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Synthesis and characterisation of neutral dialkylaluminium complexes stabilised by salicylaldiminato ligands, and their conversion to monoalkylaluminium cations †

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Treatment of the salicylaldimine ligands 3,5-Bu^t_2-2-(OH)C_6H_2CHNR [R = 2,6-$Me_2C_6H_3$ (**1a**), 2,6-$Pr^i_2C_6H_3$ (**1b**), 3,5-$(CF_3)_2C_6H_3$ (**1c**), 4-$(NO_2)C_6H_4$ (**1d**), 4-ClC_6H_4 (**1e**), 1-naphthyl (**1f**), Bu^t (**1g**)] with Me_3Al in toluene yields, after work-up, the highly crystalline (except **2c** – an oil) complexes {3,5-Bu^t_2-2-(O)C_6H_2CH=NR}$AlMe_2$ [R = 2,6-$Me_2C_6H_3$ (**2a**), 2,6-$Pr^i_2C_6H_3$ (**2b**), 3,5-$(CF_3)_2C_6H_3$ (**2c**), 4-$(NO_2)C_6H_4$ (**2d**), 4-ClC_6H_4 (**2e**), 1-naphthyl (**2f**), Bu^t (**2g**)] respectively. Reaction of these systems with $B(C_6F_5)_3$ in the presence of THF leads smoothly to [{3,5-Bu^t_2-2-(O)C_6H_2CH=NR}-AlMe(THF)]$^+$ [R = 2,6-$Me_2C_6H_3$ (**3a**), 2,6-$Pr^i_2C_6H_3$ (**3b**), 3,5-$(CF_3)_2C_6H_3$ (**3c**), 4-$(NO_2)C_6H_4$ (**3d**), 4-ClC_6H_4 (**3e**), 1-naphthyl (**3f**), Bu^t (**3g**)], as the $B(C_6F_5)_3Me^-$ salts. By contrast, the same reaction performed in dichloromethane solution without THF gives complex mixtures: the NMR spectrum of the product mixture obtained from the reaction of **2g** with $B(C_6F_5)_3$ in CD_2Cl_2 indicated, *inter alia*, the presence of both {3,5-Bu^t_2-2-(O)C_6H_2CH=NBu^t}-AlMe(C_6F_5)] and $B(C_6F_5)_2Me$. Compounds **2a** and **2b** have been characterised by single crystal X-ray structure determinations and shown to have virtually identical conformations. In both systems there is a marked distortion in the tetrahedral geometry at the aluminium centre.

Introduction

Organoaluminium complexes are currently generating considerable interest due to their increasing role in polymerisation chemistry, *e.g.*, in cationic,[1,2] anionic[3–6] and ring-opening[7] polymerisation, and as cocatalysts/activators in transition metal-catalysed olefin polymerisation.[8] In addition, neutral aluminium alkyls have long been known to promote the oligomerisation of ethylene to α-olefins at elevated temperature and pressure.[9] More recently, cationic aluminium alkyls have been shown to polymerise ethylene under mild conditions.[10,11] These polymerisation-active cationic aluminium alkyls are stabilised by means of monoanionic ligands, namely the bidentate *N*,*N* amidinate ligand and the tridentate *N*,*N*,*N* pyridylimineamide ligand as reported by Jordan *et al.*[10] and ourselves[11], respectively. We have subsequently described[12] an extension of this work to include a series of aluminium alkyl cations employing tridentate *O*,*N*,*N* and *O*,*N*,*O* Schiff base ligands derived from salicylaldimine and bearing a pendant donor arm joined at the imine nitrogen. These monoalkylaluminium cations, which are formed from the corresponding neutral dialkylaluminium systems, were similarly found to be active in the polymerisation of ethylene.

The readily accessible potentially *bidentate* salicylaldimine ligand family is closely related to the *tridentate* family referred to above but, by having no pendant arm, the former constitutes a simpler *N*,*O* ligand type. In our programme directed at stabilising both mono- and di-alkylaluminium systems we decided to target these simpler chelates. We noted in an earlier communication[12] that it appeared possible to employ the *N*,*O* bidentate ligands to stabilise cationic monoalkylaluminium species provided they were used in conjunction with an independent donor ligand such as THF. Here we report the synthesis and characterisation of a series of neutral aluminium alkyls stabilised by bidentate salicylaldimine ligands and the conversion of these to the corresponding THF-coordinated monoalkylaluminium cations.

Results and discussion

All of the salicylaldimine ligands studied were prepared in good yields (61–95%) as yellow to orange crystalline solids by condensation of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde with the appropriate aniline in refluxing ethanol in the presence of a catalytic amount of formic acid. Satisfactory elemental analyses were obtained for all of the ligands. Spectroscopic data are consistent with the formulations depicted in Scheme 1.

The ^{1}H NMR spectra of **1a–1g** in C_6D_6 exhibit resonances in the region δ 7.60–8.13 for the imine C*H* proton, with the corresponding ^{13}C NMR signals occurring in the range δ 161.1–168.4. Ligands **1a–1g** also display two characteristic doublets (^4J(HH) *ca.* 2.5 Hz) in the ^{1}H NMR for the aromatic ring protons of the $Bu^t_2C_6H_2$(OH)CHNR ring, whilst the phenolic protons appear as low field resonances in the region δ 13.1–14.9. The infrared absorption band of the imine is clearly visible between 1587 and 1655 cm^{-1}, and molecular ion peaks are observed in the EI mass spectrum for all of the compounds.

Reaction of these new ligands **1a–1g** with Me_3Al (one equivalent) in toluene at ambient temperature affords, after work-up, the corresponding highly crystalline yellow to orange/red complexes {3,5-Bu^t_2-2-(O)C_6H_2CH=NR}$AlMe_2$, **2a–2g**; the exception is the 3,5-$(CF_3)_2C_6H_2$ derivative **2c** which is an orange oil (see Scheme 1). The complexes are presumed to form *via* formal loss of methane, and their spectroscopic data indicate that all are constituted similarly to the crystallographically characterised examples (*vide infra*).

Crystals of **2a** and **2b** suitable for X-ray analysis were grown from acetonitrile at room temperature. The structures of **2a** and

† Electronic supplementary information (ESI) available: further synthetic details and characterisation for ligands and for aluminium compounds and cations. See http://www.rsc.org/suppdata/dt/b1/b100743m/

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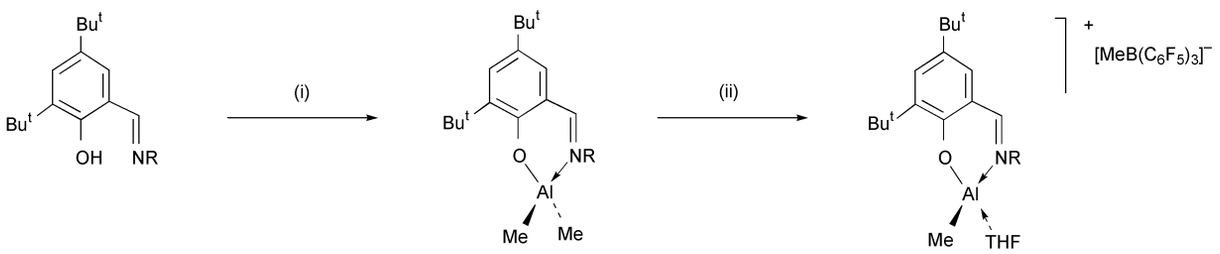
Table 1 Selected bond lengths (Å) and angles (°) for **2a** and **2b**

	2a	**2b**		**2a**	**2b**
Al–O	1.755(3)	1.773(3)	Al–N	1.972(3)	1.972(3)
Al–C(1)	1.950(5)	1.959(5)	Al–C(2)	1.960(5)	1.948(5)
O–C(3)	1.319(5)	1.321(4)	N–C(9)	1.285(5)	1.300(5)
N–C(10)	1.457(5)	1.460(5)	C(3)–C(4)	1.411(5)	1.413(5)
C(4)–C(9)	1.433(6)	1.442(5)			
O–Al–C(1)	111.8(2)	114.0(2)	O–Al–N	93.9(2)	93.6(1)
O–Al–C(2)	111.8(2)	110.4(2)	C(1)–Al–N	111.8(2)	109.7(2)
C(2)–Al–N	111.2(2)	112.2(2)	C(3)–O–Al	133.5(3)	132.2(2)
C(1)–Al–C(2)	114.5(3)	115.1(2)	C(9)–N–Al	121.9(3)	122.6(3)
C(9)–N–C(10)	117.4(3)	117.2(3)	O–C(3)–C(4)	120.7(4)	121.3(3)
C(10)–N–Al	120.7(3)	120.3(2)	N–C(9)–C(4)	127.7(4)	126.8(4)
C(3)–C(4)–C(9)	122.2(4)	122.0(3)			



1a R = 2,6-$Me_2C_6H_3$ **2a** R = 2,6-$Me_2C_6H_3$ **3a** R = 2,6-$Me_2C_6H_3$
1b R = 2,6-$Pr^i_2C_6H_3$ **2b** R = 2,6-$Pr^i_2C_6H_3$ **3b** R = 2,6-$Pr^i_2C_6H_3$
1c R = 3,5-$(CF_3)_2C_6H_3$ **2c** R = 3,5-$(CF_3)_2C_6H_3$ **3c** R = 3,5-$(CF_3)_2C_6H_3$
1d R = 4-$(NO_2)C_6H_4$ **2d** R = 4-$(NO_2)C_6H_4$ **3d** R = 4-$(NO_2)C_6H_4$
1e R = 4-ClC_6H_4 **2e** R = 4-ClC_6H_4 **3e** R = 4-ClC_6H_4
1f R = 1-naphthyl **2f** R = 1-naphthyl **3f** R = 1-naphthyl
1g R = Bu^t **2g** R = Bu^t **3g** R = Bu^t

Scheme 1 Reagents: (i) $AlMe_3$, C_7H_8; (ii) $B(C_6F_5)_3$, THF in C_6D_6 or C_7H_8.

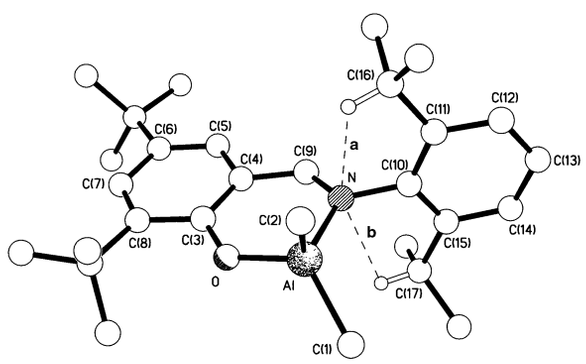


Fig. 1 The molecular structure of **2b** (that of **2a** has an essentially identical conformation) showing also the weak C–H ··· N(pπ) stabilising interactions; the H ··· N distances (Å) and C–H ··· N angles (°) are **a**, 2.46, 109; **b**, 2.48, 108.

2b show the complexes to have virtually identical geometries, the principal difference being in the relative orientations of the *tert*-butyl groups – Fig. 1. In both structures the aluminium centre has a distorted tetrahedral geometry with angles ranging between 93.9(2) and 114.5(3)° in **2a** and 93.6(1) and 115.1(2)° in **2b**, the most "acute" angle in each case being associated with the bite of the chelating ligand (Table 1). The chelate ligand in each structure binds to the aluminium in an unsymmetrical fashion with the bond to the oxygen atom being typical of an alkoxide [1.755(3) and 1.773(3) Å in **2a** and **2b** respectively], whilst that to the imino nitrogen atom is, as expected, appreciably longer at 1.972(3) Å in each complex. In both structures the chelate C=N bond retains its double bond character, being 1.285(5) Å in **2a** and 1.300(5) Å in **2b**. There are small differences in the geometries of the six-membered chelate rings in the two structures with that in **2b** having a slightly folded, sofa conformation (the aluminium atom lying 0.17 Å out of the plane of the other five atoms which are co-planar to within 0.04 Å) whereas in **2a** the chelate ring is essentially planar (the maximum deviation from planarity being only 0.02 Å).

In both structures the pendant 2,6-dialkylphenyl rings are oriented virtually orthogonally (89°) to the plane of the six-membered metallocyclic ring. There is evidence in **2b** that this conformation is stabilised by a pair of weak C–H ··· N(pπ) interactions between the isopropyl methine hydrogen atoms and the non-bonding p orbitals of the ring nitrogen atom (linkages **a** and **b** in Fig. 1).[13] In neither structure are there any notable intermolecular interactions, the packing being dominated by the hydrophobic methyl and *tert*-butyl groups resulting in very low packing densities (D_c = 1.047 and 1.053 g cm^{-3} in **2a** and **2b** respectively).

The ^{1}H NMR spectra (in C_6D_6) of compounds **2a**–**2g** exhibit resonances in the region δ 7.05–7.83 due to the imine groups, with corresponding ^{13}C NMR signals between δ 169.1 and 174.8. Characteristic Al–Me signals appear in the region δ −0.20 to −0.36 in the ^{1}H NMR, and δ −6.4 to −9.1 in the ^{13}C NMR. The NMR data for the structurally characterised systems **2a** and **2b** indicate that the solid state forms remain essentially unchanged in solution. The infrared absorption band for the imine C=N stretches of **2a–2g** occur in the region 1613–1618 cm^{-1}. Satisfactory elemental analyses were obtained for all the compounds.

Arene solutions of the dimethyl complexes **2a–2g**, when treated sequentially with one equivalent of tetrahydrofuran and then with one equivalent of $B(C_6F_5)_3$, were observed to separate into two layers. Isolation of the lower layer and evaporation of this to dryness yielded the cationic systems [{3,5-Bu^t_2-2-$(O)C_6H_2CH{=}NR$}$AlMe(THF)]^+$, **3a–3g**, with $[MeB(C_6F_5)_3]^-$ as

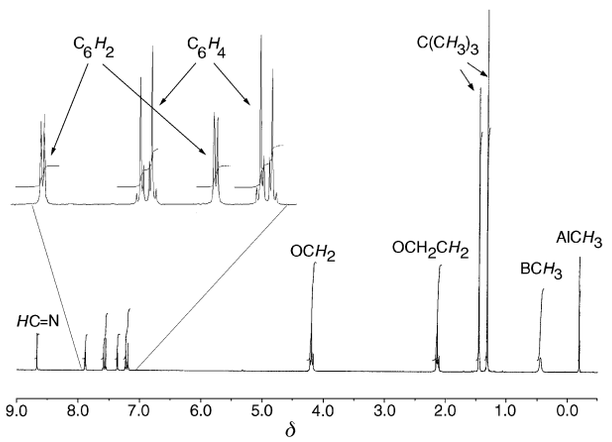


Fig. 2 The ^{1}H NMR spectrum of **3e** in CD_2Cl_2.

the counter ion (see Scheme 1). It was also found possible to generate the cations by adding the THF donor after the addition of $B(C_6F_5)_3$, but the cleanest products were obtained when the donor was added first. However, in the absence of the THF donor, no immediate reaction was observed, *e.g.* when **2b** and $B(C_6F_5)_3$ were mixed in C_6D_6 solution at ambient temperature. In CD_2Cl_2, by contrast, all of **2a–2g** reacted rapidly with $B(C_6F_5)_3$ to form complex mixtures. For example, the ^{1}H NMR spectrum of a solution of **2g** and $B(C_6F_5)_3$ in CD_2Cl_2 (after standing for 24 hours at ambient temperature) revealed *inter alia* a high field triplet at δ −0.31 [J(HF) 1.5 Hz] characteristic of an Al–Me resonance coupled to the α-fluorines of a coordinated C_6F_5 group. This suggests the presence of the species {3,5-Bu$^t_2$-2-(O)C_6H_2CH=NBu^t}AlMe(C_6F_5) which is formed, presumably, by abstraction of a C_6F_5 group from $[B(C_6F_5)_3Me]^-$ by the first-formed coordinatively unsaturated and therefore highly reactive cationic intermediate (*i.e.* not having the THF donor to stabilise it). Further evidence for the abstraction of a C_6F_5 group is the appearance of a quintet in the same ^{1}H NMR spectrum at δ 1.33 [J(HF) 1.8 Hz] which is assigned to the methyl of the resulting $MeB(C_6F_5)_2$, this methyl being coupled to the four equivalent α-fluorines of the C_6F_5 groups. Our observations parallel those of Smith and coworkers[14] for the similar reaction of the β-diketiminato complex [(2,6-Pr$^i_2C_6H_3$)NC(Me)CHC(Me)N(2,6-Pr$^i_2C_6H_3$)]$AlMe_2$ with $B(C_6F_5)_3$, in the absence of a donor, which led to the isolation and characterisation of the analogous [ligand]-AlMe(C_6F_5) system.

The THF coordinated aluminium methyl cations, **3a–3g**, were formed in high purity, as demonstrated by their ^{1}H, ^{13}C (and in some cases ^{19}F) NMR spectra recorded in CD_2Cl_2. Crystalline materials were however not obtained. A typical ^{1}H NMR spectrum is shown in Fig. 2 (*i.e.* as obtained for **3e**). The ^{1}H NMR spectra of this series of cations have the imine resonance appearing in the range δ 8.74 to 8.41 and the resonance of the remaining aluminium methyl in the range δ −0.16 to −0.43; the corresponding ^{13}C NMR signals lie between δ 174.8 and 179.9 and between δ −10.9 and −14.5 respectively. A comparison of the ^{1}H NMR spectra of *e.g.* **2a** and **3a** (both run in CD_2Cl_2) shows that the resonances for the cation are shifted downfield relative to the corresponding resonances for the neutral $AlMe_2$ precursor compound, with the largest shift being that for the Al–Me resonance (from δ −0.83 to −0.43). This effect is ascribed principally to the presence of the positive charge in **3a**. The methyl resonance of $[B(C_6F_5)_3Me]^-$ in **3a–3g**, which is broadened by the boron quadrupole, is seen in the range δ 0.39 to 0.44, as is anticipated for the free ion.[15] This observation supports our formulation of the complexes as separated ions as opposed to the ion pairs (*i.e.* with Al ··· Me–B association) observed by Coles and Jordan.[16] Moreover, the fact that the positions of the broad BMe ^{13}C resonance (at *ca.* δ 10.4) and the C_6F_5 ^{19}F resonances (at δ −135.5, −167.5, −170.0) in the anion are virtually identical throughout the series is further evidence that this charge separated arrangement occurs in all the products **3a–3g**.

When excess THF is added to CD_2Cl_2 solutions of the cations **3a–3g**, the original two resonances of the coordinated THF are replaced by two more intense resonances shifted towards those of free THF (*i.e.* δ 3.68, 1.82 in CD_2Cl_2). With **3c**, for example, a 1.5 molar excess of THF led to a shift in the resonance positions from δ 4.21, 2.15 to δ 3.90, 1.95. The fact that only one set of resonances is seen in the presence of excess THF implies that a rapid intermolecular exchange process occurs between the bound and the free ligand. This behaviour demonstrates the highly labile nature of the coordinated THF which we anticipate will be important in chemical processes involving these cationic species.

Concluding remarks

This work provides an extension of our earlier study[12] of aluminium alkyl systems employing salicylaldiminate ligands bearing pendant donor arms. Here we have shown that it is possible to access cleanly and in high yield a family of cationic aluminium alkyls bearing an *independent* donor ligand (THF), as opposed to one that is pendant to the salicylaldiminate group. The synthetic pathway is crucial to the successful isolation of these bidentate cationic alkylaluminium species; the reactions are best carried out by addition of one mole equivalent of THF to the neutral precursor in an aromatic solvent prior to the addition of $B(C_6F_5)_3$. In the absence of the donor ligand, abstraction of C_6F_5 by the electron-deficient aluminium centre occurs. The ability to use an independent rather than a pendant donor group to stabilise the $(L,X)AlMe^+$ system broadens appreciably the scope and potential of the original study as now, clearly, a much wider array of other potential donors may be employed. We are currently exploring the role of these cations and their derivatives in facilitating various polymerisation processes; the results of these studies will be presented elsewhere.

Experimental

General

All manipulations were carried out under an atmosphere of dry nitrogen either using standard Schlenk and cannula techniques, or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Imperial College or by Medac Ltd. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in C_6D_6 for the ligands and neutral compounds (unless stated otherwise), and in CD_2Cl_2 for the cationic complexes, on Bruker DRX400 or AC250 machines at ambient temperature; chemical shifts were referenced to the residual protio impurity of the deuterated solvent; ^{13}C chemical shift assignments were based on DEPT experiments. Infrared spectra (Nujol mulls, KBr/CsI windows) were run on Perkin-Elmer 577 and 457 grating spectrophotometers and mass spectra were measured either on a VG Autospec or a VG Platform II spectrometer. Selected synthetic details are given below, the remainder are supplied as ESI.†

Preparation of ligands

3,5-Bu$^t_2$-2-(OH)C_6H_2CHN-2,6-Me$_2C_6H_3$ (1a). 2,6-Dimethylaniline (5.72 cm^3, 46.4 mmol) was added *via* syringe to a solution of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (10.88 g, 46.4 mmol) in EtOH (120 cm^3). Formic acid (5 drops) was added, and the solution refluxed for 20 h. The resulting solution was

dried over $MgSO_4$ and filtered. Slow concentration of the EtOH solution yielded large yellow plates of **1a**. Yield 14.47 g, 92%. Found C 81.6; H 9.0; N 4.2%; $C_{23}H_{31}NO$ requires C 81.9; H 9.3; N 4.2%. IR/cm^{-1}: 3375w, br (O–H stretch), 1774m, 1748s, 1705s, 1655m (C=N stretch), 1625s, 1588s, 1312m, 1287m, 1274s, 1252s, 1216s, 1193s, 1171s, 1133m, 1095m, 1026m, 979m, 919w, 887w, 863s, 825s, 803s, 768s, 734m, 646m, 602m. ^{1}H NMR: δ 13.84 (br s, 1H, –O*H*), 7.66 (s, 1H, C*H*=N), 7.65 [d, 1H, ^4J(HH) 2.5 Hz, OAr–*H*], 6.99 [d, 1H, ^4J(HH) 2.5 Hz, OAr–*H*], 6.94–6.91 (m, 3H, NAr–*H*), 1.97 (s, 6H, Ar–CH_3), 1.65 [s, 9H, C(CH_3)$_3$], 1.33 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR: δ 168.4 (*C*H=N), 158.1, 148.9, 140.9, 137.6, 128.6, 128.4, 127.6, 127.2, 125.0, 118.8 (all Ar–*C*), 35.5 [*C*(CH$_3$)$_3$], 34.3 [*C*(CH$_3$)$_3$], 31.7 [C(*C*H$_3$)$_3$], 29.8 [C(*C*H$_3$)$_3$], 18.4 (NAr–*C*H$_3$). MS (EI, *m*/*z*) 337 $[M]^+$, 322 $[M - CH_3]^+$.

3,5-Bu$^t_2$-2-(OH)C$_6$H$_2$CHN-2,6-Pr$^i_2$C$_6$H$_3$ (1b). 2,6-Diisopropylaniline (4.19 cm^3, 22.2 mmol) was added *via* syringe to a solution of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (5.21 g, 22.2 mmol) in EtOH (100 cm^3). Formic acid (5 drops) was added, and the solution refluxed for 20 h. The solution was dried over $MgSO_4$, filtered, and the volatiles removed under reduced pressure. Extraction into pentane (5 cm^3) followed by cooling to −30 °C afforded yellow crystals of **1b**. Yield 5.30 g, 61%. Found C 82.5; H 10.0; N 3.4%; $C_{27}H_{39}NO$ requires C 82.4; H 10.0; N 3.4%. IR/cm^{-1}: 3397w, br (O–H stretch), 1776m, 1749m, 1705s, 1654m, 1624s (C=N stretch), 1586s, 1322m, 1274s, 1251s, 1231m, 1203s, 1169s, 1133m, 1109m, 1058m, 1043m, 1026m, 980m, 933m, 881m, 862s, 823m, 796s, 773m, 758s, 731m, 720m, 644w, 603w. ^{1}H NMR: δ 13.94 (br s, 1H, –O*H*), 7.98 (s, 1H, C*H*=N), 7.64 [d, 1H, ^4J(HH) 2.5 Hz, OAr–*H*], 7.14–7.10 (m, 3H, NAr–*H*), 7.09 [d, 1H, ^4J(HH) 2.5 Hz, OAr–*H*], 3.02 [sept., 2H, ^3J(HH) 6.9 Hz, C*H*(CH$_3$)$_2$], 1.64 [s, 9H, C(CH_3)$_3$], 1.30 [s, 9H, C(CH_3)$_3$], 1.06 [d, 12H, ^3J(HH) 6.9 Hz, CH(CH_3)$_2$]. ^{13}C NMR: δ 168.4 (*C*H=N), 159.2, 147.1, 141.0, 139.1, 137.8, 127.2, 127.1, 125.7, 123.5, 118.6 (all Ar–*C*), 35.5 [*C*(CH$_3$)$_3$], 34.3 [*C*(CH$_3$)$_3$], 31.6 [C(*C*H$_3$)$_3$], 29.8 [C(*C*H$_3$)$_3$], 28.5 [*C*H(CH$_3$)$_2$], 23.5 [CH(*C*H$_3$)$_2$]. MS (EI, *m*/*z*) 393 $[M]^+$, 378 $[M - CH_3]^+$

Preparation of complexes

{3,5-Bu$^t_2$-2-(O)C$_6$H$_2$CH=N-2,6-Me$_2$C$_6$H$_3$}AlMe$_2$ (2a). Trimethylaluminium (2.0 M, 1.60 cm^3, 3.2 mmol) was added dropwise to a solution of **1a** (1.05 g, 3.11 mmol) in toluene (30 cm^3) at −78 °C. The reaction was allowed to warm to room temperature and then stirred for 12 h. Volatiles were removed *in vacuo*, and the product was extracted into hot MeCN (20 cm^3). Filtration followed by cooling to room temperature afforded large golden blocks of **2a**. Yield 0.87 g, 71%. Found C 75.9; H 9.1; N 3.7%. $C_{25}H_{36}AlNO$ requires C, 76.3; H 9.2; N 3.6%. IR/cm^{-1}: 1613s, 1598s, 1588s, 1555s, 1540s, 1408m, 1359m, 1336m, 1323m, 1279m, 1257s, 1237m, 1211m, 1199m, 1173s, 1137m, 1097m, 1025w, 996w, 966w, 927w, 918w, 878m, 857s, 813w, 783m, 768s, 760m. ^{1}H NMR: δ 7.72 [d, 1H, ^4J(HH) 2.6 Hz, OAr–*H*], 7.17 (s, 1H, C*H*=N), 6.92–6.80 (m, 3H, NAr–*H*), 6.71 [d, 1H, ^4J(HH) 2.6 Hz, OAr–*H*], 1.97 (s, 6H, Ar–CH_3), 1.60 [s, 9H, C(CH_3)$_3$], 1.28 [s, 9H, C(CH_3)$_3$], −0.32 (s, 6H, Al–CH_3). ^{1}H NMR (CD_2Cl_2): δ 8.07 (s, 1H, C*H*=N), 7.61 [d, 1H, ^4J(HH) 2.6 Hz, OAr–*H*], 7.15 (m, 3H, NAr–*H*), 7.05 [d, 1H, ^4J(HH) 2.6 Hz, OAr–*H*], 2.22 (s, 6H, Ar–CH_3), 1.44 [s, 9H, C(CH_3)$_3$], 1.30 [s, 9H, C(CH_3)$_3$], −0.83 (s, 6H, Al–CH_3). ^{13}C NMR: δ 174.8 (*C*H=N), 163.0, 145.2, 141.3, 139.3, 133.0, 131.9, 129.4, 129.0, 127.3, 119.1 (all Ar–*C*), 35.6 [*C*(CH$_3$)$_3$], 34.2 [*C*(CH$_3$)$_3$], 31.5 [C(*C*H$_3$)$_3$], 29.6 [C(*C*H$_3$)$_3$], 18.5 (NAr–*C*H$_3$), −8.5 (Al–*C*H$_3$). MS (EI, *m*/*z*) 379 $[M - CH_3]$; (CI, NH_4^+) 395 $[M - CH_3 + NH_4]^+$, 378 $[M - CH_3 + H]^+$.

{3,5-Bu$^t_2$-2-(O)C$_6$H$_2$CH=N-2,6-Pr$^i_2$C$_6$H$_3$}AlMe$_2$ (2b). Trimethylaluminium (2.0 M, 1.30 cm^3, 2.6 mmol) was added dropwise to a solution of **1b** (1.00 g, 2.54 mmol) in toluene (30 cm^3). The reaction was stirred at room temperature for 12 h and then the volatiles were removed *in vacuo*. The product was extracted into hot MeCN (10 cm^3). Filtration and cooling to room temperature afforded **2b** as bright yellow crystals. Yield 0.99 g, 87%. Found C 77.6; H 9.6; N 3.1%. $C_{29}H_{44}AlNO$ requires C 77.5; H 9.9; N 3.1%. IR/cm^{-1}: 1614s, 1598s, 1587s, 1557m, 1541s, 1407m, 1364s, 1321s, 1276m, 1256s, 1235m, 1202m, 1190m, 1170s, 1134m, 1109m,1097m, 1057m, 1043m, 1029m, 935m, 921m, 889w, 876m, 854m, 800m, 785m, 764s, 723m, 700m, 678s, 659m, 641m, 608m, 544w, 525w.^{1}H NMR: δ 7.85 (s, 1H, *p*-NAr–*H*), 7.73 [d, 1H, ^4J(HH) 2.5 Hz, OAr–*H*], 7.15–7.0 (m, 2H, NAr–*H*), 7.05 (s, 1H, C*H*=N), 6.91 [d, 1H, ^4J(HH) 2.6 Hz, OAr–*H*], 3.16 [sept., 2H, ^3J(HH) 6.8 Hz, C*H*(CH$_3$)$_2$], 1.59 [s, 9H, C(CH_3)$_3$], 1.25 [s, 9H, C(CH_3)$_3$], 1.19 [d, 6H, ^3J(HH) 6.8 Hz, CH(CH_3)$_2$], 0.81 [d, 6H, ^3J(HH) 6.8 Hz, CH(CH_3)$_2$], −0.27 (s, 6H, Al–CH_3). ^{13}C NMR: δ 174.5 (*C*H=N), 163.2, 142.83, 142.76, 141.6, 139.8, 133.3, 129.0, 124.5, 118.8 (all Ar–*C*, one peak obscured), 35.7 [*C*(CH$_3$)$_3$], 34.1 [*C*(CH$_3$)$_3$], 31.3 [C(*C*H$_3$)$_3$], 29.6 [C(*C*H$_3$)$_3$], 28.4 [*C*H(CH$_3$)$_2$], 25.8 [CH(*C*H$_3$)$_2$], 22.8 [CH(*C*H$_3$)$_2$], −9.0 (Al–*C*H$_3$).MS (EI, *m*/*z*) 434 $[M - CH_3]^+$.

Preparation of cations

[{3,5-Bu$^t_2$-2-(O)C$_6$H$_2$CH=N-2,6-Me$_2$C$_6$H$_3$}AlMe(THF)]$^+$ [B(C$_6$F$_5$)$_3$Me]$^-$ (3a). The compound **2a** (23.6 mg, 0.06 mmol) was dissolved in C_6D_6 (0.5 ml). THF (4.86 μl, 0.06 mmol) was added to the solution *via* syringe and then a solution of $B(C_6F_5)_3$ (30.72 mg, 0.06 mmol) in C_6D_6 (0.8 ml) was added dropwise; this caused the formation of two layers. The solution of the aluminium compound was agitated during the addition. Residual $B(C_6F_5)_3$ was washed into the reaction solution using C_6D_6 (0.6 ml). The resulting mixture was shaken briefly and was then left to stand for 20 minutes. After this period the upper layer was carefully separated and discarded. The lower layer was evaporated to dryness leaving a yellow foam (37 mg). ^{1}H NMR: δ 8.44 (s, 1H, C*H*=N), 7.91 [d, 1H, ^4J(HH) 2.5 Hz, C$_6H_2$], 7.30 [d, 1H, ^4J(HH) 2.5 Hz, C$_6H_2$], 7.30 (m, 3H, C$_6H_3$Me$_2$), 4.25 (m, 4H, OCH_2CH$_2$), 2.21 (m, 4H, OCH$_2$CH_2), 2.19 [s, 6H, C$_6$H$_3$(CH_3)$_2$], 1.49 (s, 9H, C$_4H_9$), 1.32 (s, 9H, C$_4H_9$), 0.45 (br s, 3H, BCH_3), −0.43 (s, 3H, AlCH_3). ^{13}C NMR: δ (cation part only) 179.86 (*C*H=N), 160.53, 144.08, 141.25, 118.88 [four quaternary resonances of *C*$_6$H$_2$Bu$^t_2$(O)C ring], 141.98 (one quaternary of C$_6$H$_3$Me$_2$ ring, the other is obscured), 137.30, 131.38 [2 *C*H resonances of C$_6$H$_2$Bu$^t_2$(O)C ring], 130.26, 129.45 (two *C*H resonances of C$_6$H$_3$Me$_2$N ring), 75.76 (O*C*H$_2$), 35.69 (*C*Me$_3$), 34.65 (*C*Me$_3$), 31.03 [C(*C*H$_3$)$_3$], 29.57 [C(*C*H$_3$)$_3$], 25.70 (OCH$_2$*C*H$_2$), 18.46 [C$_6$H$_3$(*C*H$_3$)$_2$], −14.50 (br, Al*C*H$_3$), also *C*H$_3$B of anion seen as broad resonance at δ 10.3. ^{19}F NMR: δ −135.5 (6F, BC$_6F_5$), −167.6 (3F, BC$_6F_5$), −170.2 (6F, BC$_6F_5$).

[{3,5-Bu$^t_2$-2-(O)C$_6$H$_2$CH=N-2,6-Pr$^i_2$C$_6$H$_3$}AlMe(THF)]$^+$ [B(C$_6$F$_5$)$_3$Me]$^-$ (3b). This complex was prepared similarly to **3a** but using **2b** (27.0 mg, 0.06 mmol) and toluene was used in place of benzene-d_6. ^{1}H NMR: δ 8.41 (s, 1H, C*H*=N), 7.91 [d, 1H, ^4J(HH) 2.5 Hz, C$_6H_2$], 7.49 [dd, 1H, ^3J(HH) 8.7 Hz, ^3J(HH) 6.7 Hz, C$_6H_3$Pr$^i_2$], 7.36 [d, 1H, ^3J(HH) 8.7 Hz, C$_6H_3$Pr$^i_2$], 7.36 [d, 1H, ^3J(HH) 6.7 Hz, C$_6H_3$Pr$^i_2$], 7.26 [d, 1H, ^4J(HH) 2.5 Hz, C$_6H_2$], 4.25 (m, 4H, OCH_2), 2.68 (sept., 2H, ^3J(HH) 6.8 Hz, C*H*Me$_2$), 2.21 (m, 4H, OCH$_2$CH_2), 1.49 (s, 9H, C$_4H_9$), 1.32 (s, 9H, C$_4H_9$), 1.32 [d, 6H, ^3J(HH) 6.8 Hz, CH(CH_3)$_2$], 1.14 [d, 6H, ^3J(HH) 6.8 Hz, CH(CH_3)$_2$], 0.44 (br s, 3H, BCH_3), −0.37 (s, 3H, AlCH_3). ^{13}C NMR: δ (cation part only) 179.02 (*C*H=N), 160.61, 144.38, 141.32, 118.51 [four quaternary resonances of *C*$_6$H$_2$Bu$^t_2$(O)C ring], 137.60, 131.05 [2 *C*H resonances of *C*$_6$H$_2$Bu$^t_2$(O)C ring], 130.42, 125.57 (2 *C*H resonances of *C*$_6$H$_3$Pr$^i_2$N ring), 129.32, 128.52 (two quaternary resonances of *C*$_6$H$_3$Pr$^i_2$N ring), 75.82 (O*C*H$_2$), 35.74 (*C*Me$_3$), 34.71

(CMe_3), 31.05 [$C(CH_3)_3$], 29.62 [$C(CH_3)_3$], 29.33 ($CHMe_2$), 26.00 [$(CH(CH_3)_2$], 25.69 (OCH_2CH_2), 22.76 [$(CH(CH_3)_2$], −14.52 (br, $AlCH_3$), also CH_3B of anion seen as broad resonance at δ 10.3.

Crystallography

Crystal data for **2a**: $C_{25}H_{36}NOAl$, $M = 393.5$, orthorhombic, *Pbca* (no. 61), $a = 13.865(2)$, $b = 15.721(3)$, $c = 22.912(4)$ Å, $V = 4994(1)$ Å^3, $Z = 8$, $D_c = 1.047$ g cm^{-3}, μ(Mo-Kα) = 0.95 cm^{-1}, $T = 293$ K, orange prisms; 4355 independent measured reflections, F^2 refinement, $R_1 = 0.066$, $wR_2 = 0.141$, 2118 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta \leq 50°$], 254 parameters.

Crystal data for **2b**: $C_{29}H_{44}NOAl$, $M = 449.6$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 9.316(2)$, $b = 10.277(1)$, $c = 29.617(1)$ Å, $V = 2835.5(6)$ Å^3, $Z = 4$, $D_c = 1.053$ g cm^{-3}, μ(Cu-Kα) = 7.52 cm^{-1}, $T = 203$ K, yellow plates; 2616 independent measured reflections, F^2 refinement, $R_1 = 0.052$, $wR_2 = 0.129$, 2257 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 126°$], 290 parameters. The absolute structure was determined by a combination of *R*-factor tests [$R_1^+ = 0.0524$, $R_1^- = 0.0531$] and by use of the Flack parameter [$x^+ = +0.22(8)$, $x^- = +0.78(8)$]. CCDC reference numbers 157073 and 157074. See http://www.rsc.org/suppdata/dt/b1/b100743m/ for crystallographic data in CIF or other electronic format.

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