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Alkali Metal "ate" Complexes and Complex Metal Hydrides of Beryllium

E. C. ASHBY* and H. S. PRASAD

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The reactions of $LiAlH_4$ and AlH_3 with "ate" complexes of beryllium ($Li_nBe_mR_{2m+n}$) in ether solvents were investigated as a possible route to complex metal hydrides of beryllium. Both the 1:1 and 2:1 complexes of methyllithium and dimethylberyllium [$LiBe(CH_3)_3$ and $Li_3Be(CH_3)_4$] yielded Li_2BeH_4 when allowed to react with $LiAlH_4$ in diethyl ether. Li_3BeH_5 was obtained by a similar reaction of methyllithium and dimethylberyllium in 3:1 molar ratio followed by the reduction of the "ate" complex $Li_3Be(CH_3)_5$ with $LiAlH_4$ in diethyl ether. The 1:2 complex of methyllithium and dimethylberyllium $LiBe_2(CH_3)_5$ yielded a compound of indefinite composition. $LiBeH_3$ was prepared by the reaction of AlH_3 and [$LiBe(CH_3)_3$] in a 1:1 molar ratio in diethyl ether. The hydrides were characterized by elemental analysis, X-ray powder diffraction, and DTA–TGA analysis. Proton NMR spectra of diethyl ether solutions of methyllithium and dimethylberyllium in 1:1, 2:1, 3:1, and 1:2 molar ratios have been obtained over a wide temperature range. The spectra show that there is rapid exchange of methyl groups between methyllithium and the complexes formed. Evidence for the existence of more than one complex at equilibrium is discussed.

Introduction

Recently we have reported the synthesis of complex metal hydrides of zinc,[1] magnesium,[2] and copper.[3] The preparation of these compounds involves the reduction of an "ate" complex ($M_nM'_mR_{2m+n}$) with either $LiAlH_4$ or AlH_3.

$$\mathrm{CH_3Li + (CH_3)_2M} \rightarrow$$

$$\begin{tikzcd} \mathrm{LiM(CH_3)_3} \arrow[r, "\mathrm{CH_3Li}"] \arrow[d, "\mathrm{LiAlH_4}"] & \mathrm{Li_2M(CH_3)_4} \arrow[r, "\mathrm{CH_3Li}"] \arrow[d, "\mathrm{LiAlH_4}"] & \mathrm{Li_3M(CH_3)_5} \arrow[d, "\mathrm{LiAlH_4}"] \\ \mathrm{LiMH_3} & \mathrm{Li_2MH_4} & \mathrm{Li_3MH_5} \end{tikzcd} \qquad (1)$$

$$\mathrm{CH_3Li + 2(CH_3)_2M \rightarrow LiM_2(CH_3)_5 \xrightarrow{LiAlH_4} LiM_2H_5} \qquad (2)$$

$M = Zn$ or Mg

In 1968, Coates and Bell[4] reported the preparation of Li_2BeH_4 by the reaction of beryllium chloride and $Li(C_2H_5)_2BeH$. Attempts were also made to prepare other complex metal hydrides of beryllium, e.g., $LiBeH_3$; however no evidence was found to support the existence of this compound.

Recently Seitz and coworkers[5,6] studied lithium-7 and proton NMR spectra of methyllithium with $(CH_3)_2Mg$, $(CH_3)_2Zn$, and $(CH_3)_2Cd$ in diethyl ether. The spectra show that complexes of the type $Li_2M(CH_3)_4$ and $Li_3M(CH_3)_5$ (where M = Mg, Zn, or Cd) are formed in solution. No attempts were made to isolate these complexes in pure form. No evidence was available for or against the formation of a 1:1 complex. In our earlier work,[2,7] we studied the system methyllithium–dimethylmagnesium in diethyl ether by high-resolution infrared spectroscopy and found in general that at any given concentration there are several "ate" complex species in equilibrium and at no time does a single complex exist in solution.

In view of our recent preparation of complex metal hydrides of zinc, magnesium, and copper by the reaction of $LiAlH_4$ with the corresponding "ate" complexes, we decided to carry out a similar study involving the reactions of "ate" complexes of beryllium with $LiAlH_4$ or AlH_3. In this paper, we describe the preparation and characterization of $LiBeH_3$, Li_2BeH_4, and Li_3BeH_5. Also the system CH_3Li–$(CH_3)_2Be$ in diethyl ether was studied by proton NMR and high-resolution infrared spectroscopy in order to define the composition of the "ate" complex in solution prior to reaction with $LiAlH_4$.

Experimental Section

All operations were carried out either in a nitrogen-filled glove box equipped with a recirculating system to remove oxygen and moisture[8] or on the bench top using typical Schlenk-tube techniques.[9]

Instrumentation. Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solid samples were obtained as mulls in Nujol between CsI plates. Solutions were run in matched 0.10-mm path length 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 8–10 hr. *d* spacings were evaluated using a precalibrated scale equipped with viewing apparatus. Line intensities were estimated visually. DTA–TGA data were obtained under vacuum using a modified Mettler Thermoanalyzer II. Proton NMR spectra were obtained at 60 MHz using a Varian A-60 NMR spectrometer.

Analytical Procedures. Gas analyses were carried out by hydrolyzing samples on a standard vacuum line equipped with a Toepler pump. Aluminum analyses were carried out by complexometric titration with EDTA. Beryllium was determined by adding excess sodium fluoride to the solution at pH 7.8 and then back-titrating to pH 7.8 using standard hydrochloric acid. Lithium analysis was carried out by flame photometry. Analysis for chloride was carried out using a modified Volhard procedure. Analyses for carbon-bonded and oxygen-bonded metals were carried out by the Watson and Eastham[10] method using 2,2'-biquinoline and phenolphthalein indicators.

Materials. Diethyl ether (Fisher anhydrous ether) was distilled over $LiAlH_4$ immediately prior to use. Benzene (Fisher Certified reagent) was distilled over sodium aluminum hydride. Lithium aluminum hydride was obtained as a gray powder from Ventron, Metal Hydrides Division. Solutions of $LiAlH_4$ in diethyl ether were prepared by stirring the solid hydride for 24 hr with freshly distilled solvent, followed by filtration in a glove box to yield a clear, colorless solution.

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

LiH		BeH_2		Li_2BeH_4		Li_3BeH_5		$LiBH_3$		"$LiBe_2H_5$"	
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
3.85	w	3.85	s	3.85	w	3.65	w	6.60	vw	6.60	ww
2.65	w	3.45	w	3.69	vw	3.48	s	3.82	mw	4.85	vs
2.60	w	2.32	s	3.52	w	2.92	s	3.45	vw	3.80	m
2.35	s	2.225	vvw	3.25	w	2.75	ms	3.25	vw	3.50	vw
2.25	m	2.17	vvw	2.95	s	2.55	w	2.95	s	3.25	vvw
2.03	s	2.02	w	2.80	vw	2.42	w	2.77	w	2.92	s
1.95	w	1.96	w	2.57	s	2.30	vw	2.55	s	2.85	w
1.59	w	1.72	ms	2.40	w	2.18	vvw	1.98	w	2.55	m
1.440	s		w	2.32	vw	2.02	vvw	1.80	w	2.40	w
1.225	m			2.17	vw	1.80	vvw			2.30	w
1.175	w			2.04	w					1.97	mw
0.935	w			1.96	m					1.80	w
0.911	w			1.81	s						
				1.55	ms						
				1.47	w						

Anhydrous beryllium chloride was obtained from Alfa Inorganics. Solutions of beryllium chloride in diethyl ether were prepared by adding excess diethyl ether (50% excess based on the bis(etherate) of beryllium chloride) to a slurry of $BeCl_2$ in benzene cooled to 5°.[11] Ether solutions of $BeBr_2$ were prepared as previously reported.[12] Ether-soluble aluminum hydride was prepared by the reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether.[13] Methyllithium was obtained as a 5.4% solution in ether from Foote Mineral Co. and stored at −20° until ready to use. Sodium hydride was prepared by hydrogenation of metallic sodium in benzene at 4000 psi for 24 hr. A slurry of sodium hydride in diethyl ether was prepared in the usual manner. Lithium hydride was prepared by hydrogenolysis of *tert*-butyllithium in pentane at 4000 psi for 24 hr.

Preparation of Dimethylberyllium in Diethyl Ether. A solution of methyllithium in ether was added slowly to a solution of beryllium chloride in ether in a 2:1 molar ratio. Lithium chloride precipitated immediately and was separated by filtration. The filtrate was evaporated to dryness under vacuum at room temperature and dimethylberyllium (white solid) was purified by sublimation under vacuum (0.05 mm Hg) at 110°. A solution of dimethylberyllium in ether was then prepared by dissolving the purified compound in ether. Analysis showed a Be:CH_4 ratio of 1.00:1.98.

Preparation of $(n\text{-}C_4H_9)_2Be$ in Diethyl Ether. $n\text{-}C_4H_9Li$ (20 mmol) in hexane was added slowly with stirring to a cold solution (0°) of $BeCl_2$ (10 mmol) in diethyl ether. Lithium chloride precipitated and was filtered. The filtrate was concentrated and analyzed for beryllium and the *n*-butyl group in the usual manner (Be:C_4H_{10} = 1.0:1.92).

Infrared Study of the Reaction of $(CH_3)_2Be$ with CH_3Li in Diethyl Ether. To 2 ml of $(CH_3)_2Be$ (0.623 *M*) in a 10-ml volumetric flask was added a volume of CH_3Li in ether (1.586 *M*) calculated to give the desired $(CH_3)_2Be$ to CH_3Li ratio. The solution was then adjusted to the 10-ml mark and stirred. $(CH_3)_2Be$:CH_3Li ratios of 1:1, 1:2, 1:3, and 2:1 were studied by infrared spectroscopy in this manner. The infrared spectra of these solutions are shown in Figure 1.

Proton NMR Study of the Reaction of $(CH_3)_2Be$ with CH_3Li in Diethyl Ether. Ether solutions of CH_3Li and $(CH_3)_2Be$ were mixed in the appropriate molar ratios to form $Li_nBe_m(CH_3)_{2m+n}$ (n = 1, 2, 3 when m = 1; n = 0.5 when m = 2). The solutions were transferred into 5-mm NMR tubes under nitrogen and stored in Dry Ice.

Reactions Involving $(CH_3)_2Be$ with CH_3Li. (a) Reaction of $LiAlH_4$ with $LiBe(CH_3)_3$ in Diethyl Ether. Attempted Preparation of $LiBeH_3$. Methyllithium (5 mmol) in diethyl ether was added to 5 mmol of dimethylberyllium in diethyl ether. The resulting solution was stirred at room temperature for 1 hr; then 5 mmol of $LiAlH_4$ in diethyl ether was added. A white precipitate appeared immediately. This mixture was stirred at room temperature for another hour and filtered. The white solid was dried at room temperature under vacuum and analyzed. Anal. Calcd for $LiBeH_3$: Li, 36.56; Be, 47.49; H, 15.94. Found: Li, 46.83; Be, 28.39; H, 12.76. The molar ratio of Li:Be:H was 2.08:1.00:4.01. The filtrate contained only aluminum and a trace of beryllium and lithium. The infrared spectrum of the filtrate showed no Al–H stretching vibrations but instead was about identical with the spectrum observed for $(CH_3)_3Al$. The X-ray powder diffraction pattern of the solid product contained lines due to Li_2BeH_4 only.

(b) Reaction of $LiAlH_4$ with $Li_2Be(CH_3)_4$ in Diethyl Ether. Preparation of Li_2BeH_4. Dimethylberyllium (20 mmol) in diethyl ether was added to 40 mmol of methyllithium in diethyl ether. The resulting solution was stirred for 1 hr at room temperature, followed by addition of 40 mmol of $LiAlH_4$ in diethyl ether. There was an immediate precipitation of a white solid. The mixture was stirred for an additional 1 hr at room temperature, filtered, and dried under vacuum. Anal. Calcd for $Li_2BeH_4\cdot0.047Et_2O$:[14] Li, 45.65; Be, 29.64; H, 13.24. Found: Li, 46.82; Be, 25.58; H, 13.04. The molar ratio of Li:Be:H in the solid is 2.13:1.00:4.09. The X-ray powder diffraction pattern, given in Table I, was almost identical with the pattern reported earlier for Li_2BeH_4.[4]

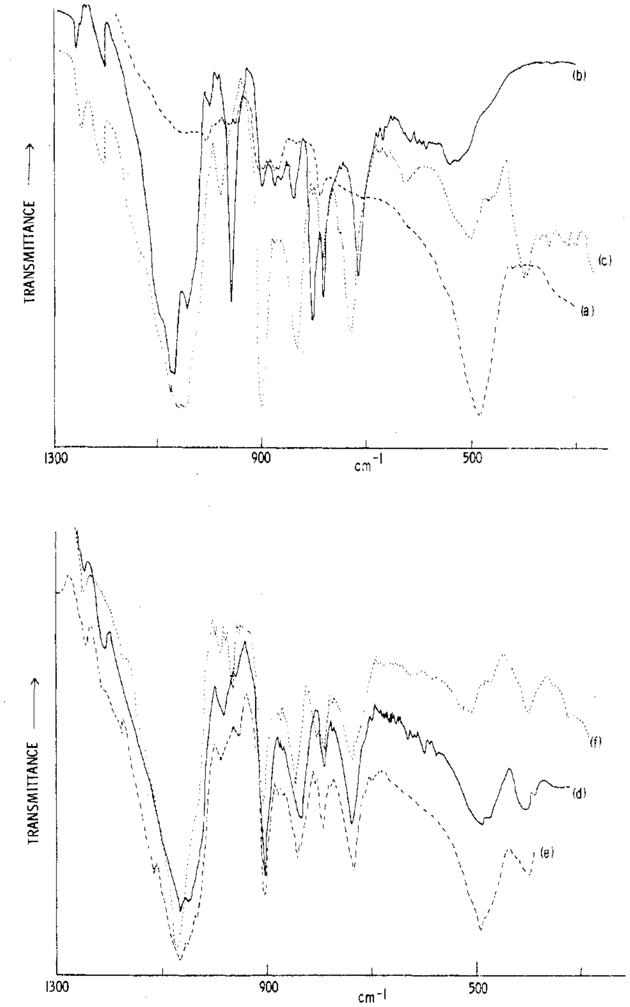


Figure 1. Infrared spectra of CH_3Li, $(CH_3)_2Be$, and mixtures of CH_3Li and $(CH_3)_2Be$ in diethyl ether: (a) CH_3Li; (b) $(CH_3)_2Be$; (c) 1:1 CH_3Li + $(CH_3)_2Be$; (d) 2:1 CH_3Li + $(CH_3)_2Be$; (e) 3:1 CH_3Li + $(CH_3)_2Be$; (f) 1:2 CH_3Li + $(CH_3)_2Be$.

(c) Reaction of $LiAlH_4$ with $Li_3Be(CH_3)_5$ in Diethyl Ether. Preparation of Li_3BeH_5. Methyllithium (42 mmol) in diethyl ether was added to 14 mmol of dimethylberyllium in diethyl ether. The resulting solution was stirred for 1 hr at room temperature, followed by addition of 35 mmol of $LiAlH_4$ in diethyl ether. A white precipitate appeared immediately. The mixture was stirred for 1 additional hr at room temperature and filtered. The resulting white solid was then dried at room temperature under vacuum and analyzed. Anal. Calcd for $Li_3BeH_5 \cdot 0.23Et_2O$:[14] Li, 40.09; Be, 17.35; H, 9.70. Found: Li, 38.14; Be, 18.07; H, 10.40. The molar ratio of Li:Be:H was 2.73:1.00:5.17. The amount of Li_3BeH_5 recovered was 100% of the theoretical value. The X-ray powder diffraction data are given in Table I. Infrared analysis of the solid (Nujol mull) showed a broad strong band at 1400–1800 cm^{-1} (centered at 1600 cm^{-1}).

(d) Reaction of $LiAlH_4$ with $LiBe_2(CH_3)_5$ in Diethyl Ether. Attempted Preparation of $LiBe_2H_5$. Methyllithium (10 mmol) in diethyl ether was added to 20 mmol of dimethylberyllium in diethyl ether. The resulting solution was stirred for 1 hr, followed by addition of 17.5 mmol of $LiAlH_4$ in diethyl ether. There was an immediate precipitation of a white solid. The mixture was stirred overnight at room temperature and then filtered. The white solid was then dried at room temperature under vacuum. The X-ray powder diffraction data are given in Table I. Anal. Calcd for $LiBe_2H_5$: Li, 23,12; Be, 60.07; H, 16.79. Found: Li, 31.11; Be, 31.14; H, 11.61. The molar ratio of Li:Be:H was 1.28:1.00:3.31.

(e) Reaction of NaH with $(n\text{-}C_4H_9)_2Be$ in Diethyl Ether. Attempted Preparation of $NaBe(n\text{-}C_4H_9)_2H$. A slurry of sodium hydride (10 mmol) in diethyl ether was added to 10 mmol of $(n\text{-}C_4H_9)_2Be$ in diethyl ether. The resulting mixture was stirred for 48 hr at room temperature and then filtered. An analysis of the filtrate showed Be:H in the ratio of 0.976:0.309 and the analysis of the white residue showed it to be unreacted sodium hydride.

(f) Reaction of $LiAlH_4$ with $BeBr_2$ in Diethyl Ether. Preparation of BeH_2. $LiAlH_4$ (14 mmol) solution in diethyl ether was added to 7 mmol of $BeBr_2$ solution in diethyl ether and the mixture was stirred for 1 hr at room temperature. The resulting white solid was filtered, washed with ether several times, and dried at room temperature under vacuum. Anal. Calcd for $BeH_2 \cdot 0.21Et_2O$:[14] Be, 33.88; H, 7.58. Found: Be, 34.54; H, 7.25. The molar ratio of Be:H was 1.00:1.89. The X-ray powder diffraction data are given in Table I.

(g) Reaction of AlH_3 with $LiBe(CH_3)_3$ in Diethyl Ether. Preparation of $LiBeH_3$. To a solution of $LiBe(CH_3)_3$ (10 mmol) in diethyl ether prepared by the method described above, a solution of AlH_3 (10 mmol) in ether was added slowly with stirring. A white precipitate appeared immediately. The mixture was stirred for 1 hr at room temperature and then filtered and washed with ether. The white solid was dried at room temperature under vacuum and analyzed. Anal. Calcd for $LiBeH_3 \cdot 0.27Et_2O$:[14] Li, 17.89; Be, 23.24; H, 7.79. Found: Li, 17.05; Be, 21.96; H, 7.53. The amount of $LiBeH_3$ recovered was 100% of the theoretical value. The X-ray powder diffraction data are given in Table I. Infrared analysis of the filtrate obtained after isolation of solid $LiBeH_3$ showed the presence of only $(CH_3)_3Al$ in the solution. The infrared spectrum of the solid showed a broad band at 1400–1800 cm^{-1}.

(h) Reaction of AlH_3 with $LiBe_2(CH_3)_5$ in Diethyl Ether. Attempted Preparation of $LiBe_2H_5$. A solution of $LiBe_2(CH_3)_5$ in diethyl ether was obtained by adding a solution of methyllithium (12.9 mmol) to a solution of dimethylberyllium (25.8 mmol) in ether. The mixture was stirred for 1 hr followed by addition of a solution of AlH_3 (21.5 mmol) in ether. A white solid precipitated immediately. The mixture was stirred for 2 hr at room temperature and then filtered and washed with ether, and the solid was dried at room temperature under vacuum. The infrared spectrum of the filtrate showed a broad strong band centered at 1650 cm^{-1}. The elemental analysis of the filtrate showed a Li:Be:Al:gas (hydrolyzable) ratio of 0.63:1.00:0.34:2.14. The hydrolyzed gas contained about 75% methane and 25% hydrogen. Infrared analysis of the solid showed a broad band at 1400–1800 cm^{-1}. The elemental analysis of the solid showed a Li:Be:H ratio of 1.23:1.00:3.15. The X-ray powder diffraction data are given in Table I.

Results and Discussion

Reactions of $LiAlH_4$ with "ate" Complexes of CH_3Li and $(CH_3)_2Be$. (a) Reaction of $LiAlH_4$ with $LiBe(CH_3)_3$ in Diethyl Ether. Attempted Preparation of $LiBeH_3$. The reaction of $(CH_3)_2Be$ with CH_3Li in diethyl ether yields a clear solution.

Table II. Chemical Shifts from the Center of the Methyl Triplet of Diethyl Ether

	Chem shifts, ppm		
Sample	Room temp	−65°	−96°
CH_3Li	3.08	3.08	
$(CH_3)_2Be$	2.28	2.38	2.550
$CH_3Li + (CH_3)_2Be$	2.21	2.22	2.25 (128) 2.67 (6)
$2CH_3Li + (CH_3)_2Be$	2.40	2.27 (46) 3.07 (14)	2.23 (82) 2.69 (134) 3.14 (22)
$3CH_3Li + (CH_3)_2Be$	2.55	2.30 (26) 3.08 (13)	2.23 (50) 2.70 (150) 3.15 (63)
$4CH_3Li + (CH_3)_2Be$	2.62	2.31 (31) 3.07 (28)	2.22 (48) 2.68 (138) 3.13 (122)
$CH_3Li + 2(CH_3)_2Be$			2.34
$CH_3Li + 3(CH_3)_2Be$			2.35
$6CH_3Li + (CH_3)_2Be$			2.19 (20) 2.64 (32) 3.11 (90)

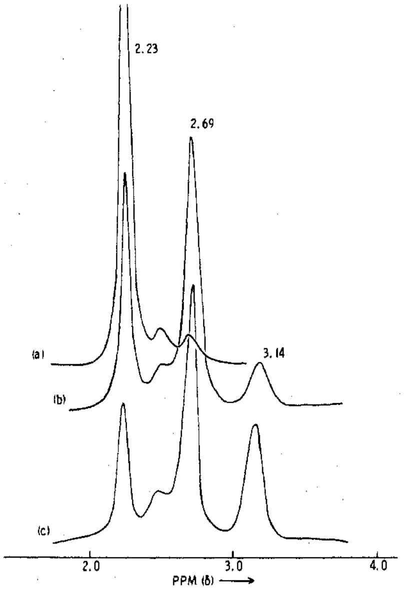


Figure 2. ^1H NMR spectra in diethyl ether at −96°: (a) $CH_3Li + (CH_3)_2Be$; (b) $2CH_3Li + (CH_3)_2Be$; (c) $3CH_3Li + (CH_3)_2Be$. The chemical shifts are shown upfield from the center of the ether triplet.

The infrared spectrum of the resultant solution is recorded in Figure 1. Although no assignment has been made for M–C stretching vibrations, the absence of the 483-cm^{-1} band characteristic of methyllithium and the absence of the medium strong band at 960 cm^{-1} present in dimethylberyllium indicate the formation of a complex involving methyllithium and dimethylberyllium. The infrared spectrum of the solution shows two medium strong bands at 500 and 400 cm^{-1} and a weak band at 450 cm^{-1}.

At room temperature the proton chemical shifts of methyllithium and dimethylberyllium are 3.08 and 2.28 ppm, respectively, upfield from the center of the ether triplet (Table II). The proton spectrum of methyllithium–dimethylberyllium complex consists of a single sharp resonance at room temperature which implies either formation of a compound with only one type of methyl group or rapid exchange involving different species in solution. At low temperature (−96°) the exchange is slowed such that a multiplet structure occurs, as shown in Figure 2. The resonance peak at 2.23 ppm may be assigned to the methyl protons of the 1:1 complex, whereas

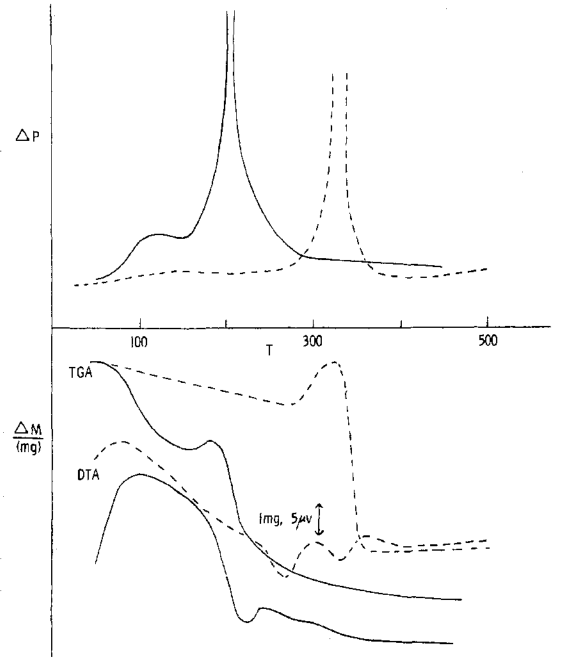


Figure 3. Vacuum DTA-TGA of BeH_2 (—) and Li_2BeH_4 (- - -).

the resonance peak at 2.65 ppm may be assigned to the methyl protons of the complex $Li_2Be(CH_3)_4$. The presence of the broad peak at 2.45 ppm is not well understood; however, it may be due to some kind of impurity which could not be removed from the starting materials although considerable effort was made in this direction. The occurrence of this peak at low temperature has also been noted by Seitz and Little[6] while studying the methyllithium–dimethylcadmium system. It appears, therefore, that at room temperature there is a rapid exchange between 2:1 and 1:1 complexes of methyllithium and dimethylberyllium giving a single sharp resonance and at low temperature this exchange is slowed to the extent that $LiBe(CH_3)_3$ and $Li_2Be(CH_3)_4$ exhibit individual methyl signals. It is clear that $LiBe(CH_3)_3$ is by far the most predominant species in solution; however, it is in equilibrium with $Li_2Be(CH_3)_4$ at room temperature.

The reaction of $LiAlH_4$ and $LiBe(CH_3)_3$ gave a solid which was shown to be Li_2BeH_4 instead of $LiBeH_3$. The infrared spectrum of the filtrate showed no bands due to Al–H stretching vibrations between 1900 and 1700 cm^{-1}; however, it did exhibit a spectrum almost identical with that of $(CH_3)_3Al$. The infrared spectrum of the white solid (in Nujol mull) contained broad absorptions centered at 1600 cm^{-1}. The X-ray powder diffraction pattern showed only lines for Li_2BeH_4 (Table I). The route by which Li_2BeH_4 is formed from $LiBe(CH_3)_3$ and $LiAlH_4$ is not clear but probably takes place by a series of reactions that can be represented in a simplified way by eq 3 and 4. The vacuum TGA diagram shown in Figure 3 contained one very broad peak at 330°. This observation in addition to the pressure differential curve peaking at 330° is indicative of the evolution of a noncondensable gas (H_2) and represents the only weight loss or gas evolution up to 500°. The thermal effect (DTA) of this gas evolution is a small endotherm (330°) which is preceded by another small endotherm at 270° indicative of a structural change not involving a weight loss or gas evolution. The weight loss at 330° (8%) corresponds to the loss of 1 mol of hydrogen present in Li_2BeH_4. Thus, the decomposition takes place according to eq 5 and 6 with Li_2BeH_4 dissociating to LiH and BeH_2 at 270° (no weight loss) followed by decomposition of the BeH_2 at 330°.

$$LiBe(CH_3)_3 + LiAlH_4 \rightarrow Li_2Be(CH_3)_3H + AlH_3 \quad (3)$$

$$Li_2Be(CH_3)_3H + AlH_3 \rightarrow Li_2BeH_4 + Al(CH_3)_3 \quad (4)$$

$$Li_2BeH_4 \rightarrow 2LiH + BeH_2 \quad \text{(endotherm, 270°)} \quad (5)$$

$$BeH_2 \rightarrow Be + H_2 \quad \text{(endotherm, 330°)} \quad (6)$$

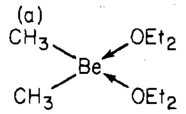
(b) Reaction of $LiAlH_4$ with $Li_2Be(CH_3)_4$ in Diethyl Ether. Preparation of Li_2BeH_4. The reaction of CH_3Li with $(CH_3)_2Be$ in a 2:1 molar ratio also yields a clear solution. The infrared spectrum of the resultant solution shown in Figure 1 is identical with the infrared spectrum of the 1:1 complex except that the band at 500 cm^{-1} is masked by the strong band of methyllithium at 483 cm^{-1}. The proton NMR spectrum of $Li_2Be(CH_3)_4$ in diethyl ether at room temperature is shown in Figure 2. At room temperature the proton spectrum consists of a single sharp resonance peak which again implies either a single compound or a rapid exchange among different species in solution. The low-temperature (−96°) proton spectrum (Figure 2) can be interpreted in terms of an equilibrium mixture of 1:1, 2:1, and 3:1 complexes of methyllithium and dimethylberyllium.

$$^1/_4(CH_3Li)_4 + (CH_3)_2Be \rightarrow LiBe(CH_3)_3 \quad (7)$$

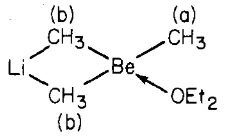
$$LiBe(CH_3)_3 + {}^1/_4(CH_3Li)_4 \rightleftharpoons Li_2Be(CH_3)_4 \quad (8)$$

$$Li_2Be(CH_3)_4 + {}^1/_4(CH_3Li)_4 \rightleftharpoons Li_3Be(CH_3)_5 \quad (9)$$

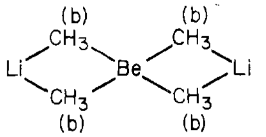
The methyl group (a) bonded directly to the beryllium atom in $(CH_3)_2Be{\cdot}2OEt_2$ should be similar to one of the methyl groups in $LiBe(CH_3)_3{\cdot}OEt_2$ and $Li_3Be(CH_3)_5$. On the other hand the methyl group (b) bridged to Li and Be(Li–CH_3–Be) should be similar to the methyl group (b) in $Li_2Be(CH_3)_4$ and $Li_3Be(CH_3)_3$. Furthermore, the methyl group (c) bridged only to Li(Li–CH_3–Li) should be similar to the methyl group in $(CH_3Li)_4$ and $Li_3Be(CH_3)_5$ designated (c). The resonance furthest downfield is assigned to the methyl group (a) attached only to beryllium since $(CH_3)_2Be{\cdot}2OEt_2$ absorbs in this region. The methyl group (c) has been assigned to the absorption furthest upfield because this methyl group is attached only to Li and therefore should resemble $(CH_3Li)_4$ which absorbs the furthest upfield. The methyl group (b) bonded to lithium and beryllium atoms should exhibit a chemical shift somewhere in between $(CH_3)_3Be{\cdot}2OEt_2$ and $(CH_3Li)_4$. Using these ideas, the assignment of the resonance peaks can be made to substantiate the existence of equilibria 7–9.



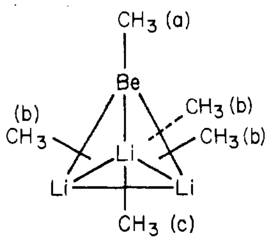
$(CH_3)_2Be{\cdot}2OEt_2$



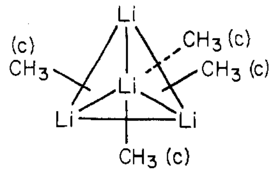
$LiBe(CH_3)_3{\cdot}OEt_2$



$Li_2Be(CH_3)_4$



$Li_3Be(CH_3)_5$



$(CH_3Li)_4$

The amount of each complex, namely, $LiBe(CH_3)_3$,

$Li_2Be(CH_3)_4$, and $Li_3Be(CH_3)_5$ at equilibrium can be calculated by measuring the areas of each peak and taking into consideration the fact that each peak may be due either to methyl protons of only one species or to methyl protons of different species present in solution. For example, the resonance peak furthest downfield may be due to both of the methyl groups of $(CH_3)_2Be{\cdot}2OEt_2$ as well as due to the methyl group bonded to the beryllium atom in $Li_3Be(CH_3)_5$. Similarly, the resonance peak observed for the 2:1 complex, $Li_2Be(CH_3)_4$, may also be due to the three methyl groups which are bonded to both lithium and beryllium atoms in $Li_3Be(CH_3)_5$. The resonance peak furthest upfield may only be due to the methyl group bonded to the three lithium atoms in the complex $Li_3Be(CH_3)_5$ or to the presence of methyllithium. It has been found from the measured areas (Table II) that $LiBe(CH_3)_3$, $Li_2Be(CH_3)_4$, and $Li_3Be(CH_3)_5$ exist in a 1:1:1 molar ratio in solution at –96° when CH_3Li and $(CH_3)_2Be$ are admixed in a 2:1 ratio.

The reaction of $LiAlH_4$ and the "ate" complex mixture produced on allowing CH_3Li and $(CH_3)_2Be$ to react in a 2:1 ratio yielded a white solid of empirical formula Li_2BeH_4. The infrared spectrum of the white solid contained a broad absorption band centered on 1600 cm^{-1}. The X-ray powder diffraction pattern showed it to be Li_2BeH_4 (Table I). The vacuum DTA–TGA of this compound was identical with the one discussed earlier. The major weight loss (7.7%) occurred at 330° corresponding to 1 mol of hydrogen.

(c) Reaction of $LiAlH_4$ with $Li_3Be(CH_3)_5$ in Diethyl Ether. Preparation of Li_3BeH_5. The infrared spectrum of the solution obtained by stirring a solution of CH_3Li with $(CH_3)_2Be$ in diethyl ether in a 3:1 molar ratio is recorded in Figure 1. The infrared spectrum of the solution shows two medium strong bands at 405 and 335 cm^{-1} which are tentatively assigned to Be–C stretching vibrations. The strong band at 480 cm^{-1} is assigned to the Li–C stretching vibrations. The proton spectrum of the same solution consists of a single sharp resonance at room temperature. This implies either the presence of a single compound or a rapid exchange between different species in solution. At –96° three major absorptions are observed (Figure 2). The assignments of these resonance peaks are made as before describing the system as an equilibrium of the type

$$^{1}/_{4}(CH_3Li)_4 + Li_2Be(CH_3)_4 \rightleftharpoons Li_3Be(CH_3)_5 \qquad (10)$$

In order to establish the stoichiometry of these complexes at equilibrium the areas of all absorptions in the low-temperature proton spectra were measured. A calculation of the relative peak intensities shows $Li_3Be(CH_3)_5$ to be the major species in solution with ~10% dissociation to CH_3Li and $Li_2Be(CH_3)_4$ (Table II).

Reaction of $LiAlH_4$ with $Li_3Be(CH_3)_5$ produced an insoluble white compound which exhibited the empirical formula Li_3BeH_5. The infrared spectrum of the solid showed a broad absorption band centered on 1600 cm^{-1}. The X-ray powder diffraction pattern showed it to be a new compound and not a physical mixture of LiH and Li_2BeH_4. The vacuum DTA–TGA of this compound showed a weight loss (1.21%) at 218° and another weight loss (4.71%) at 300°, the total weight loss being 5.92% which is quite in agreement with the theoretical value (5.78%) calculated for the loss of 1 mole of hydrogen. Although this total weight loss due to evolution of hydrogen gas leads us to suggest eq 11–13 as the steps of decomposition, the weight loss in two stages is somewhat puzzling.

$$\text{step I:}\quad Li_3BeH_5 \rightarrow Li_2BeH_4 + LiH \qquad (11)$$

$$\text{step II:}\quad Li_2BeH_4 \rightarrow 2LiH + BeH_2 \qquad (12)$$

$$\text{step III:}\quad BeH_2 \rightarrow Be + H_2 \qquad (13)$$

Table III. Thermal Decomposition of Complex Metal Hydrides of Beryllium

Compd (sample wt, mg)	Thermicity	Range of transition (peak max), °C	% wt Loss
BeH_2 (21.5)	Exo	80–150 (125)	11.6 (loss of ether)
	Endo	170–230 (208)	13.95
Li_2BeH_4	Endo	250–290 (270)	Phase change
	Endo	280–360 (330)	8.0
Li_3BeH_5		210–226 (218)	1.21
	Endo	240–290 (262)	Phase change
	Endo	300–340 (315)	4.71
$LiBeH_3$	Exo	130–190 (164)	5.27
	Endo	250–275 (265)	Phase change
	Endo	270–325 (308)	5.1
BeH_2 + Li_2BeH_4 (52.1) (1:1 molar ratio)	Exo	90–150 (130)	7.4 (loss of ether)
	Endo	170–250 (205)	6.1
	Endo	250–280 (270)	Phase change
	Endo	260–330 (295)	4.8

(d) Reaction of $LiAlH_4$ with $LiBe_2(CH_3)_5$ in Diethyl Ether. $LiBe_2H_5$. The infrared spectrum of the resultant mixture obtained after stirring CH_3Li with $(CH_3)_2Be$ in a 1:2 molar ratio is identical with the infrared spectrum of the so-called complex $LiBe(CH_3)_3$. The proton NMR spectrum of the solution consists of a single sharp resonance at room temperature as well as at low temperature (–96°) indicating a single compound or very rapid exchange of methyl groups between the complex $LiBe(CH_3)_3$ and dimethylberyllium. The reaction of $LiAlH_4$ with the 1:2 CH_3Li–$(CH_3)_2Be$ solution resulted in a solid of indefinite analysis. The X-ray powder diffraction of the solid gave very weak lines similar to those for Li_2BeH_4, but with different intensities. It appears that the compound is a physical mixture of Li_2BeH_4 and BeH_2.

Reactions of AlH_3 with "ate" Complexes of CH_3Li and $(CH_3)_2Be$. (a) Reaction of AlH_3 with $LiBe(CH_3)_3$ in Diethyl Ether. Preparation of $LiBeH_3$. The reaction of AlH_3 and $LiBe(CH_3)_3$ in diethyl ether produced a white solid of empirical formula $LiBeH_3$. The infrared spectrum of this compound also contained a broad band centered on 1600 cm^{-1}. The X-ray powder diffraction pattern showed it to be different from either a physical mixture of Li_2BeH_4 and BeH_2 or a mixture of LiH and BeH_2. Although the strong lines at 2.95 and 2.55 Å are common in both $LiBeH_3$ and Li_2BeH_4, other lines are quite different. Moreover, the strong lines at 1.81 and 1.55 Å present in Li_2BeH_4 and the lines at 3.85 and 2.32 Å present in BeH_2 are absent in $LiBeH_3$. Therefore, the compound appears to have its own identity.

The vacuum DTA–TGA of $LiBeH_3$ is reported in Table III. It contained noncondensable gas evolutions at 164 and 308°, respectively. The gas evolution at 164° was accompanied by a small exothermal effect and is probably due to decomposition of BeH_2 into beryllium and hydrogen (step 1). The thermal effect (DTA) of the gas evolution at 308° is a small endotherm which is preceded by another small endotherm at 265° indicative of a structural change not involving a weight loss or gas evolution. The weight loss at 164° (5.27%) corresponds to the loss of one atom of hydrogen present in $LiBeH_3$.

Similarly, the weight loss at 308° (5.1%) corresponds to the weight loss of one atom of hydrogen. Therefore, the thermal decomposition of $LiBeH_3$ is believed to occur in essentially two steps below 500° (see eq 14–17).

$$\text{step I}\begin{cases}2LiBeH_3 \rightarrow Li_2BeH_4 + BeH_2 & (14)\\ BeH_2 \rightarrow Be + H_2 & (15)\end{cases}$$

$$\text{step II}\begin{cases}Li_2BeH_4 \rightarrow 2LiH + BeH_2 & (16)\\ BeH_2 \rightarrow Be + H_2 & (17)\end{cases}$$

(b) Reaction of AlH_3 with $LiBe_2(CH_3)_5$ in Diethyl Ether. Attempted Preparation of $LiBe_2H_5$. The reaction of AlH_3 and $LiBe_2(CH_3)_5$ resulted in a solid of indefinite analysis. The X-ray powder diffraction of the solid gave very weak lines similar to those of Li_2BeH_4, but with different intensities. The vacuum DTA–TGA of the solid showed three noncondensable gas evolutions at 165, 243, and 308°, respectively. The thermal effect (DTA) of gas evolution at 165° is a small endotherm which probably represents the decomposition of BeH_2 into beryllium and hydrogen. The gas evolution at 243° is accompanied by an exotherm whereas the gas evolution at 308° is accompanied by a small endotherm. The weight loss (1%, 2.8%, and 5.7%, respectively) indicates the presence of one or more species in the sample.

A potential route to complex metal hydrides of beryllium of the type $Na_nBe_mH_{2n+m}$ and $K_nBe_mH_{2n}$ involves the reaction of NaH or KH with $(CH_3)_2Be$ followed by reaction of the resulting complex with $LiAlH_4$. Attempts to prepare $KBe(CH_3)_2H$ and $NaBe(s\text{-}C_4H_9)_2H$ in diethyl ether resulted in incomplete reaction between potassium or sodium hydride and corresponding dialkylberyllium compounds.

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Registry No. LiH, 7580-67-8; BeH_2, 7787-52-2; Li_2BeH_4, 19321-21-2; Li_3BeH_5, 56792-70-2; $LiBeH_3$, 25282-11-5; CH_3Li, 917-54-4; $(CH_3)_2Be$, 506-63-8; $LiAlH_4$, 16853-85-3; $Li_2Be(CH_3)_4$, 20860-58-6; $Li_3Be(CH_3)_5$, 56829-59-5; $LiBe_2(CH_3)_5$, 56829-60-8; $(n\text{-}C_4H_9)_2Be$, 7367-41-1; Et_2O, 60-29-7; $BeBr_2$, 7787-46-4; AlH_3, 7784-21-6; $LiBe(CH_3)_3$, 56792-71-3.

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Contribution from the Department of Chemistry,
The University of Florida, Gainesville, Florida 32611

Trends in the Proton Nuclear Magnetic Resonance Spectra of Some Amine–Haloboranes. Steric Effects[1]

W. H. MYERS,*[2] G. E. RYSCHKEWITSCH, M. A. MATHUR, and R. W. KING

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Borane adducts of trimethylamine and diethylamine were halogenated using free halogens or hydrogen halides, and the proton NMR spectra of these amine–haloborane adducts were obtained. The resonances of these adducts showed a shift to lower field with increased size of halogen or with increased number of halogens on boron. This shift to lower field had been previously attributed to inductive effects, but in this work it was shown that the shift to lower field was due to steric interaction between halogens on boron and alkyl groups on nitrogen. Proton NMR spectra for diethylamine–haloboranes were complex and showed patterns attributable to nonequivalent methylene protons. Computer analyses of the spectra allowed assignments consistent with preferred rotational configurations.

Introduction

There can be no question as to the place of nuclear magnetic resonance in chemistry today. NMR has become one of the most powerful tools available for studying a wide variety of chemical systems, including such diverse problems as reaction kinetics, structure, product yields, product identification, and reaction mechanisms. However, in spite of its usefulness, there is still considerable controversy in the literature concerning the origin of chemical shifts.

A variety of physical evidence has established that the acid strengths of the boron trihalides increase in the order $BF_3 < BCl_3 < BBr_3 < BI_3$. This evidence includes calorimetric studies,[3] dipole moment determinations,[4] gas-phase displacement studies,[5-7] and structural determinations involving X-ray and microwave techniques.[8-10] Attempts have been made, with varying success, to correlate this property of the boron trihalides with various spectral properties of their donor–acceptor complexes. Thus, correlations have been attempted between acidity of the boron trihalides and infrared data,[11-16] mass spectral data,[17] ^{11}B NMR data,[18-22] and ^1H NMR data[23-27] obtained on the donor–acceptor complexes formed by the boron trihalides. The one characteristic common to these various correlations is the assumption that the relative ability of the coordinated boron trihalides to remove electron density from the donor to which they are coordinated is in the same order as the order of acid strengths of the free boron trihalides.

In particular the ^1H NMR spectra of trimethylamine–trihaloboranes have been examined[25-27] and the conclusion was reached that the trend observed in the spectra, a downfield shift of the methyl resonance with larger halogens on boron, is consistent with an inductive effect due to the increased acidity of the borane. To evaluate this argument, consider first the reason that the order of acid strength is $BF_3 < BCl_3 <$