

Novel aluminium- and gallium-nitrogen heteronorbornanes†

Christian Lustig and Norbert W. Mitzel*

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany.
E-mail: n.mitzel@lrz.tu-muenchen.de

Received (in Basel, Switzerland) 5th May 2000, Accepted 16th June 2000

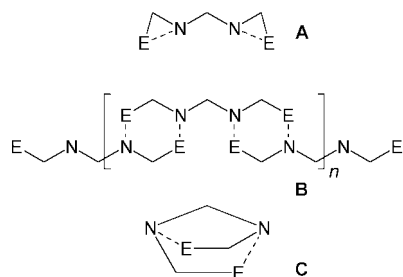
Published on the Web 6th July 2000

Selective formation of 2,5-dialumina-3,6-diaza- and 2,5-digalla-3,6-diaza-norbornane is achieved by reaction of bis(thiomethyl-methylamino)methane with dimethylaluminium and dimethylgallium chloride by simultaneous formation of two metal-carbon and two metal-nitrogen bonds accompanied by two ring closure reactions; the norbornane-basket structures are favoured over potential isomers containing three-membered rings and over polymeric aggregation.

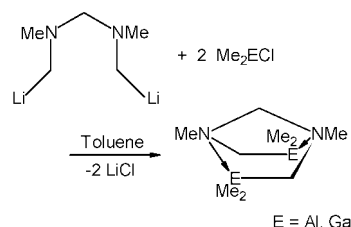
Small molecule nitrogen compounds of aluminium and gallium are the subjects of recent interest owing their potential as molecular precursors for III/V materials.¹ Investigations on both donor-acceptor adducts and metal amides have been intensely pursued.² Recent interest in compounds with acceptor and donor atoms in geminal position revealed various types of possible aggregates, either intramolecular *via* formation of three-membered ring systems as in compounds containing BCN,³ BNN,⁴ AICN⁵ and AINN⁶ but also SiON,⁷ GeON⁸ and SnON⁹ units or intermolecular *via* formation of dimers with cyclohexane-like six-membered rings as in [(H₂BCH₂SMe₂)₂],¹⁰ [Me₂Al(CH₂PMe₂)₂]₂ and [Al(CH₂PMe₂)₃]₂,¹¹ and [(Me₃C-CH₂)₂InCH₂PPh₂]₂.¹² We intended to construct systems with two ECN functions joined by a bridging unit which have at least three possibilities for aggregation as depicted in Scheme 1 two three-membered rings (A), six-membered rings in either polymeric aggregation (B) or aggregated to form a norbornane-like structure (C).

In this contribution we demonstrate by preparation of the first alumina- and galla-azanorbornanes that the structural motif C is preferred for the saturated AICN and GaCN systems. The reaction of a slurry of Karsch's dilithiated aminal [LiCH₂(Me)₂N]₂CH₂¹³ with 2 equiv. of dimethylaluminium chloride or dimethylgallium chloride in toluene at -78 °C leads to a simultaneous formation of four chemical bonds and two ring closures to give the norbornane-like aggregates depicted in Scheme 2.† The reactions proceeds uniformly, and no sign of structures of type A and B were observed.

Compounds **1** and **2** show the typical NMR spectra of norbornane units with two non-equivalent signals for the two geminal methyl groups at Al or Ga (E) and the geminal hydrogen atoms at the carbon atom connecting E and N. These signals do not coalesce upon heating toluene solutions to



Scheme 1



Scheme 2

110 °C, proving the absence of rapid rearrangement reactions involving cleavage of the donor acceptor bonds, required for a positional exchange of the metal bound methyl groups.

Single crystals of both compounds, obtained from toluene solutions upon cooling, were examined by X-ray diffraction, and the structure of **1** is shown in Fig. 1.‡§ Compound **1** and the isostructural **2** are the first structurally characterised aminomethyl-aluminium and -gallium compounds. The molecules reside on C₂ axes passing through the aminal carbon atom and are chiral, but occur in the crystal as a racemate. The methylene bridge between the two N atoms causes the E₂C₂N₂ six-membered ring to adopt a boat conformation with compressed angles at the metal centres [**1**: 86.2(1)°, **2**: 85.1(1)°] and widened angles at the methylene groups in the six-membered ring [**1**: 105.8(1), **2**: 106.3(2)°] relative to the C_{2v} symmetric hydrocarbon norbornane where the C-C-C angles at the methylene groups in the six-membered ring are 102.7°.¹⁴ This leads to a geometry at the metal atoms which deviates drastically from an ideal tetrahedron. The endocyclic E-N and E-C bond lengths are long when compared to the gas phase values of simple reference compounds such as Me₃Al-NMe₃ [Al-N 2.099(10), Al-C 1.987(5) Å]¹⁵ and Me₃Ga-NMe₃ [Ga-N 2.09(3), Ga-C 1.992(6) Å].¹⁶

The N-C bonds involving the metallated carbon atoms in the norbornane cages of **1** and **2** (N-C2) are *ca.* 3 pm longer than the N-C1 and N-C2 bonds. This elongation of bonds within the ring system indicates the presence of some strain. B3LYP/6-311G(d) calculations were conducted to obtain an estimate for

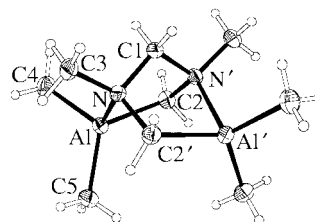


Fig. 1 Molecular structure of (Me₂AlCH₂MeN)₂CH₂ **1**. Selected interatomic distances (Å) and angles (°) for **1**: Al-C2 2.020(1), Al-C4 1.971(1), Al-C5 1.962(1), Al-N 2.028(1), N-C1 1.481(1), N-C2 1.514(1), N-C3 1.482(1); Al'-C2-N 105.8(1), Al-N-C2' 110.2(1), N-C1-N' 106.2(1), N-Al-C2 86.2(1), C1-N-Al 102.2(1), C1-N-C2 107.1(1), C2-Al-C4 112.3(1), C2-Al-C5 120.6(1). Selected interatomic distances (Å) and angles (°) for isostructural **2**: Ga-C2 2.026(3), Ga-C4 1.991(4), Ga-C5 1.977(4), Ga-N 2.124(3), N-C1 1.476(4), N-C2 1.503(4), N-C3 1.475(4); Ga'-C2-N 106.3(2), Ga-N-C2' 110.7(2), N-C1-N' 106.7(3), N-Ga-C2 85.1(1), C1-N-Ga 100.7(2), C1-N-C2 108.5(2), C2-Ga-C4 112.9(2), C2-Ga-C5 122.0(2).

† Electronic supplementary information (ESI) available: selected geometry parameters for **1** and **2** (X-ray and DFT). See <http://www.rsc.org/suppdata/cc/b0/b003813j/>

the difference in energy between the monomolecular structures **A** and **C**, which were predicted to be 162 and 206 kJ mol⁻¹ for **1** and **2**, respectively, and their three-membered ring isomers. As the norbornane structures of **1** and **2** cannot be regarded as strain-free, although much less strained than the three-membered-ring isomers, these values indicate that the *AICN* units in the three-membered-ring isomers contain at least 80 kJ mol⁻¹ more strain energy relative to their six-membered ring dimers. The observation of compounds containing *AICN* and also *AINN* three-membered rings can therefore only be rationalised by steric shielding of the small ring unit.

The compact structures of **1** and **2** leads to their comparatively high volatility, and both can be sublimed at ca. 90 °C under a pressure of 0.01 mbar without decomposition. The volatility of **1** and **2** leads to the expectation of a small molecular dipole moment for **1** and **2**. Calculations give estimates for dipole moments of 3.95 and 3.43 D for **1** and **2**. The value for **1** is higher than for its three-membered-ring isomer (2.14 D).

We have shown that introduction of two linkages containing acceptor and donor atoms in geminal positions are useful for the synthesis of organometallic heterocyclic systems without the necessity for sterically demanding ligands. Variations of the donor and acceptor centres and the bridging unit opens a field for many novel structural motifs generated through intra- and inter-molecular coordination and for the construction of new macrocyclic compounds.

We are grateful to the Deutsche Forschungsgemeinschaft, the Leonhard-Lorenz-Stiftung and the Fonds der Chemischen Industrie for financial support. Selected geometry parameters for crystalline **1** and **2** accompanied by the results of B3LYP/6-311G(d) calculations is available as ESI.†

Notes and references

† Preparation of **1** and **2**: Me₂ECl (E = Al, Ga) (10 ml of a 1 M solution in *n*-hexane, 10 mmol) was slowly added at -78 °C to a stirred suspension of [LiCH₂N(Me)]₂CH₂ (0.57 g, 5.00 mmol) in toluene (40 ml). The reaction mixture was gradually warmed to room temperature and stirred for 1 day. The solvents were evaporated under reduced pressure and the residue was dissolved in *n*-hexane (20 ml) and filtered. Storage at -20 °C afforded colourless crystals.

Compound 1: yield: 0.72 g (67%), mp 118–119 °C. CI-MS [*m/z* (%): 198 (100), [M⁺ - CH₃]; ¹H NMR (400.05 MHz, 298 K, C₆D₆): δ -0.67 (s, 6 H, AlCH₃), -0.34 (s, 6 H, AlCH₃), 0.97 (d, ¹J_{HH} 12.8 Hz, 2 H, AlCH₂N), 1.82 (s, 6 H, NCH₃), 2.11 (d, ¹J_{HH} 12.8 Hz, 2 H, AlCH₂N), 2.16 (s, 2 H, NCH₂N); ¹³C{¹H} NMR (100.50 MHz, 298 K, C₆D₆): δ -10.50 (AlCH₃), -8.92 (s, AlCH₃), 45.88 (NCH₃), 47.52 (AlCH₂N), 81.71 (AlCH₂N); ²⁷Al NMR (104.05 MHz, 298 K, C₆D₆): δ 178 (ν₂ 1700 Hz).

Compound 2: yield: 1.11 g (74%), mp 114–116 °C. CI-MS [*m/z* (%): 284 (100), [M⁺ - CH₃]; ¹H NMR (400.05 MHz, 298 K, C₆D₆): δ -0.35 (s, 6 H,

GaCH₃), -0.09 (s, 6 H, GaCH₃), 1.16 (d, ¹J_{HH} 11.35 Hz, 2 H, GaCH₂N), 1.88 (s, 6 H, NCH₃), 2.11 (s, 2 H, NCH₂N), 2.26 (d, ¹J_{HH} = 11.35, 2 H, GaCH₂N), ¹³C{¹H} NMR (100.50 MHz): δ -7.32 (GaCH₃), -5.93 (GaCH₃), 45.73 (NCH₃), 49.21 (GaCH₂N), 82.32 (GaCH₂N).

§ *Crystal data*: **1**, C₉H₂₄Al₂N₂, *M* = 214.26, monoclinic, space group *P2*/*n*, *a* = 7.802(2), *b* = 7.351(1), *c* = 11.923(2) Å, β = 101.36(1)°, *V* = 670.4(2) Å³, *D*_c(*Z* = 2) = 1.061 g cm⁻³. 2067 reflections collected on a Turbo-CAD4 four circle diffractometer [ω-scan, 2θ_{max} = 54°, Mo-Kα radiation, λ = 0.71073 Å, *T* = 143(2) K] merged to 1463 unique (*R*_{int} = 0.036) refining to *R*₁ = 0.023 for 1347 data [*F*_o > 4σ(*F*_o)] and *wR*₂ = 0.069 for all 1463 data. Anisotropic refinement of all thermal displacement parameters for non-H-atoms, isotropic for H-atoms.

2, C₉H₂₄Ga₂N₂, *M* = 299.74, monoclinic, space group *P2*/*n*, *a* = 7.7786(3), *b* = 7.4037(3), *c* = 11.8506(6) Å, β = 101.475(3)°, *V* = 668.8(2) Å³, *D*_c(*Z* = 2) = 1.488 g cm⁻³. 2447 reflections collected on a Nonius DIP2020 image plate diffractometer [2θ_{max} = 53°, Mo-Kα radiation, λ = 0.71073 Å, *T* = 133(2) K] merged to 1372 unique (*R*_{int} = 0.011) refining to *R*₁ = 0.034 for 1220 data [*F*_o > 4σ(*F*_o)] and *wR*₂ = 0.090 for all 1372 data. Anisotropic refinement of all thermal displacement parameters for non-H-atoms, isotropic for H-atoms.

CCDC 182/1689. See <http://www.rsc.org/suppdata/cc/b0/b003813j/> for crystallographic files in .cif format.

- 1 A. H. Cowley and R. A. Jones, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1208.
- 2 *Chemistry of Aluminum, Gallium and Indium*, ed. A. J. Downs, Blackie-Chapman Hall, London, 1993; *Coordination Chemistry of Aluminum*, ed. G. H. Robinson, VCH Publishers, Weinheim, 1993.
- 3 T. H. Hseu and L. H. Larsen, *Inorg. Chem.*, 1975, **14**, 330.
- 4 S. Diemer, H. Nöth and W. Storch, *Eur. J. Inorg. Chem.*, 1999, 1765.
- 5 W. Uhl, U. Schütz, W. Hiller and M. Heckel, *Chem. Ber.*, 1994, **127**, 1587.
- 6 W. Uhl and F. Hannemann, *Eur. J. Inorg. Chem.*, 1999, 201.
- 7 N. W. Mitzel and U. Losehand, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2807; N. W. Mitzel and U. Losehand, *J. Am. Chem. Soc.*, 1998, **120**, 7320.
- 8 N. W. Mitzel and U. Losehand, *Eur. J. Inorg. Chem.*, 1998, 2023.
- 9 N. W. Mitzel, U. Losehand and A. Richardson, *Organometallics*, 1999, **18**, 2610.
- 10 H. Nöth and D. Sedlak, *Chem. Ber.*, 1983, **116**, 1479.
- 11 H. H. Karsch and A. Appelt, *Phosphorus Sulfur Relat. Elem.*, 1983, **18**, 287; H. H. Karsch, A. Appelt, F. H. Köhler and G. Müller, *Organometallics*, 1985, **4**, 231.
- 12 O. T. Beachley, M. A. Banks, M. R. Churchill, W. G. Feighery and J. C. Fettinger, *Organometallics*, 1991, **10**, 3036.
- 13 H. H. Karsch, *Chem. Ber.*, 1996, **129**, 483.
- 14 N. L. Allinger, H. J. Geise, W. Pyckhout, L. A. Paquette and J. C. Gallucci, *J. Am. Chem. Soc.*, 1989, **111**, 1106.
- 15 G. A. Anderson, F. R. Forgaard and A. Haaland, *Acta Chem. Scand.*, 1972, **26**, 1947.
- 16 V. S. Mastryukov, V. P. Novikov, L. V. Vil'kov, A. V. Golubinskii, L. M. Golubinskaya and V. I. Bregadze, *Zh. Strukt. Khim.*, 1987, **28**, 143; *J. Struct. Chem. (Engl. Transl.)*, 1987, **28**, 122.