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Preparation and Characterization of Lithium Imidoalanate Complexes $Li_2[(RN)_4(AlH_2)_6]$ (R = Me or ^{t}Bu): First Examples of Aluminum-Rich Imidoalanes with an Adamantoid Structure

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Whereas methylammonium chloride, $[MeNH_3]Cl$, reacts with $LiGaH_4$ in an ether solution to give, according to the conditions, either the adduct $MeH_2N \cdot GaH_3$ or the cationic derivative $[(MeH_2N)_2GaH_2]^+Cl^-$, the corresponding reaction of $[MeNH_3]Cl$ or $[^tBuNH_3]Cl$ with $LiAlH_4$ proceeds mainly, with H_2 elimination, to the imidoalane $Li_2[(RN)_4(AlH_2)_6]$ (R = Me, **1**, or ^{t}Bu, **2**). The crystal structure of **1**·$2Et_2O$ reveals, for the first time, anionic units with an adamantane-like Al_6N_4 skeleton. The Li cations exist at two distinct sites, each linked via Li(μ-H)Al bridges to two $[(MeN)_4(AlH_2)_6]^{2-}$ cages. Despite disordering of the ^{t}Bu groups, the crystal structure of **2** evidently includes analogous anionic units. By contrast, the main product of the reaction between $[^iPrNH_3]Cl$ and $LiAlH_4$ under similar conditions is the known neutral, hexameric imidoalane $[^iPrNAlH]_6$, **3**, the crystal structure of which has been redetermined.

Introduction

Imidoalanes with the generic empirical formula RNAlX (where R = an organic group and X = H, an organic group, or a halogen) can be prepared in various ways, but an appropriate primary amine and aluminum(III) compound are the usual precursors, as exemplified by eqs 1 and 2.[1−9] An alternative synthesis recently reported[10] involves the reaction

$$AlX_3 + RNH_3Cl \xrightarrow[-HX]{} 1/n[RHNAlX_2]_n \xrightarrow[-HX]{\Delta} 1/m[RNAlX]_m \tag{1}$$

$$LiAlH_4 + RNH_3Cl \rightarrow 1/m[RNAlH]_m + 3H_2 + LiCl \tag{2}$$

between the organoaluminum(I) compound $[Cp^*Al]_4$ ($Cp^* = C_5Me_5$) and a trialkylsilyl azide RR'_2SiN_3, which proceeds in accordance with eq 3 with N_2 elimination and formation

$$^1/_4[Cp^*Al]_4 + RR'_2SiN_3 \rightarrow 1/m[Cp^*AlNSiRR'_2]_m + N_2 \tag{3}$$

of the corresponding imidoalane $[Cp^*AlNSiRR'_2]_m$. Imidoalanes are noteworthy on two counts.

First, with the exception of $HC(MeCDippN)_2AlNC_6H_3$-2,6-$Trip_2$ (Dipp = C_6H_3-2,6-$^iPr_2$ and Trip = C_6H_2-2,4,6-$^iPr_3$), where a monomeric structure may well be enforced by the uncommon bulk of the substituents R and X,[11] the compounds display considerable diversity of nuclearity and structure, as illustrated in Figure 1, in the cluster forms they adopt. The frameworks range from the heterocubane Al_4N_4 of $[RNAlX]_4$ (**I**),[4,8,12] through the hexagonal prismatic Al_6N_6

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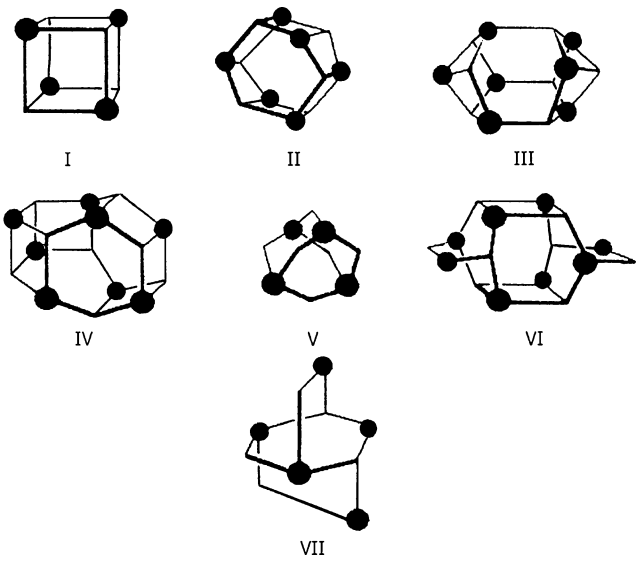

Figure 1. Cages formed by known imidoalanes.[4]

of $[RNAlX]_6$ (**II**),[4,8,13] to the more complex Al_7N_7 and Al_8N_8 frameworks of $[RNAlX]_7$ (**III**) and $[RNAlX]_8$ (**IV**), respectively.[4,8] The last two may be regarded as being formed by the fusion of either two pseudocubic fragments or of a cubic and hexagonal prismatic fragment. The nature of the product is a sensitive function of the substituents R and X, the temperature, and the solvent used. That there is but a fine balance in the choice of product is demonstrated by the finding that ^{i}PrNAlH may be either a tetramer or a hexamer and that ^{n}PrNAlH occurs as either a hexamer or an octamer.[4,8] Coordination by acidic or basic functions results in rupture of some of the bonds in the cage and distortion of the regular geometry, as in $[Me_2N(CH_2)_3NAlH]_6{\cdot}2LiH$[14] and $[^iPrNAlH]_6{\cdot}AlH_3$.[15] In addition, mixed imides add further variety to the cage structures. For example, the cores of the compounds $(ClAl)_4(NMe)_2(NMe_2)_4$[16] and $(ClAl)_2(OAl)(MeNAl)(NMe_2)_6$[17] are Al_4N_6 and Al_4N_5O cages, respectively, each with an adamantane-like structure (**V**); the structure of $(MeNAlMe)_6(Me_2AlNHMe)_2$ can be derived from a hexagonal prism with two edges being broken to insert two $Me_2AlNHMe$ bridges (**VI**);[18] and $(^iPrNAlH)_2(^iPrHNAlH_2)_3$ presents an Al_5N_5 cage with the structure **VII**.[19]

Second, imidoalanes share with amidoalanes an $(AlN)_n$ cagelike or cyclic skeleton that gives them the potential to act as precursors for the chemical vapor or thermal deposition of aluminum nitride, one of the best electrical insulators for microelectronic applications.[20]

We have reported recently on how the reaction of an amine hydrochloride, $[RNH_3]Cl$, with $LiGaH_4$ in an ether solution can be made to deliver gallane adducts of the type $RH_2N{\cdot}GaH_3$ (R = Me or ^{t}Bu);[21] these are labile, decomposing at or near ambient temperatures with the elimination of H_2 and formation of the corresponding amido derivative $[RHNGaH_2]_n$. The corresponding aluminum derivatives are much more labile, with dehydrogenation typically proceeding in accordance with eq 2 to produce the imide $[RNAlH]_m$ under comparable conditions.[2,4,7,22,23] Somewhat unexpectedly, therefore, we find that the reaction in an ether solution of 1 mol of $LiAlH_4$ with about 1.5 mol of $[RNH_3]Cl$ (R = Me, **1**, or ^{t}Bu, **2**) indeed results in H_2 elimination but yields as the major aluminum product a new lithium imidoalanate with the composition $Li_2Al_6N_4R_4$. This has been authenticated by elemental analysis and by its vibrational, solid-state ^{27}Al NMR and mass spectra, while single-crystal X-ray diffraction of **1**$\cdot 2Et_2O$ and **2** at 150 K establishes the formulations $Li[Li(OEt_2)_2][(MeN)_4(AlH_2)_6]$ and $Li_2[(^tBuN)_4(AlH_2)_6]$, respectively, incorporating adamantane-like $[(RN)_4(AlH_2)_6]^{2-}$ anionic cages (R = Me and ^{t}Bu). In the case of **1**$\cdot 2Et_2O$, these anions are linked through $Al{-}H{\cdots}Li$ bridges to Li^+ cations of two quite distinct types. By contrast, the main product of the reaction between $[^iPrNH_3]Cl$ and $LiAlH_4$ carried out under similar conditions is the known hexameric isopropylimidoalane, $[^iPrNAlH]_6$,[24] **3**, the crystal structure of which has been redetermined.

Experimental Section

The vacuum-line methods used for the preparation of the new lithium imidoalanates **1** and **2** have been described elsewhere.[25] Diethyl ether and other solvents were dried by standard methods and distilled before use. The source materials ($LiAlH_4$, $[MeNH_3]Cl$, $[^iPrNH_3]Cl$, $[^sBuNH_3]Cl$ (^{s}Bu = *sec*-butyl), and $[^tBuNH_3]Cl$), from Aldrich Chemicals, were recrystallized before use.

IR measurements on a KBr disc were made in transmission using a Nicolet Magna-IR 560 FTIR spectrometer; detection was with a liquid N_2-cooled MCTB detector covering the range 400–4000 cm^{-1}, typically at a resolution of 0.5 cm^{-1}. Raman spectra, excited at $\lambda = 514.5$ nm with an Ar^+ laser, were recorded with a Dilor Labram 300 spectrometer having a CCD detector. ^{27}Al magic-angle spinning (MAS) NMR spectra were measured for solid powder samples at 104.2 MHz (9.4 T) on a Varian/Chemagnetics Infinity spectrometer using a 4 mm double-resonance probe and a sample rotation rate of 15 kHz. To obtain quantitative spectra, a

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Table 1. Crystallographic Data for Compounds **1**·$2Et_2O$, **2**, and **3**

param	**1**·$2Et_2O$	**2**	**3**
empirical formula	$C_{12}H_{44}Al_6Li_2N_4O_2$	$C_{16}H_{48}Al_6Li_2N_4$	$C_{18}H_{48}Al_6N_6$
fw	452.28	472.36	510.51
cryst dimens (mm)	0.10 × 0.12 × 0.24	0.20 × 0.20 × 0.20	0.20 × 0.40 × 0.50
cryst system	monoclinic	cubic	triclinic
space group	$P2_1/c$	$Fd\bar{3}m$	$P\bar{1}$
unit cell dimens			
a (Å)	13.0826(2)	18.3521(9)	10.5708(2)
b (Å)	12.1616(2)	18.3521(9)	16.5470(4)
c (Å)	18.1906(4)	18.3521(9)	17.0406(4)
α (deg)	90	90	92.1463(9)
β (deg)	94.7891(8)	90	93.8153(9)
γ (deg)	90	90	91.3870(11)
V (Å^3)	2884.1	6181.0	2970.90
Z	4	8	4
d(calcd) (Mg m^{-3})	1.042	1.015	1.141
abs coeff (mm^{-1})	0.234	0.216	0.233
θ_{max} (deg)	27.5	24.962	27.536
reflns measd	38 223	850	23 915
unique reflns (R_{int})	6851 (0.060)	299 (0.063)	13 578 (0.1078)
no. of params	286	25	589
conventional R [$R > 3\sigma(F)$]	0.0494	0.0878	0.0405
weighted R (F^2 and all data)	0.0584	0.0802	0.0449
GOF on F^2 (S)	1.0630	2.6310	1.0872
largest difference peak/hole (e Å^{-3})	+0.68/−0.51	+0.42/−0.26	+0.31/−0.32

single pulse excitation was applied using a short pulse length (0.83 μs). Each spectrum resulted from 600 scans separated by a 5 s delay. The ^{27}Al chemical shifts were referenced to an aqueous solution of $Al(NO_3)_3$ (0 ppm). Mass spectrometric measurements were made with a Micromass GC-TOF instrument with field ionization, using a temperature-programmed solid probe inlet. C, H, and N analyses were carried out by the Elemental Analysis Service at London Metropolitan University.

Synthesis and Authentication. Lithium tetrakis(methylimido)-hexakis(aluminate), $Li_2[(MeN)_4(AlH_2)_6]$, **1**, was synthesized by a procedure similar to that used for methylamine−gallane, $MeH_2N·GaH_3$,[21] and involving the reaction of $LiAlH_4$ (in place of $LiGaH_4$) with the freshly recrystallized amine hydrochloride $[MeNH_3]Cl$ in dry Et_2O solution at room temperature. In a typical experiment, $LiAlH_4$ (20 mmol) was treated with a 50% mol excess of $[MeNH_3]Cl$ (31 mmol). After filtering and concentrating by evaporating the solvent under vacuum, the solution was left for 4−6 weeks at room temperature; white crystals (identified by X-ray analysis of a single crystal at 150 K as the dietherate of **1**) were then observed to separate, typically in yields of about 58% based on the amount of $LiAlH_4$ taken. Similar results were achieved irrespective of whether the reaction occurred exclusively at room temperature or the temperature of the mixture was gradually raised from 195 K to ambient. However, the first procedure was preferred in this and subsequent experiments, since the second was apt to lead to poorer yields and less pure products, presumably through the survival of one or more reaction intermediates. The crystals release 2 mol of Et_2O relatively easily but are otherwise lastingly stable under moisture-free conditions at ambient temperatures. Indeed, there was no sign of significant decomposition at temperatures up to ca. 160 °C, whereupon the solid began to turn yellow and dihydrogen was evolved. The compound was insufficiently soluble in any organic solvent with which it did not react to permit satisfactory solution NMR measurements. Anal. Calcd for ether-free solid $C_4H_{24}N_4Al_6Li_2$: C, 15.80; H, 7.96; N, 18.43. Found: C, 15.90; H, 7.85; N, 18.56. IR spectrum of a KBr disc (wavenumbers in cm^{-1}): 2961 ms, 2893 m, 2817 m, 1844 s [ν(Al−H)], 1473 m, 1262 s, 1099 ms, 1020 s, 956 s, 804 s, 706 s, 648 ms. Raman spectrum of the solid (wavenumbers in cm^{-1}): 2969 sh, 2932 s, 2899 m, 2881 sh, 2820 s, 1852 s [ν(Al−H)], 1467/1435 mw, 987 mw, 956 mw, 841 w, 695 mw, 607 mw, 464 w, 368 s, 261 mw, 185 w. ^{27}Al MAS NMR spectrum of the solid powder: δ_{Al} +112. Field ionization MS (m/z): 429 $[Al_9(NMe)_6H_{12}]^+$, 369 $[Al_9N_4(NMe)_2H_{12}]^+$, 355 $[Al_9N_3(NMe)_2H_{12}]^+$, 295 $[Al_7N_3(NMe)_2H_6]^+$, 281 $[Al_7N_2(NMe)_2H_6]^+$, 221 $[Al_6N_4H_3]^+$, 207 $[Al_6N_3H_3]^+$, 147 $[Al_3(NMe)_2H_8]^+$, 73 $[Al_2NH_5]^+$, 57 $[MeNAlH]^+$.

Similar experiments were carried out with $LiAlH_4$ and each of the hydrochlorides of $^iPrNH_2$, $^sBuNH_2$, and $^tBuNH_2$. However, only $[^tBuNH_3]Cl$ gave in the white solid $Li_2[(^tBuN)_4(AlH_2)_6]$, **2**, a major product analogous to **1**; yields of the pure crystals were typically about 45% based on the amount of $LiAlH_4$ taken. Anal. Calcd for $C_{16}H_{48}N_4Al_6Li_2$: C, 40.68; H, 10.24; N, 11.86. Found: C, 40.52; H, 10.25; N, 11.61. IR spectrum of a KBr disc (wavenumbers in cm^{-1}): 2974 m, 2957 s, 2900 m, 2865 m, 1837/1805/1732 s,vbr [ν(Al−H)], 1469 m, 1392 m, 1364 ms, 1228 m, 1186 ms, 1094 w, 1070 m, 1033 w, 942 ms, 890 mw, 788 s, 738 m, 693 s, 639 w, 487 w. Raman spectrum of the solid (wavenumbers in cm^{-1}): 2986 m, 2964 m, 2936 m, 2908 m, 1850 s,br [ν(Al−H)], 1482 m, 1455 m, 1233 m, 919 m, 843 mw, 796 mw, 774 mw, 518 m, 465 s, 415 w, 390 w, 356 mw, 237 mw, 225 s. ^{27}Al MAS NMR spectrum of the solid powder: δ_{Al} +105.

The reaction with $[^sBuNH_3]Cl$ gave no crystals at room temperature and only a liquid mixture of inseparable products on removal of the solvent. That with $[^iPrNH_3]Cl$ gave, by contrast, mainly the known[24] neutral hexamer of isopropylimidoalane, $[^iPrNAlH]_6$, **3**. Yields of the pure crystals were typically about 30%. Anal. Calcd for $C_{18}H_{48}Al_6N_6$: C, 42.35; H, 9.47; N, 16.47. Found: C, 42.23; H, 9.56; N, 16.38. IR spectrum of a KBr disc (wavenumbers in cm^{-1}): 2974 s, 2870 ms, 2726 w, 2625 m, 1850/1788/1700 s [ν(Al−H)], 1467 m, 1385 m, 1364 m, 1327 mw, 1261 mw, 1164 ms, 1131 s, 1094 ms, 954 s, ca. 800 s,vbr, 510/490/462 mw. Raman spectrum of the solid (wavenumbers in cm^{-1}): 2967 ms, 2933 ms, 2902 m, 2864 ms, 2716 w, 2629 w, 1864 s [ν(Al−H)], 1462 m, 1440 mw, 1382 w, 1358 mw, 1330 mw, 1164 w, 1133 ms, 992 w, 960 w, 937 m, 847 ms, 808 m, 763 m, 695 mw, 658 m, 524 m, 495 w, 446 mw, 419 vs, 331 mw, 310 w, 288 m, 254 ms.

X-ray Crystallography. Table 1 gives crystal data and other information relating to the structure determination and refinement for single crystals of **1**·$2Et_2O$, **2**, and **3**. Two independent sets of measurements were made on single crystals of **1**·$2Et_2O$, each mounted under perfluoropolyether oil on a glass fiber. X-ray diffraction data (λ (Mo Kα) = 0.710 73 Å) were then collected on a Bruker Smart Apex diffractometer in one case and on an Enraf-Nonius Kappa CCD diffractometer in the second. Single crystals of **2** and **3**, grown by slow crystallization from Et_2O solution aided by petroleum infusion, were each similarly mounted under perfluoropolyether oil, and X-ray data (λ(Mo Kα = 0.710 73 Å) were collected on an Enraf-Nonius Kappa CCD diffractometer. In every case, the temperature of the crystal was maintained at 150 K by an Oxford Cryosystems Cryostream device.[26] Semiempirical absorption corrections were made from equivalent reflections.[27] The intensity data were processed using the *DENZO-SMN* package.[27]

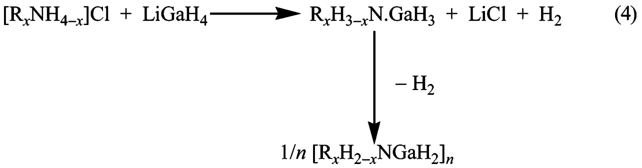
Examination of the systematic absences showed the space group of the monoclinic crystals of **1**$\cdot 2Et_2O$ to be $P2_1/c$. With the direct methods program *SIR92*,[28] the structure was solved, the Al, O, N, and methyl C atoms of the anion being located. The Li and remaining C atoms were located in a Fourier difference map. Subsequent full-matrix least-squares refinement was carried out with the *CRYSTALS* program suite.[29] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. The AlH_2 hydrogen atoms were located in a Fourier difference map and their coordinates and isotropic thermal parameters subsequently refined. Other hydrogen atoms were positioned geometrically after each cycle of refinement. A three-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give $R = 0.0494$, $R_w = 0.0584$.

The crystal structure of **2** was modeled in $Fd\bar{3}m$, with the $[(^tBuN)_4(AlH_2)_6]^{2-}$ anion located about a site of $\bar{4}3m$ (T_d) symmetry. The pivot carbon atom (C1) of the ^{t}Bu group sits on a site of $0.3m$ (C_{3v}) symmetry, but the methyl groups (C2) do not lie in the associated mirror planes and are therefore disordered over two orientations. The anisotropic displacement parameters of the carbon atoms are large, and it is likely that the description presented here is an approximate, average structure; though detailed analysis of the geometry would be inappropriate, this structure does establish the atomic connectivity in **2**. Attempts to model the structure in $Fd\bar{3}$ or with the methyl groups represented as a diffuse ring of density were no more successful, yielding no improvement in the data-fitting. The C1−C2 distance was restrained to 1.50(1) Å during refinement. The Li and the H atoms attached to Al were located in a difference map, and it was even possible to refine the hydride positional and isotropic displacement parameters freely. The H atoms of the ^{t}Bu group were placed in calculated positions. All non-H atoms were modeled with anisotropic displacement parameters. At 8%, the final *R* factor is high by modern standards, but the value reflects the difficulties of modeling the disorder.

There were no problems of disordering with the triclinic crystal of the hexamer **3**. The structure determined for the crystal at 150 K proved not to be significantly different from that determined previously when the crystal was presumably at room temperature.[24]

Results and Discussion

Selected primary and secondary amine adducts of gallane with the general formula $R_xH_{3-x}N\cdot GaH_3$ ($x = 1$, R = Me or ^{t}Bu,[21] $x = 2$, R = Me[30]) have been characterized, being relatively long-lived at or near ambient temperatures despite their innate susceptibility to decomposition through elimination of dihydrogen and formation of the corresponding amidogallane, $[R_xH_{2-x}NGaH_2]_n$. They have been prepared by the interaction of the appropriate amine hydrochloride with $LiGaH_4$ in Et_2O solution. However, the reaction represented by eq 4 is by no means the only one taking place in such a mixture and, depending on the conditions and particularly the reacting proportions, other products may be isolated, including, for example, the cationic gallane derivatives $[H_2Ga(NH_2R)_2]^+Cl^-$ (R = Me, ^{i}Pr, ^{s}Bu, or ^{t}Bu)[31,32] and $[H_2Ga(NH_2{}^iPr)NH(^iPr)GaH_2NH(^iPr)GaH_2(NH_2{}^iPr)]^+Cl^-$.[32]



$$\begin{tikzcd} {[R_xNH_{4-x}]Cl + LiGaH_4} \arrow[r] & {R_xH_{3-x}N.GaH_3 + LiCl + H_2} \arrow[d, "-H_2"] \\ & {1/n\,[R_xH_{2-x}NGaH_2]_n} \end{tikzcd} \quad (4)$$

$$2[RNH_3]Cl + LiGaH_4 \rightarrow [(RH_2N)_2GaH_2]^+Cl^- + LiCl + 2H_2 \quad (5)$$

$$2[(RH_2N)_2GaH_2]^+Cl^- + LiGaH_4 \rightarrow [H_2Ga(NH_2R)NH(R)GaH_2NH(R)GaH_2(NH_2R)]^+Cl^- + LiCl + 2H_2 \quad (6)$$

Primary and secondary amine adducts of alane are much more labile than their gallane counterparts, decomposing rapidly with the elimination of H_2 at ambient temperatures. By carrying out the reaction between $[Me_2NH_2]^+Cl^-$ and $LiAlH_4$ in an ether solution at ca. 248 K and causing crystallization to occur at 203 K, however, it has been possible to isolate the dimethylamine adduct $Me_2(H)N\cdot AlH_3$.[31] Adducts that are thermally robust at room temperature can be formed, though only with sterically demanding secondary amines such as 2,2,6,6-tetramethylpiperidine.[33] Spurred by the success of recent experiments aimed at isolating primary amine adducts of gallane, we have carried out similar experiments to see whether, by working at appropriately low temperatures, analogous alane derivatives can be intercepted before they start to decompose. In no case has this yet proved feasible, but we have found that the reaction of $LiAlH_4$ with about 1.5 mol of $[RNH_3]Cl$ (R = Me or ^{t}Bu) in an ether solution results in dihydrogen elimination even at 195 K and that the filtered solution yields on standing at or near room-temperature white crystals of a new, major product shown by its elemental analysis, spectroscopic properties, and single-crystal X-ray analysis to be the dilithium salt of the anion $[(RN)_4(AlH_2)_6]^{2-}$ (R = Me, **1**, or ^{t}Bu, **2**).

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Similar experiments involving the hydrochlorides of other primary amines, viz., [^{i}PrNH$_3$]Cl and [^{s}BuNH$_3$]Cl, were likewise unable to forestall dihydrogen elimination but have failed so far to deliver any products analogous to **1** and **2**. Instead, [^{i}PrNH$_3$]Cl gives under these conditions mainly the neutral isopropylimidoalane known previously[24] to occur as a crystalline hexamer [^{i}PrNAlH]$_6$. Evaporation of the solvent from the products of the reaction with [^{s}BuNH$_3$]Cl yielded only a viscous liquid mixture from which no pure product could be isolated.

X-ray analysis of the crystals formed at 273 K and then held at 150 K indicated that **1** was first isolated as a diethyl ether solvate. Warming to room temperature, however, resulted in the slow loss of the ether with breakup of the individual crystals, and subsequent elemental and spectroscopic analysis then found the solid to be more-or-less ether-free. Thus, C, H, and N elemental analyses were consistent with the empirical formula $R_2H_6N_2Al_3Li$ for **1** (R = Me) and **2** (R = ^{t}Bu), respectively. The vibrational spectra gave no hint of significant features in the range of 3100−3500 cm^{-1} suggestive of the presence of N−H bonds.[34] On the other hand, they did include distinctive strong absorption or scattering near 1850 cm^{-1} that was clearly indicative of the presence of Al−H bonds,[7,23] as in [Me$_2$NAlH$_2$]$_3$, for example,[35] as well as a pattern of bands at 2800−3000, 1400−1500, and 900−1200 cm^{-1} that was consistent with the presence of an NMe or N^{t}Bu moiety.[21,34]

The mass spectrum of **1** gave no hint of molecular fragments exhibiting the isotopic patterns characteristic of Li, while the lack of a second naturally abundant isotope of Al or N prevented any unambiguous interpretation of the results. However, the pattern of the mass peaks suggested as a recurring feature the Al$_3$N$_2$ unit in monomeric, dimeric, or trimeric guises, with varying numbers of H and Me substituents attached. Thus, the strongest peak (at $m/z = 221$) appeared to correspond to [Al$_6$N$_4$H$_3$]$^+$, and the different progressions implied that fragmentation of clusters was occurring with the progressive loss of H, Me, N, and Al constituents.

With solution NMR measurements being precluded by the low solubility of **1** and **2** in organic solvents with which they did not react, the ^{27}Al MAS NMR spectra of each of the solid powders at room-temperature revealed a single resonance with $\delta_{Al} = +112$ (**1**) or +105 (**2**), a shift characteristic of a tetrahedrally coordinated aluminum center.[36]

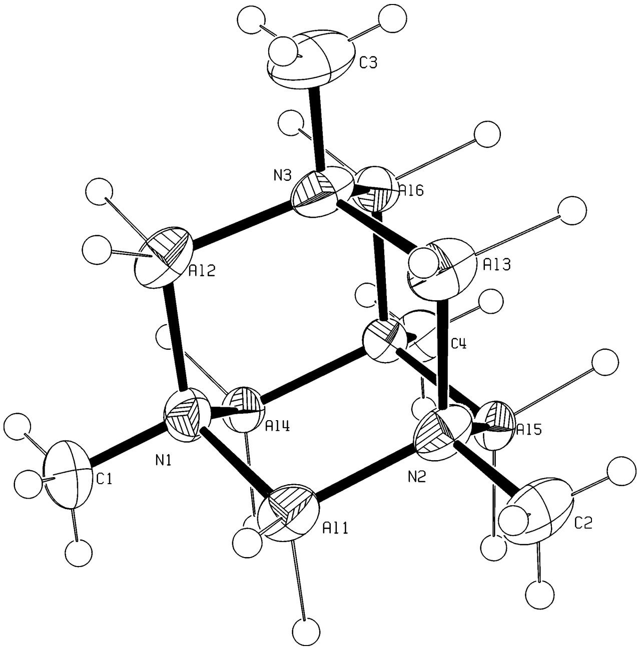

Figure 2. Structure and atom labeling of the [(MeN)$_4$(AlH$_2$)$_6$]$^{2-}$ anion in **1**·2Et$_2$O.

Two independent structural analyses were carried out on single crystals of **1**·2Et$_2$O isolated from an ether solution at ambient temperatures, mainly to check the reproducibility of the method of synthesis, with results that were identical within the limits of experimental uncertainty. The most striking feature of the structure is the [(MeN)$_4$(AlH$_2$)$_6$]$^{2-}$ anion, which occupies a site with no crystallographic symmetry. This is accompanied by one [Li(OEt$_2$)$_2$]$^+$ cation, also on a site with no crystallographic symmetry, and two unsolvated Li$^+$ cations on crystallographic centers of inversion. As illustrated in Figure 2, the anion has an Al$_6$N$_4$ adamantoid framework subject to only minor deviations from ideal T_d symmetry. Salient bond lengths and angles are listed in Table 2. The Al−N distances, ranging from 1.890(3) to 1.912(3) Å, average 1.900 Å, that is, well within the range normally associated with AlN cluster compounds.[37] Despite the negative charge, the distances are quite short by the standards of heterocubane imides of the type [RNAlX]$_4$ (1.89−1.948 Å)[4,8,12] but neither more nor less than average length by the standards of the hexagonal faces of hexagonal prismatic imides of the type [RNAlX]$_6$ (1.873−1.926 Å).[4,8,13] The Al−N−Al angles vary between 109.9(2)° and 115.5(2)° and the N−Al−N angles between 103.9(2)° and 105.7(2)°. There is no hint of Al···Al interaction within the Al$_6$N$_4$ cage, with Al···Al distances at 3.11−3.22 Å appreciably longer than those in either aluminum metal (2.86 Å) or a heterocubane imidoalane of the type [RNAlX]$_4$ (ca. 2.7 Å).[4,8,12] With Al−H and N−C bonds measuring on average 1.52 and 1.514 Å, respectively, and H−Al−H angles near 112°, the bonding of the substituents is plainly not out of the ordinary.[37] Although the charge and the spatial and electronic demands of the substituents attached to the Al and N atoms undoubtedly play their part in determining the Al−N distances in an AlN cage such as this, mutual Al···Al and N···N repulsions are likely also to be a factor, so that Al−N distances tend to shorten as the Al−N−Al and N−Al−N angles are able to widen. Neither of the compounds (ClAl)$_4$(NMe)$_2$(NMe$_2$)$_4$[16] and (ClAl)$_2$(OAl)(MeNAl)(NMe$_2$)$_6$,[17] previously described as featuring adamantoid frameworks, is

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Table 2. Selected Distances (Å) and Interbond Angles (deg) for the Compound **1**·2Et$_2$O

	Distances[a]		
Al(1)−N(1)	1.890(3)	N(1)−C(1)	1.519(5)
Al(1)−N(2)	1.912(3)	N(2)−C(2)	1.512(4)
Al(1)−H(1)	1.46(4)	N(3)−C(3)	1.515(5)
Al(1)−H(2)	1.57(3)	N(4)−C(4)	1.510(4)
Al(2)−N(1)	1.904(3)		
Al(2)−N(3)	1.909(3)	Li(1)−H(4)	2.06(3)
Al(2)−H(3)	1.47(5)	Li(1)−H(8)	2.00(4)
Al(2)−H(4)	1.50(3)	Li(1)−H(12)	2.18(4)
Al(3)−N(2)	1.907(3)	Li(2)−H(5)	1.98(4)
Al(3)−N(3)	1.897(3)	Li(2)−H(10)	2.21(4)
Al(3)−H(5)	1.60(4)	Li(2)−H(11)	2.13(3)
Al(3)−H(6)	1.48(4)	Li(3)−O(1)	1.961(6)
Al(4)−N(1)	1.896(3)	Li(3)−O(2)	1.961(7)
Al(4)−N(4)	1.903(2)	Li(3)−H(2)	1.92(3)
Al(4)−H(7)	1.54(4)	Li(3)−H(7)	2.56(4)
Al(4)−H(8)	1.51(3)	Li(3)−H(9)	2.03(4)
Al(5)−N(2)	1.898(3)		
Al(5)−N(4)	1.889(2)	O(1)−C(5)	1.430(4)
Al(5)−H(9)	1.58(4)	O(1)−C(7)	1.455(5)
Al(5)−H(10)	1.50(3)	O(2)−C(9)	1.410(6)
Al(6)−N(3)	1.898(3)	O(2)−C(11)	1.436(6)
Al(6)−N(4)	1.893(3)		
Al(6)−H(11)	1.48(3)		
Al(6)−H(12)	1.56(4)		
	Angles[a]		
N(1)−Al(1)−N(2)	105.67(12)	N(1)−Al(4)−N(4)	105.36(11)
N(1)−Al(1)−H(1)	116.5(17)	N(1)−Al(4)−H(7)	109.8(14)
N(2)−Al(1)−H(1)	110.9(17)	N(4)−Al(4)−H(7)	109.6(13)
N(1)−Al(1)−H(2)	107.3(12)	N(1)−Al(4)−H(8)	107.5(13)
N(2)−Al(1)−H(2)	106.2(12)	N(4)−Al(4)−H(8)	108.1(13)
H(1)−Al(1)−H(2)	109.6(21)	H(7)−Al(4)−H(8)	116.0(19)
N(1)−Al(2)−N(3)	103.85(12)	N(2)−Al(5)−N(4)	105.40(11)
N(1)−Al(2)−H(3)	113.4(18)	N(2)−Al(5)−H(9)	109.4(13)
N(3)−Al(2)−H(3)	113.9(17)	N(4)−Al(5)−H(9)	108.3(13)
N(1)−Al(2)−H(4)	108.4(13)	N(2)−Al(5)−H(10)	109.7(14)
N(3)−Al(2)−H(4)	105.9(13)	N(4)−Al(5)−H(10)	107.5(14)
H(3)−Al(2)−H(4)	110.9(22)	H(9)−Al(5)−H(10)	116.0(18)
N(2)−Al(3)−N(3)	104.23(12)	N(3)−Al(6)−N(4)	105.36(12)
N(2)−Al(3)−H(5)	106.6(13)	N(3)−Al(6)−H(11)	110.3(13)
N(3)−Al(3)−H(5)	107.0(14)	N(4)−Al(6)−H(11)	110.0(13)
N(2)−Al(3)−H(6)	112.3(17)	N(3)−Al(6)−H(12)	108.9(14)
N(3)−Al(3)−H(6)	115.4(17)	N(4)−Al(6)−H(12)	113.1(14)
H(5)−Al(3)−H(6)	110.8(22)	H(11)−Al(6)−H(12)	109.2(19)
Al(1)−N(1)−Al(2)	112.92(15)	Al(2)−N(3)−Al(3)	115.49(16)
Al(1)−N(1)−Al(4)	110.65(14)	Al(2)−N(3)−Al(6)	110.43(14)
Al(2)−N(1)−Al(4)	111.39(14)	Al(3)−N(3)−Al(6)	110.10(15)
Al(1)−N(1)−C(1)	107.5(2)	Al(2)−N(3)−C(3)	106.2(3)
Al(2)−N(1)−C(1)	108.0(2)	Al(3)−N(3)−C(3)	107.7(2)
Al(4)−N(1)−C(1)	106.1(2)	Al(6)−N(3)−C(3)	106.4(3)
Al(1)−N(2)−Al(3)	113.36(14)	Al(4)−N(4)−Al(5)	111.56(12)
Al(1)−N(2)−Al(5)	110.85(13)	Al(4)−N(4)−Al(6)	110.90(13)
Al(3)−N(2)−Al(5)	109.90(15)	Al(5)−N(4)−Al(6)	111.75(12)
Al(1)−N(2)−C(2)	107.5(2)	Al(4)−N(4)−C(4)	106.49(19)
Al(3)−N(2)−C(2)	108.0(2)	Al(5)−N(4)−C(4)	108.56(19)
Al(5)−N(2)−C(2)	106.9(2)	Al(6)−N(4)−C(4)	107.3(2)

[a] See Figure 2 for atom labeling.

strictly comparable with the [(MeN)$_4$(AlH$_2$)$_6$]$^{2-}$ anion. Not only is there a reversal of the roles of metal and nonmetal atoms but the cages are also made less regular by the inclusion of more than one type of metal or nonmetal site. A similar reversal of roles in an adamantoid framework is also experienced when N is traded for other nonmetal atoms, as in (Et$_2$Al)$_4$[(PH)$_4$(Si^{i}Pr$_2$)$_2$].[38]

As in the case of solid LiAlH$_4$[39] and related lithium derivatives,[40] the lithium cations fulfill a vital role in directing the packing of the [(MeN)$_4$(AlH$_2$)$_6$]$^{2-}$ anions, as indicated in the packing diagram of Figure 3. The ether-free Li$^+$ cations occupy roughly octahedral sites, forming tridentate Al(μ-H)$_3$Li bridges to each of two neighboring anions, and thus establishing a network of infinite chains. The Li$\cdots$H distances cover the range of 1.98(4)−2.21(4) Å, with a mean of 2.09 Å. The [Li(OEt$_2$)$_2$]$^+$ ions, with Li−O coordinate links measuring 1.961(7) Å, are each linked to a single [(MeN)$_4$(AlH$_2$)$_6$]$^{2-}$ anion via a bidentate Al(μ-H)$_2$Li bridge with Li$\cdots$H distances of 1.92(3) and 2.03(4) Å. The impression of a distorted tetrahedral coordination geometry is, however, qualified by the perception of a further, monodentate Al(μ-H)Li bridge to a second anion, this time with a significantly longer Li$\cdots$H distance of 2.56(4) Å. At 1.961(7) Å, the Li−O coordinate links are slightly longer than those in [LiCl(OEt$_2$)]$_4$ and [LiI(OEt$_2$)]$_4$ (1.91−1.92 Å)[41] and considerably longer than those in [LiBr(OEt$_2$)]$_4$ (1.84 Å).[42] The ethyl groups of the ether molecules appeared to display a distorted geometry with abnormally large thermal parameters, suggesting that they are disordered. Attempts to resolve this disorder did not lead to any significant improvement in agreement between the calculated and observed intensities. In view of the relatively loose binding of the ether molecules, however, such disorder in the crystal would come as no surprise.

Although disorder permitted the determination of only a rather imprecise crystal structure for **2**, the results are wholly consistent with the presence of an anion [(^{t}BuN)$_4$(AlH$_2$)$_6$]$^{2-}$ analogous to that in **1**·2Et$_2$O. The Al$_6$N$_4$ framework has crystallographic T_d symmetry, and the refinements revealed a ^{t}Bu-substituted anion having mean Al−N, C−N, and Al−H distances estimated to be 1.899(3), 1.532(13), and 1.42(6) Å, respectively, and therefore entirely in keeping with the precedents set by the Me-substituted anion of **1**·2Et$_2$O. With the location of the Li atoms in the crystal, it was apparent that the structure consists of Al$_6$N$_4$ clusters linked through hydride bridges to six-coordinate Li atoms to build up a three-dimensional framework (see Figure 4).

The structure determined for the triclinic crystals of the neutral alane, [^{i}PrNAlH]$_6$, **3**, did not differ significantly from that reported previously by Cesari et al. in 1974.[24] Hence the individual molecules consist of hexagonal prismatic Al$_6$N$_6$ cages (**II**) built up from two six-membered, planar (AlN)$_3$ rings joined together by transverse Al−N bonds. Within the rings, the Al−N distances span the range 1.889(3)−1.912(3) Å, averaging 1.900 Å, whereas the transverse Al−N distances, spanning the range of 1.948(3)−1.963(3) Å and averaging 1.956 Å, are somewhat longer. This difference can be explained by the justifiable assumption of

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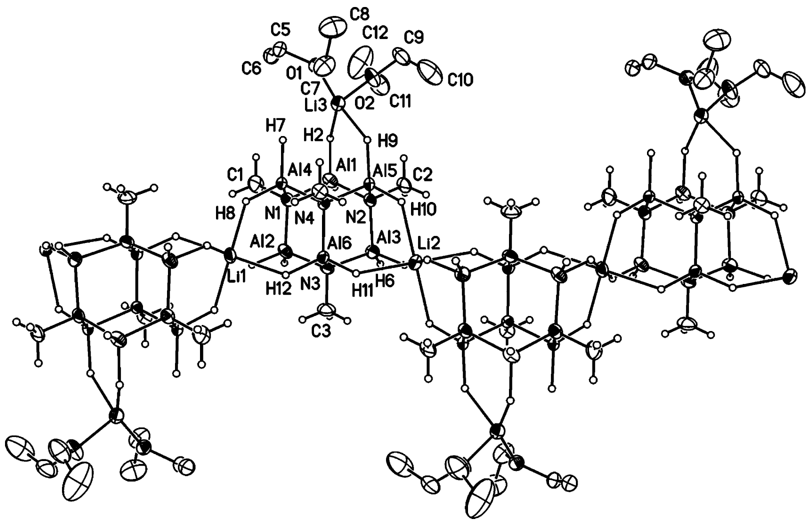


Figure 3. Chain formation via interactions with Li^+ ions in the crystal structure of $\mathbf{1}\cdot 2Et_2O$. Ellipsoids are drawn at the 30% probability level, and H atoms are shown as circles of arbitrary radius.

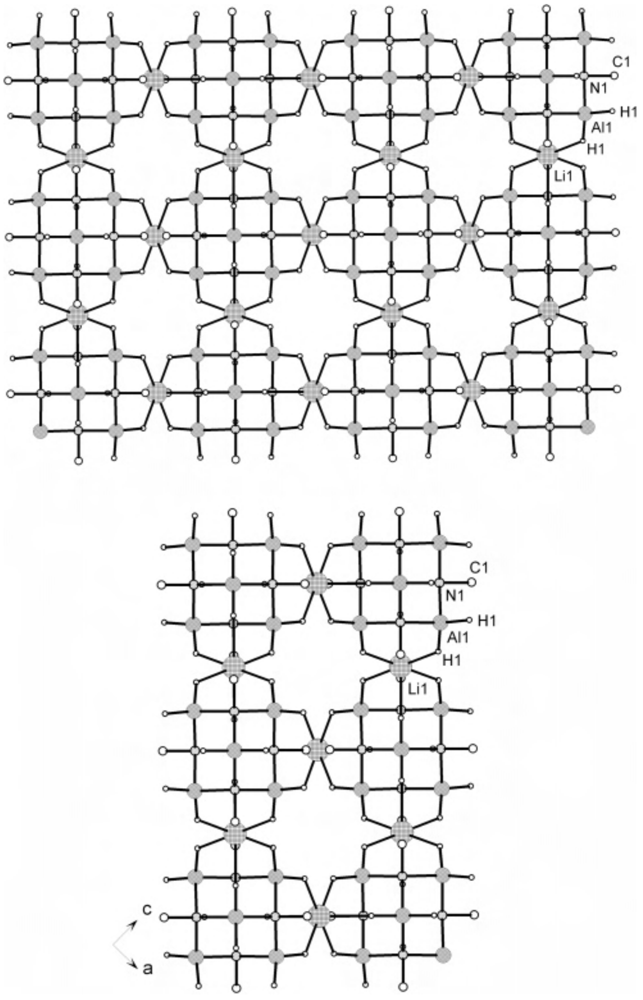
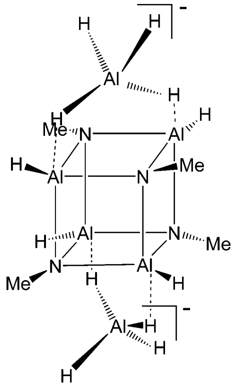


Figure 4. (a) Crystal structure of **2** viewed along *b* and showing how the Li^+ ions link the $[(^t\mathrm{BuN})_4(\mathrm{AlH}_2)_6]^{2-}$ anions into a three-dimensional array. The methyl groups have been omitted for clarity. Ellipsoids are drawn at the 30% probability level. (b) Alternative ball-and-stick representation.

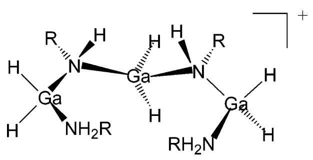
Scheme 1



greater s character in the bonds of the $(AlN)_3$ faces. Within these faces, the Al−N−Al and N−Al−N bond angles average 123.2° and 116.5°, respectively, while the corresponding angles made by the transverse bonds are 88.7° and 91.2°. The mean extracage distances N−C and Al−H average 1.512 and 1.50 Å, respectively. The packing of the molecules is essentially determined by the methyl···methyl contacts.

With a reaction mixture that offers a variety of possible chemical pathways, it is not easy to judge how the adamantoid anion $[(RN)_4(AlH_2)_6]^{2-}$ (R = Me or ^{t}Bu) comes to be formed. Perhaps the most obvious starting point is the alane adduct $RH_2N\cdot AlH_3$. In contrast to its gallane counterpart,[21] this may be expected to suffer H_2 elimination even at subambient temperatures, very likely to form the corresponding alkylimidoalane, which may well be a tetramer, $[RNAlH]_4$, with a heterocubane framework analogous to that of one form of the corresponding isopropylimido derivative.[4,8] This may then react with 2 mol of AlH_4^- (see Scheme 1) with retention of the tetrahedral $(NR)_4$ fragment but expansion of the Al_4 tetrahedron to an Al_6 octahedron. Alternatively, the tetramer $[RNAlH]_4$ may react with 2 mol of $RH_2N\cdot AlH_3$ in a similar manner but with H_2 elimination to form the neutral hexamer $[RNAlH]_6$. Considerable circumstantial evidence suggests that AlN cages are susceptible to quite facile changes of nuclearity and form,[4,8,12,13] with the faces of the cages open to nucleophilic attack.[43]

However, the reactions of primary amine hydrochlorides with $LiGaH_4$ are also instructive, since intermediate gallane derivatives are less reactive and so are more amenable to isolation and characterization. With an excess of the hydrochloride, the reactions have been shown to afford cationic gallane derivatives of the type $[(RH_2N)_2GaH_2]^+Cl^-$, where R = Me, ^{i}Pr, ^{s}Bu, or ^{t}Bu, as in eq 5.[30,31] Cationic alane derivatives have also been prepared. For example, treatment of $Me_3N{\cdot}AlH_3$ with a tridentate or tetradentate nitrogen base L yields products of the type $[H_2AlL]^+[AlH_4]^-$,[44] in which the cationic centers are stabilized by penta- or hexacoordination of the metal atom (cf. tetracoordination of the gallane cations). In the case where R = ^{i}Pr, a further reaction of 2 mol of $[(RH_2N)_2GaH_2]Cl$ with $LiGaH_4$ results, according to eq 6, in the elimination of LiCl and 2 mol of H_2 with the formation of the trigallane derivative $[H_2Ga(NH_2R)NH(R)GaH_2NH(R)GaH_2(NH_2R)]^+Cl^-$, in which the cation has the structure **4**.[32] There is no reason to think that a product analogous to this cannot be formed when $[RNH_3]Cl$ reacts with $LiAlH_4$, with the difference that the more acidic and coordinatively unsaturated Al atoms would be expected to induce further, facile reactions. For example, dimerization with deprotonation at the bridging amido functions (before, during, or after the event) and expulsion of the coordinated primary amine molecules would provide a feasible route to $[(RN)_4(AlH_2)_6]^{2-}$. Such a mechanism seems more in keeping with the conditions favored in our experiments (with an excess of the hydrochloride) than the earlier postulate involving tetrameric $[RNAlH]_4$.



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With the discovery of anions of the type $[(RN)_4(AlH_2)_6]^{2-}$ (R = Me or ^{t}Bu) with an adamantoid framework, we have thus been able to add a new aluminum-rich example to the remarkable range of cage structures open to imidoalanes.[4,8] In the process we have revealed a hitherto unknown excursion taken by the interaction of a primary amine with an aluminum(III) hydride. Our results thus add to the experience of previous studies[4,8,12,13] in demonstrating how critical to the outcome the reaction conditions can be. That this outcome is also markedly dependent on the nature of the alkyl substituent at nitrogen is underlined, moreover, by the different responses of the amine hydrochlorides $[RNH_3]Cl$ to $LiAlH_4$, even under a given set of conditions, according to whether R = Me, ^{i}Pr, ^{s}Bu, or ^{t}Bu.

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Supporting Information Available: Crystallographic data in CIF format for the compounds $\mathbf{1}{\cdot}2Et_2O$, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) Perhaps the clearest evidence of this is seen in the structure of the loosely bound complex $Pr^iN{=}NPr^i{\cdot}[Pr^iNAlH]_4$. See Uhl, W.; Molter, J.; Neumüller, B. *Chem.—Eur. J.* **2001**, *7*, 1512.

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