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Synthesis and Characterization of Heteroscorpionate Rare-Earth Metal Dialkyl Complexes and Catalysis on MMA Polymerization

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Keywords: Rare earths / Tridentate ligands / Polymerization

A series of rare-earth metal alkyl complexes supported by a heteroscorpionate ligand were prepared and structurally characterized. X-ray diffraction analysis revealed that the heteroscorpionate ligand is face-capping on the rare-earth metal in k^3 mode, making the configuration of the afforded dialkyl metal complexes similar to that of half-metallocenes. These complexes are capable of polymerizing methyl methacrylate, with the lutetium complex displaying the highest activity even at low temperature. The poly(methyl methacrylate) obtained is syndiotactically enriched with narrow molecular weight distribution.

Introduction

Synthesis of organo rare-earth metal alkyl complexes is of great importance because most are able to initiate polymerizations of monomers such as ethylene,[1] styrene,[2] conjugated dienes,[3] lactide,[4] and methyl methacrylate etc.[5] However, as rare-earth metals have large ion radii and the metal–carbon bond is highly active, in the formation of such complexes, dimerization, ligand scrambling, formation of ate complexes and C–H activation usually take place to afford unexpected products, which significantly influence their catalytic activity.[6] Thus, ancillary ligands with multiple coordinating sites and large steric bulkiness are favoured to prevent these side reactions. Cyclopentadienyls, which can provide a more steric environment around the central metal in η^5-mode via five carbon atoms, are among the most commonly adopted ligands,[7] and have been widely employed to stabilize rare-earth metal alkyl species. However, structural modification is difficult in cyclopentadienyl compounds, hampering improvement in the catalytic performances of the attached (half) metallocenes. Heteroscorpionate compounds (Figure 1) derived from bis(pyrazolyl)methane are tridentate ligands and may face-cap on the metal in κ^3-fashion, representing a probable alternative to the cyclopentadienyls.[8] In addition, heteroscorpionates are easily structurally modified either by varying the substituents of the heterocycle to change the spatial sterics or by changing the functional groups to tune the electronic properties, which is believed to be responsible for the catalytic activity and stereoselectivity in catalytic reactions. Although heteroscorpionates have been widely used in main group and d-block metals,[8b,8c,9] their applications as anionic ancillary ligands in rare-earth metals have been explored less in spite of the fact that highly efficient rare-earth metal catalysts have been synthesized.[10] Herein we report the synthesis and characterization of heteroscorpionate rare-earth metal dialkyl complexes. Their application as a catalyst for the polymerization of methyl methacrylate is also included for the first time.

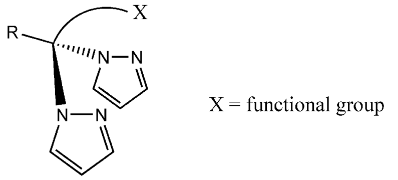

Figure 1. Structure of the heteroscorpionate ligand.

Results and Discussion

The ligand precursor 2,2-[bis(3,5-dimethylpyrazolyl)]-1,1-diphenylethanol was prepared according to reported method with a minor modification.[11] Bis(3,5-dimethylpyrazolyl)methane was synthesized first by the reaction of 3,5-dimethylpyrazole with excess dichloromethane under refluxing for 1 d with the assistance of tetrabutylammonium bromide, a kind of phase-transfer catalyst (Scheme 1). Lithiation in tetrahydrofuran (THF) resulted in an off-white suspension, to which purified benzophenone was added. The reaction mixture was warmed up to room temperature

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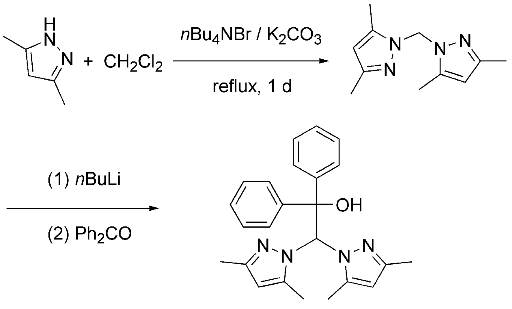
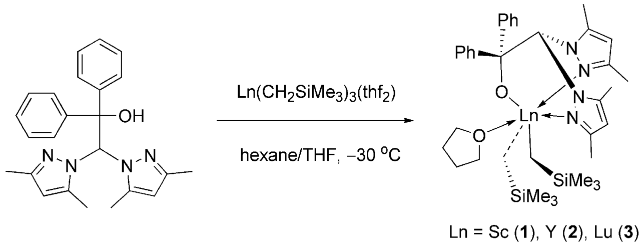
and stirred for another 8 h (Scheme 1). The targeted ligand precursor was obtained by recrystallization from a minimal dichloromethane solution at low temperature.



Scheme 1. Synthesis of heteroscorpionate ligand precursor.

Reaction of this heteroscorpionate ligand in THF with an equimolar amount of trialkyl rare-earth metal Ln[$CH_2Si(CH_3)_3$]$_3$(thf)$_2$ in hexane at –30 °C for 10 h gave the desired dialkyl rare-earth metal complexes (**1**: Ln = Sc, **2**: Ln = Y, and **3**: Ln = Lu) with the release of tetramethylsilane (Scheme 2). The formation of complex **1** was evidenced by ^{1}H NMR spectroscopic analysis. The resonance of the hydroxy proton (originally at δ = 7.95 ppm) of the ligand had disappeared. Meanwhile two sets of resonances at δ = 2.20 and 1.64 ppm ascribed to the methyl groups on the pyrazole ring were observed which were different to the singlet in the ligand spectrum, suggesting that the two methyl groups on one pyrazole ring were inequivalent. Two broad peaks at δ = 3.77 and 1.39 ppm were assigned to the THF molecule. The methylene protons of Sc–CH_2SiMe_3 gave a singlet resonance at δ = 0.16 ppm. The integrated intensity of the resonances demonstrated there are two alkyl groups and one heteroscorpionate ligand in complex **1**. In addition, one THF molecule coordinates to the scandium through an oxygen atom to satisfy the high coordinating number.



Scheme 2. Preparation of heteroscorpionate rare-earth metal dialkyl complexes **1**, **2** and **3**.

The solid-state structure of **1** was further confirmed by X-ray diffraction analysis. Each unit cell contains two molecules of complex **1** (Figure 2). Four molecules of free THF are trapped in a lattice. Complex **1** is a monomer of a THF solvate, consistent with its solution-state structure. Each scandium ion bonds to a THF molecule and two alkyl moieties. Meanwhile, the heteroscorpionate ligand facially coordinates to the scandium ion via the oxygen atom and the two nitrogen atoms of the pyrazole rings in a κ^3 mode, like an umbrella, which limits the rotation of the pyrazole rings (Figure 1). This observation further corroborated the results of ^{1}H NMR spectrum analysis that two types of methyl groups were nonequivalent by giving two sets of resonances. The ligands generate a distorted octahedral geometry around the central metal with the two oxygen atoms occupying apices while the N1, N3, C25, C29 atoms form the horizontal plane. Furthermore, Sc1, O1 and C24 define a mirror plane bisecting the molecule. The bond lengths of Sc–C and Sc–N [2.278(3) and 2.279(3) Å vs. 2.423(2) and 2.375(2)] are slightly longer than those reported by Antionio Otero ([2.213(5) and 2.232(5) Å vs. 2.279(4) Å] (Table 1).[12] ^{1}H NMR spectra of complexes **2** and **3** were similar to that of complex **1**, indicating that **2** and **3** were homologues of **1**. Singlet resonance at δ = –0.22 ppm for **2** (δ = –0.37 ppm for **3**) was ascribed to the methylene of the alkyl bound to yttrium. Single crystals of complexes **2** and **3** were easily isolated from THF solution at low temperature (–30 °C), which were further characterized by X-ray analysis (Figures 3 and 4). The space group (*C*2/*c*) and symmetry (monoclinic) differ from that of **1** ($P\bar{1}$, triclinic, Table 3). In addition eight molecules of **2** (or **3**) in each unit cell and eight molecules of THF were detected. The Y–C bond lengths of 2.443(4) and 2.452(4) Å and the Y–N bond lengths of 2.540(3) and 2.578(3) Å in **2** fall within the nor-

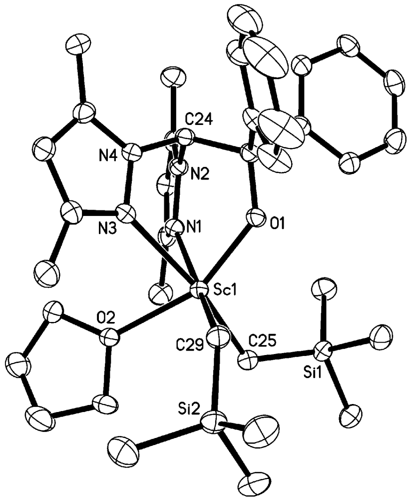


Figure 2. ORTEP drawing of complex **1** with thermal ellipsoids at 35% probability levels. The hydrogen atoms and the free THF molecule are omitted for clarity.

Table 1. Selected bond lengths [Å] and bond angles [°] for complexes **1**–**3**.

	Ln = Sc	Ln = Y	Ln = Lu
Ln–C(25)	2.279(3)	2.443(4)	2.388(4)
Ln–C(29)	2.278(3)	2.452(4)	2.391(4)
Ln–O(1)	1.9662(2)	2.099(2)	2.067(3)
Ln–O(2)	2.2730(2)	2.401(3)	2.353(3)
Ln–N(1)	2.423(2)	2.540(3)	2.472(4)
Ln–N(3)	2.375(2)	2.578(3)	2.535(4)
C(25)–Ln(1)–C(29)	97.80(1)	99.22(1)	99.23(2)
O(1)–Ln(1)–O(2)	155.55(7)	151.79(9)	152.85(1)
N(1)–Ln(1)–N(3)	75.85(7)	71.44(9)	72.60(1)

mal range reported in the literature,[10] which are slightly longer than those of Lu–C [2.388(4) and 2.391(4) Å] and Lu–N [2.472(4) and 2.535(4) Å] in **3**, but are obviously longer than those in **1**, in good agreement with the ionic radii.

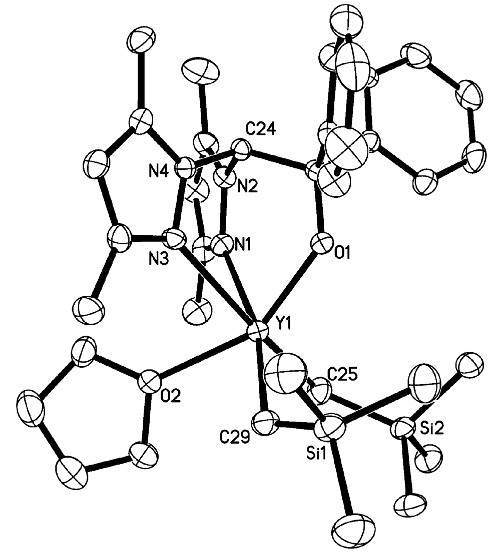


Figure 3. ORTEP drawing of complex **2** with thermal ellipsoids at 35% probability levels. The hydrogen atoms and the free THF molecule are omitted for clarity.

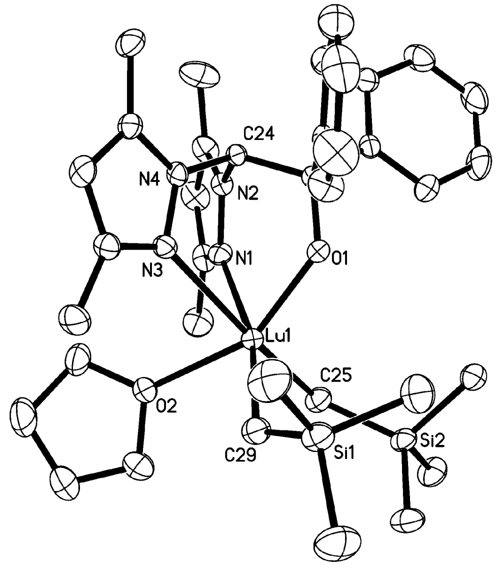


Figure 4. ORTEP drawing of complex **3** with thermal ellipsoids at 35% probability levels. The hydrogen atoms and the free THF molecule are omitted for clarity.

These dialkyl rare-earth complexes were evaluated as catalysts for the polymerization of methyl methacrylate (MMA) and the results are collected in Table 2. All three complexes were able to polymerize MMA at room temperature and the polymerization reaction was dependent on the metal centre. When polymerization was performed in THF complex **3** displayed the highest activity as compared with its scandium and yttrium analogues **1** and **2** (runs 1–3). When the temperature decreased to 0 °C a higher conversion of 92% could be achieved within 15 min. Meanwhile, the molecular weight increased to 76600 from 31000 at 25 °C (run 4). However, with a further decrease of the temperature to –20 °C, the catalytic activity clearly dropped, but with enhanced syndiotacticity of the resultant PMMA (run 5). Below a temperature of –40 °C, almost no polymerization occurred (runs 6, 7). Moreover, bimodal distribution could be observed when the polymerization was carried out at low temperature (runs 5, 7). Meanwhile, the polymerization medium showed also an obvious influence on the catalytic activity, although this seemed to have no effect on the regularity of the resultant PMMA. When the polymerization was carried out in toluene it showed higher activity as compared to that in THF. For instance with complex **3**, completeness could be achieved within 0.25 h at –20 °C, and an up to 95% conversion could be reached even at –40 °C in 0.25 h. Likewise, polymers with bimodal distribution were obtained at low temperature.

Table 2. Polymerization of methyl methacrylate by complexes **1**, **2** and **3**.[a]

Run	Cat	Solvent	T_p [°C]	Conv. [%]	Tacticity[b] mr	rr	M_n[c] (10^3)	PDI[c]
1	**1**	thf	25	18.3	37.0	63.0	22.4	1.4
2	**2**	thf	25	49	43.9	56.1	19.6	1.3
3	**3**	thf	25	74.5	37.2	62.8	31.0	1.3
4	**3**	thf	0	92	34.2	65.8	76.6	1.2
5[d]	**3**	thf	–20	76	31.8	68.2	299.8/42.3	1.4/1.2
6	**3**	thf	–40	no				
7[d,e]	**3**	thf	–40	49	26.9	73.1	259.3/57.7	1.3/1.2
8	**3**	tol	0	100	38	62.0	98.0	2.0
9[d]	**3**	tol	–20	100	38.5	61.5	336.0/58.2	1.3/1.3
10[d]	**3**	tol	–40	95	35.1	64.9	916.8/56.3	1.4/1.2

[a] Conditions: catalyst: 10 µmol, $[MMA]_0/[Ln]_0$ = 500, solvent: 1 mL, time = 15 min. [b] Determined by ^1H NMR spectroscopy. [c] Determined by GPC against polystyrene standards. [d] Bimodal distribution. [e] Time: 17 h.

It seemed that the two alkyls behaved differently under low temperature which was responsible for the generation of bimodal peaks, which we have observed in our previous report.[4b] Thus, we attempted to obtain a monoalkyl rare-earth metal complex of the formula L_2LnR (L is the heteroscorpionate ligand). However, both treating trialkyl yttrium (or trialkyl lutetium) with 2 equiv. of ligand precursor directly at low temperature or a stepwise methodology from complex **2** or **3** with 1 equiv. of ligand precursor proved unsuccessful. We suggest that a highly spacious environment is required if a sandwich complex is to form in which the metal centre will be seven-coordinate or more. In complex **2** or **3** each metal centre is six-coordinate, which inhibits the formation of a sandwich complex. This assumption might be partly supported by Otero's report where only one of the two pyrazole rings could coordinate to the scandium or yttrium centre.[12]

Conclusions

We have demonstrated the synthesis and characterization of alkyl rare-earth metal complexes supported by a heteroscorpionate ligand. The ligand facially coordinated to the rare-earth metal via O, N, N' atoms in k^3 mode, quite like a cylopentadienyl ligand. These dialkyl complexes were all effective catalysts for the polymerization of methyl methacrylate albeit with low specific control on the resulting polymers and a little higher PDI values compared to living polymerization. This might be a consequence of the existence of two alkyl groups bound to the metal centre, both of which are able to initiate polymerization of MMA. Further work will be focused on the design and optimization of the heteroscorpionate ligand to produce PMMA with high stereoregularity.

Experimental Section

General: All reactions were carried out under a dry and oxygen-free argon atmosphere using Schlenk techniques or under a nitrogen atmosphere in a glovebox. Solvents such as n-hexane, toluene were purified by an MBraun SPS system. THF was dried by distillation over sodium potassium alloy with benzophenone as indicator under a nitrogen atmosphere and was stored over freshly cut sodium in a glovebox. 3,5-Dimethylpyrazole was purchased and purified by recrystallization from hot cyclohexane prior to use. Benzophenone was purified by recrystallization from hot ethanol followed by drying over anhydrous $MgSO_4$ in CH_2Cl_2. CH_2Cl_2, anhydrous K_2CO_3 and $n\text{Bu}_4\text{NBr}$ were used as received. Bis(3,5-dimethylpyrazolyl)methane and 1,1-diphenyl-2,2-bis(3,5-dimethylpyrazolyl)ethanol were synthesized according to modified literature procedures and structurally characterized by the ^{1}H NMR technique. The synthesis of rare-earth metal tris(alkyl)s followed the established method with a little modification.[13] The molecular weight and molecular weight distribution of the polymers were measured by the TOSOH HLC 8220 GPC at 40 °C using THF as eluent against polystyrene standards. Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox by use of NMR tubes and then sealed by paraffin film. ^{1}H, ^{13}C NMR spectra were recorded with a Bruker AV400 (FT, 400 MHz for ^{1}H NMR; 100 MHz for ^{13}C NMR) spectrometer.

Bis(3,5-dimethylpyrazolyl)methane: 3,5-Dimethylpyrazole (6 g, 62 mmol), $n\text{Bu}_4\text{NBr}$ (1.54 g, 4.8 mmol), KOH (5.4 g, 96 mmol), anhydrous K_2CO_3 (13.2 g, 95.5 mmol) and CH_2Cl_2 (150 mL) were charged into a three-neck round-bottom flask filled with nitrogen in advance. The reactants were stirred vigorously and heated at reflux for 1 d. When the reaction mixture was cooled to room temperature, a colourless dichloromethane solution was obtained by suction filtration. The residue was extracted with $CHCl_3$ (3×50 mL) and the extractant was combined with the previous dichloromethane solution. Then the organic solvents were removed by rotary evaporation to afford white solids. The pure products (2.87 g, 73% yield) were isolated as white solids by recrystallization from hot *n*-hexane solution. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 6.15 (s, 2 H, Pz-*H*), 5.80 (s, 2 H, CH_2), 2.43 (s, 6 H, CH_3), 2.19 (s, 6 H, CH_3) ppm.

1,1-Diphenyl-2,2-bis(3,5-dimethylpyrazolyl)ethanol: Bis(3,5-dimethylpyrazolyl)methane (4.08 g, 20 mmol) was dissolved in dry THF (100 mL) and then transferred to an ampoule (200 mL). When it was cooled to –80 °C an equimolar amount of *n*BuLi (20 mmol, in hexane) was added dropwise to the stirred solution under nitrogen to yield a white suspension. The mixture was stirred for another 1 h at this temperature, and benzophenone was added (3.64 g, 20 mmol). The mixture was warmed up to room temperature and stirred for an additional 8 h to generate a yellow suspension. White solids were isolated by suction filtration and washed with a small amount of THF. Then water and CH_2Cl_2 were added to form a suspension. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×40 mL). The combined organic solution was dried with anhydrous $MgSO_4$ overnight. Crude products were isolate by suction filtration and removal of CH_2Cl_2. The pure products (1.7 g, 44%) were obtained after crystallization from hot CH_2Cl_2 solution. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 7.94 (s, 1 H, O*H*), 7.29 (m, 4 H, Ph-*H*), 7.24 (s, 2 H, Ph-*H*), 7.15 (m, 4 H, Ph-*H*), 6.95 (s, 1 H, C*H*), 5.66 (s, 2 H, Pz-*H*), 2.01 (s, 12 H, CH_3) ppm.

Complex 1: In a glovebox 1,1-diphenyl-2,2-bis(3,5-dimethylpyrazolyl)ethanol (0.1546 g, 0.4 mmol) in THF (8 mL) was slowly added to the stirred solution of $Sc(CH_2SiMe_3)_3THF_2$ (0.18 g, 0.4 mmol) in hexane (10 mL) at –30 °C. The reaction was slowly warmed to room temperature and stirring was continued for a further 8 h to form a white suspension. The product was isolated by suction filtration followed by washing with cold THF in 63% yield. Single crystals suitable for X-ray analysis were obtained by recrystallization from THF solution at –30 °C for several days. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.83 (d, 4 H, *o-H*-Ar), 7.22 (br., 4 H, *m-H*-Ar), 7.04 (t, 2 H, *p-H*-Ar), 6.59 (s, 1 H, C*H*), 5.33 (s, 2 H, C*H*), 3.77 (s, 4 H, THF), 2.20 (s, 6 H, CH_3), 1.64 (s, 6 H, CH_3), 1.39 (s, 4 H, THF), 0.65 [s, 18 H, $Si(CH_3)_3$], 0.16 (s, 4 H, Si-CH_2) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 150.3, 147.2, 140.4 ($C^{3,3'}$ and $C^{5,5'}$), 127.9, 127.6, 127.4 (Ph), 106.6 ($C^{4,4'}$), 72.7 (THF), 69.4 (*C*H), 32.0 [$ScCH_2Si(CH_3)_3$], 26.1 (THF), 15.1 ($Me^{3,3'}$), 11.5 ($Me^{5,5'}$), 5.4 [$ScCH_2Si(CH_3)_3$] ppm.

Complex 2: Following the same protocol as that for preparation of complex **1**, complex **2** was isolated as a white solid (0.228 g) in 72% yield by treatment of $Y(CH_2SiMe_3)_3THF_2$ (0.2 g, 0.4 mmol) with 1,1-diphenyl-2,2-bis(3,5-dimethylpyrazolyl)ethanol (0.1546 g, 0.4 mmol). Single crystals suitable for X-ray analysis were isolated from THF solution at –30 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.86 (d, 4 H, *o-H*-Ar), 7.23 (br., 4 H, *m-H*-Ar), 7.05 (t, 2 H, *p-H*-Ar), 6.60 (s, 1 H, C*H*), 5.33 (s, 2 H, C*H*), 3.66 (br., 8 H, THF), 2.14 (s, 6 H, CH_3), 1.61 (s, 6 H, CH_3), 1.47 (br., 8 H, THF), 0.70 [s, 18 H, $Si(CH_3)_3$], –0.22 (s, 4 H, Si-CH_2) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 151.5, 141.2, 141.0 ($C^{3,3'}$ and $C^{5,5'}$), 127.9, 127.5, 127.4, 126.1 (Ph), 106.7, 106.4 ($C^{4,4'}$), 73.8 (THF), 73.2 (THF), 69.0 (*C*H), 28.3 [$YCH_2Si(CH_3)_3$], 28.1 [$YCH_2Si(CH_3)_3$], 27.9 (THF), 26.1 (THF), 14.8 ($Me^{3,3'}$), 11.5 ($Me^{5,5'}$), 5.6 [$YCH_2Si(CH_3)_3$], 5.5 [$YCH_2Si(CH_3)_3$] ppm.

Complex 3: By using the same protocol complex **3** was synthesized in 66% yield as a white solid from the reaction between 1,1-diphenyl-2,2-bis(3,5-dimethylpyrazolyl)ethanol (0.1546 g, 0.4 mmol) and $Lu(CH_2SiMe_3)_3THF_2$ (0.232 g, 0.4 mmol). Single crystals suitable for X-ray analysis were isolated from mixed THF/hexane solution at –30 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.88 (d, 4 H, *o-H*-Ar), 7.23 (br., 4 H, *m-H*-Ar), 7.07 (t, 2 H, *p-H*-Ar), 6.59 (s, 1 H, C*H*), 5.34 (s, 2 H, C*H*), 3.65 (br., 16 H, THF), 2.14 (s, 6 H, CH_3), 1.62 (s, 6 H, CH_3), 1.48 (br., 16 H, THF), 0.70 [s, 18 H, $Si(CH_3)_3$], –0.37 (s, 4 H, Si-CH_2) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 150.0, 146.9, 140.4 ($C^{3,3'}$ and $C^{5,5'}$), 127.8, 127.6, 127.5, 126.9 (Ph), 106.8 ($C^{4,4'}$), 73.8 (THF), 67.8 (*C*H), 33.5 [$LuCH_2Si(CH_3)_3$], 31.9 [$LuCH_2Si(CH_3)_3$], 25.7 (THF), 23.0 (THF), 14.3 ($Me^{3,3'}$), 11.0 ($Me^{5,5'}$), 5.2 [$LuCH_2Si(CH_3)_3$], 5.1 [$LuCH_2Si(CH_3)_3$] ppm.

Crystal Structure Determination (Table 3): Crystals for X-ray analysis were obtained as described in the Exp. Section. Data collection was performed at –86.5 °C with a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo-K_r radiation (λ = 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.

Table 3. Summary of crystallographic data for complexes **1**, **2** and **3**.

	1·THF$_2$	**2**·THF	**3**·THF
Formula	$C_{44}H_{71}N_4O_4Si_2Sc$	$C_{40}H_{63}N_4O_3Si_2Y$	$C_{40}H_{63}LuN_4O_3Si_2$
Fw	821.19	793.03	879.09
T [K]	185(2)	185(2)	185(2)
Wavelength	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	*C*2/*c*	*C*2/*c*
a [Å]	9.2843(6)	39.924(5)	39.9625(1)
b [Å]	13.4158(9)	11.9231(1)	11.8662(4)
c [Å]	19.9517(1)	20.819(2)	20.7896(7)
α [°]	99.8860(1)	90	90
β [°]	97.6680(1)	119.058(2)	119.1800(1)
γ [°]	101.4970(1)	90	90
V [Å^3]	2362.6(3)	8663.0(2)	8607.4(5)
Z	2	8	8
D_c [Mg/m^3]	1.154	1.216	1.357
μ [mm^{-1}]	0.249	1.440	2.388
F(000)	888	3376	3632
Reflections collected	13400	23781	23531
R_int	9108 (0.0170)	8520 (0.0580)	8538 (0.0333)
$2\theta_\mathrm{max}$ [°]	52.08	52.10	52.22
GOF	1.033	0.999	1.049
R_1	0.0564	0.0535	0.0368
wR_2	0.1375	0.1188	0.0892
R_1 (all data)	0.0707	0.0955	0.0486
wR_2 (all data)	0.1488	0.1365	0.0970

CCDC-767818 (for **1**), -767819 (for **2**) and -767820 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Typical Procedure for Polymerization of Methyl Methacrylate: Catalyst **1** (6.8 mg, 10 µmol) was dissolved in THF (1 mL) in a glovebox. Methyl methacrylate (0.5 g, 0.5 mmol) was added dropwise under vigorous agitation at room temperature. After a designated time the polymerization was quenched with alcohol containing 10% HCl. The afforded polymer was precipitated from a large amount of alcohol and dried under vacuum to constant weight. Its tacticity was determined by ^{1}H NMR spectroscopy in $CDCl_3$ and the number-average molecular weight was determined by GPC against polystyrene standards.

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