Synthesis and Characterization of Homoleptic Lanthanide Guanidinate Complexes and Their Catalytic Activity for the Ring-Opening Polymerization of Trimethylene Carbonate

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Keywords: Insertion / Lanthanides / N ligands / Polymerization

Two methods to synthesize homoleptic guanidinate lanthanide complex are described. The samarium guanidinate complex $[Sm\{Ph_2NC(NCy)_2\}_3]\cdot 2C_7H_8$ (**1**) can be synthesized by the metathesis reaction of lithium guanidinate with anhydrous samarium trichloride in a 3:1 molar ratio. The analogous complexes $[Ln\{Ph_2NC(NCy)_2\}_3]\cdot 2C_7H_8$ [Ln = Yb (**2**), Nd (**3**)] can also be synthesized by the insertion reaction of *N*,*N'*-dicyclohexylcarbodiimide into the Ln–N bond of $[(THF)_4Li][Ln(NPh_2)_4]$ in a 3:1 molar ratio in good yield. Complexes **1**–**3** were characterized by elemental analysis, IR and ^1H NMR spectroscopy. The molecular structures of complexes **1** and **3** were further determined by X-ray diffraction techniques. These complexes showed high activity for the ring-opening polymerization of trimethylene carbonate (TMC), giving polymers with M_w/M_n ranging from 1.41–1.73.

Introduction

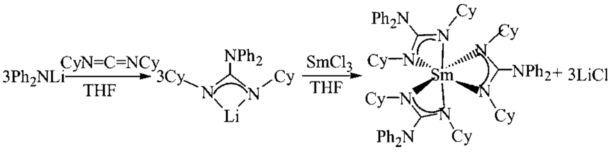
Lanthanocene complexes exhibit a variety of catalytic abilities for the polymerization of olefins, polar monomers and for organic transformations, such as hydrogenation, cyclic hydroamination of both alkynes and alkenes and so on.[1] Although guanidinate ligands have been well established as a versatile and flexible ligand system that is a potential alternative to cyclopentadienyl-based systems, and its application in organolanthanide complexes has led to the synthesis of a number of guanidinate derivatives of lanthanides,[2−7] the catalytic behavior of these complexes was not investigated until quite recently, when it was first reported that a monoguanidinate derivative of lanthanum $[La\{CyNC[N(SiMe_3)_2]NCy\}(OC_6H_3tBu_2\text{-}2,6)_2]$ can catalyze the ring-opening polymerization of D,L-lactide.[6] Very recently, methyllanthanide bis(guanidinate) complexes were found to be effective catalysts not only for the polymerization of ε-caprolactone and MMA,[5] but also for the polymerization of styrene,[8] which is normally quite difficult to polymerize with organolanthanide complexes. These fascinating results prompted us to study the chemistry of lanthanide guanidinate complexes further.

In this paper we report the synthesis of the homoleptic guanidinate lanthanides $[Ln\{Ph_2NC(NCy)_2\}_3]\cdot 2C_7H_8$ (Ln = Sm, Yb, and Nd) by a metathesis reaction (Sm) or by the insertion of *N*,*N'*-dicyclohexylcarbodiimide into the Ln−N bond of $[(THF)_4Li][Ln(NPh_2)_4]$ (Yb and Nd). All these complexes show good catalytic activity for the ring-opening polymerization of trimethylene carbonate (TMC).

Results and Discussion

Synthesis and Characterization of the Lanthanide Guanidinate Complexes

The metathesis reaction is one of the most versatile methods for the synthesis of organolanthanide derivatives. Thus, the new complex $[Sm\{Ph_2NC(NCy)_2\}_3]$ was prepared in good yields by the metathesis reaction of anhydrous $SmCl_3$ with $Li[Ph_2NC(NCy)_2]$, freshly prepared by the reaction of $LiNPh_2$ with CyN=C=NCy in THF [Equation (1)].



(1)

It has been reported that the insertion of one equivalent of the carbodiimide into the Ln−N bond of lanthanide amides leads to the formation of the corresponding lanthanide

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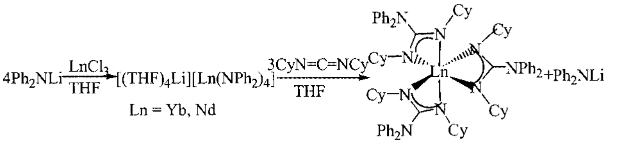
DOI: 10.1002/ejic.200300856

monoguanidinate derivatives,[6,7] so we wondered whether three molecules of the carbodiimide could insert into three Ln−N bonds of homoleptic lanthanide amides to give the corresponding homoleptic lanthanide guanidinate complexes. To answer this question, the reaction of *N,N′*-dicyclohexylcarbodiimide with $[(THF)_4Li][Ln(NPh_2)_4]$ in a 3:1 molar ratio was tried in THF. After workup, the homoleptic lanthanide guanidinate complexes $[Ln\{Ph_2NC(NCy)_2\}_3]\cdot 2C_7H_8$ [Ln = Yb (**2**), Ln = Nd (**3**)] were isolated in good yields. It is interesting that neither $LiLn[Ph_2NC(NCy)_2]_4$ nor $Li[Ph_2NC(NCy)_2]$ was obtained; the only Li product recovered was $LiNPh_2$ [Equation (2)]. This result indicates that the insertion of carbodiimide into the Ln−N bond is easier than into the Li−N bond.



(2)

All these lanthanide complexes are air and moisture sensitive, and are soluble in toluene, THF, and diethyl ether. They were characterized by elemental analysis and IR spectroscopy. The IR spectra of these complexes exhibit strong absorptions in the range of 1600−1640 cm^{-1}, which are consistent with a partial C=N double-bond character, indicating that the π-electrons are delocalized within the double bond of the N−C−N linkage.

Crystal Structure Analyses

The molecular structures of **1** and **3** were further determined by X-ray diffraction. Crystals of **1** and **3** suitable for X-ray diffraction were grown from toluene solutions. The molecular structures of **1** and **3** are shown in Figure 1 and 2, respectively. Selected bond lengths and angles are given in Table 1.

As shown in Figure 1 and 2, complexes **1** and **3** have analogous solid-state structures: they are both monomeric with a six-coordinate lanthanide center ligated by six nitrogen atoms of three chelating bidentate guanidinate ligands. The coordination geometry around the lanthanide ion for each complex is best described as a distorted trigonal prism. The C−N distances within the chelating guanidinate ligands (see Table 1) are approximately equivalent and significantly shorter than C−N single bond lengths, indicating that the π-electrons in these complexes are delocalized within the N−C−N fragment. The Sm−N bond lengths in complex **1** range from 2.425(6) to 2.460(6) Å, giving an average of 2.442(6) Å. This value is similar to that in $[Sm\{CH(SiMe_3)_2\}\{CyNC[N(SiMe_3)_2]NCy\}_2]$ [av. 2.417(4) Å].[3] As expected, the coordinated guanidinate group and the lanthanide atom form essentially a planar four-membered ring [N(1)−Sm(1)−N(2) = 54.6(2)°, C(1)−N(1)−Sm(1) = 94.4(5)°, C(1)−N(2)−Sm(1) = 94.9(4)°, N(1)−C(1)−N(2) = 115.9(7)°; sum of angles: 359.8°]. The N(1)−Sm(1)−N(2), N(4)−Sm(1)−N(5), and N(7)−Sm(1)−N(8) bond angles are 54.6(2)°, 55.2(2)°, and 54.8(2)°, respectively, and are similar to the corresponding angles in $[Sm\{CH(SiMe_3)_2\}\{CyNC[N(SiMe_3)_2]NCy\}_2]$ [55.06(13)°, and 55.59(13)°][3] and $[Yb\{CyNC(Ph)NCy\}_3]\cdot 2THF$ [58.1(2)° and 57.98(17)°].[9]

The Nd−N bond lengths vary from 2.464(4) to 2.494(4) Å, similar to those in $[\{(Me_3Si)_2NC(N\mathit{i}Pr)_2\}_2Nd(\mu\text{-}Me)_2Li(TMEDA)]$ [2.476(7) to 2.523(6)Å].[5] The guanidinate groups bind to Nd through two nitrogen atoms to yield a

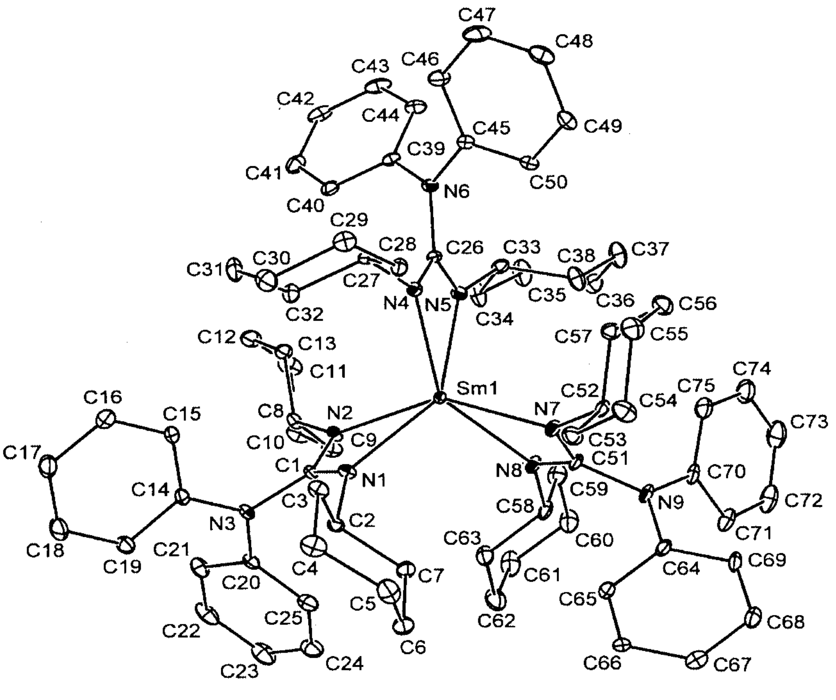


Figure 1. The molecular structure of complex **1**

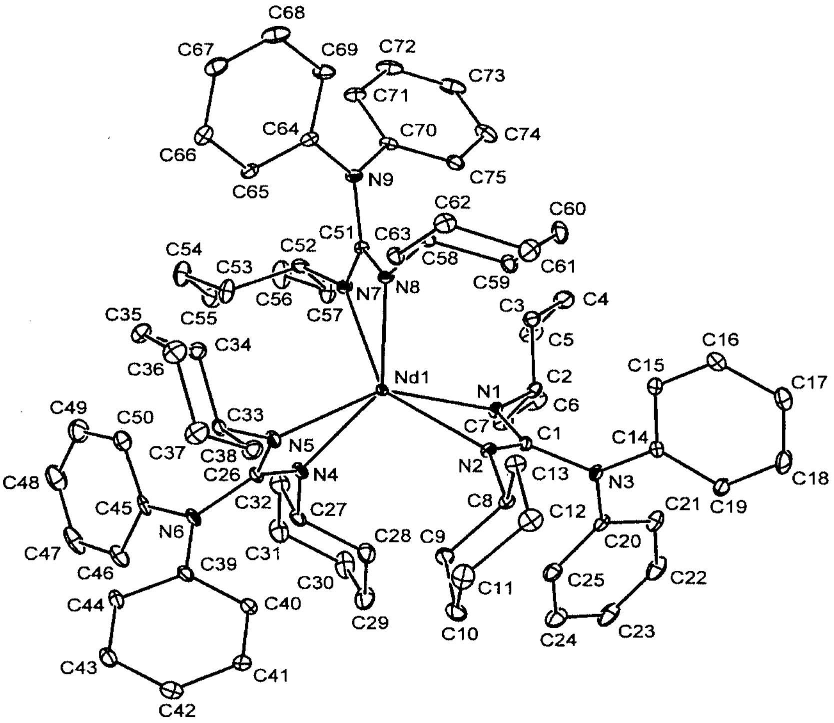


Figure 2. The molecular structure of complex **3**

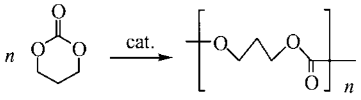
Table 1. Selected bond lengths (Å) and angles (°) for **1** and **3**

Bond length (Å)	**1**	**3**	Bond length (Å)	**1**	**3**
Ln(1)−N(1)	2.442(7)	2.478(4)	Ln(1)−N(2)	2.435(6)	2.485(4)
Ln(1)−N(4)	2.448(4)	2.464(4)	Ln(1)−N(5)	2.440(4)	2.494(4)
Ln(1)−N(7)	2.460(6)	2.475(3)	Ln(1)−N(8)	2.425(6)	2.477(2)
Ln(1)−C(26)	2.863(4)	2.889(5)	Ln(1)−C(51)	2.858(8)	2.891(3)
N(1)−C(1)	1.32(1)	1.312(5)	N(3)−C(1)	1.46(1)	1.324(5)
N(2)−C(1)	1.316(9)	1.324(6)	N(5)−C(26)	1.332(7)	1.327(5)
N(4)−C(26)	1.326(8)	1.332(6)	N(7)−C(51)	1.309(8)	1.324(5)
N(6)−C(26)	1.431(6)	1.441(6)	N(9)−C(51)	1.44(1)	1.439(4)
N(8)−C(51)	1.33(1)	1.314(5)			
Angle (°)	**1**	**3**	**Angle (°)**	**1**	**3**
N(1)−Ln(1)−N(2)	54.6(2)	53.9(1)	C(51)−N(8)−Ln(1)	94.6(4)	94.4(2)
N(4)−Ln(1)−N(5)	55.2(2)	54.7(1)	N(1)−C(1)−N(2)	115.9(7)	117.0(4)
N(7)−Ln(1)−N(8)	54.8(2)	54.1(1)	N(4)−C(26)−N(5)	116.7(4)	117.8(4)
C(1)−N(1)−Ln(1)	94.4(5)	94.8(3)	N(7)−C(51)−N(8)	116.9(7)	117.2(3)
C(1)−N(2)−Ln(1)	94.9(4)	94.2(3)	C(26)−Ln(1)−C(51)	119.1(2)	118.4(1)
C(26)−N(4)−Ln(1)	93.9(3)	94.4(3)	Ln(1)−C(26)−N(6)	178.3(4)	178.8(3)
C(26)−N(5)−Ln(1)	94.1(3)	93.1(3)	Ln(1)−C(51)−N(9)	177.4(5)	177.9(3)
C(51)−N(7)−Ln(1)	93.6(4)	94.2(2)			

planar four-membered ring (sum of angles 359.9°) with bite angles of 53.9(1)°, 54.7(1)° and 54.7(1)°, respectively, which are similar to those in complex **1**, and [{$(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2Nd(\mu\text{-}Me)_2Li(TMEDA)$] [53.5(2)° and 54.0(2)°].[5]

Ring-Opening Polymerization of Trimethylene Carbonate (TMC)

Polycarbonate is a biomaterial with good biodegradability, biocompatibility, and low toxicity, and therefore the study of its preparation has attracted much attention. The ring-opening polymerization of a cyclic carbonate is an easy way to get a polycarbonate, and several Lewis acids are effective catalysts for this polymerization reaction. However, there are only a few papers dealing with the polymerization of cyclic carbonates catalyzed by organolanthanide complexes.[10−15] Evans et al. have found that a Sm^{II} complex can catalyze the copolymerization of ε-caprolactone (ε-CL) and ethylene carbonate, but cannot catalyze the homopolymerization of ethylene carbonate,[10] and Yasuda et al. have reported that Sm^{II} complexes show catalytic activity for the homopolymerization of trimethylene carbonate and the copolymerization of trimethylene carbonate with ε-CL.[11] Recently, Shen et al. have found that homoleptic lanthanide(III) aryloxides are effective initiators for the ring-opening polymerization of 2,2-dimethyltrimethylene carbonate.[12b] We therefore decided to examine the catalytic activity of the homoleptic guanidinate lanthanide complexes in the ring-opening polymerization of TMC (Scheme 1).



Scheme 1

The preliminary results are listed in Table 2, where it can be seen that all the complexes tested show high activity for the ring-opening polymerization of TMC. The monomer conversion is over 85% for all the polymerizations under the conditions of [M]/[I] = 500 (mole ratio) at 40 °C in 30 min (entries 1, 5, and 10). An effect of the central metal on the catalytic activity can also be observed. For example, the conversion reaches 95% in the case of [M]/[I] = 700 at 40 °C in 30 min using **2** as the initiator, while it is only 56% and 12% for complexes **1** and **3**, respectively (entries 2, 7 and 11). The conversion was still 89.5% even when the [M]/[I] ratio was increased to 1000 with **2** as the initiator (entry 8). Therefore, the activity order under the present polymerization conditions is Yb > Sm > Nd, which is opposite to the order of the ionic radii.

An effect of the polymerization temperature on the conversion can also be observed. The conversion increases with an increase of temperature from 20 to 60 °C with **1** or **3** as the initiator (entries 2, 3, 9, 10).

The catalytic activity of these tris(guanidinate) lanthanide complexes is similar to that of $La(OAr)_3$ (OAr = 2,6-di-*tert*-butyl-4-methyl phenolate) for the ring-opening polymerization of TMC,[12c] but is higher than that of $LnCl_3$ [12e] and $BX_3{\cdot}Et_2O$.[16] In comparison with the above catalysts, our lanthanide tris(guanidinate) complexes give polymers with a relatively narrow molecular-weight distribution.

Conclusion

In summary, homoleptic guanidinate lanthanide complexes can be easily prepared in good yield by the metathesis reaction of lithium guanidinate with anhydrous lanthanide trichlorides or by the insertion reaction of carbodiimide into the Ln−N bonds of $[(THF)_4Li][Ln(NPh_2)_4]$ in a 3:1 molar ratio. Their structural features have been determined by X-ray diffraction. These complexes show good catalytic activity for the ring-opening polymerization of trimethylene carbonate and the polymerization gives polymers with a relatively narrow molecular-weight distribution (M_w/M_n = 1.41−1.73).

Experimental Section

General Procedures: All manipulations were performed under pure Ar with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl prior to use. Anhydrous $LnCl_3$,[17] $[Li(THF)_4][Ln(NPh_2)_4]$[18] and trimethylene carbonate (TMC)[19] were prepared according to the literature procedures. *N,N′*-Dicyclohexylcarbodiimide was purchased from Aldrich and used as received without further purification. Melting points were determined in sealed Ar-filled capillary tubes. Metal analyses were carried out by complexometric titration. Carbon, hydrogen and nitrogen analyses were performed by direct combustion on a Carlo−Erba EA = 1110 instrument. The IR spectra were recorded on a Magna-IR 550 spectrometer. Molecular weight and molecular weight distributions were determined against

Table 2. Polymerization of TMC initiated by homoleptic lanthanide guanidinate complexes[a]

Entry	Init	[M]/[I]	Temp (°C)	Time (min)	Yield[b] (%)	M_n ($\times 10^4$)	M_w/M_n [c]
1	**1**	500	20	30	86.4	1.15	1.70
2	**1**	700	40	30	56.11	0.87	1.69
3	**1**	700	60	30	100	1.47	1.75
4	**2**	500	20	30	94.9	2.08	1.73
5	**2**	500	40	30	92.0	2.65	1.64
6	**2**	500	60	30	94.4	2.95	1.56
7	**2**	700	40	30	95.7	1.79	1.62
8	**2**	1000	60	30	89.5	1.68	1.59
9	**3**	500	20	30	21.26	0.89	1.41
10	**3**	500	40	30	85.65	2.43	1.66
11	**3**	700	40	30	12.4	0.90	1.63

[a] Polymerization conditions: toluene, [TMC] = 1 mol/L. [b] Yield = weight of polymer obtained/weight of monomer used. [c] Measured by GPC (calibrated with standard polystyrene samples).

a polystyrene standard by gel-permeation chromatography (GPC) on a waters 1515 apparatus with three HR columns (HR-1, HR-2 and HR-4); THF was used as an eluent at 30 °C. ^{1}H NMR spectra were measured on a Unity Inova-400 spectrometer.

Synthesis of [Sm{Ph$_2$NC(NCy)$_2$}$_3$]·2C$_7$H$_8$ (1): A Schlenk flask was charged with Ph$_2$NH (2.1 mL,15.0 mmol), THF (30 mL), and a stir bar. The solution was cooled to 0 °C, and *n*BuLi (9.6 mL, 15.0 mmol, 1.56 M in hexane) was added. It was then slowly warmed to room temperature and stirred for 1 h. *N*,*N′*-Dicyclohexylcarbodiimide (3.15 g, 15.3 mmol in 10 mL of THF) was then added to this solution at 0 °C. The solution was slowly warmed to room temperature, stirred for 1 h and then added slowly to a pale-gray slurry of SmCl$_3$ (1.28 g 5.11 mmol) in 20 mL of THF. The resulting solution was stirred for 1 h at 273 K and then stirred for 48 h at room temperature. The solvent was removed in vacuo and the residue was extracted with toluene and LiCl removed by centrifugation. After the extracts were concentrated, colorless crystals (5.50 g, 74%)were obtained at room temperature after a few days. M.p. 212 °C (dec.). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 6.88−7.39 (m, 42 H, Ph), 3.62 (m, 6 H, unique H-Cy), 0.34−2.15 (br., 60 H, C$_6$H$_{10}$) ppm. C$_{89}$H$_{112}$N$_9$Sm (1458.3): calcd. C 73.30, H 7.75, N 8.64, Sm 10.31; found C 73.24, H 7.20, N 8.63, Sm 9.85. IR (KBr pellet): $\tilde{\nu}$ = 3426 cm^{-1} (s), 2928 (m), 2855 (w), 1636 (s), 1590 (m), 1559 (w), 1493 (m), 1454 (w), 1400 (w), 1366 (w), 1235 (s), 1158 (s), 891 (w), 756 (w), 694 (w), 625 (w), 505 (m).

Synthesis of [Yb{Ph$_2$NC(NCy)$_2$}$_3$]·2C$_7$H$_8$ (2): A Schlenk flask was charged with a solution of [Li(THF)$_4$][Yb(NPh$_2$)$_4$] (4.56 g, 4.0 mmol) in 30 mL of THF and a stir bar. Then, a solution of *N*,*N′*-dicyclohexylcarbodiimide (2.47 g, 12.0 mmol) in 20 mL of THF was added slowly. The color of the solution slowly became yellow. The solution was then stirred for another 48 h and the solvents evaporated to dryness in vacuo. The residue was extracted with toluene and LiCl was removed by centrifugation. The solution was concentrated and stored at room temperature for crystallization. Complex **2** was obtained as yellow crystals (4.62 g, 78%). M.p. 287−289 °C (dec.). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 6.88−7.40 (m, 42 H, Ph), 3.16−3.98 (m, 6 H, unique H-Cy), 0.34−2.15 (br., 60 H, C$_6$H$_{10}$) ppm. C$_{89}$H$_{112}$N$_9$Yb (1481.0): calcd. C 72.18, H 7.62, N 8.51, Yb 11.69; found C 71.96, H 8.05, N 8.79, Yb 10.73. IR (KBr pellet): $\tilde{\nu}$ = 3430 cm^{-1} (s), 2928 (s), 2855 (m), 1640 (s), 1590 (m), 1493 (m), 1451 (w), 1308 (w), 1235 (w), 1154 (w), 1076 (w), 1030 (w), 891 (w), 752 (m), 694 (m).

Table 3. Details of the crystallographic data collection and refinement for **1** and **3**

	1	**3**
Empirical formula	C$_{89}$H$_{112}$N$_9$Sm	C$_{89}$H$_{112}$N$_9$Nd
Molecular weight	1458.32	1452.16
Temperature (K)	193.1	193.1
Wavelength (Å)	0.7107	0.7107
Size (mm)	0.40 × 0.42 × 0.25	0.60 × 0.55 × 0.30
Crystal system	monoclinic	monoclinic
Space group	$P2_1$ (no. 4)	$P2_1$ (no. 4)
a (Å)	14.086(2)	14.1338(13)
b (Å)	21.782(2)	21.7685(13)
c (Å)	14.541(2)	14.5916(13)
α (°)	90	90
β (°)	117.843(5)	118.017(3)
γ (°)	90(5)	90
V (Å^3)	3945.0(8)	3963.3(6)
Z	2	2
$D_{\text{calcd.}}$ (g cm^{-3})	1.228	1.217
Absorption coefficient (mm^{-1})	0.796	0.705
F (000)	1542.00	1538.00
Theta range for collection (°)	3.0−27.5	3.2−27.5
Reflection collected	87950	79450
Independent reflections	17924	18014
Variables	918	918
R [$I > 3\sigma(I)$]	0.045	0.035
Rw	0.106	0.091
Goodness-of-fit on F^2	0.973	1.023

Synthesis of [Nd{Ph$_2$NC(NCy)$_2$}$_3$]·2C$_7$H$_8$ (3): Following the procedure for the synthesis of **2**, the reaction of *N*,*N′*- dicyclohexylcarbodiimide (1.36 g, 6.6 mmol) in 20 mL of THF with [Li(THF)$_4$][Nd(NPh$_2$)$_4$] (2.45 g, 2.2 mmol) in 30 mL of THF afforded **3** as light-blue crystals (2.88 g, 65%). M.p. 131 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 6.87−7.40 (m, 42 H, Ph), 3.56−3.62 (m, 6 H, unique H-Cy), 0.34−2.15 (br., 60 H, C$_6$H$_{10}$) ppm. C$_{89}$H$_{112}$N$_9$Nd (1452.2): calcd. C 73.61, H 7.77, N 8.68, Nd 9.94; found C 73.25, H 7.96, N 8.92, Nd 9.55. IR (KBr pellet): $\tilde{\nu}$ = 3442 cm^{-1} (s), 3280 (m), 3257 (m), 2964 (m), 1628 (m), 1405 (w), 1266 (m), 1088 (s), 1027 (s), 918 (w), 888 (w), 803 (s), 695 (w), 533 (w), 440 (w).

Typical Procedure for the Polymerization Reactions: A 50-mL Schlenk flask equipped with a magnetic stir bar was charged with a solution of TMC (0.3583 g, 3.51 mmol) in 2.8 mL of toluene. To this solution was added 0.7 mL of a solution of complex **2** in toluene (1.0×10^{-2} M, 7.00×10^{-3} mmol) with a syringe. The contents of the flask were then vigorously stirred for 30 min at 20 °C. The polymerization was quenched by adding a 5% solution of HCl in methanol,. The polymer precipitated from methanol and was dried under vacuum.

X-ray Structural Determination of 1 and 3: Suitable single crystals of complexes **1** and **3** were each sealed in a thin-walled glass capillary, and intensity data were collected on a Rigaku Mercury CCD equipped with graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation. Details of the intensity data collection and crystal data are given in Table 3. The crystal structures of these complexes were solved by direct methods and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix least-squares analysis on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically with assigned appropriate isotropic thermal parameters. CCDC-224364 (for **1**) and -224365 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We are indebted to the Chinese National Natural Science Foundation for financial support.

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Received November 20, 2003
Early View Article