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Investigation of the "bent sandwich-like" divalent lanthanide pyrazolylborates $Ln(Tp^{iPr2})_2$ (Ln = Sm, Eu, Yb)

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SUPPLEMENTARY INFORMATION

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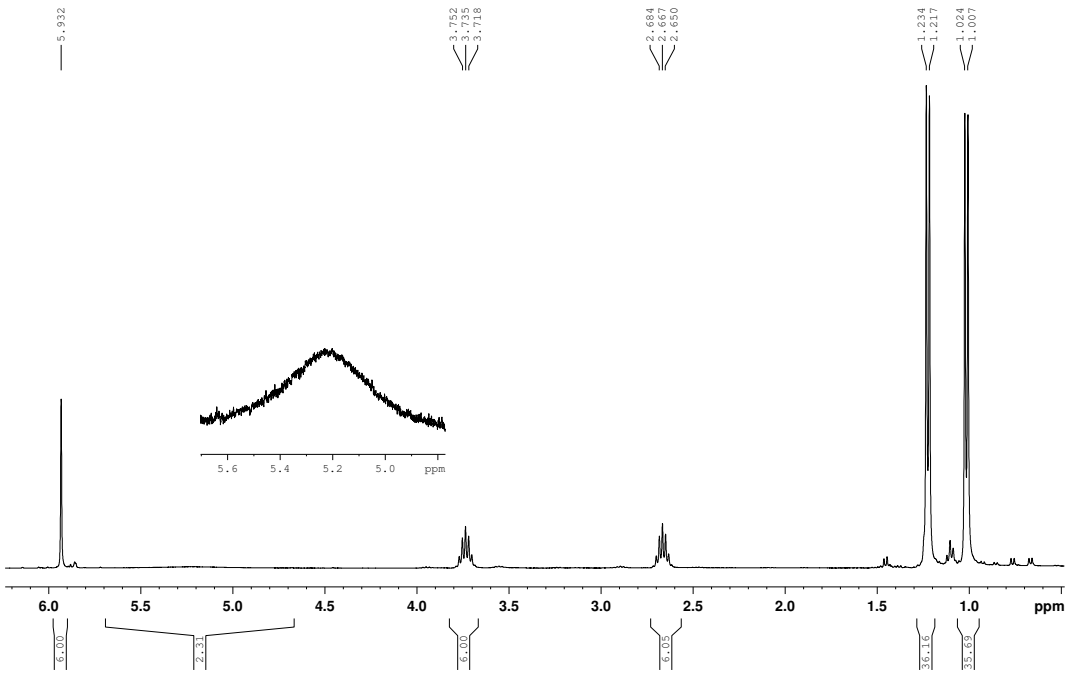

Figure S1. ^{1}H NMR spectrum of Yb(Tp^{iPr2})$_2$ (**4**)

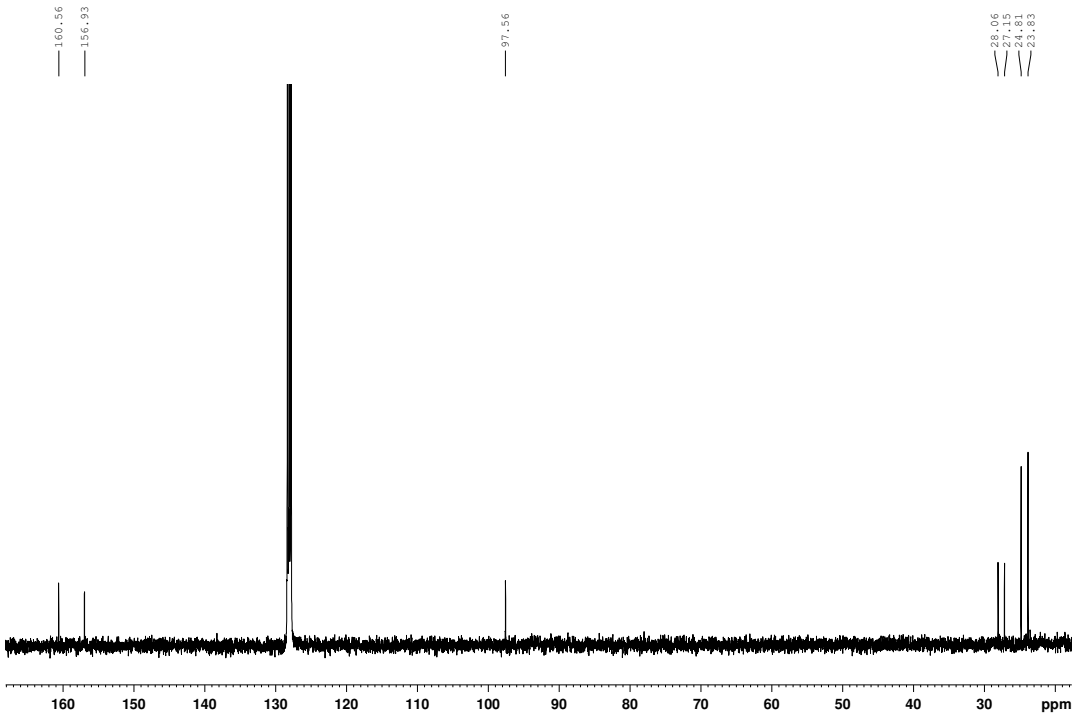

Figure S2. ^{13}C NMR spectrum of Yb(Tp^{iPr2})$_2$ (**4**)

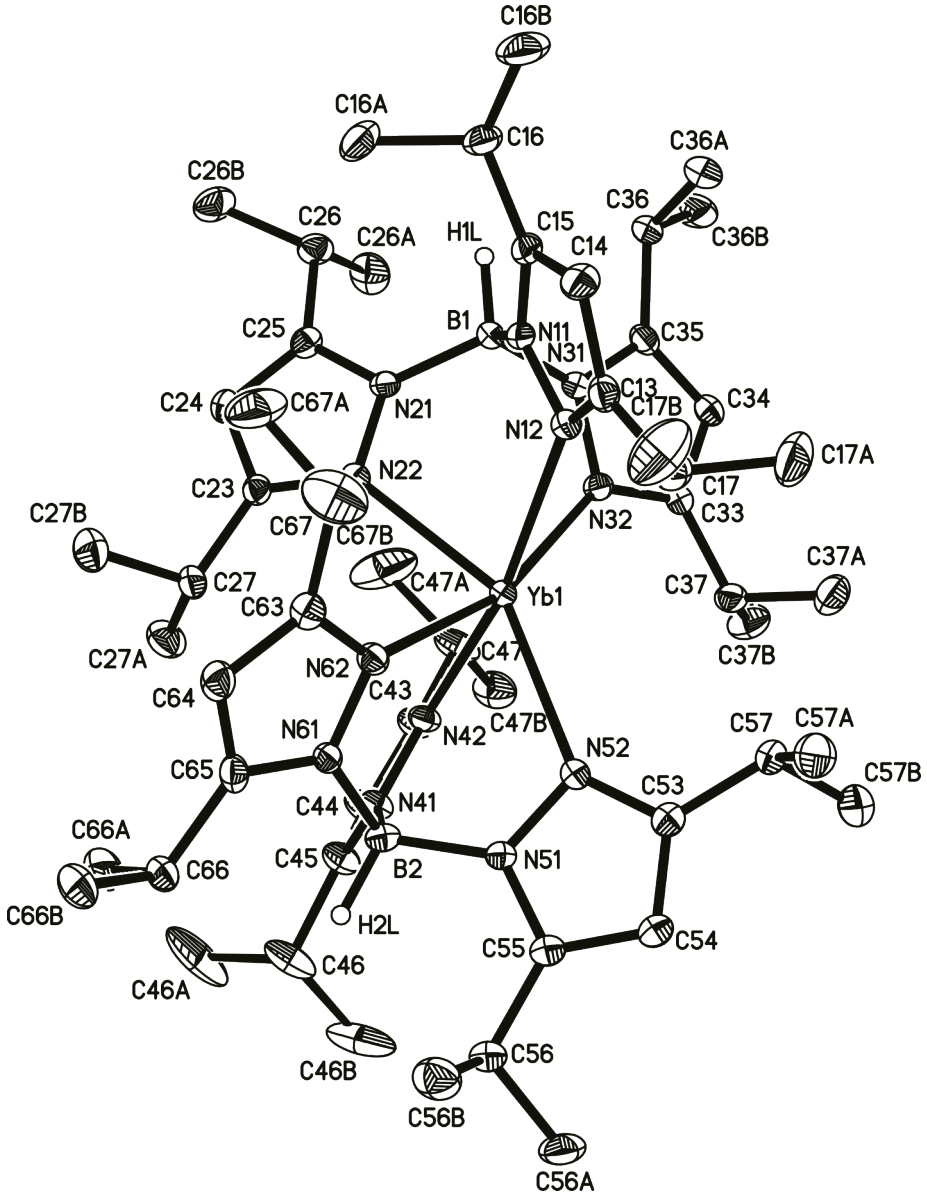

Figure S3. Perspective view of the Yb(Tp^{iPr2})$_2$ (**4**) molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the B–H groups, and are not shown for the remaining groups.

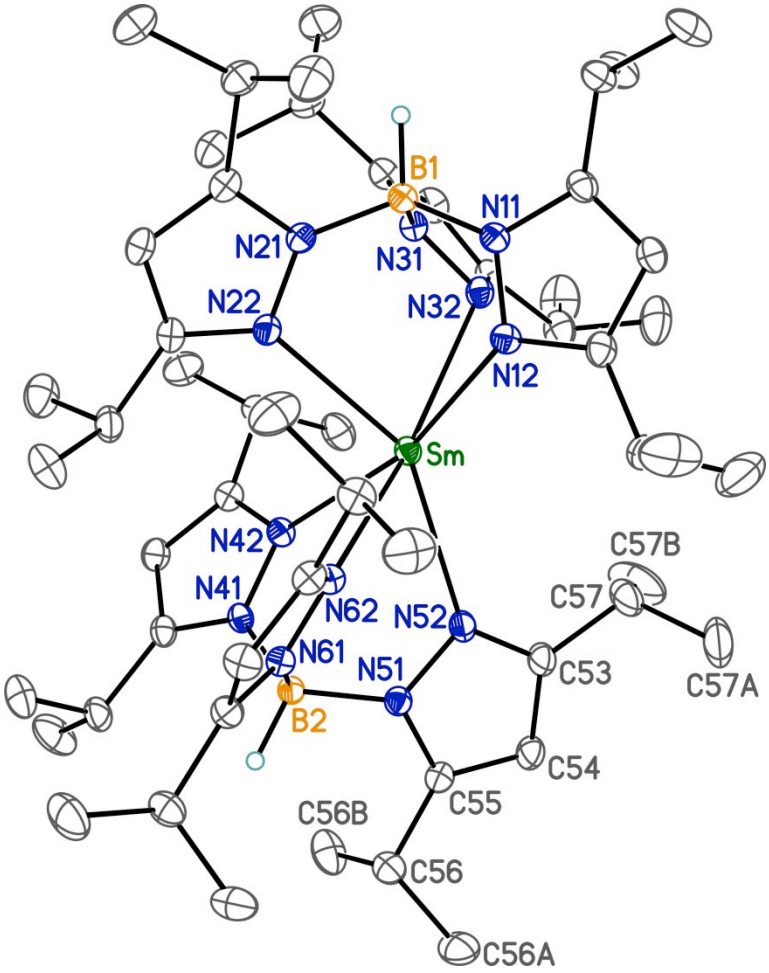

Figure S4. Perspective view of the [{HB(3,5-^{i}Pr$_2$-pyrazolyl)$_3$}$_2$Sm]•CH$_3$CN (**5**) molecule showing the atom labelling scheme. The lattice solvate acetonitrile is not shown. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 30% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the B–H groups, and are not shown for the remaining groups.

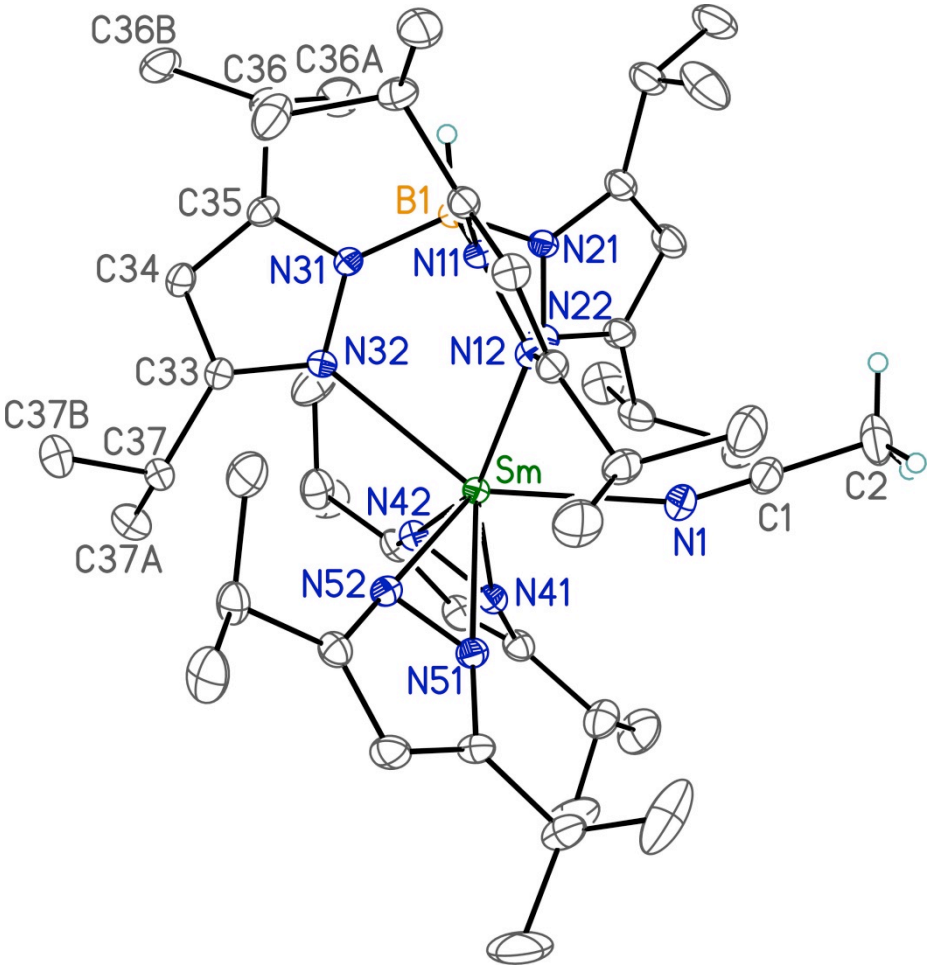

Figure S5. Perspective view of the [{HB(3,5-^{i}Pr$_2$-pyrazolyl)$_3$Sm(3,5-^{i}Pr$_2$-pyrazolyl)$_2$(NCMe)] (**6**) molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 30% probability level. Hydrogen atoms attached to C2 and B1 are shown with arbitrarily small thermal parameters; all other hydrogens are not shown.

Table S1. Interatomic Distances (Å) and Angles (°) for previously published $Sm(Tp^{iPr2})_2$ and $Tm(Tp^{iPr2})_2$, and $Sm(Tp^{iPr2})_2 \cdot CH_3CN$ (5) and $Yb(Tp^{iPr2})_2$ (4)

	Sm(A)[a,b]	Sm(B)[a,b]	Sm•CH_3CN	Tm(A)[a,b]	Tm(B)[a,b]	Yb[a]	Yb'[a]
Ln-N12	2.638(2)	2.664(2)	2.642(2)	2.534(2)	2.538(2)	2.528(2)	2.525(2)
Ln-N22	2.668(2)	2.639(2)	2.638(2)	2.543(2)	2.536(2)	2.530(2)	2.522(2)
Ln-N32	2.645(2)	2.664(2)	2.735(2)	2.553(2)	2.534(2)	2.550(2)	2.528(2)
Ln-N42	2.587(2)	2.624(2)	2.631(2)	2.500(2)	2.518(2)	2.487(2)	2.498(2)
Ln-N52	2.680(2)	2.643(2)	2.634(2)	2.599(2)	2.554(2)	2.589(2)	2.540(2)
Ln-N62	2.605(2)	2.616(2)	2.661(2)	2.488(2)	2.503(2)	2.478(2)	2.502(2)
$Ln\text{-}N_{range}$	2.59 – 2.68	2.62 – 2.66	2.63 – 2.74	2.49 – 2.60	2.50 – 2.55	2.48 – 2.59	2.50 – 2.54
N-Ln-N(intra)							
N12-Ln-N22	78.68(5)	77.34(5)	78.37(5)	81.80(7)	80.59(7)	81.93(6)	84.11(6)
N12-Ln-N32	69.08(5)	70.85(5)	69.93(5)	71.42(7)	71.41(7)	71.61(6)	71.61(6)
N22-Ln-N32	77.52(5)	78.85(5)	84.17(5)	81.87(7)	83.53(7)	82.31(6)	81.04(6)
N42-Ln-N52	69.71(5)	73.80(5)	69.68(5)	76.12(7)	76.45(7)	76.31(6)	73.14(6)
N42-Ln-N62	81.45(5)	83.05(5)	80.92(5)	86.03(5)	87.69(7)	86.51(6)	88.33(6)
N52-Ln-N62	72.96(5)	68.86(5)	71.27(5)	72.61(7)	72.54(7)	73.52(6)	76.79(6)
$N\text{-}Ln\text{-}N(inter)_{cis}$							
N12-Ln-N52	127.86(5)	122.71(6)	122.50(5)	119.32(7)	118.87(7)	118.34(6)	116.55(6)
N12-Ln-N62	101.05(5)	102.59(5)	95.81(5)	99.84(7)	100.62(7)	99.25(6)	98.28(6)
N22-Ln-N42	84.17(5)	87.48(5)	87.58(5)	84.94(7)	86.31(7)	85.22(6)	87.90(6)
N22-Ln-N62	84.93(5)	87.93(5)	84.82(5)	84.33(7)	87.59(7)	83.57(6)	86.10(6)
N32-Ln-N42	104.24(5)	100.09(5)	110.81(5)	99.42(7)	98.32(7)	99.47(6)	100.06(6)
N32-Ln-N52	125.83(5)	124.92(6)	123.03(5)	122.61(7)	117.86(8)	122.11(6)	118.23(6)

N–Ln–(inter)$_{trans}$							
N12–Ln–N42	162.34(5)	163.49(5)	165.82(5)	164.40(7)	164.10(7)	165.21(6)	169.24(6)
N22–Ln–N52	147.69(5)	151.43(5)	148.94(5)	150.88(7)	153.94(7)	151.18(6)	154.59(6)
N32–Ln–N62	161.18(6)	166.20(6)	163.50(5)	164.60(7)	168.91(8)	164.13(6)	164.32(6)
Torsion Angles							
Ln–N12N11–B1	8.5(2)	33.3(2)	26.3(2)	32.6(3)	30.9(3)	32.2(2)	3.3(2)
Ln–N22N21–B1	23.5(2)	28.7(2)	26.7(2)	22.5(3)	24.1(3)	20.8(2)	23.9(2)
Ln–N32N31–B1	32.8(2)	17.2(2)	62.4(2)	6.6(3)	3.9(3)	5.5(2)	30.3(2)
Ln–N42N41–B2	22.8(2)	7.4(2)	23.6(2)	9.1(3)	11.6(3)	9.0(2)	28.0(2)
Ln–N52N51–B2	1.3(2)	2.5(2)	3.8(2)	2.3(3)	0.6(3)	2.4(2)	0.1(2)
Ln–N62N61–B2	7.1(2)	30.7(2)	14.4(2)	22.8(3)	28.2(3)	22.0(2)	11.5(2)
B1–Ln–B	148.34(5)	151.79(5)	151.19(5)	151.13(7)	153.40(7)	151.1	153.9

[a]There are two independent molecules per asymmetric unit.

[b]A. Momin *et al. Inorg. Chem.,* 2014, **53**, 12066.