Electronic Supplementary Information

Half-Sandwich Scandium Boryl Complexes Bearing a Silylene-Linked Cyclopentadienyl−Amido Ligand

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Experimental Section

General Information

All manipulations of air- and moisture-sensitive compounds were performed under an argon atmosphere by use of standard Schlenk techniques or a nitrogen atmosphere in an MBRAUN Labmaster 130 glovebox. Argon and nitrogen (Takachiho Chemical Industrial Co., Ltd.) were purified by being passed through a Dryclean column (4 A molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi–Analyzer (MBRAUN) to ensure both were always below 0.1 ppm. Elemental analyses were performed by a MICRO CORDER JM10. Organic solvents were obtained from Kanto Kagaku Co., purified by an MBRAUN SPS-800 Solvent Purification System and dried over fresh Na chips in a glovebox. Nitric oxide, carbon monoxide and ^{13}C-enriched carbon monoxide (99 atom%, ISOTEC) were used as received without further purification. $Me_2Si(C_5Me_4H)(NHPh)$ ligand[1] and boryl lithium[2] were synthesized according to literature procedures. Scandium chloride complex **1** was synthesized as a modified procedure.[3] $ScCl_3$ was purchased from STREM Co., and $ScCl_3(THF)_3$ was prepared from $ScCl_3$ with THF at 70 ˚C for 12 hours. *N,N'*-Diisopropylcarbodiimide was purchased from TCI, dried over CaH_2, vacuum-transferred, degassed by two freeze-pump-thaw cycles and kept in the glovebox. All ^{1}H, ^{13}C and ^{11}B NMR spectra of complexes were recorded on a JEOL AL-400 or JEOL AL-500 instrument in C_6D_6 with tetramethylsilane (TMS) as an internal standard, unless otherwise mentioned. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, sep = septet, m = multiplet, br = broad signal), coupling constant (Hz), integration. Infrared spectra were recorded on a Nicolet 380 (Thermo Electron) spectrometer using nujol mulls sandwiched between KBr plates.

X-ray Crystallographic Studies

A crystal was sealed in a thin-walled glass capillary under a microscope in the glove box. Data collections were performed at –100 ˚C on a Bruker SMART APEX diffractometer with a CCD area detector using graphite-monochromated MoK$_\alpha$ radiation (λ= 0.71069 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package.[4] The raw frame data was processed using SAINT[5] and SADABS[6] to yield the reflection data file. The structures were solved by using SHELXTL program.[7] Refinements were performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis using SHELXTL program. The disordered THF (C20, C21) on complex **1** was separated into two parts (C30, C31) and were treated with 50% and 50% occupancy, respectively. The oxygen atoms of disordered DME ligands in complex **3** (O1, O3, O5, O6) were treated with 50%. Some of the carbon and oxygen atoms of DME ligands were refined isotropically due to the serious disorder. The disordered phenyl group on the N3 in complex **4** (C13-17) was separated into two parts (C54-57, C64) and were treated with 55% and 45% occupancy, respectively. The disordered phenyl carbons (C20-22) and (C60-62) on N2 in **4** were treated with 60% and 40% occupancy, respectively. The disordered methyl groups (C39, C40, C49, C50, C51-53, C58) of isopropyl units on N4 and C37 in **4** were treated with 50% occupancy. The disordered methylene carbons (C46, C48) of THF in **5** were treated with 50% occupancy. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance.

CCDC numbers 981558 (**1**), 981559 (**2**), 988055 (**3**), 981560 (**4**) and 981564 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request/cif

Synthesis and Characterization of Scandium Chloride (Complex 1)

^{n}BuLi (8.5 mL, 2.6 M, hexane) was slowly added to a THF solution (20 mL) of $Me_2Si(C_5Me_4H)(NHPh)$ (3.000 g, 11.05 mmol), then stirred for 5 h. The THF suspension of $\{Me_2Si(C_5Me_4H)(NHPh)\}Li_2$ was added to the THF suspension (10 mL) of $ScCl_3(THF)_3$ (4.062 g, 11.05 mmol) and reacted overnight at room temperature. The solvent was removed under reduced pressure. The residue was extracted with benzene and removed benzene under reduced pressure. The residue was dissolved in mixture solution of toluene and hexane and was cooled down to –30 ˚C to afford colorless crystals dimeric **1** (2.359 g, 25%). Recrystallization from toluene gave single crystals suitable for X-ray analysis (Figure S1). ^{1}H NMR (400 MHz, C_6D_6, 25 ˚C): δ 0.80 (s, 12H, Si(*Me*)$_2$), 0.97–1.00 (m, 8H, THF), 2.07 (s, 12H, Cp(*Me*)$_4$), 2.18 (s, 12H, Cp(*Me*)$_4$), 3.44–3.47 (m, 8H, THF), 6.78 (t, 7.3 Hz, 2H, Aryl), 7.08 (d, 7.8 Hz, 4H, Aryl), 7.18–7.22 (m, 4H, Aryl); ^{13}C NMR (100 MHz, C_6D_6, 25 ˚C, δ_{C6D6} = 128.06): δ 4.3 (s, 4C, Si(*Me*)$_2$), 11.9 (s, 4C, Cp(*Me*)$_4$), 14.3 (s, 4C, Cp(*Me*)$_4$), 24.9 (s, 4C, THF), 72.2 (s, 4C, THF), 109.4, 118.2, 120.7, 127.9, 129.6, 131.0, 153.9 (aromatic and Cp ring carbons). Anal. Calcd. for $C_{42}H_{62}Cl_2N_2O_2Sc_2Si_2$: C 59.77; H 7.40; N 3.32. Found: C 59.84; H 7.38; N 3.44.

Synthesis and Characterization of Scandium Boryl (Complex 3)

A 1,2-dimethoxyethane (DME, 5 mL) solution of complex **2** (0.369 g, 0.38 mmol) was stirred at room temperature for 30 min. After most solvent removal under reduced pressure, the residue dissolved in mixture of DME, hexane and benzene. The solution crystallized at –30 ˚C to give **3** as colorless crystals (0.355 g, 91%). ^{1}H NMR (400 MHz, THF-d8, 25 ˚C): δ 0.31 (s, 3H, Si(*Me*)$_2$), 0.37 (s, 3H, Si(*Me*)$_2$), 0.75 (d, 6.8 Hz, 6H, CH(*Me*)$_2$), 0.87 (d, 6.8 Hz, 6H, CH(*Me*)$_2$), 1.14 (d, 6.8 Hz, 6H, CH(*Me*)$_2$), 1.20 (s, 3H, Cp(*Me*)$_4$), 1.42 (d, 6.8 Hz, 6H, CH(*Me*)$_2$), 1.77 (s, 3H, Cp(*Me*)$_4$), 1.84 (s, 3H, Cp(*Me*)$_4$), 2.11 (s, 3H, Cp(*Me*)$_4$), 3.23 (s, 18H, C*H*$_3$OCH$_2$CH$_2$OC*H*$_3$), 3.31–3.79 (m, 2H, *CH*(Me)$_2$), 3.40 (s, 12H, CH$_3$OC*H*$_2$C*H*$_2$OCH$_3$), 3.50–3.70 (m, 2H, *CH*(Me)$_2$), 5.90 (s, 2H, N–C*H*=C*H*–N), 6.23 (t, 6.9 Hz, 1H, Aryl), 6.74–7.05 (m, 10H, Aryl). (See Figure S7 for ^{1}H NMR spectrum). ^{13}C NMR (100 MHz, C_6D_6, 25 ˚C, $\delta_{THF\text{-}d8}$ = 67.21): δ 4.3, 4.6 (s, 2C, Si(*Me*)$_2$), 12.2, 13.2, 13.6, 15.4 (s, 4C, Cp(*Me*)$_4$), 22.5, 24.4, 25.6, 27.5 (s, 8C, CH(*Me*)$_2$), 28.3, 29.4 (s, 4C, *C*H(Me)$_2$), 58.7 (s, 6C, DME), 72.5 (s, 6C, DME), 120.3, 120.4 (s, 2C, N–*C*H=*C*H–N), 105.5, 114.0, 122.3, 123.1, 123.8, 124.0, 125.3, 127.0, 127.4, 128.1, 146.4, 146.8, 147.1, 157.1 (aromatic and Cp ring carbons). ^{11}B NMR (160 MHz, THF-d8, 25 ˚C): δ 38.7 (br). Anal. Calcd. for $C_{55}H_{83}BClN_3O_3ScSi$: C 65.11; H 8.84; N 4.14. Found: C 65.45; H 8.63; N 4.24.

Synthesis and Characterization of Borylamidinate (Complex 4)

A hexane solution (5 mL) of *N,N’*-diisopropylcarbodiimide (0.049 g, 0.55 mmol) was slowly added into a benzene solution (5 mL) of **2** (0.531 g, 0.55 mmol) at room temperature and the mixture was stirred for 3 hours at 60 ˚C. After solvent removal under reduced pressure, the residue was extracted with hexane. The filtrate was further concentrated to afford colorless crystals of **3** (0.307 g, 67%) at room temperature (Figure S2). ^{1}H NMR (400 MHz, C_6D_6, 25 ˚C): δ 0.65 (d, 6.0 Hz, 6H, N–CH(*Me*)$_2$), 0.71 (s, 6H, Si(*Me*)$_2$), 0.78 (d, 6.4 Hz, 6H, N–CH(*Me*)$_2$), 0.97–1.01 (m, 12H, CH(*Me*)$_2$), 1.10 (d, 6H, 6.9 Hz, CH(*Me*)$_2$), 1.30 (d, 6H, 6.9 Hz, CH(*Me*)$_2$), 2.02 (s, 6H, Cp(*Me*)$_4$), 2.32 (s, 6H, Cp(*Me*)$_4$), 3.09–3.20 (m, 4H, *CH*(Me)$_2$), 3.30 (sep, 6.2 Hz, 2H, N–*CH*(Me)$_2$), 6.22 (d, 2.3 Hz, 1H, N–C*H*=C*H*–N), 6.25 (d, 2.3 Hz, 1H, N–C*H*=C*H*–N), 6.61–6.63 (m, 2H, Aryl), 6.84–6.88 (m, 1H, Aryl), 7.06–7.21 (m, 8H, Aryl); ^{13}C NMR (100 MHz, C_6D_6, 25 ˚C, δ_{C6D6} = 128.06): δ 4.3 (s, 2C, Si(*Me*)$_2$), 12.7, 14.6 (s, 4C, Cp(*Me*)$_4$), 22.1, 23.0, 26.0, 26.3 (s, 8C, CH(*Me*)$_2$), 26.8, 27.1 (s, 2C, N–CH(*Me*)$_2$), 28.6, 29.1 (s, 2C, *C*H(Me)$_2$), 50.3 (s, 2C, N–*C*H(Me)$_2$), 121.66, 121.72 (s, 2C, N–*C*H=*C*H–N), 108.6, 118.3, 123.6, 124.3, 124.7, 126.3, 128.5, 129.2, 139.9, 140.4, 144.4, 145.3, 155.7 (aromatic and Cp ring carbons). The chemical shift of carbon linked with boryl was not found because of widening effect from boryl group. ^{11}B NMR (160 MHz, C_6D_6, 25 ˚C): δ 20.3 (br). Anal. Calcd. for $C_{50}H_{73}BN_5ScSi$: C 72.53; H 8.89; N 8.46. Found: C 72.50; H 8.81; N 8.51.

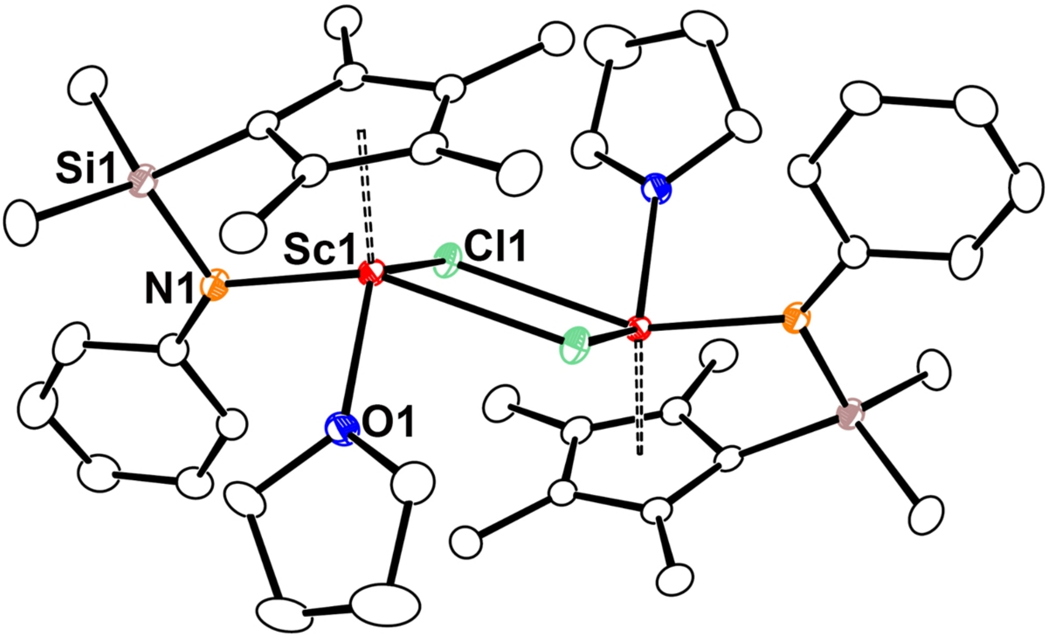

Figure S1. ORTEP drawing of **1** with thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Sc1–N1 2.142(2), Sc1–Cl1 2.5454(9), Sc1–C1 2.378(3), Sc1–C2 2.461(3), Sc1–C3 2.573(3), Sc1–C4 2.568(3), Sc1–C5 2.442(3), Sc1–centroid of Cp 2.171, Sc1–O1 2.2245(19).

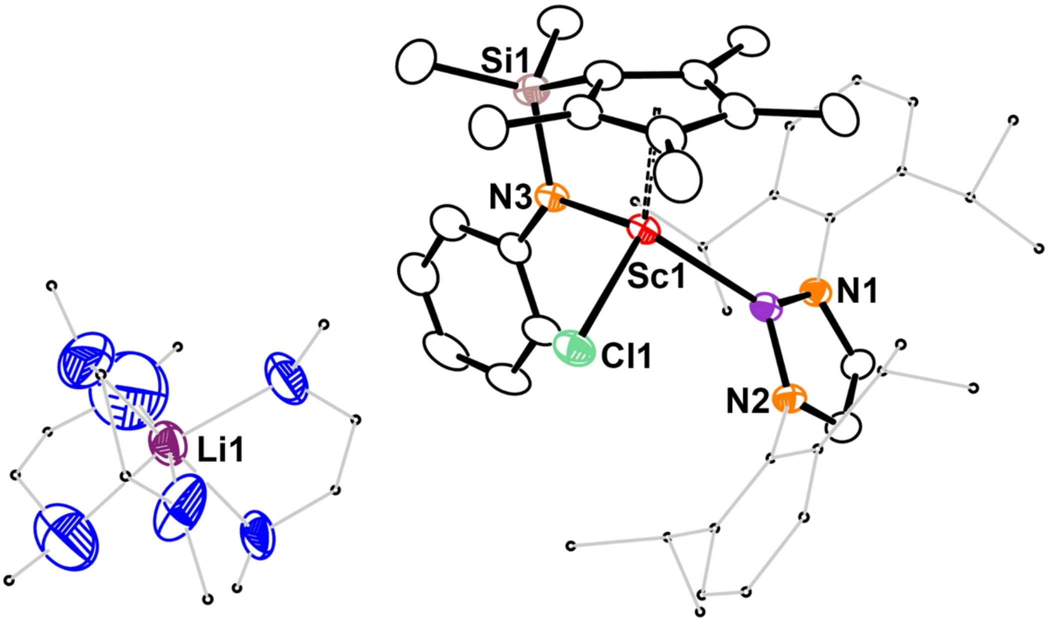

Figure S2. ORTEP drawing of **3** with thermal ellipsoids at the 30% level except for the 2,6-$(^{i}Pr)_2C_6H_3$ groups in the boryl unit and three DME molecules. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Sc1–B1 2.499(5), Sc1–N3 2.132(4), Sc1–Cl1 2.403(1), Sc1–centriod of Cp 2.193, N1–B1 1.468(6), N2–B1 1.482(6).

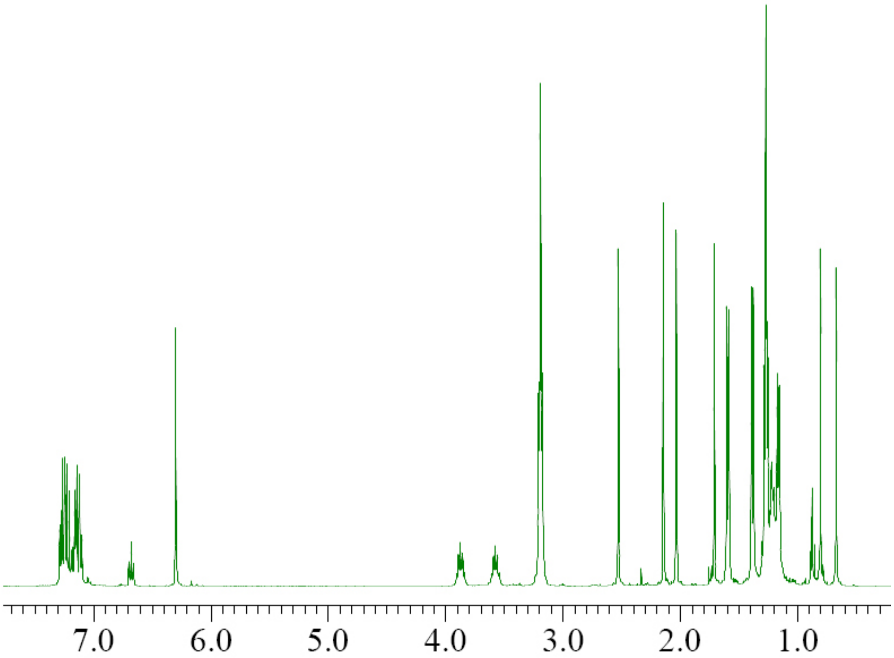

Figure S6. ^{1}H NMR spectrum of complex **2**

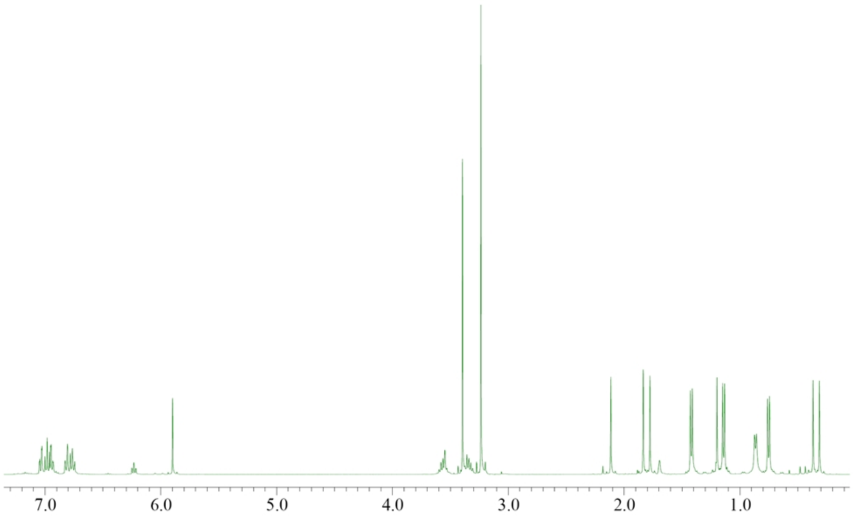

Figure S7. ^{1}H NMR spectrum of complex **3**

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