F-block N-heterocyclic carbene complexes

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N-Heterocyclic carbenes (NHCs) can bind as two-electron σ-donor ligands to lanthanide and actinide metal cations. In this review we summarise how the incorporation of an anionic group (alkoxide or amido), to form heterobidentate NHC ligands, allows the synthesis of a range of f-block NHC adducts. The tethering group also allows the lability of the NHC group, and its subsequent reactivity, to be studied. We include a brief survey of the known, structurally characterised f-element–NHC bond distances, and a range of substrates that react to displace the metal-bound NHC group.

Introduction

N-Heterocyclic carbene (NHC) ligands are heterocycles that bind as soft, two-electron σ-donors through the NCN carbon atom, and are now used widely as strongly basic phosphine analogues, to support late transition metal complexes.[1] The range of N-functionalised NHCs is expanding rapidly since a large number and range of homogeneous catalysts now rely on NHC-based supporting ligands for steric and electronic control. Increasingly, the strongly σ-basic NHCs find use as additives in homogeneous Lewis acidic, metal-catalysed processes.[2] In contrast to alkyl phosphines, carbenes are also recognised now as effective ligands for high oxidation state metal complexes.[3] However, very little chemistry of the electropositive metal–NHC fragment has been reported to date. We have been investigating the use of alkoxides, and alkylamides, linked to the NHC donor by a C_2 alkyl chain, to generate asymmetric, heterobidentate ligands, Chart 1, through which we can explore the NHC binding to f-block, and early metal cations.

The first lanthanide NHC complexes were isolated by Arduengo *et al*. in 1994, who synthesised the first lanthanide(II) and lanthanide(III) complexes.[4] Following the development of lanthanide–phosphine complexes such as $[M(Cp^*)_2(X)]$ ($Cp^* = C_5Me_5$, M = Eu, Yb; X = bis(dimethylphophino)methane, bis(dimethylphosphino)ethane),[5] they demonstrated the facile substitution of thf by the least bulky kinetically inert NHC, tetramethyl imidazol-2-ylidene, in lanthanocene complexes, to form **A**, Scheme 1, and that the addition of a second equivalent of NHC, allowed the isolation of a second adduct **B**.

The addition of an NHC to $[Eu(thd)_3]$ (thd = tetramethylheptanedioate), also affords **C**, Fig. 1.[4] The solid state X-ray crystal structures of both **B** and **C** indicate that the carbene is bound to the lanthanide and that the M–C bond is longer than in σ-bonded alkyl lanthanide complexes. In solution, the ^{13}C NMR spectrum of the yttrium(III) analogue contains a high frequency C_{cene} ($C_{carbene}$) resonance at 199 ppm, with a 33 Hz coupling constant to yttrium, indicating the carbene remains bound in solution and that the NHC does not dissociate on the NMR time scale (yttrium(III) is diamagnetic, ^{89}Y, I = ½,

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Polly L. Arnold obtained her DPhil in 1997 from the University of Sussex, supervised by Professor Geoff Cloke. She was awarded a Fulbright Scholarship for postdoctoral research with Professor Kit Cummins at MIT, and returned to the UK to take up a lectureship at the University of Nottingham in 1999. She held an EPSRC Advanced Research Fellowship between 2000 and 2005, and was promoted to Associate Professor this year. Her research is focused on the synthesis of lanthanide and actinide inorganometallic complexes, and the study of their bonding, small molecule activation chemistry, and catalytic applications.

Steve Liddle

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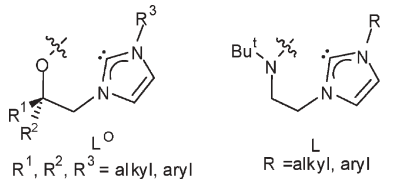
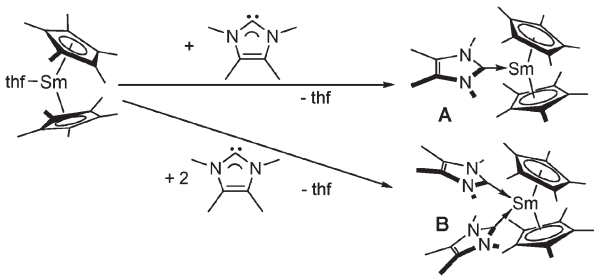


Chart 1



Scheme 1

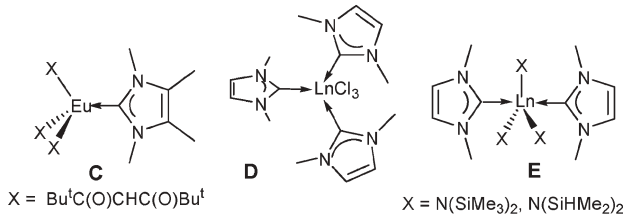


Fig. 1 Monodentate NHC adducts of trivalent lanthanide complexes.

100%). Solvent displacement reactions were also used to form lanthanide tris(silylamido) and halide adducts **D**, and **E**,[6] and ytterbocene derivatives.[7]

Two analogues of **A**, ligated by a bulkier NHC, $[Sm(Cp^*)_2(C\{NPr^iCMe\}_2)]$, and $[Sm(Cp^t)_2(C_3H_5)(C\{NPr^iCMe\}_2)]$, ($Cp^t = C_5H_4Bu^t$) have been studied as catalysts for methyl methacrylate and isoprene polymerisation, although it is unclear whether the NHC remains bound in the active catalyst species.[8]

More recently, the first organometallic uranyl complex, **F**,[9] Fig. 2, as well as monodentate NHC adducts have been reported for tri- and tetravalent uranium (**G**[10] and **H**[11]).

Salt elimination and protonolysis routes to metal–carbene complexes

Silver(I) NHC adducts of the form [Ag(NHC)]Cl are widely used as transmetallation agents for late metal NHC complexes, since the silver complexes are labile, but less air-sensitive than

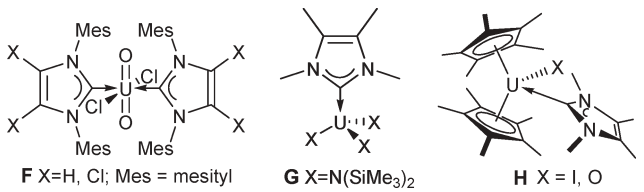
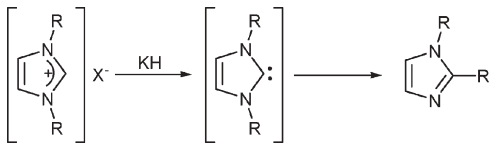


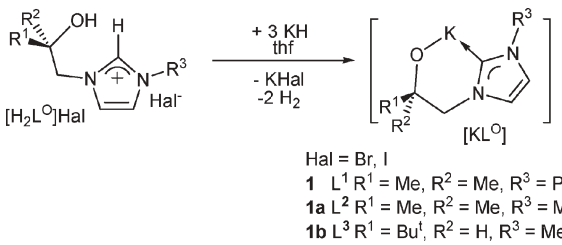
Fig. 2 Monodentate NHC adducts of uranium complexes.



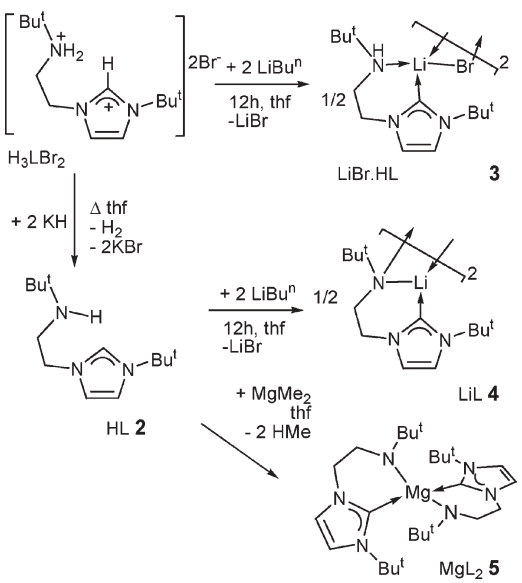
Scheme 2

the free carbene (although they are light sensitive).[12] However, more electropositive metals are less able to compete with the silver cation for the soft NHC, so silver carbene complexes have so far been unsuitable for the synthesis of early metal complexes. The deprotonation of an imidazolium salt, carbene precursor, at the C2 position, with a Group 1 base, which can form s-block adducts, is preferable. A few lithium(I) NHC complexes have been isolated as stable crystalline solids,[2a,13] and are now being shown to be effective and less costly transmetallation reagents than silver adducts. However, the isolation of heavier Group 1 metal-containing NHC complexes can be hindered by a 1,2-shift of the N-substituents, Scheme 2.[14]

The OH and NH functional groups of our functionalised ligands HL° and HL in Schemes 3 and 4, may be deprotonated to form s-block alkoxide or amido salts, respectively, in which the NHC group in the chelate ligand now binds as an additional solvating donor. The alkoxide adducts that we have characterised are generally monomeric, or highly fluxional



Scheme 3



Scheme 4

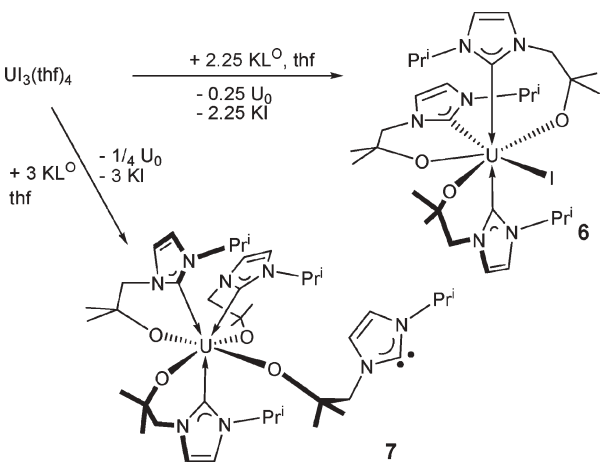
aggregates in benzene or thf solution, but crystallise as tetrameric alkoxide cubane clusters with bridging alkoxide vertices in the solid state.[15] The amido adducts are generally mono- or dimeric.[16]

The O-functionalised ligands make the isolation of potassium NHCs straightforward; complexes based on **1**,[15] Scheme 3, are thermally-, and relatively air-stable, reagents for salt elimination reactions to generate metal NHC complexes.

The N-functionalised NHC ligands, such as the aminocarbene **2**, are readily prepared by deprotonation of the ammonium imidazolium salt precursors, Scheme 4.[17] If the counterion in the salt precursor forms thf-soluble lithium salts (*i.e.* LiBr or LiI), then these salts are inevitably incorporated into the carbene ligand to form [LiBr·HL] **3**, Scheme 4. This is also observed for the L° ligand chemistry, for example the lithium tetramer $[LiI{\cdot}Li(L^{\circ})(OEt_2)]_2$ is isolated from the deprotonation of $[H_2L^{\circ}]I$ (R^1 = Bu^t, R^2 = H, R^3 = Pr^i) with lithium alkyl or lithium amide bases.[2a]

The salt free lithium amide $[Li(L)]_2$ **4**[16] forms a dimeric structure with a distorted metal–carbene bond, in spite of the presence of ether donor solvents, *vide infra*. It is extremely air-sensitive. The lithium salt **4**, as well as the salt-free, magnesium amido carbene complex $[Mg(L)_2]$ **5**[16] are excellent reagents for f-block chemistry.

Treatment of the potassium alkoxide **1** with $UI_3(thf)_4$ in thf affords a tetravalent uranium complex, regardless of stoichiometry, since U(IV) is a thermodynamic sink in this system. Thus the reaction using 2.25 equivalents of KL° affords the uranium iodide complex **6**, $[U(L^{\circ})_3I]$ as a dark golden-coloured powder, in excellent yield, Scheme 5.[18] The reaction with three equivalents of KL° affords an emerald green complex formulated as $[U(L^{\circ})_4]$, **7**,[18] isolated in good yield. Complex **6** is difficult to isolate as anything other than a powder, but **7** crystallises readily, even from crude reaction mixtures. This surprised us since it is the first example of a metal complex that contains a free NHC, to the best of our knowledge. The molecular structure is shown in Fig. 3. The ^{1}H NMR spectrum of **7** at room temperature contains only two very broad resonances of approximately equal intensity, centred at 17 ppm and −6 ppm.



Scheme 5

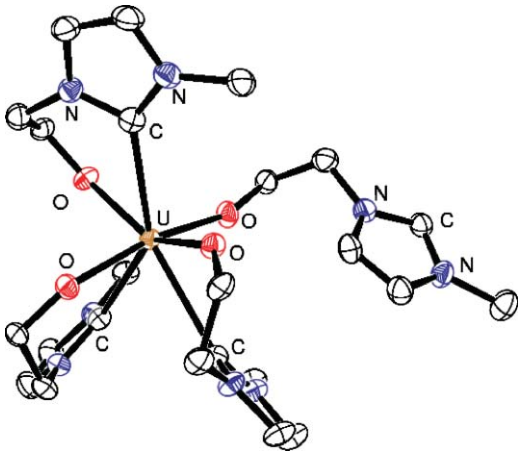


Fig. 3 Thermal ellipsoid drawing of **7** (50% probability).

Cooling a d_8-toluene solution of **7** to 228 K demonstrates that this is due to a dynamic equilibrium process, and at 228 K, the sharp ^{1}H NMR spectrum anticipated for a U(IV) complex is observed. The fluxional process is associated with a large change in proton chemical shifts, assumed to be the exchange of free- for uranium-coordinated NHC groups.

The alkoxide **1** also reacts with uranyl dichloride $[UO_2Cl_2(thf)_2]_2$ to afford orange $[UO_2(L^{\circ})_2]$ **8**,[19] whilst the amide **4** affords red $[UO_2(L)_2]$ **9**, Fig. 4.[16]

Metathesis reactions between **4** and half an equivalent of $[CeI_3(thf)_4]$, or $CeCl_3$, in ethereal or aromatic solvents, were also attempted. However, in all instances only variable quantities of **2** were recovered, along with intractable halide-containing and imidazolium products.[20]

The *in situ* reaction at low temperature (−78 °C) of KMe with **2**, then addition of this to half an equivalent of $[CeI_3(thf)_4]$ in diethyl ether–DME, was also carried out with the aim of preparing $[Ce(L)_2I]$. However, following work-up a dark red solution was obtained, from which only crystals of the cerium reagent could be isolated, and in low yield.[20]

The imidazolium proton, and the alcohol and amino protons are all sufficiently acidic that the monoprotonated proligands HL° and HL can also be used in acid–base reactions to make f-block functionalised-NHC adducts.

Transamination of the lithium bromide carbene-amine **3** with $[Sm(N'')_3]$ [N″ = $N(SiMe_3)_2$] proceeds cleanly to afford $[Sm(L)(N'')_2]$ **10**, Scheme 6, as dark yellow, very air-sensitive crystals.[17] The LiBr adduct gives better product yields than the free base; no lithium or bromide ions remain in the coordination sphere of the lanthanide metal, and no samarium bromide-containing complexes were found in the product mixture.

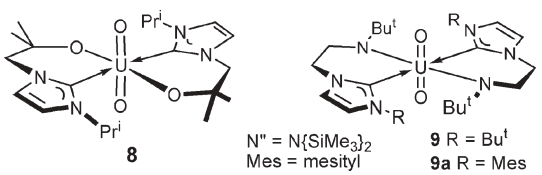
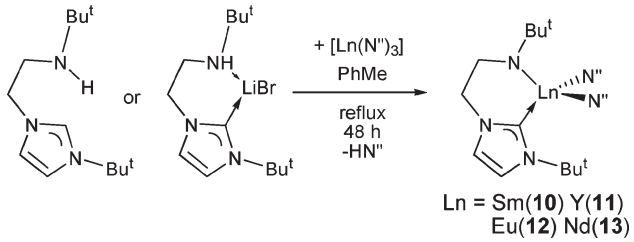


Fig. 4 Uranyl amido-carbene adducts.



Scheme 6

The crystals may be isolated by recrystallisation 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.

The Y(III) analogue **11** is colourless and has a very large $^{1}J_{YC}$ coupling constant, of 54.7 Hz. The Ln–C_{cene} bond distances are shorter than those of the monodentate Ln–NHC adducts reported, and at the short end of normal two-electron σ-alkyl bonds. The molecular structure of **10** is shown in Fig. 5. The Y(III) **11**,[17] Eu(III) **12**[21] and Nd(III) **13**[22] analogues have also been isolated, although the larger Nd(III) centre renders the complex **13** significantly more air-sensitive, and they are all isomorphous with **10**.

We were keen to extend this chemistry to cerium, since no Ce(III)–NHC complexes had been reported at that time. Reaction of one equivalent of **3** with [Ce(N″)$_3$] in toluene, Scheme 7, affords a sticky yellow solid which we anticipated would be [Ce(L)(N″)$_2$] **14**. On all except one occasion, we have isolated yellow, crystalline **14**.[20]

However, once, a bright yellow microcrystalline solid was isolated in moderate yield, and characterised as [Ce(L)(N″)(μ-Br)]$_2$ **15**, Scheme 7.[20] Complex **15** is the result of a ligand exchange reaction between the LiBr, provided by **3**, and compound **14**.

The isolation of **15** was unexpected but, despite varied reaction conditions, all subsequent attempts to make **15** have generated **14**. However, the reaction of LiI with **14** (Scheme 7) in toluene at 80 °C affords, after work-up, a bright yellow microcrystalline solid which is insoluble in diethyl ether again, and characterised as **16**.[20]

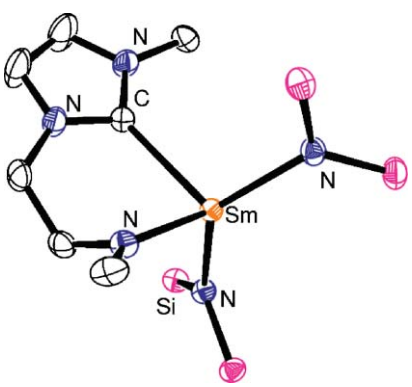
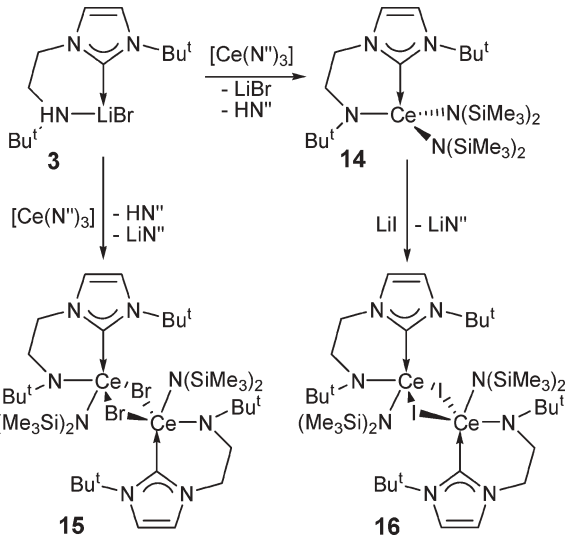


Fig. 5 Thermal ellipsoid drawing of **10** (50% probability).



Scheme 7

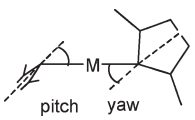
Compounds **15** and **16** are synthetically more desirable than **14** since they provide access to more straightforward metathesis salt-elimination chemistry. Unfortunately, these two amide–halide exchange reactions are somewhat capricious, although scrupulously removing thf shuts down the amide–halide exchange. The neodymium system **13** is also susceptible to amide–halide exchange, but to a much lesser extent than cerium.

The isolation of **15** and **16** is notable on two counts: Firstly, in our laboratory we have never observed any evidence for ligand exchange reactions in the later lanthanide complexes, and yields are typically excellent (>85%). Presumably the Lewis acidity of Ce (and Nd), which is less than that of Y, Sm, and Eu, is such that Li, which is exceptionally Lewis acidic, can compete for the amide ligand; secondly, heteroleptic lanthanide complexes of the type [LnLL′L″] are far rarer than complexes of the type [LnLL′$_2$], and are usually restricted to the heavier, and smaller, lanthanides.

Distorted geometries in the metal–carbene bonding

Interestingly, in the solid-state structure of **1**,[15] the carbene heterocycles display a wide range of K–CN_2 geometries other than the anticipated trigonal planar carbon. The range of pitch angles, measured as the vertical angle between M–C and the NCN plane are between 9 and 52°, Fig. 6, distortions previously unseen in late metal carbene complexes.

The lithium NHC complex **4**,[16] which crystallises as a dimer with a *transoid* [LiN_{amide}]$_2$ core has a very distorted Li–CN_2 shape. However, the lithium–carbene bonds are significantly shorter than the non-distorted magnesium–carbene distances in **5**.[16] These data are summarised in Fig. 7.



metal:	K4	K5	K8	K3	K6	K1	K2	K7
pitch(°):	9	13	17	21	36	41	43	52
yaw(°):	5	7	3	7	6	10	7	12
M-C(Å):	3.16	3.07	3.06	3.13	2.95	2.98	3.05	2.99

Fig. 6 Potassium carbene fragments in the structure of **1**: metrics ordered by pitch angle.

complex:	4	5	9	9a
pitch (°):	18	2	23	9
	20	4		
yaw (°):	20	10	17	3
	22	11		

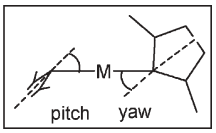


Fig. 7 Measured pitch and yaw angles of M–CN_2C_2 fragments of **4**, **5**, **9** and **9a** (°).

As part of our studies of the complexation of NHCs to d^0 metals, we have made uranyl NHC complexes **9** and **9a**, Fig. 4, with two amido-NHC ligands which differ only in that one is *N-tert*-butyl functionalised (L), whereas the other is *N*-mesityl functionalised (L^{Mes}), Fig. 8.

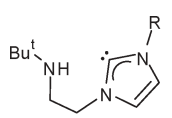
Treatment of $[UO_2Cl_2(thf)_2]$ with two equivalents of **4** (or treatment of $[UO_2(N'')_2(thf)_2]$ with two equivalents of **2**) affords red $[UO_2(L)_2]$ **9**, *vide supra*. The *N*-mesityl salt $[UO_2(L^{Mes})_2]$ **9a** was also made, from the reaction of two equivalents of $[Li(L^{Mes})]$ and $[UO_2Cl_2(thf)_2]$.[16]

Crystallographic analyses of **9** and **9a** show that the *tert*-butyl substituted ligand is too large to fit around the equatorial belt of the linear, axial uranyl cation, but the more planar mesityl ligands can pack more effectively. Thus the metal–carbene MCN_2 group is significantly more distorted in the former, **9,** than in the latter, **9a**. However, the metal–carbene distances are all 2.64 Å (within standard uncertainty) in **9** and **9a**, and also in the monodentate NHC adduct $[UO_2Cl_2\{C(NMesCH)_2\}_2]$ (**F**).[9]

The stretching vibration of the linear UO_2^{2+} cation is a more sensitive indicator than the U=O bond length, of the strength of the equatorial ligand set. In the FTIR spectra, the asymmetric UO_2 ν_3 stretches are essentially identical, identified as **9** = 929 cm^{-1} and **9a** = 933 cm^{-1}.

To summarise, the differences in carbene distortion, but similarities in U–C length and UO_2 vibrations of the two uranyl complexes **9** suggest that the NHC group can bend to form distorted metal–NHCs for these electropositive metals, without reducing the strength of the electrostatic bonding interaction.

We note that complex **B**[4] has the largest M–carbene distortion for Sm–NHC complexes with a pitch angle of 21.4°, **C** has the largest deviation of Eu–NHC complexes with a pitch and yaw of 2.5 and 9.7° and $[Y\{N(SiHMe_2)_2\}_3\{C(NMeCH)_2\}_2]$ has the largest deviation of Y–NHC complexes with a pitch and yaw of 9.3 and 0.9°.[6] One monodentate NHC adduct $[Y(N'')_3\{C(NMeCH)_2\}]$ displays a deviation of 8°,[6] but the complex also contains agostic interactions that could have contributed to the asymmetry in the structure. We also measured an 8° angle in the complex **11**, and note that the lithium alkoxy-carbene $[Li\{OCHBu^tCH_2(1\text{-}CNCHCHNBu^t)\}\cdot LiI]_2$ which also has a flexible C2-alkyl backbone, has a very short Li–C distance, 2.135 Å, and a yaw of 19°.[2a]



HL R = Bu^t,
HL^{Mes} R = mesityl

Fig. 8 Amino carbenes.

Table 1 contains a list of M–C_{cene} distances for crystallographically characterised f-element NHC complexes and the ^{13}C chemical shifts of the carbene carbon for diamagnetic complexes. Although direct comparisons are difficult to make as the tabulated complexes exhibit different coordination numbers, and the ancillary ligands all have different steric requirements, it is clear that the use of an anionic tether results in a more tightly bound carbene, and that the M–NHC bond distances fall within the range of corresponding M–alkyl bonds.

Labilisation reactions of the carbene

The strength of the metal–amide or –alkoxide bond in complexes such as ours makes a controlled study of the reactivity of the electropositive metal–NHC fragment possible, precluding ligand redistribution processes that can complicate lanthanide coordination chemistry, and allows us to monitor the fate of both the metal cation and the nucleophilic NHC. A series of competition reactions of **11** with potential donor ligands was carried out, exemplified by Scheme 8.[17] The f^0 yttrium complex, which displays a large $^1J_{YC}$ coupling constant, is the easiest complex with which to test this reactivity. Table 2 lists a selection of substrates that do or do not react to displace the NHC group from the metal, in a d_6-benzene NMR spectral solution, at room temperature.

The first lanthanide–NHC complexes were prepared by displacement of ether solvents by strongly basic and nucleophilic NHCs;[4] it is therefore not surprising to observe that thf and diethyl ether fail to displace the NHC in **11**. Somewhat surprising, however, is the observation that dme fails to displace the NHC in **11** even though it has the potential to form a strong chelate. This contrasts to the reaction with tmeda which does displace the NHC (δ_{cene} 211 ppm), which is commensurate with the greater basicity of the N-centres compared to the O-centres in dme. Triphenylphosphine and trimethylamine oxide fail to displace the NHC. However, triphenylphosphine oxide does successfully displace the NHC, Scheme 8,[17] and this is conveniently monitored by NMR spectroscopy; the ^{13}C NMR spectrum loses the doublet resonance for the carbene which is replaced by a singlet resonance consistent with a pendant NHC (δ_{cene} 210 ppm) and the ^{31}P NMR spectrum exhibits a doublet resonance ($^2J_{PY}$ = 6 Hz) at 57 ppm. Reaction of **11** with $BH_3{\cdot}SMe_2$ proceeds analogously to **7** (see below) as confirmed by the collapse of the carbene resonance due to coupling to the quadrupolar boron centre. However, steric factors are clearly important since the corresponding reaction with BPh_3 fails to displace the carbene from yttrium. Interested in the C(II)–C(IV) couple of the carbene we investigated reactions with azides to see if oxidative addition at the carbene centre would occur (with concomitant elimination of dinitrogen). However, Me_3SiN_3 forms the adduct $[Y(L)(N'')_2(N_3SiMe_3)]$ as evidenced by the ^{13}C NMR spectrum (δ_{cene} 192 ppm, $^1J_{YC}$ = 42 Hz) and adamantyl azide fails to coordinate (presumably for steric reasons). Triphenylphosphine sulfide is desulfurised by **11** and the carbene centre is converted to the corresponding thione as

Table 1 Metal–NHC M–C bond lengths in structurally characterised f-block NHC adducts; C_{cene} chemical shifts and $^1J_{YC}$ coupling constants included where relevant[a]

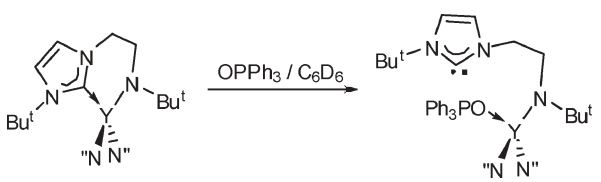
Compound	M–C_{cene} bond length/Å	^{13}C δ/ppm, J_{YC}/Hz	No. (this article)	Lit. ref.
$[Ce(L)(N'')_2]$	2.670(2)		**14**	20
$[Ce(L)(N'')(\mu\text{-Br})]_2$	2.699(2)		**15**	20
$[Ce(L)(N'')(\mu\text{-I})]_2$	2.700(3)		**16**	20
$[Ce(L')(N'')(\mu\text{-I})]_2$	2.728(8)		**26**	22
$[Nd(L)(N'')_2]$	2.609(3)		**13**	22
$[Nd(L')(N'')_2]$	2.648(3)		**27**	22
$[Nd(L')(N'')(\mu\text{-I})]_2$	2.656(5)		**25**	22
$[Nd(L')(N'')(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}N_3)]_2$	2.672(3)		**28**	22
$[Sm(L)(N'')_2]$	2.579(2)		**10**	17
$[Sm(L)(N'')(\mu\text{-}OCH_3)]_2$	2.682(3)		**23**	26
$[Eu(L)(N'')_2]$	2.562(3)		**12**	21
$[Y(L)(N'')_2]$	2.501(5)	185.8, 55	**11**	17
$[Y(\mu\text{-}L^-)(N'')(\mu\text{-}N'')K(dme)]_2$	2.447(2)*	167.5,[a] 62; 199.2	**20**	26
$[Sm(\mu\text{-}L^-)(N'')(\mu\text{-}N'')K(dme)]_2$	2.509(3)*		**22**	26
$[UO_2(L)_2]$	2.640(5)	263	**9**	16
$[UO_2(L^{Mes})_2]$	2.633(7)	NR	**9a**	16
$[U(L^\circ)_4]$	2.740 (av)		**7**	18
$[U(L^\circ)_3(L^\circ\text{-}BH_3)]$	2.740 (av)		**17**	18
$[Ce(Cp^*)_2I\{C(NMeCMe)_2\}]$	2.724(4)			11*a*
$[Ce(C_5H_4Bu^t)_3\{C(NMeCMe)_2\}]$	2.797(4)			11*a*
$[Sm(Cp^*)_2\{C(NMeCMe)_2\}_2]$	2.837(7), 2.845(7)		**B**	4
$[Sm(Cp^*)_2\{C(NPr^iCMe)_2\}]$	2.782(3)			8*a*
$[Sm(C_5H_4Bu^t)_2Cl\{C(NPr^iCMe)_2\}]$	2.62(2)			8*b*
$[Eu(thd)_3\{C(NMeCMe)_2\}]$	2.663(4)	46.5	**C**	4
$[Yb(C_5Me_4Et)_2\{C(NMeCMe)_2\}]$	2.552(4)	205		7*a*
$[Yb(C_5H_3Bu^t{}_2)_2\{C(NMeCMe)_2\}]$	2.598(3)	201.8		7*b*
$[Y\{N(SiHMe_2)_2\}_3\{C(NMeCH)_2\}]$	2.560(9), 2.55(1)	190.3, 49.6	**E**	6
$[Y\{N(SiHMe_2)_2\}_3\{C(NMeCH)_2\}_2]$	2.648(8), 2.671(9)	194.0, NR	**E**	6
$[UO_2Cl_2\{C(NMesCH)_2\}_2]$	2.626(7)		**F**	9
$[UO_2Cl_2\{C(NMesCCl)_2\}_2]$	2.609(4)		**F**	9
$[U(N'')_3\{C(NMeCMe)_2\}]$	2.672(5)		**G**	10
$[U\{tacn(OAr)_3\}\{C(NMeCMe)_2\}]$	2.789(14)			10
$[U(Cp^*)_2I\{C(NMeCMe)_2\}]$	2.687(5)		**H**	11*a*
$[U(C_5H_4Bu^t)_3\{C(NMeCMe)_2\}]$	2.768(5)			11*a*
$[UCl_4(NC_5H_3\text{-}2,6\text{-}\{CNC_2H_2N(2,6\text{-}Pr^i{}_2C_6H_3)\}_2)]$	2.573(5), 2.587(5)			43
$[U(Cp^*)_2(O)\{C(NMeCMe)_2\}]$	2.636(9)		**H**	11*b*

[a] * = carbanion, dme = dimethoxyethane, tacn = triazacyclononane, Mes = mesityl, NR = not reported, av = average.

evidenced by NMR spectroscopy; the formation of triphenylphosphine is confirmed in the ^{31}P spectrum and the doublet carbene resonance is lost in the ^{13}C spectrum. Propylene sulfide and *tert*-butyl isonitrile do not react with the carbene at room temperature and heating solutions results in oligomerisation/polymerisation of these substrates. The addition of D,L-lactide to **11** results in rapid ring-opening of the cyclic ester and polymerisation by **11**, which acts as a bifunctional catalyst.[23]

Treatment of the U(IV) complex **7**, which already has one free NHC group, with Lewis acids or 16 valence electron organometallic fragments generates complexes which no longer display any dynamic processes on the ^1H NMR spectral time scale.

The reaction of **7** with the borane $BH_3{\cdot}SMe_2$ affords the green borane adduct, $[U(L^\circ)_3(L^\circ{\cdot}BH_3)]$ **17**[18], Scheme 9. The

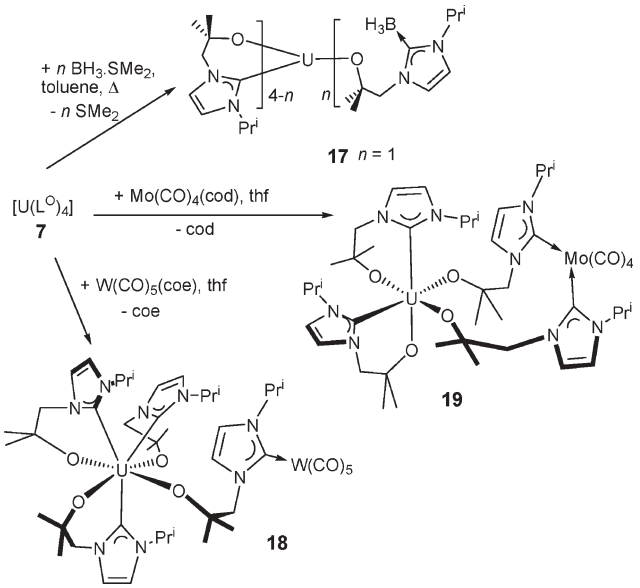


Scheme 8

Table 2 Substrates studied as potential competitor ligands with the metal-coordinated NHC group in **11** (published data are in reference 17 unless otherwise indicated)

Substrate	Displaces NHC?	Observation
thf	N	
Diethyl ether	N	
Triphenylphosphine	N	
Tetramethylethylenediamine (tmeda)	Y	tmeda adduct formed
Trimethylamine oxide	N	
Triphenylphosphine oxide	Y	Phosphine oxide adduct formed
D,L-Lactide	Y	Rapid polymerisation to afford polylactic acid[23]
BH_3	Y	J_{YC} lost due to quadrupolar B[a]
BPh_3	N	No reaction[a]
Me_3SiN_3	N	Azide adduct formed[a]
AdN_3	N	No reaction[a]
CO	N	No reaction[a]
NO	N	No reaction[a]
CO_2	Y	Intractable oil in NMR tube[a]
S_8	Y	Thione formed[a]
$Ph_3P{=}S$	Y	Thione formed[a]
Propylene sulfide	N	Polymerisation of sulfide[a]
Bu^tNC	N	Cyclisation of isonitrile[a]
$[W(CO)_5(coe)]$	Y	Forms a benzene-insoluble oil + free coe in solution[a]

[a] Unpublished results.



Scheme 9

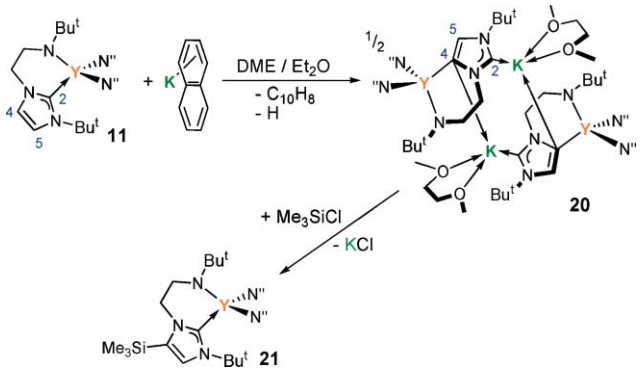
reaction is essentially quantitative, and there is no evidence of SMe_2 incorporation. Furthermore, up to four equivalents of $BH_3{\cdot}SMe_2$ may be consumed by **7**. Treatment of **7** with one equivalent of [W(coe)$(CO)_5$] (coe = cyclo-octene) results in the liberation of coe and the formation of a compound formulated as the eighteen-electron tungsten complex [U$(L^\circ)_3$(μ-L°)W$(CO)_5$] **18**, Scheme 9.[18] Similarly, **7** reacts with one equivalent of [Mo(cod)$(CO)_4$] (cod = cyclo-octadiene) to afford a poorly soluble product formulated as the eighteen-electron molybdenum complex [U$(L^\circ)_2$(μ-L°)$_2$Mo$(CO)_4$] **19**, Scheme 9.[18]

Backbone reactions of the carbene

Regioselective C4 C–H activation/deprotonation

The use of a σ-bound, amido-tethered NHC group in complexes **10** and **11** brings a potentially reactive 6e π-system proximal to the lanthanide metal centre; trivalent f-element cations have recently begun to show a rich small molecule activation chemistry when substituted 6e π-heterocycles such as pyrroles and aromatic solvents are used to stabilise low-oxidation state complexes.[24] Since the solid-state structure of **1** exhibits a range of electrostatic interactions between the potassium cation and the π-system of the heterocycle,[15] 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, in order to stabilise f-element cations in low oxidation states, or to participate in the reductive activation of small molecules such as dinitrogen. Indeed, it is suggested that the potassium K(I)/K(0) couple may be instrumental in the lanthanide-mediated dinitrogen reduction in the reaction between [Ln$(N'')_3$] and potassium metal to afford [{Ln$(N'')_2$(thf)}$_2$(μ-η^2:η^2-N_2)]; this occurs for yttrium and lanthanides which have yet to be isolated in the divalent state.[25]

The combination of a π-heterocycle with the silylamide anion in **10** and **11** led us to study the chemistry of Y(III), and



Scheme 10

the more easily reducible Sm(III) with reductants. We found that neither low oxidation state, nor dinitrogen reduced compounds, were obtained. Instead, regioselective deprotonation at the C4 position of the NHC occurred, or the products of more traditional metal-based, ether-cleavage reactions were observed.

Treatment of colourless **11** 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 colourless **20** can be isolated in 52% yield, Scheme 10. The product was characterised as the bimetallic dimer [Y(μ-L^-)(N″)(μ-N″)K(dme)]$_2$ (**20**); the molecular structure is shown in Fig. 9.[26]

Complex **20** is formally a product of deprotonation and a migration of the C2-binding carbene from the yttrium(III) centre to the incorporated potassium(I) cation. To the best of our knowledge, this is the first instance of a negatively charged, 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 by *N-tert*-butyl cleavage of the NHC[27]). The ^{13}C NMR resonances for C2 and C4 in **20** are observed at 199.2 and 167.5 ppm, respectively. These compare with shifts of 185.8 ppm for the C2 carbene carbon in **11**,[17] and 208.4 ppm for the only other thermally stable potassium–NHC

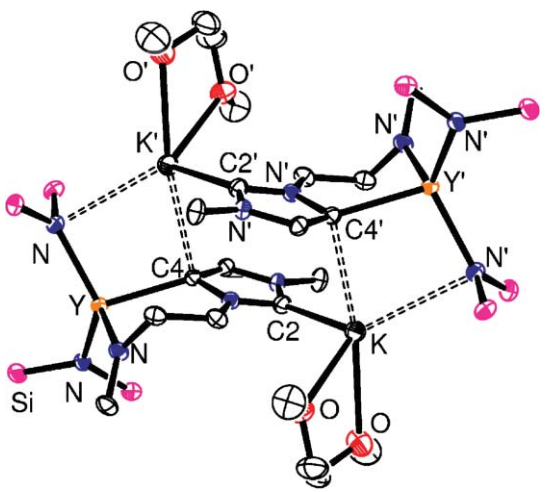


Fig. 9 Thermal ellipsoid drawing of **20** (50% probability), Si and Bu^t methyl groups omitted for clarity.

complex, **1**.[15] The $^{1}J_{YC}$ coupling constant of 62 Hz is the largest reported to date, and in line with those observed for the 2-metallated thiophene and furan, and terphenyl complexes $[Y(Cp^*)_2(2\text{-}EC_4H_3)(thf)_n]$ (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.[28]

X-Ray crystallography reveals that **20** is dimeric in the solid state. Each yttriate centre 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 is significantly shorter than the Y–C2 distance in **11** and is at the short end of the Y–C single σ-bond range. The NHC is bound, normally, *via* C2 to K1 and the C2-bound K–NHC moiety is essentially planar. The potassium cation is five-coordinate with a close contact to a silyl methyl carbon atom, the O donor atoms of a coordinated dme molecule, and, more interestingly, an additional K–NHC interaction to the '*exo*' p orbital of C4′, which enables construction of the dimer. The C–N and C–C bond lengths do not suggest a fully rehybridised sp^3 C4 carbon.

In a rational synthesis, treatment of **11** with methyl potassium at low temperature in diethyl ether, followed by addition of dme, affords **20** 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 **11**. However, this would in principle limit the maximum yield to 50% and this is exceeded, albeit marginally. Also, **11** does not react with KN″ until heated at reflux for 48 h, which yields only 5% **20**, and decomposition products.

Treatment of **11** with KC_8 in thf, in an analogous manner to the reaction that affords $[\{Y(N'')_2(thf)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$,[29] gave no reaction products. Repetition of this reaction in dme–diethyl ether afforded only **11**. The use of potassium–18-crown-6 mixtures instead of KC_8 also resulted in the recovery of **11**, but complete consumption of the crown; the ^{1}H NMR spectra indicated that alkoxide products had been formed instead.

Complex **20** 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 $[Y(L')(N'')_2]$ (**21**) (where L′ = $Bu^tNCH_2CH_2[C\{NC(SiMe_3)CHNBu^t\}]$) in quantitative yield, with concomitant elimination of KCl, Scheme 10. This is conveniently monitored by NMR spectroscopy; in the ^{13}C NMR spectrum the characteristic signal for the C2 carbon in **20** at 199.2 ppm is replaced by a signal at 172.73 ppm, which exhibits one-bond coupling to yttrium ($^{1}J_{YC}$ = 55.8 Hz), and is indicative of 'normal' coordination of the NHC to yttrium, as in **11**.

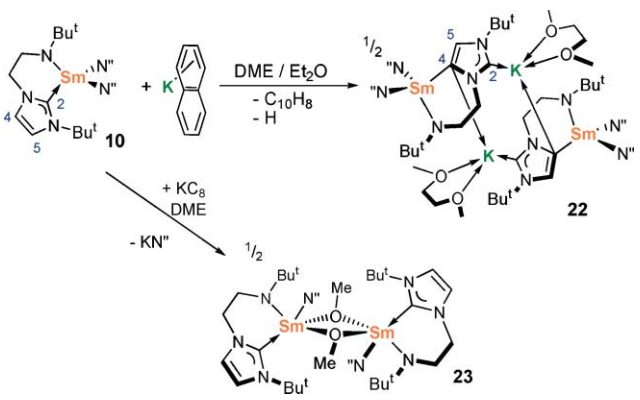
The isolation of **20** was surprising, but suggests the reaction is most likely proceeding through a regioselective deprotonation of the C4 hydrogen atom, mediated either by a base or a reductant. Therefore, the NHC ring presumably plays a non-innocent role in the reduction chemistry. Given that there is no literature precedent for a molecular Y(II) species the assertion of non-innocence 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 should afford different products to that of NHC-based reductive chemistry.

The divalent oxidation state of samarium is readily accessible by treatment with potassium reductants; for example, the reaction of $[Sm(N'')_3]$ with KC_8 affords the purple and divalent complex $[Sm(N'')_3K]$.[25,30] The reaction of $[Sm(L)(N'')_2]$ (**10**) with either $KC_{10}H_8$ or KC_8 affords a purple-coloured solution, assumed to contain a Sm(II) complex, but from which no purple-coloured complex could be isolated, Scheme 11. Interestingly, even in an ether solvent, the naphthalenide anion appears to stabilise a K-incorporated complex; this is presumed to be a precursor to the metallated $[Sm(\mu\text{-}L^-)(N'')(\mu\text{-}N'')K(dme)]_2$ (**22**) (isostructural with **20**),[26] which is obtained in low yield after crystallisation from hexane, analogously to **20**. 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 spectrum on freshly reduced **10** 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 by-product.[25,29] Also, attempts to prepare Sm(II) amido-NHC complexes from divalent $[Sm(N'')_2]_2$ give **10** as the only isolable product.[17] Briefly heating a solution of the KC_8 reduced Sm species results in the purple solution instantaneously turning red giving $[Sm(L)(N'')(\mu\text{-}OCH_3)]_2$ **23**, the ether cleavage product, after work-up, Scheme 11.[26]

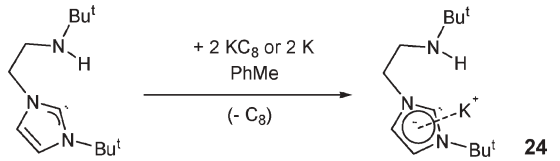
Thus, the relative stability of the divalent oxidation state of samarium suggests that the electron resides more on the metal than on the NHC ring; this supports the intermediacy of a one-electron reduced NHC in the formation of **20**, since reduction of yttrium is unlikely.

The suggestion of NHC-based reduction prompted us to investigate the reduction of the neutral parent amine-NHC, **2**. Heating a mixture of HL and potassium to reflux in toluene results in a colour change from yellow to dark red, forming a complex characterised as the stable radical anion of the ligand, $[K]^+[Bu^tNHCH_2CH_2\{C(NCHCHNBu^t)\}]^{\bullet-}$ (**24**), in about 50% yield, Scheme 12.[26]

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).[31] The ^{1}H NMR



Scheme 11



Scheme 12

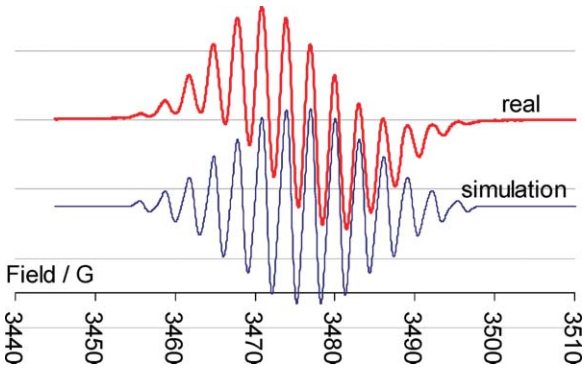


Fig. 10 EPR spectrum (upper, red trace) of radical anion **24**. Simulated (lower, navy trace) with g_{iso} = 2.004719, A_K = 3.07 G, A_N = 6.02 G, and A_H = 3.27 G.

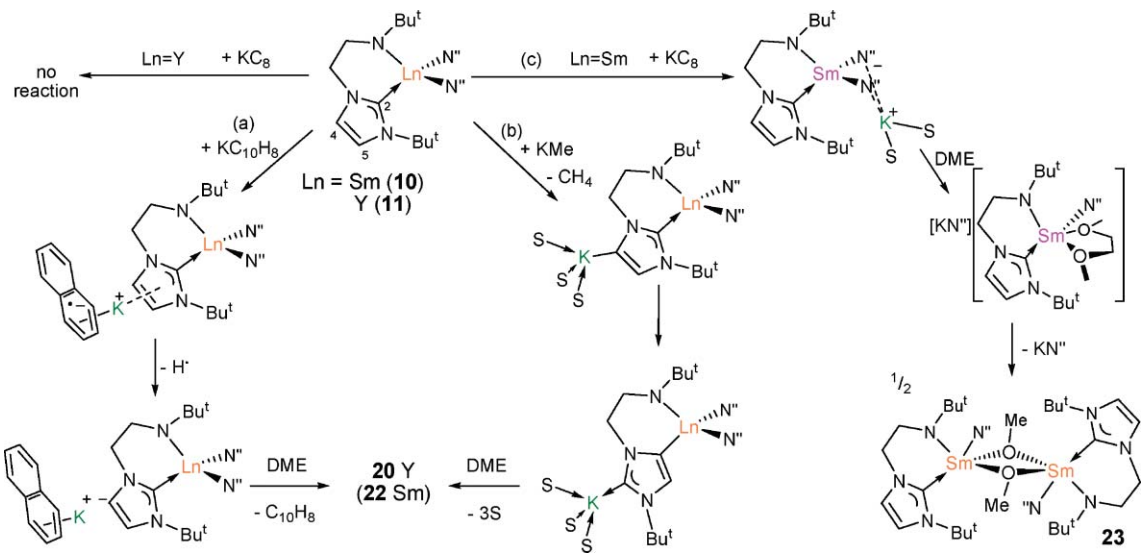
spectrum of an *in situ* generated sample of **24** after forty eight hours' reaction shows ~50% unconverted starting material, and two broadened resonances near 1 ppm attributed to the two *tert*-butyl groups, but no other features.

The EPR spectrum of **24**, Fig. 10, 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.[32] In the recently reported radical anions of gallium and germylene NHC analogues such as $[Ge(NBu^tCH)_2]^{\cdot -}$ and $[Ga(P'')_2(NBu^tCH)_2]^{\cdot -}$ (P″ = $P(SiMe_3)_2$) the radical resides on the C_2N_2 portion of the heterocycle.[33] Interestingly, a diradical is formed for the amido analogue $[Ga(N'')_2(NBu^tCH)_2\{4\text{-}Ga(N'')(Me)(NBu^tCHCNBu^t)_2\}]^{2\cdot -}$ as a formal product of HN″ elimination from a gallium cation and the heterocycle C4 hydrogen.[34]

This suggests 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 subsequent to the reduction.

Observing the stability of **24** we propose the mechanistic processes outlined in Scheme 13. For **11**, reduction with potassium naphthalenide facilitates reduction of the NHC ring which is stabilised by naphthalene (route a). This primes the system for loss of H· 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 **20**.

In the absence of stabilising naphthalene no reduction occurs, presumably because the strongly nucleophilic NHC renders the Y centre too electron rich, increasing the reduction potential for an already 'unreducible' metal, and reduction of the 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 **20** is obtained (route b). The yttrium complex **11** does not react significantly with KN″, indicating that if the potassium naphthalenide route to **20** also involves a selective C4-deprotonation, then potassium reductants generate a base that is stronger than KN″ in the reaction mixture that forms **20**. 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).[35]



Scheme 13 Proposed mechanistic routes to **20**, **22**, and **23**. S = ether solvent.

We have not observed any fluxional processes for any of the complexes, and measure only one yttrium–carbon coupling constant for **11**. We also find that prolonged heating of samples in deuterated solvents eventually results in decomposition to release HL, and we have not observed any deuterium-incorporated HL. This suggests that a mechanism involving dissociation of the NHC, H-migration from C4 to C2, and subsequent deprotonation at C2 is unlikely. For **10**, the same reduction process with potassium naphthalenide occurs to give **22**. 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 **22** compared to **20**.

The widespread use of metal 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.* **I**, Fig. 11.[36] It has also been predicted that the C4-NHC ligand is a stronger electron donor than a C2-NHC,[37] and shown that C4-bound derivatives *e.g.* **J**, Fig. 11, can function as better catalysts.[1b,38] With the increasing use of NHCs to enhance early metal catalyst systems for reactions such as C–C bond formation and polymerisation, the behaviour and occurrence of abnormally-bound carbene adducts is now of widespread relevance and importance in homogeneous catalysis and small molecule reactivity.[39] The reduction chemistry described here in addition to the growing number of abnormal carbenes indicates that caution should be employed when generating catalysts *in situ*.

Regioselective C4 silylation

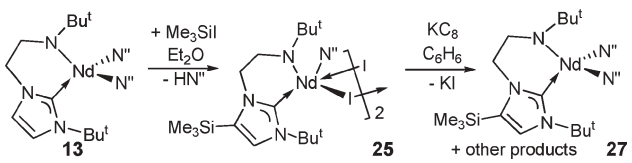
The widespread use of metal NHC complexes in homogeneous catalysis presents the long standing challenges of facile control over the nature of all NHC substituent positions in order to gain maximum steric and electronic control over catalyst properties. However, whilst protocols now exist for functionalising both backbone C4 and C5 carbons with halogen or deuterium (by reaction of the free NHC with CCl_4 or base and D_2O, respectively)[40] the control of the migration, or a specific functionalisation of the carbene backbone remains a challenge. In the course of our reduction studies we discovered a facile reaction which not only selectively substitutes one N″ ligand for iodide, but also simultaneously, and regioselectively, silylates the backbone of the NHC at the C4 position in a one-pot reaction.

The initial impetus for this avenue of research was to extend the reduction chemistry described above to lanthanides which possess reduction potentials between yttrium(III) and samarium(III) and we therefore selected cerium(III) and neodymium(III) [E° ($Ln^{3+/2+}$) Ce = −2.92, Nd = −2.62 V].[41] The preparation of the Nd analogue of **10** [Nd(L)(N″)$_2$] (**13**) was readily accomplished in the same manner which affords **10–12**. However, in our hands compound **13** shows no reaction with KC_8 in arene or ether solvents, in contrast to the reaction between KC_8 and [Nd(N″)$_3$] which affords [{Nd(N″)$_2$(thf)}$_2$(μ-η^2:η^2-N_2)] in low yield,[25] showing the subtlety of the electronic requirements for this reductive activation system. We therefore sought to identify a straightforward and high yielding route to iodide precursors since we reasoned reduction chemistry would be much more favourable when driven by the elimination of KI.

As has been observed in Group 4 chemistry previously, we reasoned that reaction of Me_3SiI with **13** should proceed to eliminate N‴ [N(SiMe$_3$)$_3$] and afford [Nd(L)(N″)(μ-I)]$_2$, analogously to the way Group 4 bis(dimethylamide) compounds are smoothly converted to the corresponding dichlorides by treatment with Me_3SiCl, along with concomitant elimination of Me_3SiNMe_2. Although amide–iodide exchange does indeed occur, we were surprised to observe simultaneous, and regioselective, silylation of the backbone of the NHC at the C4 position (and elimination of HN″ rather than N‴) to afford [Nd(L′)(N″)(μ-I)]$_2$ (**25**) (L′ = Bu^{t}NCH$_2$CH$_2$[C{NC(SiMe$_3$)CHNBu^t}]), Scheme 14, Fig. 12.[22] As far as we are aware, this is the first functionalisation of an NHC backbone which need not proceed *via* a refunctionalisation of the basic C2 atom, or 1,3-proton or -alkyl migration.

In terms of suggesting a mechanism for this regioselective silylation, we immediately discount a process involving a 1,3-shift, as seen in the formation of 'wrong carbenes', because no product containing a C2-bound trimethylsilyl group is observed and the yield of **25** is excellent (∼85%).

Notably, the functionalised atom, C4, is the same distance from the tether amide as the bound C2 which raises the 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 chemistry, but not yet for carbene complexes. In Scheme 15, path a, labilisation of the



Scheme 14

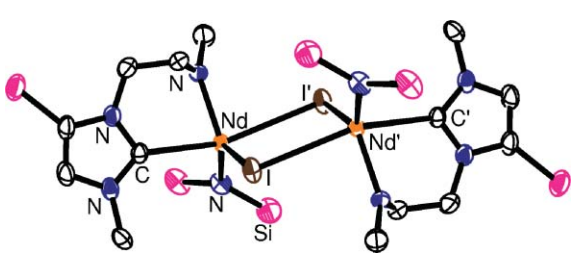


Fig. 12 Thermal ellipsoid drawing of **25** (50% probability).

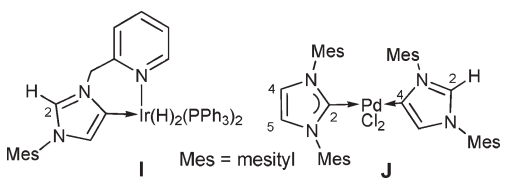
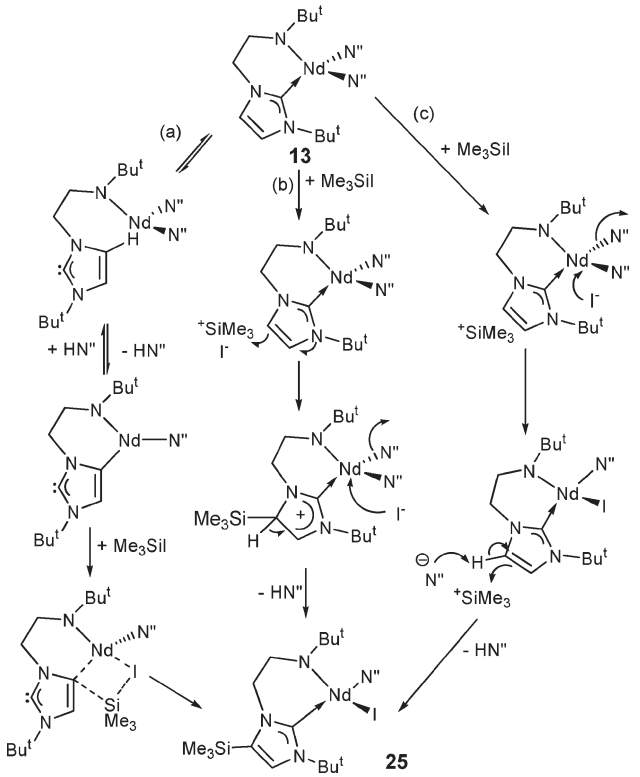


Fig. 11 Late metal complexes with abnormally bound carbene ligands.



Scheme 15

NHC 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 subsequent incorporation of Me_3SiI. However, we discount this mechanism since we do not find any evidence of C–H activated intermediates (and see above).

An alternative and plausible route, path b, since the reaction works best in diethyl ether, is a direct electrophilic attack on the NHC ring by an ether-stabilised trimethylsilyl cation, with subsequent loss of HN″ and coordination of the iodide anion. However, we observe a significant dependence of the reaction on the size of the metal; whereas silylation proceeds smoothly and in high yield to afford **25**, and the Ce congener $[Ce(L')(N'')(\mu\text{-}I)]_2$ (**26**),[22] no reaction is observed when **11** is treated with Me_3SiI, even over prolonged periods of time. This could suggest that the reaction is affected by steric congestion at the metal.

A mechanism closer to path c seems most likely; an associative mechanism involving nucleophilic substitution of N″ by iodide at the metal centre could generate an amide base of sufficient strength to form a C4-carbanion which is readily quenched by the trimethylsilyl cation. This is consistent with steric congestion at the metal centre hindering the silylation and, germane to this proposed mechanism, is the fact that trimethylsilyl cations are long-lived species in ethereal solvents,[42] and the C4-carbanion in **20** is also readily quenched by a trimethylsilyl cation in ethereal solvent to give **21**.[26]

Successful in finding a facile and high-yielding route to iodide precursors, albeit with the surprising concomitant C4-functionalisation, we investigated the reduction chemistry of **25**. Compound **25** reacts with KC_8 in thf with elimination of KI to afford a green oil. Unfortunately, we have been unable to isolate any product from this reaction so the outcome remains unknown. The reduction with KC_8 in an arene solvent instead affords a brown solution from which blue crystals of $[Nd(L')(N'')_2]$ (**27**) were isolated in low yield, Scheme 14.[22]

Complex **27** is a product of ligand redistribution/disproportionation of the putative Nd(II) intermediate [Nd(L′)(N″)] and is consistent with our observations that, so far, our attempts to isolate Sm(II) NHC complexes (even starting with stable Sm(II) precursors) have resulted in the isolation of Sm(III) species[17,26] due to their inherent instability (the strongly basic NHC renders the metal too electron rich) and ligand redistribution/disproportionation reactions.

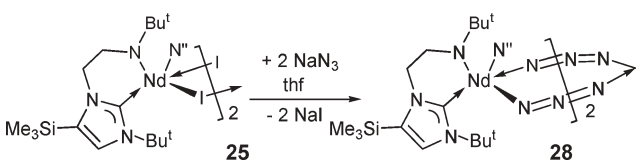
Compounds **13**, **25**, **26**, and **27** have all been characterised by single crystal X-ray diffraction. Compounds **25** and **26** are dimeric, isostructural, and adopt structures essentially identical to **16**, except for the presence of the additional $SiMe_3$ group at the C4 position, and are noteworthy as further examples of unusually stable heteroleptic complexes (with respect to ligand scrambling) for such large lanthanide metal centres. Complex **27** is essentially isostructural with complexes **10–13**, save for substitution of H by $SiMe_3$ at the C4 position. The almost identical conformations of **13** and **27** in the solid state presents an opportunity to directly probe the effect of silylation at the C4 position; not surprisingly, the C2–Nd bond length in **27** is longer than in **13** which is commensurate with incorporation of the electropositive Si atom into the σ-framework of the NHC which renders the L′ NHC a softer donor than L.

Although the reduction chemistry of **13** has thus far proven unsuccessful in terms of small molecule activation, or isolation of low oxidation state complexes, it has ultimately provided a convenient entry-point to NHC lanthanide mono-iodide precursors and we are currently exploring their metathesis chemistry; for example, **25** reacts readily with NaN_3 to afford dimeric $[Nd(L')(N'')(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}N_3)]_2$ (**28**), Scheme 16.[22]

Concluding remarks

It is clear that NHCs are better than trialkyl or aryl phosphines as donor ligands in f-block coordination chemistry. However, the metal–carbene bond is significantly weaker and more reactive in these electropositive metal systems than it is in late metal systems. The use of bidentate ligands containing NHC groups is still a relatively small area in early metal chemistry. Those that combine an anionic group with the NHC can be particularly effective in the stabilisation of f-block NHC complexes, generating systems with short metal–carbene bonds.

Although the range of complexes reported to date is still small, these electropositive metal organometallics already display a range of chemistry as yet unseen in late metal–NHC



Scheme 16

complexes, and of potential relevance to homogeneous catalysis, and small molecule activation chemistry.

Due to the strongly basic character of the donor carbene, the reactions that result in (reversible) NHC displacement can readily lead to other reaction chemistry, such as atom abstraction, or polymerisation catalysis.

The π-system of the carbene can also become involved in reaction chemistry: for example, the deprotonation of a backbone CH affords bimetallic complexes that bridge through the σ-framework of the carbene, and the metal coordinated carbene is readily silylated to generate asymmetric metal carbene complexes.

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