

## Synthesis, Structure, and Reaction Chemistry of Samarium(II), Europium(II), and Ytterbium(II) Complexes of the Unsymmetrical Benzamidinate Ligand $[\text{PhC}(\text{NSiMe}_3)(\text{NC}_6\text{H}_3\text{Pr}^i_{2-2,6})]^-$

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Neutral mononuclear lanthanide(II) bis(amidinate) complexes  $[\text{LnL}_2(\text{THF})_x]$  [ $\text{L} = \text{PhC}(\text{NSiMe}_3)(\text{NC}_6\text{H}_3\text{Pr}^i_{2-2,6})^-$ ;  $\text{Ln} = \text{Sm}$ ,  $x = 2$  (**3**);  $\text{Ln} = \text{Eu}$ ,  $x = 2$ , (**4**);  $\text{Ln} = \text{Yb}$ ,  $x = 1$  (**5**)] were synthesized by the reaction of the appropriate  $\text{LnL}_2(\text{THF})_2$  with potassium amidinate  $[\text{KL}]_n$  (**2**). The reduction chemistry of **3–5** was also examined. The reaction of the Sm(II) and Eu(II) amidinates **3** and **4** with diphenyl dichalcogenides  $\text{PhEPh}$  ( $\text{E} = \text{Se}$ ,  $\text{Te}$ ) led to the binuclear lanthanide(III) amidinate-chalcogenolate complexes  $[\text{LnL}_2(\mu\text{-EPh})_2]$  [ $\text{Ln} = \text{Sm}$ ,  $\text{E} = \text{Se}$  (**6**);  $\text{Ln} = \text{Eu}$ ,  $\text{E} = \text{Se}$  (**7**);  $\text{Ln} = \text{Sm}$ ,  $\text{E} = \text{Te}$  (**9**)], whereas reacting the Yb(II) bis(amidinate) **5** with  $\text{PhSeSePh}$  yielded the mononuclear  $[\text{YbL}_2(\text{SePh})(\text{THF})]$  (**8**). The reaction of **5** with iodine led to the Yb(III) bis(amidinate) iodide complex  $[\text{YbL}_2(\text{I})(\text{THF})]$  (**10**). Treatment of **3** with *N,N'*-dicyclohexylcarbodiimide afforded the mixed-ligand Sm(III) tris(amidinate)  $[\text{SmL}_2\{\text{CyNC}(\text{H})\text{NCy}\}]$  (**11**) ( $\text{Cy} = \text{cyclohexyl}$ ). The molecular structures of complexes **2–5** and **7–11** were elucidated by X-ray diffraction analyses.

### Introduction

Over the past decades, tremendous research efforts have been devoted to the development of various types of ancillary ligands as alternatives for cyclopentadienyl ligands.<sup>1,2</sup> Among those cyclopentadienyl alternatives, amidinate ligands  $[\text{R}^1\text{NC}(\text{R}^2)\text{NR}^1]^-$  have proved to be versatile, forming stable complexes with a wide range of metals.<sup>3,4</sup> Their steric

and electronic properties can be readily modified by introduction of various  $\text{R}^1$  and  $\text{R}^2$  substituents. Amidinates are useful ligands in organolanthanide chemistry,<sup>5</sup> and a number of trivalent lanthanide amidinates have been reported.<sup>1,5–12</sup> In contrast, the chemistry of their divalent counterparts remains an underdeveloped area. Edelmann and co-workers<sup>13</sup> have reported a series of mononuclear Yb(II) benzamidinate complexes  $[\text{Yb}\{(\text{RC}_6\text{H}_4)\text{C}(\text{NSiMe}_3)_2\}_2(\text{THF})_2]$  ( $\text{R} = \text{H}$ ,  $\text{OMe}$ ,  $\text{Ph}$ ). The reactivity of some of these complexes toward reduction of diaryl dichalcogenides  $\text{REER}$  ( $\text{R} = \text{Ph}$ ,  $\text{Me}$ ;  $\text{E} = \text{Se}$ ,  $\text{Te}$ ) was also studied.<sup>13b</sup> Recently, Junk and co-workers<sup>14</sup> have reported the sterically hindered complex

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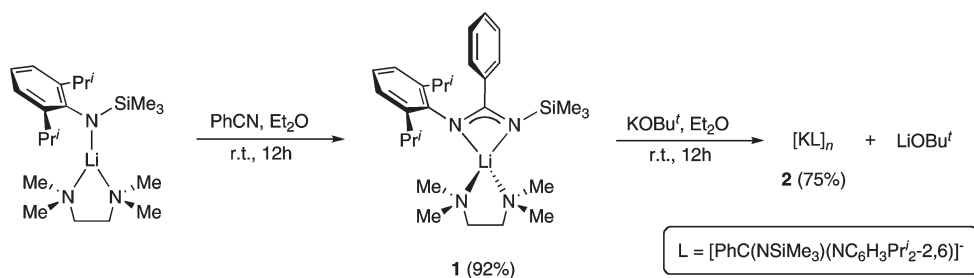
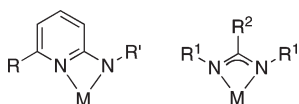
Scheme 1. Synthesis of Complexes **1** and **2**

Chart 1



[Sm{HC(NC<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2-2,6</sub>)<sub>2</sub>}(THF)<sub>2</sub>], which represents the first example of a Sm(II) bis(amidinate) to be synthesized and structurally characterized. This Sm(II) complex can be readily converted to its homoleptic Sm(III) counterpart.

Our current research interest focuses on the chemistry of metal complexes supported by anionic nitrogen-based ligands.<sup>15</sup> Earlier, we have reported on the coordination chemistry of the chelating 2-pyridyl amido ligand [N(SiBu<sup>*t*</sup>Me<sub>2</sub>)-(2-C<sub>5</sub>H<sub>3</sub>N-6-Me)]<sup>-</sup> toward trivalent lanthanides.<sup>15d</sup> Besides, we have also reported a series of divalent transition metal (Mn–Ni) complexes derived from the unsymmetrical benzamidinate ligand [PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)]<sup>-</sup>.<sup>15e</sup> One common feature of the 2-pyridyl amido system and the amidinato system is the presence of a NCN ligand backbone. This results in the formation of four-membered MNCN metallacyclic rings when these ligands coordinate to metal centers in a chelating fashion (Chart 1). Continuing our work on the unsymmetrical amidinato ligand system,<sup>15e</sup> we have extended our studies to the lanthanide series using a sterically more bulky 2,6-diisopropylphenyl substituted [PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2-2,6</sub>)]<sup>-</sup> (L) ligand.<sup>16</sup> Herein, we report on the synthesis and structural characterization of lanthanide(II) bis(amidinate) complexes [LnL<sub>2</sub>(THF)<sub>*x*</sub>] (Ln = Sm and Eu, *x* = 2; Ln = Yb, *x* = 1). To the best of our knowledge, complex [EuL<sub>2</sub>(THF)<sub>2</sub>] is the first structurally authenticated Eu(II) amidinate. The reaction chemistry of the present lanthanide(II) amidinates toward reduction of diphenyl dichalcogenides PhEPh (E = Se, Te), iodine, and *N,N'*-dicyclohexylcarbodiimide was also examined in our studies.

## Results and Discussion

**Synthesis of Lithium and Potassium Salts of [PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2-2,6</sub>)]<sup>-</sup> (L).** The lithium benzamidinate complex [LiL(TMEDA)] (**1**) (TMEDA = *N,N,N'*,

*N'*-tetramethylethylenediamine) was readily prepared by the reaction of the lithium amide [Li{N(SiMe<sub>3</sub>)(C<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2-2,6</sub>)}(TMEDA)]<sup>17</sup> with benzonitrile (Scheme 1). The reaction involves nucleophilic attack of the [N(SiMe<sub>3</sub>)-(C<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2-2,6</sub>)]<sup>-</sup> anion to the C≡N functional group of benzonitrile, followed by 1,3-silyl migration. Complex **1** gave satisfactory elemental analysis. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1** showed one set of resonance signals due to the L ligand and TMEDA. It is noteworthy that the methyl protons of the isopropyl substituents of the L ligand occurred as two doublets at 1.22 and 1.25 ppm, respectively, indicating that the isopropyl methyl groups are diastereotopic. This may be attributed to hindered rotation about the N–C<sub>*ipso*</sub> bond.<sup>18</sup>

X-ray diffraction analysis revealed that **1** is mononuclear with the Li atom coordinated by a κ<sup>2</sup>-bound L<sup>-</sup> anion and a chelating TMEDA ligand (Figure 1).<sup>19</sup> The coordination geometry around the lithium atom can be described as distorted tetrahedral. The almost identical C(13)–N(1) (1.319(1) Å) and C(13)–N(2) (1.330(2) Å) distances indicate delocalization of the anionic charge over the amidinato NCN moiety. The Li(1)–N(1) and Li(1)–N(2) distances of 2.041(3) and 2.052(4) Å, respectively, are only marginally longer than the corresponding bond lengths of 2.009(3) and 2.032(3) Å in the closely related [Li{PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)}(TMEDA)].<sup>15e</sup>

The potassium salt of the L ligand was prepared by a transmetalation reaction of [LiL(TMEDA)] (**1**) with KOBu<sup>*t*</sup>. Addition of **1** to a slurry of KOBu<sup>*t*</sup> in diethyl ether at room temperature yielded potassium benzamidinate **2**, which was isolated as very air-sensitive, colorless crystals. Compound **2** is soluble in THF, but only sparingly soluble in toluene, diethyl ether, and hexane. Its <sup>1</sup>H and <sup>13</sup>C NMR spectra showed one set of resonance signals, which were assignable to the L ligand. The methyl groups of the isopropyl substituents of the L ligand in **2** are also diastereotopic, as revealed by the occurrence of two doublets at 1.10 and 1.17 ppm, respectively, in its <sup>1</sup>H NMR spectrum.

The solid-state structure of **2** was determined by X-ray crystallography. Compound **2** crystallizes as a one-dimensional polymer made up of linked binuclear K<sub>2</sub>L<sub>2</sub> subunits (Figure 2). Each potassium atom in **2** is bound by

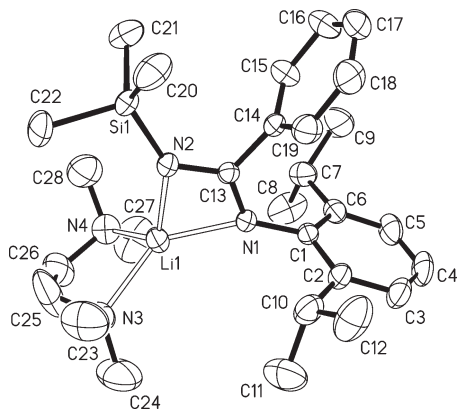
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(16) As compared to the less hindered [PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)]<sup>-</sup> ligand reported previously by our group (ref <sup>15e</sup>), the sterically more bulky L ligand was anticipated to be a potential candidate, providing sufficient steric shielding, for the preparation of neutral, mononuclear lanthanide(II) complexes.

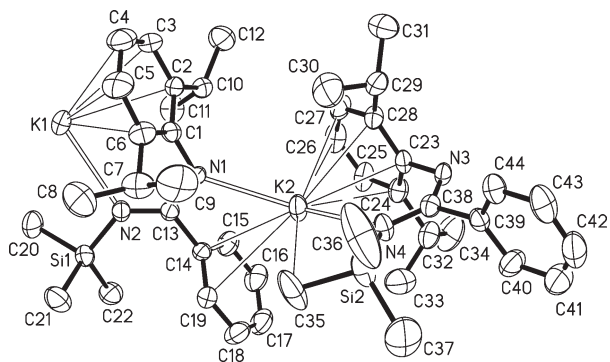
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(19) Selected bond distances (Å) and angles (deg) for complexes **1–5**, **7**, **8**, **9**–**7**H<sub>8</sub>, **10**, and **11** are provided in Tables S1–10, respectively. See Supporting Information.



**Figure 1.** Molecular structure of [LiL(TMEDA)] (**1**) (30% thermal ellipsoids) with atom labeling.

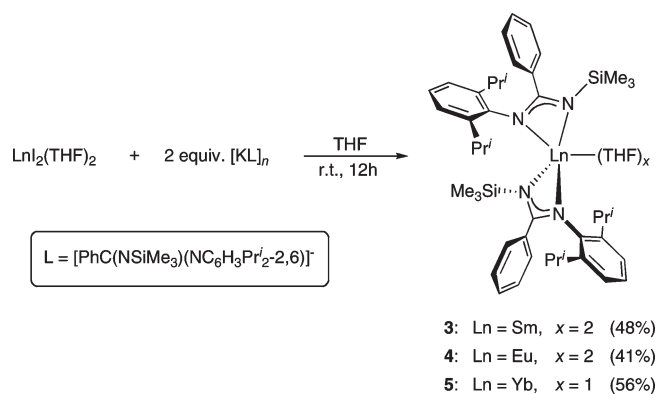


**Figure 2.** Polymeric structure of [KL]<sub>n</sub> (**2**) (30% thermal ellipsoids) with atom labeling.

a L ligand in an unusual  $\eta^1$ -amide: $\eta^6$ -arene fashion. A similar  $\eta^1$ : $\eta^6$ -binding mode of amidinate ligands has been observed in the potassium formamidinate complexes [K(FMes)(FMes)] [FMes = HC(NC<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)<sub>2</sub>]<sup>20</sup> and [K(DippForm)<sub>2</sub>K(THF)<sub>2</sub>]<sub>n</sub> · xTHF (DippForm = HC(NC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sub>2</sub>)<sup>21</sup>. The potassium–nitrogen distances of 2.846(6) Å [K(1)–N(2)] and 2.824(7) Å [K(2)–N(4)] in **2** are longer than the corresponding distance in [K(FMes)(FMes)] (2.719(1) Å),<sup>20</sup> but comparable to that of 2.863(4) Å in [K(DippForm)<sub>2</sub>K(THF)<sub>2</sub>]<sub>n</sub> · xTHF.<sup>21</sup> The K(1)–C(centroid) and K(2)–C(centroid) distances in complex **2** are 2.908 Å and 2.864 Å, respectively. They are similar to the corresponding distance of 2.887(7) Å in [K(FMes)(FMes)],<sup>20</sup> but slightly shorter than that (3.034(9) Å) in [K(DippForm)<sub>2</sub>K(THF)<sub>2</sub>]<sub>n</sub> · xTHF.<sup>21</sup> Each potassium atom in **2** is further coordinated to the C=N bond of the NCN moiety of a neighboring L ligand, completing the one-dimensional polymeric structure of the compound [K(1)–N(3)#1 2.760(6) Å, K(1)–C(38)#1 3.505(9) Å, K(2)–N(1) 2.807(6) Å, and K(2)–C(13) 3.488(8) Å].

**Synthesis and Structures of Lanthanide(II) Bis(amidinate) Complexes.** The potassium benzamidinate [KL]<sub>n</sub> (**2**) was used as a ligand-transfer reagent in subsequent studies. Divalent samarium, europium, and ytterbium complexes with the L ligand were readily prepared by metathesis reactions of the appropriate LnI<sub>2</sub>(THF)<sub>2</sub> (Ln = Sm, Eu and Yb) with **2**. As outlined in Scheme 2,

**Scheme 2.** Synthesis of Complexes **3–5**



addition of two molar equivalents of **2** to a solution of SmI<sub>2</sub>(THF)<sub>2</sub> in THF at room temperature yielded the Sm(II) bis(amidinate) [SmL<sub>2</sub>(THF)<sub>2</sub>] (**3**) as deep greenish blue crystals in a moderate yield. A 1:1 reaction of SmI<sub>2</sub>(THF)<sub>2</sub> and **2** was also examined. In our hands, treatment of SmI<sub>2</sub>(THF)<sub>2</sub> with one molar equivalent of **2** led to **3** as the only isolable product. Analogous reactions of EuI<sub>2</sub>(THF)<sub>2</sub> and YbI<sub>2</sub>(THF)<sub>2</sub> with two molar equivalents of **2** in THF led to [EuL<sub>2</sub>(THF)<sub>2</sub>] (**4**) (orange crystals) and [YbL<sub>2</sub>(THF)] (**5**) (dark red crystals), respectively. All of the complexes **3–5** are extremely sensitive to air and moisture. They are readily soluble in common organic solvents. Their formulations were confirmed by elemental analysis and NMR spectroscopy (for the diamagnetic Yb(II) complex **5**). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5** showed one set of resonance signals which were assignable to a pair of L ligands and one THF molecule. Similar to the lithium and potassium derivatives **1** and **2**, the methyl groups of the isopropyl substituents in **5** are also diastereotopic. This is indicated by the occurrence of two doublet signals at 1.27–1.40 ppm in its <sup>1</sup>H NMR, as well as two resonance signals at 22.9 and 25.9 ppm in its <sup>13</sup>C NMR spectrum.

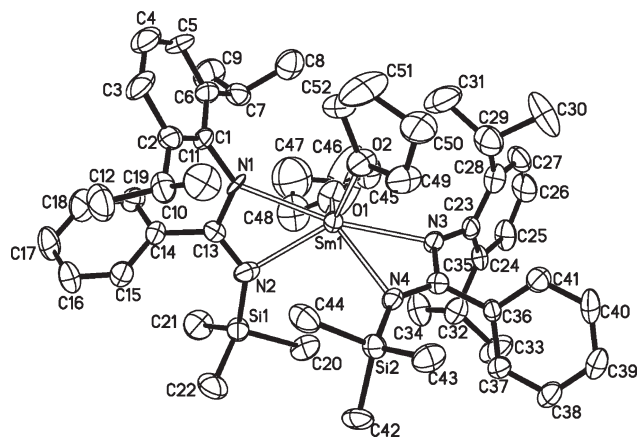
Single crystals of complexes **3–5** suitable for X-ray diffraction analysis were obtained from *n*-hexane. The Sm(II) bis(amidinate) **3** crystallizes in the monoclinic space group *Cc*. Figure 3 shows the crystal structure of complex **3**, with selected bond distances and angles provided in Supporting Information, Table S3.<sup>22</sup> The asymmetric unit of **3** consists of four independent molecules of nearly the same structure. Each Sm atom is bound by a pair of  $\kappa^2$ -bound L ligands and two THF molecules. The complex exhibits a *cisoid* structure with a crystallographic C<sub>2</sub> axis passing through the Sm(II) center. The Sm–N distances in **3**, which fall within the range of 2.49(1)–2.67(1) Å, are comparable to those reported for [Sm{HC(NC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sub>2</sub>}(THF)<sub>2</sub>] (2.529(3) and 2.617(3) Å)<sup>14</sup> and the four-coordinate Sm(II) bis(guanidinate) [Sm{(2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>N)<sub>2</sub>C(NC<sub>2</sub>Y)<sub>2</sub>}] (2.529(2)–2.570(2) Å).<sup>23</sup> The Sm–O(THF) bond lengths of 2.61(1)–2.64(1) Å in **3** are similar to the corresponding distances in [Sm{HC(NC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sub>2</sub>}(THF)<sub>2</sub>] (2.599(3) and 2.560(3) Å).<sup>14</sup> The acute N–C–N bite angles of the L ligands in **3** (51.3(3)–53.7(4)°)

(22) The carbon atoms of the coordinated THF molecules in complex **3** exhibit large thermal motion. They were refined with isotropic thermal parameters and subjected to atom-atom distance restraints.

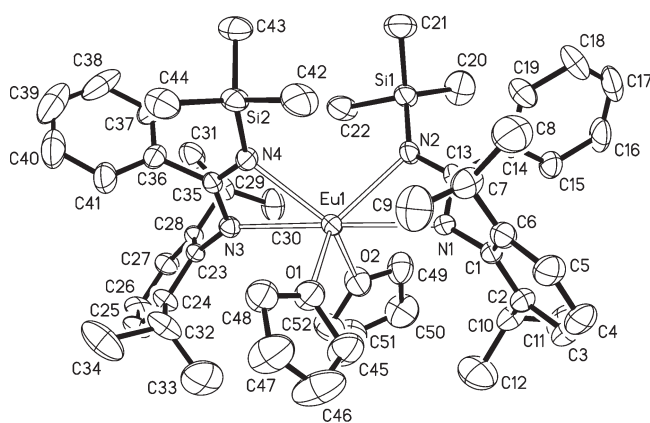
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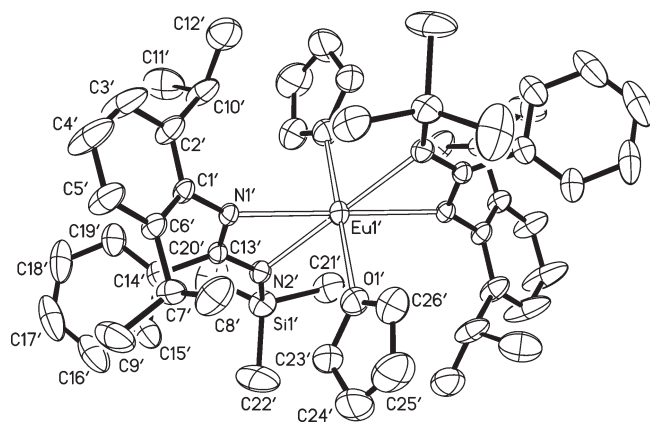
**Figure 3.** Molecular structure of  $[\text{SmL}_2(\text{THF})_2]$  (**3**) (30% thermal ellipsoids) with atom labeling. Only one of the four independent molecules in the asymmetric unit is shown.



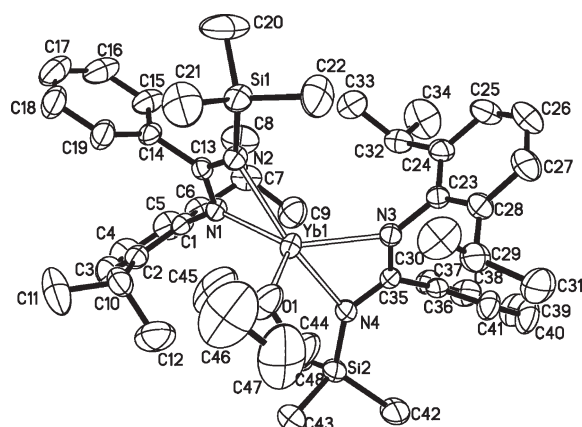
**Figure 4.** Molecular structure of the *cisoid* isomer in the crystal structure of  $[\text{EuL}_2(\text{THF})_2]$  (**4**). Each asymmetric unit consists of one molecule of a *cisoid* isomer. Thermal ellipsoids were plotted at 30% probability level.

are similar to that of  $52.9(1)^\circ$  reported for  $[\text{Sm}\{\text{HC}(\text{NC}_6\text{H}_3\text{Pr}^i_2\text{-}2,6)_2\}_2(\text{THF})_2]$ ,<sup>14</sup> and those of  $52.55(7)^\circ$  and  $52.18(7)^\circ$  in  $[\text{Sm}\{(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3\text{N})_2\text{C}(\text{NCy}_2)_2\}]_2$ .<sup>23</sup>

Complex **4** crystallizes in the monoclinic space group  $P2_1/c$ . Interestingly, the asymmetric unit consists of one molecule of a *cisoid* isomer and a “half” molecule of a *transoid* isomer. The molecular structures of the *cisoid* and *transoid* isomers of **4** are depicted in Figures 4 and 5, respectively. Selected bond lengths and angles for the complex are listed in Supporting Information, Table S4. The *cisoid* isomer exhibits non-crystallographic  $C_2$  symmetry with two  $\kappa^2$ -bound L ligands and two “*cis*” THF molecules [ $\text{O}(1)\text{—Eu}(1)\text{—O}(2) = 109.0(1)^\circ$ ]. The coordination geometry around the Eu(II) center in this isomer can be described as distorted octahedral. On the other hand, the *transoid* isomer is located at an inversion center and conforms closely to  $C_{2h}$  symmetry. Four amidinato nitrogen atoms form an equatorial plane, while two “*trans*” THF molecules occupy the axial positions [ $\text{O}(1')\text{—Eu}(1')\text{—O}(1'') = 180.0(2)^\circ$ ]. The Eu—N distances of the two isomeric forms of **4** are similar, covering the range of  $2.526(4)\text{—}2.768(4)$  Å. They are comparable to the corresponding distances of  $2.525(2)\text{—}2.563(2)$  Å reported for the related Eu(II) bis(guanidinate) complex  $[\text{Eu}\{(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3\text{N})_2\text{C}(\text{NCy}_2)_2\}]_2$ .<sup>23</sup> Similar Eu(II)—N distances were also reported for the Eu(II) diamide  $[\text{Eu}\{\text{N}(\text{Si}$



**Figure 5.** Molecular structure of the *transoid* isomer in the crystal structure of complex **4**. The Eu atom is located at an inversion center. Thermal ellipsoids were plotted at 30% probability level. Symmetry transformation:  $1-x, 1-y, 1-z$ .



**Figure 6.** Molecular structure of  $[\text{YbL}_2(\text{THF})]$  (**5**) (30% thermal ellipsoids) with atom labeling.

$\text{Me}_3\}_2(\text{DME})_2]$  (Eu—N =  $2.530(4)$  Å, DME = 1,2-dimethoxyethane).<sup>24a</sup> However, they are slightly longer than the terminal Eu—N distance of  $2.448(4)$  Å in  $[\text{Na-Eu}\{\text{N}(\text{SiMe}_3)_2\}_3]$ .<sup>24b</sup> The Eu—O(THF) bond distance of the *transoid* isomer ( $2.604(4)$  Å) is slightly longer than those of the *cisoid* form ( $2.527(4)$  and  $2.570(4)$  Å). The N—C—N bite angles of the L ligands in **4** are acute, falling within the range of  $50.9(1)$  to  $52.4(1)^\circ$ .

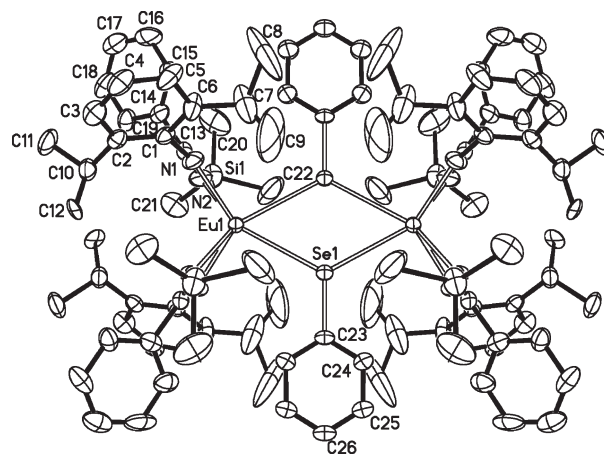
The Yb(II) bis(amidinate) **5** is present as a mono-THF adduct. The molecular structure of **5** is illustrated in Figure 6, with selected bond distances and angles provided in Supporting Information, Table S5. The complex has a five-coordinate ligand environment, which consists of four amidinato nitrogen atoms from a pair of  $\kappa^2$ -bound L ligands and one oxygen atom of a coordinated THF molecule. It is believed that the smaller ionic radius of  $\text{Yb}^{2+}$  in **5** (as compared with those of  $\text{Sm}^{2+}$  and  $\text{Eu}^{2+}$  in **3** and **4**, respectively) can allow the coordination of only one THF ligand. The Yb—N distances of  $2.399(3)\text{—}2.453(4)$  Å are marginally shorter than the corresponding distances in the six-coordinate  $[\text{Yb}\{\text{PhC}(\text{NSiMe}_3)_2\}_2(\text{THF})_2]$  ( $2.468(2)$  and  $2.478(2)$  Å).<sup>13</sup> However, they are comparable to those

(24) (a) Tilley, T. D.; Zalkin, A.; Andersen, R. A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 551–554. (b) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, *23*, 2271–2276.

(2.378(2)–2.430(2) Å) reported for the mononuclear Yb(II) bis(guanidinate) [Yb{(2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>N)<sub>2</sub>C(NC<sub>2</sub>Y)<sub>2</sub>}]<sub>2</sub>, and 2.373(3) and 2.426(3) Å for the binuclear [Yb{(2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>N)<sub>2</sub>C(NC<sub>2</sub>Y)<sub>2</sub>}(THF)(μ-I)]<sub>2</sub>.<sup>23</sup>

**Reduction Chemistry of Complexes 3–5.** Divalent lanthanide complexes are strong reducing agents. The reduction potentials of the Eu<sup>3+</sup>/Eu<sup>2+</sup>, Yb<sup>3+</sup>/Yb<sup>2+</sup>, and Sm<sup>3+</sup>/Sm<sup>2+</sup> couples were reported to be –0.35, –1.15, and –1.55 V (versus NHE), respectively.<sup>25</sup> Their reducing properties have been well documented,<sup>26,27</sup> particularly the use of SmI<sub>2</sub> as a coupling or reducing agent in synthetic chemistry.<sup>28</sup> Early work on the redox chemistry of organolanthanide(II) compounds was focused on divalent metallocene complexes. Evans and co-workers have studied the redox chemistry of samarocene complexes in detail.<sup>27,29</sup> Recently, the reduction of *N,N'*-dicyclohexylcarbodiimide by [Sm(MeC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>(THF)] has also been reported.<sup>30</sup> Andersen and co-workers<sup>31</sup> have studied the reduction of dichalcogenides by divalent ytterbocene complexes. Beside cyclopentadienyl complexes, there were also a few reports on the reduction chemistry of organolanthanide(II) complexes supported by non-cyclopentadienyl ligands. Edlmann and co-workers<sup>13</sup> have studied the reactivity of [Yb{RC<sub>6</sub>H<sub>4</sub>C(NSiMe<sub>3</sub>)<sub>2</sub>}(THF)]<sub>2</sub> (R = H, OMe) toward reduction of diaryl dichalcogenides. The reduction of carbodiimides by Sm(II) amido complexes of the [N(SiMe<sub>3</sub>)<sub>2</sub>]<sup>–</sup> ligand has been examined by Junk and co-workers as well.<sup>32</sup> In the present work, we have examined the reduction chemistry of complexes 3–5 toward diphenyl dichalcogenides PhEPh (E = Se, Te), iodine and *N,N'*-dicyclohexylcarbodiimide.

**1. Reactions of Complexes 3–5 with PhEPh (E = Se, Te).** Treatment of two molar equivalents of [SmL<sub>2</sub>(THF)<sub>2</sub>] (3) with PhSeSePh in hexane resulted in a gradual color change of the reaction mixture from deep greenish blue to yellow, from which Sm(III) benzamidinate-selenolate complex 6 was isolated as yellow crystals. The Eu(II) bis(amidinate) 4 reacted smoothly with PhSeSePh under similar reaction condition yielding the dark red, crystalline Eu(III) derivative 7 (Scheme 3). Results of elemental analyses were in good agreement with the formulation of 6 and 7 as shown in Scheme 3. The molecular structure of complex 7 was determined by X-ray diffraction.<sup>33</sup> As depicted in Figure 7, complex 7 crystallizes as a dimer with a planar Eu<sub>2</sub>Se<sub>2</sub> core. The complex conforms closely to C<sub>2h</sub> symmetry with a crystallographic 2-fold axis passing through both Eu atoms. Each Eu atom



**Figure 7.** Molecular structure of [EuL<sub>2</sub>(μ-SePh)<sub>2</sub>] (7) (30% thermal ellipsoids) with atom labeling. The [PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)]<sup>–</sup> (L) ligand is 2-fold disordered and only one of the two possible orientations is shown for clarity.

is coordinated by two κ<sup>2</sup>-bound benzamidinate ligands and two bridging phenylselenolate ligands. The coordination geometry around the Eu(III) center can be described as distorted octahedral. The L ligands bind to the Eu atom in a slightly unsymmetrical manner, as revealed by the slightly different Eu(1)–N(1) and Eu(1)–N(2) bond distances of 2.362(5) Å and 2.442(5) Å, respectively. This may be ascribed to a difference in the size of the C<sub>6</sub>H<sub>3</sub>-Pr<sup>i</sup><sub>2</sub>-2,6 and SiMe<sub>3</sub> substituents attached to N(1) and N(2), respectively. The observed Eu(1)–Se(1) bond length in 7 is 3.0813(6) Å.

On the other hand, treatment of [YbL<sub>2</sub>(THF)] (5) with PhSeSePh under a similar reaction condition yielded the mononuclear [YbL<sub>2</sub>(SePh)(THF)] (8) (Scheme 3). The molecular structure of 8 is shown in Figure 8, with selected bond distances and angles listed in Supporting Information, Table S7. The Yb(III) center in 8 exhibits hexacoordinate geometry surrounded by two chelating L ligands, one terminal PhSe<sup>–</sup> ligand and one THF molecule. The difference in the molecular structures of 7 and 8 (binuclear versus mononuclear) may be attributed to a smaller ionic radius of Yb<sup>3+</sup> (0.868 Å) than that of Eu<sup>3+</sup> (0.947 Å).<sup>34</sup> The L ligands also coordinate in a slightly unsymmetrical fashion to the Yb(II) center in 8: the observed Yb–N–(C<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6) bond lengths are 2.385(4) Å [Yb(1)–N(1)] and 2.406(4) Å [Yb(1)–N(3)], whereas the corresponding Yb–N(SiMe<sub>3</sub>) distances are 2.313(4) Å [Yb(1)–N(2)] and 2.277(4) Å [Yb(1)–N(4)]. The Yb–N distances in 8 are comparable to those of 2.265(7)–2.366(7) Å reported for the related [Yb{PhC(NSiMe<sub>3</sub>)<sub>2</sub>}(SePh)(THF)].<sup>13</sup> The observed Yb(1)–Se(1) distance in complex 8 is 2.7604(7) Å, which is slightly shorter than the corresponding distance of 2.805(1) Å in the latter complex.<sup>13</sup>

The successful isolation of complexes 7 and 8 prompted us to extend our studies on the reactivity of 3–5 toward the heavier diphenyl ditelluride. Addition of PhTeTePh to [SmL<sub>2</sub>(THF)<sub>2</sub>] (3) in toluene resulted in a color change of the solution from deep greenish blue to orange. Work-up of the resultant solution yielded the Sm(III) benzamidinate-tellurate complex [SmL<sub>2</sub>(μ-TePh)]<sub>2</sub> (9) as orange crystals. Attempts to prepare the analogous Eu(III) and

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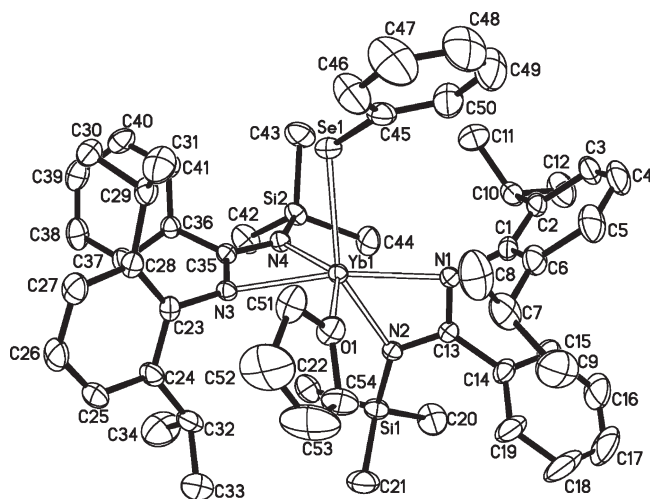
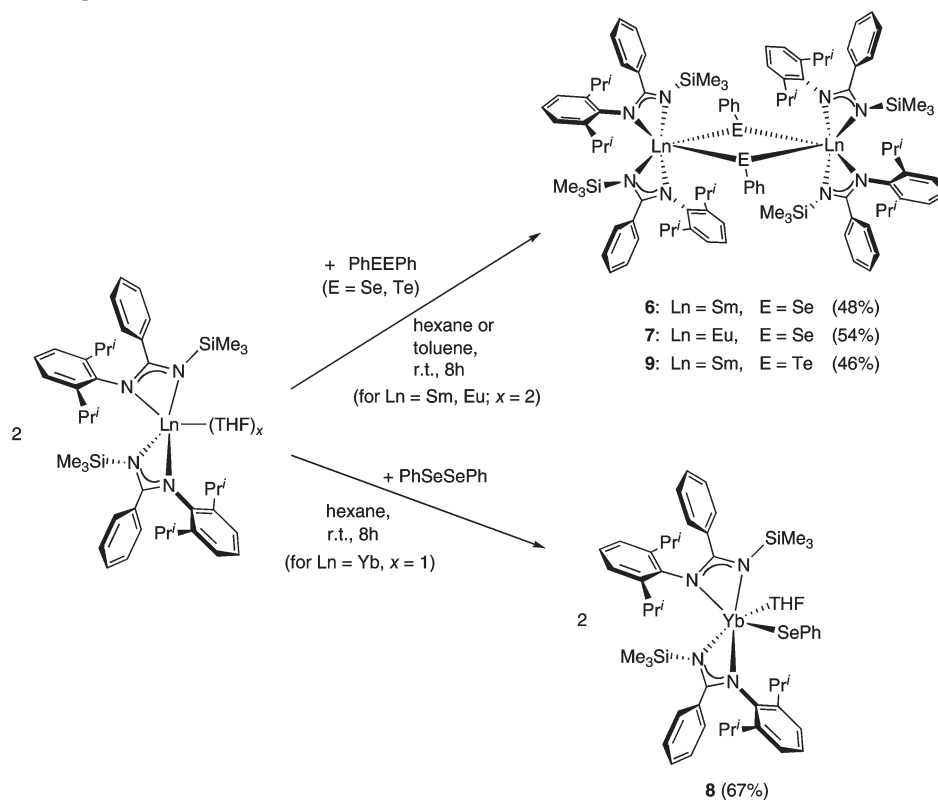
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(33) Unfortunately, attempts to obtain X-ray quality crystals of the Sm(III) derivative 6 were unsuccessful. On the basis of results of elemental analysis and the fact that Sm<sup>3+</sup> (0.958 Å) and Eu<sup>3+</sup> (0.947 Å) have similar ionic radii, it is expected that complex 6 may have a similar molecular structure as that of the Eu(III) counterpart 7.

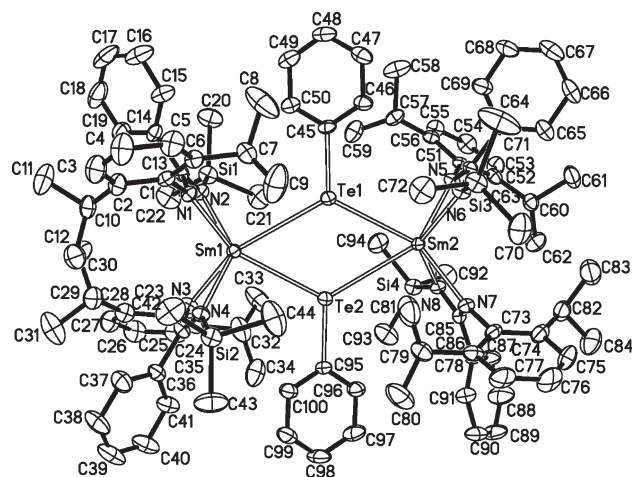
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Scheme 3. Synthesis of Complexes 6–9



**Figure 8.** Molecular structure of  $[\text{YbL}_2(\text{SePh})(\text{THF})]$  (**8**) (30% thermal ellipsoids) with atom labeling.

Yb(III) tellurate complexes by reacting **4** and **5**, respectively, with  $\text{PhTeTePh}$  were unsuccessful, as only an intractable oil was obtained. Figure 9 shows the solid-state structure of the solvated complex  $\mathbf{9} \cdot \text{C}_7\text{H}_8$ , and selected bond distances and angles are listed in Supporting Information, Table S8. Complex **9** conforms closely to  $D_2$  symmetry with a planar  $[\text{Sm}_2\text{Te}_2]$  core. Each Sm atom exhibits hexacoordinate geometry, with its coordination sphere consisting of two chelating L ligands and two bridging  $\text{PhTe}^-$  anions. In fact, the coordination geometry around each Sm atom in **9** is similar to that observed in the Eu(II) selenolate counterpart  $[\text{EuL}_2(\mu\text{-SePh})_2]$  (**7**). The Sm–N distances in **9** fall within the range



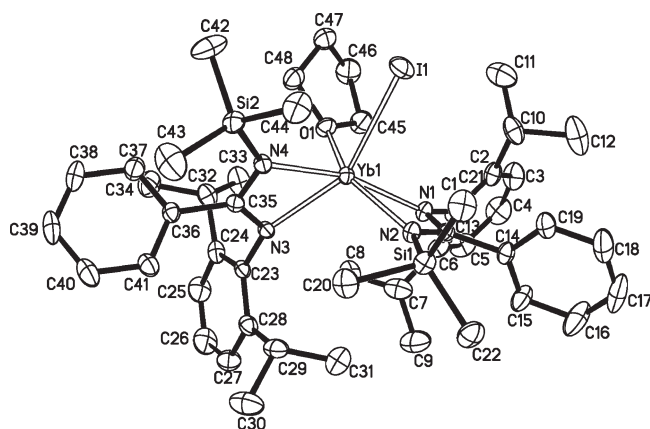
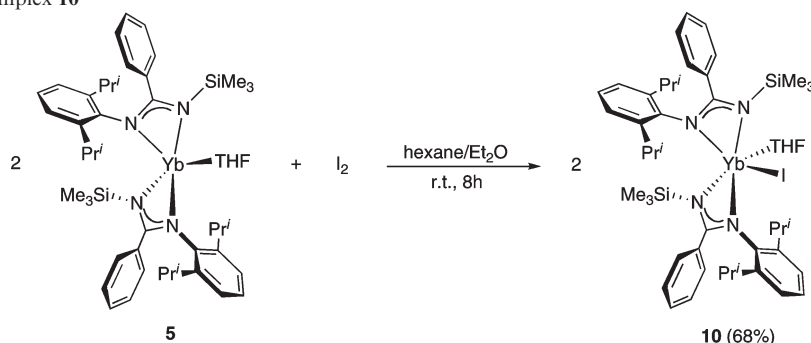
**Figure 9.** Molecular structure of  $[\text{SmL}_2(\mu\text{-TePh})_2] \cdot \text{C}_7\text{H}_8$  ( $\mathbf{9} \cdot \text{C}_7\text{H}_8$ ) (30% thermal ellipsoids) with atom labeling. The toluene solvate molecule is omitted for clarity.

of 2.367(5)–2.453(5) Å, and the Sm–Te distances are 3.2463(6)–3.3360(6) Å. The Sm–Te distances are comparable to corresponding distances of 3.2627(4) Å in dimeric  $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-TePh})_2]$ ,<sup>35</sup> but slightly longer than the terminal Sm–Te bond length of 3.1279(3) Å in monomeric  $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{TePh})(\text{THF})]$ .<sup>35</sup>

**2. Reaction of Complex 5 with Iodine.** Direct reaction of  $[\text{YbL}_2(\text{THF})]$  (**5**) with iodine resulted in formation of the mononuclear Yb(III) bis(amidinate) iodide complex  $[\text{YbL}_2(\text{I})(\text{THF})]$  (**10**), which was isolated as yellow

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Scheme 4. Synthesis of Complex 10



**Figure 10.** Molecular structure of  $[\text{YbL}_2(\text{I})(\text{THF})]$  (**10**) (30% thermal ellipsoids) with atom labeling.

crystals in 68% yield (Scheme 4). Attempts to prepare the analogous Sm(III) and Eu(III) derivatives by reacting **3** and **4** with iodine under a similar reaction condition were unsuccessful, yielding only an intractable oil. The molecular structure of **10** is illustrated in Figure 10, with selected bond lengths and angles provided in Supporting Information, Table S9. The Yb(III) center in **10** exhibits six-coordinate geometry with the Yb–N distances falling within the range of 2.290(3)–2.367(3) Å, which are comparable to those of 2.277(4)–2.406(4) Å found in the selenolate counterpart  $[\text{YbL}_2(\text{SePh})(\text{THF})]$  (**8**). Similar Yb(III)–N distances were also reported for the Yb(III) benzamidinate complex  $[\text{Yb}\{\text{PhC}(\text{NCy})_2\}_3]$  (2.321(5)–2.333(5) Å),<sup>36</sup> and the guanidinate complex  $[\text{Yb}\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2\{\text{N}(\text{SiMe}_3)_2\}]$  (2.30(1)–2.33(1) Å).<sup>37</sup> Comparison of the structural parameters of complexes **8** and **10** revealed the different steric properties of the  $\text{PhSe}^-$  and  $\text{I}^-$  ligands in these two complexes. It is noteworthy that the C(13)–Yb(1)–C(35) angle of 134.7(1)° formed by the two L ligands in **10** is similar to corresponding angle of 134.0(1)° in **8**. On the other hand, the O(1)–Yb(1)–I(1) angle of 85.66(7)° in **10** is much smaller than the O(1)–Yb(1)–Se(1) angle of 101.7(1)° in **8**.

**3. Reaction of Complex 3 with *N,N'*-dicyclohexylcarbodiimide.** Addition of *N,N'*-dicyclohexylcarbodiimide (DCC) to an equimolar amount of **3** in THF resulted in

a color change of the reaction mixture from deep greenish blue to yellow, indicative of the oxidation of Sm(II) to Sm(III) (Scheme 5). Workup of the resulting solution yielded the mononuclear, mixed-ligand tris(amidinate)  $[\text{SmL}_2\{\text{CyNC}(\text{H})\text{NCy}\}]$  (**11**) as the only isolable product in moderate yield.

Crystals of complex **11** suitable for X-ray diffraction were obtained from hexane. The solid-state structure of **11** is depicted in Figure 11, with selected bond distances and angles provided in Supporting Information, Table S10. The Sm atom is coordinated by two benzamidinate L ligands and one formamidinate anion  $[\text{CyNC}(\text{H})\text{NCy}]^-$ , all of which being bound in a  $\kappa^2$ -fashion. The coordination geometry around the Sm atom can be described as highly distorted octahedral. Unsymmetrical binding of the L ligands to the Sm atom is revealed by the different Sm(1)–N(1) and Sm(1)–N(2) distances of 2.517(2) Å and 2.398(2) Å, respectively. The Sm–N(formamidinate) distance [Sm(1)–N(3)] is 2.394(2) Å, which is similar to that of Sm(1)–N(2) but slightly shorter than the corresponding distances reported for the homoleptic Sm(III) formamidinate  $[\text{Sm}\{\text{HC}(\text{NC}_6\text{H}_3\text{Pr}^{i-2,6})_2\}_3]$  (2.448(6)–2.467(6) Å).<sup>14</sup> The N–C–N bite angles of the amidinate ligands in **11** are acute, falling within the range of 54.82(8)–56.6(1)°.

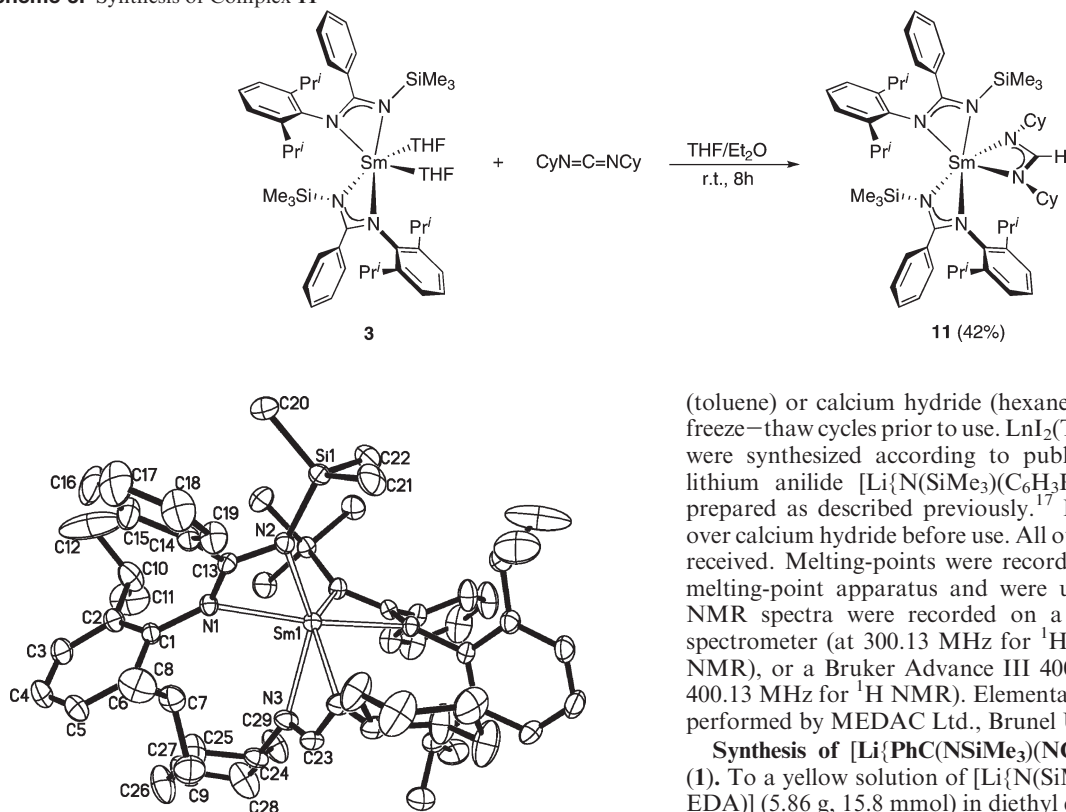
Carbodiimides are important substrates for metal-based reactivity studies. Reactions of carbodiimides with organosamarium(II) complexes have been reported. Reduction of  $\text{RN}=\text{C}=\text{NR}$  (R = Cy, Pr<sup>i</sup>) by the divalent samarocene  $[\text{Sm}(\text{MeC}_5\text{H}_4)_2(\text{THF})]$  led to the coupled oxalamidinate products  $[\{(\text{MeC}_5\text{H}_4)_2\text{Sm}(\text{HMPA})\}_2(\mu\text{-C}_2\text{N}_4\text{R}_4)]$ .<sup>30</sup> More interestingly, reactions of  $\text{RN}=\text{C}=\text{NR}$  (R = Cy, C<sub>6</sub>H<sub>3</sub>Pr<sup>i-2,6</sup>) with the non-metallocene complexes  $[\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$  and  $[\text{NaSm}\{\text{N}(\text{SiMe}_3)_2\}_3]$  gave unexpected results.<sup>32</sup> Direct reactions of  $[\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$  and  $[\text{NaSm}\{\text{N}(\text{SiMe}_3)_2\}_3]$  with  $\text{CyN}=\text{C}=\text{NCy}$  afforded the binuclear Sm(III) oxalamidinate  $[\{[\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2\}_2(\mu\text{-C}_2\text{N}_4\text{Cy}_4)]$ . An analogous reaction of  $[\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$  with the more bulky (2,6-Pr<sup>i-2</sup>-C<sub>6</sub>H<sub>3</sub>)N=C=N(C<sub>6</sub>H<sub>3</sub>Pr<sup>i-2,6</sup>) led to an unusual binuclear complex, in which a C–C coupling of two isopropyl methine carbon atoms was observed. A similar reaction of  $[\text{NaSm}\{\text{N}(\text{SiMe}_3)_2\}_3]$  with (2,6-Pr<sup>i-2</sup>-C<sub>6</sub>H<sub>3</sub>)N=C=N(C<sub>6</sub>H<sub>3</sub>Pr<sup>i-2,6</sup>) resulted in a  $\gamma$  C–H activation of a  $\text{N}(\text{SiMe}_3)_2^-$  ligand to give a C-substituted amidinate complex.

In our hands, the reduction of  $\text{CyN}=\text{C}=\text{NCy}$  by **3** afforded the mononuclear, mixed-ligand  $[\text{SmL}_2\{\text{CyNC}(\text{H})\text{NCy}\}]$  (**11**) as the only isolable product. It is believed

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Scheme 5. Synthesis of Complex 11



**Figure 11.** Molecular structure of  $[\text{SmL}_2\{\text{CyNC}(\text{H})\text{NCy}\}]$  (**11**) (30% thermal ellipsoids) with atom labeling.

that the present reaction may involve a one-electron reduction of  $\text{CyN}=\text{C}=\text{NCy}$  by  $\text{Sm}(\text{II})$  which generates the corresponding “ $\text{C}(\text{NCy})_2^{\cdot-}$ ” radical anionic species. Apparently, the latter species undergoes subsequent hydrogen abstraction from the reaction solvent (THF) and/or the coordinated THF molecules in **3** to give complex **11**. In a further investigation, the reaction of **3** with DCC was repeated with toluene as the reaction solvent. In the latter case, complex **11** was still obtained as the only isolable product. Conceivably, the coordinated THF molecules in **3** may also provide a source of the hydride yielding complex **11**, even though the reaction was carried out in a solvent other than THF.

### Summary

Utilization of the bulky unsymmetrical benzamidinate ligand  $[\text{PhC}(\text{NSiMe}_3)(\text{NC}_6\text{H}_3\text{Pr}'_2\text{-}2,6)]^-$  (**L**) has led to the synthesis of neutral, mononuclear lanthanide(II) bis(amidinate) complexes  $[\text{LnL}_2(\text{THF})_x]$  [ $\text{Ln} = \text{Sm}$ ,  $x = 2$  (**3**);  $\text{Ln} = \text{Eu}$ ,  $x = 2$ , (**4**);  $\text{Ln} = \text{Yb}$ ,  $x = 1$  (**5**)]. Complexes **3–5** act as one-electron reductants, which react readily with diphenyl dichalcogenides, iodine and *N,N'*-dicyclohexylcarbodiimide to give the corresponding lanthanide(III) chalcogenides (**6–9**), iodide (**10**), and a mixed-ligand tris(amidinate) complex (**11**), respectively.

### Experimental Section

**General Methods.** All manipulations were carried out under a purified nitrogen atmosphere using modified Schlenk techniques. Solvents were dried over and distilled from sodium benzophenone (diethyl ether and tetrahydrofuran), Na/K alloy

(toluene) or calcium hydride (hexane), and degassed twice by freeze–thaw cycles prior to use.  $\text{LnI}_2(\text{THF})_2$  ( $\text{Ln} = \text{Sm}$ ,  $\text{Eu}$ ,  $\text{Yb}$ ) were synthesized according to published procedures.<sup>38</sup> The lithium amidate  $[\text{Li}\{\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{Pr}'_2\text{-}2,6)\}(\text{TMEDA})]$  was prepared as described previously.<sup>17</sup> Benzocyanide was distilled over calcium hydride before use. All other reagents were used as received. Melting-points were recorded on an Electrothermal melting-point apparatus and were uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX300 NMR spectrometer (at 300.13 MHz for  $^1\text{H}$  and 75.47 MHz for  $^{13}\text{C}$  NMR), or a Bruker Avance III 400 NMR spectrometer (at 400.13 MHz for  $^1\text{H}$  NMR). Elemental analyses (C, H, N) were performed by MEDAC Ltd., Brunel University, U.K.

**Synthesis of  $[\text{Li}\{\text{PhC}(\text{NSiMe}_3)(\text{NC}_6\text{H}_3\text{Pr}'_2\text{-}2,6)\}(\text{TMEDA})]$  (**1**).** To a yellow solution of  $[\text{Li}\{\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{Pr}'_2\text{-}2,6)\}(\text{TMEDA})]$  (5.86 g, 15.8 mmol) in diethyl ether (40 mL) at 0 °C was slowly added  $\text{C}_6\text{H}_5\text{CN}$  (1.6 mL, 15.8 mmol) via a syringe. The reaction mixture was stirred at room temperature for 12 h, and concentrated under reduced pressure to about 20 mL to yield **1** as colorless crystals. Yield: 6.89 g, 14.6 mmol, 92%. Mp 155–158 °C.  $^1\text{H}$  NMR (300.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.32–7.29 (m, 2H, ArH), 7.05 (t,  $J = 1.5$  Hz, 1H, ArH), 7.03 (s, 2H,  $\text{C}_6\text{H}_5$ ), 7.01–6.98 (m, 1H,  $\text{C}_6\text{H}_5$ ), 6.96–6.89 (m, 2H,  $\text{C}_6\text{H}_5$ ), 3.61 (septet,  $J = 6.9$  Hz, 2H,  $\text{CHMe}_2$ ), 2.06 (s, 12H,  $\text{NMe}_2$ ), 1.83 (s, 4H,  $\text{NCH}_2$ ), 1.25 (d,  $J = 6.9$  Hz, 6H,  $\text{CHMe}_2$ ), 1.22 (d,  $J = 6.9$  Hz, 6H,  $\text{CHMe}_2$ ), 0.14 (s, 9H,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR (75.47 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  173.9, 148.3, 143.4, 141.5, 128.0, 127.2, 126.6, 122.8, 122.0, 56.7, 45.8, 28.1, 26.0, 23.5, 4.14. Anal. Calcd for  $\text{C}_{28}\text{H}_{47}\text{N}_4\text{SiLi}$ : C, 70.84; H, 9.98; N, 11.80%. Found: C, 70.90; H, 10.13; N, 11.77%.

**Synthesis of  $[\text{K}\{\text{PhC}(\text{NSiMe}_3)(\text{NC}_6\text{H}_3\text{Pr}'_2\text{-}2,6)\}]_n$  (**2**).** To a stirring suspension of  $\text{KOBu}^t$  (1.52 g, 13.6 mmol) in diethyl ether (10 mL) was slowly added a solution of **1** (6.42 g, 13.5 mmol) in the same solvent (30 mL) at room temperature. The reaction mixture was stirred under ambient conditions for 12 h, whereupon a white solid precipitated out. The precipitate was collected and redissolved in THF. The resulting solution was filtered and concentrated under reduced pressure to about 20 mL to give **2** as colorless crystals. Yield: 3.95 g, 10.1 mmol, 75%. Mp 90–93 °C.  $^1\text{H}$  NMR (300.13 MHz,  $\text{THF-d}_8$ ):  $\delta$  7.26 (br, 2H, ArH), 7.09 (t,  $J = 6.9$  Hz, 2H,  $\text{C}_6\text{H}_5$ ), 7.01, (t,  $J = 6.9$  Hz, 1H,  $\text{C}_6\text{H}_5$ ), 6.96–6.90 (m, 2H,  $\text{C}_6\text{H}_5$ ), 6.68 (br, 1H, ArH), 3.49 (septet,  $J = 6.9$  Hz, 2H,  $\text{CHMe}_2$ ), 1.17 (d,  $J = 6.9$  Hz, 6H,  $\text{CHMe}_2$ ), 1.10 (d,  $J = 6.9$  Hz, 6H,  $\text{CHMe}_2$ ),  $-0.36$  (s, 9H,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR (75.47 MHz,  $\text{THF-d}_8$ ):  $\delta$  168.2, 142.5, 141.7, 128.5, 128.1, 127.5, 125.8, 122.6, 119.5, 28.8, 24.3, 23.5, 3.76. Anal. Calcd for  $\text{C}_{22}\text{H}_{31}\text{N}_2\text{SiK}$ : C, 67.64; H, 8.00; N, 7.17%. Found: C, 67.00; H, 8.26; N, 6.80%.

**Synthesis of  $[\text{Sm}\{\text{PhC}(\text{NSiMe}_3)(\text{NC}_6\text{H}_3\text{Pr}'_2\text{-}2,6)\}_2(\text{THF})_2]$  (**3**).** A solution of **2** (1.64 g, 4.2 mmol) in THF (30 mL) was added dropwise to a deep blue solution of  $\text{SmI}_2(\text{THF})_2$  (1.19 g, 2.2 mmol) in THF (20 mL) at room temperature. The resulting

(38) Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, 1999–2009.



Table 1. Selected Crystallographic Data<sup>a</sup> for Complexes 1–4

	1	2	3	4
molecular formula	C <sub>28</sub> H <sub>47</sub> LiN <sub>4</sub> Si	C <sub>44</sub> H <sub>62</sub> K <sub>2</sub> N <sub>4</sub> Si <sub>2</sub>	C <sub>52</sub> H <sub>78</sub> N <sub>4</sub> O <sub>2</sub> Si <sub>2</sub> Sm	C <sub>52</sub> H <sub>78</sub> N <sub>4</sub> O <sub>2</sub> Si <sub>2</sub> Eu
molecular weight	474.73	731.36	997.71	999.33
crystal size, mm <sup>3</sup>	0.40 × 0.40 × 0.30	0.30 × 0.20 × 0.10	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20
crystal system	triclinic	orthorhombic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>Cc</i>	<i>P2</i> <sub>1</sub> / <i>c</i>
<i>a</i> , Å	9.6479(3)	18.520(2)	26.150(4)	11.3897(11)
<i>b</i> , Å	10.5509(3)	20.284(3)	25.969(4)	20.474(2)
<i>c</i> , Å	15.3111(5)	25.347(3)	32.829(5)	35.475(3)
$\alpha$ , deg	92.0060(10)	90	90	90
$\beta$ , deg	90.0550(10)	90	95.941(4)	98.248(2)
$\gamma$ , deg	97.8830(10)	90	90	90
<i>Z</i>	2	8	16	6
<i>V</i> , Å <sup>3</sup>	1542.88(8)	9522(2)	22175(6)	8186.9(14)
density, g cm <sup>-3</sup>	1.022	1.090	1.195	1.216
abs coeff., mm <sup>-1</sup>	0.096	0.281	1.141	1.232
temperature, K	293(2)	293(2)	293(2)	293(2)
reflections collected	21808	49739	59373	55492
independent reflections	7271 ( <i>R</i> <sub>int</sub> = 0.0298)	8386 ( <i>R</i> <sub>int</sub> = 0.2482)	28036 ( <i>R</i> <sub>int</sub> = 0.0876)	19706 ( <i>R</i> <sub>int</sub> = 0.0770)
obs. data with <i>I</i> ≥ 2σ( <i>I</i> )	4374	2770	16280	8847
final <i>R</i> indices [ <i>I</i> ≥ 2σ( <i>I</i> )] <sup>b</sup>	<i>R</i> 1 = 0.0534 <i>wR</i> 2 = 0.1357	<i>R</i> 1 = 0.0967 <i>wR</i> 2 = 0.2103	<i>R</i> 1 = 0.0566 <i>wR</i> 2 = 0.1105	<i>R</i> 1 = 0.0502 <i>wR</i> 2 = 0.1077
<i>R</i> indices (all data) <sup>b</sup>	<i>R</i> 1 = 0.0993 <i>wR</i> 2 = 0.1588	<i>R</i> 1 = 0.2676 <i>wR</i> 2 = 0.3681	<i>R</i> 1 = 0.1263 <i>wR</i> 2 = 0.1468	<i>R</i> 1 = 0.1499 <i>wR</i> 2 = 0.1523

<sup>a</sup>Data collected on a Bruker SMART CCD diffractometer or a Bruker KAPPA APEX II diffractometer with graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) using  $\omega$  scan. <sup>b</sup>*R*1 =  $\sum||F_o| - |F_c||/\sum|F_o|$ ; *wR*2 =  $\{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)\}^{1/2}$ .

Table 2. Selected Crystallographic Data<sup>a</sup> for Complexes 5, 7, and 8

	5	7	8
molecular formula	C <sub>48</sub> H <sub>70</sub> N <sub>4</sub> OSi <sub>2</sub> Yb	C <sub>100</sub> H <sub>134</sub> N <sub>8</sub> Se <sub>2</sub> Si <sub>4</sub> Eu <sub>2</sub>	C <sub>54</sub> H <sub>75</sub> N <sub>4</sub> OSeSi <sub>2</sub> Yb
molecular weight	948.30	2022.35	1104.36
crystal size, mm <sup>3</sup>	0.50 × 0.40 × 0.30	0.50 × 0.40 × 0.30	0.40 × 0.30 × 0.20
crystal system	triclinic	orthorhombic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>Cmca</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	11.5584(14)	32.583(6)	10.404(2)
<i>b</i> , Å	13.1786(16)	18.221(3)	11.636(2)
<i>c</i> , Å	17.986(2)	18.365(3)	25.142(5)
$\alpha$ , deg	87.540(2)	90	85.181(3)
$\beta$ , deg	78.050(2)	90	86.664(3)
$\gamma$ , deg	72.646(2)	90	64.703(3)
<i>Z</i>	2	4	2
<i>V</i> , Å <sup>3</sup>	2557.8(5)	10903(3)	2741.2(9)
density, g cm <sup>-3</sup>	1.231	1.232	1.338
abs coeff., mm <sup>-1</sup>	1.910	1.895	2.452
temperature, K	293(2)	173(2)	293(2)
reflections collected	13866	27305	14837
independent reflections	8980 ( <i>R</i> <sub>int</sub> = 0.0255)	4893 ( <i>R</i> <sub>int</sub> = 0.0528)	9599 ( <i>R</i> <sub>int</sub> = 0.0338)
obs. data with <i>I</i> ≥ 2σ( <i>I</i> )	7336	3393	8206
final <i>R</i> indices [ <i>I</i> ≥ 2σ( <i>I</i> )] <sup>b</sup>	<i>R</i> 1 = 0.0347 <i>wR</i> 2 = 0.0811	<i>R</i> 1 = 0.0468 <i>wR</i> 2 = 0.1389	<i>R</i> 1 = 0.0389 <i>wR</i> 2 = 0.0933
<i>R</i> indices (all data) <sup>b</sup>	<i>R</i> 1 = 0.0494 <i>wR</i> 2 = 0.0953	<i>R</i> 1 = 0.0663 <i>wR</i> 2 = 0.1541	<i>R</i> 1 = 0.0492 <i>wR</i> 2 = 0.1040

<sup>a</sup>Data collected on a Bruker SMART CCD diffractometer or a Bruker KAPPA APEX II diffractometer with graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) using  $\omega$  scan. <sup>b</sup>*R*1 =  $\sum||F_o| - |F_c||/\sum|F_o|$ ; *wR*2 =  $\{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)\}^{1/2}$ .

deep green reaction mixture was stirred for 12 h, after which all the volatiles were removed in vacuo. The residue was extracted with hexane (40 mL). Filtration and concentration of the solution to about 5 mL, followed by standing the solution at room temperature for 1 day yielded complex **3** as deep greenish blue crystals. Yield: 1.05 g, 1.05 mmol, 48%. Mp 164–167 °C (dec.). Anal. Calcd for C<sub>52</sub>H<sub>78</sub>N<sub>4</sub>O<sub>2</sub>Si<sub>2</sub>Sm: C, 62.60; H, 7.88; N, 5.61%. Found: C, 62.28; H, 7.88; N, 6.08%.

**Synthesis of [Eu{PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup>-2,6)}<sub>2</sub>(THF)]<sub>2</sub> (4).** Complex **4** was synthesized by a procedure similar to that of **3**. Reaction of EuI<sub>2</sub>(THF)<sub>2</sub> (1.06 g, 1.9 mmol) with **2** (1.44 g, 3.7 mmol) in THF (30 mL) gave **4** as orange crystals. Yield: 0.78 g, 0.77 mmol, 41%. Mp 188–191 °C (dec.). Anal. Calcd for

C<sub>52</sub>H<sub>78</sub>N<sub>4</sub>O<sub>2</sub>Si<sub>2</sub>Eu: C, 62.50; H, 7.87; N, 5.60%. Found: C, 62.32; H, 8.09; N, 5.87%.

**Synthesis of [Yb{PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup>-2,6)}<sub>2</sub>(THF)]<sub>2</sub> (5).** Complex **5** was prepared by a procedure similar to that of **3**. Treatment of YbI<sub>2</sub>(THF)<sub>2</sub> (1.16 g, 2.0 mmol) in THF (20 mL) with a solution of **2** (1.52 g, 3.9 mmol) in the same solvent (30 mL) afforded the title compound as dark red crystals. Yield: 1.03 g, 1.09 mmol, 56%. Mp 193–196 °C (dec.). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.25 (d, *J* = 7.2 Hz, 4H, ArH), 7.02 (d, *J* = 7.2 Hz, 4H, C<sub>6</sub>H<sub>5</sub>), 6.97 (t, *J* = 7.2 Hz, 6H, C<sub>6</sub>H<sub>5</sub>), 6.85 (t, *J* = 7.2 Hz, 2H, ArH), 3.77 (br, 4H, CHMe<sub>2</sub>), 3.60 (br, 4H, THF), 1.40–1.27 (2d, *J* = 6.0 Hz, 28H, CHMe<sub>2</sub> and THF), –0.01 (s, 18H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (75.47 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  174.9,

Table 3. Selected Crystallographic Data<sup>a</sup> for Complexes **9**·C<sub>7</sub>H<sub>8</sub>, **10**, and **11**

	<b>9</b> ·C <sub>7</sub> H <sub>8</sub>	<b>10</b>	<b>11</b>
molecular formula	C <sub>107</sub> H <sub>142</sub> N <sub>8</sub> Te <sub>2</sub> Si <sub>4</sub> Sm <sub>2</sub>	C <sub>48</sub> H <sub>70</sub> IN <sub>4</sub> OSi <sub>2</sub> Yb	C <sub>57</sub> H <sub>85</sub> N <sub>6</sub> Si <sub>2</sub> Sm
molecular weight	2208.55	1075.20	1060.84
crystal size, mm <sup>3</sup>	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20
crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	13.7791(17)	14.241(2)	14.513(3)
<i>b</i> , Å	19.970(2)	14.095(2)	18.376(3)
<i>c</i> , Å	22.393(3)	25.946(4)	22.516(4)
$\alpha$ , deg	114.055(2)	90	90
$\beta$ , deg	103.082(2)	95.391(2)	102.796(3)
$\gamma$ , deg	92.451(2)	90	90
<i>Z</i>	2	4	4
<i>V</i> , Å <sup>3</sup>	5417(1)	5185.1(13)	5855.7(18)
density, g cm <sup>-3</sup>	1.354	1.377	1.203
abs coeff., mm <sup>-1</sup>	1.692	2.481	1.082
temperature, K	293(2)	293(2)	293(2)
reflections collected	29381	27640	19827
independent reflections	18944 ( <i>R</i> <sub>int</sub> = 0.0334)	9125 ( <i>R</i> <sub>int</sub> = 0.0452)	7111 ( <i>R</i> <sub>int</sub> = 0.0461)
obs. data with <i>I</i> ≥ 2σ( <i>I</i> )	13719	7315	5892
final <i>R</i> indices [ <i>I</i> ≥ 2σ( <i>I</i> )] <sup>b</sup>	<i>R</i> 1 = 0.0592 <i>wR</i> 2 = 0.1690	<i>R</i> 1 = 0.0315 <i>wR</i> 2 = 0.0750	<i>R</i> 1 = 0.0377 <i>wR</i> 2 = 0.0909
<i>R</i> indices (all data) <sup>b</sup>	<i>R</i> 1 = 0.0830 <i>wR</i> 2 = 0.1832	<i>R</i> 1 = 0.0466 <i>wR</i> 2 = 0.0840	<i>R</i> 1 = 0.0520 <i>wR</i> 2 = 0.0993

<sup>a</sup>Data collected on a Bruker SMART CCD diffractometer or a Bruker KAPPA APEX II diffractometer with graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) using  $\omega$  scan. <sup>b</sup>*R*1 =  $\sum||F_o| - |F_c|| / \sum|F_o|$ ; *wR*2 =  $\{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)\}^{1/2}$ .

145.6, 141.7, 141.2, 127.6, 127.4, 127.1, 123.6, 122.9, 69.2, 28.6, 25.9, 25.4, 22.9, 3.03. Anal. Calcd for C<sub>48</sub>H<sub>70</sub>N<sub>4</sub>OSi<sub>2</sub>Yb: C, 60.79; H, 7.44; N, 5.91%. Found: C, 60.51; H, 7.76; N, 6.19%.

**Synthesis of [Sm{PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2</sub>-2,6)}<sub>2</sub>( $\mu$ -SePh)]<sub>2</sub> (**6**).** A solution of PhSeSePh (0.298 g, 0.96 mmol) in hexane (25 mL) was slowly added to a solution of **3** (1.92 g, 1.92 mmol) in the same solvent (35 mL) at room temperature. The reaction mixture turned gradually from deep greenish blue to yellow. Stirring was continued for 8 h at room temperature. The solution was filtered and concentrated to about 10 mL to give **6** as yellow crystals. Yield: 0.93 g, 0.46 mmol, 48%. Mp 156–159 °C. Anal. Calcd for C<sub>100</sub>H<sub>134</sub>N<sub>8</sub>Se<sub>2</sub>Si<sub>4</sub>Sm<sub>2</sub>: C, 59.48; H, 6.69; N, 5.55%. Found: C, 59.66; H, 6.92; N, 5.53%.

**Synthesis of [Eu{PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2</sub>-2,6)}<sub>2</sub>( $\mu$ -SePh)]<sub>2</sub> (**7**).** Complex **7** was prepared by a procedure similar to that of **6**. A solution of PhSeSePh (0.38 g, 1.2 mmol) in hexane (35 mL) was slowly added to a solution of **4** (2.42 g, 2.4 mmol) in the same solvent (25 mL). The reaction mixture turned gradually from orange to dark red, from which complex **7** was isolated as dark red crystals. Yield: 1.31 g, 0.65 mmol, 54%. Mp 128–131 °C (dec.). Anal. Calcd for C<sub>100</sub>H<sub>134</sub>N<sub>8</sub>Se<sub>2</sub>Si<sub>4</sub>Eu<sub>2</sub>: C, 59.39; H, 6.68; N, 5.54%. Found: C, 59.55; H, 7.02; N, 5.32%.

**Synthesis of [Yb{PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2</sub>-2,6)}<sub>2</sub>(SePh)(THF)] (**8**).** Complex **8** was synthesized by a procedure similar to that of **6**. Treatment of **5** (2.44 g, 2.2 mmol) with PhSeSePh (0.34 g, 1.1 mmol) in hexane yielded **8** as orange crystals. Yield: 1.62 g, 1.47 mmol, 67%. Mp 180–183 °C. Anal. Calcd for C<sub>54</sub>H<sub>75</sub>N<sub>4</sub>OSi<sub>2</sub>SeYb: C, 58.73; H, 6.84; N, 5.07%. Found: C, 59.02; H, 6.99; N, 5.28%.

**Synthesis of [Sm{PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2</sub>-2,6)}<sub>2</sub>( $\mu$ -TePh)]<sub>2</sub>·C<sub>7</sub>H<sub>8</sub> (**9**·C<sub>7</sub>H<sub>8</sub>).** A solution of PhTeTePh (0.37 g, 0.9 mmol) in toluene (25 mL) was added dropwise to a solution of **3** (1.79 g, 1.8 mmol) in the same solvent (30 mL) at room temperature. The reaction mixture was stirred for 8 h whereupon its color changed from deep greenish blue to orange. The solution was filtered and concentrated to about 10 mL to yield the title compound as orange crystals. Yield: 0.90 g, 0.41 mmol, 46%. Mp 145–148 °C. Anal. Calcd for C<sub>100</sub>H<sub>134</sub>N<sub>8</sub>Si<sub>4</sub>Sm<sub>2</sub>Te<sub>2</sub>·C<sub>7</sub>H<sub>8</sub>: C, 58.19; H, 6.48; N, 5.07%. Found: C, 58.14; H, 6.52; N, 5.03%.

**Synthesis of [Yb{PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2</sub>-2,6)}<sub>2</sub>(I)(THF)] (**10**).** To a solution of **5** (1.91 g, 2.0 mmol) in hexane (20 mL)

was slowly added a solution of iodine (0.26 g, 1.0 mmol) in Et<sub>2</sub>O (20 mL) at room temperature. The resulting solution was stirred at room temperature for 8 h, whereupon its color changed from dark red to orange red and finally to yellow. All the volatiles were removed in vacuo, and the residue was extracted with hexane (40 mL). Filtration and concentration of the solution to about 10 mL yielded **10** as yellow crystals. X-ray quality crystals of **10** were obtained by recrystallization from a hexane/toluene solvent mixture. Yield: 1.46 g, 1.36 mmol, 68%. Mp 233–236 °C. Anal. Calcd for C<sub>48</sub>H<sub>70</sub>N<sub>4</sub>IOSi<sub>2</sub>Yb: C, 53.62; H, 6.56; N, 5.21%. Found: C, 54.10; H, 7.02; N, 5.48%.

**Synthesis of [Sm{PhC(NSiMe<sub>3</sub>)(NC<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2</sub>-2,6)}<sub>2</sub>{HC(NCy)<sub>2</sub>}] (**11**).** To a solution of **3** (1.21 g, 1.2 mmol) in THF (30 mL) was slowly added a solution of *N,N'*-dicyclohexylcarbodiimide (1.8 M, 0.8 mL, 1.4 mmol) in Et<sub>2</sub>O (20 mL). The resulting solution turned from deep greenish blue to yellow. After stirring at room temperature for 8 h, the solution was pumped to dryness and the residue was extracted with hexane (40 mL). Filtration and concentration of the solution to about 5 mL afforded the title compound as pale yellow crystals. Yield: 0.53 g, 0.50 mmol, 42%. Mp 215–218 °C. Anal. Calcd for C<sub>57</sub>H<sub>85</sub>N<sub>6</sub>Si<sub>2</sub>Sm: C, 64.53; H, 8.08; N, 7.92%. Found: C, 64.47; H, 8.29; N, 7.82%.

**X-ray Crystallographic Analysis.** Single crystals of compounds **1**–**5**, **7**, **8**, **9**·C<sub>7</sub>H<sub>8</sub>, **10**, and **11** suitable for X-ray diffraction studies were mounted in glass capillaries and sealed under nitrogen. Data were collected on a Bruker SMART CCD diffractometer or a Bruker KAPPA APEX II diffractometer with graphite-monochromatized Mo–K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 293 K (for **1**–**5**, **8**, **9**·C<sub>7</sub>H<sub>8</sub>, **10**, and **11**) and 173 K (for **7**). An empirical absorption correction was applied using the SADABS program.<sup>39</sup> The structures were solved by direct phase determination using the computer program SHELX-97 and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms.<sup>40</sup> Hydrogen atoms

(39) Sheldrick, G. M. SADABS: *Program for Empirical Absorption Correction of Area Detector Data*. University of Göttingen: Göttingen, Germany, 1996.

(40) Sheldrick, G. M.; *SHELXTL 5.10 for Windows NT, Structure Determination Software Programs*. Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1997.

were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factors. Details of the data collection and crystallographic data are given in Tables 1, 2, and 3.

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**Supporting Information Available:** Crystallographic information files (CIF), and selected bond distances (Å) and angles (deg) of complexes **1–5**, **7**, **8**, **9**·C<sub>7</sub>H<sub>8</sub>, **10**, and **11**. This material is available free of charge via the Internet at <http://pubs.acs.org>.