Intrinsic reactivity of a uranium metallacyclopropene toward unsaturated organic molecules†

Lei Zhang, Bo Fang, Guohua Hou, Lin Ai, Wanjian Ding, Marc D. Walter and Guofu Zi*

The uranium metallacyclopropene \( [\eta^5-\text{C}_8\text{Me}_8\text{C}_2\text{SiMe}_3]_2\text{Th} (\eta^5-C_2\text{Me}_2\text{C}_2\text{SiMe}_3) \) (1) reacts with various small unsaturated organic molecules. For example, replacement of bis(trimethylsilylacetylene occurs when complex 1 is exposed to alkynes, conjugated alkenes, nitriles and quinones. Reaction of 1 with internal phenyl(alkyl) acetylene PhC==CMe selectively yields the \( \text{C}_2\text{ symmetric} \) uranium metallacyclopentadiene \( [\eta^5-\text{C}_8\text{Me}_8\text{C}_2\text{SiMe}_3]_2\text{U} [\eta^5-\text{C}(\text{Ph})==\text{C}(\text{Me})==\text{C}(\text{Ph})==\text{C}(\text{Me})] \) (6) after the loss of bis(trimethylsilylacetylene, while treatment of 1 with phenyl(alkyl)acetylenes (PhC==CRR, \( \text{R} = \text{SiHMe}_2, \text{SiMe}_3 \)) gives the corresponding \( \text{C}_2\text{ symmetric} \) isomers \( [\eta^5-\text{C}_8\text{Me}_8\text{C}_2\text{SiMe}_3]_2\text{U} [\eta^5-\text{C}(\text{R})==\text{C}(\text{Ph})==\text{C}(\text{R})==\text{C}(\text{R})] \) (R = SiHMe_2 (7), SiMe_3 (8)). Furthermore, while no deprotonation occurs between complex 1 and pyridine derivatives, cyclohexaneone can be inserted into the uranium metallacyclopropene moiety of 1 to yield the five-membered, heterocyclic complex \( [\eta^5-\text{C}_8\text{Me}_8\text{C}_2\text{SiMe}_3]_2\text{U}[\text{OC} (\text{CH}_3)_{15}(\text{SiMe}_3)]_2 \) (14) in quantitative conversion. Density functional theory (DFT) studies have been performed to complement the experimental studies.

Introduction

Metallacyclopropenes have various synthetic and catalytic applications, e.g., metallacyclopropenes of group 4 metallocenes have been employed for the preparation of complex organic molecules or heterocyclic main group element compounds. Therefore group 4 metallacyclopropenes bearing the Cp′2M fragment (where Cp′ = substituted or unsubstituted \( \eta^5\)-cyclopentadienyl) represent synthetically useful synths liberating the coordinated alkene under mild conditions and transferring the Cp′2M[η] fragment when reacted with unsaturated substrates. While group 4 chemistry is now well established, the corresponding actinide and lanthanide metallacycles have been neglected. This is remarkable considering the recent advances in actinide mediated small molecule activation, in which the influence of 6d and 5f orbitals on the reactivity of these species has been evaluated. In the course of our investigations, we have recently reported on stable actinide metallacyclopropenes \( [\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_2\text{H}_2\text{Th}[\eta^5-\text{C}_2\text{Ph}_2]_2 ] \) and \( [\eta^5-\text{C}_8\text{Me}_8\text{C}_2\text{SiMe}_3]_2[\eta^5-\text{C}_2\text{Ph}_2]_2 \) strongly coordinated and reacts as a nucleophile towards hetero-unsaturated molecules or as a strong base inducing intramolecular \( \text{C}-\text{H} \) bond activation, replacement of the coordinated alkylène occurs when the uranium metallacyclopropene \( [\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_2\text{H}_2\text{Th}[\eta^5-\text{C}_2\text{Ph}_2]_2 ] \) reacts with unsaturated molecules such as alkynes, imines, bipy, carbodiimide, organic azides, and diazene derivatives. Encouraged by these remarkably different reactivities, we have now extended the substrate scope, and report herein on its reaction with pyridine derivatives, imines, (un)symmetrically substituted internal alkynes, conjugated alkenes, quinones, ketones and nitriles. These studies are also compared to those with related thorium metallacyclopropenes.

Results and discussion

The reaction of the thorium metallacyclopropene \( [\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_2\text{H}_2\text{Th}[\eta^5-\text{C}_2\text{Ph}_2]_2 ] \) with pyridine derivatives induces \( \text{C}-\text{H} \) bond activation to give pyridyl alkynyl thorium compounds. Nevertheless, similar to group 4 metallacycloprope complexes, no deprotonation is observed between the uranium metallacyclopropene \( [\eta^5-\text{C}_8\text{Me}_8\text{C}_2\text{SiMe}_3]_2[\eta^5-\text{C}_2\text{Ph}_2]_2 \) (1) and pyridine or 4-(dimethylamino)pyridine (DMAP) even when heated at 50 °C overnight, instead, the corresponding adducts...
Scheme 1  Synthesis of complexes 2 and 3.

($\eta^5$-C$_5$Me$_5$)$_2$U[($\eta^2$-C$_2$(SiMe$_3$)$_2$)](L) (L = Py (2), DMAP (3)) are formed in quantitative yields (Scheme 1). The molecular structures of 2 and 3 are shown in Fig. 1 and 2, and the selected bond distances and angles are listed in Table 1. In the U($\eta^5$-C$_5$Me$_5$)$_2$5 fragment, the average U–C distances are 2.357(8) Å and 2.385(6) Å for 2 and 3, respectively, and the C–U–C angles are 33.0(3)° and 33.8(2)° for 2 and 3, respectively. These structural parameters are comparable to those found in the base-free complex 1 with an average U–C distance of 2.333(9) Å and the C–U–C angle of 33.3(3)°. The relatively long U–N distances of 2.625(8) Å (for 2) and 2.632(6) Å (for 3) are consistent with those of a datively coordinated nitrogen atom, which, however, are longer than that found in [$\eta^5$-1,2,4-(Me$_2$C)$_3$C$_6$H$_4$]$_2$U (DMAP) (2.535(4) Å).10 Nevertheless, deprotonation occurs when complex 1 is exposed to di[naphthalen-1-yl]methanamine (1-C$_{10}$H$_8$)$_2$CNH to form the alkenyl iminato [(C$_{10}$H$_8$)$_2$C][N=C(1-C$_{10}$H$_8$)$_2$] (4) (Scheme 2). The molecular structure of 4 is shown in Fig. 3, and the selected bond distances and angles are listed in Table 1. The C(21)–C(22) distance of 1.330(14) Å is in the typical range of a C=C bond, whereas the U–C(21) distance of 2.436(9) Å is slightly longer than those in 2 and 3 (Table 1). The short U–N distance of 2.191(8) Å and the angle of U–N–C(29) of 177.8(8)° suggest some nitrogen π donation to the uranium atom. These structural parameters may be compared to those found in [$\eta^5$-C$_5$Me$_5$]$_2$U(NCP$\beta$)$_2$ with the U–N distances of 2.169(6)–2.185(3) Å and the U–N–C angles of 172.8(6)–176.5(5)°,6,11 and those in imidazolin-2-iminato uranium compounds with the U–N distances in the range of 2.118(8)–2.143(4) Å and the U–N–C angles of 169.5(5)–169.8(4)°.12

However, in contrast to the thorium metallacyclopropanes,7a,9 the coordinated bis(trimethylsilylacetylene in 1 can be exchanged with the internal alkyne. Mixing the uranium metallacyclopentadiene 1 with internal alkyne PhC=C(Me) in toluene at ambient temperature forms the corresponding metallacyclopentadienes [$\eta^5$-C$_5$Me$_5$]$_2$U($\eta^2$-C$_2$(Ph)) (Scheme 3), which is presumably a consequence of the more open coordination sphere in the metallacyclopentadiene intermediate [$\eta^5$-C$_5$Me$_5$]$_2$U($\eta^2$-C$_2$(Ph)) (R = Ph (5), Me (6)) in quantitative conversions. Our previous DFT computations suggest that one molecule of PhC=C(Me) initially reacts with 1 to displace bis(trimethylsilylacetylene and to form the corresponding metallacyclopentadienes [$\eta^5$-C$_5$Me$_5$]$_2$U($\eta^2$-C$_2$(Ph)) (Scheme 3), which is presumably a consequence of the more open coordination sphere in the metallacyclopentadiene intermediate [$\eta^5$-C$_5$Me$_5$]$_2$U($\eta^2$-C$_2$(Ph)) (R = Ph (5), Me (6)). Similar to the formation of thorium metallacyclopentadienes,7c the C=C bond formation is selective, i.e., the methyl-end of PhC=C(Me) couples with the phenyl-substituted terminus of a second acetylene, leading to the C$_{2v}$-symmetric U[($\eta^2$-C(Ph))=C(Me)=C(Ph)=C(Me)] fragment. DFT studies confirm that the formation of this C$_{2v}$-symmetric U[($\eta^2$-C(Ph))=C(Me)=C(Ph)=C(Me)] fragment is thermodynamically more favourable ($\Delta$G(298 K) = –17.7 kcal mol$^{-1}$) than the C$_{2v}$-symmetric isomer U[($\eta^2$-C(Ph))=C(Me)=C(Ph)=C(Ph)] (P6b; $\Delta$G(298 K) = –16.4 kcal mol$^{-1}$) or U[($\eta^2$-C(Me)=C(Ph)=C(Ph)=C(Ph)) (P6a; $\Delta$G(298 K) = –15.2 kcal mol$^{-1}$) and also proceeds with the lower activation barrier $\Delta$G$^{\ddagger}$(298 K) = 21.3 kcal mol$^{-1}$ (Fig. 4). This selectivity in the C–C bond formation observed for complex 6 may be rationalized by the Mulliken charges in the free alkyne PhC=C(Me), the uranium metallacyclopentadiene intermediate [$\eta^5$-C$_5$Me$_5$]$_2$U($\eta^2$-C$_2$(Ph)) (Me) and the transition state TS6 (Fig. 5). The more negatively charged end of the internal alkyne coordinates to the electropositive U(iv) atom and therefore electronic effects prevail over steric effects. Moreover, the formation of 6 may also proceed by two different reaction pathways, i.e., via transition state TS6 or TS6c (Fig. 4C), but the insertion via TS6 ($\Delta$G$^{\ddagger}$(298 K) = 21.3 kcal mol$^{-1}$) is computed to be energetically more favour-
able than that proceeding via TS6c ($\Delta G^\ddagger(298 \text{ K}) = 21.9 \text{ kcal mol}^{-1}$), which is consistent with the electronic arguments developed above. When phenyl(silylacetylene) PhC≡SiHMe$_2$ or PhC≡SiMe$_3$ is added to compound 1, the metallacyclopentadienes ($\eta^5$-C$_5$Me$_5$)$_2$U[($\eta^2$-C(R)=C(Ph)-C(Ph)=C(R)] (R = SiHMe$_2$ (7), SiMe$_3$ (8)) are isolated exclusively, but the selectivity in the C–C bond formation changes (Scheme 3), that is, the phenyl-substituted terminus of PhC≡C(R) couples with the phenyl-substituted one of a second acetylene to give a $C_{2v}$-symmetric $\text{U}[\eta^2$-C(R)=C(Ph)-C(Ph)=C(R)] moiety. Our DFT investigations also reproduce this change in selectivity. The $C_{2v}$-symmetric isomer ($\eta^5$-C$_5$Me$_5$)$_2$U[($\eta^2$-C(SiHMe$_2$)=C(Ph)=C(Ph)=C(SiHMe$_2$)] is energetically more favorable (7; $\Delta G(298 \text{ K}) = -11.8 \text{ kcal mol}^{-1}$) than the $C_{2v}$-symmetric [P7a; $\Delta G(298 \text{ K}) = -2.8 \text{ kcal mol}^{-1}$] and $C_5$-symmetric isomers [P7b; $\Delta G(298 \text{ K}) = -9.2 \text{ kcal mol}^{-1}$], and it also forms with the lowest barrier of activation $\Delta G^\ddagger(298 \text{ K}) = 21.8 \text{ kcal mol}^{-1}$ (Fig. 6). As discussed above, the selectivity of the C–C bond formation to give complex 7 can also be explained by the Mulliken charges computed for the free alkyne PhC≡C(SiHMe$_2$), the intermediate ($\eta^5$-C$_5$Me$_5$)$_2$U[($\eta^2$-C(Ph)=SiHMe$_2$)] and the transition state TS7 (Fig. 5). However, in

### Table 1  Selected distances (Å) and angles (°) for compounds 2–4, 6–8 and 11–14

<table>
<thead>
<tr>
<th>Compound</th>
<th>C(Cp)-U</th>
<th>C(Cp)-U</th>
<th>Cp(cent)-U</th>
<th>U-X</th>
<th>Cp(cent)-U-Cp(cent)</th>
<th>X-U-X/Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.794(9)</td>
<td>2.754(9)</td>
<td>2.830(9)</td>
<td>2.520(9)</td>
<td>C26: 2.369(8), C27: 2.346(8)</td>
<td>133.4(3)</td>
</tr>
<tr>
<td>3</td>
<td>2.831(6)</td>
<td>2.792(6)</td>
<td>2.876(6)</td>
<td>2.555(6)</td>
<td>N1: 2.625(8)</td>
<td>133.4(2)</td>
</tr>
<tr>
<td>4</td>
<td>2.787(9)</td>
<td>2.746(8)</td>
<td>2.813(9)</td>
<td>2.514(8)</td>
<td>C21: 2.436(9), N1: 2.191(8)</td>
<td>134.8(3)</td>
</tr>
<tr>
<td>6</td>
<td>2.748(8)</td>
<td>2.714(8)</td>
<td>2.774(8)</td>
<td>2.471(8)</td>
<td>C22: 2.399(9), C25: 2.365(8)</td>
<td>141.7(3)</td>
</tr>
<tr>
<td>7</td>
<td>2.752(11)</td>
<td>2.734(10)</td>
<td>2.777(11)</td>
<td>2.476(10)</td>
<td>C21: 2.400(11), C24: 2.382(11)</td>
<td>137.0(4)</td>
</tr>
<tr>
<td>8</td>
<td>2.764(7)</td>
<td>2.755(7)</td>
<td>2.780(7)</td>
<td>2.497(7)</td>
<td>C14: 2.370(8), C14A: 2.370(8)</td>
<td>136.9(4)</td>
</tr>
<tr>
<td>11</td>
<td>2.766(10)</td>
<td>2.715(10)</td>
<td>2.827(10)</td>
<td>2.495(10)</td>
<td>N1: 2.447(10), N2: 2.364(11)</td>
<td>131.8(4)</td>
</tr>
<tr>
<td>12</td>
<td>2.714(8)</td>
<td>2.684(8)</td>
<td>2.749(8)</td>
<td>2.434(8)</td>
<td>O1: 2.191(5), O2: 2.202(5)</td>
<td>139.2(2)</td>
</tr>
<tr>
<td>13</td>
<td>2.750(11)</td>
<td>2.655(11)</td>
<td>2.805(10)</td>
<td>2.476(10)</td>
<td>O1: 2.130(6), O2A: 2.127(6)</td>
<td>133.3(2)</td>
</tr>
<tr>
<td>14</td>
<td>2.810(14)</td>
<td>2.734(14)</td>
<td>2.886(11)</td>
<td>2.556(12)</td>
<td>O1: 2.062(8), C21: 2.512(12)</td>
<td>130.4(3)</td>
</tr>
</tbody>
</table>

$^a$ Cp = cyclopentadienyl ring. $^b$ Average value. $^c$ Range. $^d$ The angle of C–U–C.
contrast to the uranium metallacyclopentadiene 5,8 no thermal degradation is observed for complexes 6–8, in line with the previous observations establishing that the substituents on the acetylene significantly influenced the reactivity of the actinide metallacycles.7c The molecular structures of 6–8 are shown in Fig. 7–9, and the selected bond distances and angles are provided in Table 1. Furthermore, the U–C distances of 2.365(8)–2.400(11) Å are comparable to those of the U–C(sp²) σ-bonds found in complexes 1–4 (2.315(9)–2.436(9) Å). The C–C distances within the metallacyclopentadiene fragments are 1.344(10), 1.503(11) and 1.363(11) Å for 6, 1.372(15), 1.510(15) and 1.352(15) Å for 7 and 1.374(9), 1.558(12) and

Fig. 4 Free energy profile (kcal mol⁻¹) for the reaction of (η⁵-C₅Me₅)₂U [η²-C(Ph)=C(Me)] + PhC≡CMe (U was treated with ECP60WB). [U] = (η⁵-C₅Me₅)₂U.

Fig. 6 Free energy profile (kcal mol⁻¹) for the reaction of (η⁵-C₅Me₅)₂U [η²-C(Ph)=C(SiHMe₂)] + PhC≡CSiHMe₂ (U was treated with ECP80MWB). [U] = (η⁵-C₅Me₅)₂U.

Fig. 5 Mulliken charges of the free alkynes, their respective uranium metallacyclopropenes and transition state complexes. [U] = (η⁵-C₅Me₅)₂U.
1.374(9) Å for 8, and therefore are very close to those previously reported for related actinide metallacyclopentadiene compounds, e.g., \((\eta^5-C_5Me_5)_2U(\eta^4-C_4Ph_4)\) (1.365(3), 1.509(4) and 1.365(4) Å).4

The coordinated bis(trimethylsilyl)acetylene in 1 may also be replaced with conjugated alkynes or olefins. For example, reaction of 1 with 1 equiv. of 1,4-diphenylbutadiyne (PhC≡CH≡CHPh) or 1,4-diphenylbutadiene (PhCH=CH=CHPh) yields the uranium metallacyclopenta-

triene \((\eta^5-C_5Me_5)_2U[\eta^4-C_4Ph_2]\) (9) (Scheme 3) and the metallacyclopentene \((\eta^5-C_5Me_5)_2U[\eta^2-CH(Ph)CH=CHCH(Ph)]\) (10) (Scheme 4), respectively, in quantitative conversions. However, no reaction occurs when 1 is exposed to olefins such as RCH=CHR \((R = H, Ph, Me)\) even when heated at 100 °C for one week.

The bis(trimethylsilyl)acetylene moiety in 1 can also be replaced with hetero-unsaturated organic molecules. For example, complex 1 reacts with three equivalents of the nitrile C6H11CN to yield the C–C and N–C coupling product \((\eta^5-C_5Me_5)_2U[\eta^3-N=C(C_6H_{11})C(C_6H_{11})=NC(C_6H_{11})=N]\) (11) (Scheme 5). This contrasts the reaction of the related thorium metallacyclopropene \([\eta^5-1,2,4-(Me_3C)_3C_5H_2]_2Th(\eta^2-C_2Ph_2)\) with PhCN,7,9 for which an insertion product was isolated. In analogy to the reactivity of group 4 metallacyclopropene \((\eta^5-C_5Me_5)_2M[\eta^2-C_2(SiMe_3)_2]\) (M = Ti, Zr),2,3,6 we propose that C6H11CN initially replaces the bis(trimethylsilyl)acetylene frag-

---

**Fig. 7** Molecular structure of 6 (thermal ellipsoids drawn at the 35% probability level).

**Fig. 8** Molecular structure of 7 (thermal ellipsoids drawn at the 35% probability level).

**Fig. 9** Molecular structure of 8 (thermal ellipsoids drawn at the 35% probability level).

**Scheme 4** Synthesis of complex 10.

**Scheme 5** Synthesis of complex 11.
ment to give a metal $\eta^3$-nitrile intermediate,$^{13}$ which immediately couples with a second molecule of $\text{C}_6\text{H}_5\text{CN}$ to give a five-membered metallaheterocycle,$^2$ that further reacts with a third molecule of $\text{C}_6\text{H}_5\text{CN}$ to afford 11 (Scheme 5). Fig. 10 shows the molecular structure of 11 and the selected bond distances and angles are provided in Table 1. These structural parameters suggest some degree of electron delocalization with the $\text{N}(1)\cdots\text{C}(21)\cdots\text{N}(2)\cdots\text{C}(28)\cdots\text{C}(35)\cdots\text{N}(3)$ fragment. The U–N distances are 2.447(10) Å for N(1) and 2.364(11) Å for N(2) and 2.270(11) Å for N(3), which are longer than that found in 4 (2.191(8) Å). Addition of 9,10-phenanthrenequinone (9,10-$\text{C}_1\text{H}_8\text{O}_2$) to 1 forms the monomeric uranium quinonate ($\eta^3\text{-C}_3\text{Me}_3)_2\text{U}(9,10-\text{O}_2\text{C}_1\text{H}_8)$) concomitant with free bis(trimethylsilyl)acetylene (Scheme 6), whereas the less sterically encumbered $\sigma$-benzoquinone affords the dimeric quinonate $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}]_2(\mu-\text{O}_2\text{C}_6\text{H}_4)_2$ (13) (Scheme 6). The molecular structures of 12 and 13 are shown in Fig. 11 and 12, and the selected bond distances and angles are listed in Table 1. The average U–O distance is 2.191(5) Å for 12, which is larger than that found in 13 (2.127(6) Å). Nevertheless, in contrast to the reaction with quinones, but similar to the reactivity of the thorium metallacycloprenopene $[\eta^3\text{-1,2,4-(Me}_3\text{C})_3\text{C}_3\text{H}_2\text{Th}](\eta^3\text{-C}_3\text{Ph}_3)]$ towards ketones (for details see the ESI†), insertion of 1 equiv. of cyclohexanone ([(CH$_2$)$_5$CO]) into the uranium metallacycloprenopene moiety of 1 is observed at ambient temperature to exclusively yield the five-membered uranium heterocycle ($\eta^3\text{-C}_3\text{Me}_3)_2\text{U}[\text{OC}(\text{CH}_2)\text{C}_6\text{H}_5\text{SiMe}_3]$) (14) (Scheme 6). The molecular structure of 14 is shown in Fig. 13, and the selected bond distances and angles are compiled in Table 1. The U–O distance is 2.062(8) Å, which is comparable to those in 12 and 13 (Table 1), whereas the U–C(21) distance is 2.512(12) Å, which is significantly longer than those of the U–C(sp$^2$) $\sigma$-bonds found in compounds 1–4 (2.315(9)–2.436(9) Å).
Conclusions

While the coordinated alkyne in the thorium metallacyclopropenes is inert towards alkyne exchange, it can react as a nucloephile towards hetero-ununsaturated molecules or as a strong base inducing inter- or intramolecular C-H bond activations. 7,9 In contrast, addition of pyridine derivatives to the bonding in the uranium metallacyclopropene U-(η^5-C=C=Csime3L) (L = Py (2), DMAP (3)) without C-H bond activations. The reactivity difference observed for uranium relative to thorium can be rationalized by the more covalent bonds between the enhanced 5f orbitals contributing to the bonding in the uranium metallacyclopropene U-(η^5-C=C=Csime3L) moiety. 8 Furthermore, in contrast to the thorium metallacyclopropenes, 7,9 replacement of the coordinated alkyne occurs when complex 1 is exposed to alkyynes, conjugated alkenes, nitriles and quinones. These distinct reactivity patterns are similar to those of the more covalent group 4 metallacyclopro- pene complexes. 1,2 Nevertheless, thorium and uranium metallacyclopropenes exhibit similar reactivity patterns when exposed to ketones, which are inserted into the actinide metallacycloproene moieties to yield the five-membered heterocyclic compounds. Further investigations regarding the intrinsic reactivity of actinide metallacyclopropenes and of uranium metallacycles 9 and 10 are currently in progress.

Experimental

General methods

All reactions and product manipulations were carried out under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glove box. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. (η^5-C=C=Csime3L) (1) was prepared according to literature methods. 5 All other chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. and used as received unless otherwise noted. Infrared spectra were recorded in KBr pellets on an Avatar 360 Fourier transform spectrometer. 1H and 13C{1H} NMR spectra were recorded at 25 °C on a Bruker AV 400 spectrometer at 400 and 100 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents, which served as internal standards, for proton and carbon chemical shifts. Melting points were measured on a X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

Syntheses

Preparation of (η^5-C=C=Csime3L)U[η^2-C(=Csime3L)](Py) (2). A toluene (5 mL) solution of pyridine (32 mg, 0.40 mmol) was added to a toluene (10 mL) solution of (η^5-C=C=Csime3L)U[η^2-C(=Csime3L)] (1; 272 mg, 0.40 mmol) with stirring at room temperature. After this solution was stirred at room temperature for one hour, the solvent was evaporated. The residue was dried in a vacuum at 50 °C overnight to give 2 as a brown solid in quantitative yield (Found: C, 52.30; H, 7.02; N, 1.86. C35H58N2Si2U requires C, 52.29; H, 7.05; N, 1.85%) M.p.: 93–95 °C (dec.). 1H NMR (CD2D): δ 25.95 (br s, 1H, py), 14.96 (s, 9H, SiC5H3), 6.38 (s, 1H, py), -2.07 (s, 1H, py), -3.27 (s, 30H, CpC6H3CH3), -3.94 (s, 9H, SiC5H3), -6.56 (s, 1H, py), -10.67 (br s, 1H, py) ppm. 13C{1H} NMR (CD2D): δ 133.4 (ring C), 125.6 (py C), 99.7 (py C), 79.8 (py C), 60.4 (SiC5H3), -54.7 (SiC5H3), -66.8 (CpC6H3CH3) ppm; carbons of UC5H5SiMe5 were not observed. IR (KBr, cm⁻¹): 2962 (s), 2895 (s), 1598 (m), 1570 (m), 1433 (s), 1402 (s), 1342 (s), 1282 (s), 1082 (s), 1018 (s), 839 (s). Brown crystals of 2 suitable for X-ray structure analysis were grown from an n-hexane solution at room temperature.

Preparation of (η^5-C=C=Csime3L)U[η^2-C(=Csime3L)](DMAP) (3). This compound was prepared as a brown solid in quantitative yield from the reaction of (η^5-C=C=Csime3L)U[η^2-C(=Csime3L)] (1; 272 mg, 0.40 mmol) and DMAP (49 mg, 0.40 mmol) in toluene (15 mL) at room temperature and dried in a vacuum at 50 °C by a similar procedure to that in the synthesis of 2 (Found: C, 52.46; H, 7.32; N, 3.48. C49H63NSi2U requires C, 52.48; H, 7.30; N, 3.50%). M.p.: 107–109 °C (dec.). 1H NMR (CD2D): δ 16.13 (br s, 9H, SiC5H3), 14.52 (br s, 9H, SiC5H3), -0.50 (s, 1H, py), -2.94 (s, 6H, NCH3), -3.36 (s, 30H, CpC6H3), -3.52 (s, 1H, py) ppm; two protons were not observed. 13C{1H} NMR (CD2D): δ 128.5 (py C), 128.1 (py C), 127.9 (py C), 113.3 (ring C), 62.3 (SiC5H3), 36.1 (NCH3), -65.9 (CpC6H3) ppm; carbons of UC5H5SiMe5 were not observed. IR (KBr, cm⁻¹): 2960 (s), 1608 (s), 1527 (s), 1438 (s), 1384 (s), 1228 (s), 1062 (s), 1004 (s), 839 (s), 804 (s). Brown crystals of 3 suitable for X-ray structure analysis were grown from an n-hexane solution at room temperature.

Preparation of (η^5-C=C=Csime3L)U[C(=Csime3L)](C=CH(SiMe3))N=C(C(=Csime3L)C6H4) (4). Method A. A toluene (5 mL) solution of (1-C10H7)2C=CH(SiMe3)CNH (113 mg, 0.43 mmol) was added to a toluene (10 mL) solution of (η^5-C=C=Csime3L)U[η^2-C(=Csime3L)] (1; 272 mg, 0.40 mmol) with stirring at room temperature. After the solution was stirred at room temperature overnight, the solvent was removed. The residue was extracted with benzene (10 mL × 3) and filtered. The volume of the filtrate was reduced to 5 mL, and brown crystals of 4 were isolated when this solution was kept at room temperature for one week. Yield: 338 mg (88%) (Found: C, 61.26; H, 6.60, N, 1.47. C49H63NSi2U requires C, 61.29; H, 6.61; N, 1.46%). M.p.: 177–179 °C (dec.). 1H NMR (CD2D): δ 19.01 (s, 9H, SiC5H3), 15.05 (br s, 9H, SiC5H3), 9.23 (s, 2H, aryl), 7.60 (m, 2H, aryl), 4.59 (s, 1H, C=C=CH), 1.23 (s, 2H, aryl), 0.89 (s, 2H, aryl), 0.32 (s, 2H, aryl), -1.80 (s, 30H, CpC6H3), -9.78 (s, 9H, SiC5H3) ppm. 13C{1H} NMR (CD2D): δ 233.8 (UC), 142.1 (ring C), 132.1 (aryl C), 129.3 (aryl C), 128.5 (aryl C), 127.9 (aryl C), 125.6 (aryl C), 124.4 (aryl C), 44.9 (N=C=CH), 19.9 (SiC5H3), 15.0 (SiC5H3), -33.5 (CH) -51.6 (CpC6H3) ppm. IR (KBr, cm⁻¹): 2958 (s), 2899 (s), 1595 (s), 1579 (s), 1538 (s), 1402 (s), 1259 (s), 1246 (s), 1095 (s), 840 (s), 775 (s).

Method B. NMR Scale. A toluene (0.3 mL) solution of (1-C10H7)2C=CH(SiMe3)CNH (5.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with (η^5-C=C=Csime3L)U[η^2-C(=Csime3L)]
(1; 14 mg, 0.02 mmol) and C₆D₆ (0.2 mL). Resonances of 4 were observed by ¹H NMR spectroscopy (100% conversion).

Preparation of [η⁵-C₅Me₅]₂U[η³-C(Ph)]−C(Me)(Ph)−C(Me)⁻[0.5C₅H₄ (6-0.5C₅H₄). Method A. This compound was prepared as brown crystals from the reaction of [η⁵-C₅Me₅]₂U[η³-C(SiMe₃)₂] (1; 272 mg, 0.40 mmol) and PhC≡CMe (93 mg, 0.8 mmol) in toluene (15 mL) at room temperature and recrystallized from a benzene solution by a similar procedure as that in the synthesis of 4. Yield: 234 mg (75%) (Found: C, 63.13; H, 6.32. C₄₆H₄₄U requires C, 63.15; H, 6.33%). M.p.: 103–105 °C (dec.). ¹H NMR (C₆D₆): δ 7.15 (s, 3H, C₅H₅), 6.14 (s, 4H, phenyl), 5.58 (s, 3H, CH₃), 2.94 (s, 15H, CpCH₃), 2.72 (s, 1H, phenyl), 1.28 (s, 15H, CpCH₃), −1.39 (s, 2H, phenyl), −6.00 (s, 3H, CH₃), −13.65 (s, 2H, phenyl), −20.74 (s, 1H, phenyl) ppm. ¹³C{¹H} NMR (C₆D₆): δ 278.4 (U), 260.2 (U), 197.4 (ring C), 188.4 (ring C), 130.3 (phenyl C), 129.6 (phenyl C), 129.3 (phenyl C), 128.0 (C₅H₄), 124.7 (phenyl C), 122.9 (phenyl C), 122.5 (phenyl C), 122.4 (phenyl C), 121.9 (phenyl C), 112.2 (C=Ph), 104.5 (C=C), 91.2 (U), 69.7 (C=CH₂), −41.2 (CpCH₃), −45.3 (CpCH₃). IR (KBr, cm⁻¹): 2960 (s), 2922 (s), 1438 (s), 1402 (s), 1259 (s), 1074 (s), 1018 (s), 798 (s).

Method B. NMR Scale. A C₆D₆ (0.3 mL) solution of PhC≡CMe (4.6 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with [η⁵-C₅Me₅]₂U[η³-C(SiMe₃)₂] (1; 14 mg, 0.02 mmol) and C₆D₆ (0.2 mL). Resonances of 6 and those of Me₃Si≡C≡SiMe₃ (¹H NMR (C₆D₆): δ 0.15 (s, 18H, SiCH₃) ppm) were observed by ¹H NMR spectroscopy (100% conversion).

Reaction of [η⁵-C₅Me₅]₂U[η³-C(SiMe₃)₂] (1) with PhC≡CMe. NMR Scale. A C₆D₆ (0.2 mL) solution of PhC≡CMe (2.3 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η⁵-C₅Me₅]₂U[η³-C(SiMe₃)₂] (1; 14 mg, 0.02 mmol) and C₆D₆ (0.3 mL). Resonances of 6 along with those of unreacted 1 and Me₃Si≡C≡SiMe₃ were observed by ¹H NMR spectroscopy (50% conversion based on 1).

Preparation of [η⁵-C₅Me₅]₂U[η³-C(SiMe₃)₂]−C(Ph)(Ph)−C(Me)⁻[0.5C₅H₄ (6-0.5C₅H₄). Method A. This compound was prepared as brown crystals from the reaction of [η⁵-C₅Me₅]₂U[η³-C(SiMe₃)₂] (1; 272 mg, 0.40 mmol) and PhC≡CMe (93 mg, 0.8 mmol) in toluene (15 mL) at room temperature and recrystallized from an n-hexane solution by a similar procedure as that in the synthesis of 4. Yield: 281 mg (82%) (Found: C, 58.81; H, 6.87. C₄₆H₄₄Si₂U requires C, 58.85; H, 6.82%). M.p.: 104–106 °C (dec.). ¹H NMR (C₆D₆): δ 7.28 (d, 4H, J = 7.6 Hz, phenyl), 6.81 (t, 4H, J = 7.4 Hz, phenyl), 5.83 (t, 2H, J = 7.0 Hz, phenyl), 4.21 (s, 1H, SiCH₃), 3.86 (s, 30H, CpCH₃), −4.78 (s, 6H, SiCH₃) ppm. ¹³C{¹H} NMR (C₆D₆): δ 217.4 (UCSI), 146.5 (ring C), 132.2 (phenyl C), 127.0 (phenyl C), 125.9 (phenyl C), 123.9 (phenyl C), 110.7 (CPh), 0.0 (SiCH₃), −39.7 (CpCH₃), −65.1 (SiCH₃) ppm. IR (KBr, cm⁻¹): 2949 (m), 2906 (s), 1395 (m), 1487 (m), 1438 (s), 1400 (s), 1259 (s), 1236 (s), 1070 (s), 1018 (s), 935 (s), 827 (s).

Method B. NMR Scale. A C₆D₆ (0.3 mL) solution of PhC≡CMe (7.0 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with [η⁵-C₅Me₅]₂U[η³-C(SiMe₃)₂] (1; 14 mg, 0.02 mmol) and C₆D₆ (0.2 mL). Resonances of 8 and those of Me₃Si≡C≡SiMe₃ were observed by ¹H NMR spectroscopy (100% conversion).

Reaction of [η⁵-C₅Me₅]₂U[η³-C(SiMe₃)₂] (1) with PhC≡CMe. NMR Scale. A C₆D₆ (0.2 mL) solution of PhC≡CMe (3.5 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η⁵-C₅Me₅]₂U[η³-C(SiMe₃)₂] (1; 14 mg, 0.02 mmol) and C₆D₆ (0.3 mL). Resonances of 8 along with those of unreacted 1 and Me₃Si≡C≡SiMe₃ were observed by ¹H NMR spectroscopy (50% conversion based on 1).

Preparation of [η⁵-C₅Me₅]₂U[η³-C(Ph)₃] (9). Method A. This compound was prepared as brown microcrystals from the reaction of [η⁵-C₅Me₅]₂U[η³-C(SiMe₃)₂] (1; 272 mg, 0.40 mmol) and PhC≡C−C≡CPh (81 mg, 0.4 mmol) in toluene (15 mL) at room temperature and recrystallized from a benzene solution by a similar procedure as that in the synthesis of 4. Yield: 219 mg (77%) (Found: C, 60.81; H, 7.71. C₄₆H₄₄O requires C, 60.84; H, 6.57%). M.p.: 136–138 °C (dec.). ¹H NMR (C₆D₆): δ 6.69 (t, 2H, J = 7.0 Hz, phenyl), 5.18 (t, 4H, J = 6.8 Hz, phenyl), 2.09 (m, 4H, phenyl), −0.95 (s, 30H, CpCH₃) ppm. ¹³C{¹H} NMR (C₆D₆): δ 237.7 (UCPh), 190.6 (PhC≡C), 157.1 (ring C), 137.6 (phenyl C), 128.5 (phenyl C), 117.0 (phenyl C), 51.4 (CpCH₃) ppm. IR (KBr, cm⁻¹): 2962 (s), 2905 (s), 1612 (m), 1586 (m), 1439 (s), 1403 (s), 1383 (s), 1260 (s), 1068 (s), 1020 (s), 799 (s).

Method B. NMR Scale. A C₆D₆ (0.3 mL) solution of PhC≡C−C≡CPh (4.0 mg, 0.02 mmol) was slowly added to a J. Young
NMR tube charged with ($\eta^5$-C$_5$Me$_5$)$_2$U[$\eta^5$-C$_5$(SiMe$_3$)$_2$] (1; 14 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). Resonances of 9 and those of Me$_5$SiC$_5$SiMe$_3$ were observed by $^1$H NMR spectroscopy (100% conversion).

**Preparation of ($\eta^5$-C$_5$Me$_5$)$_2$U[$\eta^5$-CH(Ph)CH=CHCH(Ph)] (10). Method A.** This compound was prepared as brown micro-crystals from the reaction of ($\eta^5$-C$_5$Me$_5$)$_2$U[$\eta^5$-C$_5$(SiMe$_3$)$_2$] (1; 272 mg, 0.40 mmol) and PhCH=CHCH=CHPh (83 mg, 0.4 mmol) in toluene (15 mL) at 70 °C and recrystallized from a toluene solution by a similar procedure as that in the synthesis of 4. Yield: 234 mg (82%) (Found: C, 60.51; H, 6.18.

$^1$H NMR (C$_6$D$_6$): $\delta$ 47.19 (s, 2H, CH=C), 12.58 (s, 15H, CpCH$_2$), $-0.21$ (d, 4H, $J$ = 8.9 Hz, phenyl), $-0.32$ (s, 15H, CpCH$_3$), $-10.91$ (d, 2H, $J$ = 11.7 Hz, phenyl), $-20.32$ (d, 4H, $J$ = 9.2 Hz, phenyl), $-171.11$ (s, 2H, PhCH) ppm. IR (KBr, cm$^{-1}$): 2962 (s), 2922 (s), 1617 (m), 1560 (m), 1400 (s), 1386 (s), 1259 (s), 1089 (s), 1016 (s), 979 (s).

**Method B. NMR Scale.** A C$_6$D$_6$ (0.3 mL) solution of PhCH=CHCH=CHPh (4.1 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with ($\eta^5$-C$_5$Me$_5$)$_2$U[$\eta^5$-C$_5$(SiMe$_3$)$_2$] (1; 14 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). Resonances of 10 and those of Me$_5$SiC$_5$SiMe$_3$ were observed by $^1$H NMR spectroscopy (100% conversion) after this solution was kept at 70 °C for two days.

**Preparation of ($\eta^5$-C$_5$Me$_5$)$_2$U[$\eta^5$-N=C(C$_6$H$_5$)$_2$(C$_6$H$_5$)$_2$]=NC (C$_6$H$_5$)$_2$-N=0.5C$_6$H$_6$ (11.0.5C$_6$H$_6$). Method A.** This compound was prepared as brown crystals from the reaction of ($\eta^5$-C$_5$Me$_5$)$_2$U[$\eta^5$-C$_5$(SiMe$_3$)$_2$] (1; 272 mg, 0.40 mmol) and C$_6$H$_5$CN (131 mg, 1.20 mmol) in toluene (15 mL) at room temperature and recrystallized from a benzene solution by a similar procedure as that in the synthesis of 4. Yield: 273 mg (78%) (Found: C, 60.36; H, 7.58; N, 4.82. C$_{34}$H$_{58}$N$_2$U requires C, 60.39; H, 7.60; N, 4.85%)

$^1$H NMR (C$_6$D$_6$): $\delta$ 6.151 (m, 1H, CH$_3$), 14.55 (m, 2H, CH$_2$), 14.01 (m, 2H, CH$_2$), 7.15 (s, 3H, C$_6$H$_5$), 7.04 (m, 2H, CH$_2$), 6.09 (m, 2H, CH$_2$), 5.76 (m, 2H, CH$_2$), 4.89 (m, 1H, CH$_3$), 4.70 (m, 1H, CH$_3$), 3.73 (m, 2H, CH$_2$), 2.98 (m, 2H, CH$_2$), 2.63 (m, 1H, CH$_2$), 1.88 (m, 3H, CpCH$_2$), 0.20 (m, 4H, CpCH$_2$), $-1.23$ (m, 1H, CH$_2$), $-3.39$ (m, 1H, CH$_2$), $-4.84$ (m, 2H, CH$_2$), $-5.20$ (m, 2H, CH$_2$), $-6.71$ (m, 1H, CH$_2$), $-13.12$ (m, 2H, CH$_2$), $-13.50$ (m, 1H, CH$_2$), $-19.15$ (m, 2H, CH$_2$), $-83.76$ (s, 1H, CH$_2$) ppm. 13C$^1$(H) NMR (C$_6$D$_6$): $\delta$ 195.3 (ring C), 166.6 (C=O), 164.9 (C=N), 128.0 (C$_6$H$_5$), 107.0 (C=O), 64.2 (CH$_3$), 64.1 (CH$_3$), 63.3 (CH$_3$), 34.1 (CH$_3$), 31.9 (CH$_3$), 31.7 (CH$_3$), 29.1 (CH$_3$), 27.3 (CH$_3$), 27.2 (CH$_3$), 26.6 (CH$_3$), 18.6 (CH$_3$), 11.5 (CH$_3$), $-40.8$ (CpCH$_2$) ppm. IR (KBr, cm$^{-1}$): 2962 (m), 2922 (s), 1617 (m), 1560 (m), 1400 (s), 1386 (s), 1259 (s), 1089 (s), 1016 (s), 979 (s).

**Method B. NMR Scale.** A C$_6$D$_6$ (0.3 mL) solution of 0-benzquinone (2.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with ($\eta^5$-C$_5$Me$_5$)$_2$U[$\eta^5$-C$_5$(SiMe$_3$)$_2$] (1; 14 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). Resonances of 13 and those of Me$_5$SiC$_5$SiMe$_3$ were observed by $^1$H NMR spectroscopy (100% conversion).

**Preparation of ($\eta^5$-C$_5$Me$_5$)$_2$U[OC(CHO)$_2$(C$_5$(SiMe$_3$)$_2$)] (14). Method A.** This compound was prepared as orange crystals from the reaction of ($\eta^5$-C$_5$Me$_5$)$_2$U[$\eta^5$-C$_5$(SiMe$_3$)$_2$] (1; 272 mg, 0.40 mmol) and cyclohexane (40 mg, 0.40 mmol) in toluene (15 mL) at room temperature and recrystallized from an n-hexane solution by a similar procedure as that in the synthesis of 4. Yield: 261 mg (84%) (Found: C, 52.53; H, 7.51. C$_{34}$H$_{48}$O$_2$SiU requires C, 52.53; H, 7.52%)

$^1$H NMR (C$_6$D$_6$): $\delta$ 57.94 (d, 2H, $J$ = 16.3 Hz, CH$_2$), 48.10 (t, 2H, $J$ = 11.9 Hz, CH$_2$), 37.06 (q, 2H, $J$ = 13.1 Hz, CH$_2$), 24.90 (d, 1H, $J$ = 10.1 Hz, CH$_2$), 23.00 (d, 2H, $J$ = 13.8 Hz, CH$_2$), 18.20 (d, 1H, $J$ = 9.0 Hz, CH$_2$), 5.93 (s, 9H, SiCH$_3$), $-0.27$ (s, 30H,
Cp(CH₃)₃, −22.08 (s, 6H, SiCH₃), −38.94 (s, 3H, SiCH₃) ppm.¹³C
¹¹H NMR (CD₂Cl₂): δ 198.5 (UC), 143.3 (CH₂), 142.5 (UC=CD), 141.5 (CH₃), 118.7 (CO), 112.3 (ring C), 56.7 (CH₃), 55.4 (CH₂), 54.2 (CH₃), 4.1 (SiCH₃), −59.3 (CpCH₃) ppm. IR (KBr, cm⁻¹): 2958 (s), 2927 (s), 2854 (s), 1436 (s), 1377 (s), 1247 (s), 1076 (s), 1018 (s), 840 (s).

**Method B. NMR Scale.** A C₆D₆ (0.3 mL) solution of cyclohexanone (2.0 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η5-C₅Me₅]U[η5-C₅SiMe₃] (1; 14 mg, 0.02 mmol) and C₆D₆ (0.2 mL). Resonances of 14 were observed by ¹H NMR spectroscopy (100% conversion).

**X-ray crystallography**

Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart APEX II CCD diffractometer at 100(2) K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.¹⁵ All structures were solved by direct methods and refined by full-matrix least squares on F² using the SHELXL program package.¹⁶ All the hydrogen atoms were geometrically fixed using the riding model. Disordered solvents in the voids of 15 were modelled or removed by using the SQUEEZE program.¹⁷ The crystal data and experimental data for 2–4, 6–8 and 11–16 are summarized in the ESL.† Selected bond lengths and angles are listed in Table 1.

**Computational methods**

All calculations were carried out with the Gaussian 09 program (G09),¹⁸ employing the B3PW91 functional, plus a polarizable continuum model (PCM) (denoted as B3PW91-PCM), with the standard 6-31G(d) basis set for C, H and Si elements and a quasi-relativistic 5f-in-valence effective-core potential (ECP60MWB) or 5f-in-core effective-core potential (ECP80MWB) treatment for the core region of U and the corresponding optimized segmented basis set for the valence shells of U,¹⁹ to fully optimize the structures of reactants, complexes, transition states, intermediates, and products, and also to mimic the experimental toluene-solvent conditions (dielectric constant ε = 2.379). All stationary points were subsequently characterized by vibrational analyses, from which their respective zero-point (vibrational) energies (ZPE) were extracted and used in the relative energy determinations; in addition, frequency calculations were also performed to ensure that the reactant, complex, intermediate, product and transition state structures resided at minima and 1st order saddle points, respectively, on their potential energy hypersurfaces.

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (Grant No. 21472013, 21573021, 21672024), and the Deutsche Forschungsgemeinschaft (DFG) through the Heisenberg program (WA 2513/6).

**Notes and references**


4 Selected actinide and lanthanide metallacycles, see: (a) P. J. Fagan, J. M. Manriquez, T. J. Marks, C. S. Day,


For comparison, the reactivity of the thorium metallacyclopropanes is outlined in the ESIF.


12 For selected well-characterized $n^2$-nitride metal complexes, see: (a) T. C. Wright, G. Wilkinson, M. Motevali and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1986, 1987–1988; (b) P. A. Chetcuti, C. B. knobler and M. F. Hawthorne, *Organometallics*, 1988, 7, 650–660. Complex 12 could also be prepared in 66% yield from $\left[\text{[N}_5\text{C}_5\text{Me}_3\text{H}]\text{UCl}_3\right]$ and $9,10\text{C}_{14}\text{H}_{14}\text{O}_2$ in the presence of sodium amalgam, see ref. 4a.

13 G. M. Sheldrick, SADAB, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 1996.


