# **ORGANOMETALLICS**

# 2,5-Bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl Complexes of the Heavy Alkaline Earth Metals: Synthesis, Structures, and Hydroamination Catalysis

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Supporting Information

**ABSTRACT:** The heteroleptic iodo complexes  $[(DIP_2pyr)MI(THF)_n]$  (M = Ca, Sr (n = 3); Ba (n = 4); (DIP\_2pyr)<sup>-</sup> = 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl) were synthesized by reaction of  $[(DIP_2pyr)$ K] with anhydrous alkaline earth metal diiodides. All complexes are monomeric in the solid state. A  $\kappa^3$ -coordination mode of the (DIP\_2pyr)<sup>-</sup> ligand was observed for the strontium and the barium compounds, while the analogous calcium derivative is  $\kappa^2$ -coordinated in the solid state. However, VT-<sup>1</sup>H NMR studies of  $[(DIP_2pyr)CaI(THF)_3]$  indicate a symmetrically coordinated (DIP\_2pyr)<sup>-</sup> ligand in solution. Computational studies confirm the different coordination modes in solution and in the solid state. The preferred  $\kappa^2$ coordination mode observed in the solid state might be a result of temperature or/and crystal-packing effects. Furthermore, the calcium and strontium amido complexes  $[(DIP_2pyr)M{N(SiMe_3)_2}(THF)_2]$  (M = Ca, Sr) were prepared by reaction of  $[(DIP_2pyr)MI(THF)_n]$  (M = Ca, Sr (n = 3)) with



 $[K{N(SiMe_3)_2}]$ . Both compounds were investigated for the intramolecular hydroamination of aminoalkenes. Both catalysts showed a good activity, and the best results were obtained for the calcium complex  $[(DIP_2pyr)Ca{N(SiMe_3)_2}(THF)_2]$ .

# INTRODUCTION

Amines have been largely applied in the chemical industry as bulk chemicals, fine chemicals, pharmaceuticals, and dyes.<sup>1</sup> In order to avoid chemical waste produced in time-consuming multistep syntheses, hydroamination was discovered as an alternative access to nitrogen-containing molecules. Hydroamination, the direct addition of amine N-H bonds to C-C multiple bonds, attracted the attention of many researchers and thus was intensely studied for the last decades.<sup>1–19</sup> Catalytic hydroamination was investigated for a wide range of complexes of various metals, such as alkali metals, <sup>3,5,15,20,21</sup> early transition metals, <sup>1,7,9,12,14,15,20</sup> and lanthanides and actinides, <sup>1,7–9,11–13,15–17</sup> and very recently aluminum compounds were studied for hydroamination reactions.<sup>22,23</sup> Early transition metal and late transition metal catalysts have to be distinguished. Complexes of early transition metals, such as group  $4^{4,6,7,12,13,18}$ and the rare earth elements, 1,7-9,11-13,15-17 are highly efficient catalysts for the hydroamination, but the synthetic application is limited by their high sensitivity toward moisture and air and their low tolerance to polar functional groups. In contrast, compounds of the late transition metals such as nickel,<sup>24</sup> palladium,<sup>7,9,12,15,20</sup> platinum,<sup>9,20</sup> copper,<sup>9</sup> and gold<sup>25–31</sup> show high polar functional group tolerance, but are mostly based on relatively expensive or toxic metals, and thus some of them have a limited use for the synthesis of pharmaceuticals. In addition, late transition metal catalysts show low reaction rates and moderate selectivity for the

hydroamination of nonactivated substrates. Recently some research groups started to investigate alkaline earth metal complexes as catalysts for the hydroamination reaction.<sup>32-43</sup> In 2005 Hill et al. reported first on this topic by using  $\beta$ -diketiminato calcium amide  $[{(DIPNC(Me))_2CH}Ca{N(SiMe_3)_2}(THF)]$  (DIP = 2,6-diisopropylphenyl) as catalyst for the intramolecular hydroamination of aminoalkenes.<sup>36</sup> As expected, high conversions and short reaction times at low temperatures were observed, which is similar to rare earth metal catalyzed hydroamination. Recently, Hill et al. expanded their experimental and computational studies by synthesizing analogous  $\beta$ -diketiminato complexes of magnesium, strontium, and barium.<sup>33,35</sup> The hydroamination by using either the barium or the strontium catalyst failed, since ligand redistribution occurred and homoleptic complexes were formed. Consequently, the calcium catalyst remains superior, while computational studies predict the  $\beta$ -diketiminato strontium amide to be the most active catalyst. Recently, the synthesis of  $[\{H_2B(Im^{tBu})_2\}M\{N(SiMe_3)_2\}(THF)_n] (M = Ca, n = 1; M = Sr, n = 2, Im^{tBu} = 1$ -tert-butylimidazole) as catalytically active species for the intramolecular hydroamination of aminoalkenes was reported.<sup>32</sup> Different from the  $\beta$ -diketiminato alkaline earth metal complexes, no ligand redistribution was observed for the strontium compound; on the contrary, the strontium derivative

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was proven to be the most active catalyst. Furthermore, aminotroponiminate alkaline earth metal amides were synthesized by our group and proved to be catalytically active for the intramolecular hydroamination of aminoalkenes.<sup>37–39</sup> While heteroleptic complexes of calcium and strontium [{(*i*Pr)<sub>2</sub>ATI}M{N(Si- $Me_3_2$  (THF)<sub>2</sub> (M = Ca, Sr; (*i*Pr)<sub>2</sub>ATI = N-isopropyl-2-(isopropylamino)troponiminate) were obtained, barium forms only the homoleptic complex  $[{(iPr)_2ATI}_2Ba(THF)_2]$ . In our studies, the activity of the catalysts decreases with increasing ionic radius of the metal, and the best result was obtained for the calcium compound. This is contrary to the results observed previously for the alkaline earth metal complexes containing either the  $\beta$ -diketiminato<sup>33,35</sup> or the bis(imidazolin-2-ylidene-1yl)borate ligand,<sup>32</sup> and consequently the reaction rates and selectivities of alkaline earth metal catalysts cannot be simply related to the ionic radius of the center metal.

Now, we were interested in extending our studies to a new ligand system. Since the 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl ligand ((DIP\_pyr)<sup>-</sup>) was proven to stabilize rare earth metal(III) complexes,<sup>44–48</sup> we recently introduced the ligand into the coordination chemistry of the divalent lanthanides, which resulted in new structures with interesting coordination modes.<sup>49</sup> As a result of the same oxidation state and the similar ionic radii,<sup>50,51</sup> the reactivity and coordination behavior of the divalent lanthanides and the heavier alkaline earth metals are related.<sup>37,52–56</sup> In this context we were interested in studying the differences and similarities in the coordination chemistry of the (DIP\_2pyr)<sup>-</sup> ligand in alkaline earth metals compared to the divalent lanthanides.<sup>57</sup> Furthermore, we studied the new compounds as catalysts for the hydroamination and thus extended the short list of catalytically active alkaline earth metal species.

# EXPERIMENTAL SECTION

General Procedures. 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  $(10^{-3} \text{ Torr})$  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 or on a Bruker Avance II 300 MHz NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were obtained by means of an ATR unit on a Bruker FTIR IFS 113v spectrometer. Mass spectra were recorded at 70 eV on a Varian Mat SM 11. Elemental analyses were carried out with an Elementar Vario EL.  $(DIP_2pyr)H^{58,59}$  and  $[(DIP_2pyr)K](1)^{45,60}$  were prepared according to literature procedures.

[(DIP<sub>2</sub>pyr)MI(THF)<sub>n</sub>] (2–4). General Procedure. THF (20 mL) was condensed at -78 °C onto a mixture of MI<sub>2</sub> (M = Ca, Sr, Ba) (1.00 mmol) and [(DIP<sub>2</sub>pyr)K] (1) (480 mg, 1.00 mmol), and the resulting yellow reaction mixture was stirred at 60 °C for 16 h (M = Ca, 60 h). The yellow solution was filtered off and concentrated until a yellow precipitate appeared. The mixture was heated carefully until the solution became clear. The solution was allowed to stand at room temperature to obtain the product as yellow crystals after several hours.

[(DIP<sub>2</sub>pyr)Cal(THF)<sub>3</sub>] (2). Cal<sub>2</sub> (294 mg, 1.00 mmol). Yield: 505 mg, 0.61 mmol, 61% (single crystals). <sup>1</sup>H NMR (THF- $d_{s}$ , 300 MHz, 25 °C):  $\delta$  1.20 (d, 24 H, CH(CH<sub>3</sub>),  $J_{H,H}$  = 6.9 Hz), 3.22 (sept, 4 H, CH(CH<sub>3</sub>),  $J_{H,H}$ 

= 6.9 Hz), 6.79 (s, 2 H, 3,4-pyr), 7.03 (dd, 2 H, p-Ph,  $J_{H,H,1} = 8.7$  Hz,  $J_{H,H,2} = 6.6$  Hz), 7.11–7.14 (m, 4 H, Ph), 8.24 (br, 2 H, N=CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (THF- $d_8$ , 100.4 MHz, 25 °C):  $\delta$  25.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 116.0 (3,4-pyr), 123.2 (Ph), 124.3 (br, Ph), 138.2 (Ph), 139.5 (br, 2,5-pyr), 150.9 (Ph), 161.4 (br, N=CH) ppm. Anal. Calcd for C<sub>42</sub>H<sub>62</sub>CaIN<sub>3</sub>O<sub>3</sub> (2) (823.94): C, 61.22, H, 7.58, N, 5.10. Found: C, 60.83, H, 7.69, N, 4.78. Variable-temperature (VT)-<sup>1</sup>H NMR studies of **2** (65 and -70 °C): <sup>1</sup>H NMR (THF- $d_8$ , 300 MHz, 65 °C):  $\delta$  1.19 (d, 24 H, CH(CH<sub>3</sub>),  $J_{H,H} = 6.9$  Hz), 3.17 (sept, 4 H, CH(CH<sub>3</sub>),  $J_{H,H} = 6.9$  Hz), 6.80 (s, 2 H, 3,4-pyr), 7.01 (dd, 2 H, *p*-Ph,  $J_{H,H,1} = 8.4$  Hz,  $J_{H,H,2} = 6.6$  Hz), 7.09–7.12 (m, 4 H, Ph), 8.23 (s, 2 H, N=CH) ppm. <sup>1</sup>H NMR (THF- $d_8$ , 300 MHz, -70 °C):  $\delta$  1.09–1.28 (m, 24 H, CH(CH<sub>3</sub>), 3.03–3.18 (m, 4 H, CH(CH<sub>3</sub>)), 6.59 (s, 2 H, 3,4-pyr), 7.00–7.16 (m, 6 H, Ph), 8.07 (s, 2 H, N=CH) ppm.

[(DIP<sub>2</sub>pyr)Srl(THF)<sub>3</sub>] (3). SrI<sub>2</sub> (341 mg, 1.00 mmol). Yield 634 mg, 0.73 mmol, 73%. <sup>1</sup>H NMR (THF- $d_8$ , 300 MHz, 25 °C):  $\delta$  1.17–1.21 (m, 24 H, CH(CH<sub>3</sub>)), 3.22 (sept, 4 H, CH(CH<sub>3</sub>),  $J_{H,H}$  = 6.9 Hz), 6.59 (s, 2 H, 3,4-pyr), 7.05 (dd, 2 H, *p*-Ph,  $J_{H,H,1}$  = 8.8 Hz,  $J_{H,H,2}$  = 6.3 Hz), 7.13–7.15 (m, 4 H, Ph), 8.01 (s, 2 H, N=CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (THF- $d_8$ , 100.4 MHz, 25 °C):  $\delta$  25.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 117.3 (3,4-pyr), 122.5 (Ph), 123.8 (Ph), 139.4 (Ph), 142.5 (2,5-pyr), 150.9 (Ph), 161.5 (N=CH) ppm. Anal. Calcd for C<sub>46</sub>H<sub>70</sub>IN<sub>3</sub>O<sub>4</sub>Sr (3 + THF) (943.59): C, 58.55, H, 7.48, N, 4.45. Found: C, 58.54, H, 7.48, N, 4.66.

 $\begin{array}{l} \textbf{[(DIP_2pyr)Bal(THF)_4]} \ \textbf{(4).} BaI_2 \ (391 mg, 1.00 mmol). Yield: \\ 455 mg, 0.46 mmol, 46% \ (single crystals). {}^{1}H NMR \ (THF-d_8, 400 MHz, 25 °C): \delta 1.16-1.32 \ (m, 24 H, CH(CH_3)), 3.22 \ (sept, 4 H, CH(CH_3), J_{H,H} = 6.9 Hz), 6.59 \ (s, 2 H, 3,4-pyr), 7.07 \ (dd, 2 H, p-Ph, J_{H,} H_1 = 8.4 Hz, J_{H,H,2} = 6.8 Hz), 7.13-7.17 \ (m, 4 H, Ph), 8.03 \ (s, 2 H, N=CH) ppm. {}^{13}C{}^{1}H} NMR \ (THF-d_8, 100.4 MHz, 25 °C): \delta 26.1 \ (CH(CH_3)_2), 28.4 \ (CH(CH_3)_2), 118.1 \ (3,4-pyr), 123.3 \ (Ph), 124.5 \ (Ph), 140.1 \ (2,5-pyr), 143.7 \ (Ph), 151.3 \ (Ph), 162.4 \ (N=CH) ppm. \\ Anal. Calcd for C_{46}H_{70}BaIN_3O_4 \ (4) \ (993.30): C, 55.62, H, 7.10, N, \\ 4.23. Found: C, 55.21, H, 6.71, N, 4.53. \\ \end{array}$ 

 $[(DIP_2pyr)M{N(SiMe_3)_2}(THF)_2]$  (5, 6). General Procedure. THF (15 mL) was condensed at -78 °C onto a mixture of  $[(DIP_2pyr)MI(THF)_3]$  (M = Ca (2), Sr (3)) (0.5 mmol) and  $[K{N(SiMe_3)_2}]$  (100 mg, 0.5 mmol), and the resulting yellow reaction mixture was stirred at 60 °C for 16 h. The yellow solution was filtered off and concentrated until a yellow precipitate appeared. The mixture was heated carefully until the solution became clear. The solution was allowed to stand at room temperature to obtain the product as yellow crystals after several hours.

[(DIP<sub>2</sub>pyr)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF)<sub>2</sub>] (5). [(DIP<sub>2</sub>pyr)CaI(THF)<sub>3</sub>] (2) (411 mg, 0.5 mmol). Yield: 270 mg, 0.34 mmol, 69% (single crystals). <sup>1</sup>H NMR (THF- $d_8$ , 300 MHz, 25 °C):  $\delta$  -0.21 (s, 18 H, SiMe<sub>3</sub>), 1.21 (d, 24 H, CH(CH<sub>3</sub>),  $J_{H,H}$  = 6.9 Hz), 3.07 (sept, 4 H, CH(CH<sub>3</sub>),  $J_{H,H}$  = 6.9 Hz), 6.71 (s, 2 H, 3,4-pyr), 7.07 (dd, 2 H, p-Ph,  $J_{H,1}$  = 8.7 Hz,  $J_{H,H,2}$  = 6.0 Hz), 7.13-7.16 (m, 4 H, Ph), 8.07 (s, 2 H, N=CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (THF- $d_8$ , 100.4 MHz, 25 °C):  $\delta$  5.0 (SiMe<sub>3</sub>), 25.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 118.8 (3,4-pyr), 122.6 (Ph), 124.0 (Ph), 140.0 (Ph), 142.5 (2,5-pyr), 150.5 (Ph), 161.3 (N=CH) ppm. Anal. Calcd for C<sub>48</sub>H<sub>80</sub>CaN<sub>4</sub>O<sub>3</sub>Si<sub>2</sub> (5 + THF) (857.42): C, 67.24, H, 9.40, N, 6.53. Found: C, 67.36, H, 9.11, N, 6.32.

[(DIP<sub>2</sub>pyr)Sr{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF)<sub>2</sub>] (6). [(DIP<sub>2</sub>pyr)SrI(THF)<sub>3</sub>] (3) (436 mg, 0.5 mmol). Yield: 300 mg, 0.36 mmol, 72% (single crystals). <sup>1</sup>H NMR (THF- $d_8$ , 300 MHz, 25 °C):  $\delta$  -0.29 (s, 18 H, SiMe<sub>3</sub>), 1.15-1.32 (m, 24 H, CH(CH<sub>3</sub>)), 3.06 (sept, 4 H, CH(CH<sub>3</sub>)),  $J_{H,H} = 6.9$  Hz), 6.62 (s, 2 H, 3,4-pyr), 7.07 (dd, 2 H, p-Ph,  $J_{H,H,1} = 9.0$  Hz,  $J_{H,H,2} = 6.0$  Hz), 7.13-7.16 (m, 4 H, Ph), 8.03 (s, 2 H, N=CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (THF- $d_8$ , 100.4 MHz, 25 °C):  $\delta$  5.0 (SiMe<sub>3</sub>), 25.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 118.1 (3,4-pyr), 122.6 (Ph), 124.0 (Ph), 139.0 (Ph), 142.5 (2,5-pyr), 150.8 (Ph), 162.0 (N=CH) ppm.

Table 1. Crystallographic Details of 2-6

|  | 2·THF  | 3·2THF                               | 4·THF  | 5.THF                               | 6.THF                      |
|--|--|--------------------------------------|--|-------------------------------------|----------------------------|
| chemical formula                                     | C <sub>46</sub> H <sub>70</sub> CaIN <sub>3</sub> O <sub>4</sub> | $\mathrm{C_{50}H_{78}IN_{3}O_{5}Sr}$ | C <sub>50</sub> H <sub>78</sub> BaIN <sub>3</sub> O <sub>5</sub> | $\mathrm{C_{48}H_{80}CaN_4O_3Si_2}$ | $C_{48}H_{80}N_4O_3Si_2Sr$ |
| fw   | 896.03   | 1015.67                              | 1065.39  | 857.42                              | 904.96                     |
| a/Å  | 17.187(3)  | 15.253(3)                            | 10.979(2)  | 16.426(3)                           | 16.605(3)                  |
| b/Å  | 15.177(3)  | 31.967(6)                            | 31.676(6)  | 10.568(2)                           | 10.727(2)                  |
| c/Å  | 19.291(4)  | 11.330(2)                            | 15.769(3)  | 29.727(6)                           | 29.874(6)                  |
| $eta/{ m deg}$                                       | 107.76(3)  | 107.95(3)                            | 109.07(3)  | 97.67(3)                            | 96.87(3)                   |
| unit cell volume/Å $^3$                              | 4792(2)  | 5256(2)                              | 5183(2)  | 5114(2)                             | 5283(2)                    |
| temperature/K  | 150(2)   | 200(2)                               | 200(2)   | 150(2)                              | 200(2)                     |
| space group  | $P2_{1}/c$   | $P2_{1}/c$                           | $P2_1$   | $P2_1/c$                            | $P2_{1}/c$                 |
| no. of formula units per unit cell, $\boldsymbol{Z}$ | 4  | 4                                    | 4  | 4                                   | 4                          |
| radiation type                                       | Μο Κα  | Μο Κα                                | Μο Κα  | Μο Κα                               | Μο Κα                      |
| absorp coeff, $\mu/\text{mm}^{-1}$                   | 0.816  | 1.657                                | 1.406  | 0.210                               | 1.105                      |
| no. of reflns measd                                  | 30 443   | 42 462                               | 39 822   | 22 279                              | 39 441                     |
| no. of indep reflns                                  | 8441   | 9253                                 | 23 278   | 10 661                              | 10 530                     |
| R <sub>int</sub>                                     | 0.1016   | 0.2298                               | 0.0492   | 0.0614                              | 0.0968                     |
| final $R_1$ values $(I > 2\sigma(I))$                | 0.0729   | 0.0885                               | 0.0397   | 0.0689                              | 0.0653                     |
| final $wR(F^2)$ values (all data)                    | 0.1963   | 0.2350                               | 0.0992   | 0.1790                              | 0.1564                     |
| goodness of fit on F <sup>2</sup>                    | 0.986  | 0.933                                | 1.010  | 0.970                               | 1.057                      |

Anal. Calcd for C<sub>48</sub>H<sub>80</sub>SrN<sub>4</sub>O<sub>3</sub>Si<sub>2</sub> (6 + THF) (904.96): C, 63.71, H, 8.91, N, 6.19. Found: C, 64.30, H, 8.58, N, 6.23.

**Hydroamination Studies.** The catalyst was weighed under argon gas into an NMR tube.  $C_6D_6$  (~0.5 mL) was condensed into the NMR tube, and the mixture was frozen to -196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before insertion into the core of the NMR machine ( $t_0$ ). The ratio between the reactant and the product was calculated by comparison of the integrations of the corresponding signals. Ferrocene was used as an internal standard for the kinetic measurements. The substrates 2,2diphenyl-pent-4-enylamine (7a),<sup>61</sup> C-(1-allylcyclohexyl)methylamine (8a),<sup>61</sup> 2,2-dimethylpent-4-enylamine (9a),<sup>61</sup> and 2-amino-5-hexene (via hex-5-en-2-one oxime<sup>62</sup>) (10a)<sup>63</sup> were synthesized according to the literature procedures. <sup>1</sup>H NMR spectra of 2-methyl-4,4-diphenylpyrrolidine (7b),<sup>61</sup> 3-methyl-2-aza-spiro[4.5]decane (8b),<sup>61</sup> 2,4,4-trimethylpyrrolidine (9b),<sup>61</sup> and 2,5-dimethylpyrrolidine (10b)<sup>63</sup> conform with the literature.

**Isomerization Product 10c**, *in Situ* <sup>1</sup>**H NMR Data.** Compound **10c** was detected within a mixture and not further purified.

**2-Amino-4-hexene (10c).** <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 25 °C):  $\delta$  0.73 (br, 2 H, NH<sub>2</sub>), 0.92 (d, 3 H, Me,  $J_{H,H}$  = 6.3 Hz), 1.47–1.50 (m, 3 H, Me-C=C), 1.92 (t, 2 H, C=C-CH<sub>2</sub>,  $J_{H,H}$  = 6.9 Hz), 2.71 (m<sub>s</sub>, 1 H, CH), 5.28–5.38, 5.44–5.54 (2 m, 2 H, HC=CH) ppm.

X-ray Crystallographic Studies of 2–6. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to either the -73 or -123 °C cold stream of a STOE IPDS 2T diffractometer. Subsequent computations were carried out on an Intel Pentium Core2Duo PC.

All structures were solved by the Patterson method (SHELXS-97<sup>65</sup>). The remaining non-hydrogen atoms were located from successive difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function  $(F_o - F_c)^2$ , where the weight is defined as  $4F_o^2/2(F_o^2)$  and  $F_o$  and  $F_c$  are the observed and calculated structure factor amplitudes using the program SHELXL-97.<sup>65</sup> Carbon-bound hydrogen atom positions were calculated. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

#### RESULTS AND DISCUSSION

The salt metathesis reaction of  $[(DIP_2pyr)K]$  (1) with anhydrous alkaline earth metal diiodides in THF at elevated temperature gave the corresponding complexes  $[(DIP_2pyr)MI-(THF)_n]$  (M = Ca (2), Sr (3) (*n* = 3); Ba (4) (*n* = 4)), as shown in Scheme 1. While the strontium and barium complexes 3 and 4 were obtained within 16 h, the synthesis of the calcium compound 2 required a reaction time of 60 h.<sup>57</sup>

Complexes 2-4 were characterized by standard analytical/ spectroscopic techniques, and the solid-state structures were analyzed by single-crystal X-ray diffraction. Compounds 2-4 are monomeric in the solid state (Scheme 1). Interestingly, the  $(DIP_2 pyr)^-$  ligand in the calcium complex 2 shows a  $\kappa^2$ -coordination mode, while the ligands in 3 and 4 coordinate in a  $\kappa^3$ fashion to the metal centers. The <sup>1</sup>H NMR spectrum of compound 2 shows a broad singlet for the imino N=CH moieties  $(\delta = 8.24 \text{ ppm})$ , while for the isopropyl groups one doublet ( $\delta =$ 1.20 ppm) and one septet ( $\delta$  = 3.22 ppm) were observed, indicating that the 2,6-diisopropylaniline moieties of the ligand can freely rotate in solution. These observations can be ascribed to a similar chemical environment in solution at room temperature for both 2,6-diisopropylaniline moieties, which is in contrast to the solid-state structures of 2 (see below). Further VT-<sup>1</sup>H NMR studies of 2 were performed, in order to investigate the coordination mode of the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand in solution. At 65 °C the <sup>1</sup>H NMR spectrum of compound **2** is very similar to the one measured at room temperature, except the imino N=CH moieties showing a clear singlet ( $\delta$  = 8.23 ppm), which is certainly caused by the thermal motion. This thermal motion includes the rotation of the 2,6-diisopropylaniline groups as well as flipping of the imino N=CH moieties. Upon lowering the temperature to -70 °C, a multiplet for the isopropyl CH<sub>3</sub> groups  $(\delta = 1.09 - 1.28)$  was observed, indicating a restricted rotation of the 2,6-diisopropylaniline groups of the ligand at low temperature.

#### Scheme 1



In addition, the pyrrolyl hydrogen atoms as well as the imino N=CH moieties show a clear singlet ( $\delta = 6.59$  ppm and  $\delta = 8.07$  ppm), which can be attributed to a similar chemical environment for both 2,6-diisopropylaniline moieties of the ligand. In solution even at a low temperature, there is no evidence of an asymmetrical coordination mode of the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand in the calcium complex **2**. The <sup>1</sup>H NMR spectra of **3** and **4** show a multiplet ( $\delta = 1.17-1.21$  (**3**), 1.16-1.32 (**4**) ppm) and a clear septet ( $\delta = 3.22$  (**3**), 3.22 (**4**) ppm) for the isopropyl groups of the (DIP<sub>2</sub>pyr)<sup>-</sup> ligands, which indicates a restricted rotation of the 2,6-diisopropylaniline groups. In addition, the sharp singlet for the imino N=CH units ( $\delta = 8.01$  (**3**), 8.03 (**4**) ppm) confirms the symmetrical coordination mode of the ligands in **3** and **4**.

Compound **2** crystallizes in the monoclinic space group  $P2_1/c$ with four molecules of the complex and four THF molecules in the unit cell. The  $(DIP_2pyr)^-$  ligand of 2 coordinates with one Schiff-base function and the pyrrolyl moiety (Ca-N1 2.510(5) Å and Ca-N2 2.408(5) Å) to the metal center (Figure 1). As expected, the coordinated imino N=CH unit exhibits a slightly larger N-C bond length (N1-C1 1.296(8) Å) than the noncoordinated N=CH moiety (N3-C6 1.262(7) Å). The 6-fold coordination sphere around the metal center is formed by the  $\kappa^2$ coordinated (DIP<sub>2</sub>pyr)<sup>-</sup> ligand, the iodine atom, and three THF molecules, showing a distorted octahedral geometry. The iodine atom and the coordinated Schiff-base moiety are in trans position and show a nearly linear setup  $(N1-Ca-I 178.34(12)^\circ)$ . The remaining square area of the distorted octahedron is formed by the pyrrolyl moiety and the three THF molecules, and the almost planar arrangement of the CaO<sub>3</sub>N fragment is confirmed by the sum of the four corresponding valence angles (360.2°). The Ca-I bond distance (3.0782(13) Å) in 2 is similar to the Yb-I bond length (3.100(2) Å) of the analogous ytterbium compound  $[(DIP_2pyr)YbI(THF)_3]^{49}$  and to those in  $[{(Me_3SiNPPh_2)_2C-}$ H}CaI(THF)<sub>2</sub>] or [{ $(iPr)_2ATI$ }CaI(THF)<sub>3</sub>] ( $(iPr)_2ATI = N$ isopropyl-2-(isopropylamino)troponiminate).<sup>56,66</sup> Usually, analogous calcium and ytterbium derivatives tend to form isostructural complexes. $^{37,53-56}$  In the present case, the calcium complex 2 exhibits a  $\kappa^2$ -coordinated (DIP<sub>2</sub>pyr)<sup>-</sup> ligand, which is coordinated



Figure 1. Perspective ORTEP view of the molecular structure of 2. Thermal ellipsoids are drawn to encompass 30% probability. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [deg]: Ca-N1 2.510(5), Ca-N2 2.408(5), Ca-O1 2.367(4), Ca-O2 2.371(5), Ca-O3 2.368(4), Ca-I 3.0782(13), N1-C1 1.296(8), N3-C6 1.262(7); N1-Ca-N2 71.6(2), N1-Ca-O1 90.31(15), N1-Ca-O2 87.8(2), N1-Ca-O3 89.74(15), N2-Ca-O1 92.0(2), N2-Ca-O2 159.4(2), N2-Ca-O3 85.13(15), N1-Ca-I 178.34(12), N2-Ca-I 107.21(11), O1-Ca-I 90.84(11), O2-Ca-I 93.41(13), O3-Ca-I 89.05(11), O1-Ca-O2 88.0(2), O2-Ca-O3 95.1(2), O1-Ca-O3 176.9(2).

only by one Schiff-base function and the pyrrolyl moiety, while the analogous ytterbium compound  $\left[(\text{DIP}_2\text{pyr})\text{YbI}(\text{THF})_3\right]^{49}$  additionally shows a long interaction with the second Schiffbase unit.

Compound 3 crystallizes in the monoclinic space group  $P2_1/c$  with four molecules of the complex and eight THF molecules in the unit cell. As a result of "twining" problems, the data quality is low but the connectivity of the atoms could be clearly assigned. Compound 3 is isostructural to the analogous samarium and



**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]: Sr-N1 2.964(7), Sr-N2 2.478(7), Sr-N3 2.966(7), Sr-O1 2.566(6), Sr-O2 2.589(6), Sr-O3 2.562(6), Sr-I 3.2282(12); N1-Sr-N2 61.1(2), N1-Sr-N3 121.7(2), N2-Sr-N3 60.7(2), N1-Sr-O1 89.0(2), N1-Sr-O2 76.0(2), N1-Sr-O3 152.1(2), N2-Sr-O1 82.4(2), N2-Sr-O2 136.2(2), N2-Sr-O3 143.3(2), N3-Sr-O1 80.3(2), N3-Sr-O2 158.6(2), N3-Sr-O3 83.6(2), N1-Sr-I 98.44(14), N2-Sr-I 104.2(2), N3-Sr-I 98.59(13), O1-Sr-I 171.8(2), O2-Sr-I 89.7(2), O3-Sr-I 88.04(15), O1-Sr-O2 88.7(2), O2-Sr-O3 77.0(2), O1-Sr-O3 83.7(2).

europium compounds [(DIP<sub>2</sub>pyr)LnI(THF)<sub>3</sub>] (Ln = Sm, Eu).<sup>49</sup> The (DIP<sub>2</sub>-pyr)<sup>-</sup> ligand coordinates as a tridentate chelate ligand in an almost symmetrical fashion to the metal center, as shown in Figure 2. The Sr-N distances reflect the differences in bond strength and character. Accordingly, the Sr-N(Schiffbase) bonds display a rather weak  $\sigma$ -donor character, while the short Ln–N(pyrrole) bonds signal a strong interaction as result of the negatively charged nitrogen atom. Thus, the Sr-N bond distances to the pyrrole ring (Sr-N1 2.964(7) Å, Sr-N2 2.478(7) Å, Sr-N3 2.966(7) Å) are about 0.5 Å shorter than the distance to the Schiff-base nitrogen atoms. The coordination sphere of the metal center of 3 is formed by the  $(DIP_2pyr)^{-1}$ ligand, the iodine atom, and three THF molecules, which resulted in a distorted pentagonal bipyramidal geometry. The iodine atom and one THF molecule are arranged in a nearly linear setup (O1-Sr-I 171.8(2)°) and form the apexes of the distorted pentagonal bipyramid. The almost planar arrangement of the  $SrN_3O_2$  fragment is confirmed by the sum of the corresponding five valence angles  $(358.4^{\circ})$ . The iodine atom occupies a *cisoid* position to all three nitrogen atoms of the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand (N1-Sr-I 98.44(14)°, N2-Sr-I 104.2(2)°, N3-Sr-I 98.59(13)°).

Compound 4 crystallizes in the monoclinic space group  $P_{21}$  with four molecules of the complex and four THF molecules in the unit cell. The asymmetric unit contains two independent molecules of 4 and two THF molecules. Similarly to 3, the  $(DIP_2pyr)^-$  ligand of 4 is coordinated almost symmetrically to the metal center (Figure 3). The metal—imine nitrogen bond distances (Ba1-N1 3.196(4) Å, Ba1-N3 3.145(3) Å, Ba2-N4 3.214(4) Å, Ba2-N6 3.156(3) Å) are longer than the Ba- $N_{pyrrolyl}$  distance (Ba1-N2 2.690(3) Å, Ba2-N5 2.679(3) Å). Remarkably, the coordination sphere of the metal center is satisfied by four additionally coordinated THF molecules, instead of forming a dimer. Consequently, the 8-fold coordination sphere is formed by the (DIP\_2pyr)<sup>-</sup> ligand, the iodine atom, and four THF molecules. The iodine atom of 4 is not arranged linearly



Figure 3. Perspective ORTEP view of the molecular structure of 4. Thermal ellipsoids are drawn to encompass 30% probability. Only one of the two independent molecules is shown. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [deg]: Ba1-N1 3.196(4), Ba1-N2 2.690(3), Ba1-N3 3.145(3), Ba1-O1 2.812(3), Ba1-O2 2.801(3), Ba1-O3 2.806(3), Ba1-O4 2.877(3), Ba1-I1 3.4950(8), Ba2-N4 3.214(4), Ba2-N5 2.679(3), Ba2-N6 3.156(3), Ba2-O5 2.819(3), Ba2-O6 2.774(4), Ba2-O7 2.865(3), Ba2-O8 2.776(3), Ba2-I2 3.4922(7); N1-Ba1-N2 57.13(10), N1-Ba1-N3 115.04(9), N2-Ba1-N3 57.94(10), N1-Ba1-O1 79.94(9), N1-Ba1-O2 147.02(10), N1-Ba1-O3 74.46(10), N1-Ba1-O4 77.66(10), N2-Ba1-O1 74.37(9), N2-Ba1-O2 119.27(10), N2-Ba1-O3 126.22(11), N2-Ba1-O4 71.75(9), N3-Ba1-O1 84.92(9), N3-Ba1-O2 72.28(10), N3-Ba1-O3 156.64(9), N3-Ba1-O4 81.52(10), N1-Ba1-II 128.59(6), N2-Ba1-II 148.40(7), N3-Ba1-II 106.04(7), O1-Ba1-II 134.84(7), O2-Ba1-II 73.56(7), O3-Ba1-I1 79.99(8), O4-Ba1-I1 79.31(7), O1-Ba1-O2 68.43(10), O1-Ba1-O3 75.58(10), O1-Ba1-O4 145.75(9), O2-Ba1-O3 88.44(11), O2-Ba1-O4 134.71(11), O3-Ba1-O4 121.82(10) N4-Ba2-N5 56.92(9), N4-Ba2-N6 115.20(9), N5-58.28(10), N4-Ba2-O5 85.62(9), N4-Ba2-O6 Ba2-N6 159.73(11), N4-Ba2-O7 79.68(10), N4-Ba2-O8 73.89(10), N5-Ba2-O5 74.66(9), N5-Ba2-O6 126.08(10), N5-Ba2-O7 147.29(9), N5-Ba2-O8 118.65(11), N6-Ba2-O5 78.57(9), N6-Ba2-O6 71.77(10), N6-Ba2-O7 81.55(10), N6-Ba2-O8 143.67(9), N4-Ba2-I2 106.90(6), N5-Ba2-I2 149.15(7), N6-Ba2-I2 128.84(7), O5-Ba2-I2 133.86(6), O6-Ba2-I2 78.85(8), O7-Ba2-I2 78.65(7), O8-Ba2-I2 74.35(7), O5-Ba2-O6 77.00(11), O5-Ba2-O7 147.29(9), O5-Ba2-O8 66.78(10), O6-Ba2-O7 120.59(12), O6-Ba2-O8 89.53(12), O7-Ba2-O8 134.24(10).

with respect to any of the nitrogen atoms of the  $(DIP_2pyr)^$ ligand (e.g., N1–Ba1–II 128.59(6)°, N2–Ba1–II 148.40(7)°, N3–Ba1–II 106.04(7)°). The Ba–I bond distances (Ba1–II 3.4950(8) Å and Ba2–I2 3.4922(7) Å) are similar to that observed for the monomeric barium iodo complex stabilized by the very bulky tris[3-(2-methoxy-1,1-dimethyl)pyrazolyl]hydroborate (TpC\*) ligand (Ba–I 3.5008(2) Å).<sup>67</sup>

Similarly to the previously described divalent lanthanide compounds,<sup>49</sup> all complexes **2**–**4** are monomeric in the solid state, which is remarkable since strontium and barium tend to form dimeric complexes, bridged by iodine atoms.<sup>56,66,68–71</sup> Only few monomeric heteroleptic iodo complexes of strontium and barium are known. For example, [TpC\*SrI(THF)] and [TpC\*BaI], which contain a very bulky hexadentate ligand, form monomers in the solid state.<sup>67</sup> In addition, the monomeric cluster compounds [IM(OtBu)<sub>4</sub>{Li(THF)}<sub>4</sub>(OH)] of calcium, strontium, and barium are known.<sup>72</sup> All these compounds contain very bulky ligands, which saturate the coordination sphere of the



Figure 4. Energy diagram of compounds 2 and 4 based on computational studies.

corresponding metal center to form monomeric structures and thus cannot be compared to complexes **3** and **4**, in which the coordination sphere is satisfied by additionally coordinated THF molecules. Furthermore, it is very interesting that the solid-state structure of the calcium complex **2** shows a  $\kappa^2$ -coordinated (DIP<sub>2</sub>pyr)<sup>-</sup> ligand, while the VT-<sup>1</sup>H NMR studies indicate a symmetrical coordination of the ligand in solution even at low temperatures. In order to obtain more insight into the coordination behavior of the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand in the calcium complex **2**, computational studies of **2** and the barium derivative **4** were performed.

**Computational Studies.** The possible local minima on the corresponding energy hyperfaces were calculated within the framework of density functional theory  $(\text{RI-DFT})^{73,74}$  at the BP86-level<sup>75–78</sup> (basis set of def2-SVP quality for each atom),<sup>79–81</sup> as this theoretical level provides reliable data on this kind of highly ionic complexes. Due to the huge size of the molecules, frequency calculations to check on imaginary frequencies as indicators for a negative curvature of the energy hypersurface were not possible. Instead the calculations were performed without symmetry constraints to ensure that minima calculated are "real". All of the calculations entailed the use of the TURBOMOLE package.<sup>82</sup> As the size of the ligand may be of importance for the complexation of the unsymmetrical or symmetrical isomer of the ligand, the molecular structures of the most different compounds, which are 2 and 4, were calculated without simplification of the ligands (Figure 4).

The energy differences between the symmetrically (SYM) coordinated  $(DIP_2pyr^{SYM})^-$  ligand and the asymmetrically (ASYM) coordinated  $(DIP_2pyr^{ASYM})^-$  ligand for both the barium and the calcium compound were calculated. In both cases, the symmetrically coordinated solvent-free species  $[(DIP_2pyr^{SYM})MI]$  exhibit a lower energy than the asymmetrically coordinated ones  $[(DIP_2pyr^{ASYM})MI]$  by 57 kJ/mol (M = Ba) and 49 kJ/mol (M = Ca), respectively.

We compared the energy of the possible isomer  $[(DIP_2p-yr^{SYM})MI(THF)_4]$  as realized for M = Ba with that of

[(DIP<sub>2</sub>pyr<sup>SYM</sup>)MI(THF)<sub>3</sub>] (with one further unbound THF molecule) as realized for M = Ca. For M = Ca we found that [(DIP<sub>2</sub>pyr<sup>SYM</sup>)MI(THF)<sub>4</sub>] is not formed and spontaneously "decomposes" into [(DIP<sub>2</sub>pyr<sup>SYM</sup>)MI(THF)<sub>3</sub>] plus an unbound THF during the relaxation process of the calculation. The coordination sphere of Ca is obviously not large enough to allow the aggregation of four THF donor molecules. [(DIP<sub>2</sub>pyr<sup>ASYM</sup>) CaI(THF)<sub>3</sub>] and [(DIP<sub>2</sub>pyr<sup>SYM</sup>)CaI(THF)<sub>3</sub>] are of comparable energy at this level of theory so that the shape of the realized isomer is obviously due to temperature or/and crystal-packing effects.<sup>57</sup> For M = Ba we confirmed the experimental finding: [(DIP<sub>2</sub>pyr<sup>SYM</sup>)BaI(THF)<sub>4</sub>] is energetically favored by 31 kJ/mol with respect to [(DIP<sub>2</sub>pyr<sup>ASYM</sup>)BaI(THF)<sub>3</sub>] plus an unbound THF. The theoretical species [(DIP<sub>2</sub>pyr<sup>ASYM</sup>)BaI(THF)<sub>4</sub>].

Amido Complexes. In order to form catalytically active species based on 2 and 3 for the intramolecular hydroamination catalysis, the {N(SiMe<sub>3</sub>)<sub>2</sub>}<sup>-</sup> ligand was introduced as a leaving group.<sup>35–37,39</sup> Since our previous studies resulted in decreased catalytic activity by increasing the ionic radius of the alkaline earth metal, we were not interested in synthesizing the analogous barium compound. The reaction of  $[(DIP_2pyr)MI(THF)_3]$  (M = Ca (2), Sr (3)) with  $[K{N(SiMe_3)_2}]$  in THF at elevated temperature gave  $[(DIP_2pyr)M{N(SiMe_3)_2}]$  (M = Ca (5), Sr (6)), as shown in Scheme 2.<sup>57</sup>

Complexes **5** and **6** were characterized by standard analytical/ spectroscopic techniques, and the solid-state structures were analyzed by single-crystal X-ray diffraction. The <sup>1</sup>H NMR spectra of **5** and **6** show a singlet for the imino N=CH groups ( $\delta = 8.07$ (**5**), 8.03 (**6**) ppm) of the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand, which confirms the  $\kappa^3$ -coordination mode. While for **6** a multiplet and a septet are observed for the isopropyl groups of the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand (1.15–1.32, 3.06 ppm), the <sup>1</sup>H NMR spectrum of **5** shows a doublet and a septet ( $\delta = 1.21$ , 3.07 ppm), indicating a free rotation of the 2,6-diisopropylaniline moieties in **5**. In the <sup>1</sup>H NMR spectra of **5** and **6** one singlet for the {N(SiMe<sub>3</sub>)<sub>2</sub>}<sup>-</sup> ligand

#### Scheme 2





Figure 5. Perspective ORTEP view of the molecular structure of 5. Thermal ellipsoids are drawn to encompass 30% probability. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [deg]: Ca-N1 3.022(3), Ca-N2 2.374(3), Ca-N3 2.888(3), Ca-N4 2.372(3), Ca-O1 2.368(2), Ca-O2 2.363(3); N1-Ca-N2 61.08(8), N1-Ca-N3 124.98(7), N1-Ca-N4 123.60(9), N2-Ca-N3 63.90(8), N2-Ca-N4 174.96(11), N3-Ca-N4 111.42(9), N1-Ca-O1 85.23(9), N1-Ca-O2 87.42(10), N2-Ca-O1 86.85(9), N2-Ca-O2 86.75(10), N3-Ca-O1 92.98(9), N3-Ca-O2 88.55(10), N4-Ca-O1 91.62(9), N4-Ca-O2 95.17(10), O1-Ca-O2 171.96(11), Ca-N4-Si1 113.86(15), Ca-N4-Si2 122.55(14).

 $(\delta = -0.21 \text{ (5)}, -0.29 \text{ (6) ppm})$  is observed. The <sup>13</sup>C{<sup>1</sup>H} NMR data are consistent with the information obtained from the <sup>1</sup>H NMR spectra.

Compounds 5 and 6 crystallize in the monoclinic space group  $P2_1/c$  with four molecules of the corresponding complex and four THF molecules in the unit cell. As shown in Figures 5 and 6, the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand coordinates in both compounds 5 and 6 in a tridentate fashion. In compound 6 an almost symmetrical coordination of the ligand to the metal center (Sr-N1 3.034(3) Å, Sr-N3 2.994(3) Å) is seen, while due to the smaller ionic radius of Ca<sup>2+</sup>, the Schiff-base functions of the ligand in 5 coordinate in an asymmetrical fashion (Ca-N1 3.022(3) Å, Ca-N3 2.888(3) Å). In contrast to the different coordination modes of the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand in 2 and 3, in both products 5 and 6 the ligand is thus  $\kappa^3$ -coordinated in the solid state. The



**Figure 6.** Perspective ORTEP view of the molecular structure of 6. Thermal ellipsoids are drawn to encompass 30% probability. Hydrogen atoms are omitted for clarity. The THF molecule around O2 is disordered, and bond lengths and angles are given for both positions O2A and O2B. Selected distances [Å] and angles [deg]: Sr–N1 3.034(3), Sr–N2 2.515(3), Sr–N3 2.994(3), Sr–N4 2.516(3), Sr–O1 2.527(3), Sr–O2A 2.539(9), Sr–O2B 2.509(9), Sr–C31 3.299(5); N1–Sr–N2 59.79(9), N1–Sr–N3 120.63(8), N1–Sr–N4 125.43(9), N2–Sr–N3 60.85(9), N2–Sr–N4 174.35(10), N3–Sr–N4 113.93(9), N1–Sr–O1 85.85(10), N1–Sr–O2A 82.9(2), N1–Sr–O2B 92.7(2), N2–Sr–O1 86.37(10), N2–Sr–O2A 84.5(2), N2–Sr–O2B 88.9(2), N3–Sr–O1 91.66(11), N3–Sr–O2A 90.6(2), N3–Sr–O2B 85.1(2), N4–Sr–O1 91.75(10), N4–Sr–O2B 92.9(2), O1–Sr–O2A 168.1(2), O1–Sr–O2B 175.1(2), Sr–N4–Si1 112.23(15), Sr–N4–Si2 121.7(2).

6-fold coordination sphere of each complex is formed by the  $(DIP_2pyr)^-$  ligand, the  $\{N(SiMe_3)_2\}^-$  ligand, and two THF molecules, showing a distorted octahedral geometry. The apexes of each polyhedron are formed by the two THF molecules, which are arranged linearly  $(O1-Ca-O2\ 171.96(11)^\circ$  (5) and  $O1-Sr-O2B\ 175.1(2)^\circ$  (6)). The planar arrangement of the CaN<sub>4</sub> fragment is confirmed by the sum of the four corresponding valence angles (360.0° in 5 and 6)). The M–N bond distances to the pyrrolyl units of the (DIP\_2pyr)<sup>-</sup> ligands in 5 and 6 (Ca-N2 2.374(3) Å (5) and Sr-N2 2.515(3) Å (6)) are similar to the M–N bond length observed for the  $\{N(SiMe_3)_2\}^-$  ligands (Ca-N4 2.372(3) Å (5) and Sr-N4 2.516(3) Å (6)). Furthermore, the different M–N4–Si angles (Ca–N4–Si1 113.86(15)°

| Entry | Substrate                | Product              | Cat       | Т    | t    | Yield <sup>b</sup> |
|-------|--------------------------|----------------------|-----------|------|------|--------------------|
|       |                          |                      | (5 mol %) | [°C] | [h]  | [%]                |
| 1     | Ph Ph<br>NH <sub>2</sub> | HN                   | 5         | r.t. | 0.03 | 99                 |
| 2     | 7a                       | Ph´ `Ph<br><b>7b</b> | 6         | r.t. | 0.5  | 98                 |
| 3     |                          | HN                   | 5         | r.t. | 0.33 | quant              |
| 4     | 8a                       | 8b                   | 6         | r.t. | 4    | quant              |
| 5     | Me Me                    | HN                   | 5         | r.t  | 0.5  | 92                 |
| 6     | 9a                       | Me´`Me<br>9b         | 6         | 60   | 2    | 92                 |
| 7     |                          |                      | 5         | r.t. | 46   | 82°                |
| 8     |                          | $\square$            |           |      |      | (1:13)"            |
|       | 10a                      | N<br>H<br>10b        | 5         | 60   | 5    | 60 <sup>c</sup>    |
|       |                          |                      |           |      |      | $(1:8)^{d}$        |
|       |                          |                      | 6         | r.t. | 48   | 29 <sup>c</sup>    |
|       |                          |                      |           |      |      | (-) <sup>e</sup>   |

Table 2. Hydroamination Reactions of Terminal Aminoalkenes and Alkynes Catalyzed by 5 and  $6^a$ 

<sup>*a*</sup> Conditions: cat. 15–20 mg (5 mol %),  $C_6 D_6$ . <sup>*b*</sup> Calculated by <sup>1</sup>H NMR, ferrocene as internal standard. <sup>*c*</sup> Products were accompanied by alkene isomerization byproduct **10c** (see text for details). <sup>*d*</sup> Ratio *cis:trans.* <sup>*c*</sup> *Cis/trans* signals obscured by other signals.

versus Ca–N4–Si2 122.55(14)° (5); Sr–N4–Si1 112.23(15)° versus Sr–N4–Si2 121.7(2)° (6)) of the {N(SiMe<sub>3</sub>)<sub>2</sub>}<sup>-</sup> ligands indicate a distorted geometry. The Si1–N4–Si2 angles are 123.5(2)° (5) and 126.1(2)° (6). In contrast to [Me<sub>2</sub>Si(Flu)-(C<sub>5</sub>Me<sub>5</sub>)DyN(SiMe<sub>3</sub>)<sub>2</sub>] (Flu = C<sub>13</sub>H<sub>8</sub>, fluorenyl), in which agostic interactions between the dysprosium ion and one methyl group of the {N(SiMe<sub>3</sub>)<sub>2</sub><sup>-</sup> ligand were observed, <sup>83</sup> the difference between the two angles is smaller in the present case. As a reason for the slightly asymmetrical arrangement of the {N(SiMe<sub>3</sub>)<sub>2</sub><sup>-</sup> ligands in 5 and 6, crystal packing effects are suggested.<sup>57</sup>

Recently, Hill et al. reported the  $\beta$ -diketiminato complexes [{(DIPNC(Me))<sub>2</sub>CH}M{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF)] (DIP = 2,6-diisopropylphenyl; M = Ca, Sr, Ba) and on the problem of ligand redistribution, observed for the heavier homologues strontium and barium.<sup>35</sup> The desired products were accompanied by the homoleptic complexes, and obviously the ligand was not able to stabilize the heteroleptic compounds in the case of strontium and barium. In the present work, no problematic ligand redistribution occurred and the desired heteroleptic compounds 5 and 6 were obtained without byproducts. In contrast to the different coordination modes of the (DIP<sub>2</sub>pyr)<sup>-</sup> ligand in 2 and 3, in both products 5 and 6 the ligand is  $\kappa^3$ -coordinated in the solid state.

Hydroamination Studies. The catalytic activity of complexes 5 and 6 was investigated for the intramolecular hydroamination of nonactivated aminoalkenes. All experiments were carried out under rigorously anaerobic reaction conditions by using dry, degassed substrates and a catalyst loading of 5 mol % and were monitored by <sup>1</sup>H NMR spectroscopy, by using ferrocene as an internal standard.<sup>57</sup> As presented in Table 2, both complexes 5 and 6 are catalytically active. The calcium species 5 was more active than the strontium compound 6, which is consistent with the results from our previously studies by using aminotroponiminate alkaline earth metal amides as catalysts.<sup>37</sup> As shown in Table 2, substrates 7a, 8a, and 9a were cyclized selectively to the corresponding pyrrolidines 7b, 8b, and 9b (entries 1-6) in high yields under mild conditions, while the reactions of the  $\alpha$ branched aminoalkene 10a catalyzed by either 5 or 6 were accompanied by a side reaction (entries 7-9). The side product 10c illustrated in Scheme 3 was determined via <sup>1</sup>H NMR spectroscopy.

The cyclization of **10a** by using either catalyst **5** or **6** afforded the desired product **10b** and additionally **10c**, which was formed in a competitive alkene isomerization reaction (Table 2, entries 7–9). **10c** was not further cyclized by the catalysts, since internal



alkenes are less reactive than terminal aminoalkenes. A similar alkene isomerization was observed by Hill et al. by using  $[{(DIPNC(Me))_2CH}Ca{N(SiMe_3)_2}(THF)]$  as a catalyst.<sup>35</sup> The alkene isomerization depends on the reaction temperature and the type of catalyst. By using **5** as a catalyst, the cyclization of **10a** at an elevated temperature of 60 °C within 5 h led to 40% of the rearrangement product **10c** (Table 2, entry 8). However, by performing the same reaction at room temperature within 46 h, the selectivity could be improved, and only 18% of **10c** was detected (Table 2, entry 7). Furthermore, by lowering the temperature the *cis/trans* selectivity of the product **10b** was improved from *cis:trans* = 1:8 at 60 °C to 1:13 at room temperature. By using **6** as a catalyst, the alkene isomerization reaction is favored even at room temperature, and 71% of **10c** was determined (Table 2, entry 9).

However, substrates 7a, 8a, and 9a were cyclized without the formation of undesired side products. On the basis of the Thorpe–Ingold effect,<sup>88–91</sup> the reaction rate increases with increasing steric bulk of the substituents in  $\beta$ -position to the amino group, and thus aminoalkenes 7a and 8a were converted rapidly to their cyclic products at room temperature. Substrate 9a, which contains less bulky substituents, was cyclized by the more active catalyst 5 within 0.5 h at room temperature (Table 2, entry 5), whereas by using 6 as a catalyst an elevated temperature of 60 °C was required and the conversion was complete after two hours (Table 2, entry 6). The best result was obtained by using 5 as the catalyst and 7a as the substrate, and 99% of the corresponding product 7b was formed at room temperature within 2 min (Table 2, entry 1).

# SUMMARY

The heteroleptic iodo complexes  $[(DIP_2pyr)MI(THF)_n]$  (M = Ca (2), Sr (3) (n = 3); Ba (4) (n = 4);  $(DIP_2pyr)^- = 2,5$ bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl) were synthesized by reaction of  $[(DIP_2pyr)K](1)$  with anhydrous alkaline earth metal diiodides. Further treatment of 2 and 3 with  $[K{N(SiMe_3)_2}]$  resulted in the amido complexes  $[(DIP_2pyr)_2]$  $M{N(SiMe_3)_2}(THF)_2$  (M = Ca (5), Sr (6)). Both compounds were investigated for the intramolecular hydroamination of aminoalkenes. Both complexes 5 and 6 are catalytically active systems, although the formation of rearrangement products by alkene isomerization led to a limited reaction scope. In particular, the calcium complex 5 showed high activity and can be compared to the  $\beta$ -diketiminato calcium amide [{(DIPNC(Me))<sub>2</sub>CH}- $Ca{N(SiMe_3)_2}(THF)]$ , the aminotroponiminate calcium amide  $[{(iPr)_2ATI}Ca{N(SiMe_3)_2}(THF)_2]$   $((iPr)_2ATI = N$ -isopropyl-2-(isopropylamino)troponiminate), and the bis(imidazolin-2-ylidene-1-yl)borate alkaline earth metal amides [{H<sub>2</sub>B- $(Im^{tBu})_{2}M{N(SiMe_{3})_{2}}(THF)_{n}]$  (M = Ca, n = 1; M = Sr, n = 2; Im<sup>tBu</sup> = 1-*tert*-butylimidazole).<sup>32,35,37</sup>

## ASSOCIATED CONTENT

**Supporting Information.** Details of the computational studies and X-ray crystallographic files in CIF format for the

structure determinations of 2-6 are available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

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