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Synthesis of a Phosphorano-Stabilized U(IV)-Carbene via One-Electron Oxidation of a U(III)-Ylide Adduct

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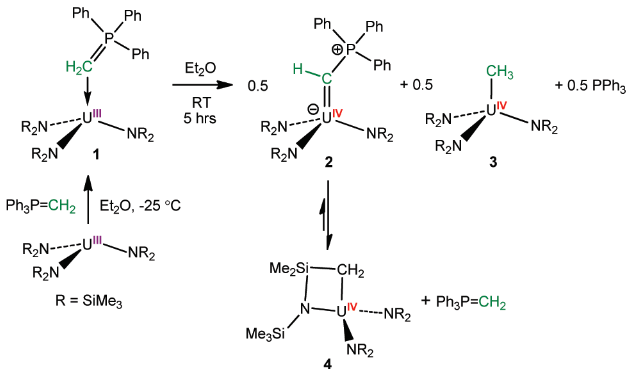
S Supporting Information

ABSTRACT: Addition of the Wittig reagent $Ph_3P{=}CH_2$ to the U(III) tris(amide) $U(NR_2)_3$ ($R = SiMe_3$) generates a mixture of products from which the U(IV) complex $U{=}CHPPh_3(NR_2)_3$ (**2**) can be obtained. Complex **2** features a short U═C bond and represents a rare example of a uranium carbene. In solution, **2** exists in equilibrium with the U(IV) metallacycle $U(CH_2SiMe_2NR)(NR_2)_2$ and free $Ph_3P{=}CH_2$. Measurement of this equilibrium as a function of temperature provides $\Delta H_{rxn} = 11$ kcal/mol and $\Delta S_{rxn} = 31$ eu. Additionally, the electronic structure of the U═C bond was investigated using DFT analysis.

Scheme 1



While transition metal alkylidenes and carbenes are well established,[1,2] actinide carbene complexes (excluding those possessing *N*-heterocyclic carbene ligands) remain exceedingly rare.[3] Uranium carbenes have been observed in inert gas matrices and are postulated as intermediates in McMurry-type reactions,[4,5] but well-defined, isolable examples are limited. The first uranium carbenes to be synthesized, $Cp_3U{=}CHPMe_2R$ ($Cp = \eta^5$-C_5H_5; R = Ph[6] and Me[7]), were generated by treatment of Cp_3UCl with the lithiated phosphoylide $Li[(CH_2)_2PMeR]$. These complexes feature a short uranium−carbon bond distance, suggestive of a formal U═C interaction. Nearly 30 years passed before other uranium carbenes were reported, specifically $[U\{C(PPh_2S)_2\}(BH_4)_2(THF)_2]$[8,9] and $[U\{C(PPh_2NMes)_2\}_2]$ (Mes = 2,4,6-$Me_3C_6H_2$).[10] These U(IV) complexes utilize a chelating methandiide ligand which serves to stabilize the U═C interaction. Interestingly, every uranium carbene isolated thus far features at least one phosphorus substituent attached to the α-carbon.

The paucity of actinide complexes possessing An═C interactions likely results from an energetic disparity between the carbon and metal valence orbitals, as has been reasoned for the absence of lanthanide alkylidene and carbene complexes.[11] However, the ability of uranium to form multiple bonds with heteroatoms, such as nitrogen and oxygen,[3] suggests that complexes possessing U═C double bonds should be attainable. Isolating new uranium carbenes would both serve to provide insight into the role of the 5f and 6d orbitals in actinide metal−ligand bonding and potentially reveal unprecedented modes of reactivity.

Our laboratory has been investigating the reactivity of the highly reducing U(III) tris(amide) $U(NR_2)_3$ ($R = SiMe_3$) with atom transfer reagents, in an attempt to form uranium complexes possessing metal−ligand multiple bonds.[12] We have turned our attention toward the reactivity of $U(NR_2)_3$ with Wittig reagents ($R_3P{=}CHR'$) with the goal of forming complexes possessing U═C bonds. While a rare transformation, Wittig reagents are capable of effecting alkylidene transfer in some transition metal systems, with concomitant generation of PR_3.[13]

Treatment of a diethyl ether solution of $U(NR_2)_3$ with 1 equiv of $Ph_3P{=}CH_2$ rapidly generates the U(III)-ylide adduct $U(CH_2PPh_3)(NR_2)_3$ (**1**) in good yield (Scheme 1), which can be isolated as a deep purple crystalline solid. Inspection of the solid-state molecular structure of **1** (see the Supporting Information) reveals a U−C bond distance of 2.686(6) Å. This is comparable to the U−C distance (2.672(5) Å) found in the U(III) *N*-heterocyclic carbene adduct $U(ImMe_4)[N(SiMe_3)_2]_3$ ($ImMe_4$ = tetramethylimidazol-2-ylidene),[14] signifying a simple Lewis acid−base interaction between the U(III) metal center and the phosphoylide ligand in **1**. The ^1H NMR spectrum of **1** in C_6D_6 indicates the U(III)-Wittig interaction is retained in solution, as the methylene protons of the Wittig reagent appear at −110.55 ppm. Similarly, the $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at −46.9 ppm, which is shifted significantly from that observed for the uncomplexed ylide.[15] Complex **1** exhibits an effective magnetic moment of 3.01 μ_B at 300 K which decreases to 2.12 μ_B at 4 K, as determined by SQUID magnetometry. This is consistent with the proposed U(III) oxidation state.[16]

Solutions of **1** can be stored for several weeks at −25 °C; however, upon standing at room temperature, the deep purple

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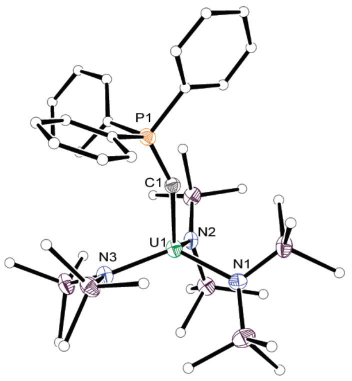

Figure 1. Solid-state molecular structure of $U{=}CHPPh_3(N(SiMe_3)_2)_3$ (**2**) with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): U1−C1 = 2.278(8), C1−P1 = 1.679(8), U1−C1−P1 = 151.7(4), U1−N1 = 2.287(6), U1−N2 = 2.304(6), U1−N3 = 2.290(6).

color of these solutions bleaches to a light red-orange within several hours. From these solutions, the U(IV) carbene $U{=}CHPPh_3(NR_2)_3$ (**2**) can be isolated (Scheme 1) in moderate yield. Complex **2** can also be obtained, in better yield (70% yield, 35% based on $U(NR_2)_3$), by direct reaction of $U(NR_2)_3$ with excess $Ph_3P{=}CH_2$ in Et_2O.

Analysis of **2** by X-ray crystallography reveals a complex possessing a short uranium−carbon bond distance (U1−C1 = 2.278(8) Å) and a large U1−C1−P1 bond angle (151.7(4)°) (Figure 1). For comparison, this U−C distance is significantly shorter than a typical $U{-}C_{alkyl}$ distance (2.4−2.5 Å), such as that found for $Cp^*_2UMe_2$ (2.41(1) Å) ($Cp^* = \eta^5$-C_5Me_5) or [Na(18-crown-6)THF][$U(NR_2)(CH_2SiMe_2NR)_2$] (2.457(6) Å) (R = $SiMe_3$).[17−19] Moreover, the U−C bond length is comparable to the U=C distance found in $Cp_3U{=}CHPMe_2Ph$ (2.29(3) Å)[6] and in [$Cp_2U\{C(PPh_2S)_2\}$] (2.336(4) Å),[9] but shorter than those observed in [$U\{C(PPh_2NMes)_2\}_2$] (2.427(8) Å, 2.448(9) Å).[10] Finally, the P−C bond length (P1−C1 = 1.679(8) Å) in **2** is identical to that of the uncoordinated ylide, $Ph_3P{=}CH_2$ (1.661(8) Å)[20] suggesting that carbene formation does not greatly affect the P−C interaction. Finally, complex **2** exhibits an effective magnetic moment of 2.84 μ_B at 300 K which decreases to 0.97 μ_B at 4 K, as determined by SQUID magnetometry. This temperature response is consistent with the proposed U(IV) oxidation state.[16]

The ^1H NMR spectrum of **2** in C_6D_6 exhibits a broad singlet at −147.1 ppm, assignable to the methine proton of the carbene ligand, while its $^{31}P\{^1H\}$ NMR spectrum reveals a singlet at 172.1 ppm, which is shifted dramatically downfield from the methylene signal observed for **1**. Interestingly, the ^1H and $^{31}P\{^1H\}$ NMR spectra of **2** show that, in solution, the complex exists in equilibrium with uncoordinated $Ph_3P{=}CH_2$ and the U(IV) metallacycle $U(CH_2SiMe_2NR)(NR_2)_2$ (**4**)[21,22] (Scheme 1). This equilibrium is highly dependent upon solvent and temperature. For instance, the metallacycle is favored in a 5:1 ratio over **2** in 25 mM toluene solutions at room temperature, whereas the ratio changes to 1:5, respectively, in 30 mM diethyl ether solutions of **2** at −30 °C. Accordingly, **2** can be isolated in 59% yield by addition of 1.2 equiv of $Ph_3P{=}CH_2$ to a concentrated diethyl ether solution of **4** at −25 °C, where the lower temperature favors the formation of **2**. In contrast, in polar solvents such as THF or pyridine, **2** converts completely to **4** and $Ph_3P{=}CH_2$, irrespective of temperature.

The formation of **2** differs from the salt elimination reactions employed in the syntheses of previous uranium carbenes (vide supra).[6−10] Instead, **2** arises from the one-electron oxidation of **1** concomitant with the formal loss of H· from the coordinated Wittig ligand. To determine the fate of this hydrogen atom, we monitored solutions of **1** by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. This revealed the formation of **2** along with two new products, namely PPh_3 and the U(IV) methyl complex $U(CH_3)(NR_2)_3$ (**3**), in a 1:1:1 ratio (Scheme 1). The presence of **3** was confirmed by comparison of its spectral properties with independently prepared samples and by elemental analysis of isolated material.[23] Monitoring the reaction of $U(CD_2PPh_3)(NR_2)_3$ (**1-*d*$_2$**) by ^2H and ^1H NMR spectroscopies reveals the formation of $U(CDPPh_3)[N(SiMe_3)_2]_3$ (**2-*d*$_1$**) and $U(CD_3)[N(SiMe_3)_2]_3$ (**3-*d*$_3$**), as anticipated. However, this process is complicated by the scrambling of the ^2H label between the ylide methylene group and the $N(SiMe_3)_2$ ligands in **1-*d*$_2$** (see the Supporting Information). This scrambling occurs prior to its conversion into **2-*d*$_1$** and **3-*d*$_3$**. As a result, we observe small amounts of ^1H incorporation into the methine position of **2-*d*$_1$** and the methyl position of **3-*d*$_3$**. We also observe ^2H incorporation into the $SiMe_3$ groups of **2-*d*$_1$**, **3-*d*$_3$**, and **4**. The mechanism by which the scrambling occurs in **1-*d*$_2$** is currently under investigation; however, a related uranium system has been observed to undergo similar scrambling.[21]

Given these results, the generation of **2** appears to arise from an intermolecular hydrogen atom transfer between ylide ligands. This is similar to the H· transfer reactivity observed between $U(NR_2)_3$ and the U(V) imido complex $U({=}NAr)(NR_2)_3$ (Ar = *p*-tolyl), which yields the U(IV) metallacycle, **4**, and the U(IV) amide $U(N\mathit{H}Ar)(NR_2)_3$.[24] A related hydrogen atom transfer between ylide ligands in **1** would result in the formation of the phosphoranyl radical $[Ph_3PCH_3]\cdot$, a known source of $CH_3\cdot$ via $P{-}C_{alkyl}$ bond homolysis.[25,26]

To test for hydrogen atom transfer, the reaction between complex **1** and a substoichiometric amount of TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl) in C_6D_6 was explored.[27] Addition of 10 mol % TEMPO to **1** results in the rapid formation of complexes **2**, **3**, and Ph_3P. The reaction is complete after 2.5 h, a nearly 4-fold decrease from the normal reaction time in this solvent. The final product distribution also reveals a deficiency of **3** and Ph_3P, relative to **2**, equivalent to the amount of TEMPO added to the reaction. The only TEMPO-derived product observed in the final reaction mixture is tetramethylpiperidine. Its formation may be due to an O-atom transfer side reaction[28] or decomposition of the hydroxylamine, TEMPO-H. Overall, these observations support the premise that the reaction proceeds via an initial H· atom transfer event.

The solution phase interconversion of **2** and **4** was monitored by variable-temperature NMR spectroscopy from 243 to 295 K in toluene-d_8, and the thermodynamic parameters were extracted from the equilibrium concentrations of the reactants. The van't Hoff plot is linear (see the Supporting Information) and reveals that the forward reaction is endothermic (ΔH = 11 kcal/mol) and entropically driven (ΔS = 31 eu). Assuming that ΔH_{rxn} is solely due to the two bond breaking events and the two bond making events (Scheme 1), and the contribution of solvation effects is negligible, then ΔH_{rxn} can be represented by eq 1.

$$-\Delta H_{rxn} = D(C{-}H)_{Wittig} + D(U{-}C) - D(C{-}H)_{SiMe3} - D(U{=}C) \qquad (1)$$

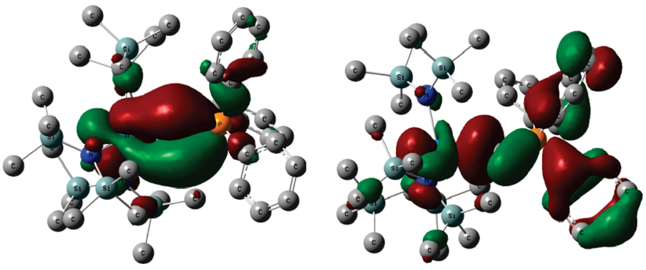

Figure 2. Kohn−Sham orbital representations of the π (left) and σ (right) bonds of the U═C interaction in **2**, plotted at the 0.02 isolevel.

The strengths of $U-C_{alkyl}$ bonds are highly sensitive to the coordination environment provided by the ancillary ligands,[29,30] making it difficult to calculate an absolute D(U═C) value. Nonetheless, using eq 1 it is possible to determine the relative difference between D(U═C) and D(U−C). A reliable bond enthalpy is known for $D(C-H)_{SiMe_3}$; however, to our knowledge, the D(C−H) for an $R_3P{=}CH-H$ ylide has not been measured. Thus we were required to use the calculated D(C−H) for the parent phosphonium salt, $[Me_3PCH_2-H]^+$, the closest analogue for which data are available. Substituting these literature values into eq 1 ($D(C-H)_{SiMe_3}$ = 99 kcal/mol[31] and $D(C-H)_{Wittig}$ = 103 kcal/mol[32]) provides an estimate of the relative difference between D(U═C) and D(U−C) of 15 kcal/mol. Previously reported D(U−C) values for uranium alkyls vary from 29 kcal/mol for $Cp'_3U(^nBu)$ ($Cp' = Me_3SiC_5H_4$)[30] to 75 kcal/mol for $Cp^*_2U(Me)Cl$,[29] allowing us to assess an upper limit of 90 kcal/mol for D(U═C). Given this, it is apparent that D(U═C) of **2** is only slightly greater than a typical uranium carbon single bond, such as that found for $Cp^*_2U(Me)Cl$.[29] It is also clear that D(U═C) of **2** is significantly weaker than the D(Ta═C) = 126 kcal/mol for $Ta{=}CHR(CH_2R)_3$ ($R = SiMe_3$),[33] highlighting the difference between M═C bond strengths of an actinide carbene and a traditional transition metal alkylidene.

To gain further insight into the electronic structure of the U═C bond, a DFT analysis was performed on **2** at the B3LYP level of theory. The bond distances compare well with those obtained experimentally: the calculated U−C bond distance is 2.284 Å, while the calculated U−N bond distances are 2.313, 2.324, and 2.331 Å. The Mulliken spin density of 2.133 is consistent with a U(IV) complex having two unpaired 5f electrons. These reside in HOMO−1 and HOMO−2, which are both predominantly metal based and nonbonding (see Supporting Information). The main orbitals involved in the uranium−carbon interaction are the HOMO, which constitutes the π interaction, and HOMO-6, which constitutes the main σ interaction (Figure 2). According to Mulliken population analysis, the HOMO is mostly carbon 2p character with 22% uranium character (51% C2p, 16% U5f and 6% U6d). This is slightly more U character than that calculated for previous uranium carbenes.[8,10] HOMO−6 is also mostly carbon centered (24% C2p, 4% C2s, 9% U6d, 4% U5f).

A natural bond orbital (NBO) analysis was also conducted on complex **2**, and on $Cp_3U{=}CHPMe_2Ph$,[6] for comparison. The U−C σ-bond (HOMO-6) in complex **2** includes 12% U character (10% 7s, 15% 7p, 35% 6d, 40% 5f) while the U−C π-bond is composed of 8% U character (18% 7s, 11% 7p, 54% 6d, 17% 5f). The corresponding C2p contributions are 88% and 92% for the σ- and π-bonds, respectively. For Gilje's carbene complex,[6] the results are nearly identical with 12% and 7% U character for the U−C σ-bond (HOMO) and π-bond (HOMO-9), respectively. The corresponding C2p contributions are 88% and 93% for the σ- and π-bonds, respectively. Overall, the calculations reveal that the U−C interaction is highly polarized with modest π character, consistent with conclusions drawn from the thermochemistry data.

In summary, the U(III) ylide adduct $U(CH_2PPh_3)(NR_2)_3$ undergoes an intermolecular H· atom transfer between ylide ligands, to form the U(IV) carbene complex $U{=}CHPPh_3(NR_2)_3$, the U(IV) methyl complex $U(CH_3)(NR_2)_3$, and Ph_3P, revealing a new mode of ylide reactivity with a metal complex. This result also highlights the propensity of $U(NR_2)_3$, and U(III) reagents more generally, to favor one-electron redox chemistry.[12,34−36] Given that the formation of a metal carbene by group transfer typically requires a formal two-electron oxidation at the metal center, new carbene transfer reagents exploiting the one-electron redox chemistry of U(III) appear necessary for the synthesis of carbenes from U(III). Utilizing this knowledge, we intend to investigate this strategy of carbene synthesis with the goal of generating new uranium carbene complexes in which the carbene ligand is not stabilized by a phosphorano substituent.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, crystallographic details (as CIF files), and spectral data for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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