

Synthesis and characterization of aluminum complexes of 2-pyrazol-1-yl-ethenolate ligands

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Abstract

The synthesis and the characterization of some new aluminum complexes with bidentate 2-pyrazol-1-yl-ethenolate ligands are described. 2-(3,5-Disubstituted pyrazol-1-yl)-1-phenylethanones, 1-PhC(O)CH₂-3,5-R₂C₃HN₂ (**1a**, R = Me; **1b**, R = Bu^t), were prepared by solventless reaction of 3,5-dimethyl pyrazole or 3,5-di-*tert*-butyl pyrazole with PhC(O)CH₂Br. Reaction of **1a** or **1b** with AlR₃¹ (R¹ = Me, Et) yielded *N,O*-chelate alkylaluminum complexes [R₂¹AlOC(Ph)CH{(3,5-R₂C₃HN₂)-1}] (**2a**, R = R¹ = Me; **2b**, R = Bu^t, R¹ = Me; **2c**, R = Me, R¹ = Et). Compound **1a** was readily lithiated with LiBu^t in thf or toluene to give lithiated species **3**. Treatment of **3** with 0.5 equiv of MeAlCl₂ or AlCl₃ yielded five-coordinated aluminum complexes [XAl(OC(Ph)CH{(3,5-Me₂C₃HN₂)-1})₂] (**4**, X = Me; **5**, X = Cl). Reaction of **5** with an equiv of LiHBEt₃ generated [Al(OC(Ph)CH{(3,5-Me₂C₃HN₂)-1})₃] (**6**). Complex **6** was also obtained by reaction of **3** with 1/3 equiv of AlCl₃. Treatment of **5** with 2 equiv of AlMe₃ yielded complex **2a**, whereas with an equiv of AlMe₃ afforded a mixture of **2a** and [Me(Cl)AlOC(Ph)CH{(3,5-Me₂C₃HN₂)-1}] (**7**). Compounds **1a**, **1b**, **2a–2c** and **4–6** were characterized by elemental analyses, NMR and IR (for **1a** and **1b**) spectroscopy. The structures of complexes **2a** and **5** were determined by single crystal X-ray diffraction techniques. Both **2a** and **5** are monomeric in the solid state. The coordination geometries of the aluminum atoms are a distorted tetrahedron for **2a** or a distorted trigonal bipyramid for **5**. © 2005 Elsevier B.V. All rights reserved.

Keywords: 2-Pyrazol-1-yl-ethenolate ligands; Aluminum complexes; Synthesis; Structures

1. Introduction

Organoaluminum compounds have attracted much attention in recent years due to their use as catalysts or co-catalysts for olefin polymerization [1,2], as initiators in ROP of cyclic esters [3] and as synthetic reagents or catalysts [4]. These compounds also exhibited interesting structure features and versatile reactivities [5]. *N,O*-Chelate ligands have been widely used in main group and transition metal coordination chemistry. For example, nickel complexes with *N,O*-

chelate ligands have been investigated as catalysts for olefin polymerization [1a,6]. Aluminum complexes with *N,O*-ligands also showed versatile coordination mode and unique applications [7]. For example, tris(8-quinolinolato)aluminum is one of the most widely used complexes for organic light emitting devices (OLED) [8]. A series of *N,O*-chelate aluminum complexes such as ketiminate and SALEN aluminum complexes exhibited excellent catalytic activity toward the ring opening polymerization of cyclic esters [7f,9]. *N,O*-Bidentate ligands were also found to be able to stabilize cationic monoalkylaluminum species [10]. Here we report synthesis and characterization of aluminum complexes stabilized by 2-pyrazol-1-yl-ethenolate ligands.

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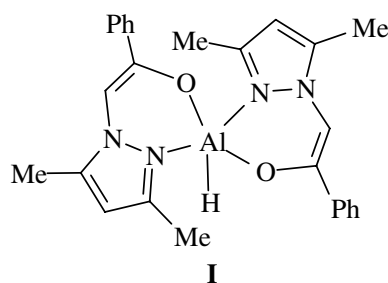
E-mail address: zxwang@ustc.edu.cn (Z.-X. Wang).

2. Results and discussion

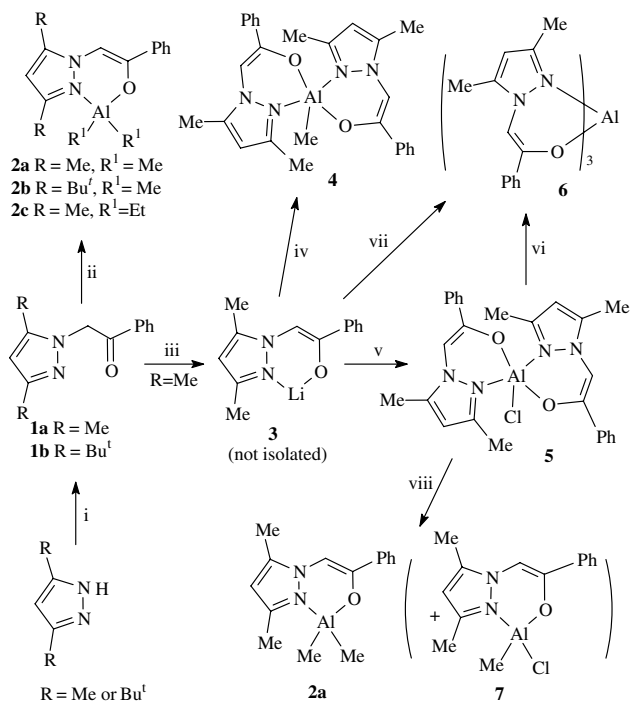
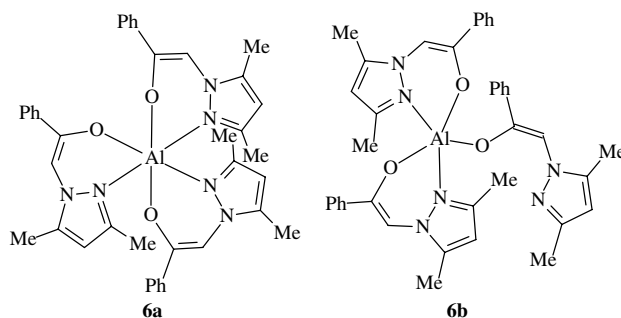
Preparation and reactions of 2-(3,5-disubstituted pyrazol-1-yl)-1-phenylethanones are summarized in Scheme 1.

A mixture of 3,5-dimethylpyrazole, $\text{PhC(O)CH}_2\text{Br}$ and Na_2CO_3 in a mortar was ground with a pestle for 20 min to give 2-(3,5-dimethylpyrazol-1-yl)-1-phenylethanone (**1a**). Similar treatment of 3,5-di-*tert*-butylpyrazole and $\text{PhC(O)CH}_2\text{Br}$ in the presence of Na_2CO_3 formed a mixture of 2-(3,5-di-*tert*-butylpyrazol-1-yl)-1-phenylethanone (**1b**) and starting materials. However, the reaction can reach almost completeness under microwave radiation conditions. The minor unreacted starting materials were removed at 80 °C under vacuum. Both **1a** and **1b** reacted readily with AlMe_3 or AlEt_3 in a 1:1 molar ratio, giving four-coordinated *N,O*-chelate alkylaluminum complexes **2a–2c**. The reactions proceed along with the elimination of an equivalent of methane or ethane. However, reaction of **1a** or **1b** with trimethylaluminum in a 2:1 molar ratio can not form bis(2-pyrazol-1-yl-ethenolate) aluminum complexes, only **2a** or **2b** being obtained. Compound **1a** was readily lithiated with LiBu^t in thf or toluene from about –80 °C to room temperature to give lithiated species, supposing **3**. Treatment of **3** with 0.5 equiv of MeAlCl_2 prepared [11] in situ from AlMe_3 and AlCl_3 in toluene generated five-

coordinated aluminum complex **4**. Similar reaction between **3** and 0.5 equiv of AlCl_3 afforded another five-coordinated aluminum complex **5**. Attempts to methylate **5** by treatment with MeLi were unsuccessful. The reaction produced a complicated mixture. Treatment of complex **5** with an equiv of LiHBET_3 in thf afforded complex **6**. The reaction could proceed via a hydride intermediate **I**, which transformed into **6** via a dismutation reaction. The other product of the dismutation reaction may be AlH_3 because no other complexes can be isolated. Complex **6** was also obtained by reaction of **3** with 1/3 equiv of AlCl_3 . Reaction of **5** with an equiv of AlMe_3 gave a mixture of **2a** and **7**. Similar reaction between **5** and 2 equiv of AlMe_3 afforded complex **2a**. These are attributed to a redistribution of ligands and then the methylation of **7** with AlMe_3 . Ligand redistributions often occur between aluminum complexes. A number of examples have been reported in the literature [11–13]. In addition, attempts to prepare complex **7** by reaction of **3** with an equiv of MeAlCl_2 were unsuccessful. The reaction gave a complicated mixture.



Compounds **1a** and **1b** were characterized by elemental analyses, ^1H and ^{13}C NMR and IR spectroscopy. Each of complexes **2a–2c** and **4–6** was characterized by elemental analyses, ^1H and ^{13}C NMR spectroscopy. The NMR spectra of complexes **4** and **5** showed that two 2-pyrazol-1-yl-ethenolate ligands are equivalent in the respective molecule. Complex **6** is six-coordinated in the solid state shown by single crystal X-ray diffraction (see **6a**). However, its ^1H NMR spectrum exhibited two sets of ligand signals in a 2:1 integral ratio, showing that two of the ligands have same coordination environment. Its ^{27}Al NMR spectrum (δ 60 ppm) supported a five-coordinated aluminum center [14]. Hence we assume that in the solution it exists as structure **6b**.



Scheme 1. Reagents and conditions: i, $\text{PhC(O)CH}_2\text{Br}$, grinding (R = Me) or MW radiation (R = Bu^t); ii, AlR_3^1 (R^1 = Me, Et), toluene, r.t., 15 h.; iii, LiBu^t , thf or toluene, –80 °C–r.t., 6 h.; iv, 1/2 MeAlCl_2 , toluene, –80 °C–r.t., 15 h.; v, 1/2 AlCl_3 , thf, –80 °C–r.t., 15 h.; vi, LiHBET_3 , thf, –80 °C–r.t., 15 h.; vii, 1/3 AlCl_3 , thf, –80 °C–r.t., 15 h.; viii, 1 or 2 equiv. of AlMe_3 , toluene, r.t., 15 h.

The structures of complexes **2a** and **5** were further characterized by single crystal X-ray diffraction. The structure of **2** is presented in Fig. 1 along with selected bond lengths and angles. Crystalline **2a** is monomeric. The fused six-membered ring Al1N1N2C6C7O1 is coplanar with the pyrazolato moiety as well as the phenyl ring. The geometry at the aluminum atom is a distorted tetrahedron with angles ranging from 94.81(13)° to 114.9(2)°. The most acute angle is associated with the bite angle of the chelate ligand, which is close to corresponding those in [Et₂Al{OC(Me)CHC(Me)N(2,6-Pr₂C₆H₃)}₂] [94.56(9)°] [13] and [Et₂Al{Sal(Bu^t)}] [94.97(6)°] [14]. The Al1–N1 distance of 1.940(3) Å is a little shorter than those found in [R₂Al{OC(Me)CHC(Me)N(2,6-Pr₂C₆H₃)}₂] (R = Me, 1.954(6) Å; R = Et, 1.958(2) Å) [15] and in [Et₂Al{Sal(Bu^t)}] (1.976(2) Å) [16]. The Al1–O1 distance of 1.747(3) Å is also shorter than corresponding those in [Me₂Al{OC(Me)CHC(Me)N(2,6-Pr₂C₆H₃)}₂] and [Et₂Al{Sal(Bu^t)}] (1.795(5) and 1.772(1) Å, respectively). However, The distances of Al1–N1 and Al1–O1 are still within the normal ranges for a four-coordinated alkyl aluminum complex [10b,17]. The C6–C7 distance of 1.327(5) Å shows a double bond between the atoms.

The structure of **5** is presented in Fig. 2 along with selected bond lengths and angles. Complex **5** is monomeric in the solid state and the aluminum atom is five-coordinated. The coordination geometry is a distorted trigonal bipyramid with N1 and N3 atoms in axial positions and Cl1, O1 and O2 atoms in equatorial positions. The Cl1, O1, O2 and Al1 atoms are coplanar, the total angles of the trigonal plane being 360°. The N1–Al1–N3 angle of 176.68(8)° shows that the arrange of the atoms is close

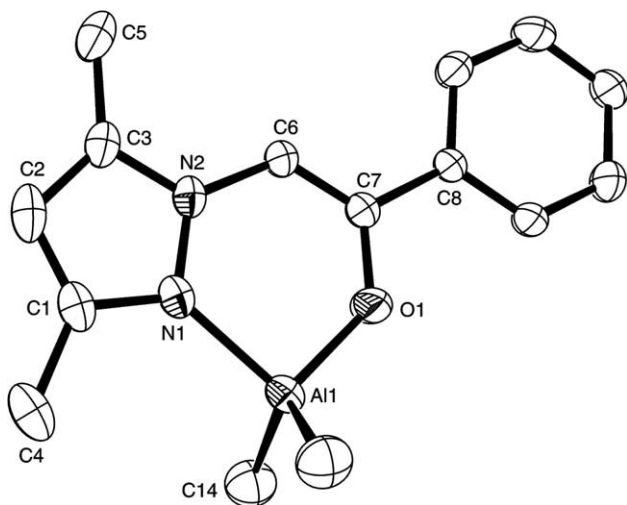


Fig. 1. ORTEP drawing of complex **2a** with 30% probability thermal ellipsoids. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al1–C14 1.948(3), Al1–O1 1.747(3), Al1–N1 1.940(3), C7–O1 1.322(4), C6–C7 1.327(5), C6–N2 1.419(4); N1–Al1–O1 94.81(13), O1–Al1–C14 112.54(12), C14–Al1–C14' 114.9(2), N1–Al1–C14 110.16(12), C7–O1–Al1 130.9(2), N2–N1–Al1 122.6(2), N2–C6–C7 125.6(3).

to linear. The bite angles N1–Al1–O1 and N3–Al1–O2 (90.30(8)° and 90.89(8), respectively) are narrower than that in **2a**, but wider than those in [RAl{OC(Me)CHC(Me)N(2,6-Pr₂C₆H₃)}₂] (R = Me, Et. av. 87.58° and 87.43°, respectively) [15]. The Al–N distance of average 2.0317 Å is normal for a five-coordinated aluminum complex with *N,O*-chelate ligands. For example, the Al–N distances in [RAl{OC(Me)CHC(Me)N(2,6-Pr₂C₆H₃)}₂] (R = Cl, Me, Et) range from 2.021(12) to 2.0678(17) Å [15]. The Al–O distance of average 1.7463 Å is close to that in **2a**, but shorter than in the five-coordinated complexes [RAl{OC(Me)CHC(Me)N(2,6-Pr₂C₆H₃)}₂] (R = Cl, Me, Et), which ranging between 1.799(9) and 1.8202(16) Å.

The structure of complex **6** was also determined by single crystal X-ray diffraction, but the data quality is poor due to the crystal quality. However, the structure has been solved and proves that the central aluminum atom is six-coordinated in the solid state as shown in **6a**. This coordination mode is different from that in the solution proved by ¹H and ²⁷Al NMR spectroscopy.

3. Experimental

3.1. General methods

All experiments were performed under nitrogen using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium (toluene),

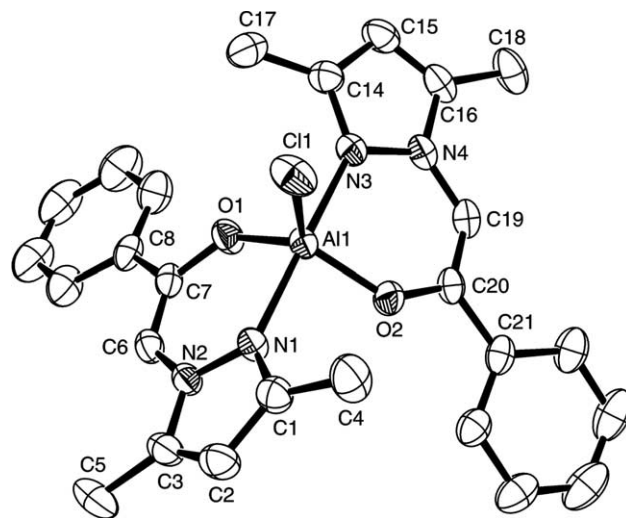


Fig. 2. ORTEP drawing of complex **5** with 30% probability thermal ellipsoids. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al1–Cl1 2.1816(9), Al1–O1 1.7468(16), Al1–N1 2.0347(18), Al1–O2 1.7459(16), Al1–N3 2.0287(19), O1–C7 1.333(3), O2–C20 1.328(2), C6–C7 1.331(3), C19–C20 1.331(3), C6–N2 1.393(3), C19–N4 1.403(3); Cl1–Al1–O1 118.82(7), Cl1–Al1–O2 117.53(7), Cl1–Al1–N1 91.95(6), Cl1–Al1–N3 91.36(6), N1–Al1–N3 176.67(8), N1–Al1–O1 90.30(8), N1–Al1–O2 87.91(8), N3–Al1–O1 87.79(8), N3–Al1–O2 90.89(8), O1–Al1–O2 123.65(9).

sodium–benzophenone (thf, Et₂O and *n*-hexane) or CaH₂ (CH₂Cl₂) and degassed prior to use. C₆D₆ were purchased from Acros Organics and stored over Na/K alloy and degassed prior to use. CDCl₃ was purchased from Acros Organics and stored over 4 Å molecular sieve. AlMe₃, AlEt₃, LiBu^{*n*} and LiHBET₃ were purchased from Alfa Aesar and used as received. 3,5-Disubstituted pyrazoles were prepared according to the literature [18]. NMR spectra were recorded on a Bruker av300 spectrometer at ambient temperature. The chemical shifts of ¹H and ¹³C NMR spectra are referenced to internal solvent resonances and the ²⁷Al NMR spectra are referenced to external AlCl₃ in D₂O. IR spectra were determined on a Bruker VECTOR-22 spectrometer. Elemental analyses were performed by the Analytical Center of University of Science and Technology of China.

3.2. Synthesis of 1-PhC(O)CH₂-3,5-Me₂C₃HN₂ (**1a**)

A mixture of 3,5-dimethylpyrazole (3.84 g, 40 mmol), PhC(O)CH₂ Br (7.96 g, 40 mmol) and Na₂CO₃ (2.12 g, 20 mmol) in a mortar was ground using a pestle for 20 min. The mixture was set aside for 4 h. The resulted solid was washed with water and dried in air to give **1a** · H₂O (6.51 g, 70%), m.p. 80–84 °C. Anal. Calc. for C₁₃H₁₆N₂O₂: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.02; H, 7.14; N, 12.03%. ¹H NMR (CDCl₃): δ 1.75 (s, 2H, H₂O), 2.16 (s, 3H, Me), 2.24 (s, 3H, Me), 5.45 (s, 2H, CH₂), 5.91 (s, 1H, CH), 7.48–7.53 (m, 2H, Ph), 7.59–7.63 (m, 1H, Ph), 7.96–7.99 (m, 2H, Ph). ¹³C NMR (CDCl₃): δ 11.14, 13.61, 55.45, 106.02, 128.27, 129.06, 134.07, 134.88, 140.69, 148.51, 192.90. IR (KBr disc): ν_{C=O} 1689 cm⁻¹. **1a** can be obtained by heating **1a** · H₂O under vacuum.

3.3. Synthesis of 1-PhC(O)CH₂-3,5-Bu^{*t*}₂C₃HN₂ (**1b**)

A mixture of 3,5-di-*tert*-butylpyrazole (1.29 g, 7.17 mmol), PhC(O)CH₂Br (1.43 g, 7.18 mmol) and Na₂CO₃ (0.38 g, 3.58 mmol) was radiated using microwave (80 W) for 15 min. The mixture was added water and extracted with Et₂O. The ether layer was dried with Na₂SO₄ and then concentrated to give **1b** with minor starting materials. The mixture was heated at 80 °C under vacuum for 1 h and then recrystallized from Et₂O to give colorless crystals of **1b** (1.66 g, 78%), m.p. 143–144 °C. Anal. Calc. for C₁₉H₂₆N₂O: C, 76.47; H, 8.78; N, 9.39. Found: C, 76.65; H, 8.98; N, 9.54%. ¹H NMR (CDCl₃): δ 1.21 (s, 9H, Bu^{*t*}), 1.22 (s, 9H, Bu^{*t*}), 5.58 (s, 2H, CH₂), 5.88 (s, 1H, CH), 7.41 (t, *J* = 7.8 Hz, 2H, Ph), 7.53 (t, *J* = 7.8 Hz, 1H, Ph), 7.85–7.88 (m, 2H, Ph). ¹³C NMR (CDCl₃): δ 30.41, 30.70, 31.38, 32.05, 57.95, 100.82, 128.12, 128.93, 133.75, 135.21, 152.21, 160.85, 193.75. IR: ν_{C=O} 1699 cm⁻¹.

3.4. Synthesis of [Me₂AlOC(Ph)CH{(3,5-Me₂-C₃HN₂)-1}] (**2a**)

A solution of **1a** (0.306 g, 1.43 mmol) in toluene (10 ml) was cooled to about –80 °C. To the solution was added AlMe₃ (2.3 M solution in hexane, 0.65 ml, 1.49 mmol) with stirring. The mixture was stirred overnight at room temperature and the resulted solution was filtered. Concentration of the filtrate afforded colorless crystals of **2a** (0.213 g, 55%), m.p. 160–162 °C. Anal. Calc. for C₁₅H₁₉N₂OAl: C, 66.65; H, 7.08; N, 10.36. Found: C, 66.48; H, 7.12; N, 10.29%. ¹H NMR (C₆D₆): δ –0.05 (s, 6H, AlMe₂), 1.47 (s, 3H, Me), 2.10 (s, 3H, Me), 5.29 (s, 1H, CH), 6.26 (s, 1H, CH), 7.25–7.35 (m, 3H, Ph), 7.96–7.99 (m, 2H, Ph). ¹³C NMR (C₆D₆): δ –8.90, 10.42, 12.32, 96.76, 106.35, 125.78, 128.53, 128.67, 138.66, 139.06, 146.31, 149.57.

3.5. Synthesis of [Me₂AlOC(Ph)CH{(3,5-Bu^{*t*}₂-C₃HN₂)-1}] (**2b**)

2b was prepared using a similar method to that for **2a**. Reaction of **1b** (0.262 g, 0.88 mmol) with AlMe₃ (2.3 M solution in hexane, 0.40 ml, 0.92 mmol) in toluene (10 ml) gave colorless crystals of **2b** (0.21 g, 68%), m.p. 144–148 °C. Anal. Calc. for C₂₁H₃₁N₂OAl: C, 71.16; H, 8.81; N, 7.90. Found: C, 70.74; H, 8.80; N, 7.79%. ¹H NMR (C₆D₆): δ 0.10 (s, 6H, AlMe₂), 1.11 (s, 9H, Bu^{*t*}), 1.41 (s, 9H, Bu^{*t*}), 6.02 (s, 1H, CH), 7.01 (s, 1H, CH), 7.22–7.34 (m, 3H, Ph), 8.06–8.09 (m, 2H, Ph). ¹³C NMR (C₆D₆): δ 1.42, 28.94, 30.98, 31.69, 32.62, 100.62, 102.77, 125.76, 128.17, 128.71, 128.88, 138.44, 150.09, 152.36, 161.33.

3.6. Synthesis of [Et₂AlOC(Ph)CH{(2,4-Me₂-C₃HN₂)-1}] (**2c**)

2c was prepared using a similar method to that for **2a**. Reaction of **1a** (0.307 g, 1.43 mmol) with AlEt₃ (1.8 M solution in hexane, 1.5 ml, 2.70 mmol) in toluene (10 ml) gave colorless crystals of **2c** (0.136 g, 32%), m.p. 102–104 °C. Anal. Calc. for C₁₇H₂₃N₂OAl: C, 68.44; H, 7.77; N, 9.39. Found: C, 68.54; H, 7.46; N, 9.54%. ¹H NMR (C₆D₆): δ 0.48–0.89 (m, 4H, AlCH₂), 1.49 (s, 3H, Me), 1.50 (t, *J* = 8.1 Hz, 6H, Me), 2.14 (s, 3H, Me), 5.35 (s, 1H, CH), 6.27 (s, 1H, CH), 7.24–7.35 (m, 3H, Ph), 7.96–7.99 (m, 2H, Ph). ¹³C NMR (C₆D₆): δ 0.99, 9.50, 10.48, 12.25, 96.76, 106.34, 125.72, 128.55, 128.69, 138.62, 139.37, 146.48, 149.92.

3.7. Synthesis of [MeAl(OC(Ph)CH{(2,4-Me₂C₃HN₂)-1})₂ · C₆H₅Me] (**4** · C₆H₅Me)

To a suspension of AlCl₃ (0.123 g, 0.92 mmol) in toluene (10 ml) was added AlMe₃ (2.3 M solution in hexane, 0.20 ml, 0.46 mmol) at room temperature with

stirring. After stirring for 4 h, the solution was cooled to about $-80\text{ }^{\circ}\text{C}$ and a solution of $[\text{LiOC}(\text{Ph})\text{CH}\{(3,5\text{-Me}_2\text{C}_3\text{HN}_2)\text{-1}\}]$ prepared from **1a** (0.59 g, 2.76 mmol) and LiBu^n (2.89 M solution in hexane, 0.95 ml, 2.76 mmol) in toluene was added. The mixture was warmed to room temperature and stirred overnight. The solution was filtered and the filtrate was concentrated to generate pale yellow crystalline $4 \cdot \text{C}_6\text{H}_5\text{Me}$ (0.306 g, 40%), m.p. $190\text{--}192\text{ }^{\circ}\text{C}$. Calc. for $\text{C}_{34}\text{H}_{37}\text{N}_4\text{O}_2\text{Al}$: C, 72.84; H, 6.65; N, 9.99. Found: C, 72.87; H, 6.45; N, 9.88%. ^1H NMR (C_6D_6): 0.04 (s, 3H, Me), 1.66 (s, 6H, Me), 2.20 (3H, PhMe), 2.68 (s, 6H, Me), 5.66 (s, 2H, CH), 6.52 (s, 2H, CH), 7.10–7.36 (m, 11H, Ph), 7.90–7.94 (m, 4H, Ph). ^{13}C NMR (C_6D_6): δ 10.60, 14.41, 21.42, 97.80, 106.41, 125.64, 125.70, 126.64, 127.85, 128.56, 129.34, 136.38, 137.90, 140.01, 146.97, 147.70.

3.8. Synthesis of $[\text{ClAl}(\text{OC}(\text{Ph})\text{CH}\{(2,4\text{-Me}_2\text{-C}_3\text{HN}_2)\text{-1}\})_2]$ (**5**)

LiBu^n (2.89 M solution in hexane, 0.97 ml, 2.80 mmol) was added to a solution of **1a** (0.60 g, 2.80 mmol) in thf (10 ml) at about $-80\text{ }^{\circ}\text{C}$ with stirring. After stirring for 4 h at room temperature, the solution was recooled to about $-80\text{ }^{\circ}\text{C}$ and AlCl_3 (0.187 g, 1.40 mmol) was added. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo and the residue was extracted with CH_2Cl_2 . The mixture was filtered and the filtrate was concentrated to about 1 ml. Several drops of Et_2O was added to form colorless crystals of **5** (0.50 g, 73%), m.p. $218\text{--}221\text{ }^{\circ}\text{C}$. Anal. Calc. for $\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_2\text{ClAl}$: C, 63.68; H, 5.36; N, 11.46. Found: C, 63.72; H, 5.41; N, 11.65%. ^1H NMR (CDCl_3): δ 2.31 (s, 6H, Me), 2.46 (s, 6H, Me), 5.97 (s, 2H, CH), 6.63 (s, 2H, CH), 7.18–7.26 (m, 6H, Ph), 7.54–7.57 (m, 4H, Ph). ^{13}C NMR (CDCl_3): δ 11.62, 14.87, 98.10, 107.36, 125.13, 128.01, 128.27, 129.22, 137.03, 138.27, 146.46, 148.33.

3.9. Synthesis of $[\text{Al}(\text{OC}(\text{Ph})\text{CH}\{(3,5\text{-Me}_2\text{-C}_3\text{HN}_2)\text{-1}\})_3 \cdot \text{C}_6\text{H}_5\text{Me}]$ (**6** · $\text{C}_6\text{H}_5\text{Me}$)

To a stirred solution of **5** (0.143 g, 0.29 mmol) in thf (10 ml) was added LiHBEt_3 (1 M solution in thf, 0.29 ml, 0.29 mmol) at about $-80\text{ }^{\circ}\text{C}$. The mixture was warmed to room temperature and stirred overnight. Solvents were removed and the residue was dissolved in toluene. The solution was filtered and the filtrate was concentrated to give colorless crystals of complex **6** · $\text{C}_6\text{H}_5\text{Me}$ (0.088 g, 59%), m.p. $194\text{--}196\text{ }^{\circ}\text{C}$. Anal. Calc. for $\text{C}_{46}\text{H}_{47}\text{N}_6\text{O}_3\text{Al}$: C, 72.80; H, 6.24; N, 11.07. Found: C, 72.67; H, 6.28; N, 10.98%. ^1H NMR (C_6D_6): 1.63–1.72 (b, 6H, Me), 1.77 (s, 3H, Me), 2.17 (s, 6H, Me), 2.20 (s, 3H, MePh), 2.30 (s, 3H, Me), 5.58 (s, 1H, CH), 5.66 (s, 2H, CH), 6.60 (s, 1H, CH),

7.09–7.23 (m, 7H, Ph + CH), 7.25 (s, 5H, Ph), 7.33 (t, $J = 7.5\text{ Hz}$, 4H, Ph), 7.87–7.90 (m, 2H, Ph), 8.01 (d, $J = 7.5\text{ Hz}$, 4H, Ph). ^{13}C NMR (C_6D_6): δ 10.91, 13.03, 14.21, 14.34, 21.42, 96.11, 98.21, 105.59, 106.95, 125.54, 125.70, 125.90, 127.37, 127.57, 127.91, 128.57, 129.34, 135.95, 136.35, 137.25, 137.90, 139.29, 141.69, 146.24, 148.12, 150.79, 151.42. ^{27}Al NMR (C_6D_6): δ 60.

Complex **6** was also obtained by reaction between lithiated **1a** and AlCl_3 . Compound **1a** (0.642 g, 3 mmol) was lithiated by reaction with LiBu^n (2.89 M in hexane, 1.04 ml, 3 mmol) in thf. The solution was cooled to about $-80\text{ }^{\circ}\text{C}$ and AlCl_3 (0.133 g, 1 mmol) was added. The mixture was warmed to room temperature and stirred overnight. Solvents were removed in vacuo and the residue was extracted with toluene. The mixture was filtered and the filtrate concentrated to afford colorless crystalline complex **6** · $\text{C}_6\text{H}_5\text{Me}$ (0.559 g, 74%).

3.10. Reaction of complex **5** with AlMe_3

To a solution of complex **5** (0.446 g, 0.91 mmol) in toluene (10 ml) was added AlMe_3 (2.3 M solution in hexane, 0.83 ml, 1.82 mmol) at room temperature with stirring. The mixture was stirred for 12 h and then

Table 1
Details of the X-ray structure determinations of complexes **2a** and **5**

	2a	5
Empirical formula	$\text{C}_{15}\text{H}_{19}\text{N}_2\text{OAl}$	$\text{C}_{26}\text{H}_{26}\text{ClN}_4\text{O}_2\text{Al}$
FW	270.30	488.94
Crystal system	Orthorhombic	Triclinic
Space group	$Pnma$	$P\bar{1}$
a (Å)	9.3911(16)	9.6016(16)
b (Å)	7.2864(19)	9.7544(16)
c (Å)	22.101(6)	13.453(2)
α (°)	90	83.340(2)
β (°)	90	85.521(3)
γ (°)	90	83.632(3)
V (Å ³)	1512.3(6)	1241.0(4)
Z	4	2
D_{calc} (g/cm ³)	1.187	1.308
$F(000)$	576	512
μ (mm ⁻¹)	0.128	0.220
θ range for data collections (°)	1.84 to 25	1.53 to 26.36
Number of reflections collected	7372	7161
Number of independent reflections (R_{int})	1448 (0.0496)	4982 (0.0200)
Number of data/restraints/parameters	1448/0/115	4982/0/311
Goodness-of-fit on F^2	1.150	1.025
Final R indices ^a [$I > 2\sigma(I)$]	$R_1 = 0.0482$ $wR_2 = 0.1341$	$R_1 = 0.0447$ $wR_2 = 0.1144$
R indices (all data)	$R_1 = 0.0812$ $wR_2 = 0.1759$	$R_1 = 0.0713$ $wR_2 = 0.1344$
Largest difference peak and hole (e · Å ⁻³)	0.248 and -0.336	0.185 and -0.214

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

filtered. The filtrate was concentrated to form colorless crystalline complex **2a** (0.272 g, 55%).

The similar reaction of complex **5** (0.17 g, 0.35 mmol) with an equiv of AlMe₃ (2.3 M solution in hexane, 0.16 ml, 0.35 mmol) gave colorless crystals (0.086 g) identified by NMR spectroscopy as a mixture of **2a** and **7**. The ratio of **2a** to **7** is about 3.6:1.

3.11. X-ray crystallography

Single crystals of complexes **2a** and **5** were mounted in Lindemann Capillaries under nitrogen. Diffraction data were collected on a Siemens CCD area-detector with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods using SHELXS-97 [19] and refined against F^2 by full-matrix least-squares using SHELXL-97 [20]. Crystal data and experimental details of the structure determinations are listed in Table 1.

4. Supplementary materials

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 266571 and 266572 for **2a** and **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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