Mixed Sandwich Thorium Complexes Incorporating Bis(tri-*iso*propylsilyl)cyclooctatetraenyl and Pentamethylcyclopentadienyl Ligands: Synthesis, Structure and Reactivity

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Electronic Supporting Information

Contents

Selected views of the molecular structure of 3

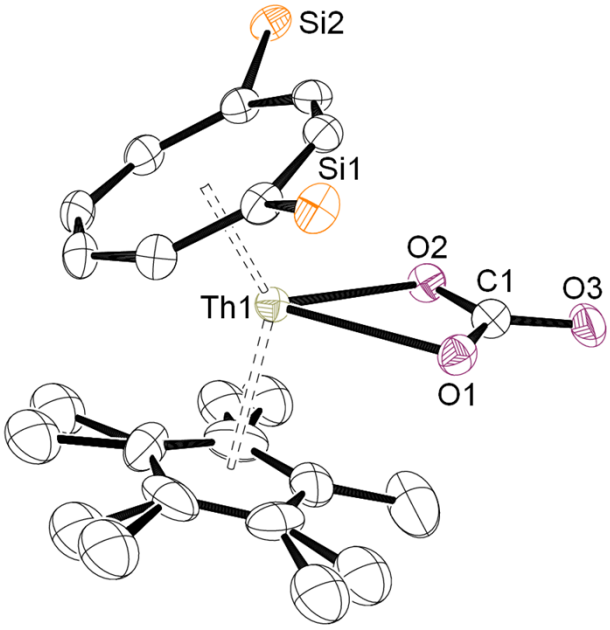

Figure S1. ORTEP representation of the asymmetric unit of **3**, showing modelling of carbonate ligand.

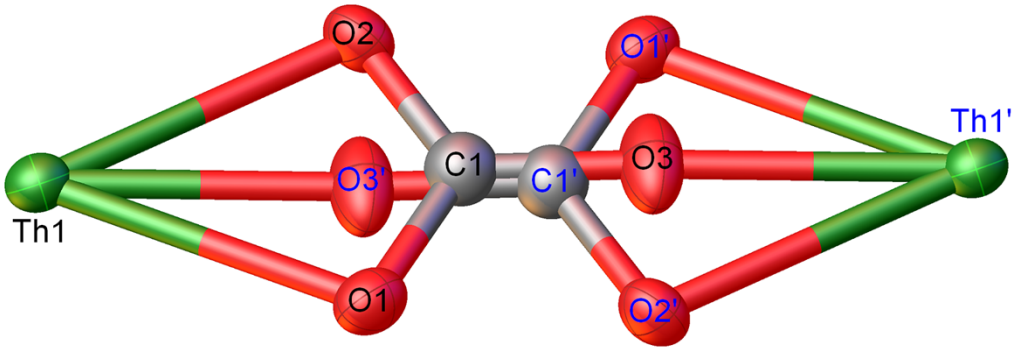

Figure S2. OLEX2-generated graphic of the grown structure of **3**, showing only overlapping 50:50 occupancy core: label colours black and blue represent asymmetric unit and symmetry-generated molecule respectively.

Unrefined molecular structure of 6

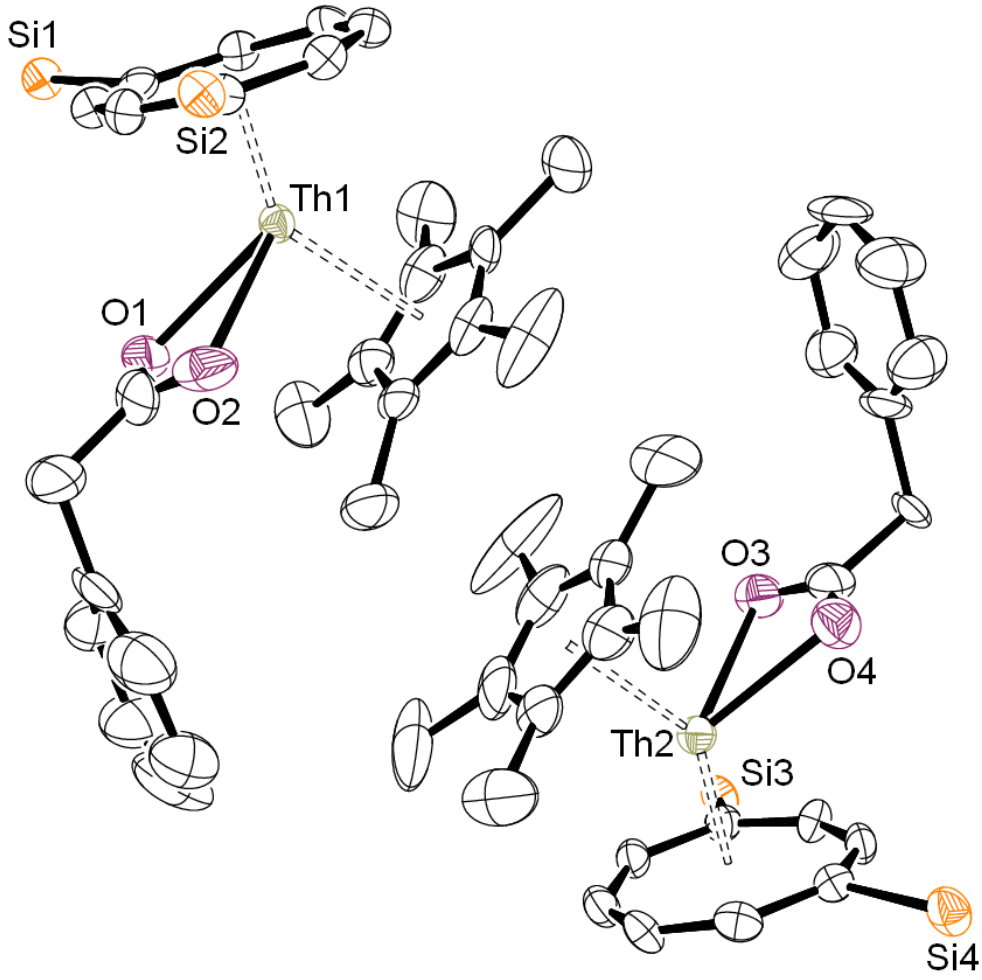

Figure S3. ORTEP representation of the molecular structure of **6**. Refinement not complete; residual electron density also observed above the COT ring, thought to be a result of poor-quality twinned crystals for which a sufficient model could not be found.

Table S1. Crystal data and structure refinement details for **1**-**4**.

	1	**2**	**3**	**4**
Formula	$C_{36}H_{63}Si_2ClTh.(C_6H_{12})$	$C_{36}H_{63}Si_2ITh$	$C_{36.5}H_{63}O_{1.5}Si_2Th.(C_7H_8)$	$C_{88}H_{142}O_4Si_4Th_2$
FW	903.69	910.98	906.22	1840.46
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P -1	P -1	P -1	P -1
a/Å	8.67790(1)	8.7050(4)	12.283(3)	12.3722(5)
b/Å	12.8594(2)	12.5835(6)	13.356(3)	13.3983(4)
c/Å	20.8423(4)	18.1400(8)	15.689(3)	15.7276(7)
α/°	92.8860(10)	89.126(2)	65.93(3)	65.525(2)
β/°	99.1770(10)	83.109(2)	67.92(3)	67.618(2)
γ/°	109.519(2)	71.906(3)	72.30(3)	72.722(2)
V/Å^3	2150.66(6)	1874.63(15)	2142.8(11)	2163.84(15)
Z	2	2	2	1
Crystal size/mm^3	0.2 x 0.04 x 0.04	0.36 x 0.22 x 0.06	0.16 x 0.08 x 0.06	0.04 x 0.02 x 0.02
θ range/°	3.42 – 27.06	3.15 – 27.53	3.396 - 27.880	2.61 – 27.54
Completeness	97.9	99.5	98.6	98.3
Reflections collected, *R*(int)	26587, 0.0673	35632, 0.057	31500, 0.0581	28262, 0.0534
Independent reflections	9259	8609	9765	9819
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0465	R1 = 0.041	R1 = 0.0277	R1 = 0.0346
	wR2 = 0.0992	wR2 = 0.098	wR2 = 0.0605	wR2 = 0.0667
R indices (all data)	R1 = 0.0628	R1 = 0.053	R1 = 0.0329	R1 = 0.0476
	wR2 = 0.1055	wR2 = 0.103	wR2 = 0.0624	wR2 = 0.0707

Table S2. Crystal data and structure refinement details for **5** and **8**.

	5	**8**
Formula	$C_{43}H_{70}Si_2Th$	$C_{74}H_{128}Si_4O_4Th_2$
FW	875.21	1904.23
Crystal system	Triclinic	Triclinic
Space group	P -1	P -1
a/Å	13.0170(2)	11.9293(4)
b/Å	17.3983(3)	13.9229(6)
c/Å	20.0305(3)	14.3584(5)
α/°	82.3334(9)	95.881(3)
β/°	75.2024(9)	113.241(3)
γ/°	69.8092(7)	113.851(3)
V/Å^3	4111.27(12)	1904.24(14)
Z	4	1
Crystal size/mm^3	0.14 x 0.08 x 0.06	0.2 x 0.1 x 0.04
θ range/°	2.106 – 27.47	2.68 – 26.32
Completeness	99.2	99.8
Reflections collected, *R*(int)	70490, 0.0603	14686, 0.0379
Independent reflections	18670	6696
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0339	R1 = 0.0376
	wR2 = 0.0580	wR2 = 0.0852
R indices (all data)	R1 = 0.0677	R1 = 0.0508
	wR2 = 0.0869	wR2 = 0.0907

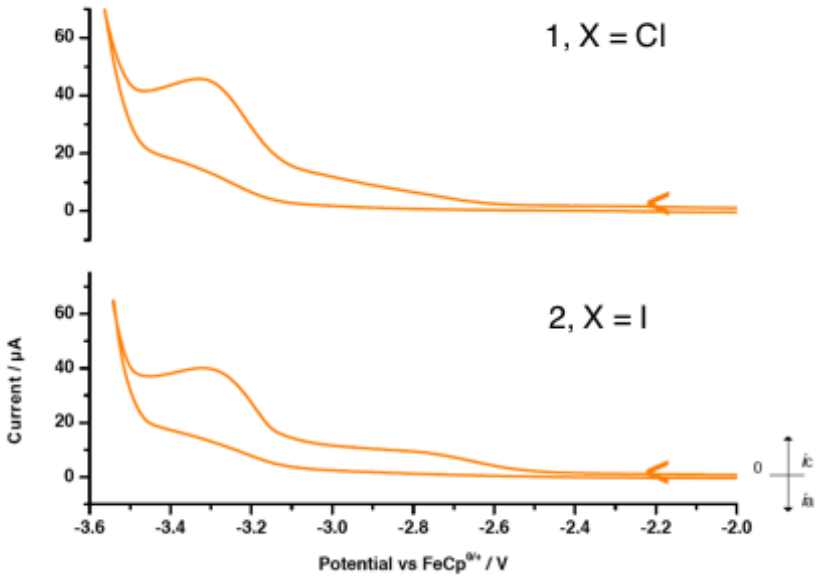

Figure S4: Cyclic voltammograms of **1** (7.70 mM) and **2** (5.27 mM) in THF containing 0.1 M [N^{n}Bu$_4$][PF$_6$]. The scan rate was 100 mV.s^{-1}.