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Synthesis and crystal structure of one carbon-atom bridged lutetium complex $[Ph_2C(Flu)(Cp)]LuN(TMS)_2$ and catalytic activity for polymerization of polar monomers

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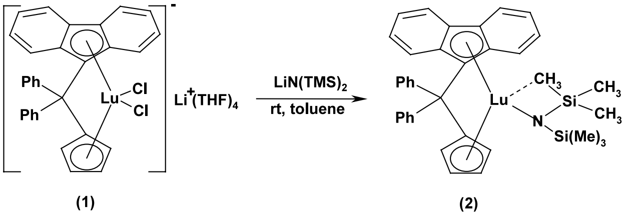
Abstract

The one-carbon atom bridged amide complex $[Ph_2C(Flu)(Cp)]LuN(TMS)_2$ (**2**) (Flu = $C_{13}H_8$, Cp = C_5H_4, TMS = $SiMe_3$) has been synthesized by reaction of its chloride precursor with $LiN(TMS)_2$ in toluene. An X-ray structure of the amide complex **2** exhibits apparently intramolecular $^{\beta}$Si–C agostic interaction with Lu. Polymerization of methyl methacrylate (MMA) and lactones with this complex has also been investigated.

Keywords: Ansa-Lanthanoidocene; Lutetium; Crystal structure; Poly(MMA); Poly(lactone)

1. Introduction

Since the discovery of the first stereorigid chiral ansa-metallocene complex [1] and their application as homogeneous catalysts in stereospecific polymerization of α-olefins to polymers with stereoregular microstructures, a wide variety of metallocene catalysts from Group 3 and 4 have now been prepared. The tactility of polypropylene varies predictably with the structure of the ansa-metallocene catalysts: C_2 symmetric metallocenes produce highly isotactic polypropylene; C_1 metallocenes also produce isotactic polypropylene, but generally with less stereospecificity; syndiotactic polypropylene has been produced using essentially a single type of C_s symmetric ansa-metallocene catalyst [2]. However, the chemistry of ansa-lanthanocene has been very limited, especially when compared with that of the Group 4 metallocenes. Since the metallocenes of the rare earth elements are isoelectronic structure with Group 4 cationic alkyl metallocene complexes Cp_2MR^+ d^0 ($Cp=C_5H_5$), they are single-component catalysts for olefin polymerization. This fact facilitates significantly the study of olefin polymerization mechanism and the influence of the metal ligation environment on the structure and properties of the resultant polymer for that the intermediates can be isolated more easily than in the case of the Group 4 matallocenes [3,4]. They can also catalyze polymerization of polar monomers [4–8] and block copolymerization of olefins with polar monomers [4,9,10].



Scheme 1.

Until now most of the work reported was on compounds stabilized by bis(pentamethylcyclopoentadienyl) or closely related ligand systems [4,6,10,11]. Most of the works for study of one-atom bridged lanthanoidocenes are using silicon as the bridging atom. In connection with our previous investigation on a series study of the synthesis and structural characterization of one-atom (Si and C) bridged fluorenyl cyclopentadienyl lan-

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Table 1
X-ray diffraction data collection parameters for complex **2**

Empirical formula	$C_{37}H_{40}LuNSi_2$
Formula weight	729.87
Crystal system	Triclinic
Color	red
a (Å)	15.777(3)
b (Å)	17.147(6)
c (Å)	14.434(5)
α (°)	110.10(3)
β (°)	93.46(2)
γ (°)	91.39(2)
V (Å^3)	3656(1)
F(000)	1472.00
μ (cm^{-1})	27.89
Z	2
Space group	$P\bar{1}$
D_{calc} (g cm^{-3})	1.326
Reflections	10369
Observations	7747
Final R, wR [a]	0.057; 0.073
peak, hole (e Å^{-3})	1.64; −1.98

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{0.5}$.

Table 2
Selected bond lengths (Å) and internal angles (°) for complex **2**

Bond lengths			
Lu–C(32)	2.74(1)	Lu–C(7)	2.558(9)
Lu–N	2.167(8)	Lu–C(8)	2.568(10)
Lu–Si(1)	3.020(3)	Lu–C(13)	2.741(9)
Si(2)–N	1.722(9)	Lu–C(15)	2.541(10)
Si(1)–N	1.687(10)	Lu–C(16)	2.533(9)
Si(1)–C(32)	1.89(1)	Lu–C(17)	2.59(1)
Si(2)–C(37)	1.87(2)	Lu–C(18)	2.58(1)
Lu–C(1)	2.731(10)	Lu–C(19)	2.588(9)
Lu–C(6)	2.621(9)	C(32)–H(23)	0.97
Lu–H(23)	2.50	C(32)–H(24)	0.96
Lu–H(24)	2.50	C(32)–H(25)	0.94
Lu–H(25)	3.50		
Bond angles			
Lu–N–Si(1)	102.5	C(20)–C(14)–C(26)	103.2(8)
Lu–N–Si(2)	131.9(5)	C(17)–Lu–N	93.3(4)
Si(2)–N–Si(1)	125.6(5)	C(18)–Lu–N	103.1(4)
C(7)–C(14)–C(15)	101.1(7)		
Dihedral angles			
Plan (1) and (5)	74.38		

thanocenes [12,13]. We wish to report here the synthesis and structure of a new diphenylmethene bridged fluorenyl cyclopentadienyl lutetium amide $[Ph_2C(C_{13}H_8)(C_5H_4)]LuN(SiMe_3)_2$ and their application of catalyst to polar monomer polymerization.

2. Results and discussion

2.1. Synthesis

By reaction of the chloride compound $[Ph_2C(C_{13}H_8)(C_5H_4)Lu(Cl)_2][Li(THF)_4]$ [13a] (**1**) with $LiN(TMS)_2$ in toluene, we isolated the monomeric salt-free and solvent-free amide complex $[Ph_2C(C_5H_4)(C_{13}H_8)]LuN(TMS)_2$ (**2**) (Scheme 1). Compound **2** can also be made by one-pot synthesis procedure that is by reaction of anhydrous $LuCl_3$ with dilithium salt of the diphenylmethylene-bridged ligand in ether, followed by the treatment with the $KN(TMS)_2$ in toluene. The amide complex **2** is very soluble in toluene and benzene, and sparingly soluble in hexane. It has also been further characterized by Elemental Analysis, MS, FT-Raman, and X-ray diffraction analysis.

2.2. Molecular structure

X-ray diffraction quality crystal was grown from toluene solution. Detail of the crystal data and refinements for complex **2** is shown in Table 1, and selected bond lengths and internal angles are given in Table 2. The X-ray structure of **2** is shown in Fig. 1.

The first aspect is involved with the bonding modes of the two five-membered ring fragments to Lu when compared with its chloride precursor. This neutral structure of complex **2** is very different from that of the 'ate' complex **1**. As can be seen from the bond distance data in Table 2, the distances of five Lu–C(ring) range from 2.558(9) to 2.741(9) Å for fluorenyl fragment and 2.533(9)–2.59(1) Å for cyclopentadienyl ligand are shorter when compared with those of 2.570(6)–2.841(5) and 2.561(5)–2.626(5) Å in complex **1**, showing the typical pattern of normal η^5-bonding fashion instead of the η^3-bonding mode in **1**. This difference might be due to the steric decreasing around the rare-earth center when one of the amide group $N(TMS)_2$ takes place of the two chloride ligands coordinated on it in the ate complex **1**. The smaller angle of 101.1(7)° among the two $C_{bridgehead}$–CPh_2–$C_{bridgehead}$ bonds and the acute dihedral angle of 74.38° between two π-ring plans compared with those (102.4(3), 96.98°) observed in complex **1** also indicate the reduced steric effect around the central metal atom.

Although the bite angle of **2** is smaller than that in the corresponding ate chloride **1**, it is still larger when compared with that of the dimethylsilyl-bridged fluorenyl cyclopentadienyl lanthanide amides such as in $[Me_2Si(C_5H_4)(C_{13}H_8)]DyN(TMS)_2$ [12], the bite angle is 99.7(3)°; $[Me_2Si(C_5H_4)(C_{13}H_8)]ErN(TMS)_2$ [12], 99.5(2)°, and $[Me_2Si(C_5Me_4)(C_{13}H_8)]YN(TMS)_2$ [14], 100.4(9)°. Remarkably, such large bite angle is assumed to facilitate the agostic approach of the bis(trimethylsilyl)amide moiety to the Lewis acidic metal ion. Complex **2** features a Lu–N bond length of 2.167(8) Å, which is shorter than in the dimethylsilyl-bridged fluorenyl cyclopentadienyl lanthanocene amides (for example, in $[Me_2Si(C_5H_4)(C_{13}H_8)]DyN(TMS)_2$ (Dy–N = 2.207(5) Å), $[Me_2Si(C_5H_4)(C_{13}H_8)]ErN(TMS)_2$

(Er–N = 2.194(4) Å) and $[Me_2Si(C_5Me_4)(C_{13}H_8)]$-$YN(TMS)_2$ (Y–N = 2.243(11)Å)) and five-coordinate amide precursor (2.184(3)–2.238(3) Å) [15]. The shortest Ln–N bond reported so far was observed in the complex: *rac*-$Me_2Si(2\text{-}Me\text{–}Ind)_2LuN(TMS)_2$ (2.159(4) Å) [16], in which both of the Si–H moieties approach the Lu(III) center in an agostic manner.

The second interesting structural feature in complex **2** is the possible presence of an agostic interaction between the $^{\beta}$Si–C bond and the central metal atom. In this amide complex, one of the trimethylsilyl substituent approaches the Ln^{3+} center at an acute $\angle$Ln–C_{α}–Si_{β}(1). In this one carbon atom bridged complex **2** (Fig. 1), one of the Lu–N–Si angles is 102.5°, the other is 131.9(5)°. This multicenter Ln–Me–Si interaction has been observed in numerous organolanthanide amide complexes, for example $(C_5Me_5)_2LnN(TMS)_2$ [17], (*S*)–$[Me_2Si(C_5Me_4)((+)-\text{neomenthylCp})]LnN(TMS)_2$ [18], (*S*)–$[Me_2Si(C_5Me_4)((-)\text{menthylCp})]LnN(TMS)_2$ [19], $[Me_2Si(C_5Me_4)(C_{13}H_8)]YN(TMS)_2$ [14] with the two $\angle$Ln–N–Si_{β} angles ranging from 103.6(6) to 109.4(3)° for $\angle$Ln–N–Si_{β}(1) and from 121.5(5) to 132.0(7)° for $\angle$Ln–N–Si_{β}(2). The larger C(7)–C(14)–C(15) angle of 101.1(7)° and the dihedral angles of 74.38°, compared to that of the Si-bridged ligands, makes the metal center more open and induces the Lu–C(32) of 2.71(1) Å much shorter than that of Si-bridged amide complexes, for example, in our previous reported Si-bridged amides the Ln–C distances are equal to 2.834–2.901 Å [12]. The longer distances of the central metal atom Lu to the two hydrogens H (23, 24) on the γ-methyl group (equal to 2.50 Å) further demonstrate that there is the $^{\beta}$Si–Me–metal agostic interaction not the ($^{\gamma}$C)H–metal interaction [20]. The ^{1}H-NMR data of **2** show only one signal of the methyls of TMS groups at δ 0.00. This is inconsistent with the agostic structure shown in the X-ray structure, implying the fluxionality of **2** in THF solution.

2.3. Polymerization of MMA and lactones

To investigate the catalytic ability of compound **2** toward polar monomers, polymerization of methyl methacrylate (MMA) and lactones has been examined. Polymerization of MMA and lactones was performed in toluene and after a fixed time was quenched with acidic methanol, the polymers were isolated as colorless solids and characterized by GPC in THF using standard polystyrene. Triad microstructures analysis of the PMMA was carried out using ^{1}H-NMR spectra. The results of polymerization are summarized in Table 3. This one-carbon atom bridged ansa-complex initiates MMA polymerization to yield PMMA with rich-syndiotacticity (rr 59%; mm 18%; mr 23%). Its activity is

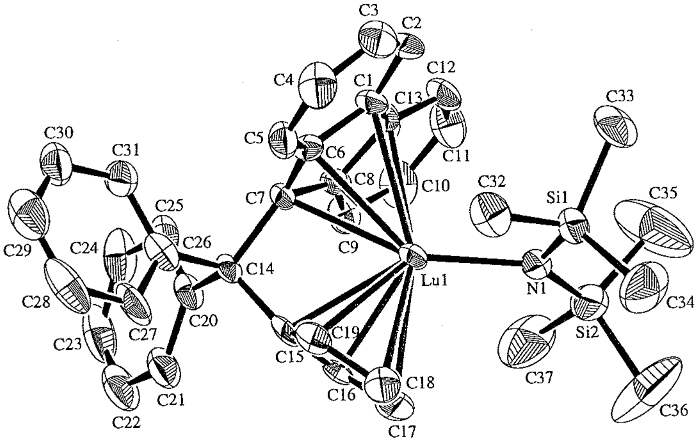

Fig. 1. ORTEP diagram of $[(C_{13}H_8)CPh_2(C_5H_4)LuN(TMS)_2]$ (**2**) with the adopted atom numbering (only one of the two molecules of the unit cell is shown).

Table 3
Data for the polymerization reactions

Entry	Mon.	[mon]/[cat]	T_p (°C)	Y (%)	M_w ($\times 10^{-4}$)	M_n ($\times 10^{-4}$)	M_w/M_n
1	MMA	200	0	12.3	5.44	2.40	2.27
2	MMA	200	−78	0	–	–	–
3	CL	600	25	53	8.15	4.38	1.85
4	VL	600	25	17	3.90	2.32	1.68

Reaction conditions: time, 2 h; solv/$[M_0]$ = 2 vol/vol; solvent, toluene.

less than those of $[Ln(C_5Me_5)_2H]_2$ and $[Ln(C_5Me_5)_2Me]_2$ [5]. The low activity of **2** is mainly due to the slow initial 1,4-addition of the $Ln–N(TMS)_2$ functionality to MMA compared with those of Ln–R (R = H, Me) functionality[6]. In connection with the slow initial 1,4-addition, the polymer formed by **2** shows broader polydisperisity than those obtained by $[Ln(C_5Me_5)_2H]_2$ and $[Ln(C_5Me_5)_2Me]_2$. The activity of **2** is also less than those of our previously reported one-silylcane bridged fluorenyl cyclopentadienyl lanthanocene derivatives [12]. The stereoselectivity of **2** is less than those of $[Ln(C_5Me_5)_2H]_2$ and $[Ln(C_5Me_5)_2Me]_2$. The complex **2** also initiate ring opening polymerization of ε-Caprolactone (CL) and δ-Valerolactone (VL). In the case of CL polymerization, the activity of this complex is higher than that of $[Yb(C_5Me_5)_2Me]_2$, and its activity can compare with that of $[Sm(C_5Me_5)_2Me]_2$ considering the reaction time [7]. The PCL and PVL formed are of moderate polydisperisities ($M_w/M_n = 1.85$, 1.68).

3. Experimental

3.1. General procedure

All operation involving organometallic was carried out under an inert atmosphere of Ar using standard schlenk techniques. Toluene and C_6H_{14} were distilled from Na–benzophenone Ketyl. $[Ph_2C(C_{13}H_8)(C_5H_4)Lu(Cl)_2]Li(THF)_4$ (**1**) was synthesized using the method described in literature [13a]. Methyl methacrylate was purified by distillation from CaH_2 followed by storage over activated molecular sieves (3A) and then vacuum transferred using a high-vacuum line prior to use. ε-Caprolactone (CL) was dried over CaH_2 for 10 days, distilled in vacuo, and stored over molecular sieves. δ-Valerolactone (VL) was distilled in vacuo and stored over molecular sieves. Mass spectra were recorded on a Hp 5989A spectrometer ($T = 50–400$ °C, 1.3 KV). The solvents C_6D_6 was degassed and dried over a Na–K alloy. ^{1}H-NMR on IX-90Q (300 MHz) spectrometer. Elemental analyses were performed by the Analytical Laboratory of the Shanghai Institute of Organic Chemistry.

3.2. Synthesis of $[Ph_2C(C_5H_4)(C_{13}H_8)]LuN(TMS)_2$ (2)

A solution of 230 mg (1.15 mmol) $KN(TMS)_2$ was added dropwise to a stirred suspension of 770 mg (1.27 mmol) of **1** in 50 ml $C_6H_5CH_3$ at − 78 °C under Ar. The reaction mixture was then slowly warmed to room temperature (r.t.) and stirred for 1 day, and then warmed to 60 °C and stirred for 1 day. The precipitate was filtered off. The solvent was decanted, concentrated slightly to 30 ml, and then cooled overnight at − 20 °C for crystallization. Orange crystal 92 mg (12.6%) was formed, which is suitable for X-ray analysis. Anal. Calc. for $C_{37}H_{40}LuNSi_2$ (**2**): C, 60.91; H, 5.49; N, 1.92. Found: C, 62.64; H, 5.63; N, 2.09%. ^{1}H-NMR (300 MHz; $[^2H_8]$THF, 25 °C): δ (J/Hz) 8.45 (d, 2H, $J = 8.2$ Hz, CH(Ar)), 8.34 (d, 2H, $J = 6.5$ Hz, CH(Ar)), 8.20 (d, 2H, $J = 8.1$ Hz, CH(Ar)), 7.2–7.7 (m, CH(Ar)), 6.31 (m, 2H,CH(Cp)), 6.50 (m, 2H, CH(Cp)), 0.00 (s, 18H, CH_3(Si)). EI mass spectrum (70 eV, 50–400 °C): m/z 730 (19.14, $[M]^+$), 654 (21.91, $[M-Ph]^+$), 146 (65.71, $[N(SiMe_3)_2]^+$). FT-Raman (cm^{-1}): 3056 (m), 2898 (m), 1528 (m), 1435 (m), 1327 (vs), 1003 (s), 741 (m), 667 (m), 618 (m), 522 (w), 440 (m), 285 (m).

3.3. Polymerization of MMA

A solution of preweighted catalyst (0.5 mmol) in $C_6H_5CH_3$ was adjusted to a constant temperature using an external bath. Into the well-stirred solution was syringed 100 mmol of methyl methacrylate, and the reaction was continuously stirred for an appropriate period at that temperature. Polymerization was stopped by addition of the acidic MeOH. The resulting precipitated PMMA was collected, washed with MeOH several times, and dried in vacuum at 50 °C for 12 h.

3.4. Polymerization of Lactones

To a solution of the catalyst (0.5 mmol) in $C_6H_5CH_3$ was added lactone using a syringe at r.t. with vigorous stirring. After 120 min, the polymerization was quenched by addition of MeOH and the solvent was removed. The polymer was redissolved in $CHCl_3$ (5 ml) and precipitated with MeOH (50 ml). The polymer was filtered and dried under vacuum.

3.5. X-ray structure determination

Single crystals were sealed in thin-walled glass capillaries under an atmosphere of Ar. X-ray diffraction data were collected at a r.t. using the w-2θ scan technique to a maximum 2θ value of 21.5°. The intensities of three representative reflections were measured after every 200 reflections. Over the course of data collection, the standards decreased by 0.9%. A linear correction factor was applied to the data to account for this phenomenon. The data were corrected for Lorentz polarization effects. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation [21].

4. Conclusion

In summary, we have successfully synthesized one new carbon-bridged fluorenyl cyclopentadienyl trivalent lutetium amide complex with C_s-symmetry, and characterized its structural features by X-ray diffraction studies. This complex initiates polymerization of polar monomers.

5. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 171166 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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