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Organolanthanide Complexes

Anionic Amido N-Heterocyclic Carbenes: Synthesis of Covalently Tethered Lanthanide–Carbene Complexes**

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Deprotonation of a bidentate amine-imidazolium bromide affords a new amine-functionalized carbene, and by a protonolysis reaction, the first f-element complex with a covalently bound, potentially hemilabile, N-heterocyclic carbene.

Since the early use of di-*N*-phenyl, -methyl, and -adamantyl functionalized imidazolium salts and electron-rich alkenes as precursors for metal–carbene complexes and stable nucleophilic carbenes,[1] it is now apparent that a wide range of *N*-functional groups are tolerated in nucleophilic

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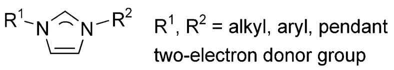
imidazol-2-ylidenes (**A**) or N-heterocyclic carbenes (NHCs). These bind as two-electron donors to almost all metals in the



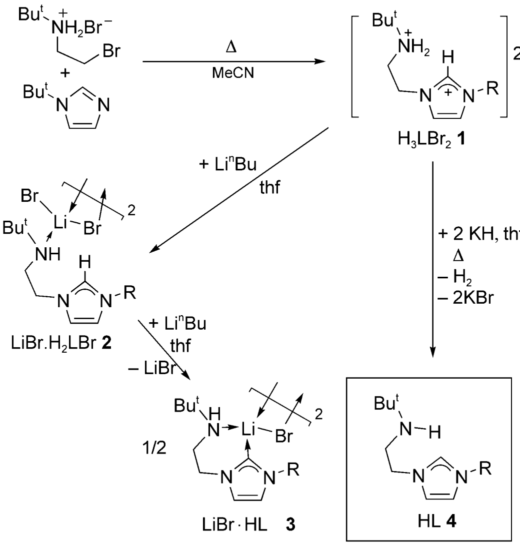
periodic table.[2] NHCs form extremely strong dative bonds to late d-block metals such as ruthenium and palladium, with little or no backbonding,[3] and are easily *N*-functionalized. The overwhelming majority of these ligands are neutral, and incorporate chiral hydrocarbyl groups, or additional donor groups (e.g. pyridyl, ether, NHC), to tune the catalytic activity of the complexes in reactions such as C–Si, C–C, C–N, and now methane C–H activation.[4] To date, the NHC complexes of the most electropositive metals, including Groups 4, 5, and the s- and f-block, have been reported only as "curiosities", in which the NHC binds simply as a solvate.[5] Although interesting electronic properties of the early metal–NHC bond has been suggested,[6] no complexes have been available in which the strength or reactivity of the bound NHC may be studied. Monodentate, unfunctionalized NHCs have already been used to good effect in Al^{III} mediated C–C bond forming reactions,[7] so the development of NHC-functionalized ligands which are asymmetric, and in which the NHC is hemilabile, has potential in areas of homogeneous catalysis.

We have been studying NHC ligands that incorporate a pendant anionic functional group for this purpose.[8] We now report a synthesis of the first amido-functionalized NHC ligand, and syntheses of trivalent samarium(III) and yttrium(III) adducts of this asymmetric bidentate ligand.

The reaction of 2-bromoethyl-*tert*-butyl-ammonium bromide with *N*-*tert*-butyl imidazole proceeds cleanly in acetonitrile to afford the alkylammonium imidazolium bromide $t\mathrm{BuNH_2CH_2CH_2[HC\{}t\mathrm{BuN(CHCH)N\}]Br}$ $\mathrm{H_3LBr_2}$, **1** (Scheme 1). A single crystal X-ray diffraction study (see Supporting Information) shows that both cationic groups—amine NH$_2$ and imidazolium CH—form networks of hydrogen bonds through lattice bromide ions.

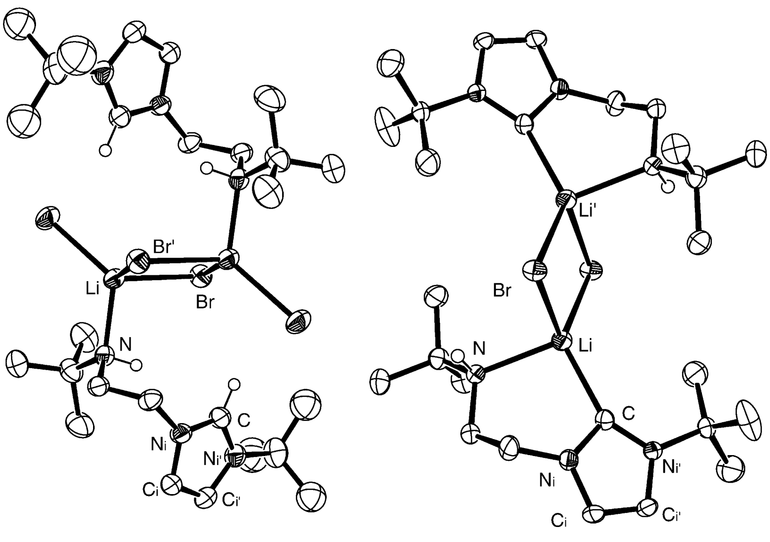
Complex **1** may be deprotonated in sequential steps: The reaction of **1** with an equivalent of lithium *n*-butyl affords the amine-imidazolium bromide H$_2$LBr. Removal of volatiles, and recrystallization from THF affords the LiBr adduct [LiBr(H$_2$LBr)] **2**. The reaction of **2** with a further equivalent of lithium *n*-butyl yields the lithium bromide adduct of the target amine–carbene [LiBr(HL)] **3**, Scheme 1. Whilst it is possible to crystallize salt-free H$_2$LBr from a solution of **2**, (see Supporting Information), the dative bonds from the amine and NHC in **3** bind to the Li cation; we could not displace the bound LiBr from **3** by trituration or other extraction procedures.

Figure 1 shows the structures of **2** and **3**. The molecular structures obtained for all three complexes, and the LiBr-free H$_2$LBr, show the typical change in C–N distance (increase) and ∢ NCN angle (decrease) of the unsaturated NCN fragment upon deprotonation, reflecting the increase in s character in the carbene lone pair.[9]



Scheme 1. Syntheses of complexes **1–4**

Lithium carbenes are extremely rare; in **3** the Li–C distance is longer than the 2.155 Å bond length measured in the only other simple lithium NHC adduct, $\mathrm{[Li\{C_5H_2(SiMe_3)_3\}\{C(N}t\mathrm{BuCH)_2\}]}$, and longer than the average Li–C$_{\mathrm{NHC}}$ distance of 2.162 Å (calculated by including bridging Li–C distances in the other two reported structures).[10] The *tert*-butyl groups of the two molecules of the dimer are geared with a short C–C closest distance of 3.91 Å (H···H separation = 2.41 Å), and although the [LiCN$_i$N$_{i'}$] fragment is planar, Li···N$_{i'}$ is shorter than Li···N$_{i'}$, which suggests the ligand is too large for the lithium cation. The geometry of the neutral chelate in **3** compares closely with the recently reported [PdCl$_2$(L′)] and [Rh(cod)(L′)][BF$_4$] (L′ = [1-{C(MesN(CHCH)N)-3-{CH=C(*t*Bu)NH*i*Pr]; Mes = 2,4,6-Me$_3$C$_6$H$_2$) complexes of a bidentate neutral imine–NHC [1-



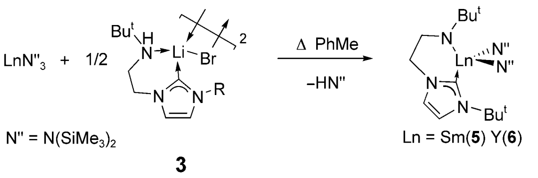
2 **3**

Figure 1. X-ray crystal structures of **2** and **3** (ORTEP, thermal ellipsoids set at the 50% probability level).

{C(MesN(CHCH)N)-3-{CH_2C(*t*Bu)=N*i*Pr], which tautomerizes to an enamine upon binding.[11]

To preclude salt incorporation, a mixture of **1** and two equivalents of potassium hydride was heated to reflux in THF for 12 h; filtration and removal of volatiles afforded the carbene–amine HL **4** in 86 % yield as a distillable yellow oil.

Transamination of the lithium carbene–amine **3** with [Sm{$(NSiMe_3)_2\}_3$] proceeded cleanly in toluene over 48 h to afford **5** [Eq (1)] with complete displacement of lithium bromide from the coordination sphere. No samarium bromide-containing complexes were found in the product mixture. After removal of the volatiles, dark yellow, very air-sensitive crystals of [Sm(L){$N(SiMe_3)_2\}_2$] **5** were isolated by recrystallization from diethyl ether, or by sublimation (140 °C, 10^{-3} mbar). The paramagnetism of the complex precludes ^{13}C NMR spectroscopic identification of the carbenoid carbon, but a carbene–samarium bond in solution is inferred from the absence of the carbene ^{13}C NMR spectral resonance, and strongly shifted CH backbone resonances of the heterocycle. Single crystals of **5** suitable for structural analysis were grown by sublimation; the structure is shown in Figure 2.



(1)

The geometry at the Sm ion is pseudo-tetrahedral, with one possible close contact with a silicon atom suggested by a Sm–Si distance of 3.3334(5) Å. The amido α-CH_2 group is also close to the metal at 2.918 Å. The Sm–$C_{carbene}$ distance of 2.588(2) Å is the shortest yet recorded, compared to the three published monodentate Sm–NHC complexes (av 2.76 Å, range 2.62–2.83 Å).[12] The Sm–$N_{silylamide}$ bonds (av 2.216(2) Å) are short (average for simple samarium amido derivatives = 2.37 Å; range 2.19–2.70 Å). The N-Sm-N angle between the two silylamides of 129° is wider than the tetrahedral angle measured in unconstrained four-coordinate Sm(III) silylamides (av 112.7°).[13]

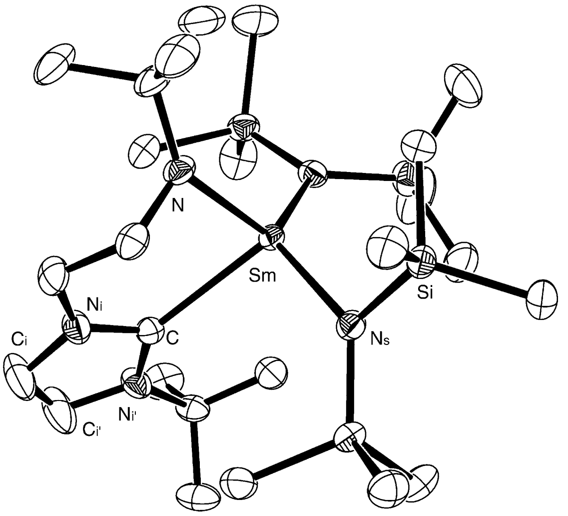


Figure 2. X-ray crystal structures of **5** (ORTEP, thermal ellipsoids set at the 50% probability level).

The long C–N distances and narrow ∢ NCN angle that were observed for **3** are again observed, but in this structure, the Sm-heterocycle fragment is almost completely planar and now symmetrically bifurcates the external N_i-C-$N_{i'}$ angle, which suggests the bite angle of this ligand is well-suited to the large cation.

The only isolable complex obtained from the reaction of the divalent compound [Sm{$(NSiMe_3)_2\}_2$] with **4** is the trivalent **5**, in a lower yield. We have yet to identify the byproducts arising from the oxidation of the Sm^{II} centre.

Compelling evidence of NHC binding in this system was obtained by the synthesis of the analogous f^0 yttrium complex. The complex [Y(L){$N(SiMe_3)_2\}_2$] **6**, made from [Y{$N(SiMe_3)_2\}_3$] by the same method as **5**, is isostructural (see Supporting Information) but the Y–$C_{carbene}$ distance is 2.501(5) Å. In NMR spectroscopic solution, the ^{13}C $C_{carbene}$ resonates at 186 ppm with a ^1J ^{89}Y–$C_{carbene}$ coupling of 54.7 Hz, larger than any $^1J_{YC}$ value reported for a σ-bound yttrium alkyl or an yttrium-NHC adduct.[14]

These are the first complexes that combine a metal–amide bond and a metal–NHC bond in a ligand. The strength of the metal–amide bond in **5** and **6** makes a controlled study of the reactivity of the electropositive metal–NHC fragment possible for the first time by precluding ligand redistribution processes that can complicate lanthanide coordination chemistry and allowing us to monitor the fate of both the metal cation and the nucleophilic NHC. It is suggested that the softness of the NHC makes it a poor donor for a lanthanide. A preliminary series of competition reactions of **6** with potential donor ligands was carried out to determine the lability of the NHC bond in this system: THF, diethyl ether, triphenylphosphane, and trimethylamine oxide are unreactive; tetramethylethlenediamine (TMEDA) and triphenylphosphane oxide successfully displace the NHC group and bind to the metal; the ^{13}C NMR spectra lose $^1J_{YC}$ coupling, and the latter solution NMR spectrum shows a ^{31}P chemical shift of 57 ppm, with $^2J_{PY}$ 6 Hz.

In summary, the first anionic, amido-functionalized *N*-heterocyclic-carbene ligand has been prepared and used to tether covalently the unusual σ-donor NHC group to an electropositive metal atom to afford new organolanthanide complexes. This has allowed the first systematic study of the lability of an early-metal–NHC moiety. The tethered, hemilabile carbene in these complexes may find use in catalysis, for example, as a new Lewis acid–Lewis base catalyst,[15] and a study of the reactivity of the metal-labilized NHC group is now in progress.

Experimental Section

CCDC-218135–218140 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).CCDC, codes. Selected characterizing data for **3**: Yield 77%. ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.17$ (9H, s, *t*Bu), 1.62 (9H, s, *t*Bu), 2.41 (2H, t, CH_2), 4.02 (2H, t, CH_2), 6.15 (1H, d, CH), 6.51 ppm (1H, d, CH); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 197$ ppm ($C_{carbene}$). Elemental analysis calcd (%) for $C_{13}H_{25}N_3LiBr$: C 50.33, H 8.12, N 13.54; found C 50.13, H 8.00, N 13.30.

4: Yield 86%.^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.95$ (9H, s, *t*Bu), 1.47 (9H, s, *t*Bu), 2.81 (2H, q, CH_2), 3.96 (2H, t, CH_2), 6.59 (1H, s, CH), 6.69 ppm (1H, s, CH); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 211.0$ ppm ($C_{carbene}$). Elemental analysis calcd (%) for $C_{13}H_{25}N_3$: C 69.91, H 11.28, N 18.81; found C 69.94, H 11.49, N 18.75.

5: Yield 20% ^{1}H NMR (300 MHz, C_6D_6): $\delta = -0.97$ (9H, s, *t*Bu), -0.29 (9H, s, *t*Bu), 0.13 (36H, s, 2 ($N(SiMe_3)_2$)), 3.97 (1H, s, CH), 5.2 (1H, s, CH), 6.42 (2H, br s, CH_2), 11.52 ppm (2H, br s, CH_2). Elemental analysis calcd (%) for $C_{25}H_{60}N_5Si_4Sm\cdot 2Et_2O$: C 47.09, H 7.18, N 8.32; found: C 33.59, H 6.79, N 8.08.

6: Yield 25%. ^{1}H NMR (300 MHz, C_6D_6): $\delta = -0.97$ (9H, s, *t*Bu), -0.29 (9H, s, *t*Bu), 0.13 (36H, s, ($N(SiMe_3)_2$)), 3.97 (1H, s, CH), 5.2 (1H, s, CH), 6.42 (2H, br s, CH_2), 11.52 ppm (2H, br s, CH_2); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 186.28$ ppm ($C_{carbene}$, $J_{C\text{-}Y}$ 53 Hz). Elemental analysis calcd (%) for $C_{25}H_{60}N_5Si_4Y.Et_2O$: C 49.32, H 8.56, N 9.92; found: C 43.32, H 8.71, N 9.64.

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