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Synthesis and Reactivity of a Silylalkyl Double Tuck-in Uranium Metallocene $[(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2CH_2)_2U]$ and its Conversion to Bis(tethered) Metallocenes

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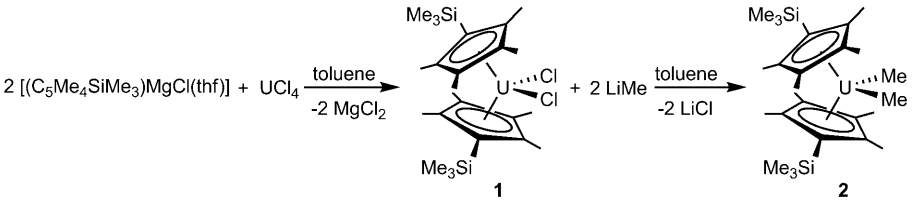
The development of actinide reaction chemistry has benefited enormously from the metallocene coordination environment provided by two pentamethylcyclopentadienyl ligands in complexes such as $[(C_5Me_5)_2UCl_2]$ and $[(C_5Me_5)_2UMe_2]$ [1] Actinide metallocenes have been used as starting materials for many studies on the transformations possible at these large heavy-metal centers.[2] Although much has been learned with these metallocenes, there are still many reaction systems that could not be fully identified or defined with the $[(C_5Me_5)_2]^{2-}$ ligand set. Indeed, major efforts are being made to examine "non-metallocene" actinide chemistry.[3]

Herein, we report a new approach to studying actinide metallocene reaction chemistry that has the benefit of having the reactive ligands tethered within the complex. The value of tethering reactive ligands in exploring and defining reaction chemistry is well established.[4] The tethered ligand platform is generated for uranium by two C–H bond activation reactions involving the $(C_5Me_4SiMe_3)^-$ ligand. The synthesis of a bis(tethered alkyl) complex is described as well as two representative insertion reactions that show it can provide both crystallographic data elusive with $[(C_5Me_5)_2UX_2]$ complexes and enhanced reactivity over the untethered analogues. The resulting bis(tethered alkoxide) and bis(tethered iminoacyl) complexes show that this system provides a general entry into uranium reactivity studies by using tethered ligands.

Synthesis of actinide complexes with the $(C_5Me_4SiMe_3)^-$ ligand were initially being explored as part of an effort to obtain more soluble actinide metallocenes. The $(C_5Me_4SiMe_3)^-$ ligand was shown to be a viable replacement for $(C_5Me_5)^-$ with early transition metals[5–13] and lanthanides.[14–20] With the latter metals, this ligand has led to spectacular mono-ring chemistry.[14–19]

UCl_4 reacts with two equivalents of $[(C_5Me_4SiMe_3)MgCl(thf)]$ to produce $[(C_5Me_4SiMe_3)_2UCl_2]$ (**1**) as a crystalline maroon product in 92% yield in a reaction analogous to the formation of $[(C_5Me_5)_2UCl_2]$ (Scheme 1).[1] The structural parameters of **1**, determined by X-ray crystallography, are very similar to those of $[(C_5Me_5)_2UCl_2]$.[21] The large trimethylsilyl groups of the $(C_5Me_4SiMe_3)^-$ ligand point up and away from the uranium center and therefore do not distort the metallocene moiety significantly from that of the $(C_5Me_5)^-$ complex.



Scheme 1. Synthesis of $[(C_5Me_4SiMe_3)_2UCl_2]$ (**1**) and $[(C_5Me_4SiMe_3)_2UMe_2]$ (**2**).

The addition of two equivalents of solid LiMe to a solution of **1** in toluene over 5 min generates $[(C_5Me_4SiMe_3)_2UMe_2]$ (**2**) as an orange crystalline product in 93% yield after 12 h of stirring (Scheme 1). Complex **2** is isolated from the reaction mixture by removal of a white solid by centrifuging, followed by removal of the solvent under vacuum. Similar to **1**, complex **2** has a structure analogous to that of $[(C_5Me_5)_2UMe_2]$.[22]

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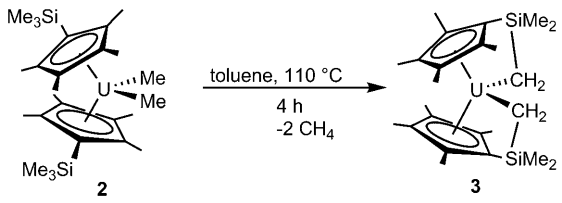
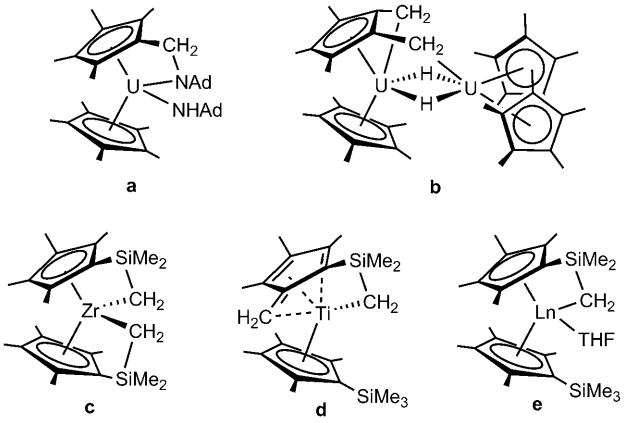
In contrast to $[(C_5Me_5)_2UMe_2]$,[1] complex **2** is unstable at elevated temperature. Heating complex **2** in toluene at 110 °C for 4 h eliminates methane and forms $[(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2CH_2)_2U]$ (**3**) as a red crystalline solid in 94% yield (Scheme 2). Complex **3** is the result of metalation of



Scheme 2. Formation of complex **3** from **2** upon heating.

the trimethylsilyl groups of both $(C_5Me_4SiMe_3)^-$ ligands in **2**, that is, a silylalkyl double "tuck-in"[23] complex is formed. Complex **3** was characterized by ^{1}H NMR and IR spectroscopy and elemental analysis and structurally identified by X-ray crystallography (Figure 1). The ^{1}H NMR spectrum of **3** showed six major resonances, assignable to the four methyl substituents of the cyclopentadienyl rings and two silicon bound methyl groups, consistent with the solid-state structure. The methylene hydrogen atoms were not observed in the ^{1}H NMR spectrum, which is not uncommon for alkyl groups directly bound to a paramagnetic uranium center.[24] A similar situation was observed with metalated $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2CH_2)^-$ complexes of paramagnetic lanthanides[20] and with metalated $[(Me_3C)_2C_5H_2CMe_2CH_2]^{2-}$ complexes of cerium[25] and neodymium.[26]

Crystallographically characterized examples of actinide metallocenes with $\eta^5{:}\eta^1$-cyclopentadienyl ligands are rare: the only previously reported examples are shown in Scheme 3 (**a**[27] and **b**[28]). Metalation of the $(C_5Me_4SiMe_3)^-$ ligand has previously been observed in zirconocene and titanocene chemistry, as shown in Scheme 3 (**c**[10] and **d**[13]) and recently with lanthanides, Scheme 3 (**e**).[20]



Scheme 3. Examples of $\eta^5{:}\eta^1$-cyclopentadienyl uranium complexes (**a**, **b**) and transition metal and lanthanide complexes involving metalated $(C_5Me_5SiMe_3)^-$ ligands (**c**–**e**).

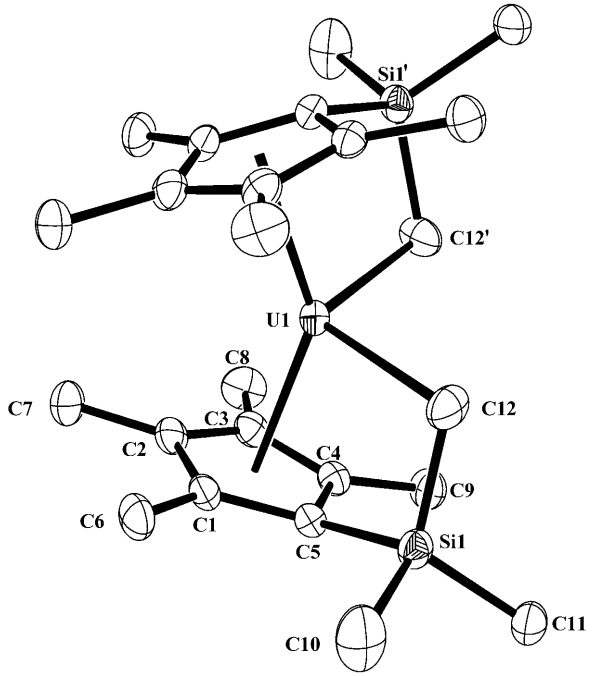


Figure 1. Thermal ellipsoid plot of $[(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2CH_2)_2U]$ (**3**) drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: U1–(ring centroid) 2.419, U1–C12 2.453(2), (ring centroid)-U1-(ring centroid) 144.1, (ring centroid)-U1-C12 95.7, C12-U-C12′ 102.52(1).

Complex **3** maintains a metallocene geometry, despite the formation of two additional rings in the molecule. The 2.453(2) Å U1–C12 bond in **3** is similar to the 2.425(2) Å U–C(Me) distance in **2**, but the 2.419 Å U1–(ring centroid) bond length in **3** is shorter than the 2.471 Å U–(ring centroid) bond in **2**. The main structural differences in the tethered compound are the 144.1° (ring centroid)-U1-(ring centroid) and the 102.5(1)° C12-U1-C12′ bond angles versus 139.5° and 91.26(9)° in **2**, respectively. Complex **3** is not isomorphous with the zirconium complex in Scheme 3,[10] which has significantly different bond lengths and angles due to the difference in the eight-coordinate ionic radii: 1.00 Å for U^{IV} versus 0.84 Å for Zr^{IV}.[29]

The effects of tethering a uranium alkyl bond were studied with insertion reactions by using CO and the isoelectronic substrate *tert*-butyl isocyanide, *t*Bu–N≡C. Both substrates are known to react with $[(C_5Me_5)_2UMe_2]$,[30,31] but in each case it was not possible to obtain crystallographic data on the products. As shown in Figures 2 and 3, the tethered complex **3** gave fully characterizable products in both cases.

As shown in Scheme 4, each U–C bond in **3** reacts with CO and the double insertion product $[\{\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2C(=CH_2)O\}_2U]$ (**4**) is isolated. Complex **4** does not contain acyl ligands that would result from direct CO insertion, but instead contains enolate ligands presumably formed by a silyl rearrangement. This type of rearrangement has been observed before in both actinide[30,32] and early-transition-

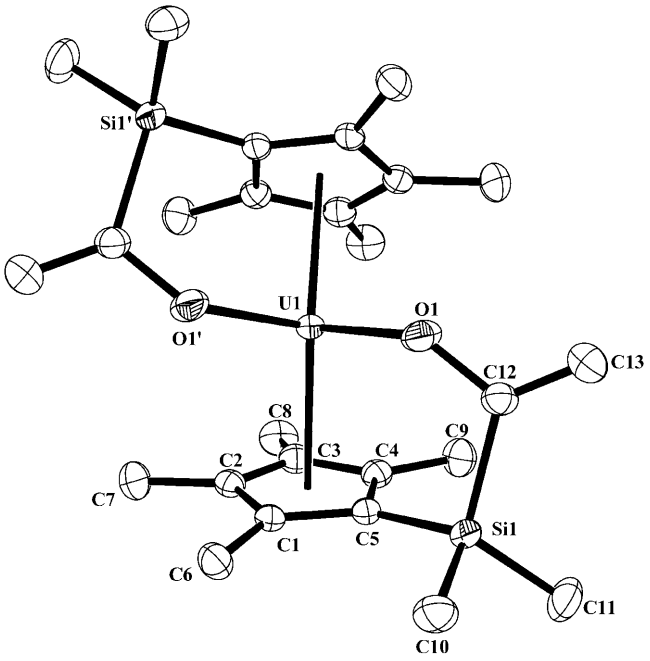
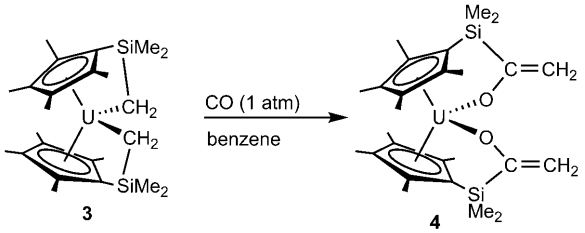
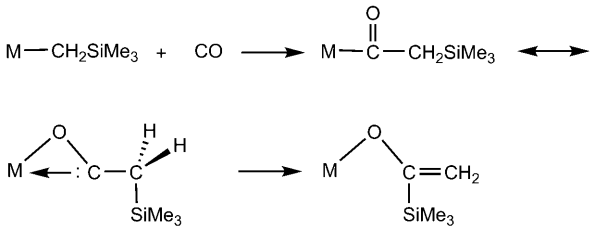


Figure 2. Thermal ellipsoid plot of $[\{\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2C(=CH_2)O\}_2U]$ (**4**) drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: U1–(ring centroid) 2.453, U1–O1 2.132(2), C12–C13 1.324(4), (ring centroid)-U1-(ring centroid) 135.0, (ring centroid)-U1-O1 100.5, O1-U1-O1′ 101.6(1), U1-O1-C12 135.5(2).



Scheme 4. Formation of complex **4** from **3** by treatment with CO.

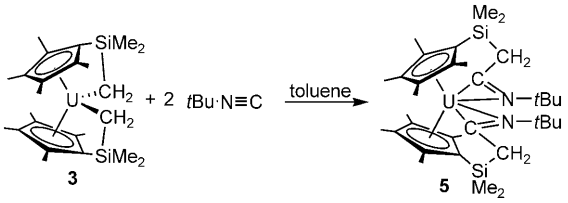
metal complexes[33–37] and has been explained by CO insertion into a M–C bond to form a carbene-like intermediate that can formally insert into a Si–C bond (Scheme 5).[30] Complex **4** provides the first crystallographic evidence that this silyl rearrangement accompanies CO insertion in actinide chemistry (Figure 2).[30,32,38] In addition, complex **4** is a



Scheme 5. CO insertion and silyl rearrangement.

bis(alkoxide) metallocene that is suitable for further studies of U–O bond reactivity in a tethered environment.

Double insertion reactivity is also observed with the substrate *t*Bu–N≡C. The 1,1-insertion product $[(\eta^5{:}\eta^2\text{-}C_5Me_4SiMe_2CH_2C{=}N\mathit{t}Bu)_2U]$ (**5**) was isolated (Scheme 6)



Scheme 6. Formation of complex **5** from **3** by treatment with *t*Bu–N≡C. yp

and was structurally characterizable by X-ray crystallography (Figure 3). In contrast to the insertion reaction in Scheme 6, analytical and spectroscopic evidence indicates that only a single insertion occurs with $[(C_5Me_5)_2UMe_2]$.[31] The insertion of *t*Bu–N≡C into both of the uranium–carbon bonds of **3** results in a bis(tethered iminoacyl) actinide metallocene and will allow this ligand system to be explored in a tethered environment. Each nitrogen atom of the dihapto iminoacyl points out from the middle of the metallocene wedge, but these ligands are not coplanar with one another. The dihedral angle between the N1-U1-C13 and N2-U1-C30 planes is 28.5°.

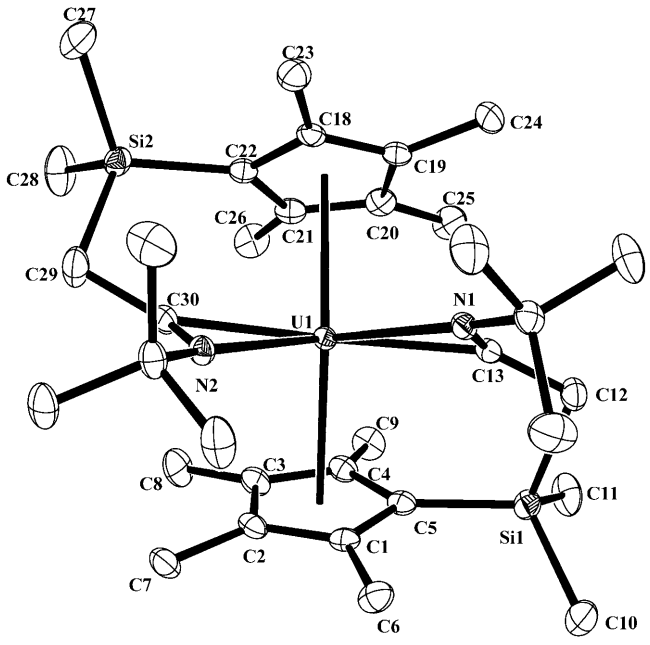


Figure 3. Thermal ellipsoid plot of $[(\eta^5{:}\eta^2\text{-}C_5Me_4SiMe_2CH_2C{=}N\mathit{t}Bu)_2U]$ (**5**) drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: U1–(ring centroid) 2.524, 2.531, U1–C13 2.385(2), U1–C30 2.397(2), U1–N1 2.489(2), U1–N2 2.481(2), C13–N1 1.280(3), C30–N2 1.275(3), (ring centroid)-U1-(ring centroid) 132.5, C13-U1-C30 151.09(7), N1-U1-N2 93.15(5).

The isolation of **5** suggests that the tethered nature of **3** may allow investigation of reactions sterically prohibited with $[(C_5Me_5)_2UMe_2]$. It was argued that the steric bulk of the $(MeC{=}NtBu)^-$ group, assumed to be side-on bound based on the spectra, prevented a second insertion from occurring with $[(C_5Me_5)_2UMe_2]$.[31] The second insertion may be possible in **3** because it has a (ring centroid)-U1-(ring centroid) angle approximately 5° larger than that in $[(C_5Me_5)_2UMe_2]$ and the 102.5(1)° C12-U1-C12′ angle in **3** is larger than the 94.6(2)° C(Me)-U-C(Me) angle of $[(C_5Me_5)_2UMe_2]$ [22] In addition, ring strain in the tether could lead to higher reactivity.

Complex **5** also provides an interesting contrast to the insertion of *t*BuN≡C into the U−C bond in the amide metallacycle, $[\{(Me_3Si)_2N\}_2U\{CH_2SiMe_2N(SiMe_3)\}]$.[32] In that case, a silyl rearrangement occurred, similar to that in the CO insertions above, to form a product with uranium ligated only by nitrogen, $[\{(Me_3Si)_2N\}_2U\{tBuNC(=CH_2)SiMe_2N(SiMe_3)\}]$.[32] In the case of **3**, a silyl rearrangement accompanies insertion only with CO.

Tethering the alkoxide and iminoacyl ligands in **4** and **5**, respectively, also affects metrical parameters compared with untethered metallocene complexes. For example, the 135.5(2)° U1-O1-C12 bond angle in **4** is significantly different from the 170.2(5)° to 178(1)° bond angles found in other uranium alkoxides.[28,39,40] The 2.132(2) Å U1−O1 bond length in **4** is also longer than the 2.05(1) Å U−O bond length reported for the terminal alkoxide uranium metallocene, $[\{(C_5Me_5)_2U(OMe)\}_2PH]$.[39] The 2.385(2) and 2.397(2) Å U−C and 2.489(2) and 2.481(2) Å U−N bond lengths in **5** mirror the 2.36(2) Å U−C and 2.40(2) Å U−N bond lengths in the mono(iminoacyl) complex $[(C_5H_5)_3U(MeC{=}NCy)]$ ($Cy = C_6H_{11}$), although the latter U−C and U−N bond lengths are indistinguishable at the 3σ level.[41] Due to the side-on coordination of the iminoacyl ligands in **5**, there is a significant difference in the C13-U1-C30 bond angle in **5** (151.09(7)°), compared with that in **2** (91.26(9)°) or **3** (102.5(1)°), whereas the N1-U1-N2 bond angle of 93.15(5)° is similar to the C(Me)-U-C(Me) bond angle in **2**. The 135.0° and 132.5° (ring centroid)-U1-(ring centroid) bond angles in **4** and **5**, respectively, are smaller than the 144.1° angle in **3** most likely because the new tethers contain one additional atom.

In summary, the use of $(C_5Me_4SiMe_3)^-$ ligands in place of $(C_5Me_5)^-$ provides an opportunity by C−H bond activation to generate bis(tethered alkyl) uranium metallocenes. These tethered U−C bonds engage in insertion reactions with CO and *t*Bu−N≡C to form complexes containing tethered alkoxide and tethered iminoacyl ligands, respectively. The larger bond angles in $[(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2CH_2)_2U]$ (**3**) compared with $[(C_5Me_5)_2UMe_2]$ appear to allow double insertion in the isocyanide reaction and this suggests that the tethered systems have the potential to deliver enhanced reactivity. Since each insertion reaction generates a new tethered complex, the diversity of tethered actinide complexes accessible from **3** for further reactivity studies is substantial.

Experimental Section

Experimental details for the syntheses of **1**, **2**, **3**, **4**, and **5** are given in the Supporting Information.

CCDC-739777 (**1**), 739778 (**2**), 739779 (**3**), 73980 (**4**), and 739781 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: cyclopentadienyl ligands · insertion · metalation · tethers · uranium

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