Supplementary Material (ESI) for Chemical Communications
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Tetravalent Cerium Carbene Complexes
Supplementary Information

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Experimental and Crystallographic Details

General Procedures

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a MBraun Unilab glove box unless otherwise stated. The solvents used (THF, diethyl ether, hexanes) were purified by passage through activated alumina towers and degassed prior to use. Benzene-d_6, THF-d_8 and Pyridine-d_5 were refluxed over potassium and vacuum transferred prior to use. Benzoquinone was sublimed prior to use. A 0.5 M solution of 9-BBN in THF was freeze-pump-thaw degassed three times prior to use. [KL][1] and [$CeI_3(THF)_4$][2] were synthesised according to literature procedures. All other reagents were purchased from Aldrich or Strem and used as received.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX300, at 300 K unless otherwise stated, spectrometer and referenced internally to residual protio solvent. Elemental analyses were determined by Mr. Stephen Boyer at London Metropolitan University.
Crystallographic intensity data were collected using Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART 1000 CCD area detector diffractometer using ω scans. Structure solution and refinement was carried out using the SHELXTL suite of programs.[3]

Preparations

[CeL_3] 1

To a stirred, cooled mixture of [$CeI_3(THF)_4$] (9.14 g, 11.29 mmol) and [KL] (7.39 g, 33.54 mmol) was added cooled THF (100 ml, −78 °C). The yellow suspension was allowed to warm to room temperature over 12 h, during which time it became a bright orange solution containing a colorless precipitate. Filtration and removal of volatiles from the filtrate under reduced pressure afforded an orange solid **1** (6.04 g, 78 %). Attempts to grow single, X-ray quality crystals have so far proved unsuccessful.
Found: C 52.58, H 7.60, N 12.20. Calc. for $C_{30}H_{51}CeN_6O_3$: C 52.68, H 7.53, N 12.29 %. λ_{max} = 292 nm, ε = 3244 $dm^3mol^{-1}cm^{-1}$. ^{1}H NMR (C_6D_6); δ 11.71 (bs, 2H, N-CH_2-C), 9.64 (bs, 6H, N-CH-(CH_3)$_2$), 6.05 (bs, 1H, N-C*H*-CH-N), 3.22 (bs, 1H, N-CH-C*H*-N), -2.94 (bs, 6H, O-C-(CH_3)$_2$), -5.56 (bs, 1H, N-C*H*-(CH_3)$_2$). MS (EI) m/z: 683 (M^+, 10 %). μ_{eff} (Evans method, benzene, 300 K) 2.21 μ_B.

[CeL_4] 2

Method A:
To a mixture of **1** (0.35 g, 0.51 mmol) and benzoquinone (27.6 mg, 0.26 mmol) was added THF (10 ml). A dark brown suspension formed immediately and was stirred at room temperature for 12 h. Filtration and removal of volatiles from the filtrate under reduced pressure afforded **2** as a yellow solid (0.17 g, 38 %)

Method B:
To a mixture of **1** (3.0 g, 4.39 mmol), [KL] (0.97 g, 4.39 mmol) and benzoquinone (0.24 g, 2.19 mmol) was added diethyl ether (50 ml). A dark brown suspension formed immediately and was stirred at room temperature for 12 h. Filtration and removal of volatiles from the filtrate under reduced pressure afforded **2** as a yellow solid (2.97 g, 78 %). Pale yellow crystals suitable for an X-ray diffraction study were grown from a THF solution at −30 °C.

Found: C 55.41, H 8.07, N 12.83. Calc. for $C_{40}H_{68}CeN_8O_4$: C 55.52, H 7.94, N 12.95 %. λ_{max} = 241 nm, ε = 23,065 $dm^3mol^{-1}cm^{-1}$. ^{1}H NMR (C_6D_6); δ 7.01 (s, 1H, N-C*H*-CH-N), 6.50 (s, 1H, N-CH-C*H*-N), 5.28 (sept, 1H, $^3J_{H-H}$ 6 Hz, N-C*H*-$(CH_3)_2$), 4.03 (s, 2H, N-CH_2), 1.29 (s, 6H, O-C-(CH_3)$_2$), 1.23 (d, 6H, $^3J_{H-H}$ 6 Hz, N-C*H*-$(CH_3)_2$). ^{13}C; 212.60 ($C_{carbene}$), 122.03 (N-*C*-C-N), 113.08 (N-C-*C*-N), 78.51 (O-*C*Me_2), 64.35 (N*C*H_2), 51.04 (N-*C*HMe_2), 30.00 (N-C(*C*H_3)$_2$), 24.13 (O-C(CH_3)$_2$). ^{1}H NMR (C_6D_6) at −75 °C; δ 7.31, 7.29, 7.18, 7.16, 7.15, 7.13, 7.09, 7.03 (s, 1H, N-C*H*-C*H*-N), 1.32 (bd, 24H, indistinguishable, N-C*H*-$(CH_3)_2$), 1.04 (bs, 24H, O-C-(CH_3)$_2$). The complex precipitates out of solution at this temperature; no further resonances could be identified. MS (EI) m/z: 699 (7 %, L_3CeO), 683 (95, CeL_3). μ_{eff} (Evans method, benzene, 300 K) 0.00 μ_B.

Oxidation of 1 with XeF_2 or [Fe(Cp)$_2$][OTf]

Each reaction was carried out according to method A, as above, but with the benzoquinone reagent replaced by XeF_2 (37.0 mg, 0.22 mmol) and **1** (300 mg, 0.44 mmol), or [Fe(Cp)$_2$][OTf] (290 mg, 0.88 mmol) and **1** (600 mg, 0.88 mmol) in diethyl ether (10 ml). Dark orange solutions formed in both cases and after an analogous work-up, [CeL_4] was isolated as a yellow solid in 32 %, and <10 % yield, respectively.

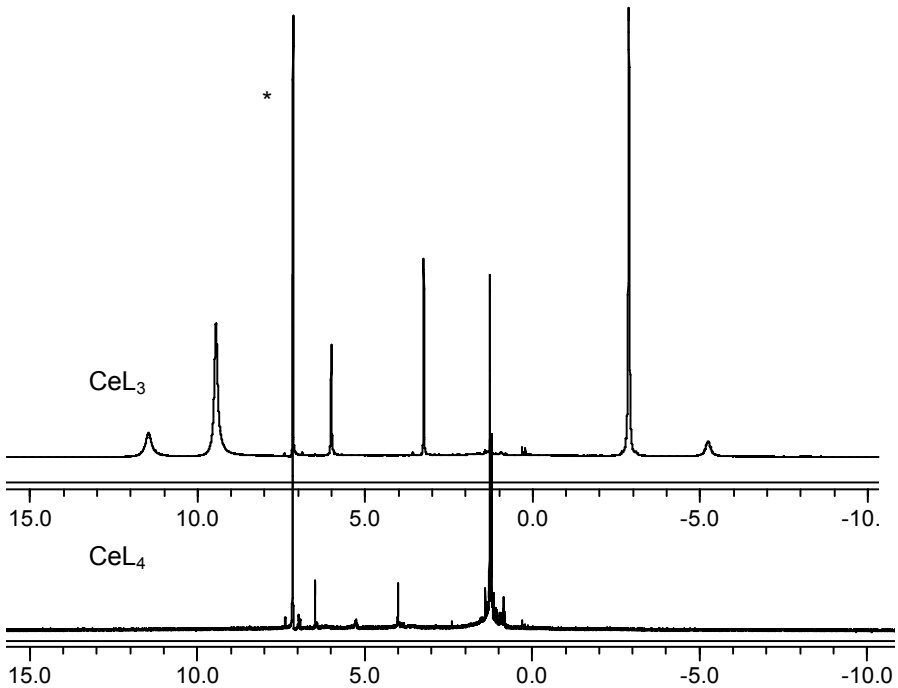


Figure S1. ^{1}H NMR spectra of **1** (upper trace) and **2** (lower) (* = solvent residual H resonance)

[Ce(L)$_2$(L-9BBN)$_2$] 3

To a cooled solution of **2** (1.30 g, 1.50 mmol) in THF (30 ml, −78 °C), was added a solution of 9-BBN (0.5 M, 6.0 ml, 3.00 mmol) dropwise. A yellow/ brown suspension formed and was allowed to warm to room temperature with stirring for 12 h. The volatiles were removed from the dark brown solution under reduced pressure, affording a brown solid which was recrystallised from benzene, yielding **3** as yellow crystals (1.34 g, 80 %). Crystals suitable for X-ray diffraction were grown *via* slow cooling of a hot benzene solution to room temperature.
Found: C 60.74, H 9.00, N 10.06. Calc. for $C_{56}H_{98}B_2CeN_8O_4$: C 60.03, H 8.92, N 10.10 %. ^{1}H NMR (C_5D_5N); δ 9.00, 7.37 (s, 1H, H(c), H(c')), 7.18, 7.04 (s, 1H, H(d), H(d')), 7.37 (s, 2H, H(C)), 7.20 (s, 2H, H(D)), 5.42 (broad sept, 2H, $^3J_{H-H}$ 6 Hz, H(e), H(e')), 5.19 (sept, 2H, $^3J_{H-H}$ 6 Hz, H(E)), 4.51 (bs, 2H, H(b)), 4.00 (bs, 2H, H(b')), 3.92 (s, 4H, H(B)), 2.95-3.96 (m, 28H, 9-BBN), 2.51, 2.49 (d, 12H, $^3J_{H-H}$ 6 Hz, N-C*H*-

$(CH_3)_2$), 2.29, 2.25 (s, 12H, O-C-(CH_3)$_2$). ^{13}C; δ 212.53 (both Ce-bound $C_{carbene}$), 125.61, 124.0 (C(c), C(c')), 123.40 (C(C)), 116.62 (C(D)), 115.88, 115.11 (C(d), C(d')), 81.62, 80.29 (O-C), 70.65 (O-C), 65.64, 61.34 (C(b), C(b')), 59.23 (C(B)), 53.01, 49.83 (C(e), C(e')), 51.10 (C(E)), 39.67, 32.85 (C(f), C(f')), 34.08 (C(F)), 34.33 (9-BBN-CH), 30.61, 26.20, 25.95 (9-BBN-CH_2), 24.86 (C(A)), 24.86, 24.67 (C(a), C(a')). ^{11}B (C_5D_5N); δ -15.4. The boron-coordinated $C_{carbene}$ resonance is not observed due to coupling to the quadrupolar B nucleus. μ_{eff} (Evans method, pyridine, 300 K) 0.0 μ_B.

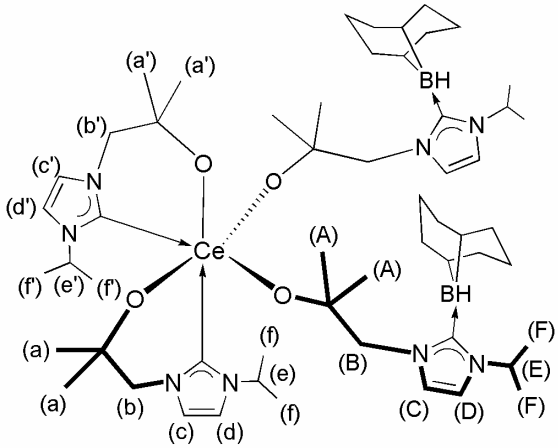


Figure S2. Labelling scheme for assignment of NMR spectra of **3**

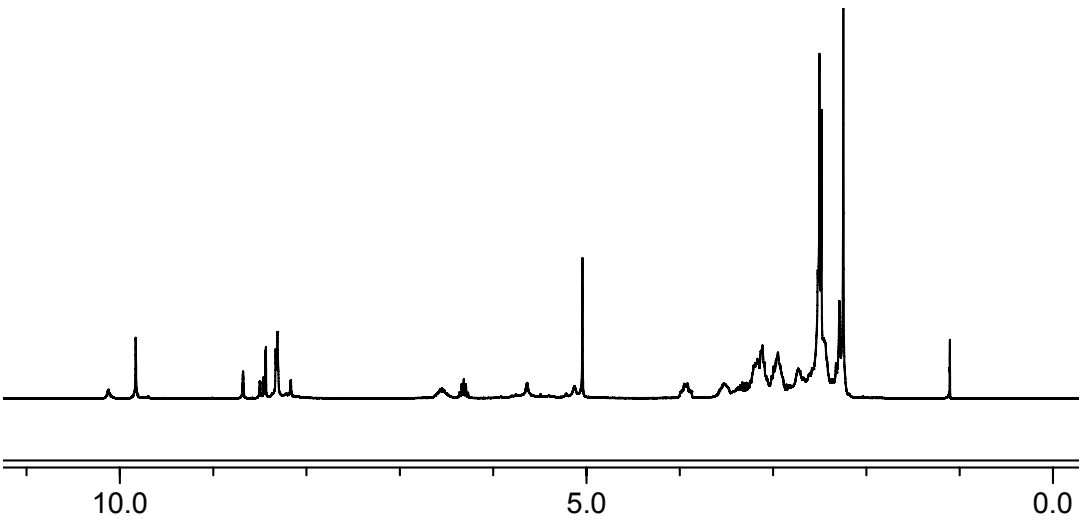
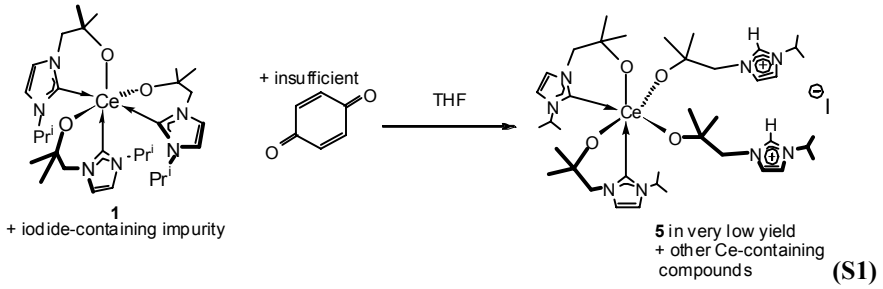


Figure S3. ^{1}H NMR spectrum of **3**. No resonances are observed outside this spectral window

[CeL$_2$(LH)$_2$]I 5



(S1)

To a mixture of **1** (0.5 g, 0.73 mmol) and benzoquinone (3.9 mg, 0.04 mmol) was added THF (15 ml), equation S1. An orange solution formed immediately and was stirred for 12 h. Filtration and removal of volatiles from the filtrate under reduced pressure afforded an orange solid (0.47 g). The ^{1}H NMR spectra in C_6D_6 showed predominantly **1** and **2** to be present. A small crop of **5** was isolated from the solution, and a yellow single crystal suitable for X-ray structure determination was grown from a benzene solution at 25 °C, although there was insufficient quantity of **5** to enable further characterisation. Structural characterisation confirms that complex **5** is a Ce^{III} analogue of **2**, Fig. S4.

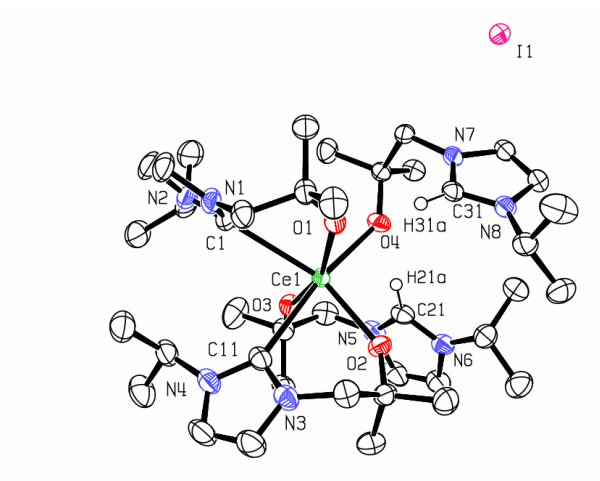


Figure S4. Displacement ellipsoid drawing of the molecular structure of **5** (50 % probability ellipsoids). Solvent and hydrogens omitted, except H21a and H31a. Selected distances (Å) and angles (º): Ce-O1 2.332(2), Ce-O3 2.279(2), Ce-O$_{(av)}$ 2.309; range 2.12-2.41, Ce1-C1 2.798(3), Ce1-Ce11 2.806(3), N1-C1 1.366(4), N5-C21 1.335(4), N1-C1-N2 103.0(2), N5-C21-N6 108.8(2).

References

1) P.L. Arnold, M. Rodden, C. Wilson, *Chem. Commun.*, 2005, 1743.
2) K. Izod, S.T. Liddle, W. Clegg, *Inorg. Chem*, 2004, **43**, 214.
3) Bruker, 1997, SHELXTL 5.10. Bruker AXS Inc., Madison, Wisconsin, USA., G.M. Sheldrick, *Acta. Cryst. A*, 1990, **46**, 467, G.M. Sheldrick, 1997, SHELXL97, University of Goettingen, Germany.