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C–H bond activation induced by thorium metallacyclopropene complexes: a combined experimental and computational study†

Bo Fang,‡[a] Lei Zhang,‡[a] Guohua Hou,[a] Guofu Zi,*[a] De-Cai Fang*[a] and Marc D. Walter*[b]

Inter- and intramolecular C–H bond activations by thorium metallacyclopropene complexes were comprehensively studied. The reduction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2ThCl_2$ (**1**) with potassium graphite (KC_8) in the presence of internal alkynes (PhC≡CR) yields the corresponding thorium metallacyclopropenes $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph(R))$ (R = Ph (**2**), Me (**3**), ^{i}Pr (**4**), C_6H_{11} (**5**)). Complexes **3–5** derived from phenyl(alkyl)acetylenes are very reactive resulting in an intramolecular C–H bond activation of the 1,2,4-$(Me_3C)_3C_5H_2$ ligand. In contrast, no intramolecular C–H bond activation is observed for the diphenylacetylene derived complex **2**, but it does activate α-C–H bonds in pyridine or carbonyl derivatives upon coordination. Density functional theory (DFT) studies complement the experimental studies and provide additional insights into the observed reactivity.

Introduction

Highly strained metallacyclopropenes are reactive functionalities and can serve as precursors for the synthesis of highly functionalized organic molecules and heterocyclic main group compounds.[1–3] In this context metallacyclopropenes of group 4 metallocenes have been of particular interest[1,2] and are readily prepared by the reaction of Cp'_2M (Cp′ = (un)substituted η^5-cyclopentadienyl) with alkynes or by the reduction of Cp'_2MCl_2 in the presence of a suitable alkyne.[1b] However, group 4 metallacyclopropenes derived from differently substituted alkynes are exceptionally rare,[2j–m] see *e.g.* $[\eta^5\text{-}C_5H_5]_2Zr(\eta^2\text{-}RC_2SiMe_2H)$ (R = ^{t}Bu, Ph, $SiMe_3$).[2j] One reason for this is that especially for the heavier (and therefore larger) group 4 metals the use of less sterically demanding alkynes generally produces the more stable metallacyclopentadienes, and therefore detailed investigations on metallacyclopropenes have been limited to bulky and symmetrically substituted alkynes such as PhC≡CPh and $Me_3SiC{\equiv}CSiMe_3$.[1b,2n,o] In addition, the metallacyclopropenes derived from $Me_3SiC{\equiv}CSiMe_3$ are also more susceptible to substitutions and to participate in C–H bond activation processes.[1b,2n,o] Nevertheless, in contrast to the rich group 4 chemistry, actinide metallacyclopropenes have remained rare,[4] and only recently the first stable metallacyclopropene $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph_2)$ (**2**) has been prepared.[5] Several studies have now established that in actinide chemistry the 5f orbitals have significant influence on the reactivity.[6] Thorium with its $7s^26d^2$ ground state stands on the borderline between group 4 metals and the actinides and it is therefore a very attractive element for further investigations. Complex **2** reacts with a variety of hetero-unsaturated molecules such as aldehydes, ketones, CS_2, carbodiimides, nitriles, isothiocyanates, organic azides, and diazoalkane derivatives.[5] The $Th(\eta^2\text{-}PhCCPh)$ moiety in complex **2** shows no reactivity towards additional alkynes to form metallacyclopentadienes and no exchange with added alkynes. Therefore it is of interest to explore the reduction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2ThCl_2$ (**1**) in the presence of unsymmetrically substituted alkynes such as PhC≡CR to prepare novel thorium metallacyclopropenes that can be tuned in their steric and electronic properties and to investigate their ability to participate in C–H bond activation processes that are a highly topical field in organoactinide research[7] and also to correlate this reactivity to group 4 metal chemistry. These studies are described in this article.

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

[a]Department of Chemistry, Beijing Normal University, Beijing 100875, China. E-mail: gzi@bnu.edu.cn; dcfang@bnu.edu.cn; Fax: +86-10-58802075; Tel: +86-10-58806051

[b]Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany. E-mail: mwalter@tu-bs.de; Fax: +49-531-3915387; Tel: +49-531-3915312

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‡ These authors contributed equally to this work.

glove box. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. KC_8,[8] [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2ThCl_2$ (**1**)[9] and [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$-Th(η^2-C_2Ph_2) (**2**)[5] 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. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 and 100 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents, which served as internal standards, for proton and carbon chemical shifts. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

Syntheses

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2$][η^5,σ-1,2-$(Me_3C)_2$-4-(CH_2CMe_2)C_5H_2]Th[C(Ph)=CH^{i}Pr] (7). KC_8 (1.20 g, 8.80 mmol) was added to a toluene (20 mL) solution of [η^5-1,2,4-$(Me_3C)_3$-$C_5H_2]_2ThCl_2$ (**1**; 2.00 g, 2.6 mmol) and PhC≡C^{i}Pr (0.38 g, 2.6 mmol) with stirring at room temperature. After this solution was stirred one day at 80 °C, the solvent was removed. The residue was extracted with benzene (10 mL × 3) and filtered. The volume of the filtrate was reduced to 10 mL, colorless crystals of **7** were isolated when this solution was kept at room temperature for two days. Yield: 1.64 g (75%) (found: C, 64.08; H, 8.43. $C_{45}H_{70}Th$ requires C, 64.11; H, 8.37%). M.p.: 202–204 °C. ^{1}H NMR (C_6D_6): δ 7.36 (t, J = 7.7 Hz, 2H, phenyl), 7.21 (d, J = 7.2 Hz, 2H, phenyl), 6.97 (t, J = 7.4 Hz, 1H, phenyl), 6.49 (d, J = 3.4 Hz, 1H, ring C*H*), 6.10 (d, J = 3.5 Hz, 1H, ring C*H*), 5.92 (d, J = 3.4 Hz, 1H, ring C*H*), 5.75 (d, J = 3.5 Hz, 1H, ring C*H*), 5.41 (d, J = 7.2 Hz, 1H, C=C*H*^{i}Pr), 2.95 (m, 1H, C*H*$(CH_3)_2$), 1.71 (s, 3H, C$(CH_3)_2$), 1.66 (s, 3H, C$(CH_3)_2$), 1.57 (s, 9H, C$(CH_3)_3$), 1.50 (s, 9H, C$(CH_3)_3$), 1.48 (s, 9H, C$(CH_3)_3$), 1.47 (s, 9H, C$(CH_3)_3$), 1.22 (s, 9H, C$(CH_3)_3$), 1.06 (m, 7H, ThCH_2 and CH$(CH_3)_2$), −0.01 (d, J = 13.0 Hz, 1H, ThCH_2) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 219.6 (Th*C*Ph), 151.5 (phenyl *C*), 143.9 (phenyl *C*), 142.2 (phenyl *C*), 140.4 (phenyl *C*), 139.5 (ring *C*), 138.3 (ring *C*), 128.5 (ring *C*), 124.6 (ring *C*), 124.2 (ring *C*), 124.1 (C=*C*H^{i}Pr), 123.7 (ring *C*), 116.9 (ring *C*), 115.5 (ring *C*), 114.0 (ring *C*), 112.0 (ring *C*), 49.8 (ThCH_2), 35.8 (*C*$(CH_3)_3$), 35.5 (*C*$(CH_3)_3$), 35.0 (C$(CH_3)_3$), 34.9 (C$(CH_3)_3$), 34.7 (*C*$(CH_3)_3$), 34.4 (C$(CH_3)_3$), 34.3 (*C*$(CH_3)_3$), 34.2 ($CH_2C(CH_3)_2$), 34.0 (C$(CH_3)_3$), 33.9 (*C*$(CH_3)_3$), 32.6 (C$(CH_3)_3$), 30.4 ($CH_2C(CH_3)_2$), 28.5 (CH_2*C*$(CH_3)_2$), 23.5 (*C*H$(CH_3)_2$), 23.4 (CH$(CH_3)_2$) ppm. IR (KBr, cm^{-1}): ν 2954 (s), 1589 (m), 1485 (s), 1456 (s), 1384 (s), 1357 (s), 1238 (s), 1165 (s), 1070 (s), 1028 (s), 904 (m), 813 (s).

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2$][η^5,σ-1,2-$(Me_3C)_2$-4-(CH_2CMe_2)C_5H_2]Th[C(Ph)=CH(C_6H_{11})] (8). This compound was prepared as colorless crystals from the reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2ThCl_2$ (**1**; 2.00 g, 2.6 mmol) and PhC≡C(C_6H_{11}) (0.48 g, 2.6 mmol) in the presence of KC_8 (1.20 g, 8.80 mmol) in toluene (20 mL) at 100 °C and recrystallization from a benzene solution by a similar procedure as in the synthesis of **7**. Yield: 1.84 g (80%) (found: C, 65.30; H, 8.43. $C_{48}H_{74}Th$ requires C, 65.28; H, 8.45%). M.p.: 180–182 °C. ^{1}H NMR (C_6D_6): δ 7.36 (t, J = 7.6 Hz, 2H, phenyl), 7.24 (d, J = 7.4 Hz, 2H, phenyl), 6.96 (t, J = 7.2 Hz, 1H, phenyl), 6.49 (d, J = 3.4 Hz, 1H, ring C*H*), 6.10 (d, J = 3.5 Hz, 1H, ring C*H*), 5.93 (d, J = 3.4 Hz, 1H, ring C*H*), 5.78 (d, J = 3.5 Hz, 1H, ring C*H*), 5.48 (d, J = 7.2 Hz, 1H, C=C*H*Cy), 2.74 (m, 1H, cyclohexyl-C*H*), 1.83 (br s, 2H, cyclohexyl-CH_2), 1.72 (s, 3H, C$(CH_3)_2$), 1.71 (s, 3H, C$(CH_3)_2$), 1.58 (s, 9H, C$(CH_3)_3$), 1.51 (s, 9H, C$(CH_3)_3$), 1.50 (s, 18H, C$(CH_3)_3$), 1.44 (m, 4H, cyclohexyl-CH_2), 1.22 (s, 9H, C$(CH_3)_3$), 1.07 (m, 5H, ThCH_2 and cyclohexyl-CH_2), 0.01 (d, J = 13.0 Hz, 1H, ThCH_2) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 220.3 (Th*C*Ph), 151.6 (phenyl *C*), 144.0 (phenyl *C*), 142.2 (phenyl *C*), 140.4 (phenyl *C*), 139.6 (ring *C*), 138.4 (ring *C*), 128.5 (ring *C*), 124.2 (C=*C*HCy), 124.1 (ring *C*), 123.7 (ring *C*), 123.6 (ring *C*), 117.0 (ring *C*), 115.6 (ring *C*), 114.0 (ring *C*), 112.1 (ring *C*), 49.7 (ThCH_2), 38.2 (*C*H), 35.8 (*C*$(CH_3)_3$), 35.5 (*C*$(CH_3)_3$), 35.4 (*C*$(CH_3)_3$), 35.1 (C$(CH_3)_3$), 34.9 (C$(CH_3)_3$), 34.7 (*C*$(CH_3)_3$), 34.5 (C$(CH_3)_3$), 34.4 (CH_2), 34.1 (C$(CH_3)_3$), 34.0 ($CH_2C(CH_3)_2$), 33.9 (*C*$(CH_3)_3$), 33.4 (CH_2*C*$(CH_3)_2$), 32.6 (C$(CH_3)_3$), 32.5 (CH_2), 30.6 ($CH_2C(CH_3)_2$), 26.2 (CH_2), 26.1 (CH_2), 26.0 (CH_2) ppm. IR (KBr, cm^{-1}): ν 2955 (s), 2925 (s), 1599 (m), 1448 (s), 1360 (s), 1260 (s), 1096 (s), 1028 (s), 808 (s).

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2$][η^5,σ-1,2-$(Me_3C)_2$-4-(CH_2CMe_2)C_5H_2]Th[η^3-CH(Ph)CHCH_2]·C_6H_6 (9·C_6H_6). This compound was prepared as orange crystals from the reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2ThCl_2$ (**1**; 2.00 g, 2.6 mmol) and PhC≡CCH_3 (0.30 g, 2.6 mmol) in the presence of KC_8 (1.20 g, 8.80 mmol) in toluene (20 mL) at 70 °C and recrystallization from a benzene solution by a similar procedure as in the synthesis of **7**. Yield: 1.97 g (85%) (found: C, 65.88; H, 8.16. $C_{49}H_{72}Th$ requires C, 65.89; H, 8.13%). M.p.: 216–218 °C. ^{1}H NMR (C_6D_6): δ 7.37 (d, J = 7.8 Hz, 2H, phenyl), 7.25 (t, J = 7.7 Hz, 2H, phenyl), 7.15 (s, 6H, C_6H_6), 7.00 (t, J = 7.3 Hz, 1H, phenyl), 6.67 (m, 1H, PhCH=C*H*), 6.10 (d, J = 3.4 Hz, 1H, ring C*H*), 6.01 (d, J = 3.5 Hz, 1H, ring C*H*), 5.94 (d, J = 3.4 Hz, 1H, ring C*H*), 5.30 (d, J = 3.5 Hz, 1H, ring C*H*), 4.64 (d, J = 15.6 Hz, 1H, PhC*H*=CH), 2.59 (m, 1H, ThCH_2CH=CHPh), 2.47 (m, 1H, ThCH_2CH=CH), 1.53 (br s, 12H, C$(CH_3)_3$ and C$(CH_3)_2$), 1.52 (s, 9H, C$(CH_3)_3$), 1.40 (s, 9H, C$(CH_3)_3$), 1.33 (s, 9H, C$(CH_3)_3$), 1.29 (s, 9H, C$(CH_3)_3$), 1.03 (s, 3H, C$(CH_3)_2$), 0.27 (d, J = 12.7 Hz, 1H, ThCH_2), −0.09 (d, J = 12.7 Hz, 1H, ThCH_2) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 142.9 (phenyl *C*), 142.0 (phenyl *C*), 140.2 (phenyl *C*), 139.8 (phenyl *C*), 139.6 (ring *C*), 139.3 (ring *C*), 129.3 (ring *C*), 128.7 (ring *C*), 128.5 (ring *C*), 128.0 (C_6H_6), 124.9 (ring *C*), 124.7 (ring *C*), 123.4 (ring *C*), 114.3 (ring *C*), 112.2 (ring *C*), 111.8 (Ph*C*H=CH), 100.8 (PhCH=*C*H), 66.1 (ThCH_2CH=CHPh), 45.6 (ThCH_2), 35.4 (*C*$(CH_3)_3$), 35.2 (*C*$(CH_3)_3$), 35.0 (C$(CH_3)_3$), 34.9 (*C*$(CH_3)_3$), 34.8 (C$(CH_3)_3$), 34.3 (*C*$(CH_3)_3$), 34.0 (C$(CH_3)_3$), 33.6 (*C*$(CH_3)_3$), 33.5 (C$(CH_3)_3$), 33.4 ($CH_2C(CH_3)_2$), 32.9 (C$(CH_3)_3$), 32.8 ($CH_2C(CH_3)_2$), 30.2 (*C*$(CH_3)_2$) ppm. IR (KBr, cm^{-1}): ν 2956 (s), 2904 (s), 1473 (s), 1460 (s), 1386 (s), 1361 (s), 1238 (s), 1070 (s), 1022 (s), 812 (s).

When the isotopically labeled alkyne PhC≡CCD_3 was used, the resonance at δ = 4.64 ppm corresponding to PhC*H*=CH in complex **9** disappeared, indicating that indeed a [1,3]-hydrogen migration had occurred in the PhC=CHCH_3 fragment resulting in the formation of **9**.

Preparation of [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$Th[C(Ph)=CHPh]-(η^2-*C,N*–C_5H_4N) (10)

Method A. A toluene solution (5 mL) of pyridine (20 mg, 0.25 mmol) was added to a toluene (10 mL) solution of [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$Th(η^2-C_2Ph_2) (**2**; 220 mg, 0.25 mmol) with stirring at room temperature. After the solution was stirred at room temperature four days, the solvent was removed. The residue was extracted with benzene (10 mL × 3) and filtered. The volume of the filtrate was reduced to 2 mL, colorless crystals of **10** were isolated when this solution was kept at room temperature for one week. Yield: 206 mg (86%) (found: C, 66.63; H, 7.62; N, 1.43. $C_{53}H_{73}$NTh requires C, 66.57; H, 7.70; N, 1.46%). M.p.: 192–194 °C. ^{1}H NMR (C_6D_6): δ 7.90 (d, J = 7.5 Hz, 1H, pyridyl), 7.45 (m, 5H, phenyl), 7.36 (t, J = 7.6 Hz, 2H, phenyl), 7.12 (m, 2H, phenyl), 7.06 (s, 1H, C=C*H*), 6.98 (m, 1H, pyridyl), 6.93 (t, J = 7.4 Hz, 1H, pyridyl), 6.87 (m, 1H, phenyl), 6.58 (d, J = 3.2 Hz, 2H, ring C*H*), 6.38 (t, J = 6.0 Hz, 1H, pyridyl), 6.33 (d, J = 3.2 Hz, 2H, ring C*H*), 1.51 (s, 18H, C(CH_3)$_3$), 1.45 (s, 18H, C(CH_3)$_3$), 1.04 (s, 18H, C(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 229.8 (Th*C*Ph), 210.1 (Th*C*N), 154.0 (aryl *C*), 145.5 (aryl *C*), 142.7 (aryl *C*), 142.5 (aryl *C*), 141.2 (aryl *C*), 137.7 (aryl *C*), 136.3 (aryl *C*), 134.9 (aryl *C*), 133.4 (aryl *C*), 129.7 (aryl *C*), 128.5 (aryl *C*), 128.4 (aryl *C*), 126.4 (ring *C*), 126.3 (ring *C*), 124.1 (ring *C*), 122.8 (ring *C*), 118.1 (ring *C*), 112.6 (C=*C*HPh), 34.9 (*C*(CH$_3$)$_3$), 34.8 (C(*C*H$_3$)$_3$), 34.5 (*C*(CH$_3$)$_3$), 34.0 (C(*C*H$_3$)$_3$), 33.0 (C(*C*H$_3$)$_3$) ppm; one *C* resonance of Me$_3$*C*-groups overlapped. IR (KBr, cm^{-1}): ν 2958 (s), 1590 (s), 1480 (s), 1458 (s), 1357 (s), 1237 (s), 1001 (s), 825 (s).

Method B. NMR scale. A C_6D_6 (0.3 mL) solution of pyridine (1.6 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$Th(η^2-C_2Ph_2) (**2**; 18 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The NMR sample was maintained at room temperature and monitored periodically by ^{1}H NMR spectroscopy. After one day, conversion to **10** was 40% complete, and after four days, conversion to **10** was complete.

When perdeuterated pyridine C_5D_5N was used, the resonance at δ = 7.06 ppm corresponding to the PhC*H*=C fragment in **10** disappeared completely, confirming that a deuterium atom was transferred to the alkenyl group.

Preparation of [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$Th[C(Ph)=CHPh]-(η^2-*C,N*-4-Me_2N-C_5H_3N) (11)

Method A. This compound was prepared as colorless microcrystals from the reaction of [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$Th(η^2-C_2Ph_2) (**2**; 220 mg, 0.25 mmol) and DMAP (31 mg, 0.25 mmol) in toluene (15 mL) at room temperature and recrystallization from an *n*-hexane solution by a similar procedure as in the synthesis of **10**. Yield: 217 mg (87%) (found: C, 66.13; H, 7.79; N, 2.83. $C_{55}H_{78}N_2$Th requires C, 66.11; H, 7.87; N, 2.80%). M.p.: 176–178 °C. ^{1}H NMR (C_6D_6): δ 7.55 (d, J = 7.3 Hz, 2H, phenyl), 7.48 (m, 3H, phenyl), 7.41 (t, J = 7.6 Hz, 2H, phenyl), 7.27 (s, 1H, pyridyl), 7.12 (m, 3H, phenyl and C=C*H*), 6.94 (t, J = 7.3 Hz, 1H, phenyl), 6.72 (d, J = 5.8 Hz, 1H, pyridyl), 6.62 (d, J = 3.2 Hz, 2H, ring C*H*), 6.34 (d, J = 3.2 Hz, 2H, ring C*H*), 5.83 (dd, J = 6.4, 2.4 Hz, 1H, pyridyl), 2.27 (s, 6H, (CH_3)$_2$N), 1.55 (s, 36H, C(CH_3)$_3$), 1.19 (s, 18H, C(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 225.0 (Th*C*Ph), 210.3 (Th*C*N), 154.6 (aryl *C*), 153.6 (aryl C), 144.6 (aryl *C*), 142.1 (aryl *C*), 142.0 (aryl *C*), 140.6 (aryl *C*), 138.0 (aryl *C*), 133.3 (aryl *C*), 129.7 (aryl *C*), 128.4 (aryl *C*), 128.3 (aryl *C*), 126.5 (aryl *C*), 126.1 (ring *C*), 122.5 (ring *C*), 117.8 (ring *C*), 116.9 (ring *C*), 112.3 (ring *C*), 109.2 (C=*C*HPh), 38.6 ((*C*H$_3$)$_2$N), 35.0 (C(*C*H$_3$)$_3$), 34.8 (*C*(CH$_3$)$_3$), 34.7 (*C*(CH$_3$)$_3$), 34.6 (*C*(CH$_3$)$_3$), 34.1 (C(*C*H$_3$)$_3$), 33.1 (C(*C*H$_3$)$_3$) ppm. IR (KBr, cm^{-1}): ν 2956 (s), 1582 (s), 1490 (s), 1434 (s), 1363 (s), 1257 (s), 1238 (s), 1165 (s), 996 (s), 825 (s).

Method B. NMR scale. A C_6D_6 (0.3 mL) solution of DMAP (2.5 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$Th(η^2-C_2Ph_2) (**2**; 18 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The NMR sample was maintained at room temperature and monitored periodically by ^{1}H NMR spectroscopy. After one day, conversion to **11** was 70% complete, and after two days, conversion to **11** was complete.

Preparation of [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$Th[C(Ph)=CHPh]-(κ^2-*C,O*–C_5H_4NO) (12)

Method A. This compound was prepared as colorless crystals from the reaction of [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$Th(η^2-C_2Ph_2) (**2**; 220 mg, 0.25 mmol) and pyridine *N*-oxide (24 mg, 0.25 mmol) in toluene (15 mL) at room temperature and recrystallization from an *n*-hexane solution by a similar procedure as in the synthesis of **10**. Yield: 219 mg (90%) (found: C, 65.43; H, 7.59; N, 1.43. $C_{53}H_{73}$NOTh requires C, 65.48; H, 7.57; N, 1.44%). M.p.: 136–138 °C. ^{1}H NMR (C_6D_6): δ 7.46 (m, 4H, phenyl), 7.36 (t, J = 7.6 Hz, 2H, phenyl), 7.12 (t, J = 7.8 Hz, 2H, phenyl), 7.05 (t, J = 7.2 Hz, 1H, pyridyl), 6.92 (t, J = 6.6 Hz, 2H, phenyl), 6.82 (s, 1H, C=C*H*), 6.70 (d, J = 3.1 Hz, 2H, ring C*H*), 6.46 (d, J = 3.1 Hz, 2H, ring C*H*), 6.38 (t, J = 7.0 Hz, 1H, pyridyl), 6.29 (br s, 1H, pyridyl), 6.15 (m, 1H, pyridyl), 1.55 (s, 18H, C(CH_3)$_3$), 1.49 (s, 18H, C(CH_3)$_3$), 1.21 (s, 18H, C(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 215.7 (Th*C*Ph), 202.2 (Th*C*N), 152.6 (aryl *C*), 143.7 (aryl *C*), 141.2 (aryl *C*), 137.6 (aryl *C*), 136.9 (aryl *C*), 134.4 (aryl *C*), 129.8 (aryl *C*), 128.4 (aryl *C*), 128.3 (aryl *C*), 128.1 (aryl *C*), 127.9 (aryl *C*), 127.2 (aryl *C*), 127.1 (ring *C*), 126.5 (ring *C*), 122.9 (ring *C*), 122.4 (ring *C*), 117.8 (ring *C*), 112.9 (C=*C*HPh), 35.2 (*C*(CH$_3$)$_3$), 34.9 (*C*(CH$_3$)$_3$), 34.6 (C(*C*H$_3$)$_3$), 34.5 (*C*(CH$_3$)$_3$), 34.4 (C(*C*H$_3$)$_3$), 33.1 (C(*C*H$_3$)$_3$) ppm. IR (KBr, cm^{-1}): ν 2957 (s), 1590 (s), 1481 (s), 1450 (s), 1387 (s), 1237 (s), 1171 (s), 1026 (s), 821 (s).

Method B. NMR scale. A C_6D_6 (0.3 mL) solution of pyridine *N*-oxide (1.9 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$Th(η^2-C_2Ph_2) (**2**; 18 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The color of the solution immediately changed from pale yellow to colorless, and the NMR resonances of **12** were observed by ^{1}H NMR spectroscopy (100% conversion in 10 min).

Preparation of [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$Th[C(Ph)=CHPh]-[O–C(=CH_2)NMe_2] (13)

Method A. This compound was prepared as colorless crystals from the reaction of [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$Th(η^2-C_2Ph_2) (**2**; 220 mg, 0.25 mmol) and CH_3CONMe_2 (22 mg, 0.25 mmol) in toluene (15 mL) at room temperature and recrystallization from a benzene solution by a similar procedure as in the synthesis of **10**. Yield: 202 mg (84%) (found: C, 64.75; H, 8.02; N, 1.42. $C_{52}H_{77}$NOTh requires C, 64.77; H, 8.05; N, 1.45%). M.p.: 176–178 °C. ^{1}H NMR (C_6D_6): δ 7.48 (d, J = 7.1 Hz, 2H, phenyl), 7.39 (m, 3H, phenyl and C=C*H*Ph), 7.23 (t, J = 7.7 Hz, 2H, phenyl), 7.06 (t, J = 7.7 Hz, 2H, phenyl), 6.99 (t, J = 7.3 Hz, 1H, phenyl), 6.92 (t, $J = 7.4$ Hz, 1H, phenyl), 6.77 (s, 4H, ring C*H*), 3.59 (s, 2H, OC=C*H*$_2$), 2.56 (s, 6H, N(C*H*$_3$)$_2$), 1.58 (s, 18H, C(C*H*$_3$)$_3$), 1.45 (s, 18H, C(C*H*$_3$)$_3$), 1.37 (s, 18H, C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 225.3 (Th*C*Ph), 169.9 (O*C*=C), 149.4 (phenyl *C*), 145.7 (phenyl *C*), 145.4 (phenyl *C*), 144.6 (phenyl *C*), 137.0 (phenyl *C*), 130.2 (phenyl *C*), 129.1 (phenyl *C*), 128.5 (phenyl *C*), 128.2 (ring *C*), 127.8 (ring *C*), 126.9 (ring *C*), 124.9 (ring *C*), 117.0 (ring *C*), 116.8 (C=*C*HPh), 70.0 (C=*C*H$_2$), 40.8 (N(*C*H$_3$)$_2$), 35.3 (*C*(CH$_3$)$_3$), 35.0 (*C*(CH$_3$)$_3$), 34.8 (C(*C*H$_3$)$_3$), 34.5 (C(*C*H$_3$)$_3$), 33.2 (C(*C*H$_3$)$_3$) ppm; one *C* resonance of Me$_3$*C*-groups overlapped. IR (KBr, cm^{-1}): ν 2955 (s), 1610 (s), 1485 (s), 1326 (s), 1237 (s), 1194 (s), 1098 (s), 1075 (s), 1021 (s), 987 (s), 806 (s).

Method B. NMR scale. A C_6D_6 (0.3 mL) solution of CH_3CONMe_2 (1.8 mg; 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(η^2-C$_2$Ph$_2$) (**2**; 18 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The color of the solution immediately changed from pale yellow to colorless, and the NMR resonances of **13** were observed by ^{1}H NMR spectroscopy (100% conversion in 10 min).

X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker SMART CCD diffractometer at 100(2) K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). An

Table 1 Crystal data and experimental parameters for compounds **7–10**, **12** and **13**

Compound	**7**	**8**	**9**·C$_6$H$_6$	**10**	**12**	**13**
Formula	C$_{45}$H$_{70}$Th	C$_{48}$H$_{74}$Th	C$_{49}$H$_{72}$Th	C$_{53}$H$_{73}$NTh	C$_{53}$H$_{73}$NOTh	C$_{52}$H$_{77}$NOTh
F_w	843.05	883.11	893.10	956.16	972.16	964.18
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	*Pc*	*P*2$_1$/*n*	*P*($\bar{1}$)	*P*($\bar{1}$)	*P*2$_1$/*c*	*P*($\bar{1}$)
a (Å)	12.658(7)	10.699(3)	10.468(3)	11.109(2)	15.278(3)	10.962(2)
b (Å)	10.480(6)	26.148(6)	11.297(3)	21.888(5)	12.306(3)	11.091(2)
c (Å)	18.889(8)	17.831(4)	18.569(5)	21.958(5)	25.718(5)	21.157(3)
α (deg)	90	90	80.10(1)	97.05(1)	90	77.21(1)
β (deg)	127.00(3)	98.27(5)	82.09(1)	90.20(1)	90.31(1)	84.12(1)
γ (deg)	90	90	78.99(1)	90.93(1)	90	75.93(1)
V (Å^3)	2001.2(19)	4936(2)	2110.9(9)	5298.4(19)	4835.2(17)	2315.1(6)
Z	2	4	2	4	4	2
D_{calc} (g cm^{-3})	1.399	1.188	1.405	1.199	1.335	1.383
μ(Mo/Kα)$_{calc}$ (cm^{-1})	3.754	3.047	3.563	2.844	3.119	3.257
Size (mm)	0.10 × 0.10 × 0.10	0.20 × 0.10 × 0.10	0.20 × 0.20 × 0.15	0.30 × 0.20 × 0.20	0.40 × 0.35 × 0.30	0.30 × 0.25 × 0.20
F(000)	860	1808	912	1952	1984	988
2θ range (deg)	3.88 to 50.50	3.12 to 55.22	3.72 to 55.28	3.66 to 50.50	3.68 to 56.57	3.84 to 55.40
No. of reflns, collected	10 858	33 781	14 481	19 085	34 068	16 026
No. of obsd reflns	6764	11 412	9716	19 085	11 961	10 665
No. of variables	434	462	468	992	523	516
Abscorr (T_{max}, T_{min})	0.75, 0.62	0.75, 0.62	0.75, 0.61	0.75, 0.57	0.75, 0.63	0.75, 0.64
R	0.060	0.056	0.046	0.082	0.029	0.054
R_w	0.129	0.112	0.094	0.204	0.065	0.123
R_{all}	0.078	0.096	0.058	0.111	0.038	0.065
G_{of}	1.03	0.98	1.00	1.03	1.02	1.02
CCDC	1058993	1058994	1058995	1058996	1058997	1058998

Table 2 Selected distances (Å) and angles (deg) for compounds **7–10**, **12** and **13**[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
7	2.84(3)	2.68(1) to 3.01(3)	2.58(3)	C(34) 2.57(2), C(41) 2.57(3)	142.5(2)	109.7(2)
8	2.867(7)	2.705(6) to 2.969(7)	2.579(7)	C(16) 2.544(7), C(41) 2.480(6)	142.2(2)	112.6(2)
9	2.852(5)	2.693(5) to 2.987(5)	2.583(5)	C(34) 2.545(5), C(35) 2.632(6) C(36) 2.851(6), C(37) 2.984(6)	139.8(2)	124.0(2)[d], 95.9(2)[e] 73.1(2)[f]
10	2.904(13)	2.832(12) to 2.964(12)	2.640(12)	C(42) 2.555(12), C(49) 2.440(11) N 2.422(10)	137.1(4)	31.8(4)[g], 78.0(4)[h] 109.6(4)[i]
12	2.917(3)	2.843(3) to 3.019(3)	2.653(3)	C(41) 2.569(3), C(49) 2.640(3) O 2.406(2), N 2.990(2)	138.0(2)	77.1(1)[j], 130.7(1)[k] 53.9(1)[l]
13	2.870(6)	2.834(6) to 2.917(6)	2.603(6)	C(41) 2.537 (7), O 2.198(4)	134.7(2)	110.5(2)

[a] Cp = cyclopentadienyl ring. [b] Average value. [c] Range. [d] The angle of C(34)–Th(1)–C(35). [e] The angle of C(34)–Th(1)–C(36). [f] The angle of C(34)–Th(1)–C(37). [g] The angle of C(49)–Th(1)–N(1). [h] The angle of C(42)–Th(1)–N(1). [i] The angle of C(42)–Th(1)–C(49). [j] The angle of C(41)–Th(1)–C(49). [k] The angle of C(41)–Th(1)–O(1). [l] The angle of C(49)–Th(1)–O(1).

empirical absorption correction was applied using the SADABS program.[10] All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL program package.[11] All the hydrogen atoms were geometrically fixed using the riding model. Disordered solvents in the voids of **8** and **10** were modeled or removed by using the SQUEEZE program.[12] The crystal data and experimental data for **7–10**, **12** and **13** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

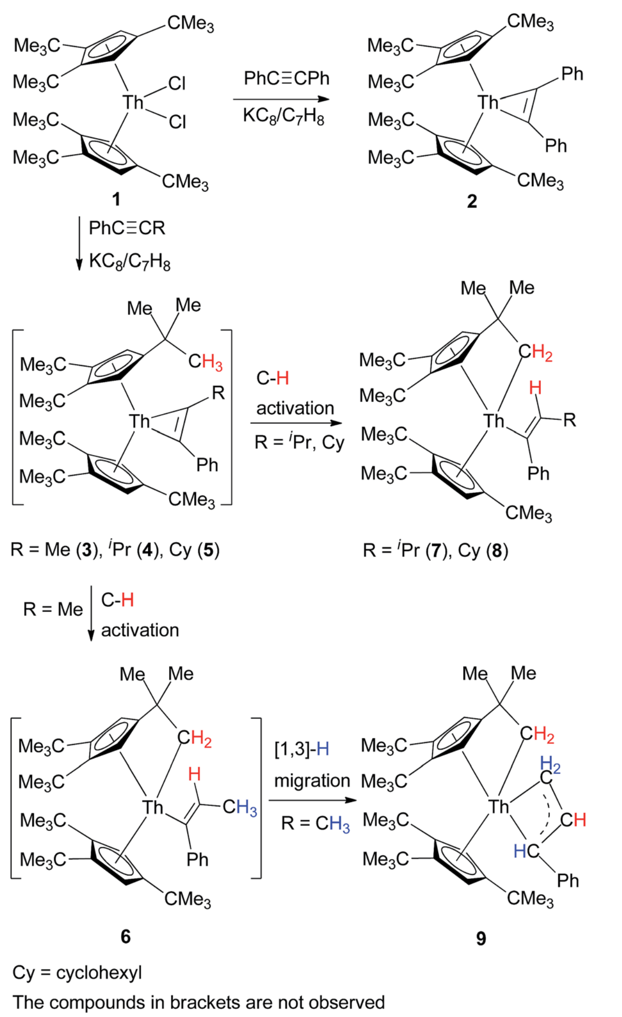
Computational methods

All calculations 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 and N elements and Stuttgart RLC ECP from the EMSL basis set exchange (https://bse.pnl.gov/bse/portal) for Th,[14] to fully optimize the structures of reactants, complexes, transition state, intermediates, and products, and also to mimic the experimental toluene-solvent conditions (dielectric constant $\varepsilon = 2.379$). 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 hyper surfaces. In order to consider the dispersion effect for the reaction **2** + py, single-point B3PW91-PCM-D3 (ref. 15) calculations, based on B3PW91-PCM geometries, have been performed.

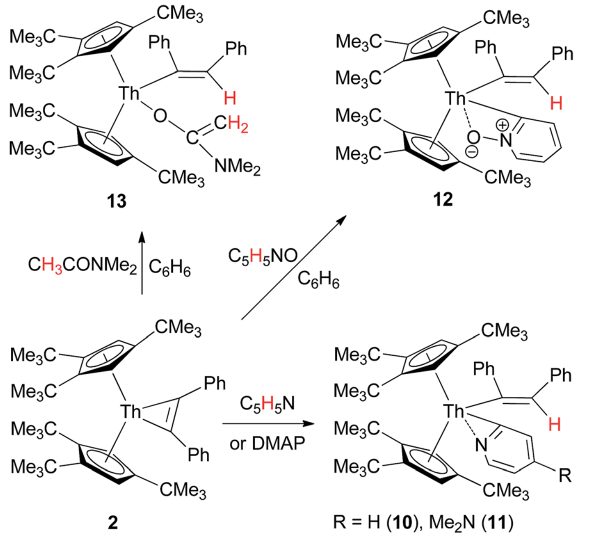
Results and discussion

Reaction of 1 : 1 mixture of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2ThCl_2$ (**1**) and diphenylacetylene (PhC≡CPh) with an excess of KC_8 in toluene solution gives the metallacyclopropene, [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2Th(\eta^2$-$C_2Ph_2)$ (**2**) (Scheme 1).[5] However, under similar reaction conditions, the treatment of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2ThCl_2$ (**1**) and phenyl(alkyl)acetylenes PhC≡CR (R = Me, ^{i}Pr, C_6H_{11}) with KC_8 does not yield the expected metallacyclopropenes [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2Th(\eta^2$-$C_2Ph(R))$ (R = Me (**3**), ^{i}Pr (**4**), C_6H_{11} (**5**)), instead, the cyclometalated alkenyl complexes [η^5-1,2,4-$(Me_3C)_3C_5H_2$][η^5,σ-1,2-$(Me_3C)_2$-4-$(CH_2CMe_2)C_5H_2$]Th[C(Ph)=CHR] (R = ^{i}Pr (**7**), C_6H_{11} (**8**)) and [η^5-1,2,4-$(Me_3C)_3C_5H_2$][η^5,σ-1,2-$(Me_3C)_2$-4-$(CH_2CMe_2)C_5H_2$]Th[η^3-CH(Ph)CHCH$_2$] (**9**) are isolated, respectively, in good yields (Scheme 1). Moreover, in contrast to the [$(\eta^5$-$C_5Me_5)_2$An] (An = Th, U) fragment,[16] no thorium metallacyclopentadiene complexes were isolated for the sterically more demanding 1,2,4-$(Me_3C)_3C_5H_2$ ligand regardless of the amount of added internal alkynes. We propose in analogy to the PhC≡CPh reaction that the metallacyclopropenes **3–5** are initially formed, but they are unstable and convert by an intramolecular C–H bond activation to yield [η^5-1,2,4-$(Me_3C)_3C_5H_2$][η^5,σ-1,2-$(Me_3C)_2$-4-$(CH_2CMe_2)C_5H_2$]Th[C(Ph)=CHR] (R = Me (**6**), ^{i}Pr (**7**), C_6H_{11} (**8**)). However, it is noteworthy that the C–H bond activation occurs selectively at the alkyl-end of the disubstituted acetylene. Moreover, in contrast to complexes **7** and **8**, the least sterically hindered complex **6** further undergoes an [1,3]-hydrogen migration to form the cyclometallated allyl complex **9** (Scheme 1).

In contrast to the metallacyclopropenes **3–5**, complex **2** is stable and no ligand cyclometalation was observed, even when heated at 100 °C for one week. Nevertheless, in contrast to zirconium metallacyclopropenes,[1b] complex **2** is capable of activating C–H bonds of different substrates, such as those of pyridine or carbonyl derivatives containing an α-H atom upon coordination. For example, treatment of complex **2** with 1 equiv of pyridine, DMAP, pyridine *N*-oxide or CH_3CONMe_2, the pyridyl alkenyl thorium complexes [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[C(Ph)=CHPh](η^2-*C*,*N*-C_5H_4N) (**10**), [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[C(Ph)=CHPh](η^2-*C*,*N*-4-$Me_2NC_5H_3N$) (**11**) and [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[C(Ph)=CHPh](κ^2-*C*,*O*-C_5H_4NO) (**12**), and enolyl alkenyl thorium complex [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th[C(Ph)=CHPh][O–C(=CH$_2$)NMe$_2$] (**13**) are formed, respectively, in quantitative conversions (Scheme 2), in which an α-H of the pyridine, DMAP,



Scheme 1 Synthesis of compounds 7–9.



Scheme 2 Synthesis of complexes **10–13**.

pyridine *N*-oxide or CH_3CONMe_2 is transferred to the metallacyclopropene $Th(\eta^2\text{-}C_2Ph_2)$ moiety.

Complexes **7–13** are stable in dry nitrogen atmosphere, but they are moisture sensitive. They were characterized by various spectroscopic techniques and elemental analyses. In addition, the solid-state structures of complexes **7–10**, **12** and **13** were determined by single crystal X-ray diffraction analyses (Table 1). Selected bond distances and angles for these compounds are listed in Table 2. The molecular structures of **7** and **8** are shown in Fig. 1 and 2. The Th–C(CH_2CMe_2Cp) distance of 2.57(2) Å in **7** is comparable to that (2.544(7) Å) found in **8**, but significantly longer than that in $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2ThMe_2$ (2.480(3) Å).[9] Furthermore, the Th–C(alkenyl) distances (2.57(3) Å for **7** and 2.480(6) Å for **8**) are in the range of previously reported Th–C(sp^2) σ-bonds (2.420(3)–2.654(14) Å),[17] but are slightly longer than that (2.395(2) Å) found in the metallacyclopropene $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(\eta^2\text{-}C_2Ph_2)$.[5]

Fig. 3 depicts the molecular structure of **9**. The C–C distances of the allyl fragment are of 1.385(8) Å for C(35)–C(36) and 1.372(8) Å for C(36)–C(37). Nevertheless, the Th–C(35), Th–C(36) and Th–C(37) distances of 2.632(6) Å, 2.851(6) Å and 2.984(6) Å, respectively, become progressively longer, suggesting that the η^3-coordination allyl moiety observed in the solid state is weak and that hapticity switch ($\eta^3 \rightarrow \eta^1$) is likely to occur in solution. Indeed, in the $^{13}C\{^1H\}$ NMR spectrum the corresponding allyl resonances are found at δ = 66.1, 100.8 and 111.8 ppm, respectively, which would be more consistent with a η^1-coordination mode in solution.[18] Furthermore, while the Th–C(35) distance of 2.632(6) Å is longer than those found in $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2ThMe_2$ (2.480(3) Å)[9] and $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(CH_2Ph)_2$ (2.521(3) and 2.527(3) Å),[19] it is consistent with the value of *ca.* 2.73 Å found in $[\eta^3\text{-}1,3\text{-}(Me_3Si)_2C_3H_3]_4Th$.[20] In contrast, the Th–C(34) distance of 2.545(5) Å is comparable to those found in **7** (2.57(2) Å) and **8** (2.544(7) Å).

The solid state molecular structures of **10** and **12** are shown in Fig. 4 and 5 and for selected bond distances and angles see Table 2. The Th–C(alkenyl) distances (2.555(12) Å for **10** and

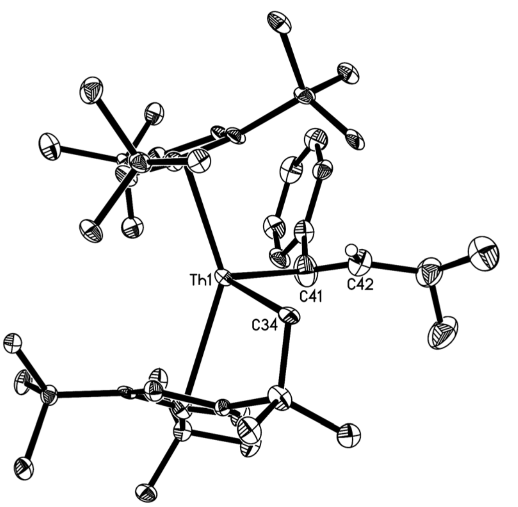


Fig. 1 Molecular structure of **7** (thermal ellipsoids drawn at the 35% probability level).

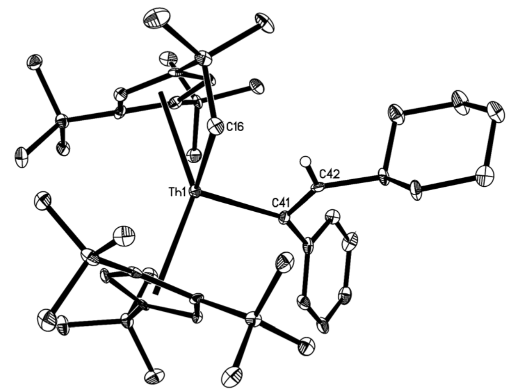


Fig. 2 Molecular structure of **8** (thermal ellipsoids drawn at the 35% probability level).

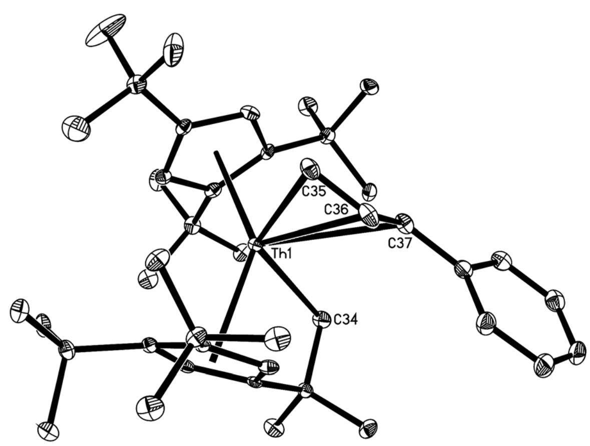


Fig. 3 Molecular structure of **9** (thermal ellipsoids drawn at the 35% probability level).

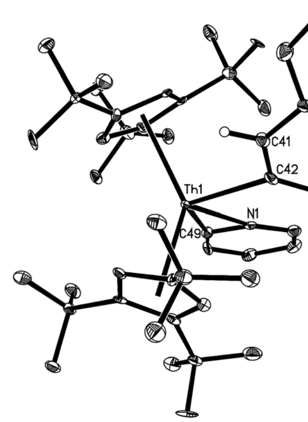


Fig. 4 Molecular structure of **10** (thermal ellipsoids drawn at the 35% probability level).

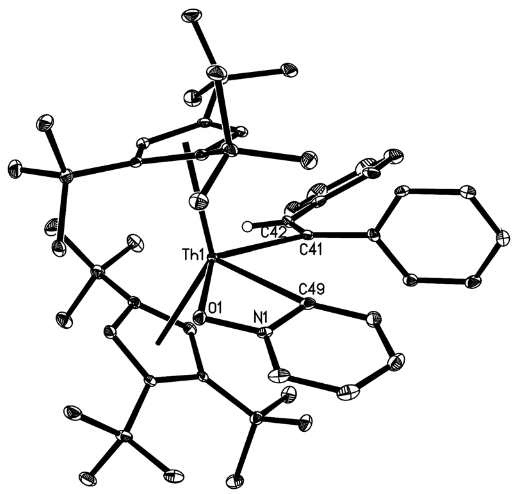


Fig. 5 Molecular structure of **12** (thermal ellipsoids drawn at the 35% probability level).

2.569(3) Å for **12**) are in the same range as those found in **7** (2.57(3) Å), **8** (2.480(6) Å), and **9** (2.632(6) Å). In **10**, the Th–C(pyridyl) distance is 2.440(11) Å, and the Th–N distance is 2.422(10) Å. Nevertheless, the Th–C(pyridyl) distance of 2.640(3) Å in **12** is close to that found (η^5-C_5Me_5)$_2$Th(CH_2Ph)(κ^2-*C*,*O*-ONC_5H_4) (2.621(3) Å).[21] Furthermore, the Th–O distance (2.406(2) Å) in **12** is shorter than that expected for a dative interaction,[22] but is comparable to that found in (η^5-C_5Me_5)$_2$-Th(CH_2Ph)(κ^2-*C*,*O*-ONC_5H_4) (2.416(2) Å).[21] The N–O distance (1.369(3) Å) is slightly longer than that in the free pyridine *N*-oxide (1.330(9) Å),[23] but virtually identical to that found in (η^5-C_5Me_5)$_2$Th(CH_2Ph)(κ^2-*C*,*O*-ONC_5H_4) (1.360(3) Å).[21]

The solid state molecular structure of **13** is depicted in Fig. 6. The Th^{4+} ion is η^5-bound to two Cp-rings and one σ-coordinate carbon atom and one oxygen atom with the average Th–C(Cp) distance of 2.870(6) Å and the angle Cp(cent)–Th–Cp(cent) of 134.7(2)°. The Th–C(41) distance (2.537(7) Å) is comparable to those found in **7** (2.57(3) Å), **8** (2.480(6) Å), **9** (2.632(6) Å), **10** (2.555(12) Å), and **12** (2.569(3) Å), and the Th–O distance (2.198(4) Å) is comparable to those found in [η^5-1,2,4-

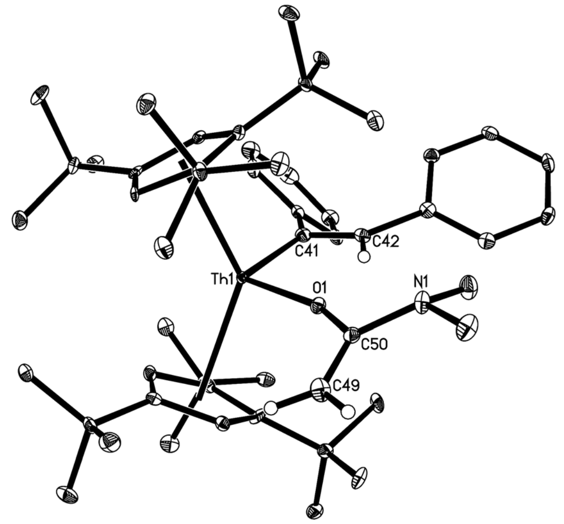


Fig. 6 Molecular structure of **13** (thermal ellipsoids drawn at the 35% probability level).

$(Me_3C)_3C_5H_2]_2$Th[O_2CPh_2] (2.202(3) Å),[24] and [η^5-1,2,4-$(Me_3C)_3$-$C_5H_2]_2$Th[($OCPh_2$)$_2$] (2.182(2) Å).[5]

Thorium metallacyclopropenes derived from phenyl(alkyl) acetylenes are very reactive species that are capable to undergo a selective intramolecular C–H bond activation of the cyclopentadienyl ligand 1,2,4-$(Me_3C)_3C_5H_2$. However, while complex **2** derived from diphenylacetylene cannot promote intramolecular C–H bond activations, it activates intermolecularly C–H bonds upon coordination, such as those of pyridine or carbonyl derivatives containing an α-H atom. To further understand these observations, DFT calculations were performed at the B3PW91 level of theory. As a representative example of the phenyl(alkyl)acetylene derivatives complex **5** was chosen. We first compared the energetics of the intramolecular C–H bond activation and its selectivity for complexes **2** and **5** (Fig. 7). These computations revealed several interesting features: (1) The intramolecular C–H bond activation of a methyl group of the 1,2,4-$(Me_3C)_3C_5H_2$ ligand in **2** is energetically unfavorable (ΔG(298 K) = 3.9 kcal mol^{-1}), while that promoted by complex **5** is exergonic (Fig. 7), presumably because of electronic effects. In a simple physical organic picture, an alkyl-group introduces a stronger + I-effect than a phenyl group, which should therefore more strongly destabilize the negative charge on a dianionic [η^2-alkenediyl]$^{2-}$ ligand and protonation should occur preferentially at the more basic, alkyl-substituted end. Therefore the thermal stability of the diphenylacetylene derived thorium metallacyclopropene **2** may also reflect the reduced basicity of the diphenyl-substituted [η^2-alkenediyl]$^{2-}$ ligand, so that only those metallacyclopropene complexes derived from phenyl(alkyl)acetylenes are thermally converted to the cyclometalated complexes *via* an intramolecular C–H bond activation of the 1,2,4-$(Me_3C)_3C_5H_2$ ligand. (2) Furthermore, the DFT computations also explain the selectivity of the C–H bond activation: only the R*C* (R = cyclohexyl) end of phenyl(cyclohexyl)-substituted metallacyclopropene in **5** is capable to undergo σ-bond metathesis (ΔG(298 K) = −4.6

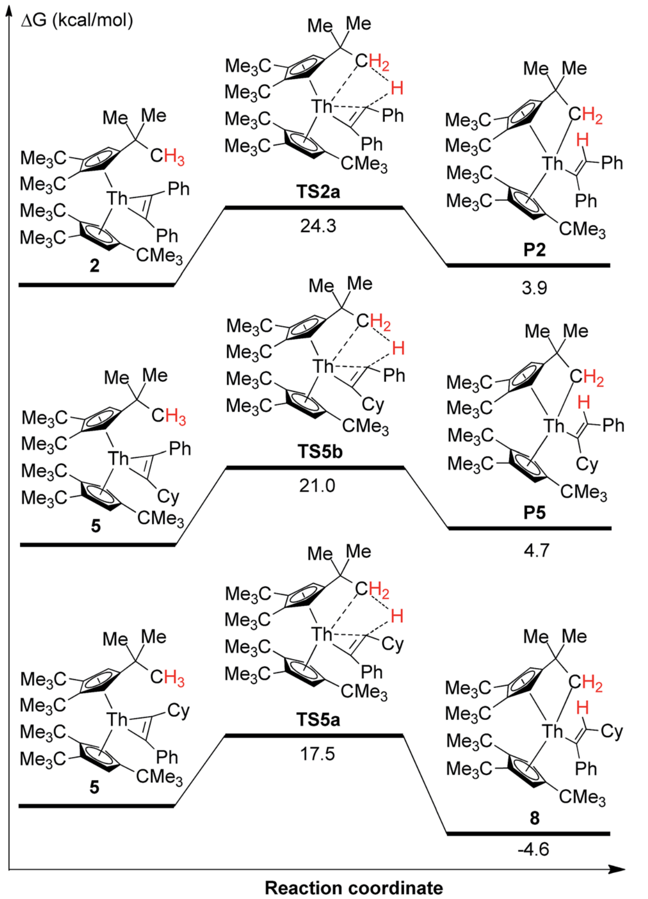


Fig. 7 Free energy profile (kcal mol^{-1}) for the conversions of **2** and **5**. Cy = cyclohexyl.

kcal mol^{-1}), while the reaction at the Ph*C*-position is energetically unfavorable ($\Delta G(298\ K) = 4.7$ kcal mol^{-1}) (Fig. 7). Again, this difference in reactivity might be ascribed to the electronic effect as just mentioned above. (3) Moreover, the barrier for the conversion of **5** to **8** is only $\Delta G^{\ddagger}(298\ K) = 17.5$ kcal mol^{-1} and can be overcome under the reaction conditions. The computational results are also consistent with the experimentally observed stability of complex **2** upon heating. The energetic profile for the intermolecular reaction of **2** with pyridine is

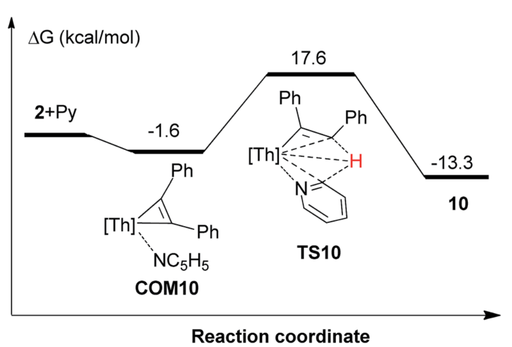


Fig. 8 Free energy profile (kcal mol^{-1}) for the reaction of **2** + Py. [Th] = [η^5-1,2,4-$(Me_3C)_3C_5H_2$]$_2$Th.

shown in Fig. 8 and it involves the adduct **COM10** and the transition state **TS10**. In the σ-bond metathesis transition state **TS10** the two forming bond distances of Th–C and C–H are 2.687 and 1.513 Å, respectively, *ca.* 0.22 and 0.42 Å longer than those in product **10**. The conversion of **COM10** to the product **10** is energetically favorable by $\Delta G(298\ K) = -13.3$ kcal mol^{-1}, and proceeds *via* transition state **TS10** with an activation barrier ($\Delta G^{\ddagger}(298\ K)$) of 19.2 kcal mol^{-1}, which can be overcome at ambient temperature and therefore is consistent with the experimental observations.

Conclusions

In conclusion, the first examples of inter- and intramolecular C–H bond activations mediated by thorium metallacyclopropenes were comprehensively investigated. When the substitutents on the thorium metallacyclopropene are changed from phenyl to alkyl, a distinctive change in reactivity is observed, which is also illustrated by their relative stabilities. The thorium metallacyclopropenes derived from phenyl(alkyl) acetylenes are very reactive and cannot be isolated, instead, they thermally convert to cyclometalated complexes *via* an intramolecular C–H bond activation of the 1,2,4-$(Me_3C)_3C_5H_2$ ligand. In contrast, the thorium metallacyclopropene **2** derived from diphenylacetylene is thermally stable. The change in relative stability is also reflected in DFT computations, which showed that the intramolecular C–H bond activation of the ligand 1,2,4-$(Me_3C)_3C_5H_2$ induced by **5** is energetically favourable, while that promoted by **2** is not. Nevertheless, in contrast to zirconium metallacyclopropenes,[1b] complex **2** is capable of promoting the intermolecular C–H bond activations of substrates, such as pyridine or carbonyl derivatives containing α-H atoms upon coordination. This leads to the formation of the corresponding pyridyl alkenyl or enolyl alkenyl complexes. The further development of new actinide metallacyclopropene complexes and the exploration of the thorium cyclometalated complexes and pyridyl alkenyl complexes in organic syntheses are ongoing projects in these laboratories.

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Notes and references

1 For selected reviews, see: (*a*) S. L. Buchwald and R. B. Nielsen, *Chem. Rev.*, 1988, **88**, 1047–1058; (*b*) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann and A. Spannenberg, *Organometallics*, 2003, **22**, 884–900; (*c*) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann,

A. Spannenberg and V. B. Shur, *Eur. J. Inorg. Chem.*, 2004, 4739–4749; (*d*) U. Rosenthal, *Angew. Chem., Int. Ed.*, 2004, **43**, 3882–3887; (*e*) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann and A. Spannenberg, *Organometallics*, 2005, **24**, 456–471; (*f*) U. Rosenthal, V. V. Burlakov, M. A. Bach and T. Beweries, *Chem. Soc. Rev.*, 2007, **36**, 719–728; (*g*) H. S. La Pierre and K. Meyer, *Prog. Inorg. Chem.*, 2014, **58**, 303–415; (*h*) K. D. J. Parker and M. D. Fryzuk, *Organometallics*, 2015, **34**, 2037–2047.

2 Selected papers on group 4 metallacyclopropenes, see: (*a*) M. D. Walter, C. D. Sofield and R. A. Andersen, *Organometallics*, 2008, **27**, 2959–2970; (*b*) T. Beweries, C. Fischer, S. Peitz, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, D. Heller and U. Rosenthal, *J. Am. Chem. Soc.*, 2009, **131**, 4463–4469; (*c*) K. Kaleta, M. Ruhmann, O. Theilmann, T. Beweries, S. Roy, P. Arndt, A. Villinger, E. D. Jemmis, A. Schulz and U. Rosenthal, *J. Am. Chem. Soc.*, 2011, **133**, 5463–5473; (*d*) M. Haehnel, M. Ruhmann, O. Theilmann, S. Roy, T. Beweries, P. Arndt, A. Spannenberg, A. Villinger, E. D. Jemmis, A. Schulz and U. Rosenthal, *J. Am. Chem. Soc.*, 2012, **134**, 15979–15991; (*e*) M. Haehnel, S. Hansen, K. Schubert, P. Arndt, A. Spannenberg, H. Jiao and U. Rosenthal, *J. Am. Chem. Soc.*, 2013, **135**, 17556–17565; (*f*) S. K. Podiyanachari, G. Kehr, C. Mück-Lichtenfeld, C. Daniliuc and G. Erker, *J. Am. Chem. Soc.*, 2013, **135**, 17444–17456; (*g*) L. Becker, P. Arndt, H. Jiao, A. Spannenberg and U. Rosenthal, *Angew. Chem., Int. Ed.*, 2013, **52**, 11396–11400; (*h*) Ò. Àrias, A. R. Petrov, T. Bannenberg, K. Altenburger, P. Arndt, P. G. Jones, U. Rosenthal and M. Tamm, *Organometallics*, 2014, **33**, 1774–1786; (*i*) D. J. Mindiola, L. A. Watson, K. Meyer and G. L. Hillhouse, *Organometallics*, 2014, **33**, 2760–2769; (*j*) N. Peulecke, A. Ohff, P. Kosse, A. Tillack, A. Spannenberg, R. Kempe, W. Baumann, V. V. Burlakov and U. Rosenthal, *Chem.–Eur. J.*, 1998, **4**, 1852–1861; (*k*) M. Zirngast, C. Marschner and J. Baumgartner, *Organometallics*, 2008, **27**, 2570–2583; (*l*) U. Rosenthal, A. Ohff, M. Michalik, H. Görls, V. V. Burlakov and V. B. Shur, *Angew. Chem., Int. Ed.*, 1993, **32**, 1193–1195; (*m*) V. V. Burlakov, A. V. Polyakov, A. I. Yanovsky, Y. T. Struchkov, V. B. Shur, M. E. Vol'pin, U. Rosenthal and H. Görls, *J. Organomet. Chem.*, 1994, **476**, 197–206; (*n*) J. Hiller, U. Thewalt, M. Polášek, L. Petrusová, V. Varga, P. Sedmera and K. Mach, *Organometallics*, 1996, **15**, 3752–3759; (*o*) D. Thomas, N. Peulecke, V. V. Burlakov, B. Heller, W. Baumann, A. Spanneberg, R. Kempe, U. Rosenthal and R. Beckhaus, *Z. Anorg. Allg. Chem.*, 1998, **624**, 919–924.

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

4 (*a*) L. Andrews, G. P. Kushto and C. J. Marsden, *Chem.–Eur. J.*, 2006, **12**, 8324–8335; (*b*) M. Foyentin, G. Folcher and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1987, 494–495.

5 B. Fang, W. Ren, G. Hou, G. Zi, D.-C. Fang, L. Maron and M. D. Walter, *J. Am. Chem. Soc.*, 2014, **136**, 17249–17261.

6 Selected papers about the bonding of organoactinide complexes, see: (*a*) T. Cantat, C. R. Graves, K. C. Jantunen, C. J. Burns, B. L. Scott, E. J. Schelter, D. E. Morris, P. J. Hay and J. L. Kiplinger, *J. Am. Chem. Soc.*, 2008, **130**, 17537–17551; (*b*) N. Barros, D. Maynau, L. Maron, O. Eisenstein, G. Zi and R. A. Andersen, *Organometallics*, 2007, **26**, 5059–5065; (*c*) A. Yahia and L. Maron, *Organometallics*, 2009, **28**, 672–679; (*d*) W. Ren, X. Deng, G. Zi and D.-C. Fang, *Dalton Trans.*, 2011, 9662–9664; (*e*) E. Ciliberto, S. D. Bella, A. Gulino, I. Fragala, J. L. Petersen and T. J. Marks, *Organometallics*, 1992, **11**, 1727–1737; (*f*) K. Tatsumi and A. Nakamura, *J. Am. Chem. Soc.*, 1987, **109**, 3195–3206; (*g*) J. R. Walensky, R. L. Martin, J. W. Ziller and W. J. Evans, *Inorg. Chem.*, 2010, **49**, 10007–10012; (*h*) B. M. Gardner, P. A. Cleaves, C. E. Kefalidis, J. Fang, L. Maron, W. Lewis, A. J. Blake and S. T. Liddle, *Chem. Sci.*, 2014, **5**, 2489–2497.

7 Selectedreviews, see: (*a*) K. R. D. Johnson and P. G. Hayes, *Chem. Soc. Rev.*, 2013, **42**, 1947–1960; (*b*) P. L. Arnold, M. W. McMullon, J. Rieb and F. E. Kühn, *Angew. Chem., Int. Ed.*, 2015, **54**, 82–100.

8 M. A. Schwindt, T. Lejon and L. S. Hegedus, *Organometallics*, 1990, **9**, 2814–2819.

9 W. Ren, G. Zi, D.-C. Fang and M. D. Walter, *Chem.–Eur. J.*, 2011, **17**, 12669–12682.

10 G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Göttingen, Germany, 1996.

11 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 2008, **64**, 112–122.

12 SQUEEZE: P. V. D. Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 194–201.

13 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, 2009.

14 W. Küchle, M. Dolg, H. Stoll and H. Preuss, *Mol. Phys.*, 1991, **74**, 1245–1263.
15 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
16 Selected actinide metallacyclopentadienes, see: (*a*) P. J. Fagan, J. M. Manriquez, T. J. Marks, C. S. Day, S. H. Vollmer and V. W. Day, *Organometallics*, 1982, **1**, 170–180; (*b*) P. J. Fagan, J. M. Manriquez, E. A. Maatta, A. M. Seyam and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 6650–6667; (*c*) J. M. Manriquez, P. J. Fagan, T. J. Marks, S. H. Vollmer, C. S. Day and V. W. Day, *J. Am. Chem. Soc.*, 1979, **101**, 5075–5078; (*d*) W. J. Evans, S. A. Kozimor and J. W. Ziller, *Chem. Commun.*, 2005, 4681–4683; (*e*) B. Fang, G. Hou, G. Zi, D.-C. Fang and M. D. Walter, *Dalton Trans.*, 2015, **44**, 7927–7934.
17 (*a*) L. A. Seaman, E. A. Pedrick, T. Tsuchiya, G. Wu, E. Jakubikova and T. W. Hayton, *Angew. Chem., Int. Ed.*, 2013, **52**, 10589–10592; (*b*) I. Korobkov, B. Vidjayacoumar, S. I. Gorelsky, P. Billone and S. Gambarotta, *Organometallics*, 2010, **29**, 692–702; (*c*) I. Korobkov, A. Arunachalampillai and S. Gambarotta, *Organometallics*, 2004, **23**, 6248–6252; (*d*) W. Ren, E. Zhou, B. Fang, G. Zi, D.-C. Fang and M. D. Walter, *Chem. Sci.*, 2014, **5**, 3165–3172.
18 T. J. Marks and W. A. Wachter, *J. Am. Chem. Soc.*, 1976, **98**, 703–710.
19 W. Ren, N. Zhao, L. Chen and G. Zi, *Inorg. Chem. Commun.*, 2013, **30**, 26–28.
20 C. N. Carlson, T. P. Hanusa and W. W. Brennessell, *J. Am. Chem. Soc.*, 2004, **126**, 10550–10551.
21 J. A. Pool, B. L. Scott and J. L. Kiplinger, *J. Am. Chem. Soc.*, 2005, **127**, 1338–1339.
22 (*a*) A. Haskel, T. Straub and M. S. Eisen, *Organometallics*, 1996, **15**, 3773–3775; (*b*) M. A. Edelman, P. B. Hitchcock, J. Hu and M. F. Lappert, *New J. Chem.*, 1995, **19**, 481–489.
23 R. E. Marsh, M. Kapon, S. Hu and F. H. Herbstein, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 62–77.
24 W. Ren, G. Zi, D.-C. Fang and M. D. Walter, *J. Am. Chem. Soc.*, 2011, **133**, 13183–13196.

