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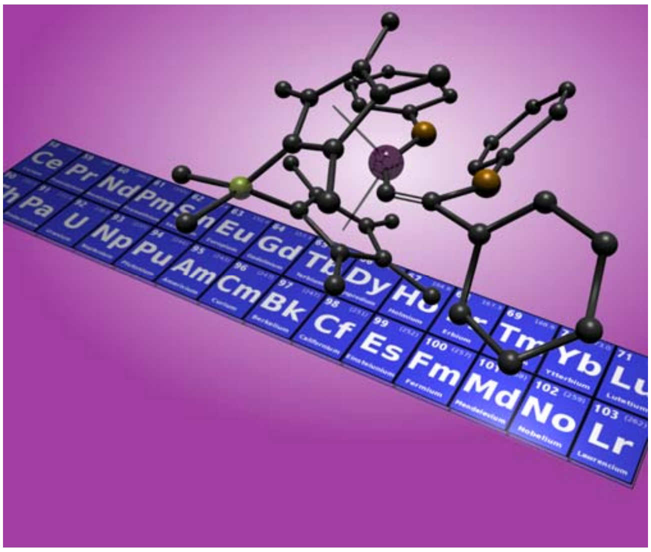

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Synthesis of linked half sandwich rare-earth metal chlorido and borohydrido complexes and their catalytic behavior towards MMA polymerization†

Zhongbao Jian,[a,b] Wei Zhao,[a,b] Xinli Liu,[a] Xuesi Chen,[a] Tao Tang[a] and Dongmei Cui*[a]

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A series of rare-earth metal complexes attached by an amino-functionalized cyclopentadienyl ligand (C_5Me_4H-C_6H_4-*o*-NMe_2) (**1**) was prepared. The metathesis reaction of the ligand lithium salt [C_5Me_4-C_6H_4-*o*-NMe_2]Li with $LnCl_3(THF)_n$ afforded the dichlorido complexes [(C_5Me_4-C_6H_4-*o*-NMe_2)$_2Ln_2Cl_4$][LiCl(THF)$_2$] (Ln = Y (**2a**), Lu (**2b**)), which are trinuclear connected by μ_3-Cl and μ_2-Cl multiple bridges. The straightforward metathesis reaction of $Ln(BH_4)_3(THF)_n$ with equimolar [C_5Me_4-C_6H_4-*o*-NMe_2]Li in THF medium yielded the first linked half sandwich ligand stabilized THF-free rare-earth metal bis(borohydrido) complexes (C_5Me_4-C_6H_4-*o*-NMe_2)Ln(BH_4)$_2$ (Ln = Sc (**3a**), Sm (**3b**)), respectively. The single component borohydrido complex **3a** showed high activity towards the bulk polymerization of methyl methacrylate without specific control, which showed high iso-selectivity (mm = 80%) when the polymerization was performed in benzene medium, and switched to syndio-selectivity (rr = 74% at –20 °C) in polar THF medium, whilst the metal chlorido species was inert. The binary catalyst system of **3a**/Mg^nBu_2 had similar catalytic performances when compared with **3a** in THF medium, but provided enriched syndio-control in benzene solution that was in contrast to the iso-control of **3a**. Surprisingly, **3a** upon activation with ^{n}BuLi displayed an extremely high activity (1.1×10^6 g mol_{Sc}^{-1} h^{-1}) and afforded syndiotactic PMMA (rr = 75%) at low polymerization temperature (–20 °C) in THF.

Introduction

During the past decades, organolanthanide complexes have experienced rapid development and have exerted marvelous performances in various chemical transformations and polymerizations of polar and non-polar monomers.[1] The extensively investigated complexes usually contain Ln–σ-C, Ln–σ-H bonds, which usually encounter problems of thermo-stability, ligand redistribution, solvent-addition as well as sensitivity to moisture and oxygen.[2] Meanwhile the more stable lanthanide chlorides are noted for their sparing solubility in common solvents. Thus lanthanide borohydrides have attracted increasing attention as an alternative owing to their stability, good solubility and structural diversity as compared with their chloride counterparts. In the past few years, the use of borohydride as a reactive ligand has been common in organolanthanide chemistry, but rather limited. Further exploration on their catalytic activity towards the polymerization of polar and non-polar monomers remained rather limited.[3–5]

On the other hand, polymerization of methyl methacrylate (MMA) *via* coordination mechanism has been a research hot topic since the landmark $(C_5Me_5)_2LnR$ (R = alkyl, H) realized syndioselective (>95% rr) polymerization of MMA in a living mode (M_w/M_n = 1.02–1.05) albeit at a very low temperature (–95 °C).[6,7] Henceforth, lanthanide complexes containing Ln–C (alkyl, allyl or benzyl), Ln–N (amido), or Ln–H bonds have been synthesized and applied for the specific selective polymerization of MMA.[8,9] However lanthanide borohydrides had not been found as efficient initiators for MMA polymerization until 2005 when samarium borohydride complexes bearing diamide–diamine ligands showed activity albeit with low selectivity.[10] Hence investigations have been directed to the lanthanide homoleptic borohydrides and their analogues bearing one or two bulky ligands.[11–14] It is noteworthy that the involved complexes are based on larger rare-earth metals providing unsatisfactory catalytic activity for MMA polymerization, and those attached to smaller rare-earth metals such as scandium have been less explored. The main reason might be the synthetic difficulty of scandium borohydrido complexes that usually suffer ligand scrambling, coordination of THF and especially ring-opening of THF when performing the reaction in the presence of THF, which are attributed to the less steric environment of the borohydrides and the high oxophilicity of scandium ion. Therefore only two borohydrido scandocenes, $Cp_2Sc(BH_4)$ and $[Cp^{(TMS)_2}]_2Sc(BH_4)$, have been reported in the literature (Cp = cyclopentadienyl).[15] Very recently, mono-Cp scandium bis(borohydride)s was successfully obtained that was accompanied by byproducts of a borohydrido scandocene and a THF ring-opening complex;[3k,16] meanwhile, the first bis-THF solvated borohydrido La and Lu complexes bearing a non-Cp pyrrolyl bis(imido) ligand were isolated although BH_4 addition to the C=N group of the ligand took place.[17]

Herein, we report the synthesis and structures of rare-earth metal chlorido and borohydrido complexes that are stabilized

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[a] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin street, Changchun, 130022, China. E-mail: dmcui@ciac.jl.cn; Fax: +86 431 85262774; Tel: +86 431 85262773*

[b] *Graduate School of the Chinese Academy of Sciences, Beijing, 100039, China*

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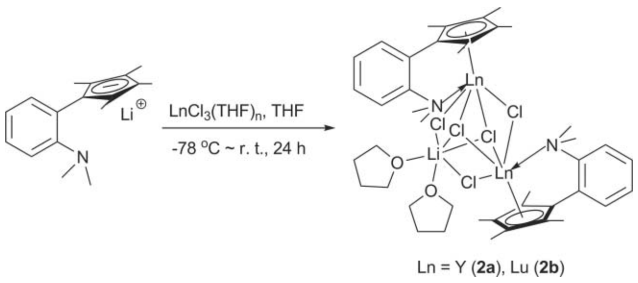
by a rigid aminophenyl-functionlized-cyclopentadienyl, a linked-half-sandwich ligand. Although the linked-half-sandwich ligands have been widely employed to stabilize metal complexes,[18] the rigid phenyl linked half-sandwich ligands and the corresponding lanthanide complexes are scarce.[19] All the complexes reported here are novel, which alone or under the activation of cocatalysts, display varied catalytic performances towards the polymerization of MMA. The factors that influence the catalytic activity and the specific regularity of the isolated polymer will also be presented.

Results and discussion

Synthesis and characterization of dichlorido complexes 2

The aminophenyl-functionalized-Cp compound **1**, (C_5Me_4H-C_6H_4-*o*-NMe_2), was prepared according to the literature by treatment of ortholithiated N,N-dimethylaniline (LiC_6H_4-*o*-NMe_2) with 2,3,4,5-tetramethylcyclopentenone ($C_5H_2Me_4O$) followed by acidic workup and further treatment with ammonia as a yellow viscous liquid (54% yield).[20] Lithiation of **1** with an equimolar amount of ^{n}BuLi at −78 °C gave [C_5Me_4-C_6H_4-*o*-NMe_2]Li that reacted with $LnCl_3(THF)_n$ to generate the corresponding dichlorides [(C_5Me_4-C_6H_4-*o*-NMe_2)$_2Ln_2Cl_4$][LiCl(THF)$_2$] (Ln = Y (**2a**), Lu (**2b**)) in moderate to high yields (Scheme 1). As **1** exists in three isomers, the Cp-proton gives multi resonances around δ 3.5 ppm and the four Cp-methyl groups show multi signals accordingly.[20] Thus the formation of complexes **2** can be easily recognized by the disappearance of the multiple Cp-proton resonances and the presence of more clearer two singlet resonances assigned to Cp-methyl groups (δ 1.94, 2.04 ppm in **2a** *vs* δ 1.96, 2.18 ppm in **2b**). X-Ray diffraction analyses reveal that complexes **2** are trinuclear in the solid state. The aminophenyl-functionalized-Cp ligand coordinates to the Ln ion in a η^5/κ^1 linked-half-sandwich mode. Two such units and a two-THF solvated lithium chloride are connected by the chloride multiple bridges in Ln–μ_3-Cl–Li, Ln–μ_2-Cl–Ln and Ln–μ_2-Cl–Li modes, respectively (Fig. 1). For the yttrium complex **2a**, the bond length of Y–μ_2-Cl–Li (Y(1)–Cl(2)), 2.624(1) Å, is shorter than 2.760(1) Å of Y–μ_2-Cl–Y (Y(1)–Cl(3)) and 2.717(1) Å of Y–μ_3-Cl–Li (Y(1)–Cl(1)), which is comparable to the terminal Y–$Cl_{terminal}$ bond length (av. 2.617 Å and 2.60 Å) in the literature (Table 1).[21] Meanwhile, the distance between Y(1) and Y(1A) (3.909(7) Å) is out of a reasonable bonding range.[22]



Scheme 1 Synthesis of trinuclear rare-earth metal dichlorido complexes **2a** and **b**.

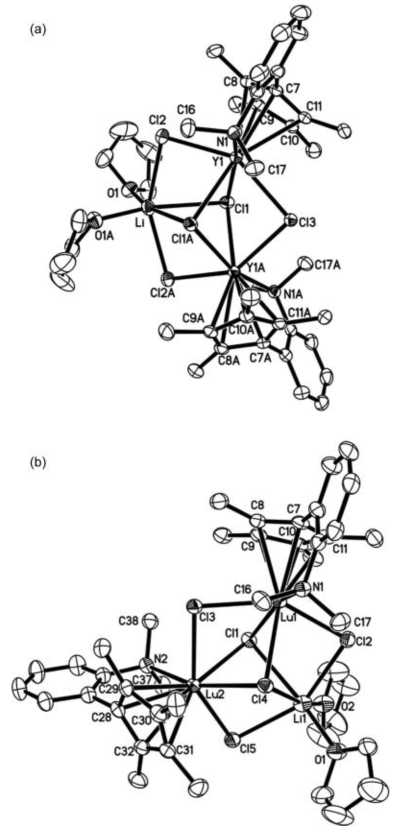


Fig. 1 X-Ray structures of complexes **2a** and **2b** with 35% probability of thermal ellipsoids. Hydrogen atoms and solvents are omitted for clarity.

Synthesis and characterization of bis(borohydrido) complexes 3

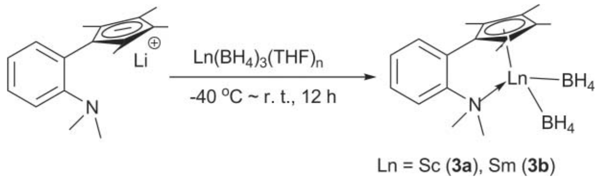
The straightforward metathesis reaction of $Ln(BH_4)_3(THF)_n$ with one equivalent of [C_5Me_4-C_6H_4-*o*-NMe_2]Li in THF medium at −40 °C to r.t., followed by an extraction with toluene, yielded off-white solids of complexes (C_5Me_4-C_6H_4-*o*-NMe_2)Ln(BH_4)$_2$, (Ln = Sc (**3a**), Sm (**3b**)), respectively (yields: 80%, 73%) (Scheme 2). The ^{1}H NMR spectroscopic analysis of the scandium complex **3a** (**3b** is paramagnetic) clearly indicated that no THF ring-opening and even no THF coordination can be observed. The very broad signals appearing in the upfield region between δ 0.71 and δ 1.53 are assignable to the borohydrido protons of Sc–BH_4, which are comparable to those in (C_5Me_5)Sc(BH_4)$_2$(THF) (δ 0.3 and 1.7).[3k] In the ^{11}B NMR spectra, a single peak was seen at δ −19.72 ppm in C_6D_6, which shifted to δ −22.63 ppm in THF-d_8,

Table 1 Selected bond distances (Å) and angles (°) for **2a** and **2b**

Parameter	**2a** (Ln = Y)	**2b** (Ln = Lu)
Ln(1)–C(Cp)(av.)	2.632(8)	2.599(8)
Ln(1)–C_{cent}	2.340(3)	2.303(5)
Ln(1)–Cl(1)	2.717(1)	2.673(1)
Ln(1)–Cl(2)	2.624(1)	2.582(1)
Ln(1)–Cl(3)	2.760(1)	2.692(1)
Li–Cl(1)	2.833(8)	2.794(1)
Ln(1)–Li	3.726(8)	3.705(1)
Ln(1)–Ln(1A/2)	3.909(7)	3.850(3)
N(1)–Ln(1)–C_{cent}	94.6(4)	95.8(7)
Ln(1)–Cl(1)–Ln(1A/2)	90.01(3)	89.25(4)
Ln(1A/2)–Cl(3)–Ln(1)	90.16(4)	91.47(4)

Table 2 Summary of crystallographic data for **2a**, **2b**, and **3a**

	2a·toluene	**2b**·2THF	**3a**
Formula	$C_{49}H_{68}Cl_5Li$–$N_2O_2Y_2$	$C_{50}H_{76}Cl_5Li$–$N_2O_4Lu_2$	$C_{17}H_{30}B_2$-NSc
Crystal size/mm	0.25 × 0.20 × 0.19	0.23 × 0.19 × 0.16	0.20 × 0.18 × 0.09
Fw	1079.00	1303.26	315.00
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$
a/Å	21.3695(16)	12.5151(8)	9.4847(9)
b/Å	13.2414(10)	14.1980(9)	8.6593(9)
c/Å	18.2197(14)	15.5689(10)	22.574(2)
α/°	90	88.6990(10)	90
β/°	98.6180(10)	80.8860(10)	92.259(2)
γ/°	90	84.2540(10)	90
V/Å^3	5097.3(7)	2717.7(3)	1852.6(3)
Z	4	2	4
D_c/g cm^{-3}	1.396	1.593	1.129
Radiation (λ)/Å	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
$2\theta_{max}$/°	52.12	52.08	52.32
μ/cm^{-1}	25.66	38.99	3.90
F(000)	2200	1304	680
No. of obsd reflns	5043	10 475	3696
No. of params refnd	271	539	228
GOF	1.010	1.062	0.761
R_1	0.0457	0.0380	0.0409
wR_2	0.1210	0.1027	0.1355



Scheme 2 Synthesis of rare-earth metal bis(borohydrido) complexes **3a** and **b**.

confirming further the existence of BH_4 groups. Complexes **3a** and **3b** showed good solubility in THF and toluene but were slightly soluble in hexane. Colorless crystals of **3a** were readily grown from a mixture of toluene and hexane at −30 °C within 12 h, which allowed the resolution of its molecular structure in the solid state by X-ray diffraction analysis (Table 2, Fig. 2). Complex **3a** is monomeric bis(borohydride)s, THF-free, consistent with that deduced in the solid state. The aminophenyl-functionalized-Cp ligand coordinates to the Sc^{3+} ion in a η^5/κ^1 CGC-mode. Meanwhile both borohydrido groups BH_4 bond to the Sc^{3+} ion in a tridentate η^3-mode evidenced by the short Sc–B bond lengths of 2.334(3) Å and 2.348(3) Å, as the bidentate coordinating borohydrido moiety gives a longer metal–boron bond (2.551(5) Å).[23] The Cp centroid together with the N, B and Sc atoms generate a pseudo tetrahedral geometry. The strong influence of the geometry of this linked-half-sandwich ligand is reflected by the shorter bond length of Sc–C_{cent}, 2.138(3) Å, compared to 2.156 Å of Sc–C_{cent} in the non-linked mono-Cp $(C_5Me_5)Sc(BH_4)_2(THF)$.[3k] Complex **3a** represents the first linked half sandwich scandium bis(borohydride)s.

Catalysis on the polymerization of MMA

In preliminary experiments, the chlorido complexes **2a** and **2b** were tested for the polymerization of MMA in THF medium but were completely inactive after 120 min, which could be attributed to the stronger bridging Ln–Cl bonds. To our delight, the borohydrido complexes **3a** and **3b** displayed various catalytic activity and specific selectivity, suggesting that Ln–BH_4 species could initiate the MMA polymerization.[10,13] As shown in Table 3, **3a** alone displayed high activity for the bulk polymerization of MMA but afforded atactic product (mm 42%, mr 39%, rr 19%) (run 1). When the polymerization was performed in non-polar solvent benzene with **3a**, high specific control could be achieved albeit with a decreased activity. The resultant poly(methyl methacrylate) (PMMA) had high isotacticity (mm 80%) and narrow molecular weight distribution ($M_w/M_n = 1.58$) (run 2), suggesting the single-site nature of the active species. Thus with the increase of monomer-to-initiator ratio varying from 500 and 800 to 1000, respectively, the molecular weight of the resultant PMMA increased correspondingly from 12.5×10^3 and 14.8×10^3 to 16.6×10^3 g mol^{-1}, meanwhile, the molecular weight distribution and tacticity remained unchanged (runs 2–4), indicating the controllable nature of this polymerization even though not livingness. When polar solvent THF was employed instead of benzene, **3a** exhibited an obvious improved activity, but, in contrast, switched to syndio-selectivity (rr 61%, run 5), meaning that solvent played a decisive role in governing the catalyst performances. Noteworthy was that lowering the polymerization temperature to −20 °C gave rise in specific selectivity (rr 74%) but sacrificed the activity (run 7).

The addition of cocatalyst also exhibited dramatic influence on both catalytic activity and specific selectivity[3f,11] but in a different way from that of solvent. Upon addition of 2 equiv. Mg^nBu_2, the resultant binary system **3a**/Mg^nBu_2 showed a comparable syndio-selectivity with the single component **3a** when the polymerization was carried out in THF solution albeit with a worse activity (run 10); whilst in benzene medium the binary catalyst system provided syndiotactic-enriched PMMA (run 11) in contrast to **3a** that displayed iso-control under the same condition. When 3 equiv. of ^nBuLi was used to replace Mg^nBu_2, we found that the conversion of monomer was 80% even though the polymerization time was prolonged to 360 min at 20 °C (run 12), which was ascribed to

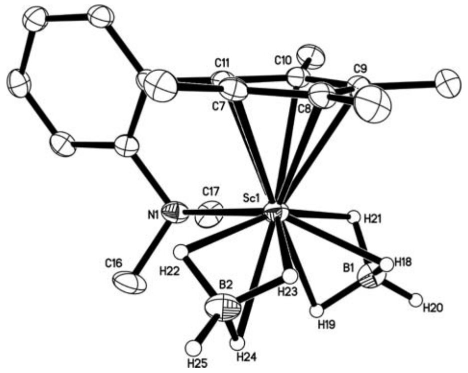


Fig. 2 X-Ray structure of **3a** with 35% probability of thermal ellipsoids. Hydrogen atoms are partially omitted for clarity. Selected bond distances (Å) and angles (°): Sc(1)–C(Cp)(av.) 2.453(2), Sc(1)–C_{cent} 2.138(2), Sc(1)–H_B (av.) 2.15(3), Sc(1)–B(1) 2.334(3), Sc(1)–B(2) 2.348(3), Sc(1)–B (av.) 2.341(3), Sc(1)–N(1) 2.378(2), B–H_T 1.10(3), B–H_B 1.15(3); C_{cent}–Sc(1)–N(1) 102.8(3), C_{cent}–Sc(1)–B(1) 121.10(2), C_{cent}–Sc(1)–B(2) 118.50(3), B(2)–Sc(1)–B(1) 107.97(1). H_B = bridged hydrogen atom, H_T = terminal hydrogen atom.

Table 3 Results of MMA polymerization using **3a** and **b** as precursors[a]

Run	Cat.	Co-cat.	Solvent	T/°C	t/min	Activity[b]	M_n[c] ($\times 10^{-3}$)	M_w/M_n[c]	Tacticity[d] mm-mr-rr (%)
1	**3a**			20	12	130	11.4	1.67	42-39-19
2	**3a**		Benzene	20	120	13	12.5	1.58	80-14-6
3[e]	**3a**		Benzene	20	120	10	14.8	1.52	76-20-4
4[f]	**3a**		Benzene	20	120	8	16.6	1.49	73-25-2
5	**3a**		THF	20	120	70	14.1	1.68	5-34-61
6	**3a**		THF	0	150	50	25.7	1.99	5-30-65
7	**3a**		THF	–20	720	4	92.2	2.51	2-24-74
8	**3b**		Benzene	20	150	4	15.3	1.39	43-37-20
9	**3b**		THF	20	60	42	21.6	1.62	9-33-58
10	**3a**	Mg^nBu_2	THF	20	90	15	19.1	1.59	7-26-67
11	**3a**	Mg^nBu_2	Benzene	20	90	15	8.2	4.17	19-24-57
12	**3a**	^nBuLi	THF	20	360	7	11.1	1.56	14-35-51
13	**3a**	^nBuLi	THF	–20	2.5	1116	68.4	2.06	0-25-75
14	**3a**	^nBuLi	THF	–40	5	552	190	2.01	0-20-80
15	**3a**	^nBuLi	Benzene	20	360	2	10.8	1.54	56-32-12
16	**3b**	^nBuLi	THF	20	60	40	15.6	1.58	8-38-54
17	**3b**	^nBuLi	THF	0	40	56	46.9	1.81	8-29-63
18	**3b**	^nBuLi	THF	–20	5	396	119.7	1.97	7-27-66
19	**3b**	^nBuLi	THF	–40	60	13	246.3	2.26	4-24-72

[a] Conditions: Ln (10 μmol), solvent (1 ml), [MMA]/[Cat.] = 500, [Mg^nBu_2]/[Cat.] = 2, [^nBuLi]/[Cat.] = 3. [b] Given in kg of PMMA mol_{Ln}^{-1} h^{-1}. [c] Measured by GPC calibrated with standard polystyrene samples. [d] Determined by ^1H NMR spectroscopy in $CDCl_3$. [e] [MMA]/[Cat.] = 800. [f] [MMA]/[Cat.] = 1000.

the decomposition of the catalyst and inevitable side reactions.[24] Surprisingly when the polymerization temperature was dropped to –20 °C, the system showed extremely high activity meaning almost completeness could be reached in 2.5 min, meaning a TOF of 1.1×10^6 g mol_{Sc}^{-1} h^{-1}. As far as we are aware, this is the highest catalytic activity for the MMA polymerization with lanthanide borohydrido complexes reported to date that simultaneously display a syndio-selectivity up to 75%. Although the bridged-indenyl yttrium benzyl complex was reported to show the highest activity (6.0×10^6 g mol_Y^{-1} h^{-1}) in the research field of MMA polymerization using rare-earth metal complexes, unfortunately, the isolated PMMA was completely without stereo-control (mm 30.0%, mr 31.5%, rr 38.5%).[9k] The activity was halved with a further decrease in temperature to –40 °C. Correspondingly, the syndio-selectivity improved with the lowering of the temperature to reach rr = 80%. Similarly, carrying out the polymerization in non-polar benzene, the addition of ^nBuLi caused a decrease in activity at room temperature, however, which seemed not to bring about the switch of iso-to-syndio selectivity (run 15) as that of Mg^nBu_2.

It has been reported that the central metal type influenced the catalytic performances and the microstructures of the isolated polymers from the polymerizations of both the polar or non-polar monomers. For MMA polymerization, research usually focuses on the samarium or neodymium based complexes since these larger metals are well known to afford efficient polymerization catalysts.[10,13,24] In this work it was seen that the scandium complex **3a** was more active and provided better stereo-control as compared to the samarium **3b** in non-polar benzene or polar THF medium, or in the presence of cocatalysts or not (runs 16–19).

Conclusions

We have demonstrated that by introduction of a linked-half-sandwich ligand, aminophenyl-functionalized-Cp, new lanthanide trinuclear dichlorido complexes, and especially the first non-solvated scandium and samarium bis(borohydride)s without ligand scrambling, coordination of THF and/or ring-opening of THF, have been successfully synthesized and well defined. Moreover, the borohydrido complexes alone or in the presence of cocatalysts showed various catalytic performances depending on the nature of reaction medium, the type of the cocatalysts as well as the polymerization temperature. Whatever the nature of the complexes and co-catalysts, syndiotactic PMMA was obtained in polar THF medium. The PMMA stereoregularity was changed by adding Mg^nBu_2 to **3a** from iso-control to syndio-control but retained iso-control by adding ^nBuLi, when polymerization was carried out in non-polar benzene. The scandium borohydrido complex was found to be better than its samarium counterpart regarding stereocontrol and activity, in contrast to the previous reported large lanthanide effect, moreover, which upon activation of ^nBuLi exhibited extremely high activity at low polymerization temperature.

Experiment

General methods

All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. All solvents were purified from MBraun SPS system. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed by paraffin film. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by ^1H–^1H COSY and ^1H–^{13}C HMQC experiments when necessary. ^{11}B NMR spectrum was referenced to an external standard of $BF_3 \cdot Et_2O$ (0.0 ppm) in C_6D_6 or THF-d_8. The molecular weight and molecular weight distribution of the polymers were measured by a TOSOH HLC-8220 GPC. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). Mg^{n}Bu$_2$ (1.0 M in heptane), ^{n}BuLi (2.5 M in hexane), LnCl$_3$, and NaBH$_4$ were purchased from Aldrich or Fluka. Methyl methacrylate (MMA) was dried over CaH$_2$ under stirring for 48 h and distilled under vacuum before use. Ln(BH$_4$)$_3$(THF)$_n$[25] was prepared according to the literature. Ligand **1** (1-(2-N,N-dimethylaminophenyl)-2,3,4,5-tetramethylcyclopentadiene) was prepared by following the known procedure.[20]

X-Ray crystallographic studies

Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at −86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

Synthesis of complex [(C$_5$Me$_4$-C$_6$H$_4$-*o*-NMe$_2$)$_2$Y$_2$Cl$_4$][LiCl(THF)$_2$] (2a)

Under a nitrogen atmosphere, to a THF suspension (20 mL) of YCl$_3$(THF)$_{3.5}$ (0.448 g, 1.0 mmol), 1 equiv. of [C$_5$Me$_4$-C$_6$H$_4$-*o*-NMe$_2$]Li (0.247 g, 1.0 mmol) prepared by the reaction of ligand **1** with ^{n}BuLi, was added slowly at −78 °C. The reaction mixture was allowed to warm to room temperature gradually and was stirred for 24 h. Removal of volatiles under reduced pressure, extracting the residue with toluene and evaporating toluene to dryness, afforded **2a** as white powder (0.322 g, 65%). Single crystals (with one toluene molecule in the lattice) for X-ray analysis grew from a mixture of THF and toluene at −30 °C within several days. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.78 (br s, 8H, THF), 1.94 (s, 12H, C$_5$*Me*$_4$), 2.04 (s, 12H, C$_5$*Me*$_4$), 2.80 (s, 12H, NMe$_2$), 3.69 (br s, 8H, THF), 7.11–7.34 ppm (m, 8H, C$_6$H$_4$). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ 12.42 (s, 4C, C$_5$*Me*$_4$), 12.88 (s, 4C, C$_5$*Me*$_4$), 26.57 (s, 4C, THF), 54.57 (s, 4C, NMe$_2$), 69.48 (s, 4C, THF), 115.98 (s, 4C, *C*$_5$Me$_4$), 117.14 (s, 4C, *C*$_5$Me$_4$), 122.24 (s, 2C, *o*-N*C*$_6$H$_4$), 123.42 (s, 2C, *ipso*-*C*$_5$Me$_4$), 129.06 (s, 2C, *p*-N*C*$_6$H$_4$), 130.74 (s, 2C, *m*-N*C*$_6$H$_4$), 133.97 (s, 2C, *o*-C$_5$Me$_4$*C*$_6$H$_4$), 136.12 (s, 2C, *ipso*-C$_5$Me$_4$*C*$_6$H$_4$), 158.27 ppm (s, 2C, *ipso*-N*C*$_6$H$_4$). Anal. calcd for C$_{49}$H$_{68}$N$_2$O$_2$Cl$_5$LiY$_2$ (%): C, 54.54; H, 6.35; N, 2.60. Found: C, 54.21; H, 6.20; N, 2.49.

Synthesis of complex [(C$_5$Me$_4$-C$_6$H$_4$-*o*-NMe$_2$)$_2$Lu$_2$Cl$_4$][LiCl(THF)$_2$] (2b)

Following a similar procedure described for the preparation of **2a**, complex **2b** was isolated from the reaction of LuCl$_3$(THF)$_3$ (0.498 g, 1.0 mmol) with 1 equiv. of [C$_5$Me$_4$-C$_6$H$_4$-*o*-NMe$_2$]Li (0.247 g, 1.0 mmol) in a 74% yield (0.430 g). Single crystals (with two THF molecules in the lattice) for X-ray analysis grew from the mixture of THF and toluene at −30 °C within several days. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.77 (br s, 8H, THF), 1.96 (s, 12H, C$_5$*Me*$_4$), 2.18 (s, 12H, C$_5$*Me*$_4$), 2.90 (s, 12H, NMe$_2$), 3.67 (br s, 8H, THF), 7.18 (d, $J_{\text{H–H}} = 3.0$ Hz, 3H, C$_6$*H*$_4$), 7.32–7.35 (m, 3H, C$_6$*H*$_4$), 7.39–7.42 ppm (m, 2H, C$_6$*H*$_4$). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ 12.58 (s, 4C, C$_5$*Me*$_4$), 13.04 (s, 4C, C$_5$*Me*$_4$), 26.34 (s, 4C, THF), 59.14 (s, 4C, NMe$_2$), 69.35 (s, 4C, THF), 117.08 (s, 4C, *C*$_5$Me$_4$), 118.92 (s, 4C, *C*$_5$Me$_4$), 123.15 (s, 2C, *o*-N*C*$_6$H$_4$), 124.62 (s, 2C, *ipso*-*C*$_5$Me$_4$), 130.16 (s, 2C, *p*-N*C*$_6$H$_4$), 132.04 (s, 2C, *m*-N*C*$_6$H$_4$), 135.68 (s, 2C, *o*-C$_5$Me$_4$*C*$_6$H$_4$), 137.52 (s, 2C, *ipso*-C$_5$Me$_4$*C*$_6$H$_4$), 160.07 ppm (s, 2C, *ipso*-N*C*$_6$H$_4$). Anal. calcd for C$_{50}$H$_{76}$N$_2$O$_4$Cl$_5$LiLu$_2$ (%): C, 46.08; H, 5.88; N, 2.15. Found: C, 45.79; H, 5.68; N, 2.07.

Synthesis of complex (C$_5$Me$_4$-C$_6$H$_4$-*o*-NMe$_2$)Sc(BH$_4$)$_2$ (3a)

Under a nitrogen atmosphere, to a THF suspension (20 mL) of Sc(BH$_4$)$_3$(THF)$_{1.5}$ (0.198 g, 1.0 mmol), 1 equiv. of [C$_5$Me$_4$-C$_6$H$_4$-*o*-NMe$_2$]Li (0.247 g, 1.0 mmol) prepared by the reaction of ligand **1** with ^{n}BuLi, was added slowly at −40 °C. The reaction mixture was allowed to warm to room temperature gradually and was stirred for 12 h. Removal of volatiles under reduced pressure, extracting the residue with toluene, and evaporating the toluene to dryness afforded **3a** as white powder (0.254 g, 80%). Single crystals for X-ray analysis grew from a mixture of toluene and hexane at −30 °C within 12 h. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ between 0.71 and 1.53 (very br s, 8H, BH$_4$), 2.11 (s, 6H, C$_5$*Me*$_4$), 2.24 (s, 6H, C$_5$*Me*$_4$), 2.53 (s, 6H, NMe$_2$), 6.71–6.73 (m, 1H, C$_6$*H*$_4$), 7.05–7.16 ppm (m, 3H, C$_6$*H*$_4$). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 12.87 (s, 2C, C$_5$*Me*$_4$), 14.27 (s, 2C, C$_5$*Me*$_4$), 53.81 (s, 2C, NMe$_2$), 121.50 (s, 1C, *o*-N*C*$_6$H$_4$), 125.02 (s, 2C, *C*$_5$Me$_4$), 126.15 (s, 2C, *C*$_5$Me$_4$), 126.61 (s, 1C, *ipso*-*C*$_5$Me$_4$), 128.11 (s, 1C, *p*-N*C*$_6$H$_4$), 129.76 (s, 1C, *m*-N*C*$_6$H$_4$), 132.60 (s, 1C, *o*-C$_5$Me$_4$*C*$_6$H$_4$), 133.68 (s, 1C, *ipso*-C$_5$Me$_4$*C*$_6$H$_4$), 155.99 ppm (s, 1C, *ipso*-N*C*$_6$H$_4$). ^{11}B NMR (96.3 MHz, C$_6$D$_6$, 25 °C): δ −19.72 ppm. ^{11}B NMR (96.3 MHz, THF-*d*$_8$, 25 °C): δ −22.63 ppm. Anal. calcd for C$_{17}$H$_{30}$NB$_2$Sc (%): C, 64.82; H, 9.60; N, 4.45. Found: C, 64.41; H, 9.43; N, 4.34.

Synthesis of complex (C$_5$Me$_4$-C$_6$H$_4$-*o*-NMe$_2$)Sm(BH$_4$)$_2$ (3b)

Following a similar procedure described previously, treatment of [C$_5$Me$_4$-C$_6$H$_4$-*o*-NMe$_2$]Li (0.247 g, 1.0 mmol) with 1 equiv. of Sm(BH$_4$)$_3$(THF)$_3$ (0.411 g, 1.0 mmol) afforded **3b** as white powder (0.304 g, 73%). Anal. calcd for C$_{17}$H$_{30}$NB$_2$Sm (%): C, 48.57; H, 7.19; N, 3.33. Found: C, 48.27; H, 7.08; N, 3.24.

MMA polymerization

A detailed polymerization procedure (run 13, Table 3) is described as a typical example. In a glove box, 3.2 mg of complex **3a** (1.0×10^{-5} mol) was dissolved in 1 mL of dry and degassed THF. Three equivalents of ^{n}BuLi (3.0×10^{-5} mol) were then added with a microsyringe. Several seconds later the solution turned to pale yellow. The glass ampule was then taken outside, placed in a −20 °C thermostatic bath and stirred for 20 min. 0.5 g of MMA (0.005 mol) was added and the reaction was carried out for 2.5 min to generate a viscous solution. Methanol was injected to terminate the polymerization. The reaction mixture was poured into a large quantity of methanol and then dried under vacuum at ambient temperature to a constant weight (0.465 g, 93%).

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