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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$[Sc([9]aneS_3)(CH_2SiMe_3)_3]$, the first rare earth organometallic complex of 1,4,7-trithiacyclonane, is a precursor to ethylene and α-olefin polymerisation catalysts upon activation with BAr^F_3 or $[CPh_3][BAr^F_4]$ ($Ar^F = C_6F_5$); these are the first cationic rare earth organometallic catalysts supported by an all-sulfur donor ligand.

Non-cyclopentadienyl Group 3 and lanthanide organometallic chemistry is a topic of considerable current activity,[1] especially with regard to the development of olefin polymerisation catalysts.[2] Over the last 5 years in particular the focus in these regards has almost exclusively been on cationic alkyl systems.[3]

Bercaw et al. showed that when the trimethyl complex **I-Sc** (Chart 1) was treated with BAr^F_3 ($Ar^F = C_6F_5$) in THF-d_8 a species formulated as $Sc(Me_3[9]aneN_3)Me_2(\mu\text{-}Me)BAr^F_3$ "proved competent" for ethylene polymerization (no activity data were given).[4a] Subsequently,[4b] we found that the tris(trimethylsilylmethyl) homologue **II-Sc** and the podand ligand system **III-Sc** were the most active ethylene polymerisation catalysts reported to date for Sc (a re-evaluation of **I-Sc** found it to be only ca 15% as active as **II-Sc**[4c]). The yttrium analogues **I-Y**, **II-Y** or **III-Y** showed no activity. However, Hessen and co-workers' amide-functionalised yttrium systems **IV** do polymerise ethylene upon activation with $[PhNMe_2H][BAr^F_4]$.[5] Okuda et al. were the first to report structurally authenticated (but catalytically inactive) rare earth alkyl cations (e.g. **V**)[6] with crown ethers, and also showed that mono-alkyl di-cations of the type $[Ln(CH_2SiMe_3)(solvent)_x]^{2+}$ (modelled by **VI**) were active ethylene polymerisaton catalysts.[7] Hessen et al. and Piers et al. have reported recently on catalytically active cationic alkyl complexes with monoanionic N_2-donor ligands (e.g. **VII**).[8] Very recently, Gade et al. reported that the C_3-symmetric $[Sc(^iPr\text{-}trisox)(CH_2SiMe_3)_3]$ **VIII** (featuring a podand-like ligand akin to **III**) catalysed the isoselective polymerisation of 1-hexene on activation with 2 equivs. of $[CPh_3][BAr^F_4]$ and a di-cationic active species was postulated.[9]

Concurrent with these rapid advances for cationic rare earth alkyl catalysts (all with hard N- or O-donor co-ligands) have been reports that the presence of neutral S-donor groups may be beneficial to the performance of cationic Group 4 alkyl polymerisation catalysts.[10a] Such an effect has yet to be tested for cationic Group 3 alkyl catalysts and indeed no such complexes with S-donor ligands have been described.[10b] Stimulated by the capacity of the Sc compounds **I-Sc**, **II-Sc** and **III-Sc** for ethylene polymerisation and the recent demonstration of 1-hexene polymerisation by **VIII** (all with neutral fac-N_3 donor ligands) we set out to explore the use of the all-sulfur donor macrocycle 1,4,7-trithiacyclononane ($[9]aneS_3$). Although $[9]aneS_3$ has an extensive coordination chemistry of the mid to late transition and p-block metals (nearly 250 organometallic compounds alone have been described),[11] no organometallic rare earth or transition metal compound before Group 6 has ever been reported. Indeed the first rare earth coordination complexes at all of $[9]aneS_3$ (La and U triiodides) have only recently appeared.[12]

Reaction of $[Sc(CH_2SiMe_3)_3(THF)_2]$ with one equivalent of $[9]aneS_3$ in cold toluene afforded $[Sc([9]aneS_3)(CH_2SiMe_3)_3]$ **1** as a white solid in 75% isolated yield (Scheme 1). Compound **1** was characterised by NMR and IR spectroscopy and elemental analysis.† The ^1H NMR spectrum of **1** indicates a product of C_{3v} symmetry. The ring methylene protons appear as two sets of sharp, mutually-coupled second order multiplets consistent with the macrocycle being κ^3 bound to the $Sc(CH_2SiMe_3)_3$ fragment, the resonances for which are as expected. Diffraction-quality crystals of **1** were grown from a toluene–pentane mixture and the molecular structure is shown in Fig. 1 together with selected bond distances.‡

As expected the $[9]aneS_3$ ligand adopts a fac-coordination mode and the geometry at Sc is approximately octahedral. The average Sc–S bond length of 2.793 Å in **1** is comparable to the limited literature data for S–Sc dative bonds (av. = 2.833; range = 2.744–2.872 Å for one report).[10b] The average Sc–CH_2 distance of 2.249 Å in **1** is somewhat less than in **II-Sc** (2.279 Å).[4c]
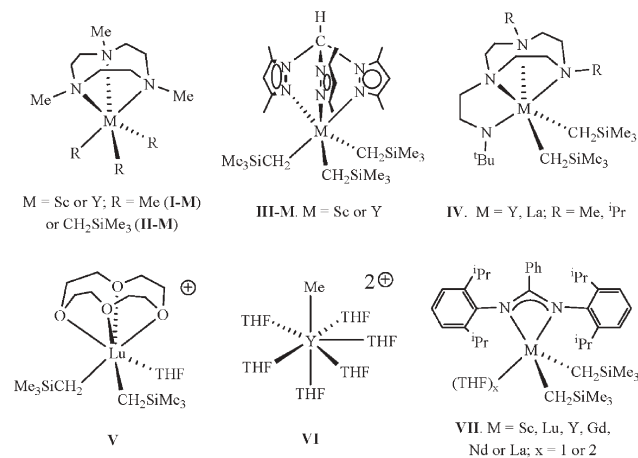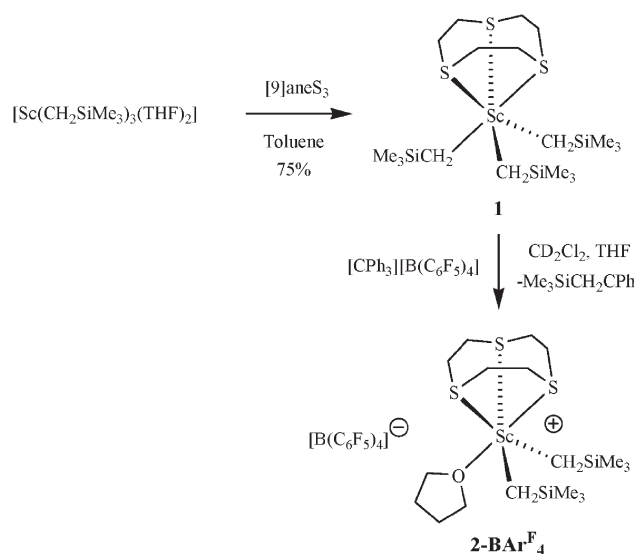

Chart 1

M = Sc or Y; R = Me (**I-M**) or CH_2SiMe_3 (**II-M**)

III-M. M = Sc or Y

IV. M = Y, La; R = Me, ^iPr

V

VI

VII. M = Sc, Lu, Y, Gd, Nd or La; x = 1 or 2

Scheme 1 Synthesis of **1** and *in situ* synthesis of **2**-BAr$^F_4$.

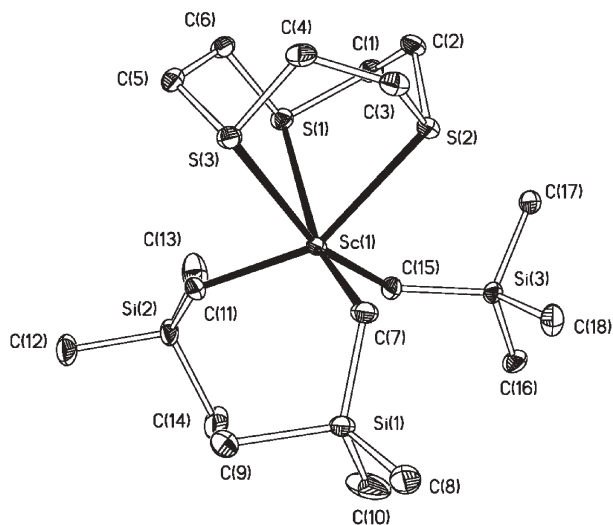**Fig. 1** Molecular structure of [Sc([9]aneS$_3$)(CH$_2$SiMe$_3$)$_3$] **1**. Selected distances and angles: Sc(1)–S(1) 2.7947(7), Sc(1)–S(2) 2.7799(6), Sc(1)–S(3) 2.8039(6), Sc(1)–C(7) 2.250(2), Sc(1)–C(11) 2.265(2), Sc(1)–C(15) 2.231(2) Å; S(1)–Sc(1)–S(2) 74.439(18), S(1)–Sc(1)–S(3) 74.240(17), S(2)–Sc(1)–S(3) 74.380(18)°.

Reaction of **1** with [CPh$_3$][BAr$^F_4$] in CD$_2$Cl$_2$ gave a fluxional compound assigned as the five-coordinate cation [Sc([9]aneS$_3$)-(CH$_2$SiMe$_3$)$_2$]$^+$ along with the expected side-product Ph$_3$CCH$_2$SiMe$_3$. Addition of ethylene gas (1 atm) to the sample produced a fine white precipitate of polyethylene. Addition of THF (1 equiv.) to samples of [Sc([9]aneS$_3$)(CH$_2$SiMe$_3$)$_2$]$^+$ afforded the Lewis base adduct [Sc([9]aneS$_3$)(CH$_2$SiMe$_3$)$_2$(THF)]$^+$ **2**$^+$ (Scheme 1) which showed resonances for a firmly bound THF and *fac*-coordinated [9]aneS$_3$ ligands.† While relatively stable over several days when made on the NMR tube scale, **2**-BAr$^F_4$ could not be isolated cleanly on a preparative scale. Analogous observations were made for **II-Sc**.[4b]

Under identical conditions to those described for **I-Sc**, **II-Sc** and **III-Sc**[4b,c] reaction of **1** (20 μmol) with BAr$^F_3$ (1 equiv.)

in toluene (250 cm^3) in the presence of Al^{i}Bu$_3$ (250 equivs.) under 5 bar ethylene pressure afforded 11.4 g of free-flowing polyethylene after 1 h and acidic work-up. The polymerisation activity of **1** (110 kg mol^{-1} h^{-1} bar^{-1}) is superior to that of **I-Sc** (30 kg(PE) mol^{-1} h^{-1} bar^{-1}) and indeed most scandium based ethylene polymerisation catalysts described to date.[3] However, **1** is significantly less active than either **II-Sc** (220–240 kg(PE) mol^{-1} h^{-1} bar^{-1}) or **III-Sc** (290 kg(PE) mol^{-1} h^{-1} bar^{-1}). As a control experiment we found that [Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$] afforded no polyethylene when activated in the same way, demonstrating the ability of the [9]aneS$_3$ macrocycle to stabilise the presumed cationic alkyl initiating and propagating species.

There has been only one very recent report of 1-hexene polymerisation by a cationic rare earth alkyl catalyst,[9] and none at all for styrene. Activation of **1** with [CPh$_3$][BAr$^F_4$] (1 equiv.) at room temperature† in C$_6$H$_5$Cl followed by addition of 1-hexene led to the slow formation of poly(1-hexene) (*ca.* 30% conversion after 15 min, activity 200 kg(PH) mol^{-1} h^{-1}) Mindful of Okuda and co-workers' report that di-cationic alkyls can also be effective polymerisation catalysts we examined the polymerisation of 1-hexene by **1** when activated with 2 equivs. of [CPh$_3$][BAr$^F_4$]. At room temperature the reaction was extremely vigorous, almost immediately boiling the 1-hexene monomer. Even at −30 °C the polymerisation was very rapid and exothermic with 90% conversion (activity 3660 kg(PH) mol^{-1} h^{-1}) of 1-hexene to essentially atactic poly-1-hexene (32% *mmmm* pentads (isotactic component) as judged by ^{13}C NMR) within 2.5 mins but with very poor control of molecular weight (M_w = 769,500, M_n = 33,400, M_w/M_n = 23.0§). Repeating the room temperature reaction at a higher dilution and lower [monomer] : [catalyst] ratio† predictably gave lower reaction rates (50% conversion after 10 mins; activity 144 kg(PH) mol^{-1} h^{-1}) but much better control of molecular weight (M_w = 77,390, M_n = 13,280, M_w/M_n = 5.8§). Again an otherwise identical control experiment with [Sc(CH$_2$SiMe$_3$)$_3$-(THF)$_2$] showed negligible conversion, confirming once more the strong beneficial role of the S$_3$-donor macrocycle.

Finally we report our preliminary observation that styrene is also very rapidly polymerised in the presence of **1** when activated with 2 equivs. of [CPh$_3$][BAr$^F_4$] at −30 °C (100% conversion after 1 min, activity 13 600 kg(PS) mol^{-1} h^{-1}). Full characterisation of the polymer and mechanistic investigations are underway.

In conclusion, we have demonstrated for the first time that neutral S-donor ligands may be used as supporting groups for catalytically active, rare earth organometallic cations and have shown that α-olefins can also be polymerised with them. Remarkably, although sulfur donors are often viewed as "poisons" for late transition metal catalysts, such ligands do indeed give rise to activity comparable to complexes of their N-donor analogues for the systems reported here.[13] However, additional ligand substitution may be necessary to control the stereochemistry of insertion for α-olefins and molecular weight distributions. We are actively developing the stoichiometric and catalytic chemistry (including other monomers, other functionalisation reactions of unsaturated substrates and the optimisation of catalytic conditions in general) of rare earth alkyl complexes with different families[14] of *fac*-N$_3$ and *fac*-S$_3$ donor ligands and their mixed-donor atom homologues.

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Notes and references

‡ Crystal data for [Sc([9]aneS₃)(CH₂SiMe₃)₃]·0.5(C₇H₈) (**1**·0.5(C₇H₈)): C₁₈H₄₅S₃ScSi₃·C₃.₅H₄, M_w = 533.04, monoclinic, C2/c, a = 20.0776(4), b = 15.6656(3), c = 20.0619(4) Å, α = 90.00, β = 100.0286(9), γ = 90.00°, U = 6213.6(2) Å³, Z = 8, F(000) = 2312, T = 150 K, Nonius Kappa CCD, Mo-Kα radiation, 5.13 ≤ 2θ ≤ 27.48°, 7044 independent reflections, 5027 reflections I > 3σ(I), R = 0.0350, R_w = 0.0436. CCDC 267474. See http://www.rsc.org/suppdata/cc/b5/b503967c/ for crystallographic data in CIF or other electronic format.
§ GPC data recorded at 30 °C in THF referenced to polystyrene standards.

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