

## Organometallic Chemistry

# Uranium versus Thorium: Synthesis and Reactivity of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}[\eta^2-\text{C}_2\text{Ph}_2]$

Deqiang Wang,<sup>[a]</sup> Wanjian Ding,<sup>[a]</sup> Guohua Hou,<sup>[a]</sup> Guofu Zi,<sup>\*[a]</sup> and Marc D. Walter<sup>\*[b]</sup>

**Abstract:** The synthesis, electronic structure, and reactivity of a uranium metallacyclopropene were comprehensively studied. Addition of diphenylacetylene ( $\text{PhC}\equiv\text{CPh}$ ) to the uranium phosphinidene metallocene  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}=\text{P}-2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$  (**1**) yields the stable uranium metallacyclopropene,  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}[\eta^2-\text{C}_2\text{Ph}_2]$  (**2**). Based on density functional theory (DFT) results the 5f orbital contributions to the bonding within the metallacyclopropene  $\text{U}-(\eta^2-\text{C}=\text{C})$  moiety increases significantly compared to the related  $\text{Th}^{\text{IV}}$  compound  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}[\eta^2-\text{C}_2\text{Ph}_2]$ , which also results in more covalent bonds between

the  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}^{2+}$  and  $[\eta^2-\text{C}_2\text{Ph}_2]^{2-}$  fragments. Although the thorium and uranium complexes are structurally closely related, different reaction patterns are therefore observed. For example, **2** reacts as a masked synthon for the low-valent uranium(II) metallocene  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}^{\text{II}}$  when reacted with  $\text{Ph}_2\text{E}_2$  ( $\text{E}=\text{S}, \text{Se}$ ), alkynes and a variety of hetero-unsaturated molecules such as imines, ketazine, bipy, nitriles, organic azides, and azo derivatives. In contrast, five-membered metallaheterocycles are accessible when **2** is treated with isothiocyanate, aldehydes, and ketones.

## Introduction

Metallacyclopropenes, especially those of d-transition metals, have been extensively studied for the last three decades.<sup>[1]</sup> Within this class of compounds group 4 metallacyclopropenes bearing a  $\text{Cp}'_2\text{M}$  fragment (where  $\text{Cp}'$  = substituted or unsubstituted  $\eta^5$ -cyclopentadienyl) are probably the most thoroughly investigated class. In the presence of a suitable unsaturated substrate, the coordinated alkyne is readily displaced releasing a  $\text{Cp}'_2\text{M}^{\text{II}}$  fragment which reacts with the provided substrate to yield highly functionalized organic molecules or heterocyclic main group element compounds.<sup>[1,2]</sup> The reactivity of these group 4 metallacyclopropenes varies with the steric and electronic properties exerted by the  $\text{Cp}'$  and alkyne ligands.<sup>[1,2]</sup> In contrast to this well-established chemistry of group 4 metals, metallacycles of the lanthanides and actinides have only recently attracted renewed attention after many years of inactivi-

ty.<sup>[3]</sup> These studies should be considered in the context of current developments in the actinide field focusing on small molecule activation<sup>[4]</sup> and the impact of 5f orbital contributions on bonding and the reactivity.<sup>[5]</sup>

We have been interested in thorium and uranium metallacycles for some time,<sup>[6]</sup> which we recently documented with the synthesis of two stable actinide metallacyclopropenes  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}[\eta^2-\text{C}_2\text{Ph}_2]$ <sup>[6a]</sup> and  $(\eta^5-\text{C}_5\text{Me}_5)_2\text{U}[\eta^2-\text{C}_2(\text{SiMe}_3)_2]$ .<sup>[6f]</sup> The alkyne in the thorium metallacyclopropene  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}[\eta^2-\text{C}_2\text{Ph}_2]$  reacts as a nucleophile towards hetero-unsaturated molecules such as aldehydes, ketones,  $\text{CS}_2$ , carbodiimides, nitriles, isothiocyanates, organic azides, and diazoalkane derivatives or as a strong base inducing intermolecular C–H bond activation.<sup>[6a,b]</sup> In contrast, the uranium metallacyclopropene  $(\eta^5-\text{C}_5\text{Me}_5)_2\text{U}[\eta^2-\text{C}_2(\text{SiMe}_3)_2]$  acts as a masked synthon for the  $(\eta^5-\text{C}_5\text{Me}_5)_2\text{U}(\text{II})$  fragment when reacted with unsaturated molecules.<sup>[6f,g]</sup> Unfortunately, at the time we could not directly compare  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}[\eta^2-\text{C}_2\text{Ph}_2]$  to its uranium analogue  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}[\eta^2-\text{C}_2\text{Ph}_2]$  (**2**), so that some of the differences observed for  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}[\eta^2-\text{C}_2\text{Ph}_2]$  and  $(\eta^5-\text{C}_5\text{Me}_5)_2\text{U}[\eta^2-\text{C}_2(\text{SiMe}_3)_2]$  may also be traced to the different steric requirements of the coordinated ligands. Only recently, we could serendipitously isolate the missing uranium counterpart  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}[\eta^2-\text{C}_2\text{Ph}_2]$  (**2**), while studying the reactivity of  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}=\text{P}-2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$  (**1**).<sup>[7]</sup> This now allowed us to directly evaluate both actinide metallacyclopropenes and to establish differences and similarities in the reactivity of these compounds. These results are described in this manuscript.

[a] D. Wang, Dr. W. Ding, Dr. G. Hou, Prof. G. Zi  
Department of Chemistry, Beijing Normal University, Beijing 100875 (China)  
E-mail: gzi@bnu.edu.cn

[b] Prof. Dr. M. D. Walter  
Institut für Anorganische und Analytische Chemie  
Technische Universität Braunschweig, Hagenring 30  
38106 Braunschweig (Germany)  
E-mail: mwalter@tu-bs.de

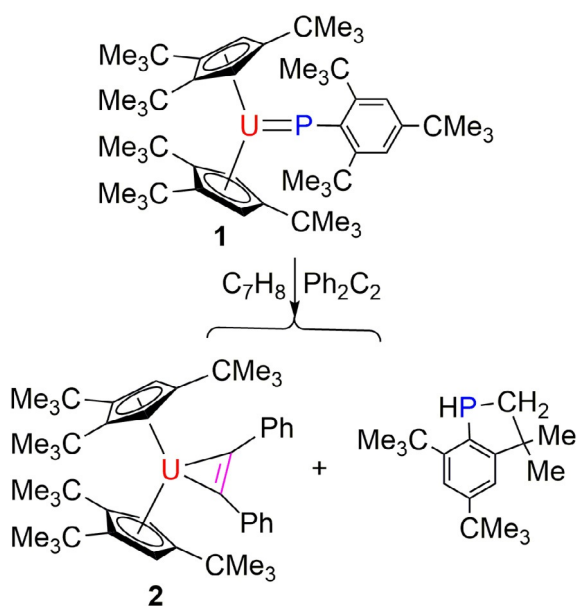
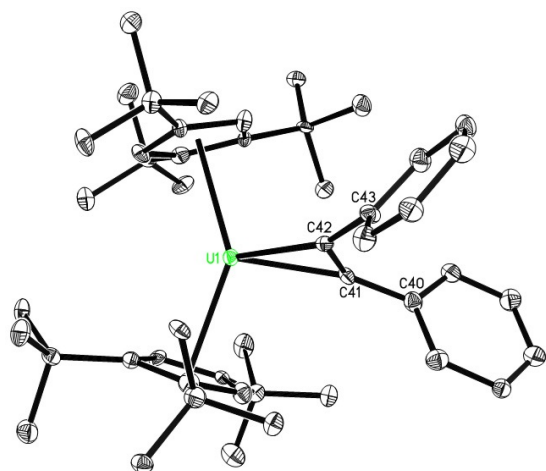
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:  
<https://doi.org/10.1002/chem.202100089>.

© 2021 The Authors. Chemistry - A European Journal published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

## Results and Discussion

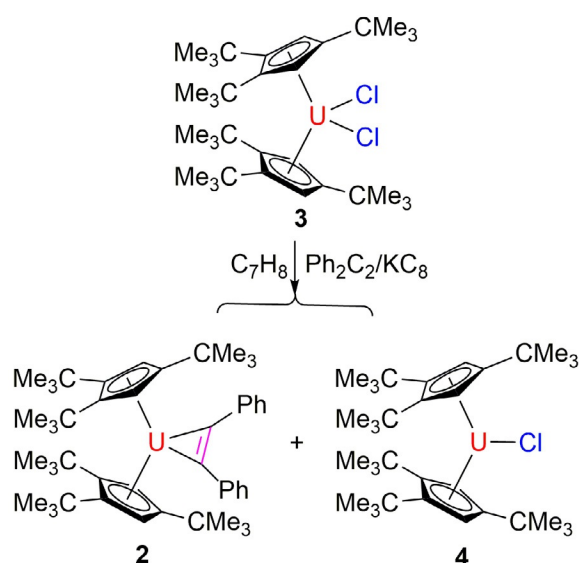
Synthesis of  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**)

Heating a mixture of the uranium phosphinidene metallocene  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}=\text{P}-2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$  (**1**) with  $\text{PhC}\equiv\text{CPh}$  in toluene at  $50^\circ\text{C}$  forms the air and moisture sensitive metallacyclopropene,  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**), which can be isolated as brown crystals in 80% yield, while the phosphinidane 3,3-Me<sub>2</sub>-5,7-*t*Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>P is formed as the side-product (Scheme 1).<sup>[7]</sup> Complex **2** is very soluble in and readily recrystallized from an *n*-hexane solution. The molecular structure of **2** is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. The relevant C(41)–C(42) distance of 1.33(2) Å agrees with the value found for a typical double bond

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

(1.331 Å)<sup>[6a]</sup> and is essentially identical to those found in the uranium metallacyclopropene  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (1.338(11) Å)<sup>[6f]</sup> and the thorium metallacyclopropenes  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$  (1.343(4) Å)<sup>[6a]</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>[6e]</sup> indicating a doubly reduced alkyne ligand,  $[\eta^2\text{-C}_2\text{Ph}_2]^{2-}$ . The angle ( $33.2(6)^\circ$ ) of C(41)–U(1)–C(42) also parallels that in the uranium metallacyclopropene  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  ( $33.3(3)^\circ$ )<sup>[6f]</sup> and the C–Th–C angle ( $32.6(1)^\circ$ ) in the related thorium metallacyclopropene  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$ .<sup>[6a]</sup> Furthermore, the angles of C(41)–C(42)–C(43) ( $127(2)^\circ$ ) and C(40)–C(41)–C(42) ( $130(2)^\circ$ ) approach a value of  $120^\circ$ , which is the expectation value for  $\text{sp}^2$ -hybridized carbon atoms. The U–C distances are 2.35(2) Å for C(41) and 2.298(19) Å for C(42), which are similar but slightly more asymmetric than those in  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$  (2.315(9) and 2.350(9) Å).<sup>[6f]</sup> For comparison the Th–C distance in the thorium metallacyclopropene  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$  is 2.395(2) Å,<sup>[6a]</sup> which is longer than expected based on the different ionic radii of Th<sup>IV</sup> (1.05 Å) and U<sup>IV</sup> (1.00 Å) (with a coordination number of 8).<sup>[8]</sup>

Nevertheless, in contrast to the formation of the thorium metallacyclopropene  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$ ,<sup>[6a]</sup> the reduction of  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{UCl}_2$  (**3**) in the presence of an excess of potassium graphite ( $\text{KC}_8$ ) and diphenylacetylene ( $\text{PhC}\equiv\text{CPh}$ ) does not cleanly yield the desired uranium metallacyclopropene **2**, but a mixture of the uranium metallacyclopropene **2** and the uranium(III) chloride species  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{UCl}$  (**4**)<sup>[9]</sup> is formed (Scheme 2), which can be explained by the moderate reduction potential of  $\text{U}^{\text{IV}}/\text{U}^{\text{III}}$  ( $E^\circ = -0.63\text{ V}$ ).<sup>[10]</sup> The ratio of **2** and **4** is roughly 1:3 (as confirmed by <sup>1</sup>H NMR spectroscopy). Unfortunately, this mixture cannot be converted to pure **2** upon prolonged reduction with excess potassium graphite ( $\text{KC}_8$ ) in the presence of diphenylacetylene. Furthermore, attributed to a remarkably similar solubility the mixture of complexes **2** and **4** could not be separated by recrystallization.

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

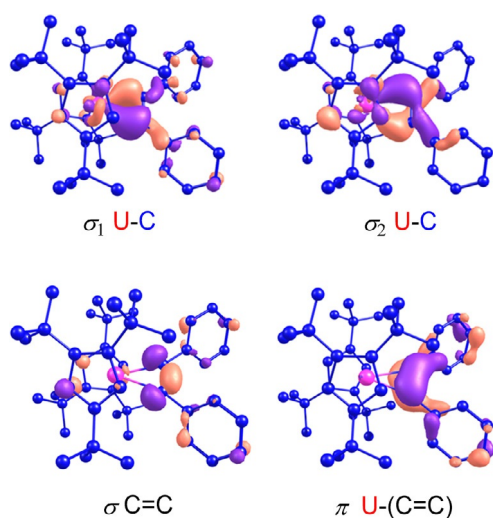
**Table 1.** Selected distances (Å) and angles (deg) for compounds **2**, **5**, **9**, **10**, **12**, **14**, **16–18** and **20–23**.<sup>[a]</sup>

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>	2.79(2)	2.71(2) to 2.890(18)	2.51(2)	C(41) 2.35(2), C(42) 2.298(19)	141.2(6)	33.2(6)
<b>2'</b> (Th) <sup>[6a]</sup>	2.861(2)	2.798(2) to 2.950(2)	2.592(2)	Th—C 2.395(2), 2.395	138.7(2)	32.6(1)
<b>5</b>	2.803(5)	2.746(5) to 2.855(5)	2.528(5)	C(41) 2.475(5), C(42) 2.449(5) C(43) 2.448(5), C(44) 2.463(5)	139.4(2)	92.4(2) <sup>[d]</sup>
<b>9</b>	2.798(3)	2.737(3) to 2.873(3)	2.523(3)	N(1) 2.222(2), N(2) 2.214(2)	149.2(1)	72.3(1)
<b>10</b>	2.817(5)	2.731(6) to 2.927(6)	2.544(6)	N(1) 2.252(5), N(1A) 2.252(5)	144.3(2)	70.9(3)
<b>12</b>	2.818(5)	2.748(5) to 2.914(5)	2.546(5)	N(1) 2.208(4), C(35) 2.482(6)	136.4(2)	69.3(2)
<b>14</b>	2.806(3)	2.749(3) to 2.888(3)	2.532(2)	N(1) 1.977(3), N(2) 1.974(3)	139.2(1)	98.7(1)
<b>16</b>	2.841(5)	2.729(5) to 2.976(5)	2.570(5)	N(1) 1.968(4)	134.1(3)	
<b>17</b>	2.787(5)	2.725(5) to 2.846(5)	2.511(5)	N(1) 2.227(4), N(2) 2.418(4) C(39) 2.517(6)	140.4(2)	33.4(2) <sup>[e]</sup>
<b>18</b>	2.804(5)	2.709(5) to 2.931(4)	2.530(5)	S(1) 2.659(1), S(2) 2.628(1)	142.5(1)	100.4(1)
<b>20</b>	2.795(10)	2.699(10) to 2.895(10)	2.522(10)	S(1) 2.649(2), C(37) 2.480(10)	140.9(2)	76.0(2)
<b>21</b>	2.828(3)	2.731(3) to 2.962(3)	2.557(3)	O(1) 2.062(2), C(37) 2.581(3)	133.6(1)	67.6(1)
<b>22</b>	2.817(4)	2.726(3) to 2.953(4)	2.546(4)	O(1) 2.069(2), C(43) 2.577(4)	133.8(1)	67.5(1)
<b>23</b>	2.833(5)	2.735(5) to 2.916(5)	2.562(5)	O(1) 2.076(4), C(35) 2.572(6)	126.7(2)	67.1(2)

[a] Cp = cyclopentadienyl ring. [b] Average value. [c] Range. [d] The angle of C(41)—U(1)—C(44). [e] The angle of N(1)—U(1)—N(2).

## Bonding studies

Density functional theory (DFT) computations at the B3PW91 level of theory were performed to probe the interaction between the  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}^{2+}$  and the  $[\eta^2-\text{C}_2\text{Ph}_2]^{2-}$  fragments, which also allows the bonding in **2** to be compared to its thorium analogue  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2-\text{C}_2\text{Ph}_2)$  (**2'**). Computed and experimentally determined molecular structure of **2** are in good agreement and reproduce the asymmetry within the An $[\eta^2-\text{C}_2\text{Ph}_2]$  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 2. The natural localized molecular orbital (NLMO) analysis (Table 2) suggests that  $\sigma_1(\text{U}-\text{C})$  bond combines a carbon hybrid orbital (72.9.0%; 25.7% s and 74.3% p) and a uranium hybrid orbital (22.0%; 41.1% 5f and 54.0% 6d), whereas  $\sigma_2(\text{U}-\text{C})$  bond is formed by a carbon hybrid orbital (72.9%; 25.7% s and 74.3% p) and a ura-



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

nium hybrid orbital (22.2%; 40.9% 5f and 54.2%). In addition, two bonding orbitals are identified for the C—C bond: the  $\sigma$ -bond ( $\sigma(\text{C}=\text{C})$ ) composes of two carbon hybrid orbitals (47.7%; 29.0% s and 71.0% p; and 47.7%; 28.9% s and 71.1% p), whereas the  $\pi$ -bond ( $\pi[\text{U}(\text{C}=\text{C})]$ ) is made up by 84.6% carbon occupancy consisting of only p orbitals and a 11.7% contribution from a uranium hybrid orbital (48.5% 5f and 50.6% 6d). These results implicate that electron density is also shifted from the alkyne  $\pi$ -orbital to the electron deficient metal uranium atom.

However, in the thorium counterpart  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2-\text{C}_2\text{Ph}_2)$  (**2'**), the metal contribution to the bonding of the Th $(\eta^2-\text{C}_2\text{Ph}_2)$  moiety is significantly reduced (16.0% and 16.1% Th for Th—C  $\sigma_1$  and  $\sigma_2$  bond, respectively, and 8.4% Th for Th—(C=C)  $\pi$  bond) (Table 2). An increased charge separation result, which increases the electrostatic interaction between the individual  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{An}^{2+}$  and  $[\eta^2-\text{C}_2\text{Ph}_2]^{2-}$  fragments, that is, 1.56 for U (**2**) and 2.12 for Th (**2'**) (Table 2). Furthermore, the Wiberg bond order of the An—C $_2\text{Ph}_2$  is reduced from 0.801 and 0.804 (for **2**) to 0.678 and 0.681 (for **2'**) (Table 2). Both observations reflect the increased polarization and ionicity within the bonding between the metallocene  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}^{2+}$  and the alkyne  $[\eta^2-\text{C}_2\text{Ph}_2]^{2-}$  fragments. Also the  $\pi$ -donation from the  $\pi$ -MO of the coordinated alkyne to the metal atom is significantly less efficient, which is due to an increase in the 5f orbital energy of the thorium atom relative to that of the uranium atom.<sup>[5g,h]</sup> The evaluation of the 5f orbital contribution to the U—C  $\sigma$  (41.1% and 40.9% for  $\sigma_1$  and  $\sigma_2$  bond, respectively) and U—(C=C)  $\pi$  (48.5%) bonds in **2** reveals it to be substantially larger than that of the 5f orbitals in **2'** (16.7% and 16.6% for Th—C  $\sigma_1$  and  $\sigma_2$  bond, respectively, and 31.2% for Th—(C=C)  $\pi$  bond), which is in line with the previously investigated systems.<sup>[5d,f,6c,f,i]</sup> Overall, this difference should also manifest itself in divergent reactivities of the uranium complex **2** relative to that of the thorium metallacyclopropenes.<sup>[6a,b,11]</sup>

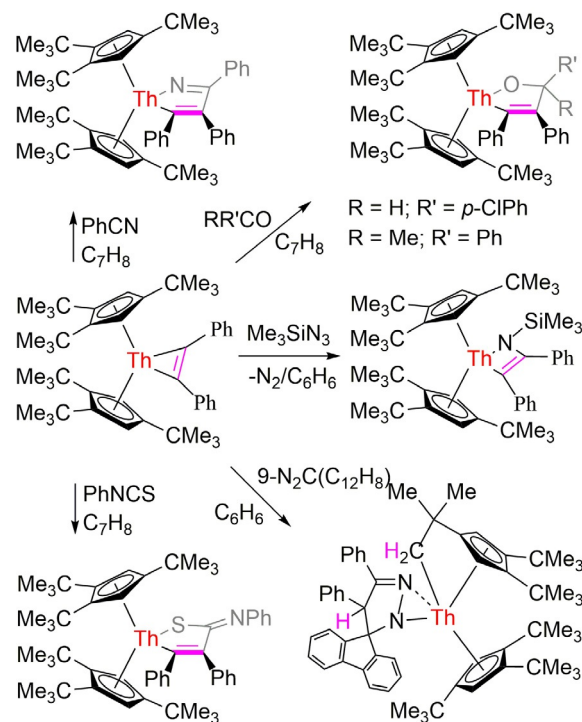
**Table 2.** Natural localized molecular orbital (NLMO) analysis of An–(C<sub>2</sub>Ph<sub>2</sub>) bonds,<sup>[a]</sup> bond order, and the natural charges for the [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>An and [η<sup>2</sup>-C<sub>2</sub>Ph<sub>2</sub>] units.

		2 (U)	2' (Th)	
σ <sub>1</sub> An–C	%An	22.0	16.0	
	%s	3.6	5.1	
	%p	1.3	1.9	
	%d	54.0	76.3	
	%f	41.1	16.7	
	%C	72.9	79.0	
	%s	25.7	25.6	
	%p	74.3	74.6	
	σ <sub>2</sub> An–C	%An	22.2	16.1
		%s	3.6	5.0
%p		1.3	1.8	
%d		54.2	76.6	
%f		40.9	16.6	
%C		72.9	79.0	
%s		25.7	25.4	
%p		74.3	74.6	
σ C=C		%An	3.0	2.9
		%s	1.8	2.7
	%p	3.3	3.5	
	%d	44.0	51.1	
	%f	50.9	42.7	
	%C	47.7	47.9	
	%s	29.0	31.6	
	%p	71.0	68.4	
	π An(C=C)	%An	11.7	8.4
		%p	0.9	2.1
%d		50.6	66.7	
%f		48.5	31.2	
%C		42.3	44.0	
%p		100	100	
%C		42.3	44.1	
%p		100	100	
Wiberg bond order (An–C <sub>2</sub> Ph <sub>2</sub> )			0.801	0.678
NBO charge (An)			0.804	0.681
NBO charge (Cp <sub>2</sub> An)		1.31	1.60	
NBO charge (C <sub>2</sub> Ph <sub>2</sub> )		0.78	1.06	
NBO charge (C <sub>2</sub> Ph <sub>2</sub> )		–0.78	–1.06	

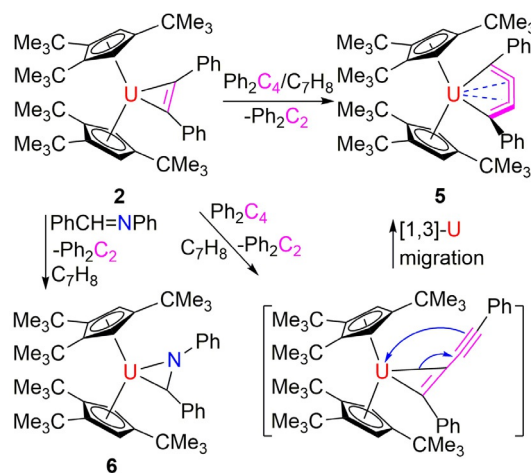
[a] The contributions by atom and orbital are averaged over all the ligands of the same type (complexes of U and Th) and over alpha and beta orbital contributions (complex of U).

## Reactivity studies

We then investigated the reactivity of **2** towards a series of organic substrates and compared the reaction outcomes to those obtained for the thorium metallacyclopropene complex [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th(η<sup>2</sup>-C<sub>2</sub>Ph<sub>2</sub>) (**2'**). Figure 3 summarizes the products obtained for **2'**.


**Figure 3.** Selected reactivity of [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th(η<sup>2</sup>-C<sub>2</sub>Ph<sub>2</sub>) (**2'**).

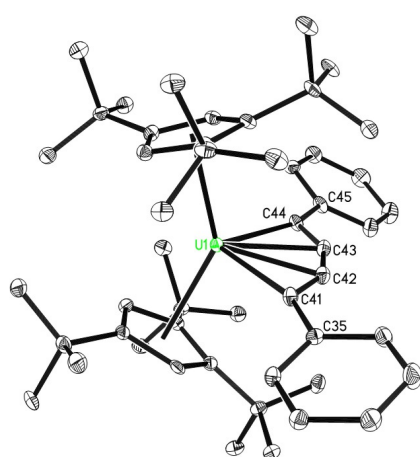
In accordance with the thorium metallacyclopropene [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th(η<sup>2</sup>-C<sub>2</sub>Ph<sub>2</sub>),<sup>[6a]</sup> no alkyne dissociation could be detected by NMR spectroscopy within the temperature range of 20–100 °C. However, contrary to the thorium metallacyclopropene [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th(η<sup>2</sup>-C<sub>2</sub>Ph<sub>2</sub>),<sup>[6a]</sup> the coordinated diphenylacetylene ligand in **2** is labile enough to be exchanged by internal alkynes. For example, addition of 1,4-diphenylbutadiyne (PhC≡CC≡CPh) at 40 °C gives the uranium metallacyclopentatriene complex [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>U(η<sup>4</sup>-C<sub>4</sub>Ph<sub>2</sub>) (**5**) and diphenylacetylene (PhC≡CPh) (Scheme 3). To account for this transformation, it is proposed that diphenylbutadiyne replaces diphenylacetylene to give a metallacyclopro-


**Scheme 3.** Synthesis of complexes **5** and **6**.

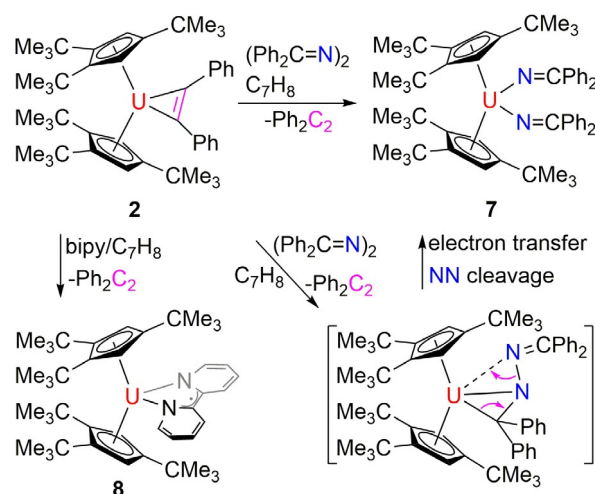
ene complex, which converts by a [1,3]-U migration to yield complex **5** (Scheme 3). The molecular structure of **5** is provided in Figure 4, and selected bond distances and angles are listed in Table 1. The C–C distances of C(41)–C(42), C(42)–C(43) and C(43)–C(44) are 1.307(7), 1.305(8) and 1.300(7) Å, respectively, which suggest a delocalized cumulene moiety. The angles of C(35)–C(41)–C(42) and C(45)–C(44)–C(43) are 127.5(5) and 128.3(5)°, respectively, approach the value of 120°, consistent with  $sp^2$ -hybridization at the carbon atoms. Nevertheless, the cumulene fragment itself remains rather strained with C(41)–C(42)–C(43) and C(44)–C(43)–C(42) angles of 150.2(5)° and 149.9(5)°, respectively. Similar structural parameters were also found for the previously reported actinide metallacyclopentatrienes ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An( $\eta^4$ -C<sub>4</sub>Ph<sub>2</sub>) (An = Th,<sup>[6d]</sup> U<sup>[3p]</sup>), ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U[ $\eta^4$ -C<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>]<sup>[6f]</sup> [ $\eta^5$ -1,3-(Me<sub>3</sub>C)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>]<sub>2</sub>U( $\eta^4$ -C<sub>4</sub>Ph<sub>2</sub>)<sup>[6g]</sup> and ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th[ $\eta^4$ -C<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>]<sup>[6h]</sup>.

Diphenylacetylene displacement in **2** is also encountered in the presence of hetero-unsaturated organic molecules. For example, complex **2** reacts with the aldimine PhCH=NPh to yield the metallazaaziridine [ $\eta^5$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>U( $\eta^2$ -CHPhNPh) (**6**) (Scheme 3). Nevertheless, treatment of **2** with the hydrazine derivative (Ph<sub>2</sub>C=N)<sub>2</sub> yields the bisiminato 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(N=CPh<sub>2</sub>)<sub>2</sub> (**7**) and diphenylacetylene (Scheme 4). Like in the reaction with PhCH=NPh, presumably diphenylacetylene replacement with (Ph<sub>2</sub>C=N)<sub>2</sub> furnishes a metallazaaziridine, which converts by N–N bond cleavage to **7** (Scheme 4). Moreover, it is of note that the uranium bipy 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(bipy) (**8**)<sup>[9]</sup> can also be accessed by the addition of 2,2'-bipyridine (bipy) to **2** (Scheme 4).

Diphenylacetylene substitution is also encountered in the reaction of **2** with the nitriles RCN (R = C<sub>6</sub>H<sub>11</sub>, Ph<sub>2</sub>CH), in which five-membered metallaheterocycles [ $\eta^5$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>U[(N=CR)] (R = C<sub>6</sub>H<sub>11</sub> (**9**), Ph<sub>2</sub>CH (**10**)) are formed (Scheme 5). Again, in analogy to the reaction with PhCH=NPh, RCN may initially replace the diphenylacetylene ligand to give a  $\eta^2$ -coordinated nitrile intermediate,<sup>[6g]</sup> which spontaneously incorporates a second molecule of RCN to give the five-membered heterometallacycles **9–10** (Scheme 5). The molecular

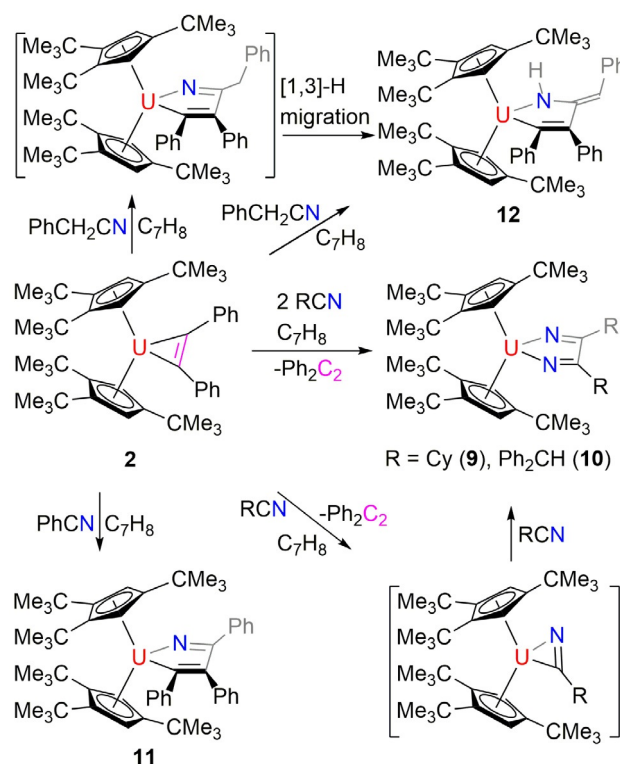


**Figure 4.** Molecular structure of **5** (thermal ellipsoids drawn at the 35% probability level).



The compound in brackets is not observed

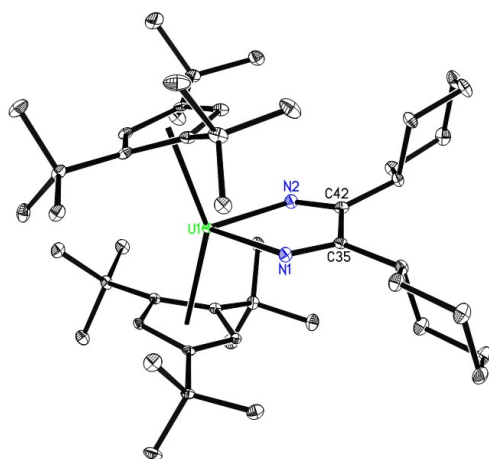
**Scheme 4.** Synthesis of complexes **7** and **8**.



The compounds in brackets are not observed

**Scheme 5.** Synthesis of complexes **9–12**.

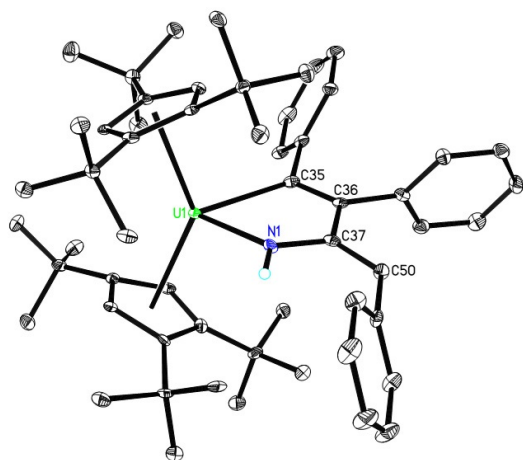
structure of **9** is shown in Figure 5, whereas the structure of **10** is provided in the Supporting Information. The U–N distances are 2.222(2) and 2.214(2) Å for **9**, and 2.252(5) Å for **10**, and the N–U–N angles are 72.3(1)° for **9** and 70.9(3)° for **10**. Nevertheless, when the slightly less sterically encumbered PhCN is used, only the insertion of 1 equiv of PhCN into the uranium metallacyclopentatriene moiety of **2** occurs at room temperature to yield the five-membered heterocyclic complex [ $\eta^5$ -1,2,4-



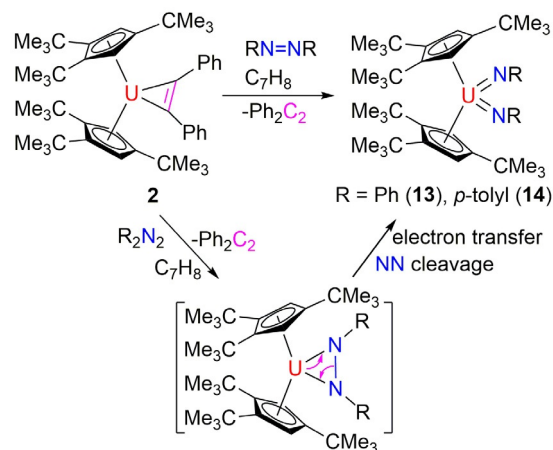
**Figure 5.** Molecular structure of **9** (thermal ellipsoids drawn at the 35% probability level).

( $\text{Me}_3\text{C}_3\text{C}_5\text{H}_2$ )<sub>2</sub>U[N=C(Ph)(C<sub>2</sub>Ph<sub>2</sub>)] (**11**) in quantitative conversion (Scheme 5). A similar reaction was also observed for the thorium metallacyclopropene [ $\eta^5$ -1,2,4-( $\text{Me}_3\text{C}_3\text{C}_5\text{H}_2$ )<sub>2</sub>Th( $\eta^2$ -C<sub>2</sub>Ph<sub>2</sub>)] with PhCN (Figure 3).<sup>[6a]</sup> However, when benzyl nitrile PhCH<sub>2</sub>CN is added to **2** the five-membered heterocyclic complex [ $\eta^5$ -1,2,4-( $\text{Me}_3\text{C}_3\text{C}_5\text{H}_2$ )<sub>2</sub>U[NHC(=CHPh)(C<sub>2</sub>Ph<sub>2</sub>)] (**12**) formed in quantitative conversion (Scheme 5). We assume that **2** initially reacts with PhCH<sub>2</sub>CN to give a five-membered heterocyclic intermediate (analogous to compound **11**), which converts by [1,3]-H migration to yield the final product **12** (Scheme 5). Figure 6 illustrates the molecular structure of **12** and selected bond lengths and angles are collected in Table 1. The C(37)–C(50) distance is 1.379(8) Å, and C(37)–N(1) distance is 1.384(7) Å. The U–N distance is 2.208(4) Å, whereas U–C(35) distance is 2.482(6) Å, and the angle of N(1)–U–C(35) is 69.3(2)°.

However, complex **2** yields with the diazenes RN=NR (R = Ph, *p*-tolyl) the bisimido uranium(VI) complexes [ $\eta^5$ -1,2,4-( $\text{Me}_3\text{C}_3\text{C}_5\text{H}_2$ )<sub>2</sub>U(=NR)<sub>2</sub>] (R = Ph (**13**), *p*-tolyl (**14**)) in quantitative conversion (Scheme 6). Analogously to the reaction with



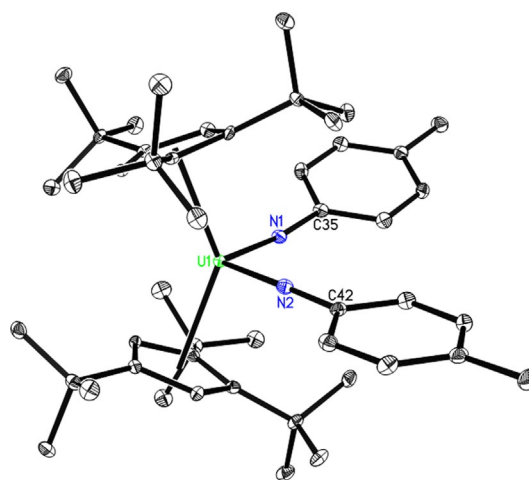
**Figure 6.** Molecular structure of **12** (thermal ellipsoids drawn at the 35% probability level).



The compound in brackets is not observed

**Scheme 6.** Synthesis of complexes **13** and **14**.

PhCH=NPh, RN=NR replaces the diphenylacetylene fragment to form a three-membered metallacyclic intermediate, which transforms by electron transfer and NN bond cleavage to yield the bisimido products **13**–**14** (Scheme 6). The molecular structure of **14** is shown in Figure 7, and the selected bond distances and angles are listed in Table 1. The short U–N distances (1.977(3) Å for N(1) and 1.974(3) Å for N(2)) and the angles of U–N(1)–C(35) (168.4(2) and U–N(2)–C(42) (173.0(3)°) are consistent with a U=N double bond.<sup>[12]</sup> These structural parameters may be compared to those found in [ $\eta^5$ -1,2,4-( $\text{Me}_3\text{C}_3\text{C}_5\text{H}_2$ )<sub>2</sub>U(=NPh)<sub>2</sub>] (**13**) with the U–N distances of 1.985(4) and 1.981(4) Å and the U–N–C angles of 171.4(4) and 172.8(4)°,<sup>[7]</sup> [ $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(=N-*p*-tolyl)<sub>2</sub>] with the U–N distances of 1.971(4) and 1.975(3) Å and the U–N–C angles of 178.8(3) and 179.1(3)°,<sup>[6f]</sup> and [ $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(=NPh)<sub>2</sub>] with the U–N distance of 1.952(7) Å and the U–N–C angle of 177.8(6)°.<sup>[13]</sup> It is of note that the uranium metallocenes such as [ $\eta^5$ -1,2,4-( $\text{Me}_3\text{C}_3\text{C}_5\text{H}_2$ )<sub>2</sub>U(bipy)],<sup>[9]</sup> ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(bipy),<sup>[6k]</sup> [ $\eta^5$ -1,2,4-( $\text{Me}_3\text{C}_3\text{C}_5\text{H}_2$ )<sub>2</sub>U=P-2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**1**)],<sup>[7]</sup> ( $\eta^5$ -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>],<sup>[6f,g]</sup> [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>UH]<sub>2</sub>,<sup>[14]</sup> ( $\eta^5$ -



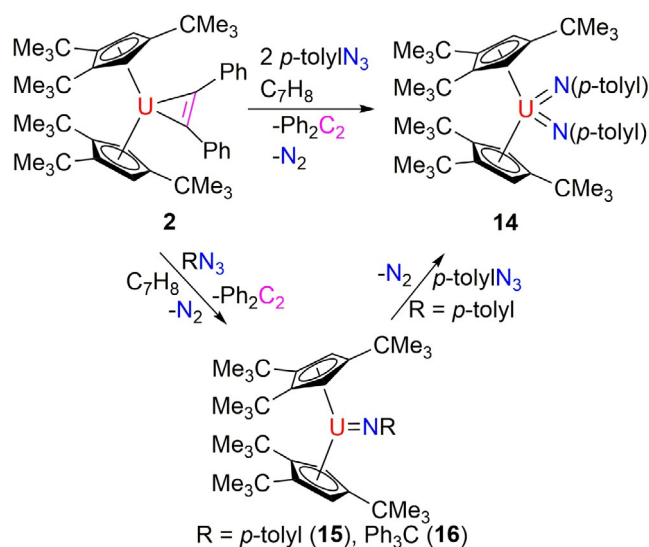
**Figure 7.** Molecular structure of **14** (thermal ellipsoids drawn at the 35% probability level).

$C_5Me_5U[(\mu\text{-Ph})_2BPh_2]$ ,<sup>[13g,15]</sup>  $[(C_5Me_5)_2U]_2(\mu\text{-}\eta^6\text{-}C_6H_6)$ ,<sup>[16]</sup> and  $(\eta^5\text{-}C_5Me_5)U[P(SiMe_3)(2,4,6\text{-}Me_3Ph)](THF)$ <sup>[17]</sup> may also act as  $Cp_2U^{II}$  synthons forming bisimido uranium(VI) complexes.

Moreover, complex **14** may also be formed from the reaction of **2** with *p*-tolylN<sub>3</sub> (Scheme 7). This contrasts the transformation of the thorium metallacyclopropene  $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph_2)$  with organic azides,<sup>[6a]</sup> in which insertion or isomerization products were isolated. Instead the reactivity of **2** more closely resembles that observed for the bipy complexes  $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2An(\text{bipy})$  (*An* = Th, U) towards *p*-tolylN<sub>3</sub>.<sup>[9,18]</sup> *p*-TolylN<sub>3</sub> displaces the diphenylacetylene in **2** and releases N<sub>2</sub> to give the imido complex  $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U=N(p\text{-tolyl})$  (**15**), which reacts with a second molecule of *p*-tolylN<sub>3</sub> to yield the bisimido uranium(VI) compound **14** concomitant with N<sub>2</sub> evolution (Scheme 7).

Moreover, in analogy to the reactivity of the bipy complex  $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(\text{bipy})$  towards Ph<sub>3</sub>CN<sub>3</sub>,<sup>[18]</sup> the bulky trityl azide Ph<sub>3</sub>CN<sub>3</sub> displaces the diphenylacetylene in **2** and releases N<sub>2</sub> to give the uranium(IV) imido complex  $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U=NPh_3$  (**16**) in quantitative conversion (Scheme 7). The molecular structure of **16** is provided in Figure 8, while selected bond distances and angles are presented in Table 1. The short U–N distance (1.968(4) Å) and the angle of U–N(1)–C(35) (169.3(3)°) are consistent with a U=N double bond.<sup>[12]</sup> These structural parameters may be compared to those found in  $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U=N(p\text{-tolyl})$  (**15**) with the U–N distance of 1.988(5) Å and the U–N–C angle of 172.3(5)°.<sup>[9]</sup>

Moreover, for the reaction of the thorium metallacyclopropene  $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph_2)$  with 9-diazafluorene (C<sub>12</sub>H<sub>8</sub>)CN<sub>2</sub> insertion or isomerization products are isolated.<sup>[6a]</sup> This contrasts the uranium(V) imido cyanido  $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(=NN=CHSiMe_3)(CN)$  (**17**) isolated from the reaction of **2** with Me<sub>3</sub>SiCHN<sub>2</sub> (Scheme 8). To rationalize this product formation it is proposed that **2** initially reacts with 2 equiv of Me<sub>3</sub>SiCHN<sub>2</sub> resulting in diphenylacetylene replacement fol-



Scheme 7. Synthesis of complexes **14**–**16**.

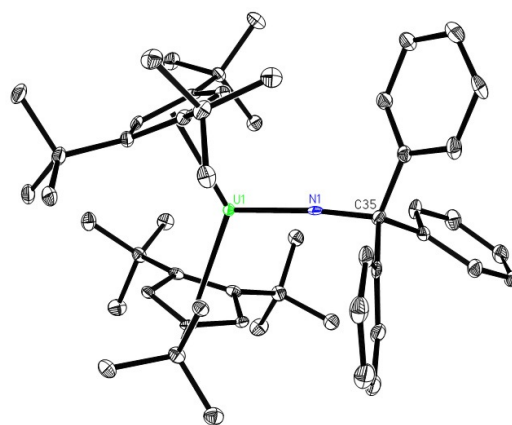
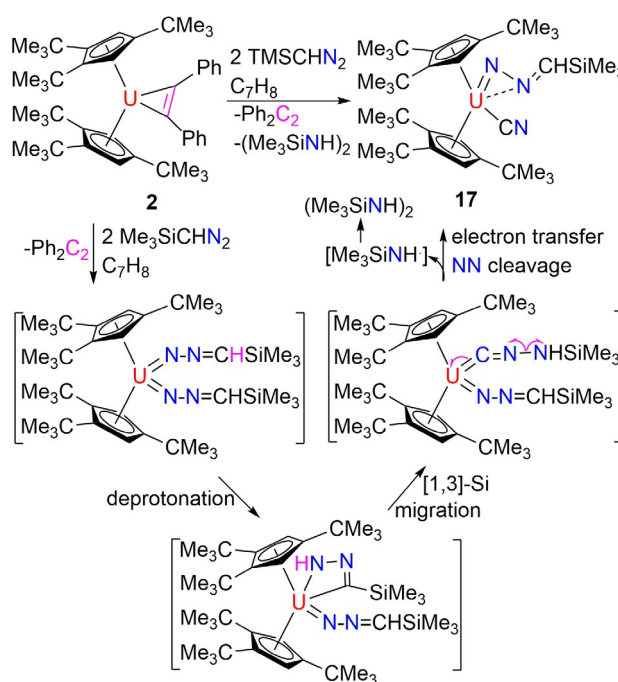
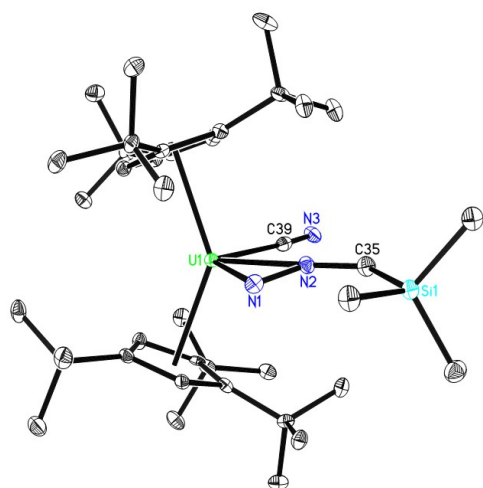


Figure 8. Molecular structure of **16** (thermal ellipsoids drawn at the 35% probability level).



Scheme 8. Synthesis of complex **17**.

lowed by electron transfer to yield a uranium(VI) bisimido complex. In the next step, this bisimido complex forms a four-membered intermediate, which converts via [1,3]-Si migration to yield a uranium(VI) isonitrile complex, in which the N–N bond is homolytically cleaved to yield **17** and the amine radical Me<sub>3</sub>SiNH·. The latter further dimerizes to the hydrazine derivative (Me<sub>3</sub>SiNH)<sub>2</sub> (Scheme 8). The molecular structure of **17** is presented in Figure 9, whereas relevant bond distances and angles are compiled in Table 1. The U–N distances are 2.227(4) Å for N(1) and 2.418(4) Å for N(2), whereas the U–C(39) distance is 2.517(6) Å. The C(39)–N(3) distance is 1.145(8) Å, whereas the C(35)–N(2) distance is 1.293(7) Å. The angle of N(1)–U–N(2) is 33.4(2)°, whereas the linear angle of U–



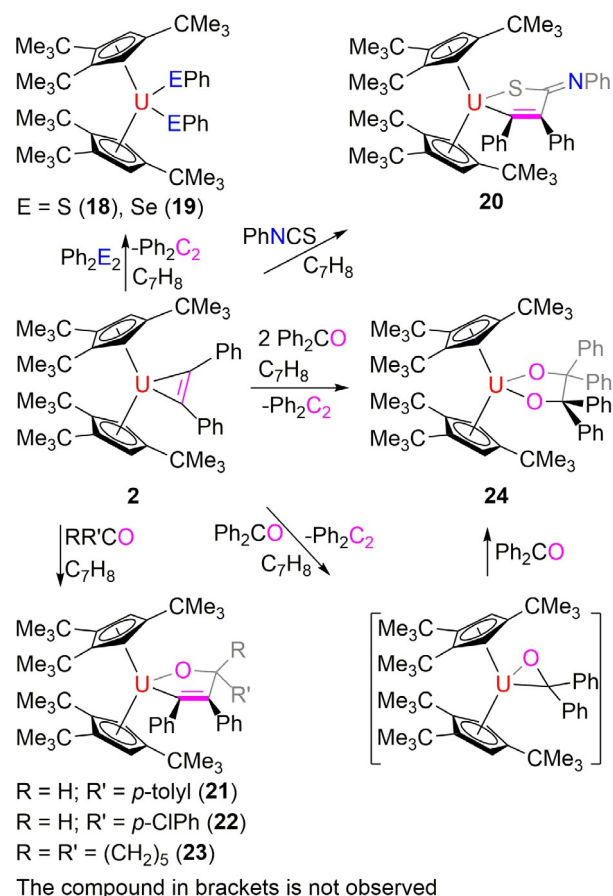
**Figure 9.** Molecular structure of **17** (thermal ellipsoids drawn at the 35% probability level).

C(39)–N(3) is  $176.6(5)^\circ$ . The N(1)–N(2) distance is  $1.348(7)$  Å, and the N(2)–C(35) distance is  $1.293(7)$  Å.

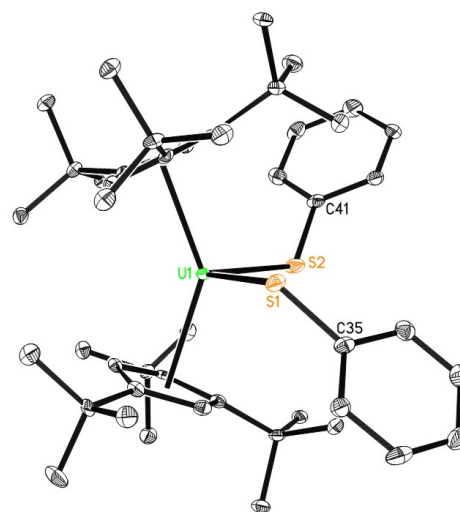
Furthermore, replacement of the coordinated diphenylacetylene with S–S and Se–Se bond cleavage are observed in the reaction of **2** with  $\text{Ph}_2\text{S}_2$  or  $\text{Ph}_2\text{Se}_2$ , in which the disulfido complex  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{U(SPh)}_2$  (**18**) and the diselenido complex  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{U(SePh)}_2$  (**19**) are formed, respectively (Scheme 9). Figure 10 shows the molecular structure of **18** and selected bond distances and angles are compiled in Table 1. The U–S distances are  $2.659(1)$  Å for S(1) and  $2.628(1)$  Å for S(2), and the angle of S(1)–U–S(2) is  $100.4(1)^\circ$ .

Nevertheless, in the presence of suitable substrates, the reactivity of the uranium metallacyclopropene **2** may also parallel its thorium analogue  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$  (Figure 3).<sup>[6a,11]</sup> For example, insertion of 1 equiv of PhNCS into the uranium metallacyclopropene moiety of **2** is observed at room temperature to yield the five-membered heterocyclic complex  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{U}[\text{SC}(\text{NPh})(\text{C}_2\text{Ph}_2)]$  (**20**) (Scheme 9). The molecular structure of **20** can be found in Figure 11 and selected bond distances and angles are compiled in Table 1. The U–S distance is  $2.649(2)$  Å, whereas U–C(37) distance is  $2.480(10)$  Å, and the angle of S(1)–U–C(37) is  $76.0(2)^\circ$ .

Moreover, treatment of **2** with 1 equiv of aldehydes RCHO (R = *p*-tolyl, *p*-ClPh) or ketone  $(\text{CH}_2)_5\text{CO}$  also gives the five-membered heterocyclic compounds  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{U}[\text{OCR}(\text{R}')(\text{C}_2\text{Ph}_2)]$  (R = H, R' = *p*-tolyl (**21**), *p*-ClPh (**22**); R = R' =  $(\text{CH}_2)_5$  (**23**)) (Scheme 9). The molecular structure of **23** is shown in Figure 12, whereas the structures of **21** and **22** are provided in the Supporting Information. The U–O distances are  $2.062(2)$  Å for **21**,  $2.069(2)$  Å for **22** and  $2.076(4)$  Å for **23**, whereas the U–C distances are  $2.581(3)$  Å for **21** (C37),  $2.577(4)$  Å for **22** (C43) and  $2.572(6)$  Å for **23** (C35), and the angles of O–U–C are  $67.6(1)^\circ$  for **21** (C37),  $67.5(1)^\circ$  for **22** (C43) and  $67.1(2)^\circ$  for **23** (C35). However, when the bulky ketone  $\text{Ph}_2\text{CO}$  is used as substrate, the diphenylacetylene moiety is replaced to form the uranium pinacolate  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{U}[(\text{OCPh}_2)_2]$  (**24**) (Scheme 9), irrespectively of the



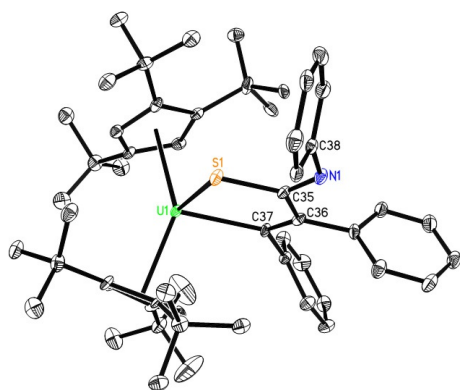
**Scheme 9.** Synthesis of complexes **18**–**24**.



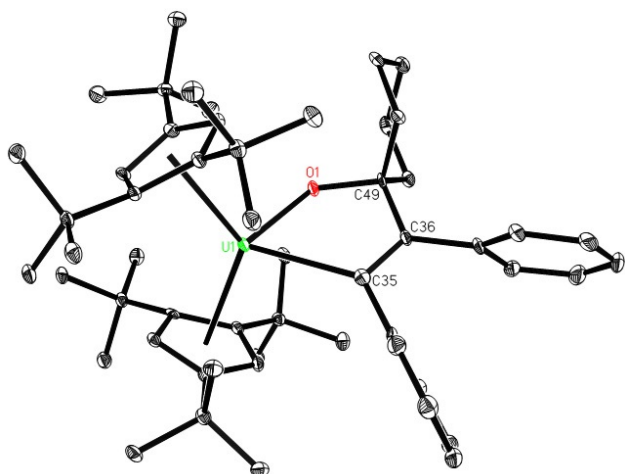
**Figure 10.** Molecular structure of **18** (thermal ellipsoids drawn at the 35% probability level).

quantity of added  $\text{Ph}_2\text{CO}$ . Product formation may be explained by diphenylacetylene substitution to form a uranium  $\eta^2$ -ketone intermediate,<sup>[7]</sup> which immediately reacts with a second molecule of  $\text{Ph}_2\text{CO}$  to furnish **24** (Scheme 9).





**Figure 11.** Molecular structure of **20** (thermal ellipsoids drawn at the 35% probability level).



**Figure 12.** Molecular structure of **23** (thermal ellipsoids drawn at the 35% probability level).

## Conclusions

The intrinsic reactivity of a stable uranium metallacyclopropene 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( $\eta^2$ -C<sub>2</sub>Ph<sub>2</sub>), was evaluated and compared to that of the other uranium and thorium metallacyclopropenes. In analogy to the uranium metallacyclopropene derivative ( $\eta^5$ -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>),<sup>[6f]</sup> density functional theory (DFT) suggests that the 5f orbitals contribution to the  $\sigma$  and  $\pi$ -bonds of the U-( $\eta^2$ -C=C) moiety increases substantially compared to the related thorium metallacyclopropene complex, which also renders the bonds between the [ $\eta^5$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>U<sup>2+</sup> and [ $\eta^2$ -C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> fragments more covalent than those found in the related thorium metallacyclopropene. Whereas the coordinated alkyne in the thorium metallacyclopropenes is inert to ligand substitution,<sup>[6a]</sup> it reacts as a nucleophile towards hetero-unsaturated molecules or as a strong base inducing the inter- or intramolecular C–H bond activations.<sup>[6a,b,11]</sup> However, in analogy to the uranium metallacyclopropene ( $\eta^5$ -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>),<sup>[6f,g]</sup> the reactivity patterns of the uranium complex **2** change considerably, that is, the uranium complex **2** serves as a synthetically useful [ $\eta^5$ -1,2,4-

(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>U(II) synthon in the reaction with Ph<sub>2</sub>E<sub>2</sub> (E=S, Se) and unsaturated molecules such as alkynes, imines, ketazine, bipy, nitriles, organic azides, and azo derivatives, in which the coordinated diphenylacetylene was readily replaced during the reaction.

Nevertheless, thorium and uranium metallacyclopropenes also exhibit similar reactivity patterns, e.g., when exposed to isothiocyanates, aldehydes and ketones, for which mono insertion of these substrates into the actinide metallacyclopropene moieties occurs to yield the five-membered heterometallacycles.<sup>[6a,f,g,11]</sup> However, like the thorium metallacyclopropene [ $\eta^5$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>Th( $\eta^2$ -C<sub>2</sub>Ph<sub>2</sub>),<sup>[6a,11]</sup> the coordinate PhCCPh in **2** is readily displaced, when the sterically encumbered Ph<sub>2</sub>CO is used as substrate, but the metallaoxirane intermediate [ $\eta^5$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>U( $\eta^2$ -Ph<sub>2</sub>CO) is too reactive to be observed and a second molecule of Ph<sub>2</sub>CO inserts to yield the uranium pinacolate [ $\eta^5$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>U[(OCPh<sub>2</sub>)<sub>2</sub>] (**24**). Further investigations concerning the intrinsic reactivity of actinide metallacycles 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 glove box. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Diphenylacetylene was purified by sublimation. [ $\eta^5$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>U=P-2,4,6-tBu<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**1**)<sup>[7]</sup> and [ $\eta^5$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>UCl<sub>2</sub> (**3**)<sup>[9]</sup> were prepared according to literature procedures. 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. 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 [ $\eta^5$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>U( $\eta^2$ -C<sub>2</sub>Ph<sub>2</sub>) (**2**)

**Method A:** A toluene (10 mL) solution of PhC≡CPh (178 mg, 1.0 mmol) was added to a toluene (10 mL) solution of [ $\eta^5$ -1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>U=P-2,4,6-tBu<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**1**; 981 mg, 1.0 mmol) with stirring at room temperature. After the solution was stirred at 50 °C overnight, the solvent was removed. The residue was extracted with *n*-hexane (10 mL×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 two days. Yield: 706 mg (80%). M.p.: 178–180 °C (dec.). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 26.59 (s, 4H, phenyl), 16.62 (s, 4H, phenyl), 10.79 (d, *J* = 5.6 Hz, 2H, phenyl), 9.30 (br s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), –15.00 (br s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), –32.03 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>) ppm; ring C–H atoms were not observed. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 202.7 (UC), 201.8 (phenyl C), 201.0 (phenyl C), 151.4 (phenyl C), 138.4 (phenyl C), 137.9 (C(CH<sub>3</sub>)<sub>3</sub>), 137.3 (C(CH<sub>3</sub>)<sub>3</sub>), 136.7 (C(CH<sub>3</sub>)<sub>3</sub>), 85.8 (C(CH<sub>3</sub>)<sub>3</sub>), –50.1 (ring C), –51.1 (ring C) ppm; one ring C overlapped. IR (KBr):  $\tilde{\nu}$  = 2960 (s), 1460 (m), 1384 (m),

1259 (s), 1093 (s), 1020 (s), 800 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{48}\text{H}_{68}\text{U}$ : C, 65.28; H, 7.76. Found: C, 65.35; H, 7.73.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{PhC}\equiv\text{CPh}$  (3.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}=\text{P-}2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$  (**1**; 20 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **2** along with those of 3,3-Me<sub>2</sub>-5,7-tBu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>P (<sup>1</sup>H NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.46 (dd,  $J$  = 3.8, 1.5 Hz, 2H, phenyl), 4.39 (ddd,  $J$  = 181.6, 11.9, 7.9 Hz, 1H, PH), 1.59 (d,  $J$  = 3.6 Hz, 1H, CH<sub>2</sub>), 1.56 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 1.34 (s, 3H, CH<sub>3</sub>), 1.31 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 1.29 (d,  $J$  = 3.6 Hz, 1H, CH<sub>2</sub>), 1.11 (s, 3H, CH<sub>3</sub>) ppm)<sup>[5b]</sup> were observed by <sup>1</sup>H NMR spectroscopy (100% conversion) after the sample was kept at 50 °C overnight.

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$ (**2**) and $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UCI}$ (**4**)

$\text{KC}_8$  (1.20 g, 8.80 mmol) was added to a toluene (20 mL) solution of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UCI}_2$  (**3**; 1.94 g, 2.5 mmol) and diphenylacetylene (0.45 g, 2.5 mmol) with stirring at room temperature. After this solution was stirred one day at 40 °C, the solvent was removed. The residue was extracted with *n*-hexane (20 mL  $\times$  3) and filtered. The volume of the filtrate was reduced to 15 mL, green microcrystals were isolated when this solution was kept at  $-20$  °C for 2 days. The <sup>1</sup>H NMR spectrum recorded in  $\text{C}_6\text{D}_6$  showed the presence of **2** and **4** (<sup>1</sup>H NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  =  $-7.95$  (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>),  $-25.40$  (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>) ppm; protons of the rings were not observed)<sup>[9]</sup> in a 1:3 ratio. Unfortunately, this mixture could not be converted to exclusively yield **2** upon prolonged reduction in the presence of diphenylacetylene with an excess of potassium graphite ( $\text{KC}_8$ ). Under these conditions, some other yet unidentified species were formed. In addition, on a synthetic scale the mixture of complex **2** and **4** could not be separated to yield pure materials because of their similar solubilities. However, a few green crystals of **4** suitable for X-ray diffraction analysis were selected from those microcrystals that recrystallized from an *n*-hexane at  $-20$  °C, and the molecular structure of **4** was further verified by X-ray diffraction analysis (see Supporting Information for details).

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_4\text{Ph}_2)$ (**5**)

**Method A:** A toluene (10 mL) solution of  $\text{PhC}\equiv\text{CC}\equiv\text{CPh}$  (51 mg, 0.25 mmol) was added to a toluene (10 mL) solution of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) with stirring at room temperature. After the solution was stirred at 40 °C for one week, 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 **5** were isolated when this solution was kept at  $-20$  °C for two days. Yield: 186 mg (82%). M.p.: 117–119 °C (dec.). <sup>1</sup>H NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 14.35 (s, 4H, phenyl), 10.23 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 8.70 (s, 4H, phenyl), 8.30 (s, 2H, phenyl),  $-1.28$  (br s, 18H, C(CH<sub>3</sub>)<sub>3</sub>),  $-15.18$  (br s, 18H, C(CH<sub>3</sub>)<sub>3</sub>) ppm; ring C–H atoms were not observed. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 294.5 (UCPh), 207.7 (UC), 179.1 (ring C), 175.5 (ring C), 139.2 (phenyl C), 132.7 (phenyl C), 129.2 (phenyl C), 128.3 (phenyl C), 49.4 (C(CH<sub>3</sub>)<sub>3</sub>), 32.3 (C(CH<sub>3</sub>)<sub>3</sub>), 31.9 (C(CH<sub>3</sub>)<sub>3</sub>), 29.8 (C(CH<sub>3</sub>)<sub>3</sub>) ppm; other carbon atoms overlapped. IR (KBr):  $\tilde{\nu}$  = 2958 (s), 1952 (w, C=C=C), 1460 (s), 1361 (s), 1238 (s), 1097 (s), 1070 (s), 1024 (s), 825 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{50}\text{H}_{68}\text{U}$ : C, 66.20; H, 7.56. Found: C, 66.25; H, 7.53.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{PhC}\equiv\text{CC}\equiv\text{CPh}$  (4.0 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **5** along with those of

$\text{PhC}\equiv\text{CPh}$  were observed by <sup>1</sup>H NMR spectroscopy (100% conversion) after the sample was kept at 40 °C for one week.

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-CHPhNPh})$ (**6**)

**Method A:** This compound was prepared as brown microcrystals from the reaction of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $\text{PhCH}=\text{NPh}$  (46 mg, 0.25 mmol) in toluene (15 mL) at 100 °C and recrystallization from an *n*-hexane solution by a similar procedure as that in the synthesis of **5**. Yield: 177 mg (80%). <sup>1</sup>H NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 129.18 (s, 1H, CHPh), 34.03 (s, 1H, phenyl), 26.49 (s, 2H, phenyl), 23.78 (s, 1H, phenyl), 13.63 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 13.36 (s, 2H, phenyl), 12.24 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 7.42 (s, 1H, phenyl),  $-0.60$  (s, 1H, phenyl),  $-2.57$  (s, 1H, phenyl),  $-10.04$  (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>),  $-17.56$  (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>),  $-35.03$  (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>),  $-42.50$  (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>),  $-68.53$  (s, 1H, phenyl) ppm; ring C–H atoms were not observed. These spectroscopic data agreed with those reported in the literature.<sup>[7]</sup>

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{PhCH}=\text{NPh}$  (3.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **6** along with those of  $\text{PhC}\equiv\text{CPh}$  were observed by <sup>1</sup>H NMR spectroscopy (100% conversion) after the sample was kept at 100 °C for 5 days.

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\text{N}=\text{CPh}_2)$ (**7**)

**Method A:** This compound was prepared as brown microcrystals from the reaction of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $(\text{Ph}_2\text{C}=\text{N})_2$  (90 mg, 0.25 mmol) in toluene (15 mL) at 100 °C and recrystallization from a benzene solution by a similar procedure as that in the synthesis of **5**. Yield: 221 mg (83%). <sup>1</sup>H NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 33.06 (br s, 2H, ring CH), 14.59 (br s, 6H, C(CH<sub>3</sub>)<sub>3</sub>), 12.45 (br s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 7.70 (s, 1H, phenyl), 7.41 (s, 2H, phenyl), 7.37 (s, 1H, phenyl), 7.04 (s, 2H, phenyl), 2.29 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.45 (s, 9H, phenyl), 1.28 (s, 5H, phenyl),  $-23.34$  (br s, 12H, C(CH<sub>3</sub>)<sub>3</sub>),  $-75.71$  (br s, 2H, ring CH) ppm. These spectroscopic data were in line with those reported in the literature.<sup>[7]</sup>

**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  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **7** along with those of  $\text{PhC}\equiv\text{CPh}$  were observed by <sup>1</sup>H NMR spectroscopy (100% conversion) after the sample was kept at 100 °C for 5 days.

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\text{bipy})$ (**8**)

**Method A:** This compound was prepared as green microcrystals from the reaction of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and bipy (39 mg, 0.25 mmol) in toluene (15 mL) at 100 °C and recrystallization from a benzene solution by a similar procedure as that in the synthesis of **5**. Yield: 181 mg (84%). <sup>1</sup>H NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 1.26 (s, 4H, ring CH), 1.17 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>),  $-7.47$  (d,  $J$  = 4.9 Hz, 2H, bipy),  $-9.01$  (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>),  $-58.93$  (s, 2H, bipy),  $-99.40$  (s, 2H, bipy),  $-125.80$  (s, 2H, bipy) ppm. These spectroscopic data agreed with those reported in the literature.<sup>[7]</sup>

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of bipy (3.1 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **8** along with those of  $\text{PhC}\equiv\text{CPh}$  were observed by <sup>1</sup>H NMR spectroscopy (100% conversion) after the sample was kept at 100 °C for 3 days.

### Preparation of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\text{N}=\text{C}(\text{C}_6\text{H}_{11}))_2$ (**9**)

**Method A:** This compound was prepared as brown microcrystals from the reaction of  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $\text{C}_6\text{H}_{11}\text{CN}$  (55 mg, 0.50 mmol) in toluene (15 mL) at room temperature and recrystallization from a benzene solution by a similar procedure as that in the synthesis of **5**. Yield: 188 mg (78%). M.p.: 165–167 °C (dec.).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 19.82 (br s, 2H, Cy), 18.03 (s, 2H, CH), 15.00 (br s, 2H, Cy), 13.53 (br s, 2H, Cy), 12.61 (br s, 2H, Cy), 11.47 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 9.55 (br s, 2H, Cy), 8.89 (br s, 2H, Cy), 6.30 (br s, 4H, Cy), 5.32 (d,  $J$  = 15.2 Hz, 2H, Cy), 4.93 (d,  $J$  = 12.8 Hz, 2H, Cy), –10.01 (s, 36H,  $\text{C}(\text{CH}_3)_3$ ) ppm; protons of  $\text{C}_6\text{H}_{11}$  were not observed.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 216.1 (N=C), 77.0 (CH), 41.6 ( $\text{C}(\text{CH}_3)_3$ ), 32.5 ( $\text{C}(\text{CH}_3)_3$ ), 31.7 ( $\text{C}(\text{CH}_3)_3$ ), 16.7 ( $\text{CH}_2$ ), 5.7 ( $\text{CH}_2$ ), –18.9 (ring C), –38.8 (ring C) ppm; other carbons overlapped. IR (KBr):  $\tilde{\nu}$  = 2928 (s), 1450 (s), 1359 (s), 1240 (s), 1180 (m), 964 (s), 763 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{48}\text{H}_{80}\text{N}_2\text{U}$ : C, 62.45; H, 8.73; N, 3.03. Found: C, 62.41; H, 8.76; N, 3.02. Brown crystals of  $9 \cdot 0.5\text{C}_6\text{H}_{14}$  suitable for X-ray structural analysis were grown from an *n*-hexane solution.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{C}_6\text{H}_{11}\text{CN}$  (4.4 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **9** along with those of  $\text{PhC}\equiv\text{CPh}$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion) after the sample was kept at room temperature overnight.

### Reaction of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$ (**2**) with $\text{C}_6\text{H}_{11}\text{CN}$

**NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{C}_6\text{H}_{11}\text{CN}$  (2.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **9** along with those of unreacted **2** and  $\text{PhC}\equiv\text{CPh}$  were observed by  $^1\text{H}$  NMR spectroscopy (50% conversion based on **2**) after the sample was kept at room temperature overnight.

### Preparation of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\text{N}=\text{C}(\text{CHPh}_2))_2$ (**10**)

**Method A:** This compound was prepared as brown crystals from the reaction of  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $\text{Ph}_2\text{CHCN}$  (97 mg, 0.50 mmol) in toluene (15 mL) at room temperature and recrystallization from an *n*-hexane solution by a similar procedure as that in the synthesis of **5**. Yield: 218 mg (80%). M.p.: 104–106 °C (dec.).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 39.49 (s, 1H, phenyl), 29.51 (s, 1H, phenyl), 23.77 (s, 3H, phenyl), 16.10 (s, 3H, phenyl), 13.97 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 11.00 (s, 3H, phenyl), 10.45 (s, 1H, phenyl), –1.31 (s, 2H, CH), –13.12 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), –16.00 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), –21.16 (s, 7H, phenyl), –62.00 (s, 1H, phenyl) ppm; protons of the rings were not observed.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 235.1 (C=N), 160.1 (phenyl C), 158.5 (phenyl C), 145.8 (phenyl C), 141.0 (phenyl C), 137.8 (phenyl C), 135.7 (phenyl C), 131.5 (phenyl C), 123.7 (phenyl C), 120.6 (phenyl C), 52.9 ( $\text{C}(\text{CH}_3)_3$ ), 49.9 ( $\text{C}(\text{CH}_3)_3$ ), 35.1 ( $\text{C}(\text{CH}_3)_3$ ), 17.0 ( $\text{C}(\text{CH}_3)_3$ ), –3.4 (ring C), –42.8 (ring C), –50.3 (ring C) ppm; other carbons overlapped. IR (KBr):  $\tilde{\nu}$  = 2957 (s), 1595 (s), 1554 (s), 1492 (s), 1452 (s), 1359 (s), 1238 (s), 964 (s), 812 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{62}\text{H}_{80}\text{N}_2\text{U}$ : C, 68.23; H, 7.39; N, 2.57. Found: C, 68.21; H, 7.36; N, 2.60.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{Ph}_2\text{CHCN}$  (7.7 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **10** along with those

of  $\text{PhC}\equiv\text{CPh}$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion) after the sample was kept at room temperature overnight.

### Reaction of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$ (**2**) with $\text{Ph}_2\text{CHCN}$

**NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{Ph}_2\text{CHCN}$  (3.9 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **10** along with those of unreacted **2** and  $\text{PhC}\equiv\text{CPh}$  were observed by  $^1\text{H}$  NMR spectroscopy (50% conversion based on **2**) after the sample was kept at room temperature overnight.

### Preparation of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\text{N}=\text{C}(\text{Ph})(\text{C}_2\text{Ph}_2))$ (**11**)

**Method A:** This compound was prepared as brown microcrystals from the reaction of  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $\text{PhCN}$  (26 mg, 0.25 mmol) in toluene (15 mL) and recrystallization from an *n*-hexane solution by a similar procedure as in the synthesis of **5**. Yield: 212 mg (86%). M.p.: 107–109 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 36.09 (s, 2H, ring CH), 18.02 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 17.73 (s, 2H, phenyl), 14.80 (s, 3H, phenyl), 10.61 (s, 2H, phenyl), 9.98 (s, 1H, phenyl), 3.67 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), –2.35 (s, 2H, phenyl), –3.66 (s, 1H, phenyl), –9.08 (s, 1H, phenyl), –12.03 (s, 1H, phenyl), –22.14 (s, 2H, phenyl), –22.84 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), –33.17 (s, 2H, ring CH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 266.2 (UCPh), 230.6 (CPh), 181.4 (C=N), 155.4 (phenyl C), 134.2 (phenyl C), 134.0 (phenyl C), 130.4 (phenyl C), 126.9 (phenyl C), 126.3 (phenyl C), 119.7 (phenyl C), 116.0 (phenyl C), 114.8 (phenyl C), 108.3 (phenyl C), 107.4 (phenyl C), 101.7 (phenyl C), 86.7 ( $\text{C}(\text{CH}_3)_3$ ), 84.9 ( $\text{C}(\text{CH}_3)_3$ ), 52.2 ( $\text{C}(\text{CH}_3)_3$ ), 47.4 ( $\text{C}(\text{CH}_3)_3$ ), 44.1 ( $\text{C}(\text{CH}_3)_3$ ), –1.3 (ring C), –1.8 (ring C), –2.4 (ring C), –4.9 (ring C), –57.2 (ring C) ppm; one C resonance of  $\text{Me}_3\text{C}$ -groups overlapped. IR (KBr):  $\tilde{\nu}$  = 2958 (s), 1458 (s), 1361 (s), 1261 (s), 1238 (s), 1095 (s), 1072 (s), 1022 (s), 806 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{55}\text{H}_{73}\text{NU}$ : C, 66.98; H, 7.46; N, 1.42. Found: C, 67.02; H, 7.43; N, 1.41.

**Method B, NMR Scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{PhCN}$  (2.1 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **11** were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion in 10 min).

### Preparation of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\text{NHC}(\text{=CHPh})(\text{C}_2\text{Ph}_2))$ (**12**)

**Method A:** This compound was prepared as brown crystals from the reaction of  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $\text{PhCH}_2\text{CN}$  (30 mg, 0.25 mmol) in toluene (15 mL) and recrystallization from an *n*-hexane solution by a similar procedure as in the synthesis of **5**. Yield: 205 mg (82%). M.p.: 123–125 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 16.49 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 14.85 (s, 1H, NH), 8.72 (s, 2H, ring CH), 6.00 (s, 2H, phenyl), 4.51 (t,  $J$  = 6.5 Hz, 1H, phenyl), 3.90 (t,  $J$  = 6.8 Hz, 2H, phenyl), 3.62 (s, 1H, phenyl), 3.09 (d,  $J$  = 6.2 Hz, 1H, phenyl), 2.24 (d,  $J$  = 7.2 Hz, 2H, phenyl), 0.68 (d,  $J$  = 7.8 Hz, 2H, phenyl), –0.50 (s, 1H, PhCH), –1.68 (s, 1H, phenyl), –2.08 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), –6.64 (t,  $J$  = 6.4 Hz, 1H, phenyl), –8.30 (s, 2H, ring CH), –19.26 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), –38.49 (d,  $J$  = 4.6 Hz, 2H, phenyl) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 322.1 (UCPh), 318.5 (CPh), 302.8 (CNH), 214.5 (phenyl C), 155.8 (phenyl C), 142.0 (phenyl C), 123.6 (phenyl C), 118.8 (phenyl C), 115.0 (phenyl C), 107.8 (ring C), 98.6 (ring C), 97.3 (ring C), 97.1 (ring C), 96.9 (ring C), 78.4 (CHPh), 48.8 ( $\text{C}(\text{CH}_3)_3$ ), 43.2 ( $\text{C}(\text{CH}_3)_3$ ) ppm; other carbons overlapped. IR (KBr):  $\tilde{\nu}$  = 2958 (s), 1591 (m), 1456 (m), 1361 (s), 1240

(s), 1072 (s), 1028 (s), 808 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_6\text{H}_7\text{N}_3\text{U}$ : C, 67.24; H, 7.56; N, 1.40. Found: C, 67.26; H, 7.53; N, 1.41.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{PhCH}_2\text{CN}$  (2.4 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 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 in 10 min).

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U(=NPh)}_2$ (**13**)

**Method A:** This compound was prepared as brown crystals from the reaction of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $\text{PhN=NPh}$  (46 mg, 0.25 mmol) in toluene (15 mL) at  $50^\circ\text{C}$  and recrystallization from a benzene solution by a similar procedure as that in the synthesis of **5**. Yield: 186 mg (84%).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 9.48 (t,  $J$  = 7.5 Hz, 4H, phenyl), 4.99 (s, 4H, ring CH), 3.07 (d,  $J$  = 6.6 Hz, 4H, phenyl), 1.65 (s, 36H,  $\text{C}(\text{CH}_3)_3$ ), 1.62 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 0.17 ppm (t,  $J$  = 7.2 Hz, 2H, phenyl). These spectroscopic data agreed with those reported in the literature.<sup>[7]</sup>

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{PhN=NPh}$  (3.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **13** along with those of  $\text{PhC}\equiv\text{CPh}$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion) after the sample was kept at  $50^\circ\text{C}$  for 5 days.

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U(=N}(p\text{-tolyl)})_2$ (**14**)

**Method A:** This compound was prepared as brown crystals from the reaction of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and bis(*p*-tolyl)diazene (53 mg, 0.25 mmol) in toluene (15 mL) at  $50^\circ\text{C}$  and recrystallization from a benzene solution by a similar procedure as that in the synthesis of **5**. Yield: 183 mg (80%). M.p.:  $185\text{--}187^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 9.34 (d,  $J$  = 7.6 Hz, 4H, phenyl), 8.08 (s, 6H,  $\text{CH}_3$ ), 5.00 (s, 4H, ring CH), 2.83 (d,  $J$  = 4.8 Hz, 4H, phenyl), 1.67 (s, 36H,  $\text{C}(\text{CH}_3)_3$ ), 1.63 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 187.2 (phenyl C), 166.7 (phenyl C), 142.8 (phenyl C), 140.3 (phenyl C), 118.8 (ring C), 105.9 (ring C), 104.6 (ring C), 38.1 ( $\text{C}(\text{CH}_3)_3$ ), 37.9 ( $\text{C}(\text{CH}_3)_3$ ), 35.8 ( $\text{C}(\text{CH}_3)_3$ ), 31.5 ( $\text{C}(\text{CH}_3)_3$ ), 23.6 ( $\text{CH}_3$ ) ppm. IR (KBr):  $\tilde{\nu}$  = 2958 (s), 1460 (s), 1361 (s), 1240 (s), 1099 (s), 821 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{48}\text{H}_{72}\text{N}_2\text{U}$ : C, 63.00; H, 7.93; N, 3.06. Found: C, 63.04; H, 7.93; N, 3.04.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of bis(*p*-tolyl)diazene (4.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **14** along with those of  $\text{PhC}\equiv\text{CPh}$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion) after the sample was kept at  $50^\circ\text{C}$  for 5 days.

**Method C, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of *p*-tolyl $\text{IN}_3$  (5.3 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **14** along with those of  $\text{PhC}\equiv\text{CPh}$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion) after the sample was kept at room temperature overnight.

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U=NCPh}_3$ (**16**)

**Method A:** This compound was prepared as brown microcrystals from the reaction of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $\text{Ph}_3\text{CN}_3$  (72 mg, 0.25 mmol) in toluene (15 mL) at room temperature and recrystallization from a benzene solution by a similar procedure as that in the synthesis of **5**. Yield: 209 mg

(83%). M.p.:  $173\text{--}175^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 85.85 (s, 2H, ring CH), 37.79 (s, 6H, phenyl), 18.84 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 12.51 (s, 6H, phenyl), 10.19 (s, 3H, phenyl),  $-18.22$  (s, 18H,  $\text{C}(\text{CH}_3)_3$ ),  $-45.33$  (s, 18H,  $\text{C}(\text{CH}_3)_3$ ),  $-47.73$  (s, 2H, ring CH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 172.6 (phenyl C), 171.9 (phenyl C), 170.8 (phenyl C), 159.5 (phenyl C), 143.6 (ring C), 141.0 (ring C), 139.5 (ring C), 100.3 ( $\text{CPh}_3$ ), 58.2 ( $\text{C}(\text{CH}_3)_3$ ), 57.8 ( $\text{C}(\text{CH}_3)_3$ ), 31.9 ( $\text{C}(\text{CH}_3)_3$ ), 31.8 ( $\text{C}(\text{CH}_3)_3$ ) ppm; other carbons overlapped. IR (KBr):  $\tilde{\nu}$  = 2957 (s), 1485 (m), 1357 (m), 1236 (m), 1089 (s), 1066 (s), 1030 (s), 806 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{53}\text{H}_{73}\text{N}_3\text{U}$ : C, 66.16; H, 7.65; N, 1.46. Found: C, 66.14; H, 7.69; N, 1.44. Brown crystals of **16**· $0.5\text{C}_6\text{H}_{14}$  suitable for X-ray structural analysis were grown from an *n*-hexane solution.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{Ph}_3\text{CN}_3$  (5.7 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **16** along with those of  $\text{PhC}\equiv\text{CPh}$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion) after the sample was kept at room temperature overnight.

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U(=NN=CHSiMe}_3\text{)}(\text{CN})$ (**17**)

**Method A:** This compound was prepared as orange crystals from the reaction of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $\text{Me}_3\text{SiCHN}_2$  (58 mg, 0.50 mmol) in toluene (15 mL) at room temperature and recrystallization from an *n*-hexane solution by a similar procedure as that in the synthesis of **5**. Yield: 152 mg (72%). M.p.:  $149\text{--}151^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 4.40 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ),  $-1.65$  (s, 18H,  $\text{C}(\text{CH}_3)_3$ ),  $-1.81$  (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ),  $-3.46$  (s, 18H,  $\text{C}(\text{CH}_3)_3$ ) ppm; protons of  $\text{CpH}$  and  $\text{CHSi}$  were not observed.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 198.2 (CN), 90.1 (CHSi), 38.1 ( $\text{C}(\text{CH}_3)_3$ ), 35.0 ( $\text{C}(\text{CH}_3)_3$ ), 34.9 ( $\text{C}(\text{CH}_3)_3$ ), 33.3 ( $\text{C}(\text{CH}_3)_3$ ), 30.1 ( $\text{C}(\text{CH}_3)_3$ ), 29.6 ( $\text{C}(\text{CH}_3)_3$ ),  $-2.6$  (ring C),  $-3.2$  (ring C),  $-7.0$  (ring C),  $-7.2$  (ring C),  $-8.9$  ( $\text{Si}(\text{CH}_3)_3$ ),  $-10.4$  (ring C) ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  =  $-1.1$  ppm. IR (KBr):  $\tilde{\nu}$  = 2957 (s), 2069 (s), 1944 (w, CN), 1599 (m), 1564 (s), 1492 (m), 1458 (m), 1357 (s), 1242 (s), 1166 (m), 839 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{39}\text{H}_{68}\text{N}_3\text{SiU}$ : C, 55.43; H, 8.11; N, 4.97. Found: C, 55.44; H, 8.09; N, 5.00.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{Me}_3\text{SiCHN}_2$  (4.6 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **17** along with those of  $\text{PhC}\equiv\text{CPh}$  and  $(\text{Me}_3\text{SiNH})_2$  ( $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 2.43 (s, 2H, NH), 0.28 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ) ppm) were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion) after the sample was kept at room temperature overnight.

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U(SPh)}_2$ (**18**)

**Method A:** This compound was prepared as brown crystals from the reaction of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $\text{Ph}_2\text{S}_2$  (55 mg, 0.25 mmol) in toluene (15 mL) at  $50^\circ\text{C}$  and recrystallization from an *n*-hexane solution by a similar procedure as that in the synthesis of **5**. Yield: 201 mg (87%). M.p.:  $168\text{--}170^\circ\text{C}$  (dec.).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 6.08 (s, 36H,  $\text{C}(\text{CH}_3)_3$ ),  $-0.28$  (d,  $J$  = 5.8 Hz, 2H, phenyl),  $-0.35$  (s, 4H, phenyl),  $-9.47$  (s, 18H,  $\text{C}(\text{CH}_3)_3$ ),  $-24.22$  (s, 4H, phenyl) ppm; ring C–H atoms were not observed.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 165.4 (ring C), 164.6 (ring C), 163.7 (ring C), 133.4 (phenyl C), 133.2 (phenyl C), 103.0 (phenyl C), 102.8 (phenyl C), 67.4 ( $\text{C}(\text{CH}_3)_3$ ), 46.0 ( $\text{C}(\text{CH}_3)_3$ ), 39.2 ( $\text{C}(\text{CH}_3)_3$ ) ppm; other carbons overlapped. IR (KBr):  $\tilde{\nu}$  = 2958 (s), 1577 (s), 1473 (s), 1361 (s), 1238 (s), 1080 (s), 1024 (s),

831 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{46}\text{H}_{68}\text{S}_2\text{U}$ : C, 59.85; H, 7.42. Found: C, 59.82; H, 7.43.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{Ph}_2\text{S}_2$  (4.4 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **18** along with those of  $\text{PhC}\equiv\text{CPh}$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion) after the sample was kept at  $50^\circ\text{C}$  overnight.

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\text{SePh})_2$ (**19**)

**Method A:** This compound was prepared as brown microcrystals from the reaction of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $\text{Ph}_2\text{Se}_2$  (78 mg, 0.25 mmol) in toluene (15 mL) at  $50^\circ\text{C}$  and recrystallization from an *n*-hexane solution by a similar procedure as that in the synthesis of **4**. Yield: 193 mg (82%). M.p.:  $134\text{--}136^\circ\text{C}$  (dec).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 5.76$  (br s, 36H,  $\text{C}(\text{CH}_3)_3$ ), 0.99 (s, 2H, phenyl),  $-8.42$  (s, 18H,  $\text{C}(\text{CH}_3)_3$ ),  $-20.14$  (s, 4H, phenyl),  $-21.06$  (s, 4H, phenyl),  $-22.64$  (s, 4H, ring CH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 174.1$  (ring C), 173.4 (ring C), 172.6 (ring C), 134.0 (phenyl C), 129.2 (phenyl C), 118.6 (phenyl C), 103.9 (phenyl C), 69.1 ( $\text{C}(\text{CH}_3)_3$ ), 48.4 ( $\text{C}(\text{CH}_3)_3$ ), 32.6 ( $\text{C}(\text{CH}_3)_3$ ), 31.5 ( $\text{C}(\text{CH}_3)_3$ ) ppm. IR (KBr):  $\tilde{\nu} = 2958$  (s), 1575 (s), 1471 (s), 1361 (s), 1238 (s), 1020 (s), 831 (m), 732 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{40}\text{H}_{63}\text{Se}_2\text{U}$ : C, 51.12; H, 6.76. Found: C, 51.14; H, 6.73.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{Ph}_2\text{Se}_2$  (6.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **19** along with those of  $\text{PhC}\equiv\text{CPh}$  were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion) after the sample was kept at  $50^\circ\text{C}$  overnight.

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}[\text{SC}(=\text{NPh})(\text{C}_2\text{Ph}_2)]$ (**20**)

**Method A:** This compound was prepared as brown crystals from the reaction of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $\text{PhNCS}$  (34 mg, 0.25 mmol) in toluene (15 mL) at room temperature and recrystallization from a benzene solution by a similar procedure as in the synthesis of **5**. Yield: 209 mg (82%). M.p.:  $155\text{--}157^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 53.36$  (s, 2H, ring CH), 21.16 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 4.29 (s, 1H, phenyl), 4.04 (s, 2H, phenyl), 3.52 (s, 2H, phenyl), 3.03 (d,  $J = 5.8$  Hz, 2H, phenyl), 2.52 (s, 1H, phenyl), 1.88 (d,  $J = 3.6$  Hz, 2H, phenyl), 1.22 (s, 1H, phenyl),  $-5.65$  (s, 2H, phenyl),  $-7.25$  (s, 18H,  $\text{C}(\text{CH}_3)_3$ ),  $-7.87$  (s, 2H, phenyl),  $-18.18$  (s, 18H,  $\text{C}(\text{CH}_3)_3$ ),  $-33.80$  (s, 2H, ring CH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 204.7$  (UCPh), 143.6 (phenyl C), 125.1 (phenyl C), 123.4 (phenyl C), 122.4 (phenyl C), 120.2 (phenyl C), 118.9 (phenyl C), 110.5 (ring C), 110.3 (ring C), 103.7 (ring C), 97.9 (ring C), 97.1 (ring C), 96.3 (CPh), 92.2 (C=N), 60.3 ( $\text{C}(\text{CH}_3)_3$ ), 41.7 ( $\text{C}(\text{CH}_3)_3$ ), 41.6 ( $\text{C}(\text{CH}_3)_3$ ) ppm; other carbons overlapped. IR (KBr):  $\tilde{\nu} = 2957$  (s), 1593 (m), 1491 (s), 1384 (s), 1361 (s), 1217 (s), 1112 (s), 823 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{55}\text{H}_{73}\text{NSU}$ : C, 64.87; H, 7.23, N, 1.38. Found: C, 64.85; H, 7.24, N, 1.35.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{PhNCS}$  (2.7 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **20** were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion) after the sample was kept at room temperature overnight.

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}[\text{OCH}(p\text{-tolyl})\text{-(C}_2\text{Ph}_2)]\cdot 0.5\text{C}_6\text{H}_6$ (**21**·**0.5C}\_6\text{H}\_6)**

**Method A:** This compound was prepared as orange crystals from the reaction of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and *p*-tolylCHO (30 mg, 0.25 mmol) in toluene (15 mL) at room temperature and recrystallization from a benzene solution by a similar procedure as in the synthesis of **5**. Yield: 219 mg (84%). M.p.:  $139\text{--}141^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 126.96$  (s, 1H, ring CH), 77.14 (s, 1H, ring CH), 41.94 (s, 2H, phenyl), 19.77 (s, 2H, phenyl), 17.39 (br s, 20H, phenyl, OCH and  $\text{C}(\text{CH}_3)_3$ ), 15.38 (s, 2H, phenyl), 9.44 (s, 1H, phenyl), 9.32 (s, 2H, phenyl), 9.11 (s, 3H,  $\text{CH}_3$ ), 7.15 (s, 3H,  $\text{C}_6\text{H}_6$ ),  $-4.06$  (s, 9H,  $\text{C}(\text{CH}_3)_3$ ),  $-4.51$  (s, 2H, phenyl),  $-5.80$  (s, 2H, phenyl),  $-11.94$  (s, 9H,  $\text{C}(\text{CH}_3)_3$ ),  $-17.51$  (s, 9H,  $\text{C}(\text{CH}_3)_3$ ),  $-19.11$  (s, 9H,  $\text{C}(\text{CH}_3)_3$ ),  $-31.77$  (s, 1H, ring CH),  $-58.53$  ppm (s, 1H, ring CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 247.6$  (UCPh), 171.1 (CPh), 154.5 (phenyl C), 149.5 (phenyl C), 134.5 (phenyl C), 128.5 ( $\text{C}_6\text{H}_6$ ), 123.3 (ring C), 119.1 (ring C), 112.4 (ring C), 100.1 (ring C), 66.0 (CHO), 45.6 ( $\text{C}(\text{CH}_3)_3$ ), 29.1 ( $\text{C}(\text{CH}_3)_3$ ), 27.1 ( $\text{C}(\text{CH}_3)_3$ ), 16.6 ( $\text{CH}_3$ ) ppm; other carbons overlapped. IR (KBr):  $\tilde{\nu} = 2958$  (s), 1384 (m), 1359 (s), 1240 (s), 1060 (s), 1003 (s), 821 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{59}\text{H}_{79}\text{OU}$ : C, 67.99; H, 7.64. Found: C, 67.97; H, 7.62.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of *p*-tolylCHO (2.4 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **21** were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion) after the sample was kept at room temperature overnight.

#### Preparation of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}[\text{OCH}(p\text{-ClPh})\text{-(C}_2\text{Ph}_2)]\cdot 1.5\text{C}_6\text{H}_6$ (**22**·**1.5C}\_6\text{H}\_6)**

**Method A:** This compound was prepared as orange crystals from the reaction of  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and *p*-ClPhCHO (35 mg, 0.25 mmol) in toluene (15 mL) at room temperature and recrystallization from a benzene solution by a similar procedure as in the synthesis of **5**. Yield: 245 mg (86%). M.p.:  $143\text{--}145^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 122.11$  (s, 1H, ring CH), 74.37 (s, 1H, ring CH), 40.61 (s, 2H, phenyl), 19.46 (s, 2H, phenyl), 15.39 (br s, 20H, phenyl, OCH and  $\text{C}(\text{CH}_3)_3$ ), 14.95 (s, 2H, phenyl), 9.36 (s, 1H, phenyl), 9.19 (s, 2H, phenyl), 7.15 (s, 9H,  $\text{C}_6\text{H}_6$ ),  $-3.62$  (s, 9H,  $\text{C}(\text{CH}_3)_3$ ),  $-4.31$  (s, 2H, phenyl),  $-5.50$  (s, 2H, phenyl),  $-11.38$  (s, 9H,  $\text{C}(\text{CH}_3)_3$ ),  $-16.82$  (s, 9H,  $\text{C}(\text{CH}_3)_3$ ),  $-18.65$  (s, 9H,  $\text{C}(\text{CH}_3)_3$ ),  $-30.75$  (s, 1H, ring CH),  $-53.49$  (s, 1H, ring CH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 245.5$  (UCPh), 171.1 (CPh), 150.6 (phenyl C), 149.6 (phenyl C), 148.7 (phenyl C), 147.8 (phenyl C), 134.5 (phenyl C), 129.3 (phenyl C), 128.5 ( $\text{C}_6\text{H}_6$ ), 125.6 (phenyl C), 123.3 (ring C), 119.4 (ring C), 112.2 (ring C), 112.0 (ring C), 100.6 (ring C), 65.1 (CHO), 46.2 ( $\text{C}(\text{CH}_3)_3$ ), 25.5 ( $\text{C}(\text{CH}_3)_3$ ), 17.8 ( $\text{C}(\text{CH}_3)_3$ ), 7.9 ( $\text{C}(\text{CH}_3)_3$ ) ppm. IR (KBr):  $\tilde{\nu} = 2958$  (s), 1487 (s), 1361 (s), 1240 (s), 1087 (s), 1070 (s), 1004 (s), 821 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{64}\text{H}_{82}\text{ClOU}$ : C, 67.38; H, 7.24. Found: C, 67.36; H, 7.22.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of *p*-ClPhCHO (2.8 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **22** were observed by  $^1\text{H}$  NMR spectroscopy (100% conversion) after the sample was kept at room temperature overnight.

### Preparation of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}[\text{OC}[(\text{CH}_2)_3](\text{C}_2\text{Ph}_2)]$ (**23**)

**Method A:** This compound was prepared as orange microcrystals from the reaction of  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $(\text{CH}_2)_5\text{CO}$  (25 mg, 0.25 mmol) in toluene (15 mL) at room temperature and recrystallization from a benzene solution by a similar procedure as in the synthesis of **5**. Yield: 195 mg (76%). M.p.: 161–163 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 55.40 (s, 2H, ring CH), 28.55 (br s, 4H, phenyl), 22.65 (s, 2H, phenyl), 19.72 (s, 4H, phenyl), 12.95 (s, 1H, Cy), 10.86 (s, 4H, Cy), 9.88 (s, 2H, Cy), –5.09 (s, 3H, Cy), –6.57 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), –15.85 (br s, 45H,  $\text{C}(\text{CH}_3)_3$ ), –32.54 (s, 2H, ring CH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 170.1 (CPh), 134.0 (phenyl C), 132.3 (phenyl C), 129.4 (phenyl C), 127.9 (phenyl C), 122.4 (ring C), 120.2 (ring C), 117.9 (ring C), 99.0 (ring C), 61.3 (CO), 47.0 ( $\text{C}(\text{CH}_3)_3$ ), 44.1 ( $\text{C}(\text{CH}_3)_3$ ), 35.7 ( $\text{CH}_2$ ), 30.5 ( $\text{CH}_2$ ), 29.7 ( $\text{CH}_2$ ) ppm; other carbons were not observed. IR (KBr):  $\tilde{\nu}$  = 2960 (s), 1384 (s), 1259 (s), 1089 (s), 1022 (s), 798 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{54}\text{H}_{78}\text{OU}$ : C, 66.10; H, 8.01. Found: C, 66.08; H, 8.02. Brown crystals of **23**·0.5 $\text{C}_6\text{H}_{14}$  suitable for X-ray structural analysis were grown from an *n*-hexane solution.

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $(\text{CH}_2)_5\text{CO}$  (2.0 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **23** were observed by  $^1\text{H NMR}$  spectroscopy (100% conversion) after the sample was kept at room temperature overnight.

### Preparation of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}[\text{OCPh}_2]$ (**24**)

**Method A:** This compound was prepared as orange crystals from the reaction of  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 221 mg, 0.25 mmol) and  $\text{Ph}_2\text{CO}$  (91 mg, 0.50 mmol) in toluene (15 mL) at 60 °C and recrystallization from a benzene solution by a similar procedure as that in the synthesis of **5**. Yield: 224 mg (84%).  $^1\text{H NMR}$  (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 61.95 (s, 2H, ring CH), 27.41 (s, 1H, phenyl), 23.01 (s, 1H, phenyl), 16.08 (s, 1H, phenyl), 13.84 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 13.42 (s, 1H, phenyl), 9.72 (s, 2H, phenyl), 8.43 (s, 2H, phenyl), 7.66 (s, 4H, phenyl), 7.01 (s, 5H, phenyl), 4.61 (s, 1H, phenyl), 2.90 (s, 1H, phenyl), –1.30 (s, 1H, phenyl), –5.29 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), –23.24 (s, 2H, ring CH), –43.97 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ) ppm. These spectroscopic data agreed with those reported in the literature.<sup>[7]</sup>

**Method B, NMR scale:** A  $\text{C}_6\text{D}_6$  (0.3 mL) solution of  $\text{Ph}_2\text{CO}$  (7.3 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL). Resonances of **24** along with those of  $\text{PhC}\equiv\text{CPh}$  were observed by  $^1\text{H NMR}$  spectroscopy (100% conversion) after the sample was kept at 60 °C for 5 days.

### Reaction of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$ (**2**) with $\text{Ph}_2\text{CO}$

**NMR scale:** A  $\text{C}_6\text{D}_6$  (0.2 mL) solution of  $\text{Ph}_2\text{CO}$  (3.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with  $[\eta^5-1,2,4-(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{U}(\eta^2\text{-C}_2\text{Ph}_2)$  (**2**; 18 mg, 0.02 mmol) and  $\text{C}_6\text{D}_6$  (0.3 mL). Resonances of **24** along with those of unreacted **2** and  $\text{PhC}\equiv\text{CPh}$  were observed by  $^1\text{H NMR}$  spectroscopy (50% conversion based on **2**) after the sample was kept at 60 °C for 5 days.

### X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Rigaku Saturn CCD diffractometer at 100(2) K using graphite monochromated  $\text{Cu}_{\text{K}\alpha}$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). An empirical absorption

correction was applied using the SADABS program.<sup>[19]</sup> All structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  using the SHELXL program package.<sup>[20]</sup> All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **2**, **5**, **9**, **10**, **12**, **14**, **16–18** and **20–23** are summarized in the Supporting Information. Selected bond lengths and angles are listed in Table 1. It is of note that the structural data of **2** were relatively poor due to crystal twinning, which led to a large positive residual density ( $9.77 \text{ e \AA}^{-3}$ ) close to the uranium atom (0.99 Å) and also to low bond precision within the C–C distances (0.02776 Å). These B level alerts in the checkCIF could not be removed on refinement.

Deposition numbers 2054372 (**2**), 2054384 (**5**), 2054379 (**9**), 2054374 (**10**), 2054373 (**12**), 2054376 (**14**), 2054375 (**16**), 2054377 (**17**), 2054382 (**18**), 2054378 (**20**), 2054381 (**21**), 2054383 (**22**), and 2054380 (**23**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

### Computational methods

All calculations were carried out with the Gaussian 09 program (G09),<sup>[21]</sup> employing the B3PW91 functional, plus a polarizable continuum model (PCM) (denoted as B3PW91-PCM), with standard 6-31G(d) basis set for C and H 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>[22]</sup> to fully optimize the geometries of the complexes.

### Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21871029, 21573021, 21672024), and the Deutsche Forschungsgemeinschaft (DFG) through the Heisenberg program (WA 2513/6). Open access funding enabled and organized by Projekt DEAL.

### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** actinides · bonding · metallacyclopropene complexes · reactivity · uranium

- [1] For selected reviews, see: a) S. L. Buchwald, R. B. Nielsen, *Chem. Rev.* **1988**, *88*, 1047–1058; b) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics* **2003**, *22*, 884–900; c) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, V. B. Shur, *Eur. J. Inorg. Chem.* **2004**, 4739–4749; d) U. Rosenthal, *Angew. Chem. Int. Ed.* **2004**, *43*, 3882–3887; *Angew. Chem.* **2004**, *116*, 3972–3977; e) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics* **2005**, *24*, 456–471; f) U. Rosenthal, V. V. Burlakov, M. A. Bach, T. Beweries, *Chem. Soc. Rev.* **2007**, *36*, 719–728; g) S. Roy, U. Rosenthal, E. D. Jemmis, *Acc. Chem. Res.* **2014**, *47*, 2917–2930; h) K. D. J. Parker, M. D. Fryzuk, *Organometallics* **2015**, *34*, 2037–2047; i) G. Zi, *Chem. Commun.* **2018**, *54*, 7412–7430; j) U. Rosenthal, *Angew. Chem. Int. Ed.* **2018**, *57*, 14718–14735; *Angew. Chem.* **2018**, *130*, 14932–14950; k) U. Rosenthal, *Eur. J. Inorg. Chem.* **2019**, 895–916; l) U. Rosenthal, *ChemistryOpen* **2019**, *8*, 1036–1047; m) U. Rosenthal, *Organometallics* **2020**, *39*, 4403–4414.



- [13] D. S. J. Arney, C. J. Burns, D. C. Smith, *J. Am. Chem. Soc.* **1992**, *114*, 10068–10069.
- [14] W. J. Evans, K. A. Miller, S. A. Kozimor, J. W. Ziller, A. G. DiPasquale, A. L. Rheingold, *Organometallics* **2007**, *26*, 3568–3576.
- [15] W. J. Evans, K. A. Miller, W. R. Hillman, J. W. Ziller, *J. Organomet. Chem.* **2007**, *692*, 3649–3654.
- [16] a) W. J. Evans, S. A. Kozimor, J. W. Ziller, N. Kaltsoyannis, *J. Am. Chem. Soc.* **2004**, *126*, 14533–14547; b) W. J. Evans, C. A. Traina, J. W. Ziller, *J. Am. Chem. Soc.* **2009**, *131*, 17473–17481.
- [17] P. Rungthanaphatsophon, C. L. Barnes, S. P. Kelley, J. R. Walensky, *Dalton Trans.* **2018**, *47*, 8189–8192.
- [18] W. Ren, G. Zi, M. D. Walter, *Organometallics* **2012**, *31*, 672–679.
- [19] G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Göttingen, Germany, **1996**.
- [20] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.
- [21] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Menucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A., Jr., Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cio-slawski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.
- [22] a) W. Küchle, M. Dolg, H. Stoll, H. Preuss, *J. Chem. Phys.* **1994**, *100*, 7535–7542; b) X. Cao, M. Dolg, H. Stoll, *J. Chem. Phys.* **2003**, *118*, 487–496; c) X. Cao, M. Dolg, *THEOCHEM* **2004**, *673*, 203–209.

---

Manuscript received: January 9, 2021

Accepted manuscript online: February 9, 2021

Version of record online: March 16, 2021