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Preparation and Characterization of $HMgAlH_4$, $HMgBH_4$, and $H_4AlMgBH_4$

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The reactions of alane and diborane with an active form of magnesium hydride in THF were used to prepare $HMgAlH_4$ and $HMgBH_4$. These products were also prepared by the reaction of $NaAlH_4$ and $NaBH_4$ with HMgCl in THF. The hydridomagnesium chloride was prepared by the reaction of magnesium chloride with magnesium hydride in THF. Both $HMgAlH_4$ and $HMgBH_4$ are soluble in THF and exhibit well-defined infrared absorption spectra. When the THF solvent was removed from $HMgAlH_4$, a mixture of MgH_2 and $Mg(AlH_4)_2$ was isolated rather than the expected $HMgAlH_4$, while in the case of $HMgBH_4$, a highly viscous liquid was obtained which differs from a physical mixture of solid MgH_2 and $Mg(BH_4)_2$. For the first time, a triple metal hydride of empirical formula, AlH_4MgBH_4, has been successfully prepared in pure form by the reaction of sodium aluminum hydride with chloromagnesium borohydride. The $ClMgBH_4$ was prepared by the reaction of HMgCl with diborane in 1:1 ratio. The infrared spectrum of AlH_4MgBH_4 in THF showed strong bands at 2366 and 2155 cm^{-1} due to B–H stretching vibrations and a very strong band at 1713 cm^{-1} due to Al–H stretching. X-ray powder diffraction and DTA–TGA studies of this compound are also presented.

Introduction

The preparation of $HMgAlH_4$ and $HMgBH_4$ has been attempted in several laboratories including our own over a period of years. In 1951, Schlesinger and co-workers[2] reported that if diethylmagnesium in diethyl ether is added to a large excess of $LiAlH_4$ in ether solution, a clear solution results from which a compound possessing the empirical formula $HMgAlH_4$ precipitates on addition of benzene. Unfortunately, the compound was not characterized further. An attempt to repeat this result failed to produce $HMgAlH_4$ but instead resulted in the formation of MgH_2 and $Mg(AlH_4)_2$ regardless of the reaction conditions.[3] Our earlier attempts to prepare $HMgAlH_4$ and $HMgBH_4$ by several possible reaction routes failed[4] and in each case a mixture of MgH_2 and either $Mg(AlH_4)$ or $Mg(BH_4)_2$ was isolated rather than the expected products.

$$LiAlH_4 + Et_2Mg \rightarrow HMgAlH_4 + \text{other products} \tag{1}$$

Wiberg and co-workers reported that $LiAlH_4$ and $NaAlH_4$ react with diborane in THF to form a new class of unusually stable compounds which they refer to as "triple metal hydrides" (e.g., $LiAlH_2(BH_4)_2$, $NaAlH_3BH_4$).[5] The reactions were reported to take place according to eq 2. We have studied[6] the same reactions reported by Wiberg under a variety of conditions but were not able to isolate the reported compounds. Instead we found (when $n = 2$) that $LiBH_4$ and H_2AlBH_4 are formed according to eq 3.

$$LiAlH_4 + nBH_3 \rightarrow LiAlH_4{\cdot}nBH_3 \quad (\text{where } n = 1\text{–}4) \tag{2}$$

$$LiAlH_4 + nBH_3 \rightarrow LiBH_4 + H_{4-n}Al(BH_4)_n \tag{3}$$

Our recent preparation of THF-soluble HMgX compounds (where X = Cl or Br) suggests that the reaction of HMgCl with $LiAlH_4$ and $LiBH_4$ should form $HMgAlH_4$ and $HMgBH_4$, respectively. In addition, if it is possible to prepare $HMgAlH_4$ and $HMgBH_4$, it should be possible to prepare AlH_4MgBH_4 by the reaction of $ClMgAlH_4$ with $NaBH_4$ or $ClMgBH_4$ with $NaAlH_4$.

Experimental Section

All operations were carried out either in a nitrogen-filled glovebox equipped with a recirculating system to remove oxygen and moisture or at the bench using typical Schlenk tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

Instrumentation. Infrared spectra were recorded in KBr cells using a Perkin-Elmer 621 high-resolution infrared spectrophotometer. X-ray powder diffraction of all samples was obtained on a Philips-Norelco x-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Single-walled capillaries of 0.5 mm diameter were used. The *d* spacings were evaluated using a precalibrated scale equipped with a viewing apparatus. Line intensities were estimated visually. DTA–TGA data were obtained under vacuum using a modified Mettler Thermoanalyzer II.

Analytical Procedures. Gas analyses were carried out by hydrolyzing samples on a standard vacuum line equipped with a Toepler pump. Aluminum analyses were carried out by complexometric titration with EDTA at pH 4. Magnesium analyses in the presence of aluminum were carried out by masking the aluminum with triethanolamine and titrating with EDTA at pH 10. Boron was determined as boric acid by titration with standard base in the presence of mannitol. Chloride was determined by Volhard titration.

Materials. Tetrahydrofuran and benzene (Fisher Certified reagent) were distilled over sodium aluminum hydride just prior to use, and diethyl ether was distilled over $LiAlH_4$. Magnesium chloride in THF was prepared[7] by the reaction of mercuric chloride with excess magnesium in THF. Lithium and sodium aluminum hydride were obtained from Ventron Metal Hydrides Division and prepared as a solution in diethyl ether and in THF as described previously.[8] Aluminum hydride in THF was prepared[9] by the reaction of 100% sulfuric acid on lithium aluminum hydride in THF at −10 °C. Diborane in THF was obtained from Ventron Metal Hydrides Division. Diethylmagnesium was prepared by the reaction of diethylmercury at 60 °C with excess magnesium metal.[10]

Preparation of Active MgH_2 Slurry in THF. To diethylmagnesium (20 mmol) in diethyl ether (35 mL) was added dropwise lithium aluminum hydride (20 mmol) in diethyl ether (40 mL) with constant stirring at room temperature. An exothermic reaction resulted and immediate precipitation of MgH_2 was observed. This reaction mixture was stirred for about 15 min and then centrifuged. The supernatant solution was removed via syringe and the white solid was washed with fresh amounts of diethyl ether and centrifuged and the supernatant solution again removed via syringe. This process was repeated three times in order to ensure the removal of the $LiAlH_2Et_2$ formed as a by-product in the reaction. The ether-wet solid was now added to freshly distilled THF and the resulting slurry analyzed. Analysis of the solid showed a Mg:H ratio of 1.00:2.02.

Reaction of AlH_3 with MgH_2 Slurried in THF in 1:1 ratio. To 4.0 mmol of magnesium hydride slurried in THF (15 mL) was added aluminum hydride (4.0 mmol) in THF (25 mL) dropwise with continued stirring. The reaction mixture was stirred for 0.5 h, during which time all of the insoluble MgH_2 dissolved. A slight terbidity was separated by centrifuging and removing the supernatant solution by syringe. An infrared spectrum of this solution gave a band at 1715 cm^{-1} due to Al–H stretching. Anal. Calcd for $HMgAlH_4$: Mg:Al:H = 1.00:1.00:5.00. Found: 1.00:1.05:5.06.

No precipitation occurred when the solution was allowed to sit overnight. When the solvent was removed under pressure, precipitation began when the concentration of the solution was about 0.10 M. This white crystalline solid was dried under reduced pressure at 25 °C (0.1 mm) for about 0.5 h and analyzed. Anal. Calcd for $HMgAlH_4{\cdot}1.5THF$: Mg:Al:H:THF = 1.00:1.00:5.00:1.50. Found: 1.00:1.06:4.87:1.53. An infrared spectrum of the solid (Nujol mull) showed bands at 1830 and 1720 cm^{-1} due to Al–H stretching. An x-ray powder diffraction pattern of this solid showed weak lines due to $Mg(AlH_4)_2{\cdot}4THF$ along with some new lines different from that of $Mg(AlH_4)_2\cdot 4THF$. The main lines were 8.6 (w), 7.4 (w), 7.1 (w), 5.40 (s), 5.25 (s), 4.60 (s), 4.12 (m), 3.00 (s), 2.82 (m), 2.50 (m), 1.87 (m), 1.77 (w), 1.66 (s), 1.52 (w), 1.49 (w), 1.25 (s), 1.21 (s).

The above reaction was repeated in the same manner except that this time the solvent was removed within 1 h after addition of the reagents. The resulting white solid was dried under similar conditions of temperature and pressure as reported above and then analyzed. Anal. Calcd for $HMgAlH_4\cdot 2THF$: Mg:Al:H:THF = 1.00:1.00:5.00:2.00. Found: 1.00:1.07:5.10:2.02. X-ray powder pattern = 8.75 (m), 7.41 (m), 7.10 (s), 5.83 (m), 5.50 (m), 4.60 (w), 4.13 (3), 3.80 (m), 3.22 (m), 3.08 (w), 2.90 (w), 2.80 (w), 2.72 (w). These lines were comparable to that of $Mg(AlH_4)_2\cdot 4THF$.

Preparation of HMgCl in THF Solution.[11] Twenty-five milliliters of a 0.30 M solution of magnesium chloride (7.5 mmol) in THF was added dropwise to well-stirred magnesium hydride slurried in THF (7.50 mmol) at room temperature. The reaction was exothermic. The reaction mixture was stirred for 1 h and the clear solution analyzed. Anal. Calcd for HMgCl: H:Mg:Cl = 1.00:1.00:1.00. Found: 0.98:1.00:1.03.

Reaction of $NaAlH_4$ in THF in 1:1 Ratio. To 5 mL of a 0.81 M solution of HMgCl (4.05 mmol) in THF was added 8.1 mL of a 0.5 M THF solution of $NaAlH_4$ (4.05 mmol) dropwise with continuous stirring at room temperature. The reaction was exothermic and a white precipitate appeared just after beginning the addition of $NaAlH_4$. This reaction mixture was stirred for 0.5 h and the white insoluble solid was separated by centrifuging the reaction mixture and removing the supernatant solution by means of a syringe. The resulting white solid was washed with THF, and both the solid and the supernatant solution separated earlier were analyzed. (White insoluble solid. Anal. Calcd for NaCl: Na:Cl = 1.00:1.00. Found 1.00:1.03. A negligible amount of magnesium and aluminum was also detected. Supernatant solution. Anal. Calcd for $HMgAlH_4$: Mg:Al:H = 1.00:1.00:5.00. Found: 1.00:1.02:5.03. IR spectrum of the solution: 1715 (s), 1380 (m), 1350 (w), 1320 (w), 790 (m), 765 (s) cm^{-1}.) The THF solvent was removed under reduced pressure about 2 h after reagent addition and the resulting white crystalline product was dried under reduced pressure at 25 °C (0.1 mm) for 0.5 h and analyzed. Anal. Calcd for $HMgAlH_4\cdot 2THF$ or $MgH_2 + Mg(AlH_4)_2\cdot 4THF$: Mg:Al:H:THF = 1.00:1.00:5.00:2.00. Found: 1.00:1.03:5.02:2.01. X-ray powder pattern: 8.75 (m), 7.41 (m), 7.10 (m), 7.10 (s), 5.83 (m), 5.50 (m), 4.60 (w), 4.13 (s), 3.80 (m), 3.22 (m), 3.08 (w), 2.90 (w), 2.80 (w), 2.72 (corresponds to $Mg(AlH_4)_2\cdot 4THF$).

Reaction of Magnesium Hydride with $Mg(AlH_4)_2\cdot 4THF$ in THF. A freshly prepared slurry of magnesium hydride (4.0 mmol) in THF and $Mg(AlH_4)_2$ (4.0 mmol) were mixed in THF and stirred for 2 h at room temperature. Some white solid remained undissolved even after stirring for 4 h. It was filtered and both the filtrate and insoluble solid were analyzed.

Filtrate anal. Calcd for $HMgAlH_4$: Mg:Al:H = 1.00:1.00:5.00. Found: 1.00:1.15:4.92. Filtrate contained about 60% of the total magnesium. IR (in THF): 1715 (m), 1381 (m), 1349 (w), 1320 (w), 790 (m), 7.65 (s) cm^{-1}.

Insoluble solid anal. Found: Mg:Al:H = 1.13:1.00:4.82. X-ray pattern: 8.76 (m), 7.40 (m), 7.10 (s), 5.83 (m), 5.50 (m), 4.60 (w), 4.13 (s), 3.80 (m), 3.22 (m), 3.08 (w), 2.90 (w) (corresponds to $Mg(AlH_4)_2\cdot 4THF$).

Reaction of $NaBH_4$ with HMgCl in THF. Sodium borohydride (3.02 mmol) in THF (25 ml) was added dropwise to a well-stirred solution of HMgCl (3.0 mmol) in THF (15 mL) at room temperature. Immediate reaction took place and an insoluble white solid resulted. This reaction mixture was stirred for 0.5 h and the white solid was removed by filtration. Analysis of the solid revealed that it contained Na and Cl in ratios 1.00:1.02. The filtrate exhibited infrared bands at 2372 and 2158 cm^{-1} due to B–H stretching.

Anal. Calcd for $HMgBH_4$: Mg:B:H = 1.00:1.00:5.00. Found: 1.00:1.07:5.09.

Reaction of MgH_2 with $Mg(BH_4)_2$ in THF in 1:1 Ratio. $Mg(BH_4)_2$ (4.5 mmol) was prepared in THF by the reaction of diborane (9.0 mmol) with a slurry of magnesium hydride (4.5 mmol). The THF solution of $Mg(BH_4)_2$ was added dropwise to a well-stirred slurry of MgH_2 (4.5 mmol) prepared freshly in THF. This reaction mixture was stirred for 3 h, and the insoluble solid was filtered and washed with THF and both the insoluble white solid and filtrate were analyzed. Analysis of the insoluble solid showed that it contained Mg, B, and H in ratios 1.07:0.07:2.12. The solid contained about 30% of the total magnesium as magnesium hydride.

Filtrate anal. Calcd. for $HMgBH_4$: Mg:B:H = 1.00:1.00:5.00. Found: 1.00:1.19:5.02. The infrared spectrum exhibited bands at 2378, 2265, and 2158 cm^{-1} characteristic of B–H stretching vibrations.

Reaction of Diborane with MgH_2 in THF in 1:1 Ratio. To a slurry of MgH_2 (4.60 mmol) in THF was added 5.0 mL of a 0.92 M solution of diborane (4.60 mmol) in THF with stirring. The reaction was exothermic and was stirred for 0.5 h at room temperature resulting in an almost clear solution. The slight turbidity present was removed by centrifuging and separating the supernatant solution. The insoluble solid corresponded to 4–5% of the total magnesium hydride used in the reaction. The supernatant solution was analyzed. Anal. Calcd for $HMgBH_4$: Mg:B:H = 1.00:1.00:5.00. Found: 1.00:1.06:5.10. The infrared spectrum showed strong bands at 2365 and 2160 cm^{-1} characteristic of B–H stretching vibrations. Other bands were at 2220 (sh), 2055 (sh), 1348 (m), 1110 (m), 805 (w), and 625 (w) cm^{-1}. The solvent from the supernatant solution was removed under reduced pressure and the residue dried in vacuo at 25 °C (0.1 mm) for 1 h to give a highly viscous colorless liquid which could not be further dried. The physical state of this compound looked different than the mixture of MgH_2 and $Mg(BH_4)_2$ which are both solids.

Preparation of $ClMgBH_4$ in THF Solution.[11] To a well-stirred solution of HMgCl (20 mmol) in THF (30 mL) was added $BH_3\cdot THF$ (20 mmol in 30 mL of THF) slowly at room temperature. The reaction was exothermic and resulted in a clear solution. The solution was characterized by its infrared spectrum and elemental analysis. Anal. Calcd for $ClMgBH_4$: Mg:B:H:Cl = 1.00:1.00:4.00:1.00. Found: 1.00:1.02:4.06:1.03. An infrared spectrum exhibited strong absorption bands at 2375 and 2158 cm^{-1} characteristic of the B–H stretching.

Reaction of $ClMgBH_4$ with $NaAlH_4$ in THF in 1:1 Ratio. Sodium aluminum hydride (7.5 mmol) in THF (12 mL) was added slowly to a well-stirred solution of $ClMgBH_4$ (7.5 mmol) in THF (35 mL) at room temperature. The reaction was exothermic and an insoluble white solid was formed immediately on addition of the $NaAlH_4$. The reaction mixture was stirred for 0.5 h and the white insoluble solid separated from the clear supernatant solution by centrifugation followed by removal of the supernatant solution (syringe). Both the insoluble solid and the supernatant solution were analyzed. (Insoluble solid. Anal. Calcd for NaCl: Na:Cl = 1.00:1.00. Found: 1.00:1.02. The NaCl was formed quantitatively. X-ray pattern: 3.26 (m), 2.82 (vs), 2.00 (vs), 1.70 (w), 1.628 (m), 1.410 (w), 1.261 (m), 1.152 (w). Supernatant solution. Anal. Calcd for AlH_4MgBH_4: Mg:Al:B:H = 1.00:1.00:1.00:8.00. Found: 1.00:0.98:1.01:8.06. Infrared spectrum (in THF): 2366 (s), 2220 (sh), 2155 (s), 2050 (w), 1820 (w), 1713 (s), 1370 (m), 1110 (w), 960 (w), 790 (sh), 755 (s) cm^{-1}.)

When about 15 mL of THF from this solution was removed under vacuum, some insoluble white solid precipitated from solution. The solid and the filtrate were analyzed. (Insoluble white solid: Anal. Found: Mg:Al:B:H = 1.00:1.27:0.83:8.11. The total magnesium in this solid was about 10% of the initial magnesium involved in the reaction. X-ray pattern: 8.7 (w), 7.4 (w), 7.1 (w), 6.4 (vw), 5.25 (vw), 4.15 (vw), 3.80 (vw). These weak lines correspond to $Mg[AlH_4]_2\cdot 4THF$. Filtrate. Anal. Calcd for AlH_4MgBH_4: Mg:Al:B:H = 1.00:1.00:1.00:8.00. Found: 1.00:0.94:1.05:8.01. An infrared spectrum of the filtrate exhibited absorption bands at 2365 (s), 2220 (sh), 2155 (s), 2050 (w), 1715 (s), 1380 (m), 792 (sh), 755 (s), and 670 (m) cm^{-1}.) The filtrate was then concentrated to 8 mL by removing solvent under vacuum and the resulting insoluble solid separated from the clear supernatant. Both solid and supernatant were analyzed. (Insoluble solid. Anal. Calcd for $AlH_4MgBH_4\cdot 2THF$: Mg:Al:B:H:THF = 1.00:1.00:1.0018.00:2.00. Found: 1.00:1.05:0.99:8.14:1.95. X-ray pattern: 9.85 (m), 8.80 (m), 7.90 (m), 7.40 (m), 7.10 (w), 5.65 (w), 5.32 (m), 5.25 (w), 4.90 (vw), 4.15 (m), 3.91 (w), 2.80 (vw), 2.75 (vw) Å. Supernatant solution. Anal. Calcd for AlH_4MgBH_4: Mg:Al:B:H = 1.00:1.00:1.00:8.00. Found: 1.00:0.82:1.17:7.93.)

Reaction of $Mg(BH_4)_2$ with $Mg(AlH_4)_2$ in THF. When a THF solution of $Mg(BH_4)_2$ (3.05 mmol) was added dropwise to a well-stirred slurry of $Mg(AlH_4)_2$ (3.82 mmol) in THF and the reaction mixture stirred at room temperature for 2 h, an almost clear solution resulted. The slight insoluble solid was filtered and analyzed. The analysis showed that it contained Mg, Al, B, and H in ratios 1.00:1.52:0.35:7.78. It contained about 15% of the initial magnesium taken as $Mg(AlH_4)_2$.

Filtrate anal. Calcd for AlH_4MgBH_4: Mg:Al:B:H = 1.00:1.00:1.00:8.00. Found: 1.00:0.91:1.10:7.97. An infrared spectrum of the filtrate exhibited bands at 2368 and 2155 cm^{-1} characteristic of B–H stretching vibrations and a strong band at 1715 cm^{-1}

characteristic of Al–H stretching vibrations.

Results and Discussion

Some time ago[4] we attempted to prepare $HMgAlH_4$ and $HMgBH_4$, the half complex metal hydrides of $Mg(AlH_4)_2$ and $Mg(BH_4)_2$. The major interest was to impart solubility to a Mg–H compound so that it might find utility as a soluble reducing agent toward organic substrates. In addition it would be reasonable to suppose that such compounds would be more thermally stable than either $Mg(AlH_4)_2$ or $Mg(BH_4)_2$ due to their Mg–H component and therefore, their resemblance to MgH_2 (320 °C dec). Although we failed in our initial attempts to prepare these compounds, new attractive routes opened up recently when we found that $MgCl_2$ and $MgBr_2$ will react with an active form of MgH_2 in THF to form a clear, colorless solution of HMgCl and HMgBr, respectively. We immediately considered the possibility that $HMgAlH_4$ and $HMgBH_4$ could be prepared by the reaction of one of these HMgX compounds with $NaAlH_4$ and $NaBH_4$ to produce the desired compounds (eq 4–6). The active form of MgH_2 used to prepare HMgCl was obtained by reaction of $LiAlH_4$ with diethylmagnesium in ether (eq 7). Indeed when $NaAlH_4$ in THF was added to a THF solution of HMgCl, NaCl precipitated quantitatively and the remaining clear colorless solution analyzed for the compound $HMgAlH_4$. If instead a mixture of MgH_2 and $Mg(AlH_4)_2$ was formed, both compounds would have precipitated from solution since both of these compounds are insoluble in THF. The infrared spectrum showed the Al–H stretching absorption in $HMgAlH_4$ to be at 1715 cm^{-1}; however, it was not possible to observe the Mg–H absorption band. When the THF solvent was removed from the solution of $HMgAlH_4$ and the solid material analyzed by x-ray powder diffraction, the data clearly showed that some disproportionation had taken place according to eq 8. Since MgH_2 and $Mg(AlH_4)_2$ have such a high heat of formation and are so insoluble in THF, it seems reasonable that when the THF solvent is removed from $HMgAlH_4$ the compound would disproportionate.

$$MgH_2 + MgCl_2 \xrightarrow{THF} 2HMgCl \quad (4)$$

$$HMgCl + NaAlH_4 \xrightarrow{THF} HMgAlH_4 + NaCl \quad (5)$$

$$HMgCl + NaBH_4 \xrightarrow{THF} HMgBH_4 + NaCl \quad (6)$$

$$LiAlH_4 + (C_2H_5)_2Mg \rightarrow MgH_2 + LiAlH_2(C_2H_5)_2 \quad (7)$$

$$2HMgAlH_4 \rightarrow MgH_2 + Mg(AlH_4)_2 \quad (8)$$

Likewise, $HMgBH_4$ was prepared in a similar manner (eq 6) to $HMgAlH_4$, that is, by the reaction of HMgCl with $NaBH_4$ in THF. The reaction was quantitative and $HMgBH_4$ formed as a clear colorless solution in THF. An infrared spectrum showed absorption bands at 2365 and 2160 cm^{-1} due to terminal and bridging B–H stretching vibrations. Unlike $HMgAlH_4$, when THF is removed from a solution of $HMgBH_4$, it appears that disproportion does not take place.

It was also possible to prepare $HMgAlH_4$ and $HMgBH_4$ by the reactions of an active form of MgH_2 with AlH_3 in THF and BH_3 in THF, respectively (eq 9 and 10). When a clear solution of either AlH_3 in THF or BH_3 in THF was added to a slurry of MgH_2 in THF, the MgH_2 dissolved within a matter of a few minutes. The infrared spectra of these solutions were identical with the solutions of $HMgAlH_4$ and $HMgBH_4$ prepared earlier from the reaction of HMgCl with $NaAlH_4$ and $NaBH_4$, respectively. Elemental analysis indicated the correct empirical formulas for $HMgAlH_4$ and $HMgBH_4$ as would be expected since the MgH_2 dissolved in equal molar proportions with respect to the AlH_3 and BH_3. Once again when THF solvent was removed from the solution of $HMgAlH_4$, MgH_2 and $Mg(AlH_4)_2$·4THF were detected by x-ray powder diffraction analysis. On the other hand, when the THF solvent was removed from a solution of $HMgBH_4$, a viscous liquid was formed from which no further THF could be removed. The infrared spectrum of this liquid was different from that of a prepared mixture of MgH_2 and $Mg(BH_4)_2$.

$$MgH_2 + AlH_3 \xrightarrow{THF} HMgAlH_4 \quad (9)$$

$$MgH_2 + BH_3 \xrightarrow{THF} HMgBH_4 \quad (10)$$

An attempt was made to prepare $HMgAlH_4$ by the reaction of MgH_2 with $Mg(AlH_4)_2$ in THF. When these reagents were stirred at room temperature for 4 h, only 60% of the initial magnesium taken as MgH_2 dissolved. However, the analysis of the solution showed $HMgAlH_4$ to be present. Similarly, when MgH_2 and $Mg(BH_4)_2$ were allowed to react in THF for 3 h, about 30% of the MgH_2 reactant remained unreacted. The solution contained both $HMgBH_4$ and $Mg(BH_4)_2$ as characterized by elemental and infrared analysis. The above reactions cannot be carried out for longer periods of time in order to ensure complete reaction without some THF cleavage taking place. Because of incomplete reaction, it appears that the reactions of HMgCl with $NaAlH_4$ or $NaBH_4$ or the reaction of MgH_2 with AlH_3 or BH_3 are better for the preparation of $HMgAlH_4$ and $HMgBH_4$.

We have recently reported[11] the preparation of $ClMgBH_4$ by the reaction of HMgCl with diborane in THF (eq 11). We now find that when a THF solution of $NaAlH_4$ is added to a THF solution of $ClMgBH_4$ in 1:1 ratio, a white solid is produced which analyzes as pure NaCl. Since $Mg(AlH_4)_2$ is insoluble in THF, the presence of a clear solution of empirical formula $H_4AlMgBH_4$ represents the formation of this stable and soluble "triple metal hydride". An infrared spectrum of the product solution exhibited absorption bands at 2366 and 2155 cm^{-1} due to terminal and bridging B–H stretching vibrations and a strong band at 1713 cm^{-1} characteristic of the Al–H stretching vibration. Since $Mg(BH_4)_2$ in THF shows B–H absorptions at 2380 and 2270 cm^{-1} and $Mg(AlH_4)_2$ is not soluble in THF, it is clear that $H_4AlMgBH_4$ is a true compound and not a mixture of $Mg(AlH_4)_2$ and $Mg(BH_4)_2$.

$$2HMgCl + B_2H_6 \xrightarrow{THF} 2ClMgBH_4 \quad (11)$$

In an attempt to determine something about the integrity of $H_4AlMgBH_4$ in the solid state, a fractional crystallization of a THF solution of $H_4AlMgBH_4$ was carried out. Four fractions were collected. By elemental analysis it was shown that the first solid fraction was enriched with $Mg(AlH_4)_2$ and by x-ray powder pattern analysis it was shown that some $Mg(AlH_4)_2$ was present. The middle two fractions analyzed were for $H_4AlMgBH_4$ and the x-ray powder patterns showed the absence of $Mg(AlH_4)_2$ (all lines being other than those ascribed to $Mg(AlH_4)_2$). The middle fractions ($H_4AlMgBH_4$·2THF) were shown to be completely soluble in benzene, once again demonstrating the integrity of these fractions as a single compound since $Mg(AlH_4)_2$·4THF is not soluble in benzene. The product AlH_4MgBH_4 could also be prepared in almost 90% purity by the reaction of $Mg(AlH_4)_2$ with $Mg(BH_4)_2$ in THF. When $Mg(BH_4)_2$ in THF was added dropwise to a well-stirred slurry of $Mg(AlH_4)_2$ in THF, an almost clear solution resulted after 2 h. An infrared spectrum of the solution showed the presence of B–H and Al–H stretching bands at 2368, 2155, and 1715 cm^{-1}, respectively. The vacuum DTA–TGA of AlH_4MgBH_4·2THF is shown in Figure 1. AlH_4MgBH_4·2THF decomposes evolving condensable gas (THF) at 125 °C and noncondensable gases (H_2) at 165 and 300 °C. The first decomposition is endothermic,

$$Mg(AlH_4)_2 + Mg(BH_4)_2 \xrightarrow{THF} 2AlH_4MgBH_4 \quad (12)$$

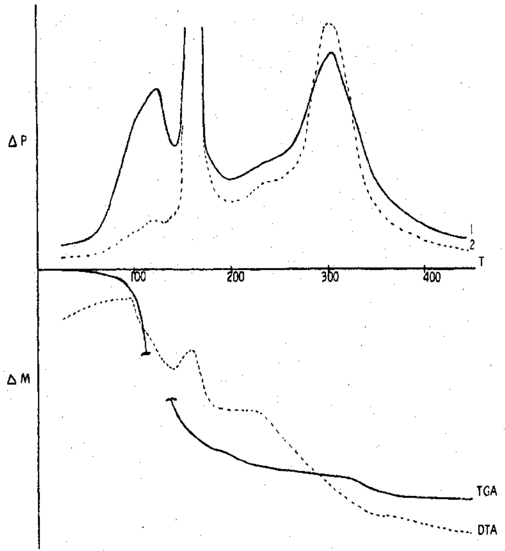

Figure 1. Vacuum DTA–TGA of $H_4AlMgBH_4$: (1, —) change in pressure, (2, ---) pressure change after liquid nitrogen trap.

the second decomposition is exothermic followed by an endothermic effect, and the third decomposition is a broad endotherm. The first gas evolution is attributed to the evolution of solvated THF. The second decomposition at 165 °C, accompanied by noncondensable gas evolution, can be attributed to decomposition of AlH_4MgBH_4 to $BH_3{\cdot}AlH_3$ and MgH_2 with simultaneous decomposition of $BH_3{\cdot}AlH_3$ to give H_2. The last endotherm is due to the decomposition of MgH_2. The steps involved in the decomposition are shown below. No

$$\text{step 1:}\quad AlH_4MgBH_4{\cdot}2THF \rightarrow AlH_4MgBH_4 + 2THF \qquad (13)$$

$$\text{step 2:}\quad AlH_4MgBH_4 \rightarrow Al{\cdot}B + MgH_2 + 3H_2 \qquad (14)$$

$$\text{step 3:}\quad MgH_2 \rightarrow Mg + H_2 \qquad (15)$$

THF cleavage was observed during the thermal decomposition process.

Registry No. $HMgAlH_4$, 12693-01-5; HMgCl, 22106-77-0; NaCl, 7647-14-5; $HMgBH_4$, 12693-03-7; $ClMgBH_4$, 62816-03-9; AlH_4MgBH_4, 62881-85-0; AlH_3, 7784-21-6; MgH_2, 7693-27-8; $NaAlH_4$, 13770-96-2; $Mg(AlH_4)_2{\cdot}4THF$, 25610-40-6; $NaBH_4$, 16940-66-2; $Mg(BH_4)_2$, 16903-37-0; diborane, 19287-45-7; $BH_3{\cdot}THF$, 14044-65-6.

References and Notes

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S_4: An ab Initio Study

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The relative stability of ten possible electronic and conformational states of S_4 has been studied by ab initio STO-3G and 44-31G calculations. The STO-3G optimized geometry is significantly different from the 44-31G optimized geometry and the standard routine to carry out single 4-31G calculations at STO-3G optimized geometries is not appropriate here. Based on the present study in conjunction with previous experimental and theoretical enthalpies of formation for S_4, the triplet helix diradical is predicted to be the most stable among all possible forms including the *c*-S_4. The branched molecule, sulfur trithiotrioxide (trigonal S_4), which has been proposed by extended Hückel calculations, seems unlikely to exist according to the present study. The validity of the use of molecular total overlap population to explain the order of relative stability is also examined.

Elemental sulfur,[1,2] which has been known and used for several thousand years, can exist in a polymeric form and as a variety of rings containing different numbers of sulfur atoms. Many of them have been isolated and structurally elucidated. However, the structure of S_4 remains an interesting unsolved problem.[1,2]

The S_4 molecule is known to exist in the gas and the liquid phase. Several possible structures have been proposed including a ring, a diradical, a bipolar compound, or a chain with double bonds. But, none of these has been experimentally determined. Recent extended Hückel calculations,[1,3] based on spectroscopic atomic parameters, gave a special stability to a branched structure, sulfur trithiotrioxide. Our molecular mechanics calculations[4] suggest that the existence of *cyclo*-tetrasulfur as the most stable structure is unlikely since it is highly strained with a steric energy almost 10 times that found in *cyclo*-hexasulfur and an S–S bond energy about 12 kcal/mol smaller than the corresponding value for *cyclo*-hexasulfur. However, thermodynamic[5] and photoionization[6] data seem to favor the ring although they are insufficient to determine the structure of S_4.[1] It seems to us that there is no unique answer so far about the most stable structure of the S_4 molecule.

An alternative way to attack this problem is ab initio molecular orbital theory which has been described in detail elsewhere.[7] In this paper, ab initio molecular orbital theory is employed to study the structures and stabilities of ten possible electronic and conformational states of S_4.

Computational Aspects and Results

The results presented here were obtained using the Gaussian 70 system of programs.[8,9] The linear-chain, branched-chain, branched-ring, and single-ring forms were all examined at the STO-3G level since its small size permits full optimization under reasonable cost for a molecule as large as S_4. This