**Introduction**

Ceium is a cheap, non-toxic, redox-active, early lanthanide. It is earth-abundant, being more common than copper or nickel, its salts are six times less toxic than those of iron, and it is the only rare earth with a readily accessible +III/+IV redox couple.\(^1\)-\(^4\) It has been used widely as a stoichiometric oxidant in organic chemistry, as a redox active heterogeneous catalyst support, and increasingly in the development of homogeneous catalysts for a range of small molecule transformations.\(^1\) The Ce\(^{III/IV}\) redox potential can be easily tuned across an extremely large window by appropriate ligand choice, for example from \(E^0 = +1.30\) V vs. Fe/Fe\(^{3+}\) for Ce(\(\text{ClO}_4\))\(_2\) in 8 M HClO\(_4\) to \(E_{\text{pc}} = -2.39\) V vs. Fe/Fe\(^{3+}\) in [Ce(\(\text{O}^\text{Bu})_2(\text{THF})]_2\). Rare examples of molecular, dinuclear Ce\(^{III}\) and Pr\(^{III}\) complexes with robust Ln-coordination are accessible by use of the tetraphenolate pTP as a supporting, chelating O-donor ligand platform, pTP = \([2-\{(\text{OC}_6\text{H}_4\text{R}_2\text{-2,4})\text{CH}\}-\text{C}_6\text{H}_4\cdot\text{-1,4}]^{-}\) that favours the higher formal oxidation states accessible to rare earths. Two classes of complexes have been made from the platforms; one metallacyclic 2 + 2 \([\text{Ln}_2(\text{pTP})_2]\) framework with a rigid, letterbox-shaped geometry and \([\text{Ln}\text{(arylolate)}_4]\) core, and one more flexible \([\text{Ln}X_2(\text{pTP})]\) with one rare earth ion at either end of the platform. The Ln\(^{III}\) letterbox complexes have two K\(^{+}\) counter-cations, one of which sits inside the letterbox, binding the two central arenas of the platform sufficiently strongly that it cannot be displaced by solvent molecules (THF and pyridine) or crown ethers. Oxidation of the Ce\(^{III}\) letterboxes is facile and forms the unusual neutral molecular (Ce\(^{IV}\))\(_2\) letterbox in which the Ce\(^{IV}\) reduction potential is \(-1.83\) V vs. Fe/Fe\(^{3+}\). The electronic structure of the Ce(\(\text{en/iv}\)) complexes was investigated using HERFD-XAS (high energy resolution fluorescence detection X-ray absorption spectroscopy).

Anionic oxygen-donor alkoxide and aryloxide ligands have been used most use in stabilising the higher oxidation state in the Ce\(^{III/IV}\) redox couple,\(^7,12,17-21\) and applications of cerium reagents in molecular chemistry have largely been focused on mononuclear cerium complexes.\(^6,20,22\) We have used functionalised aryloxide ligands to support cerium(\(\text{iii}\)) catalysts [Ce(\(\text{L}^\text{R}\))\(_3\)]\(_2\) (\(\text{L}^\text{R} = \text{ortho-NHC-aryloxide} = \text{O}(\text{o-C}_6\text{H}_4\text{-Bu}_2\text{-2,6-CN}(\text{CH}_2)\)).
active form of the classical cerium oxidant, aqueous Ce(IV), is
However, it has been shown by EXAFS spectroscopy that the
cations in a molecule has received considerably less attention.
dinuclear,24 so the development of robust and well-defined
previously reported the synthesis of their UIII/III and UIV/IV com-
via
ories
able ester L-lactide.3
for the ring-opening polymerisation (ROP) of the bio-renew-
molecular [Ce]2 complexes that can combine two readily acces-
feature not usually achievable in molecular f-block chemistry.
observe two-electron separated redox states in the system, a
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previously reported the synthesis of their UIII/III and UIV/IV com-
The tetraphenol ligands H4(pTP), [α,α',α'-tetra(3-tert-butyl-5-
R-2-hydroxyphenyl)p-xylene, R = Me, 'Bu], (Scheme 1) are syn-
thesised via a straightforward condensation reaction. We have
previously reported the synthesis of their UIII/III and UIV/IV com-
plexes, and others have reported the use of pTP ligands to
support catalysis by both partially deprotonated potassium salts
[K2H2(pTP)],30 or VV and MoVI-imido complexes which have
shown catalytic reactivity for the ring-opening polymerisation of
e-caprolactone.26,31 In the case of the potassium complexes, the
authors attributed the remarkable stability of the doubly deproto-
nated salt [K2H2(pTP)] to the formation of potassium-arene
interactions with the central arene of the platform, and capacity
for the remaining protons to bridge the two aryloxide O atoms
on each side.30 In our hands, the tetra-potassium salt 1k,
[[K4(pTP)]2(THF)11, R = Me], is readily isolated from the reaction
between H4(pTP)[THF]11, with four equivalents of KN+ (N+ = N(SiMe)3)
in THF at room temperature, Scheme 1, although we note that it
is extremely sensitive to hydrolysis. It has been fully character-
ised, including by a single crystal X-ray diffraction study, but the
syntheses of the cerium complexes below are most straight-
forward when samples of 1k are made in situ (R = Me, 'Bu).
The tetrapotassium salt 1k crystallises as a THF-solvated
dimer [K6(pTP)4Me2(THF)11] in the monoclinic space group
P2(1)/c, with four molecules in the unit cell. In the crystal
structure (Fig. 1), four K+ ions (K3–K6) and four oxygen atoms
(O3–O6) form a near-planar ladder-like [K4O4] skeleton. This
type of coordination has previously been reported in the
family of K(OAr)(sol) salts, for various aryl groups such as
2,6-dimethyl, and potassium p-halide-substituted aryloxides,
[(4-X-C6H4OK)6·(dioxane)6], (X = F, Cl, Br). Each of these K+
coordinates to three phenolate oxygen atoms while oxygen
atoms bridge two K+ ions. The K–O bond distances range from
2.552(4) Å (K4–O5) to 3.132(4) Å (K6–O5), falling in the
reported range of K–O bonds of 2.432(6) Å to 3.194 Å. The
two ions in the middle of the skeleton of the structure, K4 and
K5, coordinate to the phenyl linker via π interactions with an
average distance of 2.868 Å and 3.046 Å, respectively.
Syntheses of rare earth complexes of pTP
Reactions of complex 1k and [LnCl3(THF)3] (Ln = Ce, Pr) in a
1 : 1 Ln : pTP ratio in THF affords the targeted binuclear rare
earth metal letterbox complexes as their ate salts
[K(THF)n][KLn4(pTP)2(THF)4] 2k–Ln, (Ln = Ce, Pr; R = Me, 'Bu)
in good yields (~80%). Analogous reactions of 1bu with
[LnCl3(THF)3] (Ln = Ce, Pr) in a 2 : 1 Ln : pTP ratio in THF
affords the binuclear (Ln1bu) complexes [[LnCl(THF)3]2(pTP)3]2.
The products are purified by evaporation of the filtered solu-

Results and discussion
The tetraphenol ligands H4(pTP), [α,α,α',α'-tetra(3-tert-butyl-5-
R-2-hydroxyphenyl)p-xylene, R = Me, 'Bu], (Scheme 1) are syn-
thesised via a straightforward condensation reaction. We have
previously reported the synthesis of their UIII/III and UIV/IV com-
plexes, and others have reported the use of pTP ligands to
support catalysis by both partially deprotonated potassium salts
[K2H2(pTP)],30 or VV and MoVI-imido complexes which have
shown catalytic reactivity for the ring-opening polymerisation of
e-caprolactone.26,31 In the case of the potassium complexes, the

Scheme 1 Synthesis of tetrapotassium salt 1k.

Fig. 1 Solid-state structure of complex 1kMe. Thermal ellipsoids of non-
carbon atoms are shown at 30% probability. All hydrogen atoms and
lattice solvent molecules are omitted for clarity.

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The complexes 2-Ce are paramagnetic so $^1$H NMR spectra of the complexes contain broadened and shifted, but still assignable, resonances for the ligands. The Ce(III) complexes should have one unpaired electron on each f-block cation. Accordingly, they were analysed by EPR spectroscopy. As anticipated, no EPR signal was visible in solutions of 2-mu-Ce at room temperature or 100 K. However, an EPR resonance was observed at 9 K for a solid-state sample; a weak resonance is observed at 200 mT which is attributed to the disallowed $S=1\rightarrow S=0$ transition. The K$^+$ counter-cation is the 2 half-field signal that corresponds to the S = −1 to S = 1 state of the [Ce$^{III}$] system, see ESI†.

The letterbox-encapsulated K$^+$ is remarkably difficult to remove: addition of pyridine or excess 18-crown-6 in THF solution to 2-mu-Ce yields the pyridine-solvated 2-mu-Ce-py, [K(py)$_3$][KCe$_2$(py)$_4$(TP)$_2$] (R = Me, Bu) (see ESI†), or external-K-18-crown-6 solvate 2-mu-Ce-cr, [K(18-crown-6)(THF)$_2$][KCe$_2$(TP)$_2$(THF)$_2$] (R = Me), respectively. Almost no change in the $^1$H NMR chemical shifts other than those of the solvating donor ligands is observed even when the THF solution of 2-mu-Ce-cr is heated at 60 °C for 24 hours. The structures of 2-mu-Ce and 2-mu-Ce-cr (see ESI†) have been confirmed by single crystal XRD.

Single crystals of complex 3-mu-Ln, [[LnX(py)$_3$](TP)$_2$] (LnX = CeCl, PrCl), suitable for X-ray diffraction were grown by
vapour diffusion of hexane into a saturated pyridine solution at room temperature. The solid-state structure of $^{3}\text{Pr}\text{u}-\text{Ce}$ is shown in Fig. 3a. That of the pyridine solvate of $^{3}\text{Pr}\text{u}-\text{Ce}$, grown from a saturated pyridine solution at $-30^\circ\text{C}$, is shown in the ESL.$^\dagger$

The Ce and Pr analogues are isostructural (see ESI), with a trans-disposition of the two metal bis(aryloxide) fragments, on either side of the phenyl-linker, displaying a trans-configuration. The Ln1–Cl1 bond in $3\text{-Ce}$ is 2.7789(6) Å, 0.02 Å longer than in $3\text{-Pr}$ in line with the similarity between their ionic radii. However, a cis-configuration is observed in the borohydride analogue, $\left[[\text{Ce}(\text{BH}_4)(\text{py})_4]_2(\text{pTP}^\text{Bu})\right]$ (Fig. 3b), where two borohydride groups reside on the same side of the phenyl ring. The average Ce–B distance of 2.832 Å is slightly longer than the reported value of 2.678(6) Å and 2.704(7) Å in the complex $\left[[\text{Ce}(\text{BH}_4)_2(\text{THF})_5]\right][\text{BPh}_4]$.34

The Ce$^{\text{III}}$ complexes $2\text{-Ce}$ are extremely sensitive to oxidation by even trace amounts of $\text{O}_2$. Accordingly, stoichiometric reactions with a variety of oxidants, such as $\text{I}_2$ or CuX$_2$ ($X = \text{Cl}$ or OTf), leads to the instant formation of intensely blue-coloured products characterised as the Ce$^{\text{IV}}$ complexes $4^R$, $\left[[\text{Ce}(\text{pTP}^\text{Bu})_2(\text{THF})_3]\right]$ ($R = \text{Me}$, $^3\text{Bu}$) (Scheme 3). The blue colour observed in these complexes is attributed to a ligand–π to vacant Ce-4f charge-transfer band (LMCT) that is observed in many Ce$^{\text{IV}}$ complexes.12,17,15,36 In the UV-Vis spectrum of a THF solution of $^{4}\text{Bu}$, the broad absorption band is centred at 576 nm (see ESI†), a relatively low energy compared to other Ce$^{\text{IV}}$ aryloxide complexes (e.g. 487 nm in the complex $[\text{Li}_3(\text{thf})_3\text{Ce}^{\text{IV}}(\text{BINOLate})\text{Cl}]$).20,37

Redox chemistry

Reactions of $2^\text{R}-\text{Ce}$ with a range of oxidants have been studied. The cleanest oxidations of $2^\text{R}-\text{Ce}$ are with CuX$_2$ ($X = \text{Cl}$ or OTf), affording Cu$^0$ metal and KX by-products. Reactions with other oxidants ($\text{I}_2$, XeF$_2$ and HgX$_2$ ($X = \text{Cl}$, I, OAc)) are described in the ESL.$^\dagger$ This reaction can be monitored by $^1\text{H}$ NMR spectroscopy as the paramagnetically shifted resonances of the starting material $2$ disappear immediately and are replaced by a set of diamagnetic ligand resonances attributable to a Ce$^{\text{IV}}$/Ce$^{\text{IV}}$ complex.

The reaction with just a single equivalent of $\text{I}_2$ or CuX$_2$ ($X = \text{Cl}$ or OTf) generates the new (Ce$^{\text{IV}}$), product $4^\text{R}$ and unreacted (Ce$^{\text{III}}$), starting material $2^\text{R}-\text{Ce}$ in equal amounts. This represents a rare, concerted, two-electron redox process for a single molecular lanthanide complex.

Single crystals of $^{4}\text{Bu}$ were grown by slow evaporation of hexane into a concentrated THF solution but the diffraction data are of poor quality, so only the connectivity can be deduced (Fig. 4). Complex $4\text{Me}$ was analysed only by NMR spectroscopy, see ESL.$^\dagger$ In the molecular structure of $4\text{Bu}$ each Ce atom is coordinated by four phenolate oxygen atoms and two THF molecules. With the loss of $\text{K}^+$ from the letterbox, the dihedral angle between the two central arene rings decreases to 25° while their inter-centroid distance decreases to 4.538 Å. The X-ray data are poor, and the precision of the metrics is not reliable, but the average Ce–O$_{\text{Ar}}$ bond length is around 2.15 Å so appreciably shorter than that in Ce(u) complexes (2.382 Å for $2\text{Me}-\text{Ce}$, 2.350 Å for $2\text{Bu}-\text{Ce}$), consistent with the decrease in Ce radius upon oxidation to f$^0$ (from 1.01 Å to 0.87 Å).38

The cyclic voltammograms of Ce$^{\text{III}}$ complex $2\text{Bu}-\text{Ce}$ shows a small current increase corresponding to an irreversible oxidation at +0.76 V which is tentatively assigned to the Ce$^{\text{III}}$–IV process, but is increasingly difficult to observe with additional scans; this may be the result of decomposition of the complex in supporting electrolyte solution (see ESI† for details).
However, the CeIV complex is considerably more robust, and cyclic voltammetry of a THF solution of $^{4}$tBu using 0.1 M $[nBu_4N][PF_6]$ as supporting electrolyte shows a quasi-reversible reduction at $E_{pc} = −1.31$ V with a small return oxidation wave at $E_{pa} = −1.02$ V. This may correspond to the one-electron reduction of one CeIV ion. A larger reduction wave is observed at $E_{pc} = −1.83$ V vs. Fc/Fc$^+$ (Fig. 5). It is not clear yet whether in the electrochemical experiment, the return oxidation wave is due to an impurity or a process occurring at the ligand first. It has been observed on multiple occasions in repeated measurements and using different batches of material, and in two different laboratories. The O-donor ligands, and the observed higher stability of the CeIV complex compared with the CeIII complex 2 all support the expected stabilisation of the +4 oxidation state in the complex, although more in-depth characterisation is warranted. Our previous electrochemical analyses of the free ligand, and the potassium salt, were not helpful. The couples can be compared to a range of related O-ligated CeIV complexes such as $[Ce(O^tBu)_4(py)_2]$ ($E_{pc} = −1.99$ V vs. Fc/Fc$^+$ in DCM), Ce$[2-\{BuNO\}py)_4$ ($E_{pc} = −1.95$ V vs. Fc/Fc$^+$ in DCM), CeL(O^tBu)$_4$ ($E_{pc} = −2.39$ V vs. Fc/Fc$^+$ in THF) and imidophosphorane supported complexes Ce[NPPip]$_4$ (reduction range of $−2.30 < E_{pc} < −2.47$ V vs. Fc/Fc$^+$ in THF).10

In order to obtain a more chemically accurate view on the Ce complex oxidation state, HERFD-XAS (high energy resolution fluorescence detection X-ray absorption spectroscopy) was employed. HERFD-XAS provides a method to probe the 5d density of states in detail. Specifically, this enables a fingerprinting determination of whether a complex can be formally considered Ce(III) vs. Ce(IV). HERFD-XAS spectra (Fig. 6) of sample $^{2}$tBu·Ce shows a single peak, indicative of formal Ce(III). Sample $^{4}$tBu, however, shows two main peak features approximately 10 eV apart. This doublet peak is indicative of formal Ce(IV), and is also observed in CeO$_2$, which serves as a fingerprinting standard (Fig. 6). Thus, electronically, $^{2}$tBu can be referred to as Ce(III) and $^{4}$tBu as Ce(IV), as it contains considerable f$^0$ character.41,42

Under certain conditions, praseodymium can exist in the formal PrIV oxidation state in some solid-state compounds such as NaPrF$_5$, PrF$_4$, and Pr oxides or even in the +V oxidation state in the gas-phase. However, molecular PrIV complexes remain an elusive and interesting target. Recent reports on the synthesis and isolation of the TbIV complexes51,52 have shown great potential for the stabilisation of rare earth metals in the +IV oxidation state with bespoke ligand systems. Here, unlike the cerium counterpart, the (PrII)$^2$ complex $^{2}$tBu·Pr is inert to most of the oxidants under the same reaction conditions. No reactivity with oxidants such

![Fig. 4](https://example.com/fig4.png)

**Fig. 4** Solid-state structure of complex $^{4}$tBu. All hydrogen atoms and lattice solvent molecules are omitted for clarity. The inter-arene distance (4.538 Å) is represented by the blue double-headed arrow.

![Fig. 5](https://example.com/fig5.png)

**Fig. 5** Cyclic voltammogram of complex $^{4}$tBu at different scan rates versus Fc/Fc$^+$ measured in THF with 0.1 M $[nBu_4N][PF_6]$.

![Fig. 6](https://example.com/fig6.png)

**Fig. 6** Normalised HERFD-XAS spectra at the Ce LIII absorption edge. The increased edge energy and doublet peak for $^{4}$tBu (blue) compared with $^{2}$tBu·Ce (red) confirm the Ce(IV) oxidation state of $^{4}$tBu. The doublet peaks of $^{4}$tBu also match those observed for CeO$_2$ (black, dotted), which serves as a Ce(IV) fingerprinting standard. Peak splitting in the CeO$_2$ HERFD spectrum has been attributed to 5d state splitting.43
as \( \text{O}_2 \), \( \text{CuX}_2 \) (\( \text{X} = \text{Cl}, \text{OTf} \)), \( \text{Ph}_3\text{CCl} \) or benzoquinonone was observed in solutions monitored by \(^1\text{H} \) NMR spectroscopy. Addition of \( \text{I}_2 \) to solutions of complex \( 2^{3\text{Bu}-\text{Pr}} \) showed no reaction at room temperature, but the mixture changes colour from brown to green when heated at 60 °C for 8 hours. A reaction monitored by solution NMR spectroscopy shows the full transformation of starting material into several different products (see ESI†), from which, work-up yields a white powder that is characterised as the dinuclear \( \text{Pr}^{\text{III}} \) complex \( \{[\text{Pr}[(\text{thf})]_2(p\text{TP})]\} \) \( R = '\text{Bu} \), 5, with a yield of 29% (Fig. 7). It is evident from this that one of the chelating ligand platforms has been de-coordinated, and the other material that is isolated from the reaction is the product of ligand oxidation, a bicyclic ether that we have also characterised by X-ray crystallography (see ESI†).\(^{31}\)

In the solid-state structure of 5, each \( \text{Pr} \) atom displays a pseudo-octahedral configuration with three THF molecules, two phenolate oxygen atoms and one iodine atom, similarly to \( 3^{\text{Bu}-\text{Pr}} \). The two metal centres are bonded to the opposite ends of the tetraphenolate ligand, in a trans-geometry. The \( \text{Pr}-1 \) bond is 3.1697(5) Å while two \( \text{Pr}-\text{O} \) bonds are labelled in the figure as 2.176(4) Å and 2.202(4) Å. These are slightly longer than those observed in the homoleptic aryloxide \( \{[\text{PrI}(\text{thf})_3]_2(p\text{TP})\} \) but are ~0.1 Å shorter than the average length (2.30 Å) measured in \( 2^{3\text{Bu}-\text{Pr}} \).

**Conclusions**

In summary, we have successfully synthesised a series of tetraphenolate supported bi-metallic \( \text{Ce}^{\text{III}} \) and \( \text{Pr}^{\text{III}} \) complexes with robust Ln-coordination and which favour the higher formal oxidation states accessible for rare earths. Two types of geometry are accessible; complexes with the new, rigid, letterbox-shaped geometries and \( [\text{Ln}(\text{aryloxide})_4] \) cores in a \( 2 + 2 \) \( [\text{Ln}_2(p\text{TP})_2] \) framework, and flexible complexes with one rare earth ion at either end of the single ligand platform in the form \( [[\text{LnX}_2(p\text{TP})]] \) are readily accessible. The binding of one \( \text{K}^- \) cation inside the letterbox shape of the \( [\text{Ln}_2(p\text{TP})_2] \) complexes in a bis(arene) motif is sufficiently strong that it cannot be extracted by crown ethers, although it can be removed through salt elimination by oxidation of the complex to the neutral \( \text{Ce}^{\text{IV}} \) letterbox complex. Solution electrochemical experiments showed that the \( \text{Ce}^{\text{IV}} \) cation is particularly well stabilised by the ligand with a measured \( \text{Ce}^{\text{IV}} \) reduction potential of ~1.83 V vs. \( \text{Fc}/\text{Fc}^- \). HERFD-XAS data on the \( \text{Ce}^{\text{IV}} \) complex confirms the formal +4 oxidation state for complex \( 4^{3\text{Bu}-\text{Pr}} \) based on a doublet peak that indicates considerable \( f^0 \) character. Chemical oxidation reactions show that only two-electron redox processes occur at the bimetallic letterbox-shaped complexes. Oxidation of the \( \text{Pr}^{\text{III}} \) complexes to target molecular \( \text{Pr}^{\text{IV}} \) yields products of ligand oxidation although there may be opportunities for judicious oxidant choice to enable the stabilisation of reaction intermediates.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**