An unsolvated lithium trihydroaluminate and the correponding trialkynylaluminates supported by an anionic triazacyclononane ligand

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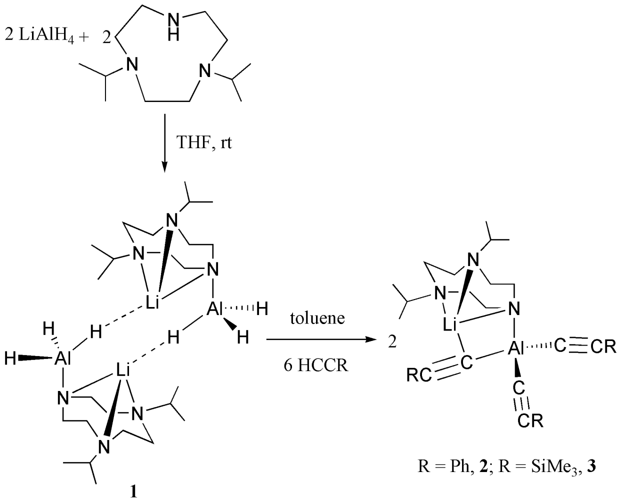
Reaction of the anionic tacn ligand ((tacn)H = 1,4-diisopropyl-1,4,7-triazacyclononane) with $LiAlH_4$ in THF afforded a dimeric, unsolvated lithium trihydroaluminate, which upon treatment with terminal acetylenes HCCR (R = Ph, $SiMe_3$) yielded the corresponding monomeric trialkynylaluminates in which one acetylide ligand bridges the Li and Al atom at the C_α atom while the two terminal acetylide ligands are coordinated to the Al atom.

Hydroaluminates are well known reducing agents in organic chemistry. In recent years, there has been increased attention on the structural characterization of well-defined molecular trihydroaluminates incorporating bulky organic ligands due to their interesting structural features and their potential use for selective reductions.[1] By comparison, the related acetylide derivatives have received relatively little attention; nonetheless, their importance in the selective alkynylation of carbonyl compounds[2a,b] and other catalytic transformations has been noted recently.[2c,d] They have been generated *in situ* for the applications, but very little is known regarding their structures, probably due to their intrinsic tendency to form large aggregates in the solid state as well as their low solubility in common organic solvents.[3]

Our studies of transition metal complexes incorporating the anionic tacn ligand ((tacn)H = 1,4-diisopropyl-1,4,7-triazacyclononane) have shown that this ligand can function as either a tridentate, six-electron donor or may partially dissociate thus freeing coordination sites for further reactivity. In the latter mode, the ligand is also able to stabilize unusual bimetallic complexes *via* coordination of a second metal to the uncomplexed nitrogen donor atoms.[4,5] As both hydride and acetylide are very strong bridging ligands, we reasoned that this anionic macrocyclic ligand system could stabilize some interesting unsolvated and low molecularity hydro- and alkynyl-aluminates with unusual coordination geometries. Here we report the first isolation of an unsolvated lithium trihydroaluminate **1** and the related trialkynylaluminates **2** and **3** supported by the $tacn^-$ ligand.

Results and discussion

The reaction of 1,4-diisopropyl-1,4,7-triazacyclononane ((tacn)H) with $LiAlH_4$ in THF at room temperature afforded a solvent free lithium trihydroaluminate **1** in excellent yield (Scheme 1). Complex **1** has been characterized by ^1H, ^7Li, and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis. The most notable features of the ^1H NMR spectrum are the absence of resonances attributable to incorporated solvent or the Al–*H* protons; evidence for the latter is, nevertheless, provided by the IR spectrum, which shows a broad Al–H absorption centered at 1707 cm^{-1}. The ^7Li NMR is not especially informative and serves only to confirm the results of a positive lithium flame test. These data alone give little indication of the molecular structure of the molecules, so we turned to diffraction methods to address this issue.



Scheme 1

The molecular structure (Fig. 1) was determined by single crystal X-ray analysis. The final model shows a weakly bound dimeric structure in which one hydride ligand bridges between aluminium and lithium. The molecular structure of **1** is unique in comparison to several known solvated lithium aluminates such as $[(SiMe_3)_2NAlH(\mu\text{-}H)_2Li(OEt_2)]_2$[1a] and $(PhMe_2Si)_3CAlH(\mu\text{-}H)_2Li(THF)_2]_2$,[1d] all of which feature $Al_2Li_2H_4$ rings in the solid state. The aluminium atom in **1** is coordinated to the amido nitrogen atom of the $tacn^-$ ligand, and three hydride ligands, one of which bridges to a lithium atom. The three Al–H distances (both terminal and bridging) are essentially the same (average 1.57 Å), and are in good agreement with literature values.[6] The Li–H bond length (1.91(3) Å) may be compared to those found in solid LiH (2.040 Å)[7] and $LiAlH_4$ (1.88–2.16 Å),[8] but is significantly longer than those in $[(SiMe_3)_2NAlH(\mu\text{-}H)_2Li(OEt_2)]_2$ (1.777 Å).[1a]

Addition of three equivalents of terminal acetylenes, HCCPh or $HCCSiMe_3$, to **1** at room temperature leads to the elimination of H_2 and the formation of trialkynylaluminates **2** and **3** in high yield (Scheme 1). Compounds **2** and **3** were characterized by ^1H, ^7Li, and ^{13}C NMR spectroscopy, IR spectra, and elemental analysis. All three alkyne ligands are equivalent

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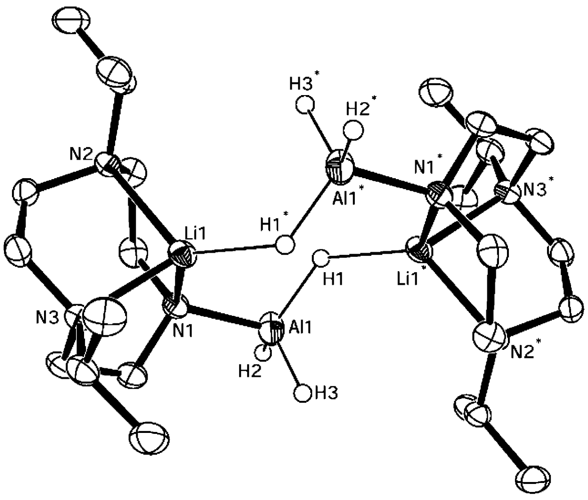

Fig. 1 ORTEP[17] drawing of **1**. Selected bond lengths [Å] and angles [°]: Al1–N1 1.877(2), Al1–H1 1.56(3), Al1–H2 1.58(3), Al1–H3 1.57(3), Li1–H1 1.91(3), Li1–N1 2.028(4), Li1–N2 2.095(4), Li1–N3 2.094(4); H1–Al1–H2 108(1), H2–Al1–H3 113(1), N1–Al1–H2 109(1), N1–Li1–H1* 120.3(8).

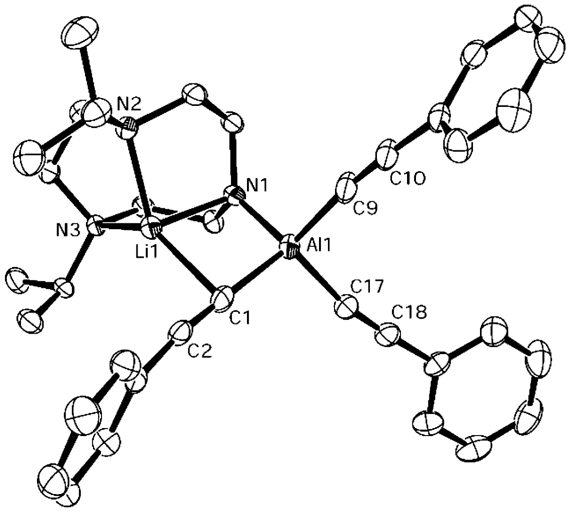

Fig. 2 ORTEP drawing of **2**. Selected bond lengths [Å] and angles [°]: Al1–N1 1.843(2), Al1–C1 1.981(3), Al1–C9 1.948(3), Al1–C17 1.950(3), Li1–N1 2.083(4), Li1–N2 2.032(4), Li1–N3 2.027(5), Li1–C1 2.230(5), Li1–C(2) 2.718, C1–C2 1.212(3), C9–C10 1.212(3), C17–C18 1.207(4); Al1–C1–C2 178.1(2), Al1–C9–C10 174.1(2), Al1–C17–C18 169.2(2), C1–C2–C3 172.6(3), C9–C10–C11 176.9(3), C17–C18–C19 177.3(3), Al1–N1–Li1 88.9(1), Al1–C1–Li1 81.5(1).

in solution at room temperature according to ^1H and ^{13}C NMR spectroscopy and again, the ^7Li data renders no structural information.

The molecular structure of **2** (Fig. 2) represents the first structurally characterized alkynylaluminate. The compound is monomeric in the solid state, with a four-coordinate aluminium atom bound to two terminal acetylides, one novel bridging acetylide group, and the tacn amido nitrogen. The Al1–C1 bond length (1.981(3) Å) is slightly longer than the Al–C (terminal) distances (average 1.949 Å), and also longer than those in the neutral aluminium acetylide compound $\{tBu_2PzAl(CCPh)_2\}_2$ (tBu_2Pz = 3,5 di-*tert*-butylpyrazolate) (1.92 Å).[9] The Al1–C1–C2 (178.1(2)°) angle is nearly linear, whereas the angles between the aluminium atom and the two terminal acetylides (174.1(2)° and 169.2(2)°) deviate slightly from linearity. The Li1–C1 distance (2.230(5) Å) is only slightly longer than those found in $(tBuCCLi)_4(THF)_4$ (2.19 Å),[10] and is in the range reported for those in $(LiCCSiMe_2C_6H_4OMe)_6$ (2.13–2.92 Å).[11] The Li1–C2 distance (2.718(5) Å) is long, inferring only weak electrostatic interaction between the lithium atom and the acetylide π electrons.[11] Interestingly, DFT calculations[12] (B3LYP method; 6-31G** basis set) predicted an optimized geometry almost identical to that found experimentally with Li–C1 = 2.248 Å and the same minor elongation of the Li-coordinated acetylene (1.206 Å *vs.* 1.200 Å for the non-coordinated acetylenes).

Compounds **1**, **2** and **3** represent the first known Group 13 compounds supported by anionic tridentate macrocyclic tacn ligands,[13] and the latter two species are the first well-characterized alkynylaluminates. Efforts to exchange the Li ion in these complexes for transition metals in attempts to prepare μ-acetylides have been unsuccessful to date, although further studies on related systems are in progress.

Experimental

Standard Schlenk-line and glove box techniques were used throughout. Pentane, diethyl ether, and toluene were passed through a column of activated alumina and degassed with argon. $LiAlH_4$ was crystallized from Et_2O before use. C_6D_6 was vacuum transferred from sodium/benzophenone ketyl. Unless otherwise specified, ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in C_6D_6 at ambient temperature on a Bruker DRX-500 spectrometer. ^1H NMR chemical shifts are given relative to C_6D_5H (δ 7.15). ^{13}C NMR chemical shifts are relative to C_6D_6 (δ 128.39). ^7Li NMR chemical shifts were referenced to an external LiCl (3 M in D_2O) standard at 0 ppm. IR samples were prepared as Nujol mulls and taken between KBr plates. Elemental analyses were determined by the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley. Single crystal X-ray structure determinations were performed at CHEXRAY, University of California, Berkeley.

Synthesis of 1

To a solution of $LiAlH_4$ (0.38 g, 10.00 mmol) in THF (20 mL) was added 1,4-diisopropyl-1,4,7-triazacyclononane ((tacn)H) (2.12 g, 10.00 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 15 h. The solvent was removed under vacuum. The resulting oily residue was dissolved in diethyl ether (50 mL), and stored at −40 °C overnight to give colorless crystals of **1** (2.4 g, 92%). ^1H NMR (C_6D_6): δ 0.86 (d, J = 6.7 Hz, 6 H, Me), 0.98 (d, J = 6.8 Hz, 6 H, Me), 3.03, 2.49, 2.10, 1.82 (m, 12 H, CH_2CH_2) 3.16 (sept, J = 6.6 Hz, 2 H, CH). ^{13}C NMR (C_6D_6): δ 18.8, 19.1 (CH_3), 48.9 (CH), 50.5, 53.7 (CH_2CH_2). ^7Li NMR (C_6D_6): δ 2.44. IR (Nujol, KBr): ν = 1707 cm^{-1}. Anal. calc. for $C_{12}H_{29}N_3LiAl$ (249.30): C, 57.82; H, 11.73; N, 16.85. Found: C, 57.82; H, 11.69; N, 16.75%.

Synthesis of 2 and 3

To a solution of **1** (0.50 g, 2.01 mmol) in toluene (15 mL) was added phenylacetylene (0.66 g, 6.50 mmol) at room temperature. Gas evolution was observed immediately upon addition. The mixture was stirred for 15 h at room temperature. The solvent was removed under vacuum to afford a white powder, which was subsequently crystallized from toluene at −10 °C to give colorless crystals of **2** (1.0 g, 85%). **3** was prepared similarly, and crystallized from pentane–toluene (10 : 1) to give **3** as a colorless crystalline solid (90%).

2: ^1H NMR (C_6D_6): δ 0.67 (d, J = 6.8 Hz, 6 H, Me), 0.80 (d, J = 6.8 Hz, 6 H, Me), 1.84, 1.92, 2.13, 2.51, 2.63 (m, 12 H, CH_2CH_2), 3.63 (sept, J = 6.8 Hz, 2 H, CH), 6.92–7.05 (m, 9 H, Ar–H), 7.53 (m, 6 H, Ar–H). ^{13}C NMR (C_6D_6): δ 17.0, 18.4 (CH_3), 47.1 (CH), 50.1, 53.1 (CH_2CH_2), 106.1 (Al–*C*), 124.8 (*C*Ph), 125.2, 126.1, 130.9, 131.0 (Ph). ^7Li NMR (C_6D_6): δ 2.74. IR (Nujol, KBr): ν = 1520, 1592 (Ph), 2108, 2122 (*C*CPh) cm^{-1}.

Anal. calc. for $C_{36}H_{41}N_3AlLi$ (549.66): C, 78.67; H, 7.52; N, 7.64. Found: C, 78.14; H, 7.85; N, 7.95%.

3: ^{1}H NMR (C_6D_6): δ 0.07 (s, 27 H, $SiMe_3$), 0.78 (m, 6 H, CH_3), 0.89 (m, 6 H, CH_3), 2.30–2.62 (m, 6 H, CH_2CH_2), 1.96 (m, 6 H, CH_2CH_2), 3.30 (m, 2 H, CH). ^{13}C NMR (C_6D_6): δ 0.4 ($SiMe_3$), 18.2, 18.4, 19.4, 19.6 (CH_3), 48.0 (CH), 49.5, 49.7, 54.1, 54.3 (CH_2CH_2), 93.7, 94.1 ($CSiMe_3$), 113.5 (Al–C). ^{7}Li NMR (C_6D_6, 194 MHz): δ 2.33. IR (Nujol, KBr): ν = 2060, 1948 cm^{-1}. Anal. calc. for $C_{27}H_{53}N_3AlLiSi_3$: C, 60.29; H, 9.93; N, 7.81. Found: C, 59.42; H, 10.30; N, 8.05%.

X-Ray structural analyses for 1 and 2

A fragment of a colorless block of **1** or **2** was mounted in a glass capillary. Data were collected on a Siemens Smart diffractometer. Data were integrated by the program SAINT[14] to a maximum 2θ value of 49.4°. The structure was solved by direct methods[15] and expanded using Fourier techniques.[16] The nonhydrogen atoms were refined anisotropically. The three hydrogen atoms bound to the aluminium ion were refined isotropically, while the rest were included in fixed positions.

Crystal data for 1. $C_{12}H_{29}N_3LiAl$, $M = 249.30$, crystal dimensions 0.32 × 0.28 × 0.13 mm, monoclinic, space group $P2_1/n$, $a = 9.1950(1)$, $b = 13.4305(3)$, $c = 13.0959(3)$ Å, $\beta = 106.265(1)°$, $V = 1552.53(5)$ Å^3, $Z = 4$, $d_{calc} = 1.067$ g cm^{-3}; $F(000) = 552.00$, $\lambda = 0.71069$ Å, $T = 139$ K, μ(Mo-Kα) = 1.15 cm^{-1}, $R_1 = 0.0590$, $wR_2 = 0.0559$. Of the 6935 reflections that were collected, 2678 were unique ($R_{int} = 0.042$).

Crystal data for 2. $C_{36}H_{41}N_3AlLi$, $M = 549.66$, crystal dimensions 0.34 × 0.22 × 0.18 mm, monoclinic, space group $P2_1/c$, $a = 8.3268(4)$, $b = 18.0244(9)$, $c = 22.140(1)$ Å, $\beta = 99.666(1)°$, $V = 3275.7(2)$ Å^3, $Z = 4$, $d_{calc} = 1.114$ g cm^{-3}, $F(000) = 1176.00$, μ(Mo-Kα) = 0.89 cm^{-1}, $T = 130$ K, $2\theta_{max} = 49.4°$, $R_1 = 0.0672$, $wR_2 = 0.0534$. Of the 14627 reflections collected, 5617 were unique ($R_{int} = 0.048$).

CCDC reference numbers 173850 (**1**) and 173851 (**2**).

See http://www.rsc.org/suppdata/dt/b2/b202238a/ for crystallographic data in CIF or other electronic format.

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