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

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Inter- and intramolecular C–H bond activations by thorium metallacyclopropene complexes were comprehensively studied. The reduction of \([\eta^5-1,2,4-(\text{Me}_3\text{C})_5\text{C}_2\text{H}_2]\text{ThCl}_2\) (1) with potassium graphite (K\(\text{C}_6\)) in the presence of internal alkynes (Ph\(\text{C}R\)) yields the corresponding thorium metallacyclopropenes \([\eta^5-1,2,4-(\text{Me}_3\text{C})_5\text{C}_2\text{H}_2]\text{Th}(\eta^5-\text{C}_2\text{Ph(R)}\) \(R = \text{Ph}\)) (2) has been prepared. Several studies have now established that in actinide chemistry the 5f orbitals have significant influence on the reactivity. Thorium with its 7s\(^2\)6d\(^2\) ground state stands on the borderline between group 4 metals and the actinides and is therefore a very attractive element for further investigations. Complex 2 reacts with a variety of hetero-unsaturated molecules such as aldehydes, ketones, \(\text{CS}_2\), carbodiimides, nitriles, isothiocyanates, organic azides, and diazoalkane derivatives. 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 \([\eta^5-1,2,4-(\text{Me}_3\text{C})_5\text{C}_2\text{H}_2]\text{Th}(\eta^5-\text{C}_2\text{Ph}_3)\) (1) in the presence of unsymmetrically substituted alkynes such as \(\text{PhC}\equiv\text{CPh}\) and \(\text{Me}_6\text{SiC}\equiv\text{CMe}_3\) 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. 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...
glove box. All organic solvents were freshly distilled from sodium benzoephonone ketyl immediately prior to use. KC8−(THF)6−[(CH2)2CMe2]C5H2]ThCl2 (1) and KC8−(THF)6−[(CH2)2CMe2]C5H2]Th(μ-C(N)Ph)2 (2) were prepared according to literature methods. All other chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. and used as received unless otherwise noted. Infrared spectra were recorded in KBr pellets on an Avatar 360 Fourier transform spectrometer. 1H and 13C{1H} NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 and 100 MHz, respectively. All chemical shifts are reported in δ units with respect 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 [n][C5H2TH]2−[C(CH3)3]−**

This compound was prepared as colorless crystals from the reaction of [n][C5H2TH]2−(THF)6−[(CH2)2CMe2]C5H2]Th(μ-N(CH3))2 (1) with stirring at room temperature. A 151.5 (phenyl 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. C49H72Th requires C, 65.28; H, 8.45%). M.p.: 180–182 °C. 1H NMR (CD2Cl2): 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 CH), 6.10 (d, J = 3.5 Hz, 1H, ring CH), 5.93 (d, J = 3.4 Hz, 1H, ring CH), 5.78 (d, J = 3.5 Hz, 1H, ring CH), 5.48 (d, J = 7.2 Hz, 1H, C=C=CH2), 2.74 (m, 1H, cyclohexyl-CH), 1.83 (br s, 2H, cyclohexyl-CH2), 1.72 (s, 3H, C(CH3)3), 1.71 (s, 3H, C(CH3)3), 1.58 (s, 9H, C(CH3)3), 1.51 (s, 9H, C(CH3)3), 1.50 (s, 18H, C(CH3)3), 1.44 (m, 4H, cyclohexyl-CH2), 1.22 (s, 9H, C(CH3)3), 1.07 (m, 5H, ThCH2 and cyclohexyl-CH2), 0.01 (d, J = 13.0 Hz, 1H, ThCH2) ppm. 13C{1H} NMR (CD2Cl2): δ 220.3 (ThC=CH), 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=CH2), 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), 97.7 (ThC=CH2), 38.2 (CH), 35.8 (C(CH3)3), 35.3 (C(CH3)3), 35.1 (C(CH3)3), 34.9 (C(CH3)3), 34.7 (C(CH3)3), 34.5 (C(CH3)3), 34.4 (CH3), 34.1 (C(CH3)3), 34.0 (CH2C(CH3)3), 33.9 (C(CH3)3), 33.4 (CH2C(CH3)3), 32.6 (C(CH3)3), 32.5 (C(CH3)3), 30.6 (CH2C(CH3)3), 26.2 (CH2), 26.1 (CH2), 26.0 (CH2) 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 [n][C5H2TH]2−[C(CH3)3]−**

This compound was prepared as orange crystals from the reaction of [n][C5H2TH]2−(THF)6−[(CH2)2CMe2]C5H2]Th(μ-N(CH3))2 (1) with stirring at room temperature. yield: 1.97 g (85%) (found: C, 65.88; H, 8.16. C50H70Th requires C, 65.89; H, 8.13%). M.p.: 216–218 °C. 1H NMR (CD2Cl2): δ 7.37 (t, J = 7.8 Hz, 2H, phenyl), 7.25 (t, J = 7.7 Hz, 2H, phenyl), 7.15 (s, 6H, C(CH3)3), 7.00 (t, J = 7.3 Hz, 1H, phenyl), 6.77 (m, 1H, PhC=CH2), 6.10 (d, J = 3.4 Hz, 1H, ring CH), 6.01 (d, J = 3.5 Hz, 1H, ring CH), 5.94 (d, J = 3.4 Hz, 1H, ring CH), 5.30 (d, J = 3.5 Hz, 1H, ring CH), 4.64 (d, J = 15.6 Hz, 1H, PhCH=CH2), 2.59 (m, 1H, ThCH2CH=CHPh), 2.47 (m, 1H, ThCH2CH=CHPh), 1.53 (br s, 12H, C(CH3)3 and C(CH3)3), 1.52 (s, 9H, C(CH3)3), 1.40 (s, 9H, C(CH3)3), 1.33 (s, 9H, C(CH3)3), 1.29 (s, 9H, C(CH3)3), 1.03 (3H, C(CH3)3), 0.27 (d, J = 12.7 Hz, 1H, ThCH2), −0.09 (d, J = 12.7 Hz, 1H, ThCH2) ppm. 13C{1H} NMR (CD2Cl2): 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(CH3)3), 124.9 (ring C), 124.7 (ring C), 123.4 (ring C), 114.3 (ring C), 112.2 (ring C), 111.8 (PhCH=CH2), 100.8 (PhCH=CH2), 66.1 (ThCH2CH=CHPh), 45.6 (ThCH2), 35.4 (C(CH3)3), 35.2 (C(CH3)3), 35.0 (C(CH3)3), 34.9 (C(CH3)3), 34.8 (C(CH3)3), 34.3 (C(CH3)3), 34.0 (C(CH3)3), 33.6 (C(CH3)3), 33.5 (C(CH3)3), 33.4 (CH2C(CH3)3), 32.9 (C(CH3)3), 32.8 (CH2C(CH3)3), 30.2 (C(CH3)3) 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 allyl PhC=CCD3 was used, the resonance at δ = 4.64 ppm corresponding to PhCH=CH2 in complex 9 disappeared, indicating that indeed a [1,3]-hydrogen migration had occurred in the PhC=CHCH2 fragment resulting in the formation of 9.
Preparation of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_2\text{C}_3\text{H}_2\text{Th}[\text{C}(\text{Ph})]\text{CHPh}]$ (10)

Method A. A toluene solution (5 mL) of pyridine (20 mg, 0.25 mmol) was added to a toluene (10 mL) solution of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_2\text{C}_3\text{H}_2\text{Th}[\text{C}(\text{Ph})], ( \eta^5-\text{C}_3\text{N}-\text{C}_3\text{H}_2\text{N})]$ (2; 220 mg, 0.25 mmol) with stirring at room temperature. After the solution was stirred at room temperature for four days, the solvent was removed. The residue was extracted with benzene (10 mL $\times$ 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, 7.78; N, 8.80). C$_{54}$H$_{173}$N$_7$Th requires C, 66.57; H, 7.70; N, 1.46%.

Method B. A toluene solution (5 mL) of pyridine (20 mg, 0.25 mmol) was slowly added to a J. Young NMR tube charged with $[\eta^5-1,2,4-(\text{Me}_3\text{C})_2\text{C}_3\text{H}_2\text{Th}[\text{C}(\text{Ph})]$, (2; 18 mg, 0.02 mmol) and C$_6$D$_6$ (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 $[\eta^5-1,2,4-(\text{Me}_3\text{C})_2\text{C}_3\text{H}_2\text{Th}[\text{C}(\text{Ph})] \text{CHPh}]$ (c$_5$-C$_3$N-C$_3$H$_2$NO) (12)

Method A. This compound was prepared as colorless crystals from the reaction of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_2\text{C}_3\text{H}_2\text{Th}[\text{C}(\text{Ph})]$; (2; 18 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$_{78}$N$_2$Th requires C, 65.48; H, 7.57; N, 1.44%). M.p.: 136–138°C. $^1$H NMR (C$_6$D$_6$): δ 7.46 (m, 4H, phenyl), 7.36 (t, $J = 7.6$ Hz, 2H, phenyl), 6.72 (d, $J = 7.6$ Hz, 2H, ring C$^6$H$_4$N), 6.31 (d, $J = 7.6$ Hz, 2H, phenyl), 6.20 (d, $J = 7.6$ Hz, 2H, ring C$^6$H$_4$N). 13C{1H} NMR (C$_6$D$_6$): δ 143.9 (aryl C), 133.4 (aryl C), 128.4 (aryl C), 128.0 (aryl C), 127.2 (aryl C), 127.0 (aryl C), 126.5 (ring C), 126.3 (ring C), 124.1 (ring C), 122.8 (ring C), 118.1 (ring C), 112.6 (C=CHPh), 34.9 (C(CH$_3$)$_3$), 34.5 (C(CH$_3$)$_3$), 34.0 (C(CH$_3$)$_3$), 33.0 (C(CH$_3$)$_3$) ppm. One $^1$H resonance of Me$_3$C groups overlapped. IR (KBr, cm$^{-1}$): ν 2956 (s), 1590 (s), 1480 (s), 1458 (s), 1357 (s), 1237 (s), 1001 (s), 825 (s).

Preparation of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_2\text{C}_3\text{H}_2\text{Th}[\text{C}(\text{Ph})] \text{CHPh}]$ (c$_5$-C$_3$N-4-Me-C$_3$H$_2$N) (11)

Method A. This compound was prepared as colorless microcrystals from the reaction of $[\eta^5-1,2,4-(\text{Me}_3\text{C})_2\text{C}_3\text{H}_2\text{Th}[\text{C}(\text{Ph})]$; (2; 18 mg, 0.02 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$_{88}$N$_2$Th requires C, 66.11; H, 7.87; N, 2.80%). M.p.: 176–178°C. $^1$H NMR (C$_6$D$_6$): 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=CHPh), 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$^6$H$_4$N), 6.34 (d, $J = 3.2$ Hz, 2H, ring C$^6$H$_4$N), 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{1H} NMR (C$_6$D$_6$): δ 122.5 (ThC$^1$Ph), 210.3 (ThCN), 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), 112.3 (ring C), 109.2 (C=CHPh), 38.6 (CH$_3$), 35.0 (C(CH$_3$)$_3$), 34.8 (C(CH$_3$)$_3$), 34.7 (C(CH$_3$)$_3$), 34.6 (C(CH$_3$)$_3$), 34.1 (C(CH$_3$)$_3$), 33.1 (C(CH$_3$)$_3$) 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$_6$D$_6$ (0.3 mL) solution of DMAP (2.5 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with $[\eta^5-1,2,4-(\text{Me}_3\text{C})_2\text{C}_3\text{H}_2\text{Th}[\text{C}(\text{Ph})]$; (2; 18 mg, 0.02 mmol) and C$_6$D$_6$ (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.
6.92 (t, J = 7.4 Hz, 1H, phenyl), 6.77 (s, 4H, ring CH), 3.59 (s, 2H, OC=CH₂), 2.56 (s, 6H, N(CH₃)₃), 1.58 (s, 18H, C(CH₃)₃), 1.45 (s, 18H, C(CH₂CH₃)₃), 1.37 (s, 18H, C(CH₂H)₃) ppm. 

Method B. NMR scale. A C₆D₆ (0.3 mL) solution of CH₃-CONE₂ (1.8 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with [η⁵-C₅H₅]₂Th(η⁵-C₅H₅) (2; 18 mg, 0.02 mmol) and C₈D₈ (0.2 mL). The color of the solution immediately changed from pale yellow to colorless, and the NMR resonances of 13 were observed by ¹H 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 (λ = 0.71073 Å). An

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

| Compound | 7  | 8  | 9  | 10  | 12  | 13  |
|----------|----|----|----|-----|-----|-----|
| Formula  | C₄₅H₇₀Th | C₄₅H₇₀Th | C₄₅H₇₀Th | C₄₅H₇₀Th | C₄₅H₇₀Th | C₄₅H₇₀Th |
| R∞       | 0.76 | 0.81 | 0.82 | 0.77 | 0.78 | 0.80 |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Triclinic | Monoclinic | Triclinic |
| Space group | Pc | P2₁/n | P(1) | P(1) | P2₁/c | P(1) |
| Z         | 2  | 4  | 4  | 4  | 4  | 4  |
| Dₐcc (g cm⁻³) | 1.399 | 1.888 | 1.405 | 1.199 | 1.335 | 1.383 |
| μ(Mo/Kα), (cm⁻¹) | 3.754 | 3.047 | 3.563 | 2.844 | 3.119 | 3.257 |
| Size (mm) | 0.10 × 0.10 | 0.20 × 0.10 | 0.20 × 0.20 | 0.30 × 0.20 | 0.40 × 0.35 | 0.30 × 0.25 |
| θ (deg) | 3.88 to 50.50 | 0.10 × 0.10 | 0.20 × 0.10 | 0.20 × 0.20 | 0.30 × 0.20 | 0.40 × 0.35 |
| No. of refls, collected | 10 858 | 33 781 | 14 481 | 19 085 | 34 068 | 16 026 |
| No. of obsd refls | 6764 | 11 412 | 9716 | 19 085 | 11 961 | 10 665 |
| No. of variables | 434 | 462 | 468 | 992 | 323 | 516 |
| Abscorr (Rmax, Rmin) | 0.75, 0.62 | 0.75, 0.62 | 0.75, 0.62 | 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 |
| Rw | 0.129 | 0.112 | 0.094 | 0.204 | 0.065 | 0.123 |
| Rp | 0.078 | 0.096 | 0.058 | 0.111 | 0.038 | 0.065 |
| GOF | 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*

| Compound | C(Cp)-Th | C(Cp)-Th | Cp(cen)-Th | Th-X | C(Cp)-Th | Cp(cen)-Th | X-Th/X/Y |
|----------|---------|---------|-----------|------|---------|-----------|---------|
| 7        | 2.84(3) | 2.68(1) | 3.01(3) | 2.58(3) | C(34)2.57(2), C(41)2.57(3) | 142.5(2) | 109.7(2) |
| 8        | 2.86(7) | 2.70(6) | 2.96(7) | 2.57(9) | C(34)2.54(4), C(41)2.48(60) | 142.2(2) | 112.6(2) |
| 9        | 2.83(25) | 2.69(5) | 2.98(5) | 2.58(5) | C(34)2.54(5), C(35)2.63(26) | 139.8(2) | 124.0(2)*, 95.9(2)* |
| 10       | 2.90(13) | 2.83(12) | 2.96(12) | 2.64(12) | C(42)2.55(12), C(49)2.44(10) | 137.1(4) | 73.1(2)* |
| 11       | 2.91(3) | 2.84(3) | 3.01(3) | 2.65(3) | C(41)2.56(9), C(49)2.64(30) | 138.0(2) | 77.1(2)*, 130.7(1) |
| 12       | 2.87(6) | 2.84(6) | 2.91(6) | 2.60(6) | C(41)2.53(7), O 2.19(84) | 134.7(2) | 110.5(2) |

*Cp = cyclopentadienyl ring. *Average value. *Range. *The angle of C(34)-Th(1)-C(35). *The angle of C(34)-Th(1)-C(36). *The angle of C(49)-Th(1)-N(1). *The angle of C(42)-Th(1)-N(1). *The angle of C(42)-Th(1)-C(49). *The angle of C(41)-Th(1)-C(49). *The angle of C(41)-Th(1)-O(1). *The angle of C(49)-Th(1)-O(1).
empirical absorption correction was applied using the SADABS program. All structures were solved by direct methods and refined by full-matrix least squares on \( F^2 \) using the SHELXL program package. 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. 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), 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, U) fragment, internal alkynes. We propose in analogy to the PhC(H)n complex 

\[
\text{PhC}_n\text{H}_{11} (8) \]

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 metallacyclopentadienes 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, complex 2 is capable of activating C–H of different substrates, such as those of pyridine or carbonyl derivatives containing an \(\alpha\)-H atom upon coordination. For example, treatment of complex 2 with 1 equiv of pyridine, DMAP, pyridine N-oxide or CH3CONMe2, the pyridyl alkynyl thorium complexes \([\eta^5,1,2,4-\{\text{Me}_2\text{C},\text{C}_5\text{H}_2\}\text{Th}(\eta^2-\text{C}_2\text{Ph}_2)] (10), [\eta^5,1,2,4-\{\text{Me}_2\text{C},\text{C}_5\text{H}_2\}\text{Th}(\eta^2-\text{C}_2\text{Ph}_2)] (11) and [\eta^5,1,2,4-\{\text{Me}_2\text{C},\text{C}_5\text{H}_2\}\text{Th}(\eta^2-\text{C}_2\text{Ph}_2)] (12), and enolyl alkynyl thorium complex \([\eta^5,1,2,4-\{\text{Me}_2\text{C},\text{C}_5\text{H}_2\}\text{Th}(\eta^2-\text{C}_2\text{Ph}_2)] (13) are formed, respectively, in quantitative conversions (Scheme 2), in which an \(\alpha\)-H of the pyridine, DMAP,
pyridine N-oxide or CH$_3$CONMe$_2$ is transferred to the metallacyclopentene Th($\eta^5$-C$_2$Ph$_2$) 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$_2$CMe$_3$) 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 [ψ$^5$-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$ThMe$_2$ (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 metallacyclopentene [ψ$^5$-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th($\eta^5$-C$_2$Ph$_2$).$^5$

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 $\eta^3$-coordination allyl moiety observed in the solid state is weak and that hapticity switch ($\eta^3$ → $\eta^1$) is likely to occur in solution. Indeed, in the $^{13}$C($^1$H) NMR spectrum the corresponding allyl resonances are found at $\delta$ = 66.1, 100.8 and 111.8 ppm, respectively, which would be more consistent with a $\eta^1$-coordination mode in solution.$^{18}$ Furthermore, while the Th–C(35) distance of 2.632(6) Å is longer than those found in [ψ$^5$-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$ThMe$_2$ (2.480(3) Å)$^9$ and [ψ$^5$-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(CH$_2$Ph)$_2$ (2.521(3) and 2.527(3) Å)$^{19}$ it is consistent with the value of ca. 2.73 Å found in [ψ$^5$-1,3-(Me$_3$Si)$_2$C$_3$H$_3$]$_4$Th.$^{20}$ In contrast, the Th–C(34) distance of 2.545(5) Å is comparable to those found in 7 (2.572(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
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 [\(\eta^2-C_2Me_3\)2Th(CH2Ph)(k2-C,O-ONC5H4)] (2.621(3) Å). 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 [\(\eta^2-C_2Me_3\)2Th(CH2Ph)(k2-C,O-ONC5H4)] (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),22 but virtually identical to that found in [\(\eta^2-C_2Me_3\)2Th(CH2Ph)(k2-C,O-ONC5H4)] (1.360(3) Å).21

The solid state molecular structure of 13 is depicted in Fig. 6. The ThIV ion is \(\eta^2\)-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 [\(\eta^2\)-1,2,4-

\[
\begin{align*}
[\text{Me}_3C_2C_2H_2\text{C}_2\text{O}_2\text{CPh}_2] & (2.202(3) \text{ Å}), \\
[\eta^5\text{-1,2,4-}\{\text{Me}_3C_2\}C_2H_2\text{C}_2\text{O}_2\text{CPh}_2] & (2.182(2) \text{ Å}). \\
\end{align*}
\]

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-{Me3C}2C2H2. 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 \(\alpha\)-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-{Me3C}2C2H2 ligand in 2 is energetically unfavorable (\(\Delta G(298 \text{ K}) = 3.9 \text{ kcal mol}^{-1}\)), 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 \(\eta^2\)-alkenediyll2− 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 \(\eta^2\)-alkenediyll2− 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-{Me3C}2C2H2 ligand. (2) Furthermore, the DFT computations also explain the selectivity of the C–H bond activation: only the RC (R = cyclohexyl) end of phenyl(cyclohexyl)-substituted metallacyclopropene in 5 is capable to undergo \(\sigma\)-bond metathesis (\(\Delta G(298 \text{ K}) = -4.6 \text{ kcal mol}^{-1}\)).
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 ΔG(298 K) = –13.3 kcal mol\(^{-1}\), and proceeds via transition state TS10 with an activation barrier (ΔG\(^{\ddagger}\)(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 metallocyclopropenes were comprehensively investigated. When the substituents on the thorium metallocyclopropene are changed from phenyl to alkyl, a distinctive change in reactivity is observed, which is also illustrated by their relative stabilities. The thorium metallocyclopropenes 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\(_3\)C)\(_3\)C\(_5\)H\(_2\) ligand. In contrast, the thorium metallocyclopropene 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\(_3\)C)\(_3\)C\(_5\)H\(_2\) induced by 5 is energetically favourable, while that promoted by 2 is not. Nevertheless, in contrast to zirconium metallocyclopropenes,\(^{1b}\) 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 metallocyclopropene complexes and the exploration of the thorium cyclometalated complexes and pyridyl alkenyl complexes in organic syntheses are ongoing projects in these laboratories.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant no. 21472013, 21172022, 21272026, 21373030), the Program for Changjiang Scholars and Innovative Research Team in University, and the Deutsche Forschungsgemeinschaft (DFG) through the Emmy-Noether and Heisenberg program (WA 2513/2 and WA 2513/6, respectively). We thank Dr Xuebin Deng for his help with the crystallography, and Prof. Richard A. Andersen for helpful discussions.

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