The inverse-trans-influence in tetravalent lanthanide and actinide bis(carbene) complexes

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Across the periodic table the trans-influence operates, whereby tightly bonded ligands selectively lengthen mutually trans metal-ligand bonds. Conversely, in high oxidation state actinide complexes the inverse-trans-influence operates, where normally cis strongly donating ligands instead reside trans and actually reinforce each other. However, because the inverse-trans-influence is restricted to high-valent actinyls and a few uranium(V/VI) complexes, it has had limited scope in an area with few unifying rules. Here we report tetravalent cerium, uranium and thorium bis(carbene) complexes with trans $C = M = C$ cores where experimental and theoretical data suggest the presence of an inverse-trans-influence. Studies of hypothetical praseodymium(IV) and terbium(IV) analogues suggest the inverse-trans-influence may extend to these ions but it also diminishes significantly as the 4f orbitals are populated. This work suggests that the inverse-trans-influence may occur beyond high oxidation state 5f metals and hence could encompass mid-range oxidation state actinides and lanthanides. Thus, the inverse-trans-influence might be a more general f-block principle.
The trans-influence is a long-established, well-documented concept of broad relevance across inorganic chemistry. This thermodynamic ground-state phenomenon classically occurs in square-planar and pseudo-octahedral d-block complexes where tightly bonded ligands selectively lengthen mutually trans metal–ligand bonds. The trans-influence is fundamentally important and underpins the trans-effect, a kinetic rate effect where the order of substitution of ligands at a metal centre can be controlled; this is a key parameter to control, for example, the syntheses of cis- or trans-\([\text{PtCl}_2(\text{NH}_3)_2]\), whose isomerism is important regarding cancer treatment.

Although the bonding of lanthanide(II) and low/mid oxidation state early actinide ions is considered more ionic than in the d-block, there are crystallographic, and in some instances computationally supported, examples of complexes where metrical parameters are consistent with the presence of the trans-influence.

In high oxidation state actinide complexes the opposite phenomenon of the inverse-trans-influence (ITI) can be found. Here, strongly donating ligands that normally adopt cis orientations to avoid destabilizing the respective metal–ligand bonds via the trans-influence in fact reside trans to one another and even mutually reinforce each other. The classical, dominant example of the ITI is the uranyl(VI) dication, \([\text{UO}_2]^{2+}\), that adopts a trans-linear geometry and is chemically robust because of strong ITI-strengthened uranium–oxygen bonds. Indeed, linear \(\text{trans-dioxo}\) actinyls \([\text{AnO}_2]^{n+}\) (An = U, Np, Pu) are well known and prevalent, but \(\text{trans-dioxos}\) in the d-block are unusual and require strong equatorial \(\sigma\)-donor ligands to weaken the metal-oxo linkages sufficiently to enable them to reside mutually trans. Two isosctructural complexes that demonstrate the trans-influence and the ITI are \([\text{MoO}_2\text{Cl}_2(\text{OPPh}_3)_2]\) (I)\(^{22}\) and \([\text{UO}_2\text{Cl}_2(\text{OPPh}_3)_2]\) (II)\(^{23}\), respectively (Fig. 1); in the former the oxos are cis, whereas in the latter they are trans.

The ITI often plays a structure-dictating role, but this is not a criterion that must be met to make invoking the ITI valid; there are examples of high valent uranium complexes where ligands are constrained by their own architecture such that they have no choice but to place donor groups trans to a strongly donating ligand like a nitride or oxo, but despite this they present very short metal–ligand distances despite their unfavourable bonding situation. For example, in the complexes \([\text{U}\{\text{Tren-TIPS}\}(\text{E})]\) [Tren\(^\text{TIPS} = \text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\); E = N (III), O (IV)] (Fig. 1)\(^{24,25}\) the \(\text{U–N}_{\text{amine}}\) distances are short at 2.465(5) and 2.482(6) Å, respectively, despite being trans to nitride and oxo ligands, whereas such \(\text{U–N}_{\text{amine}}\) distances are normally 2.5–2.7 Å (ref. 26). In these systems there is no ITI structure-dictating role, and as part of a polydentate Tren-ligand with minimal reorganization energy\(^{27}\) the Tren amines are forced to be unfavourably trans to a nitride or oxo\(^{28}\), but the \(\text{U–N}_{\text{amine}}\) distances are short, not long, that credibly invokes the ITI.

The origin of the ITI is complex, but is in part rationalized on the basis that in high oxidation state early actinides \(6p\) orbitals are semi-core and transfer electron density to vacant \(5f\) orbitals, creating an electron hole that is compensated for by additional donation of electron density from trans ligands\(^{17–21}\). For many years the ITI was limited to uranyl(VI) complexes\(^{29}\) or structurally analogous complexes such as \([\text{UOCl}_3]^-\) (ref. 29), but in recent years a limited number of uranium(V) and (VI) ITI complexes have emerged\(^{30,31}\). The unifying theme has been high oxidation state (V or VI) metal complexes combined with hard, polarizing, charge-loaded oxo, imide and nitride ligands. Because it is limited to high oxidation state early actinides, the question of whether the ITI is a niche concept or in fact has a broader underpinning role for the \(f\)-block has remained unanswered for around a quarter of a century in an area with few unifying rules.

When considering if the ITI could have a broader basis, it would have to be demonstrated to operate over a larger range of oxidation states, and be expanded beyond actinides to include the lanthanides. The IV oxidation state is the logical next step to take in terms of the general synthetic availability of uranium and thorium complexes, as the only two actinides that can be routinely handled without specialist facilities, and also because a IV oxidation state opens the door to extend this concept to the lanthanides; cerium has an accessible IV oxidation state under normal conditions, presenting the opportunity to compare cerium, uranium and thorium together\(^{34,35}\). Although hard, formally di- and trianionic oxygen and nitrogen ligands have so far exclusively supported the ITI with high oxidation state metals, by moving to a mid-range oxidation state a softer, isoelectronic dianionic carbon-based ligand might be arguably desirable to approximately maintain the relative energy matching of frontier metal and ligand orbitals, and we note that the only examples of uranium and even thorium in the +2 oxidation state under ambient conditions are stabilized by carbon-based ligands\(^{36–38}\). Indeed, carbon should be a good ligand for the ITI more generally because of its generally high-lying frontier orbitals compared with uranium\(^{31}\). However, a paucity of synthetically accessible families of complexes where the metal can be varied in a common mid-range oxidation state has limited testing the above hypothesis.

Here, we report the realization of our aim by the synthesis of cerium, uranium and thorium \(\text{bis(carbene)}\) complexes that exhibit linear \(\text{C} = \text{M} = \text{C}\) units and thus would conventionally be expected to present long \(\text{M–C}\) distances, in fact exhibit exceedingly short \(\text{M–C}\) distances, and for cerium among the shortest experimental Ce-C distance on record. Theoretical calculations reveal that when the pseudo-core \(5p\) (cerium) or \(6p\) (uranium or thorium) orbitals are isolated from the valence manifold the \(\text{M–C}\) distances increase. Taken together with the short \(\text{M–C}\) distances, and considering that they are disposed trans, this suggests that the ITI may extend beyond high oxidation state \(5f\) metals to operate in mid-range oxidation state
Results
Synthesis. Treating the cerium(III) carbene-methanide complex $\text{Ce}[\text{BIPM(TMS)}(\text{ODipp})_2]$ with benzyl potassium and 18C6 in THF gives the yellow cerium(III) bis(carbene) complex $\text{Ce}[\text{BIPM(TMS)}(\text{THF})]$ in 52% yield (Fig. 2). Although cerium(IV) is regarded as a difficult oxidation state to access in an organometallic context because cerium(IV) oxidizing and organometallic ligands are reducing, we find that oxidation of 2Ce can be straightforwardly accomplished by AgBPh$_4$ to give the green cerium(IV) bis(carbene) complex $\text{Ce}[\text{BIPM(TMS)}(\text{THF})]$ in 43% yield after work-up and recrystallization (Fig. 2). The oxidation of 2Ce to 3Ce is so favourable that even small traces of dry air will effect oxidation. This suggests that the two carbeneres are together well suited to stabilizing cerium(IV) and producing a robust C = Ce = C unit, cf, the stability of the ITI-stabilized uranyl O = U = O dication. The corresponding uranium and thorium bis(carbene) complexes [M(BIPM(TMS))$_2$][Li(THF)] (M = U, 3U; Th, 3Th) were prepared by a different methodology (Fig. 2). The mono (carbene) dichloride complexes [M(BIPM(TMS))Cl$_2$Li(THF)] (M = U, 4U; Th, 4Th) were converted to the corresponding dialkyls [M(BIPM(TMS))(CH$_2$SiMe$_3$)$_2$] (M = U, 5U; Th, 5Th) by subsequence thermolysis with BIPM(TMS)$_2$H$_2$ to give 3U and 3Th in 75% and 52% yields as brown and colourless crystals, respectively, after work-up.

Characterization data. The $^1$H nuclear magnetic resonance (NMR) spectra of 3Ce and 3Th span 0–10 p.p.m. and are characteristic of diamagnetic complexes, whereas that of paramagnetic 3U spans ±33 p.p.m. The $^{31}$P NMR spectra of 3Ce, 3U and 3Th exhibit resonances at −13.7, −219.7 and 6.3 p.p.m., respectively; the $^{31}$P NMR resonance for 3Ce compares well with that of $[\text{Ce(BIPM(TMS)}(\text{ODipp})_2)]^{-}$ (−10.2 p.p.m., Dipp = 2,6-diisopropylphenyl) (43), and those of 3U and 3Th are typical of such complexes (41,44). The $^{13}$C NMR carbene resonances for 3U and 3Th could not be located, even utilizing $^{13}$C-$^{31}$P 2D NMR techniques, but the equivalent carbeneres in 3Ce were observed at 345.5 p.p.m. (J$_{PC} = 170$ Hz); this is more deshielded than that of $[\text{Ce(BIPM(TMS)}(\text{ODipp})_2)]^{-}$ (324.6 p.p.m., J$_{PC} = 149$ Hz) (43), possibly suggesting that the carbeneres in 3Ce are donating more strongly to cerium than in $[\text{Ce(BIPM(TMS)}(\text{ODipp})_2)]^{-}$ despite their trans arrangement. This might be expected for an ITI, and is also within the 200–400 p.p.m. range of covalent transition metal carbeneres rather than that observed for ionic yttrium(III) analogues (10–40 p.p.m.) (44).

As expected for a $^1S_0$ 4f$^0$ cerium(IV) ion, the ultraviolet/visible/near-infrared (UV/Vis/NIR) spectrum of 3Ce exhibits no absorbances in the NIR region where f–f transitions associated with multiconfigurational character might occur (Supplementary Methods). Two absorptions (Fig. 3a), the broadness of which is a defining feature in many cerium(IV) complexes (45), are observed in the visible region at 17,000 and 24,700 cm$^{-1}$ (ε = 4,895 and 14,387 M$^{-1}$cm$^{-1}$, respectively), and the latter absorbance is responsible for the green colour of 3Ce. In order to understand the electronic transitions responsible for the green colour of 3Ce we modelled the spectrum using time-dependent density functional theory (TD-DFT) calculations at the statistical
average of orbital potentials (SAOP)/zeroth order regular approximation (ZORA)/triple zeta basis set with one polarization function (TZP) level and the profile of the electronic manifold of the $^3H_4$ ground term, a strongly axial field would stabilize the $|3H_4\rangle$ state and hence even at low temperatures the complex is paramagnetic. This phenomenon has been observed before in uranium(IV) complexes with weak $\tau$ character, and the crystal field of 3Ce reveals a well-resolved, quasi-reversible single redox process assigned to the CeIV/CeIII redox couple (Supplementary Fig. 5), complex 3U retains a high $\gamma T$ value over most of the temperature range and the low-temperature $\gamma T$ value is much higher than expected from temperature-independent paramagnetism alone. This suggests that the crystal field of two strongly donating axial ligands is sufficient to stabilize low-lying paramagnetic states (consistent with low-temperature magnetization data) separated widely from higher energy states assuming a $^3H_4$ ground term, a strongly axial field would stabilize the $|n_l=4\rangle$ non-Kramers doublet, and hence even at low temperatures the complex is paramagnetic. This phenomenon has been observed before in uranium(IV) complexes with strongly donating, multiply bonded axial ligands\textsuperscript{17–32}. Complexes 3Ce and 3Th are diamagnetic, and the essentially nil or small negative $\gamma T$ slope for the latter rule out any temperature-independent paramagnetism behaviour, suggesting there is no 

The characterization data for 3Ce, 3U and 3Th support their IV oxidation state formulations. To unequivocally confirm that 3Ce is a $^1S_0$ complex we subjected it to X-ray absorption

Figure 3 | Spectroscopic and magnetic characterization data. (a) The UV/Vis/NIR spectrum of 3Ce, illustrating the broad nature of the two principal transitions in the visible region. (b) Cyclic voltammogram of 0.2 mM 3Ce in THF at selected sweep rates (0.1 M $[\text{N(Pr)}_4][\text{BArF}_4^-$ supporting electrolyte, $E_{\text{CeIV/CeIII}}=\text{tetraakis(3,5-trifluoromethylphenyl)borate}$) versus $[\text{Fe(Cp)}_2]^{0/+}$ showing a single quasi-reversible redox process assigned to the CeIV/CeIII redox couple. (c) Variable temperature magnetic susceptibility data for 3Ce, 3U and 3Th indicative of populated low-lying paramagnetic states for 3U and diamagnetic, closed-shell assignments for 3Ce and 3Th. (d) Cerium LIII-edge XANES spectrum of the cerium(IV) complex 3Ce (red trace) in comparison with its cerium(III) precursor 2Ce (black trace). As references, spectra of 0.01M cerium(III) nitrate in water (green trace) and of cerium(IV) dioxide (blue trace) are given. The XANES spectra of 2Ce and 3Ce were recorded at 15 K and the references were recorded at 298 K.
Reactivity. To give experimental support to the formulation of $\text{3Ce}$, $\text{3U}$ and $\text{3Th}$ as carbene complexes, we examined their reactivity towards PhCHO. In all cases the Wittig–alkene product PhC(H) = C(PhH$_2$NSiMe$_3$)$_2$ was formed in essentially quantitative yield. Although $\text{3Th}$ reacts too quickly to be monitored (reaction complete in $< 5 \text{ min}$), and $\text{3U}$ reacts quickly ($> 80\%$ consumed in $15 \text{ min}$) and is paramagnetic, hence reliable data could not be extracted from questionable NMR integrations, was found to be amenable to a full study (Supplementary Figs 15–17). The reaction of $\text{3Ce}$ with two equivalents of PhCHO was fitted to second-order kinetics overall (first order with respect to both $\text{3Ce}$ and PhCHO) with $k$ ($298 \text{ K}$) = $1.28 \times 10^{-4} \pm 0.25 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^{3} \text{ s}^{-1}$. Eyring and Arrhenius analyses yielded $\Delta H^\ddagger = + 57.2 \pm 2 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = - 194.4 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$, affording $\Delta G^\ddagger = + 95.2 \pm 2 \text{ kJ mol}^{-1}$ ($298 \text{ K}$) and $E_a = +40.0 \pm 2 \text{ kJ mol}^{-1}$. These data are consistent with the reaction conditions and the metalloexetane intermediates formed from a double ($2 + 2$)-cycloaddition/bond metathesis reaction to produce CeO$_2$ and PhC(H) = C(PhH$_2$NSiMe$_3$)$_2$. This reactivity is characteristic of covalent early metal carbenes and contrasts with more ionic yttrium(III)–methanediide BIPMTMS complexes that activate aryl C–H bonds of carbonyl compounds. We note that the order of reactivity of $\text{3Ce}$, $\text{3U}$ and $\text{3Th}$ with PhCHO is $\text{3Th} > \text{3U} > \text{3Ce}$, this is principally consistent with the ionic radii of the metals but is also consistent with the increasing level of covalency in the $\text{M} = \text{C}$ bonds of $\text{3Ce} > \text{3U} > \text{3Th}$ suggested by our calculations.

Theoretical calculations. To probe the electronic structures of $\text{3Ce}$, $\text{3U}$ and $\text{3Th}$, we undertook DFT calculations on their full structures. The geometry-optimized calculations match closely the experimentally determined structures within 0.05 Å and 2° (Supplementary Tables 3–11), and the TD-DFT calculations model the experimentally determined electronic absorption spectrum of $\text{3Ce}$ well. We thus conclude that the theoretical models provide a qualitative description of the electronic manifolds of $\text{3Ce}$, $\text{3U}$ and $\text{3Th}$. Although the analysis that follows shows that the dominant feature of the metal–carbon interactions in $\text{3Ce}$, $\text{3U}$ and $\text{3Th}$ is electrostatic bonding, covalent contributions are present and the discussion focuses on this latter aspect.

For $\text{3Ce}$, $\text{3U}$ and $\text{3Th}$, the calculated MDC$_n$ metal charges are 1.99, 2.77 and 2.48, respectively, and the MDC$_n$ carbene charges

Differences in $\text{2Ce}$, and $\sim 0.04 \text{ Å}$ shorter than the $\text{Ce} = \text{C}$ distances in $[\text{Ce}(\text{BIPMTMS})(\text{ODipp})_2]^{13}$ and the special case of cerium confined within an endohedral fullerene. Significantly, considering they are trans, the Ce–C bond distances in $\text{3Ce}$ are the shortest experimentally determined Ce–C distances to date in discrete molecular compounds, being surpassed only by short (2.247(17)–2.334(15) Å) cerium–carbon distances in periodic ethynediide–halide clusters. Short molecular Ce–C distances have been found in theoretical models of experimentally unknown $\text{CeC}_2^+$ and $[\text{Cp}_2\text{CeCH}_2]$ that are sterically unimpeded and, in the case of the former, benefit from the reduced electronic repulsion from a net positive charge.

The U1–C1 and U1–C32 distances in $\text{3U}$ (2.410(6) and 2.421(6) Å, respectively) are statistically equivalent to the corresponding distances in $\text{3Ce}$ (ionic radii of Ce$^{IV}$ = 0.87 Å versus U$^{IV}$ = 0.89 Å$^{62}$). However, the Th1–C1 and Th1–C32 distances in $\text{3Th}$ (2.514(3) and 2.516(3) Å, respectively) are $\sim 0.05 \text{ Å}$ longer than would be predicted purely based on the increase in ionic radius of Th$^{IV}$ (0.94 Å)$^{62}$. The short M = C bond lengths in $\text{3Ce}$, and to some extent $\text{3U}$, are all the more notable for the fact they are trans, and suggest that an ITI, rather than trans-influence, may be operating.

The solid-state structures of $\text{3Ce}$, $\text{3U}$ and $\text{3Th}$ were determined by single crystal X-ray diffraction and were found to be essentially isostuctural. Complex $\text{3Ce}$ is illustrated in Fig. 4 and further details of that and all other structurally determined complexes in this study can be found in Supplementary Figs 9–14 and Supplementary Tables 1 and 2. In each case, pseudo-octahedral metal centres present with mutually trans carbenes (3Ce, 176.98(7)$^5$; 3U, 177.5(2)$^5$; 3Th, 176.21(8)$^5$) with deviations from the octahedral ideal because of the BIPMTMS N–M–N bite angles resulting in the imino nitrogen atoms residing above and below the hypothetical equatorial plane. The carbenes adopt essentially planar T-shaped geometries with sum of angles spanning the range 357.23(18)–359.00(15)$^5$ and the metal–BIPMTMS 6-membered chelate rings are essentially planar contrasting with some BIPMTMS complexes to 360.00(15)$^5$ geometries with sum of angles spanning the range 357.23(18)–359.00(15)$^5$. The carbenes adopt essentially planar T-shaped imino nitrogen atoms residing above and below the hypothetical BIPMTMS ligands are disposed essentially orthogonally to one another, with dihedral angles between the two N–M–N planes of 92.5(2), 92.4(2) and 91.4(2)$^5$, respectively. The Ce1–C1 and Ce1–C32 distances in $\text{3Ce}$ (2.385(2) and 2.399(3), respectively) are exceedingly short, $> 0.2 \text{ Å}$ shorter than the corresponding

Figure 4 | Molecular structure of $\text{3Ce}$ at 150 K with displacement ellipsoids set to 30%. Hydrogen atoms and lattice solvent are omitted for clarity. The structures of $\text{3U}$ and $\text{3Th}$ are very similar. Selected bond lengths (Å) and angles (°): C1–P1 1.664(2), C1–P2 1.664(2), C32–P3 1.665(5), C32–P4 1.663(4), P1–N1 1.6128(18), P2–N2 1.6174(19), P3–N3 1.6247(18), P4–N4 1.6202(18), Ce1–C1 2.385(2), Ce1–C32 2.399(3), Ce1–N1 2.4766(17), Ce1–N2 2.5122(17), Ce1–N3 2.4726(18), Ce1–N4 2.4966(16), P1–C1 2.1763(15), P2–C2 2.1761(15), P3–C3 2.1751(15), P4–C4 2.1758(15), P1–C1–P2 150.31(14), P2–N2–P3 150.32(14), P3–N3–P4 150.33(14), P4–N4–P1 150.34(14), N1–Ce1–N2 127.16(6), N3–Ce1–N4 127.36(6), C1–Ce1–C32 176.98(7)$^7$.
Figure 5 | Selected CASSCF-calculated natural orbitals of truncated models of bis(carbene) complexes. Only strongly occupied M–C bonding orbitals and 5f orbitals are shown. Pronounced multiconfigurational character is present among the 5f orbitals in the truncated U complex, but the rest of the electronic manifold comprises orbitals with occupations close to integer values showing at best weak multiconfigurational character. All orbitals rendered at an isosurface of 0.02 atomic units (a.u.).

are \(-1.79/-1.80, -2.03/-2.06\) and \(-1.95/-2.01\), respectively. Although care must be taken when analysing calculated charges, they are indicative of metal(IV) ions \(^{44,64}\) and that perhaps the cerium ion in \(^{3}\)Ce is better matched to receiving electron donation from the ligands than the uranium and thorium ions in \(^{3}\)U and \(^{3}\)Th. However, the calculated MDC\(_m\) spin density of \(-2.27\) for the uranium ion in \(^{3}\)U is certainly consistent with charge donation from the BIPMTMS ligand to uranium and also with its \(5f^2\) uranium(IV) formulation.

Inspection of the Kohn Sham frontier orbitals of \(^{3}\)Ce, \(^{3}\)U and \(^{3}\)Th (Supplementary Figs 18–20) clearly shows twofold bonding interactions between each carbene and the respective metal. Each M–C bond is polarized, however, as evidenced by M–C Nalewajski–Mrozek bond orders averaging 1.10, 1.30 and 0.73 for \(^{3}\)Ce, \(^{3}\)U and \(^{3}\)Th, respectively. For comparison, the Ce = C bond order in Ce(BIPMTMS)(ODipp)\(_2\) is also 1.1 (ref. 43), whereas uranium(IV)-BIPM complexes typically have U=C double and U–C single bond orders of \(-1.4\) and \(-0.5\), respectively\(^{44,64}\), and thorium is polarized with Th–C bond orders of \(-0.7\) (ref. 64). Therefore, the data presented here fit the overall literature trends.

A clearcut view of the M = C bonding in \(^{3}\)Ce, \(^{3}\)U and \(^{3}\)Th from the Kohn Sham frontier orbitals is precluded because of the delocalized nature of molecular orbital calculations. We therefore turned to natural bond orbital (NBO) analysis (Supplementary Figs 21 and 22) that is suited to the treatment of chemical bonding in molecular complexes. For \(^{3}\)Ce, the Ce = C σ-bonds are composed of \(-13\%\) cerium and 87% carbon character; in each case the cerium contribution is \(-46\%\) 5d and \(-53\%\) 4f, with the remaining \(-1\%\) being 6s. For the Ce = C π-bonds, cerium contributes only \(-8\%\) to these bonds and the cerium component is predominantly 4f character \((-80\%)\) with a modest 5d component \((-19\%)\), with the remaining being 5p character. These data compare well with those of Ce(BIPMTMS)(ODipp)\(_2\)\(^{142}\), and indeed there is growing evidence that cerium(IV) is suited to utilizing its 4f orbitals in bonding to ligands \(^{43,53,63,66}\). This may be important, because a study on lanthanide(III) chalcogenide complexes found a trans-influence where the lanthanide utilizes predominantly d orbitals\(^{12}\); in contrast the metal(IV) complexes, certainly for cerium and uranium, are deploying predominantly f orbitals, in line with the general theory of the ITI\(^{17–21}\). For \(^{3}\)U, the U–C σ-bonds are composed of \(-14.5\%\) uranium character and \(-85.5\%\) carbon character. As for \(^{3}\)Ce, the 5f/6d contributions of \(^{3}\)U are well balanced at \(-51:47\%), with the remaining 7% character. The U–C, π-bond is \(-18.86\%\) uranium/carbon and, like for cerium, is within the uranium component, principally 5f \((-86\%)\) with modest 6d \((-13\%)\), with the remaining \(-1\%\) being 6p character. For \(^{3}\)Th, NBO does not return any Th = C interactions, suggesting that the Th = C bonding is highly ionic.

To better understand the nature of the M = C interactions in these compounds we turned to complete/restricted active space self-consistent field (CASSCF/RASSCF) methodologies that allows us to consider electron correlation through a rigorous configuration-interaction-based approach to directly compare open- and closed-shell compounds. The computational cost of such calculations required truncation and symmetrization of the experimentally determined structures to produce tractable models, but by retaining key structural motifs near identical electronic structures are obtained (Supplementary Tables 12–14).

RASSCF calculations were employed in order to identify an appropriate active space for each system. Because of the computational expense of such calculations, RAS1, RAS2 and RAS3 subspaces were constrained to consist of 12, 7 and 12 orbitals, respectively. The 7 RAS2 orbitals comprise the 4f/5f manifold, whereas the RAS1 and RAS3 orbitals account for orbitals with significant C/N 2s and 2p character and natural orbitals whose occupation numbers most deviate from integer values. This active space ensured that all M = C and M–N interactions were accurately modelled. State-averaged RASSCF calculations indicated a degenerate \(^3\)B\(_1\)/\(^3\)B\(_2\) ground state in the \(^3\)U model complex, corresponding to a state of E symmetry in the full idealized D\(_{2d}\) point group. The natural orbital occupation numbers resulting from these calculations allowed complete active spaces to be defined. Subsequent CASSCF calculations correlated 8 electrons in 8 orbitals in the cases of \(^{3}\)Ce and \(^{3}\)Th model complexes, and 10 electrons in 12 orbitals in the case of the U complex.

CASSCF calculations revealed that all complexes are dominated by M(IV) configurations, (Fig. 5), contributing 96.0%, 96.0% and 95.4% to the ground state wavefunctions of the \(^{3}\)Ce, \(^{3}\)U and \(^{3}\)Th model complexes, respectively. Maximum deviations from integer values in natural orbital occupations were 0.026, 0.021 and 0.026 for the \(^{3}\)Ce, \(^{3}\)U and \(^{3}\)Th model complexes, respectively, indicating at most weak multiconfigurational character. The resultant electronic structure is almost identical to that obtained from the RASSCF simulations, and the dominant M(IV) character in all systems is commensurate with all experimental measures. Notably, as shown in Fig. 5, \(^{3}\)Ce, \(^{3}\)U and \(^{3}\)Th show σ-bonding combinations that are strongly reminiscent of uranyl, a feature that also emerges from the DFT analysis that is consistent with an ITI in these complexes.
To further probe the covalent contribution to bonding in these compounds, we directly analyse the resultant electron densities via the quantum theory of atoms in molecules (QTAIM) and focus on two parameters: the delocalization index between two bonded atomic centres (δ) and the magnitude of the electron density at the bond critical point between the centres (ρBCP). The delocalization index, formally a two-electron property of the system, is a measure of the number of electrons shared between two atoms, and is large when orbital mixing because of energetic near degeneracy between the two atoms is pronounced. In this sense, it probes similar properties to those given by orbital decomposition via NBO analysis or, experimentally, by X-ray absorption spectroscopy that probes orbital energy near degeneracy. On the other hand, ρBCP quantifies electronic charge concentration in the bond between two atoms. Combined, these measures give an indication as to whether orbital mixing leads to charge accumulation in the bonding region (and hence bond stabilization) and hence provide a more complete method for assessing bond covalency than orbital analysis alone (Supplementary Table 15).

QTAIM-derived atomic charges are more consistent than those obtained via NBO analysis, with \( q(Ce) < q(U) < q(Th) \). Carbene charges reflect this trend that therefore provides some evidence for a greater covalent interaction in the 3Ce complex. Stronger evidence is provided by the delocalization indices, δ(M,C), that are notably larger for 3Ce than either 3U or 3Th. Consideration of ρBCP demonstrates that this electron sharing corresponds to charge accumulation in the M = C bonding region: ρBCP follows a similar trend to δ(M,C), with the Ce and U complexes exhibiting significantly larger values than that of Th. Inspection of the ellipticity parameter \( \epsilon \) for the M = C bond reveals values that are consistent with an asymmetric distribution of electron density around the M = C bond comparable to those found for alkynes and \([M(BIPMTMPD)(ODipp)M]^{3+}\), confirming that in 3Ce, 3U and 3Th there is a M = C bonding interaction involving two electron pairs donated from a carbene to a metal.

Probing the inverse-trans-influence. To probe whether the ITI is operating in 3Ce, 3U and 3Th, we adopted the method of O’Grady and Kaltsoyannis. Here, 3Ce, 3U and 3Th were geometry optimized with a frozen core, up to 4\(d\) for 3Ce and 5\(d\) for 3U and 3Th and with the pseudo-core 5 or 6\(p\) orbitals, respectively, either explicitly included as valence orbitals or placed in the frozen core. Although the ITI is a complex phenomenon that involves several factors, it is clear that \( p \) orbitals are involved in the ITI and that this method isolates the contributions that the pseudo-core 5/6\(p\) orbitals have on the bonding. Although the carbene ligands in 3Ce, 3U and 3Th clearly exhibit polarized M = C bonds, the ITI is predominantly dependent on the charge and polarization nature of the coordinated ligands. To rule out coincidental systematic errors from a particular method, we examined the effect of varying the functional (BP86 versus PBE) and the basis set (normal all-electron basis set versus a normal frozen core up to 4 or 5\(d\) for 3Ce, 3U, and 3Th, respectively) separately or simultaneously, and found no significant changes in equilibrium geometries. However, when the 5 or 6\(p\) orbitals for 3Ce, 3U and 3Th, respectively, were additionally also placed in the frozen core, significant changes to the equilibrium geometries were observed in all cases. Specifically, the M = C distances lengthen by ~0.05 Å when the relevant \( p \) orbitals are placed in the frozen core that are very similar shifts to those found previously for \([MOX]^-\) anions (M = U, Np; X = F, Cl, Br) and this represents the \( p \) orbital contributions to the ITI. It should be noted that, on inclusion of the relevant \( p \) orbitals into the frozen cores, the M–N\(_{imino}\) distances also elongate; however, the latter lengthen by only ~0.02 Å, less than half of that of the change to the M–C linkages. As expected, with \( p \) orbitals in the frozen cores the metal and carbene charges increase, indicating more polarized and presumably weakened interactions. For example, in 3Ce the cerium and carbene charges rise from 1.83 and −1.71 when 5\(p\) orbitals are included in the valence region to 2.54 and −1.82 when 5\(p\) orbitals are placed in the frozen core. Inspection of the differences of the total energies of the geometry-optimized structures of 3Ce, 3U and 3Th with the \( p \) orbitals in the frozen core or in the valence region yields energy differences of 12.5, 20.5 and 18.2 kcal mol\(^{-1}\) for 3Ce, 3U and 3Th, respectively. This provides a qualitative bracketing of the stabilizing energy that the inclusion of the pseudo-core \( p \) orbitals in the bonding to a \( bis(\text{carbene}) \) ligand set provides, and compares well with the ITI of 6 kcal mol\(^{-1}\) calculated for a uranium(VI)-mono(oxo) unit in a tris(aryl oxide) triazacyclononane complex.

As 3Ce, 3U and 3Th all appear to exhibit the ITI, we investigated the synthesis of the analogous praseodymium(IV) and terbium(IV) \( bis(\text{BIPM}) \) complexes 3Pr and 3Tb, respectively. We targeted these complexes because after cerium they have the next two lowest fourth ionization energies of all lanthanides. Nevertheless, the fourth ionization energies of these two elements are still considerable, and we could not access 3Pr and 3Tb experimentally. Attempting AgBPH\(_4\)-mediated oxidations of 2Pr and 2Tb (Fig. 1) results not in oxidation to give 3Pr and 3Tb but instead elimination of \([\text{K}(\text{18C6})(\text{THF})][\text{BPH}_4]\) and isolation of \([M(BIPMTMPD)_2\text{Ag}] (M = Pr, 6Pr; M = Tb, 6Tb); photolysis or electrochemistry experiments on 6Pr and 6Tb resulted in intractable decomposition products. However, although we could not prepare 3Pr and 3Tb, 3Ce, 3U, 3Th, 2Pr and 2Tb provide experimentally calibrated benchmarks with which to provide confidence in the calculated hypothetical geometry-optimized structures of 3Pr and 3Tb. Inspection of the equilibrium geometries of 3Pr and 3Tb calculated with their respective 5\(p\) orbitals in-core and included in the valence regions reveals that the ITI persists but diminishes on moving from Ce to Pr to Tb (Supplementary Tables 16–19). Specifically, the Pr = C distances elongate by 0.02 Å when the 5\(p\) orbitals are placed in the frozen core, and the Pr–N distances elongate by only 0.006 Å. For Tb, the effect is significantly reduced, with a 0.007 Å elongation of the Tb = C distance when the 5\(p\) orbitals are placed in the frozen core and the Tb–N distances elongate by 0.006 Å. We conclude from these data that the ITI may, in principle, apply across the lanthanide(IV) series, but as 4\(f\) electron occupancy increases the ITI diminishes. This is consistent with the theory of the ITI as donation of \( n/p \) electron density into the \((n−1)/f\) orbital manifold will become less favourable as the \((n−1)/f\) occupancy increases because of interelectronic repulsion. Furthermore, the appearance of a trend suggests greater levels of \( f\)-orbital covalency that is supported by the characterization data more widely, whereas for lanthanide(III) systems when the trans-influence has been studied and principally \( d\)-orbital participation has been invoked then the trans-influence trend is uniform, suggestive of mainly ionic bonding character. Thus, the observations of uniform trans-influence with \( d\)-orbital bonding for lanthanide(III) ions versus diminishing ITI for lanthanide(IV) ions where \( f\)-orbital bonding is principally invoked is internally consistent.

The delocalized nature of the molecular orbital approach makes the identification of key molecular orbitals involved in the ITI difficult. Thus, inspection of individual molecular orbitals would not be expected to provide clear-cut information, as has proven to be the case even in highly symmetric complexes. However, an examination of the electronic manifolds of 3Ce, 3U and 3Th reveals a common molecular orbital that may...
be significant. All three complexes exhibit a molecular orbital at $\sim -16.4$ eV (3Ce, -16.483; 3U, -16.485; 5Th, -16.494 eV) $\sim 12$ eV below the highest occupied molecular orbital (2 for $5f^2$ 3U). In each case contributions from the 2s orbitals of each carbene (normalized to 34%) and 5 or 6p orbitals for cerium or uranium and thorium, respectively (normalized to 5%) are found. Interestingly, a similar orbital is computed for 3Pr at $\sim -16.476$ eV, although here the carbon (normalized to 32%) and praseodymium (normalized to 2.5%) contributions are notably less well matched. In contrast, for 3Tb the closest match is now a molecular orbital at $-20.455$ eV with normalized carbon and terbium contributions of 9% and 3%, respectively. We suggest that this molecular orbital is common to 3Ce, 3U, 3Tb and 3Pr but not 3Tb may represent a signature in this instance of the ITI20,29.

**Discussion**

We have prepared three new metal bis(carbene) complexes that contain linear C = M = C cores and the characterization data show these complexes to be unequivocally metal(IV) complexes and thus valid to compare with one another. For the cerium and uranium derivatives the M = C bonds are short, and for the former one of the shortest Ce-C bonds on record; that they are so short despite the fact that they are strongly donating diazines disposed trans with respect to one another suggests that the ITI is operating instead of the more classical trans influence. Theoretical calculations suggest the presence of an ITI in cerium, uranium and thorium derivatives, as removal of carbyne disposed trans with respect to one another results in elongation of the M-imino bonds. Interestingly, the characterisation data and theoretical data taken together suggest a consistent trend of covalency of 3Ce ~ 3U > 3Th. This work suggests that the ITI concept, first established a quarter of a century ago, may extend beyond high oxidation state $5f$ metals to now encompass mid-range oxidation state $5f$ actinides and $4f$ lanthanides. Calculations also suggest, however, that the ITI may diminish on moving from left to right in the lanthanide series and with increasing ($n-1$) occupation number. Although an opposite trend may operate for the actinides29, it may be that the more diffuse $5f$ orbitals could tolerate occupancy more; however, thus far the radioactivity of those elements has precluded any detailed body of experimental work from being compiled and hence further work will be required to provide the necessary benchmarks with which to investigate this. The observations of uniform trans-influence with d-orbital bonding for lanthanide(III) ions$^2$ versus the trend reported here of diminishing ITI for the lanthanide(IV) ions investigated, where f-orbital bonding is principally invoked, is gratifyingly internally consistent. Thus, the ITI might be a more general f-block principle.

**Methods**

**General.** Experiments were carried out under a dry, oxygen-free dinitrogen atmosphere using Schlenk-line and glove-box techniques. All solvents and reagents were rigorously dried and deoxygenated before use. Compounds were variously characterized by elemental analyses, electrochemistry, NMR, Fourier transform infrared spectroscopy (FTIR), EPR, XANES and UV/Vis/NIR electronic absorption spectroscopies, single crystal X-ray diffraction studies (Supplementary Data 1–11), Evans methods and SQUID magnetometry, and DFT, NBO, QTAIM, CASSCF and RASSCF computational methods.

**Synthesis of [Ce(BIPMTMS)$_2$](K[18C6](THF)$_2$) (2Ce).** THF (10 ml) was added to a precooled ($\sim -78$ °C) mixture of [U(BIPMTMS)$_2$](Cl)$_2$(Li)(THF)$_2$ (1.09 g, 1 mmol) and LiCH$_2$SiMe$_3$ (0.19 g, 2 mmol). The mixture was then allowed to slowly warm to room temperature with stirring over 6 h to afford a yellow solution. All volatiles were removed in vacuo and the resulting brown solid was extracted with toluene (20 ml). Volatiles were removed in vacuo and the resulting brown solid was recrystallized from hexane (3 ml) and stored at $\sim -30$ °C to afford 5U as brown crystals. Yield 0.67 g (69%). Anal Calcld for C$_{38}$H$_{54}$N$_2$P$_2$Si$_4$U: C, 47.22; H, 6.00; N, 2.98. Found: C, 46.53; H, 5.92; N, 2.97. The carbon is consistently low over five independently synthesized batches that we attribute to carbide formation. $^1$H NMR (CD$_2$Cl$_2$, 298 K): $\delta$ 0.95 (16H, s, NSi(CH$_3$)$_2$), 7.08 (24H, d, J$\neq$Ar-H, 7.24 (16H, m, o-Ar-H) ppm. $^3$[P(CH$_3$)$_3$] NMR (CD$_2$Cl$_2$, 298 K): $\delta$ -16.35 (CeCP$_2$) ppm. $^3$[P(H)CH$_2$SiMe$_3$] NMR (CD$_2$Cl$_2$, 298 K): $\delta$ -2.17 (NSi(CH$_3$)$_3$) ppm. FTIR v/cm$^{-1}$ (Nujol): 1294 (w), 1246 (w), 1164 (s), 843 (m), 757 (w), 693 (w), 656 (w), 597 (w), 509 (m).

**Preparation of [U(BIPMTMS)(CH$_2$SiMe$_3$)$_2$] (3U).** Toluene (15 ml) was added to a precooled ($\sim -78$ °C) mixture of [U(BIPMTMS)(Cl)$_2$(Li)(THF)$_2$] (1.09 g, 1 mmol) and LiCH$_2$SiMe$_3$ (0.19 g, 2 mmol). The mixture was then allowed to slowly warm to room temperature with stirring over 6 h to afford a yellow solution. All volatiles were removed in vacuo and the resulting brown solid was extracted with toluene (20 ml). Volatiles were removed in vacuo and the resulting brown solid was recrystallized from hexane (3 ml) and stored at $\sim -30$ °C to afford 5U as brown crystals. Yield 0.67 g (69%). Anal Calcld for C$_{38}$H$_{54}$N$_2$P$_2$Si$_4$U: C, 47.22; H, 6.00; N, 2.98. Found: C, 46.53; H, 5.92; N, 2.97. The carbon is consistently low over five independently synthesized batches that we attribute to carbide formation. $^1$H NMR (CD$_2$Cl$_2$, 298 K): $\delta$ -7.76 (18H, Si(CH$_3$)$_3$), 0.41 (18H, Si(CH$_3$)$_3$), 5.21 (m, 4H, Ar-H), 5.49 (br, 8H, Ar-H), 5.85 (br, 8H, Ar-H), 7.15 (br, 4H). IR v/cm$^{-1}$ (Nujol): 1305 (w), 1305 (w), 1248 (m, br), 1108 (m), 1019 (m), 836 (w). Magnetic moment (Evans method, CD$_2$Cl$_2$, 298 K): 2.65 $\mu_B$.

**Preparation of [Th(BIPMTMS)(CH$_2$SiMe$_3$)$_2$] (3Th).** Toluene (15 ml) was added to a precooled ($\sim -78$ °C) mixture of [Th(BIPMTMS)(Cl)$_2$(Li)(THF)$_2$] (1.09 g, 1 mmol) and LiCH$_2$SiMe$_3$ (0.19 g, 2 mmol). The mixture was then allowed to slowly warm to room temperature with stirring over 6 h to afford a yellow solution. All volatiles were removed in vacuo and the resulting brown solid was extracted with toluene (20 ml). Volatiles were removed in vacuo and the resulting brown solid was recrystallized from hexane (3 ml) and stored at $\sim -30$ °C to afford 5U as brown crystals. Yield 0.67 g (69%). Anal Calcld for C$_{38}$H$_{54}$N$_2$P$_2$Si$_4$U: C, 47.22; H, 6.00; N, 2.98. Found: C, 46.53; H, 5.92; N, 2.97. The carbon is consistently low over five independently synthesized batches that we attribute to carbide formation. $^1$H NMR (CD$_2$Cl$_2$, 298 K): $\delta$ -33.88 (36H, s, NSi(CH$_3$)$_3$), 12.04 (3H, 9H, Ar-H), 13.76 (17H, Ar-H), 30.42 (br, 14H, Ar-H). $^3$[P(CH$_3$)$_3$] NMR (CD$_2$Cl$_2$, 298 K): $\delta$ -219.70 (br, UCP$_2$) ppm. FTIR v/cm$^{-1}$ (Nujol): 1958 (w), 1450 (s), 1334 (s), 1281 (m), 1245 (m), 1178 (w), 1153 (w), 1103 (s), 1055 (m), 745 (m), 669 (m), 628 (m), 514 (w), 489 (w). Magnetic moment (Evans method, CD$_2$Cl$_2$, 298 K): $\mu_B = 2.61$.
Preparation of [Th(BIPMTMS)2] (3Th). Toluene (10 ml) was added to a mixture of [Th(BIPMTMS)(CH2Ph)3] (0.87 g, 0.90 mmol) and BIPMTMSH2 (0.51 g, 0.53 mmol). The resulting pale yellow solution was stirred at 50 °C for 20 h, and then was dried in vacuo to afford sticky yellow solid. The crude product was washed with hexanes (2 x 10 ml) and then dried in vacuo to afford 3Th as a colourless powder. Yield: 0.63 g, 52%. Recrystallization of a small portion from toluene at 5 °C afforded colourless crystal suitable for single crystal X-ray diffraction. Anal. Calcd for C62H76N4P4Si4Th: C 55.34; H 5.69; N 4.16%. Found: C 55.02; H 5.78; N 3.91%. FTIR ν/cm−1 (Nujol): 3084 (m), 1462 (m), 1245 (s), 1011 (s), 693 (m). Magnetic moment (Evans method, THF, 298 K): μeff = 9.90 μB.

Reaction of [Ce(BIPMTMS)2] with PhCHO. Benzaldehyde (2.5 mg, 0.04 mmol) was added to a solution of [Ce(BIPMTMS)2] (11 mg, 0.04 mmol) in toluene (0.5 ml). The reaction mixture was then heated to 60 °C and then analysed by multinuclear NMR that revealed a small amount of conversion to (Me3SiNPPh2)2C(H)Ar. The reaction mixture was then heated to 60 °C for 48 h. Analysis of the crude mixture showed qualitative conversion to (Me3SiNPPh2)2C(H)Ar. All spectroscopic data matched previously reported data.

Reaction of [U(BIPMTMS)2] with ArCHO. d5-benzene (0.4 mmol) was added to a mixture of 9-anthracene carboxaldehyde (4.9 mg, 24 μmol) and [U(BIPMTMS)2] (15 mg, 12 μmol). The reaction mixture was then heated to 60 °C and then analysed by multinuclear NMR that revealed 95% conversion to (Me3SiNPPh2)2C(H)Ar. All spectroscopic data matched previously reported data.

Reaction of [U(BIPMTMS)2] with PhCHO. Benzaldehyde (6.4 mg, 0.60 μmol) was added to a solution of [U(BIPMTMS)2] (40.5 mg, 30 μmol) in d5-benzene (0.4 ml). The reaction mixture was then heated to 60 °C and then analysed by multinuclear NMR that revealed 90% conversion to (Me3SiNPPh2)2C(H)Ar. All spectroscopic data matched previously reported data.

Reaction of [Ce(BIPMTMS)2] with PhCHO. Benzaldehyde (12.4 mg, 60 μmol) and [Ce(BIPMTMS)2] (40.5 mg, 30 μmol). The reaction mixture was then heated to 60 °C and then analysed by multinuclear NMR that revealed 95% conversion to (Me3SiNPPh2)2C(H)Ar. All spectroscopic data matched previously reported data.

Reaction of [Ce(BIPMTMS)2] with PhCHO. Benzaldehyde (12.4 mg, 60 μmol) and [Ce(BIPMTMS)2] (40.5 mg, 30 μmol). The reaction mixture was then heated to 60 °C and then analysed by multinuclear NMR that revealed 95% conversion to (Me3SiNPPh2)2C(H)Ar. All spectroscopic data matched previously reported data.

Data availability. The X-ray crystallographic coordinates (ccif format) for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 1500929-1500939. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. All other data are available from the corresponding authors on request.

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**Author contributions**

M.G., E.L. and D.P.M. synthesized and characterized the compounds. F.T. and E.J.L.M. recorded and analysed the EPR and SQUID data. C.H. and A.C.S. recorded and analysed the XANES data. J.M. and S.T.L. conducted and analysed the DFT and NBO calculations. W.L. and A.J.B. carried out the single crystal X-ray diffraction work. A.K. conducted and analysed the CASSCF/RASSCF and QTAIM data. S.T.L. originated the central idea, supervised the work, analysed the data and wrote the manuscript with contributions from all co-authors.

**Additional information**

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The original version of this Article contained a typographical error in Fig. 2, where reagent H$_2$C(Ph$_2$PNSiMe$_3$)$_2$ was incorrectly given as H$_2$C(PNSiMe$_3$)$_2$. This has now been corrected in both the PDF and HTML versions of the Article.