in THF showed the chemical shift separation between the highest peaks of the two multiplets to be 0.68 ppm in both cases.

Ebulliscopic molecular weight data for PhMgH in THF showed it to be monomer at infinite dilution with the molecular weight increasing sharply with concentration [mol wt of PhMgH (molality vs. association): 0.0284 *m*, 1.27; 0.0712 *m*, 1.95; 0.124 *m*, 3.02; 0.1774 *m*, 4.10]. However, the molecular weight of $PhMg_2H_3$ could not be determined as it cleaved THF at reflux to give an insoluble product of empirical formula $PhMg_2(O\text{-}n\text{-}Bu)_3$.

The product PhMgH·0.5THF gave x-ray powder diffraction pattern lines at 8.05 (s), 6.60 (m), 5.40 (w), 4.80 (m), 4.60 (w), 4.21 (vs), 3.85 (w), 3.60 (w), 3.40 (w), 3.30 (w), 3.05 (w), 2.80 (w), 2.43 (w), and 2.40 (w) Å. The amorphous solid $PhMg_2H_3$ which contains an indefinite amount of ether did not give any x-ray powder pattern. Vacuum DTA–TGA studies of PhMgH·0.5THF showed loss of THF at 100 °C after which a continued weight loss with an increase in temperature was observed. The maximum weight loss was observed at 300 °C due to benzene evolution. No hydrogen gas evolution was noticed. In the case of the etherate of $PhMg_2H_3$, the first weight loss was observed at 100–120 °C (due to loss of ether) after which a continued weight loss with an increase in temperature was observed. Hydrogen evolution was observed at 300–360 °C. The trapped gases were ether, benzene, and some ethanol.

The difference between the infrared, NMR, and powder diffraction data for Ph_2Mg and MgH_2 as compared to the products PhMgH and $PhMg_2H_3$ provides additional evidence for the integrity of the latter compounds as true compounds rather than physical mixtures of Ph_2Mg and MgH_2.

Registry No. Ph_2Mg, 555-54-4; $LiAlH_4$, 16853-85-3; $LiAlPh_4$, 62126-57-2; $PhMg_2H_3$, 62139-40-6; MgH_2, 7693-27-8; PhMgH, 62086-01-5; $LiAlH_2Ph_2$, 27662-04-0; $LiAlHPh_3$, 62126-58-3.

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Nature of Alkyl–Hydrogen Exchange Reactions Involving Aluminum and Zinc. 1. Reactions of $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ with Aluminum Hydride

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When AlH_3 is allowed to react with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ in tetrahydrofuran in 1:1 molar ratio, $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ are formed as soluble complexes. These two compounds are the first reported triple metal hydride complexes involving lithium, aluminum, and zinc. Their solution composition is inferred from spectroscopic and colligative property studies. The mechanisms of formation of these compounds by the reaction of AlH_3 with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ in THF are discussed in light of the spectroscopic results.

Introduction

Recently we have reported the synthesis of several complex metal hydrides of zinc:[1-3] Li_3ZnH_5, Li_2ZnH_4, $LiZnH_3$, Na_2ZnH_4, $NaZnH_3$ [4], $NaZn_2H_5$, K_2ZnH_4, $KZnH_3$, and KZn_2H_5. All but two of these complex metal hydrides were prepared by alkyl–hydrogen exchange reactions between either $LiAlH_4$, $NaAlH_4$, or AlH_3 and an ate complex of zinc. Li_3ZnH_5, Li_2ZnH_4, and $LiZnH_3$ were prepared by reacting the ate complexes $Li_3Zn(CH_3)_5$, $Li_2Zn(CH_3)_4$, and $LiZn(CH_3)_3$ with $LiAlH_4$ in diethyl ether. $NaZnH_3$ was obtained by the reaction of $NaZn(CH_3)_2H$ with $NaAlH_4$ in THF, and $KZnH_3$ was prepared by the analogous reaction of $KZn(CH_3)_2H$ with $LiAlH_4$. The reactions of AlH_3 with $NaZn(CH_3)_2H$ and $KZn(CH_3)_2H$ in THF produced $NaZn_2H_5$ and KZn_2H_5.

Since our discovery of the use of aluminohydrides in the synthesis of main-group complex metal hydrides, we have been very interested in the nature of exchange reactions between Al–H species and main-group alkyl–metal species. The reaction of $LiZn(CH_3)_2H$ with AlH_3, while it would have been expected to give $LiZnH_3$ in a manner similar to the above reactions, resulted instead in the formation of the THF-soluble complex $LiZn(CH_3)_2AlH_4$. The similar complex $LiZn_2(CH_3)_4AlH_4$ was then prepared by reacting $LiZn_2(CH_3)_4H$ with AlH_3 in THF. We feel that, in addition to providing a possible route to triple metal hydrides, an in depth study of the formation of these complexes could provide insight into the nature of exchange reactions between aluminohydride compounds and ate complexes of zinc.

Experimental Section

Apparatus. Reactions were performed under nitrogen using Schlenk-tube techniques.[5] Filtrations and other manipulations were carried out in a glovebox equipped with a recirculating system.[6]

Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solutions were studied in matched 0.10-mm path length NaCl or KBr cells. X-ray powder data were obtained on a Philips-Norelco x-ray unit with 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. *d* Spacings were read on a precalibrated scale equipped with viewing apparatus. Intensities were estimated visually. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer equipped with a standard variable-temperature unit. Ebullioscopic molecular association studies were carried out in THF under vacuum (240 mmHg absolute) using the technique developed by Walker and Ashby.[7]

Analytical Work. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[5] Methane in the presence of hydrogen was determined in a previously described tensimeter.[5] 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 other metals was determined by EDTA titration.

Materials. Lithium hydride was prepared by hydrogenolysis of *tert*-butyllithium at 4000 psi for 24 h. Dimethylzinc was prepared by the procedure of Noller.[8] Methyl iodide was obtained from Fisher Scientific. The iodide was dried over anhydrous $MgSO_4$ and distilled prior to use. The zinc–copper couple was obtained from Alfa Inorganics. The reaction of the zinc–copper couple with methyl iodide was allowed to proceed overnight. The dimethylzinc was distilled from the reaction mixture under nitrogen. Tetrahydrofuran (Fisher Certified reagent grade) was distilled under nitrogen over $NaAlH_4$. Ultrapure hydrogen (99.9995%) obtained from the Matheson Corp. was used for hydrogenation experiments. Aluminum hydride was prepared by the reaction of 100% H_2SO_4 with $LiAlH_4$ in THF. Li_2SO_4 was removed by filtration resulting in a clear and colorless solution of AlH_3 in THF.[9]

Reaction of AlH_3 with $LiZn(CH_3)_2H$ in Tetrahydrofuran. Five millimoles of dimethylzinc in THF was added to 5 mmol of lithium hydride slurry in THF. This mixture was stirred until all of the lithium hydride dissolved; then 5 mmol of AlH_3 in THF was added. After 1 h of stirring, an infrared spectrum, NMR spectrum, and ebullioscopic molecular weight were obtained on the clear solution. The infrared spectrum is shown in Figure 1 in addition to the spectra of $(CH_3)_2Zn$, AlH_3, and $LiZn(CH_3)_2H$ in THF. The infrared spectrum of the solution does not correspond to a mixture of AlH_3 and $LiZn(CH_3)_2H$. The NMR spectrum in the region upfield from TMS is shown in Figure 4. The molecular weight measurement gave an *i* value of 1 in the concentration range 0.06–0.18 M when based on aluminum concentration.

Infrared spectra were recorded for a 0.18 M solution obtained by the reaction of $LiZn(CH_3)_2H$ with AlH_3 at time periods of 1 h, 5 h, 24 h, 2 days, 4 days, 7 days, 2 weeks, and 3 weeks after the initial mixing of the reactants. In every case the infrared spectrum of the supernatant solution was the same as that shown in Figure 1d, except the spectra became less intense with time. After the first four hours a black solid began to precipitate and continued to do so during the remainder of the 3-week period. At the end of this time period, the supernatant solution contained a little less than half of the starting zinc (2.47 mmol of the starting 5 mmol of zinc). The black solid was separated by filtration, washed with THF, and dried under vacuum overnight at room temperature. Analysis revealed that it contained Li, Zn, H, and Al in the molar ratio 1.06:2.00:1.93:0.07. An x-ray powder diffraction pattern of the solid contained lines due to $LiZnH_3$ and Zn metal only.

In a separate experiment, $LiZn(CH_3)_2H$ and AlH_3 were allowed to react at room temperature for 1 week and at a concentration of 0.18 M. At the end of this time, a black solid had formed and was separated by filtration, washed with THF, and dried under vacuum. Analysis of the black solid indicated a Li:Zn:H:Al molar ratio of 1.04:2.00:3.28:0.04. An x-ray powder diffraction pattern of the solid contained lines due to $LiZnH_3$ and Zn metal only.

In another experiment, $LiZn(CH_3)_2H$ and AlH_3 were allowed to react at a concentration of 0.02 M. This reaction produced instead of a clear solution a white solid. The solid was separated by filtration, washed with THF, and dried under vacuum. Analysis of the solid indicated Li:Zn:H:Al molar ratios of 0.01:1.00:1.98:0.03. An x-ray powder diffraction pattern showed the solid to be ZnH_2.

Attempts were made to obtain the compound formed by reacting $LiZn(CH_3)_2H$ with AlH_3 as a solid by stripping off the THF solvent at room temperature because of our interest in obtaining x-ray powder diffracion and DTA–TGA analysis on this material. However, these attempts always gave a black, gummy material which was unsuitable for use. An attempt was made to separate the compound as a solid by crystallization at reduced temperature but no crystals formed. The solution of this compound in THF stayed clear and did not precipitate any black solid for indefinite periods of time when cooled to dry ice–acetone temperature. An attempt to obtain the solid compound by stripping THF from solution at reduced temperatures resulted in a gum which turned black on warming to room temperature.

Reaction of AlH_3 with $LiZn_2(CH_3)_4H$ in THF. $(CH_3)_2Zn$ in THF (8.35 mmol) was added to 4.17 mmol of LiH slurried in THF. A clear solution resulted to which was added 4.17 mmol of AlH_3 in THF. The mixture remained clear even after 1 h of stirring. The infrared spectrum, NMR spectrum, and ebullioscopic molecular weight were obtained on the solution. The infrared spectrum is shown in Figure 2d along with the infrared spectra of $(CH_3)_2Zn$, AlH_3, and $LiZn_2(CH_3)_4H$ in THF. The infrared spectrum of the solution does not correspond to a mixture of AlH_3 and $LiZn_2(CH_3)_4H$. The NMR spectrum is shown in Figure 4. The molecular weight measurement gave an *i* value of 1 in the concentration range 0.04–0.12 M when based on aluminum concentration.

The solution obtained from the reaction of $LiZn_2(CH_3)_4H$ with AlH_3 stood overnight before any black solid was observed. Attempts to obtain a solid sample of soluble product from this reaction failed.

Reaction of AlH_3 with $LiZn(CH_3)_2AlH_4$ in THF. $(CH_3)_2Zn$ in THF (5 mmol) was added to 5 mmol of LiH slurried in THF. A clear solution resulted to which was added 5 mmol of AlH_3 in THF. The resulting solution, which was 0.18 *m* in $LiZn(CH_3)_2AlH_4$, was stirred for 1 h; then 5 mmol more of AlH_3 was added. A white precipitate appeared immediately. The solid was slurried for 1 h and then separated by filtration, washed with THF, and dried under vacuum. Analysis of the solid indicated Li:Zn:H:Al molar ratios of 0.03:1.00:2.04:0.00. An x-ray powder diffraction pattern and vacuum DTA–TGA showed the solid to be ZnH_2. The filtrate contained 4% of the starting zinc and Li, Al, Zn, CH_3, and H in the molar ratio 1.00:1.91:0.03:1.96:4.89. An infrared spectrum of the filtrate (bands in the metal–hydrogen stretching region at 1745 and 1693 cm^{-1}) indicated the presence of $(CH_3)_2AlH$ and $LiAlH_4$.

Reaction of AlH_3 with $LiZn_2(CH_3)_4AlH_4$ in THF. $(CH_3)_2Zn$ in THF (8.35 mmol) was added to 4.18 mmol of LiH slurried in THF. A clear solution resulted to which was added 4.17 mmol of AlH_3 in THF. The resulting solution which was 0.12 M in $LiZn_2(CH_3)_4AlH_4$ was stirred for 1 h; then 4.17 mmol more of AlH_3 was added. A white precipitate appeared immediately. The solid was slurried for 1 h and then separated by filtration, washed with THF, and dried under vacuum. Analysis of the solid indicated a Li:Zn:H:Al molar ratio of 0.02:1.00:2.08:0.06. An x-ray powder diffraction pattern showed the solid to be ZnH_2. The filtrate contained 5% of the starting zinc and Li, Al, Zn, CH_3 and H in the molar ratio 1.00:1.93:0.10:3.93:1.99. An infrared spectrum of the filtrate (bands in the terminal Al–H stretching region at 1747 and 1660 cm^{-1}) indicated the presence of $(CH_3)_2AlH$ and $LiAl(CH_3)_2H_2$.

Reaction of $LiAlH_4$ with $LiZn(CH_3)_2AlH_4$ in THF. $(CH_3)_2Zn$ in THF (5 mmol) was added to 5 mmol of LiH slurried in THF. A clear solution resulted to which was added 5 mmol of AlH_3 in THF. The resulting solution was stirred for 1 h; then 5 mmol of $LiAlH_4$ in THF was added. The solution still remained clear. It was stirred for 2 h and an infrared spectrum run on the solution. The spectrum corresponded to a mixture of $LiAlH_4$ and $LiZn(CH_3)_2AlH_4$.

Reactions of $LiAlH_4$ with $LiZn_2(CH_3)_4AlH_4$ in THF. A solution of $LiZn_2(CH_3)_4AlH_4$ (2.5 mmol) was prepared as described above; then 5 mmol of $LiAlH_4$ in THF was added. The solution which remained clear was stirred for 2 h and the infrared spectrum recorded. The spectrum corresponded to a mixture of $LiAlH_4$ and $LiZn_2(CH_3)_4AlH_4$.

Results and Discussion

When AlH_3 was allowed to react with $NaZn(CH_3)_2H$ and $KZn(CH_3)_2H$ in THF, the insoluble complex metal hydrides $NaZn_2H_5$ and KZn_2H_5 were formed according to eq 1 and 2.

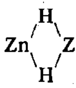
$$2NaZn(CH_3)_2H + 2AlH_3 \rightarrow NaZn_2H_5 + NaAl_2(CH_3)_4H_3 \quad (1)$$

$$2KZn(CH_3)_2H + 2AlH_3 \rightarrow KZn_2H_5 + KAl_2(CH_3)_4H_3 \quad (2)$$

On the other hand, the reaction of AlH_3 with $LiZn(CH_3)_2H$ did not yield a precipitate but only a clear solution. This behavior indicates that $LiZn_2H_5$ was not formed since this compound would be expected to be insoluble in THF. Information concerning the nature of the species present in solution can be obtained by examining the infrared spectrum, NMR spectrum, and colligative properties of the reaction solution.

Ebullioscopic molecular weight measurements on the solution from the reaction of $LiZn(CH_3)_2H$ with AlH_3 over a concentration range of 0.06–0.18 M (based on aluminum) yielded *i* values ranging from 1.01–1.08. GLC analysis of hydrolyzed samples both before and after the molecular weight experiment showed the absence of any THF cleavage products. An analysis of the reaction mixture showed Li, Zn, Al, CH_3, and H to be present in a 1.05:1.00:0.98:2.11:3.99 molar ratio. Since the *i* value is based on the concentration of aluminum in the solution, a singular compound of the stoichiometry

Table I. Infrared Spectral Bands (cm^{-1}) for $(CH_3)_2Zn$, AlH_3, $LiZn(CH_3)_2H$, $LiZn_2(CH_3)_4H$, $LiZn(CH_3)_2AlH_4$, and $LiZn_2(CH_3)_4AlH_4$ in THF[a,b]

$(CH_3)_2Zn$	AlH_3	$LiZn(CH_3)_2H$	$LiZn_2(CH_3)_4H$	$LiZn(CH_3)_2$-AlH_4[d]	$LiZn_2(CH_3)_4$-AlH_4[e]	Approx assignment
550 s		498 s	521 s	475 s	479 s	Zn–C str
674 vs		680 vs	668 vs	690 vs	700 vs	CH_3 rock
	728 vs 755 w 795 s			720 sh, s 775 s		Al–H def
840 m		795 w				Solvent O–C str
1153 m		1118 m	1120 m	1118 m 1162 m	1140 m 1170 w	CH_3 def
		1450 br,[c] s	1290 br,[c] s			Zn–H str
				1400 br,[c] s	1400 br,[c] s	 str
	1740 vs			1660 br,[c] vs		Terminal Al–H str

[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 broad. The frequency given is approximately the center of the band. [d] Concentration 0.15 M. [e] Concentration 0.10 M.

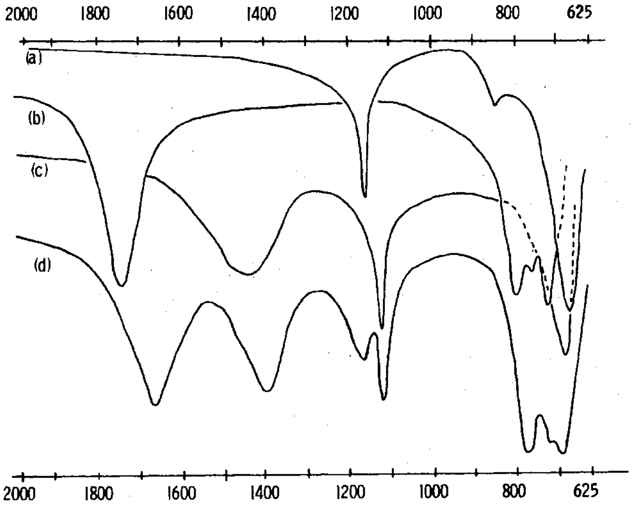


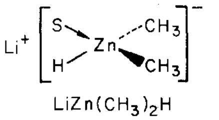
Figure 1. Infrared spectra of (a) $(CH_3)_2Zn$ in THF, (b) AlH_3 in THF, (c) $LiZn(CH_3)_2H$ in THF, and (d) $LiZn(CH_3)_2AlH_4$ in THF.

$LiZn(CH_3)_2AlH_4$ is indicated.

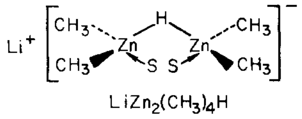
$$LiZn(CH_3)_2H + AlH_3 \rightarrow LiZn(CH_3)_2AlH_4 \qquad (3)$$

The infrared spectrum of the reaction mixture (Table I and Figure 1d) contains two strong broad bands in the metal–hydrogen stretching region, one at 1660 cm^{-1} and the other at 1400 cm^{-1}. The fact that these bands are shifted to 1180 and 1015 cm^{-1} in the infrared spectrum of $LiZn(CH_3)_2AlD_4$ (prepared from $LiZn(CH_3)_2D$ and AlD_3) shows that they actually are due to metal–hydrogen stretching modes.

Shriver and co-workers[10] have suggested structures I and



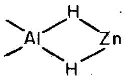
I



II

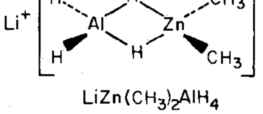
II for $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$. Referring to the data generated in this study (Table I), one can see that the Zn–H stretching frequency for $LiZn_2(CH_3)_4H$ (1290 cm^{-1}) is lower than that for $LiZn(CH_3)_2H$ (1450 cm^{-1}). These data are consistent with the suggested structures since one would expect the bridging Zn–H–Zn band in $LiZn_2(CH_3)_4H$ to have a lower stretching than the nonbridging Zn–H in $LiZn(CH_3)_2H$.[11] The infrared spectra of the deuterated compounds $LiZn(CH_3)_2D$ and $LiZn_2(CH_3)_4D$ show that the bands at 1450 and 1290 cm^{-1} for the hydride complexes are shifted to 1041 and 896 cm^{-1}, establishing that these bands are indeed due to zinc–hydrogen bonds.

The band at 1400 cm^{-1} for $LiZn(CH_3)_2AlH_4$ is close to the terminal Zn–H stretching band for $LiZn(CH_3)_2H$, but at a lower frequency. The data in Table I suggest that stretching bands due to Al–H absorb at somewhat higher frequencies than those due to Zn–H. Therefore, the structural unit Al–H–Zn should have a stretching band at higher frequency than the band due to Zn–H–Zn in $LiZn_2(CH_3)_4H$ although it might be expected to be roughly equivalent to the terminal Zn–H band for $LiZn(CH_3)_2H$. With this in mind, the band at 1400 cm^{-1} in $LiZn(CH_3)_2AlH_4$ could be assigned to the double hydrogen bridge structure III. These conclusions,



III

together with the fact that the band at 1660 cm^{-1} corresponds to a terminal Al–H stretching vibration, leads to the conclusion that $LiZn(CH_3)_2AlH_4$ has structure IV, where the zinc and



IV

aluminum atoms are tetrahedrally coordinated. The position of the CH_3 groups in this structure is consistent with the infrared spectrum in the metal–carbon stretching region. There are no bands in the Al–C stretching region, 700–550 cm^{-1}.[12] The observed band at 475 cm^{-1} is consistent with terminal Zn–C stretching modes. For $(CH_3)_2Zn$ in THF, this band is at 547 cm^{-1}, but it shifts to lower frequency (500–400 cm^{-1}) upon complex formation.[10,13]

The reaction of $LiZn_2(CH_3)_4H$ with AlH_3, like the reaction of $LiZn(CH_3)_2H$ with AlH_3, yielded a clear solution. Ebullioscopic molecular weight measurements on the reaction mixture over a concentration range of 0.04–0.12 M (based on aluminum) yielded *i* values ranging from 0.98–1.07. Again, GLC analysis of hydrolyzed samples both before and after the molecular weight experiment showed the absence of THF cleavage products. An analysis of the reaction mixture showed Li, Zn, Al, Me, and H to be present in the molar ratio 0.97:2.00:1.02:3.97:3.99. Since the *i* value is based on the aluminum concentration, these data indicate the presence of a compound of stoichiometry $LiZn_2(CH_3)_4AlH_4$. The infrared spectrum of the reaction mixture (Figure 2d) did not contain any bands in the terminal Al–H stretching region (1900–1600

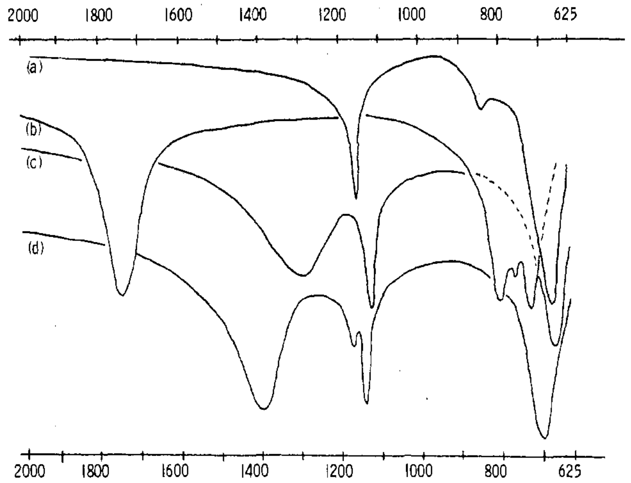


Figure 2. Infrared spectra of (a) $(CH_3)_2Zn$ in THF, (b) AlH_3 in THF, (c) $LiZn_2(CH_3)_4H$ in THF, and (d) $LiZn_2(CH_3)_4AlH_4$ in THF.

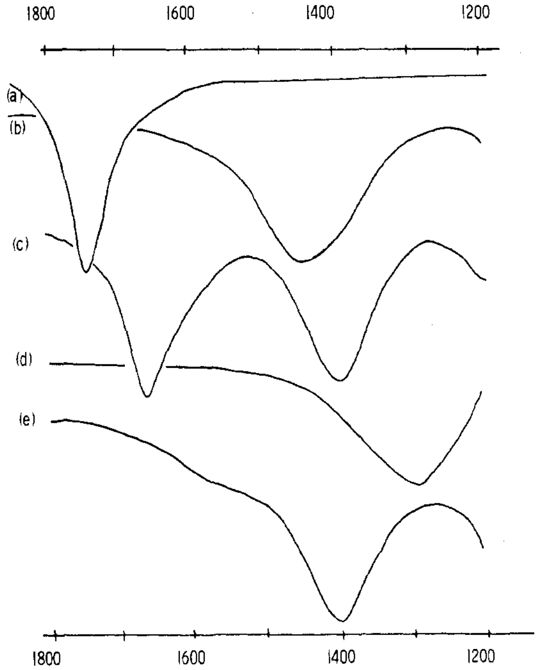
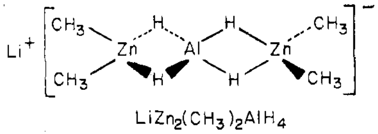


Figure 3. The 1800–1200 cm^{-1} region of the infrared spectra for (a) AlH_3 in THF, (b) $LiZn(CH_3)_2H$ in THF, (c) $LiZn(CH_3)_2AlH_4$ in THF, (d) $LiZn_2(CH_3)_4H$ in THF, and (e) $LiZn_2(CH_3)_4AlH_4$ in THF.

cm^{-1}), but only a broad peak centered at 1400 cm^{-1}. Also there is no terminal Al–H deformation band in its characteristic region (800–700 cm^{-1}); but there is a Zn–CH_3 stretching band at 479 cm^{-1}. With the exception of the band at 1660 cm^{-1} and the bands in the terminal Al–H deformation region, the spectrum of $LiZn_2(CH_3)_4AlH_4$ exactly matched the spectrum of $LiZn(CH_3)_2AlH_4$ (Figure 3). On the basis of the arguments used above for $LiZn(CH_3)_2AlH_4$, $LiZn_2(CH_3)_4AlH_4$ would be expected to have structure V, where the zinc and



$LiZn_2(CH_3)_2AlH_4$

V

aluminum atoms are tetrahedrally coordinated. In view of the fact that there are no terminal aluminum–hydrogen bands in the infrared spectrum of the complex and that the molecular weight measurements indicate the presence of a single species, the above structure seems to be the only reasonable one which can be drawn. Thus, the assignment of the band at 1400 cm^{-1} in the infrared spectrum of $LiZn(CH_3)_2AlH_4$ to the unit III appears to be justified.

Table II. Chemical Shifts for Methyl Groups in $(CH_3)_2Zn$, $LiZn(CH_3)_2H$, $LiZn_2(CH_3)_4H$, $LiZn(CH_3)_2AlH_4$, and $LiZn_2(CH_3)_4AlH_4$ in THF[a]

Sample	Concn, M	Chem shifts,[b] τ
$(CH_3)_2Zn$		10.79
$LiZn_2(CH_3)_4H$		10.90
$LiZn(CH_3)_2H$		10.97
$LiZn(CH_3)_2AlH_4$	0.10	10.95 (10.7), 10.98 (1.0), 11.02 (2.3)
$(LiZn(CH_3)_2H + AlH_3)$	0.18	10.96 (6.5), 10.98 (2.4), 11.02 (1.0)
$LiZn_2(CH_3)_4AlH_4$ $(LiZn_2(CH_3)_4H + AlH_3)$	0.12	10.96 (3.1), 11.02 (1.0)

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

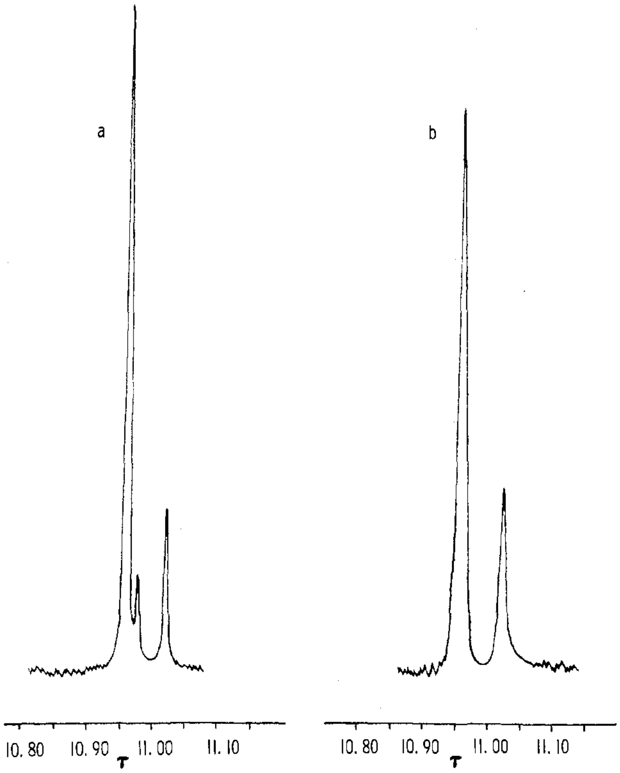
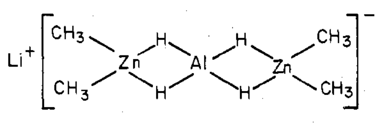
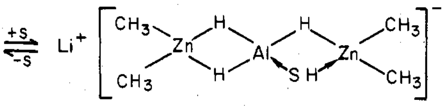


Figure 4. ^1H NMR spectra in THF at 35 °C for (a) $LiZn(CH_3)_2AlH_4$ and (b) $LiZn_2(CH_3)_4AlH_4$.

The ^1H NMR resonances for the organozinc methyl groups in $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ are given in Table II and Figure 4. The organozinc methyl resonance shifts progressively upfield on proceeding from $(CH_2)_2Zn$ to $LiZn_2(CH_3)_4H$ to $LiZn(CH_3)_2H$. This behavior is consistent with the assignment of structures I and II suggested for these compounds. One would have expected the methyl resonance to shift upfield from $(CH_3)_2Zn$ upon formation of the anionic hydride complex $LiZn(CH_3)_2H$. A similar shift upfield would also be expected for $LiZn_2(CH_3)_4H$; however, the shift would not be expected to be as great as that observed for $LiZn(CH_3)_2H$. The methyl resonances for $LiZn_2(CH_3)_4AlH_4$ are upfield from $(CH_3)_2Zn$ indicating the formation of an anionic hydride complex or complexes. These two signals are believed to be due to the methyl groups on V and VI which are in equilibrium as shown in eq 4. The low-field resonances



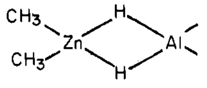
V



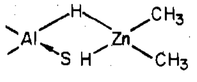
(4)

VI

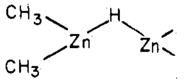
are assigned to the methyl groups in the structural unit VII whereas the high-field resonances would be due to the methyl groups in VIII. One can readily see that V and VI would give rise to just two NMR signals and fit the observed infrared and molecular association data. Also, on the basis of the position of the methyl resonances for $(CH_3)_2Zn$, $LiZn_2(CH_3)_4H$, and $LiZn(CH_3)_2H$, the two signals for $LiZn_2(CH_3)_4AlH_4$ are about where one would predict for structures like V and VI. For example, on formation of the structural unit IX from $(CH_3)_2Zn$, the methyl resonance shifted 0.11 ppm upfield. Thus, one would expect a similar upfield shift on the formation of the structural unit X from $(CH_3)_2Zn$. However, on formation of the double hydrogen bridge structure XI from the above unit, one would not expect to see another full 0.11-ppm upfield shift. The upfield shift should only be about 60% of this amount.[14] So the position of the methyl resonance for the double hydrogen bridge unit should be about 0.17 ppm upfield from $(CH_3)_2Zn$. This is what one observes. Similarly, the position of the methyl resonance for the structural unit VIII should be about 0.22 ppm upfield from $(CH_3)_2Zn$. Again this is what one observes.



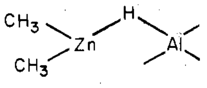
VII



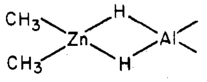
VIII



IX

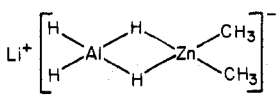


X

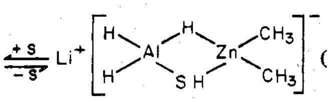


XI

Three methyl resonances are observed for $LiZn(CH_3)_2AlH_4$. The low-field and high-field resonances are the same as those observed for $LiZn_2(CH_3)_4AlH_4$ and can be assigned, using the local environment hypothesis,[15] to the methyl groups in the structures IV and XII, which are in equilibrium as shown in eq 5. The middle resonance, which is 0.19 ppm upfield from $(CH_3)_2Zn$, is due to the dimer form of $LiZn(CH_3)_2AlH_4$.[16] This assignment is consistent with the fact that the relative intensity of the center resonance increases as the solution becomes more concentrated. At lower temperatures (to −83 °C) the same signals are observed for $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$. Thus at room temperature the methyl group exchange between structures like IV and XII is slow on the NMR time scale.



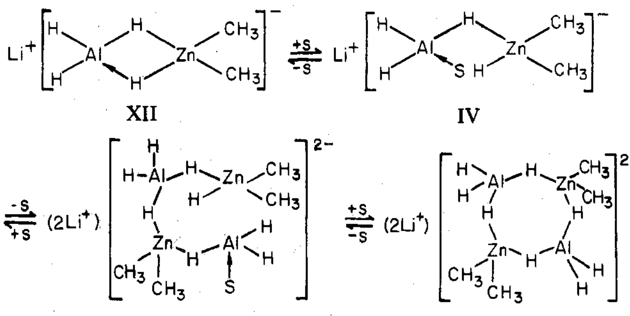
IV



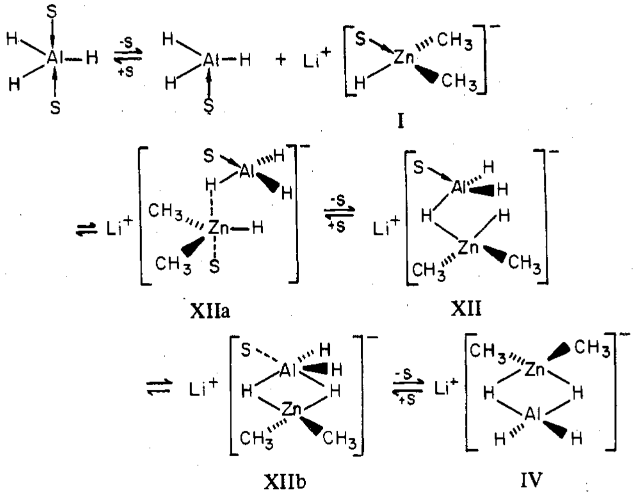
XII

(5)

Scheme I



Scheme II



It was felt that the triple metal ate complexes $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ could be used as precursors in the synthesis of the triple metal hydride complexes $LiZnAlH_6$ and $LiZn_2AlH_8$. Along this line, the two ate complexes were reacted with both AlH_3 and $LiAlH_4$. The reactions of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ with AlH_3 produced ZnH_2 according to eq 6 and 7, while the addition of $LiAlH_4$ to each of these resulted in no reaction.

$$LiZn(CH_3)_2AlH_4 + AlH_3 \rightarrow ZnH_2 + HAl(CH_3)_2 + LiAlH_4 \qquad (6)$$

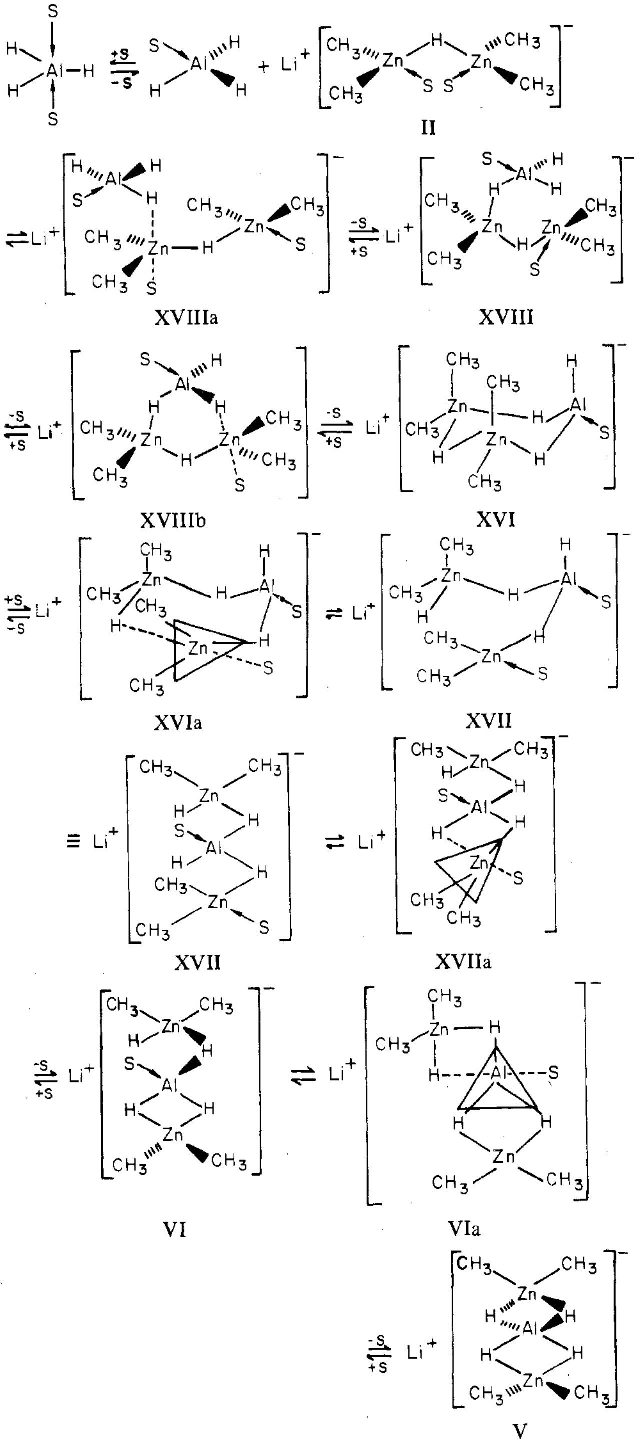
$$LiZn_2(CH_3)_4AlH_4 + AlH_3 \rightarrow 2ZnH_2 + HAl(CH_3)_2 + LiAl(CH_3)_2H_2 \qquad (7)$$

Conclusions

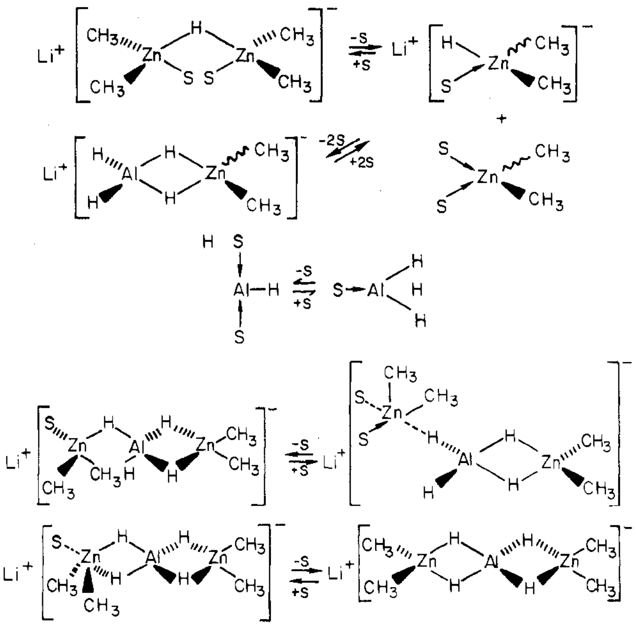
In paper 2 of this series,[16] we shall report that $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ can also be made by the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in 1:1 and 1:2 molar ratios. Ebullioscopic molecular weight measurements on these $LiZn(CH_3)_2AlH_4$ solutions, which were somewhat more concentrated than those used in this study, gave *i* values intermediate between 1 and 2, indicating an equilibrium between monomeric and dimeric forms of this compound. ^1H NMR spectra have been obtained for solutions of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$. The results for $LiZn(CH_3)_2AlH_4$ are consistent with the equilibrium mixture of compounds shown in Scheme I. The amount of dimer XIV ⇌ XV is favored as the concentration of the solution is increased. At the concentrations used in this study reported here, i.e. about 0.1 M, the equilibrium is shifted in favor of the monomeric structures XII and IV.

Structures IV and XII can give some insight into the mechanism by which $LiZn(CH_3)_2AlH_4$ is formed in the reaction of $LiZn(CH_3)_2H$ with AlH_3. Scheme II shows the steps

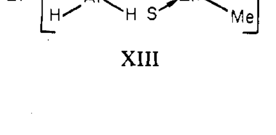
Scheme III



Scheme IV



which we believe take place in this reaction. First aluminum hydride reacts with $LiZn(CH_3)_2H$ in a nucleophilic solvent displacement reaction on zinc to yield the intermediate XII via transition state XIIa. The result of this nucleophilic solvent displacement is the formation of a three-center Al–H–Zn bond. It would be unreasonable to assume that $LiZn(CH_3)_2H$ attacks AlH_3 via a nucleophilic solvent displacement reaction on aluminum since the coordination bonds between aluminum and solvent are stronger than those between zinc and solvent. In addition, such a reaction would yield, instead of XII, an intermediate such as XIII and no evidence was found in the NMR spectrum for this species. Aluminum hydride, which is known to be in four-coordinate–five-coordinate equilibrium in THF,[17] would most likely react as the four-coordinate species in order to minimize steric interactions in the transition state XIIa. The product IV is formed when XII undergoes an intramolecular nucleophilic solvent displacement on aluminum via transition state XIIb. The strength of the aluminum–coordinated solvent bond is shown by the fact that XII is observed in the NMR spectrum. Failure to detect any of the starting materials indicates that the zinc–coordinated solvent bond is much weaker than the Al–H–Zn bridge bond. The fact that AlH_3 is monomeric in THF indicates that the aluminum-coordinated solvent bond is stronger than the Al–H–Al bridge bond in THF. However, in the solvent the Al–H–Zn bridge bond must be slightly stronger than the aluminum–solvent bond since the VI:XII ratio as shown by NMR is about 6. All of the steps shown in Scheme II are suggested to be reversible; however, the equilibrium must lie predominantly in the direction of XII and IV.



XIII

The ^1H NMR spectrum of $LiZn_2(CH_3)_4AlH_4$ indicates the presence of both a solvated and unsolvated monomer in THF solution, with the solvent coordinated to aluminum in the solvated form. A reasonable mechanism for the formation of these two compounds by the reaction of AlH_3 with $LiZn_2(CH_3)_4H$ is shown in Scheme III. Another, but equally reasonable, mechanism which recognizes that $LiZn_2(CH_3)_4H$ is subject to equilibrium 8 in THF[10] is shown in Scheme IV.

$$LiZn_2(CH_3)_4H \rightleftharpoons LiZn(CH_3)_2H + (CH_3)_2Zn \tag{8}$$

Of course, it could be argued that both schemes are operative. We, however, believe Scheme III to be the most reasonable in light of the observed chemistry. The reaction of AlH_3 with either $LiZn_2(CH_3)_4AlH_4$ or $NaZn_2(CH_3)_4AlH_4$ [18] produces ZnH_2, but the reaction of $KZn_2(CH_3)_4H$ with either 1 or 2 equiv of AlH_3 yields KZn_2H_5. The only way that one can rationalize the formation of KZn_2H_5 is to assume that direct alkyl–hydrogen exchange has occurred between $KZn_2(CH_3)_4H$ and AlH_3 through an intermediate such as X shown in Scheme III. Infrared spectra obtained upon reaction of AlH_3 with $KZn_2(CH_3)_4H$[18] do indicate the existence of an intermediate such as XV. In light of this, it seems reasonable to us that

$LiZn_2(CH_3)_4H$ would also react with AlH_3 to give an intermediate like XVI which would then undergo an intramolecular rearrangement to give VI and V. The critical step in this type of rearrangement would be a solvent-aided breakage of the Zn–H–Zn bond in XVI to give XVII through transition state XVIa. If, when the cation is K, the Zn–H–Zn bridge bond in XVI is too strong to be broken by a solvent attack on zinc, then XVI would be observed and not VI or V. With the lifetime of XVI increased, it could then undergo exchange with AlH_3 to give KZn_2H_5. Our studies show that in solutions where the alkali metal:zinc ratio is 1:2, the percent $MZn_2(CH_3)_4H$ present (see equation 8) is 60, 71, and 85 when the cation is Li, Na, and K, respectively. This certainly does indicate that the Zn–H–Zn bond in XVI would be stronger when the cation is K than when it is Li or Na.

In the mechanism shown in Scheme III, the first step involves the loss of solvent in five-coordinate alane to form four-coordinate alane, which then reacts with $LiZn_2(CH_3)_4H$ to give intermediate XVIII via transition state XVIIIa. Intermediate XVI is then formed via transition state XVIIIb. The Zn–H–Zn bridge bond in X is then cleaved by reaction with solvent via transition state XVIa to form intermediate XVII. Intermediate XVII then undergoes loss of solvent from zinc and aluminum via transition states XIIa and VIa, respectively, to form the final products VI and V. Again, the equilibrium lies largely in favor of VI and V since they are the species observed spectroscopically.

A discussion of why a solid with a Li:Zn ratio of 1:2 forms when $LiZn(CH_3)_2AlH_4$ is allowed to stand at room temperature will be more appropriately included in a later paper[18] dealing with the mechanisms of the reactions of $NaZn(CH_3)_2H$ and $NaZn_2(CH_3)_4H$ with AlH_3 in THF. The mechanisms of the reactions of $KZn(CH_3)_2H$ and $KZn_2(CH_3)_4H$ with AlH_3 to produce KZn_2H_5 will also be discussed at that time.

The discovery of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ provides some insight into the nature of alkyl–hydrogen exchange reactions between zinc and aluminum. For example, the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ in diethyl ether is a standard method for the preparation of zinc hydride.[19] One would expect this reaction to involve an intermediate such as $LiZn(CH_3)_2AlH_4$. A study of the reaction of $(CH_3)_2Zn$ and $LiAlH_4$ in THF does provide evidence concerning this point.[16]

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Registry No. $LiZn(CH_3)_2AlH_4$, 59092-43-2; $LiZn_2(CH_3)_4AlH_4$, 62166-60-3; $LiZn(CH_3)_2H$, 26520-83-2; $LiZn_2(CH_3)_4H$, 62126-56-1; $(CH_3)_2Zn$, 544-97-8; AlH_3, 7784-21-6.

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The Reaction of Amines, Ammonia, and Pyridine with Tetra- and Trifluorophosphorane. The Formation of HPF_5^- and $H_2PF_4^-$ Anions

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The liquid-phase reactions of HPF_4 and H_2PF_3 with $(CH_3)_3N$, $(CH_3)_2NH$, CH_3NH_2, NH_3, and pyridine have been investigated. Treatment of HPF_4 with these bases results in the production of the pentafluorophosphate anion, HPF_5^-, as its ammonium, substituted ammonium, or pyridinium salt. The liquid-phase reaction of H_2PF_3 with $(CH_3)_3N$ or $(CH_3)_2NH$ results in the production of the tetrafluorophosphate anion, $H_2PF_4^-$, as its substituted ammonium salt. However, treatment of H_2PF_3 with CH_3NH_2, NH_3, or pyridine produces unidentified insoluble orange precipitates which do not contain detectable quantities of the $H_2PF_4^-$ anion. NMR data are reported for the HPF_5^- and $H_2PF_4^-$ anions and mechanisms are suggested for their formation reactions.

Introduction

It is widely recognized[2] that PF_5 exhibits a Lewis acid behavior comparable to that of BF_3. Thus, treatment of PF_5 with a variety of Lewis bases such as the fluoride anion, dimethyl sulfoxide, and amines yields adducts of the composition base→PF_5. Octahedral coordination around the phosphorus atom has been confirmed by x-ray crystallography in the cases of the PF_6^- anion[3] and the pyridine adduct of PF_5.[4] Much less attention, however, has been paid to the acceptor capabilities of substituted phosphorus(V) fluorides. In part this stems from the fact that the acceptor strength[5] is known to decrease in the sequence $PF_5 > ArylPF_4 > AlkylPF_4 >> R_2PF_3$. Nevertheless, tetrafluorophosphoranes can function as acceptors toward sufficiently strong donors[5,6] and trifluorophosphoranes can be induced into intramolecular N→P coordinate bonding in certain cyclic systems.[7] However, in many cases, treatment of a tetrafluorophosphorane with a Lewis base leads to products other than simple adducts. For