A New Class of Aluminum Cations Based upon Tetradentate (N_2O_2) Chelating Ligands

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Herein are described the synthesis and characterization of the complexes of formula LAlR (where R = Cl and L = Salen (**1**), SalenCl (**2**), Acen (**3**) and where R = Me and L = Salen (**4**), SalenCl (**5**), Acen (**6**); Salen = *N*,*N*′-ethylenebis((2-hydroxyphenyl)methylimine), SalenCl = *N*,*N*′-ethylenebis((2-hydroxy-5-chlorophenyl)methylimine), Acen = *N*,*N*′-ethylenebis((2-hydroxyphenyl)-1-ethylimine)). The LAlCl derivatives dissolve in water and MeOH to yield the cationic complexes $[LAl(H_2O)_2]^+Cl^-$ (L = Salen (**7**), SalenCl (**8**), Acen (**9**)) and $[LAl(MeOH)_2]^+Cl^-$ (L = Salen (**10**), SalenCl (**11**), Acen (**12**)), respectively. An alternative preparation of the cationic species involves the reaction of the LAlCl derivative with $NaBPh_4$. This leads to complexes of formula $[LAl(MeOH)_2]^+BPh_4^-$ (L = Salen (**13**), SalenCl (**14**), Acen (**15**)). Complexes **4**−**6** can be reacted with either MeOH or 4-chloro-3,5-dimethylphenol (Ph′) to form complexes of general formula LAlOR (R = Me, L = Salen (**16**), SalenCl (**17**), Acen (**18**); R = Ph′, L = Salen (**19**), SalenCl (**20**), Acen (**21**)). All of the compounds were characterized by IR, melting points, elemental analyses, and, when soluble, NMR. Additionally, the crystal structures of **7**, **13**, **15**, and **18** were obtained.

Introduction

Organometallic aluminum reagents are used widely in organic synthesis. Some transformations that can be achieved with these reagents include the reduction of ketones and aldehydes[1] and the "living" polymerization of oxiranes.[2] These reactions are facilitated by the fact that aluminum reagents are strong Lewis acids and, consequently, may form strong bonds to an oxygen-containing substrate such as an aldehyde, ketone, or oxirane. In order for the aluminum reagent to be effective, it must be coordinatively unsaturated. This has traditionally been accomplished through the use of nonpolar solvents. Unfortunately, low coordination numbers, combined with the inherent oxophilicity of aluminum, make these reagents both oxygen and moisture sensitive. More recently the use of a sterically congested three-coordinate aluminum center, as found for MeAl(2,6-di-*tert*-butylphenolate)$_2$[3] and MeAl(2,6-diphenylphenolate)$_2$,[4] was shown to be of great catalytic utility in the reduction of aldehydes. Alternatively, chelating ligands may be used which occupy five coordination sites but presumably leave the sixth site open for substrate coordination. Chelated examples include Schiff base−[2b−e] and porphyrin−AlCl complexes.[2e−g] Complexes of this genre are of demonstrated utility in the ring-opening ("living") polymerization of epoxides.

For applications in Lewis acid catalysis, the use of a cationic aluminum reagent would be ideal. Cations are naturally electron deficient and provide a strong electrostatic component to substrate coordination. However, such cations have not been available as a class of fully characterized molecules until recently when a preliminary report on the synthesis and structural characterization of air-stable, cationic aluminum complexes of general formula $[(\text{Schiff base})Al(solv)_2]^+X^-$ was published.[5] Depending on the nature of the solvent, these molecules were shown to effectively coordinate and polymerize propylene oxide. Thus, by judicious choice of solvent, these cations may behave as coordinatively unsaturated in the presence of a more basic substrate.

The present work will expand upon these initial studies and broaden the scope of the cationic aluminum complexes. The details of the polymerization of oxiranes with these cations will be published in a separate report. This paper, then, describes the synthesis and characterization of the complexes of formulas LAlR (R = Cl, L = Salen (**1**), SalenCl (**2**), Acen (**3**); R = Me, L = Salen (**4**), SalenCl (**5**), Acen (**6**)), $[LAl(H_2O)_2]^+Cl^-$, (L = Salen (**7**), SalenCl (**8**), Acen (**9**)), $[LAl(MeOH)_2]^+Cl^-$ (L = Salen (**10**), SalenCl (**11**), Acen (**12**)), $[LAl(MeOH)_2]^+BPh_4^-$ (L = Salen (**13**), SalenCl (**14**), Acen (**15**)), and LAlOR (R = Me, L = Salen (**16**), SalenCl (**17**), Acen (**18**); R = 4-chloro-3,5-dimethlyphenyl, L = Salen (**19**), SalenCl (**20**), Acen (**21**)) (Salen = *N*,*N*′-ethylenebis((2-hydroxyphenyl)methylimine), SalenCl = *N*,*N*′-ethylenebis((2-hydroxy-5-chlorophenyl)methylimine), Acen = *N*,*N*′-ethylenebis((2-hydroxyphenyl)-1-ethylimine)). All of the compounds were characterized by IR, melting points, elemental analyses, and, when soluble, NMR. Additionally, the crystal structures of **7**, **13**, **15**, and **18** were obtained.

Results and Discussion

Complexes **1**−**6** are prepared by combining the appropriate $SalenH_2$ ligand with either R_3Al or R_2AlCl (Scheme 1).[6] Upon addition of the aluminum reagent to the ligand, the complex begins precipitating immediately. This apparent insolubility

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(1) (a) *Selectivities in Lewis Acid Promoted Reactions*; Schinzer, D., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989. (b) Yamamoto, H. In *Organometallics in Synthesis*; Schlosser, M., Ed.; John Wiley & Sons Ltd.: West Sussex, England, 1994; Chapter 7.

(2) (a) Vandenberg, E. J. *J. Polym. Sci., Part A-1* **1969**, *7*, 525. (b) Jun, C. L.; Le Borgne, A.; Spassky, N. *J. Polym. Sci., Polym. Symp*. **1986**, *74*, 31. (c) Vincens, V.; Le Borgne, A.; Spassky, N. *Makromol. Chem. Rapid Commun*. **1989**, *10*, 623. (d) Le Borgne, A.; Vincens, V.; Jouglard, M.; Spassky, N. *Makromol. Chem. Macromol. Symp*. **1993**, *73*, 37. (e) Sugimoto, H.; Kawamura, C.; Kuroki, M.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 2013. (f) Aida, T.; Mizutta, R.; Yoshida, Y.; Inoue, S. *Makromol. Chem*. **1981**, *182*, 1073. (g) Shimasaki, K.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 3076. (h) Asano, S.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun*. **1985**, 1148.

(3) (a) Maruoka, K.; Nagahara, S.; Yamamoto, H. *J. Am. Chem. Soc*. **1990**, *112*, 6115. (b) Maruoka, K.; Nagahara, S.; Yamamoto, H. *Tetrahedron Lett*. **1990**, *31*, 5475.

(4) Maruoka, K.; Concepcion, A. B.; Murase, N.; Oishi, M.; Hirayama, N.; Yamamoto, H. *J. Am. Chem. Soc*. **1993**, *115*, 3943.

(5) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *J. Am. Chem. Soc*. **1995**, *117*, 6779.

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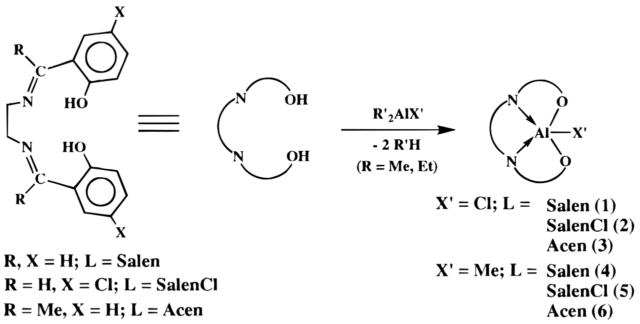
Scheme 1. Synthesis of **1**−**6**



leads to reasonable yields of the product in the range 70−96%, although subsequent redissolution in NMR solvents is problematic (vide infra). Neither the chloride nor the methyl derivatives are air or moisture sensitive. The reaction shown in Scheme 1 is very similar to that used to prepare SalenAlEt. This product was shown by X-ray crystallography to consist of a monomeric complex in which the Al atom is in a square-pyramidal geometry.[7] An analogous structure may be inferred for **4**−**6**. No structural information is available for the chloride derivatives (**1**−**3**). Indeed, on the basis of traditional alkyl group 13 halide chemistry, a chloride-bridged dimer would be expected to result.[8] Such dimerization is motivated by a tendency for aluminum to take a coordination number of 4, or higher. In **1**−**3** the aluminum may be considered to have a saturated coordination sphere, and thus, in the absence of steric and electronic factors, a monomeric structure may be envisioned. Indeed, this type of formulation is observed for structurally characterized porphyrin−MCl complexes (where M = Ga[9] and In[10]).

Dissolution of **1**−**3** in water leads to dissociation of the chloride anion from the aluminum center and the consequent formation of the cationic dihydrate derivatives, **7**−**9** (Scheme 2a). This conversion is essentially quantitative, and the complexes are indefinitely stable in water and air. The infrared data display a broad resonance in the range 3024−3115 cm^{-1}, which can be attributed to the bound H_2O groups. The elemental analyses also confirm that there are two molecules of water present in the sample.

An X-ray crystallographic study of **7** indicates that the H_2O groups occupy the axial positions of an octahedral coordination environment around Al with an O−Al−O′ angle of 176.0(3)°. The molecular structure and atom-numbering scheme of the cation are shown in Figure 1. Selected bond distances and angles can be found in Table 3. There are no close intermolecular contacts between the cation and the chloride ion. The Salen ligand adopts a planar geometry (maximum deviation 0.041 Å for O2) and occupies the equatorial positions around the central aluminum atom. The most significant deviation from O_h geometry is found for the N1−Al−N2 angle (80.5°) and represents the constraints imposed by the ethylenediimino backbone of the ligand. This also may contribute to the widened O1−Al−O2 angle (94.8(3)°).

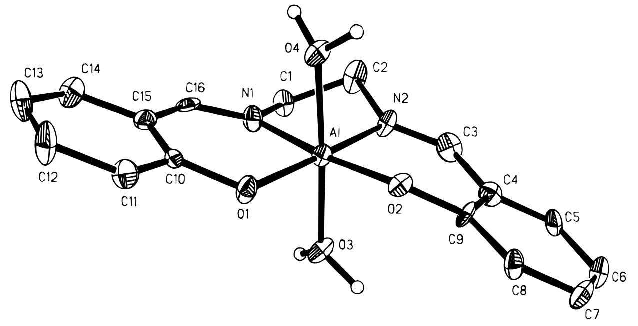
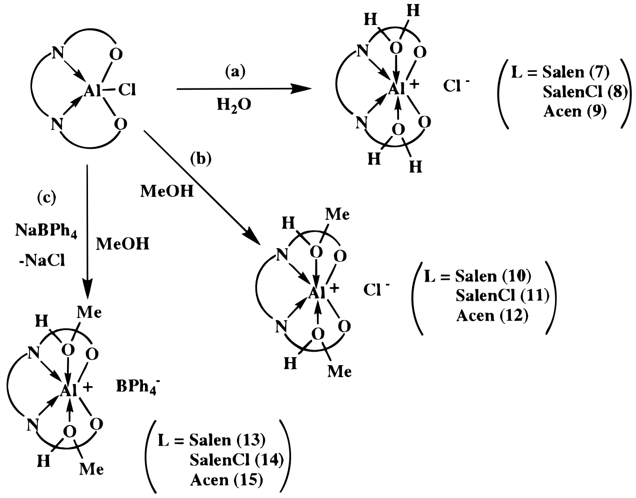


Figure 1. Molecular structure and atom-numbering scheme for $[SalenAl(H_2O)_2]^+$ (**7**).

Scheme 2. Syntheses of the Cationic Aluminum Complexes **7**−**15**



The Al−O distances to the salen ligand (average 1.82 Å) are somewhat shorter than those to the coordinating water molecules (average 1.95 Å), in keeping with the differences in bond length on going from covalent to coordinate covalent bonding. Structurally characterized complexes of aluminum with water are extremely rare. The Al−O bond distances in structurally characterized inorganic examples such as $[Al(H_2O)_6{}^{3+}][IO_3{}^-]_2[HI_2O_6{}^-]\cdot HIO_3$ and $[Al(H_2O)_6{}^{3+}][NO_3{}^-]_3\cdot 3H_2O$ (average 1.88 Å)[11,12] are only marginally shorter than those found for **7**.

The chloride groups in **1**−**3** can also be displaced by the relatively weak base MeOH. Thus, complexes **10**−**12** form when **1**−**3** are dissolved in MeOH at ambient temperature. Fortunately, these complexes demonstrate solubility in MeOH and are amenable to study by NMR techniques. Such ^1H NMR data are given in Table 1. The ligand ethyl group for **10**−**12** is manifested as a singlet in the range δ 3.94−3.97 ppm. The presence of a broad singlet for this group is significant, as it has previously been shown that aluminum[13] and gallium[14]

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(6) The synthesis of compound **4** and a wide range of other Salen-AlOR complexes has been reported previously: Gurian, P. L.; Cheatham, L. K.; Ziller, J. W.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1991**, 1449.

(7) Dzugan, S. L.; Goedken, V. L. *Inorg. Chem.* **1986**, *25*, 2858.

(8) See, for example, the structures of $[R_2GaCl]_2$ for R = Me_5C_5 (Beachley, O. T., Jr.; Hallock, R. B.; Zhang, H. M.; Atwood, J. L. *Organometallics* **1985**, *4*, 1675) and *t*-Bu (Atwood, D. A.; Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Atwood, J. L.; Bott, S. G. *J. Coord. Chem.* **1992**, *25*, 233).

(9) Kadish, K. M.; Boisselier-Cocolios, B.; Coutsolelos, A.; Mitaine, P.; Guilard, R. *Inorg. Chem.* **1985**, *24*, 4521.

(10) Cocolios, P.; Moise, C.; Guilard, R. *J. Organomet. Chem.* **1982**, *228*, C43.

(11) Cradwick, P. S.; de Endredy, A. S. *J. Chem. Soc., Dalton Trans.* **1977**, 146.

(12) In order to provide a direct comparison of Al−OH_2 distances with compound **7**, the crystal structure of $[Al(H_2O)_6{}^{3+}][NO_3{}^-]_3\cdot 3H_2O$ was determined: space group monoclinic $P2_1/c$ with $a = 13.872(1)$ Å, $b = 9.643(1)$ Å, $c = 10.906(1)$ Å, $\beta = 95.68(1)°$, $V = 1451.6(2)$ Å^3, and Z = 4. There were 1528 observed reflections with $F > 4.0\sigma(F)$ refined on 202 parameters resulting in $R = 0.037$, $R_w = 0.035$, and GOF = 1.06.

(13) Atwood, D. A.; Jegier, J. A.; Martin, K. J.; Rutherford, D. *Organometallics* **1995**, *14*, 1453.

(14) (a) Atwood, D. A.; Rutherford, D. *Organometallics* **1995**, *14*, 2880. (b) *Ibid.* **1995**, *14*, 3988.

Table 1. ^{1}H NMR Data for Compounds **1**, **4−6**, **10−16**, and **18−21**[a]

compound	CH_2CH_2	Ph*H*	PhC*H*	PhCH_3	other
SalenAlCl (**1**)	3.83 (m)	6.76−7.44 (m)	8.38 (s)		
	4.23 (m)				AlCH_3
SalenAlMe (**4**)	3.66 (m)	6.69−7.36 (m)	8.21 (s)		−1.06 (s)
	3.98 (m)				
SalenClAlMe (**5**)	3.75 (m)	7.00−7.32 (m)	8.22 (s)		−1.07 (s)
	4.08 (m)				
AcenAlMe (**6**)	3.79 (m)	6.66−7.49 (m)		2.46 (m)	−1.15 (s)
					CH_3OH
[SalenAl(MeOH)$_2$]Cl (**10**)	3.94 (s)	6.74−7.43 (m)	8.55 (s)		3.26 (s), 4.85 (s (br))
[SalenClAl(MeOH)$_2$]Cl (**11**)	3.97 (s)	6.91 (d)	8.55		3.26 (s), 4.85 (s (br))
		7.33−7.43 (m)			
[AcenAl(MeOH)$_2$]Cl (**12**)	3.95 (s)	6.71−7.73 (m)		2.58 (s)	3.26 (s), 4.88 (s (br))
[SalenAl(MeOH)$_2$]BPh$_4$ (**13**)	3.72 (s (br))	6.65−7.35 (m)	8.31 (s (br))		3.28 (s), 4.78 (s (br))
[SalenClAl(MeOH)$_2$]BPh$_4$ (**14**)	3.66 (s)	6.74−7.36 (m)	8.19 (s)		3.26 (s), 4.78 (s (br))
[AcenAl(MeOH)$_2$]BPh$_4$ (**15**)	3.69 (m (br))	6.65−7.39 (m)		2.44 (m (br))	3.26 (s), 4.80 (s (br))
					OCH_3
[SalenAlOMe]$_2$ (**16**)	3.08−4.19 (m)	6.51−7.48 (m)	8.11 (s (br))		2.93 (s)
[AcenAlOMe]$_2$ (**18**)	3.11−3.89 (m)	6.4−7.52 (m)		2.24 (s), 2.36 (s)	2.82 (s)
					PhCH_3
SalenAlOC$_6$H$_2$(CH$_3$)$_2$Cl (**19**)	3.68 (m)	6.18 (s, Ph′)	8.28 (s)		2.00 (s)
	4.00 (m)	7.16−7.38 (m)			
SalenClAlOC$_6$H$_2$(CH$_3$)$_2$Cl (**20**)	3.78 (m)	6.20 (s, Ph′)	8.30 (s)		2.00 (s)
	4.09 (m)	7.07−7.41			
AcenAlOC$_6$H$_2$(CH$_3$)$_2$Cl (**21**)	3.81 (m)	6.13 (s, Ph′)		2.42 (s)	2.02 (s)
		6.73−7.50 (m)			

[a] Compounds **2**, **3**, **7−9**, and **17** are insoluble.

Table 2. Crystal Data for [SalenAl(H$_2$O)$_2$]Cl (**7**), [SalenAl(MeOH)$_2$]BPh$_4$ (**13**), [AcenAl(MeOH)$_2$]BPh$_4$ (**15**), and 2[AcenAlOMe]$_2$·7MeOH (**18**)

compound	**7**	**13**	**15**	**18**
formula	$C_{16}H_{20}AlN_2O_4$	$C_{43}H_{46}AlBN_2O_5$	$C_{46}H_{54}AlBN_2O$	$C_{41.5}H_{56}Al_2N_4O_{9.5}$
fw	366.8	708.6	768.7	1633.7
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Pna*2$_1$	*P*2$_1$/*n*	*P*2$_1$/*n*	*P*2$_1$/*c*
a (Å)	7.462(2)	10.751(1)	12.788(3)	17.497(3)
b (Å)	15.810(4)	22.518(2)	23.324(3)	22.098(3)
c (Å)	13.866(3)	15.637(2)	14.849(3)	22.066(2)
β (deg)		95.60(1)	104.84(2)	99.27(1)
V (Å^3)	1635.9(7)	3767.7(7)	4281.2(14)	8420(2)
Z	4	4	4	4
D_{calc} (g/cm^3)	1.489	1.249	1.193	1.289
crystal size (mm)	0.4^3	0.2 × 0.6 × 0.6	0.8 × 0.6 × 0.4	1.0 × 0.5 × 0.4
temp (K)	298	298	298	298
2θ range (deg)	3.5−45	2.0−45	2.0−45	3.5−45
scan type	$2\theta-\theta$	$2\theta-\theta$	$2\theta-\theta$	$2\theta-\theta$
scan speed (deg/min)	8−60	8−60	8−60	8−60
scan range (deg)	0.50	0.40	0.40	0.50
no. of reflns collected	1416	6222	6849	13 051
no. of indp reflns	1118	4932	5578	11 005
no. of obsd reflns ($F > X\sigma(F)$)	888	2768	2009	6011
x	4.0	6.0	4.0	4.0
no. of params	214	469	505	1027
R	0.0576	0.0483	0.0686	0.0724
R_w	0.0631	0.0493	0.0723	0.0732
GOF	2.06	1.67	3.49	4.20
largest diff peak (e/Å^3)	0.40	0.22	0.29	0.56

complexes of hydrogenated Salen (Salan) can adopt a rigid solution state geometry. This geometry is manifested in AB coupling of protons on the same carbon atom. For instance, the ethylenediimino backbone protons would be manifested as a doublet of doublets. Thus, the appearance of a singlet for the backbones of **10−12** may imply the presence of a fluxional process such as the rapid exchange of MeOH with CD_3OD. The ability for the coordinating solvents on these cations to freely dissociate will have important ramifications in the potential use of these molecules as catalysts. The hydrogens on the methanol molecules appear as a moderately broad single resonance at 3406−3426 cm^{-1} in the infrared spectra.

An alternative route to cationic complexes involves the reaction of the LAlCl derivatives with NaBPh$_4$ (Scheme 2c). This reaction yields complexes **13−15** which consist of separate aluminum cations and borate anions. The infrared data confirm the presence of coordinating MeOH with O−H absorbances in the range 3464−3555 cm^{-1}. The elemental analyses are also correct when these molecules are included in the calculation (along with the solvents that are hydrogen-bonded to these in a second-sphere coordination (see below)). This also indicates that the MeOH groups cannot be removed under the reduced pressure (10^{-4} Torr) experienced during sample preparation. As was the case for **10−12**, these complexes also manifest a singlet for the ethylene backbone of the ligand in the ^{1}H NMR.

The six-coordinate geometry implied by the spectroscopic data is confirmed for **13** and **15** by X-ray analysis. The molecular structures and atom-numbering schemes for these two

Table 3. Bond Lengths (Å) and Angles (deg) for $[\mathrm{SalenAl(H_2O)_2}]\mathrm{Cl}$ (**7**), $[\mathrm{SalenAl(MeOH)_2}]\mathrm{BPh_4}$ (**13**), and $[\mathrm{AcenAl(MeOH)_2}]\mathrm{BPh_4}$ (**15**)

	7	**13**	**15**
Distances			
Al−O(1)	1.829(8)	1.808(3)	1.806(8)
Al−O(2)	1.806(8)	1.797(4)	1.783(9)
Al−O(3)	1.963(8)	2.002(3)	1.945(8)
Al−O(4)	1.936(9)	1.975(4)	1.966(9)
Al−N(1)	1.983(10)	1.981(4)	1.997(11)
Al−N(2)	1.976(10)	1.982(4)	1.970(10)
O(1)−Ph	1.366(15)	1.333(6)	1.327(15)
O(2)−Ph	1.345(15)	1.330(6)	1.309(17)
N(1)−$\mathrm{CH_2CH_2}$	1.465(14)	1.470(6)	1.467(15)
N(1)−$\mathrm{CH_2Ph}$	1.273(18)	1.291(7)	1.289(17)
N(2)−$\mathrm{CH_2CH_2}$	1.486(15)	1.476(6)	1.481(16)
N(2)−$\mathrm{CH_2Ph}$	1.288(18)	1.282(7)	1.310(19)
Angles			
O(1)−Al−O(2)	94.8(3)	92.3(2)	93.3(4)
O(1)−Al−O(3)	90.0(4)	92.5(2)	92.5(3)
O(2)−Al−O(3)	92.0(4)	91.4(1)	93.4(4)
O(1)−Al−O(4)	89.9(4)	91.8(2)	90.6(4)
O(2)−Al−O(4)	92.0(4)	88.3(2)	88.8(4)
O(3)−Al−O(4)	176.0(3)	175.8(2)	176.1(3)
O(1)−Al−N(1)	93.0(4)	93.2(2)	91.3(4)
O(2)−Al−N(1)	172.0(4)	174.3(2)	174.4(4)
O(3)−Al−N(1)	89.4(4)	87.4(2)	89.6(4)
O(4)−Al−N(1)	86.6(4)	92.5(2)	87.9(4)
O(1)−Al−N(2)	172.8(4)	174.5(2)	174.3(5)
O(2)−Al−N(2)	91.7(4)	92.8(2)	92.3(4)
O(3)−Al−N(2)	86.6(4)	85.6(2)	87.7(4)
O(4)−Al−N(2)	93.0(4)	90.3(2)	89.0(4)
N(1)−Al−N(2)	80.5(4)	81.6(2)	83.1(4)

Table 4. Positional Parameters ($\times 10^5$) and Equivalent Isotropic Thermal Parameters for $[\mathrm{SalenAl(H_2O)_2}]\mathrm{Cl}$ (**7**)

atom	*x*	*y*	*z*	*U*(eq) (Å^2)
Al	1764	3505	1158	23(1)
Cl	3190(5)	5152(2)	−3081(4)	51(1)
O(1)	1195(13)	2873(5)	2218(6)	33(3)
O(2)	1973(12)	2608(5)	359(6)	26(3)
O(3)	−793(11)	3632(4)	859(7)	32(3)
O(4)	4273(12)	3451(5)	1508(7)	33(3)
N(1)	1682(16)	4584(5)	1886(9)	31(4)
N(2)	2212(16)	4306(6)	90(8)	31(4)
C(1)	1663(20)	5353(6)	1298(9)	32(4)
C(2)	2757(22)	5170(7)	395(10)	43(5)
C(3)	1927(23)	4125(8)	−802(11)	41(6)
C(4)	1465(20)	3301(7)	−1175(10)	32(5)
C(5)	992(20)	3224(9)	−2128(10)	38(5)
C(6)	521(21)	2445(9)	−2516(10)	46(5)
C(7)	575(22)	1741(9)	−1950(11)	43(6)
C(8)	1087(21)	1781(7)	−983(10)	32(5)
C(9)	1472(19)	2575(8)	−572(9)	30(5)
C(10)	1564(17)	3077(8)	3155(9)	25(4)
C(11)	1602(20)	2422(9)	3816(9)	38(5)
C(12)	1961(25)	2600(9)	4778(9)	50(6)
C(13)	2238(23)	3418(9)	5077(11)	54(6)
C(14)	2122(22)	4069(8)	4423(10)	42(5)
C(15)	1794(19)	3905(8)	3454(10)	28(4)
C(16)	1796(18)	4618(7)	2802(10)	29(5)

molecules are shown in Figures 2 and 3, respectively. Selected bond lengths and angles are located in Table 3. Each molecule adopts a distorted octahedral geometry and both are of the same morphology as **7**. Thus, the coordinated solvents occupy axial positions while the ligand occupies the equatorial sites. The largest deviation from 90° for the equatorial groups occurs for the N1−Al−N2 angles which are 81.5(2) and 83.1(4)° for **13** and **15**, respectively. This angle for **7** was 80.5(4)°.

The average Al−O(ligand) bond distances in **7**, **13**, and **15** are 1.82, 1.80, and 1.80 Å, respectively. These distances compare closely to the average values seen for the central five-coordinate aluminum atoms in $[\mathrm{(SalenAl)_2O}]$ (1.82 Å)[6] and SalenAlEt (1.82 Å).[7] The same distances for the coordinating solvents in **7**, **13**, and **15** are somewhat longer (average 1.95, 1.99, and 1.96 Å, respectively). These are similar to the Al−O donor bond distances in representative examples such as $\mathrm{Et_2O{\rightarrow}Al(Bzyl)_3}$ (1.90 Å)[15] and $\mathrm{THF{\rightarrow}Al(mesityl)_3}$ (1.97 Å)[16]

Table 5. Positional Parameters ($\times 10^5$) and Equivalent Isotropic Thermal Parameters for $[\mathrm{SalenAl(MeOH)_2}]\mathrm{BPh_4}$ (**13**)[a]

atom	*x*	*y*	*z*	*U*(eq) (Å^2)
Al	1680(2)	4767(1)	1048(1)	44(1)
O(1)	1845(3)	4793(1)	−91(2)	48(1)
O(2)	1004(3)	5497(1)	1038(2)	48(1)
O(3)	3395(3)	5099(1)	1349(2)	46(1)
O(4)	−28(3)	4441(2)	843(3)	73(2)
O(5)	4582(4)	5205(2)	2916(3)	91(2)
N(1)	2435(4)	3967(2)	1185(3)	47(2)
N(2)	1621(4)	4679(2)	2305(3)	46(2)
C(1)	2140(4)	4364(2)	−624(3)	40(2)
C(2)	2026(4)	4474(2)	−1504(3)	44(2)
C(3)	2328(5)	4048(2)	−2084(3)	57(2)
C(4)	2767(5)	3498(2)	−1798(3)	61(2)
C(5)	2883(5)	3378(2)	−936(3)	54(2)
C(6)	2566(4)	3803(2)	−334(3)	43(2)
C(7)	2724(4)	3639(2)	556(3)	48(2)
C(8)	2754(5)	3775(2)	2078(3)	57(2)
C(9)	1865(5)	4073(2)	2641(3)	58(2)
C(10)	1530(4)	5118(2)	2817(3)	50(2)
C(11)	1301(4)	5727(2)	2544(3)	46(2)
C(12)	1345(5)	6161(3)	3182(3)	62(2)
C(13)	1134(6)	6745(3)	2985(4)	74(3)
C(14)	858(5)	6906(3)	2132(4)	67(2)
C(15)	812(5)	6488(2)	1488(3)	56(2)
C(16)	1042(4)	5888(2)	1678(3)	44(2)
C(17)	3950(5)	5562(3)	882(3)	73(2)
C(18)	−615(5)	3916(3)	960(4)	75(3)
C(19)	4718(7)	5788(4)	3244(4)	110(4)

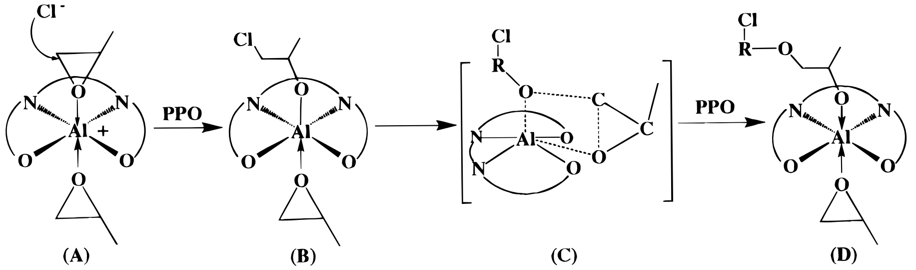
[a] The coordinates of the $\mathrm{BPh_4^-}$ group are located in the Supporting Information.

Table 6. Positional Parameters ($\times 10^5$) and Equivalent Isotropic Thermal Parameters ($\times 10^4$) for $[\mathrm{AcenAl(MeOH)_2}]\mathrm{BPh_4}$ (**15**)[a]

atom	*x*	*y*	*z*	*U*(eq) (Å^2)
Al(1)	20090(30)	57040(15)	12028(23)	388(13)
O(1)	6654(61)	60025(31)	8133(50)	414(32)
O(2)	23266(68)	58446(33)	1228(49)	464(34)
O(3)	26134(59)	64271(30)	17516(46)	423(30)
O(4)	14640(68)	49465(34)	7213(53)	560(36)
O(5)	37357(68)	65244(39)	34969(55)	614(38)
O(6)	230(97)	43027(49)	11251(64)	1072(56)
N(1)	17404(81)	54772(39)	24209(61)	392(40)
N(2)	34361(81)	53561(40)	17415(65)	428(42)
C(1)	1676(95)	62868(49)	13568(75)	361(46)
C(2)	−5809(98)	66961(51)	9513(84)	447(50)
C(3)	−11436(105)	70217(56)	14366(104)	608(64)
C(4)	−9790(116)	69115(58)	23842(102)	634(68)
C(5)	−2698(109)	64842(54)	28190(91)	553(57)
C(6)	2986(93)	61687(49)	22929(79)	374(48)
C(7)	10251(95)	56964(53)	27930(78)	422(49)
C(8)	9001(98)	54861(56)	37231(78)	631(61)
C(9)	24427(109)	49948(53)	28213(91)	589(59)
C(10)	35479(109)	50767(58)	26570(85)	635(62)
C(11)	43113(111)	54066(52)	14439(82)	474(55)
C(12)	53739(102)	51674(59)	19871(91)	751(67)
C(13)	42473(104)	57051(51)	5582(85)	420(51)
C(14)	52239(128)	58116(56)	3081(112)	713(72)
C(15)	52384(129)	60779(62)	−4999(124)	778(80)
C(16)	42833(143)	62822(59)	−10983(107)	720(73)
C(17)	33409(115)	62013(58)	−8749(90)	602(64)
C(18)	32696(111)	59068(46)	−589(83)	405(53)
C(19)	24843(102)	69732(46)	13110(81)	529(55)
C(45)	31595(112)	68306(62)	40329(94)	799(72)
C(46)	−4289(121)	43445(66)	18708(117)	973(85)

[a] The coordinates of the $\mathrm{BPh_4^-}$ group are located in the Supporting Information.

Scheme 3. Proposed Mechanism of Propylene Oxide Oligomerization



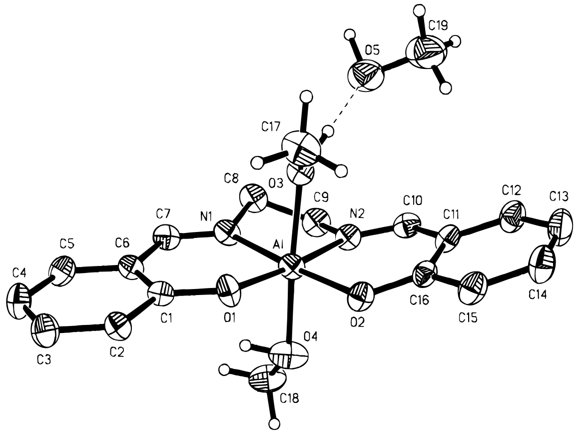


Figure 2. Molecular structure and atom-numbering scheme for $[SalenAl(MeOH)_2]^+ \cdot MeOH$ (**13**).

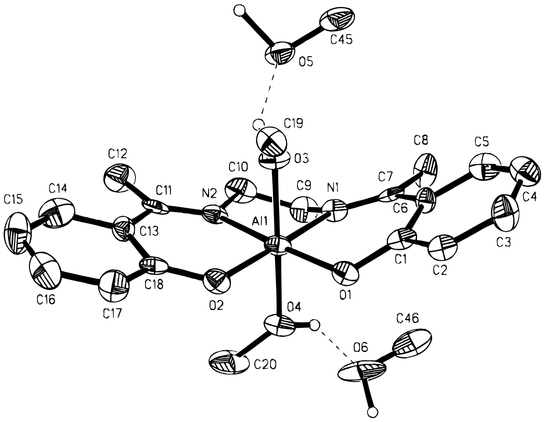


Figure 3. Molecular structure and atom-numbering scheme for $[AcenAl(MeOH)_2]^+ \cdot 2MeOH$ (**15**).

but somewhat longer than those found for donors containing phosphine oxide functionalities such as $Ph_3P{=}O{\rightarrow}AlX_3$ (where X = Cl (1.73 Å) and Br (1.74 Å)).[17] On the basis of this comparison of the bond distances and bond angles (Table 3) for **7**, **13**, and **15**, one may conclude that there is very little change at the aluminum center as a result of changes in the coordinated solvent, ligand, and counteranion.

Compounds **13**, **15**, and **18** (see below) possess solvents of crystallization in their unit cells. For **13** and **15**, these solvent molecules are within bonding distance (<3.2 Å) of the groups coordinated to the aluminum cation. Thus, for **13**, a third MeOH molecule is hydrogen-bonded to the coordinated solvent at a distance of 1.50 Å (O5---H). In **15**, each of the coordinated solvents is hydrogen-bonded to an additional MeOH group in the second coordination sphere (four total MeOH groups). These distances are 1.77 Å (H46---O5) and 1.919 Å (H47---O6). Nevertheless, there is still only a single peak in the IR spectra (3555 and 3464 cm^{-1}) which can be attributed to the MeOH groups in **13** and **15**, respectively. Additionally, the Al−O(solvent) bond distances do not appear lengthened.

The relative ease with which the counteranion (Cl$^-$) dissociates for **7**−**12** may serve to indicate that a similar process is occurring in the reported Lewis acid catalyses with Schiff base−AlCl complexes.[2b−e] Thus, the catalytically active species in all Schiff base−aluminum complexes may well be an aluminum cation. The polymerization of propylene oxide (PPO) for example, may be envisioned to proceed as follows. One of the two coordinated substrates is activated by the counter anion (Scheme 3A). (This step has been confirmed in reactions of (TPP)AlCl with 1 equiv of PPO which, after hydrolysis, yields 1-chloro-2-propanol (Scheme 3B).[2f]) Subsequently, each additional PPO group is added to the Al−O bond through a four-centered intermediate (Scheme 3C), resulting in a lengthening of the polyether (Scheme 3D). A similar type of mechanism has been postulated to occur for the polymerization of propylene with $[Cp_2ZrMe^+][MAO^-]$.[18]

When **4**−**6** are dissolved in MeOH, an alkane elimination occurs, resulting in the formation of the methoxy species **16**−**18**. These complexes are indefinitely stable in air and water. The ^1H NMR data for **16** and **18** display multiplets across the ranges δ 3.08−4.19 and 3.11−3.89 ppm, respectively. The PhCH resonance for **16** is a very broad singlet centered at δ 8.11 ppm, while two resonances are manifested for the PhCMe groups at δ 2.24 and 2.36 ppm. This indicates that these complexes may exist as methoxy-bridged dimers. This would also follow the precedent established for other alkoxy-bridged group 13 complexes.[19] This supposition is confirmed in the solid state for **18**.

As determined by X-ray crystallography, **18** adopts a methoxy-bridged dimeric structure. In this structure, there are two independent dimers in the unit cell. These two molecules are essentially identical, so only one representative molecule will be described here. The molecular structure and atom-numbering scheme for this molecule are shown in Figure 4. Selected bond distances and angles can be found in Table 7. In the structure, the Al_2O_2 four-membered ring is planar with somewhat widened Al−O−Al′ angles (103°) compared to the O−Al−O′ angles (77°). The disparity in these angles can be attributed to the sterically encumbered nature of the molecule. The Al−O distances are actually somewhat longer than usual ((average) = 1.90 Å). This may be compared to the same distances in $[Me_2AlOMe]_3$ (Al−O = 1.851(3) Å) for which the bridging

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(15) Srini, V.; de Mel, J.; Oliver, J. P. *Organometallics* **1989**, *8*, 2312.

(16) Rahman, A. F. M.; Siddiqui, K. F.; Oliver, J. P. *J. Organomet. Chem.* **1987**, *319*, 161.

(17) Burford, N.; Royan, B. W.; Spence, R. E.; Cameron, T. S.; Linden, A.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **1990**, 1521.

(18) For a recent review on metallocene-based Ziegler−Natta catalysis see: Mohring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1.

(19) Oliver, J. P.; Kumar, R.; Taghiof, M. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH Publishers, Inc.; New York, 1993; p 167.

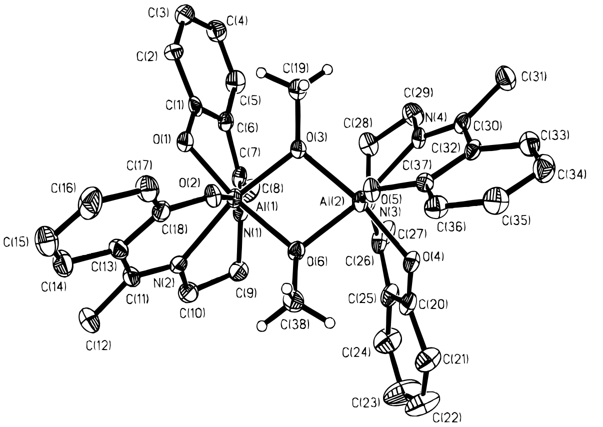


Figure 4. Molecular structure and atom-numbering scheme for [AcenAlOMe]$_2$ (**18**).

Table 7. Bond Lengths (Å) and Angles (deg) for One Molecule of [AcenAlOMe]$_2$ (**18**)

Distances					
Al(1)−Al(2)	2.968(3)	Al(1)−O(6)	1.910(5)	Al(2)−O(5)	1.813(5)
Al(1)−O(1)	1.840(6)	Al(1)−N(1)	2.038(7)	Al(2)−O(6)	1.885(5)
Al(1)−O(2)	1.818(5)	Al(1)−N(2)	2.058(6)	Al(2)−N(3)	2.046(6)
Al(1)−O(3)	1.883(4)	Al(2)−O(3)	1.908(5)	Al(2)−N(4)	2.052(5)
		Al(2)−O(4)	1.844 (6)		

Angles			
Al(2)−Al(1)−O(1)	133.2(2)	Al(1)−Al(2)−O(3)	38.2(1)
Al(2)−Al(1)−O(2)	99.4(2)	Al(1)−Al(2)−O(4)	132.5(2)
O(1)−Al(1)−O(2)	93.1(2)	O(3)−Al(2)−O(4)	169.5(2)
Al(2)−Al(1)−O(3)	38.8(2)	Al(1)−Al(2)−O(5)	99.4(2)
O(1)−Al(1)−O(3)	94.9(2)	O(3)−Al(2)−O(5)	94.7(2)
O(2)−Al(1)−O(3)	98.9(2)	O(4)−Al(2)−O(5)	91.8(2)
Al(2)−Al(1)−O(6)	38.3(1)	Al(1)−Al(2)−O(6)	38.9(2)
O(1)−Al(1)−O(6)	169.6(2)	O(3)−Al(2)−O(6)	77.1(2)
O(2)−Al(1)−O(6)	94.6(2)	O(4)−Al(2)−O(6)	93.9(2)
O(3)−Al(1)−O(6)	77.0(2)	O(5)−Al(2)−O(6)	98.8(2)
Al(2)−Al(1)−N(1)	91.5(2)	Al(1)−Al(2)−N(3)	93.7(2)
O(1)−Al(1)−N(1)	85.1(2)	O(3)−Al(2)−N(3)	90.1(2)
O(2)−Al(1)−N(1)	166.4(2)	O(4)−Al(2)−N(3)	85.7(3)
O(3)−Al(1)−N(1)	94.6(2)	O(5)−Al(2)−N(3)	164.3(2)
O(6)−Al(1)−N(1)	89.0(2)	O(6)−Al(2)−N(3)	96.9(2)
Al(2)−Al(1)−N(2)	129.8(2)	Al(1)−Al(2)−N(4)	130.7(2)
O(1)−Al(1)−N(2)	95.2(2)	O(3)−Al(2)−N(4)	93.0(2)
O(2)−Al(1)−N(2)	88.5(2)	O(4)−Al(2)−N(4)	95.4(2)
O(3)−Al(1)−N(2)	167.1(3)	O(5)−Al(2)−N(4)	88.2(2)
O(6)−Al(1)−N(2)	92.0(2)	O(6)−Al(2)−N(4)	168.2(3)
N(1)−Al(1)−N(2)	78.2(2)	N(3)−Al(2)−N(4)	76.6(2)

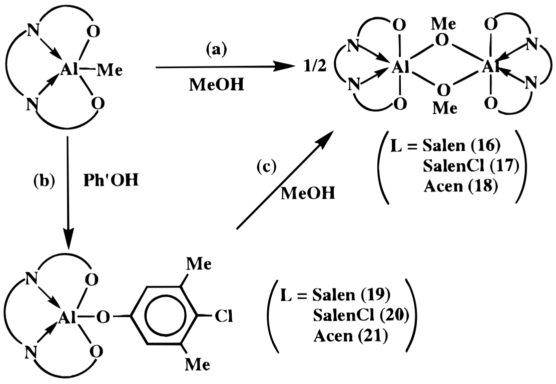
oxygen atoms adopt distorted tetrahedral geometries.[20] Additionally, the shortest intramolecular contacts between the methanol hydrogens and the ligand are 2.43 Å (H38A−C20) and 2.60 Å (H19A−C1). These short distances are indicative of a very sterically crowded complex despite the relatively small steric requirements of the methoxy substituent. The methoxy groups and the ligand amine backbones adopt a cis configuration in which steric repulsions are minimized. It is evident that the use of more bulky groups in these systems will lead to the formation of monomeric species.

In fact, the use of mesityl alcohol does result in a monomeric species. For example, the complex SalenAlO(Mes) is monomeric as determined by X-ray crystallography.[6] In the present study the synthesis of LAl(OPh′) (where Ph′ = 5-chloro-4,6-dimethylphenol) proceeds as described in Scheme 4b. By analogy to SalenAlO(Mes), compounds **19**−**21** are proposed to be monomeric. Additionally, each of these complexes can be converted to its OMe analog by dissolution in MeOH (Scheme 4c).

Table 8. Positional Parameters (×10^5) and Equivalent Isotropic Thermal Parameters (×10^4) for [AcenAlOMe]$_2$ (**18**)

atom	*x*	*y*	*z*	*U*(eq) (Å^2)
Al(1)	41707(12)	22058(10)	56378(9)	301(7)
Al(2)	39935(13)	22329(10)	69526(9)	306(7)
O(1)	49866(27)	20227(22)	52382(20)	349(18)
O(2)	42456(28)	30133(22)	55022(21)	364(18)
O(3)	47589(25)	21663(21)	64306(19)	297(17)
O(4)	31357(28)	22310(22)	73407(20)	347(18)
O(5)	41564(28)	30324(21)	71053(20)	345(18)
O(6)	34057(25)	22902(21)	61598(20)	312(17)
N(1)	39442(34)	13010(28)	55844(25)	330(22)
N(2)	33395(32)	21574(29)	48649(26)	357(23)
N(3)	39583(37)	13105(28)	70236(26)	361(23)
N(4)	47752(33)	20542(26)	77297(24)	307(21)
C(1)	54766(43)	15675(36)	53912(30)	343(28)
C(2)	62471(41)	16398(40)	53054(34)	425(31)
C(3)	67934(48)	12046(43)	54801(36)	508(34)
C(4)	65877(50)	6734(41)	57514(37)	497(34)
C(5)	58369(50)	5843(38)	58236(36)	486(33)
C(6)	52541(43)	10154(34)	56366(31)	336(28)
C(7)	44395(45)	8662(34)	56255(31)	338(28)
C(8)	42145(50)	2102(36)	56396(41)	561(36)
C(9)	31041(42)	12160(37)	53900(34)	414(29)
C(10)	28985(45)	15890(40)	48177(35)	494(32)
C(11)	32564(44)	25265(39)	43954(33)	410(30)
C(12)	27143(49)	23793(44)	38109(35)	601(36)
C(13)	36672(42)	31056(37)	44355(33)	380(29)
C(14)	35709(51)	34867(45)	39172(38)	552(36)
C(15)	38907(55)	40477(48)	39369(45)	655(41)
C(16)	43067(54)	42744(43)	44872(43)	606(38)
C(17)	44147(46)	39113(36)	49948(37)	465(32)
C(18)	41114(42)	33197(35)	49901(34)	352(28)
C(19)	55442(41)	23482(36)	65831(32)	404(29)
C(20)	25418(47)	18649(37)	71989(34)	419(31)
C(21)	18032(50)	20949(42)	72665(40)	567(36)
C(22)	11497(59)	17474(52)	70933(55)	837(51)
C(23)	12070(63)	11631(55)	69015(62)	1010(61)
C(24)	19187(55)	9176(43)	68657(45)	659(41)
C(25)	26035(47)	12494(36)	70179(35)	415(30)
C(26)	33606(51)	9700(35)	70423(33)	416(31)
C(27)	34195(51)	2917(35)	71294(40)	546(35)
C(28)	47571(46)	10897(34)	71857(34)	441(31)
C(29)	51176(47)	14441(35)	77523(34)	474(31)
C(30)	49191(42)	24105(35)	81990(31)	359(28)
C(31)	54672(47)	22224(40)	87731(34)	512(32)
C(32)	45608(40)	30083(33)	82025(32)	318(26)
C(33)	45753(45)	33258(36)	87470(35)	408(30)
C(34)	42695(49)	38929(40)	87692(39)	511(35)
C(35)	39435(46)	41714(36)	82255(38)	459(32)
C(36)	39129(42)	38780(34)	76763(36)	388(29)
C(37)	42024(38)	32930(32)	76428(30)	284(25)
C(38)	27939(44)	27118(38)	60337(35)	480(31)

Scheme 4. Syntheses of **16**−**21**



Conclusion

Solvated, cationic aluminum chelate complexes have been established as a distinct class of compounds. A wide range of examples are accessible through variations in ligand, solvent,

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[20] Drew, D. A.; Haaland, A.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1973**, *398*, 241.

and counteranion. On the basis of the crystal structures of these compounds, a four-centered transition state, requiring two open coordination sites and a cationic aluminum center, is proposed for the polymerization of oxiranes with Schiff base−aluminum catalysts. Such polymerizations are currently being conducted.

Experimental Section

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction with an inert-atmosphere glovebox. All solvents were rigorously dried prior to use. The SalenH$_2$ ligands were synthesized as previously described.[21] NMR data were obtained on JEOL-GSX-400 and -270 instruments at 270.17 (^{1}H) and 62.5 (^{13}C) MHz. Chemical shifts are reported relative to SiMe$_4$ and are in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}.

Preparation of SalenAlCl (1). To a solution of SalenH$_2$ (5.000 g, 18.64 mmol) in toluene (125 mL) was added a solution of dimethylaluminum chloride (1.724 g, 18.64 mmol) in toluene (50 mL). The addition took place over 2−3 min, resulting in a yellow solution and pale yellow solid. The mixture was allowed to stir for 2 h at 25 °C and then filtered. The solid was dried *in vacuo,* yielding 5.807 g (95%) of **1**. Mp: 156−60 °C dec. ^{1}H NMR (CDCl$_3$): δ 3.83 (m, 2H, CH_2), 4.23 (m, 2H, CH_2), 6.76−7.44 (m, 8H, PhH), 8.38 (s, 2H, PhCH). IR: 3040 w, 2974 w, 1647 s, 1550 s, 1477 s, 1340 s, 912 m, 756 s, 659 s. Anal. Calcd: C, 58.46; H 4.29. Found: C, 58.26; H, 4.54.

Preparation of SalenClAlCl (2). The procedure was as described for **1** with SalenClH$_2$ (5.000 g, 14.65 mmol) in toluene (150 mL) and dimethylaluminum chloride (1.356 g, 14.65 mmol) in toluene (50 mL). Yield: 5.498 g (93%) of **2**. Mp: 146−50 °C dec. IR: 3051 w, 2953 m, 2933 m, 1641 s, 1539 s, 1465 s, 1383 s, 1302 s, 850 s, 715 s. Anal. Calcd: C, 48.33; H, 3.04. Found: C, 48.60; H, 3.09.

Preparation of AcenAlCl (3). The procedure was as described for **1** with AcenH$_2$ (5.000 g 16.87 mmol) in toluene (150 mL) and dimethylaluminum chloride (1.561 g, 16.87 mmol) in toluene (50 mL). Yield: 5.754 g (96%) of **3**. Mp: 179−82 °C dec. IR: 3065 w, 2931 m, 1604 s, 1560 s, 1446 s, 1359 m, 1244 s, 877 m, 771 s, 665 s. Anal. Calcd: C, 60.60; H, 5.09. Found: C, 60.72; H, 5.34.

Preparation of SalenAlMe (4). This preparation is an alternate to that described in ref 6. To a solution of SalenH$_2$ (10.000 g, 37.27 mmol) in toluene (90 mL) was added a solution of trimethylaluminum (2.955 g, 37.27 mmol) in toluene (10 mL). The vigorous reaction subsided after a few minutes, resulting in a mass of pale yellow needles. An additional 50 ml of toluene was added, and the mixture was stirred at reflux for 1 h, cooled to 25 °C, and filtered. The pale yellow needles were dried *in vacuo,* yielding 9.851 g (86%) of **4**. Mp: 192−196 °C dec. ^{1}H NMR (CDCl$_3$): δ −1.06 (s, 3H, AlCH_3), 3.66 (m, 2H, CH_aH$_b$), 3.98 (m, 2H, CH$_a$$H_b$), 6.69−7.36 (m, 8H, Ph$H$), 8.21 (s, 2H, PhC$H$). IR: 3048 m, 3018 m, 2918, m, 1624 s, 1546 s, 1473 s, 1391 s, 1335 m, 1208 m, 1148 m, 807 s, 656 s. Anal. Calcd: C, 66.23; H, 5.56. Found: C, 66.61; H, 5.48.

Preparation of SalenClAlMe (5). To a solution of SalenClH$_2$ (5.000 g, 14.65 mmol) in toluene (125 mL) was added a solution of trimethylaluminum (1.056 g, 14.65 mmol) in toluene (25 mL). The vigorous reaction subsided after a few minutes, resulting in a yellow solution and yellow solid. The mixture was stirred at reflux for 1 h, cooled to 25 °C, and then filtered. The solid was dried *in vacuo,* yielding 3.881 g (69%) of **5** as a yellow solid. Mp: 200−205 °C dec. ^{1}H NMR (CDCl$_3$): δ −1.07 (s, 3H, AlCH_3), 3.75 (m, 2H, CH_aCH$_b$), 4.08 (m, 2H, CH$_a$CH_b), 7.00−7.32 (m, 6H, PhH), 8.22 (s, 2H, PhCH). IR: 3113 m, 2920 m, 1631 s, 1539 s, 1462 s, 1379 s, 1184 s, 711 s, 679 s, 631 s, 621 m. Anal. Calcd: C, 54.13; H, 4.01. Found: C, 54.47; H, 4.26.

Preparation of AcenAlMe (6). The procedure was as described for **5** with AcenH$_2$ (10.000 g, 33.74 mmol) in toluene (90 mL) and trimethylaluminum (2.432 g, 33.74 mmol) in toluene (20 mL). Yield: 2.09 g (92%) of **6** as a pale yellow solid. Mp: 223−25 °C dec. ^{1}H NMR (CDCl$_3$): δ −1.15 (s, 3H, AlCH_3), 2.46 (s, 6H, C-CH_3), 3.79 (m, 4H, CH_2H_2), 6.66−7.49 (m, 8H, PhH). IR: 3081 m, 2918 m, 1602 s (br), 1543 s, 1446 s, 1334 s, 1248 s, 877 s, 752 s, 665 s. Anal. Calcd: C, 67.84; H, 6.29. Found: C, 67.53; H, 6.13.

Preparation of [SalenAl(H$_2$O)$_2$]$^+$Cl$^-$ (7). To **1** (1.00 g, 3.04 mmol) was added H$_2$O (20 mL). The bright yellow mixture was allowed to stir for 2 h at 25 °C, resulting in a pale yellow solution and solid. Filtration of the mixture afforded 0.73 g (66%) of **7** as a pale yellow powder. Addition of 90 mL of H$_2$O to the original mixture resulted in complete dissolution of the solid. Slow evaporation of the H$_2$O over a period of 3 days resulted in a nearly quantitative yield of **7** as a crystalline solid. Mp: 162−65 °C dec. IR: 3057 s (br), 1639 s, 1560 m, 1473 s, 1400 s, 1296 s, 814 m, 760 s. Anal. Calcd: C, 52.69; H, 4.97. Found: C, 52.65; H, 5.02.

Preparation of [SalenClAl(H$_2$O)$_2$]$^+$Cl$^-$ (8). To **2** (1.00 g, 2.52 mmol) was added H$_2$O (20 mL). The bright yellow mixture was allowed to stir for 2 h at 25 °C, resulting in a pale yellow solution and solid. Filtration of the mixture afforded 0.90 g (83%) of **8** as a pale yellow solid. Mp: 152−55 °C dec. IR: 3115 s (br), 1647 s, 1545 m, 1489 s, 1384 s, 1288 m, 817 m, 717 m. Anal. Calcd: C, 44.32; H, 3.72. Found: C, 44.17; H, 3.75.

Preparation of [AcenAl(H$_2$O)$_2$]$^+$Cl$^-$ (9). To **3** (1.00 g, 2.80 mmol) was added H$_2$O (25 mL). The bright yellow mixture was allowed to stir for 2 h at 25 °C, resulting in a yellow solution and solid. Filtration of the mixture afforded 0.77 g (70%) of **9** as a light yellow solid. Mp: 158−160 °C dec. IR: 3088 s (br), 1608 s, 1554 m, 1446 m, 1308 m, 1251 s, 748 s. Anal. Calcd: C, 55.04; H, 5.65. Found: C, 55.16; H, 5.87.

Preparation of [SalenAl(MeOH)$_2$]$^+$Cl$^-$ (10). To **1** (2.000 g, 6.080 mmol) at 25 °C was added MeOH (40 mL). The solid dissolved within 10 min, resulting in a yellow solution. The solution was allowed to stir for 2 h and the solvent removed under reduced pressure, yielding 2.190 g (92%) of **10** as a very pale yellow crystalline solid. Mp: >260 °C. ^{1}H NMR (CD$_3$OD): δ 3.26 (s, CH_3OH), 3.94 (s, 4H, CH_2CH_2), 4.85 (s (br), CH$_3$OH), 6.74−7.43 (m, 8H, PhH), 8.55 (s, 2H, PhCH). IR: 3426 w, 3011 s (br), 2745 m, 1641 s, 1604 m, 1550 m, 1454 m, 1400 s, 1298 s, 910 m, 814 m, 760 s. Anal. Calcd: C, 55.04; H, 5.44. Found: C, 54.92; H, 5.44.

Preparation of [SalenClAl(MeOH)$_2$]$^+$Cl$^-$ (11). To **2** (2.000 g, 4.979 mmol) at 25 °C was added MeOH (40 mL). The solid dissolved within 10 min, resulting in a yellow solution. The solution was allowed to stir for 2 h and the solvent removed under reduced pressure, yielding 2.02 g (87%) of **11** as a yellow crystalline solid. Mp: >260 °C. ^{1}H NMR (CD$_3$OD): δ 3.26 (s, CH_3OH), 3.97 (s, 4H, CH_2CH_2), 4.85 (s (br), CH$_3$OH), 6.91 (d, 2H, PhH), 7.33−7.43 (m, 4H, PhH), 8.55 (s, 2H, PhCH). IR: 3406 w, 2991 s (br), 2779 m, 1641 s, 1537 m, 1467 s, 1381 s, 1307 s, 1186 m, 1012 m, 817 s, 713 s. Anal. Calcd: C, 46.83; H, 4.37. Found: C, 46.40; H, 4.30.

Preparation of [AcenAl(MeOH)$_2$]$^+$ Cl$^-$ (12). To **3** (2.000 g, 5.606 mmol) at 25 °C was added MeOH (40 mL). The solid dissolved within 2 min, resulting in a deep yellow solution. The solution was allowed to stir for 2 h and the solvent removed under reduced pressure, yielding 2.051 g (87%) of **12** as a pale yellow crystalline solid. Mp: >260 °C. ^{1}H NMR (CD$_3$OD): δ 2.58 (s, 6H, CCH_3), 3.26 (CH_3OH), 3.95 (s, 4H, CH_2CH_2), 4.88 (s (br), CH$_3$OH), 6.71−7.73 (m, 8H, PhH). IR: 3416 w, 3063 s (br), 2769 m, 1606 s, 1554 m, 1446 s, 1319 m, 1249 m, 1018 m, 877 m, 748 s. Anal. Calcd: C, 57.08; H, 6.23. Found: C, 56.96; H, 5.93.

Preparation of [SalenAl(MeOH)$_2$]$^+$BPh$_4$$^-$·2MeOH (13). To a mixture of **1** (1.921 g, 5.844 mmol) and sodium tetraphenylborate (2.000 g, 5.844 mmol) was added THF (50 mL). The pale yellow suspension was refluxed for 2 h, resulting in a pale yellow solution and a white solid. The THF was removed under reduced pressure, and MeOH (50 mL) was added. The pale yellow solution was filtered off a white solid and cooled to 0 °C for 24 h, yielding 2.34 g (52%) of **13** as pale yellow platelike crystals. Mp: 140−44 °C dec. ^{1}H NMR (CD$_3$OD): δ 3.28 (s (br), CH_3OH), 3.72 (s (br), 4H, CH_2CH_2), 4.78 (s (br), CH$_3$OH), 6.65−7.35 (m, (br), 28H, PhH), 8.31 (s (br), 2H, PhCH). IR: 3555 m, 3055 m, 2964 m, 1631 s, 1554 s, 1479 s, 1450 s, 1340 s, 1018 s, 734 s, 705 s. Anal. Calcd: 71.35; H, 6.81. Found: C, 71.46; H, 6.42.

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(21) Atwood, D. A.; Benson, J.; Jegier, J. A.; Lindholm, N. F.; Martin, K. J.; Pitura, R. J.; Rutherford, D. *Main Group Chem.* **1995**, *1*, 99.

Preparation of $[SalenClAl(MeOH)_2]^+BPH_4^-\cdot MeOH$ (14). The procedure was as described for **13** with **2** (2.000 g, 4.979 mmol), sodium tetraphenylborate (1.704 g, 4.979 mmol), and THF (30 mL). Yield: 1.993 g (51%) of **14** as thin yellow needles. Mp: 146−48 °C dec. ^1H NMR (CD_3OD): δ 3.26 (s, CH_3OH), 3.66 (m, 4H, CH_2CH_2), 4.78 (s(br), CH_3OH), 6.74−7.36 (m, 26H, Ph*H*), 8.19 (s, 2H, PhC*H*). IR: 3539 m, 3117 m (br), 3055 m, 2986 m, 1633 s, 1539 m, 1465 s, 1384 s, 1028 m, 817 s, 709 s. Anal. Calcd: C, 66.43; H, 5.70. Found: C, 66.62; H, 5.73.

Preparation of $[AcenAl(MeOH)_2]^+BPh_4^-\cdot MeOH$ (15). The procedure was as described for **13** with **3** (2.000 g, 5.606 mmol), sodium tetraphenylborate (1.92 g, 5.606 mmol), and THF (50 mL). Yield: 2.073 g (50%) of **15** as colorless cubelike crystals. Mp: 153−55 °C dec. ^1H NMR (CD_3OD): δ 2.44 (m (br), 6H, CCH_3), 3.26 (s (br), CH_3OH), 3.69 (m (br), 4H, CH_2CH_2), 4.80 (m (br), CH_3OH), 6.65−7.39 (m (br), 28H, Ph*H*). IR: 3464 m, 3163 m (br), 3036 m, 2796 m, 1606 s, 1548 s, 1446 s, 1400 s, 1323 m, 748 s, 705 m. Anal. Calcd: C, 73.37; H, 6.84. Found: C, 73.30; H, 6.76.

Preparation of $[SalenAlOMe]_2\cdot MeOH$ (16). To **4** (2.000 g, 6.487 mmol) was added MeOH (40 mL). The mixture was stirred at reflux for 30 min, resulting in a yellow solution and white solid. The mixture was cooled to 25 °C and filtered. The white solid was dried *in vacuo*, yielding 1.653 g (75%) of **16** as a white crystalline solid. Mp: 160−165 °C. ^1H NMR ($CDCl_3$): δ 2.93 (s (br), 6H, $AlOCH_3$), 3.08−4.19 (m, 8H, CH_2CH_2), 6.51−7.48 (m, 16H, Ph*H*), 8.11 (s (br), 4H, PhC*H*). IR: 3383 m (br), 3032 m, 2922 m, 2831 m, 1635 s, 1477 m, 1454 s, 1334 m, 773 m, 570 s. Anal. Calcd: C, 61.77; H, 5.63. Found: C, 61.97; H, 5.22.

Preparation of $[SalenClAlOMe]_2$ (17). The procedure was as described for **16** with **5** (2.000 g, 5.246 mmol) and MeOH (60 mL). Yield: 1.90 g (91%) of **17** as a pale yellow crystalline solid. Mp: >260 °C. IR: 3412 m (br), 3146 m, 2945 m, 2833 m, 1637 s, 1533 m, 1392 m, 1327 m, 1037 m, 823 s, 707 s. Anal. Calcd: C, 51.93; H, 3.85. Found: C, 52.22; H, 3.76.

Preparation of $[AcenAlOMe]_2\cdot 2MeOH$ (18). The procedure was as described for **16** with **6** (2.000 g, 5.946 mmol) and MeOH (75 mL). Yield: 1.08 g (54%) of **18**. Mp: > 260 °C. ^1H NMR ($CDCl_3$): δ 2.24 (s, 6H, CCH_3), 2.36 (s, 6H, CCH_3), 2.82 (s, 6H, OCH_3), 3.11−3.89 (m, 8H, CH_2CH_2), 6.43−7.52 (m, 16H, Ph*H*). IR: 3136 s (br), 3024 m, 2979 m, 2831 m, 1606 s, 1541 s, 1448 s, 1400 m, 1332 m, 1035 m (br), 762 s, 585 s. Anal. Calcd: C, 62.55; H, 6.56. Found: C, 62.18; H, 6.67.

Preparation of $SalenAlOC_6H_2(CH_3)_2Cl$ (19). To a suspension of **4** (1.000 g, 3.243 mmol) in toluene (40 mL) was added 4-chloro-3,5-dimethylphenol (0.508 g, 3.243 mmol). The mixture was brought to reflux, resulting in a yellow solution and no solid. As the solution was stirred at reflux over a period of 1 h, a very pale yellow solid precipitated. The mixture was cooled to 25 °C and filtered. The solid was dried *in vacuo*, yielding 1.251 g (86%) of **19** as a very pale yellow crystalline solid. Mp: 248−253 °C dec. ^1H NMR ($CDCl_3$): δ 2.00 (s, 6H, $PhCH_3$), 3.68 (m, 2H, CH_aCH_b), 4.00 (m, 2H, CH_aCH_b), 6.18 (s, 2H, Ph*H*), 6.76−7.38 (m, 8H, Ph*H*), 8.28 (s, 2H, PhC*H*). IR: 3038 w, 2980 m, 2852 w, 1635 s, 1587 m, 1548 s, 1481 s, 1338 s, 1149 m, 740 s, 653 m. Anal. Calcd: C, 64.22; H, 4.94. Found: C, 63.96; H, 4.82.

Preparation of $SalenClAlOC_6H_2(CH_3)_2Cl$ (20). The procedure was as described for **19** with **5** (2.000 g, 5.303 mmol) in toluene (40 mL) and 4-chloro-3,5-dimethylphenol (0.822 g, 5.303 mmol). Yield: 2.142 g (78%) of **20** as yellow needles. Mp: 258−260 °C dec. ^1H NMR ($CDCl_3$): δ 2.06 (s, 6H, $PhCH_3$), 3.78 (m, 2H, CH_aCH_b), 4.09 (m, 2H, CH_aCH_b), 6.20 (s, 2H, Ph*H*), 7.07−7.41 (m, 6H, Ph*H*), 8.30 (s, 2H, PhC*H*). IR: 3036 w, 2951 m, 1629 s, 1535 s, 1467 s, 1389 s, 1307 s, 1184 s, 927 m, 758 s, 715 s. Anal. Calcd: C, 55.68; H, 3.89. Found: C, 55.94; H, 3.70.

Preparation of $AcenAlOC_6H_2(CH_3)_2Cl$ (21). The procedure was as described for **19** with **6** (1.000 g, 2.973 mmol) in toluene (40 mL) and 4-chloro-3,5-dimethlyphenol (0.466 g, 2.973 mmol). Yield: 1.212 g (86%) of **21** as a very pale yellow crystalline solid. Mp: >260 °C. ^1H NMR ($CDCl_3$): δ 2.02 (s, 6H, $PhCH_3$), 2.42 (s, 6H, CCH_3), 3.81 (m, 4H, CH_2CH_2), 6.13 (s, 2H, PhH), 6.73−7.50 (m, 8H, Ph*H*). IR: 3051 w, 2947 m, 2918 m, 2856 w, 1599 s (br), 1547 s, 1465 s, 1352 s, 1271 s, 1049 m, 879 s, 752 s. Anal. Calcd: C, 65.48; H, 5.50. Found: C, 65.75; H, 5.31.

X-ray Experimental Details. For **7**, crystals suitable for X-ray analysis were grown from the filtrate over several weeks at 5 °C. For **13** and **15**, the product crystals were suitable for X-ray analysis. For **18**, crystals suitable for X-ray analysis were obtained from a solution of **21** in MeOH which was stored at 0 °C for several days. Details of the crystal data and a summary of data collection parameters for the complexes are given in Table 2. 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 for each compound, 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.

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Supporting Information Available: Tables of X-ray experimental details, bond lengths and angles, positional parameters, and anisotropic thermal parameters and unit cell views (52 pages). Ordering information is given on any current masthead page.

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