shifts in the complexes could equally well be caused by the electronegative bridging groups reducing the σ-bonding ability of the ligands. It should be noted that some comparisons are being made here between frequencies obtained from different solvents and hence the conclusions may not be meaningful.

The final compounds to be discussed are the products $(ffars)_2RhCl_3$ and $(ffos)_2RhCl_3$. The analytical data for the ffos complex (Table I) are not very good; in fact, it seems difficult to get consistent analysis figures for this type of complex. However, there is little doubt that the formula is correct. The infrared spectrum of Table II indicates that the di(tertiary phosphine) is bonded in the usual way and the structures are probably the same as that of the analogous diars complex which Nyholm[16] found to be a 1:1 electrolyte and formulated as $[(diars)_2RhCl_2]^+Cl^-$.

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[16] R. S. Nyholm, *J. Chem. Soc.*, 857 (1950).

Notes

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The Tetrakis(dimethylamino)diborane(4)–Diborane(6) System[1,2]

BY J. D. CUMMINS, M. YAMAUCHI,[3] AND B. WEST

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The similarity in the structures of tetrakis(dimethylamino)diborane(4) and of tetrakis(dimethylamino)ethene and the possibility of forming some novel aminoboron hydrides prompted us to investigate the tetrakis(dimethylamino)diborane(4)–diborane(6) system.

Tetrakis(dimethylamino)diborane(4) dissolved in 2-methylbutane reacts with 1 mole of diborane(6) at −78° to form a white insoluble solid. On warming to −23°, 1 mole of dimethylaminoborane is formed along with a colorless nonvolatile liquid which slowly converts to a yellow glass. At temperatures above −78°, the diborane(6) to tetrakis(dimethylamino)diborane(4) mole ratio varies from 1:1 to 2:1 owing primarily to the formation of dimethylaminodiborane(6). Similar results were obtained although not as reproducibily in the absence of a solvent, in hydrocarbon solvents, and in methyl ether.

Physical data which give direct evidence for the structure of the 1:1 adduct could not be obtained owing to its insolubility and its thermal instability. However, on the basis of chemical arguments, it is reasonable to propose that the adduct has a tetraborane(10)-like structure which results from the symmetrical cleavage of diborane(6) by tetrakis(dimethylamino)diborane(4). This adduct then loses 1 mole of dimethylaminoborane on warming and the remaining B–B bonded fragment polymerizes into the nonvolatile liquid. With this hypothesis in mind, two attempts, both unsuccessful, were made to minimize polymerization and isolate a stable monomeric species. Apparently if the adduct has a tetraborane(10)-like structure, the B–B bonded fragment polymerizes too rapidly and thus prevents the formation of stable monomers.

Experimental Section

Standard high-vacuum line and inert-atmosphere techniques were used to carry out the experiments described below. Tetra(dimethylamino)diborane(4)[4] was used without further purification. The desired amount of reagent was measured volumetrically to the nearest 0.001 ml with a 2-ml micrometer syringe. The density of the liquid at room temperature (0.858 g/ml) was determined by weighing liquid delivered by the syringe. No corrections were made for changes in density due to temperature fluctuations. All solvents were fractionally distilled and stored over either metallic sodium, calcium hydride, or lithium aluminum hydride under vacuum. The diborane(6) (pressure at −111°, 225 mm; lit.[5] 225 mm) was always fractionally distilled in the vacuum line just prior to use.

B_2H_6 + $[(CH_3)_2N]_4B_2$ in Hydrocarbon Solvents.—In a typical run 5.36 mmoles of B_2H_6 were added at −78° to 0.852 mmole of $[(CH_3)_2N]_4B_2$ dissolved in 5 ml of 2-methylbutane. The formation of a white precipitate and a drop in pressure indicated that a reaction had occurred. After allowing the reaction mixture to stand at −78° for several hours, the substances volatile at −78° were removed. Hydrolysis of the nonvolatile substances in aqueous NaOH yielded 5.92 mmoles of hydrogen, in good agreement with the 5.96 mmoles expected if 0.852 mmole of $B_2H_6\cdot[(CH_3)_2N]_4B_2$ had formed.

In three other experiments the $B_2H_6:[(CH_3)_2N]_4B_2$ ratio in the nonvolatile solid was found to be 1.17:1, 1.11:1, and 1.02:1. The ratio was determined by acid hydrolysis of the unreacted diborane in these runs.

When the temperature of the reaction mixture was allowed to rise above −78° for even a few minutes, higher ratios (1.45:1 and 1.8:1) were obtained.

Similar results were obtained in the absence of a solvent, in methyl ether, and in other hydrocarbon solvents such as 3-methylpentane, methylcyclohexane, and toluene.

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[1] Taken in part from the Ph.D. thesis of J. D. C., University of New Mexico, Sept 1966.

[2] A report on a brief study of this sytem by J. L. Boone and co-workers, U. S. Borax Research Corp., Anaheim, Calif. 92803, is contained among the U. S. Government classified literature.

[3] Communications should be addressed to this author at Eastern Michigan University Ypsilanti, Mich. 48197.

[4] Complimentary sample from the U. S. Borax Co., Anaheim, Calif.

[5] I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik, and G. B. L. Smith, *J. Am. Chem. Soc.*, **74**, 901 (1952).

Separation of $(CH_3)_2NBH_2$ from $B_2H_6\cdot[(CH_3)_2N]_4B_2$.—The 1:1 adduct (1.30 mmoles) prepared in the above manner was washed several times with fresh portions of 2-methylbutane. Precautions were taken to keep the temperature of the system at or below −78°. The white solids which remained on the filter frit decomposed into a white volatile solid and a viscous nonvolatile liquid on warming to −23°. The solid was sublimed away from the liquid at room temperature and was identified as $(CH_3)_2NBH_2$ (1.11 mmoles) by its vapor-phase infrared spectrum. Thus the $(CH_3)_2NBH_2$:$B_2H_6\cdot[(CH_3)_2N]_4B_2$ rato is 0.86:1. In a second experiment 2.27 mmoles of $(CH_3)_2NBH_2$ was isolated from the decomposition of 1.95 mmoles of the 1:1 adduct giving a $(CH_3)_2NBH_2$:$B_2H_6\cdot[(CH_3)_2N]_4B_2$ ratio of 1.17:1.

Attempted Isolation of Stable, Monomeric, B–B Bonded Species.—In an attempt to prepare a stable trimethylamine derivative of the fragment remaining after the 1:1 adduct had lost 1 mole of $(CH_3)_2NBH_2$, an excess of the Lewis base was added to the adduct and the mixture was allowed to stand at −23°. From this mixture only a trace of a substance which might be a monomeric B–B bonded species was detected. Most of the fragment formed a nonvolatile liquid which slowly converted to a yellow glass.

Since hydride–dimethylamino exchange occurred in the reaction of B_2H_6 and $[(CH_3)_2N]_4B_2$, an attempt was made to synthesize NaB_3H_8 by allowing a large excess of $NaBH_5$ and B_2H_6 to react with a dilute tetrahydrofuran solution of $[(CH_3)_2N]_4B_2$. No chemical evidence for the presence of $[B_3H_8]^-$ was found in this reaction mixture.

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The Hydrolysis of Carbon Monoxide Borane

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In a recent study of the aqueous chemistry of potassium boranocarbonate ($K_2H_3BCO_2$) the following observations were reported: (a) rapid acidification of $K_2H_3BCO_2$ solutions produces H_3BCO in good yields;[1] (b) titration data indicate that the H_3BCO thus formed is produced *via* the boranobicarbonate ion and boranocarbonic acid[1]

$$H_3BCO_2^{2-} \overset{H^+}{\rightleftharpoons} H_3BCOOH^- \overset{H^+}{\rightleftharpoons} H_3BC(OH)_2 \rightleftharpoons H_3BCO + H_2O$$

and (c) little H_3BCO can be isolated by slow acidification under dilute conditions at room temperature; however, up to 1.5 moles of hydrogen is produced per mole of $K_2H_3BCO_2$ hydrolyzed. Formaldehyde is also formed when slow acidification is carried out exposed to the air.[2]

These points suggest that when H_3BCO is generated slowly in aqueous solution it reacts with water to form products that differ from those expected from the previously reported reaction of H_3BCO and water[3]

$$H_3BCO + 3H_2O \xrightarrow{100°} B(OH)_3 + 3H_2 + CO \qquad (1)$$

The purpose of this work is to elucidate the reactions that occur between H_3BCO and water.

Experimental Section

Standard vacuum procedures and ₸ apparatus were used throughout.

Materials.—Diborane[4] and potassium boranocarbonate[1] were prepared by previously published procedures. In the preparation of potassium boranocarbonate the carbon monoxide was passed through an aqueous sodium hydroxide solution to remove any carbon dioxide present and then three −78° traps to remove water. The carbon monoxide borane used in these experiments was generated as needed by the action of 85% phosphoric acid on an appropriate amount of the boranocarbonate.[1]

The Reaction of Gaseous H_3BCO and Water.—A 20-ml quantity of water in a 100-ml round-bottomed flask equipped with a vacuum adapter was evacuated. The flask and contents were then cooled to −196° and 1.00 mmole of H_3BCO was condensed into the flask. The stopcock on the adapter was closed and the system was kept at 0° for 2 days. After that time the contents volatile at room temperature were passed through a trap at −78° and two at −196°. The noncondensable gases were measured by a Toepler pump system. An infrared spectrum of these gases showed the presence of carbon monoxide. The traps cooled to −196° were found to contain a small amount of unreacted H_3BCO which was identified by its infrared spectrum. Vapor-phase chromatography of the water trapped at −78° confirmed that no other reaction products volatile at room temperature were formed.

The residue left in the reaction flask was found to be a mixture of boric acid and hydroxymethylboronic acid anhydride. The boronic acid anhydride could be sublimed under vacuum at 100° to a cold finger maintained at 0°. The anhydride was identified by its melting point of 146–149° (lit.[5] 147–148°) and analysis. *Anal.* Calcd for $(BO_2CH_3)_n$: B, 18.68; C, 20.70; H, 5.15. Found: B, 18.48; C, 20.75; H, 4.99. Molecular weight measurements indicated that the anhydride was dimeric in ketone solutions. *Anal.* Calcd for the dimer: 115.8. Found: 108 (acetone), 120 (methyl ethyl ketone). These values were obtained by vapor-phase osmometry. The anhydride hydrolyzes to the monomer hydroxymethylboronic acid $[(HO)_2BCH_2OH]$ in aqueous solution as shown by its molecular weight in water which was determined cryoscopically. *Anal.* Calcd: 57.8. Found: 57.0. The equivalent weight of the anhydride in water was also determined by titration in the presence of mannitol. *Anal.* Calcd: 57.8. Found: 57.8.

Similar procedures were employed when the reaction was run at 50°. The reaction of H_3BCO with water at 0° was run at higher initial pressures of H_3BCO in sealed Pyrex tubes equipped with break tips.

The Reaction of $K_2H_3BCO_2$ Solutions and Dilute HCl.—In a typical experiment 136 mg (1.00 mmole) of $K_2H_3BCO_2$ was dissolved in 20 ml of water in a 100-ml round-bottomed flask. A 4.0-ml quantity of 0.50 *N* HCl was then frozen into a rimless 13 × 100 ml test tube. The test tube was placed upright in the flask containing the boranocarbonate solution and the flask was then attached to an adapter equipped with a vacuum stopcock. The system was evacuated while the contents of the test tube were still frozen. The stopcock on the adapter was closed and the apparatus was removed from the vacuum line and allowed to equilibrate to 0°. The apparatus was then tipped slightly to allow a few drops of HCl solution to run out of the test tube and

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