The Aminolysis of Beryllium Dichloride with Diisopropylamine and Reactions of Some Aminoberyllium Chlorides[‡]

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Dedicated to Prof. Dr. D. Fenske on the occasion of his 60th birthday

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$BeCl_2$ is not aminolyzed by diisopropylamine. An excess of this amine reacts with $BeCl_2$ or $BeCl_2·2OEt_2$ to give $BeCl_2·HNiPr_2$ (**1**). This compound, on deprotonation with LiBu at low temperature, gives rise predominantly to dimers of ClBe(N*i*Pr$_2$) (**2**), together with Be(N*i*Pr$_2$)$_2$ (**3**). Compound **2** adds diisopropylamine to give the adduct ClBe(N*i*Pr$_2$)·HN*i*Pr$_2$ (**4**), which provides **3** on treatment with LiBu. Compound **2** reacts with $LiBH_4$ to give dimeric *i*Pr$_2$NBeBH$_4$ (**17**). The BH_4 group is μ^2-bonded to the Be centers, as shown by NMR spectroscopic data and an X-ray structure determination. Moreover, a number of dimeric organylberyllium diisopropylamides *i*Pr$_2$NBeR have been prepared by treatment of **2** with LiR. In analogy, *tert*-butoxyberyllium diisopropylamide (**20**) has also been synthesized. Moreover, several 2,2,6,6-tetramethylpiperidinoberyllium and bis(trimethylsilyl)amino derivatives are reported. ^{9}Be NMR spectroscopic data of the new compounds are consistent with tricoordinated Be centers and dimeric units (MS, cryoscopy).

Introduction

The principles of the chemistry of beryllium−nitrogen compounds were explored particularly by Coates and coworkers, beginning in the 1950s.[2] Research focussed on dimethylamino derivatives, which in most cases proved to be dimeric (for RBeNMe$_2$; R = alkyl, aryl),[3] and the status of beryllium−nitrogen chemistry has been summarized by Lappert et al.[4] Unlike the trimeric Be(NMe$_2$)$_2$, and also Be(NEt$_2$)$_2$, which is dimeric, the silylamide Be[N(SiMe$_3$)$_2$]$_2$ proved to be monomeric.[5] Another monomeric beryllium bis(amide) is the 2,2,6,6-tetramethylpiperidino derivative (tmp)$_2$Be.[6] For (*i*Pr$_2$N)$_2$Be, a monomer/dimer equilibrium in solution has been established.[6] Obviously, the steric requirements of the diisopropylamino group allow stabilization of both association states with a preference for the dimer in the solid, and it may therefore be expected that diisopropylamides of beryllium of type *i*Pr$_2$NBeX should be monomeric for bulky groups X. In order to verify this we have been examining a number of beryllium amides of this kind.

Results

Reactions

So far, no systematic study of the aminolysis of beryllium dichloride has been performed.

Bis(dialkylamino)beryllium compounds are readily obtained from $BeCl_2·2OEt_2$ and 2 equiv. of LiNR$_2$ as shown in Equation (1). This is the only known route to the sterically demanding monomeric bis(amides) (tmp)$_2$Be, [*t*Bu(Me$_3$Si)N]$_2$Be,[6] and [(Me$_3$Si)$_2$N]$_2$Be.[5] For sterically less bulky amine groups, one may also deprotonate adducts of secondary amines and beryllium dichloride with LiR [Equation (2)].[7] However, this route has not often been used. To date, most of the reported amine adducts of $BeCl_2$ have the composition $BeCl_2·n$(amine) ($n = 2-4$).[8,9] In order to characterize the various steps from $BeCl_2$ to (R$_2$N)$_2$Be we have studied the reaction between beryllium dichloride and diisopropylamine in more detail.

No adduct of $BeCl_2$ and HN*i*Pr$_2$ has yet been described. The amine may not form a well-defined product, as has been found for the triethylamine adduct of $BeCl_2$.[9] We found that solid $BeCl_2$ does not react with an excess of HN*i*Pr$_2$ at ambient temperature. Under reflux conditions, however, the crystals of $BeCl_2$ turned into a gray powder of composition $BeCl_2·HNiPr_2$ (**1**) [Equation (3)]. This compound is more readily obtained by treatment of $BeCl_2·2OEt_2$ with a large excess of diisopropylamine in diethyl ether solution. In this case the 1:1 adduct was formed

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$$BeCl_2{\cdot}2OEt_2 + 2\ LiNR_2 \rightarrow \underset{\mathbf{3}}{Be(NR_2)_2} + 2\ LiCl \qquad (1)$$

$$BeCl_2{\cdot}2HNR_2 + 2\ LiR' \rightarrow Be(NR_2)_2 + 2\ LiCl + R'H \qquad (2)$$

$$BeCl_2 + HN\mathit{i}Pr_2 \rightarrow \underset{\mathbf{1}}{Cl_2Be{\cdot}HN\mathit{i}Pr_2} \qquad (3)$$

$$Cl_2Be{\cdot}HN\mathit{i}Pr_2 + LiBu \rightarrow \underset{\mathbf{2}}{\mathit{i}Pr_2NBeCl} + LiCl + BuH \qquad (4)$$

$$BeCl_2{\cdot}2OEt_2 + LiN\mathit{i}Pr_2 \rightarrow \mathit{i}Pr_2NBeCl + LiCl \qquad (5)$$

$$\mathit{i}Pr_2NBeCl + HN\mathit{i}Pr_2 \rightleftarrows \underset{\mathbf{4}}{\mathit{i}Pr_2NBeCl{\cdot}NH\mathit{i}Pr_2} \qquad (6)$$

$$\mathit{i}Pr_2NBeCl{\cdot}HN\mathit{i}Pr_2 + LiBu \rightarrow BuH + LiCl + (\mathit{i}Pr_2N)_2Be \qquad (7)$$

as an oily product, which became solid on removal of all volatile substances in vacuo. An excess of the amine is therefore not able to deprotonate **1**. This was to be expected, because it is unlikely that the amine would be able to remove a proton from $BeCl_2{\cdot}HN\mathit{i}Pr_2$, as the beryllium amide should be more basic than diisopropylamine. A stronger base, such as LiR, is therefore needed for deprotonation.

Astonishingly, the reaction between LiBu and **1** at ambient temperature provided not only $\mathit{i}Pr_2NBeCl$ (**2**), but also by-products such as $\mathit{i}Pr_2NBeBu$ and $(\mathit{i}Pr_2N)_2Be$ (**3**). This latter compound was actually the main product. Moreover, **2** could not be separated from the other products by sublimation in vacuo. Obviously, **2** reacted more rapidly than **1** with LiBu, to give $\mathit{i}Pr_2NBeBu$, and, moreover, a $BeN\mathit{i}Pr_2$/LiBu exchange, resulting in the formation of $Li(\mathit{i}NPr_2)$, competes favorably with other reactions and provides an opportunity to generate **3**.

At present, the 1:1 reaction between $LiN\mathit{i}Pr_2$ and $BeCl_2{\cdot}2OEt_2$ in diethyl ether at 0 °C is the best choice for the preparation of **2** [Equation (5)]. Some $\mathit{i}Pr_2NBeOEt$ and $(\mathit{i}Pr_2N)_2Be$ is also formed in this reaction, but the chloride **2** can be separated by sublimation. In contrast, neither ligand exchange between $BeCl_2$ and $(\mathit{i}Pr_2N)_2Be$ in boiling benzene nor the reaction between $(\mathit{i}Pr_2N)_2Be$ and $BeCl_2{\cdot}2OEt_2$ in boiling THF or toluene afford **2**.

Molecular mass values and spectroscopic data for **2** indicate that the compound is dimeric in solution, containing tricoordinated Be atoms. These should be able to act as Lewis acidic centers. It was therefore expected that **2** might add a Lewis base. In the context of aminolysis, the addition of diisopropylamine to **2** was studied. The existence of a compound $\mathit{i}Pr_2NBeCl{\cdot}HN\mathit{i}Pr_2$ (**4**) was indicated in the reaction between $BeCl_2$ and 2 equiv. of the amine in diethyl ether after addition of 1 equiv. of LiBu. Needles separated from the resulting solution, their NMR spectroscopic data being consistent with compound **4** in admixture with $\mathit{i}Pr_2NBeBu$ and **3**.

Actually, after 10−20 min, the ^{1}H NMR spectrum of the 1:1 mixture of **2** and $HN\mathit{i}Pr_2$ showed only the components, and about 24 h were required until the new signals attained maximum intensity. These signals can be interpreted in terms of the equilibrium according to Equation (6). Heating of this mixture to 75 °C restored the original situation (i.e., only the signals for diisopropylamine and **2** were visible), and it again took more than 24 h at ambient temperature to reform the equilibrium situation, which in solution lies

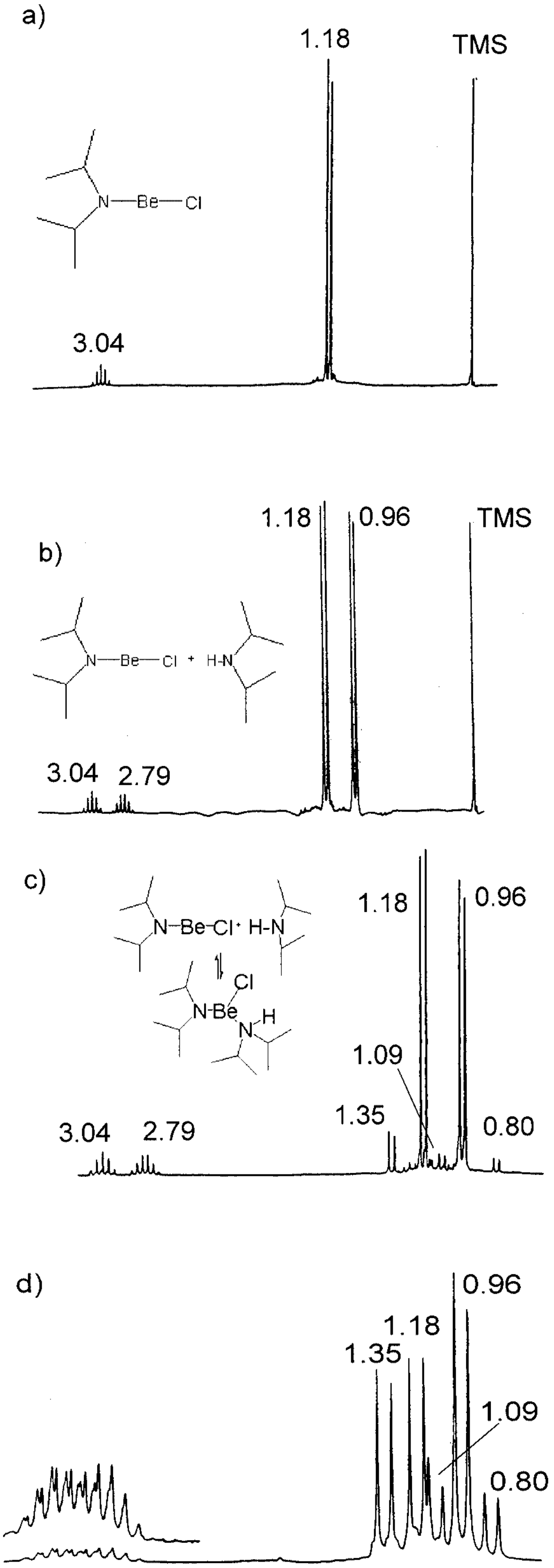


Figure 1. Time-dependent ^{1}H NMR spectra of the reaction mixture of diisopropylamine and (diisopropylamino)beryllium chloride; a) $(\mathit{i}Pr_2NBeCl)_2$ at 200 MHz; b) $(\mathit{i}Pr_2NBeCl)_2$ + $\mathit{i}Pr_2NH$ (1:2) at 200 MHz; 30 min after addition; c) as b) but 210 min after addition; d) equilibrium situation, 90 MHz spectrum after 68 h

to 75% on the side of the adduct **4**. Figure 1 depicts some NMR spectra to illustrate this kind of interaction.

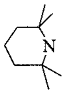
As was to be expected, the adduct $\mathrm{ClBe(N}i\mathrm{Pr_2)\cdot HN}i\mathrm{Pr_2}$ did not react further with an excess of the amine. However, it was deprotonated by LiBu at low temperature, as shown in Equation (7), to produce bis(diisopropylamino)beryllium (**3**).[6] At ambient temperature, $i\mathrm{Pr_2NBeBu}$ is a by-product. Thus, *direct aminolysis* of $\mathrm{BeCl_2}$ by diisopropylamine is not possible, most probably because the *Be*-bonded amino group is more basic than the amine itself.[10]

Similarly, it was expected that $\mathrm{BeCl_2\cdot 2OEt_2}$ should react with *N*-lithio-2,2,6,6-tetramethylpiperidine [Li(tmp)] in a 1:1 ratio to give (tmp)BeCl (**5**). In hexane solution, however, the main product (was tmp)$_2$Be (**6**). On the other hand, when the reaction was performed at −78 °C in the presence of diethyl ether, a viscous oil was obtained, and this was analyzed by NMR spectroscopy as a mixture of **6** (15%) and (tmp)BeOEt (**7**, 85%). These components could not be separated by fractional distillation. Analogously, the 1:1 reaction between $\mathrm{BeCl_2}$ and $t\mathrm{Bu(Me_3Si)NLi}$ in diethyl ether afforded a mixture of $[t\mathrm{Bu(Me_3Si)N]_2Be}$ (**8**), $t\mathrm{Bu(Me_3Si)NBeCl}$ (**9**), and $t\mathrm{Bu(Me_3Si)_2NBeOEt}$ (**10**). From this mixture the bis(amide) **8** was separated by distillation. However, when the reaction was started at −100 °C, compound **8** was not present, and **9** and **10** were obtained in a 1:1.8 ratio. Compound **9** was separated by fractional sublimation. Similar behavior was observed for the 1:1 reaction between $\mathrm{BeCl_2}$ and $\mathrm{LiN(SiMe_3)_2}$ in diethyl ether. At room temperature, only $\mathrm{[(Me_3Si)_2N]_2Be}$ (**11**) was obtained besides $\mathrm{BeCl_2\cdot 2OEt_2}$. At −78 °C, a 1:4:2 mixture of **11**, $\mathrm{(Me_3Si)_2NBeCl}$ (**12**), and $\mathrm{(Me_3Si)_2NBeOEt}$ (**13**) resulted. When the reaction was started at −100 °C, however, only **12** and **13** were detected by NMR, and these two compounds could be separated by fractional sublimation.

(tmp)BeCl **5**

(tmp)$_2$Be **6**

(tmp)BeOEt **7**



= tmp

$[(t\mathrm{Bu})\mathrm{Me_3SiN]_2Be}$ **8**

$(t\mathrm{Bu})\mathrm{Me_3SiNBeCl}$ **9**

$(t\mathrm{Bu})\mathrm{Me_3SiNBeOEt}$ **10**

$\mathrm{[(Me_3Si)_2N]_2Be}$ **11**

$\mathrm{(Me_3Si)_2NBeCl}$ **12**

$\mathrm{(Me_3Si)_2NBeOEt}$ **13**

Reactions of $i\mathrm{Pr_2NBeCl}$ and other Aminoberyllium Chlorides

The aminoberyllium chlorides offer potential as reagents for the synthesis of other aminoberyllium compounds by nucleophilic substitution of the Cl atoms. $[i\mathrm{Pr_2NBeCl}]_2$ was used as a model compound for this kind of reaction. Treatment with LiBu in hexane gave a 68% yield of liquid $i\mathrm{Pr_2NBeBu}$ (**14**), as shown in Equation (8).

$$[i\mathrm{Pr_2NBeCl}]_2 + 2\ \mathrm{LiBu} \rightarrow [i\mathrm{Pr_2NBeBu}]_2 + 2\ \mathrm{LiCl} \tag{8}$$

14

$$[i\mathrm{Pr_2NBeCl}]_2 + 2\ \mathrm{Li}t\mathrm{Bu} \rightarrow [i\mathrm{Pr_2NBe}(t\mathrm{Bu})]_2 + 2\ \mathrm{LiCl} \tag{9}$$

15

$$2\ t\mathrm{BuBeCl} + 2\ \mathrm{LiN}i\mathrm{Pr_2} \rightarrow [i\mathrm{Pr_2NBe}(t\mathrm{Bu})]_2 + 2\ \mathrm{LiCl} \tag{10}$$

At 0 °C the reaction according to Equation (9) produced some gas, which may be due to elimination of isobutene and formation of the hydride $[i\mathrm{Pr_2NBeH}]_n$. However, workup by sublimation yielded compound **15** as a solid in 48% yield. The residue from the sublimation provided evidence for the formation of the hydride, because hydrogen was generated by hydrolysis with hydrochloric acid. When the reaction according to Equation (9) was performed at −78 °C the yield of **15** increased to 78%. This yield was also obtained in the reaction according to Equation (10).

In order to obtain information on the steric effect of the tmp group, $\mathrm{[tmpBeCl]_2}$ was treated with LiBu and LitBu. The reaction between **5** and LiBu gave dimeric (tmp)BeBu (**16**) [Equation (11)]. This is a viscous oil, and its dimeric nature was determined by molecular mass measurement in cyclohexane. Temperature-dependent ^{9}Be NMR spectroscopy provided no evidence for a monomer/dimer equilibrium.

$$\mathrm{[(tmp)BeCl]_2} + 2\ \mathrm{LiBu} \rightarrow \mathrm{[(tmp)BeBu]_2} + 2\ \mathrm{LiCl} \tag{11}$$

16

$$\mathrm{[(tmp)BeCl]_2} + 2\ \mathrm{Li}t\mathrm{Bu} \rightarrow [\mathrm{(tmp)Be}(t\mathrm{Bu})]_2 + 2\ \mathrm{LiCl} \tag{12}$$

17

$$\mathrm{[(tmp)BeCl]_2} + 2\ \mathrm{Li}t\mathrm{Bu} \rightarrow 2/n\ \mathrm{[(tmp)BeH]}_n + \mathrm{LiCl} + \mathrm{H_2C{=}CMe_2} \tag{13}$$

$$t\mathrm{BuBeCl\cdot OEt_2} + \mathrm{(tmp)Li} \rightarrow \mathrm{(tmp)BeH} + \mathrm{LiCl\cdot H_2C{=}CMe_2} \tag{14}$$

$$[i\mathrm{Pr_2NBeCl}]_2 + 2\ \mathrm{LiBH_4} \rightarrow [i\mathrm{Pr_2NBeBH_4}]_2 + 2\ \mathrm{LiCl} \tag{15}$$

18

$$[i\mathrm{Pr_2NBeCl}]_2 + 2\ \mathrm{KO}t\mathrm{Bu} \rightarrow [i\mathrm{Pr_2NBeO}t\mathrm{Bu}]_2 + 2\ \mathrm{KCl} \tag{16}$$

19

$$[i\mathrm{Pr_2NBeCl}]_2 + 2\ \mathrm{py} \rightarrow [i\mathrm{Pr_2NBeCl\cdot py}]_2 \tag{17}$$

20

$$[i\mathrm{Pr_2NBeCl}]_2 + 2\ \mathrm{EX_3} \rightarrow [i\mathrm{Pr_2NBeCl\cdot EX_3}]_2 \tag{18}$$

21

$\mathrm{(EX_3{=}BCl_3)}$

22

$\mathrm{(EX_3{=}BBr_3)}$

23

$\mathrm{(EX_3{=}AlCl_3)}$

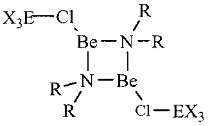
When LitBu was allowed to react with $\mathrm{[(tmp)BeCl]_2}$ in hexane according to Equation (12), gas evolution was noted. The ^{1}H and ^{13}C NMR spectra of the solution showed only very-low-intensity signals for a tBu group. When the reaction was performed at −78 °C, LiCl precipitated slowly [see Equation (13)]. On warming, gas evolution started at about 10 °C. When the reaction mixture obtained at −78 °C was subjected to NMR analysis, no signals for a *Be*-bonded tBu group could be observed. The ^{9}Be NMR signal found at δ = 11.9 ppm ($h_{1/2}$ = 140 Hz) shows the same shielding as for compound **16**, an indication of the formation of $[\mathrm{(tmp)Be}(t\mathrm{Bu})]_2$.

An attempt to prepare **17** by using monomeric $t\mathrm{BuBeCl\cdot OEt_2}$ as a starting material might have allowed a more straightforward substitution using (tmp)Li. Neither at 0 °C nor at −78 °C was this possible, however. Gas evolution was observed in both cases, and the filtrate from the suspension gave no evidence for the formation of **17** by NMR analysis. However, 1 equiv. of LiCl was formed, and the filtrate was virtually free of chloride. The yield of the crude material was 90% calculated for (tmp)BeH.[11] The reaction therefore has to be as shown in Equation (14).

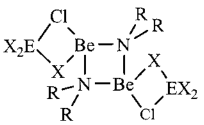
Since ether cleavage has been observed in reactions between the aminoberyllium chlorides and $LiNR_2$ compounds in diethyl ether, resulting in ethoxy derivatives, we treated **2** with KO*t*Bu. The *tert*-butoxy derivative **19** was obtained in good yield, as shown in Equation (16) (see below for the structures of R_2NBeOR compounds).

Unlike the alkyl or alkoxy groups, which are usually unidentate substituents, the BH_4 group may be variously mono-, di-, or even tridentate. The reaction between **2** and $LiBH_4$ was therefore expected to give $i$$Pr_2NBe(BH_4)$, which might be monomeric in the case of a structure such as $i$$Pr_2NBe(\mu\text{-}H_3BH)$ but proved to be dimeric $[iPr_2NBeH_4]_2$ (**18**) as shown in Equation (15). However, analysis of the solution by ^{11}B NMR spectroscopy showed that the main product was iPr_2NBH_2, together with $(iPr_2N)_2BH$, $[iPr_2NB(H)Cl]_2$, and $Be(BH_4)_2$. Moreover, several ^9Be NMR signals were noted, but none could be reliably assigned. When the reaction according to Equation (15) was performed at −78 °C and the mixture was allowed to come to room temperature, however, crystals of **18** separated from a concentrated solution at −20 °C. The tetrahydroborate **18** is stable up to 85 °C, but very moisture-sensitive, although not spontaneously inflammable in contact with air. Its molecular structure was determined by X-ray crystallography.

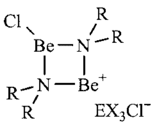
While $[iPr_2NBeCl]_2$ should have Lewis-acidic properties, due to its tricoordinated Be atoms, only Lewis base behavior can be expected from its Cl atoms. Compound **2** reacts readily with pyridine (py) to form a deep red solution in hexane [Equation (17)]. The isolated product is $[iPr_2NBeCl\cdot py]_2$ (**20**), with tetracoordinate Be atoms as shown by ^9Be NMR spectroscopy ($\delta = 4.8$, $w_{1/2} = 1.5$ Hz). Triethylamine gave no stable adduct.[9] Surprisingly, **2** reacted with strong Lewis acids, provided they were strong chloride acceptors. Thus, 1:2 adducts $[iPr_2NBeCl]_2\cdot 2ECl_3$ resulted from treatment of **2** with BCl_3, BBr_3, and $AlCl_3$ [Equation (18)]. One of the constitutions **A**−**C** would be expected for these adducts. Structure **A** can be ruled out, as the ^9Be NMR signal is typical of tetracoordinate Be. Structure **C** also does not have to be considered, primarily because two ^9Be NMR signals would be expected at low field for a tri- and a dicoordinated Be atom. The latter would have only an electron quadruplet, and the cation would certainly be a high-energy species. All NMR spectroscopic data, however, are in agreement with structure **B**, and we assume that the structure has C_{2v} symmetry.



A



B



C

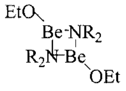
Spectroscopic Data

Beryllium is a single-isotope element. Its nuclear spin is 3/2, and it has a favorable longitudinal relaxation time. Although its nuclear quadrupole moment of $5.2\cdot 10^{-2}$ ($e\cdot 10^{-24}$ cm^2) is about 70% that of ^{11}B, the linewidths of the signals may become rather broad for Be atoms residing in asymmetric environments. On the other hand, the sensitivity of the ^9Be nucleus is smaller than that of ^{11}B only by a factor of 10. Nevertheless, the nuclear properties of ^9Be are very favorable for use of ^9Be NMR as a tool for obtaining structural information. As has been shown previously, chemical shifts and linewidths depend not only on the substituents but also, to a large extent, on the coordination number of Be.[12] Table 1 summarizes the ^9Be chemical shifts and ^1H, ^{13}C, and ^{14} N NMR spectroscopic data for the compounds reported in this study.

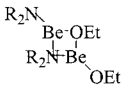
Because of the low solubility of $Cl_2Be\cdot HNiPr_2$ in most solvents, all of its NMR spectroscopic data were collected at 60 °C in C_6D_6 solutions. The ^9Be NMR signal at $\delta = 5.84$ ppm, and particularly its linewidth (see Table 1), shows that the compound contains tricoordinated Be atoms. No ^{14}N resonance could be recorded. The ammonium-type character of the coordinated amine is represented by a ^1H NMR signal for the NH group at $\delta = 5.05$ ppm, 4.5 ppm downfield from the free amine. The proton signal for the CH group is also shifted downfield ($\delta = 1.97$ ppm).

While the ^9Be chemical shifts and the linewidths of the aminoberyllium chlorides **2**, **5**, **9**, and **13** (see Table 1) are consistent with a coordination number of three for the Be atoms, the ^1H and the ^{13}C NMR signals are less strongly influenced than in compound **2**. Tetracoordination at ^{14}N is confirmed by chemical shifts in the range from $\delta = -120$ to −140 ppm.[13]

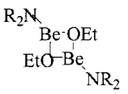
Unexpectedly, only two ^1H NMR signals were observed for the 36 protons of dimeric (tmp)BeCl. The eight methyl groups are represented by a single sharp signal at $\delta = 1.30$ ppm, contrasting with a broad, unresolved multiplet for the CH_2 groups. Again in contrast, four ^{13}C NMR signals were found. Assignment to the four equivalent C atoms (atoms C1/C5, C2/C4, C3, and Me) of the tmp units was possible with the aid of $^{13}C(^1H\text{-}NOE)$ experiments. Dimeric (tmp)BeOEt provided similar NMR spectra, the ^{13}C NMR spectrum showed clearly resolved signals for the two magnetically equivalent ethoxy groups. Those of the tmp groups are at higher field than in tmpH, except for the atoms C1/C5, which are bonded to a tetracoordinated N atom. Almost the same chemical shifts as for Et_2O were noted for the EtO groups. This is further evidence that the EtO group does not bridge the Be atoms (i.e., of the three possible dimeric aminoberyllium ethoxide structures **D**−**F** only the symmetrical amino-bridged species were formed).



D



E



F

Table 1. NMR spectroscopic data of the aminoberyllium compounds (in C_6D_6)

	δ^9Be [ppm]	$w_{1/2}$ [Hz]	δ^1H [ppm]	δ^{13}C [ppm]
$i\text{Pr}_2\text{NH}\cdot\text{BeCl}_2$	5.84	48	5.05 (NH)	
$i\text{Pr}_2\text{NBeCl}$[a]	10.37	82	1.20 (d), 3.06 (sept)	23.77 (q, Me),
$(i\text{Pr}_2\text{N})_2\text{Be}$[b]	12.7	288	1.06 (d), 2.92 (sept)	26.10 (Me), 17.33 (CH)
(tmp)BeCl[c]	9.4	60	1.30 (s), 1.64 (m)	19.13 (d), 34.46 (q), 39.55 (d),50.38 (s)
(tmp)BeOEt[d]	7.7	40	1.08 (s), 1.16 (m), 1.36 (t),3.79 (q) (EtO)	17.63, 31.18, 36.81, 52.30 (tmp), 17.87, 61.15 (Et)
$(\text{tmp})_2\text{Be}$	15.3	230	1.28 (s), 1.59(m)	19.07, 34.31, 39.85, 50.33
$(t\text{Bu})\text{Me}_3\text{SiNBeCl}$	11.6	90	0.25(s), 1.29(s)	4.40 (q, SiMe); 35.77, 51.52 (*t*Bu)
$(t\text{Bu})\text{Me}_3\text{SiNBeOEt}$	9.12	85	0.16(s), 1.15(s), 1.23(Me), 2.78(CH_2)	3.27 (SiMe); 33.19, 50.42 (*t*Bu), 18.89, 65.44 (Et)
$[(t\text{Bu})\text{Me}_3\text{SiN}]_2\text{Be}$	15.1	260	0.22(s), 1.32 (s)	4.30 (SiMe); 35.60, 51.67 (*t*Bu)
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Be}$	12.5	195	0.19 (s)	3.98
$(\text{Me}_3\text{Si})_2\text{NBeCl}$	6.93	60	0.25	4.08
$(\text{Me}_3\text{Si})_2\text{NBeOEt}$	9.10	63	0.40 (s), 1.41 (Me),4.31 (CH_2)	4.96 (SiMe); 17.47, 63.15 (Et)
$i\text{Pr}_2\text{NBeBu}$	16.6	180	1.14 (d), 3.04 (sept), 0.14, 0.88, 1.67 (Bu)	14.32, 30.68, 30.96 (Bu), 24.22, 45.74 (*i*Pr)
$i\text{Pr}_2\text{NBe}(t\text{Bu})$	19.1	190	0.92 (s), 1.26 (d), 3.31 (sept)	33.60 (*t*Bu), 24.67, 46.27 (*i*Pr)
$i\text{Pr}_2\text{NBeBH}_4$	7.76	43	1.13(d), 3.04(sept)	23.53, 46.31

[a] $\delta^{14}N = -183$. [b] $\delta^{14}N = -280$. [c] $\delta^{14}N = -134$. [d] $\delta^{14}N = -112$.

The ^{9}Be nuclei of the alkylberyllium amides are strongly deshielded in relation to the aminoberyllium chlorides and ethoxides. This corresponds to similar shielding effects seen in aluminium chemistry.[14] Neither for $(\text{R}_2\text{NBeBu})_2$ nor for $[\text{R}_2\text{NBe}(t\text{Bu})]_2$ were signals observed for the C atoms bound to Be. This phenomenon is due to short transversal relaxation times T_2, which result in line broadening, an effect well known in organoboron chemistry.[15] In the case of $[i\text{Pr}_2\text{NBe}(t\text{Bu})]_2$, the NMR spectra show no change with temperature (20−80 °C). No partial monomerization is therefore observed up to 80 °C.

As indicated previously, compound (tmp)Be(*t*Bu) is unstable and decomposes with gas evolution, most probably with formation of the hydride (tmp)BeH. Its ^{9}Be NMR spectrum should show a doublet due to $^1J(^9\text{Be}^1\text{H})$, but only a broad signal ($h_{1/2} = 140$ Hz) at δ^9 Be = 11.9 ppm was observed. Both observations correspond to tricoordinated Be. Because a small coupling constant is to be expected for this compound, the linewidth may prevent detection of the coupling, as is the case with, for example, $[(\text{tmp})_2\text{AlH}]_2$.[16] No $^1J(^9\text{Be}^1\text{H})$ coupling can be observed in the ^{1}H NMR spectrum of $[i\text{Pr}_2\text{NBe}(\mu\text{-H}_2\text{BH}_2)]_2$, while the ^{11}B resonance appears as a 1:4:6:4:1 quintuplet, showing that the four hydrogen atoms bonded to the B atoms are magnetically equivalent. This is typical for almost all metal tetrahydroborates and can be explained for covalent species by a rapid exchange between terminal and bridging positions.[17] In comparison with the shielding of the boron center in NaBH_4 [$\delta^{11}\text{B} = -41.7$ ppm, $^1J(^{11}\text{B},^1\text{H}) = 80.8$ Hz[18]] or $(\text{Me}_3\text{Si})_2\text{NMg}(\mu\text{-H}_2\text{BH}_2)\cdot 2\text{THF}$ [$\delta^{11}\text{B} = -39.1$ ppm, $^1J(^{11}\text{B},^1\text{H}) = 81.8$ Hz][19] the boron nuclei in $[i\text{Pr}_2\text{NBe}(\mu\text{-H}_2\text{BH}_2)]_2$ are deshielded while the coupling constant remains the same.

IR spectroscopy, unlike NMR, did not prove to be very helpful for obtaining structural information. In case of the adduct $\text{BeCl}_2\cdot\text{HN}i\text{Pr}_2$, a sharp band at 3224 cm^{-1} corresponds to ν(NH), while the NH stretching band for the free amine is very broad, with a maximum at about 3250 cm^{-1}. A strong and sharp band at 555 cm^{-1} may be attributed to ν(BeCl_2). For the chlorides $(\text{R}_2\text{N}{-}\text{BeCl})_2$ a strong band at 615±35 cm^{-1} is most likely due to ν(BeCl). We found no band characteristic for a Be−C stretching frequency, but the double-bridge bonding of the BH_4 group was readily noticeable by two bands for two bridging and two terminal hydrogen atoms (2500, 2430, 2120, 2090 cm^{-1}).

The NMR spectroscopic data of the Lewis acid adducts of **2** do not differ too much from the parent compound. Actually, there is also no pronounced difference in the ^{13}C chemical shifts for **2** and for diisopropylamine. The ammonium-type character of the diisopropylamino group is reflected in lowfield shifts for both the Me and the CH groups, while $^1J_{\text{H,H}}$ remains constant. The lowfield shifts observed for the BBr_3 adduct in relation to boron and aluminium trichloride adducts most probably reflects a paramagnetic downfield shift resulting from the bromine atoms. Moreover, one might have expected better shielding of the ^{9}Be nuclei in the EX_3 adducts of **3**. It is the smaller linewidth that points to the presence of tetracoordinated Be atoms. That the interaction between the halide atoms of the Lewis acids and the beryllium centers is weak can be seen from the ^{11}B and ^{27}Al chemical shifts. In case of the BCl_3 adduct the resonance is at higher field than that of BCl_3 but significantly deshielded with respect to free BCl_4^- ($\delta^{11}\text{B} = 7$ ppm)[20] while the ^{27}Al NMR signal of the AlCl_3 adduct is slightly better shielded than in the anion AlCl_4^- ($\delta^{27}\text{Al} = 110$ ppm).[21]

X-ray Structure of $i\text{Pr}_2\text{NBeBH}_4$

Single crystals of $i\text{Pr}_2\text{NBeBH}_4$ were obtained from a hexane solution at −20 °C. The compound crystallized in the monoclinic space group $P2_1/c$ with $Z = 4$ dimeric units. Figure 2 displays the molecular structure.

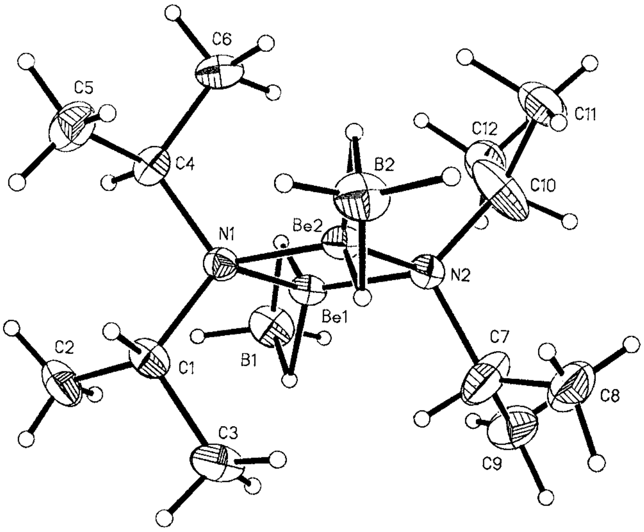


Figure 2. Molecular structure of [$i$$Pr_2NBeBH_4$]$_2$; thermal ellipsoids are depicted on a 50% probability level; selected bonds lengths [Å] and bond angles [°] (estimated standard deviations are represented in parentheses): Be1−N1 1.690(4), Be1−N2 1.703(4), Be2−N1 1.690(4), Be2−N2 1.697(4), Be1···B1 1.925(5), Be2···B2 1.950(5), Be1−H1a 1.50(3), Be1−H1b 1.53(3), B1−H1a 1.19(3), B1−H2a 1.23(3), B1−H3a 1.06(3), B1−H4a 1.11(3), B2−H1b 1.26(3), B2−H2b 1.25(3), B2−H3b 1.10(4), B1−H4b 1.06(4), N1−C1 1.513(4), N1−C4 1.504(4), N2−C7 1.520(5), N2−C10 1.486(4); N1−Be1−N2 99.9(2), N1−Be2−N2 100.1(2), Be1−N1−Be2 80.3(2), Be1−N2−Be2 79.7(2), H1a−Be1−H2a 78(2), H1b−Be2−H2b 80(2), H1a−B1−H2a 104(3), H1b−B2−H2b 100(2), H3a−B1−H4a 117(3), H3b−B2−H4b 112(3), C1−N1−C4 110.0(2), C7−N2−C10 110.9(2), Be1−N1−C1 117.7(2), Be1−N1−C4 113.3(2), Be2−N1−C1 116.0(2), Be2−N1−C4 117.0(2), Be2−N2−C7 111.2(3), Be2−N2−C10 120.1(3), Be1−N2 C10 121.2(3)

The central part of the molecule is an oblique four-membered Be_2N_2 ring with a comparatively short Be···Be distance of 2.179 Å, while the N···N distance is 2.697 Å. The Be−N bond lengths vary from 1.690(4) to 1.703(4) Å. Each Be atom is surrounded not only by two N atoms but also by two H atoms, with Be−H bond lengths of 1.46(3) and 1.53(3) Å. The Be−B distances are 1.938 and 1.942 Å, respectively.

As would be expected, the bridging hydrogen atoms show B−H bonds longer [av. 1.23(3) Å] than the terminal B−H bonds [1.17(3) Å]. The terminal H−B−H bond angles are more open [117(3)° at B1, 113(2)° at B2] than those of the bridging hydrogen atoms [104(2)° at B1, 100(2)° at B2]. The H−Be−H bond angles are more acute, with 78(2)° at Be1 and 80(2)° at Be2. It follows from the longer N···N distance in relation to the Be···Be distance that the bond angles at the N atoms are more acute [Be1−N1−Be2 80.3(3)°, Be1−N2−Be 2 79.7(2)°] than those at the Be atoms [N1−Be1−N2 99.9(2)°, N1−Be2−N2 100.1(2)°].

Discussion

Of the two possible routes to aminoberyllium chlorides considered, ligand exchange between $(R_2N)_2Be$ and $BeCl_2$ (or $BeCl_2{\cdot}2OEt_2$) was unsuccessful, unlike 1:1 reactions between $BeCl_2$ and $LiNR_2$ compounds [R_2N = N$i$$Pr_2$, tmp, $N(SiMe_3tBu)_2$, $N(SiMe_3)_2$] in diethyl ether solution. Low temperatures are necessary to retard or suppress the formation of beryllium bis(amides), because the aminoberyllium chlorides formed react more rapidly than $BeCl_2$ with $LiNR_2$ at ambient temperature. However, the formation of ethoxyberyllium amides could not be prevented. This indicates that ether cleavage by $LiNR_2$ occurs to a considerable extent even at low temperature. All compounds of type R_2NBeX (X = R, Cl, EtO) are dimeric. Dimerization occurs through the N atoms, producing four-membered Be_2N_2 rings. No beryllates $Li[Be(NR_2)_nCl_mY_o]$ (Y = OEt; $n + m + o = 3$) could be detected in the diethyl ether solutions. Beryllates have been observed by Anderson and Coates[22] in reactions between $BeCl_2$ and $LiNMe_2$ in diethyl ether.

(tmp)Be(tBu) could not be prepared, because it decomposes with gas evolution and presumably forms (tmp)BeH. This latter compound was, however, not obtained in a pure state. Isobutene elimination from tBu−metal compounds is not unusual, as even LitBu itself decomposes into LiH and isobutene.[23]

Direct aminolysis of $BeCl_2$, either as the crystalline material or as $BeCl_2{\cdot}2OEt_2$, with diisopropylamine could not be achieved. The reactions stopped at the $BeCl_2{\cdot}HNiPr_2$ adduct stage. Obviously, the NH proton is not sufficiently acidic to react with additional amine to achieve aminolysis to either R_2NBeCl or $(R_2N)BeCl{\cdot}HNR_2$ (R = iPr). This latter adduct is indeed formed, though only slowly, in the reaction between ($i$$Pr_2NBeCl$)$_2$ and diisopropylamine, but it readily disintegrates into the components in solution at higher temperatures. In this respect the aminolysis of $BeCl_2$ matches the aminolysis of $AlCl_3$ with secondary amines, which also stops at the adduct stage,[24] unlike the case of BCl_3, which is aminolyzed to give not only R_2NBCl_2 but also $(R_2N)_2BCl$ and even $B(NR_2)_3$ with many secondary amines.[25] The main reason for the lack of aminolysis of $BeCl_2$ and $AlCl_3$ is most probably that the amides formed have more strongly basic nitrogen centers than the amine itself, while in the boron case the basicity of the amino group is reduced due to B−N π-bonding. However, $BeCl_2{\cdot}HNiPr_2$ can be deprotonated with LiBu or $LiNR_2$ (i.e., with strong bases).

Experimental Section

General: All experiments were performed under anhydrous conditions with use of Schlenk techniques. Dinitrogen or argon were used as protecting gases. Anhydrous $BeCl_2$ was purchased from Aldrich and the amines from Fluka, while the LiR compounds were gifts from Chemetall GmbH (usually as 1.5 M solutions in hexane). The amines and the solvents used were dried in a conventional manner ($LiAlH_4$, CaH_2, P_2O_5). $BeCl_2$−diethyl ether was prepared from Be powder and HCl in diethyl ether.[26] All necessary safety measures were practiced in the experimental procedures, as Be compounds are toxic. After the experiments, the glassware was washed with conc. HCl and the solutions were collected in plastic flasks. These collected solutions were concentrated in vacuo using a rotary evaporator. The oily or pasty residues were properly labeled and disposed as special waste.

Physical Measurements: Molecular masses were determined by cryoscopy in cyclohexane solutions or by mass spectrometry. NMR: JEOL 90 or Bruker WP200 instruments. ^{1}H (int. TMS, int. CD_2Cl_2, int. C_6D_6), ^{9}Be (1 M solution of $BeCl_2$ in 1 M HCl/D_2O), ^{13}C (int. TMS, int. $CDCl_3$, or int. $C_6D_{6'}$), ^{14}N (ext. 1 M solution of NH_4NO_3 in D_2O). MS: Atlas CH7. IR: Perkin-Elmer 235 spectrometer. Elemental analysis: Automatic C/H/N analyzer, chloride titration with a Metroohm instrument. M.p.: Mel-Temp. in capillaries.

X-ray Analysis: Siemens P4 diffractometer, Mo-K_α radiation, graphite monochromator, LT2 device. Data collection at −80 °C, data reduction with the program SAINT,[27] structure solution with SHELX79,[28] data refinement with SHELXTL. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions of the BH_4 group were taken from the difference Fourier map. These were freely refined with individual isotropic thermal parameters. H atoms of the isopropyl groups were placed in calculated positions and included in the final refinements as riding on their C atoms. Crystallographic data for **18** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC-195196. Copies can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; E-mail: deposit@ccdc.ac.uk.

Beryllium Dichloride−Diisopropylamine (1). a) Anhydrous crystalline $BeCl_2$ (1.50 g, 19 mmol) was covered with diisopropylamine (13.5 mL, 100 mmol) in a two-necked flask, and the mixture was kept at reflux for 3 h. During this time the crystals disappeared and turned into a gray mass. The solid was isolated by filtration, washed with pentane, and dried in vacuo. Yield: 2.40 g (100%) of **1**, m.p. 65 °C. NMR recorded at 70 °C: see Table 1. $C_6H_{14}BeCl_2N$ (180.12): calcd. C 39.79, H 8.37, Cl 39.14, N 7.74; found C 39.22, H 8.41, Cl 39.20, N 7.83. **b)** Diisopropylamine (12.5 mL, 90 mmol) was dissolved in diethyl ether (25 mL). A solution of $BeCl_2$ in diethyl ether (4.5 M, 10 mL, 45 mmol) was added dropwise to the stirred solution over 15 min. An oily phase formed. The mixture was kept at reflux for 1 h (this is not actually necessary). No crystals formed from the oily phase in a refrigerator within 24 h. All volatile components were then removed in vacuo. A gray mass was left behind, and this, after drying in vacuo, gave 18.12 g (99.5%) of **1**, m.p. 65 °C. NMR spectroscopic and analytical data are the same within standard errors as for the compound obtained by procedure a).

Deprotonation of $BeCl_2$·HN*i*Pr$_2$ with LiBu: Diisopropylamine (14.1 mL, 100 mmol) was added to $BeCl_2$ (7.99 g, 100 mmol) and the mixture was heated at reflux for 3 h. The resulting gray solid mass was then suspended in hexane (50 mL) and the stirred suspension was treated with a solution of LiBu in hexane (1.58 M, 66.7 mL, 100 mmol) over 2 h. The resulting suspension was kept at reflux for 2 h, insoluble material (4.9 g) was removed by filtration, and the solvent was removed from the filtrate in vacuo. An oily residue (17.5 g) remained. Half of the material was distilled. This afforded two fractions: fraction 1 (0.8 g), b.p. up to 60 °C/0.1 Torr; fraction 2 (5.67 g), b.p. 60−63 °C/0.1 Torr, showing three ^{9}Be NMR signals at δ = 9.9 (main product), 15.9, and 3.2 ppm. Redistillation of fraction 2 yielded 3.25 g of product with b.p. 61−62 °C/0.1 Torr. It showed the following NMR signals: δ^1H = 0.1 ppm (m), 0.87 (d, $^3J_{H,H}$ = 6.69 Hz), 1.04 (d, $^3J_{H,H}$ = 6.75 Hz), 1.21 (d, $^3J_{H,H}$ = 5.86 Hz), 1.52 (m), 2.9 (m), 3.7 (m). δ^9Be = 10.2 ppm with a shoulder at δ = 16 ppm. On standing, this fraction became partly crystalline. The crystals (0.72 g) were separated and washed with pentane. They showed a ^{1}H NMR spectrum fairly similar to that described above, with the most intense signal at δ = 1.21 ppm (d). δ^9Be = 1.7 and 15.4 ppm (broad, $h_{1/2}$ = 170 Hz). The chloride content of all fractions was very low by qualitative analysis. From comparison of NMR spectroscopic data, all fractions contained **3**, **14**, and small amounts of **2**. Several attempts to produce crystals from various solvents with the second part of the crude product failed at −20 and −78 °C.

Ligand Exchange between $BeCl_2$ and (*i*Pr$_2$N)$_2$Be: (*i*Pr$_2$N)$_2$Be (10.0 g, 48 mmol) and hexane (50 mL) were added to $BeCl_2$ (3.83 g, 48 mmol). The mixture was kept at reflux for 48 h. Hexane was removed from a sample in vacuo. The oily residue showed ^{1}H NMR signals at δ = 1.09 (d) and 2.92 ppm (sept) typical of **3**. Irradiation of the mixture by an Hg lamp in the presence or absence of hexane also did not induce any reaction; 3.87 g of $BeCl_2$ was recovered. Similarly, a mixture of (*i*Pr$_2$N)$_2$Be (3.14 g, 15 mmol) and $BeCl_2$·2OEt$_2$ (6 mL of a 2.5 M solution in ether) showed no reaction after being kept at reflux for 24 h, as evidenced by ^{9}Be NMR resonance [signals at δ = 12.7 ppm (amide) and δ = 1.15 ppm for beryllium chloride−diethyl ether].

(Diisopropylamino)beryllium Chloride (2). a) $BeCl_2$·2OEt$_2$ (16.8 mL of a 2.59 M solution in diethyl ether, 50 mmol) was diluted with diethyl ether (20 mL). A suspension of LiN*i*Pr$_2$ (37 mmol) in hexane (50 mL) was added with stirring over 2 h. Insoluble material was removed by filtration after 16 h, and the solvent was stripped off from the filtrate in vacuo. The oily residue was distilled (b.p. ca. 85 °C/0.1 Torr), and the distillate afforded colorless crystals of **2**, m.p. 72 °C. NMR: see Table 1. $C_6H_{14}BeClN$ (144.65): calcd. C 49.82, H 9.76, Cl 24.51, N 9.68; found C 48.65, H 9.78, Cl 23.93, N 9.65. Molecular mass: 286. **b)** The reaction was performed similarly at 0 °C (16.8 mL of a 2.98 M $BeCl_2$ solution in diethyl ether, 50 mmol, diluted with 25 mL of ether) with freshly prepared LiN*i*Pr$_2$ (50 mmol) in hexane (75 mL). Stirring at 0 °C for 3 h, and then at ambient temperature overnight gave LiCl (2.05 g, 97%), which was isolated from the suspension by filtration. The filtrate contained 7.42 g of a solid crude product. Its sublimation at 95 °C/0.005 Torr provided waxy crystals of **2**, m.p. 72 °C; yield 6.62 g (86%). MS: Correct isotope pattern for [$M^{+\cdot}$] (288). All other data are as stated under a).

(Diisopropylamino)beryllium Chloride−Diisopropylamine Adduct 4: $BeCl_2$ (2.05 g, 26 mmol) was allowed to react at reflux with diisopropylamine (7.45 mL, 53 mmol) for 2 h. Hexane (50 mL) was then added to the cooled (0 °C) suspension, followed by LiBu (1.56 M in hexane, 16.9 mL, 26 mmol). This produced a white suspension. After the mixture had been heated at reflux for 2 h, some crystals had separated on the walls of the flask. Insoluble material was then rapidly removed by filtration (1.11 g) and the filtrate was reduced to 30 mL in vacuo. Crystal settled from the filtrate at −20 °C. Yield 4.18 g (68%) of **4**; m.p. 65 °C with decomp. NMR: see Table 1. $C_{12}H_{29}BeClN_2$ (245.84): calcd. C 58.63, H 11.89, Cl 14.42, N 11.39; found C 59.19, H 12.43, Cl 14.33, N 10.75.

(2,2,6,6-Tetramethylpiperidino)beryllium Chloride (5): A diethyl ether solution of $BeCl_2$ (3.5 M, 13.3 mL) was diluted with diethyl ether (50 mL) and cooled to −100 °C. A suspension of (tmp)Li (7.36 g, 50 mmol) in pentane/hexane (1:1) was added dropwise with vigorous stirring over a period of 3 h. Stirring was continued for another 3 h, and the suspension was then allowed to come to room temperature overnight with continuous stirring. Insoluble material (2.08 g) was removed by filtration, and the solvents were stripped off from the filtrate in vacuo. A brownish solid (10.4 g) was left. This crude product showed the following NMR spectroscopic data:

$\delta^{1}H$ = 1.08 ppm (t), 1.16 (s), 3.9 [q, ^{3}J(H.H) = 7.08 Hz; (tmp)BeOEt, **7**], 1.30 (s), 1.64 [m, (tmp)BeCl, **5**], ratio of the singlets 2.2:1 (95% **5**, 5% **7**). $\delta^{9}Be$ = 9.4 ppm (**5**). Sublimation of the crude material at 110 °C/0.006 Torr yielded 6.84 g (74%) of **5**, m.p. 105−107 °C. NMR: see Table 1. $C_9H_{18}BeClN$ (184.74): calcd. C 58.31, H 9.84, Cl 19.19, N 7.89; found C 56.47, H 9.08, Cl 19.08, N 6.95. Molecular mass: 366. MS: 369 for [$M^{+\cdot}$] (correct isotopic pattern).

[*tert*-Butyl(trimethylsilyl)amino]beryllium Chloride (9): Analogously to the preparation of **5**, a diethyl ether solution of $BeCl_2$ (3.75 M, 13.3 mL, 50 mmol), diluted with diethyl ether (50 mL), was added at −100 °C to a suspension of $LiN(SiMe_3)CMe_3$ (6.66 g, 50 mmol) in pentane/hexane (1:1) (75 mL). Stirring was continued at −100 °C for 3 h and at −78 °Cfor 2 h. After the suspension had reached room temperature, the solid was filtered and the solvents were removed from the filtrate in vacuo. Residue: 8.43 g of a waxy solid. Sublimation at 125 °C/0.0049 Torr gave 3.4 g (36%) of **9**. NMR: see Table 1. $C_7H_{18}BeClNSi$ (188.81): cald. C 44.53, H 9.63, Cl 18.78, N 7.42; found C 43.92, H 9.05, Cl 18.54, N 6.86. Molecular mass: 375.

[Bis(trimethylsilyl)amino]beryllium Chloride (12) and Ethoxyberyllium Bis(trimethylsilyl)amide (13): This compound was prepared analogously to **9**, from $BeCl_2$ (25 mmol) in diethyl ether/pentane (1:1, 50 mL) and $LiN(SiMe_3)_2$ (4.18 g, 25 mmol) suspended in pentane/hexane (1:1, 50 mL) at −100 °C. After workup, 4.83 g of a slightly yellow, waxy solid was obtained, and this was shown by NMR analysis to be a 1:2.5 mixture of **12**/**13**. Fractional sublimation gave three fractions: a) at 110 °C/ 0.004 Torr, 1.24 g of compound **13**, m.p. 147−149 °C;NMR spectroscopic data see Table 1; b) at 110−117 °C/0.004 Torr, 2.18 g, this fraction was shown by NMR to be a mixture of **12** and **13**; c) 117 °C/0.004 Torr, 0.6 g of compound **12**, NMR: see Table 1. $C_6H_{18}BeClNSi_2$ (204.89): calcd. C 35.17, H 8.87, Cl 17.36, N 6.84; found C 34.23, H 8.25, Cl 17.21, N 6.23.

Butyl(diisopropylamino)beryllium (14): iPr_2NBeCl (3.18 g, 22 mmol) was dissolved in hexane (25 mL), and the solution was cooled to 0 °C. A solution of LiBu in hexane (1.56 M, 14.1 mL) was added dropwise, with stirring. The mixture was then kept at reflux for 1 h. After the solid material (LiCl) had been removed by filtration and the hexane had been distilled from the filtrate, the oily residue was distilled. Compound **14** had a b.p. of 78 °C/ 0.1 Torr. Yield 2.49 g (88%). NMR: see Table 1. $C_{10}H_{23}BeN$ (166.35): calcd. C 72.20, H 13.98, N 8.42; found C 71.08, H 12.41, N 7.95. Molecular mass: 426.

***tert*-Butyl(diisopropylamino)beryllium (15): a)** The compound was prepared as described for **14**, from iPr_2NBeCl(2.60 g, 18 mmol) in hexane (25 mL) and a solution of Li*t*Bu (1.50 M, 12 mL, 18 mmol), withstirring at ambient temperature for 3 h. Compound **15** showed a b.p. of 90 °C/0.005 Torr, Yield 1.44 g (48%), m.p. 84−86 °C. When the reaction was performed at −78 °C the yield rose to 78%. NMR spectroscopic data: see Table 1. $C_{10}H_{23}BeN$ (166.35): calcd. C 72.20, H 13.98, N 8.42; found C 69.58, H 13.05, N 7.93 (low C/H values due to insufficient protection against oxidation during the weighing process). Molecular mass: 331. **b)** $tBuBeCl\cdot OEt_2$ (1.41 g, 8.0 mmol), dissolved in pentane (15 mL), was treated at −78 °C, with vigorous stirring, with a suspension of $LiNiPr_2$ (0.l86 g, 8 mmol) in pentane/hexane (1:1). After the mixture had been allowed to come to room temperature, the solid was removed by filtration and the solvents were removed in vacuo. The residue was distilled, b.p. 90 °C (oil bath)/0.005 Torr. Yield 1.01 g (76%) of **15**, m.p. 84−86 °C. NMR spectroscopic data are as found for compound **15** prepared by procedure a).

Butyl(2,2,6,6-tetramethylpiperidino)beryllium (16): (tmp)BeCl (2.03 g, 11 mmol) was dissolved in hexane (20 mL) and treated, whilst stirring, with LiBu (7.05 mL, 1.56 M solution in hexane diluted with 10 mL of hexane). The mixture was kept at reflux for 30 min. Insoluble material was removed by filtration and the solvents were removed in vacuo. The residue had a b.p. of 98−104 °C/ 0.006 Torr. Yield 1.32 g (58%) of **16**. NMR spectroscopic data: see Table 1. $C_{13}H_{27}BeN$ (206.42): calcd. C 75.67, H 13.21, N 6.79; found C 74.98, H 12.88, N 6.25. Molecular mass: 410.

Attempt to Prepare (tmp)Be(*t*Bu) (17): a) (tmp)BeCl (2.77 g, 15 mmol) dissolved in pentane (40 mL) was cooled to −78 °C. A solution of Li*t*Bu (1.5 M, 10.0 mL, 15 mmol), diluted with pentane (15 mL), was then added with stirring over 3 h. After additional stirring for 2 h, the mixture was allowed to come to ambient temperature, whereupon vigorous gas evolution started at ca. 10 °C. Insoluble material was removed after stirring for additional 20 min, followed by stripping off of the solvents in vacuo. The residue (2.04 g), a yellowish, viscous oil, decomposed during attempted distillation. The residue was practically free of chloride. NMR (crude product): $\delta^{1}H$ = 1.01 ppm (s), 1.18 (s), 1.31 (s), 1.62 (m) in a ratio of 1.0:1.7:14.7:8.8. $\delta^{13}C$ = 18.55 ppm, 32.22, 32.76, 33.21, 34.37,

Table 2. NMR spectroscopic data of diisopropylamine, diisopropylaminoberyllium chloride, and its addition products with boron trihalides and aluminium trichloride (δ [ppm], linewidths $w_{1/2}$ [Hz])

	$\delta^{9}Be/\delta^{11}B/\delta^{27}Al$ ($w_{1/2}$)	$\delta^{1}H$(Me, CH)	^{1}J(H,H)	$\delta^{13}C$(Me, CH)
$HN(CHMe)_2$	−	0.96, 2.97	6.60	23.78, 45.50
$[ClBe[N(CHMe_2)_2]_2$	10.70/−/− (82)	1.20, 3.04	6.59	23.77, 45.84
$[ClBe[N(CHMe_2)_2]_2\cdot 2BCl_3$	9.96/30.8/− (60)/(108)/−	1.19, 3.08	6.59	23.94, 45.66
$[ClBe[N(CHMe_2)_2]_2\cdot 2BBr_3$	10.65/22.1/− (60)/(125)/−	1.37, 3.27	6.59	25.43, 47.12
$[ClBe[N(CHMe_2)_2]_2\cdot 2AlCl_3$	10.04/−/104.5 (55)/−/(154)	1.18, 3.09	6.60	23.78, 45.30
$[ClBe[N(CHMe_2)_2py]_2$	4.82/−/− (1.5)	1.13 (d), 3.03 (sept), 6.72 (m), 7.08 (m), 8.89 (m)	6.45	24.22 (q), 45.71 (d), 124.62 (d), 138.70 (d), 148.29 (d)

37.75. 39.87, 50.40, 52.21. δ^9Be = 11.9 ppm ($h_{1/2}$ = 145 Hz). **b)** *t*BuBeCl·OEt$_2$ (1.58 g, 9.00 mmol) was dissolved in pentane (20 mL) and the solution was cooled to −78 °C. A suspension of (tmp)Li (1.32 g, 9.00 mmol) in pentane/hexane (1:1) (20 mL) was added over 2 h. The solid that had formed was removed by filtration and the solvents were stripped off in vacuo. The NMR spectroscopic data are essentially the same as from experiment a), demonstrating that no single compound was produced [main product 90%; δ^1H = 1.31 ppm (s), 1.67 (m), by-products ca. 4 and 6%]. The product was essentially free of chloride.

(Diisopropylamino)beryllium Tetrahydroborate (18): A solution of LiBH$_4$ in diglyme (1.0 M, 5.8 mL, 5.8 mmol), to which diethyl ether (5 mL) had been added, was added to a solution of (*i*Pr$_2$NBeCl)$_2$ (0.83 g, 2.9 mmol) in diethyl ether (10 mL). After the addition, the mixture was kept at reflux for 1 h. Insoluble material was removed by filtration (G4), all solvents were stripped off in vacuo, and the residue was crystallized from pentane at −20 °C. Colorless, extremely moisture-sensitive crystals (0.54 g, 75%) were obtained, dec. at ca. 85 °C. NMR: see Table 1. IR: ν(BH): 2428, (st), 2405 (st), 2138 (st), 2068 (m) cm^{-1}. $C_{12}H_{36}B_2Be_2N_2$ (248.14): calcd. C 58.08, H 14.65, N 11.29; found C 56.46, H 9.53, N 10.59. The low H content seems to be due to insufficient protection of the compound during the weighing process. In addition, combustion occurred explosively. Molecular mass: 246.

***tert*-Butoxyberyllium Diisopropylamide (19):** (*i*Pr$_2$NBeCl)$_2$ (1.72 g, 5.94 mmol) was dissolved in hexane (30 mL) and treated with KO*t*Bu (1.47 g, 13.0 mmol) in hexane (15 mL). After the mixture had been heated at reflux for 30 min, the insoluble part was removed by filtration, the solvents were stripped off from the filtrate in vacuo, and the light brown residue was subjected to sublimation. Yield 1.70 g (78.5%) of **19** obtained at 150 °C/0.005 Torr, m.p. 138−139 °C. NMR: see Table 1. $C_{10}H_{23}BeNO$ (182.35): calcd. C 65.86, H 12.74, N 7.68; found C 63.47, H 11.65, N 7.08. Molecular mass: 359.

Adduct of (Diisopropylamino)beryllium Chloride and Boron Trichloride (21): (*i*Pr$_2$NBeCl)$_2$ (0.83 g, 2.9 mmol) was dissolved in dichloromethane (10 mL) and the solution was cooled to −78 °C. At this temperature, liquid BCl$_3$ (1 mL) was added and the mixture was stirred for 2 h. Excess BCl$_3$ and solvent were then removed in vacuo, and the dark brown solid residue was crystallized from pentane (3 mL). Yield 0.99 g (65%) of **22**, yellow solid, dec. at 132−140 °C. NMR: data see Table 2. $C_6H_{24}BBeCl_4N$ (261.83): calcd. C 27.52, H 4.89, Cl 54.16, N 5.35; found C 26.58, H 4.02, Cl 53.95, N 4.98.

Adduct of (Diisopropylamino)beryllium Chloride and Boron Tribromide (22): Analogously to the preparation of **22**, (*i*Pr$_2$NBeCl)$_2$ (0.62 g, 2.1 mmol) was treated with BBr$_3$ (0.47 mL, 5 mmol), dissolved in CH$_2$Cl$_2$. After removal of the dichloromethane from the solution, the dark brown residue was subjected to crystallization from pentane (9 mL) to give 0.98 g (58%) of dark brown **23**, dec. at 95−98 °C. NMR: see Table 2. $C_6H_{14}BBeBr_3ClN$ (395.18): calcd. C 18.23, H 3.58, N 3.55; found C 17.18, H 2.87, N 3.05; total halide contents: 0.41 mmol in 0.1 mol of compound **23**.

Adduct of (Diisopropylamino)beryllium Chloride and Aluminium Trichloride (23): Freshly sublimed AlCl$_3$ (0.69 g, 5.2 mmol) was added to a solution of (*i*Pr$_2$NBeCl)$_2$ (0.75 g, 2.6 mmol) in dichloromethane (10 mL). No reaction was observed after the mixture had been stirred for 1 h. After the mixture had been heated at reflux for 2 h, the AlCl$_3$ had dissolved. The solvent was then removed in vacuo and the yellow/brown solid was crystallized from pentane (8 mL). Yield: 0.89 g (62%) adduct as a light yellow solid, dec. at 115−117 °C. NMR: see Table 2. $C_6H_{14}AlBeCl_4N$ (278.04): calcd. C 25.92, H 5.09, N 5.04; found C 24.83, H 4.18, N 4.67.

Pyridine Adduct of (Diisopropylamino)beryllium Chloride (20): A solution of pyridine (0.70 mL, 6.6 mmol) in CH$_2$Cl$_2$ (5 mL) was added with stirring to a solution of (*i*Pr$_2$NBeCl)$_2$ (0.69 g, 3.3 mmol) in the same solvent (15 mL). A deep red solution formed. After 2 h, the solvent was removed in vacuo and the remaining brown solid was dissolved in pentane (5 mL). No crystals separated from this solution at −20 °C. On removal of the solvent a dark brown/red solid remained (1.48 g, 99%), dec. at 132−134 °C. NMR: see Table 2. $C_{11}H_{19}BeClN_2$ (223.78): calcd. C 59.04, H 8.58, Cl 15.84, N 12.52; found C 56.84, H 8.88, Cl 15.66, N 9.28.

Crystallographic Data and Structure Refinement Parameters for (*i*Pr$_2$NBeBH$_4$)$_2$: Empirical formula: $C_{12}H_{36}B_2Be_2N_2$, formula mass: 248.07, crystal color: colorless, crystal size: 0.32 × 0.30 × 0.42 mm, crystal system: monoclinic, space group: $P2_1/n$, unit cell dimensions: a = 7.813(2), b = 21.927(6), c = 10.437(4) Å, β = 93.60(3)°, V = 1784.5(9) Å^3, Z = 4, density (calcd.) = 0.923 g/cm^3, linear absorption coefficient: 0.46 cm^{-1}, F(000) = 559, wavelength: λ= 0.71073 Å, 2θ range for data collection: 3−46°, speed: 2.2−29.3 °/min, T = 18 °C, index ranges: h, k, ±l, reflections collected: 2910, independent reflections: 2494, reflections observed (2.5σ): 1898, parameters refined: 273, R_i = 0.0281, structure solution: direct methods, R_1 = 0.0876, R_w = 0.080, largest residual electron density: 0.41 e/Å^3.

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