Homoleptic Lanthanide(II)-Bis(Guanidinate) Complexes, $[Ln(Giso)_2]$ (Giso = $[(ArN)_2CN(C_6H_{11})_2]^-$, Ar = $C_6H_3Pr^i_2$-2,6): Planar 4-Coordinate (Ln = Sm or Eu) vs Distorted Tetrahedral (Ln = Yb) Geometries

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SUPPLEMENTARY MATERIAL

Preparation of compounds 1 – 5. (see main text for spectroscopic data)

General experimental details

All manipulations were performed under an inert atmosphere (nitrogen or argon) under anhydrous conditions using Schlenk line and glove box techniques. Solvents were dried by reflux over molten potassium or Na/K alloy under an atmosphere of nitrogen. SmI_2 was purchased from Aldrich as a 0.1 m solution in THF. THF solutions of YbI_2 and EuI_2 were prepared by reaction of the metal with $C_2H_4I_2$ in THF.[1] Solutions of K[(Giso)] in THF were typically prepared by treating GisoH (1.0 eq) with $K[N(SiMe_3)_2]$ (1.02 eq) in THF (20 cm^3) and stirring for 1 h. Reproducible microanalyses on all compounds could not be obtained due to the presence of solvent of crystallisation in all cases and the extreme air sensitivity of the compounds.

1. *Synthetic Methods of Organometallic and Inorganic Chemistry*, W.A. Herrmann (ed.), Georg Thieme Verlag, Stuttgart, **1997**, vol. 6, pg. 26 – 28.

Preparation of $[Sm(Giso)_2]$ 1: SmI_2 (31.4 cm^3 of a 0.1 m solution in THF, 3.14 mmol) was added to a solution of K[(Giso)] (4.47 mmol) in THF (30 cm^3) at –80°C. The mixture was slowly warmed to room temperature with stirring. Volatiles were removed under reduced pressure and the residue was extracted with hexane (60 cm^3). The extract was filtered and the filtrate concentrated to *ca.*

15 cm^3, placed at –30°C overnight yielding dark violet crystals of **1**. Yield: 1.76 g (1.42 mmol, 64 %). Crystals suitable for x-ray crystallography were grown from benzene.

Preparation of [Eu(Giso)$_2$] 2: EuI_2 (40 cm^3 of a 0.035 m solution in THF, 1.40 mmol) was added to a solution of K[(Giso)] (2.15 mmol) in THF (30 cm^3) at –80°C. The mixture was slowly warmed to room temperature with stirring. Volatiles were removed under reduced pressure and the residue was extracted with hexane (60 cm^3). The extract was filtered and the solvent removed *in vacuo*. The residue was recrystallised from benzene (*ca.* 3 cm^3) (40°C to 20°C) yielding red-orange crystals of **2**. Yield: 0.64 g (0.52 mmol, 48 %).

Preparation of [Yb(Giso)$_2$] 3, [{Yb(Giso)I(THF)}$_2$] 4 and [{Yb(Giso)I}$_2$] 5: YbI_2 (72.5 cm^3 of a 0.02 m solution in THF, 1.45 mmol) was added to a solution of K[(Giso)] (2.07 mmol mmol) in THF (30 cm^3) at –80°C. The mixture was slowly warmed to room temperature with stirring. Volatiles were removed under reduced pressure and the residue was extracted with hexane (60 cm^3). The extract was filtered and the solvent removed *in vacuo*. The residue was recrystallised from toluene (*ca.* 3 cm^3) (40°C to 20°C) yielding deep green crystals of **3**. Yield: 0.65 g (0.52 mmol, 50 %). Concentration of the mother liquor afforded a mixture of yellow crystals of **4** (6% yield) and red crystals of **5** (5% yield) which were separated manually. Dissolution of **5** in THF led to its quantitative conversion to **4**. X-ray quality crystals of **4** were obtained by recrystallising a mixture of **4** and **5** from benzene.

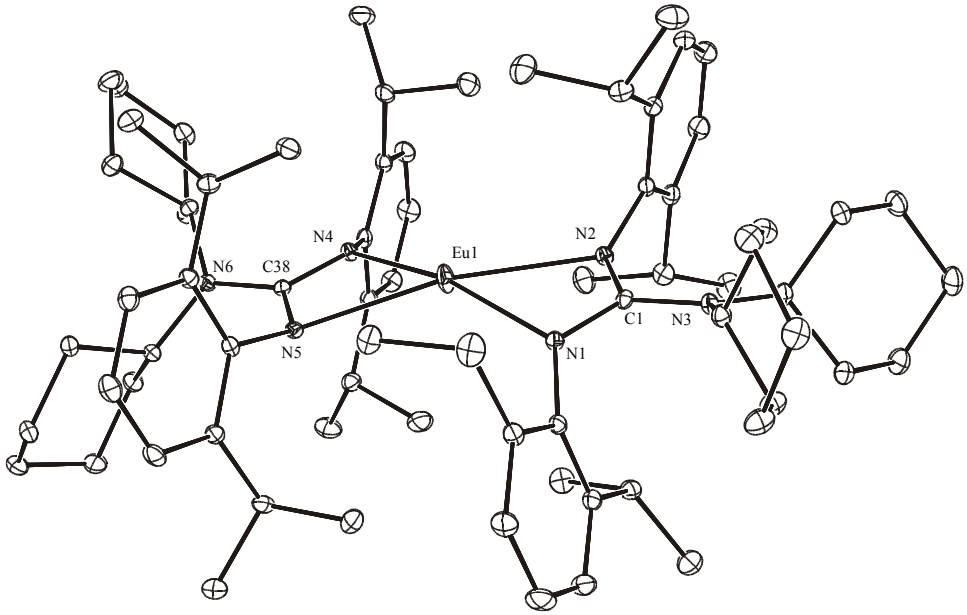

Fig. 1S: ORTEP diagram of compound **2** (hydrogen atoms omitted, ellipsoids at the 25% probability level).

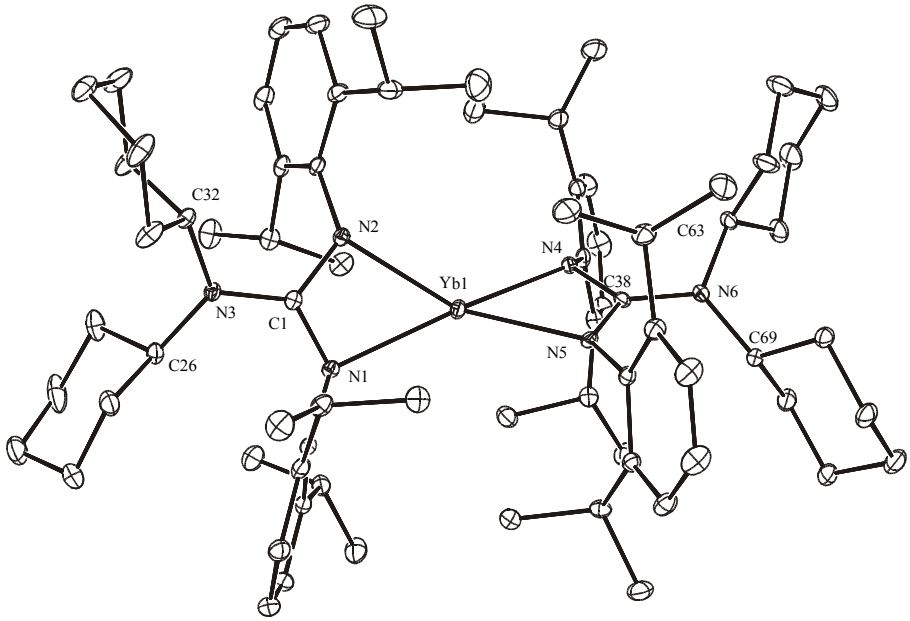

Fig. 2S: ORTEP diagram of compound **3** (hydrogen atoms omitted, ellipsoids at the 25% probability level).