

give SiMe₄, PhNMe₂ and an ionic yttrium alkyl species formulated as $\{[\text{PhC}(\text{NAr})_2\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF-}d_8)_n]\text{[B}(\text{C}_6\text{F}_5)_4]\}$ (**5**). In the ¹³C NMR spectrum,¹¹ the YCH₂ resonance in **5** is shifted downfield and the *J*_{YC} is increased somewhat relative to the neutral dialkyl **3**, which is similar to the behaviour observed previously for cationic YCH₂SiMe₃ species.³ In a more weakly coordinating polar solvent, bromobenzene-*d*₅, the resulting cationic species was found to be too unstable for characterisation.

When activated by [PhNMe₂H][B(C₆F₅)₄] in toluene in the presence of ethene, **3** readily polymerises the monomer to yield polyethene. In Table 1, the data are given for ethene polymerisation runs at 50 °C with varying run times, from 5 min to 30 min. It was observed that the *M*_w of the product increases from 430.10³ over 5 min to 1211.10³ over 30 min, with a remarkably low polydispersity *M*_w/*M*_n of around 1.2. Simple calculations indicate that about 1.1(1) polymer chain per yttrium is produced in all the runs. This suggests that the polymerisation of ethene by **3**/[PhNMe₂H][B(C₆F₅)₄] has living character, *i.e.* that chain transfer *via* β-H elimination is unfavourable. The exact study of this phenomenon in this system is complicated by experimental difficulties, such as inhomogeneity of the reaction mixture by precipitation of the polymer during the run. This may be associated with the observation that, although the catalyst productivity per unit of time decreases with increasing run time (from 1037 kg(PE) mol⁻¹ h⁻¹ bar⁻¹ over 5 min to 400 kg(PE) mol⁻¹ h⁻¹ bar⁻¹ over 30 min), the low polydispersity of the polymer is retained.

In contrast with the results for **3**, the combination of the bis-THF adduct **4** with [PhNMe₂H][B(C₆F₅)₄] in the presence of ethene did not result in catalytic polymerisation. Apparently the bonding of the second molecule of THF to the cationic metal species is sufficiently strong to suppress catalytic activity, suggesting that the (amidinate)Y(alkyl)(THF)-cation is responsible for olefin capture and subsequent insertion. In the presence of an excess of partially hydrolysed tris(isobutyl)aluminium (TIBAO) scavenger¹² (Al to Y ratio 10:1), the combination **4**/[PhNMe₂H][B(C₆F₅)₄] is effective as ethene polymerisation catalyst (Table 1, bottom two entries). The *M*_w of the polyethene is lower than in the absence of TIBAO, and its polydispersity is around 2. The polymer *M*_w does increase with run time to some extent, and it can be calculated that in both runs approximately 5 polymer chains per yttrium are produced. This behaviour may be similar to that observed in the polymerisation of ethene by some group 3 and group 4 metal metallocene catalysts in the presence of main group metal alkyls, where a polymer chain may be transferred from the group 3 metal to the main group metal and *vice versa*, and where chain termination by β-H transfer is insignificant.¹³

In conclusion, the use of a sterically encumbered benzamidinate ancillary ligand has enabled the synthesis of a mono-(amidinate) yttrium dialkyl that, with the Brønsted acid activator [PhNMe₂H][B(C₆F₅)₄], can be converted into a cationic monoalkyl species. The latter provides an active ethene polymerisation catalyst system in which chain transfer *via* β-H

abstraction appears to be unfavourable, and that can produce polyethene with a narrow polydispersity. There are several examples of cationic transition-metal catalysts that can effect living linear insertion polymerisation of ethene,^{14,15} but such behaviour at a relatively high reaction temperature of 50 °C is quite unusual.

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Notes and references

‡ Crystallographic data: for **3**: C₄₃H₆₉N₂O₂Si₂Y, *M* = 775.11, triclinic, space group *P*1̄, *a* = 12.537(1), *b* = 13.340(1), *c* = 13.925(1) Å, α = 101.964(9), β = 98.18(1), γ = 93.65(1)°, *U* = 2244.6(3) Å³, *T* = 130 K, *Z* = 2, *D*_c = 1.147 g cm⁻³, μ = 13.8 cm⁻¹, Enraf-Nonius CAD4-F diffractometer, λ(Mo-Kα) = 0.71073 Å, 9732 unique reflections, final residuals *wR*(*F*²) = 0.1390, *R*(*F*) = 0.0547 for 7479 reflections with *F*_o ≥ 4σ(*F*_o) and 702 parameters. For **4**: C₄₇H₇₇N₂O₂Si₂Y, *M* = 847.22, triclinic, space group *P*1̄, *a* = 10.8885(6), *b* = 11.7658(6), *c* = 20.830(1) Å, α = 80.246(1), β = 85.581(1), γ = 69.055(1)°, *U* = 2455.8(2) Å³, *T* = 90 K, *Z* = 2, *D*_c = 1.146 g cm⁻³, μ = 12.71 cm⁻¹, Bruker SMART APEX CCD diffractometer, λ(Mo-Kα) = 0.71073 Å, 11035 unique reflections, final residuals *wR*(*F*²) = 0.0782, *R*(*F*) = 0.0306 for 9712 reflections with *F*_o ≥ 4σ(*F*_o) and 795 parameters. CCDC reference numbers 192682 and 192683. See <http://www.rsc.org/suppdata/cc/b2/b208502j/> for crystallographic files in CIF format.

- H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143; A. L. McKnight and R. M. Waymouth, *Chem. Rev.*, 1998, **98**, 2587; G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428 and references therein.
- S. Haleja, W. P. Schaefer and J. E. Bercaw, *J. Organomet. Chem.*, 1997, **532**, 45; J. A. M. Canich, T. D. Schaffer, J. N. Christopher and K. R. Squire, *World Pat.*, WO00/18808, 2000; P. G. Hayes, W. E. Piers and R. McDonald, *J. Am. Chem. Soc.*, 2002, **124**, 2132.
- S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen and J. H. Teuben, *Chem. Commun.*, 2001, 637; B. Hessen and S. Bambirra, *World Pat.*, WO02/32909, 2002.
- S. Bambirra, M. J. R. Brandsma, E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Organometallics*, 2000, **19**, 3197.
- S. Ogata, A. Mochizuki, M.-A. Kakimoto and Y. Imai, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2171.
- R. T. Boeré, V. Klassen and G. Wolmershäuser, *J. Chem. Soc., Dalton Trans.*, 1998, 4147.
- K. B. Aubrecht, K. Chang, M. A. Hillmyer and W. B. Tolman, *J. Polym. Sci. A*, 2001, **39**, 284.
- M. F. Lappert and R. Pearce, *J. Chem. Soc., Chem. Commun.*, 1973, 126.
- W. J. Evans, J. C. Brady and J. W. Ziller, *J. Am. Chem. Soc.*, 2001, **123**, 7711.
- Selected NMR data for **3**: ¹H NMR (300 MHz, C₆D₆): δ 3.69 (m, 4 H α-THF), 1.14 (m, 4 H β-THF), -0.11 (d, ²*J*_{YH} = 3.0 Hz, 4 H, CH₂SiMe₃). ¹³C NMR (75.4 MHz, C₆D₆): δ 70.7 (t, ¹*J*_{CH} = 147.6 Hz, α-THF), 39.5 (dt, ¹*J*_{YC} = 40.3 Hz, ¹*J*_{CH} = 100.1 Hz, YCH₂SiMe₃), 24.9 (t, ¹*J*_{CH} = 124.4 Hz, β-THF).
- Selected NMR data for **5**: ¹H NMR (500 MHz, THF-*d*₈): δ -0.15 (d, ²*J*_{YH} = 3.0 Hz, 2 H, CH₂SiMe₃). ¹³C{¹H} NMR (125.7 MHz, THF-*d*₈): δ 42.3 (d, ¹*J*_{YC} = 42.7 Hz, YCH₂SiMe₃).
- Prepared according to: J. F. van Baar, P. A. Schut, A. D. Horton, T. Dall'occo and G. M. M. van Kessel, *World Pat.*, WO 00/35974, 2000.
- J.-F. Pelletier, A. Mortreux, X. Olonde and K. Bujadoux, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1854; E. G. Samsel, *US Pat.*, 5210338, 1993.
- M. Brookhart, J. M. DeSimone, B. E. Grant and M. J. Tanner, *Macromolecules*, 1995, **28**, 5378; K. Mashima, S. Fujikawa, Y. Tanaka, H. Urata, T. Oshiki, E. Tanaka and A. Nakamura, *Organometallics*, 1995, **14**, 2633; J. Saito, M. Mitani, J. Mohri, Y. Yoshida, S. Matsui, S. Ishii, S. Kojoh, N. Kashiwa and T. Fujita, *Angew. Chem., Int. Ed.*, 2001, **40**, 2918; M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 3327.
- For a recent review on living olefin insertion polymerisation, see: G. W. Coates, P. D. Hustad and S. Reinartz, *Angew. Chem., Int. Ed.*, 2002, **41**, 2236.

Table 1 Catalytic ethene polymerisation with **3** and **4** in conjunction with [PhNMe₂H][B(C₆F₅)₄] activator^a

Dialkyl	Time/min	PE yield/g	Activity ^c	10 ⁻³ <i>M</i> _w	<i>M</i> _w / <i>M</i> _n
3 ^a	5	4.2	1.04	430	1.2
3 ^a	10	6.4	0.79	644	1.2
3 ^a	20	7.6	0.46	854	1.2
3 ^a	30	10.0	0.40	1269	1.1
4 ^a	10	0.0	0.0	—	—
4 /TIBAO ^{a,b}	5	11.1	2.67	361	2.1
4 /TIBAO ^{a,b}	20	18.9	1.15	689	1.9

^a Conditions: toluene solvent (150 ml), 50 °C, 10 μmol Y dialkyl complex, 10 μmol activator, 5 bar ethene pressure. ^b Toluene solvent (200 ml), 100 μmol Al. ^c 10³ kg(PE) mol(Y)⁻¹ h⁻¹ bar⁻¹.