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Intrinsic reactivity of a uranium metallacyclopropene toward unsaturated organic molecules†

Lei Zhang,^a Bo Fang,^a Guohua Hou,^a Lin Ai,^a Wanjian Ding,^{*a} Marc D. Walter^{*b} and Guofu Zi^{*a}

The uranium metallacyclopropene ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**) reacts with various small unsaturated organic molecules. For example, replacement of bis(trimethylsilyl)acetylene occurs when complex **1** is exposed to alkynes, conjugated alkenes, nitriles and quinones. Reaction of **1** with internal phenyl(alkyl) acetylene $\text{PhC}\equiv\text{CMe}$ selectively yields the C_s symmetric uranium metallacyclopentadiene ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}(\text{Ph})=\text{C}(\text{Me})\text{-C}(\text{Ph})=\text{C}(\text{Me})]$ (**6**) after the loss of bis(trimethylsilyl)acetylene, while treatment of **1** with phenyl(silyl)acetylenes ($\text{PhC}\equiv\text{CR}$, $\text{R} = \text{SiHMe}_2$, SiMe_3) gives the corresponding C_{2v} symmetric isomers ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}(\text{R})=\text{C}(\text{Ph})\text{-C}(\text{Ph})=\text{C}(\text{R})]$ ($\text{R} = \text{SiHMe}_2$ (**7**), SiMe_3 (**8**)). Furthermore, while no deprotonation occurs between complex **1** and pyridine derivatives, cyclohexanone can be inserted into the uranium metallacyclopropene moiety of **1** to yield the five-membered, heterocyclic complex ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\text{OC}(\text{CH}_2)_5\text{C}_2(\text{SiMe}_3)_2]$ (**14**) in quantitative conversion. Density functional theory (DFT) studies have been performed to complement the experimental studies.

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Introduction

Metallacyclopropenes have various synthetic and catalytic applications,^{1–3} e.g., metallacyclopropenes of group 4 metallocenes have been employed for the preparation of complex organic molecules or heterocyclic main group element compounds.^{1–3} Therefore group 4 metallacyclopropenes bearing the $\text{Cp}'_2\text{M}$ fragment (where $\text{Cp}' =$ substituted or unsubstituted $\eta^5\text{-cyclopentadienyl}$) represent synthetically useful synthons liberating the coordinated alkyne under mild conditions and transferring the $\text{Cp}'_2\text{M}(\text{II})$ fragment when reacted with unsaturated substrates.^{1,2} While group 4 chemistry is now well established, the corresponding actinide and lanthanide metallacycles have been neglected.^{1g,4} This is remarkable considering the recent advances in actinide mediated small molecule activation,^{1g,5} in which the influence of 6d and 5f orbitals on the reactivity of these species has been evaluated.⁶ In the course of our investigations, we have

recently reported on stable actinide metallacyclopropenes [$\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{)}_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$ ^{7a} and ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**).⁸ Interestingly, whereas the alkyne in the thorium metallacyclopropene [$\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{)}_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$] is strongly coordinated and reacts as a nucleophile towards hetero-unsaturated molecules or as a strong base inducing intermolecular C–H bond activation,^{7a,b} replacement of the coordinated alkyne occurs when the uranium metallacyclopropene ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**) reacts with unsaturated molecules such as alkynes, imines, bipy, carbodiimide, organic azides, and diazene derivatives.⁸ 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.⁹

Results and discussion

The reaction of the thorium metallacyclopropene [$\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{)}_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$] with pyridine derivatives induces C–H bond activation to give pyridyl alkenyl thorium compounds.^{7b,9} Nevertheless, similar to group 4 metallacyclopropene complexes,^{1,2} no deprotonation is observed between the uranium metallacyclopropene ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**) and pyridine or 4-(dimethylamino)pyridine (DMAP) even when heated at 50 °C overnight, instead, the corresponding adducts

^aDepartment of Chemistry, Beijing Normal University, Beijing 100875, China.

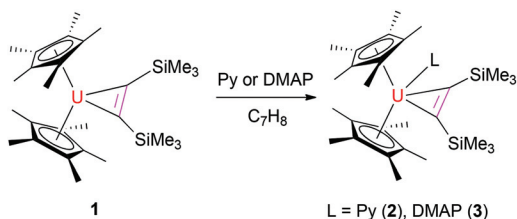
E-mail: dingwanjian@bnu.edu.cn, gzi@bnu.edu.cn

^bInstitut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany.

E-mail: mwalter@tu-bs.de

† Electronic supplementary information (ESI) available: Reactivity of thorium metallacyclopropenes, molecular structures of **15** and **16**, additional experiments and crystal parameters and Cartesian coordinates of all stationary points optimized at the B3PW91-PCM level. CCDC 1496477–1496481, 1496483–1496486 and 1496488–1496490. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt03005j





Scheme 1 Synthesis of complexes 2 and 3.

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2](\text{L})$ (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 $\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ 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,

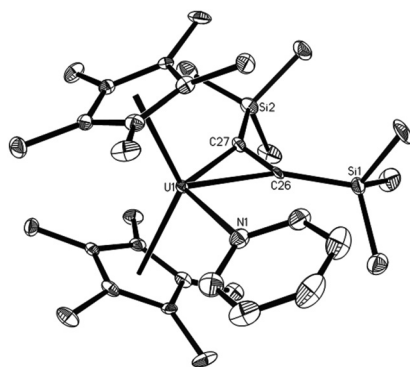


Fig. 1 Molecular structure of 2 (thermal ellipsoids drawn at the 35% probability level).

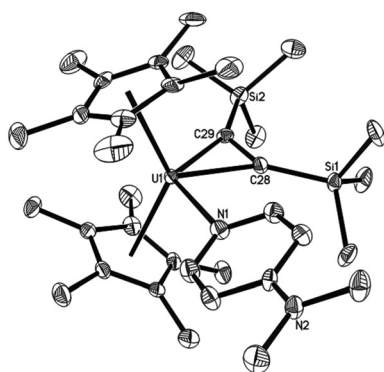


Fig. 2 Molecular structure of 3 (thermal ellipsoids drawn at the 35% probability level).

are longer than that found in $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UO}$ (DMAP) (2.535(4) Å).¹⁰ Nevertheless, deprotonation occurs when complex 1 is exposed to di(naphthalen-1-yl)methanimine (1-C₁₀H₇)₂CNH to form the alkenyl iminato $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\text{C}(\text{SiMe}_3)=\text{CH}(\text{SiMe}_3)][\text{N}=\text{C}(1\text{-C}_{10}\text{H}_7)_2]$ (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(6)° suggest some nitrogen π donation to the uranium atom. These structural parameters may be compared to those found in $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\text{NCPPh}_2)_2$ with the U–N distances of 2.169(6)–2.185(5) Å and the U–N–C angles of 172.8(6)–176.5(5)°,^{8,11} 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

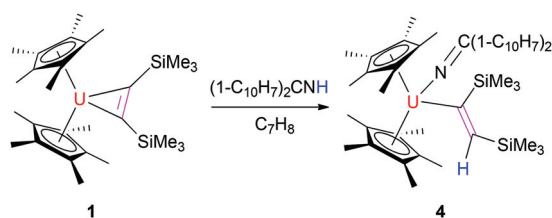
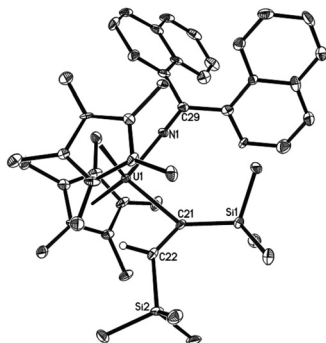
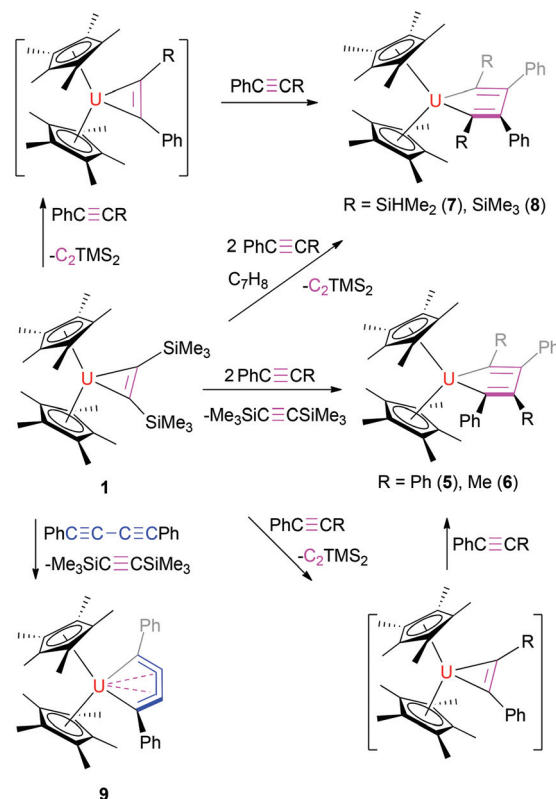
However, in contrast to the thorium metallacycloprenes,^{7a,9} the coordinated bis(trimethylsilyl)acetylene in 1 can be exchanged with the internal alkynes. Mixing the uranium metallacycloprenes 1 with internal alkynes PhC≡CR (where R = Ph, Me) in toluene at ambient temperature forms the corresponding metallacyclopentadienes $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}(\text{Ph})=\text{C}(\text{R})-\text{C}(\text{Ph})=\text{C}(\text{R})]$ (R = Ph (5),⁸ Me (6)) in quantitative conversions (Scheme 3). Our previous DFT computations suggest that one molecule of PhC≡CR initially reacts with 1 to displace bis(trimethylsilyl)acetylene and to form the corresponding metallacycloprenes $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2\text{Ph}(\text{R})]$, followed by a second insertion of PhC≡CR to yield the thermodynamically preferred metallacyclopentadienes (Scheme 3),⁸ which is presumably a consequence of the more open coordination sphere in the metallacycloprenes intermediates $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2\text{Ph}(\text{R})]$. Similar to the formation of thorium metallacyclopentadienes,^{7c} the C–C bond formation is selective, *i.e.*, the methyl-end of PhC≡CMe couples with the phenyl-substituted terminus of a second acetylene, leading to the *C_s*-symmetric $\text{U}[\eta^2\text{-C}(\text{Ph})=\text{C}(\text{Me})-\text{C}(\text{Ph})=\text{C}(\text{Me})]$ fragment. DFT studies confirm that the formation of this *C_s*-symmetric $\text{U}[\eta^2\text{-C}(\text{Ph})=\text{C}(\text{Me})-\text{C}(\text{Ph})=\text{C}(\text{Me})]$ fragment is thermodynamically more favourable ($\Delta G(298\text{ K}) = -17.7\text{ kcal mol}^{-1}$) than the *C_{2v}*-symmetric isomer $\text{U}[\eta^2\text{-C}(\text{Ph})=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{C}(\text{Ph})]$ (**P6b**; $\Delta G(298\text{ K}) = -16.4\text{ kcal mol}^{-1}$) or $\text{U}[\eta^2\text{-C}(\text{Me})=\text{C}(\text{Ph})-\text{C}(\text{Ph})=\text{C}(\text{Me})]$ (**P6a**; $\Delta G(298\text{ K}) = -15.2\text{ kcal mol}^{-1}$) and also proceeds with the lower activation barrier $\Delta G^\ddagger(298\text{ K}) = 21.3\text{ kcal mol}^{-1}$ (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≡CMe, the uranium metallacycloprenes intermediate $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2\text{Ph}(\text{Me})]$ and the transition state **TS6** (Fig. 5). The more negatively charged end of the internal alkyne coordinates to the electro-positive 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** ($\Delta G^\ddagger(298\text{ K}) = 21.3\text{ kcal mol}^{-1}$) is computed to be energetically more favour-



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

Compound	C(Cp)–U ^b	C(Cp)–U ^c	Cp(cent)–U ^b	U–X	Cp(cent)–U–Cp(cent)	X–U–X/Y
2	2.794(9)	2.754(9) to 2.830(9)	2.520(9)	C26: 2.369(8), C27: 2.346(8) N1: 2.625(8)	133.4(3)	33.0(3) ^d
3	2.831(6)	2.792(6) to 2.876(6)	2.555(6)	C28: 2.387(6), C29: 2.382(6) N1: 2.632(6)	133.4(2)	33.8(2) ^d
4	2.787(9)	2.746(8) to 2.813(9)	2.514(8)	C21: 2.436(9), N1: 2.191(8)	134.8(3)	99.0(3)
6	2.748(8)	2.714(8) to 2.774(8)	2.471(8)	C22: 2.399(9), C25: 2.365(8)	141.7(3)	78.4(3)
7	2.752(11)	2.734(10) to 2.777(11)	2.476(10)	C21: 2.400(11), C24: 2.382(11)	137.0(4)	79.7(4)
8	2.764(7)	2.755(7) to 2.780(7)	2.497(7)	C14: 2.370(8), C14A: 2.370(8)	136.9(3)	85.6(3)
11	2.766(10)	2.715(10) to 2.827(10)	2.495(10)	N1: 2.447(10), N2: 2.364(11) N3: 2.270(11)	131.8(4)	N1–U–N2: 54.5(4) N1–U–N3: 120.2(5) N2–U–N3: 67.8(4)
12	2.714(8)	2.684(8) to 2.749(8)	2.434(8)	O1: 2.191(5), O2: 2.202(5)	139.2(2)	73.1(2)
13	2.750(11)	2.655(11) to 2.805(10)	2.476(10)	O1: 2.130(6), O2A: 2.127(6)	133.3(2)	98.3(2)
14	2.810(14)	2.734(14) to 2.886(11)	2.556(12)	O1: 2.062(8), C21: 2.512(12)	130.4(3)	67.9(3)

^a Cp = cyclopentadienyl ring. ^b Average value. ^c Range. ^d The angle of C–U–C.

**Scheme 2** Synthesis of complex 4.**Fig. 3** Molecular structure of 4 (thermal ellipsoids drawn at the 35% probability level).**Scheme 3** Synthesis of complexes 5–9.

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(silyl)acetylene $\text{PhC}\equiv\text{CSiHMe}_2$ or $\text{PhC}\equiv\text{CSiMe}_3$ is added to compound 1, the metallacyclopentadienes ($\eta^5\text{-C}_5\text{Me}_5$)₂U[$\eta^2\text{-C(R)=C(Ph)-C(Ph)=C(R)}$] (R = SiHMe₂ (7), SiMe₃ (8)) are isolated exclusively, but the selectivity in the C–C bond formation changes (Scheme 3), that is, the phenyl-substituted terminus of $\text{PhC}\equiv\text{CR}$ couples with the phenyl-substituted one of a second acetylene to give a C_{2v} -symmetric U[$\eta^2\text{-C(R)=C(Ph)-C(Ph)=C(R)}$] moiety. Our DFT investigations also reproduce this change in selectivity. The C_{2v} -symmetric isomer ($\eta^5\text{-C}_5\text{Me}_5$)₂U[$\eta^2\text{-C(SiHMe}_2)=\text{C(Ph)-$

$\text{C(Ph)=C(SiHMe}_2)]$ 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_s -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 $\text{PhC}\equiv\text{CSiHMe}_2$, the intermediate ($\eta^5\text{-C}_5\text{Me}_5$)₂U[$\eta^2\text{-C}_2\text{Ph(SiHMe}_2)]$ and the transition state **TS7** (Fig. 5). However, in



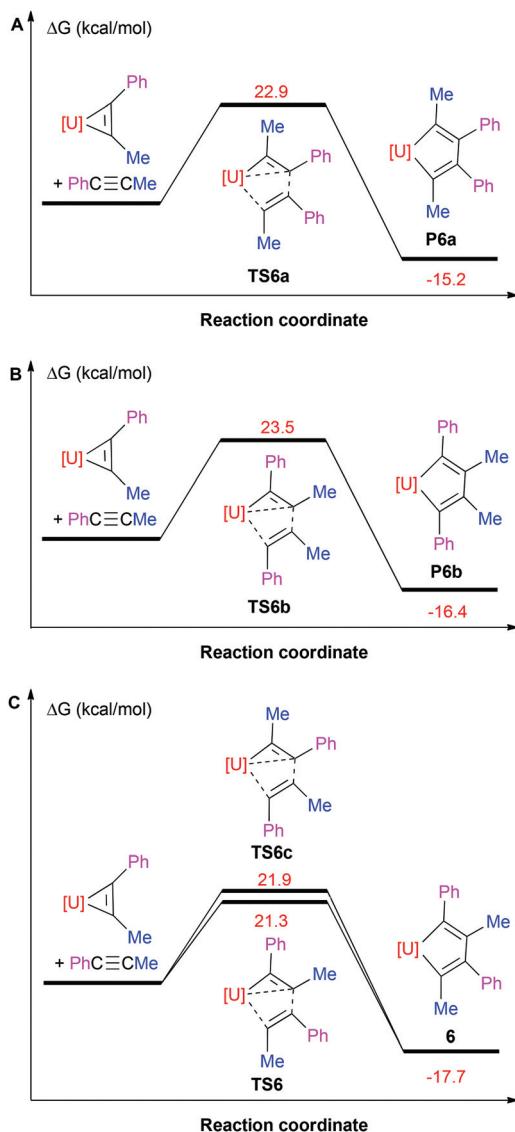


Fig. 4 Free energy profile (kcal mol⁻¹) for the reaction of (η⁵-C₅Me₅)₂U [η²-C(Ph)=C(Me)] + PhC≡CMe (U was treated with ECP60MWB). [U] = (η⁵-C₅Me₅)₂U.

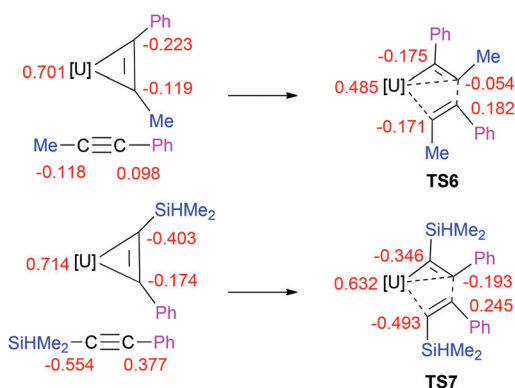


Fig. 5 Mulliken charges of the free alkynes, their respective uranium metallacycloprenes and transition state complexes. [U] = (η⁵-C₅Me₅)₂U.

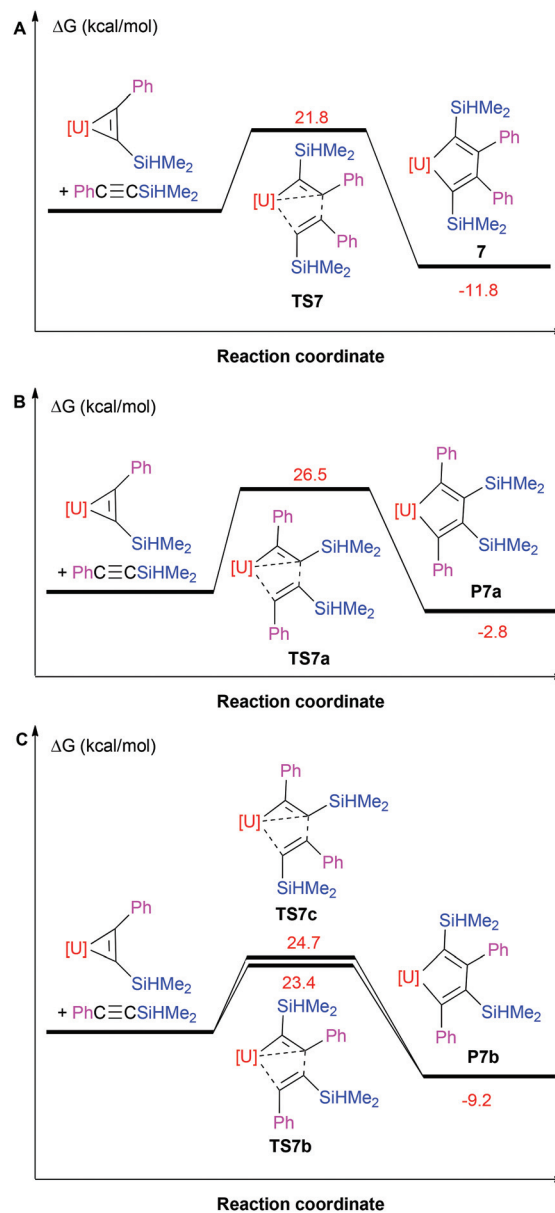


Fig. 6 Free energy profile (kcal mol⁻¹) for the reaction of (η⁵-C₅Me₅)₂U [η²-C(Ph)=C(SiHMe₂)] + PhC≡CSiHMe₂ (U was treated with ECP80MWB). [U] = (η⁵-C₅Me₅)₂U.

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



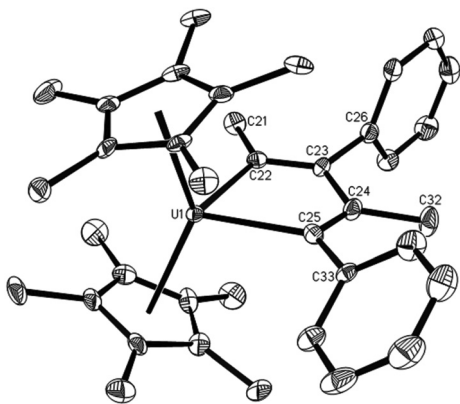


Fig. 7 Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level).

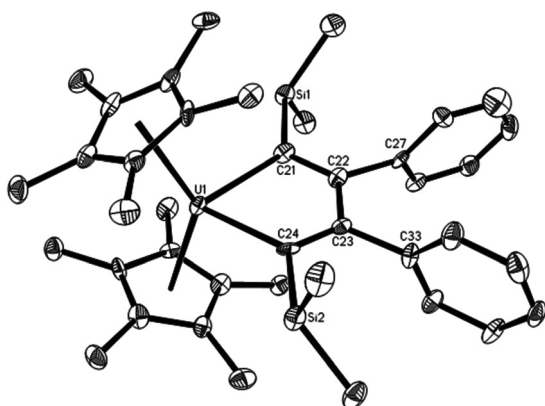


Fig. 8 Molecular structure of **7** (thermal ellipsoids drawn at the 35% probability level).

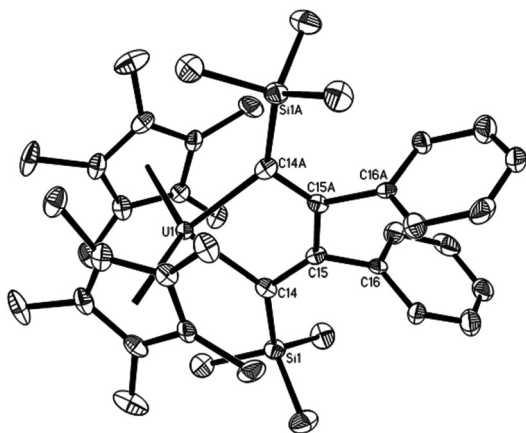


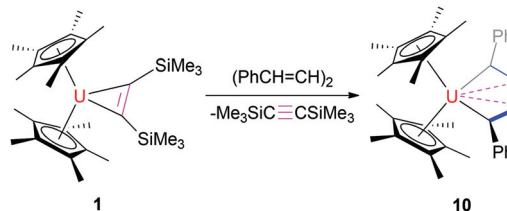
Fig. 9 Molecular structure of **8** (thermal ellipsoids drawn at the 35% probability level).

1.374(9) Å for **8**, and therefore are very close to those previously reported for related actinide metallacyclopentadiene compounds,^{4,7c} e.g., $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\eta^2\text{-C}_4\text{Ph}_4)$ (1.365(3), 1.509(4) and

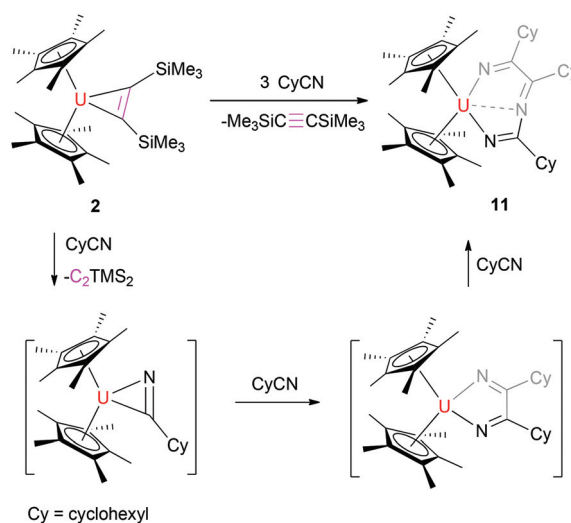
1.365(3) Å)^{4e} and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\eta^2\text{-C}_4\text{Me}_4)$ (1.354(4), 1.521(6) and 1.354(4) Å).⁴ⁿ

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 ($\text{PhC}\equiv\text{CC}\equiv\text{CPh}$) or 1,4-diphenylbutadiene ($\text{PhCH}=\text{CHCH}=\text{CHPh}$) yields the uranium metallacyclopentatriene $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\eta^4\text{-C}_4\text{Ph}_2)$ (**9**) (Scheme 3) and the metallacyclopentene $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-CH(Ph)CH}=\text{CHCH(Ph)}]$ (**10**) (Scheme 4), respectively, in quantitative conversions. However, no reaction occurs when **1** is exposed to olefins such as $\text{RCH}=\text{CHR}$ ($\text{R} = \text{H, Ph, Me}$) 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 $\text{C}_6\text{H}_{11}\text{CN}$ to yield the C–C and N–C coupling product $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^3\text{-N}=\text{C}(\text{C}_6\text{H}_{11})\text{C}(\text{C}_6\text{H}_{11})=\text{NC}(\text{C}_6\text{H}_{11})=\text{N}]$ (**11**) (Scheme 5). This contrasts the reaction of the related thorium metallacyclopentene $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$ with PhCN ,^{7a,9} for which an insertion product was isolated. In analogy to the reactivity of group 4 metallacyclopentene $(\eta^5\text{-C}_5\text{Me}_5)_2\text{M}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ ($\text{M} = \text{Ti, Zr}$),^{2h,l} we propose that $\text{C}_6\text{H}_{11}\text{CN}$ initially replaces the bis(trimethylsilyl)acetylene frag-



Scheme 4 Synthesis of complex **10**.



Cy = cyclohexyl

Scheme 5 Synthesis of complex **11**.



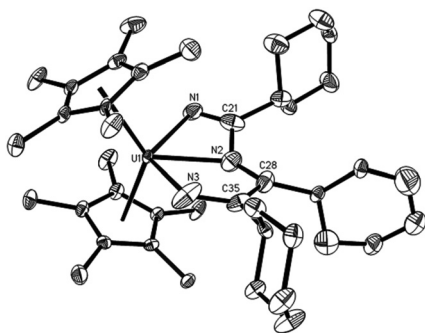


Fig. 10 Molecular structure of **11** (thermal ellipsoids drawn at the 35% probability level).

ment to give a metal η^2 -nitrile intermediate,¹³ which immediately couples with a second molecule of $C_6H_{11}CN$ to give a five-membered metallaheterocycle,^{2h,l} that further reacts with a third molecule of $C_6H_{11}CN$ 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 N(1)–C(21)–N(2)–C(28)–C(35)–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- $C_{14}H_8O_2$) to **1** forms the monomeric uranium quinonate (η^5 - C_5Me_5)₂U(9,10- $O_2C_{14}H_8$) (**12**)¹⁴ concomitant with free bis(trimethylsilyl)acetylene (Scheme 6), whereas the less sterically encumbered *o*-benzoquinone affords the dimeric quinonate [$(\eta^5$ - C_5Me_5)₂U]₂(μ -*o*- $O_2C_6H_4$)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

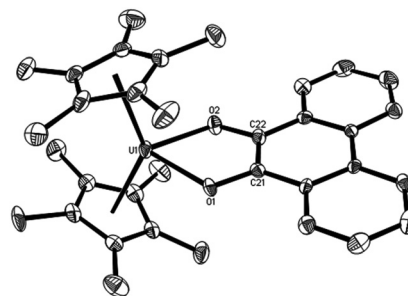


Fig. 11 Molecular structure of **12** (thermal ellipsoids drawn at the 35% probability level).

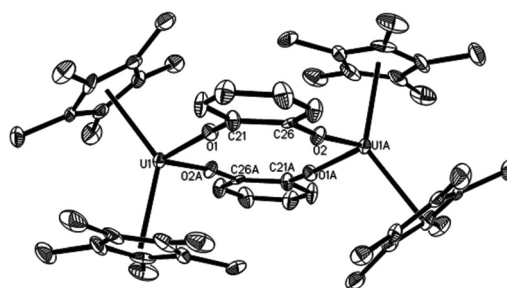
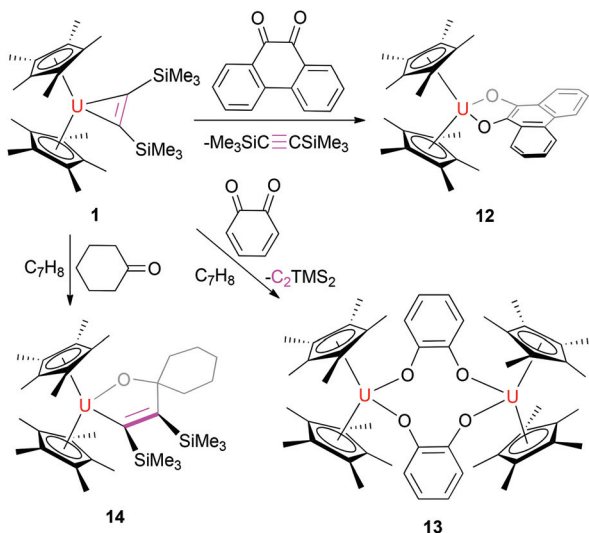


Fig. 12 Molecular structure of **13** (thermal ellipsoids drawn at the 35% probability level).

reaction with quinones, but similar to the reactivity of the thorium metallacyclopropene [η^5 -1,2,4-(Me_3C)₃ C_5H_2]₂Th(η^2 - C_2Ph_2) towards ketones (for details see the ESI[†]), insertion of 1 equiv. of cyclohexanone ($(CH_2)_5CO$) into the uranium metallacyclopropene moiety of **1** is observed at ambient temperature to exclusively yield the five-membered uranium heterocycle (η^5 - C_5Me_5)₂U[OC(CH_2)₅($C_2(SiMe_3)_2$)] (**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) σ -bonds found in compounds **1–4** (2.315(9)–2.436(9) Å).



Scheme 6 Synthesis of complexes **12–14**.

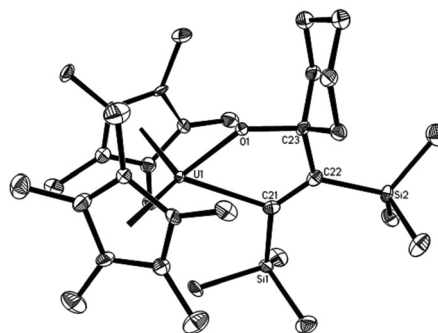


Fig. 13 Molecular structure of **14** (thermal ellipsoids drawn at the 35% probability level).



Conclusions

While the coordinated alkyne in the thorium metallacyclopropenes is inert towards alkyne exchange, it can react as a nucleophile towards hetero-unsaturated molecules or as a strong base inducing inter- or intramolecular C–H bond activations.^{7,9} In contrast, addition of pyridine derivatives to the uranium complex ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**) forms the corresponding Lewis-base adducts ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**L**) (**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 ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}^{2+}$ and $[\eta^2\text{-C}_2(\text{SiMe}_3)_2]^{2-}$ fragments and is a consequence of the enhanced 5f orbitals contributing to the bonding in the uranium metallacyclopropene $\text{U}(\eta^2\text{-C}=\text{C})$ moiety.⁸ Furthermore, in contrast to the thorium metallacyclopropenes,^{7,9} replacement of the coordinated alkyne occurs when complex **1** is exposed to alkynes, conjugated alkenes, nitriles and quinones. These distinct reactivity patterns are similar to those of the more covalent group 4 metallacyclopropene complexes.^{1,2} Nevertheless, thorium and uranium metallacyclopropenes exhibit similar reactivity patterns when exposed to ketones, which are inserted into the actinide metallacyclopropene 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. ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**) was prepared according to literature methods.⁸ 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 $^{13}\text{C}\{^1\text{H}\}$ 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 X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

Syntheses

Preparation of ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2](\text{Py})$ (2**).** A toluene (5 mL) solution of pyridine (32 mg, 0.40 mmol) was added to a toluene (10 mL) solution of ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**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. $\text{C}_{33}\text{H}_{53}\text{NSi}_2\text{U}$ requires C, 52.29; H, 7.05; N, 1.85%). M.p.: 93–95 °C (dec.). ^1H NMR (C_6D_6): δ 25.95 (br s, 1H, py), 14.96 (s, 9H, SiCH_3), 6.38 (s, 1H, py), –2.07 (s, 1H, py), –3.27 (s, 30H, CpCH_3), –3.94 (s, 9H, SiCH_3), –6.56 (s, 1H, py), –10.67 (br s, 1H, py) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 133.4 (ring C), 125.6 (py C), 99.7 (py C), 79.8 (py C), 60.4 (SiCH_3), –54.7 (SiCH_3), –66.8 (CpCH_3) ppm; carbons of UCSiMe_3 were not observed. IR (KBr, cm^{-1}): 2962 (s), 2895 (s), 1598 (m), 1570 (m), 1433 (s), 1402 (s), 1242 (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 ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2](\text{DMAP})$ (3**).** This compound was prepared as a brown solid in quantitative yield from the reaction of ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**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. $\text{C}_{35}\text{H}_{58}\text{N}_2\text{Si}_2\text{U}$ requires C, 52.48; H, 7.30; N, 3.50%). M.p.: 107–109 °C (dec.). ^1H NMR (C_6D_6): δ 16.13 (br s, 9H, SiCH_3), 14.52 (br s, 9H, SiCH_3), –0.50 (s, 1H, py), –2.94 (s, 6H, NCH_3), –3.36 (s, 30H, CpCH_3), –3.52 (s, 1H, py) ppm; two protons were not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 128.5 (py C), 128.1 (py C), 127.9 (py C), 113.3 (ring C), 62.3 (SiCH_3), 36.1 (NCH_3), –65.9 (CpCH_3) ppm; carbons of UCSiMe_3 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 ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\text{C}(\text{SiMe}_3)=\text{CH}(\text{SiMe}_3)][\text{N}=\text{C}(1\text{-C}_{10}\text{H}_7)_2]$ (4**).** **Method A.** A toluene (5 mL) solution of ($1\text{-C}_{10}\text{H}_7\text{)}_2\text{CNH}$ (113 mg, 0.4 mmol) was added to a toluene (10 mL) solution of ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**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 \times 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. $\text{C}_{49}\text{H}_{63}\text{NSi}_2\text{U}$ requires C, 61.29; H, 6.61; N, 1.46%). M.p.: 177–179 °C (dec.). ^1H NMR (C_6D_6): δ 19.01 (s, 9H, SiCH_3), 15.05 (br s, 4H, aryl), 9.23 (s, 2H, aryl), 7.60 (m, 2H, aryl), 4.59 (s, 1H, $\text{C}=\text{CH}$), 1.23 (s, 2H, aryl), 0.89 (s, 2H, aryl), 0.32 (s, 2H, aryl), –1.80 (s, 30H, CpCH_3), –9.78 (s, 9H, SiCH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 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 ($\text{N}=\text{C}$), 19.9 (SiCH_3), 15.0 (SiCH_3), –33.5 (CH) –51.6 (CpCH_3) ppm. IR (KBr, cm^{-1}): 2958 (s), 2899 (s), 1595 (s), 1579 (s), 1558 (s), 1402 (s), 1259 (s), 1246 (s), 1095 (s), 1018 (s), 840 (s), 775 (s).

Method B. NMR Scale. A C_6D_6 (0.3 mL) solution of ($1\text{-C}_{10}\text{H}_7\text{)}_2\text{CNH}$ (5.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with ($\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$



(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[η²-C(Ph)=C(Me)C(Ph)=C(Me)]·0.5C₆H₆ (6·0.5C₆H₆). Method A. This compound was prepared as brown crystals from the reaction of (η⁵-C₅Me₅)₂U[η²-C₂(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. C₄₁H₄₉U requires C, 63.15; H, 6.33%). M.p.: 103–105 °C (dec.). ¹H NMR (C₆D₆): δ 7.15 (s, 3H, C₆H₆), 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 (UCPh), 260.2 (UCCH₃), 197.4 (ring C), 188.4 (ring C), 130.3 (phenyl C), 129.6 (phenyl C), 129.3 (phenyl C), 128.0 (C₆H₆), 124.7 (phenyl C), 122.9 (phenyl C), 122.5 (phenyl C), 122.4 (phenyl C), 121.9 (phenyl C), 112.2 (C=C(Ph)), 104.5 (C=C(Me)), 91.2 (UCCH₃), 69.7 (C=CCH₃), -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[η²-C₂(SiMe₃)₂] (1; 14 mg, 0.02 mmol) and C₆D₆ (0.2 mL). Resonances of 6 and those of Me₃SiC≡CSiMe₃ (¹H NMR (C₆D₆): δ 0.15 (s, 18H, SiCH₃) ppm) were observed by ¹H NMR spectroscopy (100% conversion).

Reaction of (η⁵-C₅Me₅)₂U[η²-C₂(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[η²-C₂(SiMe₃)₂] (1; 14 mg, 0.02 mmol) and C₆D₆ (0.3 mL). Resonances of 6 along with those of unreacted 1 and Me₃SiC≡CSiMe₃ were observed by ¹H NMR spectroscopy (50% conversion based on 1).

Preparation of (η⁵-C₅Me₅)₂U[η²-C(SiHMe₂)=C(Ph)C(Ph)=C(SiHMe₂)] (7). Method A. This compound was prepared as brown crystals from the reaction of (η⁵-C₅Me₅)₂U[η²-C₂(SiMe₃)₂] (1; 272 mg, 0.40 mmol) and PhC≡CSiHMe₂ (128 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: 279 mg (84%) (Found: C, 57.98; H, 6.61. C₄₀H₅₄Si₂U requires C, 57.95; H, 6.57%). M.p.: 118–120 °C. ¹H NMR (C₆D₆): δ 6.74 (d, 4H, *J* = 7.4 Hz, phenyl), 6.29 (t, 4H, *J* = 7.2 Hz, phenyl), 5.27 (t, 2H, *J* = 6.9 Hz, phenyl), 3.66 (s, 30H, CpCH₃), -6.10 (s, 12H, SiCH₃), -30.20 (s, 2H, SiH) ppm. ¹³C{¹H} NMR (C₆D₆): δ 266.9 (UCSi), 231.4 (ring C), 128.5 (phenyl C), 127.9 (phenyl C), 124.3 (phenyl C), 123.4 (phenyl C), 105.1 (CPh), -1.5 (SiCH₃), -41.4 (CpCH₃) ppm. IR (KBr, cm⁻¹): 2960 (s), 2902 (s), 2083 (s), 1593 (m), 1408 (s), 1259 (s), 1070 (s), 1018 (s), 937 (s), 887 (s).

Method B. NMR Scale. A C₆D₆ (0.3 mL) solution of PhC≡CSiHMe₂ (6.4 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with (η⁵-C₅Me₅)₂U[η²-C₂(SiMe₃)₂] (1; 14 mg, 0.02 mmol) and C₆D₆ (0.2 mL). Resonances of 7 and those of Me₃SiC≡CSiMe₃ were observed by ¹H NMR spectroscopy (100% conversion).

Reaction of (η⁵-C₅Me₅)₂U[η²-C₂(SiMe₃)₂] (1) with PhC≡CSiHMe₂. NMR Scale. A C₆D₆ (0.2 mL) solution of PhC≡CSiHMe₂ (3.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with (η⁵-C₅Me₅)₂U[η²-C₂(SiMe₃)₂] (1; 14 mg, 0.02 mmol) and C₆D₆ (0.3 mL). Resonances of 7 along with those of unreacted 1 and Me₃SiC≡CSiMe₃ were observed by ¹H NMR spectroscopy (50% conversion based on 1).

Preparation of (η⁵-C₅Me₅)₂U[η²-C(SiMe₃)=C(Ph)C(Ph)=C(SiMe₃)] (8). Method A. This compound was prepared as brown crystals from the reaction of (η⁵-C₅Me₅)₂U[η²-C₂(SiMe₃)₂] (1; 272 mg, 0.40 mmol) and PhC≡CSiMe₃ (140 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. C₄₂H₅₈Si₂U 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, 12H, 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), 1595 (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≡CSiMe₃ (7.0 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with (η⁵-C₅Me₅)₂U[η²-C₂(SiMe₃)₂] (1; 14 mg, 0.02 mmol) and C₆D₆ (0.2 mL). Resonances of 8 and those of Me₃SiC≡CSiMe₃ were observed by ¹H NMR spectroscopy (100% conversion).

Reaction of (η⁵-C₅Me₅)₂U[η²-C₂(SiMe₃)₂] (1) with PhC≡CSiMe₃. NMR Scale. A C₆D₆ (0.2 mL) solution of PhC≡CSiMe₃ (3.5 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with (η⁵-C₅Me₅)₂U[η²-C₂(SiMe₃)₂] (1; 14 mg, 0.02 mmol) and C₆D₆ (0.3 mL). Resonances of 8 along with those of unreacted 1 and Me₃SiC≡CSiMe₃ were observed by ¹H NMR spectroscopy (50% conversion based on 1).

Preparation of (η⁵-C₅Me₅)₂U[η⁴-C₄Ph₂] (9). Method A. This compound was prepared as brown microcrystals from the reaction of (η⁵-C₅Me₅)₂U[η²-C₂(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, 5.71. C₃₆H₄₀U requires C, 60.84; H, 5.67%). 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), 136.8 (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 $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**; 14 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **9** and those of $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ were observed by ^1H NMR spectroscopy (100% conversion).

Preparation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-CH(Ph)CH=CHCH(Ph)]$ (10**).** **Method A.** This compound was prepared as brown microcrystals from the reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**; 272 mg, 0.40 mmol) and $\text{PhCH}=\text{CHCH}=\text{CHPh}$ (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. $\text{C}_{36}\text{H}_{44}\text{U}$ requires C, 60.49; H, 6.20%). M.p.: 153–155 °C (dec.). ^1H NMR (C_6D_6): δ 47.19 (s, 2H, $\text{CH}=\text{C}$), 12.58 (s, 15H, CpCH_3), -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. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 463.2 (UC), 219.8 ($\text{CH}=\text{C}$), 169.8 (ring C), 155.4 (phenyl C), 155.1 (phenyl C), 127.9 (phenyl C), 74.3 (phenyl C), -11.5 (CpCH_3), -49.8 (CpCH_3) ppm. IR (KBr, cm^{-1}): 2962 (s), 2910 (s), 1492 (m), 1438 (s), 1402 (s), 1384 (s), 1259 (s), 1072 (s), 1020 (s), 800 (s).

Method B. NMR Scale. A C_6D_6 (0.3 mL) solution of $\text{PhCH}=\text{CHCH}=\text{CHPh}$ (4.1 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**; 14 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **10** and those of $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ were observed by ^1H NMR spectroscopy (100% conversion) after this solution was kept at 70 °C for two days.

Preparation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^3\text{-N}=\text{C}(\text{C}_6\text{H}_{11})\text{C}(\text{C}_6\text{H}_{11})=\text{NC}(\text{C}_6\text{H}_{11})=\text{N}]\cdot 0.5\text{C}_6\text{H}_6$ (11**·0.5 C_6H_6).** **Method A.** This compound was prepared as brown crystals from the reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**; 272 mg, 0.40 mmol) and $\text{C}_6\text{H}_{11}\text{CN}$ (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. $\text{C}_{44}\text{H}_{66}\text{N}_3\text{U}$ requires C, 60.39; H, 7.60; N, 4.80%). M.p.: 235–237 °C (dec.). ^1H NMR (C_6D_6): δ 16.51 (m, 1H, CH_2), 14.55 (m, 2H, CH_2), 14.01 (m, 2H, CH_2), 7.15 (s, 3H, C_6H_6), 7.04 (m, 2H, CH_2), 6.09 (m, 2H, CH_2), 5.76 (m, 2H, CH_2), 4.89 (m, 1H, CH_2), 4.70 (m, 1H, CH_2), 3.70 (m, 2H, CH_2), 2.98 (m, 2H, CH_2), 2.63 (m, 1H, CH_2), 1.88 (s, 30H, CpCH_3), 0.20 (m, 2H, CH_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. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 195.3 (ring C), 166.6 ($\text{C}=\text{N}$), 164.9 ($\text{C}=\text{N}$), 128.0 (C_6H_6), 107.0 ($\text{C}=\text{N}$), 64.2 (CH), 64.1 (CH), 63.3 (CH), 34.1 (CH_2), 31.9 (CH_2), 31.7 (CH_2), 29.1 (CH_2), 27.3 (CH_2), 27.2 (CH_2), 26.6 (CH_2), 18.6 (CH_2), 11.5 (CH_2), -40.8 (CpCH_3) ppm. IR (KBr, cm^{-1}): 2962 (s), 2922 (s), 1617 (m), 1560 (m), 1400 (s), 1386 (s), 1259 (s), 1089 (s), 1016 (s), 798 (s).

Method B. NMR Scale. A C_6D_6 (0.3 mL) solution of $\text{C}_6\text{H}_{11}\text{CN}$ (6.6 mg, 0.06 mmol) was slowly added to a J. Young NMR tube charged with $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**; 14 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **11** and those of

$\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ were observed by ^1H NMR spectroscopy (100% conversion).

Preparation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(9,10\text{-O}_2\text{C}_{14}\text{H}_8)$ (12**).** **Method A.** This compound was prepared as brown crystals from the reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**; 272 mg, 0.40 mmol) and 9,10-phenanthrenequinone (85 mg, 0.40 mmol) in toluene (15 mL) at room temperature and recrystallized from a toluene solution by a similar procedure as that in the synthesis of **4**. Yield: 258 mg (90%) (Found: C, 57.01; H, 5.31. $\text{C}_{34}\text{H}_{38}\text{O}_2\text{U}$: C, 56.98; H, 5.34%). M.p.: >300 °C (dec.). ^1H NMR (C_6D_6): δ 3.76 (s, 30H, CpCH_3), 2.82 (d, 2H, $J = 8.2$ Hz, phenyl), 2.04 (t, 2H, $J = 9.3$ Hz, phenyl), -1.58 (d, 2H, $J = 9.0$ Hz, phenyl), -25.39 (d, 2H, $J = 7.7$ Hz, phenyl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 132.4 (ring C), 125.6 (aryl C), 115.6 (aryl C), 115.2 (aryl C), 113.7 (aryl C), 109.5 (aryl C), 97.0 (aryl C), 95.4 (aryl C), -27.3 (CpCH_3) ppm. IR (KBr, cm^{-1}): 2960 (s), 2906 (s), 1595 (m), 1517 (s), 1477 (s), 1409 (s), 1365 (s), 1109 (s), 1028 (s), 920 (s), 756 (s).

Method B. NMR Scale. A C_6D_6 (0.3 mL) solution of 9,10-phenanthrenequinone (4.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**; 14 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **12** and those of $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ were observed by ^1H NMR spectroscopy (100% conversion).

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}]_2(\mu\text{-}o\text{-O}_2\text{C}_6\text{H}_4)_2\cdot\text{C}_6\text{H}_6$ (13**· C_6H_6).** **Method A.** This compound was prepared as orange crystals from the reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**; 272 mg, 0.40 mmol) and *o*-benzoquinone (43 mg, 0.40 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: 220 mg (84%) (Found: C, 53.08; H, 5.71. $\text{C}_{58}\text{H}_{74}\text{O}_4\text{U}_2$ requires C, 53.13; H, 5.69%). M.p.: >300 °C (dec.). ^1H NMR (C_6D_6): δ 7.15 (s, 6H, C_6H_6), 2.11 (s, 4H, phenyl), 1.78 (s, 60H, CpCH_3), -12.33 (s, 4H, phenyl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 147.1 (ring C), 128.0 (C_6H_6), 125.6 (phenyl C), 108.4 (phenyl C), 108.2 (phenyl C), -36.5 (CpCH_3) ppm. IR (KBr, cm^{-1}): 2962 (m), 1581 (m), 1479 (s), 1402 (s), 1263 (s), 1224 (s), 1097 (s), 1018 (s), 904 (s), 825 (s).

Method B. NMR Scale. A C_6D_6 (0.3 mL) solution of *o*-benzoquinone (2.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**; 14 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **13** and those of $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ were observed by ^1H NMR spectroscopy (100% conversion).

Preparation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\text{OC}(\text{CH}_2)_5(\text{C}_2(\text{SiMe}_3)_2)]$ (14**).** **Method A.** This compound was prepared as brown crystals from the reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**; 272 mg, 0.40 mmol) and cyclohexanone (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. $\text{C}_{34}\text{H}_{58}\text{OSi}_2\text{U}$ requires C, 52.55; H, 7.52%). M.p.: 115–117 °C (dec.). ^1H NMR (C_6D_6): δ 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,



CpCH₃), -22.08 (s, 6H, SiCH₃), -38.94 (s, 3H, SiCH₃) ppm. ¹³C {¹H} NMR (C₆D₆): δ 198.5 (UC), 143.3 (CH₂), 142.5 (UC=C), 141.5 (CH₂), 118.7 (CO), 112.3 (ring C), 56.7 (CH₂), 55.4 (CH₂), 54.2 (CH₂), 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)₂U[η²-C₂(SiMe₃)₂] (**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 ESI.† 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.

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