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Reduction chemistry yields stable and soluble divalent lanthanide tris(pyrazolyl)borate complexes†

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Reduction of the heteroleptic Ln(III) precursors [Ln(Tp)$_2$(OTf)] (Tp = hydrotris(1-pyrazolyl)borate; OTf = triflate) with either an aluminyl(I) anion or KC$_8$ yielded the adduct-free homoleptic Ln(II) complexes dimeric 1-Eu [{Eu(Tp)(μ-κ^1:η^5-Tp)}$_2$] and monomeric 1-Yb [Yb(Tp)$_2$]. Complexes 1-Ln have good solubility and stability in both non-coordinating and coordinating solvents. Reaction of 1-Ln with 2 Ph$_3$PO yielded 1-Ln(OPPh$_3$)$_2$. All complexes are intensely coloured and 1-Eu is photoluminescent. The electronic absorption data show the 4f–5d electronic transitions in Ln(II). Single-crystal X-ray diffraction data reveal first μ-κ^1:η^5-coordination mode of the unsubstituted Tp ligand to lanthanides in 1-Eu.

Divalent lanthanide Ln(II) ions have remarkable physical and chemical properties.[1] Complexes of Ln(II) are electron-transfer reagents in important synthetic transformations.[1a,2] The physical properties of Ln(II) include single-molecule magnetism,[3] and unique optical properties.[4] Judicious choice of ancillary ligand is essential to supporting Ln(II) ions.[5]

The tridentate nitrogen donor scorpionate ligand hydrotris(1-pyrazolyl)borate (Tp) ligand has been shown to support Ln(II) in homoleptic [Ln(Tp^R)$_2$] complexes where Tp^R = 3 and/or 5-substituted-pyrazolyl.[6] These [Ln(Tp^R)$_2$] complexes display a wide range of chemical reactivity,[7] and are also useful synthons for organometallic Ln complexes,[8] and heterometallic Ln and transition metal complexes.[9] The [Ln(Tp^{iPr2})$_2$] (Ln = Eu, Yb) complexes exhibit properties intermediate between Ln nitrides and metallocenes in light-emitting diodes (LEDs).[10] The first molecular Eu(II)-based electroluminescent thin film device was synthesised using [Eu(Tp$^{3,5\text{-}R}$)$_2$] (R = Me).[11] Recently the potential of [Eu(Tp$^{3\text{-}R}$)$_2$] (R = Me, CF$_3$) complexes have been demonstrated in organic LEDs (OLEDs).[6h]

In contrast to Cp^R Ln(II) chemistry (Cp^R = substituted cyclopentadienyl), the synthetic routes to [Ln(Tp^R)$_2$] complexes, with one exception,[6d] have always utilised Ln(II) precursors.[6,7] Lanthanide chemistry of the unsubstituted Tp ligand has remained largely unexplored. Moreover the THF-adduct complexes [Ln(Tp)$_2$(THF)$_2$] were reported to be unstable in solution.[6b,12] Here we report the reduction chemistry of the heteroleptic Ln(III) precursors [Ln(Tp)$_2$(OTf)],[13] to synthesise stable adduct-free homoleptic Ln(II) complexes [Ln(Tp)$_2$] **1-Ln** (Ln = Eu, Yb), and Ph$_3$PO adduct complexes **1-Ln(OPPh$_3$)$_2$**.

The formal reduction potentials (E^0) of Ln^{3+}/Ln^{2+} for Ln = Eu −0.35 V and Yb −1.15 V in aqueous solution *vs.* the Normal Hydrogen Electrode (NHE) make them the most accessible Ln(III) candidates for reduction.[14] Upon reduction of the parent Ln(III), the stability of these classical Ln(II) is achieved by either the attainment of half-filled 4f orbitals in Eu(II) or full 4f orbitals in Yb(II). It is of note that the redox potentials of Ln(III) depend on the ancillary ligand environment, for example [Ln(C$_5$H$_4$SiMe$_3$)$_3$] (Ln = Eu, Yb) were recently reported to be *ca.* 1 V more difficult to reduce than their formal reduction potentials.[15] There are no data in the literature for the E^0 of Ln^{3+}/Ln^{2+} in a Tp ligand environment, but the reduction potentials are expected to be intermediate between the above examples. We therefore explored the reduction chemistry of our Ln(III) (Ln = Eu, Yb) precursors with various reductants.

Complex **1-Yb** was first isolated by reduction of [Yb(Tp)$_2$(OTf)] with [{K[Al(NON$^{\text{Dipp}}$)]}$_2$][16] (NON$^{\text{Dipp}}$ = {O(SiMe$_2$NDipp)$_2$}$^{2-}$, Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$, see ESI,† SIIa). This demonstrates the utility of aluminium(I)[17] in lanthanide reduction chemistry. However, the reaction of [Y(Tp)$_2$(OTf)] with [{K[Al(NON$^{\text{Dipp}}$)]}$_2$] yielded the Y(III) '*ate*'-salt [Y(Tp)$_2$(μ-OTf)$_2$K(18-crown-6)] **2-Y** (see ESI,† SV).

Our previous work on the metathesis chemistry of [Ln(Tp)$_2$(OTf)][13] had shown that elimination of K(OTf) in non-coordinating solvents was most effective, and this is also the case for the reduction chemistry. Neither clean reduction nor K(OTf) elimination could be achieved in ethereal solvents (see Fig. S68 for the crystal structure of **1-Yb(DME)** co-crystallised with KOTf, DME = 1,2-dimethoxyethane, ESI†). While metallic K

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† Electronic supplementary information (ESI) available. CCDC 2161063–2161071 and 2195976. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d2cc03189b

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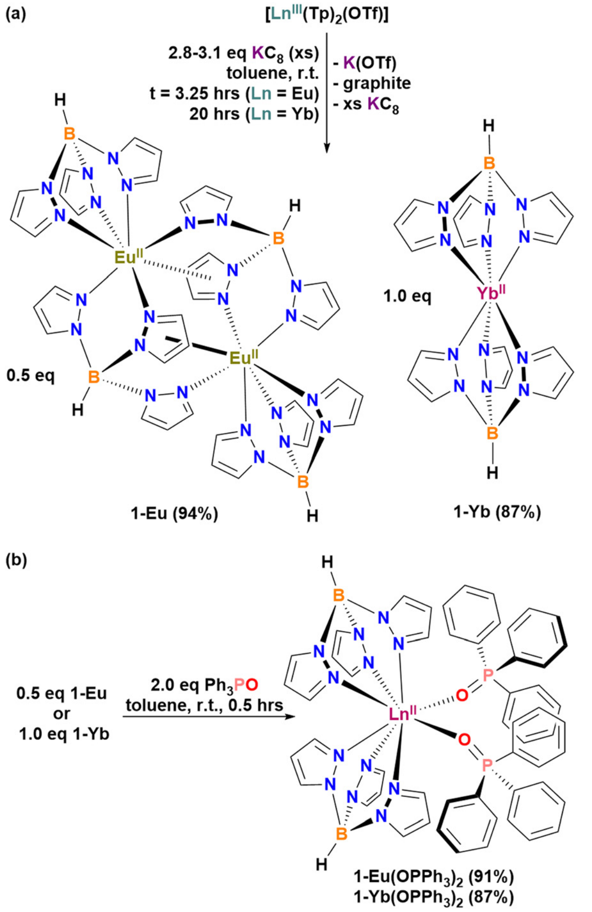

Scheme 1 (a) Synthesis of [{Eu(Tp)(μ-κ^1:η^5-Tp)}$_2$] **1-Eu** and [Yb(Tp)$_2$] **1-Yb** complexes by reduction of the Ln(III) precursor complexes [Ln(Tp)$_2$(OTf)]. (b) Synthesis of *bis*-adduct complexes [Ln(Tp)$_2$(OPPh$_3$)$_2$] **1-Ln(OPPh$_3$)$_2$** (Ln = Eu, Yb) by reaction of two Ph$_3$PO with **1-Ln**.

does reduce [Ln(Tp)$_2$(OTf)] the reaction conditions could not be adequately controlled to achieve clean formation of Ln(II). Therefore, the adduct-free divalent lanthanide complexes **1-Ln** were synthesised by the reduction of [Ln(Tp)$_2$(OTf)] with excess KC$_8$ (Scheme 1) at ambient temperature in toluene with stirring, followed by filtration and subsequent removal of volatiles *in vacuo* (**1-Eu** [{Eu(Tp)(μ-κ^1:η^5-Tp)}$_2$] 94%, **1-Yb** [Yb(Tp)$_2$] 87%). Complexes **1-Ln** have good solubility and stability in both coordinating and non-coordinating solvents. Furthermore, reaction of **1-Ln** with two equivalents of Ph$_3$PO in toluene resulted in the isolation of the *bis*-adduct complexes **1-Ln(OPPh$_3$)$_2$** (**1-Eu(OPPh$_3$)$_2$** 91%, **1-Yb(OPPh$_3$)$_2$** 87%). Elemental analyses of **1-Ln** and **1-Ln(OPPh$_3$)$_2$** are consistent with their respective formulations.

No resonances were observed by NMR spectroscopy for the paramagnetic complexes **1-Eu** and **1-Eu(OPPh$_3$)$_2$**, consistent with the half-filled 4f^7 electronic configuration of Eu(II). The corrected Evans' method magnetic moments (μ_{eff}) for **1-Eu** and **1-Eu(OPPh$_3$)$_2$** in d_6-benzene at room temperature were found to be in the ranges of 7.62–7.78 μ_B and 7.19–7.46 μ_B, respectively. These data are consistent with the calculated spin-only magnetic moment (μ_{so}) of 7.94 μ_B for 4f^7 Gd(III),[18] and Eu(II) literature examples, for both organometallics,[19] and coordination compounds.[20] Complexes **1-Yb** and **1-Yb(OPPh$_3$)$_2$** are full-shell 4f^{14} and diamagnetic as expected, with NMR data similar to [Yb(Tp^R)$_2$] complexes.[6b–d,f] In d_6-benzene the Tp-pyrazolyl protons in **1-Yb** are observed by ^{1}H NMR spectroscopy at δ = 5.97, 7.42 and 7.67 ppm and the Tp-borohydride at δ = 4.96 ppm, in the expected 6 : 6 : 6 : 2 ratio. The Tp-pyrazolyl protons are observed at very similar chemical shifts in the ^{1}H NMR of **1-Yb(OPPh$_3$)$_2$**.

Diffusion-ordered NMR spectroscopy (^{1}H 2D-DOSY) of **1-Yb**, and **1-Yb** with 1 or 2 equivalents of Ph$_3$PO show that **1-Yb** is monomeric, and that in solution there is an equilibrium between Ph$_3$PO and **1-Yb(OPPh$_3$)$_x$** (see ESI,† S1.6). The resonances assigned to **1-Yb(OPPh$_3$)$_2$** in the ^{1}H and ^{31}P NMR data are therefore an equilibrium average. The phenyl protons of Ph$_3$PO, appear at δ = 6.92, 7.02 and 7.49 ppm in the expected 12 : 6 : 12 ratio for two equivalents of Ph$_3$PO, slightly shifted from free Ph$_3$PO (δ = 6.97–7.08 and 7.72–7.82 ppm in a 9 : 6 ratio). By ^{31}P NMR the singlet resonance at δ = 27.63 ppm assigned to **1-Yb(OPPh$_3$)$_2$**, is shifted from free Ph$_3$PO (δ = 24.72 ppm). The Tp-borohydrides of both **1-Yb** and **1-Yb(OPPh$_3$)$_2$** were observed as doublet resonances at δ = −1.85 ppm by ^{11}B NMR. The pyrazolyl carbon resonances of **1-Yb** and **1-Yb(OPPh$_3$)$_2$** were assigned *via* 2D ^{1}H–^{13}C HSQC NMR experiments (see ESI†). The IR spectra of **1-Ln** are near-identical, with weak absorptions between 2350–2560 cm^{-1} assigned to the ν_{BH} of the Tp ligands.[6d,f,13] The IR data for **1-Ln(OPPh$_3$)$_2$** are consistent with **1-Ln** but additionally display strong $\nu_{\text{P=O}}$ at 1117 cm^{-1}. The $\nu_{\text{P=O}}$ is shifted from 1184 cm^{-1} in free Ph$_3$PO to lower wavenumbers upon coordination to the Ln(II).[21]

Complexes **1-Ln** and **1-Ln(OPPh$_3$)$_2$** are intensely coloured due to Laporte allowed 4f^{n-1}–5d^1 transitions characteristic of Ln(II).[22] The electronic absorption spectra of **1-Ln** in both non-coordinating (a) and coordinating (b) solvents, and **1-Ln(OPPh$_3$)$_2$** in MeCN (c) are shown in Fig. 1. In toluene (Fig. 1a) or hexane (Fig. S53 and S54 in ESI†) complexes **1-Ln** display broad and strong absorptions (Ln = Eu ε = 1.45–3.67 × 10^3 M^{-1} cm^{-1}; Ln = Yb ε = 0.68–1.93 × 10^3 M^{-1} cm^{-1}) in the near UV and visible, with λ_{max} of 395 nm for **1-Eu**, and λ_{max} of 341 nm and 520 nm for **1-Yb**.

Photoluminescence (PL) of **1-Eu** is also shown in Fig. 1, in the solid-state under a UV lamp (d) and the excitation and emission spectra in toluene solution (e). Complex **1-Eu** shows emission at 590 nm (λ_{Ex} of 389 nm), and the Excitation-Emission Matrix data (EEM, Fig. S61, ESI†) demonstrate that the emission of **1-Eu** originates only from the parity-allowed 4f^{6}5d^1 to 4f^7 transition of Eu(II). The PL data for **1-Eu** are very similar to those reported for [Eu(Tp$^{\text{3-CH3}}$)$_2$][6h] and consistent with other [Eu(Tp^R)$_2$] examples.[6f–h,10] The λ_{max} and λ_{Em} values in [Eu(Tp^R)$_2$] complexes correlate well to the relative donor-strength of the Tp ligand. The energy of the excitation and emission from molecular Ln(II) complexes in solution follows the spectrochemical series. The energy gap between the 4f and the 5d reduces in magnitude as the interaction with the ancillary ligands increases O < N < C, for example the data for [Ln(Cp^R)$_2$] are significantly red-shifted from [Ln(Tp^R)$_2$].[22a] In acetonitrile, the transition envelopes for **1-Ln** (Fig. 1b) are in very similar spectral positions. In **1-Yb(MeCN)** there is also no

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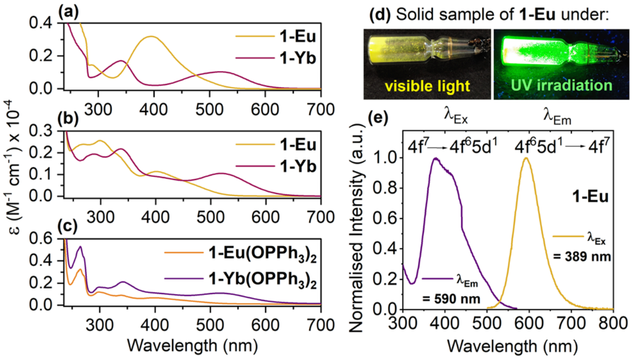

Fig. 1 Overlay of the electronic absorption spectra of **1-Ln** in either toluene (a) or in MeCN (b) and overlay of the electronic absorption spectra of **1-Ln(OPPh$_3$)$_2$** (c) in MeCN, all spectra recorded at room temperature. The traces are coloured in the colour of the complex. Data (λ_{max} and ε) are tabulated in ESI,† Table S3. Photoluminescence of a solid sample of **1-Eu** under a UV lamp (d). Excitation (LHS, λ_{Em} = 590 nm) and emission (RHS, λ_{Ex} = 389 nm) spectra of **1-Eu**, recorded in toluene (e).

change in magnitude of molar extinction co-efficient, however, in **1-Eu(MeCN)** ε decreases significantly. The increased solvent cut-off in MeCN allows for the observation of additional absorptions in the UV for **1-Ln**. No spectral features in these data originate from the Tp ligand. The data for **1-Ln(OPPh$_3$)$_2$** in acetonitrile are near-identical to **1-Ln**, with the addition of the π–π^* transitions arising of Ph$_3$PO (λ_{max} = 265–272, ε = 2.6–5.3 × 10^3 M^{-1} cm^{-1}).[23]

The solid-state molecular structures of **1-Eu** (a), **1-Yb** (b), **1-Yb(THF)** (c), and **1-Eu(OPPh$_3$)$_2$** (d) are shown in Fig. 2. The structures of **1-Eu(THF)$_2$** are shown in Fig. S63 and S64 and **1-Yb(OPPh$_3$)** in Fig. S69 (ESI†). Important structural metrics are tabulated in the ESI† (see S4), data comparison in Table S4 and crystallographic information in Table S5. The Ln–N(κ^3-Tp),[6a,d,f,10] Eu–(η^5-Tp),[24] Ln-O(THF),[1a,b] and Ln–O(OPPh$_3$)[21c,23] bond distances in **1-Ln**, **1-Ln(THF)$_x$** and **1-Ln(OPPh$_3$)$_x$** (Ln = Eu, x = 2; Yb, x = 1) fall within the expected ranges. All data are consistent with the lanthanide contraction[25] and the increase in ionic radius upon reduction from Ln(III) to Ln(II).[13] In the absence of coordinating solvents, complex **1-Eu** (a) is an unusual example of a dimeric structure, whereas complex **1-Yb** (b) is monomeric as expected.[6a,c,d,f] In **1-Eu** (a) each Eu(II) is bound by a κ^3-Tp ligand and an μ-κ^1:η^5 Tp ligand. The μ-κ^1:η^5 binding mode has been seen in Eu(II) pyrazolyl complexes,[24] but this is the first example of μ-κ^1:η^5 Tp binding with bridging of lanthanide metal centres.[6f–h,d,10] In **1-Eu** a significantly longer bond distance is observed for Eu–N(μ-κ^1:η^5-Tp). Either dissolution in THF of **1-Ln** or the addition of 2 Ph$_3$PO to **1-Ln** in toluene, and recrystallisation resulted in single-crystals of the Lewis base adduct complexes **1-Ln(THF)$_x$** (c) or **1-Ln(OPPh$_3$)$_x$** (d) (Ln = Eu, x = 2; Yb, x = 1). Complexes **1-Ln(THF)$_x$** and **1-Ln(OPPh$_3$)$_x$** are all monomeric, with two axial κ^3-coordinated Tp ligands bound to each Ln metal centre, and either one (Yb) or two (Eu) adduct molecules bound in the equatorial plane. In the single-crystal of **1-Yb(OPPh$_3$)** the binding of one Ph$_3$PO ligand is attributed to the specific crystallisation conditions.

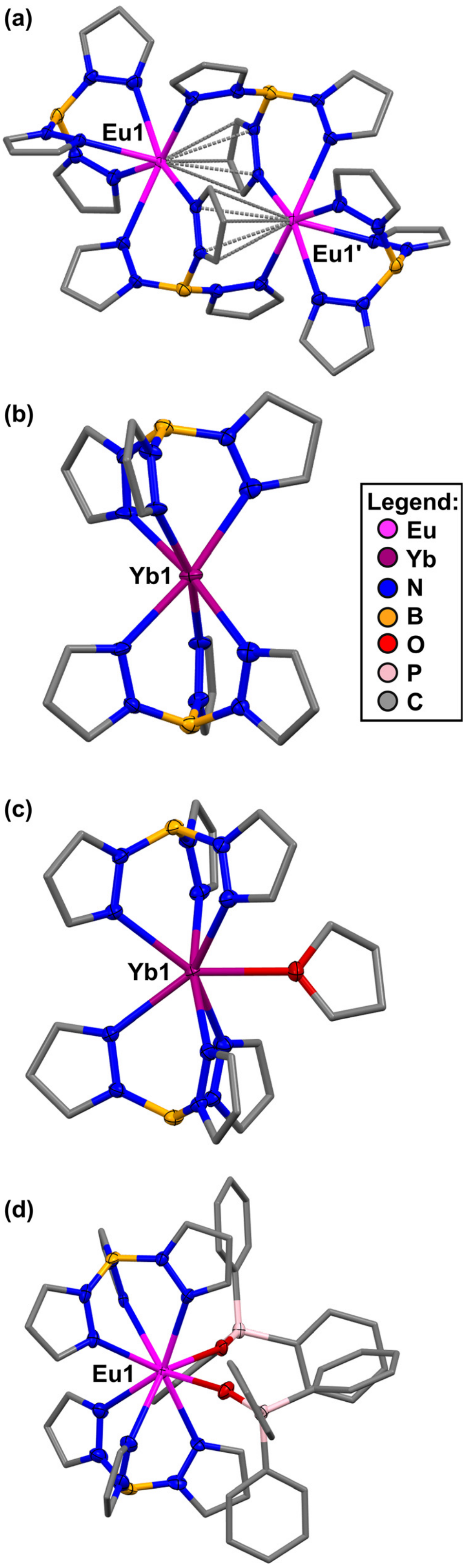

Fig. 2 Crystal structures of **1-Eu** (a), **1-Yb** (b), **1-Yb(THF)** (c), **1-Eu(OPPh$_3$)$_2$** (d). Hydrogen atoms and lattice solvent molecules omitted for clarity and pyrazolyl carbon atoms of Tp, backbone carbon atoms of THF, phenyl carbon atoms of Ph$_3$PO displayed in wireframe. Displacement ellipsoids drawn at 50% probability. Data and crystallographic information can be found in the ESI,† S4 and Tables S4, S5.

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Reduction of Ln(III) in [Ln(Tp)$_2$(OTf)] has been demonstrated to be an excellent route to Ln(II) in [Ln(Tp)$_2$] (Ln = Eu, Yb). The binding strength in combination with ability of the unsubstituted Tp ligand to bridge, bend and flex, results in very stable and soluble Ln(II) complexes. Enabling in turn the collection of both solid-state and solution-state spectroscopic data. Highlights include the direct observation of the effect of solvent on 4f–5d electronic transitions in Ln(II), PL from Eu(II) and first example of μ-κ^1:η^5 Tp binding to lanthanides. Exploration of the chemistry of [Ln(Tp)$_2$] is ongoing in our laboratory, and we anticipate future study of the chemical and physical properties of these Ln(II) complexes.

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Conflicts of interest

There are no conflicts to declare.

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