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Journal of Organometallic Chemistry 672 (2003) 94–99

Journal
of Organo
metallic
Chemistrywww.elsevier.com/locate/jorganchem

Insertion of carbodiimide into the Ln–N σ -bond of organolanthanide complexes. Synthesis and characterization of organolanthanide guanidinate complexes (C_5H_5)₂Ln[ⁱPrN=C(NⁱPr)₂–NⁱPr] (Ln = Yb, Dy, Gd)

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Received 28 January 2003; received in revised form 5 March 2003; accepted 6 March 2003

Abstract

The synthesis and structures of three new lanthanide complexes incorporating tetra-substituted guanidinate ligand [ⁱPrN=C(NⁱPr)₂–NⁱPr] are described. Treatment of Cp₂LnNⁱPr₂(–THF) (Ln = Yb, Dy, Gd) with *N,N'*-di-*isopropyl*-carbodiimide results in mono-insertion of carbodiimide into the Ln–N σ -bond to yield Cp₂Ln[ⁱPrN=C(NⁱPr)₂–NⁱPr] (Ln = Yb(1), Dy(2), Gd(3)), providing an efficient method for the synthesis of organolanthanide guanidinate complexes. It was found that an excess of *N,N'*-di-*isopropyl*-carbodiimide did not affect the nature of the final product. Complexes 1–3 were characterized by elemental analysis, IR and mass spectroscopies. Complexes 1 and 2 were determined by the X-ray single crystal diffraction analysis.

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Keywords: Organolanthanide; Insertion; Carbodiimide; Structures; Cyclopentadienyl

1. Introduction

Recently, nitrogen-based anionic ligands receive considerable attention from the desire to mimic the flexibility and remarkable reactivity of metallocene-based systems [1]. For example, the amidinate ligands have been well established as a versatile and flexible ligand system for a potential alternative to cyclopentadienyl-based system in organometallic chemistry [2–6]. Among the important features of these species are the donor ability of the nitrogen centers and the potential to exploit both the steric and electronic effects induced by the variation of organic substituents on the ligand framework. As the isoelectronic analogues of amidinates, guanidinate ligands [RⁱN=C(NR₂)–NRⁱ] also attract recent attention in coordination and organometallic chemistry [7–22]. The investigation results showed that the presence of an additional nitrogen center with

the lone pair of electrons for the guanidinate ligands may provide a potential coordinated site and make the π -conjugated contribution to the NCN moiety, which is a result of the balance of electronic and steric effects, besides possessing the similar versatility and flexibility to amidinate ligands in bonding fashion [23,24]. However, guanidinate ligands have been limitedly explored in organometallic chemistry of rare earths. In fact, only three reports have been found in Group 3 metal and lanthanide chemistry [25–27].

On the other hand, the insertion of an organic functional group into a lanthanide–ligand bond has come increased interest in recent years, since it represents a fundamental step for many lanthanide-promoted transformations and may provide some valuable new methods for synthesis of new organometallic derivatives [28]. The accumulated information in this field indicates that the occurrence of the insertion strongly depends on the degree of steric saturation around the central metal ion and the nature of the ligand. It is noteworthy that although the insertion chemistry of the Ln–N bond has been extensively explored, only one example of insertion

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of carbodiimide into the Ln–N bond is reported to date [26]. Continuing our recent investigations of systems on the insertion chemistry of carbodiimide [29] and to learn more about the guanidinate group as a ligand, we herein report the insertion of carbodiimide into the Ln–N σ -bond of lanthanocene amino complexes, which provides an efficient method for synthesis of organolanthanide guanidinate complexes.

2. Experimental

2.1. Materials and methods

All operations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified argon or nitrogen using standard Schlenk techniques. The solvents of THF, toluene, *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen prior to use. $\text{Cp}_2\text{LnN}^i\text{Pr}_2(\text{THF})$ was prepared from the reaction of Cp_2YbCl with LiN^iPr_2 in 1:1 mole ratio in THF solution at -30°C by a slightly modified literature method [30]. *n*-Butyllithium and *N,N'*-di-isopropyl-carbodiimide were purchased from Aldrich and were used without purification. Elemental analyses for C, H and N were carried out on a Rapid CHN–O analyzer. Infrared spectra were obtained on a NICOLET FT-IR 360 spectrometer with samples prepared as Nujol mulls. Mass spectra were recorded on a Philips HP5989A instrument operating in EI mode. Crystalline samples of the respective complexes were rapidly introduced by the direct inlet techniques with a source temperature of 200°C . The values of *m/z* are referred to the isotopes ^{12}C , ^1H , ^{14}N , ^{157}Gd , ^{163}Dy and ^{174}Yb .

2.2. Synthesis of $\text{Cp}_2\text{Yb}[\text{PrN}=\text{C}(\text{N}^i\text{Pr}_2)=\text{N}^i\text{Pr}]$ (1)

2.2.1. Method A

To a 20 ml THF solution of $\text{Cp}_2\text{YbN}^i\text{Pr}_2(\text{THF})$ (0.324 g, 0.68 mmol), *N,N'*-di-isopropyl-carbodiimide (0.086 g, 0.68 mmol) was slowly dropped at -30°C . After being stirred for 30 min at the low temperature, the mixture solution was warmed to room temperature and the solution color slowly turned from dark green to orange in several hours. After being stirred for 3 h, the solvent was removed under vacuum to give an orange powder. Recrystallization of the powder from the solvent mixture of THF and toluene gave **1** as orange red prismatic crystals. Yield: 0.241 g (67%). Anal. Calc. for $\text{C}_{23}\text{H}_{38}\text{N}_3\text{Yb}$: C, 52.16; H, 7.23; N, 7.93. Found: C, 52.04; H, 7.29; N, 7.94%. IR (Nujol, cm^{-1}): 3165 w, 1631 s, 1301 m, 1232 m, 1160 s, 1118 s, 1050 w, 1013 s, 959 m, 913 w, 888 s, 768 m, 663 s. EIMS: *m/z* [fragment, relative intensity (%)] = 530 (M, 10), 515 (M–CH₃, 13), 465 (M–CpH, 17), 430 (M–N^{*i*}Pr₂, 26), 366 (M–Cp–

N^{*i*}Pr₂, 33), 304 (Cp₂Yb, 37), 226 (L, 85), 184 (L–^{*i*}Pr+H, 17), 127 (L–N^{*i*}Pr₂+H, 21), 100 (N^{*i*}Pr₂, 40), 43 (^{*i*}Pr, 100) [L = (^{*i*}PrN)₂C(N^{*i*}Pr₂)].

2.2.2. Method B

N,N'-Di-isopropyl-carbodiimide (0.102 g, 0.81 mmol) was slowly dropped into a 30 ml toluene solution of $\text{Cp}_2\text{YbN}^i\text{Pr}_2(\text{THF})$ (0.385 g, 0.81 mmol) at -30°C . After being stirred for 30 min at the low temperature, the mixture solution was warmed to room temperature and the solution color quickly turned from dark green to orange in several minutes. After stirred for 1 h, the solvent was removed under vacuum to give an orange powder. Recrystallization of the powder from the solvent mixture of toluene and THF gave **1** as orange crystals. Yield: 0.317 g (74%). The physical, analytical, and spectroscopic properties of the compound were identical with those obtained above.

2.3. Synthesis of $\text{Cp}_2\text{Dy}[\text{PrN}=\text{C}(\text{N}^i\text{Pr}_2)=\text{N}^i\text{Pr}]$ (2)

N,N'-Di-isopropyl-carbodiimide (0.141 g, 1.12 mmol) was slowly dropped to a solution of $\text{Cp}_2\text{DyN}^i\text{Pr}_2(\text{THF})$ (0.521 g, 1.12 mmol) in 30 ml THF at -30°C . After being stirred for 30 min at the low temperature, the reaction mixture was subsequently worked up by the method described above. 0.355 g of yellow prismatic crystals was obtained in 61% yield. Anal. Calc. for $\text{C}_{23}\text{H}_{38}\text{DyN}_3$: C, 53.22; H, 7.38; N, 8.09. Found: C, 53.09; H, 7.33; N, 8.14%. IR (Nujol, cm^{-1}): 3165 w, 1631 s, 1302 m, 1230 m, 1164 s, 1120 s, 1053 w, 1011 s, 965 m, 913 w, 890 s, 767 m, 663 s. EIMS: *m/z* [fragment, relative intensity (%)] = 504 (M–CH₃, 2), 477 (M–^{*i*}Pr+H, 10), 420 (M–N^{*i*}Pr₂, 7), 356 (M–Cp–N^{*i*}Pr₂, 14), 293 (Cp₂Dy, 88), 226 (L, 19), 184 (L–^{*i*}Pr+H, 8), 127 (L–N^{*i*}Pr₂+H, 7), 100 (N^{*i*}Pr₂, 8), 66 (CpH, 100), 43 (^{*i*}Pr, 46) [L = (^{*i*}PrN)₂C(N^{*i*}Pr₂)].

2.4. Synthesis of $\text{Cp}_2\text{Gd}[\text{PrN}=\text{C}(\text{N}^i\text{Pr}_2)=\text{N}^i\text{Pr}]$ (3)

Using the procedure described for **1**, the reaction of *N,N'*-di-isopropyl-carbodiimide (0.117 g, 0.93 mmol) and $\text{Cp}_2\text{GdN}^i\text{Pr}_2(\text{THF})$ (0.425 g, 0.93 mmol) in THF afforded **3** as colorless prismatic crystals. Yield: 0.258 g (54%). Anal. Calc. for $\text{C}_{23}\text{H}_{38}\text{GdN}_3$: C, 53.76; H, 7.45; N, 8.18. Found: C, 53.61; H, 7.38; N, 8.29%. IR (Nujol, cm^{-1}): 3165 w, 1632 s, 1306 m, 1230 m, 1160 s, 1120 s, 1056 w, 1011 s, 976 m, 913 w, 890 s, 764 m, 663 s. EIMS: *m/z* [fragment, relative intensity (%)] = 498 (M–CH₃, 8), 226 (L, 63), 184 (L–^{*i*}Pr+H, 21), 169 (L–^{*i*}Pr–CH₃+H, 27), 155 (L–^{*i*}Pr–CH₂CH₃+H, 33), 142 (L–2^{*i*}Pr+2H, 34), 127 (L–N^{*i*}Pr₂+H, 16), 100 (N^{*i*}Pr₂, 34), 43 (^{*i*}Pr, 100) [L = (^{*i*}PrN)₂C(N^{*i*}Pr₂)].

2.5. X-ray data collection, structure determination and refinement for complexes **1** and **2**

Suitable crystals of complexes **1** and **2** were sealed under argon in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART CCD diffractometer using graphite-monochromated Mo- K_{α} ($\lambda = 0.71073$ Å) radiation. During the collection of the intensity data, no significant decay was observed. For **1**, frames were integrated to the maximum 2θ angle of 52.00° with the Siemens SAINT program to yield a total 10 694 reflections, of which 4605 were independent ($R_{\text{int}} = 0.0354$). For **2**, frames were integrated to the maximum 2θ angle of 52.02° with the Siemens SAINT programme to yield a total 10 753 reflections, of which 4618 were independent ($R_{\text{int}} = 0.0235$). Laue symmetry revealed a monoclinic crystal system and the final unit cell parameters were determined from the full-matrix least-squares on F^2 refinement of three-dimensional centroids of 4605 reflections for **1** and 4618 reflections for **2**. The intensities were corrected for Lp and empirical absorption with SADABS program [31]. A summary of the crystallographic data is given in Table 1.

The structure was solved by the direct method using the SHELXL-97 program [32]. All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in the refinement. Further refinement led to final convergence at $R = 0.0423$ for **1**, and $R = 0.0535$ for **2**. All calculations were performed using the Bruker SMART program.

3. Results and discussion

3.1. Synthesis and characterization of $\text{Cp}_2\text{Ln}[\text{PrN}=\text{C}(\text{N}^i\text{Pr}_2)=\text{N}^i\text{Pr}]$ ($\text{Ln} = \text{Yb}(\mathbf{1}), \text{Dy}(\mathbf{2}), \text{Gd}(\mathbf{3})$)

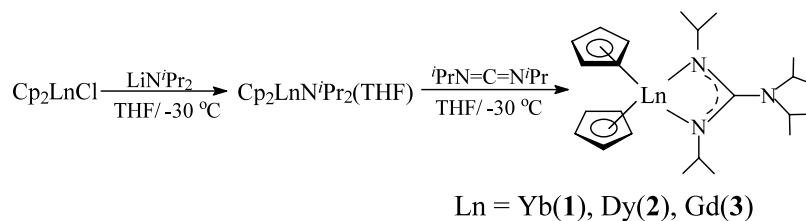
Treatment of $\text{Cp}_2\text{LnN}^i\text{Pr}_2(\text{THF})$ ($\text{Ln} = \text{Yb}, \text{Dy}, \text{Gd}$) with N,N' -di-*isopropyl*-carbodiimide under mild conditions gave guanidinate complexes $\text{Cp}_2\text{Ln}[\text{PrN}=\text{C}(\text{N}^i\text{Pr}_2)=\text{N}^i\text{Pr}]$ ($\text{Ln} = \text{Yb}(\mathbf{1}), \text{Dy}(\mathbf{2}), \text{Gd}(\mathbf{3})$), indicating that one carbodiimide molecule is inserted into the Ln–N σ -bond of $\text{Cp}_2\text{LnN}^i\text{Pr}_2(\text{THF})$ (Scheme 1). The reaction rate significantly depends on the nature of solvents. For example, the change of the solution color from dark green to orange indicated that for **1** the reaction needs several hours in THF, but only several minutes in toluene. This demonstrates that carbodiimide is possibly activated by coordinating to the Lewis acidic Yb^{3+} ion, and is then attacked by the bound amino ligand to form guanidinate complex via concerted four-centered σ bond metathesis processes [33]. Since the THF molecule can be coordinated to Yb^{3+} ion, which

Table 1
Crystal and data collection parameters of complexes **1** and **2**

	1	2
Empirical formula	$\text{C}_{23}\text{H}_{38}\text{N}_3\text{Yb}$	$\text{C}_{23}\text{H}_{38}\text{N}_3\text{Dy}$
Molecular weight	529.60	519.06
Temperature (K)	298(2)	298(2)
Crystal color	Red	Yellow
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/n$
Unit cell dimensions		
a (Å)	8.790(3)	8.769(1)
b (Å)	29.824(10)	29.929(4)
c (Å)	9.517(3)	9.532(1)
β ($^{\circ}$)	108.712(4)	108.324(2)
V (Å ³)	2362.9(13)	2374.5(5)
Z	4	4
D_{calc} (g cm ⁻³)	1.489	1.452
μ (cm ⁻¹)	3.969	3.158
$F(000)$	1068	1052
Crystal dimensions (mm)	$0.30 \times 0.15 \times 0.15$	$0.30 \times 0.15 \times 0.15$
Radiation	Mo- K_{α}	Mo- K_{α}
($\lambda = 0.71073$ Å)		
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
θ Range ($^{\circ}$)	2.36–26.00	2.35–26.01
Index ranges	$-10 \leq h \leq 10,$ $-35 \leq k \leq 36,$ $-11 \leq l \leq 7$	$-10 \leq h \leq 10,$ $-32 \leq k \leq 36,$ $-11 \leq l \leq 11$
Reflections measured	10 694	10 753
Unique reflections	4605 ($R_{\text{int}} = 0.0354$)	4618 ($R_{\text{int}} = 0.0235$)
Completeness to θ	99.2% ($\theta = 26.00$)	98.7% ($\theta = 26.01$)
Max/min transmission	0.5874 and 0.3822	0.6487 and 0.4509
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4605/0/253	4618/0/252
Goodness-of-fit on F^2	1.119	1.166
Final R indices	$R_1 = 0.0423,$ $[I > 2\sigma(I)]$ $wR_2 = 0.0764$	$R_1 = 0.0399,$ $wR_2 = 0.0692$
R indices (all data)	$R_1 = 0.0539,$ $wR_2 = 0.0802$	$R_1 = 0.0535,$ $wR_2 = 0.0723$
Largest difference peak and hole (e Å ⁻³)	1.315 and –0.954	0.819 and –1.837

interferes the interaction of $\text{Cp}_2\text{YbN}^i\text{Pr}_2(\text{THF})$ with carbodiimide, the reaction in toluene took place more rapidly than in THF.

In contrast to phenyl isocyanate insertion into the Ln–N σ bond, where excess PhNCO can be catalyzed to polymer [30], we found that N,N' -di-*isopropyl*-carbodiimide only can mono-insert into the Ln–N σ -bond even in presence of a large excess of carbodiimide with a higher reaction temperature and a longer reaction time, without further subsequent reactions. This might be attributed to the differences of the steric hindrance and the reactivity between PhNCO and N,N' -di-*isopropyl*-carbodiimide. For the more sterically crowding $\text{Cp}_2\text{Ln}[\text{PrN}=\text{C}(\text{N}^i\text{Pr}_2)=\text{N}^i\text{Pr}]$ system, since the inter-



Scheme 1.

action of the second *N,N'*-di-*isopropyl*-carbodiimide molecule with the center metal is prevented by the absence of a free coordination site on complex 1–3 as well as the lower reactivity of *N,N'*-di-*isopropyl*-carbodiimide compared with phenyl isocyanate, no further reaction involved *N,N'*-di-*isopropyl*-carbodiimide was observed.

Complexes 1–3 are air- and moisture-sensitive. They are readily dissolved in THF and toluene, but are sparingly soluble in *n*-hexane. All these complexes were characterized by elemental analysis, IR and mass spectroscopies, which were in good agreement with the proposed structure. In the mass spectra, complexes 1–3 are characterized by the readily loss of the methyl group from the molecule ions. In the IR spectra, the characterized absorption at ca. 2100 cm⁻¹ for the $\nu_{\text{as}}(\text{N}=\text{C}=\text{N})$ stretch of free carbodiimide is absent, but a new strong band at ca. 1630 cm⁻¹ attributable to the delocalized $-\text{N}=\text{C}=\text{N}-$ stretching mode is present [34].

3.2. Description of crystal structures of 1 and 2

Complex 1 and 2 crystallize from the solvent mixture of tetrahydrofuran and toluene at -20 °C in monoclinic system, space group *P2*₁/*n* for 1 and 2. The molecular structures of 1 and 2 are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are given in Tables 2 and 3, respectively. The X-ray structure

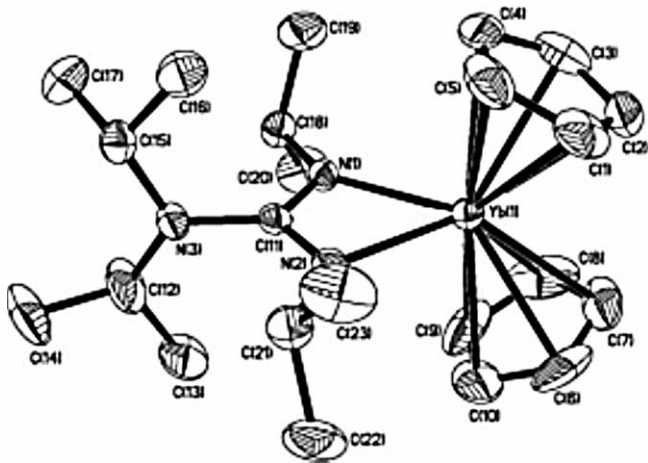


Fig. 1. ORTEP diagram of Cp₂Yb[ⁱPrN=C(NⁱPr₂)=NⁱPr] (1) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms omitted for clarity.

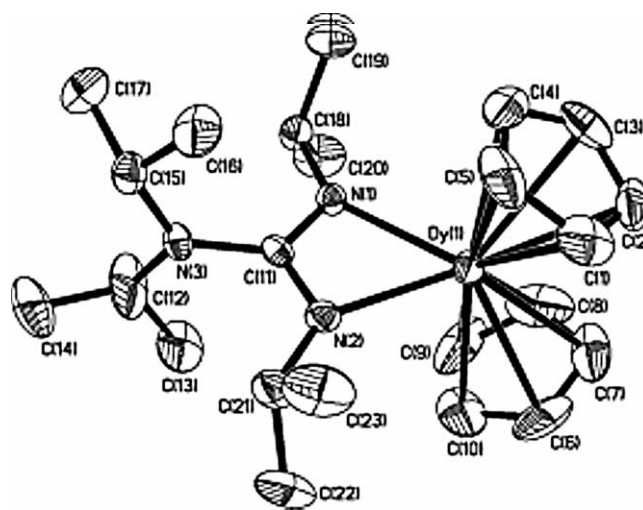


Fig. 2. ORTEP diagram of Cp₂Dy[ⁱPrN=C(NⁱPr₂)=NⁱPr] (2) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms omitted for clarity.

Table 2
Bond lengths (Å) and angles (°) for 1

Bond lengths			
Yb(1)–N(1)	2.278(4)	Yb(1)–C(2)	2.617(7)
Yb(1)–N(2)	2.288(5)	Yb(1)–C(4)	2.619(7)
Yb(1)–C(7)	2.585(8)	N(1)–C(11)	1.337(7)
Yb(1)–C(6)	2.585(8)	N(1)–C(18)	1.459(7)
Yb(1)–C(8)	2.590(8)	N(2)–C(11)	1.329(7)
Yb(1)–C(5)	2.596(7)	N(2)–C(21)	1.466(7)
Yb(1)–C(10)	2.597(8)	N(3)–C(12)	1.415(8)
Yb(1)–C(9)	2.605(8)	N(3)–C(11)	1.427(7)
Yb(1)–C(3)	2.605(7)	N(3)–C(15)	1.473(7)
Yb(1)–C(1)	2.606(7)		
Bond angles			
N(1)–Yb(1)–N(2)	58.73(15)	N(2)–C(11)–N(1)	114.2(5)
C(11)–N(1)–Yb(1)	93.6(3)	N(2)–C(11)–N(3)	122.1(5)
C(11)–N(2)–Yb(1)	93.4(3)	N(1)–C(11)–N(3)	123.7(5)
C(12)–N(3)–C(11)	120.4(5)	N(2)–C(11)–Yb(1)	57.3(3)
C(12)–N(3)–C(15)	120.5(5)	N(1)–C(11)–Yb(1)	56.9(3)
C(11)–N(3)–C(15)	118.5(4)	N(3)–C(11)–Yb(1)	179.0(4)

analysis results show that 1 and 2 are isostructural. Both are solvent-free monomers with the lanthanide atom bonded to two η⁵-cyclopentadienyl rings and one chelating guanidinate ligand to form a distorted tetrahedron geometry similar to lanthanocene amidinates Cp₂Ln[ⁱBuN=C(ⁱBu)=NⁱBu] (Ln = Er, Y) [29]. The

Table 3
Bond lengths (Å) and angles (°) for **2**

Bond lengths			
Dy(1)–N(1)	2.319(4)	Dy(1)–C(4)	2.650(5)
Dy(1)–N(2)	2.321(4)	Dy(1)–C(3)	2.651(5)
Dy(1)–C(6)	2.622(6)	N(1)–C(11)	1.330(5)
Dy(1)–C(7)	2.625(6)	N(1)–C(18)	1.455(5)
Dy(1)–C(10)	2.628(6)	N(2)–C(11)	1.323(5)
Dy(1)–C(8)	2.632(7)	N(2)–C(21)	1.463(6)
Dy(1)–C(1)	2.639(6)	N(3)–C(12)	1.411(7)
Dy(1)–C(2)	2.641(6)	N(3)–C(11)	1.427(5)
Dy(1)–C(5)	2.645(6)	N(3)–C(15)	1.469(6)
Dy(1)–C(9)	2.646(7)		
Bond angles			
N(1)–Dy(1)–N(2)	57.50(12)	N(2)–C(11)–N(1)	114.6(4)
C(11)–N(1)–Dy(1)	93.9(3)	N(2)–C(11)–N(3)	122.2(4)
C(11)–N(2)–Dy(1)	94.0(3)	N(1)–C(11)–N(3)	123.3(4)
C(12)–N(3)–C(11)	120.2(4)	N(2)–C(11)–Dy(1)	57.3(2)
C(12)–N(3)–C(15)	120.3(4)	N(1)–C(11)–Dy(1)	57.3(2)
C(11)–N(3)–C(15)	119.1(4)	N(3)–C(11)–Dy(1)	178.5(3)

coordination number of the central Ln³⁺ is eight. As expected, the coordinated guanidinate group forms essentially a planar four-membered ring with the lanthanide atom within experimental errors. The bond angles around C(11) are consistent with sp² hybridization. The cent-Ln-cent (cent = the center of cyclopentadienyl ring) plane relative to the LnNCN plane is approximately perpendicular. This disposition is likely the result of steric interactions between bulky isopropyl groups and two cyclopentadienyl ligands.

In **1**, the C(11)–N(1) and C(11)–N(2) distances of the guanidinate group are approximately equivalent and significantly shorter than the C–N single bond distances, indicating that the π -electrons of the C=N double bond in the present structure are delocalized over the N–C–N unit [35]. Consistent with this observation, the Yb–N(1) and Yb–N(2) distances, 2.278(4) and 2.288(5) Å, are intermediate between the values observed for the Yb–N single bond distance and the Yb–N donor bond distance (2.19–2.69 Å) [36–39], and are comparable to the corresponding values found in [(C₅H₄Me)Yb(PzMe₂)(OSiMe₂PzMe₂)₂] (Yb–Nav = 2.293(6) Å) [37] and {CyNC[N(SiMe₃)₂]NCy}₂YbN(SiMe₃)₂ (Yb–Nav = 2.317(13) Å) [25].

Characteristically, the dihedral angle formed by the planar NⁱPr₂ function and the YbNCN plane of 87.96° militates against the π -overlap between these two moieties. The nearly perpendicular disposition results likely from the steric interaction between these isopropyl groups. Consistent with this, the C(11)–N(3) bond length of 1.427(7) Å in **1** is originally a single bond, rather than in the range of the conjugated C–N system. In fact, this orientation of the bulky NⁱPr₂ effectively adds a third dimension to the steric bulk of the essentially planar guanidinate ligand. The Yb–C(Cp) distances range from 2.585(8) to 2.619(7) Å, and are in

the normal ranges observed for lanthanocene complexes. The average Yb–C(Cp) distance of 2.601(7) Å is similar to those found in other Cp₂Yb-containing compounds, such as (C₅H₅)₂Yb(PzMe₂)(HPzMe₂), 2.62(1) Å [39]; [(C₅H₅)₂Yb(OCMe=C=CHMe)₂], 2.63(1) Å [40]; (C₅H₅)₂Yb(CH₃)(THF), 2.60(2) Å [41].

The structural parameters of **2** (Table 3) are very similar to those found in complex **1**. The complex has no unusual distances or angles in the Cp₂Dy unit. The Dy–C(Cp) distances range from 2.622(6) to 2.651(5) Å. The average value of 2.638(5) Å is similar to those found in other Cp₂Dy-containing compounds, such as [Cp₂Dy(OCMe=CHMe)₂], 2.668(6) Å [42] and [MeCpDy(η^2 -PzMe₂)(μ -OSiMe₂PzMe₂)₂], 2.684(16) Å [43]. The Dy–N distances of 2.319(4) and 2.321(4) Å are similar to the corresponding distances in complex **1**, when the difference in the metal ionic radii is considered [44].

4. Conclusions

We have demonstrated that lanthanocene amino derivatives exhibit high activity toward carbodiimide. Carbodiimide inserts readily into the Ln–N σ bonds of organolanthanide amides Cp₂LnNⁱPr₂(THF) under mild conditions, which provides a new way to the synthesis of lanthanide guanidinate complexes. It was found that an excess carbodiimide does not affect the nature of the final complexes, a single insertion only being observed. It seemed that the reaction in toluene took place more rapidly than in THF.

5. Supplemental material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 202428 and 202429 for compounds **1** and **2**, respectively. 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>).

Acknowledgements

We thank the National Natural Science Foundation of China and the Research Funds of Excellent Young Teacher and the New Century Distinguished Scientist of National Education Ministry of China for financial support.

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