other batches of solvent, the original results were found to be irreproducible. It is conceivable that the exchanged samples arose because of catalysis by an impurity (e.g., peroxides or alcohols) in the original diglyme sample. Although exchanged samples could have been gained from alternative sources, the mixtures of $NaBH_nD_{4-n}$ obtained from these preliminary experiments proved more than adequate sources of spectral information.
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Nature of Alkyl–Hydrogen Exchange Reactions Involving Aluminum and Zinc. 2. Reaction of $(CH_3)_2Zn$ with $LiAlH_4$ in Tetrahydrofuran

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When $(CH_3)_2Zn$ was added to a THF solution of $LiAlH_4$ in 2:1, 3:2, and 1:1 molar ratios, $LiZn_2(CH_3)_4AlH_4$ and $LiZn(CH_3)_2AlH_4$ were formed according to eq 1–3. When the order of addition was reversed and $LiAlH_4$ was added to a THF solution of $(CH_3)_2Zn$ in 1:1, 2:3, and 1:2 molar ratios, $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ were again formed according to eq 1–3. Infrared and ^1H NMR spectroscopic studies, as well as ebullioscopic molecular weight measurements, were used to define the solution composition of the products obtained from these reactions. The role of $LiZn(CH_3)_2AlH_4$ as the intermediate involved in the formation of ZnH_2 from the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ is discussed in light of the spectroscopic studies carried out on this reaction.

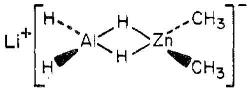
$$2(CH_3)_2Zn + LiAlH_4 \rightleftharpoons LiZn_2(CH_3)_4AlH_4 \quad (1)$$

$$3(CH_3)_2Zn + 2LiAlH_4 \rightleftharpoons LiZn_2(CH_3)_4AlH_4 + LiZn(CH_3)_2AlH_4 \quad (2)$$

$$(CH_3)_2Zn + LiAlH_4 \rightleftharpoons LiZn(CH_3)_2AlH_4 \quad (3)$$

Introduction

Recently we reported the first synthesis of triple metal ate complexes involving an alkali metal, zinc, and aluminum, i.e., $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$.[1] These compounds were formed by the reaction of AlH_3 with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ in THF and are believed to have the structures represented by I and II. In that report we noted that a study of these triple metal complexes could provide clues as to the nature of alkyl–hydrogen exchange reactions between zinc and aluminum.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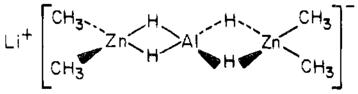

II

In this paper we will report on the formation of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ by reaction of $(CH_3)_2Zn$ with $LiAlH_4$ in THF under a variety of conditions. The fact that the triple metal complex, $LiZn(CH_3)_2AlH_4$, can be prepared by allowing $LiAlH_4$ to react with $(CH_3)_2Zn$ offers the first indication of what could be the intermediate involved in the formation of ZnH_2 from these two reagents in diethyl ether.[2] An infrared spectral study of the reaction between $(CH_3)_2Zn$ and $LiAlH_4$ in THF does indeed provide evidence that $LiZn(CH_3)_2AlH_4$ is involved.

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. Solutions were run in matched 0.10-mm path length NaCl or KBr 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. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer with a standard variable-temperature unit. Ebullioscopic molecular association studies were carried out in THF

Table I. Infrared Spectra of $(CH_3)_2Zn$, $LiAlH_4$, $LiZn(CH_3)_2AlH_4$, $LiZn_2(CH_3)_4AlH_4$, and the Products Obtained by Mixing $LiAlH_4$ and $(CH_3)_2Zn$ in THF[a]

Obsd IR bands,[b] cm^{-1}							
$(CH_3)_2Zn$	$LiAlH_4$	$LiZn(CH_3)_2$-AlH_4[d]	$LiZn_2(CH_3)_4$-AlH_4[e]	1:1 $LiAlH_4$ + $(CH_3)_2Zn$[f]	2:3 $LiAlH_4$ + $(CH_3)_2Zn$[g]	1:2 $LiAlH_4$ + $(CH_3)_2Zn$[h]	Approx assignt
550 s		475 s	479 s	472 s	475 s	475 s	Zn–C stretch
674 vs		690 vs	700 vs	690 vs	697 vs	700 vs	CH_3 rock
	760 m	720 sh, s		720 sh, s	720 sh, w		Al–H def
		775 s		775 s	775 m		
840 m							Solvent O–C stretch
1153 m		1118 m	1140 m	1118 m	1130 sh, w	1140 m	CH_3 def
		1162 m	1170 w	1162 m	1164 w	1170 w	
		1400 br,[c] s	1400 br,[c] s	1400 br,[c] s	1400 br,[c] s	1400 br,[c] s	Double H bridge stretch
				1500 sh, s	1500 sh, s	1500 sh, s	Zn–H–Al stretch
	1691 s	1660 br, vs		1660 br, vs	1660 br, vs		Terminal Al–H stretch

[a] All spectra were run with THF as reference. [b] Abbreviations: w, weak; m, medium; s, strong; sh, shoulder; v, very; br, broad. [c] These bands were very broad. The frequency given is approximately the center of the band. [d] Concentration = 0.15 M. [e] Concentration = 0.10 M. [f] Concentration = 0.52 M. [g] Concentration = 0.47 M. [h] Concentration = 0.40 M.

under vacuum (240 mmHg absolute) using the technique developed earlier.[5]

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 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 in the absence of aluminum was determined directly by EDTA titration.

Materials. Solutions of $LiAlH_4$ (Ventron, Metal Hydrides Division) were prepared in THF in the usual manner.[1] Dimethylzinc was prepared by the procedure of Noller.[6] 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 $NaAlH_4$.

Reactions of $LiAlH_4$ with $(CH_3)_2Zn$ in THF at Molar Ratios of 1:1, 2:3, and 1:2. In three separate reactions 10, 7.5, and 5 mmol of a 0.386 M solution of $LiAlH_4$ in THF were added to 10 mmol of a 0.820 M solution of $(CH_3)_2Zn$ in THF. In each case, the resulting clear solution was stirred for about 15 min, then a small sample was subjected to infrared analysis. The resulting infrared spectra, in addition to the spectra of $(CH_3)_2Zn$, $LiAlH_4$, $LiZn(CH_3)_2AlH_4$,[1] and $LiZn_2(CH_3)_4AlH_4$,[1] are shown in Figure 1. Table I contains a listing of the infrared bands observed for the spectra given in this figure. NMR spectra and ebullioscopic molecular association studies were run on the 1:1 and 1:2 mixtures of $LiAlH_4$ and $(CH_3)_2Zn$. Analysis of these solutions indicated the presence of Li, Al, CH_3, H, and Zn in 1.03:1.00:1.91:3.96:0.98 ratio for the 1:1 mixture and 0.98:1.00:4.02:3.91:2.02 ratio for the 1:2 mixture.

In a separate experiment 10 mmol of 0.386 M $LiAlH_4$ in THF was added to 10 mmol of 0.820 M $Zn(CH_3)_2$ in THF. The resulting clear solution was divided into two portions. One was set aside to stand for 1 week at room temperature. The other was diluted 20-fold immediately with THF. Within 5 min a white precipitate began to form in the diluted solution (ca. 0.01 M). The initial concentrated solutions remained clear for almost 3 h before any black solid began to precipitate. Infrared spectra of both the concentrated and diluted solutions (or supernatants if a solid is present) were recorded after 15 min, 30 min, 2 h, 4 h, 1 day, 3 days, and 1 week. In each case the infrared spectra corresponded to the spectrum of $LiZn(CH_3)_2AlH_4$. The white solid that formed after the 0.253 M solution of $LiZn(CH_3)_2AlH_4$ had been diluted was found to be ZnH_2. The solids in both the concentrated and diluted samples had turned black after sitting a week at room temperature under THF. In each case the solids were separated by filtration, washed with THF, and dried under vacuum at room temperature. The solid from the more concentrated solution of $LiZn(CH_3)_2AlH_4$ exhibited Li:Zn:H:Al in molar ratios of 1.06:2.00:3.20:0.05 and contained 22.4% of the starting zinc. (The remainder of the zinc was in the supernatant.) An x-ray powder pattern of this solid revealed that it contained $LiZnH_3$ and Zn metal only. The solid from the more dilute solution of $LiZn(CH_3)_2AlH_4$ was found to exhibit Li:Zn:H:Al in molar ratios of 0.04:1.00:1.42:0.05 and contained 48.2% of the starting zinc. An x-ray powder pattern of this solid revealed that it contained ZnH_2 and Zn metal.

In another, separate experiment, 10 mmol of 0.820 M $(CH_3)_2Zn$ in THF was added to 724 mL of freshly distilled THF, then 10 mmol of 0.386 M $LiAlH_4$ in THF was added. The mixture was stirred for 30 s, then an infrared spectrum was obtained on the solution while it was still clear. This infrared spectrum was the same as that of $LiZn(CH_3)_2AlH_4$. Within 5 min after the $LiAlH_4$ had been added to the $(CH_3)_2Zn$, a white solid began to form. This white solid was found to be ZnH_2. When the reaction mixture was allowed to stand at room temperature for 1 week, the white solid turned black. An infrared spectrum of the supernatant remaining at this point showed that $LiZn(CH_3)_2AlH_4$ was still present. An analysis of the black solid revealed that it contained Li:Zn:H:Al in molar ratios of 0.06:1.00:1.31:0.05. A little less than half of the initial zinc added (46.4%) was found in the black solid. An x-ray powder pattern of the solid revealed that it contained ZnH_2 and Zn metal.

Reactions of $(CH_3)_2Zn$ with $LiAlH_4$ in THF at Molar Ratios of 1:1, 3:2, and 2:1. In three separate reactions 10, 15, and 20 mmol of a 0.820 M solution of $(CH_3)_2Zn$ in THF were added to 10 mmol of a 0.386 M solution of $LiAlH_4$ in THF. In each case, the resulting clear solution was stirred for about 15 min, followed by infrared analysis (Figure 2). Table I contains a listing of the infrared bands observed for the spectra given in this figure. On standing in THF at room temperature and on dilution with THF, the mixture obtained on adding $(CH_3)_2Zn$ to $LiAlH_4$ in 1:1 ratio behaved in the same way as described earlier for the mixture obtained on adding $LiAlH_4$ to $(CH_3)_2Zn$.

Results and Discussion

In an earlier report[1] we described the synthesis of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ in THF by the reaction of AlH_3 with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$, respectively. An infrared spectral analysis revealed the structures of these two triple metal hydrides to be those given by I and II. The infrared spectra recorded for these complexes are shown in Figure 1 and the characteristic vibrational frequencies tabulated in Table I. The addition of either $LiAlH_4$ to $(CH_3)_2Zn$ or $(CH_3)_2Zn$ to $LiAlH_4$ in a 1:1 molar ratio in THF yields a clear solution whose infrared spectrum corresponds closely

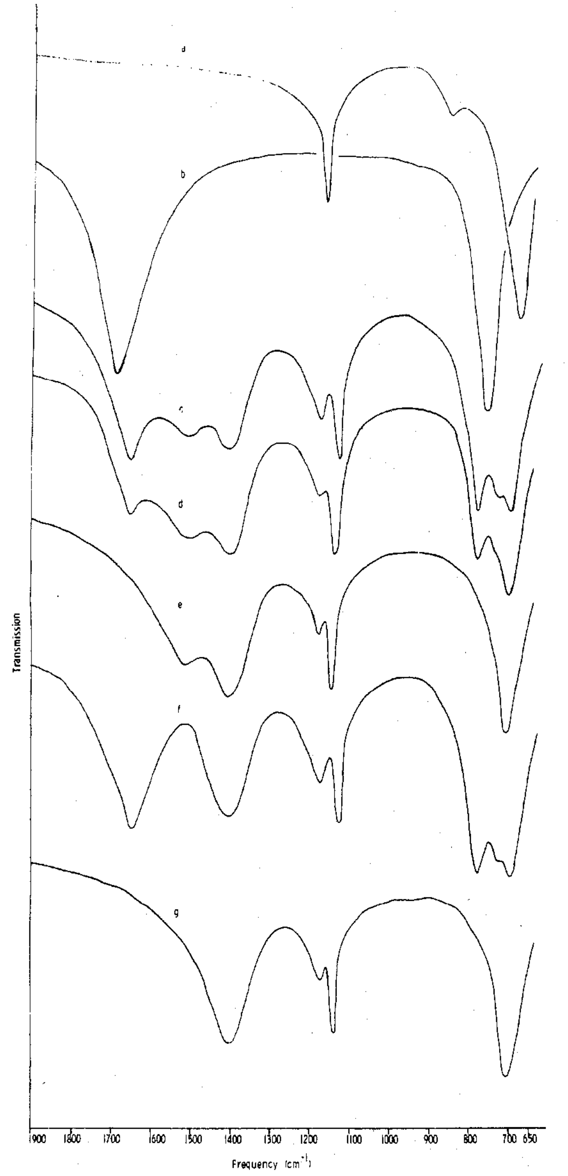


Figure 1. Infrared spectra of solutions obtained by adding $LiAlH_4$ to $(CH_3)_2Zn$ in THF: (a) $(CH_3)_2Zn$; (b) $LiAlH_4$; (c) 1:1 $LiAlH_4$ + $(CH_3)_2Zn$; (d) 2:3 $LiAlH_4$ + $(CH_3)_2Zn$; (e) 1:2 $LiAlH_4$ + $(CH_3)_2Zn$; (f) $LiZn(CH_3)_2AlH_4$; (g) $LiZn_2(CH_3)_4AlH_4$.

to that of $LiZn(CH_3)_2AlH_4$ prepared from $LiZn(CH_3)_2H$ and AlH_3, the only difference being the presence of a band at 1500 cm^{-1} in the infrared spectrum of the 1:1 $LiAlH_4$ and $(CH_3)_2Zn$ mixture. Likewise, the addition of either $LiAlH_4$ to $(CH_3)_2Zn$ in 1:2 ratio or $(CH_3)_2Zn$ to $LiAlH_4$ in 2:1 ratio in THF yields a clear solution whose infrared spectrum corresponds closely to that of $LiZn_2(CH_3)_4AlH_4$, again the difference being the occurrence of a band at 1500 cm^{-1}. Also the addition of $LiAlH_4$ to $(CH_3)_2Zn$ in 2:3 ratio or $(CH_3)_2Zn$ to $LiAlH_4$ in 3:2 ratio in THF yields a clear solution whose infrared spectrum corresponds to a mixture of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ except for the band at 1500 cm^{-1}. The infrared spectra of the $LiAlH_4$–$(CH_3)_2Zn$ mixtures are recorded in Figures 1 and 2. The observed infrared bands are tabulated in Table I for a more convenient comparison with the reported[1] bands for $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$. We reported[1] previously that the terminal Zn–H stretching band in $LiZn(CH_3)_2H$ occurs at 1450 cm^{-1}, whereas the bridging Zn–H–Zn stretching band in $LiZn_2(CH_3)_4H$ occurs at 1290 cm^{-1}. Formation of a bridging zinc–hydrogen bond compound to a terminal one results in a shifting of the asymmetric stretching band to a lower frequency by 160 cm^{-1}. Based on this, one would expect the terminal Al–H stretching band in $LiZn(CH_3)_2AlH_4$ to shift about 160 cm^{-1} to lower frequency on formation of an Al–H–Zn bridging bond. Since the terminal Al–H stretching band in $LiZn(CH_3)_2AlH_4$ occurs at 1660 cm^{-1}, one would expect an Al–H–Zn bridging hydride absorption in this compound to be at about 1500 cm^{-1}. This seems reasonable since the band at 1400 cm^{-1} in $LiZn(CH_3)_2AlH_4$ has been assigned to the double hydrogen bridged unit

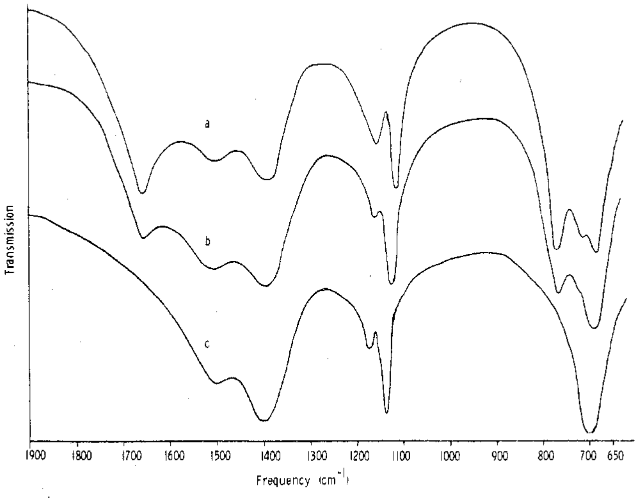
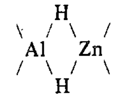
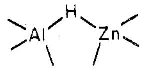


Figure 2. Infrared spectra of solutions obtained by adding $(CH_3)_2Zn$ to $LiAlH_4$ in THF: (a) 1:1 $(CH_3)_2Zn$ + $LiAlH_4$; (b) 2:3 $(CH_3)_2Zn$ + $LiAlH_4$; (c) 1:2 $(CH_3)_2Zn$ + $LiAlH_4$.



and one would expect a single hydrogen bridging unit to absorb at somewhat higher frequency. In light of this reasoning, the band observed at 1500 cm^{-1} for solutions obtained by mixing $LiAlH_4$ and $(CH_3)_2Zn$ is assigned the structural unit



In the solutions of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ prepared by reacting AlH_3 with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$, the compounds were present in concentrations of 0.15 and 0.10 M when the infrared spectra were recorded. The solutions of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ prepared in this study by mixing $LiAlH_4$ and $(CH_3)_2Zn$ had concentrations in the range 0.4–0.5 M when the infrared spectra were recorded. The observation of a band, due to a single hydrogen bridging unit, at higher concentrations, when it was not seen at lower concentration, leads one to conclude that this type of unit might be the result of higher associated species. In this connection, molecular association studies were carried out on solutions of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ prepared by mixing $LiAlH_4$ with $(CH_3)_2Zn$. The resulting association values are shown in Figure 3 for $LiZn(CH_3)_2AlH_4$ and Figure 4 for $LiZn_2(CH_3)_4AlH_4$. The data in these figures show that in the concentration range 0.4–0.5 M significant association to a dimer unit is occurring. At concentrations near 0.10 M, little association beyond the monomer is observed. Therefore, an equilibrium of the type shown in eq 4 is indicated for $LiZn(CH_3)_2AlH_4$ in THF. A similar equilibrium could be written for $LiZn_2(CH_3)_4AlH_4$. Structure III, the dimer of $LiZn(CH_3)_2AlH_4$, does contain the single hydrogen bridged unit. It is easy for one to see how the observed infrared spectra could arise when two compounds

Table II. Chemical Shifts for $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4$ at Various Concentrations in THF[a]

Sample	Concn, M	Chem shifts,[b] τ	Calcd assocn (i)
$LiZn(CH_3)_2AlH_4$ ($LiAlH_4$ + $(CH_3)_2Zn$)	0.48	10.96 (1.9, 10.98 (1.8), 11.02 (1.0)	1.42
	0.39	10.96 (3.3), 10.98 (2.5), 11.01 (1.0)	1.32
	0.28	10.95 (3.4), 10.98 (2.0), 11.02 (1.0)	1.27
	0.19	10.96 (6.1), 10.98 (2.3), 11.03 (1.0)	1.18
$LiZn(CH_3)_2AlH_4$ ($LiZn(CH_3)_2H$ + AlH_3)	0.18	10.96 (6.5), 10.98 (2.4), 11.02 (1.0)	1.18
	0.10	10.95 (10.7), 10.98 (1.0), 11.02 (2.3)	1.04
$LiZn_2(CH_3)_4AlH_4$ ($LiAlH_4$ + $2(CH_3)_2Zn$)	0.46	10.96 (6.7), 10.98 (3.1), 11.01 (1.0)	1.86
$LiZn_2(CH_3)_4AlH_4$ ($LiZn_2(CH_3)_4H$ + AlH_3)	0.12	10.96 (3.1), 11.02 (1.0)	1.00

[a] Spectra were recorded at 35 °C. [b] Relative integration is given in parentheses.

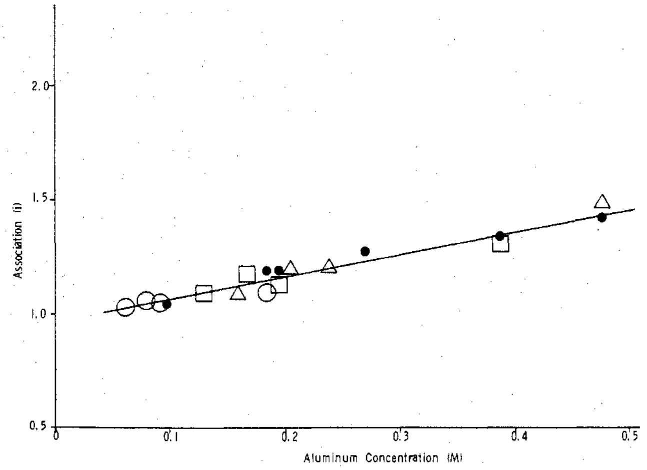
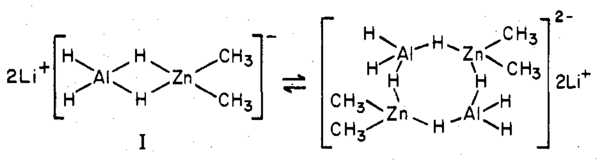


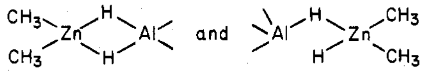
Figure 3. Molecular association values for $LiZn(CH_3)_2AlH_4$: ○, $LiZn(CH_3)_2H + AlH_3$, $C_0 = 0.18$ M; □, $LiAlH_4 + (CH_3)_2Zn$, $C_0 = 0.39$ M; △, $LiAlH_4 + (CH_3)_2Zn$, $C_0 = 0.48$ M; ●, calculated from NMR data.



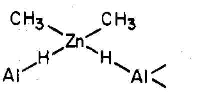
(4)

with the structures of I and III are present.

The ^1H NMR chemical shifts observed for $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ (prepared from $LiAlH_4$ and $(CH_3)_2Zn$) are listed in Table II. The chemical shifts are the same as those observed for $LiZn(CH_3)_2AlH_4$ prepared from AlH_3 and $LiZn(CH_3)_2H$. The resonances at τ 10.96 and 11.02 have been previously assigned to methyl groups in the structural units[1]



respectively. The resonance at τ 10.98 is seen to become more intense as the concentration of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ is increased (Table II and Figure 5). This suggests that the resonance is due to the dimer of these compounds. The dimer structure III contains the structural unit



which would provide a magnetic environment somewhat different from the two units above. Therefore the resonance at τ 10.98 is assigned to this unit. The NMR data suggest an equilibrium between structures which contain the three units shown above. Such an equilibrium is shown in Scheme I. The NMR integration data can be used to calculate the relative amounts of I, III, IV, and V and with these an apparent association can be calculated. Such association values are shown in Table II and plotted in Figures 3 and 4. It is seen that the calculated association values based on Scheme I agree well with the experimentally determined values, thus indicating that Scheme I provides a very reasonable picture of the composition of $LiZn(CH_3)_2AlH_4$ in THF. The NMR data for $LiZn_2(CH_3)_4AlH_4$ suggest that a similar equilibrium can be written to describe its solution composition.

The chemical shifts recorded with variable-temperature NMR for selected samples of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ are shown in Table III. The same three

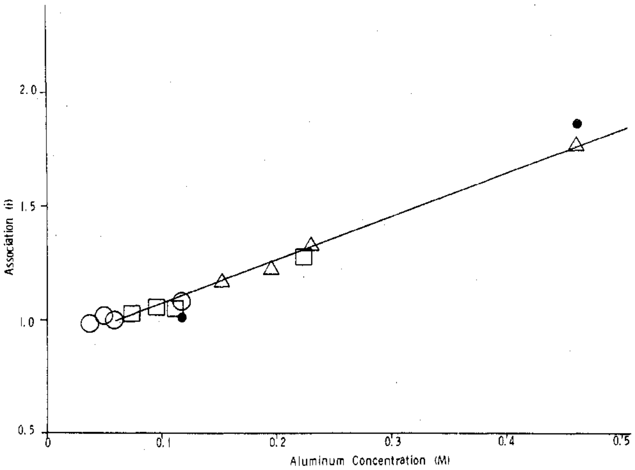


Figure 4. Molecular association values for $LiZn_2(CH_3)_4AlH_4$: ○, $LiZn(CH_3)_4H + AlH_3$, $C_0 = 0.12$ M; □, $LiAlH_4 + 2(CH_3)_2Zn$, $C_0 = 0.23$ M; △, $LiAlH_4 + 2(CH_3)_2Zn$, $C_0 = 0.46$ M; ●, calculated from NMR data.

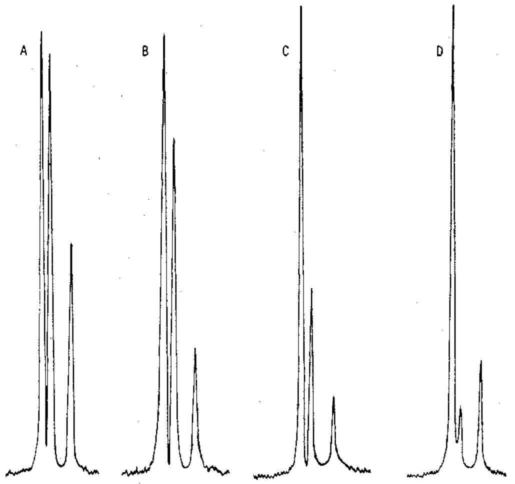
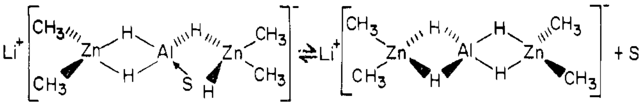


Figure 5. ^1H NMR spectra of $LiZn(CH_3)_2AlH_4$ in THF at various concentrations: (A) 0.48 M, (B) 0.39 M, (C) 0.19 M, (D) 0.10 M.

Table III. Chemical Shifts for $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ at Various Temperatures in THF

Sample	Concn, M	Temp, °C	Chem shifts, τ	Rel integration
$LiZn(CH_3)_2AlH_4$	0.39	35	10.96, 10.98, 11.01	3.3:2.5:1.0
($LiAlH_4$ + $(CH_3)_2Zn$)		21	10.98, 11.00, 11.03	3.9:2.8:1.0
		4	10.99, 11.01, 11.03	4.8:2.9:1.0
		−19	10.99, 11.01, 11.04	5.6:3.1:1.0
		−36	11.00, 11.02, 11.07	6.1:3.4:1.0
		−51	11.01, 11.04, 11.11	6.8:3.5:1.0
		−63	11.02, 11.06, 11.14	7.6:3.7:1.0
		−81	11.02, 11.06, 11.17	8.6:3.8:1.0
$LiZn_2(CH_3)_4AlH_4$	0.46	35	10.96, 10.98, 11.01	6.7:3.1:1.0
($LiAlH_4$ + $2(CH_3)_2Zn$		−63	10.98, 10.99, 11.08	9.5:4.3:1.0
$LiZn_2(CH_3)_4AlH_4$	0.12	−35	10.96, 11.02	3.1:1.0
($LiZn_2(CH_3)_4H$ + AlH_3		−63	10.99, 11.11	5.0:1.0

Table IV. Equilibrium Constants at Various Temperatures for the Reaction

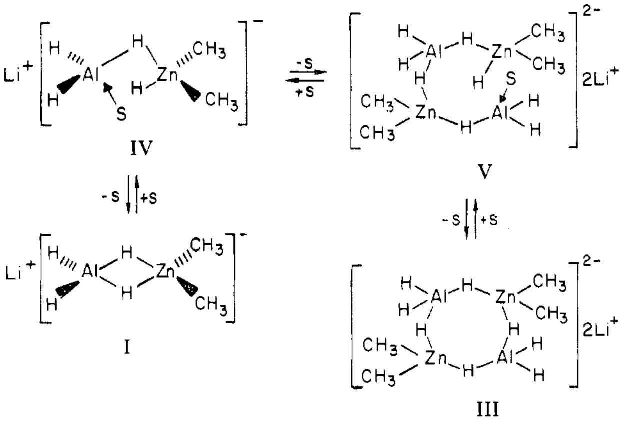


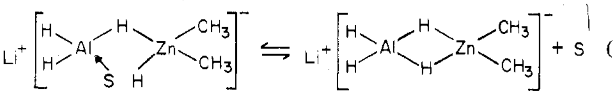
in Tetrahydrofuran

Temp, °C	K^a	Ln K	$1/T$ (K^{-1}) X 10^3
35	4.60	1.53	3.2
21	5.16	1.64	3.4
4	6.12	1.81	3.6
−19	7.03	1.95	3.9
−36	7.67	2.04	4.2
−51	8.46	2.14	4.5
−63	9.79	2.28	4.8
−81	10.27	2.33	5.2

[a] An exponential curve fit to the data yields $K = 1.36e^{404/T}$ with a correlation factor of $R^2 = 0.96$. This equation gives the following thermodynamic parameters: $\Delta H = -803$ cal/mol, $\Delta S = 0.61$ eu.

Scheme I





(5)

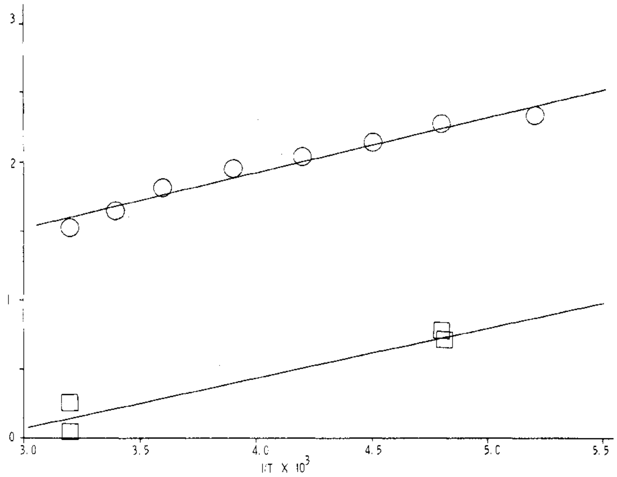
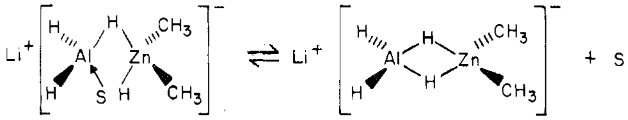


Figure 6. Plot of ln K vs. $1/T$ for the following reactions: ○, $LiZn(CH_3)_2AlH_4{\cdot}S = LiZn(CH_3)_2AlH_4 + S$; □, $LiZn_2(CH_3)_4AlH_4{\cdot}S = LiZn_2(CH_3)_4AlH_4 + S$.

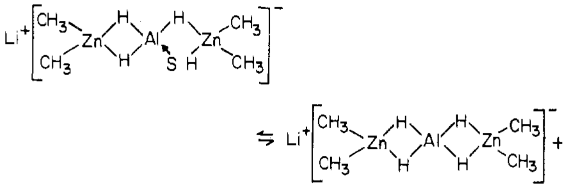
Table V. Equilibrium Constants at Various Temperatures for the Reaction



in Tetrahydrofuran

Temp, °C	K^a	Ln K	$1/T$ (K^{-1}) X 10^3
35	1.04	0.04	3.2
35	1.29	0.25	3.2
−63	2.02	0.70	4.8
−63	2.14	0.76	4.8

[a] An exponential curve fit to the data yields $K = 0.36e^{364/T}$ with a correlation factor of $R^2 = 0.93$. This equation gives the following thermodynamic parameters: $\Delta H = -724$ cal/mol, $\Delta S = -2.02$ eu.



(6)

resonances are observed, but they move to higher field as the temperature is decreased due to solvent anisotropy.[7] Integration of these signals shows that, in the case of $LiZn(CH_3)_2AlH_4$, the equilibrium in Scheme I is shifted in favor of I as the temperature is decreased; i.e., the amounts of solvated structures IV and V decrease with decreasing temperature. Using the NMR integration data, equilibrium constants can be calculated for this process (eq 5). The equilibrium constants are given in Table IV and plotted as ln K vs. $1/T$ in Figure 6. Equilibrium constants for the similar process involving $LiZn_2(CH_3)_4AlH_4$ (eq 6) are given in Table V and plotted in Figure 6. The enthalpy and entropy of the reaction as written in eq 5 are calculated to be −0.80 kcal/mol and 0.61 eu. For eq 6, ΔH and ΔS are calculated to be −0.72 kcal/mol and −2.02 eu. The enthalpy of reactions 5 and 6 would be expected to be about equal since an aluminum–solvent coordinate bond is broken and an Al–H–Zn bridge bond is formed in both. Of course the calculated enthalpies support

$$\Delta H(\text{reaction}) = \Delta H(\text{solvation}) + \Delta H(\text{bond energy})$$

our suggestions, since they are equal within the uncertainty that lies in this type of calculation. The negative enthalpy of reaction indicates that the Al–H–Zn bridge bond is stronger than the aluminum solvent bond. The entropy of reaction 5 is positive, which is expected since the partition function for two molecules translating independently should be greater than that for the vibration of the solvent coordinate bond. The magnitude of ΔS is, however, not as great as one would have expected (generally in the range of 10 eu[8]) since formation of the double hydrogen bridge restricts the degrees of freedom of the molecules. In eq 6, two double hydrogen bridge units are formed which leads to a negative entropy of reaction.

A simple representation of the basic solvation equilibrium is shown in eq 7. The forward reaction should be endothermic

$$\mathrm{M{\cdot}S} \rightleftharpoons \mathrm{M} + \mathrm{S} \tag{7}$$

($\Delta H > 0$ kcal/mol) since a coordinate bond breaks and the entropy should be positive ($\Delta S > 0$ eu). Both reactions 5 and 6 violate this principle, so the solvation equilibrium cannot be as simple as that of eq 7. Indeed, the solvation equilibrium is complicated by simultaneous formation of a double hydrogen bridge. There is, however, a precedent for this type of behavior. The Schlenk equilibrium for C_2H_5MgBr (eq 8) is

$$(C_2H_5)_2Mg + MgBr_2 \rightleftharpoons 2C_2H_5MgBr \tag{8}$$

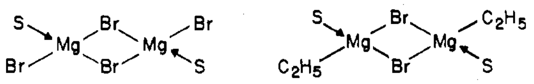
reported to have ΔH and ΔS values of 6.1 kcal/mol and 23.7 eu in THF,[9] whereas these values become −3.7 kcal/mol and −0.3 eu in diethyl ether.[10] In THF, $(C_2H_5)_2Mg$, C_2H_5MgBr, and $MgBr_2$ are all monomeric.[11] Typical organomagnesium halides have been shown to form disolvates in THF,[12] as do the diorganomagnesium compounds.[13] The magnesium halides form tetrasolvates with THF.[14] This leads one to revise eq 8 for the Schlenk equilibrium to eq 9 so that the solvation

$$(C_2H_5)_2Mg{\cdot}2S + MgBr_2{\cdot}4S \rightleftharpoons 2C_2H_5MgBr{\cdot}2S + 2S \tag{9}$$

effects of THF can be included.[8] The signs of ΔH and ΔS for this reaction should follow the predictions based on the solvation equilibrium in eq 7, since only monomeric species are present; i.e., no bridge bonds are being formed. The data, of course, are consistent with this suggestion. In diethyl ether $(C_2H_5)_2Mg$ is monomeric while C_2H_5MgBr is essentially dimeric. Magnesium bromide is more highly associated than even a dimer.[11] The Schlenk equilibrium in eq 8 should then be revised to eq 10, so solvation effects can be included. (For

$$(C_2H_5)_2Mg{\cdot}2S + {}^1/_2[(MgBr_2)_2{\cdot}2S] \rightleftharpoons (C_2H_5MgBr)_2{\cdot}2S + S \tag{10}$$

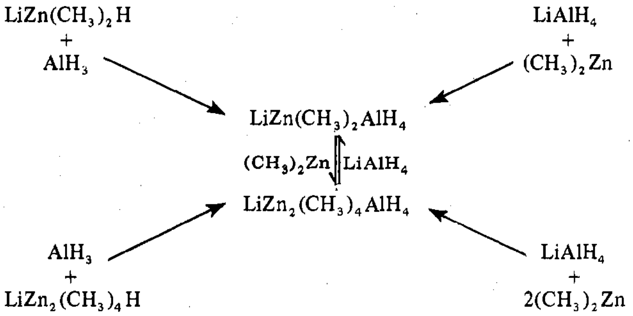
simplicity magnesium bromide is written as the dimer in this equation.) Diorganomagnesium compounds are known to form bis(diethyl etherates), whereas dimeric $MgBr_2$ and C_2H_5MgBr would have one solvent molecule per magnesium as shown by the structures below. The reaction in eq 10 is similar to



reactions 5 and 6 above in that coordinated solvent is displaced with the formation of a double halogen bridge. Both the ΔH and ΔS for this reaction are negative, not what one would predict based on the simple solvation equilibrium of eq 7, but indeed consistent with the thermodynamic parameters observed for reactions 5 and 6.

The concentrations of the THF solutions of $LiZn(CH_3)_2AlH_4$ studied initially by infrared analysis were about 0.2–0.4 M. These solutions, after preparation, remained clear for a few hours at room temperature but then began to deposit a black solid. It was found that even after sitting 1 week not all of the zinc deposited from these solutions. Analysis of the black solid revealed that it contained Li:Zn:H:Al in a molar ratio of 1.06:2.00:3.20:0.05. An x-ray powder diffraction pattern of the solid contained lines due to $LiZnH_3$ and Zn metal only. It is suggested that $LiZn_2H_5$[15] precipitated from the solution of $LiZn(CH_3)_2AlH_4$ in THF and then decomposed rapidly to $LiZnH_3$ and ZnH_2, with the ZnH_2 undergoing subsequent decomposition to Zn metal. On the other hand, when a 0.2 M solution of $LiZn(CH_3)_2AlH_4$ was diluted 20-fold or greater with THF, a white precipitate of ZnH_2 formed within 5 min. Also if $LiAlH_4$ is added to a dilute solution of $(CH_3)_2Zn$ in THF, i.e., about 0.01 M, a white precipitate of ZnH_2 begins to form within 5 min. The yields of ZnH_2, however, are low, never being greater than 50%. The fact that $LiZnH_3$ is formed at concentrations greater than 0.1 M, but at concentrations less than this, suggests that this hydride results from III, the dimer of $LiZn(CH_3)_2AlH_4$. The complex metal hydride only precipitates from solutions of $LiZn(CH_3)_2AlH_4$ where the association value is at least 1.10. Solutions of $LiZn(CH_3)_2AlH_4$, which contain for the most part only the monomeric form I, result in the precipitation of ZnH_2 only. The fact that ZnH_2 is formed by way of $LiZn(CH_3)_2AlH_4$ in THF is good evidence that $LiZn(CH_3)_2AlH_4$ is the intermediate involved in the alkyl–hydrogen exchange reaction between $LiAlH_4$ and $(CH_3)_2Zn$ to give ZnH_2. It has been known for quite some time that the reaction of a dialkylzinc compound with $LiAlH_4$ in diethyl ether produces ZnH_2;[2] however, no attempts have been made to determine the intermediates involved in the reaction. This work suggests that $LiZn(CH_3)_2AlH_4$ is an intermediate in this reaction. The fact that $LiZn(CH_3)_2AlH_4$ can be detected in the reaction mixture of $LiAlH_4$ with $(CH_3)_2Zn$ which produces ZnH_2 in THF is strong evidence to support the above statement.

Scheme II

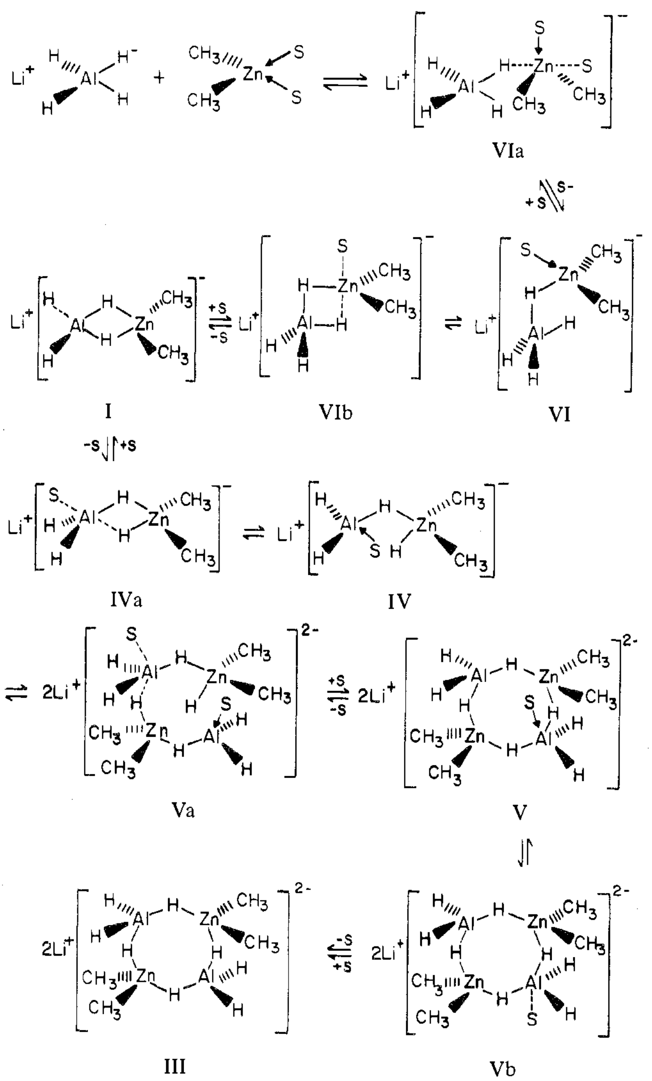


Conclusions

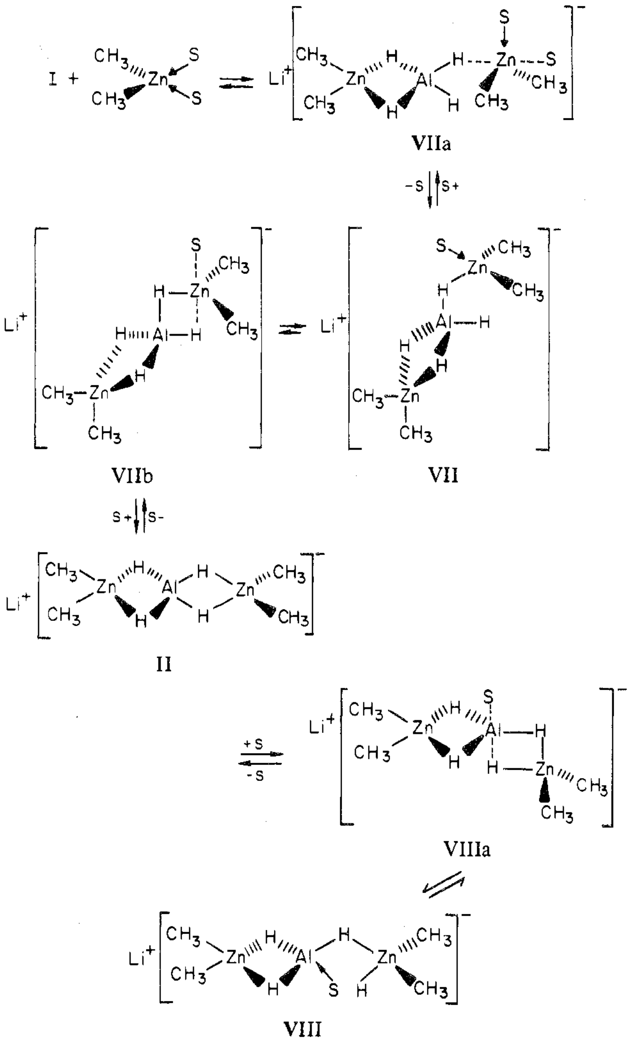
Whether $LiAlH_4$ is added to $(CH_3)_2Zn$ or $(CH_3)_2Zn$ is added to $LiAlH_4$ makes no difference as far as the final products of the reaction are concerned. The infrared spectra observed when the ratio of $(CH_3)_2Zn$ to $LiAlH_4$ is 1:1, 3:2, or 2:1 are the same. As $LiAlH_4$ is added to $(CH_3)_2Zn$, there is a smooth conversion of the $(CH_3)_2Zn$ to $LiZn_2(CH_3)_4AlH_4$ and then to $LiZn(CH_3)_2AlH_4$. On the other hand, when $(CH_3)_2Zn$ is added to $LiAlH_4$, there is a smooth conversion of $LiAlH_4$ to $LiZn(CH_3)_2AlH_4$ and then to $LiZn_2(CH_3)_4AlH_4$. These reactions are shown in Scheme II. Thus, $LiZn_2(CH_3)_4AlH_4$ can be converted to $LiZn(CH_3)_2AlH_4$ by addition of $LiAlH_4$, and $LiZn(CH_3)_2AlH_4$ can be converted to $LiZn_2(CH_3)_4AlH_4$ by addition of $(CH_3)_2Zn$. These interconversions indicate that there exists a mobile equilibrium between $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$. This statement is supported by the fact that a 3:2 mixture of $(CH_3)_2Zn$ and $LiAlH_4$ gives rise to both $LiZn_2(CH_3)_4AlH_4$ and $LiZn(CH_3)_2AlH_4$.

The mechanism for the formation of $LiZn(CH_3)_2AlH_4$ when $(CH_3)_2Zn$ and $LiAlH_4$ are allowed to react in THF can be visualized as occurring in the manner shown in Scheme III. Lithium aluminum hydride (solvent-separated ion pair[16]) reacts with the THF solvate of dimethylzinc by nucleophilic attack of AlH_4^- on zinc displacing solvent to give VI by way of transition state VIa. In this reaction one of the zinc–THF

Scheme III



Scheme IV



solvate bonds is broken with formation of a zinc–hydrogen bridge bond. The forward reaction should be exothermic ($\Delta H < 0$ kcal/mol) and the entropy should be positive ($\Delta S > 0$ eu), thus making the formation of VI from $LiAlH_4$ and $(CH_3)_2Zn$ very favorable. One would expect ΔH to be negative since a zinc–THF solvate bond, which should be weaker than an aluminum–THF solvate bond, is being replaced by a Zn–H–Al bridge bond. Our studies here have shown that Al–H–Zn bridge bonds are stronger than aluminum–THF solvate bonds. Intermediate VI then proceeds to form I via transition state VIb by an intramolecular nucleophilic displacement of solvent on zinc. In the latter intramolecular reaction, the remaining zinc–THF solvate bond is broken with formation of a second zinc–hydrogen bridge bond. This reaction would also be expected to be very favorable for the same reasons just given. The equilibrium between I and VI would be expected to be shifted largely in favor of I. This is shown to be true experimentally since no signals for a compound such as VI are observed in the NMR. Moreover, the entire equilibrium represented by reaction 11 would be expected to be shifted

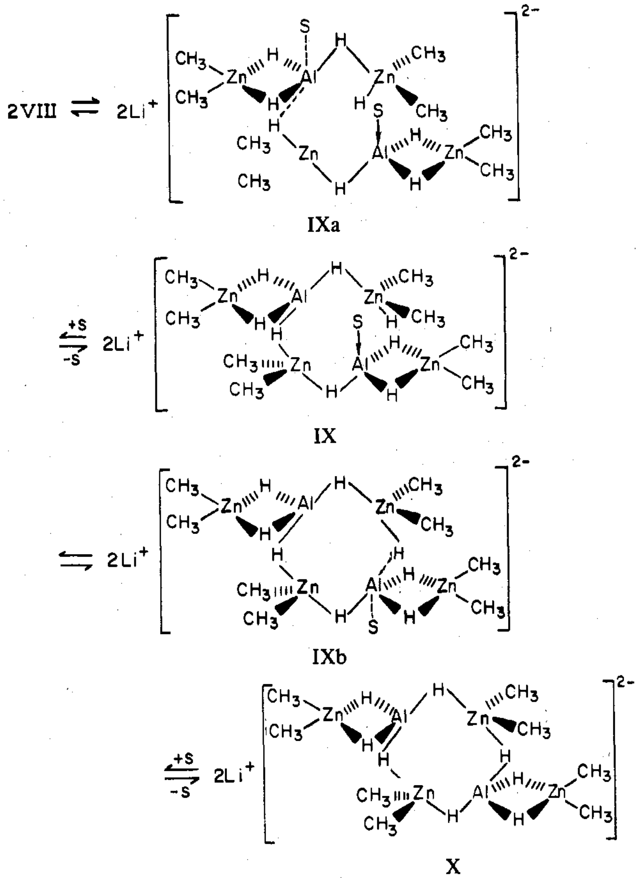
$$LiAlH_4 + (CH_3)_2Zn{\cdot}2S \rightleftharpoons LiZn(CH_3)_2AlH_4 + 2S \qquad (11)$$

entirely in favor of $LiZn(CH_3)_2AlH_4$, again, for the reasons cited above. The forward reaction should be strongly exothermic[17] and the entropy positive. This again is shown experimentally, since spectroscopic studies on $LiZn(CH_3)_2AlH_4$ failed to show any evidence to indicate the presence of $LiAlH_4$ or $(CH_3)_2Zn$. Solvate IV is then formed via transition state IVa by a nucleophilic solvent attack on the aluminum in I. In this reaction, the Al–H–Zn bridge bonds are broken with formation of an aluminum–THF solvate bond. The equilibrium between I and IV which was discussed earlier lies slightly in favor or I. If the concentration of the solution is such that dimers will be present, then the dimer forms V and III will be formed through transition states Va and Vb, respectively. The equilibrium between V and III lies in favor of III. The amount of III relative to I depends upon both the concentration and temperature of the solution.

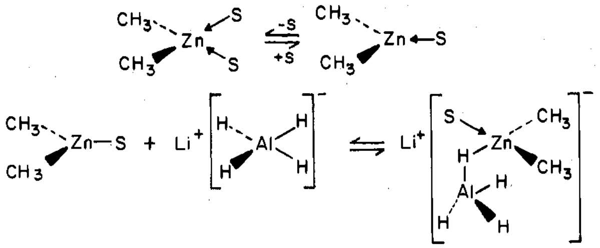
The mechanism for the formation of $LiZn_2(CH_3)_4AlH_4$ when $LiAlH_4$ and $(CH_3)_2Zn$ are allowed to react in THF can be visualized as occurring in the manner shown in Scheme IV. Lithium aluminum hydride reacts with the THF solvate of $(CH_3)_2Zn$ to give I by the mechanism shown in Scheme III. I then reacts with the THF solvate of $(CH_3)_2Zn$ to form VII by way of transition state VIIa. This reaction is similar to the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ to form VI in Scheme III. Nucleophilic displacement of a THF solvent molecule from the tetrahedral zinc (transition state VIIb) then results in the formation of another zinc–hydrogen bridge bond and the formation of II. On the whole, this mechanism is very similar to that shown in Scheme III. II then reacts through VIIIa to give VIII. For solutions where dimers are present, VIII reacts through IXa to give IX, which then gives X through IXb (Scheme V). VIII, IX, and X could also be formed by the reactions of IV, V, and III with $(CH_3)_2Zn$.

In both Schemes III and IV, the transition states are pictured as involving five-coordinate, trigonal-bipyramidal zinc.

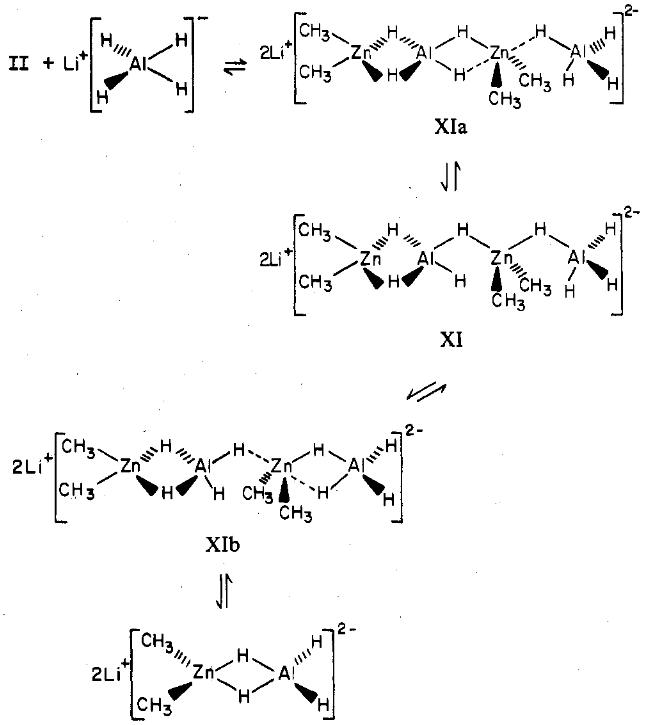
Scheme V



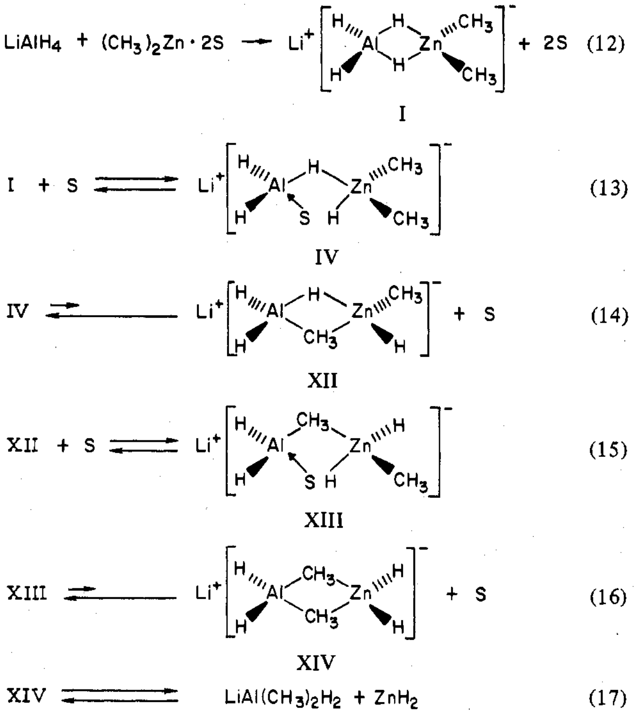
Scheme VI



Scheme VII



Scheme VIII



This geometry assumes an S_N2-type displacement of solvent from zinc. Loss of solvent via an S_N1-type reaction was considered; however, this type of mechanism would necessarily imply the existence of three-coordinate zinc as shown in Scheme VI. Since four- and five-coordinate organozinc species are much more common than three-coordinate ones,[18] an S_N2-type nucleophilic displacement mechanism is favored.

The mechanism of conversion of $LiZn_2(CH_3)_4AlH_4$ to $LiZn(CH_3)_2AlH_4$ in THF by the addition of $LiAlH_4$ (see Scheme II) is pictured in Scheme VII. Lithium aluminum hydride reacts with $LiZn_2(CH_3)_4AlH_4$ to give XI by way of transition state XIa. One of the zinc–hydrogen bridge bonds in $LiZn_2(CH_3)_4AlH_4$ is broken by S_N2 attack of AlH_4 on one of the terminal zinc atoms and a new zinc–hydrogen bridge bond is formed between the terminal zinc and the incoming AlH_4^- group. Intermediate XI then forms two molecules of $LiZn(CH_3)_2AlH_4$ by way of XIb.

Concerning the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ to produce ZnH_2, the work reported here clearly establishes that $LiZn(CH_3)_2AlH_4$ is the primary intermediate involved in this reaction. Scheme VIII shows a reasonable mechanism for this reaction using the intermediates that have been detected by spectroscopic means in this study. Intermediates I and IV are formed rapidly from $LiAlH_4$ and $(CH_3)_2Zn$, since they were detected immediately after mixing the two reactants. The formation of the mixed-bridge intermediate XII in reaction 14 is probably very slow and could very well be the rate-limiting step. This reaction would be expected to be slow since an aluminum–THF solvate bond is being broken by the formation of a methyl bridge bond between zinc and aluminum. The methyl bridge bond would be expected to be weaker than the aluminum solvate bond.[8] Formation of the double methyl bridged intermediate XIV in reaction 16 would be slow also, perhaps slower than reaction 14. Reaction 17 completes the sequence with XIV disproportionating to

$LiAl(CH_3)_2H_2$ 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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(7) The magnetic field experienced by a solute molecule will depend in part on the bulk magnetic susceptibility of the solution. The average orientation of molecules in the bulk solvent surrounding a solute molecule is temperature and concentration dependent and as this average orientation changes so will the chemical shift. These effects are usually small compared to specific solvation effects but may amount to a tenth of a part per million in chemical shift or more in specific cases. Solvent anisotropy in connection with concentration changes was not observed here, since the concentration was never much greater than 0.5 M. In studies on Grignard reagents these effects were not observed until the concentration became 2.0 M.

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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.