Supplementary Information

Group 3 Dialkyl Complexes of a Rigid Monoanionic NNN-Donor Pincer Ligand: Synthesis, Structures, Unexpected Reactivity with CPh₃⁺, and Hydroamination Catalysis

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Figure S1: ¹H NMR spectrum of H[AII₂] (600 MHz, C₆D₆).



Figure S2: Expanded region of the ¹H NMR spectrum of H[AII₂] (600 MHz, C₆D₆).



Figure S3: Expanded region of the ¹H NMR spectrum of H[AII₂] (600 MHz, C₆D₆).



Figure S4: ${}^{13}C{}^{1}H$ NMR spectrum of H[AII₂] (151 MHz, C₆D₆).



Figure S5: Expanded region of the ${}^{13}C{}^{1}H$ NMR spectrum of H[AII₂] (151 MHz, C₆D₆).



Figure S6: Expanded region of the ${}^{13}C{}^{1}H$ NMR spectrum of H[AII₂] (151 MHz, C₆D₆).



Figure S7: ¹H NMR spectrum of [(AII₂)Y(CH₂SiMe₃)₂] (1) (600 MHz, C₆D₆).



Figure S8: Expanded region of the ¹H NMR spectrum of [(AII₂)Y(CH₂SiMe₃)₂] (1) (600 MHz, C₆D₆).



Figure S9: Expanded region of the ¹H NMR spectrum of [(AII₂)Y(CH₂SiMe₃)₂] (1) (600 MHz, C₆D₆).



Figure S10: ¹³C{¹H} NMR spectrum of [(AII₂)Y(CH₂SiMe₃)₂] (1) (151 MHz, C₆D₆).



Figure S11: Expanded region of the ${}^{13}C{}^{1}H$ NMR spectrum of $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) (151 MHz, C_6D_6).



Figure S12: Expanded region of the ${}^{13}C{}^{1}H$ NMR spectrum of $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) (151 MHz, C_6D_6).



Figure S13: Expanded region of the ${}^{13}C{}^{1}H$ NMR spectrum of $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) (151 MHz, C_6D_6).



Figure S14: Expanded region of the ${}^{13}C{}^{1}H$ NMR spectrum of $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) (151 MHz, C_6D_6).



Figure S15: ¹H NMR spectrum of [(AII₂)Sc(CH₂SiMe₃)₂] (2) (600 MHz, C₆D₆).



Figure S16: Expanded region of the ¹H NMR spectrum of [(AII₂)Sc(CH₂SiMe₃)₂] (2) (600 MHz, C₆D₆).



Figure S17: Expanded region of the ¹H NMR spectrum of [(AII₂)Sc(CH₂SiMe₃)₂] (2) (600 MHz, C₆D₆).



Figure S18: ${}^{13}C{}^{1}H$ NMR spectrum of $[(AII_2)Sc(CH_2SiMe_3)_2]$ (2) (151 MHz, C₆D₆).



Figure S19: Expanded region of the ${}^{13}C{}^{1}H$ NMR spectrum of $[(AII_2)Sc(CH_2SiMe_3)_2]$ (2) (151 MHz, C_6D_6).



Figure S20: Expanded region of the ${}^{13}C{}^{1}H$ NMR spectrum of $[(AII_2)Sc(CH_2SiMe_3)_2]$ (2) (151 MHz, C_6D_6).



Figure S21: Expanded region of the ${}^{13}C{}^{1}H$ NMR spectrum of $[(AII_2)Sc(CH_2SiMe_3)_2]$ (2) (151 MHz, C_6D_6).



Figure S22: Expanded region of the ${}^{13}C{}^{1}H$ NMR spectrum of $[(AII_2)Sc(CH_2SiMe_3)_2]$ (2) (151 MHz, C_6D_6).



Figure S23: ¹H NMR spectrum (600 MHz, 298 K, C_6D_5Br) of [(AII₂-CH₂SiMe₃)Y(CH₂SiMe₃)₂][B(C_6F_5)₄] (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of [(AII₂)Y(CH₂SiMe₃)₂] (**1**) with [CPh₃][B(C_6F_5)₄]. Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species.



Figure S24: Expanded region of the ¹H NMR spectrum (600 MHz, 298 K, C_6D_5Br) of [(AII₂-CH₂SiMe₃)Y(CH₂SiMe₃)₂][B(C₆F₅)₄] (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of [(AII₂)Y(CH₂SiMe₃)₂] (**1**) with [CPh₃][B(C₆F₅)₄]. Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species.



Figure S25: Expanded region of the ¹H NMR spectrum (600 MHz, 298 K, C_6D_5Br) of [(AII₂-CH₂SiMe₃)Y(CH₂SiMe₃)₂][B(C₆F₅)₄] (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of [(AII₂)Y(CH₂SiMe₃)₂] (**1**) with [CPh₃][B(C₆F₅)₄]. Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species.



Figure S26: ¹H NMR (500 MHz, 298 K, C_6D_5Br) spectra of (a) top, red spectrum: $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) with naphthalene as an internal standard, before the addition of $[CPh_3][B(C_6F_5)_4]$, and (b) bottom, blue spectrum: $[(AII_2-CH_2SiMe_3)Y(CH_2SiMe_3)_2][B(C_6F_5)_4]$ (3) generated in-situ after the addition of $[CPh_3][B(C_6F_5)_4]$.



Figure S27: ¹³C{¹H} NMR (298 K, 151 MHz) spectrum of $[(AII_2-CH_2SiMe_3)Y(CH_2SiMe_3)_2][B(C_6F_5)_4]$ (3) generated in-situ (in ~20% spectroscopic yield) from the reaction of $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) with $[CPh_3][B(C_6F_5)_4]$ in C_6D_5Br . Other reaction products are HCPh₃ (~2 equiv. relative to 3) and an unidentified paramagnetic species.



Figure S28: Expanded region of the ${}^{13}C{}^{1}H$ NMR (298 K, 151 MHz) spectrum of $[(AII_2-CH_2SiMe_3)Y(CH_2SiMe_3)_2][B(C_6F_5)_4]$ (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of $[(AII_2)Y(CH_2SiMe_3)_2]$ (**1**) with $[CPh_3][B(C_6F_5)_4]$ in C_6D_5Br . Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species.



Figure S29: Expanded region of the ${}^{13}C{}^{1}H$ NMR (298 K, 151 MHz) spectrum of [(AII₂-CH₂SiMe₃)Y(CH₂SiMe₃)₂][B(C₆F₅)₄] (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of [(AII₂)Y(CH₂SiMe₃)₂] (**1**) with [CPh₃][B(C₆F₅)₄] in C₆D₅Br. Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species.



Figure S30: ¹¹B NMR spectrum (161 MHz, 298 K, C_6D_5Br) of [(AII₂-CH₂SiMe₃)Y(CH₂SiMe₃)₂][B(C_6F_5)₄] (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of [(AII₂)Y(CH₂SiMe₃)₂] (**1**) with [CPh₃][B(C_6F_5)₄]. Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species.



Figure S31: ¹⁹F NMR spectrum (471MHz, 298 K, C₆D₅Br) of $[(AII_2-CH_2SiMe_3)Y(CH_2SiMe_3)_2][B(C_6F_5)_4]$ (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of $[(AII_2)Y(CH_2SiMe_3)_2]$ (**1**) with $[CPh_3][B(C_6F_5)_4]$. Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species.



Figure S32: VT- ¹⁹F NMR spectra (471 MHz, C_6D_5Br) of [(AII₂-CH₂SiMe₃)Y(CH₂SiMe₃)₂][B(C₆F₅)₄] (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of [(AII₂)Y(CH₂SiMe₃)₂] (**1**) with [CPh₃][B(C₆F₅)₄]. Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species.



Figure S33: ${}^{1}H{}^{-13}C$ HSQC (258 K, 500, 126 MHz) spectrum of [(AII₂-CH₂SiMe₃)Y(CH₂SiMe₃)₂][B(C₆F₅)₄] (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of [(AII₂)Y(CH₂SiMe₃)₂] (**1**) with [CPh₃][B(C₆F₅)₄] in C₆D₅Br. Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species.



Figure S34: Expanded region of the ¹H-¹³C HSQC (258 K, 500, 126 MHz) spectrum of $[(AII_2-CH_2SiMe_3)Y(CH_2SiMe_3)_2][B(C_6F_5)_4]$ (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of $[(AII_2)Y(CH_2SiMe_3)_2]$ (**1**) with $[CPh_3][B(C_6F_5)_4]$ in C_6D_5Br . Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species.



Figure S35: Expanded region of the ¹H-¹³C HSQC (258 K, 500, 126 MHz) spectrum of $[(AII_2-CH_2SiMe_3)Y(CH_2SiMe_3)_2][B(C_6F_5)_4]$ (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of $[(AII_2)Y(CH_2SiMe_3)_2]$ (**1**) with $[CPh_3][B(C_6F_5)_4]$ in C_6D_5Br . Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species.



S36: 2D $^{1}H^{-13}C$ HMBC NMR 151 MHz, Figure spectrum (600, 298 K) of [(AII₂-CH₂SiMe₃)Y(CH₂SiMe₃)₂][B(C₆F₅)₄] (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of [(AII₂)Y(CH₂SiMe₃)₂] (1) with [CPh₃][B(C₆F₅)₄] in C₆D₅Br. Other reaction products are HCPh₃ (~2 equiv. relative to 3) and an unidentified paramagnetic species. On the axes, YCH₂SiMe₃ peaks are indicated in blue and red, and NCH₂SiMe₃ peaks are highlighted in green. See below for expansions of the regions within the dashed boxes.



Figure S37: Expanded region of the 2D ${}^{1}H^{-13}C$ HMBC NMR spectrum (600, 151 MHz, 298 K) of [(AII₂-CH₂SiMe₃)Y(CH₂SiMe₃)₂][B(C₆F₅)₄] (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of [(AII₂)Y(CH₂SiMe₃)₂] (**1**) with [CPh₃][B(C₆F₅)₄] in C₆D₅Br. Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species. On the axes, YCH₂SiMe₃ peaks are indicated in blue and red, and NCH₂SiMe₃ peaks are highlighted in green.



Figure S38: Expanded region of the 2D ${}^{1}H{}^{-13}C$ HMBC NMR spectrum (600, 151 MHz, 298 K) of [(AII₂-CH₂SiMe₃)Y(CH₂SiMe₃)₂][B(C₆F₅)₄] (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of [(AII₂)Y(CH₂SiMe₃)₂] (**1**) with [CPh₃][B(C₆F₅)₄] in C₆D₅Br. Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species. On the axes, YCH₂SiMe₃ peaks are indicated in blue and red, and NCH₂SiMe₃ peaks are highlighted in green.



Figure S39: Expanded region of the 2D ${}^{1}H{}^{-13}C$ HMBC NMR spectrum (600, 151 MHz, 298 K) of [(AII₂-CH₂SiMe₃)Y(CH₂SiMe₃)₂][B(C₆F₅)₄] (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of [(AII₂)Y(CH₂SiMe₃)₂] (**1**) with [CPh₃][B(C₆F₅)₄] in C₆D₅Br. Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species.



NMR 151 Figure **S40:** 2D $^{1}\text{H}-^{1}\text{H}$ NOESY spectrum (600, MHz, 298 K) of [(AII₂-CH₂SiMe₃)Y(CH₂SiMe₃)₂][B(C₆F₅)₄] (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of [(AII₂)Y(CH₂SiMe₃)₂] (1) with [CPh₃][B(C₆F₅)₄] in C₆D₅Br. Other reaction products are HCPh₃ (~2 equiv. relative to 3) and an unidentified paramagnetic species. On the axes, YCH₂SiMe₃ peaks are indicated in blue and red, and NCH₂SiMe₃ peaks are highlighted in green. See below for expansions of the regions within the dashed boxes.



Figure S41: Selected region of the 2D ¹H-¹H NOESY NMR spectrum (600, 151 MHz, 298 K) of $[(AII_2-CH_2SiMe_3)Y(CH_2SiMe_3)_2][B(C_6F_5)_4]$ (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of $[(AII_2)Y(CH_2SiMe_3)_2]$ (**1**) with $[CPh_3][B(C_6F_5)_4]$ in C_6D_5Br . Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species. Crosspeaks involving the CH₂SiMe₃ groups are highlighted in yellow. On the axes, YCH₂SiMe₃ peaks are indicated in blue and red, and NCH₂SiMe₃ peaks are highlighted in green.



Figure S42: Selected region of the 2D ¹H-¹H NOESY NMR spectrum (600, 151 MHz, 298 K) of $[(AII_2-CH_2SiMe_3)Y(CH_2SiMe_3)_2][B(C_6F_5)_4]$ (**3**) generated in-situ (in ~20% spectroscopic yield) from the reaction of $[(AII_2)Y(CH_2SiMe_3)_2]$ (**1**) with $[CPh_3][B(C_6F_5)_4]$ in C_6D_5Br . Other reaction products are HCPh₃ (~2 equiv. relative to **3**) and an unidentified paramagnetic species. Crosspeaks involving the CH₂SiMe₃ groups are highlighted in yellow. On the axes, YCH₂SiMe₃ peaks are indicated in blue and red, and the NCH₂SiMe₃ peak is highlighted in green.



Figure S43: Experimental (top; blue) and simulated (bottom; red) solution X-band EPR spectra of the purple solution formed upon reaction of reaction of $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) with $[CPh_3][B(C_6F_5)_4]$ (this reaction afforded diamagnetic **3** (in ~20% yield), HCPh₃ (~2 equiv. relative to **3**), and an unidentified paramagnetic product). Temp. = 25 °C, Microwave frequency = 9.6036 GHz, Modulation amplitude = 0.5 G. Simulation parameters: g = 2.0035, Gaussian line broadening = 0.435, Hyperfine coupling = 10.9 (2 × ¹H), 12.8 (2 × ¹H), 15.5 (2 × ¹H) and 13.1 (1 × ¹⁴N) MHz (3.9, 4.6, 5.5 and 4.7 G, respectively).



Figure S44: ¹H NMR (500 MHz; 298 and 248 K) spectra of the reaction of $[(AII_2)Sc(CH_2SiMe_3)_2]$ (2) with $[CPh_3][B(C_6F_5)_4]$ in C_6D_5Br .



Figure S45: Cyclic voltammograms of $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) at a scan rate of 2000 mV/s in 1,2-difluorobenzene with $[N^nBu_4][B(C_6F_5)_4]$ base electrolyte (Pt working and counter electrode, Ag pseudo-reference electrode). The bottom CV contains added $[FeCp_2]$ ($E_{1/2} = -0.60$ V vs $[FeCp_2]^{0/+}$) as an internal calibrant.



Figure S46: Cyclic voltammograms of $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) at scan rates of 200 mV/s (top) and 20 mV/s (bottom) in 1,2-difluorobenzene with $[N^nBu_4][B(C_6F_5)_4]$ base electrolyte (Pt working and counter electrode, Ag pseudo-reference electrode).

INTRAMOLECULAR HYDROAMINATION CATALYSIS



Figure S47: In-situ ¹H NMR spectrum of the intramolecular hydroamination product formed from 1amino-2,2-diphenylpent-4-ene and $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) / $[CPh_3][B(C_6F_5)_4]$ (2 mol%) after 8 min at 24 °C (600 MHz,C_6D_5Br).



Figure S48: In-situ ¹H NMR spectrum of the intramolecular hydroamination product formed from 1-amino-2,2-diphenyl-4-methylpent-4-ene and $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) / $[CPh_3][B(C_6F_5)_4]$ (5 mol%) after 1 hour at 24 °C (600 MHz, C₆D₅Br).



Figure S49: In-situ ¹H NMR spectrum of the intramolecular hydroamination product formed from 1amino-2,2-diphenylhex-5-ene and $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) / $[CPh_3][B(C_6F_5)_4]$ (5 mol%) after 1.1 hours at 24 °C (600 MHz, C₆D₅Br).



Figure S50: Hydroamination of 1-amino-2,2-diphenylpent-4-ene by $[(AII_2)Y(CH_2SiMe_3)_2]$ (1; 5 mol%) in C₆D₆: a) Concentration of product (mol/L) vs. time, b) % conversion to product vs. time.

a)



b)



Figure S51: Hydroamination of 1-amino-2,2-diphenyl-4-methylpent-4-ene by $[(AII_2)Y(CH_2SiMe_3)_2](1) / [CPh_3][B(C_6F_5)_4](2 \text{ mol}\%)$ at 24 °C in C₆D₅Br: a) concentration of product (mol/L) vs. time, b) % conversion to product vs. time.



Figure S52: Hydroamination of 1-amino-2,2-diphenylhex-5-ene by $[(AII_2)Y(CH_2SiMe_3)_2]$ (1) / $[CPh_3][B(C_6F_5)_4]$ (4 mol%) at 24 °C in C_6D_5Br : a) Concentration of product (mol/L) vs. time, b) % conversion of substrate to product vs. time.