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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.<sup>1</sup> 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<sup>2</sup> and main group elements,<sup>3</sup> and even by free singlet carbenes,<sup>4</sup> 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.<sup>2c</sup>

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.<sup>5</sup> Also, although P–P bonds are broken in almost all cases,  $P_4$  is

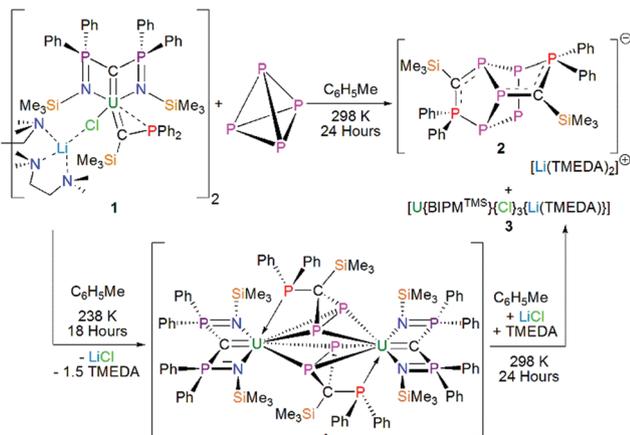
not fragmented into smaller phosphorus-containing units which are suited for functionalisation. In previous work, we reported uranium-mediated aggregation of  $P_4$ , generating the triuranium- $[P_7]$  Zintl complex  $\{[U(Ts^{Tot})\{(\mu_3-\eta^2:\eta^2:\eta^2-P_7)\}]_3\}$  (**I**,  $Ts^{Tot} = HC(SiMe_2NC_6H_4-4-Me)_3$ ),<sup>5d</sup> as well as the diuranium inverted-sandwich cyclo- $P_5$  complex  $\{[U(Tren^{TIPS})\{(\mu-\eta^5:\eta^5-cyclo-P_5)\}]_2\}$  (**II**,  $Tren^{TIPS} = N(CH_2CH_2NSiPr^1_3)_3$ ).<sup>5c</sup> 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.<sup>5d</sup> Recently, we described the synthesis of a family of uranium(IV)–silyl–phosphino–carbene complexes,<sup>6</sup> which are the first actinide carbene complexes to be free of carbene-stabilising phosphorus(v)-substituents.<sup>7</sup> 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.<sup>8,9</sup> 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.<sup>3e</sup> 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**,  $BIPM^{TMS} = C(PPh_2NSiMe_3)_2$ )<sup>6</sup> with one molar equivalent of finely-divided  $P_4$  in toluene at room temperature afforded orange crystals of

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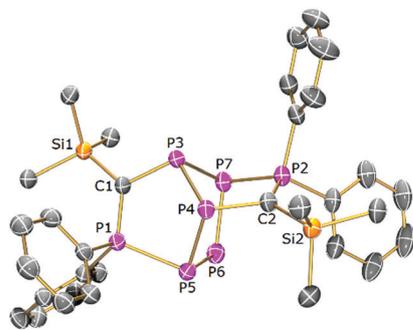
† Electronic supplementary information (ESI) available: Synthetic, structural, and spectroscopic details. CCDC 2060876–2060878. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1cc01741a



**Scheme 1** Activation of P<sub>4</sub> by the uranium(IV)-silyl-phosphino-carbene complex **1**, yielding complexes **2**, **3**, and **4**.

the diorgano-P<sub>5</sub> compound [P<sub>5</sub>C(SiMe<sub>3</sub>)(PPh<sub>2</sub>)<sub>2</sub>][Li(TMEDA)<sub>2</sub>] (**2**) in 32% isolated yield after work-up (Scheme 1).<sup>10</sup> 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<sup>TMS</sup>}(Cl)(μ-Cl)<sub>2</sub>Li(TMEDA)] (**3**), isolated in 26% yield.<sup>10</sup>

The solid-state structure of **2** (Fig. 1) reveals it consists of a central cyclo-P<sub>5</sub> core, which resembles the envelope conformation of cyclopentane. The P<sub>5</sub>-ring is non-planar and does not show signs of aromaticity, in contrast to the cyclo-P<sub>5</sub> unit in **II**.<sup>5c</sup> Two adjacent phosphorus atoms of the P<sub>5</sub>-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<sub>5</sub>-phosphorus atom adjacent to that coordinated by the other [SiPC]  $\alpha$ -carbon (P1-P5/P2-P7). The P-P distances of the P<sub>5</sub>-ring (P3 to P7) (av. 2.212(2) Å) are consistent with P-P single bonds.<sup>11</sup> The only two-coordinate phosphorus centre of the P<sub>5</sub>-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<sub>5</sub> 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)<sub>2</sub>]<sup>+</sup> 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).<sup>11</sup> 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.<sup>10</sup> The structural parameters of this complex are typical for uranium(IV)-BIPM<sup>TMS</sup> complexes,<sup>7b</sup> and very similar to those of the closely related complex [U(BIPM<sup>TMS</sup>)(Cl)(μ-Cl)<sub>2</sub>Li(THF)<sub>2</sub>],<sup>12</sup> which is the starting material used to prepare **1**.<sup>6</sup>

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<sub>4</sub>, induced by **1**, with formation of two P-C bonds and two new P-P bonds.<sup>5</sup>

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<sub>4</sub> 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<sup>TMS</sup>)(μ-η<sup>2</sup>:η<sup>2</sup>-P<sub>2</sub>)C(SiMe<sub>3</sub>)(PPh<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (**4**), isolated in 46% yield.<sup>10</sup>

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-η<sup>2</sup>:η<sup>2</sup>-P<sub>2</sub>)C(SiMe<sub>3</sub>)(PPh<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> groups. The formally dianionic R<sub>2</sub>CP<sub>2</sub> unit features a three-membered CP<sub>2</sub>-ring, formed by insertion of 0.5 equivalents of P<sub>4</sub> into the U=C<sub>carbene</sub> double bond. Additionally, each uranium centre in **4** is coordinated by the [BIPM<sup>TMS</sup>]<sup>2-</sup> methanediide and a κ<sup>1</sup>-phosphino group.

The P2-P3 distance within the CP<sub>2</sub> ring of **4** (2.1762(11) Å) is similar to the average measured for the cyclo-P<sub>5</sub> unit in **2** (2.212(2) Å), and typical of a P-P single bond.<sup>11</sup> 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**.<sup>6</sup> 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<sub>BIPM</sub> bonding interaction. The U=C bond distance within **4** is typical of a uranium(IV) complex,<sup>7b</sup> 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

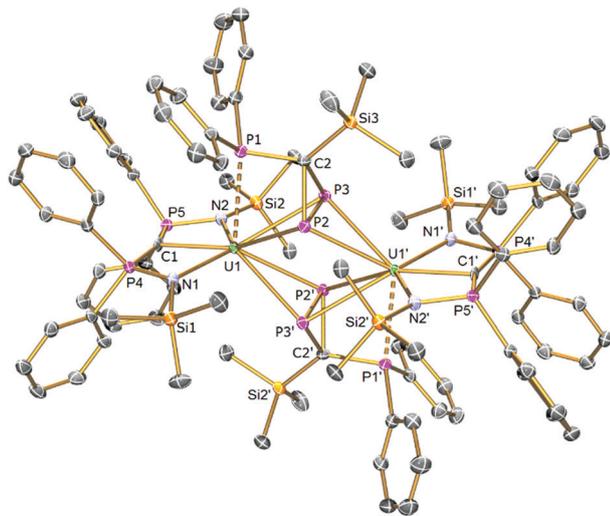


Fig. 2 Molecular structure of **4** at 100 K with displacement ellipsoids set at 50% probability. Hydrogen atoms and lattice solvent are omitted for clarity.

(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).<sup>11</sup> However, values between 2.9 and 3.1 Å are typical of dative P(III) → U(IV) interactions.<sup>13</sup> 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.<sup>11</sup> This is likely due to the bridging nature of the  $[(\mu-\eta^2:\eta^2-P_2)C(SiMe_3)(PPh_2)]^{2-}$  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†).<sup>10,14</sup> At 300 K the effective magnetic moment is 3.81  $\mu_B$  per molecule (2.70  $\mu_B$  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  $\mu_{eff}$  occurs to 1.06  $\mu_B$  per molecule (0.75  $\mu_B$  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.<sup>6,7a,9,14,15</sup>

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<sub>4</sub> at room temperature. This suggests that the formation of **2** does not involve the reaction of **4** with unreacted P<sub>4</sub>, 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<sub>4</sub> 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%).<sup>6</sup> 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<sub>4</sub> at room temperature produces the organo-P<sub>5</sub> compound **2**, as well as the uranium methanediide complex **3**. If the reaction of **1** with P<sub>4</sub> is carried out at low temperature an intermediate complex **4**, which results from P<sub>4</sub> 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<sub>4</sub> activation/insertion into any metal–carbon double bond and also of an actinide complex generating an organophosphorus compound directly from P<sub>4</sub>. Whereas actinide reactivity with P<sub>4</sub> usually results only in reductive ring-opening of P<sub>4</sub> and/or catenation, this work reveals a catenation that surprisingly proceeds *via* fragmentation of P<sub>4</sub> to functionalised P<sub>2</sub> 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<sub>4</sub> 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<sub>4</sub> 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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