The Synthesis and Characterisation, including *X*-ray Diffraction Study, of $[Th\{\eta\text{-}C_5H_3(SiMe_3)_2\}_3]$; the First Thorium(III) Crystal Structure†

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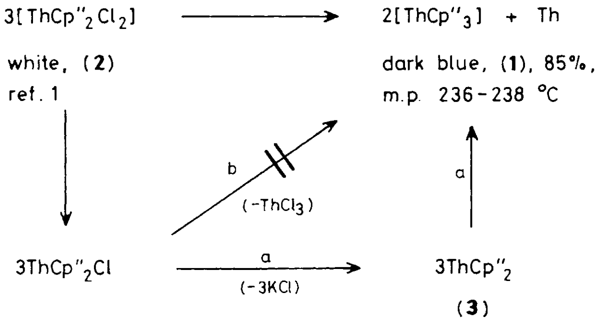
Reduction of $[ThCp''_2Cl_2]$ [$Cp'' = \eta\text{-}C_5H_3(SiMe_3)_2$] with Na–K in PhMe yields $[ThCp''_3]$, which is monomeric in the solid state, as determined by *X*-ray crystallography, and is the first crystalline tri-η-cyclopentadienylmetal complex, <Th–C(η-)> 2.80(2) Å.

We report the synthesis and *X*-ray characterisation of the exceedingly air- and moisture-sensitive but thermally stable, hydrocarbon-soluble, blue, paramagnetic, crystalline f^1 complex $[ThCp''_3]$ [$Cp'' = \eta\text{-}C_5H_3(SiMe_3)_2$] (**1**). As far as we are aware, there are no previous *X*-ray single-crystal structural data either for a Th^{III} complex or a homoleptic tris(η-cyclopentadienyl)metal complex.

Complex (**1**) was obtained by an unexpected reductive disproportionation from the colourless f^0 complex $[ThCp''_2Cl_2]$ (**2**)[1] and a five-fold excess of Na–K alloy in toluene. We believe that (**1**) is formed (pathway a in Scheme 1) *via* the transient thorocene (**3**), because (i) the yield of (**1**) was virtually quantitative in Cp″ and Th metal was a coproduct; (ii) metathesis (pathway b in Scheme 1) *via* $ThCp''_2Cl$ is unlikely, *cf.*,[2] the stable $[\{UCp''_2(\mu\text{-}Cl)\}_2]$ (**4**); (iii) we find that (**4**) is reduced by Na–K alloy in PhMe to U; and (iv) there is trapping evidence both for UCp^*_2 ($Cp^* = \eta\text{-}C_5Me_5$)[3] and $ThCp^*_2$[4] {*e.g.*, $[ThCp^*_2Cl_2]$ + Mg(buta-1,3-diene) → $[ThCp^*_2(\eta\text{-}C_4H_6)]$}.

It is evident that the thorocene(IV) chloride (**2**) is difficult to reduce. Thus, it did not react with Na–Hg in toluene upon prolonged reflux, although[3] $[UCp^*_2Cl_2]$ and Na–Hg in tetrahydrofuran (thf) gave $[UCp^*_2(\mu\text{-}Cl)_2Na(thf)_2]$. Furthermore,[5] $[ThCp^*_2Cl_2]$ did not undergo electrochemical reduction in tetrahydrofuran (thf) or MeCN below −2.7 V [*cf.*, for the U analogue, $-E_{\frac{1}{2}} = 1.30$ (MeCN) or 1.22 (thf)].

Complex (**1**) is monomeric in the crystal, with the three equivalent $\eta\text{-}C_5H_3(SiMe_3)_2$ groups distributed symmetrically



$Cp'' = \eta\text{-}C_5H_3(SiMe_3)_2$

Scheme 1. *Reagents and conditions:* Na–K, PhMe, 20 °C, 24 h. Compound (**1**) was characterised by microanalysis, ^1H n.m.r. spectroscopy [a broad single peak ($w_{\frac{1}{2}}$ 900 Hz) centred at 5.3 p.p.m. attributed to $SiMe_3$ protons], and *X*-ray diffraction (Figure 1).

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† No reprints available.

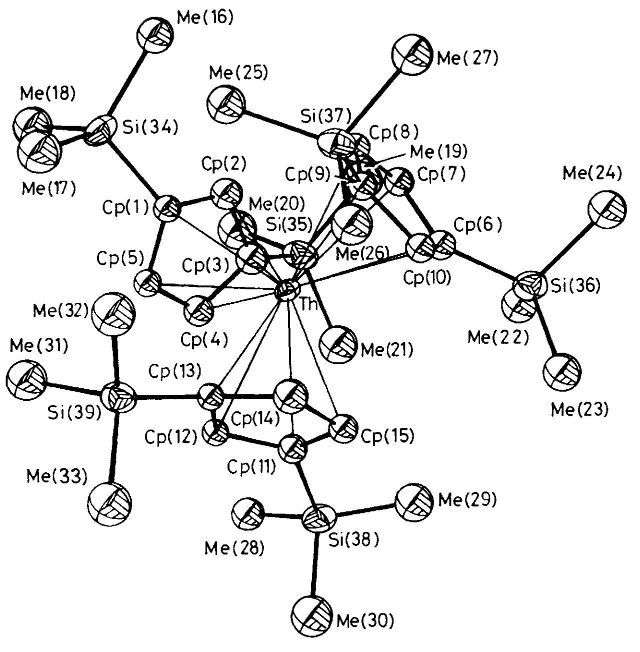

Figure 1. The molecular structure, and atom labelling scheme, for [ThCp″$_3$] (**1**). Relevant dimensions are: Th–Cp(1) aver. 2.80(2), Th–Cp(2) aver. 2.81(2), Th–Cp(3) aver. 2.79(2), Th–cent.(1) 2.519, Th–cent.(2) 2.526, Th–cent.(3) 2.509 Å; cent.(1)–Th–cent.(2) 121.11(4), cent.(1)–Th–cent.(3) 118.86(3), cent.(2)–Th–cent.(3) 120.03(4)°. [Cent.(1), cent.(2), and cent.(3) are the centroids of the cyclopentadienyl rings.]

about the quasi-nine-co-ordinate thorium atom, Figure 1.‡ The average Th–C(η-) distance of 2.80(2) Å in [ThCp″$_3$] (**1**) is close to that in [ThCp″$_2$Cl$_2$] (**2**), 2.78(1) Å.[1] The co-ordination environment around Th can alternatively be described as trigonal planar, the average of the three cent.–Th–cent. angles = 120° (cent. denotes the centroid of each Cp″ ligand); <Th–cent.> 2.52 Å [*cf.*, 2.51 Å in (**2**)].

The organometallic chemistry of the actinides, and especially of U and Th, is developing rapidly, mainly for complexes in oxidation state +4.[7] The +3 state is also readily accessible for U, and *X*-ray data for several compounds are available, including [{UCp*$_2$(μ-Cl)}$_3$],[3] [{UCp″$_2$(μ-X)}$_2$] (X = Cl or Br),[2] [UCp*$_2$H(dmpe)] (dmpe = Me$_2$P[CH$_2$]$_2$PMe$_2$),[8] [UCp$_3$(thf)],[9] [U(η-indenyl)$_3$],[10] [U(η-C$_5$H$_4$SiMe$_3$)$_3$(CNEt)],[11] and [UCp$_3$(Bu^n)]$^-$.[12] Thorium(III) complexes are very rare, but the hydrocarbon-insoluble compounds ThCp$_3$, Th(C$_5$H$_4$Me)$_3$, and Th(indenyl)$_3$ have been reported.[7,13]

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‡ *Crystal data* for [ThCp″$_3$] (**1**): M = 860.42, space group $P2_1/c$, a = 18.006(5), b = 13.783(5), c = 19.359(8) Å, β = 112.83(5)°, U = 4427.95 Å^3, Z = 4, D_c = 1.29 g cm^{-3}, μ = 45.52 cm^{-1} (Mo-K_α).

The structure of complex (**1**) was solved by routine heavy atom methods and refined to R = 0.049, R' = 0.067 for 2224 observed reflections, measured on a CAD-4 diffractometer. Details of the data collection process have previously been given.[6]

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

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