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Silyl-Phosphino-Carbene Complexes of Uranium(IV)

Erli Lu, Josef T. Boronski, Matthew Gregson, Ashley J. Wooles, and Stephen T. Liddle*

Abstract: We report unprecedented silyl-phosphino-carbene complexes of uranium(IV), where before all covalent actinide-carbon double bonds were stabilised by phosphorus(V) substituents or restricted to matrix isolation experiments. Conversion of $[U(BIPM^{TMS})(Cl)(\mu-Cl)_2Li(THF)_2]$ (**1**, $BIPM^{TMS} = C(PPh_2NSiMe_3)_2$) to $[U(BIPM^{TMS})(Cl)\{CH(Ph)(SiMe_3)\}]$ (**2**), and addition of $[Li\{CH(SiMe_3)(PPh_2)\}(THF)]$ and $Me_2NCH_2CH_2NMe_2$ (TMEDA) gave $[U\{C(SiMe_3)(PPh_2)\}(BIPM^{TMS})(\mu-Cl)Li(TMEDA)(\mu-TMEDA)_{0.5}]_2$ (**3**) by α -hydrogen abstraction. Addition of 2,2,2-cryptand or two equivalents of 4-*N,N*-dimethylaminopyridine (DMAP) to **3** gave $[U\{C(SiMe_3)(PPh_2)\}(BIPM^{TMS})(Cl)][Li(2,2,2-cryptand)]$ (**4**) or $[U\{C(SiMe_3)(PPh_2)\}(BIPM^{TMS})(DMAP)_2]$ (**5**). The characterisation data for **3-5** suggest that whilst there is evidence for 3-centre P-C-U π -bonding character, the U=C double bond component is dominant in each case. These U=C bonds are the closest to a 'true' uranium-alkylidene, yet outside of matrix isolation experiments.

In contrast to the well-developed nature of transition metal-carbenes with covalent M=C double bonds, the analogous uranium chemistry is far more sparse.^[1] The first uranium-carbene with a covalent U=C double bond, stabilised by one phosphorus(V) substituent, $[U(CHPM_2Ph)(\eta^5-C_5H_5)_3]$ (**1**),^[2] was reported in 1981 and its reactivity was well elaborated.^[3] After a pause of some three decades the area was revived with various examples of uranium-carbene complexes with one or two phosphorus(V) substituents that stabilise the carbene.^[4] The majority of these complexes exhibit covalent U=C double bond interactions, i.e. uranium plays a significant role in stabilising the carbene by accepting charge from it, but in all cases the phosphorus(V)-substituents introduce the competing carbene and ylid resonance forms $R_3P^+-C(R)=U \leftrightarrow R_3P=C(R)-U$ (R = H or R'₃P), where in the latter the phosphorus(V) substituent plays a significant stabilising role by accepting charge from the carbene. So, those U=C double bonds are not as fully developed as they might otherwise be.^[1a,c]

Apart from fleeting reactive intermediates,^[5] the only reports of unfettered uranium-carbon multiple bonds pertain to fundamental species such as $[U\equiv C]$, $[C\equiv U\equiv C]$, $[U\equiv CH]$, $[C\equiv U=O]$, $[F_3U\equiv CH]$, and $[X_2U=CH_2]$ (X = H, F, Cl),^[6] prepared on microscopic scales in matrix isolation experiments at cryogenic temperatures (<10 K). Thus, the synthesis of a covalent U=C double bond, where the carbene substituents do not significantly affect the U=C component, in a 'true' uranium-alkylidene is yet to be reported under ambient conditions after synthetic efforts spanning four decades.^[1a,c,2] Without exception, outside of matrix isolation all uranium-carbenes with covalent U=C double bonds are stabilised with phosphorus(V) substituents,^[1a,c] which has posed the question as to whether U=C double bonds free of phosphorus(V) substituents are accessible under ambient conditions. A full understanding of U=C double bonds is thus lacking, but is key to informing the on-going debate over the nature of actinide chemical bonding and to providing organouranium reactivity benchmarks.

The complex $[Sc\{C(SiMe_3)(PPh_2)\}\{HC(MeCNAr)_2\}(THF)]$ (**II**, Ar = 2,6-diisopropylphenyl) was recently reported.^[7] In this compound, the Sc=C bond is highly polarised, and consequently a π -delocalised Sc-C-P 3-centre unit is found. Inspired by that report, and related early d-block analogues,^[8] we reasoned that using $\{C(SiMe_3)(PPh_2)\}^2$, never before deployed in actinide chemistry, might present, if synthetically accessible, a U=C double bond that would be more fully developed than in phosphorus(V)-substituted variants because the phosphorus(III) substituent should be less able to accept charge from the carbene. This U=C double bond might thus be anticipated to be closer to matrix isolation examples,^[6] since 5f uranium(IV) might be expected to better stabilise the carbene than 3d scandium(III).

We report here the synthesis, characterisation, and reactivity benchmarking of silyl-phosphino-carbene complexes of uranium(IV). Outside of matrix isolation these are the first examples of covalent actinide-carbon double bonds prepared without phosphorus(V) substituents. Our strategy exploited α -hydrogen abstraction, and so they represent a significant advance towards isolating a 'true' uranium-alkylidene under ambient conditions. In contrast to **II**,^[7] whilst we find evidence for 3-centre P-C-U π -bonding character, the U=C double bond component is dominant because the uranium ions are the dominant acceptor of charge from the carbene. So, these U=C bonds can be considered to be the closest to a 'true' uranium-alkylidene thus far prepared outside of matrix isolation experiments.

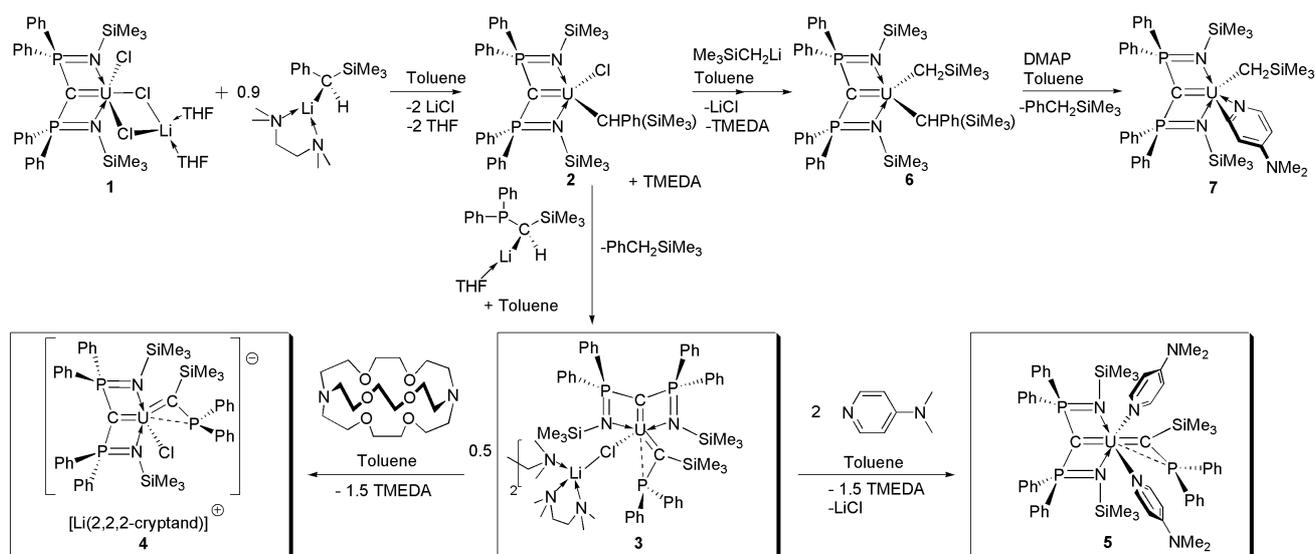
After extensive screening of multiple types and combinations of alkyl ligands - e.g. CH_3 , CH_2Bu^t , CH_2SiMe_3 , $CH(SiMe_3)_2$, $CH_2C_6H_5$, $CH(C_6H_5)_2$, none of which facilitate α -hydrogen abstraction in any combinations nor under thermolysis or photolysis conditions - we deduced^[9] that installation of $\{PhC(H)SiMe_3\}^-$ at uranium in $[U(BIPM^{TMS})(Cl)(\mu-Cl)_2Li(THF)_2]$ (**1**, $BIPM^{TMS} = C(PPh_2NSiMe_3)_2$)^[4j] produces the carbene precursor complex $[U(BIPM^{TMS})(Cl)\{CH(Ph)(SiMe_3)\}]$ (**2**), Scheme 1. Complex **2** is best used *in situ*, and when treated with $[Li\{CH(SiMe_3)(PPh_2)\}(THF)]$ ^[10] in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) elimination of $PhCH_2SiMe_3$ by α -hydrogen abstraction results in isolation of the red complex $[U\{C(SiMe_3)(PPh_2)\}(BIPM^{TMS})(\mu-Cl)Li(TMEDA)(\mu-TMEDA)_{0.5}]_2$ (**3**) in 36% crystalline yield, Scheme 1. It would seem that the occluded $(TMEDA)_{1.5}LiCl$ fragment acts as a protecting group blocking the coordination site left otherwise vacant by the eliminated $PhCH_2SiMe_3$, preventing decomposition or dimerisation.

Addition of 2,2,2-cryptand to **3** eliminates the TMEDA to give $[U\{C(SiMe_3)(PPh_2)\}(BIPM^{TMS})(Cl)][Li(2,2,2-cryptand)]$ (**4**). Alternatively, treatment of **3** with two equivalents of 4-*N,N*-dimethylaminopyridine (DMAP) eliminates the $(TMEDA)_{1.5}LiCl$ entirely to yield $[U\{C(SiMe_3)(PPh_2)\}(BIPM^{TMS})(DMAP)_2]$ (**5**). Complexes **4** and **5** are isolated as red crystalline solids in 86 and 65% yields, respectively, Scheme 1.^[9]

The solid state molecular structures of **3-5** were determined,^[9] and **5** is shown in Figure 1. The salient features of **3-5** are the presence of a meridionally-coordinated $BIPM^{TMS}$ ligand and a silyl-phosphino-carbene ligand to uranium. In **3** and **4** the coordination sphere of each uranium ion is completed by the occluded $(TMEDA)_{1.5}LiCl$ and chloride components, respectively.

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Scheme 1. Synthesis of the uranium(IV)-alkylidene complexes **3**, **4**, and **5** from precursors **1** and **2**, and sequential alkylation of **2** (to give **6**) and reactivity of **6** with 4-*N,N*-dimethylaminopyridine (DMAP) to give the C-H activated product **7** which contrasts to the adduct formation of **5**.

In **3-5**, the U=C_{carbene}/U=C_{BIPM} distances are 2.270(10)/2.405(9), 2.265(2)/2.459(2), and 2.296(5)/2.424(5) Å, respectively. Considering the different uranium coordination environments and formal charge states these U=C_{carbene} distances are invariant and short. In contrast, the longer but typical U=C_{BIPM} bond lengths vary more, suggesting that the U=C_{carbene} unit is the more robust, structure-dictating unit. The U=C_{carbene} distances are in-between the sum of covalent uranium-carbon single (2.45 Å) and double (2.01 Å) bond radii,^[11] and fit with the trend of uranium-carbon quadruple ([C≡U=O], 1.77 Å), triple ([F₃U=CH], 1.94 Å), and double ([F₂U=CH₂], 2.07 Å) bond distances found computationally^[6] when considering the major differences in these species of uranium coordination number, oxidation state, and steric encumbrance. Considering their differing natures, the U=C_{carbene} distances in **3-5** compare very well to the U=C distances in [U(CHPM₂Ph)(η⁵-C₅H₅)₃] (U(IV), 2.293(2) Å),^[2] [U(CHPPPh₃){N(SiMe₃)₂}₃] (U(IV), 2.278(8) Å),^[41] **1** (U(IV), 2.310(4) Å), [U(BIPM^{TMS})(Cl)₂(I)] (U(V), 2.268(10) Å), and [U(BIPM^{TMS})(O)(Cl)₂] (U(VI), 2.183(3) Å).^[4b,j]

The U...P distances in **3-5** are 2.774(3), 2.8277(5), and 2.8371(13) Å, respectively, and are at the limit of, or exceed, the covalent single bond radii of uranium and phosphorus (2.81 Å).^[11] Further, it is clear from the solid state structures that due to the orientations of the Ph₂P groups the phosphorus lone pairs do not point towards the uranium ions in **3-5**. However, there is clearly a U-P bond in [U(PH₂){N(CH₂CH₂NSiPr₃)₃}] even though the U-P distance in that complex is 2.883(2) Å,^[12] and the U=C-P angles in **3-5** are acute (~88°), and the U=C-Si angles are obtuse (~140°; Si-C-P angles ~132°). It is interesting to note that in sterically unencumbered alkylidenes such as [X₂U=CH₂] (X = H, F, Cl, Br, I)^[6e,g,h] one of the U=C-H angles is also ~88°. On balance, we surmise that there are U...P interactions in **3-5**, but due to the geometric disposition they must be weak. We note that the P-C_{carbene} distances are relative short [e.g. 1.739(5) Å in **5**, cf 1.743(3) Å in **II**^[7]], which suggests some P-C negative hyperconjugation and thus some phosphorus π-stabilisation of the carbene.

The ¹H NMR spectra of **3-5** span the ranges -32 to +25, -33 to +59, and -16 to +48 ppm, respectively. The ³¹P NMR spectra of **3-5** reveal broad BIPM^{TMS} phosphorus resonances at -598, -582, and -402 ppm, respectively, but the phosphine resonances could not be located. Both sets of NMR data are characteristic of 5f² uranium(IV)-BIPM^{TMS} complexes.^[4b,c,d] Due to low solubilities post-crystallisation, reliable UV/Vis/NIR spectra of **3** and **4** could not be obtained. However, the spectrum of **5**^[9] is consistent with the uranium(IV) formulation.^[1b,41,13] The ATR-IR spectra of **3-5** all exhibit strong absorptions at ~650 and ~595 cm⁻¹, which are shown by analytical frequencies calculations, computed to within 25 cm⁻¹ of experiment in each case, to be the main U=C_{carbene} bond stretches in **3-5**.

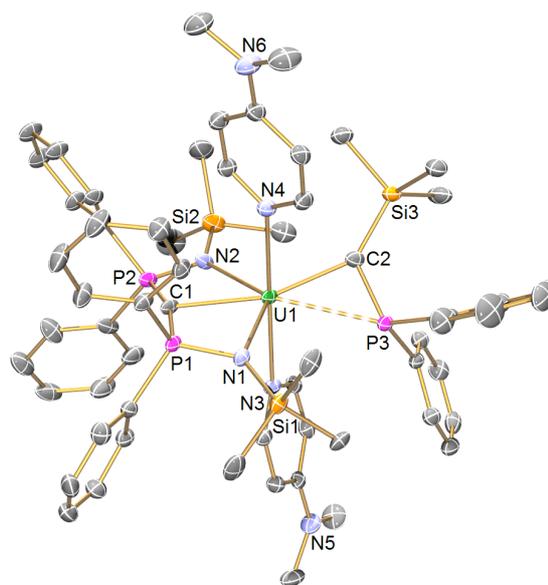


Figure 1. Molecular structure of **5** at 150 K with 40% probability ellipsoids. Hydrogen atoms, minor disorder components, and lattice solvent are omitted for clarity. The weak U=C-P interaction is represented by a dashed-bond between uranium and phosphorus.

Table 1. Selected computed DFT, NBO, and QTAIM data for the U=C bonds in **3'**, **4'**, **5** and **I**.

Entry ^a	Bond length and index ^{b,c}		Charges		NBO			NBO			QTAIM ^e			
	U=C	BI	q_U^d	q_C^e	U[%]	σ -component ^f C[%]	U 7s/7p/6d/5f	U[%]	π -component ^f C[%]	U 7s/7p/6d/5f	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$	$\epsilon(r)$
3'	2.277	1.78	2.87	-1.88	19	81	2:1:53:44	20	80	0:0:19:81	0.12	0.13	-0.04	0.52
	2.392	1.26		-2.00	14	86	1:0:32:67	11	89	0:0:33:67	0.08	0.06	-0.02	0.26
4'	2.286	1.71	2.69	-1.95	15	85	0:1:54:45	13	87	0:0:21:79	0.11	0.12	-0.04	0.48
	2.448	1.13		-1.79	11	89	0:0:38:62	8	92	1:1:31:67	0.08	0.08	-0.02	0.26
5	2.273	1.78	3.10	-2.02	19	81	0:0:42:58	21	79	0:0:35:65	0.12	0.11	-0.05	0.46
	2.394	1.25		-1.84	15	85	0:0:30:70	13	87	0:0:36:64	0.09	0.12	-0.03	0.22
I	2.354	1.64	2.49	-1.97	0	100	-	25	75	0:0:6:94	0.09	0.14	-0.03	0.25

^a All molecules geometry optimised without symmetry constraints at the LDA VWN BP86 TZP/ZORA level; for **3'**, **4'**, and **5** the first entry is the U=C_{carbene} bond and the second entry is the U=C_{BIPM} bond. ^b Calculated U=C distances (Å). ^c U=C Nalewajski-Mrozek bond indices. ^d MDC-q charge on U. ^e MDC-q charge on carbene carbon. ^f Natural Bond Orbital (NBO) analyses. ^g QTAIM topological electron density [$\rho(r)$], Laplacian [$\nabla^2\rho(r)$], electronic energy density [$H(r)$], and ellipticity [$\epsilon(r)$] bond critical point data.

Confirmation of the uranium(IV) assignments of **3-5** is provided by SQUID magnetometry.^[9] The magnetic moments per uranium ion of **3-5** are all ~3.0 μ_B at 298 K, in each case changing little until ~50 K where the magnetic moment drops sharply to ~0.8 μ_B by 2 K and is tending to zero. The magnetic moment of uranium(IV) usually smoothly decreases over the temperature range 298 to 2 K and tends to zero as this ion is a magnetic singlet at low temperature with a residual magnetic moment from temperature independent paramagnetism (~0.4 μ_B).^[1b,13,14] The retention of higher than usual magnetic moments until 50 K and also at 2 K is atypical of most uranium(IV) magnetism, but is characteristic of cases where one or more strongly donating multiply bonded ligands are coordinated to uranium(IV).^[4a-c,15,16]

In order to probe the U=C_{carbene} linkages in **3-5**, we modelled them with DFT.^[9] We replaced the bridging TMEDA in **3** with a NMe₃ surrogate to provide the computationally tractable monomer model [U{C(SiMe₃)(PPh₂)}(BIPM^{TMS})(μ -Cl)Li(TMEDA)(NMe₃)] (**3'**) whilst retaining the charge balance and steric profile, we computed the full [U{C(SiMe₃)(PPh₂)}(BIPM^{TMS})(Cl)]⁻ anion component of **4** (**4'**), and used the full model of **5**. The geometry optimised structures of **3'**, **4'**, and **5** are in excellent agreement with their experimental structures, Table 1, and we include data for **I** for comparison.^[1a,4f] The computed U and C charges are consistent with their formulations.

For **3'**, **4'**, and **5** the HOMO and HOMO-1 are singularly-occupied and of essentially pure 5f character. The next orbitals in each case, which are doubly-occupied, are the U=C_{carbene} π -bond (HOMO-2), followed by the U=C_{carbene} σ -bond (HOMO-3). Slightly lower in energy in the HOMO-4 to HOMO-8 regions are the U=C_{BIPM} π - then σ -bonds. However, in all complexes there is extensive and variable mixing of orbital contributions from the U=C_{BIPM}, U=C_{carbene}, and phosphine lone pairs, so, since other orbital coefficients also intrude into these molecular orbitals, the overall bonding picture of these energetically similar orbitals is convoluted by the inherently delocalised nature of the DFT calculations.

In order to obtain a localised, more chemically intuitive description of the bonding in **3'**, **4'**, and **5** we turned to NBO analysis, Table 1. The U=C_{carbene} σ - and π -bonds in **3'** and **5** are remarkably similar and for charge-rich **4'** the σ - and π -bonds show lower uranium contributions. We conclude that the 6d and 5f contributions to the U=C_{carbene} σ -bonds are generally fairly equal, but for the corresponding π -bonds 5f contributions dominate these more angular interactions. The data for **3'**, **4'**, and **5** are similar to computed data for simpler, fundamental [X₂U=CH₂] (X = F, Cl) species prepared in matrix isolation experiments,^[6a,e,g] where average uranium σ - and π -contributions to those U=C double bonds of ~21 and ~26% are found. It is also instructive to compare **I** to the U=C_{carbene} units in **3'**, **4'**, and **5**; for **I** the

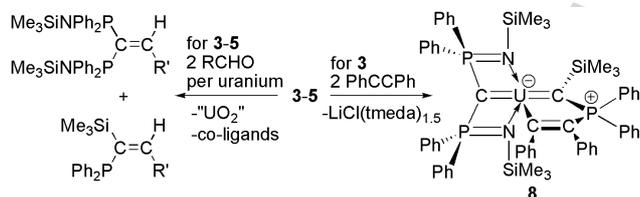
σ -bond is essentially electrostatic, but the π -bond is slightly more covalent. The U=C_{carbene} bonds can also be internally compared to the U=C_{BIPM} cases within each of **3'**, **4'**, and **5**, and we note that the uranium contributions to the U=C_{BIPM} bonds are consistently 4-9% lower than the corresponding U=C_{carbene} for each pair. We also note that the U=C_{BIPM} uranium contributions are lower than in other uranium(IV)-BIPM^{TMS} complexes,^[1a] presumably reflecting the strongly donating nature of the silyl-phosphino-carbene.

Nalewajski-Mrozek bond order analyses, Table 1, reveals U=C_{carbene} bond orders which are consistently higher than the U=C_{BIPM} bond orders that are slightly lower than usually found for uranium(IV)-BIPM^{TMS} complexes,^[1a] underscoring the strongly donating nature of the carbene group. The U=C_{carbene} values are also higher than for **I** and bond orders of ~1.45 for [X₂U=CH₂] (X = F, Cl).^[6a,d] For comparison, the BIPM^{TMS} imino donors exhibit U-N bond orders of ~0.8, the coordinated DMAP ligands in **5** exhibit U-N bond orders of ~0.6, and the phosphine U-P bond orders vary from ~0.3 in **3** and **4** - which derives from indirect mixing of the phosphine orbitals into the uranium-carbene bonding orbitals rather than any direct U-P interaction - to 0 in **5**.^[17] Supporting this latter point, the P-C_{carbene} bond orders average 1.20, reflecting the aforementioned mixing by negative hyperconjugation. So, some 3-centre U-C-P π -topology is found in **3-5**, however the U=C double bonds in **3-5** with U=C bond orders ~1.5 times the P-C bond orders contrast to the more delocalised 3-centre Sc-C-P π -bonding scenario in **II** where the situation is reversed with the C-P bond order ~1.6 times than the S=C bond order.^[7] Thus, the bonding situation in **3-5** is closer to the localised one found in [Ta(CHPM₂)(η^5 -C₅Me₅)₂(PMe₃)]^[8f] than in **II**.^[7] This underscores the key, dominant role of uranium-stabilisation of the carbenes in **3-5** that is also rather different to the situation found in related free carbenes such as Me₃SiCP(NPr₂)₂.^[18]

In addition to orbital-based DFT and NBO methods, we performed a topological bond analysis using QTAIM, Table 1.^[19] For a chemical bond at the Bond Critical Point (BCP) the topological electron density ($\rho(r)$) tends to be <0.1 when the bond is ionic and >0.2 when it is covalent. For all complexes U=C BCPs were found with $\rho(r)$ values ordered U=C_{carbene} > U=C_{BIPM} ~ **I**, indicating the presence of covalent uranium-carbon chemical bonds, albeit polarised ones. Single or triple bonds present cylindrical distributions of electron density around the inter-nuclear bond axis at the BCP ($\epsilon(r) = 0$). Double bonds, however, are asymmetric when viewed down the inter-nuclear bond axis ($\epsilon(r) > 0$). For comparison, the carbon-carbon bonds in ethane, benzene, and ethylene have $\epsilon(r)$ values of 0, 0.23, and 0.45, and transition metal-alkylidene complexes generally have $\epsilon(r)$ values of ~0.5.^[20] The QTAIM analysis consistently returns non-zero U=C_{carbene} and U=C_{BIPM}

ellipticities, thus both are clearly U=C double bond interactions but with the former clearly better developed than the latter, and this is in line with those of **1** and uranium-BIPM complexes generally.^[1a] The $P-C_{\text{carbene}}$ $\epsilon(r)$ values of **3-5** are consistently ~ 0.1 , which only deviating modestly from zero gives clarity over the true extent of negative hyperconjugation and 3-centre U-C-P π -character that could be otherwise over-estimated from visual inspection of molecular orbitals alone. Interestingly, no U-P BCPs are found in **3-5**. Since there are no U-P BCPs, and the structural and NBO data suggest phosphine lone pairs that point away, not to, uranium, it is concluded that any U \cdots P interactions must be relatively weak. Furthermore, ring CPs between the BIPM^{TMS} phosphorus centres and uranium ions in **3'**, **4'**, and **5** are found by QTAIM, and we have found U-P BCPs in other compounds with U-P bonds,^[12,17] suggesting that the absence of uranium-phosphine BCPs in three independent calculations is not spurious.

Experimentally, it is interesting to note that addition of DMAP to **3** only forms the DMAP adduct **5**, whereas addition of DMAP to **II**^[7] results in rapid C-H activation of DMAP. The coordination of two DMAP molecules in **5** suggests that there are no steric barriers, and thus the lack of DMAP C-H activation by **3** experimentally supports the notion that the U=C_{carbene} bonds in **3-5** are more covalent, and thus less reactive units than that in **II**.^[7] In support of this notion, when **2** is converted to [U(BIPM^{TMS}){CH(Ph)(SiMe₃)}(CH₂SiMe₃)] (**6**), which does not undergo α -hydrogen abstraction, and then treated with DMAP C-H activation occurs under mild conditions to give [U(BIPM^{TMS})(NC₅H₃-4-NMe₂)(CH₂SiMe₃)] (**7**), Scheme 1.^[9] This underscores the more basic, ionic nature of U-C single bonds compared to U=C double bonds.



Scheme 2. Synthesis of the Wittig alkene products and **8** from complexes **3-5**. R' = phenyl or 9-anthracene.

Preliminary reactivity studies reveal divergent carbene- and phosphine-centred reactivities, Scheme 2. Complexes **3-5** all react with benzaldehyde and 9-anthracenecarboxaldehyde to produce alkenes by Wittig-type chemistry. Two equivalents of aldehyde are consumed per uranium each time, irrespective of reactant ratios, to produce (Ph₂P)(Me₃Si)C=C(H)(R') and (Me₃SiNPPH₂)₂C=C(H)(R') (R' = anthracene or phenyl). Potentially of more interest, **3** reacts with PhCCPh to give [U{C(SiMe₃)(Ph₂PCPhCPh)}(BIPM^{TMS})] (**8**) where the alkyne has formed a metalocycle between the phosphine and uranium centres. This complex is notable on two counts. The U=C_{carbene} double bond is so robust that reactivity has preferentially occurred at the phosphine, and indeed the U=C_{carbene} distance of 2.316(7) Å in **8** is by the 3 σ -criterion barely perturbed from **3-5** whilst the U=C_{BIPM} distance [2.405(7) Å] is comparable to that in **3**. Despite the fact there is clearly a vacant coordination site *trans* to the alkenyl unit in **8** the carbene resides essentially *trans* to the central BIPM^{TMS} carbon [C=U=C = 173.8(2) °] even though there is no obvious constraining steric reason for it to do so. If the *trans*-influence is operating here this would not be expected since there is clearly space for the C=U=C angle

to decrease further, and this hints at the possible presence of an inverse-*trans*-influence.^[4a-c,21]

To conclude, by utilising a silyl-phosphino-carbene we have prepared three uranium(IV)-carbenes by α -hydrogen abstraction. These are the first actinide-carbon double bonds outside of matrix isolation conditions to be free of phosphorus(V) substituents, and the first use of such a ligand in f-block chemistry; as such they exhibit uranium(IV)-carbon bond distances that are amongst the shortest on record. Although there is evidence for the presence of a 3-centre U-C-P π -interaction facilitated by negative hyperconjugation, the characterisation data all suggest the presence of U=C_{carbene} double bonds that dominate the bonding picture. These U=C_{carbene} bonds can be considered to be the closest to a 'true' uranium-alkylidene yet prepared outside of matrix isolation experiments. Complexes **3-5** take us a step further towards isolable uranium-alkylidenes, and preliminary reactivity studies have revealed divergent carbene- and phosphine-centred reactivities.

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Keywords: uranium • carbene • phosphine • alkylidene • metal-ligand multiple bonding

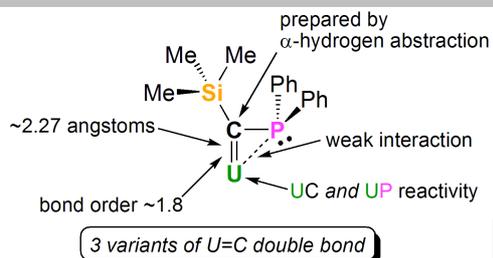
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Entry for the Table of Contents

COMMUNICATION

Do U=C?: The first covalent actinide-carbon double bonds free of P(V) substituents are reported. The U=C bond is so dominant that although some 3-centre U-C-P π -character is found it is minimal. Diverent reactivity centred at the carbene and phosphine are found.



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Silyl-Phosphino-Carbene Complexes of Uranium(IV)