Ring-opening in the actinide cyclopropyl complexes [Cp_3U(2,2-diphenylcyclopropyl)]$^{n-}$ (n = 0, 1)

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Abstract

The reaction of [Cp_3UCl] with *in situ* generated 1-lithium-2,2-dipenylcyclopropane results in the formation of [Cp_3U(2,2-diphenylcyclopropyl)] (**1**), in good yield. Reduction of **1** with KC_8, in the presence of 2.2.2-cryptand, results in formation of a rare U(III) alkyl complex, [K(2.2.2-cryptand)][Cp_3U(2,2-diphenylcyclopropyl)] (**2**). Thermolysis or photolysis of **1** for 10 d in toluene results in isomerization to the U(IV) η^1-allyl complex, [$Cp_3U(\eta^1$-3,3-diphenylallyl)] (**3**). Moreover, photolysis of **2** in THF for 9 h at room temperature results in isomerization to the U(III) η^1-allyl complex, [K(2,2,2-cryptand)][$Cp_3U(\eta^1$-3,3-diphenylallyl)] (**4**). Both **3** and **4** were fully characterized. In addition, selective labelling of the C_α positions of **1** and **2** with deuterium revealed that cyclopropyl ring-opening occurs via distal C-C bond cleavage via a hypothesized η^3-allyl intermediate.

Introduction

The synthetic methods used by transition metal chemists to make carbene complexes do not often translate to the actinides.[1-4] For example, addition of diphenyldiazomethane to [Cp*$_2$U^{IV}(NAr)] (Ar = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) results in formation of the U(VI) hydrazido complex, [Cp*$_2$U^{VI}(NAr)(N$_2$CPh$_2$)], and not in N_2 elimination and carbene formation, as intended.[5] Similarly, reaction of [(($^{t\text{-Bu}}$ArO)$_3$tacn)U^{III}] with diphenyldiazomethane results in formation of [(($^{t\text{-Bu}}$ArO)$_3$tacn)U^{IV}(η^2-NNCPh$_2$)], which features an unusual open-shell mono-anionic hydrazido ligand.[6] Several other examples of similar diazoalkane reactivity with the actinides are also known.[6-13] α-H elimination, another common way to make transition metal carbenes,[14] has also never been seen in the actinides. Instead, other modes of reactivity are observed. For example, thermolysis of [Cp*$_2$Th(CH$_2$^{t}Bu)$_2$] result in formation of [Cp*$_2$Th(*cyclo*-*C*H$_2$CMe$_2$*C*H$_2$)] and neopentane via γ-H activation of a neopentyl ligand.[15] At this point, the only reliable synthetic route to an An=C bond is ligation of a deprotonated Wittig reagent or bis(iminophosphorane) to an actinide ion, which results in formation of heteroatom-stabilized actinide carbene complexes,[4, 16-21] such as [Cp*$_2$U(X)(CHPPh$_3$)] (X= Cl, Br, I),[17] [U{C(SiMe$_3$)(PPh$_2$)}(BIPM^{TMS})(Cl)]$^-$ (BIPM^{TMS} = C(PPh$_2$NSiMe$_3$)$_2$),[22] and [An(CHPPh$_3$)(NR$_2$)$_3$] (An = Th, U; R = SiMe$_3$).[23, 24]

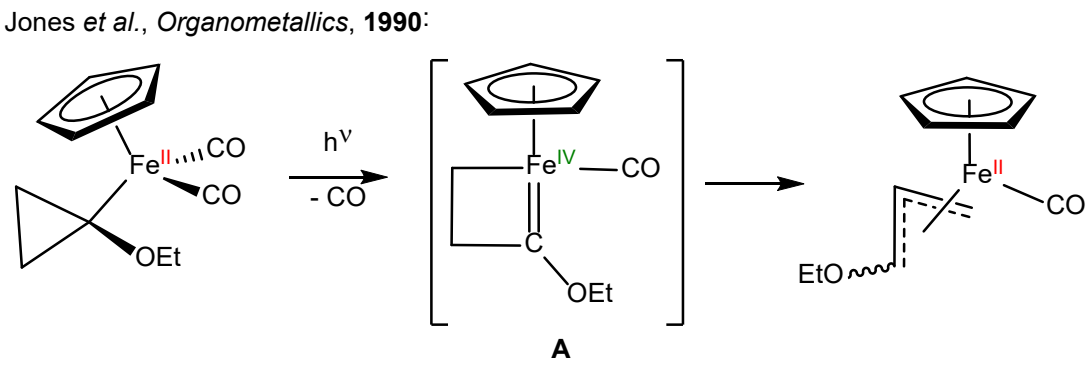
In an effort to find new routes to An=C and An≡C bonds, we have turned our attention to less common carbene and carbyne sources. For example, we recently reported the isolation of the first An allenylidenes, [{(NR$_2$)$_3$}An(CCCPh$_2$)]$^-$ (An = U, Th; R = SiMe$_3$), which were accessed by deprotonation of the An-allenyl complexes [{(NR$_2$)$_3$}An(CH=C=CPh$_2$)],[25] which themselves were made via reaction of

[AnCl$(NR_2)_3$] with 1-lithium-3,3-diphenylcyclopropene. Notably, [{$(NR_2)_3$}An$(CCCPh_2)$]$^-$ were the first reported An carbenes that contain no heteroatom stabilization. In addition, we reported the thermal ring-opening of [Cp_3Th(3,3-diphenylcyclopropenyl) to give [Cp_3Th(3-phenyl-1*H*-inden-1-yl)].[26] Calculations suggest that this reaction proceeds via a triplet metallocarbene. However, this proposed intermediate could not be observed. Similarly, the U(III) bis(diisopropylamino)cyclopropenylidene adduct, [$(NR_2)_3$U(BAC)] (R = $SiMe_3$) rearranges upon heating to give the ring-opened U(IV) product, [$(NR_2)_2$U{*N*(R)($SiMe_2$CH=C(N^iPr_2)C(N^iPr_2)=*C*H)}], which we hypothesized was also formed via an unobserved carbene intermediate.[27] Finally, reduction of the U(III) isocyanide, [U$(NR_2)_3$(CN-2,6-$Me_2C_6H_3)_2$], resulted in isocyanide coupling, and not aminocarbyne formation, as originally hoped.[28, 29]

Building on this work, we have continued to search for non-traditional routes to actinide carbenes. One possible route to a metal carbene is the ring-opening of a cyclopropyl ligand via a proximal C-C bond (Scheme 1).[30, 31] In particular, Jones and co-workers reported that photolysis of [CpFe$(CO)_2$(1-ethoxycyclopropyl)] generates a transient metallocyclocarbene **A**, which was identified by an Fe=C resonance at 335.0 ppm in its ^{13}C NMR spectrum.[30] This species subsequently isomerized to an η^3-allyl complex on standing. Also of note, [Cp^*_2Y(μ-*cyclo*-$C_3H_5)_2$Li(THF)], [Tp^{Me2}NbCl(*cyclo*-C_3H_5)(η^2-MeC≡CMe)], and [^{Me}LSc(*cyclo*-$C_3H_5)_2$] (^{Me}L = ArNC(Me)CHC(Me)NAr, Ar = 2,6-$^i Pr_2C_6H_3$) exhibit α-C–C agostic interactions in the solid-state, which can be viewed as a prelude to proximal C-C activation.[32-34] However, ring-opening via a distal C-C bond has also be observed. This mechanism of

cyclopropyl ring-opening directly provides an η^3-allyl complex and is likely operative in [Cp*W(NO)(*cyclo*-C_3H_5)R] (R = CH_2SiMe_3, CH_2Ph, $CH_2{}^tBu$)[35, 36] and [Tp^{Me2}Nb(*cyclo*-C_3H_5)(C_6F_5)(η^2-MeC≡CMe)].[37] The mechanism of cyclopropyl ring opening in [$Cp^*{}_2$Sm(*cyclo*-1-Me-2-Ph-C_3H_3)] has also been calculated using DFT. In this particular case, distal C-C activation was calculated to occur with an activation barrier of 27-35 kcal/mol, depending on the conformer.[38] Intriguingly, coordination of the phenyl substituent to the Sm center was found to lower the barrier of activation.

Scheme 1. Generation of an iron carbene via cyclopropyl ring-opening.[30]

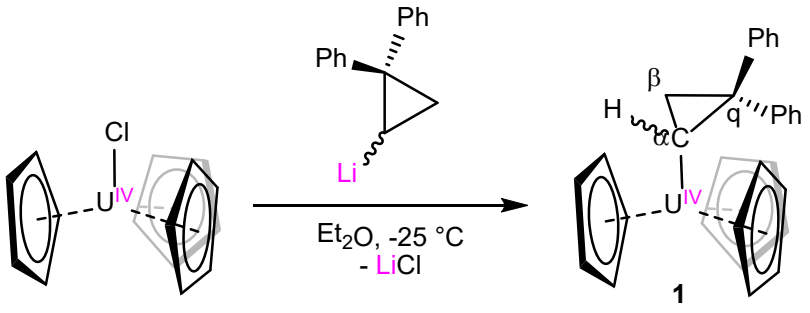


Herein, we report the synthesis, isolation, and ring-opening reactivity of [Cp_3U(2,2-diphenylcyclopropyl)] and its isostructural U(III) analogue, which represent the first structurally-characterized f element cyclopropyl complexes. Additionally, we investigate the mechanism of ring-opening by selectively labelling the cyclopropyl ligand with deuterium. This cyclopropyl ligand was chosen, in part, because we thought the phenyl groups at the 2-position would bias the ring in favor of proximal activation, either via steric or electronic effects.

Results and discussion

Reaction of [Cp_3UCl] with *in situ* generated 1-lithium-2,2-diphenylcyclopropane[39] in Et_2O results in formation of [Cp_3U(2,2-diphenylcyclopropyl)] (**1**), which can be isolated as brown plates in 63% yield after removal of the volatiles, extraction into toluene, filtration, and crystallization (Scheme 2). The ^{1}H NMR spectrum of **1** in benzene-d_6 features a diagnostic H_α resonance at –170.26 ppm and diastereotopic H_β resonances at –17.07 and –23.12 ppm. These three resonances are present in a 1:1:1 ratio, consistent with the proposed formulation. In addition, complex **1** exhibits a single Cp environment at –3.41 ppm (Figure S3). The UV-vis spectrum of **1** features a broad transition centered at 475 nm ($\varepsilon = 835\ cm^{-1}\cdot M^{-1}$), which we have tentatively assigned to a LMCT transition (Figure S23). This spectrum also features many sharp, weak absorptions between 500 to 750 nm, which are assignable to Laporte forbidden 5f → 5f transitions.[12, 40, 41] Complex **1** represents a rare example of an actinide cyclopropyl complex. To our knowledge, only one other example is known, namely, [Cp^*_2Th(*cyclo*-$C_3H_5)_2$], but it was not structurally characterized.[42]

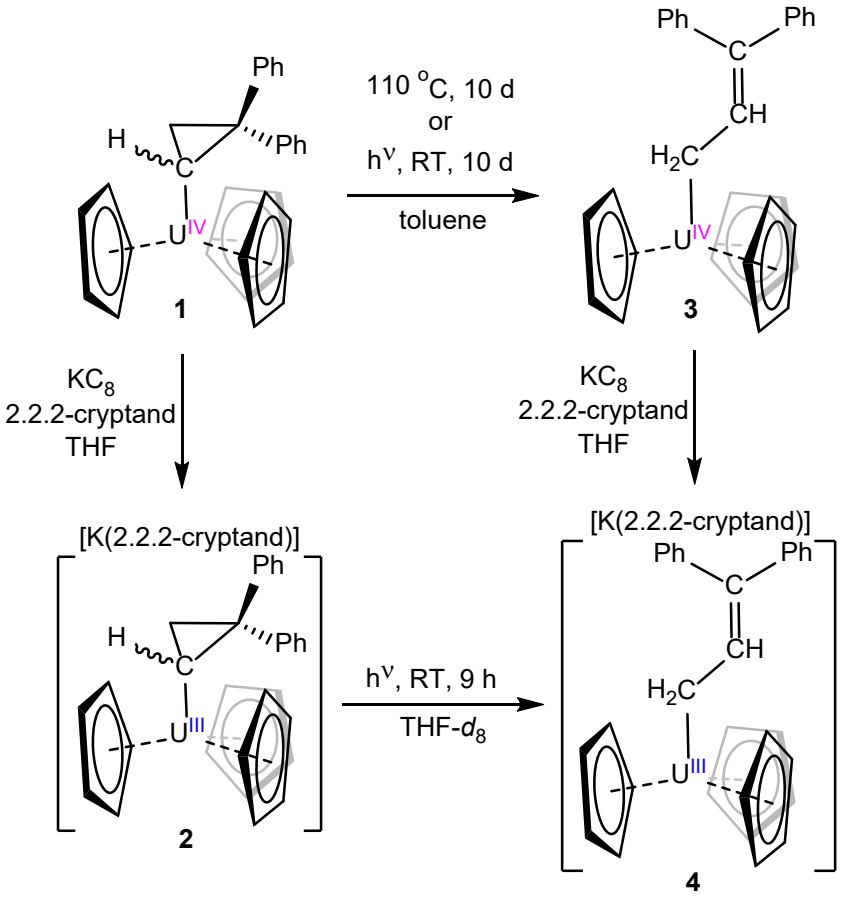
Scheme 2. Synthesis of complex **1**



Complex **1** crystallizes in the orthorhombic space group *C*mca. It exhibits substantial positional disorder of both the Cp and 2,2-diphenylcyclopropyl ligands. Due to the extreme positional disorder, H atoms were not assigned to either the Cp and 2,2-diphenylcyclopropyl

ligands. Nonetheless, the connectivity of **1** was confirmed (Figure S1). In an attempt to grow crystals of complex **1** in a different crystal system, it was crystalized from Et_2O, THF, dichloromethane, chlorobenzene, and dimethoxyethane. In all instances, however, these crystallizations result in nicely-diffracting needles that still featured the same *C*mca unit cell.

Scheme 3. Synthesis of complexes **2**, **3**, and **4**.



Reaction of **1** with 1 equiv of KC_8 in THF, in the presence of 2.2.2-cryptand, results in formation of a dark red solution, from which [K(2.2.2-cryptand)][Cp_3U(2,2-diphenylcyclopropyl)] (**2**) can be isolated in 88% yield after work-up (Scheme 3). The ^{1}H NMR spectrum of **2** in THF-d_8 features a diagnostic H_α resonance at –88.03 ppm and diastereotopic

H_β resonances at –1.32 and –5.46 ppm. These resonances are present in a 1:1:1 ratio. In addition, complex **2** exhibits a single Cp environment at –15.05 ppm (Figure S6). Its UV-vis spectrum of **2** features broad transitions centered at 385 nm (ε = 880 $cm^{-1}\cdot M^{-1}$) and 478 (ε = 765 $cm^{-1}\cdot M^{-1}$), which we have tentatively assigned to 6d → 5f transitions. In addition, we observe several weak, broad absorptions between 530 to 800 nm, which are consistent with Laporte forbidden 5f → 5f transitions (Figure S24).

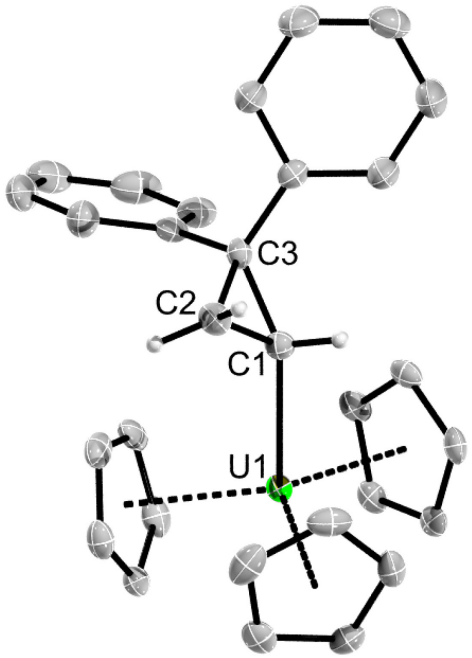


Figure 1. Solid state molecular structure of **2**·0.5THF, shown with thermal ellipsoids set at 50% probability. The $[K(2.2.2\text{-cryptand})]^+$ cation, THF solvate, and hydrogen atoms (except those of C_α and C_β) are omitted for clarity. Selected bond lengths [Å] and angles [deg]: U–C1 = 2.526(4), C1–C2 = 1.533(5), C1–C3 = 1.525(5), C2–C3 = 1.506(5), U–C1–C2 = 126.7(3), U–C1–C3 = 142.8(3).

Complex **2** crystallizes in the triclinic space group $P\bar{1}$ as the THF solvate, **2**·0.5THF (Figure 1). Unlike **1**, complex **2** crystallizes without disorder, permitting an accurate assessment of its metrical parameters. The U-C distance in **2** is 2.526(4) Å, which is similar to those of other σ-bonded uranium(III) hydrocarbyl complexes.[43-46] For example, the U–C bond distances in [Li(2.1.1-cryptand)][$Cp_3U(n\text{-}C_4H_9)$], [$Tp^*U(CH_2Ph)_2(THF)$], [Tp^*_2UMe], and [$Cp^*TpU(CH_2SiMe_3)(THF)$] are 2.557(9), 2.604(9) and 2.615(7), 2.54(3), and 2.557(12) Å, respectively.[43, 44, 47, 48] Moreover, the C_α–C_β (1.533(5) Å), C_α–C_q (1.525(5) Å), and C_β–C_q (1.506(5) Å) distances in **2** are consistent with the presence of C-C single bonds. Additionally, the sum of interatomic angles around C_α (329°) is consistent with sp^3 hybridization at this atom. To our knowledge, complexes **1** and **2** represent the first structurally characterized cyclopropyl complexes of the actinides, although many actinide metallacycles are known.[49]

Given the reactivity reported for [$CpFe(CO)_2$(1-ethoxycyclopropyl)],[30] we hypothesized that thermolysis of **1** could induce isomerization to afford a ring-opened uranium carbene complex. To this end, a red-brown toluene solution of **1**, in an NMR tube equipped with a J-Young valve, was thermolyzed for 10 d at 110 °C. The reaction mixture gradually changed from red-brown to dark yellow. Work-up of the resulting dark yellow solution resulted isolation of the U(IV) allyl complex, [$Cp_3U(\eta^1$-3,3-diphenylallyl)] (**3**), as dark yellow blocks in 35% yield (Scheme 3). The ^{1}H NMR spectrum of **3** in toluene-d_8 features a diagnostic H_α resonance at –212.5 ppm and an H_β resonance at –31.76 ppm. These resonances are present in a 2:1 ratio, consistent with the proposed formulation. In addition, complex **3** exhibits a single Cp environment at –2.87 ppm (Figure S9). Complex **3** can also be accessed by photolysis of **1**. In particular, photolysis of a red-brown toluene solution of **1**, using a water-jacketed, medium-pressure Hg

lamp, for 10 d at room temperature also results in formation of a dark yellow solution. Work-up of this solution results in the isolation of **3** in 38% yield (Scheme 3). Note that the ^{1}H NMR spectra of the crude reaction mixtures, for either the photolysis or thermolysis reactions, are quite clean, suggesting that the modest yields are due to challenges with crystallization. To our knowledge, these reactions represent the first examples of cyclopropyl ring-opening in complexes of the actinides.

Complex **2** can also undergo cyclopropyl ring opening. In particular, photolysis of a dark red THF solution of **2** using a water-jacketed, medium-pressure Hg lamp, in an NMR tube equipped with a J-Young valve, for 9 h at room temperature resulted in a color change to dark yellow-orange. Work-up of the reaction mixture resulted the isolation of the ring-opened product, [K(2.2.2-cryptand)][$Cp_3U(\eta^1$-3,3-diphenylallyl)] (**4**), as dark yellow plates in 53% yield (Scheme 3). The ^{1}H NMR spectrum of **4** in THF-d_8 features a diagnostic H_α resonance at –118.19 ppm and a H_β resonance at –20.13 ppm, which are present in a 2:1 ratio, respectively. In addition, complex **4** exhibits a single Cp environment at –14.98 ppm (Figure S16). Complex **4** can also be access by reduction of **3**. In particular, reaction of **3** with 1 equiv of KC_8 in THF, in the presence of 2.2.2-cryptand, affords **4** in 40% yield after work-up (Scheme 3). Interestingly, attempts to effect the thermal ring-opening of complex **2** were unsuccessful. Complex **2** is insoluble in toluene, which precluded thermolysis in that solvent, while thermolysis of a THF solution of **2** at 65 °C resulted in no reaction over the course of 48 h.

Complexes **3** and **4** both crystallize in the triclinic space group $P\bar{1}$ (Figures 2 and S2). Complex **3** crystallizes as the toluene solvate, **3**·C_7H_8, whereas **4** crystallizes as the THF solvate, **4**·THF. The U-C distance in **3** is 2.532(4) Å, which is consistent with those found in other U(IV) η^1-

allyl complexes. For example, the relevant U-C distances in [Cp*$_2$U(η^3-$CH_2C(R)CH_2$)(η^1-$CH_2C(R)=CH_2$)] (R = H, Me) are 2.526(3) Å and 2.538(1) Å, respectively.[50] Not surprisingly, the U-C distance in **4** (2.59(1) Å) is longer than that observed for **3**, consistent with the larger ionic radius of U(III).[51] The C_α–C_β distances in **3** and **4** are 1.463(6) Å and 1.42(1) Å, respectively, which are consistent with C-C single bonds, whereas the C_β–C_γ distances in **3** (1.364(6) Å) and **4** (1.39(1) Å) are consistent with double bond character. The sum of angles around C_γ are also consistent with sp^2 hybridization (**3**: Σ(C-C_γ-C) = 360°; **4**: Σ(C-C_γ-C) = 360°). Overall, these data confirm the presence of a η^1-allyl ligand in **3** and **4**.

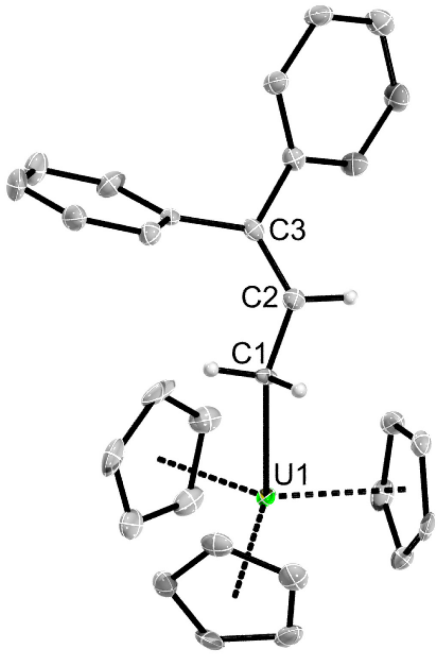


Figure 2. Solid state molecular structure of **3**, shown with thermal ellipsoids set at 50% probability. The toluene solvate and hydrogen atoms (except those of C_α and C_β) are omitted for clarity. Selected bond lengths [Å] and angles [deg]: **3**: U–C1 = 2.532(4), C1–C2 = 1.463(6),

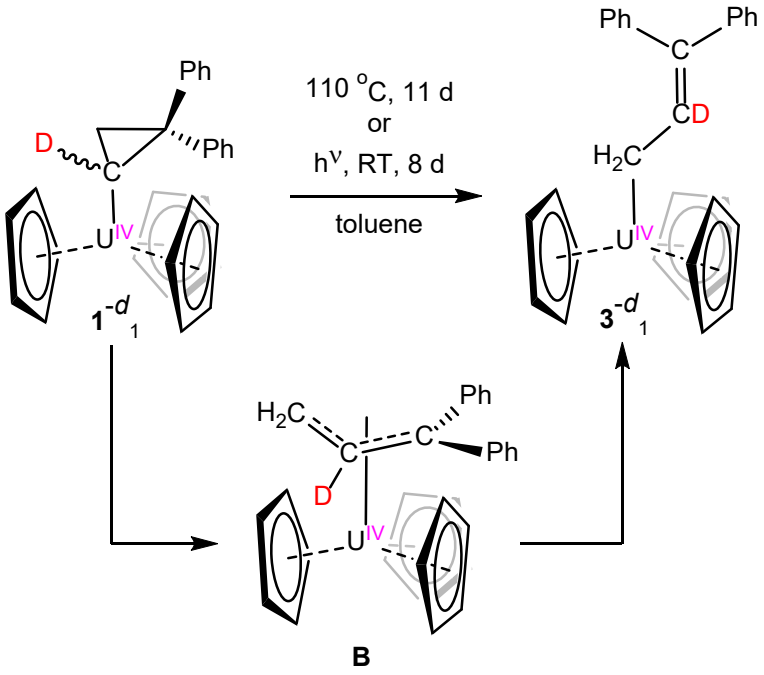
C2–C3 = 1.364(6), U–C1–C2 = 119.5(3), C1–C2–C3 = 129.7(4). **4**: U–C1 = 2.59(1), C1–C2 = 1.42(1), C2–C3 = 1.39(1), U–C1–C2 = 121.1(8), C1–C2–C3 = 133(1).

To probe if the cyclopropyl ring-opening is occuring via proximal or distal C-C activation, we selectively labelled the C_α position of **1** with deuterium. Access to **1**-d_1 was achieved by reaction of [Cp_3UCl] with *in situ* generated 1-lithium-1-deuterio-2,2-diphenylcyclopropane in Et_2O.[52] Complex **1**-d_1 can be isolated as brown plates in 65% yield after work up. Its ^{1}H NMR spectrum is nearly identical to that of **1**, except that the H_α resonance is absent (Figure S4). As expected, the ^{2}H NMR spectrum of **1**-d_1 features a single resonance at –171.54 ppm, assignable to the D_α environment (Figure S5). Subsequent reaction of **1**-d_1 with 1 equiv of KC_8 in THF, in the presence of 2.2.2-cryptand, results in formation of a dark red solution, from which **2**-d_1 can be isolated in 67% yield. Its ^{2}H NMR spectrum features a single resonance at –87.43 ppm assignable to the D_α environment (Figure S8). Importantly, no other resonances are present in the ^{2}H NMR spectra of **1**-d_1 and **2**-d_1, indicative of selective labelling at the C_α position without any deuterium scrambling.

Thermolysis of a red-brown toluene solution of **1**-d_1, in an NMR tube equipped with a J-Young valve, at 110 °C for 11 d resulted in formation of a deep yellow solution. Work-up of this solution provided the U(IV) allyl complex, [Cp_3U(η^1-2-deutero-3,3-diphenylallyl)] (**3**-d_1), as dark yellow blocks in 42% yield (Scheme 4). Its ^{2}H NMR spectrum in toluene-h_8 features one resonance at –31.82 ppm assignable to the D_β environment (Figure S12). No other resonances are present in this spectrum. In addition, the ^{1}H NMR spectrum of **3**-d_1 in toluene-d_8 features a diagnostic H_α resonance at –212.5 ppm (Figure S11). No resonance is observed for the H_β environment in this spectrum. Overall, the ^{2}H and ^{1}H NMR spectra are consistent with a distal

ring-opening pathway to afford an η^3-allyl intermediate (**B**), which then isomerizes to give the η^1-allyl product, **3**-d_1. Photolysis of a red-brown toluene solution of **1**-d_1 using a water-jacketed, medium-pressure Hg lamp for 8 d at room temperature, also results in formation of **3**-d_1. The ^{1}H and ^{2}H NMR spectra of this material are also consistent with isomerization via selective distal C-C bond cleavage (Figure S13 and S14).

Scheme 4. Synthesis of complex **3**-d_1.



We also examined the cyclopropyl ring-opening of complex **2**. In particular, photolysis of a dark red THF solution of **2**-d_1 using a water-jacketed, medium-pressure Hg lamp, in an NMR tube equipped with a J-Young valve, for 24 h at room temperature resulted in a color change to dark yellow-orange. The ^{2}H NMR spectrum of this mixture in THF-h_8 featured a single resonance at –19.36 ppm, which assignable to the D_β environment of **4**-d_1 (Figure S18). The ^{1}H NMR spectrum of a comparably generated reaction mixture in THF-d_8 features a diagnostic

H_α resonance at –118.30 ppm, but no resonance assignable to the H_β environment (Figure S17). As was observed for **3**-d_1, the spectral data for **4**-d_1 are consistent with selective distal C-C bond cleavage. Interestingly, Chen and co-workers also utilized selective deuterium labelling to investigate cyclopropyl reactivity. In their case, they discovered that cyclopropane elimination from [$L^{Me}Sc(cyclo\text{-}C_3H_5)_2$] occurs via direct hydrogen abstraction from an isopropyl methine carbon.[33]

Conclusion

In summary, we isolated [Cp_3U(2,2-diphenylcyclopropyl)] via salt metathesis of [Cp_3UCl] with *in situ* generated 1-lithium-2,2-diphenylcyclopropane. Thermolysis or photolysis of this complex results in ring-opening of the cyclopropyl ring, which results in formation of an η^1-allyl complex, [$Cp_3U(\eta^1$-3,3-diphenylallyl)]. Similar results are observed upon photolysis of its U(III) analogue, [K(2.2.2-cryptand)][Cp_3U(2,2-diphenylcyclopropyl)]. Deuterium labelling studies demonstrate that ring-opening occurs exclusively via distal C-C bond cleavage, via an unobserved η^3-allyl intermediate, despite the apparent steric unfavorability of the diphenyl-substituted η^3-3,3-diphenylallyl ligand. Notably, we observed no evidence for proximal activation, regardless of uranium oxidation state or mechanism of activation (i.e., thermolysis or photolysis), demonstrating that the phenyl substituents cannot override the preference for distal activation. This reactivity contrasts with that observed for [$CpFe(CO)_2$(1-ethoxycyclopropyl)],[30] which can exhibit proximal C-C cleavage, and highlights the potential importance of the α-carbon substituent in directing the mode of activation (Scheme 1). Moving forward, we plan to further examine the reactivity of actinide cyclopropyl complexes,

especially cyclopropyl complexes with heteroatom substituents on the α-carbon, in pursuit of non-traditional routes to access actinide carbon multiple bonds.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, crystallographic details, computational results, and spectral data for complexes **1**, **2**·THF, **3**·toluene, and **4**·THF (PDF). This material is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interests.

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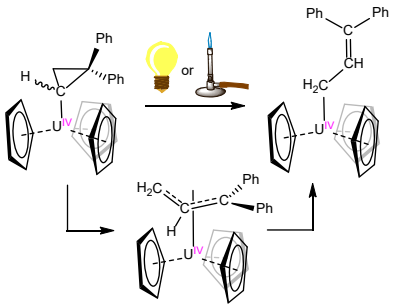
References

1. Hayton, T. W., Recent developments in actinide-ligand multiple bonding. *Chem. Commun.* **2013**, *49*, 2956-2973.
2. Hayton, T. W., Metal-ligand multiple bonding in uranium: structure and reactivity. *Dalton Trans.* **2010**, *39*, 1145-1158.
3. Liddle, S. T., The Renaissance of Non-Aqueous Uranium Chemistry. *Angew. Chem. Int. Ed.* **2015**, *54*, 8604-8641.
4. Gregson, M.; Wooles, A. J.; Cooper, O. J.; Liddle, S. T., Covalent Uranium Carbene Chemistry. *Comments Inorg. Chem.* **2015**, *35*, 262-294.
5. Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J., Enhancing the reactivity of uranium(vi) organoimido complexes with diazoalkanes. *Chem. Commun.* **2002**, 30-31.
6. Lam, O. P.; Feng, P. L.; Heinemann, F. W.; O'Connor, J. M.; Meyer, K., Charge-Separation in Uranium Diazomethane Complexes Leading to C-H Activation and Chemical Transformation. *J. Am. Chem. Soc.* **2008**, *130*, 2806-2816.
7. Roussel, P.; Boaretto, R.; Kingsley, A. J.; Alcock, N. W.; Scott, P., Reactivity of a triamidoamine complex of trivalent uranium. *J. Chem. Soc., Dalton Trans.* **2002**, 1423-1428.
8. Ren, W.; Zhou, E.; Fang, B.; Hou, G.; Zi, G.; Fang, D.-C.; Walter, M. D., Experimental and Computational Studies on the Reactivity of a Terminal Thorium Imidometallocene towards Organic Azides and Diazoalkanes. *Angew. Chem. Int. Ed.* **2014**, *53*, 11310-11314.
9. Matson, E. M.; Fanwick, P. E.; Bart, S. C., Diazoalkane Reduction for the Synthesis of Uranium Hydrazonido Complexes. *Eur. J. Inorg. Chem.* **2012**, *2012*, 5471-5478.
10. Settineri, N. S.; Shiau, A. A.; Arnold, J., Two-electron oxidation of a homoleptic U(III) guanidinate complex by diphenyldiazomethane. *Chem. Commun.* **2018**, *54*, 10913-10916.
11. Cantat, T.; Graves, C. R.; Scott, B. L.; Kiplinger, J. L., Challenging the Metallocene Dominance in Actinide Chemistry with a Soft PNP Pincer Ligand: New Uranium Structures and Reactivity Patterns. *Angew. Chem. Int. Ed.* **2009**, *48*, 3681-3684.
12. Gardner, B. M.; Patel, D.; Lewis, W.; Blake, A. J.; Liddle, S. T., Photochemically Promoted Bond-Cleavage and -Capture in a Diazomethane Derivative of a Triamidoamine Uranium(IV) Complex. *Angew. Chem. Int. Ed.* **2011**, *50*, 10440-10443.
13. Kiplinger, J. L.; John, K. D.; Morris, D. E.; Scott, B. L.; Burns, C. J., [(C5Me5)2U(Me)(OTf)]2: A New Reagent for Uranium Metallocene Chemistry. Preparation of the First Actinide Hydrazonato Complexes. *Organometallics* **2002**, *21*, 4306-4308.
14. Crabtree, R. H., The Organometallic Chemistry of the Transition Metals. 3rd ed.; John Wiley & Sons: New York, 2001; pp 292-337.
15. Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M., C-H Activation Mechanisms and Regioselectivity in the Cyclometallation Reactions of Bis(pentamethylcyclopentadienyl)thorium Dialkyl Complexes. *J. Am. Chem. Soc.* **1986**, *108*, 40-56.
16. Rungthanaphatsophon, P.; Bathelier, A.; Castro, L.; Behrle, A. C.; Barnes, C. L.; Maron, L.; Walensky, J. R., Formation of Methane versus Benzene in the Reactions of $(C_5Me_5)_2Th(CH_3)_2$ with $[CH_3PPh_3]X$ (X=Cl, Br, I) Yielding Thorium-Carbene or Thorium-Ylide Complexes. *Angew. Chem. Int. Ed.* **2017**, *56*, 12925-12929.
17. Rungthanaphatsophon, P.; Huang, P.; Walensky, J. R., Phosphorano-Stabilized Carbene Complexes with Short Thorium(IV)– and Uranium(IV)–Carbon Bonds. *Organometallics* **2018**, *37*, 1884-1891.
18. Cantat, T.; Arliguie, T.; Noël, A.; Thuéry, P.; Ephritikhine, M.; Floch, P. L.; Mézailles, N., The U=C Double Bond: Synthesis and Study of Uranium Nucleophilic Carbene Complexes. *J. Am. Chem. Soc.* **2009**, *131*, 963-972.
19. Ma, G.; Ferguson, M. J.; McDonald, R.; Cavell, R. G., Actinide Metals with Multiple Bonds to Carbon: Synthesis, Characterization, and Reactivity of U(IV) and Th(IV) Bis(iminophosphorano)methandiide Pincer Carbene Complexes. *Inorg. Chem.* **2011**, *50*, 6500-6508.

20. Gregson, M.; Lu, E.; Mills, D. P.; Tuna, F.; McInnes, E. J. L.; Hennig, C.; Scheinost, A. C.; McMaster, J.; Lewis, W.; Blake, A. J.; Kerridge, A.; Liddle, S. T., The inverse-trans-influence in tetravalent lanthanide and actinide bis(carbene) complexes. *Nat. Commun.* **2017**, *8*, 14137.
21. Ren, W.; Deng, X.; Zi, G.; Fang, D.-C., The Th=C double bond: an experimental and computational study of thorium poly-carbene complexes. *Dalton Trans.* **2011**, *40*, 9662-9664.
22. Lu, E.; Boronski, J. T.; Gregson, M.; Wooles, A. J.; Liddle, S. T., Silyl-Phosphino-Carbene Complexes of Uranium(IV). *Angew. Chem. Int. Ed.* **2018**, *57*, 5506-5511.
23. Fortier, S.; Walensky, J. R.; Wu, G.; Hayton, T. W., Synthesis of a Phosphorano-Stabilized U(IV)-Carbene via One-Electron Oxidation of a U(III)-Ylide Adduct. *J. Am. Chem. Soc.* **2011**, *133*, 6894-6897.
24. Smiles, D. E.; Wu, G.; Hrobárik, P.; Hayton, T. W., Synthesis, Thermochemistry, Bonding, and ^{13}C NMR Chemical Shift Analysis of a Phosphorano-Stabilized Carbene of Thorium. *Organometallics* **2017**, *36*, 4519-4524.
25. Kent, G. T.; Yu, X.; Wu, G.; Autschbach, J.; Hayton, T. W., Synthesis and electronic structure analysis of the actinide allenylidenes, $[\{(NR_2)_3\}An(CCCPh_2)]^-$ (An = U, Th; R = $SiMe_3$). *Chem. Sci.* **2021**, *12*, 14383-14388.
26. Kent, G. T.; Yu, X.; Wu, G.; Autschbach, J.; Hayton, T. W., Ring-opening of a thorium cyclopropenyl complex generates a transient thorium-bound carbene. *Chem. Commun.* **2022**, *58*, 6805-6808.
27. Nguyen, T. H.; Yu, X.; Kent, G. T.; Autschbach, J.; Hayton, T. W., U-C Bond Insertion, Ring-opening, and C-H activation in a Uranium Bis(diisopropylamino)cyclopropenylidene (BAC) Adduct. *Organometallics* **2023**, *42*, 1005–1012.
28. Staun, S. L.; Kent, G. T.; Gomez-Torres, A.; Wu, G.; Fortier, S.; Hayton, T. W., Reductive Coupling of Xylyl Isocyanide Mediated by Low-Valent Uranium. *Organometallics* **2021**, *40*, 2934-2938.
29. Mokhtarzadeh, C. C.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S., A Highly-Reduced Cobalt Terminal Carbyne: Divergent Metal- and α-Carbon-Centered Reactivity. *J. Am. Chem. Soc.* **2018**, *140*, 8100-8104.
30. Conti, N. J.; Crowther, D. J.; Tivakornpannarai, S.; Jones, W. M., Rearrangements of cyclopropanes .sigma. bonded to iron: .alpha.-eliminations to carbene complexes and ring opening to .pi.-allyl complexes. *Organometallics* **1990**, *9*, 175-184.
31. Omrčen, T.; Conti, N. J.; Jones, W. M., Synthesis and ring-opening reactions of .alpha.-fluoro-substituted cyclopropanes .sigma.-bonded to iron. *Organometallics* **1991**, *10*, 913-917.
32. Jaffart, J.; Etienne, M.; Reinhold, M.; McGrady, J. E.; Maseras, F., An unprecedented α-C–C agostic interaction in a cyclopropyl tris(pyrazolyl)boratoniobium complex. *Chem. Commun.* **2003**, 876-877.
33. Xu, C.; Li, G.; Etienne, M.; Leng, X.; Chen, Y., α-C–C agostic interactions and C–H bond activation in scandium cyclopropyl complexes. *Inorganic Chemistry Frontiers* **2020**, *7*, 4822-4831.
34. Escudié, Y.; Dinoi, C.; Allen, O.; Vendier, L.; Etienne, M., An Unsymmetrical bis C-C Agostic Heterobimetallic Lithium Yttrium Complex. *Angew. Chem. Int. Ed.* **2012**, *51*, 2461-2464.
35. Parker, K. D. J.; Labat, S.; Sotiropoulos, J.-M.; Miqueu, K.; Pimienta, V.; Vendier, L.; Etienne, M., Allyl Complexes of Tungsten from the Rearrangement of Transient Cyclopropyl Precursors. *Eur. J. Inorg. Chem.* **2019**, *2019*, 4555-4563.
36. Parker, K. D. J.; Vendier, L.; Etienne, M., Synthesis, Characterization, and Ligand Rearrangement of Tungsten Cyclopropyl Complexes. *Organometallics* **2018**, *37*, 1221-1224.
37. Oulié, P.; Dinoi, C.; Li, C.; Sournia-Saquet, A.; Jacob, K.; Vendier, L.; Etienne, M., CH Bond Activation of Unsaturated Hydrocarbons by a Niobium Methyl Cyclopropyl Precursor. Cyclopropyl Ring Opening and Alkyne Coupling Reaction. *Organometallics* **2017**, *36*, 53-63.
38. Tobisch, S., Organolanthanide-Mediated Ring-Opening Ziegler Polymerization (ROZP) of Methylenecycloalkanes: A Theoretical Mechanistic Investigation of Alternative Mechanisms for Chain Initiation of the Samarocene-Promoted ROZP of 2-Phenyl-1-methylenecyclopropane. *Chemistry – A European Journal* **2005**, *11*, 3113-3126.
39. Maercker, A.; Oeffner, K. S.; Girreser, U., Polylithiumorganic compounds. Part 29: C,C Bond cleavage of phenyl substituted and strained carbocycles using lithium metal. *Tetrahedron* **2004**, *60*, 8245-8256.
40. Morris, D. E.; Da Re, R. E.; Jantunen, K. C.; Castro-Rodriguez, I.; Kiplinger, J. L., Trends in Electronic Structure and Redox Energetics for Early-Actinide Pentamethylcyclopentadienyl Complexes. *Organometallics* **2004**, *23*, 5142-5153.
41. Mills, D. P.; Moro, F.; McMaster, J.; van Slageren, J.; Lewis, W.; Blake, A. J.; Liddle, S. T., A delocalized arene-bridged diuranium single-molecule magnet. *Nat. Chem.* **2011**, *3*, 454-460.

42. Fendrick, C. M.; Marks, T. J., Actinacyclobutanes. Thermochemistry based strategies for the ring-opening stoichiometric activation of saturated and olefinic hydrocarbons. *Journal of the American Chemical Society* **1986**, *108*, 425-437.
43. Matson, E. M.; Kiernicki, J. J.; Fanwick, P. E.; Bart, S. C., Expanding the Family of Uranium(III) Alkyls: Synthesis and Characterization of Mixed-Ligand Derivatives. *European Journal of Inorganic Chemistry* **2016**, *2016*, 2527-2533.
44. Matson, E. M.; Forrest, W. P.; Fanwick, P. E.; Bart, S. C., Synthesis and Reactivity of Trivalent Tp*U(CH2Ph)2(THF): Insertion vs Oxidation at Low-Valent Uranium–Carbon Bonds. *Organometallics* **2013**, *32*, 1484-1492.
45. Johnson, S. A.; Bart, S. C., Achievements in uranium alkyl chemistry: celebrating sixty years of synthetic pursuits. *Dalton Transactions* **2015**, *44*, 7710-7726.
46. Matson, E. M.; Forrest, W. P.; Fanwick, P. E.; Bart, S. C., Functionalization of Carbon Dioxide and Carbon Disulfide Using a Stable Uranium(III) Alkyl Complex. *J. Am. Chem. Soc.* **2011**, *133*, 4948-4954.
47. Arnaudet, L.; Charpin, P.; Folcher, G.; Lance, M.; Nierlich, M.; Vigner, D., Characterization of the anion $[(\eta^5\text{-}C_5H_5)_3U^{III}\text{-}n\text{-}C_4H_9]^-$. Synthesis and crystal structure of tricyclopentadienyl n-butyluranium(III) lithium cryptate: $[(C_5H_5)_3UC_4H_9]^-[LiC_{14}H_{28}N_2O_4]^+$. *Organometallics* **1986**, *5*, 270-274.
48. Matson, E. M.; Forrest, W. P.; Fanwick, P. E.; Bart, S. C., Use of Alkylsodium Reagents for the Synthesis of Trivalent Uranium Alkyl Complexes. *Organometallics* **2012**, *31*, 4467-4473.
49. Zi, G., Recent developments in actinide metallacycles. *Chem. Commun.* **2018**, *54*, 7412-7430.
50. Webster, C. L.; Ziller, J. W.; Evans, W. J., Synthesis and CO2 Insertion Reactivity of Allyluranium Metallocene Complexes. *Organometallics* **2012**, *31*, 7191-7197.
51. Shannon, R. D., Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halide and Chalcogenides. *Acta Crystallogr. Sect. A* **1976**, *A32*, 751-767.
52. Baird, M. S.; Nizovtsev, A. V.; Bolesov, I. G., Bromine–magnesium exchange in gem-dibromocyclopropanes using Grignard reagents. *Tetrahedron* **2002**, *58*, 1581-1593.



Photolysis or thermolysis of the U(IV) cyclopropyl complex, [Cp_3U(2,2-diphenylcyclopropyl)], results in formation of the U(IV) η^1-allyl complex, [Cp_3U(η^1-3,3-diphenylallyl)], via a hypothesized η^3 allyl intermediate.