Cationic alkyl aluminium ethylene polymerization catalysts based on monoanionic *N,N,N*-pyridyliminoamide ligands

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Treatment of the 2,6-bis(imino)pyridines {[2,6-(ArNCR)$_2$C$_5$H$_3$N]} [R = H, Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$ or 2,4,6-Me$_3$C$_6$H$_2$; R = Me, Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$] with AlMe$_3$ at elevated temperature gives, *via* migration of a methyl group to the ligand backbone, the pseudo-five coordinate dimethyl-aluminium species {2-[ArNCR(Me)],6-(ArNCR)C$_5$H$_3$N}-AlMe$_2$ (1a–c); upon treatment with B(C$_6$F$_5$)$_3$, 1a–c cleanly afford the cationic methyl complexes [{2-[ArNCR(Me)],6-(ArNCR)C$_5$H$_3$N}AlMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (2a–c) which are active for ethylene polymerization.

Neutral aluminium alkyls are well known to act as ethylene oligomerization[1] and polymerization[2] catalysts. However, the potential of cationic aluminium alkyls as catalysts is just emerging. Recent advances by Coles and Jordan[3] have utilised a number of chelating *N,N*-amidinate ligands, *viz.* {RC(NR′)$_2$} (R = Me, R′ = *i*-Pr, Cy; R = *t*-Bu, R′ = *i*-Pr, Cy, SiMe$_3$) which, upon reaction with Me$_3$Al, afford complexes of the form [{RC(NR′)$_2$}AlMe$_2$]. Cationic species are readily generated on further reaction with B(C$_6$F$_5$)$_3$ or [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$], the latter giving amine adducts. In the case of R = *t*-Bu, R′ = *i*-Pr the derived cation [from B(C$_6$F$_5$)$_3$] polymerizes ethylene at ambient temperature, albeit with low activity.

In a separate study, we[4] and Brookhart and coworkers[5] have recently shown that iron and cobalt complexes bearing neutral, 6-electron donor 2,6-bis(imino)pyridine ligands afford exceptionally active polymerization catalysts when activated with methylaluminoxane (MAO). We became interested in extending the range of *N,N,N*-chelate ligands to monoanionic derivatives in which one of the imino groups is transformed into an amido functionality, and nucleophilic attack on the imine carbon using an alkylaluminium reagent offered a convenient approach.[6] The aluminium complexes so-derived can be used to provide a source of free pyridyliminoamine ligands (*via* hydrolysis); details of the synthetic utility of this reaction will be reported elsewhere.[7] Here, we show that the dimethylaluminium complexes bearing such tridentate *N,N,N*-ligands also can be converted cleanly to cationic alkyl derivatives which are

active as ethylene polymerization catalysts. The significance of this observation is highlighted by a recent report that bidentate *N,N*-chelate ligand systems can lead to undesirable exchange reactions which thwart the generation of a polymerization-active site.[8]

Reaction of the parent 2,6-bis(imino)pyridines {[2,6-(ArNCR)$_2$C$_5$H$_3$N]} [R = H, Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$ or 2,4,6-Me$_3$C$_6$H$_2$; R = Me, 2,6-*i*-Pr$_2$C$_6$H$_3$] with AlMe$_3$ in refluxing toluene (12 h) results in alkylation of the ligand backbone to give the dimethylaluminium species {2-[ArNCR(Me)],6-(ArNCR)C$_5$H$_3$N}AlMe$_2$ [R = H; Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$ **1a**; R = H; Ar = 2,4,6-Me$_3$C$_6$H$_2$ **1b**; R = Me, Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$ **1c**] in high yield (Scheme 1).†

Crystals of **1b** suitable for an X-ray structure determination were grown from MeCN. The molecular structure‡ of **1b** shows the N(9)–C(9)–py–C(7)–N(7) portion of the ligand to be co-planar to within 0.06 Å (Fig. 1), a geometry very similar to that observed for the closely related bis(imino)pyridine ligand in its iron complex.[4] Here the aluminium atom lies 0.33 Å out of this plane and adopts a severely distorted tetrahedral geometry with
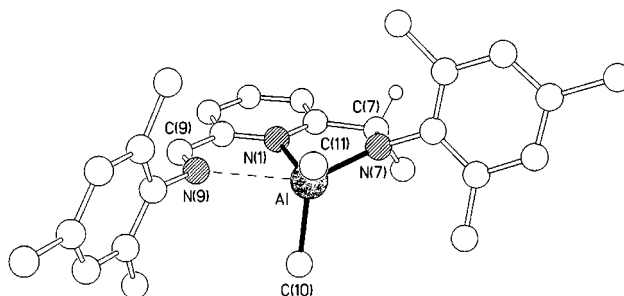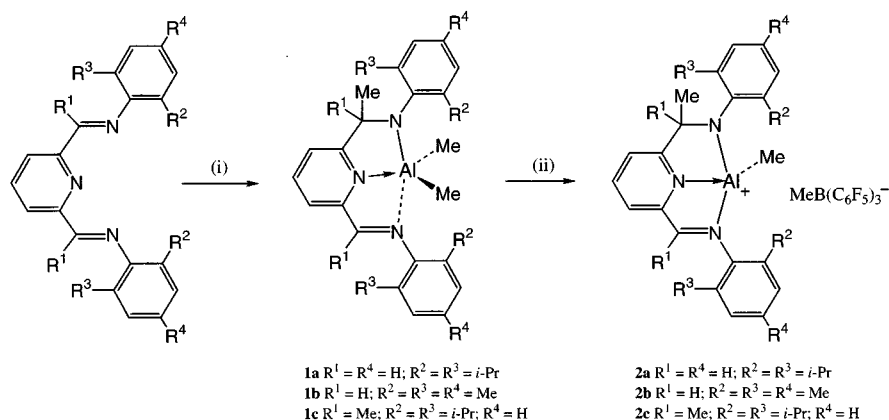

Fig. 1 The molecular structure of **1b**. Selected bond lengths (Å) and angles (°): Al–N(1) 2.029(4), Al–N(7) 1.876(4), Al–N(9) 2.575(4), Al–C(10) 1.990(6), Al–C(11) 1.951(5), C(7)–N(7) 1.444(6), C(9)–N(9) 1.273(5), N(7)–Al–C(11) 103.6(2), N(7)–Al–C(10) 113.8(2), C(11)–Al–C(10) 114.0(3), N(7)–Al–N(1) 81.3(2), C(11)–Al–N(1) 136.0(2), C(10)–Al–N(1) 102.8(2).

1a R^1 = R^4 = H; R^2 = R^3 = *i*-Pr
1b R^1 = H; R^2 = R^3 = R^4 = Me
1c R^1 = Me; R^2 = R^3 = *i*-Pr; R^4 = H

2a R^1 = R^4 = H; R^2 = R^3 = *i*-Pr
2b R^1 = H; R^2 = R^3 = R^4 = Me
2c R^1 = Me; R^2 = R^3 = *i*-Pr; R^4 = H

Scheme 1 *Reagents and conditions:* (i) AlMe$_3$, toluene, 110 °C, 12 h; (ii) B(C$_6$F$_5$)$_3$, toluene, rt.

Table 1 Results of ethylene polymerization runs with cations **2a–c**

Run[a]	Cation[b]	Yield/g	Activity/ g mol^{-1} h^{-1} bar^{-1}	M_n[c]	M_w[c]	M_w[c]/M_n[c]	M_{pk}[c]
1	**2a**	0.10	80	7800	23 000	2.9	19 000
2	**2b**	0.08	60	5200	33 000	6.3	13 000
3	**2c**	0.15	120	2400	13 000	5.5	9 800

[a] All runs performed in toluene at 5 bar of ethylene, 40 °C, 60 min, using 0.25 mmol of cation. [b] Generated *in situ* from the reaction of equimolar (0.25 mmol) amounts of **1a–c** and B(C$_6$F$_5$)$_3$. [c] Determined by GPC at 160 °C.

angles at aluminium ranging between 81.3(2) and 136.0(2)°. There is a slight asymmetry in the Al–Me distances [1.990(6) Å to C(10) and 1.951(5) Å to C(11)] but a more marked difference between the two Al–N bonds, with that to the formally negatively charged nitrogen N(7) being significantly shorter [at 1.876(4) Å] than that to the pyridyl nitrogen [2.029(4) Å]. Perhaps the most interesting feature of the structure is the directing of the imino nitrogen N(9) into the flattened 'basal' face of the tetrahedron—the aluminium atom lies only 0.3 Å out of the N(1)–C(10)–C(11) plane whereas it lies between 0.6 and 0.9 Å out of the other tetrahedral faces. The distance is long at 2.575(4) Å, but bearing in mind the potential for this nitrogen and the pyridyl nitrogen to adopt an *anti* relationship in the absence of a metal ion[7] we believe that this interaction is real and indeed a key feature in the subsequent cation formation in **2**.

The ^{1}H NMR spectra are consistent with the solid-state structures of **1** being maintained in solution. For **1a**, the pyridyl *meta*-protons resonate at δ 8.49 and 7.67 while the coordinated methyl groups appear as singlets at δ −0.67 and −0.89 reflecting the C_1 symmetry of the complex.

The cationic complexes [{2-[ArNCR(Me)],6-(ArNCR)-C$_5$H$_3$N}AlMe]$^+$ (**2a–c**) are readily generated on treatment of one equivalent of [B(C$_6$F$_5$)$_3$] in toluene at ambient temperature (Scheme 1).† For example, the ^{1}H NMR spectrum arising from **2a** reveals a sharp singlet at δ −0.70 for the methyl group coordinated to aluminium, while the methyl group coordinated to boron of the [MeB(C$_6$F$_5$)$_3$]$^-$ counter-anion is clearly seen as a broad singlet at δ 0.43. The upfield shift of this resonance is consistent with a free anion[9] and contrasts with the more downfield resonance (δ 1.67) observed by Coles and Jordan in which a B–Me···Al association is invoked.[3]

All the cationic complexes **2a–c** are active for ethylene polymerization (see Table 1) affording solid polyethylene with activities between 80 and 120 g mol^{-1} h^{-1} bar^{-1}. The polymer products in each case are low molecular weight, with M_ws ranging from 33 000 (run 2) to 13 000 (run 3). It is noteworthy that by changing the ligand backbone (otherwise identical) in **2a** from a single methyl group to three methyl groups in **2c** has the effect of reducing the molecular weight by almost half (*cf.* runs 1 and 3).

In a series of experiments on the iron and cobalt catalyst systems, we have shown that the bis(imino)pyridine ligands bonded to iron and cobalt are not attacked by AlMe$_3$ or MAO under the conditions of the polymerization experiment: free bis(imino)pyridine can be isolated in quantitative yield following hydrolytic work-up after the polymerization, *i.e.* no alkylation of the ligand backbone occurs of the type described here.

Notes and references

† Satisfactory microanalyses have been obtained. *Selected spectroscopic data:* For **1a**: ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ 8.61 (s, 1H, N=CH), 8.49 [d, 1H, ^3J(HH) 7.6, Py-H$_m$], 8.15 [app. t, 1H, ^3J(HH) 7.6 Py-H$_p$], 7.67 [d, 1H, ^3J(HH) 7.6, Py-H$_m$], −0.67 (s, 3H, AlMe), −0.89 (s, 3H, AlMe). For **1b**: ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ 8.57 (s, 1H, N=CH), 8.30 [d, 1H, ^3J(HH) 7.6, Py-H$_m$], 8.11 [app. t, 1H, ^3J(HH) 7.6, Py-H$_p$], 7.68 [d, 1H, ^3J(HH) 7.6, Py-H$_m$], −0.73 (s, 3H, AlMe), −1.01 (s, 3H, AlMe). For **1c**: ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ 8.31 [app. t, 1H, ^3J(HH) 7.6 Py-H$_p$], 8.03 [d, 1H, ^3J(HH) 7.6, Py-H$_m$], 7.78 [d, 1H, ^3J(HH) 7.6, Py-H$_m$], 2.31 (s, 3H, N=CMe), 1.82 (s, 6H, NCMe$_2$), −0.72 (s, 3H, AlMe), −0.89 (s, 3H, AlMe). For **2a**: ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ 8.68 (s, 1H, N=CH), 8.15 [app. t, 1H, ^3J(HH) 7.6, Py-H$_p$], 8.17 [d, 1H, ^3J(HH) 7.6, Py-H$_m$], 8.13 [d, 1H, ^3J(HH) 7.6, Py-H$_m$], 0.43 (s, 3H, BMe), −0.70 (s, 3H, AlMe). For **2b**: ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ 8.57 (s, 1H, N=CH), 8.33 [app. t, 1H, ^3J(HH) 7.6, Py-H$_p$], 8.01 [d, 1H, ^3J(HH) 7.6, Py-H$_m$], 7.98 [d, 1H, ^3J(HH) 7.6, Py-H$_m$], 4.67 [q, 1H, ^3J(HH) 6.7, C*H*Me], 1.26 (d, 3H, CH*Me*), 0.33 (s, 3H, BMe), −0.85 (s, 3H, AlMe). For **2c**: ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ 8.29 [app. t, 1H, ^3J(HH) 7.6, 7.6, Py-H$_p$], 8.07 [d, 1H, ^3J(HH) 7.6 Py-H$_m$], 8.03 [d, 1H, ^3J(HH) 7.6, Py-H$_m$], 2.30 (s, 3H, N=CMe), 1.79 (s, 6H, NCMe$_2$), 0.40 (s, 3H, BMe), −0.77 (s, 3H, AlMe).

‡ *Crystal data for* **1b**: C$_{28}$H$_{36}$N$_3$Al, M = 441.6, triclinic, space group $P\bar{1}$ (no. 2), a = 7.992(2), b = 8.169(1), c = 20.979(3) Å, α = 82.28(1), β = 82.93(2), γ = 71.92(1)°, V = 1285.4(4) Å^3, Z = 2, D_c = 1.141 g cm^{-3}, μ(Cu-Kα) = 8.21 cm^{-1}, F(000) = 476, T = 183 K; orange/red platy needles, 0.23 × 0.17 × 0.03 mm, Siemens P4/RA diffractometer, ω-scans, 3810 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give R_1 = 0.073, wR_2 = 0.169 for 2432 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°$] and 290 parameters. CCDC 182/1059.

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