Pendant arm Schiff base complexes of aluminium as ethylene polymerisation catalysts

Paul A. Cameron, Vernon C. Gibson,* Carl Redshaw, John A. Segal, Michael D. Bruce, Andrew J. P. White and David J. Williams

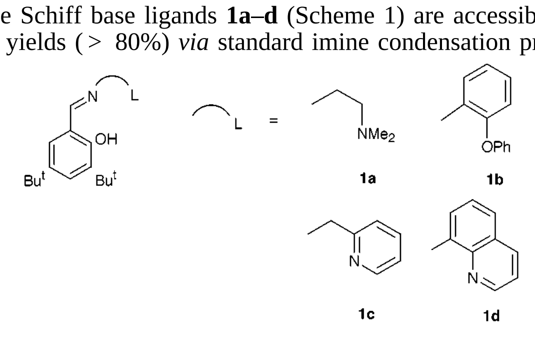
Department of Chemistry, Imperial College, South Kensington, London, UK, SW7 2AY. E-mail: v.gibson@ic.ac.uk

Received (in Cambridge, UK) 25th June 1999, Accepted 9th August 1999

The potentially tridentate Schiff base ligands [3,5-Bu^t_2-2-(HO)C_6H_2CH=NL] 1, on reaction with Me_3Al at room temperature, afford the complexes [(3,5-Bu^t_2-2-(O)C_6H_2CH=NL)$AlMe_2$] [L = $CH_2CH_2NMe_2$ 2a, (2-PhO)C_6H_4 2b, 2-$CH_2C_5H_4N$ 2c and 8-C_9H_6N (quinoline) 2d], 2a and 2c have been characterised crystallographically; further reaction of the dimethyl compounds with $B(C_6F_5)_3$ affords the cationic systems [(3,5-Bu^t_2-2-(O)C_6H_2CH=NL)-AlMe]$^+$ 3a–d of which 3a and 3b are ethylene polymerisation catalysts.

Recent reports by Coles and Jordan[1] and ourselves[2] have revealed the potential for cationic aluminium alkyls as ethylene polymerisation catalysts. The aluminium procatalysts reported thus far are bi- and tri-dentate chelates (L) of the general form [{L}$AlMe_2$], which are synthesised by the reaction of the relevant ligand system with Me_3Al. To obtain an active catalyst system, cationic species are generated on further reaction with $B(C_6F_5)_3$ in hydrocarbon or chlorocarbon solvents. The cationic aluminium alkyls so derived display low activities as ethylene polymerisation catalysts and they produce polymers of high[1] (M_w 176000–272000) or moderate[2] (M_w 13000–23000) molecular weight. In studies directed at extending the family of cationic aluminium catalysts to N,O-Schiff base chelate ligands, we first targeted bidentate chelates *e.g.* 3,5-Bu^t_2-2-(HO)C_6H_2CH=NR (R = alkyl or aryl), which led to the isolation of a range of systems of the type [(3,5-Bu^t_2-2-(O)C_6H_2CH=NR)$AlMe_2$].[3] However attempts to obtain clean alkylaluminium cations by way of reaction with $B(C_6F_5)_3$ (in toluene or dichloromethane) were unsuccessful, always leading to a mixture of species. ^{1}H NMR spectra of the product mixtures show *inter alia* the presence of high field methyl resonances that are characteristic of (ligand)AlMe(C_6F_5) species[4] formed by arylation of the Al centre by the boron reagent. In view of this undesired reactivity, the investigation was extended to Schiff base chelates bearing a pendant donor arm which it was envisaged might, through coordination, lend stability to the cationic methyl product. Here we show not only that such ligands afford stable cationic alkyl species but also that these cationic alkyls are active catalysts for ethylene polymerisation. Homogeneous olefin polymerisation catalysts hitherto described which are derived from N,O-Schiff bases are limited to complexes of transition metals, namely Ti,[5,6] Zr,[6,7] Cr[8] and Ni.[9]

The Schiff base ligands **1a–d** (Scheme 1) are accessible in good yields (> 80%) *via* standard imine condensation procedures. Treatment of these potentially tridentate ligands with Me_3Al in toluene at room temperature readily affords the corresponding dimethyl complexes [3,5-Bu^t-2-(O)C_6H_2CH=N-L]$AlMe_2$ **2a–d** with concomitant elimination of methane (Scheme 2).†

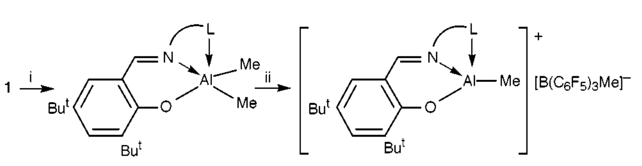


Scheme 1 Ligands **1a**–**d**.

Crystals of **2a** suitable for an X-ray structure determination‡ were grown from MeCN at room temperature. Deprotonated **1a** is seen to act as a tridentate ligand, binding to aluminium *via* the oxygen and the imino and amino nitrogen atoms [Fig. 1(a)]. The geometry at aluminium can best be described as distorted trigonal bipyramidal though with the bond to the axial amino nitrogen N(1) [2.413(5) Å] being substantially longer than that to the equatorial imino centre N(4) [1.998(4) Å]. With the exception of Al–N(1), the Al–X bonds are all clearly single in nature. These bonds, however, are noticeably longer than the corresponding linkages in the simple chelate analogues, *e.g.* {3,5-Bu^t_2-2-(O)C_6H_2CH=N(2,6-$Me_2C_6H_3$)}$AlMe_2$[3] [Al–O 1.773(3), Al–N 1.972(3), Al–Me 1.948(5), 1.959(5) Å] reflecting the presence of the additional donor in **2a** with subsequent competition for electron density. It is interesting that the aluminium atom is displaced significantly out of the equatorial plane (0.16 Å) in the direction of the ligand oxygen. The six-membered N,O chelate ring adopts a sofa conformation, the aluminium lying *ca.* 0.5 Å out of the plane of the other five atoms (which are co-planar to within 0.03 Å). The ring C=N bond has clearly retained its double bond character [N(4)–C(5) 1.294(6) Å], there being no evidence of significant delocalisation into any of the adjacent linkages. The structure of complex **2c** [Fig. 1(b)] is very similar to that of **2a**, in particular with respect to the geometry around Al, the only significant difference of note being a substantial reduction in the bond distance between the aluminium and the pyridyl nitrogen [Al–N(1) 2.254(2) Å *cf.* the dimethylamino nitrogen in **2a** [Al–N(1) 2.413(5) Å]. The remaining bond lengths and angles at aluminium do not differ significantly from those in **2a**.

The cationic complexes [(3,5-Bu^t_2-2-(O)C_6H_2CH=NL)-AlMe]$^+$ **3a–d** are readily generated on treatment with 1 equiv. of [$B(C_6F_5)_3$] in CD_2Cl_2 or toluene at ambient temperature (Scheme 2) as illustrated by the ^{1}H NMR spectrum of **3a** (Fig. 2); the systems exist as free cations as opposed to the ion pairs (*i.e.* with Al···Me–B association) observed by Coles and Jordan.[1] The pendant arm is likely to stabilise the cationic aluminium centre; in its absence, as noted above, the analogous reaction with [$B(C_6F_5)_3$] gave complicated NMR spectra corresponding to multiple products.

Complexes **2a–d** were combined with 1 equiv. of $B(C_6F_5)_3$ to test for ethylene polymerisation activity. Polymerisations were run with 0.25 mmol catalyst in 200 mL toluene solution under 5 bar ethylene pressure at 50 °C for 60 min. Procatalysts **2a** and



Scheme 2 *Reagents:* i. $AlMe_3$, toluene; ii, $B(C_6F_5)_3$, CD_2Cl_2 or toluene.

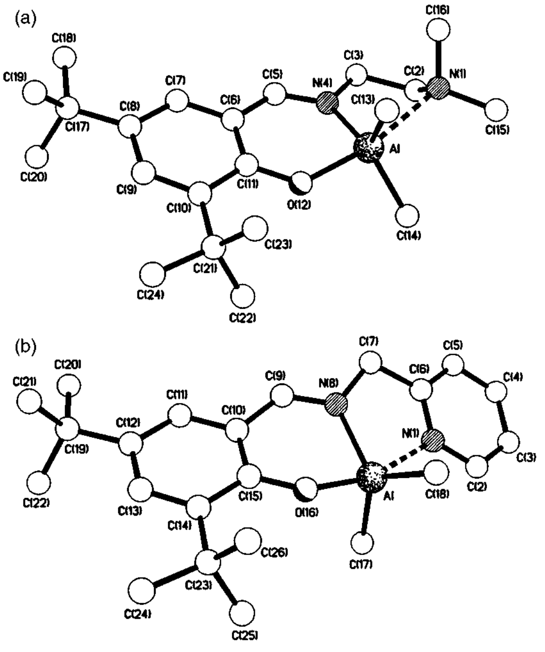


Fig. 1(a) The molecular structure of **2a**, showing the trigonal bipyramidal geometry at aluminium and the very long Al–N(amino) linkage. Selected bond lengths (Å) and angles (°): Al–N(1) 2.413(5), Al–N(4) 1.998(4), Al–O(12) 1.854(4), Al–C(13) 1.978(6), Al–C(14) 1.976(5), N(4)–C(5) 1.294(6), O(12)–Al–C(14) 96.6(2), O(12)–Al–C(13) 98.3(2), C(14)–Al–C(13) 123.7(3), O(12)–Al–N(4) 88.2(2), C(14)–Al–N(4) 116.0(2), C(13)–Al–N(4) 118.4(2), O(12)–Al–N(1) 163.0(2), C(14)–Al–N(1) 91.4(2), C(13)–Al–N(1) 89.5(2), N(4)–Al–N(1) 74.9(2). (b) Complex **2c**.

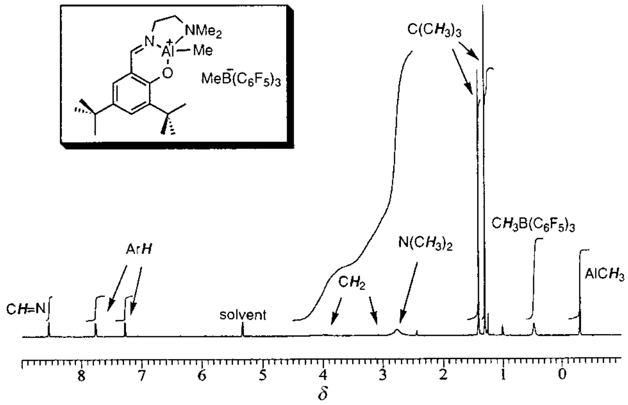


Fig. 2 ^{1}H NMR spectrum (250 MHz) of **3a**.

2b produced solid polyethylene but procatalysts **2c** and **2d** did not display any polymerisation activity. Procatalyst **2a** gave a productivity of 50 g(PE) mol^{-1} h^{-1} bar^{-1} and yielded polyethylene with M_w = 172000, M_n = 2400, whilst procatalyst **2b** gave 110 g(PE) mol^{-1} h^{-1} bar^{-1} with polymer M_w = 218000, M_n = 5200.

In contrast to our previous tridentate aluminium alkyls,[2] the present system affords higher molecular weights, as exemplified by the much higher M_w values, although the activities are similar. The results suggest that lability of the pendant donor arm, as in the cations derived from **2a**, **2b**, is an important feature of the polymerisation catalysis mechanism, providing a pathway for ethylene to approach the aluminium centre. The observation that **2c** and **2d**, which have N-heterocycles as the donor arms, did not provide active systems accords with this view as these compounds are likely to form cations with stronger donor to metal bonds (as evidenced by the significantly shorter Al–N(1) bond length in **2c** *cf.* **2a**) thereby reducing the propensity for dissociation of the coordinating arm to generate an active centre.

In summary, we have shown that Schiff base ligands are capable of stabilising cationic methylaluminium centres only when they possess an additional donor arm. We reasoned, however, that it might be possible to form cations from the analogous Schiff bases without the donor arm if a *free* donor ligand, *e.g.* THF, were added to stabilise the system. This is indeed the case, and our subsequent study of the formation of these closely related cationic species will be published elsewhere.

We thank the EPSRC for a studentship (to P. A. C.), BP-Amoco Chemicals and ICI Acrylics for financial support, and the Royal Society and the Leverhulme Trust for Fellowships (to J. A. S. and C. R.). Mr G. Audley is gratefully acknowledged for GPC measurements.

Notes and references

† Satisfactory microanalyses were obtained for compounds **2a**–**d**, cations **3a**–**d** were characterised spectroscopically. *Selected spectroscopic data* (*J*/Hz): for **2a**: ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ 7.66 [d, 1H, ^4J(HH) 2.4, C_6H_2], 7.39 (s, 1H, CH=N), 6.80 [d, 1H, ^4J(HH) 2.6, C_6H_2], 2.86 [t, 2H, ^3J(HH) 6.8, CH_2CH_2], 2.08 [t, 2H, ^3J(HH) 6.2, CH_2CH_2], 1.85 [s, 6H, $N(CH_3)_2$], 1.63, [s, 9H, $C(CH_3)_3$], 1.30 [s, 9H, $C(CH_3)_3$], −0.26 (s, 6H, $AlCH_3$). For **2c**: ^{1}H NMR (C_6D_6, 298 K): δ 8.31–8.28 (m, 1H, C_5H_4N), 7.72 [d, 1H, ^4J(HH) 2.6, C_6H_2], 7.38 [t, 1H, ^4J(HH) 1.3, CH=N), 6.83 [d, 1H, ^4J(HH) 2.5, C_6H_2], 6.80 [dt, 1H, ^3J(HH) 7.7, ^4J(HH) 1.7, C_5H_4N], 6.50–6.39 (m, 1H, C_5H_4N), 6.22–6.14 (m, 1H, C_5H_4N), 3.81 (br s, 2H, CH_2), 1.76 [s, 9H, $C(CH_3)_3$], 1.38 [s, 9H, $C(CH_3)_3$], −0.15 (s, 6H, $AlCH_3$). For **3a**: ^{1}H NMR (CD_2Cl_2, 298 K): δ 8.55 (s, 1H, CH=N), 7.76 [d, 1H, ^4J(HH) 2.6, C_6H_2], 7.27 [d, 1H, ^4J(HH) 2.6, C_6H_2], 4.0 (br, CH_2CH_2), 3.0 (br, CH_2CH_2), 2.77 [br s, 6H, $N(CH_3)_2$], 1.41 [s, 9H, $C(CH_3)_3$], 1.31 [s, 9H, $C(CH_3)_3$], 0.47 (s, 3H, BCH_3), −0.31 (s, 3H, $AlCH_3$). For **3c**: ^{1}H NMR (CD_2Cl_2, 298 K): δ 8.46 (s, 1H, CH=N), 8.05 [dt, 1H, ^3J(HH) 7.9, ^4J(HH) 1.5, C_5H_4N], 8.00 [d, 1H, ^4J(HH) 2.5, C_6H_2], 7.82 [d, 1H, ^3J(HH) 5.3, C_5H_4N], 7.51 [d, 1H, ^3J(HH) 8.0, C_5H_4N], 7.20 (m, 1H, C_5H_4N), 7.20 [dt, 1H, ^3J(HH) 6.3, ^4J(HH) 1.1, C_5H_4N), 7.07 [d, 1H, ^4J(HH) 2.5, C_6H_2], 5.15 [AB q, 2H, ^3J(HH) 1.5, CH_2CH_2], 4.98 [AB q, 2H, ^3J(HH) 1.5, CH_2CH_2], 1.75 [s, 9H, $C(CH_3)_3$], 1.26 [s, 9H, $C(CH_3)_3$], 0.48 (s, 3H, BCH_3), −0.47 (s, 3H, $AlCH_3$).

‡ *Crystal data* for **2a**: $C_{21}H_{37}N_2OAl$, M = 360.5, monoclinic, space group $P2_1/c$ (no. 14), a = 10.332(2), b = 24.982(4), c = 9.729(2) Å, β = 115.98(1)°, V = 2257.4(7) Å^3, Z = 4, D_c = 1.061 g cm^{-3}, μ(Mo-Kα) = 1.00 cm^{-1}, $F(000)$ = 792, T = 293 K, 2934 independent reflections. For **2c**: $C_{23}H_{33}N_2OAl$, M = 380.5, monoclinic, space group $P2_1/c$ (no. 14), a = 15.009(2), b = 12.207(2), c = 14.129(1) Å, β = 116.36(1)°, V = 2319.5(4) Å^3, Z = 4, D_c = 1.090 g cm^{-3}, μ(Mo-Kα) = 1.01 cm^{-1}, $F(000)$ = 824, T = 293 K, 5299 independent reflections. Data were collected on Siemens P4/PC diffractometers using ω-scans, and the non-hydrogen atoms were refined anisotropically using full matrix least squares based on F^2 to give R_1 = 0.067 (0.054), wR_2 = 0.156 (0.136) for 1646 (3526) independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 45°$ (45°)] and 226 (245) parameters for **2a** (**2c**) respectively.

CCDC 182/1366. See http://www.rsc.org/suppdata/cc/1999/1883/ for crystallographic files in .cif format.

1 M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1997, **119**, 8125.
2 M. Bruce, V. C. Gibson, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 2523.
3 P. A. Cameron, V. C. Gibson, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, manuscript in preparation.
4 B. Qian, D. L. Ward and M. L. Smith III, *Organometallics*, 1998, **17**, 3070.
5 S. Doherty, R. J. Errington, A. P. Jarvis, S. Collins, W. Clegg and M. R. J. Elsegood, *Organometallics*, 1998, **17**, 3408; J. P. Corden, W. Errington, P. Moore and M. G. H. Wallbridge, *Chem. Commun.*, 1999, 323.
6 T. Fujita, Y. Tohi, M. Mitani, S. Matsui, J. Saito, M. Nitabaru, K. Sugi, H. Makio and T. Tsutsui (Mitsui Chemicals), *Eur. Pat.*, 0874005A1, 1998.
7 E. B. Tjaden and R. F. Jordan, *Macromol. Symp.*, 1995, **89**, 231.
8 V. C. Gibson, C. Newton, C. Redshaw, G. A. Solon, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1999, 827.
9 C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben and M. W. Day, *Organometallics*, 1998, **17**, 3149.

Communication 9/05120A