Supplementary Material (ESI) for Dalton Transactions

This journal is ® The Royal Society of Chemistry

Cationic Rare-Earth Metal Bis(tetrahydridoborato) Complexes: Direct Synthesis, Structure and Ring Opening Polymerisation Activtiy Toward Cyclic Esters

Dominique Robert, Małgorzata Kondracka and Jun Okuda*

Institute for Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, D-52074
Germany

General comments

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Toluene and thf were distilled from sodium benzophenone ketyl. Pentane was distilled from sodium benzophenone ketyl triglyme. [D_8]thf was dried over sodium, and distilled prior to use. [NEt_3H][BPh_4] was prepared by 1:1 reaction of [NEt_3H][Cl] with [$NaBPh_4$] in water followed by filtration, washing with water and ether and drying to constant weight. [$Ln(BH_4)_3(thf)_3$] were prepared according to a modified literature procedure,[1] and recrystallised from thf before use. All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded at room temperature on a Bruker DRX 400 spectrometer (^{1}H 400.1 MHz, ^{11}B 128.4 MHz) or on a Varian Unity 500 spectrometer (^{1}H 499.6 MHz, ^{11}B 160.3 MHz). All chemical shifts are given in ppm. Chemical shifts for ^{1}H NMR spectra were referenced internally using the residual solvent resonances and reported relative to $SiMe_4$. ^{11}B NMR spectra were referenced externally to a saturated solution of $NaBH_4$ in D_2O.

Procedure for the synthesis of $[Ln(BH_4)_2(thf)_5]^+[BPh_4]^-$ (1–4): A thf solution of $[NEt_3H]^+[BPh_4]^-$ was added dropwise at room temperature to a –30 °C cold thf solution of $[Ln(BH_4)_3(thf)_3]$. Gas evolution was instantaneously observed. After stirring the solution for two hours, the volatiles were removed under vacuum, and the resulting solid extracted with toluene (3 × 20 mL) to remove unreacted $[Ln(BH_4)_3(thf)_3]$. The remaining solid was washed with pentane (3 × 20 mL) and dried under vacuum to afford the product as microcrystals. All compounds were recrystalised from saturated thf solutions at –40 °C, upon what diffraction quality crystals could be obtained for complexes **1**, **3** and **4**.

Synthesis of $[Y(BH_4)_2(thf)_5]^+[BPh_4]^-$ (1): Following the procedure described above, $[Y(BH_4)_3(thf)_3]$ (350 mg, 1 mmol) was reacted with $[NEt_3H]^+[BPh_4]^-$ (400 mg, 0.95 mmol) to give **1** as a white powder (678 mg, 85%). $C_{44}H_{68}B_3O_5Y$ (798.35): calcd. C 66.20, H 8.59; found C 66.44, H 8.49 %. ^{1}H NMR ([D$_8$]thf): $\delta = 0.42$ (q, $^1J_{BH} = 82$ Hz, 8 H, BH_4), 1.77 (m, 20 H, β-CH_2, thf), 3.62 (m, 20 H, α-CH_2, thf), 6.70 (t, $^3J_{HH} = 7.3$ Hz, 4 H, Ph-4), 6.85 (t, $^3J_{HH} = 7.3$ Hz, 8 H, Ph-3), 7.27 (br m, 8 H, Ph-2). ^{11}B{^{1}H} NMR ([D$_8$]thf): $\delta = -6.55$ (BPh_4), –26.89 (BH_4).

Synthesis of $[La(BH_4)_2(thf)_5]^+[BPh_4]^-$ (2): Following the procedure described above, $[La(BH_4)_3(thf)_3]$ (800 mg, 2 mmol) was reacted with $[NEt_3H]^+[BPh_4]^-$ (800 mg, 1.9 mmol) to give **2** as a white powder (1075 mg, 67%). $C_{44}H_{68}B_3LaO_5$ (848.35): calcd. C 62.29, H 8.08; found C 62.42, H 7.69 %. ^{1}H NMR ([D$_8$]thf): $\delta = 0.98$ (q, $^1J_{BH} = 85$ Hz, 8 H, BH_4), 1.77 (m, 20 H, β-CH_2, thf), 3.62 (m, 20 H, α-CH_2, thf), 6.70 (t, $^3J_{HH}$ = 7.3 Hz, 4 H, Ph-4), 6.85 (t, $^3J_{HH}$ = 7.3 Hz, 8 H, Ph-3), 7.27 (br m, 8 H, Ph-2). $^{11}B\{^1H\}$ NMR ([D$_8$]thf): δ = –6.54 (BPh_4), –20.76 (BH_4).

Synthesis of $[Nd(BH_4)_2(thf)_5]^+[BPh_4]^-$ (3): Following the procedure described above, $[Nd(BH_4)_3(thf)_3]$ (910 mg, 2 mmol) was reacted with $[NEt_3H]^+[BPh_4]^-$ (800 mg, 1.9 mmol) to give **3** as a light pink powder (1312 mg, 81%). $C_{44}H_{68}B_3NdO_5$ (853.69): calcd. C 61.91, H 8.03; found C 61.84, H 7.70 %. ^1H NMR ([D$_8$]thf): δ = 1.78 (m, 20 H, β-CH_2, thf), 3.62 (m, 20 H, α-CH_2, thf), 6.73 (t, $^3J_{HH}$ = 7.3 Hz, 4 H, Ph-4), 6.87 (t, $^3J_{HH}$ = 7.3 Hz, 8 H, Ph-3), 7.30 (br m, 8 H, Ph-2), 89.77 (br, 8 H, BH_4). $^{11}B\{^1H\}$ NMR ([D$_8$]thf): δ = 154.13 (BH_4), –6.51 (BPh_4).

Synthesis of $[Sm(BH_4)_2(thf)_5]^+[BPh_4]^-$ (4): Following the procedure described above, $[Sm(BH_4)_3(thf)_3]$ (411 mg, 1 mmol) was reacted with $[NEt_3H]^+[BPh_4]^-$ (400 mg, 0.95 mmol) to yield **4** as an off-white powder (786 mg, 84%). $C_{44}H_{68}B_3O_5Sm$ (859.81): calcd. C 61.46, H 7.97; found C 60.79, H 7.76 %. ^1H NMR ([D$_8$]thf): δ = –5.56 (br q, 8 H, BH_4), 1.77 (m, 24 H, β-CH_2, thf), 3.62 (m, 24 H, α-CH_2, thf), 6.70 (t, $^3J_{HH}$ = 7.0 Hz, 4 H, Ph-4), 6.85 (t, $^3J_{HH}$ = 7.4 Hz, 8 H, Ph-3), 7.27 (br m, 8 H, Ph-2). $^{11}B\{^1H\}$ NMR ([D$_8$]thf): δ = –6.54 (BPh_4), –31.84 (BH_4).

Polymerisation Procedure. Compounds **1–4** were disolved in thf, and neat ε-CL was added at once under vigorous stirring. The initial volume of thf was calculated so that the total volume was 4 mL after addition of ε-CL. The reaction media became too viscous to allow stirring after less than 0.5 minute in all cases. The polymerisation mixture was then immediatly quenched with methanol and the polymer precipitated in pentane, washed and dried to constant weight. The weight- and number-average molecular weight M_w and M_n were determined by GPC on an Agilent 1100 Series instrument at 35 °C in thf against polystyrene standards.

Crystal structure analysis. Relevant crystallographic data are summarised in Table S1. The data of complexes **1**, **3** and **4** were collected with a Bruker AXS diffractometer and reduced with the program system SMART.[2] The structures were solved by direct methods (SHELXS-86)[3] and all independent reflections were used in the refinement by full-matrix least-squares against all F^2 data (SHELXL-97)[4].

CCDC reference numbers 674068 (**1**), 674069 (**3**) and 674070 (**4**).

Reference

1 S. M. Cendrowski-Guillaume, M. Nierlich, M. Lance and M. Ephritikhine, *Organometallics*, 1998, **17**, 786.

2 *Siemens. ASTRO, SAINT and SADABS. Data Collection and Processing Software for the SMART System.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1996.

3 G. M. Sheldrick, *SHELXS-86, A Program for Crystal Structure Solution*, University of Göttingen, Germany, 1986.

4 G. M. Sheldrick, *SHELXL-97, A Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.

Table S1. Crystallographic and Data Collection Parameters for $[Y(BH_4)_2(thf)_5]^+[BPh_4]^-$ (**1**), $[Nd(BH_4)_2(thf)_5]^+[BPh_4]^-$ (**3**) and $[Sm(BH_4)_2(thf)_5]^+[BPh_4]^-$ (**4**).

Compound	**1**	**3**	**4**
Empirical formula	$C_{44}H_{68}B_3O_5Y$	$C_{44}H_{68}B_3NdO_5$	$C_{44}H_{68}B_3O_5Sm$
M_r	798.32	853.65	859.76
Crystal size (mm)	0.30 × 0.27 × 0.16	0.30 × 0.22 × 0.20	0.30 × 0.19 × 0.16
Crystal colour and habit	Colourless rod	Colourless block	Colourless block
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	13.516(2)	13.033(2)	13.070(6)
b (Å)	13.118(2)	13.516(2)	13.534(6)
c (Å)	24.745(4)	24.968(4)	24.936(11)
α (°)	90	90	90
β (°)	90.817(4)	90.071(9)	90.071(9)
γ (°)	90	90	90
V (Å^3)	4386.9(12)	4398.2(12)	4411(3)
Z	4	4	4
D_{calc} (g.cm^{-3})	1.209	1.289	1.295
T (K)	130(2)	130(2)	130(2)
μ(Mo Kα) (mm^{-1})	1.371	1.221	1.372
F(000)	1704	1788	1796
θ Range (°)	2.16–21.64	2.17–28.91	3.12–22.44
Number of reflections collected	59767	31868	54897
Number of reflections observed [$I > 2\sigma(I)$]	7098	10062	7937
Number of independent reflections (R_{int})	10938 (0.0919)	12299 (0.0354)	11001 (0.0843)
Data/restraints/parameters	10938/0/510	12299/3/497	11001/10/503
Goodness-of-fit on F^2	1.039	1.070	1.007
R_1, wR_2 [$I > 2\sigma(I)$]	0.0417, 0.0669	0.0384, 0.0814	0.0464, 0.0855
R_1, wR_2 (all data)	0.0771, 0.0708	0.0531, 0.0867	0.0638, 0.0884
Largest difference in peak and hole (e Å^{-3})	0.984 and –0.520	1.484 and –0.988	1.448 and –2.868