Insertion Reactions of Phenyl Isocyanate and Phenyl Isothiocyanate into the Nd−S Bond of $[(CH_3C_5H_4)_2Nd(\mu\text{-}SPh)(THF)]_2$: Synthesis and Crystal Structures

Qi Shen,*[†,‡] Huanrong Li,[†] Changsheng Yao,[†] Yingming Yao,[†] Lilu Zhang,[†] and Kaibei Yu[§]

Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, People's Republic of China, Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academia Sinica, Shanghai 200032, People's Republic of China, and Chengdu Institute of Organic Chemistry, Academia Sinica, Chengdu 610041, People's Republic of China

Received January 3, 2001

The two insertion reactions of $[(CH_3C_5H_4)_2Nd(\mu\text{-}SPh)(THF)]_2$ (**1**) with PhNCO and PhNCS in a 1:1 mole ratio in tetrahydrofuran (THF) solution were studied. The first reaction gives the dimeric complex $[(CH_3C_5H_4)_2Nd]_2[\mu\text{-}\eta^2\text{-}OC(SPh)NPh]_2$ (**2**), which has an interlinked tricyclic structure formed via two bridged Nd−O bonds, while the second reaction affords the complex $(CH_3C_5H_4)_2Nd[\eta^2\text{-}SC(SPh)NPh](THF)$ (**3**), containing a η^2-coordinated ligand of SC(SPh)NPh. The new complexes, including **1**, were fully characterized by IR, elemental analysis, and single-crystal X-ray diffraction.

Introduction

The reactions of organic isocyanates with main-group-metal and transition-metal complexes have already been studied extensively. It is well-known that organic isocyanates can insert into metal−carbon, metal−nitrogen, metal−hydrogen, and metal−oxygen bonds to give the corresponding insertion products.[1−3] However, studies on the reactivity of lanthanide complexes with organic isocyanates are still limited. We reported that phenyl isocyanate could react easily with the lanthanocene amide $(CH_3C_5H_4)_2LnN(i\text{-}Pr)_2(THF)$ (Ln = Y, Er, Yb) to give the insertion product $[(CH_3C_5H_4)_2Ln(THF)(\eta^2\text{-}OCN(i\text{-}Pr)_2NPh)]$.[4] In addition, Evans et al. presented the insertion of phenyl isocyanate into the Ln−C π-bond of $(C_5Me_5)_3Ln$ to generate $(C_5Me_5)_2Sm[\eta^2\text{-}OC(C_5Me_5)N(Ph)C(NPh)O]$.[5] However, the insertion of isocyanate into a Ln−S bond has not been found in the literature.

During our studies of the reactivity of lanthanocene thiolate, we have examined the reactions of $[(CH_3C_5H_4)_2Nd(\mu\text{-}SPh)(THF)]_2$(**1**) with phenyl isocyanate and phenyl isothiocyanate and found that the two reactions could take place; the corresponding products $[(CH_3C_5H_4)_2Nd]_2[\mu\text{-}\eta^2\text{-}OC(SPh)NPh]_2$ (**2**) and $(CH_3C_5H_4)_2Nd[\eta^2\text{-}SC(SPh)NPh](THF)$ (**3**) were obtained. Herein, we wish to report the syntheses, characterizations, and crystal structures of the products obtained in the insertion reactions of phenyl isocyanate and phenyl isothiocyanate into the Nd−S bond of **1**.

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, all experiments were performed under pure argon with rigorous exclusion of air and water using Schlenk techniques. Solvents were dried and freed of oxygen by refluxing over sodium/benzophenone ketyl and distilled prior to use. PhNCO and PhNCS were dried over molecular sieves and degassed prior to use.

Melting point temperatures were determined in sealed argon-filled capillaries and are uncorrected. The IR spectra were recorded on a Magna550 spectrometer. Elemental analyses (C, H, N) were performed by direct combustion on a Carlo Erba 1110 instrument.

Anhydrous $NdCl_3$[6] and $(CH_3C_5H_4)_3Nd$[7] were prepared according to the literature methods.

Synthesis of $[(CH_3C_5H_4)_2Nd(\mu\text{-}SPh)(THF)]_2$ (1). To a solution of $(CH_3C_5H_4)_3Nd$ (1.36 g, 3.56 mmol) in 30 mL of THF was added 0.36 mL (3.56 mmol) PhSH with a syringe. After the mixture was stirred at room temperature for 48 h, the reaction solution was concentrated and cooled to −10 °C. Blue-purple crystals were formed. Yield: 1.19 g (60%). Mp: 141−144 °C. Anal. Calcd for $C_{44}H_{54}O_2S_2Nd_2$: C, 54.62; H, 5.63; Nd, 29.82. Found: C, 54.20; H, 5.39; Nd, 29.75. IR: 2966 (w), 2928 (w), 1628 (w), 1477 (w), 1377 (w), 1084 (w), 1045 (w), 887 (w), 740 (m), 694 (w), 547 (w).

Synthesis of $[(CH_3C_5H_4)_2Nd]_2[\mu\text{-}\eta^2\text{-}OC(SPh)NPh]_2$ (2). To a solution of **1** (1.19 g, 2.46 mmol) in THF (40 mL) was added 0.27 mL (2.46 mmol) of phenyl isocyanate (PhNCO). The reaction mixture was stirred at room temperature overnight.

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* To whom correspondence should be addressed. E-mail: qshen@suda.edu.cn. Fax: 0086-512-5112371.

[†] Suzhou University.

[‡] Chinese Academia Sinica.

[§] Academia Sinica.

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10.1021/om0100131 CCC: $20.00
Publication on Web 06/12/2001

Table 1. Crystal Data and Structure Refinement for Complexes 1, 2 and 3

	1	2	3
formula	$C_{22}H_{27}NdOS$	$C_{50}H_{48}N_2O_2S_2Nd_2$	$C_{29}H_{32}NNdOS_2$
fw	483.74	1061.50	618.92
temp (K)	293(2)	294(2)	291(2)
cryst syst	monoclinic		
space group	$P2_1/n$ (No. 14)		
a (Å)	8.541(2)	13.589(1)	10.0310(10)
b (Å)	18.048(3)	17.643(1)	23.988(3)
c (Å)	14.618(2)	18.711(1)	11.685(2)
β (deg)	106.58(2)	95.93(1)	95.570(10)
V (Å^3)	2159.6(7)	4462.0(5)	2798.4(7)
Z	4		
F(000)	972	2120	1252
D(calcd) (Mg/m^3)	1.488	1.580	1.469
μ (mm^{-1})	2.507	2.436	2.025
diffractometer	Siemens P4	Rigaku Raxis II C	Siemens P4
radiation	Mo Kα		
θ range (deg)	2.26−26.00	1.77−25.55	1.70−24.99
cryst size (mm)	0.70 × 0.50 × 0.40	0.30 × 0.40 × 0.80	0.54 × 0.40 × 0.22
no.of rflns collected	5473	13 007	5584
no. of obsd rflns ($I > 2\sigma(I)$)	3208	6539	3015
no. of variables	226	523	310
R_F, R_{wF}	0.0406, 0.0877	0.0731, 0.1961	0.0316, 0.0553
goodness of fit	1.019	1.082	0.793

The reaction mixture was concentrated and cooled to −10 °C. Blue-purple crystals (1.17 g, 88.2%) of compound **2** were obtained from THF−toluene. Mp: 164−167 °C dec. Anal. Calcd for $C_{50}H_{48}N_2O_2S_2Nd_2$: C, 56.57; H, 4.56; N, 2.64; Nd, 27.17. Found: C, 55.80; H, 4.30; N, 2.53; Nd, 27.10. IR (Nujol, cm^{-1}): 3059 (m), 2924 (w), 2858 (w), 1675 (m), 1610 (s), 1597 (s), 1520 (s), 1430 (s), 1307 (s), 1238 (m), 1192 (s), 1026 (s), 918 (m), 821 (m), 756 (s), 690 (s), 505 (w), 439 (w).

Synthesis of $(CH_3C_5H_4)_2Nd[\eta^2\text{-}SC(SPh)NPh](THF)$ (3). To a THF (30 mL) solution of $[(CH_3C_5H_4)_2Nd(\mu\text{-}SPh)(THF)]_2$ (1.63 g, 3.37 mmol) was added phenyl isothiocyanate (0.4 mL, 3.37 mmol); the resulting solution was stirred overnight at room temperature. After the clear solution was concentrated, blue-purple crystals of **3** (1.22 g, yield 60.5%) were isolated. Mp: 138−141 °C. Anal. Calcd for $C_{29}H_{32}NOS_2Nd$: C, 56.28; H, 5.21; N, 2.26; Nd, 23.30. Found: C, 56.03; H, 5.10; N, 2.18; Nd, 23.10. IR (Nujol, cm^{-1}): 3071 (w), 2886 (w), 2732 (w), 1651 (w), 1589 (m), 1466 (s), 1342 (w), 1204 (m), 1026 (s), 972 (s), 864 (m), 756 (m), 694 (w), 594 (w), 493 (w).

X-ray Data Collection and Structure Determination. Suitable single crystals of complexes **1**−**3** were sealed in thin-walled glass capillaries for single-crystal structure determinations. The data were collected at room temperature on a Siemens P4 diffractometer (for **1** and **3**) or a Rigaku Raxis II C diffractometer (for **2**) using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. Intensity data were corrected for Lorentz−polarization and empirical absorption effects. A summary of crystallographic data is given in Table 1. The structures were solved by direct methods and refined with full-matrix least squares on F^2. All the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in idealized positions.

Results and Discussion

Synthesis of 1. Lanthanocene thiolate complex usually can be synthesized by the following methods: reaction of lanthanide metal with ArSSAr,[8] metathesis of $LnCl_3$ with MSR,[9] and the reaction of Cp'_3Ln with HSR.[10] Here the third method was used for the synthesis of **1**. The expected **1** was obtained as blue-purple crystals in 60% yield when $(CH_3C_5H_4)_3Nd$ reacted with 1 equiv of HSPh in THF at room temperature (eq 1).

$$2(CH_3C_5H_4)_3Nd + 2HSPh \rightarrow \underset{\mathbf{1}}{[(CH_3C_5H_4)_2Nd(\mu\text{-}SPh)(THF)]_2} \quad (1)$$

The complex **1** is soluble in THF and slightly soluble in aromatic solvents. It is thermally stable and decomposes at 141−144 °C.

Insertion of Phenyl Isocyanate into the Nd−S Bond of 1. The insertion reaction of PhNCO into the Nd−S bond of complex **1** went smoothly when equivalent phenyl isocyanate was added into the THF solution of **1** at room temperature. The insertion product as blue-purple crystals was isolated in good yield after workup. The IR spectra of the product show two strong absorptions at 1597 and 1520 cm^{-1}, which can be assigned to bidentate CN and CO vibrations.[11] The results indicate that in this reaction the new amido ligand [OC(SPh)-NPh] was formed through transferring the SPh group to the isocyanate carbon atom (eq 2), which is similar to the analogous reaction of $(CH_3C_5H_4)_2LnN(i\text{-}Pr)_2(THF)$ with PhNCO, in which $-N(i\text{-}Pr)_2$ was moved to the isocyanate carbon atom.[4] The new amido ligand that is formed, [OC(SPh)NPh], is coordinated to the central metal Nd in an η^2 fashion. An X-ray determination shows the complex to be a dimer (see Description of the Molecular Structure).

$$[(CH_3C_5H_4)_2Nd(\mu\text{-}SPh)(THF)]_2 + 2PhNCO \rightarrow \underset{\mathbf{2}}{[(CH_3C_5H_4)_2Nd]_2[\mu\text{-}\eta^2\text{-}OC(SPh)NPh]_2} \quad (2)$$

Insertion of Phenyl Isothiocyanate into the Nd−S Bond of 1. We consider that the coordination behavior of phenyl isothiocyanate is similar to that of phenyl isocyanate, for they are isoelectronic analogues. Therefore, a similar reaction with phenyl isothiocyanate has also been studied, even though this kind of reaction has not yet been found in the literature. The reaction proceeded smoothly when equivalent phenyl isothiocyanate had been added into THF solution of complex **1**. The product $(CH_3C_5H_4)_2Nd[\eta^2\text{-}SC(SPh)NPh](THF)$ (**3**) was isolated in good yield, as shown in eq 3. The formation of **3** can be confirmed by the IR data for complex **3**. There was no band at ca. 2150 cm^{-1} assigned to the asymmetric stretching frequency of −N═C═S in the IR spectra. Two strong absorptions at 1466 and 1026

$$[(CH_3C_5H_4)_2Nd(\mu\text{-}SPh)(THF)]_2 + 2PhNCS \rightarrow \underset{\mathbf{3}}{2(CH_3C_5H_4)_2Nd[\eta^2\text{-}SC(SPh)NPh](THF)} \quad (3)$$

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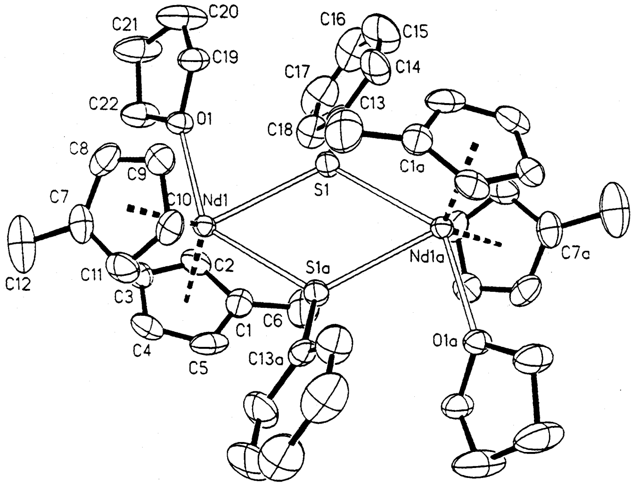

Figure 1. ORTEP diagram of the molecular structure of $[(CH_3C_5H_4)_2Nd(\mu\text{-}SPh)(THF)]_2$ (**1**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 1[a]

Nd(1)−S(1)	2.9216(14)	S(1)−Nd(1)#1	2.9364(13)
Nd(1)−C(1)	2.809(5)	Nd(1)−C(2)	2.782(5)
Nd(1)−C(3)	2.733(5)	Nd(1)−C(4)	2.729(5)
Nd(1)−C(5)	2.753(5)	Nd(1)−O(1)	2.542(5)
Nd(1)−Cp(1)	2.493	Nd(1)−Cp(2)	2.497

O(1)−Nd(1)−C(10)	113.55(14)	C(10)−Nd(1)−S(1)	106.30(13)
C(9)−Nd−S(1)	96.74(13)	C(2)−Nd(1)−S(1)	98.01(12)
C(1)−Nd(1)−S(1)	88.98(12)	C(4)−Nd(1)−C(9)	124.74(18)
C(4)−Nd−S(1)	137.55(14)	Nd−S(1)−Nd(1)#1	116.90(4)
Cp(1)-Nd(1)-Cp(2)	124.5		

[a] Cp(1) represents the centroid of the C(1)−C(5) ring; Cp(2) represents the centroid of the C(7)−C(11) ring.

cm^{-1} appeared. The two bands can be attributed to the characteristic absorptions of bidentate CN and CS in the *N*-phenylthioacetamide ligand, respectively.[11,12] The IR data indicated complex **3** should contain a CS_2N fragment of the η^2-coordinated ligand.

Description of the Molecular Structure. Complex **1** is a centrosymmetric binuclear molecule, with the benzenethiol ligand as the bridging groups. The structure is common (Figure 1). The lanthanide metal Nd is coordinated by two $CH_3C_5H_4$ rings, two sulfur atoms from the benzenethiol ligands and one oxygen atom of THF. The coordination number of Nd metal is 9. Selected bond distances and angles are listed in Table 2. The two Nd−S distances are 2.9216(14) and 2.9364(13) Å with an average of 2.9290(13) Å for **1**, which agrees with the value found in the related sulfur-bridged complex $[(Me_3CC_5H_4)_2Ce(\mu\text{-}SCHMe_2)]_2$, 2.882(6) Å,[13] when the difference in metallic ionic radii is considered.

Complex **2** is a dimeric complex in which two $(CH_3C_5H_4)_2Nd$ groups are connected by two $[OC(SPh)NPh]^-$ anions. The eight atoms Nd1, O2, C44, N2, Nd2, O1, C19, and N1 form an interlinked tricyclic structure via the two bridged Nd−O bonds (Nd1−O1 and Nd2−O2 bonds). The central metal is coordinated by two $CH_3C_5H_4$ rings, two O atoms, and one N atom from the phenyl isocyanate groups. The formal coordination number of each Nd is 9. Selected bond distances and angles are listed in Table 3. The molecular structure shown in Figure 2 is similar to those for the complexes $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^4\text{-}(PhN)OCCO(NPh)]$[14] and $\{Me_2Al(\mu\text{-}Et_2N)_2Mg[(Ph)NC(CH_3)O]\}_2$.[15] The former complex was synthesized by the reaction of $(C_5Me_5)_2Sm(Ph)N{=}N(Ph)\text{-}Sm(C_5Me_5)_2$ with CO, while the latter was formed by the reaction of $[Me_2Al(\mu\text{-}Et_2N)_2Mg(\mu\text{-}Me)]_2$ and PhNCO. The C−N and C−O bond distances associated with sp^2 carbon atoms are 1.297(8), 1.281(8) Å and 1.301(8), 1.292(8) Å, respectively, which are intermediate between a double-bond distance (N=C, 1.26 Å; C=O, 1.20−1.22 Å) and a single-bond distance (N−C, 1.51 Å; C−O, 1.43 Å).[16,17] The bond parameters indicate some electronic delocalization over the O−C−N unit. The observed Nd1−N1 (2.543(6) Å) and Nd2−N2 (2.573(6) Å) bond distances are longer than a normal Nd−N σ bond (2.283 Å)[18] and shorter than the donating bond distance (2.682

Table 3. Selected Bond Distances (Å) and Angles(deg) for Complex 2[a]

Nd(1)−O(1)	2.535(5)	Nd(1)−O(2)	2.411(4)
Nd(1)−N(1)	2.543(6)	N(1)−C(19)	1.297(8)
C(19)−O(1)	1.281(8)	Nd(2)−O(2)	2.553(5)
Nd(2)−O(1)	2.402(4)	Nd(2)−N(2)	2.573(6)
N(2)−C(44)	1.301(8)	C(44)−O(2)	1.292(8)
Nd(1)−C(7)	2.759(8)	Nd(1)−C(8)	2.761(9)
Nd(1)−C(9)	2.749(9)	Nd(1)−C(10)	2.718(9)
Nd(1)−C(11)	2.726(9)	Nd(1)−Cp(1)	2.471
Nd(1)−Cp(2)	2.477	Nd(2)−Cp(3)	2.463
Nd(2)−Cp(4)	2.475		

O(2)−Nd(1)−O(1)	66.53(16)	O(2)−Nd(1)−N(1)	117.90(16)
O(1)−Nd(1)−N(1)	51.65(16)	O(1)−Nd(2)−O(2)	66.37(16)
O(1)−Nd(2)−N(2)	117.39(17)	O(2)−Nd(2)−N(2)	51.28(16)
O(1)−C(19)−N(1)	118.1(6)	Nd(2)−O(1)−Nd(1)	114.02(18)
O(2)−C(44)−N(2)	117.6(6)		

[a] Cp(1) represents the centroid of the C(1)−C(5) ring; Cp(2) represents the centroid of the C(7)−C(11) ring; Cp(3) represents the centroid of the C(26)−C(30) ring; Cp(4) represents the centroid of the C(32)−C(36) ring.

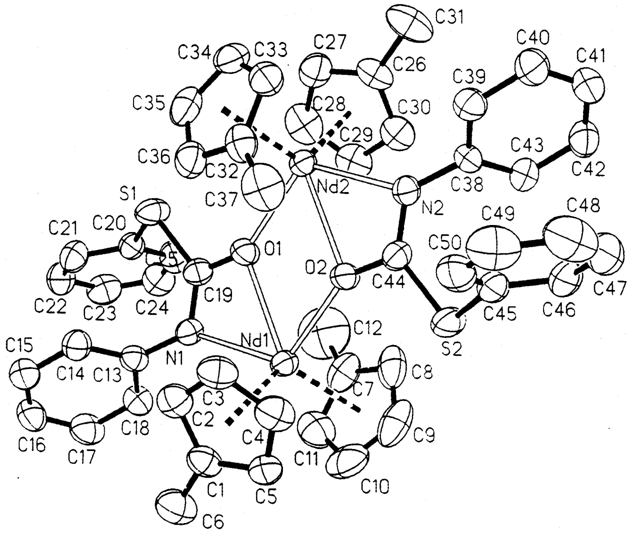

Figure 2. ORTEP diagram of the molecular structure of $[(CH_3C_5H_4)_2Nd]_2[\mu\text{-}\eta^2\text{-}OC(SPh)NPh]_2$ (**2**).

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Å).[18] Nd1−O1 (2.535(5) Å) and Nd2−O2 (2.553(5) Å) fall in the range for typical Nd−O (2.552 Å) donating bond lengths.[19] The Nd−N and Nd−O bond distances can be compared to Sm−N (2.384(7) Å) and Sm−O (2.342(6) Å) distances in the complex $(C_5Me_5)_2Sm[\mu\text{-}\eta^2{:}\eta^1\text{-}(Ph)NN(CO_2)(Ph)]Sm(C_5Me_5)_2(THF)$[20] when the difference between ionic radii for Sm^{3+} and Nd^{3+} is considered.[21] Nd−Cp(centroid) bond lengths range from 2.463 to 2.477 Å and average 2.472 Å, which is comparable to 2.451 Å in the complex $\{NdCp^R{}_2(\mu\text{-}Cl)\}_2$.[22] The data are almost the same in complex **3** (average 2.483 Å). The Nd−Cp(centroid) bond length is fairly close to those in other bis(cyclopentadienyl)neodymium complexes.[23,24]

Complex **3** has a monomer structure. The central metal is coordinated by two $CH_3C_5H_4$ rings, one THF, and S and N atoms from the SC(SPh)NPh ligand which was formed from insertion of the SPh group into the phenyl isothiocyanate moiety. The molecular structure is shown in Figure 3. Selected bond lengths and angles are listed in Table 4. The ring formed by Nd, N, C1, and S1 is nearly planar. The C(1)−N and C(1)−S(1) bond distances, 1.291(5) and 1.716(4) Å, are intermediate between single- and double-bond distances.[16,25] These parameters show that the electrons are delocalized over the N−C−S unit. The Nd−N bond length of 2.534(4) Å is identical with 2.535(8) Å found in complex **2**, which also is intermediate between a normal Nd−N σ bond (2.283 Å)[18] and a donating bond distance (2.682 Å).[19] The bond distance of Nd−S (2.883(3) Å) is somewhat shorter than the average distance (2.9290(13) Å) of complex **1**.

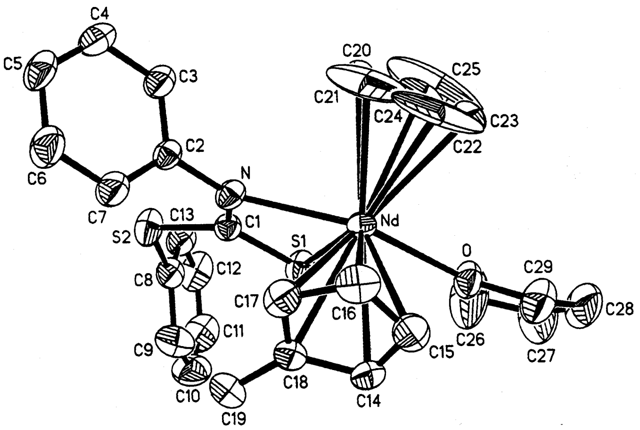

Figure 3. ORTEP diagram of the molecular structure of $(CH_3C_5H_4)_2Nd[\eta^2\text{-}SC(SPh)NPh](THF)$ (**3**).

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 3[a]

Nd−S(1)	2.881	Nd−N	2.534(4)
Nd−C(14)	2.757(4)	Nd−C(15)	2.713(5)
Nd−C(16)	2.730(5)	Nd−C(17)	2.764(5)
Nd−C(18)	2.796(4)	Nd−Cp′(1)	2.484
Nd−Cp′(2)	2.481	S(1)−C(1)	1.716(4)
N−C(1)	1.291(5)		
O−Nd−N	135.02(12)	C(1)−S(1)−Nd	79.7(2)
C(1)−N−Nd	102.3(3)	N−C(1)−S(1)	120.4(4)
Cp′(2)−Nd−S(1)	122.1	Cp′(1)−Nd−S(1)	109.8
Cp′(2)−Nd−N	100.2	Cp′(1)−Nd−N	100.2
Cp′(2)−Nd−O	98.8	Cp′(1)−Nd−O	100.0

[a] Cp′(1) represents the centroid of the C(14)−C(18) ring; Cp′(2) represents the centroid of the C(20)−C(24) ring.

Acknowledgment. We gratefully acknowledge the Chinese National Foundation of Natural Science and the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academia Sinica, for financial support.

Supporting Information Available: Tables of crystal data, atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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