pounds, it should be mentioned that no alkylaminofluorophosphorane exhibits a P–F coupling constant of more than 900 cps[12] although the P–F coupling constant of $(CH_3)_2NPF_2$ is 1194 cps.[19] This strongly suggests that the compound is a phosphine, not a phosphorane. Under higher resolution it can be seen that each member of the fluorine resonance doublet is split into a 1:6:15:20:15:6:1 septet owing to coupling with the six equivalent protons ($J_{HF} = 3.1$ cps).

The bands observed in the ir spectrum of $(CH_3)_2NPFBr$ may be fairly easily assigned by analogy with the ir assignments based on normal-coordinate calculations for $(CH_3)_2NPF_2$ and $(CH_3)_2NPBr_2$ recently made by Farran.[20] The complete spectrum may be summarized by the following absorptions (in cm^{-1}, with intensity and tentative assignments, respectively): 2950 (m), 2905 (mw), 2855 (w), and 2810 (w) (symmetric C–H stretch); 1475, 1460, and 1445 (m) (methyl deformation); 1290 (ms) (C–N stretch); 1185 (ms), 1175 (sh), and 1060 (mw) (methyl rock); 815 (ms) (P–F stretch); 458 (m) (?); 387 (ms) (C–N–C deformation or P–Br stretch).

The mass spectra of a sample of $(CH_3)_2NPFBr$ show ions which correspond to the anticipated fragmentation pattern. Two peaks of about equal intensity at *m/e* 175 and 173 correspond to parent ions $(CH_3)_2NPF^{79}Br^+$ and $(CH_3)_2NPF^{81}Br^+$. The most abundant peak appears at *m/e* 94 and corresponds to the loss of a bromine atom from $(CH_3)_2NPFBr$. The mass spectra of other dialkylaminofluorophosphines and dialkylaminofluorophosphoranes generally exhibit a fragmentation pattern which suggests that the P–N is most easily cleaved.[21] This does not appear to be the case with dialkylaminohalofluorophosphines and -phosphoranes.[22]

It has been mentioned in the Experimental Section that the principal volatile products of the reaction between BrCN and $(CH_3)_2NPF_2$ are $(CH_3)_2NPF_3(CN)$ and $(CH_3)_2NPFBr$. It is possible to suggest that the reaction proceeds according to the equation

$$2(CH_3)_2NPF_2 + BrCN \longrightarrow (CH_3)_2NPF_3(CN) + (CH_3)_2NPFBr$$

The nonvolatile solid also obtained in this reaction may be accounted for by postulating the presence of a polymeric cyanophosphine or further reaction of the alkylamino moiety with BrCN. Such reactions are well known.[23] It is of interest to note that PF_3, in contrast to $(CH_3)_2NPF_2$, does not interact with BrCN, even at 75°. This may suggest that the electron-donating ability of the $(CH_3)_2N$ group (which increases the negativity of the phosphorus atom) allows attack of BrCN.

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Synthesis of the Hydrides of Germanium, Phosphorus, Arsenic, and Antimony by the Solid-Phase Reaction of the Corresponding Oxide with Lithium Aluminum Hydride[1]

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When SiO_2, GeO_2, P_2O_5, As_2O_3, or Sb_2O_3 was heated with a deficit of $LiAlH_4$ in the absence of solvent at 148–170°, a rapid reaction took place to give SiH_4, a mixture of GeH_4, Ge_2H_6, and Ge_3H_8, PH_3, AsH_3, and SbH_3, respectively. No volatile tin, boron, or titanium hydrides were formed when SnO_2, B_2O_3, or TiO_2 was heated with $LiAlH_4$.

It has been demonstrated by Weiss and Fisher[2] that when lithium aluminum hydride is heated to approximately 200° with excess powdered silicon dioxide in the absence of solvent, silane, SiH_4, is formed. Approximately 7.1% of the hydrogen present in the lithium aluminum hydride appeared in the SiH_4 produced. This is a most convenient method for the small-scale synthesis of SiH_4 since no volatile reagents or solvents, from which the SiH_4 must be subsequently separated, are employed; the apparatus and experimental procedure are also extremely simple. The present study was undertaken in order to ascertain whether this procedure could be used for the convenient synthesis of other volatile hydrides.

[1] This report is based on portions of a thesis submitted by J. M. Bellama to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work was supported in part by the Advanced Research Projects Agency, Office of the Secretary of Defense.

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The following oxides were heated with a deficit of lithium aluminum hydride in the absence of solvent at 148–170°: SiO_2, GeO_2, SnO_2, P_2O_5, As_2O_3, Sb_2O_3, B_2O_3, TiO_2. In view of the apparent complexity of the reaction between germanium dioxide and lithium aluminum hydride, the yields of all hydrides obtained are expressed in terms of the percentage of hydrogen in the lithium aluminum hydride employed which finally appeared in a given hydride. They are: SiH_4, 6.9%; GeH_4, 4.4%; Ge_2H_6, 2.7%; Ge_3H_8, 0.6%; PH_3, 8.0%; AsH_3, 10.9%; and SbH_3, 0.2%; no volatile tin, boron, or titanium hydrides were detected. In most systems the ratio of reactants was varied; this resulted in a change in yield. Although the above percentage yields are small, useful quantities of most of the hydrides can readily be obtained in the pure state in a short time by this method.

With the exception of germanium dioxide, all of the oxides employed are relatively inexpensive and hence the low conversion of oxide to hydride is of no great practical concern. When the germanium dioxide residue, after appropriate pretreatment, was reheated with further quantities of lithium aluminum hydride in nine consecutive experiments, the yields of germanium hydrides obtained in each experiment were found to be essentially identical with those observed in the first experiment.

The production of Ge_2H_6 and Ge_3H_8 in addition to GeH_4 is difficult to explain although it is possible that the higher hydrides may arise from the preliminary formation of a lower oxide of germanium which contained germanium–germanium bonds.

Experimental Section

All work was carried out in a borosilicate (Pyrex) glass vacuum system. Commercial grade chemicals were used.

General Procedure.—The oxide and fresh, finely ground $LiAlH_4$ were placed in a long-necked 250-ml round-bottom reaction flask and were mixed by manual shaking. The reaction flask, which contained a loose plug of glass wool in the neck to prevent solid particles from being carried into the vacuum system, was attached to the vacuum system by a ground-glass joint sealed to the top of the neck of the flask. A 500-ml surge bulb was provided to protect the apparatus from the large volume of hydrogen suddenly evolved in the preparation of PH_3 and AsH_3. The reaction vessel was evacuated and a stopcock was then turned so that any volatile material formed in the reaction vessel would be pumped continuously through five traps in series immersed in liquid nitrogen. The reaction vessel was then heated in a syrupy phosphoric acid bath.

Some samples of $LiAlH_4$ were found to contain small amounts of diethyl ether impurity which was given off (sometimes together with ethylene) when the temperature of the reaction vessel was between 110 and 150°. Since the reaction between most of the oxides and $LiAlH_4$ is either very slight or does not occur at all in this temperature range, the diethyl ether and/or ethylene, if liberated, was removed from the liquid-nitrogen collection traps before the temperature was raised further. If desired, the $LiAlH_4$ may be heated under these conditions and then cooled, before adding the oxide. The reaction vessel was raised from room temperature to the temperature at which reaction occurred (approximately 148–170°) during about 0.5 hr. Reaction generally occurred suddenly and rapidly and it was usually complete within 1–2 min after the reaction commenced. The hydrogen evolved was continuously pumped away through the traps immersed in liquid nitrogen.

Preparation of SiH_4.—A mixture of SiO_2, in the form of fresh, dry, 200-mesh silica gel (7.2524 g, 120.69 mmol) and $LiAlH_4$ (0.8946 g, 23.57 mmol), started to react at 170°. Reaction was complete after several minutes. The only volatile material recovered was pure SiH_4 [52.5 mg, 1.64 mmol, 6.94% yield; mol wt, 32.0 (calcd 32.1); confirmed by infrared[3] and mass spectra].

When more $LiAlH_4$ was added to the cooled residue in the reactor vessel which was again heated, only a very small amount of SiH_4 was evolved. After repeating this operation twice more, no SiH_4 was evolved. However, when aqueous hydrogen chloride was added to the solid residue, small quantities of SiH_4 were evolved. It is believed that the SiO_2 was deactivated by the presence of a protective coating of one or more of the following substances which might have been formed on the surface of the SiO_2 particles: Li_2O, Al_2O_3, Si, Li_4Si, Al_4Si_3. The last two species could react with the hydrochloric acid to give SiH_4.

Preparation of GeH_4, Ge_2H_6, and Ge_3H_8.—In a typical experiment a mixture of GeO_2 (5.0558 g, 48.339 mmol) and $LiAlH_4$ (0.2242 g, 5.980 mmol) in the molar ratio 8.21:1.00 began to react at 165°. Reaction was complete within 1 min. Infrared examination of the volatile products isolated showed that they consisted of GeH_4, Ge_2H_6, and Ge_3H_8 only. Pure GeH_4 [13.5 mg, 0.176 mmol, 4.37% yield; mol wt, 76.1 (calcd 76.61); confirmed by infrared[4] and mass spectra] was obtained by passing the mixture through a trap held at −134° in which the GeH_4 did not condense. The condensate in the −134° trap was then passed through a trap held at −78° in which Ge_3H_8 (approximately 1 mg, 0.004 mmol, 0.6% yield; identified by infrared[5] and mass spectra) condensed. The more volatile material was Ge_2H_6 [8.4 mg, 0.11 mmol, 2.72% yield; mol wt, 150.3 (calcd 151.25); confirmed by infrared[6] and mass spectra].

Addition of further quantities of $LiAlH_4$ to the residue from the reaction, followed by heating, yielded only negligible quantities of germanes; however, the addition of aqueous hydrogen chloride to the residue gave GeH_4 (3.2 mg) and Ge_2H_6 (1.5 mg). These observations might be explained by an hypothesis analogous to that proposed for the SiO_2–$LiAlH_4$ reaction system.

Optimum yields of Ge_2H_6 resulted when the molar ratios of $LiAlH_4$ to GeO_2 were approximately 1 to 8–10. If the ratio of GeO_2 was increased, the over-all yields of germanium hydrides decreased; if the GeO_2 to $LiAlH_4$ ratio was decreased to below 5:1, only GeH_4 was produced. Also, with the lower ratio, the reaction took place with almost explosive violence.

The GeO_2-rich residue remaining from the reaction could be readily reactivated by heating it in a furnace (in the presence of air) at 900° for approximately 15 min. When the resulting solid was treated with $LiAlH_4$ and heated, germanes were obtained in essentially undiminished yield. Thus 10 g of GeO_2 was treated with ~0.3–0.4 g of $LiAlH_4$ in each of nine separate experiments, each experiment being followed by reactivation of the GeO_2. This complete operation resulted in the formation of 170 mg of pure GeH_4, 75 mg of pure Ge_2H_6, and 7.5 mg of pure Ge_3H_8. It is believed that the air-heating process oxidizes at least some of the species which form the protective coating on the GeO_2 particles.

Preparation of PH_3.—A mixture of P_2O_5 (7.134 g, 50.24 mmol) and $LiAlH_4$ (0.2111 g, 5.826 mmol) in the molar ratio 8.26:1.00 was heated to 165°. A very vigorous reaction which was complete in a few seconds took place. The only volatile material recovered was pure PH_3 [15.8 mg, 0.465 mmol, 8.0% yield; mol wt, 33.8 (calcd 34.0); confirmed by infrared[7] and mass spectra]. Since both white and red phosphorus are produced in this reaction, the reaction vessel should be filled with nitrogen before disconnecting it from the vacuum system at the completion of the experiment.

Preparation of AsH_3.—A mixture of As_2O_3 (9.7752 g, 49.420

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mmol) and $LiAlH_4$ (0.1757 g, 4.360 mmol) in the molar ratio 10.67:1.00 was heated to 148°. A very vigorous reaction which was complete in a few seconds took place. The only volatile material recovered was pure AsH_3 [39.3 mg, 0.504 mmol, 10.9% yield; mol wt, 78.5 (calcd 77.93); confirmed by infrared[7] and mass spectra].

Preparation of SbH_3.—A mixture of Sb_2O_3 (15.363 g, 52.707 mmol) and $LiAlH_4$ (0.1983 g, 5.225 mmol) in the molar ratio 9.08:1.00 was heated to 165° at which temperature a rapid reaction, which was complete in few a seconds, took place. The only volatile material recovered was pure SbH_3 (approximately 1 mg, 0.008 mmol, 0.2% yield; identified by infrared[8] and mass spectra).

Reaction with Miscellaneous Oxides and Oxide Mixtures.—When $LiAlH_4$ was heated with the following oxides, no volatile hydride species were obtained: SnO_2, B_2O_3, TiO_2. When $LiAlH_4$ was heated with a mixture of B_2O_3 and SiO_2, only SiH_4 was evolved. On heating a mixture of SiO_2 and GeO_2 with $LiAlH_4$, no species such as SiH_3GeH_3[9] was formed. Only SiH_4 and the expected mixture of germanes were obtained. When $LiAlH_4$ was heated with a mixture of GeO_2 and As_2O_3, only germanes and AsH_3 were evolved. No species such as GeH_3AsH_2[10] was formed.

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Metalloboranes. II.[1] Transition Metal Complexes of $B_{10}H_{12}{}^{2-}$

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Initial studies suggest a substantial scope and chemistry for metalloboranes based on the $B_{10}H_{12}{}^{2-}$ ligand and transition metal ions. Three types of complexes have been established: (A) $M(B_{10}H_{12})_2{}^{2-}$ with M representing cobalt, nickel, palladium, and platinum; (B) $M(B_{10}H_{12})L_2$ for palladium or platinum with L representing triorganophosphines; (C) $M(B_{10}H_{12})L_3{}^-$ for cobalt, rhodium, and iridium with carbon monoxide and phosphine ligands. It is proposed that the $B_{10}H_{12}{}^{2-}$ moiety interacts with the transition metal atom primarily as a bidentate ligand to form an 11-atom icosahedral fragment. The two extra hydrogen atoms bridge edges of the open pentagonal face of the icosahedral fragment. Spectral and diffraction data fully support this ligand–metal interaction for all three types of complexes.

Introduction

Metalloborane chemistry is extensive and quite large in scope.[2] The transition metal chemistry of $B_{10}H_{12}{}^{2-}$ is the subject of this report. This borane anion has been reportedly isolated in the form of the sodium salt by Wilks and Carter[3] from the prolonged reaction of decaborane with sodium hydride. In addition, Greenwood and Travers reported that the reaction of zinc and cadmium dialkyls with decaborane in ether yields $M(B_{10}H_{12})(ether)_2$ derivatives.[4–7] Upon dissolution of the $M(B_{10}H_{12})(ether)_2$ derivatives in water, $M(B_{10}H_{12})_2{}^{2-}$ complexes of zinc and cadmium are obtained. An analogous mercury complex has also been reported.[7] Greenwood and Travers proposed tetrahedral coordination of the metal atom through direct metal–boron bonds with the 6,9 boron atoms of an unrearranged decaborane cage[4–7] in both types of $B_{10}H_{12}{}^{2-}$ complexes.

We report here the synthesis and characterization of transition metal complexes of the $B_{10}H_{12}{}^{2-}$ ligand of the types: $M(B_{10}H_{12})_2{}^{2-}$, where M = Co, Ni, Pd, Pt; $M(B_{10}H_{12})L_2$, where M = Pd, Pt; L = triorganophosphines; and $M(B_{10}H_{12})L_3{}^-$, where M = Co, Rh, Ir; L = CO and $P(C_6H_5)_3$.

Discussion

Synthesis.—The most general synthesis of $B_{10}H_{12}{}^{2-}$ metalloboranes is the reaction of excess $B_{10}H_{13}{}^-$ ion with transition metal halide complexes. The $B_{10}H_{13}{}^-$ reagent gives $M(B_{10}H_{12})_2{}^{2-}$ compounds with cobalt, nickel, palladium, and platinum halide complexes. In addition, phosphine and carbonyl complexes of cobalt, rhodium, and iridium give $M(B_{10}H_{12})L_3{}^-$ anions as illustrated with Vaska's iridium compound. Initial metal complexation of $B_{10}H_{13}{}^-$ may enhance[8] the proton release either directly by capture with relatively weak bases such as $B_{10}H_{13}{}^-$, $Co(CO)_4{}^-$, and R_3P, or by hydrogen transfer to the metal.

$$4B_{10}H_{13}{}^- + [(C_6H_5)_3P]_2NiCl_2 \longrightarrow Ni(B_{10}H_{12})_2{}^{2-} + 2B_{10}H_{14} + 2(C_6H_5)_3P + 2Cl^- \quad (1)$$

$$2B_{10}H_{13}{}^- + [(C_2H_5)_3P]_2PtCl_2 \longrightarrow Pt(B_{10}H_{12})[P(C_2H_5)_3]_2 + B_{10}H_{14} + 2Cl^- \quad (2)$$

$$2B_{10}H_{13}{}^- + [(C_6H_5)_3P]_2Ir(CO)Cl \longrightarrow Ir(B_{10}H_{12})(CO)[P(C_6H_5)_3]_2{}^- + B_{10}H_{14} + Cl^- \quad (3)$$

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