

Syntheses of cationic four-coordinated aluminum complexes: counter-ion induced aggregation through the N–H···I hydrogen bonds

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Abstract

Synthesis of cationic aluminum complexes from the reactions of Lewis bases with Me_2AlI is reported. The reactions of two molar equivalents of (*S*)-(–)-1-phenylethylamine, (*R*)-(–)-pantolactone (PL–H), or (*S*)-(–)-ethyl lactate (EL–H) with Me_2AlI (**1**), generated in situ from the reaction of Me_3Al with one molar equivalent of I_2 in toluene at room temperature, afford white crystalline solids $[\text{Me}_2\text{Al}((\text{S})\text{-NH}_2(\text{Ph})\text{C}(\text{H})\text{CH}_3)_2]^+\text{I}^-$ (**2**), $[(\text{PL})_2\text{Al}]^+\text{I}^-$ (**3**) or $[(\text{EL})_2\text{Al}]^+\text{I}^-$ (**4**), respectively. However, Me_3Al reacts with one molar equivalent of PL–H producing $[(\text{Me}_2\text{Al}(\mu\text{-PL}))_2]^+$ (**5**). The reaction of Me_2AlI with 2,2'-ethylidene-bis-(4,6-di-*tert*-butylphenol) (EDBP–H₂) yields $[\text{Al}(\text{EDBP})\text{I}(\text{Et}_2\text{O})]^+$ (**6**) which further reacts with one molar equivalent or two molar equivalents of OPPh_3 giving a neutral complex $[\text{Al}(\text{EDBP})(\text{OPPh}_3)_2\text{I}]$ (**7**) or a cationic complex $[\text{Al}(\text{EDBP})(\text{OPPh}_3)_2]^+\text{I}^-$ (**8**). However, the cationic aluminum derivative $[\text{Al}(\text{EDBP})(\text{HMPA})_2]^+\text{I}^-$ (**9**) is prepared from the reaction of **6** with excess of HMPA. Crystal structures of **2**, **5**, and **8** determined by X-ray diffraction method are also presented. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Aluminum; Cation; Aggregation; Hydrogen bond

1. Introduction

Cationic aluminum complexes are of great interest because of their potential use as living polymerization catalysts [1] as well as their role in the Lewis acid promoted Diels–Alder reactions [2]. Although many cationic aluminum complexes have been reported; however, four-coordinated aluminum cations are relatively rare but are still remain attractive as these complexes are not completely coordinated saturate and are electron deficient [3]. Recently Atwood and Jegier have demonstrated that the formation of aluminum cations is affected by the nature of halogen in Me_2AlX [4]. In which he describes that Me_2AlBr reacts with excess *tert*-butyl amines resulting in a cationic aluminum complex $[(\text{tBuNH}_2)_2\text{AlMe}_2]^+\text{Br}^-$ formation, whereas, Me_2AlCl reacts with *tert*-butyl amines leading only to a neutral adduct $[(\text{tBuNH}_2)\text{Al}(\text{Cl})\text{Me}_2]$. Recently, we have been

directed toward the preparation and use of aluminum derivatives as Lewis acid for the catalysis of Diels–Alder reactions and ring-opening polymerization [5]. Our interest in cationic aluminum chemistry has led us to investigate a feasible way for the preparation of a variety of cationic aluminum complexes. Me_2AlI is chosen as a starting material because of the weak Al–I bond, therefore, it is easy to break the Al–I bond using Lewis bases. In this paper, we report the preparation and characterization of several four-coordinated cationic aluminum complexes. The first examples that cationic aluminum complexes are stabilized by lactate or lactonate ligand and the formation of supramolecular structure via N–H···I hydrogen bonds will be presented.

2. Experimental

2.1. General

All manipulations were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing at

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least 24 h over sodium–benzophenone (toluene, hexane, diethyl ether, tetrahydrofuran) or phosphorus pentoxide (CH_2Cl_2) and freshly distilled prior to use. Deuterated solvents were dried over molecular sieves. AlMe_3 (2.0 M in toluene), (*S*)-(–)-1-phenylethylamine, (*R*)-(–)-pantolactone, (*S*)-(–)-ethyl lactate, 2,2'-ethyldiene-bis-(4,6-di-*tert*-butylphenol), iodine, triphenylphosphine oxide, hexamethylphosphoramide were purchased and used without further purification. Melting points were determined with a Buchi 535 digital melting point apparatus. ^1H - and ^{13}C -NMR spectra were recorded on a Varian VXR-300 (300 MHz) or a Mercury-400 (400 MHz) spectrometer with chemical shifts given in ppm from the internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Infrared spectra were obtained from a Bruker Equinox 55 spectrometer.

2.2. Preparation of $[\text{Me}_2\text{Al}((\text{S})-\text{NH}_2\text{PhCH}(\text{CH}_3)_2)^+ \text{I}^-]$ (2)

To an ice cold solution (0°C) of iodine (0.52 g, 2.0 mmol) in toluene (20 ml), an AlMe_3 (1.0 ml, 2.0 M in toluene, 2.0 mmol) solution was added slowly. The solution changes color from purple to colorless in 20 min, followed by the addition of (*S*)-(–)-1-phenylethylamine (0.52 ml, 4.0 mmol). The resulting mixture was stirred for 2 h, during which a white precipitate formed and then was dried in vacuo. The residue was extracted with 30 ml of CH_2Cl_2 and recrystallized from 3:1 hexane– CH_2Cl_2 . Colorless crystals were obtained after 24 h. Yield: 0.81 g (95%). Anal. Calc. for $\text{C}_{18}\text{H}_{28}\text{AlIN}_2$: C, 50.71; H, 6.62; N, 6.57. Found: C, 50.53; H, 6.65; N, 6.65%. ^1H -NMR (CDCl_3 , ppm): δ 7.41–7.30 (m, 10H, Ph); 5.14 (br, 4H, NH_2); 4.15 (q, 2H, $\text{CH}(\text{CH}_3)$, $J = 6.8$ Hz); 1.60 (d, 6H, $\text{CH}(\text{CH}_3)$, $J = 6.8$ Hz); –1.05 (AlCH_3). ^{13}C -NMR (CDCl_3 , ppm): δ 139.94, 129.05, 128.68, 126.82 (Ph); 52.72 ($\text{CH}(\text{CH}_3)$); 24.34 ($\text{CH}(\text{CH}_3)$); –10.43 (AlCH_3).

2.3. Preparation of $[(\text{R})\text{-pantolactonato}]_2\text{Al}^+ \text{I}^-$ (3)

To an ice cold solution (0°C) of iodine (0.52 g, 2.0 mmol) in CH_2Cl_2 (20 ml), AlMe_3 (1.0 ml, 2.0 mmol) was added slowly. After the mixture was stirred for 30 min, (*R*)-(–)-pantolactone (0.52 g, 4.0 mmol) was added and the resulting mixture was stirred for 3 h. The volatile materials were removed in vacuo and the residue was extracted with 20 ml of CH_2Cl_2 . Colorless crystalline solids were obtained 24 h after the addition of hexane (40 ml). Yield: 0.65 g (79%). Anal. Calc. for $\text{C}_{12}\text{H}_{18}\text{O}_6\text{AlI}$: C, 34.97; H, 4.40. Found: C, 35.41; H, 4.51%. ^1H -NMR (CDCl_3 , ppm): δ 4.11 (s, 2H), 4.04 (d, 2H, CH_2 , $J = 8.8$ Hz), 3.95 (d, 2H, CH_2 , $J = 8.8$ Hz), 1.25 (s, 6H, CH_3), 1.09 (s, 6H, CH_3). IR (KBr, ν_{CO}): 1736 cm^{-1} . M.p. 179°C (dec.).

2.4. Preparation of $[\text{Al}((\text{S})\text{-OC}(\text{H})(\text{CH}_3)\text{-COOEt})_2]^+ \text{I}^-$ (4)

To an ice cold solution (0°C) of iodine (0.52 g, 2.0 mmol) in CH_2Cl_2 (20 ml), AlMe_3 (1.0 ml, 2.0 mmol) was added slowly and stirred for 30 min. (*S*)-(–)-ethyl lactate (0.46 ml, 4.0 mmol) was added and the resulting mixture was stirred for 3 h. The volatile materials were removed in vacuo and the residue was extracted with 20 ml of CH_2Cl_2 . Colorless crystalline solids were obtained 24 h after the addition of hexane (40 ml). Yield: 0.48 g (62%). Anal. Calc. for $\text{C}_{10}\text{H}_{18}\text{O}_6\text{AlI}$: C, 30.95; H, 4.67. Found: C, 30.83; H, 5.19%. ^1H -NMR (CDCl_3 , ppm): δ 4.26 (q, 2H, CH , $J = 6.8$ Hz), 4.25 (q, 4H, OCH_2CH_3 , $J = 7.0$ Hz); 1.42 (d, 6H, CH_3 , $J = 6.8$ Hz); 1.31 (t, 6H, OCH_2CH_3 , $J = 7.0$ Hz). IR (KBr, ν_{CO}): 1646 cm^{-1} . M.p. 160°C (dec.).

2.5. Preparation of $[\text{Me}_2\text{Al}(\mu\text{-(R)-pantolactonato})]_2$ (5)

To an ice cold solution (0°C) of (*R*)-pantolactone (0.26 g, 2.0 mmol) in ether (30 ml), an AlMe_3 (1.2 ml, 2.0 M in toluene, 2.4 mmol) solution was added slowly. The mixture was stirred for 2.5 h and then was dried in vacuo to give a white powder. The residue was extracted with 30 ml of ether and then concentrated to ca. 20 ml. Colorless crystals were obtained, after cooling to –20°C overnight. Yield: 0.29 g (79%). Anal. Calc. for $\text{C}_{16}\text{H}_{30}\text{Al}_2\text{O}_6$: C, 51.61; H, 8.12. Found: C, 51.23; H, 7.89%. ^1H -NMR (CDCl_3 , ppm): δ 4.94 (s, 1H, OCH); 4.15 (s, 2H, OCH_2); 1.32, 1.09 (s, 6H, $\text{C}(\text{CH}_3)_2$), –0.82 (s, 6H, AlCH_3). ^{13}C -NMR (CDCl_3 , ppm): δ 182.86 ($\text{C}=\text{O}$), 79.47 (OCH), 77.44 (OCH_2), 42.43 ($\text{C}(\text{CH}_3)_2$), 22.46, 18.46 ($\text{C}(\text{CH}_3)_2$), –8.96 (AlCH_3). IR (KBr, ν_{CO}): 1757 cm^{-1} .

2.6. Preparation of $[\text{Al}(\text{EDBP})\text{I}(\text{Et}_2\text{O})]$ (6)

To an ice cold solution (0°C) of iodine (1.04 g, 4.0 mmol) in toluene (30 ml), an AlMe_3 (2.0 ml, 2.0 M in toluene, 4.0 mmol) solution was added slowly. After 20 min the mixture became colorless, 2,2'-ethyldiene-bis(4,6-di-*tert*-butylphenol) (1.76 g, 4.0 mmol) in ether (20 ml) was added. The resulting mixture was stirred for 2 h and then dried in vacuo. The residue was extracted with 35 ml of ether and the extraction was then concentrated to ca. 20 ml and cooled to –20°C to furnish colorless crystals. Yield: 2.10 g (79%). Anal. Calc. for $\text{C}_{34}\text{H}_{54}\text{AlIO}_3$: C, 61.44; H, 8.19. Found: C, 60.76; H, 7.44%. ^1H -NMR (CDCl_3 , ppm): δ 7.38 (d, 2H, Ph, $J = 2.4$ Hz), 7.14 (d, 2H, Ph, $J = 2.4$ Hz); 4.51 (br, 4H, OCH_2CH_3); 4.40 (q, 1H, $\text{CH}(\text{CH}_3)$, $J = 7.2$ Hz); 1.68 (d, 3H, $\text{CH}(\text{CH}_3)$, $J = 7.2$ Hz); 1.53 (br, 6H, OCH_2CH_3); 1.42 (s, 18H, $\text{C}(\text{CH}_3)_3$); 1.30 (s, 18H, $\text{C}(\text{CH}_3)_3$). ^{13}C -NMR (CDCl_3 , ppm): δ 150.7, 140.9, 137.6, 133.4, 121.6, 120.9 (Ph); 70.1 (OCH_2CH_3); 35.3,

34.5, 31.8, 30.5 ('Bu); 30.9 (CH(CH₃)); 22.4 (CH(CH₃)); 13.9 (OCH₂CH₃).

2.7. Preparation of [(Ph₃P=O)Al(EDBP)I] (7)

A solution of triphenylphosphine oxide (0.56 g, 2.0 mmol) in toluene (20 ml) was added to a rapidly stirring solution of [Al(EDBP)I(Et₂O)] (1.33 g, 2.0 mmol) in toluene (30 ml). The reaction mixture was stirred at room temperature (r.t.) for 2 h, during which a white precipitate formed. The volatiles were removed under vacuum and the residue was dissolved in hot toluene (50 ml). The hot toluene solution was allowed to cool to –20°C, affording colorless crystalline product after 24 h. Yield: 1.56 g (90%). Anal. Calc. for C₄₈H₅₉AlIO₃P: C, 66.36; H, 6.84. Found: C, 66.92; H, 6.73%. ¹H-NMR (CDCl₃, ppm): δ 7.79–7.39 (m, 15H, Ph); 7.38, 7.30, 7.10, 7.02 (d, 4H, Ph, *J* = 2.4 Hz); 4.88, 4.64 (q, 1H, CH(CH₃), *J* = 7.2 Hz); 1.68, 1.46 (d, 3H, CH(CH₃), *J* = 7.2 Hz); 1.42, 1.29 (s, 18H, C(CH₃)₃); 1.19 (s, 18H, C(CH₃)₃).

2.8. Preparation of [Al(EDBP)(O=PPh₃)₂]⁺I[–] (8)

To a rapidly stirring solution of [Al(EDBP)I(Et₂O)] (1.33 g, 2.0 mmol) in toluene (30 ml), triphenylphosphine oxide (1.12 g, 4.0 mmol) in toluene (20 ml) was added. The reaction mixture was stirred at r.t. for 2 h, during which a white precipitate formed. The volatile materials were removed under vacuum and the residue was extracted with 40 ml of THF and was then concentrated to ca. 30 ml and cooled to –20°C to furnish colorless crystals. Yield: 2.04 g (89%). Anal. Calc. for C₆₆H₇₄AlIO₄P₂: C, 69.10; H, 6.50. Found: C, 68.95; H, 6.08%. ¹H-NMR (CDCl₃, ppm): δ 7.79–7.39 (m, 30H, Ph); 7.21 (d, 2H, Ph, *J* = 2.0 Hz), 7.06 (d, 2H, Ph, *J* = 2.0 Hz); 4.09 (q, 1H, CH(CH₃), *J* = 6.8 Hz); 1.27 (s, 18H, C(CH₃)₃); 1.18 (s, 18H, C(CH₃)₃); 0.93 (d, 3H, CH(CH₃), *J* = 6.8 Hz). ¹³C-NMR (CDCl₃, ppm): δ 150.5, 140.4, 136.1, 133.1, 120.9, 120.8 (Ph); 135.0, 132.2 (d), 132.1 (d), 129.8 (d), 129.5 (d), 124.4 (d), 123.8 (d) (PPh); 35.0, 34.2, 29.9, 29.7 ('Bu); 31.6 (CH(CH₃)); 21.6 (CH(CH₃)).

2.9. Preparation of [Al(EDBP)(HMPA)₂]⁺I[–] (9)

Hexamethylphosphoramide (1.40 ml, 8.0 mmol) was added to a rapidly stirring solution of [Al(EDBP)I(Et₂O)] (1.33 g, 2.0 mmol) in toluene (30 ml). The reaction mixture was stirred overnight at r.t., during which a white precipitate formed. The volatile materials were removed under vacuum to give a white powder. The residue was dissolved in hot toluene (40 ml). The hot toluene solution was allowed to cool to 5°C, affording colorless crystals after 48 h. Yield: 1.51 g (80%). Anal. Calc. for C₄₂H₇₆AlIN₆O₄P₂: C, 53.39; H, 8.11; N,

8.89. Found: C, 53.45; H, 8.32; N, 8.74%. ¹H-NMR (CDCl₃, ppm): δ 7.33 (d, 2H, Ph, *J* = 2.4 Hz), 7.05 (d, 2H, Ph, *J* = 2.4 Hz); 4.33 (q, 1H, CH(CH₃), *J* = 7.2 Hz); 2.80 (d, 18H, OP[N(CH₃)₂]₃, *J*_{H-P} = 10 Hz), 2.79 (d, 18H, OP[N(CH₃)₂]₃, *J*_{H-P} = 10 Hz), 1.63 (d, 3H, CH(CH₃), *J* = 7.2 Hz); 1.37 (s, 18H, C(CH₃)₃); 1.28 (s, 18H, C(CH₃)₃). ¹³C-NMR (CDCl₃, ppm): δ 150.8, 140.1, 135.9, 133.2, 121.0, 120.8 (Ph); 36.96, 36.91 (d, P[N(CH₃)₂]₃, *J*_{C-P} = 18.4 Hz); 35.1, 34.3, 31.7, 29.9 ('Bu); 31.1 (CH(CH₃)); 22.8 (CH(CH₃)).

2.10. X-ray crystallographic studies

Suitable crystals of **2**, **5**, and **8** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Siemens P4 diffractometer. The crystallographic data were collected using a ω–2θ scan mode with Mo–K_α radiation. Cell constants were obtained by least-squares analysis on positions of at least 25 randomly selected reflections in the 2θ range of 4–28°. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a Siemens SHELXTL PLUS package [6]. All non-H atoms and hydrogen atoms attached on nitrogen were located from successive Fourier maps. Other H-atoms were refined using a riding model [7]. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Crystallographic data of **2**, **5** and **8** are listed in Table 1.

3. Results and discussion

3.1. Synthesis and spectroscopic studies of 1–5

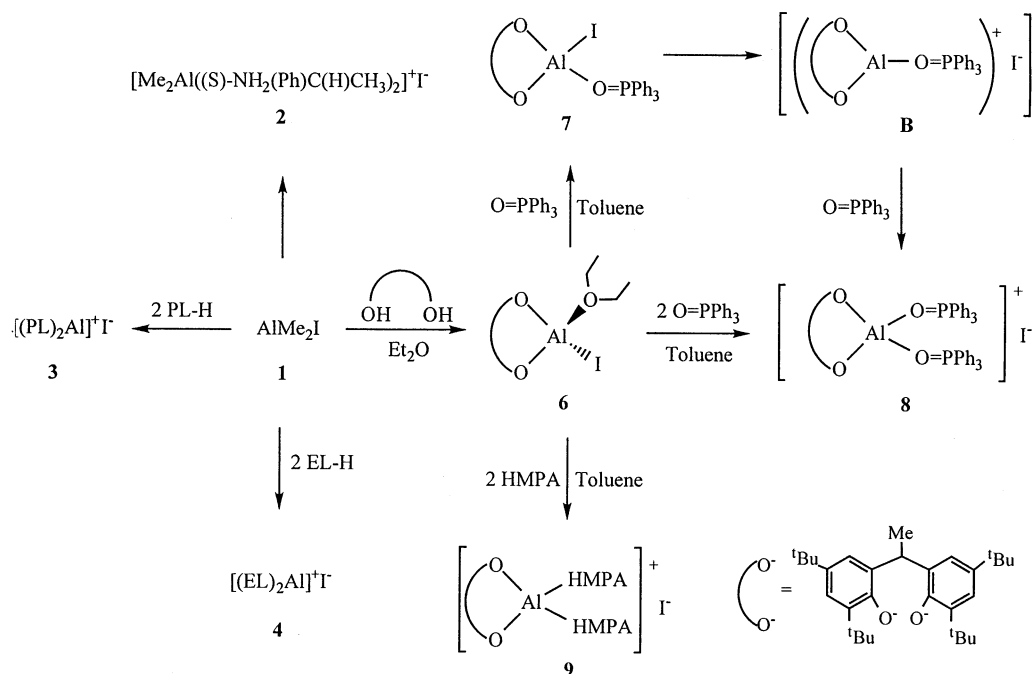
The reactions of two molar equivalents of (S)-(–)-1-phenylethylamine, (R)-(–)-pantolactone (PL-H), or (S)-(–)-ethyl lactate (EL-H) with Me₂AlI (**1**), generated in situ from the reaction of Me₃Al with one molar equivalent of I₂ in toluene at 0°C, afford cationic aluminum complexes [Me₂Al((S)-NH₂(Ph)C(H)CH₃)₂]⁺I[–] (**2**), [(PL)₂Al]⁺I[–] (**3**) or [(EL)₂Al]⁺I[–] (**4**), respectively (shown in Scheme 1). However, the reaction of one molar equivalent of (R)-(–)-pantolactone with Me₃Al yields a neutral pentacoordinated aluminum complex [(μ-PL)AlMe₂]₂ (**5**). Compound **5** is readily dissolved in toluene. However, compounds **2**, **3** and **4** are sparingly soluble in warm toluene but readily dissolve in cold dichloromethane indicating an ionic feature of these compounds. Despite attempts in vain to obtain the solid state structure of **3** and **4**, the ionic feature of **3** and **4** can be established by IR spectroscopic studies. A systematic decrease in the carbonyl stretching frequency (ν_{CO}) from the free (R)-pantolactone (1760

cm⁻¹) to the neutral compound [Me₂Al(μ-PL)]₂ (**5**) (1757 cm⁻¹) and to cationic compound **3** (1736 cm⁻¹) is observed. Similarly, ν_{CO} decreases from the free ethyl lactate (1738 cm⁻¹) to neutral compound [Me₂Al(μ-(S)-(-)OC(H)(Me)C(O)OEt)]₂ (**A**) (1687 cm⁻¹) [8] and to cationic compound **4** (1646 cm⁻¹). This dra-

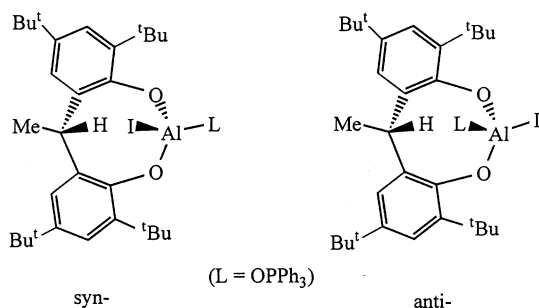
matic decrease in ν_{CO} ($21\text{--}41\text{ cm}^{-1}$) from the neutral compound (**A** or **5**) to the cationic compound (**3** or **4**) is consistent with our expectation. There is more electron density donating from the carbonyl to aluminum center in cationic aluminum complex than that in neutral complex resulting in the weaken of C=O bond.

Table 1
Crystallographic data of compounds **2**, **5**, and **8**

	2	5	8·2THF
Formula	C ₁₈ H ₃₀ AlIN ₂ O	C ₁₆ H ₃₀ Al ₂ O ₆	C ₇₄ H ₉₀ AlIO ₆ P ₂
Formula weight	444.3	372.4	1291.3
Crystal system	Colorless needle	Colorless parallelepiped	Colorless parallelepiped
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>A</i> (Å)	6.888(1)	13.269(2)	13.823(2)
<i>B</i> (Å)	17.782(4)	17.244(2)	18.068(2)
<i>C</i> (Å)	19.090(2)	18.763(2)	29.100(3)
β (°)	—	—	100.22(2)
<i>V</i> (Å ³)	2338.2(9)	4293.2(9)	7152.5(15)
<i>Z</i>	4	8	4
<i>D</i> _{calc} (Mg m ^{−3})	1.262	1.152	1.199
λ (Mo–K α) (Å)	0.7107	0.7107	0.7107
Absorption coefficient (mm ^{−1})	1.414	0.159	0.553
2 θ Range (°)	3.5–48.0	4.0–45	3.5–45
Scan type	2 θ – θ	2 θ – θ	2 θ – θ
Reflections collected	4205	6240	9688
Observed reflections	2421 (<i>F</i> > 4 σ (<i>F</i>))	4791 (<i>F</i> > 4 σ (<i>F</i>))	6240 (<i>F</i> > 4 σ (<i>F</i>))
No. of refined parameters	210	433	766
<i>R</i> ^a for significant reflections (%)	4.63	3.98	5.74
<i>R</i> _w ^b for significant reflections (%)	4.36	4.30	6.36
Goodness-of-fit ^c	1.13	1.18	1.83

$$^a R = |\Sigma(|F_o - F_c|)/\Sigma|F_o||.$$
^b $R_w = |\Sigma_{\sqrt{w}}(F_o - F_c)| / |\Sigma_{\sqrt{w}} F_o|$; $w = 1/[\sigma^2(F) + 0.0006]F^2$ for **2**; $w = 1/[\sigma^2(F) + 0.001]F^2$ for **5** and **8**.^c Goodness-of-fit = $[\sum w(|F_o - F_c|)^2 / (N_{\text{reflns}} - N_{\text{params}})]^{1/2}$.

Scheme 1.



Scheme 2.

Though previous work in this area has shown that a variety of Lewis bases such as amines, crown ethers, TMEDA, THF, acac, etc. [9] has led to the formation of aluminum cations; to our knowledge, there has been no example available on aluminum cation stabilized with lactone or lactate as coordinating ligand. Thus, compounds **3** and **4** stand as the first example of aluminum cations stabilized by lactate or lactonate ligand.

3.2. Synthesis and spectroscopic studies of **6–9**

[Al(EDBP)I(Et₂O)] (**6**) was synthesized in 79% yield from the reaction of 2,2'-ethyldiene-bis(4,6-di-*tert*-butylphenol) (EDBP-H₂) with Me₂AlI in diethyl ether, followed by the recrystallization from diethyl ether. Treatment of **6** with one molar equivalent of Ph₃P=O, yielded a neutral complex [Al(EDBP)I(OPPh₃)] (**7**). The cationic aluminum derivative [Al(EDBP)(OPPh₃)₂]⁺I[−] (**8**) is prepared either from the reaction of **7** with one molar equivalent of Ph₃P=O or from the reaction of **6** with two molar equivalents of Ph₃P=O. In addition, the reaction of **6** with excess of HMPA in toluene yields cationic complex [Al(EDBP)(HMPA)₂]⁺I[−] (**9**). The ¹H-NMR data of **6**, **8** and **9** reveal only one set of resonances for *tert*-butyl groups of phenyl ring in EDBP^{2−} ligand. Similarly, one set of two resonances for the two hydrogens on both aryl moieties was observed. These observations suggest that these two aryl moieties are chemically equivalent and that requires a σ-plane of symmetry pass through the C-7 methine carbon and the

Table 2

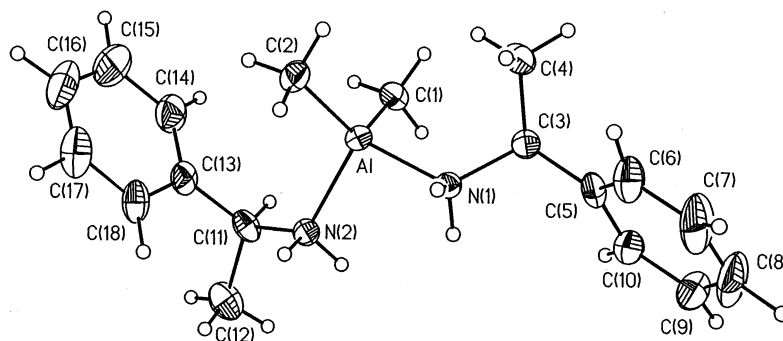
Selected bond distances (Å) and bond angles (°) of **2**

Bond lengths			
Al–N(1)	1.977(6)	Al–N(2)	1.971(7)
Al–C(1)	1.958(10)	Al–C(2)	1.960(9)
Bond angles			
N(1)–Al–N(2)	98.4(3)	N(1)–Al–C(1)	108.8(3)
N(2)–Al–C(1)	105.9(3)	N(1)–Al–C(2)	108.3(4)
N(2)–Al–C(2)	110.2(4)	C(1)–Al–C(2)	122.6(4)

aluminum atom. However, two sets of resonances are observed for compound **7** with a relative ratio of 3:1 indicating the presence of two geometric isomers for compound **7** as shown in Scheme 2. It is believed that the formation of **8** from **7** involves initial generation of the 3-coordinate Al derivative [(EDBP)Al(OPPh₃)]⁺ (**B**), which is rapidly trapped by OPPh₃.

3.3. Molecular structure of **2**, **5** and **8**

The ionic feature of **2** is further verified by the X-ray crystal structure determination and the ORTEP of [Me₂Al((*S*)-NH₂(Ph)CH(CH₃))₂]⁺ as shown in Fig. 1. Selected bond distances (Å) and bond angles (°) of **2** are listed in Table 2. The aluminum center is tetrahedrally coordinated by two amine molecules and two methyl groups in which the bond distances of Al–N bond are found to be similar with Al–N(1) 1.977(7) and Al–N(2) 1.971(7) Å, respectively. It is worth noting the polymeric feature of compound **2** in solid state in which [Me₂Al((*S*)-NH₂(Ph)CH(CH₃))₂]⁺ cations are connected through the N–H⋯I hydrogen bonds with iodide counterions to form a polymeric aggregate as shown in Fig. 2. Iodide anion is bonded to four hydrogen atoms from three independent amine molecules with the (N)H–I distances ranging from 2.773 to 3.242 Å and the correspondent I–N distances ranging from 3.542 to 3.790 Å as shown in Table 3. The N–H⋯I hydrogen bond distances and angles lie in the range generally expected for N–H⋯I hydrogen bonding [10]. Strong hydrogen bonds in the formation of supramolecular

Fig. 1. The ORTEP of [Me₂Al((*S*)-NH₂PhCH(CH₃))₂]⁺ with the atom labeling scheme.

structures have played important role among the organic and inorganic compounds and have been widely investigated [11].

Suitable crystals for structure determination of **5** are obtained from ether solution at -18°C and its ORTEP is shown in Fig. 3. Selected bond distances ($\text{\AA}$) and bond angles ($^{\circ}$) of **5** are listed in Table 4. The structure of **5** shows a dimeric feature which contains 5.5.4.5.5-fused rings with an Al_2O_2 core and a lactonate group bonded to Al through the $\text{C}=\text{O}$. The coordination

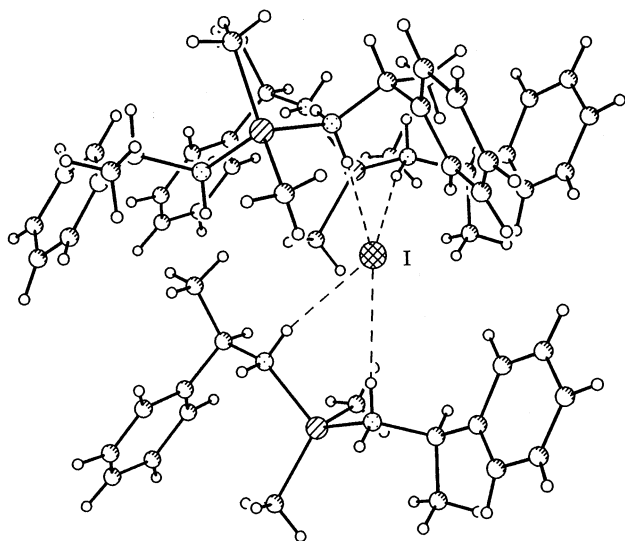


Fig. 2. Structure of **2** in the solid state demonstrates polymeric feature through $\text{N}-\text{H}\cdots\text{I}$ interactions.

Table 3
Selected hydrogen bond lengths ($\text{\AA}$) and angles ($^{\circ}$) in $2\cdot\text{H}_2\text{O}$

$\text{N}-\text{H}\cdots\text{I}$	$\text{H}\cdots\text{I}$	$\text{N}\cdots\text{I}$	$\text{N}-\text{H}\cdots\text{I}$	Symmetry
$\text{N}(1)-\text{H}(1\text{a})\cdots\text{I}$	3.242	3.790	156.1	$x-1, y, z$
$\text{N}(1)-\text{H}(1\text{b})\cdots\text{I}$	2.981	3.691	165.1	x, y, z
$\text{N}(2)-\text{H}(2\text{a})\cdots\text{I}$	2.859	3.586	159.1	$-1/2+x, 1/2-y, 2-z$
$\text{N}(2)-\text{H}(2\text{b})\cdots\text{I}$	2.773	3.542	158.0	x, y, z

Table 4

Selected bond distances ($\text{\AA}$) and bond angles ($^{\circ}$) of **5**

Bond lengths			
$\text{Al}(1)-\text{O}(1)$	1.865(2)	$\text{Al}(1)-\text{O}(2)$	2.315(3)
$\text{Al}(1)-\text{C}(1)$	1.953(4)	$\text{Al}(1)-\text{C}(2)$	1.956(4)
$\text{Al}(1)-\text{O}(4)$	1.934(2)	$\text{O}(1)-\text{Al}(2)$	1.933(2)
$\text{Al}(2)-\text{O}(4)$	1.873(2)	$\text{Al}(2)-\text{O}(5)$	2.355(3)
$\text{Al}(2)-\text{C}(21)$	1.947(4)	$\text{Al}(2)-\text{C}(22)$	1.957(4)
Bond angles			
$\text{O}(1)-\text{Al}(1)-\text{O}(2)$	78.3(1)	$\text{O}(1)-\text{Al}(1)-\text{C}(1)$	116.9(2)
$\text{O}(2)-\text{Al}(1)-\text{C}(1)$	87.9(2)	$\text{O}(1)-\text{Al}(1)-\text{C}(2)$	118.1(2)
$\text{O}(2)-\text{Al}(1)-\text{C}(2)$	88.3(1)	$\text{C}(1)-\text{Al}(1)-\text{C}(2)$	122.7(2)
$\text{O}(2)-\text{Al}(1)-\text{Al}(2)$	116.7(1)	$\text{C}(1)-\text{Al}(1)-\text{Al}(2)$	124.5(2)
$\text{C}(2)-\text{Al}(1)-\text{Al}(2)$	107.9(1)	$\text{O}(1)-\text{Al}(1)-\text{O}(4)$	76.8(1)
$\text{O}(2)-\text{Al}(1)-\text{O}(4)$	154.9(1)	$\text{C}(1)-\text{Al}(1)-\text{O}(4)$	106.0(2)
$\text{C}(2)-\text{Al}(1)-\text{O}(4)$	100.7(1)	$\text{O}(1)-\text{Al}(2)-\text{O}(4)$	76.7(1)
$\text{Al}(1)-\text{Al}(2)-\text{O}(5)$	115.7(1)	$\text{O}(1)-\text{Al}(2)-\text{O}(5)$	153.6(1)
$\text{O}(4)-\text{Al}(2)-\text{O}(5)$	77.1(1)	$\text{Al}(1)-\text{Al}(2)-\text{C}(21)$	125.4(1)
$\text{O}(1)-\text{Al}(2)-\text{C}(21)$	107.3(1)	$\text{O}(4)-\text{Al}(2)-\text{C}(21)$	117.2(2)
$\text{O}(5)-\text{Al}(2)-\text{C}(21)$	87.6(2)	$\text{Al}(1)-\text{Al}(2)-\text{C}(22)$	108.2(1)
$\text{O}(1)-\text{Al}(2)-\text{C}(22)$	100.8(1)	$\text{O}(4)-\text{Al}(2)-\text{C}(22)$	118.6(2)
$\text{O}(5)-\text{Al}(2)-\text{C}(22)$	89.0(1)	$\text{C}(21)-\text{Al}(2)-\text{C}(22)$	121.6(2)

polyhedron of the central five-coordinated aluminum atom is somewhat distorted from perfect trigonal bipyramidal geometry with two carbons, and one of two bridging oxygen atoms siting on equatorial positions. The aluminum atom, two ligating carbon atoms, and one of two bridging oxygen atoms are almost coplanar. The two equatorial $\text{Al}-\text{C}$ bonds average $1.953 \text{ \AA}$ that are similar to normal $\text{Al}-\text{C}$ bonds in five-coordinated complexes. However, the average $\text{Al}-\text{O}$ distance for the dative $\text{C}=\text{O} \rightarrow \text{Al}$ bond in **5** is $2.335(4) \text{ \AA}$ which is $0.36 \text{ \AA}$ longer than its lactate congener $[\text{Me}_2\text{Al}(\mu-(S)-(-)\text{OC}(\text{H})(\text{Me})\text{C}(\text{O})\text{OEt})_2]$ [8] and is about $0.62 \text{ \AA}$ longer than the longest dative bond from an oxygen to a four-coordinated aluminum for an ester group [12]. The longer $\text{Al}-\text{O}$ distance in **5** than that in $[\text{Me}_2\text{Al}(\mu-(S)-(-)\text{OC}(\text{H})(\text{Me})\text{C}(\text{O})\text{OEt})_2]$ is resulting from the ring strain of pantolactone group.

The cationic formulation was confirmed by the X-ray determination of **8** and the molecular structure of the cation is shown in Fig. 4. Selected bond distances ($\text{\AA}$) and bond angles ($^{\circ}$) of **8** are listed in Table 5. The cation consists of a central four-coordinate aluminum atom in a distorted tetrahedral geometry where aluminum is bonded to two oxygens of aryloxides and two oxygens of phosphine oxides with $\text{Al}-\text{O}(1) = 1.693(4)$, $\text{Al}-\text{O}(2) = 1.721(4)$, $\text{Al}-\text{O}(3) = 1.750(4)$, $\text{Al}-\text{O}(4) = 1.743(4) \text{ \AA}$. The short average $\text{Al}-\text{O}$ bond length of $1.747 \text{ \AA}$ (phosphine oxide), which is only slightly longer than that of $\text{Al}-\text{O}$ $1.707 \text{ \AA}$ (aryl oxide), and the linearity $\text{Al}-\text{O}-\text{P}$ angles of $157.9(3)$ and $171.1(3)^{\circ}$, respectively, indicate the existence of a strong interaction between Al and OPPh_3 . It is interesting to note that the $\text{Al}-\text{O}(4)$ distance of $1.743(4) \text{ \AA}$ is similar to the $\text{Al}-\text{O}(3)$ distance of $1.750(4) \text{ \AA}$ indicating that no steric hin-

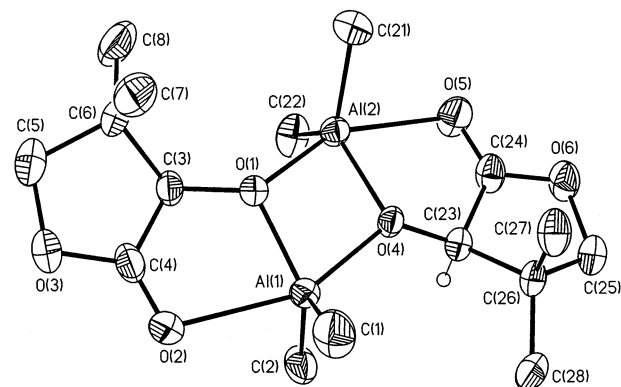


Fig. 3. Molecular structure and atom numbering scheme for $[(\mu\text{-PL})\text{AlMe}_2]_2$ (**5**).

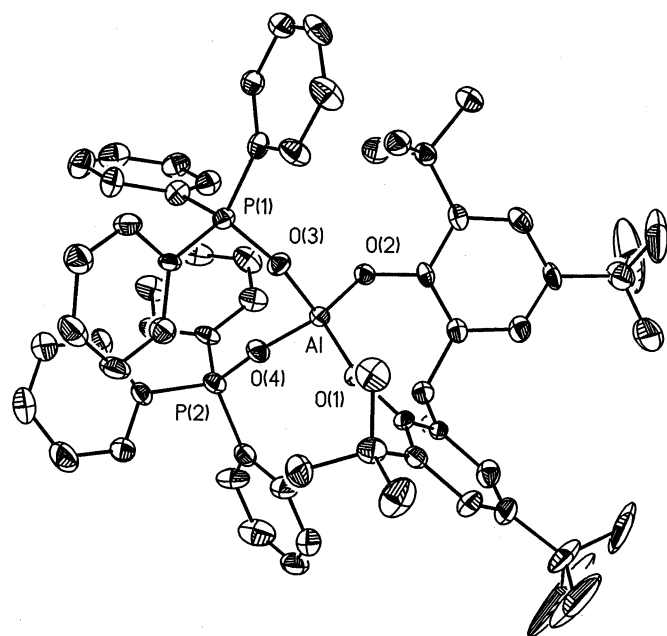


Fig. 4. Molecular structure and atom numbering scheme for [(EDBP)Al(OPPh₃)₂]⁺.

Table 5
Selected bond distances (Å) and bond angles (°) of **8**

<i>Bond lengths</i>			
Al–O(1)	1.693(4)	Al–O(2)	1.721(4)
Al–O(3)	1.750(4)	Al–O(4)	1.743(4)
P(1)–O(3)	1.527(4)	P(2)–O(4)	1.518(4)
<i>Bond angles</i>			
O(1)–Al–O(2)	117.8(2)	O(1)–Al–O(3)	107.2(2)
O(2)–Al–O(3)	109.7(2)	O(1)–Al–O(4)	108.9(2)
O(2)–Al–O(4)	109.4(2)	O(3)–Al–O(4)	102.7(2)
O(3)–P(1)–C(31)	109.4(3)	Al–O(3)–P(1)	157.9(3)
Al–O(4)–P(2)	171.1(3)		

drance difference for the phosphine oxide ligand *trans/cis* to the C(7) hydrogen.

In conclusion, cationic aluminum complexes were synthesized easily from the reactions of Lewis bases with Me₂AlI. The first characterized examples of aluminum cations stabilized by lactate or lactonate ligands are reported. The formation of supramolecular structure via strong N–H⋯I hydrogen bonds has been observed for compound **2**.

4. Supplementary material

The crystal data have been deposited with the Cambridge Crystallographic Data Centre with CCDC Nos.

135271 for compound **2**, 135272 for compound **5**, and 135273 for compound **8**.

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