The first rare earth organometallic complex of 1,4,7-trithiacyclononane: a precursor to unique cationic ethylene and α-olefin polymerisation catalysts supported by an all-sulfur donor ligand

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Electronic supporting information

Characterising data for [Sc([9]aneS_3)(CH_2SiMe_3)$_3$] (1). ^{1}H NMR (C_6D_6, 300.0 MHz, 293 K): 2.25 (6 H, m, SCH_2), 1.45 (6 H, m, SCH_2), 0.47 (27 H, s, $SiMe_3$), 0.15 (6 H, s, $ScCH_2$) ppm. ^{13}C NMR (C_6D_6, 75.0 Hz, 293 K): 43.0 ($ScCH_2$), 31.2 (SCH_2), 4.3 ($SiMe_3$) ppm. IR (NaCl plates, Nujol): 1413 (w), 1234 (w), 1246 (s), 875 (s), 823 (m), 745 (m) cm^{-1}. EI-MS: *m/z* = 225.3 (12 %) [M – $3CH_2SiMe_3$]$^+$, 179.8 (100 %) [[9]aneS_3]$^+$. Anal. found (calcd. for $C_{18}H_{45}S_3ScSi_3$): C, 44.1 (44.0); H, 9.2 (9.3).

Characterising data for [Sc([9]aneS_3)(CH_2SiMe_3)$_2$(THF)][BAr$^F{}_4$] (2-BAr$^F{}_4$). ^{1}H NMR (CD_2Cl_2, 300.0 MHz, 293 K): 4.38 (4 H, m, $OC\underline{H}_2CH_2$), 3.25 (6 H, m, SCH_2), 3.05 (6 H, m, SCH_2), 2.27 (4 H, m, $OCH_2C\underline{H}_2$), 0.28 (4 H, d, ^2J = 7.2 Hz, $C\underline{H}_2SiMe_3$), 0.02 (18 H, s, $Si\underline{Me}_3$) ppm. ^{19}F NMR (CD_2Cl_2, 300.0 MHz, 293 K): -133.53 (d, *o*-C_6F_5), -163.88 (t, *m*-C_6D_6), -167.80 (t, *p*-C_6F_5) ppm. ^{13}C NMR (CD_2Cl_2, 75.0 Hz, 293 K): 57.2 ($O\underline{C}H_2CH_2$), 32.9 ($S\underline{C}H_2$) 25.8 ($OCH_2\underline{C}H_2$), 3.2 ($Si\underline{Me}_3$) ppm.

Ethylene polymerisation conditions. Steel autoclave equipped with removable glass liner, magnetically coupled mechanical stirrer (stirring rate 750 rpm); 20 µmol **1**, 20 µmol $B(C_6F_5)_3$ cocatalyst; 250 cm^3 total volume toluene; 5 bar ethylene pressure delivered on request; run time 60 min; 250 equivs. Al^iBu_3. Quenching with methanol and water and then washing with 10% HCl and finally water and drying yielded 11.14 g of polyethylene.

1-Hexene polymerisation studies: Procedure 1. A solution of [CPh$_3$][BAr$^F{}_4$] (*ca* 1 or 2 equiv.) in C_6H_5Cl (1.5 - 5.0 cm^3) was added to solid **1** (20 μmol) and cooled to the desired temperature (-30 to r.t.). To this stirred solution was added 1-hexene (5 cm^3, 3.39 g) at the desired temperature and the progress of the reaction (% conversion of 1-hexene) was monitored by ^{1}H NMR aliquots. The reaction was terminated by addition of wet THF and the PH precipitated by adding this with stirring to ethanol. **Procedure 2.** To a solution of [CPh$_3$][BAr$^F{}_4$] (2 equiv.) and 1-hexene (1.48 cm^3, 1.08 g) in C_6H_5Cl (2.5 cm^3), a solution of **1** in C_6H_5Cl (2.5 cm^3) was added. The progress of the reaction (% conversion of 1-hexene) was monitored by ^{1}H NMR aliquots and the reaction was terminated by addition of wet THF and the PH precipitated by adding this with stirring to ethanol.

1-Styrene polymerisation. A solution of [CPh$_3$][BAr$^F{}_4$] (2 equiv.) in C_6H_5Cl (5.0 cm^3) was added to solid **1** (20 μmol) and cooled to -30 °C. To this stirred solution was added styrene (5 cm^3, 4.55 g) at the desired temperature and the progress of the reaction (% conversion of styrene) was monitored by ^{1}H NMR aliquots. After 1 min 100 % conversion was observed. The reaction was terminated by addition of wet THF and the PS precipitated by adding this with stirring to ethanol. The solid was isolated by filtration and dried to yield 3.5 g polystyrene.