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Insertion of Carbodiimide into the Ln−C σ-Bond of Organolanthanide Complexes. Synthesis, Reaction, and Characterization of Organolanthanide Amidinates $(C_5H_5)_2Ln[^t\text{BuN}\overset{\cdots}{-}\text{C}(^n\text{Bu})\overset{\cdots}{-}\text{N}^t\text{Bu}]$ (Ln = Er, Gd, Y)

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The synthesis, structures, and reactivity of new lanthanocene complexes incorporating amidinate ligand $[^t\text{BuN}\overset{\cdots}{-}\text{C}(^n\text{Bu})\overset{\cdots}{-}\text{N}^t\text{Bu}]$ are described. Treatment of $Cp_2Ln^n\text{Bu}$ (Ln = Er (**1**), Y (**2**), Gd (**3**)) with *N*,*N*′-di-*tert*-butylcarbodiimide results in monoinsertion of carbodiimide into the Ln−C σ-bond to yield the title compounds $Cp_2Ln[^t\text{BuN}\overset{\cdots}{-}\text{C}(^n\text{Bu})\overset{\cdots}{-}\text{N}^t\text{Bu}]$ (Ln = Er (**4**), Y (**5**), Gd (**6**)). Complexes **4**−**6** were characterized by elemental analysis and IR and mass spectroscopies. The structures of complexes **4** and **5** were determined through X-ray single-crystal diffraction analysis. It is shown that compound **5** is a fine catalyst for cyclotrimerization of phenyl isocyanate.

Introduction

Amidinate ligands $[R'N\overset{\cdots}{-}C(R)\overset{\cdots}{-}NR'']$ continue to be a focus of much attention in organometallic chemistry,[1] because their steric and electronic effects can be manipulated through programmed variation of the C- and N-substituents.[2] It has been confirmed that the amidinate group is a potential alternative for the Cp ligand and can be used extensively in coordination chemistry and organometallic chemistry of main group and transition metals.[3] In recent years, some group 3 metal and lanthanide amidinate complexes have also been reported.[2c,4,5a] But all these compounds were synthesized by the metathesis reaction of the corresponding amidinate salt with lanthanide chlorides.[5]

On the other hand, as the isoelectronic analogues of carbodiimides, insertions of PhNCO, PhNCS, CO_2, COS, and CS_2 into Ln−C σ-bonds have been extensively studied by our group and other groups,[6] providing many new methods for the Ln−C bond transformation into Ln−N, Ln−O, and Ln−S bonds. However, to our knowledge, no example of insertion of carbodiimides into the Ln−C σ-bond of organolanthanide complexes has been reported. To investigate the reactivity of carbodiimide toward organolanthanide alkyl complexes, we herein report the insertion of carbodiimide into the Ln−C σ-bond, which provides an efficient synthesis of organolanthanide amidinate complexes.

Experimental Section

General Procedures. All operations involving air- and moisture-sensitive compounds were carried out under an inert

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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. Cp_2LnCl[7a] and Cp_2Ln^nBu[7b] were prepared according to the procedures described in the literatures. *n*-Butyllithium and *N*,*N*′-di-*tert*-butylcarbodiimide 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, ^{89}Y, ^{155}Gd, and ^{166}Er. ^1H NMR data were obtained on a Bruker DMX-500 NMR spectrometer and were referred to residual aryl protons in C_6H_6 (δ 7.15).

Synthesis of $Cp_2Er[^tBuN\underset{\cdot\cdot}{-}C(^nBu)\underset{\cdot\cdot}{-}N^tBu]$ (4). A solution of ^nBuLi (2.31 M, 0.33 mL in cyclohexane) was added dropwise to a 20 mL THF solution of Cp_2ErCl (0.254 g, 0.76 mmol) at −30 °C. After stirring for 30 min at the low temperature, the mixture solution was slowly warmed to room temperature and stirred for 3 h. The clear pink solution became orange. To the reaction mixture was slowly added dropwise *N*,*N*′-di-*tert*-butylcarbodiimide (0.120 g, 0.78 mmol) at −30 °C. After being stirred for 1 h at the low temperature, the reaction mixture was slowly warmed to ambient temperature and stirred for 12 h. The solvent was removed under vacuum, and the solid residue was extracted with 30 mL of toluene. The orange extract solution was concentrated and cooled at −20 °C to give a pink powder. Recrystallization of the powder from the mixture solvent of THF and toluene gave **4** as pink crystals. Yield: 0.325 g (82%). Anal. Calcd for $C_{23}H_{37}N_2Er$: C, 54.29; H, 7.33; N, 5.50. Found: C, 53.84; H, 7.40; N, 5.51. IR (Nujol, cm^{-1}): 1737(w), 1653(s), 1629(m), 1527(w), 1357(s), 1272(s), 1237(s), 1196(s), 1086(s), 1010(s), 836(s), 766(s), 692(w), 648(w). EI-MS: *m*/*z* [fragment, rel int (%)] 508 (M, 5), 493 ($M-CH_3$, 29), 296 (Cp_2Er, 8), 213 (L+H, 11), 155 ($L-^nBu$, 3), 141 ($L-N^tBu$, 25), 114 ($L-N^tBu-C_2H_3+H$, 8), 99 ($L-2^tBu+H$, 8), 84 ($L-N^tBu-C_4H_8$, 14), 71 (N^tBu, 13), 57 (Bu, 100) [$L = (^tBuN)_2C(^nBu)$].

Synthesis of $Cp_2Y[^tBuN\underset{\cdot\cdot}{-}C(^nBu)\underset{\cdot\cdot}{-}N^tBu]$ (5). ^nBuLi (2.31 M, 1.14 mL in cyclohexane) was added to a solution of Cp_2YCl (0.670 g, 2.63 mmol) in 30 mL of THF at −30 °C. After being stirred for 3 h, *N*,*N*′-di-*tert*-butylcarbodiimide (0.409 g, 2.65 mmol) was added to the mixture solution at −30 °C. The reaction mixture was subsequently worked up by the method described above. Pale yellow crystals of **5** were obtained in 76% yield, 0.875 g. Anal. Calcd for $C_{23}H_{37}N_2Y$: C, 64.17; H, 8.66; N, 6.51. Found: C, 63.89; H, 8.65; N, 6.50. IR (Nujol, cm^{-1}): 1739(w), 1649(s), 1623(m), 1524(w), 1352 (s), 1268(s), 1232(s), 1194(s), 1083(s), 1010(s), 836(m), 762(s), 688(w), 645(m). ^1H NMR (C_6H): δ 6.42 (s, 10H), 2.06 (t, 2H, $CH_2CH_2CH_2CH_3$), 1.45−1.47 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.25−1.30 (m, 2H, $CH_2CH_2CH_2CH_3$), 0.92 (t, 3H, $CH_2CH_2CH_2CH_3$), 1.56 (s, 9H, $C(CH_3)_3$), 1.50 (s, 9H, $C(CH_3)_3$). EI-MS: *m*/*z* [fragment, rel int (%)] 415 ($M-CH_3$, 8), 349 ($M-CH_3-CpH$, 3), 219 (Cp_2Y, 2), 212 (L, 8), 155 (L−Bu, 4), 141 ($L-N^tBu$, 30), 114 ($L-N^tBu-C_2H_3+H$, 9), 99 ($L-2^tBu+H$, 10), 84 ($L-N^tBu-C_4H_8$, 14), 71 (N^tBu, 16), 58 (^tBuH, 100).

Synthesis of $Cp_2Gd[^tBuN\underset{\cdot\cdot}{-}C(^nBu)\underset{\cdot\cdot}{-}N^tBu]$ (6). Following the procedure described for **4**, reaction of Cp_2GdCl (0.329 g, 1.02 mmol) with ^nBuLi (2.31 M, 0.44 mL in cyclohexane) and subsequently with *N*,*N*′-di-*tert*-butylcarbodiimide (0.158 g, 1.02 mmol) gave **6** as yellow crystals. Yield: 0.274 g (54%). Anal. Calcd for $C_{23}H_{37}N_2Gd$: C, 55.38; H, 7.48; N, 5.62. Found: C, 55.10; H, 7.48; N, 5.65. IR (Nujol, cm^{-1}): 1734(w), 1651(s), 1628(m), 1523(w), 1353(s), 1272(s), 1235(s), 1195(s), 1086(s), 1009(s), 868(w), 837(s), 762(s), 688(w), 649(m). EI-MS: *m*/*z* [fragment, rel int (%)] 483 ($M-CH_3$, 4), 212 (L, 7), 155 ($L-^nBu$, 4), 141 ($L-N^tBu$, 32), 114 ($L-N^tBu-C_2H_3+H$, 10), 99 ($L-2^tBu+H$, 11), 84 ($L-N^tBu-C_4H_8$, 15), 71 (N^tBu, 16.76), 58 (^tBuH, 100).

Catalytic Cyclotrimerization of Phenyl Isocyanate by Complex 5. To a 30 mL THF solution of complex **5** (0.039 g, 0.078 mmol) was added phenyl isocyanate (0.139 g, 1.17 mmol) at −78 °C. Then the mixture solution was slowly warmed to room temperature and stirred for overnight. The solution slowly became orange-red. The red solution was concentrated to ca. 2 mL and cooled at −20 °C to give pale yellow crystals of $(PhNCO)_3$ (**7**). Yield: 0.107 g (77%). EI-MS: *m*/*z* [fragment, rel int (%)] 357 (M, 100), 238 (M−PhNCO, 8), 119 (PhNCO, 84), 77 (Ph, 12). The identify of $(PhNCO)_3$ was confirmed by comparison of X-ray crystallographic analysis data with literature values.[6a]

X-ray Data Collection, Structure Determination, and Refinement for Complexes 4 and 5. Suitable crystals of complexes **4** and **5** 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 Kα (λ = 0.71073 Å) radiation. During the collection of the intensity data, no significant decay was observed. For **4**, frames were integrated to the maximum 2θ angle of 50.04° with the Siemens SAINT program to yield a total of 4804 reflections, of which 3848 were independent ($R_{int} = 0.0256$). For **5**, frames were integrated to the maximum 2θ angle of 53.82° with the Siemens SAINT program to yield a total of 5524 reflections, of which 4656 were independent ($R_{int} = 0.0241$). 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 3848 reflections for **4** and 4656 reflections for **5**. The intensities were corrected for Lorentz−polarization effects and empirical absorption with the SADABS program.[8] A summary of the crystallographic data is given in Table 1.

The structure was solved by the direct method using the SHELXL-97 program.[9] 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 $R = 0.0340$ for **4** and $R = 0.0464$ for **5**. All calculations were performed using the Bruker Smart program.

Results and Discussion

Synthesis of *N*,*N*′-Di-*tert*-butylcabodiimide Insertion Products $Cp_2Ln[^tBuN\underset{\cdot\cdot}{-}C(^nBu)\underset{\cdot\cdot}{-}N^tBu]$ (Ln = Er, Gd, Y). $Cp_2Ln^nBu(THF)$ (Ln = Er (**1**), Y (**2**), Gd-(**3**)) were allowed to react with *N*,*N*′-di-*tert*-butylcabodiimide giving amidinate lanthanide complexes $Cp_2Ln[^tBuN\underset{\cdot\cdot}{-}C(^nBu)\underset{\cdot\cdot}{-}N^tBu]$ (Ln = Er (**4**), Y (**5**), Gd(**6**)), indicating that one carbodiimide molecule is inserted into the Ln−C σ-bond of $Cp_2Ln^nBu(THF)$ (Scheme 1).

Complexes **4**−**6** are air- and moisture-sensitive. They are readily dissolved in THF and toluene and sparing soluble in *n*-hexane. All amidinate complexes were characterized by elemental analysis and IR and mass spectroscopies, which were in good agreement with the proposed structures. In the mass spectra, all the amidi-

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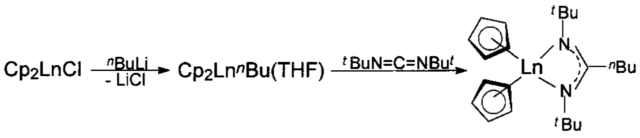
Table 1. Crystal and Data Collection Parameters of Complexes 4 and 5

	4	**5**
formula	$C_{23}H_{27}N_2Er$	$C_{23}H_{37}N_2Y$
molecular weight	508.81	430.46
cryst color	pink	pale yellow
cryst dimens (mm)	0.60 × 0.50 × 0.30	0.60 × 0.40 × 0.30
cryst syst	monoclinic	monoclinic
space group	$P2_1/m$	$P2_1$
unit cell dimens		
a (Å)	8.4495(11)	8.470(4)
b (Å)	15.786(2)	15.807(7)
c (Å)	9.1663(12)	9.215(4)
β (deg)	109.054(2)	109.109(5)
V (Å^3)	1155.6(3)	1165.8(8)
Z	2	2
D_c (g cm^{-3})	1.433	1.226
μ (mm^{-1})	3.638	2.509
F(000)	494	456
radiation ($\lambda = 0.71073$ Å)	Mo Kα	Mo Kα
temperature (K)	298.2	293.2
scan type	$\omega-2\theta$	$\omega-2\theta$
θ range (deg)	2.35 to 25.02	2.34 to 26.91
h,k,l range	$-9 \leq h \leq 10$, $-18 \leq k \leq 18$ $-10 \leq l \leq 6$	$-4 \leq h \leq 10$ $-18 \leq k \leq 20$ $-11 \leq l \leq 9$
no. of reflns measd	4804	5524
no. of unique reflns	3848 ($R_{int} = 0.0256$)	4656 ($R_{int} = 0.0241$)
completeness to θ	99.5% ($\theta = 25.02$)	99.0% ($\theta = 26.91$)
max. and min. transmn	0.4083 and 0.2188	0.5198 and 0.3144
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	3848/1/243	4656/1/235
goodness-of-fit on F^2	1.043	1.039
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0334$, $wR_2 = 0.0916$	$R_1 = 0.0359$, $wR_2 = 0.0862$
R indices (all data)	$R_1 = 0.0340$, $wR_2 = 0.0923$	$R_1 = 0.0464$, $wR_2 = 0.0924$
absolute structure param	−0.07(2)	−0.008(8)
largest diff peak and hole (e Å^{-3})	1.121 and −0.982	0.441 and −0.355

Scheme 1



Ln = Er (**4**), Y (**5**), Gd (**6**)

nate complexes are characterized by the ready loss of the methyl group from the molecule ions. In the IR spectra, the characterized absorption at ca. 2100 cm^{-1} for the ν_{as}(N═C═N) stretch of free carbodiimides is absent, but a new strong band at ca. 1650 cm^{-1} attributable to the delocalized $-N{\cdots}C{\cdots}N-$ stretching mode is present.[10]

In contrast to phenyl isocyanate insertion into the Ln−C bond, where excess PhNCO can be incorporated into the first insertion products[5c] or is catalyzed to polymerize isocyanurate $(PhNCO)_3$,[5a] we found that *N*,*N*′-di-*tert*-butylcarbodiimide only monoinserts into the Ln−C σ-bond even in the 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-*tert*-butylcarbodiimide. For the more sterically crowded $Cp_2Ln[{}^tBuN{\cdots}C({}^nBu){\cdots}N{}^tBu]$ system, neither a double insertion product nor cyclization/polymerization product is obtained, since the interaction of the second *N*,*N*′-di-*tert*-butylcarbodiimide molecule with the center metal is prevented by the absence of a free coordination site on complexes **4**−**6** as well as the lower reactivity of *N*,*N*′-di-*tert*-butylcarbodiimide compared with phenyl isocyanate.

Crystal Structures of 4 and 5. Complexes **4** and **5** crystallize from the solvent mixture of tetrahydrofuran and toluene at −20 °C in the monoclinic system, space group $P2_1/m$ for **4** and $P2_1$ for **5**. The molecular structures of **4** and **5** are shown in Figure 1 and Figure 2. Selected bond lengths and angles are given in Tables 2 and 3, respectively. The X-ray structure analysis results show that **4** and **5** are isostructural. Both are solvent-free monomers with the lanthanide atom bonded to two η^5-cyclopentadienyl rings and one chelating amidinate ligand to form distorted tetrahedron geometry. The coordination number of the central metal Ln^{3+} is eight. As expected, the coordinated amidinate group forms essentially a planar four-membered ring with the lanthanide atom within experimental error. The bond angles around C(11) are consistent with sp^2 hybridization. The cent−Ln−cent (cent = the center of cyclopentadienyl ring) plane relative to the NCNLn plane is approximately perpendicular. This disposition is likely the result of steric interactions between bulky *tert*-butyl groups and two cyclopentadienyl ligands.

In **5**, the C(11)−N(1) and C(11)−N(2) distances of the amidinate 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.[11] Consistent with this observation,

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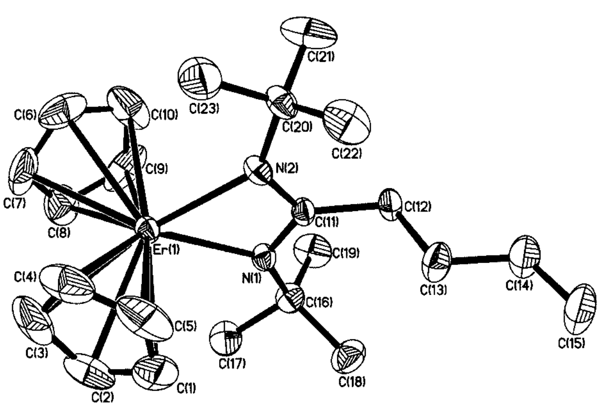

Figure 1. ORTEP diagram of $\mathrm{Cp_2Er[{}^tBuN\overset{\dots}{-}C({}^nBu)\overset{\dots}{-}N{}^tBu]}$ (**4**) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms omitted for clarity.

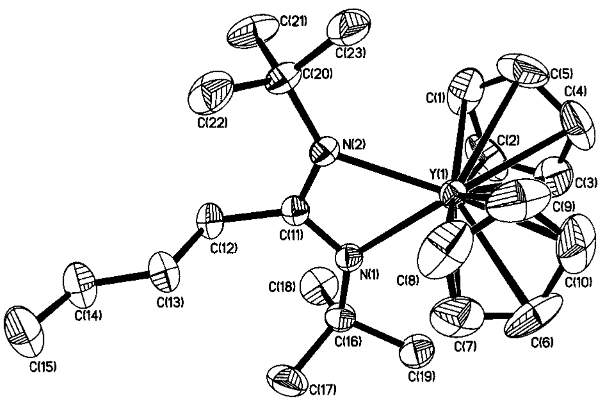

Figure 2. ORTEP diagram of $\mathrm{Cp_2Y[{}^tBuN\overset{\dots}{-}C({}^nBu)\overset{\dots}{-}N{}^tBu]}$ (**5**) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms omitted for clarity.

Table 2. Bond Lengths (Å) and Angles (deg) for 4

Er(1)−N(1)	2.280(4)	Er(1)−C(7)	2.657(9)
Er(1)−N(2)	2.282(5)	Er(1)−C(8)	2.663(10)
Er(1)−C(4)	2.625(10)	Er(1)−C(1)	2.667(9)
Er(1)−C(3)	2.624(9)	N(1)−C(11)	1.325(11)
Er(1)−C(2)	2.633(8)	N(1)−C(16)	1.484(10)
Er(1)−C(6)	2.636(10)	N(2)−C(11)	1.348(9)
Er(1)−C(10)	2.638(10)	N(2)−C(20)	1.479(9)
Er(1)−C(5)	2.636(10)	C(11)−C(12)	1.527(10)
Er(1)−C(9)	2.657(10)		
N(1)−Er(1)−N(2)	58.5(3)	C(20)−N(2)−Er(1)	137.4(5)
C(11)−N(1)−C(16)	128.3(5)	N(1)−C(11)−N(2)	113.1(5)
C(11)−N(1)−Er(1)	94.5(4)	N(1)−C(11)−C(12)	124.2(6)
C(16)−N(1)−Er(1)	136.8(6)	N(2)−C(11)−C(12)	122.7(6)
C(11)−N(2)−C(20)	128.7(6)	C(12)−C(11)−Er(1)	176.9(5)
C(11)−N(2)−Er(1)	93.8(4)		

Table 3. Bond Lengths (Å) and Angles (deg) for 5

Y(1)−N(2)	2.301(3)	Y(1)−C(3)	2.661(5)
Y(1)−N(1)	2.302(2)	Y(1)−C(4)	2.665(6)
Y(1)−C(10)	2.642(5)	Y(1)−C(2)	2.665(5)
Y(1)−C(7)	2.642(5)	N(1)−C(11)	1.326(5)
Y(1)−C(1)	2.644(5)	N(1)−C(16)	1.481(5)
Y(1)−C(8)	2.649(5)	N(2)−C(11)	1.336(5)
Y(1)−C(5)	2.651(5)	N(2)−C(20)	1.481(5)
Y(1)−C(6)	2.655(4)	C(11)−C(12)	1.515(6)
Y(1)−C(9)	2.653(5)		
N(2)−Y(1)−N(1)	57.51(13)	C(20)−N(2)−Y(1)	135.6(3)
C(11)−N(1)−C(16)	128.4(3)	N(1)−C(11)−N(2)	112.6(3)
C(11)−N(1)−Y(1)	95.1(2)	N(1)−C(11)−C(12)	124.3(4)
C(16)−N(1)−Y(1)	136.1(3)	N(2)−C(11)−C(12)	123.1(4)
C(11)−N(2)−C(20)	129.3(3)	C(12)−C(11)−Y(1)	177.0(3)
C(11)−N(2)−Y(1)	94.8(2)	C(20)−N(2)−Y(1)	135.6(3)

the Y−N(1) and Y−N(2) distances, 2.301(3) and 2.302(2) Å, are intermediate between the values observed for a Y−N single bond distance and a Y−N donor bond distance[12] and are comparable to the corresponding values found in $[\mathrm{CpY}(\eta^2\text{-}\mathrm{PzMe_2})(\mu\text{-}\mathrm{PzMe_2})]_2$ ($\mathrm{Y{-}N_{av}} = 2.324(3)$ Å).[13] However, the average Y−N distance (2.301(8) Å) is slightly but significantly shorter than those observed in complexes $\mathrm{Cp^*[PhC(NSiMe_3)_2]Y(\mu\text{-}Me_2)Li(TMEDA)}$ ($\mathrm{Y{-}N_{av}} = 2.418(7)$ Å),[4d] $\mathrm{[PhC(NSiMe_3)_2]_2YR}$ (R = H, $\mathrm{Y{-}N_{av}} = 2.356(3)$ Å;[4c] R = C≡CH, $\mathrm{Y{-}N_{av}} = 2.366(4)$ Å[2b]), and $[p\text{-}\mathrm{MeOC_6H_4C(NSiMe_3)_2}]_2\mathrm{YCH(SiMe_3)_2}$ ($\mathrm{Y{-}N_{av}} = 2.338(4)$ Å).[2b] This may be attributed to the higher electrophilicity and less steric hindrance of $\mathrm{Cp_2Y}$ compared to the corresponding moiety of the latter in the systems, which results in a stronger interaction between Y and nitrogen.[14] The Y−C(Cp) distances range from 2.642(5) to 2.665(6) Å and are in the normal range observed for the lanthanide metallocenes. The average Y−C(Cp) distance of 2.644(6) Å is similar to those found in other $\mathrm{Cp_2Y}$-containing compounds, such as $[(\mathrm{C_5H_5})_2\mathrm{Y}(\mu\text{-}\mathrm{CH_3})]_2$, 2.66(2) Å,[15a] and $[(\mathrm{C_5H_5})_2\mathrm{Y}(\mu\text{-}\mathrm{Me})_2\mathrm{AlMe_2}]$, 2.62(4) Å.[15b]

The structural parameters of **4** (Table 2) are very similar to those for complex **5**, the Er−C(Cp) 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 $\mathrm{[Li(THF)_4]\{[(C_5H_5)_2ErH]_3Cl\}}$,[16a] 2.65 Å, and $\mathrm{(C_5H_5)ErCl_2(THF)_3}$,[16b] 2.67 Å. The Er−N distances of 2.280(4) and 2.282(5) Å are in the range expected for the Er−N bond interaction with partial single and donor bond character.[17] The average Er−N distance of 2.281(5) Å is comparable to the corresponding distance in complex **5**, when the differences in the metal ionic radii are considered.[18]

Cyclopolymerization of Phenyl Isocyanate Catalyzed by Complex 5. Recently, Shen and co-workers found that phenyl isocyanate can insert into the Ln−N σ-bond of the lanthanide amide complexes $\mathrm{Cp_2LnN{}^iPr_2(THF)}$.[19] To explore the reactivity of lanthanide amidinates and further study the effect of the nature of ligands on the isocyanate insertion into the Ln−N bond, we studied the reaction of complex **5** with phenyl isocyanate. The results indicate that the only observable products are cyclotrimer $\mathrm{(PhNCO)_3}$ (**7**) and complex **5** in the reaction of **5** with an equivalent or excess of phenyl isocyanate. A similar reaction is observed in the amidinate complexes of Sn(IV).[20] Further investigations

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into the mechanism of the formation of $(PhNCO)_3$ and its scope and generality are underway.

Conclusions

We have demonstrated that organolanthanide alkyl derivatives exhibit high activity toward carbodiimide. Carbodiimide inserts readily into the Ln−C σ-bond of organolanthanide alkyl complexes Cp_2Ln^nBu under mild conditions, which provides a new way to prepare new lanthanocence derivatives incorporating amidinate ligands $[R'N\overset{...}{-}C(R)\overset{...}{-}NR']$. The further investigation results suggest that the carbodiimide insertion is independent of stoichiometry and excess carbodiimide does not undergo any other reaction. But complex **5** can catalyze cyclotrimerization of phenyl isocyanate.

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Supporting Information Available: Tables of 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.

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