$LiAl(CH_3)_2H_2$ and ZnH_2, which precipitates from solution. All the reactions, except 12, are actual equilibria which are never displaced entirely toward ZnH_2. This is supported by the fact that after standing 1 week, sufficient time for full equilibrium to be reached, the supernatant solution above ZnH_2 still contained about 50% of the original zinc.

It would be reasonable also to assume that the reaction between $LiAlH_4$ and $(CH_3)_2Zn$ in diethyl ether, which is known to produce ZnH_2, proceeds through an intermediate such as $LiZn(CH_3)_2AlH_4$. This assumption is borne out in our study of the reaction between $LiAlH_4$ and $(CH_3)_2Zn$ in diethyl ether.[19]

Registry No. $LiZn(CH_3)_2AlH_4$, 59092-43-2; $LiZn_2(CH_3)_4AlH_4$, 62166-60-3; $(CH_3)_2Zn$, 544-97-8; $LiAlH_4$, 16853-85-3; ZnH_2, 14018-82-7; $LiZnH_3$, 38829-83-3.

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Nature of Alkyl–Hydrogen Exchange Reactions Involving Aluminum and Zinc. 3. Reaction between $(CH_3)_2Zn$ and $LiAlH_4$ in Diethyl Ether

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The reaction between lithium aluminum hydride and dimethylzinc in diethyl ether has been studied in detail. The course of the reaction was found to be dependent upon the mode of addition, the ratio, and concentration of the reactants. When $(CH_3)_2Zn$ was added to $LiAlH_4$, the reaction was found to proceed according to the equations

$$(CH_3)_2Zn + 2LiAlH_4 \rightarrow ZnH_2 + LiAl(CH_3)H_3$$

$$(CH_3)_2Zn + LiAlH_4 \rightarrow ZnH_2 + LiAl(CH_3)_2H_2$$

$$3(CH_3)_2Zn + 2LiAlH_4 \rightarrow 3ZnH_2 + 2LiAl(CH_3)_3H$$

$$2(CH_3)_2Zn + LiAlH_4 \rightarrow 2ZnH_2 + LiAl(CH_3)_4$$

The identity of the aluminum-containing products was established by spectral comparison with the products formed on redistribution of $LiAlH_4$ with $LiAl(CH_3)_4$. On the other hand, addition of $LiAlH_4$ to $(CH_3)_2Zn$ in 1:2 ratio produced the soluble complex $LiZn_2(CH_3)_4AlH_4$. The same addition in 1:1 ratio yielded a mixture of $LiZnH_3$ and ZnH_2 by way of the intermediate $LiZn(CH_3)_2AlH_4$. In 2:1 ratio the reaction gave ZnH_2 only. The mechanism of the reaction between $LiAlH_4$ and $(CH_3)_2Zn$ is discussed in light of these results.

Introduction

Recently, we reported the synthesis of the trimetal complexes $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ in THF.[1] These compounds were formed by the reactions of AlH_3 with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ and by the reactions of $LiAlH_4$ with $(CH_3)_2Zn$ in 1:1 and 1:2 ratios. In paper 2 of this series, it was shown that $LiZn(CH_3)_2AlH_4$ is the intermediate involved in the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in THF to give ZnH_2. At that time, it was proposed that this same compound would be the intermediate involved in the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ to give ZnH_2 in diethyl ether. (The synthesis of ZnH_2 by this method was reported by Schlesinger and co-workers[2] in 1951.) In view of this interesting possibility, and the fundamental nature of this reaction, a more detailed study seemed appropriate.

Experimental Section

Apparatus. Reactions were performed under nitrogen using Schlenk tube techniques.[3] Filtrations and other manipulations were carried out in a glovebox equipped with a recirculating system using manganese oxide columns to remove oxygen and dry ice–acetone traps to remove solvent vapors.[4] Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Spectra of solid samples were obtained as Nujol mulls between CsI plates. Spectra of solutions were obtained using matched 0.10-mm path length NaCl cells. X-ray powder data were obtained on a Philips-Norelco x-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to x rays for 6 h. The *d* spacings were read on a precalibrated scale equipped with a viewing apparatus. Intensities were estimated visually.

Analytical Procedure. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[3] Methane in the presence of hydrogen was determined by volume in a previously described tensimeter.[3] Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration. Zinc in the presence of aluminum was determined by masking the aluminum with triethanolamine and titrating the zinc with EDTA. Zinc alone was determined by EDTA titration.

Materials. $LiAlH_4$ was obtained as gray, lumpy solids from Ventron, Metal Hydrides Division. Solutions of $LiAlH_4$ in diethyl ether were prepared by stirring the solid hydride for 24 h with freshly distilled solvent, followed by filtration, to yield a clear, colorless solution. The solution of $LiAlH_4$ in diethyl ether was standardized by aluminum analysis and transferred volumetrically. Dimethylzinc was prepared by the procedure of Noller.[5] Methyl iodide was obtained from Fisher Scientific Co. The iodide was dried over anhydrous $MgSO_4$ and distilled prior to use. Zinc–copper couple was obtained from Alfa Inorganics. The reaction of zinc–copper couple with methyl iodide was allowed to proceed overnight. The $(CH_3)_2Zn$ was distilled from the reaction mixture at atmospheric pressure under nitrogen. Diethyl ether was distilled under nitrogen over $LiAlH_4$.

Lithium tetramethylaluminate ($LiAl(CH_3)_4$) was prepared by the reaction of CH_3Li with $(CH_3)_3Al$. Trimethylaluminum was obtained from Texas Alkyls, Inc., and distilled through a 12-in. glass-helix-packed column at reduced pressure. Methyllithium was prepared by the reaction of excess lithium metal with $(CH_3)_2Hg$ in diethyl ether at −20 °C. Dimethylmercury was obtained from Org—Met and used without any further purification. Lithium metal was obtained as a 30% dispersion in petrolatum from Alfa-Ventron. The diethyl ether solution of $LiAl(CH_3)_4$ was standardized by aluminum analysis.

Infrared Spectral Study of the Reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in Diethyl Ether. A 1.16 M solution of $LiAlH_4$ in diethyl ether was placed in a two-neck round-bottom flask fitted with a condenser and a three-way stopcock. Increments of 0.83 M solution of $(CH_3)_2Zn$ in diethyl ether were added via syringe under nitrogen to the magnetically stirred $LiAlH_4$ solution. After each addition, the solution was stirred for 5 min at room temperature, then the stirring was stopped in order to allow the precipitate to settle. Infrared spectra were obtained by withdrawing samples of the supernatant solution by syringe under nitrogen. The additions were continued until the ratio of $(CH_3)_2Zn$ to the original $LiAlH_4$ was 2:1. The infrared spectra obtained in this way are shown in Figure 1.

In a similar manner a 1.16 M solution of $LiAlH_4$ in diethyl ether was added in increments to a 0.83 M solution of $(CH_3)_2Zn$. The infrared spectra obtained from this study are shown in Figure 2.

Redistribution of $LiAlH_4$ and $LiAl(CH_3)_4$. Reactions between $LiAlH_4$ and $LiAl(CH_3)_4$ were performed by mixing standard solutions of the reagents in ratios appropriate to produce $LiAl(CH_3)_3H$, $LiAl(CH_3)_2H_2$, and $LiAl(CH_3)H_3$. After stirring for 1 h at room temperature, infrared spectra were obtained on the resulting solution.

Reactions between $LiAlH_4$ and $(CH_3)_2Zn$ in Diethyl Ether. A. Reactions Where $(CH_3)_2Zn$ is Added to $LiAlH_4$. (1) 2.0 $LiAlH_4$–1.0 $(CH_3)_2Zn$. A diethyl ether solution of $(CH_3)_2Zn$ (0.83 M) was added dropwise by syringe (under nitrogen flush) to a magnetically stirred 1.16 M solution of $LiAlH_4$ in diethyl ether until the ratio of reactants was 1.0:2.0 ($(CH_3)_2Zn$:$LiAlH_4$). A white precipitate formed immediately. After stirring for 1 h at room temperature, the mixture was filtered. The resulting solid was washed with diethyl ether and dried under vacuum at room temperature. Analysis of the solid showed it to contain Li, Zn, H, and Al in molar ratios of 0.02:1.00:2.04:0.03 and all the starting zinc. An x-ray powder diffraction pattern of the solid showed it to be zinc hydride. Analysis of the filtrate showed it to contain Li, Al, CH_3, H, and Zn in molar ratios of 1.04:1.00:0.98:3.11:0.00.

(2) 1.0 $LiAlH_4$–1.0 $(CH_3)_2Zn$. This reaction was performed in a manner identical with that above. The precipitate, after isolating and drying, was found to contain Li, Zn, H, and Al in molar ratios of 0.04:1.00:2.03:0.03 and 98.2% of the starting zinc. An x-ray powder diffraction pattern showed the solid to be ZnH_2. The filtrate contained Li, Al, CH_3, H, and Zn in molar ratios of 1.01:1.00:2.01:1.99:0.02.

(3) 0.67 $LiAlH_4$–1.0 $(CH_3)_2Zn$. In this reaction 95.7% of the starting zinc was recovered in the precipitate which contained Li, Zn, H, and Al in molar ratios of 0.01:1.00:2.08:0.02. An x-ray powder diffraction pattern showed the solid to be ZnH_2. The filtrate contained Li, Al, CH_3, H, and Zn in molar ratios of 1.03:1.00:2.97:0.96:0.04.

(4) 0.50 $LiAlH_4$–1.0 $(CH_3)_2Zn$. In this reaction 97.4% of the starting zinc was recovered in the precipitate which contained Li, Zn, H, and Al in molar ratios of 0.03:1.00:2.05:0.02. An x-ray powder diffraction pattern showed the solid to be ZnH_2. The filtrate contained Li, Al, CH_3, H, and Zn in molar ratios of 1.04:1.00:3.98:0.00:0.03.

B. Reactions Where $LiAlH_4$ is Added to $(CH_3)_2Zn$. (1) 0.50 $LiAlH_4$–1.0 $(CH_3)_2Zn$. A diethyl ether solution of $LiAlH_4$ (1.16 M) was added dropwise by syringe (under nitrogen flush) to a magnetically stirred solution of 0.83 M $(CH_3)_2Zn$ in diethyl ether until the ratio of reactants was 1.0:2.0 ($LiAlH_4$:$(CH_3)_2Zn$). The clear solution was stirred for 1 h, but still no precipitate was visible. An analysis of the solution showed it to contain Li, Zn, Al, CH_3, and H in molar ratios of 1.02:2.00:0.99:3.98:4.02. The infrared spectrum of the solution (Figure 3-1) was the same as that shown in Figure 2-2 (taken after 5 min of stirring).

(2) 1.0 $LiAlH_4$–1.0 $(CH_3)_2Zn$. This reaction was performed in a manner identical with that above. This time a white precipitate formed. After stirring for 1 h at room temperature, the mixture was filtered. The resulting solid was washed with diethyl ether and dried under vacuum at room temperature. An analysis of the solid showed it to contain Li, Zn, H, and Al in molar ratios of 0.62:2.00:4.63:0.00 and 97.1% of the starting zinc. An x-ray powder diffraction pattern of the solid showed it to be a mixture of $LiZnH_3$ and ZnH_2. An analysis of the filtrate showed it to contain Li, Al, CH_3, H, and Zn in molar ratios of 0.69:1.00:1.98:1.70:0.03. The infrared spectrum of this solution is shown in Figure 3-2.

(3) 2.0 $LiAlH_4$–1.0 $(CH_3)_2Zn$. In this reaction all of the starting zinc was recovered in the precipitate which contained Li, Zn, H, and Al in molar ratios of 0.01:1.00:2.02:0.00. An x-ray powder diffraction pattern showed the solid to be ZnH_2. An analysis of the filtrate showed it to contain Li, Al, CH_3, H, and Zn in molar ratios of 1.01:1.00:1.03:3.04:0.00. The infrared spectrum of this solution is shown in Figure 3-3.

Reaction of $LiZn(CH_3)_2AlH_4$ with $LiAlH_4$ in Diethyl Ether. A 1.16 M solution of $LiAlH_4$ (10 mmol) was added with stirring to a 0.83 M solution of $(CH_3)_2Zn$ (10 mmol) in diethyl ether. A clear solution resulted, but after 30 s of stirring a white precipitate began to form. The mixture was stirred for 5 min, then the stirring stopped and the small amount of solid that was present allowed to settle for 1 min. A sample of the supernatant solution gave an infrared spectrum similar to that shown in Figure 2-4. Analysis of this sample showed that Zn and Al were present in a 0.91:1.00 ratio.

As soon as the sample had been taken, 10 mmol of 1.16 M $LiAlH_4$ was added to the mixture with stirring. There was an immediate formation of more solid. After stirring for 5 min at room temperature, the mixture was filtered. The resulting solid was washed with diethyl ether and dried under vacuum at room temperature. An analysis of the solid showed that it contained Li, Zn, H, and Al in molar ratios of 0.03:1.00:2.01:0.00 and all of the starting zinc. An x-ray powder diffraction pattern of the solid showed it to be essentially ZnH_2. The filtrate contained Li, Al, CH_3, H, and Zn in molar ratios of 1.02:1.00:1.03:3.05:0.00. The infrared spectrum showed $LiAl(CH_3)H_3$ to be present.

Reaction Where $LiAlH_4$ is Added to a Dilute Solution of $(CH_3)_2Zn$ in 1:1 Ratio. A 0.83 M solution of $(CH_3)_2Zn$ (5 mmol) in diethyl ether was added to 100 mL of diethyl ether. A 1.16 M solution of $LiAlH_4$ (5 mmol) was added dropwise by syringe (under nitrogen flush) to the above solution while stirring. A white precipitate formed. After stirring for 1 h at room temperature, the mixture was filtered. The resulting solid was washed with diethyl ether and dried under vacuum at room temperature. An analysis of the solid showed that it contained Li, Zn, H, and Al in molar ratios of 0.03:1.00:2.03:0.00 and 98.3% of the starting zinc. An x-ray powder diffraction pattern showed the solid to be ZnH_2. An analysis of the filtrate showed it to contain Li, Al, CH_3, H, and Zn in molar ratios of 1.01:1.00:1.93:2.01:0.02. An infrared spectrum of the concentrated solution showed $LiAl(CH_3)_2H_2$ to be present.

Results and Discussion

Schlesinger and co-workers[2] have reported that the most satisfactory method of preparing ZnH_2 involves the addition of one part $(CH_3)_2Zn$ to two parts $LiAlH_4$ in diethyl ether solution. They did not report the results that would be obtained if one were to vary the ratio of reactants or reverse the mode of addition. Because of some observations that we made

Table I. Products Obtained from Various Reactions between $LiAlH_4$ and $(CH_3)_2Zn$ in Diethyl Ether

Ratio $(CH_3)_2Zn/LiAlH_4$	Anal. of solid Li:Zn:H:Al	Components of solid as inferred from powder diffraction	$Li:Al:CH_3:H:Zn$	Components of solution as inferred from IR spectra
		Reactions Where $(CH_3)_2Zn$ Was Added to $LiAlH_4$[a]		
0.5	0.02:1.00:2.04:0.03	ZnH_2	1.04:1.00:0.98:3.11:0.00	$LiAl(CH_3)H_3$
1.0	0.01:1.00:2.03:0.03	ZnH_2	1.01:1.00:2.01:1.99:0.02	$LiAl(CH_3)_2H_2$
1.5	0.01:1.00:2.08:0.02	ZnH_2	1.03:1.00:2.97:0.96:0.04	$LiAl(CH_3)_3H$
2.0	0.03:1.00:2.05:0.02	ZnH_2	1.04:1.00:3.98:0.00:0.03	$LiAl(CH_3)_4$
		Reactions Where $LiAlH_4$ Was Added to $(CH_3)_2Zn$[a]		
2.0			1.02:0.99:3.98:4.02:2.00	$LiZn(CH_3)_4AlH_4$
1.0	0.62:2.00:4.63:0.00	$LiZnH_3 + ZnH_2$	0.69:1.00:1.98:1.70:0.03	$(CH_3)_2AlH + LiAl(CH_3)_2H_2$
0.5	0.01:1.00:2.02:0.00	ZnH_2	1.01:1.00:1.03:3.04:0.00	$LiAl(CH_3)H_3$

[a] Reactions were stirred for 1 h before the products were separated.

in a previous study, we had reason to believe that the results of this reaction may be different if carried out under different conditions than those reported by Schlesinger and co-workers. We have now studied this reaction under a variety of conditions and the results are summarized in Table I. The data indicate that the course of the reaction is greatly influenced by both the mode of addition and the ratio of reactants. These results are quite unusual, since previous studies in this laboratory have shown that the reactions of $LiAlH_4$ with $(C_2H_5)_2Mg$,[6] $(CH_3)_2Mg$,[7] and $(C_6H_5)_2Mg$[8] in diethyl ether are not sensitive to either of these parameters.

When $(CH_3)_2Zn$ was added to $LiAlH_4$ in four equal increments such that the ratio of total zinc to aluminum was 0.5:1, 1:1, 1.5:1, and 2:1 after each of the four additions, the reaction proceeded in a stepwise fashion exchanging methyl groups on zinc for hydrogen on aluminum as shown in eq 1–4.

$$(CH_3)_2Zn + 2LiAlH_4 \rightarrow ZnH_2 + 2LiAl(CH_3)H_3 \tag{1}$$

$$(CH_3)_2Zn + 2LiAl(CH_3)H_3 \rightarrow ZnH_2 + 2LiAl(CH_3)_2H_2 \tag{2}$$

$$(CH_3)_2Zn + 2LiAl(CH_3)_2H_2 \rightarrow ZnH_2 + 2LiAl(CH_3)_3H \tag{3}$$

$$(CH_3)_2Zn + 2LiAl(CH_3)_3H \rightarrow ZnH_2 + 2LiAl(CH_3)_4 \tag{4}$$

Support for these reactions proceeding as shown is provided by the infrared spectra of the supernatant solutions remaining after each incremental addition. These spectra (Figure 1) are identical with the infrared spectra of $LiAl(CH_3)H_3$, $LiAl(CH_3)_2H_2$, $LiAl(CH_3)_3H$, and $LiAl(CH_3)_4$ in diethyl ether solution prepared by allowing $LiAl(CH_3)_4$ to redistribute with $LiAlH_4$ according to the stoichiometry shown in eq 5–7.

$$3LiAlH_4 + LiAl(CH_3)_4 \rightarrow 4LiAl(CH_3)H_3 \tag{5}$$

$$LiAlH_4 + LiAl(CH_3)_4 \rightarrow 2LiAl(CH_3)_2H_2 \tag{6}$$

$$LiAlH_4 + 3LiAl(CH_3)_4 \rightarrow 4LiAl(CH_3)_3H \tag{7}$$

Lithium tetramethylaluminate was prepared by reacting CH_3Li with $(CH_3)_3Al$ in diethyl ether.[9] Further support for these reactions proceeding as shown is provided by the fact that the aluminum complexes $LiAl(CH_3)_2H_2$, $LiAl(CH_3)_3H$, and $LiAl(CH_3)_4$ were formed according to eq 2–4 when $(CH_3)_2Zn$ was added to authentic preformed samples of $LiAl(CH_3)H_3$, $LiAl(CH_3)_2H_2$, and $LiAl(CH_3)_3H$ in 1:2 ratio in diethyl ether.

When $(CH_3)_2Zn$ was added separately to $LiAlH_4$ in 0.5:1, 1:1, 1.5:1, and 2:1 molar ratios, the reactions proceeded according to eq 8–11. Support for these reactions is provided by data in Table I. In each case, the solid isolated from these reactions was found to be ZnH_2. Infrared spectra of the supernatant solutions showed the presence of the aluminum complexes listed in reactions 8–11.

$$(CH_3)_2Zn + 2LiAlH_4 \rightarrow ZnH_2 + LiAl(CH_3)H_3 \tag{8}$$

$$(CH_3)_2Zn + LiAlH_4 \rightarrow ZnH_2 + LiAl(CH_3)_2H_2 \tag{9}$$

$$3(CH_3)_2Zn + 2LiAlH_4 \rightarrow 3ZnH_2 + 2LiAl(CH_3)_3H \tag{10}$$

$$2(CH_3)_2Zn + LiAlH_4 \rightarrow 2ZnH_2 + LiAl(CH_3)_4 \tag{11}$$

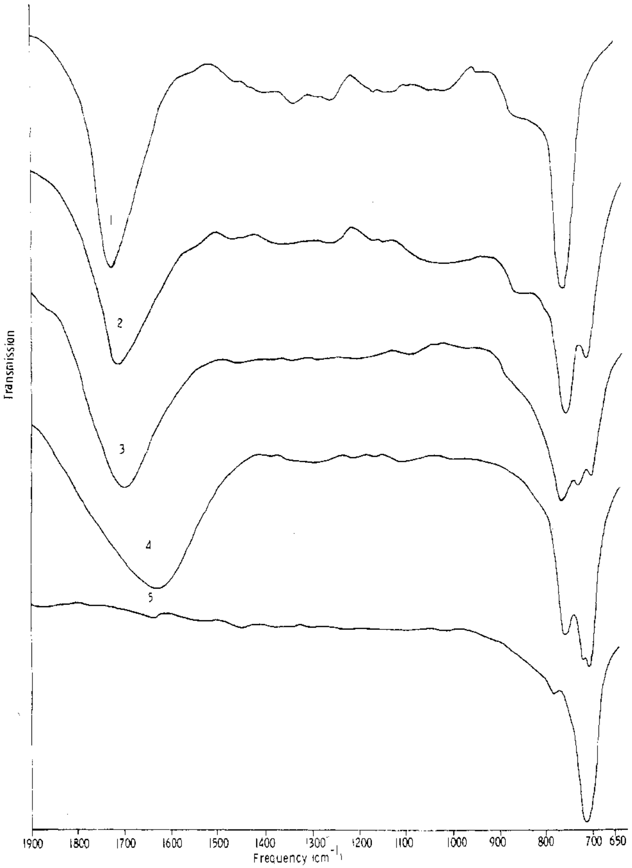


Figure 1. Infrared spectra of supernatant solutions obtained by adding $(CH_3)_2Zn$ to $LiAlH_4$ in diethyl ether. $(CH_3)_2Zn:LiAlH_4$ ratio: (1) pure $LiAlH_4$, (2) 0.5:1.0, (3) 1.0:1.0, (4) 1.5:1.0, (5) 2.0:1.0.

The infrared spectra of the solutions that resulted when $LiAlH_4$ was added to $(CH_3)_2Zn$ in four increments, such that the ratio of total aluminum to zinc was 0.5:1, 0.75:1, 1:1, and 2:1, are shown in Figure 2. After the addition of each increment, the resulting mixture was stirred for 5 min before the infrared spectrum was recorded. Upon the addition of the first increment, a clear solution resulted. The infrared spectrum of the solution (bands at 1500 (sh, s), 1400 (br, s), 795 (w), and 705 cm^{-1} (s)) corresponded very closely to that of $LiZn_2(CH_3)_4AlH_4$ in THF.[1] Evidently, when one part $LiAlH_4$ is added to two parts $(CH_3)_2Zn$, the two reagents do not react to give ZnH_2 and $LiAl(CH_3)_4$ but instead form $LiZn_2(CH_3)_4AlH_4$ according to eq 12. Upon addition of the second increment, some solid began to precipitate. The infrared spectrum of the solution (1700 (sh), 1640 (br, s), 1500

$$LiAlH_4 + 2(CH_3)_2Zn \rightarrow LiZn_2(CH_3)_4AlH_4 \tag{12}$$

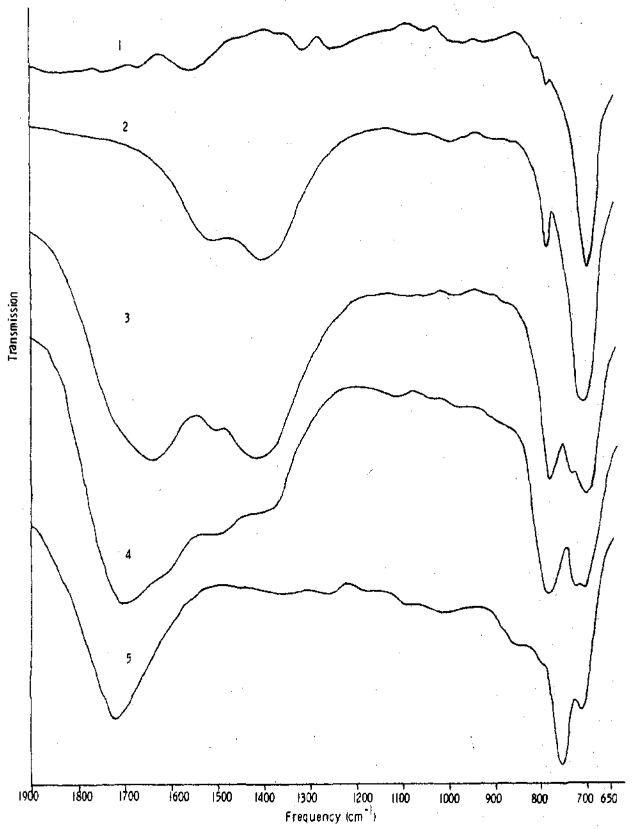


Figure 2. Infrared spectra of supernatant solutions obtained by adding $LiAlH_4$ to $(CH_3)_2Zn$ in diethyl ether. $LiAlH_4$:$(CH_3)_2Zn$ ratio: (1) pure $(CH_3)_2Zn$, (2) 0.5:1.0, (3) 0.75:1.0, (4) 1.0:1.0, (5) 2.0:1.0. Reaction time was 5 min.

(sh, s), 1400 (br, s), 780 (s), 735 (sh, m), 700 cm^{-1} (s)) was characteristic of a mixture of $LiAl(CH_3)_2H_2$ (ν(Al–H) 1700 cm^{-1}), $LiZn(CH_3)_2AlH_4$ (1660 (br, s), 1500 (sh, s), 1400 (br, s), 775 (s), 720 cm^{-1} (sh, s) in THF), and $LiZn_2(CH_3)_4AlH_4$ (1500 (sh, s), 1400 (br, s), 700 cm^{-1} (s)). The reaction which occurred upon addition of this increment is shown in eq 13.

$$\mathrm{LiAlH_4 + 2LiZn_2(CH_3)_4AlH_4 \rightarrow 2LiZn(CH_3)_2AlH_4 + LiZn_2(CH_3)_4AlH_4} \tag{13}$$

The precipitate and $LiAl(CH_3)_2H_2$ arise through the disproportionation of $LiZn(CH_3)_2AlH_4$. Equation 13 is supported by the fact that in THF $LiZn(CH_3)_2AlH_4$ decomposes to give $LiAl(CH_3)_2H_2$ as one of its products.[1] Equation 13 shows that $LiAlH_4$ reacts with $LiZn_2(CH_3)_4AlH_4$ to produce two parts $LiZn(CH_3)_2AlH_4$; a reaction which is known to occur in THF.[1] Upon addition of the third increment more solid precipitated. The infrared spectrum of the solution (1700 (br, s), 1640 (sh), 1500 (sh), 1400 (sh, s), 780 (s), 720 cm^{-1} (s)) corresponded to a mixture of $LiAl(CH_3)_2H_2$ and $LiZn(CH_3)_2AlH_4$ (eq 14).

$$\mathrm{LiAlH_4 + 2LiZn(CH_3)_2AlH_4 + LiZn_2(CH_3)_4AlH_4 \rightarrow 4LiZn(CH_3)_2AlH_4} \tag{14}$$

Again $LiAl(CH_3)_2H_2$ and the precipitate arise through disproportionation of $LiZn(CH_3)_2AlH_4$. Upon addition of the last increment copious quantities of solid precipitated. The infrared spectrum of the resulting supernatant solution showed it to contain $LiAl(CH_3)H_3$ and the solid was found to be mostly ZnH_2 (eq 15). It is known that in THF, AlH_3 reacts

$$\mathrm{LiAlH_4 + LiZn(CH_3)_2AlH_4 \rightarrow ZnH_2 + 2LiAl(CH_3)H_3} \tag{15}$$

with $LiZn(CH_3)_2AlH_4$[1] to produce ZnH_2 according to eq 16.

$$\mathrm{AlH_3 + LiZn(CH_3)_2AlH_4 \xrightarrow{THF} ZnH_2 + (CH_3)_2AlH + LiAlH_4} \tag{16}$$

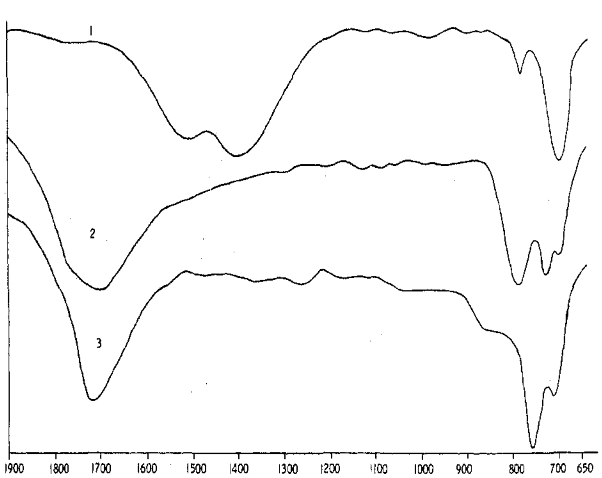


Figure 3. Infrared spectra of supernatant solution obtained by adding $LiAlH_4$ to $(CH_3)_2Zn$ in diethyl ether. $LiAlH_4$:$(CH_3)_2Zn$ ratio: (1) 0.5:1.0, (2) 1.0:1.0, (3) 2.0:1.0. Reaction time was 1 h.

Therefore, it seems reasonable that a similar reaction would occur in diethyl ether between $LiAlH_4$ and $LiZn(CH_3)_2AlH_4$.

The infrared spectra of the solutions that result when $LiAlH_4$ is added separately to $(CH_3)_2Zn$ in molar ratios of 0.5:1, 1:1, and 2:1 ($LiAlH_4$:$(CH_3)_2Zn$) are shown in Figure 3. After the three additions were made, the resulting mixtures were stirred for 1 h before the infrared spectra were recorded on the supernatant solutions. The data in Table I summarize the composition of the supernatant solutions and the solids that resulted from these reactions. The additions of $LiAlH_4$ to $(CH_3)_2Zn$ in 0.5:1 ratio again produced a solution which remained clear even after stirring for 1 h. The infrared spectrum of the solution corresponded to $LiZn_2(CH_3)_4AlH_4$.

The addition of $LiAlH_4$ to $(CH_3)_2Zn$ in 1:1 ratio produced, after 1 h of stirring, a solid which corresponded to 1:2.2 mixture of $LiZnH_3$ and ZnH_2. The infrared spectrum of the supernatant solution (1760 (sh), 1700 (s), 780 (s), 725 (s), 700 cm^{-1} (sh)) corresponded to a mixture of $(CH_3)_2AlH$ (ν(Al–H) 1760 cm^{-1}) and $LiAl(CH_3)_2H_2$. Analysis of the supernatant solution indicated that $(CH_3)_2AlH$ and $LiAl(CH_3)_2H_2$ were present in a 1:2.2 ratio; hence, eq 17. The

$$\mathrm{LiAlH_4 + (CH_3)_2Zn \rightarrow 0.31LiZnH_3 + 0.69ZnH_2 + 0.31(CH_3)_2AlH + 0.69LiAl(CH_3)_2H_2} \tag{17}$$

products arise through disproportionation of the initially formed $LiZn(CH_3)_2AlH_4$. This suggestion is reasonable since $LiZn(CH_3)_2AlH_4$ was observed spectroscopically after a reaction time of 5 min and, in addition, $LiZn(CH_3)_2AlH_4$ is known to decompose in THF giving a solid which contains $LiZnH_3$ and ZnH_2.[1] The addition of $LiAlH_4$ to $(CH_3)_2Zn$ in 2:1 ratio produced, after 1 h of stirring, a solid which was found to be ZnH_2. An infrared spectrum of the supernatant solution showed $LiAl(CH_3)H_3$ to be present. The reaction then proceeds as shown in eq 18.

$$\mathrm{2LiAlH_4 + (CH_3)_2Zn \rightarrow ZnH_2 + 2LiAl(CH_3)H_3} \tag{18}$$

It is very unusual to see only ZnH_2 formed in this reaction (eq 18), when the two previous reactions produced $LiZnH_3$ as well. The following explanation is presented for this behavior. The first equivalent of $LiAlH_4$ reacts with $(CH_3)_2Zn$ to form $LiZn(CH_3)_2AlH_4$, which can then decompose to give $LiZnH_3$ and ZnH_2. But, before this happens, it is possible for the second equivalent of $LiAlH_4$ to react with $LiZn(CH_3)_2AlH_4$ to yield ZnH_2 and $LiAl(CH_3)H_3$. This explanation assumes that $LiZn(CH_3)_2AlH_4$ decomposes to $LiZnH_3$ and ZnH_2 at a rate much slower than it reacts with additional $LiAlH_4$. This assumption is reasonable since when $LiAlH_4$

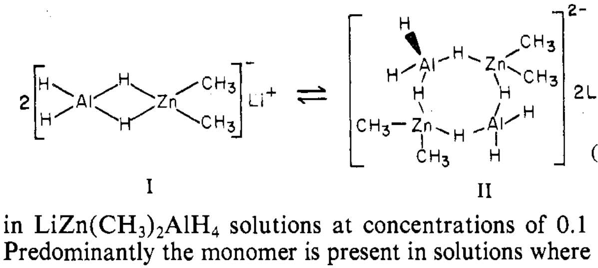
was added incrementally to $(CH_3)_2Zn$ in 1:1 ratio $LiZn(CH_3)_2AlH_4$ was observed spectroscopically after a reaction time of only 5 min and about 90% of the zinc was still in solution. The subsequent addition of an equivalent of $LiAlH_4$ to this solution caused an immediate precipitation of all the remaining zinc as ZnH_2 and the formation of $LiAl(CH_3)H_3$ in the solution.

The addition of $LiAlH_4$ to a 0.05 M solution of $(CH_3)_2Zn$ in 1:1 molar ratio produced, after 1 h of stirring, a solid which was found to be ZnH_2 (no $LiZnH_3$ was present). The resulting supernatant solution was found to contain only $LiAl(CH_3)_2H_2$. Evidently $LiZn(CH_3)_2AlH_4$ is formed in this reaction also, but in the dilute solution (less than 0.10 M), it disproportionated to give only ZnH_2. In the more concentrated solution, i.e., greater than 0.2 M, $LiZn(CH_3)_2AlH_4$ disproportionates to give mixtures of $LiZnH_3$ and ZnH_2. This same behavior was observed in the reaction between $LiAlH_4$ and $(CH_3)_2Zn$ in THF.[1] The disproportionation to ZnH_2 in dilute solution was shown to occur through the monomer form of $LiZn(CH_3)_2AlH_4$, whereas $LiZnH_3$ resulted from the dimer of $LiZn(CH_3)_2AlH_4$. This indicates that $LiZn(CH_3)_2AlH_4$ is capable of existing as an equilibrium between monomer and dimer forms in diethyl ether also.

There have been two recent studies where the synthesis of ZnH_2 has been reported.[10,11] Earlier we reported that the addition of $LiAlH_4$ to a solution of $(CH_3)_2Zn$ in diethyl ether in a 1.5:1.0 ratio resulted in the precipitation of a solid which contained Zn and H in a ratio of 1.00:2.02. On the other hand, Shriver and co-workers, who did not report any experimental details except to say that the procedure of Schlesinger[2] was used, obtained a solid with Zn and H in a ratio of 1.00:2.26. The solid gave a positive flame test for Li, but the authors did not report the ratio of Li:Zn. The x-ray powder diffraction pattern of the solid did, however, contain lines due to $LiZnH_3$,[12] showing that the solid was a mixture of $LiZnH_3$ and ZnH_2. Therefore, it is likely that these workers added $LiAlH_4$ to $(CH_3)_2Zn$ in about a 1:1 ratio in diethyl ether. These two reports indicate a trend similar to what we have reported here. The addition of $LiAlH_4$ to $(CH_3)_2Zn$ in a ratio greater than 1:1 yields ZnH_2, but addition at this ratio or less leads to mixtures of $LiZnH_3$ and ZnH_2.

Conclusions

The results of this study allow us to say something about the mechanism by which $LiAlH_4$ and $(CH_3)_2Zn$ react to give ZnH_2 in diethyl ether. In THF when $LiAlH_4$ and $(CH_3)_2Zn$ were allowed to react (the mode of addition did not matter), $LiZn(CH_3)_2AlH_4$, $LiZn_2(CH_3)_4AlH_4$, or mixtures of the two were obtained depending on the ratio of reactants. On standing, solutions of $LiZn(CH_3)_2AlH_4$ (where the concentrations were greater than 0.1 M) precipitated a mixture of $LiZnH_3$ and ZnH_2. More dilute solutions of $LiZn(CH_3)_2AlH_4$ (concentrations in the range 0.04–0.01 M) precipitated ZnH_2 only. Molecular weight measurements, coupled with NMR and infrared spectral studies, showed that an equilibrium between the monomer and dimer units I and II (eq 19) exists in $LiZn(CH_3)_2AlH_4$ solutions at concentrations of 0.1 M. Predominantly the monomer is present in solutions where the concentration is in the range 0.04–0.01 M. It was proposed that $LiZnH_3$ arises from intramolecular exchange of the methyl groups on zinc for the hydrogens on aluminum in an intermediate like II, since $LiZnH_3$ is only precipitated from solutions where II is observed. Likewise, in dilute solutions where only I is observed, ZnH_2 is precipitated as a result of intramolecular exchange within I. It is easy to see how the proper mixed bridge intermediates could arise from I.



I II (19)

Scheme I

$$LiAlH_4 + (CH_3)_2Zn \rightarrow LiZn(CH_3)_2AlH_4$$

$$LiZn(CH_3)_2AlH_4 + LiAlH_4 \rightarrow ZnH_2 + 2LiAl(CH_3)H_3$$

When $LiAlH_4$ is added to solutions of $(CH_3)_2Zn$ in diethyl ether such that $LiAlH_4$ is never in excess, the results indicate that the same phenomena are occurring. The addition of $LiAlH_4$ to $(CH_3)_2Zn$ in 1:1 ratio initially gives a solution of $LiZn(CH_3)_2AlH_4$. At concentrations greater than 0.1 M this solution precipitates a mixture of $LiZnH_3$ and ZnH_2; however, solutions less than 0.1 M precipitate ZnH_2 only. It is reasonable, therefore, to propose that in diethyl ether $LiZnH_3$ results from intramolecular exchange in an intermediate like II, whereas ZnH_2 results from intramolecular exchange in I.

When $LiAlH_4$ is added to $(CH_3)_2Zn$, such that $LiAlH_4$ is in excess, the mechanism of the reaction appears to be different. The solid product from the reaction is always ZnH_2. Since the addition of $LiAlH_4$ to a solution of $LiZn(CH_3)_2AlH_4$ results in the immediate precipitation of ZnH_2, it seems reasonable that the above reaction would be proceeding by the pathway shown in Scheme I.

When $(CH_3)_2Zn$ is added to $LiAlH_4$, the reaction proceeds in a similar manner. As the $(CH_3)_2Zn$ is added, $LiAlH_4$ is always in excess. This results in the initial formation of $LiZn(CH_3)_2AlH_4$ followed by a rapid reaction with $LiAlH_4$ to give ZnH_2. As the addition of $(CH_3)_2Zn$ is continued, a point is reached where the ratio of total Al to Zn is 2. At this point all the $LiAlH_4$ has reacted, all the zinc has precipitated as ZnH_2, and all the aluminum is present as $LiAl(CH_3)H_3$. Subsequent addition of more $(CH_3)_2Zn$ results in reaction between $(CH_3)_2Zn$ and $LiAl(CH_3)H_3$ (which is in large excess now) to give ZnH_2 in a manner similar to that shown in Scheme I except that now $LiAl(CH_3)_2H_2$ is formed. With continued $(CH_3)_2Zn$ addition the ratio of total Al to Zn soon becomes 1. At this point all the $LiAl(CH_3)H_3$ has reacted, all the zinc has precipitated as ZnH_2, and all the aluminum is present as $LiAl(CH_3)_2H_2$. If the addition of $(CH_3)_2Zn$ is continued further, one sees reaction of $(CH_3)_2Zn$ with $LiAl(CH_3)_2H_2$ and finally with $LiAl(CH_3)_3H$ to give ZnH_2. Throughout the entire course of the reaction when $(CH_3)_2Zn$ is added to $LiAlH_4$ (if the addition is done in a slow dropwise fashion), there will always be an aluminohydride species present in excess over $(CH_3)_2Zn$. This is then what always causes the precipitation of zinc hydride.

The results of this study have shown that if one is to obtain relatively pure ZnH_2 by reacting $LiAlH_4$ and $(CH_3)_2Zn$ in diethyl ether, the reaction must be carried out by adding $(CH_3)_2Zn$ slowly to $LiAlH_4$ not allowing the ratio of total Al to total Zn to drop below 2.

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Registry No. $LiAlH_4$, 16853-85-3; $(CH_3)_2Zn$, 544-97-8; $LiAl(CH_3)H_3$, 62816-23-3; $LiAl(CH_3)_2H_2$, 19528-78-0; $LiAl(CH_3)_3H$, 62816-22-2; $LiAl(CH_3)_4$, 14281-94-8; $LiZn(CH_3)_2AlH_4$, 59092-43-2; ZnH_2, 14018-82-7; $LiZnH_3$, 38829-83-3; $(CH_3)_2AlH$, 865-37-2; $LiZn_2(CH_3)_4AlH_4$, 62166-60-3.

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Nature of Alkyl–Hydrogen Exchange Reactions Involving Aluminum and Zinc. 4. Reactions of $MZn(CH_3)_2H$ and $MZn_2(CH_3)_4H$ with AlH_3 and $MAlH_4$ with $(CH_3)_2Zn$ (Where M = Na and K) in Tetrahydrofuran

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When AlH_3 was allowed to react with $NaZn(CH_3)_2H$ in THF, the reaction products were found to be dependent on the initial concentration of $NaZn(CH_3)_2H$. The reaction with dilute solutions of $NaZn(CH_3)_2H$ produced ZnH_2; whereas $NaZn_2H_5$ was produced from the more concentrated solutions. The reaction of AlH_3 with $NaZn_2(CH_3)_4H$ produced the soluble trimetal complex $NaZn_2(CH_3)_4AlH_4$. The reaction between $NaAlH_4$ and $(CH_3)_2Zn$ in 1:1 and 1:2 molar ratios produced $NaZn(CH_3)_2AlH_4$ and $NaZn_2(CH_3)_4AlH_4$. Concentrated solutions of $NaZn(CH_3)_2AlH_4$ were found to disproportionate giving $NaZn_2H_5$; whereas the more dilute solutions formed ZnH_2. The mechanism for the formation of KZn_2H_5 or $NaZn_2H_5$ from the reaction of AlH_3 with $KZn(CH_3)_2H$ or $NaZn(CH_3)_2H$ is discussed in light of the results which are presented. The mechanism by which KZn_2H_5 is formed in the reaction of $KZn_2(CH_3)_4H$ with AlH_3 is discussed.

Introduction

Earlier reports in this series[1] were concerned with the properties and solution composition of the two trimetal complexes $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$. It was found that the complexes could be prepared either by reacting $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ with AlH_3 or by reacting $LiAlH_4$ with $(CH_3)_2Zn$ in an appropriate ratio. We have reported elsewhere[2] that $NaZn(CH_3)_2H$ and $KZn(CH_3)_2H$ react with AlH_3 to give the complex metal hydrides $NaZn_2H_5$ and KZn_2H_5, respectively. One might have predicted that $LiZn(CH_3)_2H$ would have undergone a similar reaction with AlH_3, but it apparently gave only the soluble complex $LiZn(CH_3)_2AlH_4$. However, this complex was found to decompose slowly at room temperature to give a black solid with contained Li and Zn in a molar ratio of 1:2. The black solid was identified as a mixture of $LiZnH_3$ and partially decomposed ZnH_2. This information would lead one to propose that the complex $LiZn(CH_3)_2AlH_4$ was not actually decomposing but undergoing a disproportionation reaction to yield $LiZn_2H_5$, which then decomposed to $LiZnH_3$ and ZnH_2. If this were the case, the $LiZn(CH_3)_2AlH_4$ would be the primary intermediate in the reaction of $LiZn(CH_3)_2H$ with AlH_3 to give $LiZn_2H_5$. Also, then, the reactions of $NaZn(CH_3)_2H$ and $KZn(CH_3)_2H$ with AlH_3, which yield $NaZn_2H_5$ and KZn_2H_5, should proceed via an intermediate similar to $LiZn(CH_3)_2AlH_4$, e.g., $NaZn(CH_3)_2AlH_4$ and $KZn(CH_3)_2AlH_4$. In this connection, an infrared spectral study of these two reactions has been carried out in an effort to provide evidence concerning the existence of these intermediates.

Experimental Section

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques.[3] Filtrations and other manipulations were carried out in a glovebox equipped with a recirculating system.[4]

Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Spectra of solutions were obtained in matched 0.10-mm path length NaCl cells. X-ray powder data were obtained using a Philips-Norelco x-ray unit using a 114.6-mm camera with nickel-filtered Cu K α radiation. Samples were sealed in 0.5-mm capillaries and exposed to x rays for 6 h. The *d* spacings were read on a precalibrated scale equipped with a viewing apparatus. Intensities were estimated visually.

Analytical Procedure. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump. Methane in the presence of hydrogen was determined using a previously described tensimeter.[3] Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration. Zinc in the presence of aluminum was determined by masking the aluminum with triethanolamine and titrating the zinc with EDTA. Zinc alone was determined by EDTA titration.

Materials. Potassium and sodium hydride were obtained from Alfa Inorganics as a slurry in mineral oil. Solutions of lithium and sodium aluminum hydride (Ventron, Metal Hydride Division) were prepared in THF in the usual manner. Dimethyl zinc was prepared by the procedure of Noller.[5] Methyl iodide was obtained from Fisher Scientific. The iodide was dried over anhydrous $MgSO_4$ and distilled prior to use. Zinc–copper couple was obtained from Alfa Inorganics. The reactions of zinc–copper couple with methyl iodide were allowed to proceed overnight. The dimethylzinc was distilled from the reaction mixture under nitrogen. Tetrahydrofuran (Fisher Certified Reagent Grade) was distilled under nitrogen over $NaAlH_4$. Aluminum hydride was prepared by the reaction of 100% H_2SO_4 with $LiAlH_4$ in THF. Li_2SO_4 was removed by filtration and a lithium-free solution of AlH_3 in THF was obtained.[6]

Reaction of $NaZn(CH_3)_2H$ with AlH_3 in THF. (a) AlH_3 Added to 0.45 M $NaZn(CH_3)_2H$. Five millimoles of a 0.820 M solution of $(CH_3)_2Zn$ in THF was added to 5 mmol of a 1.00 M slurry of NaH in THF. A clear solution of $NaZn(CH_3)_2H$ formed. Next 5 mmol of a 0.332 M solution of AlH_3 was added. An off-white precipitate appeared immediately. Infrared spectra were obtained on the $(CH_3)_2Zn$ solution, the $NaZn(CH_3)_2H$ solution, and the supernatant left after 5 min and 24 h. The infrared spectra are shown in Figure 1. After sitting 1 day the precipitate was filtered, washed with THF, and dried at room temperature under vacuum. The ratio of Na:Zn:H in the solid was 1.02:2.00:4.86 and it contained all the starting zinc. An x-ray powder diffraction pattern showed the solid to be $NaZn_2H_5$. The filtrate contained Na, Al, CH_3, H, and Zn in molar ratios of 1.03:2.00:3.89:3.08:0.061. An infrared spectrum of the filtrate showed a broad band in the Al–H stretching region centered at 1625 cm^{-1}. $(CH_3)_2AlH$ absorbs at 1720 cm^{-1} in THF; thus the filtrate was not a mixture of $NaAl(CH_3)_2H_2$ and $(CH_3)_2AlH$.

(b) AlH_3 Added to 0.01 M $NaZn(CH_3)_2H$. The reaction was performed in a manner identical with that above except the $NaZn(CH_3)_2H$ solution was diluted to 0.01 M before the addition