Fragmentation, Catenation, and Direct Functionalisation of White Phosphorus by a Uranium(IV)-Silyl-Phosphino-Carbene Complex†

Josef T. Boronski, John A. Seed, Ashley J. Wooles, and Stephen T. Liddle*

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

Organophosphorus compounds have numerous vital uses.1 Industrially, organophosphorus compounds are derived from \(\text{PCl}_3\), which is in turn formed by chlorination of white phosphorus \((\text{P}_4)\). Thus, there is significant interest in discovering new, direct paths to the derivatisation of \(\text{P}_4\). Indeed, the activation and functionalisation of \(\text{P}_4\) 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/functionality of \(\text{P}_4\) in processes which directly yield organophosphorus compounds is challenging and only beginning to be realised.26

In contrast to burgeoning studies of \(\text{P}_4\) activation by transition metal and main group compounds, reports of \(\text{P}_4\) activation by actinide elements are scarce, being limited to six examples.5 Also, although P-P bonds are broken in almost all cases, \(\text{P}_4\) is not fragmented into smaller phosphorus-containing units which are suited for functionalisation. In previous work, we reported uranium-mediated aggregation of \(\text{P}_4\), generating the triuranium-\([\text{P}_3]\) Zintl complex \([\text{U}]{\text{Ts}^\text{TMS}}\{\mu-\text{η}^2:\text{η}^2:\text{η}^2-\text{P}_3\})\) (I, \(\text{Ts}^\text{TMS} = \text{HCl}(\text{SiMe}_2\text{NC}_{6}\text{H}_4\text{-4-Me})\)) as well as the diuranium inverted-sandwich cyclo-P_3 complex \([\text{U}]{\text{Tren}^\text{TMS}}\{\mu-\text{η}^3:\text{η}^3-\text{cyco-P}_3\})\) (II, \(\text{Tren}^\text{TMS} = \text{N}(\text{CH}_3\text{CH}_3\text{NSiPr}_3)\)).5c Complex I is the only actinide-mediated \(\text{P}_4\) activation product which has been functionalised further, in two steps, 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 \(\text{P}_4\).

Scheme 1. Activation of \(\text{P}_4\) by the uranium(IV)-silyl-phosphino-carbene complex 1, yielding complexes 2, 3, and 4.

Here, we report activation and direct functionalisation of \(\text{P}_4\) by a uranium-silyl-phosphino-carbene complex. This is an unprecedented example of cooperative metal-carbene \(\text{P}_4\) activation/insertion into any metal-carbon double bond and also of an actinide complex reacting with \(\text{P}_4\) to directly generate an organophosphorus species.5e Overall, a diorgano-\(\text{P}_4\) 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 \(\text{P}_4\), yielding functionalised \(\text{P}_2\) 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_3)][BIPM(TMS)](μ-Cl)(Li(TMEDA))_3]_2 (1, BIPM(TMS) = C(PPh_3NSiMe_3)) with one molar equivalent of finely-divided P_4 in toluene at room temperature afforded orange crystals of the diorganophosphorus compound [P_4(C(SiMe_3)(PPh_3))][Li(TMEDA)] (2) in 32% isolated yield after work-up (Scheme 1). Decanting and slow evaporation of the mother liquid resulted in isolation of yellow crystals of the uranium-containing product of this reaction, the methanediide complex [U[BIPM(TMS)](μ-Cl)]_2(Li(TMEDA))] (3), isolated in 26% yield.  

The solid-state structure of 2 (Figure 1) reveals it consists of a central cyclo-P_3 core, which resembles the envelope conformation of cyclcopentane. The P_3-ring is non-planar and does not show signs of aromaticity, in contrast to the cyclo-P_5 unit in II. Two adjacent phosphorus atoms of the P_3-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_3-phosphorus atom adjacent to that coordinated by the other [SiPC] α-carbon (P1-P5/P2-P7). The P-P distances of the P_3-ring (P3 to P7) (av. 2.212(2) Å) are consistent with P-P single bonds. The only two-coordinate phosphorus center of the P_3 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_3 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 Pykkö’s covalent single- and double-bond radii for carbon and phosphorus (1.86 and 1.69 Å, respectively). However, the C1-P1 and C2-P2 distances are even shorter, at 1.710(4) and 1.705(4) Å, 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 structural parameters of this complex are typical for uranium(IV)-BIPM(TMS) complexes, and very similar to those of the closely related complex [U[BIPM(TMS)](μ-Cl)Li(THF)]_2, which is the starting material used to prepare 1. 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. 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)](μ-η^2:η^2-P_2)(C(SiMe_3)(PPh_2))]] (4), isolated in 46% yield.

The formulation of 4 was confirmed by its solid-state structure (Figure 2), revealing the salient feature of two uranium ions bridged by two cyclo-1,2-diphosphapropan-1,2-diene ([μ-η^2:η^2-P_2]C(SiMe_3)(PPh_2))]^2 groups. The formally dianionic R_6CP_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^2-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_3 unit in 2 (2.212(2) Å), and typical of a P-P single bond. Additionally, the C2-P2/C3-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. 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=CP bonding interaction.

![Figure 1](image1.png)

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

![Figure 2](image2.png)

Figure 2. Molecular structure of 4 at 100 K with displacement ellipsoids set at 50% probability. Hydrogen atoms and lattice solvent are omitted for clarity.
U=Si bond distance within 4 is typical of a uranium(IV) complex, 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 aligned 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 (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). However, values between 2.9 and 3.1 Å are typical of dative P(III)→U(IV) interactions. The U1-P2/P2’ and U1-P3/P3’ distances within 4 are 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. This is likely due to the bridging nature of the \([\mu-\eta^2:1\eta^2]C(SiMe_3)C(PPh_3)^2\) 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 (Figure S7). 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.

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 \([\{U(TMEDA)\}C(H)C(H)(SiMe_3)\] to 3 at ~78 °C generates 1 in comparable isolated yield (39%) to the published procedure (36%). 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-\(P_4\) 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=Si 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 \(P_4\) 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.

**Notes and references**


See the ESIF for full details.


Unprecedented insertion of \( P_4 \) into a \( M=C \) double bond is reported, revealing overall catenation via \( P_4 \)-fragmentation into \( R_2 CP_2 \) units.