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Electronic Supporting Information

A Structural Investigation of Heteroleptic Lanthanide Substituted Cyclopentadienyl Complexes

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1. Crystallographic method

The crystal data for complexes **1**, **2a-b**, **2a·THF** and **3**-**6** are compiled in Table S1-S2. Crystals were examined on CCD area detector diffractometers using graphite- or mirror-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensities were integrated from data recorded on 1° frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. A Gaussian grid face-indexed absorption correction with a beam profile correction was applied. The structures were solved variously by direct and heavy atom methods and were refined by full-matrix least-squares on all unique F^2 values, 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. CrysAlisPro was used for control and integration, and SHELXTL and OLEX2 were employed for structure solution and refinement and for molecular graphics. CCDC 1056158–1056165 (**1**, **2a-b**, **2a·THF** and **3**-**6**) 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.

2. Crystallographic data

Table S1: Crystallographic data for **1**, **2a-b** and **2a·THF**

	1	**2a**	**2b**	**2a·THF**
Formula	$C_{19}H_{37}KO_2Si_2$	$C_{44}H_{84}I_2La_2Si_8$	$C_{44}H_{84}Ce_2I_2Si_8$	$C_{26}H_{50}ILaOSi_4$
Fw	392.76	1369.45	1371.87	756.83
cryst size, mm	0.17 x 0.19 x 0.97	0.14 x 0.24 x 0.38	0.14 x 0.16 x 0.24	0.15 x 0.35 x 0.42
crystal syst	monoclinic	triclinic	triclinic	orthorombic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a, Å	10.0903(5)	10.7116(19)	10.7177(7)	11.0319(4)
b, Å	10.8463(5)	11.485(3)	11.5326(7)	16.0851(11)
c, Å	21.9151(11)	13.285(3)	13.3332(8)	20.1692(7)
α, °	90	72.517(19)	72.794(5)	90
β, °	93.491(4)	83.217(15)	83.327(5)	90
γ, °	90	79.146(17)	78.870(5)	90
V, Å^3	2394.0(2)	1527.7(6)	1541.59(18)	3579.0(3)
Z	4	1	1	4
ρ_{calcd}, g cm^3	1.090	1.489	1.478	1.405
μ, mm^{-1}	0.330	2.572	2.640	2.205
F(*000*)	856	680	682	1520
no. of reflections (unique)	5817(1872)	7661(5556)	10168(5615)	30648(6552)
S[a]	1.029	1.06	1.09	1.11
$R_1(wR_2)$ ($F^2 > 2\sigma(F^2)$)	0.0549(0.1377)	0.0976(0.1642)	0.0534(0.0887)	0.0453(0.0809)
R_{int}	0.042	0.075	0.044	0.069
min., max. diff map, e Å^{-3}	−0.38, 0.41	−1.62, 2.61	−0.81, 1.74	−0.95, 0.87

Table S2: Crystallographic data for **3**-**6**

	3	**4**	**5**	**6**
Formula	$C_{52}H_{84}Ce_2I_2$	$C_{22}H_{45}CeI_2O_2Si_3$	$C_{32}H_{66}CeIOSi_6$	$C_{26}H_{65}CeN_2Si_7$
Fw	1243.23	819.77	902.40	742.55
cryst size, mm	0.28 x 0.38 x 0.69	0.10 x 0.15 x 0.27	0.21 x 0.30 x 0.41	0.14 x 0.18 x 0.27
crystal syst	triclinic	orthorhombic	monoclinic	monoclinic
space group	*P*−1	$P2_12_12_1$	$P2_1/c$	$C2/c$
a, Å	10.5085(5)	11.8979(7)	16.9173(4)	38.4377(14)
b, Å	11.3227(4)	14.6707(7)	13.0450(3)	17.9044(5)
c, Å	23.7712(8)	37.397(2)	20.6985(6)	25.5605(7)
α, °	90.523(3)	90	90	90
β, °	98.515(3)	90	92.959(2)	109.755(3)
γ, °	104.372(3)	90	90	90
V, Å^3	2706.58(18)	6527.7(6)	4561.8(2)	16555.6(9)
Z	2	8	4	16
ρ_{calcd}, g cm^3	1.525	1.668	1.314	1.192
μ, mm^{-1}	2.831	3.411	1.853	1.319
F(*000*)	1236	3192	1844	6256
no. of reflections (unique)	17833(9896)	13441(5937)	18836(8343)	15128(9642)
S[a]	1.03	1.07	1.04	1.02
$R_1(wR_2)$ ($F^2 > 2\sigma(F^2)$)	0.0393(0.0641)	0.0589(0.0700)	0.0416(0.0725)	0.0957(0.2443)
R_{int}	0.041	0.056	0.045	0.1159
min., max. diff map, e Å^{-3}	−0.84, 0.74	−0.98, 0.83	−0.78, 0.74	−4.26, 5.32

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $S = [\Sigma w(F_o^2 - F_c^2)^2/\text{no. data} - \text{no. params})]^{1/2}$ for all data.

3. Molecular structure of 1

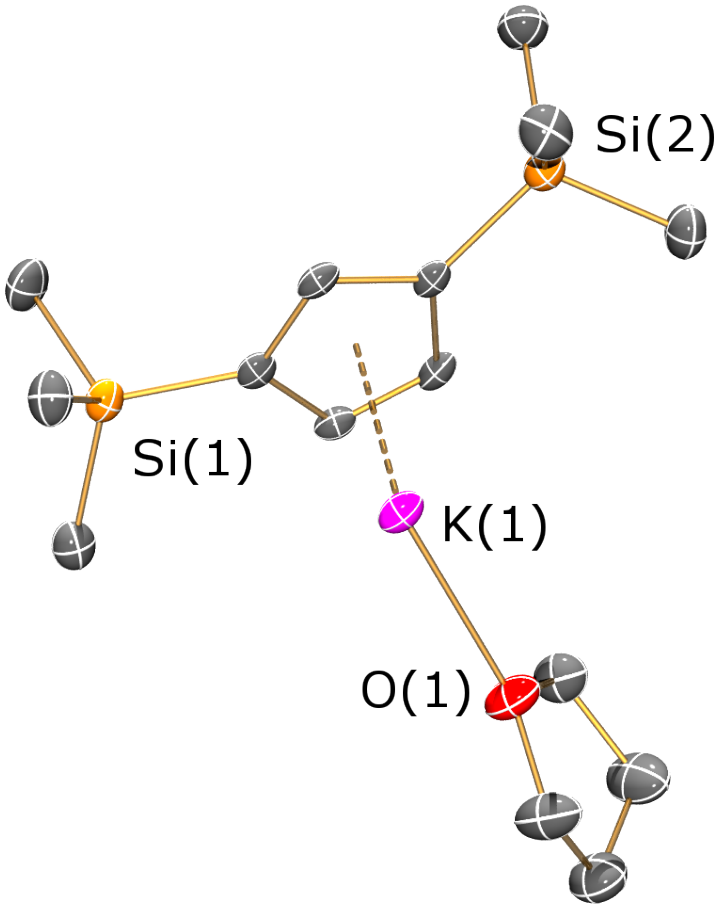

Figure S1: Molecular structure of **1** with selective atom labelling, with displacement ellipsoids set at the 50 % probability level; hydrogen atoms have been omitted for clarity. Selected bond distances [Å] for **1**: K(1)−O(1) = 2.671(4), K(1)···$Cp_{centroid}$ = 2.837(3).

4. Molecular structure of 2a

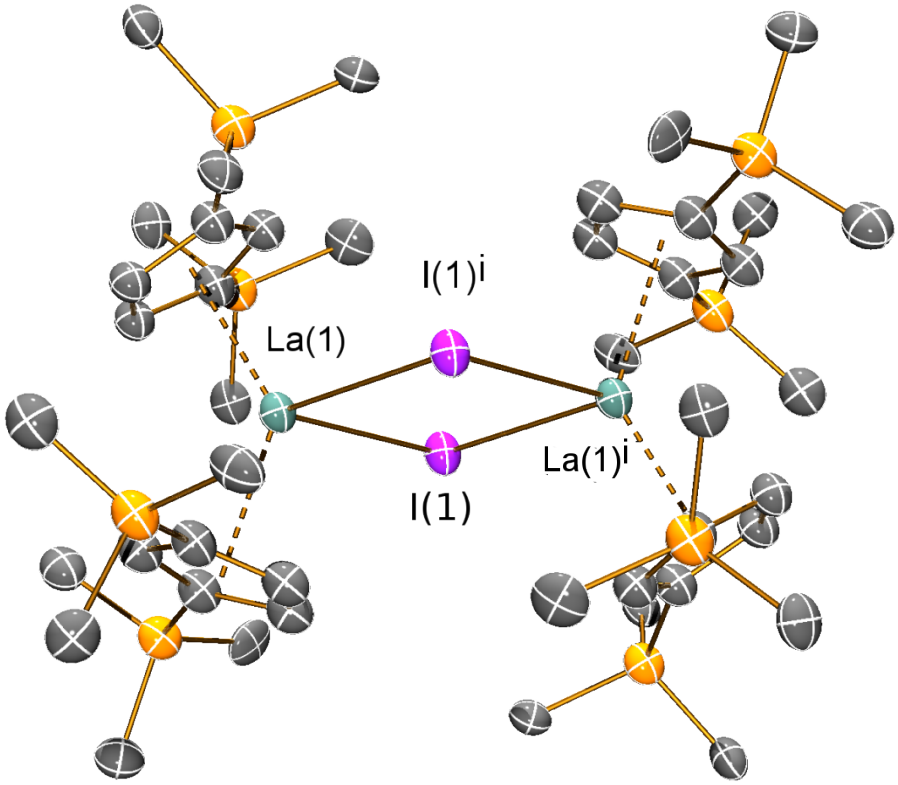

Figure S2: Molecular structure of **2a** with selective atom labelling, with displacement ellipsoids set at the 50 % probability level; hydrogen atoms have been omitted for clarity. Symmetry operation to generate equivalent atoms: *i* = 2−*x*, −*y*, −*z*. Selected bond distances [Å] and angles [°] for **2a**: La(1)–I(1) 3.2153(16), La(1)–I(1^{i}) 3.2103(14), La(1)···Cp$_{centroid}$(1) 2.519(7), La(1)···Cp$_{centroid}$(2) 2.518(7), La(1)···La(1^{i}) 4.758(2), I(1)–La(1)–I(1^{i}) 84.46(4), La(1)–I(1)–La(1^{i}) 95.54(4).

5. References

1. *CrysAlis PRO*, Agilent Technologies: Yarnton, England, 2010.
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