Neutral and cationic yttrium alkyl complexes with linked 1,4,7-triazacyclononane-amide monoanionic ancillary ligands: synthesis and catalytic ethene polymerisation†‡

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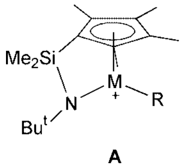
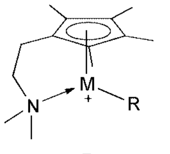
Yttrium dialkyl complexes [*N*,*N*′-R_2-tacn-*N*″-$(CH_2)_2NBu^t$]-$Y(CH_2SiMe_3)_2$ (R = Me, Pr^i; tacn = 1,4,7-triazacyclononane) were prepared; when activated with $[PhNMe_2H][B(C_6F_5)_4]$ these complexes form cationic alkyl species that are active ethene polymerisation catalysts.

Cationic group 4 metal alkyl species with linked dianionic cyclopentadienyl-amide ancillary ligands, such as $[C_5Me_4SiMe_2NBu^t]M(alkyl)^+$ **A** (M = Ti, Zr), are highly efficient catalysts for the polymerisation of alkenes.[1] The isoelectronic group 3 metal alkyl complexes with these ligands are neutral, and much less effective in alkene polymerisation.[2] One approach that might allow the generation of cationic group 3 metal alkyl species is to replace either one of the monoanionic moieties of the ancillary ligand (amide or cyclopentadienyl) by a neutral functionality. A recent patent showed that replacement of the amide group by an amine donor can lead to $[C_5Me_4CH_2CH_2NMe_2]M(alkyl)^+$ **B**, (M = Sc) species that are active in catalytic alkene polymerisation.[3] We have designed a ligand in which an amido functionality is attached to a substituted 1,4,7-triazacyclononane (tacn) group, and that allowed us to generate cationic tacn-amide group 3 metal alkyl complexes of type **C**. These species were found to be highly active in the catalytic polymerisation of ethene.



A



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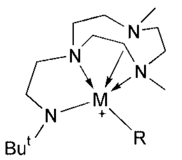
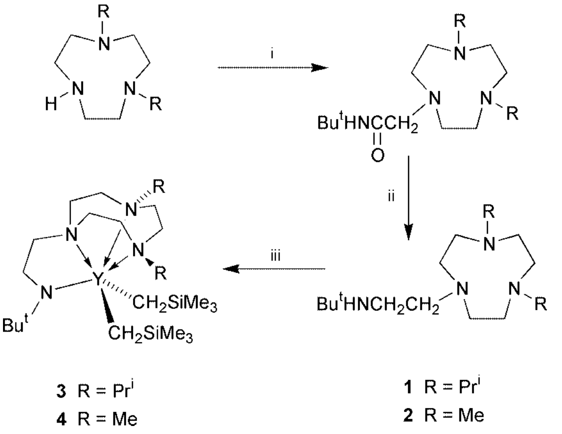


C

1,4,7-Triazacyclononane ligands have been successfully used as 6-electron *fac*-tridentate ligands on a wide range of transition metals, and various neutral and anionic tacn derivatives have appeared in the literature recently.[4] The new tacn-amine derivatives *N*,*N*′-R_2-tacn-*N*″-$(CH_2)_2NBu^tH$ (R = Pr^i, **1**; Me, **2**) were prepared in two steps from the known corresponding *N*,*N*′-dialkyl-1,4,7-triazacyclononanes[5] (Scheme 1). Reaction of these *N*,*N*′-dialkyltriazacyclononanes with *N*-*tert*-butylchloroacetamide in refluxing actonitrile, with a catalytic amount of NaI, yielded the corresponding *N*-*tert*-butyl-(4,7-dialkyl-1,4,7-triazacyclonon-1-yl)acetamides. These were then reduced with $LiAlH_4$ in refluxing diglyme and purified, after hydrolysis and acid–base extraction, by Kugelrohr distillation (**2**) or column chromatography (**1**).

Reaction of the amine **1** with the yttrium trialkyl $Y(CH_2SiMe_3)_3(thf)_2$[6] in C_6D_6 results in formation of $SiMe_4$, free thf, and the yttrium dialkyl complex [*N*,*N*′-Pr^i_2-tacn-*N*″-$(CH_2CH_2)NBu^t]Y(CH_2SiMe_3)_2$ **3**, (Scheme 1), as seen by NMR spectroscopy. The same reaction in pentane solvent (0.5 mmol scale), followed by crystallization, yielded analytically pure, white crystalline **3**. The isolated yield (28%) was rather modest, mainly due the high solubility of the product. An X-ray structure determination of **3**§ confirmed its identification as a monomeric, thf-free yttrium dialkyl (Fig. 1). As expected, the three nitrogens of the tacn moiety are bound in *fac* arrangement to the metal centre. There is considerable asymmetry in the structure of the complex, as seen *e.g.* in the angle N(1)–Y–C(19) 113.8(2)° *vs.* N(1)–Y–C(23) 95.9(2)°, and the groups are



Scheme 1 *Reagents and conditions*: i, *N*-*tert*-butylchloroacetamide, MeCN, cat. NaI, reflux, 1 h; ii, $LiAlH_4$, diglyme, reflux, 3 h (**2**) or 100 h (**1**), followed by hydrolysis and acid–base extraction; iii, $Y(CH_2SiMe_3)_3(thf)_2$, pentane, 14 h, 20 °C.

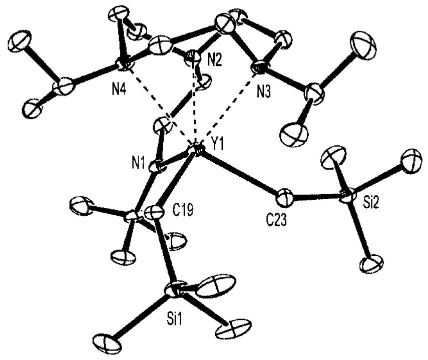


Fig. 1 Molecular structure of **3** (hydrogen atoms omitted for clarity, unlabeled atoms are carbon, thermal ellipsoids drawn at 30% probability level). Selected interatomic distances (Å) and angles (°): Y–N(1) 2.231(5), Y–N(2) 2.541(5), Y–N(3) 2.618(5), Y–N(4) 2.740(5), Y–C(19) 2.476(5), Y–C(23) 2.421(7); C(19)–Y–C(23) 101.1(2), N(1)–Y–N(2) 72.4(2), N(2)–Y–N(3) 68.8(2), N(2)–Y–N(4) 65.5(2), N(3)–Y–N(4) 68.9(2), N(3)–Y–C(23) 86.7(2), N(4)–Y–C(19) 82.7(2), Y–C(19)–Si(1) 134.2(3), Y–C(23)–Si(2) 145.4(4).

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† Electronic supplementary information (ESI) available: experimental, spectroscopic and polymerization details. See http://www.rsc.org/suppdata/cc/b1/b101012n/

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Table 1 Catalytic ethene polymerisation with **3** and **4** in conjunction with $[PhNMe_2H][B(C_6F_5)_4]$ activator[a]

Dialkyl	T/°C	PE yield/g	Productivity/ 10^3 kg(PE) mol(Y)$^{-1}$ h^{-1} bar^{-1}	10^{-3} M_w	M_w/M_n
4	30	5.62	0.70	471	4.0
4	50	9.40	1.18	325	4.9
4	80	14.30	1.79	98	6.0
3[b]	30	11.95	0.96	—[c]	—[c]

[a] *Conditions:* toluene solvent (150 ml), 10 μmol Y dialkyl complex, 10 μmol activator, 5 bar ethene pressure, 10 min run time. [b] 15 min run time. [c] Not determined.

arranged in such a way as to prevent the eclipsing of the ligand Pr$^{\mathrm{i}}$ and Y–alkyl groups. The Y–N distances for the tacn nitrogens span a considerable range, the shortest being the distance to the bridgehead nitrogen Y–N(2), 2.541(5) Å, and the longest the Y–N(4) distance, 2.740(5) Å, N(4) being practically *trans* to C(23). This asymmetry appears to be retained in solution, as the ambient temperature ^{1}H and ^{13}C NMR spectra show resonances consistent with an asymmetric species (*e.g.* four resonances for the diastereotopic CH_2SiMe_3 methylene protons).[7] The alkyl methylene carbon resonances are found at δ 33.7 and 31.0, with rather large $^1J_{YC}$ coupling constants (*ca.* 38 Hz) and relatively small $^1J_{CH}$ coupling constants of 95 Hz.

Reaction of the amine **2** with $Y(CH_2SiMe_3)_3(thf)_2$ in pentane yielded the corresponding dialkyl complex $[N,N'\text{-}Me_2\text{-tacn-}N''\text{-}(CH_2CH_2)NBu^t]Y(CH_2SiMe_3)_2$ **4**, analytically pure in 86% isolated yield. The smaller size of the alkyl substituents makes the complex more fluxional, as the room temperature ^{1}H NMR spectrum of **4** shows broad resonances consistent with a species with an average C_s symmetry. Cooling a toluene-d_8 solution of **4** to −60 °C slows down this dynamic process, revealing spectra with four Y–alkyl methylene and two Y–C resonances, again consistent with an asymmetric ground state structure.[8]

The dialkyl complex **4** reacts cleanly with the Brønsted acid $[PhNMe_2H][B(C_6F_5)_4]$[9] in C_6D_5Br solvent to give $SiMe_4$, free $PhNMe_2$, and an ionic species formulated as $\{[N,N'\text{-}Me_2\text{-tacn-}N''\text{-}(CH_2CH_2)NBu^t]Y(CH_2SiMe_3)\}[B(C_6F_5)_4]$ **6**.[10] The ^{1}H NMR spectrum shows a single resonance at δ −1.06 for the YCH_2 group (J_{YH} not resolved), and the ^{13}C NMR YCH_2 resonance at δ 37.0 (J_{YC} 40.7 Hz), shifted downfield and with a larger J_{YC} relative to the dialkyl **4**. The ionic species **6** is thermally relatively stable, and remains essentially unchanged over 1 h at ambient temperature in bromobenzene solution. In contrast, reaction of the dialkyl complex **3** with $[PhNMe_2H][B(C_6F_5)_4]$ leads to rapid formation of propene and 2 equiv. of $SiMe_4$ (as seen by ^{1}H NMR spectroscopy), and an ill-defined yttrium species. Apparently, an Pr$^{\mathrm{i}}$ substituent on the ancillary ligand is metallated on one of its methyl groups, followed by elimination of propene. When the reaction is performed in the presence of an excess of d_8-thf, the cationic alkyl species is trapped before ligand metallation occurs, giving a species formulated (based on its ^{1}H NMR characteristics) as $\{[N,N'\text{-}Pr^i_2\text{-tacn-}N''\text{-}(CH_2CH_2)NBu^t]Y(CH_2SiMe_3)(d_8\text{-thf})\}[B(C_6F_5)_4]$ (**5**·d_8-thf), with YCH_2 resonances at δ −1.29 and −1.35 (dd, $^2J_{HH}$ 11.0 Hz, J_{YH} 3.0 Hz).[11]

Ethylene homopolymerisation experiments (toluene solvent) showed that the dialkyls **3** and **4**, in combination with the Brønsted acid activator $[PhNMe_2H][B(C_6F_5)_4]$, yield active ethene polymerisation catalysts, with observed productivities up to 1.79×10^3 kg(PE) mol(Y)$^{-1}$ h^{-1} bar^{-1}. Relatively short run times (10–15 min) were chosen to minimise inhomogeneity and mass transfer effects. Over the run period the catalysts show a modest (25–30%) decrease in ethene uptake rate. The results listed in Table 1 show that the productivity of the Me_2-tacn system is enhanced by increasing the reaction temperature, but that the polydispersity of the polyethene produced also increases substantially. One possible explanation for this is that the initial cationic alkyl catalyst is thermally transformed into another species that is also active in the polymerisation of ethene, thus leading to bimodal product distributions. The polymerisation behaviour of this type of catalyst and its dependence on various parameters (ligand substitution pattern, activator species, *etc.*) is subject of further study.

In conclusion, we have prepared new yttrium dialkyl species with monoanionic tetradentate triazacyclononane-amide ancillary ligands. Reactions of these dialkys with $[PhNMe_2H][B(C_6F_5)_4]$ generate the ionic species **5**·thf-d_8 and **6**, rare examples of spectroscopically characterised cationic group 3 metal alkyls.[12] These cationic alkyl species are active catalysts for the polymerisation of ethene.

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Notes and references

§ *Crystallographic data* for **3**: $C_{26}H_{61}N_4Si_2Y$, M = 574.87, triclinic, space group $P\bar{1}$, a = 9.815(1), b = 9.859(1), c = 17.291(1) Å, α = 95.60(1), β = 90.68(1), γ = 98.63(1)°, U = 1645.7(4) Å^3, T = 130 K, Z = 2, D_c = 1.160 g cm^{-3}, μ = 18.6 cm^{-1}, Enraf-Nonius CAD4-F diffractometer, λ(Mo-Kα) = 0.71073 Å, 6433 unique reflections, final residuals $wR(F^2)$ = 0.1800, $R(F)$ = 0.0731 for 3940 reflections with $F_o \geqslant 4\sigma(F_o)$ and 311 parameters. CCDC 157466. See http://www.rsc.org/suppdata/cc/b1/b101012n/ for crystallographic data in .cif or other electronic format.

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7. *Selected NMR data* for **3**: ^{1}H NMR (500 MHz, C_6D_6) δ −0.26 (dd, J_{HH} 10.5, J_{YH} 3.3 Hz, 1H, YC*H*H), −0.53 (dd, J_{HH} 10.8, J_{YH} 2.1 Hz, 1H, YC*H*H), −0.83 (dd, J_{HH} 10.8, J_{YH} 3.0 Hz, 1H, YCH*H*), −1.00 (dd, J_{HH} 10.8, J_{YH} 2.1 Hz, 1H, YCH*H*). ^{13}C NMR (125.7 MHz, C_6D_6) δ 33.7 (dt, J_{YC} 36.9, J_{CH} 95.1 Hz, YCH_2), 31.0 (t, J_{YC} 38.7, J_{CH} 95.0 Hz, YCH_2).
8. *Selected NMR data* for **4**: ^{1}H NMR (500 MHz, −60 °C, C_7D_8) δ −0.62 (d, J_{HH} 11.0 Hz, 1H, YC*H*H), −0.86 (d, J_{HH} 11.0 Hz, 1H, YC*H*H), −0.94 (d, J_{HH} 11.0 Hz, 1H, YCH*H*), −1.06 (d, J_{HH} 10.5 Hz, 1H, YCH*H*). The J_{YH} coupling on the YCH_2 protons is unresolved. ^{13}C NMR (125.7 MHz, −60 °C, C_7D_8) δ 29.8 (dt, J_{YC} 35.4, J_{CH} 93.3 Hz, YCH_2), 28.5 (dt, J_{YC} 38.9, J_{CH} 97.3 Hz, YCH_2).
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10. *NMR data* for the cation of **6**: ^{1}H NMR (500 MHz, −30 °C, C_6D_5Br) δ 2.58–2.22 (m, 16H, NCH_2), 2.18 (s, 6H, NMe), 1.09 (s, 9H, Bu$^{\mathrm{t}}$), 0.11 (s, 9H, CH_2SiMe_3), −1.06 (br, 2H, YCH_2). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_5Br, −30 °C) δ 60.09 (NCH_2), 56.05 (NCH_2), 53.33 (CMe_3), 53.75 (NCH_2), 51.78 (NCH_2), 46.51 (NMe), 46.16 (NCH_2), 37.02 (d, $^1J_{YC}$ 40.7 Hz, YCH_2), 30.17 (CMe_3), 4.31 (SiMe).
11. *NMR data* for the cation of **5**·thf-d_8: ^{1}H NMR (500 MHz, −30 °C, C_6D_5Br–thf-d_8) δ 3.48 (sept, J_{HH} 6.0 Hz, 1H, C*H*Me_2), 3.40 (t, J_{HH} 13.0 Hz, 1H, NCH_2), 2.79–2.75 (m, 2H, NCH_2), 2.68–2.59 (m, 3H, NCH_2), 2.55–2.48 (m, 2H, NCH_2), 2.42–2.29 (m, 3H, NCH_2), 2.25–2.17 (m, 3H, NCH_2), 1.27 (br, 1H, CH*Me*$_2$), 1.18 (d, J_{HH} 6.0 Hz, 6H, CH*Me*$_2$), 1.15 (s, 9H, Bu$^{\mathrm{t}}$), 0.84 (d, J_{HH} 5.5 Hz, 3H, CH*Me*$_2$), 0.80 (d, J_{HH} 5.5 Hz, 3H, CH*Me*$_2$), 0.09 (s, 9H, *Me*$_3$SiCH$_2$), −1.29 (dd, J_{HH} 11.0, J_{YH} 3.0 Hz, 1H, YC*H*H), −1.35 (dd, J_{HH} 11.0, J_{YH} 3.0 Hz, 1H, YCH*H*).
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