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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 $MAIH_4$ 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 series¹ 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 elsewhere² 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 $Cu K \alpha$ 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, CH₃, 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

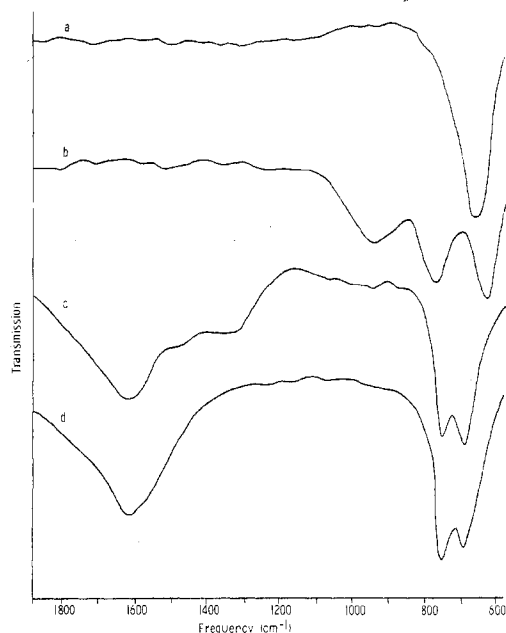


Figure 1. Infrared spectra of $\text{NaZn}(\text{CH}_3)_2\text{H}$ and THF-soluble products from its reaction with AlH_3 : (a) $(\text{CH}_3)_2\text{Zn}$ in THF, (b) $\text{NaZn}(\text{CH}_3)_2\text{H}$ in THF, (c) $\text{NaZn}(\text{CH}_3)_2\text{H} + \text{AlH}_3$ in THF after 5 min, and (d) $\text{NaZn}(\text{CH}_3)_2\text{H} + \text{AlH}_3$ in THF after 24 h— $\text{NaAl}_2(\text{CH}_3)_4\text{H}_3$.

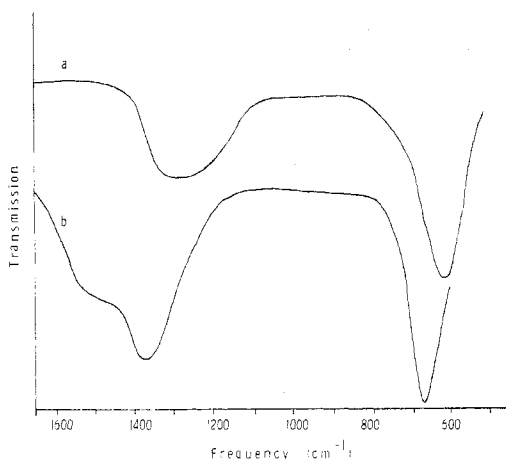


Figure 2. Infrared spectra of (a) $\text{NaZn}_2(\text{CH}_3)_4\text{H}$ and (b) $\text{NaZn}_2(\text{CH}_3)_4\text{AlH}_4$.

of AlH_3 . After this addition the clear solution remained for about 3 h, then a white precipitate began to form. The mixture was stirred overnight, then the precipitate was filtered, washed, and dried. The solid which was gray at this point contained Na, Zn, H, and Al in molar ratios of 0.02:1.00:1.86:0.01 and 51.8% of the starting zinc. (Repeating the reaction for longer periods of time did not produce any more solid.) An x-ray powder diffraction pattern of the solid showed it to be essentially ZnH_2 .

Reaction of $\text{NaZn}_2(\text{CH}_3)_4\text{H}$ with AlH_3 in Tetrahydrofuran. Ten millimoles of a 0.820 M solution of $(\text{CH}_3)_2\text{Zn}$ in THF was added to 5 mmol of NaH slurried in THF, followed by 5 mmol of a 0.557 M solution of AlH_3 in THF. A clear solution resulted which was believed to be $\text{NaZn}_2(\text{CH}_3)_4\text{AlH}_4$. An analysis of the solution indicated that Na, Al, CH₃, H, and Zn were present in ratios of 1.00:1.00:3.84:3.91:0.98. Infrared spectra were obtained on the $\text{NaZn}_2(\text{CH}_3)_4\text{H}$ solution and the adduct between $\text{NaZn}_2(\text{CH}_3)_4\text{H}$ and AlH_3 . These spectra are shown in Figure 2. Five millimoles of AlH_3 was then added to the $\text{NaZn}_2(\text{CH}_3)_4\text{AlH}_4$ solution. A white precipitate formed immediately. This mixture was stirred about 1 h and then filtered, and the precipitate was washed and dried. The solid contained Na, Zn, H, and Al in a ratio of 0.00:1.00:2.01:0.00 and all the starting zinc. An x-ray powder diffraction pattern of the solid showed it to

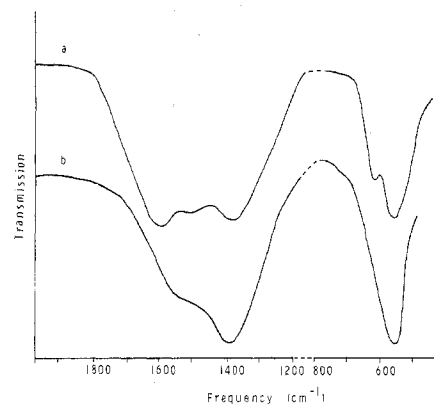


Figure 3. Infrared spectra of solutions obtained when $(\text{CH}_3)_2\text{Zn}$ is added to NaAlH_4 in tetrahydrofuran: NaAlH_4 to $(\text{CH}_3)_2\text{Zn}$ (a) 1:1, (b) 1:2.

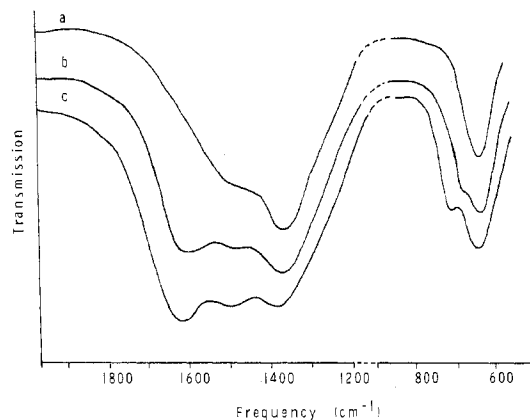


Figure 4. Infrared spectra of solutions obtained by adding NaAlH_4 to $(\text{CH}_3)_2\text{Zn}$ in tetrahydrofuran: (a) 1:2 NaAlH_4 to $(\text{CH}_3)_2\text{Zn}$, (b) 2:3 NaAlH_4 to $(\text{CH}_3)_2\text{Zn}$, (c) 1:1 NaAlH_4 to $(\text{CH}_3)_2\text{Zn}$.

be ZnH_2 . The filtrate corresponded to $\text{NaAl}_2(\text{CH}_3)_4\text{H}_3$ by infrared spectra and analysis (ratio Na:Al:CH₃:H:Zn was 1.01:2.00:3.88:3.11:0.00).

Infrared Study of the Reaction of NaAlH_4 with $(\text{CH}_3)_2\text{Zn}$ in THF.

A 0.82 M solution of $(\text{CH}_3)_2\text{Zn}$ in THF was placed in a round-bottom flask fitted with a three-way stopcock. A 0.813 M solution of NaAlH_4 was added in increments by syringe under nitrogen flush to the magnetically stirred $(\text{CH}_3)_2\text{Zn}$ solution. After each addition, the solution was stirred for 15 min at room temperature, then an infrared spectrum was obtained on the resulting solution. The addition of NaAlH_4 was made in three increments such that after each addition the ratio of total zinc to aluminum was 2:1, 4:3, and 1:1. The resulting infrared spectra are shown in Figure 3. Clear solutions were present after the first two additions, but the third addition caused the formation of a precipitate.

In like manner, a 0.82 M solution of $(\text{CH}_3)_2\text{Zn}$ in THF was added in two increments to a solution of 0.813 M NaAlH_4 . The resulting infrared spectra are shown in Figure 4. The two increments were made such that the ratio of total zinc to aluminum would be 1:1 and 2:1. After the first addition a precipitate formed, but upon the second addition the entire precipitate redissolved and a clear solution resulted.

Reaction of NaAlH_4 with $(\text{CH}_3)_2\text{Zn}$ in a 1:1 Molar Ratio. Ten millimoles of a 0.921 M solution of $(\text{CH}_3)_2\text{Zn}$ in THF was added to 10 mmol of a 0.813 M solution of NaAlH_4 in THF. Initially a white precipitate appeared, but it quickly disappeared and an off-white precipitate formed. Infrared spectra were obtained on the supernatant solution 5 min, 2.5 h, 28 h, 4 days, and 7 days after the initial addition. The infrared spectra are shown in Figure 5.

In a separate experiment, 10 mmol of $(\text{CH}_3)_2\text{Zn}$ was added to 10 mmol of NaAlH_4 in THF. The resulting solution was stirred for about 3 h and filtered. The solid contained Na, Zn, and H in a molar ratio of 1.00:2.00:4.87 and about 31.0% of the starting zinc. An x-ray powder diffraction pattern showed the solid to be NaZn_2H_5 . The molar ratio of Na:Al:Zn in the filtrate was 1.75:2.00:1.38.

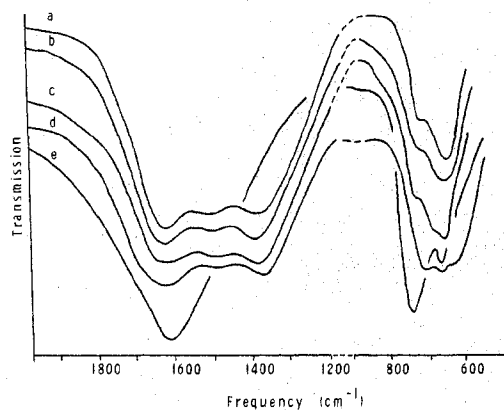


Figure 5. Infrared spectra of solutions obtained by adding NaAlH_4 to $(\text{CH}_3)_2\text{Zn}$ in tetrahydrofuran: (a) 1:1 NaAlH_4 to $(\text{CH}_3)_2\text{Zn}$ after 5 min, (b) 1:1 NaAlH_4 to $(\text{CH}_3)_2\text{Zn}$ after 2.5 h, (c) 1:1 NaAlH_4 to $(\text{CH}_3)_2\text{Zn}$ after 28 h, (d) 1:1 NaAlH_4 to $(\text{CH}_3)_2\text{Zn}$ after 4 days, and (e) 1:1 NaAlH_4 to $(\text{CH}_3)_2\text{Zn}$ after 7 days.

In another separate experiment, $(\text{CH}_3)_2\text{Zn}$ and NaAlH_4 were allowed to react in a 1:1 molar ratio. After stirring for 9 days, the mixture was filtered. An x-ray powder diffraction pattern of the resulting solid showed NaZn_2H_5 and zinc metal to be present. An analysis of the filtrate showed the presence of Na, Al, CH_3 , H, and Zn in ratios of 1.01:2.00:3.99:2.82:0.00. An infrared spectrum showed bands corresponding to $\text{NaAl}_2(\text{CH}_3)_4\text{H}_3$.

Reaction of AlH_3 with $(\text{CH}_3)_2\text{Zn}$ in THF. Five millimoles of a 0.820 M solution of $(\text{CH}_3)_2\text{Zn}$ in THF was added to 5 mmol of a 0.555 M solution of AlH_3 in THF. A white precipitate formed immediately. The mixture was stirred about 1 h and filtered. The ratio of Zn:H in the solid was 1.00:2.03 and an x-ray powder pattern showed it to be ZnH_2 . No zinc remained in the filtrate. An infrared spectrum of the filtrate showed it to be $\text{Al}(\text{CH}_3)_2\text{H}$.

Reaction of ZnH_2 with $\text{NaAl}(\text{CH}_3)_2\text{H}_2$ in THF. Zinc hydride (2.5 mmol) slurried in THF was added to 2.5 mmol of $\text{NaAl}(\text{CH}_3)_2\text{H}_2$ in THF. All the ZnH_2 dissolved in less than 1 min and a clear solution formed. An infrared spectrum was obtained on this clear solution and it corresponded to $\text{NaZn}(\text{CH}_3)_2\text{AlH}_4$. After about 20 min an off-white precipitate began to appear. This mixture was stirred for a day and filtered. The solid contained Na:Zn:H in a molar ratio of 1.06:2.00:4.81 and an x-ray powder pattern showed it to be NaZn_2H_5 . The filtrate was allowed to stand another week. After this time more solid appeared. The mixture was refiltered. The molar ratio of Na:Zn in the solid was 1.05:2.00. The molar ratio of Na:Al:Zn in the filtrate was now 1.03:2.00:0.17. An infrared spectrum of the filtrate corresponded to $\text{NaAl}_2(\text{CH}_3)_4\text{H}_3$.

Preparation of KAlH_4 . Ten millimoles of KH slurried in THF was added to 10 mmol of a 0.1025 M solution of AlH_3 in THF. The mixture was stirred for a few days, then a sample of the solid isolated and analyzed. The molar ratio of K:Al:H in the solid was 1.03:1.00:3.91. The KAlH_4 was stored under THF and used as a slurry.

Reaction of $\text{KZn}(\text{CH}_3)_2\text{H}$ with AlH_3 in THF. Five millimoles of KH slurried in THF was added to 5 mmol of $(\text{CH}_3)_2\text{Zn}$ in THF. An infrared spectrum was obtained on the solution formed. Next 5 mmol of a 0.1025 M solution of AlH_3 in THF was added to the solution of $\text{KZn}(\text{CH}_3)_2\text{H}$. As quickly as possible an infrared spectrum was obtained on the supernatant in the hope of seeing the spectrum of the intermediate which leads to the products KZn_2H_5 and $\text{KAl}_2(\text{CH}_3)_4\text{H}_3$. The spectra are shown in Figure 6.

Reaction of KAlH_4 with $(\text{CH}_3)_2\text{Zn}$ in THF in 1:1 Molar Ratio. A 0.921 M solution of $(\text{CH}_3)_2\text{Zn}$ (2.5 mmol) in THF was added to 2.5 mmol of KAlH_4 slurried in THF. The mixture was stirred for 30 min during which time a solid remained throughout. After this period of time, an infrared spectrum was obtained on the supernatant solution. The spectrum is shown in Figure 6. After an additional 2 h the mixture was filtered and the solid was found to contain K:Zn:H in a molar ratio of 0.99:2.00:4.92. The x-ray powder diffraction pattern of the solid showed it to be KZn_2H_5 . The ratio of K:Al:Zn in the filtrate was 1.01:2.00:0.00.

Reaction of KAlH_4 with $(\text{CH}_3)_2\text{Zn}$ in THF in a 1:2 Molar Ratio. Five millimoles of a 0.921 M solution of $(\text{CH}_3)_2\text{Zn}$ in THF was added

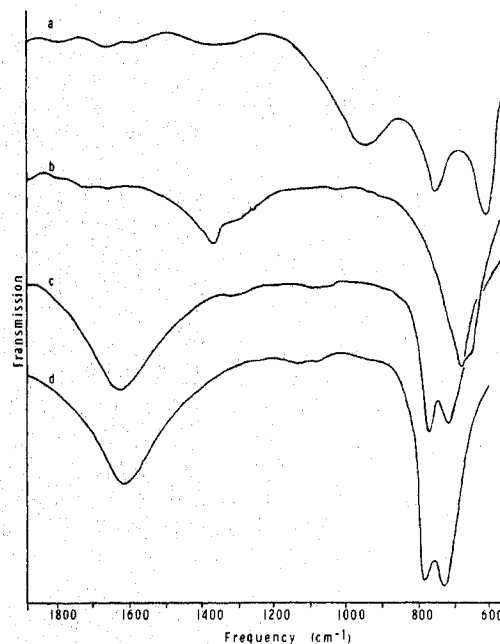


Figure 6. Infrared spectra of $\text{KZn}(\text{CH}_3)_2\text{H}$, THF products from its reaction with AlH_3 , and the products from the reaction of KAlH_4 with $(\text{CH}_3)_2\text{Zn}$ in tetrahydrofuran: (a) $\text{KZn}(\text{CH}_3)_2\text{H}$ in THF, (b) 1:1 KAlH_4 + $(\text{CH}_3)_2\text{Zn}$ after 3 min, (c) 1:1 $\text{KZn}(\text{CH}_3)_2\text{H}$ to AlH_3 after 3 h, and (d) 1:1 KAlH_4 + $(\text{CH}_3)_2\text{Zn}$ after 3 h.



Figure 7. Infrared spectra of $\text{KZn}_2(\text{CH}_3)_4\text{H}$, products from the reaction of KAlH_4 with $(\text{CH}_3)_2\text{Zn}$ in 1:2 ratio, and products from the reaction of $\text{KZn}_2(\text{CH}_3)_4\text{H}$ with AlH_3 in tetrahydrofuran: (a) 1:2 KAlH_4 to $(\text{CH}_3)_2\text{Zn}$ after 5 min, (b) 1:2 KAlH_4 to $(\text{CH}_3)_2\text{Zn}$ after 20 min, (c) 1:2 KAlH_4 to $(\text{CH}_3)_2\text{Zn}$ after 4 h, (d) 2:1 $\text{KZn}_2(\text{CH}_3)_4\text{H}$ to AlH_3 , and (e) 1:1 $\text{KZn}_2(\text{CH}_3)_4\text{H}$ to AlH_3 after 5 min, (f) 1:1 $\text{KZn}_2(\text{CH}_3)_4\text{H}$ to AlH_4 after 4 h, (g) 1:2 $\text{KZn}_2(\text{CH}_3)_4\text{H}$ to AlH_3 ($\text{Al}(\text{CH}_3)_2\text{H}$), and (h) $\text{KZn}_2(\text{CH}_3)_4\text{H}$.

to 2.5 mmol of KAlH_4 slurried in THF. A clear solution formed within seconds. As quickly as possible an infrared spectrum was obtained on this solution. After 10 min a white solid began to appear. The mixture was stirred for 4 h and then filtered. The solid contained K:Zn:H in a molar ratio of 1.02:2.00:4.87. An x-ray powder diffraction pattern of the solid showed it to be KZn_2H_5 . The molar ratio of K:Zn:Al in the filtrate was 1.01:2.00:5.09. An infrared spectrum obtained on the filtrate is shown in Figure 7.

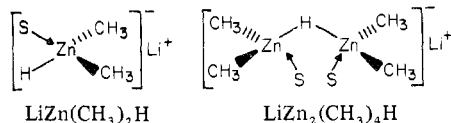
Reaction of $\text{KZn}_2(\text{CH}_3)_4\text{H}$ with AlH_3 in THF at Molar Ratios of 2:1, 1:1, and 1:2. Potassium hydride (2.5 mmol) slurried in THF was added to 5 mmol of a 0.921 M solution of $(\text{CH}_3)_2\text{Zn}$ in THF. After the solution turned clear, marking the formation of $\text{KZn}_2(\text{CH}_3)_4\text{H}$, 1.25 mmol of a 0.1025 M solution of AlH_3 in THF was added. The resulting clear solution was stirred 15 min then an infrared spectrum was obtained. Another 1.25 mmol of a 0.1025 M solution of AlH_3 in THF was then added to this solution which still was clear. A white precipitate began forming immediately. An infrared spectrum was obtained on the supernatant solution. Next, another 2.5 mmol of AlH_3 was added. The mixture was stirred 15 min and then another infrared spectrum obtained, and finally the mixture was filtered. The solid contained K:Zn:H in a molar ratio of 1.02:2.00:4.85, and an x-ray powder diffraction pattern showed it to be KZn_2H_5 . The infrared spectrum showed the filtrate to be $(\text{CH}_3)_2\text{AlH}$. All spectra are shown in Figure 7.

In a separate experiment, 2.5 mmol of AlH_3 in THF was added to 2.5 mmol of $\text{KZn}_2(\text{CH}_3)_4\text{H}$ in THF. The resulting slurry was stirred for 4 h then filtered. The solid contained K:Zn:H in a molar ratio of 1.06:2.00:4.91. An x-ray powder diffraction pattern showed the solid to be KZn_2H_5 . The molar ratio of K:Zn:Al in the filtrate was 1.02:2.00:5.05.

Results and Discussion

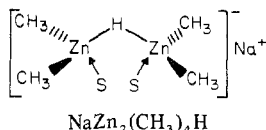
With the aid of our earlier reports¹ concerning the solution composition of $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$ and $\text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4$, one can begin to rationalize the unusual results of the reaction of AlH_3 with $\text{NaZn}(\text{CH}_3)_2\text{H}$ and $\text{KZn}(\text{CH}_3)_2\text{H}$, that is the formation of NaZn_2H_5 and KZn_2H_5 .

First, it is important to consider the structures of $\text{NaZn}(\text{CH}_3)_2\text{H}$ and $\text{KZn}(\text{CH}_3)_2\text{H}$ in THF. The Zn-H stretching frequency for $\text{LiZn}_2(\text{CH}_3)_4\text{H}^1$ (1290 cm^{-1}) is lower than that for $\text{LiZn}(\text{CH}_3)_2\text{H}^1$ (1450 cm^{-1}). These data are consistent with the structures Shriver and Kubas⁷ have suggested for $\text{LiZn}(\text{CH}_3)_2\text{H}$ and $\text{LiZn}_2(\text{CH}_3)_4\text{H}$, since one would expect the



bridging Zn-H-Zn bond in $\text{LiZn}_2(\text{CH}_3)_4\text{H}$ to have a lower stretching frequency than the terminal Zn-H bond in $\text{LiZn}(\text{CH}_3)_2\text{H}$. Bell and Coates⁸ have reported that a terminal zinc-hydrogen stretching vibration should occur somewhere in the range $1600\text{--}2100\text{ cm}^{-1}$. The Zn-H bond in $\text{LiZn}(\text{CH}_3)_2\text{H}$ is a terminal one, but solvent coordination to zinc in the complex probably causes the shift to a frequency lower than 1600 cm^{-1} .

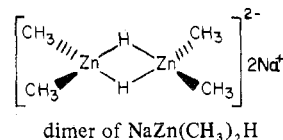
The Zn-H stretching mode for $\text{NaZn}(\text{CH}_3)_2\text{H}$ (Figure 1) appears as a broad band extending from $1050\text{ to }750\text{ cm}^{-1}$ with the center at 920 cm^{-1} . This unusually low Zn-H stretching frequency cannot be explained as being the result of solvent cleavage, since an analysis of the solution, just prior to obtaining the spectrum, showed that Na, Zn, CH₃, and H were present in ratios of 1.03:1.00:1.96:0.91. Kubas and Shriver⁷ have reported that $\text{NaZn}(\text{CH}_3)_2\text{H}$ and $\text{NaZn}_2(\text{CH}_3)_4\text{H}$ are monomeric in THF. The asymmetric Zn-H stretching vibration for $\text{NaZn}_2(\text{CH}_3)_4\text{H}$ (Figure 2) appears as a broad



band between $1400\text{ and }1150\text{ cm}^{-1}$ with the peak maximum occurring at 1260 cm^{-1} . This corresponds very closely to the Zn-H stretching vibration for $\text{LiZn}_2(\text{CH}_3)_4\text{H}$ at 1290 cm^{-1} , which indicates that the structures of the two compounds in THF should be similar. The fact that $\text{LiZn}(\text{CH}_3)_2\text{H}$ displays a Zn-H stretching vibration close to the terminal metal-hydrogen region indicates that a terminal Zn-H bond is

present and that the monomeric structure shown above represents the compound adequately. If $\text{NaZn}(\text{CH}_3)_2\text{H}$ is indeed monomeric in the solutions used in this study, then one would have expected to see a Zn-H stretching band for this compound somewhere in the region $1400\text{--}1450\text{ cm}^{-1}$. Since this was not observed, $\text{NaZn}(\text{CH}_3)_2\text{H}$ cannot have the same monomeric structure as $\text{LiZn}(\text{CH}_3)_2\text{H}$. However, the solutions of $\text{NaZn}(\text{CH}_3)_2\text{H}$ used in this work had concentrations in the range $0.8\text{--}1.0\text{ M}$ and therefore $\text{NaZn}(\text{CH}_3)_2\text{H}$ could be present as a dimer. Since Kubas and Shriver⁷ did not report the concentration range over which their association data apply, the possibility exists that their solutions were more dilute than ours. (Some of the results from this study do suggest that $\text{NaZn}(\text{CH}_3)_2\text{H}$ is monomeric at lower concentration.)

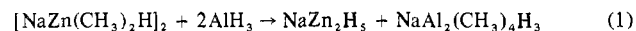
A dimer of $\text{NaZn}(\text{CH}_3)_2\text{H}$ would be expected to have the structure shown below where the two zinc atoms are tetra-



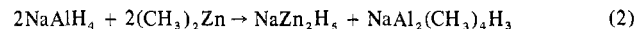
hedrally coordinated and connected by a double hydrogen bridge. One would expect the asymmetric Zn-H stretching vibration for such a structure to be lower than the corresponding frequency for $\text{NaZn}_2(\text{CH}_3)_4\text{H}$ which has only one Zn-H-Zn bridge bond. This is what one observes. Therefore, it is not unreasonable that a 1.0 M solution of $\text{NaZn}(\text{CH}_3)_2\text{H}$ in THF exists as a dimer in solution. Kubas and Shriver⁹ have also reported that the complex $\text{NaZn}(\text{C}_6\text{F}_5)_2\text{H}$ exists as a dimer with double hydrogen bridge bonds in diethyl ether. They report that the asymmetric Zn-H stretching vibration for the dimer appears as a strong broad band between $1300\text{ and }1700\text{ cm}^{-1}$. However, their spectra were recorded as Nujol mulls of the completely desolvated solid and not as solutions in diethyl ether.

The infrared spectrum of an approximately 1.0 M solution of $\text{KZn}(\text{CH}_3)_2\text{H}$ in THF is shown in Figure 6. It exactly matches the spectrum observed for $\text{NaZn}(\text{CH}_3)_2\text{H}$ in THF. Therefore, $\text{KZn}(\text{CH}_3)_2\text{H}$ is also believed to be a dimer in THF with a structure similar to that suggested for the $\text{NaZn}(\text{CH}_3)_2\text{H}$ dimer.

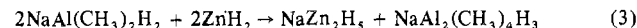
When a 0.9 M solution of $\text{NaZn}(\text{CH}_3)_2\text{H}$ in THF was allowed to react with an equimolar quantity of AlH_3 , an off-white precipitate which was NaZn_2H_5 appeared immediately. After 2 h all the zinc disappeared from the solution, indicating complete conversion to NaZn_2H_5 . The THF soluble product, $\text{NaAl}_2(\text{CH}_3)_4\text{H}_3$, remained in solution. The stoichiometry of the reaction is given by eq 1. The reaction of



NaAlH_4 with $(\text{CH}_3)_2\text{Zn}$ in 1:1 molar ratio also yielded NaZn_2H_5 and $\text{NaAl}_2(\text{CH}_3)_4\text{H}_3$ according to eq 2. In this



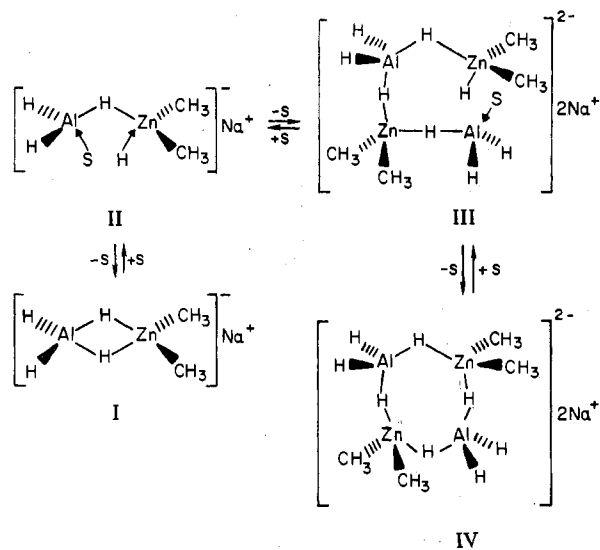
case, however, a precipitate did not appear until a few minutes after the reactants had been mixed and in addition all the zinc disappeared from solution only after a period of 1 week. The reaction of $\text{NaAl}(\text{CH}_3)_2\text{H}_2$ with ZnH_2 in a 1:1 molar ratio yielded NaZn_2H_5 and $\text{NaAl}_2(\text{CH}_3)_4\text{H}_3$ according to eq 3. In



this case a clear solution remained for about 20 min before any solid began to form. After sitting for a period of 1 week all the zinc finally disappeared from solution.

In each of these three cases the intermediate leading to the products could be observed by infrared spectroscopy. Figure 5 contains infrared spectra of the supernatant solution from

Scheme I

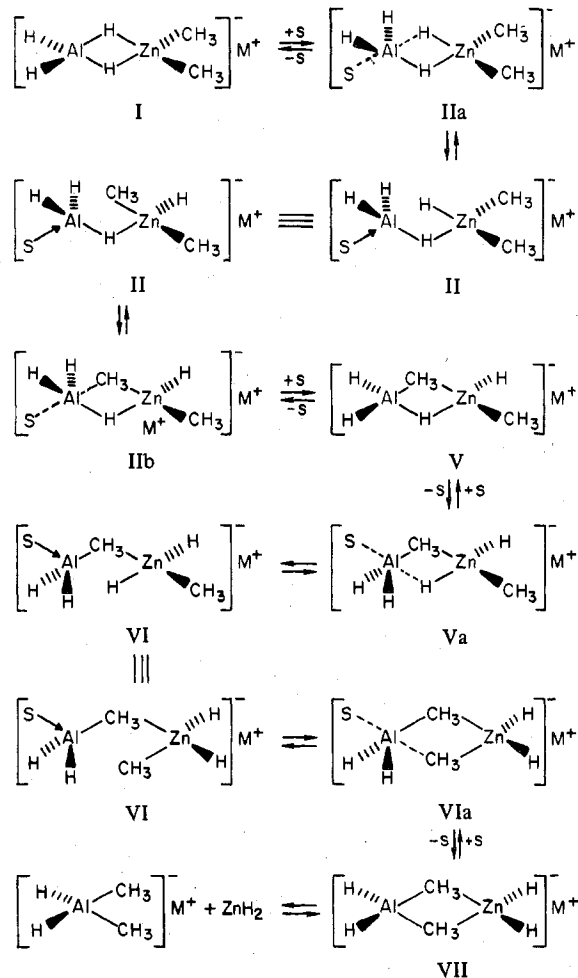


the reaction of NaAlH_4 with $(\text{CH}_3)_2\text{Zn}$ in a 1:1 molar ratio after 5 min, 2.5 h, 28 h, 4 days, and 7 days. Only after 7 days does the spectrum approach that of $\text{NaAl}_2(\text{CH}_3)_4\text{H}_3$. The remainder of the spectra, which are of the intermediate leading to the product, are essentially identical; therefore, the spectrum of the reaction mixture after 5 min is representative and will be studied in detail. There is a very broad band in the metal-hydrogen stretching region extending from 1800 to 1200 cm^{-1} . This spectrum is very similar to the one observed for $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$ prepared from LiAlH_4 and CH_3Zn^1 except that in this case the terminal Al-H asymmetric stretching vibration occurs at 1615 cm^{-1} . The solution composition of $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$ which gave rise to such spectra was found to consist of an equilibrium between monomer and dimer forms of this compound.¹ In view of the very close correspondence between the infrared spectra, the intermediate in the above reaction is probably $\text{NaZn}(\text{CH}_3)_2\text{AlH}_4$, which would have a solution composition similar to that of $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$ (see Scheme I).

The intermediate involved in the formation of NaZn_2H_5 by the reaction of $\text{NaAl}(\text{CH}_3)_2\text{H}_2$ with ZnH_2 must also be $\text{NaZn}(\text{CH}_3)_2\text{AlH}_4$, since an infrared spectrum of the clear solution, which was initially formed, contained these same bands.

In our earlier reports,¹ it was mentioned that solutions of $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$ decompose on standing to give a solid containing Li and Zn in a ratio of 1:2. However, the solutions were never observed to precipitate all of the zinc. Solutions of $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$ when diluted to about 0.01 M were found to precipitate ZnH_2 . Also the reactions of $\text{LiZn}(\text{CH}_3)_2\text{H}$ with AlH_3 or LiAlH_4 with $(\text{CH}_3)_2\text{Zn}$ in 1:1 ratio, when carried out in dilute solution, were found to precipitate ZnH_2 . Similar behavior occurs when either $\text{NaZn}(\text{CH}_3)_2\text{H}$ and AlH_3 or NaAlH_4 and $(\text{CH}_3)_2\text{Zn}$ are allowed to react in dilute solution. Both reactions produce ZnH_2 . However, when these same two reactions are carried out at concentrations greater than 0.2 M, NaZn_2H_5 is precipitated and not ZnH_2 . Earlier it was mentioned that $\text{NaZn}(\text{CH}_3)_2\text{H}$ appears to be dimeric at concentrations above 0.2 M but monomeric in more dilute solutions. Solutions of $\text{LiZn}(\text{CH}_3)_2\text{H}$ appeared to be monomeric at all the concentrations employed in these studies.¹ Based on these observations, it appears that monomeric $\text{MZn}(\text{CH}_3)_2\text{H}$ compounds react with alane to give $\text{MZn}(\text{CH}_3)_2\text{AlH}_4$ which can then undergo alkyl-hydrogen exchange to yield either MZn_2H_5 or ZnH_2 , depending on the concentration of the solution. In solutions above 0.2 M in concentration, $\text{MZn}(\text{CH}_3)_2\text{AlH}_4$ yields MZn_2H_5 . In more dilute

Scheme II

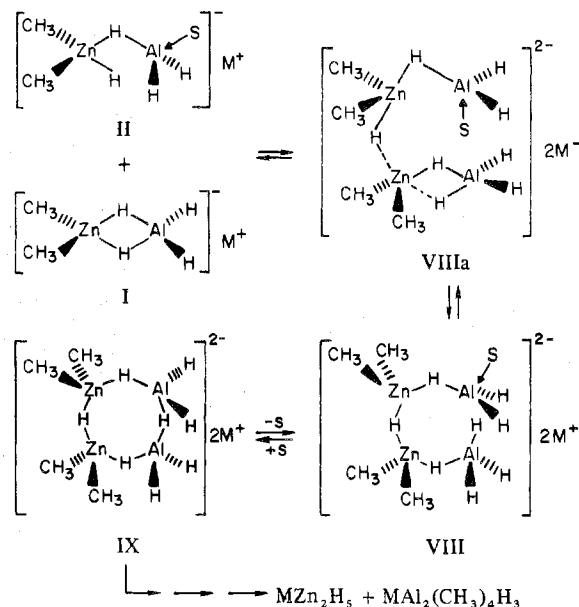


solutions, it gives ZnH_2 . Reactions of MAlH_4 compounds with $(\text{CH}_3)_2\text{Zn}$ proceed in a similar way since they also produce the intermediate $\text{MZn}(\text{CH}_3)_2\text{AlH}_4$. It seems that the concentration of the intermediate is the factor which determines the products, either MZn_2H_5 or ZnH_2 , in these reactions. This leads one to conclude that a species similar to the dimer form of $\text{MZn}(\text{CH}_3)_2\text{AlH}_4$ (IV) would be the primary intermediate in the exchange reactions which lead to MZn_2H_5 . This statement is supported by the fact that association studies on solutions of $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$,¹ when the concentration is greater than 0.2 M, indicate the presence of a considerable amount of a dimeric species. The primary intermediate in the exchange reactions which lead to ZnH_2 must be the monomeric form of $\text{MZn}(\text{CH}_3)_2\text{AlH}_4$ (I). This statement is supported by the fact that ZnH_2 is only precipitated from solution of $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$ where the association value is one.

A reasonable mechanism by which $\text{MZn}(\text{CH}_3)_2\text{AlH}_4$ can undergo intramolecular exchange to produce ZnH_2 is shown in Scheme II. This scheme of reactions is essentially identical with the mechanism given in an earlier report¹ for the reaction between LiAlH_4 and $(\text{CH}_3)_2\text{Zn}$ to produce ZnH_2 . The mechanism was discussed in some detail in that report. The rate limiting step in the scheme is thought to be formation of the mixed bridged intermediate V, since formation of a methyl bridge bond with simultaneous breakage of an aluminum-THF solvate bond should be unfavorable.¹

A reasonable mechanism by which $\text{MZn}(\text{CH}_3)_2\text{AlH}_4$ can undergo exchange to produce MZn_2H_5 is shown in Scheme III. Intermediate VIII results from the reaction of I with II through transition-state VIIIa. In this reaction one of the Al-H-Zn bridge bonds in I is broken with subsequent for-

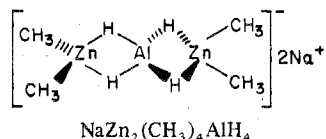
Scheme III



mation of the Zn-H-Zn bridge bond in VIII. Intermediate VIII then undergoes an intramolecular displacement of the solvent on aluminum with simultaneous formation of an Al-H-Al bridge bond to give intermediate IX. It is easy for one to see how IX could undergo intramolecular methyl hydride exchange to produce MZn_2H_5 and $\text{MAI}_2(\text{CH}_3)_4\text{H}_3$.

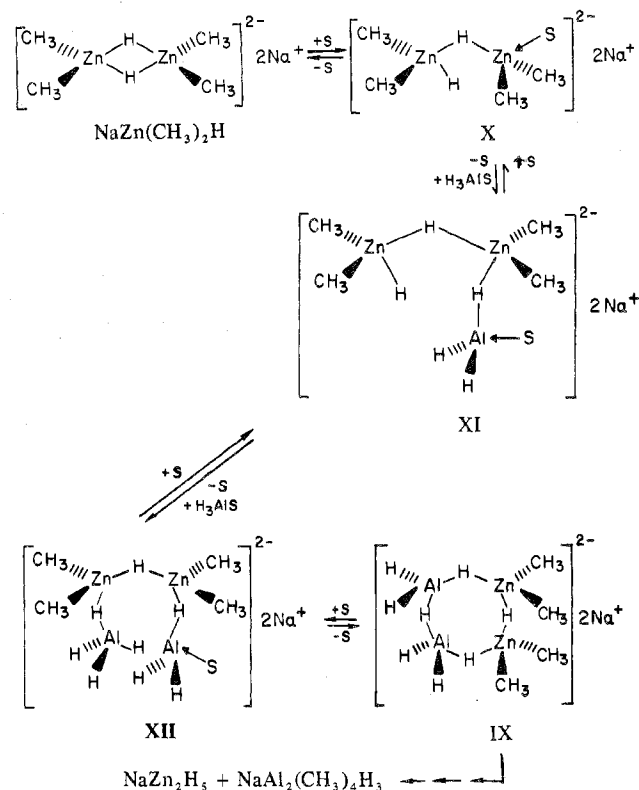
Figure 1 contains infrared spectra of the supernatant solution from the reaction of $\text{NaZn}(\text{CH}_3)_2\text{H}$ with AlH_3 after 5 min and 24 h. The spectrum of the supernatant left after 5 min contained a broad band extending from 1550 to 1200 cm^{-1} with no well-defined maximum. The rest of the spectrum corresponded to $\text{NaAl}_2(\text{CH}_3)_4\text{H}_3$ which was also formed. The broad band extending from 1550 to 1200 cm^{-1} could be due to $\text{NaZn}(\text{CH}_3)_2\text{AlH}_4$, but this seems unlikely due to the rate at which NaZn_2H_5 is formed in this reaction. If $\text{NaZn}(\text{CH}_3)_2\text{AlH}_4$ were the actual intermediate leading to NaZn_2H_5 , then one would have expected it to take about 1 week for all the zinc to disappear from solution, but instead it takes only a few hours. However, the intermediate must be similar to $\text{NaZn}(\text{CH}_3)_2\text{AlH}_4$, since the bands observed in the infrared are similar to those found for this compound. A likely candidate for this intermediate is IX, since it should give rise to an infrared spectrum similar to $\text{NaZn}(\text{CH}_3)_2\text{AlH}_4$. But in addition to this, IX is a necessary intermediate in any mechanistic scheme for the production of NaZn_2H_5 . A reasonable mechanism then for the reaction between $\text{NaZn}(\text{CH}_3)_2\text{H}$ and AlH_3 to give NaZn_2H_5 is shown in Scheme IV. The first step in this mechanism is solvent cleavage of one of the two bridging Zn-H-Zn bonds, then two molecules of alane can add rapidly to give intermediate IX. This intermediate then undergoes intramolecular alkyl-hydrogen exchange to yield NaZn_2H_5 .

The reaction of $\text{NaZn}_2(\text{CH}_3)_4\text{H}$ with alane behaves in a similar way to the reaction of $\text{LiZn}_2(\text{CH}_3)_4\text{H}$ with alane in that $\text{NaZn}_2(\text{CH}_3)_4\text{AlH}_4$ is formed. The infrared spectra of



$\text{NaZn}_2(\text{CH}_3)_4\text{H}$ and $\text{NaZn}_2(\text{CH}_3)_4\text{AlH}_4$ are shown in Figure 2. The spectrum of $\text{NaZn}_2(\text{CH}_3)_4\text{AlH}_4$ is very similar to that of $\text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4$. There is a very broad peak in the

Scheme IV



metal-hydrogen stretching region with a shoulder at 1480 cm^{-1} and maximum at 1380 cm^{-1} . There is no band in the terminal Al-H stretching or deformation region. The structure of $\text{NaZn}_2(\text{CH}_3)_4\text{AlH}_4$, therefore, must be similar to that of $\text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4$.

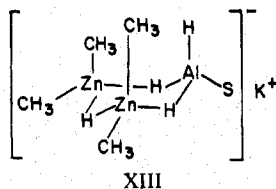
The reactions of $\text{KZn}(\text{CH}_3)_2\text{H}$ with alane and KAlH_4 with $(\text{CH}_3)_2\text{Zn}$ in 1:1 molar ratio behave differently than the corresponding sodium system, although KZn_2H_5 is formed in both reactions. The difference is due to the fact that there is no concentration dependence by the reaction product and the rate of formation of KZn_2H_5 is much faster than in the sodium system. The reaction of KAlH_4 with $(\text{CH}_3)_2\text{Zn}$ in 1:1 molar ratio is complete within 3 h regardless of the concentration of the starting materials and the reaction of $\text{KZn}(\text{CH}_3)_2\text{H}$ with alane is complete within 5 min. In view of this large rate increase and the nonconcentration dependence of the product, the mechanism for the formation of KZn_2H_5 could be different from that presented for the sodium systems. One would expect $\text{KZn}(\text{CH}_3)_2\text{AlH}_4$ to be involved in the reaction of KAlH_4 with $(\text{CH}_3)_2\text{Zn}$; however, infrared spectral analysis of the reaction mixture in its intermediate stages failed to show the bands characteristic of the $[\text{Zn}(\text{CH}_3)_2\text{AlH}_4]^-$ system. One such spectrum is shown in Figure 6. There is a broad band extending from 1500 to 1150 cm^{-1} in the metal-hydrogen stretching region. This band has its maximum absorption at 1380 cm^{-1} and has a shoulder at 1300 cm^{-1} . In the 700-600- cm^{-1} region there is a band at 675 cm^{-1} which has a shoulder at 650 cm^{-1} . Attempts to record infrared spectra of the intermediates involved in the reaction of $\text{KZn}(\text{CH}_3)_2\text{H}$ with alane were unsuccessful. It may be that the mechanism of these reactions is similar to those given for the sodium system, but due to lack of evidence we cannot say definitely whether this is true or not.

The reaction of $\text{KZn}_2(\text{CH}_3)_4\text{H}$ with alane differs considerably from the reaction of $\text{LiZn}_2(\text{CH}_3)_4\text{H}$ and $\text{NaZn}_2(\text{CH}_3)_4\text{H}$ with alane. While the latter two reactions yield $\text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4$ and $\text{NaZn}_2(\text{CH}_3)_4\text{AlH}_4$, $\text{KZn}_2(\text{CH}_3)_4\text{H}$ reacts with either 1 or 2 equiv of alane to yield KZn_2H_5 and

apparently not $\text{KZn}_2(\text{CH}_3)_4\text{AlH}_4$. More evidence along this line is provided by considering the reactions of $\text{LiZn}_2(\text{CH}_3)_4\text{H}$ and $\text{NaZn}_2(\text{CH}_3)_4\text{H}$ with AlH_3 in 1:2 ratio. Both these reactions produce ZnH_2 , presumably by the reaction of AlH_3 with the initially formed $\text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4$ and $\text{NaZn}_2(\text{CH}_3)_4\text{AlH}_4$. Since $\text{KZn}_2(\text{CH}_3)_4\text{H}$ reacts with AlH_3 in 1:2 ratio to produce KZn_2H_5 , the indication is that $\text{KZn}_2(\text{CH}_3)_4\text{AlH}_4$ was not formed.

When KAlH_4 and $(\text{CH}_3)_2\text{Zn}$ are allowed to react in a 1:2 molar ratio, a clear solution results. The infrared spectrum of this solution, shown in Figure 7, is exactly like the infrared spectrum of $\text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4$ and $\text{NaZn}_2(\text{CH}_3)_4\text{AlH}_4$. If this clear solution is allowed to stand, after about 10 min a white solid which is KZn_2H_5 begins to precipitate. But if immediately after the clear solution is formed an equivalent of alane is added, ZnH_2 is formed. In view of this evidence one can conclude that $\text{KZn}_2(\text{CH}_3)_4\text{AlH}_4$ is formed by the reaction of KAlH_4 with $(\text{CH}_3)_2\text{Zn}$ in a 1:2 molar ratio.

Now when alane is added to $\text{KZn}_2(\text{CH}_3)_4\text{H}$ in a 1:1 molar ratio, a white precipitate begins to form immediately. An infrared spectrum of the supernatant left after 5 min reaction time is shown in Figure 7. This spectrum is clearly not that of $\text{KZn}_2(\text{CH}_3)_4\text{AlH}_4$ but is assigned to the compound XIII. The compound is the same as intermediate X shown in Scheme III of the first report in this series.¹ The infrared spectrum of XIII contains three bands in the metal-hydrogen stretching region, one at 1610, another at 1490, and the third at 1340 cm^{-1} . The band at 1610 cm^{-1} is assigned to the stretching



modes of the terminal Al-H group in XIII. The band at 1490 cm^{-1} is assigned to the stretching modes of the bridging hydrogen between aluminum and zinc. The band at 1340 cm^{-1} is assigned to the stretching modes of the bridging hydrogen between the two zinc atoms. These assignments are reasonable based on our earlier reports.¹ The terminal Al-H stretching vibration for $\text{NaZn}(\text{CH}_3)_2\text{AlH}_4$ was assigned to the Al-H-Zn bridging unit. The stretching vibrations for the Zn-H-Zn bonds in $\text{LiZn}_2(\text{CH}_3)_4\text{H}$ and $\text{NaZn}_2(\text{CH}_3)_4\text{H}$ occur at 1290 and 1260 cm^{-1} .

In an earlier report,¹ it was pointed out that the critical step in the formation of $\text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4$ is the attack of a solvent molecule on an intermediate like XIII to cleave the Zn-H-Zn bridge bond. Evidently, in the reaction of $\text{KZn}_2(\text{CH}_3)_4\text{H}$ with

alane, the Zn-H-Zn bridge bond in XIII is too strong to be cleaved by a solvent molecule and $\text{KZn}_2(\text{CH}_3)_4\text{AlH}_4$ is never formed. Instead of forming $\text{KZn}_2(\text{CH}_3)_4\text{AlH}_4$, XIII undergoes intramolecular exchange to yield KZn_2H_5 . In Scheme III of the first report in this series, it was pointed out that a mobile equilibrium exists between $\text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4$ and an intermediate like XIII. When lithium or sodium is the cation, the equilibrium lies in the direction of $\text{MZn}_2(\text{CH}_3)_4\text{AlH}_4$; however, when potassium is the cation, the equilibrium lies in the direction of XIII. Thus, when KAlH_4 and $(\text{CH}_3)_2\text{Zn}$ are allowed to react in a 1:2 molar ratio, the initial product is $\text{KZn}_2(\text{CH}_3)_4\text{AlH}_4$; however, it is converted to XIII after a few minutes. Intermediate XIII then undergoes intramolecular exchange to give KZn_2H_5 . Proof that both reactions proceed by way of the same intermediates is offered by the fact that an infrared spectrum of the supernatant solution (taken about 10 min after KZn_2H_5 began to precipitate) was exactly the same as the spectrum observed after 5 min in the reaction of $\text{KZn}_2(\text{CH}_3)_4\text{H}$ with alane in a 1:1 molar ratio. This spectrum is shown in Figure 7.

In this paper we have tried to present reasonable mechanisms, based on the information gathered in this study, for the exchange reactions of the zincate complexes $\text{MZn}(\text{CH}_3)_2\text{H}$ and $\text{MZn}_2(\text{CH}_3)_4\text{H}$ with alane. In these mechanisms we have tried to indicate the importance of the role of the solvent in exchange reactions of this type and have shown the dependence of the reaction between $(\text{CH}_3)_2\text{Zn}$ and MAlH_4 on solvent concentration.

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Registry No. NaZn_2H_5 , 39356-34-8; KZn_2H_5 , 37276-96-3; $\text{NaZn}(\text{CH}_3)_2\text{H}$, 26520-81-0; $\text{KZn}(\text{CH}_3)_2\text{H}$, 41202-98-6; $\text{NaZn}_2(\text{CH}_3)_4\text{AlH}_4$, 62881-84-9; $\text{NaAl}_2(\text{CH}_3)_4\text{H}_3$, 62816-24-4; $\text{NaZn}(\text{CH}_3)_2\text{AlH}_4$, 62881-83-8; $\text{KAl}_2(\text{CH}_3)_4\text{H}_3$, 62816-25-5; $(\text{CH}_3)_2\text{AlH}$, 865-37-2; $\text{NaZn}_2(\text{CH}_3)_4\text{H}$, 62816-26-6; $\text{NaAl}(\text{CH}_3)_2\text{H}_2$, 19528-79-1; $\text{KZn}_2(\text{CH}_3)_4\text{H}$, 62816-04-0; $(\text{CH}_3)_2\text{Zn}$, 544-97-8; NaAlH_4 , 13770-96-2; ZnH_2 , 14018-82-7; KAlH_4 , 16903-34-7; AlH_3 , 7784-21-6; NaH , 7646-69-7; KH , 7693-26-7.

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