## ORGANOMETALLICS

## 2,5-Bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl Complexes of the Divalent Lanthanides: Synthesis and Structures

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Summary: The reaction of potassium 2,5-bis{N-(2,6-diisopro $pylphenyl)iminomethyl}pyrrolyl, [(DIP<sub>2</sub>pyr)K], with the anhy$ drous lanthanide diiodides resulted in the heteroleptic complexes[(DIP<sub>2</sub>pyr)LnI(THF)<sub>3</sub>] (Ln = Sm, Eu, Yb). All complexes aremonomeric in the solid state, which is remarkable, since samarium and europium complexes tend to form dimeric complexesbridged by iodine ions. The (DIP<sub>2</sub>pyr)<sup>-</sup> ligands are coordinated $almost symmetrically in a <math>\kappa^3 N, N', N''$  mode to the metal center in the samarium and europium compounds. In contrast, for the ytterbium complex an asymmetric coordination mode was observed.

Recently we and other groups were attracted by 2,5-bis-(*N*-aryliminomethyl)pyrrolyls, which can serve as unique monoanionic nitrogen ligands in coordination chemistry. Some actinide complexes in which the 2,5-bis(*N*-aryliminomethyl)pyrrole structural motif was part of a larger oligodentate macrocyclic ligand were published as the first examples in this area.<sup>1-3</sup> Later some macrocyclic multinuclear nickel compounds were reported.<sup>4,5</sup> The first transition-metal complexes with the tridentate 2,5-bis(*N*-aryliminomethyl)pyrrolyl ligands were reported by Bochmann et al.<sup>6</sup> Today alkali-metal,<sup>7,8</sup> aluminum,<sup>9</sup> group 4,<sup>6</sup> iron,<sup>6</sup> chromium,<sup>8</sup> copper,<sup>10</sup> and rare-earth-metal

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complexes<sup>11–14</sup> ligated by 2,5-bis(*N*-aryliminomethyl)pyrrolyls are known. The coordination mode of the resulting complexes depends on the steric bulk of the aryl substituents of the ligand, the number of ligands coordinated, the ionic radius of the metal center, and the bulkiness of additional ligands coordinated to the metal atom. In most of the reported compounds the ligand binds in a tridentate fashion with the two Schiff base nitrogen atoms and the pyrrolyl moiety onto the metal centers (Scheme 1A), but in a few cases also a bidentate binding mode was observed (Scheme 1B). Some of the reported complexes have been used as catalysts for the polymerization of ethylene<sup>8,9,15,16</sup> and the oligomerization of ethylene and propylene to linear and branched products.<sup>15</sup>

In 2001, Mashima et al. introduced 2,5-bis(*N*-aryliminomethyl)pyrrolyl compounds into rare-earth-metal chemistry by forming some yttrium complexes.<sup>11</sup> These compounds were obtained by amine elimination reactions from the corresponding pyrroles with  $[Y{N(SiMe_3)_2}_3]$ . The coordination mode and the number of the 2,5-bis(*N*-aryliminomethyl)pyrrolyl ligands introduced to a metal center were controlled by varying the bulkiness on the aryl group of the ligands. We have been working now for some time with the sterically very demanding 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl (DIP<sub>2</sub>pyr)<sup>-</sup> ligand in trivalent rareearth-metal chemistry.<sup>12-14</sup> In this context a number of chloride and borohydride complexes were synthesized, and some of these compounds were used as Ziegler–Natta catalysts for the polymerization of 1,3-butadiene to poly-*cis*-1,4butadiene.<sup>14</sup>

Since the  $(DIP_2pyr)^-$  ligand was proven to show a rich coordination chemistry for the trivalent rare-earth metals, we are now interested in extending this chemistry to the divalent lanthanides. Herein we report on the synthesis and structure of the monomeric lanthanide iodo complexes [(DIP\_2pyr)LnI(THF)\_3] (Ln = Sm, Eu, Yb).<sup>17</sup>

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## **Results and Discussion**

As reported earlier, 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole, (DIP<sub>2</sub>pyr)H, can be deprotonated with KH to give the corresponding potassium salt [(DIP<sub>2</sub>pyr)K].<sup>13</sup> Reaction of [(DIP<sub>2</sub>pyr)K] with anhydrous lanthanide diiodides in THF at elevated temperature resulted in the heteroleptic complexes [(DIP<sub>2</sub>pyr)LnI(THF)<sub>3</sub>] (Ln = Sm (1), Eu (2), Yb (3)) in good yields (Scheme 2).

The new complexes were characterized by standard analytical/spectroscopic techniques, and the solid-state structures were established by single-crystal X-ray diffraction. The diamagnetic compound **3** was also investigated by NMR techniques. The NMR spectra show the expected set of signals for the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand and point to a symmetrical coordination of the ligand in solution. This is in contrast to the solid-state structure and indicates a dynamic behavior of the ligand in solution. In the <sup>1</sup>H NMR spectrum, one doublet ( $\delta$  1.25 ppm) and one septet ( $\delta$  3.25 ppm) were observed for the isopropyl groups, indicating that the 2,6-diisopropylaniline moieties of the ligand can freely rotate in solution. The <sup>13</sup>C{<sup>1</sup>H} NMR data are consistent with these observations.

Compounds 1 and 2, which are isostructural in the solid state, crystallize in the monoclinic space group  $P2_1/c$  with four molecules of the corresponding complex and eight THF molecules in the unit cell (Figure 1). Data collection parameters and selected bond lengths and angles are given in Table S1 (Supporting Information) and in the caption of Figure 1. The coordination polyhedron of the lanthanide atoms in both compounds is formed by the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand, the iodine atom, and three THF molecules and shows a distorted-pentagonal-bipyramidal geometry. The apexes of each bipyramid are formed by the iodine atom and one THF molecule with an almost linear setup (O1-Sm-I) = $171.25(14)^{\circ}$  (1) and O1-Eu-I =  $169.8(2)^{\circ}$  (2)). The nearly planar arrangement of the LnN<sub>3</sub>O<sub>2</sub> fragments is confirmed by the sums of the corresponding five valence angles  $(358.1^{\circ} (1)$ and 358.5° (2)). The (DIP<sub>2</sub>pyr)<sup>-</sup> ligands are coordinated almost symmetrically in a  $\kappa^3$  N, N', N'' mode to the metal center (Sm-N1 = 2.928(7) Å, Sm-N2 = 2.474(7) Å, Sm-N3 = 2.934(7) Å (1) and Eu–N1 = 2.934(8) Å, Eu–N2 = 2.464(8) Å, Eu-N3 = 2.969(8) A (2)). The Ln-I bond distances Sm-I = 3.2233(9) Å and Eu-I = 3.2088(11) Å are in the expected range.<sup>18,19</sup> The iodine atoms are in the apex of the pentagonal bipyramid (N1-Sm-I =  $98.91(14)^\circ$ , N2-Sm-I =  $104.8(2)^\circ$ ,  $N3-Sm-I = 98.85(13)^{\circ}$  (1) and  $N1-Eu-I = 98.3(2)^{\circ}$ ,  $N2-Eu-I = 104.6(2)^{\circ}, N3-Eu-I = 98.5(2)^{\circ}(2)).$ 

Compound 3 crystallizes as green plates in the monoclinic space group  $P2_1/c$  with four molecules of the complex and



Figure 1. Perspective ORTEP view of the molecular structure of 1. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg) are given for 1 and the isostructural complex 2. Complex 1: Sm-N1=2.928(7), Sm-N2=2.474(7), Sm-N3=2.934(7), Sm-O1= 2.600(6), Sm-O2=2.596(6), Sm-O3=2.580(6), Sm-I=3.2233(9); N1-Sm-N2 = 61.3(2), N1-Sm-N3 = 121.9(2), N2-Sm-N3 =60.7(2), N1-Sm-O1 = 89.3(2), N1-Sm-O2 = 75.7(2), N1-Sm-O3 = 151.3(2), N2-Sm-O1 = 81.8(2), N2-Sm-O2 =135.9(2), N2-Sm-O3 = 143.3(2), N3-Sm-O1 = 79.1(2), N3-Sm-O1 = 79Sm-O2=158.1(2), N3-Sm-O3=83.7(2), N1-Sm-I=98.91(14), N2-Sm-I = 104.8(2), N3-Sm-I = 98.85(13), O1-Sm-I =171.25(14), O2-Sm-I = 90.40(14), O3-Sm-I = 88.47(13),O1-Sm-O2 = 88.7(2), O1-Sm-O3 = 82.9(2), O2-Sm-O3 = 82.9(2), O2-Sm-O3 = 82.9(2), O2-Sm-O3 = 82.9(2), O2-Sm-O3 = 82.9(2), O3 = 876.7(2). Complex 2: Eu-N1 = 2.934(8), Eu-N2 = 2.464(8), Eu-N3 = 2.969(8), Eu-O1 = 2.472(9), Eu-O2 = 2.598(8), Eu-O3 = 2.595(8), Eu-I=3.2088(11); N1-Eu-N2=61.6(3), N1-Eu-N3= 122.3(2), N2-Eu-N3 = 60.9(3), N1-Eu-O1 = 90.5(3), N1-Eu-O2 = 76.0(3), N1-Eu-O3 = 152.7(3), N2-Eu-O1 = 84.2(3),N2-Eu-O2 = 136.7(3), N2-Eu-O3 = 142.4(3), N3-Eu-O1 = 80.9(3), N3-Eu-O2 = 158.3(3), N3-Eu-O3 = 82.5(3), N1-Eu-I = 98.3(2), N2-Eu-I = 104.6(2), N3-Eu-I = 98.5(2),O1-Eu-I=169.8(2), O2-Eu-I=89.0(2), O3-Eu-I=87.7(2), O1-Eu-O2 = 88.1(3), O1-Eu-O3 = 82.1(3), O2-Eu-O3 = 77.5(3).

two *n*-pentane molecules in the unit cell (Figure 2). Due to twinning problems, the quality of the structure is low. As observed for compounds 1 and 2, the coordination polyhedron of complex 3 consists of a distorted pentagonal bipyramid in the solid state. In contrast to 1 and 2, the apexes of the bipyramid are formed by two THF molecules, which are arranged almost linearly  $(O1-Yb-O3 = 170.8(5)^\circ)$ . The sum of the corresponding five valence angles shows a nearly planar arrangement of the YbN<sub>3</sub>OI fragment (360.1°). As a result of the smaller ion radius of Yb, the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand in 3 is coordinated asymmetrically to the metal center, which is in contrast to the case for compounds 1 and 2. In complex 3 one Schiff-base function (N1) shows an Yb-N bond distance of 2.757(12) Å, while the other function exhibits a long interaction to the metal center (Yb-N1 = 3.1997(6) Å). Obviously the asymmetrical coordination of the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand is caused by the smaller ionic radius of the metal center in 3 compared with those of 1 and 2. Additionally, crystal packing may also be considered. The Yb-I bond distance (3.100(2) Å) of **3** is within the same range observed for other monomeric ytterbium(II) iodo complexes.<sup>20-22</sup>

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**Figure 2.** Perspective ORTEP view of the molecular structure of **3**. Thermal ellipsoids are drawn to encompass 30% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å)] and angles (deg): Yb-N1 = 2.757(12), Yb-N2 = 2.387(13), Yb-N3 = 3.1997(6), Yb-O1 = 2.431(11), Yb-O2 = 2.439(12), Yb-O3 = 2.415(14), Yb-I=3.100(2); N1-Yb-N2 = 65.0(4), N1-Yb-N3 = 123.08(4), N2-Yb-N3 = 58.13(4), N1-Yb-O1 = 92.2(4), N1-Yb-O2 = 168.0(5), N1-Yb-O3 = 94.5(4), N2-Yb-O1 = 87.8(4), N2-Yb-O2 = 127.0(5), N2-Yb-O3 = 89.4(5), N3-Yb-O1 = 84.55(4), N3-Yb-O2 = 68.63(4), N3-Yb-O3 = 86.50(4), N1-Yb-I = 83.9(3), N2-Yb-I = 148.8(3), N3-Yb-I = 152.96(3), O1-Yb-I = 92.8(3), O2-Yb-I = 84.4(3), O3-Yb-I = 94.2(3), O1-Yb-O2 = 86.1(4), O1-Yb-O3 = 170.8(5), O2-Yb-O3 = 89.4(5).

Interestingly, complexes 1-3 are all monomeric in the solid state, which is remarkable, since samarium and europium with larger ionic radii tend to form dimeric complexes bridged by iodine ions:<sup>20,23-30</sup> e.g., [{(Me<sub>3</sub>SiNPPh<sub>2</sub>)<sub>2</sub>CH}-Ln( $\mu$ -I)(THF)]<sub>2</sub> (Ln = Eu, Sm)<sup>20,23</sup> and [{(Me<sub>3</sub>Si)<sub>2</sub>N}Sm( $\mu$ -I)-(DME)(THF)]<sub>2</sub>.<sup>30</sup> To the best of our knowledge, only a few monomeric heteroleptic iodo complexes of divalent samarium and europium have been reported in the literature. For divalent europium there has also been only one structurally characterized monomeric heteroleptic iodo complex reported, which is the cluster [IEu(OtBu)<sub>4</sub>{Li(THF)}<sub>4</sub>(OH)].<sup>18</sup> This compound is stabilized by a bulky alkali-metal cage on one side and thus cannot be compared with our complexes.

There are two examples for structurally characterized monomeric samarium(II) iodo complexes in the literature. One of these is a complex with the very bulky ligand  $\{C_5Me_4-SiMe_2(iPr_2-tacn)\}^-$  (tacn = 1,4-diisopropyl-1,4,7-triazacyclononane).<sup>19</sup> This ligand coordinates via the cyclopentadienyl moiety and the three nitrogen atoms of the triazacyclononane

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ring to the samarium(II) center. Consequently, the coordination sphere is already saturated and a monomer is formed. This complex cannot be compared with our compounds, because the  $(DIP_2pyr)^-$  ligand is less sterically demanding and the coordination spheres of compounds 1 and 2 are satisfied by three solvent molecules. The other example is the samarium(II) compound  $[Sm(L^{Ph, tBu})I(THF)_4] (L^{Ph, tBu} = {N(C(Ph)=N)_2})^{-1}$  $C(tBu)Ph^{-}$ , which coordinates four THF molecules to saturate the coordination sphere instead of forming a dimer.<sup>31</sup> In addition, the nitrogen atom of the monodentate  $(L^{Ph,tBu})^{-1}$ ligand and the iodine atom exhibit a relatively small angle  $(N1-Sm-I = 100.25(9)^{\circ})$  instead of building a nearly linear N-Sm-I unit. This arrangement was also observed for 1 and 2, as described above. The reason for the formation of the cisoid isomers is unclear. The crystal structures of the diodides of samarium(II) and europium(II) coordinated by different solvents have been comprehensively described in the literature, and transoid as well as cisoid isomers were observed.<sup>32–37</sup> No doubt a subtle interplay of crystal packing and steric effects are the dominant factors for the differences.

## **Experimental Section**

General Considerations. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high-vacuum  $(10^{-3})$ Torr) line, or in an argon-filled MBraun glovebox. THF was distilled under nitrogen from potassium benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were dried using an MBraun solvent purification system (SPS-800). All solvents for vacuum line manipulations were stored in vacuo over LiAlH<sub>4</sub> in resealable flasks. Deuterated solvents were obtained from Aldrich (99 atom % D). NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were obtained on a Bruker IFS 113v FTIR spectrometer. Mass spectra were recorded at 70 eV on a Varian Mat SM 11 instrument. Elemental analyses were carried out with an Elementar Vario EL apparatus.  $LnC_{13}^{,38}$ ,  $LnI_{2}^{,39-41}$  (DIP<sub>2</sub>pyr)H,<sup>42,43</sup> and [(DIP<sub>2</sub>pyr)K]<sup>13,44</sup> were prepared according to literature procedures.

[(DIP<sub>2</sub>pyr)LnI(THF)<sub>3</sub>] (1–3). General Procedure. THF (20 mL) was condensed at -78 °C onto a mixture of LnI<sub>2</sub>(THF)<sub>n</sub>

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(Ln = Sm, Eu, Yb) and  $[(DIP_2pyr)K]$ , and the resulting reaction mixture was stirred for 16 h at 60 °C. The deeply colored solution was filtered off and concentrated until a precipitate appeared. The mixture was heated carefully until the solution became clear. For Ln = Yb the solution was layered with *n*-pentane. The products were obtained at room temperature overnight as deeply colored crystals.

[(**DIP**<sub>2</sub>**pyr**)**SmI**(**THF**)<sub>3</sub>] (1). SmI<sub>2</sub>(THF)<sub>2.5</sub> (643 mg, 1.10 mmol), [(**DIP**<sub>2</sub>**pyr**)**K**] (480 mg, 1.00 mmol). Black crystals from hot THF; yield 706 mg, 0.76 mmol, 76% IR (KBr,  $\nu/\text{cm}^{-1}$ ): 731 (m), 766 (m), 800 (m), 860 (m), 1039 (m), 1093 (m), 1155 (s), 1254 (w), 1315 (m), 1360 (w), 1437 (m), 1574 (m), 1616 (s), 1714 (w), 2046 (w), 2181 (w), 2864 (w), 2927 (w), 2963 (m), 3450 (m). Anal. Calcd for C<sub>40</sub>H<sub>58</sub>N<sub>3</sub>O<sub>2.5</sub>ISm (1·0.5THF; 935.83): C, 53.49; H, 6.51; N, 4.68. Found: C, 53.33; H, 6.63; N, 4.26.

[(DIP<sub>2</sub>pyr)EuI(THF)<sub>3</sub>] (2). EuI<sub>2</sub>(THF)<sub>2</sub> (412 mg, 0.75 mmol), [(DIP<sub>2</sub>pyr)K] (360 mg, 0.75 mmol). Red crystals from hot THF; yield 360 mg, 0.39 mmol, 51% (single crystals). IR (KBr,  $\nu/\text{cm}^{-1}$ ): 735 (m), 769 (m), 796 (m), 860 (m), 1039 (m), 1097 (m), 1155 (s), 1230 (w), 1319 (m), 1360 (w), 1437 (m), 1574 (m), 1616 (s), 1710 (w), 2046 (w), 2181 (w), 2868 (w), 2924 (w), 2962 (m), 3450 (m). Anal. Calcd for C<sub>42</sub>H<sub>62</sub>N<sub>3</sub>O<sub>3</sub>IEu (**2**; 935.83): C, 53.90; H, 6.68; N, 4.49. Found: C, 53.58; H, 6.70; N, 4.21.

[(DIP<sub>2</sub>pyr)YbI(THF)<sub>3</sub>] (3). YbI<sub>2</sub>(THF)<sub>2</sub> (286 mg, 0.50 mmol), [(DIP<sub>2</sub>pyr)K] (240 mg, 0.50 mmol). Green crystals from THF/ *n*-pentane; yield 200 mg, 0.21 mmol, 42% (single crystals). <sup>1</sup>H NMR (THF- $d_8$ , 400 MHz, 25 °C):  $\delta$  1.25 (d, 24 H, CH(CH<sub>3</sub>),  $J_{\rm H,H} = 6.9$  Hz), 3.25 (sept, 4 H, CH(CH<sub>3</sub>),  $J_{\rm H,H} = 6.9$  Hz), 6.75 (s, 2 H, 3,4-pyr), 7.07–7.12 (m, 2 H, p-Ph), 7.17–7.19 (m, 4 H, Ph), 8.21 (s, 2 H, N=CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (THF- $d_8$ , 100.4 MHz, 25 °C):  $\delta$  28.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 34.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 118.0 (3,4-pyr), 123.1 (Ph), 124.4 (Ph), 139.7 (Ph), 143.8 (2,5-pyr), 151.4 (Ph), 161.5 (N=CH) ppm. Anal. Calcd for C<sub>42</sub>H<sub>62</sub>N<sub>3</sub>O<sub>3</sub>IYb (3; 956.90): C, 52.72; H, 6.53; N, 4.39. Found: C, 52.86; H, 6.63; N, 4.23.

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Supporting Information Available: CIF files and a table giving X-ray crystallographic data for the structure determinations of 1-3. This material is available free of charge via the Internet at http://pubs.acs.org.