

# Investigations on Organolanthanide Derivatives with the Hydrazonido (<sup>-</sup>NHN=CPh<sub>2</sub>) Ligand: Synthesis, Crystal Structure, and Reactivity

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Two organolanthanide complexes with the benzophenone hydrazonido(1–) ligand,  $[Cp_2Yb(\mu-NHN=CPh_2)]_2$  (1) and  $Cp_2Er[\eta^2-NHN=CPh_2](THF)$  (2), were synthesized by abstraction of cyclopentadienyl from  $Cp_3Ln$  with 1 equiv of benzophenone hydrazone in THF. Reaction of 1 and 2 with phenyl isocyanate gives Ln-N bond insertion with the 1,3-H migration products  $Cp_2Ln(\eta^2-OC (NHPh)NN=CPh_2)(HMPA)$  (Ln = Yb (3), Er (4)). However, 1 and 2 react with PhNCS to give Ln-N bond insertion without the 1,3-H migration products  $Cp_2Ln(\eta^2-SC(NHN=CPh_2)NPh)(HMPA)$  (Ln = Yb (5), Er (6)) under the same conditions. PhCN inserts into the Er-N bond of 2 with 1,3-hydrogen migration to form the organolanthanide heterometallacycles  $Cp_2Er[\eta^2-NHC(Ph)NN=CPh_2]$  (7). However, <sup>1</sup>BuNC does not insert into the Er-N bond of 2 under the same conditions, and treatment of 2 with <sup>1</sup>BuNC leads to the isolation of the solvent-free dimer  $[Cp_2Er(\mu-\eta^1:\eta^2-NHN=CPh_2)]_2$  (2'). All new compounds have been characterized through X-ray single-crystal diffraction analysis.

## Introduction

There has been considerable and growing interest in metal hydrazido complexes and in their role as catalysts for the stoichiometric and catalytic reduction of dinitrogen to ammonia;<sup>1</sup> further, the terminal hydrazido(2–) ligands are believed to participate in alkyne hydrohydrazination<sup>2</sup> and iminohydrazination<sup>3</sup> catalysis. Although many transition-metal hydrazido complexes have been synthesized in recent years,<sup>4,5</sup> informa-

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The activation of organolanthanides on unsaturated organic small molecules is an important field in organolanthanide chemistry.<sup>7,8</sup> As one flourishing subdiscipline of this field, insertion reactions have been studied extensively over the past decade, because they permit unusual organolanthanide derivatives to be prepared and provide new bond-forming methods for organic synthesis with exquisite selectivity and effectiveness.<sup>9–11</sup> Recently, our interest has been focused on the investigation of the addition of the N–H bonds of organolanthanide

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derivatives to some unsaturated organic small molecules to construct a novel neutral or anionic ligand or an N-heterocyclic skeleton.<sup>12</sup> As part of this program, we were interested in the reactivity of lanthanide hydrazonido complexes toward heteroallenes. Therefore, herein we report the synthesis of organolanthanide derivatives bearing the benzophenone hydrazonido(1–) ligand and their reactions with PhNCO, PhNCS, and PhCN.

## **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 or a glovebox. The solvents THF, toluene, and *n*hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use.  $(C_5H_5)_3Ln$  was prepared by literature methods.<sup>13</sup> PhNCO, PhNCS, PhCN, 'BuNC, Ph<sub>2</sub>C=NNH<sub>2</sub>, and HMPA (hexamethylphosphoric triamide) 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. <sup>1</sup>H NMR data were obtained on a Bruker DMX-400 NMR spectrometer.

**Synthesis of [Cp<sub>2</sub>Yb(\mu-NHN=CPh<sub>2</sub>)]<sub>2</sub> (1).** (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Yb (0.943 g, 2.56 mmol) and Ph<sub>2</sub>C=NNH<sub>2</sub> (0.504 g, 2.56 mmol) were mixed in 50 mL of THF. After the mixture was stirred for 24 h at room temperature, all volatile substances were removed under vacuum to give an orange powder. Red crystals of 1 were obtained by recrystallization from THF at -20 °C for several days. Yield: 1.12 g (87%). Anal. Calcd for C<sub>46</sub>H<sub>42</sub>N<sub>4</sub>Yb<sub>2</sub>: C, 55.42, H, 4.25; N, 5.62. Found: C, 55.31; H, 4.21; N, 5.69. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 7.16):  $\delta$  64.25 (4H, C<sub>6</sub>H<sub>5</sub>), 26.43 (4H, C<sub>6</sub>H<sub>5</sub>), 23.39 (4H, C<sub>6</sub>H<sub>5</sub>), 18.87 (2H, NH), 12.49 (4H, C<sub>6</sub>H<sub>5</sub>), 11.85 (4H, C<sub>6</sub>H<sub>5</sub>), -17.37 (20H, C<sub>5</sub>H<sub>5</sub>). IR (Nujol): 3178 m, 1598 w, 1574 m, 1549 m, 1535 m, 1493 s, 1440 s, 1391 s, 1158 m, 1074 w, 1010 s, 955 s, 777 s, 704 m, 661 m cm<sup>-1</sup>.

Synthesis of Cp<sub>2</sub>Er[ $\eta^2$ -NHN=CPh<sub>2</sub>](THF) (2). Following the procedure described for 1, reaction of  $(C_5H_5)_3$ Er (0.972 g, 2.68 mmol) with Ph<sub>2</sub>C=NNH<sub>2</sub> (0.528 g, 2.68 mmol) gave 2 as pink crystals. Yield: 1.26 g (83%). Anal. Calcd for C<sub>27</sub>H<sub>29</sub>ON<sub>2</sub>Er: C, 57.42; H, 5.17; N, 4.96. Found: C, 57.33; H, 5.15; N, 5.05. IR (Nujol): 3548 s, 3422 m, 3260 m, 1574 s, 1436 s, 1194 s, 1071 s, 1009 s, 950 m, 913 m, 866 s, 769 s, 707 m, 656 w cm<sup>-1</sup>.

Synthesis of Cp<sub>2</sub>Yb $|\eta^2$ -OC(NHPh)NN=CPh<sub>2</sub>](HMPA) (3). PhNCO (0.081 g, 0.67 mmol) was slowly added to a 20 mL THF solution of 1 (0.332 g, 0.33 mmol) at room temperature, and the mixture was stirred for 1 h. Then HMPA (0.120 g, 0.66 mmol) was added into the solution, and this mixture was continuously stirred overnight. The reaction solution was concentrated to ca. 5 mL under reduced pressure. Orange crystals of **3** were obtained by slow diffusion of *n*-hexane. Yield: 0.373 g (71%). Anal. Calcd for C<sub>36</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>PYb: C, 54.27; H, 5.57; N, 10.55. Found: C, 54.21; H, 5.53; N, 10.61. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  26.01

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Synthesis of Cp<sub>2</sub>Er $|\eta^2$ -OC(NHPh)NN=CPh<sub>2</sub>](HMPA) (4). Following the procedure described for 3, reaction of PhNCO (0.055 g, 0.46 mmol) with 2 (0.260 g, 0.46 mmol) and HMPA (0.083 g, 0.46 mmol) gave 4 as pink crystals. Yield: 0.276 g (76%). Anal. Calcd for C<sub>36</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>PEr: C, 54.66; H, 5.61; N, 10.62. Found: C, 54.53; H, 5.57; N, 10.66. IR (Nujol): 3351 m, 1605 m, 1589 s, 1571 s, 1530 s, 1443 s, 1071 w, 1011 s, 989 s, 748 s, 697 m, 658 w cm<sup>-1</sup>.

Synthesis of Cp<sub>2</sub>Yb $|\eta^2$ -SC(NHN=CPh<sub>2</sub>)NPh](HMPA) (5). Following the procedure described for 3, reaction of 1 (0.339 g, 0.34 mmol) with phenyl isothiocyanate (0.092 g, 0.68 mmol) and HMPA (0.122 g, 0.68 mmol) gave 5 as orange crystals. Yield: 0.370 g (67%). Anal. Calcd for C<sub>36</sub>H<sub>44</sub>N<sub>6</sub>OSPYb: C, 53.20; H, 5.46; N, 10.34. Found: C, 53.12; H, 5.47; N, 10.43. IR (Nujol): 3299 m, 1589 m, 1562 w, 1531s, 1445 s, 1400 m, 1169 s, 1073 w, 1012 s, 984 s, 770 s, 745 s, 705 m, 665 w cm<sup>-1</sup>. No valuable <sup>1</sup>H NMR spectra on this ytterbium compound could be obtained.

Synthesis of Cp<sub>2</sub>Er[ $\eta^2$ -SC(NHN=CPh<sub>2</sub>)NPh](HMPA) (6). Following the procedure described for 3, reaction of 2 (0.327 g, 0.58 mmol) with phenyl isothiocyanate (0.079 g, 0.58 mmol) and HMPA (0.104 g, 0.58 mmol) gave 6 as pink crystals. Yield: 0.300 g (64%). Anal. Calcd for C<sub>36</sub>H<sub>44</sub>N<sub>6</sub>OSPEr: C, 53.58; H, 5.49; N, 10.41. Found: C, 53.43; H, 5.43; N, 10.54. IR (Nujol): 3300 s, 1588 m, 1573 w, 1562 w, 1530 s, 1445 s, 1399 s, 1167s, 1071 w, 1006 s, 994 s, 778 s, 745 s, 705 m, 665 w cm<sup>-1</sup>.

Synthesis of Cp<sub>2</sub>Er[ $\eta^2$ -NHC(Ph)NN=CPh<sub>2</sub>] (7). PhCN (0.046 g, 0.45 mmol) was slowly added to a 20 mL THF solution of 2 (0.254 g, 0.45 mmol) at room temperature, and the mixture was stirred for 24 h. The reaction solution was concentrated to ca. 5 mL by reduced pressure. Pink crystals of 7 were obtained by slow diffusion of *n*-hexane. Yield: 0.212 g (79%). Anal. Calcd for C<sub>30</sub>H<sub>26</sub>N<sub>3</sub>Er: C, 60.48; H, 4.40; N, 7.05. Found: C, 60.41; H, 4.37; N, 7.11. IR (Nujol): 3366 m, 1584 s, 1529 s, 1502 s, 1426 m, 1406 w, 1215 m, 1016 s, 785 s, 768 s, 705 m, 660 w cm<sup>-1</sup>.

1406 w, 1215 m, 1016 s, 785 s, 768 s, 705 m, 660 w cm<sup>-1</sup>. Synthesis of  $[Cp_2Er(\mu-\eta^1:\eta^2-NHN=CPh_2)]_2$  (2'). 'BuNC (0.034 g, 0.40 mmol) was slowly added to a 20 mL THF solution of 2 (0.226 g, 0.40 mmol) at room temperature, and the mixture was stirred for 24 h. The reaction solution was concentrated to ca. 5 mL by reduced pressure. Pink crystals of 2' were obtained by slow diffusion of *n*-hexane. Yield: 0.124 g (63%). Anal. Calcd for C<sub>46</sub>H<sub>42</sub>N<sub>4</sub>Er<sub>2</sub>: C, 56.07; H, 4.30; N, 5.69. Found: C, 55.95; H, 4.27; N, 5.77. IR (Nujol): 3251 m, 3243 w, 1598 w, 1574 w, 1529 m, 1514 m, 1494 s, 1442 s, 1041 s, 1021 s, 959 m, 770 s, 697 m, 660 w cm<sup>-1</sup>.

Structure Determination of Complexes 1-7 and 2'. X-ray structure determination details and crystallographic refinement parameters of complexes 1-7 and 2' are given in the Supporting Information.

#### **Results and Discussion**

Synthesis and Characterization of Organolanthanide Hydrazonido Complexes  $[Cp_2Yb(\mu-NHN=CPh_2)]_2$  (1) and  $Cp_2Er$  $(\eta^2-NHN=CPh_2)\cdot THF$  (2). The known samarium and scandium hydrazido complexes were synthesized by the oxidation reaction of  $Cp^*_2Sm$  with excess hydrazine  $(H_2NNH_2)^{6a}$ or the protonolysis reaction of  $Cp^*_2ScCH_3$  with 1 equiv of the hydrazine  $H_2NNH_2$  or  $H_2NN(CH_3)_2$ .<sup>6b</sup> Here we synthesized the complexes  $[Cp_2Yb(\mu-NHN=CPh_2)]_2$  (1) and  $Cp_2Er$  $(\eta^2-NHN=CPh_2)\cdot THF$  (2) by the protonolysis reaction of  $Cp_3Ln$  with 1 equiv of  $H_2NN=CPh_2$  in THF at room temperature, as shown in Scheme 1. The structural analysis

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results show that 1 is a solvent-free dimer, while 2 is a solvated monomer.

Both 1 and 2 are sensitive to air and moisture and are soluble in THF and toluene and slightly soluble in *n*-hexane. They have been characterized by elemental analysis, IR, and <sup>1</sup>H NMR. In the IR spectra, **1** exhibits two characteristic absorptions at 3178 and  $1574 \text{ cm}^{-1}$ , which can be attributed to the hydrazonido ligand;<sup>5a</sup> 2 exhibits three absorptions at  $3548, 3422, \text{ and } 3260 \text{ cm}^{-1} \text{ attributable to the N-H bond and}$ two well-defined bands at 1071 and 913 cm<sup>-1</sup> for the coordinated THF. The solid-state structures of complexes 1 and 2 have been identified by X-ray single-crystal diffraction analysis, as shown in Figures 1 and 2. Crystal data confirm the centrosymmetric dimeric structure of 1, with the hydrazonido(1-) group as a monodentate bridging ligand. Each Yb atom is coordinated by two  $\eta^{5}$ -cyclopentadienyl rings and two bridging nitrogen atoms to form a distorted-tetrahedral geometry. The coordination number of the central  $Yb^{3+}$  is 8. Two Yb-N bond distances (Yb1-N1 = 2.349(10) Å; Yb1-N1A = 2.340(10) Å) are almost equivalent and are between those expected for an  $Yb^{3+} - N$  single bond and an  $Yb^{3+} - N$ N donor bond (2.19-2.69 Å).<sup>9,12</sup> The C1–N2 double-bond distance (1.289(15) Å) is comparable to the accepted value for the N(sp<sup>2</sup>)=C(sp<sup>2</sup>) double bond (1.28 Å).<sup>14</sup>

In 2, the hydrazonido ligand is coordinated to the erbium ion in a side-on bonding mode. The metal ion is bonded to two Cp rings, one chelating hydrazonido ligand, and one THF molecule to form a distorted-bipyramidal geometry. The coordination number of the central  $Er^{3+}$  is 9. As expected, the Er1-N1 bond distance, 2.227(4) Å, is shorter than the average Yb-N(bridging) distance observed in 1 and is similar to the values found in Yb(NHC<sub>6</sub>H<sup>i</sup><sub>3</sub>Pr<sub>2</sub>- $2,6)_3$ (THF)<sub>2</sub> (average 2.17 Å),<sup>15</sup> when the difference in the metal ionic radii and the effect of coordination number are considered.<sup>16</sup> The Er1-N2 distance of 2.372(4) Å is comparable to the Ln-N donor bond distance. Notably, the N1-N2 distance of 1.339(5) Å in 2 is much shorter than that observed in 1 (N1-N2 = 1.432(13) Å), while the C1-N2 distance of 1.311(5) Å is slightly longer than the corresponding value in **1**, 1.289(15) Å.

**Reactions of Complexes 1 and 2 with PhNCO and PhNCS.** To explore the reactivity of complexes 1 and 2, we first investigate their reactions with phenyl isocyanate. PhNCO was dropped into a clear THF solution of 1 or 2 at room temperature, and after the mixture was stirred for 1 h, a small amount of precipitate was formed. Then 1 equiv of HMPA was added to the turbid solution, and after it was stirred overnight, the solution became clear. After workup, the Ln-N bond insertion with 1,3-H migration products  $Cp_2Ln(\eta^2-OC(NHPh)NN=CPh_2)(HMPA)$  (Ln = Yb (3), Er (4)) were obtained in moderate yields, as shown in Scheme 2.

To gain more insight into the reactivity of 1 and 2, the reactions of them with phenyl isothiocyanate (PhNCS) were also investigated. Interestingly, treatment of 1 and 2 with PhNCS under the same conditions yields the Ln–N bond insertion products  $Cp_2Ln(\eta^2-SC(NPh)NHN=CPh_2)$  (HMPA) (Ln = Yb (5), Er (6)). X-ray analysis results indicate that PhNCS simply inserts into the Ln–N bond without any hydrogen migration, which is significantly different from the observations in the formation of 3 and 4. It is yet unclear why complexes 5 and 6 do not undergo the subsequent 1,3-hydrogen migration as observed in complexes 3 and 4.

It should be noted that complexes 3-6 are almost insoluble in THF and other organic solvents without HMPA. Complexes 3-6 have been characterized by elemental analysis, IR, and <sup>1</sup>H NMR, and their structures were also identified by X-ray single-crystal diffraction analysis. The X-ray analysis shows that, although the cell parameters of complexes 3 and 4 are different (Table 1, Supporting Information), their structures are similar and that both of them are monomeric structures (Figure 3) in which the newly formed ureido ligand (OC(NHPh)NN=CPh<sub>2</sub>) contacts the lanthanide atom in a  $\eta^2$ -bonding mode. The Ln atom is coordinated by two  $\eta^5$ -cyclopentadienyl groups, one chelating OC(NHPh)NN=CPh<sub>2</sub> ligand, and one oxygen atom from the HMPA molecule, such that the Ln atom has a coordination number of 9. In 3, the 1.271(13) Å C1-O1 distance is between the 1.293-1.407 Å range of C(sp<sup>2</sup>)-O distances and the 1.192-1.256 Å range of C(sp<sup>2</sup>)=O distances.17 The distance of C1-N2 (1.337(14) Å) is also between the values observed for a C-N single-bond distance (1.321-1.416 Å) and a C=N double-bond distance (1.279-1.416 Å)1.329 Å).<sup>20</sup> The bond angles around C14 are consistent with sp<sup>2</sup> hybridization. This suggests some electronic delocalization over the O-C-N unit. Consistent with this observation, the Yb-O1 and the Yb-N2 distances, 2.233(8) and 2.593(9) Å, both lie between the values observed for a Yb-O(N) single-bond distance and a Yb-O(N) donor-bond distance.9a,9c,11b Interestingly, the C1-N3 distance (1.338 (14) Å) is significantly shorter than the expected value for  $C(sp^2)-N(sp^3)$  single bonds ( $C-N_{av} = 1.416$ ),<sup>18</sup> indicating a strong p $-\pi$  conjugation between the lone-pair electron on noncoordinated nitrogen and the N-C-N unit. The C8-N1 and N1-N2 distances (1.309(13), 1.401(12) Å) are in the expected range.

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Figure 1. Thermal ellipsoid plot of  $[Cp_2Yb(\mu-NHN=CPh_2)]_2$ (1), with ellipsoids at the 30% probability level. Selected bond lengths (Å): Yb(1)-N(1A) = 2.340(10), Yb(1)-N(1) = 2.349-(10), N(1)-N(2) = 1.432(13), N(2)-C(1) = 1.289(15). Selected bond angles (deg): N(1A)-Yb(1)-N(1) 80.0(4), N(2)-N(1)-Yb(1A) = 122.3(7), N(2)-N(1)-Yb(1) = 111.6(7), C(1)-N-(2)-N(1) = 117.3(10).



Figure 2. Thermal ellipsoid plot of  $Cp_2Er[\eta^2-NHN=CPh_2]$ (THF), (2), with ellipsoids at the 30% probability level. Selected bond lengths (Å): Er(1)-N(1) = 2.227(4), Er(1)-N(2) = 2.372(4), Er(1)-O(1) = 2.376(4), N(1)-N(2) = 1.339(5), C(1)-N-(2) = 1.311(5). Selected bond angles (deg): N(1)-Er(1)-N(2) =33.66(13), C(1)-N(2)-N(1) = 124.9(4), C(1)-N(2)-Er(1) =164.3(3), N(1)-N(2)-Er(1) = 67.2(2).

The bond parameters for **4** are also in normal ranges (Figure 3), indicating that the hydrazonido ligand is transformed to the ureido ligand via a formal insertion of a phenyl isocyanate into the N-H bond. Complex **4** is also a monomer, in which the ureido ligand is chelated to the erbium ion  $\text{Er}^{3+}$  in a  $\eta^2$ -bonding mode. The bond distances and angles in **4** are similar to the corresponding values in **3**, if the difference in metal radii is considered.

The X-ray determination indicates that complex  $\mathbf{6}$  is a solvent-free monomeric structure. As shown in Figure 4, the



Cp<sub>2</sub>Er fragment connects with one SC(NPh)NHN=CPh<sub>2</sub> unit and one HMPA molecule. The N3-C1 and S1-C1 bond lengths, 1.360(12) and 1.722(10) Å, are between the corresponding C-N and C-S single- and double-bond distances, respectively.<sup>9b,11a</sup> These bond parameters indicate substantial electronic delocalization over the S-C-N unit. Significantly, the distance of N2-C1 (1.360(12) Å) in 7 is slightly shorter than the corresponding value found in Cp<sub>2</sub>Yb(SC(Ptz)NPh) (THF) (N2-C17 = 1.395(7) Å), which may indicate that the lone-pair electrons on the N2 atom are partially delocalized on the S-C-N unit. The C8-N1 and N1-N2 distances (1.291 (11), 1.369(11) Å) are also in the normal ranges. The Er-O1 distance is 2.237(7) Å, significantly shorter than that of the Er-:OR donor bond.<sup>19</sup>

Complex 5 is isostructural with 6. The central metal also contacts the nitrogen and sulfur atoms from the PhNCS unit, whereas the hydrazonido group shifts to the center carbon of PhNCS and is not coordinated to the metal atom. Its bond lengths and angles are comparable to the corresponding values observed in 6, when the differences in the metal ionic radii are considered.

**Reaction of 2 with PhCN.** In recent years, organic nitriles have been useful reagents in organic synthesis for the construction of many important N-heterocyclic compounds, and thus their reactivity toward organometallic chemistry.<sup>20</sup> Upon comparison with the investigations on the reactivity of organolanthanide hydrides and alkyl complexes with nitriles, which have provided many important organometallic reactions and interesting structures,<sup>21,22</sup> examples of

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Figure 3. Thermal ellipsoid plot of  $Cp_2Ln(\eta^2-OC(NHPh))$ NN=CPh<sub>2</sub>)(HMPA) (Ln = Yb (3), Er (4)), with ellipsoids at the 30% probability level. Selected bond lengths in 3 (Å): Yb-(1)-O(2) = 2.230(7), Yb(1)-O(1) = 2.233(8), Yb(1)-N(2) =2.593(9), N(1)-C(8) = 1.309(13), N(1)-N(2) = 1.401(12), N-(2)-C(1) = 1.337(14), N(3)-C(1) = 1.338(14), O(1)-C(1) =1.271(13), O(2)-P(1) = 1.474(7). Selected bond angles in 3 (deg): O(1)-Yb(1)-N(2) = 53.7(3), C(8)-N(1)-N(2) = 121.6(9), C(1)-N(2)-N(1) = 108.5(9), C(1)-N(2)-Yb(1) = 86.1(7),N(1)-N(2)-Yb(1) = 164.0(7). Selected bond lengths in 4 (Å): Er(1)-O(2) = 2.244(9), Er(1)-O(1) = 2.332(8), Er(1)-N(2) =2.486(10), N(1)-C(8) = 1.314(15), N(1)-N(2) = 1.376(14), N-(2)-C(1) = 1.329(15), N(3)-C(1) = 1.390(16), O(1)-C(1) =1.248(15), O(2)-P(1) = 1.466(9). Selected bond angles in 4 (deg): O(1)-Er(1)-N(2) = 54.7(3), C(8)-N(1)-N(2) = 118(1),C(1)-N(2)-N(1) = 111(1), C(1)-N(2)-Er(1) = 87(1), O(1)-C(1)-N(2) = 119(1), O(1)-C(1)-N(3) = 120(1), N(2)-C(1)-N(3) = 121(1), O(1)-C(1)-N(2) = 115(1), O(1)-C(1)-N-(3) = 120(1), N(2)-C(1)-N(3) = 125(1), N(1)-N(2)-Er-(1) = 144(1).

reactions of organolanthanide amides with nitriles have scarcely been reported.<sup>22c,22e,22g</sup> Recently, we found that the cyano group of anthranilonitrile can continuously insert into the Ln-N(primary amide) bond to construct a quinazolinate moiety.<sup>12f</sup> With the organolanthanide hydrazonido complex 2 in hand, we also explored its reactivity toward benzonitrile and tert-butyl isocyanide. As shown in Scheme 3, when phenyl isocyanate was added to a THF solution of 2 at room temperature, the new organolanthanide heterometallacycle  $Cp_2Er[\eta^2-NHC(Ph)NN=CPh_2]$  (7) was obtained, indicating that PhCN inserts into the lanthanide-nitrogen (hydrazonido) bond in concert with a 1,3hydrogen migration.<sup>6b</sup> However, treatment of 2 with 'BuNC gave only the solvent-free dimer  $[Cp_2Er(\mu-\eta^1:\eta^2-\eta^2)]$ NHN= $CPh_2$ ]<sub>2</sub> (2'), indicating that <sup>t</sup>BuNC cannot insert into the lanthanide-nitrogen bond of 2.

The molecular structure and important bond lengths and angles of 7 ares shown in Figure 5. The X-ray crystal analysis shows that the hydrazonido group in 7 has combined with benzonitrile, forming a five-membered heterometallacycle. As expected, the bond angles around C14 are consistent with  $sp^2$  hybridization, and the resulting heterometallacycle is planar within experimental error (the sum of angles in this ring is 537.5°). The C14–N2 bond distance, 1.295(14) Å, is





Figure 4. Thermal ellipsoid plot of  $Cp_2Ln(\eta^2-SC(NHN=CPh_2))$ NPh)(HMPA) (Ln = Yb (5), Er (6)), with ellipsoids at the 30%probability level. Selected bond lengths for 5 (Å): Yb(1)-O-(1) = 2.215(8), Yb(1)-N(3) = 2.520(9), Yb(1)-S(1) = 3.146(3), N(1)-N(2) = 1.442(8), N(1)-C(8) = 1.497(14), N(2)-C-(1) = 1.534(14), N(3)-C(1) = 1.471(15), O(1)-P(1) = 1.437(8), S(1)-C(1) = 1.676(12). Selected bond angles for 5 (deg): N-(3)-Yb(1)-S(1) = 54.9(2), N(2)-N(1)-C(8) = 131.2(9), N-(1)-N(2)-C(1) = 128.0(9), C(1)-N(3)-Yb(1) = 108.2(6), C-108.2(6)(1)-S(1)-Yb(1) = 79.8(4), N(3)-C(1)-N(2) = 130.3(9), N-(3)-C(1)-S(1) = 116.0(8), N(2)-C(1)-S(1) = 113.7(8). Selected bond lengths for 6 (Å): Er(1)-O(1) = 2.237(7), Er(1)-N-(3) = 2.500(8), Er(1) - S(1) = 2.744(3), S(1) - C(1) = 1.722(10),N(1)-C(8) = 1.291(11), N(1)-N(2) = 1.369(11), N(2)-C(1) =1.360(12), N(3)-C(1) = 1.312(12), O(1)-P(1) = 1.491(7).Selected bond angles for 6 (deg): N(3)-Er(1)-S(1) = 58.9(2), C(1)-S(1)-Er(1) = 82.4(3), C(8)-N(1)-N(2) = 117.0(8),C(1)-N(2)-N(1) = 119.1(8), C(1)-N(3)-Er(1) = 101.1(6), N-(2)-C(1)-S(1) = 120.8(8).

Scheme 3



comparable to the accepted value for the  $N(sp^2)=C(sp^2)$ double bond.<sup>14</sup> The N1–N2 and C1–N1 distances, 1.388 (13) and 1.268(14)Å, are in the normal ranges. Consistent with this observation, two different Er–N distances have been observed in 7. The Er1–N1 distance of 2.407(10) Å is significantly longer than the Er1–N3 distance of 2.156(10) Å. The former falls in the range of Er–N donor-bond lengths, while the latter is consistent with the Er–N singlebond length. The relative bond parameters reveal that the hydrogen atom of the hydrazido group is shifted toward the nitrogen atom on the benzonitrile moiety.<sup>6b</sup>

Positive structural verification of 2' was also provided by a single-crystal X-ray analysis. The solid-state structural analysis shows that 2' has a solvent-free centrosymmetric



Figure 5. Thermal ellipsoid plot of  $Cp_2Er[\eta^2-NHC(Ph) NN=CPh_2]$  (7), with ellipsoids at the 30% probability level. Selected bond lengths (Å): Er(1)-N(3) = 2.156(10), Er(1)-N(1) = 2.407(10), N(1)-C(1) = 1.268(14), N(1)-N(2) = 1.388 (13), N(2)-C(14) = 1.295(14), N(3)-C(14) = 1.333(16), C-(14)-C(15) = 1.504(14). Selected bond angles (deg): N(3)-Er(1)-N(1) = 66.7(4), N(2)-N(1)-Er(1) = 116.4(8), C(14)-N(2)-N(1) = 110.9(10), C(14)-N(3)-Er(1) = 121.6(8), N(2)-C(14)-N(3) = 121.9(11), N(2)-C(14)-C(15) = 113.3 (11), N(3)-C(14)-C(15) = 124.7(11).

dimeric structure (Figure 6) in which the hydrazido ligand acts as both a bridging and a side-on chelating group. The bonding mode of the hydrazonido groups in 2' is significantly different from those observed in 1 and 2. The six atoms Er1, N1, N2, Er1A, N1A, and N2A form an interlinked tricyclic structure via two bridged nitrogen atoms.

#### Conclusions

We have synthesized three new organolanthanide hydrazonido(1–) complexes, wherein three kinds of bonding modes of the hydrazonido ligand to lanthanide metals were observed. Further studies on their reactivity toward unsaturated organic molecules indicate that PhNCO and PhCN can formally monoinsert into the N–H bond of these organolanthanide hydrazonido(1–) complexes, while PhNCS can



Figure 6. Thermal ellipsoid plot of  $[Cp_2Er(\mu-\eta^1:\eta^2-NHN=CPh_2)]_2$ (2'), with ellipsoids at the 30% probability level. Selected bond lengths (Å): Er(1)-N(1) = 2.37(2), Er(1)-N(2) = 2.40(2), Er(1)-N(1A) = 2.41(2), N(1)-N(2) = 1.36(3), N(2)-C(1) =1.29(3). Selected bond angles (deg): N(1)-Er(1)-N(2) = 33.2(7), N(1)-Er(1)-N(1A) = 80.8(7), N(2)-Er(1)-N(1A) =109.9(7), N(2)-N(1)-Er(1) = 74.6(13), N(2)-N(1)-Er(1A) =151.3(17), Er(1)-N(1)-Er(1A) = 99.2(7), C(1)-N(2)-N(1) = 120(2), C(1)-N(2)-Er(1) = 158(2), N(1)-N(2)-Er-(1) = 72.3(13).

only insert the lanthanide–nitrogen bond. These results clearly demonstrate that the hydrazonido(1-) ligand bound to the lanthanide metal can undergo versatile reactions to afford a variety of novel organolanthanide complexes.

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Supporting Information Available: Text, tables, and CIF files giving X-ray structure determination details for 1-7 and 2'. This material is available free of charge via the Internet at http://pubs.acs.org.