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\((\text{L}^1)\), supported by bidentate ortho-aryloxide-NHC ligands are reported \((\text{L}^1 = \text{O(o-C}_{6}\text{H}_{4}\text{-Bu}_{2}-2,6-\text{CN(C}_{4}\text{H}_{3})\text{NR}; \text{R} = '\text{Pr}, '\text{Bu}, '\text{Mes}; \text{Ln} = \text{Ce, Sm, Eu})\). The cerium complexes react cleanly and quantitatively insert carbon dioxide exclusively into all three cerium carbene bonds, forming Ce\((\text{L}^1)\text{CO}_{3}\)). The insertion is reversible only for the mesityl-substituted complex Ce\((\text{L}^1)\). Analysis of the capacity of Ce\((\text{L}^1)\) to insert a range of heteroallenes that are isoelectronic with CO reveals the solvent and ligand size dependence of the selectivity. This is important because only the complexes capable of reversible CO\(_2\)-insertion are competent catalysts for catalytic conversions of CO\(_2\). Preliminary studies show that only Ce\((\text{L}^1)\text{CO}_{3}\)) catalyses the formation of propylene carbonate from propylene oxide and 1 atmosphere pressures of carbon dioxide. The mono-ligand complexes can be isolated from reactions using LiCe\((\text{NP}_3)\) as a starting material; LiBr adducts [Ce\((\text{L}^1)\text{(NP}_3)\)Br.LiBr(THF)]; \((\text{R} = \text{Me, 'Pr})\) are reported, along with a hexanuclear N-heterocyclic dicarbene \([\text{Li}_2\text{Ce}(\text{OArC}_{6}\text{H}_{4})_2\text{NP}_3)\text{Br}_2(\text{THF})]_3\) by-product. The analogous para-aryloxide-NHC proligand \([p\text{-L}^1\text{Bu}_2\text{-2,6- CN(C}_4\text{H}_3)\text{NMes}]\) has been made for comparison, but the rare earth tris-ligand complexes \(\text{Ln}(p\text{-L}^1\text{Bu}_2\text{-2,6- CN(C}_4\text{H}_3)\text{NMes})\) are too reactive for straightforward Lewis pair separated chemistry to be usefully carried out.

Carbon dioxide can be a useful and renewable C\(_1\) 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 imidazolidine carboxylates,\(^{7,8}\) imidazolidine amidates\(^{9}\) and imidazolidine carboximidodithioates\(^{10}\) respectively (Chart 1). While imidazolidine carboxylates can successfully catalyse carbamate formation,\(^{11}\) NHCs react as organocatalysts with isocyanates to form cyclic ureas as through an azolium 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 \(\sigma\)-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.\(^{16-19}\) 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 \(-\text{Sc-NHC-CO}_2\)\(_2\))\(_n\) containing network owing to the flexible alkoxide tether.\(^{20}\)

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d Electronic Supplementary Information [ESI] available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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J. Name., 2013, 00, 1-3 | 1
Chemical Science

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

1Ce\textsuperscript{iv}:

1Ce\textsuperscript{v}:

1Ce\textsuperscript{vi}:

1Ce\textsuperscript{vi}:

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
Fig. 1 Molecular structures of $1\text{Ce}^{\text{Mes}}$ (upper) and $1\text{Ce}^{\text{iPr}}$ (lower) with Ce, O and C$_{\text{ar}}$ 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 $1\text{Ce}^{\text{Mes}}$: Ce1-C11 2.747(6), Ce1-C21 2.694(6), Ce1-C31 2.785(7), Ce1-O11 2.349(4), Ce1-O21 2.277(4), Ce1-O31 2.283(5), C11-Ce1-C21 88.28(18), C11-Ce1-C31 172.93(18), C21-Ce1-C31 88.53(18), O11-Ce1-O21 154.05(15), O11-Ce1-O31 107.42(15), O21-Ce1-O31 97.45(16), C11-Ce1-O21 65.85(9), O21-Ce1-O31 66.82(8), O31-Ce1-O31 66.25(9), O11-Ce1-C21 101.48(9), O11-Ce1-C31 93.66(8), O11-Ce1-O31 96.58(8), O21-Ce1-C31 94.23(8), Ce1-C11 2.251(2), C11-Ce1-C21 105.49(9), C11-Ce1-C31 100.01(9), C21-Ce1-C31 101.48(9), O11-Ce1-O21 93.66(8), O11-Ce1-O31 97.45(16), C11-Ce1-O21 65.85(9), O21-Ce1-O31 66.82(8), O31-Ce1-O31 66.25(9).

These ligand orientation differences are rationalized by consideration that three planar mesityl groups pack more easily than the aryloxide tert-butylic groups would, and that the tert-butylic iso-propyl steric repulsions are less prescriptive. The C$_{\text{ar}}$-symmetric complex would also be favoured if π-stacking between the mesityl substituent and an adjacent imidazole-ylidine ring is possible. This high degree of steric crowding is used to rationalise the failed synthesis of related but bulkier diisopropylphenyl containing aryloxide-carbene ligands. Reactions aimed at targeting the mono- and bis-alkoxy-NHC analogues using this synthetic method yielded only the tris-ligand complex and unreacted LnCl$_3$ while the targeted synthesis of a Sm(II) analogue results in spontaneous oxidation and isolation of Sm(III) compound, $1\text{Sm}^{\text{Mes}}$ (see SI).

Single crystal X-ray analyses show that the fac- and mer-isomers are retained in the solid state for $1\text{Ce}^{\text{Mes}}$ and $1\text{Ce}^{\text{iPr}}$ respectively (see Figure 1). The coordination geometry of cerium in each is a pseudo-octahedral geometry defined by average C–Ce–C bond angles ($172.93(18)^\circ$), $O8.41(18)^\circ$ and $102.33(9)^\circ$) and OArCeOAr 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 $2.742(6)$ Å and $2.742(6)$ Å, within the upper limits of face-centred π-stacking.

Reactivity of $1\text{Ce}^{\text{R}}$ complexes

Exposure of a solution of $1\text{Ce}^{\text{R}}$ to an atmosphere of carbon dioxide results in the instant and quantitative formation of $2\text{Ce}^{\text{Bu}}$ (Ln[CO$_3$)$_3$] as observed by the precipitation of a beige solid (hexanes reaction solvent) or monitoring by $^1$H NMR spectroscopy (benzene reaction solvent), Scheme 2. As anticipated for a complex with a hemilabile metal–NHC bond, the CO$_2$ exclusively inserts into the three Ce–C bonds, and pleasingly, 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 $2\text{Ce}^{\text{Mes}}$ held at elevated temperatures under dynamic vacuum (100 °C, 10$^{-3}$ mbar) show no loss of CO$_2$. However, a sample of $2\text{Ce}^{\text{Mes}}$ shows some loss of 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 CO$_2$.

$^1$H NMR spectroscopic analysis reveals that the N-alkyl functionalised $2\text{Ce}^{\text{R}}$ complexes have C$_3$ symmetry, i.e. a fac-conformation of the three bidentate ligands. The $^1$H NMR spectra contain diagnostic CO$_2$ carbon resonances for $2\text{Ce}^{\text{iPr}}$ and $2\text{Ce}^{\text{Mes}}$ ($\delta = 173.1$ ppm and 173.5 ppm respectively) at significantly higher frequency than known organic NHC.CO$_2$ compounds ($\leq 20$ ppm)$^{38}$, as might be anticipated from proximity to the paramagnetic metal center. The FTIR spectrum of $2\text{Ce}^{\text{iPr}}$ shows a characteristic absorption at 1666 cm$^{-1}$ (typical range ~1630–1690)$^{8, 33, 34}$. The conversion of $1\text{Ce}^{\text{Mes}}$ to $2\text{Ce}^{\text{Mes}}$ results in a lowering of symmetry from C$_3$ to C$_2$ 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 CO₂ insertion products 2Ce[IPr] and 2Ce[Bu] have a pseudo-trigonal prismatic geometry with C₅-symmetric fac- arrangement described by the average O²⁻–Ce–O⁶⁻ bond angles (97.03(10)° and 95.94(8)° respectively) and O¹Ce–O⁶Ce–O₁CO bond angles (77.77(10)° and 80.48(8)°). The average Ce–O₁CO 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.

Interestingly, treatment of a benzene solution of 1Ce[IPr] 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 CS₂ into two (of the three) M--C bonds was characterized. The higher reactivity of CO₂ compared to CS₂ in this system is reasonable considering the stronger affinity of Ce for oxygen, and the lower dipole moment in the latter reagent.

![Diagram](image)

Scheme 3 Treatment of 1Ce[IPr] with reagents isoelectronic to CO₂

Treatment of a benzene or THF solution of 1Ce[IPr] with three equivalents of mesityl isocyanate immediately results in the insertion of isocyanate into all three Ce–NHC bonds, affording a pale-yellow solution from which the tris-azoliumamidate complex D 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 cyclohexyllallene shows no reactivity with 1Ce[IPr].

In the reaction of 1Ce[IPr] with three equivalents of tert-butylisocyanate in benzene or THF, two molecules of isocyanate insert to form 3Ce[IPr](MesNCO), however in DME solution, three molecules insert to form 3Ce[IPr](BuNCO)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-butyl 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 1Ce[IPr] is treated with 3 equivs of tert-butylisothiocyanate at 80 °C in benzene or THF, a single equivalent of thiocarbamate inserts to form 3Ce[IPr](BuNC) while in DME two equivalents of thiocarbamate insert to form 3Ce[IPr](BuNC).
Single crystals of $3\text{Ce}^{\text{iv}}(\text{BuNCS})_2$ 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 $1\text{Ce}^{\text{iv}}$ (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$_{\text{Ar}}$ (78.75° avg.) and C–Ce–O$_{\text{Ar}}$ (69.93°).

**Catalytic applications of $2\text{Ce}^{\text{iv}}$ 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 $2\text{Ce}^{\text{iv}}$ 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

Catalytic formation of propylene carbonate from propylene oxide in an atmosphere of carbon dioxide using 2CeMes and 2CeMe.

**Scheme 5** Catalytic formation of propylene carbonate from propylene oxide in an atmosphere of carbon dioxide using 2CeMes and 2CeMe.

**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-H₄L⁺][Br], R = Me, Pr and equimolar amounts of Li[THF][CeH₃(P₃)]. 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 4Ce⁻ and 4Ce⁺ (Ce₂Br₂Li₂[P₃]₂Li₂THF₂) to a moderate level (20 % and 38 % respectively, see Scheme 6).

Cryolographic analysis reveals a dimeric structure still containing unreacted base and lithium ions (see SI). A complicated bis(ligand) Li₂Ce₂ cluster 5CeMe, in which each ligand has been deprotonated at the NHC backbone (in the 4-position) yielding a diatomic 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 arylxide 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 prolagn synthesis using saturated-backbone imidazole analogues allows access to the para-functionalized prolagn in 15% yield.27 Treatment of this N-mesyli functionalized prolagn [p-H₂L₃][X]. (p-L₃ = [O(p-C₆H₄Ph⁻Bu₂-2,6-CN(C₆H₄)N-C₆H₄Ph⁻2,4,6-Mes₃)]) with either MN(SiMe₃)₃ (M = Na or K) in THF at room temperature affords the group 1 NHC salts 6Me₃ [(M[p-L₃]Me)₃] (M = Na, K) in quantitative yield, Scheme 7. The solid-state structures of both are polymeric, according to single crystal X-ray data, with 6Na₃ displaying repeating C-[[Na-\(\mu-\text{ArO}\)]-Na]-C diamond units, while 6K₃ displays a perpendicular ArO-K-C arrangement, see SI.

Salt 6Na₃ can be treated with YCl₃ or CeCl₃ at –20°C to synthesise 7Ln₃ [(Ln[p-L₃]Me)₃(THF)] where Ln = Y, Ce). In 56% and 30% yield as yellow powders. Due to their high reactivity

![Fig. 4 Molecular structure of 5CeMe with imidazolium, Ce, O and Li atoms shown at 50 % ellipsoid probability, framework atoms drawn capped stick and coordinated solvents, peripheral carbon atoms wireframe, and H and lattice solvent omitted for clarity.](Image)

![Scheme 6 Reactions to target mono-NHC Ln complexes that afford 4CeMe, 4CeMe and the hexagonal 5CeMe that is the by-product isolated as single X-ray quality crystals for R = Me.](Image)

**Scheme 6** Reactions to target mono-NHC Ln complexes that afford 4CeMe, 4CeMe and the hexagonal 5CeMe that is the by-product isolated as single X-ray quality crystals for R = Me.
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-HL\textsubscript{Mes})\textsubscript{3})(THF)]\textsubscript{2}⋅X\textsubscript{3}.

\begin{align*}
\text{Scheme 7 Reaction to target the para-ligand adducts 7Ln}^{\text{Mas}} (\text{Ln} = \text{Y, Ce})
\end{align*}

Analysis of 7\text{Y}^{\text{Mas}} by \textsuperscript{13}C 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 SI).

**Conclusions**

The tris(ortho-aryloxide-NHC) rare earth complexes Ln(L\textsubscript{Mas})\textsubscript{3} are readily isolated and are the thermodynamic sink in this system. Insertion of CO\textsubscript{2} or a range of isoelectronic (hetero)allenes into the labile cerium carbene bond in Ce(L\textsubscript{Mas})\textsubscript{3} shows a dependence on solvent and N-R group on L\textsubscript{Mas} 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 substituted Ce(L\textsubscript{Mas})\textsubscript{3}. The reversibility of the CO\textsubscript{2} insertion appears to be crucial for further reactivity as only Ce(L\textsubscript{Mas}.CO)\textsubscript{3}\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\textsubscript{Mas}.CO)\textsubscript{3} the complexes are inactive. We propose that the catalyst 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(N\textsubscript{Pr})\textsubscript{3} as a starting material; LiBr adducts [Ce(L\textsubscript{Mas})(N\textsubscript{Pr})\textsubscript{3}]LiBr(THF)]\textsubscript{2} (R = Me, iPr) are reported, along with a hexanuclear N-heterocyclic dicarbene complex [Li\textsubscript{2}Ce(OAr\textsubscript{Mes}-H)\textsubscript{2}(N\textsubscript{Pr})\textsubscript{3}(THF)]\textsubscript{2} which is formed as a by-product. The analogous para-aryloxide-NHC proligand (p-L\textsubscript{Mas})\textsubscript{3} = O(p-C\textsubscript{6}H\textsubscript{4})\textsubscript{2}Bu-2,6-CN(C\textsubscript{6}H\textsubscript{4})NMe\textsubscript{3} has been made for comparison. The group 1 salts [Na(p-L\textsubscript{Mas})\textsubscript{3}]\textsubscript{2} and [K(p-L\textsubscript{Mas})\textsubscript{3}]\textsubscript{2} form two different types of infinite coordination polymers through metal carbene-bonds. Synthesis of the analogous lanthanide para-aryloxide-NHC complexes Ln(p-L\textsubscript{Mas})\textsubscript{3}(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 Ce\textsubscript{7}-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.

**Acknowledgements**

We thank the EPSRC for funding through the Centre for Doctoral Training in Critical Resource Catalysis (CRITICAT, EP/L016419/1, R.W.F.K.), EP/J018139/1 and the UK Catalysis Hub (EP/K014714/1 P.L.A., C.W.), EP/M010554/1 (P.L.A.). This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No 740311, P.L.A.). K.W. thanks the China Scholarship Council (CSC) for a postgraduate fellowship. P.L.A., M.W.M., J.R. and F.E.K. thank the Technische Universität München – Institute for Advanced Study, funded by the German Excellence Initiative. A.D.S. thanks the Royal Society for a Wolfson Research Merit Award. C.J. thanks the DAAD for a scholarship, and C.J. and J.R. thank the TUM Graduate School for financial support.

**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 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 stored over 4 Å molecular sieves. Deuterated solvents, benzene-d\textsubscript{6}, THF-d\textsubscript{8} and pyridine-d\textsubscript{5} 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, AVAS00, or PRO500 spectrometers at 300 K. Chemical shifts are reported in parts per million, δ,
NMR 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.

General procedure 1 – Synthesis of 1Ln

To a suspension of [o-H2Ln][Br] (3 equiv) in DME (0.1 mL) KN(SiMe3)2 (6 equiv) was added and the resulting mixture was stirred for 5 min at room temperature. LnCl2(thf)2 (1 equiv) 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.

1CeIV – Using general procedure 1 – 3-(3,5-di-tert-butyl-2,5-dihydrophenyl)-1-mesityl-1H-imidazol-3-ium [o-H2Ce][Br] (353 mg, 0.75 mmol) KN(SiMe3)2 (300 mg, 1.5 mmol) CeCl3(thf)1.15 (80 mg, 0.25 mmol) and DME (2.5 mL) gave after extraction and recrystallization in benzene title compound 1CeIV 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) δ: −8.50 (9H, ArCH3), −3.80 (27H, s, C(CH3)2), 1.51 (9H, s, C(CH3)3), 3.37–3.32 (9H, m, C(CH3)2), 5.43 (3H, s, CH3), 7.60 (1H, s, CH), 7.08 (1H, app d, J = 2.7, CH), 6.70 (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, 2xCH), 10.39 (1H, s, CH), 11.01 (1H, s, CH), 11.22 (1H, s, CH); 13C(H) NMR (126 MHz, C6D6) δ: 144.1, 137.3, 123.4, 123.1, 124.6, 24.7, 130.1, 31.9, 32.0, 32.5, 33.3, 33.9, 34.2, 35.4, 36.2, 36.5, 39.4, 40.1, 42.8, 46.4, 51.4, 114.4, 115.6, 118.9, 119.3, 119.5, 121.3, 122.2, 122.7, 122.8, 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 C67H58CeNO2: C 66.70%, H 8.12%, N 7.78% calculated. C 66.72%, H 8.13%, N 7.78% found; APPI (NSI) Ce6H72CeNO2+ [M]+ requires 1307.6833, found 1307.6810 (−1.7 ppm).

1SmIV – Using general procedure 1 – 3-(3,5-di-tert-butyl-2,5-dihydrophenyl)-1-mesityl-1H-imidazol-3-ium [o-H2Sm][Br] (296 mg, 0.75 mmol), KN(SiMe3)2 (300 mg, 1.5 mmol), SmCl3(thf)1.15 (100 mg, 0.1575 mmol) and DME (2.5 mL) gave after recrystallization title compound 1SmIV as a yellow solid (171 mg, 7.66 mmol, 63%). 1H NMR (400 MHz, C6D6) δ: −9.17 (−9.07) (1H, m, CH(CH2)), −4.24 (3H, app d, J = 5.8, CH(CH2)), −2.42 (3H, app d, J = 5.5, CH(CH2)), −1.13 (9H, s, C(CH3)), −0.85 (−0.73) (6H, m, 2xCH(CH2)), −0.63 (−0.59) (1H, m, CH(CH2)), 1.08 (9H, s, C(CH3)), 1.65–1.70 (3H, m, CH(CH2)), 1.81 (10H, s, C(CH3)), 1.85 (10H, s, C(CH3)), 2.02 (10H, s, C(CH3)), 2.39 (10H, s, C(CH3)), 3.24 (3H, app d, J = 5.5, CH(CH2)), 4.99 (1H, app p, J = 6.8, CH(CH2)), 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, J = 1.7, ArH).
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$_{61}$H$_{58}$CeO$_{4}$N$_{2}$: C 66.07%, H 8.04%, N 7.70% calculated. C 60.10%, H 8.33%, N 7.54% found. APPI (NSI$^+$) C$_{60}$H$_{58}$CeO$_{4}$N$_{2}$ [M]$^+$ requires 1093.67, found 1093.676 (+3 ppm).

1Eu$^{3+}$ – Using general procedure 1 – 3-(3,5-di-tert-butyl-2-hydroxyphenyl)-1-isopropyl-1H-imidazol-3-ium bromide [e-H$_{2}$Br$^{+}$][Br] (296 mg, 0.75 mmol), KN(SiMe$_3$)$_2$ (300 mg, 1.5 mmol), EuCl$_3$(thf)$_2$ (110 mg, 0.1575 mmol) and DME (2.5 mL) gave after recrystallization title compound 1Eu$^{3+}$ as an orange-red solid (121 mg, 0.11 mmol, 45%); $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$: –21.12 (1H, s), –14.06 (9H, s, CH$_3$), –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, CH$_3$)$_2$, –0.72 (1H, s, CH), –0.64 (1H, s, CH), –1.73 (3H, s, CH$_3$), 2.65 (1H, s, CH), 4.76 (3H, s, CH$_3$), 5.71 (1H, s, CH), 6.20 (1H, CH$_3$), 7.20 (1H, CH), 7.39 (1H, CH), 11.89 (9H, s, CH$_3$), 15.05 (3H, s, CH(CH$_3$)$_2$), 15.83 (1H, s, CH), 17.88 (1H, s, CH), 24.72 (3H, s, CH$_3$), 33.23 (3H, s, CH$_3$), 40.9X (1H, s, CH), 96.66 (1H, s, CH); Elemental analysis C$_{61}$H$_{58}$CeO$_{4}$N$_{2}$: 65.97%, H 8.03%, N 7.69% calculated. C 66.00%, H 8.01%, N 7.67% found; APPI (NSI$^+$) C$_{60}$H$_{58}$CeO$_{4}$N$_{2}$ [M]$^+$ requires 1092.6052, found 1092.6095 (+3 ppm).

**General procedure 2 – Synthesis of 2Ce$^{8+}$**

A solution of 1Ce$^{8+}$ (3 equiv) in benzene or THF (0.5 m) was freeze-pump-thaw degassed 3 times and exposed to an atmosphere of dry CO$_2$ 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.

2Ce$^{8+}$ – Using general procedure 2 – 1Ce$^{8+}$ (3.0 g, 2.78 mmol) in toluene (50 mL) was charged with an atmosphere of CO$_2$ and after recrystallization gave the title product 2Ce$^{8+}$ as a colourless solid (202 mg, 0.16 mmol, 50%); $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$: 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, 34.5, 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, 141.5, 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. v$_{max}$ (nujol mull): 1678, 1716.

Elemental analysis C$_{61}$H$_{58}$CeO$_{4}$N$_{2}$: C 67.52% H 6.93% N 5.83% calculated. C 67.21% H 7.25% N 5.66% found.

3Ce$^{8+}$ (Mes$_2$NCO$_2$) – To a solution of 1Ce$^{8+}$ (108 mg, 0.11 mmol) in C$_6$H$_6$ (2 mL), MesNCO$_2$ (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%); $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$: –6.53 (9H, s, C(H$_2$)$_3$), –5.17 (3H, s, C(CH$_3$)$_2$), –4.52 (3H, s, CH$_3$), –3.89 (3H, s, CH$_3$), –0.21 (3H, s, CH$_3$), 0.05 (3H, s, CH$_3$), 1.10 (3H, s, CH$_3$), 1.37 (9H, s, C(CH$_3$)$_2$), 1.53 (6H, s, Mes$_2$(2,6)CH$_3$), 1.72 (2H, s, Mes$_2$(3)H), 1.99 (9H, s, C(CH$_3$)$_2$), 2.00 (6H, s, Mes$_2$(2,6)CH$_3$), 2.22 (3H, s, CH$_3$), 2.56 (9H, s, C(CH$_3$)$_2$), 2.58 (3H, s, CH$_3$), 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, 4.34 (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(CH3)3), 10.64 (1H, s, CH), 10.85 (1H, s, CH), 12.62 (1H, s, CH). Elemental analysis C90H95Ce2O4N8S2 requires 1394.8052, found 1394.8394, 0.93% C, 64.32% H, 8.54% N, 8.73% S (M+H+). 

3CeIPy(BuNCO)3 – To a solution of 1CeIPy (108 mg, 0.1 mmol) in DMF (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, CDCl3) and crystallographic data. 

Notes and references


hemilabile Ce-C bonds

only reversible for R=Mes

catalytic for R=Mes

hemilabile Ce-C bonds

$\Delta_R \leftarrow \text{Pr, } \text{Bu, Mes} \rightarrow \text{vacuum}$

only reversible for R=Mes

catalytic for R=Mes