Results and Discussion

When pentaborane(9) was treated with excess potassium hydroxide powder at −80 °C in tetrahydrofuran, the $B_5H_8^-$ anion was produced slowly in the solution. The rate of the $B_5H_8^-$ formation was fast at −40 °C, and the reaction was complete in 15 min. At −20 °C further reactions and/or the decomposition of the $B_5H_8^-$ anion was observed. These secondary reactions appeared to proceed only very slowly at −40 °C. The above observation was made on the boron-11 NMR spectra of the reaction mixture. The sample was prepared by mixing B_5H_9, KOH powder (ca. 0.37 g per mmol of B_5H_9), and tetrahydrofuran at −80 °C in a 10-mm o.d. sample tube. This experiment confirmed the formation of the $B_5H_8^-$ ion and the stability of the $B_5H_8^-$ solution below −40 °C in the presence of solid potassium hydroxide. An appropriate equation for the reaction would be

$$B_5H_9 + 2KOH(s) \xrightarrow[\text{THF}]{<-40\ ^\circ C} KB_5H_8 + KOH \cdot H_2O(s)$$

The extent of the KB_5H_8 dissociation in the solution phase and the synthetic utility of the $B_5H_8^-$ solution thus prepared were examined by performing two established reactions of the $B_5H_8^-$ ions.[6] The deprotonation reaction of B_5H_9 was performed at −45 °C in a larger reaction vessel with use of a larger excess of potassium hydroxide (0.7–1.5 g per mmol of B_5H_9). The solid in the resulting reaction mixture was filtered quickly and washed briefly with tetrahydrofuran in the cold. The volatile components were removed from the filtrate, and then the residue was treated with anhydrous hydrogen chloride for the conversion of the $B_5H_8^-$ ion to B_5H_9. The pentaborane(9) recovery was 95% or higher. Very small amounts of hydrogen gas and tetraborane(10) were produced during the process of the HCl treatment. In another experiment, the KB_5H_8 solution was filtered directly into a flask containing mercuric chloride. The reaction gave μ,μ'-$(B_5H_8)_2Hg$ in a 74% yield on the basis of the amount of mercuric chloride used.

Pentaborane(9) is a stronger Brønsted acid than cyclopentadiene as demonstrated by the reaction

$$B_5H_9 + C_5H_5^- \xrightarrow[\text{THF}]{<-20\ ^\circ C} B_5H_8^- + C_5H_6$$

which was used by Grimes and his co-workers to generate the $B_5H_8^-$ ion in situ for the preparations of certain metallaboranes.[4a] Thus, the deprotonation of pentaborane(9) with solid potassium hydroxide was not an unexpected reaction, but the stability of the $B_5H_8^-$ ion in the presence of solid KOH had been unknown. The observations described in this note suggest that the Jolly's method[5a] can be adapted to the metallaborane and metallacarborane syntheses for which $B_5H_8^-$ anion is utilized.

Experimental Section

General Data. Conventional vacuum-line techniques were used for the handling of volatile compounds. Potassium hydroxide powder was prepared by pulverizing KOH pellets (approximately 85%, ACS reagent grade) with use of a Waring Blendor.[5a] Pentaborane(9) (Callery Chemical Co.) and hydrogen chloride (Matheson Gas Products) were purified by fractional condensation on the vacuum line. Laboratory stock tetrahydrofuran, which had been stored over $LiAlH_4$, was condensed directly in the reaction vessels from the solvent container. Commercially obtained reagent grade mercuric chloride was used as received.

Monitoring of the Reaction. Potassium hydroxide powder (0.5 g) was placed at the bottom of a tube (10-mm o.d. × 25 cm long, Pyrex, equipped with a stopcock at the upper end), and tetrahydrofuran (ca. 2 mL) and pentaborane(9) (1.35 mmol) were condensed above the powder. The tube was shaken gently in a −80 °C bath for mixing of the reactants and then placed in the probe of a Varian XL-100-15 NMR spectrometer. The spectra of the sample were recorded at various temperatures beginning at −80 °C. During the measurements, the sample tube was transferred frequently from the probe to cold baths of appropriate temperatures and the reaction mixture was agitated in the bath.

The HCl Reaction. A mixture containing B_5H_9 (2.30 mmol) and KOH powder (3.5 g) in about 30 mL of tetrahydrofuran was stirred in a 100-mL vessel for 45 min at −45 °C. The solution was then filtered into another 100-mL flask through a coarse glass frit, and the solid on the frit was washed twice with cold tetrahydrofuran. Upon removal of the volatile components from the filtrate by pumping at −45 °C, a heavy liquid remained in the flask. An excess of HCl (3.7 mmol) was condensed in the flask, and the flask was warmed to −45 °C. The absorption of the HCl by the residue was evident at this temperature. The flask was eventually warmed to room temperature, and the volatile components were distilled out into the other part of the vacuum line where the mixture was treated with boron trifluoride (to complex tetrahydrofuran) and then fractionated. A 2.28 mmol quantity of pentaborane(9), which was slightly contaminated by tetraborane(10) (identified by IR), was recovered.

The $HgCl_2$ Reaction. Pentaborane(9) (9.58 mmol) was treated with KOH powder (7.0 g) in about 30 mL of tetrahydrofuran in the same manner as described above. The resulting solution was filtered into a 100-mL flask in which 1.17 g (4.31 mmol) of $HgCl_2$ had been placed. The washing of the solid on the frit was not performed. The reaction mixture was stirred for 3 h at −45 °C, and then the volatile components were pumped out at −45 °C and finally at room temperature. The residue was washed with dichloromethane repeatedly by recycling the solvent until nothing could be leached out. The solvent was pumped out from the leachate, and the white solid product was sublimed under vacuum at 100 °C for 11 h. The yield of the sublimed product $Hg(B_5H_8)_2$ was 1.04 g (3.18 mmol) or 73.7% on the basis of the $HgCl_2$ used.[7] The product in a dichloromethane solution gave the ^{11}B NMR signals at −8.4, −9.7, and 45.1 ppm.[8] The J_{BH} value for the 45.1 ppm doublet was 176 Hz.[8] The ^{11}B NMR spectra of the sublimation residue (suspended in CH_2Cl_2) contained strong signals of $Hg(B_5H_8)_2$, indicating the sublimation was incomplete.

Acknowledgment. The authors acknowledge support of this work by the U.S. Army Research Office through Grants DAAG 29-76-G-0120 and DAAG 29-79-C-0129.

Registry No. B_5H_9, 19624-22-7; KOH, 1310-58-3; $Hg(B_5H_8)_2$, 70850-80-5.

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[6] For the reaction of $B_5H_8^-$ with HCl, see ref 1. For the reaction of $B_5H_8^-$ with $HgCl_2$, see ref 3c.

[7] A yield of 90% was reported for the synthesis of $Hg(B_5H_8)_2$ which was described in ref 3c.

[8] The reported values in ref 3c are −7.92, −9.60, and −43.85 ppm, the coupling constant for the most shielded doublet being 176 Hz.

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Reaction of Azide Ion with Some Hexafluorides

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Received December 31, 1980

This work arose as a part of a study of the complexing of simple anions by binary fluorides.[1] It is known that the azide ion forms weak complexes with sulfur dioxide,[2] but there is no evidence of interaction with acetonitrile. A compound containing the elements of WF_6 and N_3^- is WF_5N_3 which has been synthesized from trimethylsilyl azide and WF_6.[3] Reactions of some of the title compounds have been found to give

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easy synthetic routes to a few species otherwise difficult to obtain.

Experimental Section

Standard high-vacuum line techniques were employed to handle all volatile compounds. Moisture-sensitive solids were manipulated under nitrogen in a drybox. Infrared spectra of the solid samples as KBr pellets were recorded on Beckman Acculab 4 and Perkin-Elmer 621 spectrometers. Raman spectra of the solid products and liquid SO_2 or CH_3CN solutions were observed with a Jarrell-Ash 25-300 Raman spectrometer with excitation by the 514.5-nm line of an argon ion-laser. Fluorine resonance spectra of the SO_2 and CH_3CN solutions were obtained with a Varian Associates XL-100 spectrometer with a Nicolet Fourier transform attachment at 94.1 MHz. Chemical shifts, positive to low field, are referenced to $CFCl_3$ as internal standard. X-ray powder diffraction patterns were taken with Cu radiation in 114-mm diameter Debye–Scherrer cameras. Tungsten hexafluoride (Ozark-Mahoning), uranium hexafluoride (Varlacoid), molybdenum hexafluoride (Cerac), and tellurium and selenium hexafluorides (Ozark-Mahoning) were used as received. Lithium, cesium, and tetramethylammonium (TMA) azides were prepared from the corresponding hydroxide and hydrazoic acid, while sodium azide was a commercial product. Sulfur dioxide and acetonitrile were dried by repeated distillation over P_2O_5.

Synthesis of WF_5N_3 and $CsWF_7$. A total of 0.0265 g of vacuum-dried cesium azide was dissolved in 0.67 g of anhydrous sulfur dioxide, and a threefold excess of tungsten hexafluoride (0.157 g) was added. The reagents reacted together to give a yellow solution and a white precipitate. The solution was decanted to a side arm and the precipitate washed by distillation of SO_2 from the solution onto it followed by decantation. All readily volatile materials were removed by pumping under vacuum to yield 0.0655 g (96%) of $CsWF_7$ and 0.0488 g (100%) of WF_5N_3. The identity of the $CsWF_7$ was confirmed by the identity of its Raman spectrum and its X-ray powder pattern with those already reported.[4,5] WF_5N_3 was identified by its fluorine resonance spectrum ($\delta(F_{eq}) = 137.4$, $\delta(F_{ax}) = 100.1$, $J_{F-F} = 73.0$ Hz, $J_{W-F_{eq}} = 36.9$ Hz) and Raman spectrum. It is shock and moisture sensitive and must be handled with care.

Synthesis of $CsUF_6$. A total of 0.0309 g of vacuum-dried CsN_3 dissolved in 0.64 g of anhydrous sulfur dioxide was mixed with 0.0736 g of UF_6. Vigorous evolution of nitrogen commenced immediately. All volatile materials were removed under vacuum to give 0.0875 g of $CsUF_6$. Its identity was confirmed by X-ray powder diffraction[6] and elemental analysis. Anal. Calcd: Cs, 27.4; U, 49.1; F, 23.5. Found: Cs, 27.5; U, 46.6; F, 22.3.

Synthesis of $TMAMoF_6$. A total of 0.1069 g of vacuum-dried $TMAN_3$ dissolved in 1.048 g of anhydrous sulfur dioxide was mixed with 0.195 g of MoF_6 and the solution, initially blood red, allowed to warm to room temperature. The solution turned pale orange and evolved 1.32 mmol of nitrogen gas (theoretical 1.38 mmol). All volatile materials were removed under vacuum to give 0.2626 g of $TMAMoF_6$ (theoretical 0.2616 g). Anal. Calcd: Mo, 33.8; F, 40.1. Found: Mo, 33.2; F, 39.4.

Results and Discussion

The reactions of tungsten, molybdenum, and uranium hexafluorides with azide ion may be described by eq 1–3.

$$MF_6 + N_3^- \rightarrow MF_6N_3^- \qquad (1)$$

$$2MF_6 + N_3^- \rightarrow MF_7^- + MF_5N_3 \qquad (2)$$

$$MF_6 + N_3^- \rightarrow MF_6^- + {}^3/_2N_2 \qquad (3)$$

Reaction 1 is the predominant reaction with WF_6 and tetramethyl- or tetrabutylammonium azide in SO_2 or CH_2Cl_2 as solvent although the products of reaction 2 are produced slowly and to a slight extent when more than 1 equiv of WF_6 is initially present in the reaction mixture.[7] It has also been shown that there is rapid exchange via a displacement mechanism between free and complexed WF_6.[7] With lithium, sodium, and cesium azides and WF_6 only products specified by reaction 2 are observed with sulfur dioxide as solvent. In the cases of Li and Na pure MWF_7 cannot be isolated since it gradually decomposes to MF and WF_6. In acetonitrile as solvent reaction 1 occurs rapidly with Li, Na, Cs, and TMA azide followed by a slow reaction (eq 3) causing evolution of nitrogen. It is therefore possible to synthesize pure $CsWF_7$ and WF_5N_3 but not MWF_6 since reaction 3 is slow.

The reaction of UF_6 with azide ion may be described by eq 3 in every case. In SO_2 as solvent complete reaction occurs with cesium and tetramethylammonium as cations. With lithium and sodium as cations and 1 equiv of UF_6 reaction is slow, is incomplete, and depends upon the state of aggregation of the azide. In the presence of an excess of UF_6 the reaction is more vigorous. However it is possible to have complete reaction of Li and NaN_3 by conducting the reaction in acetonitrile as solvent, where reaction 3 proceeds smoothly with an excess of UF_6. The reaction of MoF_6 with azide ion is described by eq 3. TeF_6 reacts with $TMAN_3$ slowly and incompletely in SO_2 solution to give many fluorine containing species. SeF_6 does not react with $TMAN_3$ under similar conditions.

A somewhat analogous situation is the reaction of trimethylsilyl azide with hexafluorides. The reaction of WF_6 to yield WF_5N_3 has already been described.[3] With UF_6 there is evolution of nitrogen, and the only fluorinated species observed by fluorine resonance spectroscopy is trimethylsilyl fluoride. Similar results are observed in the room-temperature reaction with MoF_6, however at −70 °C a doublet and quintuplet are found in the fluorine resonance from MoF_5N_3 (δ 182.4 and 237.6, $J = 94.4$ Hz) and a pair of triplets from *cis*-$MoF_4(N_3)_2$ (δ 147.1 and 179.0, $J = 91.1$ Hz). These chemical shifts are consistent with those predicted by the equation $\delta(F) = pC + qT$ for substituted octahedral fluorinated species[8] and the magnitudes of C and T are appropriate.[1]

Registry No. WF_5N_3, 75900-58-2; $CsWF_7$, 57373-25-8; $CSUF_6$, 17374-59-3; $TMAMoF_6$, 78199-46-9; WF_6, 7783-82-6; UF_6, 7783-81-5; MoF_6, 7783-77-9; MoF_5N_3, 75900-59-3; *cis*-$MoF_4(N_3)_2$, 78198-91-1; N_3^-, 14343-69-2.

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Thermal Decomposition of $[Rh(NH_3)_5Cl]Cl_2$

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Received October 20, 1980

Recently Kohata and co-workers reported the preparation of $[Rh(NH_3)_4Cl_2]Cl$ by heating $[Rh(NH_3)_5Cl]Cl_2$ at 296 °C for 130 min to simply expel one molecule of ammonia from the latter complex.[1] We have studied the thermal decomposition of this compound under the same conditions as described by Kohata et al., with a substantially different outcome. We found that the thermal decomposition of this complex results in the formation of rhodium metal as well as $[Rh(NH_3)_4Cl_2]Cl$.

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