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Deprotonation of N-Heterocyclic Carbenes to Afford Heterobimetallic Organolanthanide Complexes

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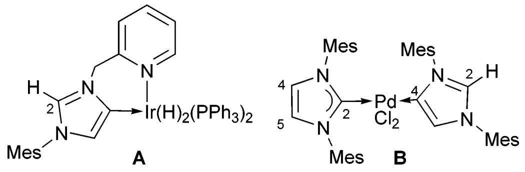
Amido-tethered N-heterocyclic carbene (NHC) lanthanide complexes, [Ln(L)N″$_2$] [L = *t*-BuNCH$_2$CH$_2${C(NCHCHN*t*-Bu)}; N″ = N(SiMe$_3$)$_2$; Ln = Y (**1**), Sm (**4**)], when treated with potassium naphthalenide, undergo regiospecific deprotonation at the NHC backbone to generate the Ln(III)−K(I) heterobimetallic complexes [N″$_2$Ln(L$^-$)K(DME)]$_2$ [Ln = Y (**2**), Sm (**5**); L$^-$ = the dianion *t*-BuNCH$_2$CH$_2${C(NCCHN*t*-Bu)}], which are the first examples of NHC ligands that C,C′-bridge two metals. For yttrium(III), which has a high reduction potential, it appears that reduction injects an electron into the heterocycle ring, thus priming the NHC for selective H atom abstraction. However, when complex **4**, which has a much lower and accessible reduction potential, is treated with potassium naphthalenide, a higher proportion of metal-centered reduction chemistry is observed; only a small percentage of **4** is reduced at the NHC, giving correspondingly much lower yields of **5**. Attempts to isolate the Sm(II) species observed in the reduction of **4** resulted in isolation of KN″ and **4**; the putative Sm(II) complex is apparently unstable with respect to disproportionation and ligand redistribution. Treatment of **1** with KC$_8$ affords no reaction; treatment of **4** with KC$_8$ affords [Sm(L)N″(μ-OCH$_3$)]$_2$ (**6**), a product of metal-mediated radical C−O activation and cleavage of the DME solvent. Compound **2** reacts quantitatively with Me$_3$SiCl to eliminate KCl and generate the complex [Ln(L′)N″$_2$] (**3**) [L′ = *t*-BuNCH$_2$CH$_2${C(NCSiMe$_3$CHN*t*-Bu)}]. The potassium-reduced NHC complex [K]$^+$[*t*-BuNHCH$_2$CH$_2${C(NCHCHN*t*-Bu)}]$^{\bullet-}$ (**7**) is also reported; **7** is the first chemically generated, stable NHC radical anion. Compounds **2**, **5**, and **6** have been characterized by X-ray crystallography, ^{1}H and ^{13}C NMR spectroscopy, and CHN microanalyses. Compound **3** has been characterized by ^{1}H and ^{13}C NMR spectroscopy, and compound **7** by EPR and ^{1}H NMR spectroscopy.

Introduction

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] Occasionally, this can result in 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, e.g., **A**, Chart 1.[2] It has also been predicted that the C4-NHC ligand is a stronger electron donor than a C2-NHC[3] and proposed that C4-bound derivatives, e.g., **B**, can function as better catalysts.[4] With the increasing use of NHCs to enhance early metal catalyst systems for reactions such as C−C bond formation and polymerization,[5] the behavior and occurrence of "wrong-carbene" adducts is now of widespread relevance and importance in homogeneous catalysis and small molecule reactivity.[6]

Chart 1



We have been studying the f-element chemistry of NHCs, using N-alkyl-functionalized amido and alkoxide substituents to stabilize σ-bound complexes such as **1** in Scheme 1.[7] The NHC group in these complexes brings a potentially reactive π-system proximal to the metal. Trivalent f-element cations have recently begun to show a rich small molecule activation chemistry when substituted 6π-heterocycles such as pyrroles and aromatic solvents are used to stabilize formally low-oxidation-state complexes.[8] We recently found that the alkoxide-functionalized NHC [$^-$OCMe$_2$CH$_2$(C{NCHCHN*i*-Pr})] al-

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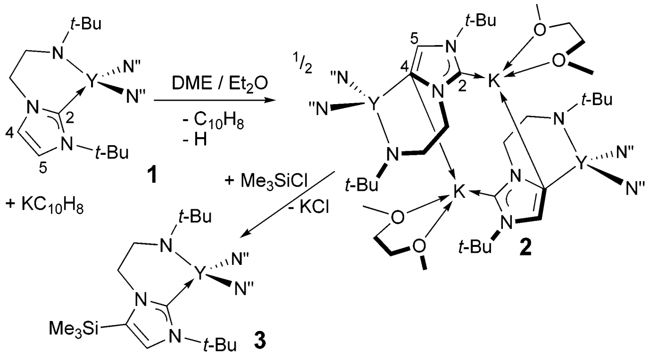
Scheme 1



lowed the synthesis of the first stable K(I)-NHC complexes (which normally decompose via a 1,2-alkyl rearrangement); the solid-state structure exhibits a range of electrostatic interactions between the potassium cation and the π-system of the heterocycle.[9] We were interested as to whether the NHC could bind K(I) solely as a 6π-electron heterocycle, in combination with an f-element complex, to stabilize f-element cations in unusual oxidation states or participate in the reductive activation of small molecules. Indeed, although the mechanism is still unclear,[10] it is suggested that the potassium K(I)/K(0) couple may be instrumental in the lanthanide-mediated dinitrogen reduction in the reaction between $[LnN''_3]$ ($N'' = N(SiMe_3)_2$) and potassium metal to afford $[\{N''_2(THF)Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$; this occurs for yttrium and lanthanides, which have yet to be isolated in the divalent state.

The combination of a π-heterocycle with the silylamide anion in **1** has led us to study the chemistry of Y(III) and the more easily reducible Sm(III). We report herein both reduction and C−H activation reactions that regiospecifically deprotonate the C4 backbone carbon of the ring to give the first carbene-carbanion-bridged heterobimetallic complexes, C−O bond activation of DME to give a methoxide complex, and the first stable, chemically generated radical anion NHC complex.

Results and Discussion

Treatment of the colorless amido-tethered NHC complex $[Y(L)N''_2]$ (**1**) with potassium naphthalenide in a DME/diethyl ether mixture at −78 °C affords an emerald green solution, which becomes dark red upon warming to room temperature, from which a colorless crystalline solid, **2**, can be isolated in good yield, Scheme 1. Complex **2** is characterized as the bimetallic dimer $[N''_2Y(L^-)K(DME)]_2$ by NMR spectroscopy, elemental analysis, and a single-crystal X-ray diffraction study; the molecular structure is shown in Figure 1.

Complex **2** is formally a product of deprotonation and, in addition, a migration of the C2-binding carbene from the yttrium(III) center to the incorporated potassium(I) cation. To the best of our knowledge, this is the first instance of a C,C-bridged NHC complex. A Ni(II) complex that is both C and N bound (as a carbene and an imidazolate) has been reported recently, formed from N-*tert*-butyl cleavage of the NHC.[11] The ^{13}C NMR resonances for C2 and C4 in **2** are observed at 199.2 and 167.5 ppm, respectively. These compare with shifts of 185.8 ppm for the C2 carbene carbon in **1**[7a] and 208.4 ppm for the only other thermally stable potassium-NHC complex, $[KOCMe_2CH_2(C\{NCHCHN\textit{i}\text{-}Pr\})]$.[9] The $^1J_{YC}$ coupling constant of 62 Hz is the largest reported to date and in line with those observed for the 2-metalated thiophene and furan, and terphenyl complexes $[Y(C_5Me_5)_2(2\text{-}SC_4H_3)(THF)_n]$ (E = S, $n = 1$, E = O, $n = 2$) and $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)_2(2\text{-}SC_4H_3)(THF)]$, and $[Y(dmp)Cl_2(THF)_3]$ (dmp = 2,6-dimesitylphenyl), respectively, which are low-coordinate and have anisotropic electron density at the bound carbon.[12]

X-ray crystallography reveals that **2** is dimeric in the solid state, residing over a crystallographic inversion center; selected bond lengths and angles in Table 1 are also compared with distances and angles measured for the samarium analogue **5** (vide infra). Each yttriate center is four-coordinate, N-bound to two N″ ligands, the amide N2 atom of the NHC tether, and the newly formed C4 carbanion of the NHC backbone. The Y1−C4 distance of 2.447(2) Å in **2** is significantly shorter than the Y−C2 distance in **1** of 2.501(5) Å and is at the short end of the Y−C single σ-bond range.[13] The NHC is bound, normally, via C2 to K1, and the C2-bound K−NHC moiety is essentially planar, exhibiting a K1−C2 distance of 2.954(2) Å, which is shorter than in the only other structurally characterized potassium NHC complex (mean $K-C_{carbene} = 3.048$ Å).[9] The potassium cation is five-coordinate with a close contact to a silyl methyl carbon atom (C20′), the O1 and O2 donor atoms of a coordinated DME molecule, and, more interestingly, an additional K−NHC interaction to C4′ of 3.182(2) Å, which enables the construction of the dimer. While the Y1−C4−K1′ angle is small (92°), the M−C4−centroid angle is 153° for Y and 112.3° for K. The C−N and C−C bond lengthening is insufficient to suggest a fully rehybridized sp^3 C4 carbon. In the crystal structure of the polymeric potassium carbene complex $[KOCMe_2CH_2(C\{NCHCHN\textit{i}\text{-}Pr\})]_8{\cdot}thf$,[9] three close contacts between the K(I) and other NHC ring carbons are within the sum of the potassium and carbon covalent radii; distances of 3.083(4), 3.135(5), and 3.161(4) Å compare with 3.182(2) Å here and a mean K−C distance of 3.10 Å in crystallographically characterized potassium cyclopentadienide complexes. The distance from K1 to the atoms adjacent to C4′ in the heterocycle are much longer: 3.831 Å to the other backbone carbon C5′ and 3.787 Å to the nitrogen N3′.

In a rational synthesis, treatment of **1** with methyl potassium at low temperature in diethyl ether, followed by addition of DME, affords **2** in 82% (higher) yield. A reductant could generate a base, e.g., KN″, from half of the starting material (with loss of the fragment [Y(L)N″]), which deprotonates C4 in **1**. However, this would in principle limit the maximum yield to 50%, and this is exceeded, albeit marginally. Also, **1** does

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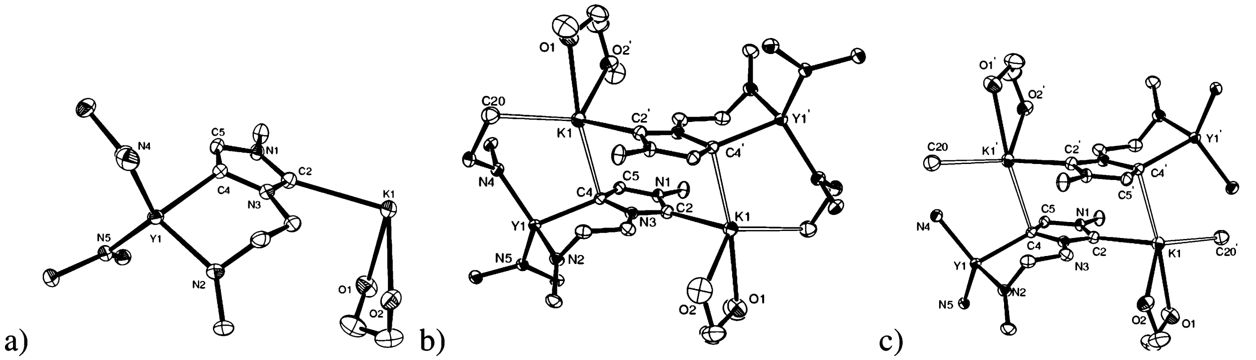


Figure 1. Thermal ellipsoid drawing of **2** (50% probability); the structure of **5** is essentially identical. (a) Half of the dimer; asymmetric unit (hydrogen and methyl groups omitted for clarity); (b) full dimeric molecule (hydrogen, CMe, and SiMe groups without close metal contacts omitted); and (c) core showing metals and closest bonding atoms/groups.

Table 1. Selected Distances (Å) and Angles (deg) for the Molecular Structures of 2 and the Samarium Analogue 5 (vide infra)

distance/angle	**2**, Ln = Y	**5**, Ln = Sm
Ln1-C4	2.447(2)	2.509(3)
K1−C2	2.954(2)	2.954(4)
K1−C4′	3.182(2)	3.173(3)
K1−C20′ (K1−C26′ for **5**)	3.225	3.232
Ln1−N2	2.1786(18)	2.220(3)
K1−N4	3.3550(19)	3.310(3)
N3−C2	1.365(3)	1.366(4)
N3−C4	1.421(3)	1.425(4)
N2−Ln1-C4	86.75(7)	84.83(10)
N3−C2−N1	101.85(18)	101.8(3)

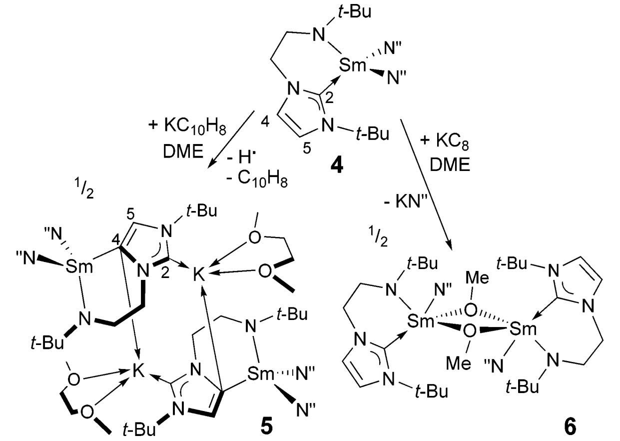
not react with KN″ until heated at reflux for 48 h, which yields only 5% **2** and decomposition products; we are currently investigating the mechanism of this reaction.

Treatment of **1** with KC_8 in THF, in a manner analogous to the reaction that affords $[\{N''_2(THF)Y\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$,[14] gave no reaction products. Repetition of this reaction in DME/diethyl ether afforded only **1**. The use of potassium/18-crown-6 mixtures instead of KC_8 also resulted in the recovery of **1** in good yield, but complete consumption of the crown, the ^{1}H NMR spectra indicating that ethoxide products had been formed instead (cf. **6**).

Complex **2** may be quenched with a variety of electrophiles; for example the reaction with Me_3SiCl in d_8-THF smoothly silylates the NHC backbone to afford $[Y(L')N''_2]$ (**3**) in quantitative yield, with concomitant elimination of KCl (there is no other soluble, diamagnetic species in the ^{1}H NMR spectrum of the reaction mixture), Scheme 1. The reaction is conveniently monitored by NMR spectroscopy; in the ^{13}C NMR spectrum the characteristic signal for the C2 carbon in **2** at 199.2 ppm is replaced by a signal at 172.73 ppm, which exhibits one-bond coupling to yttrium ($^1J_{YC} = 55.8$ Hz), and is indicative of "normal" coordination of the NHC to yttrium, as in **1**.

The isolation of **2** was surprising, but suggests the reaction is most likely proceeding through a regioselective deprotonation of the C4 hydrogen atom, mediated by either a base or a reductant. Therefore, the NHC ring presumably plays a noninnocent role in the reduction chemistry. Given that there is no literature precedent for a molecular Y(II) species, the assertion of noninnocence of the NHC is all the more credible, and we therefore investigated reduction chemistry with the much more easily reducible metal samarium, since metal-based reductive chemistry might be expected to be different from that of NHC-based reductive chemistry.

Scheme 2



The divalent oxidation state of samarium is readily accessible by treatment with potassium reductants; for example, the reaction of SmN''_3 with KC_8 affords the purple divalent $[KSmN''_3]$.[10,15] The reaction of $[Sm(L)N''_2]$ (**4**) with either $KC_{10}H_8$ or KC_8 affords a purple-colored solution, assumed to contain a Sm(II) complex, but from which no purple-colored complex could be isolated, Scheme 2. Interestingly, even in an ether solvent, the naphthalenide anion appears to stabilize a K-incorporated complex; this is presumed to be a precursor to the metalated $[N''_2Sm(L^-)K(DME)]_2$ (**5**) (isostructural with **2**; see Table 1 for selected bond lengths and angles), which is obtained in low yield after crystallization from hexane, analogously to **2**. However, KC_8 reduction appears to allow DME coordination to a divalent samarium complex, which loses K(I) more readily; a crude ^{1}H NMR spectra on freshly reduced **4** shows two separate N″ resonances (in a 1:1 ratio) consistent with formation of KN″ and [Sm(L)N″(DME)]; germane to this, the lanthanide silylamide complexes that reduce dinitrogen also eliminate KN″ as a byproduct.[10,14] Attempts to recrystallize the reduced product from nonpolar solvents afforded only pale-colored crystalline material identified as either KN″ or **4**, leaving the purple oil apparently unchanged but diminished in quantity. Apparently the putative divalent Sm complex is unstable with respect to ligand redistribution/disproportionation reactions, and this observation is in agreement with the fact that attempts to prepare Sm(II) amido-NHC complexes from divalent $[SmN''_2]_2$ give **4** as the only isolable product.[7a] Briefly heating a solution of the KC_8-reduced Sm species results in the purple solution instantaneously turning red, giving $[N''Sm(L)(\mu\text{-}OMe)]_2$, **6**, the

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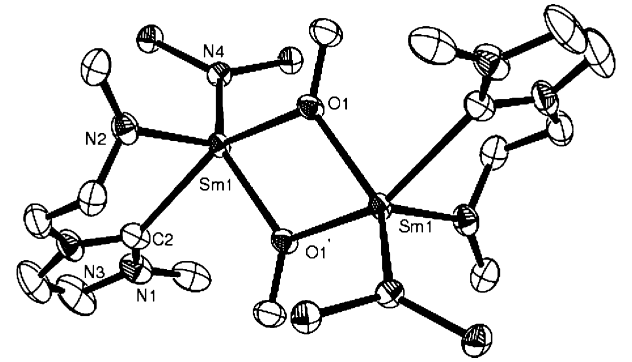


Figure 2. Thermal ellipsoid drawing of **6** (50% probability). Hydrogen, CMe, and SiMe groups are omitted for clarity.

Table 2. Selected Distances (Å) and Angles (deg) for 6

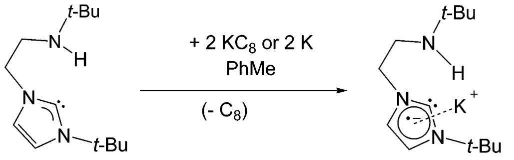
distance/angle	
Sm1−C2	2.682(3)
Sm1−N2	2.239(3)
Sm1−N4	2.401(2)
Sm1−O1, Sm1−O1′	2.349(2), 2.353(2)
Sm1− Sm1′	3.870
N2−Sm1−C2	80.68(10)
C11−N2−Sm1	105.6(2)
N3−C2	1.362(4)
N3−C4	1.386(5)
N3−C2−N1	103.3(3)

ether cleavage product, after workup.[16] Crystals of **6** suitable for a single-crystal X-ray diffraction study were grown from a hexane solution. The molecular structure is shown in Figure 2, and selected bond lengths and angles are in Table 2.

The structure of **6** is dimeric, constructed around a *transoid* Sm_2O_2 four-membered ring, which is strictly planar as a consequence of residing over a crystallographic inversion center. Each Sm is coordinated by two O atoms (O1 and O1′) of μ-methoxide ligands, the N4 atom of a N″ ligand, and the N2 and C2 atoms of the chelating amido-NHC ligand, adopting a distorted trigonal bypyramidal geometry such that C2 and O1 are axial. The Sm1−C2 bond length is 2.682(3) Å, which is longer than the Sm−NHC bond length of 2.588(2) Å in **4** (the shortest Sm−NHC bond length yet reported)[7a] and within the typical range of Sm−NHC bond lengths.[17] The Sm1−N2 bond length of 2.239(3) Å is shorter than the Sm1−N4 bond length of 2.401(2) Å, as befits the more electron rich nature of the dialkyl amide compared to the organosilicon-substituted amide; the Sm1−N4 bond length is well within the range of literature $\mathrm{Sm{-}N_{silylamide}}$ bond lengths (range 2.19−2.70 Å).[15,18] A close contact of Sm1 to C11 (the CH_2 group bound to N2) is suggested by a distance of 3.044 Å and an N2−Sm1−C11 angle of 105.6(2)°.

Thus the relative stability of the divalent oxidation state of samarium suggests that the electron resides more on the metal than on the NHC ring; this is reflected by the low yield of C4-deprotonated product **5** and supports the intermediacy of a one-electron-reduced NHC in the formation of **2**, since reduction of yttrium is unlikely.

Scheme 3



7

The question as to whether distinct NHC-based or metal-based reductive processes were occurring (or a combination), which lead to the selective deprotonation or ether cleavage, respectively, prompted us to investigate the reduction of the neutral parent amine-NHC, HL. Heating a mixture of HL and potassium to reflux in toluene results in a color change from yellow to dark red, forming a complex characterized as the stable radical anion of the ligand, $[\mathrm{K}]^+[t\text{-}\mathrm{BuNHCH_2CH_2\{C(NCHCHN}t\text{-}\mathrm{Bu)\}]^{\bullet-}}$ (**7**), Scheme 3.

While the free ligand HL shows no reaction with KN″, the reaction with potassium metal or potassium graphite in refluxing toluene affords a stable radical anion of the ligand, **7**, in about 50% yield, Scheme 3. To the best of our knowledge, this is the first stable radical anion of an NHC and the first to be chemically generated (rather than electrochemically generated).[19] The ^{1}H NMR spectrum of an in situ generated sample of **7** after 48 h reaction shows 50% unconverted starting material and two broadened resonances near 1 ppm attributed to the two *tert*-butyl groups, but no other features. There is some precipitated material, but the solution is very clean.

The EPR spectrum of **7**, Figure 3, is clearly resolved at room temperature in fluid solution in toluene. The spectrum is simulated by incorporating a coupling of the electron to a potassium cation (with a notably high hyperfine coupling constant for an organic radical-potassium complex, perhaps reflecting the absence of suitable donor solvents such as THF) and a symmetrical coupling to two nitrogen atoms and two hydrogen atoms. This indicates that the electron resides in the NHC π-system and is reminiscent of the potassium-pyrrole and potassium-permethylcyclopentadienide electrostatic π-bound fragments observed in reduced systems.[20] The fact that our previous attempts to isolate the potassium salt KL has resulted in decomposition via a 1,2 alkyl migration also supports the retention of the NH proton in the reduction.[9] In the recently reported radical anions of gallium and germylene NHC analogues $[\mathrm{Ge\{N}t\text{-}\mathrm{BuCH\}_2]^{\bullet-}}$ and $[\mathrm{P''_2Ga\{N}t\text{-}\mathrm{BuCH\}_2]^{\bullet-}}$ ($\mathrm{P''} = \mathrm{P(SiMe_3)_2}$) the radical resides on the C_2N_2 portion of the heterocycle.[21] Interestingly, a diradical is formed for the amido analogue $[\mathrm{N''_2Ga\{N}t\text{-}\mathrm{BuCH\}_2\text{-}(4\text{-}[GaN''Me\{N}t\text{-}\mathrm{BuCHCN}t\text{-}\mathrm{Bu\}_2])]^{2\bullet-}}$ (one electron residing on

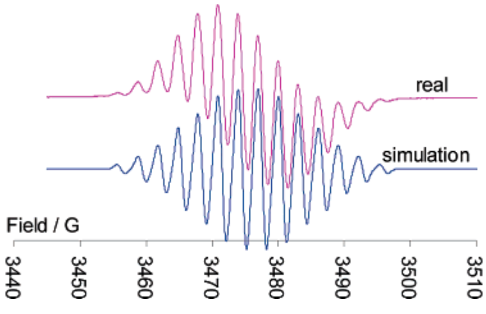


Figure 3. EPR spectrum (upper trace) of radical anion **7**. Simulated (lower trace) with $g_{\mathrm{iso}} = 2.004719$, $A_{\mathrm{K}} = 3.07$ G, $A_{\mathrm{N}} = 6.02$ G, and $A_{\mathrm{H}} = 3.27$ G.

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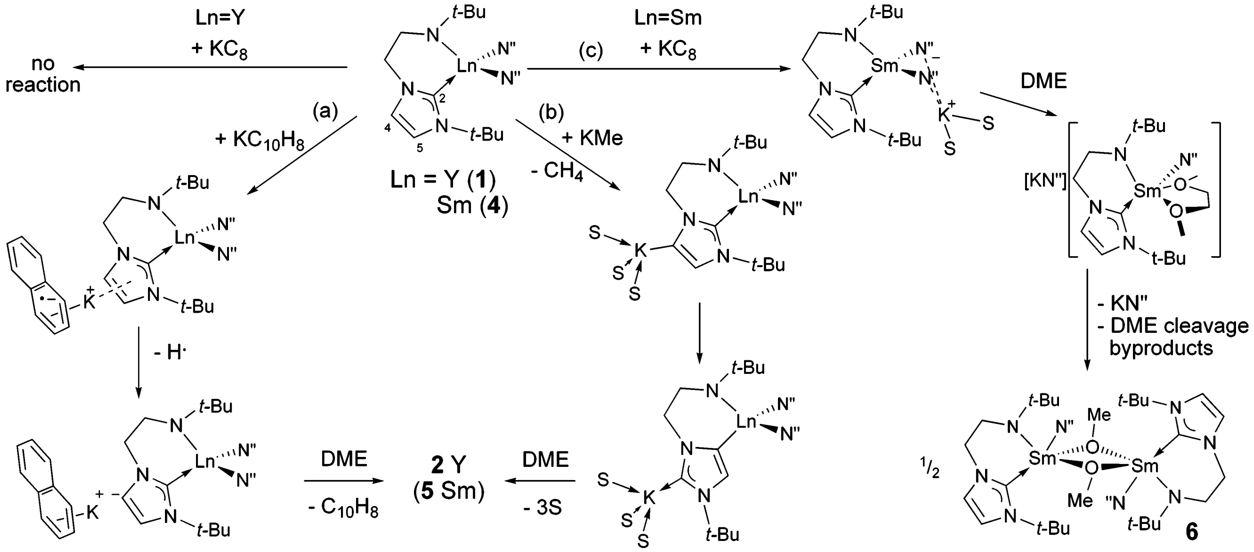
Scheme 4. Proposed Mechanistic Routes to 2, 5, and 6[a]



[a] S = ether solvent.

each of the two diazabutadiene fragments in the dimer) as a formal product of HN″ elimination from a gallium cation and the heterocycle C4 hydrogen, although greater spin densities on the backbone CHs of the heterocycles would be expected in these softer element systems.[22]

This result indicates that the NHC is capable of engaging in reduction chemistry and presumably allows a mechanism for the metal systems with high reduction potentials to undergo deprotonation chemistry at the NHC ring after the reduction. The C4 selectivity observed in this reduction-activated H elimination is supported by observations of charge separation across the heavier group 14 heterocycle analogues such as silylenes and germylenes.[21]

Observing the stability of **7**, we propose the mechanistic processes outlined in Scheme 4. For **1**, reduction with potassium naphthalenide facilitates reduction of the NHC ring, which is stabilized by naphthalene (route a). This primes the system for loss of H$^\bullet$ and rotation of the NHC unit, which is commensurate with the respective electronegativities of Y(III) and K(I) since the newly formed carbanion coordinates to the more electropositive Y(III), to afford the heterobimetallic system **2**. In the absence of stabilizing naphthalene no reduction occurs, presumably because the strongly nucleophilic NHC renders the Y center too electron rich, increasing the reduction potential for an already "unreducible" metal, and reduction of the bound NHC is disfavored in the absence of naphthalene. The selective deprotonation of the sterically most accessible H atom is most likely for the strongly basic, but solid reagent methyl potassium; a high isolated yield of **2** is obtained (route b). The yttrium complex **1** does not react significantly with KN″, indicating that if the potassium naphthalenide route to **2** also involves a selective C4 deprotonation, then potassium reductants generate a stronger base than KN″ in the formation of **2**. The complexes [Ln(L)N″$_2$] that we have studied to date (Y, Ce, Nd, Sm, and Eu) can be sublimed intact in moderate yield (10^{-5} mbar, ca. 200 °C) with poorer yields for the larger lanthanides, analogous to the sublimation yields of [LnN″$_3$].[23] We have not observed any fluxional processes for any of the complexes and measure only one yttrium−carbon coupling constant for **1**. We also find that prolonged heating of samples in deuterated solvents eventually results in decomposition to release HL, as identified by NMR spectroscopy, and we have not observed any deuterium-incorporated HL (we do not observe the NH group in the ^{1}H NMR spectrum).[24] This suggests that a mechanism involving dissociation of the NHC, H-migration from C4 to C2, and subsequent deprotonation at C2 is unlikely. For **4**, the same reduction process with potassium naphthalenide occurs to give **5**. However, since Sm is more easily reduced, metal reduction occurs as well, which directly competes with NHC reduction, and therefore drastically reduces the yield of **5** compared to **2**. Reduction of **4** with KC$_8$ gives a metal-reduced, ether-stabilized species, which, upon heating, follows a more traditional redox-mediated, ether-cleavage reaction to afford **6**.

Conclusions

The first chemically generated stable radical anion of an NHC has been characterized and is proposed to be involved in the reduction chemistry of NHC adducts of lanthanides with high reduction potentials. This reduction chemistry leads to selective deprotonation and syntheses of the first carbene-carbanion-bridged bimetallic complexes, and in contrast to the homoleptic silylamides, in no case is dinitrogen reduction observed. Further substitution chemistry of these complexes occurs cleanly and regioselectively. The more readily reduced Sm(III) cation competes with the NHC group for the reducing electron and forms reactive divalent complexes capable of cleaving DME by C−O activation. Work is in hand to develop bimetallic compounds of the bridging carbene that combine magnetically interesting metals.

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Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen. Hexane, toluene, diethyl ether, and THF were dried by passage through activated alumina towers and degassed before use. DME was distilled from potassium under an atmosphere of dry nitrogen. All solvents were stored over potassium mirrors (with the exception of THF and DME, which were stored over activated 4 Å molecular sieves). Deuterated solvents were distilled from potassium, degassed by three freeze−pump−thaw cycles, and stored under dinitrogen. Trimethylsilyl chloride was distilled from activated magnesium turnings, degassed by three freeze−pump−thaw cycles, and stored over copper under an atmosphere of dinitrogen. Potassium and naphthalene were purchased from Aldrich and used without further purification. The compounds $[LnN''_3]$ (Ln = Y, Sm),[23] $[HL\cdot 2LiBr]$, $[(L)Ln(N'')_2]$ (Ln = Y, Sm),[7a] KMe,[25] and KC_8[26] were prepared by published literature procedures.

^1H and $^{13}C\{^1H\}$ 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 $SiMe_4$. EPR spectra were recorded on a Bruker ESP 300E spectrometer and simulated using Bruker SimFonia version 1.25. Elemental microanalyses were carried out by Mr. Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK.

Preparation of $[N''_2Y(L^-)K(DME)]_2$ (2). Method a: DME (15 mL) and diethyl ether (15 mL) were added to a cold (−78 °C) mixture of **1** (1.26 g, 2.00 mmol), potassium (0.078 g, 2.00 mmol), and naphthalene (0.26 g, 2.00 mmol) to give a viscous emerald green solution. The mixture was allowed to warm to room temperature and stirred for 19 h, during which time it turned deep red. Volatiles were removed under reduced pressure to give a sticky red solid. Hexane (4 mL) was added and the mixture heated to give, upon cooling, **2** as a colorless crystalline solid, which was isolated by filtration. Storage of the mother liquor at 5 °C for 24 h gave a further crop of crystals of **2** suitable for an X-ray diffraction study. Combined yield: 0.79 g, 52%.

Method b: Precooled diethyl ether (30 mL, 0 °C) was added to a mixture of KMe (0.34 g, 6.00 mmol) and **1** (1.90 g, 3.00 mmol) with stirring. Gas evolution was observed immediately. The mixture was allowed to warm to room temperature with stirring over 17 h. Filtration (cannula), then stirring with an added portion of DME (5 mL) for 5 min, followed by removal of volatiles under reduced pressure, afforded an orange-yellow oil. This was washed with warm hexanes (5 mL), then dried under reduced pressure to afford 1.86 g of **2** (82%). Samples made by the two routes were confirmed to be the same compound by ^1H and ^{13}C NMR spectroscopy. Anal. Calcd for $C_{58}H_{138}K_2N_{10}O_4Si_8Y_2$: Y, 11.69; C, 45.82; H, 9.15; N, 9.21. Found: Y, 11.61; C, 40.29; H, 8.87; N, 8.49. Problems of incomplete combustion have been observed for **1** as well as related lanthanide organometallics.[7a] ^1H NMR (d_8-THF, 295 K): δ 0.10 (s, 72H, $SiMe_3$), 1.25 (s, 18H, *t*-Bu), 1.50 (s, 18H, *t*-Bu), 3.30 (s, 12H, OCH_3), 3.48 (s, 8H, OCH_2), 3.44 (m, 4H, CH_2), 4.25 (m, 4H, CH_2), and 6.60 (s, 2H, CH). $^{13}C\{^1H\}$ NMR (d_8-THF, 295 K): δ 5.23 ($SiMe_3$), 31.03 (*t*-Bu), 31.33 (*t*-Bu), 48.12 (CH_2), 53.07 (C), 53.66 (C), 57.45 (CH_2), 58.02 (OCH_3), 71.69 (OCH_2), 121.19 (CH), 167.52 (d, J_{YC} = 62.0 Hz, CY), and 199.22 ($C_{carbene}$).

Preparation of $[Y(L')N''_2]$ (3). In a glovebox, Me_3SiCl (0.013 mL, 0.10 mmol) was added to a solution of **2** (0.076 g, 0.10 mmol) in d_8-THF (0.55 mL) in a Young's tap NMR tube. The tube was sealed and shaken for 1 min, and the resulting KCl precipitate allowed to settle. The generation of $Y(L')N''_2$ (**3**) is quantitative by ^1H NMR spectroscopy. ^1H NMR (d_8-THF, 295 K): δ 0.07 (s, 36H, $SiMe_3$), 0.60 (s, 9H, $SiMe_3$), 1.20 (s, 9H, *t*-Bu), 1.66 (s, 9H, *t*-Bu), 3.44 (m, 2H, CH_2), 4.55 (m, 2H, CH_2), and 7.07 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (d_8-THF, 295 K): δ 4.60 ($=CSiMe_3$), 4.76 ($SiMe_3$), 31.30 (*t*-Bu), 31.50 (*t*-Bu), 47.51 (CH_2), 53.45 (C), 55.71 (C), 57.73 (CH_2), 127.33 (CH), 145.16 (CSi), and 172.73 (d, J_{YC} = 55.8 Hz, $C_{carbene}$).

Reaction of 1 with KN″. In a Young's tap NMR tube DME (0.50 mL) and C_6D_6 (0.05 mL) were added to a mixture of **1** (0.10 g, 0.16 mmol) and KN″ (0.032 g, 0.16 mmol). The pale yellow solution was heated to 90 °C for 48 h, during which time it became dark red. The tube was then cooled to room temperature, and NMR spectra were recorded. The resulting ^1H and $^{13}C\{^1H\}$ NMR spectra indicated a mixture predominantly of LH (∼85%), with minor amounts of **1** (∼10%) and **2** (∼5%). No evidence of deuterium incorporation into the NHC ring was observed in the NMR spectra.

Preparation of $[N''_2Sm(L^-)K(DME)]_2$ (5). DME (15 mL) and diethyl ether (15 mL) were added to a cold (−78 °C) mixture of **4** (2.08 g, 3.00 mmol), potassium (0.12 g, 3.00 mmol), and naphthalene (0.39 g, 3.00 mmol) to give a viscous emerald green solution, which rapidly became dark red upon warming to room temperature. Volatiles were removed under reduced pressure, and the resulting red oil was extracted into hexane (5 mL) and filtered. Storage at −30 °C afforded a small crop of yellow crystals of **5** suitable for an X-ray diffraction. Yield: 0.22 g, 9.0%. Crystals of **5** were contaminated with a red oil, which we could not separate by any method. Consequently we were unable to obtain accurate CHN microanalysis or NMR spectra that could be unambiguously interpreted.

Preparation of $[Sm(L)N''(\mu\text{-}OCH_3)]_2$ (6). A solution of **4** (2.08 g, 3.00 mmol) in DME/diethyl ether (5/5 mL) was dropwise to a cold (−78 °C) slurry of KC_8 (0.41 g, 3.00 mmol) in DME/diethyl ether (5/5 mL) to give a dark purple solution. The solution was allowed to warm to room temperature and stirred for 18 h. The solution was filtered and volatiles were removed under reduced pressure to give a purple oil. The oil was dissolved in toluene (5 mL) and briefly heated to boiling point, whereupon the solution turned red. The solution was cooled to room temperature, volatiles were removed under reduced pressure, and the resulting red oil was extracted into hexane (4 mL) and filtered. Storage at −30 °C afforded a crop of yellow crystals of $\mathbf{6}\cdot 1/2C_6H_{14}$ suitable for an X-ray diffraction study. Yield: 0.87 g, 25%. Anal. Calcd for $C_{40}H_{90}N_8Si_4Sm_2\cdot 1/2C_6H_{14}$: C, 44.09; H, 8.35; N, 9.57. Found: C, 42.90; H, 8.48; N, 9.47. ^1H NMR (d_6-benzene, 295 K): δ −0.86 (s, 18H, *t*-Bu), −0.20 (s, 18H, *t*-Bu), 0.23 (s, 36H, $SiMe_3$), 3.13 (s, 2H, CH_2), 3.16 (s, 6H, OCH_3), 4.11 (s, 2H, CH), 5.32 (s, 2H, CH), 6.55 (s, 2H, CH_2), 7.27 (s, 2H, CH_2), and 11.77 (s, br, 2H, CH_2).

Preparation of $[K]^+[t\text{-}BuNHCH_2CH_2\{C(NCHCHNt\text{-}Bu)\}]^{\bullet-}$ (7). Method a: In a Young's tap-equipped ampule toluene (4 mL) was added to HL (0.026 g, 0.116 mmol) and potassium (0.005 g, 0.128 mmol), and the mixture was heated to 100 °C for 20 h. An aliquot (0.4 mL) was removed and its EPR spectrum recorded. Another aliquot was removed, and its ^1H NMR spectrum recorded. Estimated yield (based on HL) = 50%. ^1H NMR (d_6-benzene, 295 K): δ 1.21 (br s, fwhm 60 Hz, 18H, *t*-Bu), 0.25 (br s, fwhm 60 Hz, 18H, *t*-Bu). The NH is never observed in the spectra of HL, and all other protons are assumed to be too close to the unpaired electron to be observed.

Method b: In a Young's tap-equipped ampule toluene (7 mL) was added to HL (0.050 g, 0.22 mmol) and KC_8 (0.033 g, 0.24 mmol), and the mixture was heated to 100 °C for 20 h. Estimated yield (based on HL) = 30%.

Method c: In a Young's tap-equipped ampule THF (25 mL) was added to HL (0.47 g, 2.10 mmol) and K (0.12 g, 3.07 mmol), and the mixture was heated to 70 °C for 5 days to afford a lemon yellow solution. Estimated yield (based on HL) = 10%.

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Table 3. Crystallographic Data for 2, 5, and 6

	2	**5**	**6**
formula	$C_{58}H_{138}K_2N_{10}O_4Si_8Y_2$	$C_{58}H_{138}K_2N_{10}O_4Si_8Sm_2$	$C_{40}H_{90}N_8O_2Si_4Sm_2 \cdot 1/2C_6H_{14}$
fw	1520.52	1643.40	1171.35
cryst size, mm	0.70 × 0.69 × 0.52	0.47 × 0.47 × 0.41	0.79 × 0.52 × 0.42
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2(1)/n$	$P2(1)/n$	$C2/c$
a, Å	12.8586(12)	12.897(2)	26.899(7)
b, Å	17.7064(17)	17.735(3)	11.136(3)
c, Å	19.2653(18)	19.302(3)	21.979(6)
β, deg	96.674(2)	96.474(2)	112.692(4)
V, Å^3	4356.6 (7)	4386.8(12)	6074(3)
Z	2	2	4
$\rho_{\mathrm{calcd},}$ g cm^{-3}	1.159	1.244	1.281
μ, mm^{-1}	1.573	1.571	2.029
no. of reflns measd	26 645	49 914	25 421
no. of unique reflns, R_{int}	9792	10 115	6935
no. of reflns with $F^2 > 2\sigma(F^2)$	7404	7815	4462
transmn coeff range	0.406−0.495	0.526−0.565	0.297−0.483
R, $R_w{}^a$ ($F^2 > 2\sigma$)	0.0366, 0.0892	0.0366, 0.0896	0.0298, 0.0680
R, $R_w{}^a$ (all data)	0.0595, 0.0978	0.0601, 0.1060	0.0536, 0.0739
S^a	1.005	1.102	0.948
no. of params	399	399	266
max., min. diff map, e Å^{-3}	+0.49, −1.14	+2.59, −1.37	+1.17, −0.55

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$; $S = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\text{no. data} - \text{no. params})]^{1/2}$ for all data.

EPR spectrum of **7** (X-band, modulation amplitude 1.0 G): fluid toluene, referenced to dpph, simulated with $g_{\mathrm{iso}} = 2.004719$. Spectral features simulated according to a hyperfine coupling to potassium, two nitrogen, and two hydrogen atoms, resolved as $A_K = 3.07$ G, $A_N = 6.02$ G, and $A_H = 3.27$ G, line width 1.1 G.

X-ray Crystallography. Crystal data for compounds **2**, **5**, and **6** are given in Table 3, and further details of the structure determinations are in the Supporting Information. Bond lengths and angles are listed in Tables 1 and 2. Crystals were examined on a Bruker AXS 1000 or APEX CCD area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). 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. Semiempirical 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. Crystals of **6** contained highly disordered hexane hemisolvent molecules, which were treated by the PLATON SQUEEZE procedure.[27] Programs were Bruker AXS SMART (control) and SAINT (integration)[28] and SHELXTL for structure solution, refinement, and molecular graphics.[29]

Acknowledgment. The authors thank the EPSRC (S.T.L., P.L.A.), the Nuffield Foundation, and the Royal Society for financial support.

Supporting Information Available: For **2**, **5**, and **6** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters in cif format. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

OM050895U

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