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Formation of the Unprecedented Trilithio-Capped Heteroadamantanyl Iminoalane Anion $[(HAl)_4(NPh)_6\{Li(OEt_2)\}_3]^-$: An Open Cage Derived from a Rhombododecahedron**

Kenneth W. Henderson,* Alan R. Kennedy,
Arlene E. McKeown, and Robert E. Mulvey

There is a great deal of current interest in the preparation of organometallic compounds containing combinations of p-block elements due to their uses in the electronics industry,[1] in catalysis,[2] and in the search for new types of π bonding.[3] As a result, a wide variety of heterodimetallic species that adopt polyhedral cage frameworks have been characterized, and structural patterns within their mixed-metal cores are now emerging. A notable example exists for the isovalent series of compounds with general formulas $M_4E_6Li_4$ (where M = AlH, E = AsSi*i*Pr$_3$; M = AlMe or Sn, E = PC$_6$H$_{11}$)[4] or $M_2E_6Li_6$ (where M = Sb, E = NCH$_2$CH$_2$Ph, NC$_6$H$_{11}$, N*t*Bu, NC$_6$H$_3$(OMe)$_2$, or PC$_6$H$_{11}$;[5] M = Ge*t*Bu, E = AsSi*i*Pr$_3$;[6] M = SiR, E = NR′,[7] where R = H, R′ = Me$_3$Si; R = Me, *t*Bu or Ph, R′ = Me$_3$Si; R = Me or Ph, R′ = *t*Bu; R = Me or *t*Bu, R′ = Me; M = SiEt, E = PSi*i*Pr$_3$), which all adopt structures containing very similar 14-membered rhombododecahedral cage cores (Lewis base complexants within the compounds are ignored for simplicity). In contrast, we now report the synthesis of the novel, charge-separated complex **1**, which though isovalent with the above compounds adopts a unique molecular geometry.

$[Li(OEt_2)_3]^+[(HAl)_4(NPh)_6\{Li(OEt_2)\}_3]^-$ **1**

Complex **1** was originally prepared from the equimolar reaction between the primary amidolithium PhN(H)Li and the alane adduct $H_3Al\cdot N(Me)C_5H_8$ (where N(Me)C$_5$H$_8$ = 1-methyl-1,2,3,6-tetrahydropyridine)[8] in diethyl ether solution. However, measurement of H$_2$ evolution from the reaction has established that the ideal stoichiometry for the preparation of **1** is that shown in Equation (1). Crystallographic analysis of **1** revealed a remarkable structure consisting of a cage anion (**1a**; Figure 1) and a solvent-separated countercation, with no discernible close contacts between the two.[9]

$$6\,PhN(H)Li + 4\,H_3Al\cdot N(Me)C_5H_8 \xrightarrow[-4\,MeNC_5H_8]{Et_2O} \mathbf{1} + 2\,LiH + 6\,H_2 \qquad (1)$$

Solution NMR data (^{27}Al and low-temperature ^{7}Li) appear to be consistent with the solid-state structure of **1**, indicating the presence of two distinct signals (apical/equatorial Al, and cation/anion Li). However, a full understanding of the

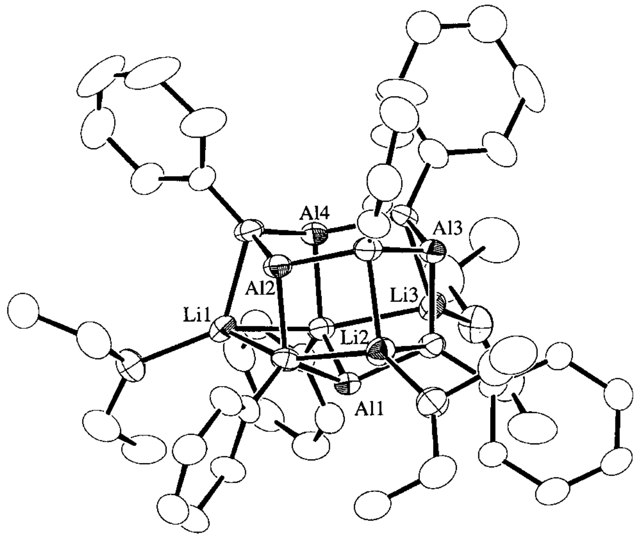

Figure 1. Molecular structure of **1a** with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Al1-N1 1.882(6), Al1-N3 1.901(7), Al1-N4 1.895(6), Al2-N1 1.914(6), Al2-N2 1.873(7), Al2-N5 1.881(7), Al3-N2 1.860(7), Al3-N3 1.918(6), Al3-N6 1.890(7), Al4-N4 1.924(6), Al4-N5 1.881(7), Al4-N6 1.868(7), Li1-O1 1.929(14), Li2-O2 1.950(14), Li3-O3 1.930(13), Li1-N1 2.205(15), Li1-N4 2.227(15), Li1-N5 2.106(14), Li2-N1 2.218(15), Li2-N2 2.059(14), Li2-N3 2.227(15), Li3-N3 2.225(14), Li3-N4 2.221(14), Li3-N6 2.069(13); N-Li-N 84.97 (mean), N-Al1-N 104.17 (mean), N-Al2-N 105.40 (mean), N-Al3-N 105.40 (mean), N-Al4-N 105.73 (mean).

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[*] Dr. K. W. Henderson, Dr. A. R. Kennedy, A. E. McKeown,
Prof. R. E. Mulvey
Department of Pure and Applied Chemistry
University of Strathclyde
Glasgow, G1 1XL (UK)
Fax: (+44) 141-552-0876
E-mail: k.w.henderson@strath.ac.uk

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complex dynamic processes occurring in solution has yet to be determined.

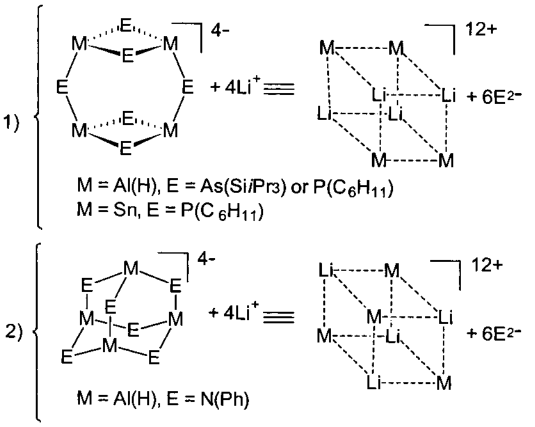
The fascinating feature of the "missing" vertex of the cage can be explained in terms of the cavity size of the Al_3N_3 rings. Analysis of the bond lengths within **1a** indicate only small differences for the Al–N distances (range from 1.860(7) to 1.924(6) Å; mean 1.890 Å). These are consistent with the distance of 1.888(5) Å found in both of the related Li/Al amide dimers **2** and **3**.[10] Significantly, the Li–N distances

$[\{Me_2AlN(Ph)Li(thf)_2\}_2]$ **2**

$[\{iBu_2AlN(Ph)Li(thf)\}_2]$ **3**

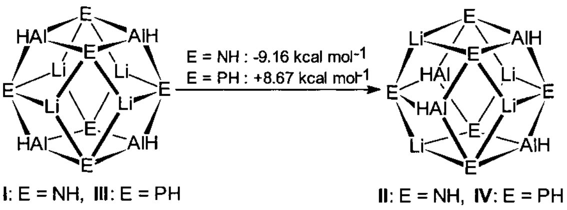
show much greater variance, ranging from 2.059(14) to 2.227(15) Å, and the mean distance of 2.173 Å is much longer than those found in **2** and **3** (2.023(12) and 1.980(17) Å, respectively). Each Li center in **1a** asymmetrically caps a Al_3N_3 ring, with one relatively short contact to the nitrogen atom on the open face of the cage (mean 2.078 Å), and two long contacts, to the remaining nitrogen atoms (mean 2.220 Å). The overall effect is that the uncapped Al_3N_3 face of the cage is more open (less puckered) than the three Li-capped Al_3N_3 faces. Further evidence for this distortion is the differences in the transannular N⋯N distances, which are 2.94 Å (mean) for the capped faces and 3.18 Å (mean) for the open face. The widening of the fourth Al_3N_3 ring results in a larger cavity, which can no longer accommodate (or trap) a Li center, leading to the preferential formation of a charge-separated complex.

Further examination of **1a** reveals a surprising difference in the arrangement of the atoms within the cage skeleton compared to the previously mentioned isovalent 14-membered cage compounds.[4–7] These complexes, with the general core formula $M_4E_6Li_4$ (M = Al, E = As or P; M = Sn, E = P), have almost identical frameworks. They consist of a pair of dimeric M_2E_2 rings connected through two additional bridging E ligands, leading to a tetraanionic polycycle (Scheme 1). Another view is to consider the structures composed of two orthogonal rectangular planes of metals, M_4/Li_4. This view can be extended to include the compounds with the general core formula $M_2E_6Li_6$ (M = Sb or Si, E = N and M = Ge, E = As), where one rectangular plane of metals is composed of a dimetallic M_2Li_2 ring. In contrast, **1a** breaks with this structural pattern by adopting a unique $(HAl)_4(NPh)_6$ heteroadamantanyl tetraanionic core, which has three of the four six-membered Al_3N_3 rings capped by μ_3-Li centers. In theory, placement of a fourth Li atom to make a closed cage structure would result in two interpenetrating tetrahedra of metals, that is an isomer of the related heterodimetallic complexes (Scheme 1).



Scheme 1. Simplified view of the alternative cores in the dimetallic cages, 1) bridged dimers and 2) heteroadamantanyl.

Ab initio molecular orbital calculations (HF/6-31G*) were carried out for two isomers of the model complex $[(HAl)_4(NH)_6Li_4]$: 1) bisecting planes of metals (**I**) and 2) interpenetrating tetrahedra of metals (**II**) (Scheme 2).[11]



Scheme 2. Generalized view of the calculated molecules.

Interestingly, **II** was found to be more stable than **I** by 9.16 kcal mol^{-1}, in agreement with the heteroadamantanyl core found for **1a**. This preference is due to an alleviation of metal–metal repulsions in the heteroadamantanyl isomer. In **I** there are two short Al⋯Al and Li⋯Li distances of 2.656 and 2.345 Å (mean), respectively (transannular repulsions in the M_2N_2 rings); however, in **II** the metals are separated by 3.357 and 3.889 Å (mean), respectively. Other distances in **I** and **II** are similar (Li–N 2.063 and 2.074 Å (mean), respectively, and Al–N 1.920 and 1.909 Å (mean), respectively).

Calculations on the related P-bridged model complexes $[(HAl)_4(PH)_6Li_4]$ (**III** and **IV**) indicate that all the metal–metal separations are > 3 Å for both isomers as a consequence of the larger bridging anion. Moreover, and consistent with experimental data,[4b] the bridged dimers isomer **III** was found to be favored over the heteroadamantanyl isomer **IV** by 8.67 kcal mol^{-1}.

Therefore, the formation of the heteroadamantanyl core in **1a** is driven principally by minimizing the metal–metal repulsions, while maintaining strong metal–N interactions. Furthermore, the factors governing the generation of the charge-separated species are complex and include the aromatic nature of the phenyl groups attached to the imido nitrogen atoms, the effect of solvation by Et_2O, and the cavity size of the Al_3N_3 rings.

Experimental Section

1: *n*BuLi (10 mmol, 5.9 mL of a 1.7 M solution in hexanes) was added to a Schlenk tube by syringe, and all solvent was removed in vacuo. The resulting yellow oil was dissolved in Et_2O (10 mL), the solution was cooled to −78 °C, and aniline (10 mmol, 0.91 mL) was then added dropwise by syringe. This solution was stirred at −78 °C for 30 min, then allowed to warm to ambient temperature and stirred for a further 2 h. After dilution with Et_2O (30 mL), the solution was recooled to −78 °C. $H_3Al \cdot N(Me)C_5H_8$ (10 mmol, 1.27 g; where $N(Me)C_5H_8$ = 1-methyl-1,2,3,6-tetrahydropyridine[8]) was added to the solution through a solids addition tube, and the reaction mixture was stirred for 1 h before it was allowed to warm to ambient temperature. After the mixture had been stirred for a further 24 h, a cloudy yellow/brown solution was produced. The mixture was filtered through Celite, cooled to $-20\,^{\circ}C$, and left to stand for 12 h, resulting in the precipitation of small, colorless crystals of **1**. Yield 60.5 %; m.p. > 300 °C; IR (Nujol): $\tilde{\nu} = 1775\ cm^{-1}$ (Al–H); elemental analysis calcd for $C_{60}H_{94}Al_4Li_4N_6O_6$ (%): C 63.72, H 8.32, N 7.43; found: C 63.45, H 7.55, N 8.70; ^{1}HNMR (variable-temperature studies showed only one set of resonances (with broadening) in the range 300–193 K; 400.13 MHz, C_6D_6, 300 K): $\delta = 7.76$ (d, 2H; *o-H*, Ph), 7.16 (t, 2H; *m-H*, Ph), 6.74 (t, 1H; *p-H*, Ph), 5.40 (v br., 1H; Al*H*), 2.88 (q, 4H; OCH_2), 0.60 (t, 6H; CH_3); ^{13}CNMR (100.62 MHz, C_6D_6, 300 K): $\delta = 156.70$ (*i-C*; Ph), 129.21 (*m-C*; Ph), 124.88 (*o-C*; Ph), 117.58 (*p-C*; Ph), 65.33 (OCH_2), 13.66 (CH_3); ^{7}Li NMR (variable-temperature studies showed only a single resonance in the range 300–213 K but the appearance of a second resonance at 193 K; 155.51 MHz, referenced to LiCl in D_2O, [D$_8$]toluene, 193 K): $\delta = 6.75$, δ 6.58; ^{27}Al NMR (C_6D_6, 298 K, 52.12 MHz, referenced to $AlCl_3$ in D_2O): $\delta = 131.30$, 69.91.

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New Fused Bicyclic Cyclotrigermanes from Cycloaddition Reactions of Cyclotrigermene[**]

Norihisa Fukaya, Masaaki Ichinohe, and
Akira Sekiguchi[*]

The chemistry of three- and four-membered ring systems consisting of Group 14 elements heavier than carbon is a subject of considerable interest.[1] The thermal and photochemical conversion of cyclotrigermanes into digermenes and germylenes is well established and has been used for the synthesis of a variety of novel germanium compounds.[2] However, cyclotrigermane derivatives incorporating a bicyclic system are completely unknown for synthetic reasons.[3, 4] Most of the cyclotrigermane derivatives were synthesized by the simple reductive coupling reaction of the corresponding diorganodihalogermane with the appropriate reducing agents.[1, 2] Recently, we succeeded in synthesizing a variety of cyclotrigermene analogues of cyclopropene by reaction of the cyclotrigermenium ion with nucleophiles.[5] The reactivity of the cyclotrigermenes is of special interest, since cycloaddition to the endocyclic Ge=Ge bond could provide access to new bicyclic compounds. We now report the synthesis of the first bicyclic cyclotrigermane derivatives by the reaction of a mesityl-substituted cyclotrigermene with isoprene, 2,3-dimethyl-1,3-butadiene, and phenylacetylene.

After the successful synthesis of tetrakis(tri-*tert*-butylsilyl)cyclotrigermene $(tBu_3Si)_4Ge_3$ (**1a**)[6] and tetrakis(tri-*tert*-butylgermyl)cyclotrigermene $(tBu_3Ge)_4Ge_3$ (**1b**)[6] by reaction of $GeCl_2$(dioxane) with tBu_3SiNa or tBu_3GeLi, we presumed that the cyclotrigermenes should be suitable as precursors of

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[*] Prof. Dr. A. Sekiguchi, Dipl.-Chem. N. Fukaya, Dr. M. Ichinohe
Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305-8571 (Japan)
Fax: (+81) 298-53-4314
E-mail: sekiguch@staff.chem.tsukuba.ac.jp

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