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). In this field, white phosphorus activation by early d-transition metal complexes has been extensively investigated as the direct preparation of organophosphorus reagents from elemental phosphorus would skip the protracted chlorination and derivatisation steps used industrially. Whilst U(III) small molecule activation chemistry has also started to flourish, the analogous Th(III) chemistry is currently limited to the serendipitous reaction of Lappert’s [Th(C5H3Bu−1,3)2{C8H6(SiMe3)2-1,4}] (2-P4) with white phosphorus in refluxing toluene to give [Th(C5H3Bu−1,3)2(μ-η1-η1-P4)], with [Th(C5H3Bu−1,3)2(μ-η1-η1-P4)]{Th(C5H3Bu−1,3)2(θ−1-P4)}14 of most relevance here. For Th(IV) chemistry, Scherer has reported the reaction of [Th(C5H3Bu−1,3)2(θ−1-P4)] with white phosphorus in refluxing toluene to give [Th(C5H3Bu−1,3)2(μ-η1-η1-P4)], with [Th(C5H3Bu−1,3)2(μ-η1-η1-P4)]{Th(C5H3Bu−1,3)2(θ−1-P4)}14 isolated when half an equivalent of MgCl2 was added to the reaction mixture.15

The reaction of [Th(Cp″)3]16 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 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(C5Me3)3]14, has previously been shown to activate P4, and the reduction potential of P4 is reported at 1.53 and 1.98 V, depending on the conditions employed.17

†Electronic supplementary information (ESI) available: Full synthetic details, crystallography and DFT studies. CCDC 1426081. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt04528b. Additional research data supporting this publication are available from The University of Manchester eScholar repository at DOI: 10.15127/1.294611.

‡Scheme 1 Synthesis of complex 1.

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The $^{31}$P($^1$H) NMR spectrum of 1 in $d_6$-benzene at 298 K exhibits two triplet signals [$\delta_P$: 227.59 (t, $J_{PP} \approx 400$ Hz) and 328.86 ppm (t, $J_{PP} \approx 400$ Hz)] and two broad unresolved multiplets [$\delta_P$: $-246.55$ (br m, $\Delta \nu \approx 2000$ Hz) and 10.35 ppm (br m, $\Delta \nu \approx 2000$ 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$_2$P$_4$ [$\delta_P$: 348 ppm (s)]. 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 reproduced 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 $^{31}$P($^1$H) NMR spectroscopy of 1 in toluene/$d_6$-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, $\delta_P$: 216 (t, $J_{PP} = 411$ Hz), 220 (t, $J_{PP} = 411$ Hz), 317 (t, $J_{PP} = 411$ Hz), and 323 (t, $J_{PP} = 411$ 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. $^{31}$P($^1$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 $^{29}$Si($^1$H) NMR spectrum of 1 at 298 K [$\delta_{Si}$: −8.02 ppm], showing that a pseudo-high symmetry environment of the silyl groups is adopted in solution at room temperature. The $^1$H and $^{13}$C($^1$H) NMR spectra of 1 were unremarkable and two signals were observed for the silyl groups in each spectrum [$\delta_H$: 0.58 and 0.60 ppm; $\delta_{C}$: 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 ($\epsilon = 30 400$ M$^{-1}$ cm$^{-1}$) is assigned as the cyclo-P$_4$ π → π$^*$ transition and the broad absorptions at 425 nm (9000 M$^{-1}$ cm$^{-1}$) and 477 nm (11 200 M$^{-1}$ cm$^{-1}$), assigned as LMCT bands based on the similarity of this spectrum with closely related “slipped” cyclo-P$_4$ transition metal systems.$^{1,9}$ The spectral data for 1 are typical of a diamagnetic formulation, with two Th($^n$) centres and a cyclo-P$_4$ $^{3e}$ 6s-electron aromatic bridging diad.

The solid state structure of 1-C$_7$H$_8$ was determined by single crystal XRD (Fig. 1). Complex 1 adopts the cubic space group $Pa$3, with a crystallographic threefold rotation axis through the Th(1)–P(1) bond and the centre of the cyclo-P$_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 μ–η$^1$–η$^1$-P$_4$ binding mode, which we attribute to the presence of three bulky Cp$^*$ groups at each thorium centre. Steric effects have previously been accounted for the “slipped” cyclo-P$_4$ binding mode in

$\left[\left(U(C_5M_5)[C_5H_6(SiPr_3)_2Cl]\right)_2(\mu–\eta^1–\eta^1–P_4)\right]^{1,4b}$ The Th–P distances in 1 [2.919(4) Å] are unremarkable, being similar to those observed in $\left[\left(Th(C_5H_4Bu_2^*\eta^1–3)\right)_2(\mu–\eta^1–\eta^1–P_4)\left(Th(C_5H_4Bu_2^*\eta^1–3)\right)_2(CI)\right]$ [2.913(7) Å mean].$^{1,5}$ The Th...Cp$_{centroid}$ distances in 1 [2.543(5) Å] are longer than those in $\left[Th(Cp^*\eta^1)\right]$ [2.519(2) Å mean]$^{7a}$ and are more similar to those reported for $\left[Th(Cp^*\eta^1)\right]$ [2.565 Å mean],$^{20}$ in agreement with a formal Th($^n$) 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 $\left[\left(U(C_5Me_5)[C_5H_6(SiPr_3)_2Cl]\right)_2(\mu–\eta^1–\eta^1–P_4)\right]^{1,4b}$ The P–P distances in 1 [2.051(9) Å mean] are remarkably short compared with those in $\left[\left(Th(C_5H_4Bu_2^*\eta^1–3)\right)_2(\mu–\eta^1–\eta^1–P_4)\left(Th(C_5H_4Bu_2^*\eta^1–3)\right)_2(CI)\right]$ [2.150(2) Å mean]$^{3,14b}$ and $\left[\left(Th(C_5H_4Bu_2^*\eta^1–3)\right)_2(\mu–\eta^1–\eta^1–P_4)\left(Th(C_5H_4Bu_2^*\eta^1–3)\right)_2(CI)\right]$ [2.185(9) Å mean].$^{1,5}$ Being more similar to a P=P double bond length (2.04 Å),$^{21}$ this observation can be attributed to the unusual μ–η$^1$–η$^1$-binding mode of the cyclo-P$_4$ unit in 1. In this orientation σ-donation of phosphorus sp$^3$-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 TURBOMOLE (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 (2.340 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 σ1- and π1-levels that are formally degenerate in the free P4\(^{2-}\) dianion, with the σ1-level split by 1.11 eV/0.52 eV at the experimental/PBE0-optimised geometry and the corresponding π1-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 (\(\rho_{\text{BCP}}\)) of the Th–P bond is 0.047 a.u., indicative of a largely unperturbed aromatic \(\pi\)-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\(_3\) 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 6z-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 \([\text{Th(Cp}^\text{‴}]{_3}\) over \([\text{U(Cp}^\text{‴}]{_3}\) with \(P_4\) necessitates future investigations into the reactivity of Th\(_{n}\) complexes. We are especially interested in Th\(_{n}\)-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.

Notes and references


