Molecularly Simple Dimethylaminomethyl Compounds of Aluminum, Gallium, and Indium

Christian Lustig and Norbert W. Mitzel*

Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Strasse 8, 48149 Münster, Germany

Received August 20, 2002

The dimethylaminomethyl compounds $(Me_2AlCH_2NMe_2)_2$ (**1**), $(Me_2GaCH_2NMe_2)_2$ (**2**), $(Me_2InCH_2NMe_2)_2$ (**3**), $(Me_2AlCH_2NMe_2)\cdot(MeClAlCH_2NMe_2)$ (**4**), $[ClAl(CH_2NMe_2)_2]_2$ (**5**), and $[Al(CH_2NMe_2)_3]_2$ (**6**) have been prepared by reacting $LiCH_2NMe_2$ with the corresponding element or organoelement chlorides. Characterization was undertaken by means of elemental analyses, NMR spectroscopy (^1H, ^{13}C, ^{27}Al), and mass spectrometry. An unusually low ^{27}Al NMR chemical shift of **6** (62 ppm) was observed indicating a possible coordination number higher than four at aluminum in solution. The crystal structures of all compounds but **3** have been determined and confirm that all form dimers with six-membered $M_2C_2N_2$ rings in the chair conformation. The mass spectra indicate that the dimers are retained in the gas phase, and for **1** the molecular dynamics of ring inversion was monitored in solution by variable-temperature NMR spectroscopy, showing that the barrier for the inversion process (9 kcal mol^{-1}) is comparable to that of cyclohexane. Calculations at the B3LYP/6-311G(d) level of theory confirm that the molecular structures of **1** and **2** are almost undistorted in the solid state. DFT calculations (B3LYP/6-311G(d)) for the monomeric three-membered ring isomers of **1** and **2** show these to be much higher in energy (81 and 77 kJ mol^{-1} per monomer) than the corresponding six-membered ring dimers.

The presence of geminal donor and acceptor sites in the same molecule is often the source of characteristic types of reactivity. Important examples based on this principle include the carbenoid reactivity of Köbrich's α-halogen-methyllithium reagents,[1] the carbenoids of the type Li−C−O,[2] and corresponding nitrenoids[3] and oxenoids[4] containing Li−N−O and Li−O−O units. Extrusion of the bridging unit under final formation of a chemical bond between the geminal donor and acceptor centers is also reported for silicon-containing species such as the nitrene generators $R_3Si-N(R)-OSiMe_3$[5] and the carbene-generating α-fluoromethylsilanes R_3Si-CH_2-F.[6] Recently Steinborn and co-workers found the compound $LiCH_2SPh$ to show carbene transfer capability.[7] Examples involving transition metal acceptor atoms also include the well-known Simmon−Smith reagent[8] $I-CH_2-Zn-I$ or the carbene-generating Seyferth reagent $Ph-Hg-CCl_2Br$.[9] Other compounds with the geminal donor acceptor motif do not extrude the linking unit and behave in a more classical sense, for example the reagents for nucleophilic aminomethylation[10] and phosphinomethylation.[11]

In recent years investigations with focus on the structural chemistry of such compounds revealed that there are a number of ways for the acceptor atoms in such compounds to saturate their demand for electron density by either intramolecular coordination leading to three-membered rings or intermolecularly by formation of higher aggregates, the simplest being six-membered ring dimers.

Many but not all of the three-membered ring systems undergo such extrusion reactions, but so far the body of structural information is still not large enough for a sound structure-based reactivity prediction, in particular in the light of so many possible different combinations of donors, acceptors, and linking units. Nevertheless, it would have far-reaching consequences if one could find a unified plan for numerous reactions of geminal systems based on their molecular structures and dynamics.[12]

Only a few representatives of organometallic compounds with group 13 acceptors and geminal donor atoms occurring as three-membered rings are known. Among these are boron compounds of the formula R_2B-

---

* Corresponding author. E-mail: Mitzel@uni-muenster.de.

[1] (a) Kirmse, W. *Angew. Chem.* **1965**, *77*, 1; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1. (b) Köbrich, G. *Angew. Chem.* **1972**, *84*, 557; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 473. (c) Siegel, H. *Top. Curr. Chem.* **1982**, *106*, 55.

[2] Boche, G.; Bosold, F.; Lohrenz, J. C. W.; Opel, A.; Zulauf, P. *Chem. Ber.* **1993**, *126*, 1873.

[3] (a) Boche, G.; Boie, C.; Bosold, F.; Harms, K.; Marsch, M. *Angew. Chem.* **1994**, *106*, 90; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 115. (b) Schverdina, N. I.; Kotscheschkov, Z. *J. Gen. Chem. USSR* **1938**, *8*, 1835. (c) Beak, P.; Kokko, B. J. *J. Org. Chem.* **1982**, *47*, 2822. (d) Erdik, E.; Ay, M. *Chem. Rev.* **1989**, *89*, 1947.

[4] (a) Boche, G.; Bosold, F.; Lohrenz, J. C. W. *Angew. Chem.* **1994**, *106*, 1228; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1161. (b) Boche, G.; Möbus, K.; Harms, K.; Lohrenz, J. C. W.; Marsch, M. *Chem. Eur. J.* **1996**, *2*, 604.

[5] Chang, Y. H.; Chiu, F.-T.; Zon G. *J. Org. Chem.* **1981**, *46*, 352.

[6] Beckers, H.; Bürger, H. *J. Organomet. Chem.* **1990**, *385*, 207.

[7] Rüffer, T.; Bruhn, C.; Maulitz, A. H.; Ströhl, D.; Steinborn, D. *Organometallics* **2000**, *19*, 2829.

[8] Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256.

[9] Seyferth, D. *Acc. Chem. Res.* **1972**, *5*, 65.

[10] Peterson, D. J. *J. Org. Chem.* **1967**, *32*, 1717.

[11] Karsch, H. H.; Schmidbaur, H. *Z. Naturforsch.* **1977**, *32b*, 762.

[12] Kostyanovskii, R. G.; Prokov'ev, A. K. *Dokl. Akad. Nauk SSSR* **1965**, *164*, 1054.

10.1021/om020687r CCC: $25.00
Publication on Web 12/20/2002

$CR'_2{-}NR''_2$. Two of them have been structurally elucidated in the solid state and represent three-membered ring compounds with BCN rings.[13,14] Six-membered ring dimers of systems containing geminal acceptors and donors are found in a few representatives including the compounds with B−C−S,[15] Al−C−S,[16,17] Ga−C−S,[17] Al−C−P,[18] and In−C−P[19] linkages.

In this contribution we present investigations on simple systems containing the saturated linkage M−C−N for M being an earth metal atom. Apart from the heteronorbornane type compounds $[Me_2MCH_2N(Me)]_2CH_2$ (M = Al, Ga) we reported recently[20] such compounds are so far unknown. In contrast to the saturated systems, compounds of the general formula $R_2Al{-}CH{=}NR'$ are known and said to be six-membered ring dimers.[21] There also exists a compound with Al−C═N linkages and an Al−C−N three-membered ring resulting from insertion of an isonitrile into an Al−Al bond, which however should be viewed as nonclassically bonded. [22]

Experimental Section

General Methods. All experiments were carried out under a dry nitrogen atmosphere with standard Schlenk and high-vacuum techniques or in a glovebox operated under argon. Solvents were purified and dried by standard techniques. Dimethylaluminum chloride was prepared from trimethylaluminum and aluminum trichloride. Dimethylgallium chloride[23] and dimethylindium chloride[24] were obtained according to literature procedures. Pure dimethylaminomethyllithium was obtained via transmetalation of dimethylaminomethyltri-*n*-butyltin[25] with *n*-butyllithium. CAUTION: $LiCH_2NMe_2$ spontaneously ignites and burns vigorously on contact with air. Chemical ionization (CI) mass spectra were obtained with a Varian MAT 311A spectrometer. All NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (400.05 MHz ^{1}H, 100.50 MHz ^{13}C, 104.05 MHz ^{27}Al) in C_6D_6 or toluene-d_8 as solvent dried over K/Na alloy.

(Dimethylaminomethyl)dimethylaluminum ($\mathbf{(Me_2AlCH_2NMe_2)_2}$) (1). To a stirred suspension of dimethylaminomethyllithium (6.92 mmol, 0.45 g) in 45 mL of *n*-pentane was slowly added a solution of dimethylaluminum chloride (6.88 mmol, 6.88 mL of an 1 M solution in *n*-hexane) at −78 °C. The reaction mixture was slowly warmed to room temperature. Colorless crystals were obtained after filtration, concentration to 10 mL, and storage at −78 °C. Yield: 0.49 g (62%), mp 121 °C; sublimation point 65 °C (0.01 mbar). ^{1}H NMR (C_6D_6): δ −0.65 (s, $\mathrm{AlC}H_3$), 1.56 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.97 (s, $\mathrm{NC}H_3$). ^{13}C{^{1}H} NMR: δ −9.92 (br s, $\mathrm{Al}C\mathrm{H}_3$), 50.45 (s, $\mathrm{N}C\mathrm{H}_3$), 51.78 (br s, $\mathrm{Al}C\mathrm{H}_2\mathrm{N}$). ^{27}Al NMR ($C_6D_6$): δ 166 ($\nu_{1/2}$ = 950 Hz). CI-MS [m/z (%)]: 215 (100), [M^+ − Me]; 172 (39) [$M^+ - CH_2NMe_2$], 115 (14) [$Me_2AlCH_2NMe_2^+$], 100 (20) [$Me_2AlCH_2NMe_2^+$ − Me]. Anal. Calcd for $C_{10}H_{28}Al_2N_2$: C 52.15, H 12.25, N 12.16. Found: C 52.08, H 11.98, N 11.87.

(Dimethylaminomethyl)dimethylgallium ($\mathbf{(Me_2GaCH_2NMe_2)_2}$) (2). The synthesis of $(Me_2GaCH_2NMe_2)_2$ is analogous to the one for $(Me_2AlCH_2NMe)_2$, but employing dimethylaminomethyllithium (6.15 mmol, 0.40 g) and dimethylgallium chloride (6.14 mmol, 0.83 g). Yield: 0.67 g (69%), mp 118 °C; sublimation point 70 °C (0.01mbar). ^{1}H NMR (C_6D_6): δ −0.36 (s, $\mathrm{GaC}H_3$), 1.78 (s, $\mathrm{GaC}H_2\mathrm{N}$), 1.99 (s, $\mathrm{NC}H_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ −7.57 (s, $GaCH_3$), 50.72 (s, NCH_3), 54.12 (s, $GaCH_2N$). CI-MS [m/z (%)]: 301 (100), [M^+ − Me]; 258 (63) [$M^+ - CH_2NMe_2$], 156 (28) [$Me_2GaCH_2NMe_2^+$]. Anal. Calcd for $C_{10}H_{28}Ga_2N_2$: C 38.03, H 8.94, N 8.87. Found: C 38.01, H 8.93, N 8.86.

(Dimethylaminomethyl)dimethylindium ($\mathbf{(Me_2InCH_2NMe_2)_2}$) (3). At −78 °C 45 mL of diethyl ether was condensed onto a mixture of dimethylaminomethyllithium (6.31 mmol, 0.41 g) and dimethylindium chloride (6.31 mmol, 1.13 g). The mixture was allowed to warm slowly to room temperature. The solid residue was separated by centrifugation. Filtration, concentration, and storage at −78 °C yielded a colorless powder. Yield: 0.61 g (48%), mp 187 °C. ^{1}H NMR (C_6D_6): δ −0.21 (s, $InCH_3$), 1.93 (s, $InCH_2N$), 2.02 (s, NCH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ −8.66 (s, $InCH_3$), 51.94 (s, NCH_3), 56.70 (s, $InCH_2N$). CI-MS [m/z (%)]: 391 (100) [M^+ − Me]; 348 (95) [$M^+ - CH_2NMe_2$], 318 (32) [M^+ − 2Me, CH_2NMe_2], 202 (10) [$Me_2InCH_2NMe_2^+$], 145 (21) [$InMe_2^+$], 115 (31) [In^+]. Anal. Calcd for $C_{10}H_{28}In_2N_2$: C 29.59, H 6.95, N 6.90. Found: C 29.34, H 6.98, N 6.88.

(Dimethylaminomethyl)dimethylaluminum(dimethylaminomethyl)(chloro)methylaluminum [$\mathbf{Cl(Me)AlCH_2NMe_2{\cdot}Me_2AlCH_2NMe_2}$] (4). The synthesis of [$Cl(Me)AlCH_2NMe_2{\cdot}Me_2AlCH_2NMe_2$] is analogous to the one for $(Me_2AlCH_2NMe_2)_2$, but employing dimethylaminomethyllithium (5.23 mmol, 0.34 g) and trichlorotrimethyldialuminum (5.23 mmol, 1.07 g). Yield: 0.31 g (48%), mp 122 °C; sublimation point 65 °C (0.01 mbar). The following description of NMR data represents the spectroscopic data obtained from a solution of single crystalline material, and obviously there are complex mixtures in solution. ^{1}H NMR (C_6D_6): δ −0.74 (s, $\mathrm{AlC}H_3$), −0.67 (s, $\mathrm{AlC}H_3$), −0.63 (s, $\mathrm{AlC}H_3$), −0.61 (s, $\mathrm{AlC}H_3$), −0.57 (s, $\mathrm{AlC}H_3$), −0.50 (s, $\mathrm{AlC}H_3$), 1.32 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.37 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.44 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.47 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.48 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.51 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.56 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.57 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.59 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.60 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.62 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.66 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.71 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.72 (s, $\mathrm{AlC}H_2\mathrm{N}$), 1.76 (s, $\mathrm{NC}H_3$), 1.82 (s, $\mathrm{NC}H_3$), 1.9 (s, $\mathrm{NC}H_3$), 1.95 (s, $\mathrm{NC}H_3$) 1.96 (s, $\mathrm{NC}H_3$), 1.99 (s, $\mathrm{NC}H_3$), 2.14 (s, $\mathrm{NC}H_3$), 2.19 (s, $\mathrm{NC}H_3$). ^{13}C{^{1}H} NMR: δ −9.7 (vbr s, $\mathrm{Al}C\mathrm{H}_3$), 49.32 (br s, $\mathrm{Al}C\mathrm{H}_2\mathrm{N}$), 49.81 (s, $\mathrm{N}C\mathrm{H}_3$), 49.93 (s, $\mathrm{N}C\mathrm{H}_3$), 49.97 (s, $\mathrm{N}C\mathrm{H}_3$), 50.11 (s, $\mathrm{N}C\mathrm{H}_3$), 50.36 (s, $\mathrm{N}C\mathrm{H}_3$), 50.49 (s, $\mathrm{N}C\mathrm{H}_3$) 50.74 (s, $\mathrm{N}C\mathrm{H}_3$). ^{27}Al NMR: δ 148 ($\nu_{1/2}$ = 2400 Hz), 166 ($\nu_{1/2}$ = 950 Hz).

Bis(dimethylaminomethyl)aluminum Chloride [$\mathbf{ClAl(CH_2NMe_2)_2]_2}$ (5) and Tris(dimethylaminomethyl)aluminum [$\mathbf{Al(CH_2NMe_2)_3]_2}$ (6). The various experiments can generally be described as follows. To stirred suspensions of dimethylaminomethyllithium in an inert solvent (pentane, hexane, toluene) was slowly added an understoichiometric amount of aluminum chloride at temperatures between −78 °C and ambient temperature. After different conditions for reaction time (12 h to 1 week) and temperature (RT to reflux) the resulting suspensions were filtered and the solvent was removed from the filtrate to yield a solid residue, which was always a mixture of different compounds, giving complex ^{1}H and ^{13}C NMR spectra. From hexane solutions of these mixtures a few crystals of **5** and **6** besides precipitates of other compounds were isolated and identified by crystal structure analyses (see below). This material did not contain significant

---

(13) Ansorge, A.; Brauer, D. J.; Bürger, H.; Hagen, T.; Pawelke, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 384

(14) Brauer, D. J.; Bürger, Buchheim-Spiegel, S., T.; Pawelke, G. *Eur. J. Inorg. Chem.* **1999**, 255.

(15) Nöth, H.; Sedlak, D. *Chem. Ber.* **1983**, *116*, 1479.

(16) (a) Dickson, P. M.; Oliver, J. P. *Organometallics* **1994**, *13*, 3300. (b) Rüffer, T. Doctoral Thesis, Martin-Luther-Universität Halle-Wittenberg 1999. (c) Rüffer, T.; Bruhn, C.; Brusanov, E.; Nordhoff, K.; Steinborn, D. *Z. Anorg. Allg. Chem.* **2002**, *628*, 421.

(17) Lustig, C.; Mitzel, N. W. *Organometallics* **2002**, *21*, 3471.

(18) (a) Karsch, H. H.; Appelt A. *Phosphorus Sulfur Related Elements* **1983**, *18*, 287. (b) Karsch, H. H.; Appelt, A.; Köhler, F. H.; Müller, G. *Organometallics* **1985**, *4*, 231.

(19) Beachley, O. T.; Banks, M. A.; Churchill, M. R.; Feighery, W. G.; Fettinger, J. C. *Organometallics* **1991**, *10*, 3036.

(20) Lustig, C.; Mitzel, N. W. *Chem. Commun.* **2000**, 1393.

(21) Hoberg, H.; Bukowski, P. *Liebigs. Ann. Chem.* **1975**, 1124.

(22) Uhl, W.; Schütz, U.; Hiller W.; Heckel, M. *Chem. Ber.* **1994**, *127*, 1587.

(23) Armer, B.; Schmidbaur, H. *Chem. Ber.*, **1967**, *100*, 1521.

(24) Clark, H. C.; Pickard, A. L. *J. Organomet. Chem.*, **1967**, *9*, 427.

(25) Peterson, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 4027.

Table 1. Data for the Single Crystal X-ray Diffraction Experiments

	1	**2**	**4**	**5**	**6**
formula	$C_{10}H_{28}N_2Al_2$	$C_{10}H_{28}N_2Ga_2$	$C_9H_{25}N_2Al_2Cl$	$C_{12}H_{32}N_4Al_2Cl_2$	$C_{18}H_{48}N_6Al_2$
M_r	115.15	315.78	125.36	178.64	201.29
T [K]	143(2)	133(2)	123(2)	148(2)	143(2)
cryst syst	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a [Å]	6.8100(4)	6.7886(4)	6.749(2)	21.910(4)	10.053(2)
b [Å]	7.664(2)	7.6420(5)	7.229(2)	7.652(1)	12.629(1)
c [Å]	9.0129(11)	9.0194(7)	8.883(3)	12.041(2)	10.718(2)
α [deg]	94.21(2)	94.553(4)	75.89(2)	90	90
β [deg]	110.81(1)	110.708(4)	68.94(3)	99.470(10)	109.31(1)
γ [deg]	116.20(2)	116.117(4)	64.81(2)	90	90
V [Å^3]	379.37(12)	377.34(4)	363.85(19)	1991.2(6)	1284.2(4)
Z, D_{calc} [g cm^{-3}]	1, 1.008	1, 1.390	1, 1.144	4, 1.192	2, 1.041
cryst size [mm]	0.3 × 0.2 × 0.2	0.4 × 0.2 × 0.2	0.3 × 0.2 × 0.1	0.4 × 0.3 × 0.3	0.7 × 0.5 × 0.4
reflns$_{collected/unique}$	1856/1654	11608/1450	3192/1596	6038/4333	2936/2792
R_{int}	0.0195	0.045	0.0174	0.0368	0.0449
$2\theta_{max}$	27.0	26.6	27.0	27.0	27.0
completeness [%]	99.7	91.6	99.5	99.4	99.4
no. of data/restraints/params	1654/0/120	1450/ 0/120	1596/1/97	4333/0/309	2792/0/215
extinction coeff					0.011(6)
R_1/wR_2	0.0257/0.0665	0.0309/0.0779	0.0411/0.1115	0.0329/0.0735	0.0526/0.1539
R_1/wR_2 (all data)	0.0340/0.0697	0.0321/0.0788	0.0435/0.1131	0.0705/0.0853	0.0623/0.1637
$\Delta\rho_{fin}$ [e Å^{-3}]	0.290/−0.125	0.521/−0.641	0.529/−0.241	0.363/−0.231	0.441/−0.333

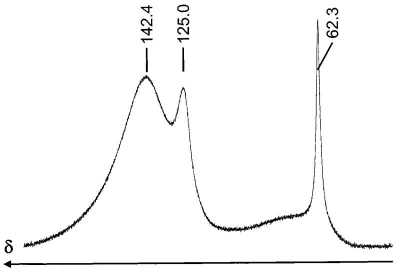


Figure 1. ^{27}Al NMR spectrum of a sample (dissolved in C_6D_6) resulting from an attempt to prepare $Al(CH_2NMe_2)_3$ from $LiCH_2NMe_2$ (excess) and $AlCl_3$.

amounts of lithium and also gave complex NMR spectra with too many lines to be interpretable. The ^{27}Al NMR of one of such samples is shown in Figure 1. Dissolution of the crystallographically examined crystals also gave complex ^{1}H and ^{13}C spectra, but ^{27}Al NMR spectra with clearly enhanced signals at 125 ppm for **5** and 62 ppm for **6**, while the other signals shown in Figure 1 were always present, but less strong.

Crystal Structure Determinations. Single crystals of compounds **1**, **2**, **4**, **5**, and **6** were mounted under inert perfluoropolyether at the tip of a glass fiber and cooled in the cryostream of the diffractometer. Data were collected on a Nonius Turbo-CAD4 diffractometer for all structures but $(Me_2GaCH_2NMe_2)_2$ (**2**), for which a Nonius DIP 2020 was used. Both diffractometers were operated with monochromatic Mo Kα radiation (λ = 0.71073 Å). No absorption corrections were applied for **1**, **4**, **5**, and **6**, and the scattering intensities of **2** were corrected by the program SCALEPACK.[26] The structure solutions were carried out using direct methods, and the refinements of the structure were undertaken with the program SHELXTL 5.01.[27] Non-hydrogen atoms were refined with anisotropic thermal displacement parameters, hydrogen atoms isotropically. Further details of data collection and refinement are listed in Table 1.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-190387 $(Me_2AlCH_2NMe_2)_2$ (**1**), CCDC-190388 $(Me_2GaCH_2NMe_2)_2$ (**2**), CCDC-190389 $(Me_2AlCH_2NMe_2)\cdot(MeClAlCH_2NMe_2)$ (**4**), CCDC-190390 $[ClAl(CH_2NMe_2)_2]_2$ (**5**), and CCDC-190391 $[Al(CH_2NMe_2)_3]_2$ (**6**). 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).

Results and Discussion

Preparation and Characterization of the Compounds. The dimethylaminomethyl compounds $(Me_2AlCH_2NMe_2)_2$, $(Me_2GaCH_2NMe_2)_2$, and $(Me_2InCH_2NMe_2)_2$ were prepared by reacting dimethylaminomethyllithium $LiCH_2NMe_2$ with the corresponding dimethylmetal chlorides in hexane (eq 1).

$$2\ Me_2NCH_2Li + 2\ Me_2MCl \rightarrow (Me_2MCH_2NMe_2)_2 + 2\ LiCl \quad (1)$$

$$M = Al\ (\mathbf{1}),\ Ga\ (\mathbf{2}),\ In\ (\mathbf{3})$$

The Al, Ga, and In compounds **1**, **2**, and **3** were identified by elemental analyses and NMR spectroscopy of the nuclei ^{1}H, ^{13}C (and ^{27}Al for **1**). Mass spectra proved the presence of dimers in the gas phase. The occurrence of mass peaks corresponding to the monomer cations is also observed. These can be formed either by ionization of monomers present in the gas phase and/or by decay upon ionization of the dimers.

The Al and Ga compounds **1** and **2** were obtained as crystalline materials upon cooling solutions in hydrocarbon solvents. The new compounds are all well soluble in nonpolar solvents such as pentane, hexane, and toluene and even better in ethers. The indium compound $(Me_2InCH_2NMe_2)_2$ (**3**) is much less soluble in nonpolar solvents, but dissolves to some extent in diethyl ether and easily in THF. The compounds are thermally stable up to about 100 °C in the solid state and in solution. The compounds **1** and **2** can be sublimed at 65 °C/70 °C in a vacuum (10^{-2} mbar).

In one experiment according to eq 1, a mixture of Me_2AlCl and $MeAlCl_2$ was employed close to a stoichiometry of $Me_2AlCl\cdot MeAlCl_2$. This reaction yielded among other compounds an aggregate of the formula $[(Me_2AlCH_2$-

---

(26) SCALEPACK: Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(27) *SHELXTL*; Siemens Analytical X-Ray Instrumentation Inc.: Madison, WI, 1995. Refinement: Sheldrick, G. M. *SHELXL93*; Universität Göttingen: Germany, 1993.

$NMe_2)\cdot(MeClAlCH_2NMe_2)]$ (**4**, eq 2), which was obtained as a crystalline product described by its crystal structure below. The ^1H and ^{13}C NMR spectra are not as simple as the formula $[(Me_2AlCH_2NMe_2)\cdot(MeClAlCH_2NMe_2)]$ suggests and consist of a number of lines, which indicate the presence of at least three different species, namely, $(Me_2AlCH_2NMe_2)_2$, $[(Me_2AlCH_2NMe_2)\cdot(MeClAlCH_2NMe_2)]$, and $(MeClAlCH_2NMe_2)_2$. However, as there are more lines than would be possible for the three species, we have to assume the presence of further compounds in this mixture, which could not be separated, as the only compound we could crystallize from such solutions is **4**. Dissolution of crystals of **4** leads to the same distribution of products, which obviously result from redistribution reactions of the monomers with one another. The simple appearance of the ^{27}Al NMR spectrum does not reflect this complexity in solution, as it comprises only two broad lines at $\delta = 148$ ($\nu_{1/2} =$ 2400 Hz) and 166 ppm ($\nu_{1/2} = 950$ Hz), which stem from Me_2AlCH_2 and $MeClAlCH_2$ units.

$$2\ Me_2NCH_2Li + Me_2AlCl\cdot MeAlCl_2 \rightarrow \underset{\mathbf{4}}{[(Me_2AlCH_2NMe_2)\cdot(MeClAlCH_2NMe_2)]} + 2\ LiCl \quad (2)$$

To prepare the homoleptic compound $[Al(CH_2NMe_2)_3]_2$, we reacted aluminum trichloride and Me_2NCH_2Li in the stoichiometric ratio 1:3. However, a complex mixture of compounds resulted from these synthetic attempts. At least two of the compounds could be obtained in crystalline form and are $(MeClAlCH_2NMe_2)_2$ (**5**) and $[Al(CH_2NMe_2)_3]_2$ (**6**), which were identified by X-ray crystallography (vide infra). Variation of the reaction conditions resulted in a variation of the ratio of the products formed. The major problem with these reactions is the limited solubility of Me_2NCH_2Li in hydrocarbon solvents (pentane, hexane, toluene) and diethyl ether and the slow decomposition in THF. At temperatures of −78 °C or lower both Me_2NCH_2Li and $AlCl_3$ are not well soluble even in ethers, and despite applying stoichiometric amounts of the reactants, the reactions remained incomplete with respect to the desired homoleptic compound. The search for optimum conditions (solvents, temperatures, reaction times (varied from 12 h to 1 week) proved to be rather difficult, and finally we cannot provide a simple recipe to prepare large amounts of $(MeClAlCH_2NMe_2)_2$ (**5**) or $[Al(CH_2NMe_2)_3]_2$ (**6**) in a selective way and high yields. The use of aluminum bromide and iodide also did not lead to an improvement of the preparation procedures. Furthermore are there no suitable separation procedures for the products like distillation or sublimation, and the rather incomplete fractional crystallization is the only way we found so far to solve this problem in part.

$$Me_2NCH_2Li + AlCl_3 \rightarrow \underset{\mathbf{5}}{[ClAl(CH_2NMe_2)_2]_2},\ \underset{\mathbf{6}}{[Al(CH_2NMe_2)_3]_2} \quad (3)$$

It should also be noted that other attempts to prepare the Al-chlorinated compounds by chlorination of the compounds $Me_2MCH_2NMe_2$ [M = Al (**1**), Ga (**2**)] with trimethyltin chloride according to a recently reported procedure[28] failed, and only a number of products were produced, which could neither be separated nor identified.

Table 2. ^{27}Al NMR Spectroscopy Data for the Five New Compounds and Two Reference Compounds in Solution (C_6D_6) at 21 °C

compound	chemical shift [ppm] (half width)
$(Me_2AlCH_2NMe_2)_2$ (**1**)	166 ($\nu_{1/2} = 950$ Hz)
$(Cl(Me)AlCH_2NMe_2)\cdot$	148 ($\nu_{1/2} = 2400$ Hz),
$(Me_2AlCH_2NMe_2)$ (**2**)	166 ($\nu_{1/2} = 950$ Hz)
$[ClAl(CH_2NMe_2)_2]_2$ (**5**)	141 ($\nu_{1/2} = 2500$ Hz)
$[Al(CH_2NMe_2)_3]_2$ (**6**)	62 ($\nu_{1/2} = 250$ Hz)
$[Cl_2AlCH_2NMe_2]_2$ (**7**)	125 ($\nu_{1/2} = 1200$ Hz)
$Me_3Al\cdot NMe_3$	179 ($\nu_{1/2} = 1000$ Hz)
$Cl_3Al\cdot NMe_3$	109 ($\nu_{1/2} = 100$ Hz)

All compounds reported in this section are sensitive to oxygen and water, with the sensitivity decreasing in the series aluminum, gallium, and indium for the compounds $(Me_2MCH_2NMe_2)_2$. Solutions in hydrocarbons contain the dimers as described in more detail below in a section dealing with the molecular dynamics in solution. The dimeric structure of the compounds seems also to be retained in ethers or upon adding triethylamine to the solutions, as the NMR chemical shifts do not change significantly, with respect to C_6D_6 solutions without base addition. This is in contrast to the corresponding sulfur compounds $(Me_2MCH_2SMe)_2$,[17] which undergo ring opening and coordinate the stronger bases ethers and trialkylamines to their metal atoms upon addition of those. Hence we can conclude that either the geminal nitrogen atoms are stronger donors or the formation of six-membered ring dimers is otherwise thermodynamically favored.

^{27}Al NMR Spectroscopy. For those compounds containing aluminum ^{27}Al NMR spectroscopy has proven to be a valuable tool in identification of products and in obtaining information about the coordination of the metal atoms in solution. Table 2 shows a list of ^{27}Al NMR data for the compounds described above and some relevant reference compounds.

The more alkyl groups bound to the Al atoms, the higher the frequency of the NMR signal. This trend is manifest from the data for $Me_3Al\cdot NMe_3$ (179 ppm) and $(Me_2AlCH_2NMe_2)_2$ (166 ppm). More chlorine substituents shift the signals to lower frequencies, as shown for $[ClAl(CH_2NMe_2)_2]_2$ (141 ppm) and $Cl_3Al\cdot NMe_3$ (109 ppm). The resonance at 125 ppm in mixtures resulting from reactions of Me_2NCH_2Li with $AlCl_3$ (one example displayed in Figure 1) could be used to tentatively assign it to $[Cl_2Al(CH_2NMe_2)]_2$ (**7**). The only exception in the series of chemical shifts is the value of 62 ppm, which was assigned $[Al(CH_2NMe_2)_3]_2$ (**6**), as samples containing crystallographically identified $[Al(CH_2NMe_2)_3]_2$ displayed signals with this chemical shift beside others when dissolved in C_6D_6. Resonances at 62 ppm are also always present in various contributions in the spectra of mixtures resulting from preparation attempts of **6**, as described above and shown in Figure 1. A value of 62 ppm indicates that the aluminum atoms should adopt coordination numbers higher than four in solution, which is not too difficult to imagine in the presence of three dimethylaminomethyl groups per aluminum atom. For the homoleptic $Al(CH_2SMe)_3$ five-coordinate Al atoms were also found in the solid state structure.[16] Crystallographic investigation of the compound $[Al(CH_2-$

---

(28) Schnitter, C.; Klimek, K.; Roesky, H. W.; Albers, T.; Schmidt, H.-G.; Röpken, C.; Parisini, E. *Organometallics* **1998**, *17*, 2249.

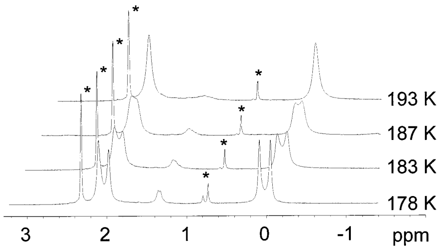


Figure 2. ^{1}H NMR spectra (resolution 0.4 Hz) at various temperatures of $(Me_2AlCH_2NMe_2)_2$ dissolved in [D$_8$]toluene. The signals marked with an asterisk are due to toluene (2.2 ppm) and an impurity (0.8 ppm).

$NMe_2)_3]_2$ (**6**) in the solid state reveals the aluminum centers to adopt the coordination number four (vide infra), and we have to assume this to be the primary coordination type also in solution. There is, however, no basis for a decision whether the remaining dimethylaminomethyl groups coordinate intra- or intermolecularly.

For the homoleptic sulfur compound $Al(CH_2SMe)_3$ a ^{27}Al NMR chemical shift of 160 ppm was reported in [D$_8$]toluene,[16c] but in the thesis of Rüffer[16b] this value is discussed more controversially, as the spectrum illustrated in this work shows only a very weak peak, while for $Al(CH_2SPh)_3$ no ^{27}Al NMR spectrum could be recorded at all.[16b] The proton NMR data of **6** and $Al(CH_2SMe)_3$ cannot be compared, as samples of **6** were not pure and thus gave complex spectra, while the proton NMR spectrum of $Al(CH_2SMe)_3$ was recorded in [D$_8$]THF, in which Al−S donor bonds are broken and $Al(CH_2SMe)_3$ is monomeric and coordinated to THF. In this light the coordination of both the homoleptic sulfur and nitrogen compound remains unclear in solution.

Contamination of the samples of $[Al(CH_2NMe_2)_3]_2$ (**6**) by ate-complexes resulting from the reaction of **6** with an excess of Me_2NCH_2Li could be excluded on the basis of chemical analyses and ^{7}Li NMR spectroscopy, which both showed the absence of lithium in the samples under investigation.

Molecular Dynamics of $(Me_2AlCH_2NMe_2)_2$ in Solution. The dynamic behavior of the heterocyclohexane ring systems was examined with a sample of $(Me_2AlCH_2NMe_2)_2$ dissolved in [D$_8$]toluene by recording proton NMR spectra at various temperatures. A graphical representation of these results is depicted in Figure 2. At low temperatures (178 K) signals are apparent, which can clearly be assigned to the chemically distinguishable axial and equatorial methyl groups at both nitrogen and aluminum atoms. The signal for the methylene group is also split at low temperature, but not resolved into the expected two doublets at the lowest temperature of our experiments, which was 178 K. At higher temperatures these signals tend to merge and finally are mean signals representing the rapid exchange of equatorial and axial sites. The coalescence temperature is found at 187 K, a value that can be converted by the Eyring equation into a barrier of inversion of 9.0 ± 0.3 kcal mol^{-1} for the ring inversion process. This value is remarkably close to that of cyclohexane (10.2 ± 0.2 kcal mol^{-1}).[29]

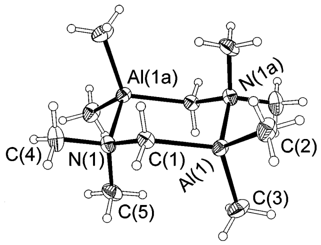


Figure 3. Molecular structure of $(Me_2AlCH_2NMe_2)_2$ (**1**) as obtained by low-temperature X-ray crystallography. $(Me_2GaCH_2NMe_2)_2$ (**2**) is isostructural, and a plot is given in the Supporting Information.

Crystal Structures of $(Me_2AlCH_2NMe_2)_2$ and $(Me_2GaCH_2NMe_2)_2$. The compounds $(Me_2AlCH_2NMe_2)_2$ (**1**) and $(Me_2GaCH_2NMe_2)_2$ (**2**) are isomorphous and both crystallize in the triclinic space group $P\bar{1}$ with $Z = 1$ formula unit of the dimer in the unit cell. The structures of both compounds are illustrated in Figure 3. The dimers have a crystallographic inversion center at the middle of the six-membered $M_2C_2N_2$ rings formed by Al−N and Ga−N donor−acceptor bonds. The rings adopt chair conformations. This formation of six-membered rings for saturated M−C−N units was already described for the heteronorbornane systems $[(Me_2MCH_2NMe)_2CH_2]$ (M = Al, Ga), but in these cases the $M_2C_2N_2$ rings have boat conformations.[20] Note that compounds containing the lighter homologous element boron $[(F_3C)_2B-CR_2-NR'_2]$ have been found to crystallize as monomers with an intramolecular B···N donor−acceptor bond leading to a three-membered ring.[13,14] More similar to the structures of $(Me_2AlCH_2NMe_2)_2$ and $(Me_2GaCH_2NMe_2)_2$ are the sulfur analogous compounds $(Me_2AlCH_2SMe)_2$ and $(Me_2GaCH_2SMe)_2$, which have the same chairlike six-membered ring motif and were described by us earlier.[17]

That the M−C−N angles in both compounds are distinctly larger [121.0(1)° and 119.7(2)°] than the tetrahedral angle is consistent with the absence of any significant attractive interaction between the acceptor centers (Al, Ga) and the donor atoms (N) in the same $Me_2MCH_2NMe_2$ monomer unit. The sums of angles C−M−C about the metal atoms are larger than expected for tetrahedral geometries and are 339.7° for $(Me_2AlCH_2NMe_2)_2$ and 343.9° for $(Me_2GaCH_2NMe_2)_2$. Remarkable are the very different C−M−C angles, with the C1−M−C3 angles (ring to the exocyclic axial methyl group) being the largest [117.0(1)° and 118.8(2)°], the angles C2−M−C3 enclosed by the metal atoms and the two exocyclic carbon atoms being intermediate [113.9(1)° and 114.7(2)°], and the C1−M−C2 angles involving the equatorial methyl groups being the smallest [108.8(1)° and 110.4(1)°].

The M−N distances in the rings of crystalline $(Me_2AlCH_2NMe_2)_2$ and $(Me_2GaCH_2NMe_2)_2$ are 2.010(1) and 2.093(2) Å. For the aluminum compound this may be compared with solid $Me_3N{\cdot}AlH_3$ [2.063(7) Å][30] or solid $Me_3N{\cdot}AlMe_3$ [2.045(1) Å].[31] The Ga−N distance is slightly longer than in solid $Me_3N{\cdot}GaH_3$ [2.081 Å][32] and equal to that of gaseous $Me_3N{\cdot}GaMe_3$ [2.09(5) Å].[33]

---

[29] Friebolin, H.; Ein- und zweidimensionale NMR-Spektroskopie: e. Einf.; VCH: Weinheim, 1988; p 252.

[30] (a) Warner, H. E.; Wang, Y.; Ward, C.; Gillies, C. W.; Interrante, L. *J. Phys. Chem.* **1994**, *98*, 12215. (b) Almenningen, A.; Gundersen, G.; Haugen, T.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 3928.

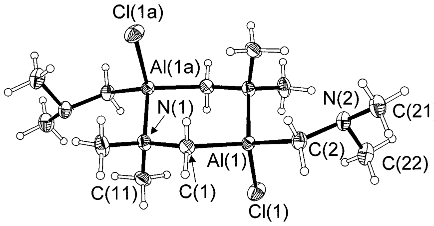


Figure 4. Molecular structure of $[ClAl(CH_2NMe_2)_2]_2$ (**5**) as obtained by low-temperature X-ray crystallography.

Crystal Structure of $(Me_2AlCH_2NMe_2)\cdot(MeClAlCH_2NMe_2)$. The unsymmetrical heterocyclohexane $(Me_2AlCH_2NMe_2)\cdot(MeClAlCH_2NMe_2)$ crystallizes in the centrosymmetric space group $P\bar{1}$, which requires the molecule to be disordered about the center of inversion. It is only the axial sites of the cyclohexane skeleton that are adopted by the chlorine atoms. An alternative refinement in the space group $P1$ with the assumption of a racemic twin turned out to be a less suitable description of the situation, resulting in a slightly worse fit to the experimental scattering intensities. The diffraction experiment was carried out two times with different crystals and led to the following values for the occupation factors for Cl and CH_3 groups at the sites of disorder: first experiment 0.46/0.54, second experiment 0.58/0.42, which finally led us to fix the occupation site factors to 0.5. The desired separation of the electron density maxima between carbon and chlorine positions was achieved by tying the Al−C distance of the disordered methyl group to the Al−C distance of the adjacent methyl group.

Although the total fit of the structure model to the experimental data and the estimated standard deviations are good, the disorder does not allow deriving accurate structural parameters for the molecule, as the structural parameters of the corresponding units in the $(Me_2AlCH_2NMe_2)$ and $(MeClAlCH_2NMe_2)$ parts of the molecule are necessarily averaged. A figure of the structure and these mean values are given in the Supporting Information. Nevertheless, the structure is rather similar to that of $(Me_2AlCH_2NMe_2)_2$, vide supra. In particular the Al−C−N angles are very similar, at 121.0(1)° in $(Me_2AlCH_2NMe_2)_2$ and 122.2(1)° in the monochlorine derivative. Expectedly, the Al−N bonds are slightly shorter in $(Me_2AlCH_2NMe_2)\cdot(MeClAlCH_2NMe_2)$ due to the electronegative chlorine atom attached to the Lewis acidic Al center.

Crystal Structure of $[ClAl(CH_2NMe_2)_2]_2$. The compound $[ClAl(CH_2NMe_2)_2]_2$ (**5**) crystallizes in the monoclinic space group $P2_1/c$, whereby the molecules are arranged about the center of inversion (Figure 4). As in $(Me_2AlCH_2NMe_2)\cdot(MeClAlCH_2NMe_2)$ (**4**) the chlorine substituents are only found to occupy the axial sites of the heterocyclohexane ring, which again adopts a chair conformation. Consistent with the solution ^{27}Al NMR spectra is that the aluminum atoms are only four- and not five-coordinate, despite the presence of two nitrogen donor sites per aluminum center. Therefore, two types of Me_2NCH_2 groups are present: one involved in ring formation with the nitrogen atom being tetracoordinate and bound to the aluminum atom of the second monomer and one “free” dimethylaminomethyl group, which has a free donor site at its nitrogen center. The endocyclic methylene group has a wider Al−C−N valence angle of 122.8(1)° (similar to the three compounds described above) than the exocyclic one, which is 116.6(1)°. However, this is still larger than an ideal tetrahedral angle, but cannot be attributed to a deformation occurring upon ring formation. It is best compared to the also widened B−C−C angle in triethylborane, which was rationalized by hyperconjugation of the p-orbital at boron into C−H orbitals.[34]

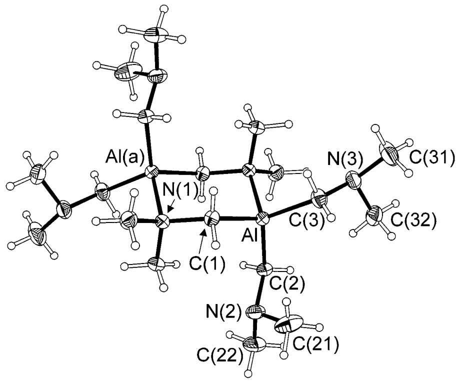


Figure 5. Molecular structure of $[Al(CH_2NMe_2)_3]_2$ (**6**) as obtained by low-temperature X-ray crystallography.

Due to the electronegative chlorine substituent, the lengths of other bonds to aluminum are shorter than in $(Me_2AlCH_2NMe_2)_2$, i.e., the Al−C bonds to the endocyclic methylene groups [1.989(2) vs 2.016(1) Å] and the Al−N bonds [1.974(2) vs 2.010(1) Å].

Crystal Structure of $[Al(CH_2NMe_2)_3]_2$. The homoleptic compound $[Al(CH_2NMe_2)_3]_2$ (**6**) crystallizes in the monoclinic space group $P2_1/n$, with the molecules surrounding the crystallographic center of inversion (Figure 5). The salient point in this structure is the coexistence of coordinate and noncoordinate nitrogen atoms, and the formation of the central six-membered ring with four coordinate Al atoms despite the NMR experiments in C_6D_6 solution seems to indicate higher coordination numbers at Al and therefore involvement of more than one of the three CH_2NMe_2 groups coordinating the Al centers via their nitrogen functions. In common with the crystal structures described above, the six-membered ring adopts a chair conformation and has wide Al−C−N angles of 121.8(1)°, whereas the exocyclic Al−C−N angles are much closer to the tetrahedral angle at 114.9(1)°. Accordingly the endocyclic $(H_2)C$−N bond [1.514(2) Å] is longer, while the exocyclic ones [1.466(2), 1.481(2) Å] resemble more typical values found for instance in the N−C bond lengths to the methyl groups [1.448(3)−1.455(3) Å] at the exocyclic N atoms.

---

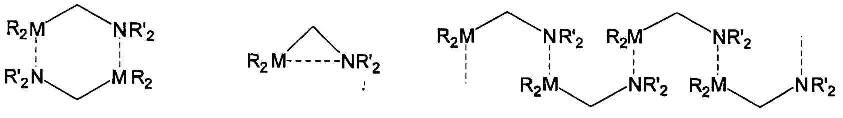
(31) (a) Crystal structure: Gelbrich, T.; Sieler, J.; Dümichen, U. *Z. Kristallogr.* **2000**, *215*, 127. Gas-phase structures: (b) Anderson, G. A.; Forgaard, F. R.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 1947. (c) Anderson, G. A.; Forgaard, F. R.; Haaland, A. *J. Chem. Soc. D* **1971**, 480.

(32) (a) Shriver, D. F.; Nordman, C. E. *Inorg. Chem.* **1963**, *2*, 1298. (b) Andrews, P. C.; Gardiner, M. G.; Raston, C. L.; Tolhurst, V. A. *Inorg. Chim. Acta* **1997**, *259*, 249. (c) Brain, P. T.; Brown, H. E.; Downs, A. J.; Greene, T. M.; Johnsen, E.; Parsons, S.; Rankin, D. W. H.; Smart, B. A.; Tang, C. Y. *J. Chem. Soc., Dalton Trans.* **1998**, 3685.

(33) Mastryukov, V. S.; Novikov, V. P.; Vilkov, L. V.; Golubinskii, A. V.; Golubinskaya, L. M.; Bregadze, V. I. *Zh. Strukt. Khim./J. Struct. Chem. (Engl. Transl.)* **1987**, *28*, 143/122.

(34) Boese, R.; Bläser, D.; Niederprüm, N.; Nüsse, M.; Brett, W. A.; Schleyer, P. v. R.; Bühl, M.; van Eikema Hommes, N. J. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 314.

Scheme 1



1 (M = Al, R = R' = CH_3) **1a**

2 (M = Ga, R = R' = CH_3) **2a**

Table 3. Bond Lengths [Å] and Angles [deg] for $[Me_2AlCH_2NMe_2]_2$ (1) and $[Me_2GaCH_2NMe_2]_2$ (2) as Obtained from Low-Temperature X-ray Crystallography and Quantum Chemical Calculations

	$[Me_2AlCH_2NMe_2]_2$		$[Me_2GaCH_2NMe_2]_2$	
	XRD	B3LYP/ 6-311G(d)	XRD	B3LYP/ 6-311G(d)
M(1)−C(1)	2.016(1)	2.042	2.019(3)	2.051
M(1)−C(2)	1.979(1)	1.994	1.994(3)	2.010
M(1)−C(3)	1.980(1)	1.996	1.998(4)	2.012
M(1)−N(1a)	2.010(1)	2.071	2.093(2)	2.174
N(1)−C(5)	1.482(2)	1.483	1.475(4)	1.477
N(1)−C(4)	1.486(2)	1.485	1.487(4)	1.481
N(1)−C(1)	1.509(1)	1.509	1.459(4)	1.499
C(2)−M(1)−C(3)	113.9(1)	115.1	114.7(2)	116.4
C(2)−M(1)−N(1a)	106.8(1)	106.3	104.6(1)	104.3
C(3)−M(1)−N(1a)	105.2(1)	105.1	103.5(1)	103.0
C(2)−M(1)−C(1)	108.8(1)	108.5	110.4(1)	109.5
C(3)−M(1)−C(1)	117.0(1)	117.1	118.8(2)	119.0
N(1a)−M(1)−C(1)	104.0(1)	103.5	102.8(1)	102.2
C(5)−N(1)−C(4)	108.1(1)	108.2	108.5(4)	108.5
C(5)−N(1)−C(1)	109.5(1)	110.0	110.2(2)	110.6
C(4)−N(1)−C(1)	110.0(1)	110.4	109.7(2)	110.2
C(5)−N(1)−M(1a)	110.9(1)	110.0	110.6(2)	110.3
C(4)−N(1)−M(1a)	110.7(1)	110.4	109.2(2)	108.6
C(1)−N(1)−M(1a)	107.6(1)	107.9	108.6(2)	108.7
N(1)−C(1)−M(1)	121.0(1)	112.0	119.7(2)	121.2

Three-Membered Monomers vs Six-Membered Ring Dimers: Calculations. The formation of six-membered ring dimers as described in the preceding section is only one of a number of alternatives one can imagine to saturate the coordinative demand of the Lewis acidic earth metal centers (Scheme 1). In particular the highly strained three-membered rings with an intra-monomer donor−acceptor bond have been found to exist in compounds with B−C−N[13,14] and Al−N−N[35] units (and also in Si−O−N compounds).[36] The differences in energies between the six-membered ring dimers and the three-membered ring monomers should be dominated by the ring strain. We optimized both types of geometries for the Al and Ga compounds **1** and **2** and their three-membered ring monomers **1a** and **2a** with HF and DFT methods up to the B3LYP/6-311G(d) level of theory. The geometries of the compounds **1** and **2** are so close to their crystal structures that they do not need to be displayed separately. Their geometry parameters may be compared with the experimental results in Table 3. The small ring monomer geometry of **1a** is shown in Figure 6, and the bond lengths and angles of the $Me_2AlCH_2NMe_2$ and $Me_2GaCH_2NMe_2$ monomers (**1a** and **2a**) are listed in Table 6. The structure of **1a** was also calculated at the higher MP2/6-311G(d,p) level, but the geometry is quite close to that optimized at the B3LYP/6-311G(d) level of theory, making us confident that the DFT method is suitable to predict the structures with suitable accuracy.

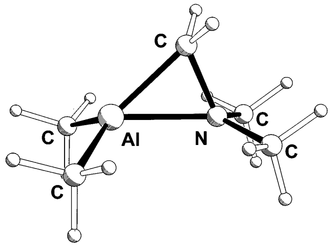


Figure 6. Molecular structures of the three-membered ring isomer $Me_2AlCH_2NMe_2$ (**1a**) as calculated at the B3LYP/6-311G(d) level of theory.

Table 4. Bond Lengths and Angles for $[Cl(Me_2NCH_2)_2Al]_2$ (5)

distance [Å]	value	angle [deg]	value
Al(1)−C(2)	1.973(2)	C(2)−Al(1)−N(1a)	108.5(1)
Al(1)−N(1a)	1.974(2)	C(2)−Al(1)−C(1)	109.8(1)
Al(1)−C(1)	1.989(2)	N(1a)1−Al(1)−C(1)	106.2(1)
Al(1)−Cl(1)	2.171(1)	C(2)−Al(1)−Cl(1)	114.7(1)
N(1)−C(12)	1.486(3)	N(1a)−Al(1)−Cl(1)	104.0(1)
N(1)−C(11)	1.489(3)	C(1)−Al(1)−Cl(1)	113.1(1)
N(1)−C(1)	1.510(2)	C(12)−N(1)−C(11)	107.5(2)
N(1)−Al(1a)	1.974(2)	C(12)−N(1)−C(1)	110.0(2)
N(2)−C(22)	1.449(3)	C(11)−N(1)−C(1)	110.2(2)
N(2)−C(21)	1.456(3)	C(12)−N(1)−Al(1a)	112.7(1)
N(2)−C(2)	1.482(2)	C(11)−N(1)−Al(1a)	107.8(1)
		C(1)−N(1)−Al(1a)	108.6(1)
		N(1)−C(1)−Al(1)	122.8(1)
		C(22)−N(2)−C(21)	109.2(2)
		C(22)−N(2)−C(2)	110.7(2)
		C(21)−N(2)−C(2)	111.2(2)
		N(2)−C(2)−Al(1)	116.6(1)

Concerning the bonding situation in **1a** and **2a**, a closer look at the geometries reveals that the C_2M-CH_2 units in **1a** and **2a** are almost planar, which seems surprising at first glance. However, this geometry compares nicely to the crystal structure data of the related compounds $(F_3C)_2BC(SiMe_3)(CH_2Ph)NMe_2$[13] and $(F_3C)_2BC(Ph)_2NMe_2$,[14] where it was also noted that the substituent planes BCC and CCSi do not bisect the corresponding angles of the three-membered rings. In this case it was attributed to steric interactions between the substituents at the ring atoms B and C, but in light of our quantum chemical results for the closely related **1a** we have to favor electronic interactions as the superior way to rationalize this behavior.

---

(35) (a) Uhl, W.; Molter, J.; Neumüller, B. *Eur. J. Inorg. Chem.* **2001**, 1510. Related compounds can be found in: (b) Uhl, W.; Molter, J.; Neumüller, B.; Schmock, F. *Z. Anorg. Allg. Chem.* **2001**, *627*, 909. (c) Uhl, W.; Molter, J.; Koch, R. *Eur. J. Inorg. Chem.* **1999**, 2021. (d) Uhl, W.; Molter, J.; Koch, R. *Eur. J. Inorg. Chem.* **2000**, 2255. (e) Uhl, W.; Molter, J.; Neumüller, B.; Saak, W. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2284. (e) (f) Uhl, W.; Molter, J.; Neumüller, B. *Organometallics* **2000**, *19*, 4422. (g) Uhl, W.; Molter, J.; Neumüller, B. *Inorg. Chem.* **2001**, *20*, 2011. (h) Uhl, W.; Molter, W.; Neumüller, B. *Chem. Eur. J.* **2001**, *7*, 1510.

(36) (a) Mitzel, N. W.; Losehand, U. *Angew. Chem.* **1997**, *109*, 2897; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2807. (b) Losehand, U.; Mitzel, N. W. *Inorg. Chem.* **1998**, *37*, 3175. (c) Mitzel, N. W.; Losehand, U. *J. Am. Chem. Soc.* **1998**, *120*, 7320. (d) Mitzel, N. W.; Losehand, U.; Wu, A.; Cremer, D.; Rankin, D. W. H. *J. Am. Chem. Soc.* **2000**, *122*, 4471.

Table 5. Bond Lengths and Angles for $[(Me_2NCH_2)_3Al]_2$ (6)

distance [Å]	value	angle [deg]	value
Al(1)−N(1)	1.999(2)	N(1)−Al(1)−C(2)	104.5(1)
Al(1)−C(2)	2.009(2)	N(1)−Al(1)−C(1)	104.8(1)
Al(1)−C(1)	2.009(2)	C(2)−Al(1)−C(1)	116.0(1)
Al(1)−C(3)	2.013(2)	N(1)−Al(1)−C(3)	104.3(1)
N(1)−C(11)	1.484(2)	C(2)−Al(1)−C(3)	120.2(1)
N(1)−C(12)	1.484(2)	C(1)−Al(1)−C(3)	105.5(1)
N(1)−C(1a)	1.514(2)	C(11)−N(1)−C(12)	108.0(1)
C(1)−N(1a)	1.514(2)	C(11)−N(1)−C(1a)	110.1(1)
C(2)−N(2)	1.466(2)	C(12)−N(1)−C(1a)	109.1(1)
N(2)−C(21)	1.448(3)	C(11)−N(1)−Al(1)	110.5(1)
N(2)−C(22)	1.455(3)	C(12)−N(1)−Al(1)	110.7(1)
N(3)−C(32)	1.450(3)	C(1a)−N(1)−Al(1)	108.5(1)
N(3)−C(31)	1.455(3)	N(1a)−C(1)−Al(1)	121.8(1)
N(3)−C(3)	1.481(2)	N(2)−C(2)−Al(1)	114.9(1)
		C(21)−N(2)−C(22)	110.0(2)
		C(21)−N(2)−C(2)	110.5(2)
		C(22)−N(2)−C(2)	111.2(2)
		C(32)−N(3)−C(31)	109.1(2)
		C(32)−N(3)−C(3)	109.6(2)
		C(31)−N(3)−C(3)	112.0(2)
		N(3)−C(3)−Al(1)	114.9(1)

Table 6. Geometry Parameters for the Hypothetical Three-Membered Ring Compounds $Me_2AlCH_2NMe_2$ (1a) and $Me_2GaCH_2NMe_2$ (1b) as Calculated Quantum Chemically[a]

	$Me_2AlCH_2NMe_2$		$Me_2GaCH_2NMe_2$
compound	MP2/ 6-311G(d,p)	B3LYP/ 6-311G(d)	B3LYP/ 6-311G(d)
$M-CH_3$	1.973	1.972	1.992
$M-CH_2$	1.972	1.979	1.993
$N-CH_2$	1.533	1.538	1.513
$N-CH_3$	1.465	1.466	1.459
M−N	2.035	2.068	2.282
M−C−N	69.7	71.0	80.0
H_2C-M-N	44.9	45.9	40.7
H_2C-N-M	65.4	64.4	59.3
$H_2C-M-CH_3$	119.6	119.9	118.9
$H_3C-M-CH_3$	120.5	119.9	122.0
$H_2C-N-CH_3$	112.7	113.5	113.6
$H_2C-N-CH_3$	110.8	111.4	112.0

[a] Bond lengths are given in Å and angles in deg.

A further compound that may be compared with **1a** is the three-membered BNN ring in (Mes)ClBN[BCl(Mes)]NMe_2,[37] which also has the substituent plane BClC at the ring boron atom deviating substantially from the bisector of the ring valence angle at this boron atom.

The metal−carbon distances for the bonds to the methyl groups and the methylene units are very similar, unlike in the structures of the dimers, where the $M-CH_2$ distances are slightly longer. However, the endocyclic N−C distances are predicted to be 1.538 and 1.513 Å for **1a** and **2a** and are thus substantially widened with respect to the exocyclic N−C distances of 1.466 and 1.459 Å, which are in the normal range for such bonds. This parallels the widening of the N−O bonds in the three-membered ring SiON compounds with Si···N donor−acceptor interactions recently investigated by our group.[36]

The coordination sphere MC_3 about the Al and Ga atoms in **1a** and **2a** are flat, as indicated by the sum of angles CMC. These are 358.7° and 358.8° for **1a** and **2a**. Together with the equally long M−C distances this could be interpreted as a three-coordinate metal atom, with the geminal nitrogen center being attracted by purely electrostatic forces, i.e., not leading to a pyramidalization under formation of an at least partially covalently bonded adduct.

The energy differences **1**/**1a** and **2**/**2a** (81 and 77 kJ mol^{-1} per monomer) give a rough estimate for the driving force of preference for the dimeric six-membered ring structures.

We have prepared simple organometallic compounds containing saturated M−C−N linkages for the metals aluminum, gallium, and indium. Like the simple boron compound $H_2BCH_2NMe_2$,[38] our new compounds are dimeric with $M_2C_2N_2$ rings. Electronegative or large substituents at boron have allowed the isolation of compounds with BCN three-membered rings. Calculations on the alternative aggregation motifs for Al−C−N and Ga−C−N compounds favor clearly the dimerization into six-membered rings over three-membered monomers. At present we are going to explore the effects of substituents at the metal and the nitrogen atom for the aluminum, gallium, and indium compounds. The possibility for higher aggregation than into dimers or intramolecular coordination of aminomethyl groups to the metal atoms as is evident for $Al(CH_2NMe_2)_3$ in solution still remains incompletely understood and deserves further investigations.

Dimerization rather than three-membered ring formation is found to be the preferred way of aggregation in a variety of dimethylaminomethyl compounds of Al, Ga, and In. These are compounds with geminal nitrogen donor and metal acceptor centers, which were prepared and their coordination investigated in different phases, accompanied by studies of the dynamic behavior by NMR and theoretical studies.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and the Leonhard-Lorenz-Stiftung. We are grateful to Professor H. Schmidbaur for generous support.

Supporting Information Available: Crystal structure plots of compounds **2** and **4**, a table of structural parameters for **4**, tables of crystal data, atomic coordinates, and equivalent isotropic thermal parameters for all crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020687R

---

[37] Diemer, S.; Nöth, H.; Storch, W. *Eur. J. Inorg. Chem.* **1999**, 1765.

[38] (a) Miller, N. E.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 1196. (b) Miller, N. E.; Murphy, M. D.; Reznicek, D. L. *Inorg. Chem.* **1966**, *5*, 1832. (c) Hseu, T. H.; Larsen, L. A. *Inorg. Chem.* **1975**, *14*, 330.