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Experimental and Computational Studies on a Base-Free Terminal Uranium Phosphinidene Metallocene

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In memory of Professor Richard A. Andersen, who passed away a year ago.

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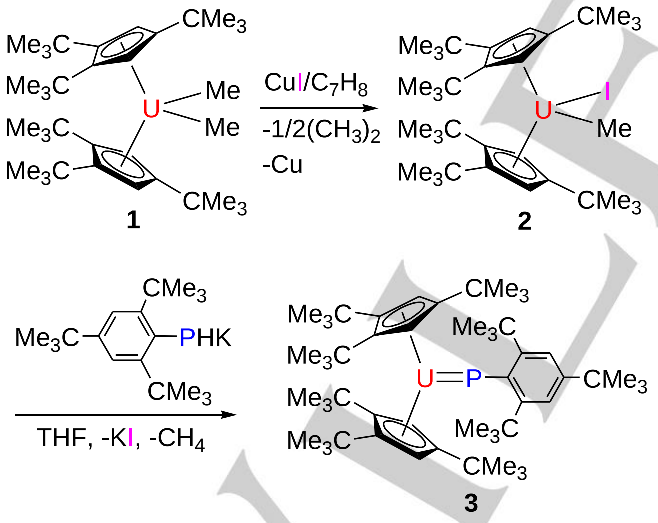
Abstract: The first stable base-free terminal uranium phosphinidene metallocene is presented; and its structure and reactivity have been studied in detail and compared to that of the corresponding thorium derivative. Salt metathesis reaction of the methyl iodide uranium metallocene Cp‴$_2$U(I)Me (**2**, Cp‴ = η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$) with Mes*PHK (Mes* = 2,4,6-(Me$_3$C)$_3$C$_6$H$_2$) in THF yields the base-free terminal uranium phosphinidene metallocene, Cp‴$_2$U=PMes* (**3**). In addition, density functional theory (DFT) studies suggest substantial 5f orbital contributions to the bonding within the uranium phosphinidene [U]=PAr moiety, which results in a more covalent bonding between the [Cp‴$_2$U]$^{2+}$ and [Mes*P]$^{2-}$ fragments than that for the related thorium derivative. This difference in bonding besides steric reasons causes different reactivity patterns for both molecules. Therefore, the uranium derivative **3** may act as a Cp‴$_2$U(II) synthon releasing the phosphinidene moiety (Mes*P:) when treated with alkynes or a variety of hetero-unsaturated molecules such as imines, thiazoles, ketazines, bipy, organic azides, diazene derivatives, ketones, and carbodiimides.

Introduction

For more than 20 years d-transition metal phosphinidene complexes have been extensively studied and various derivatives have been prepared and their intrinsic reactivity and chemical and physical properties are now thoroughly investigated,[1-4] resulting in interesting applications in the synthesis of phosphorus compounds, organometallic derivatives, and new materials.[1-3] Furthermore, because of the high reactivity terminal phosphinidene compounds have been particularly sought-after, since they are also more efficient in phosphorus-element bond synthesis and more useful in catalytic transformations than bridged phosphinidene derivatives.[1-3] So while the field of phosphinidene complexes of d-transition metals has flourished, only a few derivatives containing 5f-elements have emerged over the last two decades.[4,5] The scarcity of actinide derivatives can be traced to the sensitivity of these multiple-bonded actinide complexes to steric effects imposed by the ligand environment at the metal atom,[6] which makes a judicial choice of the employed ligand set imperative. Attributed to these challenges a more detailed reactivity study of these species is still missing.[5] Moreover, this may also present a rewarding endeavor since organoactinide chemistry has not only witnessed a renaissance in recent years attributed to potential applications of organoactinides in small molecule activation and functionalization,[7] but it also addresses the more fundamental question concerning the influence of 5f orbital occupation on bonding and reactivity in general.[8] Several studies have confirmed that already subtle changes in the 5f orbital contributions can have a significant influence on the reactivity of organoactinide compounds.[8] In this context, we compared the reactivity of thorium and uranium metallacyclopropene complexes and noted some remarkable divergence in their reactivity.[9] For example, while the alkyne moiety in the thorium metallacyclopropene Cp‴$_2$Th(η^2-C$_2$Ph$_2$) (Cp‴ = η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$) reacts as a nucleophile towards hetero-unsaturated molecules or as a strong base inducing the intermolecular C-H bond activations,[9e,f] the related uranium metallacyclopropene Cp*$_2$U[η^2-C$_2$(SiMe$_3$)$_2$] (Cp* = η^5-C$_5$Me$_5$) serves as an efficient synthon for the Cp*$_2$U(II) fragment when reacted with unsaturated molecules.[9j] More recently we have also reported on terminal phosphinidene thorium complexes including the first isolable base-free terminal actinide phosphinidene metallocene Cp‴$_2$Th=PMes* (**3′**; Mes* = 2,4,6-(Me$_3$C)$_3$C$_6$H$_2$).[10a] The strong coordination of the phosphinidene moiety in **3′** resulted in unusual reactivity toward various small molecules such as CS$_2$, isothiocyanate, nitriles, isonitriles, and organic azides, yielding carbodithioates, imido complexes, metallaaziridines, and azido compounds.[10a] To evaluate the difference between terminal thorium and uranium phosphinidenes, we set out to prepare the first stable base-free terminal uranium phosphinidene metallocene, Cp‴$_2$U=PMes* (**3**), which indeed shows distinctively different reactivity patterns to those found for its thorium counterpart Cp‴$_2$Th=PMes* (**3′**).

Results and Discussion

Synthesis of Cp'''_2U=PMes* (3). Addition of CuI (1 equiv) to the uranium dimethyl complex Cp'''_2UMe_2 (**1**) in toluene forms the methyl iodide complex $Cp'''_2U(I)Me$ (**2**) in 85% yield (Scheme 1). The molecular structure of **2** is shown in Figure 1, and selected bond distances and angles are listed in Table 1. The U-C(35) distance is 2.423(5) Å, whereas the U-I distance is 2.990(1) Å, and the angle of C(35)-U-I is 92.5(2)º. Subsequent treatment of **2** with 1 equiv of Mes*PHK in THF allows the isolation of the targeted base-free terminal phosphinidene uranium metallocene, Cp'''_2U=PMes* (**3**), in 75% yield (Scheme 1).[11] The molecular structure of **3** is presented in Figure 2, and selected bond distances and angles are given in Table 1. To the best of our knowledge, complex **3** represents the first structurally authenticated base-free terminal phosphinidene uranium metallocene, and therefore constitutes a notable addition to the class of other structurally characterized actinide metallocenes featuring a phosphinidene functionality, Cp'''_2Th=PMes*,[10a] {Cp''_2Th(=PMes*)(ClK)}$_2$ (Cp″ = η^5-1,3-$(Me_3C)_2C_5H_3$),[10c] {Cp''_2Th(=P-2,4,6-$^i Pr_3C_6H_2$)(ClK)}$_2$,[10d] Cp^*_2U(=PMes*)($OPMe_3$),[5b] {[Cp^*_2Th(=P-2,4,6-$^i Pr_3C_6H_2$)(PH-2,4,6-$^i Pr_3C_6H_2$)]K}$_2$,[5g] and [Cp^*_2Th(=P-2,4,6-$^i Pr_3C_6H_2$)(PH-2,4,6-$^i Pr_3C_6H_2$)][K(2,2,2-cryptand)].[5g] The short U-P distance of 2.495(1) Å and the essentially linear U-P-C(35) angle (177.4(1)º) are in line with a U=P double bond.[12] Furthermore, the U-P distance of 2.495(1) Å is only moderately elongated relative to the predicted value by Pyykkö for a U=P double bond (2.36 Å),[13] but it is shorter than those values found for Cp^*_2U(=PMes*)($OPMe_3$) (2.562(3) Å),[5b] [($^i Pr_3SiNCH_2CH_2)_3NU$=PH][K(B15C5)$_2$] (2.613(2) Å),[5c] and [($^i Pr_3SiNCH_2CH_2)_3NU$=PH][Na(12C4)$_2$] (2.685(2) Å).[5f] Overall, these structural parameters observed for **3** fully support the description of a uranium phosphinidene.



Scheme 1. Synthesis of complexes **2** and **3**.

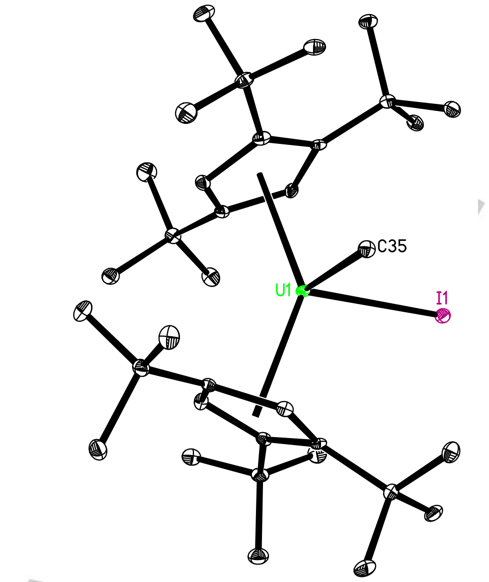


Figure 1. Molecular structure of **2** (thermal ellipsoids drawn at the 35% probability level).

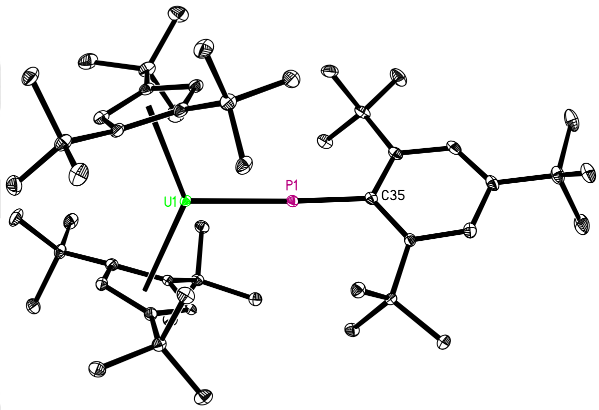


Figure 2. Molecular structure of **3** (thermal ellipsoids drawn at the 35% probability level).

Bonding Studies. Density functional theory (DFT) computations at the B3PW91 level of theory were performed to evaluate the interaction between the $[Cp'''_2U]^{2+}$ and the $[PMes^*]^{2-}$ fragments, which also allows the bonding in **3** to be compared to its thorium analogue Cp'''_2Th=PMes* (**3′**).[10a] The computed structures for **3** and **3′** in gas phase reproduce the experimental solid-state data very well and show that the $[Mes^*P]^{2-}$ fragment is coordinated to the $[Cp'''_2An]^{2+}$ moiety by one An-P σ-bond and two An-P π-bonds, as illustrated in Figure 3. The natural localized molecular orbital (NLMO) analysis (Table 2) performed on **3** reveals that U-P σ-bond, σ(U=P), combines a phosphorus hybrid orbital (73.4%; 78.5% 3s and 21.5% 3p) and a uranium hybrid orbital (25.3%; 55.8% 6d and 26.0% 5f). The two orthogonal U-P π bonds, π_1 and π_2, have similar compositions and consist of a pure 3p phosphorus-based orbital (62.7%) and a uranium hybrid orbital (32.0%; 53.1% 6d and 44.7% 5f) and a pure 3p phosphorus-based orbital (58.9%) and a uranium hybrid orbital (37.1%; 47.2% 6d and 51.1% 5f), respectively. Within this description additional electron density is transferred from the π-orbitals of $[Mes^*P]^{2-}$ fragment to the electron deficient

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metallocene unit $[Cp'''_2U]^{2+}$. Nevertheless, in the related thorium complex **3′**, the metal contribution to the bonding of the Th=PMes* moiety decreases notably (20.6% Th for Th=P σ bond, and 25.2% and 30.9% Th for Th=P π_1 and π_2 bonds, respectively) (Table 2). A direct comparison of the 5f orbital contributions to the bonding in the uranium complex **3** (U=P σ (26.0%) and U=P π bonds (44.7% and 51.1% for π_1 and π_2 bonds, respectively) and its thorium analogue **3′** (15.0% for the Th=P σ bond and 33.9% and 24.0% for the Th=P π_1 and π_2 bonds, respectively) shows a significantly larger 5f orbital contribution in **3** than that in **3′**, which is consistent with the previously investigated systems.[8d,e,9g,j,m] Therefore the thorium derivative shows an increased charge separation, and hence an increased electrostatic interaction between the individual $[Cp'''_2An]^{2+}$ and $[Mes^*P]^{2-}$ fragments, that is, 0.58 for the uranium complex (**3**) and 0.80 for thorium complex (**3′**) (Table 2). The decreased Mayer bond order of the An=P of 1.76 (for **3**) to 1.53 (for **3′**)) (Table 2) points in the same direction. These render the bonding between the metallocene $[Cp'''_2Th]^{2+}$ and the $[Mes^*P]^{2-}$ fragment more ionic, which is also consistent with an increased 5f orbital energy of the thorium atom relative to those of the uranium atom,[8f,g] the efficiency of the π-donation from the π-MO of the phosphinidene fragment to the thorium atom decreases. Hence a different reactivity of the uranium complex **3** can be expected compared to related thorium phosphinidenes.[10,14]

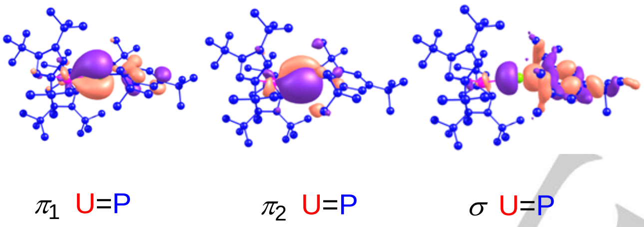
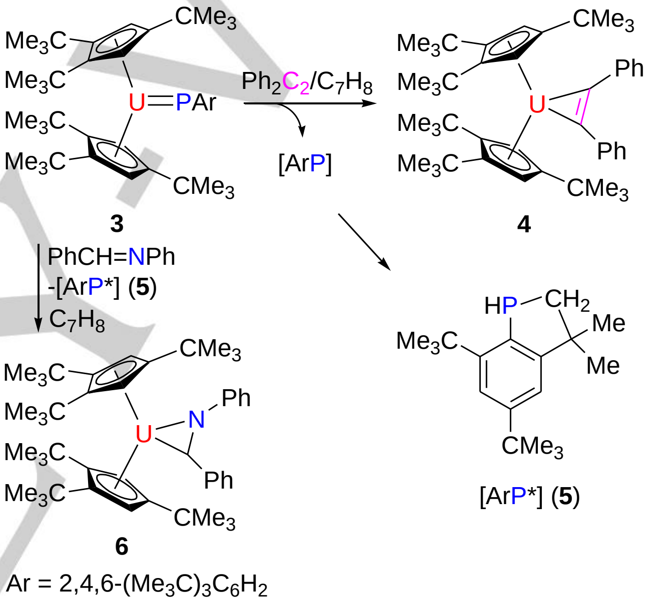


Figure 3. Plots of HOMOs for **3** (the hydrogen atoms have been omitted for clarity).

Reactivity Studies. As previously established for the base-free thorium derivative, $Cp'''_2Th=PMes^*$ (**3′**),[10a] no phosphinidene dissociation occurs when **3** is heated to 100 °C in toluene solution, which is in line with a strong coordination of the phosphinidene moiety to the uranium atom. However, in contrast to the thorium derivatives (see Figure S1),[10,14] the coordinated phosphinidene in the uranium species **3** is susceptible to exchange with internal alkynes. For example, addition of PhC≡CPh at 50 °C yields the - so far unknown – uranium(IV) metallacyclopropene $Cp'''_2U(\eta^2\text{-}C_2Ph_2)$ (**4**) besides the phosphaindane derivative $3,3\text{-}Me_2\text{-}5,7\text{-}{}^tBu_2C_8H_5P$ (**5**) in quantitative conversion (Scheme 2). According to DFT computations, it can be assumed that **3** initially reacts with PhC≡CPh to yield a metallacyclopropene adduct **INT4** (Figure 4), then the phosphinidene $2,4,6\text{-}{}^tBu_3C_6H_2P$ dissociates from **INT4** to give the metallacyclopropene **4**. Finally, the phosphinidene $2,4,6\text{-}{}^tBu_3C_6H_2P$ converts to the phosphaindane $3,3\text{-}Me_2\text{-}5,7\text{-}{}^tBu_2C_8H_5P$ (**5**) *via* C-H bond activation. The energetically favorable (ΔG(298 K) = -152.2 kJ mol^{-1}) formation of **4** + **5** and the overall reaction barrier of $\Delta G^{\ddagger}$(298 K) = 112.4 kJ mol^{-1} agree with the experimental observations. Figure 5 shows the molecular structure of **4**, whereas selected bond distances and angles can be found in Table 1. The C(35)-C(36) distance is 1.342(4) Å, and the U-C distances are 2.318(3) Å for C(35) and 2.331(3) Å for C(36), and the angle of C(35)-U-C(36) is 33.6(1)°. These structural parameters are essentially identical to those observed for the known $Cp^*_2U[\eta^2\text{-}C_2(SiMe_3)_2]$ with the U-C distances of 2.315(9) and 2.350(9) Å, and with a C=C distance of 1.338(11) Å, and a C-N-C angle of 33.3(3)°.[9i] Nevertheless, contrary to the reactivity of the thorium phosphinidene complex $\{Cp''_2Th(=PMes^*)(ClK)\}_2$ toward PhC≡CPh,[10c] no [2+2] cycloaddition product is formed between complex **3** and PhC≡CPh, presumably caused by steric hindrance.[10a] However, while no reaction was observed for the thorium phosphinidene complex $Cp'''_2Th=PMes^*$ (**3′**),[10a] the sterically more encumbered uranium species **3** undergoes a ligand replacement reaction, which cannot be exclusively attributed to steric effects, and the different electronic structures at the metal atoms also need to be taken into considerations.



Scheme 2. Synthesis of complexes **4** and **6**.

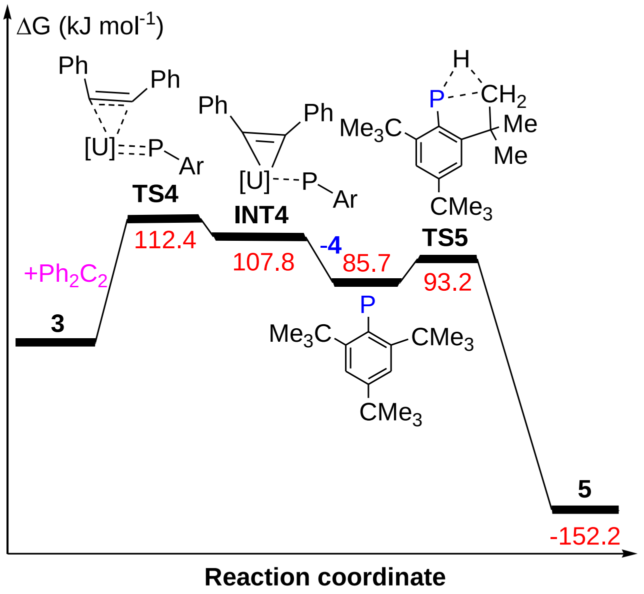


Figure 4. Energy profile (kJ mol^{-1}) for the reaction of **3** + PhC≡CPh (computed at *T* = 298 K). [U] = Cp‴$_2$U. Ar = 2,4,6-^{t}Bu$_3$C$_6$H$_2$.

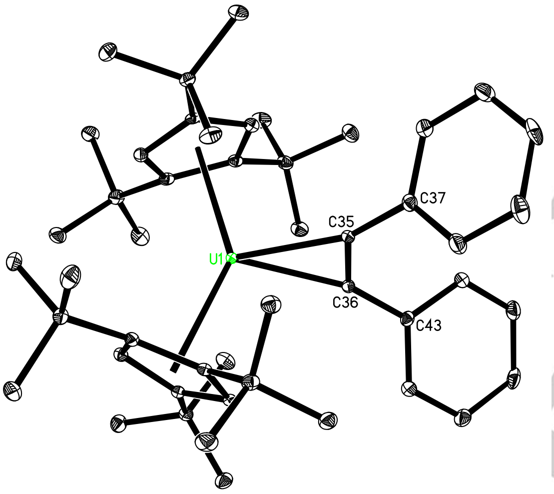


Figure 5. Molecular structure of **4** (thermal ellipsoids drawn at the 35% probability level).

Moreover, hetero-unsaturated organic molecules can also replace the phosphinidene moiety in **3**. For example, contrary to the reactivity of the thorium phosphinidene complex {Cp″$_2$Th(=PMes*)(ClK)}$_2$ toward PhCH=NPh (see Supporting Information, Figure S1),[10c,14] complex **3** reacts with this substrate to yield the metallaaziridine Cp‴$_2$U(η^2-CHPhNPh) (**6**) and the phosphaindane 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) (Scheme 2). Figure 6 shows the molecular structure of **6**, while selected bond distances and angles are provided in Table 1. The U-N and U-C(18) distances are 2.227(6) and 2.439(8) Å, respectively, whereas the N(1)-U-C(18) angle amounts to 35.6(2)º. Also in contrast to the reactivity of the thorium phosphinidene complexes **3′** and {Cp″$_2$Th(=PMes*)(ClK)}$_2$ with thiazole (see Supporting Information, Figure S1),[10b,c] thiazole replaces the phosphinidene fragment in the uranium derivative **3** to yield the six-membered heterocyclic complex Cp‴$_2$U(SCH=CHN=CH) (**7**) and the phosphaindane **5** (Scheme 3). To account for this reactivity we propose a mechanism similar to the reaction with PhCH=NPh, in the first step thiazole substitutes the phosphinidene fragment to yield a metallaaziridine complex, which is, however, unstable and converts *via* C-S cleavage to a zwitterionic intermediate, which then spontaneously forms **7** (Scheme 3). Figure 7 shows the molecular structure of **7** and selected bond distances and angles are listed in Table 1. The U-N and U-C(37) distances amount to 2.243(6) and 2.389(11) Å, respectively, whereas the U-S distance is much longer with 2.813(2) Å. Nevertheless, under similar reaction conditions, treatment of **3** with (Ph$_2$C=N)$_2$ gives a diiminato complex Cp‴$_2$U(N=CPh$_2$)$_2$ (**8**) and phosphaindane 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) in quantitative conversion (Scheme 4). A plausible mechanism may include phosphinidene exchange with (Ph$_2$C=N)$_2$ to also furnish a metallaaziridine, which opens *via* N-N cleavage to **8** (Scheme 4). The solid-state molecular structure of **8** is provided in Figure 8, while selected bond distances and angles are given in Table 1. The U-N distances are 2.214(3) Å for N(1) and 2.227(3) Å for N(2), and the U-N-C angles are 177.0(3)º for N(1) and 176.6(3)º for N(2), and the N(1)-U-N(2) angle is 111.4(1)º. These structural parameters may be compared to those found in Cp*$_2$U(N=CPh$_2$)$_2$ with the U-N distances of 2.172(7) and 2.169(6) Å, and the U-N-C angles of 172.8(6) and 174.7(6)º, and the N-U-N angle of 107.2(2)º.[9j] In analogy to the bis(phosphide) thorium complex [H$_2$B(3-Mes-C$_3$H$_2$N$_2$)$_2$]$_2$Th(PHMes)$_2$ (Mes = 2,4,6-Me$_3$Ph) towards bipy,[15] reductive elimination occurs in the reaction of compound **3** and bipy, that is, the known compound Cp‴$_2$U(bipy) (**9**)[6a] is accessible by the addition of 2,2’-bipyridine (bipy) to compound **3** (Scheme 4). Figure 9 presents the molecular structure of **9** and selected bond distances and angles are listed in Table 1. The U-N(1) and U-N(1A) distances are 2.420(6) Å, and the N(1)-U-N(1A) angle is 66.1(2)º.

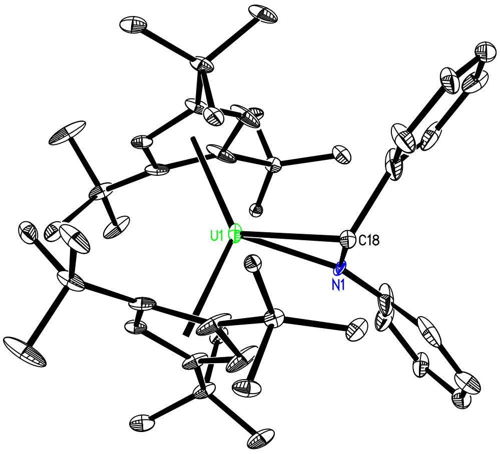
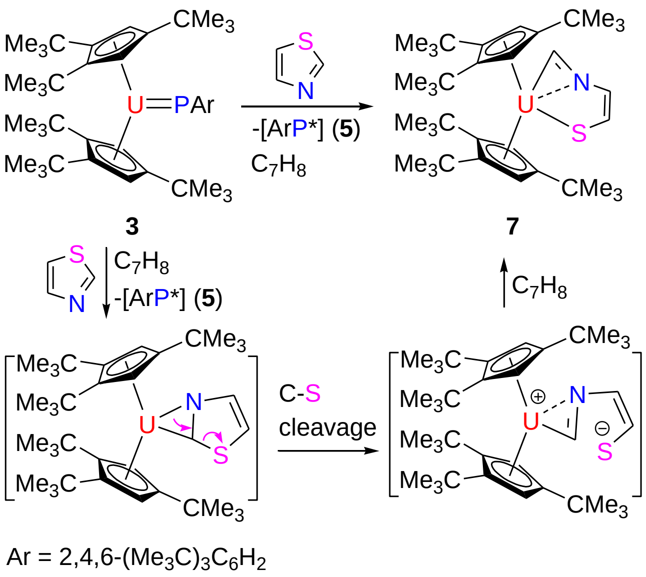


Figure 6. Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level).



Scheme 3. Synthesis of complex **7**.

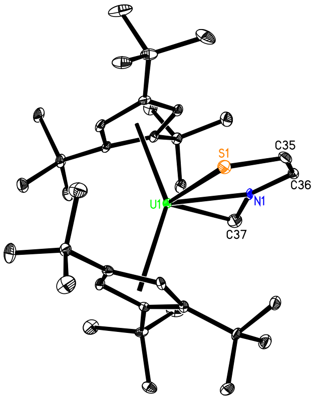
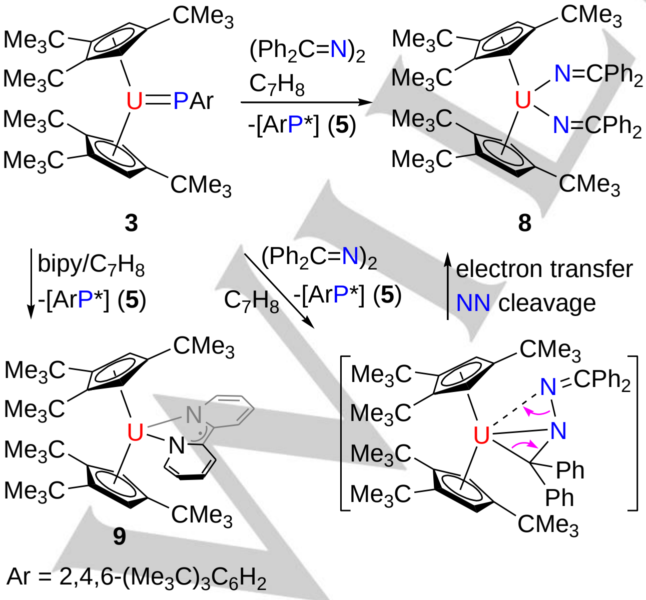


Figure 7. Molecular structure of **7** (thermal ellipsoids drawn at the 35% probability level).



Scheme 4. Synthesis of complexes **8** and **9**.

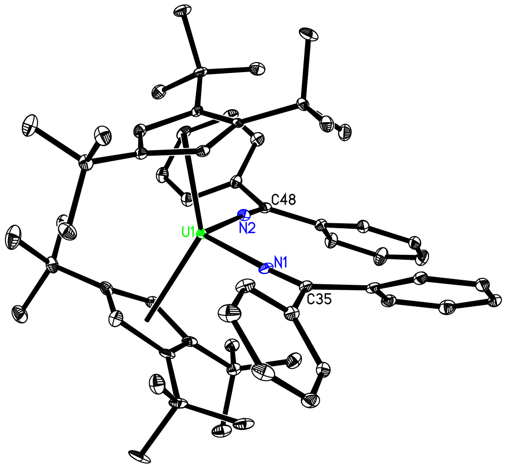


Figure 8. Molecular structure of **8** (thermal ellipsoids drawn at the 35% probability level).

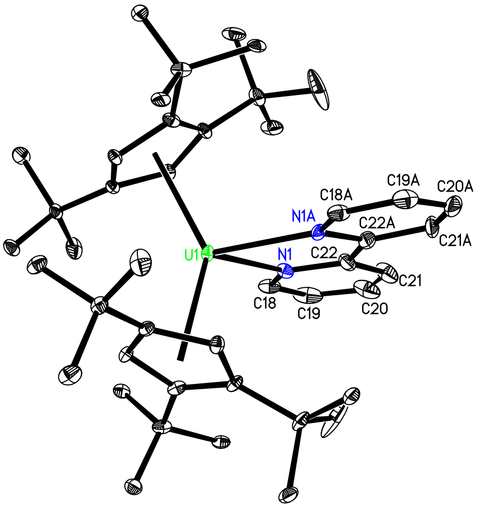
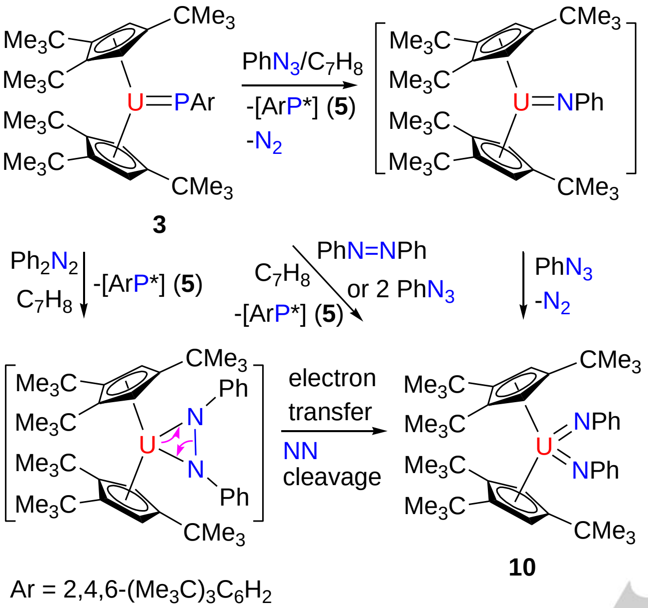


Figure 9. Molecular structure of **9** (thermal ellipsoids drawn at the 35% probability level).

In contrast, treatment of **3** with 1,2-diphenyldiazene (PhN=NPh) gives the uranium(VI) bisimido species Cp‴$_2$U(=NPh)$_2$ (**10**) besides the phosphaindane **5** in quantitative conversion (Scheme 5). It is reasonable to postulate that the reaction sequence commences with a substitution of phosphinidene fragment by PhN=NPh to form a metalladiazirine, then an electron transfer ensues to cleave the N-N bond to give the bisimido complex **10** (Scheme 5). Complex **10** may also be prepared by the reaction of **3** with phenyl azide (PhN$_3$) in quantitative conversion (Scheme 5), and the reaction outcome remains unaffected regardless of the amount of azide employed. It is reasonable to propose that PhN$_3$ displaces the phosphinidene fragment in **3** and releases N$_2$ to give a uranium(IV) imido complex, which subsequently reacts with a second molecule of PhN$_3$ to yield the bisimido uranium(VI) compound **10** and N$_2$ (Scheme 5). The molecular structure of **10** can be found in Figure 10, while the selected bond distances and angles are available in Table 1. The short U-N distances (1.985(4) Å for N(1) and 1.981(4) Å for N(2)) and the angles of U-N(1)-C(35) (171.4(4)º) and U-N(2)-C(41) (172.8(4)º) are in line with a U=N double bond description.[12] These structural parameters matches those previously found in related compounds such as Cp*$_2$U(=N-*p*-tolyl)$_2$ with the U-N distances of 1.971(4) and 1.975(3) Å and the U-N-C angles of 178.8(3) and 179.1(3)°,[9j] Cp*$_2$U(=NPh)$_2$ with the U-N distance of 1.952(7) Å and the U-N-C angle of 177.8(6)°,[16] and Cp′′′$_2$U=N(*p*-tolyl) with the U-N distance of 1.988(5) Å and the U-N-C angle of 172.3(5)°.[6a]



Scheme 5. Synthesis of complex **10**.

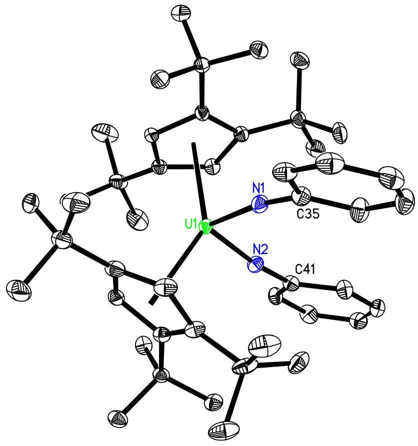
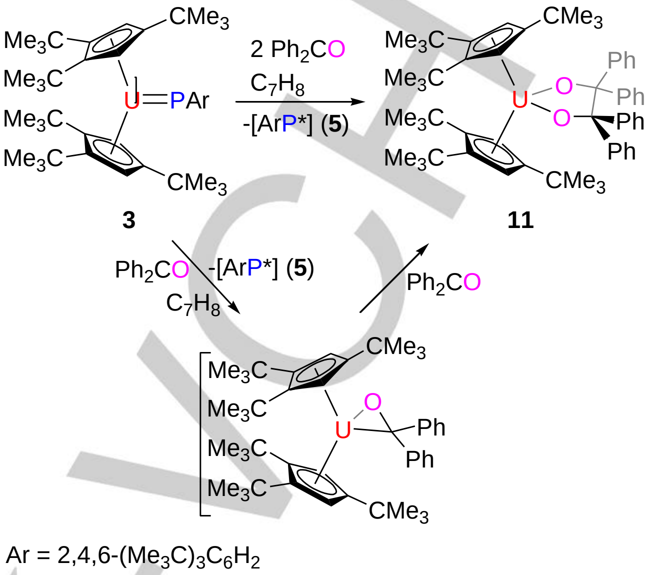


Figure 10. Molecular structure of **10** (thermal ellipsoids drawn at the 35% probability level).

Addition of Ph$_2$CO to **3** also releases the coordinated phosphinidene to yield the uranium pinacolate Cp′′′$_2$U[(OCPh$_2$)$_2$] (**11**) and the phosphaindane **5** (Scheme 6). However, no change in product formation is observed when the equivalents of Ph$_2$CO added to the reaction are varied. Presumably, on replacement of phosphinidene fragment with Ph$_2$CO an unstable metallaoxirane intermediate forms,[9e,10c] which subsequently couples with a second molecule of Ph$_2$CO to furnish the pinacolate **11** (Scheme 6). Figure 11 shows the molecular structure of **11** and selected bond distances and angles are given in Table 1. The U-O distances are 2.132(2) Å for O(1) and 2.146(2) Å for O(2), and the O(1)-U-O(2) angle is 68.0(1)°.



Scheme 6. Synthesis of complex **11**.

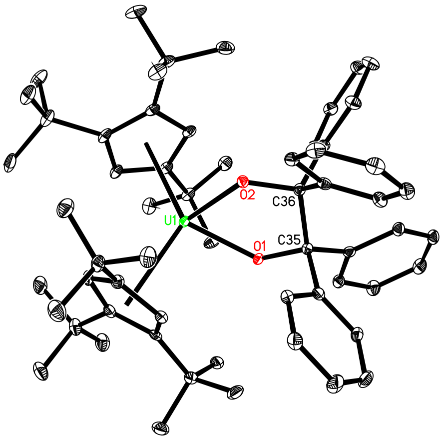
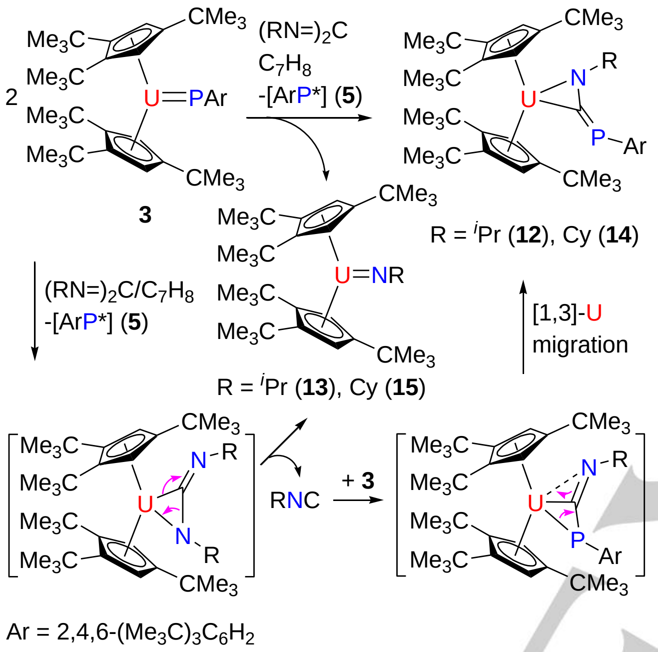


Figure 11. Molecular structure of **11** (thermal ellipsoids drawn at the 35% probability level).

However, when **3** is exposed to carbodiimides (RN=)$_2$C a mixture of products is formed, which consists of the metallaaziridines Cp′′′$_2$U[C(=PMes*)N(R)] (R = ^{i}Pr (**12**), C$_6$H$_{11}$ (**14**)), the imido complexes Cp′′′$_2$U=NR (R = ^{i}Pr (**13**), C$_6$H$_{11}$ (**15**)) and phosphaindane **5** (Scheme 7). The ^{1}H NMR spectroscopy data show that the complexes **12** and **13** as well as **14** and **15** are formed in a 1:1 ratio. Again, we assume that the initial step involves the replacement of the phosphinidene fragment by (RN=)$_2$C to give a metallaaziridine, which gives rise to the imido complexes **13** and **15** by isonitrile RNC loss (Scheme 7). However, the released isonitrile RNC may also react with a second molecule of **3** in a [2+1] cycloaddition to furnish the three-membered metallaheterocycles, followed by a [1,3]-U migration to yield the metallaaziridines **12** and **14** (Scheme 7). To verify this conjecture, we established that complexes **12** and **14** may also be accessed by the direct reaction of **3** with isonitriles RNC (for details see Experimental Section). It should also be noted that the similar actinide metallaaziridines can also be accessed by the reaction of bis(phosphido) actinide complexes with isocyanides.[17] The molecular structure of **14** is shown in Figure 12, whereas the structure of **12** is provided in the Supporting Information. The U-N distances are 2.245(2) Å for **12** and 2.250(3) Å for **14**, whereas the U-C distances are 2.369(3) Å for **12** and 2.353(3) Å for **14**. These structural parameters are comparable to those found in $Cp^*_2U[C{=}P(2,4,6\text{-}Me_3Ph)N^tBu](CN^tBu)$ with the U-C distance of 2.369(4) Å, and the U-N distance of 2.293(4) Å,[17c] and $Cp^*_2U[C{=}P(Ph)N^tBu](CN^tBu)$ with the U-C distance of 2.383(3) Å, and the U-N distance of 2.273(2) Å.[17b]



Scheme 7. Synthesis of complexes **12**-**15**.

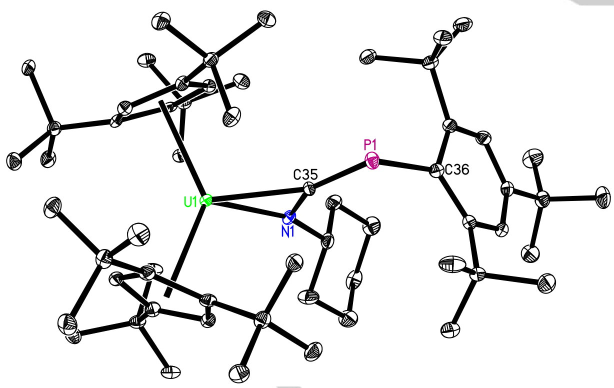


Figure 12. Molecular structure of **14** (thermal ellipsoids drawn at the 35% probability level).

Conclusion

In conclusion, the first stable base-free terminal phosphinidene uranium metallocene, $Cp'''_2U{=}PMes^*$ (**3**), was comprehensively studied. Density functional theory (DFT) shows that 5f orbitals contribute substantially to the σ and π-bonds of the uranium phosphinidene U=PAr moiety and that the bonds between the $[Cp'''_2U]^{2+}$ and $[Mes^*P]^{2-}$ fragments are more covalent than those of the related thorium phosphinidene complex. The coordinated phosphinidene in the terminal phosphinidene thorium metallocenes is inert to ligand exchange,[10,14] but it reacts with unsaturated molecules *via* a [2+2], [2+1] or [2+3] cycloaddition process or acts as a strong base inducing the intermolecular E-H (E = C, Si, N) bond activations.[10,14] In contrast, the uranium phosphinidene complex **3** behaves differently, it serves as a synthetically useful $Cp''_2U(II)$ synthon in the reactions with unsaturated molecules such as alkynes, imines, thiazoles, ketazines, bipy, organic azides, diazene derivatives, ketones, and carbodiimides, in which the coordinated phosphinidene is readily replaced during the reactions. It is interesting to note that **3** adds to the series of uranium metallocenes which may act as $Cp_2U(II)$ synthons such as $Cp'''_2U(bipy)$,[6a] $Cp^*_2U[(\mu\text{-}Ph)_2BPh_2]$,[18] and $Cp^*_2U[P(SiMe_3)(2,4,6\text{-}Me_3Ph)](THF)$.[19] Although no phosphorus-containing species were obtained, it allows us to isolate species which are so far not accessible by other synthetic routes. Further investigations on the intrinsic reactivity of terminal phosphinidene actinide metallocenes and uranium metallacyclopropene complex **4** are in progress and will be detailed in due course.

Experimental Section

General Procedures. All reactions and product manipulations were carried out under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glove box. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Cp'''_2UMe_2 (**1**),[6a] 2,4,6-$^tBu_3C_6H_2PH_2$ (Mes^*PH_2),[20] and 2,4,6-$^tBu_3C_6H_2PHK$ (Mes^*PHK)[21] 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, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AV 400 spectrometer at 400, 100 and 162 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, and to external 85% H_3PO_4 (0.00 ppm) for phosphorus chemical shifts. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

Preparation of $Cp'''_2U(I)Me$ (2). Solid CuI (0.38 g, 2.0 mmol) was slowly added to a stirred toluene (20 mL) solution of Cp'''_2UMe_2 (**1**; 1.47 g, 2.0 mmol) at room temperature. During the reaction copper metal (Cu) and ethane CH_3CH_3 were formed. After this solution was stirred at room temperature 3 days, the solvent was removed. The residue was extracted with *n*-hexane (10 mL × 3) and filtered. The volume of the combined filtrate was reduced to 10 mL, orange crystals of **2** were isolated after this solution was kept at -20 ºC for one day. Yield: 1.44 mg (85%). M.p.: 139-141 °C (dec.). ^1H NMR (400 MHz, C_6D_6): δ = 9.12 (s, 18H, $C(CH_3)_3$), 6.45 (s, 18H, $C(CH_3)_3$), -13.02 (s, 18H, $C(CH_3)_3$), -102.51 (s, 3H, UCH_3) ppm; ring C-*H* atoms were not observed. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 64.0 ($C(CH_3)_3$), 46.4 ($C(CH_3)_3$), 44.0 ($C(CH_3)_3$), 42.0 ($C(CH_3)_3$), 41.3 ($C(CH_3)_3$), 40.6 ($C(CH_3)_3$), -20.9 (UCH_3) ppm; ring *C* atoms were not oberved. IR (KBr): $\tilde{\nu}$ = 2958 (s), 1479 (s), 1458 (s), 1363 (s), 1238 (s), 1107 (s), 1020 (s), 997 (s), 837 (s), 808 (s) cm^{-1}. Anal. Calcd for $C_{35}H_{61}IU$: C, 49.64; H, 7.26. Found: C, 49.73; H, 7.30.

Preparation of $Cp'''_2U{=}PMes^*$ (3). A THF (10 mL) solution of Mes^*PHK (316 mg, 1.0 mmol) was added to a THF (10 mL) solution of $Cp'''_2U(I)Me$ (**2**; 847 mg, 1.0 mmol) with stirring at room temperature. After the solution was stirred at room temperature overnight, the solvent was removed. The residue was extracted with *n*-hexane (10 mL × 3) and filtered. The volume of the filtrate was reduced to 10 mL, brown crystals of **3** were isolated when this solution was kept at -20 ºC for two days. Yield: 736 mg (75%). M.p.: 130-132 ºC (dec.). ^1H NMR (400 MHz, C_6D_6): δ = 44.95 (s, 2H, ring C*H*), 21.71 (s, 2H, ring C*H*), 19.26 (s, 2H, phenyl), 3.50 (s, 9H, $C(CH_3)_3$), 1.73 (s, 18H, $C(CH_3)_3$), 0.48 (s, 18H, $C(CH_3)_3$), -0.99 (s, 18H, $C(CH_3)_3$), -35.78 (s, 18H, $C(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 311.4 (phenyl *C*), 281.2 (phenyl *C*), 251.5 (phenyl *C*), 172.6 (phenyl *C*), 89.1 ($C(CH_3)_3$), 61.6 ($C(CH_3)_3$), 50.2 ($C(CH_3)_3$), 44.6 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$), 31.2 (d, $J_{P\text{-}C}$ = 10.0 Hz, $C(CH_3)_3$), 8.6 ($C(CH_3)_3$), 7.5 ($C(CH_3)_3$), 3.3 ($C(CH_3)_3$), 1.5 ($C(CH_3)_3$), -57.5 (ring *C*), -58.5 (ring *C*), -59.5 (ring *C*), -60.8 (ring *C*) ppm. IR (KBr): $\tilde{\nu}$ = 2955 (s), 1477 (s), 1384 (s), 1357 (s), 1259 (s), 1070 (s), 1016 (s), 812 (s) cm^{-1}. Anal. Calcd for $C_{52}H_{87}PU$: C, 63.65; H, 8.94. Found: C, 63.68; H, 8.96.

Please note that we also attempted to record a ^{31}P{^{1}H} NMR spectrum, however, no resonances were observed even when the sample was measured for two days.

Preparation of Cp‴$_2$U(η^2-C$_2$Ph$_2$) (4). Method A. A toluene (5 mL) solution of PhC≡CPh (45 mg, 0.25 mmol) was added to a toluene (10 mL) solution of Cp‴$_2$U=PMes* (**3**; 245 mg, 0.25 mmol) with stirring at room temperature. After the solution was stirred at 50 ºC two days, the solvent was removed. The residue was extracted with *n*-hexane (10 mL × 3) and filtered. The volume of the filtrate was reduced to 2 mL, brown crystals of **4** were isolated when this solution was kept at room temperature for two days. Yield: 245 mg (82%). M.p.: 178-180 ºC (dec.). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 26.59 (s, 4H, phenyl), 16.62 (s, 4H, phenyl), 10.79 (d, *J* = 5.6 Hz, 2H, phenyl), 9.30 (br s, 18H, C(C*H*$_3$)$_3$), -15.00 (br s, 18H, C(C*H*$_3$)$_3$), -32.03 (s, 18H, C(C*H*$_3$)$_3$) ppm; ring C-*H* atoms were not observed. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 202.7 (U*C*), 201.8 (phenyl *C*), 201.0 (phenyl *C*), 151.4 (phenyl *C*), 138.4 (phenyl *C*), 137.9 (C(*C*H$_3$)$_3$), 137.3 (C(*C*H$_3$)$_3$), 136.7 (*C*(CH$_3$)$_3$), 85.8 (*C*(CH$_3$)$_3$), -50.1 (ring *C*), -51.1 (ring *C*) ppm; one ring *C* overlapped. IR (KBr): $\tilde{\nu}$ = 2960 (s), 1460 (m), 1384 (m), 1259 (s), 1093 (s), 1020 (s), 800 (s) cm^{-1}. Anal. Calcd for C$_{48}$H$_{68}$U: C, 65.28; H, 7.76. Found: C, 65.35; H, 7.73. Brown crystals of **4**·4C$_6$H$_6$ suitable for X-ray structural analysis were grown from a benzene solution.

Method B. NMR Scale. A C$_6$D$_6$ (0.3 mL) solution of PhC≡CPh (3.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). Resonances of **4** along with those of 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) (^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 7.46 (dd, *J* = 3.8, 1.5 Hz, 2H, phenyl), 4.39 (ddd, *J* = 181.6, 11.9, 7.9 Hz, 1H, P*H*), 1.59 (d, *J* = 3.6 Hz, 1H, C*H*$_2$), 1.56 (s, 9H, (C*H*$_3$)$_3$C), 1.34 (s, 3H, C*H*$_3$), 1.31 (s, 9H, (C*H*$_3$)$_3$C), 1.29 (d, *J* = 3.6 Hz, 1H, C*H*$_2$), 1.11 (s, 3H, C*H*$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ = -79.5 ppm)[10a] were observed by NMR spectroscopy (100% conversion) when this solution was kept at 50 ºC for 2 days.

Preparation of Cp‴$_2$U(η^2-CHPhNPh) (6). Method A. This compound was obtained as brown crystals from the reaction of Cp‴$_2$U=PMes* (**3**; 245 mg, 0.25 mmol) and PhCH=NPh (46 mg, 0.25 mmol) in toluene (15 mL) at 50 ºC and recrystallization from an *n*-hexane solution by a similar procedure as that in the synthesis of **4**. Yield: 184 mg (83%). M.p.: 215-217 ºC (dec.). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 129.18 (s, 1H, C*H*Ph), 34.03 (s, 1H, phenyl), 26.49 (s, 2H, phenyl), 23.78 (s, 1H, phenyl), 13.63 (s, 9H, C(C*H*$_3$)$_3$), 13.36 (s, 2H, phenyl), 12.24 (s, 9H, C(C*H*$_3$)$_3$), 7.42 (s, 1H, phenyl), -0.60 (s, 1H, phenyl), -2.57 (s, 1H, phenyl), -10.04 (s, 9H, C(C*H*$_3$)$_3$), -17.56 (s, 9H, C(C*H*$_3$)$_3$), -35.03 (s, 9H, C(C*H*$_3$)$_3$), -42.50 (s, 9H, C(C*H*$_3$)$_3$), -68.53 (s, 1H, phenyl) ppm; ring C-*H* atoms were not observed. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 228.0 (U*C*), 213.3 (phenyl *C*), 201.5 (phenyl *C*), 173.3 (phenyl *C*), 173.1 (phenyl *C*), 159.7 (phenyl *C*), 139.6 (phenyl *C*), 134.4 (phenyl *C*), 125.8 (phenyl *C*), 54.6 (C(*C*H$_3$)$_3$), 35.1 (*C*(CH$_3$)$_3$), 21.1 (*C*(CH$_3$)$_3$), 20.2 (*C*(CH$_3$)$_3$), -43.5 (ring *C*), -66.1 (ring *C*), -78.5 (ring *C*) ppm; other carbons overlapped. IR (KBr): $\tilde{\nu}$ = 2958 (s), 1602 (s), 1506 (s), 1359 (s), 1261 (s), 1097 (s), 1028 (s), 748 (s) cm^{-1}. Anal. Calcd for C$_{47}$H$_{69}$NU: C, 63.71; H, 7.85; N, 1.58. Found: C, 63.75; H, 7.83; N, 1.52.

Method B. NMR Scale. A C$_6$D$_6$ (0.3 mL) solution of PhCH=NPh (3.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). Resonances of **6** along with those of 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) were observed by ^{1}H NMR spectroscopy (100% conversion) when this solution was kept at 50 ºC for 2 days.

Preparation of Cp‴$_2$U(SCH=CHN=CH) (7). Method A. This compound was obtained as brown crystals from the reaction of Cp‴$_2$U=PMes* (**3**; 245 mg, 0.25 mmol) and thiazole (22 mg, 0.25 mmol) in toluene (15 mL) at 50 ºC and recrystallization from an *n*-hexane solution by a similar procedure as that in the synthesis of **4**. Yield: 198 mg (86%). M.p.: 98-100 ºC (dec.). ^{1}H NMR (C$_6$D$_6$): δ 70.47 (s, 1H, C*H*), 40.47 (s, 1H, C*H*), 17.59 (br s, 2H, ring C*H*), 15.97 (br s, 2H, ring C*H*), 7.47 (s, 1H, C*H*), 0.38 (s, 18H, C(C*H*$_3$)$_3$), -1.87 (s, 18H, C(C*H*$_3$)$_3$), -10.49 (s, 18H, C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 271.5 (U*C*), 158.9 (CH=*C*HN), 152.2 (*C*H=CHN), 46.9 (*C*(CH$_3$)$_3$), 41.9 (C(*C*H$_3$)$_3$), 36.8 (*C*(CH$_3$)$_3$), 35.6 (*C*(CH$_3$)$_3$), 34.8 (C(*C*H$_3$)$_3$), -4.4 (ring *C*), -20.6 (ring *C*), -20.7 (ring *C*), -71.2 (ring *C*) ppm; other *C* atoms overlapped. IR (KBr, cm^{-1}): *v* 2957 (s), 1595 (m), 1479 (s), 1460 (s), 1390 (s), 1359 (s), 1261 (s), 1240 (s), 1095 (s), 1020 (s), 808 (s). Anal. Calcd for C$_{37}$H$_{61}$NSU: C, 56.25; H, 7.78; N, 1.77. Found: C, 56.22; H, 7.83; N, 1.72.

Method B. NMR Scale. A C$_6$D$_6$ (0.3 mL) solution of thiazole (1.7 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). Resonances of **7** along with those of 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) were observed by ^{1}H NMR spectroscopy (100% conversion) when this solution was kept at 50 ºC for 2 days.

Preparation of Cp‴$_2$U(N=CPh$_2$)$_2$ (8). Method A. This compound was obtained as brown crystals from the reaction of Cp‴$_2$U=PMes* (**3**; 245 mg, 0.25 mmol) and (Ph$_2$C=N)$_2$ (90 mg, 0.25 mmol) in toluene (15 mL) at 50 ºC and recrystallization from a benzene solution by a similar procedure as that in the synthesis of **4**. Yield: 226 mg (85%). M.p.: 155-157 ºC (dec.). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 33.06 (br s, 2H, ring C*H*), 14.59 (br s, 6H, C(C*H*$_3$)$_3$), 12.45 (br s, 18H, C(C*H*$_3$)$_3$), 7.70 (s, 1H, phenyl), 7.41 (s, 2H, phenyl), 7.37 (s, 1H, phenyl), 7.04 (s, 2H, phenyl), 2.29 (s, 18H, C(C*H*$_3$)$_3$), 1.45 (s, 9H, phenyl), 1.28 (s, 5H, phenyl), -23.34 (br s, 12H, C(C*H*$_3$)$_3$), -75.71 (br s, 2H, ring C*H*) ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 160.1 (phenyl *C*), 155.3 (phenyl *C*), 151.7 (phenyl *C*), 148.8 (phenyl *C*), 138.8 (phenyl *C*), 136.4 (phenyl *C*), 129.7 (phenyl *C*), 122.6 (phenyl *C*), 104.7 (N=*C*), 56.2 (*C*(CH$_3$)$_3$), 38.5 (*C*(CH$_3$)$_3$), 34.9 (*C*(CH$_3$)$_3$), 34.8 (C(*C*H$_3$)$_3$), 34.2 (C(*C*H$_3$)$_3$), 34.1 (C(*C*H$_3$)$_3$), -28.4 (ring *C*) ppm; other carbons were not observed. IR (KBr): $\tilde{\nu}$ = 2958 (s), 1600 (s), 1583 (s), 1562 (s), 1359 (s), 1238 (s), 1028 (m), 825 (s) cm^{-1}. Anal. Calcd for C$_{60}$H$_{78}$N$_2$U: C, 67.65; H, 7.38; N, 2.63. Found: C, 67.68; H, 7.33; N, 2.62.

Method B. NMR Scale. A C$_6$D$_6$ (0.3 mL) solution of (Ph$_2$C=N)$_2$ (7.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). Resonances of **8** along with those of 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) were observed by ^{1}H NMR spectroscopy (100% conversion) when this solution was kept at 50 ºC for 36 h.

Preparation of Cp‴$_2$U(bipy) (9). Method A. This compound was obtained as green crystals from the reaction of Cp‴$_2$U=PMes* (**3**; 245 mg, 0.25 mmol) and bipy (39 mg, 0.25 mmol) in toluene (15 mL) at 50 ºC and recrystallization from a benzene solution by a similar procedure as that in the synthesis of **4**. Yield: 177 mg (82%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.26 (s, 4H, ring C*H*), 1.17 (s, 36H, C(C*H*$_3$)$_3$), -7.47 (d, *J* = 4.9 Hz, 2H, bipy), -9.01 (s, 18H, C(C*H*$_3$)$_3$), -58.93 (s, 2H, bipy), -99.40 (s, 2H, bipy), -125.80 (s, 2H, bipy) ppm. These spectroscopic data agreed with those reported in the literature.[6a]

Method B. NMR Scale. A C$_6$D$_6$ (0.3 mL) solution of bipy (3.1 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). Resonances of **9** along with those of 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) were observed by ^{1}H NMR spectroscopy (100% conversion) when this solution was kept at 50 ºC 36 h.

Preparation of Cp‴$_2$U(=NPh)$_2$ (10). Method A. This compound was obtained as brown crystals from the reaction of Cp‴$_2$U=PMes* (**3**; 245 mg, 0.25 mmol) and PhN=NPh (46 mg, 0.25 mmol) in toluene (15 mL) at 50 ºC and recrystallization from a benzene solution by a similar procedure as that in the synthesis of **4**. Yield: 177 mg (80%). M.p.: 195-197 ºC (dec.). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 9.48 (t, *J* = 7.5 Hz, 4H, phenyl), 4.99 (s, 4H, ring C*H*), 3.07 (d, *J* = 6.6 Hz, 4H, phenyl), 1.65 (s, 36H, C(C*H*$_3$)$_3$), 1.62 (s, 18H, C(C*H*$_3$)$_3$), 0.17 (t, *J* = 7.2 Hz, 2H, phenyl) ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 186.6 (phenyl *C*), 167.4 (phenyl *C*), 156.4 (phenyl *C*), 146.7 (phenyl *C*), 125.5 (ring *C*), 107.9 (ring *C*), 107.5 (ring *C*), 38.1 (C(*C*H$_3$)$_3$), 38.0 (C(*C*H$_3$)$_3$), 31.4 (*C*(CH$_3$)$_3$), 29.5 (*C*(CH$_3$)$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 2951 (s), 1573 (m), 1464 (s), 1357 (s), 1261 (s), 1236 (s), 1093 (s), 1020 (s), 800 (s) cm^{-1}. Anal. Calcd for C$_{46}$H$_{68}$N$_2$U: C, 62.28; H, 7.73; N, 3.16. Found: C, 62.31; H, 7.72; N, 3.12.

Method B. NMR Scale. A C$_6$D$_6$ (0.3 mL) solution of PhN=NPh (3.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). Resonances of **10** along with those of 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) were observed by ^{1}H NMR spectroscopy (100% conversion) when this solution was kept at 50 ºC for 2 days.

Method C. NMR Scale. A C$_6$D$_6$ (0.3 mL) solution of PhN$_3$ (4.8 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). Resonances of **10** along with those of 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) were observed by ^{1}H NMR spectroscopy (100% conversion in 10 min).

Reaction of Cp‴$_2$U=PMes* (3) with PhN$_3$. NMR Scale. A C$_6$D$_6$ (0.2 mL) solution of PhN$_3$ (2.4 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C$_6$D$_6$ (0.3 mL). Resonances of **10** along with those of unreacted **3** and 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) were observed by ^{1}H NMR spectroscopy (50% conversion based on **3**, in 10 min).

Preparation of Cp‴$_2$U[(OCPh$_2$)$_2$]·0.5C$_6$H$_6$ (11·0.5C$_6$H$_6$). Method A. This compound was obtained as orange crystals from the reaction of Cp‴$_2$U=PMes* (**3**; 245 mg, 0.25 mmol) and Ph$_2$CO (91 mg, 0.50 mmol) in toluene (15 mL) at 50 ºC and recrystallization from a benzene solution by a similar procedure as that in the synthesis of **4**. Yield: 227 mg (82%). M.p.: 154-156 ºC (dec.). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 61.95 (s, 2H, ring C*H*), 27.41 (s, 1H, phenyl), 23.01 (s, 1H, phenyl), 16.08 (s, 1H, phenyl), 13.84 (s, 18H, C(C*H*$_3$)$_3$), 13.42 (s, 1H, phenyl), 9.72 (s, 2H, phenyl), 8.43 (s, 2H, phenyl), 7.66 (s, 4H, phenyl), 7.15 (s, 3H, C$_6$*H*$_6$), 7.01 (s, 5H, phenyl), 4.61 (s, 1H, phenyl), 2.90 (s, 1H, phenyl), -1.30 (s, 1H, phenyl), -5.29 (s, 18H, C(C*H*$_3$)$_3$), -23.24 (s, 2H, ring C*H*), -43.97 (s, 18H, C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 138.3 (phenyl *C*), 137.9 (phenyl *C*), 136.7 (phenyl *C*), 132.0 (phenyl *C*), 130.2 (phenyl *C*), 130.1 (phenyl *C*), 128.5 (*C*$_6$H$_6$), 89.4 (O*C*), 65.3 (C(*C*H$_3$)$_3$), 63.4 (*C*(CH$_3$)$_3$), 33.9 (C(*C*H$_3$)$_3$), 32.2 (C(*C*H$_3$)$_3$), 29.7 (*C*(CH$_3$)$_3$), 28.8 (C(*C*H$_3$)$_3$), -65.3 (ring *C*) ppm; other carbons were not observed. IR (KBr): $\tilde{\nu}$ = 2958 (s), 1599 (s), 1446 (s), 1317 (s), 1276 (s), 1028 (s), 920 (s), 763 (s) cm^{-1}. Anal. Calcd for C$_{63}$H$_{81}$O$_2$U: C, 68.27; H, 7.37. Found: C, 68.31; H, 7.32.

Method B. NMR Scale. A C$_6$D$_6$ (0.3 mL) solution of Ph$_2$CO (7.3 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C$_6$D$_6$ (0.2 mL). Resonances of **11** along with those of 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) were observed by ^{1}H NMR spectroscopy (100% conversion) when this solution was kept at 50 ºC for 36 h.

Reaction of Cp‴$_2$U=PMes* (3) with Ph$_2$CO. NMR Scale. A C_6D_6 (0.2 mL) solution of Ph_2CO (3.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C_6D_6 (0.3 mL). Resonances of **11** along with those of unreacted **3** and 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) were observed by ^{1}H NMR spectroscopy (50% conversion based on **3**) after the sample was kept at 50 ºC for 36 h.

Preparation of Cp‴$_2$U[C(=PMes*)N(^{i}Pr)] (12). Method A. This compound was obtained as brown crystals from the reaction of Cp‴$_2$U=PMes* (**3**; 245 mg, 0.25 mmol) and (^{i}PrN=)$_2$C (17 mg, 0.13 mmol) in toluene (15 mL) at 50 ^{o}C and recrystallization from an *n*-hexane solution by a similar procedure as that in the synthesis of **4**. Yield: 100 mg (38% based on U). M.p.: 115-117 ^{o}C (dec.). ^{1}H NMR (400 MHz, C_6D_6): δ = 116.29 (s, 1H, NC*H*), 41.10 (s, 3H, C*H*$_3$), 29.49 (s, 3H, C*H*$_3$), 22.45 (s, 1H, phenyl), 17.61 (s, 1H, phenyl), 16.05 (s, 18H, C(C*H*$_3$)$_3$), 10.99 (s, 9H, C(C*H*$_3$)$_3$), 8.76 (s, 9H, C(C*H*$_3$)$_3$), 3.56 (s, 9H, C(C*H*$_3$)$_3$), 3.54 (s, 9H, C(C*H*$_3$)$_3$), -19.83 (br s, 18H, C(C*H*$_3$)$_3$), -38.81 (s, 9H, C(C*H*$_3$)$_3$) ppm; protons of the rings were not observed. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 129.3 (phenyl *C*), 126.7 (phenyl *C*), 125.6 (phenyl *C*), 121.8 (phenyl *C*), 59.7 (N*C*), 40.1 (C(*C*H$_3$)$_3$), 37.8 (C(*C*H$_3$)$_3$), 32.7 (*C*H$_3$), 32.6 (*C*H$_3$), 31.5 (C(*C*H$_3$)$_3$), 30.9 (C(*C*H$_3$)$_3$) ppm; other carbons were not observed. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = 857.4 ppm. IR (KBr): $\tilde{\nu}$ = 2960 (s), 1591 (m), 1512 (s), 1460 (s), 1388 (s), 1359 (s), 1238 (s), 1020 (m), 812 (s) cm^{-1}. Anal. Calcd for $C_{56}H_{94}NPU$: C, 64.04; H, 9.02; N, 1.33. Found: C, 64.08; H, 8.99; N, 1.32.

Method B. NMR Scale. A C_6D_6 (0.3 mL) solution of (^{i}PrN=)$_2$C (2.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **12** along with those of Cp‴$_2$U=N^{i}Pr (**13**) (^{1}H NMR (400 MHz, C_6D_6): δ = 37.20 (br s, 1H NC*H*), 1.71 (s, 3H, C*H*$_3$), 1.67 (s, 3H, C*H*$_3$), -18.33 (br s, 18H, C(C*H*$_3$)$_3$), -25.45 (br s, 18H, C(C*H*$_3$)$_3$), -35.10 (br s, 18H, C(C*H*$_3$)$_3$) ppm; protons of the rings were not observed) and 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) were observed by ^{1}H NMR spectroscopy (100% conversion) when this solution was kept at 50 ^{o}C overnight. Complex **13** was not isolated as a pure compound on a synthetic scale, since it was an oily residue and very soluble in solvents such as benzene and *n*-hexane and **12** could not be removed completely.

Method C. NMR Scale. A C_6D_6 (0.3 mL) solution of ^{i}PrNC (1.4 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **12** were observed by ^{1}H NMR spectroscopy (100% conversion) after the sample was kept at room temperature overnight.

Preparation of Cp‴$_2$U[C(=PMes*)N(C$_6$H$_{11}$)] (14). Method A. This compound was obtained as brwon crystals from the reaction of Cp‴$_2$U=PMes* (**3**; 245 mg, 0.25 mmol) and DCC (52 mg, 0.25 mmol) in toluene (15 mL) at 50 ºC and recrystallization from an *n*-hexane solution by a similar procedure as that in the synthesis of **4**. Yield: 93 mg (34% based on U). M.p.: 170-172 ºC (dec.). ^{1}H NMR (400 MHz, C_6D_6): δ = 115.37 (s, 1H, NC*H*), 54.77 (s, 1H, Cy), 37.96 (s, 1H, Cy), 30.76 (s, 1H, Cy), 26.32 (s, 1H, Cy), 22. 65 (s, 1H, Cy), 21.23 (s, 2H, phenyl), 20.27 (s, 1H, Cy), 17.22 (s, 1H, Cy), 16.53 (s, 18H, C(C*H*$_3$)$_3$), 15.79 (s, 1H, Cy), 12.73 (s, 1H, Cy), 12.37 (s, 1H, Cy), 10.70 (s, 9H, C(C*H*$_3$)$_3$), 8.10 (s, 9H, C(C*H*$_3$)$_3$), 4.02 (s, 9H, C(C*H*$_3$)$_3$), -19.91 (br s, 18H, C(C*H*$_3$)$_3$), -38.77 (s, 18H, C(C*H*$_3$)$_3$) ppm; protons of the rings were not observed. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 165.7 (*C*=P), 161.9 (phenyl *C*), 150.4 (phenyl *C*), 145.9 (phenyl *C*), 136.9 (phenyl *C*), 63.0 (NCH), 60.7 (Cy *C*), 54.7 (Cy *C*), 46.9 (Cy *C*), 43.4 (*C*(CH$_3$)$_3$), 43.2 (*C*(CH$_3$)$_3$), 39.6 (C(*C*H$_3$)$_3$), 37.0 (C(*C*H$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 19.7 (*C*(CH$_3$)$_3$), -49.4 (ring *C*), ppm; other carbons were not observed. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = 874.6 ppm. IR (KBr): $\tilde{\nu}$ = 2957 (s), 2928 (s), 1506 (s), 1460 (s), 1386 (s), 1357 (s), 1292 (s), 1226 (s), 1097 (s), 1022 (s), 875 (s), 808 (s) cm^{-1}. Anal. Calcd for $C_{59}H_{98}NPU$: C, 64.99; H, 9.06; N, 1.28. Found: C, 64.98; H, 9.09; N, 1.30.

Method B. NMR Scale. A C_6D_6 (0.3 mL) solution of DCC (2.1 mg, 0.01 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **14** along with those of Cp‴$_2$U=NC$_6$H$_{11}$ (**15**) (^{1}H NMR (400 MHz, C_6D_6): δ = 31.26 (br s, 2H, C*H*$_2$), 25.10 (br s, 2H, C*H*$_2$), 21.48 (s, 1H, C*H*N), 20.12 (s, 2H, C*H*$_2$), 16.10 (s, 2H, C*H*$_2$), 14.24 (s, 2H, C*H*$_2$), 12.65 (br s, 18H, C(C*H*$_3$)$_3$), -14.39 (br s, 18H, C(C*H*$_3$)$_3$), -35.89 (s, 18H, C(C*H*$_3$)$_3$) ppm; protons of the rings were not observed) and 3,3-Me$_2$-5,7-^{t}Bu$_2$C$_8$H$_5$P (**5**) were observed by ^{1}H NMR spectroscopy (100% conversion) when this solution was kept at 50 ºC overnight. Complex **15** was not isolated as a pure compound on a synthetic scale, since it was an oily residue and very soluble in solvents such as benzene and *n*-hexane and **14** could not be removed completely.

Method C. NMR Scale. A C_6D_6 (0.3 mL) solution of C$_6$H$_{11}$NC (2.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with Cp‴$_2$U=PMes* (**3**; 20 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **14** were observed by ^{1}H NMR spectroscopy (100% conversion) after the sample was kept at room temperature overnight.

***X*-ray Crystallography.** Single-crystal X-ray diffraction measurements were carried out on a Rigaku Saturn CCD diffractometer at 100(2) K using Cu Kα radiation (λ = 1.54184 Å). An empirical absorption correction was applied using the SADABS program.[22] All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL program package.[23] The hydrogen atoms were geometrically fixed using a riding model. The crystal data and experimental data for **2**-**4**, **6**-**12**, **14** and **17** are summarized in Tables S1-3. Selected bond lengths and angles are listed in Table 1.

CCDC 2002932 (**2**), 2002931 (**3**), 2002929 (**4**), 2002930 (**6**), 2002928 (**7**), 2002936 (**8**), 2002933 (**9**), 2002934 (**10**), 2002939 (**11**), 2002937 (**12**), 2002942 (**14**), and 2004059 (**17**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Methods. All calculations were carried out with the Gaussian 09 program (G09),[24] employing the B3PW91 functional, plus a polarizable continuum model (PCM) (denoted as B3PW91-PCM), with standard 6-31G(d) basis set for C, H and P elements and a quasi-relativistic 5f-in-valence effective-core potential (ECP60MWB) treatment with 60 electrons in the core region for U and the corresponding optimized segmented ((14s13p10d8f6g)/[10s9p5d4f3g]) basis set for the valence shells of U,[25] 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 1st order saddle points, respectively, on their potential energy hypersurfaces. In order to consider the dispersion effect for the reactions **3**+PhC≡CPh, single-point B3PW91-PCM-D3[26] calculations, based on B3PW91-PCM geometries, have been performed.

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Conflict of interest

The authors declare no conflict of interest.

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Table 1. Selected Distances (Å) and Angles (deg) for Compounds **2**-**4**, **6**-**12** and **14**[a]

compound	C(Cp)-U[b]	C(Cp)-U[c]	Cp(cent)-U[b]	U-X	Cp(cent)-U-Cp(cent)	X-U-X/Y
2	2.790(4)	2.733(4) to 2.870(4)	2.514(4)	C(35) 2.423(5), I(1) 2.990(1)	140.8(2)	92.5(2)
3	2.793(4)	2.719(3) to 2.899(4)	2.517(4)	P(1) 2.495(1)	138.0(1)	
4	2.804(3)	2.744(3) to 2.884(3)	2.530(3)	C(35) 2.318(3), C(36) 2.331(3)	139.1(1)	33.6(1)
6	2.808(5)	2.678(5) to 2.950(5)	2.538(5)	C(18) 2.439(8), N(1) 2.227(6)	138.0(2)	35.6(2)
7	2.803(4)	2.763(4) to 2.857(4)	2.528(4)	C(37) 2.389(11), N(1) 2.243(4) S(1) 2.813(2)	143.7(2)	66.6(1)[d], 33.3(3)[e]
8	2.835(4)	2.776(4) to 2.898(4)	2.563(4)	N(1) 2.214(3), N(2) 2.227(3)	140.2(1)	111.4(1)
9	2.843(5)	2.790(5) to 2.904(5)	2.573(5)	N(1) 2.429(4), N(1A) 2.429(4)	140.6(1)	66.1(2)
10	2.800(5)	2.760(5) to 2.833(5)	2.526(5)	N(1) 1.985(4), N(2) 1.981(4)	141.9(2)	99.8(2)
11	2.844(3)	2.715(3) to 3.040(3)	2.634(3)	O(1) 2.132(2), O(2) 2.146(2)	121.3(1)	68.0(1)
12	2.818(3)	2.718(3) to 2.960(3)	2.545(3)	N(1) 2.245(2), C(35) 2.369(3)	133.4(1)	33.8(1)
14	2.831(4)	2.724(4) to 2.958(4)	2.560(4)	N(1) 2.250(3), C(35) 2.353(4)	133.2(1)	34.0(1)

[a] Cp = cyclopentadienyl ring. [b] average value. [c] Range. [d] The angle of S(1)-U(1)-N(1). [e] The angle of N(1)-U(1)-C(37).

Table 2. Natural Localized Molecular Orbital (NLMO) Analysis of An=PAr Bonds,[a] Bond Order, and the Natural Charges for the $[Cp'''_2An]$ and [ArP] Units.

		3 (U)	**3′** (Th)[10a]
σ An-P	%An	25.3	20.6
	%s	7.8	9.4
	%p	10.4	10.1
	%d	55.8	65.5
	%f	26.0	15.0
	%P	73.4	78.7
	%s	78.5	76.7
	%p	21.5	23.3
π_1 An=P	%An	32.0	25.2
	%p	2.2	1.8
	%d	53.1	64.3
	%f	44.7	33.9
	%P	62.7	70.7
	%p	100	100
π_2 An=P	%An	37.1	30.9
	%p	1.7	2.0
	%d	47.2	74.0
	%f	51.1	24.0
	%P	58.9	66.0
	%p	100	100
Mayer bond order (An=P)		1.76	1.53
NBO charge (An)		0.52	0.62
NBO charge (P)		-0.01	-0.12
NBO charge (Cp_2An)		0.29	0.40
NBO charge (ArP)		-0.29	-0.40

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

Captions

Scheme 1. Synthesis of complexes **2** and **3**.

Scheme 2. Synthesis of complexes **4** and **6**.

Scheme 3. Synthesis of complex **7**.

Scheme 4. Synthesis of complexes **8** and **9**.

Scheme 5. Synthesis of complex **10**.

Scheme 6. Synthesis of complex **11**.

Scheme 7. Synthesis of complexes **12**-**15**.

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

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

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

Figure 4. Energy profile (kJ mol^{-1}) for the reaction of **3** + PhC≡CPh (computed at T = 298 K). [U] = Cp'''_2U. Ar = 2,4,6-$^tBu_3C_6H_2$.

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

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

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

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

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

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

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

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

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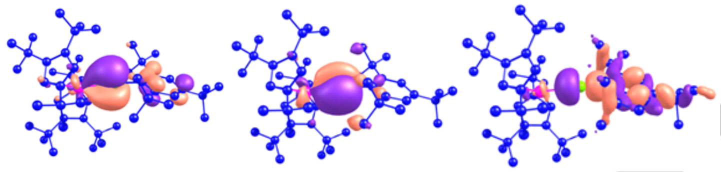

π_1 U=P π_2 U=P σ U=P

The first base-free terminal uranium phosphinidene metallocene was prepared and it showed a distinctively different reactivity compared to the related thorium phosphinidenes.