Supporting Information

The scandium terminal imido complexes induced C-H bond selenation and the formation of Sc-Se bond

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General. All operations were carried out under an atmosphere of argon using Schlenk techniques or in a nitrogen filled glovebox. Toluene, hexane, and C_6D_6 were dried over Na/K alloy, distilled under vacuum, and stored in the glovebox. 2,6-Diisopropylaniline for the protonlysis reaction was purchased from Aldrich, dried over 4Å molecular sieves, distilled under vacuum, and degassed by freeze-pump-thaw cycle under high vacuum prior to use. 2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one[1] and N^1-(2-aminoethyl)-N^1,N^2,N^2-trimethylethane-1,2-diamine[2] were prepared according to literature procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer at 400 MHz and 100 MHz, respectively. ^{77}Se NMR spectrum was recorded on a Bruker AV 500 MHz spectrometer at 95.5 MHz. All chemical shifts are reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, and to diphenyldiselenide in C_6D_6 [^{77}Se = -460 ppm] for selenium chemical shifts.[3] Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

Synthesis of LH. 2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one (1.79 g,6.89 mmol), N^1-(2-aminoethyl)-N^1,N^2,N^2-trimethylethane-1,2-diamine (1.00 g,6.89 mmol), a catalytic amount of *p*-toluenesulfonic acid (250 mg), and toluene (30 mL) were introduced into a 100 mL flask equipped with a Dean-Stark apparatus. After refluxing for 12 hours, the solution was allowed to cool to room temperature, washed with saturated aqueous Na_2CO_3 (15 mL), and then dried over anhydrous Na_2SO_4 overnight. The solvent was removed under vacuum to give the crude product as a yellow oil, which was purified by flash column chromatography to give the product as a yellow viscous oil (1.67 g, 4.32 mmol, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.79 (s, 1H; MeC(N*H*)CH), 7.10-7.08 (m, 2H; Ar*H*), 7.02-6.98 (m, 1H; Ar*H*), 4.64 (s, 1H; MeC(NAr)C*H*), 3.33 (t, $^3J_{HH}$ = 7.2 Hz, 2H; NCH_2), 2.86 (sept, $^3J_{HH}$ = 7.2 Hz, 2H; ArC*H*Me$_2$), 2.51-2.47 (m, 2H; NCH_2), 2.45-2.41 (m, 2H; NCH_2), 2.26-2.23 (m, 2H; NCH_2), 2.22 (s, 3H; N*Me*), 2.13 (s, 6H; NMe_2), 2.01 (s, 3H; *Me*C), 1.62 (s, 3H; *Me*C), 1.15 (d, $^3J_{HH}$ = 7.2 Hz, 6H; ArCHMe_2), 1.11 (d, $^3J_{HH}$ = 7.2 Hz, 6H; ArCHMe_2). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 11.01 (s, 1H; MeC(N*H*)CH), 7.22-7.21 (m, 2H; Ar*H*), 7.14-7.10 (m, 1H; Ar*H*), 4.71 (s, 1H; MeC(NAr)C*H*), 3.19 (sept, $^3J_{HH}$ = 7.2 Hz, 2H; ArC*H*Me$_2$), 2.98 (br, 2H; NCH_2), 2.39-2.36 (m, 2H; NCH_2), 2.34 (sept, $^3J_{HH}$ = 6.0 Hz, 2H; NCH_2), 2.21-2.18 (m, 2H; NCH_2), 2.04 (s, 3H; N*Me*), 2.02 (s, 6H; NMe_2), 1.69 (s, 3H; *Me*C), 1.66 (s, 3H; *Me*C), 1.29 (d, $^3J_{HH}$ = 7.2 Hz, 6H; ArCHMe_2), 1.25 (d, $^3J_{HH}$ = 7.2 Hz, 6H; ArCHMe_2). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 165.8, 155.3 (imine *C*), 147.0, 137.9, 122.6, 122.3 (Ar*C*), 93.0 (MeC(N)*C*H), 58.3, 57.4, 56.2 (N*C*H$_2$), 45.8 (NMe_2), 42.5 (N*C*H$_2$), 41.2 (N*Me*), 28.0, 23.8, 22.7, 21.5, 19.5 (Ar^i*Pr* and *Me*C). HRMS (EI): calcd for $C_{24}H_{42}N_4$ (M^+): 386.3409; found 386.3405.

Synthesis of 2. 1 (100 mg, 0.149 mmol) and elemental selenium (11.8 mg, 0.149 mmol) were mixed in 5 mL of toluene. The reaction mixture was stirred at room temperature for 3.5 hours and then filtered. The deep brown filtrate was concentrated to approximately 0.5 mL and stored under –35 °C for 12 hours to afford **2** as brownish yellow crystals (62.0 mg, 0.0827 mmol, 56%). Anal. Calcd for $C_{40}H_{61}N_6ScSe\cdot(0.75\cdot C_7H_8)$: C, 66.36; H, 8.25; N, 10.26. Found: C, 66.63; H, 8.32; N, 9.90. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.48 (d, $^3J_{HH}$ = 6.8 Hz, 1H; H^2 of DMAP), 7.25-7.21 (m, 2H; Ar*H*), 7.13 (m, 2H; ArH^3 of toluene), 7.07-7.01 (m, 3H; Ar*H*), 7.02 (m, 3H; Ar$H^{2\ or\ 4}$ of toluene), 6.91 (t, $^3J_{HH}$ = 7.2 Hz, 1H; Ar*H*), 6.54 (br, 1H; $H^{3\ or\ 5}$ of DMAP), 6.12 (s, 1H; ArN*H*Sc), 5.77 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.4 Hz, 1H; $H^{3\ or\ 5}$ of DMAP), 4.97 (s, 1H; MeC(N)C*H*), 3.96 (sept, $^3J_{HH}$ = 7.2 Hz, 1H; ArC*H*Me$_2$), 3.69 (sept, $^3J_{HH}$ = 7.2 Hz, 2H; ArC*H*Me$_2$), 3.23-3.16 (m, 1H; NCH_2), 3.07-2.99 (m, 2H; NCH_2), 2.49 (br, 1H; ArC*H*Me$_2$), 2.28-2.07 (m, 6H; CH$_2$NMe_2), 2.11 (s, 3H; ArCH_3 of toluene), 2.04 (s, 6H; NMe_2), 1.87 (s, 3H; *Me*C), 1.95-1.89 (m, 1H; NCH_2), 1.75 (s, 3H; *Me*C), 1.50 (d, $^3J_{HH}$ = 6.8 Hz, 6H; ArCHMe_2), 1.38 (d, $^3J_{HH}$ = 6.8 Hz, 6H; ArCHMe_2), 1.34 (d, $^3J_{HH}$ = 6.8 Hz, 3H; ArCHMe_2), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 3H; ArCHMe_2), 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 3H; ArCHMe_2), 0.81 (d, $^3J_{HH}$ = 6.8 Hz, 3H; ArCHMe_2). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 167.5, 166.8 (imine *C*), 166.1 (N*C*Se), 155.5, 153.4, 146.6, 145.9, 144.7, 142.6, 134.4, 129.3, 128.6, 126.2, 125.6, 125.0, 123.6, 123.5, 116.1, 112.4, 102.1 (Ar*C*, and DMAP-*C*), 98.1 (MeC(N)*C*H), 58.8, 49.0 (N*C*H$_2$), 38.1 (NMe_2), 28.9, 28.3, 27.9, 26.2, 25.9, 25.5, 25.4, 25.3, 24.3, 23.8, 21.4, 21.1 (Ar^iPr, *Me*C and *Me* of toluene). ^{77}Se NMR (95.5 MHz, C_6D_6, 25 °C) δ = -653.7.

Synthesis of 3. LH (305 mg, 0.789 mmol) and $Sc(CH_2SiMe_3)_3(thf)_2$ (355 mg, 0.789 mmol) were mixed in 5 mL of hexane at –35 °C. The reaction mixture was gradually warmed to room temperature. After standing at room temperature for 2 hours, the volatiles were removed under vacuum and the residual orange solid was extracted with hexane (3×2 mL). The extract was concentrated to approximately 0.5 mL and cooled to –35 °C to afford **3** as an orange crystalline solid (350 mg, 0.579 mmol, 73% yield). Anal. Calcd for $C_{32}H_{63}N_4ScSi_2$: C, 63.53; H, 10.50; N, 9.26. Found: C, 63.57; H, 10.27; N, 9.06. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.20-7.18 (m, 3H; Ar*H*), 4.97 (s, 1H; MeC(N)C*H*), 3.36 (br, 2H; NCH_2), 3.14 (br, 2H; ArC*H*Me$_2$), 3.05 (br, 2H; NCH_2), 2.79 (br, 2H; NCH_2), 2.40 (s, 3H; N*Me*), 2.24 (br, 2H; NCH_2), 2.02 (s, 6H; NMe_2), 1.71 (s, 3H; *Me*C), 1.68 (s, 3H; *Me*C), 1.48 (d, $^3J_{HH}$ = 6.8 Hz, 6H; ArCHMe_2), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 6H; ArCHMe_2), 0.19 (s, 18H; CH$_2$SiMe_3), -0.12 (d, $^2J_{HH}$ = 11.6 Hz, 2H; CH_2SiMe$_3$), -0.27 (d, $^2J_{HH}$ = 11.6 Hz, 2H; CH_2SiMe$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 166.5, 165.6 (imine *C*), 147.7, 142.5, 126.0, 124.4 (Ar*C*), 99.0 (MeC(N)*C*H), 53.1, 53.0, 52.9, 47.4, 45.6, 41.5 (N*C*H$_2$, N*Me* and NMe_2), 28.1, 25.1, 25.0, 24.7, 22.8 (*Me*C and Ar^iPr), 4.2 (CH$_2$SiMe_3).

Synthesis of 4. 2,6-Diisopropylaniline (59.0 mg, 0.331 mmol) in 5 mL of hexane was added to **3** (195 mg, 0.331 mmol) in 5 mL of hexane in one portion at room temperature. The reaction mixture was stirred at 50

^{o}C for 6 hours. After cooling to room temperature, the volatiles were removed under vacuum to give an orange solid. Recrystallization of the orange solid from hexane afforded **4** as orange crystals (102 mg, 0.147 mmol, 44 % yield). Anal. Calcd for $C_{40}H_{70}N_5ScSi$: C, 69.22; H, 10.17; N, 10.99. Found: C, 69.49; H, 10.31; N, 10.50. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ = 7.20-7.17 (m, 2H; Ar*H*), 7.15-7.12 (m, 3H; Ar*H*), 6.84 (br, 1H; Ar*H*), 5.50 (br, 1H; ArN*H*Sc), 4.97 (s, 1H; MeC(N)C*H*), 3.60 (br, 1H; NCH_2), 3.31 (m, 2H; ArC*H*Me$_2$), 3.18 (m, 1H; NCH_2), 2.99 (m, 3H; ArC*H*Me$_2$ and NCH_2), 2.86 (m, 1H; NCH_2), 2.46 (br, 2H; NCH_2), 2.33 (m, 1H; NCH_2), 2.23 (m, 1H; NCH_2), 1.99-1.90 (m, 6H; NMe_2), 1.77 (s, 3H; N*Me*), 1.71 (s, 3H; *Me*C), 1.67 (s, 3H; *Me*C), 1.44 (d, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 3H; ArCHMe_2), 1.37 (d, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 6H; ArCHMe_2), 1.31 (d, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 6H; ArCHMe_2), 1.29 (d, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 3H; ArCHMe_2), 1.11 (d, $^3J_{\mathrm{HH}}$ = 6.4 Hz, 3H; ArCHMe_2), 1.09 (d, $^3J_{\mathrm{HH}}$ = 6.4 Hz, 3H; ArCHMe_2), 0.12 (s, 9H; CH$_2$SiMe_3), -0.15 (d, $^2J_{\mathrm{HH}}$ = 10.4 Hz, 1H; CH_2SiMe$_3$), -0.28 (d, $^2J_{\mathrm{HH}}$ = 10.4 Hz, 1H; CH_2SiMe$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 ^{o}C): δ = 167.2, 166.6 (imine *C*), 150.6, 146.7, 144.1, 142.8, 134.0, 126.3, 124.9, 124.6, 123.3, 116.4 (Ar*C*), 99.6 (MeC(N)*C*H), 54.9, 52.9, 52.5, 51.3, 50.4, 48.2, 47.8, 45.5, 43.7 (N*C*H$_2$, N*Me* and NMe_2), 40.1 (Sc*C*H$_2$SiMe$_3$), 38.7 (N*C*H$_2$), 29.4, 28.8, 27.6, 25.7, 25.6, 25.4, 25.1, 25.0, 24.8, 24.3, 23.1 (*Me*C and Ar^i*Pr*), 4.0 (CH$_2$SiMe_3).

Synthesis of 5. 4 (170 mg, 0.2449mmol) was dissolved in 3 mL of hexane and kept at 50 ^{o}C for 3 days. Red crystals precipitated from the reaction solution were washed with hexane (3 x 1 mL), and recrystallized from toluene to afford **5** as red crystals (61.0 mg, 0.101 mmol, 48 % yield). Anal. Calcd for $C_{36}H_{58}N_5Sc$: C,71.37; H, 9.65; N, 11.56. Found: C, 70.68; H, 9.53; N, 11.68. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ = 7.25-7.21 (m, 3H; Ar*H*), 7.10 (t, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 1H; Ar*H*), 7.01-6.98 (m, 1H; Ar*H*), 6.78 (t, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 1H; Ar*H*), 5.15 (s, 1H; MeC(N)C*H*), 4.23 (sept, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 1H; ArC*H*Me$_2$), 4.16 (sept, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 2H; ArC*H*Me$_2$), 3.52-3.40 (m, 2H; NCH_2), 2.82 (sept, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 1H; ArC*H*Me$_2$), 2.75 (dd, $^2J_{\mathrm{HH}}$ = 10.4 Hz, $^3J_{\mathrm{HH}}$ = 4.0 Hz, 1H; NCH_2), 2.56 (s, 3H; N*Me*), 2.10 (m, 1H; NCH_2), 2.08 (s, 3H; NMe_2), 2.02 (dd, $^2J_{\mathrm{HH}}$ = 10.4 Hz, $^3J_{\mathrm{HH}}$ = 4.4 Hz, 1H; NCH_2), 1.97-1.94 (m, 1H; NCH_2), 1.92 (s, 3H; *Me*C), 1.92-1.89 (m, 1H; NCH_2), 1.86-1.84 (m, 1H; NCH_2), 1.84 (s, 3H; *Me*C), 1.51 (d, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 6H; ArCHMe_2), 1.42 (d, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 6H; ArCHMe_2), 1.35 (d, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 3H; ArCHMe_2), 1.28 (s, 3H; NMe_2), 1.19 (d, $^3J_{\mathrm{HH}}$ = 6.8Hz, 3H; ArCHMe_2), 1.00 (d, $^3J_{\mathrm{HH}}$ = 6.4 Hz, 3H; ArCHMe_2), 0.95 (d, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 3H; ArCHMe_2). ^{13}C NMR (100 MHz, C_6D_6, 25 ^{o}C): δ = 167.0, 165.6 (imine *C*), 156.3, 146.6, 146.0, 141.7, 137.8, 125.5, 125.4, 123.2, 121.7, 110.3 (Ar*C*), 98.0 (MeC(N)*C*H), 62.5, 57.8, 57.0, 49.0, 48.1, 45.1, 43.2 (N*Me*, NMe_2 and N*C*H$_2$), 28.4, 28.2, 27.6, 25.7, 25.3, 25.2, 25.1, 25.0, 23.4, 23.2 (*Me*C and Ar^i*Pr*).

Synthesis of 6. 5 (100 mg, 0.165 mmol) and elemental selenium (13 mg, 0.165 mmol) were mixed in 5 mL of toluene. The reaction mixture was stirred at room temperature for 12 hours and then filtered. The yellow filtrate was concentrated to approximately 0.5 mL and stored at –35 ^{o}C for 12 hours to give a yellow solid, which was recrystallized from a toluene/hexane mixture to afford **6** as yellow crystals (72.3 mg, 0.106

mmol, 64% yield). Anal. Calcd for $C_{36}H_{58}N_5ScSe\cdot(0.5C_6H_{14})$: C, 64.35; H, 9.00; N, 9.62. Found: C, 64.41; H, 8.74; N, 9.43. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.20-7.16 (m, 5H; Ar*H*), 6.88 (t, $^3J_{HH}$ = 7.6 Hz, 1H; Ar*H*), 5.84 (s, 1H; ArN*H*Sc), 4.79 (s, 1H; MeC(N)C*H*), 4.05 (d, $^2J_{HH}$ = 9.6 Hz, 1H; SeC*H*$_2$), 3.84 (sept, $^3J_{HH}$ = 6.8 Hz, 1H; ArC*H*Me$_2$), 3.54 (sept, $^3J_{HH}$ = 6.8 Hz, 2H; ArC*H*Me$_2$), 3.46 (d, $^2J_{HH}$ = 9.6 Hz, 1H; SeC*H*$_2$), 3.24 (sept, $^3J_{HH}$ = 6.8 Hz, 1H; ArC*H*Me$_2$), 3.20-3.11 (m, 1H; NC*H*$_2$), 3.03-2.96 (m, 1H; NC*H*$_2$), 2.90-2.81 (m, 2H; NC*H*$_2$), 2.53 (s, 3H; N*Me*), 2.11-2.04 (m, 1H; NC*H*$_2$), 2.02 (s, 3H; N*Me*), 1.82-1.78 (m, 1H; NC*H*$_2$), 1.73 (s, 3H; *Me*C), 1.67 (s, 3H; *Me*C), 1.68-1.64 (m, 1H; NC*H*$_2$), 1.61-1.56 (m, 1H; NC*H*$_2$), 1.50 (d, $^3J_{HH}$ = 6.8 Hz, 3H; ArCH*Me*$_2$), 1.41 (d, $^3J_{HH}$ = 6.8 Hz, 6H; ArCH*Me*$_2$), 1.38 (d, $^3J_{HH}$ = 6.8 Hz, 3H; ArCH*Me*$_2$), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 6H; ArCH*Me*$_2$), 1.14 (d, $^3J_{HH}$ = 6.8 Hz, 3H; ArCH*Me*$_2$), 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 3H; ArCH*Me*$_2$), 0.89 (t, $^3J_{HH}$ = 6.8 Hz, *n*-hexane). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 168.5, 165.7 (imine *C*), 151.2, 147.2, 144.9, 141.9, 134.7, 126.3, 125.2, 123.9, 123.4, 123.1, 116.7 (Ar*C*), 97.7(MeC(N)*C*H), 56.8, 56.5, 53.6, 49.7, 49.2, 44.6, 44.4 (N*C*H$_2$Se, N*Me* and N*C*H$_2$), 28.7, 28.6, 28.4, 26.7, 26.6, 26.0, 25.2, 25.1, 25.0, 23.3, 22.5 (Ar^i*Pr* and *Me*C). ^{77}Se NMR (95.5 MHz, C_6D_6, 25 °C) δ = -760.0.

X-ray Crystallography. Single crystals of **2** and **4** suitable for X-ray diffraction analysis were grown up from the toluene solutions, those of **3** and **5** were grown up from hexane solutions, and those of **6** were grown up from a toluene/hexane mixture. The single crystals were sealed in thin-walled glass capillaries, and data collection was performed at 20°C on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using the ω-scan mode. The *SMART* program package[4] was used to determine the unit-cell parameters. Unit cell parameters refinement and data reduction were performed with *SAINT* program package.[5] The absorption correction was performed semi-empirically from equivalents with *SADABS* program.[6] All structures were solved by direct methods[7] and refined on F^2 by full-matrix least squares techniques.[8] Except of the case of the minor component of a disordered trimethylsilyl group carbon atoms in **2** [site occupancy factor (*sof*) 0.131(14)], all non-hydrogen atoms were treated anisotropically. Except of the hydrogen atom of anilide functional groups in **2**, **4** and **6**, all H-atoms were placed in calculated positions and refined in an isotropic approximation using the riding model. The specified above anilide H-atoms were found from difference Fourier syntheses and refined isotropically. To facilitate data processing, *OLEX2* program[9] was used during the structure solution and refinement routines. The absolute structure of racemic **3** (polar space group *Pna*2_1) was established as described by Flack[10] [resultant Flack parameter 0.04 (4)]. The nature and *sof*-s of the solvent molecules in **2** (toluene, *sof* 0.75) and **6** (hexane, *sof* 1.00) was proved with the intrinsic *SQUEEZE* procedure of the *PLATON* program package.[11] Exhaustive details of the disorder treatment, structure refinement and restrains applied can be found in supplied CIF-files in _publ_section_exptl_refinement sections. Crystal data and refinement details for **2-6** are summarized in the Table S1.

Table S1. Crystal data and refinement parameters for **2-6**.

Compound	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{45.25}H_{67}N_6ScSe$	$C_{32}H_{63}N_4ScSi_2$	$C_{40}H_{70}N_5ScSi$	$C_{36}H_{58}N_5Sc$	$C_{42}H_{72}N_5ScSe$
Formula weight	818.97	605.00	694.06	605.83	770.97
Crystal size, mm	0.35 × 0.19 × 0.11	0.37 × 0.30 × 0.23	0.40 × 0.35 × 0.32	0.30 × 0.26 × 0.25	0.38 × 0.30 × 0.28
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$Pna2_1$	$P2_1/c$	$P{-1}$	$P2_1/c$
Unit cell dimensions:					
a [Å]	16.9407(16)	20.686(2)	9.4600(7)	10.9539(10)	15.693(5)
b [Å]	10.3275(10)	10.7668(10)	23.0011(16)	13.6426(12)	18.073(6)
c [Å]	27.971(3)	17.2813(17)	20.5013(14)	14.4239(13)	15.637(5)
α [°]	90	90	90	74.071(2)	90
β [°]	103.202(2)	90	101.978(2)	69.856(2)	90.126(8)
γ [°]	90	90	90	67.166(2)	90
Volume [Å^3]	4764.3(8)	3848.9(7)	4363.8(5)	1840.2(3)	4445(3)
Z	4	4	4	2	4
Density (calculated) [g·cm^{-3}]	1.142	1.044	1.056	1.093	1.152
Absorption coefficient [mm^{-1}]	0.95	0.277	0.227	0.229	1.02
F(000)	1742	1328	1520	660	1656
θ range [°]	2.1 to 25.1	2.0 to 25.1	2.03 to 25.1	1.64 to 25.1	2.2 to 25.1
Index ranges	$-20 \le h \le 19$ $-12 \le k \le 12$ $-20 \le l \le 33$	$-21 \le h \le 24$ $-10 \le k \le 12$ $-20 \le l \le 20$	$-11 \le h \le 11$ $-21 \le k \le 27$ $-24 \le l \le 24$	$-13 \le h \le 13$ $-15 \le k \le 16$ $-17 \le l \le 16$	$-16 \le h \le 18$ $-21 \le k \le 21$ $-18 \le l \le 18$
Reflections collected / unique	23727 / 8464 [$R_{int} = 0.077$]	18940 / 6798 [$R_{int} = 0.068$]	22169 / 7770 [$R_{int} = 0.052$]	9489 / 6492 [$R_{int} = 0.020$]	22328 / 7897 [$R_{int} = 0.177$]
Completeness [%] to θ = 25.1°	99.6	100	99.8	99.1	99.8
Unique reflections I>2σ(I)	4390	4499	4897	5107	3182
Min. and Max. transmission	0.732 and 0.902	0.904 and 0.939	0.915 and 0.931	0.934 and 0.945	0.699 and 0.764
Data/restraints/parameters	8464 / 199 / 554	6798 / 177 / 423	7770 / 93 / 475	6492 / 0 / 392	7897 / 48 / 458
Goodness-of-fit on F^2	0.93	0.99	1.00	1.03	0.86
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0680$ $wR_2 = 0.1570$	$R_1 = 0.0652$ $wR_2 = 0.1248$	$R_1 = 0.0630$ $wR_2 = 0.1492$	$R_1 = 0.0549$ $wR_2 = 0.1360$	$R_1 = 0.0812$ $wR_2 = 0.1640$
R indices (all data)	$R_1 = 0.1424$ $wR_2 = 0.1807$	$R_1 = 0.1031$ $wR_2 = 0.1388$	$R_1 = 0.1061$ $wR_2 = 0.1666$	$R_1 = 0.0701$ $wR_2 = 0.1443$	$R_1 = 0.1988$ $wR_2 = 0.1981$
Largest diff. peak and hole [e·Å^{-3}]	0.530 and –0.487	0.206 and –0.173	0.354 and –0.227	0.300 and –0.206	0.504 and –0.605

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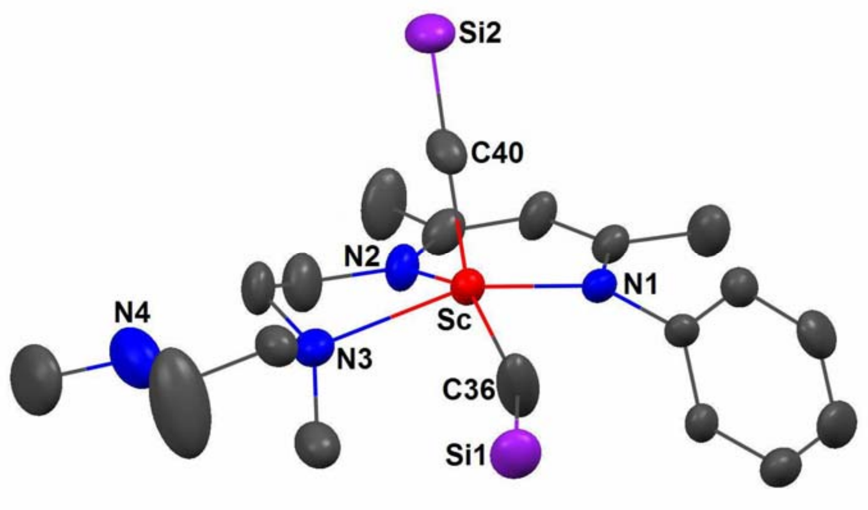

Fig. S1 Molecular structure of **3** with thermal ellipsoids at 30% probability level. Isopropyl groups at the Ar substitutents, methyl groups at silicon atoms, minor component of the disordered C36 atom and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sc-C36 2.240(10), Sc-C36' 2.228(17), Sc-C40 2.211(4), Sc-N1 2.210(3), Sc-N2 2.216(4), Sc-N3 2.360(4).

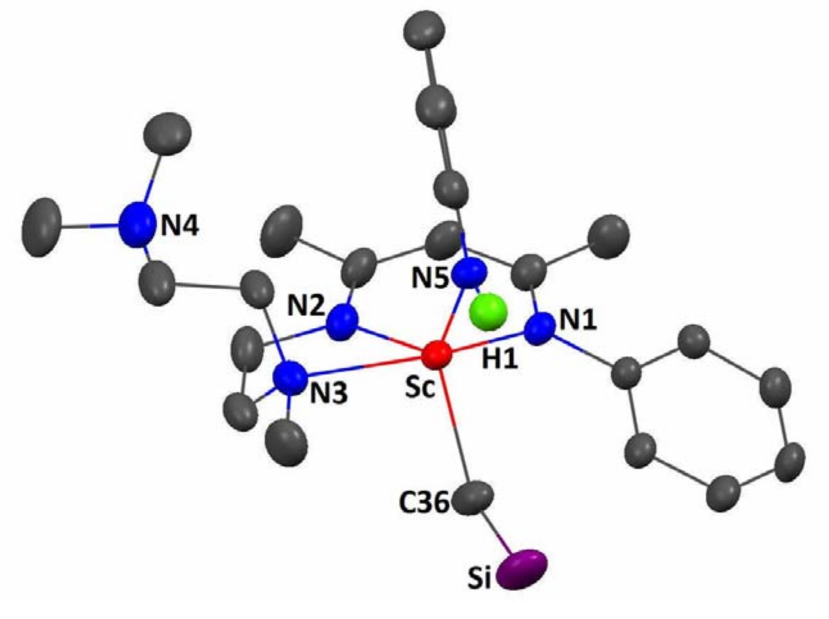

Fig. S2 Molecular structure of **4** with thermal ellipsoids at 30% probability level. Isopropyl groups at the Ar substitutents, disordered methyl groups at the silicon atom and hydrogen atoms (except of the anilide hydrogen atom) are omitted for clarity. Selected bond lengths (Å) and angles (°): Sc-N5 2.054(3), Sc-C36 2.217(3), Sc-N1 2.221(2), Sc-N2 2.172(3), Sc-N3 2.392(3), Sc-N5-C40 147.8(2).