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Lanthanide mono(borohydride) complexes of diamide-diamine donor ligands: novel single site catalysts for the polymerisation of methyl methacrylate[†]

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Samarium chloride and borohydride complexes of the diamide-diamine ligands $(2-C_5H_4N)CH_2N(CH_2CH_2NR)_2$ (R = SiMe₃ or mesityl) are described; the borohydride compounds are the first polydentate amide-supported single component lanthanide catalysts for the controlled polymerisation of polar monomers, and also represent the first lanthanide borohydride complex for the polymerisation of methyl methacrylate.

The search for non-cyclopentadienyl ligand environments for the lanthanide metals is mainly driven by the potentially superior control over metal-centred reactivity that may be gained.¹ This is especially relevant for the design of new polymerisation catalysts.^{1*a,b*} The lanthanides are large, "hard" ions and thus the quest for non-metallocene, activatorless catalysts of the type $[(L)_n M(X)]$ (M = trivalent lanthanide, $(L)_n$ is a dianionic supporting ligand or ligand set; X = "active group" for initiation) had led to an increased focus on N- and O-donor ligands. Sterically tuneable, *poly*dentate ligands are deemed to be important so as to restrain the coordination sphere with regard to ligand redistribution reactions and protect against aggregation of low-coordinate complexes or intermediates.

Very recently, several reports² of the controlled polymerisation of polar α -olefin monomers by catalysts supported by tetradentate, bis(phenoxide) ligands have appeared $(e.g.,^{2a}$ I, Chart 1). Dianionic, chelating diamide-based ligands have been remarkably successful in controlling polymerisation activity and polymer structure for the comprehensively studied Group 4 metals.3 However, the track record of tri- and tetra-dentate diamide ligands in the polymerisation of α -olefins by lanthanide complexes $[(L)_n M(X)]$ has been undistinguished.¹ For example, compounds II (Chart 1) provide poor activity and control of methyl methacrylate (MMA) polymerisation for all but the smallest Group 3 metal,4 possibly indicating that the tridentate diamide-pyridine ligand in II does not offer sufficient stabilisation for the larger metals. Lanthanide borohydrides have only very recently been introduced as effective lanthanide (pre)catalysts.⁵ For example, they are able to initiate the ring opening polymerisation of ε-caprolactone (CL) with good control of molecular weights.5a They also afford trans-specific diene polymerisation catalysts in the presence of MgBu₂.5b However, lanthanide borohydrides have not yet been shown to initiate the controlled polymerisation of methyl methacrylate, nor have any non-metallocene derivatives been exploited in any a-olefin polymerisation. Here we report the first nonhydrocarbyl lanthanide complexes of the type $[(L)_n M(X)]$ (X = BH₄). They are also the first BH₄-derived single site and single component catalysts for the controlled polymerisation of MMA.

We recently showed how the lithiated diamide-diamine salt $Li_2N_2NN^{\text{TMS}}$ (1, Chart 1) and its protio analogue $H_2N_2NN^{\text{TMS}}$ allow entry to a range of early metal complexes of the



type $[M(N_2NN^{TMS})(X)_n]$ (no f-element derivatives or catalytic chemistry for these ligands has yet been described).⁶ The dianionic tetradentate ligands N_2NN^{TMS} are clearly relatives of the bis(phenoxide) ligands successfully exploited in complexes **I**, but have the added advantage that the steric and electronic effects of the amide N-substituents are well-expressed, since they are attached to the atom directly bonded to the metal. Since amide N-substituents are well-known³ to profoundly influence catalyst performance we have also prepared[†] a new amide *N*-mesityl protio ligand $H_2N_2NN^{Mes}$ and its lithiated derivate $Li_2N_2NN^{Mes}$ **2** (Chart 1). $H_2N_2NN^{Mes}$ was prepared in 97% yield from (2- $C_5H_4N)CH_2N(CH_2CH_2NH_2)_{2^{6a}}$ and mesityl bromide, employing the catalytic system 1.5 mol% Pd₂(dba)₃, 3.8 mol% *rac*-BINAP and NaO'Bu (3 equivs.). Treatment of $H_2N_2NN^{Mes}$ with BuⁿLi (2 equivs.) gave **2** in 82% yield.

Preliminary studies indicate that chloride and borohydride lanthanide complexes of N_2NN^{TMS} or/and N_2NN^{Mes} can be prepared for a range of lanthanides from La to Lu. We focus here on the samarium complexes since this larger metal is well known to afford efficient polymerisation catalysts. The new complexes were synthesised by addition of a THF solution of the dilithium salt to a cold slurry of the metal trichloride or tris(borohydride) salts in THF. The resultant dimeric complexes [Sm(N₂NN^{TMS})Cl]₂ **3** and [Sm(N₂NN^{TMS})BH₄]₂ **4** [Sm(N₂NN^{Mes})Cl]₂ **5**, [Sm(N₂NN^{Mes})(BH₄)₂Li]₂ **6** were obtained in good yields (Scheme 1).† Clearly complexes **3** and **5** are potentially useful synthons through halide metathesis reactions.



Scheme 1 Reagents and yields: (i) SmCl₃, 34% (3) and 81% (5); (ii) $[Sm(BH_4)_3(THF)_2]$, 76% (4) and 79% (6).

The structures of 3, 5 and 6 were confirmed by X-ray crystallography,[‡] and those of 5 and 6 are shown in Figs. 1 and 2, respectively. All three compounds possess dimeric structures in the solid state with chloride or lithium borohydride bridges.

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[†] Electronic supplementary information (ESI) available: Selected characterising data. See http://www.rsc.org/suppdata/dt/b4/b417279p/



 $\label{eq:Fig.1} Fig. 1 \quad Displacement ellipsoid plot of [Sm(N_2NN^{Mes})Cl]_2 \ \textbf{5}.$



Fig. 2 Displacement ellipsoid plot of [Sm(N₂NN^{Mes})(BH₄)₂Li]₂ 6.

Compounds 3 and 5 feature 6-coordinate, distorted octahedral metal centres. Compound 6 was obtained as an "ate" complex with one residual LiBH₄ per Sm (confirmed by ¹H and ⁷Li NMR spectroscopy); the coordination number of each Sm in **6** is 9 including 5 Sm \cdots H(B) contacts [one BH₄ is tridentate; the other is bidentate with Sm-B distances of Sm(1)-B(1) 2.927 and Sm(1)-B(2) 2.764 Å]. In this structure the lithium atoms are the bridges for the two samarium amido borohydride fragments and both are linked to three hydrogen atoms of three different BH4 groups. The lithium atoms are each further supported by coordination to a mesityl aromatic ring. There is no donor solvent in the coordination sphere. This is a new structure of this type, and the most similar one was for an ytterbocene borohydride "ate" complex reported by Khvostov et al. which was polymeric and contained two THF molecules per metal centre.⁷ The additional interaction between the mesityl rings and the lithiums appears to be important in the formation of this "ate" complex. Compound 4 is not an "ate" complex and features one BH₄ ligand per N₂NN^{TMS} ligand in its ¹H NMR spectrum and no evidence for bound lithium in its ⁷Li NMR spectrum. The IR data for **4** are not consistent with a terminal η^3 -bound BH₄ group,⁸ but are consistent with a BH₄-bridged dimer.⁸

Polymerisation reactions of ɛ-caprolactone were carried out with the borohydride complexes 4 and 6. The reactions were performed in toluene with added THF in order to dissolve the catalyst and, we believe based on NMR experiments, cleave the dimeric structures. Upon addition of the monomer the solution rapidly became viscous. The polymerisation of 250 equivs. of Ecaparolcatone by complex 4 was complete within 1 min, affording poly(ϵ -caprolactone) in 96% yield with $M_{n(exp)} = 24000$ and $M_{\rm n}/M_{\rm w} = 1.17.$ § The molecular weight is in accordance with the expected value ($M_{n(\text{theory})} = 26700$), calculated on the basis of a single chain growing per samarium centre. In contrast, the otherwise identical chloride analogue 3 showed very low activity (only 32% yield after 2 h) with very poor control of the molecular weight ($M_{n(exp)} = 26900$ vs. $M_{n(theory)} = 14800$; $M_{\rm n}/M_{\rm w} = 1.80$). This shows that while the Sm–N_{amide} linkages are slightly reactive, this is negligeable in comparison to the BH₄ centered initiation which affords quantitative (100%) ε caprolactone conversion within 1 min with a good molecular weight control. The borohydride compound 6 was half as active as 4 under the same conditions. This may be due to the greater steric encumbrance of the mesityl groups.

We also investigated the polymerisation of methyl methacrylate9 with the lanthanide borohydride complexes 4 and 6. The results of MMA polymerisation experiments are summarised in Table 1. Both complexes 4 and 6 afford poly(methyl methacrylate) under these conditions. Compound 4 is the most active, leading to very narrow polydispersity indices of ca. 1.2. The polymerisation with 4 occurs at a wide range of temperatures, from +25 °C to -78 °C. The microstructure of the poly(methyl methacrylate) is dependent on the temperature, and the syndiotactic ratio increases from 34.8% at 25 °C to 64.5% at -78 °C. Compound 6 has not been evaluated at low temperature, its activity being already low at room temperature. This is the first example of the polymerisation of MMA by a lanthanide borohydride compound. The chloride compound 3 was also tested for the polymerisation of MMA at 25 °C and was found to be completely inactive even after 24 h, which is again consistent with the BH₄ group (or a hydride derived therefrom) initiating the polymerisation.

In conclusion, we have described the first polydentate amidesupported single component and single site lanthanide catalysts for the controlled polymerisation of polar monomers, and also the first lanthanide borohydride complex for the polymerisation of methyl methacrylate. These systems clearly have considerable scope for development (metal, diamide-donor ligand set and Nsubstituents). Further studies on other lanthanide borohydride complexes of N_2NN^{TMS} , N_2NN^{Mes} and related ligands are in progress and will be reported in due course.

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Table 1 Methyl methacrylate polymerisation experiments with borohydride complexes 4 and 6^a

						Tacticity (%) ^c			
Complex	$T/^{\circ}\mathrm{C}$	t/h	Yield (%)	$M_{\rm n(exp)}{}^{b}/{ m g}~{ m mol}^{-1}$	PDI ^b	mm	mr	rr	
4 4 4 6	25 0 -78 25	3 3 1.5 12	50 50 7.6 26	35,660 52,800 $-d^{d}$ 12,400	1.21 1.25 ${d}$ 1.64	27 7 11 25	38 35 24.5 40	35 58 64.5 35	

^{*a*} Conditions: solvent = 1 mL of toluene and 0.1 mL of THF, [MMA]/[catalyst] = 400. ^{*b*} Measured by gel permeation chromatography at 30 °C in THF relative to PS standards with Mark–Houwink corrections for M_n . ^{*c*} Measured by ¹H NMR in CDCl₃. ^{*d*} Polymer not soluble in THF

Notes and references

‡ *Crystal Data*: for $C_{62}H_{78}Cl_2N_8Sm_2$ (**5**), M = 1307.06, monoclinic, space group $P2_1/n$, a = 16.165(3), b = 21.332(4), c = 17.402(4) Å, $\beta = 97.46(3)^\circ$, V = 5949.8(21) Å³, T = 150 K, Z = 4, $\mu = 2.089$ mm⁻¹, 26058 reflections measured, 13576 unique, $R_{int} = 0.03$. Final *R* values were RI = 0.0346 and $R_w = 0.0387$ (for $I > 3\sigma(I)$). For $C_{28}H_{44}B_2LiN_4$ Sm (**6**), M = 615.65, triclinic, space group $P\overline{I}$, a = 10.5720(1), b = 11.6396(2), c = 12.6413(2) Å, a = 101.4560(6), $\beta = 105.0218(7)$, $\gamma = 93.5125(10)^\circ$, V = 1461.99(4) Å³, T = 150 K, Z = 2, $\mu = 2.031$ mm⁻¹, 15945 reflections measured, 8786 unique, $R_{int} = 0.018$. Final *R* values were RI = 0.0293 and wR2 = 0.0540 (for all data). RI = 0.0243 and wR2 = 0.0524 (for $I > 2\sigma(I)$). (Data for 3 have been made available to referees and will be disclosed in a future publication.) CCDC reference numbers 251360 and 251361. See http://www.rsc.org/suppdata/dt/b4/b417279p/ for crystallographic data in .cif or other electronic format.

 \S Molecular weights (corrected using Mark–Howink coefficients for ε caprolactone) and polydispersity index of the poly(ε -caparolcatone) were determined by GPC at 30 °C in THF against PS standards.

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