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Diuranium Complexes

A Crystallizable f-Element Tuck-In Complex: The Tuck-in Tuck-over Uranium Metallocene $[(C_5Me_5)U\{\mu\text{-}\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_3(CH_2)_2\}(\mu\text{-}H)_2U(C_5Me_5)_2]$**

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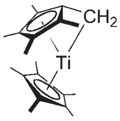
One of the features of the $C_5Me_5^-$ group that makes it such a desirable ligand in organometallic chemistry is the fact that it is relatively inert to the C–H activation that often complicates the chemistry of $C_5H_5^-$ metallocene complexes.[1–4] Although $C_5Me_5^-$ is more resistant to attack on the C–H bond, its methyl groups can be metalated with some highly reactive metal species.[5–10] Since these C–H activated ligands arise from extremes in reactivity, they have been involved in unprecedented reactions. For example, the homogeneous C–H activation of methane was first discovered with $[\{(C_5Me_5)_2LuMe\}_n]$[5] based on a mechanism involving the "tucked-in"[6] complex "$[(C_5Me_5)\{C_5Me_4(CH_2)\}Lu]$". Tuck-in[6] intermediates have also played prominent roles in explaining the C–H activation in complexes such as $[(C_5Me_5)_2ScMe]$[6] and $[(C_5Me_5)_2Th(CH_2CMe_3)_2]$.[11] Despite the repeated use of tuck-in complexes in mechanistic schemes involving f elements, no spectroscopic or crystallographic evidence has ever been presented to support the existence of such an intermediate in a lanthanide or actinide complex.

Tuck-in complexes have been crystallographically characterized with transition metals.[7,9,10,12] For example, in the $\{(C_5Me_5)_2TiH\}$ system, $[(C_5Me_5)Ti\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)\}]$ (**1**) could be isolated.[7] However, in these transition-metal tuck-in compounds, low-oxidation-state tetramethylfulvalene resonance structures can contribute to the stability of the complexes.[7,9,10,12,13] With the limited oxidation states available for f elements, this is less likely.

Crystallographic evidence for an alternative type of $C_5Me_5^-$ metalation has been obtained with lanthanides in the form of "tuck-over" complexes $[(C_5Me_5)_2Ln(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5)]$ (**2**; Ln = Y,[14] La,[15] Sm,[16] and Lu[17]) in which the methylene group formed by C–H activation is attached to a second metal atom. In some cases, double C–H activation at two methyl groups resulted in $C_5Me_3(CH_2)_2^{3-}$ ligands, for example, in $[\{(C_5Me_5)_3Ln_2[C_5Me_3(CH_2)_2]\}_2]$ (**3**; Ln = Ce[18] and Sm[19]).[13,20])



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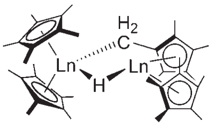

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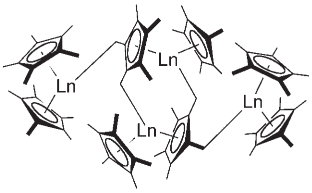

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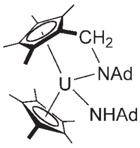

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The only crystallographic evidence for this type of C–H activation of a $C_5Me_5^-$ ligand in an actinide complex involves a methylene group attached to nitrogen not the metal. Thermolysis of the U^{6+}–imido complex $[(C_5Me_5)_2U(=NAd)_2]$ (Ad = 1-adamantyl) formed $[(C_5Me_5)U\{\eta^1{:}\eta^5\text{-}NAd(CH_2C_5Me_4)\}(NHAd)]$ (**4**,[21])—a reaction that could involve a tuck-in (or tuck-over) intermediate. The only other suggestion of $C_5Me_5^-$ metalation in actinide chemistry is kinetic data on a multiple-pathway transformation involving formation of $[(C_5Me_5)_2Th(\mu\text{-}CH_2)_2EMe_2]$ from $[(C_5Me_5)_2ThR_2]$ (R = CH_2EMe_3; E = C, Si).[11]

We report here the first crystallographically characterized tuck-in complex of an f element and the first crystallographic data on uranium tuck-in and tuck-over structures. Both are found in the same structure (Figure 1). This bonding mode has not been observed previously in any metal complex of ligands derived from $C_5Me_5^-$ to our knowledge.

Recent results on the chemistry of actinide hydride complexes[22,23] made it desirable to determine if the equilibrium between tetravalent $[\{(C_5Me_5)_2UH_2\}_2]$ (**5**)[24] and trivalent $[\{(C_5Me_5)_2UH\}_2]$ (**6**)[24] could be shifted to form pure **6** by heating. When the mixture of **5** and **6** was heated to 110 °C in toluene, complex **7** was generated [Equation (1)].

X-ray crystallography revealed the structure of complex **7** (Figure 1). A doubly-metalated $[\mu\text{-}\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_3(CH_2)_2]^{3-}$ ligand is engaged in both tuck-in and tuck-over binding to uranium. The large thermal ellipsoids in the C1–C5 ring are likely the result of multiple ring orientations. However,

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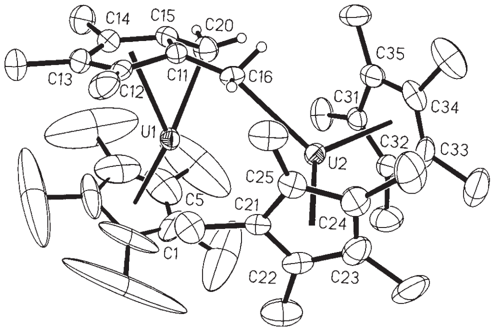
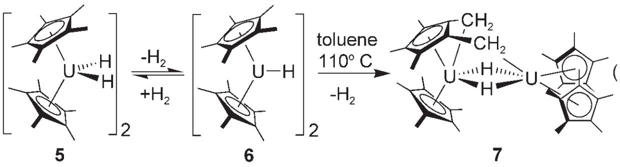


Figure 1. Molecular structure of **7** (thermal ellipsoid drawn at the 50% probability level).



(1)

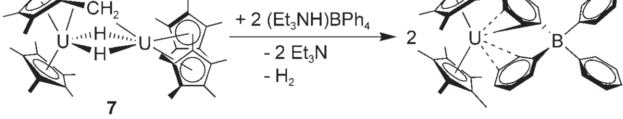
5 **6** **7**

resolution limits in the X-ray data were not adequate to propose a disordered model. Consequently, the disorder was treated as high thermal activity. Although the bridging hydride ligands were not located in the X-ray crystal structure, their presence was established by other means. Attempts to prepare a diamagnetic thorium analog according to Equation (1) were unsuccessful.

The infrared spectrum of **7** displayed a broad band centered at 1164 cm^{-1} in the region typical for U-H-U stretching modes. This absorption band is similar to those observed for both **5** and **6**,[22,24] which give rise to broad bands centered at 1188 and 1176 cm^{-1}, respectively. Attempts to synthesize a deuterium analog of **7** were thwarted by the fact that neither $[\{(C_5Me_5)_2UD_2\}_2]$ nor $[\{(C_5Me_5)_2UD\}_2]$ were accessible due to hydride exchange with the $C_5Me_5^-$ rings.[24] The infrared spectrum of the product made according to Equation (1), but from precursors synthesized from $[(C_5Me_5)_2UMe_2]$ and D_2, was identical to that of **7**.

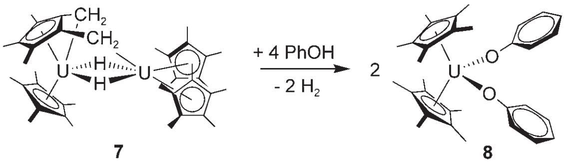
The presence of hydrides in **7** was probed by measuring the gas evolution during the synthesis of **7** from **6**[22] by means of a Toepler pump. Only one equivalent of dihydrogen per two uranium atoms was obtained as shown in Equation (1). Two equivalents of dihydrogen would be expected, if a U^{3+} complex without hydride ligands was formed instead of **7**.

The presence of hydrides was also shown by the reactions in Equation (2) and (3). Complex **7** reacts with $(Et_3NH)BPh_4$ to form the cation $[(C_5Me_5)_2U]BPh_4$[25] cleanly with evolution of hydrogen as monitored by ^1H NMR spectroscopy and Toepler pump [Eq. (2)]. The yield of H_2 was only 53% of that expected, but if no hydrides were present in **7**, only simple protonation of the methylene groups would occur.



(2)

7



(3)

7 **8**

The reactions of **7** with phenol and C_6H_5OD gave further support for the presence of hydrides. Reaction of **7** with phenol yields H_2 and the bis(phenoxide) complex $[(C_5Me_5)_2U(OPh)_2]$ (**8**) in 92% yield [Eq. (3)]. The identity of **8** was confirmed by X-ray crystallography (Figure 2). Reaction of **7** with C_6H_5OD gave HD[28] and a product that had ^2D NMR resonances at 3.1 ppm consistent with the presence of deuterium in place of hydrogen in $C_5Me_5^-$ rings of **8**.

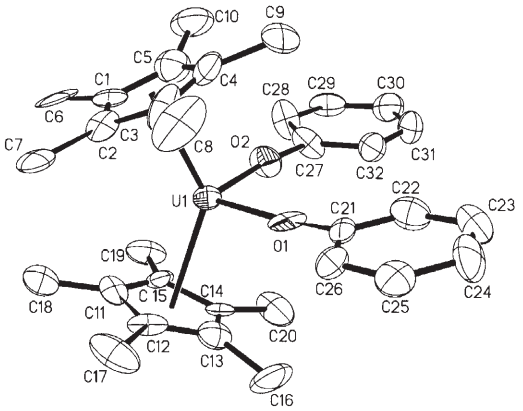


Figure 2. Molecular structure of **8** (thermal ellipsoid drawn at the 50% probability level). The structure is similar to those of $[(C_5Me_5)_2U(EPh)_2]$ (E = S, Se)[26] except the U-O1-C21 and U-O2-C27 angles (174(1) and 172(1)°) are larger.[27]

The structure of **7** contains two uranium atoms separated by 3.7917(5) Å, a distance intermediate between the U⋯U distances in tetravalent **5** (3.606(6) Å) and trivalent **6** (3.8530(7) and 3.8651(7) Å).[22] The larger distance in **7** vs **5** is consistent with the more extensive bridging structure that includes the tuck-over unit. The presence of the two “tuck” units in the C11–C15 ring led to significant variation of the U−C bond lengths to that ring, although the ring planarity is not affected and the C−C distances are equivalent within the error limits. The ring carbon atoms attached to the methylene groups, C11 and C15, have the shortest $U1{-}C_{ring}$ distances (2.422(6) and 2.436(7) Å), for C12 and C14 these distances are 2.709(6) and 2.783(8) Å, and the ring carbon most distant from the methylene groups has a U1−C13 bond length of 2.935(7) Å.

The U2−C16 tuck-over linkage (2.640(1) Å) is longer than typical $U{-}C_{alkyl}$ single bonds (for example, 2.414(7) and 2.424(7) Å for $U{-}C_{Me}$ in $[(C_5Me_5)_2UMe_2]$[29]). This is consistent with the long Ln−C bonds of the CH_2 tuck-over groups observed in lanthanide complexes.[14–19] The U1−C16 distance (2.722(8) Å) is in the broad range of $U{-}C_{C_5Me_5}$ distances, and hence C16 may also transfer electron density to U1. A similar situation is seen in the lanthanide tuck-over complexes.[14–19]

The U1–C20 distance, the first structurally characterized bond length between an f element and the carbon atom of a CH_2 tuck-in group, is 2.564(1) Å. Hence, this bond is longer than a terminal alkyl bond, as expected for bridging ligands, but it is not as long as for a methylene bridge attached to a second metallocene. In comparison, the Ti–CH_2 distance in **1** is very similar to a Ti^{3+}–C_{alkyl} bond.[7]

The isolation of **7** raises several basic questions about the reactivity of U–H groups. Although it is reasonable that a U–H group in **6** can metalate a methyl group in $C_5Me_5^-$, as has previously been observed with Ln–H bonds,[14,16] a sigma-bond metathesis with elimination of H_2 would lead to a trivalent $[(C_5Me_5)U(C_5Me_4CH_2)]$ moiety from one of the $\{(C_5Me_5)_2UH\}$ units in dimeric **6**. It is not clear how or why a second metalation would occur at the $C_5Me_4CH_2^{2-}$ ligand to form the observed tuck-in and tuck-over structure. It is possible that the hydride ligands in **7** are formed by reduction of H_2 with U^{3+} ions in the same way that hydride ligands in **5** are formed from H_2 and **6** in the reverse of the equilibrium in Equation (1). Hence, as the $C_5Me_5^-$ rings are being metalated, the H_2 produced in this process may react with the U^{3+} centers before it leaves the metal coordination sphere.

Clearly, the chemistry of uranium metallocene hydrides has some extra dimensions that have not yet been fully explored. New uranium hydrides are accessible that combine hydride and alkyl functionality. In addition, double C–H activation is possible in this class of compounds to form tuck-in and tuck-over structures in a single complex. In any case, the long sought crystallographic evidence for the postulated f element tuck-in intermediates has been obtained and the existence of both tuck-in and tuck-over structures for actinides has been established.

Experimental Section

7: In a glovebox, a green-brown solution of a 1:1 mixture of **5** and **6** (248 mg, 0.244 mmol) in toluene (10 mL) was heated to 110 °C for 3 minutes with frequent venting. The mixture was allowed to cool slowly to room temperature, and solvent was removed under reduced pressure to yield a green oil. A concentrated solution in toluene (3 mL) produced dark green crystals of **7** (188 mg, 0.185 mmol, 75 %) after 2 days at −35 °C. ^1H NMR (C_6D_6, 298 K): $\delta = -23.9$ (br s, 30 H, $C_5\mathit{Me}_5$, $\Delta\nu_{1/2} = 600$ Hz), −2.6 ppm (s, 15 H, $C_5\mathit{Me}_5$, $\Delta\nu_{1/2} = 8$ Hz), [−0.3 (s, 2 H), 1.5 (s, 3 H), 1.1 (s, 2 H), $C_5Me_5(CH_2)_2$]. ^1H NMR (C_6D_6, 343 K): $\delta = -19.3$ (s, 30 H, $C_5\mathit{Me}_5$, $\Delta\nu_{1/2} = 70$ Hz), −7.7 (s), −1.5 (s, 15 H, $C_5\mathit{Me}_5$, $\Delta\nu_{1/2} = 11$ Hz), 3.4 (s), 1.2(s), 0.4(s). ^{13}C NMR (C_6D_6, 343 K): $\delta = -47.5$ ($C_5\mathit{Me}_5$), −58.6 ($C_5\mathit{Me}_5$), 126.0 (C_5Me_5), 129.7 ppm (C_5Me_5). IR (KBr): $\tilde{\nu} = 2966$ (m), 2903 (vs), 2854 (vs), 2722 (w), 1434 (m), 1377 (m), 1164 (s), 1020 (s), 903 (m), 799 (m), 586 (m) cm^{-1}. Elemental analysis calcd for $C_{40}H_{60}U_2$: C 47.24, H 5.95, U 46.81; found: C 47.58, H 5.91, U 46.43.

7: A sealable Schlenk flask fitted with a Teflon stopper was charged with **6** (499 mg, 0.490 mmol) in toluene (20 mL). After four freeze-pump-thaw cycles, the solution was heated to 110 °C for 20 minutes. The reaction mixture was frozen in liquid nitrogen and evacuated using a Toepler pump equipped with a U-trap cooled in liquid nitrogen. The non-condensable gas was collected (9.8 μmol, 0.93 equiv) and subsequently analyzed by ^1H NMR spectroscopy in C_6D_6 to be H_2 (single resonance at 4.46 ppm). The solvent from the reaction mixture was evaporated to dryness yielding **7** as a dark brown crystalline material (0.469 g, 94 %).

8: In a glovebox, a solution of PhOH (56 mg, 0.59 mmol) in toluene (3 mL) was added to a stirred solution of dark green **7** (152 mg, 0.150 mmol) in toluene (5 mL). The solution immediately turned dark orange. After the mixture was stirred overnight, the solution was evaporated to dryness to yield **8** as a dark orange crystalline powder (192 mg, 92 %). Crystals of **8** suitable for X-ray diffraction studies were grown at −35 °C from a concentrated toluene solution. ^1H NMR (500 MHz, C_6D_6): $\delta = 3.19$ (s, 30 H, C_5Me_5, $\Delta\nu_{1/2} = 5$ Hz), 3.9 (t, 2 H, $^3J_{H,H} = 8$ Hz, *p*-H), 1.8 (t, 4 H, $^3J_{H,H} = 8$ Hz, *m*-H), −13.6 ppm (d, 4 H, $^3J_{H,H} = 8$ Hz, *p*-H). ^{13}C NMR (125 MHz, C_6D_6): $\delta = -32.8$ ($C_5\mathit{Me}_5$), 141.1 (C_5Me_5), 125.1 (*m*-Ph), 104.1 (*o*-Ph), 108.1 ppm (*p*-Ph). IR (KBr): $\tilde{\nu} = 2972$ (m), 2907 (m), 2857 (m), 1588 (vs), 1489 (vs), 1475 (vs), 1377 (w), 1252 (vs), 1276 (vs), 1160 (s), 1065 (m), 998 (m), 873 (vs), 863 (vs), 754 (vs), 691, 604 (s) cm^{-1}. C,H analysis calcd for $C_{32}H_{40}O_2U$: C 55.33, H 5.80; found: C 55.62, H 5.50.

In a similar experiment, **7** (12 mg, 0.012 mmol) in C_6D_6 was added to a J-Young tube containing a frozen slurry of $(Et_3NH)BPh_4$ (10 mg, 0.024 mmol) in C_6D_6. The J-Young tube was capped immediately and a color change from brown-green to brown was observed. ^1H NMR spectroscopy showed quantitative conversion of starting material to the previously characterized $[(C_5Me_5)_2U]BPh_4$[25] and H_2, which exhibited a ^1H NMR resonance at 4.46 ppm.

Compound **7** crystallizes in the space group $P\bar{1}$ with $a = 10.5198(17)$, $b = 11.0156(17)$, $c = 16.281(3)$ Å, $\alpha = 89.529(3)$, $\beta = 81.943(3)$, $\gamma = 80.842(3)°$, $V = 1844.0(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.828$ Mg m^{-3}, $R1 = 0.0436$ [$I > 2\sigma(I)$], $wR2 = 0.1114$, GOF = 1.047. Compound **8** crystallizes in the space group $P\bar{1}$ with $a = 9.409(2)$, $b = 9.667(2)$, $c = 17.020(4)$ Å, $\alpha = 99.753(4)$, $\beta = 96.714(4)$, $\gamma = 108.070(4)°$, $V = 1426.6(6)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.617$ Mg m^{-3}, $R1 = 0.078$ [$I > 2\sigma(I)$], $wR2 = 0.184$.

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