

# Influence of the 5f Orbitals on the Bonding and Reactivity in Organoactinides: Experimental and Computational Studies on a Uranium Metallacyclopentene

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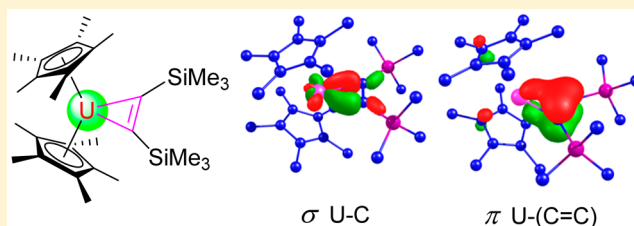
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**S** Supporting Information

**ABSTRACT:** The synthesis, structure, and reactivity of a uranium metallacyclopentene were comprehensively studied. Reduction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{UCl}_2$  (**1**) with potassium graphite ( $\text{KC}_8$ ) in the presence of bis(trimethylsilyl)acetylene ( $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ ) allows the first stable uranium metallacyclopentene  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**) to be isolated. Magnetic susceptibility data confirm that **2** is a U(IV) complex, and density functional theory (DFT) studies indicate substantial 5f orbital contributions to the bonding of

the metallacyclopentene  $\text{U}(\eta^2\text{-C}=\text{C})$  moiety, leading to more covalent bonds between the  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}^{2+}$  and  $[\eta^2\text{-C}_2(\text{SiMe}_3)_2]^{2-}$  fragments than those in the related Th(IV) compound. Consequently, very different reactivity patterns emerge, e.g., **2** can act as a source for the  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\text{II})$  fragment when reacted with alkynes and a variety of heteroatom unsaturated molecules such as imines, bipy, carbodiimide, organic azides, hydrazine, and azo derivatives.



## INTRODUCTION

Highly strained metallacyclopentenes have found various synthesis and catalysis applications.<sup>1–6</sup> For example, group 4 metallacyclopentenes formed by a  $\text{Cp}'_2\text{M}$  ( $\text{Cp}' =$  substituted or unsubstituted  $\eta^5$ -cyclopentadienyl) fragment have been of particular interest as precursors for the preparation of highly functionalized organic molecules and heterocyclic main group element compounds<sup>1,2,6</sup> because they can serve as a useful synthon for the metallocene fragment liberating the coordinated alkyne under mild conditions when reacted with unsaturated substrates.<sup>1,2</sup> In general, the reactivity depends significantly on the identity of the metallocene  $\text{Cp}'_2\text{M}$  fragment and the steric and electronic properties of the coordinated alkyne. Although metallacyclopentenes of the group 4 metals have been extensively studied and their intrinsic reactivity patterns are now well-established,<sup>1</sup> the analogous actinide compounds have essentially been neglected since the early work by Marks reported more than 30 years ago.<sup>1g,7</sup> This is especially true for actinide metallacyclopentenes, and the first isolable actinide metallacyclopentene  $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$  has only recently been prepared.<sup>8a</sup> The lack of general interest in this class of compounds is very surprising considering the resurgence of organoactinide chemistry, which is driven by the potential of actinide complexes in small molecule activation.<sup>1g,9</sup> A particular focus of the actinide community has traditionally been the influence of the 5f orbitals on the bonding and the reactivity of (organo)actinide compounds.<sup>10</sup> Previous studies established that the  $\pi\text{-U(III)}$  alkyne complex  $(\eta^5\text{-C}_5\text{H}_5)_3\text{U}(\eta^2\text{-$

$\text{PhC}\equiv\text{CPh})$  exhibits only limited stability,<sup>7g</sup> whereas the alkyne in the thorium metallacyclopentene  $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$  is strongly bound and gives rise to interesting reactivity with various heteroatom unsaturated molecules such as aldehydes, ketones,  $\text{CS}_2$ , carbodiimides, nitriles, isothiocyanates, organic azides, and diazoalkane derivatives.<sup>8a</sup> Motivated by this difference and encouraged by the rich chemistry of the thorium metallacyclopentene  $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$  and by the fact that so far no uranium metallacyclopentenes have been isolated and structurally characterized, we have recently decided to also expand our studies to uranium. Furthermore, we also wish to address the influence of 5f orbitals on the bonding and reactivity in organoactinide compounds leading to distinctively different reactivity between uranium and thorium and expect that it may act as a U(II) synthon similar to the reactivity observed for group 4 metallacyclopentenes.<sup>1,2</sup> In this paper we report on some observations concerning the synthesis, electronic structure, and structure–reactivity relationship of the first stable uranium metallacyclopentene. A comparison to the corresponding thorium and group 4 metallocenes is also included.

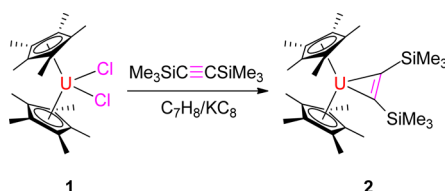
Received: February 6, 2016

Published: April 12, 2016

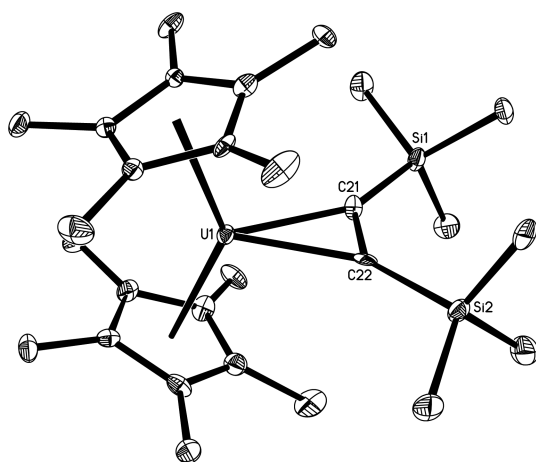
## RESULTS AND DISCUSSION

**Synthesis of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**).** Treatment of a 1:1 mixture of bis(trimethylsilyl)acetylene ( $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ ) and  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{UCl}_2$  (**1**) with an excess of  $\text{KC}_8$  in toluene solution gives brown crystals of air and moisture sensitive metallacyclopropene  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**) in 75% yield (Scheme 1). In contrast to the thorium

Scheme 1



metallacyclopropenes,<sup>8b,c</sup> **2** can be stored under a dry nitrogen atmosphere in solution or solid state without degradation via C–H bond activation or deprotonation. Complex **2** is soluble in and readily recrystallized from an *n*-hexane solution, and it was fully characterized by various spectroscopic techniques, elemental analysis, and single-crystal X-ray diffraction. The molecular structure of **2** is shown in Figure 1, and selected



**Figure 1.** Molecular structure of **2** (thermal ellipsoids drawn at the 35% probability level).

bond distances and angles are listed in Table 1. To the best of our knowledge, **2** is the first structurally characterized uranium metallacyclopropene, and it also represents an important addition to the family of structurally characterized actinide metallacyclopropenes,  $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$  and  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\eta^2\text{-C}_2\text{Ph}(\text{SiMe}_3))(\text{Cl})][\text{Li}\{\text{MeO}(\text{CH}_2\text{CH}_2\text{O})_2\text{Me}\}_2]$ .<sup>8a,c</sup> The relevant C(21)–C(22) distance of 1.338(11) Å is close to the value of a typical double bond (1.331 Å)<sup>11</sup> and comparable to those found in thorium metallacyclopropenes  $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$  (1.343(4) Å)<sup>8a</sup> and  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\eta^2\text{-C}_2\text{Ph}(\text{SiMe}_3))(\text{Cl})][\text{Li}\{\text{MeO}(\text{CH}_2\text{CH}_2\text{O})_2\text{Me}\}_2]$  (1.360(7) Å).<sup>8c</sup> The angle (33.3(3)°) of C(21)–U(1)–C(22) can also be compared to the C–Th–C angle (32.6(1)°) in the related thorium metallacyclopropene  $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$ .<sup>8a</sup> Furthermore, the angles of C(21)–C(22)–Si(2) (134.7(7)°) and C(22)–C(21)–Si(1) (134.5(7)°) differ significantly from 180° (expected for an sp-hybridized C atom) approaching a value of 120°, which is typical for sp<sup>2</sup>-hybridized carbon atoms. The U–C distances are 2.315(9) Å for C(21) and 2.350(9) Å for C(22), which are at the lower end of reported U–C(sp<sup>2</sup>) σ-bonds (2.340(5)–2.650(7) Å)<sup>10f,12</sup> and slightly shorter than the Th–C distance in  $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$  (2.395(2) Å)<sup>8a</sup> because of the smaller size of the U<sup>4+</sup> ion.<sup>13</sup> Overall, these structural parameters clearly support the description of **2** as a uranium metallacyclopropene complex.

**Solid-State Magnetic Susceptibility Studies (SQUID).** To elucidate the electronic ground state in **2**, magnetic susceptibility studies were undertaken. Collecting magnetic data on air and moisture sensitive compounds requires attention to detail and extreme care. Therefore, independently prepared samples of **2** were sealed in quartz tubes and the magnetic susceptibility was recorded (see Experimental Section for details). The detailed analysis of the uranium magnetism can be difficult because crystal field splitting and spin–orbit coupling are of the same order of magnitude (i.e., on the order of kT). Therefore, spin–orbit and crystal field terms can mix in the free ion term, and the magnetic moment U(IV) is much lower than expected for a <sup>3</sup>H<sub>4</sub> ground state (i.e., μ<sub>eff</sub> = 3.59 μ<sub>B</sub>). This makes it difficult to differentiate U(III) and U(IV) only on the basis of the magnetic moment at 300 K. However, a very important difference in the magnetic susceptibility of U(III) and U(IV) is apparent at low temperature. Temperature-independent paramagnetism is a strong indication for U(IV) because only a U(IV) ground-state singlet can be realized that

**Table 1.** Selected Distances (Å) and Angles (°) for Compounds **2**, **4–8**, and **11–13**<sup>a</sup>

compound	C(Cp)–U <sup>b</sup>	C(Cp)–U <sup>c</sup>	Cp(cent)–U <sup>b</sup>	U–X	Cp(cent)–U–Cp(cent)	X–U–X/Y
<b>2</b>	2.737(9)	2.713(9) to 2.765(9)	2.453(9)	C(21) 2.315(9), C(22) 2.350(9)	138.9(3)	33.3(3)
<b>4</b>	2.790(4)	2.733(4) to 2.826(4)	2.516(4)	C(23) 2.528(3), C(24) 2.498(4)	127.8(1)	34.4(1)
<b>5</b>	2.747(13)	2.709(11) to 2.784(13)	2.470(13)	C(21) 2.422(13), C(30) 2.388(12)	138.5(4)	109.6(4)
<b>6</b>	2.745(5)	2.731(5) to 2.772(5)	2.470(5)	C(24) 2.515(5), C(25) 2.434(5)	134.0(2)	92.2(2) <sup>d</sup>
<b>7</b>	2.794(4)	2.755(4) to 2.826(4)	2.521(4)	C(26) 2.435(5), C(27) 2.487(5)	131.3(1)	69.6(1)
<b>8</b>	2.753(14)	2.708(14) to 2.820(11)	2.484(14)	N(1) 2.296(3), N(2) 2.287(3)	132.9(3)	80.8(3)
<b>11</b>	2.767(5)	2.721(5) to 2.819(4)	2.492(5)	C(28) 2.750(11), C(29) 2.748(10)	132.3(1)	60.6(1)
<b>12</b>	2.775(4)	2.724(4) to 2.819(4)	2.507(4)	N(1) 2.255(8), N(2) 2.274(7)	127.6(1)	87.3(1) <sup>e</sup>
<b>13</b>	2.742(7)	2.701(5) to 2.781(7)	2.470(7)	C(21) 2.433(5), C(22) 2.490(4)	145.7(1)	103.7(1)

<sup>a</sup>Cp = cyclopentadienyl ring. <sup>b</sup>Average value. <sup>c</sup>Range. <sup>d</sup>Angle of C(24)–U(1)–C(27). <sup>e</sup>Angle of C(21)–U(1)–N(2).

is nonmagnetic and possesses a first excited state close in energy.<sup>14</sup> Figure 2 shows the magnetic susceptibility data for **2**,

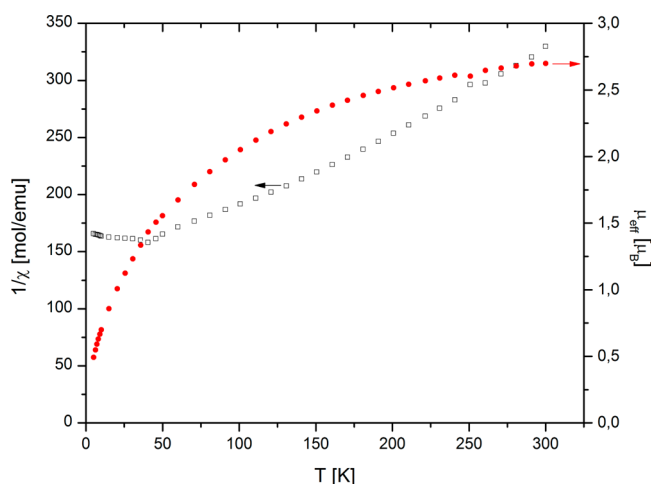


Figure 2.  $1/\chi$  and  $\mu_{\text{eff}}$  vs  $T$  for **2**.

which clearly exhibits temperature-independent paramagnetism below 50 K. This is, as pointed out above, indicative for a U(IV) compound. Moreover, the magnetic moment ( $\mu_{\text{eff}}(4\text{ K}) = 0.47(1)\ \mu_{\text{B}}$ ) (see Supporting Information for details) is in good agreement with typical U(IV) compounds (ca. 0.5–0.8  $\mu_{\text{B}}$  at approximately 4 K).<sup>14</sup> Overall, these results are consistent with the uranium(IV) metallacyclopropene description developed on the basis of the structural data of **2**.

**Bonding Studies.** The Dewar–Chatt–Duncanson model was originally applied to explain the bonding in metal olefin complexes,<sup>15</sup> but it can also be extended to metallacyclopropenes.<sup>1,16</sup> Two resonance structures have to be considered,  $\pi$ -complex (A) and metallacyclopropene (B) (Figure 3), in which

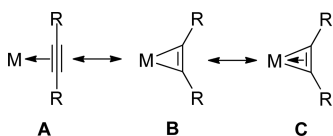


Figure 3. Resonance structures of metallacyclopropene.

the alkyne acts as a two-electron donor ligand.<sup>17</sup> However, the resonance structures A and B differ in their extent of  $\pi$ -back-bonding between the metal atom and the alkyne ligand so that resonance structure B can also be interpreted as a  $M^{2+}$  fragment being coordinated by a  $[\eta^2\text{-alkenediy}]^{2-}$  anion. Furthermore, for electron-poor metal atoms the coordinated alkyne may also act as an additional  $\pi$ -donor providing electron density to the metal atom via the orthogonal  $\pi$ -system and therefore serves as a four-electron donor ligand (Figure 3, C).<sup>17</sup> To probe further the interaction between the uranium atom and the  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  moiety, density functional theory (DFT) computations at the B3PW91 level of theory were undertaken. The bonding in **2** was also compared to its hypothetical thorium analogue ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>Th $[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2'**). The computed structure of **2** is in excellent agreement with the experimental data and shows an An $[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  metallacyclopropene moiety with two in-plane An–C  $\sigma$ -bonds and one out-of-plane  $\pi$ -bond interacting with the metal center, as illustrated in Figure 4. The natural localized molecular orbital (NLMO) analysis (Table 2) also reveals that U–C  $\sigma$ -bonds,  $\sigma(\text{U}-\text{C})$ , are formed by a

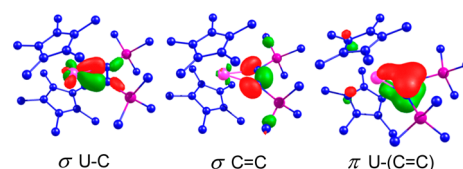


Figure 4. Plots of HOMOs for **2**. (Hydrogen atoms have been omitted for clarity.)

Table 2. Natural Localized Molecular Orbital (NLMO) Analysis of An– $[\text{C}_2(\text{SiMe}_3)_2]$  Bonds<sup>a</sup>

		2 (U)	2' (Th)
$\sigma$ An–C	%An	23.9	18.2
	%s	7.0	7.6
	%p	1.6	1.6
	%d	55.4	78.4
	%f	36.0	12.4
$\sigma$ C=C	%C	71.8	77.9
	%s	25.5	23.6
	%p	74.5	76.4
	%An	2.9	2.7
	%s	1.7	1.5
$\pi$ An(C=C)	%p	2.5	2.6
	%d	53.4	51.4
	%f	42.4	44.5
	%C	96.2	96.7
	%s	28.4	30.9
	%p	71.6	69.1
	%An	10.7	7.8
	%p	2.0	4.0
	%d	46.5	68.3
	%f	51.5	27.7
	%C	86.8	89.7
	%p	100	100

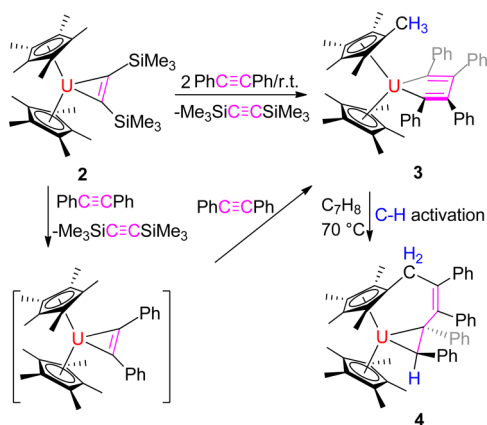
<sup>a</sup>The contributions by atom and orbital are averaged over all the ligands of the same character (complexes of U and Th) and over alpha and beta orbital contributions (complex of U).

carbon hybrid orbital (71.8%; 25.5% s and 74.5% p) and a uranium hybrid orbital (23.9%; 36.0% 5f and 55.4% 6d). In addition, two bonding orbitals are found for the C–C bond: one is a  $\sigma$ -bond ( $\sigma(\text{C}=\text{C})$ ) with 96.2% carbon occupancy with hybridization of 28.4% s and 71.6% p; the other bonding orbital is a  $\pi$ -bond ( $\pi[\text{U}(\text{C}=\text{C})]$ ) with 86.8% carbon occupancy consisting of only p orbitals and with a 10.7% contribution from a uranium hybrid orbital (51.5% 5f and 46.5% 6d). These results indicate electron donation of the alkyne  $\pi$ -orbital to the electron-deficient metal uranium atom, consistent with the notion that the alkyne fragment acts in this case as a four-electron donor ligand (Figure 3, resonance structure C). In addition, the percent contribution of metal to U–C  $\sigma$  (23.9%) and U–(C=C)  $\pi$  (10.7%) bonds is close to those computed for the related zirconium (28.3% for Zr–C  $\sigma$  bond and 10.2% for Zr–(C=C)  $\pi$  bond) and hafnium (24.5% for Hf–C  $\sigma$  bond and 10.1% for Hf–(C=C)  $\pi$  bond) metallacyclopropenes.<sup>18</sup> Therefore, the bonding in **2** carries some resemblance to that of the delocalized metallacyclopropene moiety reported

for group 4 compounds.<sup>18</sup> However, in the hypothetical thorium complex ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>Th[ $\eta^2\text{-C}_2(\text{SiMe}_3)_2$ ] (2'), the metal contribution to the bonding of the Th[ $\eta^2\text{-C}_2(\text{SiMe}_3)_2$ ] moiety decreases notably (18.2% Th for Th–C  $\sigma$  bond and 7.8% Th for Th–(C=C)  $\pi$  bond) (Table 2), suggesting a more polarized and therefore more ionic bond between ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>Th and alkyne fragment [ $\eta^2\text{-C}_2(\text{SiMe}_3)_2$ ], and the  $\pi$ -donation from the  $\pi$ -MO of the coordinated alkyne to the metal atom is significantly less pronounced (resonance structure B in Figure 3). A direct comparison of the bonding in 2 to that of the hypothetical thorium complex ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>Th[ $\eta^2\text{-C}_2(\text{SiMe}_3)_2$ ] (2') shows that the 5f orbital contribution to the U–C  $\sigma$  (36.0%) and U–(C=C)  $\pi$  (51.5%) bonds in 2 is substantially larger than that of the 5f orbitals in 2' (12.4% for Th–C  $\sigma$  bond and 27.7% for Th–(C=C)  $\pi$  bond), which is consistent with the previously investigated systems.<sup>7h,10e,f</sup> This difference reflects itself in the reactivity of the uranium complex 2 when compared to the thorium metallacyclopropenes.<sup>8,19</sup>

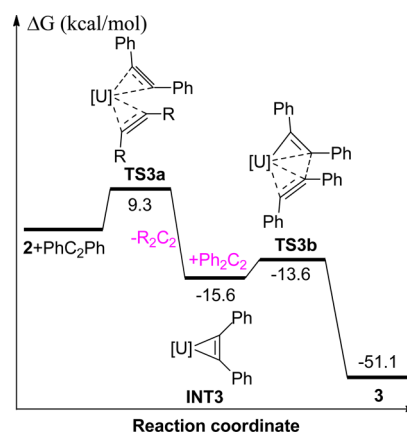
**Reactivity Studies.** In contrast to the uranium(III) complex ( $\eta^5\text{-C}_5\text{H}_5$ )<sub>3</sub>U( $\eta^2\text{-PhC}\equiv\text{CPh}$ )<sup>7g</sup> but similar to the thorium metallacyclopropene [ $\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2$ ]<sub>2</sub>Th( $\eta^2\text{-C}_2\text{Ph}_2$ ),<sup>8a</sup> variable-temperature (20–100 °C) <sup>1</sup>H NMR investigations reveal that no alkyne dissociation occurs when 2 is heated to 100 °C. This is consistent with a strong coordination of the bis(trimethylsilyl)acetylene moiety to the uranium atom, and therefore the metallacyclopropene fragment stays intact in toluene solution even at high temperatures. However, in contrast to the thorium metallacyclopropenes,<sup>8,19</sup> the coordinated bis(trimethylsilyl)acetylene in 2 can be exchanged with internal alkynes. For example, addition of diphenylacetylene (PhC≡CPh) at room temperature gives the metallacyclopentadiene complex ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>U( $\eta^2\text{-C}_4\text{Ph}_4$ ) (3)<sup>7a–e</sup> in quantitative conversion (Scheme 2). This reactivity

Scheme 2



connects 2 to group 4 metallacyclopropene complexes, which also react with added alkynes forming other metallacycles.<sup>12</sup> One molecule of diphenylacetylene initially reacts with 2 to displace bis(trimethylsilyl)acetylene and to form the uranium metallacyclopropene ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>U( $\eta^2\text{-C}_2\text{Ph}_2$ ). However, unlike the sterically more congested thorium metallacyclopropene [ $\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2$ ]<sub>2</sub>Th( $\eta^2\text{-C}_2\text{Ph}_2$ ),<sup>8a</sup> ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>U( $\eta^2\text{-C}_2\text{Ph}_2$ ) then immediately inserts a second molecule of PhC≡CPh to yield the thermodynamically preferred metallacyclopentadiene 3 (Scheme 2). DFT computations support this mechanistic proposal: The metallacyclopropene complex

INT3 is initially formed during the reaction of 2 with PhC≡CPh (Figure 5). The formation of INT3 is energetically



**Figure 5.** Free energy profile (kcal/mol) for the reaction of 2 + Ph<sub>2</sub>C<sub>2</sub> + Ph<sub>2</sub>C<sub>2</sub> (computed at T = 298 K). [U] = ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>U. R = Me<sub>3</sub>Si.

favorable ( $\Delta G(298\text{ K}) = -15.6\text{ kcal/mol}$ ), and proceeds via the transition state TS3a with a reaction barrier of  $\Delta G^\ddagger(298\text{ K}) = 9.3\text{ kcal/mol}$  (Figure 5). However, reaction of INT3 with a second molecule of PhC≡CPh to form 3 is thermodynamically preferred ( $\Delta G(298\text{ K}) = -51.1\text{ kcal/mol}$ ) and proceeds via the transition state TS3b with a low activation barrier ( $\Delta G^\ddagger(298\text{ K})$ ) of 2.0 kcal/mol. This is completely consistent with the rapid formation of 3 at ambient temperature. In addition, we also found that complex 3 is thermally unstable and undergoes an intramolecular C–H bond activation of the Cp\* ligand to give the uranium metallacyclopropane ( $\eta^5\text{-C}_5\text{Me}_5$ )[ $\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{C(Ph)=C(Ph)C(Ph)CHPh}$ ]U (4) in quantitative conversion (Scheme 2) with an activation barrier of  $\Delta G^\ddagger(343\text{ K})_{3\rightarrow 4} = 25.3\text{ kcal/mol}$ , which was determined by a <sup>1</sup>H NMR kinetic study (see Supporting Information for details). Although complex 3 was originally prepared in 1978, the intramolecular C–H bond activation of 3 has not been reported.<sup>7a–e</sup> DFT computations show that the conversion of 3 to 4 is energetically favorable ( $\Delta G(343\text{ K}) = -10.3\text{ kcal/mol}$ ; Figure S3). Moreover, the computed barrier for the conversion of 3 to 4 is  $\Delta G^\ddagger(343\text{ K}) = 25.1\text{ kcal/mol}$ , which can be overcome at a reaction temperature of 70 °C and is in excellent agreement with the experimental barrier of 25.3 kcal/mol. The molecular structure of 4 is shown in Figure 6, and selected bond distances and angles are listed in Table 1. The C(23)–C(24) distance is 1.486(5) Å, the U–C distances are 2.528(3) Å for C(23) and 2.498(4) Å for C(24), and the angle of C(23)–U–C(24) is 34.4(1)°. However, when the terminal alkyne phenylacetylene (PhC≡CH) is used as substrate, deprotonation occurs, and the alkenyl alkynyl uranium complex ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>U(C<sub>2</sub>Ph)[C(SiMe<sub>3</sub>)=CHSiMe<sub>3</sub>] (5) is formed in quantitative conversion (Scheme 3). The molecular structure of 5 is shown in Figure 7, and the selected bond distances and angles are given in Table 1. The C(21)–C(22) distance of 1.220(17) Å is in the typical range of a C≡C bond. U–C(30) (2.388(12) Å) is comparable to the reported U–C(sp<sup>2</sup>)  $\sigma$ -bonds (2.340(5)–2.650(7) Å),<sup>10f,12</sup> whereas U–C(21) (2.422(13) Å) is close to that found in ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>U(C<sub>2</sub>Ph)<sub>2</sub> (2.398(5) Å).<sup>20</sup>

Under similar reaction conditions, the coordinated bis(trimethylsilyl)acetylene in 2 can also be replaced by 1,4-bis(trimethylsilyl)butadiyne (Me<sub>3</sub>SiC≡CC≡CSiMe<sub>3</sub>) to yield

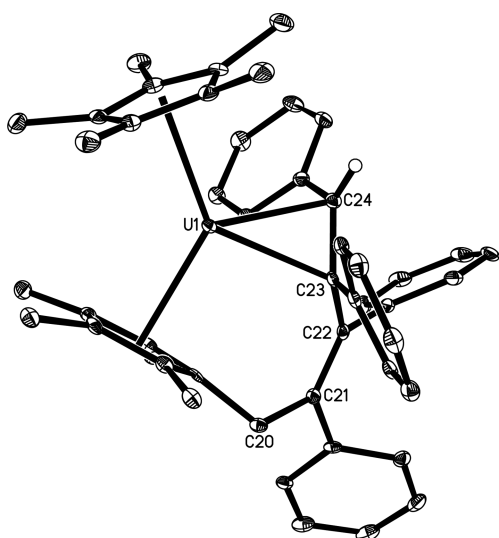


Figure 6. Molecular structure of 4 (thermal ellipsoids drawn at the 35% probability level).

### Scheme 3

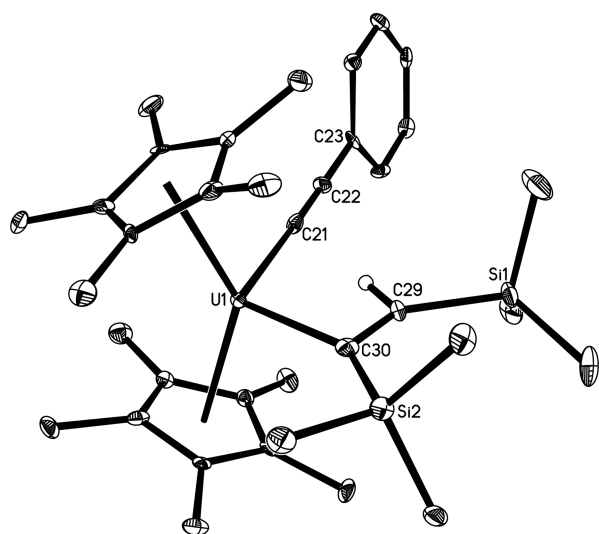
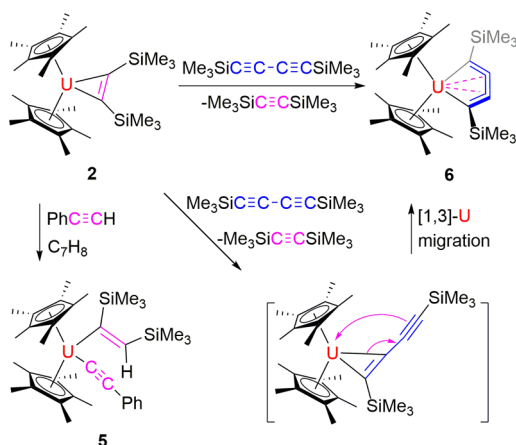


Figure 7. Molecular structure of 5. (Thermal ellipsoids drawn at the 35% probability level.)

the uranium metallacyclopentatriene complex ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>U[ $\eta^4\text{-C}_4(\text{SiMe}_3)_2$ ] (6) in quantitative conversion (Scheme 3).

Similar to the reaction with tolane ( $\text{PhC}\equiv\text{CPh}$ ), bis(trimethylsilyl)butadiyne replaces the bis(trimethylsilyl)acetylene fragment to give a metallacyclopentatriene complex,<sup>21</sup> which converts by a [1,3]-U migration to give complex 6 (Scheme 3). To the best of our knowledge, complex 6 (Figure 8) represents the first structurally characterized uranium

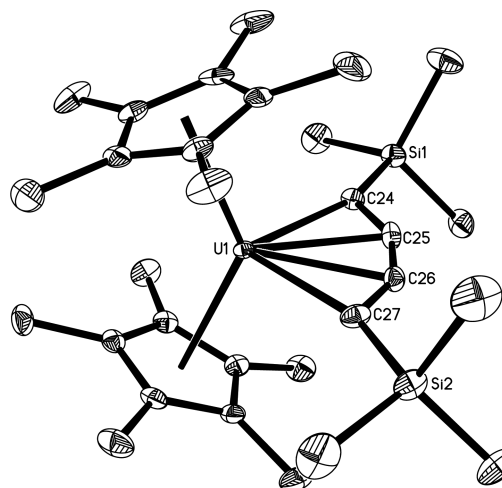


Figure 8. Molecular structure of 6. (Thermal ellipsoids drawn at the 35% probability level.)

metallacyclopentatriene, and the crystal structure of the related thorium metallacyclopentatriene, ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>Th( $\eta^4\text{-C}_4\text{Ph}_2$ ),<sup>71</sup> is the only other reported actinide metallacyclopentatriene. The C–C distances for C(24)–C(25), C(25)–C(26), and C(26)–C(27) are 1.299(7), 1.314(7), and 1.295(7) Å, respectively; they agree with a delocalized cumulene fragment. The angles of 129.2(4)° for Si(1)–C(24)–C(25) and 127.9(4)° for Si(2)–C(27)–C(26) differ substantially from 180° and approach a value of 120°, which is typical for  $\text{sp}^2$ -hybridized carbon atoms. Nevertheless, the cumulene remains highly strained with bond angles of 152.6(5)° and 151.3(5)° for C(24)–C(25)–C(26) and C(25)–C(26)–C(27), respectively. These structural parameters, besides those listed in Table 1, are consistent with a uranium metallacyclopentatriene as previously shown for the thorium derivative ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>Th( $\eta^4\text{-C}_4\text{Ph}_2$ ).<sup>71</sup>

Interestingly, the bis(trimethylsilyl)acetylene moiety in 2 can also be replaced by heterounsaturated organic molecules. For example, complex 2 reacts with two equivalents of the imine  $\text{PhCH}=\text{NPh}$  to yield the five-membered heterocyclic complex ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>U[ $\eta^2\text{-N}(\text{Ph})\text{CH}(\text{Ph})\text{CH}(\text{Ph})\text{N}(\text{Ph})$ ] (7) by replacing the bis(trimethylsilyl)acetylene moiety and C–C coupling (Scheme 4). For the formation of 7 the following reaction pathway may be proposed:  $\text{PhCH}=\text{NPh}$  replaces the bis(trimethylsilyl)acetylene fragment to give a metallazaaziridine,<sup>22</sup> which is very reactive and immediately couples with a second molecule of  $\text{PhCH}=\text{NPh}$  to give 7 (Scheme 4). Figure 9 shows the molecular structure of 7, and selected bond distances and angles are compiled in Table 1. The U–N distances are 2.296(3) Å for N(1) and 2.287(3) Å for N(2), and the N(1)–U–N(2) angle is 69.6(1)°. In contrast to the thorium metallacyclopentatriene [ $\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2$ ]<sub>2</sub>Th( $\eta^2\text{-C}_2\text{Ph}_2$ ),<sup>19</sup> replacement of the coordinated alkyne is also observed in the reaction of 2 with the diazabutadiene (*p*-tolylN=CH)<sub>2</sub>, in which the five-membered heterocyclic complex ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>U[ $\eta^2\text{-N}(\textit{p}\text{-tolyl})\text{CH}=\text{CHN}(\textit{p}\text{-tolyl})$ ] (8) is formed (Scheme 5). Similar to the reaction with

Scheme 4

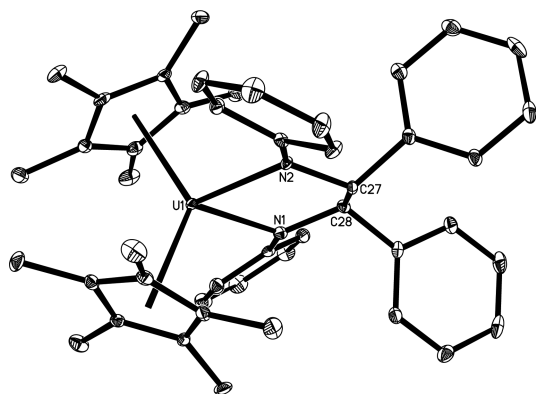
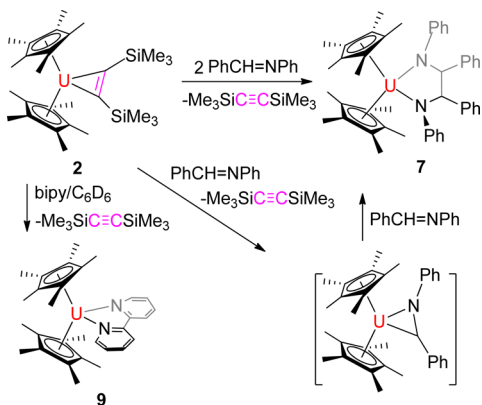
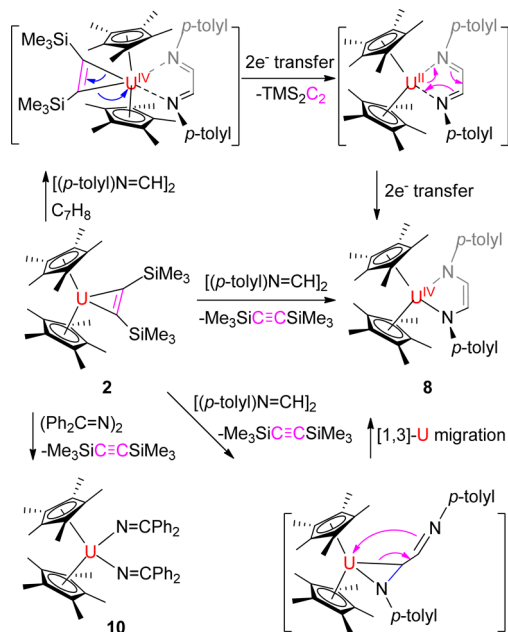


Figure 9. Molecular structure of 7. (Thermal ellipsoids drawn at the 35% probability level.)

Scheme 5



PhCH=NPh, (*p*-tolylN=CH)<sub>2</sub> also replaces the bis-(trimethylsilyl)acetylene fragment to give a metallaziridine,<sup>22</sup> which converts by a [1,3]-U migration to complex 8 (Scheme 5). An alternative reaction pathway similar to that proposed for the formation of the group 4 and ytterbium(III) diazabutadiene complexes<sup>23</sup> includes the replacement of the coordinated

alkyne by the diazabutadiene (*p*-tolylN=CH)<sub>2</sub> forming a diazabutadiene U(II) adduct,<sup>24</sup> followed by instantaneous electron transfer to yield 8 (Scheme 5). The molecular structure of 8 is shown in Figure 10, and the selected bond

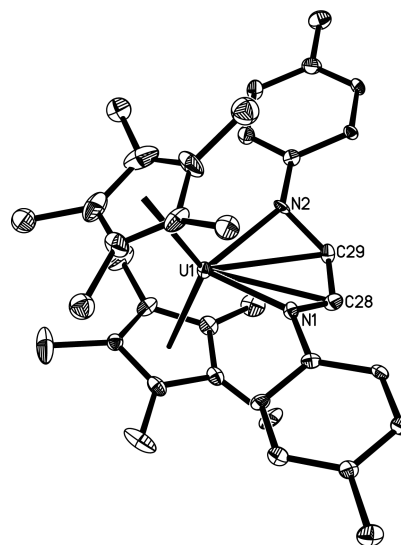
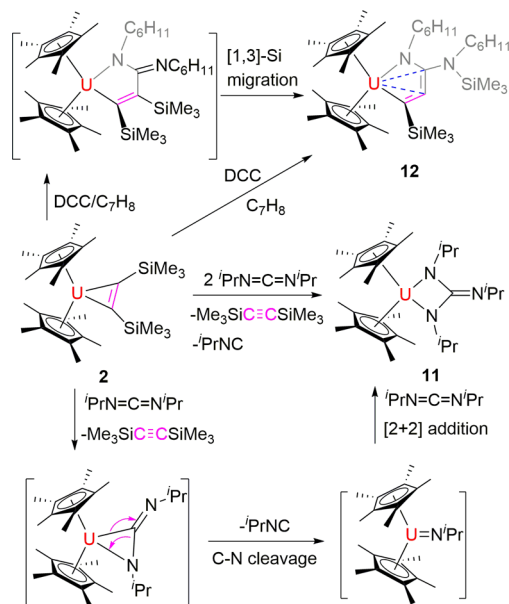


Figure 10. Molecular structure of 8. (Thermal ellipsoids drawn at the 35% probability level.)

distances and angles are listed in Table 1. The C(28)–C(29) distance of 1.377(13) Å is in the typical range of a C=C bond. The U–C distances are 2.750(11) Å for C(28) and 2.748(10) Å for C(29), which are longer than those found in 2 and 6. The U–N distances are 2.255(8) Å for N(1) and 2.274(7) Å for N(2), which are close to those observed in 7, whereas the N(1)–U–N(2) angle (80.8(3)°) is larger than that found in 7 (69.6(1)°). It should be noted that the uranium bipy complex ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(bipy) (9)<sup>25</sup> can also be formed by addition of 2,2'-bipyridine (bipy) to compound 2 (Scheme 4). However, under similar reaction conditions, treatment of 2 with (Ph<sub>2</sub>C=N)<sub>2</sub> gives a diiminato complex ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(N=CPh<sub>2</sub>)<sub>2</sub> (10)<sup>26</sup> in quantitative conversion (Scheme 5), in which the proposed mechanisms for this transformation, similar to those proposed for the reaction with (*p*-tolylN=CH)<sub>2</sub> (Scheme 5), are outlined in the Scheme S1.

Moreover, the coordinated alkyne in 2 is also replaced on addition of carbodiimides. For example, treatment of 2 with *N,N'*-diisopropylcarbodiimide gives a four-membered heterocyclic complex ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U[ $\eta^2$ -N(*i*-Pr)C(=N-*i*-Pr)N(*i*-Pr)] (11) (Scheme 6). Similar to the reaction with PhCH=NPh, *N,N'*-diisopropylcarbodiimide replaces the bis(trimethylsilyl)acetylene fragment to give a metallaziridine,<sup>22</sup> which converts to an imido complex by isonitrile *i*-PrNC loss. Unlike the sterically more congested uranium imido complex [ $\eta^5$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>U=NMe,<sup>27</sup> the Cp\* derivative is less sterically crowded and immediately converts with a second molecule of *N,N'*-diisopropylcarbodiimide in a [2 + 2] cycloaddition reaction to 11 (Scheme 6). DFT investigations show that 2 initially reacts with *N,N'*-diisopropylcarbodiimide to give the metallaziridine INT11a (Figure S4). In a next step, metallaziridine INT11a degrades to the imido *i*-PrNC adduct INT11b; then, *i*-PrNC dissociates from INT11b to yield the imido complex INT11c. Subsequently, an adduct INT11d is formed when a second molecule of *N,N'*-diisopropylcarbodiimide coordinates to INT11c. Finally, the energetically more

Scheme 6



favorable product **11** ( $\Delta G(298\text{ K}) = -27.5\text{ kcal/mol}$ ) is formed in a concerted [2 + 2] cycloaddition. The molecular structure of **11** is shown in Figure 11, and selected bond distances and

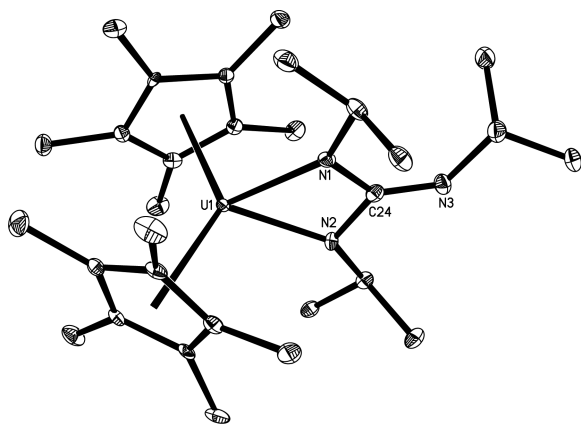


Figure 11. Molecular structure of **11**. (Thermal ellipsoids drawn at the 35% probability level.)

angles are shown in Table 1. The U–N distances are 2.258(4) Å for N(1) and 2.218(4) Å for N(2), which are comparable to those found in 7 and 8 (Table 1).

However, under similar reaction conditions, treatment of **2** with *N,N'*-dicyclohexylcarbodiimide (DCC) gives ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>U[ $\eta^4\text{-N}(\text{C}_6\text{H}_{11})\text{C}\{\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_{11})\}=\text{C}=\text{C}(\text{SiMe}_3)$ ] (**12**) in quantitative conversion (Scheme 6), and no displacement of bis(trimethylsilyl)acetylene was detected. Analogous to the reaction of the thorium metallacyclopentene [ $\eta^5\text{-1,2,4}(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2$ ]<sub>2</sub>Th( $\eta^2\text{-C}_2\text{Ph}_2$ ) with DCC,<sup>8a</sup> the following reaction pathway can be proposed: DCC inserts into the U[ $\eta^2\text{-C}_2(\text{SiMe}_3)_2$ ] moiety to give a five-membered heterocyclic intermediate, which undergoes [1,3]-Si migration to give complex **12** (Scheme 6). The molecular structure of **12** is shown in Figure 12, and selected bond distances and angles are listed in Table 1. The C–C distances of 1.295(6) Å for C(21)–C(22), 1.389(6) Å for C(22)–C(23) Å, and C(23)–N(2) distance of 1.367(6) Å suggest a delocalization of the negative

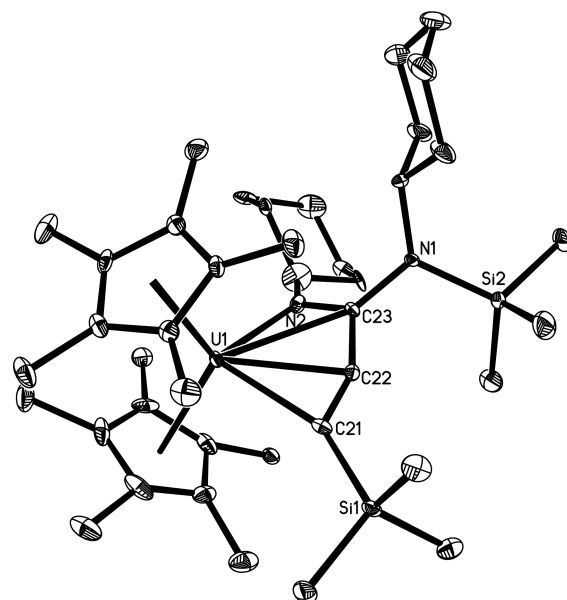
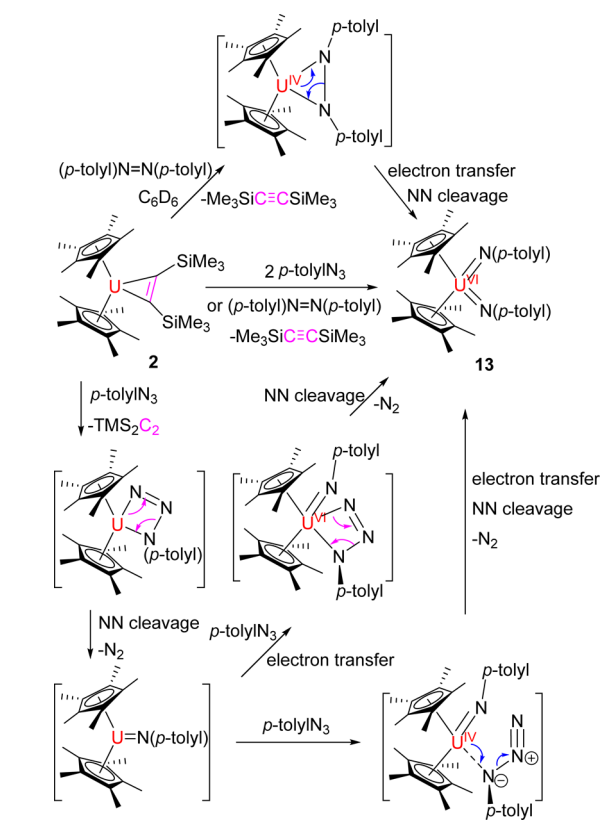


Figure 12. Molecular structure of **12**. (Thermal ellipsoids drawn at the 35% probability level.)

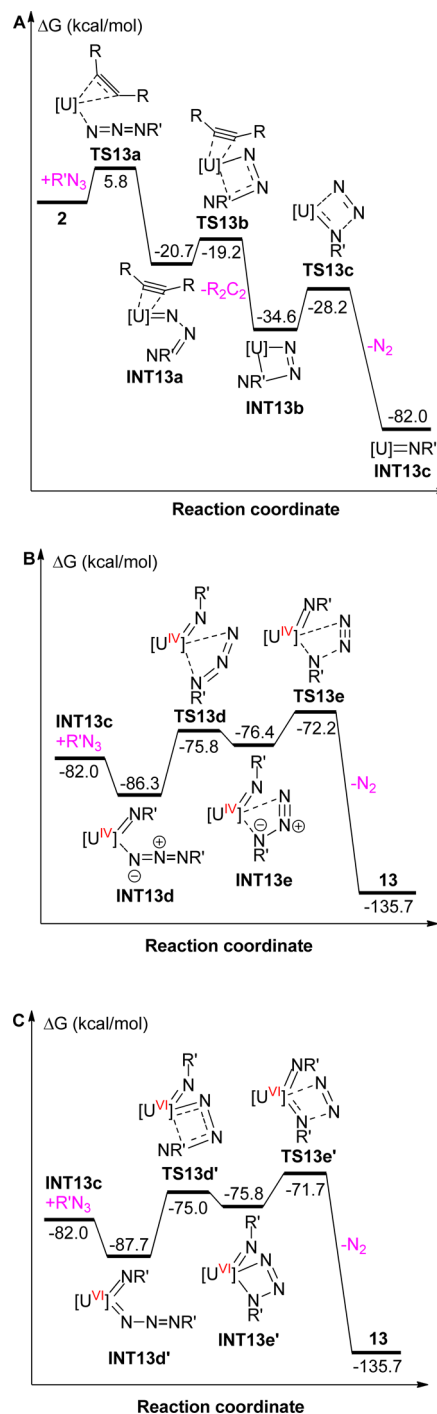
charge within the [ $\eta^4\text{-N}(\text{C}_6\text{H}_{11})\text{C}\{\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_{11})\}=\text{C}=\text{C}(\text{SiMe}_3)$ ] fragment. The U–N(2) distance (2.321(4) Å) is comparable to those found in 7, 8, and 11 (Table 1). In addition, the U–C distances of 2.433(5) Å for C(21) and 2.490(4) Å for C(22) are close to those observed in 2 and 6 but shorter than U–C(23) (2.713(4) Å). Nevertheless, the cumulene moiety remains strained, and the bond angle C(21)–C(22)–C(23) of 155.7(4)° differs markedly from 180°.

In contrast to the thorium metallacyclopentene [ $\eta^5\text{-1,2,4}(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2$ ]<sub>2</sub>Th( $\eta^2\text{-C}_2\text{Ph}_2$ ),<sup>8a</sup> no insertion or isomerization products are isolated from the reaction of **2** with *p*-tolylN<sub>3</sub>, but the diimido complex ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>U[ $=\text{N}(\textit{p}\text{-tolyl})$ ]<sub>2</sub> (**13**) is formed (Scheme 7). This reactivity may be compared to that observed for the bipy complexes [ $\eta^5\text{-1,2,4}(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2$ ]<sub>2</sub>An-(bipy) (An = Th, U) toward *p*-tolylN<sub>3</sub>.<sup>28</sup> *p*-TolylN<sub>3</sub> initially displaces the bis(trimethylsilyl)acetylene in **2** and forms a four-membered complex, which releases N<sub>2</sub> to give the imido complex ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>U= $\text{N}(\textit{p}\text{-tolyl})$ . However, the Cp\* ligand is not sterically demanding enough to sufficiently stabilize the imido complex, which immediately reacts with a second molecule of *p*-tolylN<sub>3</sub> to form an adduct, followed by electron transfer, NN bond cleavage, and N<sub>2</sub> release to yield diimido uranium(VI) compound **13** (Scheme 7). Alternatively, when the imido complex is formed, it immediately converts with a second molecule of *p*-tolylN<sub>3</sub> via electron transfer to give a four-membered complex, followed by NN bond cleavage and N<sub>2</sub> release to yield diimido complex **13** (Scheme 7). In contrast to the reaction of the imido thorium complex [ $\eta^5\text{-1,2,4}(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2$ ]<sub>2</sub>Th= $\text{N}(\textit{p}\text{-tolyl})$  with *p*-tolylN<sub>3</sub>,<sup>29</sup> no [2 + 3] cycloaddition product uranium tetraazametallacyclopentene was observed. DFT investigations suggest that *p*-tolylN<sub>3</sub> initially reacts with **2** to form the intermediate INT13a with a low barrier of  $\Delta G^\ddagger(298\text{ K}) = 5.8\text{ kcal/mol}$  (Figure 13A). In a next step, bis(trimethylsilyl)acetylene dissociates from INT13a to give the four-membered heterocyclic intermediate INT13b. Then, the INT13b releases N<sub>2</sub> to yield the energetically very favorable imido complex INT13c ( $\Delta G(298\text{ K}) = -82.0\text{ kcal/mol}$ ) with a low barrier of only  $\Delta G^\ddagger(298\text{ K}) = 6.4\text{ kcal/mol}$ .

Scheme 7



Subsequently, coordination of a second molecule of *p*-tolylN<sub>3</sub> to intermediate INT13c forms the adduct INT13d (Figure 13B), which isomerizes via a [1,3]-U migration to the adduct INT13e, followed by N<sub>2</sub> loss to give thermodynamically more stable product 13 ( $\Delta G(298\text{ K}) = -135.7\text{ kcal/mol}$ ), and the conversion from INT13d proceeds with a low barrier of  $\Delta G^\ddagger(298\text{ K}) = 14.1\text{ kcal/mol}$ . Alternatively, when the imido complex INT13c is formed, coordination of a second molecule of *p*-tolylN<sub>3</sub> to intermediate INT13c gives the intermediate INT13d' (Figure 13C). Subsequently, a four-membered heterocyclic intermediate INT13e' is formed, followed by N<sub>2</sub> loss to give thermodynamically more stable product 13 ( $\Delta G(298\text{ K}) = -135.7\text{ kcal/mol}$ ), and the conversion from INT13d' proceeds with a low barrier of  $\Delta G^\ddagger(298\text{ K}) = 16.0\text{ kcal/mol}$ . These computational results are consistent with the rapid formation of 13 at ambient temperature. Moreover, the results show that the two potential energy surfaces are so close in energy that the crossing will be easy. However, despite our efforts it has not been possible to locate the crossing point between U(IV, f<sup>2</sup>) to U(VI, f<sup>0</sup>). Complex 13 can also be accessed by the reaction of 2 with bis(*p*-tolyl)diazene (Scheme 7). Similar to the reaction with PhC≡CPh, bis(*p*-tolyl)diazene replaces the bis(trimethylsilyl)acetylene fragment to form a three-membered metallacycle, followed by electron transfer and NN bond cleavage to give diimido complex 13 (Scheme 7). The molecular structure of 13 is shown in Figure 14, and the selected bond distances and angles are listed in Table 1. The short U–N distances (1.971(4) Å for N(1) and 1.975(3) Å for N(2)) and the angles of U–N(1)–C(21) (178.8(3)°) and U–N(2)–C(28) (179.1(3)°) are consistent with a U=N double bond.<sup>30</sup> These structural parameters may be compared to those in  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\text{=NPh})_2$  with the U–N distance of 1.952(7)



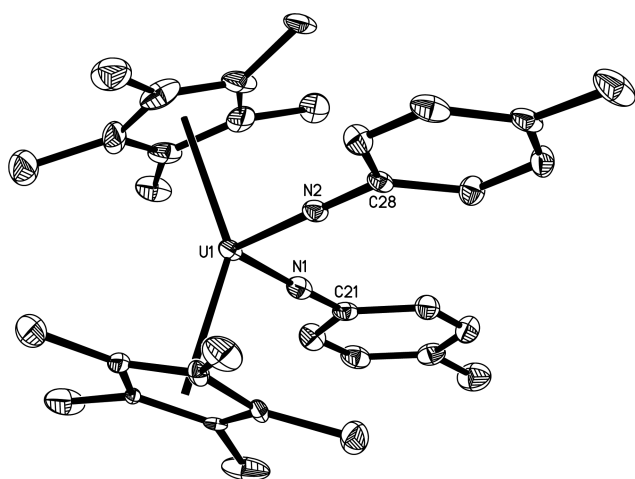
**Figure 13.** Free energy profile (kcal/mol) for the reaction of 2 + *p*-tolylN<sub>3</sub> + *p*-tolylI<sub>3</sub> (computed at  $T = 298\text{ K}$ ). [U] =  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}$ . R = Me<sub>3</sub>Si. R' = *p*-tolyl.

Å and the U–N–C angle of 177.8(6)°,<sup>31</sup>  $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_3\text{H}_2]_2\text{U}=\text{N}(\textit{p}\text{-tolyl})$  with the U–N distance of 1.988(5) Å and the U–N–C angle of 172.3(5)°,<sup>28a</sup> and thorium imido complex  $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_3\text{H}_2]_2\text{Th}=\text{N}(\textit{p}\text{-tolyl})$  with the Th–N distance of 2.038(3) Å and the Th–N–C angle of 172.8(3)°.<sup>32</sup>

## CONCLUSIONS

The first stable uranium(IV) metallacyclopropene complex,  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (2), was thoroughly investi-





**Figure 14.** Molecular structure of **13** (thermal ellipsoids drawn at the 35% probability level).

gated. Density functional theory (DFT) shows that 5f orbitals contribute substantially to the  $\sigma$ - and  $\pi$ -bonds of the U-( $\eta^2$ -C=C) moiety and that the bonds between the ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U<sup>2+</sup> and [ $\eta^2$ -C<sub>2</sub>(SiMe<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> fragments are more covalent than those of the related thorium metallacyclopropene complex. Although the coordinated alkyne in the thorium metallacyclopropenes is inert to alkyne exchange,<sup>8</sup> it reacts as a nucleophile toward heterounsaturated molecules or as a strong base inducing the inter- or intramolecular C–H bond activations.<sup>8,19</sup> In contrast, uranium complex **2** serves as a synthetically useful Cp\*<sub>2</sub>U(II) synthon, as illustrated by its reaction with unsaturated molecules such as alkynes, imines, bipy, carbodiimide, organic azides, hydrazine, and azo derivatives in which the coordinated alkyne was readily replaced during the course of the reaction. This relates complex **2** to group 4 metallacyclopropenes.<sup>1,2</sup> Further investigations on the intrinsic reactivity of actinide metallacyclopropenes and uranium metallacyclopropene complex **6** are ongoing and will be reported in due course.

## EXPERIMENTAL SECTION

**General Procedures.** 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 glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. KC<sub>8</sub><sup>33</sup> and *p*-tolylN<sub>3</sub><sup>34</sup> were prepared according to literature methods. 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. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 and 100 MHz, respectively. All chemical shifts are reported in  $\delta$  units with reference to the residual protons of the deuterated solvents, which served as internal standards for proton and carbon chemical shifts. The magnetic susceptibility data were recorded on a Quantum Design MPMS XL5 SQUID magnetometer. The sample for magnetic susceptibility measurements was sealed in quartz tubes according to literature procedures.<sup>35</sup> Magnetic susceptibility data were corrected for diamagnetism using Pascal's constants<sup>36</sup> for all the constituent atoms. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

**Preparation of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>UCl<sub>2</sub> (**1**): Modified Method.<sup>7b</sup>** To a toluene (50 mL) suspension of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)K (3.48 g, 20.0 mmol) and UCl<sub>4</sub> (3.80 g, 10.0 mmol), 2 mL of pyridine was added. After this mixture was refluxed for 3 days, the mixture was filtered, and the residue was washed with toluene (10 mL  $\times$  3). The volume of the

filtrate was reduced to ca. 20 mL, and maroon crystals of **1** were isolated when this solution was kept at  $-20$  °C for 2 days. Yield: 4.92 g (85%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 13.47 (s, 30H, CH<sub>3</sub>).

**Preparation of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U[ $\eta^2$ -C<sub>2</sub>(SiMe<sub>3</sub>)<sub>2</sub>] (**2**).** KC<sub>8</sub> (1.42 g, 10.5 mmol) was added to a toluene (20 mL) solution of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>UCl<sub>2</sub> (**1**; 2.00 g, 3.5 mmol) and bis(trimethylsilyl)acetylene (0.60 g, 3.5 mmol) with stirring at room temperature. After this solution was stirred 1 day at room temperature, the solvent was removed. The residue was extracted with *n*-hexane (10 mL  $\times$  3) and filtered. The volume of the filtrate was reduced to 10 mL; brown crystals of **2** were isolated when this solution was kept at  $-20$  °C for 2 days. Yield: 1.78 g (75%). M.p.: 123–125 °C (dec.). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 8.20 (s, 18H, SiCH<sub>3</sub>),  $-6.25$  (s, 30H, CpCH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 168.3 (ring C), 53.1 (Si(CH<sub>3</sub>)<sub>3</sub>),  $-75.3$  (CpCH<sub>3</sub>) ppm; carbons of UCSI Me<sub>3</sub> were not observed. IR (KBr, cm<sup>-1</sup>) 2960 (s), 2920 (s), 2854 (s), 1602 (m), 1454 (s), 1377 (s), 1242 (s), 1082 (s), 1020 (s), 840 (s). Anal. Calcd for C<sub>28</sub>H<sub>48</sub>Si<sub>2</sub>U: C, 49.54; H, 7.13. Found: C, 49.51; H, 7.16.

**Reaction of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U[ $\eta^2$ -C<sub>2</sub>(SiMe<sub>3</sub>)<sub>2</sub>] (**2**) with PhC $\equiv$ CPh: NMR-Scale.** A C<sub>6</sub>D<sub>6</sub> (0.2 mL) solution of PhC $\equiv$ CPh (3.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U[ $\eta^2$ -C<sub>2</sub>(SiMe<sub>3</sub>)<sub>2</sub>] (**2**; 14 mg, 0.02 mmol) and C<sub>6</sub>D<sub>6</sub> (0.3 mL). Resonances of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U[ $\eta^2$ -C<sub>4</sub>Ph<sub>4</sub>] (**3**)<sup>7b</sup> (<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 6.13 (s, 30H, CpCH<sub>3</sub>), 5.58 (t, *J* = 7.1 Hz, 4H, phenyl), 5.48 (t, *J* = 6.9 Hz, 2H, phenyl), 4.11 (d, *J* = 7.4 Hz, 4H, phenyl),  $-0.65$  (t, *J* = 6.9 Hz, 2H, phenyl),  $-1.72$  (d, *J* = 6.1 Hz, 4H, phenyl),  $-34.83$  (d, *J* = 5.5 Hz, 4H, phenyl) ppm) along with those of unreacted **2** and Me<sub>3</sub>SiC $\equiv$ CSiMe<sub>3</sub> (<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 0.15 (s, 18H, SiCH<sub>3</sub>) ppm) were observed by <sup>1</sup>H NMR spectroscopy (50% conversion on the basis of **2**). To this NMR sample, a C<sub>6</sub>D<sub>6</sub> (0.2 mL) solution of PhC $\equiv$ CPh (3.6 mg; 0.02 mmol) was added; resonances of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U[ $\eta^2$ -C<sub>4</sub>Ph<sub>4</sub>] (**3**) and Me<sub>3</sub>SiC $\equiv$ CSiMe<sub>3</sub> were observed by <sup>1</sup>H NMR spectroscopy (100% conversion). The NMR sample was maintained at 70 °C and monitored periodically by <sup>1</sup>H NMR spectroscopy. After 0.5 h, new resonances attributed to **4** (see below) were observed by <sup>1</sup>H NMR spectroscopy (60% conversion based on **3**). After 3 h, only resonances of **4** were observed by <sup>1</sup>H NMR spectroscopy (100% conversion).

**Preparation of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)[ $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>C(Ph)=C(Ph)C(Ph)-CHPh]U (**4**).** A toluene (5 mL) solution of PhC $\equiv$ CPh (142 mg, 0.80 mmol) was added to a toluene (10 mL) solution of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U[ $\eta^2$ -C<sub>2</sub>(SiMe<sub>3</sub>)<sub>2</sub>] (**2**; 272 mg, 0.40 mmol) with stirring at room temperature. After the solution was stirred at 70 °C overnight, the solvent was removed. The residue was extracted with benzene (10 mL  $\times$  3) and filtered. The volume of the filtrate was reduced to 5 mL; brown crystals of **4** were isolated when this solution was kept at room temperature for 1 week. Yield: 298 mg (86%). M.p.: 179–181 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 58.18 (s, 1H, phenyl), 50.84 (d, *J* = 14.4 Hz, 1H, phenyl), 35.93 (d, *J* = 14.3 Hz, 1H, phenyl), 18.93 (s, 4H, CH<sub>3</sub> and phenyl), 14.66 (s, 2H, phenyl), 11.02 (s, 2H, phenyl), 9.14 (s, 4H, CH<sub>3</sub> and phenyl), 8.41 (d, *J* = 10.5 Hz, 1H, phenyl), 8.03 (d, *J* = 9.3 Hz, 1H, phenyl), 7.11 (s, 18H, CH<sub>3</sub> and phenyl), 4.12 (s, 2H, CH<sub>2</sub>), 3.88 (s, 2H, phenyl), 1.39 (s, 1H, phenyl),  $-1.07$  (s, 4H, CH<sub>3</sub> and phenyl),  $-23.23$  (s, 3H, CH<sub>3</sub>),  $-28.65$  (s, 1H, phenyl),  $-29.51$  (s, 1H, phenyl),  $-31.46$  (s, 1H, PhCH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 318.6 (U–CPh), 278.1 (phenyl C), 224.0 (phenyl C), 184.5 (phenyl C), 178.3 (ring C), 176.8 (ring C), 171.6 (ring C), 170.2 (ring C), 135.7 (phenyl C), 134.5 (phenyl C), 130.8 (phenyl C), 129.3 (phenyl C), 128.5 (phenyl C), 127.9 (phenyl C), 125.6 (C=C), 120.1 (phenyl C), 119.5 (C=C),  $-32.9$  (CH<sub>3</sub>),  $-36.1$  (CH<sub>3</sub>),  $-57.1$  (CH<sub>2</sub>),  $-112.9$  (CH) ppm; other carbons overlapped. IR (KBr, cm<sup>-1</sup>) 2962 (s), 2926 (s), 1595 (m), 1440 (s), 1382 (s), 1259 (s), 1087 (s), 1018 (s), 798 (s). Anal. Calcd for C<sub>48</sub>H<sub>50</sub>U: C, 66.65; H, 5.83. Found: C, 66.60; H, 5.88.

**Preparation of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)U(C<sub>2</sub>Ph)[C(SiMe<sub>3</sub>)=CHSiMe<sub>3</sub>] (**5**). Method A.** This compound was prepared as red crystals from the reaction of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U[ $\eta^2$ -C<sub>2</sub>(SiMe<sub>3</sub>)<sub>2</sub>] (**2**; 272 mg, 0.40 mmol) and PhC $\equiv$ CH (41 mg, 0.40 mmol) in toluene (15 mL) at room temperature and recrystallization from a benzene solution by a procedure similar to that in the synthesis of **4**. Yield: 281 mg (90%).

M.p.: 129–131 °C (dec.).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 10.30 (t,  $J = 7.2$  Hz, 1H, phenyl), 9.33 (d,  $J = 7.6$  Hz, 2H, phenyl), 9.27 (s, 9H,  $\text{SiCH}_3$ ), 5.96 (t,  $J = 7.1$  Hz, 2H, phenyl), 1.62 (s, 30H,  $\text{CpCH}_3$ ),  $-8.69$  (s, 9H,  $\text{SiCH}_3$ ),  $-39.68$  (s, 1H,  $\text{C}\equiv\text{CH}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 361.9 ( $\text{UC}\equiv\text{C}$ ), 202.1 ( $\text{U}-\text{CSi}$ ), 185.3 (ring C), 136.7 ( $\text{SiCH}_3$ ), 128.6 (phenyl C), 127.9 (phenyl C), 111.5 (phenyl C), 67.3 (phenyl C), 31.4 ( $\text{SiCH}_3$ ),  $-13.5$  (CH),  $-13.7$  ( $\text{UC}\equiv\text{C}$ ),  $-40.4$  ( $\text{CpCH}_3$ ) ppm. IR (KBr,  $\text{cm}^{-1}$ ) 2958 (s), 2910 (s), 2295 (w), 1597 (w), 1442 (s), 1381 (s), 1246 (s), 1068 (s), 1022 (s), 839 (s). Anal. Calcd for  $\text{C}_{36}\text{H}_{54}\text{Si}_2\text{U}$ : C, 55.36; H, 6.97. Found: C, 55.23; H, 7.01.

**Method B: NMR-Scale.** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{PhC}\equiv\text{CH}$  (2.0 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **5** were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion).

**Preparation of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^4\text{-C}_4(\text{SiMe}_3)_2]$  (**6**).** **Method A.** This compound was prepared as brown crystals from the reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 272 mg, 0.40 mmol) and  $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$  (78 mg, 0.40 mmol) in toluene (15 mL) at room temperature and recrystallization from an *n*-hexane solution by a procedure similar to that in the synthesis of **4**. Yield: 219 mg (78%). M.p.: 168–170 °C (dec.).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 2.21 (s, 18H,  $\text{SiCH}_3$ ),  $-2.52$  (s, 30H,  $\text{CpCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 108.4 (ring C), 9.7 ( $\text{SiCH}_3$ ),  $-63.3$  ( $\text{CpCH}_3$ ) ppm; carbons of UC were not observed. IR (KBr,  $\text{cm}^{-1}$ ) 2962 (s), 2909 (s), 2068 (m), 1582 (m), 1404 (s), 1377 (s), 1259 (s), 1084 (s), 1018 (s), 800 (s). Anal. Calcd for  $\text{C}_{30}\text{H}_{48}\text{Si}_2\text{U}$ : C, 51.26; H, 6.88. Found: C, 51.23; H, 7.01.

**Method B: NMR-Scale.** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$  (3.9 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **6** and those of  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion).

**Preparation of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-N(Ph)CH(Ph)CH(Ph)N(Ph)]$  (**7**).** **Method A.** This compound was prepared as purple crystals from the reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 272 mg, 0.40 mmol) and  $\text{PhCH}=\text{NPh}$  (145 mg, 0.80 mmol) in toluene (15 mL) at room temperature and recrystallization from a benzene solution by a procedure similar to that in the synthesis of **4**. Yield: 286 mg (82%). M.p.: 257–259 °C (dec.).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 33.62 (s, 2H, CH), 10.80 (s, 30H,  $\text{CH}_3$ ), 8.30 (s, 4H, phenyl), 6.83 (s, 4H, phenyl), 6.36 (t,  $J = 6.1$  Hz, 2H, phenyl), 1.23 (s, 4H, phenyl), 0.88 (s, 4H, phenyl),  $-9.96$  (t,  $J = 7.1$  Hz, 2H, phenyl) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 338.4 (CH), 182.8 (ring C), 129.3 (phenyl C), 128.5 (phenyl C), 127.1 (phenyl C), 126.1 (phenyl C), 125.7 (phenyl C), 123.9 (phenyl C), 102.3 (phenyl C), 102.1 (phenyl C),  $-19.1$  ( $\text{CH}_3$ ) ppm. IR (KBr,  $\text{cm}^{-1}$ ) 2960 (w), 2897 (w), 1585 (s), 1483 (s), 1448 (s), 1257 (s), 1089 (s), 1020 (s), 887 (s). Anal. Calcd for  $\text{C}_{46}\text{H}_{52}\text{N}_2\text{U}$ : C, 63.44; H, 6.02; N, 3.22. Found: C, 63.39; H, 6.10; N, 3.19.

**Method B: NMR-Scale.** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{PhCH}=\text{NPh}$  (7.2 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **7** and those of  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion).

**Reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**) with  $\text{PhCH}=\text{NPh}$ : NMR-Scale.** A  $\text{C}_6\text{D}_6$  (0.2 mL) solution of  $\text{PhCH}=\text{NPh}$  (3.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.3 mL). Resonances of **7** along with those of unreacted **2** and  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  were observed by  $^1\text{H}$  NMR spectroscopy (50% conversion based on **2**).

**Preparation of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-N(p-tolyl)CH=CHN(p-tolyl)}]$  (**8**).** **Method A.** This compound was prepared as brown crystals from the reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 272 mg, 0.40 mmol) and  $(p\text{-tolylN}=\text{CH})_2$  (94 mg, 0.40 mmol) in toluene (15 mL) at room temperature and recrystallization from a benzene solution by a procedure similar to that in the synthesis of **4**. Yield: 274 mg (92%). M.p.: 147–149 °C (dec.).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 5.16 (s, 30H,  $\text{CpCH}_3$ ), 1.41 (s, 2H, CH), 0.14 (s, 6H,  $\text{tolylCH}_3$ ),  $-1.06$  (s, 4H, phenyl),  $-31.56$  (s, 2H, phenyl),  $-34.73$  (br s, 2H, phenyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR

( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 331.3 (CH), 138.2 (phenyl C), 129.3 (phenyl C), 128.5 (phenyl C), 123.9 (phenyl C), 100.2 (ring C), 9.6 ( $\text{tolylCH}_3$ ),  $-27.6$  ( $\text{CpCH}_3$ ) ppm. IR (KBr,  $\text{cm}^{-1}$ ) 2962 (s), 1612 (m), 1514 (s), 1382 (s), 1259 (s), 1089 (s), 1018 (s), 800 (s). Anal. Calcd for  $\text{C}_{36}\text{H}_{46}\text{N}_2\text{U}$ : C, 58.05; H, 6.23; N, 3.76. Found: C, 58.00; H, 6.30; N, 3.74.

**Method B: NMR-Scale.** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $(p\text{-tolylN}=\text{CH})_2$  (4.7 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **8** and those of  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion).

**Reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**) with 2,2'-Bipyridine: NMR-Scale.** A  $\text{C}_6\text{D}_6$  (0.2 mL) solution of bipy (3.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.3 mL). Resonances of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\text{bipy})$  (**9**)<sup>25c</sup> ( $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 0.14 (s, 30H,  $\text{CpCH}_3$ ),  $-20.27$  (d,  $J = 9.0$  Hz, 2H, bipy),  $-41.28$  (s, 2H, bipy),  $-81.37$  (s, 2H, bipy),  $-95.28$  (s, 2H, bipy) ppm) and  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion).

**Preparation of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\text{N}=\text{CPh})_2$  (**10**).**<sup>26</sup> **Method A.** This compound was prepared as brown crystals from the reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 272 mg, 0.40 mmol) and  $(\text{Ph}_2\text{C}=\text{N})_2$  (144 mg, 0.40 mmol) in toluene (15 mL) at room temperature and recrystallization from a benzene solution by a procedure similar to that in the synthesis of **4**. Yield: 274 mg (95%). M.p.: 200–202 °C (dec.).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 7.69 (d,  $J = 6.8$  Hz, 4H, phenyl), 7.35 (d,  $J = 7.4$  Hz, 4H, phenyl), 7.10 (m, 6H, phenyl), 7.02 (m, 6H, phenyl),  $-1.83$  (s, 30H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 160.1 (phenyl C), 154.3 (ring C), 150.1 (phenyl C), 138.8 (phenyl C), 136.4 (phenyl C), 129.8 (phenyl C), 129.2 (phenyl C), 128.8 (phenyl C), 112.2 (phenyl C), 58.0 ( $\text{N}=\text{C}$ ),  $-50.8$  ( $\text{CH}_3$ ) ppm. IR (KBr,  $\text{cm}^{-1}$ ) 3057 (m), 2900 (s), 1959 (w), 1660 (s), 1598 (s), 1566 (s), 1446 (s), 1386 (m), 1317 (s), 1276 (s), 1076 (s), 1026 (s), 889 (m), 765 (s). Anal. Calcd for  $\text{C}_{46}\text{H}_{50}\text{N}_2\text{U}$ : C, 63.58; H, 5.80; N, 3.22. Found: C, 63.54; H, 5.89; N, 3.17. Furthermore, this complex was further identified by X-ray diffraction analysis; for details, see the Supporting Information.

**Method B: NMR-Scale.** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $(\text{Ph}_2\text{C}=\text{N})_2$  (7.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **10** and those of  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion).

**Preparation of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-N(i-Pr)C(=Ni-Pr)N(i-Pr)}]$  (**11**).** **Method A.** This compound was prepared as brown crystals from the reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 272 mg, 0.40 mmol) and  $i\text{-PrN}=\text{C}=\text{Ni-Pr}$  (101 mg, 0.80 mmol) in toluene (15 mL) at room temperature and recrystallization from an *n*-hexane solution by a procedure similar to that in the synthesis of **4**. Yield: 238 mg (86%). M.p.: 121–123 °C (dec.).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 18.61 (s, 1H, CH), 11.80 (s, 1H, CH), 6.31 (s, 6H,  $\text{CH}_3$ ), 4.91 (s, 15H,  $\text{CpCH}_3$ ), 2.89 (s, 1H, CH),  $-0.03$  (s, 15H,  $\text{CpCH}_3$ ),  $-2.26$  (s, 6H,  $\text{CH}_3$ ),  $-4.20$  (s, 6H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 102.2 (ring C), 48.5 (CH), 43.9 (CH), 31.9 ( $\text{CH}_3$ ), 25.8 ( $\text{CH}_3$ ), 12.2 ( $\text{CH}_3$ ),  $-31.0$  ( $\text{C}=\text{N}$ ),  $-55.3$  ( $\text{CpCH}_3$ ),  $-56.0$  ( $\text{CpCH}_3$ ) ppm; other carbons overlapped. IR (KBr,  $\text{cm}^{-1}$ ) 2962 (s), 2914 (s), 1633 (s), 1575 (s), 1442 (s), 1379 (s), 1257 (s), 1080 (s), 1018 (s), 837 (s). Anal. Calcd for  $\text{C}_{30}\text{H}_{51}\text{N}_3\text{U}$ : C, 52.09; H, 7.43; N, 6.07. Found: C, 52.03; H, 7.51; N, 6.05.

**Method B: NMR-Scale.** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $i\text{-PrN}=\text{C}=\text{Ni-Pr}$  (5.0 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **11** and those of  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  and  $i\text{-PrNC}$  ( $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 3.34 (sep,  $J = 7.4$  Hz, 1H, CH), 1.04 (d,  $J = 7.4$  Hz, 6H,  $\text{CH}_3$ ) ppm) were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion).

**Reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**) with  $i\text{-PrN}=\text{C}=\text{Ni-Pr}$ : NMR-Scale.** A  $\text{C}_6\text{D}_6$  (0.2 mL) solution of  $i\text{-PrN}=\text{C}=\text{Ni-Pr}$  (2.5 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (**2**; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.3 mL). Resonances of **11** along with those of unreacted **2** and  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  and  $i\text{-PrNC}$  were observed by  $^1\text{H}$  NMR spectroscopy (50% conversion based on **2**).

**Preparation of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^4\text{-N}(\text{C}_6\text{H}_{11})\text{C}(\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_{11}))\text{C}=\text{C}(\text{SiMe}_3)]$  (12).** *Method A.* This compound was prepared as brown crystals from the reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (2; 272 mg, 0.40 mmol) and DCC (82 mg, 0.40 mmol) in toluene (15 mL) at room temperature and recrystallization from an *n*-hexane solution by a procedure similar to that in the synthesis of 4. Yield: 305 mg (86%). M.p.: 150–152 °C (dec.).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 6.19 (s, 4H,  $\text{CH}_2$ ), 5.78 (s, 2H,  $\text{CH}_2$ ), 5.02 (s, 30H,  $\text{CpCH}_3$ ), 4.16 (s, 2H,  $\text{CH}_2$ ), 2.76 (m, 1H, CH), 2.38 (s, 1H, CH), 0.04 (s, 9H,  $\text{SiCH}_3$ ),  $-2.56$  (s, 9H,  $\text{SiCH}_3$ ),  $-4.09$  (s, 4H,  $\text{CH}_2$ ),  $-7.18$  (s, 2H,  $\text{CH}_2$ ),  $-7.49$  (m, 2H,  $\text{CH}_2$ ),  $-10.43$  (s, 4H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 320.9 (U–C), 148.4 (ring C), 137.9 (C=C), 125.7 (C=C), 58.5 (NCH), 51.1 (NCH), 31.9 ( $\text{CH}_2$ ), 28.3 ( $\text{CH}_2$ ), 28.2 ( $\text{CH}_2$ ), 27.3 ( $\text{CH}_2$ ), 25.6 ( $\text{CH}_2$ ), 23.0 ( $\text{CH}_2$ ), 10.9 ( $\text{SiCH}_3$ ), 5.3 ( $\text{SiCH}_3$ ),  $-30.3$  ( $\text{CpCH}_3$ ) ppm. IR (KBr,  $\text{cm}^{-1}$ ) 2927 (s), 2852 (s), 1645 (m), 1570 (m), 1446 (s), 1379 (s), 1259 (s), 1091 (s), 1020 (s), 800 (s). Anal. Calcd for  $\text{C}_{41}\text{H}_{70}\text{N}_2\text{Si}_2\text{U}$ : C, 55.63; H, 7.97; N, 3.16. Found: C, 55.60; H, 7.85; N, 3.11.

*Method B: NMR-Scale.* A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of DCC (4.1 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (2; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of 12 were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion).

**Preparation of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\text{N}(\text{p-tolyl})_2]$  (13).** *Method A.* This compound was prepared as brown crystals from the reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (2; 272 mg, 0.40 mmol) and *p*-tolylN<sub>3</sub> (107 mg, 0.80 mmol) in toluene (15 mL) at room temperature and recrystallization from a benzene solution by a procedure similar to that in the synthesis of 4. Yield: 230 mg (80%). M.p.: 126–128 °C (dec.).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 9.14 (d,  $J = 8.1$  Hz, 4H, phenyl), 7.59 (s, 6H, tolyl $\text{CH}_2$ ), 4.10 (s, 30H,  $\text{CpCH}_3$ ), 2.70 (d,  $J = 8.1$  Hz, 4H, phenyl) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ) 181.8 (phenyl C), 155.5 (phenyl C), 136.1 (phenyl C), 108.4 (ring C), 107.5 (phenyl C), 9.0 (tolyl $\text{CH}_2$ ), 7.9 ( $\text{CpCH}_3$ ) ppm. IR (KBr,  $\text{cm}^{-1}$ ) 2962 (s), 2910 (s), 1618 (m), 1452 (s), 1377 (s), 1261 (s), 1097 (s), 1020 (s), 908 (s), 817 (s). Anal. Calcd for  $\text{C}_{34}\text{H}_{44}\text{N}_2\text{U}$ : C, 56.82; H, 6.17; N, 3.90. Found: C, 56.78; H, 6.26; N, 3.85.

*Method B: NMR-Scale.* A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of *p*-tolylN<sub>3</sub> (5.3 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (2; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of 13 and those of  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion).

**Reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (2) with *p*-tolylN<sub>3</sub>: NMR-Scale.** A  $\text{C}_6\text{D}_6$  (0.2 mL) solution of *p*-tolylN<sub>3</sub> (2.7 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (2; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.3 mL). Resonances of 13 along with those of unreacted 2 and  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  were observed by  $^1\text{H}$  NMR spectroscopy (50% conversion based on 2).

**Reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (2) with Bis(*p*-tolyl)-diazene: NMR-Scale.** A  $\text{C}_6\text{D}_6$  (0.2 mL) solution of bis(*p*-tolyl)-diazene (4.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (2; 14 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.3 mL). Resonances of 13 and  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  were observed by  $^1\text{H}$  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 K $\alpha$*  radiation ( $\lambda = 0.71073$  Å). An empirical absorption correction was applied using the SADABS program.<sup>37</sup> All structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXL program package.<sup>38</sup> All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for 2, 4–8, and 10–13 are summarized in the [Supporting Information](#). Selected bond lengths and angles are listed in [Table 1](#).

**Computational Methods.** All calculations were carried out with the Gaussian 09 program (G09),<sup>39</sup> employing the B3PW91 functional, plus a polarizable continuum model (PCM) (denoted as B3PW91-PCM), with standard 6-31G(d) basis set for C, H, N, and Si elements and a quasi-relativistic 5f-in-valence effective-core potential

(ECP60MWB) treatment with 60 electrons in the core region for U and the corresponding optimized segmented ((14s13p10d8f6g)/[10s9p5d4f3g]) basis set for the valence shells of U,<sup>40</sup> to fully optimize the structures of reactants, complexes, transition state, intermediates, and products and also to mimic the experimental toluene–solvent conditions (dielectric constant  $\epsilon = 2.379$ ). All stationary points were subsequently characterized by vibrational analyses, from which their respective zero-point (vibrational) energy (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 residing at minima and first-order saddle points, respectively, on their potential energy hypersurfaces. To consider the dispersion effect for the reactions  $2+\text{Ph}_2\text{C}_2+\text{Ph}_2\text{C}_2$  and  $2+(i\text{-PrN}=\text{C})_2\text{C}+(i\text{-PrN}=\text{C})_2\text{C}$ , single-point B3PW91-PCM-D3<sup>41</sup> calculations, based on B3PW91-PCM geometries, have been performed.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b01391.

Reactivity of thorium metallacyclopropenes; crystal parameters for compounds 2, 4–8, and 10–13; kinetic, magnetic susceptibility and computational studies; NMR spectra. (PDF)

Cartesian coordinates of all stationary points optimized at the B3PW91-PCM level. (XYZ)

X-ray crystallographic data for compounds 2, 4–8, and 10–13. (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21472013, 21272026, and 21573021), and the Deutsche Forschungsgemeinschaft (DFG) through the Emmy-Noether and Heisenberg program (WA 2513/2 and WA 2513/6, respectively).

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