Regioselective C–H activation of lanthanide-bound N-heterocyclic carbenes†

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The reaction of Ln(L)N$''_2$ (Ln = Nd, Ce; L = *t*-BuNCH$_2$CH$_2$[C{NCHCHN*t*-Bu}], N$''$ = N(SiMe$_3$)$_2$) with trimethylsilyl iodide regiospecifically functionalises the carbene backbone at the C4-carbene ring position to afford the silylated complex Ln(L$'$)N$''$I; Ln(L$'$)N$''_2$ is isolated after attempted reduction (L$'$ = *t*-BuNCH$_2$CH$_2$[C{NC(SiMe$_3$)CHN*t*-Bu}]) which allows a comparison of the structurally characterised complexes Nd(L)N$''_2$, [Nd(L$'$)N$''$I]$_2$, and Nd(L$'$)N$''_2$.

The widespread use of metal N-heterocyclic carbene (NHC) complexes in homogeneous catalysis includes many systems in which the carbene is generated by an *in situ* deprotonation.[1] Increasingly, complexes are being isolated which contain abnormally bound carbenes, *i.e.* ligands bound through a backbone C4 or C5 carbon, as a result of an H migration from the backbone to C2.[2–5] However, while protocols now exist for functionalising both backbone C4 and C5 carbons with halogen or deuterium (by reaction of the free NHC with CCl$_4$ or base and D$_2$O, respectively)[6,7] the control of the migration, or a specific functionalisation of the carbene backbone has yet to be reported. Such a functionalisation would allow new planar, asymmetric NHC ligands to be generated.[8–11]

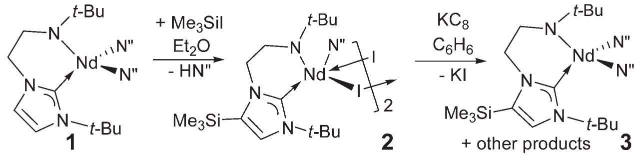
Recently, we have been studying the chemistry of electropositive metal NHC complexes, using *N*-alkyl functionalised anionic groups to stabilise the σ-bound complexes.[12–14] We reported the heteroleptic [Ce(L)N$''$(μ-X)]$_2$ (X = Br, I; N$''$ = N(SiMe$_3$)$_2$), which is isolated in moderate yield from the reaction of [CeN$''_3$] with [HL.LiX].[15] Heteroleptic lanthanide complexes such as **2** are rare since the complexes are so prone to redistribution reactions, but lanthanide iodides are particularly useful precursors for metathesis chemistry due to the insolubility of displaced potassium iodide. They are even more interesting as precursors for the reductive activation of small molecules, as they should be more readily reduced than traditional coordination complexes by potassium reductants.[16]

The neodymium complex [Nd(L)N$''_2$] **1**, is prepared in an analogous manner to [Ln(L)N$''_2$] (Ln = Y, Sm, Ce).[12,15] In our hands, it shows no reaction with potassium graphite, in contrast with [NdN$''_3$] which affords [{N$''_2$(THF)Nd}$_2$(μ-η^2:η^2-N$_2$)] in low yield,[16] showing the subtlety of the electronic requirements of the reductive activation system. The Nd(III) cation is slightly easier to reduce to the divalent state than Ce(III): E° (Ln$^{3+/2+}$) Nd = −2.62, Ce = −2.92 V.[17] Observing this, we have sought to identify a straightforward and high-yielding route to the iodide complexes of Ce and Nd, since we reasoned that this might allow access to reductive activation chemistry of the carbene complexes. Herein, we present this successful methodology, and an additional, surprisingly straightforward regioselective functionalisation of the carbene backbone that accompanies the reaction.

Complex **1** was treated with Me$_3$SiI at room temperature for 60 h, Scheme 1, in the anticipation of yielding [Nd(L)N$''$(μ-I)]$_2$ and N(SiMe$_3$)$_3$ as the byproduct. However, the reaction generates the silylated-carbene iodide [Nd(L$'$)N$''$(μ-I)]$_2$ **2**, (L$'$ = the silylated *t*-BuNCH$_2$CH$_2$[C{NC(SiMe$_3$)CHN*t*-Bu}]) and HN$''$ is eliminated rather than N(SiMe$_3$)$_3$. This appears, to the best of our knowledge, to be the first functionalisation of an NHC backbone carbon that need not proceed *via* a refunctionalisation of the basic carbene C2 atom, or 1,3 proton or alkyl migration, so we were interested to investigate the mechanism, and to understand if this is a generally applicable NHC functionalisation, or desymmetrisation strategy.

In terms of suggesting a mechanism for this silylation, we immediately discount a process involving a 1,3 shift, as seen in the formation of the 'wrong' carbenes.[2–5] This is because no product containing a C2-bound trimethylsilyl group is observed.

Notably, the functionalised atom—C4—is the same distance from the tether amide as the bound C2, which raises a question as to whether the C–H bond is activated by metal insertion prior to functionalisation. C–H bond activation is well known in organolanthanide alkyl chemistry, but not yet for carbene complexes.[18–23] In Scheme 2, path (a), labilisation of the NHC group is shown to place the C4 C–H group in the ideal position for a σ-bond metathesis reaction, after elimination of amine, and allowing a subsequent incorporation of Me$_3$SiI. However, we discount this mechanism since we cannot find any evidence of the C–H-activated intermediates: also, heating a *d$_6$*-benzene solution of the diamagnetic yttrium analogue of **1**, [Y(L)N$''_2$], shows no loss of Y–C$_{\text{carbene}}$ coupling, *i.e.* no fluxionality, and no evidence of incorporation of deuterium from the solvent (usually a reactive substrate in organoalkyl lanthanide σ bond methathesis systems) is seen in heated solutions of [Ln(L)N$''_2$] (Ln = Y, Ce, Nd, Sm, Eu).



Scheme 1

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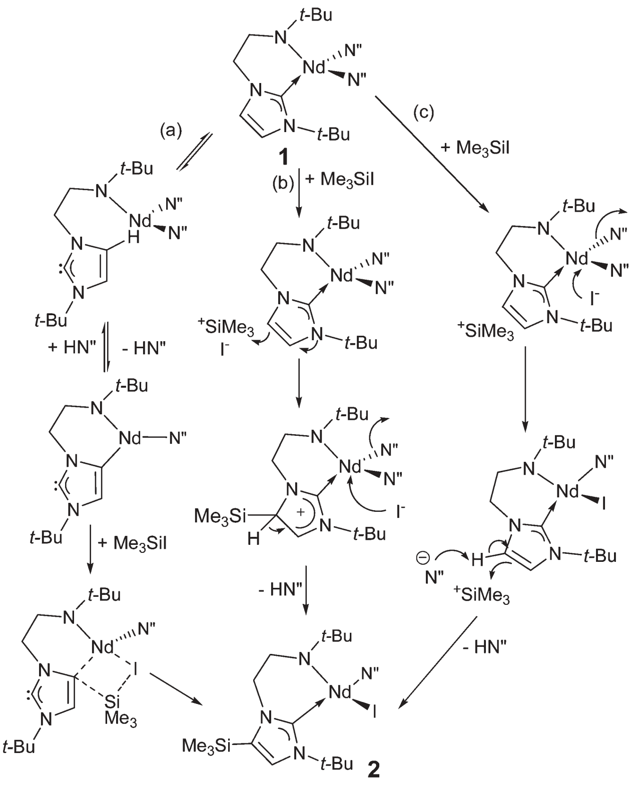
† Electronic supplementary information (ESI) available: preparative and reactivity data for complexes **1**–**5**. See DOI: 10.1039/b511265f



Scheme 2

An alternative plausible route, path (b), since the reaction works best in diethyl ether, is a direct electrophilic attack of the NHC ring by the ether-stabilised trimethylsilyl cation,[24,25] with subsequent loss of HN'' and coordination of the iodide anion. However, we observe a significant dependence on the reaction on the size of the metal: the complex $[Ce(L')N''(\mu\text{-}I)]_2$ **4** is readily made from $[Ce(L)N''_2]$ by the same procedure as for **2** (see ESI‡). However, treatment of $[Y(L)N''_2]$ with trimethylsilyl iodide for prolonged periods (up to six days in diethyl ether) does not afford the silylated $[Y(L')N''(\mu\text{-}I)]_2$ or $[Y(L')N''_2]$ (the Y analogue of **3**). The failure of this smaller metal to form the analogue of **2** suggests that the rate of this reaction is affected by steric congestion at the metal.[26]

Thus, a mechanism closer to path (c) seems most likely: an associative mechanism involving the nucleophilic substitution of N'' by the iodide anion at the metal centre could also generate the amide base of sufficient strength to form the carbanion which is readily quenched by the trimethylsilyl cation, which is a long-lived species stabilised by the ether solvent.[24,25,27]

Further, treatment of the iodide **2** with KC_8 in benzene under a dinitrogen atmosphere affords **3**, the silylated ligand complex $Nd(L')(N'')_2$, rather than a reduced Nd complex, as the only isolable product, in low yield. This is a ligand redistribution/disproportionation product, and again demonstrates the subtlety of the electronic requirements for reductive activation at these metals.

Solutions of all three complexes gave crystals suitable for X-ray diffraction studies‡ (see ESI); the molecular structures are depicted in Fig. 1.

The crystals of **1** are isomorphous with the Ce, Sm, and Y congeners.[12,15] 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 characterised Nd–carbene bond lengths for comparison in the literature, but this value compares with values of 2.699(2) Å for the Ce congener.[15] The Nd1–N2, Nd1–N4, Nd1–N5, and $Nd–N_{silylamide}$ bond lengths are as expected.[28–32] The Nd1···Si4 and Nd1···C11 distances of 3.354 and 2.933 Å, respectively, are suggestive of close contacts.

Compound **2** is dimeric in the solid state, constructed around a *transoid* Nd_2I_2 four-membered ring which resides over a crystallographic inversion center. Each Nd is a five-coordinate, distorted trigonal bipyramid with C2 and I1 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, and the softer nature of the silylated NHC. However, the Nd1–N2 (dialkyl amide) bond length is 2.205(4) Å, shorter than that 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. 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 range 3.040–3.287 Å).[33,34] As in **1**, close contacts of Nd1 to Si3 and C11 are suggested by distances of 3.408 and 2.907 Å, respectively.

In compound **3** the Nd atom adopts a distorted tetrahedral geometry. 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

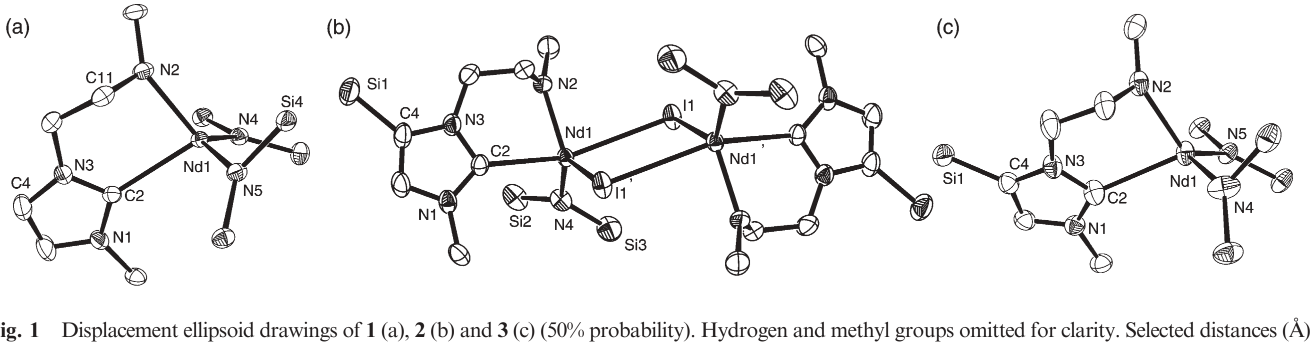
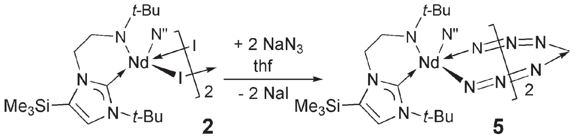


Fig. 1 Displacement ellipsoid drawings of **1** (a), **2** (b) and **3** (c) (50% probability). Hydrogen and methyl groups omitted for clarity. Selected distances (Å) and angles (°) (listed for **1**, **2**, and **3** in order): Nd1–C2 2.609(3), 2.656(5), 2.648(3), Nd1–N2, 2.243(2), 2.205(4), 2.248(3), Nd1–I1, Nd1–I1′ (for **1**, **3**) 3.2492(6), 3.2087(7), Nd1–Nd1′ (for **2**) 5.010, N2–Nd1–C2, 84.07(8), 81.91(16), 81.59(10), 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).

than the corresponding bond length in **1**. Since **1** and **3** are the same, save for substitution of H by $SiMe_3$ 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 $Nd–N_{silylamide}$ bond lengths are again typical.[28–32] 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).

We also note that although the reduction of **2** has so far been unsuccessful, salt methathesis chemistry proceeds smoothly, for example the azide complex **5** is readily prepared from the treatment of **2** with stoichiometric NaN_3, eqn. 1 (see ESI for the synthesis and single crystal X-ray structure data for **5**‡). In **5** the $Nd–C_{carbene}$ distance is longer than in the other five-coordinate Nd complex **2** (2.672(3) Å), and the N–N distances in the two bridging azides (ave. 1.16 Å) are consistent with the bond orders drawn in eqn. 1. Other distances and angles are unremarkable.



(1)

To conclude, a silylation reaction of a metal-coordinated NHC heterocycle occurs regioselectively, allowing the controlled C–H functionalisation of one backbone carbon of the ring, and generation of a softer NHC ligand by a mild and straightforward route. The isolation of $[Nd(L)N''_2]$ and $[Nd(L')N''_2]$ allows a direct probe of the effect of incorporation of the electropositive silicon into the σ-framework of the NHC. Work is in hand to study the small molecule chemistry of the silylated NHC adducts.

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Notes and references

‡ ESI available: full synthetic details for complexes and crystallographic data for **1–5**. Selected experimental and crystallographic data: **1**: yield: 4.30 g, 85%. Anal. Calcd for $C_{25}H_{60}N_5NdSi_4$: C, 43.68; H, 8.80; N, 10.19. Found: C, 43.87; H, 8.89; N, 10.05. $C_{25}H_{60}N_5NdSi_4$ block, blue M_r = 687.38 Monoclinic, $P2_1/c$ a = 18.1289(12) b = 11.6659(8) c = 17.7378(12) Å β = 102.709(2)° V = 3659.5(4) $Å^3$ μ = 1.570 mm^{-1} Z = 4 D_x = 1.248 Mg m^{-3} 8348 independent reflections. Final R_1 [6977 $F > 4\sigma(F)$] = 0.0264 and wR (all F^2) was 0.0654. **2**: Yield: 4.07 g, 70%. Anal. Calcd for $C_{44}H_{100}I_2N_8Nd_2Si_6\cdot½C_6H_5CH_3$: C, 38.08; H, 7.00; N, 7.48. Found: C, 37.98; H, 7.11; N, 7.49. $C_{47.50}H_{104}I_2N_8Nd_2Si_6$ Needle, blue M_r = 1498.21 Triclinic, P-1 a = 11.280(2) b = 14.204(3) c = 14.632(3) Å α = 63.675(3) β = 70.505(3) γ = 74.060(3)° V = 1958.5(6) $Å^3$ μ = 2.221 mm^{-1} Z = 1 D_x = 1.270 Mg m^{-3} 6877 independent reflections. Final R_1 [6106 $F > 4\sigma(F)$] = 0.0440 and wR (all F^2) was 0.1120. **3**: Yield (based on Nd): 0.42 g, 28%. Anal. Calcd for $C_{28}H_{68}N_5NdSi_5$: C, 44.27; H, 9.02; N, 9.22. Found: C, 44.17; H, 8.93; N, 9.36. $C_{28}H_{68}N_5NdSi_5$ Block, pale blue M_r = 759.56 Triclinic, P-1 a = 10.9100(10) b = 12.3766(11) c = 17.1729(16) Å α = 108.306(2) β = 97.810(2) γ = 104.318(2)° V = 2074.8(3) $Å^3$ μ = 1.418 mm^{-1} Z = 2 D_x = 1.216 Mg m^{-3} 9420 independent reflections. Final R_1 [7757 $F > 4\sigma(F)$] = 0.0391 and wR (all F^2) was 0.0895. **4**: Yield: 1.22 g, 74%. Anal. Calcd for $C_{44}H_{100}Ce_2I_2N_8Si_6$: C, 36.60; H, 6.98; N, 7.76. Found: C, 36.51; H, 6.92; N, 7.64. $C_{58}H_{116}Ce_2I_2N_8Si_6$ block, yellow M_r = 1628.17 Monoclinic, $P2_1/c$ a = 11.7912(12) b = 14.8947(15) c = 22.118(2) Å β = 95.838(2)° V = 3864.4(7) $Å^3$ μ = 2.09 mm^{-1} Z = 2 D_x = 1.399 Mg m^{-3} 8860 independent reflections. Final R_1 [6128 $F > 4\sigma(F)$] = 0.056 and wR (all F^2) was 0.168. **5**: Yield: 0.77 g, 39%. Anal. Calcd for $C_{58}H_{116}N_{14}Nd_2Si_6$: C, 47.50; H, 7.97; N, 13.17. Found: C, 36.79; H, 6.86; N, 12.67. $C_{58}H_{116}N_{14}Nd_2Si_6$ block, pale blue M_r = 1466.67 Monoclinic, $P2_1/c$ a = 11.2143(6) b = 15.5058(9) c = 22.3542(13) Å β = 97.695(2)° V = 3852.1(4) $Å^3$ μ = 1.468 mm^{-1} Z = 2 D_x = 1.264 Mg m^{-3} 8805 independent reflections. Final R_1 [7138 $F > 4\sigma(F)$] = 0.0298 and wR (all F^2) was 0.0810. CCDC 280856–280860. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511265f

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