Synthesis and characterization of lithium, aluminium and zinc complexes supported by pyrazolyl-based N,N′-chelate ligands†

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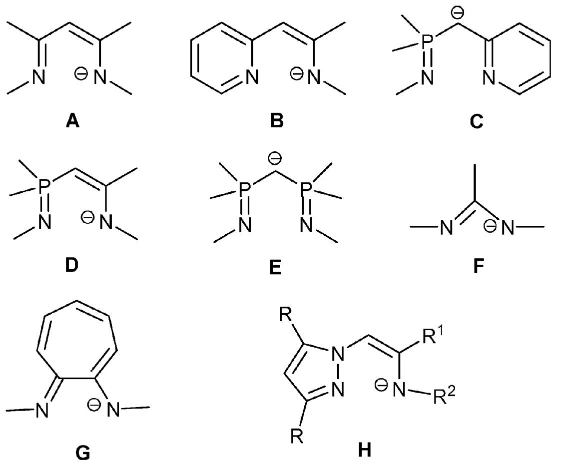
A series of lithium, aluminium and zinc complexes bearing $[3,5\text{-}R_2C_3HN_2CHC(R^1)N(R^2)]^-$ ligands were synthesized and characterized. Treatment of 1-(Me_3SiCH_2)-3,5-$R_2C_3HN_2$ (R = Me, Bu^t) with LiBu^n and then $\mathrm{Bu}^t\mathrm{CN}$ afforded $[\mathrm{Li}\{\mathrm{N}(\mathrm{SiMe_3})\mathrm{C}(\mathrm{Bu}^t)\mathrm{CHN_2C_3HR_2}\text{-}3,5\}]_2$ (R = Me, **2a**; R = Bu^t, **2b**). Reaction of both **2a** and **2b** with $ZnCl_2$ gave zinc complexes $[\mathrm{Zn(Cl)}\{\mathrm{N(SiMe_3)C(Bu}^t\mathrm{)CHN_2C_3HR_2}\text{-}3,5\}]_2$ (R = Me, **3a**; R = Bu^t, **3b**). Treatment of *o*-$RC_6H_4NHC(Ph)CHN_2C_3HMe_2$-3,5 (R = OPr^i, **5a**; R = Me, **5b**) with LiBu^n yielded lithium complexes similar to **2a** or **2b**, [Li{N(*o*-RC_6H_4)C(Ph)-$CHN_2C_3HMe_2$-3,5}] (R = OPr^i, **6a**; R = Me, **6b**). Reaction of **6b** with $ZnCl_2$ generated zinc complexes [Zn(Cl){N(*o*-MeC_6H_4)C(Ph)$CHN_2C_3HMe_2$-3,5}] (**7**), and with $AlCl_3$ gave [Al(Cl_2){N(*o*-MeC_6H_4)C(Ph)$CHN_2C_3HMe_2$-3,5}] (**8**). Reaction of **5a** with $ZnEt_2$ produced [Zn{N(*o*-$\mathrm{Pr}^iC_6H_4$)C(Ph)$CHN_2C_3HMe_2$-3,5}$_2$] (**9**). Reaction of **5a** and **5b** with AlR'_3 (R′ = Me, Et) afforded aluminium complexes [Al(R'_2){N(*o*-RC_6H_4)C(Ph)$CHN_2C_3HMe_2$-3,5}] (R = OPr^i, R′ = Me, **10a**; R = Me, R′ = Me, **10b**; R = OPr^i, R′ = Et, **10c**; R = Me, R′ = Et, **10d**). A trace of species [Al(Et_2){N(*o*-MeC_6H_4)C(Ph)(Et)$CH_2N_2C_3HMe_2$-3,5}] (**11**) was also isolated from the reaction products of **5b** and $AlEt_3$. All of new compounds were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analyses. Structures of complexes **2a**, **8**, **10a**, **10d** and **11** were additionally characterized by single-crystal X-ray diffraction techniques.

Introduction

Anionic, N,N′-chelate ligands have attracted considerable attention in coordination and organometallic chemistry. The ligands as shown in Scheme 1 (**A–G**)[1–7] can stabilize various metal ions, including those with unusual oxidation states such as Mg(I)[8] and Zn(I).[9] Some of their metal complexes also show excellent catalytic properties in small molecule activation,[10] olefin polymerization[11] and the ring-opening polymerization (ROP) of cyclic esters such as ε-caprolactone and lactides.[12] For example, zinc and magnesium complexes (BDI)MOR [BDI = HC{CMeN-2,6-$^i\mathrm{Pr_2C_6H_3}$}$_2$)] are highly stereoselective initiators for the ring-opening polymerization of lactide. They exhibit high activity and good control for the conversion of *rac*-lactide into heterotactic polylactide *via* the alternating incorporation of the two monomer enantiomers.[12d–f] We have become interested in devising new N,N′-ligands that offer different steric environments and electronic characteristics, and studying synthesis and catalysis of metal complexes bearing the ligands. In this paper, we wish to describe a novel N,N′-chelate ligand which possesses a pyrazolyl as part of the ligand backbone (**H** in Scheme 1), and synthesis and characterization of lithium, aluminium and zinc complexes supported by this ligand.

Results and discussion

Synthesis of 1-trimethylsilyl-3-(pyrazol-1-yl)-1-azaallyl ligands and their lithium and zinc complexes **2a–3b** is shown in Scheme 2. Treatment of 1,3,5-trimethylpyrazole or 1-methyl-3,5-di-*tert*-butylpyrazole with LiBu^n and then Me_3SiCl gave 1-(Me_3SiCH_2)-3,5-$R_2C_3HN_2$ (R = Me, **1a**; R = Bu^t, **1b**). Reaction of **1a** or **1b** with LiBu^n and then $\mathrm{Bu}^t\mathrm{CN}$ afforded $[\mathrm{Li}\{\mathrm{N(SiMe_3)C(Bu}^t\mathrm{)CHN_2C_3HR_2}\text{-}3,5\}]_2$ (R = Me, **2a**; R = Bu^t, **2b**). In the reaction of the lithiated **1a** or **1b** with $\mathrm{Bu}^t\mathrm{CN}$, a 1,3-trimethylsilyl C → N migration was observed. Similar migration of trimethylsilyl has been



Scheme 1

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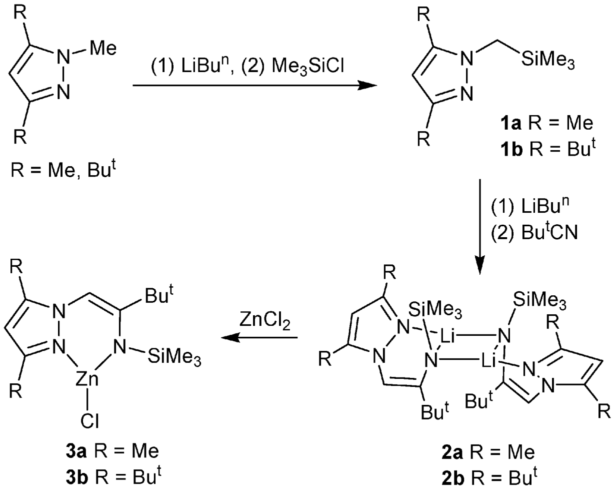


Scheme 2 Synthesis of 1-trimethylsilyl-3-(pyrazol-1-yl)-1-azaallyl-lithium and -zinc complexes.

reported previously.[2a,13] Reaction of **2a** and **2b** with an equiv. of $ZnCl_2$ afforded corresponding zinc complexes $[Zn(Cl)\{N(SiMe_3)C(Bu^t)CHN_2C_3HR_2\text{-}3,5\}]$ (**3a**, R = Me; **3b**, R = Bu^t).

Colorless oily compound **1a** has been reported previously,[14] and was characterized by ^1H and ^{13}C NMR spectra and HR-MS. Compound **1b** occurs as colorless crystals and was characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. Both **2a** and **2b** are air-sensitive colorless crystals and were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analyses. The NMR spectra showed no coordinated solvent molecules in the complexes. Single-crystal X-ray diffraction analysis of **2a** proved that it is a dimer in the solid state. Complex **2b** is expected to have the same structural mode. The ORTEP drawing of **2a** is presented in Fig. 1, along with selected bond lengths and angles. In the molecule the lithium atoms are bridged by the amido nitrogen atoms and the molecule lies about a twofold axis. The central Li_2N_2 ring is planar, with the angle at N [74.8(2)°] narrower than that at Li [105.2(2)°]. The three-coordinate lithium atoms are planar, the sum of the angles at Li being 360°. The two $SiMe_3$ groups lie on the same side of the central Li_2N_2 plane. Such cisoid structures are relatively rare in alkali metal amide chemistry although several examples have been reported.[15,16] Amido or N,N′-chelate amido lithium dimers usually adopt transoid arrangement of the amido moieties relative to the central Li_2N_2 ring.[1] For example, each of $[Li\{N(SiMe_3)C(Ph)C(H)C(R)N(SiMe_3)\}]_2$ (R = Ph, Bu^t),[17] $[Li\{N(SiMe_3)C(Ph)C(H)C_5H_4N\text{-}2\}]_2$[2a] and $[Li(tmsaq)]_2$ [tmsaq = (8-quinolyl)trimethylsilylamido][18] shows transoid conformation, being centrosymmetric dimers. In addition, the solution ^1H NMR spectrum of **2a** at room temperature exhibited only one set of signals. This showed that the solution-state structure is consistent with that observed in the solid state, rather than an equilibrium between the cisoid and transoid conformations.

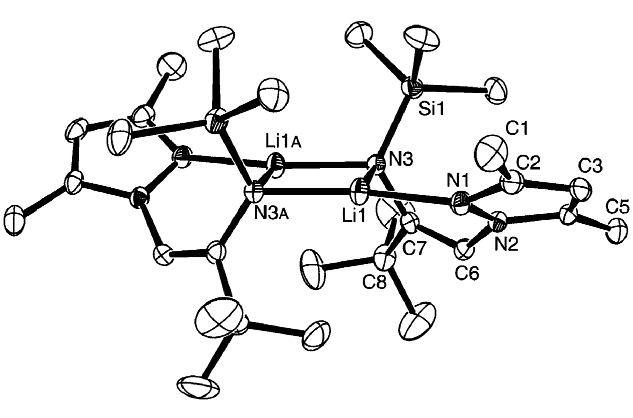
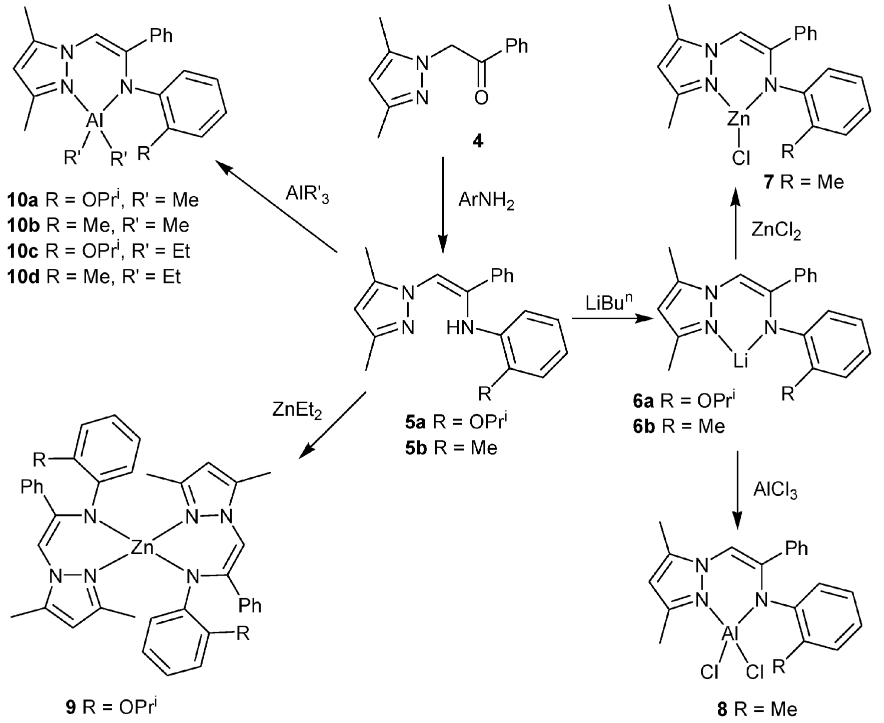


Fig. 1 ORTEP drawing of complex **2a** (20% probability thermal ellipsoids), the additional "A" letters in the atom labels indicate that these atoms are at equivalent position (1 − *x*, *y*, 1/2 − *z*). Selected bond lengths (Å) and angles (°): Li1–N1 1.992(4), Li1–N3 2.091(5), Li1A–N3 2.013(4), Li1···Li1A 2.493(8), C6–C7 1.354(3), N3–C7 1.397(3), N2–C6 1.428(3); N3–Li1–N3A 105.20(19), Li1–N3–L1A 74.80(19), N1–Li1–N3 98.1(2), N1–Li1–N3A 156.7(3).

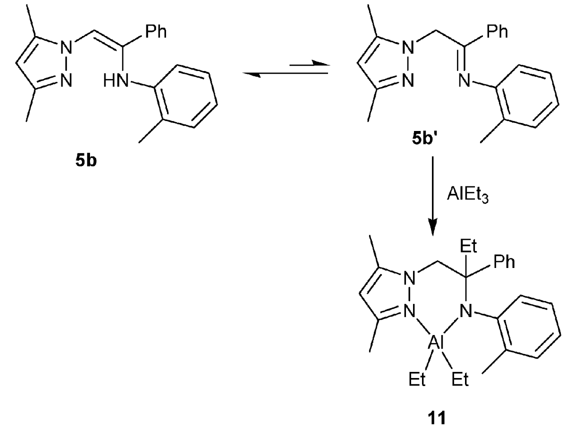
The Li1–N3 distance of 2.091(5) Å in crystalline **2a** is longer than the corresponding ones in $[Li\{N(SiMe_3)C(Ph)C(H)C(Ph)N(SiMe_3)\}]_2$ [1.965(9) Å] and $[Li\{N(SiMe_3)C(Ph)C(H)C_5H_4N\text{-}2\}]_2$ [2.012(9) Å]. The Li1A–N3 distance of 2.013(4) Å is shorter than those in $[Li\{N(SiMe_3)C(Ph)C(H)C(Ph)N(SiMe_3)\}]_2$ [2.095(2) Å] and $[Li\{N(SiMe_3)C(Ph)C(H)C_5H_4N\text{-}2\}]_2$ [2.032(6) Å]. The Li1–N1 distance of 1.992(4) Å is longer than the pyridyl nitrogen–Li distance in $[Li\{N(SiMe_3)C(Ph)C(H)C_5H_4N\text{-}2\}]_2$ [1.968(6) Å].[2a] The C6–C7 distance of 1.354(3) Å shows that it is an olefinic bond.

Complexes **3a** and **3b** are colorless (**3a**) or pale yellow (**3b**) crystals, very soluble in CH_2Cl_2 and soluble in toluene. Each of them gave satisfactory elemental analysis. The ^1H and ^{13}C NMR spectral data are consistent with their respective structure. However, we can not judge which aggregate mode they adopt, monomer or dimer, based on the data.

Synthesis of 1-aryl-3-(pyrazol-1-yl)-1-azaallyl ligands and their lithium, aluminium and zinc complexes is summarized in Scheme 3. Reaction of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-phenylethanone with *o*-$RC_6H_4NH_2$ (R = OPr^i or Me) in the presence of 4A molecular sieves and acid catalyst yielded 1-{*o*-$RC_6H_4NHC(Ph)CH$}-3,5-$Me_2C_3HN_2$ (R = OPr^i, **5a**, HL; R = Me, **5b**, HL′). Reaction of **5a** and **5b** with $LiBu^n$ afforded [LiL] (**6a**) and [LiL′] (**6b**), respectively. Treatment of **6b** with an equiv. of $ZnCl_2$ gave [Zn(Cl)L′] (**7**), and with an equiv. of $AlCl_3$ generated $[Al(Cl_2)L']$ (**8**). Reaction of **5a** with 0.5 equiv. of $ZnEt_2$ formed $[ZnL_2]$ (**9**). Attempts to prepare [Zn(Et)L] or [Zn(Et)L′] by reaction of **5a** or **5b** with an equiv. of $ZnEt_2$ were unsuccessful. The reaction gave a mixture under various conditions. Treatment of **5a** with an equiv. of AlR_3 (R = Me, Et) produced [Al(Me)L] (**10a**) and [Al(Et)L] (**10c**), respectively. Similar reaction between **5b** and $AlMe_3$ afforded **10b**, while with $AlEt_3$ gave [Al(Et)L′] (**10d**) and a trace of **11** as identified by single-crystal X-ray diffraction. Formation of complex **11** may be through addition of Et^- of $AlEt_3$ to the C=N double bond of **5b**′ (Scheme 4). Compounds **5a–11** were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analyses. The NMR spectra of **5a** and **5b** showed that both exist in an enamine form. For example, the ^1H NMR spectra of **5a** and **5b** exhibited NH signals at δ 10.05 and 9.93 ppm, respectively, no CH_2 signals of imine being



Scheme 3 Synthesis of 1-aryl-3-(pyrazol-1-yl)-1-azaallyl-lithium, -aluminium and -zinc complexes.



Scheme 4 Formation of complex **11**.

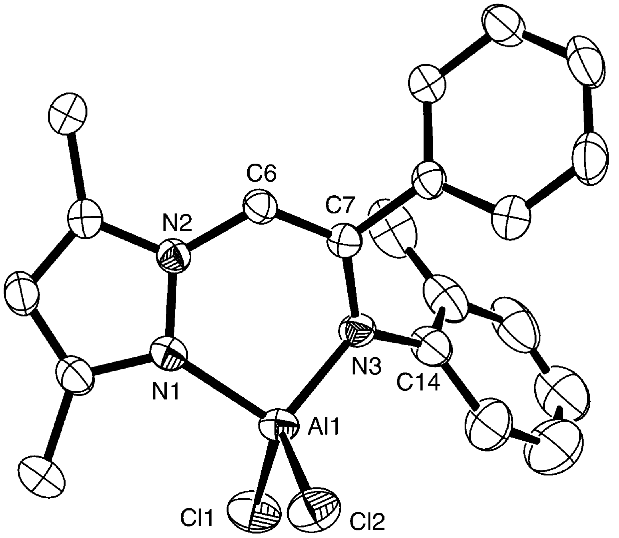


Fig. 2 ORTEP drawing of complex **8** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.890(2), Al(1)–N(3) 1.814(2), Al(1)–Cl(2) 2.1125(11), Al(1)–Cl(1) 2.1190(12), C(6)–C(7) 1.335(3), N(3)–C(7) 1.392(3); N(1)–Al(1)–N(3) 98.43(10), N(3)–Al(1)–Cl(2) 115.71(9), N(1)–Al(1)–Cl(2) 108.82(8), N(3)–Al(1)–Cl(1) 113.68(9), N(1)–Al(1)–Cl(1) 109.33(9), Cl(2)–Al(1)–Cl(1) 110.07(5), C(7)–N(3)–Al(1) 120.34(17), C(6)–C(7)–N(3) 123.4(2), C(7)–C(6)–N(2) 125.8(2).

observed. Hence, in the solution of **5a** and **5b** the imine forms must exist in an extremely small amount. Each of the ^{1}H NMR spectra of complexes **6a** and **9** displayed two doublets of the methyl groups of Pr^{i}O, showing the two methyls to be in different chemical environments. The NMR spectra of **7** displayed the existence of each group in the complex. However, as mentioned for **3a** and **3b**, we can not judge its aggregate mode based on the determined data.

Crystal structures of complexes **8**, **10a**, **10d** and **11** were determined by single-crystal X-ray diffraction techniques. The ORTEP drawing of complex **8** is presented in Fig. 2, along with selected bond lengths and angles. The crystalline molecule is monomeric and the central aluminium atom exhibits a distorted tetrahedral geometry. N2–C6–C7–N3 atoms are approximately co-planar, the torsion angle being 0.9°. The aluminium atom is out of the plane. The Al–N1 distance [1.890(2) Å] is shorter than the distance of Al–N (pyrazolyl) in [Al(Me$_2$){N(CH$_2$)$_2$N$_2$C$_3$Me$_2$-3,5}$_2$] [2.0025(10) Å][19] and comparable to that of Al–N (pyrazolyl) in [(η^1,η^1-3,5-Bu$^t_2$C$_3$HN$_2$)(μ-Al)Cl$_2$]$_2$ [1.904(2) Å].[20] The Al–N2 distance of 1.814(2) Å is shorter than most Al–N (amide) distances in four-coordinate aluminium complexes, but still within the

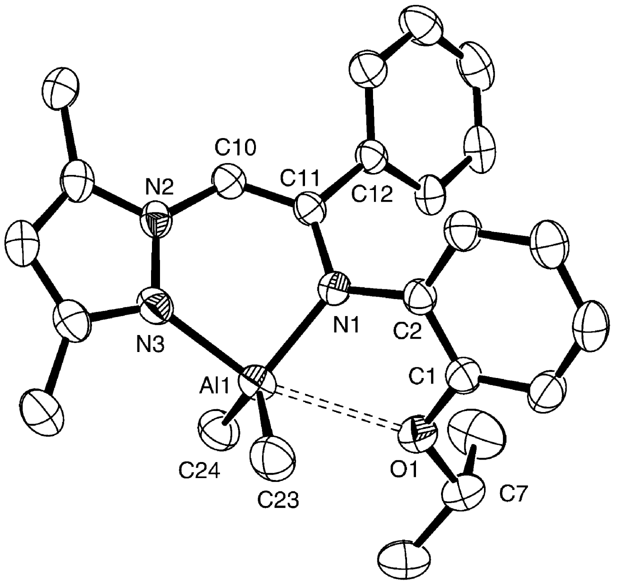


Fig. 3 ORTEP drawing of complex **10a** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.882(2), Al(1)–N(3) 1.994(2), Al(1)–C(24) 1.961(3), Al(1)–C(23) 1.962(3), Al(1)$\cdots$O(1) 2.675(2), C(10)–C(11) 1.339(3); N(1)–Al(1)–N(3) 92.70(9), N(1)–Al(1)–C(24) 118.70(12), N(1)–Al(1)–C(23) 112.53(12), C(24)–Al(1)–C(23) 121.52(14), C(24)–Al(1)–N(3) 99.25(12), C(23)–Al(1)–N(3) 104.75(13), N(1)–Al(1)–O(1) 68.45(8), 1.48(11), N(3)–Al(1)–O(1) 161.10(8).

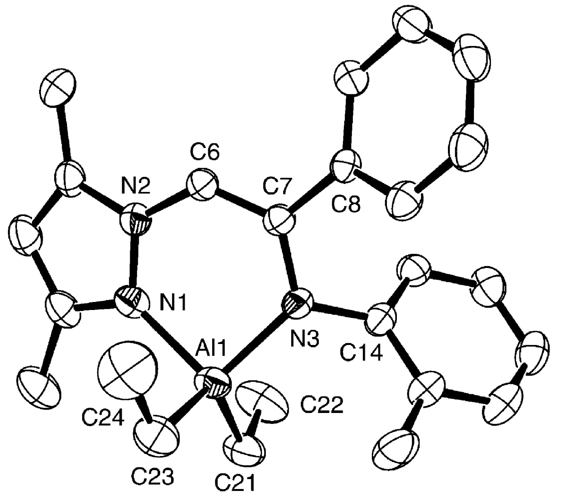


Fig. 4 ORTEP drawing of complex **10d** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.945(3), Al(1)–N(3) 1.877(3), Al(1)–C(23) 1.956(4), Al(1)–C(21) 1.965(4), C(6)–C(7) 1.346(4); N(1)–Al(1)–N(3) 95.04(13), N(3)–Al(1)–C(23) 115.94(18), N(1)–Al(1)–C(23) 103.00(17), N(3)–Al(1)–C(21) 110.28(16), N(1)–Al(1)–C(21) 108.96(17), C(23)–Al(1)–C(21) 119.98(19).

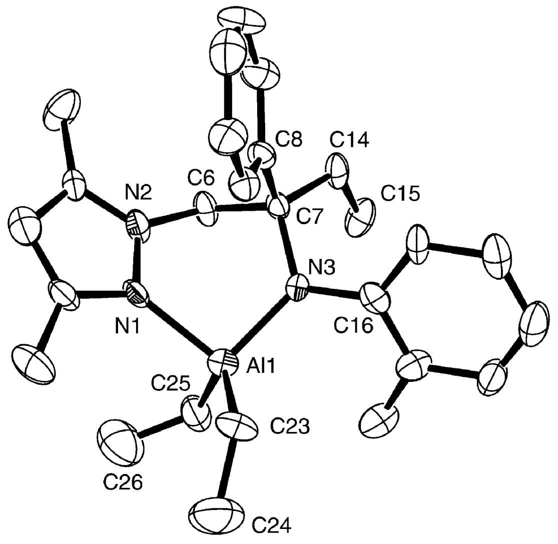


Fig. 5 ORTEP drawing of complex **11** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.939(5), Al(1)–N(3) 1.857(5), Al(1)–C(23) 1.978(7), Al(1)–C(25) 1.998(7), C(6)–C(7) 1.535(7), N(3)–C(7) 1.507(6); N(1)–Al(1)–N(3) 96.0(2), N(3)–Al(1)–C(23) 109.2(3), N(1)–Al(1)–C(23) 109.4(3), N(3)–Al(1)–C(25) 117.7(3), N(1)–Al(1)–C(25) 100.9(3), C(23)–Al(1)–C(25) 120.0(3), C(7)–N(3)–Al(1) 122.3(4), N(3)–C(7)–C(6) 106.2(5), N(2)–C(6)–C(7) 112.9(4).

normal range.[21] The N1–Al1–N3 angle of 98.43(10)° is slightly wider than those found in $[Al(Me_2)\{N(CH_2)_2N_2C_3Me_2\text{-}3,5\}_2]$ [95.02(4)°][19] and in aluminium diketiminate complexes.[22]

The ORTEP drawing of complex **10a** is presented in Fig. 3, along with selected bond lengths and angles. The crystalline **10a** is monomeric. The N2–C10–C11–N1 atoms are not co-planar. However, the C10–C11 distance of 1.339(3) Å shows that it is a double bond. The Al1–O1 distance of 2.675(2) Å is much shorter than the sum of van der Waals radii of Al and O (3.52 Å).[23] Hence there must be a strong interaction between the two atoms. The Al–N distances are longer than corresponding those in complex **8**. The N1–Al1–N3 angel is narrower [92.70(9)°] than that of complex **8** [98.43(10)°]. This may be caused partly by the Al–O interaction.

The ORTEP drawing of complex **10d** is presented in Fig. 4, along with selected bond lengths and angles. The molecule is monomeric and the central aluminium atom exhibits a distorted tetrahedral geometry. The structural skeleton is similar to that of **8**. The Al–N distances are longer than the corresponding ones in complex **8**. The N1–Al1–N3 angle [95.04(13)°] is slightly narrower than that in **8**. These are evidently caused by different coordination atoms except for the 3-(pyrazol-1-yl)-1-azaallyl ligand.

The ORTEP drawing of complex **11** is presented in Fig. 5, along with selected bond lengths and angles. The molecule is monomeric in the solid state. The central metal ring N1N2C6C7N3Al1 displays a twist geometry. The aluminium atom is four coordinate with a distorted tetrahedral geometry. The C7 atom is also tetrahedral. The C6–C7 distance of 1.535(7) Å is indicative of a C–C single bond. The Al–N distances are a little shorter than the corresponding ones in **10d**. The N–Al–N angle [96.0(2)°] is close to that of **10d** [95.04(13)°]. The C–Al–C angle [120.0(3)°] is almost same as that of **10d** [119.98(19)°].

Conclusions

New N,N′-chelate lithium complexes have been prepared by either reaction of (trimethylsilyl)(3,5-trimethyl-pyrazol-1-yl)methyllithium with Bu^{t}CN or lithiation of

N-aryl-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-phenylethenamines. Ligand transfer reactions or reactions of *N*-aryl-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-phenylethenamines with AlR_3 (R = Me, Et) or $ZnEt_2$ led to a series of N,N′-chelate aluminium and zinc complexes. Single-crystal X-ray diffractions established molecular structures of **2a**, **8**, **10a**, **10d** and **11**. The lithium complex, $[Li\{N(SiMe_3)C(Bu^t)CHN_2C_3HMe_2\text{-}3,5\}]_2$, exhibits different structural features from the related N,N′-chelate lithium dimers, the two $SiMe_3$ groups lying the same side of the plane consisting of the lithium atoms and the bridging nitrogen atoms, and the three-coordinate lithium atom having a planar geometry.

Experimental

All reactions were performed under nitrogen atmosphere using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium (toluene) or sodium/benzophenone (THF, Et_2O and hexane) and degassed prior to use. 1,3,5-trimethylpyrazole, 1-methyl-3,5-di-*tert*-butylpyrazole and 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-phenylethanone were prepared according to literature.[24,25] $AlMe_3$, $AlEt_3$, $ZnEt_2$ and $LiBu^n$ were purchased from Alfa Aesar or Acros Organics and used as received. $CDCl_3$ and C_6D_6, purchased from Cambridge Isotope Laboratories, Inc., were degassed and stored over 4A molecular sieves ($CDCl_3$) or Na/K alloy (C_6D_6). NMR spectra were recorded on a Bruker av300 spectrometer at ambient temperature. The chemical shifts of the ^1H and ^{13}C NMR spectra were referenced to TMS or internal solvent resonances. HR-MS data were recorded on an Agilent6890/Micromass GCT-MS spectrometer. Elemental analyses were performed by the Analytical Center of University of Science and Technology of China.

Preparations

$1\text{-}(Me_3SiCH_2)\text{-}3,5\text{-}Me_2C_3HN_2$ (1a). To a solution of 1,3,5-trimethylpyrazole (5.50 g, 49.93 mmol) in THF (25 cm^3) was added dropwise $LiBu^n$ (20 cm^3 of a 2.5 M solution in hexane, 50 mmol) at about −80 °C with stirring. The mixture was warmed to room temperature and stirred for 6 h. The resulting solution was re-cooled to about −80 °C and Me_3SiCl (5.50 g, 50.62 mmol) was added dropwise. The solution was warmed to room temperature and stirred overnight. Solvents were removed by rotary evaporation and the residue was extracted with CH_2Cl_2 (2 × 20 cm^3). The extract was filtered and the solvent was removed from the filtrate by rotary evaporation. The residue was distilled under reduced pressure to give colorless oil (7.11 g, 78%), bp 83–86 °C/20 mmHg. δ_H (300 MHz; $CDCl_3$) 0.05 (9 H, s, $SiMe_3$), 2.12 (3 H, s, Me), 2.16 (3 H, s, Me), 3.46 (2 H, s, CH_2), 5.69 (1 H, s, CH). δ_C (75.5 MHz; $CDCl_3$) −1.80, 11.52, 13.58, 40.12, 104.05, 138.14, 146.14. HR-MS (EI): *m*/*z* 182.1234 $[M]^+$, calc. 182.1239.

$1\text{-}(Me_3SiCH_2)\text{-}3,5\text{-}Bu^t_2C_3HN_2$ (1b). Synthesis of **1b** followed a similar procedure to **1a**. Thus, to a solution of 1-methyl-3,5-di-*tert*-butylpyrazole (4.00 g, 20.58 mmol) in THF (25 cm^3) was added dropwise $LiBu^n$ (8.5 cm^3 of a 2.5 M solution in hexane, 21.25 mmol) at about −80 °C with stirring. The mixture was warmed to room temperature and stirred for 6 h. The resulting solution was re-cooled to about −80 °C and Me_3SiCl (3.80 g, 35 mmol) was added dropwise. The solution was warmed to room temperature and stirred overnight. Solvents were removed by rotary evaporation and the residue was extracted with CH_2Cl_2 (2 × 20 cm^3). The extract was filtered and the solvent was removed from the filtrate by rotary evaporation. The residue was distilled under reduced pressure to give a colorless oil (4.17g, 76 %), bp 110–112 °C/20 mmHg (Found: C, 67.69; H, 11.24; N, 10.71. $C_{15}H_{30}N_2Si$ requires C, 67.60; H, 11.35; N, 10.51%). δ_H (300 MHz; $CDCl_3$) 0.15 (9 H, s, $SiMe_3$), 1.25 (9 H, s, Bu^t), 1.35 (9 H, s, Bu^t), 3.61 (2 H, s, CH_2), 5.77 (1 H, s, CH). δ_C (75.5 MHz; $CDCl_3$) −0.96, 29.83, 30.76, 31.17, 31.88, 39.08, 99.73, 150.95, 159.44.

$[Li\{N(SiMe_3)C(Bu^t)CHN_2C_3HMe_2\text{-}3,5\}]$ (2a). To a solution of **1a** (3.60 g, 19.74 mmol) in toluene (20 cm^3) was added dropwise $LiBu^n$ (7.9 cm^3 of a 2.5 M solution in hexane, 19.75 mmol) at about −80 °C with stirring. The mixture was warmed to room temperature and stirred for 6 h. The resulting solution was re-cooled to about −80 °C and Bu^tCN (1.70 g, 20.45 mmol) was added dropwise. The solution was stirred overnight at room temperature and then filtered. The filtrate was concentrated to afford colorless crystals (3.81 g, 71%), mp 190–192 °C (Found: C, 61.71; H, 9.63; N, 15.14. $C_{14}H_{26}N_3LiSi$ requires C, 61.96; H, 9.66; N, 15.48%). δ_H (300 MHz; C_6D_6) 0.18 (9H, s, $SiMe_3$), 1.33 (9H, s, Bu^t), 1.87 (3H, s, Me), 2.27 (3H, s, Me), 5.61 (1H, s, CH), 6.02 (1H, s, CH). δ_C (75.5 MHz; C_6D_6) 3.19, 11.36, 13.77, 30.77, 38.80, 104.71, 104.92, 140.18, 146.99, 164.15.

$[Li\{N(SiMe_3)C(Bu^t)CHN_2C_3HBu^t_2\text{-}3,5\}]$ (2b). Synthesis of **2b** followed a similar procedure to that of **2a**. Thus, to a solution of **1b** (2.66 g, 9.98 mmol) in toluene (15 cm^3) was added dropwise $LiBu^n$ (4 cm^3 of a 2.5 M solution in hexane, 10 mmol) at about −80 °C with stirring. The mixture was warmed to room temperature and stirred for 6 h. The resulting solution was re-cooled to about −80 °C and Bu^tCN (0.85 g, 10.22 mmol) was added dropwise. The solution was stirred overnight at room temperature and then filtered. The filtrate was concentrated to afford colorless crystals of **2b** (2.38 g, 67%), mp 154–156 °C (Found: C, 67.62; H, 10.75; N, 11.75. $C_{20}H_{38}LiN_3Si$ requires C, 67.56; H, 10.77; N, 11.82%). δ_H (300 MHz; C_6D_6) 0.21 (9H, s, $SiMe_3$), 1.30 (9H, s, Bu^t), 1.37 (9H, s, Bu^t), 1.47 (9H, s, Bu^t), 6.00 (1H, s, CH), 6.52 (1H, s, CH). δ_C (75.5 MHz; C_6D_6) 5.24, 29.82, 31.05, 31.35, 31.42, 31.82, 39.08, 100.65, 108.33, 151.86, 159.70, 159.83.

$[Zn(Cl)\{N(SiMe_3)C(Bu^t)CHN_2C_3HMe_2\text{-}3,5\}]$ (3a). To a solution of $ZnCl_2$ (0.20 g, 1.47 mmol) in THF (10 cm^3) was added a solution of complex **2a** (0.37 g, 1.36 mmol) in THF (10 cm^3) at about −80 °C with stirring. The mixture was warmed to room temperature and stirred overnight. Solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2. The solution was filtered and the filtrate was added toluene. The resulting solution was concentrated to give colorless crystals (0.43 g, 86%), mp 118–120 °C (Found: C, 43.03; H, 6.98; N, 10.12. $C_{14}H_{26}ClN_3SiZn\cdot 0.5CH_2Cl_2$ requires C, 42.71; H, 6.67; N, 10.30%). δ_H (300 MHz; C_5D_5N) 0.32

(9H, s, $SiMe_3$), 1.04 (9H, s, Bu^t), 2.24 (3H, s, Me), 2.59 (3H, s, Me), 6.05 (1H, s, CH), 6.33 (1H, s, CH). δ_C (75.5 MHz; C_5D_5N) 4.03, 11.06, 13.24, 28.71, 29.81, 38.01, 105.05, 107.09, 141.38, 165.36.

[Zn(Cl){N(SiMe$_3$)C(Bu^t)CHN$_2$C$_3$HBu$^t_2$-3,5}] (3b). To a solution of $ZnCl_2$ (0.16 g, 1.17 mmol) in THF (10 cm^3) was added a solution of complex **2b** (0.40 g, 1.12 mmol) in THF (5 cm^3) at about −80 °C with stirring. The mixture was warmed to room temperature and stirred overnight. Solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2. The solution was filtered and the filtrate was added toluene. The resulting mixture was concentrated to give a pale yellow solid identified as **3b**·0.15CH_2Cl_2 (0.41 g, 79%), mp 132–134 °C (Found: C, 52.25; H, 8.36; N, 9.32. $C_{20}H_{38}ClN_3SiZn\cdot 0.15CH_2Cl_2$ requires C, 52.36; H, 8.35; N, 9.09%). δ_H (300 MHz; C_6D_6) −0.08 (9H, s, $SiMe_3$), 1.21 (9H, s, Bu^t), 1.38 (9H, s, Bu^t), 1.45 (9H, s, Bu^t), 5.96 (1H, s, CH), 6.30 (1H, s, CH). δ_C (75.5 MHz; C_6D_6) 3.97, 29.40, 30.41, 31.13, 32.01, 32.43, 38.26, 77.37, 100.65, 153.55, 161.66, 162.76.

***o*-Pr^{i}OC$_6$H$_4$NHC(Ph)CHN$_2$C$_3$HMe$_2$-3,5 (5a).** A mixture of 1-PhC(O)CH_2-3,5-$Me_2C_3HN_2$ (1.57 g, 7.33 mmol), *o*-$Pr^iOC_6H_4NH_2$ (1.67 g, 11.04 mmol), 4A molecular sieves (10 g), toluene (30 cm^3) and three drops of HCO_2H was refluxed for 16 h. The mixture was cooled to room temperature and filtered. The molecular sieves were washed with CH_2Cl_2. Volatiles were removed *in vacuo*. The residue was dissolved in Et_2O. The solution was concentrated to form colorless crystals of **5a** (1.78 g, 70%), mp 126–128 °C (Found: C, 76.15; H, 7.29; N, 12.22. $C_{22}H_{25}N_3O$ requires C, 76.05; H, 7.25; N, 12.09%). δ_H (300 MHz; $CDCl_3$) 1.02 (6H, d, J = 6 Hz, Pr^i), 1.45 (3H, s, Me), 2.04 (3H, s, Me), 4.04–4.12 (1H, m, Pr^i), 5.37 (1H, s, CH), 5.65 (1H, s, CH), 6.14 (1H, d, J = 7.8 Hz, Ar), 6.24 (1H, t, J = 7.8 Hz, Ph), 6.33–6.44 (2H, m, Ar), 6.72–6.85 (3H, m, Ar), 7.22–7.24 (2H, m, Ar), 10.05 (1H, s, NH). δ_C (75.5 MHz; $CDCl_3$) 11.12, 13.63, 22.41, 55.42, 70.77, 105.95, 113.82, 115.45, 118.46, 121.23, 128.21, 129.02, 134.04, 134.78, 137.46, 140.60, 145.50, 148.44, 192.85.

***o*-MeC$_6$H$_4$NHC(Ph)CHN$_2$C$_3$HMe$_2$-3,5 (5b).** Synthesis of **5b** followed a similar procedure to that of **5a**. Thus, a mixture of 1-PhC(O)CH_2-3,5-$Me_2C_3HN_2$ (3.39 g, 15.8 mmol), *o*-$MeC_6H_4NH_2$ (2.54 g, 23.7 mmol), 4A molecular sieves (10 g), toluene (30 cm^3) and several drops of HCO_2H was refluxed for 12 h. The mixture was cooled to room temperature and filtered. The molecular sieves were washed with CH_2Cl_2. Volatiles were removed by rotary distillation. The residue was dissolved in Et_2O. The solution was concentrated to form colorless crystals (3.56 g, 74%), mp 105–107 °C (Found: C, 78.80; H, 6.94; N, 14.10. $C_{20}H_{21}N_3$ requires C, 79.17; H, 6.98; N, 13.85%). δ_H (300 MHz; $CDCl_3$) 1.45 (3H, s, Me), 1.88 (3H, s, Me), 2.24 (3H, s, Me), 5.32 (1H, s, CH), 5.71 (1H, s, CH), 6.22 (1H, d, J = 7.8 Hz, Ar), 6.36–6.50 (2H, m, Ar), 6.73–6.86 (4H, m, Ar), 7.19–7.23 (2H, m, Ar), 9.93 (1H, s, NH). δ_C (75.5 MHz; $CDCl_3$) 10.71, 13.70, 18.63, 105.01, 105.99, 119.22, 120.26, 126.46, 126.89, 127.58, 128.91, 130.67, 133.50, 137.85, 138.41, 142.24, 146.99.

[Li{N(*o*-Pr^{i}OC$_6$H$_4$)C(Ph)CHN$_2$C$_3$HMe$_2$-3,5}] (6a). To a stirred solution of **5a** (0.35 g, 1.01 mmol) in toluene (10 cm^3) was added $LiBu^n$ (0.44 cm^3 of a 2.5 M solution in hexane, 1.10 mmol) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Solvents were removed *in vacuo* and the residue was dissolved in Et_2O. The solution was filtered and the filtrate was concentrated to afford pale yellow crystals of **6a**·0.25Et_2O (0.28 g, 75%), mp 186–188 °C (Found: C, 73.98; H, 6.82; N, 11.31. $C_{22}H_{24}N_3OLi\cdot 0.25Et_2O$ requires C, 74.28; H, 7.18; N, 11.30%). δ_H (300 MHz; C_6D_6) 0.80 (3H, d, J = 5.7 Hz, Pr^i), 1.06 (3H, d, J = 6.1 Hz, Pr^i), 1.42 (3H, s, Me), 2.04 (3H, s, Me), 3.62–3.70 (1H, m, Pr^i), 5.08 (1H, s, CH), 5.29 (1H, s, CH), 5.79 (1H, d, J = 7.9 Hz, Ar), 6.07–6.11 (1H, m, Ar), 6.20–6.27 (2H, m, Ar), 6.65–6.82 (3H, m, Ar), 7.22 (2H, d, J = 7.5 Hz, Ar). δ_C (75.5 MHz; C_6D_6) 11.65, 13.64, 21.00, 23.37, 68.91, 101.14, 103.27, 112.01, 116.77, 120.84, 125.70, 126.42, 126.77, 129.04, 129.34, 137.22, 144.24, 145.79, 146.95, 148.14, 149.35.

[Li{N(*o*-MeC$_6$H$_4$)C(Ph)CHN$_2$C$_3$HMe$_2$-3,5}] (6b). To a stirred solution of **5b** (0.303 g, 1 mmol) in toluene (10 cm^3) was added $LiBu^n$ (0.44 cm^3 of a 2.5 M solution in hexane, 1.1 mmol) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. The solution was filtrated and the filtrate was concentrated to afford yellowish crystals of **6b**·0.2PhMe (0.23 g, 70%), mp 172–174 °C (Found: C, 78.46; H, 6.88; N, 12.98. $C_{20}H_{20}N_3Li\cdot 0.2PhMe$ requires C, 78.42; H, 6.64; N, 12.82%). δ_H (300 MHz; C_6D_6) 1.44 (3H, s, Me), 1.63 (3H, s, Me), 1.87 (3H, s, Me), 5.09 (1H, s, CH), 5.55 (1H, s, CH), 6.24 (1H, t, J = 7.2 Hz, Ar), 6.35 (1H, d, J = 7.7 Hz, Ar), 6.48–6.63 (3H, m, Ar), 6.74–6.86 (3H, m, Ar), 7.30 (1H, d, J = 7.1 Hz, Ar). δ_C (75.5 MHz; C_6D_6) 11.33, 13.27, 19.45, 21.42, 102.76, 104.33, 117.12, 122.70, 125.70, 126.57, 127.42, 127.91, 128.22, 128.54, 128.64, 129.33, 130.82, 137.90, 138.71, 143.57, 146.67, 155.13.

[Zn(Cl){N(*o*-MeC$_6$H$_4$)C(Ph)CHN$_2$C$_3$HMe$_2$-3,5}] (7). To a stirred solution of $ZnCl_2$ (0.22 g, 1.61 mmol) in THF (10 cm^3) was added a solution of **6b** (0.46 g, 1.49 mmol) in THF (5 cm^3) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Solvent was removed *in vacuo* and the residue was dissolved in Et_2O, filtered. The filtrate was concentrated to give a white powder of **7** (0.48 g, 78%), mp 138–140 °C. (Found: C, 57.51; H, 5.16; N, 9.84. $C_{20}H_{20}N_3ClZn\cdot 0.2CH_2Cl_2$ requires C, 57.74; H, 4.89; N, 10.00%). δ_H (300 MHz; $CDCl_3$) 2.11 (3H, s, Me), 2.44 (3H, s, Me), 2.50 (3H, s, Me), 5.56 (1H, s, CH), 6.11 (1H, s, CH), 6.80–6.83 (1H, m, Ar), 7.03–7.06 (3H, m, Ar), 7.15–7.17 (2H, m, Ar), 7.30–7.42 (3H, m, Ar). δ_C (75.5 MHz; $CDCl_3$) 10.56, 13.46, 21.38, 89.50, 104.51, 107.19, 113.26, 119.52, 122.16, 122.91, 128.38, 138.47, 139.11, 140.26, 146.91, 148.85, 150.81.

[Al(Cl$_2$){N(*o*-MeC$_6$H$_4$)C(Ph)CHN$_2$C$_3$HMe$_2$-3,5}] (8). To a solution of $AlCl_3$ (0.20 g, 1.50 mmol) in THF (8 cm^3) was added a solution of **6b** (0.45 g, 1.45 mmol) at about −80 °C with stirring. The mixture was warmed to room temperature and stirred overnight. Solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and filtered. The filtrate was added Et_2O and then concentrated to afford colorless crystals of **8** (0.52 g, 89%), mp 148–150 °C (Found: C, 59.30; H, 5.22;

N, 10.26. $C_{20}H_{20}N_3Cl_2Al{\cdot}0.1CH_2Cl_2$ requires C, 59.06; H, 4.98; N, 10.28%). δ_H (300 MHz; $CDCl_3$) 2.02 (3H, s, Me), 2.20 (3H, s, Me), 2.49 (3H, s, Me), 5.82 (1H, s, CH), 6.07 (1H, s, CH), 6.37–6.53 (1H, m, Ar), 6.72 (3H, s, Ar), 6.79–6.98 (4H, m, Ph), 7.03–7.17 (1H, m, Ar). δ_C (75.5 MHz; $CDCl_3$) 11.87, 13.30, 19.11, 98.24, 108.24, 125.05, 126.17, 127.71, 128.23, 128.72, 129.12, 130.98, 135.32, 137.51, 140.07, 143.38, 144.26, 148.06.

$[Zn\{N(o\text{-}Pr^iOC_6H_4)C(Ph)CHN_2C_3HMe_2\text{-}3,5\}_2]$ (9). To a solution of **5a** (0.347 g, 1 mmol) in toluene (10 cm^3) was added $ZnEt_2$ (0.64 cm^3 of a 0.875 M solution in hexane, 0.56 mmol) at about −80 °C with stirring. The solution was warmed to room temperature and stirred overnight. Solvents were removed *in vacuo*. The residue was dissolved in hexane and filtered. The filtrate was concentrated to give colorless crystals of **10** (0.29 g, 76%), mp 124–125 °C. Elemental analytical sample was recrystallized from a mixed solvent of Et_2O and hexane (Found: C, 69.68; H, 6.91; N, 10.43. $C_{44}H_{48}N_6O_2Zn{\cdot}0.5Et_2O$ requires C, 69.47; H, 6.72; N, 10.57%). δ_H (300 MHz; C_6D_6) 0.90 (6H, d, J = 5.7 Hz, Pr^i), 1.05 (6H, d, J = 5.7 Hz, Pr^i), 1.88 (6H, s, Me), 2.52 (6H, s, Me), 4.06–4.14 (2H, m, Pr^i), 5.56 (2H, s, CH), 6.00 (2H, s, CH), 6.06 (2H, d, J = 7.8 Hz, Ar), 6.35–6.52 (6H, m, Ar), 7.00 (2H, d, J = 7.2 Hz, Ar), 7.12 (4H, t, J = 7.5 Hz, Ar), 7.68 (4H, d, J = 7.5 Hz, Ar). δ_C (75.5 MHz; C_6D_6) 11.37, 12.52, 21.44, 21.56, 67.65, 99.66, 105.16, 111.06, 119.00, 125.43, 127.28, 129.33, 136.64, 142.88, 143.15, 145.69, 146.67, 150.21.

$[Al(Me_2)\{N(o\text{-}Pr^iOC_6H_4)C(Ph)CHN_2C_3HMe_2\text{-}3,5\}_2]$ (10a). To a solution of **5a** (0.347 g, 1 mmol) in toluene (10 cm^3) was added $AlMe_3$ (0.48 cm^3 of a 2.3 M solution in hexane, 1.1 mmol) at about −80 °C with stirring. The solution was warmed to room temperature and stirred overnight. Solvents were removed *in vacuo*. The residue was dissolved in hexane and filtered. The filtrate was concentrated to give colorless crystals of **11a** (0.27 g, 67%), mp 142–144 °C (Found: C, 71.45; H, 7.45; N, 10.57. $C_{24}H_{30}N_3OAl$ requires C, 71.44; H, 7.49; N, 10.41%). δ_H (300 MHz; C_6D_6) −0.51 (3H, br, AlMe), −0.40 (3H, br, AlMe), 1.13 (6H, br, Pr^i), 1.29 (3H, s, Me), 1.84 (3H, s, Me), 4.15–4.22 (1H, m, Pr^i), 5.04 (1H, s, CH), 5.56 (1H, s, CH), 6.24–6.28 (1H, m, Ar), 6.31–6.41 (3H, m, Ar), 6.66–6.69 (1H, m, Ar), 6.77 (2H, t, J = 7.2 Hz, Ar), 7.23–7.26 (2H, m, Ar). δ_C (75.5 MHz; C_6D_6) −7.50, 10.79, 13.09, 22.37, 22.47, 70.31, 103.13, 106.80, 111.88, 120.56, 120.97, 126.63, 127.74, 127.86, 128.06, 128.16, 128.23, 128.26, 128.30, 128.39, 128.78, 128.82, 128.86, 138.85, 140.25, 140.61, 144.07, 145.87, 150.87.

$[Al(Me_2)\{N(o\text{-}MeC_6H_4)C(Ph)CHN_2C_3HMe_2\text{-}3,5\}_2]$ (10b). To a solution of **5b** (0.303 g, 1 mmol) in toluene (10 cm^3) was added $AlMe_3$ (0.54 cm^3 of a 2.3 M solution in hexane, 1.2 mmol) at about −80 °C with stirring. The resulting solution was warmed to room temperature and stirred overnight. Solvents were removed *in vacuo*. The residue was dissolved in hexane and filtered. The filtrate was concentrated to give colorless crystals of **10b** (0.23 g, 65%), mp 110–112 °C (Found: C, 73.15; H, 7.21; N, 11.59. $C_{22}H_{26}N_3Al$ requires C, 73.51; H, 7.29; N, 11.69%). δ_H (300 MHz; C_6D_6) −0.32 (3H, s, AlMe), −0.12 (3H, s, AlMe), 1.52 (3H, s, Me), 2.07 (3H, s, Me), 2.30 (3H, s, Me), 5.28 (1H, s, CH), 5.63 (1H, s, CH), 6.76 (1H, t, J = 7.2 Hz, Ar), 6.86–6.92 (2H, m, Ar), 6.98 (3H, t, J = 7.5 Hz, Ar), 7.27 (1H, d, J = 7.5 Hz, Ar), 7.45–7.48 (2H, m, Ar). δ_C (75.5 MHz; C_6D_6) −8.92, −8.13, 10.81, 12.59, 19.54, 98.38, 106.71, 123.62, 126.34, 127.88, 127.94, 12859, 129.36, 131.15, 134.38, 137.96, 140.05, 145.64, 145.68, 147.86.

$[Al(Et_2)\{N(o\text{-}Pr^iOC_6H_4)C(Ph)CHN_2C_3HMe_2\text{-}3,5\}_2]$ (10c). To a solution of **5a** (0.347 g, 1 mmol) in toluene (10 cm^3) was added $AlEt_3$ (0.6 cm^3 of a 1.82 M solution in hexane, 1.1 mmol) at about −80 °C with stirring. The solution was warmed to room temperature and stirred overnight. Solvents were removed *in vacuo*. The residue was dissolved in hexane and filtered. The filtrate was concentrated to give colorless crystals of **10c** (0.31 g, 71%), mp 121–123 °C (Found: C, 72.53; H, 7.92; N, 9.80. $C_{26}H_{34}N_3OAl$ requires C, 72.36; H, 7.94; N, 9.74%). δ_H (300 MHz; C_6D_6) 0.43 (4H, br, $AlCH_2$), 1.22 (3H, br, $AlCH_2CH_3$), 1.35 (3H, br, Pr^i), 1.39 (3H, br, $AlCH_2CH_3$), 1.43 (3H, br, Pr^i), 1.57 (3H, s, CH_3), 2.21 (3H, s, CH_3), 4.39–4.47 (1H, m, Pr^i), 5.36 (1H, s, CH), 5.86 (1H, s, CH), 6.56–6.69 (3H, m, Ar), 6.79 (1H, d, J = 7.5 Hz, Ar), 6.97 (1H, d, J = 7.2 Hz, Ar), 7.07 (2H, t, J = 7.5 Hz, Ar), 7.60 (2H, d, J = 7.2 Hz, Ar). δ_C (75.5 MHz; C_6D_6) 1.42, 2.77, 9.91, 10.42, 10.85, 12.74, 22.42, 70.18, 102.50, 106.72, 112.47, 120.62, 121.59, 127.24, 127.74, 127.89, 128.22, 128.95, 138.18, 140.28, 140.65, 145.08, 146.01, 151.60.

$[Al(Et_2)\{N(o\text{-}MeC_6H_4)C(Ph)CHN_2C_3HMe_2\text{-}3,5\}_2]$ (10d). To a solution of **5b** (0.303 g, 1 mmol) in toluene (10 cm^3) was added $AlEt_3$ (0.66 cm^3 of a 1.82 M solution in hexane, 1.2 mmol) at about −80 °C with stirring. The resulting solution was warmed to room temperature and stirred overnight. Solvents were removed *in vacuo*. The residue was dissolved in hexane and filtered. The filtrate was concentrated to give colorless crystals of **10d** (0.27 g, 70%), mp 100–102 °C (Found: C, 74.54; H, 7.76; N, 10.93. $C_{24}H_{30}N_3Al$ requires C, 74.39; H, 7.80; N, 10.84%). δ_H (300 MHz; C_6D_6) 0.23–0.43(2H, m, $AlCH_2$), 0.53–0.64 (2H, m, CH_2), 1.15 (3H, t, J = 8.1 Hz, Me), 1.45 (3H, t, J = 8.1 Hz, Me), 1.53 (3H, s, Me), 2.15 (3H, s, Me), 2.29 (3H, s, Me), 5.33 (1H, s, CH), 5.64 (1H, s, CH), 6.78 (1H, t, J = 7.5 Hz, Ar), 6.87 (1H, d, J = 7.2 Hz, Ar), 6.93 (1H, d, J = 7.2 Hz, Ar), 7.01 (3H, t, J = 7.8 Hz, Ar), 7.36 (1H, d, J = 7.8 Hz, Ar), 7.53 (2H, d, J = 6.9 Hz, Ar). δ_C (75.5 MHz; C_6D_6) 1.43, 9.56, 10.13, 10.87, 12.44, 19.38, 98.74, 106.69, 123.61, 126.39, 127.93, 128.15, 129.37, 131.25, 134.19, 138.29, 140.02, 145.88, 146.26, 148.02.

The mother-liquor was set aside. After two days, several crystals were obtained and identified by single-crystal X-ray diffraction as $[Al(Et_2)\{N(o\text{-}MeC_6H_4)C(Ph)(Et)\text{-}CH_2N_2C_3HMe_2\text{-}3,5\}]$ (**11**).

X-Ray crystallography

Single-crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Bruker Smart CCD area-detector with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[26] and refined against F^2 by

Table 1 Details of the X-ray crystal structure determinations of complexes **2a**, **8**, **10a**, **10d** and **11**

	2a	**8**	**10a**	**10d**	**11**
Empirical formula	$C_{28}H_{52}Li_2N_6Si_2$	$C_{20}H_{20}AlCl_2N_3$	$C_{24}H_{30}AlN_3O$	$C_{24}H_{30}AlN_3$	$C_{26}H_{36}AlN_3$
M_r	542.82	400.27	403.49	387.49	417.56
T/K	294(2)	298(2)	298(2)	298(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	9.857(2)	8.6331(14)	7.4120(10)	8.4350(14)	11.977(7)
b/Å	18.365(4)	16.006(2)	24.654(2)	20.454(2)	18.109(11)
c/Å	19.384(4)	15.3112(18)	12.7840(15)	13.1771(18)	12.058(7)
β/°	99.51(3)	103.749(2)	96.660(2)	94.580(2)	108.400(10)
V/Å^3	3460.6(12)	2055.1(5)	2320.3(5)	2266.2(5)	2482(3)
Z	4	4	4	4	4
D_c/g cm^{-3}	1.042	1.294	1.155	1.136	1.118
F(000)	1184	832	864	832	904
μ/mm^{-1}	0.127	0.367	0.106	0.103	0.098
θ range for data collection/°	2.13–25.02	1.87–25.00	1.65–25.00	1.84–25.01	2.09–25.02
No. reflns collected	8771	10556	12080	11694	11862
No. indep. reflns	3058	3609	4072	3983	4315
R_{int}	0.0454	0.0301	0.0570	0.0529	0.2050
No. data/restraints/params	3058/0/180	3609/0/236	4072/3/267	3983/0/263	4315/12/278
Goodness of fit on F^2	1.022	1.031	1.006	1.086	1.060
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0522$ $wR_2 = 0.1225$	$R_1 = 0.0474$ $wR_2 = 0.1154$	$R_1 = 0.0525$ $wR_2 = 0.1181$	$R_1 = 0.0541$ $wR_2 = 0.1434$	$R_1 = 0.0927$ $wR_2 = 0.1613$
R indices (all data)	$R_1 = 0.0887$ $wR_2 = 0.1454$	$R_1 = 0.0759$ $wR_2 = 0.1271$	$R_1 = 0.1034$ $wR_2 = 0.1348$	$R_1 = 0.1224$ $wR_2 = 0.2104$	$R_1 = 0.2726$ $wR_2 = 0.1983$
$\Delta\rho_{max, min}$/e Å^{-3}	0.186, −0.199	0.619, −0.200	0.177, −0.167	0.192, −0.210	0.263, −0.310

full-matrix least-squares using SHELXL-97.[27] Hydrogen atoms were placed in calculated positions. The C8 atom in **10a** is disordered. The bonds C7–C8, C7–C8′ and C7–C9 were restrained because the bond distances showed big differences. Restraints were also applied to the displacement parameters of C24 and C26 in **11** due to the elongation of the thermal ellipsoids. Crystal data and experimental details of the structure determinations are listed in Table 1.

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