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Aluminum complexes of sterically hindered tetradentate Schiff bases: synthesis, structure, and reactivity toward ε-caprolactone

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Abstract

The sterically hindered Schiff bases tbmSalenH_2 [tbmSalen = *N,N'*-1,2-ethylenebis(3-*tert*-butyl-5-methylsalicylideneimine)] and tbmSalcenH_2 [tbmSalcen = *N,N'*-*trans*-1,2-cyclohexanediyl-bis(3-*tert*-butyl-5-methylsalicylideneimine)] afforded a series of aluminum complexes of the general formulae [Al(tbmSalen)X] and [Al(tbmSalcen)X] (X = Cl, Me, Et). The molecular structure of [Al(tbmSalcen)Cl] was determined by single-crystal X-ray structural analysis which revealed a five-coordinate aluminum center with a distorted square pyramidal geometry. The alkyl complexes were found to oligomerize ε-caprolactone. © 1997 Elsevier Science S.A.

Keywords: Aluminum; Schiff base; Ring-opening polymerization of lactones; Chiral aluminum complex

1. Introduction

Five-coordinate aluminum complexes of tetradentate ligand systems such as porphyrinato [1] and Schiff bases [2,3] have been playing an important role as initiators for the controlled polymerization of various polar monomers including methyl methacrylate, epoxides, and lactones. By using the Schiff base complex Al(Salcen)Cl [Salcen = *N,N'*-*trans*-1,2-cyclohexanediyl-bis(3-*tert*-butyl-5-methylsalicylideneiminato)], derived from the enantiomerically pure (1*R*,2*R*)-1,2-cyclohexanediamine, stereoelective ring-opening polymerization of the chiral monomers β-butyrolactone and propylene oxide became a possibility [3]. More recently, cationic aluminum Schiff base complexes were reported to initiate the ring-opening polymerization of epoxides [4]. With the aim of developing efficient chiral initiators, we have synthesized aluminum complexes containing the sterically encumbered Schiff bases ligands, tbmSalen [tbmSalen = *N,N'*-1,2-ethylenebis(3-*tert*-butyl-5-methylsalicylideneiminato)] and tbmSalcen [tbmSalcen = *N,N'*-*trans*-1,2-cyclohexanediyl-bis(3-*tert*-butyl-5-methylsalicylideneiminato)] [5,6], and tested their activity toward ring-opening polymerization of ε-caprolactone.

2. Results and discussion

The alkyl aluminum complexes of the bulky Schiff bases L, (L)AlR (L = tbmSalen, tbmSalcen), were prepared by slowly adding hexane solutions of trialkylaluminum AlR_3 (R = Me, Et) to acetonitrile suspensions of LH_2 at room temperature (Scheme 1). The use of acetonitrile was necessary, since a low concentration of both the reactants had to be maintained throughout the reaction in order to suppress the formation of polynuclear complexes [7]. The Schiff base complexes were isolated in high yields as relatively air-stable, yellow powders. The mass spectra show that these alkyl complexes are monomeric. The ^{1}H NMR spectra of the aluminum complexes show no significant differences compared to those of the free ligand, except that the proton signals for the imine groups are shifted to higher field. The methyl groups bonded to the aluminum center

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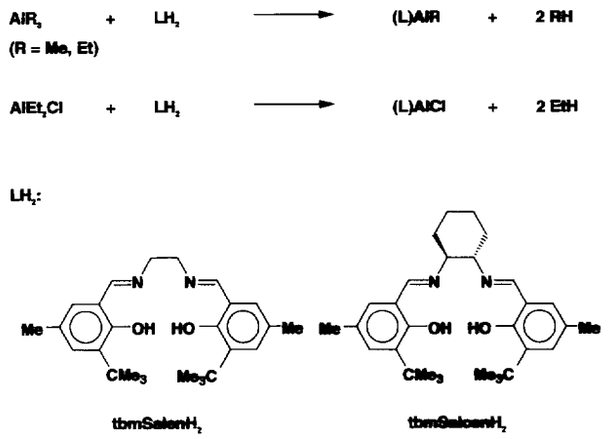


Scheme 1.

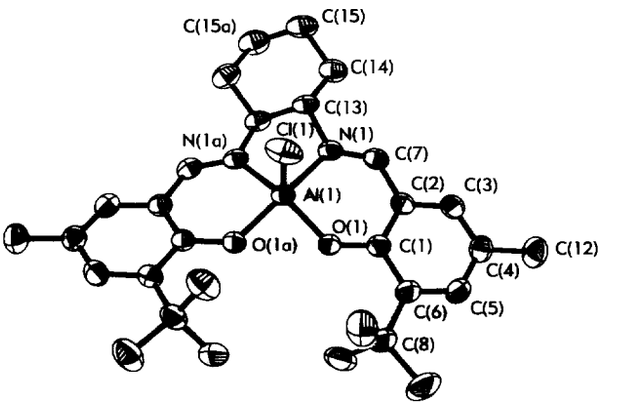


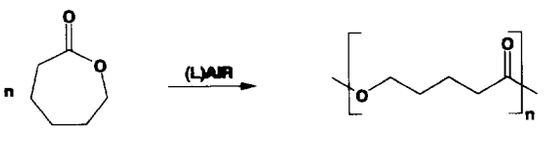
Fig. 1. Molecular structure of (tbmSalcen)AlCl. Selected bond distances (pm) and angles (deg): Al–Cl 218.4(1), Al–O1 176.9(2), Al–O1a 178.9(2), Al–N1 199.4(2), Al–N1a 199.2(2), O1–Al–O1a 90.00(7), N1–Al–N1a 79.94(8), Cl–Al–O1 112.60(6), Cl–Al–O1a 99.64(6), Cl–Al–N1 96.44(6), Cl–Al–N1a 105.98(6). Thermal ellipsoids are shown at the 50% probability level and all hydrogen atoms have been omitted for the sake of clarity.

give rise to singlets at δ −1.25 and −1.24 for (tbmSalen)AlMe and (tbmSalcen)AlMe respectively. Observation of corresponding signals in the ^{13}C NMR spectrum was hampered by the low solubility of these complexes and signal broadening. Of particular interest is the fact, that at ambient temperature the chiral complex (tbmSalcen)AlMe exhibits C_2-symmetry according to the ^1H NMR spectrum, whereas the ^{13}C NMR spectrum indicates the obvious lack of any symmetry element. Moreover, the ethyl derivative (tbmSalcen)AlEt shows the higher symmetry according to both ^1H and ^{13}C NMR spectroscopy. We assume that these complexes undergo a rapid isomerization on the NMR time scale [8].

The chloro complexes of tbmSalen and tbmSalcen (L)AlCl were obtained in high yield as yellow, air-stable powders from the reaction of diethylaluminum chloride with the ligand precursors LH_2 in hexane. Similar to the alkyl complexes, a slight shift to higher field, compared to LH_2, of the ^1H NMR signals due to tbmSalen and tbmSalcen ligand was observed. The mass spectra confirmed that the chloro complexes are also monomeric. Unlike the alkyl complexes, the chloro complex Al(tbmSalcen)Cl is unsymmetric, as shown by the loss of the C_2-symmetry of the ligand tbmSalcen upon complexation.

The crystal structure analysis of the racemic chloro complex (tbmSalcen)AlCl as dichloromethane solvate revealed a five-coordinate aluminum center with a distorted square pyramidal geometry (Fig. 1), showing the typical 'inverted umbrella' geometry commonly observed in Salen complexes of transition metals [5,6,9]. The aluminum is displaced by 44 pm from the best least-squares plane containing the chelating nitrogen and oxygen atoms. The tetradentate ligand set forms a considerably folded N_2O_2 plane with two differing aluminum–oxygen bond lengths of 176.9(2) and 178.9(2) pm. On the other hand, the two imine nitrogen atoms show identical bond lengths of average 199.3(2) pm. These features are clearly due to the chiral structure enforced by the *trans*-1,2-cyclohexanediyl backbone [6]. The angle O–Al–O was found to be 90.00(7)°, whereas the angle N–Al–N is 79.94(8)°. The sum of the angles at the aluminum center is 339.8°. The bond length between the aluminum and the apical chlorine atom is 218.4(1) pm. The chlorine atom is tilted in the direction of the oxygen atom O1a, away from the carbon atom C13 of the cyclohexanediyl backbone.

Polymerization of ε-caprolactone using (tbmSalen)AlR and (tbmSalcen)AlR was attempted in toluene at 50 °C in 2 M solutions of the monomer (Scheme 2). Number average molecular weights M_n were determined via ^1H NMR spectroscopic end group analyses and agree with the theoretically expected values. They increase linearly with conversion, suggesting that polymerization proceeds in a controlled manner. However, the activities are much lower than those of aluminum alkoxo complexes such as $Al(O^iPr)_3$. Thus with a monomer-initiator ratio of 50, poly(ε-caprolactone) of only $M_n = 2700$ was obtained after 20 h using (tbmSalen)AlR. In contrast to what was reported for the polymerization of β-butyrolactone by (Salcen)AlCl [3], the chloro complexes (L)AlCl, derived from the sterically bulky Schiff base ligands, failed to initiate ε-caprolactone polymerization.



Scheme 2.

3. Experimental

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glove-box techniques. Acetonitrile and ε-caprolactone were distilled from calcium hydride. Hexane was purified by distillation from sodium–triglyme benzophenone ketyl, toluene by distillation from sodium benzophenone ketyl. (tbmSalen)H_2 and (tbmSalcen)H_2 were prepared according to a procedure described in Ref. [10]. Trimethyl- and triethylaluminum were used as 2.0 M solutions in hexane, diethylaluminum chloride as a 1.0 M solution in hexane. ^{1}H NMR and ^{13}C NMR spectra were recorded an a Bruker ARX200 spectrometer in $CDCl_3$ at 25 °C. Mass spectra were obtained on a Varian CH7 spectrometer. Elemental analyses were determined on Heraeus CHN-Rapid apparatus.

3.1. (tbmSalen)AlMe

To a stirred suspension of (tbmSalen)H_2 (1.9 g, 4.6 mmol) in 10 ml of acetonitrile was added dropwise a solution of trimethylaluminum (2.3 ml, 4.6 mmol) in hexane at room temperature. The reaction mixture was stirred overnight at room temperature. The yellow precipitate was filtered through a glass frit and the filter bed washed with 10 ml of hexane. The precipitate was dried under vacuum to give 1.48 g (72%) of a pale yellow powder; ^{1}H NMR: δ −1.25 (s, 3 H, $AlCH_3$), 1.49 (s, 18 H, $C(CH_3)_3$), 2.24 (s, 6 H, 4-CH_3), 3.62 (m, 2 H, CH_2CH_2), 3.83 (m, 2 H, CH_2CH_2), 6.86 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, C-5), 7.22 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, C-3), 8.13 (s, 2 H, CH=N); ^{13}C{^{1}H} NMR: δ 20.5 (4-CH_3), 26.6 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 55.1 (CH_2CH_2), 118.9 (C-3), 124.1 (C-5), 130.7 (C-2), 133.8 (C-4), 141.5 (C-6), 163.4 (C-1), 168.8 (CH=N); EI MS: m/z 433 (100%, M^+ − Me), 408 (17%, tbmSalen$^+$), 217 (8%, $C_{13}H_{15}NO^+$), 204 (6%, $C_{12}H_{18}NO^+$), 174 (17%, $C_{11}H_{15}NO^+$). Anal. Calcd. for $C_{27}H_{37}AlN_2O_2$: C, 72.27, H, 8.31, N, 6.25. Found: C, 71.42, H, 8.05, N, 6.01.

3.2. (tbmSalcen)AlMe

This compound was prepared using (tbmSalcen)H_2 in a manner analogous to that described for the synthesis of (tbmSalen)AlMe and isolated as a yellow powder in 87% yield; ^{1}H NMR: δ −1.24 (s, 3 H, $AlCH_3$), 1.33 (s, 18 H, $C(CH_3)_3$), 1.40 (br m, 6 H, CH-backbone), 1.97 (s, 6 H, 4-CH_3), 2.30 (br m, 2 H, CH-backbone), 3.49 (br m, 2 H, CH-backbone), 6.31 (d, $^4J_{HH}$ = 2.0 Hz, 2 H, C-5), 7.04 (d, $^4J_{HH}$ = 2.0 Hz, 2 H, C-3), 7.68 (s, 2 H, CH=N); ^{13}C{^{1}H} NMR: δ 20.9 (4-CH_3), 14.6, 23.1, 24.2, 29.1 (CH-backbone), 30.1 ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 62.4, 65.9 (CHN), 119.4 (C-3), 124.2, 124.7 (C-5), 131.4, 131.7 (C-2), 133.6, 134.4 (C-4), 141.9 (C-6), 162.3, 164.0 (C-1), 162.3, 167.5 (CH=N); EI MS: m/z 488 (100%, M^+ − Me), 236 (10%, $C_{14}H_{21}NO^+$), 201 (10%, $C_{14}H_{27}NO^+$), 57 (16%, $C_4H_9^+$). Anal. Calcd. for $C_{31}H_{43}AlN_2O_2$: C, 74.07, H, 8.62, N, 5.57. Found: C, 74.39, H, 9.51, N, 4.99.

3.3. (tbmSalen)AlEt

This compound was prepared using (tbmSalen)H_2 and triethylaluminum in a manner analogous to that described for the synthesis of (tbmSalen)AlMe and isolated as a yellow powder in 70% yield; ^{1}H NMR: δ −0.47 (q, $^3J_{HH}$ = 8.0 Hz, 2 H, $AlCH_2$), 0.65 (t, $^3J_{HH}$ = 8.0 Hz, 3 H, $AlCH_3$), 1.51 (s, 18 H, $C(CH_3)_3$), 2.24 (s, 6 H, 4-CH_3), 3.63–3.87 (m, 4 H, CH_2CH_2), 6.74 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, C-5), 7.22 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, C-3), 8.12 (s, 2 H, CH=N); ^{13}C{^{1}H} NMR: δ 11.9 ($AlCH_3$), 22.2 (4-CH_3), 31.4 ($C(CH_3)_3$), 37.0 ($C(CH_3)_3$), 56.9 (CH_2CH_2), 120.7 (C-3), 125.7 (C-5), 132.5 (C-2), 135.6 (C-4), 143.1 (C-6), 165.4 (C-1), 170.6 (CH=N); EI MS: m/z 458 (9%, M^+), 334 (100%, M^+ − Me), 408 (13%, tbmSalen$^+$), 174 (20%, $C_{11}H_{15}NO^+$), 57 (10%, $C_4H_9^+$).

3.4. (tbmSalcen)AlEt

This compound was prepared using (tbmSalcen)H_2 and triethylaluminum in a manner analogous to that described for the synthesis of (tbmSalen)AlMe and isolated as a yellow powder in 73% yield; ^{1}H NMR: δ −0.37 (m, 4 H, $AlCH_2$), 0.71 (t, $^3J_{HH}$ = 8.0 Hz, 3 H, $AlCH_2CH_3$), 1.39 (s, 18 H, $C(CH_3)_3$), 2.27 (s, 6 H, 4-CH_3), 1.20–3.45 (br m, 8 H, CH-backbone), 7.25 (d, $^4J_{HH}$ = 2.0 Hz, 2 H, C-3), 7.67 (s, 2 H, CH=N); ^{13}C{^{1}H} NMR: δ 9.2 ($AlCH_2CH_3$), 20.8 (4-CH_3), 24.8 ($C(CH_3)_3$), 29.6 (CH-backbone), 31.2 (CH-backbone), 35.1 ($C(CH_3)_3$), 72.6 (CHN), 118.6 (C-3), 125.6 (C-5), 132.6 (C-2), 135.9 (C-4), 140.3 (C-6), 162.5 (C-1), 174.7 (CH=N); EI MS: m/z 516 (2%, M^+), 487 (100%, M^+ − Et), 57 (5%, $C_4H_9^+$). Anal. Calcd. for $C_{32}H_{45}AlN_2O_2$: C, 74.39, H, 8.78, N, 5.42. Found: C, 71.49, H, 8.93, N, 5.04.

3.5. (tbmSalen)AlCl

To a stirred suspension of (tbmSalen)H_2 (1.0 g, 2.5 mmol) in 20 ml of hexane was slowly added a hexane solution of diethylaluminum chloride (2.5 ml, 2.5 mmol) at room temperature. The reaction mixture was stirred overnight and the precipitate was filtered. Filtration followed by washing with 10 ml of hexane and drying under vacuum gave 1.2 g (96%) of yellow powder; ^{1}H NMR: δ 1.50 (s, 18 H, $C(CH_3)_3$), 2.25 (s, 6 H, 4-CH_3), 3.70 (m, 2 H, CH_2CH_2), 4.10 (m, 2 H, CH_2CH_2), 6.87 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, C-5), 7.27 (d, $^4J_{HH}$ = 2.4 Hz, 2 H, C-3), 8.28 (s, 2 H, CH=N); ^{13}C{^{1}H}

NMR: δ 20.5 (4-CH_3), 29.6 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 54.6 (CH_2CH_2), 118.7 (C-3), 125.4 (C-5), 131.0 (C-2), 134.7 (C-4), 165.0 (C-1), 169.8 (CH=N); EI MS: m/z 468 (34%, M^+), 417 (100%, Salen$^+$), 201 (18%, $C_{12}H_{15}NO^+$), 187 (16%, $C_{12}H_{15}O^+$). Anal. Calcd. for $C_{26}H_{34}AlClN_2O_2$: C, 66.95, H, 2.29, N, 3.00. Found: C, 66.64, H, 2.44, N, 3.25.

3.6. (tbmSalcen)AlCl

This compound was prepared using (tbmSalcen)H_2 in a manner analogous to that described for the synthesis of (tbmSalen)AlCl and isolated as a yellow powder in 84% yield; ^{1}H NMR: δ 1.50 (s, 9 H, $C(CH_3)_3$), 1.51 (s, 9 H, $C(CH_3)_3$), 1.60 (br m, 4 H, CH-backbone), 2.05 (br m, 2 H, CH-backbone), 2.24 (s, 3 H, 4-CH_3), 2.26 (s, 3 H, 4-CH_3), 2.30 (br m, 1 H, CH-backbone), 2.50 (br m, 1 H, CH-backbone), 3.07 (br m, 1 H, CH-backbone), 3.49 (br m, 1 H, CH-backbone), 6.84 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, C-5), 6.89 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, C-5), 7.22 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, C-3), 8.04 (s, 1 H, CH=N), 8.21 (s, 1 H, CH=N); $^{13}C\{^1H\}$ NMR: δ 20.5 (4-CH_3), 23.7, 24.1, 27.1, 27.6 (CH-backbone), 28.6, 29.6 $C(CH_3)_3$), 35.2, 35.3 ($C(CH_3)_3$), 62.4, 65.6 (CHN), 118.9 (C-3), 123.7, 124.2 (C-5), 130.9, 131.2 (C-2), 133.1, 134.0 (C-4), 141.5 (C-6), 161.8 (C-1), 162.0, 167.0 (CH=N); EI MS: m/z 522 (34%, M^+), 487 (14%, SalcenAl$^+$), 471 (100%, SalcenAl$^+$ − Me), 228 (16%, $C_{14}H_{16}NO^+$), 214 (12%, $C_{13}H_{12}NO^+$), 57 (15%, $C_4H_9^+$). Anal. Calcd. for $C_{30}H_{40}AlClN_2O_2$: C, 73.37, H, 8.21, N, 5.70. Found: C, 72.02, H, 8.07, N, 4.89.

3.7. X-ray crystallography of (tbmSalcen)AlCl

Pale yellow cubes were obtained by slow cooling of (tbmSalcen)AlCl in dichloromethane. Cell dimensions and intensity data were obtained with an Enraf–Nonius CAD-4 diffractometer: $C_{31}H_{42}AlCl_3N_2O_2$, M = 608.0, a = 1252.5(2), b = 1275.7(2), c = 1291.9(1) pm, α = 64.242(8)°, β = 63.306(8)°, γ = 64.978(9)°, Z = 2, $d_{calc.}$ = 1.268 M gm^{-3}, triclinic $P1$, Cu Kα (λ = 154.178 pm), graphite monochromator, 0.48 × 0.24 × 0.10 mm^3, T = 193 K, $4 < \theta < 60°$, $F(000)$ = 644. Number of reflections measured 4961, 4716 independent reflections [R(int) = 0.0346] of which 4093 were assigned observed [$I > 2\sigma(I)$], absorption coefficient 3.102 mm^{-1}. The structure was solved by direct methods and difference Fourier synthesis and refined against all F^2 data (SHELX-86 [11], SHELXL-93 [12]). Hydrogen atoms were calculated at their idealized positions, except those of disordered groups. The refinement converged at residuals wR_2 = 0.1251 for all reflections, corresponding to a conventional R = 0.0425 for the observed F_o data.

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depositoy number CSD406965, the names of the authors and the journal citation.

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