

**Synthesis and structural characterisation  
of novel linked bis( $\beta$ -diketiminato) rare earth metal complexes**

Daniela V. Vitanova, Frank Hampel and Kai C. Hultsch\*

**Experimental Section**

**General Considerations.** All operations were performed under an inert atmosphere of nitrogen or argon using standard Schlenk-line or glovebox techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl. Hexanes, Pentane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous  $YCl_3$  (Aldrich) and  $LaCl_3$  (Strem) were used as received.  $[Ln\{N(SiMe_3)_2\}_3]$  ( $Ln = Y, La$ )<sup>1</sup> was synthesized as described in the literature. All other chemicals were commercially available and used as received.  $^1H$  and  $^{13}C$  NMR spectra were recorded on Bruker Avance 300 or Avance 400 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of this department. Although metal complexes were combusted with  $V_2O_5$  as burning aid, some analyses gave low carbon content repeatedly, presumably due to carbide formation. Molecular weights of the polycarbonates were determined by GPC (Agilent 1100 Series using RI detector, 3 SDV Linear M  $5\mu$  columns with  $8 \times 50$  mm,  $8 \times 300$  mm and  $8 \times 600$  mm dimensions) versus polystyrene standards using THF at  $35^\circ C$  as eluent.

**4-((2,4,6-trimethylphenyl)amino)pent-3-en-2-one.** Following the procedure reported for 4-((2,6-diethylphenyl)amino)pent-3-en-2-one,<sup>2</sup> 2,4,6-trimethylaniline (13.17 g, 97.4 mmol) and excess of 2,4-pentadione (68.0 g, 679 mmol) were added to a 250 mL round-bottom flask equipped with a stirring bar. A distillation apparatus was attached to collect water and the neat solution was heated to  $150^\circ C$  for 24 h. Excess 2,4-pentadione was removed in vacuo, and the residue was distilled under vacuum at 0.02 mmHg and  $100-110^\circ C$  to give the desired compound. The obtained pale yellow solid product was recrystallised from hexanes to give 18.30 g (86%).  $^1H$  NMR ( $CDCl_3$ , 400MHz,  $25^\circ C$ ):  $\delta = 11.82$  (br s 1H, NH), 6.87 (s, 2H,  $C_6H_2$ ), 5.17 (s, 1H,  $\beta$ -CH), 2.25 (s, 3H, 4- $C_6H_2CH_3$ ), 2.13 (s, 6H, 2- $C_6H_2CH_3$ ), 2.07 (s, 3H,  $CH_3CO$ ), 1.60 (s, 3H,  $CH_3CN$ );  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100.6 MHz,  $25^\circ C$ ):  $\delta = 195.8$  (CO), 163.0 ( $CH_3CN$ ), 137.0, 135.7, 133.8, 128.8 (aryl), 95.6 ( $\beta$ -CH), 29.0 ( $CH_3CO$ ), 20.9 (4- $C_6H_2CH_3$ ), 18.8 ( $CH_3CN$ ), 18.1 (2- $C_6H_2CH_3$ ).

**4-((2,6-diisopropylphenyl)amino)pent-3-en-2-one.**<sup>3</sup> Following the procedure reported for 4-((2,6-diethylphenyl)amino)pent-3-en-2-one,<sup>2</sup> 2,6-diisopropylaniline (15.94 g, 90.1 mmol) and excess of 2,4-pentadione (56.9 g, 568 mmol) were added to a round-bottom flask equipped with a stirring bar. A distillation apparatus was attached to collect water and the neat solution was heated to 150 °C for 24 h. Excess 2,4-pentadione was removed in vacuo, and the residue was distilled under vacuum to give a reddish solid, which was crystallised from hexanes to give 12.57 g (54%) of the aimed compound. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C): δ = 12.04 (br s, 1H, NH), 7.27 (t, <sup>3</sup>J = 7.7 Hz, 1H, 4-C<sub>6</sub>H<sub>3</sub>), 7.15 (d, <sup>3</sup>J = 7.7 Hz, 1H, 3-C<sub>6</sub>H<sub>3</sub>), 5.19 (s, 1H, β-CH), 3.00 (sept, <sup>3</sup>J = 6.9 Hz, 2H, CHCH<sub>3</sub>), 2.10 (s, 3H, CH<sub>3</sub>CO), 1.61 (s, 3H, CH<sub>3</sub>CN), 1.19 (d, <sup>3</sup>J = 6.9 Hz, 6H, CHCH<sub>3</sub>), 1.12 (d, <sup>3</sup>J = 6.8 Hz, 6H, CHCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz, 25 °C): δ = 195.9 (CO), 163.2 (CH<sub>3</sub>CN), 146.2, 133.5, 128.2, 123.5 (aryl), 95.5 (β-CH), 29.0 (CH<sub>3</sub>CO), 28.4 (CHCH<sub>3</sub>), 24.5 (CHCH<sub>3</sub>), 22.6 (CHCH<sub>3</sub>), 19.1 (CH<sub>3</sub>CN).

**H<sub>2</sub>L<sup>1</sup>.** A solution of [Et<sub>3</sub>O][BF<sub>4</sub>] (2.106 g, 11.09 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was slowly added to a solution of 4-((2,4,6-trimethylphenyl)-amino)pent-3-en-2-one (2.354 g, 10.83 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) under a nitrogen atmosphere. The mixture was stirred for 2.5 h at room temperature. Et<sub>3</sub>N (1.5 mL) was added and the mixture was stirred for another 5 min. A solution of ethylene diamine (326 mg, 5.42 mmol) in Et<sub>3</sub>N (6 mL) was added to the mixture and the stirring was continued overnight. The solvent was removed in vacuo and the product was extracted with toluene. [Et<sub>3</sub>NH][BF<sub>4</sub>] was separated as an oily precipitate. Toluene was removed in vacuo and the residue was taken up in hexanes and cooled to -20 °C. The solid was separated by filtration and was washed with ethanol to remove remaining starting material. Yield 1.32 g (52%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C): δ = 10.90 (NH), 6.91 (s, 4H, C<sub>6</sub>H<sub>2</sub>), 4.60 (s, 2H, β-CH), 2.72 (s, 4H, CH<sub>2</sub>), 2.23 (s, 6H, 4-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>), 2.15 (s, 12H, 2-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>), 1.62 (s, 6H, CH<sub>3</sub>), 1.60 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 25 °C): δ = 166.5, 155.2 (CH<sub>3</sub>CN), 147.5, 131.2, 128.9, 127.7 (aryl), 94.3 (β-CH), 44.5 (CH<sub>2</sub>), 21.2 (CH<sub>3</sub>CNAr), 20.9 (4-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>), 19.1 (CH<sub>3</sub>CNHCH<sub>2</sub>), 18.6 (2-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>30</sub>H<sub>42</sub>N<sub>4</sub> (458.68): C, 78.56; H, 9.23; N, 12.21. Found: C, 78.39; H, 9.35; N, 12.27.

**H<sub>2</sub>L<sup>2</sup>.** A solution of [Et<sub>3</sub>O][BF<sub>4</sub>] (3.836 g, 20.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added slowly to a solution of 4-((2,6-diisopropylphenyl)amino)-pent-3-en-2-one (5.22 g, 20.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The reaction mixture was stirred for 3 h and then Et<sub>3</sub>N (2.8 mL) was added. After 5 min a solution of ethylene diamine (0.736 g, 12.2 mmol) in Et<sub>3</sub>N (15 mL) was added

to the mixture. After stirring at room temperature for 16 h all volatiles were removed in vacuo. Toluene was added to extract the product from the oily precipitate of  $[\text{Et}_3\text{NH}][\text{BF}_4]$ . Toluene was removed and the crude product was dissolved in ethanol. Pale yellow crystals were obtained after 12 h at  $-20\text{ }^\circ\text{C}$ . Drying in vacuo gave 4.192 g (77%) of  $\text{H}_2\text{L}^2$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $25\text{ }^\circ\text{C}$ ):  $\delta = 10.93$  (br s, 2H, NH), 7.09 (d,  $^3J = 7.2$  Hz, 4H, 3- $\text{C}_6\text{H}_2$ ), 7.01 (m, 2H, 4- $\text{C}_6\text{H}_2$ ), 4.64 (s, 2H,  $\beta$ -CH), 3.29 (s, 4H,  $\text{CH}_2$ ), 2.82 (sept,  $^3J = 6.8$  Hz, 4H,  $\text{CHCH}_3$ ), 1.95 (s, 6H,  $\text{CH}_3\text{CNAr}$ ), 1.61 (s, 6H,  $\text{CH}_3\text{CNHCH}_2$ ), 1.13 (d, 12H,  $^3J = 6.8$  Hz,  $\text{CHCH}_3$ ), 1.10 (d, 12H,  $^3J = 6.8$  Hz,  $\text{CHCH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz,  $25\text{ }^\circ\text{C}$ ):  $\delta = 166.2$ , 155.3 ( $\text{CH}_3\text{CN}$ ), 146.6, 138.1, 122.7, 122.6 (aryl), 93.8 ( $\beta$ -CH), 44.5 ( $\text{CH}_2$ ), 28.0 ( $\text{CHCH}_3$ ), 23.8 ( $\text{CHCH}_3$ ), 22.8 ( $\text{CHCH}_3$ ), 21.6 ( $\text{CH}_3\text{CNAr}$ ), 19.1 ( $\text{CH}_3\text{CNHCH}_2$ ). Anal. Calcd for  $\text{C}_{36}\text{H}_{54}\text{N}_4$  (542.84): C, 79.65; H, 10.03; N, 10.32. Found: C, 79.63; H, 9.99; N, 10.38.

**$\text{H}_2\text{L}^3$ .** A solution of  $[\text{Et}_3\text{O}][\text{BF}_4]$  (4.179, 22.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was slowly added to a solution of 4-(2,4,6-trimethylphenyl)-aminopent-3-en-4-one (5.222 g, 24.03 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) under a nitrogen atmosphere. The mixture was stirred for 2.5 h at room temperature.  $\text{Et}_3\text{N}$  (3.1 mL) was added to the clear pale solution and the mixture was stirred for another 5 min. A solution of *trans*-cyclohexane-1,2-diamine (1.256 g, 11.01 mmol) in  $\text{Et}_3\text{N}$  (15 mL) was added to the reaction mixture and the stirring was continued overnight. All volatiles were removed in vacuo and the residue was extracted with pentane ( $2 \times 20$  mL) and toluene (20 mL).  $[\text{Et}_3\text{NH}][\text{BF}_4]$  was separated as an oily precipitate. Toluene was removed in vacuo and the residue was taken up in pentane. Crystallisation at  $-20\text{ }^\circ\text{C}$  afforded 3.39 g (60%) of  $\text{H}_2\text{L}^3$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $25\text{ }^\circ\text{C}$ ):  $\delta = 11.03$  (br s, 1H, NH), 6.86 (s, 4H,  $\text{C}_6\text{H}_2$ ), 4.56 (s, 2H,  $\beta$ -CH), 3.13 (br s, 2H, ring-CH), 2.27 (s, 6H, 4- $\text{C}_6\text{H}_2\text{CH}_3$ ), 2.01 (s, 6H, 2- $\text{C}_6\text{H}_2\text{CH}_3$ ), 2.00 (s, 6H, 2- $\text{C}_6\text{H}_2\text{CH}_3$ ), 1.90-1.98 (br m, 2H, ring- $\text{CH}_2$ ), 1.94 (s, 6H,  $\text{CH}_3$ ), 1.68 (m, 2H, ring- $\text{CH}_2$ ), 1.60 (s, 6H,  $\text{CH}_3$ ), 1.15-1.35 (m, 4H, ring- $\text{CH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz,  $25\text{ }^\circ\text{C}$ ):  $\delta = 166.2$ , 155.2 ( $\text{CH}_3\text{CN}$ ), 147.2, 130.9, 128.3, 128.2, 128.0, 127.6 (aryl), 92.6 ( $\beta$ -CH), 58.0 (ring-CH), 33.4 (ring- $\text{CH}_2$ ), 24.7 (ring- $\text{CH}_2$ ), 21.2 ( $\text{CH}_3\text{CNAr}$ ), 20.7, 19.6, 18.5, 18.2 ( $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{34}\text{H}_{48}\text{N}_4$  (512.77): C, 79.64; H, 9.44; N, 10.93. Found: C, 79.54; H, 9.54; N, 11.03.

**$\text{H}_2\text{L}^4$ .** A 100 mL Schlenk flask was charged with 4-((2,6-diisopropylphenyl)amino)-pent-3-en-2-one (5.46 g, 21.1 mmol). This was dissolved in  $\text{CH}_2\text{Cl}_2$  (10 mL) and a solution of  $[\text{Et}_3\text{O}][\text{BF}_4]$  (3.80 g, 20.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was slowly added under nitrogen

atmosphere. After stirring for 3 h at room temperature Et<sub>3</sub>N (2.02 g) was added slowly. The mixture was stirred for another 15 min and then a solution of *trans*-cyclohexane-1,2-diamine (1.142 g, 10.0 mmol) in Et<sub>3</sub>N (15 mL) was added to the mixture. After stirring for 18 h at room temperature all volatiles were removed in vacuo. The product was extracted with hexanes and crystallised at -20°C to afford 3.586 g (57%) of H<sub>2</sub>L<sup>4</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C): δ = 11.02 (br s, 2H, NH), 7.10 (m, 4H, 3-C<sub>6</sub>H<sub>3</sub>), 7.02 (pt, 2H, 4-C<sub>6</sub>H<sub>3</sub>), 4.61 (s, 2H, β-CH), 3.17 (br s, 2H, ring-CH), 2.90 (m, 4H, CHCH<sub>3</sub>), 1.98 (s, 6H, CH<sub>3</sub>), 1.90 (m, 2H, ring-CH<sub>2</sub>), 1.61 (br s, 8H, CH<sub>3</sub> and ring-CH<sub>2</sub>), 1.18-1.35 (m, 4H, ring-CH<sub>2</sub>), 1.16 (d, 6H, <sup>3</sup>J = 6.8 Hz, CHCH<sub>3</sub>), 1.14 (d, 6H, <sup>3</sup>J = 6.6 Hz, CHCH<sub>3</sub>), 1.10 (d, 6H, <sup>3</sup>J = 6.6 Hz, CHCH<sub>3</sub>) 1.09 (d, 6H, <sup>3</sup>J = 6.8 Hz, CHCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz, 25 °C): δ = 166.6, 155.0 (CH<sub>3</sub>CN), 146.8, 138.3, 138.2, 122.7, 122.6, 122.5 (aryl), 92.9 (β-CH), 57.2 (ring-CH), 32.4 (ring-CH<sub>2</sub>), 28.0 (CHCH<sub>3</sub>), 27.8 (CHCH<sub>3</sub>), 24.3 (ring-CH<sub>2</sub>), 24.0 (2 C, CHCH<sub>3</sub>), 23.1, 22.8 (CHCH<sub>3</sub>), 21.7 (CH<sub>3</sub>CNAr), 19.4 (CH<sub>3</sub>CNHCH<sub>2</sub>). Anal. Calcd for C<sub>40</sub>H<sub>60</sub>N<sub>4</sub> (596.93): C, 80.48; H, 10.13; N, 9.39. Found: C, 80.43; H, 10.26; N, 9.38.

**[(L<sup>1</sup>)LaN(SiMe<sub>3</sub>)<sub>2</sub>] (1a).** A Schlenk flask was charged with H<sub>2</sub>L<sup>1</sup> (459 mg, 1.00 mmol) and [La{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>] (619 mg, 1.00 mmol). Hexanes (20 mL) was added and the mixture was stirred at 60 °C for 30 min. All volatiles were removed in vacuo to give 642 mg (85%) of **1a** in form of a pale yellow powder, which was clean according to NMR spectroscopy. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C): δ = 6.76 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 6.66 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 4.94 (s, 2H, β-CH), 3.82 (m, 2H, CH<sub>2</sub>), 3.35 (m, 2H, CH<sub>2</sub>), 2.18 (s, 6H, 4-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>), 2.05 (s, 6H, 2-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>), 1.93 (s, 6H, CH<sub>3</sub>CN), 1.52 (s, 6H, 2-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>), 1.47 (s, 6H, CH<sub>3</sub>CN), 0.33 (s, 18H, SiCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 25 °C): δ = 163.3, 162.0 (CH<sub>3</sub>CN), 143.1 (aryl-C<sub>ipso</sub>), 133.8, 133.5, 133.3, 130.2, 129.8 (aryl), 97.3 (β-CH), 52.3 (CH<sub>2</sub>), 23.3, 23.0 (CH<sub>3</sub>CN), 20.9 (4-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>), 20.3, 17.8 (2-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>), 5.0 (SiCH<sub>3</sub>). Anal. Calcd for C<sub>36</sub>H<sub>58</sub>LaN<sub>5</sub>Si<sub>2</sub> (755.97): C, 57.20; H, 7.73; N, 9.26. Found: C, 57.28; H, 7.75; N, 8.97.

**[(L<sup>1</sup>)YN(SiMe<sub>3</sub>)<sub>2</sub>] (1b).** A Schlenk flask was charged with H<sub>2</sub>L<sup>1</sup> (459 mg, 1.00 mmol) and [Y{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>] (599 mg, 1.05 mmol). Toluene (10 mL) was added and the mixture was stirred at 70 °C for 24 h. All volatiles were removed in vacuo to give 697 mg (98%) of **1b** in form of a pale yellow powder, which was clean according to NMR spectroscopy. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C): δ = 6.67 (s, 4H, C<sub>6</sub>H<sub>2</sub>), 6.59 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 4.97 (s, 2H, β-CH), 3.73 (m, 2H, CH<sub>2</sub>), 3.30 (m, 2H, CH<sub>2</sub>), 2.19 (s, 6H, 4-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>), 2.07 (s, 6H, 2-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>), 1.86 (s,

6H, CH<sub>3</sub>CN), 1.50 (s, 6H, CH<sub>3</sub>), 1.39 (s, 6H, CH<sub>3</sub>), 0.37 (s, 18H, SiCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 25 °C): δ = 165.1, 165.0 (CH<sub>3</sub>CN), 144.7 (aryl-C<sub>ipso</sub>), 133.8 (2 C), 129.94, 129.87 (aryl), 99.6 (β-CH), 51.7 (CH<sub>2</sub>), 23.5, 22.9 (CH<sub>3</sub>CN), 20.9 (4-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>), 20.8, 18.0 (2-C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>), 5.7 (SiCH<sub>3</sub>). Anal. Calcd for C<sub>36</sub>H<sub>58</sub>N<sub>5</sub>Si<sub>2</sub>Y (705.97): C, 61.25; H, 8.28; N, 9.92. Found: C, 61.08; H, 8.50; N, 9.70.

**[(L<sup>2</sup>)LaN(SiMe<sub>3</sub>)<sub>2</sub>] (2a).** A Schlenk flask was charged with H<sub>2</sub>L<sup>2</sup> (544 mg, 1.00 mmol) and [La{N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>3</sub> (621 mg, 1.00 mmol). Toluene (10 mL) was added and the mixture was stirred at 72 °C for 110 h. All volatiles were removed in vacuo to give 718 mg (80%) of **2a** in form of a pale yellow powder, which was clean according to NMR spectroscopy. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 400 MHz, 25 °C): δ = 7.00 (m, 4H, 3-C<sub>6</sub>H<sub>3</sub>), 6.91 (m, 2H, 4-C<sub>6</sub>H<sub>3</sub>), 4.95 (s, 2H, β-CH), 3.76 (m, 2H, CH<sub>2</sub>), 3.26 (br m, 4H, CH<sub>2</sub> and CHCH<sub>3</sub>), 2.71 (m, 2H, CHCH<sub>3</sub>), 1.92 (s, 6H, CH<sub>3</sub>), 1.50 (s, 6H, CH<sub>3</sub>), 1.14 (br d, 6H, CHCH<sub>3</sub>), 0.87 (br d, 12H, CHCH<sub>3</sub>), 0.70 (br d, 6H, CHCH<sub>3</sub>), 0.21 (s, 18H, SiCH<sub>3</sub>); <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 400 MHz, 80 °C): δ = 6.84-7.08 (m, 6H, C<sub>6</sub>H<sub>3</sub>), 4.92 (s, 2H, β-CH), 3.81 (br m, 2H, CH<sub>2</sub>), 3.33 (br m, 2H, CH<sub>2</sub>), 3.20 (m, 2H, CHCH<sub>3</sub>), 2.70 (m, 2H, CHCH<sub>3</sub>), 1.93 (s, 6H, CH<sub>3</sub>), 1.51 (s, 6H, CH<sub>3</sub>), 1.14 (br d, 6H, CHCH<sub>3</sub>), 0.87 (br d, 12H, CHCH<sub>3</sub>), 0.70 (br d, 6H, CHCH<sub>3</sub>), 0.21 (s, 18H, SiCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, 100.6 MHz, 80 °C): δ = 164.5, 161.6 (CH<sub>3</sub>CN), 146.8 (aryl-C<sub>ipso</sub>), 143.3, 143.0, 125.4, 124.2, 124.0 (aryl), 96.9 (β-CH), 52.1 (CH<sub>2</sub>), 28.8, 28.1 (CHCH<sub>3</sub>), 25.4 (CHCH<sub>3</sub>), 24.9 (CH<sub>3</sub>CN), 24.6, 24.5, 24.0 (CHCH<sub>3</sub>), 21.8 (CH<sub>3</sub>CN), 5.4 (SiCH<sub>3</sub>). Anal. Calcd for C<sub>42</sub>H<sub>70</sub>LaN<sub>5</sub>Si<sub>2</sub> (840.13): C, 60.05; H, 8.40; N, 8.34. Found: C, 59.48; H, 8.32; N, 7.98.

**[(L<sup>2</sup>)YN(SiMe<sub>3</sub>)<sub>2</sub>] (2b).** A Schlenk flask was charged with H<sub>2</sub>L<sup>2</sup> (543 mg, 1.00 mmol) and [Y{N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>3</sub> (570 mg, 1.00 mmol). Toluene (10 mL) was added and the mixture was stirred at 95 °C for 5 days. All volatiles were removed in vacuo to give a reddish solid. Washing with hexanes (2 × 3 mL) gave 377 mg of complex **2b** as a white powder. The hexanes washing solution was cooled to -35 °C for a few days, after which further 218 mg of **2b** were isolated. Total yield: 595 mg (77%). <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 400 MHz, -20 °C): δ = 7.11 (m, 1H, C<sub>6</sub>H<sub>3</sub>), 7.03 (m, 1H, C<sub>6</sub>H<sub>3</sub>), 6.92 (m, 1H, C<sub>6</sub>H<sub>3</sub>), 6.86 (dd, <sup>3</sup>J = 7.3 Hz, <sup>4</sup>J = 1.8 Hz, 1H, C<sub>6</sub>H<sub>3</sub>), 6.82 (dd, <sup>3</sup>J = 6.3 Hz, <sup>4</sup>J = 1.0 Hz, 1H, C<sub>6</sub>H<sub>3</sub>), 5.05 (s, 1H, β-CH), 4.89 (s, 1H, β-CH), 3.65-3.73 (m, 3H, CH<sub>2</sub> and CHCH<sub>3</sub>), 3.49 (m, 1H, CHCH<sub>3</sub>), 2.92 (m, 3H, CH<sub>2</sub> and CHCH<sub>3</sub>), 2.46 (m, 1H, CHCH<sub>3</sub>), 1.88 (s, 3H, CH<sub>3</sub>), 1.86 (s, 3H, CH<sub>3</sub>), 1.45 (d, <sup>3</sup>J = 6.6 Hz, CHCH<sub>3</sub>), 1.39 (s, 3H, CH<sub>3</sub>CN), 1.35 (m, 6H, CH<sub>3</sub>CN and CHCH<sub>3</sub>), 1.11 (d, <sup>3</sup>J = 6.1 Hz, 3H,

CHCH<sub>3</sub>), 1.10 (d, <sup>3</sup>J = 6.3 Hz, 3H, CHCH<sub>3</sub>), 0.91 (d, <sup>3</sup>J = 6.8 Hz, 3H, CHCH<sub>3</sub>), 0.89 (d, <sup>3</sup>J = 6.8 Hz, 3H, CHCH<sub>3</sub>), 0.38 (s, 18H, SiCH<sub>3</sub>), 0.32 (d, <sup>3</sup>J = 6.6 Hz, 3H, CHCH<sub>3</sub>), 0.25 (d, <sup>3</sup>J = 6.6 Hz, 3H, CHCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, 100.6 MHz, -20 °C): δ = 167.5, 167.3, 164.0, 162.8 (CH<sub>3</sub>CN), 148.2, 147.7 (aryl-*C*<sub>ipso</sub>), 143.8, 143.6, 143.3, 142.5, 126.1, 125.7, 125.0, 124.5, 124.4, 124.0 (aryl), 100.4, 99.1 (β-CH), 53.8, 49.0 (CH<sub>2</sub>), 29.7, 29.3, 28.1, 27.4 (CHCH<sub>3</sub>), 26.2, 26.1, 25.9, 25.4, 25.1, 24.8, 24.5 (2 C), 24.3, 24.2, 23.9, 21.3 (CH<sub>3</sub>), 6.4 (SiCH<sub>3</sub>). Anal. Calcd for C<sub>42</sub>H<sub>70</sub>N<sub>5</sub>Si<sub>2</sub>Y (790.13): C, 63.85; H, 8.93; N, 8.86. Found: C, 62.75; H, 8.57; N, 8.42.

**[(L<sup>3</sup>)LaN(SiMe<sub>3</sub>)<sub>2</sub>] (3).** A Schlenk flask was charged with H<sub>2</sub>L<sup>3</sup> (513 mg, 1.00 mmol) and [La{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>] (622 mg, 1.00 mmol). Toluene (10 mL) was added and the mixture was stirred for 24 h at 65 °C. All volatiles were removed in vacuo to give a pale yellow powder. A small amount of impurities was removed by washing with hexanes (5 mL) to yield 667 mg (82%) of clean **3**. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 400 MHz, -20 °C): δ = 6.88 (s, 1H, C<sub>6</sub>H<sub>2</sub>), 6.82 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 6.74 (s, 1H, C<sub>6</sub>H<sub>2</sub>), 5.10 (s, 1H, β-CH), 4.25 (s, 1H, β-CH), 4.21 (m, 1H, ring-CH), 3.09 (m, 1H, ring-CH), 2.45 (s, 3H, CH<sub>3</sub>), 2.38 (s, 3H, CH<sub>3</sub>), 2.30 (m, 2H, ring-CH<sub>2</sub>), 2.21 (s, 6H, CH<sub>3</sub>), 2.10 (s, 3H, CH<sub>3</sub>), 2.06 (s, 3H, CH<sub>3</sub>), 1.73 (s, 3H, CH<sub>3</sub>), 1.64 (s, 3H, CH<sub>3</sub>), 1.58 (m, 2H, ring-CH<sub>2</sub>), 1.54 (s, 3H, CH<sub>3</sub>), 1.41 (s, 3H, CH<sub>3</sub>), 1.05-1.30 (m, 4H, ring-CH<sub>2</sub>), 0.23 (s, 18H, SiCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, 100.6 MHz, -20 °C): δ = 162.6, 161.12, 161.08, 159.7 (CH<sub>3</sub>CN), 147.4, 147.0 (aryl-*C*<sub>ipso</sub>), 132.5, 131.7, 130.5, 130.0, 129.9, 129.6, 129.4, 129.2, 129.1, 129.0 (aryl), 94.5, 88.2 (β-CH), 71.7, 64.7 (ring-CH), 33.3, 32.6, 25.8, 25.6 (ring-CH<sub>2</sub>), 23.9, 23.8, 23.2, 21.2, 21.04, 20.99, 20.7, 18.5, 18.1 (CH<sub>3</sub>), 4.6 (SiCH<sub>3</sub>). Anal. Calcd for C<sub>40</sub>H<sub>64</sub>LaN<sub>5</sub>Si<sub>2</sub> (810.06): C, 59.31; H, 7.96; N, 8.65. Found: C, 59.12; H, 7.81; N, 8.48.

**[(L<sup>4</sup>)LaN(SiMe<sub>3</sub>)<sub>2</sub>] (4).** A Schlenk flask was charged with H<sub>2</sub>L<sup>4</sup> (602 mg, 1.01 mmol) and [La(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>] (625 mg, 1.01 mmol). Toluene (10 mL) was added and the mixture was stirred for 4 d at 95 °C. All volatiles were removed in vacuo to give 707 mg (79%) of **4** as a pale yellow powder. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C): δ = 7.02-7.18 (m, 6H, C<sub>6</sub>H<sub>3</sub>), 5.17 (s, 1H, β-CH), 4.22 (s, 1H, β-CH), 4.20 (m, 1H, ring-CH), 3.50 (sept., <sup>3</sup>J = 6.8 Hz, 1H, CHCH<sub>3</sub>), 3.16 (m, 1H, ring-CH), 3.14 (sept., <sup>3</sup>J = 6.8 Hz, 1H, CHCH<sub>3</sub>), 3.05 (sept., <sup>3</sup>J = 6.8 Hz, 1H, CHCH<sub>3</sub>), 2.54 (sept., <sup>3</sup>J = 6.8 Hz, 1H, CHCH<sub>3</sub>), 2.30 (m, 1H, ring-CH<sub>2</sub>), 2.05 (s, 3H, CH<sub>3</sub>CN), 1.75 (s, 3H, CH<sub>3</sub>CN), 1.64 (s, 3H, CH<sub>3</sub>CN), 1.50-1.70 (m, 6H, ring-CH<sub>2</sub>, obscured by other

signals), 1.54 (d,  $^3J = 6.8$  Hz, 3H, CHCH<sub>3</sub>), 1.47 (s, 3H, CH<sub>3</sub>CN), 1.42 (d,  $^3J = 6.8$  Hz, 3H, CHCH<sub>3</sub>), 1.34 (d,  $^3J = 7.1$  Hz, 3H, CHCH<sub>3</sub>), 1.27 (d,  $^3J = 6.8$  Hz, 3H, CHCH<sub>3</sub>), 1.21 (d,  $^3J = 6.6$  Hz, 3H, CHCH<sub>3</sub>), 1.10-1.14 (m, 1H, ring-CH<sub>2</sub>, obscured by other signal), 1.13 (d,  $^3J = 6.8$  Hz, 3H, CHCH<sub>3</sub>), 1.04 (d,  $^3J = 6.8$  Hz, 3H, CHCH<sub>3</sub>), 0.94 (d,  $^3J = 6.8$  Hz, 3H, CHCH<sub>3</sub>), 0.28 (s, 9H, SiCH<sub>3</sub>), 0.03 (s, 9H, SiCH<sub>3</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 25 °C):  $\delta = 164.9$ , 161.4, 160.4, 160.3 (CH<sub>3</sub>CN), 148.0, 147.3 (aryl-C<sub>ipso</sub>), 141.4, 141.1, 140.8, 140.6, 124.9, 124.1, 124.0, 123.9, 123.8, 123.0 (aryl), 95.3, 87.1 ( $\beta$ -CH), 71.5, 65.2 (ring-CH), 33.3, 32.7 (ring-CH<sub>2</sub>), 31.4, 29.3, 27.9, 27.4 (CHCH<sub>3</sub>), 27.0, 26.0 (CHCH<sub>3</sub>), 25.8, 25.7 (ring-CH<sub>2</sub>), 25.1, 25.0 (CHCH<sub>3</sub>), 24.9 (2 C, CH<sub>3</sub>CN), 24.49, 24.47 (ring-CH<sub>2</sub>), 24.0, 23.5 (CHCH<sub>3</sub>), 23.3, 21.4 (CH<sub>3</sub>CN), 5.0, 2.6 (SiCH<sub>3</sub>). Anal. Calcd for C<sub>46</sub>H<sub>76</sub>LaN<sub>5</sub>Si<sub>2</sub> (894.22): C, 61.79; H, 8.57; N, 7.83. Found: C, 60.77; H, 8.67; N, 7.43.

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