Supplementary information for: Terbocenium: completing a heavy lanthanide

metallocenium cation family with an alternative anion abstraction strategy

Conrad A. P. Goodwin, Daniel Reta, Fabrizio Ortu, Jingjing Liu, Nicholas F. Chilton* and David P. Mills*

School of Chemistry, The University of Manchester, Oxford Road, M13 9PL Manchester, UK.

Contents

1. Experimental synthesis	S2
2. Crystallography	S 6
3. NMR spectra	S11
4. FTIR spectra	S19
5. UV-vis spectra	S21
6. Magnetic measurements	S22
7. Calculations	S37
8. References	S45

1. Experimental synthesis

General methods. All manipulations were conducted under argon with rigorous exclusion of oxygen and water using Schlenk line and glove box techniques. Toluene, benzene and hexane were dried by refluxing over potassium and were stored over potassium mirrors. Dichloromethane (DCM) was dried over CaH₂ and stored over or 4 Å molecular sieves. All solvents were degassed before use. For NMR spectroscopy C₆D₆ was dried by refluxing over K and CD₂Cl₂ was dried by refluxing over CaH₂. Both NMR solvents were vacuum transferred and degassed by three freeze-pump-thaw cycles before use. Anhydrous LnCl₃ were purchased from Alfa Aesar and were used as received. KCp^{ttt},¹ [YI₃(THF)_{3.5}]² and $[Ph_3C][B(C_6F_5)_4]^3$ were prepared according to literature methods. ¹H (400 MHz), ¹³C{¹H} (100 MHz and 125 MHz), ${}^{11}B{}^{1}H{}$ (128 MHz) and ${}^{19}F{}^{1}H{}$ (376 MHz) NMR spectra were obtained on an Avance III 400 MHz or 500 MHz spectrometer at 298 K. These were referenced to the solvent used, or to external TMS (1H, 13C), H3BO3/D2O (11B) or C₇H₅F₃/CDCl₃ (¹⁹F). UV-Vis-NIR spectroscopy was performed on samples in Youngs tap appended 10 mm pathlength quartz cuvettes on an Agilent Technologies Cary Series UV-Vis-NIR Spectrophotometer from 175–3300 nm. ATR-Fourier Transform infrared (ATR-FTIR) spectra were recorded as microcrystalline powders using a Bruker Tensor 27 spectrometer. Elemental analyses were performed by Mrs Anne Davies and Mr Martin Jennings at The University of Manchester School of Chemistry Microanalysis Service, Manchester, UK.

[Tb(BH₄)₃(THF)₃] (1-Tb). THF (25 mL) was added to a mixture of TbI₃ (1.615 g, 3 mmol) and KBH₄ (1.500 g, 27.8 mmol) in an ampoule. The mixture was stirred vigorously under reflux for 96 hours, cooled to 60 °C, allowed to settle for 1 hour and filtered. Storage at – 26 °C afforded 1-Tb as large colourless crystals contaminated with ~15% iodide (1.049 g,

75%). Anal. Calcd (%) for C₁₂H_{34.4}O₃B_{2.6}I_{0.4}Tb (15% iodide contamination): C, 31.02; H, 7.46; Found: C, 30.74; H, 7.61.

[Y(BH₄)₃(THF)₃] (1-Y). THF (25 mL) was added to a mixture of [YI₃(THF)_{3.5}] (2.155 g, 3 mmol) and KBH₄ (1.618 g, 30 mmol) in an ampoule. The mixture was stirred vigorously under reflux for 96 hours, cooled to 60 °C, allowed to settle for 1 hour and filtered. Storage at -26 °C afforded **1-Y** as large colourless crystals contaminated with ~15% iodide (0.874 g, 77%). Anal. Calcd (%) for C_{11.2}H_{32.8}O_{2.8}B_{2.6}I_{0.4}Y (15% iodide contamination, 2.8 THF due to partial desolvation *in vacuo*): C, 35.39; H, 8.70; Found: C, 35.40; H, 9.03.

[Tb(Cp^{tt1})₂(BH₄)] (2-Tb). THF (20 mL) was added to a pre-cooled (-78 °C) ampoule containing **1-Tb** (0.538 g, 1.28 mmol) and KCp^{tt1} (0.698 g, 2.56 mmol). The reaction mixture was allowed to slowly warm to room temperature and then refluxed for a further 16 hours. Volatiles were removed *in vacuo* and toluene (20 mL) was added. The reaction mixture was allowed to reflux for 1 hour. The resultant suspension was allowed to settle for 3 hours and filtered. The yellow solution was concentrated to 3 mL and stored at 8 °C to afford yellow crystals (0.420 g, 51%). Anal. Calcd (%) for C₃₄H₆₂BTb·0.25C₇H₈: C, 64.70; H, 9.72; Found: C, 64.22; H, 9.98. The paramagnetism of **3** precluded assignment of its ¹¹B{¹H} and ¹³C{¹H} NMR spectra. ¹H NMR (C₆D₆, 400 MHz, 298 K): $\delta = -227.16$ (br, 18H, $v_{1/2} \sim 3200$ Hz, C(*CH*₃)₃), -108.73 (br, 18H, $v_{1/2} \sim 3000$ Hz, C(*CH*₃)₃), -6.57 (br, 18H, $v_{1/2} \sim 4950$ Hz, C(*CH*₃)₃). $\chi_M T$ product = 9.95 cm³ mol⁻¹ K (Evans method, C₆D₆, 298 K). FTIR (ATR, microcrystalline): $\tilde{v} = 3107$ (w), 2957 (s), 2904 (w), 2869 (w), 2442 (s), 2386 (m), 2139 (s), 2023 (w), 1489 (w), 1458 (s), 1389 (s), 1357 (s), 1239 (s), 1219 (w), 1164 (s), 1118 (s), 999 (s), 844 (m), 828 (s), 780 (s), 678 (s), 591 (w), 548 (w), 439 (s) cm⁻¹.

[Y(Cp^{tt})₂(BH₄)] (2-Y). THF (20 mL) was added to a pre-cooled (-78 °C) ampoule containing **1-Y** (0.639 g, 1.8 mmol) and KCp^{tt} (0.996 g, 3.6 mmol). The reaction mixture was allowed to slowly warm to room temperature and then refluxed for a further 16 hours. Volatiles were removed *in vacuo* and toluene (20 mL) was added. The reaction mixture was allowed to reflux for 16 hours. The resultant suspension was allowed to settle for 3 hours and filtered. The yellow solution was concentrated to 3 mL and stored at 8 °C to afford colourless crystals (0.444 g, 43%). Anal. Calcd (%) for C₃₄H₆₂BY: C, 71.57; H, 10.95; Found: C, 71.74; H, 11.03. ¹H NMR (C₆D₆, 400 MHz, 298 K): $\delta = 1.13$ (s, 18H, C(CH₃)₃), 1.51 (s, 36H, C(CH₃)₃), 6.67-6.72 (br m, 4H, Cp-C*H*); BH₄ signals could not be observed. ¹¹B{¹H} NMR (C₆D₆, 128 MHz, 298 K): $\delta = -14.41$ (Y-*B*H₄). ¹³C{¹H} NMR (C₆D₆, 100 MHz, 298 K): $\delta = 32.00$ (Cp-C(CH₃)₃), 34.50 (Cp-C(CH₃)₃), 34.73 (Cp-C(CH₃)₃), 35.05 (Cp-C(CH₃)₃), 129.66 (Cp-CH), 138.28 (Cp-C), 138.36 (Cp-C). FTIR (ATR, microcrystalline): $\tilde{v} = 3107$ (w), 2957 (s), 2904 (w), 2869 (w), 2442 (s), 2386 (m), 2139 (s), 2023 (w), 1489 (w), 1458 (s), 1389 (s), 1357 (s), 1239 (s), 1219 (w), 1164 (s), 1118 (s), 999 (s), 844 (m), 828 (s), 780 (s), 678 (s), 591 (w), 548 (w), 439 (s) cm⁻¹.

[**Tb**(**Cp**^{ttt})₂][**B**(**C**₆**F**₅)₄]·**CH**₂**Cl**₂ (3-**Tb**·**CH**₂**Cl**₂). Benzene (20 mL) was added to a mixture of [Ph₃C][B(C₆F₅)₄] (0.466 g, 0.505 mmol) and [Tb(Cp^{ttt})₂(BH₄)] (3) (0.324 g, 0.505 mmol) at room temperature to give a red reaction mixture. The mixture was stirred for 16 hours, forming a pale-yellow precipitate. The volatiles were removed under vacuum to give a yellow powder, which was washed with hexane (15 mL) and benzene (15 mL). The crude material was dissolved in DCM (2 mL) at -78 °C, and layered with hexane (2 mL). Storage at -25 °C afforded **3-Tb·CH₂Cl₂** as yellow crystals (0.236 g, 36%). Anal. Calcd (%) for C₅₈H₅₈BF₂₀Tb·CH₂Cl₂: C, 50.99; H, 4.35; Found: C, 50.73; H, 4.62. $\chi_M T$ product = 10.70 cm³ mol⁻¹ K (Evans method, C₆D₆, 298 K). The paramagnetism of **3-Tb·CH₂Cl₂** precluded assignment of its ¹H and ¹³C{¹H} NMR spectra. ¹¹B{¹H} NMR (CD₂Cl₂, 128 MHz, 298 K): $\delta = -27.49$ (s). ¹⁹F{¹H} NMR (CD₂Cl₂, 376 MHz, 298 K): $\delta = -182.42$ (s, *m*-*F*), -172.46 (s, *p*-*F*), -144.60 (s, *o*-*F*). FTIR (ATR, microcrystalline): $\tilde{v} = 2964$ (br, m), 2874 (w), 1643 (m), 1512 (s), 1459 (s), 1366 (m), 1275 (m), 1239 (m), 1084 (s), 976 (s), 847 (w), 774 (s), 756 (s), 683 (s), 661 (s), 603 (w), 573 (m), 437 (w) cm⁻¹.

2. Crystallography

Crystallographic methods. The crystal data for complexes 1-Ln (Ln = Tb, 1-Tb; Y, 1-Y), 2-Ln (Ln = Tb, 2-Tb; Y, 2-Y) and 3-Tb·CH₂Cl₂ are compiled in Tables S1-S2. Crystals of 1-Tb, 2-Tb and 3-Tb·CH₂Cl₂ were examined using a Rigaku XtalLAB AFC11 diffractometer with a CCD area detector and a graphite-monochromated Cu K α ($\lambda = 1.54178$ Å) or Mo K α radiation ($\lambda = 0.71073$ Å). Crystals of 1-Y were examined using a Bruker Apex II diffractometer with a CCD area detector and a graphite-monochromated Cu K α radiation (λ = 1.54178 Å). Crystals of 2-Y were examined using an Oxford Diffraction Xcalibur diffractometer, equipped with CCD area detector and mirror-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). Intensities were integrated from data recorded on 0.5° (1-Tb, 2-Tb) and 3-Tb·CH₂Cl₂), 1° (1-Y) or 0.8° (2-Y) frames by ω rotation or ω and ϕ rotation in the case of 1-Y. Cell parameters were refined from the observed positions of all strong reflections in each data set. A Gaussian grid face-indexed (1-Tb, 2-Tb, 2-Y) or multi-scan (1-Y, 3-Tb·CH₂Cl₂) absorption correction with a beam profile was applied.⁴ The structures were solved using SHELXS;⁵ the datasets were refined by full-matrix least-squares on all unique F^2 values,⁶ with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; $U_{iso}(H)$ was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. CrysAlisPro⁴ was used for control and integration, and SHELX^{5,6} was employed through OLEX2⁷ for structure solution and refinement. ORTEP-3⁸ and POV-Ray⁹ were employed for molecular graphics. CCDC 1844350–1844354 contain the supplementary crystal data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Table S1. Crystallographic data for 1-Tb and 1-Y.

^{*a*}Conventional $R = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|$; $Rw = [\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2]^{1/2}$; $S = [\Sigma w (Fo^2 - Fc^2)^2 / no. data - no. params)]^{1/2}$ for all data.

	1-Tb	1-Y
Formula	$C_{12}H_{34.4}B_{2.6}I_{0.4}O_{3}Tb$	$C_{12}H_{34.4}B_{2.6}I_{0.4}O_{3Y}$
Formula weight	460.66	394.01
Crystal size, mm	$0.24 \times 0.29 \times 0.49$	$0.01 \times 0.01 \times 0.02$
Crystal system	orthorhombic	Monoclinic
Space group	Pbcn	$P2_{1}/c$
a, Å	9.1844(2)	8.9188(2)
b, Å	14.3006(3)	12.5674(3)
c, Å	14.7076(4)	16.2017(4)
α, °	90	90
β, °	90	91.122(2)
γ, °	90	90
<i>V</i> , Å ³	1931.73(8)	1815.64(7)
Ζ	4	4
$ ho_{\text{calc}}$, g cm ³	1.584	1.441
μ , mm ⁻¹	4.244	9.781
F(<i>000</i>)	912	813
No. of reflections (unique)	12868 (1762)	27112 (3328)
S ^a	1.28	1.10
$R_1(wR_2) (F^2 > 2\sigma(F^2))$	0.0267 (0.0539)	0.0715 (0.1882)
R _{int}	0.022	0.0143
Min./max. diff map, Å ⁻³	-0.67, 0.57	-0.64, 2.01

Table S2. Crystallographic data for 2-Tb, 2-Y and 3-Tb.

^{*a*}Conventional $R = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|$; $Rw = [\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2]^{1/2}$; $S = [\Sigma w (Fo^2 - Fc^2)^2 / no. data - no. params)]^{1/2}$ for all data.

	2-Tb	2-Y	3-Tb
Formula	$C_{34}H_{62}BTb$	$C_{34}H_{62}BY$	$C_{58}H_{58}BF_{20}Tb$
Formula weight	640.26	570.55	1304.77
Crystal size, mm	$0.14 \times 0.18 \times 0.36$	$0.15\times0.22\times0.25$	$0.1 \times 0.05 \times 0.01$
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_{1}/n$	$P2_{1}/c$	<i>P</i> -1
a, Å	10.3320(2)	10.3453(5)	11.7358(4)
b, Å	15.6294(3)	15.6331(9)	12.4581(4)
c, Å	20.5234(4)	20.5613(11)	19.9710(9)
α, °	90	90	82.810(3)
β, °	99.173(2)	99.312(5)	89.321(3)
γ, °	90	90	79.728(3)
<i>V</i> , Å ³	3271.78(12)	3281.5(3)	2850.3(2)
Z	4	4	2
$ ho_{ m calc}, { m g} { m cm}^3$	1.300	1.155	1.520
μ , mm ⁻¹	2.181	1.796	1.343
F(<i>000</i>)	1343	1240	1312
No. of reflections (unique)	24081 (5942)	10183 (5931)	35372 (10291)
S^a	1.06	1.05	1.023
$R_1(wR_2) (F^2 > 2\sigma(F^2))$	0.0357 (0.1022)	0.0876 (0.2756)	0.0852 (0.1912)
$R_{ m int}$	0.028	0.052	0.101
Min./max. diff map, Å ⁻³	-1.54, 2.04	-0.99, 2.94	-1.23, 4.33



Figure S1. Molecular structure of [Tb(BH₄)₃(THF)₃] (**1-Tb**). Displacement ellipsoids set at 30 % probability level and hydrogen atoms are omitted for clarity. Selected distances: Tb1…B1, 2.69(2) Å; Tb1…B2, 2.733(6) Å; Tb1…B3, 2.69(2) Å; Tb1–O1, 2.358(3) Å; Tb1–O2, 2.434(3) Å; Tb1–O3, 2.358(3) Å.



Figure S2. Molecular structure of [Y(BH₄)₃(THF)₃] (**1-Y**). Displacement ellipsoids set at 30 % probability level and hydrogen atoms are omitted for clarity. Selected distances: Y1…B1, 2.566(10) Å; Y1…B2, 2.57(2) Å; Y1…B3, 2.60(2) Å Y1–O1, 2.304(5) Å; Y1–O2, 2.378(5) Å; Y1–O3, 2.325(5) Å.



Figure S3. Molecular structure of [Y(Cp^{ttt})₂(BH₄)] (**2-Y**). Displacement ellipsoids set at 30 % probability level and hydrogen atoms apart from those on B are omitted for clarity. Selected distances and angles: Y1...Cp_{centroid1}, 2.402(3) Å; Y1...Cp_{centroid2}, 2.397(3) Å; Y...B1, 2.646(6) Å; Cp_{centroid1}...Y1...Cp_{centroid2}, 147.53(10)°.

3. NMR spectra



Figure S4. ¹H NMR spectrum of complex 2-Tb in C₆D₆. Solvent residual marked.



Figure S5. ¹H NMR spectrum of complex 2-Tb in C₆D₆, spectrum centered at -150 ppm. Solvent residual marked.



Figure S6. ¹³C $\{^{1}H\}$ NMR spectrum of complex 2-Tb in C₆D₆. Solvent residual marked.



Figure S7. ¹H NMR spectrum of complex 2-Tb in C_6D_6 with a C_6H_6/C_6D_6 insert. Solvent residual marked.



Figure S8. ¹H NMR spectrum of complex 2-Y in C₆D₆.



Figure S9. ¹¹B NMR spectrum of complex 2-Y in C_6D_6 .



Figure S10. ¹¹B $\{^{1}H\}$ NMR spectrum of complex 2-Y in C₆D₆.



Figure S11. ${}^{13}C{}^{1}H$ NMR spectrum of complex 2-Y in C₆D₆.



Figure S12. ¹H NMR spectrum of complex 3-Tb in CD_2Cl_2 . Δ denotes solvent residual.



Figure S13. ¹¹B NMR spectrum of complex 3-Tb in CD₂Cl₂.



Figure S14. ¹¹B $\{^{1}H\}$ NMR spectrum of complex 3-Tb in CD₂Cl₂.



Figure S15. ¹³C{¹H} NMR spectrum of complex 3-Tb in CD₂Cl₂. Δ denotes solvent residual.



Figure S16. ¹⁹F NMR spectrum of complex 3-Tb in CD₂Cl₂.



Figure S17. ${}^{19}F{}^{1}H$ NMR spectrum of complex 3-Tb in CD₂Cl₂.



Figure S18. ¹H NMR spectrum of complex **3-Tb** in CD₂Cl₂ with a CH₂Cl₂/CD₂Cl₂ insert. Δ denotes solvent residual.

4. FTIR spectra



Figure S19. ATR-IR spectrum of complex 2-Tb recorded as a microcrystalline powder.



Figure S20. ATR-IR spectrum of complex 2-Y recorded as a microcrystalline powder.



Figure S21. ATR-IR spectra of **2-Tb** and **2-Y** in the region 1600–400 cm⁻¹ intended to show the similarities between all spectra.



Figure S22. ATR-IR spectrum of complex 3-Tb recorded as a microcrystalline powder.



Figure S23. UV-vis-NIR spectrum of 2-Tb between $34000-6000 \text{ cm}^{-1}$ (295–1650 nm) recorded as a 0.808 mM solution in DCM.



Figure S24. UV-vis-NIR spectrum of 3-Tb between $34000-6000 \text{ cm}^{-1}$ (295–1650 nm) recorded as a 1.023 mM solution in DCM.

6. Magnetic measurements

Solid state magnetic measurements were made using a Quantum Design MPMS-XL7 superconducting quantum interference device (SQUID) magnetometer. Crystalline samples with mass ranging between 15 and 40 mg were crushed with a mortar and pestle under an inert atmosphere, and then loaded into a borosilicate glass NMR tube along with *ca.* 5 - 20 mg powdered eicosane, which was then evacuated and flame-sealed to a length of *ca.* 5 cm. The eicosane was melted by heating the tube gently with a low-power heat gun in order to immobilise the crystallites. The NMR tube was then mounted in the centre of a plastic straw using friction by wrapping it with Kapton tape, and the straw was then fixed to the end of the sample rod. The measurements were corrected for the diamagnetism of the straw, borosilicate tube and eicosane using calibrated blanks, and the intrinsic diamagnetism of the sample using Pascals constants.¹⁰ Complex **3-Tb** is temperature sensitive so this sample was maintained below 260 K during measurement. Magnetic data is compiled in Tables S3–S9 and Figures S25–S38.

Table S3. Room temperature $\chi_M T$ products (cm³ mol⁻¹ K) for **2-Tb** and **3-Tb**. Evans method measured on an NMR spectrometer operating at 298 K, SQUID values measured in a 0.1 T field at 300 K (**2-Tb**) or 260 K (**3-Tb**).

Method	2-Tb	3-Tb	
Evans	9.95	10.70	
SQUID	10.84	11.60	
CASSCF	11.60	11.40	
Free Ion	11.82		



Figure S25. Temperature dependence of the molar magnetic susceptibility products $\chi_M T$ measured under a 0.1 T dc field for **2-Tb** (top) and **3-Tb** (bottom). Circles and solid lines are the experimental and CASSCF-SO calculated values, respectively.



Figure S26. Field dependence of magnetisation at 2 and 4 K for **2-Tb** (left) and **3-Tb** (right). Circles and solid lines are the experimental and CASSCF-SO calculated values, respectively.



Figure S27. Cole-Cole plot for **2-Tb** in a 0.1 T dc field. Solid lines are fits to the generalised Debye model, giving $0.04 \le \alpha \le 0.31$.



Figure S28. In-phase (top) and out-of-phase (bottom) ac susceptibilities for **2-Tb** in a 0.1 T dc field. Solid lines are fits to the generalised Debye model, giving $0.04 \le \alpha \le 0.2$.

Temperature	τ	Xs	Xτ	α
3.0	9.602E-04	6.995E-05	2.526E-04	2.040E-01
4.0	8.391E-04	5.682E-05	2.280E-04	1.841E-01
5.0	6.286E-04	4.884E-05	1.930E-04	1.785E-01
6.0	4.535E-04	4.472E-05	1.640E-04	1.620E-01
7.0	3.137E-04	4.126E-05	1.417E-04	1.351E-01
8.0	2.105E-04	3.805E-05	1.244E-04	1.039E-01
9.0	1.412E-04	3.545E-05	1.108E-04	7.412E-02
10.0	9.051E-05	3.078E-05	9.990E-05	6.168E-02
11.0	6.182E-05	2.845E-05	9.093E-05	3.904E-02
12.0	3.342E-05	1.978E-05	8.322E-05	4.831E-02

Table S4. Best fit parameters to the generalised Debye model for the ac data of 2-Tb.



Figure S29. Fitting of relaxation rates for **2-Tb**. Blue line is power-law (Raman) model (second line Table S5), green line is exponential (Orbach) model (first line Table S5).

Table S5. Best fit parameters to the relaxation rates for the ac data of 2-Tb.

$ au^{-1}$	$ au_0$ (s)	U_{eff} (cm ⁻¹)	<i>C</i> (s ⁻¹ K ⁻ⁿ)	n	$ au_{QTM}(s)$
$ au_{0}^{-1}e^{\left(-U_{eff}/_{kT} ight) }+ au_{QTM}^{-1}$	1.4E-6	29	-	-	8.2E-4
$CT^n + \tau_{QTM}^{-1}$	-	-	0.26	4.6	9.5E-4



Figure S30. Cole-Cole plot for 3-Tb in a 0 T dc field. Solid lines are fits to the generalised Debye model, giving $0.2 \le \alpha \le 0.38$.



Figure S31. In-phase (top) and out-of-phase (bottom) ac susceptibilities for **3-Tb** in a 0 T dc field. Solid lines are fits to the generalised Debye model, giving $0.2 \le \alpha \le 0.38$.

Temperature	τ	Xs	Xτ	α
2.00	2.1123E-02	3.4840E-05	1.9817E-04	0.37945
2.50	1.3800E-02	2.9630E-05	1.5196E-04	0.34617
3.00	1.0945E-02	2.5120E-05	1.2789E-04	0.33690
3.50	8.2874E-03	2.1910E-05	1.0534E-04	0.31733
4.00	7.0847E-03	1.9210E-05	9.2180E-05	0.31062
4.50	6.4209E-03	1.7350E-05	8.3370E-05	0.30214
5.00	5.8459E-03	1.5880E-05	7.6050E-05	0.29452
5.50	5.7323E-03	1.4690E-05	7.2460E-05	0.29759
6.00	5.2363E-03	1.3570E-05	6.6480E-05	0.28996
7.00	4.4961E-03	1.1850E-05	5.7090E-05	0.27814
8.00	3.9300E-03	1.0550E-05	5.0060E-05	0.26997
9.00	3.4570E-03	9.4400E-06	4.4630E-05	0.26552
10.00	3.0938E-03	8.7000E-06	4.0240E-05	0.25820
11.00	2.7543E-03	7.9100E-06	3.6730E-05	0.25996
12.00	2.4429E-03	7.3000E-06	3.3610E-05	0.25607
15.00	1.8117E-03	5.9700E-06	2.7180E-05	0.24945
18.00	1.4118E-03	5.2300E-06	2.2740E-05	0.23082
21.00	1.1268E-03	4.5600E-06	1.9560E-05	0.22267
24.00	9.7766E-04	4.2100E-06	1.7200E-05	0.20702
27.00	8.4849E-04	3.8600E-06	1.5360E-05	0.19030
30.00	7.5064E-04	3.5400E-06	1.3990E-05	0.19628

 Table S6. Best fit parameters to the generalised Debye model for the ac data of 3-Tb in 0

 applied field.



Figure S32. Fitting of relaxation rates for **3-Tb** in a zero applied field. Blue line is power-law (Raman) model (second line Table S7), green line is exponential (Orbach) model (first line Table S7).

Table S7. Best fit parameters to the relaxation rates for the ac data of **3-Tb**, in a zero applied field.

$ au^{-1}$	$ au_0$ (s)	U_{eff} (cm ⁻¹)	<i>C</i> (s ⁻¹ K ⁻ⁿ)	n
$ au_0^{-1} e^{\left(^{-U_{eff}}/_{kT} ight)}$	1.2E-3	6.8	-	-
CT^n	-	-	24	1.2



Figure S33. Hysteresis of **3-Tb** (mean field sweep rate of 21(8) Oe s⁻¹ for |H| < 10 kOe, 49(11) Oe s⁻¹ for 10 < |H| < 20 kOe, and 84(9) Oe s⁻¹ for 20 < |H| < 70 kOe, giving an overall mean sweep rate of 45 Oe s⁻¹.



Figure S34. Zero-field cooled (squares) and field cooled (circles) for **3-Tb**, measured at 1000 and 500 Oe external fields.

7. Calculations

We used MOLCAS 8.0¹¹ to perform CASSCF-SO calculations of **2-Tb** and **3-Tb** complexes in order to determine their electronic structures. We employed the molecular geometries from the single crystal XRD structure with no optimisation, taking the largest disorder component only. Basis sets from ANO-RCC library^{12,13} were employed with VTZP quality for Ln atoms, VDZP quality for the cyclopentadienyl C atoms, the two in-plane hydrogen atoms from the closest *t*-butyl groups and the equatorial boron atom (**2-Tb** only), and VDZ quality for all remaining atoms, in conjunction with the second-order DKH transformation. Cholesky decomposition of the two-electron integrals with a threshold of 10⁻⁸ was performed to save disk space and reduce computational demand. The molecular orbitals (MOs) were optimised in state-averaged CASSCF calculations, with eight 4f electrons in the active space of the seven f orbitals, giving spin multiplicities of 7, 5, 3and 1 with 7, 140, 472, 490 roots and 7, 140, 195, 197 states mixed by spin orbit coupling. The resulting spin-orbit wavefunctions were decomposed into their CF wavefunctions, and the magnetic susceptibility calculated (see Magnetism) using SINGLE_ANISO.¹⁴ The electronic structure is well described by the standard crystal field (CF) Hamiltonian:

$$\widehat{H}_{CF} = \sum_{k=2,4,6} \sum_{q=-k}^{k} B_k^q \,\theta_k \widehat{O}_k^q$$

where B_k^q are the CF parameters, θ_k are the operator equivalent factors and \hat{O}_k^q are the extended Steven's operator equivalents.^{15,16} The CFPs obtained by direct projection from the CASSCF-SO calculations are used to reproduce the wavefunction compositions using PHI,¹⁶ at zero and 0.1 T applied field.

Table S8 Electronic structure of **2-Tb** calculated with CASSCF-SO, and with PHI using the CFPs obtained from MOLCAS, quantised along the g_3 direction. Wavefunction contributions > 10% are shown.

MOLCAS			PHI			
Energy (cm ⁻¹)	g 3	Energy (cm ⁻¹)	g 3	Angle to quantisation axis (deg)	Wavefunction	$<\!\!J_{\rm Z}\!>$
0.00	177	0.00	170		500/1+6) + 500/176)	0.0
0.03	1/./	0.10	17.0	-	30% <u> </u> ±0/+30% +0/	0.0
147.55	141	143.6	144	1.6		0.0
148.30	14.1	143.7	14.4	1.6	45% ±5>+45% +5>	0.0
293.50	-	293.6	-	-	$33\% -3\rangle + 33\% 3\rangle + 13\% -2\rangle + 13\% 2\rangle$	0.0
313.89	-	313.7	-	-	41% -3>+41% 3>	0.0
402.99	-	403.2	-	-	$26\% -1\rangle + 26\% 1\rangle + 20\% -3\rangle + 20\% 3\rangle$	0.0
508.66	-	512.5	-	-	39% -3>+39% 3>	0.0
534.38	-	535.9	-	-	$37\% 0\rangle + 16\% -2\rangle + 16\% 2\rangle + 15\% 3\rangle + 13\% -3\rangle$	0.0
780.55	14.0	776.0	14.6	20.0	42% -2>+42% 2>	0.0
783.40	14.8	778.1	14.0	89.8	$23\% -1\rangle + 23\% 1\rangle + 25\% -3\rangle + 25\% 3\rangle$	0.0
1112.16	170	1112	17.0	<u> </u>	$43\% -1\rangle + 43\% 1\rangle$	0.0
1112.31	17.0	1112	1/.9	00.7	55% 0> + 21% -2> + 21% 2>	0.0

Table S9. Electronic structure of **2-Tb** calculated with PHI using the CFPs obtained from MOLCAS, quantised along the g_3 direction, with a 0.1 T field along the quantisation axis. Wavefunction contributions > 10% are shown.

РНІ						
Energy (cm ⁻¹)	Wavefunction	$< J_z >$				
0.00	97% -6>	-5.9				
0.84	97% 6>	5.9				
143.7	89% -5>	-4.7				
144.4	89% 5>	4.7				
294.0	$34\% -4\rangle + 32\% 4\rangle + 13\% -2\rangle + 12\%2\rangle$	-0.1				
314.1	$40\% -4\rangle+42\% 4\rangle$	0.1				
403.6	$26\% -1\rangle + 26\% 1\rangle + 20\% -3\rangle + 20\% 3\rangle$	0.0				
512.8	39% -3>+39% 3>	0.0				
536.2	$37\% 0\rangle + 16\% -2\rangle + 16\% 2\rangle + 15\% -4\rangle + 15\% 4\rangle$	0.0				
776.4	8% -4>+8% 4>+42% -2>+42% 2>	0.0				
778.5	$25\% -3\rangle + 25\% 3\rangle + 23\% -1\rangle + 23\% 1\rangle$	0.0				
1112	43% -1>+43% 1>	0.0				
1113	55% 0>+21% -2>+21% 2>	0.0				

Table S10. Electronic structure of 2-Tb calculated with CASSCF-SO, and with PHI usingthe CFPs obtained from MOLCAS, quantised along the direction normal to the plane of Cp^{ttt} -B-Cp^{ttt}. Wavefunction contributions > 10% are shown.

MOLO	CAS		РНІ			
Energy (cm ⁻¹)	g 3	Energy (cm ⁻¹)	g 3	Angle to quantisation axis (deg)	Wavefunction	$<\!\!J_{\rm Z}\!>$
0.00	177	0.00	17.8	86.0	45% -1 angle+45% 1 angle	0.0
0.03	1/./	0.12	17.0 00.9	58% 0>+20% 2>+20% -2>	0.0	
147.55	141	144.8	14.2	80.2	40% 2>+40% -2>	0.0
148.30	14.1	145.1	14.3 89.2	$24\% -1\rangle + 24\% 1\rangle + 20\% -3\rangle + 20\% 3\rangle$	0.0	
293.50	-	292.8	-	-	$37\% 0\rangle + 21\% 2\rangle + 21\% -2\rangle + 11\% -4\rangle + 11\% 4\rangle$	0.0
313.89	-	312.8	-	-	42% -3>+42% 3>	0.0
402.99	-	403.2	-	-	$25\% -3\rangle + 25\% 3\rangle + 22\% -1\rangle + 22\% 1\rangle$	0.0
508.66	-	512.2	-	-	$44\% -4\rangle+44\% 4\rangle$	0.0
534.38	-	536.9	-	-	38% -4> + 38% 4>	0.0
780.55	14.0	776.6	14.0	0.5	47% -5>+47% 5>	0.0
783.40	14.8	14.8 779.0	14.0	0.5	47% -5>+47% 5>	0.0
1112.16	17.0	1112	17.0	0.8	49% -6>+49% 6>	0.0
1112.31	17.8	1112	17.9	0.8	49% -6>+49% 6>	0.0

Table S11. Electronic structure of **2-Tb** calculated with PHI using the CFPs obtained from MOLCAS, quantised along the direction normal to the plane of Cp^{ttt} -B- Cp^{ttt} , with a 0.1 T field along the quantisation axis. Wavefunction contributions > 10% are shown.

РНІ						
Energy (cm ⁻¹)	Wavefunction	$<\!\!J_{ m z}\!>$				
0.00	45% -1 angle+45% 1 angle	0.0				
0.13	58% 0>+20% 2>+20% -2>	0.0				
144.8	$30\% 2\rangle + 30\% -2\rangle + 10\% -1\rangle + 10\% 1\rangle$	0.0				
145.1	$20\% -3\rangle + 20\% 3\rangle + 24\% -1\rangle + 24\% 1\rangle$	0.0				
292.8	$37\% 0\rangle + 20\% 2\rangle + 20\% -2\rangle + 11\% -4\rangle + 11\% 4\rangle$	0.0				
312.8	42% -3>+42% 3>	0.0				
403.2	$25\% -3\rangle + 25\% 3\rangle + 23\% -1\rangle + 23\% 1\rangle$	0.0				
512.2	$45\% -4\rangle+43\% 4\rangle$	-0.1				
536.9	38% -4> + 37% 4>	0.1				
776.5	60% -5>+35% 5>	-1.3				
779.1	34% -5> + 60% 5>	1.3				
1112	98% -6>	-5.9				
1113	98% 6>	5.9				

Table S12. Electronic structure of **3-Tb** calculated with CASSCF-SO, and with PHI using the CFPs obtained from MOLCAS, quantised along the Cp^{ttt} - Cp^{ttt} direction. Wavefunction contributions > 10% are shown.

MOLCAS		РНІ				
Energy (cm ⁻¹)	g 3	Energy (cm ⁻¹)	<i>g</i> ₃	Angle to quantisation axis (deg)	Wavefunction	$<\!\!J_{\rm Z}\!>$
0.00	17.9	0.00	18.0	0.0	$50\% \pm6 angle+50\% \mp6 angle$	0.0
0.00		0.00				0.0
313.87	14.6	313.5	15.0	0.5	50% ±5>+50% ∓5>	0.0
313.87		313.5				0.0
645.45	11.3	645.7	12.0	0.3	$50\% \pm4 angle+50\% \mp4 angle$	0.0
645.52		645.8				0.0
965.33	8.1	966.2	9.0	0.5	50% ±3>+50% ∓3>	0.0
965.81		966.6				0.0
1235.82	5.2	1233	6.0	0.9	50% ±2>+50% ∓2>	0.0
1237.14		1238				0.0
1408.20	-	1405	-	-	500/1+4) + 500/174)	0.0
1423.02	-	1426	-	-	3U% ±1)+3U% +1)	0.0
1476.96	-	1479	-	-	100% 0>	0.0

Table S13. Electronic structure of **3-Tb** calculated with with PHI using the CFPs obtained from MOLCAS, quantised along the Cp^{ttt}-Cp^{ttt} direction, with a 0.1 T field along the quantisation axis. Wavefunction contributions > 10% are shown.

РНІ						
Energy (cm ⁻¹)	Wavefunction	$<\!\!J_{ m Z}\!>$				
0.00	1000/11/0)	-6.0				
0.84	100%(±6)	6.0				
313.5		-5.0				
314.2	100%[±57	5.0				
645.9	1000/114)	-4.0				
646.5	100%(±4)	4.0				
966.5	950(1+2) + 150(1+2)	-2.1				
967.1	83%[±3] + 13%[+3]	2.1				
1233	$520(1+2) + 470(1\pm 2)$	-0.1				
1238	$53\%[\pm 2] + 47\%[\pm 2]$	0.1				
1405	500(1+1) + 500(1-1)	0.0				
1426	$30\%[\pm 1] + 30\%[\pm 1]$	0.0				
1479	100% 0>	0.0				

8. References

- F. A. Weber, H. Sitzmann, M. Schultz, C. D. Sofield and R. A. Andersen, Organometallics, 2002, 21, 3139.
- 2. K. Izod, S. T. Liddle and W. Clegg, Inorg. Chem., 2004, 43, 214.
- 3. J. C. W. Chien, W.-M. Tsai and M. D. Rausch, J. Am. Chem. Soc., 1991, 113, 8570.
- CrysAlisPRO, version 39.27b; Oxford Diffraction /Agilent Technologies UK Ltd: Yarnton, U.K., 2017.
- 5. G. M. Sheldrick, Acta Crystallogr., Sect. A., 2008, 64, 112.
- 6. G. M. Sheldrick, Acta Crystallogr., Sect. C, 2015, 71, 3.
- O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339.
- 8. L. J. Farrugia, J. Appl. Crystallogr., 2012, 45, 849.
- POV-Ray. Persistence of Vision Raytracer; Persistence of Vision Pty. Ltd.: Williamstown, Victoria, Australia, 2013.
- 10. G. A. Bain and J. F. Berry, J. Chem. Ed., 2008, 85, 532.
- F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. De Vico, I. Fernandez Galván, N. Ferré, L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. Manni, H. Lischka, D. Ma, P. Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra-Martí, M. Stenrup, D. G. Truhlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata and R. Lindh, J. Comput. Chem., 2016, 37, 506.
- B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov and P.-O. Widmark, J. Phys. Chem. A., 2004, 108, 2851.

- B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov and P.-O. Widmark, J. Phys. Chem. A., 2005, 109, 6575.
- 14. L. Ungur and L. F. Chibotaru, Chem. -Eur. J., 2017, 23, 3708.
- A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Oxford University Press, 1970.
- 16. N. F. Chilton, R. P. Anderson, D. L. Turner, A. Soncini and K. S. Murray, J. Comput. Chem., 2013, 34, 1164.