

Beryllium-9 and Hydrogen-1 Magnetic Resonance Studies of Beryllium Compounds in Solution

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Abstract: High-resolution ^9Be resonance spectroscopy of inorganic and organometallic compounds is discussed. Chemical shifts are found to be sensitive to environment and dependent only on local diamagnetic factors, the chemical shifts being determined by changes in the inductive effects of the groups bonded to beryllium. Proton magnetic resonance of methylberyllium species is reported and discussed. Dimethylberyllium is found to form 1:1 adducts with diethyl ether and trimethylamine at room temperature, but lowering the temperature favors formation of 2:1 adducts.

High-resolution ^9Be magnetic resonance spectroscopy, by analogy with ^{11}B and ^{27}Al magnetic resonance studies,^{1,2} should be a valuable technique for use in studying structure and bonding of organoberyllium compounds. A comparison of the pertinent nuclear properties³ of ^9Be , ^{11}B , and ^{27}Al (Table I) indicates that ^9Be compares favorably with ^1H , ^{27}Al , and ^{11}B with the exception of the low relative sensitivity of the ^9Be nucleus at constant field.

representative of the broad spectrum of compounds available.⁵

For example, the adducts $(\text{CH}_3)_2\text{BeN}(\text{CH}_3)_3$ and $(\text{CH}_3)_2\text{Be}(\text{N}(\text{CH}_3)_2\text{CH}_2)_2$ (three- and four-coordinate, respectively) exhibit methylberyllium proton resonance signals at τ 11.19 and 11.42, respectively.⁶ This difference was attributed to a difference in electron density (changes in local diamagnetic shielding) at the methyl protons. It is expected that these differences

Table I. Nuclear Properties

Isotope	Natural abundance, %	Relative sensitivity ^a	Spin, <i>I</i>	$Q,^b e \times 10^{-24} \text{ cm}^2$	Magnetic moment, μ , nuclear magnetons
^1H	99.98	1.0000	1/2	...	2.793
^9Be	100.00	0.0139	3/2	2×10^{-2}	-1.177
^{11}B	81.18	0.165	3/2	3.55×10^{-2}	2.688
^{27}Al	100.00	0.207	5/2	0.149	3.638

^a For equal numbers of nuclei at constant field. ^b Quadrupole moment.

In order to be useful as a spectroscopic tool, ^9Be resonance signals should (1) be sharp enough to allow accurate chemical shift measurements, (2) show a predictable dependence of the chemical shift on environment, and (3) show spin-spin coupling with other nuclei. High-resolution ^9Be magnetic resonance spectra of the following inorganic species have been reported:⁴ beryllium chloride in diethyl ether, beryllium acetylacetonate in chloroform, beryllium quinadinate in chloroform, ammonium tetrafluoroberyllate in water, and beryllium sulfate in water. The signals were sharp in all cases and the BeF_4^{2-} ion showed spin-spin coupling ($J_{^9\text{Be}-^{19}\text{F}} = 33 \pm 2 \text{ Hz}$), satisfying two of the above requirements. Unfortunately, however, no chemical shifts from the basic beryllium acetate reference were observed (due to their close proximity to the reference) except for the BeF_4^{2-} ion which had an upfield shift of about 2 ppm. This insensitivity of the chemical shift to environment was explained by postulating a high degree of ionic character in the bonding to beryllium.⁴ The compounds which were the subject of the above study, however, were not

should be evident at the beryllium nuclei also, resulting in differences in the ^9Be chemical shifts. A systematic study of organometallic systems was therefore undertaken to determine the effect of changes in environment on the ^9Be chemical shift. Proton magnetic resonance of the methylberyllium species was expected to aid in the assessment of the factors which give rise to the chemical shift.

While local diamagnetic factors are dominant in proton resonance, local paramagnetic factors are dominant in the magnetic resonance of ^{11}B and ^{19}F nuclei.⁷ Comparison of the magnitudes of ^9Be chemical shifts with those observed for ^{11}B and ^1H should reveal the relative importance of these factors. A linear plot of $J_{^{13}\text{C}-^1\text{H}}$ vs. $\tau(\text{CH}_3\text{-X})$ should also be evidence for the lack of significant paramagnetic factors for those atoms bonded to methyl groups.⁸

Experimental Section

The organoberyllium compounds which form the basis of this study are pyrophoric. All operations involving these species were therefore carried out in an inert atmosphere enclosure equipped

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- (8) R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold, New York, N. Y., 1965, p 270.

with an atmosphere circulation system for removal of trace quantities of moisture and oxygen.⁹ Dimethylberyllium,¹⁰ methylberyllium chloride,¹¹ and the 1:1 adduct of dimethylberyllium with trimethylamine¹² were synthesized by published methods. Basic adducts of dimethylberyllium, $(\text{CH}_3)_2\text{BeX}_n$, where X is dimethyl sulfide, trimethylamine, diethyl ether, and trimethylphosphine, and $n = 1$ and 2 (which may also be temperature dependent), were prepared by dissolving dimethylberyllium in the appropriate solvent. Adducts of beryllium chloride and methylberyllium chloride were prepared in an analogous manner. $\text{Be}(\text{NH}_3)_4^{2+}$ was prepared by dissolving beryllium chloride in liquid ammonia. $\text{Be}(\text{H}_2\text{O})_4^{2+}$ was prepared by dissolving beryllium nitrate in water and $\text{BeF}_2(\text{H}_2\text{O})_2$ by dissolving beryllium fluoride in water. These later species have been described previously.¹³ Bisdimethylaminoberyllium trimer, $[\text{Be}(\text{N}(\text{CH}_3)_2)_3]_3$, was synthesized by the reaction of excess dimethylamine with dimethylberyllium in ether solution. The melting point (87–89°) and the proton magnetic resonance signals at 7.03 and 7.63 (of 1:2 relative intensity, respectively) compare to the literature values of 88–89°¹⁴ and τ 7.04 and 7.66,¹⁵ respectively.

Beryllium fluoride, beryllium chloride, and beryllium nitrate were purchased from Alfa Inorganics and used without further purification. Solvents were dried prior to use by heating to reflux over calcium hydride followed by distillation. Dimethyl sulfide was purchased from Aldrich Chemical Co., Inc., diethyl ether as Baker Analyzed reagent grade solvent, and trimethylphosphine from K and K Laboratories, Inc. Trimethyl- and dimethylamine were supplied by Matheson, Inc.

Nmr samples of pyrophoric compounds were degassed and sealed on a vacuum manifold. The spectra were recorded on a Varian Associates HA-100 nuclear magnetic resonance instrument. Proton chemical shifts were recorded relative to solvent and/or internal standard (TMS) signals. Beryllium resonance spectra were obtained using a Varian V-4311 rf unit at 14.05 MHz with a field of 23.5 kG. Beryllium chemical shifts were measured by replacing the analytical sample with an audiomodulated reference sample of aqueous beryllium nitrate without interruption of the field sweep. At least two measurements were made for each sample, although the field sweep was quite linear and repetition was unnecessary. Chemical shifts are reproducible to ± 2 Hz (± 0.1 ppm).

Results and Discussion

The two major experimental problems encountered in measuring ^9Be resonance were unfavorably sensitive spin-lattice relaxation times, requiring precise setting of the rf power input for each analytical sample, and low signal strengths. The intrinsic low sensitivity of the beryllium nucleus, coupled with the low beryllium atom content of the beryllium alkyls in solution, necessitates the use of very concentrated (saturated) solutions for successful beryllium magnetic resonance analysis. The electric quadrupole moment of beryllium did not cause deleterious consequences in the room-temperature spectra of the compounds studied and, in fact, provided useful information about the symmetry of the environment. The half-height widths at room temperature ranged from 2 Hz for a saturated solution of beryllium nitrate in water (the natural width being much smaller than we could measure) to 20 Hz for $(\text{CH}_3)_2\text{Be} \cdot \text{NMe}_3$ in cyclohexane. The sharp resonance for $\text{Be}(\text{H}_2\text{O})_4^{2+}$ is indicative of a symmetrical tetrahedral arrangement of water molecules¹⁶ where quadrupolar coupling is predicted to be zero. A long spin-lattice relaxation

time is also indicated for this species, the natural line width being proportional to the reciprocal of the average time the system spends in the excited state.¹⁷

Quadrupolar broadening of the resonance signals is quite significant at lower temperatures. The half-height width of ^9Be resonance signals of a solution of dimethylberyllium in dimethyl sulfide broadens from 18 Hz at 40° to 56 and 114 Hz at –40 and –80°, respectively. Broadening of this magnitude precludes the detection of nonequivalent nuclear environments at low temperatures. The variable-temperature studies were also limited by our inability to insert the reference sample to determine the chemical shift.

Electron screening of beryllium nuclei is most conveniently considered as the sum of a number of local atomic contributions.¹⁸ These include both contributions from electron charge surrounding the nucleus and electron charge distributions of neighbor atoms in the molecule. The *diamagnetic* part arises from the total charge distribution of the atom concerned, which depends in turn on the *hybridization* of bonding orbitals and on the *inductive effects* of neighbor atoms. The chemical shifts will also be affected by the so-called neighbor anisotropy effect.¹⁹ That beryllium chemical shifts would also have a significant *paramagnetic* contribution was the conclusion of the ^{19}F resonance study of the species BeF_2 and BeF_4^{2-} in water.⁴

On the contrary, however, the effect of changes in the beryllium environment on the chemical shift is not as great as is the effect of corresponding changes on ^{11}B chemical shifts. The ^{11}B resonance of $(\text{CH}_3)_3\text{B} \cdot \text{NMe}_3$ ²⁰ is 85 ppm to higher field than that of $(\text{CH}_3)_3\text{B}$.²¹ The ^9Be resonance (Table II) of $(\text{CH}_3)_2\text{Be} \cdot 2\text{NMe}_3$ is

Table II. ^9Be and ^1H Nmr Data for Beryllium Species

Species	Solvent	^9Be chemical shift, ppm relative to $\text{Be}(\text{H}_2\text{O})_4^{2+}$	^1H chemical shift of $\text{CH}_3\text{-Be}$, τ
$\text{BeF}_2 \cdot 2\text{H}_2\text{O}$	H_2O	+0.8	
$\text{Be}(\text{H}_2\text{O})_4^{2+}$	H_2O	0.0	
$\text{Be}(\text{NH}_3)_4^{2+}$	NH_3	-1.7	
$\text{BeCl}_2 \cdot 2\text{OEt}_2$	OEt_2	-3.1	
$[\text{Be}(\text{N}(\text{CH}_3)_2)_3]_3$	Benzene		
Central Be		-3.0	
End Be		-9.8	
$\text{BeCl}_2 \cdot 2\text{SMe}_2$	SMe_2	-5.5	
$\text{CH}_3\text{BeCl} \cdot 2\text{SMe}_2$	SMe_2	-4.2	11.17
$(\text{CH}_3)_2\text{Be} \cdot \text{SMe}_2$	SMe_2	-11.6	10.77
$(\text{CH}_3)_2\text{Be} \cdot 2\text{PMe}_3$	PMe_3	-3.6	11.42
$(\text{CH}_3)_2\text{Be} \cdot 2\text{NMe}_3$	NMe_3	-12.0	11.43
$(\text{CH}_3)_2\text{Be} \cdot \text{NMe}_3$	Cyclohexane	-19.9	11.19
$(\text{CH}_3)_2\text{Be} \cdot \text{OEt}_2$	OEt_2	-20.8	11.16

only 8 ppm to higher field than that of $(\text{CH}_3)_2\text{Be} \cdot \text{NMe}_3$. The magnitude of ^{11}B resonance chemical shifts is attributed to changes in local paramagnetic deshielding, an effect orders of magnitude greater than diamagnetic factors. The smaller sensitivity of ^9Be resonance chemical shifts to environment suggests that these local paramagnetic factors are very small.

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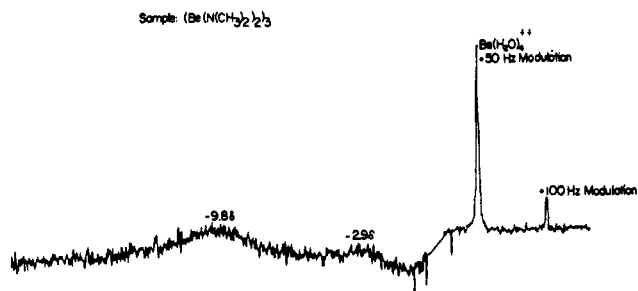
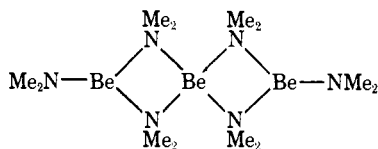


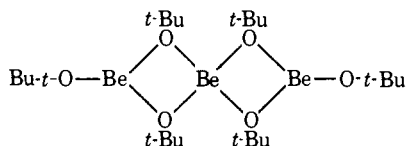
Figure 1. ^9Be resonance spectrum of bisdimethylaminoberyllium trimer.

The beryllium chemical shifts (Table II) indicate that four-coordinate beryllium atoms resonate at higher field than three-coordinate beryllium atoms. The chemical shifts of three-coordinate beryllium atoms are from -21 to -10 ppm and those of four-coordinate beryllium atoms from -12 to $+1$ ppm. Dimethylberyllium in dimethyl sulfide has been shown to be present at room temperature as a 1:1 adduct.²² The 2:1 adduct, occurring at lower temperatures, could not be measured in these experiments (*vide supra*). Proton resonance spectra indicate that both 1:1 and 2:1 adducts of trimethylamine with dimethylberyllium can be present at room temperature (as a function of amine concentration, *vide infra*). These two species exhibit ^9Be resonance signals at -19.9 and -12.0 ppm, respectively.

Two different coordination numbers in one molecule are present in bisdimethylaminoberyllium



This structure, which has recently been confirmed by X-ray diffraction,²³ contains one central, four-coordinate beryllium and two end, three-coordinate beryllium atoms. The effect of coordination number on the chemical shift is demonstrated by the ^9Be resonance spectrum (Figure 1), which has resonance signals at -3.0 (four-coordinate) and -9.8 (three-coordinate) ppm in area ratios 1:2, respectively. A similar example is beryllium *t*-butoxide trimer²⁴



The ^9Be resonance spectrum of this compound in benzene has two peaks at -1.8 and $+1.3$ ppm with half-height widths of 64 and 5 Hz, respectively. Although the chemical shifts are not greatly different, the -1.8 -ppm signal is obviously representative of the end, three-coordinate beryllium due to the concomitant quadrupolar broadening. Other examples of this class of

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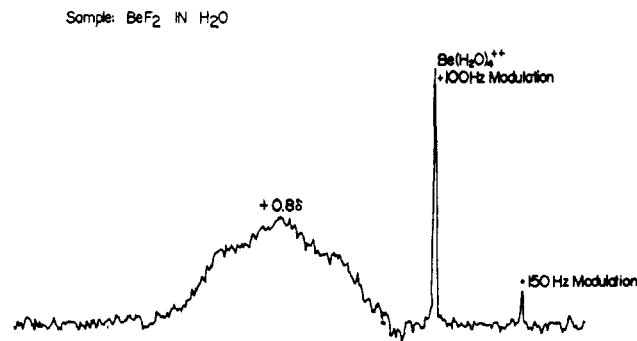


Figure 2. ^9Be resonance spectrum of $\text{BeF}_2 \cdot 2\text{H}_2\text{O}$.

compounds have been also subjected to ^9Be resonance analysis.²⁵

The chemical shifts can further be explained by changes in diamagnetic shielding, including neighbor anisotropy and electric field effects. Replacement of a group bonded to beryllium by a more electronegative group shifts the resonance to lower field. $\text{CH}_3\text{BeCl} \cdot 2\text{S}(\text{CH}_3)_2$ and $\text{BeCl}_2 \cdot 2\text{S}(\text{CH}_3)_2$ have signals at -4.2 and -5.5 ppm, respectively. Stronger bases in the adducts of beryllium species shift beryllium resonance signals to higher fields. The chemical shifts of beryllium chloride in the solvents dimethyl sulfide, diethyl ether, and ammonia occur at -5.5 , -3.1 , and -1.7 ppm, respectively, consistent with the known relative base strengths of these solvents.²⁶ The 1:1 adducts of dimethylberyllium with diethyl ether and trimethylamine have resonance signals at -20.8 and -19.9 ppm, respectively. The corresponding 1:1 adduct with dimethyl sulfide, with a peak at -11.6 ppm, is in contradiction to the above generalization and must be explained by a large neighbor anisotropy effect, perhaps arising from paramagnetic contributions because of the greater availability of d-f-type orbitals on the sulfur atom.²⁷

The only spin-spin coupling observed between ^9Be and other nuclei is for aqueous solutions of BeF_2 and $(\text{NH}_4)_2\text{BeF}_4$.⁴ Beryllium fluoride in water has a spectrum (Figure 2) which is a triplet centered at $+0.8$ ppm with $J_{^9\text{Be}-^{19}\text{F}} = 28$ Hz. These data favor a tetrahedral structure ($\text{BeF}_2 \cdot 2\text{H}_2\text{O}$) as proposed by Linnell and Haendler²⁸ in preference to the mixture of BeF^+ , BeF_2 , BeF_3^- , and BeF_4^{2-} , which was proposed on the basis of emf and conductivity measurements.²⁹ We have not been able to extend the utility of spin-spin coupling to other logical systems. The 2:1 adduct of trimethylphosphine with dimethylberyllium (the tetrahedral arrangement being indicated by the chemical shift) possesses two Be-P bonds. No $^9\text{Be}-^{31}\text{P}$ spin-spin coupling could be resolved, however. The half-height signal width of 17 Hz is the largest observed for any four-coordinate beryllium species, however, which may imply that $J_{^9\text{Be}-^{31}\text{P}}$ is some finite value less than 5 Hz but not resolvable on our instruments. No $^9\text{Be}-^1\text{H}$ coupling has been observed for several beryllium hydride derivatives³⁰ nor for any of the methyl derivatives reported in this study. Our conclusion is that the

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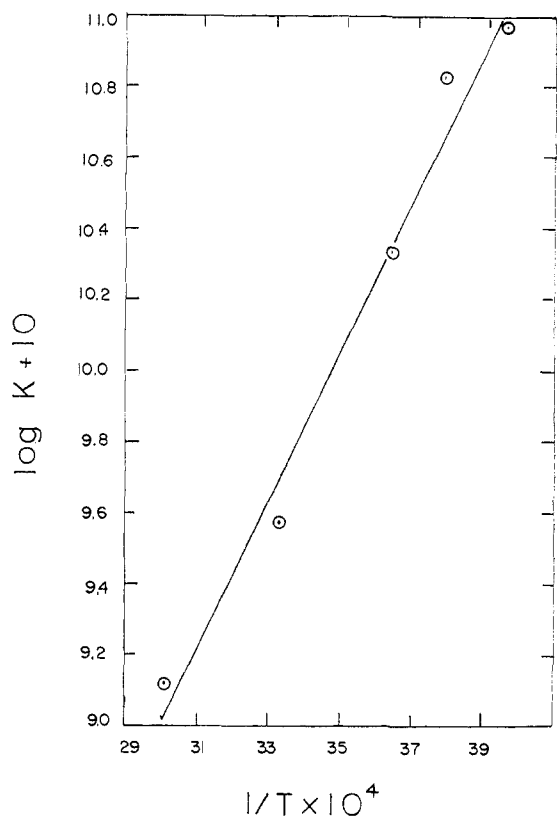


Figure 3. Plot of $\log K$ vs. $1/T$ for the equilibrium reaction $(\text{CH}_3)_2\text{Be} \cdot \text{N}(\text{CH}_3)_3 + \text{N}(\text{CH}_3)_3 = (\text{CH}_3)_2\text{Be} \cdot 2\text{N}(\text{CH}_3)_3$.

beryllium compounds are simply too ionic to manifest a useful magnitude of spin-spin coupling.

The methylberyllium proton chemical shifts of the compounds which formed the basis of the ^9Be resonance study are explained by changes in local diamagnetic shielding at the protons. This result is demonstrated by the following examples. (1) Replacement of a group bonded to beryllium with a relatively electronegative group shifts the resonance of the methyl group bonded to beryllium to lower field. $\text{CH}_3\text{BeCl} \cdot 2\text{S}(\text{CH}_3)_2$ ²² and $(\text{CH}_3)_2\text{Be} \cdot \text{S}(\text{CH}_3)_2$ resonate at τ 11.17 and 11.30, respectively. (2) Bases of increasing base strength shift the proton chemical shift of the methyl groups bonded to beryllium in the adducts to successively higher field. $(\text{CH}_3)_2\text{Be} \cdot \text{S}(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{Be} \cdot \text{OEt}_2$, and $(\text{CH}_3)_2\text{Be} \cdot \text{N}(\text{CH}_3)_3$ resonate at τ 10.77, 11.16 and 11.19, respectively. (3) The coordination number of beryllium affects the ^1H chemical shift of the methyl groups bonded to beryllium in a predictable manner. 2:1 adducts of dimethylberyllium exhibit methylberyllium resonance at higher field than the corresponding 1:1 adducts. $(\text{CH}_3)_2\text{Be} \cdot \text{S}(\text{CH}_3)_2$ and $(\text{CH}_3)_2\text{Be} \cdot 2\text{S}(\text{CH}_3)_2$ resonate at τ 10.77 and 11.30 τ respectively. $(\text{CH}_3)_2\text{Be} \cdot \text{N}(\text{CH}_3)_3$ and $(\text{CH}_3)_2\text{Be} \cdot 2\text{N}(\text{CH}_3)_3$ resonate at τ 11.19 and 11.43, respectively.

Thus it seems that both ^9Be and ^1H chemical shifts may be successfully explained on the basis of diamagnetic shielding factors. A further confirmation of this may be made by considering $J_{^{13}\text{C}-^1\text{H}}$ values for methylberyllium compounds. These values vary from 107 Hz ($(\text{CH}_3)_2\text{Be} \cdot \text{OEt}_2$, τ 11.16) to 105 Hz ($(\text{CH}_3)_2\text{Be} \cdot \text{S}(\text{CH}_3)_2$, τ 10.77). In the absence of paramagnetic and/or anisotropic effects of linear relationship is pre-

dicted for a plot of $J_{^{13}\text{C}-^1\text{H}}$ vs. $\tau(\text{CH}_3-\text{X})$. The above values indeed fit on this linear plot (illustrated on p 272 of ref 8) which may be extended to include methyl-lithium in ether.³¹ These generalizations having been made, we can now consider some specific examples in more detail.

Dimethylberyllium-Trimethylamine Adducts. The room-temperature proton magnetic resonance spectrum of dimethylberyllium in trimethylamine exhibits a single, sharp resonance line at τ 11.43 which moves 3 Hz to higher field as the temperature is lowered to -80° . These data indicate that the species present at room temperature and at -80° is the same. The methylberyllium chemical shifts of $(\text{CH}_3)_2\text{Be} \cdot \text{N}(\text{CH}_3)_3$ and $(\text{CH}_3)_2\text{Be} \cdot (\text{N}(\text{CH}_3)_2\text{CH}_2^-)_2$ are τ 11.19 and 11.52, respectively,⁶ indicating that the 2:1 adduct, $(\text{CH}_3)_2\text{Be} \cdot 2\text{N}(\text{CH}_3)_3$ is present in trimethylamine solution. In order to study the equilibrium between the 1:1 and 2:1 adducts, variable-temperature ($+40$ to -70°) proton magnetic resonance spectra of a solution containing $(\text{CH}_3)_2\text{Be} \cdot \text{N}(\text{CH}_3)_3$ plus a tenfold excess of trimethylamine in TMS were examined. The single resonance line present at all temperatures shifted from τ 11.25 at room temperature to τ 11.42 at -43° (the chemical shift was insensitive to further lowering of the temperature, being τ 11.43 at -60 and -70°), indicating a temperature-dependent equilibrium between the 1:1 and 2:1 adducts. An analogous equilibrium has been observed between diethylberyllium and trimethylamine.³² The predominance of the 1:1 adduct at room temperature is reflected in the relatively low chemical shift, whereas the 11.43 chemical shift at low temperatures indicates that all of the material has been converted to the 2:1 adduct. Although exchange could be slowed down for the 1:1 and 2:1 adducts of dimethylberyllium with dimethyl sulfide²² so that both species could be observed by nmr, it is not unreasonable that we do not observe both species in this case. The coalescence temperature of the 1:1 and 2:1 adduct signals in the dimethyl sulfide system is -48° . At this temperature the trimethylamine system is comprised entirely of the 2:1 adduct (τ 11.43). Thus the two nonequivalent environments cease to exist as such before exchange can be slowed. The equilibrium constants for this reaction (Table III) were calculated from a knowledge

Table III. Thermodynamic Parameters for the Reaction $(\text{CH}_3)_2\text{Be} \cdot \text{N}(\text{CH}_3)_3 + \text{N}(\text{CH}_3)_3 = (\text{CH}_3)_2\text{Be} \cdot 2\text{N}(\text{CH}_3)_3$

Temp, $^\circ\text{C}$	$1/T$	τ^a	K	$\log K$
45	0.00314	11.23	0.127	9.104 - 10
27	0.00334	11.26	0.370	9.568 - 10
1	0.00365	11.36	2.200	10.340 - 10
-10	0.00380	11.40	6.700	10.826 - 10
-21	0.00397	11.41	9.500	10.978 - 10

^a Chemical shift of average signal.

of the methylberyllium chemical shifts of the 1:1 and 2:1 adducts, τ 11.20 and 11.43, respectively, and the chemical shifts of the equilibrium mixture under conditions of fast exchange at each temperature, with the

(31) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Amer. Chem. Soc.*, **86**, 2135 (1964).

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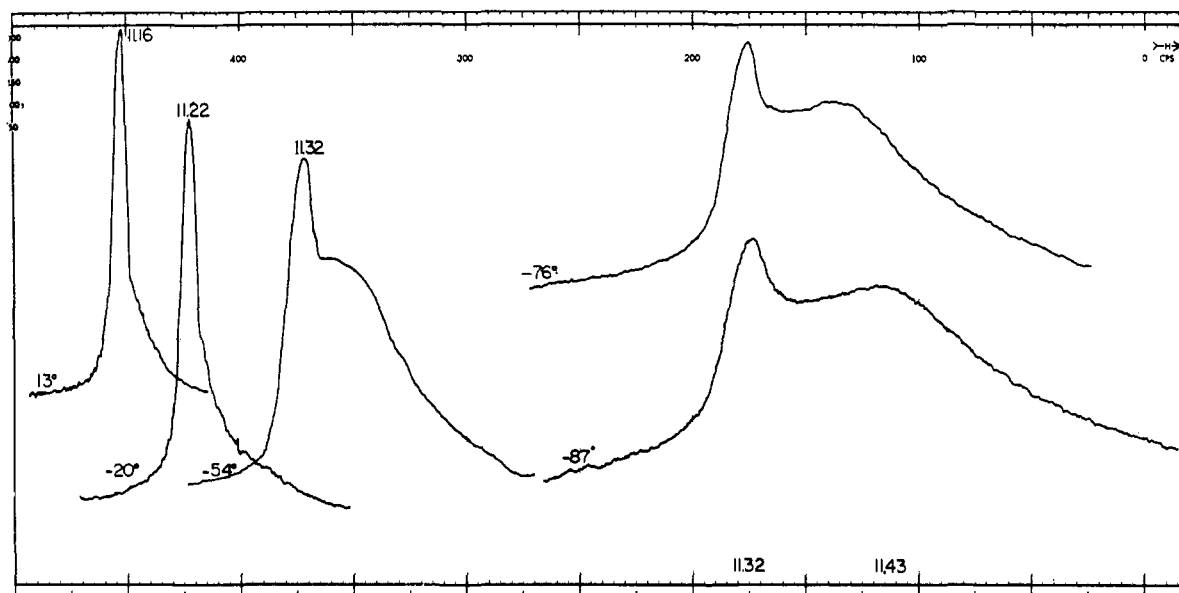


Figure 4. Variable-temperature proton magnetic resonance spectra of a solution of dimethylberyllium in diethyl ether.

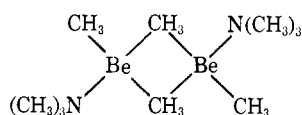
aid of the equations

$$\begin{aligned}\delta_{av} &= N_a\delta_a + N_b\delta_b \\ N_a + N_b &= 1\end{aligned}$$

where δ_{av} is the chemical shift of the averaged signal; N_a and N_b are the mole fractions of 1:1 and 2:1 adduct species, respectively, and δ_a and δ_b are the chemical shifts of the 1:1 and 2:1 adduct species. A plot of $\log K$ vs. $1/T$ is shown in Figure 3. The heat of reaction is -10.4 kcal/mol and the entropy change is -36.6 eu at 40° .

The heats of reaction for the reactions $(\text{CH}_3)_2\text{Be} + \text{N}(\text{CH}_3)_3 = (\text{CH}_3)_2\text{Be}\cdot\text{N}(\text{CH}_3)_3$ ¹² and $(\text{CH}_3)_3\text{Ga} + \text{N}(\text{CH}_3)_3 = (\text{CH}_3)_3\text{Ga}\cdot\text{N}(\text{CH}_3)_3$ ³³ are both -21 kcal/mol. The -10.4 -kcal/mol value of the heat of reaction for $(\text{CH}_3)_2\text{Be}\cdot\text{N}(\text{CH}_3)_3 + \text{N}(\text{CH}_3)_3 = (\text{CH}_3)_2\text{Be}\cdot 2\text{N}(\text{CH}_3)_3$ is logically smaller than that of the above two reactions owing both to steric and inductive considerations. On the other hand, it is larger by a factor of 3 than the -3.2 -kcal/mol value for the heat of reaction of $(\text{CH}_3)_2\text{Be}\cdot\text{S}(\text{CH}_3)_2 + \text{S}(\text{CH}_3)_2 = (\text{CH}_3)_2\text{Be}\cdot 2\text{S}(\text{CH}_3)_2$ ²² due to the much larger base strength of trimethylamine relative to dimethyl sulfide.

Although the above experiments of the dimethylberyllium-trimethylamine system failed to show evidence for polymerization as found in the dimethyl sulfide solvent study,²² the spectrum of neat, molten $(\text{CH}_3)_2\text{Be}\cdot\text{N}(\text{CH}_3)_3$ (using a benzene external standard) may show evidence of dimerization. The spectrum consists of two sharp signals at τ 7.13 ($\text{N}(\text{CH}_3)_3$) and τ 10.65 (CH_3 -Be with $J_{\text{Be}-\text{C}-\text{H}} = 105$ Hz). The low chemical shift for the methylberyllium signal is about the average of bridging methyl (τ 10.3) and terminal methyl (τ 11.2) chemical shifts and may represent the species



under conditions of rapid exchange. Further support

(33) G. E. Coates, *J. Chem. Soc.*, 2003 (1951).

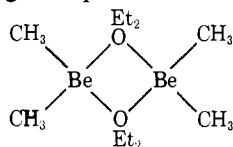
for dimerization of the neat compound is indicated by the increased magnitude of the measured heat of vaporization as the temperature is lowered.¹²

Dimethylberyllium-Diethyl Ether Adducts. Ebullioscopic measurements of solutions of dimethylberyllium in diethyl ether indicate the absence of polymers.¹¹ This study also reports variable-temperature proton chemical shifts for these solutions. These nmr data seemed rather strange to us. For example methylberyllium chemical shifts moved upfield from τ 11.16 at 40° to τ 11.3 at -75° , while in another determination the signal shifted to τ 11.43 at -85° . This latter shift of 0.13 ppm for a temperature interval of 10° seems anomalous compared with the average shift of 0.024 ppm for 10° temperature intervals above -75° . Our reexamination of this system shows that it is indeed atypical (Figure 4).

The single resonance signal present at room temperature (τ 11.16) shifts to higher field with decreasing temperature. At -54° this signal, still sharp, appears at τ 11.32, and a noticeable formation of *shoulder* on the high-field side of this signal is apparent. This shoulder continues to move upfield with decreasing temperature accompanied by an increase in relative intensity. The original signal, however, becomes insensitive to temperature changes, still being present at 11.32 at -87° .

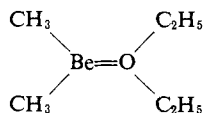
The variable-temperature nmr analysis of this system indicates that in the temperature range $+40$ to $+13^\circ$ only the 1:1 adduct is present. This is verified by the ^9Be resonance signal, which is one ppm to *lower* field than that of $(\text{CH}_3)_2\text{Be}\cdot\text{N}(\text{CH}_3)_3$, which is definitely known to have three-coordinate beryllium. Further decreasing the temperature causes the proton resonance line to move to higher field (quite analogously to the trimethylamine and dimethyl sulfide²² systems), indicating that a new "species" must be being formed. The appearance of the second, broad, signal, however, indicates that *two* species must be formed at low temperature. The relative areas of these two signals are also slightly dependent upon the concentration of the solution. The area of the broad signal (τ 11.43) appears to

increase relative to the signal at τ 11.32 as the concentration is reduced. This excludes the possibility that the τ 11.43 signal represents dimers of the type



(the methyl-bridged dimers being already excluded as they would show resonance at lower field).

We therefore suggest that the overall reaction is $(\text{CH}_3)_2\text{Be}\cdot\text{OEt}_2 + \text{OEt}_2 = (\text{CH}_3)_2\text{Be}\cdot 2\text{OEt}_2$, with the reactant and product having methyl proton chemical shifts of τ 11.16 and 11.43, respectively. The τ 11.32 signal represents an intermediate species which could possibly be the ether-bridged dimer discussed above, but which we suggest is



The Be-O system is isoelectronic with C-C and B-N and it is therefore not unreasonable to speculate on the possibility of π bonding in this case. Be-N π bonding has been previously demonstrated^{23,34} and we have been informed of X-ray studies that indicate Be-O π bonding³⁵ analogous to published work indicating Mg-O π bonding.³⁶ We therefore suggest that at lower temperatures the Be-O bond is strengthened by π bonding, causing an upfield methyl proton chemical shift. This should hinder rotation about the Be-O bond, which could be tested by using an unsymmetrical ether as the solvent, thus rendering the magnetic nonequivalence of the methyl groups bound to the beryllium.

Acknowledgment. We are indebted to the National Science Foundation for support of this work under Grant No. GP-8595.

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Reactions of the 2,4- $\text{C}_2\text{B}_5\text{H}_7$ Carborane System¹

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Abstract: The 2,4-dilithio, 2-methyl, 2,4-dimethyl, 2-bromo, and 2-trimethylsilyl derivatives of 2,4- $\text{C}_2\text{B}_5\text{H}_7$ have been prepared, but the 2-monolithio derivative is unstable with respect to polymerization in ether-hexane solvent. Electrophilic bromination of 2,4- $\text{C}_2\text{B}_5\text{H}_7$ yields the 5-bromo derivative. The parent carborane is stable in 1 M aqueous HCl, but is easily degraded to boric acid in ethanolic KOH. The dilithio salt of the $\text{C}_2\text{C}'$ -dicarboxylic acid is completely degraded by aqueous HCl.

Studies of the derivative chemistry of the polyhedral carboranes² in the $\text{C}_2\text{B}_{n-2}\text{H}_n$ series ($n = 5-12$) have centered almost exclusively upon cage systems having eight or more boron atoms. In this paper we describe some reactions of 2,4-dicarboclosoheptaborane(7) (Figure 1), a stable and relatively accessible³ carborane which seems ideally suited for research on the smaller polyhedra. Our initial work has been concerned with three types of reactions which are characteristic² of the well-studied icosahedral $\text{C}_2\text{B}_{10}\text{H}_{12}$ systems: metalation at carbon and synthesis of C-substituted organo derivatives, halogenation, and degradation by strong bases.

(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Richmond, Va., Nov 1969, Abstract No. 74; taken in part from the Ph.D. dissertation of R. R. O., University of Virginia, 1970.

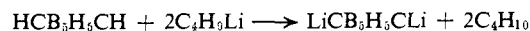
(2) For recent reviews, see V. I. Bregadze and O. Y. Okhlobystin, *Organometal. Chem. Rev., Sect. A*, 4, 345 (1969); E. L. Muettterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968; R. L. Hughes, I. C. Smith, and E. W. Lawless, "Production of the Boranes and Related Research," R. T. Holzmann, Ed., Academic Press, New York, N. Y., 1967; M. F. Hawthorne in "The Chemistry of Boron and its Compounds," E. L. Muettterties, Ed., Wiley, New York, N. Y., 1967, Chapter 5.

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Results and Discussion

Lithiation and Synthesis of C-Substituted Derivatives.

The reaction of $\text{C}_2\text{B}_5\text{H}_7$ with *n*-butyllithium is markedly sluggish in comparison with the lithiation of 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$,⁴⁻⁶ particularly in nonpolar solvents. No reaction is observed in *n*-pentane or *n*-hexane when both reactant concentrations are below 1 M, but at higher concentrations the white dilithiocarborane slowly precipitates.



Typically, 23% of the original carborane was recovered from a solution of 2.5 M $\text{C}_4\text{H}_9\text{Li}$ and 1.0 M $\text{C}_2\text{B}_5\text{H}_7$ in hexane after 20 hr at room temperature.

A considerable increase in reaction rate and yield of the dilithio derivative is obtained in a 2:1 diethyl ether-hexane solvent, compared to the pure hexane system. In ether-hexane the reaction pro-

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