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Fragmentation, catenation, and direct functionalisation of white phosphorus by a uranium(IV)–silyl–phosphino–carbene complex†

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Room temperature reaction of the uranium(IV)–carbene [U{C(SiMe$_3$)(PPh$_2$)}(BIPM^{TMS})(μ-Cl)Li(TMEDA)(μ-TMEDA)$_{0.5}$]$_2$ (1, BIPM^{TMS} = C(PPh$_2$NSiMe$_3$)$_2$) with white phosphorus (P$_4$) produces the organo-P$_5$ compound [P$_5${C(SiMe$_3$)(PPh$_2$)}$_2$][Li(TMEDA)$_2$] (2) and the uranium(IV)–methanediide [U{BIPM^{TMS}}{Cl}{μ-Cl}$_2${Li(TMEDA)}] (3). This is an unprecedented example of cooperative metal–carbene P$_4$ activation/insertion into a metal–carbon double bond and also an actinide complex reacting with P$_4$ to directly form an organophosphorus species. Conducting the reaction at low temperature permits the isolation of the diuranium(IV) complex [{U(BIPM^{TMS})([μ-η^2:η^2-P$_2$]C[SiMe$_3$][PPh$_2$])}$_2$] (4), which then converts to 2 and 3. Thus, surprisingly, in contrast to all other actinide P$_4$ reactivity, although this reaction produces catenation overall it proceeds *via* P$_4$ cleavage to functionalised P$_2$ units. Hence, this work establishes a proof of concept synthetic cycle for direct fragmentation, catenation, and functionalisation of P$_4$.

Organophosphorus compounds have numerous vital uses.[1] Industrially, organophosphorus compounds are derived from PCl$_3$, which is in turn formed by chlorination of white phosphorus (P$_4$). Thus, there is significant interest in discovering new, direct paths to the derivatisation of P$_4$. Indeed, the activation and functionalisation of P$_4$ by complexes of the transition and lanthanide metals[2] and main group elements,[3] and even by free singlet carbenes,[4] has received significant attention. However, the catalytic derivatisation/functionalisation of P$_4$ in processes which directly yield organophosphorus compounds is challenging and only beginning to be realised.[2c]

In contrast to burgeoning studies of P$_4$ activation by transition metal and main group compounds, reports of P$_4$ activation by actinide elements are scarce, being limited to six examples.[5] Also, although P–P bonds are broken in almost all cases, P$_4$ is not fragmented into smaller phosphorus-containing units which are suited for functionalisation. In previous work, we reported uranium-mediated aggregation of P$_4$, generating the triuranium-[P$_7$] Zintl complex [{U(Ts^{Tol})}$_3$(μ$_3$-η^2:η^2:η^2-P$_7$)] (**I**, Ts^{Tol} = HC(SiMe$_2$NC$_6$H$_4$-4-Me)$_3$),[5d] as well as the diuranium inverted-sandwich cyclo-P$_5$ complex [{U(Tren^{TIPS})}$_2$(μ-η^5:η^5-cyclo-P$_5$)] (**II**, Tren^{TIPS} = N(CH$_2$CH$_2$NSiPr$^i_3$)$_3$).[5c] Complex **I** is the only actinide-mediated P$_4$ activation product which has been functionalised further, in two steps overall, to generate compounds containing P–C and P–Si bonds.[5d] Recently, we described the synthesis of a family of uranium(IV)–silyl–phosphino–carbene complexes,[6] which are the first actinide carbene complexes to be free of carbene-stabilising phosphorus(V)-substituents.[7] We have found the silyl–phosphino–carbene ligand to be nucleophilic and readily transferred, allowing the formation of unusual bonding linkages, such as a uranium(V)–dinitrogen complex, or a uranium–rhodium double-dative bond.[8,9] Therefore, we set out to examine whether the nucleophilic-nature of the silyl–phosphino–carbene ligand would enable direct functionalisation of P$_4$.

Here, we report activation and direct functionalisation of P$_4$ by a uranium–silyl–phosphino–carbene complex. This is an unprecedented example of cooperative metal–carbene P$_4$ activation/insertion into any metal–carbon double bond and also of an actinide complex reacting with P$_4$ to directly generate an organophosphorus species.[3e] Overall, a diorgano-P$_5$ species is formed. Surprisingly however, by isolation of a reaction intermediate at low temperature, we find that this net catenation reaction actually initially proceeds by fragmentation of P$_4$, yielding functionalised P$_2$ units that subsequently aggregate at room temperature. The main uranium by-product is also found to be a precursor to the active uranium–carbene starting complex, thereby establishing the components of a proof of principle synthetic cycle.

Treatment of the uranium(IV)–silyl–phosphino–carbene complex [U{C(SiMe$_3$)(PPh$_2$)}(BIPM^{TMS})(μ-Cl)Li(TMEDA)(μ-TMEDA)$_{0.5}$]$_2$ (**1**, BIPM^{TMS} = C(PPh$_2$NSiMe$_3$)$_2$)[6] with one molar equivalent of finely-divided P$_4$ in toluene at room temperature afforded orange crystals of

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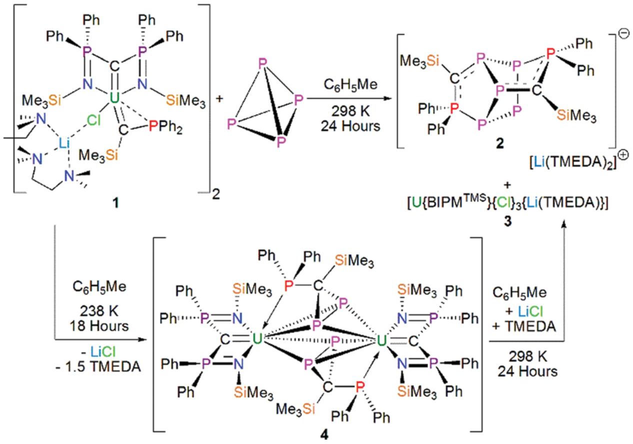

Scheme 1 Activation of P_4 by the uranium(IV)–silyl–phosphino–carbene complex **1**, yielding complexes **2**, **3**, and **4**.

the diorgano-P_5 compound $[P_5\{C(SiMe_3)(PPh_2)\}_2][Li(TMEDA)_2]$ (**2**) in 32% isolated yield after work-up (Scheme 1).[10] Decanting and slow evaporation of the mother liquor resulted in isolation of yellow crystals of the uranium-containing product of this reaction, the methanediide complex $[U\{BIPM^{TMS}\}\{Cl\}\{\mu\text{-}Cl\}_2\{Li(TMEDA)\}]$ (**3**), isolated in 26% yield.[10]

The solid-state structure of **2** (Fig. 1) reveals it consists of a central cyclo-P_5 core, which resembles the envelope conformation of cyclopentane. The P_5-ring is non-planar and does not show signs of aromaticity, in contrast to the cyclo-P_5 unit in **II**.[5c] Two adjacent phosphorus atoms of the P_5-ring are each coordinated by an individual silyl–phosphino–carbene ([SiPC]) ligand (C1-P3/C2-P4). The phosphine-substituent of each [SiPC] ligand coordinates to the P_5-phosphorus atom adjacent to that coordinated by the other [SiPC] α-carbon (P1–P5/P2–P7). The P–P distances of the P_5-ring (P3 to P7) (av. 2.212(2) Å) are consistent with P–P single bonds.[11] The only two-coordinate phosphorus centre of the P_5-ring (P6), features the two shortest P–P distances (P5–P6 : 2.174(2) Å; P6–P7 : 2.171(2) Å), with the other P–P distances ranging from 2.223(1) – 2.249(2) Å. The P1–P5 and P2–P7 interactions, between the carbene–phosphorus substituents and phosphorus atoms of the cyclo-P_5 unit, of 2.1966(14) and 2.1984(15) Å, respectively, are also consistent with P–P single bonds. The C1-P3 and C2-P4 distances are 1.786(4) and 1.776(4) Å, respectively. These values are in-between the sum of Pyykkö's covalent single- and double-bond radii for carbon and phosphorus (1.86 and 1.69 Å, respectively).[11] However, the C1-P1 and C2-P2 distances are even shorter, at 1.710(4) and 1.705(4), respectively; suggesting significant P–C multiple bonding or dipolar bond-shortening effects. The geometry of C1 and C2 are near-perfect trigonal planar, with the sum of the angles around both carbon atoms totalling 359.8(12)°.

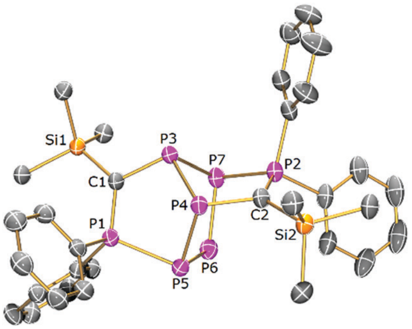

Fig. 1 Molecular structure of **2** at 100 K with displacement ellipsoids set at 30% probability. Hydrogen atoms and $[Li(TMEDA)_2]^+$ counterion are omitted for clarity.

The solid-state structure of **3** was also determined.[10] The structural parameters of this complex are typical for uranium(IV)-BIPM^{TMS} complexes,[7b] and very similar to those of the closely related complex $[U(BIPM^{TMS})(Cl)(\mu\text{-}Cl)_2Li(THF)_2]$,[12] which is the starting material used to prepare **1**.[6]

Once isolated in crystalline form, **2** is insoluble in aromatic solvents and it decomposes in ethers and other donor solvents, forming oily residues, which precluded its characterisation by multinuclear NMR and UV/Vis/NIR spectroscopies. It would appear that **2** is formed *via* the catenation/aggregation of P_4, induced by **1**, with formation of two P–C bonds and two new P–P bonds.[5]

In order to gain greater insight into the formation of **2**, we set out to isolate uranium-containing intermediates in its formation. Accordingly, reaction of **1** with a single molar equivalent of P_4 in toluene was conducted at −35 °C. The mixture was stirred for 4 hours, then left to stand at −35 °C for 4 hours (Scheme 1), resulting in the formation of red crystals of the diuranium(IV) complex $[\{U(BIPM^{TMS})([\mu\text{-}\eta^2\text{:}\eta^2\text{-}P_2]C[SiMe_3][PPh_2])\}_2]$ (**4**), isolated in 46% yield.[10]

The formulation of **4** was confirmed by its solid-state structure (Fig. 2), revealing the salient feature of two uranium ions bridged by two cyclo-1,2-diphosphapropan-1,2-diide $[(\mu\text{-}\eta^2\text{:}\eta^2\text{-}P_2)C(SiMe_3)(PPh_2)]^{2-}$ groups. The formally dianionic R_2CP_2 unit features a three-membered CP_2-ring, formed by insertion of 0.5 equivalents of P_4 into the $U{=}C_{carbene}$ double bond. Additionally, each uranium centre in **4** is coordinated by the $[BIPM^{TMS}]^{2-}$ methanediide and a κ^1-phosphino group.

The P2–P3 distance within the CP_2 ring of **4** (2.1762(11) Å) is similar to the average measured for the cyclo-P_5 unit in **2** (2.212(2) Å), and typical of a P–P single bond.[11] Additionally, the C2-P2/C2-P3 distances in **4** (1.889(3) Å and 1.892(3) Å, respectively) are typical of P–C single bonds, and somewhat longer than the C1-P3 (1.786(4) Å) and C2-P4 (1.776(4) Å) distances in **2**. In **4** the U1–C1 distance is 2.309(3) Å – somewhat shorter than the 2.405(9) Å measured for the parent uranium(IV) complex **1**.[6] This may be due to the loss of the strongly-donating silyl–phosphino–carbene ligand, allowing for an increase in the magnitude of the $U{=}C_{BIPM}$ bonding interaction. The U=C bond distance within **4** is typical of a uranium(IV) complex,[7b] with this oxidation state assignment supported by charge balancing of the coordinated ligands, and further evidenced by magnetometric measurements performed on **4** (*vide infra*). Within **4**, P1 is clearly angled towards U1, with small P1-C2-P2 and P1-C2-P3 angles (100.84(15) and 102.94(15)°, respectively), and larger Si3-C2-P2/Si3-C2-P3 angles

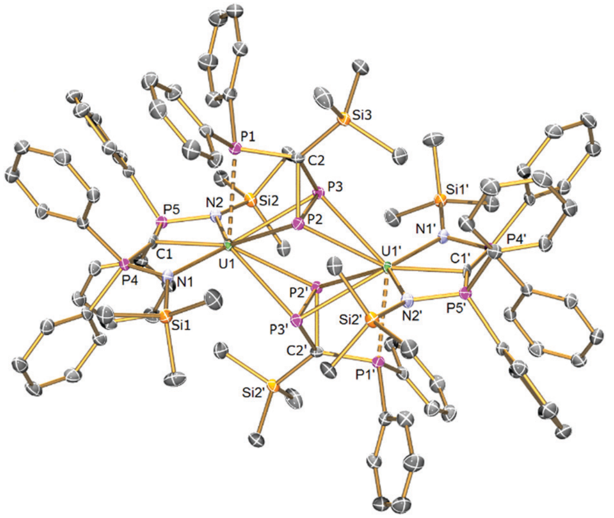

Fig. 2 Molecular structure of **4** at 100 K with displacement ellipsoids set at 50% probability. Hydrogen atoms and lattice solvent are omitted for clarity.

(117.01(16) and 117.20(16)°, respectively). The orientation of the phenyl substituents on P1 suggest that the lone pair of this phosphorus atom is directed towards U1, allowing for a dative P → U interaction. At 3.0748(7) Å, the U1–P1 distance is notably greater than the sum of the single bond covalent radii for uranium and phosphorus (2.81 Å).[11] However, values between 2.9 and 3.1 Å are typical of dative P(III) → U(IV) interactions.[13] The U1-P2/P2' and U1-P3/P3' distances within **4** (2.9753(7)/2.9565(7) and 3.0459(7)/2.9974(8) Å, respectively) are somewhat longer than expected for U–P single bonds.[11] This is likely due to the bridging nature of the $[(\mu\text{-}\eta^2{:}\eta^2\text{-}P_2)C(SiMe_3)(PPh_2)]^{2-}$ moieties between both uranium centres.

Variable temperature SQUID magnetometric measurements on a powdered sample of **4** in a 0.5 T magnetic field confirm the diuranium(IV) formulation (Fig. S7, ESI†).[10,14] At 300 K the effective magnetic moment is 3.81 μ_B per molecule (2.70 μ_B per uranium ion). The effective magnetic moment decreases slowly with decreasing temperature from 300 to 50 K, at which point a much more rapid decrease in μ_{eff} occurs to 1.06 μ_B per molecule (0.75 μ_B per uranium ion) at 2 K. The gradual decrease in effective magnetic moment between 300 and 50 K followed by a sharper decrease is indicative of the binding of strongly donating ligand(s) to uranium(IV), and this behaviour has been observed for **1** and a growing range of uranium(IV) complexes with strong donor ligands.[6,7a,9,14,15]

As for **2**, **4** decomposes in ethers and is insoluble in aromatic solvents once isolated in crystalline form, which precluded its solution-phase characterisation. To examine whether **4** is an intermediate in the formation of **2**, isolated crystalline **4** was combined with an excess of LiCl and TMEDA in toluene and allowed to stand for 24 hours (Scheme 1). After workup, both **2** and **3** were isolated in higher yields (66 and 54%, respectively) than from reaction of **1** with P_4 at room temperature. This suggests that the formation of **2** does not involve the reaction of **4** with unreacted P_4, and is perhaps instead an intermolecular process between molecules of **4** and LiCl/TMEDA. Attempts to synthesise alternative organophosphorus products from the reaction of **4** with various molar quantities of P_4 led to the isolation of **2** and **3**, albeit in reduced yields.

To examine whether a closed synthetic cycle for the formation of **2** could be devised, the use of **3** as an alternative precursor to **1** was examined. Straightforward addition of $[\{Li(TMEDA)\}C(H)(Ph)(SiMe_3)]$, followed by $[\{Li(THF)\}C(H)(PPh_2)(SiMe_3)]$, to **3** at −78 °C generates **1** in comparable isolated yield (39%) to the published procedure (36%).[6] Thus, the synthesis of **2** can be carried out within a synthetic cycle, with reuse of the uranium-containing products of the reaction.

To conclude, reaction of **1** with P_4 at room temperature produces the organo-P_5 compound **2**, as well as the uranium methanediide complex **3**. If the reaction of **1** with P_4 is carried out at low temperature an intermediate complex **4**, which results from P_4 fragmentation/insertion across the U═C bond, can be isolated and then converted to **2** and **3**, which is likely driven by the formation of strong P–C and U–Cl bonds. Furthermore, a proof of principle synthetic cycle has been established. This work reports the first example of cooperative metal–carbene P_4 activation/insertion into any metal–carbon double bond and also of an actinide complex generating an organophosphorus compound directly from P_4. Whereas actinide reactivity with P_4 usually results only in reductive ring-opening of P_4 and/or catenation, this work reveals a catenation that surprisingly proceeds *via* fragmentation of P_4 to functionalised P_2 units that subsequently aggregate. More broadly, these results suggest that the reactivity of metal–carbene complexes, particularly those of the early metals with polarised M═C bonds, with P_4 should be investigated. Such studies could provide a new, divergent, approach from the traditional two-step method of reduction followed by functionalisation, to develop the synthetic strategy of direct preparation of organophosphorus compounds from P_4 that would be a basis for further derivatisation.

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Conflicts of interest

There are no conflicts to declare.

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