Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Isolation of Reactive Ln(II) Complexes with C_5H_4Me Ligands (Cp^{Me}) Using Inverse Sandwich Countercations: Synthesis and Structure of [(18-crown-6)K(μ-Cp^{Me})K(18-crown-6)][$Cp^{Me}_3Ln^{II}$] (Ln = Tb, Ho)

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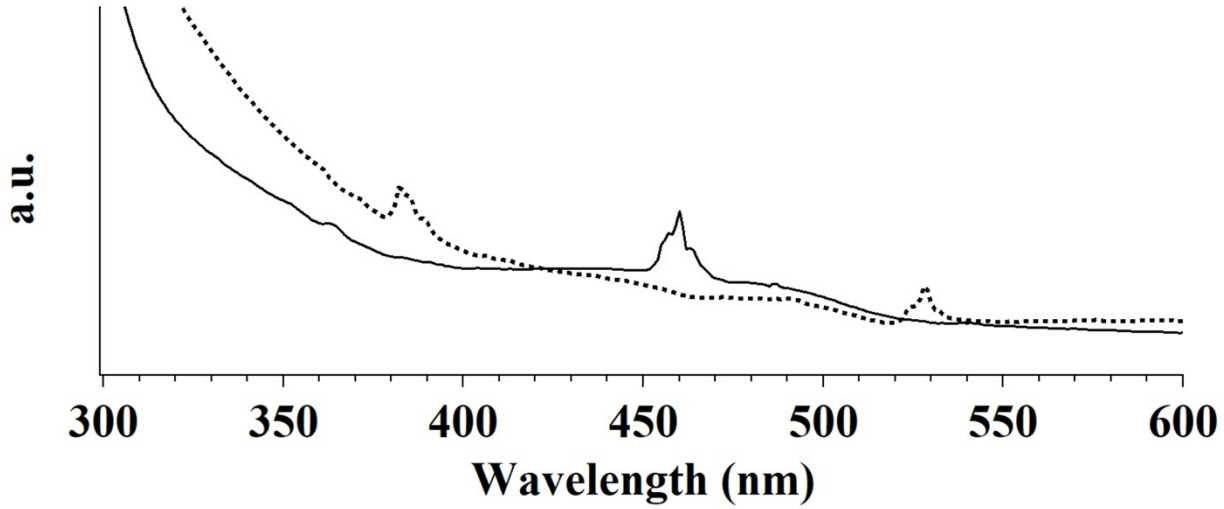

Figure S1. UV-visible spectra of **2-Ho** (solid) and **2-Er** (dashed) decomposition products.

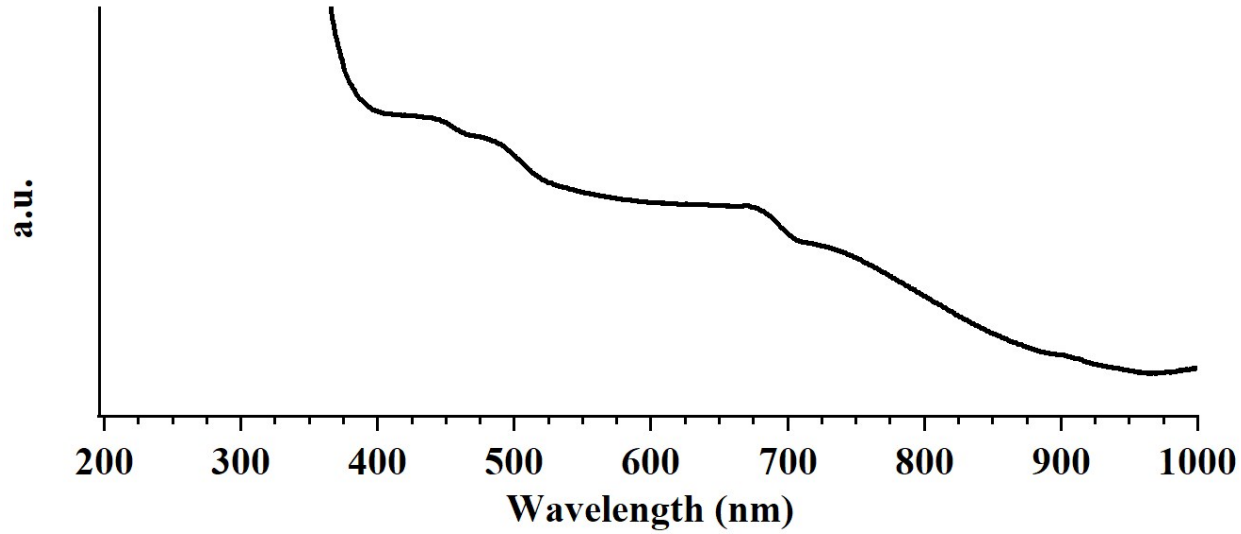

Figure S2. UV-visible spectrum of **2-Tb** in THF; λ_{max}, nm: 458, 481, 660 nm.

X-ray Data Collection, Structure Solution and Refinement for:

[(18-c-6)K(μ-Cp^{Me})K(18-c-6)][Cp$^{Me}_3$Tb], **2-Tb**

A black crystal of approximate dimensions 0.100 x 0.136 x 0.335 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (120 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were three molecules of tetrahydrofuran solvent present. One solvent molecule was disordered and included using multiple components, partial site-occupancy-factors, geometric constraints and equivalent anisotropic thermal parameters.

Least-squares analysis yielded wR2 = 0.0959 and Goof = 1.046 for 680 variables refined against 12924 data (0.80 Å), R1 = 0.0389 for those 10335 data with I > 2.0σ(I).

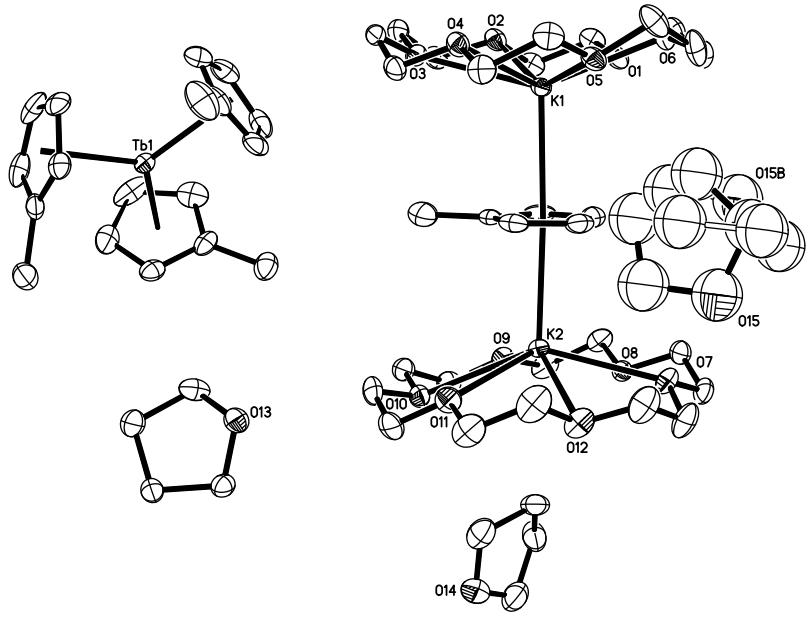

Figure S3. ORTEP representation of **2-Tb** with thermal ellipsoids drawn at the 50% probability level. Hydrogens are omitted for clarity.

Table S1. Crystal data and structure refinement for

[(18-c-6)K(μ-Cp^{Me})K(18-c-6)][Cp^{Me}_3Tb], **2-Tb**

Identification code	dnh53 (Daniel Huh)	
Empirical formula	C_{48} H_{76} Tb K_2 O_{12} • 3(C_4H_8O)	
Formula weight	1298.51	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.593(3) Å	a= 90°.
	b = 26.141(9) Å	b= 90.774(4)°.
	c = 25.231(8) Å	g = 90°.
Volume	6326(4) $Å^3$	
Z	4	
Density (calculated)	1.363 Mg/m^3	
Absorption coefficient	1.311 mm^{-1}	
F(000)	2732	
Crystal color	black	
Crystal size	0.335 x 0.136 x 0.100 mm^3	
Theta range for data collection	1.122 to 26.372°	
Index ranges	$-11 \le h \le 11$, $-32 \le k \le 32$, $-31 \le l \le 31$	
Reflections collected	68430	
Independent reflections	12924 [R(int) = 0.0476]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6436	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12924 / 0 / 680	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I) = 10335 data]	R1 = 0.0389, wR2 = 0.0886	
R indices (all data, 0.80 Å)	R1 = 0.0565, wR2 = 0.0959	
Largest diff. peak and hole	2.429 and -0.886 $e.Å^{-3}$	

Table S2. Bond lengths [Å] for [(18-c-6)K(μ-Cp^{Me})K(18-c-6)][Cp^{Me}_3Tb], **2-Tb**

Tb(1)-Cnt1	2.463	K(1)-O(6)	2.835(3)
Tb(1)-Cnt2	2.454	K(1)-O(1)	2.874(3)
Tb(1)-Cnt3	2.451	K(1)-O(5)	2.939(3)
Tb(1)-C(8)	2.675(4)	K(1)-O(4)	2.940(3)
Tb(1)-C(15)	2.687(4)	K(1)-O(2)	2.994(3)
Tb(1)-C(3)	2.708(4)	K(1)-C(23)	3.058(4)
Tb(1)-C(2)	2.708(4)	K(1)-C(19)	3.063(4)
Tb(1)-C(14)	2.713(4)	K(1)-C(22)	3.078(4)
Tb(1)-C(7)	2.721(4)	K(1)-C(21)	3.104(4)
Tb(1)-C(4)	2.722(4)	K(1)-C(20)	3.106(4)
Tb(1)-C(9)	2.723(4)	K(2)-O(9)	2.858(3)
Tb(1)-C(16)	2.726(4)	K(2)-O(11)	2.864(3)
Tb(1)-C(10)	2.740(4)	K(2)-O(7)	2.886(3)
Tb(1)-C(13)	2.741(4)	K(2)-O(8)	2.918(3)
Tb(1)-C(1)	2.753(4)	K(2)-O(12)	2.960(3)
Tb(1)-C(17)	2.767(4)	K(2)-O(10)	2.985(3)
Tb(1)-C(11)	2.774(4)	K(2)-C(23)	3.068(4)
Tb(1)-C(5)	2.785(4)	K(2)-C(22)	3.074(4)
K(1)-Cnt4	2.846	K(2)-C(19)	3.096(4)
K(2)-Cnt4	2.856	K(2)-C(21)	3.105(4)
K(1)-O(3)	2.826(3)	K(2)-C(20)	3.111(4)

Table S3. Bond angles [°] for [(18-c-6)K(μ-Cp^{Me})K(18-c-6)][Cp^{Me}_3Tb], **2-Tb**

Cnt1-Tb(1)-Cnt2	119.9
Cnt1-Tb(1)-Cnt3	119.7
Cnt2-Tb(1)-Cnt3	120.2
K(1)-Cnt4-K(2)	177.2

X-ray Data Collection, Structure Solution and Refinement for:
[(18-c-6)K(μ-Cp^{Me})K(18-c-6)][Cp$^{Me}_3$Ho], **2-Ho**

A black crystal of approximate dimensions 0.060 x 0.116 x 0.452 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (120 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were three molecules of tetrahydrofuran solvent present. One solvent molecule was disordered and included using multiple components, partial site-occupancy-factors, geometric constraints and equivalent anisotropic thermal parameters.

Least-squares analysis yielded wR2 = 0.0995 and Goof = 1.022 for 680 variables refined against 12898 data (0.80 Å), R1 = 0.0398 for those 9972 data with I > 2.0σ(I).

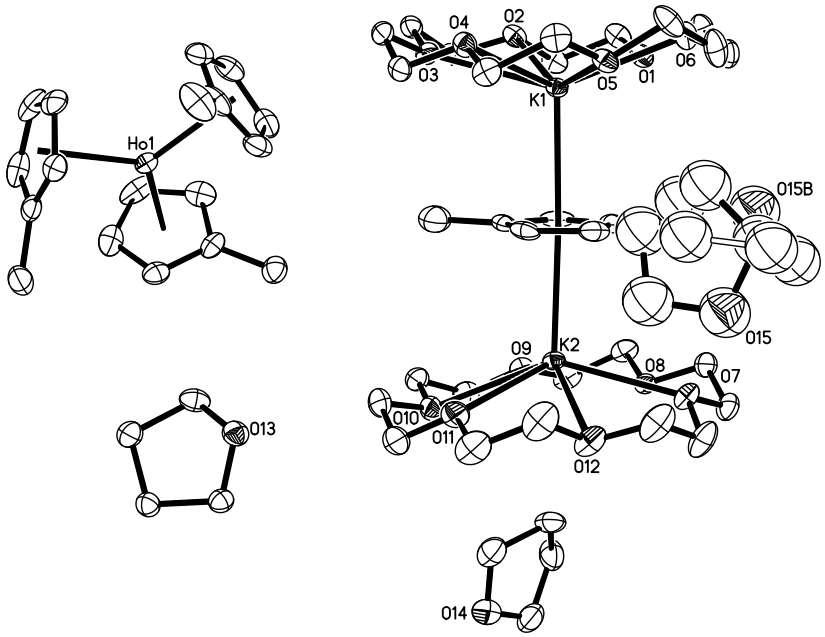

Figure S4. ORTEP representation of **2-Ho** with thermal ellipsoids drawn at the 50% probability level. Hydrogens are omitted for clarity.

Table S4. Crystal data and structure refinement for [(18-c-6)K(μ-Cp^{Me})K(18-c-6)][Cp^{Me}_3Ho], **2-Ho**

Identification code	dnh51 (Daniel Huh)	
Empirical formula	$C_{48}\ H_{76}\ Ho\ K_2\ O_{12} \bullet 3(C_4H_8O)$	
Formula weight	1304.52	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.6024(9) Å	a= 90°.
	b = 26.131(2) Å	b= 90.7143(12)°.
	c = 25.176(2) Å	g = 90°.
Volume	6316.8(10) $Å^3$	
Z	4	
Density (calculated)	1.372 Mg/m^3	
Absorption coefficient	1.446 mm^{-1}	
F(000)	2740	
Crystal color	black	
Crystal size	0.452 x 0.116 x 0.060 mm^3	
Theta range for data collection	1.756 to 26.369°	
Index ranges	$-12 \le h \le 12$, $-32 \le k \le 32$, $-31 \le l \le 31$	
Reflections collected	67781	
Independent reflections	12898 [R(int) = 0.0587]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6110	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12898 / 0 / 680	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I) = 9972 data]	R1 = 0.0398, wR2 = 0.0904	
R indices (all data, 0.8 Å)	R1 = 0.0617, wR2 = 0.0995	
Largest diff. peak and hole	2.662 and -1.171 $e.Å^{-3}$	

Table S5. Bond lengths [Å] for [(18-c-6)K(μ-Cp^{Me})K(18-c-6)][Cp^{Me}_3Ho], **2-Ho**

Ho(1)-Cnt1	2.435	K(1)-O(6)	2.835(3)
Ho(1)-Cnt2	2.432	K(1)-O(1)	2.881(3)
Ho(1)-Cnt3	2.430	K(1)-O(5)	2.940(3)
Ho(1)-C(8)	2.657(4)	K(1)-O(4)	2.946(3)
Ho(1)-C(15)	2.668(4)	K(1)-O(2)	2.999(3)
Ho(1)-C(2)	2.679(4)	K(1)-C(23)	3.065(4)
Ho(1)-C(3)	2.686(4)	K(1)-C(19)	3.070(4)
Ho(1)-C(4)	2.692(4)	K(1)-C(22)	3.080(4)
Ho(1)-C(14)	2.701(4)	K(1)-C(20)	3.103(4)
Ho(1)-C(7)	2.703(4)	K(1)-C(21)	3.106(4)
Ho(1)-C(16)	2.703(4)	K(2)-O(9)	2.862(3)
Ho(1)-C(9)	2.703(4)	K(2)-O(11)	2.862(3)
Ho(1)-C(10)	2.722(4)	K(2)-O(7)	2.886(3)
Ho(1)-C(13)	2.726(4)	K(2)-O(8)	2.918(3)
Ho(1)-C(1)	2.736(4)	K(2)-O(12)	2.968(3)
Ho(1)-C(17)	2.747(4)	K(2)-O(10)	2.982(3)
Ho(1)-C(11)	2.760(4)	K(2)-C(23)	3.076(4)
Ho(1)-C(5)	2.766(4)	K(2)-C(22)	3.078(4)
K(1)-Cnt4	2.848	K(2)-C(19)	3.095(4)
K(2)-Cnt4	2.860	K(2)-C(21)	3.114(4)
K(1)-O(3)	2.833(3)	K(2)-C(20)	3.117(4)

Table S6. Bond angles [°] for [(18-c-6)K(μ-Cp^{Me})K(18-c-6)][Cp^{Me}_3Ho], **2-Ho**

Cnt1-Ho(1)-Cnt2	120.0
Cnt1-Ho(1)-Cnt3	119.5
Cnt2-Ho(1)-Cnt3	120.3
K(1)-Cnt4-K(2)	177.5

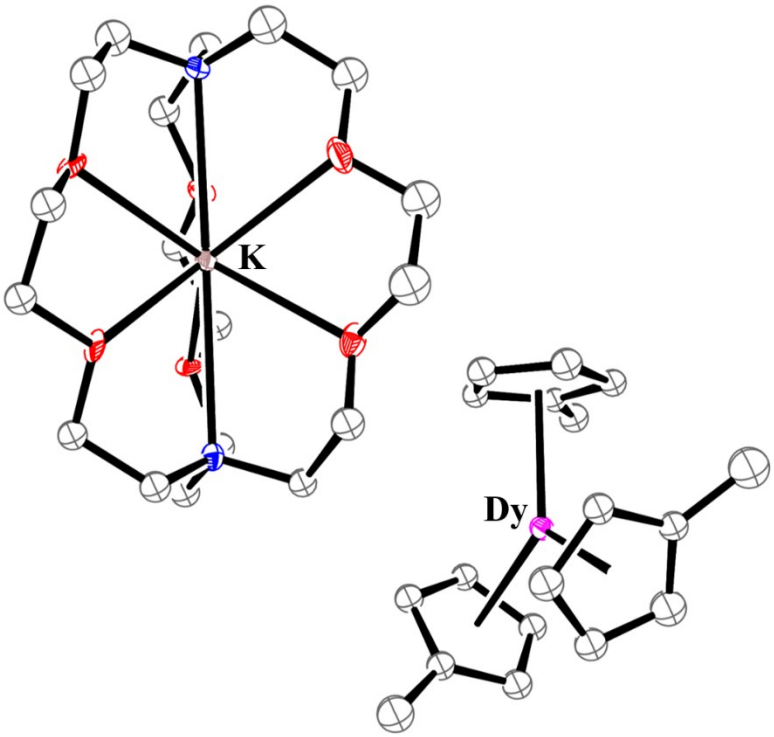

Figure S5. ORTEP representation of [K(2.2.2-cryptand)][Cp^{Me}_3Dy], **3-Dy.**

References

1. APEX2 Version 2014.11-0, Bruker AXS, Inc.; Madison, WI 2014.

2. SAINT Version 8.34a, Bruker AXS, Inc.; Madison, WI 2013.

3. Sheldrick, G. M. SADABS, Version 2014/5, Bruker AXS, Inc.; Madison, WI 2014.

4. Sheldrick, G. M. SHELXTL, Version 2014/7, Bruker AXS, Inc.; Madison, WI 2014.