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Experimental and computational studies on a three-membered diphosphido thorium metallaheterocycle [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$]†

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A three-membered thorium metallaheterocycle [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**) is readily prepared besides H_2 from [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th(PH-2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$ (**3**) upon heating in toluene solution. Density functional theory (DFT) studies were performed to elucidate the 5f orbital contribution to the bonding within Th-(η^2-P-P) revealing more covalent bonds between the [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th^{2+} and [η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$]$^{2-}$ fragments than those in the related thorium metallacyclopropene. Consequently, distinctively different reactivity patterns emerge, *e.g.*, while **4** reacts with pyridine derivatives such as 4-dimethyaminopyridnie (DMAP) and forms the DMAP adduct [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$](DMAP) (**5**), it may also act as a [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th(II) synthon when reacted with bipy, Ph_2S_2 or Ph_2Se_2. Nevertheless, no reaction of complex **4** with alkynes is observed, but it reacts as a nucleophile towards nitriles and aldehydes resulting in five- or seven-membered metallaheterocycles, respectively. DFT computations provide some additional insights into the experimental observations.

Introduction

Metal phosphido complexes are interesting starting materials for new phosphorus containing materials, molecules and organometallic compounds. This also extends to their potential applications in phosphorus–element bond formations and catalytic transformation.[1] As a result, numerous phosphido complexes of transition metals have been isolated and thoroughly characterised, whereas related actinide compounds have only sporadically been explored leaving many new avenues in this area to be explored.[2] This includes not only novel reactivity patterns including small molecule activation,[3] but also addresses the questions of how 6d and 5f orbitals effect the reactivity patterns of actinide compounds in general.[4] These inherent questions also led us to prepare and study thorium and uranium metallacycles.[5] In the course of these investigations, the thorium metallacyclopropene [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(η^2-C$_2$Ph$_2$)[5a,b] and the uranium metallacyclopropene (η^5-C$_5$Me$_5$)$_2$U[η^2-C$_2$(SiMe$_3$)$_2$] were prepared.[5f,g] Reactivity studies revealed complementary reactivity patterns: the thorium metallacyclopropene [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(η^2-C$_2$Ph$_2$) reacts as a nucleophile toward hetero-unsaturated molecules or as a strong base inducing intermolecular C–H bond activations,[5a,b] whereas the uranium metallacyclopropene (η^5-C$_5$Me$_5$)$_2$U[η^2-C$_2$(SiMe$_3$)$_2$] constitutes a useful synthon for the (η^5-C$_5$Me$_5$)$_2$U(II) fragment when treated with unsaturated organic substrates.[5f,g] As a consequent extension of these studies, we moved from all-carbon metallacycles to metallaheterocycles. Herein, we report on the synthesis, electronic structure, and structure–reactivity relationship of the three-membered diphosphido thorium metallaheterocycle complex [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**). In addition, the reactivity pattern of **4** is compared to that of the related thorium metallacyclopropenes.[5a,b]

Results and discussion

The reaction of [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$ThCl$_2$ (**1**) with 1 equiv. of 2,4,6-^{i}Pr$_3$C$_6$H$_2$PHK in benzene affords [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th

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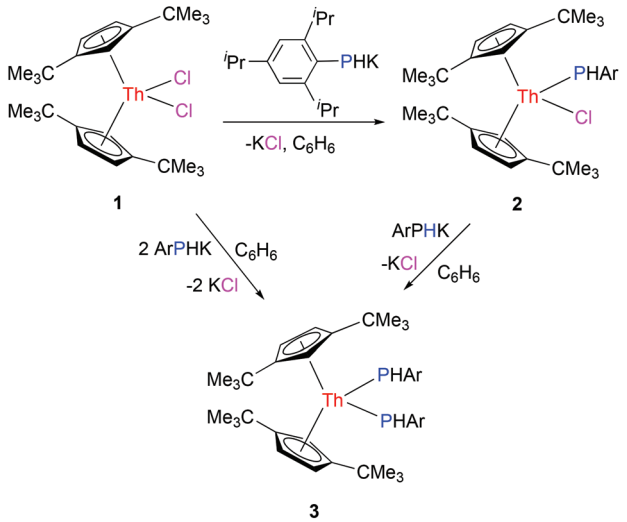
(Cl)(PH-2,4,6-$^{i}Pr_3C_6H_2$) (**2**) in 90% yield (Scheme 1). The molecular structure of **2** is shown in Fig. 1, and the selected bond distances and angles are listed in Table 1. The Th–P distance of 2.865(3) Å is *ca.* 0.2 Å longer than the Th–Cl distance of 2.637(3) Å, and the angle of P–Th–Cl is 99.7(1)°. In a subsequent salt metathesis step, **2** is exposed to a second molecule of 2,4,6-$^{i}Pr_3C_6H_2PHK$ in benzene to yield [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(PH-2,4,6-$^{i}Pr_3C_6H_2)_2$ (**3**) in 80% yield (Scheme 1). Contrary to the reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2ThCl_2$ with 2,4,6-$(Me_3C)_3C_6H_2PHK$,[2t] complex **3** can also be prepared in 70% yield when [η^5-1,3-$(Me_3C)_2C_5H_3]_2ThCl_2$ (**1**) is treated with 2 equiv. of 2,4,6-$^{i}Pr_3C_6H_2PHK$ (Scheme 1). It is noteworthy that no thorium phosphinidene [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th=P-2,4,6-$^{i}Pr_3C_6H_2$ is formed under these conditions. Complex **3** was structurally authenticated (Fig. 2) and relevant bond distances and angles are given in Table 1. The Th–P distances of 2.891(4) and 2.808(3) Å are in the same range as that found in **2**, while the P–Th–P angle is 94.6(1)°. Finally, heating of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(PH-2,4,6-$^{i}Pr_3C_6H_2)_2$ (**3**) in toluene at 75 °C affords the desired three-membered diphosphido thorium metallaheterocycle complex [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th[η^2-P_2(2,4,6-$^{i}Pr_3C_6H_2)_2$] (**4**) in 85% yield and with concomitant H_2 release (Scheme 2). We anticipate that the reaction mechanism is analogous to that proposed for the related zirconium complex (η^5-$C_5Me_5)_2$Zr(η^2-P_2Mes_2):[6] heating of the bis(phosphido) compound **3** eliminates 2,4,6-$^{i}Pr_3C_6H_2PH_2$ to give a phosphinidene intermediate, which immediately forms a phosphido hydride complex with



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

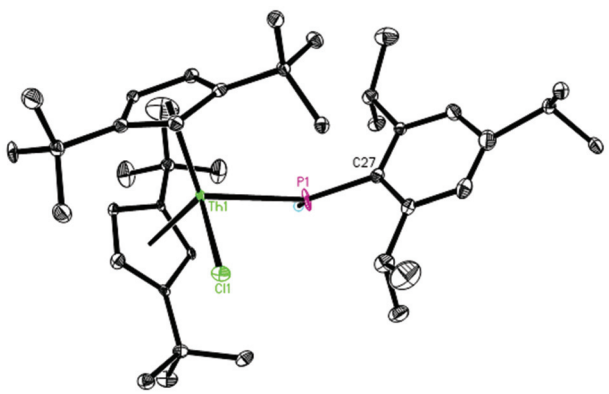


Fig. 1 Molecular structure of **2** (thermal ellipsoids drawn at the 35% probability level).

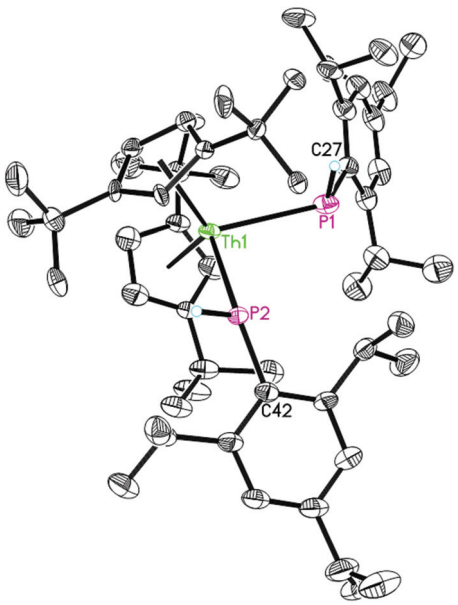
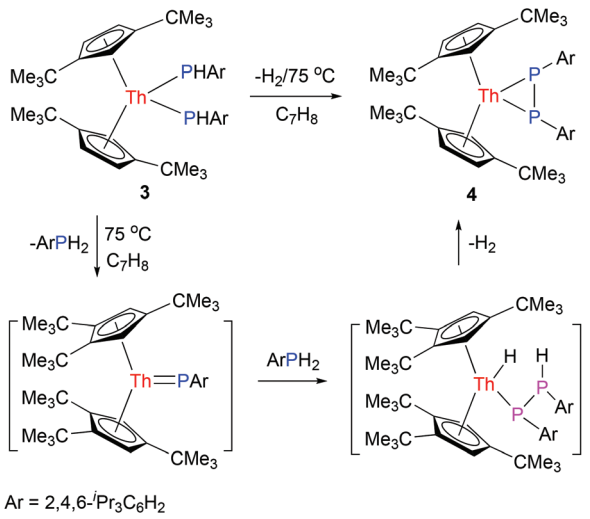


Fig. 2 Molecular structure of **3** (thermal ellipsoids drawn at the 35% probability level).

Table 1 Selected distances (Å) and angles (°) for compounds **2–3**, **5** and **9–10**[a]

Compound	C(Cp)–Th[b]	C(Cp)–Th[c]	Cp(cent)–Th[b]	Th–X	Cp(cent)–Th–Cp(cent)	X–Th–X/Y
2	2.801(14)	2.695(14) to 2.849(11)	2.528(12)	Cl1: 2.637(3), P1: 2.865(3)	127.0(3)	99.7(1)
3	2.811(12)	2.711(12) to 2.875(10)	2.540(10)	P1: 2.891(4), P2: 2.808(3)	125.9(4)	94.6(1)
5	2.853(3)	2.757(3) to 2.965(3)	2.587(3)	P1: 2.934(1), P2: 2.778(1), N1: 2.620(3)	124.6(1)	44.5(1)[d]
9	2.829(4)	2.786(4) to 2.864(4)	2.560(4)	N1: 2.227(3), P2: 2.906(1)	119.3(1)	67.4(1)
10	2.863(3)	2.808(3) to 2.945(3)	2.598(3)	O1: 2.175(2), O2: 2.138(2)	116.1(1)	84.8(1)

[a] Cp = cyclopentadienyl ring. [b] Average value. [c] Range. [d] The angle defined by P1–Th–P2.



Scheme 2 Synthesis of complex **4**.

2,4,6-$^{i}Pr_3C_6H_2PH_2$, which further releases H_2 to yield **4** (Scheme 2). Alternatively, complex **4** may also be directly formed by the elimination of H_2 from the bis(phosphido) species **3** upon heating (Scheme 2). To differentiate between these two potential reaction pathways, DFT computations were performed. These computational studies suggest that indeed **3** initially eliminates 2,4,6-$^{i}Pr_3C_6H_2PH_2$ to give the phosphinidene intermediate **INT4a** *via* the transition state **TS4a** (Fig. 3). In the next step, the phosphinidene intermediate **INT4a** reacts with 2,4,6-$^{i}Pr_3C_6H_2PH_2$ to afford a phosphido hydride intermediate **INT4b** *via* the transition state **TS4b**. Finally, H_2 is eliminated from the phosphido hydride species **INT4b** to yield **4** *via* the transition state **TS4c**. Overall, the formation of **4** + H_2 from **3** is energetically favourable (ΔG(298 K) = −11.0 kcal mol^{-1}) and occurs with a moderate reaction barrier of $\Delta G^{\ddagger}$(298 K) = 27.9 kcal mol^{-1}, which is consistent with the experimental observations. In contrast, the computed reaction barrier for the alternative reaction mechanism of a direct H_2 elimination from the bis(phosphido) **3** to form **4** *via* transition state **TS4d** is much larger ($\Delta G^{\ddagger}$(298 K) = 70.9 kcal mol^{-1}) (Fig. S1, ESI†). This is not in line with experimental findings and can therefore be discounted. To fully characterize complex **4**, various spectroscopic techniques and elemental analysis were employed. Its $^{31}P\{^{1}H\}$ NMR spectrum features a singlet at δ = 81.9 ppm, corresponding to the coordinated [η^2-P_2(2,4,6-$^{i}Pr_3C_6H_2$)$_2$] diphosphido moiety.[2] Consistent with a strong coordination of the diphosphido {[2,4,6-$^{i}Pr_3C_6H_2P$]$_2$}$^{2-}$ fragment, no dissociation is observed when **4** is heated to 100 °C as established by variable-temperature ^{1}H NMR spectroscopy (20–100 °C). Furthermore, no exchange of diphosphene (2,4,6-$^{i}Pr_3C_6H_2P$)$_2$ with internal alkynes such as MeC≡CMe, PhC≡CMe and PhC≡CPh was observed at elevated temperatures on a chemical time scale, which is analogy to the observations on thorium metallacyclopropene complexes.[5a]

To further evaluate the interaction between the thorium atom and the [(2,4,6-$^{i}Pr_3C_6H_2$)$_2$P$_2$] moiety, a computational study was undertaken at the DFT level of theory (B3PW91). Consistent with the experimental molecular structure, the computed gas-phase structure features an asymmetric Th[η^2-P$_2$(2,4,6-$^{i}Pr_3C_6H_2$)$_2$] fragment with two in-plane Th–P σ-bonds and two out-of-plane π-bonds interacting with the metal centre (Fig. 4). Based on a natural localized molecular orbital (NLMO) analysis, the P–P σ-bond is formed by two phosphorus hybrid orbitals (43.5%; 9.3% 3s and 90.7% 3p; and 46.3%; 13.5% 3s and 86.5% 3p) along with a minor contribution from a thorium hybrid orbital (8.6%; 51.4% 5f and 43.6% 6d and 2.3% 7p and 2.7% 7s). The asymmetry in the Th–P bond distances is also reflected in different orbital contributions based on the NLMO analysis. The σ_1(Th–P) bond is composed of a phosphorus hybrid orbital (72.5%; 27.3% 3s and 72.7% 3p)

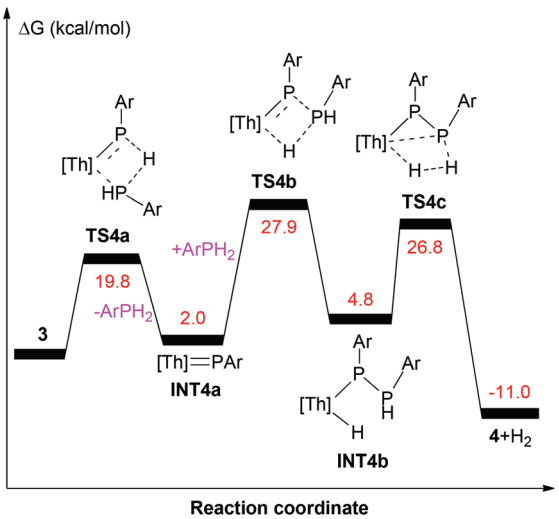


Fig. 3 Energy profile (kcal mol^{-1}) for the formation of **4** + H_2 (computed at T = 298 K). [Th] = [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th. Ar = 2,4,6-$^{i}Pr_3C_6H_2$.

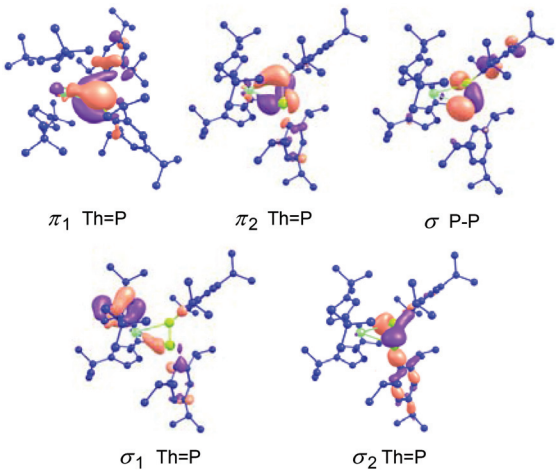
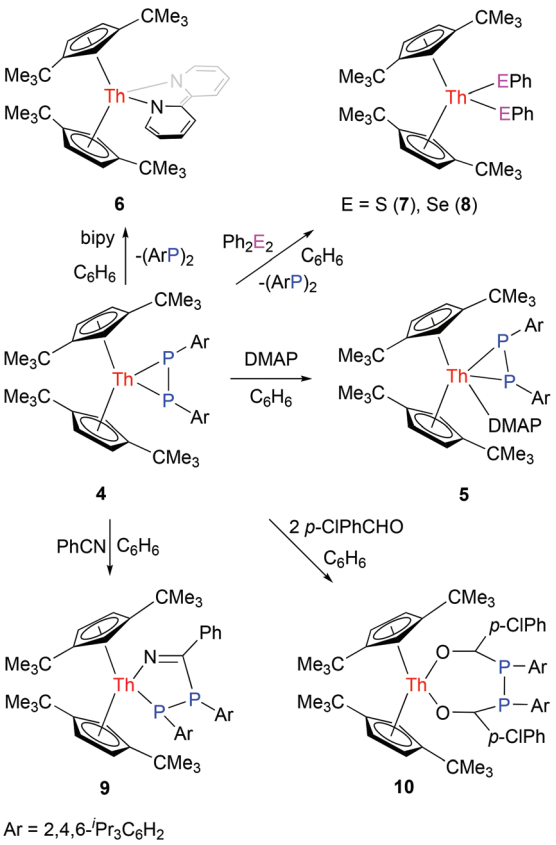


Fig. 4 Plots of HOMOs for **4** (the hydrogen atoms have been omitted for clarity).

and a thorium hybrid orbital (23.3%; 15.5% 5f and 72.0% 6d and 4.0% 7p and 8.5% 7s), whereas the σ_2(Th–P) bond consists of a phosphorus hybrid orbital (74.1%; 9.9% 3s and 90.1% 3p) and a thorium hybrid orbital (21.3%; 28.7% 5f and 68.9% 6d and 1.4% 7p and 1.0% 7s). This asymmetry also carries on to the Th–P π bonds. The π_1(Th–P) bond is composed of a phosphorus hybrid orbital (88.3%; 47.3% 3s and 52.7% 3p) with a thorium hybrid orbital (7.6%; 44.5% 5f and 28.1% 6d and 20.4% 7p and 7.0% 7s), whereas the π_2(Th–P) bond is based on a phosphorus hybrid orbital (80.0%; 53.2% 3s and 46.8% 3p) and a thorium hybrid orbital (18.1%; 22.9% 5f and 54.7% 6d and 10.3% 7p and 12.1% 7s). These computations imply that 6d and 5f orbital contributions are easily modulated and that electron density from the π-orbitals of the $[\eta^2$-$P_2(2,4,6$-$^iPr_3C_6H_2)_2]$ fragment can be readily transferred to the Lewis-acidic thorium atom. In contrast to the related thorium metallacyclopropene complexes,[5a,f] more covalent bonds between the $[1,3$-$(Me_3C)_2C_5H_3]_2Th^{2+}$ and $[\eta^2$-$P_2(2,4,6$-$^iPr_3C_6H_2)_2]^{2-}$ fragments are realized. This also causes larger Wiberg bond orders for the Th–P bonds (1.06 and 1.29) than those found for the Th–C bond in the thorium metallacyclopropene complex $[1,2,4$-$(Me_3C)_3C_5H_2]_2Th(\eta^2$-$C_2Ph_2)$ (0.53). Consequently, **4** forms the DMAP adduct $[\eta^5$-$1,3$-$(Me_3C)_2C_5H_3]_2Th[\eta^2$-$P_2(2,4,6$-$^iPr_3C_6H_2)_2](DMAP)$ (**5**) with 4-dimethylaminopyridine (DMAP) in 95% yield (Scheme 3), whereas upon the addition of pyridine derivatives to the thorium metallacyclopropene $[1,2,4$-$(Me_3C)_3C_5H_2]_2Th(\eta^2$-$C_2Ph_2)$, pyridine deprotonation is observed.[5b] Fig. 5 shows the molecular structure of **5**, and the interested reader may refer to Table 1 for the selected bond distances and angles. The Th–N distance is 2.620(3) Å, whereas the Th–P distances are significantly different with 2.934(1) and 2.778(1) Å as a direct result of the DMAP coordination, but still comparable to that found in $[1,2,4$-$(Me_3C)_3C_5H_2]_2Th(\eta^2$-$P_2Ph_2)$ (2.877(1) Å).[2t]

Similar to the reactivity of the bis(phosphido) thorium complex $[H_2B(3$-Mes-$C_3H_2N_2)_2]_2Th(PHMes)_2$ (Mes = 2,4,6-Me_3Ph) toward bipy,[2m] reductive elimination occurs in the reaction of complex **4** and bipy, that is, the coordinated diphosphene $(2,4,6$-$^iPr_3C_6H_2P)_2$ in **4** is replaced by bipy to give $[\eta^5$-$1,3$-$(Me_3C)_2C_5H_3]_2Th(bipy)$ (**6**) in quantitative conversion (Scheme 3). This contrasts the reactivity of the thorium metallacyclopropene $[1,2,4$-$(Me_3C)_3C_5H_2]_2Th(\eta^2$-$C_2Ph_2)$, but resembles that of the uranium metallacyclopropene $(\eta^5$-$C_5Me_5)_2U[\eta^2$-$C_2(SiMe_3)_2]$ towards bipy.[5f] Nevertheless, in contrast to the reactivity of the bis(phosphido) thorium complex $[H_2B(3$-Mes-$C_3H_2N_2)_2]_2Th(PHMes)_2$ toward bipy,[2m] complex **6** was not formed when **3** was exposed to bipy. In addition, the replacement of the coordinated diphosphene may also be achieved on the addition of Ph_2S_2 or Ph_2Se_2, yielding the disulfido and diselenido complexes $[\eta^5$-$1,3$-$(Me_3C)_2C_5H_3]_2Th(EPh)_2$ (E = S (**7**), Se (**8**)), respectively, in quantitative conversions (Scheme 3).

Nevertheless, despite some differences, there are also similarities with the reactivity observed for the thorium metallacyclopropene $[1,2,4$-$(Me_3C)_3C_5H_2]_2Th(\eta^2$-$C_2Ph_2)$.[5a] For example, in analogy to the reactivity of the zirconium complex $(\eta^5$-$C_5Me_5)_2Zr$



Scheme 3 Synthesis of complexes **5–10**.

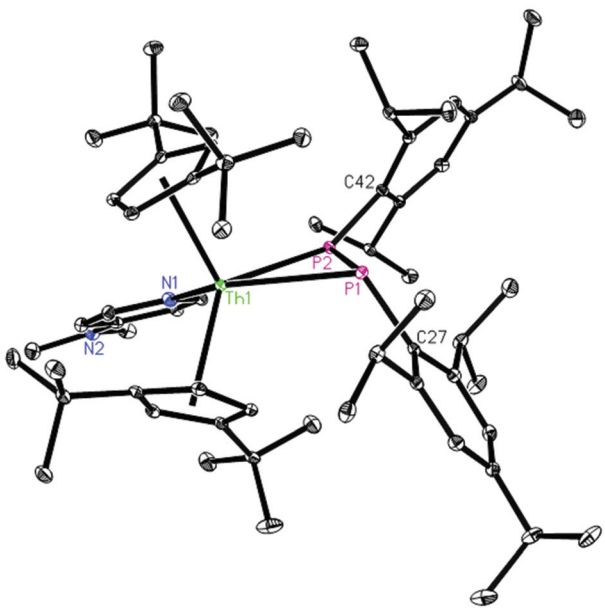


Fig. 5 Molecular structure of **5** (thermal ellipsoids drawn at the 35% probability level).

$(\eta^2$-$P_2Mes_2)$ towards hetero-unsaturated molecules,[6] complex **4** also inserts hetero-unsaturated organic substrates. The addition of 1 equiv. of PhCN to **4** yields the mono-insertion product

$[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th[NCPh\{P_2(2,4,6\text{-}^iPr_3C_6H_2)_2\}]$ (**9**) in quantitative conversion (Scheme 3). DFT computations imply that this reaction is exergonic (ΔG(298 K) = −15.0 kcal mol^{-1}), and occurs *via* the transition state **TS9** with a low activation barrier ($\Delta G^{\ddagger}$(298 K) = 17.4 kcal mol^{-1}) (Fig. 6). This is consistent with the rapid formation of **9** at ambient temperature. The molecular structure of **9** is shown in Fig. 7, and the selected bond distances and angles are provided in Table 1. The Th–N and Th–P distances of 2.227(3) Å and 2.906(1) Å, respectively, are comparable to those found in **5** (Table 1). However, when complex **4** is exposed to *p*-ClPhCHO, only the seven-membered metallaheterocycle $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th[OCH(p\text{-}ClPh)\{P_2(2,4,6\text{-}^iPr_3C_6H_2)_2\}CH(p\text{-}ClPh)O]$ (**10**) (Scheme 3) is isolated irrespective of the amount of aldehyde (*p*-ClPhCHO) added to the reaction mixture. Presumably, as in the case of PhCN, complex **4** converts initially with *p*-ClPhCHO to a five-membered metallaheterocycle, in which a second molecule of *p*-ClPhCHO can insert to yield complex **10**. Fig. 8 depicts the molecular structure of **10**, while Table 1 lists assorted bond distances and angles. The Th–O distances of 2.175(2) and 2.138(2) Å are close to those found in $(\eta^5\text{-}C_5Me_5)_2Th[OCH(p\text{-}ClPh)(C_4Ph_2)CH(p\text{-}ClPh)O]$ (2.157(4) and 2.150(4) Å).[5d]

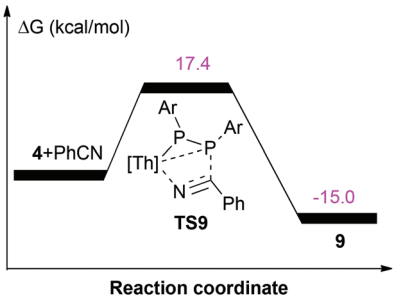


Fig. 6 Energy profile (kcal mol^{-1}) for the reaction of **4** + PhCN (computed at T = 298 K). [Th] = $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th$. Ar = 2,4,6-$^iPr_3C_6H_2$.

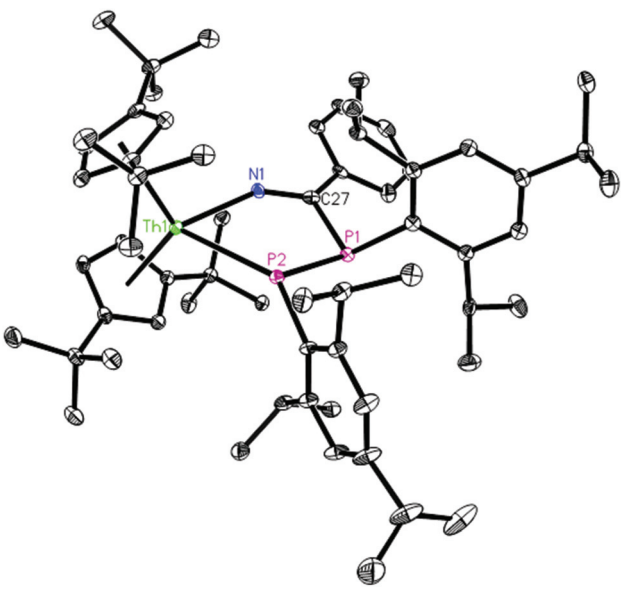


Fig. 7 Molecular structure of **9** (thermal ellipsoids drawn at the 35% probability level).

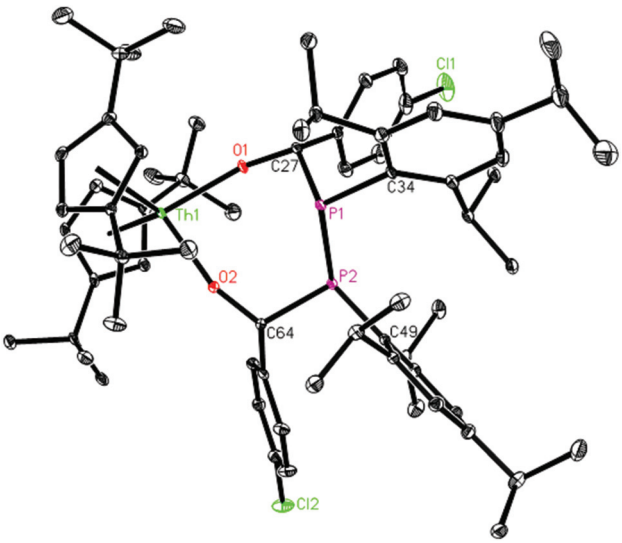


Fig. 8 Molecular structure of **10** (thermal ellipsoids drawn at the 35% probability level).

Conclusions

In conclusion, the synthesis, electronic structure and reactivity of the three-membered diphosphido thorium metallaheterocycle complex $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th[\eta^2\text{-}P_2(2,4,6\text{-}^iPr_3C_6H_2)_2]$ (**4**) were comprehensively studied. Similar to the related thorium metallacyclopropenes,[5a,f] density functional theory (DFT) studies reveal that 5f and 6d orbitals contribute to the bonding within the metallaheterocycle Th-(η^2-P-P) moiety, but the bonds between $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th^{2+}$ and $[\eta^2\text{-}P_2(2,4,6\text{-}^iPr_3C_6H_2)_2]^{2-}$ fragments and their contribution to the bonding are modulated. While the thorium metallacyclopropene $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph_2)$ reacts as a strong base inducing intermolecular C–H bond activations with pyridine derivatives,[5b] the coordinated $[\eta^2\text{-}P_2(2,4,6\text{-}^iPr_3C_6H_2)_2]$ diphosphido ligand in **4** is inert towards DMAP and only the adduct $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th[\eta^2\text{-}P_2(2,4,6\text{-}^iPr_3C_6H_2)_2](DMAP)$ (**5**) is isolated. Furthermore, whereas the coordinated alkyne in the thorium metallacyclopropene $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph_2)$ is inert towards ligand exchange,[5a,f] complex **4** may serve as a synthetic equivalent for $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th$(II) in the reaction with bipy, Ph_2S_2 or Ph_2Se_2, which results in the displacement of the coordinated diphosphene. However, in analogy to the reactivity of the related thorium metallacyclopropenes,[5a] complex **4** shows no reactivity towards alkynes, but it behaves as a nucleophile toward hetero-unsaturated molecules such as nitriles and aldehydes, resulting in five- or seven-membered metallaheterocycles. Further investigations dealing with the intrinsic reactivity of actinide metallaheterocycles are currently in progress.

Experimental

General methods

All reactions and product manipulations were carried out under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2ThCl_2$ (**1**),[4g] 2,4,6-$^{i}Pr_3C_6H_2PH_2$ [7] and 2,4,6-$^{i}Pr_3C_6H_2PHK$[8] 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 X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

Syntheses

Preparation of $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th(Cl)(PH\text{-}2,4,6\text{-}^{i}Pr_3C_6H_2)\cdot 0.5C_6H_6$ (2·0.5C$_6$H$_6$). Solid 2,4,6-$^{i}Pr_3C_6H_2PHK$ (274 mg, 1.0 mmol) was added to a benzene (20 mL) solution of $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2ThCl_2$ (**1**; 657 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, yellow crystals of **2**·0.5C$_6$H$_6$ were isolated when this solution was stored at room temperature for two days. Yield: 806 mg (90%) (found: C, 58.91; H, 7.81. $C_{44}H_{69}ClPTh$ requires C, 58.95; H, 7.76%). M.p.: 111–113 °C (dec.). ^1H NMR (C_6D_6): δ 7.22 (s, 2H, phenyl), 7.15 (s, 3H, C_6H_6), 6.60 (s, 2H, ring C*H*), 6.18 (s, 2H, ring C*H*), 6.16 (s, 2H, ring C*H*), 4.78 (d, J_{P-H} = 227 Hz, 1H, P*H*), 3.93 (m, 2H, C*H*(CH$_3$)$_2$), 2.89 (m, 1H, C*H*(CH$_3$)$_2$), 1.50 (d, J = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 1.34 (s, 18H, C(C*H*$_3$)$_3$), 1.29 (s, 18H, C(C*H*$_3$)$_3$), 1.29 (d, J = 5.8 Hz, 6H, CH(C*H*$_3$)$_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): 151.4 (d, J_{P-C} = 7.7 Hz, phenyl *C*), 151.3 (phenyl *C*), 151.0 (ring *C*), 147.2 (phenyl *C*), 137.8 (d, J_{P-C} = 16.5 Hz, phenyl *C*), 128.5 (*C*$_6$H$_6$), 120.5 (d, J_{P-C} = 4.5 Hz, ring *C*), 118.3 (ring *C*), 112.7 (ring *C*), 112.6 (ring *C*), 34.6 (*C*(CH$_3$)$_3$), 34.2 (d, J_{P-C} = 12.0 Hz, *C*(CH$_3$)$_3$), 33.6 (*C*H(CH$_3$)$_2$), 33.5 (*C*H(CH$_3$)$_2$), 32.2 (C(*C*H$_3$)$_3$), 32.1 (C(*C*H$_3$)$_3$), 24.6 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −2.6 ppm. IR (KBr, cm^{-1}): ν 2960 (s), 2902 (s), 1462 (s), 1396 (s), 1249 (s), 1097 (s), 1020 (s), 800 (s).

Preparation of $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th(PH\text{-}2,4,6\text{-}^{i}Pr_3C_6H_2)_2$ (3). Method A. Solid 2,4,6-$^{i}Pr_3C_6H_2PHK$ (137 mg, 0.5 mmol) was added to a benzene (20 mL) solution of $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th(Cl)(PH\text{-}2,4,6\text{-}^{i}Pr_3C_6H_2)$ (**2**; 429 mg, 0.5 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 and orange crystals of **3** were isolated when this solution was stored at room temperature for two days. Yield: 423 mg (80%) (found: C, 63.69; H, 8.51. $C_{56}H_{90}P_2Th$ requires C, 63.61; H, 8.58%). M.p.: 167–169 °C (dec.). ^1H NMR (C_6D_6): δ 7.23 (s, 4H, phenyl), 6.54 (s, 2H, ring C*H*), 6.23 (d, J = 1.3 Hz, 4H, ring C*H*), 4.71 (d, J_{P-H} = 233 Hz, 2H, P*H*), 4.06 (m, 4H, C*H*(CH$_3$)$_2$), 2.91 (m, 2H, C*H*(CH$_3$)$_2$), 1.49 (d, J = 6.7 Hz, 24H, CH(C*H*$_3$)$_2$), 1.31 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.25 (s, 36H, C(C*H*$_3$)$_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): 151.3 (d, J_{P-C} = 6.6 Hz, phenyl *C*), 150.8 (phenyl *C*), 147.3 (phenyl *C*), 139.1 (d, J_{P-C} = 12.7 Hz, phenyl *C*), 120.6 (d, J_{P-C} = 2.6 Hz, ring *C*), 115.7 (ring *C*), 112.4 (ring *C*), 34.6 (*C*H(CH$_3$)$_2$), 34.0 (d, J_{P-C} = 12 Hz, *C*(CH$_3$)$_3$), 33.6 (*C*H(CH$_3$)$_2$), 32.4 (C(*C*H$_3$)$_3$), 24.6 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 9.8 ppm. IR (KBr, cm^{-1}): ν 2958 (s), 1599 (m), 1460 (s), 1359 (s), 1249 (s), 1057 (s), 802 (s).

Method B. Solid 2,4,6-$^{i}Pr_3C_6H_2PHK$ (274 mg, 1.0 mmol) was added to a benzene (20 mL) solution of $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2ThCl_2$ (**1**; 329 mg, 0.5 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 and orange crystals of **3** were isolated when this solution was kept at room temperature for two days. Yield: 370 mg (70%).

Preparation of $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th[\eta^2\text{-}P_2(2,4,6\text{-}^{i}Pr_3C_6H_2)_2]$ (4). Method A. After a toluene (15 mL) solution of $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th(PH\text{-}2,4,6\text{-}^{i}Pr_3C_6H_2)_2$ (**3**; 529 mg, 0.5 mmol) was stirred at 75 °C for 3 days, the solvent was removed. The residue was extracted with THF (10 mL × 3) and filtered. The volume of the filtrate was reduced to 10 mL and orange microcrystals of **4** were isolated when this solution was stored at room temperature for two days. Yield: 448 mg (85%) (found: C, 63.79; H, 8.39. $C_{56}H_{88}P_2Th$ requires C, 63.74; H, 8.41%). M.p.: 176–178 °C (dec.). ^1H NMR (C_6D_6): δ 7.27 (s, 4H, phenyl), 6.62 (s, 2H, ring C*H*), 6.29 (d, J = 1.3 Hz, 4H, ring C*H*), 4.63 (br s, 4H, C*H*(CH$_3$)$_2$), 2.90 (m, 2H, C*H*(CH$_3$)$_2$), 1.47 (d, J = 6.7 Hz, 24H, CH(C*H*$_3$)$_2$), 1.29 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.28 (s, 36H, C(C*H*$_3$)$_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): 152.8 (phenyl *C*), 149.8 (phenyl *C*), 146.1 (phenyl *C*), 120.8 (ring *C*), 117.3 (ring *C*), 113.1 (ring *C*), 34.4 (*C*H(CH$_3$)$_2$), 33.4 (*C*(CH$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 25.8 (*C*H(CH$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$) ppm; one carbon of phenyl overlapped. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 81.9 ppm. IR (KBr, cm^{-1}): ν 2962 (s), 1404 (s), 1257 (s), 1087 (s), 1018 (s), 802 (s).

Method B. NMR scale. After a J. Young NMR tube charged with $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th(PH\text{-}2,4,6\text{-}^{i}Pr_3C_6H_2)_2$ (**3**; 21 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was stored at 75 °C for 3 days, resonances of **4** and H_2 (^1H NMR (C_6D_6): δ 4.47 ppm) were observed by ^1H NMR spectroscopy (100% conversion).

Preparation of $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th[\eta^2\text{-}P_2(2,4,6\text{-}^{i}Pr_3C_6H_2)_2]$ (DMAP) (5). A benzene (5 mL) solution of DMAP (31 mg, 0.25 mmol) was added to a benzene (10 mL) solution of $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2Th[\eta^2\text{-}P_2(2,4,6\text{-}^{i}Pr_3C_6H_2)_2]$ (**4**; 263 mg, 0.25 mmol) with stirring at room temperature. After this solu-

tion was stirred at room temperature for 1 h, the solution was filtered. The volume of the filtrate was reduced to 5 mL and orange crystals of **5** were isolated when this solution was stored at room temperature for 3 days. Yield: 280 mg (95%) (found: C, 64.29; H, 8.31; N, 2.40. $C_{63}H_{98}N_2P_2Th$ requires C, 64.26; H, 8.39; N, 2.38%). M.p.:195–197 °C (dec.). ^{1}H NMR (C_6D_6): δ 9.01 (br s, 2H, DMAP), 7.35 (s, 2H, phenyl), 7.26 (s, 2H, phenyl), 7.01 (s, 1H, ring C*H*), 6.86 (s, 1H, ring C*H*), 6.43 (br s, 2H, DMAP), 6.16 (br s, 2H, ring C*H*), 6.08 (s, 1H, ring C*H*), 5.91 (s, 1H, ring C*H*), 5.13 (br s, 2H, C*H*(CH_3)$_2$), 4.90 (br s, 2H, C*H*(CH_3)$_2$), 2.94 (br s, 2H, C*H*(CH_3)$_2$), 1.97 (s, 6H, N(C*H*$_3$)$_2$), 1.81 (br s, 12H, CH(C*H*$_3$)$_2$), 1.54 (br s, 12H, CH(C*H*$_3$)$_2$), 1.36 (br s, 24H, CH(C*H*$_3$)$_2$ and C(C*H*$_3$)$_3$), 0.97 (br s, 24H, CH(C*H*$_3$)$_2$ and C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 171.1 (aryl *C*), 150.3 (aryl *C*), 137.8 (aryl *C*), 129.3 (aryl *C*), 128.5 (aryl *C*), 128.3 (aryl *C*), 125.6 (ring *C*), 121.8 (ring *C*), 38.0 (N*C*H$_3$), 34.6 (*C*(CH$_3$)$_3$), 34.5 (*C*(CH$_3$)$_3$), 34.1 (*C*H(CH$_3$)$_2$), 32.9 (*C*H(CH$_3$)$_2$), 32.6 (C(*C*H$_3$)$_3$), 32.5(C(*C*H$_3$)$_3$), 25.8 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 21.4 (CH(*C*H$_3$)$_2$) ppm; other carbons were not observed. ^{31}P{^{1}H} NMR (C_6D_6): 14.4 (d, J_{P-P} = 233.0 Hz), −2.6 (d, J_{P-P} = 233.0 Hz) ppm. IR (KBr, cm^{-1}): ν 2960 (s), 1384 (s), 1259 (s), 1091 (s), 1020 (s), 800 (s).

Preparation of [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th(bipy) (6). Method A. A benzene (5 mL) solution of bipy (39 mg, 0.25 mmol) was added to a benzene (10 mL) solution of [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**; 263 mg, 0.25 mmol) with stirring at room temperature. After the solution was stirred at ambient 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 4 mL and purple crystals of **6** were isolated when this solution was kept at room temperature for two days. Yield: 152 mg (82%). ^{1}H NMR (C_6D_6): δ 7.29 (d, J = 6.4 Hz, 2H, bipy), 6.89 (d, J = 9.6 Hz, 2H, bipy), 6.20 (d, J = 2.4 Hz, 4H, ring C*H*), 6.14 (m, 2H, bipy), 5.95 (t, J = 2.4 Hz, 2H, ring C*H*), 5.30 (t, J = 6.0 Hz, 2H, bipy), 1.22 (s, 36H, (C*H*$_3$)$_3$C) ppm. These spectroscopic data agreed with those reported in the literature.[9]

Method B. NMR scale. A C_6D_6 (0.3 mL) solution of bipy (3.1 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**; 21 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **6** along with those of (2,4,6-^{i}Pr$_3$C$_6$H$_2$P)$_2$ (^{1}H NMR (C_6D_6): δ 7.12 (s, 2H, phenyl), 3.44 (m, 2H, C*H*(CH_3)$_2$), 2.83 (m, 1H, C*H*(CH_3)$_2$), 1.31 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.18 (d, J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$) ppm; ^{31}P{^{1}H} NMR (C_6D_6): 517.9 ppm)[10a] were observed by NMR spectroscopy (40% conversion in 2 h), and conversion to **6** was completed after the sample was stored at room temperature overnight. Nevertheless, diphosphene (2,4,6-^{i}Pr$_3$C$_6$H$_2$P)$_2$ is unstable, which dimerizes to cyclotetraphosphane (2,4,6-^{i}Pr$_3$C$_6$H$_2$P)$_4$ (^{31}P{^{1}H} NMR (C_6D_6): δ −35.9 ppm)[10] during the course of the reaction.

Preparation of [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th(SPh)$_2$ (7). Method A. This compound was isolated as colourless crystals from the reaction of [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**; 263 mg, 0.25 mmol) and Ph_2S_2 (55 mg, 0.25 mmol) in benzene (15 mL) at room temperature and recrystallization from an *n*-hexane solution by a similar procedure to that in the synthesis of **6**. Yield: 173 mg (86%). ^{1}H NMR (C_6D_6): δ 7.79 (d, J = 8.1 Hz, 4H, phenyl), 7.11 (t, J = 7.7 Hz, 4H, phenyl), 6.92 (t, J = 7.4 Hz, 2H, phenyl), 6.22 (d, J = 2.7 Hz, 4H, ring C*H*), 6.13 (t, J = 1.8 Hz, 2H, ring C*H*), 1.34 (s, 36H, C(C*H*$_3$)$_3$) ppm. These spectroscopic data agreed with those reported in the literature.[2t]

Method B. NMR scale. A C_6D_6 (0.3 mL) solution of Ph_2S_2 (4.4 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**; 21 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **7** along with those of (2,4,6-^{i}Pr$_3$C$_6$H$_2$P)$_4$ were observed by NMR spectroscopy (100% conversion) after the sample was stored at room temperature overnight.

Preparation of [η^5-1,3-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(SePh)$_2$ (8). Method A. This compound was isolated as yellow crystals from the reaction of [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**; 263 mg, 0.25 mmol) and Ph_2Se_2 (78 mg, 0.25 mmol) in benzene (15 mL) at room temperature and recrystallization from an *n*-hexane solution by a similar procedure to that in the synthesis of **6**. Yield: 189 mg (84%). ^{1}H NMR (C_6D_6): δ 8.00 (d, J = 5.2 Hz, 4H, phenyl), 7.08 (s, 4H, phenyl), 6.98 (d, J = 5.2 Hz, 2H, phenyl), 6.18 (s, 6H, ring C*H*), 1.33 (s, 36H, (C*H*$_3$)$_3$C). These spectroscopic data agreed with those reported in the literature.[9]

Method B. NMR scale. A C_6D_6 (0.3 mL) solution of Ph_2Se_2 (6.2 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**; 21 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **8** along with those of (2,4,6-^{i}Pr$_3$C$_6$H$_2$P)$_4$ were observed by NMR spectroscopy (100% conversion) after the sample was stored at room temperature overnight.

Preparation of [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[NCPh{P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$}]·C$_6$H$_6$·0.5C$_6$H$_{14}$ (9·C$_6$H$_6$·0.5C$_6$H$_{14}$). Method A. This compound was isolated as green crystals from the reaction of [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**; 263 mg, 0.25 mmol) and PhCN (26 mg, 0.25 mmol) in benzene (15 mL) at room temperature and recrystallization from an *n*-hexane solution by a similar procedure to that in the synthesis of **6**. Yield: 253 mg (79%) (found: C, 67.59; H, 8.32; N, 1.07. $C_{72}H_{106}NP_2Th$ requires C, 67.58; H, 8.35; N, 1.09%). M.p.:180–182 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.99 (d, J = 7.6 Hz, 2H, phenyl), 7.15 (s, 6H, C$_6$*H*$_6$), 6.99 (m, 7H, phenyl), 6.71 (s, 4H, ring C*H*), 6.54 (s, 2H, ring C*H*), 4.53 (br s, 1H, C*H*(CH_3)$_2$), 4.05 (br s, 2H, C*H*(CH_3)$_2$), 3.64 (m, 1H, C*H*(CH_3)$_2$), 2.77 (m, 1H, C*H*(CH_3)$_2$), 2.63 (m, 1H, C*H*(CH_3)$_2$), 1.53 (s, 18H, C(C*H*$_3$)$_3$), 1.42 (s, 18H, C(C*H*$_3$)$_3$), 1.26 (d, J = 7.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.23 (m, 16H, C*H*$_2$ and CH(C*H*$_3$)$_2$), 1.20 (d, J = 7.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.16 (d, J = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.09 (d, J = 7.4 Hz, 6H, CH(C*H*$_3$)$_2$), 0.88 (t, 3H, J = 7.8 Hz, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 156.0 (phenyl *C*), 153.9 (phenyl *C*), 153.4 (phenyl *C*), 150.4 (phenyl *C*), 149.9 (d, J_{P-C} = 21.2 Hz, N=*C*), 147.9 (phenyl *C*), 139.1 (d, J_{P-C} = 41.0 Hz, phenyl *C*), 138.2 (d, J_{P-C} = 56.8 Hz, phenyl *C*), 132.6 (phenyl *C*), 130.0 (phenyl *C*), 129.3 (phenyl *C*), 129.0 (phenyl *C*), 128.6 (phenyl *C*), 128.5 (*C*$_6$H$_6$), 125.6 (ring *C*), 123.8 (ring *C*), 122.2 (ring *C*), 121.8 (ring *C*), 111.9 (ring *C*), 34.7 (*C*(CH$_3$)$_3$), 34.5 (*C*(CH$_3$)$_3$), 33.9 (*C*H(CH$_3$)$_2$),

33.6 (C(CH_3)$_3$), 33.3 (CH(CH$_3$)$_2$), 32.7 (C(CH_3)$_3$), 32.2 (CH(CH$_3$)$_2$), 31.9 (CH_2), 31.0 (CH(CH$_3$)$_2$), 25.8 (CH(CH_3)$_2$), 24.5 (CH(CH_3)$_2$), 24.2 (CH(CH_3)$_2$), 24.2 (CH(CH_3)$_2$), 23.0 (CH_2), 14.3 (CH_3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ 104.2 (br s, ThP), −0.9 (br s, ThP') ppm. IR (KBr, cm^{-1}): ν 2960 (s), 1460 (s), 1388 (s), 1259 (s), 1093 (s), 1022(s), 800 (s).

Method B. NMR scale. A C_6D_6 (0.3 mL) solution of PhCN (2.1 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**; 21 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **9** were observed by ^{1}H NMR spectroscopy (100% conversion in 10 min).

Preparation of [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[OCH(*p*-ClPh){P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$}CH(*p*-ClPh)O]·0.5C$_6$H$_6$ (10·0.5C$_6$H$_6$). Method A. This compound was isolated as colourless crystals from the reaction of [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**; 263 mg, 0.25 mmol) and *p*-ClPhCHO (70 mg, 0.50 mmol) in benzene (15 mL) at room temperature and recrystallization from an *n*-hexane solution by a similar procedure as that in the synthesis of **6**. Yield: 292 mg (85%) (found: C, 63.71; H, 7.45. $C_{73}H_{101}Cl_2O_2P_2Th$ requires C, 63.74; H, 7.40%). M.p.: 155–157 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.34 (d, J = 7.9 Hz, 4H, phenyl), 7.15 (s, 3H, C_6H_6), 7.08 (s, 2H, ring CH), 7.00 (s, 2H, phenyl), 6.98 (s, 2H, phenyl), 6.74 (d, J = 7.8 Hz, 4H, phenyl), 6.54 (s, 2H, ring CH), 6.45 (s, 2H, ring CH), 6.30 (s, 2H, CHO), 4.53 (br s, 2H, CH(CH$_3$)$_2$), 3.92 (br s, 2H, CH(CH$_3$)$_2$), 2.60 (m, 2H, CH(CH$_3$)$_2$), 1.78 (d, J = 5.7 Hz, 6H, CH(CH_3)$_2$), 1.54 (s, 18H, C(CH_3)$_3$), 1.40 (d, J = 5.7 Hz, 12H, CH(CH_3)$_2$), 1.24 (s, 18H, C(CH_3)$_3$), 1.06 (d, J = 6.7 Hz, 12H, CH(CH_3)$_2$), 0.69 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 155.0 (phenyl C), 150.7 (phenyl C), 148.7 (phenyl C), 143.0 (d, J_{P-C} = 25.0 Hz, phenyl C), 132.8 (phenyl C), 129.8 (phenyl C), 128.6 (phenyl C), 128.5 (C_6H_6), 124.0 (phenyl C), 121.9 (ring C), 114.4 (ring C), 113.0 (ring C), 112.1 (d, J_{P-C} = 30.0 Hz, OCH), 110.7 (ring C), 109.9 (ring C), 33.6 (C(CH_3)$_3$), 33.3 (C(CH_3)$_3$), 33.0 (CH(CH$_3$)$_2$), 32.6 (C(CH_3)$_3$), 32.2 (C(CH_3)$_3$), 26.9 (CH(CH$_3$)$_2$), 25.5 (CH(CH$_3$)$_2$), 24.2 (CH(CH_3)$_2$), 23.9 (CH(CH_3)$_2$), 23.8 (CH(CH_3)$_2$) ppm. ^{31}P{^{1}H} NMR (C_6D_6): −6.8 ppm. IR (KBr, cm^{-1}): ν 2960 (s), 1560 (s), 1400 (s), 1384 (s), 1259 (s), 1089 (s), 1058 (s), 1016 (s), 800 (s).

Method B. NMR scale. A C_6D_6 (0.3 mL) solution of *p*-ClPhCHO (5.6 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**; 21 mg, 0.02 mmol) and C_6D_6 (0.2 mL). Resonances of **10** were observed by ^{1}H NMR spectroscopy (100% conversion) after the sample was kept at room temperature overnight.

Reaction of [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (4) with *p*-ClPhCHO. NMR scale. A C_6D_6 (0.2 mL) solution of *p*-ClPhCHO (2.8 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th[η^2-P$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$] (**4**; 21 mg, 0.02 mmol) and C_6D_6 (0.3 mL). Resonances of **10** along with those of unreacted **4** were observed by ^{1}H NMR spectroscopy (50% conversion based on **4**) 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.[11] All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL program package.[12] All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **2–3**, **5** and **9–10** are summarized in the ESI.† Selected bond distances and angles are listed in Table 1.

Computational methods

Computations were carried out with the Gaussian 09 program (G09),[13] employing the B3PW91 functional, plus a polarizable continuum model (PCM) (denoted as B3PW91-PCM), with standard 6-31G(d) basis set for C, H, N and P elements, and a quasi-relativistic 5f-in-valence effective-core potential (ECP60MWB) treatment with 60 electrons in the core region for Th and the corresponding optimized segmented ((14s13p10d8f6g)/[10s9p5d4f3g]) basis set for the valence shells of Th,[14] to fully optimize the structures of reactants, complexes, transition states, intermediates, and products, and also to mimic the experimental toluene-solvent conditions (dielectric constant ε = 2.379). All stationary points were subsequently characterized by vibrational analyses, from which their respective zero-point (vibrational) energy (ZPE) was extracted and used in the relative energy determinations. Furthermore, frequency calculations were performed to ensure that the reactant, complex, intermediate, product and transition state structures remained at minima and 1st order saddle points, respectively, on their potential energy hypersurfaces.

Conflicts of interest

There are no conflicts to declare.

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