N,N-Diisopropylaminomethyllithium: Synthesis, Oxidative Degradation, and Organoaluminum and -gallium Derivatives

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N,N-Diisopropylaminomethyllithium (**1**) was prepared by transmetalation from $Me_3SnCH_2N^iPr_2$ and *n*-BuLi. It was characterized by NMR spectroscopy (^1H, ^{13}C, ^7Li). Compound **1** crystallizes as a hexamer $(LiCH_2N^iPr_2)_6$ and allowed the determination of the first solvent-free structure of an α-lithiated amine. It contains a Li_6 core (distorted octahedron) 6-fold capped by $CH_2N^iPr_2$ units. **1** is very sensitive to air-oxidation. A partially $[(LiCH_2N^iPr_2)_4(LiOCH_2N^iPr_2)_2$ (**2**)] and a completely oxidized $[(LiOCH_2N^iPr_2)_6$ (**3**)] cluster compound could be isolated. **2** and **3** were characterized by multinuclear NMR spectroscopy and by single-crystal X-ray diffraction. The results show that the hexameric structure is retained upon partial or complete oxidation. **1** was used as aminomethylating agent and reacted with Me_2AlCl and Me_2GaCl to give the aminomethylaluminum and -gallium compounds $(Me_2MCH_2N^iPr_2)_2$ (M = Al, Ga), which are dimers containing six-membered rings. They were characterized by elemental analyses, NMR spectroscopy, and crystal structure determinations. They are present as dimers containing six-membered $M_2C_2N_2$ rings in solution and in the solid state.

Introduction

Within the class of α-heteroatom-substituted methyllithium compounds such as aminomethyl (R_2NCH_2Li), phosphinomethyl (R_2PCH_2Li), oxymethyl ($ROCH_2Li$), and thiomethyl lithium ($RSCH_2Li$) those with nitrogen in α-position are the most difficult to prepare due to the fact that these are formally nonstabilized carbanionic compounds. Nevertheless they are important reagents for nucleophilic introduction of the respective groups in synthetic procedures.[1] The transmetalation route developed by Seyferth et al.,[2] i.e., treating corresponding stannyl compounds with butyllithium, is still the most favorable procedure for the preparation of aminomethyl compounds of lithium as first applied by Peterson.[3] Direct deprotonation of amines is restricted to a limited number of examples, the most impressive being the double terminal lithiation of the aminal $Me_2NCH_2NMe_2$ with *tert*-butyllithium to give $LiCH_2(Me)NCH_2N(Me)CH_2Li$,[4] which has been used to prepare derivatives of Zr,[5] Ni,[6] Al, and Ga.[7] The latter Al and Ga compounds aggregate intramolecularly (heteronorbornane structure), which can be regarded as a guess for the aggregation type responsible for the intramolecularly assisted formation of the dilithium compound. Recently there was also a report on direct deprotonation of *N,N′,N″*-trimethyl-1,4,7-triazacyclononane, which probably works for the same reason.[8] Nonstabilized aminomethyl compounds are in particular reactive and highly air-sensitive and in part pyrophoric, and only a handful of structures of these compounds have been reported so far,[9] but none of these are free of donor solvent or auxiliary base molecules.

Our interest in these compounds focuses on the synthetic application for aminomethyl group transfer to organo earth metal units with the aim of preparing compounds containing saturated M−C−N units (M = Al, Ga, In). The related boron compounds with B−C−N units are known to adopt very different aggregation modes, namely, three-membered ring compounds such as $(F_3C)_2BC(SiMe_3)(CH_2Ph)NMe_2$[10] and $(F_3C)_2BC(Ph)_2NMe_2$[11] and six-membered ring dimers such as $(H_2BCH_2NMe_2)_2$ (Scheme 1).[12]

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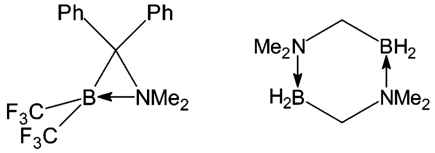
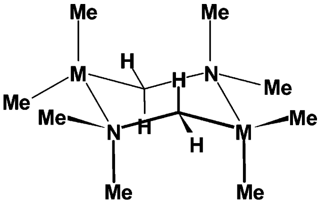
10.1021/om049631i CCC: $30.25

Scheme 1



Scheme 2



In an earlier contribution we have shown that methyl substituents at M and N lead to the formation of six-membered-ring dimers in $(Me_2AlCH_2NMe_2)_2$ and $(Me_2GaCH_2NMe_2)_2$ (Scheme 2).[13] The possibility of the formation of three-membered cyclic M−C−N units was the stimulus for this investigation, as such small M−C−N cycles could have interesting chemical properties related to those of the lithium carbenoids $LiCR_2X$ with X being Cl, OR, and other donor centers.[14] To achieve the formation of three-membered cyclic M−C−N units, we intended to increase the steric bulk of the substituents at the M−C−N backbones.

The prerequisite is of course the availability of an aminomethyllithium reagent with large groups at the N atoms, and isopropyl groups are suitable in this context. *N,N*-Diisopropylaminomethyllithium has already been reported in the literature by Strohmann and Abele,[15] but they obtained this substance as a 1:1 mixture with LiSPh by cleavage of a C−S bond in $PhS-CH_2-N^iPr_2$. This mixture has successfully been applied to the synthesis of silicon compounds, but the procedure requires aqueous workup to remove the accompanying weaker nucleophile LiSPh. As our organometal systems do not allow aqueous treatment, we had to obtain $LiCH_2N^iPr_2$ in pure form. In this paper we report on the synthesis of $LiCH_2N^iPr$, its crystal structure, its stepwise reactions with oxygen, its reactions with organoaluminum and -gallium chlorides, and the properties and structures of the resulting group 13 compounds.

Results

***N,N*-Diisopropylaminomethyllithium. Synthesis and Spectroscopy.** Transmetalation of (*N,N*-diisopropylaminomethyl)trimethylstannane with *n*-butyllithium gave *N,N*-diisopropylaminomethyllithium. The necessary stannane was prepared by amination of (iodomethyl)trimethylstannane in an established procedure.[16]

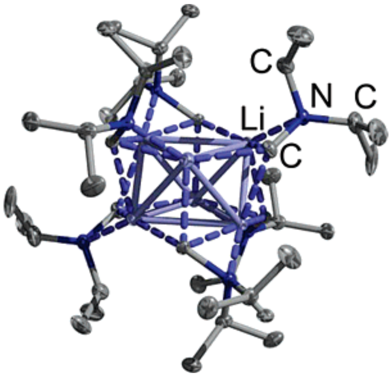


Figure 1. Crystal structure of $(LiCH_2N^iPr_2)_6$ (**1**). Hydrogen atoms are omitted for clarity.

$$Me_3SnCH_2I + 2\ HN^iPr_2 \rightarrow Me_3SnCH_2N^iPr_2 + [H_2N^iPr_2]I$$

$$6\ Me_3SnCH_2N^iPr_2 + 6\ {}^nBuLi \rightarrow 6\ {}^nBuSnMe_3 + (LiCH_2N^iPr_2)_6\ (\mathbf{1})$$

In contrast to other donor-free α-lithioamines, **1** is fairly well soluble in hydrocarbons as hexane from which it was crystallized and found to be hexameric (see below). It was also characterized by ^1H, ^{13}C, and ^7Li NMR spectroscopy. Expectedly the ^7Li NMR spectrum of **1** shows a single signal at 1.2 ppm, the region established for organolithium compounds. Although these data would be consistent with the interpretation of the presence of a single aggregation form in solution and S_6-symmetry also found approximately in the structural investigations, the line widths in the ^7Li NMR investigations do not allow a rigorous exclusion of the presence of other aggregation forms in solution nor the exclusion of a rapid exchange between such aggregates.

Crystal and Molecular Structure. Despite many attempts of crystallization under different conditions, no crystals of high quality could be grown of **1**. The crystals were quite soft and could not be mechanically stressed for crystallography preparation purposes. The structure of **1** is the first of an α-lithioamine, which was successfully crystallized without incorporation of donor solvent molecules. Such structures of α-lithioamines that were studied earlier include $(Me_2NCH_2Li)_4{\cdot}4THF$,[9d] $(Ph_2NCH_2Li)_2{\cdot}3THF$,[9c] and $(PhCH(Li)NMe_2)_2{\cdot}2Et_2O$.[9a]

The molecules of **1** are centrosymmetric and arranged about the inversion center of a triclinic cell (space group $P\bar{1}$, see Figure 1). For comparison the structural parameters are listed in Table 1 together with those obtained by geometry optimizations at the B3LYP/6-311G* level of a model compound **1a** in which the isopropyl groups have been replaced by methyl groups. In general the $(LiCN)_6$ cores of the experimentally determined and the calculated structures are in good agreement, except that the molecules of **1a** adopt higher symmetry: S_6.

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Table 1. Selected Structural Parameters for $(LiCH_2N^iPr_2)_6$ (1) as Determined by Crystallography and for $(LiCH_2NMe_2)_6$ (1a) as Calculated at the B3LYP/6-311G* Level of Theory (Å, deg)

parameter	**1**/XRD	**1a**/B3LYP
Li1−Li2	2.997(4)	2.974
Li2−Li3	2.588(4)	2.551
Li3−Li1	2.589(4)	2.551
C10−Li1	2.152(4)	2.206
C10−Li2	2.276(4)	2.214
C10−Li3	2.358(4)	2.302
C10−N10	1.524(3)	1.508
N10−Li1	2.079(3)	1.991
C11···Li1	2.733(5)	2.868
N10−C10−Li1	66.3(1)	61.5

The core of **1** consists of a trigonal antiprism of six Li atoms (strongly distorted octahedron) with six irregular triangles capped by the methylene units of the $^iPr_2NCH_2$ groups. The Li atoms of the noncapped more regular triangles have Li−Li distances between 2.973(4) and 3.002(4) Å (**1a** calculated 2.974 Å). The capped triangles include two shorter Li−Li sides of 2.588(4) and 2.605(4) Å length (calculation for **1a**: 2.551 Å). A donor bond between the nitrogen atom and a Li atom completes the primary coordination of the cluster and leads to LiCN three-membered ring units. In this respect this structure resembles that of hexameric *n*-butyllithium,[17] which also shows the described features including a weak interaction between the β-CH_2 group (instead of N) and one of the Li atoms of the Li_6 core.

Oxidation Products of $(LiCH_2N^iPr_2)_6$ (1). Oxidation Reactions. In general, the oxidation products of lithium alkyls on contact with oxygen include peroxoalkyl and alkoxide compounds,[18] which have been detected frequently in the form of their hydrolysis products.[19] There is, however, a distinct paucity of structural data for species involved in such oxidative processes. We have found two oxidation products of **1** by accident during attempts of its preparation, which were undertaken with less rigorous inert gas conditions. Oxygen reacts with **1** under formation of the corresponding alkoxide, and this reaction proceeds stepwise. We were able to isolate an intermediate of this reaction and in addition the completely oxidized product, both in crystalline form. They are aggregates of six monomers and show a strong structural relationship with **1** and one another.

$$(LiCH_2N^iPr_2)_6\,(\mathbf{1}) + O_2 \rightarrow [(LiCH_2N^iPr_2)_4(LiOCH_2N^iPr_2)_2]\,(\mathbf{2})$$

$$[(LiCH_2N^iPr_2)_4(LiOCH_2N^iPr_2)_2]\,(\mathbf{2}) + 2\,O_2 \rightarrow (LiOCH_2N^iPr_2)_6\,(\mathbf{3})$$

Only small amounts of these oxidation products **2** and **3** could be isolated in this way, which however allowed complete characterization by NMR spectroscopy and crystal structure determinations. Under these conditions of an air (diluted with inert gas) oxidation we could not exclude formation of products resulting from parallely occurring hydrolysis reactions. The pure oxidation reactions could be reproduced with dry argon containing a few percent of oxygen, but under these conditions further oxidation products were formed (detected by NMR) besides **2** and **3**, which we could neither identify nor separate.

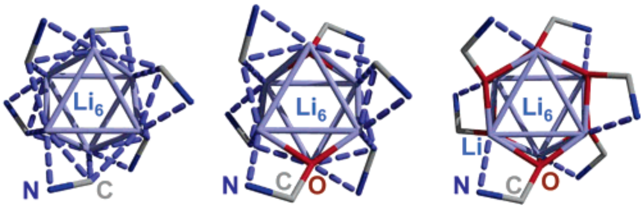

Figure 2. Cores of the crystal structures of compounds **1**, **2**, and **3** (isopropyl groups and hydrogen atoms omitted for clarity) showing the Li_6 clusters with the uncapped Li_3 triangles on top and bottom.

The isolated and in this way characterized oxidation products could be detected in these mixtures by means of their characteristic NMR signals besides other unidentified oxidation products. However, the two isolated intermediates of the oxidative degradation of **1** give interesting insight into the reaction mechanism of oxidations of organolithium compounds. **2** and **3** are further examples of α-amino lithium alkoxides, a class of compounds that has been explored by other synthetic procedures.[20]

The oxidation product formation can be monitored by NMR spectroscopy. In the proton NMR spectrum of **1** only the resonances of the $^iPr_2NCH_2$ groups are detected. The partially oxidized **2** shows similar signals (2.81, 3.04, 1.08 ppm) for the nonoxidized units and in addition peaks for the oxidized groups at 4.63 (OCH_2), 3.35 (CH), and 1.20 ppm (CH_3), both sets in the correct integral ratio 2:1, which is consistent with the composition $[(LiCH_2N^iPr_2)_4(LiOCH_2N^iPr_2)_2]$.

For **3** the ^1H NMR spectrum contains only one set of signals for the $^iPr_2NCH_2O$ units (4.64, 3.36, 1.22 ppm) and one set for the ^{13}C NMR at 46.9 (NCH) and 21.7 (CH_3). This is consistent with a molecular S_6 symmetry in the cluster $(LiOCH_2N^iPr_2)_6$.

According to this high symmetry, the ^7Li NMR spectra of **1** (1.2 ppm) and **3** (0.5 ppm) contain expectedly one signal each, but for **2** one observes three signals at 0.5, 0.7, and 1.2 ppm, which is consistent with the lower symmetry C_i and three chemically different Li sites. However, the interaggregate exchange processes cannot be excluded on the basis of our experimental data.

Crystal Structures. The most polar compound **3** formed crystals of good quality, but as in the case of **1** no crystals of high quality could be grown of **2**. These crystals of **2** were also very soft. The crystals of compounds **2** and **3** are centrosymmetric and arranged about the inversion center of their triclinic cells (space group $P\bar{1}$, see Figures 2 and 3). As for **1** geometry optimizations at the B3LYP/6-311G* level were undertaken for the simpler model compounds for **2** and **3** with the isopropyl groups replaced by methyl units: $[(LiCH_2NMe_2)_4(LiOCH_2NMe_2)_2]$ (**2a**) and $(LiOCH_2NMe_2)_6$ (**3a**). During the calculations it turned out that these mol-

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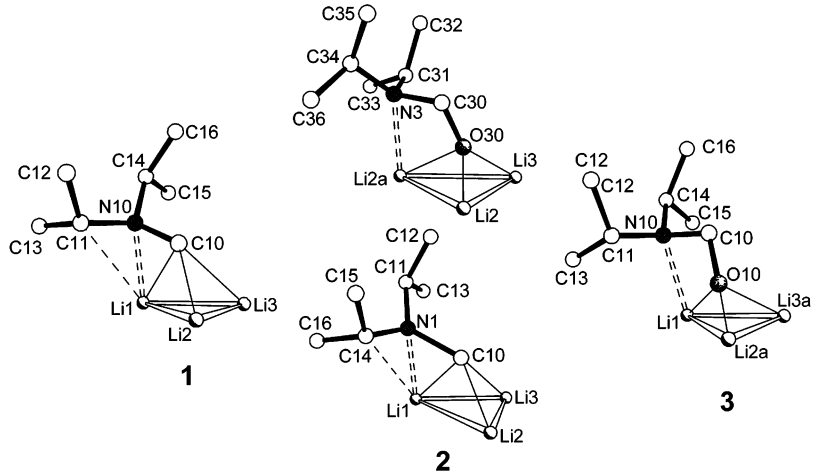

2

Figure 3. Structural elements of compounds **1**, **2**, and **3**.

Table 2. Selected Structural Parameters for $[(LiCH_2N^iPr_2)_4(LiOCH_2N^iPr_2)_2]$ (2) as Determined by Crystallography and for $[(LiCH_2NMe_2)_4(LiOCH_2NMe_2)_2]$ (2a) as Calculated at the B3LYP/6-311G* Level of Theory (Å, deg)

parameter	**2**/XRD	**2a**/B3LYP
O30−Li1	1.931(15)	1.841
O30−Li3	1.790(15)	1.926
O30−Li2a	1.940(15)	1.946
O30−C30	1.316(9)	1.377
C30−N3	1.479(9)	1.497
N3−Li2a	2.188(14)	2.174
O30−C30−N3	110.6(7)	110.2
C10−Li1	2.179(15)	2.210
C10−Li2	2.235(15)	2.254
C10−Li3	2.623(16)	2.349
C10−N1	1.742(12)[a]	1.509
C14−Li1	2.730(16)	2.805
N1−C10−Li1	65.6(5)	61.5

[a] This value is probably strongly affected by the extremely elongated thermal ellipsoid of the carbon atom C(10), which is coarsely oriented to the center of the Li triangle and seems unrealistic in comparison to the theoretical value for the related compound **3a**.

Table 3. Selected Structural Parameters for $(LiOCH_2N^iPr_2)_6$ (3) as Determined by Crystallography and for $[(LiOCH_2NMe_2)_6]$ (3a) as Calculated at the B3LYP/6-311G* Level of Theory (Å, deg)

parameter	**3**/XRD	**3a**/B3LYP
O10−Li1	1.981(4)	2.009
O10−Li2a	1.846(4)	1.862
O10−Li3a	1.951(4)	1.955
O10−C10	1.366(3)	1.370
C10−N10	1.483(3)	1.497
N10−Li1	2.197(4)	2.169
N10−C10−O10	110.2(2)	110.5
C10−O10−Li1	92.0(2)	92.4

ecules adopt the highest possible symmetry: **2a** C_i (as in the crystal) and **3a** S_6. Despite the symmetry differences between **3** and **3a**, the calculated and experimental geometries of the central parts of these molecules are in agreement for most parameters. These data are presented in Tables 2 and 3. The geometry optimization for **3a** did finally not meet the standard convergence criteria completely but approximately, probably due to a flat potential hypersurface.

In the partially oxidized **2** and the fully oxidized **3** the major structural features, the Li_6 trigonal prism, the six capped irregular triangles, and the Li···N contacts, are still present. As in **1** the noncapped triangles have the larger Li−Li distances in these structures (**2**: 3.07(2)−3.12(2) Å, **2a**: 2.998−3.206 Å, **3**: 3.133(5)−3.205(5) Å, **3a**: 3.193 Å) and the capped triangles have two short (**2**: 2.57(2)−2.62(2) Å, **2a**: 2.556−2.588 Å, **3**: 2.578(5)−2.607(5) Å, **3a**: 2.560 Å) and one long side common with the uncapped triangles. The nitrogen atoms in **2** and **3** are still linked to the vertexes of the Li_6 cluster.

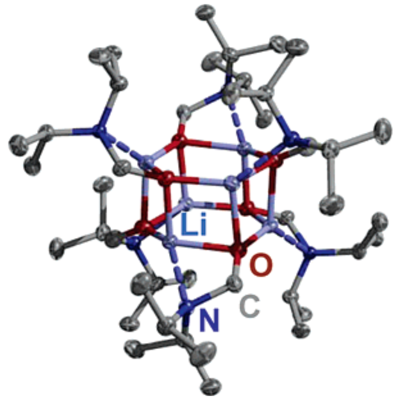

Figure 4. Crystal structure of **3** with topological Li−Li linking lines omitted showing the alternative description as drum-like structure. Hydrogen atoms are omitted for clarity.

By omitting the topological lines between the Li atoms, molecule **3** can be described alternatively as a drum-like Li_6O_6 cluster shown in Figure 4, which is an established structural motif for lithium alkoxides[18] such as $[LiOCMe_2Ph]_6$[19] and in $[LiOCH(C_6H_4Me)N(Me)CH_2CH_2NMe_2]_6$[20] (also with OCN units and Li···N contacts). Note also that mixed lithium alkoxide/lithium alkyl clusters have been described before, e.g., in the *n*-BuLi complexes with anisyl fencholate, which were employed in enantioselective *n*-BuLi additions to aldehydes.[21]

***N,N*-Diisopropylaminomethyldimethylaluminum 4 and -gallium 5. Synthesis.** $(LiCH_2N^iPr_2)_6$ (**1**) can be used as a nucleophilic reagent to transfer $CH_2N^iPr_2$ groups to other elements, which we shall demonstrate here in two examples. The reactions with dimethylaluminum and -gallium chloride give the respective

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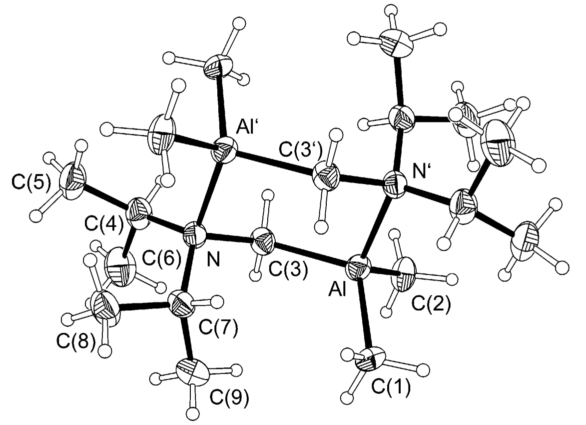

Figure 5. Crystal structure of **4**. Thermal ellipsoids are plotted at the 50% probability level. Selected bond lengths (Å) and angles (deg): Al−C(1) 2.007(2), C(1)−Al−C(2) 112.3(1), Al−C(2) 2.003(2), C(1)−Al−C(3) 118.3(1), Al−C(3) 2.024(2), C(2)−Al−C(3) 100.0(1), Al−N′ 2.042(1), Al−C(3)−N 126.5(1), N−C(3) 1.521(2); N′−Al−C(1) 105.3(1), N−C(4) 1.526(2), N′−Al−C(2) 114.5(1), N−C(7) 1.522(2), N′−Al−C(3) 106.7(1), C(4)−C(5) 1.525(3), N−C(4)−C(5) 114.8(1), C(4)−C(6) 1.529(3), N−C(4)−C(6) 115.5(2), C(7)−C(8) 1.526(3), N−C(7)−C(8) 114.4(1), C(7)−C(9) 1.533(3), N−C(7)−C(9) 116.2(2).

(diisopropylaminomethyl)dimethylmetal compounds.

$$3\ (\mathrm{Me_2AlCl})_2 + (\mathrm{LiCH_2N}^i\mathrm{Pr_2})_6 \rightarrow 3\ (\mathrm{Me_2AlCH_2N}^i\mathrm{Pr_2})_2\ (\mathbf{4}) + 6\ \mathrm{LiCl}$$

$$3\ (\mathrm{Me_2GaCl})_2 + (\mathrm{LiCH_2N}^i\mathrm{Pr_2})_6 \rightarrow 3\ (\mathrm{Me_2GaCH_2N}^i\mathrm{Pr_2})_2\ (\mathbf{5}) + 6\ \mathrm{LiCl}$$

All compounds reported in this section are sensitive to oxygen and water, with the sensitivity of the aluminum compound **4** being lower than that of the gallium compound **5**. Solutions in hydrocarbons contain the dimers, as can be seen from the NMR signals of the isopropyl groups at the nitrogen atoms and the methyl groups at the aluminum atoms, which reflect axial and equatorial positions in six-membered cyclohexane-like rings.

Crystal Structures of $(\mathbf{Me_2AlCH_2N^iPr_2})_2$ (4) and $(\mathbf{Me_2GaCH_2N^iPr_2})_2$ (5). In contrast to the earlier reported pair of methyl analogues $(\mathrm{Me_2AlCH_2NMe_2})_2$ and $(\mathrm{Me_2GaCH_2NMe_2})_2$,[13] **4** and **5** are not isomorphous. Compound **4** crystallizes in the monoclinic space group *C*2/*c* and has a chair conformation similar to $(\mathrm{Me_2AlCH_2NMe_2})_2$,[13] with a center of inversion in the middle of the six-membered $\mathrm{Al_2C_2N_2}$ ring (Figure 5). Deviating from this, **5** crystallizes in the space group $P2_1/c$ and adopts a boat conformation with the carbon atoms C(5) and C(6) in the bow and stern positions (Figure 6). This boat conformation was already found in the heteronorbornane systems $[(\mathrm{Me_2MCH_2NMe})_2\mathrm{CH_2}]$ (M = Al, Ga).[7a]

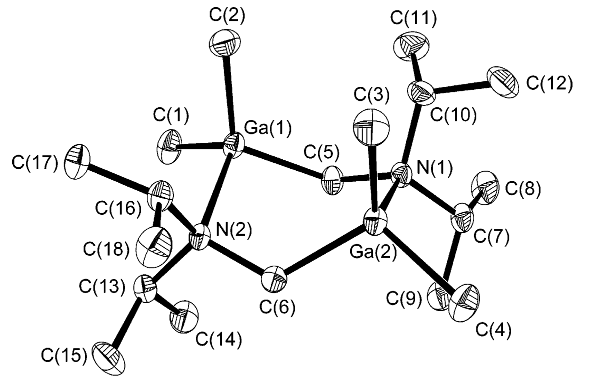

Figure 6. Crystal structure of **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are plotted at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ga(1)−C(1) 1.980(2), C(1)−Ga(1)−C(2) 108.2(1), Ga(1)−C(2) 1.985(2), C(1)−Ga(1)−C(5) 110.9(1), Ga(1)−C(5) 2.012(2), C(2)−Ga(1)−C(5) 118.4(1), Ga(1)−N(2) 2.173(2), Ga(1)−C(3)−N(1) 121.4(1), N(1)−C(5) 1.494(2), N(2)−Ga(1)−C(1) 108.6(1), N(1)−C(7) 1.517(2), N(2)−Ga(1)−C(2) 110.0(1), N(1)−C(10) 1.513(2), N(2)−Ga(1)−C(3) 100.3(1), Ga(2)−C(3) 1.988(2); C(1)−Ga(1)−C(2) 112.3(1), Ga(2)−C(4) 1.984(2), C(1)−Ga(1)−C(3) 118.3(1), Ga(2)−C(6) 2.008(2), C(2)−Ga(1)−C(3) 100.0(1), Ga(1)−N′ 2.173(2), Ga(1)−C(3)−N 126.5(1), N−C(3) 1.521(2), N′−Ga(1)−C(1) 105.3(1), N−C(4) 1.526(2), N′−Ga(1)−C(2) 114.5(1), N−C(7) 1.522(2), N′−Ga(1)−C(3) 106.7(1).

Unaffected by the conformations, the M−C−N angles in both compounds are distinctly larger than the tetrahedral angle, which is consistent with the absence of any significant attractive interaction between the acceptor centers (Al, Ga) and the donor atoms (N) in the same MCN monomer units. The Ga−C−N angles in **5** at 121.4(1)° and 122.2(2)° are only slightly larger than in $(\mathrm{Me_2GaCH_2NMe_2})_2$ [119.7(2)°],[13] whereas the Al−C−N angle in **4** at 126.5(1)° is more than 5° larger than the corresponding angle in $(\mathrm{Me_2AlCH_2NMe_2})_2$ [121.0(1)°].[13] This means that a valence angle at a four-valent carbon atom is widened by 17° with respect to the ideal tetrahedral angle, which could be expected in a strain-free situation of a six-membered ring.

The greater steric demand at the nitrogen atoms caused by the isopropyl groups is reflected by the M−N distances in the rings of crystalline **4** and **5**, 2.042(1) and 2.173(2) Å, which are larger than in the methyl compounds $(\mathrm{Me_2AlCH_2NMe_2})_2$ and $(\mathrm{Me_2GaCH_2NMe_2})_2$ at 2.010(1) and 2.093(2) Å. The latter values are closer to the stericly almost unaffected compounds $\mathrm{Me_3N{\cdot}AlH_3}$ [2.063(7) Å in the solid][25] or $\mathrm{Me_3N{\cdot}AlMe_3}$ [2.045(1) Å in the solid][26] and $\mathrm{Me_3N{\cdot}GaH_3}$ [2.081 Å in the solid][27] and $\mathrm{Me_3N{\cdot}GaMe_3}$ [2.09(5) Å in the gas phase].[28]

Experimental Section

General Methods. All experiments were carried out under a dry nitrogen atmosphere with standard Schlenk and high-

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Table 4. Crystal and Refinement Data for the Solid State Structures of Compounds 1−5

	1	**2**	**3**	**4**	**5**
	$(LiCH_2N^iPr_2)_6$	$(LiCH_2N^iPr_2)_4\cdot(LiOCH_2N^iPr_2)_2$	$(LiOCH_2N^iPr_2)_6$	$(Me_2AlCH_2N^iPr_2)_2$	$(Me_2GaCH_2N^iPr_2)_6$
formula	$C_7H_{15}LiN$	$C_{21}H_{24}Li_3N_3O$	$C_{21}H_{24}Li_3N_3O_3$	$C_9H_{22}AlN$	$C_{18}H_{44}Ga_2N_2$
cryst syst	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/c$
diffractometer	Nonius Turbo-CAD4	Bruker AXS	Nonius Kappa-CCD	Bruker Apex	Bruker Apex
λ	0.71073	1.54184	0.71073	0.71073	0.71073
a [Å]	11.485(1)	11.122(1)	11.258(1)	13.959(1)	8.645(2)
b [Å]	11.723(1)	11.801(1)	11.838(1)	16.665(1)	13.422(4)
c [Å]	11.796(1)	12.154(1)	12.303(1)	10.589(1)	19.003(5)
α [deg]	109.00(1)	117.12(1)	117.17(1)	90	90
β [deg]	109.00(1)	97.38(1)	97.53(1)	116.36(1)	100.203(5)
γ [deg]	108.37(1)	108.15(1)	108.36(1)	90	90
V [Å^3]	1272.9(1)	1278.2(1)	1309.1(2)	2207.2(3)	2170.1(10)
ρ_{calc} [g cm^{-3}]	0.940	0.986	1.044	1.031	1.310
Z	6	2	2	8	4
μ [mm^{-1}]	0.053	0.432	0.066	0.133	2.484
temp [K]	143(2)	150(2)	198(2)	198(2)	173(2)
$2\theta_{max}$ [deg]	64	125.2	55.0	55.7	30.1
no. of measd reflns	51 435	6615	8521	4326	24 334
no. of unique reflns	7775	3738	5990	2620	6322
no. of obsd reflns	6630	3457	5990		5055
R_{int}	0.034	0.138	0.025	0.019	0.056
no. of params	268	254	415	166	375
R [$I > 2\sigma(I)$]/w$R2$	0.133/0.374	0.138/0.346	0.065/0.173	0.044/0.126	0.034/0.078
ρ_{fin}(max./min.) [e Å^{-3}]	−0.53/2.06	−0.30/0.79	−0.36/0.39	−0.23/0.36	−0.58/0.95
CCDC no.	214428	214429	214430	237522	237523

vacuum techniques or in a glovebox operated under argon. Solvents were purified and dried by standard techniques. All NMR spectra were recorded on a Bruker ARX300 (^{1}H 300.1 MHz, ^{13}C 75.5 MHz), a Varian Inova 500 (^{1}H 499.8 MHz, ^{13}C 125.7 MHz, ^{7}Li 194.3 MHz), or a Varian Unity Plus 600 (^{1}H 599.8 MHz, ^{13}C 150.8 MHz) in C_6D_6 or THF-d_8 as solvent dried over K/Na alloy.

$Me_3SnCH_2N(^iPr)_2$. K_2CO_3 (27.6 g, 200 mmol) was added to a stirred solution of $HN(^iPr)_2$ (40 mL, 300 mmol) in acetonitrile (120 mL) and stirred for 10 min at 0 °C. Me_3SnCH_2I[16] (30 g, 98 mmol) in acetonitrile (20 mL) was added dropwise at 20 °C. After stirring for 10 days and filtration the phases were separated, the aqueous one washed two times with 10 mL of ether. The combined organic phases were dried ($MgSO_4$) and concentrated under vacuum. $Me_3SnCH_2N(^iPr)_2$ (17.6 g, 65%) was isolated by fractional distillation, bp 32−34 °C/0.01 Torr. ^{1}H NMR (C_6D_6): δ 0.22 (s, 9H, $SnCH_3$, $^1J_{CH} = 128.1$ Hz, $^2J_{119SnH} = 56.4$ Hz, $^2J_{117SnH} = 52.8$ Hz), 1.07 (d, 12H, $NCCH_3$, $^3J_{HH} = 6.5$ Hz, $^1J_{CH} = 124.0$ Hz), 2.61 (s, 2H, $SnCH_2N$, $^1J_{CH} = 134.2$ Hz, $^2J_{117SnH} = 24.3$ Hz, $^2J_{119SnH} = 33.9$ Hz), 2.97 (sept, 2H, NCHC, $^3J_{HH} = 6.5$ Hz). ^{13}C NMR (C_6D_6): δ −10.8 ($SnCH_3$, $^1J_{117SnC} = 290.4$ Hz, $^1J_{119SnC} = 304.4$ Hz), 20.8 ($NCCH_3$), 33.7 ($SnCH_2N$, $^1J_{117SnC} = 458.0$ Hz, $^1J_{119SnC} = 479.2$ Hz), 50.7 (NCH). MS: *m/z* 279 (M^+), 264 ($M^+ - Me$), 165 (Me_3Sn^+). Anal. Calcd for $C_{10}H_{25}NSn$ (278.01 g mol^{-1}): C 43.20 H 9.06 N 5.04. Found: C 43.43 H 9.21 N 5.19.

$[LiCH_2N(^iPr)_2]_6$. *n*-BuLi (1.6 M in hexane, 40 mL, 64 mmol) was added to a stirred solution of $Me_3SnCH_2N(^iPr)_2$ (17.6 g, 64 mmol) in 100 mL of hexane at −78 °C. After stirring overnight and concentration under reduced pressure, storage at −78 °C led to precipitation of the crude product. This was washed with 3 portions of hexane (30 mL) and dried under vacuum. Yield: 5.1 g (67%). ^{1}H NMR (C_6D_6): δ 1.02 (d, 12H, $NCCH_3$, $^3J_{HH} = 6.4$ Hz), 2.15 (s, 2H, $LiCH_2N$), 2.87 (sept, 2H, NCHC, $^3J_{HH} = 6.5$ Hz). ^{13}C NMR (C_6D_6): δ 20.9 (CH_3), 32.3 (LiCN), 51.8 (NCH). ^{7}Li NMR (C_6D_6): δ 1.2 (reference 1 M LiBr solution in H_2O). Anal. Calcd for $C_{42}H_{96}N_6Li_6$ (726.91 g mol^{-1}): C 69.40 H 13.31 N 11.56. Found: C 69.21 H 13.14 N 11.39.

Oxidation Products of $[LiCH_2N(^iPr)_2]_6$. A solution of $[LiCH_2N(^iPr)_2]_6$ in contact with small amounts of air led to the crystallization of small amounts of $[LiCH_2N(^iPr)_2]_4[LiOCH_2N(^iPr)_2]_2$ upon cooling to −25 °C. ^{1}H NMR (C_6D_6): δ 1.08 (d, 48H, $CNCCH_3$, $^3J_{HH} = 6.1$ Hz), 1.20 (d, 24H, $OCNCCH_3$, $^3J_{HH} = 6.6$ Hz), 2.81 (s, 8H, $LiCH_2N$), 4.63 (s, 4H, $LiOCH_2N$), 3.04 (sept, 8H, CNCH, $^3J_{HH} = 6.5$ Hz), 3.35 (sept, 4H, OCNCH, $^3J_{HH} = 6.9$ Hz). ^{7}Li NMR (C_6D_6): δ 0.5, 0.7, 1.2 (reference 1 M LiBr solution in H_2O). After prolonged contact with air or oxygen in argon complete oxidation led to $[LiOCH_2N(^iPr)_2]_6$, which was obtained in crystalline form upon cooling the solution to −25 °C. ^{1}H NMR (D_8-THF): δ 1.17 (d, 12H, $OCNCCH_3$, $^3J_{HH} = 6.7$ Hz), 3.31 (sept, 2H, OCNCH, $^3J_{HH} = 6.6$ Hz), 4.59 (s, 2H). ^{13}C NMR (THF): δ 21.7 (CH_3), 57.1 (NCH). ^{7}Li NMR (C_6D_6): δ 1.2 (reference 1 M LiBr solution in H_2O).

$Me_2AlCH_2N^iPr_2$. A solution of Me_2AlCl in hexane (1 M, 4.0 mL, 4.0 mmol) was added dropwise to a stirred suspension of $LiCH_2N^iPr_2$ (0.49 g, 4.0 mmol) in hexane (40 mL) at −78 °C. The reaction mixture was stirred overnight at this temperature and then allowed to warm to ambient temperature. The mixture was filtered through a sintered glass filter (porosity no. 4), and the resulting clear solution was concentrated under vacuum until it became slightly cloudy. Upon warming to room temperature, the solution became clear again. The vessel with this solution was immersed in a 1 L Dewar container filled with ethanol and allowed to cool slowly to −25 °C in refrigerator overnight. Colorless, well-formed crystals were obtained in this way. Yield: 0.37 g, 55%. Mp: 96 °C. ^{1}H NMR (C_6D_6): δ −0.37 (s, 6H, ax/eq $AlCH_3$), −0.29 (s, 6H, ax/eq $AlCH_3$), 1.01 (d, 12H, ax/eq $NCCH_3$, $^3J_{HH} = 6.8$ Hz), 1.16 (d, 12H, ax/eq $NCCH_3$, $^3J_{HH} = 6.9$ Hz), 2.03 (s, 4H, $AlCH_2N$), 3.30 (sept, 2H, ax/eq NCHC, $^3J_{HH} = 6.2$ Hz), 3.34 (sept, 2H, ax/eq NCHC, $^3J_{HH} = 7.3$ Hz). ^{13}C NMR (C_6D_6): δ −1.0 ($AlCH_3$), 19.3 (ax/eq CCH_3), 22.6 (ax/eq CCH_3), 39.6 ($AlCH_2$), 57.7 (NCH). Anal. Calcd for $C_{12}H_{30}N_2Al_2$ (342.52 g mol^{-1}): C 63.12, H 12.95, N 8.18. Found: C 62.17, H 12.80, N 7.78.

$Me_2GaCH_2N^iPr_2$. A solution of Me_2GaCl (0.69 g, 5.1 mmol) in hexane (20 mL) was added dropwise to a stirred suspension of $LiCH_2N^iPr_2$ (0.62 g, 5.1 mmol) in hexane (30 mL) at −78 °C. The reaction mixture was stirred for 4 h at this temperature and allowed to warm to ambient temperature overnight. The mixture was filtered through a sintered glass filter (porosity no. 4), and the resulting clear solution was concentrated under vacuum until it became slightly cloudy. It was allowed to warm to room temperature and became clear again. The vessel with this solution was immersed in a 1 L Dewar container filled with ethanol and allowed to cool slowly to −25 °C in a refrigerator overnight. Colorless, well-formed crystals were obtained in this way. Yield: 0.74 g, 69%. Mp: 82 °C. ^{1}H NMR (C_6D_6): δ 0.06 (s, 6H, ax/eq $GaCH_3$), 0.08 (s, 6H, ax/eq $GaCH_3$), 1.02 (d, 12H, ax/eq $NCCH_3$, $^3J_{HH} = 6.6$ Hz), 1.09 (d, 12H, ax/eq $NCCH_3$, $^3J_{HH} = 6.8$ Hz), 2.12 (s, 4H, $GaCH_2N$), 3.26 (sept., 2H, ax/eq NCHC, $^3J_{HH} = 6.5$ Hz), 3.34 (sept., 2H, ax/eq NCHC, $^3J_{HH} = 6.5$ Hz). ^{13}C NMR (C_6D_6): δ −1.4 ($GaCH_3$), 19.3 (ax/eq CCH_3), 20.5 (ax/eq CCH_3), 37.7 ($GaCH_2$), 54.1 (NCH). Anal. Calcd for $C_{12}H_{30}N_2Ga_2$ (428.00 g mol^{-1}): C 50.51, H 10.36, N 6.55. Found: C 49.35, H 9.93, N 6.75.

Crystal Structure Analyses. Single crystals of compounds **1**, **2**, **3**, **4**, and **5** were mounted under inert perfluoropolyether at the tip of a glass fiber and cooled in the cryostream of the diffractometer. Intensity corrections were applied to the data of **1** by the program SCALEPACK.[29] An absorption correction was applied to the data of **2** by means of the program SADABS.[30] The structure solutions were carried out using direct methods, and the refinements of the structure were undertaken with the program SHELXTL 5.01.[31] Non-hydrogen atoms were refined with anisotropic thermal displacement parameters, hydrogen atoms isotropically in a riding model. Further details of data collection and refinement are listed in Table 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications (nos. see Table 4). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Quantumchemical Calculations. DFT calculations were carried out using the Gaussian 98 suite of programs[32] with the methods and basis sets implemented therein.

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Supporting Information Available: Crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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