Electronic Supplementary Information for:

Molecular and Electronic Structures of Donor-Functionalized Dysprosium Pentadienyl Complexes

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General synthetic considerations. All syntheses were carried out using standard Schlenk and glove-box techniques, using an inert atmosphere of nitrogen or argon. $[(L^1)Li(tmeda)]$ (1)¹ and Cp'₃Dy² were synthesized according to literature procedures. Toluene and thf were dried by refluxing over molten potassium, followed by distillation and storage over a potassium mirror and activated 4 Å molecular sieves, respectively; all solvents were freeze-thaw degassed prior to use. FTIR spectra were recorded as Nujol mulls in KBr discs on a Perkin Elmer Spectrum BX spectrometer. Melting Points were obtained using a Stuart Scientific SMP10 melting point apparatus. Elemental analyses were carried out at London Metropolitan University, U.K.

Synthesis of $[Cp'_2Dy(L^1)]$ (3). A solution of 1 (190 mg, 0.57 mmol) in thf (10 ml) was added drop-wise to a stirring solution of Cp'_3Dy (229 mg, 0.57 mmol) in thf (10 ml). The resultant orange solution was stirred for 4 hours and then the solvent was removed *in vacuo*. The resulting orange solid was extracted into hexane and filtered to give an orange solution. The filtrate was concentrated until a solid began to precipitate. The precipitate was dissolved by gentle heating; slow cooling of the solution to room temperature resulted in the formation of 4 as orange crystals (130 mg, 43% isolated yield). Anal. Calc. (%) for C₂₄H₃₆DyNSi: C 54.48; H 6.86; N 2.65. Found: C 54.30, 54.32; H 6.91, 7.00; N 2.71, 2.79. Melting point: 135-137°C to an orange oil.

Synthesis of $[(L^1)Dy(\mu-Cl)_3\{Li(tmeda)\}]_2$ (4). A solution of 1 (86 mg, 0.26 mmol) in Et₂O (10 ml) was added drop-wise to a stirring suspension of DyCl₃ (70 mg, 0.26 mmol)in Et₂O (10 ml). The resulting orange solution was stirred for 5 hours and then filtered. The filtrate was concentrated until a solid began to precipitate from solution. Gentle heating re-dissolved the precipitate and the orange solution was stored at – 30°C overnight, which resulted in the formation of **3** as orange crystals (70 mg, 46% isolated yield). Anal. Calc. (%) for C₃₆H₇₆Cl₆Dy₂Li₂N₆Si₂: C 36.01; H 6.38; N 7.00. Found: C 35.83, 35.91; H 6.46, 6.47; N 6.91, 6.87. Melting point: decomposes to a black solid above 130°C.



Figure S1. Infrared spectrum (Nujol mull) of 3 and 4.



Figure S2. Zoomed infrared spectrum (Nujol mull) of 3 and 4 between 1750-600 cm⁻¹.

	3	4
CCDC ref. code	1045220	1045221
Formula	C ₂₄ H ₃₆ DyNSi	$C_{36}H_{76}Cl_{6}Dy_{2}Li_{2}N_{6}Si_{2} \\$
FW	529.13	1200.78
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	10.0020(5)	12.0325(3)
$b/{ m \AA}$	23.8856(10)	16.3008(4)
$c/{ m \AA}$	10.5417(6)	14.0042(4)
$\alpha/^{\circ}$	90	90
$eta /^{\circ}$	112.103(6)	91.080(2)
$\gamma/^{\circ}$	90	90
$V/\text{\AA}^3$	2333.4(2)	2746.29(12)
Ζ	4	2
Crystal size/mm ³	0.3 imes 0.3 imes 0.2	$0.2 \times 0.1 \times 0.1$
2θ range/°	5.878 to 52.74	5.784 to 52.742
Reflections collected	9267	14094
Independent reflections, <i>R</i> (int)	4772, 0.0333	5584, 0.0462
Completeness/%	99.9	99.4
Data/restraints/parameters	4772/0/248	5584/25/290
Goodness-of-fit on F^2	1.031	1.094
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0308, wR_2 = 0.0627$	$R_1 = 0.0448, wR_2 = 0.0513$
<i>R</i> indices (all data)	$R_1 = 0.0398, wR_2 = 0.0667$	$R_1 = 0.0758, wR_2 = 0.0601$

Table S1. Crystal data and structural refinement for compounds 3 and 4.

X-ray diffraction data for **3** were collected on an Oxford Instruments XCalibur2 diffractometer, and for **4** on an Agilent Technologies SuperNova diffractometer, both using MoK α radiation. Crystals were covered in an inert oil and selected under a microscope. Structures were solved with SHELXS using direct methods and refined with SHELXL using least-squares minimisation.

Ab initio calculations

Ab initio calculations were performed using the RASSCF and RASSI modules of MOLCAS 7.8,³⁻⁵ using the un-optimized X-ray geometry of **3** and **4**. For the calculation of **3**, the Dy atom was treated with the ANO-RCC-VTZP basis set, the N and C donors (aromatic Cp' atoms and C(1-3) of L¹) with the ANO-RCC-VDZP basis, while all other atoms were treated with treated with the ANO-RCC-VDZ basis.⁶⁻⁹ For the calculation of **4**, Dy(1) was treated with the ANO-RCC-VTZP basis set while Dy(1A) was replaced by the diamagnetic Lu with the ANO-RCC-VDZ basis set. The N, C (aromatic Cp' atoms and C(1-3) of L¹) and Cl donors were treated with the ANO-RCC-VDZ basis.⁶⁻⁹ The two electron integrals were Cholesky decomposed with the default thresholds. The 4f⁹ configuration of Dy^{III} was modelled with a complete active space of 9 electrons in 7 orbitals, where 21 sextets, 224 quartets and 158 doublets were included in the orbital optimization and 21 sextets, 128 quartets and 130 doublets were mixed by spin-orbit coupling.

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