

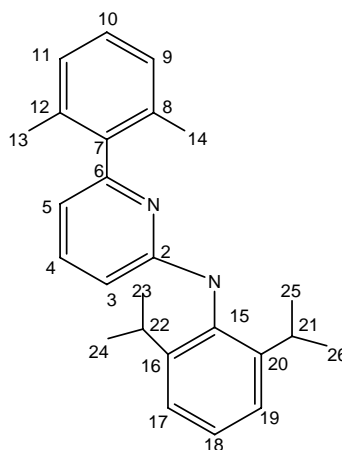
Supporting Information

Experimental details

All experiments were performed in evacuated tubes, using standard Schlenk-tube or glove-box techniques, with rigorous exclusion of traces of moisture and air. After drying over KOH, THF was purified by distillation from sodium/benzophenone ketyl, hexane and toluene by distillation from sodium/triglyme benzophenone ketyl prior to use. C₆D₆ was dried with sodium/benzophenone ketyl and condensed in vacuo prior to use. Ap'H and KAp' (Ap'-H = (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)-pyridin-2-yl]-amine) were synthesized according to previously published procedures.^{1,2} Anhydrous YCl₃³ was prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purification. NMR spectra were recorded on a Bruker DPX 200 or on a Bruker ARX 250 or on a Varian Inova 400 or on a Varian Inova 300 spectrometer. Chemical shifts for ¹H and ¹³C spectra were referenced internally using the residual solvent resonances and are reported relative to TMS. IR spectra were recorded as Nujol mulls on FSM 1201 and Specord M80 instruments. Lanthanide metal analysis were carried out by complexometric titration. The C, H elemental analysis was made in the microanalytical laboratory of IOMC and at Bayreuth University using a Vario elementar EL III elemental analyser.

Synthesis of [YAp'₂Cl(thf)] (1): A solution of KAp' (0.48 g, 1.21 mmol in 30 mL of THF) was added to a suspension of YCl₃ (0.12 g, 0.61 mmol) in THF (5 mL) and the reaction mixture was stirred for 7 h at 50 °C. After cooling to the room temperature THF was evaporated in vacuum and the remaining residue was extracted with toluene (30 mL). The extracts were filtered and the solvent was removed under vacuum and the resulting yellow solid was redissolved in THF. Slow condensation of hexane into concentrated THF solution afforded complex **1** as yellow crystals. The crystals were washed with cold hexane and dried in vacuum at room temperature (45 min). Yield (0.48 g, 87 %). IR (Nujol, KBr, cm⁻¹): 3060 m, 1584 s, 1545 s, 1349s, 1252 m, 1160 s, 1059 m,

1015 s, 856 s, 795 s, 778 s, 746 s. ^1H NMR (200 MHz, C_7D_8 , 298 K): δ = 1.10 (d, $^3J_{\text{H-H}} = 7.0$ Hz, 24H, $\text{H}^{23,24,25,26}$), 1.41 (br s, 4H, $\beta\text{-CH}_2$, THF), 2.20 (s, 12H, $\text{H}^{13,14}$), 3.29 (sept, $^3J_{\text{H-H}} = 7.0$ Hz, 4H, $\text{H}^{21,22}$), 3.54 (br, s, 4H, $\alpha\text{-CH}_2$, THF), 5.71 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 2H, H^3), 5.86 (d, $^3J_{\text{H-H}} = 8.3$ Hz, 2H, H^5), 6.37 (d, $^3J_{\text{H-H}} = 7.3$ Hz, 2H, H^4), 6.70-7.15 (m, 12H, $\text{H}^{9,10,11,17,18,19}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, C_7D_8 , 298 K): δ = 20.1 ($\text{C}^{13,14}$), 23.5 ($\text{C}^{23,24,25,26}$), 24.4 ($\text{C}^{23,24,25,26}$), 25.3 ($\beta\text{-CH}_2$, THF), 28.0 ($\text{C}^{21,22}$), 28.4 ($\text{C}^{21,22}$), 67.7 ($\alpha\text{-CH}_2$, THF), 103.4 ($\text{C}^{3,5}$), 114.2 ($\text{C}^{3,5}$), 123.8, 124.7, 127.3, 127.4, 127.6, 127.9 ($\text{C}^{9,10,11,17,18,19}$), 139.2 (C^4), 141.5 (C^7), 144.2, 147.7 ($\text{C}^{8,12,16,20}$), 156.0 (C^{15}), 159.0 (C^6), 159.6 (C^2) ppm. Anal. Calcd for $\text{C}_{54}\text{H}_{66}\text{Cl ON}_4\text{Y}$ (910.95): C, 71.19; H, 7.24; N 6.15; Y, 9.76. Found: C, 71.02; H, 7.58; N, 6.25; Y, 9.60.



Synthesis of $[\text{YAp}'_2\text{CH}_2\text{SiMe}_3(\text{thf})]$ (2**):** A hexane solution of $\text{LiCH}_2\text{SiMe}_3$ (0.021 g, 0.22 mmol in 30 mL) was added to a suspension of **1** (0.19 g, 0.21 mmol) in hexane (20 mL) and the reaction mixture was stirred for 1 h. The mixture was filtered and hexane was removed in vacuum. The yellow solid residue was dissolved in toluene-hexane mixture ($\sim 1:5$). Slow cooling of the concentrated solution of complex **2** to -20°C afforded yellow crystals of **2**. The crystals were separated from the mother liquor by decantation, washed with cold hexane and dried in vacuum at room temperature (40 min). Yield (0.13 g, 65 %). IR (Nujol, KBr, cm^{-1}): 3060 m, 1584 s, 1547 s, 1356 s, 1249 m, 1157 m, 861 s, 801 m, 778 s, 768s. ^1H NMR (200 MHz, C_6D_6 , 298 K): δ = - 0.39 (m, 2H, CH_2SiMe_3), 0.20 (s, 9H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 0.97-1.37 (m, 24H, $\text{H}^{23,24,25,26}$), 1.39 (br s, 4H, $\beta\text{-}$

CH₂, THF), 1.57, 2.24, (s, together 12H, H^{13,14}), 3.34 (m, 4H, H^{21,22}), 3.59 (br s, 4H, α-CH₂, THF), 5.70 (m, 4H, H^{3,5}), 6.68 -7.26 (m, 14 H, H^{4, 9, 10, 11, 17, 18, 19}) ppm. ¹³C NMR (50 MHz, C₆D₆, 298 K): δ = 3.9 (Si(CH₃)₃), 19.5, 20.9 (C^{13,14}), 24.4, 24.6, 24.7, 24.9 (C^{23,24,25,26}), 25.3 (β-CH₂, THF), 28.1, 29.4 (C^{21,22}), 43.3 (d, CH₂, J_{Y-C} = 43 Hz), 68.4 (α-CH₂, THF), 106.1, 109.3 (C^{3,5}), 124.1, 124.4, 127.9, 128.0 (C^{9,11,17,19}), 125.1, 128.2 (C^{10,18}), 135.8, 136.1 (C^{8,12}), 139.5 (C⁷), 140.6 (C⁴), 142.9 (C¹⁵), 143.9, 144.0 (C^{16,20}), 155.7 (C⁶), 169.1 (C²) ppm. Anal. Calcd for C₅₈H₇₇N₄OSiY (962.7): C, 72.36; H, 7.99; N, 5.82; Y, 9.23. Found: C, 72.00; H, 7.87; N, 5.78; Y, 9.43.

Synthesis of [YAp'(Ap-H)(thf)] (3): A solution of PhSiH₃ (0.057 g, 0.53 mmol) in toluene (3 mL) was added to a solution of **2** (0.51 g, 0.53 mmol) in toluene (30 mL) at room temperature and the reaction mixture was stirred for 1 h. Toluene was removed under vacuum and the solid residue was washed with cold hexane. The remaining solid residue was dissolved in heptane (30 mL) at room temperature. Slow concentration of the heptane solution afforded **3** as yellow crystals. The crystals were separated from the mother liquor by decantation, washed with cold hexane and dried in vacuum at room temperature (30 min). Yield (0.33 g, 72 %). IR (Nujol, KBr, cm⁻¹): 3064 m, 1594 s, 1584 s, 1575 s, 1362 s, 1325 m, 1260 m, 1157 m, 1804 m, 1060 m, 986 m, 846 m, 800 m, 778 m, 768 m. ¹H NMR (200 MHz, C₆D₆, 298 K): δ = 0.97-1.56 (m, together 30H, H^{23,24,25,26}, β-CH₂, THF, CH₂Y), 1.89-2.36 (m, together 9H, H^{13,14}), 3.34 (br s, 4H, H^{21,22}), 3.52 (br, s, 4H, α-CH₂, THF), 5.72 (m, 4H, H^{3,5}), 6.70 -7.27 (m, 14 H, H^{4, 9, 10, 11, 17, 18, 19}) ppm. ¹³C NMR (50 MHz, C₆D₆, 298 K): δ = 20.2, 22.3 (C^{13,14}), 24.0, 24.9 (C^{23,24,25,26}), 25.2 (β-CH₂, THF), 28.2, 28.5 (C^{21,22}), 58.3 (d, CH₂, J_{Y-C} = 30.9 Hz), 68.4 (α-CH₂, THF), 105.7, 107.7, 108.6 (C^{3,5}), 123.6, 123.9, 124.0, 124.1, 124.4, 127.0, 127.3, 127.5, 127.9, 128.1 (C^{9,10,11,17,18,19}), 139.5, 140.0, (C⁴), 134.2, 135.6, 135.9, 140.8, 143.6, 143.8, 145.0, 145.6 (C^{7,8,12,15,16,20}), 153.9, 155.8 (C⁶), 167.7, 171.9 (C²) ppm. Anal. Calcd for C₅₄H₆₅N₄OY (874.5): C, 74.16; H, 7.43; N, 6.40; Y, 10.16. Found: C, 73.82; H, 7.09; N, 6.22; Y, 9.80.

Synthesis of $\text{Ap}'_2\text{YCH}_2\text{Ph}(\text{THF})$: A mixture of $\text{Y}(\text{CH}_2\text{Ph})_3(\text{THF})_3$ (0.102 g, 0.18 mmol) and $\text{Ap}'\text{H}$ (0.126 mg, 0.35 mmol) was dissolved in THF (10 mL). After stirring the mixture for 1 h all volatiles were removed to yield $[\text{Ap}'_2\text{YCH}_2\text{Ph}(\text{THF})]$ as a pale yellow residue in almost quantitative yield.

^1H -NMR (400 MHz, THF-d_8 , 253 K): δ = 0.52 (d, 3H, $^3J(\text{H,H}) = 6.7$ Hz, $\text{H}^{23,24,25,26}$), 0.75 (d, 3H, $^3J(\text{H,H}) = 6.7$ Hz, $\text{H}^{23,24,25,26}$), 0.76 (d, 3H, $^3J(\text{H,H}) = 6.7$ Hz, $\text{H}^{23,24,25,26}$), 0.81 (d, 3H, $^3J(\text{H,H}) = 6.7$ Hz, $\text{H}^{23,24,25,26}$), 0.90 (d, 3H, $^3J(\text{H,H}) = 6.7$ Hz, $\text{H}^{23,24,25,26}$), 0.94 (d, 3H, $^3J(\text{H,H}) = 6.7$ Hz, $\text{H}^{23,24,25,26}$), 0.97 (d, 3H, $^3J(\text{H,H}) = 6.7$ Hz, $\text{H}^{23,24,25,26}$), 1.15 (d, 3H, $^3J(\text{H,H}) = 6.7$ Hz, $\text{H}^{23,24,25,26}$), 1.68 (br, 4H, $\beta\text{-CH}_2$, THF), 1.76 (s, 3H, $\text{H}^{13,14}$), 1.82 (s, 3H, $\text{H}^{13,14}$), 2.14 (s, 3H, $\text{H}^{13,14}$), 2.16 (br, 2H, CH_2Ph), 2.30 (s, 3H, $\text{H}^{13,14}$), 2.86 (sept, 1H, $^3J(\text{H,H}) = 6.7$ Hz, $\text{H}^{21,22}$), 3.06 (sept, 1H, $^3J(\text{H,H}) = 6.7$ Hz, $\text{H}^{21,22}$), 3.14 (sept, 1H, $^3J(\text{H,H}) = 6.7$ Hz, $\text{H}^{21,22}$), 3.37 (sept, 1H, $^3J(\text{H,H}) = 6.7$ Hz, $\text{H}^{21,22}$), 3.53 (br, 4H, $\alpha\text{-CH}_2$, THF), 5.65 (d, 1H, $^3J(\text{H,H}) = 8.6$ Hz, H^3), 5.74 (d, 1H, $^3J(\text{H,H}) = 8.6$ Hz, H^3), 5.80 (d, 2H, Benzyl-H, ortho), 5.92 (d, 1H, $^3J(\text{H,H}) = 7.0$ Hz, H^5), 5.97 (d, 1H, $^3J(\text{H,H}) = 7.0$ Hz, H^5), 6.10 (t, 1H, Benzyl-H, para), 6.43 (t, 2H, H^4), 6.85-7.27 (m, 14H, $\text{H}^{9,10,11,17,18,18}$ /Benzyl H, meta) ppm.

^{13}C -NMR (C_6D_6 , 298 K): δ = 19.6, 20.8 ($\text{C}^{13,14}$), 23.5, 22.6, 24.7, 25.1 ($\text{C}^{23,24,25,26}$), 25.5 ($\beta\text{-CH}_2$, THF), 28.3, 29.5 ($\text{C}^{21,22}$), 60.3 (d, CH_2 , $J_{\text{Y-C}} = 39$ Hz), 70.9 ($\alpha\text{-CH}_2$, THF), 107.3, 109.6 ($\text{C}^{3,5}$), 117.6 (C^{Ph}), 122.1 (C^{Ph}), 124.3, 124.7, 127.4, 128.2 ($\text{C}^{9,11,17,19}$), 125.5, 128.9 ($\text{C}^{10,18}$), 131.9 (C^{Ph}), 135.7, 136.2 ($\text{C}^{8,12}$), 139.8 (C^7), 140.3 (C^4), 140.9 (C^{15}), 141.3, 144.9 ($\text{C}^{16,20}$), 154.0 (C^{Ph}), 156.0 (C^6), 170.9 (C^2) ppm.

Anal. Calcd for $\text{C}_{61}\text{H}_{73}\text{N}_4\text{OY}$ (967.2): C, 75.75; H, 7.61; N, 5.79. Found: C, 75.57; H, 7.49; N, 5.59.

X-ray crystallography. The data were collected on a SMART APEX diffractometer or on a STOE IPDS II diffractometer (graphite-monochromated, MoK_α -radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and were refined on F^2 using SHELXTL⁵ package or using SIR97,⁶ SHELXL-97⁷ and WinGX⁸. All non-hydrogen atoms were refined anisotropically. SADABS⁹ or face identification (numerical) was used to perform absorption corrections.

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X-ray structure determination of complex 1.

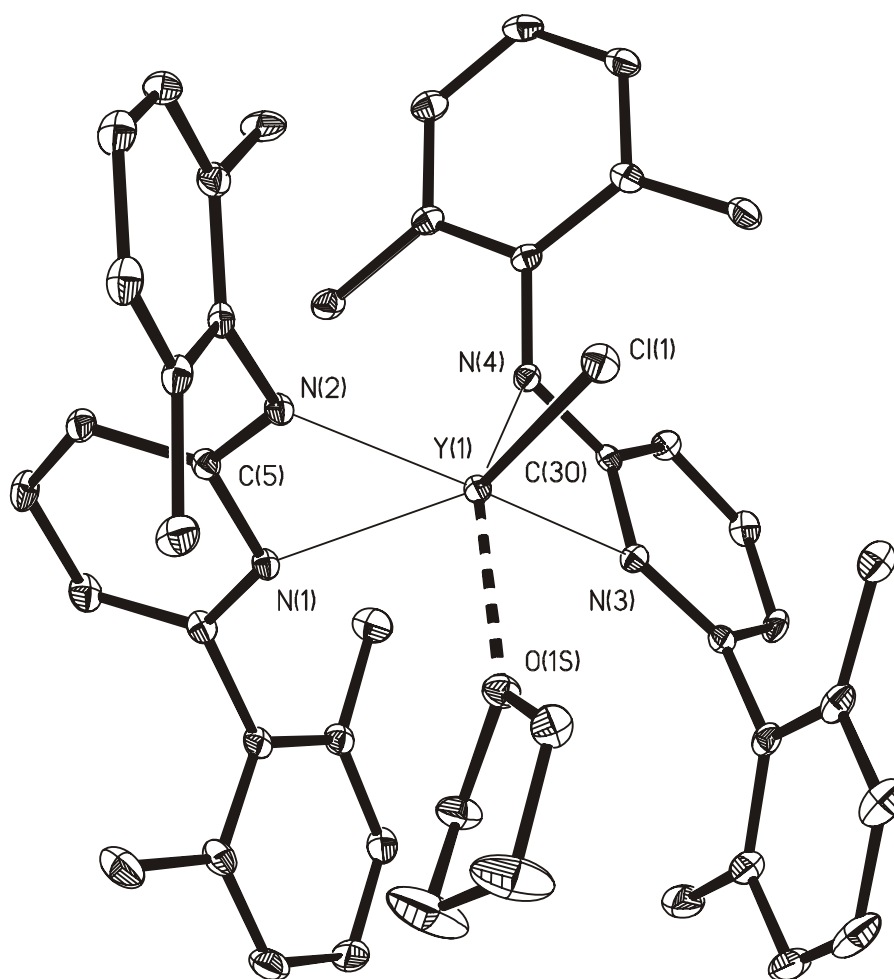


Figure 1. ORTEP diagram (30% probability thermal ellipsoids) of $\text{Ap}'_2\text{YCl}(\text{THF})$ (**1**) showing the non-hydrogen and non-carbon (except C(5) and C(30)) atom numbering scheme. Hydrogen and methyl carbon atoms of isopropyl groups are omitted. Selected bond distances [\AA] and angles [$^\circ$]: Y(1)-N(2) 2.2828(13), Y(1)-N(4) 2.3068(13), Y(1)-O(1S) 2.3314(11), Y(1)-N(3) 2.4483(13), Y(1)-N(1) 2.5097(12), Y(1)-Cl(1) 2.5154(4), N(2)-Y(1)-N(4) 106.85(4), N(2)-Y(1)-N(3) 157.95(4), N(4)-Y(1)-N(3) 57.17(4), N(2)-Y(1)-N(1) 56.20(4), N(4)-Y(1)-N(1) 95.56(4).