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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(LR)3 supported by bidentate ortho-aryloxyde–NHC ligands are reported (LR = 2-O-3,5-iBu2-C6H2(1-C(N(CH)2N(R))))). The cerium complexes cleanly and quantitatively insert carbon dioxide exclusively into all three cerium carbene bonds, forming Ce(LCO2)3. The insertion is reversible only for the mesityl-substituted complex Ce(LMes)3. Analysis of the capacity of Ce(L)3 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 cerium complexes capable of reversible CO2-insertion are competent catalysts for catalytic conversions of CO2. Preliminary studies show that only Ce(LMes)2CO2 catalyses the formation of propylene carbonate from propylene oxide under 1 atm of CO2 pressure. The mono-ligand complexes can be isolated from reactions using LiCe(NiPr2)4 as a starting material; LiBr adducts [Ce(LR)(NiPr2)Br]2 (R = Me, iPr) are reported, along with a hexanuclear N-heterocyclic dicarbene [L2Ce3(OMe)3–H3(LPR)3(THF)2]2 by-product. The analogous para-aryloxyde–NHC proligand (p-LMes = 4-O-2,6-iBu2-C6H2(1-C(NICH2)NMes))) has been made for comparison, but the rare earth tris-ligand complexes Ln[p-LMes3(THF)2]2 (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, and can provide carboxylic acids, esters and (cyclic) carbonates. Isoelectronic isocyanates and isothiocyanates are also valuable electrophilic elementary esters and (cyclic) carbonates.

Since the first reported isolation of lanthanide–NHC complexes in 1994, it has been shown that Lewis acidic rare-earth cations form hemilabile bonds with soft σ-donating NHCs. Between 2006 and 2010, Shen and co-workers published syntheses of aryloxyde–NHC lanthanide complexes, however no subsequent reactivity was reported. In 2014, we reported the activation of carbon dioxide and carbon disulfide using a scandium alkoxide-NHC complex, achieving frustrated Lewis pair (FLP) like reactivity which resulted in metal–ligand scrambling to form a polymeric –(Se–NHC–CO2)–n containing network owing to the flexible alkoxide tether. Cerium, the most abundant lanthanide has a relatively low toxicity; its trichloride is six times less toxic by ingestion than that of iron, and has many applications in heterogeneous catalysis. Previously we showed that cerium-silylamido NHC complexes [[Ce(L)(N(SiMe3)2)]2] react with CO2 to form an insoluble mixture while the uranium analogue [U(L)(N(SiMe3)2)]2 yields an equivalent of isocyanate. 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. Recently, Suresh reported the first mononuclear N-carboxylate imidazolium lanthanide compounds, suggesting their potential...
Here, we demonstrate that cerium (and other rare earth) complexes with aryloxide-tethered NHC ligands can successfully form homoleptic cerium imidazolium carboxylate complexes from CO$_2$ 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 CO$_2$ 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 CO$_2$-insertion are competent catalysts for the synthesis of cyclic carbonates from CO$_2$ 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, $[\text{o-}H_2LR\text{][Br]}$ where $L^R_1 = 2\text{-O-3,5}^\text{tBu}_2\text{C}_6\text{H}_2(1\text{-C}[\text{N(CH)2N(R)}])$ and $R = ^1\text{Pr}, ^3\text{Bu}$ and Mes were treated with 6 equivalents of KN(SiMe$_3$)$_2$ and LnCl$_3$(THF)$_n$ (Ln = Ce, Sm, Eu) in DME to afford bright yellow solutions with colourless precipitates of KCl and KBr (Scheme 1). After work-up, 1Ln$^R$ (Ln(L$^R$)$_3$) can be afforded in moderate to good yields (15–76%), while over 8 g of 1Ce$^{iPr}$ can be isolated in a single reaction.

The $^1$H NMR spectra of all four lanthanide complexes bearing alkyl R groups ($^1$Pr or $^3$Bu) contain a complex set of paramagnetic resonances indicating $C_1$ symmetry and a unique environment for each ligand. In agreement with the $^1$H spectrum of 1Ce$^{iPr}$ the $^{13}$C($^1$H) NMR spectrum is also complicated, containing three carbene chemical shifts ($\delta = 174.8$ 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 \( \approx 200–238 \) ppm for Y\(^{III}\) and Ce\(^{IV}\))\(^{13,17,19,29,30} \) However in contrast, spectra of \( 1\text{Ce}^{\text{Mes}} \) contain a single set of paramagnetically shifted resonances indicating \( C_3 \) symmetry in solution on the \(^1\text{H} \) NMR spectroscopic timescale and \(^{13}\text{C} \) NMR spectroscopy of \( 1\text{Ce}^{\text{Mes}} \) displays a single carbene resonance at 184.2 ppm.

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 \( C_3 \) symmetric complex would also be favoured if \( \pi \)-stacking between the mesityl substituent and an adjacent imidazolin-2-ylidine ring is possible. This high degree of steric crowding is used to rationalise the failed synthesis of related but bulkier diisopropophenyl containing aryloxide-carbene ligands. Reactions aimed at targeting the mono- and bis-alkoxy–NHC analogues using this synthetic method yielded only the tris-isomers are retained in the solid state for \( 2\text{CeR} \). Exposure of a solution of \( 2\text{CeR} \) to an atmosphere of carbon dioxide results in the instant and quantitative formation of \( \text{CeOAr} \) bond angles (154.05(15)\(^\circ \) and 2.814(3) \( \AA \)) with the former within the regular range of a lanthanide–carbene bond. To the best of our knowledge the latter is the longest aryloxide tethered metal–carbene bond and amongst the longest lanthanide–carbene bonds known, consistent with the proposed high degree of hemilability. For \( 1\text{Ce}^{\text{Mes}} \) there is a conceivable offset aromatic donor–acceptor interaction between the electron deficient imidazolin-2-ylidine and the electron rich mesityl with an average centroid distance of 4.36 \( \AA \), within the upper limits of face-centred \( \pi \)-stackings\(^{21,12} \).

**Reactivity of \( 1\text{Ce}^R \) complexes**

Exposure of a solution of \( 1\text{Ce}^R \) to an atmosphere of carbon dioxide results in the instant and quantitative formation of \( 2\text{Ce}^R \) (\( \text{Ln[LR}_{\text{3}} \text{CO}_3]_3 \)) as observed by the precipitation of a beige solid (hexanes reaction solvent) or monitoring by \(^1\text{H} \) NMR spectroscopy (benzene reaction solvent), Scheme 2. As anticipated for a complex with a hemilabile metal–NHC bond, the \( \text{CO}_2 \) exclusively inserts into the three Ce–C bonds, and pleasingly, and in contrast to the complexes with more flexible, bidentate alkoxy–NHCs, the rest of the molecule remains relatively unperturbed, with no evidence of ligand redistribution between metal centres. Samples of \( 2\text{Ce}^{\text{IPr}} \) and \( 2\text{Ce}^{\text{Bu}} \) held at elevated temperatures under dynamic vacuum (100 °C, 10\(^{-3} \) mbar) show no loss of \( \text{CO}_2 \). However, a sample of \( 2\text{Ce}^{\text{Mes}} \) shows some loss of \( \text{CO}_2 \) 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 a complicated mixture that could be oligomeric, but the material is quantitatively converted back to \( 2\text{Ce}^{\text{Mes}} \) upon re-exposure to an atmosphere of \( \text{CO}_2 \).

**Fig. 1** Molecular structures of \( 1\text{Ce}^{\text{IPr}} \) (upper) and \( 1\text{Ce}^{\text{Mes}} \) (lower) with Ce, O and C\(_{\text{Carbene}} \) shown at 50% ellipsoid probability, framework and peripheral carbon atoms drawn capped stick and wireframe respectively (see Fig. 1). The coordination geometry of cerium in each is a pseudo-octahedral geometry defined by average \( C–C–C \) bond angles (172.93(18)\(^\circ \) and 102.33(9)\(^\circ \) and \( \text{OAr–CeOar} \) bond angles (154.05(15)\(^\circ \)/102.44(16)\(^\circ \) and 94.82(9)\(^\circ \)). The average Ce–C bond distances of \( 1\text{Ce}^{\text{IPr}} \) and \( 1\text{Ce}^{\text{Mes}} \) are 2.742(6) \( \AA \) and 2.814(3) \( \AA \) with the former within the regular range of a lanthanide–carbene bond. To the best of our knowledge the latter is the longest aryloxide tethered metal–carbene bond and amongst the longest lanthanide–carbene bonds known, consistent with the proposed high degree of hemilability. For \( 1\text{Ce}^{\text{Mes}} \) there is a conceivable offset aromatic donor–acceptor interaction between the electron deficient imidazolin-2-ylidine and the electron rich mesityl with an average centroid distance of 4.36 \( \AA \), within the upper limits of face-centred \( \pi \)-stackings\(^{21,12} \).
results in a lowering of symmetry from \( C_3 \) to \( C_1 \) according to room temperature solution spectroscopies. The \(^1\)H 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 carboxylate units is non-coordinating in solution.

Single crystal X-ray analysis confirms that CO\(_2\) insertion products \( 2\text{Ce}^{\text{IPr}} \) and \( 2\text{Ce}^{\text{iBu}} \) have a pseudo-trigonal prismatic geometry with \( C_3 \)-symmetric fac-arrangement described by the average O\(^{\text{Ar}}\)-Ce–O\(^{\text{Ar}}\) bond angles (97.03(10)° and 95.94(8)° respectively) and O\(^{\text{CO}}\)-Ce–O\(^{\text{CO}}\) bond angles (77.77(10)° and 80.48(8)°) (Fig. 2). The average Ce–O\(^{\text{CO}}\) 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.

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 \( 1\text{Ce}^{\text{Pr}} \) 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.\(^{20}\) 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.

Treatment of a benzene or THF solution of \( 1\text{Ce}^{\text{Pr}} \) with three equivalents of mesityl isocyanate (MesNCO) immediately results in the insertion of isocyanate into all three Ce–NHC bonds, giving a pale-yellow solution from which the trisazoliumamidate \( 3\text{Ce}^{\text{Pr}}(\text{MesNCO})_3 \) can be readily isolated as colourless microcrystalline powder in 76% yield, Scheme 3. No dimer or trimer isocyanate products were observed as...
a comparison to “free” NHC isocyanate chemistry. As could be expected, the non-polar and more sterically hindered cyclohexylallene shows no reactivity with 1CePr.

In the reaction of 1CePr with three equivalents of tert-butylisonate (tBuNCO) in benzene or THF, two molecules of isocyanate insert to form 3CePr(tBuNCO)₂, however in DME solution, three molecules insert to form 3CePr(tBuNCO)₃ as a 3 : 1 mixture of the fac- and mer-isomers observable by ¹H NMR spectroscopy, Scheme 4. We suggest that in the former two solvents, the steric bulk of the tert-butyli groups restricts access to the third equivalent, but the stronger, bidentate donor solvent DME increases the lability of the NHC groups, enabling three insertions to occur. If 1CePr is treated with 3 equivs of tert-butyl isothiocyanate (tBuNCS) at 80 °C in benzene or THF, a single equivalent of isothiocyanate inserts to form 3CePr(tBuNCS) while in DME two equivalents of isothiocyanate insert to form 3CePr(tBuNCS)₂.

Single crystals of 3CePr(tBuNCS) were grown by slow diffusion of heptane into a toluene solution. An X-ray diffraction study, Fig. 3, reveals a pseudo-trigonal prismatic molecular structure of 3CePr(tBuNCS)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 3CePr(tBuNCS): 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 3 Treatment of 1CePr with reagents isoelectronic to CO₂.

Scheme 4 Differences in reactivity of 1CePr with sterically hindered isocyanates and isothiocyanates depending on solvent, and ligand substituents to afford 3CePr(tBuNCO)₂, 3CePr(tBuNCO)₃, 3CePr(tBuNCS), and 3CePr(tBuNCS)₂.
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 1CeIPr (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–OAr (78.75° avg.) and C–Ce–OAr (69.93°).

Catalytic applications of 2CeR 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) CO₂ adducts 2CeIPr and 2CeMes. 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.¹¹,¹⁵ Scheme 5 shows how under an atmosphere of carbon dioxide, 1 mol% of 2CeMes 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 2CeIPr shows no reactivity. The solid-state structures show a higher steric congestion in the LMes adduct 1CeMes, and IR and NMR spectroscopies confirm different ligand solution environments for 2CeMes, suggesting both the Ce–carbene and Ce–CO₂ interactions are weaker and more labile for the Mes system. We propose that the catalysis requires a combination of Lewis base type NHC–CO₂ activation, and Lewis acid type Ce-epoxide activation.

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 [o-H₂LR][Br], R = Me, iPr and equimolar amounts of Li(THF)[CeN(iPr₂)₄] 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 4CeIPr (Ce₂Br₄LR(iPr₂N)₂Li₂(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 ESI†). A

Scheme 6 Reactions to target mono–NHC Ln complexes that afford 4CeMes, 4CeIPr and the hexanuclear 5CeMes that is the by-product isolated as single X-ray quality crystals for R = Me.
complicated bis(ligand) Li₄Ce₆ 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 X-ray diffraction studies (Fig. 4 and ESI†). 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-L⁺ 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 imidazoline analogues allows access to the para-functionalized proligand in 15% yield.27 Treatment of this N-mesityl functionalized proligand [p-H₁₂LMes][X], (p-LMes = 4-O-2,6-·Bu₂-C₆H₄-[1-·C{N(CH)₂-NMes}]) with either MN(SiMe₃)₂(M = Na or K) in THF at room temperature affords the group 1 NHC salts 6M₁Mes [(M[p-LMes])₉]₉ (M = Na, K) in quantitative yield, Scheme 7. The solid-state structures of both are polymeric, according to single crystal X-ray data, with 6Na₉Mes displaying repeating C-·Na-·(μ·ArO)-·Na]·C diamond units, while 6K₉Mes displays a perpendicular ArO-·K-Carrangement, see ESI.† Salt 6M₁Mes can be treated with YCl₃ or CeCl₃ at −20 °C to synthesise 7Ln₁Mes (Ln[p-LMes])(THF)₂ where Ln = 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. [Ln[p-H₁₂LMes]][(THF)₉]X₉.

Analysis of 7Y₁Mes by ¹³C NMR spectroscopy reveals a characteristic carbene signal (δ 238.2 ppm) is 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 ESI†).

Scheme 7 Reaction to target the para-ligand adducts 7Ln₁Mes (Ln = Y, Ce).
**Conclusions**

The tris[ortho-aryl oxide–NHC] rare earth complexes Ln(LR)3 are readily isolated and are the thermodynamic sink in this system. Insertion of CO2 or a range of isoelectronic (hetero)allenes into the labile cerium carbene bond in Ce(LMes)3 shows a dependence on solvent and N-R group on LR that enables control of the degree of insertion. The CO2-insertion products form cleanly at ambient pressure, but only reversibly for the bulky mesityl substituted Ce(LMes)3. The reversibility of the CO2 insertion appears to be crucial for further reactivity as only Ce(LMes)3 and 13C NMR spectra were recorded on Bruker AVA400, AVA500, transferred, and freeze-dried.  

Benzene and DME were distilled from potassium and a reflux condenser. LnCl3(THF)3 (1 eq.) and [Li2Ce3(OArCMe3)13] were used as the catalyst precursor.  

**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 microfilter filters were dried in a 170 °C oven overnight before use. Benzene and DME were distilled from potassium and stored over 4 Å molecular sieves. Hexane, heptane, THF, and toluene were degassed and purified by passage through activated 4 Å molecular sieves or activated alumina towers and dried over potassium. Deuterated solvents, benzene-d8, THF-d8 and pyridine-d5 were dried over potassium, vacuum-transferred, and freeze–pump–thaw degassed prior to use.  

**1H NMR**

Natural abundance 1H NMR spectra were recorded on Bruker AVA400, AVA500, or PRO500 spectrometers at 300 K. Chemical shifts are reported in parts per million, δ, referenced to residual proton resonances, and calibrated against external TMS. Infrared spectra were recorded on a Perkin Elmer Spectrum 65 FT-IR spectrometer as nujol mulls 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(NiPr2)[Cl]3, KNiPr2[Cl]3, and the [o-H3L[Br]3] 2028 proligands were prepared according to the literature procedures. YCl3(H2O)3 and LnCl3(H2O)3 were purchased and stirred overnight with TMSCl (40 equiv.) in THF before vacuum drying for several hours.

**General procedure 1 – synthesis of LnLR**

To a suspension of [o-H3L[Br]3] (3 equiv.) in DME (0.1 M) KNiPr2[Cl]3 (6 equiv.) was added and the resulting mixture was stirred for 5 min at –20 °C while and warmed to room temperature. LnCl3(THF)3 (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**

Using general procedure 1 – 3-(3,5-di-tert-butyl-2-hydroxyphenyl)-1-isopropyl-1H-imidazol-3-ium bromide [o-H3L[Br]3] (11.82 g, 30 mmol), KNiPr2[Cl]3 (11.97 g, 60 mmol), CeCl3(THF)3 (0.15 3.29 g, 10 mmol) and DME (100 mL) gave after recrystallization the title compound 1Ce as a yellow solid (8.17 g, 7.6 mmol, 76%). X-ray quality crystals were grown from a concentrated hexane solution at –20 °C over 1 week. 1H NMR (500 MHz, C6D6) δH: –9.76 (3H, s, CH(CH3)), –6.89 (3H, s, CH(CH3)), –4.37 (3H, s, CH(CH3)), –3.38 (9H, s, C(CH3)), –1.86 (3H, s, CH(CH3)), 0.47 (3H, s, CH(CH3)), 0.77 (1H, CH), 1.51 (9H, s, C(CH3)), 1.57 (9H, s, C(CH3)), 1.75 (1H, s, CH), 1.76 (1H, s, CH), 2.10 (9H, s, C(CH3)), 2.31 (9H, s, C(CH3)), 3.37–3.32 (9H, m, C(CH3)), 3.43 (3H, s, CH(CH3)), 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, 2 × CH), 10.39 (1H, s, CH), 11.01 (1H, s, CH), 11.22 (1H, s, CH). 13C{1H} NMR (126 MHz, C6D6) δC: 14.4, 21.7, 22.3, 23.1, 24.6, 24.7, 30.1, 30.9, 31.4, 32.0, 32.5, 33.4, 33.9, 34.2, 35.4, 36.2, 36.5, 39.4, 41.0, 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 C46H37CeO2N2 requires 66.70%, H 8.12%, N 7.78% calculated. C 66.72%, H 8.13%, N 7.78% found; APPI+ C46H37CeO2N2 + [M]+ requires 1079.5894, found 1079.5711 (–17.0 ppm).

**1Ce**

Using general procedure 1 – 1-(tert-butyl)-3-(3,5-di-tert-butyl-2-hydroxyphenyl)-1H-imidazol-3-ium bromide [o-H3L[Br]3] (306 mg, 0.75 mmol), KNiPr2[Cl]3 (300 mg, 1.5 mmol), CeCl3(THF)3 (80 mg, 0.25 mmol) and DME (2.5 mL) gave after recrystallization title compound 1Ce** as a yellow solid (70 mg, 0.0625 mmol, 25%). 1H NMR (400 MHz, C6D6) δH: –18.43 (9H, s, C(CH3)), –9.47 (9H, s, C(CH3)), –4.21 (9H, s, C(CH3)), –3.27
(9H, s, C(CH3)3), −1.25 (9H, s, C(CH3)3), 1.18 (9H, s, C(CH3)3), 2.41 (9H, s, C(CH3)3), 4.02 (9H, s, C(CH3)3), 4.88 (1H, s, ArH), 6.23 (1H, s, ArH), 7.45 (1H, s, ArH), 8.66 (1H, s, ArH), 9.30−9.38 (10H, m, ArH + C(CH3)3), 9.63 (1H, s), 9.68 (1H, s), 11.97 (1H, s), 16.43 (1H, s), 16.84 (1H, s).13C[1H] NMR (126 MHz, C6D6) δC: 23.9, 25.3, 27.0, 29.0, 29.1, 30.1, 33.8, 34.2, 35.5, 35.7, 36.7, 36.9, 37.9, 38.9, 48.2, 51.8, 53.0, 57.4, 113.5, 115.1, 117.1, 118.1, 118.8, 120.6, 121.4, 123.0, 123.7, 124.3, 125.5, 130.3, 132.5, 133.4, 134.5, 137.9, 140.6, 142.4, 144.7, 147.0, 149.9, 157.3, 160.8, 163.1, 171.1, 206.2, 213.0. APPI+ C60H74CeN6O3+[M]+ requires 1121.6364, found 1121.6333 (−0.27 ppm). After several attempts, this compound did not give satisfactory elemental analysis results, presumably because of its thermal sensitivity.

1CeMes+. Using general procedure 1 – 3-(3,5-di-tert-butyl-2-hydroxyphenyl)-1-mesityl-1H-imidazol-3-ium [o-H2LMes][Br] (353 mg, 0.75 mmol), KN(SiMe3)2 (300 mg, 1.5 mmol), CeCl3·(THF)3 (1.15) (80 mg, 0.25 mmol) and DME (2.5 mL) gave after extraction and recrystallization in benzene title compound 1CeMes+ as a yellow solid (42 mg, 0.037 mmol, 15%). X-ray quality crystals were grown from a concentrated benzene solution over 1 week at room temperature.1H NMR (400 MHz, C6D6) δH: −8.50 (9H, ArH), −3.80 (27H, s, C(CH3)3), 1.51 (9H, s, ArH), 2.13 (3H, s, ArH), 2.80 (27H, s, C(CH3)3), 7.92 (9H, s, ArH), 8.33 (3H, s, ArH), 8.53 (3H, s, ArH), 9.07 (3H, s, ArH), 11.54 (3H, s, ArH), 12.01 (3H, s, ArH).13C[1H] NMR (126 MHz, C6D6) δC: 20.1 (ArCH3), 21.8 (ArCH2), 25.4 (ArCH), 32.7 (ArCH3), 34.9 (Ar(CH3)3), 36.0 (Ar(CH3)3), 122.4 (ArC), 122.3 (ImC), 123.8 (ArC), 124.8 (ArC), 125.4 (ArC), 129.5 (ArC), 130.5 (ArC), 130.5 (ImC), 135.1 (ArC), 135.7 (ArC), 138.3 (ArC), 147.9 (ArC), 148.3 (ArC), 184.2 (NCN). Elemental analysis C78H99CeN6O3+: C 71.43%, H 7.76%, N 6.31% found; APPI+ C78H99CeN6O3+[M]+ requires 1092.6052, found 1092.6095 (+3.9 ppm).

General procedure 2 – synthesis of 2CeR

A solution of 1CeR (3 equiv.) in benzene, toluene, hexane or THF (0.5 M) was freeze−pump−thaw degassed 3 times and exposed to an atmosphere of dry CO2 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 cooled to −30 °C overnight. The resulting suspension was filtered and dried under vacuum to yield the title compound which was stored at −20 °C under a nitrogen atmosphere.

2CeIPr+. Using general procedure 2 – 1CeIPr (3.0 g, 2.78 mmol) in toluene (50 mL) was charged with an atmosphere of CO2, and after recrystallization gave the title product 2CeIPr 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, C6D6) δH: 0.91 (27H, s, C(CH3)3), 1.27−1.31 (9H, m, CH(CH3)2(CH3)4), 1.72−1.76 (9H, m, CH(CH2)3(CH3)2), 2.52 (27H, s, C(CH3)3), 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(CH2)3(CH3)2).13C[1H] NMR (126 MHz, C6D6) δC: 21.4 (CH2(CH3)2(CH3)2), 24.6 (CH2(CH3)2(CH3)2), 30.1 (C(CH3)2), 33.5 (C(CH3)2), 33.6 (C(CH3)2), 36.7 (C(CH3)2), 53.1 (CH2(CH3)2(CH3)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), 171.3 (OCO). tmax (nuljel) full: 166. Elemental analysis C66H93CeO9N6: C 65.97%, H 8.03%, N 7.69% calculated. C 66.00%, H 8.01%, N 7.67% found; APPI+ C66H93CeO9N6+ [M]+ requires 1092.6052, found 1092.6095 (+3.9 ppm).

2CeBu+. Using general procedure 2 – 1CeBu (32 mg, 0.022 mmol) and THF (1 mL) was charged with an atmosphere of CO2, and after recrystallization gave the title product 2CeBu as a colourless solid (20 mg, 16 mmol, 72%).1H NMR (400 MHz, C6D6) δH: 0.87 (27H, s, C(CH3)3), 2.60 (27H, s, C(CH3)2), 2.94 (27H, s, C(CH3)2), 4.58−4.62 (3H, m, ArH), 4.84−4.88 (3H, m, ArH), 5.91 (3H, d, J = 2.5, ImH), 7.69 (3H, d, J = 2.5, ImH), 13C[1H] NMR (126 MHz, C6D6) δC: 30.0 (C(CH3)2), 30.1 (C(CH3)2), 31.1 (C(CH3)2), 33.2 (C(CH3)2), 36.4 (C(CH3)2), 62.5 (NC(CH3)2), 113.9 (ArC), 118.7 (ArC), 120.4 (ArC), 122.9 (ImC), 125.5 (ImC), 133.9 (ArC), 141.8 (ArC), 143.6 (ArC), 160.8 (ArC)2OCCe, 173.5 (OCO). Elemental analysis C60H74CeNiO3N9C: C 62.25%, H 7.46%, N 6.91% calculated. C 62.36%, H 7.58%, N 7.08% found.
2CeMes. Using a modification of general procedure 2 – 1CeMes (25 mg, 0.022 mmol) and THF (1 mL) was charged with an atmosphere of CO₂ and the resulting solution was left to slowly evaporate to give the title product 2CeMes as a bright yellow solid (31 mg, 0.022 mmol, 99%). ¹H NMR (400 MHz, d₄-THF) δH: –9.96 (3H, br. s, CH₃), –6.09 (9H, br. s, C(3H),) –5.17 (9H, br. s, C(CH₃)₃), –2.95 (9H, br. s, C(CH₃)₂), –2.11 (3H, br. s, CH₃), 0.82 (9H, br. s, C(3H),) 0.97 (3H, br. s, CH₃), 1.13 (9H, br. s, C(CH₃)₃), 2.64 (12H, appr. br. s, C(CH₃)₃ + CH₃), 3.05 (1H, br. s, CH), 3.51 (1H, br. s, CH), 4.46 (1H, br. s, CH), 4.74 (6H, appr. br. s, 2 × CH₃), 5.61 (1H, br. s, CH), 5.72 (1H, br. s, CH), 6.06 (1H, br. s, CH), 6.28 (3H, br. s, CH₃), 7.04 (1H, br. s, CH), 7.51 (1H, br. s, CH), 8.36 (1H, br. s, CH), 8.61 (1H, br. s, CH), 9.10 (3H, br. s), 10.61 (1H, br. s, CH), 12.01 (1H, br. s, CH), 12.23 (1H, br. s, CH), 12.59 (1H, br. s, CH), 13.00–3.60 (4H, m, CH₂ + CH₃). Three CH resonances could not be located. ¹³C NMR (126 MHz) d₄-THF δC: 7.3, 13.3, 16.7, 17.4, 19.5, 19.7, 20.0, 20.3, 21.1, 21.5, 22.8, 23.4, 28.2, 29.9, 30.6, 32.0, 32.5, 33.8, 34.2, 35.4, 36.3, 36.5, 113.9, 119.3, 119.5, 120.6, 121.0, 121.7, 122.4, 123.1, 123.2, 124.8, 126.3, 126.6, 127.4, 127.7, 128.1, 129.5, 130.1, 130.9, 131.8, 132.2, 132.6, 133.2, 134.3, 134.7, 135.3, 135.7, 135.9, 136.7, 137.5, 138.5, 139.3, 140.1, 141.0, 141.0, 141.5, 141.8, 142.4, 143.4, 145.7, 148.0, 160.0, 163.3, 164.7, 169.6, 170.9, 175.4, 180.4, 200.2 r. v. max (nong. null): 1678, 1716. Elementary analysis C₇₉H₁₁₄CeN₉O₆: C 67.21% H 6.75% N 5.66% found.

3CeIPr(MesNCO)₃. To a solution of 1CeIPr (108 mg, 0.1 mmol) in C₆H₆ (2 mL), MesNCO (48 mg, 0.03 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 pale-yellow powder by filtration of the solvents and drying under vacuum (76 mg, 59%). ¹H NMR (500 MHz, C₅D₅) δH: –6.95 (9H, s), –4.75 (3H, s), –2.95 (1H, s), –2.62 (3H, s), –1.00 (9H, s), –0.1 (9H, s), 0.13 (3H, s), 0.19 (9H, s), 0.59–0.64 (3H, m), 0.66 (1H, s), 1.05 (1H, s), 1.17 (3H, s), 1.35 (1H, s), 1.44 (1H, s), 1.77 (9H, s), 2.31 (9H, s), 2.52 (9H, s), 3.42 (1H, s), 4.15 (1H, s), 5.96 (3H, s), 6.28 (1H, s), 7.03 (1H, s), 7.24 (1H, s), 9.06 (1H, s), 9.38 (9H, s), 9.88 (1H, s), 10.38 (1H, s), 10.50 (1H, s), 12.30 (1H, s). APPT⁺ C₇₀H₁₀₆CeN₉O₃⁺ [M + H]⁺ requires 1278.7341, found 1278.7213 (–10.0 ppm). Elementary analysis C₇₀H₁₀₆CeN₉O₃: C 65.75%, H 8.28%, N 8.75% calculated. C 65.50%, H 8.58%, N 8.64% found.

3CeIPr[BuNOCO]₂. To a solution of 1CeIPr (108 mg, 0.1 mmol) in DME (2 mL), BuNOCO (34 µL, 0.3 mmol) was added and stirred for 2 h at 80 °C. The reaction mixture was cooled to room temperature and evaporated to dryness. Colourless X-ray quality crystals were grown by diffusion of heptane into a toluene solution of the crude product, and isolated by decanting (89 mg, 68%). ¹H NMR (500 MHz, C₅D₅) δH: –9.13 (1H, s), –8.58 (3H, s), –8.29 (1H, s), –6.14 (3H, s), –4.01 (3H, s), –3.97 (9H, s), –3.53 (3H, s), –3.00 (9H, s), –2.28 (9H, s), –1.34 (1H, s), 0.23 (9H, s), 1.38 (1H, s), 1.68 (9H, s), 3.13 (1H, s), 3.24 (3H, s), 3.25 (9H, s), 4.78 (1H, s), 6.07 (1H, s), 8.29 (1H, s), 8.37 (1H, s), 9.15 (9H, s), 9.76 (1H, s), 9.90 (1H, s), 10.86 (1H, s), 13.99 (1H, s), 14.23 (3H, s), 17.32 (1H, s), 18.17 (9H, s), 52.70 (1H br. s). Elemental analysis C₇₉H₁₁₆CeN₉O₇S: C 64.14%, H 8.07%, N 8.55% calculated. C 64.17%, H 8.35%, N 8.24% found. APPT⁺ C₇₀H₁₀₆CeN₉O₃S₂⁺ [M + H]⁺ requires 1310.6884, found 1310.6816 (–5.2 ppm).

3CeIPr[BuNCS]. To a solution of 1CeIPr (108 mg, 0.1 mmol) in DME (2 mL), BuNCS (34 µL, 0.3 mmol) was added and stirred for 2 h at 80 °C. The reaction mixture was cooled to room temperature and evaporated to dryness yielding a colourless powder (117 mg, 98%). ¹H NMR (500 MHz, C₅D₅) δH: –8.72 (3H, s), –8.44 (1H, s), –6.21 (3H, s), –4.08 (3H, s), –4.06 (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). APPT⁺ C₇₅H₁₀₂CeN₉O₃S: [M⁺] requires 1194.6350, found 1194.6571 (+18.5 ppm). Elementary analysis C₆₆H₉₈CeN₉O₃S: C
65.29%, H 8.09%, N 8.20% calculated. C 65.42%, H 8.21%, N 7.59% found.

Conflicts of interest
There are no conflicts to declare.

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Notes and references
26 G. Prabuankar and P. Suresh, ChemistrySelect, 2017, 2, 9920–9923.