

Synthesis, properties and structures of the tris(cyclopentadienyl)thorium(III) complexes $[\text{Th}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{R})_{2-1,3}\}_3]$ (R = Me or *t*Bu)

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Dedicated to Academician Oleg Nefedov, as a mark of friendship (by M.F.L.) and recognition of his many contributions to chemistry

Abstract

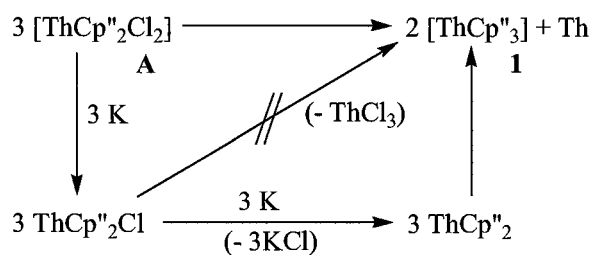
The homoleptic, dark-blue, crystalline (disubstituted-cyclopentadienyl)thorium(III) complexes $[\text{Th}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{R})_{2-1,3}\}_3]$ (R = Me **1** or *t*Bu **3**) were obtained in good yield from the appropriate tris(cyclopentadienyl)thorium(IV) chloride by treatment with an excess of sodium–potassium alloy in toluene at 20–35 °C with sonication. Complex **1** was also accessible by a similar reduction of $[\text{ThCp}''_2\text{Cl}_2]$ [$\text{Cp}'' = \eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}$]; with possibly a transient Th(II) cyclopentadienyl as intermediate. Complex **1** with wet toluene afforded $[(\text{ThCp}''_3)(\mu\text{-O})]$ (**2**); it was unreactive with THF, DME, CO or H₂, but with Na–K alloy in THF it afforded a green, diamagnetic, readily oxidisable cyclopentadienylthorium complex. Complexes **1** and **3** showed singlet EPR spectra in methylcyclohexane at 298 K, whence it is concluded that they have a 6d¹ rather than a 5f¹ electronic ground state. Variable temperature EPR spectra, magnetic measurements and optical spectra of **1** are described and discussed. The X-ray structures of crystalline **1** and **3** show that each has approximate *D*_{3h} symmetry about the Th atom, which can be regarded as bound to the centroid of each of the three cyclopentadienyl rings. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thorium(III) cyclopentadienyls; Structures; EPR spectra

1. Introduction

References to organometallic compounds of thorium in the +3 oxidation state have appeared at various times during the last three decades [1], but until 1999 only a single crystalline compound $[\text{ThCp}''_3]$ [$\text{Cp}'' = \eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}$] (**1**) had been structurally characterised [2]. Thus, in a 1986 communication we reported that treatment of colourless $[\text{ThCp}''_2\text{Cl}_2]$ (**A**) [3] in toluene with sodium–potassium alloy yielded the dark-blue, crystalline complex **1** and metallic Th, which led us to suggest that probable transient intermediates were successively $\text{ThCp}''_2\text{Cl}$ and ThCp''_2 , Scheme 1 [2]. In

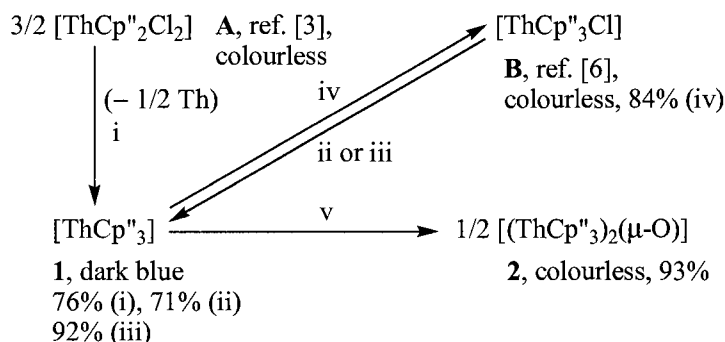
1988, we showed that the hydrocarbon-soluble **1** was EPR-active at ambient temperature with a *g*_{av} value of 1.910(1) at 300 K in methylcyclohexane and in the powdered solid from 10–300 K (calculated from $1/3(g_{\parallel} + 2g_{\perp})$); this was taken as evidence for **1** having a 6d¹, rather than 5f¹, electronic ground state [4]. For the



Scheme 1. Ref. [2].

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Scheme 2. Reagents and conditions: (i) Na–K, 20 °C, 20 h; (ii) Na–K, PhMe, 20 °C, 24 h; (iii) Na–K, C₆H₁₄, 20 °C, sonication, 6 h; (iv) Bu^tCl, C₆H₁₄, 20 °C, 5 min; (v) trace H₂O, PhMe, 20 °C.

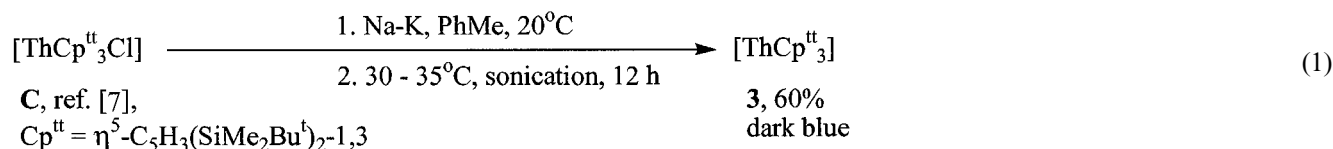
hypothetical planar (Th to the centroids (Cp) of the C₅ rings) ThCp₃ skeleton, the 6d *a*₁ orbital was calculated to be ca. 1 eV lower in energy than the lowest 5f orbital [5]; this study also predicted that a ThCp₃(L) complex (L being a neutral ligand) should destabilise this *a*₁ orbital and place it at higher energy than the 5f. The complex [K(DME)₂][Th{η⁸-C₈H₆(SiMe₂Bu^t)_{2-1,4}}₂] was also shown to be a Th(III) complex having a 6d¹ ground state [6].

In the intervening years, we have devoted considerable effort in seeking (i) other well-characterised Th(III) complexes; (ii) possible Th(II) complexes; (iii) adducts of **1** or of an analogue with a neutral ligand; and (iv) further spectroscopic and magnetic data. We now present details of the original 1986 study and extensions thereof in the directions (i)–(iv).

2. Results and discussion

The original method of synthesis (Scheme 1) of [ThCp₃'] (**1**) involved the reaction of [ThCp₂''Cl₂] (A) with Na–K alloy in toluene. Thus, **1** was formed (i in Scheme 2) from A and an excess of Na–K alloy (70% K) in toluene at ambient temperature, metallic Th being a by-product. A preferred route used [ThCp₃''Cl] (B) [7] as the precursor. Thus, from B and Na–K alloy in toluene (ii in Scheme 2), or hexane with sonication (iii in Scheme 2), **1** was obtained. The latter is a powerful reducing agent, being readily converted into B (iv in Scheme 2) or [(ThCp₃'')₂(μ-O)] (2) (v in Scheme 2) upon treatment with 2-chloro-2-methylpropane or wet toluene, respectively.

The reduction of a tris(cyclopentadienyl)thorium chloride, using Na–K alloy also proved to be a viable method for the preparation of [ThCp₃'] [Cp^{tt} = η⁵-C₅H₃-(SiMe₂Bu^t)_{2-1,3}] (**3**) from [ThCp₃''Cl] (C) [7], Eq. (1).



The dark-blue, crystalline, homoleptic (disubstituted-cyclopentadienyl) Th(III) complexes **1** and **3** gave satisfactory microanalyses (C/H) and were shown to be free of chloride. Additionally, EPR spectra and single crystal X-ray diffraction data are available. The complex [ThCp₃'] (**1**) was volatile at < 180 °C and 10⁻³ torr; this allowed Brennan and Green to record the UV photoelectron spectrum, which showed the remarkably low {cf. such data for Na (5.14 eV) and K (4.34 eV) [8]} first ionisation potential of 4.87 eV [9].

The EPR data are summarised in Table 1 and are very similar for **1** and **3**. The EPR spectrum of **1** in methylcyclohexane at 298 K is shown in Fig. 1. As discussed previously for **1** [4], results are only consistent with a 6d¹ ground state. Thus, if the 5f¹ configuration were the lowest, no room temperature signal would have been observed and the *g* values would have been markedly different from *g* = 2, while if the 7s¹ configuration were the lowest, only an isotropic EPR spectrum would be found with *g* = 2.00.

Optical spectral data for **1** in methylcyclohexane were recorded at 298, 77 and 4 K; as the latter two were very similar, only data for 298 and 4 K are shown in Table 2. The bands were broad, spanning 1000–1500 cm⁻¹ (see Fig. 2) (hence unlike the usual sharp f → f transitions) and very intense (cf. the much lower oscillation strengths, by two to three orders of magnitude, of typical lanthanide f → f transitions [10]).

Attempts were made to measure the magnetic susceptibility of various samples of powdered **1** in the 5–300 K range. From the EPR *g*_{||} and *g*_⊥ values, the calculated (cf. ref. [11]) μ_{eff} = 1.65 BM with θ = 0 K. However, although each sample of **1** followed the Curie–Weiss law [χ = C/(T – θ)], the observed values for μ_{eff} varied from ca. 0.4 to 1.56 BM with θ = 0.8 ± 0.3 K. This is attributed

Table 1
EPR results for the thorium(III) complexes **1** and **3**

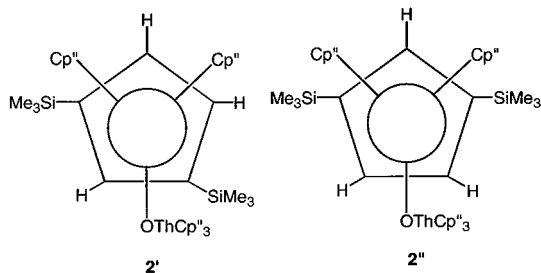
Complex	Solvent	g_{\parallel}	g_{\perp}	g_{av}	Temperature (K)
1	Methylcyclohexane			1.910(1)	300
1	Methylcyclohexane	1.9725(10)	1.879(1)	1.910 ^a	10–110
1	(Powdered solid)	1.972(1)	1.878(1)	1.909 ^a	10–300
3	Methylcyclohexane			1.910(1)	300
3	Methylcyclohexane	1.976(1)	1.894(2)	1.921 ^a	100
3	(Powdered solid)	1.972(1)	1.886(2)	1.915 ^a	300

^a Calculated from $g_{av} = 1/3(g_{\parallel} + 2 g_{\perp})$.

to varying quantities of a diamagnetic impurity in each sample, which may well have been [(ThCp^{''})₂(μ-O)] (**2**).

The molecular structure and atom numbering scheme for [ThCp^{''}]**3** is shown in Fig. 3, selected bond distances and angles being in Tables 3 and 4. Similar data for [ThCp^{''}]**1** have already been reported [2]. The two sets are closely similar, as illustrated in Table 4. The three C₅ rings in **3**, with centroids Cp(1) to Cp(3), are distributed symmetrically about the central Th atom, the coordination environment of which can be described as essentially trigonal planar; the average Cp–Th–Cp' angle is 120° (as in **1** [2]). The Th–Cp and Th–C_{sp²} bond distances are slightly longer in **3** than in **1**, consistent with Cp^{''} being more bulky than Cp'. Likewise, in **3** the Si–CMe₃ bond lengths are significantly longer than that of Si–CH₃ and the C_{sp²}–Si–CH₃ bond angles are wider than that of C_{sp²}–Si–CMe₃. The Th–Cp_{av} values for **1** (2.518 Å) and **3** (2.533 Å) may also be compared with those in [ThCp^{''}₂Cl₂] (2.506 Å) [3], [ThCp^{''}₂Cl₂] (2.525 Å) [12], [ThCp^{''}₃Cl] (2.565 Å) [7] and [ThCp^{''}₃Cl] (2.574 Å) [7].

The colourless, crystalline complex [(ThCp^{''})₂(μ-O)] (**2**) was identified by C (somewhat low) and H microanalyses and its ¹H-NMR spectrum in toluene-*d*₈. The ambient temperature spectrum was typical of a Cp^{''}-containing diamagnetic compound, having a single SiMe₃ signal and a high frequency doublet and low frequency triplet appropriate for the A₂X ring protons. As the sample was cooled, the SiMe₃ signal became increasingly broad and at 193 K split into two sharp singlets, separated by 44 Hz (corresponding to an activation energy of ΔG_{193}° K = 43.5 kJ mol⁻¹), while the ring protons finally appeared as AA'X systems. The dynamic process is believed to be due to the restricted rotation about the Cp^{''}–Th axis, which at low temperature results in the presence of the two conformers **2'** and **2''** which are no longer undergoing fast exchange on the NMR spectral time scale.



Attempts were made to prepare an adduct of [ThCp^{''}]**1**. Although **1** was soluble in THF or DME, giving in each case a deep-blue solution, there was no evidence that a reaction had occurred. Likewise, both H₂ and CO proved to be unreactive. When an excess of Na–K alloy was added to [ThCp^{''}Cl] in THF at 20 °C, the initially deep-blue solution changed within ca. 1 h to dark green. The latter was EPR-silent and the ¹H- and ¹³C-NMR spectral signals were appropriate for a dia-

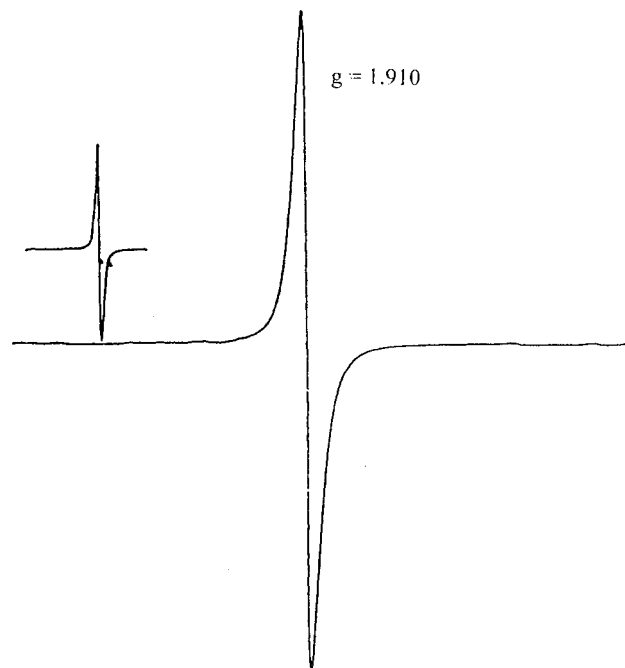


Fig. 1. The EPR spectrum of [ThCp^{''}]**1** in methylcyclohexane at 298 K (inset: DPPH as external standard).

Table 2
Optical spectra for the thorium(III) complex **1** in methylcyclohexane

Absorption max. (centre) (cm ⁻¹)	Oscillator strength × 10 ⁶	Temperature (K)
15300 (15630)	3330	298(4)
16960 (17200)	4410	298(4)
19810 (19990)	4570	298(4)
27540 (28380)	5600	298(4)

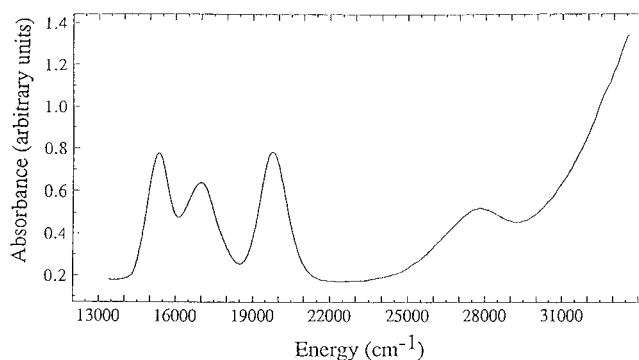


Fig. 2. The absorption spectrum of $[\text{ThCp}_3']$ (**1**) in methylcyclohexane at 298 K.

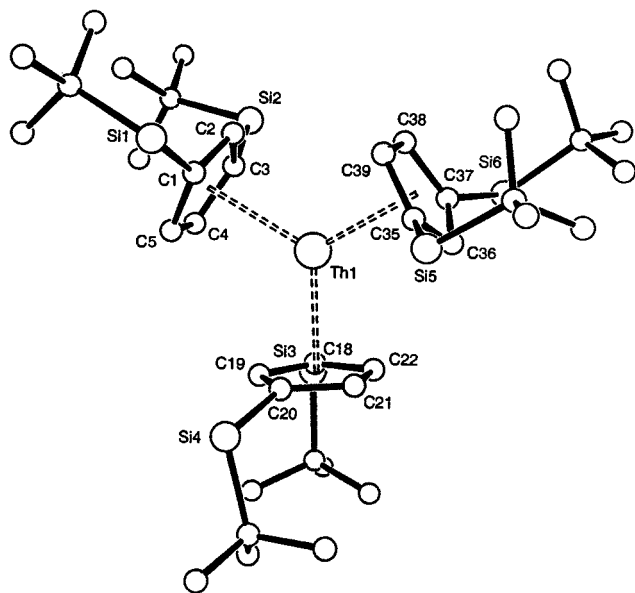


Fig. 3. The molecular structure and atomic numbering scheme for $[\text{ThCp}_3']$ (**3**). Me groups on Si atoms are omitted for clarity.

magnetic Cp''-containing compound. Numerous unsuccessful attempts were made to characterise this material, but reproducible analytical results were not

obtained. It is possible that it was a mixture of spin-paired Th(II) d^2 complexes of composition $[\text{K}(\text{THF})_x][\text{ThCp}_3']$ and/or $\text{ThCp}_2''(\text{THF})_y$. With 'BuBr it yielded $[\text{ThCp}_2''\text{Br}_2]$.

3. Experimental

3.1. Materials and procedures

All synthetic manipulations were carried out under Ar using high vacuum manifold and conventional Schlenk techniques. Solvents were dried from appropriate drying agents and were thoroughly degassed prior to use. The compounds $[\text{ThCp}_2''\text{Cl}_2]$ [3], $[\text{ThCp}_2''\text{Cl}_2]$ [12], $[\text{ThCp}_3'\text{Cl}]$ and $[\text{ThCp}_3''\text{Cl}]$ [7] were prepared by literature procedures. NMR spectra were recorded on a Bruker WM-360 instrument and EPR solution spectra were recorded at ambient temperature on a Bruker ESP-300 instrument. Elemental analyses were determined by Medac Ltd., Brunel University.

Solutions for detailed EPR and optical spectroscopy measurements at Berkeley (Tables 1 and 2) were prepared with dry, deoxygenated solvents and were sealed in appropriate quartz or Pyrex tubes. For the measurements of the intensities of the optical transitions in a $[\text{ThCp}_3']$ (**1**) in methylcyclohexane, calibrated cuvettes with a Teflon stopper were used. EPR spectral [4] and magnetic susceptibility [13] measurements were as described previously. Optical spectra were obtained on a Cary-17 spectrophotometer. For the low temperature spectra, Dewar vessels containing liquid helium and/or liquid nitrogen gas were placed in the Cary-17 sample chamber and the sample and container were immersed directly in the cryogenic fluid.

3.2. Synthesis of $[\text{ThCp}_3']$ (**1**)

(a): The compound $[\text{ThCp}_2''\text{Cl}_2]$ (**A**) (2.84 g, 3.9 mmol) was added to a stirred suspension of Na–K

Table 3
Selected intramolecular bond distances (Å) and bond angles (°) with estimated standard deviations in parentheses for $[\text{Th}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{Bu}')_2\text{-1,3}\}_3]$ (**3**) (see also Table 4)

Bond distances

Th–C(1) to Th–C(5)	2.780(6) to 2.838(6)	Si–CH ₃	1.836(9) to 1.882(10)
Th–C(18) to Th–C(22)	2.770(6) to 2.827(6)	Si–CMe ₃	1.888(8) to 1.910(7)
Th–C(35) to Th–C(39)	2.789(6) to 2.830(6)	Si–C _{sp2}	1.855(6) to 1.872(6)
Th–C _{sp2} av.	2.804	Si–C _{sp2} av.	1.863
Th–Cp av. ^a	2.533	Si–CH ₃ av.	1.859
		Si–CMe ₃ av.	1.900

Bond angles

Cp–Th–Cp' av. ^a	120	C _{sp2} –Si–CMe ₃	106.8(3) to 108.7(3)
C _{sp2} –Si–CH ₃	107.4(3)–115.0(3)	C _{sp2} –Si–CMe ₃ av.	107.8
C _{sp2} –Si–CH ₃ av.	111.2		

^a Cp or Cp' represents the centroid of a C₅ ring.

Table 4
Selected comparative bond distances (Å) and angles (°) for [Th{η⁵-C₅H₃(SiMe₂R)₂-1,3}₃] (R = Me **1** or 'Bu **3**)

	1 [2]		3 (This work)			
<i>Bond distances</i>						
Th–C _{sp²} av./C ₅ ring	2.80(2)	2.81(2)	2.79(2)	2.81(3)	2.80(3)	2.81(3)
Th–Cp ^a /C ₅ ring	2.509	2.519	2.526	2.531	2.532	2.535
Si–CH ₃ /C ₅ ring				1.87(2)	1.86(2)	1.85(2)
Si–CMe ₃ /C ₅ ring				1.90(2)	1.91(2)	1.90(2)
<i>Bond angles</i>						
Cp(1)–Th–Cp(2)						
Cp(1)–Th–Cp(3)	118.9, 120.0, 121.1			119.7, 119.8, 120.6		
Cp(2)–Th–Cp(3)						

^a Cp(1–3) represent the centroids of each of the three C₅ rings.

alloy (Na, 0.3 g; K, 0.7 g, 18 mmol) in toluene (ca. 80 ml) at ca. 20 °C. After about 4 h, an intense blue colour had developed. The mixture was stirred for a further 20 h, then filtered. The volatiles were removed from the filtrate in vacuo and the product extracted into C₆H₁₄ (ca. 60 ml), leaving a metallic residue. The extract was concentrated to ca. 20 ml and cooled at –30 °C, yielding dark-blue cubes of compound **1** (2.58 g, 76% based on Scheme 1), m.p. (dec.) 275–280 °C, subl. ca. 180 °C and 10^{–3} torr. Anal. Found: C, 45.8; H, 7.2. Calc. for C₃₃H₆₃Si₆Th: C, 46.1; H, 7.4%.

(b): Excess Na–K alloy (1.1 g, 17.5 mmol) was added to a colourless stirring solution of [ThCp₃Cl] (**B**) (3.14 g, 3.5 mmol) in toluene (ca. 50 ml) at ca. 20 °C. The mixture was stirred for 24 h. The deep-blue mixture was filtered. Volatiles were removed from the filtrate in vacuo, yielding a blue solid, which was extracted with hexane (ca. 50 ml). The extract was concentrated to ca. 25 ml and cooled at –30 °C, yielding dark-blue crystals of compound **1** (2.13 g, 71%), which was purified by multiple sublimation.

3.3. Synthesis of [(ThCp₃)₂(μ-O)] (**2**)

[ThCp₃]⁰ (**1**) (0.27 g, 0.314 mmol) was added at 20 °C to toluene (25 ml) which had not been dried. The blue colour was immediately discharged. Toluene was removed in vacuo, yielding a colourless solid, which was extracted into pentane (ca. 25 ml). The extract was concentrated to ca. 10 ml and cooled at –30 °C, affording colourless crystals of compound **2** (0.25 g, 93%). Anal. Found: C, 43.0; H, 7.30. Calc. for C₆₆H₁₂₆OSi₁₂Th₂ (**2**): C, 45.7, H, 7.27%. ¹H-NMR (toluene-*d*₈, 298 K, δ ppm): 0.38 (s, 108H, Me), 6.57 (t, 6H, H-4), 6.74 (d, 12H, H-2/H-5).

3.4. Synthesis of [ThCp₃⁰] (**3**)

Excess Na–K alloy (Na, 0.06 g; K, 0.20 g, 5.13 mmol) was added to a colourless stirring solution of

[ThCp₃⁰Cl] (**C**) (0.75 g, 0.65 mmol) in toluene (200 ml) at ca. 20 °C. A deep-blue solution was obtained after stirring for 5 d at ca. 20 °C. The mixture was sonicated for 12 h at 30–35 °C, then filtered. The precipitate was extracted with hot toluene (3 × 50 ml). The combined filtrate and extract was concentrated to ca. 10 ml and cooled at –30 °C, yielding dark-blue crystals of compound **3** (0.45 g, 60%). Anal. Found: C, 53.8; H, 8.77. Calc. for C₅₁H₉₉Si₆Th (**3**): C, 55.0; H, 8.97%.

Table 5
Crystal data and structure refinement parameters for [ThCp₃⁰] (**3**)

Empirical formula	C ₅₁ H ₉₉ Si ₆ Th
Formula weight	1112.9
Temperature (K)	293
Wavelength (Å)	0.7107
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	
<i>a</i> (Å)	12.284(3)
<i>b</i> (Å)	20.755(6)
<i>c</i> (Å)	24.139(6)
α (°)	90
β (°)	100.74(2)
γ (°)	90
<i>V</i> (Å ³)	66046.7
<i>Z</i>	4
<i>D</i> _{calc} (Mg m ^{–3})	1.22
μ Mo–Kα (cm ^{–1})	27.0
<i>F</i> (000)	2316
Crystal size (mm)	0.3 × 0.3 × 0.05
Scan mode	θ–2θ
Total reflections	11481
Unique reflections	10964
No. of variables	523
No. of observed reflections	5088
<i>R</i>	0.036
<i>R</i> _w	0.042
<i>S</i>	1.2

3.5. X-ray structure determination of crystalline $[\text{ThCp}_3^{\prime\prime}]$ (3)

Intensities were measured on an Enraf–Nonius CAD4 diffractometer at room temperature with Mo–K α radiation and a crystal sealed in a capillary. Refinement was based on F using programs from the MOLLEN package [14]. Crystal data and details of data collection are given in Table 5. Further details can be obtained directly from the authors.

Acknowledgements

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