J. Am. Chem. Soc. **1995**, *117*, 6779−6780

Communications to the Editor

Cationic Aluminum Compounds with Potential Relevance to Lewis Acid Catalysis

David A. Atwood,* Jolin A. Jegier, and Drew Rutherford

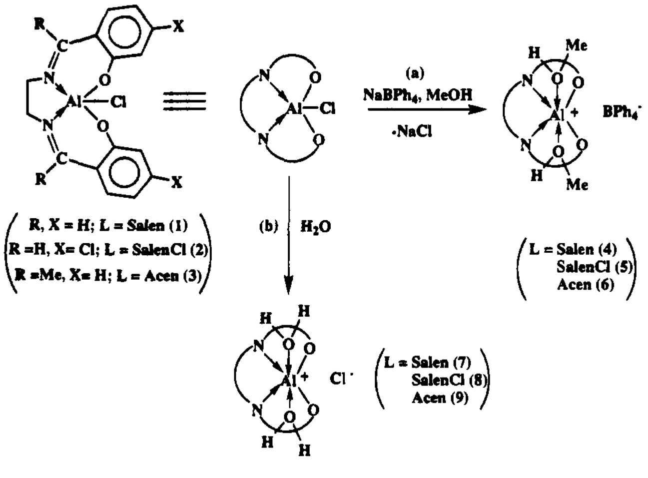
Department of Chemistry
North Dakota State University
Fargo, North Dakota 58105

Received March 13, 1995

Aluminum compounds are finding increasing importance as "living" polymerization catalysts[1] and in the Lewis acid-promoted reduction of ketones and aldehydes.[2] In order for a compound to be useful in these applications, it must be able to coordinate a substrate such as an aldehyde, ketone, or oxirane. This implies a complex that is coordinatively unsaturated and/or electron deficient. These qualities can be achieved by employing bulky substituents, as in AlMe(2,4,6-tri-*tert*-butylphenolate)$_2$,[1c] or through the use of chelating ligands, as demonstrated for SalcenAlCl (Salcen = *N,N'*-bis(2-hydroxybenzylidene)-1,2-cyclohexanediamine)[1e,f] and porphyrinAlCl complexes.[1g,h] These compounds are proven catalysts in the ring-opening living polymerization of oxiranes. For this type of application, the use of cationic aluminum reagents would be ideal. Aluminum cations are naturally electron deficient, and with the choice of loosely coordinating ligands, they may behave as coordinatively unsaturated compounds. Despite the clear relevance of such compounds, however, discrete cationic aluminum complexes have hitherto been unavailable for use in this application.

In this Communication are described the syntheses and characterization of the cationic aluminum complexes $[LAl(MeOH)_2]^+BPh_4^-$ (L = Salen (**4**), SalenCl (**5**), and Acen (**6**)) and $[LAl(H_2O)_2]^+Cl^-$ (L = Salen (**7**), SalenCl (**8**), and Acen (**9**)) (where Salen = *N,N'*-ethylenebis(2-hydroxyphenyleneimine), SalenCl = *N,N'*-ethylenebis(2-hydroxy-5-chlorophenyleneimine), and Acen = *N,N'*-ethylenebis(2-hydroxyphenylene(methyl)imine). These complexes represent the first of a new class of aluminum cations with potential relevance to Lewis acid catalysis. Additionally, **6** represents the first structurally characterized aluminum adduct of MeOH. Compounds **4−6** are prepared by reaction of the appropriate LAlCl (**1−3**) with $NaBPh_4$ according to Scheme 1a.[3] The resulting complexes are soluble in polar solvents, such as MeCN and THF, and can be isolated as crystalline solids by cooling to −30 °C in MeOH. The use of a noncoordinating anion, such as BPh_4^-, to synthesize cationic aluminum complexes is apparently unnecessary. Thus, dissolution of **1−3** in water leads to formation of the cationic dihydrate complexes $[LAl(H_2O)_2]^+Cl^-$ (L = Salen (**7**), SalenCl (**8**), and Acen (**9**)), in quantitative yield (Scheme 1b). The spectroscopic data[4] and elemental analyses[5] for **4−9** confirm the presence of the two coordinating solvent molecules.

Scheme 1. General Syntheses of Compounds **4−9**



Compounds **6** and **7** were also characterized by X-ray crystallography.[6] The molecular structures and atom labeling schemes are given in Figures 1 and 2, respectively. The figure captions contain selected bond length and angle information. The structures of **6** and **7** are morphologically similar. The aluminum atoms are bound in an octahedral fashion to the Schiff base ligand (occupying the equatorial coordination sites) and two solvent molecules (occupying axial positions). It is interesting to note that solvents possessing O−H functionalities

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(3) Synthesis: compounds **1−3** are prepared by the reaction of the appropriate ligand with either Me_2AlCl or Et_2AlCl in yields of 95%, 94%, and 96%, respectively. These are combined with $NaBPh_4$ in THF, evacuated to dryness, and extracted with MeOH to yield the $[LAl(MeOH)_2]^+BPh_4^-$ derivatives in yields of 54% (L = Salen (**4**)), 51% (L = SalenCl (**5**)), and 50% (L = Acen (**6**)). Quantitative conversion of **1−3** to **7−9** occurs after dissolution in H_2O at 25 °C.

(4) Physical data: mp **1**, 156−160 °C dec; **2**, 146−150 °C dec; **3**, 179−182 °C dec; **4**, 140−144 °C dec; **5**, 146−148 °C dec; **6**, 153−155 °C dec; **7**, 162−165 °C dec; **8**, 152−155 °C dec; **9**, 158−160 °C dec. Analyses: calcd (found) for **1**, C 58.46 (58.26), H 4.29 (4.54); **2**, C 48.33 (48.60), H 3.04 (3.09); **3**, C 60.60 (60.72), H 5.09 (5.34); **4**, C 71.35 (71.46), H 6.81 (6.42); **5**, C 66.43 (66.62), H 5.70 (5.73); **6**, C 73.37 (73.30), H 6.84 (6.76); **7**, C 52.69 (52.65), H 4.97 (5.02); **8**, C 44.32 (44.17), H 3.72 (3.75); **9**, C 55.04 (55.16), H 5.65 (5.87).

(5) Spectroscopic data: **1**, ^1H NMR ($CDCl_3$) δ 3.83 (m, 2H, CH_2), 4.23 (m, 2H, CH_2), 6.76−7.44 (m, 8H, Ph*H*), 8.38 (s, 2H, PhC*H*); IR (KBr) υ, 3040 w, 2974 w, 1647 s, 1550 s, 1477 s, 1340 s, 912 m, 756 s, 659 s cm^{-1}; **2**, IR (KBr) υ 3051 w, 2953 m, 2933 m, 1641 s, 1539 s, 1465 s, 1383 s, 1302 s, 850 s, 715 s cm^{-1}; **3**, IR (KBr) υ 3065 w, 2931 m, 1604 s, 1560 s, 1446 s, 1359 m, 1244 s, 877 m, 771 s, 665 s cm^{-1}; **4**, ^1H NMR (CD_3-OD) δ 3.28 (s (br), CH_3OH), 3.72 (s (br), 4H, CH_2CH_2), 4.78 (s (br), CH_3O*H*), 6.65−7.35 (m (br), 28H, Ph*H*), 8.31 (s (br), 2H, PhC*H*); IR (KBr) υ 3555 m, 3055 m, 2964 m, 1631 s, 1554 s, 1479 s, 1450 s, 1340 s, 1018 s, 734 s, 705 s cm^{-1}; **5**, ^1H NMR (CD_3OD) δ 3.26 (s (br), CH_3OH), 3.66 (m, 4H, CH_2CH_2), 4.78 (s, CH_3O*H*), 6.74−7.36 (m, 26H, Ph*H*), 8.19 (s, 2H, PhC*H*); IR (KBr) υ 3539 m, 3117 m (br), 3055 m, 2986 m, 1633 s, 1539m, 1465 s, 1384 s, 1028 m, 817 s, 709 s cm^{-1}; **6**, ^1H NMR (CD_3OD) δ 2.44 (m (br), 6H, CCH_3), 3.26 (m (br), CH_3OH), 3.69 (m (br), 4H, CH_2CH_2), 4.80 (m (br), CH_3O*H*), 6.65−7.39 (m (br), 28H, Ph*H*); IR (KBr) υ 3464 m, 3163 m (br), 3036 m, 2796 m, 1606 s, 1548 s, 1446 s, 1400 s, 1323 m, 748 s, 705 m cm^{-1}; **7**, IR (KBr) υ 3057 s (br) 1639 s, 1560 m, 1473 s, 1400 s, 1296 s, 814 m, 760 s cm^{-1}; **8**, IR (KBr) υ 3115 s (br), 1647 s, 1545 m, 1489 s, 1384 s, 1288 m, 817 m, 717 m cm^{-1}; **9**, IR (KBr) υ 3088 s (br), 1608 s, 1554 m, 1446 m, 1308 m, 1251 s, 748 s cm^{-1}.

(6) Crystal data: **6**, $C_{46}H_{54}AlBN_2O_6$, monoclinic, $P2_1/n$ (No. 14), a = 12.788(3) Å, b = 23.324(3) Å, c = 14.849(3) Å, β = 104.84(2)°, V = 4281.2(14) Å^3, Z = 4, with 505 parameters refined on 2009 reflections having $F > 4.0\sigma(F)$, R = 0.069 and R_w = 0.072; **7**, $C_{16}H_{20}AlClN_2O_4$, orthorhombic, $Pna2_1$ (No. 33), a = 7.462(2) Å, b = 15.810(4) Å, c = 13.866(3) Å, V = 1635.9(7) Å^3, Z = 4, with 214 parameters refined on 888 reflections having $F > 4.0\sigma(F)$, R = 0.058 and R_w = 0.063.

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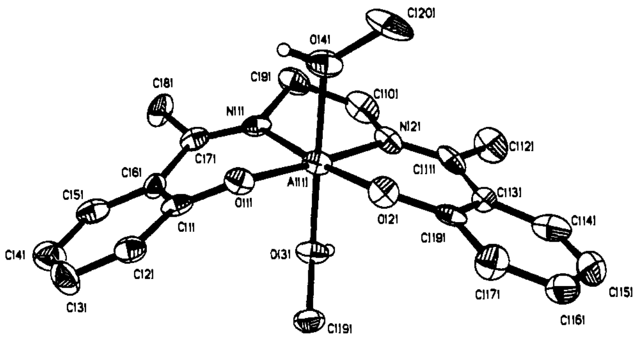

Figure 1. Molecular structure and atom numbering scheme for $[AcenAl(MeOH)_2]^+BPh_4^-$ (**6**). Selected bond distances (Å) and angles (deg): Al(1)−O(1) 1.806(8), Al(1)−O(2) 1.783(9), Al(1)−O(3) 1.945(8), Al(1)−O(4) 1.966(9), Al(1)−N(1) 1.997(11), Al(1)−N(2) 1.970(10); O(1)−Al(1)−O(2) 93.3(4), O(1)−Al(1)−O(3) 92.5(3), O(2)−Al(1)−O(3) 93.4(4), O(1)−Al(1)−O(4) 90.6(4), O(2)−Al(1)−O(4) 88.8(4), O(3)−Al(1)−O(4) 176.1(3), O(1)−Al(1)−N(1) 91.3(4), O(2)−Al(1)−N(1) 174.4(4), O(3)−Al(1)−N(1) 89.6(4), O(4)−Al(1)−N(1) 87.9(4), O(1)−Al(1)−N(2) 174.3(5), O(2)−Al(1)−N(2) 92.3(4), O(3)−Al(1)−N(2) 87.7(4), O(4)−Al(1)−N(2) 89.0(4), N(1)−Al(1)−N(2) 83.1(4).

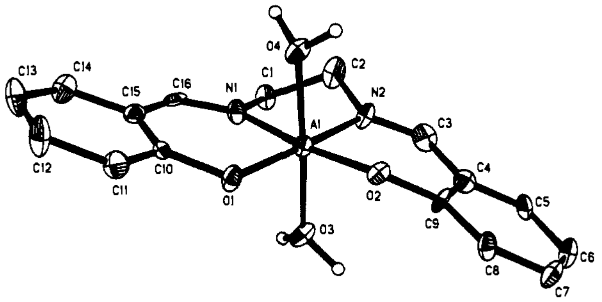

Figure 2. Molecular structure and atom numbering scheme for $[SalenAl(H_2O)_2]^+Cl^-$ (**7**). Selected bond distances (Å) and angles (deg): Al−O(1) 1.829(8), Al−O(2) 1.806(8), Al−O(3) 1.963(8), Al−O(4) 1.936(9), Al−N(1) 1.983(10), Al−N(2) 1.976(10); O(1)−Al(1)−O(2) 94.8(4), O(1)−Al(1)−O(3) 90.0(4), O(2)−Al(1)−O(3) 92.0(4), O(1)−Al(1)−O(4) 89.9(4), O(2)−Al(1)−O(4) 92.0(4), O(3)−Al(1)−O(4) 176.0(3), O(1)−Al(1)−N(1) 93.0(4), O(2)−Al(1)−N(1) 172.0(4), O(3)−Al(1)−N(1) 89.4(4), O(4)−Al(1)−N(1) 86.6(4), O(1)−Al(1)−N(2) 172.8(4), O(2)−Al(1)−N(2) 91.7(4), O(3)−Al(1)−N(2) 86.6(4), O(4)−Al(1)−N(2) 93.0(4), N(1)−Al(1)−N(2) 80.5(4).

generally form alkoxide complexes with aluminum reagents.[7] For example, the reaction of MeOH with $AlMe_3$ forms $[Me_2Al(OMe)]_3$.[8] Thus, alcohol adducts of aluminum, such as **4−6**, have been hitherto unknown. In relation to applications involving the coordination of an oxygen-containing substrate, it is important to note that complexes **4−9** may coordinate two such molecules.

The average Al−O (ligand) bond distances in **6** and **7** are 1.80 and 1.82 Å, respectively. These distances compare closely to the average values seen for the central five-coordinate aluminum atoms in $[(SalenAl)_2O]$ (1.82 Å)[9] and SalenAlEt (1.82 Å).[10] The same distances for the coordinating solvents in **6** and **7** are, as expected, somewhat longer (1.96 and 1.95 Å, respectively). These are similar to the Al−O donor bonds in representative examples, such as $Et_2O{\cdot}Al(benzyl)_3$ (1.90 Å)[11] and $THF{\cdot}Al(mesityl)_3$ (1.97 Å),[12] but somewhat longer than those found for donors containing carbonyl functionalities, such as $Ph_3P{=}O{\cdot}AlX_3$ (X = Cl (1.73 Å) and Br (1.74 Å)).[13] Additionally, the similarity of the Al−O (solvent) distances in **6** and **7** indicates that there is little or no steric effect between the ligand and solvent on going from H_2O to MeOH.

An attempted polymerization of propylene oxide (PPO) by compounds **4−9** was conducted on a vacuum line at ambient temperature and pressure. In a typical experiment, 15 mL of PPO was added to 0.5 g of the aluminum cation and then stirred for 12h. After removal of excess PPO under reduced pressure, a viscous yellow oil was obtained. Based upon an integration of the ^1H NMR and GC data, a polymeric material in the MW range of 750−1000 results for compounds **4−6**. However, compounds **7−9** did not polymerize PPO monomer under these conditions.

Compounds **4−9** represent a new class of aluminum cations which may be of importance to Lewis acid catalysis. In these complexes, the planarity of the ligand permits the coordination of two molecules of solvent, giving the central aluminum atoms a six-coordinate distorted octahedral geometry. This serves to indicate that current catalytic systems employing planar aluminum compounds may adopt a similar geometry. This would be relevant in polymerization mechanisms involving aluminum chloride complexes of Schiff bases and porphyrins. Preliminary results indicate that the MeOH-bound cations polymerize propylene oxide, while the H_2O-bound cations do not.

Acknowledgment. Gratitude is expressed to the National Science Foundation NSF-EPSCoR program (Grant RII-861075) and the NDSU Grant-in-Aid program for generous financial support.

Supplementary Material Available: Structure determination summaries, heavy atom and hydrogen atom coordinates, bond lengths and angles, anisotropic parameters, full atom labeling schemes, and unit cell views for **6** and **7** (25 pages); observed and calculated structure factors for **6** and **7** (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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