

Regioselective C-H activation of lanthanide-bound N-heterocyclic carbenes. ESI

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Experimental Section

All manipulations were carried out using standard Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen. Toluene, THF, and diethyl ether were dried by passage through activated alumina towers and degassed before use. Benzene was distilled from potassium under an atmosphere of dry nitrogen. Hexamethyldisiloxane was distilled from calcium hydride under an atmosphere of dry nitrogen. All solvents were stored over potassium mirrors (with the exception of hexamethyldisiloxane, which was stored over activated 4 Å molecular sieves). Deuteriated solvents were distilled from potassium, degassed by three freeze-pump-thaw cycles and stored under dinitrogen. Trimethylsilyliodide was distilled from activated magnesium turnings, degassed by three freeze-pump-thaw cycles, and stored over copper under an atmosphere of dinitrogen. The compounds NdN³,¹

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[HL.2LiBr],² [Ce(L)N"2],³ and KC₈⁴ were prepared by published literature procedures.

¹H, and ¹³C{¹H}, NMR spectra were recorded on a Bruker 300 spectrometer operating at 300.1, and 75.5 MHz, respectively; chemical shifts are quoted in ppm and are relative to SiMe₄. Elemental microanalyses were carried out by Mr Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK.

Preparation of Nd(L)N"2 (1) Toluene (50 ml) was added to a mixture of NdN"3 (4.60 g, 7.36 mmol) and HL.2LiBr (2.92 g, 7.36 mmol) and the resulting solution stirred for 19 hrs. The mixture was filtered to give a blue-green solution, and volatiles were removed under reduced pressure to give a sticky blue solid. The solid was extracted into diethyl ether (60 ml), filtered, and the solution concentrated under reduced pressure until incipient crystallization occurred. The mixture was warmed and then stored at -30 °C to yield blue crystals of **1** suitable for an X-ray diffraction study. Further concentration of the mother liquor and storage at -30 °C afforded a second crop of crystals. Combined yield: 4.30 g, 85 %. Anal. Calcd for C₂₅H₆₀N₅NdSi₄: C, 43.68; H, 8.80; N, 10.19. Found: C, 43.87; H, 8.89; N, 10.05. ¹H NMR (*d*₆-benzene, 295 K): δ -8.47 (s, 9H, *t*-Bu), -6.18 (s, 1H, CH), -3.65 (s, br, 2H, CH₂), -2.16 (s, 36H, SiMe₃), -1.02 (s, 1H, CH), 2.98 (s, 9H, *t*-Bu), 15.55 (s, 1H, CH₂) and 87.52 (s, br, 1H, CH₂).

The complex Nd(L)N"2 can be sublimed intact in poor yield (10⁻⁵ mbar, *ca* 200 °C) compared with the moderate yields observed for the smaller lanthanides that we have studied to date (Y, Sm, and Eu) (analogous to the sublimation yields of LnN"3). We have not observed any fluxional processes for any of the complexes, and measure only one yttrium-carbon coupling constant for the Y(III) analogue of **1**.

Preparation of [Nd(L')N''(μ -I)]₂ (2) Me₃SiI (1.14 ml, 8.00 mmol) was added to a solution of **1** (5.50 g, 8.00 mmol) in diethyl ether (10 ml). The red-blue solution was stirred for 60 hrs during which time a pale blue precipitate formed. The mother liquor was removed by filtration, the solid washed with diethyl ether (3 × 5 ml) and dried *in vacuo*. Yield: 4.07 g, 70 %. Pale blue crystals of 2.½C₆H₅CH₃ suitable for an X-ray diffraction study were grown from a cold (–30 °C) solution in toluene. Anal. Calcd for C₄₄H₁₀₀I₂N₈Nd₂Si₆.½C₆H₅CH₃: C, 38.08; H, 7.00; N, 7.48. Found: C, 37.98; H, 7.11; N, 7.49. ¹H NMR (*d*₆-benzene, 295 K): δ –8.84 (s, br, 1H, CH₂), –5.97 (s, br, 1H, CH₂), –3.53 (s, br, 9H, *t*-Bu), –2.07 (s, br, 9H, =CSiMe₃), –1.79 (s, br, 9H, *t*-Bu), –1.26 (s, br, 1H, CH), 0.21 (s, br, 18H, SiMe₃) and 1.04 (m, br, 2H, CH₂).

Reduction of 2 and isolation of Nd(L')N''₂ (3) Benzene (15 ml) was added to a mixture of **2** (1.45 g, 2.00 mmol) and KC₈ (0.28 g, 2.1 mmol) and the mixture heated to 80 °C for 20 hrs. The mixture was cooled to room temperature, filtered, and volatiles removed under reduced pressure to afford a dark red-brown oil. The oil was dissolved in hexamethyldisiloxane (1.50 ml) and stored at –30 °C to afford a crop of pale blue crystals of **3** suitable for an X-ray diffraction study. Yield (based on Nd): 0.42 g, 28 %. Anal. Calcd for C₂₈H₆₈N₅NdSi₅: C, 44.27; H, 9.02; N, 9.22. Found: C, 44.17; H, 8.93; N, 9.36. ¹H NMR (*d*₆-benzene, 295 K): δ –11.37 (s, 1H, CH₂), –8.80 (s, 9H, *t*-Bu), –5.78 (s, 1H, CH₂), –2.16 (s, 36H, SiMe₃), –0.05 (s, 1H, CH), 1.61 (s, 9H, SiMe₃), 3.12 (s, 9H, *t*-Bu), 16.93 (s, 1H, CH₂) and 90.15 (s, br, 1H, CH₂).

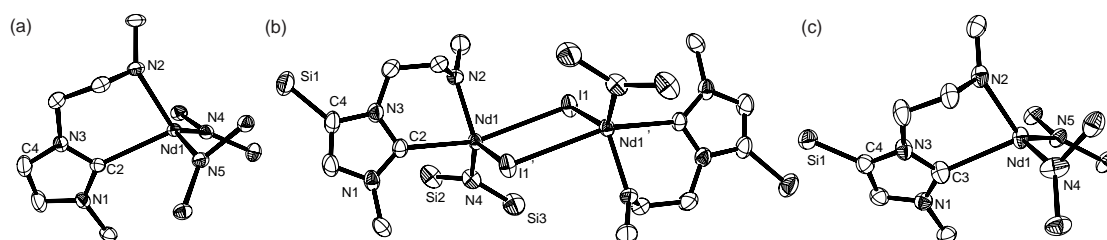
Preparation of [Ce(L')N''(μ -I)]₂ (4**)** Me₃SiI (0.32 ml, 2.27 mmol) was added to a solution of LCeN''₂ (1.55 g, 2.27 mmol) in diethyl ether (5 ml) and the mixture stirred for 8 days. The resulting yellow precipitate was isolated by filtration, washed with diethyl ether (3 × 5 ml), and dried to give **4** as a lemon yellow powder. Yield: 1.22 g, 74%. Yellow crystals of **4**·2C₆H₅CH₃ were obtained from a cold (−30 °C) solution in toluene. Anal. Calcd for C₄₄H₁₀₀Ce₂I₂N₈Si₆: C, 36.60; H, 6.98; N, 7.76. Found: C, 36.51; H, 6.92; N, 7.64. ¹H NMR (*d*₆-benzene, 295 K): δ −0.35 (s, br, 4H, CH₂), 0.20 (s, br, 36H, SiMe₃), 0.40 (s, br, 2H, CH), 1.25 (s, br, 18H, *t*-Bu), 1.63 (s, br, 18H, *t*-Bu), 2.29 (s, br, 18H, =CSiMe₃), 2.93 (s, br, 2H, CH₂) and 4.19 (s, br, 2H, CH₂).

Preparation of [Nd(L')N''(μ -N₃)]₂ (5**)** A mixture of **2** (0.99 g, 1.36 mmol) and NaN₃ (0.14 g, 2.15 mmol) were refluxed in THF (20 ml) for 6 days. The mixture was cooled to room temperature, filtered, and volatiles removed under reduced pressure. The resulting green-blue sticky solid was extracted with toluene (10 ml), filtered, concentrated to 2 ml and stored at −30 °C for 3 days to afford a crop of crystals of **5**·2C₆H₅CH₃ suitable for an X-ray diffraction study. Yield (based on Nd): 0.77 g, 39%. Anal. Calcd for C₅₈H₁₁₆N₁₄Nd₂Si₆: C, 47.50; H, 7.97; N, 13.17. Found: C, 36.79; H, 6.86; N, 12.67. ¹H NMR (*d*₆-benzene, 295 K): δ −3.75 (s, br, 36H, SiMe₃), 0.21 (s, br, 18H, *t*-Bu), 1.03 (s, br, 18H, *t*-Bu), 2.99 (s, br, 18H, =CSiMe₃), 12.65 (s, br, 2H, CH₂), 16.78 (s, br, 2H, CH), 22.62 (s, br, 2H, CH₂), 46.72 (s, br, 2H, CH₂) and 87.93 (s, br, 2H, CH₂).

Crystallography

Crystals were examined on a Bruker Smart 1000 or Apex area detector diffractometer using graphite-monochromated MoK α radiation (λ = 0.71073 Å) at 150(2) K. Intensities were integrated from a sphere of data recorded on narrow (0.3°)

frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semi-empirical absorption corrections were applied based on symmetry-equivalent and repeat reflections. The structures were solved variously by heavy-atom and direct methods and were refined by least-squares methods on all unique F^2 values, with anisotropic displacement parameters, and with constrained riding hydrogen geometries; $U(H)$ was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. The largest features in final difference syntheses were close to heavy atoms. Programs were Bruker AXS SMART (control) and SAINT (integration),⁵ and SHELXTL for structure solution, refinement, and molecular graphics.⁶



Displacement ellipsoid drawings of **1**(a) **2**(b) and **3**(c) (50 % probability). Hydrogen and methyl groups omitted for clarity.

Table 1. Selected distances (Å) and angles (°) for the molecular structures of **1**, **2** and **3**

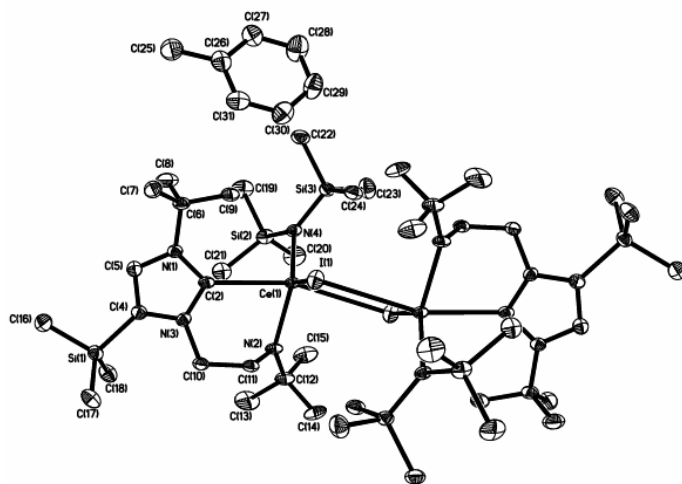
distance/angle	1	2	3
Nd1-C2	2.609(3)	2.656(5)	2.648(3)
Nd1-N2	2.243(2)	2.205(4)	2.248(3)
Nd1-N4	2.380(2)	2.322(5)	2.372(2)
Nd1-I1, Nd1-I1'	-	3.2492(6), 3.2087(7)	-
Nd1- Nd1'	-	5.010	-
N2-Nd1-C2	84.07(8)	81.91(16)	81.59(10)
C11 N2 Nd1	102.87(15)	103.5(3)	98.7(2)
N3-C2	1.360(3)	1.360(7)	1.363(4)
N3-C4	1.368(4)	1.390(7)	1.397(4)
N3-C2-N1	103.6(2)	103.4(4)	103.2(3)

Crystals of **1** are isomorphous with the Ce, Sm, and Y congeners.^{2, 3} Compound **2** is monomeric in the solid state and the geometry at Nd is distorted tetrahedral with Nd1 bonded to the C2 and N2 atoms of the amido-NHC and the N4 and N5 amide atoms of the N" ligands. The Nd1-C2 bond length is 2.609(3) Å; there are no structurally characterized Nd-carbene bond lengths for comparison in the literature, but this value compares with values of 2.699(2) and 2.588(2) Å for the Ce and Sm congeners.^{2, 3} The Nd1-N2, Nd1-N4, and Nd1-N5 bond lengths of 2.243(2), 2.380(2), and 2.379(2) Å, respectively, are as expected; terminal dialkyl amide bond lengths of 2.283 and 2.291 Å were reported for the complex (*i*-Pr₂N)₂Nd(μ -*i*-Pr₂N)₂Li(THF)⁷ and Nd-N_{silylamide} literature bond lengths are typically in the range 2.300-2.437 Å.⁸⁻¹⁴ Nd1...Si4 and Nd1...C11 distances of 3.354 and 2.933 Å, respectively, are suggestive of close contacts which we have consistently observed in the Ce, Sm, and Y congeners.

Compound **2** is dimeric in the solid state, constructed around a *transoid* Nd₂I₂ four-membered ring which is centered over a crystallographic inversion center. Each Nd is coordinated to the C2 and N2 atoms of the amido-NHC, two μ -I atoms, and the N4 atom of a N" ligand and is thus five-coordinate, adopting a distorted trigonal bipyramidal geometry such that C2 and I1 are axially disposed. The Nd1-C2 bond length is 2.656(5) Å, which is substantially longer than that observed in **1** and reflects the increased coordination number at Nd, compared to **1**, and the softer nature of the silylated NHC. However, the Nd1-N2 (dialkyl amide) bond length is 2.205(4) Å, shorter than the corresponding bond in **1**. The Nd1-N4 (silylamide) bond length of 2.322(5) Å is towards the shorter end of reported Nd-N_{silylamide} bond lengths.⁸⁻¹² The Nd1-I1 and Nd1-I1' bond lengths of 3.2492(6) and 3.2087(7) Å, respectively, are long for Nd-I bond lengths (literature bond length range 3.040-3.287 Å)¹⁵⁻²³ and are exceeded only by the Nd-I bond length of 3.287 Å in the complex

$\text{Nd}(\text{C}_8\text{H}_8)\text{I}(\text{THF})_3$.²³ As in **1**, close contacts of Nd1 to Si3 and C11 are suggested by distances of 3.408 and 2.907 Å, respectively.

Compound **3** is monomeric in the solid state; the Nd atom adopts a distorted tetrahedral geometry bonded to the C2 and N2 atoms of the amido-NHC and the N4 and N5 atoms of two N" ligands. The Nd1-C2 bond length is 2.648(3) Å; this is statistically identical to the corresponding bond length in **2**, despite the lower coordination number, but is significantly longer than the corresponding bond length in **1**. Since **1** and **3** are the same, save for substitution of H by SiMe₃ at the C4 position, this is a direct probe of the effect of silylation at the C4 position, and is commensurate with incorporation of an electropositive Si atom into the σ -framework. The Nd1-N2 bond length in **3** is 2.248(3) Å, essentially identical to that observed in **1**. The Nd1-N4 and Nd1-N5 bond lengths of 2.352(2) and 2.372(2) Å, respectively, are again typical of Nd-N_{silylamide} bond lengths.⁸⁻¹⁴ The softer nature of the NHC in **3** compared to **1** is also suggested by the short Nd1...C11 contact of 2.859 Å (*cf.* 2.933 Å in **1**), and not one, but two Nd...Si contacts (Nd1...Si2 = 3.353 Å; Nd1...Si4 = 3.466).

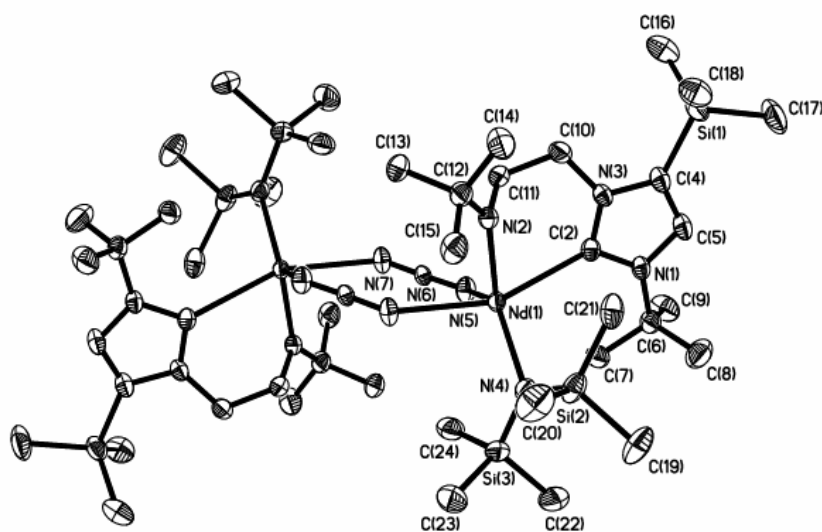


Displacement ellipsoid drawing of **4** (50 % probability). Hydrogens omitted for clarity.

Table 2. Selected distances (Å) and angles (°) for the molecular structure of **4**

Ce1	N2		2.241(6)
Ce1	N4		2.364(6)
Ce1	C2		2.728(8)
Ce1	C11		2.925(7)
Ce1	I1		3.1806(7)
Ce1	I1'		3.2354(7)
Ce1	Si3		3.479(2)
N1	C2		1.367(9)
N3	C2		1.357(9)
N2	Ce1	C2	80.0(2)
N2	Ce1	N4	119.0(2)
N2	Ce1	C2	80.0(2)
N4	Ce1	C2	101.7(2)
N2	Ce1	I1	109.97(15)
N4	Ce1	I1	130.98(15)
C2	Ce1	I1	87.28(15)
Ce1	I1	Ce1	100.650(18)
I1	Ce1	I1	79.350(18)
N3	C2	N1	103.2(6)

Crystals of **4** are isomorphous with the Nd analogue **2**. The Ce-carbene distance of 2.728(8) Å is longer by 0.07 Å than that in the Nd analogue, consistent with the larger radius of Ce(III). The carbene geometries are essentially the same for both metal complexes **2** and **4**. The Ce₂I₂ rectangle is equally distorted as the Nd-I structure; in each the difference in M-I length is 0.05 Å, but the Ce-I distances are on average 0.02 Å shorter than the Nd-I distances. Other distances and angles are as anticipated.³



Displacement ellipsoid drawing of **5** (50 % probability). Hydrogens omitted for clarity.

Table 3. Selected distances (Å) and angles (°) for the molecular structure of **5**

Nd1	N2		2.231(2)
Nd1	C2		2.672(3)
Nd1	N4		2.341(2)
Nd1	N5		2.513(3)
Nd1	N7		2.521(3)
Nd1	C11		2.907(3)
Nd1	Si3		3.4592(9)
Nd1	Si2		3.4712(9)
N1	C2		1.357(4)
N2	Nd1	N5	111.67(9)
N2	Nd1	N7	85.79(9)
N5	Nd1	N7	80.86(9)
N2	Nd1	C2	80.96(9)
N5	Nd1	C2	84.16(9)
N7	Nd1	C2	154.72(9)

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Computer programs: *Bruker SMART version 5.625* (Bruker, 2001); *Bruker SAINT version 6.36a* (Bruker, 2000); *Bruker SAINT*; *Bruker SHELXTL* (Bruker, 2001); *Bruker SHELXTL*; *SHELXL-97* (Sheldrick, 1997); *enCIFer*(Allen et al.,2004);*PLATON*(Spek,2003).