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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 $[U\{C(SiMe_3)(PPh_2)\}(BIPM^{TMS})(\mu-Cl)Li(TMEDA)(\mu-TMEDA)_{0.5}\}_2$ (**1**, $BIPM^{TMS} = C(PPh_2NSiMe_3)_2$) 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 $[U\{BIPM^{TMS}\}(Cl)(\mu-Cl)_2(Li(TMEDA))]$ (**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 $\{[U(BIPM^{TMS})(\mu-\eta^2:\eta^2-P_2)C(SiMe_3)(PPh_2)]\}_2$ (**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 metals² 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

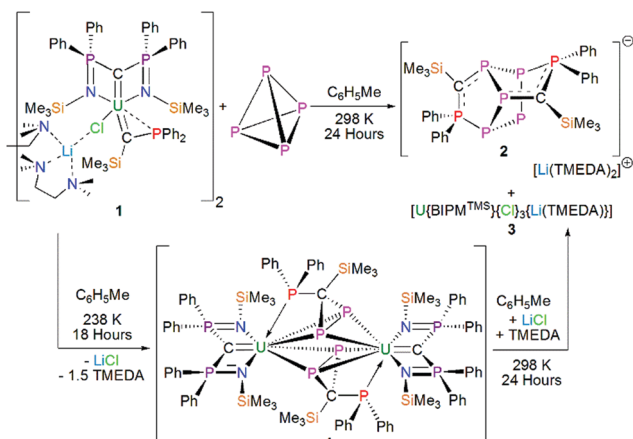
not fragmented into smaller phosphorus-containing units which are suited for functionalisation. In previous work, we reported uranium-mediated aggregation of P_4 , generating the triuranium- $[P_7]$ Zintl complex $\{[U(Ts^{Tot})(\mu_3-\eta^2:\eta^2:\eta^2-P_7)]\}_3$ (**I**, $Ts^{Tot} = HC(SiMe_2NC_6H_4-4-Me)_3$),^{5d} as well as the diuranium inverted-sandwich cyclo- P_5 complex $\{[U(Tren^{TIPS})]_2(\mu-\eta^5:\eta^5-cyclo-P_5)\}_2$ (**II**, $Tren^{TIPS} = N(CH_2CH_2NSiPr^1_3)_3$).^{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 $[U\{C(SiMe_3)(PPh_2)\}(BIPM^{TMS})(\mu-Cl)Li(TMEDA)(\mu-TMEDA)_{0.5}\}_2$ (**1**, $BIPM^{TMS} = C(PPh_2NSiMe_3)_2$)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 P₄ by the uranium(IV)-silyl-phosphino-carbene complex **1**, yielding complexes **2**, **3**, and **4**.

the diorgano-P₅ compound [P₅C(SiMe₃)(PPh₂)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){μ-Cl}₂Li(TMEDA)] (**3**), isolated in 26% yield.¹⁰

The solid-state structure of **2** (Fig. 1) reveals it consists of a central cyclo-P₅ core, which resembles the envelope conformation of cyclopentane. The P₅-ring is non-planar and does not show signs of aromaticity, in contrast to the cyclo-P₅ unit in **II**.^{5c} Two adjacent phosphorus atoms of the P₅-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 P₅-phosphorus atom adjacent to that coordinated by the other [SiPC] α -carbon (P1-P5/P2-P7). The P-P distances of the P₅-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 P₅-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-P₅ unit, of 2.1966(14) and 2.1984(15) Å, respectively, are also consistent

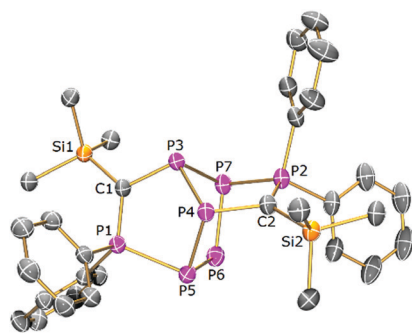


Fig. 1 Molecular structure of **2** at 100 K with displacement ellipsoids set at 30% probability. Hydrogen atoms and [Li(TMEDA)₂]⁺ counterion are omitted for clarity.

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)°.

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)(μ-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 P₄, 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 P₄ 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})([μ-η²:η²-P₂]C[SiMe₃][PPh₂])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-diphosphopropan-1,2-diide [(μ-η²:η²-P₂)C(SiMe₃)(PPh₂)]²⁻ groups. The formally dianionic R₂CP₂ unit features a three-membered CP₂-ring, formed by insertion of 0.5 equivalents of P₄ into the U=C_{carbene} double bond. Additionally, each uranium centre in **4** is coordinated by the [BIPM^{TMS}]²⁻ methanediide and a κ¹-phosphino group.

The P2-P3 distance within the CP₂ ring of **4** (2.1762(11) Å) is similar to the average measured for the cyclo-P₅ 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

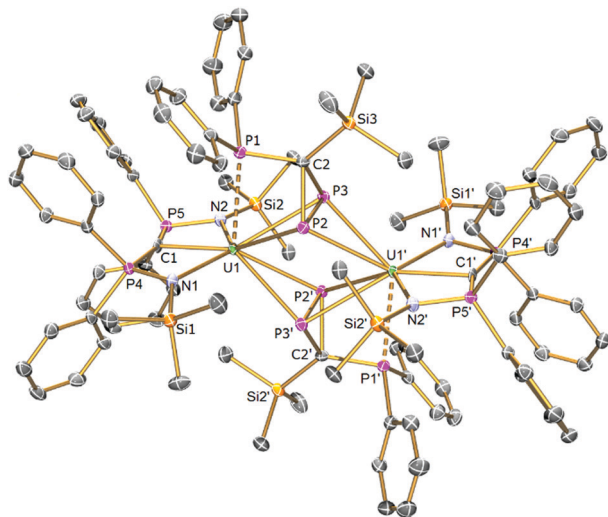


Fig. 2 Molecular structure of **4** at 100 K with displacement ellipsoids set at 50% probability. Hydrogen atoms and lattice solvent are omitted for clarity.

(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 $[(\mu-\eta^2:\eta^2-P_2)C(\text{SiMe}_3)(\text{PPh}_2)]^{2-}$ 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 P₄ at room temperature. This suggests that the formation of **2** does not involve the reaction of **4** with unreacted P₄, 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 P₄ 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 $[\{\text{Li}(\text{TMEDA})\}C(\text{H})(\text{Ph})(\text{SiMe}_3)]$, followed by $[\{\text{Li}(\text{THF})\}C(\text{H})(\text{PPh}_2)(\text{SiMe}_3)]$, 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 P₄ at room temperature produces the organo-P₅ compound **2**, as well as the uranium methanediide complex **3**. If the reaction of **1** with P₄ is carried out at low temperature an intermediate complex **4**, which results from P₄ 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 P₄ activation/insertion into any metal–carbon double bond and also of an actinide complex generating an organophosphorus compound directly from P₄. Whereas actinide reactivity with P₄ usually results only in reductive ring-opening of P₄ and/or catenation, this work reveals a catenation that surprisingly proceeds *via* fragmentation of P₄ to functionalised P₂ 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 P₄ 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 P₄ 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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