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White phosphorus activation by a Th(III) complex†

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[Th(Cp'')₃] (Cp'' = {C₅H₃(SiMe₃)₂-1,3}) activates P₄ to give [Th(Cp'')₃]₂(μ-η¹:η¹-P₄) (1), which has an unprecedented cyclo-P₄ binding mode. DFT studies were performed on a model of 1 to probe the bonding in this system.

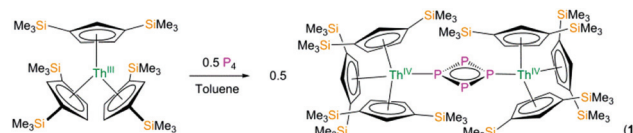
The inherent reactivity of low oxidation state early metal complexes has been widely exploited in small molecule activation chemistry for the generation of useful chemicals from abundant feedstocks (e.g. CO, CO₂, N₂).¹ In this field, white phosphorus activation by early d-transition metal complexes has been extensively investigated² as the direct preparation of organophosphorus reagents from elemental phosphorus would skip the protracted chlorination and derivatisation steps used industrially.^{3,4} Whilst U(III) small molecule activation chemistry has also started to flourish,⁵ the analogous Th(III) chemistry currently lags behind, which can be attributed to the paucity of Th(III) complexes.^{6,7} Th(III) chemistry is difficult to access as there are relatively large standard reduction potentials to overcome [*E*⁰ Th(IV) → Th(III) −3.7 V; cf. U(IV) → U(III) −0.6 V],⁸ and there are no synthetically useful Th(III)X₃ (X = halide) starting materials for salt metathesis methodologies, whereas synthetic routes to U(III) complexes from UI₃ are well-developed.⁹

The reactivity of Th(III) complexes has previously been limited to the serendipitous reaction of Lappert's [Th(Cp'')₃] with trace H₂O/O₂ to give [Th(Cp'')₃]₂(μ-O),^{6c} its purposeful oxidation with Bu^tCl to afford [Th(Cp'')₃(Cl)],^{6c,10} the reaction of [Th{C₅Me₄H}₃] with TEMPO (2,2,6,6-tetramethyl-piperidin-1-oxyl radical) to give [Th{C₅Me₄H}₃(TEMPO)] reported by Evans,¹¹ and Cloke's account of CO₂ activation with a postu-

lated Th(III) complex generated *in situ* using Na/K alloy to form carbonates and oxalates.¹² Germane to these studies, the small molecule activation chemistry of "highly reduced" thorium synthons, which formally contain Th(IV) centres and reduced ligands, has been investigated more extensively.¹³

There are currently only several examples of U(III)-mediated white phosphorus activation,¹⁴ with Cloke's account of a "slipped" cyclo-P₄ dianion in [U(C₅Me₅)[C₈H₆(SiPrⁱ)₂-1,4]]₂(μ-η²:η²-P₄) of most relevance here.^{14b} For Th(IV) chemistry, Scherer has reported the reaction of [Th(C₅H₃Bu^t-1,3)₂(η⁴-C₄H₆)] with white phosphorus in refluxing toluene to give [Th(C₅H₃Bu^t-1,3)₂]₂(μ-η³:η³-P₆), with [Th(C₅H₃Bu^t-1,3)₂]₂(μ-η³:η³-P₃)[Th(C₅H₃Bu^t-1,3)₂(Cl)] isolated when half an equivalent of MgCl₂ was added to the reaction mixture.¹⁵

The reaction of [Th(Cp'')₃]^{6a} with P₄ gives [Th(Cp'')₃]₂(μ-η¹:η¹-P₄) (1) in poor yield as the only isolable product in either a 1:0.5 or 1:0.25 stoichiometry, with the yield approximately halved when P₄ is deficient (Scheme 1). The ³¹P{¹H} NMR spectra of the reaction mixtures showed that all almost P₄ was consumed, whereas we found that [U(Cp'')₃]¹⁶ does not react with P₄, even under forcing conditions (16 hours reflux). To the best of our knowledge this is the first example of divergent reactivity profiles of isolated, structurally analogous Th(III) and U(III) complexes. This phenomenon can be attributed to differences in reduction potentials and electronic configurations of Th(III) and U(III) in [An(Cp'')₃] (see below). It is noteworthy that a U(III) complex with a similar π-donor Cp ligand environment, [U(C₅Me₅)[C₈H₆(SiPrⁱ)₂-1,4]], has previously been shown to activate P₄,^{14b} and the reduction potential of P₄ is reported at −1.53 and −1.98 V, depending on the conditions employed.¹⁷



Scheme 1 Synthesis of complex 1.

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The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in d_6 -benzene at 298 K exhibits two triplet signals [δ_{P} : 227.59 (t, $^1J_{\text{PP}} \approx 400$ Hz) and 328.86 ppm (t, $^1J_{\text{PP}} \approx 400$ Hz)] and two broad unresolved multiplets [δ_{P} : -246.55 (br m, $\Delta_{\text{v}} \approx 2000$ Hz) and 10.35 ppm (br m, $\Delta_{\text{v}} \approx 2000$ Hz)]. The multiplicity for the two low field signals correlates with the solid state structure of **1**, by comparison with the chemical shift of the signal in the ^{31}P NMR spectrum of Cs_2P_4 [δ_{P} : 348 ppm (s)].¹⁸ The two high field signals are likely due to processes involving changes in hapticity of the cyclo- P_4 ring, but could not be confidently assigned. These were reproducibly observed in separate samples of **1** but elemental analysis values obtained were in close agreement with the solid state structure (see below). To probe the identity of the unassigned signals, VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of **1** in toluene/ d_8 -toluene was performed from 193–353 K in 10 K increments (see ESI Fig. S1 and S2†). At high temperatures (>313 K) the two low field signals were not distinguishable from the baseline and the two high field multiplets simplified to broad signals. At low temperatures (<233 K) the two low field signals resolved to two pairs of triplets [data at 193 K, $\delta_{\text{P}} = 216$ (t, $^1J_{\text{PP}} = 411$ Hz), 220 (t, $^1J_{\text{PP}} = 411$ Hz), 317 (t, $^1J_{\text{PP}} = 411$ Hz), and 323 (t, $^1J_{\text{PP}} = 411$ Hz)]. We tentatively attribute this to restricted rotation about the Th...Th axis; the coalescence temperature for these signals is around 250 K (see ESI Fig. S3†). The two high field signals did not resolve sufficiently at this temperature for coupling constants to be extracted. $^{31}\text{P}\{^1\text{H}\}$ NMR COSY experiments were performed in d_6 -benzene at 298 K to determine if all four signals derived from the same molecule, but this was inconclusive despite extended acquisition times.

Only one singlet is observed in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **1** at 298 K [δ_{Si} : -8.02 ppm], showing that a pseudo-high symmetry environment of the silyl groups is adopted in solution at room temperature. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** were unremarkable and two signals were observed for the silyl groups in each spectrum [δ_{H} : 0.58 and 0.60 ppm; δ_{C} : 2.66 and 2.86 ppm]. The UV/Vis spectrum of **1** exhibits three intense absorptions (see ESI Fig. S6†). The most intense absorption at 285 nm ($\epsilon = 30\,400\text{ M}^{-1}\text{ cm}^{-1}$) is assigned as the cyclo- P_4 $\pi \rightarrow \pi^*$ transition and the broad absorptions at 425 nm ($9000\text{ M}^{-1}\text{ cm}^{-1}$) and 477 nm ($11\,200\text{ M}^{-1}\text{ cm}^{-1}$), assigned as LMCT bands based on the similarity of this spectrum with closely related “slipped” cyclo- P_4 transition metal systems.^{1,19} The spectral data for **1** are typical of a diamagnetic formulation, with two Th(IV) centres and a cyclo- P_4^{2-} 6 π -electron aromatic bridging dianion.

The solid state structure of **1**· C_7H_8 was determined by single crystal XRD (Fig. 1). Complex **1** adopts the cubic space group $Pa\bar{3}$, with a crystallographic threefold rotation axis through the Th(1)–P(1) bond and the centre of the cyclo- P_4 ring. The two phosphorus atoms that are not bonded to thorium are each located over three symmetry-equivalent positions set at 1/3 occupancy, therefore only one conformation is shown for clarity. Complex **1** exhibits a $\mu\text{-}\eta^1\text{:}\eta^1\text{-P}_4$ binding mode, which we attribute to the presence of three bulky Cp⁺ groups at each thorium centre. Steric effects have previously accounted for the “slipped” cyclo- P_4 binding mode in

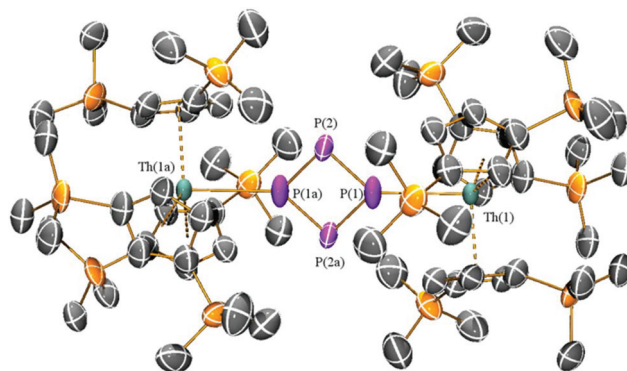


Fig. 1 Molecular structure of **1**· C_7H_8 with selected atom labelling and displacement ellipsoids set at 30% probability level. Th(1) and P(1) are on special positions, hence no equator quadratics could be generated. Hydrogen atoms, phosphorous and silyl group disorder components and lattice toluene have been removed for clarity. Symmetry operation to generate equivalent atoms: $i = -x, -y, -z$. Selected bond distances [Å] and angles [°]: Th(1)–P(1) 2.919(4), P(1)–P(2) 2.051(9), Th(1)···Cp_{centroid} 2.543(5), Th(1)–P(1)–P(2) 133.0(2), P(1)–P(2)–P(1) 85.9(4), P(2)–P(1)–P(2) 94.1(4), Cp_{centroid}···Th(1)···Cp_{centroid} 119.1(2).

[$\{\text{U}(\text{C}_5\text{Me}_5)[\text{C}_8\text{H}_6(\text{SiPr}^i_3)_2\text{-1,4}\}]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-P}_4)$].^{14b} The Th–P distances in **1** [2.919(4) Å] are unremarkable, being similar to those observed in [$\{\text{Th}(\text{C}_5\text{H}_3\text{Bu}^t_{2-1,3})_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-P}_3)\{\text{Th}(\text{C}_5\text{H}_3\text{Bu}^t_{2-1,3})_2(\text{Cl})\}\}$] [2.913(7) Å mean].¹⁵ The Th···Cp_{centroid} distances in **1** [2.543(5) Å] are longer than those in [$\text{Th}(\text{Cp}''_3)$] [2.519(2) Å mean]^{6a,7} and are more similar to those reported for [$\text{Th}(\text{Cp}''_3)(\text{Cl})$] [2.565 Å mean],²⁰ in agreement with a formal Th(IV) assignment in **1**.

The cyclo- P_4 rhombus in **1** is planar by definition, with the endocyclic P–P–P angles of 86.4(5) and 93.6(5)° skewed significantly from the approximate square arrangement observed in [$\{\text{U}(\text{C}_5\text{Me}_5)[\text{C}_8\text{H}_6(\text{SiPr}^i_3)_2\text{-1,4}\}]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-P}_4)$].^{14b} The P–P distances in **1** [2.051(9) Å mean] are remarkably short compared with those in [$\{\text{U}(\text{C}_5\text{Me}_5)[\text{C}_8\text{H}_6(\text{SiPr}^i_3)_2\text{-1,4}\}]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-P}_4)$] [2.150(2) Å mean]^{14b} and [$\{\text{Th}(\text{C}_5\text{H}_3\text{Bu}^t_{2-1,3})_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-P}_3)\{\text{Th}(\text{C}_5\text{H}_3\text{Bu}^t_{2-1,3})_2(\text{Cl})\}\}$] [2.185(9) Å mean],¹⁵ being more similar to a P=P double bond length (2.04 Å).²¹ This observation can be attributed to the unusual $\mu\text{-}\eta^1\text{:}\eta^1$ -binding mode of the cyclo- P_4 unit in **1**. In this orientation σ -donation of phosphorus sp^2 -hybridised lone pairs to vacant thorium orbitals should be the major component of the Th–P bonds, and due to the reduced π -contribution to these bonds most of the π -electron density is retained in the cyclo- P_4 ring.

A full model of **1** was studied by DFT using the TURBO-MOLE (v6.6) quantum chemistry package with the hybrid-GGA exchange–correlation functional PBE0. A gas-phase geometry optimisation was followed by vibrational frequency analysis and a local energy minimum was confirmed. Calculated Th···Cp_{centroid} distances (2.540 Å) were in excellent agreement with those calculated experimentally; Th–P bonds (2.964 Å) were in reasonable agreement, but P–P bonds (2.138 Å) were overestimated. This discrepancy was due to a small deviation from planarity in the Th– P_4 –Th unit, hence bonding analysis was performed on both PBE0-optimised and crystallographic



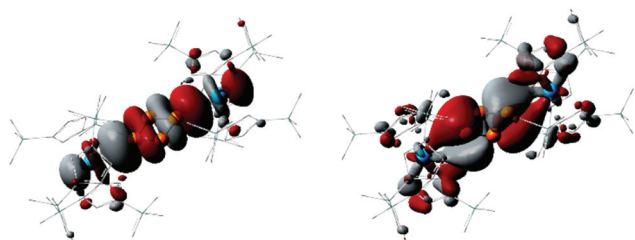


Fig. 2 σ - and π -bonding orbitals of **1**, rendered at an isosurface of 0.015 a.u.

structures. Interaction with the thorium centres manifests itself in splitting of the high-lying σ_1 - and π_1 -levels that are formally degenerate in the free P_4^{2-} dianion, with the σ_1 -level split by 1.11 eV/0.52 eV at the experimental/PBE0-optimised geometry and the corresponding π_1 -level split by 0.21 eV/0.14 eV, demonstrating the pronounced σ - and diminished π -contributions (Fig. 2).

The Quantum Theory of Atoms in Molecules (QTAIM) was employed to further investigate the bonding in **1**. Parameters obtained at experimental and PBE0-optimised geometries were very similar (see ESI†), so only the former are considered here. The calculated magnitude of the electron density at the bond critical point (ρ_{BCP}) of the Th–P bond is 0.047 a.u., indicative of a predominantly ionic interaction with slightly greater covalent character than that found in Th–S and Th–Se single bonds.²² Similar characteristics were found for the energy density, H , and the Th–P delocalisation index, $\delta(\text{Th},\text{P})$. Within the cyclo- P_4 ring, the P–P delocalisation index, $\delta(\text{P},\text{P})$, which in this situation can be regarded as a measure of bond order, was found to be 1.33, close to the formal value of 1.50 expected for an ideal aromatic system and slightly lower than the value of 1.45 calculated for free P_4^{2-} at the same level of theory. This is indicative of a largely unperturbed aromatic 6π -electron configuration. The calculated partial charge on the ring is -1.27 a.u., indicating a degree of charge transfer from the ring that is commensurate with the slight reduction in aromatic character.

We conclude that the enhanced reactivity of $[\text{Th}(\text{Cp}^{\prime\prime})_3]$ over $[\text{U}(\text{Cp}^{\prime\prime})_3]$ with P_4 necessitates future investigations into the reactivity of Th(III) complexes. We are especially interested in Th(III)-mediated small molecule activation chemistry, as these investigations could give novel reactivity profiles and bonding motifs. We thank The University of Manchester, the EPSRC (grant numbers EP/K039547/1, EP/L014416/1 and EP/J002208/1) and the Nuclear FIRST DTC for funding. AK thanks Lancaster University for access to the HEC high performance computing facility.

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