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Selective and catalytic carbon dioxide and heteroallene activation mediated by cerium N-heterocyclic carbene complexes

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A series of rare earth complexes of the form Ln(L6), supported by bidentate ortho-aryloxide-NHC ligands are reported (L6 = O(C6H4-3Bu)-2,6-CN(C6H4)NR; R = Pr, iBu, Mes; Ln = Ce, Sm, Eu). The cerium complexes react cleanly and quantitatively insert carbon dioxide exclusively into all three cerium carbene bonds, forming Ce(L6)CO2). The insertion is reversible only for the mesityl-substituted complex Ce(L6mes). Analysis of the capacity of Ce(L6) to insert a range of heteroallenes that are isoelectronic with CO2 reveals the solvent and ligand size dependence of the selectivity. This is important because only the complexes capable of reversible CO2-insertion are competent catalysts for catalytic conversions of CO2. Preliminary studies show that only Ce(L6mes)catalyses the formation of propylene carbonate from propylene oxide and 1 atmosphere pressures of carbon dioxide. The mononigand complexes can be isolated from reactions using LiCe(NPR2)2 as a starting material; LiBr adducts [Ce(L6)][NPR2]2LiBr(THF)]; (R = Me, Pr) are reported, along with a hexanuclear N-heterocyclic dicarbene [Li2Ce3(ORhOMe-H2)2(NPR3)2(THF)]2, by-product. The analogous para-aryloxide-NHC proligand (p-L6mes = O(p-C6H4-3Bu)-2,6-CN(C6H4)NMes) has been made for comparison, but the rare earth tris-ligand complexes Ln[p-L6mes]3(THF)]; (Ln = Y, Ce) are too reactive for straightforward Lewis pair separated chemistry to be usefully carried out.

Carbon dioxide can be a useful and renewable C1 building block in the fine and bulk chemical industries due to its natural abundance and reactivity,1,2 and can provide carboxylic acids, esters and (cyclic) carbonates.3 Isoelectronic isocyanates and isothiocyanates are also valuable electrophilic elementary reagents used in polymerization and cyclisations,4,6 and thus chemistry which utilizes heteroallenes is of great interest. Lewis basic N-heterocyclic carbenes (NHCs) are known to react with carbon dioxide, isocyanates and isothiocyanates as nucleophiles to form imidazolium carboxylates,7,8 imidazolium amides9 and imidazolium carbimidothioates10 respectively (Chart 1). While imidazolium carboxylates can successfully catalyse carbamate formation,11 NHCs react as organocatalysts with isocyanates to form cyclic ureas B through an azolium amide intermediate.9

Since the first reported isolation of lanthanide-NHC complexes in 1994,12,13 it has been shown that Lewis acidic rare-earth cations form hemilabile bonds with soft o-donating NHCs.14,15 Between 2006 and 2010, Shen and co-workers published syntheses of aryloxide-NHC lanthanide complexes, however no subsequent reactivity was reported.16,17 In 2014, we reported the activation of carbon dioxide C and carbon disulfide D using a scandium NHC complex, achieving frustrated Lewis pair (FLP) like reactivity which resulted in metal-ligand scrambling to form a polymeric -(Sc-NHC-CO2)-n containing network owing to the flexible alkoxy tether.18

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that of iron,21,22 and it has many applications in heterogeneous catalysis.23 Previously we showed that cerium–silylamido NHC complexes ([Ce(L)(N(SiMe3))3]) react with CO2 to form an insoluble mixture while the uranium analogue ([U(L)(N(SiMe3))3]) yields an equivalent of isocyanate.24 In the latter instance it was not possible to isolate any intermediate that confirmed whether the NHC group was definitively involved in the CO2 activation.25 Recently, Suresh reported the first mononuclear N-carboxylate imidazolium lanthanide compounds, suggesting their potential use as single-molecule magnets.26 Here, we demonstrate that cerium (and other rare earth) complexes with aryloxide-tethered NHC ligands can successfully form homoleptic cerium imidazolium carboxylate complexes from CO2 insertion into the Ce–C carbene bonds. We show how to control the reversibility for the first time, and use this, and the extent of insertion of CO2 or isoelectronic heteroallenes (isocyanates and isothiocyanates) by changing the ligand steric and electronic properties, and by solvent effects. This is important as we show that only the complexes capable of reversible CO2-insertion are competent catalysts for the synthesis of cyclic carbonates from CO2 and epoxides.

Results and discussion

Ortho-aryloxide Ln-NHC complex synthesis

One objective for synthesizing lanthanide aryloxide tethered-NHC complexes is to combine valuable hemilability within a rigid framework for selective reactivity and we envisioned that varying coordination environments arising from respective alkyl and aryl substituents could give distinctive chemistry. A suspension of an ortho-aryloxide NHC proligand,27,28 [o-H2L][Br] where L = O(o-C6H5)2·Bu2·2,6-CN(C6H2)NR and R = 1Pr, 1Bu and Mes were treated with 6 equivalents of KN(SiMe3)2 and LnCl3(THF)n (Ln = Ce, Sm, Eu) in DME to afford bright yellow solutions with colourless precipitates of KCl and KBr. After work-up, 1Ln6 (Ln(L6)3) can be afforded in moderate to good yields (15-76%), while over 8 g of 1CePr2 can be isolated in a single reaction.

The 1H NMR spectra of all four lanthanide complexes bearing alkyl R groups (1Pr or 1Bu) contain a complex set of paramagnetic resonances indicating C3 symmetry and a unique environment for each ligand. In agreement with the 1H spectrum of 1CePr2 the 13C(1H) NMR spectrum is also complicated, containing three carbene chemical shifts (δ = 174.8 ppm, 187.8 ppm, 192.3 ppm), slightly broadened compared to the rest of the spectrum (average fwhm 12 Hz), and shifted compared to similar diamagnetic lanthanide NHC complexes (normal region ≈200–238 ppm for Y3+ and Ce3+).14,17,19,29,30 However in contrast, spectra of 1CeMes contain a single set of paramagnetically shifted resonances indicating C2 symmetry in solution on the 1H NMR spectroscopic timescale and 13C NMR spectroscopy of 1CeMes displays a single carbene resonance at 184.2 ppm.

1CePr2:

1CeMes:

Scheme 1 Synthesis of homoleptic lanthanide(III) complexes 1Ln6.

Fig. 1 Molecular structures of 1CePr2 (upper) and 1CeMes (lower) with Ce, O and C carbene shown at 50% ellipsoid probability, framework and peripheral carbon atoms drawn capped stick and wireframe respectively, and H and lattice solvent omitted for clarity.
These ligand orientation differences are rationalized by consideration that three planar mesityl groups pack more easily than the aryloxide/tert-butyl groups would, and that the tert-butyl/iso-propyl steric repulsions are less prescriptive. The proposed high degree of hemilability. For the failed synthesis of related but bulkier carbene ligands, consistent with butyl groups would, and that the aryloxide/alkoxy π-stacking.

Reactivity of 1Ce8 complexes

Exposure of a solution of 1Ce8 to an atmosphere of carbon dioxide results in the instant and quantitative formation of 2Ce8 (Ln(L8- CO3)3) as observed by the precipitation of a beige solid (hexanes reaction solvent) or monitoring by 1H NMR spectroscopy (benzene reaction solvent), Scheme 2. As anticipated for a complex with a hemilabile metal–NHC bond, the CO2 exclusively inserts into the three Ce–C bonds, and pleasingly, in contrast to the complexes with more flexible, bidentate alkoxide–NHCs, the rest of the molecule remains relatively unperturbed, with no evidence of ligand redistribution between metal centres. Samples of 2Ce8Pr and 2Ce8Bu held at elevated temperatures under dynamic vacuum (100 °C, 10-3 mbar) show no loss of CO2. However, a sample of 2Ce8Mes shows some loss of CO2 under dynamic vacuum (25 to 100 °C, 10-3 mbar), that is fully reversible. Solution phase analysis of the material formed shows it to be complicated mixture that could be oligomeric, but the material is quantitatively converted back to 2Ce8Mes upon re-exposure to an atmosphere of CO2.

1H NMR spectroscopic analysis reveals that the N-alkyl functionalised 2Ce8 complexes have C3 symmetry, i.e. a fac-conformation of the three bidentate ligands. The 13C NMR spectra contain diagnostic CO and carbon resonances for 2Ce8Pr and 2Ce8Bu (δ = 173.1 ppm and 173.5 ppm respectively) at significantly higher frequency than known organic NHC.CO compounds (~20 ppm). 8 as might be anticipated from proximity to the paramagnetic metal center. The FTIR spectrum of 2Ce8Pr shows a characteristic absorption at 1666 cm-1 (typical range ~1630–1690). 8, 33, 34 The conversion of 1Ce8Mes to 2Ce8Pr results in a lowering of symmetry from C3 to C2 according to room temperature solution spectroscopies. The 1H NMR spectrum shows three broadened sets of paramagnetic ligand resonances, and two C–O stretches observable in the FTIR spectrum (1678 and 1715 cm-1). We suggest that due to steric hindrance of three mesityl groups that one of the imidazolium carbonate units is non-coordinating in solution.
respectively) and O–Ce–O bond angles (77.77(10)° and 80.48(8)°). The average Ce–O bond length is within the regular bond length range at (2.472(6) Å and 2.473(2) Å respectively) suggesting a strong degree of stabilisation despite an increase of metal chelate ring size from 6 to 8.

2Ce$_{\text{Pr}}$:

![Molecular structures of 2Ce$_{\text{Pr}}$ (upper) and 2Ce$_{\text{Bu}}$ (lower) with carboxylate and Ce atoms shown at 50 % ellipsoid probability, framework and peripheral carbon atoms drawn capped stick and wireframe respectively, and H and lattice solvent omitted for clarity. Selected distances (Å) and angles (°) for 2Ce$_{\text{Pr}}$: Ce1–O11 2.790(5), Ce1–O21 2.274(5), Ce1–O31 2.256(6), Ce1–O13 2.468(6), Ce1–O23 2.482(6), Ce1–O33 2.466(6), O11–Ce1–O21 97.18(19), O11–Ce1–O31 99.3(2), O21–Ce1–O31 94.8(2), O13–Ce1–O23 77.02(19), O13–Ce1–O33 76.68(19), O23–Ce1–O33 79.6(2), O11–Ce1–O13 75.7(2), O21–Ce1–O23 75.7(2), O31–Ce1–O33 75.9(2). For 2Ce$_{\text{Bu}}$: Ce1–O11 2.261(2), Ce1–O21 2.268(2), Ce1–O31 2.274(2), Ce1–O13 2.473(2), Ce1–O23 2.477(2), Ce1–O33 2.470(2), O11–Ce1–O21 95.38(8), O11–Ce1–O31 95.25(8), O21–Ce1–O31 97.20(8), O13–Ce1–O23 76.76(8), O13–Ce1–O33 80.89(8), O23–Ce1–O33 80.80(8), O11–Ce1–O13 75.50(8), O21–Ce1–O23 74.77(2), O31–Ce1–O33 75.03(8).](image)

Fig. 2 Molecular structures of 2Ce$_{\text{Pr}}$ (upper) and 2Ce$_{\text{Bu}}$ (lower) with carboxylate and Ce atoms shown at 50 % ellipsoid probability, framework and peripheral carbon atoms drawn capped stick and wireframe respectively, and H and lattice solvent omitted for clarity. Selected distances (Å) and angles (°) for 2Ce$_{\text{Pr}}$: Ce1–O11 2.790(5), Ce1–O21 2.274(5), Ce1–O31 2.256(6), Ce1–O13 2.468(6), Ce1–O23 2.482(6), Ce1–O33 2.466(6), O11–Ce1–O21 97.18(19), O11–Ce1–O31 99.3(2), O21–Ce1–O31 94.8(2), O13–Ce1–O23 77.02(19), O13–Ce1–O33 76.68(19), O23–Ce1–O33 79.6(2), O11–Ce1–O13 75.7(2), O21–Ce1–O23 75.7(2), O31–Ce1–O33 75.9(2). For 2Ce$_{\text{Bu}}$: Ce1–O11 2.261(2), Ce1–O21 2.268(2), Ce1–O31 2.274(2), Ce1–O13 2.473(2), Ce1–O23 2.477(2), Ce1–O33 2.470(2), O11–Ce1–O21 95.38(8), O11–Ce1–O31 95.25(8), O21–Ce1–O31 97.20(8), O13–Ce1–O23 76.76(8), O13–Ce1–O33 80.89(8), O23–Ce1–O33 80.80(8), O11–Ce1–O13 75.50(8), O21–Ce1–O23 74.77(2), O31–Ce1–O33 75.03(8).

The substrate scope was further explored with carbon disulfide and other isoelectronic (hetero)allenes shown in Scheme 3. Interestingly, treatment of a benzene solution of 1Ce$_{\text{Pr}}$ with excess carbon disulfide at temperatures up to 80 °C shows no reaction. This differs from the alkoxide-tethered carbene complex D for which the product arising from the insertion of CS$_2$ into two (of the three) M–C bonds was characterized. The higher reactivity of CO$_2$ compared to CS$_2$ in this system is reasonable considering the stronger affinity of Ce for oxygen, and the lower dipole moment in the latter reagent.

Scheme 3. Treatment of 1Ce$_{\text{Pr}}$ with reagents isoelectronic to CO$_2$.
Single crystals of $3\text{Ce}^{\text{PrP}}(\text{BuNCS})_2$ were grown by slow diffusion of heptane into a toluene solution. An X-ray diffraction study reveals a pseudo-trigonal prismatic molecular geometry at the metal center in the solid state. The Ce–S bond lengths average at 3.022 Å, and the Ce–C bond (2.716 Å) is only a little shorter than the average Ce–C bond length in the parent compound $1\text{Ce}^{\text{PrP}}$ (2.742 Å). The obtuse S–Ce–S bond angle (143.91°) and chelate angle of each bidentate ligand is within the expected range; S–Ce–O$^\text{av}$ (78.75° avg.) and C–Ce–O$^\text{av}$ (69.93°).

Catalytic applications of $2\text{Ce}^{\text{PrP}}$ complexes

The formation of cyclic carbonates from epoxides and carbon dioxide was chosen for a preliminary study of the catalytic activity of the tris(ligand) CO$_2$ adducts $2\text{Ce}^{\text{PrP}}$ and $2\text{Ce}^{\text{mes}}$. Both free base NHCs and imidazolium carboxylates can be used as catalysts for the formation of cyclic carbonates from epoxides and carbon dioxide under high temperatures and pressures (up to 120 °C and 20 atm), while rare earth initiators are known to function at lower temperatures and/or pressures, a co-catalyst is usually required. Scheme 5 shows how under an atmosphere of carbon dioxide, 1 mol% of $2\text{Ce}^{\text{mes}}$ catalyses the conversion of propylene oxide to propylene carbonate with 22% conversion at 80 °C in THF over 7 days, a much higher activity than the imidazolium carboxylates alone. On the other hand, the more compact $2\text{Ce}^{\text{PrP}}$ shows no reactivity. The solid-state structures show a higher steric congestion in the $\text{L}^{\text{mes}}$ adduct $1\text{Ce}^{\text{mes}}$, and IR and NMR spectroscopies confirm different ligand solution environments for $2\text{Ce}^{\text{mes}}$, suggesting both the Ce–C$_\text{carbene}$ and Ce–C$\text{CO}_2$ interactions are weaker and more labile for the Mes system. We propose that the catalysis requires a combination of Lewis base type NHC-CO$_2$ activation, and Lewis acid type Ce–epoxide activation.

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Fig. 3 Molecular structure of $3\text{Ce}^{\text{PrP}}(\text{BuNCS})_2$ with selected C and non-C/H atoms shown at 50% ellipsoid probability, framework and peripheral carbon atoms drawn capped stick and wireframe respectively, and H and lattice solvent omitted for clarity. Selected average distances (Å) and angles (°) for $3\text{Ce}^{\text{PrP}}(\text{BuNCS})_2$: Ce1–S10 2.996(12), Ce1–S20 3.048(12), Ce1–C31 2.716(4), Ce1–O11 2.280(3), Ce1–O21 2.273(3) Ce1–O31 2.277(3), S10–Ce1–S20 143.91(3), S10–Ce1–C31 126.96(9), S20–Ce1–C31 80.70(7), S10–Ce1–O11 78.71(8), S20–Ce1–O21 78.79(7), C31–Ce1–O31 69.93(11).

Scheme 4 Differences in reactivity of $1\text{Ce}^{\text{PrP}}$ with sterically hindered isocyanates and isothiocyanates depending on solvent, and ligand substituents to afford $3\text{Ce}^{\text{PrP}}$(BuNCO)$_2$, $3\text{Ce}^{\text{PrP}}$(BuNCO)$_3$, and $3\text{Ce}^{\text{PrP}}$(BuNCS)$_2$.

Scheme 5 Catalytic formation of propylene carbonate from propylene oxide in an atmosphere of carbon dioxide using $2\text{Ce}^{\text{mes}}$ and $2\text{Ce}^{\text{PrP}}$. 
Synthesis of the heteroleptic substituted NHC analogues

To target reactions with single equivalents of CO₂, reactions designed to make complexes containing a single NHC ligand were carried out. The reactions of the ligands \([\text{o-H}_2\text{L}^\text{L']Br}]_\text{R} = \text{Me}, \text{iPr} and \text{Pr}\) and equimolar amounts of Li(THF)[CeN(Pr₂)₃] only afford clean material in low yields and significant decomposition can be observed. Adding an additional bromide source improves the yield of the mono-NHC-Ce complexes 4CeMe and 4Ce²⁺ (Ce₂Br₃[N(Pr₂)₃]Li₂(THF)₂) to a moderate level (20 % and 38 % respectively, see Scheme 6).

Crystallographic analysis reveals a dimeric structure still containing unreacted base and lithium ions (see SI). A complicated bis(ligand) Li₅Ce₄ cluster 5CeMe in which each ligand has been deprotonated at the NHC backbone (in the 4-position) yielding a dianionic OC ligand that bridges two cerium cations, is isolated in low yield as orange crystals that are suitable for single crystal diffraction studies (Figure 3 and SI). Syntheses to target 4 or 5 in the absence of an additional bromide source, or from cerium bromide starting materials, yield only complicated mixtures of compounds in our hands.

Synthesis of the para-aryloxide substituted NHC analogues

The analogous complexes of the para-substituted aryloxide ligand p-L³ separate the Lewis acid and Lewis base centers, and thus offer a potential insight into the importance of the adjacent Ln centre and the nucleophilic NHC in the combined activation of CO₂ and the other unsaturated substrates. A modification of Wang’s proligand synthesis using saturated-backbone imidazole analogues allows access to the para-functionalized proligand in 15% yield.²⁷ Treatment of this N-mesityl functionalized proligand \([p\text{-H}_2\text{L}^\text{Mes}]^X\), \((p\text{-L}^\text{Mes} = \{\text{O}(\text{p-C}_6\text{H}_4\text{-Bu}_2\text{-2,6-CN(C}_6\text{H}_4)\text{N-C}_6\text{H}_2\text{-2,4,6-Mes})\})_3, X = \text{PF}_6, \text{Br}\) with either \(\text{MN(SiMe}_3)_2\) \((M = \text{Na} \text{or K})\) in THF at room temperature affords the group 1 NHC salts 6M⁺⁺⁺\((\text{M} = \text{Na, K})\) in quantitative yield, Scheme 7. The solid-state structures of both are polymeric, according to single crystal X-ray data, with 6Na⁺⁺⁺ displaying repeating \(\text{C}-(\mu-\text{ArO})-\text{Na}-\text{C}\) diamond units, while 6K⁺⁺⁺ displays a perpendicularly ArO-K-C arrangement, see SI.

Salt 6M⁺⁺⁺ can be treated with YCl₃ or CeCl₃ at –20°C to synthesise 7Ln⁺⁺⁺\((\text{Ln} = \text{Y, Ce})\) in 56% and 30% yield as yellow powders. Due to their high reactivity all the compounds start to degrade rapidly making further analysis difficult, and the complexes are best stored in their protonated form, i.e. \((\text{Ln}p\text{-HL}^\text{Mes})_3(\text{THF})_2\)X₃.
Analysis of 7\textsuperscript{Mes} by \textsuperscript{13}C NMR spectroscopy reveals a characteristic carbene signal (\textdelta 238.2 ppm) as observed as a singlet indicating that the carbene does not bind to yttrium in solution. These complexes were found to be extremely air sensitive, were only ever isolated as KCl and HCl salts and became highly insoluble in a range of solvents so were not pursued further (see SI).

Conclusions

The tris(ortho-aryloxide-NHC) rare earth complexes Ln(L\textsuperscript{5}) are readily isolated and are the thermodynamic sink in this system. Insertion of CO\textsubscript{2} or a range of isoelectronic (hetero)alkynes into the labile cerium carbene bond in Ce(L\textsuperscript{5}) shows a dependence on solvent and N-R group on L\textsuperscript{R} that enables control of the degree of insertion. The CO\textsubscript{2}-insertion products form cleanly at ambient pressure, but only reversibly for the bulky mesityl arylloxide. The reversibility of the CO\textsubscript{2} insertion appears to be crucial for further reactivity as only Ce(L\textsuperscript{Mes}:CO\textsubscript{2})\textsubscript{3} is an active catalyst for the conversion of propylene oxide to propylene carbonate. Although yields in these preliminary tests using low temperatures and one atmosphere of CO\textsubscript{2} are low, the catalyst is more active than a monodentate NHC and when the ligands are better fit to the metal in Ce(L\textsuperscript{Mes}:CO\textsubscript{2})\textsubscript{3} the complexes are inactive. We propose that the catalysis requires a combination of Lewis base type NHC-CO\textsubscript{2} activation, and Lewis acid type Ce-epoxide activation.

Although the tris-ligand complexes are the thermodynamic sink in the system, the mono-ligand complexes can be isolated from reactions using LiCe(NP\textsubscript{4}r)\textsubscript{3} as a starting material; LiBr adducts [Ce(L\textsuperscript{5})(NP\textsubscript{4}r)\textsubscript{2}Br][LiBr(THF)]\textsubscript{2} (R = Me, iPr) are reported, along with a hexanuclear N-heterocyclic dicarbene complex [Li\textsubscript{2}Ce\textsubscript{i}OArCM\textsubscript{3}H\textsubscript{i}][NP\textsubscript{4}r]\textsubscript{2}(THF)\textsubscript{2} which is formed as a by-product. The analogous para-aryloxide-NHC proligand (p-L\textsuperscript{Mes} = O(p-C\textsubscript{6}H\textsubscript{4}-Bu\textsubscript{2},2,6-CN(C\textsubscript{6}H\textsubscript{3}Mes)) has been made for comparison. The group 1 salts [Na(p-L\textsuperscript{Mes})]\textsubscript{n} and [K(p-L\textsuperscript{Mes})]\textsubscript{n} form two different types of infinite coordination polymers through metal carbene-bonds. Synthesis of the analogous lanthanide para-aryloxide NHC complexes Ln(p-L\textsuperscript{Mes})(THF)\textsubscript{2} (Ln = Y, Ce) is possible but they are all highly reactive leading to rapid degradation. Therefore straightforward Lewis pair separated chemistry cannot usefully be carried out.

Further work is underway to use the C\textsubscript{2}-symmetric tris(ortho-aryloxide-NHC)–CO\textsubscript{2} adducts in asymmetric catalysis and to expand the scope of the CO\textsubscript{2} functionalisation.

Conflicts of interest

There are no conflicts to declare.

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Experimental

General Details

All manipulations were carried out under a dry, oxygen-free atmosphere of nitrogen using standard Schlenk and glovebox technique. All gases were supplied by BOC gases UK. All glassware items, cannulae and Fisherbrand 1.2 µm retention glass microfibre filters were dried in a 170 °C oven overnight and stored over 4 Å molecular sieves. Heptane, THF, and toluene were degassed and purified by passage through activated 4 Å molecular sieves or activated alumina towers and stored over 4 Å molecular sieves. Deuterated solvents, benzene-d\textsubscript{δ}, THF-d\textsubscript{δ} and pyridine-d\textsubscript{δ} were dried over potassium, vacuum-transferred, and freeze–pump–thaw degassed prior to use. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on Bruker AVA400, AVA500, or PRO500 spectrometers at 300 K. Chemical shifts are reported in parts per million, \textdelta, referenced to residual proton resonances, and calibrated against external TMS. Infrared spectra were recorded on a Perkin Elmer Spectrum 65 FT-IR spectrometer as nujolulls between KBr disks. Mass spectra were acquired using a Solarix FT-ICR (12 T) (Bruker UK Ltd) equipped with a Bruker APPI source. Samples were prepared as
ca. 1 mM toluene solutions of the substrate. Elemental analyses were carried out at London Metropolitan University, London, UK.

Na[N(SiMe$_3$)$_2$], KN(SiMe$_3$)$_2$, and the [o-H$_2$L$^*$]Br$_2$ pro-ligands were prepared according to the literature procedures. YCl$_3$(H$_2$O)$_2$ and LnCl$_3$(H$_2$O)$_2$ were purchased and stirred overnight with TMSCl (40 equiv) in THF before vacuum drying for several hours.

General procedure 1 – Synthesis of 11n$^*$

To a suspension of [o-H$_2$L$^*$]Br (3 equiv) in DME (0.1 m) KN(SiMe$_3$)$_2$ (6 equiv) was added and the resulting mixture was stirred for 5 min at room temperature. LnCl$_3$(thf)$_2$ (1 eq.) was added, and the resulting mixture was stirred at room temperature for 2 h. Volatiles were removed under reduced pressure. The crude product was extracted three times with hexane and the combined filtrates were concentrated to saturation and cooled to –20 °C overnight. The resulting suspension was filtered and the solid collected and dried under vacuum to give the title compound which was stored at –20 °C under a nitrogen atmosphere.

1Ce$_{Pr}$ – Using general procedure 1 – 3-(3,5-di-tert-butyl-2-hydroxyphenyl)-1-isopropyl-1H-imidazol-3-ium bromide [o-H$_2$L$^*$]Br$_2$(11.82 g, 30 mmol), KN(SiMe$_3$)$_2$ (11.97 g, 60 mmol), CeCl$_3$(thf)$_2$ (3.29 g, 10 mmol) and DME (100 ml) gave after recrystallization the title compound 1Ce$_{Pr}$ as a yellow solid (8.17 g, 76 mmol). X-ray quality crystals were grown from a concentrated hexane solution at –20 °C over 1 week; 1H NMR (500 MHz, Cd$_2$O) $\delta$: –9.76 (3H, s, CH(CH$_3$)$_2$), –6.89 (3H, s, CH(CH$_3$)$_2$), –4.37 (3H, s, CH(CH$_3$)$_2$), –3.38 (9H, s, C(CH$_3$)$_2$), –1.62 (3H, s, CH$_2$), 0.47 (3H, s, CH(CH$_3$)$_2$), 0.77 (3H, s, H), 1.51 (9H, s, C(CH$_3$)$_2$), 1.57 (9H, s, C(CH$_3$)$_2$), 1.75 (1H, s, CH), 2.10 (9H, s, C(CH$_3$)$_2$), 2.31 (9H, s, C(CH$_3$)$_2$), 3.37–3.32 (9H, m, C(CH$_3$)$_2$), 3.43 (3H, s, CH), 5.97 (1H, s, CH), 6.70 (1H, s, CH), 7.08 (1H, app d, J 2.7, CH), 7.08 (1H, app d, J 2.7, CH), 7.62 (1H, s, CH), 7.70 (1H, app d, J 2.7, CH), 8.91 (1H, s, CH), 9.75 (1H, s, CH), 10.18 (2H, m, CH), 10.39 (1H, s, CH), 11.01 (1H, s, CH), 11.22 (1H, s, CH); 13C($^1$H)$_2$ NMR (126 MHz, Cd$_2$O) $\delta$: 14.4, 21.7, 22.3, 23.1, 24.6, 24.7, 30.1, 30.1, 31.9, 32.0, 32.5, 33.4, 33.9, 34.2, 35.4, 36.2, 36.5, 39.4, 40.1, 41.8, 46.4, 51.4, 114.4, 115.6, 118.9, 119.3, 119.5, 121.3, 122.2, 122.6, 122.7, 123.8, 124.2, 129.7, 131.4, 138.8, 140.3, 140.5, 141.9, 146.2, 147.4, 147.7, 148.6, 154.0, 155.8, 162.9, 174.8, 187.8, 192.2. Elemental analysis

$^{13}$C$_{60}$H$_{2}$Ce$_{11}$O$_{10}$C$_{6}$: C 66.70%, H 8.13%, N 7.78% calculated. C 66.7%, H 8.13%, N 7.78% found; APPi (NSi$^*$) Ce$_{60}$H$_{2}$Ce$_{11}$O$_{10}$C$_{6}$ [M]$^+$ requires 1307.6834, found 1307.6812 (–0.2 ppm).

15Ce$_{Bu}$ – Using general procedure 1 – 1-[(tert-buty13-3.5,3.5-di-tert-butyl-2-hydroxyphenyl)-1-isopropyl-1H-imidazol-3-ium bromide [o-H$_2$L$^*$]Br$_2$(296 mg, 0.75 mmol), KN(SiMe$_3$)$_2$ (300 mg, 1.5 mmol), SmCl$_3$(thf)$_2$ (100 mg, 0.1575 mmol) and DME (2.5 ml) gave after recrystallization title compound 15Ce$_{Bu}$ as a yellow solid (171 mg, 76 mmol); 1H NMR (400 MHz, Cd$_2$O) $\delta$: –9.79 (1H, m, CH$_2$), –4.24 (3H, app d, J 5.8, CH$_2$), –2.42 (3H, app d, J 5.5, CH$_2$), –1.13 (9H, s, C(CH$_3$)$_2$), –0.85–(–0.73 (6H, m, 2xCH$_2$), –0.63–(–0.59 (1H, m, CH$_2$), 1.08 (9H, s, C(CH$_3$)$_2$), 1.65–(1.70 (3H, m, CH$_2$), 1.81 (10H, s, C(CH$_3$)$_2$), 1.85 (10H, s, C(CH$_3$)$_2$), 2.02 (10H, s, C(CH$_3$)$_2$), 3.29 (10H, s, C(CH$_3$)$_2$), 3.24 (3H, app d, J 5.5, CH$_2$), 4.99 (1H, app p, J 6.8, CH$_2$), 5.54 (1H, app d, J 1.8, ArH), 6.05 (1H, app d, J 1.7, ArH), 7.26 (1H, app d, J 1.7, ArH), 7.90 (1H, app d, J 2.5, ImH), 8.06 (1H, app d, J 1.7, ArH), 8.14 (1H, app d, J 2.4, ImH), 8.15 (1H, app d, J 2.4, ImH), 8.32 (1H, app d, J 2.6, ImH), 8.43 (1H, app d, J 1.8, ArH), 8.46 (1H, app d, J 2.6, ImH), 8.53 (1H, app d, J 1.7, ArH), 8.94 (1H, app d, J 2.5, ImH). Elemental analysis

C$_{60}$H$_{2}$Sm$_{11}$O$_{10}$C$_{6}$: C 66.07%, H 8.04%, N 7.70% calculated. C 66.10%, H 8.33%, N 7.54% found; APPi (NSi$^*$) C$_{60}$H$_{2}$Sm$_{11}$O$_{10}$C$_{6}$ [M]$^+$ requires 1091.6037, found 1091.6076 (+3.6 ppm).
1EuPr — Using general procedure 1 — 3-(3,5-di-tert-butyl-2-hydroxyphenyl)-1-isopropyl-1H-imidazol-3-ium bromide \([\text{EuHLL'[Br]}\) (296 mg, 0.75 mmol), KN(SiMe_3) (300 mg, 1.5 mmol), EuCl_2(THF)_2 (110 mg, 0.1575 mmol) and DME (2.5 mL) gave after recrystallization the title compound 1EuPr as an orange-red solid (121 mg, 0.11 mmol, 45%). ¹H NMR (400 MHz, CD_2D_2): δ: −21.12 (1H, s), −14.06 (9H, s, C(CH_3)_2), −11.59 (3H, s, CH(CH_3)_2), −6.76 (9H, s, C(CH_3)_2), −5.94 (1H, s, CH), −5.90 (1H, s, CH), −5.38 (1H, s, CH), −2.60 (1H, s, CH), −1.63 (9H, s, C(CH_3)_2), −1.48 (9H, s, C(CH_3)_2), −1.44 (9H, s, C(CH_3)_2), −0.72 (1H, s, CH), −0.64 (1H, s, CH), −1.77 (3H, s, CH(CH_3)_2), 3.26 (1H, s, CH), 4.76 (3H, s, CH(CH_3)), 6.07 (1H, s, CH), 6.20 (1H, s, CH), 7.20 (1H, s, CH), 7.39 (1H, s, CH), 11.89 (9H, s, C(CH_3)_2), 15.05 (3H, s, CH(CH_3)_2), 15.85 (1H, s, CH), 17.88 (1H, s, CH), 24.72 (3H, s, CH(CH_3)), 33.23 (3H, s, CH(CH_3)), 49.20 (1H, s, CH), 96.66 (1H, s, CH); Elemental analysis: C_{60}H_{62}EuO_2N_6: C 65.97%, H 8.03%, N 7.69% calculated. C 66.00%, H 8.01%, N 7.67% found; APPi (NSi⁺) C_{60}H_{62}EuO_2N_6Si⁺ [M⁺] requires 1092.6052, found 1092.6095 (+3.9 ppm).

General procedure 2 — Synthesis of 2CeB

A solution of 1CeB (3 equiv) in benzene or THF (0.5 mL) was freeze-pump-thaw degassed 3 times and exposed to an atmosphere of dry CO₂ and then evaporated slowly in a teflon-valved ampoule. The solvent was removed under reduced pressure, and the crude product was extracted with toluene and concentrated to saturation and filtered and dried under vacuum to yield the title compound which was stored at −20 °C under a nitrogen atmosphere.

2CePr — Using general procedure 2 — 1CePr (3.0 g, 2.78 mmol) in toluene (50 mL) was charged with an atmosphere of CO₂ and after recrystallization gave the title product 2CePr as a colourless solid (2.05 g, 1.69 mmol, 61%). Colourless crystals suitable for X-ray diffraction were grown from slow diffusion of hexanes into a concentrated THF solution. ¹H NMR (400 MHz, CD_2D_2): δ: 0.91 (27H, s, C(CH_3)_2), 1.27–1.31 (9H, m, CH(CH_3)_2), 1.72–1.76 (9H, m, CH(CH_3)_2), 2.52 (27H, s, C(CH_3)_2), 4.46–4.50 (3H, m, ArH), 4.62–4.66 (3H, m, ArH), 5.97 (3H, d, J 2.6, ImH), 7.59 (3H, d, J 2.6, ImH), 8.42 (3H, m, CH(CH_3)_2). ¹C(H) NMR (126 MHz, CD_2D_2): δ: 21.4 (CH(CH_3)_2), 24.6 (CH(CH_3)_2), 30.1 (CH(CH_3)_2), 31.5 (CH(CH_3)_2), 33.6 (C(CH_3)_2), 36.7 (C(CH_3)_2), 53.1 (CH(CH_3)_2), 112.4 (NCN), 119.1 (ArC), 119.5 (ArC), 123.6 (ImC), 125.2 (ImC), 134.6 (ArC), 139.4 (ArC), 143.2 (ArC), 154.9 (ArC), 173.1 (OCO). v_max (nujol mull): 1666. Elemental analysis: C_{60}H_{62}EuO_2N_6: C 67.52%, H 6.93%, N 5.83% calculated. C 67.21% H 7.52% N 5.66% found.

3CePr(MesNCO) — To a solution of 1CePr (108 mg, 0.1 mmol) in C_6H_6 (2 mL), MesNCO (48 mg, 0.03 mmol) was added and stirred for 15 min. The reaction mixture was filtered and cooled to −30 °C and the title product was isolated as a colourless powder by filtration of the solvents and drying under vacuum (123 mg, 79%). ¹H NMR (500 MHz, CD_2D_2): δ: −6.53 (9H, s, C(CH_3)_2), −5.17 (3H, s, CH), −4.52 (3H, s, CH), −3.89 (3H, s, CH), −0.21 (3H, s, CH), 1.05 (3H, s, CH), 3.10 (3H, s, CH), 1.37 (9H, s, C(CH_3)_2), 1.53 (6H, s, Mes(2,6)CH_3), 1.72 (2H, s, Mes(3,5)H), 1.99 (9H, s, C(CH_3)_2), 2.00 (6H, s, Mes(2,6)CH_3), 2.02 (6H, s, Mes(2,6)CH_3), 2.22 (3H, s, CH), 2.56 (9H, s, C(CH_3)_2), 2.58 (3H, s, CH), 2.64 (9H, s, C(CH_3)_2), 2.99 (1H, s, CH), 3.26 (1H, s, CH), 3.44 (1H, s, CH), 3.64 (2H, s, Mes(3,5)H), 4.43 (1H, s, CH), 4.87 (1H, s, CH), 5.86 (1H, s, CH), 6.52 (2H, s, Mes(3,5)H), 6.62 (1H, s, CH), 6.79 (3H, s, CH), 7.27 (1H, s, CH), 7.35 (1H, s, CH), 7.71 (1H, s, CH), 9.07 (1H, s, CH), 10.04 (1H, s, CH), 10.58 (9H, s, C(CH_3)_2), 10.64 (1H, s, CH), 10.85 (1H, s, CH), 12.62 (1H, s, CH); Elemental analysis: C_{60}H_{62}O_2N_6: C 69.11%, H 7.73%, N 8.06% calculated. C 69.09%, H 8.11%, N 7.93% found; APPi (NSi⁺) C_{60}H_{62}EuO_2N_6Si⁺ [M⁺H⁺] requires 1563.8494, found 1563.8419 (~4.8 ppm).

3CeBu(BuNCO) — To a solution of 1CeBu (108 mg, 0.1 mmol) in DME (2 mL), BuNCO (20 mg, 0.3 mmol) was added and stirred
for 15 min. The reaction mixture was filtered into hexane (1 mL) and cooled to −30 °C and the title product was isolated as a colourless powder by filtration of the solvents and drying under vacuum (126 mg, 91%).

**1H NMR** (500 MHz, CD$_2$Cl$_2$) δ: −8.72 (3H, s), −8.44 (1H, s), −6.21 (3H, s), −4.08 (9H, s), −3.74 (1H, s), −3.61 (3H, s), −2.35 (9H, s), −1.49 (1H, s), −0.10 (1H, s), 0.32 (1H, s), 1.50 (9H, s), 1.67 (9H, s), 1.98 (9H, s), 2.82 (1H, s), 3.25 (9H, s), 3.32 (3H, s), 3.51 (1H, s), 4.69 (1H, s), 6.08 (1H, s), 6.88 (1H, s), 8.34 (1H, s), 9.25 −9.35 (9H, m), 9.82 (1H, s), 9.87 (1H, s), 14.04 (1H, s), 14.45 (3H, s), 17.40 (1H, s), 18.47 (9H, s).

**APPI (NSI+)** C$_{52}$H$_{92}$Ce$_{3}$O$_{5}$S$_{8}$ $^{[M+H]}$ requires 1194.6350, found 1194.6571 (+18.5 ppm).

**Elemental analysis** C$_{62}$H$_{62}$Ce$_{3}$O$_{5}$S$_{8}$ C 65.29%, H 8.09%, N 8.20% calculated. C 65.42%, H 8.21%, N 7.59% found.

**Notes and references**

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data. CCDC codes 1856101-1856106.

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