## Yttrium alkyl complexes with a sterically demanding benzamidinate ligand: synthesis, structure and catalytic ethene polymerisation<sup>†</sup>

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The benzamidinate yttrium dialkyl complexes [PhC- $(NAr)_2$ ]Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>n</sub> (Ar = 2,6-diisopropylphenyl; n = 1, 2) were prepared; when activated with [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], the species with n = 1 polymerises ethene to polyethene with a narrow polydispersity.

In contrast to the extensively developed families of cationic group 4 metal alkyl olefin polymerisation catalysts,1 very few examples exist to date of well-defined cationic olefin polymerisation catalysts for the group 3 and lanthanide metals.<sup>2,3</sup> In the past we reported attempts to prepare yttrium dialkyl complexes, with amidinate and amidinate-amine ancillary ligands, that could be converted to active cationic monoalkyl species.<sup>4</sup> These efforts were not successful due to the occurrence of ligand redistribution, yielding bis(amidinate) compounds, when alkyl groups other than the highly sterically demanding CH(SiMe<sub>3</sub>)<sub>2</sub> were employed. Here we report the use of a sterically demanding amidinate ancillary ligand, N,N'-bis(2,6-diisopropylphenyl)benzamidinate, in a successful synthesis of an amidinate yttrium bis(trimethylsilylmethyl) complex. This compound can be activated with the Brønsted acid activator  $[PhNMe_2H][B(C_6F_5)_4]$  to give an active ethene polymerisation catalyst, yielding polyethene with a narrow polydispersity.

The sterically demanding amidine ArN=CPh-NHAr (1, Ar = 2,6-Pri<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) was prepared from benzoic acid and the corresponding aniline with the use of silylated polyphosphoric acid, as reported for other *N,N'*-diaryl benzamidinates.<sup>5</sup> Alternatively, it can be obtained in stepwise fashion through the corresponding imidoyl chloride, as reported by Boeré *et al.* for ArN=C(*p*-tolyl)-NHAr.<sup>6</sup> The latter ligand has been used recently by Tolman *et al.* to prepare (amidinate)yttrium bisamide derivatives.<sup>7</sup>

As seen by NMR spectroscopy, the amidine **1** reacts cleanly in benzene- $d_6$  with Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (**2**)<sup>8</sup> to give SiMe<sub>4</sub> and an amidinate yttrium dialkyl species. Performing the reaction in pentane, followed by evaporation of the solvent and by removal of residual THF from the material (by stirring with additional pentane that was subsequently removed *in vacuo*), allowed crystallisation of the dialkyl complex as its mono-THF adduct, [PhC(NAr)<sub>2</sub>]Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF) (**3**, Scheme 1). Remarkably, work-up of this reaction mixture by simply concentrating and cooling the pentane solution formed initially cleanly yielded crystals of the corresponding bis-THF adduct, [PhC(NAr)<sub>2</sub>]Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub> (**4**). Both **3** and **4** were characterised by single crystal X-ray diffraction, and their structures are shown side by side in Fig. 1.

Both complexes have an N,N'-dihapto-amidinate ligand and in both cases the THF molecule(s) occupy a position roughly in the plane defined by the yttrium atom and the two ligand nitrogen atoms. The alkyl groups are located above and below that plane, oriented in such a way as to minimise interaction with the ligand 2,6-Pri<sub>2</sub>C<sub>6</sub>H<sub>3</sub> groups. The CH<sub>2</sub>–Y–CH<sub>2</sub> angle in **4** is 140.56(6)°, and relaxes to 119.48(19)° in **3**. As expected, the distances between yttrium and the ligating atoms are larger for **4** than for **3** (generally by about 0.03–0.05 Å) in response to

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b208502j/ the higher coordination number of the metal in **4**. The Y–O(2) distance in **4**, 2.451(1) Å, is elongated by 0.090 Å relative to the Y–O(1) distance in **3**. This Y–THF interaction in **4** is likely to be relatively weak, leading to facile loss of a THF molecule. Similar behaviour was recently reported for the pair of yttrium compounds  $Y(CH_2SiMe_3)_3(THF)_n$  (n = 2, 3), where one of the Y–O distances in the tris-THF adduct is very long (2.500(1) Å) and in which this THF molecule is readily lost.<sup>9</sup>

In C<sub>6</sub>D<sub>6</sub> solution, the NMR spectra of  $3^{10}$  and 4 are practically indistinguishable (apart from the shift and intensity of the THF resonances), which may indicate that one of the THF molecules in 4 is bound reversibly. For 3, the ambient temperature NMR spectrum suggests  $C_{2\nu}$  symmetry (equivalent Y-alkyl and N-aryl groups), indicating that rearrangement around the Y-centre is fast on the NMR timescale.

Reaction of **3** with the Brønsted acid activator [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in THF- $d_8$  results in a clean reaction to



Scheme 1 Reagents and conditions: i, pentane, 20 °C, 3 h, evaporation to dryness, pentane extraction; ii, pentane, 20 °C, 3 h, concentration and cooling to -30 °C.



**Fig. 1** Molecular structures of **3** (left) and **4** (right) (hydrogen atoms omitted for clarity, unlabeled atoms are carbon). Selected interatomic distances (Å) and angles (°) for **3**: Y–N(1) 2.339(3), Y–N(2) 2.369(2), Y–C(32) 2.374(4), Y–C(36) 2.384(4), Y–O 2.361(2), N(1)–Y–N(2) 57.27(9), C(32)–Y–C(36) 119.5(2), O–Y–C(32) 94.1(1), O–Y–C(36) 91.4(1), Y–C(32)–Si(1) 129.1(2), Y–C(36)–Si(2) 136.1(3); for **4**: Y–N(1) 2.395(1), Y–N(2) 2.397(1), Y–C(40) 2.427(2), Y–C(44) 2.433(2), Y–O(1) 2.427(1), Y–O(2) 2.451(1), N(1)–Y–N(2) 55.70(4), C(40)–Y–C(44) 140.56(6), O(1)–Y–O(2) 138.80(4), Y(1)–C(40)–Si(1) 137.32(9), Y–C(44)–Si(2) 135.72(9). $\ddagger$ 

give SiMe<sub>4</sub>, PhNMe<sub>2</sub> and an ionic yttrium alkyl species formulated as {[PhC(NAr)<sub>2</sub>]Y(CH<sub>2</sub>SiMe<sub>3</sub>)(THF- $d_8$ )<sub>n</sub>}-[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**5**). In the <sup>13</sup>C NMR spectrum,<sup>11</sup> the YCH<sub>2</sub> 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 YCH<sub>2</sub>SiMe<sub>3</sub> species.<sup>3</sup> 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  $[PhNMe_2H][B(C_6F_5)_4]$  in toluene in the presence of ethene,  $\hat{\mathbf{3}}$  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  $M_{\rm w}$  of the product increases from 430.10<sup>3</sup> over 5 min to 1211.10<sup>3</sup> over 30 min, with a remarkably low polydispersity  $M_w/M_p$  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  $3/[PhNMe_2H][B(C_6F_5)_4]$  has living character, *i.e.* that chain transfer via  $\beta$ -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  $[PhNMe_2H][B(C_6F_5)_4]$  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) scavenger<sup>12</sup> (Al to Y ratio 10:1), the combination  $4/[PhNMe_2H][B(C_6F_5)_4]$  is effective as ethene polymerisation catalyst (Table 1, bottom two entries). The  $M_{\rm w}$  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  $\beta$ -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 [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], can be converted into a cationic monoalkyl species. The latter provides an active ethene polymerisation catalyst system in which chain transfer via  $\beta$ -H

Table 1 Catalytic ethene polymerisation with 3 and 4 in conjunction with [PhNMe\_2H][B(C\_6F\_5)\_4] activator^a

Dialkyl	Time/min	PE yield/g	Activity <sup>c</sup>	$10^{-3}M_{\rm w}$	$M_{\rm w}/M_{\rm n}$
<b>3</b> <i>a</i>	5	4.2	1.04	430	1.2
<b>3</b> <i>a</i>	10	6.4	0.79	644	1.2
<b>3</b> <i>a</i>	20	7.6	0.46	854	1.2
<b>3</b> <i>a</i>	30	10.0	0.40	1269	1.1
<b>4</b> <i>a</i>	10	0.0	0.0	_	_
4/TIBAO <sup>a,b</sup>	5	11.1	2.67	361	2.1
4/TIBAO <sup>a,b</sup>	20	18.9	1.15	689	1.9

<sup>*a*</sup> Conditions: toluene solvent (150 ml), 50 °C, 10 μmol Y dialkyl complex, 10 μmol activator, 5 bar ethene pressure. <sup>*b*</sup> Toluene solvent (200 ml), 100 μmol Al. <sup>*c*</sup> 10<sup>3</sup> kg(PE) mol(Y)<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>.

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,<sup>14,15</sup> 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**: C<sub>43</sub>H<sub>69</sub>N<sub>2</sub>OSi<sub>2</sub>Y, *M* = 775.11, triclinic, space group *P*1, *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) Å<sup>3</sup>, *T* = 130 K, *Z* = 2, *D<sub>c</sub>* = 1.147 g cm<sup>-3</sup>, *μ* = 13.8 cm<sup>-1</sup>, Enraf-Nonius CAD4-F diffractometer, *λ*(Mo-K*α*) = 0.71073 Å, 9732 unique reflections, final residuals *wR*(*F*<sup>2</sup>) = 0.1390, *R*(*F*) = 0.0547 for 7479 reflections with *F<sub>o</sub>* ≥ 4*σ*(*F<sub>o</sub>*) and 702 parameters. For 4: C<sub>47</sub>H<sub>77</sub>N<sub>2</sub>O<sub>2</sub>Si<sub>2</sub>Y, *M* = 847.22, triclinic, space group *P*1, *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) Å<sup>3</sup>, *T* = 90 K, *Z* = 2, *D<sub>c</sub>* = 1.146 g cm<sup>-3</sup>, *μ* = 12.71 cm<sup>-1</sup>, Bruker SMART APEX CCD diffractometer, *λ*(Mo-K*α*) = 0.71073 Å, 11035 unique reflections, final residuals *wR*(*F*<sup>2</sup>) = 0.0782, *R*(*F*) = 0.0306 for 9712 reflections with *F<sub>o</sub>* ≥ 4*σ*(*F<sub>o</sub>*) and 795 parameters. CCDC reference numbers 192682 and 192683. See http://www.rsc.org/suppdata/cc/b2/b208502j/ for crystallographic files in CIF format.

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- 10 Selected NMR data for **3**: <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 3.69 (m, 4 H α-THF), 1.14 (m, 4 H β-THF), -0.11 (d, <sup>2</sup>J<sub>YH</sub> = 3.0 Hz, 4 H, CH<sub>2</sub>SiMe<sub>3</sub>). <sup>13</sup>C NMR (75.4 MHz, C<sub>6</sub>D<sub>6</sub>): δ 70.7 (t, <sup>1</sup>J<sub>CH</sub> = 147.6 Hz, α-THF), 39.5 (dt, <sup>1</sup>J<sub>YC</sub> = 40.3 Hz, <sup>1</sup>J<sub>CH</sub> = 100.1 Hz, YCH<sub>2</sub>SiMe<sub>3</sub>), 24.9 (t, <sup>1</sup>J<sub>CH</sub> = 124.4 Hz, β-THF).
- 11 Selected NMR data for **5**: <sup>1</sup>H NMR (500 MHz, THF- $d_8$ ):  $\delta$  -0.15 (d, <sup>2</sup> $J_{\rm YH}$  = 3.0 Hz, 2 H, CH<sub>2</sub>SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.7 MHz, THF- $d_8$ ):  $\delta$  42.3 (d, <sup>1</sup> $J_{\rm YC}$  = 42.7 Hz, YCH<sub>2</sub>SiMe<sub>3</sub>).
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