron–oxygen–sulfur.[1-3] The formation of the dialkyl sulfides was attributed to an electrophilic attack on the polyhedral ion by the R_2SOH^+ species. In support of this mechanism was cited the failure of the $B_{12}H_{12}^{2-}$ ion to react.[3] Believing the proposed mechanism to be essentially correct we decided to look for conditions which would remove water from the reaction mixture and replace the R_2SOH^+ intermediate with a more reactive species. Acylation of methyl sulfoxide yields an ion of the type R_2SOCOR^+ which is reactive enough, even under moderate conditions, to produce alkyl sulfide derivatives of $B_{12}H_{12}^{2-}$ in a one-step reaction. The prerequisite reaction conditions are those first reported in 1910 by Pummerer,[6] who found that sulfoxides containing at least one methyl or methylene group adjacent to sulfur react with acetic anhydride to give α-acetoxy sulfides. The mechanism of the Pummerer reaction has been investigated by a number of workers, and it would appear that two distinct steps are involved: the formation of the acetoxysulfonium ion and its subsequent rearrangement to the acetoxy sulfide.[7]

$$(RCH_2)_2SO + (CH_3CO)_2O \rightarrow (RCH_2)_2SOCOCH_3^+ + CH_3COO^- \qquad (2)$$

$$(RCH_2)_2SOCOCH_3^+ \rightarrow RCH_2SC(HR)OCOCH_3 + H^+ \qquad (3)$$

In the presence of the polyhedral ions the Pummerer reaction is inhibited, and instead of the α-acetoxy sulfide the principal products are alkyl sulfide derivatives of the polyhedral boranes. The results suggest that an electrophilic attack on the polyhedral ion followed by elimination of acetic acid occurs before the acetoxysulfonium has an opportunity to rearrange (eq 4). If an excess of sulfoxide and

$$B_{12}H_{12}^{2-} + (RCH_2)_2SOCOCH_3^+ \rightarrow B_{12}H_{11}S(CH_2R)_2^- + CH_3COOH \qquad (4)$$

anhydride is used and more time is allowed, the monosubstituted ion reacts with another acetoxysulfonium and the neutral $B_{12}H_{10}[S(CH_2R)_2]_2$ is the predominant product. Through a suitable choice of temperatures and

---

(1) H. C. Miller, W. R. Hertler, E. L. Muetterties, W. H. Knoth, and N. E. Miller, *Inorg. Chem.*, 4, 1216 (1965).

(2) W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 84, 1056 (1962).

(3) W. H. Knoth, W. R. Hertler, and E. L. Muetterties, *Inorg. Chem.*, 4, 280 (1965).

(4) H. C. Miller, N. E. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 85, 3885 (1963); H. C. Miller, N. E. Miller, and E. L. Muetterties, *Inorg. Chem.*, 3, 1456 (1964).

(5) W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 86, 3973 (1964).

(6) R. Pummerer, *Ber.*, 43, 1401 (1910).

(7) D. N. Jones, E. Helmy, and R. D. Whitehouse, *J. Chem. Soc., Perkin Trans. 1*, 11, 1329 (1972).

concentrations, yields as high as 90% of the desired products can be obtained. Sulfoxides such as phenyl sulfoxide which do not have a methyl or methylene carbon adjacent to the sulfur fail to give the expected derivatives under the reaction conditions described in this paper. Acetyl chloride has also been used as the acylating agent, but its reaction with sulfoxides is exothermic enough to create a potential hazard and therefore it is less desirable than acetic anhydride.

Since earlier workers[4,5] did not report the proton magnetic resonance spectra of the dimethyl sulfide derivatives of $B_{12}H_{12}{}^{2-}$, we were interested in seeing how the methyl protons compare with the corresponding protons in derivatives of $B_{10}H_{10}{}^{2-}$. The first thing which should be noted is the fact that despite the intervening positively charged sulfur the charge density of the adjacent boron appears to influence the chemical shift of the methyl protons. The effect shows up in two ways. Thus the conversion of the singly charged $B_{12}H_{11}S(CH_3)_2{}^-$ to the neutral $B_{12}H_{10}[S(CH_3)_2]_2$ shifts the position of the proton resonance from τ 7.79 to 7.53. At the same time these protons appear to resemble the corresponding protons in the equatorially substituted $B_{10}H_{10}{}^{2-}$ (τ 7.63 in 2-$B_{10}H_9S(CH_3)_2{}^-$) more than they do those in the apically substituted isomers[3] (τ 6.92 in 1-$B_{10}H_9S(CH_3)_2{}^-$). This fact is consistent with the charge distribution calculations which assign a value of −0.17 to each of the 12 equivalent borons in $B_{12}H_{12}{}^{2-}$ and −0.17 and −0.33, respectively, to the equatorial and apical borons in the $B_{10}H_{10}{}^{2-}$ ion.[8] In view of our results, it is surprising that the conversion of 1-$B_{10}H_9S(CH_3)_2{}^-$ to 1,10-$B_{10}H_8[S(CH_3)_2]_2$ only shifts the position of the apical methyl-proton peaks from τ 6.92 to 6.95. The equatorially substituted derivatives exhibit a similar insensitivity to the total ionic charge.[3]

Experimental Section

Instruments and Reagents. The infrared spectra were recorded on a Perkin-Elmer Model 237B spectrophotometer; the proton nuclear magnetic resonance spectra were recorded on a Varian Model A-60 spectrometer at 60 Mc. The following compounds were obtained: $Na_2B_{12}H_{12}\cdot 2H_2O$, Du Pont Chemical Co.; methyl sulfoxide, *n*D 1.4790, lot 2171, Aldrich Chemical Co.; *n*-propyl sulfoxide, *n*D 1.4633, lot 080607, Aldrich Chemical Co.; acetic anhydride, lot 702789, Fisher Chemical Co.; tetramethylammonium hydroxide, supplied as 10% aqueous solution, Eastman Organic Chemicals.

$B_{12}H_{11}S(CH_3)_2{}^-$. To a 25-ml portion of acetic anhydride, 50% vol in methyl sulfoxide, was added 1.077 g of $Na_2B_{12}H_{12}\cdot 2H_2O$. After the clear solution was maintained at 50° for 27 hr, it was poured into 450 ml of 2-propanol and stirred for 10 min; then 15 ml of aqueous tetramethylammonium hydroxide was added dropwise with continued stirring. The white precipitate which formed was filtered and dried *in vacuo*. The filtrate was saved for later recovery of the disubstituted product. The precipitate was recrystallized twice from 150-ml portions of water. The dried product weighed 0.791 g (62%): mp 192–194.5° (cor); nmr (DMSO-d_6) τ 7.79 (s, 1, $[CH_3]_2S$) and 7.12 ppm (s, 2, $[CH_3]_4N^+$); the principal ir bands (KBr wafer) are at 3015, 2490, 1475, 1415, 1325, 1175, 1065, 1040, 990, 965, 950, 835, 825, and 710 cm^{-1}. *Anal.* Calcd for $(CH_3)_4NB_{12}H_{11}S(CH_3)_2$: C, 26.01; H, 10.55; N, 5.06; B, 46.82. Found: C, 26.05; H, 10.48; N, 5.07; B, 46.62.

$B_{12}H_{10}[S(CH_3)_2]_2$. The filtrate from the precipitation described above was flash evaporated to 50 ml and stirred into 250 ml of water. The white precipitate which appeared was removed by filtration, dried *in vacuo*, and twice recrystallized from 20-ml portions of 95% ethanol. The dried crystals weighed 0.146 g (12%): mp 220.5–234.5° dec; nmr (DMSO-d_6) τ 7.53 ppm (s, 1, $[CH_3]_2S$); tlc (silica gel eluted with 1,2-dichloroethane) two isomers reducing $PdCl_2$ to black metal were distinguished; the principal ir bands (KBr wafer) are at 3015, 2500, 1425, 1325, 1025, 990, 960, 850, 800, and 720 cm^{-1}. *Anal.* Calcd for $B_{12}H_{10}[S(CH_3)_2]_2$: C, 18.19; H, 8.40; B, 49.12; S, 24.28. Found: C, 18.21; H, 8.53; B, 49.35; S, 23.88.

In another experiment a 0.7545-g sample of $Na_2B_{12}H_{12}\cdot 2H_2O$ was dissolved in a solution consisting of 10 ml of acetic anhydride in 20 ml of methyl sulfoxide and the reaction mixture was allowed to stand at room temperature for 3 weeks when it was poured into 250 ml of 2-propanol and stirred for 15 min. Addition of 20 ml of aqueous tetramethylammonium hydroxide to the 2-propanol solution precipitated $(CH_3)_4NB_{12}H_{11}S(CH_3)_2$, which was removed by filtration, recrystallized from water, and dried. It weighed 0.0875 g (9.4%). The filtrate was mixed with 500 ml of water and the resulting precipitate after two recrystallizations from 95% ethanol and drying weighed 0.7947 g. This represents a yield of 89% of $B_{12}H_{10}[S(CH_3)_2]_2$.

$B_{12}H_{11}S(CH_2CH_2CH_3)_2{}^-$. A 1.35-g portion of *n*-propyl sulfoxide was diluted to 10 ml with acetic anhydride. To this was added 1.17 g of $Na_2B_{12}H_{12}\cdot 2H_2O$. After 5 min of stirring and crushing, the solids had completely dissolved and the homogeneous reaction mixture was left standing for 13 hr at 25°. It was then quenched by dilution to 50 ml with 2-propanol and placed in a freezer overnight. The mixture was filtered cold, the small amount of solid residue discarded, and the filtrate was treated with 6 ml of aqueous tetramethylammonium hydroxide. The precipitate which appeared at this point was removed by filtration and washed with two 30-ml portions of 2-propanol and then dried *in vacuo*. The white crystals were recrystallized from 120 ml of water. Their dry weight was 1.59 g (91.5%): mp 266–266.5°; nmr (DMSO-d_6) τ 9.02 (τ 3, $[CH_3CH_2CH_2]_2S$, 8.23 (m, 2, $[CH_3CH_2CH_2]_2S$), 7.10 (t, 3, $[CH_3CH_2CH_2]_2S$), and 6.86 ppm (s, 6, $[CH_3]_4N^+$); the principal ir bands (KBr wafer) are at 3010, 2950, 2920, 2860, 2500, 1480, 1450, 1410, 1280, 1060, 1035, 265, 945, 820, and 710 cm^{-1}. *Anal.* Calcd for $(CH_3)_4NB_{12}H_{11}S(C_3H_7)_2$: C, 36.04; H, 11.19; N, 4.30; S, 9.60; B, 38.92; equiv wt, 333 g. Found: C, 35.88; H, 11.17; N, 4.47; S, 9.47; B, 38.74; equiv wt, 328 g.

Registry No. $(CH_3)_4NB_{12}H_{11}S(CH_3)_2$, 37291-09-1; $Na_2B_{12}H_{12}\cdot 2H_2O$, 12448-20-3; $B_{12}H_{10}[S(CH_3)_2]_2$, 37291-10-4; $(CH_3)_4NB_{12}H_{11}S(C_3H_7)_2$, 37291-13-7; *n*-propyl sulfoxide, 4253-91-2; acetic anhydride, 108-24-7; methyl sulfoxide, 67-68-5.

[8] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 37, 2872 (1962).

Contribution from the Department of Chemistry,
University of Southern California, Los Angeles, California 90007

Mechanism of Photosubstitution in Rhodium(III) Chloroammines

Charles Kutal and Arthur W. Adamson*

Received November 30, 1972

Previous photochemical investigations of d^6 systems have focused mainly on the ammine complexes of cobalt(III) which, although undergoing facile photoredox decomposition upon charge transfer to metal (CTTM) excitation, show little photoreactivity in the wavelength region of the first d–d transition.[1-3] The situation is quantitatively different with rhodium(III) amines. The d–d bands are very photoactive, in some cases more so than the CTTM ones.[4-8] In addition,

[1] A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, 68, 541 (1968).

[2] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970, Chapter 11.

[3] It is to be emphasized, however, that current work in this laboratory shows cobalt(III) ammines to have, in fact, a rich photosubstitutional chemistry although at a low level of quantum yield.

[4] L. Moggi, *Gazz. Chim. Ital.*, 97, 1089 (1967).

[5] T. L. Kelly and J. F. Endicott, *J. Amer. Chem. Soc.*, 94, 278 (1972).

[6] T. L. Kelly and J. F. Endicott, *J. Amer. Chem. Soc.*, 94, 1797 (1972).

[7] M. Muir, private communication.

[8] T. L. Kelly and J. F. Endicott, *J. Phys. Chem.*, 76, 1937 (1972).