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Covalency in Ce^{IV} and U^{IV} Halide and N-Heterocyclic Carbene Bonds**

Polly L. Arnold,^{1,*} Zoë R. Turner,¹ Nikolas Kaltsoyannis,^{2,*} Panagiota Pelekanaki,² Ronan M. Bellabarba,³ and Robert P. Tooze³

^[1]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

^[2]Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK.

^[3]Sasol Technology UK, Purdie Building, North Haugh, St Andrews, KY16 9SR, UK.

^[*]Corresponding authors; PLA e-mail: Polly arnold@ed.ac.uk, fax: (+44) 1316506453; NK e-mail: n.kaltsoyannis@ucl.ac.uk, fax: (+44) 2076 797463

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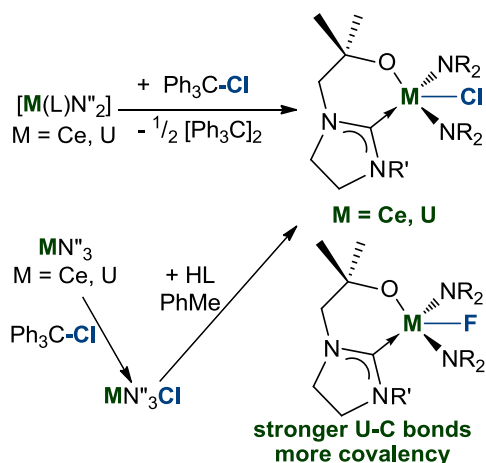
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Keywords:

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Graphical abstract:



Synopsis:

The tetravalent oxidation state of cerium is unusual, and often associated with multiconfigurational behaviour. Analysis of the bonding in *tetravalent* rather than more conventional trivalent f-block complexes shows the 5f metal bonds to softer ligands are stronger and more covalent than 4f analogues. The use of trityl chloride as a simple oxidant to access Ce^{IV} is also shown.

Abstract

Oxidative halogenation with trityl chloride provides convenient access to Ce^{IV} and U^{IV} chloroamides [M(N{SiMe₃})₂Cl] and their N-heterocyclic carbene derivatives, [M(L)(N{SiMe₃})₂Cl] (L=OCMe₂CH₂(CNCH₂CH₂NDipp) Dipp=2,6-*i*Pr₂C₆H₃). Computational analysis of the bonding in these and a fluoro analogue, [U(L)(N{SiMe₃})₂F], provides new information on the covalency in this relative rare oxidation state for molecular cerium complexes. Computational studies reveal increased Mayer bond orders in the actinide carbene bond compared with the lanthanide carbene bond, and natural and atoms-in-molecules analyses suggest greater overall ionicity in the cerium complexes than in the uranium analogues.

Introduction

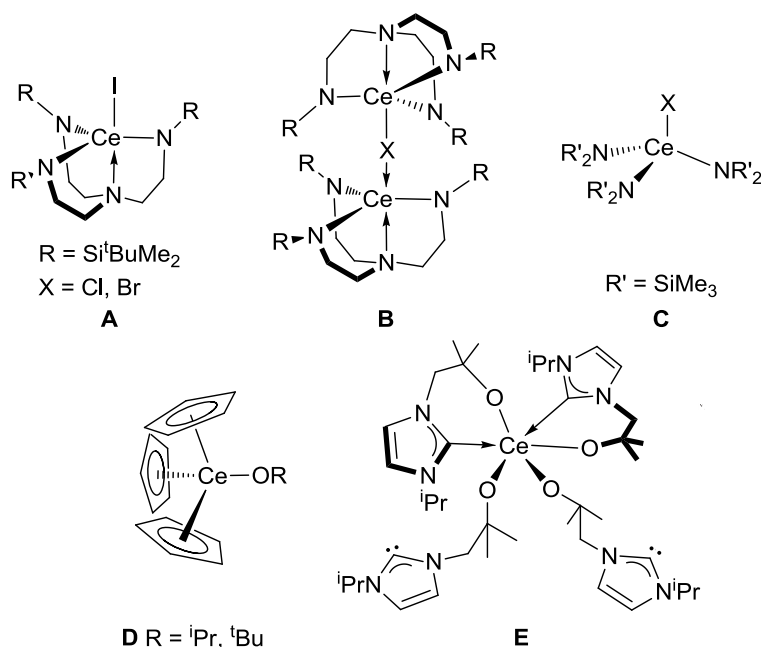
Understanding the nature of bonding and the roles of the electrons in 4f and 5f metal complexes is of fundamental academic interest and has important implications in nuclear waste management,^[1,2] and the debate over the extent of covalency in 5f-element chemistry that started decades ago is ongoing.^[3,4]

In the high-level waste streams arising from nuclear-fuel reprocessing the common oxidation state for the f-block cations encountered is +III, and the close chemical similarity of the trivalent lanthanide and actinide elements renders their separation difficult. Experimental observations that a 5f metal cation exhibits enhanced binding with a softer ligand (containing N, S, Cl, rather than O donors) than a 4f metal cation of similar size have been used as the basis for the development of chemical separators of lanthanides and actinides from these complex mixtures of cations. Trivalent 4f Ce and 5f U cations have similar ionic radii^[5] and thus the ligand affinities and bonding characteristics of pairs of their chelate complexes are often directly compared.^[6-13]

Recently, chlorine K-Edge X-ray absorption spectroscopic studies on the bonding in the series of complexes [M(Cp*)₂Cl₂] (M=Ti, Zr, Hf, Th, U; Cp*=C₅Me₅) have been used to provide direct experimental measure of the covalency in the M—Cl bond, which is significant, even for U^{IV} (at least 9 % of the Cl 3p orbital shows mixing with 6d and 5f metal-based orbitals).^[14]

By contrast to the early actinides, cerium is the only lanthanide with a chemically accessible +4 oxidation state. Indeed, due to a similar charge-to-radius ratio and solution chemistry, Ce^{IV} is often cited as a potentially useful model for Pu^{IV} complexes, which are very radioactive and difficult to manipulate.^[15,16] Unfortunately, the synthesis of such Ce^{IV} complexes is highly dependent on the choice of solvent, reaction temperature and oxidant and is often low yielding. There are only a small number of reported Ce^{IV} amide complexes, some of which are in fact Ce^{III} with ligand-centred radicals.^[17-27] Scott and co-workers reported the oxidation of the triamidoamine complex [Ce(NN')₃] (NN'=[N(CH₂CH₂NR)₃]₃, R=Si*t*BuMe₂) with molecular halogens to afford [Ce(NN')₃X] (X=I, **A**) and the mixed valence [$\{$ Ce(NN')₃]₂(μ -X)] (X=Br or Cl, **B**).^[18] Lappert and co-workers

described the preparation of $[\text{Ce}(\text{N}'')_3\text{X}]$ ($\text{N}''=\text{N}(\text{SiMe}_3)_2$, $\text{X}=\text{Cl}$ or Br , **C**) in low (24–30 %) yield by oxidation of the common silylamido reagent $[\text{Ce}(\text{N}'')_3]$ with TeX_4 ($\text{X}=\text{Cl}$ or Br) or PBr_2Ph_3 , molecular halogens resulting in no reaction.



Examples of organometallic Ce^{IV} complexes are also rare. The synthesis of $[\text{Ce}(\text{cot})_2]$ ^[28] ($\text{cot}=\text{cyclooctatetraenyl}$) and related complexes,^[29–31] combining a highly oxidising metal cation with a reducing anionic ligand, has led to intensive study and debate into assignment of the metal oxidation state.^[32–37] The first Ce^{IV} cyclopentadienyl complex^[38] was the tris(cyclopentadienyl)-supported Ce^{IV} isopropoxide (**D**) reported by Marks et al.,^[39] closely followed by the crystallographically characterised *tert*-butoxide analogue reported by Evans et al.^[40] We have demonstrated the synthesis of $[\text{CeL}_4]$ ($\text{L}=\text{OCMe}_2\text{CH}_2(\text{CNCHCHN}i\text{Pr})$; **E**).^[41, 42] The Ce^{IV} ion is supported by two bound and two unbound unsaturated backbone NHC ligands and is the only example of a $\text{Ce}^{\text{IV}}-\text{C}$ two-electron σ bond.

Computational studies comparing the extent of covalency in analogous lanthanide and actinide complexes are becoming increasingly common. Examples include studies of the bonding in 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine complexes of Cm^{III} and Eu^{III} ,^[43] backbonding in the Nd^{III} and U^{III} carbonyl complexes F_3MCO ,^[44] and our own work assessing both the extent and origin (f vs. d) of covalency in imidodiphosphinochalcogenide complexes.^[4, 12]

We have previously described the synthesis of saturated backbone NHC proligands, $\text{OCMe}_2\text{CH}_2(\text{CHNCH}_2\text{CH}_2\text{NR})$ ($\text{R}=i\text{Pr}$, 2,6-*i*PrC₆H₃, 2,4,6-MeC₆H₂), and their complexes with both low- and

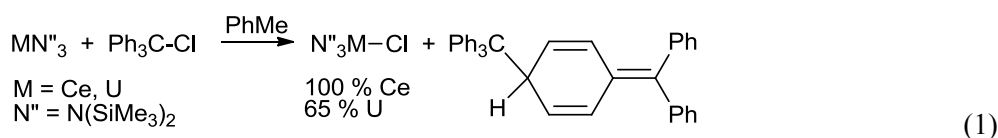
high-valent f-block cations.^[45, 46] Herein we report a new one-electron oxidation route to the synthesis of Ce^{IV} and U^{IV} starting materials and halide complexes, and the DFT computational comparison of the bonding in these two M^{IV} complexes supported by an NHC ligand.

Results and Discussion

Metal(IV) chlorides

Straightforward syntheses of [Ce(N'')₃Cl] and [U(N'')₃Cl] by one-electron oxidation using trityl chloride

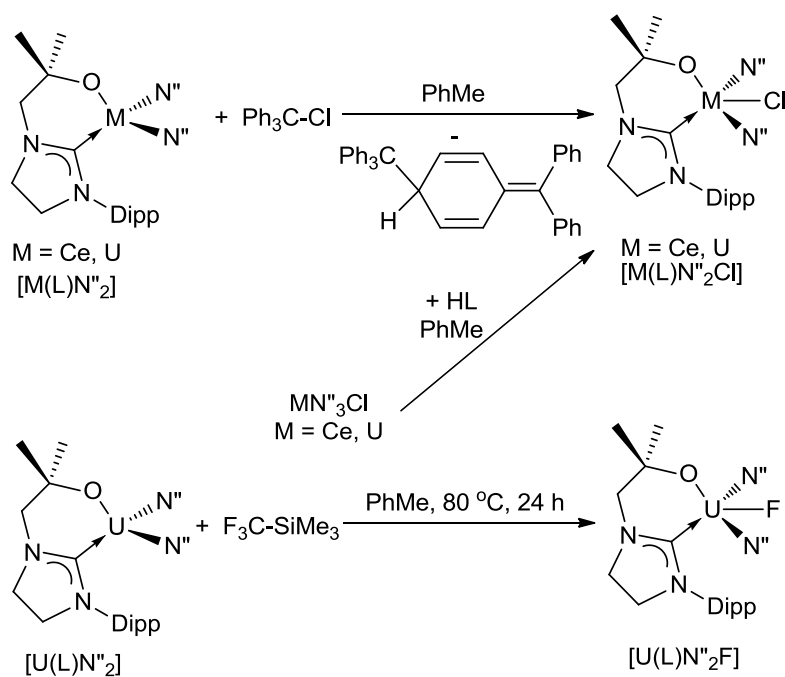
chloride: The difficulty in isolating high yields of pure Ce^{IV} amide starting materials described above led us to investigate a range of other potential oxidants. In our hands, trityl chloride, a simple, commercially available reagent, reacts with [Ce(N'')₃] to afford [Ce(N'')₃Cl] in quantitative yield before isolation [Eq. (Spiel um Platz drei)]. The yields stated in the equation are measured by integration of the NMR spectra against an internal standard, the isolated preparative scale yields are 81 (Ce) and 50 % (U). Likewise, [U(N'')₃] is readily and quantitatively converted to [U(N'')₃Cl], although the literature route to [U(N'')₃Cl] (by the reaction between UCl₄ and three equivalents of NaN'') proceeds in excellent yield.^[47] It should be noted that the use of trityl fluoride has been used previously to oxidise [U(Cp')₃] to [U(Cp')₃F] in good (45 %) yield (Cp'=C₅Me₄(SiMe₃)).^[48] The pure [M(N'')₃Cl] complexes may be readily isolated from the dimer of [CPh₃] (Gomberg's dimer, Ph₃CCH(C₆H₄)CPh₂)^[49] which is the only byproduct, by recrystallisation from a THF/hexanes mixture.



Syntheses of Ce^{IV} and U^{IV} carbene complexes [Ce(L)(N'')₂Cl], [U(L)(N'')₂Cl] and [U(L)(N'')₂F]

(L=OCMe₂CH₂(CNCH₂CH₂NDipp) Dipp=2,6-*i*Pr₂C₆H₃): In the same manner as for the metal tris(silylamido) complexes above, the yellow Ce^{III} and dark blue U^{III} complexes [M(L)(N'')₂] can be oxidised cleanly by one equivalent of Ph₃CCl in toluene, Scheme 1, to afford dark red [Ce^{IV}(L)(N'')₂Cl] and brown [U^{IV}(L)(N'')₂Cl], respectively (see the Supporting Information for full characterising data). Attempts to oxidise [Ce(L)(N'')₂] using TeCl₄ did not yield [Ce^{IV}(L)(N'')₂Cl]. We note that it is possible to convert both [M(N'')₃Cl] complexes into the [M^{IV}(L)(N'')₂Cl] carbene complexes by treatment with the proligand HL (with concomitant elimination of HN''). This suggests that now a high-yielding route to cerium(IV) amides is available, much more coordination chemistry of this strongly Lewis acidic metal cation should be accessible.

The Ce^{IV} complex is diamagnetic: the ¹H NMR spectrum is straightforward to interpret, and the carbene carbon resonance is observed at 237.4 ppm in the ¹³C NMR spectrum, a particularly high chemical shift. Single crystals of both chloride complexes were grown; the molecular structures are discussed below.



Scheme 1. Synthetic routes to the Ce^{IV} and U^{IV} carbene-alkoxide halide complexes.

During our investigations on the reactivity of the U^{III} complex, we treated [U(L)(N'')₂] with Ruppert's reagent, SiMe₃CF₃, a molecule generally used to introduce a CF₃ group.^[50] However, in our hands the only product isolable is the uranium fluoride [U^{IV}(L)(N'')₂F], which was isolated as a red-brown solid in 69 % yield after toluene workup, Scheme 1. An X-ray diffraction study of single crystals of the fluoride [U^{IV}(L)(N'')₂F] was also undertaken, see below.

The iodide [U^{IV}(L)(N'')₂I] is also accessible from the reaction of [U(L)(N'')₂] with *tert*-butyl iodide and has similar spectroscopic characteristics to the chloride and fluoride, but difficulties in the isolation of pure material led us to focus on the lighter halides.

Molecular structures of Ce^{IV} and U^{IV} carbene complexes [Ce(L)(N'')₂Cl], [U(L)(N'')₂Cl] and [U(L)(N'')₂F]: Single crystals of [Ce(L)(N'')₂Cl], [U(L)(N'')₂Cl] and [U(L)(N'')₂F] were grown from cooled

solutions of the complexes in toluene. The molecular structures are shown in Figure 1, and selected distances and angles are collated in Table 1.

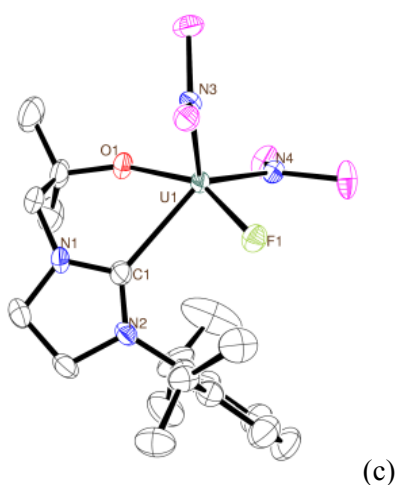
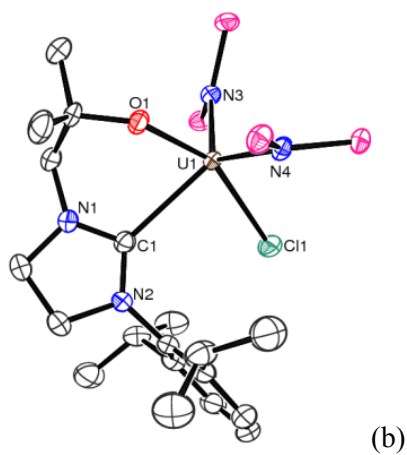
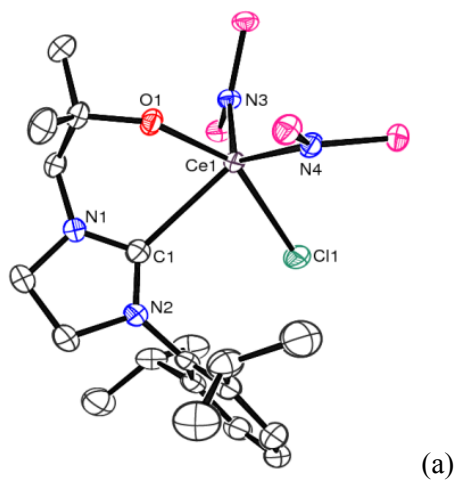


Figure 1. Displacement ellipsoid drawings of the molecular structures of a) $[\text{Ce}(\text{L})(\text{N}'')_2\text{Cl}]$, b) $[\text{U}(\text{L})(\text{N}'')_2\text{Cl}]$, and c) $[\text{U}(\text{L})(\text{N}'')_2\text{F}]$. Lattice solvent molecules, hydrogen atoms and silyl methyl groups are omitted for clarity.

Table 1. Selected experimental distances [\AA] and angles [$^\circ$] for $[\text{Ce}(\text{L})(\text{N}'')_2\text{Cl}]$, $[\text{U}(\text{L})(\text{N}'')_2\text{Cl}]$ and $[\text{U}(\text{L})(\text{N}'')_2\text{F}]$, and computational data (in square brackets) on models for these systems and the Ce–F analogue.

	$[\text{Ce}(\text{L})(\text{N}'')_2\text{F}]$	$[\text{U}(\text{L})(\text{N}'')_2\text{F}]$	$[\text{Ce}(\text{L})(\text{N}'')_2\text{Cl}]$	$[\text{U}(\text{L})(\text{N}'')_2\text{Cl}]$
M—O	[2.121]	2.082(4) [2.101]	2.061(2) [2.103]	2.072(2) [2.093]
M—N3	[2.308]	2.287(4) [2.308]	2.259(2) [2.282]	2.289(2) [2.279]
M—X (X=Cl, F)	[2.102]	2.087(3) [2.113]	2.643(7) [2.641]	2.641(6) [2.636]
M—C	[2.696]	2.654(6) [2.614]	2.692(3) [2.694]	2.668(2) [2.631]
C-M-X	[81.09]	79.90(16) [85.97]	79.87(6) [85.23]	81.83(5) [89.07]
O-M-C	[70.00]	71.59(17) [71.67]	72.18(8) [69.63]	72.89(7) [70.71]

In all three molecular structures the metal cation is five-coordinate, and the arrangement of the ligands is very similar between complexes, allowing detailed comparisons to be made. The alkoxy–carbene ligand bite angle is small in all three complexes ($72.18(8)^\circ$ in Ce—Cl, $72.89(7)^\circ$ in U—Cl and $71.59(17)^\circ$ in the U—F complex).

Inspection of the differences between the Ce and U bonds to the softer ligands should provide an initial indication of the differences in covalency between the two metal cations. The five-coordinate radius for Ce^{IV} is not recorded in the Shannon radii lists, but the six-coordinate covalent radius is 1.01 \AA , whilst six-coordinate U^{IV} has a covalent radius of 1.03 \AA , only 0.02 \AA larger. Here, the $\text{Ce}^{\text{IV}}-\text{C}_{\text{carbene}}$ bond length is $2.692(3) \text{ \AA}$. Allowing for a 0.02 \AA larger metal radius, the $\text{U}^{\text{IV}}-\text{C}_{\text{carbene}}$ lengths of $2.668(2)$ and $2.654(6) \text{ \AA}$ are not significantly (within the 3σ criterion) shorter.

It had been suggested that the short distance between the carbene carbon and a *cis*-coordinated π -donor ligand is due to the donation of electron density to the formally empty (but high-energy) carbene π orbital,^[51, 52] but we,^[53] and now others,^[54] have found no evidence for this in d^0 metal halide/NHC complexes. Again in these three complexes, the halide is close to the carbene carbon atom, but this is apparently due to packing effects once again.

Computational analysis

Molecular structures of Ce^{IV} and U^{IV} carbene complexes $[\text{Ce}(\text{L})(\text{N}'')_2\text{Cl}]$, $[\text{U}(\text{L})(\text{N}'')_2\text{Cl}]$ and $[\text{U}(\text{L})(\text{N}'')_2\text{F}]$: $[\text{Ce}(\text{L})(\text{N}'')_2\text{Cl}]$, $[\text{Ce}(\text{L})(\text{N}'')_2\text{F}]$, $[\text{U}(\text{L})(\text{N}'')_2\text{Cl}]$ and $[\text{U}(\text{L})(\text{N}'')_2\text{F}]$ were studied computationally by using DFT, with the SiMe_3 groups replaced with SiH_3 and Dipp by Me. Although it is known that formally Ce^{IV} organometallics may possess multiconfigurational ground states,^[32, 34, 35] we believe that a DFT approach is warranted in the present study as our principal aim is to assess differences in covalency between Ce^{IV} and

U^{IV} , for which DFT should be adequate. Furthermore, multiconfigurational calculations of the present low-symmetry targets are very likely intractable.

To determine if the shorter M—C bond lengths in the actinide molecules reflect increased covalency, we have probed the electronic structures at the optimised geometries using Mayer and natural analyses, and key results are collected in Table 2. Mayer bond orders (MBOs) contain all of the contributions to a bond between two atoms, that is, they take account of all bonding and antibonding interactions in a single number.^[55] It can be seen from Table 2 that the Ce—C MBOs are very similar in the F and Cl compounds, as is the case for the U—C in the analogous 5f systems. However, comparison of the Ce systems with the U shows a significantly larger MBOs in the latter, consistent with the shorter M—C bonds in 5f compounds.

Table 2. M—C Mayer bond orders, natural charges and populations (above formal values) for computational models of [Ce(L)(N'')₂F], [U(L)(N'')₂F], [Ce(L)(N'')₂Cl] and [U(L)(N'')₂Cl].

	Ce/F	U/F	Ce/Cl	U/Cl
M—C MBO	0.33	0.46	0.34	0.44
q_M	2.60	2.48	2.53	2.35
q_C	0.10	0.08	0.10	0.09
q_X	-0.65	-0.61	-0.65	-0.57
M s population	0.12	0.17	0.16	0.21
M d population	0.35	0.33	0.36	0.34
M f population	0.93	0.90	0.95	0.98

The natural charges indicate that the partial charge on the carbon atom of the NHC varies very little across the four systems studied. The charges on the halogen are the same in the two Ce compounds, while that on Cl is less negative than that for F in the U systems. Comparison of analogous Ce and U compounds reveals a less negative charge on the halogen in the latter. The metal charges vary the most across the target systems and show that the fluoride complexes have larger positive metal charges than the chloride and also that the Ce compounds have larger metal charges than the U. These data are consistent with greater ionicity in the Ce compounds.

Table 2 also presents the natural atomic populations of the metals, given as the number of electrons above the formal value expected for M^{IV} (p populations were very close to the formal value in all cases and are omitted). Such enhanced populations may be taken as evidence of participation of the orbitals in covalent bonding, and it is clear that the f orbitals have much the largest populations. Comparison between the different systems yields a mixed picture. There are larger s populations in the U compounds versus the Ce analogues, while for the d orbitals there is a slight reduction from Ce to U. The f population increases from Ce to U for the Cl compounds, but decreases slightly for the F systems. The total M population (s+d+f) decreases in the order

$[U(L)(N'')_2Cl] > [Ce(L)(N'')_2Cl] > [U(L)(N'')_2F] = [Ce(L)(N'')_2F]$, and this may be taken as evidence that covalency decreases in the same manner.

We have recently begun to use analysis of electron density topology, in the form of atoms-in-molecules (AIM) calculations, to gauge the extent of covalency in actinide systems,^[56] and have applied this approach to the current targets. Table 3 collects electron (ρ) and energy density (H) data at the metal–carbon and metal–halogen bond critical points. These data are indicative of largely ionic bonding in all four molecules,^[57] but it is noticeable that the values for the U systems are uniformly larger (in an absolute sense) than the Ce analogues. Given that, for both ρ and H , larger absolute values are associated with increased covalency, the present AIM results are entirely consistent with the conclusions from the Mayer and natural analyses in finding larger covalency in the 5f compounds.

Table 3. Characteristics of the metal–carbon and metal–halogen bond critical points for computational models of $[Ce(L)(N'')_2F]$, $[U(L)(N'')_2F]$, $[Ce(L)(N'')_2Cl]$ and $[U(L)(N'')_2Cl]$.

	Ce/F	U/F	Ce/Cl	U/Cl
M—C ρ	0.045	0.055	0.045	0.053
M—X ρ	0.105	0.110	0.059	0.064
M—C H	-0.003	-0.007	-0.004	-0.007
M—X H	-0.011	-0.013	-0.007	-0.009

Conclusion

Complexes of tetravalent Ce and U, $[Ce(L)(N'')_2Cl]$, $[U(L)(N'')_2Cl]$ and $[U(L)(N'')_2F]$ have been made and characterised by single-crystal diffraction studies. Computational models of these, and the cerium fluoride analogue, have also been studied in order to assess the degree of covalency present within the complexes.

The crystal structure data show very little difference between the complexes, within experimental error, but the slight shortening of the M—C bond in $[U(L)(N'')_2Cl]$ versus $[Ce(L)(N'')_2Cl]$ is replicated, and indeed exaggerated, computationally. A significantly larger Mayer bond order is found in the uranium–carbene bond than the cerium–carbene bond, and greater ionicity in the cerium complexes than the uranium complexes overall is supported by natural and AIM analyses.

Finally, we have also demonstrated that trityl chloride is an effective oxidant for Ce^{III} and U^{III} to make mixed ligand and organometallic Ce^{IV} and U^{IV} complexes.

Experimental Section

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.

Synthesis of [Ce(N'')₃Cl]: Toluene (10 mL) was added to a mixture of [Ce(N'')₃] (0.64 g, 1.0 mmol) and Ph₃CCl (0.36 g, 1.3 mmol) to immediately afford a dark purple solution. The reaction mixture was stirred for 1 h. The volatiles were removed in vacuo and recrystallisation from THF/hexanes (1/2) at -30 °C afforded [Ce(N'')₃Cl] as a dark purple microcrystalline solid. Yield 0.54 g (81 %); ¹H NMR (C₆D₆, 400 MHz, 298 K): δ=0.44 ppm (s, 54 H; SiMe).

Synthesis of [U(N'')₃Cl]: A solution of Ph₃CCl (0.25 g, 0.89 mmol) in toluene (5 mL) was added to a slurry of purple [U(N'')₃] (0.51 g, 0.71 mmol) in toluene (10 mL) to immediately afford a brown solution. The reaction mixture was stirred for 1 h before the volatiles were removed in vacuo. Recrystallisation from THF/hexanes (1/2) at -30 °C afforded [U(N'')₃Cl] as a brown microcrystalline solid. Yield 0.27 g (50 %); ¹H NMR (C₆D₆, 400 MHz, 298 K): δ=-2.33 ppm (s, 54 H; SiMe).

Synthesis of [Ce(L)(N'')₂Cl]: A solution of Ph₃CCl (0.22 g, 0.81 mmol) in toluene (5 mL) was added to a slurry of [Ce(L)(N'')₂] (0.62 g, 0.81 mmol) in toluene (5 mL). The reaction mixture was stirred for 12 h, during which time it turned deep orange-red. Concentration to 5 mL and cooling to -30 °C yielded red-orange microcrystalline material. This was isolated by filtration and the volatiles were then removed in vacuo to afford [Ce(L)(N'')₂Cl] as a red-orange solid. X-ray diffraction quality crystals were grown from a saturated solution of the complex in toluene at -20 °C. Yield 0.22 g (34 %); ¹H NMR (C₆D₆, 600 MHz, 298 K): δ=7.17 (t, ³J=7.2 Hz, 1 H; 4-C₆H₃), 7.12 (t, ³J=7.2 Hz, 1 H; 3,5-C₆H₃), 3.29 (t, ³J=10.6 Hz, 2 H; NCH₂CH₂N), 3.24 (sept, ³J=6.8 Hz, 2 H; HCMe₂), 3.01 (s, 2 H; OCM₂CH₂), 2.83 (t, ³J=10.6 Hz, 2 H; NCH₂CH₂N), 1.52 and 1.16 (2 d, ³J=6.8 Hz, 2×6 H; HCMe₂), 1.16 (s, 6 H; CMe₂), 0.55 ppm (s, 36 H; SiMe).

Alternative synthesis of [Ce(L)(N'')₂Cl]: A solution of HL (0.031 g, 0.10 mmol) in toluene (1 mL) was added to a dark red slurry of [Ce(N'')₃Cl] (0.068 g, 0.10 mmol) in toluene (2 mL). The reaction mixture immediately became dark purple in colour and was stirred for 2 h at room temperature. Recrystallisation from toluene (1 mL) at -30 °C afforded [Ce(L)(N'')₂Cl] as a red-orange solid. Yield 0.055 g (67 %).

Synthesis of [U(L)(N'')₂F]: F₃CSiMe₃ (14 μL, 0.094 mmol) was added to a dark blue solution of [U(L)(N'')₂] (0.081 g, 0.094 mmol) in toluene (2 mL). The reaction mixture was heated to 80 °C for 24 h to afford a dark brown solution. Recrystallisation from toluene (1 mL) at -20 °C afforded [U(L)(N'')₂F] as a red-brown solid. X-ray diffraction quality crystals were grown from a solution of the complex in toluene at -30 °C. Yield 0.057 g (69 %); ¹H NMR (C₆D₆, 360 MHz, 298 K): δ=76.40 (s, 6 H; CMe₂), 11.71 (s, 2 H; OCM₂CH₂, NCH₂CH₂N or HCMe₂), 3.21 (t, ³J=7.4 Hz, 1 H; 4-C₆H₃), 0.9 and 0.03 (2 d, ³J=7.4 Hz, 2×1 H; 3,5-C₆H₃), -4.64 (s, 12 H;

HCMe_2) -11.38 (s, 36 H; SiMe), -24.1 and -31.2 (s, 2 H; OCMe_2CH_2 , $\text{NCH}_2\text{CH}_2\text{N}$ or HCMe_2), -47.64 ppm (s, 2 H; OCMe_2CH_2 , $\text{NCH}_2\text{CH}_2\text{N}$ or HCMe_2).

Synthesis of $[\text{U}(\text{L})(\text{N}'')_2\text{Cl}]$: $[\text{U}(\text{N}'')_3\text{Cl}]$ (0.10 g, 0.13 mmol) and HL (0.040 g, 0.13 mmol) were combined in C_6D_6 (1 mL) to afford a brown solution. After 2 h, the volatiles were removed in vacuo. Recrystallisation from toluene afforded $[\text{U}(\text{L})(\text{N}'')_2\text{Cl}]$ as a brown solid. X-ray diffraction quality crystals were grown from a saturated solution of the complex in toluene at -20°C . Yield 0.043 g (36 %); $^1\text{H NMR}$ (C_6D_6 , 500 MHz, 298 K): $\delta=77.39$ (s, 6 H; CMe_2 or HCMe_2), 31.67 (s, 2 H; OCMe_2CH_2 , $\text{NCH}_2\text{CH}_2\text{N}$, HCMe_2 or 3,5- C_6H_3), 12.93 (s, 1 H; 4- C_6H_3), 7.47 (s, 2 H; OCMe_2CH_2 , $\text{NCH}_2\text{CH}_2\text{N}$, HCMe_2 or 3,5- C_6H_3), -11.05 (s, 6 H; CMe_2 or HCMe_2), -12.69 (s, 2 H; OCMe_2CH_2 , $\text{NCH}_2\text{CH}_2\text{N}$, HCMe_2 or 3,5- C_6H_3), -14.11 (s, 6 H; CMe_2 or HCMe_2), -17.61 (s, 36 H; SiMe), -27.71 ppm (s, 2 H; OCMe_2CH_2 , $\text{NCH}_2\text{CH}_2\text{N}$, HCMe_2 or 3,5- C_6H_3).

Synthesis of $[\text{U}(\text{L})(\text{N}'')_2\text{I}]$: $t\text{BuI}$ (22 μL , 0.19 mmol) was added to a solution of $[\text{U}(\text{L})(\text{N}'')_2]$ (0.16 g, 0.19 mmol) in toluene (10 mL). The reaction mixture immediately became pale brown in colour. The volatiles were removed in vacuo and a pale pink solid containing $[\text{U}(\text{L})(\text{N}'')_2\text{I}]$ as the major product was isolated from a toluene solution cooled to -20°C . Yield 0.085 g (47 %); $^1\text{H NMR}$ (C_6D_6 , 360 MHz, 298 K): $\delta=64.83$ (s, 6 H; CMe_2), 43.16 (s, 2 H; OCMe_2CH_2 , $\text{NCH}_2\text{CH}_2\text{N}$ or HCMe_2), 8.31 (s, 2 H; OCMe_2CH_2 , $\text{NCH}_2\text{CH}_2\text{N}$ or HCMe_2), 7.08 (t, $^3J=6.9$ Hz, 1 H; 4- C_6H_3), 6.99 (d, $^3J=6.9$ Hz, 1 H; 3,5- C_6H_3), 3.75 (s, 2 H; OCMe_2CH_2 , $\text{NCH}_2\text{CH}_2\text{N}$ or HCMe_2), -10.77 (s, 12 H; HCMe_2), -11.23 (s, 12 H; CMe_2), -17.19 (s, 36 H; SiMe), -17.22 ppm (s, 2 H; OCMe_2CH_2 , $\text{NCH}_2\text{CH}_2\text{N}$ or HCMe_2).

CCDC-778656 ($[\text{Ce}(\text{L})(\text{N}'')_2\text{Cl}]$), 778657 ($[\text{U}(\text{L})(\text{N}'')_2\text{Cl}]$) and 778658 ($[\text{U}(\text{L})(\text{N}'')_2\text{F}]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details: Gradient-corrected density functional theory calculations were carried out using the TPSS^[58] functional, as implemented in the Gaussian 03 Rev D.02 (G03),^[59] Gaussian 09 Rev. A.02 (G09)^[60] and Amsterdam Density Functional 2009 (ADF)^[61, 62] quantum chemistry codes. Spin-restricted calculations were performed on the Ce target molecules, and the spin-unrestricted formalism was employed for the U systems ($5f^2$). Default values for integration grids, and scf and geometry convergence criteria, were used in all cases.

Atoms-in-molecules analyses were performed using the AIMALL programme, version 09.10.24,^[63] using formatted G09 checkpoint files as input.

In the G03 calculations, (14s 13p 10d 8f)/[10s 9p 5d 4f] segmented valence basis sets with Stuttgart-Bonn variety relativistic effective core potentials (RECPs) were used for U,^[64] while an RECP plus (14s 13p 10d 8f)/[10s 8p 5d 4f] valence basis was employed for Ce.^[65] Dunning's cc-pVDZ basis sets were employed for the non f-elements.

Natural charge and population analyses^[66, 67] were carried out on all G03-optimized structures by using NBO version 3.1. We have used the default partitioning scheme, in which the actinide 6d orbitals are placed in the Rydberg basis. While there is some evidence that the 6d orbitals may be more appropriately considered as valence in the NPA scheme,^[68] we have no direct experience with such a partitioning and have decided to retain the default approach so as to better facilitate comparison with our previous studies of related systems.^[4, 12, 56]

References

- [1] K. L. Nash, *Solvent Extr. Ion Exch.* **1993**, *11*, 729.
- [2] H. H. Dam, D. N. Reinhoudt, W. Verboom, *Chem. Soc. Rev.* **2007**, *36*, 367.
- [3] G. R. Choppin, *J. Alloys Compd.* **2002**, *344*, 55.
- [4] K. I. M. Ingram, M. J. Tassell, A. J. Gaunt, N. Kaltsoyannis, *Inorg. Chem.* **2008**, *47*, 7824.
- [5] R. D. Shannon, *Acta Crystallogr., Sect.* **1976**, *A32*, 751.
- [6] T. Mehdoui, J.-C. Berthet, P. Thuery, M. Ephritikhine, *Dalton Trans.* **2004**, 579.
- [7] T. Mehdoui, J.-C. Berthet, P. Thuery, M. Ephritikhine, *Chem. Commun.* **2005**, 2860.
- [8] M. Miguirditchian, D. Guillaneux, D. Guillaumont, P. Moisy, C. Madic, M. P. Jensen, K. L. Nash, *Inorg. Chem.* **2005**, *44*, 1404.
- [9] Roger, N. Barros, T. Arliguie, P. Thuery, L. Maron, M. Ephritikhine, *J. Am. Chem. Soc.* **2006**, *128*, 8790.
- [10] M. Roger, L. Belkhiri, T. Arliguie, P. Thuery, A. Boucekkine, M. Ephritikhine, *Organometallics* **2008**, *27*, 33.
- [11] M. Mazzanti, R. Wietzke, J. Pecaut, J.-M. Latour, P. Maldivi, M. Remy, *Inorg. Chem.* **2002**, *41*, 2389.
- [12] A. J. Gaunt, S. D. Reilly, A. E. Enriquez, B. L. Scott, J. A. Ibers, P. Sekar, K. I. M. Ingram, N. Kaltsoyannis, M. P. Neu, *Inorg. Chem.* **2008**, *47*, 29.
- [13] T. Arliguie, L. Belkhiri, S.-E. Bouaoud, P. Thuery, C. Villiers, A. Boucekkine, M. Ephritikhine, *Inorg. Chem.* **2009**, *48*, 221.
- [14] S. A. Kozimor, P. Yang, E. R. Batista, K. S. Boland, C. J. Burns, D. L. Clark, S. D. Conradson, R. L. Martin, M. P. Wilkerson, L. E. Wolfsberg, *J. Am. Chem. Soc.* **2009**, *131*, 12125.
- [15] A. E. V. Gorden, J. Xu, G. z. Szigethy, A. Oliver, D. K. Shuh, K. N. Raymond, *J. Am. Chem. Soc.* **2007**, *129*, 6674.
- [16] J. Diwu, A.-G. D. Nelson, S. Wang, C. F. Campana, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2010**, *49*, 3337.
- [17] K. Tashiro, K. Konishi, T. Aida, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 856.

- [18] C. Morton, N. W. Alcock, M. R. Lees, I. J. Munslow, C. J. Sanders, P. Scott, *J. Am. Chem. Soc.* **1999**, *121*, 11255.
- [19] P. B. Hitchcock, A. G. Hulkes, M. F. Lappert, *Inorg. Chem.* **2003**, *43*, 1031.
- [20] D. B. Baudry, A. Dormond, F. Duris, J. M. Bernard, J. R. Desmurs, *J. Fluorine Chem.* **2003**, *121*, 233.
- [21] P. B. Hitchcock, M. F. Lappert, A. V. Protchenko, *Chem. Commun.* **2006**, 3546.
- [22] P. Droese, J. Gottfriedsen, *Z. Anorg. Allg. Chem.* **2008**, *634*, 87.
- [23] J. W. Buchler, A. Decian, J. Fischer, M. Kihnbotulinski, H. Paulus, R. Weiss, *J. Am. Chem. Soc.* **1986**, *108*, 3652.
- [24] J. W. Buchler, T. Dippell, *Eur. J. Inorg. Chem.* **1998**, *1998*, 445.
- [25] J. Gottfriedsen, M. Spoida, S. Blaurock, *Z. Anorg. Allg. Chem.* **2008**, *634*, 514.
- [26] P. L. Arnold, N. A. Potter née Jones, C. D. Carmichael, A. M. Z. Slawin, P. Roussel, J. B. Love, *Chem. Commun.* **2010**, *46*, 1833.
- [27] M. D. Walter, R. Fandos, R. A. Andersen, *New J. Chem.* **2006**, *30*, 1065.
- [28] A. Greco, S. Cesca, G. Bertolini, *J. Organomet. Chem.* **1976**, *113*, 321.
- [29] U. Kilimann, R. Herbst-Irmer, D. Stalke, F. T. Edelmann, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1618.
- [30] A. Ashley, G. Balazs, A. Cowley, J. Green, C. H. Booth, D. O'Hare, *Chem. Commun.* **2007**, 1515.
- [31] G. Balazs, F. G. N. Cloke, J. C. Green, R. M. Harker, A. Harrison, P. B. Hitchcock, C. N. Jardine, R. Walton, *Organometallics* **2007**, *26*, 3111.
- [32] A. Kerridge, R. Coates, N. Kaltsoyannis, *The Journal of Physical Chemistry A* **2009**, *113*, 2896.
- [33] N. M. Edelstein, P. G. Allen, J. J. Bucher, D. K. Shuh, C. D. Sofield, N. Kaltsoyannis, G. H. Maunder, M. R. Russo, A. Sella, *J. Am. Chem. Soc.* **1996**, *118*, 13115.
- [34] R. D. Fischer, *Angew. Chem.* **1994**, *106*, 2253.
- [35] M. D. Walter, C. H. Booth, W. W. Lukens, R. A. Andersen, *Organometallics* **2009**, *28*, 698.
- [36] C. H. Booth, M. D. Walter, M. Daniel, W. W. Lukens, R. A. Andersen, *Phy. Rev. Lett.* **2005**, *95*.
- [37] A. Streitwieser, Jr., S. A. Kinsley, J. T. Rigsbee, I. L. Fragala, E. Ciliberto, *J. Am. Chem. Soc.* **1985**, *107*, 7786.

- [38] G. B. Deacon, T. D. Tuong, D. G. Vince, *Polyhedron* **1983**, *2*, 969.
- [39] A. Gulino, M. Casarin, V. P. Conticello, J. G. Gaudiello, H. Mauermann, I. Fragala, T. J. Marks, *Organometallics* **1988**, *7*, 2360.
- [40] W. J. Evans, T. J. Deming, J. W. Ziller, *Organometallics* **1989**, *8*, 1581.
- [41] I. J. Casely, S. T. Liddle, A. J. Blake, C. Wilson, P. L. Arnold, *Chem. Commun.* **2007**, 5037.
- [42] P. L. Arnold, I. J. Casely, S. Zlatogorsky, C. Wilson, *Helv. Chim. Acta* **2009**, *92*, 2291.
- [43] M. A. Denecke, A. Rossberg, P. J. Panak, M. Weigl, B. Schimmelpfennig, A. Geist, *Inorg. Chem.* **2005**, *44*, 8418.
- [44] V. Vetere, P. Maldivi, B. O. Roos, C. Adamo, *J. Phys. Chem. A* **2009**, *113*, 14760.
- [45] P. L. Arnold, I. J. Casely, Z. R. Turner, C. D. Carmichael, *Chem. Eur. J.* **2008**, *14*, 10415.
- [46] Z. R. Turner, R. Bellabarba, R. P. Tooze, P. L. Arnold, *J. Am. Chem. Soc.* **2010**, *132*, 4050.
- [47] H. W. Turner, R. A. Andersen, A. Zalkin, D. H. Templeton, *Inorg. Chem.* **1979**, *18*, 1221.
- [48] M. Weydert, A. Andersen Richard, in *Inorganic Fluorine Chemistry*, American Chemical Society, Washington, DC, **1994**, pp. 383.
- [49] H. Lankamp, W. T. Nauta, C. MacLean, *Tetrahedron Lett.* **1968**, *9*, 249.
- [50] G. K. S. Prakash, A. K. Yudin, *Chem. Rev.* **1997**, *97*, 757.
- [51] C. D. Abernethy, G. M. Codd, M. D. Spicer, M. K. Taylor, *J. Am. Chem. Soc.* **2003**, *125*, 1128.
- [52] P. Shukla, J. A. Johnson, D. Vidovic, A. H. Cowley, C. D. Abernethy, *Chem. Commun.* **2004**, 360.
- [53] S. A. Mungur, A. J. Blake, C. Wilson, J. McMaster, P. L. Arnold, *Organometallics* **2006**, *25*, 1861.
- [54] B. M. Gardner, J. McMaster, S. T. Liddle, *Dalton Trans.* **2009**, 6924.
- [55] A. J. Bridgeman, G. Cavigliasso, L. R. Ireland, J. Rothery, *J. Chem. Soc., Dalton Trans.* **2001**, 2095.
- [56] M. J. Tassell, N. Kaltsoyannis, *Dalton Trans.* **2010**, *1*, DOI:10.1039/c000704h.
- [57] C. F. Matta, R. J. Boyd, in *The quantum theory of atoms in molecules* (Eds.: C. F. Matta, R. J. Boyd), Wiley-VCH, Weinheim, **2007**, pp. 1.
- [58] J. M. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phy. Rev. Lett.* **2003**, *91*, 146401.

- [59] M. J. Frisch, *et al.*, *Gaussian 03 revision D.01*, **2004**. See SI for full author list.
- [60] M. J. Frisch, *et al.*, *Gaussian 09, Revision A.2*, **2009**. See SI for full author list.
- [61] C. Fonseca Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, *Theor. Chem. Acc.* **1998**, *99*, 391.
- [62] G. te Velde, F. M. Bickelhaupt, S. Van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders, T. Ziegler, *J. Comp. Chem.* **2001**, *22*, 931.
- [63] T. A. Keith, *AIMALL*, **2009**, 09.10.24.
- [64] X. Y. Cao, M. Dolg, H. Stoll, *J. Chem. Phys.* **2003**, *118*, 487.
- [65] X. Y. Cao, M. Dolg, *J. Mol. Struct. (Theochem)* **2002**, *581*, 139.
- [66] J. E. Carpenter, F. Weinhold, *J. Mol. Struct. (Theochem)* **1988**, *169*, 41.
- [67] F. Weinhold, J. E. Carpenter, Plenum, **1988**, p. 227.
- [68] A. E. Clark, J. L. Sonnenberg, P. J. Hay, R. L. Martin, *J. Chem. Phys* **2004**, *121*, 2563.