Terminally Dimetalated Tetramethylethylenediamine (TMEDA) Compounds

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Received June 2, 2005

Terminally dilithiated tetramethylethylenediamine (TMEDA), $LiCH_2N(Me)CH_2CH_2N(Me)CH_2Li$ (**1**), was prepared by transmetalation from $Me_3SnCH_2N(Me)CH_2CH_2N(Me)CH_2SnMe_3$ and *n*-BuLi. It was isolated as a highly air-sensitive white powder and was characterized by elemental analysis and by further transmetalation reactions. Compound **1** was used as a difunctional aminomethylating agent and reacted with R_2MCl (R = Me, *t*-Bu; M = Al, Ga, In) to give the selective formation of 1,2,2,4,5,5-hexamethyl-1,4-diaza-2,5-dimetallabicyclo[2.2.2]octane (M = Al (**2**), Ga (**3**), In (**4**)) and 2,2,5,5-tetra-*tert*-butyl-1,4-dimethyl-1,4-diaza-2,5-dimetallabicyclo[2.2.2]octane (M = Al (**5**), Ga (**6**)) by simultaneous formation of two metal−carbon and two dative metal−nitrogen bonds accompanied by two ring closures. Compounds **2**−**6** were characterized by elemental analyses, by NMR spectroscopy (^1H, ^{13}C, ^{27}Al), and by crystal structure determinations. The 1,4-diazabicyclo[2.2.2]octane-like structure is favored over potential isomers containing three-membered rings and over polymeric aggregation. Despite the high steric demand of the *tert*-butyl groups, this conformation persists even in the case of **5** and **6**.

Introduction

α-Lithiated amines (R_2NCH_2Li) are important reagents for nucleophilic introduction of aminomethyl groups in synthetic procedures[1] and are difficult to prepare as compared to other α-heteroatom-substituted methyllithium compounds such as (phosphinomethyl)lithium (R_2PCH_2Li) and (thiomethyl)lithium compounds ($RSCH_2Li$), due to the fact that they are formally nonstabilized carbanionic compounds. For the synthesis of such compounds there are only a few methodologies available.[2] Among those, direct deprotonation of tertiary amines is restricted to a limited number of examples, the most impressive being the terminally dilithiated aminal $LiCH_2N(Me)CH_2N(Me)CH_2Li$,[3] which has been used to prepare derivatives of Zr,[4] Ni,[5] Al,[6−8] Ga,[6,9] and In.[8] Recently there was also a report on direct deprotonation of *N,N′,N″*-trimethyl-1,4,7-triazacyclononane, which occurred also at the position of the methyl group rather than at the methylene carbon.[10] Among the procedures of element−carbon bond cleavage, the reductive C−S bond cleavage of an S,N-acetal was employed to prepare *N,N′*-bis(lithiomethyl)piperazine, $LiCH_2N(CH_2CH_2)_2NCH_2Li$.[11] The transmetalation of α-(aminomethyl)stannanes introduced by Peterson in 1970[12] and developed by Seyferth et al.[13] is still the most generally applicable method for the preparation of (aminomethyl)lithium compounds.[2]

Tetramethylethylenediamine (TMEDA) is an important auxiliary base in reactions of alkyllithium compounds.[14] Some work on the deprotonation of TMEDA has already been reported. Treatment of TMEDA with *t*-BuLi has been reported to remove a methyl proton, while with the combination *n*-BuLi/KO^{t}Bu one obtains deprotonation at one methylene site.[15] These deprotonated species have not been isolated but were quenched with trimethylchlorostannane, and the resulting trimethylstannyl compounds were detected by NMR methods. Our interest in this context was the synthetic application of difunctional aminomethylating agents for the preparation of organo earth metal compounds containing two saturated M−C−N units (M = Al, Ga, In). Dilithiated TMEDA has already been reported in the literature by Katritzky and co-workers[16] but was then not isolated but obtained as a 1:2 mixture with LiSPh by cleavage of two C−S bonds in $PhSCH_2N(Me)CH_2CH_2N(Me)CH_2SPh$. This dilithiated species had success-

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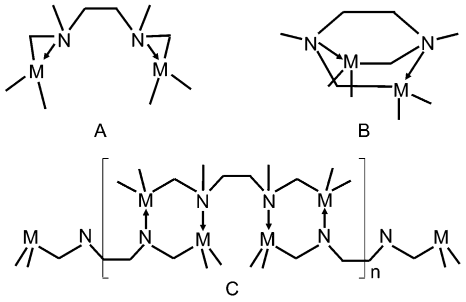
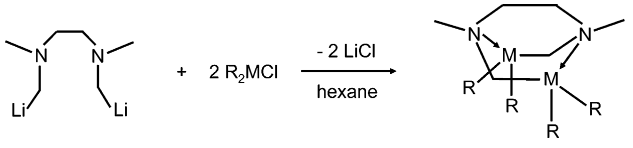
10.1021/om0504405 CCC: $30.25 © 2005 American Chemical Society
Publication on Web 09/29/2005

Chart 1



Scheme 1



(**1**)

Compound: (**2**) R = Me, M = Al
(**3**) R = Me, M = Ga
(**4**) R = Me, M = In
(**5**) R = ^{t}Bu, M = Al
(**6**) R = ^{t}Bu, M = Ga

fully been trapped by electrophiles, but the procedure requires aqueous workup to remove the accompanying weaker nucleophile LiSPh. For our purposes, the transformation into other reactive organometal compounds, an aqueous workup cannot be applied, and therefore we had to obtain $LiCH_2N(Me)CH_2CH_2N(Me)CH_2Li$ in a pure form.

In this contribution we report on the synthesis and the first isolation of doubly terminally lithiated TMEDA, its reactions with dialkylmetal chlorides of Al, Ga, and In, and the properties and aggregations of these homobiearth-metallic compounds. There are at least three possible aggregation modes for such compounds (Chart 1): two three-membered rings (A), a compact structure containing three six-membered rings (B), and six-membered rings in polymeric arrays (C). Crystal structure determinations reveal that all these compounds prefer the intramolecular hetero-1,4-diazabicyclo[2.2.2]-octane-like aggregation types (B in Chart 1).

Results

Syntheses of Dilithiated TMEDA (1) and its Organoaluminum, -gallium, and -indium Derivatives. A suitable preparative path to dilithiated TMEDA is the application of the tin/lithium exchange reaction to distannylated TMEDA, $Me_3SnCH_2N(Me)CH_2CH_2N(Me)CH_2SnMe_3$,[18] which was prepared earlier in a condensation reaction from (iodomethyl)trimethylstannane[17] and *N,N′*-dimethylethylenediamine. The tin/lithium exchange can be achieved by addition of *n*-BuLi to a solution of *N,N′*-dimethyl-*N,N′*-bis(trimethylstannylmethyl)ethylenediamine[18] in hexane. The terminally double-lithiated TMEDA, *N,N′*-bis(lithiomethyl)-*N,N′*-dimethylethylenediamine (**1**), was obtained in 78% yield

$$\begin{aligned} &Me_3SnCH_2N(Me)CH_2CH_2N(Me)CH_2SnMe_3 + \\ &\quad 2n\text{-BuLi} \rightarrow 2n\text{-BuSnMe}_3 + \\ &\quad\quad \underset{\mathbf{1}}{LiCH_2N(Me)CH_2CH_2N(Me)CH_2Li} \end{aligned}$$

as a white powder, which is highly pyrophoric in the dry state. It is insoluble in hydrocarbons (hexane, pentane, toluene) but rapidly decomposes in ethers, particularly in THF. Attempts to prepare the compound in diethyl ether or THF with the aim of yielding soluble ether adducts failed. The high reactivity to ethereal solvents and insolubility in hydrocarbons did also not allow us to record NMR spectra in solution. The identity of **1** was proven by elemental analysis and by derivatization reactions.

The reactions of the organolithium compound **1** with 2 equiv of dimethylaluminum, -gallium, and -indium chloride in hexane at −78 °C give the respective aluminum, gallium, and indium compounds with a Me_2Al (**2**)/Me_2Ga (**3**)/Me_2In (**4**) group at each end of the TMEDA skeleton. Analogous reactions can be performed with di-*tert*-butylaluminum and -gallium chlorides to yield the respective aluminum and gallium compounds with terminal $^tBu_2Al$ (**5**) and $^tBu_2Ga$ (**6**) groups (Scheme 1).

These five reactions lead to the simultaneous formation of four chemical bonds (two M−C bonds and two dative N−M bonds) and two ring closures and give 1,2,2,4,5,5-hexamethyl-1,4-diaza-2,5-dimetallabicyclo[2.2.2]octane (M = Al (**2**), Ga (**3**), In (**4**)) and 2,2,5,5-tetra-*tert*-butyl-1,4-dimethyl-1,4-diaza-2,5-dimetallabicyclo[2.2.2]octane (M = Al (**5**), Ga (**6**)).

Compounds **2**−**6** are sensitive to air and, in particular, to moisture. They were isolated as colorless crystalline materials upon cooling hexane solutions to −25 °C. They are readily soluble in nonpolar solvents such as pentane and hexane and even more soluble in toluene or ethers. All compounds are thermally stable up to their melting points, and compounds **2**−**4** can be sublimed under vacuum (10^{-2} Torr) before the onset of melting. All five compounds have been identified by elemental analysis, NMR spectroscopy of the nuclei ^1H and ^{13}C (^{27}Al for compounds **2** and **5**) in C_6D_6, and single crystal X-ray diffraction. In the NMR spectra the typical signal patterns of hetero-1,4-diazabicyclo[2.2.2]octanes are observed: two sets of signals for the two nonequivalent geminal alkyl groups at the metal atoms and the geminal hydrogen atoms of the methylene units connecting the metal and N atoms. It can be derived from the NMR spectra that all reactions in Scheme 1 proceed uniformly and no signs of the presence of other different aggregation types are observed.

Crystal and Molecular Structures of $Me_2MCH_2N(Me)CH_2CH_2N(Me)CH_2MMe_2$ (M = Al (2), Ga (3), In (4)). Compounds **2**−**4** all crystallize as the same hetero-1,4-diazabicyclo[2.2.2]octane-like aggregation type (Figures 1 and 2), but in quite different crystal systems and space groups: compound **1** crystallizes in the triclinic space group $P\bar{1}$, while **2** and **3** crystallize in the same monoclinic system with different space groups, $P2_1/n$ and $C2/c$, respectively.

The molecules of compounds **2**−**4** are C_2 symmetric (pseudo C_2 symmetry for **2** and **3**), with the C_2 axes passing through the middle points of the C−C bond in the bridging ethylene units between two N atoms. This ethylene bridge causes the $M_2C_2N_2$ six-membered ring

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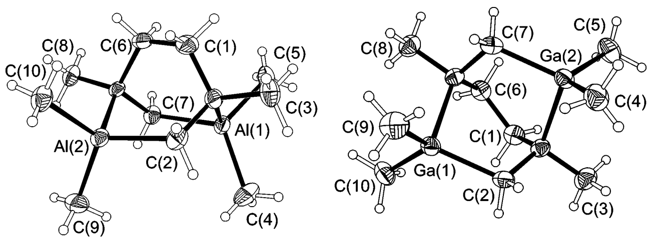

Figure 1. Molecular structures of **2** (left) and **3** (right), drawn with 50% probability ellipsoids.

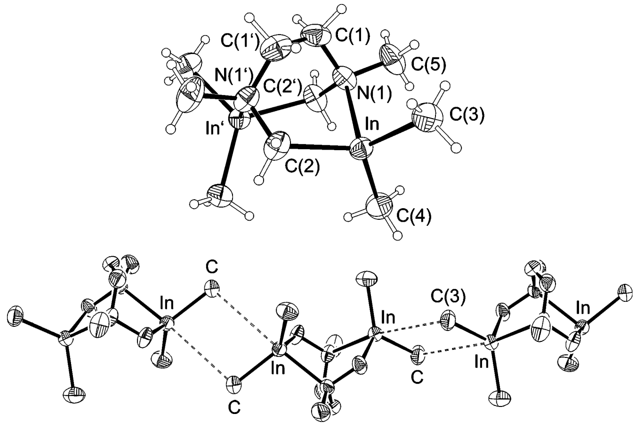

Figure 2. Molecular structure of compound **4** (top) (ORTEP drawing with 50% probability ellipsoids) and intermolecular contacts by In···C contacts (bottom) (hydrogen atoms omitted for clarity).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Solid-State Structures of Compounds 2−6[a]

	2	**3**	**4**	**5**	**6**
C(1)−C(6)	1.526(3)	1.532(4)	1.522(5)	1.541(5)	1.540(3)
C(1)−N(1)	1.485(3)	1.483(3)	1.477(3)	1.485(4)	1.483(2)
N(1)−C(2)	1.509(3)	1.505(3)	1.502(3)	1.525(4)	1.508(2)
N(1)−C(3)	1.481(3)	1.480(3)	1.483(3)	1.488(4)	1.482(2)
M(1)−C(2)	2.000(3)	2.004(3)	2.205(2)	2.006(3)	2.022(2)
M(1)−C(4)	1.961(3)	1.968(3)	2.167(3)	2.038(4)	2.045(2)
M(1)−C(5)	1.989(3)	1.986(3)	2.178(2)	2.046(4)	2.058(2)
M(1)−N(2)	1.992(2)	2.086(2)	2.327(2)	2.008(3)	2.100(2)
C(6)−N(2)	1.483(3)	1.487(3)		1.493(4)	1.484(2)
N(2)−C(7)	1.503(3)	1.497(3)		1.512(4)	1.501(2)
N(2)−C(8)	1.490(3)	1.480(3)		1.487(4)	1.487(2)
M(2)−C(7)	2.004(3)	2.011(3)		2.020(3)	2.026(2)
M(2)−C(9)	1.964(3)	1.976(3)		2.024(4)	2.039(2)
M(2)−C(10)	1.976(3)	1.980(3)		2.041(3)	2.055(2)
M(2)−N(1)	1.996(2)	2.077(2)		2.016(3)	2.106(2)
C(6)−C(1)−N(1)	116.4(2)	116.2(2)	117.6(1)	116.5(3)	116.6(2)
C(1)−N(1)−C(3)	108.3(2)	109.4(2)	109.5(2)	107.9(3)	108.1(2)
C(1)−N(1)−C(2)	107.9(2)	108.7(2)	109.4(2)	107.6(2)	108.8(2)
M(1)−C(2)−N(1)	113.9(2)	113.2(2)	113.1(1)	116.3(2)	116.2(1)
M(1)−N(2)−C(7)	108.9(2)	110.0(2)	107.3(2)	113.6(2)	114.4(1)
C(2)−M(1)−N(2)	96.2(1)	95.7(1)	91.3(1)	93.5(2)	92.4(6)
C(2)−M(1)−C(4)	116.8(1)	114.5(1)	119.0(1)	116.5(2)	117.7(7)
C(2)−M(1)−C(5)	115.8(1)	113.1(1)	114.3(1)	108.6(2)	109.0(7)
C(4)−M(1)−C(5)	115.4(1)	120.3(1)	119.7(1)	113.0(2)	113.7(7)
C(1)−C(6)−N(2)	116.3(2)	115.2(2)		116.0(3)	116.3(1)
C(6)−N(2)−C(7)	108.1(2)	108.9(2)		107.9(2)	109.0(1)
C(6)−N(2)−C(8)	108.0(2)	109.0(2)		107.8(3)	108.0(1)
M(2)−C(7)−N(2)	113.9(2)	113.2(2)		116.2(2)	116.1(1)
M(2)−N(1)−C(2)	109.2(2)	110.0(2)		112.6(2)	113.8(1)
C(7)−M(2)−N(1)	96.1(1)	95.6(1)		93.3(2)	92.4(1)
C(7)−M(2)−C(9)	115.2(1)	118.1(1)		116.0(2)	117.1(1)
C(7)−M(2)−C(10)	112.3(1)	114.2(1)		109.2(2)	109.6(1)
C(7)−M(2)−C(10)	116.2(1)	116.6(1)		113.0(2)	113.5(1)

[a] For 4 there is molecular symmetry, due to which only a half parameter set is given. Relationship of Figure 2 → Table 1: N(1′) → N(2); C(*n*′) → C(*n* + 5).

to adopt a boat conformation, typical for the 1,4-diazabicyclo[2.2.2]octane skeleton with the two N atoms at the bow and stern positions. Thus, this leads to compressed endocyclic N−M−C angles at the metal atoms (Table 1: **2**, 96.2(1) and 96.1(1)°; **3**, 95.7(1) and 95.6(1)°, **4** (even smaller), 91.3(1)°) and enlarged M−C−N angles (**2**, both 113.9(1)°; **3**, both 113.2(2)°; **4**, 113.1(1)°) related to N−C−C angles of the 1,4-diazabicyclo[2.2.2]-octane moieties in $Me_3M{\cdot}N(CH_2CH_2)_3N{\cdot}MMe_3$ (M = Al, Ga; 110.8(7)−111.7(5)°)[19] and in $H_3B{\cdot}N(CH_2CH_2)_3N{\cdot}BH_3$ (108.9(3)−109.7(3)°).[20] Both the N−M−C angles and M−C−N angles in compounds **2**−**4** are larger (the former more than 10° and the latter more than 5°) than the corresponding endocyclic N−M−C and M−C−N angles of $M_2C_2N_2$ six-membered rings in $[Me_2MCH_2N(Me)]_2CH_2$ (N−M−C angles, Al 86.2(1)°,[6] Ga 85.1(1)°,[6] In 79.6(1)°;[8] M−C−N angles, Al 105.8(1)°,[6] Ga 106.3(1)°,[6] In 107.2(1)°[8]). The much smaller N−In−C angles in **4** and $[Me_2InCH_2N(Me)]_2CH_2$ compared to those in its lighter Al and Ga analogues may be due to the distortion caused by the larger covalent radius of the In atom (In, 1.44 Å; Al, 1.18 Å; Ga, 1.26 Å).[21] These angles at the metal atoms are more than 10° smaller than the ideal tetrahedral angle, and the sums of three C−M−C angles at the metal atoms reflect the distortions from ideal tetrahedral coordination geometry: the weakest distortion is observed for **2** (346.4 and 344.0°) and a medium distortion is found for **3** (348.3 and 349.3°), while the coordination geometry at the In atoms in **4** represents the strongest deformation (353.0°) and is actually close to that in the planar Me_3In.[22] The trigonal-planar coordination of the primary bonds and an almost perpendicular orientation of the dative bond to this plane in **4** is quite similar to that formed in $[Me_2InCH_2N(Me)]_2CH_2$[8] and two other four-coordinate organoindium compounds, $Me_2In(C_6H_4CH_2NEt_2)$[23] and $(F_5C_6)_2In(CH_2)_3NMe_2$.[24] This arrangement makes the indium atoms in compound **4** accessible for short distance contacts from the side opposite to the dative In−N bond and results in intermolecular In···C distances of 3.775(2) Å (shown at the bottom of Figure 2), which is close to the sum of the van der Waals radii ($r_{VdW,C}$ = 1.70 Å; $r_{VdW,In}$ = 1.93 Å).[21]

The N−C−C angles of the bridging ethylene units (**2**, 116.2(1) and 116.5(1)°; **3**, 115.3(1) and 116.1(1)°; **4**, 117.6(1)°) are much larger than the N−C−C angles in the $N(CH_2CH_2)_3N$ skeleton in $Me_3M{\cdot}N(CH_2CH_2)_3N{\cdot}MMe_3$ (M = Al, Ga) (110.8(7)−111.7(5)°)[19] and in $H_3B{\cdot}N(CH_2CH_2)_3N{\cdot}BH_3$ (108.9(3)−109.7(3)°).[20] The endocyclic C−M bonds (**2**, 2.000(3), 2.004(3) Å; **3**, 2.004(3), 2.011(3) Å; **4**, 2.205(2) Å) and C−N bonds (**2**, 1.509(3), 1.508(3) Å; **3**, 1.505(3), 1.500(3) Å; **4**, 1.502(2) Å) in the $M_2C_2N_2$ rings are much longer compared to the C−In

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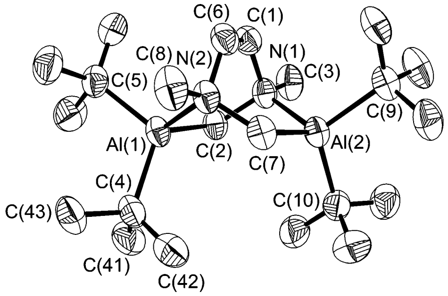

Figure 3. Molecular structure of **5** (hydrogen atoms omitted for clarity), drawn with 50% probability ellipsoids. Compound **6** is isostructural.

bonds and the C−N bonds pointing to the exocyclic methyl carbons or to the bridging ethylene carbons of the same compound. The dative M−N bonds (**2**, Al−N 1.992(2), 1.996(2) Å; **3**: Ga−N 2.086(2), 2.077(2) Å) are short with regard to the gas-phase values of the sterically almost unaffected simple reference compounds such as $Me_3Al{\cdot}NMe_3$ (2.099(10) Å)[25] and $Me_3Ga{\cdot}NMe_3$ (2.09(3) Å)[26] and also shorter than the M−N bonds in the derivatives we studied before in $[R_2MCH_2N(Me)]_2$-CH_2 (R = Me, ^{t}Bu; M = Al, Ga) (Al−N = 2.010(1)–2.042(1) Å, Ga−N = 2.093(2)–2.173(2) Å).[6,7,9] The In−N bonds in **4** (2.327(2) Å) are almost the same as those in $[Me_2NCH_2InMe_2]_2$ (2.327(2) Å)[8] and $[Me_2InCH_2N(Me)]_2$-CH_2 (2.328(2) Å).[8]

Crystal and Molecular Structures of *t*-$Bu_2MCH_2N(Me)CH_2CH_2N(Me)CH_2M$-*t*-$Bu_2$ (M = Al (5), Ga (6)). As shown in Figure 3, compounds **5** and **6** are isomorphous and crystallize in the monoclinic space group $P2_1/n$. They adopt the same intramolecular aggregation as the three compounds mentioned previously. This means that the introduction of the bulky *tert*-butyl substituents does not change the aggregation into the compact hetero-1,4-diazabicyclo[2.2.2]octane aggregates.

The greater steric demand at the metal atoms caused by the *tert*-butyl groups is reflected by the C−M bonds between metal and *tert*-butyl carbon atoms and N−M dative bonds in $M_2C_2N_2$ six-membered rings. These bonds in **5** (average values: Al−C = 2.037 Å, Al−N = 2.012 Å) and **6** (average values: Ga−C = 2.049 Å, Ga−N = 2.103 Å) are longer than their counterparts in **2** (average values: Al−C = 1.973 Å, Al−N = 1.994 Å) and **3** (average values: Ga−C = 1.988 Å, Ga−N = 1.978 Å). More convincing evidence of the impact of the bulky *tert*-butyl groups is the increase of the two M−N−C angles at the N atoms in the cage (average values: **5**, Al−N−C = 113.1°; **6**, Ga−N−C = 114.1°) and the decrease of two C−M−N angles involved in $M_2C_2N_2$ rings (average values: **5**, C−Al−N = 93.4°; **6**, C−Ga−N = 92.4°) related to their methyl analogues (average values: **2**, Al−N−C = 109.1° and C−Al−N = 96.2°; **3**, Ga−N−C = 110.0° and C−Ga−N = 95.6°). All of these changes are around 3°.

It should be noted that in all the structure parameters of compounds **5** and **6** the trends are very similar to those in the methyl analogues **2** and **3**, and thus they do not deserve a detailed discussion.

Conclusion

Terminally dilithiated TMEDA can be prepared by transmetalation recations from the respective distannylated precursor by treatment with butyllithium. It is afforded as an amorphous powder insoluble in hydrocarbons. It is pyrophoric and so highly reactive that it cannot be handled in ethers, as this leads to quick decomposition. It can serve as valuable building block for the electrophilic introduction of the $-CH_2N(Me)CH_2$-$CH_2N(Me)CH_2-$ unit, which has been demonstrated by reactions with dimethyl and di-*tert*-butyl derivatives of aluminum, gallium, and indium chlorides. These reactions lead by the formation of two metal−carbon bonds and two dative nitrogen−metal bonds to the formation of heterobicyclic compounds of the 1,4-diaza-2,5-dimetallabicyclooctane type. Other aggregation alternatives could not be observed.

Experimental Section

General Remarks. All reactions and manipulations were carried out under a dry nitrogen atmosphere with standard Schlenk and high-vacuum techniques using double manifolds or in a glovebox under argon. Solvents were purified and dried by standard methods immediately prior to use. NMR data were collected on a Bruker ARX300 (300.14 MHz for ^{1}H, 75.48 MHz for ^{13}C) and a Varian Inova 500 (499.8 MHz for ^{1}H and ^{27}Al, 125.7 MHz for ^{13}C) in C_6D_6 as solvent dried over K/Na alloy. Chemical shifts are quoted relative to TMS for ^{1}H and ^{13}C and 1 M $Al(NO_3)_3$ solution in H_2O for ^{27}Al. A Bruker Apex X-ray diffractometer (for **2** and **3**) and a Nonius Kappa-CCD X-ray diffractometer (for **4**−**6**) were used to collect the scattering intensities for the single-crystal structure determinations (both λ = 0.710 73 Å).

$LiCH_2N(Me)CH_2CH_2N(Me)CH_2Li$. $Me_3SnCH_2N(Me)CH_2$-$CH_2N(Me)CH_2SnMe_3$ was prepared by a literature method.[18] Bp: 99−102 °C/0.01 Torr. ^{1}H NMR (C_6D_6): δ 0.18 (s, 18H, $SnCH_3$, $^1J_{CH}$ = 124.6 Hz, $^2J^{117}{}_{SnH}$ = 49.1 Hz, $^2J^{119}{}_{SnH}$ = 52.4 Hz), 2.20 (s, 6H, NCH_3), 2.44 (s, 4H, $SnCH_2N$, $^2J^{117/119}{}_{SnH}$ = 23.4 Hz), 2.53 (s, 4H, NCH_2CN). ^{13}C NMR (C_6D_6): δ = −8.8 ($SnCH_3$, $^1J^{117}{}_{SnC}$ = 289.0 Hz, $^1J^{119}{}_{SnC}$ = 300.5 Hz), 47.0 (NCH_3, $^3J^{117/119}{}_{SnC}$ = 29.5 Hz), 48.4 ($SnCH_2N$, $^1J^{117}{}_{SnC}$ = 389.2 Hz, $^1J^{119}{}_{SnC}$ = 408.8 Hz), 60.2 (NCH, $^3J^{117/119}{}_{SnC}$ = 41.3 Hz).

A hexane solution of *n*-BuLi (1.6 M, 53 mL, 84.8 mmol) was added dropwise to a stirred solution of $Me_3SnCH_2N(Me)CH_2$-$CH_2N(Me)CH_2SnMe_3$ (18 g, 40.7 mmol) in hexane (100 mL) at −78 °C. The reaction mixture was stirred for 12 h, during which time it is allowed to reach ambient temperature. The liquid was separated from the precipitate through a cannula fitted with a glass wool filter, and in the same way the solid product was washed with hexane (3 × 20 mL). The product was then dried under vacuum; yield 4.1 g, 78% (based on distannylated TMEDA). Anal. Calcd for $C_6H_{14}Li_2N_2$ (mol wt 128.07): C, 56.27; H, 11.02; N, 21.87. Found: C, 56.72; H, 11.28; N, 21.73.

General Procedure for the Preparation of R_2MCH_2N-$(Me)CH_2CH_2N(Me)CH_2MR_2$ (M = Al, Ga, In; R = Me, *t*-Bu). **(a) Compounds 2−4.** A solution of Me_2MCl in hexane (20 mL) was added dropwise to a stirred suspension of $LiCH_2N(Me)CH_2$-$CH_2N(Me)CH_2Li$ in hexane (30 mL) at −78 °C.

(b) Compounds 5 and 6. $LiCH_2N(Me)CH_2CH_2N(Me)CH_2$-Li and ^{t}Bu$_2$MCl were mixed in a Schlenk tube in a glovebox. The Schlenk tube was cooled to −78 °C, and 60 mL of hexane was added slowly with vigorous stirring.

(c) All Compounds. The reaction mixtures were stirred overnight at this temperature and then warmed to ambient temperature. The mixtures were filtered through sintered-glass filters (porosity No. 4), and the resulting clear solutions were concentrated under vacuum until they became slightly

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Table 2. Crystal and Refinement Data for the Solid-State Structures of Compounds 2−6

	2	**3**	**4**	**5**	**6**
formula	$C_{10}H_{26}Al_2N_2$	$C_{10}H_{26}Ga_2N_2$	$C_{10}H_{26}In_2N_2$	$C_{22}H_{50}Al_2N_2$	$C_{22}H_{50}Ga_2N_2$
formula wt	228.29	313.77	403.97	396.60	482.08
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$P2_1/n$	$P2_1/n$
a (Å)	7.501(2)	6.934(1)	8.318(1)	12.666(2)	12.700(1)
b (Å)	8.812(3)	12.804(2)	13.125(1)	13.420(2)	13.436(1)
c (Å)	12.346(4)	16.305(2)	14.190(1)	16.304(3)	16.352(1)
α (deg)	71.95(1)	90	90	90	90
β (deg)	87.22(1)	98.16(1)	93.64(1)	111.80(1)	111.99(1)
γ (deg)	69.90(1)	90	90	90	90
V (Å^3)	727.1(4)	1432.9(4)	1546.1(2)	2573.1(7)	2587.3(3)
ρ_{calcd} (g cm^{-3})	1.043	1.454	1.736	1.024	1.238
Z	2	4	4	4	4
μ (mm^{-1})	0.173	3.732	2.957	0.121	2.091
T (K)	123(2)	173(2)	198(2)	198(2)	198(2)
T_{min}/T_{max}	0.968/0.993	0.522/0.929	0.589/0.866	0.965/0.982	0.367/0.367
$2\vartheta_{max}$ (deg)	50.00	55.00	56.56	52.60	55.76
no. of measd rflns	4588	13 622	6087	7826	15 580
no. of unique rflns	2529	3275	1882	4939	6149
no. of obsd rflns	1856	2527	1715	3188	5323
R_{int}	0.037	0.052	0.034	0.040	0.029
no. of params	231	231	68	249	249
R ($I > 2\sigma(I)$)/w$R2$	0.043/0.106	0.032/0.065	0.022/0.056	0.069/0.184	0.026/0.067
ρ_{fin}(min/max) (e Å^{-3})	−0.328/0.407	−0.272/0.533	−0.654/0.466	−0.255/0.488	−0.502/0.331
CCDC no.	236370	236369	273525	236372	236371

cloudy. When they were warmed to room temperature, the solutions became clear again. The vessels with these solutions were immersed in 1 L Dewar containers filled with ethanol and cooled slowly to −25 °C overnight. Colorless, well-formed crystals were obtained in this way.

$Me_2AlCH_2N(Me)CH_2CH_2N(Me)CH_2AlMe_2$ (2). Me_2AlCl (0.39 g, 3.0 mmol) and **1** (0.20 g, 1.6 mmol) gave **2**; yield 0.21 g (61%). Mp: 74 °C. Sublimation temperature: 62 °C/0.01 Torr. ^1H NMR (C_6D_6): δ −0.61/−0.37 (s, 12 H, CH_3Al), 1.13/1.20 (s, 4 H, $AlCH_2N$), 1.91 (s, 6 H, NCH_3), 2.06/2.13 (dd, 4H, CH_2CH_2N, $^2J_{HH} = 13.0$ Hz, $^3J_{HH} = 3.2$ Hz). ^{13}C NMR (C_6D_6): δ −9.7 (broad, CH_3Al), 49.0 (broad, $AlCH_2N$), 51.9 (NCH_3), 53.8 (CH_2CH_2N). ^{27}Al NMR (C_6D_6): δ 161 ($\nu_{1/2} = 5800$ Hz). Anal. Calcd for $C_{10}H_{26}Al_2N_2$ (mol wt 228.29): C, 52.61; H, 11.48; N, 12.27. Found: C, 52.16; H, 11.45; N, 12.20.

$Me_2GaCH_2N(Me)CH_2CH_2N(Me)CH_2GaMe_2$ (3). Me_2GaCl (0.91 g, 6.7 mmol) and **1** (0.43 g, 3.4 mmol) gave **3**; yield 0.69 g (67%). Mp: 76 °C. Sublimation temperature: 93 °C/0.01 Torr. ^1H NMR (C_6D_6): δ −0.32/−0.07 (s, 12 H, CH_3Ga), 1.39/1.43 (s, 4 H, $GaCH_2N$), 1.93 (s, 6 H, NCH_3), 2.28/2.32 (dd, 4 H, CH_2CH_2N, $^2J_{HH} = 12.1$ Hz, $^3J_{HH} = 2.4$ Hz). ^{13}C NMR (C_6D_6): δ −8.7/−6.8 (CH_3Ga), 52.4 ($GaCH_2N$), 52.7 (NCH_3), 54.4 (CH_2CH_2N). Anal. Calcd for $C_{10}H_{26}Ga_2N_2$ (mol wt 313.77): C, 38.28; H, 8.35; N, 8.93. Found: C, 37.82; H, 8.28; N,8.60.

$Me_2InCH_2N(Me)CH_2CH_2N(Me)CH_2InMe_2$ (4). Me_2InCl (0.72 g, 4.0 mmol) and **1** (0.26 g, 2.0 mmol) gave **4**; yield 0.51 g (63%). Mp: 82 °C. Sublimation temperature: 123 °C/0.01 Torr. ^1H NMR (C_6D_6): δ −0.32/−0.07 (s, 12 H, CH_3In), 1.39/1.43 (s, 4 H, $InCH_2N$), 1.93 (s, 6 H, NCH_3), 2.28/2,32 (dd, 4 H, CH_2CH_2N, $^2J_{HH} = 12.1$ Hz, $^3J_{HH} = 2.4$ Hz). ^{13}C NMR (C_6D_6): δ −8.7/−6.8 (CH_3In), 52.4 ($InCH_2N$), 52.7 (NCH_3), 54.4 (CH_2CH_2N). Anal. Calcd for $C_{10}H_{26}In_2N_2$ (mol wt 403.96): C, 29.73; H, 6.49; N, 6.93. Found: C, 29.61; H, 6.55; N, 6.91.

t-$Bu_2AlCH_2N(Me)CH_2CH_2N(Me)CH_2Al$-$t$-$Bu_2$ (5). $^tBu_2AlCl$ (0.75 g, 4.3 mmol) and **1** (0.26 g, 2.1 mmol) gave **5**; yield 0.51 g (63%). Mp: 162 °C. ^1H NMR (C_6D_6): δ 1.15/1.31 (s, 36H, $(CH_3)_3CAl$), 1.21/1.25 (s, 4H, $AlCH_2N$), 2.13 (s, 6H, NCH_3), 2.59/2.62 (dd, 4H, CH_2CH_2N, $^2J_{HH} = 14.2$ Hz, $^3J_{HH} = 3.4$ Hz). ^{13}C NMR (C_6D_6): δ 16.3 (broad, CAl), 33.1/33.5 ($(CH_3)_3CAl$), 49.7 ($AlCH_2N$), 52.7 (NCH_3), 54.8 (CH_2CH_2N). ^{27}Al NMR (C_6D_6): δ 148 ($\nu_{1/2} = 7600$ Hz). Anal. Calcd for $C_{22}H_{50}Al_2N_2$ (mol wt 396.61): C, 66.62; H, 12.71; N, 6.98. Found: C, 65.95; H, 12.63; N, 6.92.

t-$Bu_2GaCH_2N(Me)CH_2CH_2N(Me)CH_2Ga$-$t$-$Bu_2$ (6). $^tBu_2GaCl$ (0.90 g, 4.1 mmol) and **1** (0.25 g, 2.0 mmol) gave **6**; yield 0.69 g (0.73%). Mp: 189 °C. ^1H NMR (C_6D_6): δ 1.21/1.38 (s, 36H, $(CH_3)_3CGa$), 1.45/1.48 (s, 4H, $GaCH_2N$), 2.20 (s, 6H, NCH_3), 2.80/2.83 (dd, 4H, CH_2CH_2N, $^2J_{HH} = 12.1$ Hz, $^3J_{HH} = 2.9$ Hz). ^{13}C NMR (C_6D_6): δ 22.7/23.4 (CGa), 33.2/33.8 ($(CH_3)_3CGa$), 51.2 ($GaCH_2N$), 54.2 (CH_2CH_2N), 55.8 (NCH_3). Anal. Calcd for $C_{22}H_{50}Ga_2N_2$ (mol wt 482.09): C, 54.81; H, 10.45; N, 5.81. Found: C, 53.15; H, 10.28; N, 5.75.

Crystal Structure Analyses. Single crystals of compounds **2**−**6** were mounted under inert perfluoropolyether at the tips of glass fibers and cooled in the cryostream of the diffractometer (Nonius Kappa CCD for compounds **4**−**6** and Bruker AXS for for **2** and **3**, both with monochromated Mo Kα radiation; $\lambda = 0.710\,73$ Å). The structure solutions were carried out using direct methods, and the refinements of the structure were undertaken with the program SHELXTL 5.01[27] for **2** and **3** and SHELXTL version 6.10[28] for compounds **4**−**6**. Nonhydrogen atoms were refined with anisotropic thermal displacement parameters, and hydrogen atoms were included isotropically in a riding model. Further details of data collection and refinement are given in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications (for the file numbers, see Table 2). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Supporting Information Available: CIF files giving crystal data for compounds **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0504405

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