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Synthesis and Structural Characterization of $[(\text{SalpanAl})\text{Li}(\text{THF})_2]_2$ and $[(\text{SalomphanAl})\text{Li}(\text{THF})_2]_2$: A New Class of Aluminum Anion

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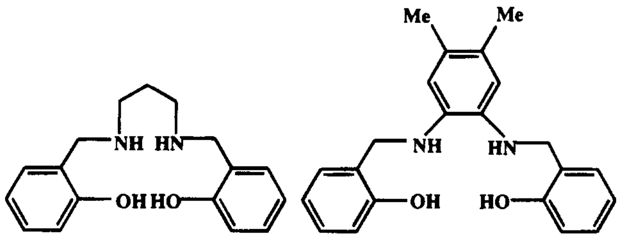
Introduction

Organometallic complexes of aluminum are useful reagents in many important applications such as living polymerizations,[1] Lewis acid promoted reductions of ketones and aldehydes,[2] and the polymerization of olefins.[3] Aluminum also figures prominently in the preparation of binary and ternary solid state electronic materials.[4] The vast majority of research into these areas has focused on neutral systems.[5] By comparison, anionic (aluminate) complexes have received somewhat less attention. Perhaps the most widely studied of the organometallic aluminates are the aluminum alkoxide[6] complexes, although reports of other aluminates[7] have appeared in the literature. An understanding of charged group 13 organometallics is of fundamental interest to main group science, and considering the widespread use of the neutral derivatives, a similar utility may be expected to develop for the charged species once that chemistry has been systematically explored.



SalpanH_4
(a)

SalomphanH_4
(b)

Figure 1. Representation of SalpanH_4 (a) and SalomphanH_4 (b).

As part of our program to explore the anionic chemistry of the group 13 elements we have chosen two members of the SalanH_4 class of ligands (Figure 1)[8] for use in preparing the anionic complexes, $[(\text{SalpanAl})\text{Li}(\text{THF})_2]_2$ (**1**) and $[(\text{SalomphanAl})\text{Li}(\text{THF})_2]_2$ (**2**). To the best of our knowledge these are the first aluminates with a 1:1 metal to ligand stoichiometry.

Results and Discussion

Compounds **1** and **2** were prepared by the reaction of LiAlH_4 with the appropriate SalanH_4 ligand according to eq 1. Yields

$$2\text{SalanH}_4 + 2\text{LiAlH}_4 \xrightarrow[-8\text{H}_2]{\text{THF}, \Delta} [(\text{SalanAl})\text{Li}(\text{THF})_2]_2 \quad (1)$$

$$\text{Salan} = \text{Salpan, Salomphan}$$

of a white, moderately air sensitive product, for the two reactions range from 80 to 95%. The compounds have been characterized by NMR (^{1}H, ^{13}C, ^{27}Al), IR, elemental analysis and show no volatility or decomposition to 260 °C. Thus, mass spectral analysis provided no useful information as to the possible oligomerization of the anions. However, the structural characterization of **1** and **2** indicate that the compounds exist as dimers. The molecular structure and atom numbering schemes for **1** and **2** are shown in Figures 2 and 3, respectively. Relevant bond length and angle information is given in the Figure captions. In each of the structures, the nitrogen atoms of the ligand act to bridge two central Al anions. The lithium cations are bridged by two oxygens from the same ligand and are coordinated to two THF molecules, forming a distorted tetrahedral geometry. The geometry of the central Al atoms in **1** is distorted trigonal bipyramidal. Using the atoms around Al(1) as an example, this is exemplified by an axial O(1)−Al(1)−N(2) angle of 166.4(5)°. The equatorial positions are then occupied by N(1), O(2), and N(4). The dimerization of **1** leads to the formation of a bent Al_2N_2 four-membered ring with the largest deviation from planarity being 0.141 Å. The two four-membered rings formed by the Al−O−Li−O atoms are planar (maximum deviation 0.051Å) and form dihedral angles of +50.0° (for Al(1)) and −53.2° (for Al(2)) atoms. It is interesting to note that the twist represented by these angles gives the structure helical chirality. This would also serve to explain the absence of a symmetry element as was found for **2**.

In **2** there is a center of inversion which makes the two $(\text{SalomphanAl})\text{Li}(\text{THF})_2$ units equivalent to one another. The coordination geometry of the Al atoms in this molecule is trigonal bipyramidal. Two nitrogens and an oxygen atom make up the equatorial coordination of the Al, while one oxygen and nitrogen atom occupy the axial positions. The equatorial Al−N

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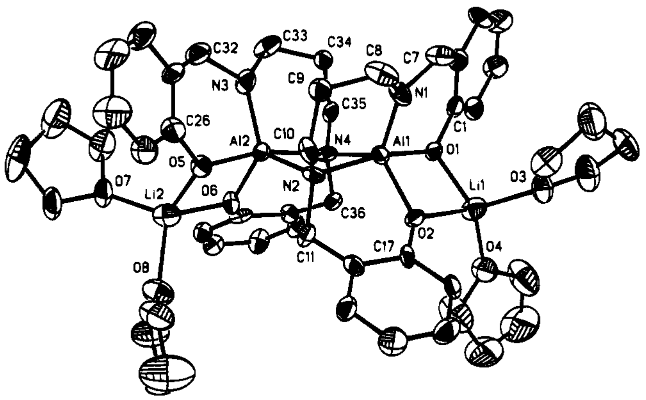

Figure 2. Molecular structure and atom numbering scheme for **1**. Important bond distances (Å) and angles (deg): Al(1)−O(1) 1.869(9), Al(1)−O(2) 1.831(9), Al(1)−N(1) 1.812 (13), Al(1)−N(2) 2.027(10), Al(1)−N(4) 1.995(12), Al(2)−O(5) 1.885(9), Al(2)−O(6) 1.839(10), Al(2)−N(2) 1.954(12), Al(2)−N(3) 1.827(11), Al(2)−N(4) 2.035(10), O(1)−Li(1) 1.854(26), O(2)−Li(1) 1.933(25), O(5)−Li(2) 1.854(29), O(6)−Li(2) 1.949(25); O(1)−Al(1)−N(1) 94.9(5), O(2)−Al(1)−N(1) 120.5(5), O(1)−Al(1)−N(2) 166.4(5), O(2)−Al(1)−N(2) 93.3(4), N(1)−Al(1)−N(2) 98.6(5), O(1)−Al(1)−N(4) 91.7(4), O(2)−Al(1)−N(4) 118.1(4), N(1)−Al(1)−N(4) 121.3(5), N(2)−Al(1)−N(4) 80.3(4), O(5)−Al(2)−O(6) 81.2, O(5)−Al(2)−N(2) 91.8(4), O(6)−Al(2)−N(2) 116.4(4), O(5)−Al(2)−N(3) 94.8(4), O(6)−Al(2)−N(3) 123.6(5), N(2)−Al(2)−N(3) 120.0(5), O(5)−Al(2)−N(4) 166.8(4), O(6)−Al(2)−N(4) 92.0(4), N(2)−Al(2)−N(4) 81.1(4), N(3)−Al(2)−N(4) 98.4(5), Al(1)−O(1)−Li(1) 100.9(9), Al(1)−O(2)−Li(1) 99.4(8), Al(2)−O(5)−Li(2) 100.6(8), Al(2)−O(6)−Li(2) 98.8(9).

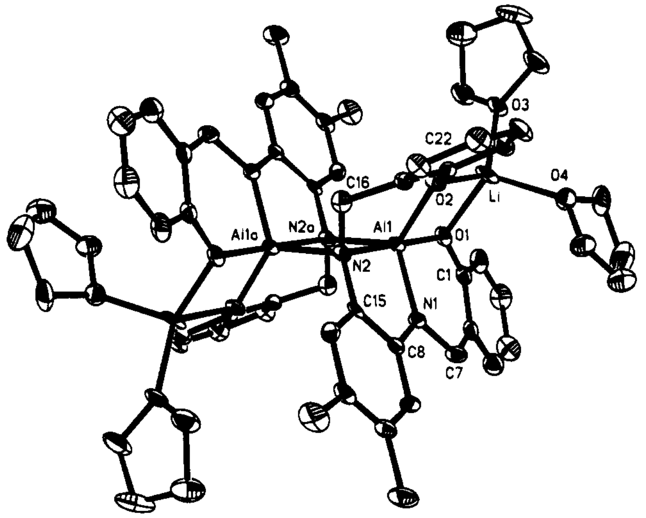

Figure 3. Molecular structure and atom numbering scheme for **2**. Important bond distances (Å) and angles (deg): Al(1)−O(1) 1.850(4), Al(1)−O(2) 1.817(6), Al(1)−N(1) 1.856(6), Al(1)−N(2) 2.029(5), Al(1)−N(2A) 1.971(6), O(1)−Li 1.927(16), O(2)−Li 1.943(12); O(1)−Al(1)−O(2) 85.7(2), O(1)−Al(1)−N(1) 94.6(2), O(2)−Al(1)−N(1) 123.8(3), O(1)−Al(1)−N(2) 179.6(3), O(2)−Al(1)−N(2) 93.9(2), N(1)−Al(1)−N(2) 85.6(2), O(1)−Al(1)−N(2A) 95.2(2), O(2)−Al(1)−N(2A) 124.1(2), N(1)−Al(1)−N(2A) 111.9(3), N(2)−Al(1)−N(2A) 85.0(2), Al(1)−O(1)−Li 96.7(4), Al(1)−O(2)−Li 97.3(5).

bonds (average 1.89 Å) are somewhat shorter than the axial bonds (2.03 Å). The same trend holds for the oxygen bonds in equatorial (1.82 Å) and axial (1.85 Å) positions. Both the Al_2N_2 and AlO_2Li four-membered rings are planar (maximum deviation 0.015Å) and form a dihedral angle of 124.8°.

The primary difference between **1** and **2** lies in the disposition of the amine backbone. In **1** the propyl amine backbones are oriented cis in relation to the Al_2N_2 four-membered ring. In **2**, the phenylamine groups are oriented in a symmetrical, trans, configuration around the Al_2N_2 ring. This configuration also allows the center of symmetry that is found in the crystal structure of **2**.

The spectroscopic characterization of **1** and **2** supported the maintenance of dimeric solution state species in keeping with the crystallographically determined structures. Thus, in **1** there were four distinct PhCH$_2$ resonances. Two of these fell in the range of δ 3.47−3.60 ppm, while the other two were manifested as doublets at δ 4.29 and 4.93 ppm. The presence of doublets for the PhCH$_2$ groups in these systems (as an AB spin system) is in keeping with a rigid solution state conformation. This is a common feature of Salan-metal complexes and has been observed in such complexes as [SalanH$_2$Zn]$_2$,[8] and SalanAlMe(AlMe$_2$)$_2$[9] (where Salan is a number of ligands including Salpan and Salomphan). The presence of such coupling in the propyl amine backbone of **1** leads to two sets of multiplets centered at δ 2.21 and 2.66 ppm. The symmetrical nature of **2** was also observed in the NMR data. Thus, the methylene groups were manifested as two sets of multiplets which were centered at δ 3.64 and 4.20 ppm. The ^{27}Al NMR chemical shifts for **1** and **2** (δ 50.10 ($W_{1/2}$ = 2083 MHz), 55.65 ($W_{1/2}$ = 1562 MHz)) were comparable to those found for the central five-coordinate aluminum atoms in the SalanAlMe(AlMe$_2$)$_2$ complexes[9] (range, 55−85 ppm ($W_{1/2}$ = 3645−6770 MHz)). This is in keeping with the supposition that geometrical, rather than electronic, factors determine ^{27}Al chemical shifts.[10] However, it is interesting to note that the peak widths for anionic **1** and **2** were much narrower than for the neutral examples.

In summary, we have demonstrated that a new class of anionic aluminum complexes with a metal−ligand stoichiometry of 1:1 can be synthesized through the use of SalanH$_4$ ligands. The type of amine backbone that is used within these ligands significantly influences the geometry of the subsequent aluminate complex. For instance, the cis orientation of the propyl amine group in **1** leads to a complex that demonstrates helical chirality. In **2**, the use of the 4,5-dimethylphenylamine group leads to a trans orientation of this group and a symmetrical molecule. Further work directed at preparing other aluminum anions, and complexes with helical chirality are currently in progress.

Experimental Section

General Data. All manipulations were conducted using Schlenk techniques in conjunction to an inert atmosphere glovebox. All solvents were rigorously dried prior to use. The ligands SalpanH$_4$ and SalomphanH$_4$ were synthesized as previously described.[8] NMR data were obtained on JEOL-GSX-400 and −270 instruments at 270.17 (^{1}H), 62.5 (^{13}C), and 104.15 (^{27}Al) MHz. Chemical shifts are reported relative to SiMe$_4$ and are in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer. Mass spectral data collections were attempted on a Hewlett-Packard 5988 spectrometer using electron impact ionization (70 eV) with a direct ionization probe (DIP). Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}.

Preparation of [(SalpanAl)(Li(THF))$_2$]$_2$ (1). SalpanH$_4$ (3.01 g, 10.52 mmol) and lithium aluminum hydride (0.420 g, 11.04 mmol) were placed in a dry, 250 mL flask under nitrogen. Dry toluene (120 mL) was added at 25 °C and the solution stirred for 10 min. Dry tetrahydrofuran (20 mL) was added and the exothermic reaction was refluxed for 10 h. After cooling to 25 °C, the solution was filtered and concentrated to one-half volume. Crystals were grown after storing at −30 °C for one week (4.32 g, 89%): mp > 260 °C; ^{1}H NMR (270 MHz, THF-d_8) δ 0.75 (m, 1H, CH$_2$C*H*$_2$), 2.20−2.22 (m, 2H, CH$_2$C*H*$_2$ and NC*H*$_2$), 2.60−2.73 (m, 3H, NC*H*$_2$), 3.47−3.60 (m, 2H, PhC*H*$_2$),

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4.29 (d, J = 15 Hz, 1H, PhCH_2), 4.93 (d, J = 15 Hz, 1H, PhCH_2), 7.04−7.18 (m, 8H, Ph−H); ^{13}C NMR (62.5 MHz, THF-d$_8$) δ 21.5 (CH$_2$$C\mathrm{H}_2$), 55.5 (N$C\mathrm{H}_2$), 58.6 (N$C\mathrm{H}_2$), 59.3 (Ph$C\mathrm{H}_2$), 67.1 (PhC$H_2$), 116.5 (Ph), 117.5, 118.2, 119.1, 126.7, 128.1, 129.3, 129.3, 130.3, 132.3, 161.2, 162.6; ^{27}Al NMR (104.15 MHz, THF-d_8) δ 50.10 ($W_{1/2}$ = 2083 Hz); IR (KBr) cm^{-1} 3057 (m), 2877 (s), 1597 (vs), 1485 (vs), 1452 (vs), 1280 (vs), 667 (s). Anal. Calcd: C, 65.22; H, 7.39; N, 6.09. Found: C, 65.50; H, 7.76; N, 5.88.

Preparation of [SalomphanAl(Li(THF))$_2$]$_2$ (2). SalomphanH$_4$ (3.05 g, 8.76 mmol) and lithium aluminum hydride (0.353 g, 9.29 mmol) were placed in a dry, 250 mL flask under nitrogen. Dry toluene (120 mL) was added at 25 °C and the solution stirred for 10 min. Dry tetrahydrofuran (20 mL) was added and the exothermic reaction was refluxed for 10 h. After cooling to 25 °C, the solution was filtered and concentrated to one-half volume. Crystals were grown after storing at −30 °C for 1 week (4.12 g, 90%): mp > 260 °C; ^{1}H NMR (270 MHz, THF-d_8) δ 1.96−2.15 (m, 6H, PhCH_3), 3.51−3.77 (m, 2H, PhCH_2), 4.03−4.38 (m, 2H, PhCH_2), 5.83−7.25 (m, 10H, Ph−H); ^{13}C NMR (62.5 MHz, THF-d_8) δ 19.91 (Ph$C\mathrm{H}_3$), 51.49 (Ph$C\mathrm{H}_2$), 55.61 (Ph$C\mathrm{H}_2$), 109.1 (Ph), 116.8, 117.3, 117.5, 118.7, 119.8, 127.0, 127.1, 127.2, 127.3, 160.4; ^{27}Al NMR (104.15 MHz, THF-d_8) δ 55.65 ($W_{1/2}$ = 1562 Hz); IR (KBr) cm^{-1} 3022 (m), 2962 (vs), 1599 (s), 1489 (vs), 1275 (vs), 1045 (vs), 891 (s), 800 (s), 671 (s). Anal. Calcd: C, 68.97; H, 6.90; N, 5.36. Found: C, 68.96; H, 6.80; N, 5.82.

X-ray Experimental Data. For each compound crystals suitable for X-ray analysis where grown from a mixture of THF and toluene after cooling to −30 °C. The crystals lost solvent readily and had to be kept at low temperature. In a typical crystal mounting session the flask containing the crystals was attached to a vacuum line while being cooled at −78 °C. The supernatant was filtered until 10 mL of solvent remained on the crystals. The flask was briefly put under vacuum, rinsed with acetone, and immediately placed into the antechamber of a drybox. After evacuation for 10 min the flask was brought into the box and placed in a freezer at −26 °C. Two crystals where mounted into glass capillaries and brought out of the drybox to be sealed with a flame. The sealed crystals were then placed into the cold stream of a low-temperature X-ray apparatus. The data collection was commenced immediately at −50 °C. Attempts to utilize a lower temperature of <−100 °C resulted in fracturing of the crystal. Many rounds of the above procedure were necessary before a full data set was obtained for **1** and **2**. Details of the crystal data and a summary of data collection parameters for **1** and **2** are given in Table 1. Data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo Kα (0.710 73 Å) radiation. The check reflections, measured every 100 reflections, indicated a less than 5% decrease in intensity over the course of data collection and hence, no correction was applied. All calculations were performed on a personal computer using the Siemens software package, SHELXTL-Plus. The structures were solved by direct methods and successive interpretation of difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters.

Table 1. Crystal Data for [SalpanAl(Li(THF))$_2$]$_2$ (**1**) and [SalomphanAl(Li(THF))$_2$]$_2$ (**2**)

compound	**1**	**2**
formula	$C_{64}H_{84}Al_2Li_2N_4O_8$	$C_{67}H_{80}Al_2Li_2N_4O_8$
formula weight	1105.2	1137.2
crystal size (mm)	1.2 × 0.6 × 0.4	0.8 × 0.5 × 0.4
crystal system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	11.894(6)	11.394(4)
b (Å)	19.076(6)	11.593(5)
c (Å)	26.862(9)	13.908(5)
α, deg	90	69.05(3)
β, deg	101.02(3)	82.46(2)
γ, deg	90	77.32(3)
V (Å^3)	5983(4)	1671.1(11)
Z	4	2
D_{calc} (g/cm^3)	1.227	2.260
temp (K)	223	223
2θ range (deg)	3.5−45	3.5−45
scan type	$2\theta-\theta$	$2\theta-\theta$
scan speed(deg/min)	8−60	5−60
scan range (deg)	0.56	0.97
reflections collected	9729	5070
indp reflections	7752	4252
obsd reflections	2637 ($F > 4.0\sigma(F)$)	2180 ($F > 4.0\sigma(F)$)
number of parameters	691	406
R	0.0770	0.0626
R_w	0.0851	0.0651
GOF	4.52	1.63
lardiff. peak (e/Å^3)	0.29	0.33

The structure solution of compound **1** was problematic. The central carbon in the propylamine backbone of the aluminate complex was disordered over two positions and was successfully refined by allocating a 50% occupancy for each position. There were also two disordered molecules of toluene in the crystal lattice. A similar model with partial occupancy was used to refine the methyl groups for these molecules.

Acknowledgment. We thank the National Science Foundation (Grant RII-861075) for generous financial support.

Supporting Information Available: Tables of bond distances, angles, atomic coordinates and thermal parameters and figures showing the full atom labeling and unit cells for **1** and **2** (28 pages). Ordering information is given on any current masthead page.

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