Electronic Supporting Information

Synthesis and characterisation of the ethylene bridged permethylindenyl cerium complex,[(EBI*)CeI(THF)]

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1. General Considerations

1.1 General Details

All organometallic manipulations were performed under an atmosphere of N_2 using standard Schlenk line techniques or a MBraun UNIlab glovebox, unless stated otherwise. Solvents used were dried by either reflux over sodium-benzophenone diketyl (THF), or passage through activated alumina (toluene, CH_2Cl_2) using a MBraun SPS-800 solvent system. Solvents were stored in dried glass ampoules, and thoroughly degassed by passage of a stream of N_2 gas through the liquid and tested with a standard sodium-benzophenone-THF solution before use. Deuterated solvents for NMR spectroscopy of oxygen or moisture sensitive materials were treated as follows: benzene-d_6 and toluene-d_8 were freeze-pump-thaw degassed and dried over a K mirror.

1.2 Solution NMR spectroscopy

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300 MHz and 75 MHz respectively, at room temperature, unless stated otherwise. The chemical shifts, δ are given relative to TMS ($\delta = 0$) in parts per million, referenced internally to the residual proton chemical shift in the deuterated solvent used. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced via the residual protio solvent peak. Oxygen or moisture sensitive samples were prepared using dried and degassed solvents under an inert atmosphere in a glovebox, and were sealed in Wilmad 5mm 505-PS-7 tubes fitted with Young's type concentric stopcocks.

1.3 Single crystal X-ray diffraction

Crystals were mounted on a glass fibre with perfluoropolyether oil and cooled rapidly to 150(2) K in a stream of N_2 using an Oxford Cryosystems Cryostream unit.

1.4 Solid state magnetic measurement

Solid-state magnetic susceptibility data were obtained using a Quantum Design MPMS-5 SQUID magnetometer. An accurately weighed sample was placed into a gelatine capsule and then loaded into a non-magnetic plastic straw, before being lowered into the cryostat. The field independence of the measurement was verified by measuring the susceptibility as a function of field between –5 and 5T. Data were then collected employing a field of 0.1T and finally corrected for the inherent diamagnetism of the sample by use of Pascal's constants.[S1]

1.5 Electrochemistry

Electrochemical experiments were performed in anhydrous CH_2Cl_2 or THF containing 0.1 $molL^{-1}$ $[N^nBu_4][PF_6]$ as supporting electrolyte, using a Princeton Applied Research VersaSTAT 3 potentiostat controlled using a PC running V3-Studio software. Cyclic voltammetric and square-wave experiments were performed using a three-electrode configuration with a N_2 inlet/outlet bubbler connected to an external oil bubbler and a side-neck fitted with a rubber septum for addition of the samples (G. Glass, Australia). The working electrode used was a Pt disc BASi MF-2013 of 1.6mm diameter, the counter electrode a Pt wire, with a Ag wire as the pseudo-reference electrode. The electrodes were polished prior to each use. Before each sample was run, the empty cell was thoroughly purged with N_2, the electrolyte solution thoroughly degassed with N_2, and a background scan of the solvent window recorded. The sample was dissolved in a small amount of electrolyte, transferred via syringe into the cell, and further degassed. After recording the CV traces, Cp_2Fe was added as an internal reference and acquisition of the voltammograms repeated. The Ag wire pseudo-reference electrode was calibrated to the Cp_2Fe/Cp_2Fe^+ couple at +0.46V *vs* the saturated calomel electrode (SCE) in CH_2Cl_2 and +0.56V in THF *vs* SCE, and all potentials are reported *vs* SCE.[5] A number of different scan rates were used and measurements were performed under an inert N_2 atmosphere. Thermodynamic half-potentials were obtained by square-wave voltammetry, and reversibility of the redox process was tested by a plot of the maximum anodic (or minimum cathodic) peak current against the square root of the scan rate, giving a straight line in the reversible cases. Comparison of the anodic to cathodic potential difference with that of the internal Cp_2Fe reference was used to confirm the number of electrons of each redox process.

2. Synthesis and NMR spectroscopy details

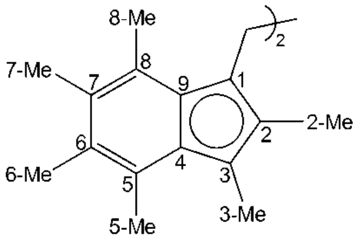
2.1 Synthesis of $[(EBI^*)K_2]$

K (0.20g, 5.04×10^{-3} mol) was stirred in THF with naphthalene (0.69g, 5.42×10^{-3} mol) for 15 hours, resulting in a deep green solution of $C_{10}H_8K$. To this was added at –78°C a solution in THF of $C_{16}H_{20}$ (1.00g, 4.71×10^{-3} mol), and the reaction mixture stirred at –78°C for 1 hour, changing to a deep red colour. After being allowed to warm to room temperature with stirring the resulting brown-beige reaction mixture was stirred for 2 hours, and the solvent removed under vacuum to afford a red-brown solid. This was washed with Et_2O and dried under vacuum to afford a buff solid. Yield: 0.84g, 71%.

^{1}H NMR (pyridine-*d*$_5$) *δ* (ppm): 2.39, 2.40, 2.52, 2.69, 2.71, 3.12 (all s, 6H, Me), 4.05 (s, 4H, C_2H_4). **^{13}C{^{1}H} NMR (pyridine-*d*$_5$) *δ* (ppm):** 13.1, 16.4, 17.3, 17.4, 18.6, 18.9 (Me), 33.5 (C_2H_4), 97.8, 105.0, 117.5, 118.1, 122.7, 123.4, 125.2, 126.0, 126.3 (ring Cs).

2.2 Synthesis of [(EBI*)CeI(THF)]

[(EBI*)K_2] (0.50g, 9.94 x 10^{-4} mol) was slurried in THF and cooled to 78°C. To this brown mixture was added [CeI_3·$(THF)_4$] (0.84g, 9.94 x 10^{-4} mol) in THF. The reaction mixture was stirred at –78°C for 1 hour. Upon warming to room temperature the reaction mixture went orange and was stirred for a further 15 hours. The solvent was removed under vacuum to afford an orange solid, which was extracted with 60°C toluene and filtered through celite. Removal of the solvent from the filtrate afforded [(EBI*)CeI(THF)] as an orange-red solid. Yield: 0.50 g, 60%.



Numbering scheme for the ^{1}H and ^{13}C{^{1}H} NMR assignment of [(EBI*)CeI(THF)]

^{1}H NMR (500MHz) (C_6D_6) *δ* (ppm): –7.85 (s, 2-Me), –2.74 (s, 8-Me), –2.19 (s, 3-Me), 1.48 (s, 7-Me), 2.98 (bs or m, C_2H_4), 9.46 (s, 5-Me), 10.22, 10.77 (both m, C_4H_8O), 13.01 (s, 6-Me). **^{13}C{^{1}H} NMR (125 MHz) (C_6D_6) *δ* (ppm):** 1.4 (2-Me), 10.3 (8-Me), 12.3 (3-Me), 14.9 (7-Me), 19.2 (5-Me), 29.3 (6-Me), 39.1 (C_2H_4), 50.6, 50.7 (both C_4H_8O), 116.7 (1-C), 125.3 (8-C), 127.5 (5-C), 129.2 (7-C), 142.6 (6-C), 170.4, 174.2, 187.2, 198.4 (all ring Cs). **Anal.** Calc for $C_{36}H_{48}CeIO$: C, 56.61; H, 6.33. Found: C, 56.72; H, 6.26.

3. X-ray crystallography

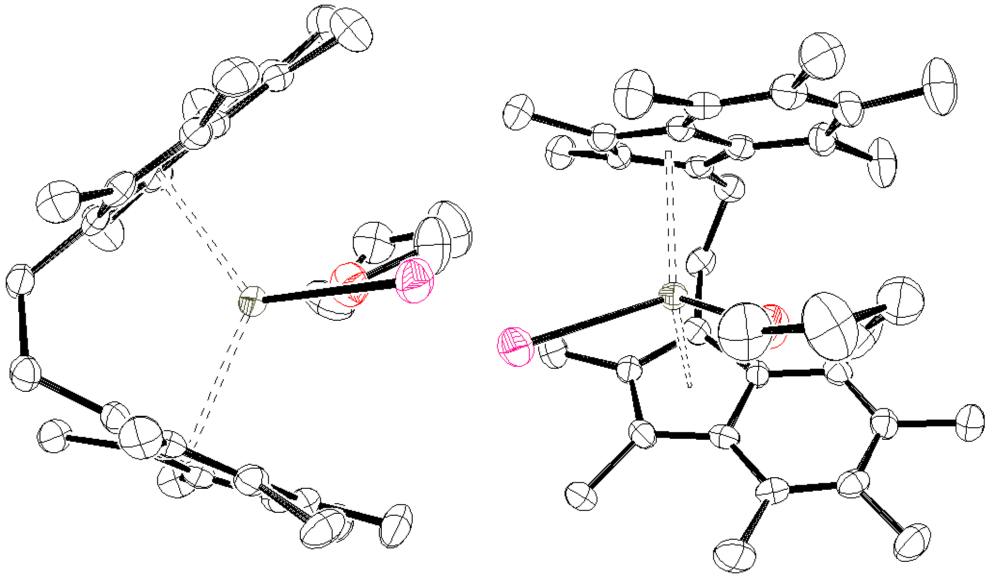


Fig S1: The complex *meso*-[(EBI*)CeI(THF)]; displacement ellipsoids shown at 50% probability.

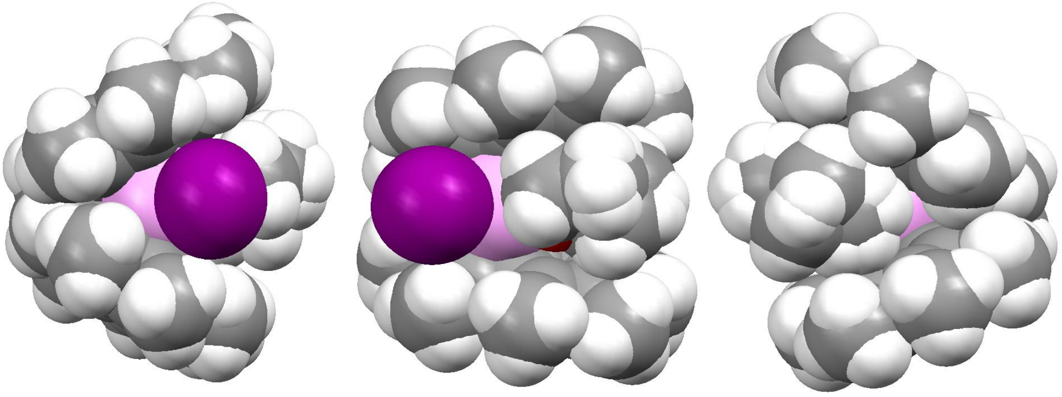


Fig S2: Space-filling models of *meso*-[(EBI*)CeI(THF)], showing steric bulk of I and THF ligands and interaction of THF molecule with Me groups on the six-membered rings.

Table S1: Selected parameters in meso-[(EBI*)CeI(THF)].

Angles (°)			
α	62.4(4)	-	
Hinge Angle	4.6(7)	Hinge Angle	5.3(6)
Rotation Angle	51.9(6)	-	

N.B. The coordinating THF ligand was found to be disordered over two positions and was modeled as such. Figs. 2 and S1 show an ordered THF for clarity.

4. ^{1}H NMR spectroscopy, variable temperature

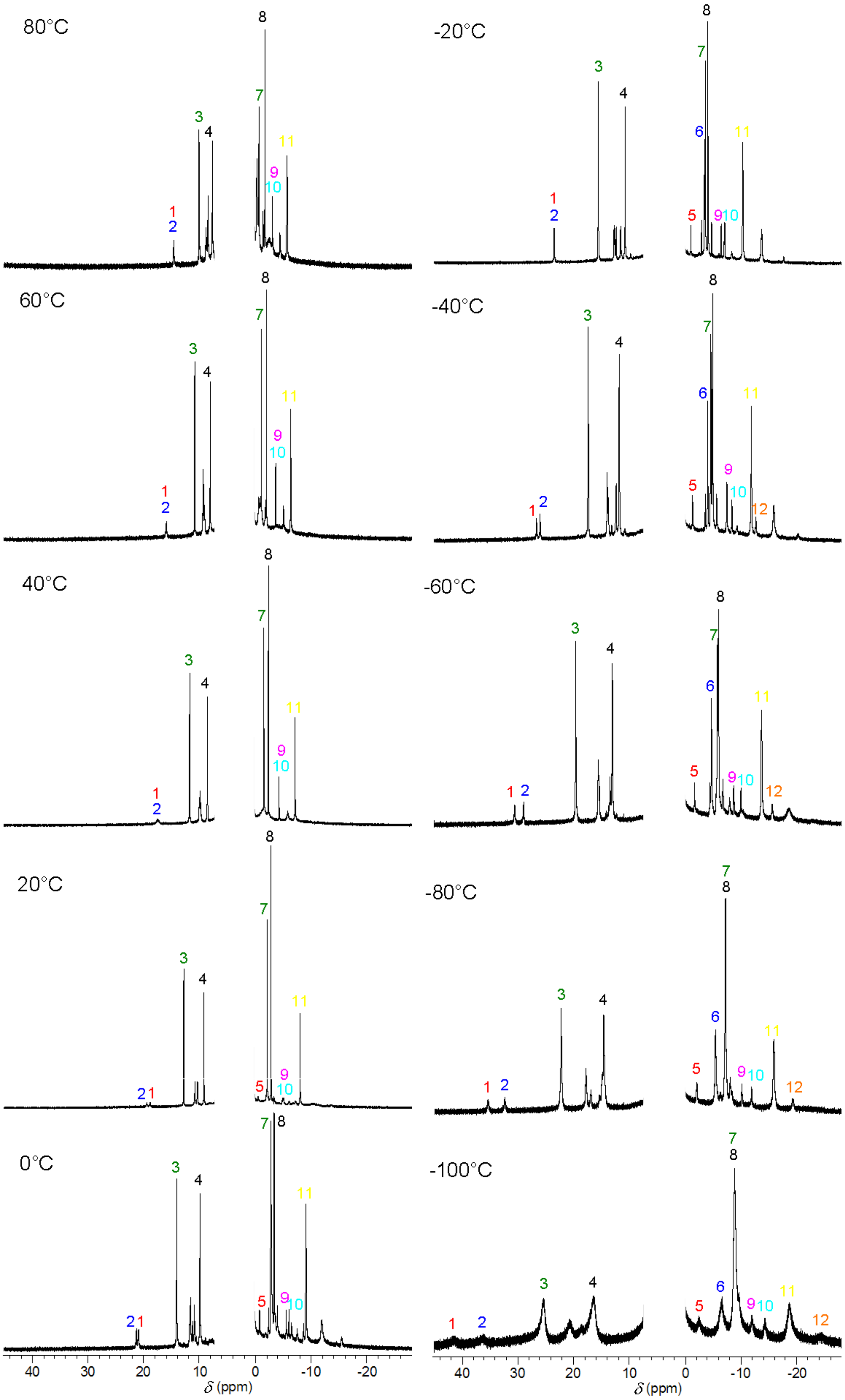


Fig. S3: ^{1}H NMR spectra of [(EBI*)CeI(THF)], toluene-d_8, over the temperature range –100°C to 80°C. The region between 0.1ppm to 7.3ppm has been omitted for clarity.

5. Depiction of the parameters RA, Ha and α

Alpha (α): An unweighted least-squares plane was calculated for the five Cp carbon atoms of each indenyl moiety (C3-7 for ***rac-EBI*ZrCl2*** shown below) and the angle measured between the two planes calculated calculated using Platon. This is the angle complementary to that calculated between the normals to the planes.

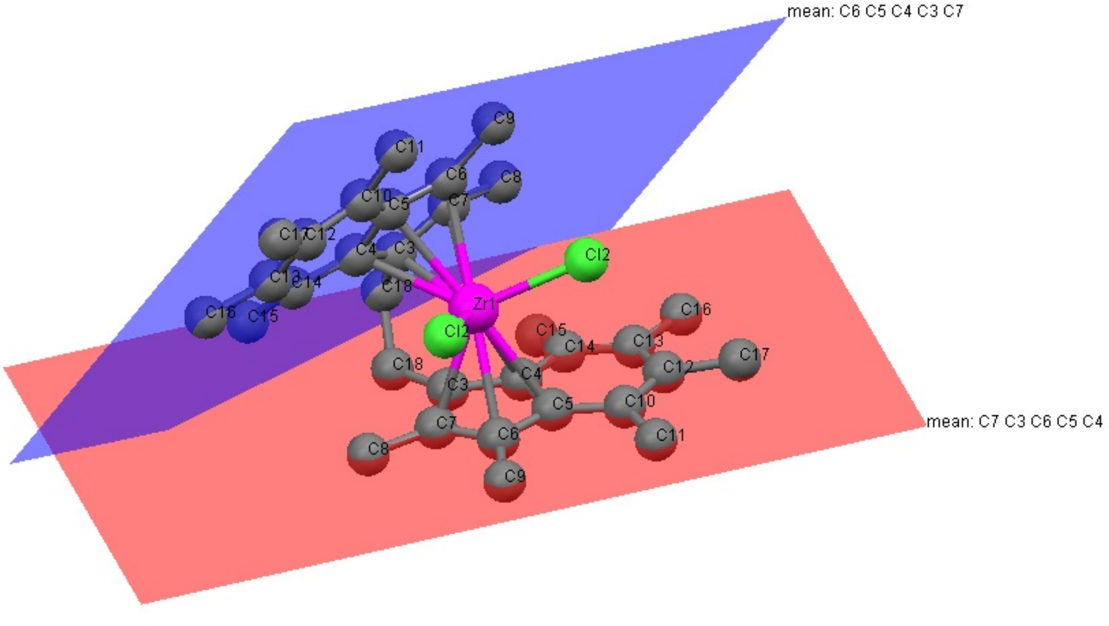


Fig. S4: Mercury depiction of the planes used to calculate α.

HA: The angle between the unweighted least-squares plane for the Cp omitting the ipso-C and the unweighted least-squares plane for the ipso-C and its two ortho-C neighbours within the Cp as calculated with Platon. i.e. the angle between the plane defined by C4-C7 below and C4, C3 and C7. This is the angle complementary to that calculated between the normals to the planes.

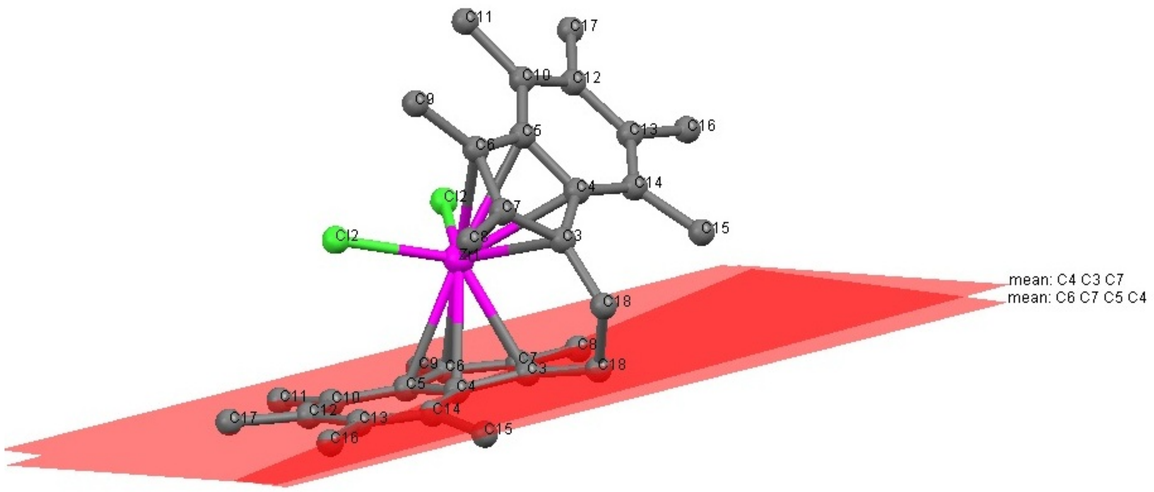


Fig. S5: Mercury depiction of the planes used to calculate HA.

RA: The angle between the two unweighted least-squares planes fitting the central metal and the bridgehead and terminal Cp atoms as calculated by Platon. This plane runs the length of the Ind fragment, approximately perpendicular to it. In the example below the plane is defined by Zr1, C4, C5 and C7 (and the second plane is the symmetry equivalent). This angle is complementary to that calculated between the normals to the planes.

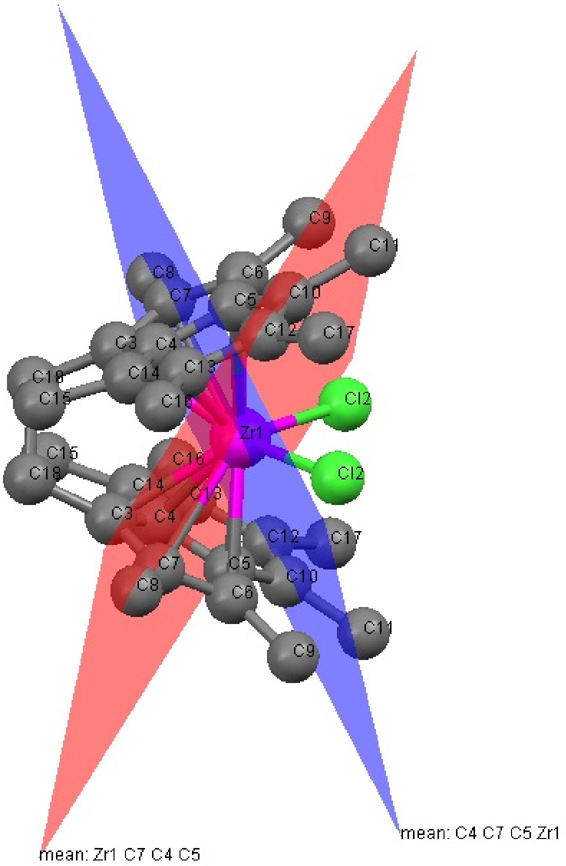


Fig. S6: Mercury depiction of the planes used to calculate RA.

6. References

S1. G. A. Bain, J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532.