

The 6-amino-6-methyl-1,4-diazepine group as ancillary ligand framework for neutral and cationic scandium and yttrium alkyls

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Supporting material: synthesis, characterization, and polymerization conditions

Experimental section

General All preparations were performed under an inert nitrogen atmosphere, using standard Schlenk or glovebox techniques, unless mentioned otherwise. Toluene, pentane, and hexane (Aldrich, anhydrous, 99.8%) were passed over columns of Al₂O₃ (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). Diethyl ether and THF (Aldrich, anhydrous, 99.8%) were dried over Al₂O₃ (Fluka). All solvents were degassed prior to use and stored under nitrogen. N, N'-dimethylethylenediamine (Aldrich, 85%), nitroethane (Acros, 98+%), formaldehyde solution (Merck, 37%) were used as received. 6-Amino-1,4,6-trimethyl-1,4-diazepine and 6-(dimethylamino)-1,4,6-trimethyl-1,4-diazepine (**L1**) were prepared following a procedure from reference 3b in the manuscript. A full description of the synthesis is given below. Deuterated solvents (C₆D₆, C₇D₈, C₄D₈O; Aldrich) were vacuum-transferred from Na/K alloy NMR spectra were recorded on Varian Gemini VXR 400, Varian Gemini VXR 300 or Varian Inova 500 spectrometers in NMR tubes equipped with a Teflon (Young) valve. The ¹H NMR spectra were referenced to resonances of residual protons in deuterated solvents. The ¹³C NMR spectra were referenced to carbon resonances of deuterated solvents and reported in ppm relative to TMS (δ 0 ppm). IR spectra were recorded on an Interspec 200-X spectrophotometer. GPC analyses were performed by A. Jekel on a Polymer Laboratories Ltd. (PL-GPC210) chromatograph with 1,2,4-trichlorobenzene (TCB) as the mobile phase at 150 °C and with polystyrene references. Elemental analyses were performed at the Microanalytical Department of the University of Groningen.

Synthesis of 6-dimethylamino-1,4,7-trimethyl-1,4-diazepine (L1)

a) Synthesis of 6-nitro-1,4,7-trimethyl-1,4-diazepine. N, N'-dimethylethylenediamine (10.0 g, 113 mmol, purity: 85%) and nitroethane (8.60 g, 115 mmol) were mixed in a two-necked flask in a ice-water bath. Formaldehyde (37% aqueous solution, 19.2 g, 236 mmol) was added dropwise at ambient temperature. After addition, a pale yellow mixture had formed. Subsequently, the reaction mixture was heated at 95°C for 15 min. The resulting dark yellow mixture was cooled to room temperature and 20 ml of water was added. The mixture was extracted twice with 100 ml of diethylether and the combined ether layer was dried over Na₂SO₄. The removal of all the volatiles gave 16.8 g brown oily liquid. The residue was purified by Kugelrohr distillation (132°C, 430 mTorr) yielding the title compound (13.10 g, 70 mmol, 62%) as a yellow liquid. The compound was characterized by ¹H and ¹³C NMR.

¹H NMR (400 MHz, CDCl₃, δ): 3.33 and 2.70 (AB system, 4H, CCH₂), 2.58 (m, 2H, NCH₂), 2.48 (m, 2H, NCH₂), 2.35 (s, 6H, NCH₃), 1.44 (s, 3H, CCH₃).

¹³C NMR (100.5 MHz, CDCl₃, δ): 91.0 (s, CMe(CH₂)₂), 65.3 (t, J_{CH} = 135.2 Hz, NCH₂), 60.9 (t, J_{CH} = 132.8 Hz, NCH₂), 48.5 (q, J_{CH} = 133.0 Hz, NCH₃), 24.8 (q, J_{CH} = 130.7 Hz, H₃CC).

b) Synthesis of 6-amino-1,4,6-trimethyl-1,4-diazepine. In a 50 mL glass miniclave (Büchi A. G., Switzerland), 6-nitro-1,4,7-trimethyl-1,4-diazepine (6.50 g, 34.7 mmol), 10 ml of absolute alcohol, and a catalytic amount of Raney-Nickel were mixed. The mixture was hydrogenated under 5 bar H₂ pressure until full conversion indicated by GC (reaction time: ~6 h). The mixture was filtered through a 2 cm pad of Celite to remove catalyst particles and the filtrate was evaporated to dryness giving 5.85 g of yellow residue. The residue was purified by Kugelrohr distillation (70°C, 430 mTorr) yielding the title compound (3.90 g, 24.8 mmol, 72%) as a colorless liquid. The compound was characterized by ¹H and ¹³C NMR.

¹H NMR (400 MHz, CDCl₃, δ): 2.57 (m, 2H, NCH₂), 2.46 (m, 2H, NCH₂), 2.41 and 2.24 (AB system, 4H, CCH₂), 2.28 (s, 6H, NCH₃), 1.54 (broad, 2H, NH₂), 0.94 (s, 3H, CCH₃).

¹³C NMR (100.5 MHz, CDCl₃, δ): 72.0 (t, J_{CH} = 132.6 Hz, NCH₂), 60.8 (t, J_{CH} = 133.9 Hz, NCH₂), 52.3 (s, CMe(CH₂)₂), 49.2 (q, J_{CH} = 132.6 Hz, NCH₃), 27.1 (q, J_{CH} = 127.3 Hz, H₃CC).

c) Synthesis of 6-dimethylamino-1,4,7-trimethyl-1,4-diazepine (L1). In a 500 mL three-necked flask equipped with a water condenser and a thermometer, 6-amino-1,4,6-trimethyl-1,4-diazepine (7.80 g, 49.6 mmol) was dissolved in 150 ml of acetonitrile, after which formaldehyde (37% aqueous solution, 19.5 ml, 241.8 mmol) was added. Sodium cyanoborohydride (4.92 g, 78 mmol) was then added in small portions. The temperature of the reaction mixture rose to about 60°C and then dropped. After stirring for about 30 min, acetic acid (about 8 ml) was added dropwise until the pH value of the mixture reached approximately 6.5 as indicated by wet pH paper. [CAUTION: when cyanoborohydride is used as reducing agent, the subsequent acidification should not proceed beyond pH = 5, as liberation of HCN might ensue.] The resulting pale brown mixture was stirred for another 30 min and then left overnight at room temperature. A few more drops of acetic acid was added and the mixture was evaporated to dryness. The residue was dissolved in water and evaporated to dryness. Then the residue was redissolved in water and made basic (pH>12) with 40% NaOH solution and extracted thrice with 100ml of diethylether. The combined ether layer was washed with 10% NaOH solution twice and then extracted twice with 1M HCl aqueous solution (100 ml). The combined water layer was made basic (pH>12) with 40% NaOH solution and extracted thrice with 100 ml of diethylether. The combined ether layer was dried with Na₂SO₄. The removal of all volatiles gave 7.47 g of slightly yellow residue. The residue was purified by Kugelrohr distillation (90°C, 270 mTorr) yielding the title compound (5.92 g, 32.0 mmol, 65%) as a colorless liquid. The compound was characterized by ¹H and ¹³C NMR. ¹H NMR (300 MHz, CDCl₃, δ): 2.65 and 2.19 (AB system, 4H, CCH₂, 2.19 overlap with 2.22 NMe₂), 2.45 (m, 4H, NCH₂), 2.27 (s, 6H, NCH₃), 1.22 (s, 6H, N(CH₃)₂), 0.91 (s, 3H, CCH₃). ¹³C NMR (75.4 MHz, CDCl₃, δ): 66.4 (t, J_{CH} = 130.7 Hz, NCH₂), 62.4 (t, J_{CH} = 130.7 Hz, NCH₂), 59.8 (s, CMe), 49.4 (q, J_{CH} = 134.2 Hz, NCH₃), 39.4 (qq, ¹J_{CH} = 133.1 Hz, ³J_{CH} = 6.2 Hz, N(CH₃)₂), 20.6 (q, J_{CH} = 126.0 Hz, H₃CC).

Synthesis of Sc(L1)(CH₂SiMe₃)₃ (1a)

(Me₃SiCH₂)₃Sc(THF)₂ (0.902 g, 2.0 mmol) was dissolved in 30 ml of cold benzene (7 °C). A solution of 6-dimethyl-1,4,6-trimethyl-1,4-diazepine **L1** (0.371 g, 2.0 mmol) in 20 ml of cold benzene was added dropwise while stirring. The mixture was allowed to warm to room temperature and stirred for 30 min. The volatiles were removed under reduced pressure and the residue was washed with pentane yielding the pure title compound (L1)Sc(CH₂SiMe₃)₃ (0.92 g, 1.87 mmol, 94%) as a slightly yellow solid. Assignment of the NMR resonances was aided by COSY and HSQC experiments.

¹H NMR (400MHz, C₆D₆, δ): 3.00 (m, 2H, NCH₂), 2.26 (d, 2H, J_{HH} = 13.7 Hz, CCHH), 2.14 (s, 6H, NCH₃), 1.91 (s, 6H, N(CH₃)₂), 1.52 (m, 2H, NCH₂), 1.22 (d, 2H, J_{HH} = 13.7Hz, CCHH), 0.47 (s, 27H, Si(CH₃)₃), -0.08 (s, 3H, CCH₃), -0.14 (s, 6H, ScCH₂). ¹³C NMR (100.6MHz, C₆D₆, δ): 68.5 (t, J_{CH} = 137.4 Hz, CCH₂), 60.0 (s, MeC), 59.2 (t, J_{CH} = 137.4 Hz, CH₂CH₂), 50.4 (q, J_{CH} = 138.9 Hz, NMe₂), 42.0 (q, J_{CH} = 138.9 Hz, NMe), 40.0 (br, ScCH₂), 10.8 (q, J_{CH} = 126.2 Hz, CMe), 4.7 (q, J_{CH} = 116.5 Hz, SiMe₃).

Anal. Calcd for C₂₂H₅₆N₃Si₃Sc: C, 53.72%; H, 11.47%; N, 8.54%. Found: C, 53.25%; H, 11.50%; N, 8.41%.

Synthesis of Y(L1)(CH₂SiMe₃)₃ (**1b**)

(Me₃SiCH₂)₃Y(THF)₂ (0.990 g, 2.0 mmol) was dissolved in 30 ml of cold benzene (7 °C). A solution of 6-dimethyl-1,4,6-trimethyl-1,4-diazepine **L1** (0.371 g, 2.0 mmol) in 20 ml of cold benzene was added dropwise while stirring. The mixture was allowed to warm to room temperature and stirred for 30 min. The volatiles were removed under reduced pressure and the residue was washed with pentane yielding the pure title compound (L1)Y(CH₂SiMe₃)₃ 1.02 g (1.9 mmol, 95%) as an off-white solid. Assignment of the NMR resonances was aided by COSY and HSQC experiments.

¹H NMR (400MHz, C₆D₆, δ): 2.78 (m, 2H, NCH₂), 2.19 (d, 2H, J_{HH} = 14.2 Hz, CCHH), 2.11(s, 6H, NCH₃), 1.89 (s, 6H, N(CH₃)₂), 1.51 (m, 2H, NCH₂), 1.18 (d, 2H, J_{HH} = 14.2 Hz, CCHH), 0.48 (s, 27H, Si(CH₃)₃), -0.11 (s, 3H, CCH₃), -0.56 (d, 6H, J_{YH} = 2.8 Hz, YCH₂). ¹³C NMR (100.6MHz, C₆D₆, δ): 68.4 (t, J_{CH} = 137.6 Hz, CCH₂), 60.9 (s, MeC), 58.8 (t, J_{CH} = 140.1 Hz, CH₂CH₂), 50.1 (q, J_{CH} = 137.1 Hz, NMe₂), 41.4 (q, J_{CH} = 136.1

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Hz, *NMe*), 36.9 (dt, $J_{CH} = 97.9$ Hz, $J_{YC} = 35.3$, *YCH*₂), 11.6 (q, $J_{CH} = 126.7$ Hz, *CMe*), 5.6 (q, $J_{CH} = 117.2$ Hz, *SiMe*₃).

Anal. Calcd for C₂₂H₅₆N₃Si₃Y: C, 49.31%; H, 10.53%; N, 7.84%. Found : C, 49.15%; H, 10.45%; N, 7.78%.

Synthesis of [Sc(L1)(CH₂SiMe₃)₂][B(C₆H₅)₄] (2a)

THF (2 ml) was added to a mixture of 73.8 mg (150 μmol) of (L1)Sc(CH₂SiMe₃)₃ and 66.2 mg (150 μmol) of [PhMe₂NH][B(C₆H₅)₄]. The solution was homogenised by agitation and allowed to stand for about 20 min. The clear, slightly yellow solution was transferred to a Tomas tube and carefully layered with cyclohexane (3 ml). After standing overnight a white solid had precipitated. The solid was washed with pentane and dried under vacuum to give 90.4 mg (114 μmol, 76%) of pure title compound as an off-white powder.

¹H NMR (400 MHz, THF-*d*₈, 298K, δ): 7.33 (br, 4 x 2H, 2-*PhB*), 6.92 (t, 4 x 2H, $J_{HH} = 7.48$ Hz, 3-*PhB*), 6.78 (t, 4 x 1H, $J_{HH} = 7.10$ Hz, 4-*PhB*), 3.04 (d, 2H, $J_{HH} = 14.0$ Hz, *CCHH*), 2.95 (m, 2H, *NCH*₂), 2.42 (s, 6H, *NCH*₃), 2.34 (m, 2H, *NCH*₂), 2.30 (s, 6H, *N(CH*₃)₂), 2.21 (d, 2H, $J_{HH} = 14.0$ Hz, *CCHH*), 0.64 (s, 3H, *CCH*₃), -0.01 (s, 18H, *Si(CH*₃)₃), -0.26 (s, 6H, *ScCH*₂). ¹³C NMR (100.6MHz, THF-*d*₈, δ): 166.4 (q, $J_{BC} = 46.5$ Hz, 1-*Ph*), 138.4 (d, $J_{CH} = 153.1$ Hz, 2-*Ph*), 127.1 (d, $J_{CH} = 152.9$ Hz, 3-*Ph*), 123.3 (d, $J_{CH} = 155.6$ Hz, 4-*Ph*), 69.7 (t, $J_{CH} = 142.7$ Hz, *CCH*₂), 63.5 (s, *MeC*), 60.6 (t, $J_{CH} = 142.7$ Hz, *CH*₂*CH*₂), 52.1 (q, $J_{CH} = 136.3$ Hz, *NMe*₂), 48.4 (br, *ScCH*₂), 43.2 (q, $J_{CH} = 137.6$ Hz, *NMe*), 12.5 (q, $J_{CH} = 128.9$ Hz, *CMe*), 4.8 (q, $J_{CH} = 119.3$ Hz, *SiMe*₃).

Anal. Calcd for C₄₆H₇₃BN₃OSi₂Sc: C, 69.41%; H, 9.24%; N, 5.28%. Found: C, 68.60%; H, 9.09%; N, 5.24%.

in situ NMR-scale generation of [Y(L1)(CH₂SiMe₃)₂][B(C₆R₅)₄] (R = H, F; 2b)

a) using [Ph₃C][B(C₆F₅)₄].

(L1)Y(CH₂SiMe₃)₃ (17.9 mg, 33 μmol) and [Ph₃C][B(C₆F₅)₄] (30.7 mg, 33 μmol) were mixed with 0.6 ml of CD₂Cl₂ and 2 drops of THF-*d*₈ were added. The obtained solution

was transferred into a NMR tube and analyzed with NMR spectroscopy, which indicated full conversion to the cationic species and $\text{Ph}_3\text{CCH}_2\text{SiMe}_3$.

^1H NMR (400 MHz, CD_2Cl_2 , 298K, δ): 3.39 (m, 2H, NCH_2), 3.23 (d, 2H, $J_{\text{HH}} = 14.4$ Hz, CCHH), 2.74 (m, 2H, NCH_2), 2.68 (s, 6H, NCH_3), 2.53 (d, 2H, $J_{\text{HH}} = 14.4$ Hz, CCHH), 2.45 (s, 6H, $\text{N}(\text{CH}_3)_2$), 0.88 (s, 3H, CCH_3), -0.02 (s, 12H, $\text{Si}(\text{CH}_3)_4$), -0.63 (d, 4H, $J_{\text{YH}} = 2.9$ Hz, YCH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6MHz, CD_2Cl_2 , 298K δ): 68.3 (CCH_2), 61.9 (CMe), 58.2 (NCH_2CH_2), 49.8 (NMe_2), 42.5 (d, $J_{\text{YC}} = 41.7$, YCH_2), 40.1 (NMe), 11.6 (CMe), 3.6 (SiMe_3). Resonances for the anion and $\text{Ph}_3\text{CCH}_2\text{SiMe}_3$ omitted.

b) using $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{H}_5)_4]$.

(L1) $\text{Y}(\text{CH}_2\text{SiMe}_3)_3$ (16.1 mg, 30 μmol) and $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{H}_5)_4]$ (13.3 mg, 30 μmol) were mixed with 0.6 ml of $\text{THF-}d_8$. The obtained solution was transferred into a NMR tube and analyzed with NMR spectroscopy, which indicated full conversion to the cationic species, SiMe_4 and PhNMe_2 .

^1H NMR (400 MHz, $\text{THF-}d_8$, 298K, δ): 7.31 (br, 8H, 2-*Ph*B), 6.90 (t, 8H, $J_{\text{HH}} = 7.47$ Hz, 3-*Ph*B), 6.76 (t, 4H, $J_{\text{HH}} = 7.07$ Hz, 4-*Ph*B), 3.07 (m, 2H, NCH_2), 3.03 (m, 2H, CCHH), 2.46 (s, 6H, NCH_3), 2.43 (m, 2H, NCH_2), 2.31 (s, 6H, NCH_3), 2.26 (m, 2H, CCHH), 0.67 (s, 3H, CCH_3), -0.028 (s, 18H, $\text{Si}(\text{CH}_3)_3$), -0.72 (d, 4H, $J_{\text{YH}} = 2.9$ Hz, YCH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6MHz, $\text{THF-}d_8$, δ): 166.4 (q, $J_{\text{BC}} = 46.5$ Hz, 1-*Ph*), 138.4 (2-*Ph*), 127.1 (3-*Ph*), 123.3 (4-*Ph*), 69.1 (CCH_2), 63.5 (s, MeC), 59.5 (CH_2CH_2), 50.8 (NMe_2), 41.5 (NMe), 41.2 (d, $J_{\text{YC}} = 41.2$ Hz, YCH_2), 12.7 (CMe), 5.3 (SiMe_3). Resonances of PhNMe_2 omitted.

Synthesis of 6-phenylaldimino-1,4,6-trimethyl-1,4-diazepine (L2)

To a 100 ml three-necked flask equipped with a water condensor and magnetic stirring bar, 3.15 g (20 mmol) of 6-amino-1,4,6-trimethyl-1,4-diazepine, 2.12 g (20 mmol) of benzaldehyde, and 60 ml of absolute ethanol were added. The solution was stirred and a drop of formic acid was added to catalyze the reaction. The mixture was heated at reflux for 6 h and then cooled to room temperature. The mixture was dried over NaSO_4 and all the volatiles were removed under reduced pressure to give a yellow residue. The residue was purified by Kugelrohr distillation (160 $^\circ\text{C}$, 430 mTorr) yielding **L2** (3.62 g, 14.8 mmol, 74%) as a yellow liquid.

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^1H NMR (400MHz, C_6D_6 , δ): 8.57 (s, 1H, N=CH), 7.83 (d, 2H, $J_{\text{HH}} = 7.89$ Hz, o-Ph), 7.17 (t, 2H, $J_{\text{HH}} = 6.65$ Hz, m-Ph), 7.14 (t, 1H, $J_{\text{HH}} = 6.88$ Hz, p-Ph), 2.81 and 2.54 (AB system, 4H, NCH₂), 2.44 (m, 4H, NCH₂CH₂), 2.22 (s, 6H, NCH₃), 1.40 (s, 3H, CCH₃).
 $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6MHz, C_6D_6 , δ): 156.6 (N=CH), 138.1 (N=CH-C), 130.2 (Ph), 128.6 (Ph), 128.4 (Ph), 70.0 (CCH₂), 63.8 (CMe), 61.9 (NCH₂CH₂), 48.8 (NMe₂), 26.5 (CMe).

IR(nujol/KBr): 2803(s), 2766 (m), 1643(vs, C=N), 1581(mw), 1308(w), 1287(m), 1122(w), 1218(w), 1122(mw), 1092(s), 1063(w), 959(w), 752(m), 963(m) cm^{-1} .

Anal. Calcd for $\text{C}_{15}\text{H}_{23}\text{N}_3$: C, 73.43%; H, 9.45%; N, 17.13%. Found : C, 72.60%; H, 9.36%; N, 16.93%.

Reaction of L2 with $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$: synthesis of 3.

$(\text{Me}_3\text{SiCH}_2)_3\text{Y}(\text{THF})_2$ (0.495 g, 1.0 mmol) was dissolved in 20 ml of cold toluene (-30 °C). A solution of L2 (0.245 g, 1.0 mmol) in 6 ml of cold toluene (-30 °C) was added dropwise while stirring. The mixture was allowed to warm to room temperature and stirred for 30 min. The volatiles were removed under reduced pressure and the residue was dissolved in the mixture of toluene and pentane. The solution was cooled to -30 °C yielding 3 as its toluene solvate ($3 \cdot 0.25(\text{C}_7\text{H}_8)$), 0.58g, 0.84mmol, 84%) as a slightly yellow crystalline solid. Assignment of the NMR resonances was aided by COSY and HSQC experiments.

^1H NMR (400MHz, C_6D_6 , δ): 7.74 (d, 2H, $J_{\text{HH}} = 7.58$ Hz, 2-Ph), 7.27 (t, 2H, $J_{\text{HH}} = 7.54$ Hz, 3-Ph), 7.08 (t, 1H, $J_{\text{HH}} = 7.01$ Hz, 4-Ph), 4.45 (dd, 1H, $J_{\text{HH}} = 12.1$ Hz, $J_{\text{HH}} = 2.87$ Hz, Ph-CH), 3.66 (m, 4H, OCH₂), 2.75 (d, 1H, $J_{\text{HH}} = 11.8$ Hz, NCHH), 2.33 (d, 1H, $J_{\text{HH}} = 11.5$ Hz, NCHH), 2.29-2.19 (m, 3H, NCH₂ and SiCHH), 2.17 (s, 3H, NCH₃), 2.13 (s, 3H, NCH₃), 2.03 (m, 1H, SiCHH), 1.78 (d, 1H, $J_{\text{HH}} = 11.8$ Hz, NCHH), 1.68 (d, 1H, $J_{\text{HH}} = 11.5$ Hz, NCHH), 1.66-1.56 (m, 2H, NCH₂), 0.68 (s, 3H, CCH₃), 0.47 (s, 18H, Si(CH₃)₃), 0.05 (s, 9H, Si(CH₃)₃), -0.43 (broad, 2H, YCH₂), -0.69 (d, $J_{\text{HH}} = 11.0$ Hz, YCH₂).
 $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6MHz, C_6D_6 , δ): 154.4 (1-Ph), 128.5 (2-Ph), 128.1 (3-Ph), 126.1 (4-Ph), 80.9 (NCH₂), 76.9 (NCH₂), 7.03 (OCH₂), 61.2 (PhCH), 58.4 (NCH₂), 57.4 (NCH₂), 57.2 (CCH₃), 50.8 (NCH₃), 50.4 (NCH₃), 30.9 (SiCH₂), 25.1 (OCH₂CH₂), 25.0 (broad, YCH₂),

21.3 (*CMe*), 5.2 ($\text{Si}(\text{CH}_3)_3$), -0.36 ($\text{Si}(\text{CH}_3)_3$). Resonances for the (proteo)toluene in the crystals omitted.

^1H NMR (500MHz, C_7D_8 , -60°C , δ): Proton signals on the phenyl group are broad and overlap with solvent C_7D_8 signals. 4.56 (d, 1H, $J_{\text{HH}} = 12.5$ Hz, PhCH), 3.53 (broad s, 2H, OCH_2), 3.341 (broad s, 2H, OCH_2), 2.72 (d, 1H, $J_{\text{HH}} = 11.0$ Hz, NCHH), 2.44 (d, 1H, $J_{\text{HH}} = 11.9$ Hz, SiCHH), 2.32 (d, 1H, $J_{\text{HH}} = 11.0$ Hz, NCHH), 2.15 (s, 3H, NCH_3), 2.12 (d, 1H, SiCHH, overlap with 2.11 ppm NCH_3), 2.11 (s, 3H, NCH_3), 2.03 (m, 2H, NCH_2), 1.66 (d, 1H, $J_{\text{HH}} = 11.0$ Hz, NCHH), 1.57 (d, 1H, $J_{\text{HH}} = 11.0$ Hz, NCHH), 1.48 (m, 2H, NCH_2), 1.34 (broad s, 4H, OCH_2CH_2), 0.68 (s, 3H, CCH_3), 0.54 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.58 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.18 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.18 (d, 1H, YCHH, overlap with 0.18 ppm singlet), -0.50 (d, 1H, $J_{\text{HH}} = 11.5$ Hz, YCHH), -0.74 (d, 1H, $J_{\text{HH}} = 11.5$ Hz, YCHH), -0.88 (d, 1H, $J_{\text{HH}} = 11.0$ Hz, YCHH). The J_{YH} coupling on the YCH_2 protons is unresolved. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7MHz, C_6D_6 , -60°C , δ): 155.4 (1-Ph), 129.2 (2-Ph), 128.3 (3-Ph), 125.9 (4-Ph), 81.0 (NCH_2), 77.1 (NCH_2), 69.8 (OCH_2), 60.9 (PhCH), 57.2 (NCH_2), 56.9 (CCH_3), 50.0 (NCH_3), 31.3 (d, $J_{\text{YC}} = 33.4$ Hz, YCH_2), 29.7 (SiCH_2), 25.8 (d, $J_{\text{YC}} = 38.5$ Hz, YCH_2), 24.3 (OCH_2CH_2), 20.5 (CCH_3), 4.67 ($\text{Si}(\text{CH}_3)_3$), 4.69 ($\text{Si}(\text{CH}_3)_3$), -0.82 ($\text{Si}(\text{CH}_3)_3$). Resonances for the (proteo)toluene in the crystals omitted.

Anal. Calcd for $2(\text{C}_{31}\text{H}_{64}\text{N}_3\text{OSi}_3\text{Y}) \cdot 0.5(\text{C}_7\text{H}_8)$: C, 56.92%; H, 9.63%; N, 6.08%. Found : C, 56.85%; H, 9.58%; N, 6.12%.

Synthesis of 6-(*o*-hydroxyphenyl)aldimino-1,4,6-trimethyl-1,4-diazepine (L3H)

To a 100 ml three-necked flask equipped with a water condenser and magnetic stirring bar, 3.15 g (20 mmol) of 6-amino-1,4,6-trimethyl-1,4-diazepine, 2.44 g (20 mmol) of salicylaldehyde, and 60 ml of absolute ethanol were added. The solution was stirred and a drop of formic acid was added to catalyze the reaction. The mixture was heated at reflux for 6 h and then cooled to room temperature. The mixture was dried over NaSO_4 and all the volatiles were removed under reduced pressure to give a yellow residue. The residue was purified by Kugelrohr distillation (180 $^\circ\text{C}$, 410 mTorr) yielding L3H (3.42 g, 13.1 mmol, 65%) as a yellow liquid. The compound was characterized with ^1H and ^{13}C NMR.

^1H NMR (400MHz, C_6D_6 , δ): 8.48 (s, 1H, N=CH), 7.14 (d, 1H, $J_{\text{HH}} = 7.89$ Hz, o-Ph), 7.08 (t, 1H, $J_{\text{HH}} = 7.89$ Hz, m-Ph), 7.02 (d, 1H, $J_{\text{HH}} = 7.42$ Hz, p-Ph), 6.70 (t, 1H, $J_{\text{HH}} = 7.42$ Hz, Ph), 2.53 and 2.30 (AB system, 4H, NCH_2 , one overlap with 2.30 multiplets 2.30 (m, 4H, NCH_2CH_2), 2.11 (s, 6H, NCH_3), 1.11 (s, 3H, CCH_3). OH proton was not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6MHz, C_6D_6 , δ): 162.6(O-CH), 162.0 (N=CH), 132.2 (Ph), 131.7 (Ph), 119.8 (N=CH-C), 118.2 (Ph), 117.7 (Ph), 69.7 (CCH_2), 63.1 (CMe), 61.7 (NCH_2CH_2), 48.6 (NMe_2), 25.0 (CMe).

IR (nujol/KBr): 2807(mw), 2768(mw), 1629 (vs, C=N), 1582(mw), 1498(mw), 1286(s), 1215(w), 1149(m), 1092(s), 1064(w), 960(vw), 943(vw), 923(vw), 897(vw), 752(s), 737(m) cm^{-1} .

Anal. Calcd for $\text{C}_{15}\text{H}_{23}\text{N}_3\text{O}$: C, 68.93%; H, 8.87%; N, 16.08%. Found : C, 68.55%; H, 8.78%; N, 15.93%.

Synthesis of $[(\text{L}3)\text{Y}(\text{CH}_2\text{SiMe}_3)_2]$ (4).

$(\text{Me}_3\text{SiCH}_2)_3\text{Y}(\text{THF})_2$ (0.495 g, 1.0 mmol) was dissolved in 20 ml of cold toluene (-30 °C). A solution of **L3H** (0.261 g, 1.0 mmol) in 6 ml of cold toluene (-30 °C) was added dropwise while stirring. The mixture was allowed to warm to room temperature and stirred for 30 min. The volatiles were removed under reduced pressure and the residue was washed with pentane yielding the title compound $(\text{L}3)\text{Y}(\text{CH}_2\text{SiMe}_3)_2$ **4** (0.41 g, 0.78 mmol, 78%) as a slightly yellow solid.

^1H NMR (500MHz, C_6D_6 , δ): 7.64 (s, 1H, N=CH), 7.29 (t, 1H, $J_{\text{HH}} = 7.26$ Hz, Ph), 7.23 (d, 1H, $J_{\text{HH}} = 7.75$ Hz, Ph), 7.12 (d, 1H, $J_{\text{HH}} = 7.75$ Hz, Ph), 6.67 (t, 1H, $J_{\text{HH}} = 7.26$ Hz, Ph), 2.87 (m, 2H, NCH_2CH_2), 2.02 (s, 6H, NMe), 1.78 (d, 2H, $J_{\text{HH}} = 13.3$ Hz), 1.55 (m, 2H, NCH_2CH_2), 1.53 (d, 2H, $J_{\text{HH}} = 13.3$ Hz), 0.42 (s, 18H, SiMe_3), 0.33 (s, 3H, CMe), -0.51 (dd, 2H, $J_{\text{YH}} = 2.9$ Hz, $J_{\text{HH}} = 11.3$ Hz), -0.55 (dd, 2H, $J_{\text{YH}} = 2.9$ Hz, $J_{\text{HH}} = 11.3$ Hz), $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7MHz, C_6D_6 , δ): 166.6 (O-Ph), 161.1 (N=CH), 135.5 (Ph), 134.7 (Ph), 122.6 (Ph), 122.6 (Ph), 115.7 (Ph), 71.5 (CCH_2), 62.1 (CMe), 57.2 (NCH_2CH_2), 49.4 (NMe_2), 30.3 (d, YCH_2 , $J_{\text{YC}} = 38.2$ Hz), 17.1 (CMe), 4.7 (SiMe_3).

IR (nujol/KBr): 1622(vs, C=N), 1599(mw), 1541(m), 1342(s), 1246(w), 1234(w), 1224(w), 1194(w), 1145(w), 1070(vw), 1043(vw), 920(mw), 886(mw), 853(br,s), 762(mw), 722(s) cm^{-1} .

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Anal. Calcd for $C_{23}H_{44}N_3OSi_2Y$: C, 52.75%; H, 8.47%; N, 8.02%. Found : C, 52.80%; H, 8.43%; N, 8.03%.

General procedure for ethene polymerization

The polymerization experiments were performed in a stirred stainless steel 1 L autoclave, fully temperature and pressure controlled, and equipped with an inert atmosphere solvent supply line and a pneumatically operated injector for the (co)catalyst solutions. Toluene (Aldrich anhydrous, 99.5%) was passed over columns of alumina, oxygen scavenger (BASF R3-11) and molecular sieves (4 Å) before being passed to the reactor. Ethene (AGA, polymer grade) was passed over columns of oxygen scavenger (BASF R3-11) and molecular sieves (4 Å) before being passed to the reactor.

In a typical experiment, solutions were prepared in a dry-box of the trialkyl complex **1** (10 μ mol) and of $[HNMe_2Ph][B(C_6F_5)]$ (10 μ mol), each in 5 ml of toluene in separate vials sealed with a serum cap. The autoclave was charged with 200ml of toluene (after injection of (co)catalyst solutions and rinsing the vials, the total volume of toluene was 250 ml), equilibrated at the desired temperature, and pressurized with ethene (5 bar). The solution of $[HNMe_2Ph][B(C_6F_5)]$ was injected first into the reactor and the reaction was started by subsequently injecting the solution of the trialkyl complex **1**. The ethene pressure was kept within 0.1 bar of the initial pressure during the reaction by replenishing flow. The polymerization was run for 10min. The obtained polymer was rinsed with ethanol and dried in a vacuum oven (70 °C).