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Lanthanide/actinide differentiation with sterically encumbered N-heterocyclic carbene ligands**

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Graphical abstract:

R = Mes, Dipp
[Ce(L^R)_2N''] readily isolated

R = Mes, Dipp
[U(L^R)_2N''] unisolable
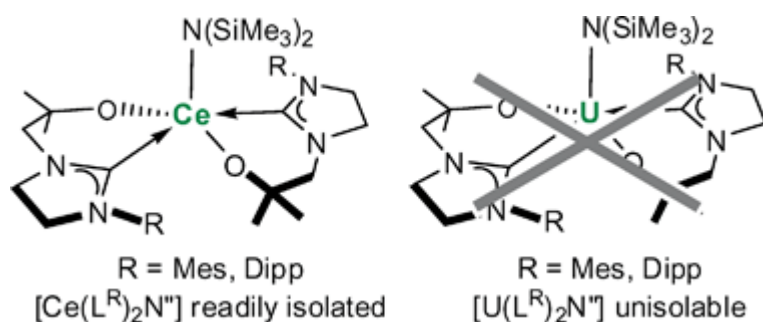
Abstract

A study is reported on the relative stability of trivalent *bis*(ligand) complexes of the form [M(L^R)$_2$N″] for trivalent group 3, lanthanide and actinide cations, using the sterically demanding N-heterocyclic carbene ligand L^R = [OCMe$_2$CH$_2${CNCH$_2$CH$_2$NR}] (R = ^{i}Pr L^P, Mes L^M, Dipp L^D; N″ = N(SiMe$_3$)$_2$). For the small Y^{III} cation (r$_{6\text{-coord}}$ = 1.040 Å) and the smallest L^R, R = ^{i}Pr, *mono*, *bis*, and *tris*(L^P) complexes can be made; [Y(L^P)$_2$N″] and [Y(L^P)$_3$] have been characterised. For the larger ligands, L^M and L^D, only the *mono*(L^R) complexes [Y(L^M)N″$_2$] and [Y(L^D)N″$_2$] can be made. For the larger Ce^{III} (r$_{6\text{-coord}}$ = 1.15 Å), *mono*(L^R) and *bis*(L^R) complexes [Ce(L^M)N″$_2$], [Ce(L^D)N″$_2$], [Ce(L^M)$_2$N″], and [Ce(L^D)$_2$N″] can be made; structural characterisation of the latter two confirm the high degree of steric congestion. The new complex [U(L^M)N″$_2$] has also been isolated. Despite the very similar radii of Ce^{III} and U^{III} (r$_{6\text{-coord}}$ = 1.165 Å), the complexes [U(L^R)$_2$N″] cannot be isolated; a surprising display of the difference between the 4f and 5f metal series. However, the six-coordinate, *bis*(ligand) U^{IV} complexes can readily be isolated if smaller ancillary ligands are used; [U(L^M)$_2$I$_2$] and [U(L^D)$_2$I$_2$] have been fully, including structurally, characterised.

1. Introduction

Much current research in the nuclear industry is focused on the use of chemoselective extractants for the separation of radionuclides from the mixtures present in spentfuel. One of the key challenges is the separation of the trivalent lanthanide and actinide cations, since this would allow for the removal and passivation of the most highly radioactive nuclides.[1] Despite very similar physical characteristics, differences between the cations can be highlighted chemically, since the 5f metal cations exhibit a higher degree of covalency in chemical bonding than 4f cations of the same charge and radius. The use of soft polypyridyl/triazine donor ligands such as in **A**, Chart 1, that can selectively bind actinides over lanthanides has been demonstrated to great effect in competition reactions between cerium and uranium.[2-5]

N-heterocyclic carbenes (NHCs) are soft donor ligands and their use as ligands in early transition metal and f-block chemistry is an expanding area.[6-12] It has recently led to the isolation of unusual compounds such as the carbene N-alkyl C–H bond activation products formed from (Tp^{tBu,Me})Yb(CH$_2$SiMe$_3$)(thf) (Tp =*tris*(pyrazolylborate)), **B** in Chart 1,[13] and silylation products **C**,[14] carbene coupling,[15] lanthanide-transition metal bonds **D**,[16] and catalysts for isoprene polymerisation **E**,[17,18] allylic alkylation,[19] alkene polymerisation,[20-22] alkene oligomerisation **F**,[23,24] and lactide polymerisation.[25-27]
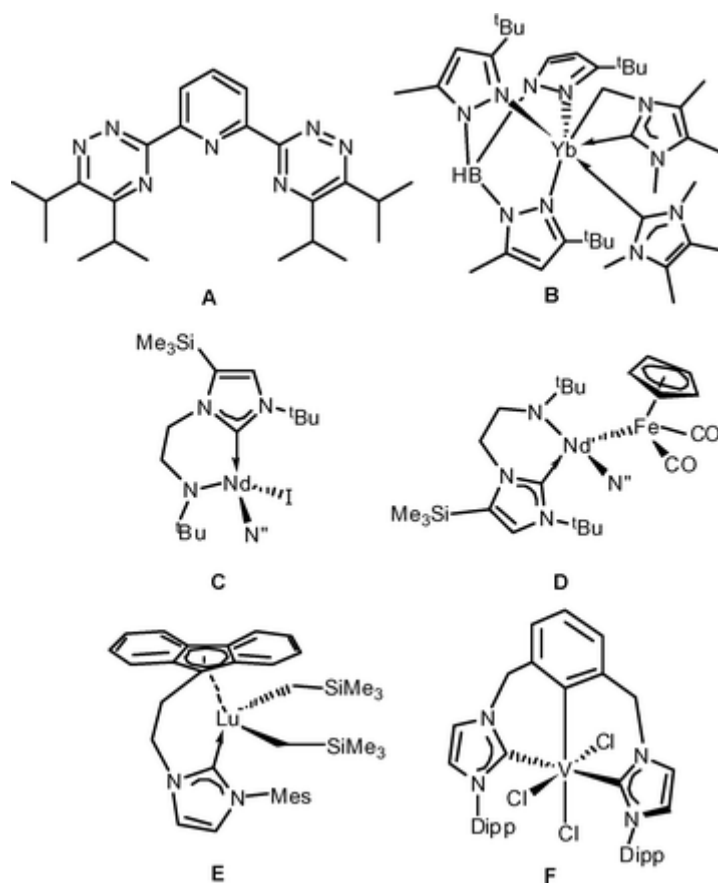
Chart 1. Selected early metal NHC complexes with unusual properties or catalytic activity.

It has been demonstrated that a single NHC ligand can afford a modest degree of selectivity for U^{III} over Ce^{III} in the complexes Cp*$_2$MI, forming [Cp*$_2$UI(NHC)] in preference to [Cp*$_2$CeI(NHC)] by a 4 : 1 ratio (Cp* = η^5-C$_5$Me$_5$).[28] We also showed that using a bidentate NHC-alkoxide as the sole ligand for Ce or U resulted in dramatically different structures; the Ce^{IV} complex CeL$_4$ (L = [OCMe$_2$CH$_2${CNCHCHN^{i}Pr}])[29,30] is six-coordinate in the solid state with two bound and two free NHC groups, whereas the uranium complex, expected to be isostructural, is seven-coordinate with three bound and one free NHC groups.[31]

Since then, we have reported the synthesis of saturated-backbone analogues of these bidentate alcohol-functionalised proligands [HL^R] (R = P denotes *iso*-propyl; R = M denotes Mes, 2,4,6-trimethylphenyl; R = D denotes Dipp, 2,6-di-*iso*propylphenyl).[32] We showed that Mg and Zn saturated-NHC complexes derived from them were good initiators for lactide ROP (ring opening polymerisation).[26] We have also reported *mono*(ligand) complexes of all three of the ligands with diamagnetic Y^{III}, [Y(L^R)N″$_2$] (R = ^{i}Pr, Mes, Dipp, N″ = N(SiMe$_3$)$_2$), and uranyl *bis*(ligand) complexes [UO$_2$(L^R)$_2$] of L^M and L^{D},[32] and recently, the reactivity of the *mono*(L^D) complexes [M(L^D)N″$_2$] M = Y^{III}, Ce^{III}, and U^{III}.[33]

The bidentate NHC-alkoxide ligands with N-aryl groups on the carbenes L^M, [OCMe$_2$CH$_2$\{CNCH$_2$CH$_2$NMes\}], and L^D, [OCMe$_2$CH$_2$\{CNCH$_2$CH$_2$NDipp\}], are very sterically demanding and we were interested in the degree of coordinative saturation that we could achieve with these. Here, we report our ability to make long-bond organometallics of Group 3 (Y), lanthanide (Ce) and actinide (U) cations, and the differences in stability between the cerium and uranium adducts of these larger carbene ligands.

2. Results and discussion

2.1. Survey of synthetic accessibility of *bis*(ligand) complexes

2.1.1 Attempted formation of *mono*, *bis*, and *tris*(L^R) Y^{III} complexes. As reported previously, treatment of YN″$_3$ with one equivalent of [HL^R] in benzene (L^P and L^M) or thf (L^D) affords yellow solutions of [Y(L^R)N″$_2$] after heating at 85 °C for 12 h (L^P), or after standing at 25 °C for 12 h (L^M and L^D), respectively, Scheme 1.[32] They were identified by the yttrium-carbene $^1J_{YC}$ coupling constants of 46 (L^P), 44 (L^M), and 42 (L^D) Hz for the carbene carbon resonance at 213.3, 215.5, and 216.3 ppm respectively. An X-ray diffraction study of [Y(L^D)N″$_2$] was also reported.
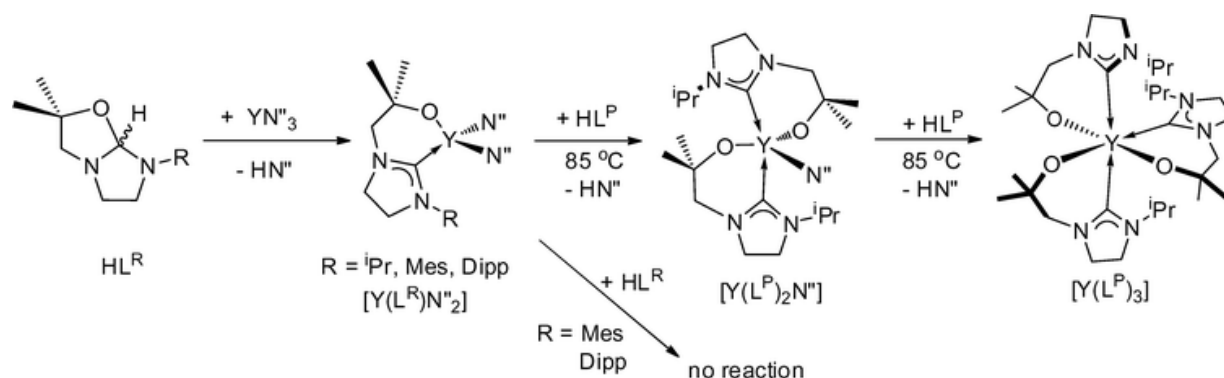
Scheme 1. Sequential NMR scale syntheses of Y^{III}-NHC complexes.

For the smallest ligand, L^P, even for small Y^{III}, it is possible to make the *bis*- and *tris*-NHC complexes [Y(L^R)$_2$N″] and [Y(L^R)$_3$]. However, the N-aryl NHC proligands [HL^M] and [HL^D] do not form the analogous complexes [Y(L^R)$_2$N″] and [Y(L^R)$_3$] even under forcing conditions, (Scheme 1). The sequential addition of one or two equivalents of [HL^P] to the NMR tube containing [Y(L^P)N″$_2$], followed by heating at 85 °C for 12 h, cleanly afforded the *bis*- and *tris*-NHC complexes [Y(L^P)$_2$N″] and [Y(L^P)$_3$], respectively, as monitored by NMR spectroscopy, Scheme 1. Heating was necessary to afford both [Y(L^P)$_2$N″] and [Y(L^P)$_3$], as mixtures were formed at room temperature regardless of the reaction stoichiometry used.

The identity of [Y(L^P)$_2$N″] and [Y(L^P)$_3$] were verified by independent treatment of YN″$_3$ with two and three equivalents of [HL^P], respectively, which after heating at 85 °C for 12 h provided identical NMR spectroscopic signatures. The ^{1}H NMR spectra of [Y(L^P)N″$_2$], [Y(L^P)$_2$N″], and [Y(L^P)$_3$] contain distinctive *iso*-propyl septets at δ = 4.37, 5.05 and 5.56 ppm, respectively. The ^{13}C NMR spectra contain yttrium-coupled carbene carbon resonances at δ = 212.3, 216.5 and 220.2 ppm ($^1J_{YC}$ = 46.4, 35.8 and 29.1 Hz), respectively. The magnitude of the $^1J_{YC}$ coupling constants are an indication of the degree of σ-character in the Y–C bond; the decreasing $^1J_{YC}$ magnitude observed across [Y(L^P)N″$_2$], [Y(L^P)$_2$N″], and [Y(L^P)$_3$] suggests that the carbenes act as progressively poorer σ-donors to the yttrium centre with the addition of each extra alkoxy-NHC ligand as the yttrium centre becomes increasingly more electron rich. The magnitude of these coupling constants is moderate compared to other examples, with values up to 62 Hz.[27]

2.1.2 Synthesis of *bis*(L^R) Ce^{III} complexes. Treatment of a solution of CeN″$_3$ with one equivalent of [HL^D] was previously shown to afford yellow [Ce(L^D)N″$_2$] in good yield;[33] the orange mesityl analogue [Ce(L^M)N″$_2$] is also readily made in hexanes at room temperature, Scheme 2. Following removal of the impurities *via* sublimation (85 °C, 10^{-5} mbar), [Ce(L^M)N″$_2$] was isolated in good yield as analytically pure orange material, displaying a set of paramagnetically shifted ligand resonances between δ = 14 and −7 ppm in the ^{1}H NMR spectrum. Storage of a pyridine solution of [Ce(L^M)N″$_2$] at −30 °C afforded single crystals of the pyridine solvate [Ce(L^M)N″$_2$(NC$_5$H$_5$)] suitable for an X-ray diffraction study (see ESI and figure ESI.4†).
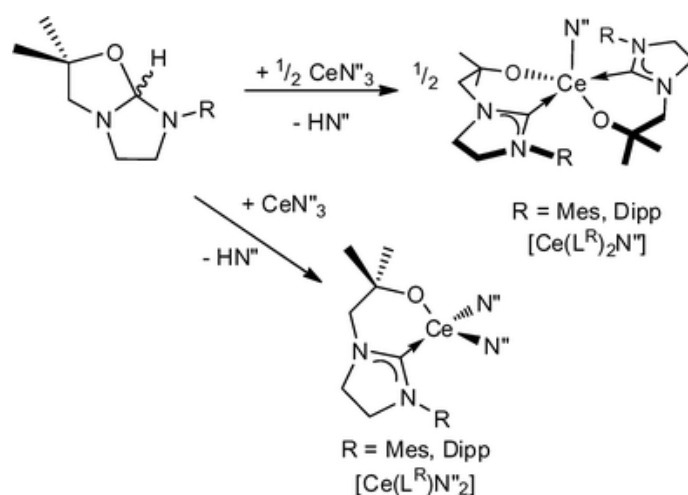
Scheme 2. Syntheses of Ce^{III}-*mono*- and *bis*(NHC) complexes.

The *bis*(ligand) cerium complexes [Ce(L^R)$_2$N″] (R = Mes, Dipp) were synthesised *via* treatment of CeN″$_3$ with two equivalents of [HL^R] in toluene or hexanes, Scheme 2. The mesityl-substituted complex [Ce(L^M)$_2$N″] crystallised as single crystals from the reaction mixture after standing at room temperature for ten minutes. Isolation and hexane washing after 12 h afforded the product in good yield. The 2,6-di-*iso*propylphenyl

substituted complex [Ce(L^D)$_2$N″] was also obtained in high yield since the product precipitates out of the reaction mixture if the reaction is conducted in hexane. Diffraction quality crystals of [Ce(L^D)$_2$N″] were grown from a toluenesolution.

The ^{1}H NMR spectrum of [Ce(L^M)$_2$N″] at room temperature displays five broadened resonances almost indistinguishable from the baseline, with the remaining three resonances observed as better resolved broad singlets, all within the range 23 to −10 ppm. These are very broad resonances compared to those observed for [Ce(L^M)N″$_2$], perhaps due to the presence of a fluxional process in solution at room temperature, such as a labilisation of the NHC groups. Similarly, the ^{1}H NMR spectrum of [Ce(L^D)$_2$N″] shows broad resonances in the range 24 to −10 ppm.

Despite the uninformative NMR spectra for [Ce(L^R)$_2$N″], both were characterised by elemental analysis and a single crystal X-ray diffraction study. The molecular structures are drawn in Fig. 1, and selected bond lengths and angles are displayed in Table 1.

Table 1. Summary of metrical data for [Ce(L^M)$_2$N″] and [Ce(L^D)$_2$N″]

Distance (Å)/angle (°)	[Ce(L^M)$_2$N″]	[Ce(L^D)$_2$N″]
Ce1–O1, –O2	2.172(3), 2.184(3)	2.1836(18), 2.201(2)
Ce1–C1, –C11	2.786(4), 2.798(4)	2.855(3), 2.813(3)
Ce1–N5	2.442(3)	2.447(3)
N–C$_{(av)}$	1.336	1.371
N–C–N$_{(av)}$	107.1	106.1
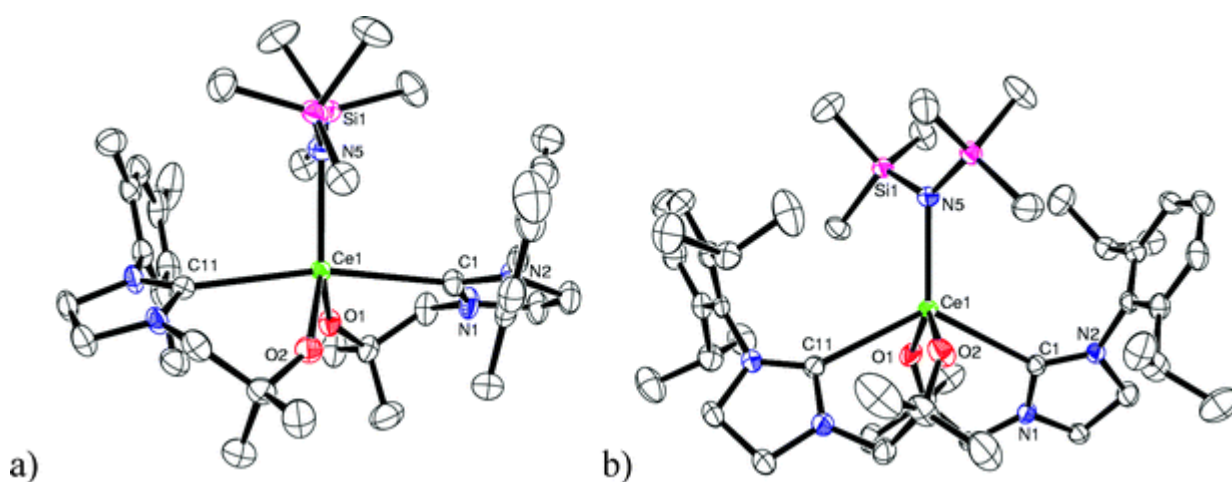
Figure 1. Displacement ellipsoid drawing of the molecular structures of a) [Ce(L^M)$_2$N″] and b) [Ce(L^D)$_2$N″] (50% probability ellipsoids). Solvent and hydrogen atoms omitted for clarity.

The cerium centre is five coordinate in each and in $[Ce(L^M)_2N'']$ adopts a distorted trigonal bipyramidal geometry, with an axial C1–Ce1–C11 angle of 167.55(10)° and equatorial O1–Ce1–O2, O1–Ce1–N5 and O2–Ce1–N5 angles of 105.00(10), 124.33(13) and 130.65(12)° respectively, with an angle sum of 359.98°. The larger N-Dipp groups in $[Ce(L^D)_2N'']$ force a further distortion away from the trigonal bipyramid, to reduce interactions between the Dipp arenes and the silylmethylgroups. The resulting square-based pyramidal geometry is thus defined by a much smaller C1–Ce1–C11 angle of 128.19(9)°, and a larger O1–Ce1–O2 angle of 127.84(8)°.

The average ligand bite angle is 71.7° in $[Ce(L^M)_2N'']$, which contributes in part to the observed distortion, and the average Ce–O and Ce–C bond lengths are 2.178 and 2.792 Å, respectively. The average ligand bite angle is 71.4° in $[Ce(L^D)_2N'']$, and the average Ce–O and Ce–C bond lengths are now 2.192 and 2.833 Å, respectively, both significantly longer than in $[Ce(L^M)_2N'']$. Interestingly, the steric congestion at the Dipp-substituted complex results in significant lengthening of the bonds to the bidentate ligand groups, but the Ce–N distance in the bound silylamido group is almost the same for both complexes, at 2.442(3) and 2.447(2) Å for the Mes and Dipp complexes, respectively. There are no structurally characterised Ce^{III} saturated backbone NHC complexes with which to compare the Ce–C bond lengths, but the five-coordinate Ce^{III}-amido-NHC complex $[Ce(L)N''(\mu\text{-}I)_2]_2$ (L = $^tBuNHCH_2CH_2[C\{^tBuNCHCHN\}]$) has a Ce–$C_{carbene}$ bond length of 2.700(3) Å.[34] The NHC heterocycle metrical data are consistent with metal-bound carbene groups.

2.1.3 Synthesis of *mono*(L^R) and attempted synthesis of *bis*(L^R) U^{III} complexes. The *mono*(ligand) complexes of U^{III} are readily accessible: Treatment of a dark purple solution of UN''$_3$ with one equivalent of [HL^D] was previously shown to afford dark blue $[U(L^D)N''_2]$ in good yield;[33] the dark blue mesityl analogue $[U(L^M)N''_2]$ is also readily made in hexanes at room temperature, in which it is very soluble, Scheme 3. The ^1H NMR spectrum of $[U(L^M)N''_2]$ shows a broadened, paramagnetically shifted set of ligand resonances between $\delta = 30$ and -20 ppm, and was also characterised by elemental analysis. The UV-vis-NIR spectrum of a $[U(L^M)N''_2]$ solution intoluene displayed a series of bands between 320 and 1313 (nm), with ε values of between 131 and 2296 (M^{-1} cm^{-1}), which are indicative of allowed d-f and forbidden f-f transitions in U^{III} ions.[35,36]

Reactions to form the *bis*(ligand) uranium complexes $[U(L^R)_2N'']$ (R = Mes, Dipp) were unsuccessful. Treatment of a dark purple solution of UN''$_3$ with two equivalents of HL^M at room temperature afforded a brown-green solution within thirty minutes which contained $[U(L^M)N''_2]$ and HL^M according to ^1H NMR spectroscopy. The same observation was recorded from the reaction of UN''$_3$ with two equivalents of HL^D and from the reaction of $[U(L^D)N''_2]$ with a further equivalent of HL^D. After longer reaction times (days) at room temperature, clear green-brown (L^M) or clear emerald green (L^D) solutions remained but ^1H NMRspectroscopic analysis showed only very few paramagnetically shifted resonances that could be ascribed

to a complex, and large quantities of free ligands HL^R and HN''. We assume that the solutions now contain simple U^{IV} salts due to the characteristic green colouration but no ligand-containing complexes were isolable in any case.
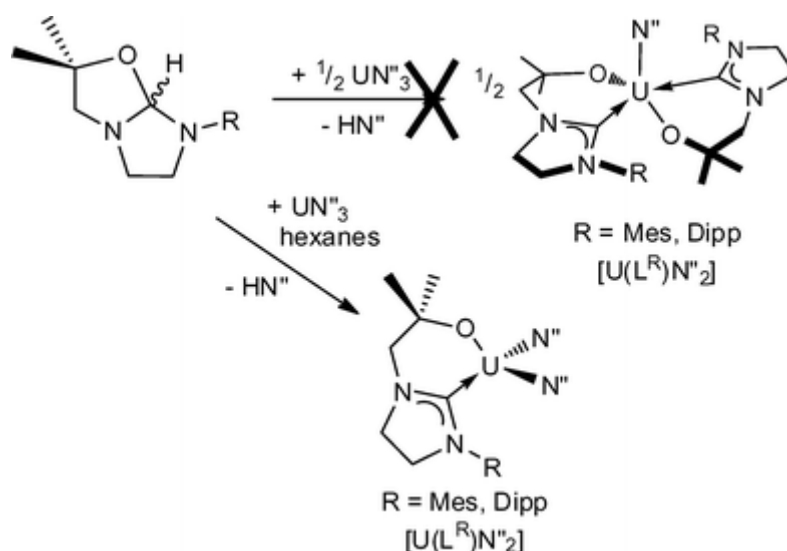

Scheme 3. Attempted syntheses of U^{III}*mono*- and *bis*(L^R) complexes.

2.2 Synthesis of *bis*(L^R) U^{IV} complexes

The ready accessibility of the diiodo complexes [U(L^R)$_2$I$_2$], Scheme 4, confirms that there is no inherent problem in coordinating two carbene ligands to the uranium centre. These complexes have been made by two alternative routes. The simplest is the use of *iso*-propyl iodide as an oxidant; at room temperature in benzene, an equimolar reaction between blue [U(L^M)N''$_2$] and *iso*-propyl iodide forms a pale brown insoluble material and pink crystals of [U(L^M)$_2$I$_2$] in a moderate yield, but the product proved difficult to separate from the brown material. Alternatively, as previously reported for the N-Dipp analogue,[33] the quaternised, silylated imidazolinium complexes [U(L^R-SiMe$_3$)N''$_2$I] regenerates the metal-carbene bond upon heating overnight (80 °C, benzene), depositing brown, insoluble precipitates and again affording pink crystals of [U(L^R)$_2$I$_2$].

A sample of the pink crystals of [U(L^M)$_2$I$_2$] were isolated by decantation of the mother liquor and brown precipitate from the crystals, followed by washing withtoluene and hexane and drying under reduced pressure. Satisfactory elemental analysis of this material was obtained but it proved insoluble in aromatic NMR solvents. A^{1}H NMR spectrum was obtained in d_5-pyridine but contained paramagnetic resonances between $\delta =$ 100 and −32 ppm; the yellow colour of the solution suggests that [U(L^M)$_2$I$_2$] has reacted with the solvent to afford (an) as yet unidentified product(s). The N-Dipp analogue [U(L^D)$_2$I$_2$] could be isolated in a similar procedure and was also shown to react with d_5-pyridine.
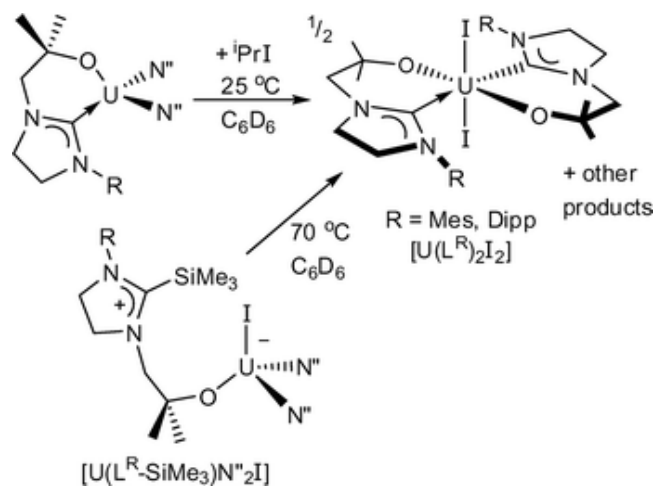
Scheme 4. Syntheses of $U^{IV}bis(L^R)$ complexes.

Dark pink single crystals of $[U(L^M)_2I_2]$ suitable for X-ray structural determination were deposited from the reaction mixture over a period of four weeks. The molecular structure is drawn in Fig. 2, and selected metrical data displayed in Table 2. The two $[U(L^R)_2I_2]$ complexes are isostructural.

Table 2. Selected metrical data for $[U(L^M)_2I_2]$ and $[U(L^D)_2I_2]$

Distance (Å)/angle (°)	$[U(L^M)_2I_2]$	$[U(L^D)_2I_2]$
U1–I1	3.0784(3)	3.0727(3)
U1–O1	2.061(3)	2.053(3)
U1–C1	2.647(4)	2.647(3)
N–C$_{(av)}$	1.336(5)	1.336(5)
N–C–N	107.6(3)	108.0(3)

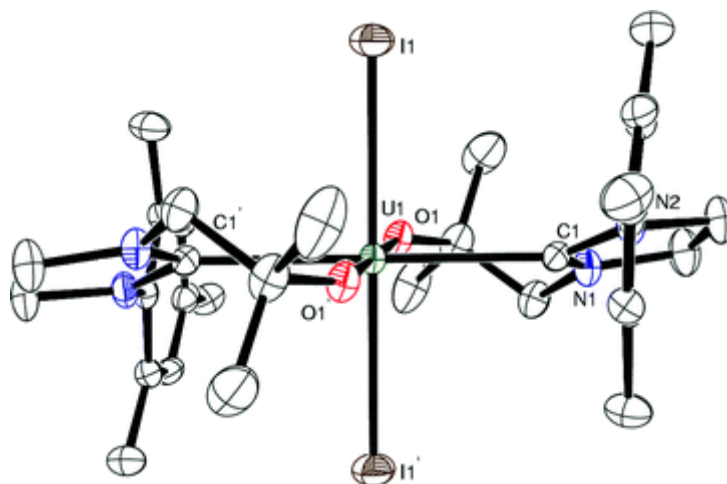**Figure 2.** Displacement ellipsoid drawing of $[U(L^M)_2I_2]$ (50% probability ellipsoids).Hydrogen atoms omitted for clarity.

As with $[U(L^D)_2I_2]$, complex $[U(L^M)_2I_2]$ possess a crystallographic C_2 axis along the I–U vector, which enforces octahedral geometry and results from the symmetry equivalence of one iodide and one ligand. The U^{IV}–I bond length in each (3.0784(3) and 3.0727(3) Å respectively) is longer than in six-coordinate $UI_4(tmu)_2$ (3.011(3) Å, tmu = tetramethyl urea).[37] The average U–$C_{carbene}$ bond length in the five structurally characterised tetravalent uranium NHC complexes in the literature is 2.677 Å.[31,38,39] Here, the short U–$C_{carbene}$ bond lengths of 2.647(4) Å suggest strong U–NHC bonding. The ligand bite angle in $[U(L^M)_2I_2]$ is 73.47(11)° (in $[U(L^D)_2I_2]$ it is 75.12(10)°) and the heterocycle parameters are standard for metal bound NHCs of this type.

3. Conclusions

For the relatively small, bidentate alkoxy-NHC ligand, with N-*iso*-propyl substituents, *mono*, *bis*, and *tris*(ligand) complexes can be made using the relatively small Y^{III} cation ($r_{6\text{-coord}}$ = 1.040 Å). However, for the larger N-aryl substituted ligands, the *bis*(ligand) complexes can only be made for the largest of the trivalent lanthanide cations, demonstrated with Ce^{III} ($r_{6\text{-coord}}$ = 1.15 Å). Structural characterisation of these shows that the complexes have very long bonds, indicative of steric crowding. This is so acute that the analogous U^{III} ($r_{6\text{-coord}}$ = 1.165 Å) complexes cannot be isolated in our hands. The straightforward isolation of the *mono*(ligand) complexes of Ce and U, and the *bis*(ligand) uranium diiodides confirms that it is steric encumbrance preventing the formation of the *bis*(ligand) silylamide complexes. These findings are summarised in Table 3. These are also the first f-block complexes with two saturated backbone NHC ligands.

Table 3. Summary of synthetically accessible complexes of Y^{III}, Ce^{III}, U^{III}, and U^{IV} with sterically demanding NHC ligands L^P, L^M and L^D. — indicates reaction not carried out. ✗ = complex not isolable in our hands

Metal	Y			Ce			U		
Ligand	L^P	L^M	L^D	L^P	L^M	L^D	L^P	L^M	L^D
mono(L^R)	$[Y(L^P)N''_2]^a$	$[Y(L^M)N''_2]^a$	$[Y(L^D)N''_2]^a$	—	$[Ce(L^M)N''_2]$	$[Ce(L^D)N''_2]^b$	—	$[U(L^M)N''_2]$	$[U(L^M)N''_2]^b$
bis(L^R)	$[Y(L^P)_2N'']$	✗	✗	—	$[Ce(L^M)_2N'']$	$[Ce(L^D)_2N'']$	—	only U^{IV} iodide isolable $[U(L^M)_2I_2]$	only U^{IV} iodide isolable $[U(L^D)_2I_2]^b$
tris(L^R)	$[Y(L^P)_3]$	✗	✗	—	✗	✗	—	✗	✗

a Complex reported previously in Ref.32. *b* Complex reported previously in Ref.33.

4. Experimental details

4.1 General procedures

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques, or in an MBraun Unilab or Vacuum Atmospheres OMNI-lab glovebox unless otherwise stated.

The solvents used were degassed and dried either by refluxing over potassium or by passage through activated alumina towers prior to use. All deuterated solvents were refluxed over potassium, vacuum transferred and freeze-pump-thaw degassed three times prior to use. The compounds [H$_2$L^R]X and [HL^R],[32] were synthesised according to literature procedures. All other reagents were used as received without further purification.

^{1}H NMR spectra were recorded on Bruker arx250 MHz, avance360 MHz or ava500 MHz spectrometers, and ^{13}C{^{1}H} on the same spectrometers at 63, 90 and 125 MHz, respectively, at 300 K unless otherwise stated, and referenced internally to residual protio solvent. Chemical shift values are quoted in ppm. Elemental analyses were determined by Mr. Stephen Boyer at London Metropolitan University.

Full X-ray crystallographic details are provided in the ESI.†

4.2 Synthesis of complexes

Synthesis of [Y(L^P)$_2$N″]. Solutions in C$_6$D$_6$ (0.75 mL) of YN″$_3$ (0.046 g, 0.08 mmol) and [HL^P] (0.03 g, 0.16 mmol) were combined and mixed well in a J-Young Teflon valve NMR tube. The combined solution turned pale yellow and was heated to 85 °C for 12 h to afford [Y(L^P)$_2$N″]. The ^{1}H NMR spectrum confirms the absence of any unreacted HL^P after this time; two other resonances are observed due to the remaining YN″$_3$ and byproduct HN″. ^{1}H NMR (C$_6$D$_6$, 298 K); 5.05 (1 H, sept, $^3J_{HH}$ = 6.7 Hz, NC*H*Me$_2$), 3.12 (2 H, bs, OCMe$_2$C*H$_2$*), 2.65 and 2.83 (2 H, m NC*H$_2$*C*H$_2$*N^{i}Pr), 1.25 (6 H, s CMe$_2$), 1.16 (6 H, d, $^3J_{HH}$ = 6.7 Hz, NCH*Me$_2$*), 0.5 (9 H, s, N(Si{C*H$_3$*}$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 298 K); 216.5 (d, $^1J_{YC}$ = 35.8 Hz, NCN), 73.4 (*C*Me$_2$), 41.6, 53.2 and 63.7 (N*C*H$_2$*C*H$_2$N^{i}Pr and OCMe$_2$*C*H$_2$), 50.3 (N*C*HMe$_2$), 31.7 (C*Me$_2$*), 21.7 (NCH*Me$_2$*), 7.03 (N(Si{*C*H$_3$}$_3$)$_2$) ppm.

Synthesis of [Y(L^P)$_3$]. Solutions in C$_6$D$_6$ (0.75 mL) of YN″$_3$ (0.026 g, 0.05 mmol) and [HL^P] (0.025 g, 0.14 mmol) were combined and mixed well in a J-Young Teflon valve NMR tube. The solution turned pale yellow and was heated to 85 °C for 12 h to afford [Y(L^P)$_3$]. ^{1}H NMR (C$_6$D$_6$, 298 K); 5.56 (1 H, sept, $^3J_{HH}$ = 6.7 Hz, NC*H*Me$_2$), 3.33 (2 H, s OCMe$_2$C*H$_2$*), 2.79 and 3.04 (2 H, m, NC*H$_2$*C*H$_2$*N^{i}Pr), 1.35 (6 H, s, CMe$_2$), 1.08 (6 H, d, $^3J_{HH}$ = 6.7 Hz, NCH*Me$_2$*) ppm. ^{13}C{^{1}H}NMR (C$_6$D$_6$, 298 K); 220.2 (d, $^1J_{YC}$ = 29.1 Hz, NCN), 72.5 (*C*Me$_2$), 42.0, 53.2 and 63.3 (N*C*H$_2$*C*H$_2$N^{i}Pr and OCMe$_2$*C*H$_2$), 50.2 (N*C*HMe$_2$), 31.7 (C*Me$_2$*), 21.5 (CH*Me$_2$*).

Synthesis of [Ce(L^M)N″$_2$]. To a solution of CeN″$_3$ (0.20 g, 0.32 mmol) in hexanes (10 mL) was added a solution of [HL^M] (0.084 g, 0.32 mmol) in hexanes (5 mL) and stirred at room temperature for 12 h. Filtration and removal of the volatiles under reduced pressure at 80 °C afforded [Ce(L^M)N″$_2$] as an orange solid. Yield 0.17 g (72%). Single crystals were grown from a pyridine solution at −30 °C. ^{1}H NMR (C$_6$D$_6$, 298 K); 14.04 (6 H, CMe$_2$), 11.36 (2 H, NC*H$_2$*C*H$_2$*NMes), 2.20 (2 H, OCMe$_2$C*H$_2$*), 2.12 (2 H, NC*H$_2$*C*H$_2$*NMes), 0.75 (3 H, *p*-Ar-*Me*), 0.3 (2 H, Ar-*H*), −5.12 (36H, N(Si{C*H$_3$*}$_3$)$_2$), −6.54 (6 H, *o*-Ar-Me) ppm. Anal. Found (calcd for C$_{38}$H$_{64}$CeN$_5$OSi$_4$) C, 46.74 (46.69); H, 8.16 (8.26); N, 7.69 (7.78).

Synthesis of [Ce(L^M)$_2$N″]. To a solution of CeN″$_3$ (0.5 g, 0.80 mmol) in toluene (10 mL) was added a solution of [HL^M] in toluene (5 mL) from which crystalline yellow blocks were formed within 10 min. After standing for 12 h, the product was isolated by filtration, washed with hexanes (2 × 5 mL) and dried under reduced pressure to afford [Ce(L^M)$_2$N″] as a crystalline yellow solid. Yield 0.44 g (67.1%). ^{1}H NMR (C$_6$D$_6$, 298 K); 22.4, 15.8, 9.6, 5.5, −9.9 (very broad), 6.45 (6 H, bs,*p*-Ar-*Me*), 0.81 (12 H, CMe$_2$), −0.97 (18 H, N(Si{CH$_3$}$_2$) ppm. Anal. Found (calcd for C$_{38}$H$_{64}$CeN$_5$O$_2$Si$_2$) C, 55.60 (55.70); H, 7.80 (7.89); N, 8.63 (8.55). Single crystals were grown from a toluene solution at room temperature.

Synthesis of [Ce(L^D)$_2$N″]. To a slurry of CeN″$_3$ (0.22 g, 0.60 mmol) in hexane (5 mL) was added a solution of [HL^D] in hexane (5 mL). The reaction mixture was stirred for 12 h during which time a pale yellow precipitate formed. This was isolated by filtration and dried *in vacuo* to afford [Ce(L^D)$_2$N″] as a pale yellow powder. From the filtrate, a second crop of product was obtained by concentration of the solution and cooling to −30 °C. Yield 0.47 g (81%). [Ce(L^D)$_2$N″] was poorly soluble and the ^{1}H NMR (C$_6$D$_6$, 298 K) spectrum showed broad overlapping resonances which could not be assigned. Anal. Found (calcd for C$_{24}$H$_{42}$CeN$_3$O$_2$Si$_2$) C, 50.67 (50.75); H, 7.44 (7.50); N, 7.24 (7.39).

Synthesis of [U(L^M)N″$_2$]. To a solution of UN″$_3$ (0.5 g, 0.7 mmol) in hexanes (10 mL) was added a solution of [HL^M] (0.18 g, 0.7 mmol) in hexanes (10 mL) at room temperature. The resulting dark blue solution was stirred for 12 h. Removal of the volatiles *in vacuo* at 90 °C afforded [U(L^M)N″$_2$] as a dark blue solid. Yield 0.51 g (89.7%). ^{1}H NMR (C$_6$D$_6$, 298 K) 28.20 and 0.62 (6 H each, *o*-Ar-Me, CMe$_2$), 26.24, 0.67, −5.69, −19.38 (2 H each, NC*H$_2$*C*H$_2$*NMes, OCMe$_2$C*H$_2$* and Ar-*H*), −9.80 (3 H, *p*-Ar-Me), −10.55 (36 H, N(Si{CH$_3$}$_2$) ppm. Anal. Found (calcd for C$_{28}$H$_{59}$N$_4$OSi$_4$U) C, 40.97 (41.09); H, 7.36 (7.28); N, 6.78 (6.85).

Attempted synthesis of [U(L^M)$_2$N″]. Treatment of a blue thf solution of UN″$_3$ (116 mg, 0.16 mmol, 5 mL) with a thf solution of [HL^M] (84 mg, 0.32 mmol, 5 mL) afforded a green-brown coloured solution over 12 h stirring at room temperature. The volatiles were removed in *vacuo*, the resulting solid was then extracted with hexanes (3 × 3 mL). Evaporation of the green hexanes extract yielded 100 mg of a pale green solid, was established by NMR spectroscopy to contain almost exclusively HL^M and small amounts of HN″. Elemental analysis of the products could not be correlated with the composition of any simple metal–ligand adduct.

Attempted synthesis of U(L^D)$_2$N″ from UN″$_3$ and 2HL^D. A J-Young Teflon valve NMR tube was charged with UN″$_3$ (0.022 g, 0.30 mmol) and HL^D (0.018 g, 0.61 mmol) in C$_6$D$_6$ (1 mL) to afford a deep blue solution instantly. The ^{1}H NMR spectrum contained resonances for U(L^D)N″$_2$ and unreacted HL^D. Over the course of 36 h, the solution became clear pale green-brown and the ^{1}H NMR spectrum contained resonances for HL^D alongside numerous small resonances over the a spectral width of 60 to −40 ppm.

Attempted synthesis of U(L^D)N″ from U(L^D)N″$_2$ and HL^D. A J-Young Teflon valve NMR tube was charged with U(L^D)N″$_2$ (0.022 g, 0.025 mmol) and HL^D(0.076 g, 0.025 mmol) in C$_6$D$_6$ (1 mL) to afford a deep blue solution. The ^{1}H NMR spectrum contained resonances for unreacted U(L^D)N″$_2$ and HL^D in a 1 : 1 ratio.

Over the course of 36 h, the solution became clear pale green-brown and HL^D was visible in the ^1H NMR spectrum alongside numerous small resonances over the a spectral width of 60 to −40 ppm.

Formation of $[UI_2(L^M)_2]$ from $[U(L^{M,Si'})N''_2I]$. A J-Young Teflon valve NMR tube containing a solution of $[U(L^{M,Si'})N''_2I]$ in C_6D_6 (0.5 mL) was heated to 70 °C for 12 h. During this time, dark pink single crystals of $[UI_2(L^M)_2]$ and a pale brown precipitate were formed. $[UI_2(L^M)_2]$ is insoluble in common NMR solvents and a satisfactory NMR spectrum was not obtained. Anal. Found (calcd for $C_{32}H_{46}I_2N_4O_2U$) C, 37.98 (38.03); H, 4.71 (4.60); N, 5.46 (5.54). Single crystals were grown by allowing a C_6D_6 solution of the reaction mixture to stand at room temperature for four weeks.

Synthesis of $[UI_2(L^M)_2]$ from $[U(L^M)N''_2]$. To a J-Young Teflon valve NMR tube containing a dark blue solution of $[U(L^M)N''_2]$ (0.057 g, 0.07 mmol) in C_6D_6(0.75 mL) was added *iso*-propyl iodide (6.9 µL, 0.07 mmol). A dark brown solution formed immediately, from which a pale brown precipitate and large dark pink crystals formed over four weeks. The cell structure of these crystals confirmed the formation of $[UI_2(L^M)_2]$.

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