ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Small Molecule Activation Mediated by a Thorium Terminal Imido Metallocene

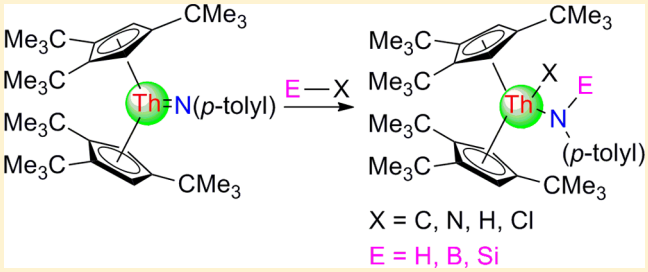
Enwei Zhou,[†,§] Wenshan Ren,[†,§] Guohua Hou,[†] Guofu Zi,*[,†] De-Cai Fang,*[,†] and Marc D. Walter*[,‡]

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

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

Supporting Information

ABSTRACT: The base-free thorium terminal imido [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th=N(*p*-tolyl) (**1**) activates a variety of small molecules such as pyridine derivatives, amines, boranes, chlorosilane, elemental selenium, and α,β-unsaturated esters. Reaction of **1** with pyridine, pyridine *N*-oxide, 2-methylpyridine *N*-oxide, *p*-toluidine, Ph_2NH, 9-borabicyclo[3.3.1]-nonane (9-BBN), $PhSiH_2Cl$, elemental selenium, PhSeSePh, and methyl methacrylate (MMA) formed the amido pyridyl complexes [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(NH-*p*-tolyl)(η^2-*C*,*N*-C_5H_4N) (**2**), [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(NH-*p*-tolyl)(κ^2-*C*,*O*-C_5H_4NO) (**3**), and [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(NH-*p*-tolyl)(κ^2-*C*,*O*-2-MeC_5H_3NO) (**4**), diamide complexes [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(NH-*p*-tolyl)$_2$ (**5**) and [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(NH-*p*-tolyl)(NPh_2) (**6**), amido hydrido complex [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(H)[N(*p*-tolyl)B(C_8H_{14})] (**7**), amido chloride complex [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(Cl)[N(*p*-tolyl)-SiH_2Ph] (**8**), amido selenido complexes [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N(*p*-tolyl)Se−Se] (**9**) and {[η^5-1,2,4-$(Me_3C)_3C_5H_2$]Th-(SePh)}$_2$[μ-N(*p*-tolyl)]$_2$ (**10**), and amido enolyl complex [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N(*p*-tolyl)CH_2C(Me)=C(OMe)O] (**11**). The new complexes **2**−**3** and **6**−**11** were characterized by various spectroscopic techniques including single crystal X-ray diffraction. Furthermore, density functional theory (DFT) studies complement the experimental investigations.



1. INTRODUCTION

Terminal imido complexes of actinide-metals containing an An=N double bond have been widely studied in the last two decades mainly because of their potential application in group transfer reactions and catalysis.[1−4] During these investigations, many uranium imido complexes have been prepared, but only some of them show significant reactivity, and most studies have therefore focused on their structural characterizations.[1−3] In contrast, only a small number of thorium imido complexes have been reported.[3j,4] The lack of interest in thorium organometallics is surprising since its $7s^26d^2$ electronic ground state configuration suggests a similar reactivity to that of group 3 and 4 metals, such as Sc, Ti, Zr, and Hf, for which several complexes with M=NR bonds are known,[5,6] and the diamagnetism of Th(IV) complexes also facilitates the NMR spectroscopic characterization. Nevertheless, more recent studies indicate that 5f orbitals play a significant part in the bonding of organothorium compounds, thus leading to a distinctively different reactivity from that of group 4 complexes.[7] In the course of our investigations in this area, we have recently prepared a base-free terminal thorium imido metallocene [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th=N(*p*-tolyl) (**1**).[8−10] Gratifyingly, complex **1** shows a rich reaction chemistry including the activation of element sulfur,[9] Si−H bonds,[11] and N≡N bonds in diazoalkanes.[12] Furthermore, it is also an important intermediate in the catalytic hydroamination of internal acetylenes,[9] an efficient catalyst for the trimerization of PhCN,[9] and a useful synthon for the preparation of oxido and sulfido thorium metallocenes [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th=E (E = O, S) by cycloaddition−elimination reactions with Ph_2C=E (E = O, S).[8] Encouraged by this broad reactivity, we are now extending our studies to small molecule activation mediated by **1**. Herein, we report on some observations concerning the reactions of the imido thorium metallocene **1** with pyridine derivatives, amines, boranes, chlorosilane, selenium, and its organic derivatives, and α,β-unsaturated organic molecules.

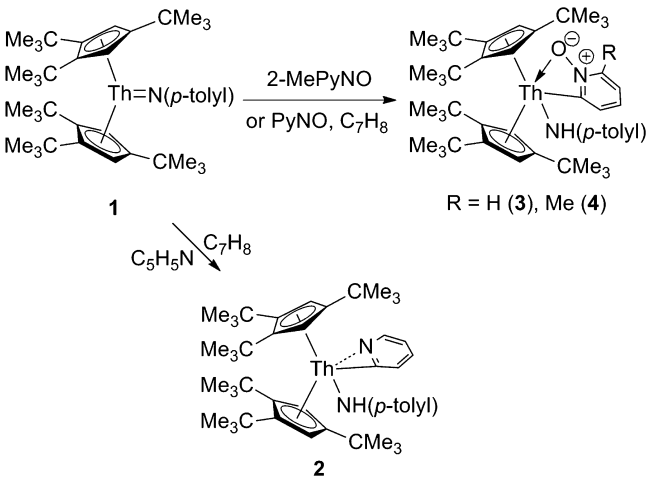
2. RESULTS AND DISCUSSION

2.1. Reaction with Pyridine Derivatives. Mixing the thorium imido [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th=N(*p*-tolyl) (**1**) with pyridine derivatives such as pyridine, pyridine *N*-oxide, or 2-methylpyridine *N*-oxide rapidly forms the amido pyridyl complexes [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(NH-*p*-tolyl)(η^2-*C*,*N*-C_5H_4N) (**2**), [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(NH-*p*-tolyl)(κ^2-*C*,*O*-C_5H_4NO) (**3**), and [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(NH-*p*-tolyl)(κ^2-*C*,*O*-2-MeC_5H_3NO) (**4**), respectively, in quantitative conversions (Scheme 1), in which an α-H atom of pyridine, pyridine *N*-oxide, or 2-methylpyridine *N*-oxide is transferred to

Received: May 27, 2015
Published: July 2, 2015

DOI: 10.1021/acs.organomet.5b00454
Organometallics 2015, 34, 3637−3647

Scheme 1



the imido Th═N(*p*-tolyl) moiety. For 2-methylpyridine *N*-oxide, no activation of sp^3 C−H bond of methyl was observed, indicating that the sp^2 C−H bond is more reactive than the sp^3 C−H bond. To further understand this transformation, DFT calculations were performed at the B3PW91 level of theory. The energetic profile for the intermolecular reaction of **1** with pyridine *N*-oxide is shown in Figure 1, and it involves the

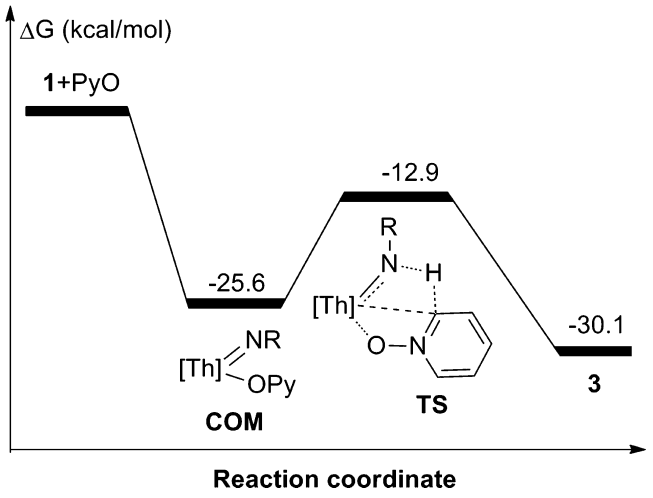


Figure 1. Free energy profile (kcal/mol) for the reaction of **1** + PyNO. [Th] = [η^5-1,2,4-$(Me_3C)_3C_5H_2$]Th. R = *p*-tolyl.

formation of the adduct **COM** and the transition state **TS**. In the σ-bond metathesis transition state **TS**, the two forming bond distances of Th−C and N−H are 3.581 and 1.295 Å, respectively, ca. 0.93 and 0.27 Å longer than those in the product **3**. The Th−C and N−H bonds are formed simultaneously, while the C−H bond is broken. The formation of the adduct **COM** from **1** + PyO is energetically favorable (ΔG(298 K) = −25.6 kcal/mol), but the final product **3** is thermodynamically more stable (−30.1 kcal/mol) than the adduct **COM**. Moreover, the potential energy profile suggests a short lifetime for the adduct **COM** since the activation barrier to form complex **3** from intermediate **COM** is only 12.7 kcal/mol. Therefore, **COM** is not isolated from the reaction mixture, and only **3** is detected by NMR spectroscopy.

The molecular structures of [η^5-1,2,4-$(Me_3C)_3C_5H_2$]$_2$Th(NH-*p*-tolyl)(η^2-*C*,*N*-C_5H_4N) (**2**), [η^5-1,2,4-$(Me_3C)_3C_5H_2$]$_2$Th(NH-*p*-tolyl)(κ^2-*C*,*O*-C_5H_4NO) (**3**) and [η^5-1,2,4-$(Me_3C)_3C_5H_2$]$_2$Th(NH-*p*-tolyl)(κ^2-*C*,*O*-2-MeC_5H_3NO) (**4**) were determined and are shown in Figures 2−4, while selected

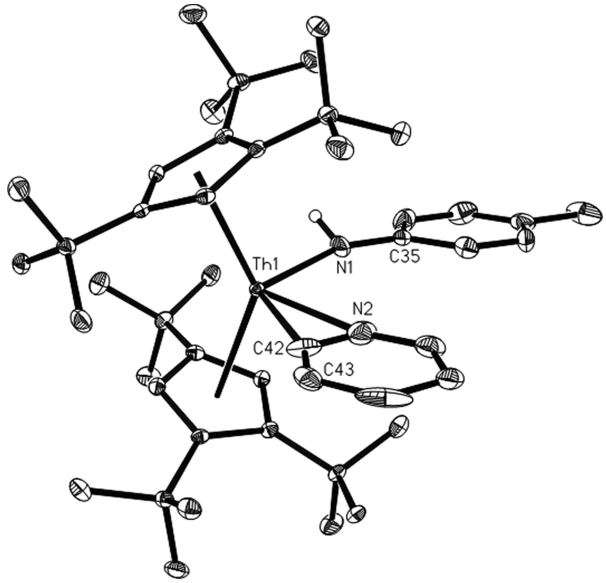


Figure 2. Molecular structure of **2** (thermal ellipsoids drawn at the 35% probability level).

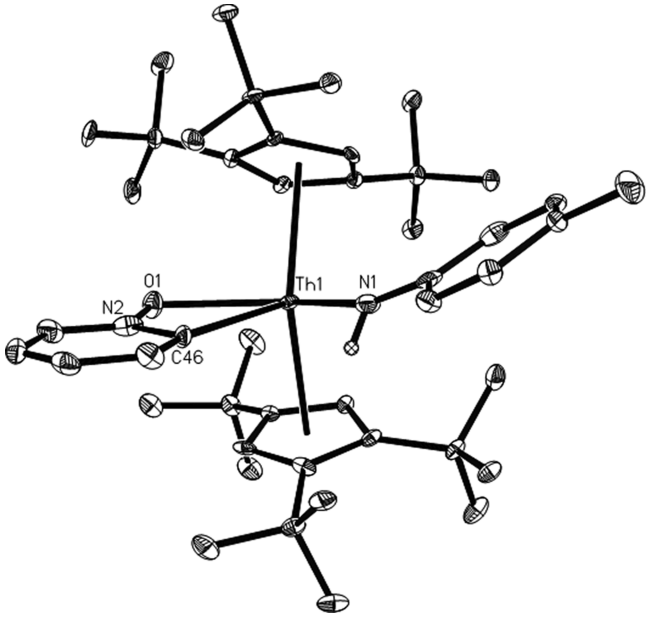


Figure 3. Molecular structure of **3** (thermal ellipsoids drawn at the 35% probability level).

bond distances and angles are listed in Table 1. In each complex, the Th^{4+} ion features a pseudotetrahedral ligand environment with two η^5-bound Cp-ring and one σ-coordinate carbon atom and two nitrogen atoms (for **2**) or one oxygen atom and one nitrogen atom (for **3** and **4**) with the average Th−C(Cp) distance of 2.886(5) Å for **2**, 2.897(7) Å for **3**, and 2.882(3) Å for **4**, respectively, and the angle Cp(cent)-Th-Cp(cent) of 137.8(2)° for **2**, 139.3(3)° for **3**, and 141.1(1)° for **4**, and the angle of Th−N−C of 160.4(4)° for **2**, 159.3(6)° for **3**, and 155.7(2)° for **4**. The Th−N(1) distances (2.257(5) Å for **2**, 2.283(7) Å for **3**, and 2.322(3) Å for **4**) can be compared

DOI: 10.1021/acs.organomet.5b00454
Organometallics 2015, 34, 3637−3647

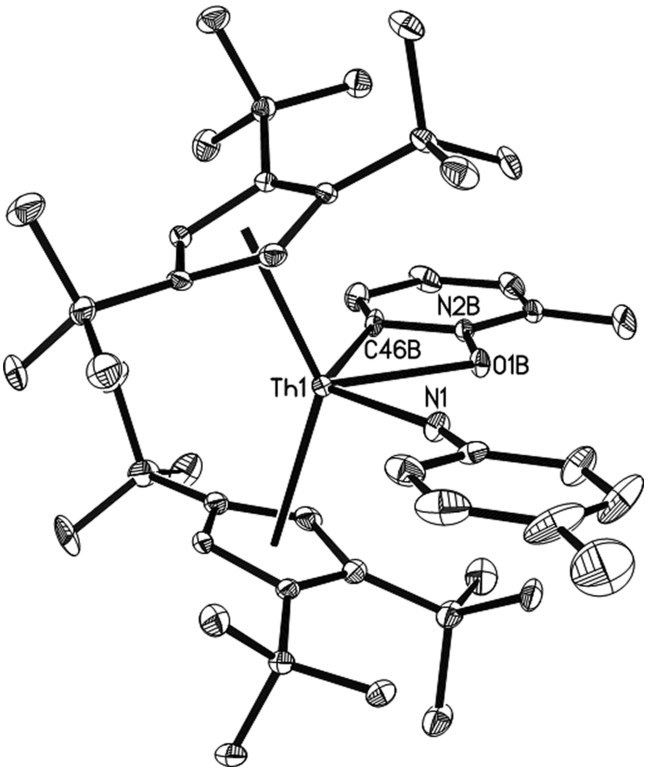
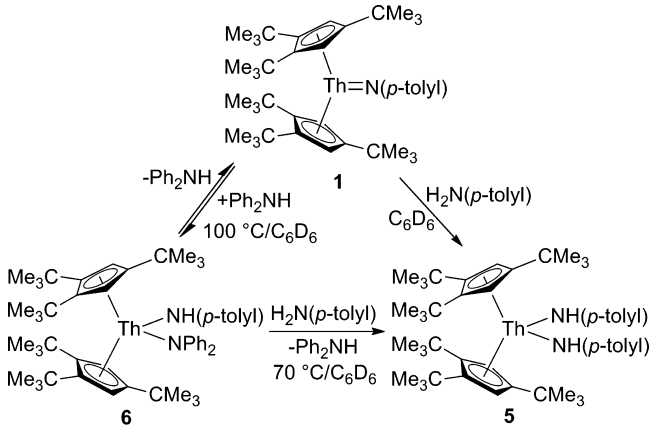


Figure 4. Molecular structure of **4** (thermal ellipsoids drawn at the 35% probability level).

to those found in $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(NH\text{-}p\text{-}tolyl)_2$ (2.279(3) and 2.286(3) Å),[9] $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[N(p\text{-}tolyl)C(S)\text{-}S]$ (2.347(6) Å),[8] $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[N(p\text{-}tolyl)C(NPh)\text{-}S]$ (2.328(3) Å),[8] $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[N(p\text{-}tolyl)N{=}NN(p\text{-}tolyl)]$ (2.366(3) and 2.354(3) Å),[12] $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(bipy)$ (2.325(5) and 2.363(4) Å),[10] and $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th(bipy)$ (2.326(7) and 2.325(7) Å).[13] However, the Th–C(pyridyl) distance of 2.486(5) Å in **2** is shorter than those found in **3** (2.687(7) Å), **4** (2.690(3) Å), and $(\eta^5\text{-}C_5Me_5)_2Th(CH_2Ph)(\kappa^2\text{-}C,O\text{-}ONC_5H_4)$ (2.621(3) Å).[14] In **2**, the Th–N(2) distance (2.497(5) Å) is as expected shorter than those observed in $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2ThO(4\text{-}Me_2NC_5H_4N)$ (2.587(5) Å)[8] and $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[(bipy)(SCPh_2)]$ (2.564(1) Å)[15] but slightly longer than those (2.257(5)–2.322(3) Å) of Th–N(1) in **2**, **3**, and **4**. In **3** and **4**, the Th–O distances (2.460(5) Å for **3** and 2.378(4) Å for **4**) are shorter than that expected for a purely dative interaction.[16] These values may also be compared to those found in $(\eta^5\text{-}C_5Me_5)_2Th(CH_2Ph)(\kappa^2\text{-}C,O\text{-}ONC_5H_4)$ (2.416(2) Å),[14] but they are longer than those observed in $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[O_2CPh_2]$ (2.202(3) Å),[8] and $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[(OCPh_2)_2]$ (2.182(2) Å).[17] The N–O distances (1.360(10) Å for **3** and 1.310(5) Å for **4**) are in the same range as those in the free pyridine *N*-oxide (1.330(9) Å)[18] and in $(\eta^5\text{-}C_5Me_5)_2Th(CH_2Ph)(\kappa^2\text{-}C,O\text{-}ONC_5H_4)$ (1.360(3) Å).[14]

2.2. Reaction with Amines. It has been demonstrated that diamide $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(NH\text{-}p\text{-}tolyl)_2$ (**5**) is readily formed on the reaction of imido $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}N(p\text{-}tolyl)$ (**1**) and *p*-toluidine (Scheme 2),[9] indicating

Scheme 2



that imido **1** activates the N–H bond in aromatic amines. Diamide **5** can be converted to imido **1** at approximately 140 °C/0.01 mmHg, but no equilibrium between diamide **5** and imido **1** is detected by ^{1}H NMR spectroscopy (in the temperature range of 20–100 °C) because of the rather small amount of formed imido or rapid chemical exchange.[9] Under similar reaction conditions, reaction of **1** with 1 equiv of Ph_2NH also affords the desired mixed diamide $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(NH\text{-}p\text{-}tolyl)(NPh_2)$ (**6**) (Scheme 2). In contrast to diamide **5**, an equilibrium between diamide **6** and imido **1** is detected at temperatures above 80 °C by ^{1}H NMR

Table 1. Selected Distances (Å) and Angles (deg) for Compounds 2–4 and 6–11[a]

compound	C(Cp)-Th[b]	C(Cp)-Th[c]	Cp(cent)-Th[b]	Th-X	Cp(cent)-Th-Cp(cent)	X-Th-X or X-Th-Y
2	2.886(5)	2.801(4) to 3.005(5)	2.621(5)	N(1) 2.257(5), N(2) 2.497(5) C(42) 2.486(5)	137.8(2)	N(1)-Th-N(2) 86.1(2) N(2)-Th-C(42) 29.2(2)
3	2.897(7)	2.807(7) to 2.933(7)	2.625(7)	N(1) 2.283(7), O(1) 2.460(5) C(46) 2.687(7)	139.3(3)	O(1)-Th-C(46) 53.5(3)
4	2.882(3)	2.813(3) to 2.945(3)	2.619(3)	N(1) 2.322(3), O(1B) 2.378(4) C(46B) 2.690(3)	141.1(1)	O(1)-Th-C(46B) 53.7(1)
6	2.890(5)	2.835(6) to 2.934(5)	2.639(5)	N(1) 2.418(5), N(2) 2.266(4)	130.4(3)	91.2(2)
7a	2.853(3)	2.783(3) to 2.939(3)	2.584(3)	N(1) 2.421(2), H(1) 1.96(3)	132.9(1)	107.9(8)
8	2.878(3)	2.824(3) to 2.964(3)	2.613(3)	N(1) 2.389(2), Cl(1) 2.663(1)	135.9(1)	97.8(1)
9	2.869(5)	2.797(5) to 2.995(5)	2.603(5)	N(1) 2.322(5), Se(1) 2.906(1)	133.8(3)	N(1)–Th-Se(1) 77.1(1)
10	2.851(5)	2.778(5) to 2.903(5)	2.584(5)	N(1) 2.170(5), Se(1) 2.918(1)		N-Th-N 74.7(2)
11	2.892(11)	2.789(11) to 3.033(11)	2.623(11)	N(1) 2.323(9), O(1) 2.197(9)	134.4(3)	N-Th-O 82.8(3)

[a]Cp = cyclopentadienyl ring. [b]Average value. [c]Range value.

DOI: 10.1021/acs.organomet.5b00454
Organometallics 2015, 34, 3637–3647

spectroscopy, suggesting that diamide **5** is more stable than diamide **6**. For example, at 100 °C, 40% of **6** converts to **1**, and the equilibrium constant of the reaction is 0.27 according to the equation K_e = ([**1**][Ph_2NH])/([**6**]). Furthermore, diamide **6** can be converted to diamide **5** by reaction with *p*-toluidine at 70 °C (Scheme 1), again supporting the notion that **5** is more stable than **6**. Overall, these results imply that the formation of an actinide-imido metallocene starting from the corresponding diamide derivatives by amine elimination strongly depends on the substituents on the amide group.[3w,9]

The molecular structure of [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(NH-*p*-tolyl)(NPh_2) (**6**) is depicted in Figure 5. The

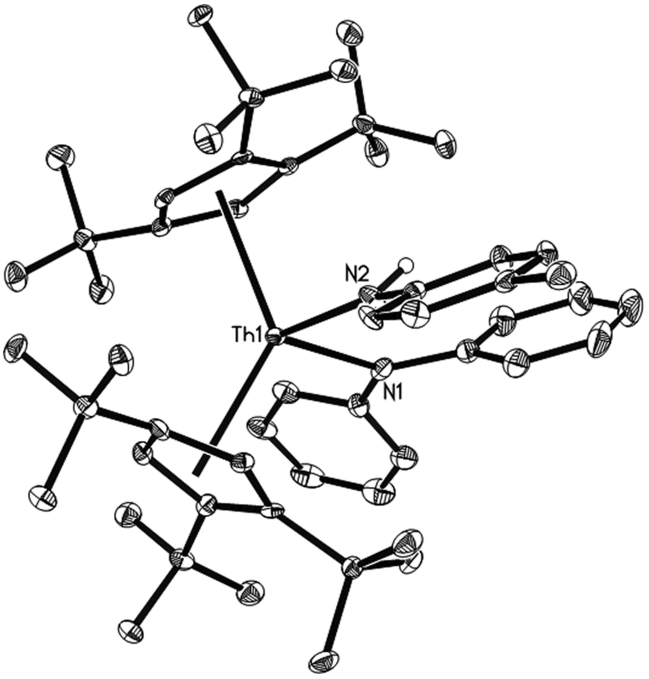
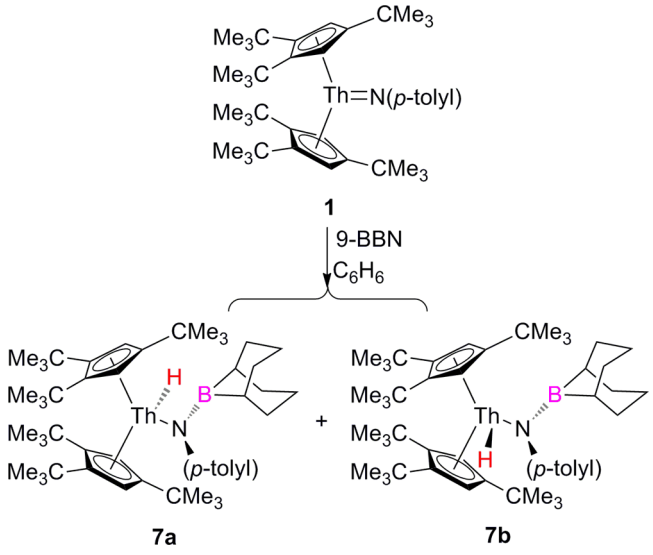


Figure 5. Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level).

orientation of the cyclopentadienyl rings is nearly eclipsed, and the two amido-groups (NH-*p*-tolyl and NPh_2) are oriented on either side of the eclipsed Me_3C-groups. The N−Th−N angle is 91.2(2)°, identical to that (91.2(1)°) found in [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(NH-*p*-tolyl)$_2$ (**5**).[9] However, the Th−N(1) distance (2.418(5) Å) is longer than that of Th−N(2) (2.266(4) Å) and the average Th−N distance (2.283(3) Å) of **5**,[9] which can presumably be attributed to the increased steric bulk of the Ph_2N group and which also contributes to the decreased stability of diamide **6** and the facile release of the Ph_2N group.

2.3. Reaction with Borane. As for the scandium imido complexes,[5k] the B−H bond of borane can also be activated by our actinide imido complex **1**. For example, the reaction of imido **1** with 1 equiv of 9-borabicyclo[3.3.1]nonane (9-BBN) rapidly forms the amido hydrido metallocene [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(H)[N(*p*-tolyl)B(C_8H_{14})] (**7**) in quantitative conversion (Scheme 3). The ^{1}H NMR spectrum of **7** clearly shows that there are two isomers, *syn* **7a** and *anti* **7b**, present in C_6D_6 solution with the ratio of 1:1.1. However, in contrast to the silane addition products,[11] the ^{1}H NMR experiment confirms that the mixture of **7a** and **7b** cannot be

Scheme 3



isomerized to only one isomer, and no degradation occurs when the mixture is heated at 100 °C for 1 week.

The cyclopentadienyl rings in [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(H)[N(*p*-tolyl)B(C_8H_{14})] (**7a**) adopt a nearly eclipsed arrangement (Figure 6). The average Th−C(ring) distance is 2.853(3)

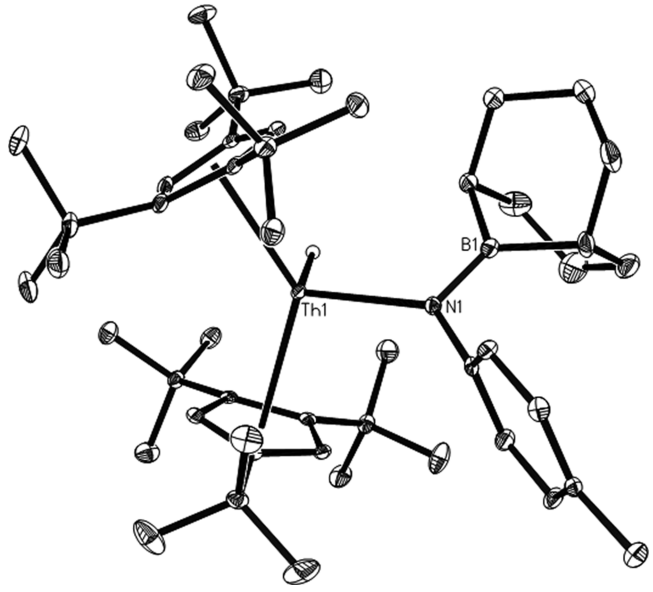


Figure 6. Molecular structure of **7a** (thermal ellipsoids drawn at the 35% probability level).

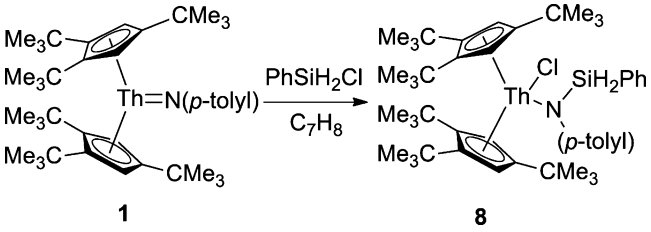
Å, and the Cp(cent)-Th-Cp(cent) angle is 132.9(1)°. Complex **7a** represents the first example of B−H bond activation induced by an actinide imido complex. The Th−N distance is 2.421(2) Å, which is comparable to those found in [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th(H)[N(*p*-tolyl)SiH_2Ph)] (2.387(2) Å),[11] [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th[(bipy)($SCPh_2$)] (2.435(1) Å),[15] [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$Th[η^2-C,N-{CH_2SiMe_2NC(=CHPh)Ph}] (2.365(2) Å),[12] (η^5-C_5Me_5)$_2$Th[N(N=CHSiMe_3)(C_4Ph_4)] (2.298(3) Å),[19] [η^5-1,2,4-(Me_3C)$_3C_5H_2$]$_2$-Th(bipy) (2.325(5) and 2.363(4) Å),[10] and [η^5-1,3-(Me_3C)$_2C_5H_3$]$_2$Th(bipy) (2.326(7) and 2.325(7) Å).[13] The Th−H distance of 1.96(3) Å is in line with those found in [η^5-

DOI: 10.1021/acs.organomet.5b00454
Organometallics 2015, 34, 3637−3647

1,2,4-$(Me_3C)_3C_5H_2]_2$Th(H)[N(*p*-tolyl)SiH_2Ph)] (2.01(3) Å)[11] and [η^5-1,3-$(Me_3C)_2C_5H_3]_3$ThH (1.99(5) Å).[20]

2.4. Reaction with Chlorosilane. DFT calculations suggest that the activation barrier in the reaction between the imido [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th=N(*p*-tolyl) (**1**) and chlorotrimethylsilane (Me_3SiCl) proceeding via the [2 + 2] addition mechanism (32.1 kcal mol^{-1}) is energetically more favorable than that for the S_N2-type process (37.4 kcal mol^{-1}).[9] This change in mechanism relative to the oxido metallocene [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th=O can be attributed to the increased steric hindrance between the reaction partners.[8] However, no reaction occurs between the imido **1** and Me_3SiCl because of the high activation barrier (32.1 kcal mol^{-1}).[9] Therefore, in order to reduce the activation barrier, a less bulky chlorosilane is required. In fact, the treatment of imido **1** with 1 equiv of $PhSiH_2Cl$, indeed, gives the chloride metallocene [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(Cl)[N(*p*-tolyl)SiH_2Ph] (**8**) in quantitative conversion (Scheme 4). The ^{1}H NMR spectrum of **8** shows a 1:1:1 pattern for the Me_3C-resonances, which is consistent with the molecular C_1-symmetry of **8**.

Scheme 4



The molecular structure of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(Cl)-[N(*p*-tolyl)SiH_2Ph] (**8**) shows nearly eclipsed cyclopentadienyl rings (Figure 7). The average Th−C(ring) distance is 2.878(3) Å, and the Cp(cent)-Th-Cp(cent) angle is 135.9(1)°. The Th−N distance is 2.389(2) Å, comparable to those found in **2**, **3**, **4**, **5**, and **7** (Table 1). The Th−Cl distance is 2.613(3) Å, which is similar to those found in [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$$ThCl_2$ (2.621(1) Å),[9] [η^5-1,3-$(Me_3C)_2C_5H_3]_2$$ThCl_2$ (2.632(1) Å),[9] and [η^5-1,3-$(Me_3Si)_2C_5H_3]_2$$ThCl_2$ (2.632(2) Å).[21]

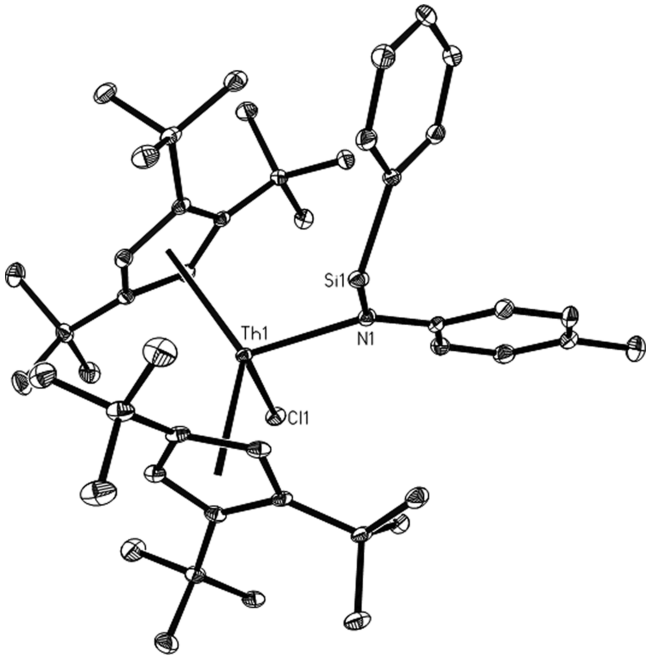
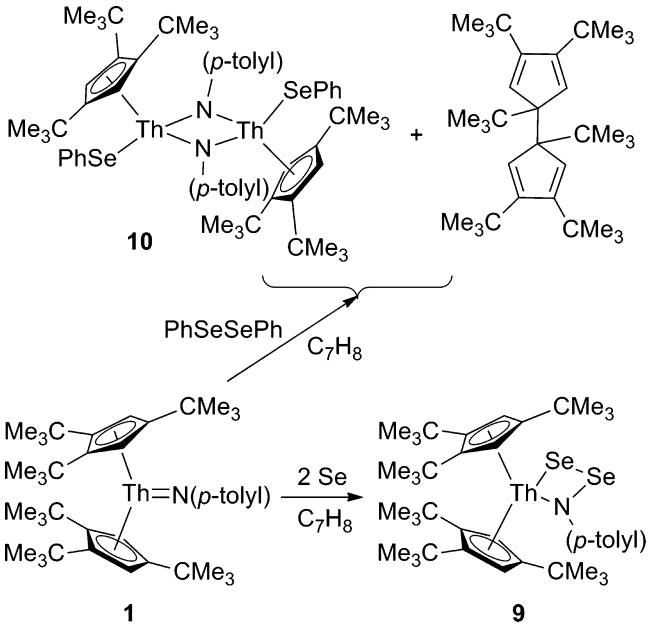


Figure 7. Molecular structure of **8** (thermal ellipsoids drawn at the 35% probability level).

2.5. Reactions with Selenium and Diphenyldiselenium. Imido [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th=N(*p*-tolyl) (**1**) reacts with elemental sulfur (S_8) to form the [2 + 2] cycloaddition product.[9] It is therefore conceivable to propose that elemental selenium (Se) might react with imido **1** in a similar manner. Indeed treatment of imido **1** with 2 equiv of selenium affords the desired cycloaddition product [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N(*p*-tolyl)Se-Se] (**9**) (Scheme 5). However, when the diselenide PhSeSePh is used, one [η^5-1,2,4-$(Me_3C)_3C_5H_2]^-$ ligand was oxidized to the dimer (2,3,5-$(Me_3C)_3C_5H_2)_2$, and the resulting anion $PhSe^-$ replaces one cyclopentadienyl ring. However, the steric demand is now no longer sufficient to prevent dimerization, and therefore, the μ-imido-bridged complex {[η^5-1,2,4-$(Me_3C)_3C_5H_2$]Th(SePh)}$_2$[μ-N(*p*-tolyl)]$_2$ (**10**) was isolated in 95% yield (Scheme 5).

Scheme 5



The molecular structure of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N-(*p*-tolyl)Se-Se] (**9**) is shown in Figure 8. The orientation of the cyclopentadienyl rings adopt a nearly eclipsed conformation, and the average Th−C(ring) distance is 2.869(5) Å, and the Cp(cent)-Th-Cp(cent) angle is 133.8(3)°. Complex **9** represents the first example of elemental selenium addition to an actinide imido complex. The Th−N distance is 2.322(5) Å, comparable to those found in **2**, **3**, **4**, **5**, **7**, and **8** (Table 1). The average Th−Se distance is 2.934(1) Å, which is in line with that found in [η^5-1,3-$(Me_3C)_2C_5H_3]_2$$Th(SePh)_2$ (2.877(1) Å).[13]

The centrosymmetric molecular structure of {[η^5-1,2,4-$(Me_3C)_3C_5H_2$]Th(SePh)}$_2$[μ-N(*p*-tolyl)]$_2$ (**10**) is depicted in Figure 9; and the Th^{4+} ion features a distorted-tetrahedral coordination environment with an average Th−C(Cp) distance of 2.851(5) Å. The Th−N distance of 2.170(5) Å is shorter than those in **2**, **3**, **4**, **6**, **7**, **8**, and **9** (Table 1). The separation of the two Th^{4+} cations (3.630(1) Å) in the dimer is in the range previously observed for {[η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th}$_2$(μ-O)$_2$

DOI: 10.1021/acs.organomet.5b00454
Organometallics 2015, 34, 3637−3647

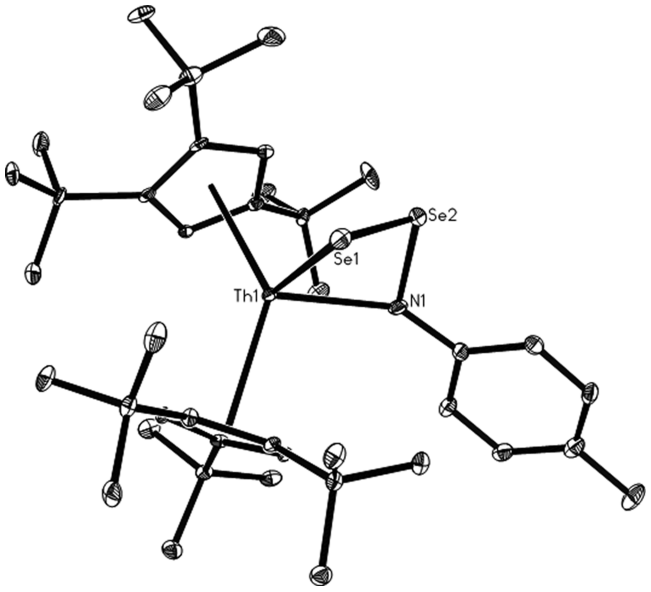


Figure 8. Molecular structure of **9** (thermal ellipsoids drawn at the 35% probability level).

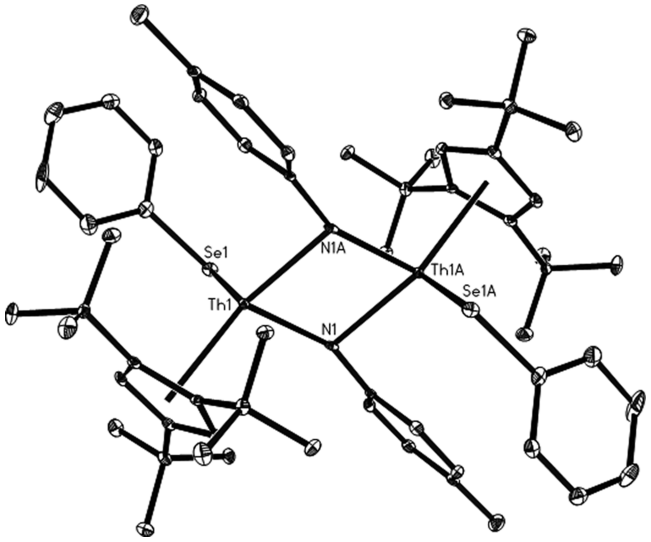
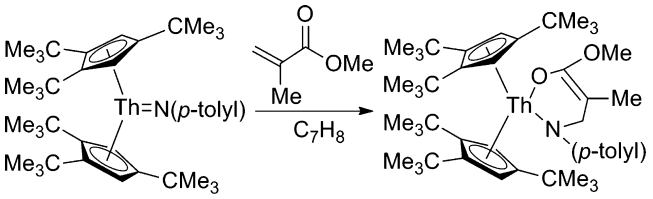


Figure 9. Molecular structure of **10** (thermal ellipsoids drawn at the 35% probability level).

Scheme 6



addition, which is a consequence of the polarized actinide imido bond An^{+}-NR^{-};[11] alternatively, this reaction could also be explained by a [4 + 2] cycloaddition reaction.

The solid state molecular structure of $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N(*p*-tolyl)CH_2C(Me)=C(OMe)O] (**11**) is depicted in Figure 10. The Th^{4+} ion features a distorted-

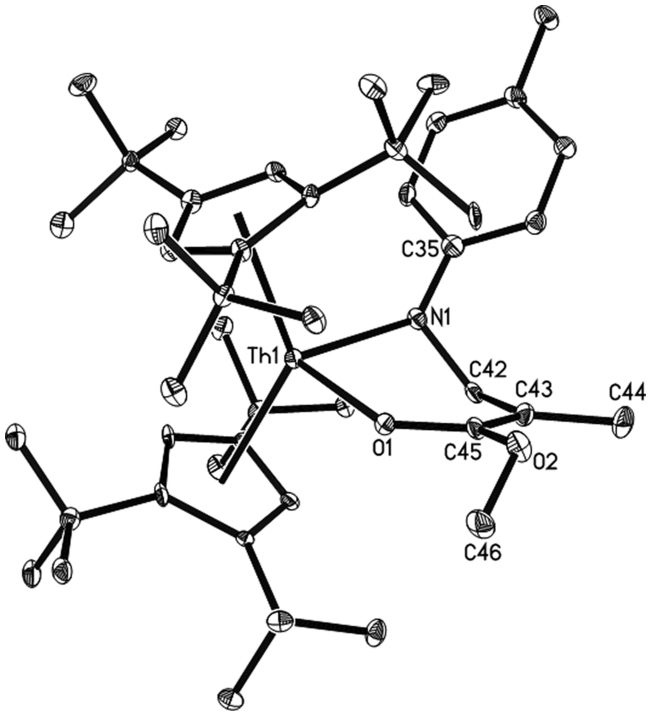


Figure 10. Molecular structure of **11** (thermal ellipsoids drawn at the 35% probability level).

(3.546(1) Å),[8] and [{[η^5-1,2,4-$(Me_3C)_3C_5H_2$]Th$(N_3)_2$}$_2${μ-N(*p*-tolyl)}$_2$][(*n*-$C_4H_9)_4N]_2$ (3.697(1) Å).[12] The Th−Se distance of 2.918(1) Å is close to the average distances found in **9** (2.934(1) Å) and [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th$(SePh)_2$ (2.877(1) Å).[13]

2.6. Reaction with α,β-Unsaturated Reagent. Imido complex [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th=N(*p*-tolyl) (**1**) reacts with unsaturated reagents such as CS_2, alkyne, and nitrile to form [2 + 2] cycloaddition products.[8,9] We were then curious to explore the reactivity of **1** with the C=C−C=O functionality of α,β-unsaturated ester, for which a similar cycloaddition reaction may occur. However, treatment of imido **1** with 1 equiv of methyl methacrylate (MMA) does not afford the [2 + 2] cycloaddition product, but an amido enolyl complex [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N(*p*-tolyl)CH_2C(Me)=C(OMe)O] (**11**) is isolated in good yield (Scheme 6). The formation of **11** can be rationalized on the basis of a Michael

tetrahedral ligand environment with two η^5-bound Cp-ring and one σ-coordinate nitrogen atom and one oxygen atom with the average Th−C(Cp) distance of 2.892(11) Å and an angle Cp(cent)-Th-Cp(cent) of 134.4(3)°. The Th−N distance (2.323(9) Å) is close to those found in **2**, **3**, **4**, **6**, **7**, **8**, and **9** (Table 1). The Th−O distance (2.197(9) Å) may be compared to those found in [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th$[O_2CPh_2]$ (2.202(3) Å),[8] [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th$[(OCPh_2)_2]$ (2.182(2) Å),[17] and [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[C(Ph)=CHPh][O−C(=CH_2)NMe_2] (2.198(4) Å).[22]

3. CONCLUSIONS

In conclusion, the base-free thorium imido metallocene, [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th=N(*p*-tolyl) (**1**), activates the C−H bond of pyridine derivatives, N−H bond of amines, B−H bond of boranes, and Si−Cl bond of chlorosilane in a 1,2-addition reaction, forming amido pyridyl, diamido, amido hydrido, and

DOI: 10.1021/acs.organomet.5b00454
Organometallics 2015, 34, 3637−3647

amido chloride compounds, respectively. However, the reaction is reversible for amines, consistent with the observation that actinide diamide complexes are efficient catalysts for the hydroamination of alkynes and the fact that these imido complexes can serve as intermediates in these reactions. In contrast, the reactions are irreversible for pyridine, borane, and chlorosilane. In addition, imido complex **1** is also capable of activating elemental selenium and its organic derivatives such as PhSeSePh in a redox process, yielding the cyclic amido selenido complex $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[N(p\text{-tolyl})Se\text{-}Se]$ (**9**) and dimeric imido selenido complex $\{[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]\text{-}Th(SePh)\}_2[\mu\text{-}N(p\text{-tolyl})]_2$ (**10**). Furthermore, with α,β-unsaturated reagents such as methyl methacrylate (MMA) imido complex **1** undergoes a Michael addition reaction or a [4 + 2] cycloaddition reaction to form the amido enolyl compound $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[N(p\text{-tolyl})CH_2C\text{-}(Me)=C(OMe)O]$ (**11**). Additional investigations of these imido, amido hydrido, and amido pyridyl complexes in the context of small molecule activation and in organic synthesis are still ongoing and will be reported in due course.

4. EXPERIMENTAL SECTION

4.1. General Methods. All reactions and product manipulations were carried out under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $PhSiH_2Cl$ was distilled under nitrogen prior to use. Ph_2NH and $p\text{-}MeC_6H_4NH_2$ were purified by sublimation. $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}N(p\text{-tolyl})$ (**1**)[8,9] was 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 obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker AV 400 spectrometer at 400, 100, and 128 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts, but they also served as the internal standard in our NMR investigations. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

4.2. Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(NH\text{-}p\text{-tolyl})(\eta^2\text{-}C,N\text{-}C_5H_4N)$ (2). *4.2.1. Method A.* A toluene (5 mL) solution of pyridine (50 mg, 0.622 mmol) was added to a toluene (10 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}N(p\text{-tolyl})$ (**1**; 500 mg, 0.622 mmol). After this solution was stirred at room temperature for 1 h, the solvent was removed. The residue was extracted with *n*-hexane (10 mL × 2) and filtered. The volume of the filtrate was reduced to ca. 2 mL, and yellow crystals **2** were isolated when this solution stood at room temperature for 2 days. Yield: 439 mg (80%). M.p.: 200−202 °C (dec). ^1H NMR (C_6D_6): δ 8.39 (d, J = 6.0 Hz, 1H, py), 8.01 (d, J = 7.2 Hz, 1H, py), 7.19 (d, J = 8.0 Hz, 2H, phenyl), 7.07 (t, J = 7.2 Hz, 1H, py), 6.93 (d, J = 8.0 Hz, 2H, phenyl), 6.62 (d, J = 6.0 Hz, 1H, py), 6.56 (d, J = 2.9 Hz, 2H, ring C*H*), 6.16 (d, J = 2.9 Hz, 2H, ring C*H*), 4.86 (s, 1H, N*H*), 2.34 (s, 3H, tolylCH_3), 1.50 (s, 18H, $(CH_3)_3C$), 1.30 (s, 18H, $(CH_3)_3C$), 1.18 (s, 18H, $(CH_3)_3C$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 236.7 (Th*C*), 156.4 (aryl *C*), 145.9 (aryl *C*), 142.0 (aryl *C*), 141.3 (aryl *C*), 141.2 (aryl *C*), 135.7 (aryl *C*), 135.6 (aryl *C*), 129.6 (aryl *C*), 124.1 (ring *C*), 124.0 (ring *C*), 118.4 (ring *C*), 115.3 (ring *C*), 114.2 (ring *C*), 34.8 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 34.1 ($C(CH_3)_3$), 33.9 ($C(CH_3)_3$), 33.4 ($C(CH_3)_3$), 33.1 ($C(CH_3)_3$), 20.8 (tolylCH_3). IR (KBr, cm^{-1}): ν 2958 (s), 2868 (s), 1622 (m), 1516 (m), 1460 (s), 1386 (s), 1361 (s), 1259 (s), 1093 (s), 1022 (s), 802 (s). Anal. Calcd for $C_{46}H_{70}N_2Th$: C,62.56; H,7.99; N,3.17. Found: C, 62.42; H, 7.98; N, 3.03.

4.2.2. Method B. 4.2.2.1. NMR Scale. A C_6D_6 (0.3 mL) solution of pyridine (1.6 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}N(p\text{-tolyl})$ (**1**; 16 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The resonances due to **2** were observed by ^1H NMR spectroscopy (100% conversion).

4.3. Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(NH\text{-}p\text{-tolyl})(\kappa^2\text{-}C,O\text{-}C_5H_4NO)$ (3). *4.3.1. Method A.* This compound was prepared as colorless crystals from the reaction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}N(p\text{-tolyl})$ (**1**; 500 mg, 0.622 mmol) and pyridine *N*-oxide (59 mg, 0.622 mmol) in toluene (15 mL) and recrystallization from an *n*-hexane solution by a procedure similar to that in the synthesis of **2**. Yield: 475 mg (85%). M.p.: 138−140 °C (dec.). ^1H NMR (C_6D_6): δ 7.99 (d, J = 6.4 Hz, 1H, py), 7.20 (d, J = 6.4 Hz, 1H, py), 7.17 (d, J = 8.0 Hz, 2H, phenyl), 7.06 (d, J = 8.0 Hz, 2H, phenyl), 6.69 (t, J = 6.4 Hz, 1H, py), 6.62 (d, J = 3.2 Hz, 2H, ring C*H*), 6.24 (t, J = 6.4 Hz, 1H, py), 6.21 (d, J = 3.2 Hz, 2H, ring C*H*), 4.37 (s, 1H, N*H*), 2.30 (s, 3H, tolylCH_3), 1.49 (s, 18H, $(CH_3)_3C$), 1.43 (s, 18H, $(CH_3)_3C$), 1.32 (s, 18H, $(CH_3)_3C$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 222.3 (Th*C*), 157.0 (aryl *C*), 142.4 (aryl *C*), 142.0 (aryl *C*), 140.8 (aryl *C*), 138.5 (aryl *C*), 134.5 (aryl *C*), 129.5 (aryl *C*), 128.3 (aryl *C*), 124.5 (ring *C*), 121.9 (ring *C*), 118.9 (ring *C*), 115.0 (ring *C*), 114.4 (ring *C*), 35.0 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 33.9 ($C(CH_3)_3$), 33.1 ($C(CH_3)_3$), 20.8 (tolylCH_3). IR (KBr, cm^{-1}): ν 2961 (s), 1603 (m), 1501 (m), 1448 (m), 1384 (s), 1260 (s), 1091 (s), 1019 (s), 799 (s). Anal. Calcd for $C_{46}H_{70}N_2OTh$: C, 61.45; H, 7.85; N, 3.12. Found: C, 61.42; H, 7.88; N, 3.03.

4.3.2. Method B. 4.3.2.1. NMR Scale. A C_6D_6 (0.3 mL) solution of pyridine *N*-oxide (1.9 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}N(p\text{-tolyl})$ (**1**; 16 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The resonances due to **3** were observed by ^1H NMR spectroscopy (100% conversion).

4.4. Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(NH\text{-}p\text{-tolyl})(\kappa^2\text{-}C,O\text{-}2\text{-}MeC_5H_3NO)$ (4). *4.4.1. Method A.* This compound was prepared as colorless crystals from the reaction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}N(p\text{-tolyl})$ (**1**; 500 mg, 0.622 mmol) and 2-methylpyridine *N*-oxide (68 mg, 0.622 mmol) in toluene (15 mL) and recrystallization from an *n*-hexane solution by a procedure similar to that in the synthesis of **2**. Yield: 471 mg (83%). M.p.: 148−150 °C (dec.). ^1H NMR (C_6D_6): δ 7.99 (d, J = 6.0 Hz, 1H, py), 7.15 (d, J = 8.0 Hz, 2H, phenyl), 7.10 (d, J = 8.0 Hz, 2H, phenyl), 6.74 (t, J = 6.0 Hz, 1H, py), 6.64 (s, 2H, ring C*H*), 6.32 (d, J = 6.0 Hz, 1H, py), 6.22 (s, 2H, ring C*H*), 4.16 (s, 1H, N*H*), 2.32 (s, 3H, tolylCH_3), 2.22 (s, 3H, pyCH_3), 1.50 (s, 18H, $(CH_3)_3C$), 1.44 (s, 18H, $(CH_3)_3C$), 1.30 (s, 18H, $(CH_3)_3C$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 211.2 (Th*C*), 157.2 (aryl *C*), 144.5 (aryl *C*), 142.4 (aryl *C*), 141.8 (aryl *C*), 140.4 (aryl *C*), 138.1 (aryl *C*), 129.5 (aryl *C*), 124.3 (aryl *C*), 122.6 (ring *C*), 118.8 (ring *C*), 115.7 (ring *C*), 115.1 (ring *C*), 114.5 (ring *C*), 35.0 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 33.9 ($C(CH_3)_3$), 33.2 ($C(CH_3)_3$), 20.8 (tolylCH_3), 16.3 (pyCH_3). IR (KBr, cm^{-1}): ν 2961 (s), 1605 (m), 1502 (m), 1451 (m), 1384 (s), 1260 (s), 1091 (s), 1019 (s), 799 (s). Anal. Calcd for $C_{47}H_{72}N_2OTh$: C, 61.82; H, 7.95; N, 3.07. Found: C, 61.72; H, 7.98; N, 3.05.

4.4.2. Method B. 4.4.2.1. NMR Scale. A C_6D_6 (0.3 mL) solution of 2-methylpyridine *N*-oxide (2.2 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}N(p\text{-tolyl})$ (**1**; 16 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The resonances due to **4** were observed by ^1H NMR spectroscopy (100% conversion).

4.5. Reaction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}N(p\text{-tolyl})$ (1) with *p*-Toluidine. *NMR Scale.* To a J. Young NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}N(p\text{-tolyl})$ (**1**; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL), *p*-toluidine (2.2 mg, 0.02 mmol) was added. The resonances due to $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(NH\text{-}p\text{-tolyl})_2$ (**5**) (^1H NMR (C_6D_6): δ 7.06 (d, J = 8.0 Hz, 4H, aryl), 6.84 (d, J = 8.0 Hz, 4H, aryl), 6.58 (s, 4H, ring C*H*), 5.07 (s, 2H, N*H*), 2.22 (s, 6H, tolylCH_3), 1.42 (s, 36H, $(CH_3)_3C$), 1.41 (s, 18H, $(CH_3)_3C$))[9] were observed by ^1H NMR spectroscopy (100% conversion).

4.6. Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(NH\text{-}p\text{-tolyl})(NPh_2)$ (6). *4.6.1. Method A.* This compound was prepared as colorless crystals from the reaction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th{=}N(p\text{-tolyl})$ (**1**; 500 mg, 0.622 mmol) and Ph_2NH (106 mg, 0.622 mmol) in toluene (15 mL) and recrystallization from an *n*-hexane solution by a procedure similar to that in the synthesis of **2**. Yield: 521

DOI: 10.1021/acs.organomet.5b00454
Organometallics 2015, 34, 3637−3647

mg (86%). M.p.: 82−84 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.26 (m, 8H, phenyl), 7.12 (m, 2H, phenyl), 7.08 (m, 2H, phenyl), 6.96 (m, 2H, phenyl), 6.85 (d, J = 3.2 Hz, 2H, ring CH), 6.66 (d, J = 3.2 Hz, 2H, ring CH), 5.73 (s, 1H, NH), 2.26 (s, 3H, tolylCH_3), 1.48 (s, 18H, (CH_3)$_3$C), 1.37 (s, 18H, (CH_3)$_3$C), 1.15 (s, 18H, (CH_3)$_3$C). ^{13}C{^{1}H} NMR (C_6D_6): δ 154.8 (phenyl C), 154.4 (phenyl C), 147.4 (phenyl C), 143.9 (phenyl C), 129.7 (phenyl C), 129.3 (phenyl C), 128.3 (phenyl C), 120.9 (phenyl C), 119.5 (ring C), 118.2 (ring C), 118.0 (ring C), 117.8 (ring C), 117.2 (ring C), 35.3 (C(CH$_3$)$_3$), 35.2 (C(CH$_3$)$_3$), 35.0 (C(CH$_3$)$_3$), 34.2 (C(CH$_3$)$_3$), 33.9 (C(CH$_3$)$_3$), 32.8 (C(CH$_3$)$_3$), 20.5 (tolyl$C$H$_3$); four phenyl C resonances overlapped. IR (KBr, cm^{-1}): ν 2961 (s), 1583 (m), 1497 (m), 1259 (s), 1090 (s), 1019 (s), 799 (s). Anal. Calcd for $C_{53}H_{76}N_2Th$: C, 65.41; H, 7.87; N, 2.88. Found: C, 65.42; H, 7.68; N, 3.03.

4.6.2. Method B. NMR Scale. To a J. Young NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th=N(*p*-tolyl) (**1**; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL), Ph_2NH (3.4 mg, 0.02 mmol) was added. The resonances due to **6** were observed by ^{1}H NMR spectroscopy (100% conversion in 10 min). When the NMR sample was heated over 80 °C, an equilibrium between diamide **6** and imido **1** was observed by ^{1}H NMR spectroscopy; however, we also observed some additional resonances attributable to small amounts of unidentified (decomposed) complexes, suggesting that complex **6** exhibits moderate stability above 80 °C precluding a closer evaluation of this equilibrium at variable temperatures.

4.7. Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(NH-*p*-tolyl)(NPh$_2$) (6) with *p*-Toluidine. *4.7.1. NMR Scale.* To a J. Young NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(NH-*p*-tolyl)(NPh$_2$) (**6**; 20 mg, 0.02 mmol) and C_6D_6 (0.5 mL), *p*-toluidine (2.2 mg, 0.02 mmol) was added. The mixture was kept at 70 °C for 1 day, and resonances due to **5** along with those of Ph_2NH (^{1}H NMR (C_6D_6): δ 7.18 (m, 4H, Ph), 6.84 (m, 6H, Ph), 4.98 (s, 1H, NH)) were observed by ^{1}H NMR spectroscopy (100% conversion).

4.8. Preparation of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(H)[N(*p*-tolyl)B-(C$_8$H$_{14}$)] (7). *4.8.1. Method A.* This compound was prepared as colorless crystals from the reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th=N(*p*-tolyl) (**1**; 500 mg, 0.622 mmol) and 9-BBN (76 mg, 0.622 mmol) in toluene (15 mL) and recrystallization from an *n*-hexane solution by a procedure similar to that in the synthesis of **2**. Yield: 426 mg (74%). M.p.: 140−142 °C (dec.). The NMR spectrum showed that there were two isomers in C_6D_6 solution. *Syn* isomer **7a**: ^{1}H NMR (C_6D_6): δ 19.28 (s, 1H, ThH), 7.87 (s, 2H, phenyl), 6.96 (d, J = 7.5 Hz, 2H, phenyl), 6.08 (m, 2H, NBCH), 5.99 (d, J = 3.0 Hz, 2H, ring CH), 5.92 (d, J = 3.0 Hz, 2H, ring CH), 2.38−1.73 (m, 12H, CH_2), 2.20 (s, 3H, tolylCH_3), 1.61 (s, 18H, (CH_3)$_3$C), 1.57 (s, 18H, (CH_3)$_3$C), 1.41 (s, 18H, (CH_3)$_3$C). ^{13}C{^{1}H} NMR (C_6D_6): δ 139.3 (phenyl C), 133.4 (phenyl C), 129.4 (phenyl C), 125.7 (phenyl C), 122.9 (ring C), 117.2 (ring C), 115.2 (ring C), 114.8 (ring C), 112.3 (ring C), 35.2 (C(CH$_3$)$_3$), 35.1 (C(CH$_3$)$_3$), 34.8 (C(CH$_3$)$_3$), 34.3 (C(CH$_3$)$_3$), 33.6 (C(CH$_3$)$_3$), 32.2 (C(CH$_3$)$_3$), 27.0 (CH), 24.1 (CH$_2$), 23.8 (CH$_2$), 23.6 (CH$_2$), 20.5 (tolylCH$_3$). ^{11}B NMR (C_6D_6): δ −2.95. *Anti* isomer **7b**: ^{1}H NMR (C_6D_6): δ 16.82 (s, 1H, ThH), 7.32 (d, J = 8.0 Hz, 2H, phenyl), 7.02 (d, J = 8.0 Hz, 2H, phenyl), 6.48 (m, 2H, NBCH), 6.34 (d, J = 3.3 Hz, 2H, ring CH), 6.11 (d, J = 3.3 Hz, 2H, ring CH), 2.38−1.73 (m, 12H, CH_2), 2.35 (s, 3H, tolylCH_3), 1.51 (s, 18H, (CH_3)$_3$C), 1.38 (s, 18H, (CH_3)$_3$C), 1.31 (s, 18H, (CH_3)$_3$C). ^{13}C{^{1}H} NMR (C_6D_6): δ 139.3 (phenyl C), 133.4 (phenyl C), 129.4 (phenyl C), 125.7 (phenyl C), 122.9 (ring C), 117.2 (ring C), 115.2 (ring C), 114.8 (ring C), 112.3 (ring C), 35.2 (C(CH$_3$)$_3$), 35.1 (C(CH$_3$)$_3$), 34.8 (C(CH$_3$)$_3$), 34.3 (C(CH$_3$)$_3$), 33.6 (C(CH$_3$)$_3$), 32.2 (C(CH$_3$)$_3$), 27.0 (CH), 24.1 (CH$_2$), 23.8 (CH$_2$), 23.6 (CH$_2$), 20.5 (tolylCH$_3$). ^{11}B NMR (C_6D_6): δ −2.95. IR (KBr, cm^{-1}): ν 2962 (s), 1448 (m), 1384 (s), 1260 (s), 1090 (s), 1019 (s), 798 (s). Anal. Calcd for $C_{49}H_{80}$NBTh: C, 63.55; H, 8.71; N, 1.51. Found: C, 63.52; H, 8.82; N, 1.43.

Note that the NMR spectra of **7a** and **7b** could not be assigned unambiguously. However, in the similar complex [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(H)[N(*p*-tolyl)SiH$_2$Ph] the resonances of Th-H at δ = 18.07 and 16.93 ppm could be attributed to the *syn* and *anti* isomers, respectively,[11] and we therefore assigned the Th−H groups and the other resonances in **7a** and **7b** accordingly. The ratio of **7a**/**7b** is ca. 1:1.1. The mixture of **7a** and **7b** could not be isomerized to one isomer, and the spectrum did not show any change even after heating at 100 °C for 1 week in C_6D_6, which was monitored by ^{1}H NMR spectroscopy in a J. Young NMR tube.

4.8.2. Method B. NMR Scale. To a J. Young NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th=N(*p*-tolyl) (**1**; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL), an excess of 9-BBN (2.5 mg, 0.02 mmol) was added. The resonances due to **7** (**7a** and **7b**) were observed by ^{1}H NMR spectroscopy (100% conversion in 10 min).

4.9. Preparation of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(Cl)[N(*p*-tolyl)-SiH$_2$Ph] (8). *4.9.1. Method A.* This compound was prepared as colorless crystals from the reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th=N(*p*-tolyl) (**1**; 500 mg, 0.622 mmol) and $PhSiH_2Cl$ (90 mg, 0.622 mmol) in toluene (15 mL) and recrystallization from an *n*-hexane solution by a procedure similar to that in the synthesis of **2**. Yield: 542 mg (92%). M.p.: 142−144 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.60 (m, 2H, phenyl), 7.30 (d, J = 8.0 Hz, 2H, phenyl), 7.08 (m, 3H, phenyl), 6.95 (d, J = 8.0 Hz, 2H, phenyl), 6.58 (d, J = 3.4 Hz, 2H, ring CH), 6.50 (d, J = 3.4 Hz, 2H, ring CH), 5.59 (s, 2H, SiH_2), 2.11 (s, 3H, tolylCH_3), 1.61 (s, 18H, (CH_3)$_3$C), 1.41 (s, 18H, (CH_3)$_3$C), 1.40 (s, 18H, (CH_3)$_3$C). ^{13}C{^{1}H} NMR (C_6D_6): δ 147.6 (phenyl C), 145.5 (phenyl C), 135.7 (phenyl C), 132.6 (phenyl C), 130.2 (phenyl C), 130.1 (phenyl C), 129.5 (phenyl C), 129.1 (phenyl C), 125.6 (ring C), 125.4 (ring C), 119.6 (ring C), 119.2 (ring C), 117.6 (ring C), 35.3 (C(CH$_3$)$_3$), 35.2 (C(CH$_3$)$_3$), 35.0 (C(CH$_3$)$_3$), 34.4 (C(CH$_3$)$_3$), 34.0 (C(CH$_3$)$_3$), 32.7 (C(CH$_3$)$_3$), 20.4 (tolylCH$_3$). IR (KBr, cm^{-1}): ν 2961 (s), 2125 (w), 1498 (m), 1383 (s), 1260 (s), 1018 (s), 1018 (s), 799 (s). Anal. Calcd for $C_{47}H_{72}$NClSiTh: C, 59.63; H, 7.67; N, 1.48. Found: C, 59.52; H, 7.82; N, 1.43.

4.9.2. Method B. 4.9.2.1. NMR Scale. To a J. Young NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th=N(*p*-tolyl) (**1**; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL), an excess of $PhSiH_2Cl$ was added. The resonances due to **8** were observed by ^{1}H NMR spectroscopy (100% conversion in 10 min).

4.10. Preparation of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th[N(*p*-tolyl)Se-Se] (9). *4.10.1. Method A.* This compound was prepared as orange crystals from the reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th=N(*p*-tolyl) (**1**; 500 mg, 0.622 mmol) and selenium (98 mg, 1.244 mmol) in toluene (15 mL) and recrystallization from an *n*-hexane solution by a procedure similar to that in the synthesis of **2**. Yield: 478 mg (80%). M.p.: 160−162 °C (dec). ^{1}H NMR (C_6D_6): δ 7.37 (d, J = 8.2 Hz, 2H, phenyl), 7.01 (d, J = 8.2 Hz, 2H, phenyl), 6.63 (br s, 4H, ring CH), 2.19 (s, 3H, tolylCH_3), 1.55 (s, 18H, (CH_3)$_3$C), 1.37 (s, 36H, (CH_3)$_3$C). ^{13}C{^{1}H} NMR (C_6D_6): δ 155.9 (phenyl C), 129.7 (phenyl C), 129.2 (phenyl C), 129.0 (phenyl C), 122.0 (ring C), 119.0 (ring C), 115.9 (ring C), 35.2 (C(CH$_3$)$_3$), 34.6 (C(CH$_3$)$_3$), 34.5 (C(CH$_3$)$_3$), 32.8 (C(CH$_3$)$_3$), 20.5 (tolylCH$_3$). IR (KBr, cm^{-1}): ν 2958 (s), 1604 (m), 1496 (s), 1360 (s), 1238 (s), 1107 (s), 1020 (s), 808 (s). Anal. Calcd for $C_{41}H_{65}NSe_2Th$: C,51.19; H,6.81; N,1.46. Found: C, 51.17; H, 6.78; N, 1.53.

4.10.2. Method B. NMR Scale. To a J. Young NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th=N(*p*-tolyl) (**1**; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL), selenium (3.2 mg, 0.04 mmol) was added. The NMR sample was maintained at room temperature for 2 days, and the resonances due to **9** were observed by ^{1}H NMR spectroscopy (100% conversion).

4.11. Preparation of {[η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]Th(SePh)}$_2$[μ-N(*p*-tolyl)]$_2$ (10). A toluene (5 mL) solution of PhSeSePh (194 mg, 0.622 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=N(*p*-tolyl) (**1**; 500 mg, 0.622 mmol). After this solution was heated at 70 °C overnight without stirring, colorless crystals were isolated from the solution, which were identified as **10** by X-ray diffraction analysis. Yield: 429 mg (95%). M.p.: 230−232 °C (dec.). IR (KBr, cm^{-1}): ν 2961 (s), 1573 (w), 1486 (s), 1384 (s), 1259 (s), 1242 (s), 1091 (s), 1019 (s), 876 (s), 799 (s). Anal. Calcd for $C_{60}H_{82}N_2Se_2Th_2$: C, 49.59; H, 5.69; N, 1.93. Found: C, 49.52; H, 5.68; N, 2.01. This compound was insoluble in deuterated solvents such as pyrdine, THF, toluene, $CDCl_3$, and CD_2Cl_2, which made the characterization by NMR spectroscopy infeasible.

DOI: 10.1021/acs.organomet.5b00454
Organometallics 2015, 34, 3637−3647

The solvent of the filtrate was removed. The residue was extracted with *n*-hexane (10 mL × 2) and filtered. The volume of the filtrate was reduced to ca. 2 mL, colorless crystals, which were identified as (2,3,5-$(Me_3C)_3C_5H_2)_2$ (^{1}H NMR (C_6D_6): δ 6.48 (s, 4H, C*H*), 1.38 (s, 36H, $(CH_3)_3C$), 1.01 (s, 18H, $(CH_3)_3C$))[3v] by ^{1}H NMR spectroscopy, were isolated in 70% yield (101 mg) when this solution stood at −20 °C for 2 days.

4.12. Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th═N(*p*-tolyl) (1) with PhSeSePh. *NMR Scale.* To a J. Young NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th═N(*p*-tolyl) (1; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL), PhSeSePh (6.2 mg, 0.02 mmol) was added. The mixture was kept at 70 °C overnight, a colorless precipitate was observed (formation of compound **10**). In addition, the resonances due to **1** disappeared, and only resonances attributed to (2,3,5-$(Me_3C)_3C_5H_2)_2$ were observed by ^{1}H NMR spectroscopy (100% conversion).

4.13. Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[N(*p*-tolyl)-CH_2C(Me)═C(OMe)O] (11). *4.13.1. Method A.* This compound was prepared as colorless crystals from the reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th═N(*p*-tolyl) (**1**; 500 mg, 0.622 mmol) and MMA (90 mg, 0.622 mmol) in toluene (15 mL) and recrystallization from an *n*-hexane solution by a procedure similar to that in the synthesis of **2**. Yield: 449 mg (80%). M.p.: 226−228 °C (dec). ^{1}H NMR (C_6D_6): δ 7.20 (d, J = 8.0 Hz, 2H, phenyl), 6.83 (d, J = 8.0 Hz, 2H, phenyl), 6.55 (d, J = 3.4 Hz, 2H, ring C*H*), 6.44 (d, J = 3.4 Hz, 2H, ring C*H*), 4.15 (s, 2H, CH_2), 3.62 (s, 3H, OCH_3), 2.26 (s, 3H, tolylCH_3), 2.09 (s, 3H, C═CCH_3), 1.53 (s, 18H, $(CH_3)_3C$), 1.41 (s, 18H, $(CH_3)_3C$), 1.33 (s, 18H, $(CH_3)_3C$). ^{13}C{^{1}H} NMR (C_6D_6): δ 158.6 (C═CO), 153.2 (phenyl *C*), 144.9 (phenyl *C*), 144.1 (phenyl *C*), 144.0 (phenyl *C*), 130.4 (ring *C*), 126.9 (ring *C*), 118.5 (ring *C*), 117.3 (ring *C*), 115.8 (ring *C*), 85.5 (*C*═CO), 55.0 (OCH_3), 54.8 (NCH_2), 35.1 ($C(CH_3)_3$), 34.9 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 33.8 ($C(CH_3)_3$), 32.8 ($C(CH_3)_3$), 20.7 (tolylCH_3), 15.0 (C═CCH_3). IR (KBr, cm^{-1}): ν 2960 (s), 1737 (w), 1620 (m), 1521 (s), 1462 (s), 1361 (s), 1257 (s), 1093 (s), 1022 (s), 806 (s). Anal. Calcd for $C_{46}H_{73}NO_2Th$: C,61.11; H,8.14; N,1.55. Found: C, 61.12; H, 8.08; N, 1.53.

4.13.2. Method B. 4.13.2.1. NMR Scale. A C_6D_6 (0.3 mL) solution of MMA (2.9 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═N(*p*-tolyl) (**1**; 16 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The resonances due to **11** were observed by ^{1}H NMR spectroscopy (100% conversion).

4.14. X-ray Crystallography. Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart APEX II CCD diffractometer at 100(2) K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.[23] All structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL-97 program package.[24] The hydride atom in **7a** was located in the difference-Fourier map and refined isotropically. All other hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **2**−**4** and **6**−**11** are summarized in the Supporting Information (Tables S1 and S2). Selected bond lengths and angles are listed in Table 1.

4.15. Computational Methods. All calculations were carried out with the Gaussian 09 program (G09),[25] employing the B3PW91 functional, plus a polarizable continuum model (PCM) and D3[26] (denoted as B3PW91-PCM+D3), with a standard 6-31G(d) basis set for C, H, N, and O elements and Stuttgart RLC ECP from the EMSL basis set exchange (https://bse.pnl.gov/bse/portal) for Th,[27] 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) was 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

Structures of stationary points along the reaction path; crystal parameters for compounds **2**−**4** and **6**−**11**; Cartesian coordinates of all stationary points optimized at the B3PW91-PCM+D3 level, in XYZ format; and X-ray crystallographic data, in CIF format, for compounds **2**−**4** and **6**−**11**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00454.

■ AUTHOR INFORMATION

Corresponding Authors

*(G.Z.) E-mail: gzi@bnu.edu.cn.
*(D.-C.F.) E-mail: dcfang@bnu.edu.cn.
*(M.D.W.) E-mail: mwalter@tu-bs.de.

Author Contributions

§E.Z. and W.R. contributed equally to this work.

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, and 21373030), the Program for Changjiang Scholars and Innovative Research Team in University, and the Deutsche Forschungsgemeinschaft (DFG) through the Emmy-Noether and Heisenberg programs (WA 2513/2 and WA 2513/6, respectively).

■ REFERENCES

(1) For selected recent reviews, see: (a) Ephritikhine, M. *Dalton Trans.* **2006**, 2501−2516. (b) Barnea, E.; Eisen, M. S. *Coord. Chem. Rev.* **2006**, *250*, 855−899. (c) Fox, A. R.; Bart, S. C.; Meyer, K.; Cummins, C. C. *Nature* **2008**, *455*, 341−349. (d) Andrea, T.; Eisen, M. S. *Chem. Soc. Rev.* **2008**, *37*, 550−567. (e) Graves, C. R.; Kiplinger, J. L. *Chem. Commun.* **2009**, 3831−3853. (f) Hayton, T. W. *Dalton Trans.* **2010**, *39*, 1145−1158. (g) Arnold, P. L. *Chem. Commun.* **2011**, *47*, 9005−9010. (h) Hayton, T. W. *Chem. Commun.* **2013**, *49*, 2956−2973. (i) Hayton, T. W. *Nat. Chem.* **2013**, *5*, 451−452. (j) Zi, G.-F.; Zhang, Z.-B.; Xiang, L.; Wang, Q.-W. *Chin. J. Org. Chem.* **2006**, *26*, 1606−1611. (k) Ren, W.; Zhao, N.; Chen, L.; Zi, G. *Youji Huaxue* **2013**, *33*, 1121−1136. (l) Zi, G. *Sci. China: Chem.* **2014**, *57*, 1064−1072.

(2) For selected papers on actinide nonmetallocenes containing terminal imido groups, see: (a) Burns, C. J.; Smith, W. H.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 3237−3239. (b) Brown, D. R.; Denning, R. G. *Inorg. Chem.* **1996**, *35*, 6158−6163. (c) Roussel, P.; Boaretto, R.; Kingsley, A. J.; Alcock, N. W.; Scott, P. *J. Chem. Soc., Dalton Trans.* **2002**, 1423−1428. (d) Castro-Rodriguez, I.; Olsen, K.; Gantzel, P.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 4565−4571. (e) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Palmer, P. D.; Batista, E. R.; Hay, P. J. *Science* **2005**, *310*, 1941−1943. (f) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Batista, E. R.; Hay, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 10549−10559. (g) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Batista, E. R. *J. Am. Chem. Soc.* **2006**, *128*, 12622−12623. (h) Castro-Rodriguez, I.; Nakai, H.; Meyer, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2389−2392. (i) Spencer, L. P.; Yang, P.; Scott, B. L.; Batista, E. R.; Boncella, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 2930−2931. (j) Bart, S. C.; Anthon, C.; Heinemann, F. W.; Bill, E.; Edelstein, N. M.; Meyer, K. *J. Am. Chem. Soc.* **2008**, *130*, 12536−12546. (k) Spencer, L. P.; Schelter, E. J.; Yang, P.; Gdula, R. L.; Scott, B. L.; Thompson, J. D.; Kiplinger, J. L.; Batista, E. R.; Boncella, J. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3795−3798. (l) Spencer, L. P.; Yang, P.; Scott, B. L.; Batista, E. R.; Boncella, J. M. *Inorg. Chem.* **2009**, *48*, 2693−2700. (m) Spencer,

DOI: 10.1021/acs.organomet.5b00454
Organometallics 2015, 34, 3637−3647

L. P.; Yang, P.; Scott, B. L.; Batista, E. R.; Boncella, J. M. *Inorg. Chem.* **2009**, *48*, 11615−11623. (n) Swartz, D. L., II; Spencer, L. P.; Scott, B. L.; Odom, A. L.; Boncella, J. M. *Dalton Trans.* **2010**, *39*, 6841−6846. (o) Seaman, L. A.; Fortier, S.; Wu, G.; Hayton, T. W. *Inorg. Chem.* **2011**, *50*, 636−646. (p) Jilek, R. E.; Spencer, L. P.; Kuiper, D. L.; Scott, B. L.; Williams, U. J.; Kikkawa, J. M.; Schelter, E. J.; Boncella, J. M. *Inorg. Chem.* **2011**, *50*, 4235−4237. (q) Matson, E. M.; Fanwick, P. E.; Bart, S. C. *Eur. J. Inorg. Chem.* **2012**, *2012*, 5471−5478. (r) Matson, E. M.; Crestani, M. G.; Fanwick, P. E.; Bart, S. C. *Dalton Trans.* **2012**, *41*, 7952−7958. (s) Lam, O. P.; Franke, S. M.; Nakai, H.; Heinemann, F. W.; Hieringer, W.; Meyer, K. *Inorg. Chem.* **2012**, *51*, 6190−6199. (t) Camp, C.; Pécaut, J.; Mazzanti, M. *J. Am. Chem. Soc.* **2013**, *135*, 12101−12111. (u) King, D. M.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Science* **2012**, *337*, 717−720. (v) King, D. M.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Nat. Chem.* **2013**, *5*, 482−488. (w) King, D. M.; McMaster, J.; Tuna, F.; McInnes, E. J. L.; Lewis, W.; Blake, A. J.; Liddle, S. T. *J. Am. Chem. Soc.* **2014**, *136*, 5619−5622.

(3) For selected papers on actinide metallocenes containing terminal imido groups, see: (a) Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 1853−1854. (b) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514−516. (c) Rosen, R. K.; Andersen, R. A.; Edelstein, N. M. *J. Am. Chem. Soc.* **1990**, *112*, 4588−4590. (d) Arney, D. S. J.; Burns, C. J.; Smith, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 10068−10069. (e) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 9840−9841. (f) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448−9460. (g) Straub, T.; Frank, W.; Reiss, G. J.; Eisen, M. S. *J. Chem. Soc., Dalton Trans.* **1996**, 2541−2546. (h) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 959−960. (i) Peters, R. G.; Warner, B. P.; Scott, B. L.; Burns, C. J. *Organometallics* **1999**, *18*, 2587−2589. (j) Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5017−5035. (k) Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Chem. Commun.* **2002**, 30−31. (l) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Chem. Commun.* **2005**, 4681−4683. (m) Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2007**, *129*, 11914−11915. (n) Graves, C. R.; Yang, P.; Kozimor, S. A.; Vaughn, A. E.; Clark, D. L.; Conradson, S. D.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Hay, P. J.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 5272−5285. (o) Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. *Organometallics* **2008**, *27*, 3335−3337. (p) Graves, C. R.; Vaughn, A. E.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Morris, D. E.; Kiplinger, J. L. *Inorg. Chem.* **2008**, *47*, 11879−11891. (q) Spencer, L. P.; Gdula, R. L.; Hayton, T. W.; Scott, B. L.; Boncella, J. M. *Chem. Commun.* **2008**, 4986−4988. (r) Evans, W. J.; Traina, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2009**, *131*, 17473−17481. (s) Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. *Chem. Commun.* **2009**, 776−778. (t) Evans, W. J.; Montalvo, E.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. *Inorg. Chem.* **2010**, *49*, 222−228. (u) Thomson, R. K.; Cantat, T.; Scott, B. L.; Morris, D. E.; Batista, E. R.; Kiplinger, J. L. *Nat. Chem.* **2010**, *2*, 723−729. (v) Zi, G.; Jia, L.; Werkema, E. L.; Walter, M. D.; Gottfriedsen, J. P.; Andersen, R. A. *Organometallics* **2005**, *24*, 4251−4262. (w) Zi, G.; Blosch, L. L.; Jia, L.; Andersen, R. A. *Organometallics* **2005**, *24*, 4602−4612.

(4) (a) Haskel, A.; Straub, T.; Eisen, M. S. *Organometallics* **1996**, *15*, 3773−3775. (b) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 814−818. (c) Schelter, E. J.; Morris, D. E.; Scott, B. L.; Kiplinger, J. L. *Chem. Commun.* **2007**, 1029−1031.

(5) Selected papers on scandium imido complexes: (a) Scott, J.; Basuli, F.; Fout, A. R.; Huffman, J. C.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 8502−8505. (b) Lu, E.; Li, Y.; Chen, Y. *Chem. Commun.* **2010**, *46*, 4469−4471. (c) Lu, E.; Chu, J.; Borzov, M.; Chen, Y.; Li, G. *Chem. Commun.* **2011**, *47*, 743−745. (d) Chu, J.; Lu, E.; Liu, Z.; Chen, Y.; Leng, X.; Song, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 7677−7680. (e) Lu, E.; Zhou, Q.; Li, Y.; Chu, J.; Chen, Y.; Leng, X.; Sun, J. *Chem. Commun.* **2012**, *48*, 3403−3405. (f) Jian, Z.; Rong, W.; Mou, Z.; Pan, Y.; Xie, H.; Cui, D. *Chem. Commun.* **2012**, *48*, 7516−7518. (g) Wicker, B. F.; Fan, H.; Hickey, A. K.; Crestani, M. G.; Scott, J.; Pink, M.; Mindiola, D. J. *J. Am. Chem. Soc.* **2012**, *134*, 20081−20096. (h) Chu, T.; Piers, W. E.; Dutton, J. L.; Parvez, M. *Organometallics* **2013**, *32*, 1159−1165. (i) Chu, J.; Lu, E.; Chen, Y.; Leng, X. *Organometallics* **2013**, *32*, 1137−1140. (j) Rong, W.; Cheng, J.; Mou, Z.; Xie, H.; Cui, D. *Organometallics* **2013**, *32*, 5523−5529. (k) Chu, J.; Han, X.; Kefalidis, C. E.; Zhou, J.; Maron, L.; Leng, X.; Chen, Y. *J. Am. Chem. Soc.* **2014**, *136*, 10894−10897. (l) Chu, J.; Kefalidis, C. E.; Maron, L.; Leng, X.; Chen, Y. *J. Am. Chem. Soc.* **2013**, *135*, 8165−8168.

(6) Selected papers on group 4 imido complexes: (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729−8731. (b) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731−8733. (c) Hill, J. E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664−665. (d) Roesky, H. W.; Voelker, H.; Witt, M.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 669−670. (e) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705−3723. (f) Dunn, S. C.; Batsanov, A. S.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2007−2008. (g) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 2179−2180. (h) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 974−985. (i) Polse, J. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 13405−13414. (j) Hoyt, H. M.; Michael, F. E.; Bergman, R. G. *J. Am. Chem. Soc.* **2004**, *126*, 1018−1019. (k) Lian, B.; Spaniol, T. P.; Horrillo-Martínez, P.; Hultzsch, K. C.; Okuda, J. *Eur. J. Inorg. Chem.* **2009**, *2009*, 429−434. (l) Tiong, P. J.; Nova, A.; Clot, E.; Mountford, P. *Chem. Commun.* **2011**, *47*, 3147−3149. (m) Tiong, P. J.; Nova, A.; Schwarz, A. D.; Selby, J. D.; Clot, E.; Mountford, P. *Dalton Trans.* **2012**, *41*, 2277−2288. (n) Schwarz, A. D.; Nielson, A. J.; Kaltsoyannis, N.; Mountford, P. *Chem. Sci.* **2012**, *3*, 819−824.

(7) For selected recent papers on 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. *Organometallics* **2009**, *28*, 672−679. (d) Walensky, J. R.; Martin, R. L.; Ziller, J. W.; Evans, W. J. *Inorg. Chem.* **2010**, *49*, 10007−10012. (e) Ren, W.; Deng, X.; Zi, G.; Fang, D.-C. *Dalton Trans.* **2011**, *40*, 9662−9664. (f) Seaman, L. A.; Pedrick, E. A.; Tsuchiya, T.; Wu, G.; Jakubikova, E.; Hayton, T. W. *Angew. Chem., Int. Ed.* **2013**, *52*, 10589−10592. (g) Gardner, B. M.; Cleaves, P. A.; Kefalidis, C. E.; Fang, J.; Maron, L.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Chem. Sci.* **2014**, *5*, 2489−2497.

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

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

(10) Ren, W.; Zi, G.; Walter, M. D. *Organometallics* **2012**, *31*, 672−679.

(11) Ren, W.; Zhou, E.; Fang, B.; Zi, G.; Fang, D.-C.; Walter, M. D. *Chem. Sci.* **2014**, *5*, 3165−3172.

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

(13) Ren, W.; Song, H.; Zi, G.; Walter, M. D. *Dalton Trans.* **2012**, *41*, 5965−5973.

(14) Pool, J. A.; Scott, B. L.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 1338−1339.

(15) Ren, W.; Lukens, W. W.; Zi, G.; Maron, L.; Walter, M. D. *Chem. Sci.* **2013**, *4*, 1168−1174.

(16) Edelman, M. A.; Hitchcock, P. B.; Hu, J.; Lappert, M. F. *New J. Chem.* **1995**, *19*, 481−489.

(17) Fang, B.; Ren, W.; Hou, G.; Zi, G.; Fang, D.-C.; Maron, L.; Walter, M. D. *J. Am. Chem. Soc.* **2014**, *136*, 17249−17261.

(18) Marsh, R. E.; Kapon, M.; Hu, S.; Herbstein, F. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 62−77.

(19) Fang, B.; Hou, G.; Zi, G.; Fang, D.-C.; Walter, M. D. *Dalton Trans.* **2015**, *44*, 7927−7934.

(20) Ren, W.; Zhao, N.; Chen, L.; Song, H.; Zi, G. *Inorg. Chem. Commun.* **2011**, *14*, 1838−1841.

DOI: 10.1021/acs.organomet.5b00454
Organometallics 2015, 34, 3637−3647

(21) Blake, P. C.; Lappert, M. F.; Taylor, R. G.; Atwood, J. L.; Hunter, W. E.; Zhang, H. *J. Chem. Soc., Dalton Trans.* **1995**, 3335−3341.
(22) Fang, B.; Zhang, L.; Hou, G.; Zi, G.; Fang, D.-C.; Walter, M. D. *Chem. Sci.* **2015**, DOI: 10.1039/c5sc01684c.
(23) Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.
(24) (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., Sect. A* **2008**, *64*, 112−122.
(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.02, Gaussian, Inc.: Wallingford, CT, 2009.
(26) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
(27) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245−1263.

DOI: 10.1021/acs.organomet.5b00454
Organometallics 2015, 34, 3637−3647