Isolation and characterization of a covalent CeIV-Aryl complex with an anomalous $^{13}$C chemical shift

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The synthesis of bona fide organometallic CeIV complexes is a formidable challenge given the typically oxidizing properties of the CeIV cation and reducing tendencies of carbanions. Herein, we report a pair of compounds comprising a CeIV−Caryl bond $[\text{Li(THF)}_4]\text{[CeIV(κ}^2\text{-ortho-oxa)}(\text{MBP})_2](3\text{-THF})$ and $[\text{Li(DME)}_3]\text{[CeIV(κ}^2\text{-ortho-oxa)(MBP})_2](3\text{-DME})$, ortho-oxa = dihydrodimethyl-2-[4-(trifluoromethyl)phenyl]-oxazolide, MBP$^2$ = 2,2′-methylenebis(6-tert-butyl-4-methylphenolate), which exhibit CeIV−Caryl bond lengths of 2.571(7) – 2.5806(19) Å and strongly-deshielded, CeIV−Cipso $^{13}$C{1H} NMR resonances at 255.6 ppm. Computational analyses reveal the Ce contribution to the CeIV−Caryl bond of 3-THF is ~12%, indicating appreciable metal-ligand covalency. Computations also reproduce the characteristic $^{13}$C{1H} resonance, and show a strong influence from spin-orbit coupling (SOC) effects on the chemical shift. The results demonstrate that SOC-driven deshielding is present for CeIV−Cipso $^{13}$C{1H} resonances and not just for diamagnetic actinide compounds.
The bonding between lanthanides and ligands has been described as purely ionic. However, modern spectroscopic and computational techniques have challenged this simple assumption. The covalency in $M - X$ interactions can result in anomalous and diagnostic nuclear magnetic resonance shifts, $X = ^{13}C, ^{15}N, ^{19}F, ^{77}Se, ^{125}Te$, resulting from participation of $f$-element orbital angular momentum. Another important aspect of detailed $f$-element electronic structure is multi-configurational character, as described in the model example of cerocene, Ce(COT)$_2$, COT = cyclooctatetraene ligand. The case for multiconfigurational character in cerocene has been made through X-ray absorption, SQUID magnetometry, and multi-reference computational studies and tied strongly to the characteristics of the cerium-carbon bonding. Despite the interest surrounding $f$-element covalency and multiconfigurational effects, there are few examples of organometallic Ce$^{IV}$ complexes. The current literature is limited to metalocene Ce$^{IV}$ complexes or $\alpha$-heteroatom stabilized Ce$^{IV}$ C $\sigma$-bonds. Reported examples of Ce$^{IV}$ – metalocene bonding include Ce$^{IV}$ complexes of cyclopentadiene, cyclooctatetraene, dianion, and bis-pentaenl dianion ligands. Complexes containing a Ce$^{IV}$ – C $\sigma$-bond, however, are limited to either an N-heterocyclic carbene (NHC) complexes, e.g., Ce[Li$_2$] (Fig. 1a), or a bis(iminophosphorano)methandiide complex, e.g., [Ce(BIPMTMS)(ODipp)$_2$] (Fig. 1a). The latter examples are expected to have electronic configurations that deviate significantly from typical organometallic alkyl, aryl, or alkynyl ligands due to the heteroatom bound to cerium are indicated with a ($NHC$) complexes, e.g., Ce[L$_4$] (Fig. 1a), or a bis(iminophosphorano)methandiide complex, e.g., [Ce(BIPMTMS)(ODipp)$_2$] (Fig. 1a). The latter examples are expected to have electronic configurations that deviate significantly from typical organometallic alkyl, aryl, or alkynyl ligands due to the heteroatom bound to cerium are indicated with a ($NHC$) complexes, e.g., Ce[L$_4$] (Fig. 1a), or a bis(iminophosphorano)methandiide complex, e.g., [Ce(BIPMTMS)(ODipp)$_2$] (Fig. 1a).

Herein, we expand our studies for the isolation of a pair of Ce$^{IV}$ – C$_{aryl}$ compounds. These compounds display unusually high $^{13}C$ NMR shifts compared to other diamagnetic M$^{IV}$ – C$_{aryl}$ compounds. Relativistic density functional calculations verify that the high NMR shifts are due to large SOC effects supported by the increased covalency of the Ce$^{IV}$ – C$_{aryl}$ bond.

Results

Synthesis and structures of Ce$^{IV}$ – C$_{aryl}$. Considering strategies to stabilize a Ce$^{IV}$ – C$_{aryl}$ bond, we hypothesized that tethering the aryl group to the Ce center would kinetically inhibit homolysis of the Ce – C bond. In addition, we sought a sterically-protected Ce center to prevent reactivity at the ipso-carbon. Lastly, we chose a supporting ligand that would stabilize the Ce$^{IV}$ oxidation state to prevent charge transfer and subsequent Ce – C bond homolysis. With these considerations in mind, we aimed to prepare a Ce$^{IV}$ – C$_{aryl}$ bond from the Ce$^{IV}$ bis(methylene bisphosphonate) complex Ce(THF)$_2$(MBP)$_2$, that was previously synthesized by members of the Schelter laboratory (1, Fig. 2). Aryloxide ligands have been previously shown to both stabilize the Ce$^{IV}$ oxidation state and high valent organometallic species of other metal species. Addition of a yellow solution of ortho-lithiated oxazoline to a purple benzene solution of Ce(THF)$_2$(MBP)$_2$ (1) at room temperature resulted in an immediate color change of the solution to dark red. The $^1H$ NMR spectrum of the reaction mixture revealed loss of the pseudo C$_{2v}$ symmetry of 1 and formation of a C$_{2v}$ symmetric product. Likewise, there was also a shift in both the $^7Li$ and $^{19}F$ NMR resonances of 2, and the two methylene protons and methyl groups of the oxazoline were no longer degenerate in the $^1H$ NMR spectrum. All $^1H$, $^7Li$, and $^{19}F$ NMR resonances were well within the range of diamagnetic signals, leading to the assignment of the product of the reaction as [Li(THF)$_4$][Ce($^{2}$-ortho-oxa)(MBP)$_2$] (3-THF).

Dark red X-ray quality crystals of 3-THF were grown over 3 days from a cooled ($-25^\circC$) mixture of 3-THF in toluene and THF layered with pentane. The crystals were collected in 66% yield (Fig. 2). Alternatively, crystallizing from a cooled ($-25^\circC$) solution of crude 3-THF in DME layered with pentane resulted in dark-red X-ray quality crystals of 3-DME over 3 days (Fig. 3). Crystals of 3-DME were collected in a slightly higher 75% yield. The differences in NMR data between 3-THF and 3-DME are negligible compared to experimental error. While compound 3-DME crystallizes with a single molecule in the asymmetric unit, compound 3-THF crystallizes with two independent molecules in the asymmetric unit, with only minor differences between the structures. The Ce – O(phenoxide) bond distances of 3-THF and 3-DME (2.1636(13)–2.202(4) Å) compare well with the Ce – O (phenoxide) bond distances observed in the reported structure of 1 (2.113(2)–2.152(2) Å). The Ce – C bond distances of 3-THF and 3-DME are 2.571(7) = 2.5806(19) Å and are shorter than reported Ce$^{III}$ – C$_{aryl}$ bond lengths: 2.621(4) = 2.64 ± 0.02 Å. The difference in ionic radii between 6-coordinate Ce$^{III}$ and Ce$^{IV}$ is 0.14 Å; however, the difference between 3-THF and 3-DME and previous Ce$^{III}$ – C$_{aryl}$ complexes is only 0.04 – 0.07 Å.

Fig. 1 Examples of Ce$^{IV}$ – C $\sigma$ bonds. a) Previous examples of complexes with formally Ce$^{IV}$ – C $\sigma$ bonds, which are stabilized by either nitrogen or phosphorus heteroatoms. b) This work detailing the synthesis and characterization of a Ce$^{IV}$ – C$_{aryl}$ bond, including computational analysis. Carbon atoms bound to cerium are indicated with a C.
We ascribe this difference to the steric demand by the MTB ligands vs. the pentamethylcyclopentadienyl ligands used in the prior work. Previously reported complexes containing CeIV−Cσ-bonds are 2.652(7)–2.705(2) Å and 2.385(2)–2.441(5) Å for the Ce−C NHC and Ce−C(bisiminophosphorano)methanide) ligands, respectively22,23,25. With this data in hand, we assign this complex as a CeIV−Caryl complex.

Electrochemical analysis. To better understand how the ortho-oxa−group impacts the stability of the CeIV cation, electrochemistry was performed on 3-THF. The Epa of 3-THF, −1.67 V vs. Fc/Fc+, shifts by −0.72 V relative to the E1/2 of 1 (−0.94 V vs. Fc/Fc+), indicating that the ortho-oxa−moiety significantly stabilizes the CeIV couple in THF. The reduction of 3-THF is not reversible under the electrochemical conditions, although the event precedes a reversible oxidation at E1/2 = −0.94 V vs. Fc/Fc+ and an irreversible oxidation at Epa = −0.43 V (Supplementary Figs. 18–19). We postulate that the reduction of the CeIV center is followed by dissociation of the ortho-oxa−fragment, producing 1 and 2. Indeed, the return anodic scan comprises waves at E1/2 = −0.94 V vs. Fc/Fc+ and Epa = −0.43 V respectively, consistent with the previous assignment for compound 1 and inferred for compound 2 (Fig. 4)29.
**13C NMR analysis.** While the 1H, 7Li, and 19F NMR of 3-THF and 3-DME showed minimal changes compared to the starting materials, the 13C[1H] NMR of the ipso-carbon of both 3-THF and 3-DME showed a significant shift (difference between 3-THF and 3-DME is less than >0.05 ppm which is within error). Indeed, the ipso-13C[1H] resonance was located at 255.6 ppm, well outside of the typical range for aryl resonances (100–170 ppm) and shifted by ~50 ppm downfield relative to the Li – Caryl resonance for the starting material, 2 (Fig. 5). This 13C[1H] shift is further downfield than observed for other characterized, diamagnetic MIV compounds as well as for CeIV methandiide) 13C{1H} shifts in the range of 324.6–343.5 ppm, depending on the secondary ligands bound to the CeIV cation; [Ce(BIPMTMS)(ODipp)2] exhibits a 13C{1H} shift of 324.6 ppm23,25. The shift of the 13C[1H] signal for the carbon atom bound to metal cations has been implicated as a reporter for the degree of covalency in element cation-carbon bonds7–9. In this light, 3-THF and 3-DME have an anomalously high covalency for a MIV-aromat bond. As with the bond distance metrics, there are few salient examples of CeIV – Cσ-bonds for comparison of the 13C[1H] NMR shifts. The compounds isolated by P. Arnold and co-workers display a 13C[1H] shift at ~213 ppm for the CeIV–NHC22. The compounds reported by Liddle contain CeIV – C (bis(methylphosphono) methandiide) 13C[1H] shifts in the range of 324.6–343.5 ppm, depending on the secondary ligands bound to the CeIV cation; [Ce(BIPMTMS)(ODipp)2] exhibits a 13C[1H] shift of 324.6 ppm23,25. Notably, these compounds contain substantially different substituents attached to the Ce–C carbon, diminishing the significance of their comparison.

**Computational bonding analysis.** To further understand the nature of the CeIV – Caryl interaction, we turned to computations to assess the electronic structure of the anionic, cerium-containing portion of 3-THF (referred to as 3). The geometry of 3 was optimized starting from the structure of 3-THF determined by X-ray crystallography, using density functional theory (DFT) with the B3LYP functional, all-electron Slater-type basis sets for all atoms, and other standard settings as detailed in the SI. The agreement between experiment and theory was excellent, with only minor differences in the CeIV – ligand bond lengths (≤0.02 Å). The MOs with the most Ce 4f character remain largely metal-centered and span the seven lowest unoccupied molecular orbitals (LUMO to LUMO + 6, Supplementary Figs. 13–19) of the complex, a common feature for CeIV compounds as well as for cerium species with a debated CeIV/CeIII oxidation state.15,16 HOMO to HOMO – 3 (Supplementary Figs. 26–29), for 3 are mostly delocalized phenoxy-centered orbitals, while HOMO – 4 (Fig. 6) corresponds to the highest occupied orbital showing significant ligand-metal (CeIV – Caryl) hybridization. The metal-ligand bonding in 3 is characterized in Fig. 6 and Table 1 in terms of natural localized molecular orbitals (NLMOs) and bond orders. There are two two-center two-electron σ bonds describing the donation bonding between the aryl carbon and oxazolinide nitrogen and Ce, and σ + π bonds describing the bonding between each of the O atoms and Ce (Supplementary Figs. 37–40). Among these, the CeIV – Caryl σ bond shown in Fig. 6 has the largest covalency, in terms of shared density, with 12% Ce contribution of which 32/62% involve 5d/4f. Previously reported CeIV – C bonds contain 8–13% Ce contribution25; Ce tends to be less covalent than UIV (UIV – C bonds 22–29% U) but similar to ThIV (ThIV – Caryl bonds 10–15%)9,25,38,40. In the remaining σ and π bonds with the N and O atoms, Ce contributes about 3–4% weight, suggesting that these bonds are mainly ionic. The bond ionocities are also reflected in the bond orders compiled in Table 1, all being significantly smaller than one (which would indicate a full single bond). In the sum of all interactions, however, Ce receives sizable electron donation from the surrounding ligands. For instance, the calculated Ce charge is +2.26 (Mulliken charge), +2.46 (Bader charge), and +2.44 (natural charge from a natural bond orbital (NBO) analysis) instead of the formal +4. The Ce natural electron configuration retrieved from the NBO analysis is 4f0.76d0.60, which deviates considerably from the formal 4f5d0. The large Ce 4f electron count of 3 (0.76), associated mainly with the sizable Ce – Caryl bonding, is comparable to the calculated and experimentally-determined Ce 4f electron counts in CeO2 and Ce(C6H5)241–43. We anticipate that this similarity has important implications.
Table 2 NLMO contributions to the $^{13}$C isotropic nuclear shielding ($\sigma_{iso}$) in $^3\sigma$.

| NLMO* | $\sigma_{iso}^{SR}$, SR-ZORA | $\sigma_{iso}^{SO}$, SO-ZORA | $\Delta^{SO}$ d |
|-------|-----------------------------|-----------------------------|--------------|
| $\Sigma(C_{aryl})$ | -103 | -156 | -52 |
| $\Sigma(C_{aryl}C_{aryl})$ | -106 | -94 | -12 |
| $\Sigma_{core}(C_{aryl})$ | 201 | 202 | 1 |
| $\Sigma_{other}$ | -26 | -25 | 0 |
| $\Sigma$(all of above) | -34 | -73 | -38 |

*All shielding contributions are in ppm. The geometry orientation is such that the $^{13}$C corresponds to the $^{13}$C-Caryl bond.

Regarding the electronic structure of $^3\sigma$, in the sense that it may potentially exhibit a multi-configurational ground-state wavefunction with $\text{Ce}^{III/IV}$ character, similar to cerocene. However, further spectroscopic studies are needed, and are under way, to confirm this assignment for $^3\sigma$.

Computational chemical shift analysis. Computed $^{13}$C NMR chemical shifts for the ipso-carbon, with various approaches, are compiled in Supplementary Table 2. The NMR shift was sensitive to the applied DFT approximations, a common observation in NMR shift calculations for compounds containing lanthanides. Indeed, with SOC in particular, the $\text{Ce}^{IV}$-aryl bond is the main contributor of the $^{13}$C SOC deshielding and this aspect is strongly related to the sizable $\text{Ce}^{IV}$ and $\text{Ce}^{V}$ character, similar to cerocene.

To rationalize the anomalous $^{13}$C shift, we carried out an analysis of the DFT/PBEh-40 $^{13}$C isotropic shielding ($\sigma_{iso}$) in terms of NLMOs. The NMR shielding data are gathered in Table 2 and the relevant NLMOs are shown in Supplementary Fig. 41. These NLMOs are used to investigate the covalent bonding between the $^3\sigma$ center and $\text{Caryl}$ is the main contributor of the $^{13}$C SOC deshielding and this aspect is strongly related to the sizable $\text{Ce}^{IV}$ and $\text{Ce}^{V}$ character, similar to cerocene.

Discussion

We have synthesized, characterized, and crystallized complexes featuring a $\text{Ce}^{IV}$-$\text{Caryl}$ bond. The synthesis of the title complexes involves a $\text{Ce}^{IV}$-$\text{aryl}$ salt 2 with 1. Electrochemical analysis revealed that the arylation interaction resulted in a notable stabilization of the $\text{Ce}^{IV}$ oxidation state, shifting the $E_{pc}$ of $\text{Ce}^{IV}$ reduction by 720 mV relative to the THF adduct. A combination of $^{13}$C/$^1$H NMR and DFT was used to investigate the covalency of the $\text{Ce}^{IV}$-$\text{Caryl}$ bonding. $^{13}$C/$^1$H NMR analysis revealed that the ipso-carbon was shifted by 255 ppm, an indicator of metal-ligand covalency in the $\text{Ce}^{IV}$-$\text{Caryl}$ bond. This result was supported by NMR analysis, which showed a 12% metal contribution to the $\text{Ce}^{IV}$-$\text{Caryl}$ bond. We expect that these results will further inform fundamental bonding in high valent f-elements and be effective in guiding the preparation of other f-element organometallic complexes.

Methods

General considerations. See Supplementary Methods for further details.

$\text{Ce(THF)}_2(\text{MBP})_2$ (1). We previously reported a synthesis of 1 that could not be separated from the lithium halide byproducts. This revised method provides clean 1. In an N$_2$-filled drybox, to a clear, colorless solution of $\text{H}_2\text{MBP}$ (0.270 g, 0.793 mmol, 2 equiv) in 4 mL of THF in a 20 mL scintillation vial with a Teflon coated stir bar, was added a yellow solution of Ce(O'Bu)$_2$(THF)$_2$ (0.200 g, 0.396 mmol, 1 equiv) in a 6 mL solution of 2:1 THF benzene at room temperature with stirring. The reaction immediately turned an intense purple color and was stirred for 1 h. The volatile materials were removed under reduced pressure, the residue was triturated with 2 mL of benzene to liberate the tert-butanol byproduct, and the volatile materials were again removed under reduced pressure. The resulting purple solid was transferred onto a medium porosity fritted filter and washed with 5 x 2 mL of pentane. The purple solid was dried under reduced pressure for 3 h. Yield: 0.311 g, 0.324 mmol, 82%.

$^1$H NMR data for this complex was not previously reported and is provided here: $^1$H NMR (400 MHz, THF-$d_8$): δ 7.15 (s, 4H), 6.79 (s, 4H), 5.01 (d, J = 13.4 Hz, 2H), 3.51 (d, J = 14.0 Hz, 2H), 2.31 (s, 12 H), 1.44 (s, 12 H).

$^{13}$C/$^1$H NMR (100 MHz, THF-$d_8$): δ 168.12, 137.25, 134.45, 129.13, 128.17, 124.12, 35.40, 34.99, 31.15, 20.93.

The quantity of THF present for 1 was verified by $^1$H-NMR in C$_2$D$_5$. $\text{Li(THF)}_2(\text{ortho-oxa})$ (2). Synthesis adapted from similar compounds. In a N$_2$-filled drybox, a solution containing H-ortho-oxa (1.217 g, 5.0 mmol, 1 equiv) and 10 mL of hexanes in a 20 mL scintillation vial with a Teflon coated stir bar was
placed in a 30 °C freezer for 30 min. The vial was removed from the freezer and, while stirring, a solution of n-butyl lithium (2.5 M, 5 mmol, 2 mL) was added dropwise over 5 min. The solution turned from colorless to yellow to brown and a yellow solid precipitated. The reaction mixture was stirred for 30 min at room temperature, after which the solid was collected by filtration over a coarse-porosity fritted-filter and washed with 3 × 2 ml of hexanes and 1 × 2 ml of pentane. The tan solid was then dried under reduced pressure for 2 h. The solid was then dissolved in 1 ml THF at rt and then placed in a 30 °C freezer overnight. Yellow crystalline blocks formed and were collected by a coarse-porosity fritted-filter and washed with 3 × 2 ml of pentane. The yellow blocks were dried for 2 h under reduced pressure. Yield: 0.831 g, 2.59 mmol, 52%.

1H NMR (400 MHz, THF-δ6): δ 8.28 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.07 (dd, J = 8.0, 2.7 Hz, 1H), 4.17 (s, 1H), 1.34 (s, 6H).

13C{1H} NMR (101 MHz, THF-δ6): 203.98, 172.88, 143.18 (q, J = 2.2 Hz), 137.45 (q, J = 3.3 Hz), 127.47 (q, J = 27.41 Hz), 127.31 (q, J = 28.2 Hz), 124.46, 119.28 (q, J = 4.0 Hz), 80.39, 66.58, 29.03.

19F NMR (376 MHz, THF-δ6): δ −64.29

Li NMR (156 MHz, THF-δ6): δ 2.08

Anal. Cal. for C70H101CeF3LiNO11: C, 62.90; H, 7.62; N, 1.05. Found C, 62.45; H, 7.32; N, 1.53.

References

1. Raymond, K. N. & Eigenbrot, C. W. Structural criteria for the mode of bonding of organoactinides and -lanthanides and related compounds. Acc. Chem. Res. 13, 276–283 (1980).

2. Kaltsoyannis, N. & Scott, P. The f elements. (Oxford University Press, 1999).

3. Lõlle, M. W. et al. Covalency in Lanthanides. An X-ray Absorption Spectroscopy and Density Functional Theory Study of LuCl₆²⁻ (x = 3, 2). J. Am. Chem. Soc. 137, 2506–2523 (2015).

4. Cheisson, T. et al. Multiple Bonding in Lanthanides and Actinides: Direct Comparison of Covalency in Thorium(IV)- and Cerium(IV)-Imido Fluoride Complex. Inorg. Chem. 53, 27–29 (2014).

5. Lewis, A. J., Carroll, P. J. & Schelter, E. J. Stable Uranium(VI) Methyl and Etheno Complex. Organometallics 11, 9190, https://doi.org/10.1021/oa9152209 (1982).

6. Kaindl, G., Schmiester, G., Sampathkumaran, E. V. & Wachter, P. Pressure-induced changes in LIII x-ray-absorption near-edge structure of CeO₂ and CeF₃: Relevance to 4f-electronic structure. Phys. Rev. B. Condens. Matter 38, 10174–10177 (1988).

7. Williams, U. J. et al. Synthesis, Bonding, and Reactivity of a Cerium(IV) Bonding and 13C NMR Chemical Shift Analysis of a Phosphorano-Stabilized Uranium(VI) Alkylidyne. J. Am. Chem. Soc. 135, 3565–3571 (2013).

8. Lewis, A. J., Carroll, P. J. & Schelter, E. J. Stable Uranium(VI) Methyl and Acetylide Complexes and the Elucidation of an Inverse Trans Influence Ligand Series. J. Am. Chem. Soc. 135, 11385–11392 (2013).

9. Multane, K. C. et al. ¹³C NMR Shifts as an Indicator of U–C Bond Covalency in Uranium(VI) Acetylene Complexes: An Experimental and Computational Study. Inorg. Chem. 58, 4152–4163 (2019).

10. Smiles, D. E., Wu, G., Hrobořík, P. & Hayton, T. W. Use of ²⁵⁷Se and ¹²⁵Te NMR Spectroscopy to Probe Covalency of the Actinide-Chalcogen Bonding in [Th(En)][N(SiMe₃)₂]₂ (E = Se, Te; n = 1, 2) and Their Oxo-Uranium(VI) Congeners. J. Am. Chem. Soc. 138, 814–825 (2016).

11. Smiles, D. E., Sergentu, D.-C., Wu, G., Autschbach, J. & Hayton, T. W. Use of ¹³C NMR spectroscopy to probe covalency in a thorium nitride. Chem. Sci. 10, 6431–6436 (2019).

12. Smiles, D. E., Wu, G., Hrobořík, P. & Hayton, T. W. Synthesis, Thermochemistry, Bonding, and ¹³C NMR Chemical Shift Analysis of a Phosphoro-Stabilized Carbene of Thorium. Organometallics 36, 4519–4524 (2017).

13. Rungtanaprasaphorn, P., Huang, P. & Walsenys, J. R. Phosphoro-Stabilized Carbene Complexes with Short Thorium(IV)– and Uranium(IV)–Carbon Bonds. Organometallics 37, 1884–1891 (2018).

14. Anderson, R. D., Booth, C. H., Lukens, W. W. & Andersen, R. A. Cerecovic Revisited: The Electronic Structure of and Intercalation Between Ce₂G₅H₈ and Ce₂G₅H₇. Organometallics 28, 698–707 (2009).

15. Smiles, D. E. et al. The duality of electron localization and covalency in lanthanide and actinide metalloccenes. Chem. Sci. 11, 2796–2809 (2020).

16. Anderson, R., Dold, M. & Edelmann, F. T. The difficult search for organouranium(IV) compounds. Chem. Soc. Rev. 46, 6697–6709 (2017).
17. Greco, A., Cesca, S. & Bertolini, W. New τ-cyclopentadienylamine and τ-cyclopentadienylamine complexes of cerium. J. Organomet. Chem. 113, 321–330 (1976).
18. Kilmann, U., Herbst-Irmer, R., Stalke, D. & Edelmann, F. T. An Efficient Access to Organocerium(IV) Complexes: Synthesis and Structure of Bis[1,3,6-tris((trimethylsilyl)cyclopentadiene]ceerium(IV). Angew. Chem. Int. Ed. 33, 1618–1621 (1994).
19. Balazs, G. et al. Cerium(III) and Cerium(IV) Bis(18-crown-6) etherate (Sandwich Complexes)synthetic, Structural, Spectroscopic, and Theoretical Studies. Organometalics 26, 3111–3119 (2007).
20. Schneider, D., Harmgarth, N., Edelmann, F. T. & Anwander, R. Ceric Cyclopentadienides Bearing Alkoxo, Aryloxo, Chlorido, or Iodido Co-Ligands. Chem. - Eur. J. 23, 12243–12252 (2017).
21. Sutton, A. D., Clark, D. L., Scott, B. L. & Gordon, J. C. Synthesis and Characterization of Cerium(IV) Metalloenes. Inorganoorg. Chem. 3, 589–596 (1995).
22. Casey, I. J., Liddle, S. T., Blake, A. J., Wilson, C. & Arnold, P. L. Tetravalent cerium carbene complexes. Chem. Commun., 5037–5039 (2007).
23. Gregson, M. et al. A Cerium(IV)–Carbon Multiple Bond. Angew. Chem. Int. Ed. 52, 13016–13019 (2013).
24. Arnold, P. L. C., Casey, I. J., Zlatogorsky, S. & Wilson, C. Organometallic Cerium Complexes from Tetravalent Coordination Complexes. Helv. Chim. Acta 92, 2291–2303 (2009).
25. Gregson, M. et al. The inverse-trans-influence in tetravalent lanthanide and actinide bis(carbone) complexes. Nat. Chem. 8, 14137 (2017).
26. Robinson, J. R., Carroll, P. J., Walsh, P. J. & Schelter, E. J. The Impact of Ligand Reorganization on Cerium(III) Oxidation Chemistry. Angew. Chem. Int. Ed. 51, 10159–10163 (2012).
27. Levin, J. R., Dorfner, W. L., Dai, A. X., Carroll, P. J. & Schelter, E. J. Density Functional Theory as a Predictive Tool for Cerium Redox Properties in Nonaqueous Solvents. Inorg. Chem. 55, 12651–12659 (2016).
28. Piro, N. A., Robinson, J. R., Walsh, P. J. & Schelter, E. J. The electrochemical behavior of cerium(III/IV) complexes: Thermodynamics, kinetics and applications in synthesis. Coord. Chem. Rev. 260, 21–36 (2014).
29. Mahoney, B. D., Piro, N. A., Carroll, P. J. & Schelter, E. J. Synthesis, Electrochemistry, and Reactivity of Cerium(III/IV) Methylene-Bis-Phenolato Complexes. Inorg. Chem. 52, 5970–5977 (2013).
30. Robinson, J. R. et al. Tuning Reactivity and Electronic Properties through Ligand Reorganization within a Cerium Heterobimetallic Framework. J. Am. Chem. Soc. 135, 19016–19024 (2013).
31. Halter, D. P. et al. Electrocatalytic H2O Reduction with f-Elements: mechanistic Insight and Overpotential Tuning in a Series of Lanthanide Complexes. J. Am. Chem. Soc. 140, 2587–2594 (2018).
32. Watanabe, T., Matsuo, T. & Kawaguchi, H. A Tantalum(V) Carbene Complex: formation of a Carbene–Bis(phenoxy) Ligand by Sequential Proton and Hydride Abstraction. Inorg. Chem. 45, 6580–6582 (2006).
33. Akagi, F., Ishida, Y., Matsuo, T. & Kawaguchi, H. Synthesis and reactivity of niobium complexes having a triply triaryloxide ligand in bidentate, tridentate, and tetradentate coordination modes. Dalton T. 40, 2375–2387 (2011).
34. Manz, T. A., Fenwick, A. E., Phomphrai, K., Rothwell, I. P. & Thomson, K. T. The nature of aryloxo and arylsulphide ligand bonding in dimethyltellurium complexes containing cyclopentadienyl ligation. Dalton Trans., 668–674, (2005).
35. Marion, L., Werkema, E. L., Perrin, L., Eisenstein, O. & Andersen, R. A. Hydrogen for Fluorine Exchange in CeF3 and CeF3H by Monomeric [1,3,4-(Me3C)3C5H2]2CeH: Experimental and Computational Studies. J. Am. Chem. Soc. 127, 279–292 (2005).
36. Werkema, E. L. & Andersen, R. A. Fluorine Hydrogen Exchange in the Hydrofluorobenzene Derivatives C6H5F2, where x = 2, 3, 4 and 5 by Monomer [1,2,4-(Me3C)3C5H2]2CeH and the Solid State Isomerization of [1,2,4-(Me3C)3C5H2]2Ce[2,3,4,5-C6H4F2] to [1,2,4-(Me3C)3C5H2]2Ce[2,3,4-C6H4F2]. J. Am. Chem. Soc. 130, 7153–7165 (2008).
37. Shannon, R. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr. Sect. A 32, 751–767 (1976).
38. Pedrick, E. A., Hrobáříková, V., Greif, A. H. & Kaupp, M. Giant Spin-Orbit Effects on NMR Shifts in Diamagnetic Actinide Complexes: Guiding the Search of Uranium(VI) Hydride Complexes in the Correct Spectral Range. Angew. Chem. Int. Ed. 51, 10884–10888 (2012).
39. Albach, J. Analyzing NMR shielding tensors calculated with two-component relativistic methods using spin-free localized molecular orbitals. J. Phys. Chem. A. 128, 164111 (2008).
40. Albach, J. & Zheng, S. Analyzing Pt chemical shifts calculated from relativistic density functional theory using localized orbitals: The role of Pt 5d lone pairs. Magn. Reson. Chem. 46, S43–S55 (2008).
41. Ianziti, K. L., Guzie, I. A. & Reich, H. J. Solution and Solid-State Structures of Lithiated Phenoxylazolines. Organometallics 25, 5390–5395 (2006).

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Author contributions G.B.P. and E.J.S conceived this project. G.B.P. performed the synthesis, electrochemical, NMR, and UV-Vis experiments. M.R.G. and P.J.C. collected and solved the X-ray structures. G.B.P., P.J.W., and E.J.S. analyzed the experimental data. D.-C.S. and J.A. conducted the theoretical computations and analyzed the results. G.B.P., D.-C.S., J.A., P.J. W. and E.J.S. participated in drafting the paper. All authors discussed the results and contributed the preparation of the final paper.

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