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Reactions of Aluminum Hydride with Group 1b, 2a, and 2b Metal Halides

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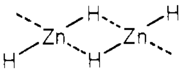
The reaction of aluminum hydride with several group 2a and 2b metal halides in diethyl ether has been studied in detail. Hydrogen–halogen exchange in the system AlH_3–MX_2 (M = Ca, Mg, Zn, Cd, Cu; X = Cl, Br, I) has been found to depend on the electronegativities of the metals concerned. Thus, calcium bromide and magnesium bromide did not undergo exchange with aluminum hydride whereas zinc chloride and zinc bromide did react with aluminum hydride to produce a new complex metal hydride of the type H_3Zn_2X (where X = Cl or Br). The reaction of zinc iodide with aluminum hydride yielded a complex of the composition $ZnI_2 \cdot AlH_3$. Cadmium bromide reacted very slowly with aluminum hydride at −40° to yield a compound of empirical formula HCdX. Cuprous chloride was shown to react with AlH_3 in ether at −78° to form CuH and $CuAlH_4$ both of which decompose when allowed to warm to room temperature. All compounds were characterized by X-ray powder diffraction, infrared spectroscopy, and elemental analyses.

Introduction

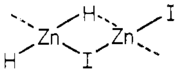
In view of our recent study of the redistribution reaction of aluminum hydride with beryllium chloride (eq 1) in diethyl ether and the possibility of the existence of HMX compounds (where M = group 2a and 2b metals and X = Cl, Br, or I), we have extended our investigation of redistribution reactions involving AlH_3 to include other group 2a and 2b metal halides in addition to $BeCl_2$ and $BeBr_2$.[1]

$$AlH_3 + BeCl_2 \rightarrow HBeCl + H_2AlCl \tag{1}$$

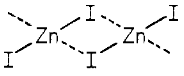
Although there have been several reports of the preparation and characterization of group 2a and 2b metal hydrides in the literature,[2] very little is known about the corresponding hydridometal halides (HMX). In 1951 Wiberg and Henle[3] reported that the addition of an ether solution of zinc chloride to a solution of aluminum hydride and aluminum chloride (1:1 mole ratio) in ether produced impure zinc hydride. These workers also reported[4] the preparation of a white solid corresponding to the formula HZnI by the reaction of zinc iodide with lithium hydride in diethyl ether. Since HZnI could not be isolated in pure form and contained different amounts of iodine, depending on the conditions of isolation, resonance structures (a, b, c) were suggested to describe the compound.



a



b



c

Wiberg and Henle[5] also studied the reaction between cadmium iodide in THF and lithium aluminum hydride in diethyl ether at −70 to −40°. In this case only cadmium hydride was obtained as a white solid which decomposed at a slow rate at −20° and decomposed spontaneously to the elements at room temperature. No evidence was obtained for either $Cd(AlH_4)_2$ or HCdI.

The preparation of hydridomagnesium halides has been reported by several workers;[6–8] however, it has been found recently[9] that these compounds actually exist as physical mixtures of magnesium hydride and the corresponding magnesium halide.

In this paper we report the reactions of aluminum hydride in ether solvent with calcium bromide, magnesium bromide, zinc halides, and cadmium bromide in several stoichiometric ratios. In this study we have isolated new complexes of zinc halides of the types H_3Zn_2X (X = Cl or Br) and $ZnI_2 \cdot AlH_3$. No conclusive evidence has been found for the existence of "HMX" species.

Experimental Section

All operations were carried out either in a nitrogen-filled glove box equipped with a recirculating system to remove oxygen and moisture[10] or on the bench using typical Schlenk-tube techniques.[11]

Instrumentation. Infrared spectra were obtained with a Perkin-Elmer Model 621 Grating infrared spectrophotometer using NaCl and CsI liquid cells. Solid samples were prepared as mulls in Nujol and the spectra were measured using polyethylene and CsI plates. X-Ray powder diffraction data were obtained using a Philips Norelco X-ray unit, using an 11.46-cm diameter camera with Ni-filtered Cu Kα radiations. The samples were exposed for 6.0 hr. *d* spacings were evaluated using a precalibrated scale equipped with viewing apparatus. Line intensities were estimated visually. DTA–TGA analyses were carried out using a Mettler Thermoanalyzer II with high-vacuum attachment.[12]

Reagents. Diethyl ether (Fisher anhydrous ether) was distilled over $LiAlH_4$ immediately prior to use. All metal halides were Fisher Certified reagent grade. Aluminum halides were purified by vacuum sublimation and ether solutions were prepared at −20° by slow addition of the aluminum halide to precooled ether. An ether solution of $MgBr_2$ was obtained by the method described previously.[13] Zinc halides were dried by heating the compounds slowly with a Bunsen flame under vacuum until they sublimed completely. Ether solutions of $ZnBr_2$ were obtained by dissolving the sublimed material in ether at room temperature. Anhydrous $CdBr_2$ was dried further by heating at 115° overnight under vacuum. Ether-soluble aluminum hydride was prepared by the reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether.[14] *Caution*! Special care must be taken while handling beryllium compounds due to their toxic character.

Analytical Procedures. Hydrogen analysis was carried out by hydrolyzing samples on a standard vacuum line equipped with a Toepler pump. Metals were determined by complexometric titration with EDTA. Zinc, magnesium, and cadmium in the presence of aluminum were determined by masking the aluminum with triethanolamine and titrating the remaining metal with EDTA. Analysis for chloride, bromide, or iodide was carried out using a modified Volhard procedure.

Infrared Study of the Reaction of AlH_3 with $AlCl_3$ and $AlBr_3$ in Diethyl Ether. The hydridoaluminum halides H_yAlX_{3-y} (where X = Cl or Br) were prepared by mixing solutions of AlH_3 and aluminum halides in ether at 0° in the appropriate ratios. Redistribution reactions between AlH_3 and aluminum halides have been discussed by a number of authors.[15] The infrared spectra are reported in Figure 1.

Reaction of AlH_3 with $MgBr_2$. (a) In 1:1 Mole Ratio. A solution of AlH_3 (10 ml, 2.732 mmol) in ether was added slowly with stirring to a solution of $MgBr_2$ (21.45 ml, 2.732 mmol) in ether. There was no immediate precipitate and the mixture remained clear even after 24 hr of stirring. The infrared spectrum of the clear solution showed strong bands at 1785 and 760 cm^{-1} and a band of medium intensity at 380 cm^{-1}. The infrared spectrum of the solid obtained by complete removal of ether from the reaction mixture showed bands at 1800 (w) and 1600 cm^{-1} (br, s). Elemental analysis of the solid gave the ratio Mg:Al:H:Br = 1.0:1.04:2.90:2.11. X-Ray powder diffraction patterns of the solid showed it to be essentially a physical mixture of $MgBr_2$ and AlH_3. When the reaction mixture was allowed to stand for a few weeks, some gray solid compound precipitated. The solid was filtered, dried under vacuum, and analyzed: Mg:Al:H:Br = 1.24:1.0:1.02:1.95. The infrared spectrum showed a very weak broad band at ~1600 cm^{-1}.

(b) In 2:1 Mole Ratio. Ether solutions of AlH_3 (8.578 mmol) and $MgBr_2$ (4.289 mmol) were mixed as described above. In this case

Table I. X-Ray Powder Pattern *d*-Spacing Data

$MgBr_2 \cdot 0.89Et_2O$		$MgBr_2 + AlH_3 \cdot 1.24Et_2O$		$MgBr_2 + 2AlH_3 \cdot 1.62Et_2O$		ZnH_2		$ZnCl_2$		$ZnCl_2 \cdot 0.11Et_2O$		$H_3Zn_2Cl \cdot 0.20Et_2O$	
d, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
9.25	vw	9.50	w	9.50	s, br	4.51	vw	4.85	s	6.85	m	7.8	s
8.0	s	8.0	s	8.25	w	4.23	s	4.70	s	5.50	m	5.80	w
7.25	s	7.25	s	7.25	w	3.80	vw	3.80	w	4.80	s	5.40	w
5.8	m	5.7	vvw	6.6	w	3.40	m	3.26	m	4.50	m	4.0	m
5.4	m	5.4	m	5.90	w	2.97	vw	3.19	m	3.80	vw	3.55	w
4.8	s	4.8	vvw	5.4	vvw	2.82	vw	3.02	s	3.55	m	3.15	w
3.95	vw	3.95	vw	4.6	vw	2.608	w	2.87	s	3.42	w	2.75	s
3.72	vvw	3.55	ms	3.62	w	2.468	vw	2.85	w	3.30	w	2.65	s
3.55	s	3.25	ms	3.50	w	2.387	m	2.35	w	3.05	s	2.37	m
3.25	s	2.97	w	3.25	m	2.290	m	2.22	w	2.87	m	2.00	w
3.01	ms	2.75	w	3.15	s	2.225	m	2.12	vw	2.57	w	1.79	vw
2.77	s	2.63	w	2.72	ms	2.135	w	1.960	vw	2.35	m	1.69	w
2.75	w	2.52	w	2.63	vvw	2.085	w	1.920	m	2.20	m	1.58	m
2.64	w	2.36	w	1.92	s	2.017	vw	1.860	s	2.06	w	1.55	w
2.52	m	2.25	vw	1.65	ms	1.905	w	1.730	s	1.97	w	1.51	w
2.42	w	2.125	vw	1.58	vw	1.764	w	1.620	w	1.95	m		
2.36	w	1.91	ms	1.255	w	1.688	vw	1.592	s	1.865	s		
2.25	vw	1.71	w	1.223	w	1.630	vw	1.490	w	1.730	m		
2.19	m					1.562	vw	1.455	w	1.620	m		
1.91	w					1.486	vw	1.280	vw	1.590	w		
1.75	w					1.464	vw	1.265	vw	1.570	m		
1.61	w					1.416	vw	1.145	vw	1.485	vw		
1.53	w							1.350	vw	1.350	vw		
1.440	w							1.265	vw	1.265	vw		
								1.215	vw	1.215	vw		
								1.095	vw	1.095	vw		

$AlH_3 \cdot 0.35Et_2O$		ZnI_2		$ZnI_2 \cdot 0.35Et_2O$		$ZnI_2AlH_3 \cdot 0.192Et_2O$		$ZnBr_2 \cdot 0.285Et_2O$				$H_3Zn_2Br \cdot 0.29Et_2O$	
d, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å[a]	I/I_0
11.5	s	3.45	s	3.45	s	8.80	m	6.5	vvw	1.95	s	10.0	w, br
4.55	m	3.05	w	3.05	vw	7.00	m	4.2	w	1.70	m	3.5	w, br
3.85	m	2.17	w	2.17	vw	5.40	vw	3.4	s	1.64	w		
2.85	m	2.12	m	2.12	m	4.90	w	2.80	vvw	1.27	w		
2.32	m	1.84	m	1.84	m	4.35	w	2.55	vw	1.150	vw		
		1.78	w	1.78	w	3.95	w	1.99	m				
		1.37	vw	1.375	vw	3.4	s						
		1.235	vw	1.245	vw								

[a] Powder diffraction lines were obtained as two broad halos and these are only approximate distances.

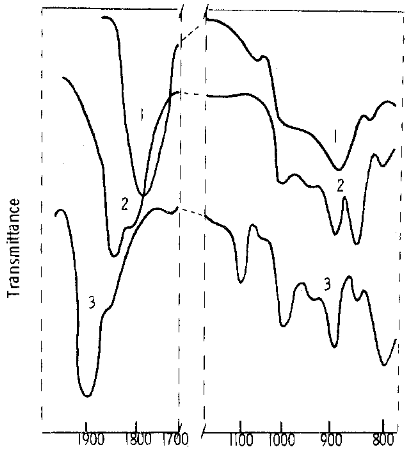


Figure 1. Infrared study of the reaction of AlH_3 with $AlCl_3$ in diethyl ether: 1, AlH_3; 2, AlH_2Cl; 3, $AlHCl_2$.

also there was no immediate precipitate and the mixture stayed clear for more than 24 hr. The infrared spectra of the clear mixture and the solid obtained after complete removal of ether were identical with the spectra obtained in part (a). Similarly X-ray powder patterns from (a) and (b) were identical. In this case, however, it was noticed that the formation of gray solid compound was faster than in (a) and in 1 week 33% of the solid (calculated on the basis of solid $MgBr_2 \cdot 2AlH_3$) precipitated from solution. Analysis of the gray powder showed: Mg:Al:H:Br = 1.0:1.70:2.22:1.41.

Reaction of AlH_3 with $ZnCl_2$. Preparation of $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$. In a typical reaction, a solution of aluminum hydride in ether was added slowly to a solution of zinc chloride in ether in an appropriate ratio (see below). An immediate precipitation of a white solid took place. The mixture was stirred for 10 min and then filtered. The white residue was washed with ether, dried under vacuum, and stored at −20°. Anal. Calcd for $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$: Zn, 66.99; H (hydrolyzable), 1.57; Cl, 18.16. Found: Zn, 66.52; H (hydrolyzable), 1.59; Cl, 17.82. The yield of product based on this analysis was 95%. The infrared spectrum of the white solid showed a very broad band with a maximum at ~1550 cm^{-1} and a weak band at ~460 cm^{-1}. The X-ray powder diffraction data given in Table I showed lines different from those of $ZnCl_2$ and AlH_3.

The reaction was repeated in the following ratios of AlH_3:$ZnCl_2$: 1:1, 1:2, 1:3, and 4:1. The white precipitate obtained in each case was subjected to complete elemental analysis and characterized by infrared spectra and X-ray powder diffraction. Similarly, the filtrate, after isolation of the white solid, was characterized by infrared spectroscopy and elemental analysis. The results are described separately.

(a) In 1:1 Mole Ratio. Aluminum hydride, 6.75 mmol in ether solvent, was mixed with zinc chloride, 6.75 mmol, in ether solvent. Analysis of the resulting white solid gave Al:Zn:H:Cl = 0.07:1.00:1.74:0.41. Infrared analysis of the solid (Nujol mull) showed two broad bands at ~1550 and 600–350 cm^{-1} centered at 460 cm^{-1}. The X-ray powder pattern of the solid was different from the patterns obtained for $ZnCl_2$ and AlH_3 (Table I). Elemental analysis of the filtrate showed H:Al:Cl:Zn = 1.60:1.00:1.57:0.00 and infrared analysis showed the bands 1898 (s), 1850 (ms), 775 (s), and 720 (s) cm^{-1}.

(b) In 1:2 Mole Ratio. AlH_3, 6.846 mmol, in ether solvent, was mixed with $ZnCl_2$, 13.692 mmol, in ether solvent. Elemental analysis of the solid residue showed Al:Zn:H:Cl = 0.05:1.00:1.56:0.486. The infrared spectrum and X-ray powder diffraction pattern were similar to the solid described earlier in part (a). The infrared spectrum of the filtrate did not show any bands at 2000–1600 and 800–700 cm^{-1}.

(c) In 1:3 Mole Ratio. AlH_3, 2.259 mmol, in ether solvent was mixed with 6.779 mmol of $ZnCl_2$ in ether solvent. Analysis of the resulting precipitate gave Al:Zn:H:Cl = 0.00:1.00:1.49:0.57. An infrared spectrum and X-ray powder pattern were obtained as in the previous cases. The analysis of the filtrate showed Al:Zn:Cl:H = 1.00:0.64:3.98:0.00. Infrared analysis did not show any absorption bands due to a hydridoaluminum halide.

(d) In 4:1 Mole Ratio. AlH_3, 5.957 mmol, in ether solvent was mixed with 1.489 mmol of $ZnCl_2$ in ether solvent. Analysis of the resulting white precipitate gave Al:Zn:H:Cl = 0.07:1.00:1.91:0.43. The infrared spectrum of the filtrate showed strong bands at 1900, 1850 (sh), 1785, and 760 cm^{-1}.

Reaction of $HAlCl_2$ with $ZnCl_2$. $HAlCl_2$, 40 ml (7.404 mmol), in ether was added slowly to a solution of zinc chloride, 21.8 ml (7.404 mmol) in ether. There was an immediate precipitation of a white solid. The mixture was stirred for about 10 min and then filtered. The residue was washed, dried under vacuum, and analyzed: Al:Zn:H:Cl = 0.12:1.00:1.40:0.76. The infrared spectrum of the filtrate showed a broad band near 1500–1400 cm^{-1}.

Reaction of AlH_3 with $ZnBr_2$. Preparation of $H_3Zn_2Br\cdot 0.29(C_2H_5)_2O$. A solution of aluminum hydride was added slowly with stirring to a solution of zinc bromide in ether and the mixture stirred about 10 min. The white solid was filtered, washed with ether, and dried under vacuum. The compound was stored at −20°. Anal. Calcd for $H_3Zn_2Br\cdot 0.29(C_2H_5)_2O$: H (hydrolyzable), 1.28; Zn, 55.51; Br, 33.93. Found: H (hydrolyzable), 1.17; Zn, 61.42; Br, 26.58. The infrared spectrum of the solid showed a broad band near 1600 cm^{-1}. X-Ray powder diffraction data are given in Table I. The above reaction was carried out in several mole ratios of AlH_3:$ZnBr_2$ and the results are described below.

(a) In 1:1 Mole Ratio. AlH_3, 6.357 mmol, in ether solvent was added to $ZnBr_2$, 6.357 mmol, in ether solvent. A white solid precipitated and was analyzed: Al:Zn:H:Br = 0.03:1.00:1.91:0.37. Infrared analysis of the solid (Nujol mull) showed a broad band near 1600 cm^{-1}. The infrared spectrum of the filtrate showed the bands 1900 (s), 1850 (sh), 765 (s), and 700 cm^{-1} (ms). The filtrate on standing overnight at room temperature deposited some gray powder which was mostly metallic zinc.

(b) In 1:2 Mole Ratio. AlH_3, 5.495 mmol, in ether solvent was added to $ZnBr_2$, 10.99 mmol, in ether solvent. Elemental analysis of the resulting solid gave Al:Zn:H:Br = 0.04:1.01:1.66:0.36. The infrared spectrum of the solid showed a broad band near 1600 cm^{-1} whereas the infrared spectrum of the filtrate did not show any band between 2000 and 1600 cm^{-1} and between 800 and 700 cm^{-1}.

(c) In 1:3 Mole Ratio. AlH_3, 7.334 mmol, in ether solvent was mixed with $ZnBr_2$, 22.00 mmol, in ether solvent. Analysis of the white precipitate gave the molar ratio Al:Zn:H:Br = 0.04:1.00:2.06:0.41. The infrared spectrum of the filtrate did not show any absorption band due to hydridoaluminum compounds.

Reaction of AlH_3 with ZnI_2. Preparation of $ZnI_2\cdot AlH_3\cdot 1.79(C_2H_5)_2O$. Solutions of aluminum hydride and zinc iodide in ether solvent were allowed to react. The white solid which precipitated immediately after mixing was filtered, washed with ether, dried under vacuum, and stored at −20°. Anal. Calcd for $ZnI_2\cdot AlH_3\cdot 1.79(C_2H_5)_2O$: Zn, 13.55; I, 52.64; Al, 5.59; H (hydrolyzable), 0.627. Found: Zn, 13.86; I, 53.07; Al, 5.99; H (hydrolyzable), 0.693. The infrared spectrum of the white solid showed the following bands in addition to bands due to diethyl ether: 1630 (vs, br), 670 (s), 520 (m), and 325 cm^{-1} (w). The X-ray powder diffraction pattern of the solid is listed in Table I. The reaction was carried out in several mole ratios of AlH_3:ZnI_2 and the results are described below.

(a) In 1:2 Mole Ratio. AlH_3, 1.473 mmol, in ether solvent was mixed with ZnI_2, 2.947 mmol, in ether solvent. Analysis of the white solid precipitate gave a molar ratio of Zn:Al:H:I = 1.0:1.07:2.99:1.97. An infrared spectrum and X-ray powder diffraction pattern were identical with those described for the reaction carried out in 1:1 ratio. Analysis of the filtrate showed Al:Zn:H:I = 0.09:1.00:0.04:2.12. An infrared spectrum of the filtrate did not show any absorption bands near 2000–1600 and 800–700 cm^{-1}. In a separate experiment, ether solutions of AlH_3 and ZnI_2 were mixed together in 1:2 mole ratio, and the mixture was stirred at 0° for 2 days. The white solid was then filtered, washed with ether, and dried under vacuum. The elemental analysis and the infrared spectrum of the white solid were identical with those described above.

(b) In 4:1 Mole Ratio. AlH_3, 5.825 mmol, in ether solvent was mixed with ZnI_2, 1.453 mmol, in ether solvent. A white solid which precipitated immediately after mixing showed a molar ratio of Al:Zn:H:I = 1.04:1.00:3.26:1.91. The infrared spectrum and X-ray powder diffraction data were identical with those described above. However, the infrared spectrum of the filtrate showed absorption bands at 1785 (s) and 760 cm^{-1} (s).

Reaction of AlH_3 with $CaBr_2$. A solution of aluminum hydride (20.1 ml, 4.794 mmol) in diethyl ether was added to a slurry of $CaBr_2$ (0.9583 g, 4.794 mmol) in 100 ml of ether. The mixture was stirred for 3 days at room temperature. It was then filtered and washed with ether, and the residue was dried under vacuum. Elemental analysis of the residue gave Ca:H:Br = 1.00:0.02:1.97. An infrared spectrum of the filtrate showed bands due to aluminum hydride only at 1785 (s) and 760 cm^{-1} (s).

Reaction of AlH_3 with $CdBr_2$. $CdBr_2$ (1.9495 g, 7.161 mmoles) was transferred to a 250-ml Schlenk tube followed by the addition of 50 ml of diethyl ether. The mixture was stirred at −40 to −30° for about 15 min and then a solution of aluminum hydride (26.0 ml, 7.161 mmol) in diethyl ether was added to the $CdBr_2$ slurry dropwise keeping the temperature of the reaction mixture always below −30°. The mixture was stirred for 4 days at −40 to −30° during which time infrared spectra of the clear solution were recorded in order to follow the progress of the reaction. When the reaction was complete, a small portion of the solution was analyzed: Al:Cd:H:Br = 1.00:0.00:2.12:0.79. The infrared spectrum of the filtrate showed bands at 1860 (s, br), 760 (s), and 700 cm^{-1} (s). The solid residue (slightly gray) was washed twice with cold (−70°) ether allowing the precipitate to settle to the bottom of the Schlenk tube while removing the clear liquid by syringe under nitrogen. The solid was analyzed: Cd:H:Br = 1.00:1.00:1.14. Hydrogen analysis was carried out by attaching the Schlenk tube with the solid directly to the vacuum line and allowing the solid to decompose at room temperature.

This reaction was studied in detail under the following conditions.

(a) Reaction Product Allowed to Warm to Room Temperature. $CdBr_2$ and AlH_3 were mixed in 1:1 mole ratio in diethyl ether in the same way as described above. The mixture was stirred for 6 hr at −78° and then allowed to warm slowly to room temperature. When the temperature of the reaction mixture reached −20°, it started turning dark and at room temperature became completely black giving off hydrogen gas. The black solid was separated by filtration, washed with ether, and dried under vacuum. The infrared spectrum of the solid did not show any absorption bands due to metal hydrides. The infrared spectrum of the filtrate on concentration showed bands at 1906 (s), 762 (s), and 700 cm^{-1} (s). Analysis of the filtrate showed Al:H:Br = 1.00:0.576:2.00 and it contained 73% of the total aluminum. Elemental analysis of the black residue gave Al:Cd:H:Br = 0.08:1.00:0.00:1.73.

(b) Reaction in THF. Since $CdBr_2$ is more soluble in THF than diethyl ether, a solution of AlH_3 (3.3 ml, 1.320 mmol) in THF was added to a solution of $CdBr_2$ (200 ml, 1.320 mmol) in THF at −78°. The mixture was stirred at −35° for 4 hr and then allowed to settle overnight inside a dewar flask. It was noticed that even after 16 hr the mixture remained turbid. The supernatant liquid was then removed carefully, with a syringe, and the remaining solid was washed with cold THF. The resulting solid was analyzed: Al:Cd:H:Br = 0.93:1.00:1.00:2.09.

(c) Reaction in 3:1 Mole Ratio in Ether. $CdBr_2$ and AlH_3 were mixed in 3:1 mole ratio in ether and the mixture stirred for 6 hr at −40 to −35°. The mixture was allowed to settle and the infrared spectrum of the clear solution showed the absence of any hydridoaluminum compound. The reaction mixture was then cooled to −76° and transferred inside the glove box as fast as possible, flushing the entryport with nitrogen for 10 min. It was then filtered and washed with cold (−40°) ether. The white solid residue turned black within a few seconds. The infrared spectrum of the filtrate on concentration did not show any absorption bands due to aluminum–hydrogen compounds. Analysis of the filtrate showed H:Al:Cd:Br = 0.00:1.00:0.00:0.76, corresponding to 36.2% of the total aluminum.

Reaction of H_2AlBr with $CdBr_2$ in Ether. H_2AlBr (61 ml, 7.585 mmol) in ether was added to a slurry of $CdBr_2$ (2.0649 g, 7.585 mmol) in ether stirred at −40°. The mixture was stirred for 5 days at −40 to −30° until the reaction was complete. The infrared spectrum of the clear solution showed a strong and broad band at 1900–1800 cm^{-1} with a maximum at 1850 cm^{-1}. The position of the band did not change on further stirring. Analysis of the solution showed Al:Cd:H:Br = 1.00:0.04:1.90:1.15, whereas the analysis of the residue on decomposition at room temperature and subsequent hydrolysis gave

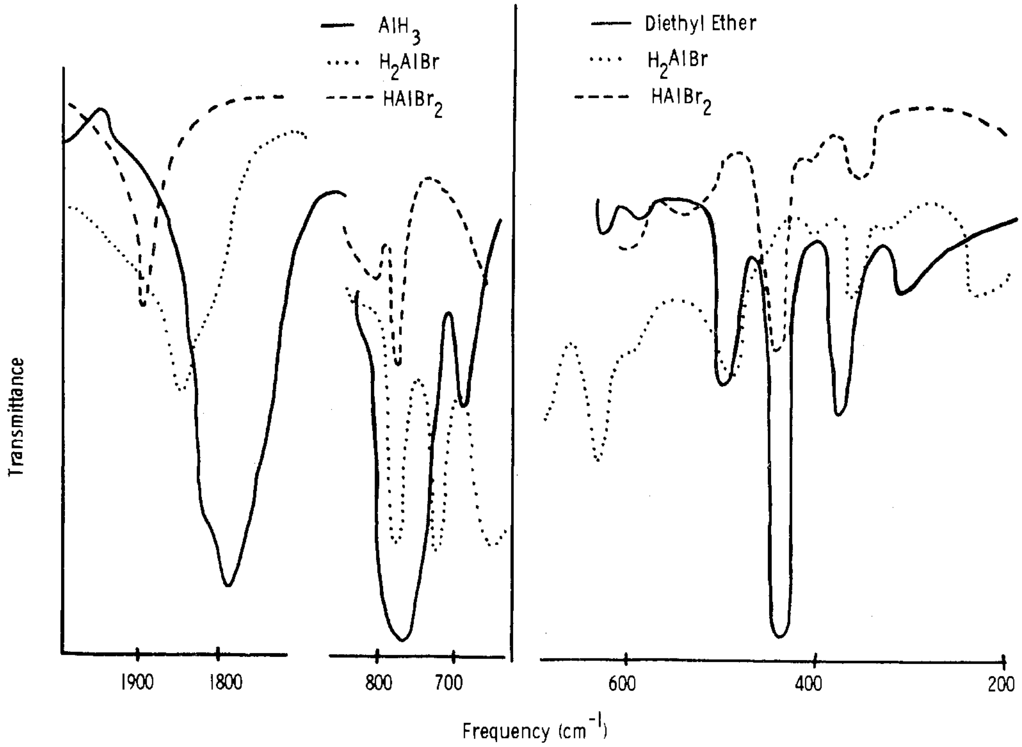


Figure 2. Infrared spectra of AlH_3, H_2AlBr, and $HAlBr_2$ in diethyl ether.

Al:Cd:H:Br = 0.09:1.00:0.19:1.94.

Reaction of AlH_3 with CuCl in Ether. Aluminum hydride solution (42.7 ml, 12.89 mmoles) in ether was added to a slurry of CuCl (1.276 g, 12.89 mmol) in ether. The mixture was stirred for 6 hr at −76° and then allowed to warm to room temperature. At −40°, the color of the reaction mixture started to turn black, and by the time the temperature rose of 0°, it was almost completely black giving off some gas and depositing a black precipitate at the bottom of the flask. It was then filtered and washed with ether, and the residue was dried at room temperature. The infrared spectrum of the filtrate showed a strong band at 1900 cm^{-1} with a shoulder at 1850 cm^{-1} and a strong band at 775 cm^{-1}. Analysis of the filtrate gave a molar ratio of Al:H:Cl = 1.04:1.00:1.80 corresponding to 44.2% of the total aluminum.

Results and Discussion

The reaction of aluminum hydride with group 1b, 2a, and 2b metal halides can be considered as a metathetical exchange reaction in which one or more hydrogen atoms of alane are exchanged with the halogen atom of the metal halide. The electronegativity differences for metal halides are calculated from the eq 2, where Q is the standard heat of formation and

$$Q = 23\Sigma(X_A - X_B)^2 \qquad (2)$$

$X_A - X_B$ is the electronegativity difference for the elements A and B.[16] The electronegativity differences for metal halides are listed in Table II. A comparison of the electronegativity differences with the experimental observations shows that if the electronegativity of the group 1 or 2 metal is higher than aluminum, the exchange reaction does not take place. However, in the case of comparable or lower electronegativity differences the exchange does take place. This simply means that in the exchange reaction between AlH_3 and metal halide the reaction will proceed to form the most thermodynamically stable products which are those resulting from the most electronegative group (halogen) residing on the most electropositive metal. Therefore, AlH_3 would not be expected to react with LiCl to form $AlCl_3$ and LiH but would be expected to react with $ZnBr_2$ to form $AlBr_3$ and ZnH_2.

As reported previously,[14] redistribution reactions are studied by mixing ether solutions of metal hydrides with metal halides in various mole ratios followed by complete elemental analysis of the resulting solution and precipitate that forms. The precipitate is further analyzed by X-ray powder diffraction, DTA–TGA, and infrared analysis whereas the solutions are analyzed further only by infrared spectroscopy.

Table II. Electronegativities of Elements and Electronegativity Difference between the Metal and Halogen

Elements	Electronegativity	Metal halide	Electronegativity difference
Ca	1.04	$CaBr_2$	1.87
Mg	1.23	$MgBr_2$	1.64
Be	1.47	$BeCl_2$	1.56
Al	1.47	$AlCl_3$	1.55
Zn	1.66	$ZnCl_2$	1.47
Cd	1.70	$AlBr_3$	1.35
Cu	1.90	$ZnBr_2$	1.30
H	2.20	$CdBr_2$	1.27
I	2.5	CuCl	1.18
Br	2.8	AlI_3	1.04
Cl	3.0	ZnI_2	1.04

Reactions of AlH_3 with AlX_3 (X = Cl, Br). Since hydrogen exchange in the AlH_3–MX_2 system would be expected to form hydridoaluminum halides, it was necessary first to prepare $HAlX_2$ and H_2AlX (where X = Cl and Br) in order to obtain the necessary infrared spectroscopic information for identification purposes. Ether-soluble AlH_3 was found to exhibit bands in its infrared spectrum at 1785 and 770 cm^{-1}. These bands are assigned to the Al–H stretching and Al–H deformation vibrations, respectively. The hydridoaluminum halides (where X = Cl and Br) were prepared in ether solvent by simply mixing ether solutions of AlH_3 and the appropriate aluminum halide at low temperature in order to avoid ether cleavage. The infrared spectra are recorded in Figures 1 and 2.

$$2AlH_3 + AlX_3 \rightarrow 3AlH_2X \qquad (3)$$

$$AlH_3 + 2AlX_3 \rightarrow 3AlHX_2 \qquad (4)$$

Reactions of AlH_3 with $CaBr_2$. Calcium bromide does not undergo an exchange reaction with AlH_3 due to the fact that calcium is more electropositive than aluminum. Elemental analysis as well as the infrared analysis of the products obtained

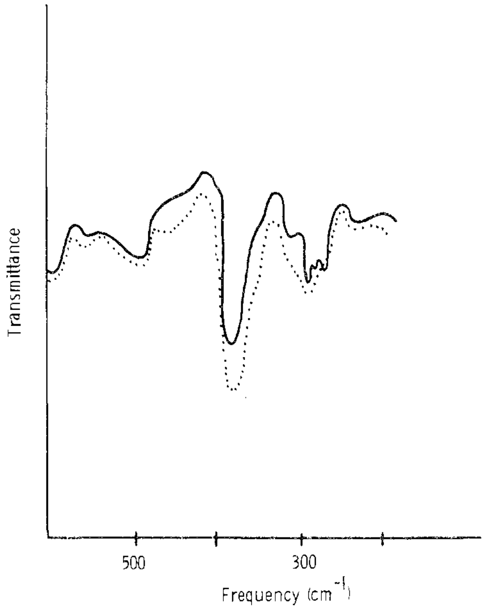


Figure 3. Infrared spectra of (a) the reaction product of $MgBr_2$ + AlH_3 (——) and (b) $MgBr_2 \cdot n(C_2H_5)_2O$ (· · ·).

after mixing an ether solution of AlH_3 with $CaBr_2$ results in a quantitative recovery of unreacted calcium bromide and AlH_3.

Reactions of AlH_3 with $MgBr_2$. Similarly, $MgBr_2$ does not react with AlH_3 in diethyl ether. Although there is no immediate precipitate after mixing an ether solution of $MgBr_2$ with AlH_3, the possibility of some soluble complex metal hydride could not be ruled out completely. Therefore, in order to isolate and characterize any possible complex, the infrared spectra of magnesium bromide and AlH_3 were determined in the near- and far-infrared regions in order to establish metal–hydrogen (deformation) and metal–halogen stretching frequencies. The infrared spectra of both $MgBr_2$ and the reaction mixture showed only one medium intense band at 380 cm^{-1} other than weak bands for diethyl ether (Figure 3). This band may be assigned to the Mg–Br stretching vibration. Powder diffraction patterns were obtained for $MgBr_2$ and AlH_3 containing nearly the same number of solvent molecules (Table I) as that of the product after solvent removal. The X-ray powder pattern of the product was consistent with a physical mixture of $MgBr_2$ and AlH_3. Similarly, the TGA analysis of the solid showed it to be either a very weak complex of AlH_3 or $AlH_3 \cdot O(C_2H_5)_2$ mixed with $MgBr_2$. On standing for several days at room temperature the reaction mixture decomposed to hydrogen and aluminum which precipitated as a gray powder. The absence of infrared absorption bands characteristic of the Mg–H stretching vibration ruled out the possibility of the existence of either MgH_2 or HMgBr in the gray solid.

Reactions of $ZnCl_2$ with AlH_3. In 1:1 mole ratio $ZnCl_2$ and AlH_3 react to produce a stable white solid of empirical formula $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$.[17] The infrared spectrum of the filtrate showed absorption bands at 1900 (s), 1850 (s), 780 (s), and 720 cm^{-1} (s), indicating the presence of $HAlCl_2$ and H_2AlCl in solution. These results suggest that the reaction takes place as in eq 5–7. The infrared spectrum as well as

$$2ZnCl_2 + 2AlH_3 \rightarrow 2H_2AlCl + 2HZnCl \quad (5)$$

$$H_2AlCl + HZnCl \rightarrow ZnH_2 + HAlCl_2 \quad (6)$$

$$ZnH_2 + HZnCl \rightarrow H_3Zn_2Cl$$

$$2ZnCl_2 + 2AlH_3 \rightarrow H_3Zn_2Cl + H_2AlCl + HAlCl_2 \quad (7)$$

the X-ray powder diffraction pattern of the solid product shows it to be a unique compound and not a physical mixture of

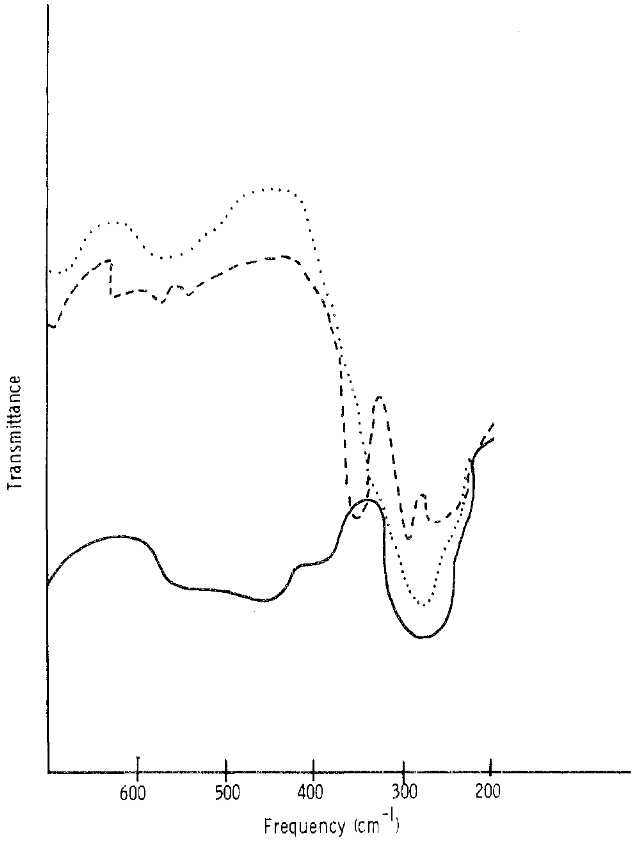


Figure 4. Infrared spectra of (a) $ZnCl_2$ (· · ·), (b) $ZnCl_2 \cdot 0.11Et_2O$ (- - -), and (c) $H_3Zn_2Cl \cdot 0.35Et_2O$ (——).

$ZnCl_2$ and ZnH_2. The infrared spectra of $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$, $ZnCl_2 \cdot 0.11Et_2O$, and $ZnCl_2$ in the solid state are reported in Figure 4 and the X-ray powder diffraction patterns are listed in Table I. An X-ray powder diffraction pattern of $ZnCl_2 \cdot 0.35(C_2H_5)_2O$ could not be obtained because the solid was quite sticky. Possibly the most convincing piece of information suggesting that H_3Zn_2Cl is a single compound and not a mixture of ZnH_2 and $ZnCl_2$ in 3:1 ratio is the fact that $ZnCl_2$ is soluble in ether, yet the H_3Zn_2Cl ratio is maintained under a variety of conditions.

In 2:1 mole ratio, $ZnCl_2$ and AlH_3 reacted to yield the same solid compound, $H_3Zn_2Cl \cdot 0.35(C_2H_5)_2O$, which was characterized by elemental analysis, X-ray powder diffraction, and infrared analysis. However, the infrared spectrum and elemental analysis of the filtrate showed it to contain only $AlCl_3$ indicating the sequence of reactions 8–11.

$$2ZnCl_2 + AlH_3 \rightarrow 2HZnCl + HAlCl_2 \quad (8)$$

$$HZnCl + HAlCl_2 \rightarrow ZnH_2 + AlCl_3 \quad (9)$$

$$ZnH_2 + HZnCl \rightarrow H_3ZnCl \quad (10)$$

$$2ZnCl_2 + AlH_3 \rightarrow H_3Zn_2Cl + AlCl_3 \quad (11)$$

The infrared spectrum and elemental analysis of the solid compound obtained by allowing $ZnCl_2$ and AlH_3 to react in a 3:1 mole ratio showed the solid product to be $H_3Zn_2Cl \cdot 0.38(C_2H_5)_2O$; however, the filtrate contained 1 mol of $AlCl_3$ as well as 1 mol of unreacted $ZnCl_2$ as expected from the results described by eq 12.

$$3ZnCl_2 + AlH_3 \rightarrow H_3Zn_2Cl + ZnCl_2 + AlCl_3 \quad (12)$$

When $ZnCl_2$ and AlH_3 were allowed to react in 1:4 mole ratio, $H_3Zn_2Cl \cdot 0.31Et_2O$ was again obtained; however, the elemental analysis gave a molar ratio of Al:Zn:H:Cl = 0.07:1.00:1.91:0.43. The high hydrogen ratio indicates that in the presence of excess AlH_3 some HZnCl reacts further with AlH_3 to form ZnH_2 rather than complex with ZnH_2 already

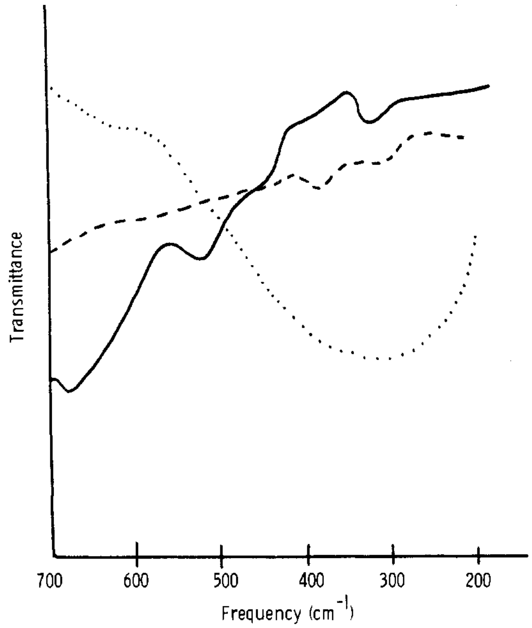


Figure 5. Infrared spectra of (a) ZnI_2 (· · ·), (b) $ZnI_2 \cdot 0.35Et_2O$ (- - -), and (c) $ZnI_2 \cdot AlH_3$ (——).

present to form H_3Zn_2Cl. Thus, the H_3Zn_2Cl formed is contaminated with ZnH_2.

In an attempt to verify the existence of HZnCl, zinc chloride and $HAlCl_2$ were allowed to react in a 1:1 mole ratio in diethyl ether. In this case a white solid was obtained corresponding to a molar ratio of Al:Zn:H:Cl = 0.12:1.00:1.40:0.76 suggesting the formation of H_3Zn_2Cl (see eq 13–17).

$$4ZnCl_2 + 4HAlCl_2 \rightarrow 4HZnCl + 4AlCl_3 \tag{13}$$

$$2HZnCl \rightarrow ZnH_2 + ZnCl_2 \tag{14}$$

$$HZnCl + ZnH_2 \rightarrow H_3Zn_2Cl \tag{15}$$

$$HZnCl \rightarrow {}^1/_2ZnH_2 + {}^1/_2ZnCl_2 \tag{16}$$

$$4ZnCl_2 + 4HAlCl_2 \rightarrow H_3Zn_2Cl + {}^1/_2ZnH_2 + {}^3/_2ZnCl_2 + AlCl_3 \tag{17}$$

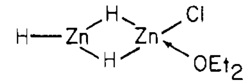
Unfortunately HZnCl was not isolated as anticipated according to eq 13. This means either that HZnCl reacts more rapidly with $HAlCl_2$ than $ZnCl_2$ to form ZnH_2 or that HZnCl disproportionates according to eq 14. Either way ZnH_2 is formed which then complexes HZnCl to form the apparently stable H_3Zn_2Cl.

Reactions of $ZnBr_2$ with AlH_3. Like $ZnCl_2$, $ZnBr_2$ was also allowed to react with AlH_3 in 1:1 and 2:1 mole ratios in ether. As in the previous case a white solid was formed closely corresponding to the empirical formula $H_3Zn_2Br \cdot 0.29Et_2O$. However, H_3Zn_2Br appears to be less stable than H_3Zn_2Cl since the white solid decomposed (producing a light gray solid) rapidly when the reaction mixture was stirred for the same period of time at room temperature. The light gray color is presumably due to the formation of zinc metal. The reactions were in general comparable with the reactions of $ZnCl_2$ with AlH_3. X-Ray powder diffraction patterns for $ZnBr_2$, $ZnBr_2 \cdot 0.28Et_2O$, and $H_3Zn_2Br \cdot 0.29Et_2O$ are shown in Table I. The fact that $ZnBr_2$ is soluble in ether and yet H_3Zn_2Br precipitated indicates that H_3Zn_2Br cannot be a mixture of ZnH_2 and $ZnBr_2$ in a 3:1 ratio.

Reactions of ZnI_2 with AlH_3. In a 2:1 mole ratio, ZnI_2 and AlH_3 in diethyl ether react to yield a white solid corresponding to the composition $ZnI_2 \cdot AlH_3 \cdot 1.79Et_2O$. Infrared analysis and X-ray powder diffraction of the solid compound showed it to be different from a physical mixture of ZnI_2 and AlH_3. The infrared spectrum as well as elemental analysis of the filtrate did not show the presence of any hydridoaluminum halides. Similarly, when the reaction was carried out in a 1:4 mole ratio (ZnI_2:AlH_3), a white solid resulted having the same composition. An infrared spectrum of the filtrate showed absorption bands due to AlH_3 alone. Therefore, it is safe to conclude that zinc iodide and AlH_3 in all stoichiometric ratios react to form $ZnI_2 \cdot AlH_3 \cdot nEt_2O$.

$$ZnI_2 + AlH_3 \rightarrow ZnI_2 \cdot AlH_3 \tag{18}$$

Very little can be said about the structures of the new zinc–hydrogen compounds (H_3Zn_2Cl, H_3Zn_2Br, $ZnI_2 \cdot AlH_3$) prepared in this study. If the compounds were soluble in some solvent, molecular weight and infrared studies could reveal much structural information. However, all of the hydrides were insoluble in all solvents in which they were tested leaving only single-crystal X-ray diffraction studies as a source of further information. In any case it might be worthwhile to point out at least some of the structural possibilities that should be considered for H_3Zn_2Cl (see **1**–**3**).



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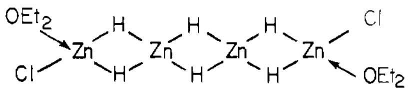

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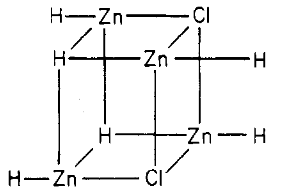

3

Reactions of $CdBr_2$ with AlH_3. In a 1:1 mole ratio, $CdBr_2$ and AlH_3 in diethyl ether were allowed to react at −40 to −30° for 40 hr with stirring to yield a slightly gray solid which exhibited a molar ratio of Cd:H:Br = 1.00:1.00:1.143. The solid decomposed to Cd, H_2, and $CdBr_2$ slowly at −20° and more rapidly at room temperature. As reported earlier by Wiberg and Henle,[2] CdH_2 was also found to decompose at −20°. Therefore, although the elemental analysis of the solid compound suggests the formation of HCdBr compound, the possibility of a physical mixture of CdH_2 and $CdBr_2$ cannot be ruled out. Elemental analysis of the filtrate showed the presence of H_2AlBr which was also supported by an infrared spectrum which exhibited bands characteristic of H_2AlBr.

In order to establish the nature of the solid product as HCdBr (eq 19) and not a mixture of $CdBr_2$ and CdH_2 (eq 20), an attempt was made to allow a mixture of $CdBr_2$ and H_2AlBr to react in diethyl ether in a 1:1 ratio at −40°. If the reaction of $CdBr_2$ and AlH_3 proceeds according to eq 20, then $CdBr_2$ is produced in the presence of H_2AlBr. Since it is possible that $CdBr_2$ is reduced in the presence of H_2AlBr (eq 21), the presence of $HAlBr_2$ would indicate the presence of $CdBr_2$ in solution. If indeed this reaction occurs (eq 21), this would indicate the absence of $CdBr_2$ in the reaction product of $CdBr_2$ and AlH_3, thus eliminating eq 20 as the reaction course. Unfortunately, no reaction took place; thus, it is not possible to tell whether the reaction product is HCdBr or a physical mixture of $CdBr_2$ and CdH_2.

$$CdBr_2 + AlH_3 \rightarrow HCdBr + H_2AlBr \tag{19}$$

$$CdBr_2 + AlH_3 \rightarrow \boxed{{}^1/_2CdH_2 + {}^1/_2CdBr_2} + H_2AlBr \tag{20}$$

$$CdBr_2 + H_2AlBr \rightarrow HCdBr + HAlBr_2 \tag{21}$$

Because of the low solubility of $CdBr_2$ in diethyl ether, an attempt was also made to study the reaction in THF; however, the reaction was found to be too slow at −40 to −30° and the reaction product decomposed above −20°.

Reactions of CuCl with AlH_3. When cuprous chloride and AlH_3 were allowed to react in 1:1 mole ratio in ether at −78° and then allowed to warm slowly to room temperature, the reaction mixture turned completely black giving off a gas. The elemental analysis as well as an infrared spectrum of the filtrate suggests that the reaction takes place according to the sequence of eq 22–25.

$$CuCl + AlH_3 \rightarrow CuH + H_2AlCl \qquad (22)$$

$$CuCl + H_2AlCl \rightarrow CuH + HAlCl_2 \qquad (23)$$

$$\underline{CuH + AlH_3 \rightarrow CuAlH_4} \qquad (24)$$

$$2CuCl + 2AlH_3 \rightarrow CuH + CuAlH_4 + HAlCl_2 \qquad (25)$$

The infrared spectrum of the filtrate showed a sharp band at 1900 cm^{-1} with a shoulder at 1850 cm^{-1}. Elemental analysis of the filtrate indicated only 43% of the total aluminum. The infrared spectrum of the black solid product did not show any absorption bands due to either hydridoaluminum compounds or hydridocopper compounds. Thus, it appears that the black solid product is a mixture of copper and aluminum metal formed according to eq 26. Since the filtrate was shown to be an ether solution of $HAlCl_2$ and since half of the aluminum was in the filtrate and half in the precipitate, it appears that there are ample data to suggest the above reaction sequence.

$$CuH + CuAlH_4 \rightarrow 2Cu + Al + {}^5/_6H_2 \qquad (26)$$

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Registry No. AlH_3, 7784-21-6; AlH_2Cl, 14644-71-4; $AlHCl_2$, 13497-97-7; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3; H_2AlBr, 54844-46-1; $HAlBr_2$, 15576-93-9; $ZnCl_2$, 7646-85-7; $H_3Zn_2Cl{\cdot}0.35(C_2H_5)_2O$, 54931-33-8; $ZnBr_2$, 7699-45-8; $H_3Zn_2Br{\cdot}0.29(C_2H_5)_2O$, 54931-35-0; ZnI_2, 10139-47-6; $ZnI_2{\cdot}AlH_3{\cdot}1.79(C_2H_5)_2O$, 54931-34-9; $CdBr_2$, 7789-42-6; CuCl, 7758-89-6.

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(17) The ether content of this compound is a result of drying the compound under vacuum for 1 hr before analysis. Further attempts to remove additional solvent by subjecting the compound to vacuum for a longer period of time resulted in decomposition of the solid.

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Syntheses, Nuclear Magnetic Resonance Spectra, and Mass Spectra of the (Halomethyl)disilanes

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The (halomethyl)disilanes $XCH_2SiH_2SiH_3$, in which X = Cl, Br, and I, have been synthesized and characterized. (Chloromethyl)disilane was prepared by the reaction of diazomethane with hexachlorodisilane, followed by $LiAlH_4$ reduction of the $ClCH_2Si_2Cl_5$ produced. (Bromomethyl)disilane was prepared by the direct reaction of bromodisilane with diazomethane. (Iodomethyl)disilane was isolated from the reaction of sodium iodide and (chloromethyl)disilane in acetone. The physical properties of these compounds are presented and correlated with the properties of related organic and organometallic compounds. The (halomethyl)disilanes represent a new type of series, the analogs of the propyl halides in which two of the carbon atoms have been replaced by silicon.

Introduction

While many silicon-functional derivatives of silane have been prepared and characterized, much less information has been reported about the related carbon-functional alkylsilanes and -germanes. We have undertaken a study of related series of XCH_2MH_2Y (M = Si, Ge) compounds and have synthesized the (halomethyl)silanes[1] and -germanes,[2] the (methoxyalkyl)silanes and -germanes,[3] and the (halomethyl)silylcobalt tetracarbonyls.[3] No carbon-functional disilanyl hydrides are known, and we here report the preparation of the (halomethyl)disilanes in order to ascertain the stability and properties of this series and to study the effects of chain extension by a $-SiH_3$ group by comparison of these compounds with the "parent" XCH_2SiH_3 species.[1,4]

In addition, mass spectra of organic molecules and their analogs in which a carbon atom is replaced by a silicon show considerable differences. Interaction between a remote electron-rich center and silicon often leads to rearranged ions in which a bond forms between the silicon and the previously not directly bonded functional group. Such interaction has previously been postulated[1,4] for the "parent" (halomethyl)silanes, and it seemed of interest to examine the effect of $-SiH_3$ chain extension by comparing the properties of XCH_2SiH_2–H and $-SiH_3$ compounds.

Although the fluoroalkyl derivatives FCH_2CH_3 and FCH_2GeH_3[5] are known, the corresponding silicon compound,