Supplementary Information

Chiral-at-metal organolanthanides: enantioselective aminoalkene hydroamination/cyclisation with non-cyclopentadienyls

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EXPERIMENTAL DETAILS

General comments. All manipulations were carried out using standard Schlenk/glove box techniques under an atmosphere of dry argon, except for the work-up procedures for the ligands which were performed under aerobic conditions. Solvents were distilled from Na/K alloy (pentane, diethyl ether), potassium (THF) or sodium (toluene) under an atmosphere of dinitrogen. Deuterated benzene and toluene were heated to reflux in vacuo over potassium for 3 d, distilled under vacuum, degassed by three freeze-pump-thaw cycles and stored in a glove box. The reagents $[M\{N(SiMe_2H)_2\}_3(THF)_2]$ (M = Y, Sm, La) were synthesised according to literature procedures.[1] Our synthesis of the Schiff base ligands H_2L^1 and H_2L^2 has been reported previously.[2]

Synthesis of $[YL^1\{N(SiMe_2H)_2\}(THF)]$.

H_2L^1 (0.30 g, 0.54mmol) and $[Y\{N(SiMe_2H)_2\}_3(THF)_2]$ (0.35g, 0.56 mmol) were loaded into a Schlenk flask. Toluene (10 ml) was added and the resulting yellow solution was stirred overnight. The solvent was removed *in vacuo* to give a foamy material. In order to remove residual traces of $HN(SiMe_2)_2$ and toluene, pentane (5 ml) was added and then removed *in vacuo* to yield a yellow solid which was dried under vacuum at 50 °C for 2 h. Pentane (~10 ml) was added, sufficient to dissolve thesolid. The solution was filtered via cannula and the filtrate was concentrated and placed in a freezer (-25 °C) for 3 d. A yellow precipitate $[Y\mathbf{L}^1\{N(SiMe_2H)_2\}(THF)]$ formed. The solid was isolated by filtration and the supernatant was concentrated and cooled to yield a further crop. Combined yield 0.39 g, 85 %. Anal. Calcd. For $C_{46}H_{63}N_3O_3Si_2Y$: C, 64.92; H, 7.46; N, 4.94. Found: C, 65.10; H, 7.31; N, 4.85. ^{1}H-NMR (d_8-tol , 297 K, 400 MHz): δ 0.10 (d, 6H, Si*Me*$_2$H), 0.17 (d, 6H, Si*Me*$_2$H), 1.28 (br, 4H, THF), 1.64 (s, 18H, [C*Me*$_3$]), 1.78 (s, 6H, Me), 2.09 (s, 6H, Me), 3.61 (br, 4H, THF), 3.72(m, 2H, Si-*H*), 6.59 (s, 2H, Ar-*H*), 6.80 (d, 2H, Ar-*H*), 6.96 (m, 2H, Ar-*H*), 7.28(s, 2H, Ar-*H*), 7.89(s, 1H, N=C*H*). $^{13}C\{^1H\}$-NMR (d_8-tol , 297 K): δ 3.2 (Si*Me*$_2$H), 20.4 (Me), 20.9 (Me), 26.0 (THF), 30.5 ([C*Me*$_3$]), 35.9 ([CMe$_3$]), 68.7 (THF), 121.8, 123.2, 124.0, 128.7, 129.5, 130.6, 133.9, 135.2, 141.2 (Ar), 166.4 (N=*C*). MS (EI) 850 $[M]^+$, 835 $[M-CH_3]^+$, 647 $[M-(THF\ and\ N(SiMe_2H)_2)]^+$, 631, 615.

Synthesis of $[LaL^1\{N(SiMe_2H)_2\}(THF)]$.

H_2L^1 (0.41 g, 0.73 mmol) and $[La\{N(SiMe_2H)_2\}_3(THF)_2]$ (0.52 g, 0.76 mmol) were loaded into a Schlenk flask. Toluene (10 ml) was added and the resulting yellow solution was stirred overnight. The solvent was removed *in vacuo* to give a foamy material. Pentane (5 ml) was added and then removed *in vacuo* to yield a yellow solid which was dried under vacuum at 50 °C for 2 h. Pentane (~10 ml) was added, sufficient to dissolve the solid. The solution was filtered via cannula, concentrated and placed in a freezer (-25 °C) for 3 d after which time a yellow precipitate $[La\mathbf{L}^1\{N(SiMe_2H)_2\}(THF)]$ had formed. The solid was isolated by filtration and the supernatant was concentrated and cooled to yield a further crop. Combined Yield 0.47 g, 71 %. Anal. Calcd. For $C_{46}H_{63}N_3O_3Si_2La$: C, 61.31; H, 7.05; N, 4.66. Found: C, 61.22; H, 6.81; N, 4.76. ^{1}H-NMR (C_6D_6, 297 K, 400 MHz): δ 0.28 (d, 6H, SiMe$_2$H), 0.34 (d, 6H, SiMe$_2$H), 1.32 (br, 4H, THF), 1.62 (s, 18H, C-*Me*$_3$), 1.78 (s, 6H, Ar-Me), 2.10 (s, 6H, Ar-Me), 2.88

(br, 4H, THF), 5.09 (p, 2H, Si-H), 6.62 (s, 2 H, Ar-H), 6.75 (d, 2H, Ar-H), 6.99 (m, 4H, Ar-H), 7.22 (s, 2H, Ar-H), 7.89 (N=CH). $^{13}C\{^1H\}$-NMR (C_6D_6, 297 K, 400 MHz): δ 3.9 (SiMe_2H), 21.0 (Me), 21.8 (Me), 27.2 (THF), 31.4 ([CMe_3]), 36.2 ([*C*Me_3]), 70.1 (THF), 124.4, 123.9, 124.2, 124.7, 129.4, 130.5, 130.6, 131.6, 134.6, 135.5, 141.2 (Ar), 166.4 (N=*C*). MS (EI): 900 $[M]^+$, 829 $[M\text{-THF}]^+$, 699 [M-(THF and $N(SiMe_2H)_2)]^+$.

Synthesis of $[YL^2\{N(SiMe_2H)_2\}(THF)]$.

H_2L^2 (0.35 g, 0.63 mmol) and $[Y\{N(SiMe_2H)_2\}_3(THF)_2]$ (0.41 g, 0.65 mmol) were loaded into a Schlenk flask. Toluene (10 ml) was added and the resulting yellow solution was stirred overnight. The solvent was removed *in vacuo* to give a foamy material. Pentane (5 ml) was added and then removed *in vacuo* to yield a yellow solid which was dried under vacuum at 50 °C for 2 h. Pentane (~10 ml) was added, sufficient to dissolve the solid. The solution was filtered via cannula, concentrated and placed in a refrigerator (0 °C) for one week, yielding a crop of pale yellow X-ray quality crystals of $[Y\mathbf{L}^2\{N(SiMe_2H)_2\}(THF)]$. The solid was isolated by filtration and the supernatant was concentrated and cooled to -30°C to yield a further crop. Combined Yield 0.36 g, 67 %. Anal. Calcd. For $C_{46}H_{63}N_3O_3Si_2Y$: C, 64.92; H, 7.46; N, 4.94. Found: C, 64.83; H, 7.60; N, 4.72. ^1H-NMR (C_6D_6, 297 K, 400 MHz): δ 0.15 (d, 6H, $SiMe_2H$), 0.22 (d, 6H, $SiMe_2H$), 1.21 (br, 4H, THF), 1.68 (s, 18H, [CMe_3]), 1.75 (s, 6H, Me), 2.05 (s, 6H, Me), 3.59 (br, 4H, THF), 4.86(br, 2H, Si-*H*), 6.33 (d, 2H, Ar-*H*), 6.77 (d, 2H, Ar-*H*), 6.90 (tr, 2H, Ar-*H*), 7.03 (d, 2H, Ar-*H*), 7.29 (d, 2H, Ar-*H*), 8.39 (s, 2H, N=C*H*). $^{13}C\{^1H\}$-NMR (C_6D_6 , 297 K): δ 4.01 (SiMe_2H), 20.3 (Me), 20.3 (Me), 25.0 (THF), 30.6 (CMe_3), 35.8 (*C*Me_3), 70.5(THF), 118.1, 122.3, 128.6, 129.7, 133.2, 137.9, 138.5, 140.6(Ar), 166.1 (N=*C*). MS (CI): 850 $[M]^+$, 779 $[M\text{-THF}]^+$, 651 [M-(THF and $N(SiMe_2H)_2)]^+$, 615.

Synthesis of $[LaL^2\{N(SiMe_2H)_2\}(THF)]$.

H_2L^2 (0.25 g, 0.45 mmol) and $[La\{N(SiMe_2H)_2\}_3(THF)_2]$ (0.32 g, 0.47 mmol) were loaded into a schlenk flask. Toluene (10 ml) was added and the resulting yellow solution stirred overnight. The solvent was removed *in vacuo* to give a foamy material. Pentane (5 ml) was added and then removed in vacuo to yield a yellow solid which was dried under vacuum at 50 °C for 2 h. Pentane (~10 ml) was added sufficient to dissolve the solid. The solution was filtered via cannula, concentrated and placed in a refrigerator (0 °C) for one week, yielding a crop of pale yellow crystalline solid $[La\mathbf{L}^2\{N(SiMe_2H)_2\}(THF)]$. The solid was isolated by filtration and the supernatant was concentrated and cooled (-30 °C) to yield a further crop. Yield = 0.25 g, 62%. Anal. Calcd. For $C_{46}H_{63}N_3O_3Si_2La$: C, 61.31; H, 7.05; N, 4.66. Found: C, 61.78; H, 6.89; N, 4.52. ^1H-NMR (C_6D_6, 297 K, 400 MHz): δ 0.23 (d, 6H, $SiMe_2H$), 0.32 (d, 6H, $SiMe_2H$), 1.30 (br, 4H, THF), 1.61 (s, 18H, CMe_3), 1.82 (s, 6H, Ar-Me), 2.11 (s, 6H, Ar-Me), 3.87 (br, 4H, THF), 5.14 (p, 2H, Si-*H*), 6.33 (d, 2H, Ar-*H*), 6.78 (tr, 2H, Ar-*H*), 7.02 (m, 4H, Ar-*H*), 7.24 (d, 2H, Ar-*H*), 8.37 (s, 2H, N=C*H*).). $^{13}C\{^1H\}$ -NMR (C_6D_6 , 297 K): δ 4.5 (SiMe_2H), 20.9 (Ar-*Me*), 26.1 (THF), 30.0 (CMe_3), 35.9 (*C*Me_3), 70.1 (THF), 118.4, 122.7, 128.2, 129.3, 133.9, 137.4, 138.1, 139.9 (Ar), 165.2 (N=C). MS (CI): 900 $[M]^+$, 842 $[M\text{- }SiMe_2H]^+$**,** 829 $[M\text{-THF}]^+$.

Synthesis of (±)-H_2L^3.

(a) Amination of catechol.

A 250 ml round bottomed flask with stirrer bar was charged with (±)-2,2´-diamino-6,6´-dimethylbiphenyl (**1**) (2.12 g, 10.0 mmol) and 3,5-di-*tert*-butylcatechol (4.44 g, 20.0 mmol). To this was added hexane (100 ml), and the mixture was stirred for 20 min, during which time it became pale green/brown. Glacial acetic acid (0.5 ml) was added and the solution was stirred for 24 h, during which time it became dark brown. Volatiles were removed under reduced pressure to yield a brown foamy solid. Analyses showed this to be the desired product (6.08 g, 98 % yield) with no detectable impurities, however recrystallisation from methanol gave a colourless solid (**2**). Volatiles were removed from the supernatant *in vacuo* and the residue was recrystallised from ethanol. Yield = 4.34 g, 70 %. Anal. Calcd for $C_{42}H_{56}N_2O_2$: C, 81.24; H, 9.09; N, 4.51. Found C, 80.81; H, 9.29; N, 4.37. ^{1}H NMR ($CDCl_3$, 297 K): δ 1.25 (s, 18H, C*Me*$_3$), 1.42 (s, 18H, C*Me*$_3$), 2.16 (s, 6H, Ar-*Me* 4.85 (s, 2H, Ar$_2$N*H*), 6.41 (s, 2H, ArO*H*), 6.47 (d, 2H, $^3J_{HH}$ = 8 Hz), 6.89 (d, 2H, Ar-*H*, $^3J_{HH}$ = 8 Hz), 6.94 (d, 2H, Ar-*H*, $^4J_{HH}$ = 2 Hz), 7.14 (t, 2H, Ar-*H*, $^3J_{HH}$ = 8 Hz), 7.21 (d, 2H, Ar-*H*, $^4J_{HH}$ = 2 Hz), ^{13}C{^{1}H}-NMR ($CDCl_3$, 297 K): δ 19.7 (*Me*), 29.4 (^{t}Bu), 31.5 (^{t}Bu), 34.2 (C*Me*$_3$), 34.9 (*C*Me$_3$), 111.8, 121.6, 121.8, 122.1,122.6, 127.5, 129.0, 135.3, 137.7, 142.2, 144.9, 149.5 (Ar). IR (CH_2Cl_2 Thin film) ν cm^{-1} 3415 (s, NH and OH), 3041, 2955, 2905, 2867, 1581, 1479, 1462, 1418, 1391, 1361, 1310, 1264, 1225 (s, C-O), 1200, 1157, 1117, 1040, 1001, 977, 922, 892, 877, 823, 778, 740, 705, 648. MS (EI) *m/z* 620 $[M]^+$.

(b) *N*-Methylation.

To a 250 ml round bottomed flask with stirrer bar was added **2** (3.00 g, 4.84 mmol). This was placed under an argon atmosphere and dissolved in dry THF (100 ml). After cooling the solution to 0 ºC an excess of *n*-butyllithium (6 ml, 2.5 M in hexanes, 15.0 mmol) was slowly added. The solution was stirred for 2 h at 0 ºC followed by stirring at room temperature for 36 h, to give a yellow solution. After cooling to 0 ºC an excess of iodomethane (0.90 ml, 14.5 ml) was slowly added. The solution became orange, and was allowed to warm to room temperature and stirred for 20 h. Ice was cautiously added to neutralise the excess *n*-butyllithium. Water (20 ml) was added and the reaction mixture was extracted with diethyl ether (100 ml). The ether layer was dried over anhydrous $MgSO_4$, filtered and the volatiles removed under reduced pressure. The resulting off-white solid, H_2L^3 was recrystallised from acetone. Yield = 2.24 g, 71 %. Anal. Calcd for $C_{44}H_{60}N_2O_2$: C, 81.43; H, 9.32; N, 4.32. Found C, 81.20; H, 9.26; N, 4.34. ^{1}H-NMR ($CDCl_3$, 297K): δ 1.09 (s, 18H, C*Me*$_3$), 1.19 (s, 18H, *C*Me$_3$), 1.19 (bs, 6H, Ar-*Me*), 2.49 (bs, 6H, N*Me*), 5.93 (bs, 2H, ArO*H*), 6.72 (bs, 2H, Ar-*H*),6.79 (bd, 2H, Ar-*H*, $^3J_{HH}$ = 8 Hz), 6.89 (d, 2H, Ar-*H*, $^4J_{HH}$ = 2 Hz), 7.19 (t, 2H, Ar-*H*, $^3J_{HH}$ = 8 Hz), 7.25 (bd, 2H, Ar-*H*, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H}-NMR ($CDCl_3$, 297 K): δ 19.1 (*Me*), 29.4 (C*Me*$_3$), 31.4 (C*Me*$_3$), 34.3 (*C*Me$_3$), 34.6 (*C*Me$_3$), 43.6 (N*Me*), 118.9, 120.2, 120.4, 126.5, 127.7, 134.9, 134.4, 137.8, 138.1, 141.0, 147.8, 148.2 (Ar). IR (CH_2Cl_2 Thin film) ν cm^{-1} 3366 (s, OH), 30.61, 2952, 2895, 2868, 2802, 1576, 1479, 1462, 1441, 1413, 1390, 1361, 1310, 1264 (s, C-O), 1244, 1223, 1202, 1095, 1007, 958, 907, 877, 822, 806, 792, 770, 742, 699, 632.MS (EI) *m/z* 648 $[M]^+$.

Synthesis of (*S*)-H_2L^3

The chiral non-racemic ligand was prepared in exactly the same manner as for (±)-H_2L^3, using (*S*)-2,2´-diamino-6,6´-dimethylbiphenyl (1.00 g, 4.72 mmol) and 3,5-di-*tert*-butylcatechol (2.10 g, 9.46 mmol). Purification of the final product was achieved by recrystallisation from diethyl ether. Overall yield = 1.63 g, 53 %.

Synthesis of (±)-H_2L^4

(a) Schiff base synthesis

The corresponding Schiff base was prepared analogously to H_2L^1 using 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde.[3,4] (2.20 g, 9.43 mmol), (±)-2,2´-diamino-6,6´-dimethylbiphenyl (1.00 g, 4.72 mmol) and ethanol (50 ml). A yellow solid was obtained and was found to be the desired product by ^{1}H-NMR spectroscopy.[3] Yield = 2.83 g, 93 %. ^{1}H NMR 250 MHz ($CDCl_3$) δ ppm, 1.25 (s, 18H, C*Me*$_3$), 1.32 (s, 18H, C*Me*$_3$), 2.07 (s, 6H, Ar-*Me*), 7.05 (d, 2H, Ar-*H*, $^3J_{HH}$ = 7 Hz), 7.08 (d, 2H, Ar-*H*, $^4J_{HH}$ = 2 Hz), 7.19 (d, 2H, Ar-*H*, $^3J_{HH}$ = 8 Hz), 7.30 (t, 2H, Ar-*H*, $^3J_{HH}$ = 8 Hz), 7.30 (d, 2H, Ar-*H*, $^4J_{HH}$ = 2 Hz), 8.49 (s, 2H, N=C*H*), 12.91 (s, 2H, ArO*H*).

(b) Schiff base reduction

A 250 ml round bottom flask with stirrer bar was charged with the Schiff base (2.83 g, 4.39 mmol). This was placed under an atmosphere of argon and dry diethyl ether (75 ml) was added. The solution was stirred vigorously while lithium aluminium hydride (0.50 g, 13.18 mmol) was added slowly. This was accompanied by evolution of a gas. After complete addition the solution was stirred for a further 20 h under a bubbler. During this time the solution became green then colourless. The mixture was cooled to 0 ºC and cautiously hydrolysed with ice, followed by neutralisation with ammonium chloride. Water (50 ml) was added and the ether layer was collected, dried over anhydrous $MgSO_4$ and filtered. Volatiles were removed *in vacuo* to yield an off-white solid. ^{1}H NMR spectroscopy showed this to be the reduced Schiff base.[4] Yield = 2.79 g, 98 %. ^{1}H-NMR ($CDCl_3$, 297 K, 300 MHz): δ 1.30 (s, 18H, C*Me*$_3$), 1.40 (s, 18H, C*Me*$_3$), 1.94 (s, 6H, Ar-*Me*$_{\mathrm{i}}$), 3.58 (m, 2H, ArN*H*), 4.37 (m, 4H, NC*H*$_2$), 6.94 – 6.87 (m, 6H, Ar-*H*), 7.01 (d, 2H, Ar-*H*, $^{4}J_{\mathrm{HH}}$ = 2 Hz), 7.26 (d, 2H, Ar-*H*, $^{4}J_{\mathrm{HH}}$ = 2 Hz), 8.47 (s, 2H, ArO*H*).

(c) *N*-methylation

The methylation of the amine was achieved analogously to H_2L^3, using the corresponding reduced Schiff base (2.79 g, 4.32 mmol), THF (100 mmol) and 2.5 M *n*-butyllithium in hexanes (6 ml, 15.0 mmol). After work-up and removal of volatiles *in vacuo* an off-white solid was obtained. Recrystallisation from ethanol yielded the white crystalline product, (±)-H_2L^4. Yield = 2.36 g, 81 %. ^{1}H-NMR ($CDCl_3$, 297 K, 300 MHz): δ 1.26 (s, 18H, [C*Me*$_3$]), 1.26 (s, 18H, [C*Me*$_3$]), 2.07 (s, 6H, Ar-*Me*), 2.51 (s, 6H, N*Me*), 3.71 (d, 2H, NC*H*$_2$, $^{2}J_{\mathrm{HH}}$ = 13 Hz), 4.04 (d, 2H, NC*H*$_2$, $^{2}J_{\mathrm{HH}}$ = 13 Hz), 6.82 (d, 2H, Ar-*H*, $^{4}J_{\mathrm{HH}}$ = 2 Hz), 7.12 (d, 2H, Ar-*H*, $^{4}J_{\mathrm{HH}}$ = 2 Hz), 7.16 (dd, 2H, Ar-*H*, $^{3}J_{\mathrm{HH}}$ = 7 Hz, $^{4}J_{\mathrm{HH}}$ = 2 Hz), 7.42 (t, 2H, Ar-*H*, $^{3}J_{\mathrm{HH}}$ = 8 Hz), 7.46 (dd, 2H, Ar-*H*, $^{3}J_{\mathrm{HH}}$ = 8 Hz, $^{4}J_{\mathrm{HH}}$ = 2 Hz), 8.87 (s, 2H, ArO*H*), ^{13}C{^{1}H}-NMR ($CDCl_3$, 297 K, 75 MHz) δ 20.2 (*Me*), 29.3 (C*Me*$_3$), 31.6 (C*Me*$_3$), 34.0 (*C*Me$_3$), 34.6 (*C*Me$_3$), 41.2 (N*Me*), 63.1 (N*C*H$_2$), 120.1, 120.5, 122.6, 123.5, 128.2, 128.7, 134.6, 135.3, 137.6, 139.7, 150.9, 153.7 (Ar). IR (CH_2Cl_2 Thin film) ν cm^{-1} 3061 (b, OH), 2955, 2866, 1597, 1574, 1481, 1462, 1454, 1434, 1426, 1390, 1361, 1301, 1258, 1235 (s, C-O), 1202, 1160, 1123, 1103, 1014, 961, 942, 878, 855, 824, 803, 791, 763, 745, 704, 676, 648. MS (EI) *m/z* 676 $[M]^+$.

Synthesis of (*S*)-H_2L^4

The chiral nonracemic ligand was prepared in exactly the same manner as (±)-H_2L^4. The corresponding Schiff base was synthesised using 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.20 g, 9.43 mmol) and (*S*)-2,2´-diamino-6,6´-dimethylbiphenyl (1.00 g, 4.72 mmol). Purification of (*S*)-H_2L^4 was achieved by column chromatography using hexane:diethyl ether, 25:1 as eluent. Overall yield = 1.20 g, 38 %.

Synthesis of (±)-$[YL^3N\{SiMe_2H\}_2THF_2]$.

An ampoule with stirrer bar was charged with (±)-H_2L^3 (300 mg, 0.46 mmol) and $[Y(N\{SiMe_2H\}_2)_3THF_2]$ (291 mg, 0.46 mmol). Toluene was added (20 ml) followed by THF (0.5 ml) and the solution was heated at 50 ºC for 3 d. The solution was then transferred to a Schlenk tube. Volatiles were removed under reduced pressure and the off-white solid was dissolved in pentane. Volatiles were removed under reduced pressure and the off-white solid was dried *in vacuo*. Yield = 400 mg, 92 %. Anal. Calcd for $C_{56}H_{86}N_3O_4Si_2Y$: C, 66.57; H, 8.58; N, 4.16. found C, 65.33; H, 8.47; N, 4.29. ^{1}H-NMR (d_6-benzene + 1 drop d_8-THF, 297 K, 300 MHz): δ 0.40 (bm, 12H, Si*Me*$_2$H), 1.28 (bm, 4H, THF), 1.29 (s, 18H, C*Me*$_3$), 1.57 (s, 6H, Ar-*Me*), 1.65 (s, 18H, C*Me*$_3$), 3.14 (bs, 6H, N*Me*), 4.02 (bm, 4H, THF), 5.30 (bm, 2H, SiMe$_2$*H*), 6.60 (d, 2H, Ar-*H*, $^{3}J_{\mathrm{HH}}$ = 7 Hz), 6.60 (d, 2H, Ar-*H*, $^{4}J_{\mathrm{HH}}$ = 2Hz), 7.01 (t, 2H, Ar-*H*, $^{3}J_{\mathrm{HH}}$ = 8 Hz), 7.17 (d, 2H, Ar-*H*, $^{4}J_{\mathrm{HH}}$ = 2 Hz),7.23 (d, 2H, Ar-*H*, $^{3}J_{\mathrm{HH}}$ = 8 Hz). ^{13}C{^{1}H}-NMR (d_6-benzene + 1 drop d_8-THF, 297K, 75 MHz): δ 4.2 (Si*Me*$_2$H), 4.0 (Si*Me*$_2$H). 21.8 (Ar-*Me*), 25.3 (THF), 30.5 (C*Me*$_3$), 31.8 (C*Me*$_3$), 34.2 (*C*Me$_3$), 35.5 (*C*Me$_3$), 71.0 (THF), 117.3, 118.0, 122.4, 126.2, 128.5, 135.7, 137.2, 140.1, 142.3, 158.7 (Ar). IR (Nujol) ν cm^{-1} 2078 (bm, Si-H), 1580, 1414, 1361, 1299, 1260 (m, C-O), 1202, 1165, 1100, 1025, 945, 889, 834, 805, 791, 747, 735, 695, 666. MS (EI) *m/z* 939 [M]$^+$, 880 [M-SiMe$_2$H]$^+$, 867 [M-THF]$^+$, 749 [M-(THF and {SiMe$_2$H}$_2$]$^+$, 735 [M-(THF and N{SiMe$_2$H}$_2$]$^+$.

Synthesis of (*S*)-[YL^{3}N(SiMe$_2$H)$_2$THF$_2$]

Using the same procedure as for (±)-[YL^{3}N(SiMe$_2$H)$_2$THF$_2$], (*S*)-H$_2$L^3 (200 mg, 0.31 mmol) and [Y(N{SiMe$_2$H}$_2$)$_3$THF$_2$] (194 mg, 0.31 mmol) were used. An off-white solid was obtained. Yield = 252 mg, 87 %.

Synthesis of (*S*)-[SmL^{3}N{SiMe$_2$H}$_2$THF$_2$]

Using the same procedure as for (±)-[YL^{3}N(SiMe$_2$H)$_2$THF$_2$], (*S*)-H$_2$L^3 (200 mg, 0.31 mmol) and [Sm(N{SiMe$_2$H}$_2$)$_3$THF$_2$] (213 mg, 0.31 mmol) were used. An off-white solid was obtained. Yield = 265 mg, 86 %. Anal. Calcd for $C_{56}H_{86}N_3O_4Si_2Sm$: C, 62.75; H, 8.09; N, 3.82. Found: C, 60.39; H, 7.93; N, 3.95. ^{1}H-NMR (d$_8$-toluene + 1 drop d$_8$-THF, 297 K, 400 MHz): δ 0.81 (bm, 12H, SiMe_2H), 1.21 (bm, THF), 1.54 (s, 18H, CMe_3), 1.75 (s, 6H, Ar-*Me*), 1.95 (bs, 6H, N*Me*), 2.62 (bs, 18H, CMe_3), 3.17 (bm, THF), 8.08 – 5.81 (bm, 10H, Ar-*H*). ^{13}C{^{1}H}-NMR (d$_8$-toluene + 1 drop d$_8$-THF, 297 K,100 MHz): δ 7.2 (SiMe_2H), 24.0 (Ar-*Me*), 27.5 (THF), 33.7 (CMe_3), 34.2 (CMe_3), 36.9 (*C*Me$_3$), 40.0 (*C*Me$_3$), 43.9 (N*Me*), 69.4 (THF), 119.8, 120.4, 125.8, 127.7, 138.3, 138.8, 139.4, 143.0, 151.5 (Ar). IR (Nujol) ν cm^{-1} 2049 (bm, Si-H), 1579, 1413, 1350, 1299, 1279, 1259 (s, C-O), 1202, 1165, 1030, 1000, 947, 694, 833, 805, 790, 758, 747, 694, 678, 662, 648. MS (CI) *m/z* 930 [M-THF]$^+$.

Synthesis of (*S*)-[La(L^3)N{SiMe$_2$H}$_2$THF$_2$]

Using the same procedure as for (±)-[YL^{3}N(SiMe$_2$H)$_2$THF$_2$], (*S*)-H$_2$L^3 (209 mg, 0.32 mmol) and [La(N{SiMe$_2$H}$_2$)$_3$THF$_2$] (219 mg, 0.32 mmol) were used. An off-white solid was obtained. Yield = 263 mg, 82 %. Anal. Calcd. for $C_{56}H_{86}N_3O_4Si_2La$: C, 63.43; H, 8.17; N, 3.96. Found C, 61.23; N, 8.34; H, 4.15. ^{1}H-NMR (d$_8$-toluene + 1 drop d$_8$-THF, 297 K, 400 MHz): δ 0.30 (d, 6H, SiMe_2H, $^3J_{\mathrm{HH}}$ = 3 Hz), 0.32 (d, 6H, SiMe_2H, $^3J_{\mathrm{HH}}$ = 3 Hz), 1.23 (s, 18H, CMe_3),1.46 (m, THF), 1.47 (bs, 6H, Ar-*Me*), 1.52 (s, 18H, CMe_{3e}), 3.01 (s, 6H, N*Me*), 3.57 (m, THF), 5.07 (m, 2H, SiMe$_2$*H*, $^3J_{\mathrm{HH}}$ = 3Hz), 6.54 (d, 2H, Ar-*H*, $^4J_{\mathrm{HH}}$ = 2 Hz), 6.56 (d, 2H, Ar-*H*, $^3J_{\mathrm{HH}}$ = 8 Hz), 6.97 (t, 2H, Ar-*H*, $^3J_{\mathrm{HH}}$ = 8 Hz), 7.04 (d, 2H, Ar-*H*, $^3J_{\mathrm{HH}}$ = 8 Hz), 7.07 (d, 2H, Ar-*H*, $^4J_{\mathrm{HH}}$ = 3 Hz). ^{13}C{^{1}H}-NMR (d$_8$-toluene + 1 drop d$_8$-THF, 297 K,100 MHz): δ 1.9 (SiMe_2H). 2.0 (SiMe_2H), 19.7 (*Me*), 24.2 (THF), 28.7 (CMe_3),30.3 (CMe_3), 32.6 (*C*Me$_3$), 33.8 (*C*Me$_3$), 43.2 (N*Me*), 66.3 (THF), 115.5, 117.4, 119.2, 120.5, 124.6, 134.2, 135.2, 135.3, 135.9, 140.1, 158.6 (Ar). IR (Nujol) ν cm^{-1} 2047 (bm, Si-H), 1577, 1415, 1360, 1301, 1280, 1259 (s, C-O), 1202, 1168, 1032, 949, 894, 833, 805, 790, 758, 746, 679. MS (EI) *m/z* 989 [M]$^+$, 930 [M-SiMe$_2$H]$^+$, 917 [M-THF]$^+$, 785 [M-(THF and N{SiMe$_2$H}$_2$]$^+$.

Synthesis of (±)-[YL^{4}N(SiMe$_2$H)$_2$THF$_2$].

A Schlenk flask equipped with a stirrer bar was charged with (±)-H$_2$L^4 (330 mg, 0.49 mg), [Y(N{SiMe$_2$H}$_2$)$_3$THF$_2$] (310 mg, 0.49 mmol) and pentane (20 ml) added at 0 ºC. The solution was stirred and allowed to warm to room temperature. All solids dissolved within 5 min and after *ca.* 30 min a white precipitate formed. The solution was stirred for 4 h at room temperature, then kept at –30 ºC overnight. The white precipitate was isolated by filtration, washed with pentane and dried *in vacuo*. Yield = 349 mg, 74 %. Anal. Calcd for $C_{58}H_{90}N_3O_4Si_2Y$: C, 67.08; H, 8.74; N, 4.05. Found: C, 65.78; H, 8.61; N, 3.90. ^{1}H-NMR (d$_8$-toluene + 1 drop d$_8$-THF, 297 K, 400 MHz): 0.39 (d, 6H, SiMe_2H, $^3J_{\mathrm{HH}}$ = 3 Hz). 0.42 (d, 6H, SiMe_2H, $^3J_{\mathrm{HH}}$ = 3 Hz), 1.35 (s, 18H, CMe_3), 1.46 (bm, THF), 1.78 (s, 18H, CMe_3), 2.22 (s, 6H, Ar-*Me*), 2.25 (s, 6H, N*Me*), 3.55 (bm, THF), 4.45 (bm, 4H, NCH_2),4.83 (m, 2H, SiMe$_2$*H*, $^3J_{\mathrm{HH}}$ = 3 Hz), 6.86 (d, 2H, Ar-*H*, $^3J_{\mathrm{HH}}$ = 8 Hz),7.12 (t, 2H, Ar-*H*, $^3J_{\mathrm{HH}}$ = 8 Hz), 7.27 (d, 2H, Ar-*H*, $^3J_{\mathrm{HH}}$

= 8 Hz), 7.48 (d, 2H, Ar-*H*, $^4J_{\mathrm{HH}}$ = 2 Hz), δ 7.51 (d, 2H, Ar-*H*, $^4J_{\mathrm{HH}}$ = 2 Hz). ^{13}C{^{1}H}-NMR (d$_8$-toluene + 1 drop d$_8$-THF, 297 K, 100 MHz): δ 2.6 (Si*Me*$_2$H), 19.0 (Ar-*Me*), 24.3 (THF), 29.7 (C*Me*$_3$), 30.5 (C*Me*$_3$), 32.8 (*C*Me$_3$), 34.1 (*C*Me$_3$), 35.9 (N*Me*), 58.3 (N*C*H$_2$), 66.2 (THF), 117.1, 120.2, 120.4, 121.7, 125.7, 126.4 , 131.4, 135.9, 136.6, 137.5, 151.9, 157.5 (Ar). IR (Nujol) ν cm^{-1} 2086 (bm, Si-H), 1574, 1411, 1361, 1338, 1302, 1260, 1240 (m, C-O), 1203, 1162, 1125, 1089, 1022, 898, 840, 794, 740, 695, 662. MS (EI) *m/z* 967 [M]$^+$, 908 [M-SiMe$_2$H]$^+$, 895 [M-THF]$^+$.

Synthesis of (*S*)-[YL^{4}N(SiMe$_2$H)$_2$THF$_2$]

Using the same procedure as for (±)-[YL^{4}N(SiMe$_2$H)$_2$THF$_2$], (*S*)-H$_2$L^4 (309 mg, 46 mmol) and [Y(N{SiMe$_2$H}$_2$)$_3$THF$_2$] (288 mg, 0.46 mmol) were used. An off-white solid was obtained. Yield = 419 mg, 95 %.

Synthesis of (±)-[SmL^{4}N(SiMe$_2$H)$_2$THF$_2$].

Using the same procedure as for (±)-[YL^{4}N(SiMe$_2$H)$_2$THF$_2$], (*S*)-H$_2$L^4 (176 mg, 0.26 mmol) and [Sm(N{SiMe$_2$H}$_2$)$_3$THF$_2$] (180 mg, 0.26 mmol) were used. An off-white solid was obtained. Yield = 268 mg, 92 %. Anal. Calcd for $C_{58}H_{90}N_3O_4Si_2Sm$: C, 63.34; H, 8.25; N, 3.82. Found: C, 62.47; H, 8.01; N, 4.04. ^{1}H-NMR (C$_6$D$_6$ + 1 drop d$_8$-THF, 297 K, 400 MHz): δ 0.33 (s, 6H, Si*Me*$_2$H), 0.51 (s, 6H, Si*Me*$_2$H), 1.68 (bm, THF), 1.82 (s, 18H, C*Me*$_3$), 2.24 (s, 6H, N*Me*),2.26 (s, 6H, Ar-*Me*), 3.51 (bm, 2H, SiMe$_2$*H*), 3.88 – 3.65 (bm, 4H, NC*H*$_2$), 4.47 (bm, THF), 4.47 (s, 18H, C*Me*$_3$), 6.85 (d, 2H, Ar-*H*, $^3J_{\mathrm{HH}}$ = 7 Hz), 7.08 (t, Ar-*H*, $^3J_{\mathrm{HH}}$ = 8 Hz), 7.55 (d, 2H, Ar-*H*, $^3J_{\mathrm{HH}}$ = 8 Hz), 8.26 (d, 2H, Ar-*H*, $^4J_{\mathrm{HH}}$ = 1 Hz), 8.78 (d, 2H, Ar-*H*, $^4J_{\mathrm{HH}}$ = 1 Hz). ^{13}C{^{1}H}-NMR (d$_6$-benzene + 1 drop d$_8$-THF, 297 K,100 MHz): δ 2.5 (Si*Me*$_2$H). 2.6 (Si*Me*$_2$H), 20.7 (Ar-*Me*$_\mathrm{i}$), 32.5 (C*Me*$_3$), 34.2 (C*Me*$_3$), 35.2 (*C*Me$_3$), 37.5 (N*Me*), 39.6 (*C*Me$_3$), 62.3 (N*C*H$_2$), 66.8 (THF), 118.6, 123.2, 123.3, 123.6, 127.9, 128.8, 132.8, 138.9, 139.1, 139.4, 153.5, 164.7(Ar). IR (Nujol) ν cm^{-1} 2053 (bm, Si-H), 1603, 1574, 1414, 1361, 1300, 1277, 1240 (s, C-O), 1203, 1166, 1132, 1024, 947, 895, 835, 812, 791, 758, 745, 697. MS (EI) *m/z* 1029 [M-H]$^+$, 971 [M-SiMe$_2$H]$^+$, 958 [M-THF]$^+$, 826 [M-(THF and N{SiMe$_2$H}$_2$]$^+$.

X-ray quality crystals of (±)-[SmL^{4}N(SiMe$_2$H)$_2$.(C$_7$H$_{16}$)], were obtained by careful addition of heptane to the off-white solid until most but not all of the solid had dissolved. The solution was then filtered from the solid via cannula and placed in a refrigerator at 0°C for 3 d yielding large colourless needles.

Synthesis of (*S*)-[SmL^{4}N(SiMe$_2$H)$_2$THF$_2$]

Using the same procedure as for (±)-[YL^{4}N(SiMe$_2$H)$_2$THF$_2$], (*S*)-H$_2$L^4 (360 mg, 0.54 mmol) and [Sm(N{SiMe$_2$H}$_2$)$_3$THF$_2$] (370 mg, 0.54 mmol) were used. An off-white solid was obtained. Yield = 0.53 mg, 95 %.

Synthesis of (*S*)-[LaL^{4}N{SiMe$_2$H}$_2$THF$_2$]

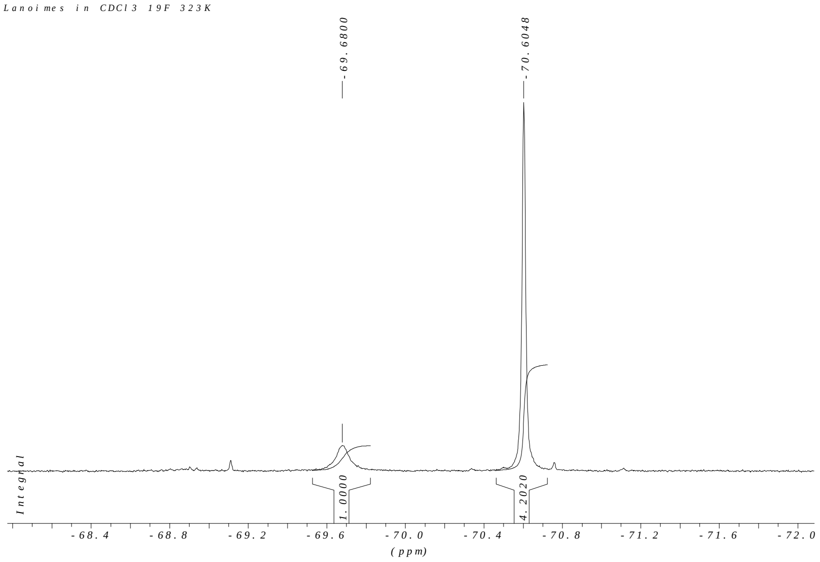
Using the same procedure as for (±)-[YL^{4}N(SiMe$_2$H)$_2$THF$_2$], (*S*)-H$_2$L^4 (180 mg, 0.27 mmol) and [La(N{SiMe$_2$H}$_2$)$_3$THF$_2$] (180 mg, 0.26 mmol) were used. An off-white solid was obtained. Yield = 241 mg, 90 %. Anal. Calcd for $C_{58}H_{90}LaN_3O_4Si_2$: C, 64.00; H, 8.33; N, 3.86. Found: C, 62.30; H, 8.00; N, 3.96. ^{1}H NMR (d$_6$-benzene + 1 drop d$_8$-THF, 297 K, 400 MHz): δ 0.46 (d, 6H, Si*Me*$_2$H, $^3J_{\mathrm{HH}}$ = 3 Hz). 0.49 (d, 6H, Si*Me*$_2$H, $^3J_{\mathrm{HH}}$ = 3 Hz),1.41 (s, 18H, C*Me*$_3$), 1.42 (bm, THF), 1.86 (s, 18H, C*Me*$_3$), 2.28 (bs, 6H, Ar-*Me*), 2.40 (s, 6H, N*Me*), 3.62 (bm, THF), 4.55 (bm, 4H, NC*H*$_2$), 4.95 (m, 1H, SiMe$_2$*H*¸$^3J_{\mathrm{HH}}$ = 3 Hz), 6.94 (d, 2H, Ar*H*$_\mathrm{j}$, $^3J_{\mathrm{HH}}$ = 8 Hz), 7.21 (t, 2H, Ar-*H*, $^3J_{\mathrm{HH}}$ = 8 Hz), 7.39 (d, 2H, Ar-*H*, $^3J_{\mathrm{HH}}$ = 8 Hz), 7.58 (d, 2H, Ar-*H*, $^4J_{\mathrm{HH}}$ = 3 Hz), 7.62 (bs, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (d$_6$-benzene + 1 drop d$_8$-THF, 297 K, 100 MHz): δ 3.6 (Si*Me*$_2$H), 20.7 (Ar-*Me*), 25.7 (THF), 30.9 (C*Me*$_3$), 32.2 (C*Me*$_3$), 34.4 (*C*Me$_3$), 35.3 (*C*Me$_3$), 37.6 (N*Me*), 58.7 (N*C*H$_2$), 67.7 (THF), 121.2, 118.6, 121.8, 123.2, 127.3, 127.8, 132.3, 136.1, 138.1, 139.2, 153.4, 160.9 (Ar). IR (Nujol) ν cm^{-1} 2047 (bm, Si-H), 1603, 1575, 1413, 1361, 1299, 1270, 1240 (s, C-O), 1203, 1166, 1132, 1061, 1026, 947, 896, 834, 810, 793, 759, 744, 688. MS (CI) *m/z* 1016 [M-H]$^+$, 945 [M-THF]$^+$.

Hydroamination/cyclisation procedure

Inside a glove box a 5 mm NMR tube equipped with a teflon stopcock was charged with between 5-10 mg of the respective catalyst. The substrate was dissolved in C_6D_6 and transferred into the NMR tube. The NMR tube was maintained at the desired temperature in a heating block until no further turnover was observed (as for [ML^{1}N{SiMe$_2$H}$_2$THF$_2$]), or until full conversion had been obtained (as for [ML^{3}N{SiMe$_2$H}$_2$THF] and [ML^{4}N{SiMe$_2$H}$_2$THF] as judged by ^{1}H-NMR spectroscopy.

Enatiomeric excess determination

The volatile components were vacuum transferred from NMR tube into a reciever flask and the enantiomeric excesses was determined by diastereomeric derivatization with (*R*)-(-)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (Mosher chloride).[5] This was achieved by a modification of the procedure of Hoye[6] in which dichloromethane (1-2 ml) was added to the distillate in the reciever flask followed by addition of 1 equiv of mosher chloride and triethylamine. The solution was stirred for 48 hours and solvent removed in in vacuo. The enantiomeric excess was then determined from the relative integration of the two resonances in the ^{19}F-NMR ($CDCl_3$) spectra recorded at 50 °C. An example spectrum for the highest recorded ee value obtained from cyclisation reaction with the pre-catalyst [LaL^{4}N{SiMe$_2$H}$_2$THF] is shown below :



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CRYSTAL STRUCTURE DATA

Crystal data and structure refinement for (±)-[YL^{2}N(SiMe2H)$_2$ (THF)].

Identification code	**(±)-**[YL^{2}N(SiMe2H)$_2$ (THF)]	
Empirical formula	C46 H64 N3 O3 Si2 Y	
Formula weight	852.09	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/a	
Unit cell dimensions	a = 15.92(2) Å	α= 90°.
	b = 17.51(3) Å	β= 95.16(13)°.
	c = 16.80(2) Å	γ = 90°.
Volume	4666(12) Å^3	
Z	4	
Density (calculated)	1.213 Mg/m^3	
Absorption coefficient	1.341 mm^{-1}	
F(000)	1808	
Crystal size	0.21 x 0.14 x 0.08 mm^3	
Theta range for data collection	1.68 to 22.50°.	
Index ranges	-17<=h<=17, -18<=k<=17, -18<=l<=18	
Reflections collected	20959	
Independent reflections	6070 [R(int) = 0.3069]	
Completeness to theta = 22.50°	99.6 %	
Absorption correction	Semi-empirical	
Max. and min. transmission	0.9003 and 0.7660	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6070 / 241 / 510	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.1607, wR2 = 0.3003	
R indices (all data)	R1 = 0.3134, wR2 = 0.3725	
Largest diff. peak and hole	1.247 and -0.668 e.Å^{-3}	

Data Collection and Processing.

Siemens SMART (Siemens, 1994) three-circle system with CCD area detector.
The crystal was held at 180(2) K with the Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986). Maximum theta was 22.50 deg. The hkl ranges were -17/ 17, -18/ 17, -18/ 18. 20959 reflections measured, 6070 unique [R(int) = 0.3069]. Absorption correction by semi-empirical method (SADABS) from equivalents; minimum and maximum transmission factors: 0.7660; 0.9003.

No crystal decay

Structure Analysis and Refinement.

Monoclinic crystal system determined but poor data quality made space group assignment difficult. Systematic absences indicated the presence of a 2(1) screw axes but we were unable to determine the presence of any glide plane. Successful solution was only possible in space group P2(1) with two molecules in the assymetric unit. Subsequent inspection of the heavy atom positions revealed the presence of an additional glide plane giving the space group P2(1)/a. The structure was subsequently refined in this non-standard setting after appropriate moving of atom position (in XP program) and alteration of symmetry settings in the shelxl instructions file. Heavy atoms were located by the Patterson interpretation section of SHELXS (Sheldrick, 1993) and the light atoms then found by E-map expansion and successive Fourier syntheses. The weak nature of the data as evidenced by the high R(int) and R(sym) values necessitated the omission of high angle data beyond 2(theta)=45 degrees, and kept the R1 value high, although the structure was stable and the solution clearly correct.

Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms, displacement and isotropic parameter restraints were applied to selected atoms due to poor data quality; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached.

The weighting scheme was calc w=1/[\s^2^(Fo^2^)+(0.0431P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3.

Refinement used SHELXTL (Sheldrick, 1997).

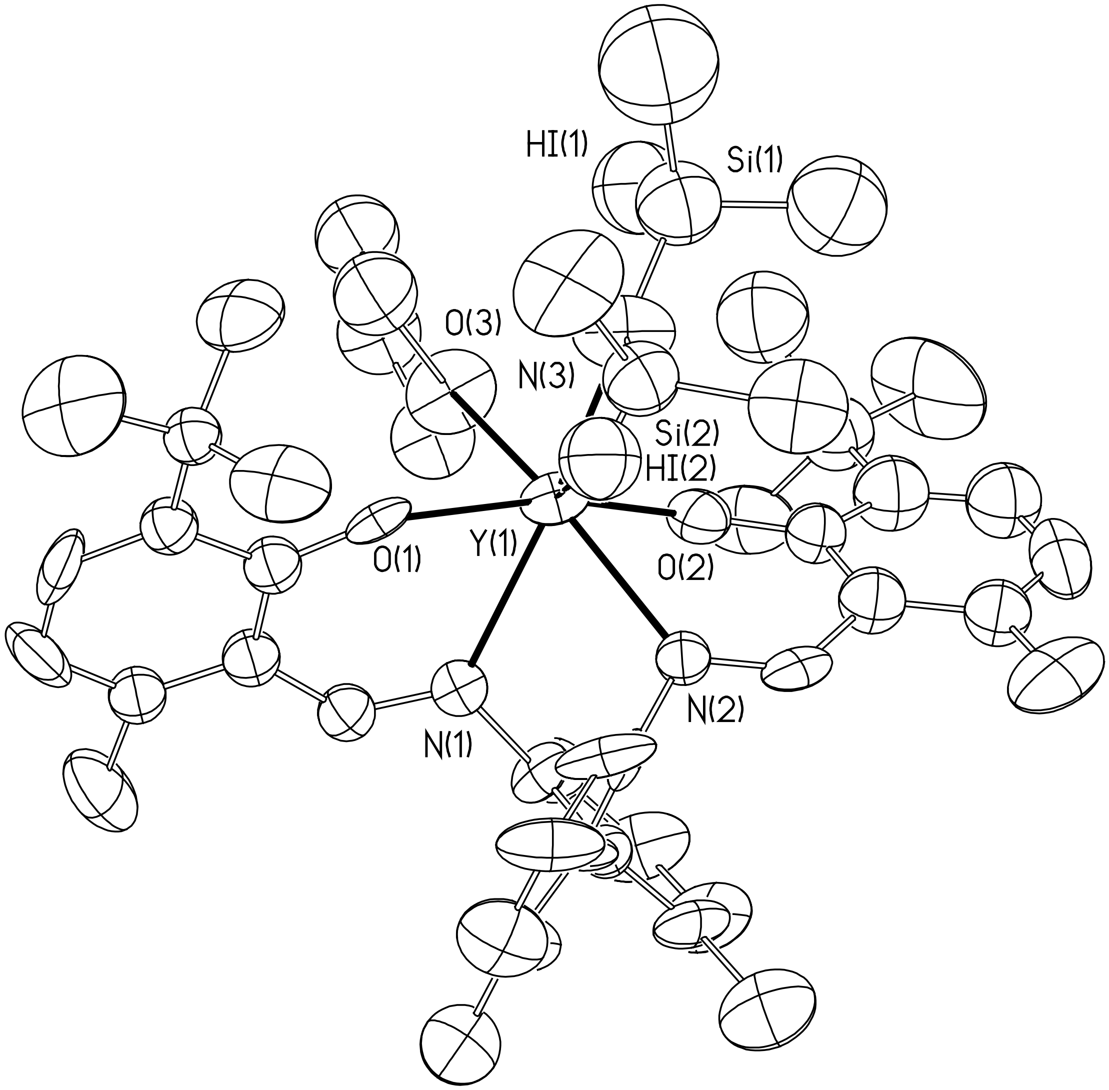

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **(±)**-[$YL^2N(SiMe2H)_2$ (THF)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y(1)	-7646(1)	9802(1)	7459(1)	40(1)
Si(1)	-7258(5)	7978(5)	6600(5)	92(3)
C(39)	-7860(20)	7166(19)	6040(20)	187(14)
C(40)	-6308(16)	7999(16)	6126(17)	130(10)
Si(2)	-8296(4)	9208(4)	5741(4)	73(2)
O(1)	-8951(7)	9974(6)	7690(7)	40(3)
O(2)	-6265(8)	9844(7)	7669(7)	51(3)
O(3)	-7576(8)	9020(8)	8610(7)	66(4)
C(43)	-7127(15)	9230(13)	9360(14)	91(4)
C(44)	-7145(15)	8519(13)	9881(14)	91(4)
C(45)	-7690(14)	7970(13)	9419(14)	91(4)
C(46)	-8108(16)	8406(14)	8724(15)	91(4)
N(1)	-7715(9)	10932(8)	8403(8)	40(4)
N(2)	-7203(10)	10866(8)	6698(9)	38(4)
N(3)	-7765(11)	8824(10)	6565(10)	81(6)
C(1)	-9438(11)	10232(11)	8199(11)	43(2)
C(2)	-10311(12)	10018(10)	8190(11)	43(2)
C(7)	-10782(12)	10250(13)	8747(15)	74(8)
C(8)	-10450(16)	10741(12)	9402(14)	72(7)
C(9)	-9632(13)	10968(10)	9391(11)	43(2)
C(11)	-9117(11)	10757(10)	8834(11)	43(2)
C(10)	-9372(14)	11502(12)	10111(12)	82(8)
C(3)	-10679(11)	9521(11)	7477(11)	43(2)
C(4)	-10592(12)	9888(13)	6678(14)	89(8)
C(5)	-11617(13)	9358(14)	7548(17)	122(11)
C(6)	-10234(13)	8733(12)	7506(14)	83(8)
C(12)	-8325(11)	11075(10)	8828(11)	43(2)
C(13)	-7005(10)	11439(10)	8451(11)	40(5)
C(14)	-6357(12)	11344(11)	9109(12)	55(6)
C(15)	-5660(14)	11807(13)	9081(14)	74(8)
C(16)	-5556(12)	12300(13)	8531(17)	79(8)
C(17)	-6187(14)	12420(11)	7911(13)	56(6)
C(19)	-6926(11)	11987(11)	7881(11)	37(5)
C(18)	-6079(13)	13015(13)	7270(14)	90(8)
C(20)	-7653(12)	12070(11)	7240(11)	44(5)
C(21)	-8209(15)	12664(13)	7266(10)	64(7)
C(23)	-8841(14)	12718(14)	6611(14)	79(7)
C(24)	-8921(15)	12181(13)	5994(13)	74(7)
C(25)	-8398(15)	11594(12)	6046(14)	74(8)
C(26)	-7727(10)	11537(10)	6655(11)	35(5)
C(22)	-8165(13)	13265(12)	7899(13)	83(7)
C(27)	-6480(12)	10930(10)	6412(9)	41(5)
C(28)	-5722(13)	10452(11)	6550(12)	58(4)
C(29)	-5053(14)	10547(12)	6071(13)	58(4)
C(31)	-4307(14)	10152(14)	6330(16)	92(9)
C(32)	-4217(15)	9718(13)	7022(14)	74(4)
C(33)	-4813(14)	9658(13)	7456(14)	74(4)
C(38)	-5638(12)	9964(10)	7229(12)	47(5)
C(30)	-5165(14)	11010(12)	5337(12)	88(8)
C(34)	-4652(14)	9203(13)	8214(14)	74(4)
C(35)	-4796(12)	9697(11)	8980(13)	78(7)
C(36)	-3711(14)	8867(15)	8410(20)	150(13)
C(37)	-5198(15)	8481(14)	8285(15)	109(9)
C(41)	-9256(15)	8676(15)	5295(14)	119(11)
C(42)	-7628(14)	9428(14)	4933(12)	96(8)

Table 3. Bond lengths [Å] and angles [°] for **(±)-** [YL^{2}N(SiMe2H)$_2$ (THF)].

Y(1)-O(1)	2.169(12)
Y(1)-O(2)	2.197(13)
Y(1)-N(3)	2.275(17)
Y(1)-O(3)	2.363(13)
Y(1)-N(2)	2.402(15)
Y(1)-N(1)	2.545(14)
Y(1)-Si(2)	3.154(8)
Si(1)-N(3)	1.685(19)
Si(1)-C(40)	1.77(2)
Si(1)-C(39)	1.92(3)
Si(2)-N(3)	1.695(17)
Si(2)-C(42)	1.84(2)
Si(2)-C(41)	1.89(2)
O(1)-C(1)	1.287(19)
O(2)-C(38)	1.31(2)
O(3)-C(46)	1.39(2)
O(3)-C(43)	1.44(2)
C(43)-C(44)	1.52(3)
C(44)-C(45)	1.47(3)
C(45)-C(46)	1.50(3)
N(1)-C(12)	1.282(19)
N(1)-C(13)	1.43(2)
N(2)-C(27)	1.292(19)
N(2)-C(26)	1.44(2)
C(1)-C(2)	1.44(2)
C(1)-C(11)	1.47(2)
C(2)-C(7)	1.31(2)
C(2)-C(3)	1.55(2)
C(7)-C(8)	1.46(3)
C(8)-C(9)	1.36(3)
C(9)-C(11)	1.35(2)
C(9)-C(10)	1.56(3)
C(11)-C(12)	1.38(2)
C(3)-C(4)	1.51(3)
C(3)-C(5)	1.54(3)
C(3)-C(6)	1.55(3)
C(13)-C(19)	1.37(2)
C(13)-C(14)	1.45(2)
C(14)-C(15)	1.38(3)
C(15)-C(16)	1.29(3)
C(16)-C(17)	1.40(3)
C(17)-C(19)	1.40(2)
C(17)-C(18)	1.52(3)
C(19)-C(20)	1.52(2)
C(20)-C(26)	1.35(2)
C(20)-C(21)	1.37(3)
C(21)-C(23)	1.42(3)
C(21)-C(22)	1.49(3)
C(23)-C(24)	1.40(3)
C(24)-C(25)	1.32(3)
C(25)-C(26)	1.42(3)
C(27)-C(28)	1.47(3)
C(28)-C(29)	1.40(3)
C(28)-C(38)	1.42(2)
C(29)-C(31)	1.41(3)
C(29)-C(30)	1.47(3)
C(31)-C(32)	1.39(3)
C(32)-C(33)	1.25(2)
C(33)-C(38)	1.44(3)
C(33)-C(34)	1.50(3)
C(34)-C(37)	1.55(3)
C(34)-C(35)	1.58(3)
C(34)-C(36)	1.61(3)

O(1)-Y(1)-O(2)	158.1(4)
O(1)-Y(1)-N(3)	101.5(6)
O(2)-Y(1)-N(3)	98.9(6)
O(1)-Y(1)-O(3)	84.8(4)
O(2)-Y(1)-O(3)	85.1(5)
N(3)-Y(1)-O(3)	95.7(6)
O(1)-Y(1)-N(2)	108.6(5)
O(2)-Y(1)-N(2)	73.9(5)
N(3)-Y(1)-N(2)	104.1(6)
O(3)-Y(1)-N(2)	153.0(5)
O(1)-Y(1)-N(1)	71.6(4)
O(2)-Y(1)-N(1)	88.4(5)
N(3)-Y(1)-N(1)	172.5(6)
O(3)-Y(1)-N(1)	86.7(5)
N(2)-Y(1)-N(1)	76.1(5)
O(1)-Y(1)-Si(2)	88.2(3)
O(2)-Y(1)-Si(2)	113.6(4)
N(3)-Y(1)-Si(2)	31.4(4)
O(3)-Y(1)-Si(2)	123.1(4)
N(2)-Y(1)-Si(2)	81.7(4)
N(1)-Y(1)-Si(2)	142.9(3)
N(3)-Si(1)-C(40)	113.1(12)
N(3)-Si(1)-C(39)	114.7(13)
C(40)-Si(1)-C(39)	101.8(14)
N(3)-Si(2)-C(42)	114.1(10)
N(3)-Si(2)-C(41)	117.1(11)
C(42)-Si(2)-C(41)	108.1(11)
N(3)-Si(2)-Y(1)	44.3(6)
C(42)-Si(2)-Y(1)	116.3(7)
C(41)-Si(2)-Y(1)	135.6(8)
C(1)-O(1)-Y(1)	144.3(11)
C(38)-O(2)-Y(1)	135.7(12)
C(46)-O(3)-C(43)	109.7(17)
C(46)-O(3)-Y(1)	125.1(12)
C(43)-O(3)-Y(1)	123.5(12)
O(3)-C(43)-C(44)	105.1(18)
C(45)-C(44)-C(43)	106(2)
C(44)-C(45)-C(46)	106(2)
O(3)-C(46)-C(45)	106(2)
C(12)-N(1)-C(13)	118.8(16)
C(12)-N(1)-Y(1)	125.2(12)
C(13)-N(1)-Y(1)	116.0(11)
C(27)-N(2)-C(26)	116.3(15)
C(27)-N(2)-Y(1)	125.4(12)
C(26)-N(2)-Y(1)	117.6(11)
Si(1)-N(3)-Si(2)	125.4(11)
Si(1)-N(3)-Y(1)	128.8(9)
Si(2)-N(3)-Y(1)	104.3(9)
O(1)-C(1)-C(2)	122.8(17)
O(1)-C(1)-C(11)	120.9(16)
C(2)-C(1)-C(11)	116.4(17)
C(7)-C(2)-C(1)	121.6(19)
C(7)-C(2)-C(3)	122(2)
C(1)-C(2)-C(3)	116.8(16)
C(2)-C(7)-C(8)	122(2)
C(9)-C(8)-C(7)	116.3(18)
C(11)-C(9)-C(8)	125(2)
C(11)-C(9)-C(10)	124.6(19)
C(8)-C(9)-C(10)	110.6(19)
C(9)-C(11)-C(12)	120.5(18)

C(9)-C(11)-C(1)	118.8(18)
C(12)-C(11)-C(1)	120.5(17)
C(4)-C(3)-C(5)	108.5(17)
C(4)-C(3)-C(6)	109.3(17)
C(5)-C(3)-C(6)	106.1(16)
C(4)-C(3)-C(2)	113.0(16)
C(5)-C(3)-C(2)	110.2(17)
C(6)-C(3)-C(2)	109.6(16)
N(1)-C(12)-C(11)	131.7(18)
C(19)-C(13)-N(1)	121.1(16)
C(19)-C(13)-C(14)	120.6(16)
N(1)-C(13)-C(14)	118.3(17)
C(15)-C(14)-C(13)	115.2(19)
C(16)-C(15)-C(14)	125(2)
C(15)-C(16)-C(17)	120(2)
C(19)-C(17)-C(16)	120(2)
C(19)-C(17)-C(18)	119.7(19)
C(16)-C(17)-C(18)	121(2)
C(13)-C(19)-C(17)	119.0(17)
C(13)-C(19)-C(20)	116.9(16)
C(17)-C(19)-C(20)	124.1(18)
C(26)-C(20)-C(21)	122.2(18)
C(26)-C(20)-C(19)	117.5(18)
C(21)-C(20)-C(19)	120.3(17)
C(20)-C(21)-C(23)	116.0(19)
C(20)-C(21)-C(22)	124.6(19)
C(23)-C(21)-C(22)	119(2)
C(24)-C(23)-C(21)	123(2)
C(25)-C(24)-C(23)	117(2)
C(24)-C(25)-C(26)	122(2)
C(20)-C(26)-C(25)	119.2(18)
C(20)-C(26)-N(2)	121.0(17)
C(25)-C(26)-N(2)	119.3(18)
N(2)-C(27)-C(28)	129.8(18)
C(29)-C(28)-C(38)	121(2)
C(29)-C(28)-C(27)	120(2)
C(38)-C(28)-C(27)	119.0(18)
C(28)-C(29)-C(31)	115(2)
C(28)-C(29)-C(30)	120(2)
C(31)-C(29)-C(30)	124(2)
C(32)-C(31)-C(29)	123(2)
C(33)-C(32)-C(31)	121(2)
C(32)-C(33)-C(38)	122(2)
C(32)-C(33)-C(34)	117(2)
C(38)-C(33)-C(34)	120(2)
O(2)-C(38)-C(28)	121.9(18)
O(2)-C(38)-C(33)	120.9(19)
C(28)-C(38)-C(33)	117.0(19)
C(33)-C(34)-C(37)	116(2)
C(33)-C(34)-C(35)	111.9(18)
C(37)-C(34)-C(35)	105.1(19)
C(33)-C(34)-C(36)	116(2)
C(37)-C(34)-C(36)	102(2)
C(35)-C(34)-C(36)	103.7(19)

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **(±)**-[YL^{2}N(SiMe2H)$_2$ (THF)]. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[$h^2 a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y(1)	45(1)	38(1)	34(1)	-3(1)	-19(1)	-11(1)
Si(1)	94(3)	92(3)	92(3)	0(1)	7(1)	-1(1)
C(39)	187(14)	187(14)	187(14)	0(1)	17(2)	0(1)
C(40)	130(10)	130(10)	130(10)	0(1)	12(1)	0(1)
Si(2)	74(2)	73(2)	72(2)	-1(1)	5(1)	-2(1)
O(1)	48(8)	26(9)	45(8)	18(6)	-4(6)	-12(5)
O(2)	63(9)	41(9)	50(8)	-9(7)	9(7)	-4(7)
O(3)	57(10)	93(12)	40(8)	7(8)	-47(7)	-5(8)
C(43)	91(4)	91(4)	91(4)	0(1)	8(1)	0(1)
C(44)	91(4)	91(4)	91(4)	0(1)	8(1)	0(1)
C(45)	91(4)	91(4)	91(4)	0(1)	8(1)	0(1)
C(46)	91(4)	91(4)	91(4)	0(1)	8(1)	0(1)
N(1)	40(4)	40(4)	40(4)	0(1)	3(1)	0(1)
N(2)	38(4)	38(4)	38(4)	0(1)	3(1)	0(1)
N(3)	111(17)	70(15)	52(12)	3(10)	-37(11)	0(11)
C(1)	43(2)	43(2)	43(2)	0(1)	4(1)	0(1)
C(2)	43(2)	43(2)	43(2)	0(1)	4(1)	0(1)
C(7)	37(13)	63(17)	130(20)	53(18)	45(15)	12(13)
C(8)	100(20)	52(18)	71(18)	-7(14)	40(15)	33(14)
C(9)	43(2)	43(2)	43(2)	0(1)	4(1)	0(1)
C(11)	43(2)	43(2)	43(2)	0(1)	4(1)	0(1)
C(10)	110(20)	90(20)	52(16)	-2(14)	26(14)	35(15)
C(3)	43(2)	43(2)	43(2)	0(1)	4(1)	0(1)
C(4)	61(16)	83(19)	120(20)	-21(16)	-42(14)	-5(13)
C(5)	34(16)	130(30)	190(30)	10(20)	-34(17)	-2(14)
C(6)	68(17)	71(19)	110(20)	-12(15)	-10(14)	-23(13)
C(12)	43(2)	43(2)	42(2)	0(1)	4(1)	0(1)
C(13)	16(11)	45(14)	58(14)	14(11)	-9(9)	-5(9)
C(14)	55(6)	55(6)	55(6)	0(1)	5(1)	0(1)
C(15)	69(18)	62(19)	81(19)	15(14)	-44(14)	-12(13)
C(16)	24(13)	68(19)	140(30)	-13(17)	-32(15)	-24(12)
C(17)	79(17)	28(14)	59(15)	15(11)	1(13)	-5(11)
C(19)	37(5)	37(5)	37(5)	0(1)	3(1)	0(1)
C(18)	79(19)	90(20)	90(20)	-7(17)	-28(15)	-27(14)
C(20)	59(14)	22(13)	47(14)	-17(10)	-11(11)	-8(10)
C(21)	130(20)	50(17)	8(11)	-3(10)	-19(12)	2(14)
C(23)	93(19)	70(20)	66(18)	15(15)	-14(15)	21(14)
C(24)	120(20)	34(16)	61(16)	9(13)	-45(14)	6(14)
C(25)	100(20)	25(15)	100(20)	16(13)	-27(16)	-18(13)
C(26)	19(12)	49(15)	37(12)	13(11)	8(9)	-10(9)
C(22)	83(7)	83(7)	83(7)	0(1)	8(1)	0(1)
C(27)	78(16)	28(13)	15(10)	-5(8)	-6(10)	-21(10)
C(28)	58(4)	58(4)	58(4)	0(1)	5(1)	0(1)
C(29)	58(4)	58(4)	58(4)	0(1)	5(1)	0(1)
C(31)	58(16)	100(20)	120(20)	-79(19)	38(15)	-40(15)
C(32)	74(4)	74(4)	74(4)	0(1)	7(1)	0(1)
C(33)	74(4)	74(4)	74(4)	0(1)	7(1)	0(1)
C(38)	47(5)	47(5)	47(5)	0(1)	4(1)	0(1)
C(30)	130(20)	80(20)	51(15)	-15(14)	-14(14)	-57(15)
C(34)	74(4)	74(4)	74(4)	0(1)	7(1)	0(1)
C(35)	56(15)	59(16)	110(20)	2(15)	-32(13)	11(12)
C(36)	49(19)	140(30)	260(40)	-30(30)	-30(20)	43(17)
C(37)	109(9)	109(9)	109(9)	0(1)	10(1)	0(1)
C(41)	100(20)	160(30)	84(19)	-32(18)	-52(16)	-65(19)
C(42)	90(20)	120(20)	71(18)	-8(15)	-36(14)	-4(15)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **(±)**-[$YL^2N(SiMe2H)_2$ (THF)].

	x	y	z	U(eq)
HI1	-7128	7826	7172	111
H(39A)	-8373	7051	6299	280
H(39B)	-7503	6710	6046	280
H(39C)	-8016	7322	5485	280
H(40A)	-6433	8126	5559	195
H(40B)	-6036	7497	6173	195
H(40C)	-5928	8385	6382	195
HI2	-8510	9712	5917	88
H(43A)	-7409	9663	9606	109
H(43B)	-6540	9378	9284	109
H(44A)	-6570	8309	9995	109
H(44B)	-7377	8641	10393	109
H(45A)	-8117	7759	9751	109
H(45B)	-7352	7544	9230	109
H(46A)	-8173	8081	8241	109
H(46B)	-8671	8588	8844	109
H(7A)	-11355	10093	8722	89
H(8)	-10785	10895	9814	87
H(10A)	-8855	11309	10402	124
H(10B)	-9825	11517	10469	124
H(10C)	-9273	12019	9915	124
H(4A)	-10903	10371	6644	134
H(4B)	-10821	9546	6251	134
H(4C)	-9994	9986	6619	134
H(5A)	-11920	9841	7589	183
H(5B)	-11677	9050	8026	183
H(5C)	-11852	9078	7074	183
H(6A)	-10525	8392	7109	125
H(6B)	-10249	8511	8040	125
H(6C)	-9646	8797	7388	125
H(12A)	-8212	11472	9208	51
H(14)	-6409	10988	9528	66
H(15A)	-5222	11758	9500	89
H(16A)	-5047	12585	8546	95
H(18A)	-6627	13245	7100	134
H(18B)	-5850	12771	6811	134
H(18C)	-5689	13412	7486	134
H(23A)	-9222	13135	6593	95
H(24A)	-9336	12236	5554	89
H(25A)	-8475	11197	5661	89
H(22A)	-8119	13022	8426	125
H(22B)	-8676	13579	7836	125
H(22C)	-7670	13588	7848	125
H(27A)	-6430	11348	6060	49
H(31A)	-3842	10186	6015	110
H(32A)	-3699	9463	7167	89
H(30A)	-5575	10762	4950	132
H(30B)	-4624	11059	5107	132
H(30C)	-5372	11519	5466	132
H(35A)	-5333	9971	8892	118
H(35B)	-4335	10065	9077	118
H(35C)	-4810	9360	9444	118
H(36A)	-3307	9290	8470	224
H(36B)	-3570	8540	7963	224
H(36C)	-3684	8567	8899	224
H(37A)	-5010	8208	8778	163
H(37B)	-5139	8148	7825	163
H(37C)	-5790	8630	8296	163
H(41A)	-9628	8563	5714	178
H(41B)	-9080	8197	5058	178
H(41C)	-9559	8991	4881	178
H(42A)	-7090	9639	5161	144
H(42B)	-7915	9802	4569	144
H(42C)	-7525	8959	4638	144

Crystal data and structure refinement for (±)-[$\mathrm{SmL^4N(SiMe_2H)_2.(C_7H_{16})}$].

Identification code	**(±)-**[$\mathrm{SmL^4N(SiMe_2H)_2.(C_7H_{16})}$]	
Empirical formula	C57 H92 N3 O2 Si2 Sm	
Formula weight	1057.87	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.1290(13) Å	a= 101.030(2)°.
	b = 14.1565(17) Å	b= 101.798(3)°.
	c = 19.349(2) Å	g = 94.828(3)°.
Volume	2904.7(6) $Å^3$	
Z	2	
Density (calculated)	1.210 Mg/m^3	
Absorption coefficient	1.092 mm^{-1}	
F(000)	1122	
Crystal size	0.32 x 0.22 x 0.08 mm^3	
Theta range for data collection	1.64 to 29.22°.	
Index ranges	-15<=h<=15, -18<=k<=18, -25<=l<=26	
Reflections collected	28296	
Independent reflections	13972 [R(int) = 0.0661]	
Completeness to theta = 29.22°	88.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9377 and 0.6965	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13972 / 81 / 636	
Goodness-of-fit on F^2	0.934	
Final R indices [I>2sigma(I)]	R1 = 0.0524, wR2 = 0.0961	
R indices (all data)	R1 = 0.0968, wR2 = 0.1082	
Largest diff. peak and hole	1.163 and -2.170	

Data Collection and Processing

Siemens SMART (Siemens, 1994) three-circle system with CCD area detector.
The crystal was held at 180(2) K with the Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986). Maximum theta was 29.22 deg. The hkl ranges were -15/ 15, -18/ 18, -25/ 26. 28296 reflections measured, 13972 unique [R(int) = 0.0661]. Absorption correction by Semi-empirical from equivalents; minimum and maximum transmission factors: 0.6965; 0.9377.

No crystal decay

Structure Analysis and Refinement.

Triclinic crystal system either space group P-1 or P1. The former was chosen on the basis of intensity statistics and shown to be correct by successful refinement. Heavy atoms were located by the Patterson interpretation section of SHELXS (Sheldrick, 1993) and the light atoms then found by E-map expansion and successive Fourier syntheses. The silicon hydride H(2A) was successfully located from a difference Fourier map.

Other hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups except for the silicon hydrogens which were freely refined. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached.

One disordered heptane solvent of crystallisation molecule was also present. The disorder was modeled across two positions and the occupancy refined.
Refinement used SHELXTL (Sheldrick, 1997).

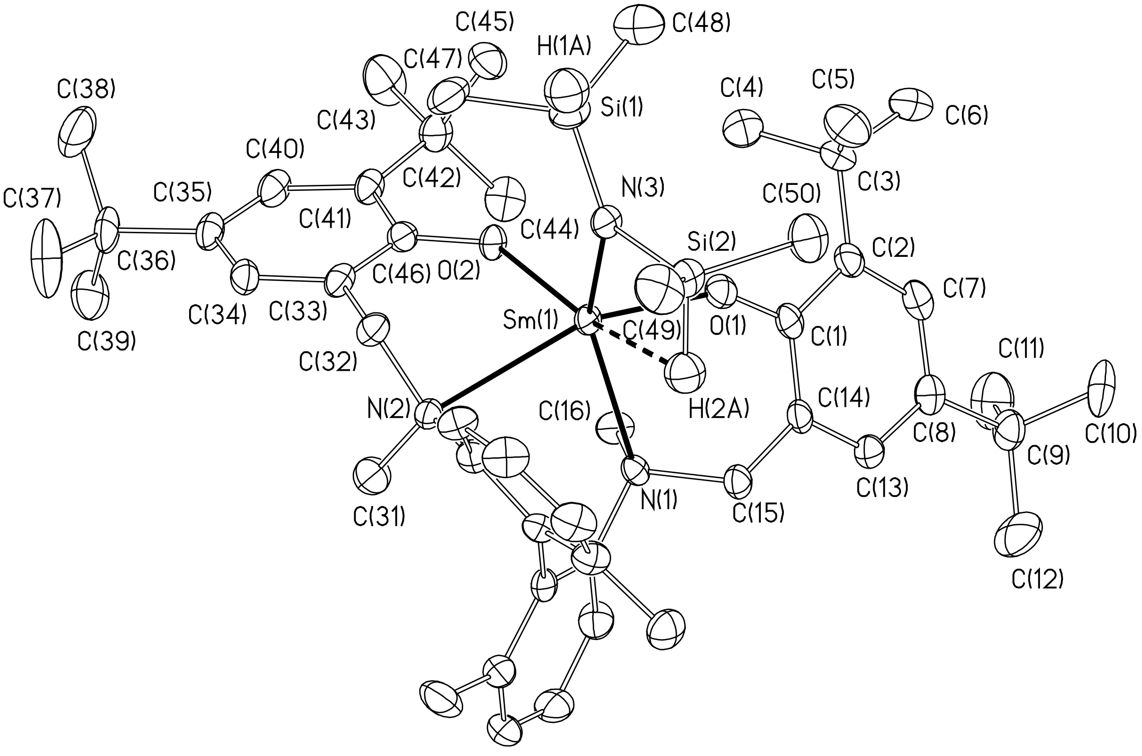
C(45)
C(48)
C(47)
H(1A)
C(38)
Si(1)
C(4)
C(5)
C(6)
C(43)
C(40)
C(42)
C(3)
N(3)
C(50)
C(37)
C(35)
C(41)
C(44)
Si(2)
C(2)
C(36)
C(46)
O(2)
C(7)
C(34)
C(33)
Sm(1)
C(49)
O(1)
C(1)
C(39)
C(11)
C(32)
C(14)
H(2A)
C(16)
N(2)
C(8)
C(10)
C(9)
N(1)
C(13)
C(31)
C(15)
C(12)

Table 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **(±)**-$[SmL^4N(SiMe_2H)_2.(C_7H_{16})]$..U(eq) is defined as one third of thetrace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Sm1	9352.7(2)	10704.1(2)	2269.0(1)	20(1)
Si1	6149.6(11)	10752.8(10)	1349.5(7)	31(1)
Si2	8370.6(12)	10978.6(10)	689.7(6)	30(1)
O1	9539(2)	9255(2)	1747.8(15)	25(1)
O2	8463(2)	10486(2)	3136.5(14)	24(1)
N1	11719(3)	10486(2)	2686.4(17)	18(1)
N2	10107(3)	12359(2)	3272.9(17)	20(1)
N3	7703(3)	10885(2)	1396.3(17)	24(1)
C1	10284(4)	8566(3)	1666(2)	22(1)
C2	9837(4)	7560(3)	1466(2)	25(1)
C3	8458(4)	7201(3)	1337(3)	32(1)
C4	8018(4)	7517(3)	2038(3)	41(1)
C5	7730(5)	7622(4)	730(3)	52(2)
C6	8193(4)	6095(3)	1115(3)	52(2)
C7	10714(4)	6911(3)	1406(2)	28(1)
C8	11985(4)	7193(3)	1537(2)	25(1)
C9	12852(4)	6411(3)	1438(2)	30(1)
C10	12434(5)	5757(4)	677(3)	46(1)
C11	12814(5)	5776(4)	1989(3)	50(1)
C12	14182(4)	6857(4)	1520(3)	53(2)
C13	12387(4)	8173(3)	1748(2)	25(1)
C14	11563(4)	8856(3)	1814(2)	22(1)
C15	12053(4)	9915(3)	2022(2)	23(1)
C16	11471(4)	9870(3)	3198(2)	26(1)
C17	12721(4)	11265(3)	3048(2)	20(1)
C18	13778(4)	11039(3)	3485(2)	28(1)
C19	14742(4)	11759(3)	3840(2)	33(1)
C20	14643(4)	12704(3)	3778(2)	32(1)
C21	13610(4)	12941(3)	3343(2)	29(1)
C22	13517(4)	13985(3)	3318(3)	42(1)
C23	12635(4)	12201(3)	2964(2)	21(1)
C24	11581(4)	12509(3)	2478(2)	22(1)
C25	11801(4)	12752(3)	1837(2)	28(1)
C26	12936(4)	12475(3)	1569(2)	34(1)
C27	10985(4)	13248(3)	1448(2)	34(1)
C28	9952(4)	13512(3)	1681(2)	34(1)
C29	9673(4)	13237(3)	2276(2)	30(1)
C30	10463(4)	12728(3)	2687(2)	24(1)
C31	10968(4)	12692(3)	3986(2)	35(1)
C32	8822(4)	12496(3)	3360(2)	26(1)
C33	8431(4)	11986(3)	3901(2)	24(1)
C34	8222(4)	12537(3)	4537(2)	26(1)
C35	7845(4)	12097(3)	5053(2)	27(1)
C36	7666(4)	12673(3)	5774(2)	33(1)
C37	7581(6)	13730(4)	5768(3)	68(2)
C38	6455(5)	12249(5)	5944(3)	65(2)
C39	8751(5)	12589(4)	6380(2)	43(1)
C40	7663(4)	11091(3)	4895(2)	27(1)
C41	7816(4)	10504(3)	4259(2)	23(1)
C42	7527(4)	9391(3)	4104(2)	28(1)
C43	7017(5)	9038(4)	4703(3)	47(1)
C44	8706(4)	8916(3)	4033(3)	37(1)
C45	6528(4)	9048(3)	3404(2)	35(1)
C46	8241(4)	10983(3)	3752(2)	22(1)
C47	5787(4)	11311(4)	2217(3)	40(1)
C48	5449(5)	9458(4)	1128(3)	55(2)
C49	7984(5)	12000(4)	238(3)	48(1)
C50	8196(5)	9866(4)	-31(2)	46(1)
C51	8673(12)	5533(9)	4251(7)	90(1)
C52	7252(13)	5277(12)	4167(8)	90(1)
C51A	6596(14)	5944(12)	4537(9)	90(1)
C52A	7416(17)	5741(14)	4073(10)	90(1)
C53	6691(7)	5520(5)	3331(4)	89(1)
C54	6871(7)	4726(5)	2752(4)	86(1)
C55	6093(7)	4635(5)	2023(4)	84(1)

C56	6238(6)	3878(5)	1430(4)	84(1)
C57	5408(6)	3815(5)	713(4)	83(1)

Table 7. Bond lengths [A] and angles [deg] for
(±)-[SmL^{4}N(SiMe$_2$H)$_2$.(C$_7$H$_{16}$)]..

Sm1-O1	2.152(3)
Sm1-O2	2.173(3)
Sm1-N3	2.294(3)
Sm1-N1	2.654(3)
Sm1-N2	2.688(3)
Sm1-C30	2.915(4)
Sm1-Si2	3.1374(12)
Si1-N3	1.705(3)
Si1-C47	1.851(5)
Si1-C48	1.863(5)
Si2-N3	1.705(3)
Si2-C50	1.860(5)
Si2-C49	1.865(5)
O1-C1	1.339(5)
O2-C46	1.342(5)
N1-C17	1.459(5)
N1-C16	1.489(5)
N1-C15	1.514(5)
N2-C30	1.446(5)
N2-C31	1.476(5)
N2-C32	1.498(5)
C1-C14	1.403(6)
C1-C2	1.421(5)
C2-C7	1.402(6)
C2-C3	1.530(6)
C3-C6	1.529(6)
C3-C5	1.533(6)
C3-C4	1.535(6)
C7-C8	1.395(6)
C8-C13	1.376(6)
C8-C9	1.539(6)
C9-C12	1.524(6)
C9-C11	1.524(6)
C9-C10	1.538(6)
C13-C14	1.394(6)
C14-C15	1.500(5)
C17-C23	1.375(5)
C17-C18	1.401(6)
C18-C19	1.382(6)
C19-C20	1.377(6)
C20-C21	1.386(6)
C21-C23	1.414(6)
C21-C22	1.500(6)
C23-C24	1.497(6)
C24-C25	1.411(5)
C24-C30	1.425(6)
C25-C27	1.383(6)
C25-C26	1.513(6)
C27-C28	1.374(6)
C28-C29	1.368(6)
C29-C30	1.402(6)
C32-C33	1.494(5)
C33-C46	1.382(6)
C33-C34	1.400(6)
C34-C35	1.388(6)
C35-C40	1.387(6)
C35-C36	1.534(6)
C36-C37	1.509(7)
C36-C39	1.532(6)
C36-C38	1.550(7)
C40-C41	1.397(5)
C41-C46	1.427(5)
C41-C42	1.540(6)
C42-C45	1.532(6)
C42-C43	1.536(6)
C42-C44	1.542(6)
C51-C52	1.561(19)
C52-C53	1.720(16)
C51A-C52A	1.42(2)
C52A-C53	1.456(18)
C53-C54	1.485(9)
C54-C55	1.471(9)
C55-C56	1.460(9)
C56-C57	1.484(9)

O1-Sm1-O2	103.71(10)
O1-Sm1-N3	95.16(11)
O2-Sm1-N3	101.75(11)
O1-Sm1-N1	73.82(10)
O2-Sm1-N1	107.23(10)
N3-Sm1-N1	150.67(11)
O1-Sm1-N2	153.54(10)
O2-Sm1-N2	76.22(10)
N3-Sm1-N2	110.88(11)
N1-Sm1-N2	80.90(10)
O1-Sm1-C30	145.67(11)
O2-Sm1-C30	104.74(11)
N3-Sm1-C30	97.46(12)
N1-Sm1-C30	79.69(11)
N2-Sm1-C30	29.56(10)
O1-Sm1-Si2	84.54(8)
O2-Sm1-Si2	133.72(8)
N3-Sm1-Si2	32.06(8)
N1-Sm1-Si2	118.68(7)
N2-Sm1-Si2	115.06(7)
C30-Sm1-Si2	89.48(9)
N3-Si1-C47	111.68(19)
N3-Si1-C48	112.9(2)
C47-Si1-C48	106.5(2)
N3-Si2-C50	116.9(2)
N3-Si2-C49	116.0(2)
C50-Si2-C49	107.5(2)
N3-Si2-Sm1	45.59(11)
C50-Si2-Sm1	115.05(17)
C49-Si2-Sm1	137.28(17)
C1-O1-Sm1	147.1(2)
C46-O2-Sm1	140.4(2)
C17-N1-C16	110.1(3)
C17-N1-C15	108.9(3)
C16-N1-C15	112.7(3)
C17-N1-Sm1	125.6(2)
C16-N1-Sm1	93.4(2)
C15-N1-Sm1	105.3(2)
C30-N2-C31	115.6(3)
C30-N2-C32	115.0(3)
C31-N2-C32	108.5(3)
C30-N2-Sm1	83.9(2)
C31-N2-Sm1	138.2(3)
C32-N2-Sm1	93.4(2)
Si2-N3-Si1	125.1(2)
Si2-N3-Sm1	102.34(16)
Si1-N3-Sm1	131.66(17)
O1-C1-C14	118.1(4)
O1-C1-C2	122.8(4)
C14-C1-C2	119.0(4)
C7-C2-C1	117.3(4)
C7-C2-C3	121.5(4)
C1-C2-C3	121.2(4)
C6-C3-C2	111.9(4)
C6-C3-C5	108.1(4)
C2-C3-C5	109.5(4)
C6-C3-C4	107.6(4)
C2-C3-C4	109.3(4)
C5-C3-C4	110.4(4)
C8-C7-C2	124.1(4)
C13-C8-C7	117.0(4)
C13-C8-C9	123.8(4)
C7-C8-C9	119.2(4)

C12-C9-C11	109.4(4)
C12-C9-C10	107.4(4)
C11-C9-C10	108.1(4)
C12-C9-C8	111.7(4)
C11-C9-C8	109.9(4)
C10-C9-C8	110.2(4)
C8-C13-C14	121.7(4)
C13-C14-C1	120.9(4)
C13-C14-C15	119.3(4)
C1-C14-C15	119.8(4)
C14-C15-N1	115.9(3)
C23-C17-C18	120.5(4)
C23-C17-N1	121.0(4)
C18-C17-N1	118.5(4)
C19-C18-C17	120.1(4)
C20-C19-C18	119.7(4)
C19-C20-C21	121.1(4)
C20-C21-C23	119.4(4)
C20-C21-C22	119.2(4)
C23-C21-C22	121.3(4)
C17-C23-C21	119.2(4)
C17-C23-C24	124.7(4)
C21-C23-C24	116.0(4)
C25-C24-C30	118.5(4)
C25-C24-C23	117.4(4)
C30-C24-C23	123.2(4)
C27-C25-C24	120.5(4)
C27-C25-C26	119.3(4)
C24-C25-C26	120.2(4)
C28-C27-C25	120.5(4)
C29-C28-C27	120.5(4)
C28-C29-C30	121.3(4)
C29-C30-C24	118.6(4)
C29-C30-N2	120.9(4)
C24-C30-N2	120.3(4)
C29-C30-Sm1	106.3(3)
C24-C30-Sm1	93.1(2)
N2-C30-Sm1	66.50(19)
C33-C32-N2	113.2(3)
C46-C33-C34	121.5(4)
C46-C33-C32	119.4(4)
C34-C33-C32	119.0(4)
C35-C34-C33	121.2(4)
C40-C35-C34	116.4(4)
C40-C35-C36	120.7(4)
C34-C35-C36	122.9(4)
C37-C36-C39	109.4(4)
C37-C36-C35	112.5(4)
C39-C36-C35	109.0(4)
C37-C36-C38	107.4(4)
C39-C36-C38	108.1(4)
C35-C36-C38	110.4(4)
C35-C40-C41	124.9(4)
C40-C41-C46	117.0(4)
C40-C41-C42	121.8(4)
C46-C41-C42	121.2(4)
C45-C42-C43	106.9(4)
C45-C42-C41	109.2(3)
C43-C42-C41	112.2(4)
C45-C42-C44	110.1(4)
C43-C42-C44	108.1(4)
C41-C42-C44	110.3(4)
O2-C46-C33	119.3(4)
O2-C46-C41	121.8(4)
C33-C46-C41	118.9(4)
C51-C52-C53	100.9(10)
C51A-C52A-C53	107.9(14)
C52A-C53-C54	124.5(10)
C52A-C53-C52	25.0(8)
C54-C53-C52	110.3(7)
C55-C54-C53	117.3(6)
C56-C55-C54	119.8(6)
C55-C56-C57	117.0(6)

Table 8. Anisotropic displacement parameters (A^2 x 10^3) for (±)-[$SmL^4N(SiMe_2H)_2.(C_7H_{16})$].. The anisotropic displacementfactor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Sm1	19(1)	26(1)	12(1)	1(1)	3(1)	3(1)
Si1	21(1)	48(1)	24(1)	11(1)	1(1)	6(1)
Si2	31(1)	44(1)	15(1)	8(1)	5(1)	4(1)
O1	24(2)	26(2)	23(2)	2(1)	1(1)	5(1)
O2	28(2)	31(2)	12(2)	1(1)	8(1)	3(1)
N1	22(2)	19(2)	13(2)	3(1)	2(2)	0(1)
N2	19(2)	25(2)	17(2)	2(2)	4(2)	4(2)
N3	22(2)	35(2)	12(2)	3(2)	3(2)	3(2)
C1	29(2)	24(2)	12(2)	1(2)	3(2)	2(2)
C2	28(2)	26(2)	17(2)	0(2)	4(2)	-1(2)
C3	25(2)	28(3)	36(3)	-4(2)	6(2)	-6(2)
C4	38(3)	39(3)	45(3)	2(2)	18(3)	-3(2)
C5	39(3)	68(4)	34(3)	-4(3)	-6(3)	-3(3)
C6	32(3)	43(3)	71(4)	-11(3)	17(3)	-11(2)
C7	39(3)	21(2)	20(2)	2(2)	7(2)	1(2)
C8	34(3)	23(2)	18(2)	6(2)	7(2)	8(2)
C9	36(3)	22(2)	35(3)	4(2)	12(2)	9(2)
C10	63(4)	44(3)	36(3)	-2(3)	22(3)	27(3)
C11	68(4)	40(3)	47(3)	14(3)	17(3)	22(3)
C12	36(3)	45(3)	83(5)	12(3)	23(3)	20(3)
C13	23(2)	30(3)	21(2)	0(2)	5(2)	3(2)
C14	28(2)	20(2)	16(2)	-1(2)	8(2)	0(2)
C15	29(2)	22(2)	19(2)	1(2)	9(2)	1(2)
C16	24(2)	37(3)	17(2)	11(2)	3(2)	0(2)
C17	20(2)	26(2)	14(2)	1(2)	6(2)	2(2)
C18	27(3)	31(3)	26(3)	6(2)	3(2)	10(2)
C19	20(2)	49(3)	25(3)	4(2)	0(2)	3(2)
C20	24(3)	39(3)	25(3)	-5(2)	2(2)	-4(2)
C21	27(3)	30(3)	27(3)	0(2)	10(2)	-3(2)
C22	36(3)	28(3)	50(3)	-4(2)	1(2)	-7(2)
C23	24(2)	25(2)	14(2)	1(2)	7(2)	3(2)
C24	21(2)	20(2)	23(2)	4(2)	3(2)	-1(2)
C25	28(2)	30(3)	27(3)	10(2)	6(2)	-1(2)
C26	37(3)	40(3)	29(3)	10(2)	14(2)	4(2)
C27	39(3)	37(3)	28(3)	18(2)	6(2)	-3(2)
C28	35(3)	36(3)	35(3)	21(2)	4(2)	6(2)
C29	23(2)	33(3)	35(3)	11(2)	7(2)	5(2)
C30	29(2)	20(2)	24(2)	6(2)	9(2)	-1(2)
C31	28(3)	49(3)	22(3)	1(2)	1(2)	3(2)
C32	22(2)	29(2)	29(3)	5(2)	9(2)	7(2)
C33	20(2)	31(3)	21(2)	5(2)	7(2)	9(2)
C34	24(2)	27(2)	23(2)	-2(2)	3(2)	9(2)
C35	23(2)	39(3)	16(2)	0(2)	3(2)	12(2)
C36	41(3)	42(3)	16(2)	-3(2)	8(2)	16(2)
C37	129(6)	53(4)	29(3)	4(3)	28(4)	43(4)
C38	48(4)	98(5)	43(4)	-14(3)	23(3)	13(3)
C39	53(3)	50(3)	23(3)	3(2)	9(2)	8(3)
C40	26(2)	41(3)	15(2)	7(2)	6(2)	8(2)
C41	24(2)	33(3)	14(2)	5(2)	4(2)	8(2)
C42	32(3)	34(3)	18(2)	6(2)	8(2)	4(2)
C43	71(4)	42(3)	28(3)	9(2)	17(3)	-7(3)
C44	41(3)	38(3)	33(3)	10(2)	8(2)	10(2)
C45	34(3)	40(3)	26(3)	0(2)	4(2)	-4(2)
C46	19(2)	29(2)	17(2)	2(2)	3(2)	2(2)
C47	25(3)	57(3)	39(3)	8(3)	12(2)	9(2)
C48	36(3)	64(4)	58(4)	4(3)	9(3)	-2(3)
C49	55(3)	58(4)	29(3)	16(3)	1(3)	5(3)
C50	53(3)	63(4)	19(3)	1(2)	7(2)	3(3)
C51	89(2)	91(2)	90(2)	18(2)	20(1)	12(2)
C52	89(2)	90(2)	89(2)	19(1)	20(1)	12(1)
C51A	89(2)	91(2)	90(2)	18(2)	20(1)	12(2)
C52A	89(1)	90(1)	90(1)	19(1)	21(1)	12(1)
C53	87(2)	90(2)	90(1)	20(1)	21(1)	12(1)
C54	84(2)	89(2)	88(1)	22(1)	22(1)	12(1)
C55	83(2)	88(2)	87(2)	24(1)	24(1)	11(2)
C56	82(2)	88(2)	87(2)	25(2)	24(2)	10(2)
C57	79(2)	90(2)	86(2)	27(2)	26(2)	8(2)

Table 9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for po17.

	x	y	z	U(eq)
H1A	5530(40)	11250(30)	870(20)	44(13)
H2A	9720(40)	11170(30)	1050(20)	37(12)
H4A	8151	8227	2185	62
H4B	8488	7239	2419	62
H4C	7135	7287	1957	62
H5A	7859	8332	870	78
H5B	6846	7391	647	78
H5C	8018	7412	286	78
H6A	8516	5867	686	78
H6B	7298	5896	1005	78
H6C	8597	5811	1512	78
H7	10424	6236	1266	33
H10A	12998	5267	618	69
H10B	12444	6152	314	69
H10C	11592	5434	615	69
H11A	13124	6173	2478	74
H11B	13334	5260	1906	74
H11C	11960	5488	1936	74
H12A	14502	7234	2014	79
H12B	14204	7284	1178	79
H12C	14694	6340	1419	79
H13	13249	8389	1850	31
H15A	11744	10216	1609	28
H15B	12966	9979	2103	28
H16A	12166	9500	3307	39
H16B	10710	9420	2977	39
H16C	11373	10283	3645	39
H18	13833	10389	3538	34
H19	15470	11604	4125	39
H20	15292	13202	4039	38
H22A	13544	14083	2834	62
H22B	14210	14396	3673	62
H22C	12735	14159	3432	62
H26A	12940	11771	1502	51
H26B	13682	12807	1925	51
H26C	12922	12668	1108	51
H27	11141	13407	1016	41
H28	9427	13889	1427	41
H29	8930	13394	2413	36
H31A	11802	12551	3947	52
H31B	10694	12354	4335	52
H31C	10980	13393	4150	52
H32A	8776	13199	3510	31
H32B	8236	12254	2886	31
H34	8341	13225	4618	31
H37A	7397	14054	6223	102
H37B	6921	13784	5362	102
H37C	8371	14038	5717	102
H38A	6537	11597	6033	97
H38B	5761	12216	5532	97
H38C	6302	12668	6374	97
H39A	8821	11903	6376	64
H39B	8607	12908	6847	64
H39C	9518	12904	6305	64
H40	7415	10777	5244	33
H43A	6320	9385	4793	70
H43B	7670	9166	5147	70
H43C	6737	8340	4552	70
H44A	8505	8208	3923	55
H44B	9329	9122	4489	55
H44C	9034	9116	3643	55
H45A	6827	9245	3003	53
H45B	5776	9341	3458	53
H45C	6342	8340	3302	53
H47A	6260	11051	2607	59

H47B	4900	11161	2187	59
H47C	6010	12016	2314	59
H48A	5584	9139	659	82
H48B	4558	9425	1105	82
H48C	5836	9130	1502	82
H49A	7175	11819	-100	72
H49B	8617	12141	-27	72
H49C	7957	12578	603	72
H50A	8480	9330	187	70
H50B	8694	9986	-376	70
H50C	7324	9695	-283	70
H51A	8981	5014	3948	135
H51B	9097	5599	4758	135
H51C	8834	6145	4101	135
H52A	6947	5693	4550	107
H52B	7031	4586	4172	107
H51D	5740	5770	4257	135
H51E	6736	6638	4762	135
H51F	6745	5566	4914	135
H52C	7845	5181	4175	107
H52D	8048	6309	4148	107
H53A	5799	5586	3270	106
H53B	7129	6141	3296	106
H54A	7748	4816	2719	104
H54B	6726	4105	2903	104
H55A	5219	4543	2061	101
H55B	6229	5265	1882	101
H56A	6113	3245	1568	101
H56B	7104	3975	1378	101
H57A	4545	3693	747	124
H57B	5592	3282	360	124
H57C	5539	4427	556	124