Insertion of a Carbodiimide into the Ln–N σ -Bond of **Organolanthanide Complexes.** Isomerization and **Rearrangement of Organolanthanides Containing Guanidinate Ligands**

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Received February 24, 2004

The reaction of (C_5H_5) YCl₂(THF)₃ with LiN/Pr₂ and subsequently with 2 equiv of N,Ndiisopropylcarbodiimide (PrN=C=NPr) in THF gave the organoyttrium guanidinates $Y[PrNC(N'Pr_2)N'Pr]_3$ (1) and $(C_5H_5)_2Y[PrNC(N'Pr_2)N'Pr]$ (2), which may be rationalized by the rearrangement reaction of the diinsertion product $(C_5H_5)Y[/PrNC(N/Pr_2)N/Pr]_2$. Treatment of PrN=C=NPr with lanthanocene primary amides $[(C_5H_5)_2LnNHR]_2$ (R = 'Bu, Ln = Yb, Er, Dy, Y; R = Ph, Ln = Yb) gave the unexpected products $(C_5H_5)_2Yb[RNC(NH'Pr)N'Pr]$ (R = 'Bu, Ln = Yb (3), Er (4), Dy (5), Y(6); R = Ph, Ln = Yb (7)), indicating that a novel isomerization reaction involving a 1,3-hydrogen shift takes place along with the insertion of carbodiimide into the Ln-N σ -bond, which provides an efficient synthesis of organolanthanide complexes with asymmetrical guanidinate ligands. All these complexes were characterized by elemental analysis and spectroscopic properties. The structures of complexes 1-5 and 7 were also determined by X-ray diffraction analysis.

Introduction

Guanidinate anions have recently received considerable attention as supporting ligands in organometallic chemistry, due to their steric and electronic tunability¹⁻⁵ and their potential as alternatives to the cyclopentadienvl group with a view to the modification of alkene and polar monomer polymerization catalysts.⁶ In principle, each of the three nitrogen atoms of the guanidinate ligand is capable of acting as a coordination site, and the bonding modes are flexible. Despite these attractive

features, studies on the reactivities of complexes possessing guanidinate ligands are still relatively limited. To our knowledge, the fluxional behaviors for the guanidinates are rarely observed,7 and the intraguanidinate hydrogen shift has yet not been reported.

On the other hand, in contrast to the extensive chemistry of bis(cyclopentadienyl)lanthanide amido complexes, little is known about the behavior of mono-(cyclopentadienyl)lanthanide bis(amido) complexes, especially for the analogous insertion reactions.^{8,9} We have previously reported the insertion of carbodiimide into the Ln-N bond of organolanthanide secondary amido complexes, which provides an efficient synthesis for organolanthanide guanidinates.^{10,11} To better understand the influence of the amido ligand and to further develop the insertion reaction, in this work we present an extension of this reaction to lanthanocene primary amido complexes, by which a novel guanidinate isomerization involving 1,3-hydrogen shift was established, yielding the first organolanthanide complexes with

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asymmetrical guanidinate ligands. Furthermore, we also studied the reaction of organolanthanide bis(amido) complexes with carbodiimide, which led to the formation of a homoleptic tris(guanidinate) lanthanide complex.

Experimental Section

General Procedure. 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 THF, toluene, and *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. (C₅H₅)YCl₂(THF)₃,^{12a} (C5H5)Y(N/Pr2)2,12b [(C5H5)2LnNH/Bu]2, and [(C5H5)2YbNHPh]212c were prepared by slightly modified literature methods. N,N-Diisopropylcarbodiimide was purchased from Aldrich and was used without purification. Melting points were determined in a sealed nitrogen-filled capillary and are uncorrected. 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/zrefer to the isotopes ¹²C, ¹H, ¹⁴N, ⁸⁹Y, ¹⁶⁴Dy, ¹⁶⁶Er, and ¹⁷⁴Yb. ¹H NMR data were obtained on a Bruker DMX-500 NMR spectrometer and were referenced to residual aryl protons in C_6H_6 (δ 7.16).

Synthesis of Y[ⁱPrNC(NⁱPr₂)NⁱPr]₃ (1) and (C₅H₅)₂Y- $[PrNC(NPr_2)NPr_3]$ (2). To a solution of $(C_5H_5)YCl_2(THF)_3$ (0.862 g, 1.95 mmol) in 30 mL of THF was added LiN/Pr2 (0.418 g, 3.90 mmol) at -30 °C. After it was stirred at this temperature for 3 h, the mixture was warmed to room temperature and was stirred for 12 h. Then, the solution was cooled to -30°C and treated with N,N-diisopropylcarbodiimide (0.492 g, 3.90 mmol). After it was stirred for 3 h at -30 °C, the reaction mixture was slowly warmed to ambient temperature and was further stirred for 24 h. Removal of the solvent left a pale yellow solid. The resulting solid was extracted with 30 mL of toluene. The extract was evaporated to ca. 5 mL. Pale yellow crystals of 1 were slowly formed at room temperature. Yield: 0.539 g (36%). Mp: 194 °C dec. Anal. Calcd for C₃₉H₈₄N₉Y: C, 60.99; H, 11.02; N, 16.41. Found: C, 60.91; H, 10.95; N, 16.42. ¹H NMR (C₆D₆): 3.57 (m, 12H, CH(CH₃)₂), 1.36 (d, 24H, CH-(CH₃)₂), 1.20 (d, 24H, CH(CH₃)₂), 0.91 (d, 24H, CH(CH₃)₂). IR (Nujol, cm⁻¹): 3175 w, 1631 s, 1160 w, 1301 m, 1222 m, 1160 s, 1118 s, 1056 m, 1019 w, 974 m, 913 w, 859 s, 822 w, 768 w, 681 w, 665 s. EI-MS (m/z (fragment, relative intensity (%)): 226 (L, 17), 184 (L - ^{*i*}Pr+H, 100), 127 (L - N^{*i*}Pr₂, 14), 100 $(N^{i}Pr_{2}, 31), 43 ({}^{i}Pr, 98) (L = {}^{i}PrNC(N^{i}Pr_{2})N^{i}Pr).$

Further crystallization by diffusion of *n*-hexane into the mother liquor yielded pale yellow crystals of **2**, which were isolated by filtration followed by a subsequent washing with a minimal amount of a mixture of THF and *n*-hexane. Yield: 0.269 g (31%). Mp: 158 °C dec. Anal. Calcd for $C_{23}H_{38}N_3Y$: C, 62.01; H, 8.60; N, 9.43. Found: C, 61.89; H, 8.65; N, 9.48. ¹H NMR (C_6D_6): δ 6.49 (m, 5H, C_5H_5), 6.29 (m, 5H, C_5H_5), 3.61 (m, 2H, $CH(CH_3)_2$), 3.38 (m, 2H, $CH(CH_3)_2$), 1.31 (d, 12H, $CH(CH_3)_2$), 1.23 (d, 6H, $CH(CH_3)_2$), 0.91 (d, 6H, $CH(CH_3)_2$). IR (Nujol, cm⁻¹): 3166 w, 1631 s, 1157 w, 1305 m, 1231 m, 1155 s, 1122 s, 1051 w, 1014 s, 959 m, 913 w, 890 s, 768 m, 663 s. EI-MS (m/z (fragment, relative intensity (%)): 430 (M – CH₃, 7), 365 (M – Cp – CH₃, 21), 226 (L, 46), 219 (Cp₂Y, 10), 184 (L – Pr + H, 17), 127 (L – $NPr_2, 25$), 100 ($NPr_2, 40$), 66 (L, 58), 43 (Pr, 100) (L = $PrNC(N/Pr_2)N/Pr$).

Synthesis of (C₅H₅)₂Yb['BuNC(NH'Pr)N'Pr] (3). To a 20 mL THF solution of [(C₅H₅)₂YbNH^{*t*}Bu]₂ (0.346 g, 0.46 mmol) was slowly added N,N-diisopropylcarbodiimide (0.116 g, 0.92 mmol) dropwise at -30 °C. After it was stirred for 30 min, the reaction mixture was slowly warmed to ambient temperature and stirred for 12 h. The solution was concentrated and cooled to -20 °C to give an orange powder. Recrystallization of the powder from a mixture of THF and toluene gave 3 as yellow crystals. Yield: 0.249 g (54%). Mp: 144 °C dec. Anal. Calcd for C₂₁H₃₄N₃Yb: C, 50.29; H, 6.83; N, 8.38. Found: C, 50.40; H, 6.95; N, 8.51. ¹H NMR: δ 6.30 (s, 10H), 3.51-3.62 (m, 2H), 2.69 (s, 1H), 0.91-1.42 (m, 21H), 1.10 (s, 9H). IR (Nujol, cm⁻¹): 3448 m, 1649 s, 1529 m, 1304 m, 1171 s, 1130 m, 1013 s, 890 s, 767 s, 701 s, 663 w. EI-MS (m/z (fragment, relative intensity (%)): 502 (M, 17), 436 (M - CpH, 24), 422 $(M - Cp - CH_3, 100), 379 (M - Cp - NH^{2}Pr, 11), 198 (L, 8),$ 142 (L – N^{*i*}Pr + H, 8) (L = ^{*i*}PrNC(NH^{*i*}Pr)N^{*i*}Bu).

Synthesis of $(C_5H_5)_2$ **Er**[**BuNC(NH'Pr)N'Pr**] **(4).** To a 20 mL THF solution of $[(C_5H_5)_2$ ErNH'Bu]_2 (0.429 g, 0.58 mmol) was slowly added *N*,*N*-diisopropylcarbodiimide (0.146 g, 1.16 mmol) dropwise at -30 °C. The reaction mixture was subsequently worked up by the method described above. Pink crystals of **4** were obtained in 67% yield (0.385 g). Mp: 162 °C dec. Anal. Calcd for C₂₁H₃₄N₃Er: C, 50.88; H, 6.91; N, 8.48. Found: C, 50.76; H, 6.98; N, 8.57. IR (Nujol, cm⁻¹): 3449 m, 1649 s, 1531 m, 1301 m, 1169 s, 1131 m, 1009 s, 892 s, 769 s, 702 s, 663 w. EI-MS (*m*/*z* (fragment, relative intensity (%)): 494 (M, 21), 428 (M – CpH, 34), 422 (M – Cp – CH₃, 71), 371 (M – Cp – NH'Pr, 34), 198 (L, 14), 142 (L – N'Pr+H, 10) (L = 'PrNC(NH'Pr)N'Bu).

Synthesis of $(C_5H_5)_2$ **Dy**['**BuNC(NH'Pr)N'Pr]** (5). By the procedure described for **3**, reaction of $[(C_5H_5)_2$ DyNH'Bu]₂ (0.314 g, 0.43 mmol) with *N*,*N*-diisopropylcarbodiimide (0.109 g, 0.86 mmol) gave **5** as pale yellow crystals. Yield: 0.321 g (76%). Mp: 168 °C dec. Anal. Calcd for C₂₁H₃₄N₃Dy: C, 51.37; H, 6.98; N, 8.56. Found: C, 51.20; H, 7.04; N, 8.73. IR (Nujol, cm⁻¹): 3443 m, 1649 s, 1530 m, 1301 m, 1169 s, 1130 m, 1009 s, 890 s, 765 s, 703 s, 663 w. EI-MS (*m*/*z* (fragment, relative intensity (%)): 491 (M, 13), 425 (M - CpH, 21), 411 (M - Cp - CH₃, 86), 368 (M - Cp - NH'Pr, 27), 198 (L, 17), 142 (L - N'Pr + H, 22) (L = 'PrNC(NH'Pr)N'Bu).

Synthesis of $(C_5H_5)_2$ **Y**['**BuNC(NH'Pr)N'Pr**] **(6).** By the procedure described for **3**, reaction of $[(C_5H_5)_2$ YNH'Bu]₂ (0.284 g, 0.49 mmol) with *N*,*N*-diisopropylcarbodiimide (0.124 g, 0.98 mmol) gave **6** as colorless crystals. Yield: 0.288 g (71%). Mp: 155 °C dec. Anal. Calcd for C₂₁H₃₄N₃Y: C, 60.42; H, 8.21; N, 10.07. Found: C, 60.29; H, 8.17; N, 10.19. ¹H NMR: δ 6.28 (s, 10H), 3.68 (s, 1H), 3.43–3.48 (m, 2H), 1.45–1.67 (m, 12H), 1.10 (s, 9H). IR (Nujol, cm⁻¹): 3445 m, 1649 s, 1528 m, 1303 m, 1170 s, 1130 m, 1011 s, 889 s, 765 s, 701 s, 661 w. EI-MS (*m*/*z* (fragment, relative intensity (%)): 417 (M, 31), 436 (M – CpH, 43), 422 (M – Cp – CH₃, 100), 379 (M – Cp – NH'Pr, 24), 198 (L, 8), 142 (L – N'Pr + H, 10) (L = 'PrNC(NH'Pr)N'Bu).

Synthesis of $(C_5H_5)_2$ **Yb**[**PhNC(NH'Pr)N'Pr**] **(7).** By the procedure described for **3**, reaction of $[(C_5H_5)_2$ YbNHPh]₂ (0.498 g, 0.63 mmol) with *N*,*N*-diisopropylcarbodiimide (0.159 g, 1.26 mmol) gave **7** as orange crystals. Yield: 0.453 g (69%). Mp: 176 °C dec. Anal. Calcd for $C_{23}H_{30}N_3$ Yb: C, 52.97; H, 5.80; N, 8.06. Found: C, 52.84; H, 5.81; N, 8.13. IR (Nujol, cm⁻¹): 3381 m, 1641 m, 1591 s, 1567 m, 1301 m, 1162 s, 1010 s, 963 m, 889 s, 771 s, 695 s, 663 w. EI-MS (*m*/*z* (fragment, relative intensity (%)): 522 (M, 55), 457 (M – Cp, 58), 399 (M – Cp – NH'Pr, 61), 218 (L', 54), 161 (L' – N'Pr, 10), 119 (L' – N'Pr – 'Pr + H, 51) (L' = 'PrNC(NH'Pr)NPh).

X-ray Data Collection, Structure Determination, and Refinement. Suitable single crystals of complexes 1-5 and 7 were sealed under argon in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphitemonochromated Mo K α ($\lambda = 0.710$ 73 Å) radiation. During the intensity data collection, no significant decay was observed.

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	2	3	4	5	7
formula	C ₂₃ H ₃₈ N ₃ Y	C ₂₁ H ₃₄ N ₃ Yb	C ₂₁ H ₃₄ N ₃ Er	C ₂₁ H ₃₄ N ₃ Dy	C ₂₃ H ₃₀ N ₃ Yb
mol wt	445.47	501.55	495.77	491.01	521.54
cryst color	colorless	red	pink	yellow	red
cryst dimens (mm)	$0.50 \times 0.20 \times 0.10$	$0.45 \times 0.40 \times 0.05$	$0.10 \times 0.10 \times 0.20$	0.10 imes 0.20 imes 0.30	$0.20\times0.10\times0.05$
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/n$	Pbac	Pbac	Pbac	$P2_1$
unit cell dimens					
a (Å)	8.803(4)	11.068(7)	11.058(5)	11.145(4)	9.0720(14)
b (Å)	30.028(12)	15.049(9)	15.086(7)	15.116(6)	8.4415(13)
c (Å)	9.573(4)	26.599(16)	26.498(12)	26.522(10)	14.682(2)
β (deg)	108.416(5)				98.600(2)
$V(Å^3)$	2401.0(16)	4430(5)	4420(3)	4468(3)	1111.8(3)
Z	4	8	8	8	2
$D_{\rm c} ({\rm g} .{\rm cm}^{-3})$	1.232	1.504	1.490	1.640	1.558
$\mu (\mathrm{mm}^{-1})$	2.440	4.229	3.804	3.352	4.217
F(000)	944	2008	1992	1976	518
radiation		Ν	Io Ka ($\lambda = 0.710~730$)	Å)	
temp (K)	293.2	298.2	293.2	298.2	298.2
scan type	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
θ range (deg)	2.34 - 25.00	2.39-26.01	1.54 - 25.01	1.54 - 25.01	1.40 - 26.01
h.k.l range	$-10 \le h \le 10$	$-13 \le h \le 12$	$-12 \le h \le 13$	$-10 \le h \le 13$	$-11 \le h \le 10$
	$-27 \le k \le 35$	$-18 \le k \le 18$	$-17 \le k \le 17$	$-17 \le k \le 16$	$-10 \le k \le 10$
	$-11 \le l \le 10$	$-15 \le l \le 32$	$-31 \le l \le 14$	$-31 \le l \le 31$	$-18 \le l \le 16$
no. of rflns measd	10 006	16 294	17 287	17 487	5134
no. of unique rflns	$4222 (R_{int} =$	$4350 (R_{int} =$	$3892 (R_{int} =$	$3935 (R_{int} =$	$3876 (R_{int} =$
not of anique times	0.0458)	0.0380)	0.0372)	0.0317)	0.0300)
completeness to θ . %	$99.3\% (\theta = 25.00)$	$99.6\% (\theta = 26.01)$	$100\% (\theta = 25.01)$	$100\% (\theta = 25.01)$	$99.5\% (\theta = 26.01)$
max and min transmissn	0.7924 and 0.3750	0.8164 and 0.2520	none	none	0.8168 and 0.4859
refinement method		full-	matrix least squares of	r_{F^2}	
no. of data/restraints/params	4222/0/252	4350/1/238	3892/0/227	3935/0/233	3876/1/248
goodness of fit on F^2	1.014	0.955	1.102	1.114	0.993
final <i>R</i> indices $(I > 2\sigma(I))$	11011	01000	11108		01000
R1	0.0495	0.0282	0.0359	0.0294	0.0356
wR2	0.0987	0.0623	0.0730	0.0640	0.0823
R indices (all data)	0.0007	0.0020	0.0700	0.0010	0.0020
R1	0.0820	0 0427	0 0464	0 0428	0 0397
wR2	0 1065	0.0659	0.0782	0.0693	0.0847
largest diff peak and	0.273 and -0.390	0.984 and -1.211	1.105 and -1.377	0.629 and -0.890	1179 and -0717
hole (e $Å^{-3}$)	0.270 4114 0.000	0.001 unu 1.211	1.100 unu 1.077	0.000 unu 0.000	1.170 unu 0.717

 Table 1. Crystal and Data Collection Parameters of Complexes 2–5 and 7

The intensities were corrected for Lorentz–polarization effects and empirical absorption with the SADABS program.¹³ The structures were solved by direct methods using the SHELXL-97 program.¹⁴ The absolute configuration of complex **7** was established by anomalous dispersion effects in diffraction measurements on the crystal. 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. All calculations were performed using the Bruker Smart program. A summary of the crystallographic data and selected experimental information are given in Table 1.

Y[^{*i*}**PrNC(N**^{*i*}**Pr**₂)**N**^{*i*}**Pr**]₃ (1). The data on crystals of 1 were sufficient to provide atom connectivity but not high-precision metrical information, due to the poor quality of data collected. Cell constants for the triclinic system at 293(2) K are as follows: a = 13.302(5) Å, b = 13.375(5) Å, c = 17.960(6) Å, $\alpha = 105.460(5)^{\circ}$, $\beta = 92.172(5)^{\circ}$, $\gamma = 119.811(4)^{\circ}$; V = 2616.1-(16) Å³, Z = 2; $D_c = 0.868$ g cm⁻³.

Results and Discussion

Reaction of $(C_5H_5)Y(N^{i}Pr_2)_2$ **with** *N*,*N*-**Diisopropylcarbodiimide.** To gain more insight into the insertion of carbodiimide into the Ln–N bond, the reaction of *N*,*N*-diisopropylcarbodiimide with $(C_5H_5)Y(N^{i}Pr_2)_2$ -

Scheme 1

(C_5H_5) YCl ₂ (THF) ₃ $\frac{1) 2 \text{ Lin'Pr}_2, \text{ THF/ -30 °C}}{2) 2 'PrN=C=N'Pr, -30 °C}$	$(C_5H_5)Y[^{i}PrNC(N^{i}Pr_2)N^{i}Pr]_2$
	r. t. ▼
$Y[^{i}PrNC(N^{i}Pr_{2})N^{i}Pr]_{3} +$	(C ₅ H ₅) ₂ Y[^{<i>i</i>} PrNC(N ^{<i>i</i>} Pr ₂)N ^{<i>i</i>} Pr]
(1)	(2)

 $(THF)_n$ was studied. It was found that the reaction of $(C_5H_5)YCl_2(THF)_3$ with LiN^{*i*}Pr₂ and subsequently with 2 equiv of N,N-diisopropylcarbodiimide (ⁱPrN=C=Nⁱ-Pr) in THF gave $Y[^{i}PrNC(N^{i}Pr_{2}) N^{i}Pr]_{3}$ (1) and $(C_{5}H_{5})_{2}Y$ - $[^{i}PrNC(N^{i}Pr_{2})N^{i}Pr]$ (2). Presumably, complexes 1 and **2** could result from the rearrangement of the diinsertion product CpY['PrNC(N'Pr2)N'Pr]2, as shown in Scheme 1. However, attempts to isolate the intermediate CpY-[^{*i*}PrNC(N^{*i*}Pr₂)N^{*i*}Pr]₂ were unsuccessful. The reactions of bis- or poly(amido) metal complexes with carbodiimides have been studied extensively,¹⁵ but multipleinsertion products are observed in only a few cases. For example, only one of the M-N bonds is reactive to carbodiimide, even under more drastic conditions for $M(NMe_2)_5$ (M = Ta, Nb).¹⁶ The present observation might be attributed to two favorable factors: (i) the presence of a vacant coordination site at the larger lanthanide metal center satisfies the need for coordina-

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tion of the carbodiimide molecule to precede insertion; (ii) the stronger ionic characteristics of the Ln–N σ bond enhance the migratory aptitude of the amino ligands. To our knowledge, few homoleptic tris(guanidinate) metal complexes have been reported in the literature, and all these compounds have been prepared by metathesis reactions. 6e,22

Syntheses and Characterizations of $(C_5H_5)_2$ Yb-[RNC(NHⁱPr)NⁱPr] (R = 'Bu, Ln = Yb (3), Er (4), Dy (5), Y (6); R = Ph, Ln = Yb (7)). Lanthanocene primary amido complexes $[(C_5H_5)_2LnNHR]_2$ were allowed to react with 'PrN=C=N'Pr to give the unexpected products $(C_5H_5)_2$ Yb[RNC(NHⁱPr)NⁱPr] (R = 'Bu, Ln = Yb (3), Er (4), Dy (5), Y (6); R = Ph, Ln = Yb (7)) (Scheme 2).

Significantly, in contrast to the observation of symmetrical coordinated guanidinate complexes in other insertions of carbodiimides into the lanthanide-nitrogen bonds, $^{10-11,15}$ reactions of $[(C_5H_5)_2LnNHR]_2$ with i -PrN=C=N/Pr gave the asymmetrically coordinated guanidinate complexes (C5H5)2Ln[RNC(NH'Pr)N'Pr] (R $= {}^{t}Bu$, Ln = Yb (3), Er (4), Dy (5), Y (6); R = Ph, Ln = Yb (7)). The formation of complexes 3-7 suggests that a novel isomerization involving a 1,3-hydrogen shift takes place along with the insertion of carbodiimide into the Ln-N bond. To our knowledge, although guanidinate complexes have been extensively studied, only one example of the guanidinate rearrangement from symmetrical to asymmetrical coordination has been reported to date.^{7a} A 1,3-hydrogen internal shift of guanidinate ligands has not observed before. This may give a new insight into the fluxionality of guanidinate ligands.

Two possible pathways for the formation of these complexes are depicted in Scheme 1. Pathway A involves 1,3-migration of the NHR group to the carbon atom of coordinated carbodiimide to form the intermediate I, analogous to the reactivity of lanthanocene secondary amido derivatives with carbodiimide,¹⁰ followed by tautomerization to the title compounds. The alternative pathway, B, involves intramolecular coupling, followed by 1,3-hydrogen migration. Insertion of carbodiimide into a Ln–N bond has been observed before, and the tautomerization of the initial product of the carbodiimide insertion, via a formal 1,3-hydrogen shift, bears some resemblance to the rearrangement that follows insertion of acetonitrile into the Sc–N bond.¹⁷ Thus, pathway A may be more plausible.

All of these complexes are air- and moisture-sensitive. They dissolve readily in THF and toluene but are sparingly soluble in *n*-hexane. They have been charac-





Figure 1. ORTEP diagram of **2** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Table 2. Bond Lengths (Å	and Angles (deg) for 2
--------------------------	------------------------

Y(1)-N(2)	2.316(3)	Y(1)-C(6)	2.654(5)
Y(1) - N(1)	2.321(3)	Y(1) - C(10)	2.657(5)
Y(1)-C(3)	2.618(5)	N(1)-C(11)	1.326(4)
Y(1) - C(2)	2.628(5)	N(1)-C(12)	1.464(5)
Y(1) - C(4)	2.638(6)	N(2) - C(11)	1.340(4)
Y(1) - C(9)	2.639(5)	N(2)-C(15)	1.464(5)
Y(1) - C(7)	2.640(5)	N(3)-C(21)	1.419(6)
Y(1) - C(8)	2.641(5)	N(3)-C(11)	1.421(5)
Y(1) - C(1)	2.643(5)	N(3)-C(18)	1.481(5)
Y(1)-C(5)	2.646(6)		
N(2) - Y(1) - N(1)	57 70(10)	N(1) - C(11) - N(2)	114 1(3)
C(11) - N(1) - C(12)	123 1(3)	N(1) - C(11) - N(3)	122 6(3)
C(11) - N(1) - V(1)	94 2(2)	N(2) - C(11) - N(3)	123 3(3)
C(11) - N(2) - Y(1)	94.0(2)	N(1) - C(11) - Y(1)	57 17(19)
C(21) - N(3) - C(11)	120.5(2)	N(2) - C(11) - V(1)	56 96(19)
C(11) - N(3) - C(18)	119 2(3)	N(3) - C(11) - Y(1)	178 4(2)
0(11) 11(0) 0(10)	110.~(0)		170.4(2)

terized by elemental analysis and spectroscopic methods. In the mass spectra, all complexes exhibit the molecule ion peak, and complexes **3**–**7** are also characterized by the easy loss of the cyclopentadienyl and the NH/Pr groups. Complexes **1**–**7** show a characteristic IR absorption band at 1630–1650 cm⁻¹ attributable to the $-N \cdot \cdot \cdot C \cdot \cdot \cdot N$ – stretching model.¹⁸ Although the crystal structure analysis indicates that the guanidinate ligands of compounds **3**–**5** and **7** are bonded to the lanthanide ions by an asymmetric mode in the solid state, it should be noted that complex **6** did not exhibit two doublets for the 'Pr groups in the ¹H NMR, which may suggest that compounds **3**–**7** are fluxional in solution. The structures of **1**–**5** and **7** were also determined by X-ray single-crystal diffraction analysis.

Crystal Structures of Complexes 1–5 and 7. The X-ray structural analysis results show that the overall structure of **2** (Figure 1, Table 2) is similar to that of the complex $(C_5H_5)_2Ln['PrNC(N'Pr_2) N'Pr]$ (Ln = Yb, Dy).¹⁰ The Y³⁺ ion is bonded to two η^5 -C₅H₅ groups and one η^2 -guanidinate ligand. The YNCN unit is coplanar. The coordination number of the Y atom is 8. The complex has no unusual distances or angles in the $(C_5H_5)_2$ Y unit. The Y–C(C₅H₅) distances range from 2.624(9) to 2.667(9) Å. The average value of 2.653(2) Å is similar to those found in other trivalent lanthanide complexes, such as $[(C_5H_5)_2Y(\mu-CH_3)]_2$ (2.66(2) Å)^{19a} and

Organolanthanides Containing Guanidinate Ligands



Figure 2. ORTEP diagram of 1 with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

 $[(C_5H_5)_2Y(\mu-Me)_2AIMe_2]$ (2.62(4) Å).^{19b} The Y-N distances of 2.280(4) and 2.282(5) Å are in the range expected for a Y-N bond interaction with partial singleand donor-bond character.²⁰ The average Y-N distance of 2.281(5) Å is comparable to the corresponding distance in organolanthanide guanidinates (C5H5)2Ln- $[{}^{i}PrNC(N{}^{i}Pr_{2})N{}^{i}Pr]$ (Ln = Yb, Dy), when the difference in the metal ionic radii is considered.²¹

Unfortunately, the quality of the crystallographic data for **1** is poor, with the value of *R* being on the high side (R1 = 0.1252, wR2 = 0.3201). The bond distances and bond angles for 1 cannot be discussed, therefore. However, the overall structure of 1 was clearly determined, as shown in Figure 2. Complex 1 is a solvent-free monomer with the ytterbium atom bonded to three chelating guanidinate ligands to form a distortedoctahedral geometry, which is similar to those of Nd-['PrNC(N'Pr_2)N'Pr]_3 6e and Ru[η^2 -(NPh)_2CNHPh]_3.^{22} The coordination number of Y^{3+} is 6.

The molecular structure of **3** is shown in Figure 3. Selected bond lengths and angles of 3 are listed in Table 3. The X-ray crystal analysis results show that the primary amino group in **3** has combined with N,Ndiisopropylcarbodiimide, forming a four-membered heterometallacycle. In contrast to the behavior observed for the guanidinate rearrangement of {[Me₂NC(Nⁱ- $Pr_{2}_{2}TiO_{2}^{7a}$ where the asymmetric guanidinate ligand shows a localized bonding situation, 3 exhibits delocalized bonding throughout the N₃C guanidinate core. The planarity of the YbN₂C ring and nearly equivalent C(11)-N(1) and C(11)-N(2) (1.333(5) and 1.343(5) Å, respectively) and Yb(1)-N(1) and Yb(1)-N(2) (2.256(3)

Parsons, S. Dalton 2000, 1887.



Figure 3. ORTEP diagrams of **3** (Ln = Yb), **4** (Ln = Er), and **5** (Ln = Dy) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Table 3.	Bond Lengths (A) and	Angles	(deg)	for
	3-5	í			

	3 (Ln = Yb)	4 (Ln = Er)	5 (Ln = Dy)
Ln(1)-N(2)	2.252(3)	2.252(5)	2.295(4)
Ln(1) - N(1)	2.256(3)	2.254(5)	2.304(4)
Ln(1)-C(9)	2.590(5)	2.586(8)	2.639(6)
Ln(1) - C(3)	2.601(5)	2.604(8)	2.648(6)
Ln(1) - C(5)	2.603(5)	2.604(8)	2.648(6)
Ln(1) - C(10)	2.603(6)	2.605(8)	2.650(6)
Ln(1) - C(7)	2.611(5)	2.609(8)	2.654(5)
Ln(1) - C(8)	2.613(5)	2.610(8)	2.656(6)
Ln(1)-C(1)	2.616(5)	2.612(8)	2.661(6)
Ln(1)-C(4)	2.617(5)	2.610(8)	2.663(6)
Ln(1) - C(6)	2.617(5)	2.616(8)	2.666(6)
Ln(1) - C(2)	2.617(5)	2.638(7)	2.667(6)
N(1)-C(11)	1.333(5)	1.342(7)	1.337(5)
N(2)-C(11)	1.344(5)	1.337(7)	1.326(5)
N(3)-C(11)	1.378(5)	1.379(7)	1.378(6)
N(2)-Ln(1)-N(1)	58.98(11)	59.18(17)	57.70(12)
C(11)-N(1)-Ln(1)	94.5(2)	94.0(3)	94.3(3)
C(11) - N(2) - Ln(1)	94.4(2)	94.3(3)	95.0(3)
N(1)-C(11)-N(2)	112.0(3)	112.3(5)	112.9(4)
N(1)-C(11)-N(3)	124.2(4)	125.0(5)	124.2(4)
N(2) - C(11) - N(3)	123.8(4)	122.7(5)	122.9(4)
N(1)-C(11)-Ln(1)	56.1(2)	56.3(3)	56.7(2)
N(2)-C(11)-Ln(1)	55.99(19)	56.2(3)	56.3(2)
N(3)-C(11)-Ln(1)	178.3(3)	177.2(4)	176.9(3)

and 2.252(3) Å, respectively) bond lengths suggest the existence of a resonance stabilization in the YbN₂C ring and no hydrogen atom at the coordinated nitrogen atom.¹⁰ This guanidinate isomerization can also be confirmed by a comparison with the structural parameters of other known guanidinate complexes.²³

Characteristically, the distance between the central carbon and noncoordinated nitrogen (C(11)-N(3)) =1.378(5) Å) is shorter than that expected for $C(sp^2)$ - $N(sp^3)$ single bonds (C-N_{av} = 1.416 Å)²⁴ and is also significantly shorter than the value observed in (C₅H₅)₂- $Yb[(^{Pr}N)_2CN^{Pr}Pr_2]$ (1.427(7) Å).¹⁰ This may be attributed to less steric repulsion between the substituents, which leads to a stronger $p-\pi$ conjugation between the lonepair electron on noncoordinated nitrogen and the N₂C⁻ unit. Consistently, the average Yb-N distance (2.254-(3) Å) is slightly shorter than the corresponding distance in (C₅H₅)₂Yb[(^{*i*}PrN)₂CN^{*i*}Pr₂] (2.288(5) Å), indicating a

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Figure 4. ORTEP diagram of **7** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

contribution from the increase of the nucleophilicity of the guanidinate anion.²⁵

Complexes 4 and 5 are isostructural with complex 3. Their structural parameters (Table 3) also indicate that the charge delocalization within the N_3C core is evident and the hydrogen linked to the nitrogen atom of the N^t-Bu group has migrated to the noncoordinated nitrogen atom. There is no unusual distance or angle in the $(C_5H_5)_2$ Er or $(C_5H_5)_2$ Dy unit. The Er-C(C₅H₅) distances range from 2.586(8) to 2.637(7) Å. The average value of 2.609(5) Å is similar to those found in other (C₅H₅)₂Ercontaining complexes, such as $(C_5H_5)_2 Er[(BuN)_2 C^n Bu]$ (2.653 Å)^{26a} and (C₅H₅)ErCl₂(THF)₃ (2.667 Å).^{26b} The $Dy-C(C_5H_5)$ distances of 2.622(6)-2.651(5) Å are in the normal range.^{10,27} The Er-N (2.252(5), 2.254(5) Å) and Dy-N (2.319(4), 2.321(4) Å) distances are similar to the corresponding distances in complex 3, when the difference in the metal ionic radii is considered.²¹

Positive structural verification of **7** was also provided by a single-crystal X-ray analysis. The solid-state structure of **7** (Figure 4) shows that the bonding mode of the 'PrNC(NH/Pr)NPh group is similar to that of 'PrNC-(NH/Pr)N'Bu observed in complexes **3**–**5**. The corresponding guanidinate isomerization, involving a 1,3Table 4. Bond Lengths (Å) and Angles (deg) for 7

	0	0	O,
Yb(1)-N(1)	2.293(6)	Yb(1)-C(9)	2.575(11)
Yb(1)-N(2)	2.297(7)	Yb(1)-C(5)	2.582(10)
Yb(1)-C(7)	2.551(11)	Yb(1)-C(10)	2.586(12)
Yb(1)-C(6)	2.560(10)	N(1)-C(11)	1.364(14)
Yb(1)-C(4)	2.562(11)	N(1)-C(12)	1.389(10)
Yb(1)-C(1)	2.567(12)	N(2)-C(11)	1.304(13)
Yb(1)-C(3)	2.569(11)	N(2)-C(18)	1.488(11)
Yb(1)-C(8)	2.572(11)	N(3)-C(11)	1.368(8)
Yb(1)-C(2)	2.572(13)		
N(1)-Yb(1)-N(2)	58.2(2)	N(1)-C(11)-N(3)	122.7(12)
C(11) - N(1) - Yb(1)	93.3(5)	N(2)-C(11)-Yb(1)	56.8(4)
C(11) - N(2) - Yb(1)	94.9(5)	N(1) - C(11) - Yb(1)	56.8(3)
N(2) - C(11) - N(1)	113.6(6)	N(3)-C(11)-Yb(1)	178.1(11)
N(2) - C(11) - N(3)	123.6(11)		

hydrogen shift, is unambiguously identified by the relative bond distances and bond angles (Table 4). 7 has no unusual distances or angles in the $(C_5H_5)_2$ Yb unit. The different C(11)–N(2) and C(11)–N(1) distances of 1.304(13) and 1.364(14) Å may be due to the additional conjugation participated in by the phenyl ring.

Conclusions

The present results demonstrate that lanthanocene amino derivatives exhibit high activity toward N, Ndiisopropylcarbodiimide. N,N-Diisopropylcarbodiimide inserts readily into each of the Ln–N σ bonds of $(C_5H_5)Y(N^{t}Pr_2)_2$ and $[(C_5H_5)_2LnNHR]_2$ (R = ^tBu, Ln = Yb, Er, Dy, Y; R = Ph, Ln = Yb) under mild conditions, which provides a new way to synthesize lanthanide guanidinate complexes. Interestingly, the insertion product derived from *N*,*N*-diisopropylcarbodiimide with $(C_5H_5)Y(N^iPr_2)_2$ is unstable at room temperature and rearranges easily to $Y[^{i}PrNC(N^{i}Pr_{2})N^{i}Pr]_{3}$ (1) and $(C_5H_5)_2Y[^{i}PrNC(N^{i}Pr_2)N^{i}Pr]$ (2). Moreover, the X-ray analyses for complexes 3-5 and 7 show that the resulting guanidinate ligands 'BuNC(NH'Pr)N'Pr and PhNC(NHⁱPr)NⁱPr readily undergo a novel isomerization via a 1,3-hydrogen shift, forming the asymmetrical guanidinate complexes.

Acknowledgment. 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.

Supporting Information Available: Figures giving additional views and CIF files giving atomic coordinates and thermal parameters, all bond distances and angles, and experimental data for all structurally characterized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049866U

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