

Dicarium letterbox-shaped tetraphenolates: f-block complexes designed for two-electron chemistry

Supplementary Information

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1. Experimental details

1.1 General experimental details

All moisture and air sensitive materials were manipulated using standard Schlenk-line techniques and stored in dinitrogen filled MBraun gloveboxes. All glassware was dried in a 160 °C oven overnight, cooled under vacuum and purged with nitrogen before use. Tetrahydrofuran, toluene and hexane were collected from a Vac Atmospheres solvent purification system, degassed and stored over activated 4 Å molecular sieves under dinitrogen. Prior to collection the solvent was cycled over a drying column containing molecular sieves for 12 hours. 1,4-Dioxane was refluxed over sodium for three days, distilled and collected into an ampoule containing 4 Å molecular sieves. Toluene-d₈, benzene-d₆ and tetrahydrofuran-d₈ were degassed, refluxed over potassium for 24 hours and distilled by trap to trap distillation under static vacuum prior to use. All solvents were purchased from Sigma-Aldrich or Fisher Scientific and purified and dried before use. ¹H, ¹³C, and ²⁹Si and ¹⁹⁹Hg(71.309 MHz) NMR spectra were recorded on Bruker AVA400, AVA500, or PRO500 spectrometers at 298 K unless otherwise specified. All ¹H NMR and ¹³C NMR spectra were referenced relative to external SiMe₄ at 0 ppm, internal residual solvent H atoms; benzene-d₆ (7.16 ppm); toluene-d₈ (7.09, 7.00, 6.98, 2.09 ppm) pyridine-d₅ (8.74, 7.58, 7.22 ppm) for ¹H NMR. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were performed by Mr Stephen Boyer at London Metropolitan University and Robertson Microlit Laboratory. Variable temperature EPR measurements were recorded using a JEOL JES-FA200 continuous wave spectrometer equipped with an X-band high-power, low-noise Dual-Gunn oscillator bridge and a high sensitivity cylindrical mode cavity and a nitrogen/helium cryostat.

CeCl₃·7H₂O was purchased from Sigma-Aldrich and dried with excess SiMe₃Cl in THF to yield anhydrous CeCl₃(THF)_n. The number of coordinated THF molecules was determined by quantitative ¹H NMR spectroscopy with an internal reference. NaN¹,¹ KBn,² KN³,³ LiN⁴ and the tetraphenol proligands H₄(pTP^R) (R = Me, ^tBu)⁵ were synthesised according to literature methods. All commercially available solid reagents for use in air sensitive reactions were dried under vacuum for a minimum of 12 hours or used as received. HgI₂, I₂ and CuCl₂ were purchased from Sigma-Aldrich and were used without further purification.

Single crystal X-ray crystallography data were collected using an Oxford Diffraction Excalibur Eos diffractometer with Mo K α radiation at 170(2) K. All structures were solved using SHELXT and least-squares refinement using SHELXL in Olex2.⁶⁻⁸ Absorption corrections were applied using *Crysalis PRO* 1.171.38.42b (Rigaku Oxford Diffraction, 2015) or 1.171.37.34 (Agilent Technologies, 2014) software. Unless otherwise stated, all non-hydrogen atoms refined with anisotropic displacement parameters and hydrogen atoms were placed and refined using a riding model.

1.2 Synthesis of complexes

1.2.1 1^{Me} [$\text{K}_8(\text{pTP}^{\text{Me}})_2(\text{THF})_{11}$]

A Schlenk flask was charged with $\text{H}_4(\text{pTP}^{\text{R}})$ ($\text{R} = \text{Me}$) (2.00 g, 0.265 mmol) and $\text{KN}(\text{SiMe}_3)_2$ (2.11 g, 1.06 mmol) and a stirrer bar. THF (20 mL) was added and the resulting yellow solution was stirred for two hours at room temperature. Hexane was subsequently added to precipitate the product as colourless crystals of 1^{Me} which were isolated by filtration and dried under vacuum. Yield: 2.85 g (85%). Colourless single crystals of 1^{Me} [$\text{K}_8(\text{pTP}^{\text{Me}})_2(\text{THF})_{11}$] were obtained from a concentrated THF solution layered with hexane at room temperature.

^1H NMR (500 MHz, benzene- d_6) δ 8.06 (d, $J = 7.6$ Hz, 2H, Ar), 7.70 (d, $J = 7.6$ Hz, 2H, Ar), 7.21 (d, $J = 8.1$ Hz, 4H, Ar), 7.06 (d, $J = 8.1$ Hz, 2H, Ar), 6.98 (m, 2H, Ar), 6.91 (m, 2H, Ar), 6.90 (m, 2H, Ar), 6.87 (s, 4H, Ar), 5.95 (s, 2H, Benzylic-CH), 5.85 (s, 2H, Benzylic-CH), 2.38 (s, 6H, Me), 2.31 (s, 6H, Me), 2.22 (s, 6H, Me), 2.15 (s, 6H, Me), 1.60 (s, 18H, ^tBu), 1.55 (s, 18H, ^tBu), 1.52 (s, 18H, ^tBu), 1.21 (s, 18H, ^tBu). Anal. Calcd $\text{C}_{144}\text{H}_{204}\text{K}_8\text{O}_{18}$ (2535.93): C, 68.20; H, 8.11. Found: C, 67.93; H, 8.05.

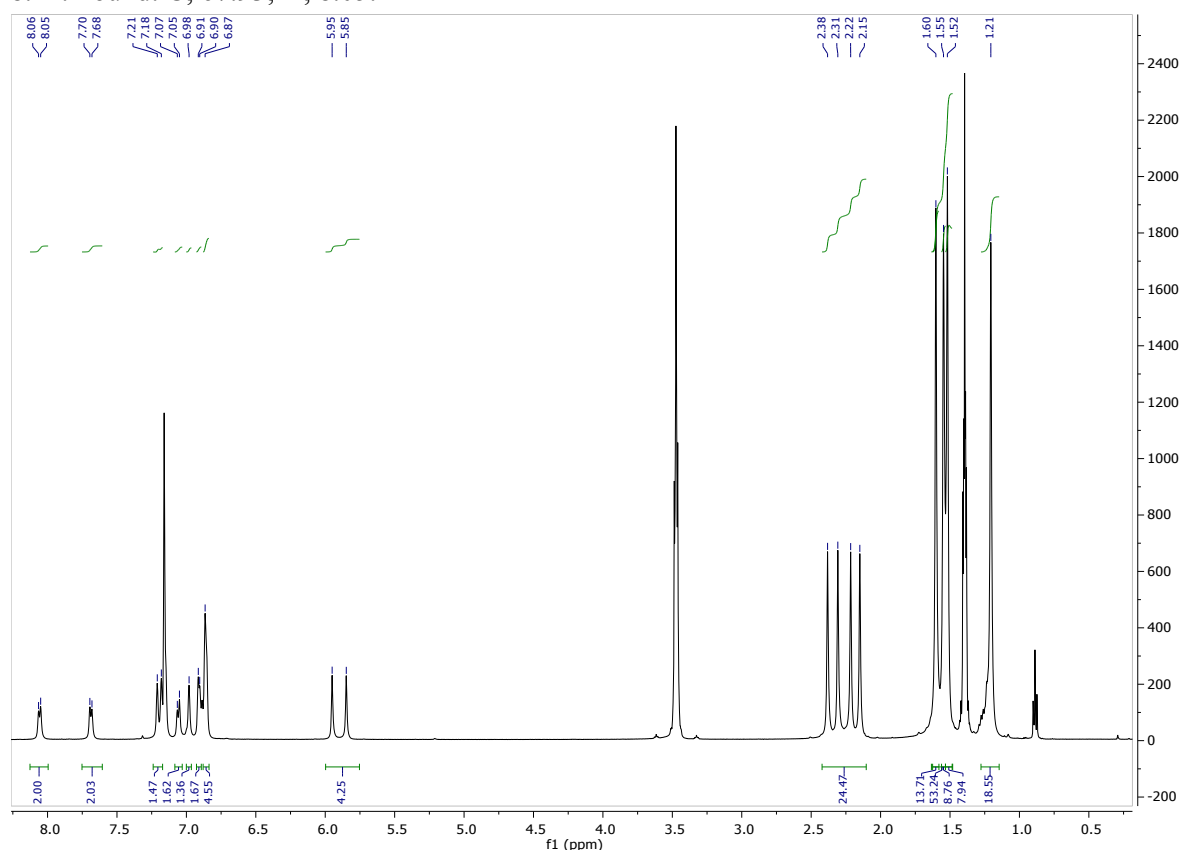


Figure S1. ^1H NMR spectrum of complex 1^{Me} in d^8 -THF.

1.2.2 2^{R} [$\text{K}(\text{THF})_5$][$\text{KCe}_2(\text{pTP}^{\text{R}})_2(\text{THF})_4$]

a) 2^{Me} , [$\text{K}(\text{THF})_5$][$\text{KCe}_2(\text{pTP}^{\text{Me}})_2(\text{THF})_4$]

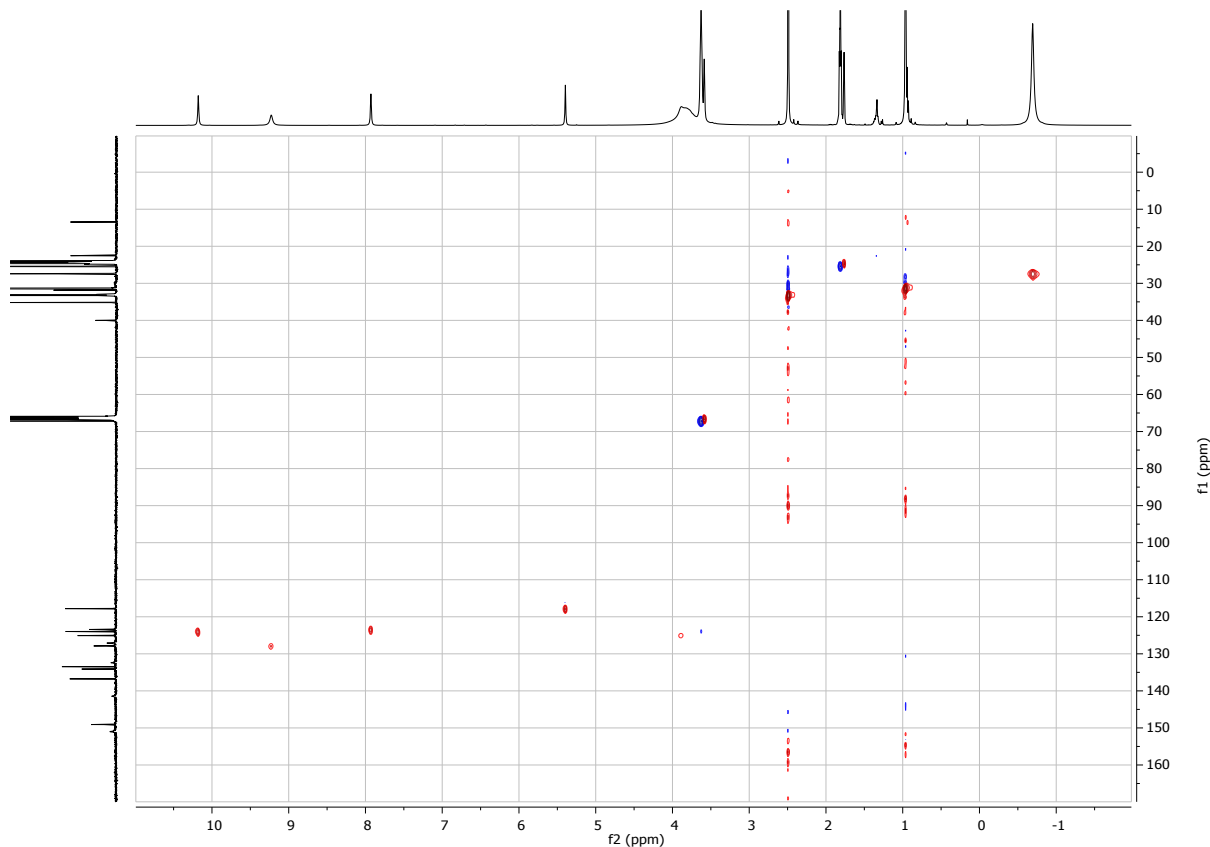
Complex 1^{Me} 1.268 g (5 mmol) was dissolved in 10 ml of THF and was then slowly added (over 2 mins) to THF suspension of $\text{CeCl}_3(\text{THF})_2$ 0.392 g (10 mmol) with stirring. The white suspension was left to stir overnight at room temperature. The afforded cloudy suspension was

the filtered off and the pale yellow filtrate was collected and the solvents of the solution were removed under reduced pressure to afford a colourless oily residue. Hexane was then added to precipitate the product 2^{Me} , $[\text{K}(\text{THF})_5][\text{KCe}_2(p\text{TP}^{\text{Me}})_2(\text{THF})_4]$ as a white powder which was collected by filtration and then washed with hexane and dried under reduced pressure. Yield: 1.43 g (85%). Colourless crystals of 2^{Me} were grown from a concentrated THF solution at -30°C . ^1H NMR (500 MHz, $\text{THF}-d_8$) δ 9.74 (s, 4H, Ar), 8.89 (s, 4H, Ar), 7.82 (s, 4H, Ar), 5.48 (s, 4H, Ar), 3.77 (s, 12H, Me), 3.45 (s, 36H, ^iBu), 2.00 (s, 12H, Me), -0.35 (s, 36H, ^iBu). Anal. Calcd $\text{C}_{150}\text{H}_{218}\text{Ce}_2\text{K}_2\text{O}_{19}$. C, 67.13; H, 8.19; Found: C, 66.81; H, 7.82.

b) 2^{tBu} , $[\text{K}(\text{THF})_5][\text{KCe}_2(p\text{TP}^{\text{tBu}})_2(\text{THF})_4]$

Following an analogous procedure to 2^{Me} , the reaction of 0.924 g (1 mmol) of $\text{H}_4(p\text{TP}^{\text{tBu}})$ and 0.802 g (1 mmol) of $\text{KN}(\text{SiMe}_3)_2$ resulted in a yellow solution of $[\text{K}_4(p\text{TP}^{\text{tBu}})]_2$ complex which was stirred for 2 hours and was then added to the THF suspension of $\text{CeCl}_3(\text{THF})_2$ 0.392 g (1 mmol) to afford 2^{tBu} , $[\text{K}(\text{THF})_5][\text{KCe}_2(p\text{TP}^{\text{tBu}})_2(\text{THF})_4]$ in a yield of 82% after work up. Single crystals were obtained from storage of a concentrated THF solution at room temperature for 6 hours.

^1H NMR (500 MHz, $\text{THF}-d_8$) δ 10.10 (s, 4H, Ar), 9.16 (s, 4H, Ar), 7.92 (s, 4H, Ar), 5.41 (s, 4H, Ar), 3.92 (s, 4H, Ar), 3.82 (s, 36H, ^iBu), 2.47 (s, 36H, ^iBu), 0.96 (s, 36H, ^iBu), -0.61 (s, 36H, ^iBu). ^{13}C NMR (126 MHz, $\text{THF}-d_8$) δ 200.19 (s, Ar), 152.22 (s, Ar), 150.31 (s, Ar), 137.98 (s, Ar), 135.34 (s, Ar), 134.68 (s, Ar), 133.64 (s, Ar), 129.10 (s, Ar), 128.33 (s, Ar), 125.20 (s, Ar), 124.65 (s, Ar), 119.02 (s, Ar), 36.41 (s, ^iBu), 34.50 (s, ^iBu), 34.36 (s, ^iBu), 34.25 (s, ^iBu), 33.11 (s, ^iBu), 32.78 (s, ^iBu), 32.58 (s, ^iBu), 28.67 (s, ^iBu). Elemental Analysis: Calcd. for $\text{C}_{148}\text{H}_{212}\text{Ce}_2\text{K}_2\text{O}_{13}$. C, 69.50; H, 8.35; Found: C, 69.04; H, 8.03.



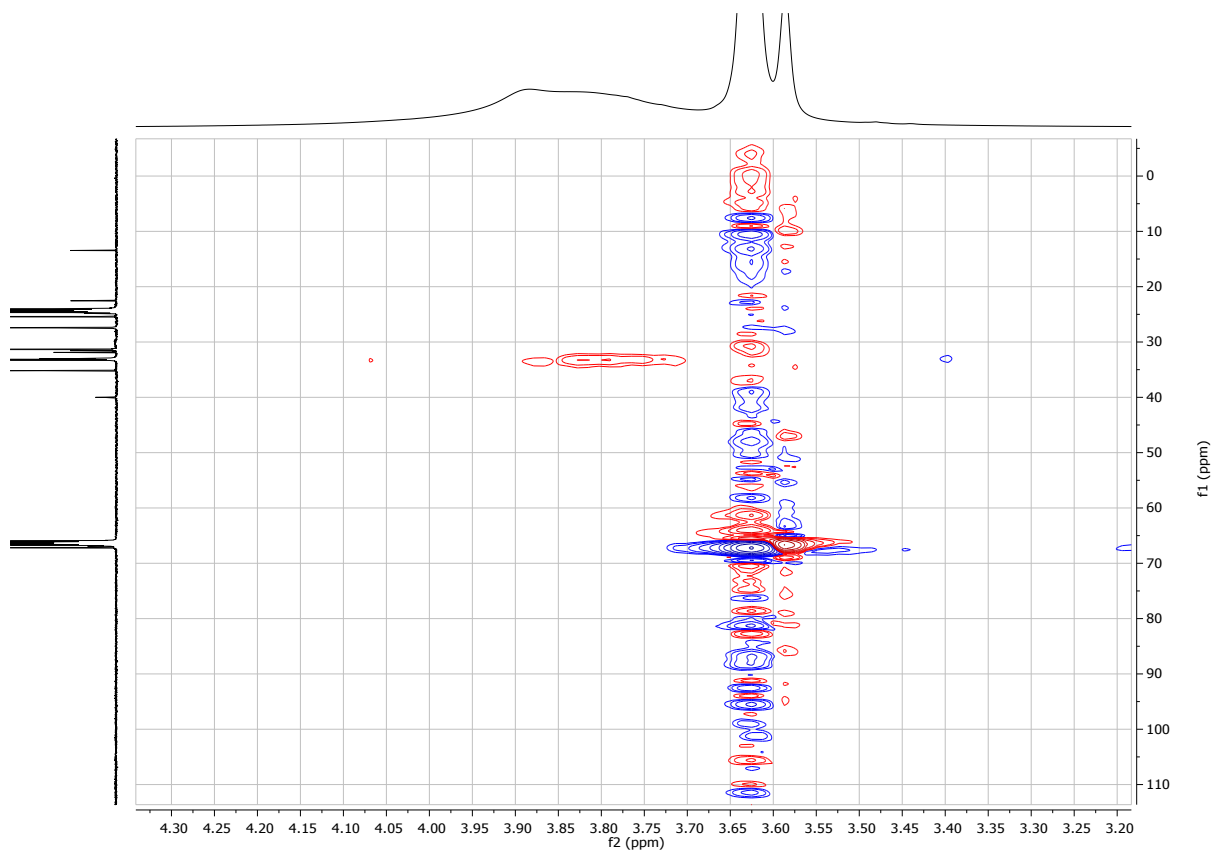


Figure S2. ^{13}C - ^1H HSQC NMR spectrum of complex 2^{tBu} (top: full spectrum; bottom: 4.3 ppm-3.20 ppm).

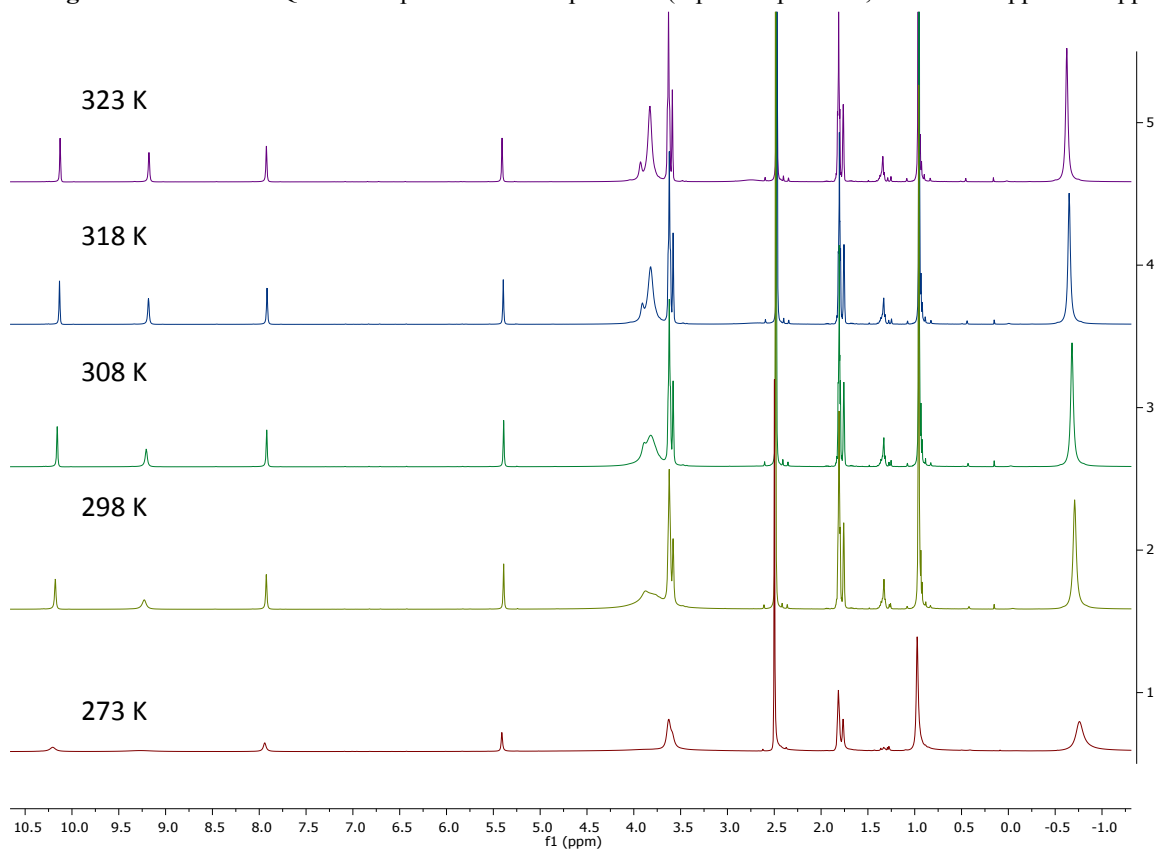


Figure S3. VT- ^1H NMR spectrum of complex 2^{tBu} .

1.2.3 2^R-solvates

a) 2^{Me}-THF, [K(THF)₃][KCe₂(pTP^{Me})₂(THF)₄]

To a yellow THF solution of complex 2^{Me} (0.215 g, 0.08 mmol, 10 ml) was added 10 ml of hexane, and the resulting solution was stored at -30 °C for a few days during which time colourless crystals of 2^{Me}-THF, [K(THF)₃][KCe₂(pTP^{Me})₂(THF)₄] formed and were isolated by decantation and drying *in vacuo*. Yield: 0.167 g (~80%). The ¹H NMR spectrum is the same as that of THF-*d*₈ solutions of 2^{Me}-py.

a) 2^{Me}-py, K(py)₆[KCe₂(pTP^{Me})₂(py)₄]

A Schlenk was charged with 2^{Me} (0.268 g, 0.1 mmol) and pyridine (5 ml) and stirred at 298K for 2 hours until dissolved. After removal of volatiles under reduced pressure, 5 ml of hexane was added to the oily residue to precipitate yellow 2^{Me}-py, [K(py)₆][KCe₂(pTP^{Me})₂(py)₄], which was isolated by filtration, washed with hexane and dried under vacuum. Pale yellow crystals were obtained from a concentrated pyridine solution stored at -30 °C. Yield: 0.264 (82%).

¹H NMR (500 MHz, Pyridine-*d*₅) δ 10.27 (s, 4H, Ar), 10.20 (s, 4H, Ar), 9.74 (s, 4H, Ar), 5.51 (s, 4H, Ar), 5.44 (s, 4H, Ar), 4.17 (s, 12H, Me), 2.91 (s, 36H, ^tBu), 2.33 (s, 12H, Me), -3.48 (s, 36H, ^tBu). ¹³C NMR (126 MHz, Pyridine-*d*₅) δ 196.64 (s, Ar), 152.18 (s, Ar), 143.58 (s, Ar), 138.55 (s, Ar), 129.50 (s, Ar), 126.37 (s, Ar), 120.24 (s, Ar), 68.37 (s, Ar), 40.29 (s, ^tBu), 36.52 (s, ^tBu), 34.90 (s, ^tBu), 34.50 (s, ^tBu), 33.54 (s, ^tBu), 33.00 (s, ^tBu), 32.14 (s, ^tBu), 27.53 (s, ^tBu), 26.40 (s, ^tBu).

Anal. Calcd C₉₅H₁₀₉CeKN₈O₄. C, 71.04; H, 6.84; N, 6.98. Found: C, 70.73; H, 6.58; N, 7.27.

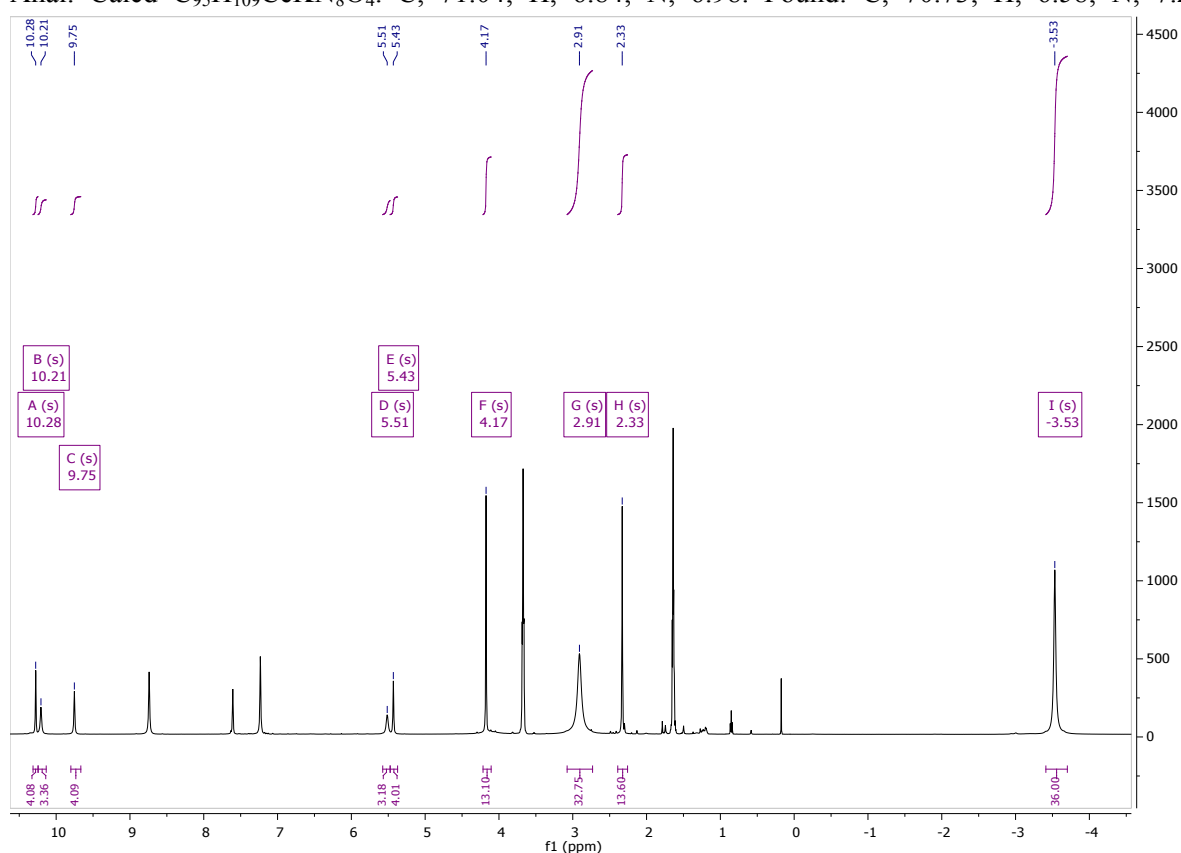


Figure S4. ¹H NMR spectrum of complex 2^{Me}-py.

b) **2^{Me}-cr**, [K(18-crown-6)(THF)₂][KCe₂(*p*TP^{Me})₂(THF)₄].

A Schlenk was charged with 18-crown-6 (0.028 g, 0.11 mmol), **2^{Me}** (0.237 g, 0.1 mmol) and THF (5 ml), and the mixture was stirred for 2 hours. 5 mL of hexane was added to the solution and the flask was stored at -30 °C. Colourless crystals of **2^{Me}-cr**, [K(18-crown-6)₃(THF)₂][KCe₂(*p*TP^{Me})₂(THF)₄] were obtained after several days and isolated by decantation of the supernatant and drying. Yield: 0.181 g (71%). ¹H NMR (500 MHz, THF-*d*₈) δ 9.77 (s, 4H, Ar), 8.94 (s, 4H, Ar), 7.89 (s, 4H, Ar), 5.54 (s, 4H, Ar), 3.81 (s, 12H, Me), 3.66 (s, 24H, CH₂), 3.44 (s, 36H, ^tBu), 2.05 (s, 12H, Me), -0.39 (s, 36H, ^tBu). ¹³C NMR (126 MHz, THF-*d*₈) δ 197.27 (s, Ar), 152.52 (s, Ar), 143.56 (s, Ar), 138.61 (s, Ar), 137.48 (s, Ar), 136.38 (s, Ar), 129.58 (s, Ar), 126.39 (s, Ar), 120.21 (s, Ar), 40.32 (s, ^tBu), 36.54 (s, ^tBu), 34.90 (s, ^tBu), 34.53 (s, ^tBu), 33.52 (s, ^tBu), 33.01 (s, ^tBu), 32.20 (s, ^tBu), 32.02 (s, ^tBu), 27.37 (s, ^tBu), 26.40 (s, ^tBu), 23.28 (s, ^tBu).

Anal. Calcd C₁₄₀H₁₉₂Ce₂K₂O₂₀. C, 65.80; H, 7.58. Found: C, 65.49; H, 7.33.

1.2.4 **2^{tBu}-Pr**, [K(THF)₅][KPr₂(*p*TP^{tBu})₂(THF)₄]

Following an analogous procedure to the synthesis of **2^{tBu}-Ce** but using PrCl₃(THF)₂, complex **2^{tBu}-Pr** is isolated in a yield of 85% after work up. Single crystals were obtained from storage of a concentrated THF solution of **2^{tBu}-Pr** at room temperature.

¹H NMR (500 MHz, THF-*d*₈) δ 34.58 (s, 4H, Ar), 27.92 (s, 4H, Ar), 26.72 (s, 36H, ^tBu), 13.14 (s, 36H, ^tBu), -2.59 (s, 36H, ^tBu), -11.41 (s, 4H, Ar), -17.64 (s, 36H, ^tBu).

¹³C NMR (126 MHz, THF-*d*₈) δ 166.77 (s, Ar), 165.80 (s, Ar), 164.64 (s, Ar), 122.49 (s, Ar), 116.63 (s, Ar), 96.75 (s, Ar), 85.26 (s, ^tBu), 51.27 (s, ^tBu), 47.37 (s, ^tBu), 33.58 (s, ^tBu), 28.92 (s, ^tBu).

Anal. Calcd C₁₆₀H₂₃₆Pr₂K₂O₁₆. C, 69.28; H, 8.58; Calcd for **2^{tBu}-Pr** + 2THF: C₁₆₈H₂₅₂Pr₂K₂O₁₈. C, 69.11; H, 8.70; Found: C, 68.87; H, 8.52.

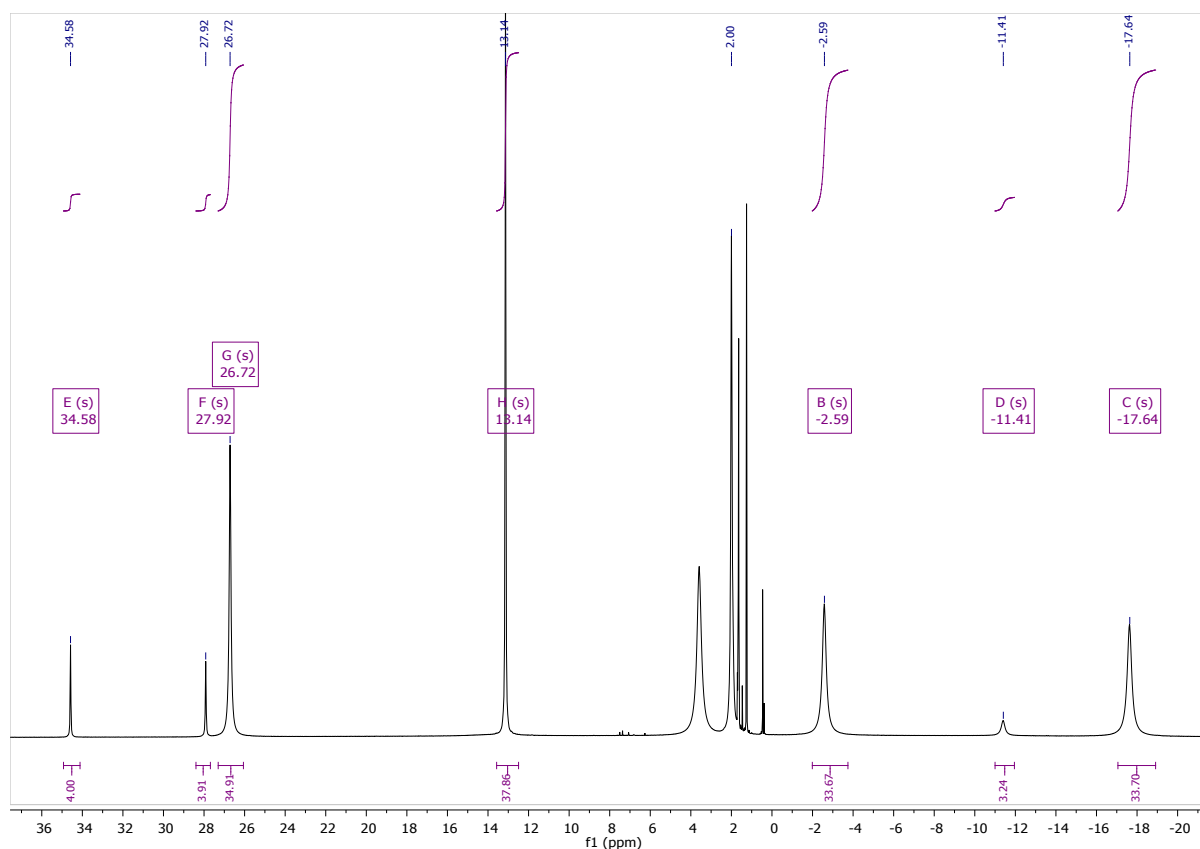


Figure S5. ^1H NMR spectrum of complex $2^{\text{Me-Pr}}$.

1.2.5 3^{tBu} , [$\{\text{LnX}(\text{THF})_2\}_2(p\text{TP}^{\text{tBu}})$] Ln = Ce,Pr X = Cl

A Teflon-valved ampoule was charged with $\text{H}_4(p\text{TP}^{\text{tBu}})$ (0.923 g, 1 mmol), KN^{III} (4 eq, 0.799 g, 0.4 mmol), THF (10 ml), and a magnetic stirrer-bar, and stirred for 1 hour. The resulting yellow solution was slowly added to a THF suspension of $\text{PrCl}_3(\text{THF})_2$, (2eq, 0.655 g, 2 mmol) and the mixture allowed to stir at room temperature for 16 h. The supernatant was isolated by filtration and evaporated to a colourless solid under reduced pressure. The solids were then extracted with pyridine (2 x 20 ml), dried, and washed with hexane, then dried *in vacuo* to afford $3^{\text{tBu-Pr}}$, [$\{\text{PrCl}(\text{THF})_2\}(p\text{TP}^{\text{tBu}})$]. Single crystals of complex $3^{\text{tBu-Pr}}$ suitable for X-ray were grown by vapour diffusion of hexane into a saturated pyridine solution at ambient temperature. Yield: 0.173 g (90%).

$3^{\text{tBu-Pr}}$

^1H NMR (500 MHz, pyridine- d_5) δ 15.35 (s, 4H, Ar), 14.18 (s, 4H, Ar), 5.33 (s, 4H, Ar), 3.91 (s, 36H, $^{\text{tBu}}$), 3.71 (s, 2H, benzylic-CH), 2.30 (s, 36H, $^{\text{tBu}}$). ^{13}C NMR (126 MHz, Pyridine- d_5) δ 157.63, 142.01, 132.28, 125.97, 35.51, 34.15, 30.37.

Anal. Calcd. $\text{C}_{104}\text{H}_{126}\text{Pr}_2\text{Cl}_2\text{N}_8\text{O}_4$. C, 65.63; H, 6.67; N, 5.89. Found: C, 65.28; H, 6.56; N, 5.71.

3^tBu-Ce

Following an analogous procedure, treatment with CeCl₃(THF)₂ led to the formation of the Ce analogue complex **3^tBu-Ce** [$\{\text{CeCl}(\text{THF})_2\}_2(p\text{TP}^{\text{tBu}})$]. Yield 90%.

¹H NMR (500 MHz, pyridine-*d*₅) δ 10.62 (s, 4H, Ar), 9.61 (s, 4H, Ar), 5.27 – 4.67 (br s, 4H, Ar), 3.68 (s, 2H, benzylic-CH), 2.03 (s, 36H, ^tBu), 0.20 (s, 36H, ^tBu). ¹³C NMR (126 MHz, Pyridine-*d*₅) δ 155.91, 140.76, 131.27, 126.54, 35.94, 33.94, 30.49. Anal. Calcd. C₁₀₄H₁₂₆Ce₂Cl₂N₈O₄. C, 65.57; H, 6.67; N, 5.88. Found: C, 65.31; H, 6.34; N, 5.73.

1.2.6 **3^tBu-Ce-BH₄** [$\{\text{Ce}(\text{BH}_4)(\text{py})_4\}_2(p\text{TP}^{\text{tBu}})$]

A pyridine solution of [K₈(*p*TP^{tBu})₂] 0.127 g (0.5 mmol) was slowly added to a Schlenk flask which was charged with pyridine solution of 0.185 g (1 mmol) Ce(BH₄)₃. The mixture was allowed to stir overnight at room temperature to form a pale yellow solution. Hexane was added to precipitate the product as a white powder. The solid was further washed with hexane and was dried under reduced pressure. Yield: 0.134 g (80%). Colourless single crystals of the pyridine solvate [$\{\text{Ce}(\text{BH}_4)(\text{py})_4\}_2(p\text{TP}^{\text{tBu}})$] were grown from a saturated pyridine solution at -30 °C.

¹H NMR (500 MHz, pyridine-*d*₅) δ 10.49 (s, 4H, Ar), 9.62 (s, 4H, Ar), 4.13 (s, 4H, Ar), 3.69 (t, *J* = 7.4 Hz, 2H), 2.09 (s, 36H, ^tBu), 0.02 (s, 36H, ^tBu). ¹³C NMR (126 MHz, Pyridine-*d*₅) δ 196.01, 155.45, 143.24, 141.10, 131.14, 125.67, 68.36, 40.44, 37.24, 35.97, 33.99, 32.27, 30.32, 26.36. ¹¹B NMR (160 MHz, pyridine-*d*₅) δ 20.9 (br s). Anal. Calcd. C₂₃₃H₂₉₃B₄Ce₄N₂₁O₈. Calcd: C, 67.93; H, 7.17; N, 7.14. Found: C, 67.61; H, 7.08; N, 7.29.

1.2.7 Reactions of H₄(*p*TP^{tBu}) with Ce(BH₄)₃ to target [$\{\text{Ce}(\text{BH}_4)(\text{py})_4\}_2(p\text{TP}^{\text{tBu}})$]

A sample of 0.185 g (1 mmol) of Ce(BH₄)₃ reacts with 0.041 g (0.5 mmol) of H₄(*p*TP^{tBu}) in THF with borane acceptors (P(Cy)₃, P(Ph)₃ or DABCO) to liberate hydrogen gas as verified by ¹H NMR spectroscopy. Monitoring these reactions by NMR spectroscopy shows that each reaction takes around 5 days to reach completion. The NMR spectra of the final product mixtures are similar and contain a set of paramagnetically shifted ligand resonances, regardless of the borane acceptor but also contain some unidentified by-products that could not be separated. Attempts to crystallize the resulting products resulted in the crystallization of the borane adduct, but yields could not be determined with confidence.

¹H NMR (500 MHz, pyridine-*d*₅) δ 10.70 (s, 4H, Ar), 9.56 (s, 4H, Ar), 4.44 (s, 2H, benzylic-CH), 3.54-2.89 (m, 8H, BH₄), 2.17 (s, 36H, ^tBu), -0.08 (s, 36H, ^tBu), -3.48 (s, 4H), -8.36 (s, 18H). ¹¹B NMR (160 MHz, Pyridine-*d*₅) δ 12.26 (br s).

1.2.8 **4^{tBu}**, [Ce₂(*p*TP^{tBu})₂(THF)₄]

To a stirred THF (5 mL) solution of 0.256 g (0.1 mmol) complex **2^{tBu}-Ce** was added over a few minutes a THF slurry of an equimolar quantity of oxidant: Cu(OTf)₂ (0.0362 g, 0.1 mmol), CuCl₂ or I₂. In each case, the solution colour changed to dark blue/purple immediately, and salts were precipitated. These salts were removed by centrifugation and the supernatant dried *in vacuo*. Hexane was added to the paste, and the resulting blue powder isolated, dried, and characterised as **4^{tBu}**, [Ce₂(*p*TP^{tBu})₂(THF)₄]. Single crystals were grown by slow diffusion of hexane into a THF solution. Yield: 0.174 g, 72 %.

¹H NMR (400 MHz, pyridine-*d*₅) δ 8.12 (d, *J* = 2.5 Hz, 4H, Ar), 8.10 (d, *J* = 2.5 Hz, 4H, Ar), 7.59 (4H, Ar), 7.57 (4H, Ar), 7.38 (s, 2H, benzylic-CH), 7.28 (d, *J* = 2.5 Hz, 4H, Ar), 1.58 (s, 36H, ^tBu), 1.42 (s, 36H, ^tBu), 1.39 (s, 36H, ^tBu), 1.17 (s, 36H, ^tBu).

¹³C NMR (101 MHz, pyridine-*d*₅) δ 170.86 (s, Ar), 166.00 (s, Ar), 143.34 (s, Ar), 141.54 (s, Ar), 141.10 (s, Ar), 140.79 (s, Ar), 138.15 (s, Ar), 132.84 (s, Ar), 132.17 (s, Ar), 130.62 (s, Ar), 124.69 (s, Ar), 124.58 (s, Ar), 119.42 (s, Ar), 119.19 (s, Ar), 47.18 (s, Benzylic-CH), 35.95 (s, ^tBu), 35.75 (s, ^tBu), 34.94 (s, ^tBu), 34.74 (s, ^tBu), 32.72 (s, ^tBu), 32.58 (s, ^tBu), 31.76 (s, ^tBu), 31.71 (s, ^tBu).

Anal. Calcd C₁₄₄H₂₀₄Ce₂O₁₂. C, 71.84; H, 8.54; Found: C: 71.18; H, 8.42. Hit for (**4^{tBu}**(THF)₂) solvate: C₁₅₂H₂₂₀Ce₂O₁₄ Calc: C, 71.55; H, 8.69.

UV-vis: λ_{max} = 576, 283, 326 nm,

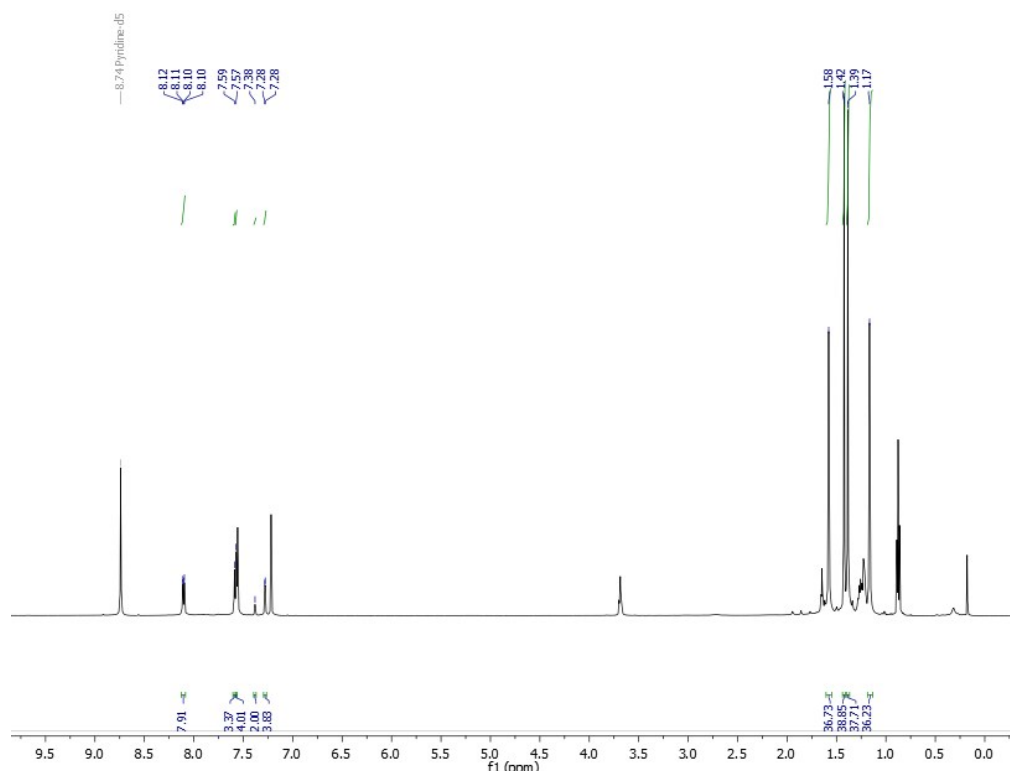


Figure S6. ¹H NMR spectrum of [Ce₂(*p*TP^{tBu})₂(THF)₄] (residual THF and hexane are visible).

1.2.9 Reaction of **2^{tbu}** with other oxidants.

Reaction of **2^{tbu}-Ce** with HgX₂

The reaction of **2^{tbu}-Ce** with HgCl₂ was carried out at -30 °C. A vial was charged with 0.02850 g (0.01 mmol) **2^{tbu}-Ce** in THF-d⁸ and was cooled to -30 °C. A cold THF-d⁸ solution of 2 eq. of HgX₂ (X = Cl, OAc) was then added into the solution of **2^{tbu}-Ce** with stirring. The colour of the solution changed to dark brown and was then transferred to a Young's tapped NMR tube. The ¹H NMR spectrum was collected at 243 K, in each case showing a paramagnetic intermediate, then at 298 K after allowing the sample to warm to ambient temperature, by which time the diamagnetic Ce(IV) product is now fully formed.

a: X = Cl. (0.0055 g, 0.02 mmol)

-30 °C (243 K): ¹H NMR (400 MHz, THF-d₈) δ 13.04 (s, 1H), 10.86 (s, 1H), 10.66 (s, 1H), 9.80 (s, 1H), 9.45 (s, 11H), 8.47 (s, 1H), 7.69 (d, *J* = 44.5 Hz, 2H), 7.51 (s, 1H), 7.31 (s, 2H), 7.19 – 6.65 (m, 11H), 6.47 (t, *J* = 11.1 Hz, 6H), 6.23 (d, *J* = 24.6 Hz, 2H), 6.00 (s, 1H), 5.68 (d, *J* = 35.1 Hz, 1H), 4.66 (d, *J* = 7.1 Hz, 1H), 3.01 (s, 9H), 1.93 (s, 9H), 1.67 – 1.45 (m, 48H), 9 0.58 (s, 9H, ^tBu), 0.33 (s, 18H, ^tBu), -0.36 (s, 18H, ^tBu), -1.94 (s, 18H, ^tBu).

25 °C (298 K): ¹H NMR (400 MHz, THF-d₈) δ 7.68 (s, 2H), 7.58 (d, *J* = 2.4 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 2.4 Hz, 3H), 7.37 (d, *J* = 2.4 Hz, 4H), 7.31 (d, *J* = 2.4 Hz, 5H), 7.08 (dd, *J* = 7.3, 2.4 Hz, 3H), 7.04 (dd, *J* = 5.8, 3.0 Hz, 7H), 6.99 (s, 2H), 6.96 (d, *J* = 8.7 Hz, 4H), 6.91 – 6.75 (m, 25H), 1.57 (s, 46H), 1.52 (d, *J* = 4.8 Hz, 32H), 1.28 (s, 17H), 1.26 (d, *J* = 4.5 Hz, 28H), 1.23 (s, 27H), 1.15 (dt, *J* = 9.7, 4.0 Hz, 101H), 1.10 (s, 12H), 1.05 (s, 16H), 0.99 (s, 16H).

b: X = OAc, (0.0064 g, 0.02 mmol)

The reaction of **2^{tbu}** and Hg(OAc)₂ at -30 °C affords a dark blue solution immediately. The ¹H NMR spectrum at -30 °C (243 K) shows 10% of paramagnetic product and one major (90%) diamagnetic product.

-30 °C (243 K): ¹H NMR (400 MHz, THF-d₈) δ 10.32 (s, 1H), 9.76 – 8.96 (m, 8H), 7.37 (d, *J* = 2.4 Hz, 4H), 7.34 (d, *J* = 2.1 Hz, 2H), 6.94 (s, 10H), 6.86 (d, *J* = 2.5 Hz, 4H), 6.75 (d, *J* = 2.2 Hz, 2H), 6.73 (s, 2H), 5.49 (s, 2H), 4.62 (s, 2H), 2.40 (d, *J* = 30.1 Hz, 36H), 1.47 (d, *J* = 8.0 Hz, 36H), 1.35 – 1.21 (m, 51H), 1.17 (s, 36H), 1.10 (s, 36H).

25 °C (298 K): ¹H NMR (400 MHz, THF-d₈) δ 7.33 (d, *J* = 12.4 Hz, 4H, Ar), 7.07 (s, 4H, Ar), 6.95 (s, 2H, benzylic-CH), 6.88 (s, 4H, Ar), 1.46 (s, 18H, ^tBu), 1.34 (s, 18H, ^tBu), 1.19 (s, 18H, ^tBu), 1.14 (s, 18H, ^tBu).

In the reaction with two equivalents of HgCl₂ at -30 °C, paramagnetic shifts at 13.04, 10.86 9.8 and -1.93 ppm *etc.* are observed which suggest the possible formation of new products (a, **Figure S7**). Given the paramagnetic ¹H NMR spectrum, an intermediate which contains Ce^{III} ions and Hg^{II} ions can still be deduced. No resonance for Hg could be found in the range from +3300 to -3300 ppm in the ¹⁹⁹Hg NMR spectrum, suggesting the cation is closely associated with the paramagnetic complex. These paramagnetically shifted products transformed to diamagnetic species when warmed up to room

temperature. As shown in **Figure S7**, two complexes can be identified upon warming. One set of the resonances (marked with an asterisk) are identified as to those of **4^{tBu}** (d) whilst the other species is a by-product that has not been determined (b, **Figure S7**).

The reaction using only one equivalent of HgCl₂ at room temperature affords the same product, leaving half equivalent of K₂L₂Ce₂ unreacted.

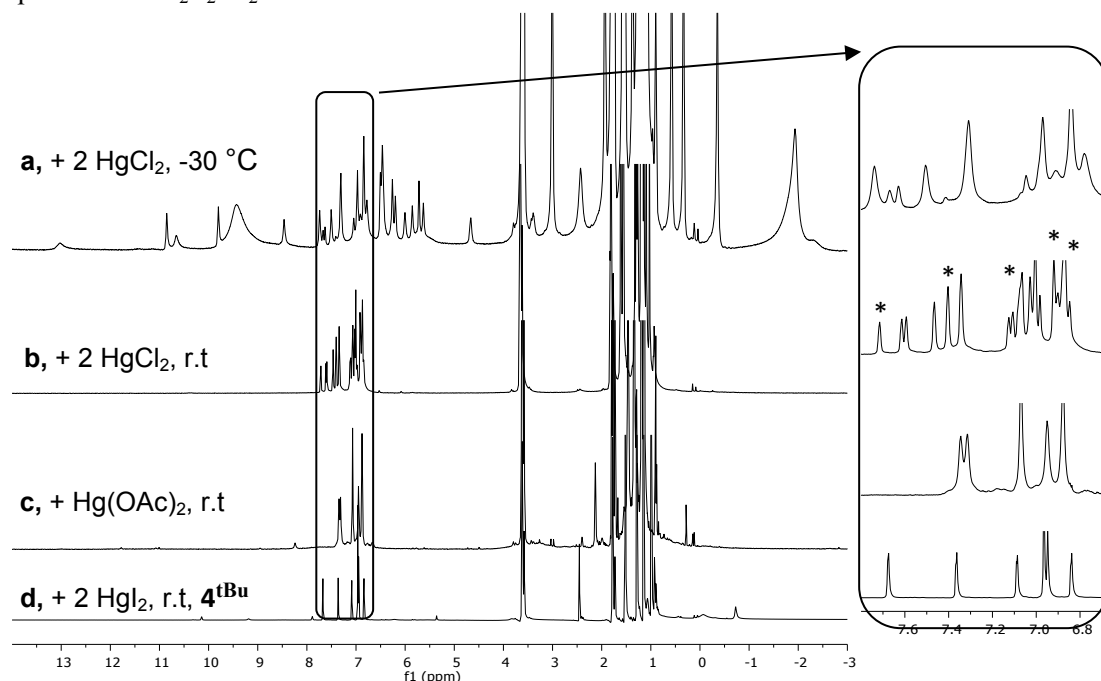


Figure S7. Reaction of **2^{tBu}-Ce** with HgX₂ (X = OAc, Cl, I).

The reaction of **2^{tBu}-Ce** with one equivalent of Hg(OAc)₂ at -30 °C takes 8 hours to reach completion. The ¹H NMR spectrum of the product (c, **Figure 7**) shows different resonances to any of those species discussed above. After compared with the NMR spectrum of **4^{tBu}** and the starting material **2^{tBu}-Ce**, the diamagnetic resonances suggest the formation of a new Ce^{IV} complex.

General procedure: To a stirring THF (5 mL) solution of 0.286 g (0.1 mmol) **2^{tBu}-Ce** was slowly added a THF solution of oxidants. The mixture was allowed to stir for 2 hours. The salt by-products were removed by centrifugation and the supernatant evaporated to dryness under reduced pressure. Hexane (5 ml) was added to the paste to triturate, then after further drying under reduced pressure, the resulting powder was collected and dried *in vacuo*.

a: 1,4-benzoquinone 0.0108 g (0.1 mmol). Dark brown/purple solution and dark brown solid obtained after work up.

¹H NMR (500 MHz, THF-*d*₈) δ 7.28 (s, 4H, Ar), 7.00 (s, 4H, Ar), 6.86 (s, 4H, Ar), 5.97 (s, 4H, Ar), 1.45 (br s, 18H, ^tBu), 1.22 (s, 18H, ^tBu), 1.13 (s, 18H, ^tBu), 1.11 – 0.96 (br s, 9H, ^tBu). UV-vis: λ_{max} = 513 nm

b: O₂. A Young's NMR tube was charged with a THF-*d*₈ (1 mL) solution of 0.143 g (0.05 mmol) **2^{tBu}-Ce**. The NMR tube was then degassed. Dry air was passed through a drying column and was added to the solution at a pressure of 1 atm. The colour of the solution changed to red-brown immediately. The NMR tube was then vigorously shaken and the mixture was open to dried air for 1 min. The generated salts were removed by centrifugation and the solution isolated and dried under reduced pressure.

Hexane was added to wash the paste, the resulting powder was collected and dried under reduced pressure.

^1H NMR (500 MHz, THF- d_8) δ 7.67 (s, 4H, Ar), 7.36 (s, 4H, Ar), 7.24 (s, 4H, Ar), 7.08 (s, 4H, Ar), 7.03 (d, $J = 8.9$ Hz, 4H, Ar), 6.95 (d, $J = 10.0$ Hz, 16H, Ar), 6.83 (s, 4H, Ar), 1.51 (s, 36H, ^tBu), 1.28 (s, 36H, ^tBu), 1.14 (d, $J = 4.8$ Hz, 36H, ^tBu), 0.98 (s, 36H, ^tBu).

UV-vis: $\lambda_{\text{max}} = 472$ nm.

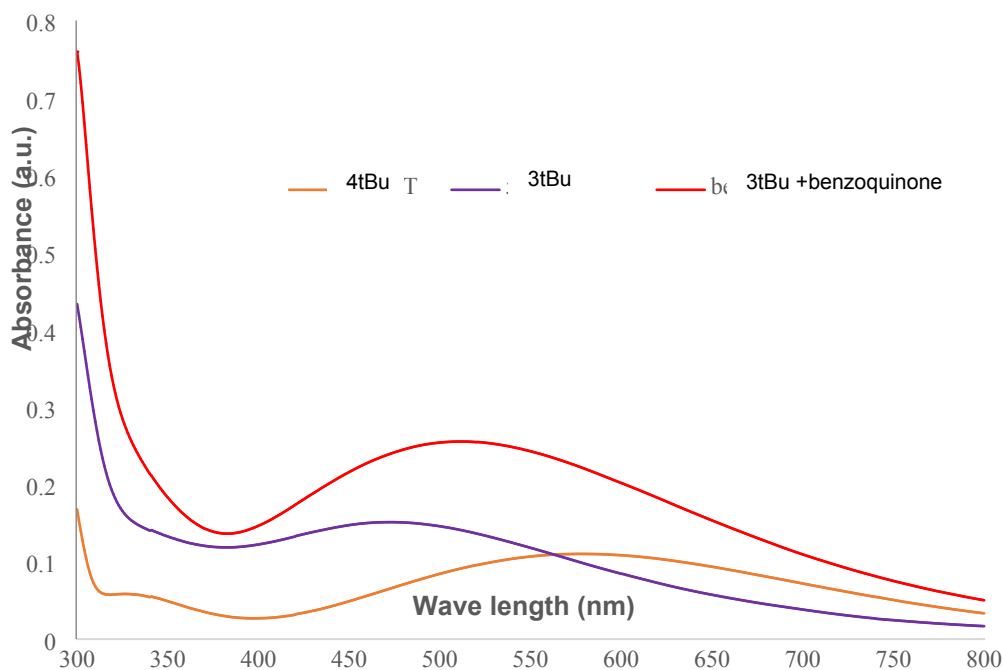


Figure S8. Electron absorption spectra for the Ce^{IV} complex 4^{tBu} (orange line) in the visible range in comparison with reactions of Ce^{III} complex 2^{tBu} with O_2 (purple line) and 1, 4-benzoquinone (red line).

1.2.10 Reaction of complex $2^{\text{tBu-Pr}}$ with I_2 .

A THF (7 mL) solution of 0.296 g (0.1 mmol) complex $2^{\text{tBu-Pr}}$ was added a THF (3 ml) solution of 0.013g (0.1 mmol) I_2 . The brown solution was then heated for 8 hours in an oil bath at 60°C . Upon heating, the solution gradually changed to dark green. After filtration, the green solution was transferred to an ampoule to remove volatiles under reduced pressure. Hexane was then added to the green paste to afford a colourless powder which was filtered and washed with more hexane and then dried under reduced pressure. The green hexane filtrate and washings were collected and combined. Removal of volatiles afforded a green solid. Crystals of complex **5** were grown by slow diffusion of hexane into a THF solution of the green solid. Yield: 0.103 g, 29%.

Colourless residue (oxidation product): ^1H NMR (500 MHz, THF- d_8) δ 13.67 (s, 4H, Ar), 12.46 (s, 4H, Ar), 10.33 (s, 36H, ^tBu), 5.15 (s, 4H, Ar), 4.48 (s, 2H, Benzylic- CH), 1.17 (s, 36H, ^tBu). ^{13}C NMR (126 MHz, Pyridine- d_5) δ 156.58, 141.93, 132.11, 125.83, 35.25, 34.33, 30.25.

Green solution: ^1H NMR (500 MHz, THF- d_8) δ 17.94 (s, 4H, Ar), 15.23 (s, 4H, Ar), 11.07 (s, 4H, Ar), 10.85 (s, 18H, Ar), 0.71 (s, 18H), -0.09 (s, 18H, ^tBu).

1.2.11 Reaction of **2^{tbu}-Pr** with XeF₂

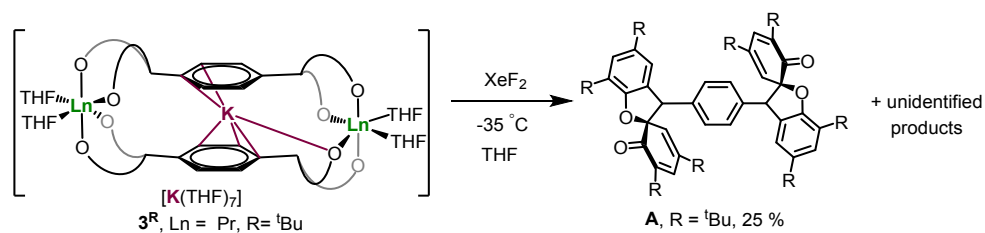


Figure S9: Reaction of Pr letterbox complex with XeF₂.

A THF solution (7ml) of 0.325 g (0.128 mmol) complex **3^{tbu}-Pr** was cooled to -35 °C in the freezer. A THF suspension of XeF₂ (0.022 g, 0.128 mmol) was then added to this solution with stirring at -35 °C. The colour of the solution changed gradually to green when solid of XeF₂ disappeared after stirring for 30 min. The volatiles of the solution were then removed at reduced pressure, affording green oily paste. Hexane was added to the paste and stirred for 10 min to extract organic product which was then decanted from the residue. Colourless crystals of product bicyclic ether **A** were grow from the concentrated hexane solution at room temperature.⁹ Yield: 0.119 g, 25%.

1.3 EPR spectra of powdered 2^{tBu}-Ce

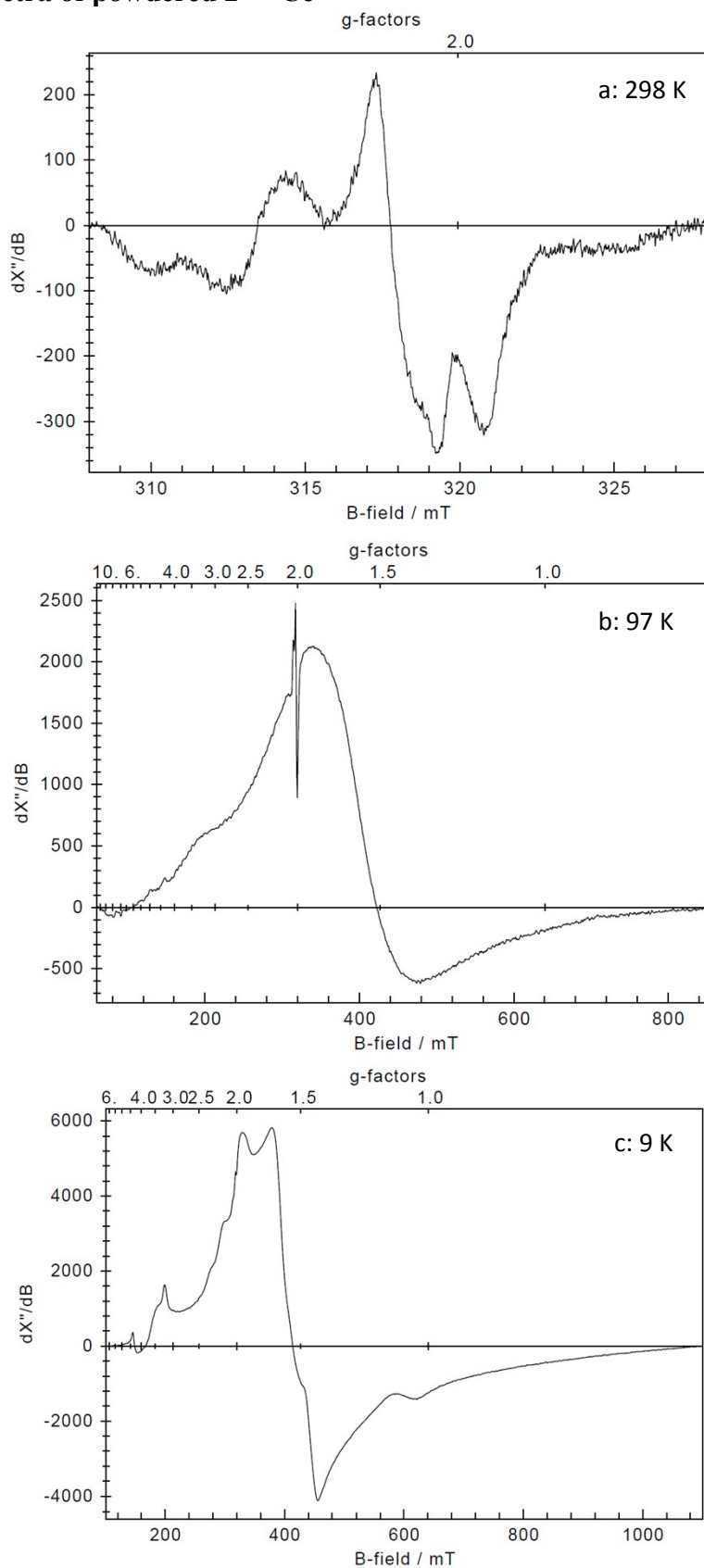


Figure S10: EPR spectrum of powdered 2^{tBu}-Ce , a) 298 K, b) 97K, c) 9 K. At 97 K the EPR spectrum shows a broadened spectrum in which the only observable transition is assigned as a g -parallel signal is to much higher field and not observed and an impurity is visible as a sharp peak at $g = 2.013$.

1.4 Electrochemistry details

Electrochemical measurements were carried out by using an Pine research WaveDriver® 200 Integrated Bipotentiostat/Galvanostat with EIS and the data processed using AfterMath Data Organizer V1.4. Experiments were undertaken at room temperature in a N₂ glovebox in a 25 mL electrochemical cell with a glassy-carbon disk working electrode, a platinum gauze as the counter electrode and a silver wire as the pseudo-reference electrode. The solution employed was 2 mM (for **2^{tBu}-Ce**) and 2 mM (for **4^{tBu}**) of the compound with 0.1 M [nBu₄N][PF₆] as the supporting electrolyte, in 10 mL dry THF. All potentials were referenced against [FcCp₂] (E_{1/2}, [Fc⁺/Fc] = 0.0 V). CVs were measured for quiescent solution at variable scan rates. Square wave voltammetry was carried out with Amplitude of 20mV and 10mV increment.

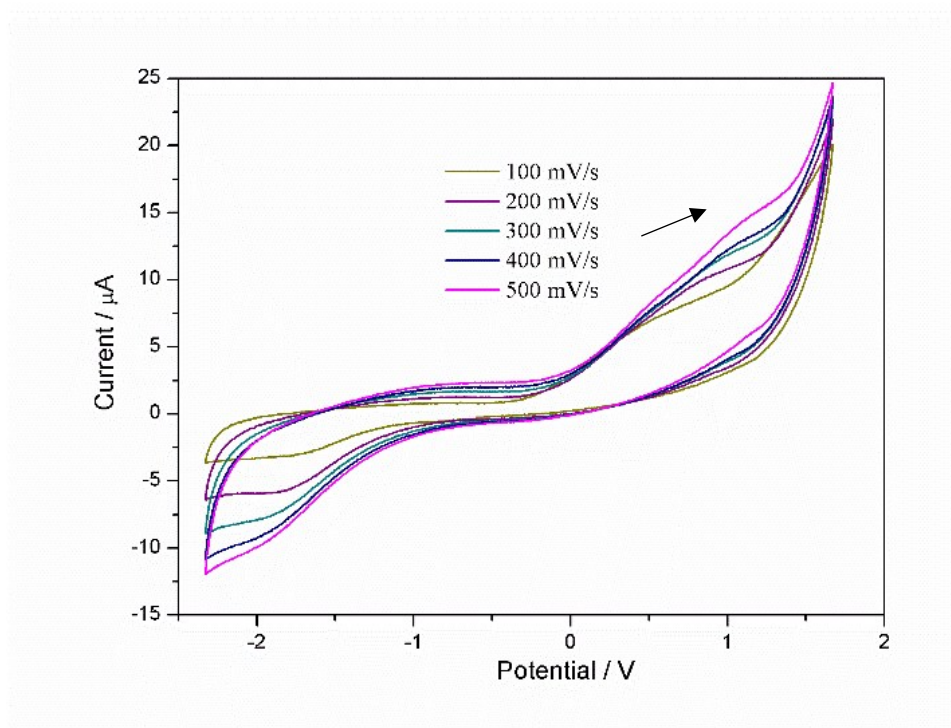


Figure S11: Cyclic voltammogram of complex **2^{tBu}-Ce** at different scan rates *versus* Fc/Fc⁺ measured in THF with 0.1 M [nBu₄N][PF₆].

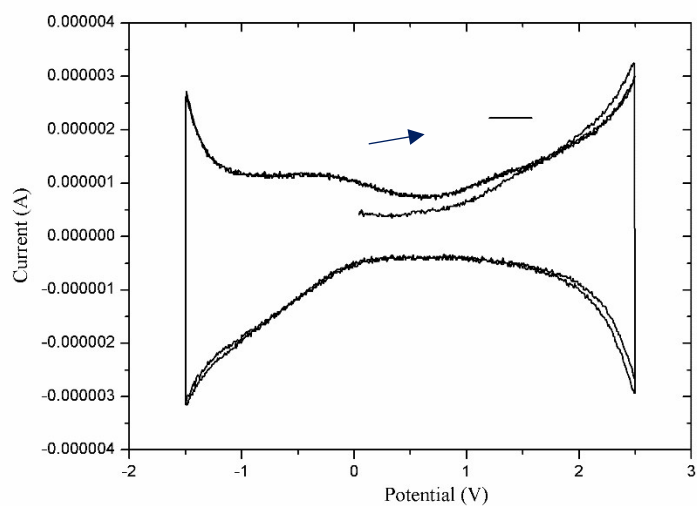


Figure S12: Square wave voltammogram of 2^tBu-Ce at scan rate of 100 mV/s.

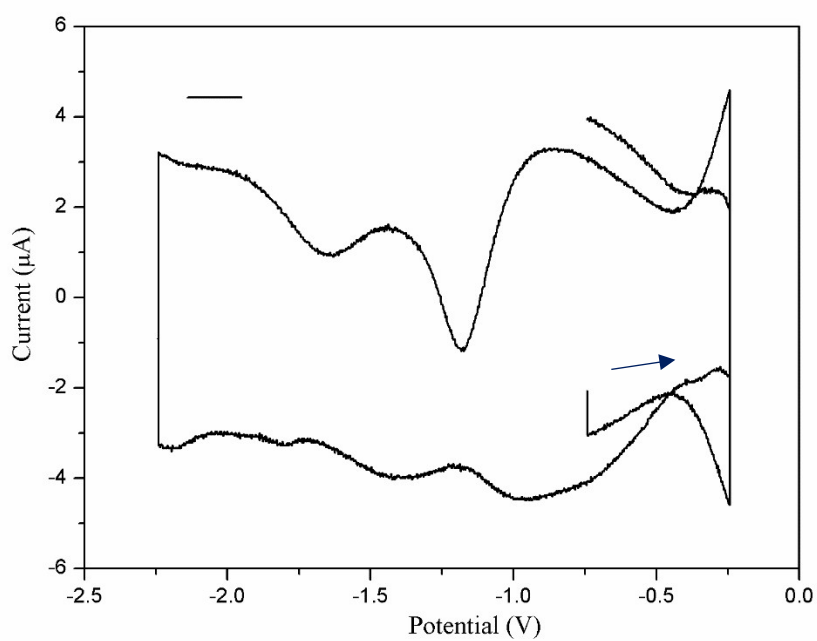


Figure S13: Square wave voltammogram of 4^tBu with step increment of 5 mV.

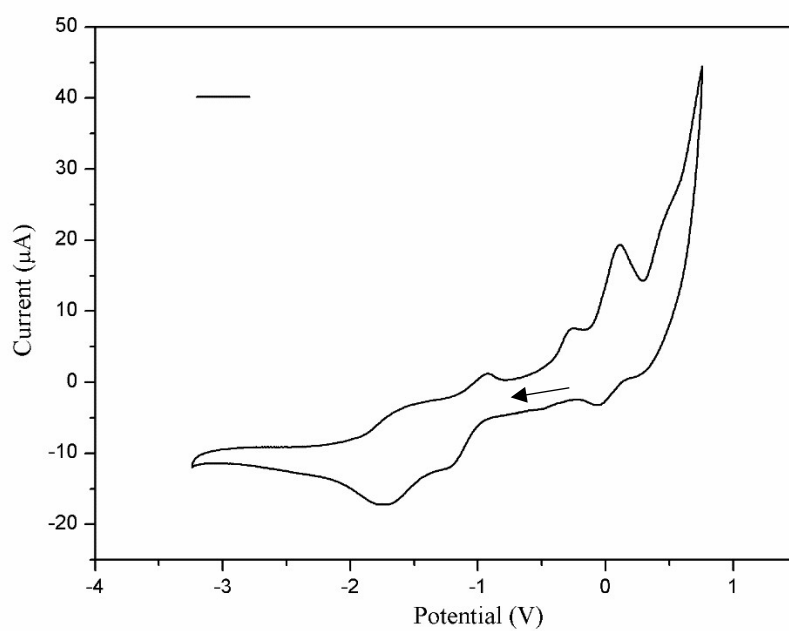


Figure S14: Cyclic voltammogram of complex 4^{Bu} versus Fc/Fc^+ measured in THF with 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$. The return oxidation wave at $E_{\text{pa}} = -0.23$ V is attributed to the oxidation of a different, as yet unidentified complex that is formed at the electrode during the reduction cycle.

1.5 HERFD methods

HERFD methods

High-energy-resolution fluorescence detection (HERFD) X-ray absorption spectroscopy measurements at the Ce L_{III} absorption edge (5723 eV) were collected at beamline 6-2 of the Stanford Synchrotron Radiation Lightsource using a 7-crystal Johann type spectrometer¹⁰ with Ge(331) analyzer crystals and a Si(311) monochromator. The beam size used for measurement was 200 μm x 400 μm. The energy was calibrated to a CeO₂ powder standard and data collected at the maximum intensity of the Ce Lα emission line (4840.2 eV). Data was processed using Athena, part of the IFEFFIT package,¹¹ which included background subtraction and normalization using the AUTOBK algorithm. Samples were prepared for measurement by first mixing with dry boron nitride and then packing them into a slotted aluminum holder sealed with indium and mylar windows. Given the air-sensitive nature of the samples, the sealed holder was kept under argon until measurement and exposed to air for less than one minute during transfer to vacuum with a helium backflow. Samples were measured at 50 K using a liquid He-cooled cryostat. To test for potential oxidation during the transfer process, an easily oxidizable complex (CeCp^{tet}₃) was measured along with the samples.

1.6 Crystallographic details

X-ray diffraction data for all complexes were recorded on an Excalibur Eos diffractometer at 170(2) K using Mo Kα radiation. All structures were solved using SHELXT¹² and least-square refined using SHELXL⁸ in Olex2.¹³ H atoms were treated by constrained refinement.

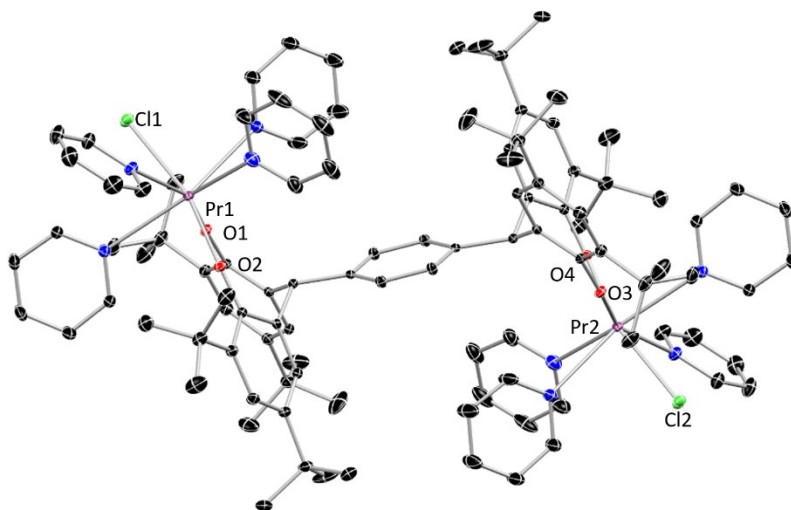


Figure S15. Solid state structure of complex **3-Pr**. Thermal ellipsoids are shown at 30% probability. All hydrogen atoms and solvents are omitted for clarity.

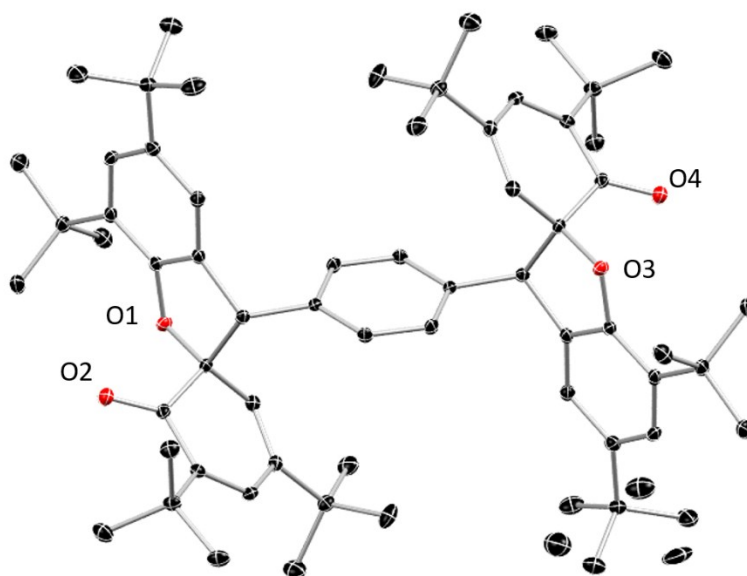


Figure S16. Solid state structure of the bicyclic ether from reaction of complex **2^{tBu}-Pr** with I_2 . Thermal ellipsoids are shown at 30% probability. All hydrogen atoms are omitted for clarity.

Table 1. Crystallographic data summary for complexes synthesised.

CCDC No.	1919080	1919083	1919084	919085	1919086
Label	1^{Me}	2^{Me}	2^{Me}-py	2^{Me}-18-c-6	2^{tBu}-Pr
Identification code	P16039_monoclinic	P15164peakhunting_monoclinic	PO16002	p16002	PO16012_reint_0p83A
Empirical formula	C ₁₄₈ H ₂₁₂ K ₈ O ₁₉	C ₁₆₄ H ₂₄₄ Ce ₂ K ₂ O ₂₃	C ₉₅ H ₁₀₉ CeKN ₈ O ₄	C ₁₃₀ H ₁₇₆ Ce ₂ K _{1.5} O ₁₆	C ₉₀ H ₁₃₈ KO _{10.5} Pr
Formula weight	2607.96	2942.02	1606.12	2333.59	1568.01
Temperature/K	170(2)	170(2)	120.00(10)	293(2)	120.01(10)
Crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	P2 ₁ /c	C2/c	P-1	P-1	P2 ₁ /c
a/Å	22.9449(7)	17.6636(3)	17.29805(13)	21.7935(6)	18.6073(7)
b/Å	27.0456(9)	33.2740(6)	21.51193(16)	23.1848(7)	31.2563(11)
c/Å	25.5786(8)	27.8553(5)	25.0448(4)	24.6660(10)	33.684(2)
α/°	90	90	97.6409(9)	112.342(3)	90
β/°	97.896(3)	92.6191(17)	103.4543(9)	91.967(3)	101.184(5)
γ/°	90	90	94.2363(6)	92.513(2)	90
Volume/Å ³	15722.5(9)	16354.5(5)	8930.03(16)	11498.9(7)	19218.7(15)
Z	4	4	4	2	8
ρ _{calc} /cm ³	1.102	1.195	1.195	0.674	1.084
μ/mm ⁻¹	0.276	0.662	4.762	0.45	4.661
F(000)	5616	6264	3376	2457	6720
Crystal size/mm ³	0.7994 × 0.5264 × 0.1778	0.5196 × 0.268 × 0.0561	0.4897 × 0.2254 × 0.0328	0.7227 × 0.5537 × 0.4425	0.176 × 0.14 × 0.03
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2θ range for data collection/°	5.692 to 48.216	6.098 to 49.426	7.018 to 152.508	5.87 to 54.97	6.256 to 136.502
Index ranges	-26 ≤ h ≤ 26, -31 ≤ k ≤ 31, -29 ≤ l ≤ 29	-20 ≤ h ≤ 20, -39 ≤ k ≤ 39, -32 ≤ l ≤ 32	-21 ≤ h ≤ 17, -26 ≤ k ≤ 27, -31 ≤ l ≤ 31	-28 ≤ h ≤ 28, -30 ≤ k ≤ 23, -32 ≤ l ≤ 30	-22 ≤ h ≤ 22, -28 ≤ k ≤ 37, -40 ≤ l ≤ 40
Reflections collected	203833	113941	181419	96714	239367
Independent reflections	24732 [R _{int} = 0.1371, R _{sigma} = 0.0945]	13888 [R _{int} = 0.0903, R _{sigma} = 0.0591]	37057 [R _{int} = 0.0832, R _{sigma} = 0.0465]	50114 [R _{int} = 0.0878, R _{sigma} = 0.1527]	34907 [R _{int} = 0.2725, R _{sigma} = 0.1478]
Data/restraints/parameters	24732/30/1608	13888/151/887	37057/37/1985	50114/231/1380	34907/18/1895
Goodness-of-fit on F ²	1.014	1.205	1.063	1.04	1.029
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0894, wR ₂ = 0.2115	R ₁ = 0.0859, wR ₂ = 0.1650	R ₁ = 0.0800, wR ₂ = 0.2095	R ₁ = 0.1039, wR ₂ = 0.2669	R ₁ = 0.1082, wR ₂ = 0.2775
Final R indexes [all data]	R ₁ = 0.1626, wR ₂ = 0.2696	R ₁ = 0.1133, wR ₂ = 0.1785	R ₁ = 0.0873, wR ₂ = 0.2168	R ₁ = 0.1604, wR ₂ = 0.3131	R ₁ = 0.1689, wR ₂ = 0.3340
Largest diff. peak/hole / e Å ⁻³	0.66/-0.43	1.56/-1.15	7.51/-2.31	2.99/-1.38	2.63/-2.06

Table 2. Crystallographic data summary for complexes synthesised (cont.).

CCDC No.	1919081	1919082	1919087	1919088	1919089
Label	3^tBu-Ce	3^tBu-Pr	4^tBu	5^tBu-Pr	5^tBu-byproduct
Identification code	P16191	P16195	4pic	PO17001_refinalized	P17095_orth
Empirical formula	C72H87CeClN6O3	C62H73ClN6O2Pr	C300H418Ce4O24	C56H91IO8Pr	C64H86O4
Formula weight	1260.04	1110.62	4968.8	1160.09	919.32
Temperature/K	293(2)	293(2)	93.15	120	120.00(14)
Crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	P-1	P-1	Pn	P-1	P21/n
a/Å	13.9455(2)	13.8885(3)	16.5331(2)	15.3646(9)	10.9580(6)
b/Å	14.0906(2)	14.0584(2)	31.1551(4)	15.4365(9)	18.2710(10)
c/Å	20.0971(3)	20.1573(3)	36.0837(6)	15.9168(8)	14.4742(7)
α/°	76.0300(10)	76.5680(10)	90	95.053(4)	90
β/°	80.3200(10)	80.439(2)	99.828(2)	116.088(5)	97.547(5)
γ/°	61.8470(10)	62.616(2)	90	115.951(6)	90
Volume/Å ³	3372.09(9)	3391.09(12)	18313.6(5)	2858.8(3)	2872.8(3)
Z	2	2	2	2	2
ρ _{calc} /cm ³	1.241	1.088	0.901	1.348	1.063
μ/mm ⁻¹	0.764	0.797	0.534	11.153	0.064
F(000)	1320	1158	5284	1206	1004
Crystal size/mm ³	0.373 × 0.129 × 0.111	? × ? × ?	0.2 × 0.2 × 0.08	0.122 × 0.118 × 0.0978	0.427 × 0.091 × 0.063
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71075)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2θ range for data collection/°	5.82 to 58.754	5.868 to 60.572	3.202 to 56.752	6.792 to 152.166	5.678 to 52.734
Index ranges	-19 ≤ h ≤ 19, -19 ≤ k ≤ 18, -27 ≤ l ≤ 27	-18 ≤ h ≤ 19, -18 ≤ k ≤ 18, -28 ≤ l ≤ 28	-21 ≤ h ≤ 21, 0 ≤ k ≤ 41, -47 ≤ l ≤ 47	-16 ≤ h ≤ 19, -19 ≤ k ≤ 18, -19 ≤ l ≤ 19	-13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -18 ≤ l ≤ 18
Reflections collected	74594	83658	149746	35153	85016
Independent reflections	16549 [Rint = 0.0440, Rsigma = 0.0452]	18379 [Rint = 0.0634, Rsigma = 0.0635]	80856 [Rint = 0.0689, Rsigma = 0.1015]	11813 [Rint = 0.0792, Rsigma = 0.0752]	5866 [Rint = 0.1614, Rsigma = 0.0787]
Data/restraints/parameters	16549/66/791	18379/0/661	80856/111/2904	11813/0/608	5866/0/350
Goodness-of-fit on F ²	1.053	1.728	1.979	1.07	1.031
Final R indexes [I ≥ 2σ (I)]	R1 = 0.0378, wR2 = 0.0822	R1 = 0.0746, wR2 = 0.2442	R1 = 0.2073, wR2 = 0.4898	R1 = 0.0655, wR2 = 0.1701	R1 = 0.0709, wR2 = 0.1331
Final R indexes [all data]	R1 = 0.0522, wR2 = 0.0884	R1 = 0.0977, wR2 = 0.2572	R1 = 0.2191, wR2 = 0.4944	R1 = 0.0809, wR2 = 0.1821	R1 = 0.1238, wR2 = 0.1525
Largest diff. peak/hole / e Å ⁻³	0.66/-0.66	3.49/-0.79	4.56/-6.57	2.41/-2.34	0.28/-0.19
Flack parameter			0.5		

Table 3. Crystallographic data summary for complexes synthesised (cont.).

CCDC No.	1920898
Label	3^tBu-Ce-BH₄
Identification code	P17023
Empirical formula	C ₂₃₃ H ₂₉₀ B ₄ Ce ₄ N ₂₁ O ₈
Formula weight	4116.56
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	19.7117(3)
b/Å	23.3826(4)
c/Å	25.9038(6)
α /°	82.210(2)
β /°	74.578(2)
γ /°	82.7970(10)
Volume/Å ³	11353.2(4)
Z	2
ρ_{calc} /cm ³	1.204
μ /mm ⁻¹	0.845
F(000)	4302
Crystal size/mm ³	0.462 × 0.176 × 0.055
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	5.702 to 51.364
Index ranges	-24 ≤ h ≤ 23, -28 ≤ k ≤ 28, -31 ≤ l ≤ 31
Reflections collected	177315
Independent reflections	42975 [R _{int} = 0.1104, R _{sigma} = 0.1341]
Data/restraints/parameters	42975/467/2616
Goodness-of-fit on F ²	1.01
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0654, wR ₂ = 0.1114
Final R indexes [all data]	R ₁ = 0.1357, wR ₂ = 0.1340
Largest diff. peak/hole / e Å ⁻³	0.94/-0.88

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