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Donor–Acceptor Interactions

Synthesis and Structure of Uranium-Silylene Complexes

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Abstract: While carbene complexes of uranium have been known for over a decade, there are no reported examples of complexes between an actinide and a „heavy carbene." Herein, we report the syntheses and structures of the first uranium-heavy tetrylene complexes: $(CpSiMe_3)_3U$-Si[PhC(NR)$_2$]R′ (R = *t*Bu, R′ = NMe_2 **1**; R = *i*Pr, R′ = PhC(N*i*Pr)$_2$ **2**). Complex **1** features a kinetically robust uranium-silicon bonding interaction, while the uranium-silicon bond in **2** is easily disrupted thermally or by competing ligands in solution. Calculations reveal polarized σ bonds, but depending on the substituents at silicon a substantial π-bonding interaction is also present. The complexes possess relatively high bond orders which suggests primarily covalent bonding between uranium and silicon. These results comprise a new frontier in actinide-heavy main-group bonding.

Studies of the fundamental coordination chemistry of the actinide elements lag behind those of the transition metals.[1] Recent experimental and computational investigations into the chemistry of the actinides incorporating new metal-element bonds have done much to challenge our understanding of actinide electronic structure. Despite the growing number of examples of bonds between actinides and heavy group 13,[2–4] group 15,[5] and group 16[6] elements, there remain few structurally characterized examples of unsupported bonds between actinides and group 14 elements heavier than carbon.[7–9]

In 2005, Ephritikhine and co-workers reported that tetramethyl imidazol-2-ylidene, an „Arduengo-type" N-heterocyclic carbene (NHC), was capable of preferential binding of uranium(III) complexes over isostructural cerium(III) analogues.[10] The propensity for the NHC to bind uranium with modest selectivity over cerium was attributed to the „softness" of the NHC ligand,[11] which has a greater capacity to interact with the diffuse and energetically accessible 5*f* orbitals of uranium than the core-like 4*f* orbitals of cerium.[12] Such differentiation between trivalent 4*f* and 5*f* elements is of particular significance to the area of nuclear waste processing and remediation.[13] While further examples of actinide–carbene complexes have since emerged,[14–16] species featuring bonds between actinides and a heavy 'tetrylene'—a formally divalent group 14 element heavier than carbon—have remained elusive. Since the heavier analogues of carbon should be „softer," we became interested in stabilizing bonds between actinides and heavy tetrylenes, as such bonding interactions may possess a higher degree of covalent character and could afford higher selectivity for trivalent 5*f* ions. Indeed, a recent theoretical study by Shi and co-workers predicted a series of polarized σ bonds between uranium and divalent heavy group 14 elements.[17] We were particularly drawn to the amidinate-supported silylenes that have emerged in recent years. The 2010 discovery by Roesky and co-workers that amidinate-supported silylenes could be prepared in high yield through dehydrochlorination pathways has caused a surge of growth in their research and application;[18,19] these silylenes have been bound to metals from nearly every group in the transition-metal series[20] as well as to lanthanides.[21] The growing application of these silylenes is largely due to the ease with which the parent chlorosilylene Si[PhC(N*t*Bu)$_2$]Cl can be derivatized to feature substituents such as alkoxy, amino, phosphino, and even alkyl groups, thus accessing an array of silylenes with varying steric and electronic properties.[20,22,23]

In 2009, we showed that the uranium(III) complex $(CpSiMe_3)_3U$ could be employed to generate species containing actinide-group 13 bonds with aluminum(I) and gallium(I).[2] $(CpSiMe_3)_3U$ has shown considerable versatility as a σ-acceptor and π-donor: this species was the first molecular uranium complex known to bind CO at room temperature.[24,25] Herein, we report the synthesis and characterization of the first actinide-heavy tetrylene complexes, obtained by reaction of $(CpSiMe_3)_3U$ with amidinate-supported silylenes. These complexes address a gap in actinide-main-group bonding and contribute to our growing understanding of covalent bonding in the actinides.

Considering the minimal steric encumbrance of the dimethylamido substituent, we targeted the silylene Si[PhC(N*t*Bu)$_2$](NMe_2) as an ideal candidate for binding $(CpSiMe_3)_3U$. Mixing room-temperature hexane solutions of $(CpSiMe_3)_3U$ and Si[PhC(N*t*Bu)$_2$](NMe_2) yielded a dark-purple solution. Concentration and cooling to −40 °C overnight afforded burgundy crystals of analytically pure $(CpSiMe_3)_3U$-Si[PhC(N*t*Bu)$_2$](NMe_2) (**1**) in 93% yield (Scheme 1). An X-ray diffraction study on single crystals of **1** revealed a uranium–silicon bond length of 3.1637(1) Å (Figure 1). While this distance is longer than the sum of the co-

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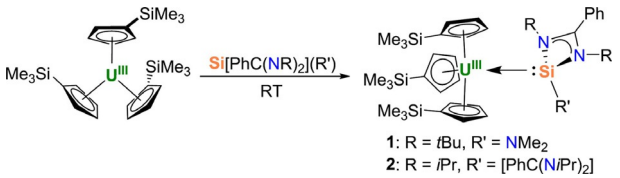

Scheme 1. Synthesis of complexes **1** and **2**.

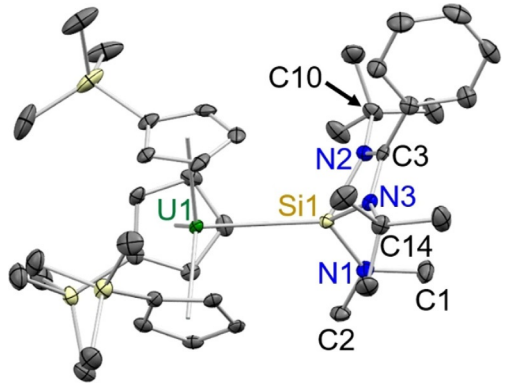

Figure 1. Crystal structure of **1** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances and angles are tabulated in the Supporting Information (Table S1).

valent radii of uranium and silicon as tabulated by Pyykkö (2.86 Å)[26] or Alvarez (3.07 Å),[27] bond lengths between *f*-elements and heavy main-group atoms have often exceeded the sums of the relevant covalent radii,[3,28–30,21] suggesting that these radii may not be the best predictor of main-group–f element bond length.[31] Compared to its 'base-free' solid-state structure,[32] the $(CpSiMe_3)_3U$ fragment has reorganized to minimize unfavorable steric interactions: the trimethylsilyl (TMS) groups on the cyclopentadienyl rings of $(CpSiMe_3)_3U$ are oriented away from the fourth ligand, an arrangement that has only been observed previously in some dimeric structures containing bridging ligands.[33–35] The bond lengths and angles of the $Si[PhC(NtBu)_2](NMe_2)$ fragment are largely unchanged upon coordination (Table S1, Supporting Information),[36] although the *tert*-butyl groups are angled further away from the silicon center (C(3)–N(2)–C(10): 129.8(2)°, C(3)–N(3)–C(14): 129.5(3)°), likely as a result of steric interactions.

The room-temperature ^1H NMR spectrum of **1** shows $Si[PhC(NtBu)_2](NMe_2)$ resonances shifted well out of their usual diamagnetic region (Figure S1, Supporting Information). Variable-temperature (VT) ^1H NMR spectroscopy did not reveal free $Si[PhC(NtBu)_2](NMe_2)$ upon heating to 84 °C, indicative of a remarkably stable and persistent bonding interaction with $(CpSiMe_3)_3U$ (Figure S3, Supporting Information). The $^{29}Si\{^1H\}$ NMR spectrum of **1** shows a sharp resonance for the cyclopentadienyl-based TMS groups at $\delta = -170$ ppm, shifted upfield by $\delta = \approx 5$ ppm from their value in $(CpSiMe_3)_3U$ (Figure S2, Supporting Information). The resonance corresponding to the silicon center of the $Si[PhC(NtBu)_2](NMe_2)$ fragment, typically located around $\delta = -2.6$ ppm,[36] was not observed between $\delta =$ 200 and −400 ppm due to its proximity to the paramagnetic uranium(III) center.

The room-temperature electronic absorption spectrum of **1** shows high energy charge-transfer (CT) bands around 460 and 500 nm; these transitions are redshifted relative to the analogous CT bands in the spectrum of isolated $(CpSiMe_3)_3U$ (Figure S11, Supporting Information). Additionally, the region between 600 and 1500 nm reveals a series of Laporte-forbidden *f–f* transitions that are characteristic of uranium(III) (Figure 2).[31,37] The energies of these transitions differ considerably from those of 'base-free' $(CpSiMe_3)_3U$ even at low concentrations (2 mM), consistent with the lower symmetry of **1** and suggestive of an $A + B \rightleftharpoons AB$ equilibrium that heavily favors the products side in solution.

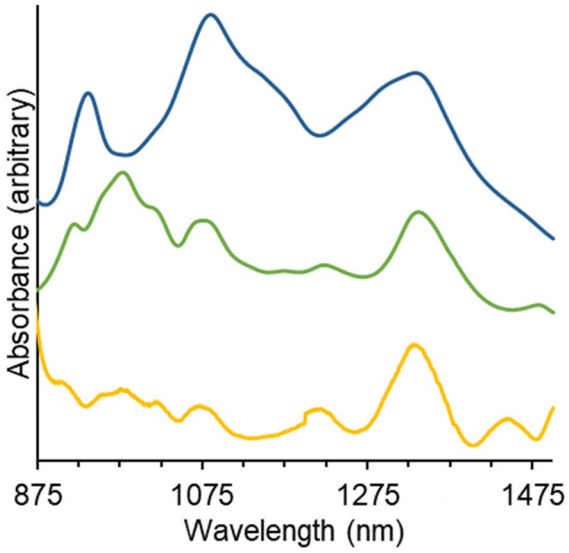

Figure 2. Solution-state NIR absorption spectra of $(CpSiMe_3)_3U$ (blue) and $(CpSiMe_3)_3U$-$Si[PhC(NtBu)_2](NMe_2)$ (**1**, green) in toluene, and the solid-state diffuse reflectance spectrum of $(CpSiMe_3)_3U$-$Si[PhC(NiPr)_2]_2$ (**2**, yellow). Since **1** and **2** are in equilibrium with their starting materials in solution, absorption spectra are reported on an arbitrary intensity scale. Furthermore, the spectra in Figure 2 have been scaled arbitrarily to highlight similarities and differences.

Having isolated a uranium-silylene complex using the sterically accessible $Si[PhC(NtBu)_2](NMe_2)$ ligand, we sought to investigate the influence of increasing steric encumbrance on the U–Si bond properties. A second example of a uranium–silylene complex (**2**) derived from the bulkier silylene $Si[PhC(NiPr)_2]_2$ was prepared similarly in 99% yield and structurally characterized (Scheme 1, Figure S16). Interestingly, and in contrast to its adducts with Lewis-acidic boron, aluminum, and transition-metal compounds,[38] the $Si[PhC(NiPr)_2]_2$ fragment in **2** has retained one monodentate amidinate ligand, likely to minimize steric strain.

The room-temperature ^1H NMR spectrum of a dilute C_6D_6 solution of **2** shows only minor shifts and broadening of the starting material peaks, indicative of dynamic behavior in solution and an equilibrium that heavily favors the reactants side (Figure S5, Supporting Information). At higher concentrations,

however, the shifts and broadening effects become more dramatic (Figure S6, Supporting Information). In the room-temperature $^{29}Si\{^1H\}$ NMR spectrum of **2**, the Cp-based TMS resonance was observed at $\delta = -164.4$ ppm (Figure S7, Supporting Information), essentially unchanged from its value in the isolated uranium(III) starting material ($\delta = -165$ ppm).[39] As with complex **1**, a resonance attributable to the silylene was not observed. To probe the temperature dependence of the solution equilibrium, we performed VT ^1H NMR spectroscopic studies on **2** from 23 to $-80\,^{\circ}C$ (Figure S8, Supportng Information). Resonances attributable to the isopropyl methyl and methyne groups of $Si[PhC(NiPr)_2]_2$ broadened and shifted out of the diamagnetic region as the temperature was lowered, indicating closer contact with the paramagnetic uranium(III) center. However, more detailed analysis of the VT ^1H NMR data was obscured by the broadness of most signals at lower temperature, which may result from fluxionality not only between the starting materials and **2** but also between the mono- vs. bidentate binding modes of the amidinato ligands bound to $Si[PhC(NiPr)_2]_2$.

In contrast to **1**, the room-temperature electronic absorption spectrum of **2** in solution is nearly identical to the summation of the spectra of the two starting materials (Figures S12, Supporting Information), providing further evidence that the solution equilibrium between the reactants and **2** lies on the reactants side at room temperature. The diffuse reflectance spectrum of solid **2**, on the other hand, bears an absorbance profile strikingly similar to the solution-state NIR spectra of **1** (Figure 2), including prominent *f–f* transitions at approximately 920, 980, 1020, 1080, 1220, and 1335 nm. The close resemblance of the spectra suggests that, while **2** readily undergoes ligand dissociation in solution, the uranium-silylene interaction is less perturbed in the solid state yielding a complex that is very similar electronically to **1**. Furthermore, the IR spectrum of **2** shows substantial differences relative to those of the starting materials (Figure S15, Supporting Information); evidently, the uranium-silicon bonding interaction in **2** changes the electronic and vibrational nature of the $Si[PhC(NiPr)_2]_2$ unit, further discounting the possibility that the uranium and silicon starting materials simply co-crystallized.

Magnetometric studies of **1** and **2** are ongoing. Preliminary results on the DC magnetic susceptibility of **2** are consistent with the trivalent oxidation state assignment for uranium (Figures S17–S18, Supporting Information).[40] Notably, the room-temperature $\chi_M T$ value of **2** is lower than that of 'base-free' $(CpSiMe_3)_3U$ (Figure S17, Supporting Information), which may reflect the stronger ligand-field splitting in **2**.

Accessing a third uranium-silylene complex via the widely utilized parent chlorosilylene, $Si[PhC(NtBu)_2]Cl$, proved impossible under our conditions: reaction between $Si[PhC(NtBu)_2]Cl$ and $(CpSiMe_3)_3U$ resulted in complete conversion to the uranium(IV) chloride, $(CpSiMe_3)_3UCl$,[41] and the bis(silylene), $Si_2[PhC(NtBu)_2]_2$,[42] as confirmed by ^1H NMR spectroscopy as well as unit-cell checks of the crystalline products (Figure S10, Supporting Information). Analogous reactivity toward $Si[PhC(NtBu)_2]Cl$ has been observed for a samarium(II)metallocene.[21] The reduction from silicon(II) to silicon(I) highlights the well-known reducing power of uranium(III) organometallic complexes.

The electronic structures of both silylene complexes have been investigated using density functional methods: natural bond orbital (NBO) analyses of geometry-optimized **1** and **2** reveal polarized σ bonds between uranium and silicon (Figure 3, Table S3, Supporting Information). The Wiberg bond

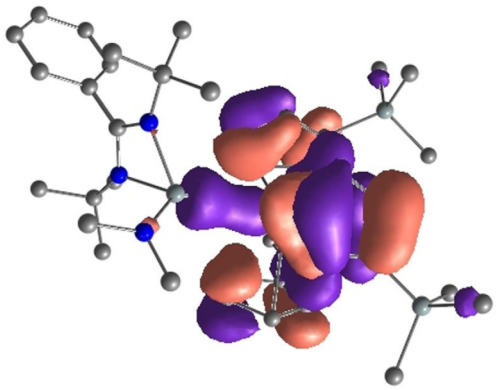

Figure 3. Kohn–Sham α-spin HOMO-4 of **1** showing the primary U–Si bonding orbital.

indices for **1** and **2** are relatively high (≈0.7) compared to those calculated for other donor–acceptor complexes containing the $(CpSiMe_3)_3U$ fragment and suggest a primarily covalent single bond between uranium and silicon.[2] In both complexes, the uranium hybrid acceptor orbital is of primarily *d* parentage (58%) but with substantial *f*-orbital contributions (12%) (Table S3, Supporting Information). Similar *f*-orbital contributions were calculated for dative bonds between U^{III} and the group 13 diyls AlCp* and GaCp*.[2] The silicon donor hybrids in both complexes are of primarily *s* character (73% *s*, 27% *p*), falling in the range of values reported for amidinato-silylene complexes of transition metals,[43] while a substantially higher percentage of *p* character was calculated for the formally X-type group 14 ligands in (^{TIPS}TREN)U-$SnMe_3$ (^{TIPS}TREN = $N(CH_2CH_2NSi(iPr)_3)_3$) and the model complex H_3Si-$U(NH_2)_3$.[8,9] Consistent with our experimental observations in the ^1H NMR and UV/vis/NIR spectra of **1** and **2**, complex **1** is calculated to have a BDE nearly twice that of complex **2**. The BDE for **1**, at 11.9 kcal mol^{-1}, is remarkably high (cf. 13.1 kcal mol^{-1} for the model complex Cp_3U-pyridine).[2] The stability of the uranium-silicon bond in **1** is further demonstrated by the low-lying nature of the bonding orbital (HOMO-4) which contrasts with the bonding orbital in **2** (HOMO); accordingly, the uranium-silicon bond in **1** should be less easily perturbed. Additionally, at the second-order NBO level, a significant π-backbonding contribution (10.3 kcal mol^{-1}) is present in **1**, while the backbonding in **2** is less than half as strong (Table S3, Supporting Information). The substantial backbonding in **1** contrasts with the NBO analysis performed on the theoretical complex $(CpSiMe_3)_3U$-$Si(NCHMes)_2$ investigated by Shi and co-workers, which found no U–Si π-bonding character.[17]

We have begun studies into the reactivity of these complexes with the aim of probing the nature of the U-Si interaction. Addition of 1 atm. of CO to a [D_6]benzene solution of **1** resulted in an equilibrium between the CO and silylene adducts of ($CpSiMe_3$)U, as monitored by ^{1}H NMR spectroscopy (Figure S4, Supporting Information). The ^{1}H NMR spectrum of **1** after the addition of CO closely resembled the spectrum of isolated **1**, indicating that the equilibrium was not dominated by ($CpSiMe_3$)$_3$U-CO.[24] The spectrum of **1** could be recovered by freeze-pump-thawing the solution and replacing the CO atmosphere with dry N_2. Although qualitative due to the unknown concentration of CO in solution, the ability of Si[PhC(N*t*-Bu)$_2$](NMe_2) to compete with CO for uranium binding further confirmed the kinetic persistence of the uranium–silylene interaction of **1** in solution, as the metal–ligand bond dissociation energy in ($CpSiMe_3$)$_3$U-CO has been estimated at 14.3 kcal mol^{-1}.[25] In contrast, addition of 1 atm. of CO to a [D_6]benzene solution of **2** showed essentially complete conversion to ($CpSiMe_3$)$_3$U–CO and free Si[PhC(N*i*Pr)$_2$]$_2$ (Figure S9, Supporting Information). These ligand substitution reactions highlight the dative bonding character of **1** and **2** while reaffirming that the U–Si bond of **1** is less easily perturbed than that of **2**.

In conclusion, we have synthesized and characterized the first complexes containing actinide-heavy tetrylene bonds. Complex **1** possesses a remarkably stable uranium–silicon bonding interaction that can compete with strong π-acids such as CO, while complex **2** shows only a weak interaction in solution that can be stabilized by cooling or crystallization. These bonds can be described as polarized covalent σ bonds, featuring high calculated bond orders and substantial *f*-orbital contributions to the bonding orbital. In the case of **1**, a significant π-backbonding contribution is present, contrasting with previous theoretical expectations for uranium-silylene species[17] and highlighting the importance of investigating actinide-heavy tetrylene bonds. Reaction of ($CpSiMe_3$)$_3$U with a chlorosilylene resulted in reduction to a silicon(I) dimer, emphasizing the importance of the silylene's supporting ligands to stabilizing uranium–silicon bonds. Current work is focused on the reactivity of **1** and **2**, experimental determination of the thermodynamic parameters for uranium-silylene binding, and the synthesis of related actinide, lanthanide, and group 14 congeners.

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Conflict of interest

The authors declare no conflict of interest.

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