Nature of the ArsoniumYlide Ph3As=CH2 and a Uranium(IV) ArsoniumCarbene Complex

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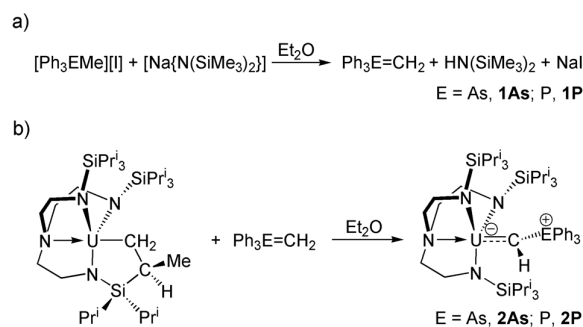# Nature of the Arsonium-Ylide Ph₃As=CH₂ and a Uranium(IV) Arsonium-Carbene Complex

John A. Seed, Helen R. Sharpe, Harry J. Futcher, Ashley J. Wooles, and Stephen T. Liddle*

Abstract: *Treatment of [Ph₃EMe][I] with [Na{N(SiMe₃)₂}] affords the ylides [Ph₃E=CH₂] (E = As, **1As**; P, **1P**). For **1As** this overcomes prior difficulties in the synthesis of this classical arsonium-ylide that have historically impeded its wider study. The structure of **1As** has now been determined, 45 years after it was first convincingly isolated, and compared to **1P**, confirming the long-proposed hypothesis of increasing pyramidalisation of the ylide-carbon, highlighting the increasing dominance of E⁺-C⁻ dipolar resonance form (sp³-C) over the E=C ene π-bonded form (sp²-C), as group 15 is descended. The uranium(IV)-cyclometallate complex [U{N(CH₂CH₂NSiPrⁱ₃)₂(CH₂CH₂SiPrⁱ₂CH(Me)CH₂)}] reacts with **1As** and **1P** by α-proton abstraction to give [U(Trenᵀᴵᴾˢ)(CHEPh₃)] (Trenᵀᴵᴾˢ = N(CH₂CH₂NSiPrⁱ₃)₃; E = As, **2As**; P, **2P**), where **2As** is an unprecedented structurally characterised arsonium-carbene complex. The short U-C distances and obtuse U-C-E angles suggest significant U=C double bond character. A shorter U-C distance is found for **2As** than **2P**, consistent with increased uranium- and reduced pnictonium-stabilisation of the carbene as group 15 is descended, which is supported by quantum chemical calculations.*

The suboptimal energetic matching of valence 5f-/6d-orbitals of mid- and high-oxidation state early actinides with 2s-/2p-frontier orbitals of carbon, as well as the contracted nature of 5f-orbitals compared to the d-orbitals of transition metals, renders actinide-carbon double bonds, that by definition require mid- and high-oxidation state metals, intrinsically polarised and thus unstable.[1] However, the stability of any M=CR₂ linkage is principally governed by the relative extent of stabilisation provided by the metal and carbon-substituents.[2] Thus, where metal-stabilisation is not optimal, sufficient stabilisation to afford isolable complexes can be provided by the carbon-substituents. Where uranium-carbene complexes with polarised-covalent, formal double bonds are concerned, this substituent stabilisation strategy has utilised phosphorus(V)- and (III)-substituents, as phosphonium and phosphine groups, respectively.[1] The latter exhibit less phosphorus stabilisation of the carbene centres than the former, resulting in more developed U=C double bonds in the latter. Whilst this approach has enabled a broad range of U=C double bonds covering uranium oxidation states of III-VI,[1,3] it is notable that, outside of microscopic cryogenic matrix isolation experiments,[4] without exception all U=C double bonds prepared and isolated on macroscopic scales from the inception of the area in the 1980s onwards are stabilised by phosphorus. Given the potential for tunability, the exclusive use of phosphorus in this arena to date is surprising, but perhaps reflects the inherent synthetic challenges in accessing suitable precursors with substituents other than phosphorus.

In order to target a formal U=C double bond with a non-phosphorus substituent, arsenic represents an attractive approach, since, as an element, it is often very different to phosphorus, e.g. smaller HOMO-LUMO gaps, light sensitivity, and a reduced ability to stabilise carbene-type groups resulting in more reactive ylide-methylene groups,[5] and thus it would present an opportunity to test the inter-play of carbene stabilisation by its substituents. When considering the construction of U=C double bonds, all involve actual or *de facto* α-proton abstraction at some stage of the synthesis with ylides or ylide-equivalents.[1a] We therefore postulated that reaction of an arsonium-ylide with a M-C bond, and preferably a strained U-C bond in a metallocycle since this has been a successful strategy for constructing actinide-element multiple bonds,[6] would generate an arsenic-stabilised U=C double bond by protonation of the cyclometallate. However, despite being established over a century ago,[7] arsonium-ylide chemistry[8] is far less developed than phosphorus,[5b,9] and indeed sulfur, -ylide areas, so some basic arsonium-ylide development work would be required, but this would bring the benefit of developing fundamental comparisons of arsonium- and phosphonium-ylides.

Here, we report an improved synthesis of the arsonium-ylide Ph₃As=CH₂ (**1As**),[5b,10] the arsenic analogue of Wittig's classical phosphonium-ylide Ph₃P=CH₂ (**1P**),[11] which resolves prior difficulties isolating **1As** cleanly, thus paving the way to its wider use and study. We report the first structural authentication of **1As**, 45 years after it was first convincingly isolated; when compared to a new polymorph of **1P** reported here, this permits structural verification of the longstanding hypothesis of increasing ylide-carbon pyramidalisation on moving from phosphorus to arsenic. Demonstrating the utility of **1As**, we report the synthesis and characterisation of the uranium(IV) arsonium carbene complex [U(Trenᵀᴵᴾˢ)(CHAsPh₃)] (Trenᵀᴵᴾˢ = N(CH₂CH₂NSiPrⁱ₃)₃, **2As**), which is an unprecedented structurally characterised arsonium-stabilised carbene complex,[12] and formally the first U=C double bond without phosphorus-stabilisation outside of matrix isolation. With the phosphonium analogue of **2As**, **2P**, prepared for comparative purposes, structural and quantum chemical studies support the notion of diminished stabilisation of the carbene by arsenic compared to phosphorus, as in the parent ylides, and thus a better-developed U-C interaction results in **2As** compared to **2P**.

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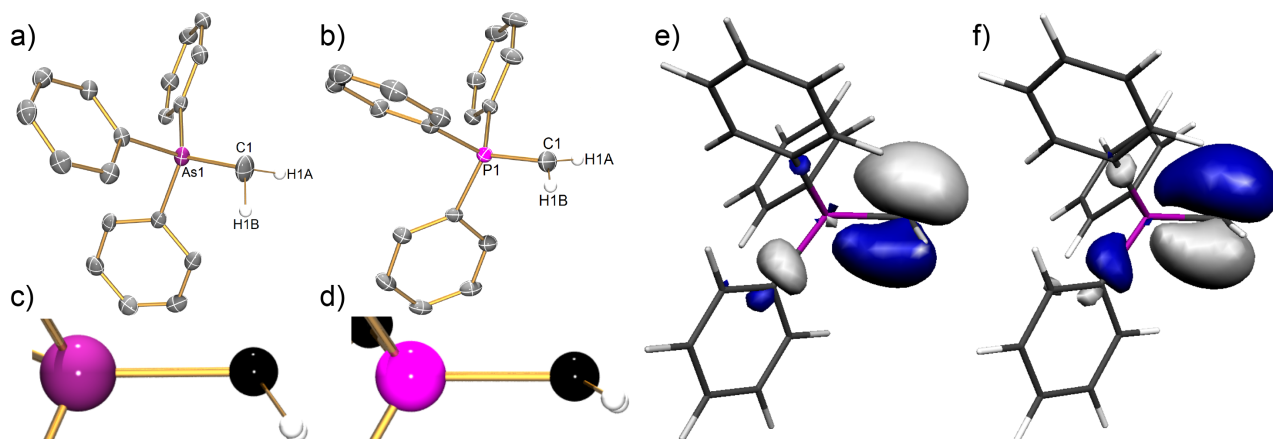   the document.

Scheme 1. a) synthesis of arsonium- and phosphonium-ylides **1As** and **1P**. b) synthesis of uranium arsonium- and phosphonium-carbene complexes **2As** and **2P**.

Figure 1. a) and b) solid state structures of **1As** and **1P**, respectively, at 150 K. Displacement ellipsoids are set at 40% and non-ylide hydrogen atoms are omitted for clarity. There are two molecules of **1As** in the crystallographic asymmetric unit, but both are very similar to one another so only one is depicted. c) and d) zoom-ins of the As=CH$_2$ and P=CH$_2$ units in the solid state structures of **1As** and **1P**, respectively, emphasising the pyramidal vs more planar geometries. e) and f) the HOMOs of **1As** (82, −4.159 eV) and **1P** (73, −4.120 eV).

We first focused on the synthesis of **1As**, since even though it was first unambiguously isolated in 1975 its synthesis is capricious and it is temperature- and light-sensitive.[5b] However, we find that treating [Ph$_3$AsMe][I] with basic but poorly nucleophilic [Na{N(SiMe$_3$)$_2$}] instead of NaNH$_2$, which is basic, nucleophilic, and protic, with strict exclusion of light, reliably produces yellow **1As** cleanly in 60% crystalline yield (Scheme 1a).[13] For comparison, we prepared orange **1P** and determined the solid state structures of **1As** and **1P** (the latter as a new polymorph[14]) as structurally authenticated arsonium-ylides are rare and none are with the parent methylene (Figures 1a and 1b).[15]

The solid-state structure of **1As** exhibits an As-C$_{ylide}$ distance of 1.826(6) Å, which is longer than the equivalent P-C$_{ylide}$ distance in **1P** (1.676(2) Å). This difference is ~0.05 Å more than the difference in single bond covalent radii of As and P (0.1 Å),[16] suggesting reduced π-stabilisation of the ylidic carbon in **1As** compared to **1P**. Consistent with this, the C$_{ylide}$ Σ∠ of 322.3(2) and 351.1(2)° for **1As** and **1P** (Figures 1c and 1d), respectively, shows that whilst the latter is virtually planar, the former is pyramidalised. This confirms predictions made on the basis of spectroscopic data in the 1970s that as group 15 is descended the ylide-carbon, in the absence of over-riding steric factors, inherently becomes more pyramidalised, reflecting the increasing dominance of the E$^+$-C$^-$ dipolar resonance form (sp^3-C) over the E=C ene π-bonded form (sp^2-C).[5] This also most likely accounts for the much lower thermal stability of **1As** compared to **1P**.[5b]

DFT calculations were performed on **1As** and **1P** (Table 1).[13] The HOMO of **1As** is more polarised than the HOMO of **1P** (Figures 1e and 1f), the E=C Nalewajski-Mrozek bond order for **1As** is lower than **1P**, and the analytical frequencies As-C$_{ylide}$ stretch (592 cm^{-1}) is lower than the P-C$_{ylide}$ value (920 cm^{-1}). QTAIM data concur, since larger ρ, more negative H (energy), and a larger ε for **1P** compared to **1As** is consistent with a better-developed covalent π-bond vs a more dipolar bond, respectively.[17] The computed MDC$_q$ charges do not seem to align with this bonding trend, but the differences are small and may reflect differences in E=C-Ph negative hyperconjugation.

Though **1As** can now be routinely isolated in crystalline form, its thermal- and light-sensitivity means that *in situ* generation for direct use is more convenient with the clean preparative method above. With strict exclusion of light, addition of *in situ* prepared **1As** to a cold (−78 °C) diethyl ether solution of [U{N(CH$_2$CH$_2$NSiPr^i$_3$)$_2$(CH$_2$CH$_2$SiPr^i$_2$CH(Me)CH$_2$)}] results in isolation of dark red [U(Tren^{TIPS})(CHAsPh$_3$)] (Tren^{TIPS} = N(CH$_2$CH$_2$NSiPr^i$_3$)$_3$, **2As**) following work-up in 65% crystalline yield

(Scheme 1b).[13] For comparison, the red phosphonium analogue, **2P**, was prepared in an analogous reaction by using **1P** instead of **1As**.[13]
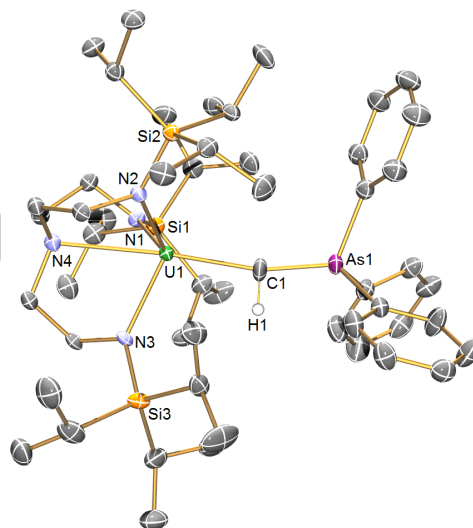

Figure 2. Molecular structure of **2As** at 150 K. Displacement ellipsoids are set at 40% with non-carbene hydrogen atoms omitted for clarity.

The solid-state structures of **2As** and **2P** were determined (Figure 2 and Supporting Information),[13] confirming their formulations. The U-C distance in **2As** of 2.272(6) Å, is between the sum of covalent uranium–carbon single (2.45 Å) and double (2.01 Å) bond radii,[16] and, noting the varying steric demands of the co-ligands, can be considered short when compared to [U(η^5-C$_5$H$_5$)$_3$(CHPMe$_2$Ph) (2.293(2) Å), [U{N(SiMe$_3$)$_2$}$_3$(CHPPh$_3$)] (2.278(8) Å), and [U(η^5-C$_5$Me$_5$)$_2$(X)(CHPPh$_3$)] (X = Cl, Br, I; U=C = 2.2428(2)-2.252(4) Å).[3c,e,18] The U-C distance in **2P** is longer (2.313(3) Å) than in **2As**, suggesting that the carbene in **2P** is a weaker donor than in **2As**. The U-N$_{amine}$ distances in **2As** and **2P**, that are *trans* to the U-C bonds, exhibit an opposite trend, being 2.709(5) and 2.683(3) Å, respectively, suggesting a stronger *trans*-influence for the carbene in **2As** compared to **2P**. The E-C$_{carbene}$ distances in **2As** and **2P** are 1.817(6) and 1.681(3) Å, respectively; like the ylides **1As** and **1P** the difference of ~0.14 Å is ~0.04 Å larger than anticipated,[16] suggesting that the carbene is less stabilised by arsenic than phosphorus. Overall, the structural data suggest stronger U-C and weaker E-C$_{carbene}$ stabilisation in **2As** than in **2P**. The U-C-E angle in **2As** is 166.1(4)° (162.1(2)° for **2P**), and more obtuse than for [U(η^5-C$_5$H$_5$)$_3$(CHPMe$_2$Ph] (142.2(1)°) and

[U{N(SiMe₃)₂}₃(CHPPh₃)] (151.7(4)°), but similar to [U(η⁵-C₅Me₅)₂(X)(CHPPh₃)] (166.09(2)-166.49(2) °).[3c,e,18]

The ¹H NMR spectra of **2As** and **2P** span the ranges +155 to −10 and +40 to −10 ppm, respectively. The corresponding ²⁹Si{¹H} NMR spectra exhibit resonances at −21.9 and −92.3 ppm, and are in the range of reported ²⁹Si chemical shifts for uranium(IV).[19] These disparate data likely reflect significant perturbations to paramagnetic shift and/or spin orbit coupling parameters as a result of changing the group 15 element. The ³¹P NMR spectrum of **2P** exhibits a resonance at 489.8 ppm, which is shifted significantly from that of **1P** (20.7 ppm in C₆D₆). Notably, in contrast to [U{N(SiMe₅)₂}₃(CHPPh₃)],[18a] spectra of **2As** and **2P** show no evidence of being in equilibrium with the cyclometallate and **1As**/**1P** starting materials.

The UV/Vis/NIR spectra of **2As** and **2P** are similar to each other and are dominated by charge-transfer bands across the UV and visible regions whilst multiple weak Laporte-forbidden f-f transitions (ε = ~5-90 M⁻¹ cm⁻¹) are observed in the NIR region that are characteristic of intra-configurational transitions of ³H₄ uranium(IV).[1b]
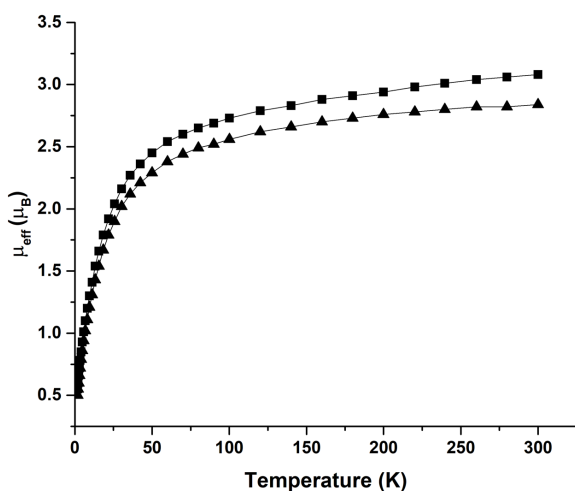

Figure 3. Variable temperature SQUID magnetic moment data (μB) for **2As** (squares) and **2P** (triangles) over the temperature range 1.8-300 K in an applied field of 0.5 Tesla. The line is a guide to the eye only.

Powdered samples of **2As** and **2P** were measured by variable-temperature SQUID magnetometry (Figure 3). The magnetic moments of **2As**/**2P** are 3.08/2.84 μB and they decrease smoothly reaching 0.55/0.50 μB at 1.8 K and tending to zero. This is characteristic behavior for ³H₄ uranium(IV), which is a magnetic triplet at room temperature and a magnetic singlet at low temperature with a small contribution from temperature independent paramagnetism that gives a non-zero low temperature magnetic moment.[1b,20] However, the magnetic profiles for **2As** and **2P** reveal two notable points: (i) the curves do not fall as quickly as is normal for uranium(IV), which is characteristic of uranium(IV) bound to strongly donating multiply

bonded ligands;[3c,f,6a,21] (ii) the magnetic moment data for **2As** are, point for point, higher than those of **2P**, and the slightly higher low temperature magnetic moment of **2As** suggests the carbene is a stronger point donor than the one in **2P**, which is consistent with the structural data.

To probe the U-C bonds in **2As** and **2P** in more detail we performed DFT calculations on the whole molecules of **2As** and **2P** (Table 1).[13] Computed, geometry optimised bond lengths and angles are in good agreement with the solid state structures, so we conclude that the computational models provide internally consistent, qualitative models of the electronic structures of **2As** and **2P**.

For **2As** and **2P** the α-spin HOMO and HOMO−1 are essentially of pure, singly occupied 5f character that corresponds to m₁ ±2 projections, and the U-C π- and σ-bonding interactions are represented by HOMOs −2 and −6. Notably, the U-C bond order for **2As** is larger than the value for **2P**, and conversely the As-C_carbene bond order is lower than the P-C_carbene bond order. The C_carbene charge in **2As** is lower than in **2P**, suggesting increased donation to uranium from the former compared to the latter since the arsenic charge is slightly higher than the phosphorus charge. Interestingly, the uranium charge is essentially the same for **2As** and **2P**, which we suggest is due to a buffering effect of the amine as suggested by the *trans*-influence trends inferred by the structural data, *i.e.* as the carbene donates more strongly the U-N_amine interaction weakens to compensate.

NBO analysis reveals a slightly increased uranium contribution to the U-C π-bond component in **2As** compared to **2P**, but for a given uranium contribution the character of each is similarly and overwhelmingly dominated by uranium 5f character with only a modest 6d orbital contribution from uranium. By the NBO method, the U-C σ bond is returned as being electrostatic and C-centred.[22]

QTAIM analysis of the U-C and E-C_carbene bond critical points in **2As** and **2P** reveals polarised-covalent bonds where the ε value is larger for **2As** than **2P**, indicating a more asymmetric distribution around the U-C bond vector consistent with greater π-character, and also that, conversely, the As-C_carbene ε term is less than the P-C_carbene value consistent with the arsenic providing less stabilisation to the carbene. The U-C *H* energy term is also larger for **2As** than **2P**, suggesting a more strongly developed U-C bond in the former than the latter.

Analytical frequency calculations on **2As**/**2P** reveal distinct behaviours. For **2As**, two absorptions at 731 and 777 cm⁻¹ correspond to 'asymmetric' and 'symmetric' stretches of the U=C and U-N_amine bonds coupled together, where in the lower energy stretch shortening/lengthening of the U-C bond is combined with lengthening/shortening of the U-N_amine bond, and for the higher energy stretch shortening/lengthening of the U-C bond is coupled to shortening/lengthening of the U-N_amine bonds. However, for **2P** the U=C stretches are now decoupled from the U-N_amine stretch with two stretches at 429 and 501 cm⁻¹, but they could not be unambiguously discerned experimentally. However, for **2As** experimental absorptions at 790 (shoulder) and 835 cm⁻¹ for **2As** could be assigned as U-C

Table 1. Selected computed DFT, NBO, and QTAIM data for the E=C, U=C, and E-C bonds in **1As**, **1P**, **2As**, and **2P** (E = As or P).

Entry[a]	Bond length and index[b,c]		Charges		NBO σ-component[f]			NBO π-component[f]			QTAIM[g]			
	Bond	BI	$q_{E/M}$[d]	q_C[e]	E/U[%]	C[%]	E ns/np/nd or U 7s/7p/6d/5f	E/U[%]	C[%]	E ns/np/nd or U 7s/7p/6d/5f	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$	$\varepsilon(r)$
1As	As=C	1.34	1.08	−0.58	50.9	49.1	33.7/66.2/0.1	0	100	-	0.15	0.07	−0.14	0.20
1P	P=C	1.43	1.03	−0.63	46.2	53.7	32.5/67.1/0.4	0	100	-	0.19	0.19	−0.20	0.39
2As	U=C	1.66	2.51	−1.63	0	100	-	17.4	82.6	0.0/0.2/12.4/87.4	0.09	0.15	−0.05	0.23
	As-C	1.23	1.13		48.6	51.4	35.0/64.9/0.1	-	-	-	0.15	0.08	−0.13	0.12
2P	U=C	1.56	2.50	−1.79	0	100	-	16.1	83.9	0.1/0.2/13.1/86.6	0.09	0.13	−0.03	0.19
	P-C	1.34	1.08		45.6	54.4	33.6/66.0/0.4	-	-	-	0.18	0.21	−0.20	0.20

[a] All molecules geometry optimised without symmetry constraints at the LDA VWN BP86 TZP/ZORA level. [b] Calculated bond of interest. [c] Nalewajski-Mrozek bond indices. [d] MDC-q charge on As, P, or U. [e] MDC-q charge on ylide or carbene C. [f] Natural Bond Orbital (NBO) analyses, E = As or P; n = 3 or 4. [g] QTAIM topological electron density [ρ(r)], Laplacian [∇²ρ(r)], electronic energy density [*H*(r)], and ellipticity [ε(r)] 3,−1 bond critical point data.

stretches. Notably, the computed values for **2As** are higher than **2P**, and for **2As** involve the N-U-C vibrating as a unit, consistent with a well-developed U-C bond, whereas for **2P** the motions involve the P-C-H units moving as a group. For comparison, analytical frequencies calculations on phosphino-silyl-stabilised U=C double bonds returned values of 595 and 650 cm^{-1},[3c] respectively, and, for wider reference, the lower end of uranyl ν_1 U=O stretches is ~790 cm^{-1}.[23] Thus, in terms of how well-developed their U-C bonds are, from these vibrational data the U-C units can be qualitatively ordered as UCHAsPh$_3$ > UC(PPh$_2$)(SiMe$_3$) > UCHPPh$_3$.

To conclude, we have developed a cleaner and more reliable synthesis of the arsonium-ylide **1As**. Structural analysis of **1As**, in conjunction with comparison to **1P**, confirms the predicted trend of increasing pyramidalisation of the ylide-carbon on moving from phosphorus to arsenic, which accounts for the greater instability of **1As** compared to **1P**. These two ylides have enabled the preparation of the uranium-carbene complexes **2As** and **2P**, the former of which is the first example of a structurally authenticated arsonium-stabilised carbene of any metal, and thus an unprecedented example outside of matrix isolation studies of a formal polarised-covalent U=C double bond without phosphorus-stabilisation. Overall, the experimental and computational characterisation data all consistently point to the U=C multiple bond being better developed in **2As**, with concomitantly weaker pnictonium-stabilisation, compared to **2P**. This is consistent with the situation found for the relative extents of ylide stabilisation in **1As** and **1P**, and the tensioned stabilisation of the carbene by the metal- and pnictide-substituents. We are currently seeking to extend the range of arsonium-ylide substituent patterns in order to develop this new class of carbene complex more widely.[24]
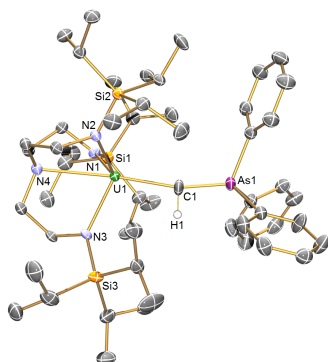
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[24] CCDC 1994476-1994479 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. All other data are available from the corresponding authors on request.

Entry for the Table of Contents

COMMUNICATION

A new route to the classical ylide Ph₃As=CH₂ resolves previous difficulties in its synthesis and isolation, its structural authentication, 45 years after it was first made, confirms that the ylide is pyramidal not planar, and it enables the synthesis of a uranium-arsonium-carbene, the first structurally characterised example of an arsonium-carbene complex of any metal.

John A. Seed, Helen R. Sharpe, Harry J. Futcher, Ashley J. Wooles, and Stephen T. Liddle*

Nature of the Arsonium-Ylide Ph₃As=CH₂ and a Uranium(IV) Arsonium-Carbene Complex