This is an open access article published under an ACS AuthorChoice License, which permits copying and redistribution of the article or any adaptations for non-commercial purposes.

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

An Actinide Metallacyclopropene Complex: Synthesis, Structure, Reactivity, and Computational Studies

Bo Fang,[†] Wenshan Ren,[†] Guohua Hou,[†] Guofu Zi,*[,†] De-Cai Fang,*[,†] Laurent Maron,*[,‡] and Marc D. Walter*[,§]

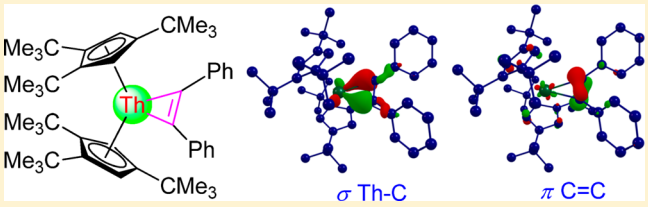
[†]Department of Chemistry, Beijing Normal University, Beijing 100875, China

[‡]LPCNO, CNRS and INSA, Université Paul Sabatier, 135 Avenue de Rangueil, 31077 Toulouse, France

[§]Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany

Supporting Information

ABSTRACT: The synthesis, structure, and reactivity of an actinide metallacyclopropene were comprehensively studied. The reduction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2ThCl_2$ (**1**) with potassium graphite (KC_8) in the presence of diphenylacetylene (PhC≡CPh) yields the first stable actinide metallacyclopropene $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph_2)$ (**2**). The magnetic susceptibility data show that **2** is indeed a diamagnetic Th(IV) complex, and density functional theory (DFT) studies suggest that the 5f orbitals contribute to the bonding of the metallacyclopropene Th—(η^2-C═C) moiety. Complex **2** shows no reactivity toward alkynes, but it reacts with a variety of heterounsaturated molecules such as aldehyde, ketone, carbodiimide, nitrile, organic azide, and diazoalkane derivatives. DFT studies complement the experimental observations and provide additional insights. Furthermore, a comparison between Th and group 4 metals reveals that Th^{4+} shows unique reactivity patterns.



INTRODUCTION

Highly strained metallacyclopropenes have attracted significant interest in the last decades because of their unusual intrinsic reactivity.[1−7] The bonding in these complexes can be rationalized by the Dewar−Chatt−Duncanson model, that was originally introduced to describe the bonding in metal olefin complexes,[8] but can be extended to metal alkyne complexes.[9] Within this model, the bonding in metallacyclopropenes can be described by two resonance structures, π-complex (**A**) and metallacyclopropene (**B**) (Figure 1). While in both cases the alkyne acts as a two-electron donor ligand,[10] the difference between the resonance structures **A** and **B** arises from the extent of π-back-bonding, which occurs between the metal atom and the alkyne ligand and resonance structure **B** can also be interpreted as a M^{2+} fragment being coordinated by a $[\eta^2\text{-alkenediyl}]^{2-}$ fragment. Furthermore, for electron-poor metal centers, the alkyne can act as an additional π-donor ligand, providing electron density to the metal atom via the orthogonal π-system and therefore acting as a four-electron donor ligand (Figure 1, **C**).[10] On the molecular orbital (MO) level, these interactions can be described by combining MOs of the metal fragment with those alkyne π-MOs of matching symmetry (Figure 1).[9] Late (and electron rich) transition metals (such as Pt, Pd, Ni, and Co) are known for their ability to undergo strong M → alkyne π-back-donation,[4] and have been used extensively in organic synthesis, e.g., mediating a variety of organic transformations such as cyclotrimerization of alkynes and preparation of pyridines and cyclopentadienones from alkynes and isonitriles, olefins, or carbon monoxide.[4a−c] In contrast, π-back-bonding is weaker in actinide metals but becomes relevant, for example, to explain the bonding in the U(III) complex $(Me_3SiC_5H_4)_3U(CO)$.[11]

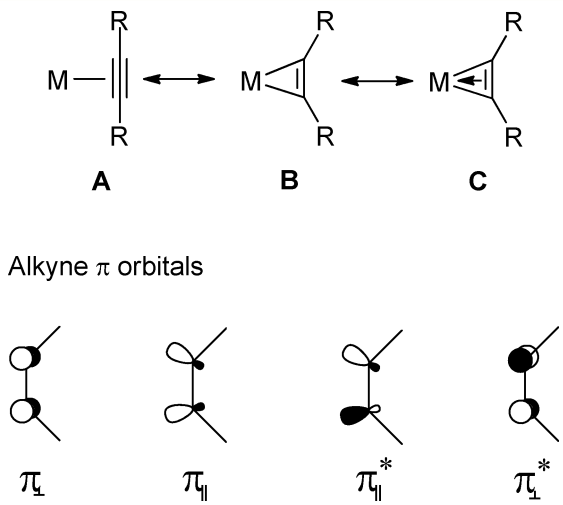


Figure 1. Resonance structures of metallacyclopropene and π-MOs of alkyne.

Received: September 22, 2014
Published: December 2, 2014

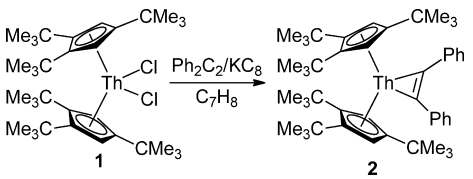
In recent years, a number of group 4 metallacyclopropenes such as $Cp'_2M(L)(\eta^2$-alkynyl) (Cp' = substituted or unsubstituted η^5-cyclopentadienyl; M = Ti, Zr, Hf; L = THF, pyridine, PMe_3) have been prepared by the reaction of Cp'_2M with alkynes or by the reduction of Cp'_2MX_2 precursors in the presence of alkynes.[1,2] Depending on the nature of the metallocene fragment Cp'_2M and the alkyne substitutents, these complexes might serve as a useful synthon for Cp'_2M when reacted with unsaturated substrates and liberate the coordinated alkyne under mild conditions.[1,2] Although the resulting metallacycles are interesting in their own right, they can also serve as precursors for the preparation of highly functionalized organic molecules and heterocyclic main group element compounds.[1,2,12] Nevertheless, in contrast to transition metal and especially group 4 complexes, to the best of our knowledge, no examples of stable actinide metallacyclopropenes have been reported in the literature.[6,7] Most notably, while the π-U(III) alkyne complex $(\eta^5\text{-}C_5H_5)_3U(\eta^2\text{-PhC}\equiv\text{CPh})$ was spectroscopically observed, it exhibited only limited stability,[7b] which presumably originates from the weak M → alkyne π-back-bonding in this U(III) complex when compared to d-transition metal complexes.[10] However, the electronic ground state of thorium is $7s^26d^2$, so one might expect a similar reactivity to that of group 4 metals, for which metallacyclopropenes are readily accessible.[1,2] Encouraged by the fascinating chemistry of group 4 metallacyclopropenes, we have therefore initiated a research program in this area. Furthermore, we also set out to address the influence of 5f orbitals in the bonding in thorium organometallics, leading to a distinctively different reactivity compared to that of d-transition metals. In this paper, we report on some observations concerning the synthesis, electronic structure, and structure−reactivity relationship of the first stable actinide metallacyclopropene $[\eta^5\text{-1,2,4-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph_2)$ (**2**) and describe the differences and similarities between the thorium and group 4 metallacyclopropenes.

■ RESULTS AND DISCUSSION

Synthesis of $[\eta^5\text{-1,2,4-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph_2)$ (2). Treatment of a 1:1 mixture of diphenylacetylene and $[\eta^5\text{-1,2,4-}(Me_3C)_3C_5H_2]_2ThCl_2$ (**1**) with an excess of KC_8 in toluene solution gives pale yellow crystals of the metallacyclopropene $[\eta^5\text{-1,2,4-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph_2)$ (**2**) in 85% yield (Scheme 1). In contrast to the $[(\eta^5\text{-}C_5Me_5)_2An]$ (An = Th, U) fragment,[6,13] no actinide metallacyclopentadiene complex was isolated in the case of the sterically more demanding 1,2,4-$(Me_3C)_3C_5H_2$ ligand regardless of the amount of PhC≡Ph employed. While **2** is air and moisture sensitive, it can be stored without degradation in a dry nitrogen atmosphere. Complex **2** is soluble in and readily recrystallized from a benzene solution, and it was fully characterized by various spectroscopic techniques, elemental analysis, and single crystal X-ray diffraction. The ^{1}H NMR resonances with chemical shifts in the range 0−10 ppm are narrow and show well-resolved coupling patterns that are consistent with a diamagnetic molecule. Furthermore, the ^{13}C NMR spectrum features a resonance at δ = 231.9 ppm, corresponding to the coordinated $[\eta^2\text{-PhC}{=}\text{CPh}]$ group.[1b,5c] Next the lability of the diphenylacetylene moiety was probed on the NMR and chemical time scale. In contrast to the uranium(III) complex $(\eta^5\text{-}C_5H_5)_3U(\eta^2\text{-PhC}\equiv\text{CPh})$,[7b] variable-temperature (20−100 °C) ^{1}H NMR investigations reveal that no dissociation of **2** occurs when it is heated to 100 °C, consistent with a strong coordination of the diphenylacetylene moiety to the thorium atom and therefore the metallacyclopropene Th—C—C ring stays intact in toluene solution even at high temperatures. Next the exchange of diphenylacetylene for MeC≡CMe, PhC≡CMe, and (*p*-tolyl)C≡C(*p*-tolyl) was investigated at elevated temperatures on a chemical time scale, but no exchange occurred in contrast to group 4 metallacyclopropene complexes.[1,2] From these observations, complex **2** is best described as a thorium metallacyclopropene (Th(IV) with a $[\eta^2\text{-alkenediyl}]^{2-}$ ligand) instead of a thorium(II) π-alkyne complex (Figure 1).

The molecular structure of **2** is shown in Figure 2, and selected bond distances and angles are listed in Table 1. To the best of our knowledge, **2** represents the first structurally characterized actinide metallacyclopropene. The carbon atoms (C(18) and C(18A)) of the alkyne and the carbon atoms (C(19) and C(19A)) are nearly coplanar with a torsion angle (C(19)−C(18)−C(18A)−C(19A)) of 8.4(1)°. The relevant C(18)−C(18A) distance of 1.343(4) Å is significantly longer than that of the free PhC≡CPh molecule (1.210(3) Å),[14] much closer to the value of a typical double bond (1.331 Å),[15] and comparable to those found in group 4 metallacyclopropenes.[1,2] In addition, the distance Th−C(18) or Th−C(18A) of 2.395(2) Å is on the lower end of the reported Th−C(sp^2) σ-bonds (2.420(3)−2.654(14) Å).[16] The C(19)−C(18)−C(18A) or C(19A)−C(18A)−C(18) angle of 128.2(1)° differs from 180° and approaches a value of 120°, which is typical for sp^2-hybridized carbon atoms. Overall, these structural parameters of **2** clearly support the formation of a thorium metallacyclopropene complex.

Scheme 1



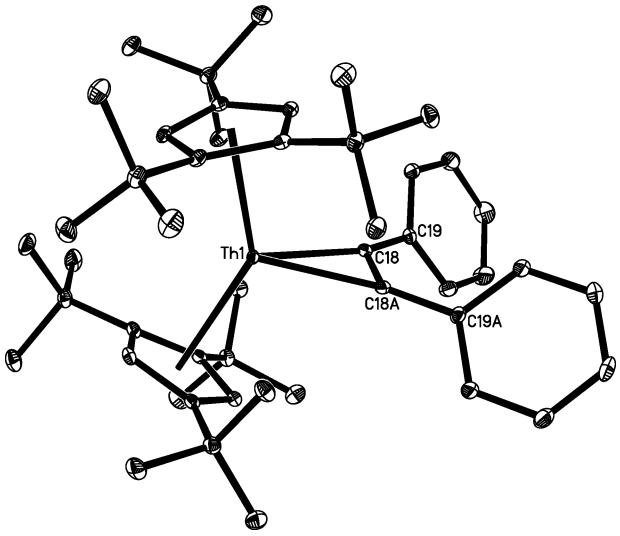


Figure 2. Molecular structure of **2** (thermal ellipsoids drawn at the 35% probability level).

Table 1. Selected Distances (Å) and Angles (deg) for Compounds 2−7, 11, and 14[a]

compound	C(Cp)−Th[b]	C(Cp)−Th[c]	Cp(cent)−Th[b]	Th−X	Cp(cent)−Th−Cp(cent)	X−Th−X/Y
2	2.861(2)	2.798(2) to 2.950(2)	2.592(2)	C(18) or C(18A) 2.395(2)	138.7(2)	32.6(1)
3	2.882(2)	2.783(3) to 2.995(3)	2.617(3)	C(41) 2.627(3), O(1) 2.123(2)	134.3(2)	67.2(1)
4	2.870(5)	2.784(4) to 2.972(5)	2.600(5)	C(37) 2.549(5), S(2) 2.766(1)	141.7(4)	70.6(1)
5	2.856(4)	2.795(4) to 2.959(4)	2.590(3)	C(41) 2.522(4), S(1) 2.741(1)	140.3(2)	72.6(1)
6	2.907(9)	2.815(9) to 3.056(8)	2.668(9)	C(41) 2.530(8), N(2) 2.309(6)	135.1(5)	68.9(3)
7	2.909(3)	2.784(3) to 3.92(3)	2.700(3)	O(1) or O(1A) 2.182(2)	122.1(2)	67.2(1)
11	2.896(3)	2.815(3) to 2.993(3)	2.632(3)	C(51) 2.442(3), N(1) 2.365(2)	138.1(2)	69.5(1)
14	2.878(12)	2.704(12) to 3.042(12)	2.613(9)	C(34) 2.554(11), N(1) 2.367(10), N(2) 2.567(10)	133.0(3)	32.3(3)[d]

[a]Cp = cyclopentadienyl ring. [b]Average value. [c]Range. [d]The angle of N(1)−Th(1)−N(2).

Solid State Magnetic Susceptibility Studies (SQUID). In a recent study, we established that $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(bipy)$ exhibits a Th(IV)(bipy^{2-}) (S = 0) ground state, but the open-shell singlet and triplet excited states are close enough in energy, so that they have to be considered in its magnetism and reaction chemistry.[17c] Nevertheless, when dealing with air and moisture sensitive samples with low magnetic moments, extreme care and attention to detail is required. To rule out impurity problems, the measurements were repeated on independently prepared samples and these samples were sealed in quartz tubes. We also recorded the magnetic susceptibility at three different temperatures (200, 250, and 300 K) and varied the applied magnetic field (H) between 0 and 70 kG. The magnetization (M_{tot}) vs H curves were plotted for complex **2** (see the Supporting Information for details). The recorded magnetization is the sum of the magnetization of the sample components including potential ferromagnetic impurities ($M_{impurity}$), and the magnetization is described by the formula $M_{tot} = \chi H + M_{impurity}$. Gratifyingly, these field sweeps confirm the absence of ferromagnetic impurities in our SQUID samples. Hence, the magnetization of the sample can be expressed by $M_{tot} = \chi H$. From the linear M_{tot} vs H plots, the magnetic susceptibility χ can be determined (see the Supporting Information for details). The χ values obtained from these analyses and collected at three different temperatures were corrected for Pascal's constants to yield a very small and negative χ value of -5.44×10^{-5} emu/mol, supporting the fact that complex **2** is indeed a diamagnetic molecule in contrast to $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(bipy)$.[17c] From these results, we conclude that exited states will have no impact on the reactivity of complex **2**.

Bonding Studies. In addition, to better understand the interaction between the thorium atom and the PhC═CPh moiety, a computational study has been carried out at the DFT level of theory (B3PW91). The optimized structure is in excellent agreement with the crystallographic data; e.g., the calculated values are 2.372 Å for the distance Th—C and 1.357 Å for C—C and 33.2° for the angle C—Th—C and 128.4° for C—C—C(Ph), which compare very favorably with the experimental values of 2.395(2) Å, 1.343(4) Å, 32.6(1)°, and 128.2(1)°, respectively.

The DFT studies further confirm that **2** is indeed best described as a metallacyclopropene, which features a $Th(\eta^2\text{-}C_2Ph_2)$ metallacyclopropene moiety with two in-plane Th−C σ-bonds and one out-of-plane π-bond interacting with the metal center (Figure 3). A natural bond orbital (NBO) analysis reveals that polarized Th−C σ-bonds (HOMO) are formed by a carbon sp-hybrid orbital (89.2%; 24% s and 76% p) and a thorium hybrid orbital (10.8%; 26% 5f and 52% 6d and 8% 7p and 14% 7s). In addition, two bonding orbitals are found for the C−C bond: one is a σ-bond (HOMO−1) with pure sp-hybrid orbitals (39% s and 61% p); the other bonding orbital is a π-bond (HOMO−2) with 99.9% occupancy consisting of only p orbitals and with a 0.1% contribution from the d orbital of Th. From these results, a metallacyclopropene moiety with a delocalized aromatic system as described for group 4 complexes[18] can be discounted. In addition, these computations reveal that the thorium 5f orbitals are indeed involved in the bonding between the metallocene and C_2Ph_2 fragments, which is consistent with previous conclusions that the 5f orbitals play a key role in the bonding of actinide complexes. Furthermore, the actinide−carbon bonds are more polarized than those in d-transition metals.[19] Therefore, the alkyne moiety in the more covalent group 4 metallacyclopropene complexes can readily be replaced by other alkynes,[1,2] whereas no exchange is observed in the thorium complex **2**.

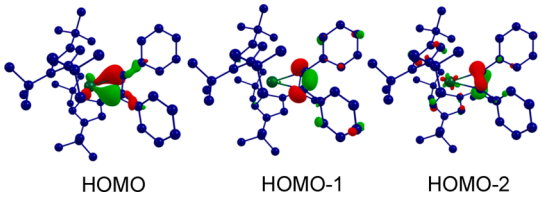
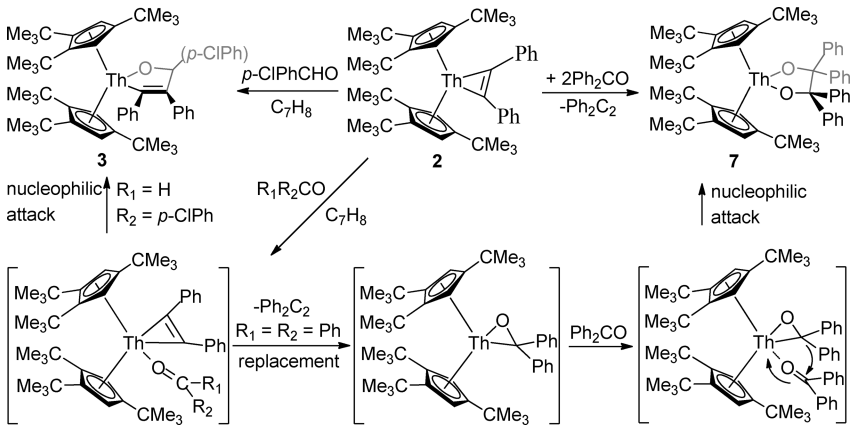


Figure 3. Plots of HOMOs for **2** (the hydrogen atoms have been omitted for clarity).

Reactivity Studies. In contrast to actinide metallacyclopentadiene complexes,[13,19f] the electronic structure and the steric strain within the moiety $Th(\eta^2\text{-}C_2Ph_2)$ should be reflected in a high reactivity toward unsaturated organic substrates. Indeed, similar to the aluminum and the group 4 metallacyclopropene complexes,[1,2,5c] complex **2** reacts readily with heterounsaturated organic substrates. For example, insertion of 1 equiv of p-ClPhCHO into the thorium metallacyclopropene moiety of **2** is observed at room temperature to yield the five-membered heterocyclic complex $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[OCH(p\text{-}ClPh)(C_2Ph_2)]$ (**3**) in quantitative conversion (Scheme 2). DFT computations show that intermediate **COM3** is initially formed during the reaction of **2** with p-ClPhCHO and that product **3** is then formed via the transition state **TS3** (Figure 4). In **TS3**, the two forming bond distances of Th−O and C−C are 2.490 and 2.912 Å, respectively, about 0.35 and 1.40 Å longer than those in product **3**. The conversion of **COM3** to product **3** is energetically very favorable by ΔG(298 K) = −47.1 kcal/mol, and proceeds via transition state **TS3** with a low activation barrier ($\Delta G^{\ddagger}$(298 K)) of only 6.8 kcal/mol. This is completely

Scheme 2



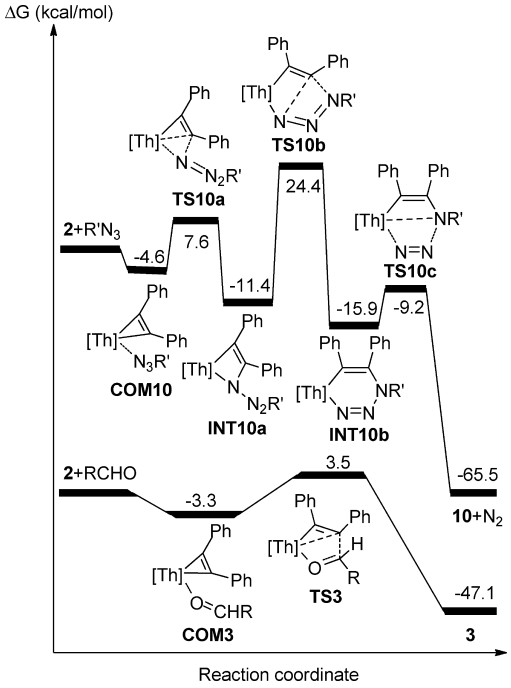
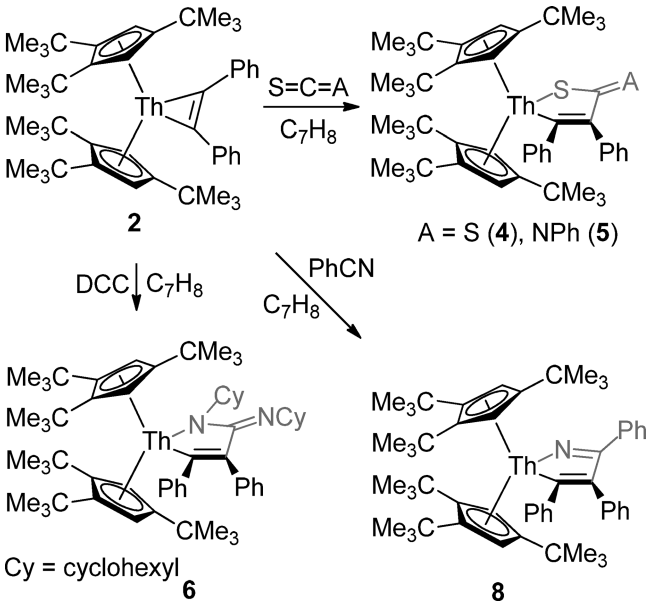


Figure 4. Free energy profile (kcal/mol) for the reactions of **2**+*p*-ClPhCHO and **2**+Me_3SiN_3 (computed at T = 298 K). [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th. R = *p*-ClPh. R′ = Me_3Si.

consistent with the rapid formation of **3** at ambient temperature.

In contrast to thorium bipy complexes,[17b] the reaction of **2** with CS_2 or PhNCS does not proceed by the replacement of the alkyne moiety to yield a thorium sulfido complex;[17b] instead, the five-membered heterocyclic complexes [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[SC(═S)(C_2Ph_2)] (**4**) and [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[SC(═NPh)(C_2Ph_2)] (**5**) are formed, respectively, in quantitative conversions (Scheme 3). Moreover, in contrast to the titanium metallacyclopropene complex (η^5-$C_5H_5)_2$Ti(η^2-$Me_3SiC_2SiMe_3$), which reacts as a π Ti(II)—alkyne complex with carbodiimides,[2b,c] reaction of **2** with carbodiimides does not involve a replacement of the alkyne to yield four-membered heterometallacycles;[2b,c] instead, treatment of **2** with 1 equiv of *N*,*N*′-dicyclohexylcarbodiimide (DCC) also gives a five-membered heterocyclic complex [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N(C_6H_{11})C(═N$C_6H_{11})(C_2Ph_2)$] (**6**) in quantitative conversion (Scheme 3).

Scheme 3



However, in contrast to the above-mentioned substrates, the alkyne moiety is replaced in the reaction of **2** with Ph_2CO to form the thorium pinacolate [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th-[$(OCPh_2)_2$] (**7**) (Scheme 2), irrespectively of the amount of Ph_2CO employed. Similar to zirconium metallacyclopropene (η^5-$C_5H_5)_2$Zr[η^2-$C_2(SiMe_3)_2$](THF),[20a] one molecule of Ph_2CO initially coordinates to **2**, but as a consequence of steric hindrance, the carbon atom of the C═O group cannot be readily attacked by the alkyne carbon atom as in the case of *p*-ClPhCHO. Therefore, Ph_2CO replaces the PhC≡CPh fragment to give a metal η^2-ketone intermediate,[20] which is highly reactive and immediately couples with a second molecule of Ph_2CO to give **7** (Scheme 2). A similar C—C coupling has been reported for the reaction between organic nitriles and aluminum[5c] or group 4[2g] metallacyclopropene complexes. However, in contrast to the latter complexes, neither replacement nor nitrile−nitrile C—C coupling reaction is observed, when complex **2** is treated with organic nitriles. In fact, complex **2** reacts with PhCN to afford the five-membered heterocyclic complex [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N═C(Ph)-(C_2Ph_2)] (**8**) in quantitative conversion (Scheme 3), once again, due to the more polarized Th(IV)—(η^2-C_2Ph_2) structure. However, when the sterically encumbered ^{t}BuCN is

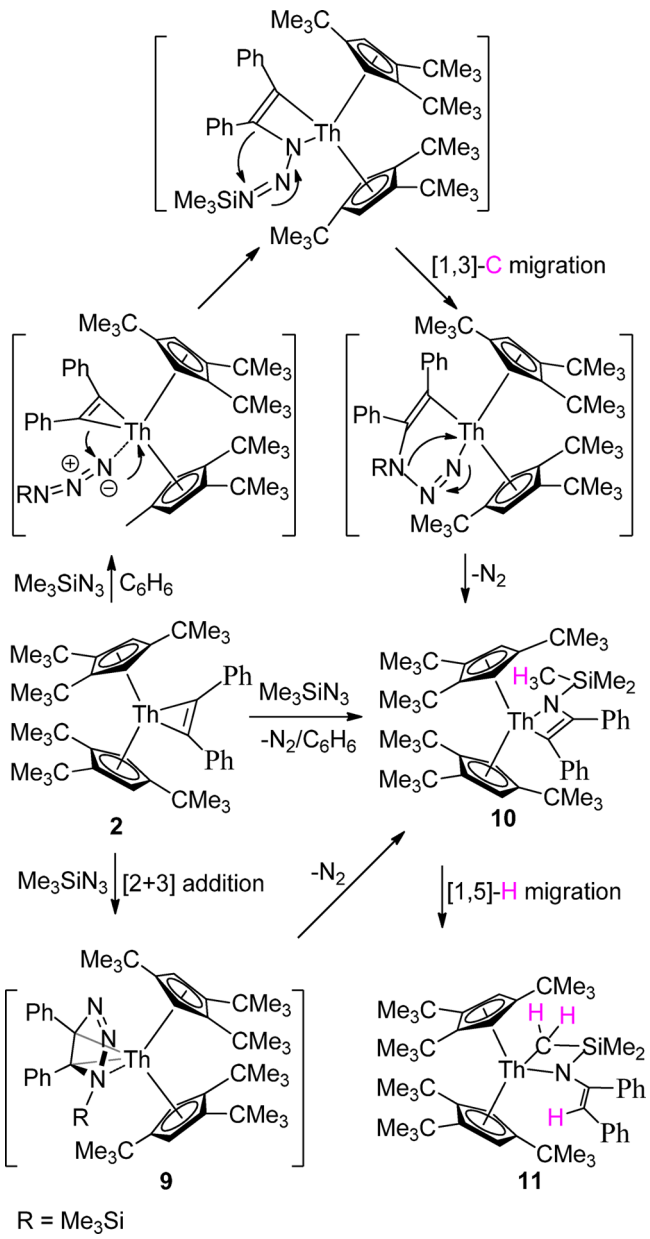
used as substrate, no reaction occurs even when heated at 100 °C for 1 week. Moreover, no insertion occurs between complex **2** and a second alkyne RC≡CR (R = Me, Ph, *p*-tolyl) even when heated at 100 °C for 1 week, most probably a consequence of steric hindrance.

Interestingly, in contrast to aluminum metallacyclopropenes,[5c] thorium bipy complexes,[17a] and zirconium metallacyclopropenes,[21] the reaction of **2** with organic azides such as Me_3SiN_3 proceeds neither by the replacement of the alkyne moiety to yield a thorium imido complex[5c,17] nor by a [3 + 1] insertion to give a four-membered metallaheterocycle;[21] instead, the rearranged complex $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[N(SiMe_3)C(Ph)=C(Ph)]$ (**10**) is unexpectedly formed in quantitative conversion (Scheme 4). It should be noted at this point that **10** cannot be prepared by the reaction of the imido complex $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}NSiMe_3$ with PhC≡CPh. Two alternative reaction pathways may be proposed for this transformation (Scheme 4). At the top of the scheme, a nucleophilic attack of the dianionic $[Ph_2C_2]^{2-}$ on Me_3SiN_3 followed by [1,3]-carbon migration and N_2 release is shown, whereas, at the bottom of the scheme, complex **2** initially reacts with Me_3SiN_3 in a [2 + 3] cycloaddition to give complex **9**. However, **9** is unstable and releases N_2 to furnish complex **10**. Furthermore, we also found that complex **10** is thermally unstable and undergoes a [1,5]-hydrogen migration at 50 °C in benzene solution to afford $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[\eta^2\text{-}C,N\text{-}\{CH_2SiMe_2NC(=CHPh)Ph\}]$ (**11**) in quantitative conversion (Scheme 4) with an activation barrier of $\Delta G^{\ddagger}(323\ K)_{10\rightarrow 11}$ = 24.2 kcal/mol, which was determined by a ^1H NMR kinetic study (see the Supporting Information for details). DFT investigations were performed to provide further insights in the underlying reaction mechanism. The two bulky 1,2,4-$(Me_3C)_3C_5H_2$ ligands prevent a direct approach of Me_3SiN_3 to the PhC=CPh moiety, initiating a [3 + 2] cycloaddition. Nevertheless, as in the case of *p*-ClPhCHO, Me_3SiN_3 initially coordinates to **2** and the intermediate **COM10** is formed. Similar to zirconium metallacyclopropenes,[21] Me_3SiN_3 inserts into the thorium metallycyclopropene moiety of **COM10** via the concerted [3 + 1] transition state **TS10a** to yield the four-membered heterocyclic complex **INT10a** (Figure 4). However, this intermediate converts in a [1,3]-carbon migration to the six-membered heterocyclic complex **INT10b**. The transformation from **COM10** to **INT10b** proceeds via intermediate **INT10a** and two transition states (**TS10a** and **TS10b**). Furthermore, the formation of **INT10b** is energetically favorable (ΔG(298 K) = −15.9 kcal/mol) and the reaction barrier is $\Delta G^{\ddagger}$(298 K) = 24.4 kcal/mol (relative to **2** + Me_3SiN_3). Moreover, N_2 loss from **INT10b** to form **10** + N_2 is exergonic by ΔG(298 K) = −65.5 kcal/mol (relative to the starting materials **2** + Me_3SiN_3) and the conversion from **INT10b** proceeds via transition state **TS10c** with a low barrier ($\Delta G^{\ddagger}$(298 K) = 6.7 kcal/mol) (Figure 4). These computational results are consistent with the experimental observations that **INT10a** and **INT10b** cannot be isolated from the reaction mixture and only **10** is observed by NMR spectroscopy. Moreover, **10** can further be converted to **11** via intermediate **INT11** and two transition states (**TS11a** and **TS11b**) (Figure 5). The barrier for the conversion of **10** to **11** is 31.8 kcal/mol (28.7 kcal/mol in the gas phase) at 323 K, which can be overcome at a reaction temperature of 50 °C, and is therefore in agreement with the experimentally detected barrier of 24.2 kcal/mol.

Nevertheless, unlike the thorium bipy complex $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(bipy)$[17a] and zirconium metallacyclopropenes,[21] complex **2** reacts with diazoalkanes such as 9-diazofluorene under similar reaction conditions to yield $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2][\eta^5,\sigma\text{-}1,2\text{-}(Me_3C)_2\text{-}4\text{-}(CH_2CMe_2)C_5H_2]Th[NC(C_{12}H_8)CH(Ph)C(Ph)=N\}]$ (**14**) (Scheme 5). As for Me_3SiN_3, one can propose the following reaction mechanism: complex **2** converts initially with 9-diazofluorene to the four-membered heterocyclic complex **12**, followed by a [1,3]-carbon migration and an intramolecular nucleophilic attack to give complex **13**, which can be detected spectroscopically (see the Experimental Section for details). However, **13** is unstable and slowly converts by an intramolecular C−H bond activation and a [1,3]-hydrogen migration to **14**.

Complexes **3**−**8**, **11**, and **14** are stable in dry nitrogen atmosphere, but they are moisture sensitive. They were characterized by various spectroscopic techniques and elemental analyses. In addition, the solid-state structures of complexes **3**−**7**, **11**, and **14** were determined by single crystal

Scheme 4



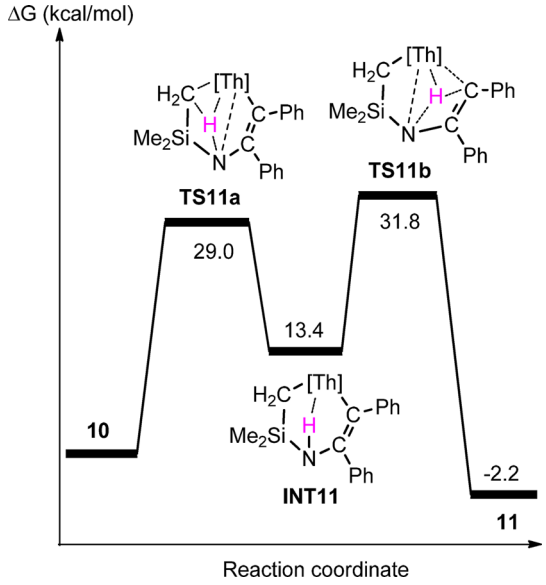


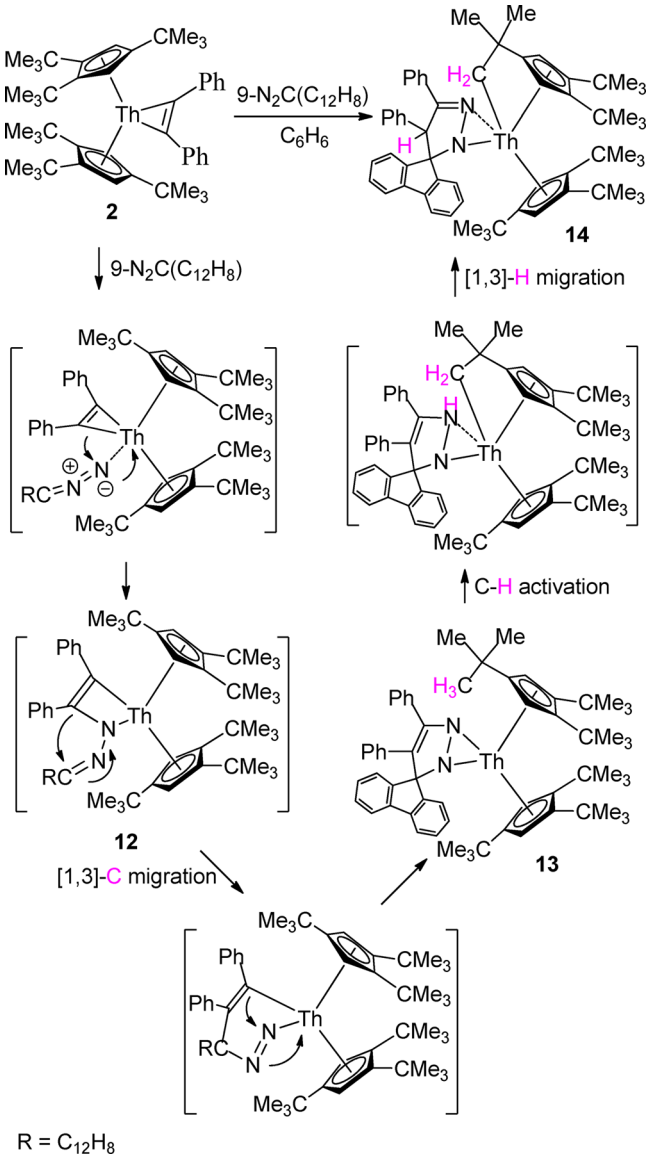
Figure 5. Free energy profile (kcal/mol) for the [1,5]-H migration of **10** (computed at T = 323 K). [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th.

X-ray diffraction analyses. The ORTEP of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[OCH(p-ClPh)(C_2Ph_2)] (**3**) is shown in Figure 6, and selected bond distances and angles are listed in Table 1. The cyclopentadienyl rings in **3** adopt a nearly staggered orientation, and the Th^{4+} ion is η^5-bound to two Cp-rings and σ-coordinated to one carbon atom and one oxygen atom of the [OCH(p-ClPh)(C_2Ph_2)] group in a distorted-tetrahedral geometry with an average Th−C(ring) distance of 2.882(2) Å. The Th−C(41) distance is 2.627(3) Å, which is longer than that found in **2** (2.395(2) Å). The Th−O distance is 2.123(2) Å, shorter than that found in [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[O_2CPh_2] (2.202(3) Å).[22]

The solid state molecular structures of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[SC(=S)(C_2Ph_2)] (**4**) and [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[SC(=NPh)(C_2Ph_2)] (**5**) are shown in Figures 7 and 8. In both complexes, the Cp-rings are nearly eclipsed. The average Th—C(Cp) distance is 2.870(5) Å for **4** and 2.856(4) Å for **5**, respectively, and the angle Cp(cent)—Th—Cp(cent) is 141.7(4)° for **4** and 140.3(2)° for **5**, respectively. The Th—C (C(37) for **4** and C(41) for **5**) distance is 2.549(5) Å for **4** and 2.522(4) Å for **5**, respectively, shorter than that found in **3** (2.627(3) Å). The Th—S distances of 2.766(1) and 2.741(1) Å for **4** and **5**, respectively, are comparable to those found in [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th-[N(p-tolyl)C(S)—S] (2.704(2) Å),[22] [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N(p-tolyl)C(NPh)—S] (2.709(1) Å),[22] [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N(p-tolyl)C($SSiMe_3$)—S] (2.890(3) Å),[22] [$(Ph_2PS)_2C]_2$Th(DME) (2.875(2), 2.909(2), 2.931(2), and 3.007(2) Å),[19d] [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th-[(bipy)($SCPh_2$)] (2.754(1) Å),[17c] and [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th[(bipy)($SCPh_2$)] (2.759(4) Å).[17c]

The molecular structure of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N-(C_6H_{11})C(=NC_6H_{11})(C_2Ph_2)] (**6**) is shown in Figure 9. The Th^{4+} ion is η^5-bound to two Cp-rings and σ-coordinated to one carbon atom and one nitrogen atom of the [N(C_6H_{11})C(=NC_6H_{11})(C_2Ph_2)] group in a distorted-tetrahedral geometry with an averaged Th—C(ring) distance of 2.907(9) Å. The Th—N distance (2.309(6) Å) is comparable to those found in [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N(p-tolyl)C(S)—S] (2.347(6) Å)[22] and [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N(p-tolyl)C(NPh)—S]

Scheme 5



(2.328(3) Å),[22] while the Th—C(41) distance (2.530(8) Å) is close to those observed in **4** and **5** (Table 1).

The cyclopentadienyl rings in [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th-[$(OCPh_2)_2$] (**7**) adopt a nearly staggered arrangement, whereby the Me_3C groups at the back of the wedge are minimizing the steric repulsion and the remaining four Me_3C groups are oriented to the left and right side of the open wedge (Figure 10). The Th^{4+} ion features a distorted-tetrahedral ligand environment with two η^5-bound Cp-rings and two σ-coordinate oxygen atoms of the pinacolate group [$(OCPh_2)_2$] with an average Th−C(ring) distance of 2.909(3) Å. The average Th−O distance is 2.182(2) Å, and therefore similar to those found in **3** (2.123(2) Å) and [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[O_2CPh_2] (2.202(3) Å).[22]

Figure 11 depicts the molecular structure of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[η^2-C,N-{CH_2SiMe_2NC(=CHPh)Ph}] (**11**), in which the Th^{4+} atom is η^5-bound to two Cp-rings and σ-coordinated to the one carbon atom and one nitrogen atom of the [η^2-C,N-{CH_2SiMe_2NC(=CHPh)Ph}] group in a distorted-tetrahedral geometry with an averaged Th—C(ring) distance of 2.896(3) Å. The Th—C(51) distance of 2.442(3) Å

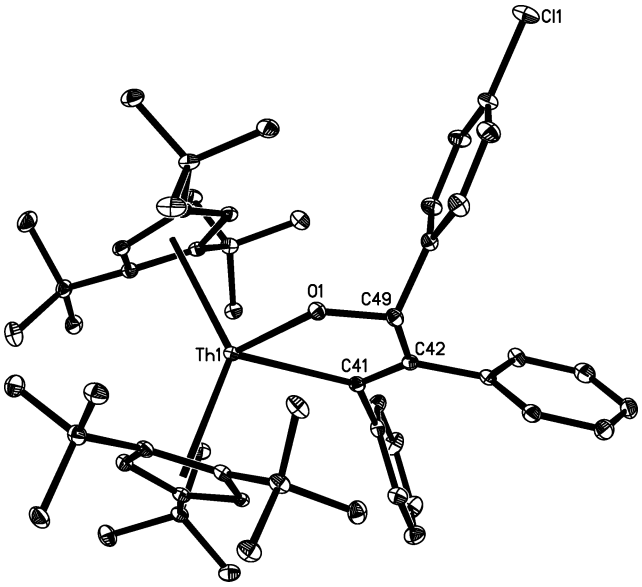


Figure 6. Molecular structure of **3** (thermal ellipsoids drawn at the 35% probability level).

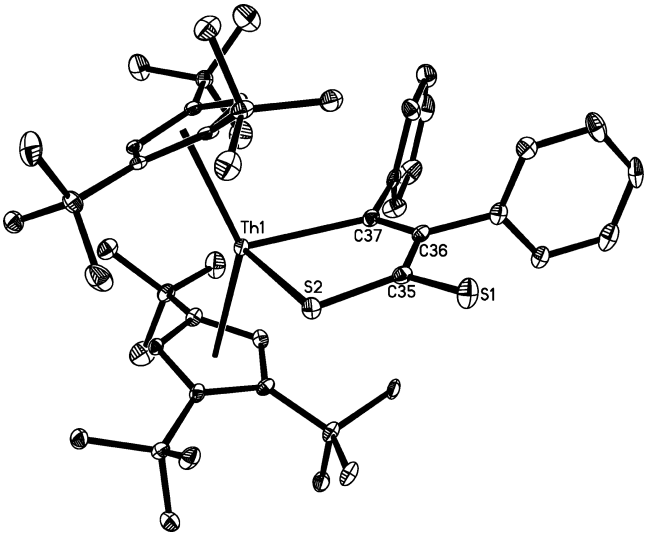


Figure 7. Molecular structure of **4** (thermal ellipsoids drawn at the 35% probability level).

is comparable to that found in $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2ThMe_2$ (2.480(3) Å).[23] The Th—N distance of 2.365(2) Å can be compared to those found in **6** (2.309(6) Å), $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[N(p\text{-tolyl})C(S)\text{—}S]$ (2.347(6) Å),[22] and $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[N(p\text{-tolyl})C(NPh)\text{—}S]$ (2.328(3) Å).[22] These structural parameters can be compared to those in $(\eta^5\text{-}C_9Me_7)_2Th(\eta^2\text{-}C,N\text{-}CH_2SiMe_2NSiMe_3)$.[24]

The molecular structure of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2][\eta^5,\sigma\text{-}1,2\text{-}(Me_3C)_2\text{-}4\text{-}(CH_2CMe_2)C_5H_2]Th[NC(C_{12}H_8)CH(Ph)C(Ph){=}N]$ (**14**) is shown in Figure 12. The Th—C(34) distance of 2.554(11) Å is longer than those found in $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2ThMe_2$ (2.480(3) Å)[23] and **11** (2.442(3) Å). However, the relatively long Th—N(2) distance of 2.567(10) Å is indicative of a datively coordinated nitrogen atom and is close to those found in $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2ThO(4\text{-}Me_2NC_5H_4N)$ (2.587(5) Å)[22] and $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[(bipy)(SCPh_2)]$ (2.564(1) Å),[17c] whereas the Th—N(1) distance of 2.367(10) Å is shorter than Th—N(2) (2.567(10) Å), and comparable to those found in **6** (2.309(6) Å), **11** (2.365(2) Å), $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[N(p\text{-tolyl})C(S)\text{—}S]$ (2.347(6) Å),[22] $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[N(p\text{-tolyl})C(NPh)\text{—}S]$ (2.328(3) Å),[22] and $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[N(p\text{-tolyl})N{=}NN(p\text{-tolyl})]$ (2.366(3) and 2.354(3) Å).[25]

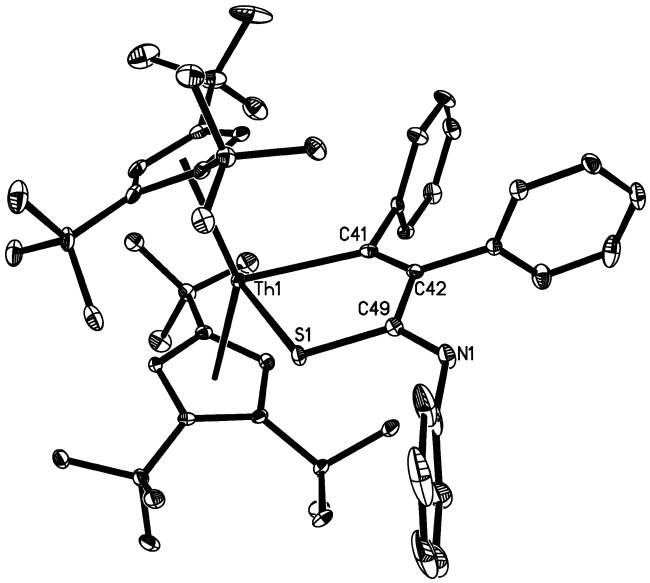


Figure 8. Molecular structure of **5** (thermal ellipsoids drawn at the 35% probability level).

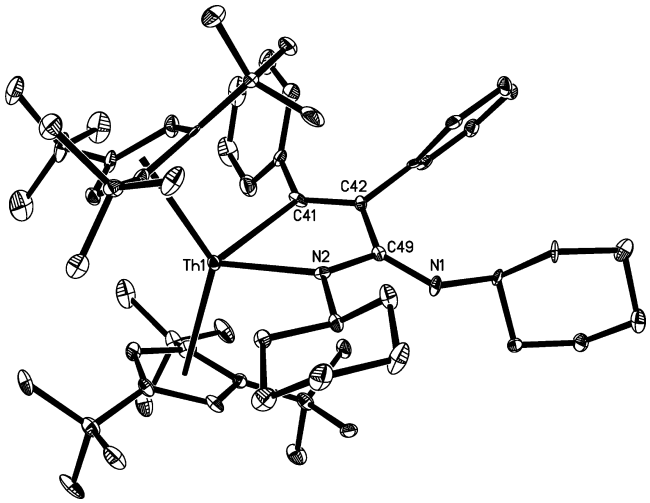


Figure 9. Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level).

■ CONCLUSIONS

In conclusion, the first stable actinide metallacyclopropene complex, $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph_2)$ (**2**), was comprehensively studied. Magnetic susceptibility studies reveal that the thorium metallacyclopropene is indeed a diamagnetic Th(IV) complex in contrast to $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(bipy)$,[17] which has been further exemplified by its reaction with CS_2, organic azides, and diazoalkane derivatives. In addition, density functional theory (DFT) shows that 5f orbitals contribute to the σ-bond of the Th—(η^2-C=C) moiety and that the bonds between the $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th^{2+}$ and the $[PhC{=}CPh]^{2-}$ fragments are

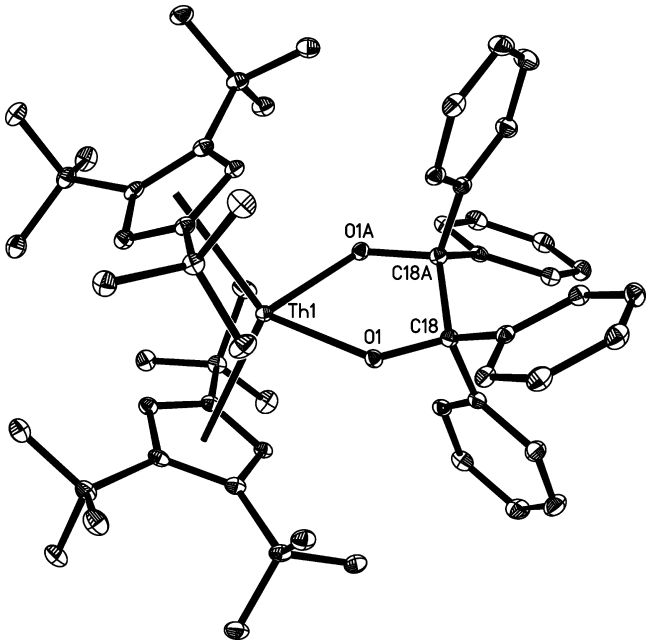


Figure 10. Molecular structure of **7** (thermal ellipsoids drawn at the 35% probability level).

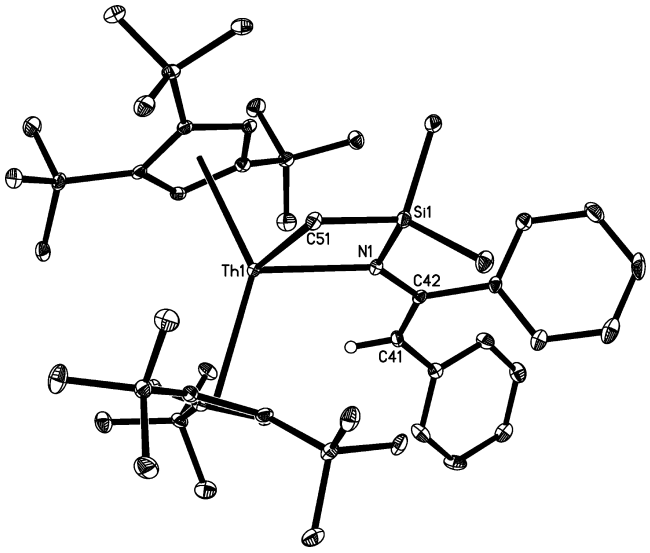


Figure 11. Molecular structure of **11** (thermal ellipsoids drawn at the 35% probability level).

very polarized. Thus, while the coordinated alkynes in the more covalent group 4 metallacyclopropenes are readily exchanged with alkynes and carbodiimides,[1,2] this is not the case in thorium complex **2**. Instead, the Th—(η^2-C═C) moiety in **2** reacts as a nucleophile. Benzaldehyde, CS_2, carbodiimide, organic nitriles, and isothiocyanate insert into the thorium metallcyclopropene. However, when the sterically encumbered Ph_2CO is used as a substrate, the PhCCPh is replaced, but the metallaoxirane intermediate [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(η^2-Ph_2CO) is too reactive to be even observed spectroscopically; however, it reacts with a second equivalent of Ph_2CO to the thorium pinacolate [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[$(OCPh_2)_2$] (**7**). Furthermore, when **2** is exposed to Me_3SiN_3, N_2 loss and formal nitrene insertion into the Th—C bond of the Th-(η^2-C═C) moiety are observed to yield [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N($SiMe_3$)C(Ph)═C(Ph)] (**10**), which converts on heating via [1,5]-H migration to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[η^2-*C,N*-{CH_2SiMe_2NC(═CHPh)Ph}] (**11**). In contrast, no N_2 loss was found, when **2** is treated with 9-diazofluorene, but after a rather complex reaction sequence, that included [1,3]-C migration, C—H bond activation of one Me group of the 1,2,4-$(Me_3C)_2C_5H_2$ ligand, and [1,3]-H migration, [η^5-1,2,4-$(Me_3C)_3C_5H_2$][η^5,σ-1,2-$(Me_3C)_2$-4-$(CH_2CMe_2)C_5H_2$]Th[NC($C_{12}H_8$)CH(Ph)C(Ph)═N}] (**14**) was isolated. Further investigations on the intrinsic reactivity of actinide metallacyclopropenes are ongoing and will be reported in due course.

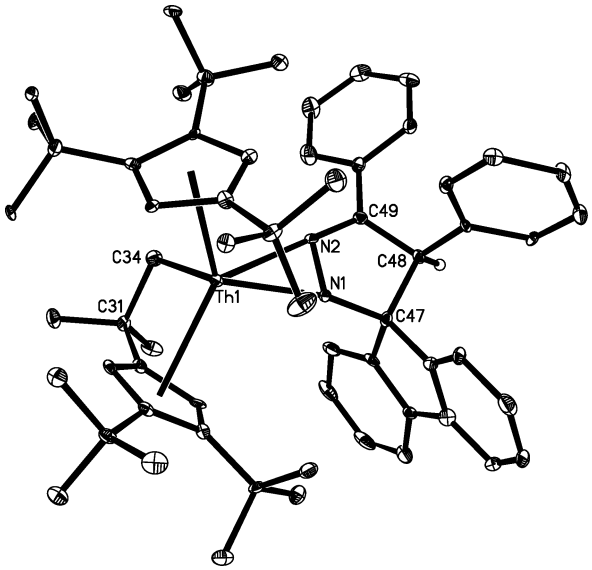


Figure 12. Molecular structure of **14** (thermal ellipsoids drawn at the 35% probability level).

■ EXPERIMENTAL SECTION

General Procedures. All reactions and product manipulations were carried out under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Diphenylacetylene was purified by sublimation prior to use. KC_8,[26] [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2ThCl_2$ (**1**),[22,23] and 9-diazofluorene[27] were prepared according to literature methods. All other chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. and used as received unless otherwise noted. Infrared spectra were recorded in KBr pellets on an Avatar 360 Fourier transform spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 and 100 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents, which served as internal standards, for proton and carbon chemical shifts. The magnetic susceptibility data were recorded on a Quantum Design MPMS XL5 SQUID magnetometer. The sample for magnetic susceptibility measurements (79 mg of **2**) was sealed in quartz tubes according to literature procedures.[28] Magnetic susceptibility data were corrected for diamagnetism using Pascal's constants[29] for all the constituent atoms. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(η^2-C_2Ph_2) (2). KC_8 (1.20 g, 8.80 mmol) was added to a toluene (20 mL) solution of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2ThCl_2$ (**1**; 2.00 g, 2.6 mmol) and diphenylacetylene (0.47 g, 2.6 mmol) with stirring at room temperature. After this solution was stirred 1 day at 40 °C, the solvent was removed. The

residue was extracted with benzene (10 mL × 3) and filtered. The volume of the filtrate was reduced to 10 mL; pale yellow crystals of **2** were isolated when this solution was kept at room temperature for 2 days. Yield: 1.94 g (85%). M.p.: 196−198 °C. ^{1}H NMR (C_6D_6): δ 7.29 (m, 8H, phenyl), 6.91 (t, J = 6.7 Hz, 2H, phenyl), 6.73 (br s, 4H, ring C*H*), 1.45 (s, 36H, C(C*H*$_3$)$_3$), 1.37 (s, 18H, C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 231.9 (ThC$_2$(Ph$_2$)), 154.7 (phenyl *C*), 140.6 (phenyl *C*), 138.2 (phenyl *C*), 128.5 (phenyl *C*), 126.0 (ring *C*), 123.5 (ring *C*), 115.3 (ring *C*), 34.5 (*C*(CH$_3$)$_3$), 34.4 (C(*C*H$_3$)$_3$), 32.8 (C(*C*H$_3$)$_3$), 27.9 (C(*C*H$_3$)$_3$) ppm. IR (KBr, cm^{-1}): 3065 (w), 2962 (s), 1587 (m), 1565 (m), 1481 (s), 1384 (s), 1260 (s), 1092 (s), 1020 (s), 810 (s). Anal. Calcd for $C_{48}H_{68}$Th: C, 65.73; H, 7.81. Found: C, 65.58; H, 7.73.

Preparation of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th[OCH(*p*-ClPh)-(C$_2$Ph$_2$)]·C$_6$H$_{12}$ (3·C$_6$H$_{12}$). Method A. A toluene solution (5 mL) of *p*-ClPhCHO (35 mg, 0.25 mmol) was added to a toluene (10 mL) solution of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(η^2-C$_2$Ph$_2$) (**2**; 220 mg, 0.25 mmol) with stirring at room temperature. During the course of the reaction, the color of the solution changed from pale yellow to colorless. After the solution was stirred at room temperature overnight, the solvent was removed. The residue was extracted with cyclohexane (10 mL × 3) and filtered. The volume of the filtrate was reduced to 5 mL; colorless crystals of **3**·C$_6$H$_{12}$ were isolated when this solution was kept at room temperature for 1 week. Yield: 237 mg (86%). M.p.: 160−162 °C. ^{1}H NMR (C_6D_6): δ 7.48 (d, J = 8.2 Hz, 2H, phenyl), 7.33 (d, J = 7.4 Hz, 2H, phenyl), 7.18 (m, 6H, phenyl), 6.89 (t, J = 7.6 Hz, 2H, phenyl), 6.83 (m, 2H, phenyl), 6.73 (d, J = 3.0 Hz, 1H, ring C*H*), 6.68 (m, 2H, C*H*O and ring C*H*), 6.45 (d, J = 3.1 Hz, 1H, ring C*H*), 6.36 (d, J = 3.1 Hz, 1H, ring C*H*), 1.81 (s, 9H, C(C*H*$_3$)$_3$), 1.67 (s, 9H, C(C*H*$_3$)$_3$), 1.59 (s, 9H, C(C*H*$_3$)$_3$), 1.40 (s, 21H, C(C*H*$_3$)$_3$ and C$_6$*H*$_{12}$), 1.05 (s, 9H, C(C*H*$_3$)$_3$), 0.99 (s, 9H, C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 212.5 (ThCPh), 162.5 (CPh), 154.3 (phenyl *C*), 145.3 (phenyl *C*), 143.9 (phenyl *C*), 143.8 (phenyl *C*), 142.8 (phenyl *C*), 142.2 (phenyl *C*), 142.0 (phenyl *C*), 141.8 (phenyl *C*), 140.6 (phenyl *C*), 133.4 (phenyl *C*), 131.4 (phenyl *C*), 129.4 (phenyl *C*), 128.5 (phenyl *C*), 128.1 (phenyl *C*), 127.8 (phenyl *C*), 127.6 (phenyl *C*), 125.8 (ring *C*), 122.7 (ring *C*), 119.6 (ring *C*), 117.8 (ring *C*), 116.5 (ring *C*), 115.2 (ring *C*), 91.9 (*C*HO), 35.3 (*C*(CH$_3$)$_3$), 35.2 (*C*(CH$_3$)$_3$), 35.1 (*C*(CH$_3$)$_3$), 35.0 (*C*(CH$_3$)$_3$), 34.7 (*C*(CH$_3$)$_3$), 34.4 (*C*(CH$_3$)$_3$), 34.3 (*C*(CH$_3$)$_3$), 33.8 (*C*(CH$_3$)$_3$), 33.6 (*C*(CH$_3$)$_3$), 32.2 (*C*(CH$_3$)$_3$), 31.9 (*C*(CH$_3$)$_3$), 30.0 (*C*(CH$_3$)$_3$), 27.2 (*C*$_6$H$_{12}$) ppm. IR (KBr, cm^{-1}): 3016 (w), 2962 (s), 1590 (m), 1457 (s), 1384 (s), 1363 (s), 1260 (s), 1089 (s), 1016 (s), 802 (s). Anal. Calcd for $C_{61}H_{85}$ClOTh: C, 66.49; H, 7.78. Found: C, 66.63; H, 7.62.

Method B. NMR Scale. A C$_6$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 [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(η^2-C$_2$Ph$_2$) (**2**; 18 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). The color of the solution immediately changed from pale yellow to colorless, and resonances corresponding to **3** were observed by ^{1}H NMR spectroscopy (100% conversion).

Preparation of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th[SC(=S)(C$_2$Ph$_2$)]·0.5C$_6$H$_6$ (4·0.5C$_6$H$_6$). Method A. This compound was prepared as green crystals from the reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(η^2-C$_2$Ph$_2$) (**2**; 220 mg, 0.25 mmol) and CS$_2$ (19 mg, 0.25 mmol) in toluene (15 mL) and recrystallization from a benzene solution by a similar procedure as in the synthesis of **3**. Yield: 223 mg (90%). M.p.: 204−206 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.17 (m, 5H, phenyl and C$_6$*H*$_6$), 7.08 (t, J = 7.6 Hz, 2H, phenyl), 7.00 (m, 4H, phenyl), 6.92 (t, J = 7.5 Hz, 1H, phenyl), 6.76 (m, 1H, phenyl), 6.60 (d, J = 3.3 Hz, 2H, ring C*H*), 6.44 (d, J = 3.4 Hz, 2H, ring C*H*), 1.70 (s, 18H, C(C*H*$_3$)$_3$), 1.43 (s, 18H, C(C*H*$_3$)$_3$), 0.99 (s, 18H, C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 240.6 (*C*S), 239.8 (ThCPh), 170.4 (*C*Ph), 150.7 (phenyl *C*), 146.8 (phenyl *C*), 145.7 (phenyl *C*), 144.4 (phenyl *C*), 130.6 (phenyl *C*), 129.3 (phenyl *C*), 128.5 (phenyl *C*), 128.0 (*C*$_6$H$_6$), 126.9 (phenyl *C*), 125.9 (ring *C*), 125.8 (ring *C*), 124.9 (ring *C*), 121.4 (ring *C*), 116.2 (ring *C*), 36.7 (*C*(CH$_3$)$_3$), 34.8 (*C*(CH$_3$)$_3$), 34.1 (*C*(CH$_3$)$_3$), 34.0 (*C*(CH$_3$)$_3$), 33.8 (*C*(CH$_3$)$_3$), 32.2 (*C*(CH$_3$)$_3$) ppm. IR (KBr, cm^{-1}): 3056 (w), 2961 (s), 1592 (w), 1665 (s), 1383 (s), 1260 (s), 1104 (s), 1019 (s), 800 (s). Anal. Calcd for $C_{52}H_{71}S_2$Th: C, 62.94; H, 7.21. Found: C, 62.76; H, 7.09.

Method B. NMR Scale. A C$_6$D$_6$ (0.3 mL) solution of CS$_2$ (1.5 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(η^2-C$_2$Ph$_2$) (**2**; 18 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). The color of the solution immediately changed from pale yellow to green, and the NMR resonances of **4** were observed by ^{1}H NMR spectroscopy (100% conversion).

Preparation of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th[SC(=NPh)(C$_2$Ph$_2$)] (5). Method A. This compound was prepared as yellow crystals from the reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(η^2-C$_2$Ph$_2$) (**2**; 220 mg, 0.25 mmol) and PhNCS (34 mg, 0.25 mmol) in toluene (15 mL) and recrystallization from a THF solution by a similar procedure as in the synthesis of **3**. Yield: 213 mg (84%). M.p.: 126−128 °C. ^{1}H NMR (C_6D_6): δ 7.34 (d, J = 7.2 Hz, 2H, phenyl), 7.27 (t, J = 7.6 Hz, 2H, phenyl), 7.10 (t, J = 7.6 Hz, 2H, phenyl), 7.04 (m, 6H, phenyl), 6.89 (m, 2H, phenyl), 6.79 (m, 1H, phenyl), 6.67 (d, J = 3.3 Hz, 2H, ring C*H*), 6.37 (d, J = 3.3 Hz, 2H, ring C*H*), 1.79 (s, 18H, C(C*H*$_3$)$_3$), 1.33 (s, 18H, C(C*H*$_3$)$_3$), 1.00 (s, 18H, C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 233.7 (ThCPh), 168.1 (*C*=N), 164.6 (*C*Ph), 153.0 (phenyl *C*), 149.9 (phenyl *C*), 146.6 (phenyl *C*), 146.2 (phenyl *C*), 144.2 (phenyl *C*), 143.1 (phenyl *C*), 130.8 (phenyl *C*), 129.0 (phenyl *C*), 128.5 (phenyl *C*), 127.2 (phenyl *C*), 127.0 (phenyl *C*), 125.7 (phenyl *C*), 124.4 (ring *C*), 122.7 (ring *C*), 120.8 (ring *C*), 120.3 (ring *C*), 116.2 (ring *C*), 36.6 (*C*(CH$_3$)$_3$), 34.7 (*C*(CH$_3$)$_3$), 34.2 (*C*(CH$_3$)$_3$), 34.0 (*C*(CH$_3$)$_3$), 33.9 (*C*(CH$_3$)$_3$), 32.3 (*C*(CH$_3$)$_3$) ppm. IR (KBr, cm^{-1}): 3053 (m), 2962 (s), 1611 (m), 1590 (s), 1443 (s), 1387 (s), 1258 (s), 1212 (s), 1096 (s), 1025 (s), 798 (s). Anal. Calcd for $C_{55}H_{73}$NSTh: C, 65.26; H, 7.27, N, 1.38. Found: C, 65.45; H, 7.33, N, 1.35.

Method B. NMR Scale. A C$_6$D$_6$ (0.3 mL) solution of PhNCS (2.7 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(η^2-C$_2$Ph$_2$) (**2**; 18 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). The NMR resonances of **5** were observed by ^{1}H NMR spectroscopy (100% conversion).

Preparation of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th[N(C$_6$H$_{11}$)C(=NC$_6$H$_{11}$)(C$_2$Ph$_2$)] (6). Method A. This compound was prepared as yellow crystals from the reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(η^2-C$_2$Ph$_2$) (**2**; 220 mg, 0.25 mmol) and DCC (52 mg, 0.25 mmol) in toluene (15 mL) and recrystallization from a benzene solution by a similar procedure as in the synthesis of **3**. Yield: 217 mg (80%). M.p.: 174−176 °C. ^{1}H NMR (C_6D_6): δ 7.33 (d, J = 7.6 Hz, 2H, phenyl), 7.18 (m, 2H, phenyl), 7.09−6.97 (m, 5H, phenyl), 6.85 (t, J = 7.3 Hz, 1H, phenyl), 6.66 (br s, 2H, ring C*H*), 6.50 (d, J = 2.8 Hz, 2H, ring C*H*), 3.93 (t, J = 10.6 Hz, 1H, NC*H*), 2.82 (br s, 3H, NC*H* and C*H*$_2$), 2.02 (br s, 2H, C*H*$_2$), 1.90 (d, J = 12.4 Hz, 2H, C*H*$_2$), 1.78 (d, J = 11.7 Hz, 2H, C*H*$_2$), 1.66 (d, J = 10.0 Hz, 4H, C*H*$_2$), 1.56 (s, 18H, C(C*H*$_3$)$_3$), 1.48 (s, 18H, C(C*H*$_3$)$_3$), 1.24 (s, 18H, C(C*H*$_3$)$_3$), 0.94 (m, 2H, C*H*$_2$); 6 cyclohexyl *H* (C*H*$_2$) overlapped with C(C*H*$_3$)$_3$ groups at 1.43−1.24 ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 221.0 (ThCPh), 158.3 (*C*Ph), 151.5 (*C*=N), 148.7 (phenyl *C*), 146.6 (phenyl *C*), 146.4 (phenyl *C*), 144.5 (phenyl *C*), 129.8 (phenyl *C*), 129.3 (phenyl *C*), 128.5 (phenyl *C*), 127.4 (phenyl *C*), 127.3 (ring *C*), 125.6 (ring *C*), 123.4 (ring *C*), 118.4 (ring *C*), 116.5 (ring *C*), 55.8 (*C*=NCH), 55.7 (*C*NCH), 36.8 (*C*(CH$_3$)$_3$), 35.7 (*C*(CH$_3$)$_3$), 35.5 (*C*(CH$_3$)$_3$), 35.2 (*C*(CH$_3$)$_3$), 34.9 (*C*(CH$_3$)$_3$), 34.8 (*C*(CH$_3$)$_3$), 32.8 (*C*H$_2$), 27.2 (*C*H$_2$), 26.6 (*C*H$_2$), 25.9 (*C*H$_2$), 25.4 (*C*H$_2$), 25.3 (*C*H$_2$) ppm. IR (KBr, cm^{-1}): 2959 (s), 1631 (m), 1570 (s), 1477 (s), 1359 (s), 1237 (s), 1194 (s), 1102 (s), 809 (s). Anal. Calcd for $C_{61}H_{90}N_2$Th: C, 67.62; H, 8.37, N, 2.59. Found: C, 67.67; H, 8.38, N, 2.63.

Method B. NMR Scale. A C$_6$D$_6$ (0.3 mL) solution of DCC (4.1 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(η^2-C$_2$Ph$_2$) (**2**; 18 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). The NMR resonances of **6** were observed by ^{1}H NMR spectroscopy (100% conversion).

Preparation of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th[(OCPh$_2$)$_2$] (7). Method A. This compound was prepared as colorless microcrystals from the reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(η^2-C$_2$Ph$_2$) (**2**; 220 mg, 0.25 mmol) and Ph$_2$CO (91 mg, 0.50 mmol) in toluene (15 mL) and recrystallization from a benzene solution by a similar procedure as in the synthesis of **3**. Yield: 199 mg (75%). M.p.: 221−223 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.13 (d, J = 7.4 Hz, 2H, phenyl), 7.76 (m, 2H,

phenyl), 7.62 (d, J = 3.2 Hz, 1H, ring CH), 7.52 (d, J = 7.4 Hz, 2H, phenyl), 7.43 (m, 2H, phenyl), 7.31 (t, J = 7.7 Hz, 2H, phenyl), 7.04 (m, 2H, phenyl), 6.94 (d, J = 7.4 Hz, 2H, phenyl), 6.87 (m, 4H, phenyl), 6.80 (m, 2H, phenyl), 6.73 (d, J = 3.2 Hz, 2H, ring CH), 6.27 (d, J = 3.2 Hz, 1H, ring CH), 1.62 (s, 9H, C(CH_3)$_3$), 1.52 (s, 9H, C(CH_3)$_3$), 1.36 (s, 9H, C(CH_3)$_3$), 1.25 (s, 9H, C(CH_3)$_3$), 1.20 (s, 9H, C(CH_3)$_3$), 1.17 (s, 9H, C(CH_3)$_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 151.3 (phenyl C), 149.0 (phenyl C), 148.0 (phenyl C), 146.3 (phenyl C), 145.8 (phenyl C), 145.6 (phenyl C), 144.9 (phenyl C), 144.3 (phenyl C), 142.8 (phenyl C), 141.9 (phenyl C), 131.5 (phenyl C), 131.2 (phenyl C), 130.8 (phenyl C), 130.3 (phenyl C), 130.0 (phenyl C), 129.3 (phenyl C), 127.5 (ring C), 127.4 (ring C), 127.3 (ring C), 127.0 (ring C), 125.8 (ring C), 122.7 (ring C), 121.3 (ring C), 119.6 (ring C), 118.0 (ring C), 115.2 (ring C), 99.7 (C-O), 36.4 (C(CH_3)$_3$), 35.3 (C(CH_3)$_3$), 35.1 (C(CH_3)$_3$), 35.0 (C(CH_3)$_3$), 34.8 (C(CH_3)$_3$), 34.4 (C(CH_3)$_3$), 34.3 (C(CH_3)$_3$), 34.2 (C(CH_3)$_3$), 33.6 (C(CH_3)$_3$), 33.3 (C(CH_3)$_3$), 33.2 (C(CH_3)$_3$), 32.4 (C(CH_3)$_3$) ppm. IR (KBr, cm^{-1}): 3054(m), 2957 (s), 1598 (s), 1478 (s), 1360 (s), 1238 (s), 1056 (s), 984 (s), 790 (s). Anal. Calcd for $C_{60}H_{78}O_2Th$: C, 67.77; H, 7.39. Found: C, 67.88; H, 7.27. Colorless crystals of **7**·4C_6H_{12} suitable for X-ray structural analysis were grown from a cyclohexane solution.

Method B. NMR Scale. A C_6D_6 (0.3 mL) solution of Ph_2CO (7.3 mg; 0.04 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(η^2-C_2Ph_2) (**2**; 18 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The color of the solution immediately changed from pale yellow to colorless, and NMR resonances attributed to **7** along with those of PhC≡CPh were observed in the ^{1}H NMR spectrum (100% conversion).

Reaction of [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(η^2-C_2Ph_2) (2) with Ph_2CO. NMR Scale. To a J. Young NMR tube charged with [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(η^2-C_2Ph_2) (**2**; 18 mg, 0.02 mmol) and C_6D_6 (0.5 mL), Ph_2CO (3.7 mg; 0.02 mmol) was added. Resonances due to **7** along with those of PhC≡CPh and unreacted **2** were observed by ^{1}H NMR spectroscopy (50% conversion based on **2**).

Preparation of [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th[N═C(Ph)(C_2Ph_2)] (8). Method A. This compound was prepared as brown-red microcrystals from the reaction of [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(η^2-C_2Ph_2) (**2**; 220 mg, 0.25 mmol) and 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 **3**. Yield: 211 mg (86%). M.p.: 186−188 °C. ^{1}H NMR (C_6D_6): δ 7.47 (d, J = 7.4 Hz, 2H, phenyl), 7.16 (m, 4H, phenyl), 7.09 (d, J = 7.4 Hz, 2H, phenyl), 7.00 (t, J = 7.4 Hz, 2H, phenyl), 6.93 (m, 3H, phenyl), 6.82 (m, 2H, phenyl), 6.47 (d, J = 2.8 Hz, 2H, ring CH), 6.45 (d, J = 2.8 Hz, 2H, ring CH), 1.69 (s, 18H, C(CH_3)$_3$), 1.53 (s, 18H, C(CH_3)$_3$), 1.15 (s, 18H, C(CH_3)$_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 230.4 (ThCPh), 178.9 (CPh), 161.5 (C═N), 152.0 (phenyl C), 144.1 (phenyl C), 142.7 (phenyl C), 142.3 (phenyl C), 141.9 (phenyl C), 140.8 (phenyl C), 130.8 (phenyl C), 130.4 (phenyl C), 128.8 (phenyl C), 128.5 (phenyl C), 127.5 (phenyl C), 127.2 (phenyl C), 127.0 (ring C), 125.6 (ring C), 123.0 (ring C), 116.9 (ring C), 114.6 (ring C), 35.2 (C(CH_3)$_3$), 34.6 (C(CH_3)$_3$), 34.4 (C(CH_3)$_3$), 33.3 (C(CH_3)$_3$), 31.7 (C(CH_3)$_3$) ppm; one C resonance of the Me_3C groups overlapped. IR (KBr, cm^{-1}): 3053 (m), 2958 (s), 1588 (s), 1541 (s), 1461 (s), 1359 (s), 1238 (s), 1020 (s), 810 (s). Anal. Calcd for $C_{55}H_{73}NTh$: C, 67.39; H, 7.51; N, 1.43. Found: C, 67.52; H, 7.46; N, 1.41.

Method B. NMR Scale. A C_6D_6 (0.3 mL) solution of PhCN (2.1 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(η^2-C_2Ph_2) (**2**; 18 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The color of the solution changed immediately from pale yellow to brown-red, and the NMR resonances of **8** were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(η^2-C_2Ph_2) (2) with ^{t}BuCN or RC≡CR (R = Me, Ph, *p*-tolyl). NMR Scale. An excess amount of ^{t}BuCN or RC≡CR (R = Me, Ph, *p*-tolyl) was added to a J. Young NMR tube charged with [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(η^2-C_2Ph_2) (**2**; 18 mg, 0.02 mmol) and C_6D_6 (0.5 mL). In each case, the sample was monitored periodically by ^{1}H NMR spectroscopy. No changes in the ^{1}H NMR spectrum were observed when heated at 100 °C for 1 week.

Preparation of [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th[N($SiMe_3$)C(Ph)═C(Ph)] (10). Method A. A benzene (10 mL) solution of Me_3SiN_3 (29 mg, 0.25 mmol) was added dropwise to a benzene (10 mL) solution of [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(η^2-C_2Ph_2) (**2**; 220 mg, 0.25 mmol) at room temperature. After this solution was stirred at room temperature for 1 h, the solvent was evaporated. The residue was dried in a vacuum at room temperature overnight to give **10** as an orange oil in quantitative yield. ^{1}H NMR (C_6D_6): δ 7.69 (d, J = 7.7 Hz, 1H, phenyl), 7.52 (d, J = 7.6 Hz, 1H, phenyl), 7.42 (d, J = 7.5 Hz, 1H, phenyl), 7.29 (m, 1H, phenyl), 7.18 (m, 3H, phenyl), 6.95 (m, 3H, phenyl), 6.64 (s, 1H, ring CH), 6.52 (s, 1H, ring CH), 6.42 (s, 1H, ring CH), 6.35 (s, 1H, ring CH), 1.50 (s, 18H, C(CH_3)$_3$), 1.43 (s, 9H, C(CH_3)$_3$), 1.39 (s, 9H, C(CH_3)$_3$), 1.38 (s, 9H, C(CH_3)$_3$), 1.26 (s, 9H, C(CH_3)$_3$), 0.54 (s, 3H, SiCH_3), 0.38 (s, 6H, SiCH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 191.9 (ThCPh), 160.7 (NCPh), 145.8 (phenyl C), 144.4 (phenyl C), 143.9 (phenyl C), 131.8 (phenyl C), 130.7 (phenyl C), 130.6 (phenyl C), 129.5 (phenyl C), 127.2 (phenyl C), 126.9 (ring C), 123.1 (ring C), 118.1 (ring C), 116.3 (ring C), 115.0 (ring C), 35.0 (C(CH_3)$_3$), 34.6 (C(CH_3)$_3$), 34.5 (C(CH_3)$_3$), 34.2 (C(CH_3)$_3$), 32.6 (C(CH_3)$_3$), 32.1 (C(CH_3)$_3$), 0.4 (SiCH_3), 0.0 (SiCH_3), −1.3 (SiCH_3) ppm. IR (KBr, cm^{-1}): 2962 (s), 1600 (w), 1443 (m), 1384 (s), 1260 (s), 1090 (s), 1019 (s), 799 (s). Anal. Calcd for $C_{51}H_{77}NSiTh$: C, 63.52; H, 8.05; N, 1.45. Found: C, 63.53; H, 8.12; N, 1.40. The NMR sample was kept at 50 °C and monitored periodically by ^{1}H NMR spectroscopy. After 1 h, new resonances of [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th[η^2-C,N-{CH_2SiMe_2NC(═CHPh)Ph] (**11**) (see below) were observed by ^{1}H NMR spectroscopy with 40% conversion. Complete conversion to **11** was achieved after 4 h.

Method B. NMR Scale. A C_6D_6 (0.3 mL) solution of Me_3SiN_3 (2.3 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(η^2-C_2Ph_2) (**2**; 18 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The color of the solution changed immediately from pale yellow to red and then to orange, and resonances due to **10** were observed by ^{1}H NMR spectroscopy (100% conversion).

Preparation of [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th[η^2-C,N-{CH_2SiMe_2NC(═CHPh)Ph}] (11). After a benzene solution (20 mL) of [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th[N($SiMe_3$)C(Ph)═C(Ph)] (**10**; 241 mg, 0.25 mmol) was stirred at 50 °C for 2 days, the solution was filtered and the volume of the filtrate was reduced to ca. 2 mL. Pale yellow crystals of **11** were isolated when this solution stood at room temperature for 2 weeks. Yield: 183 mg (76%). M.p.: 216−218 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.42 (d, J = 6.9 Hz, 2H, phenyl), 7.12 (m, 2H, phenyl), 7.08 (m, 5H, phenyl), 6.84 (m, 1H, phenyl), 6.51 (br s, 2H, ring CH), 6.44 (s, 2H, ring CH), 6.22 (s, 1H, C═CH), 2.09 (s, 2H, ThCH_2), 1.63 (s, 18H, C(CH_3)$_3$), 1.53 (s, 18H, C(CH_3)$_3$), 1.37 (s, 18H, C(CH_3)$_3$), 0.39 (br s, 6H, Si(CH_3)$_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 155.0 (NC═C), 145.1 (phenyl C), 144.7 (phenyl C), 143.8 (phenyl C), 143.2 (phenyl C), 139.7 (phenyl C), 130.6 (phenyl C), 128.5 (phenyl C), 128.1 (phenyl C), 124.1 (ring C), 117.0 (ring C), 116.8 (ring C), 114.0 (PhCH═C), 60.7 (ThCH_2), 35.3 (C(CH_3)$_3$), 35.0 (C(CH_3)$_3$), 34.6 (C(CH_3)$_3$), 34.5 (C(CH_3)$_3$), 34.2 (C(CH_3)$_3$), 32.8 (C(CH_3)$_3$), 5.6 (Si(CH_3)$_2$) ppm. IR (KBr, cm^{-1}): 3018 (w), 2959 (s), 1596 (m), 1458 (m), 1384 (s), 1258 (s), 1104 (s), 1023 (s), 799 (s). Anal. Calcd for $C_{51}H_{77}NSiTh$: C, 63.52; H, 8.05; N, 1.45. Found: C, 63.43; H, 8.16; N, 1.43.

Reaction of [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th═$NSiMe_3$ with PhC≡CPh. NMR Scale. PhC≡CPh (3.6 mg, 0.02 mmol) was added to a J. Young NMR tube charged with [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th═$NSiMe_3$[17a] (16 mg, 0.02 mmol) and C_6D_6 (0.5 mL). The sample was monitored periodically by ^{1}H NMR spectroscopy, but no change in the ^{1}H NMR spectrum was detected when the sample was heated at 100 °C for 1 week.

Preparation of [η^5-1,2,4-(Me_3C)$_3C_5H_2$][η^5,σ-1,2-(Me_3C)$_2$-4-(CH_2CMe_2)C_5H_2]Th[NC($C_{12}H_8$)CH(Ph)C(Ph)═N] (14). Method A. This compound was prepared as yellow crystals from the reaction of [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(η^2-C_2Ph_2) (**2**; 220 mg, 0.25 mmol) and 9-diazofluorene (48 mg, 0.25 mmol) in toluene (15 mL) and recrystallization from a benzene solution by a similar procedure as in the synthesis of **3**. Yield: 192 mg (72%). M.p.: 258−260 °C (dec.). ^{1}H

NMR (C_6D_6): δ 7.84 (d, J = 7.2 Hz, 1H, phenyl), 7.68 (d, J = 7.4 Hz, 2H, phenyl), 7.45 (d, J = 7.3 Hz, 1H, phenyl), 7.36 (d, J = 7.6 Hz, 1H, phenyl), 7.11 (m, 4H, phenyl), 7.00 (m, 2H, phenyl), 6.90 (m, 6H, phenyl), 6.80 (m, 1H, phenyl), 6.11 (s, 2H, ring C*H*), 6.04 (d, J = 2.6 Hz, 1H, ring C*H*), 5.82 (s, 1H, ring C*H*), 5.26 (s, 1H, C*H*), 1.67 (s, 3H, CH_3), 1.59 (s, 18H, $C(CH_3)_3$), 1.51 (s, 3H, CH_3), 1.37 (s, 18H, $C(CH_3)_3$), 1.27 (s, 9H, $C(CH_3)_3$), 0.59 (d, 1H, J = 12.6 Hz, $ThCH_2$), 0.25 (d, 1H, J = 12.6 Hz, $ThCH_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.6 (C═N), 144.7 (aryl *C*), 142.3 (aryl *C*), 142,2 (aryl *C*), 141.2 (aryl *C*), 141.1 (aryl *C*), 141.0 (aryl *C*), 140.9 (aryl *C*), 140.8 (aryl *C*), 140.1 (aryl *C*), 138.1 (aryl *C*), 133.7 (aryl *C*), 129.3 (aryl *C*), 128.9 (aryl *C*), 128.5 (aryl *C*), 128.4 (aryl *C*), 128.2 (aryl *C*), 127.8 (aryl *C*), 127.4 (aryl *C*), 127.3 (aryl *C*), 127.2 (ring *C*), 126.8 (ring *C*), 126.7 (ring *C*), 124.2 (ring *C*), 120.2 (ring *C*), 119.6 (ring *C*), 116.0 (ring *C*), 114.9 (ring *C*), 112.9 (ring *C*), 112.7 (ring *C*), 85.1 ($NC(C_{12}H_8)$), 69.6 (PhCH), 58.0 ($ThCH_2$), 35.1 ($C(CH_3)_3$), 35.0 ($C(CH_3)_3$), 34.9 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 33.5 ($C(CH_3)_3$), 33.1 ($C(CH_3)_3$), 32.7 ($C(CH_3)_3$), 32.5 ($C(CH_3)_3$) ppm; one aryl *C* resonance and three *C* resonances of the Me_3C groups overlapped. IR (KBr, cm^{-1}): 3026 (w), 2956 (s), 1600 (m), 1449 (s), 1359 (s), 1237 (s), 1042 (s), 810 (s). Anal. Calcd for $C_{61}H_{76}N_2Th$: C, 68.52; H, 7.16; N, 2.62. Found: C, 68.63; H, 7.08; N, 2.70.

Method B. NMR Scale. A C_6D_6 (0.3 mL) solution of 9-diazofluorene (3.8 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph_2)$ (**2**; 18 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The color of the solution immediately changed from pale yellow to red and then to yellow, and NMR resonances of **14** (ca. 15%) along with those of **13** (^1H NMR (C_6D_6): δ 7.80 (m, 4H, aryl), 7.51 (m, 2H, aryl), 7.28 (m, 8H, aryl), 7.24 (m, 4H, aryl), 6.62 (d, J = 3.4 Hz, 2H, ring C*H*), 6.41 (d, J = 3.4 Hz, 2H, ring C*H*), 1.59 (s, 9H, $C(CH_3)_3$), 1.48 (s, 9H, $C(CH_3)_3$), 1.45 (s, 9H, $C(CH_3)_3$), 1.59 (s, 18H, $C(CH_3)_3$), 1.39 (s, 9H, $C(CH_3)_3$) ppm) were observed by ^1H NMR spectroscopy (100% conversion). The NMR sample was kept at room temperature and monitored periodically by ^1H NMR spectroscopy. After 1 day, the conversion to **14** was 25% complete, and after 3 weeks, complete conversion of **13** to **14** was achieved. Nevertheless, complex **13** could not be isolated in pure form on a synthetic scale, since always partial degradation to **14** was observed.

X-ray Crystallography. Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart APEX II CCD diffractometer at 113(2) K using graphite monochromated M*o* Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.[30] All structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL-97 program package.[31] All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **2**−**7**, **11**, and **14** are summarized in the Supporting Information. Selected bond lengths and angles are listed in Table 1.

Computational Methods. All calculations were carried out with the Gaussian 09 program (G09),[32] employing the B3PW91 functional, plus a polarizable continuum model (PCM) and D3[33] (denoted as B3PW91-PCM+D3), with the standard 6-31G(d) basis set for C, H, N, O, Cl, and Si elements and Stuttgart RLC ECP from the EMSL basis set exchange (https://bse.pnl.gov/bse/portal) for Th,[34] to fully optimize the structures of reactants, complexes, transition state, intermediates, and products, and also to mimic the experimental toluene-solvent conditions (dielectric constant ε = 2.379). All stationary points were subsequently characterized by vibrational analyses, from which their respective zero-point (vibrational) energy (ZPE) were extracted and used in the relative energy determinations; in addition, frequency calculations were also performed to ensure that the reactant, complex, intermediate, product, and transition state structures resided at minima and first order saddle points, respectively, on their potential energy hyper surfaces.

■ ASSOCIATED CONTENT

Supporting Information

Complete list of authors for ref 32. Crystal parameters for compounds **2**−**7**, **11**, and **14**. Cartesian coordinates of all stationary points optimized at the B3PW91-PCM+D3 level and kinetic and magnetic susceptibility studies. X-ray crystallographic data, in CIF format, for compounds **2**−**7**, **11**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

gzi@bnu.edu.cn
dcfang@bnu.edu.cn
laurent.maron@irsamc.ups-tlse.fr
mwalter@tu-bs.de

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21472013, 21172022, 21272026, 21302155, 21373030) and the Deutsche Forschungsgemeinschaft (DFG) through the Emmy-Noether program (WA 2513/2). L.M. is a member of the Institut Universitaire de France. The Humboldt Foundation is also acknowledged for an experienced researcher grant (L.M.). We thank Dr. Xuebin Deng for his help with the crystallography and Professor Richard A. Andersen for helpful discussions.

■ REFERENCES

(1) For selected reviews, see: (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047−1058. (b) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2003**, *22*, 884−900. (c) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Shur, V. B. *Eur. J. Inorg. Chem.* **2004**, 4739−4749. (d) Rosenthal, U. *Angew. Chem., Int. Ed.* **2004**, *43*, 3882−3887. (e) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2005**, *24*, 456−471. (f) Rosenthal, U.; Burlakov, V. V.; Bach, M. A.; Beweries, T. *Chem. Soc. Rev.* **2007**, *36*, 719−728.

(2) For selected recent papers on group 4 metallacyclopropenes, see: (a) Beweries, T.; Fischer, C.; Peitz, S.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Heller, D.; Rosenthal, U. *J. Am. Chem. Soc.* **2009**, *131*, 4463−4469. (b) Kaleta, K.; Ruhmann, M.; Theilmann, O.; Beweries, T.; Roy, S.; Arndt, P.; Villinger, A.; Jemmis, E. D.; Schulz, A.; Rosenthal, U. *J. Am. Chem. Soc.* **2011**, *133*, 5463−5473. (c) Haehnel, M.; Ruhmann, M.; Theilmann, O.; Roy, S.; Torsten Beweries, T.; Arndt, P.; Spannenberg, A.; Villinger, A.; Jemmis, E. D.; Schulz, A.; Rosenthal, U. *J. Am. Chem. Soc.* **2012**, *134*, 15979−15991. (d) You, X.; Yu, S.; Liu, Y. *Organometallics* **2013**, *19*, 5273−5276. (e) Haehnel, M.; Hansen, S.; Schubert, K.; Arndt, P.; Spannenberg, A.; Jiao, H.; Rosenthal, U. *J. Am. Chem. Soc.* **2013**, *135*, 17556−17565. (f) Podiyanachari, S. K.; Kehr, G.; Mück-Lichtenfeld, C.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2013**, *135*, 17444−17456. (g) Becker, L.; Arndt, P.; Jiao, H.; Spannenberg, A.; Rosenthal, U. *Angew. Chem., Int. Ed.* **2013**, *52*, 11396−11400. (h) Àrias, Ò.; Petrov, A. R.; Banenberg, T.; Altenburger, K.; Arndt, P.; Jones, P. G.; Rosenthal, U.; Tamm, M. *Organometallics* **2014**, *33*, 1774−1786. (i) Mindiola, D. J.; Watson, L. A.; Meyer, K.; Hillhouse, G. L. *Organometallics* **2014**, *33*, 2760−2769. (j) Walter, M. D.; Sofield, C. D.; Andersen, R. A. *Organometallics* **2008**, *27*, 2959−2970.

(3) For selected papers on group 5 metallacyclopropenes, see: (a) Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Macromolecules* **1981**, *14*, 233−236. (b) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E.

J. Am. Chem. Soc. **1987**, *109*, 6525−6527. (c) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067−2069. (d) Hartung, J. B., Jr.; Pedersen, S. F. *Organometallics* **1990**, *9*, 1414−1417. (e) Arney, D. J.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 1282−1289. (f) Strickler, J. R.; Bruck, M. A.; Wigley, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 2814−2816. (g) Strickler, J. R.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 266−273. (h) Riley, P. N.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1996**, *15*, 5502−5506. (i) Oshiki, T.; Tanaka, K.; Yamada, J.; Ishiyama, T.; Kataoka, Y.; Mashima, K.; Tani, K.; Takai, K. *Organometallics* **2003**, *22*, 464−472. (j) Jordan, M.; Saak, W.; Haase, D.; Beckhaus, R. *Organometallics* **2010**, *29*, 5859−5870. (k) Parker, K. D. J.; Fryzuk, M. D. *Organometallics* **2014**, *33*, 6122−6131 and references therein.

(4) For selected papers on other transition metal alkyne complexes, see: (a) Collman, J. P.; Hegedus, L. P. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (b) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans.* **1973**, 977−981. (c) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855−5860. (d) Rosenthal, U.; Schulz, W. *J. Organomet. Chem.* **1987**, *321*, 103−117. (r) Casey, C. P.; Brady, J. T.; Boller, T. M.; Weinhold, F.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 12500−12511. (e) Casey, C. P.; Brady, J. T. *Organometallics* **1998**, *17*, 4620−4629. (f) Buil, M. L.; Eisenstein, O.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, *18*, 4949−4959. (g) Guillemot, G.; Solari, E.; Floriani, C.; Re, N.; Rizzoli, C. *Organometallics* **2000**, *19*, 5218−5230. (h) Frohnapfel, D. S.; Enriquez, A. E.; Templeton, J. L. *Organometallics* **2000**, *19*, 221−227. (i) Guillemot, G.; Solari, E.; Scopelliti, R.; Floriani, C. *Organometallics* **2001**, *20*, 2446−2448. (j) Müller, C.; Iverson, C. N.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 9718−9719. (k) Casey, C. P.; Boller, T. M.; Kraft, S.; Guzei, I. A. *J. Am. Chem. Soc.* **2002**, *124*, 13215−13221. (l) Müller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 1190−1196. (m) Stone, K. C.; Jamison, G. M.; White, P. S.; Templeton, J. L. *Organometallics* **2003**, *22*, 3083−3095. (n) Buccella, D.; Janak, K. E.; Parkin, G. *J. Am. Chem. Soc.* **2008**, *130*, 16187−16189. (o) Bowen, L. E.; Charernsuk, M.; Hey, T. W.; McMullin, C. L.; Orpen, A. G.; Wass, D. F. *Dalton Trans.* **2010**, *39*, 560−567. (p) Sgro, M. J.; Stephan, D. W. *Dalton Trans.* **2010**, *39*, 5786−5794. (q) Chiu, W.-H.; Zhang, Q.-F.; Williams, I. D.; Leung, W.-H. *Organometallics* **2010**, *29*, 2631−2633.

(5) For selected papers on main group metallacyclopropenes, see: (a) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5208−5209. (b) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 2337−2338. (c) Cui, C.; Kökke, S.; Herbst-Irmer, R.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Wrackmeyer, B. *J. Am. Chem. Soc.* **2001**, *123*, 9091−9098. (d) Li, X.; Song, H.; Duan, L.; Cui, C.; Roesky, H. W. *Inorg. Chem.* **2006**, *45*, 1912−1914. (e) Li, X.; Duan, L.; Song, H.; Ni, C.; Cui, C. *Organometallics* **2006**, *25*, 5665−5667.

(6) La Pierre, H. S.; Meyer, K. *Prog. Inorg. Chem.* **2014**, *58*, 303−415.

(7) The unstable actinide metallacyclopropenes An(η^2-C_2H_2) were recently reported by Andrews and co-workers, but their structures remained unknown. See: (a) Andrews, L.; Kushto, G. P.; Marsden, C. J. *Chem.—Eur. J.* **2006**, *12*, 8324−8335. In addition, the unstable complex (η^5-C_5H_5)$_3$U(η^2-PhC≡CPh) was reported by Ephritikhine and co-workers in 1987, but its molecular structure is unknown. See: (b) Foyentin, M.; Folcher, G.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1987**, 494−495.

(8) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71−C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939−2947.

(9) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466−468.

(10) Elschenbroich, C. *Organometallics*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2006.

(11) For selected papers, see: (a) Bursten, B. E.; Strittmatter, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 6606−6608. (b) Brennan, J. G.; Andersen, R. A.; Robbins, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 335−336. (c) Conejo, M. D.; Parry, J. S.; Carmona, E.; Schultz, M.; Brennann, J. G.; Beshouri, S. M.; Andersen, R. A.; Rogers, R. D.; Coles, S.; Hursthouse, M. *Chem.—Eur. J.* **1999**, *5*, 3000−3009. (d) Maron, L.; Eisenstein, O.; Andersen, R. A. *Organometallics* **2009**, *28*, 3629−3635.

(12) For selected reviews, see: (a) Negishi, E.-I.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124−130. (b) Takahashi, T.; Li, Y. Zirconacyclopentadienes in Organic Synthesis. In *Titanium and Zirconium in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2002; pp 50−85. (c) Varela, J. A.; Saá, C. *Chem. Rev.* **2003**, *103*, 3787−3802. (d) Braunschweig, H.; Kupfer, T. *Chem. Commun.* **2011**, *47*, 10903−10914. (e) Roy, S.; Rosenthal, U.; Jemmis, E. D. *Acc. Chem. Res.* **2014**, *47*, 2917−2930.

(13) For selected actinide metallacyclopentadiene complexes, see: (a) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982**, *1*, 170−180. (b) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650−6667. (c) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 5075−5078. (d) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939−3941. (e) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Chem. Commun.* **2005**, 4681−4683.

(14) Zanin, I. E.; Antipin, M. Y.; Struchkov, Y. T. *Kristallografiya* **1991**, *36*, 411−419.

(15) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

(16) (a) Ren, W.; Zhou, E.; Fang, B.; Zi, G.; Fang, D.-C.; Walter, M. D. *Chem. Sci.* **2014**, *5*, 3165−3172. (b) Seaman, L. A.; Pedrick, E. A.; Tsuchiya, T.; Wu, G.; Jakubikova, E.; Hayton, T. W. *Angew. Chem., Int. Ed.* **2013**, *52*, 10589−10592. (c) Korobkov, I.; Vidjayacoumar, B.; Gorelsky, S. I.; Billone, P.; Gambarotta, S. *Organometallics* **2010**, *29*, 692−702. (d) Korobkov, I.; Arunachalampillai, A.; Gambarotta, S. *Organometallics* **2004**, *23*, 6248−6252.

(17) (a) Ren, W.; Zi, G.; Walter, M. D. *Organometallics* **2012**, *31*, 672−679. (b) Ren, W.; Song, H.; Zi, G.; Walter, M. D. *Dalton Trans.* **2012**, *41*, 5965−5973. (c) Ren, W.; Lukens, W. W.; Zi, G.; Maron, L.; Walter, M. D. *Chem. Sci.* **2013**, *4*, 1168−1174.

(18) Jemmis, E. D.; Roy, S.; Burlakov, V. V.; Jiao, H.; Klahn, M.; Hansen, S.; Rosenthal, U. *Organometallics* **2010**, *29*, 76−81.

(19) For selected papers about the bonding of organoactinide complexes, see: (a) Cantat, T.; Graves, C. R.; Jantunen, K. C.; Burns, C. J.; Scott, B. L.; Schelter, E. J.; Morris, D. E.; Hay, P. J.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 17537−17551. (b) Barros, N.; Maynau, D.; Maron, L.; Eisenstein, O.; Zi, G.; Andersen, R. A. *Organometallics* **2007**, *26*, 5059−5065. (c) Yahia, A.; Maron, L. *Organoemtallics* **2009**, *28*, 672−679. (d) Ren, W.; Deng, X.; Zi, G.; Fang, D.-C. *Dalton Trans.* **2011**, *40*, 9662−9664. (e) Ciliberto, E.; Bella, S. D.; Gulino, A.; Fragala, I.; Petersen, J. L.; Marks, T. J. *Organometallics* **1992**, *11*, 1727−1737. (f) Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 3195−3206.

(20) For selected well-characterized η^2-ketone group 4 metal complexes, see: (a) Peulecke, N.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. *Organometallics* **1996**, *15*, 1340−1344. (b) Erker, G.; Dorf, U.; Czich, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668−676. (c) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1771−1773.

(21) Vallghan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7994−8001.

(22) Ren, W.; Zi, G.; Fang, D.-C.; Walter, M. D. *J. Am. Chem. Soc.* **2011**, *133*, 13183−13196.

(23) Ren, W.; Zi, G.; Fang, D.-C.; Walter, M. D. *Chem.—Eur. J.* **2011**, *17*, 12669−12682.

(24) Trnka, T. M.; Bonanno, J. B.; Bridgewater, B. M.; Parkin, G. *Organometallics* **2001**, *20*, 3255−3264.

(25) Ren, W.; Zhou, E.; Fang, B.; Hou, G.; Zi, G.; Fang, D.-C.; Walter, M. D. *Angew. Chem., Int. Ed.* **2014**, *53*, 11310−11314.

(26) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814−2819.

(27) Fiedler, B.; Weiß, D.; Beckert, R. *Liebigs Ann./Recl.* **1997**, 613−615.

(28) Walter, M. D.; Schultz, M.; Andersen, R. A. *New J. Chem.* **2006**, *30*, 238−246.
(29) Bain, G. A.; Berry, J. F. *J. Chem. Educ.* **2008**, *85*, 532−536.
(30) Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.
(31) (a) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structure from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.
(32) Frisch, M. J.; et al. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
(33) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
(34) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245−1263.