Tetravalent cerium carbene complexes†

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The tetravalent organometallic cerium complex [CeL_4] is readily accessible from the oxidation of the trivalent [CeL_3], L = a bidentate N-heterocyclic carbene alkoxide ligand, [C{(NPr^i)-CHCHN}CH_2CMe_2O]. The [CeL_4] complex should behave like the [UL_4] analogue, but the two complexes show significantly different structures, highlighting the differences between 4f and 5f metals.

Cerium is the only lanthanide with a readily accessible tetravalent oxidation state. As such, its chemistry offers unique opportunities for redox chemistry and, as the 4f Ce and 5f U cations are the same size, the comparison of analogues gives an insight into f-orbital covalency which is needed to improve the separation of lanthanides and actinides in nuclear waste.[1]

Much research has been invested in the isolation of genuinely f^0 examples of organometallic Ce^{IV}. Tetravalent cerium is strongly oxidising, whereas the conventional organometallic alkyl, cyclopentadienyl and cyclooctatetraenyl anions, R^-, $C_5R_5^-$, and $C_8R_8^{2-}$, are reducing in nature. Thus, although complexes such as cerocene, [Ce(η^8-C_8H_8)$_2$], and the fused-ring analogues [Ce{C_8H_4(SiPr$^i_3$-1,4)$_2$}$_2$] and [Ce(C_8Me_6)$_2$] are isolable,[2] there is no simple model that adequately describes the bonding, and they may be regarded as possessing multi-configurational ground states; cerocene has a ground state with 80% Ce^{III} 4f^1 character, with $(C_8H_8)^{1.5-}$ ligands.[3] The complexes [Ce(C_5H_5)$_3$X] and [Ce(C_5H_5)$_2X_2$] (X = OBu^t, OPr^i, halide) are closer to a formal Ce^{IV} state,[4] but to date, no examples of Ce^{IV} with σ-bound hydrocarbyl ligands have been isolated.

Other than Ce(OPr^i)$_4$, Ce(OTf)$_4$ and the ceric ammonium nitrate (CAN)-derived [Ce(OBu^t)$_2$(NO_3)$_2$(THF)$_2$],[5] routes to tetravalent complexes demand the oxidation of Ce^{III} salts. However, the outcome is rarely predictable from the redox potential of the oxidant, since ligand reorganisations contribute significantly to reaction thermodynamics. For example, oxidation with I_2 is effective for Ce[N(CH_2CH_2N{$SiMe_2$Bu^t})$_3$], but not [Ce{N($SiMe_3$)$_2$}$_3$], despite the accessibility of [Ce{N($SiMe_3$)$_2$}$_3$X] (X = Cl, Br).[6]

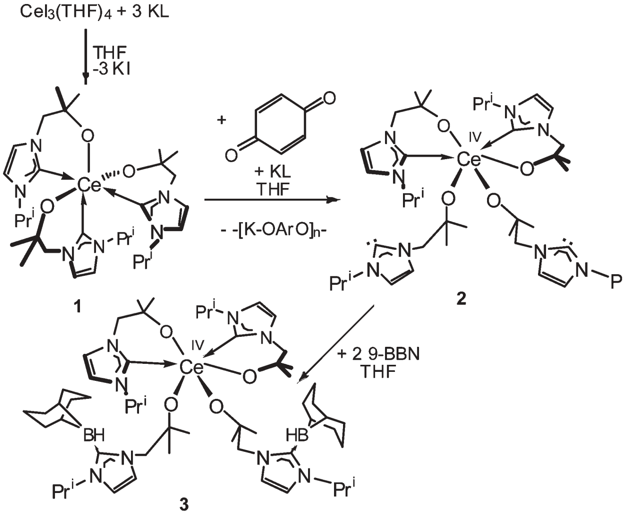
We have previously shown how the incorporation of a pendant anionic group into N-heterocyclic carbenes (NHCs) renders the synthesis of NHC adducts of electropositive metal cations easier.[7] Herein, we show how these tethered carbenes can be used to generate the first complexes with a simple, two-electron Ce^{IV}–C bond.

Treatment of [CeI_3(THF)$_4$] with three equivalents of [KL], K[$OCMe_2CH_2$(1-C{NCHCHNPr^i})], affords [CeL_3], **1**,† in good yield as a dark yellow microcrystalline powder, Scheme 1. Although no X-ray quality single crystal has been obtained, the paramagnetically shifted ligand resonances in the ^{1}H NMR spectrum of **1** are sharp and spread over a relatively narrow chemical shift range, suggestive of a high-symmetry structure.[8] The solution magnetic susceptibility of **1** at 300 K is 2.21 μ_B; the range for Ce^{III} complexes is 1.8–2.5 μ_B.

Treatment of **1** with $TeCl_4$, PBr_2Ph_3 or I_2 (reagents previously used for the oxidation of Ce^{III} amides)[6] did not yield the desired oxidation products. However, treatment of **1** with benzoquinone affords tetravalent **2**, [CeL_4], arising from oxidation and ligand redistribution, Scheme 1. Inclusion of [KL] in the reaction mixture affords an excellent yield of **2**, since no [CeL_3] is sacrificed.

Benzoquinone has been used before as an oxidant for Ce^{III} alkoxides, hinting at its generality.[9] The oxidation of **1** is also effected by XeF_2 and by [Fe(Cp)$_2$][OTf], but with lower yields.

The ^{1}H NMR spectrum of **2** is diamagnetic, as expected for a Ce^{IV} complex, with sharp ligand resonances. The carbene carbon resonance is now observed in the ^{13}C NMR spectrum at 212 ppm. One set of ligand resonances is visible in the NMR spectra, commensurate with a fast fluxional process between free and bound carbenes on the NMR timescale. In d_8-THF solution, the ^{1}H resonances decoalesce at 230 K, and at 198 K three sets of ligand resonances are observed in a 2 : 1 : 1 ratio. This is in accordance with a fast motion of the two pendant carbenes on the



Scheme 1 Synthesis of **1** and the Ce^{IV} complexes **2** and **3**.

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NMR timescale, and a sterically congested, small Ce^{IV} centre enforcing different magnetic environments on the two rigid, bound bidentate ligands.

X-ray quality yellow single crystals of **2**‡ were grown from a THF solution, Fig. 1.

The cerium cation is coordinated by two bidentate L and two monodentate L, in which the NHC groups are unbound. The Ce–O distances are average for tetravalent cerium (av. 2.135 Å; range 2.02–2.15 Å) and the Ce–C1 and Ce–C11 bond lengths are 2.693(6) and 2.652(7) Å respectively. There are no tetravalent Ce–C single bonds with which to compare these Ce^{IV}–C bond lengths, but the shortest Ce^{III}–$C_{carbene}$ distance reported is 2.670(2) Å in $[Ce(L)(N\{SiMe_3\}_2)_2]$ (L = $C\{N(Bu^t)CHCHN\}CH_2CH_2NBu$;[10] the Ce^{III} alkyl distance in $[Ce(CH\{SiMe_3\}_2)_3]$ Ce^{III}–C is 2.475 Å.[11] In a separate experiment, the analagous Ce^{III} $[CeL_2(HL)_2]I$[12] complex was structurally characterised and provides contrasting Ce^{III}–NHC and imidazolium data, which also confirm that the NHC groups in **2** have not been protonated.

The dynamic equilibria between free and coordinated carbenes may also be frozen out by treatment of **2** with two equivalents of the borane 9-BBN, 9-borabicyclo[3.3.1]nonane, Scheme 1, affording highly crystalline yellow $[Ce(L)_2(L\text{-}9BBN)_2]$, **3**.§ This also confirms the absence of any protonated imidazolium salt in **2**. The NMR spectra of **3** are characteristically diamagnetic and invariant with temperature, with only one bound carbene carbon observed in the NMR spectra (the boron-coupled carbon resonances are not observed). X-ray quality yellow single crystals of **3** were grown from a benzene solution, Fig. 2.

The geometry at the Ce^{IV} centre in **3** is pseudo-octahedral, and apart from the coordinated boranes, the structures of **2** and **3** are very similar. The $C_{carbene}$–B distances (mean 1.639 Å) are comparable to those in simple carbene-borane adducts (mean 1.667 Å).[13]

It is instructive to compare this Ce^{IV} carbene complex **2** with the U^{IV} carbene analogue $[UL_4]$, **4**,[14] reported by us, Fig. 3. Despite the nearly-identical sizes of the two cations, it is clear that the softer carbenes favour coordination to the more polarisable 5f-actinide cation than the 4f-cation, resulting in striking differences in both coordination number and geometry between them. Three carbenes coordinate to U^{IV}, at the expense of forming longer U–O and U–C bonds, Table 1.

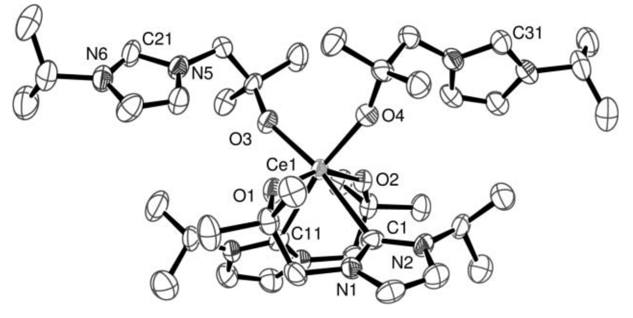

Fig. 1 Displacement ellipsoid drawing of the molecular structure of **2** (50% probability ellipsoids). Solvent and hydrogens omitted. Selected distances (Å) and angles (°); Ce–O1 2.140(4), Ce–O3 2.130(4), Ce–C1 2.693(6), Ce–C11 2.652(7), N1–C1 1.355(8), N5–C21 1.388(8), N1–C1–N2 103.5(5), N6–C21–N5 101.1(6).

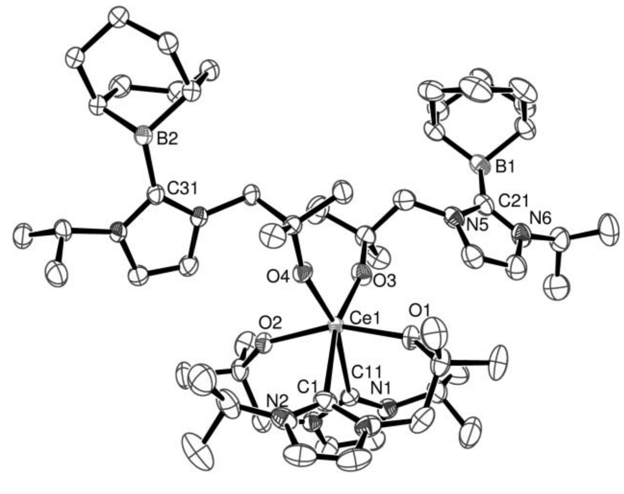

Fig. 2 Displacement ellipsoid drawing of the molecular structure of **3** (50% probability ellipsoids). Solvent and hydrogens omitted. Selected distances (Å) and angles (°); Ce–O1 2.151(1), Ce–O3 2.118(1), Ce–C1 2.705(2), Ce–C11 2.703(2), C21–B1 1.639(3), N1–C1 1.359(3), N5–C21 1.363(2), N1–C1–N2 102.9(2), N6–C21–N5 104.4(2).

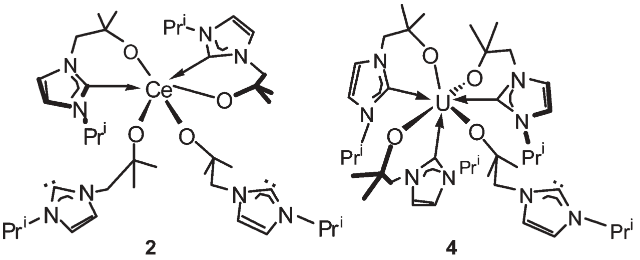

Fig. 3 Related Ce^{IV} and U^{IV} complexes.

Table 1 Comparison of structural data for **2** and **4**

Distance/Å or angle/°	M = Ce	M = U	Δ(U–Ce)	Δ(U–Ce) corr[a]
$M–O_{(av)}$	2.135(5)	2.203(3)	0.068	−0.012
$M–C_{(av)}$	2.674(7)	2.747(3)	0.073	−0.007
$N–C_{car(bound,\ av)}$	1.367(8)	1.365(4)	—	—
$N–C_{car(free,\ av)}$	1.377(9)	1.373(4)	—	—
$NCN_{(bound,\ av)}$	102.3(6)	102.1(2)	—	—
$NCN_{(free,\ av)}$	100.9(6)	101.3(2)	—	—

[a] corrected for 6- and 7-coordinate covalent radii of Ce^{IV} (1.01 Å) and U^{IV} (1.09 Å) respectively[1c]

In summary, the use of NHC-containing ligands has allowed the isolation of tetravalent organometallic cerium complexes stabilised by two-electron donor carbene ligands. These have significantly different structures to the uranium analogues, highlighting the more ionic character of these lanthanide bonds in comparison to those of the 5f metals.

Work is in progress to identify other oxidisable reagents that may be bound by the pendant NHC groups.

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Notes and references

‡ Crystal data for **2**: $C_{52}H_{92}CeN_8O_7$, M = 1081.46, monoclinic, space group $P21/n$, a = 23.188(3) Å, b = 11.1458(14) Å, c = 24.392(3) Å, α = 90.00°, β = 99.709(2)°, γ = 90.00°, V = 6213.8(14) Å^3, Z = 4,

D_c = 1.156 g cm^{-3}, μ = 0.781 mm^{-1} (MoKα, λ = 0.71073 Å), T = 150 K, R ($F^2 > 2\sigma$) = 0.0673 (6660 reflections), R_w (F^2, all data) = 0.1822, goodness-of-fit = 0.963 for all 10920 unique data (38792 measured, R_{int} = 0.11, $2\theta <$ 50°, CCD diffractometer) and 640 refined parameters. CCDC 650969. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713041d

§ Crystal data for **3**: $C_{74}H_{116}B_2CeN_8O_4$, M = 1343.49, triclinic, space group $P\bar{1}$, a = 13.6344(5) Å, b = 15.6439(6) Å, c = 19.9000(7) Å, α = 78.468(2)°, β = 74.110(2)°, γ = 66.660(2)°, V = 3728.3(2) Å^3, Z = 2, D_c = 1.197 g cm^{-3}, μ = 0.661 mm^{-1} (MoKα, λ = 0.71073 Å), T = 150 K, R ($F^2 > 2\sigma$) = 0.0323 (15594 reflections), R_w (F^2, all data) = 0.0863, goodness-of-fit = 1.065 for all 16851 unique data (34250 measured, R_{int} = 0.013, $2\theta <$ 55°, CCD diffractometer) and 826 refined parameters. CCDC 650970. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713041d

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