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

Michael Bruce, Vernon C. Gibson,* Carl Redshaw, Gregory A. Solan, Andrew J. P. White and David J. Williams

Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY. E-mail: V.Gibson@ic.ac.uk

Received (in Cambridge, UK) 13th October 1998

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 dimethylaluminium 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 coplanar 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

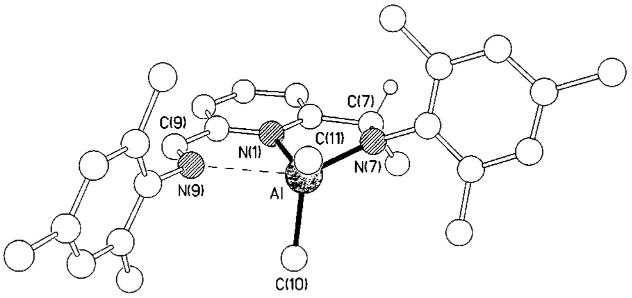
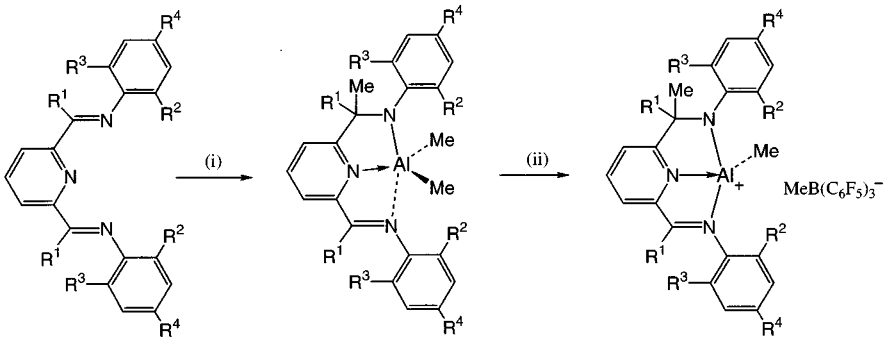


Fig. 1 The molecular structure of **1b**. Selected bond lengths (Å) and angles (°): Al–N(1) 2.029(4), Al–N(7) 1.876(4), Al–N(9) 2.575(4), Al–C(10) 1.990(6), Al–C(11) 1.951(5), C(7)–N(7) 1.444(6), C(9)–N(9) 1.273(5), N(7)–Al–C(11) 103.6(2), N(7)–Al–C(10) 113.8(2), C(11)–Al–C(10) 114.0(3), N(7)–Al–N(1) 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_6F_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_5H_3N}AlMe]$^+$ (**2a–c**) are readily generated on treatment of one equivalent of [B(C_6F_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_6F_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.

BP Chemicals Ltd is thanked for financial support. Dr J. Boyle and G. Audley are thanked for NMR and GPC measurements, respectively.

Notes and references

† Satisfactory microanalyses have been obtained. *Selected spectroscopic data:* For **1a**: ^{1}H NMR (CD_2Cl_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_2Cl_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_2Cl_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_2Cl_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_2Cl_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_2Cl_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**: $C_{28}H_{36}N_3Al$, 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.

1 K. Ziegler, H.-G. Tosel, E. Holzkamp, J. Schneider, M. Söll and W. R. Kroll, *Justus Leibigs Ann. Chem.*, 1960, **629**, 121.

2 H. Martin and H. Bretinger, *Makromol. Chem.*, 1992, **193**, 1283.

3 M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1997, **119**, 8125.

4 G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 848.

5 B. L. Small, M. Brookhart and M. A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049.

6 (*a*) J. M. Klerks, D. J. Stufkens, G. van Koten and K. Vrieze, *J. Organomet. Chem.*, 1979, **181**, 271; (*b*) V. C. Gibson, C. Redshaw, A. J. P. White and D. J. Williams, *J. Organomet. Chem.*, 1998, **550**, 453.

7 V. C. Gibson, S. Mastroianni, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, to be submitted.

8 B. Qiani, D. L. Ward and M. R. Smith III, *Organometallics*, 1998, **17**, 3070.

9 X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10015.

Communication 8/07950A