

Communications to the Editor

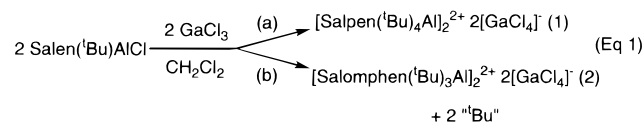
Five-Coordinate, Solvent-Free Aluminum Cations

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Cationic aluminum complexes have been of fundamental interest for many years.¹ However, there is now a growing awareness that such species can be viewed as exceedingly strong Lewis acids and thereby able to activate and catalyze reactions that would not be affected by the presence of neutral derivatives. This has been demonstrated for two-,² three-,³ and four-coordinate⁴ aluminum cations in the polymerization of olefins and for six-coordinate complexes in the oligomerization of oxiranes.⁵ The higher-coordinate derivatives are especially attractive because they are robust and not very air-sensitive.⁶ In the past, these were prepared by base-promoted displacement of halide and through salt elimination reactions.¹ These routes necessarily employed donor solvents such as H₂O, MeOH, and THF to solubilize the reactants and, in some cases, the products. Consequently the cationic products contained two base molecules. For catalytic applications, then, the monomers or substrates of interest must be of sufficient base strength to displace these preexisting base molecules. It would be far superior to have on hand a class of higher-coordinate cations without donor solvents. The present paper will detail an attempt to prepare unsolvated mononuclear aluminum cations that are not in a *T_d* geometry.



To obtain solvent-free cations a toluene or CH₂Cl₂ soluble Lewis acid, GaCl₃, is combined with either Salphen('Bu)AlCl⁷ or Salomphen('Bu)AlCl⁷ (eq 1a and b (two 'Bu groups are missing, see below)).⁸ Thus, the GaCl₃ strips the chloride from the aluminum in forming the cations, **1** and **2**. The ²⁷Al NMR data indicated that the complexes contained only five-coordinate aluminum based upon chemical shifts of ~38 ppm. Since the ligands are tetradentate, the fifth coordination site must result from dimerization.

It has been shown previously that the Salphen ligand allows a tbp geometry around a central group 13 metal alkyl or halide,⁹

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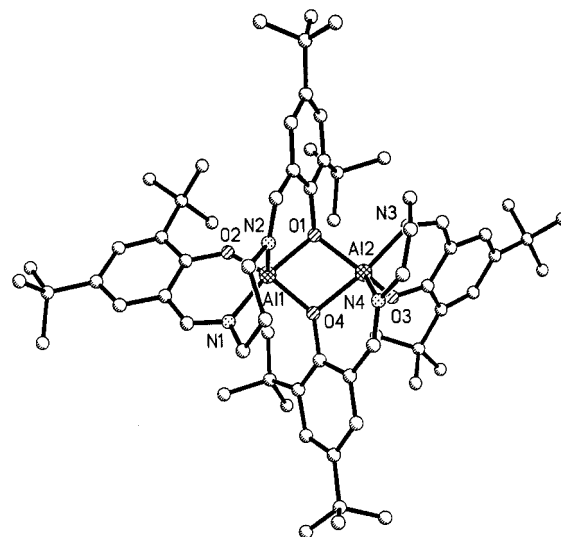


Figure 1. Molecular structure and atom numbering scheme for the cation of [Salphen('Bu)₄Al]₂²⁺ 2 [GaCl₄]⁻ (**1**). A non-thermal ellipsoid view is shown for clarity.

and thus dimerization can occur for compounds containing this ligand. The structure¹⁰ of **1** reveals this to be true and that the flexibility of the ligand -(CH₂)₃- backbone allows the aryl 'Bu groups to be oriented to reduce steric repulsion (Figure 1). The Salophen ligand does not have a flexible backbone and has only been observed to form square pyramidal complexes.⁹ In the present case removal of the chloride would lead to a potentially four-coordinate cation. The extreme Lewis acidity of such a complex with two open coordination sites means that some intermolecular base-stabilization would be desired and does occur as indicated by the ²⁷Al NMR data. In forming the dimer and filling of a fifth coordination site through intermolecular contact the ligand must remove the steric repulsion between two of the 'Bu groups. To do this a rare Friedel–Crafts dealkylation¹¹ occurs

(8) Experimental details for **1** and **2**: {[Salphen('Bu)Al]⁺]₂ 2[GaCl₄]⁻ (**1**). To a stirring solution of Salphen('Bu)AlCl (2 g, 3.56 mmol) in CH₂Cl₂ (30 mL) was added a solution of GaCl₃ (0.64 g, 3.56 mmol) in CH₂Cl₂ (20 mL) at 25 °C. The reaction mixture was stirred for 6 h, and then 20 mL of solvent was removed under vacuum. To the remaining solution 3 mL of hexanes was added, and the solution was stored at -30 °C for 1 day. The solution deposited yellow-green crystals of **1** which were isolated by filtration and dried in a vacuum. Yield 2.6 g (99%); mp 185–187 °C; ¹H NMR (CDCl₃) δ 1.00 [s, 18H, C(CH₃)₃], 1.25 [s, 18H, C(CH₃)₃], 1.32 [s, 18H, C(CH₃)₃], 1.40 [s, 18H, C(CH₃)₃], 2.02 [m, 2H, CH₂], 2.26 [m, 2H, CH₂], 2.70 [m, 2H, CH₂], 3.60 [m, 2H, CH₂], 4.12 [m, 4H, CH₂], 7.34 [d, 2H, C₆H₂], 7.57 [d, 2H, C₆H₂], 7.80 [d, 2H, C₆H₂], 7.90 [d, 2H, C₆H₂], 8.56 [s, 2H, CHN], 9.07 [s, 2H, CHN]; ²⁷Al{¹H} NMR δ 38.68 (w_{1/2} = 6922 Hz); IR (cm⁻¹) 2962 (s), 2872 (m), 2344 (w), 2363 (w), 1620 (s), 1564 (s), 1466 (s), 1424 (s), 1366 (m), 1296 (m), 1256 (m), 1204 (m), 1177 (m), 999 (w), 928 (w), 860 (m), 828 (m), 770 (m), 1144 (w), 1080 (w), 630 (w), 613 (m), 561 (w), 484 (w). Anal. Calcd for C₆₉H₁₀₂Al₂Cl₄Ga₂N₄O₄: C, 47.59; H, 5.90. Found: C, 47.46; H, 5.42. {[Salomphen('Bu)₃Al]⁺]₂ 2[GaCl₄]⁻ (**2**). The preparation of **2** proceeded in the manner described for **1** with Salomphen('Bu)AlCl (2.5 g, 3.97 mmol), GaCl₃ (0.70 g, 3.97 mmol). Yield, 2.8 g (87%); mp, >230 °C; ¹H NMR (CDCl₃) δ 0.07 [s, 18H, C(CH₃)₃], 0.09 [s, 18H, C(CH₃)₃], 1.30 [s, 9H, C(CH₃)₃], 1.46 [s, 9H, C(CH₃)₃], 2.47 [s, 6H, Ph(CH₃)₂], 2.49 [s, 6H, Ph(CH₃)₂], 7.18 (4m, 14H, C₆H_n) 7.94 [s, 2H, CHN], 8.80 [s, 2H, CHN]; ²⁷Al{¹H} NMR δ 37.99 (w_{1/2} = 5084 Hz); IR (cm⁻¹) 2961 (s), 2909 (s), 2870 (m), 1892 (w), 1618 (s), 1589 (s), 1555 (s), 1485 (m), 1464 (m), 1435 (m), 1389 (m), 1362 (m), 1256 (m), 1188 (m), 1138 (w), 1086 (m), 1022 (s), 849 (m), 781 (m). Anal. Calcd for C₈₀H₁₁₂Al₂Cl₄Ga₂N₄O₄: C, 49.16; H, 5.78. Found: C, 49.84; H, 5.40.

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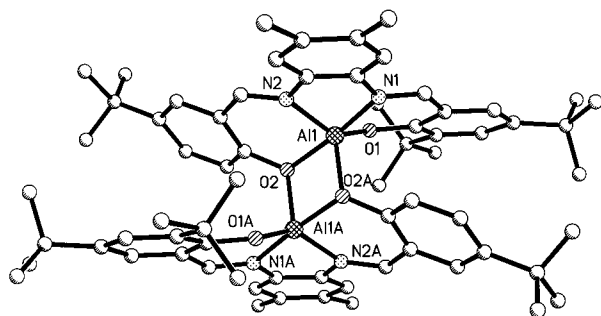


Figure 2. Molecular structure and atom numbering scheme for the cation of $[\text{Salomphen}(\text{'Bu})_3\text{Al}]_2^{2+} 2 [\text{GaCl}_4]^-$ (**1**). A 'Bu group has been lost from each ligand during the formation of the dimer. A non-thermal ellipsoid view is shown for clarity.

to eject the two 'Bu groups which would otherwise impede formation of the dimer (Figure 2). This is the first instance that has been observed for the Salen('Bu) ligands which are generally thought to be inert and unreactive when chelated to a metal. The ^1H NMR is also indicative of the loss of these groups for **2** in which there are four tBu resonances integrating to six tBu groups. For **1** the same number of resonances integrate for the expected eight tBu groups. In keeping with the dimeric formulation there are two discrete environments for the $\text{CH}=\text{N}$ groups (~ 8.6 and 9.0 ppm). By comparison, monomeric Salen('Bu) complexes display two tBu and one imine resonance. The fact that the unreactive Salen('Bu) ligand may be induced to eject a 'Bu group and dimerize rather than remain monomeric shows how difficult it will be to obtain a four-coordinate unligated aluminum cation that is not in a T_d geometry. The difficulty inherent to isolating such highly oxophilic Lewis acidic complexes may be compared to the great effort expended to prepare the silylium ion.¹²

It is likely that the aluminum cations should, at the very least, be useful as catalysts for the polymerization of substrates containing a Lewis basic atom. The substrate would dissociate

(10) X-ray Data for **1** and **2** were collected on a Siemens SMART-CCD unit with Mo $K\alpha$ radiation. A full data set $2\theta = 55^\circ$ was obtained although lower values were used in the final solution. The structures were refined using the Siemens software package SHELXTL 4.0. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into calculated positions. X-ray data for **1**: pale yellow crystals $(0.4)^3$, formula $\text{C}_{70}\text{H}_{104}\text{Al}_2\text{Cl}_{16}\text{Ga}_2\text{N}_4\text{O}_4$ (includes 4 CH_2Cl_2 molecules) FW 1826.17, Monoclinic, $P2_1/c$, $a = 15.3016(7)$ Å, $b = 27.6703(13)$ Å, $c = 22.3459(11)$ Å, $\beta = 103.655(1)^\circ$, $V = 9193.8(8)$ Å³, $Z = 4$, data 7306, parameters, 895, $R_1 = 0.0813$ (for $I \geq 2\sigma$), $wR_2 = 0.1959$, GOF (on F^2) = 1.405; for **2**: pale yellow crystals, $(0.5)^3$, formula $\text{C}_{35}\text{H}_{44}\text{AlCl}_6\text{GaN}_2\text{O}_2$, FW 834.12, Triclinic P-1, $a = 10.9634(10)$ Å, $b = 11.5890(10)$ Å, $c = 17.237(2)$ Å, $\alpha = 95.720(2)^\circ$, $\beta = 103.655(1)^\circ$, $\gamma = 97.420(2)^\circ$, $V = 2094.5(3)$ Å³, $Z = 2$, data 2155, parameters 425, $R_1 = 0.0821$ (for $I \geq 2\sigma$), $wR_2 = 0.1840$, GOF (on F^2) = 1.076.

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the dimer into substrate-supported cationic units. This is supported by the fact that **1** and **2** can be used as catalysts for the polymerization of propylene oxide (PO) and iso-butyl vinyl ether (IBVE).¹³ For PO oligomers of $M_w \approx 2000$ to 3000 and PDI ≈ 1.6 (GPC) were obtained. With IBVE polymers of $M_w \approx 9000$ to 29000 and PDI ≈ 2 were obtained. It was found that a non-oxygen containing monomer, styrene, could be polymerized to high M_w , $\sim 24,000$ with PDI ≈ 2 . However, ethylene and propylene were not polymerized under the same conditions. At lower temperatures (-78°C) the MW of the polymers increases for IBVE ($\sim 30,000$) and styrene ($\sim 110,000$). (PO did not polymerize at this temperature). Although the results here are preliminary, it appears that the observed polymerizations can be interpreted as a carbocationic polymerization with the aluminum cations serving as an initiator for the process. Further studies are currently underway to determine the exact mechanism for the polymerization of olefin-containing monomers. However, it is clear that these higher-coordinate base-free cations will prove to be of utility as either strong Lewis acid catalysts or initiators for other substrates and reactions.

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Supporting Information Available: Crystallographic data (excluding the structure factor tables) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. 10063. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. Code + (1223)336-033; e-mail: teched@chemcrs.cam.ac.uk.) Crystallographic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) Polymerizations. PO: in an inert-atmosphere glovebox (0.3 mmol) of catalyst was transferred to a 100-mL flask equipped with a magnetic stirring bar. Propylene oxide (143 mmol), freshly distilled from CaH_2 , was added via syringe. The exothermic reaction was allowed to stir for 12 h before being quenched with MeOH (2 mL) and a few drops of HCl. The polymer was dissolved in CH_2Cl_2 and washed with water. IBVE: The catalyst (0.70 mmol) was obtained in the manner described for PO (above). It was dissolved in freshly distilled CH_2Cl_2 (20 mL), and then IBVE (115 mmol), freshly distilled over CaH_2 , was added slowly over 15 min at 25°C . The polymerization proceeded as for PO. The polymer was precipitated in excess MeOH, the solvent layer was decanted off and the polymer was dried under high vacuum ($\sim 70\%$ conversion). Styrene: procedure as for PO with catalyst (0.4 mmol) and CH_2Cl_2 (50 mL) combined inside a glovebox. The solution was then cooled to -78°C , and styrene (131 mmol), freshly distilled over CaH_2 , was added slowly. The reaction was stirred for 1 h and quenched by adding MeOH (2 mL) with a few drops of HCl. The polymer was recovered as described for IBVE ($\sim 85\%$ conversion).