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A thorium metallacyclopentadiene complex: a combined experimental and computational study†

Bo Fang,^a Guohua Hou,^a Guofu Zi,^{*a} De-Cai Fang^{*a} and Marc D. Walter^{*b}

The synthesis, structure, and reactivity of a thorium metallacyclopentadiene were comprehensively studied. The reduction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ThCl}_2$ (**1**) with potassium graphite (KC_8) in the presence of diphenylacetylene ($\text{PhC}\equiv\text{CPh}$) yields the first thorium metallacyclopentadiene complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\eta^2\text{-C}_4\text{Ph}_4)$ (**2**). Density functional theory (DFT) studies suggest that the 5f orbitals are involved in the bonding of the metallacyclopentadiene $\text{Th}-(\eta^2\text{-C}=\text{C}-\text{C}=\text{C})$ moiety. Compared to the thorium metallacyclopentadiene, complex **2** shows a distinctively different reactivity towards diazoalkanes and organic azides such as $\text{Me}_3\text{SiCHN}_2$, 9-diazo fluorene and *p*-tolyl N_3 , leading to the formation of the six-membered hydrazido complexes $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}[\text{N}(\text{N}=\text{CHSiMe}_3)(\text{C}_4\text{Ph}_4)]$ (**3**) and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}[\text{N}(\text{N}=\text{C}(\text{C}_{12}\text{H}_8))(\text{C}_4\text{Ph}_4)]$ (**4**) and the seven-membered bis(triazenido) complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}[\text{N}(\text{N}=\text{N}(p\text{-tolyl}))(\text{C}_4\text{Ph}_4)\text{N}(\text{N}=\text{N}(p\text{-tolyl}))]$ (**5**), respectively.

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Introduction

Small metallacycles exhibit unusual intrinsic reactivity,¹ and within this class of compounds metallacycloprenes and metallacyclopentadienes of group 4 metallocenes have spurred particular interest.^{1,2} These metallacycles are generally prepared by the reduction of the metallocene dichlorides in the presence of a suitable alkyne.^{1c} Whereas the synthesis of metallacycloprenes requires a precise control of the alkyne stoichiometry, metallacyclopentadienes are formed in the presence of an excess alkyne.^{1c} Furthermore, metallacycles may serve as precursors for the synthesis of highly functionalized organic molecules and heterocyclic main group element compounds.^{1–3} Whereas metallacycles of the group 4 elements are well studied and understood, only a few examples of actinide elements are known.⁴ One notable exception is the reactivity of the $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}$ moiety with $\text{PhC}\equiv\text{CPh}$ to yield the uranium metallacyclopentadiene $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\eta^2\text{-C}_4\text{Ph}_4)$, which most likely proceeds *via* the uranium metallacyclopro-

pene intermediate $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\text{PhC}\equiv\text{CPh})$.^{4e} In contrast, the analogous reactivity of the $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}$ fragment has not been investigated. We have been interested in thorium organometallics for some time,^{5–8} because Th adopts with its $7s^26d^2$ electronic ground state, a special position within the actinide elements, which also relates it to group 4 metals. In order to investigate the reaction chemistry of thorium metallacycles and the influence of the 5f-orbitals we have recently prepared the thorium metallacyclopentadiene complex $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$.⁹ The sterically demanding 1,2,4-(Me_3C)₃C₅H₂ ligand prevented the double insertion of $\text{PhC}\equiv\text{CPh}$ and therefore it allowed us to investigate the reactivity of the thorium metallacyclopentadiene towards unsaturated substrates such as aldehyde, CS₂, carbodiimide, nitrile, and isothiocyanate, for which insertion into the Th–C bond was observed.⁹ With the organic azide Me_3SiN_3 the azametallacyclobutene complex $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}[\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})=\text{C}(\text{Ph})]$ was formed concomitant with N₂ loss, whereas the unusual complex $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2][\eta^5\text{-}\sigma\text{-1,2-(Me}_3\text{C)}_2\text{-4-(CH}_2\text{CMe}_2\text{)}_5\text{C}_5\text{H}_2]\text{Th}[\text{NC}(\text{C}_{12}\text{H}_8)\text{CH}(\text{Ph})\text{C}(\text{Ph})=\text{N}]$ was isolated when $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$ was treated with 9-diazo fluorene (Scheme 1).⁹ We are now interested in comparing the reactivity of a thorium metallacyclopentadiene towards these reactive nitrogen containing substrates.¹⁰ Therefore, as part of these investigations, we report herein on some observations concerning the synthesis, structure, structure–reactivity relationship of the first thorium metallacyclopentadiene $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\eta^2\text{-C}_4\text{Ph}_4)$ (**2**), and its reactivity towards organic azide and diazoalkane derivatives.

^aDepartment of Chemistry, Beijing Normal University, Beijing 100875, China.

E-mail: gzi@bnu.edu.cn, dcfang@bnu.edu.cn; Fax: +86-10-58802075;

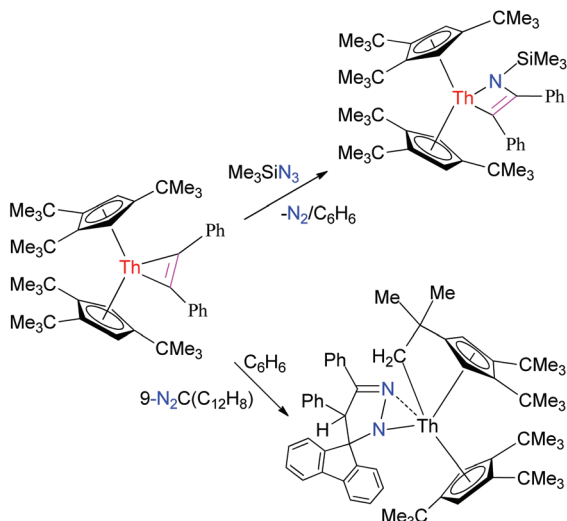
Tel: +86-10-58806051

^bInstitut 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

† Electronic supplementary information (ESI) available: Cartesian coordinates of all stationary points optimized at the B3PW91-PCM+D3 level. CCDC 1033600–1033603. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00838g



Scheme 1 Reactions of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2)$ with Me_3SiN_3 and 9-diazafluorene.

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 benzophenone ketyl immediately prior to use. Diphenylacetylene was purified by sublimation prior to use. KC_8 ¹¹ and 9-diazafluorene¹² were prepared according to literature procedures. 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 $^{13}\text{C}\{^1\text{H}\}$ 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 $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ThCl}_2$ (1).^{4b} *Modified procedure.* A toluene (50 mL) suspension of $(\text{C}_5\text{Me}_5)\text{K}$ (3.48 g, 20.0 mmol) and $\text{ThCl}_4(\text{tmeda})_2$ (6.06 g, 10.0 mmol) was refluxed for 3 days. The reaction mixture was cooled to room temperature, filtered and the residue was washed with toluene (5 mL \times 3). The volume of the filtrate was reduced to ca. 20 mL, and colorless crystals of **1** were isolated when this solution was kept at -20°C for two days. Yield: 4.99 g (87%). ^1H NMR (C_6D_6): δ 2.01 (s, 30H, CH_3).

Preparation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\eta^2\text{-C}_4\text{Ph}_4)$ (2). KC_8 (2.03 g, 15.0 mmol) was added to a toluene (20 mL) solution of

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{ThCl}_2$ (**1**; 2.00 g, 3.5 mmol) and diphenylacetylene (1.25 g, 7.0 mmol) with stirring at room temperature. After this solution was stirred overnight at room temperature, the solvent was removed. The residue was extracted with benzene (10 mL \times 3) and filtered. The volume of the filtrate was reduced to 10 mL, yellow crystals of **2** were isolated, when this solution was kept at room temperature for two days. Yield: 2.25 g (75%) (found: C, 67.20; H, 5.81. $\text{C}_{48}\text{H}_{50}\text{Th}$ requires C, 67.12; H, 5.87%). M.p.: 205–207 $^\circ\text{C}$ (decomp.). ^1H NMR (C_6D_6): δ 7.06 (t, $J = 7.7$ Hz, 4H, phenyl), 6.99 (d, $J = 7.0$ Hz, 4H, phenyl), 6.92 (t, $J = 7.6$ Hz, 4H, phenyl), 6.83 (m, 4H, phenyl), 6.65 (d, $J = 7.4$ Hz, 4H, phenyl), 1.98 (s, 30H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 221.2 (ThCPh), 151.5 (CPh), 145.2 (phenyl C), 143.7 (phenyl C), 131.3 (phenyl C), 128.9 (phenyl C), 128.5 (phenyl C), 127.5 (phenyl C), 125.6 (phenyl C), 125.3 (phenyl C), 123.7 (ring C), 11.8 (CH_3) ppm. IR (KBr, cm^{-1}): 3043 (w), 2963 (s), 2902 (s), 1586 (s), 1441 (s), 1384 (s), 1260 (s), 1093 (s), 1021 (s), 797 (s).

Preparation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}[\text{N}(\text{N}=\text{CHSiMe}_3)(\text{C}_4\text{Ph}_4)]\cdot 0.5\text{C}_6\text{H}_6$ (3·0.5 C_6H_6). *Method A.* An *n*-hexane (125 μL) solution of $\text{Me}_3\text{SiCHN}_2$ (0.25 mmol, 2 M in *n*-hexane) was added dropwise to a toluene (10 mL) solution of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\eta^2\text{-C}_4\text{Ph}_4)$ (**2**; 215 mg, 0.25 mmol) with stirring at room temperature. During the course of the reaction, the color of the solution changed from yellow to red. After the solution was stirred at room temperature overnight, 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, red crystals of 3·0.5 C_6H_6 were isolated, when this solution was kept at room temperature for one week. Yield: 217 mg (86%) (found: C, 65.32; H, 6.21; N, 2.83. $\text{C}_{55}\text{H}_{63}\text{N}_2\text{SiTh}$ requires C, 65.26; H, 6.27; N, 2.77%). M.p.: 138–140 $^\circ\text{C}$ (decomp.). ^1H NMR (C_6D_6): δ 7.15 (s, 3H, C_6H_6), 7.14 (s, 1H, NCHSi), 7.10 (t, $J = 7.5$ Hz, 4H, phenyl), 7.00 (m, 4H, phenyl), 6.90 (t, $J = 7.4$ Hz, 2H, phenyl), 6.83 (m, 6H, phenyl), 6.74 (t, $J = 7.5$ Hz, 2H, phenyl), 6.66 (m, 2H, phenyl), 2.04 (s, 30H, CH_3), 0.12 (s, 9H, $\text{Si}(\text{CH}_3)_3$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 215.2 (ThCPh), 149.7 (C=N), 148.1 (CPh), 147.2 (CPh), 146.8 (CPh), 143.2 (phenyl C), 140.0 (phenyl C), 135.3 (phenyl C), 133.8 (phenyl C), 132.7 (phenyl C), 130.4 (phenyl C), 129.5 (phenyl C), 128.9 (phenyl C), 128.5 (phenyl C), 128.0 (C_6H_6), 127.1 (phenyl C), 126.4 (phenyl C), 126.3 (phenyl C), 126.1 (phenyl C), 124.4 (phenyl C), 124.3 (phenyl C), 124.2 (phenyl C), 123.0 (ring C), 11.7 (CH_3), -0.4 ($\text{Si}(\text{CH}_3)_3$) ppm. IR (KBr, cm^{-1}): 2962 (s), 1596 (m), 1439 (m), 1383 (s), 1260 (s), 1091 (s), 1019 (s), 799 (s).

Method B. NMR scale. An *n*-hexane (10.0 μL , 2 M) solution of $\text{Me}_3\text{SiCHN}_2$ (0.02 mmol) was slowly added to a J. Young NMR tube charged with $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\eta^2\text{-C}_4\text{Ph}_4)$ (**2**; 17 mg, 0.02 mmol) and C_6D_6 (0.5 mL). The color of the solution immediately changed from yellow to red, and resonances corresponding to **3** along with those of *n*-hexane were observed by ^1H NMR spectroscopy (100% conversion in 10 min).

Preparation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}[\text{N}(\text{N}=\text{C}(\text{C}_{12}\text{H}_8))(\text{C}_4\text{Ph}_4)]\cdot \text{C}_6\text{H}_{12}$ (4· C_6H_{12}). *Method A.* This compound was prepared as green crystals from the reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\eta^2\text{-C}_4\text{Ph}_4)$ (**2**; 215 mg, 0.25 mmol) and 9-diazafluorene (48 mg, 0.25 mmol)



in toluene (15 mL) and recrystallization from a cyclohexane solution by a similar procedure as in the synthesis of **3**. Yield: 255 mg (90%) (found: C, 70.79; H, 6.30; N, 2.41. $C_{67}H_{70}N_2Th$ requires C, 70.88; H, 6.21; N, 2.47%). M.p.: 166–168 °C (decomp.). 1H NMR (C_6D_6): δ 8.19 (d, J = 7.8 Hz, 2H, aryl), 7.31 (t, J = 8.3 Hz, 2H, aryl), 7.24 (m, 4H, aryl), 7.11 (m, 6H, aryl), 7.03 (m, 4H, aryl), 6.91 (t, J = 6.1 Hz, 2H, aryl), 6.80 (m, 4H, aryl), 6.66 (t, J = 7.4 Hz, 1H, aryl), 6.43 (t, J = 7.3 Hz, 2H, aryl), 6.29 (t, J = 7.3 Hz, 1H, aryl), 2.42 (s, 15H, CH_3), 1.71 (s, 15H, CH_3), 1.40 (s, 12H, C_6H_{12}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 215.7 (ThCPh), 150.0 (CPh), 150.0 (CPh), 148.3 (CPh), 146.5 (aryl C), 143.0 (aryl C), 139.9 (aryl C), 138.8 (aryl C), 137.4 (aryl C), 135.5 (aryl C), 134.1 (aryl C), 133.9 (aryl C), 133.4 (aryl C), 132.5 (aryl C), 128.5 (aryl C), 127.6 (aryl C), 127.0 (aryl C), 126.9 (aryl C), 126.7 (aryl C), 126.6 (aryl C), 126.5 (aryl C), 126.3 (aryl C), 125.9 (aryl C), 125.6 (aryl C), 125.4 (aryl C), 125.2 (aryl C), 124.7 (aryl C), 123.3 (aryl C), 121.4 (aryl C), 120.3 (aryl C), 119.4 (ring C), 27.2 (C_6H_{12}), 12.8 (CH_3), 11.4 (CH_3) ppm. IR (KBr, cm^{-1}): 2962 (m), 1584 (m), 1434 (s), 1384 (s), 1260 (s), 1094 (s), 1019 (s), 803 (s).

Method B. NMR scale. To a J. Young NMR tube charged with ($\eta^5-C_5Me_5$)₂Th($\eta^2-C_4Ph_4$) (**2**; 17 mg, 0.02 mmol) and C_6D_6 (0.5 mL), 9-diazofluorene (3.8 mg, 0.02 mmol) was added. The color of the solution immediately changed from yellow to green, and the NMR resonances of **4** were observed by 1H NMR spectroscopy (100% conversion in 10 min).

Preparation of ($\eta^5-C_5Me_5$)₂Th[N(N=N(*p*-tolyl))(C₄Ph₄)N(N=N(*p*-tolyl))] (5**).** **Method A.** This compound was prepared as red crystals from the reaction of ($\eta^5-C_5Me_5$)₂Th($\eta^2-C_4Ph_4$) (**2**; 215 mg, 0.25 mmol) and *p*-tolylN₃ (67 mg, 0.50 mmol) in toluene (15 mL) and recrystallization from a THF solution by a similar procedure as in the synthesis of **3**. Yield: 230 mg (82%)

(found: C, 66.15; H, 5.82; N, 7.48. $C_{62}H_{64}N_6Th$ requires C, 66.18; H, 5.73; N, 7.47%). M.p.: 210–212 °C (decomp.). 1H NMR (C_6D_6): δ 7.68 (d, J = 8.4 Hz, 4H, phenyl), 7.34 (d, J = 7.0 Hz, 4H, phenyl), 7.19 (m, 8H, phenyl), 6.81 (t, J = 7.6 Hz, 4H, phenyl), 6.76 (m, 6H, phenyl), 6.58 (t, J = 7.3 Hz, 2H, phenyl), 2.24 (s, 6H, tolyl CH_3), 1.91 (s, 30H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.7 (CPh), 143.3 (CPh), 141.7 (phenyl C), 138.5 (phenyl C), 133.5 (phenyl C), 132.8 (phenyl C), 132.6 (phenyl C), 131.2 (phenyl C), 129.9 (phenyl C), 127.5 (phenyl C), 127.4 (phenyl C), 127.3 (phenyl C), 127.1 (phenyl C), 125.7 (phenyl C), 118.4 (ring C), 20.9 (tolyl CH_3), 12.9 (CH_3) ppm. IR (KBr, cm^{-1}): 2918 (s), 1605 (m), 1505 (s), 1442 (s), 1300 (s), 1258 (s), 1190 (s), 1090 (s), 1026 (s), 818 (s).

Method B. NMR scale. A C_6D_6 (0.3 mL) solution of *p*-tolylN₃ (5.2 mg, 0.04 mmol) was slowly added to a J. Young NMR tube charged with ($\eta^5-C_5Me_5$)₂Th($\eta^2-C_4Ph_4$) (**2**; 17 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The color of the solution immediately changed from yellow to red, and resonances due to **5** were observed by 1H NMR spectroscopy (100% conversion in 10 min).

Reaction of ($\eta^5-C_5Me_5$)₂Th($\eta^2-C_4Ph_4$) (2**) with *p*-tolylN₃.** **NMR scale.** A C_6D_6 (0.3 mL) solution of *p*-tolylN₃ (2.6 mg, 0.02 mmol) was slowly added to a J. Young NMR tube charged with ($\eta^5-C_5Me_5$)₂Th($\eta^2-C_4Ph_4$) (**2**; 17 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The color of the solution immediately changed from yellow to red. Resonances attributed to **5** along with those unreacted **2** were observed by 1H NMR spectroscopy (50% conversion in 10 min based on **2**).

X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker SMART CCD diffractometer at 113(2) K using

Table 1 Crystal data and experimental parameters for compounds **2–5**

Compound	2	3 ·0.5 C_6H_6	4 · C_6H_{12}	5
Formula	$C_{48}H_{50}Th$	$C_{55}H_{63}N_2SiTh$	$C_{67}H_{70}N_2Th$	$C_{62}H_{64}N_6Th$
Fw	858.92	1012.20	1135.29	1125.23
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$	$P(\bar{1})$	$C2/c$
<i>a</i> (Å)	13.662(1)	14.231(3)	11.359(3)	48.165(10)
<i>b</i> (Å)	16.932(1)	22.998(5)	11.964(3)	10.309(2)
<i>c</i> (Å)	17.245(1)	14.519(3)	20.965(5)	26.366(6)
α (°)	90	90	102.21(1)	90
β (°)	103.46(1)	91.54(1)	100.72(1)	118.01(1)
γ (°)	90	90	91.28(1)	90
<i>V</i> (Å ³)	3879.6(5)	4750.2(19)	2730.4(12)	11 558(4)
<i>Z</i>	4	4	2	8
<i>D</i> _{calc} (g cm ^{−3})	1.471	1.415	1.381	1.293
μ (Mo K α) _{calc} (cm ^{−1})	3.875	3.202	2.773	2.621
Size (mm)	0.35 × 0.27 × 0.21	0.30 × 0.20 × 0.20	0.35 × 0.30 × 0.30	0.30 × 0.20 × 0.20
<i>F</i> (000)	1712	2044	1152	4544
2 θ range (°)	3.90 to 55.14	3.96 to 55.10	3.50 to 55.24	3.50 to 55.00
No. of reflns, collected	11 305	31 258	18 754	38 230
No. of obsd reflns	4452	10 866	12 584	13 259
No. of variables	227	545	641	634
Abscorr (<i>T</i> _{max} , <i>T</i> _{min})	0.50, 0.34	0.75, 0.60	0.75, 0.64	0.75, 0.63
<i>R</i>	0.018	0.033	0.031	0.036
<i>R</i> _w	0.041	0.068	0.070	0.075
<i>R</i> _{all}	0.042	0.073	0.072	0.080
Gof	1.07	0.99	1.04	1.00
CCDC	1033600	1033602	1033601	1033603



Table 2 Selected distances (Å) and angles (°) for compounds 2–5^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	2.814(2)	2.784(2) to 2.840(2)	2.543(2)	C(17) or C(17A) 2.465(2)	144.5(1)	74.1(1)
3	2.859(4)	2.826(3) to 2.924(4)	2.592(4)	C(21) 2.545(3) N(1) 2.528(3) N(2) 2.298(3)	138.9(1)	69.4(1) ^d
4	2.850(3)	2.819(3) to 2.866(3)	2.584(3)	C(37) 2.537(3) N(1) 2.568(2) N(2) 2.304(2)	133.3(1)	68.2(1) ^e
5	2.872(4)	2.808(3) to 2.938(4)	2.592(3)	N(1) 2.537(3) N(3) 2.623(3) N(4) 2.565(3) N(6) 2.594(3)	138.9(1)	58.9(1) ^f

^a Cp = cyclopentadienyl ring. ^b Average value. ^c Range. ^d The angle of C(21)–Th(1)–N(2). ^e The angle of C(37)–Th(1)–N(2). ^f The angle of N(3)–Th(1)–N(6).

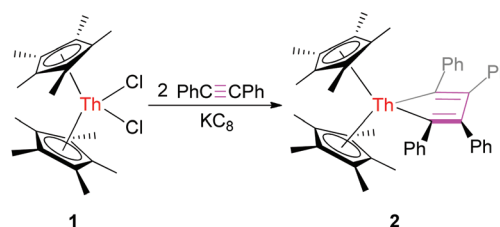
graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program.¹³ All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package.¹⁴ All the hydrogen atoms were geometrically fixed using the riding model. Disordered solvents in the voids of **5** were modeled or removed by using the SQUEEZE program.¹⁵ The crystal data and experimental data for 2–5 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),¹⁶ employing the B3PW91 functional, plus a polarizable continuum model (PCM) and D3¹⁷ (denoted as B3PW91-PCM+D3), with the standard 6-31G(d) basis set for C, H, N and Si elements and Stuttgart RLC ECP from the EMSL basis set exchange (<https://bse.pnl.gov/bse/portal>) for Th and U,¹⁸ to fully optimize the structures of reactants, complexes, transition states, intermediates, and products, and also to mimic the experimental toluene-solvent conditions (dielectric constant $\epsilon = 2.379$). 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.

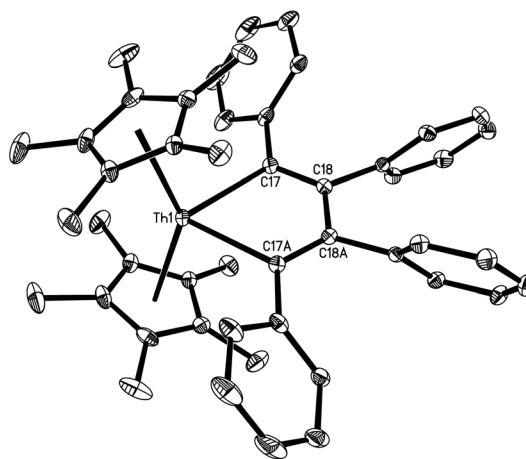
Results and discussion

Reduction of (η^5 -C₅Me₅)₂ThCl₂ (**1**) with an excess of KC₈ in the presence of PhC \equiv CPh yielded the metallacyclopentadiene, (η^5 -C₅Me₅)₂Th(η^2 -C₄Ph₄) (**2**) in 75% yield (Scheme 2). In contrast to the sterically more encumbered [η^5 -1,2,4-(Me₃C)₃C₅H₂]₂Th fragment,⁹ no thorium metallacyclopentadiene was isolated regardless of the amount of PhC \equiv CPh employed. Complex **2** is air and moisture sensitive, but it can be obtained as yellow

**Scheme 2** Synthesis of compound **2**.

crystals from a benzene solution. Various spectroscopic techniques, elemental analysis and single crystal X-ray diffraction were employed to fully characterize complex **2**. The ¹H NMR spectrum of **2** shows narrow and well-resolved resonances in the range of 0–10 ppm, which is consistent with a diamagnetic molecule. In addition, the resonance in the ¹³C NMR spectrum at $\delta = 221.2$ ppm is characteristic for the coordinated [η^2 -PhC \equiv CPh–CPh \equiv CPh] group.

The molecular structure of **2** is shown in Fig. 1. To the best of our knowledge, **2** represents the first structurally characterized thorium metallacyclopentadiene complex, and the crystal

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

structure of the related uranium metallacycle, (η^5 -C₅Me₅)₂U(η^2 -C₄Ph₄),^{4e} is the only other reported actinide metallacyclopentadiene complex. The distance Th–C(17) or Th–C(17A) of 2.465(2) Å is longer than that (2.395(2) Å) found in metallacyclopentadiene [η^5 -1,2,4-(Me₃C)₃C₅H₂]₂Th(η^2 -C₂Ph₂),⁹ but it is comparable to the other reported Th–C(sp²) σ -bonds (2.420(3)–2.654(14) Å)¹⁹ and slightly longer than the U–C distance in (η^5 -C₅Me₅)₂U(η^2 -C₄Ph₄) (2.395 (2) Å).^{4e} The angle (74.1(1)°) of C(17)–Th(1)–C(17A) is larger than that (32.6(1)°) found in metallacyclopentadiene [η^5 -1,2,4-(Me₃C)₃C₅H₂]₂Th(η^2 -C₂Ph₂).⁹ Furthermore, the distance (1.362(3) Å) of C(17)–C(18) is shorter than that (1.516(4) Å) of C(18)–C(18A), consistent with a localized metallacyclopentadiene structure as previously shown for the uranium metallacyclopentadiene (η^5 -C₅Me₅)₂U(η^2 -C₄Ph₄),^{4e} in which the C=C and C–C distances are 1.365(3) and 1.509(4) Å, respectively.^{4e} The reduced steric strain of the metallacyclopentadiene moiety should be reflected in a different reactivity compared to that of [η^5 -1,2,4-(Me₃C)₃C₅H₂]₂Th(η^2 -C₂Ph₂).⁹

In order to better understand the electronic structure of complex **2**, we undertook computational studies at the DFT level of theory. In addition, we decided to compare the bonding in **2** to its uranium analogue (η^5 -C₅Me₅)₂U(η^2 -C₄Ph₄). The DFT computations reproduce well the experimentally determined geometries of **2** and (η^5 -C₅Me₅)₂U(η^2 -C₄Ph₄), in which the butadiene fragment is coordinated to the (η^5 -C₅Me₅)₂An fragment by two An–C σ -bonds, as illustrated in Fig. 2. Furthermore, the natural bond orbital (NBO) analysis (Table 3) reveals that in complex **2**, the strongly polarized Th–C σ -bonds (σ Th–C) are composed of a carbon sp²-hybrid orbital (89.8%; 29% s and 71% p) and a thorium hybrid orbital (10.2%; 20% 5f and 48% 6d and 4% 7p and 28% 7s). In contrast, the bonding in the uranium complex (η^5 -C₅Me₅)₂U(η^2 -C₄Ph₄) is more covalent (17.4% U) and 5f orbitals also play a more important role. The percent contribution of 5f orbitals to

Table 3 Natural bond orbital (NBO) analysis of An–C₄(Ph₄) bonds

		2 (Th)	(η^5 -C ₅ Me ₅) ₂ U(η^2 -C ₄ Ph ₄)
σ An–C	%An	10.2	17.4
	%s	28	16
	%p	4	6
	%d	48	41
	%f	20	37
	%C	89.8	82.6
	%s	29	30
	%p	71	70
σ C–C	%s	31	32
	%p	69	68
σ C=C	%s	38	33
	%p	62	67
π C=C	%p	100	100

U–C σ -bonds is substantially larger in the uranium complex (η^5 -C₅Me₅)₂U(η^2 -C₄Ph₄) (37%) than that in the thorium complex **2** (20%). Furthermore, one C–C σ -bond (σ C–C) is composed of pure sp²-hybrid orbitals. Moreover, two bonding orbitals are found for the two C=C bonds: one is a σ -bond (σ C=C) with pure sp²-hybrid orbitals; the other bonding orbital is a π -bond (π C=C) with pure p orbitals. Overall, these computations reveal that the An–C bonds in actinide metallacyclopentadienes are rather ionic, but also demonstrate that actinide 5f orbitals are indeed involved in the bonding between the metallocene and C₄Ph₄ fragments. This is consistent with previous conclusions that the 5f orbitals play an important role in the bonding of actinide complexes.^{19a,20}

The next step was to probe the intrinsic reactivity of complex **2** and to compare these results to those of the thorium metallacyclopentadiene complex [η^5 -1,2,4-(Me₃C)₃C₅H₂]₂Th(η^2 -C₂Ph₂).⁹ In contrast to the thorium metallacyclopentadiene,⁹ the reaction products of **2** with one equivalent of diazoalkanes Me₃SiCHN₂ or 9-diazo fluorene yielded the six-membered hydrazido complexes (η^5 -C₅Me₅)₂Th[N(N=CHSiMe₃)(C₄Ph₄)] (**3**) and (η^5 -C₅Me₅)₂Th[N(N=C(C₁₂H₈))(C₄Ph₄)] (**4**) in quantitative conversions (Scheme 3). According to DFT computations the adduct **COM** is initially formed in the reaction of **2** with Me₃SiCHN₂ and the insertion of the coordinated Me₃SiCHN₂ proceeds *via* the transition state **TS** (Fig. 3). Interestingly, attempts to optimize a side-on bound (η^2 -N,N) adduct failed, instead the end-on bound adduct **COM** is always formed because of the steric hindrance. In the **TS** the two forming bond distances Th–N and C–N are 2.291 and 2.061 Å, respectively, which can be compared to those found in the product **3** of 2.308 and 1.376 Å, respectively. In the transition state the Th–N and C–N bonds are formed simultaneously, while the other nitrogen atom is coordinated to thorium ion. The conversion of **COM** to the product **3** is energetically very favorable by $\Delta G^\circ = -37.4$ kcal mol^{−1} and the activation barrier (ΔG^\ddagger) is 21.2 kcal mol^{−1}, which is consistent with the rapid formation of **3** at ambient temperature.

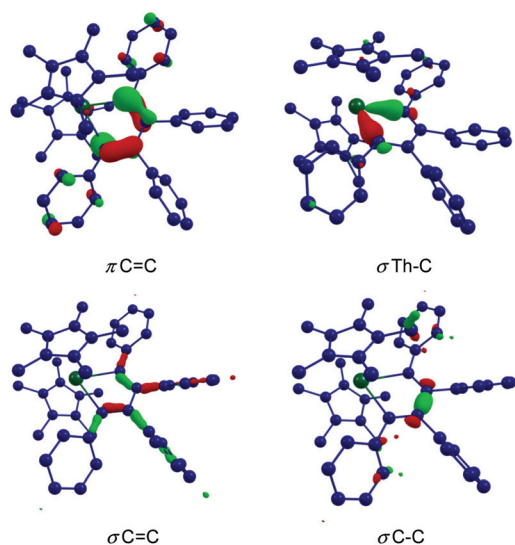
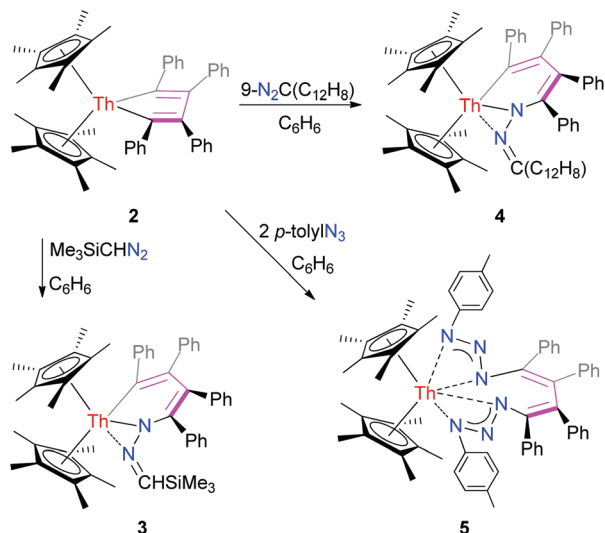
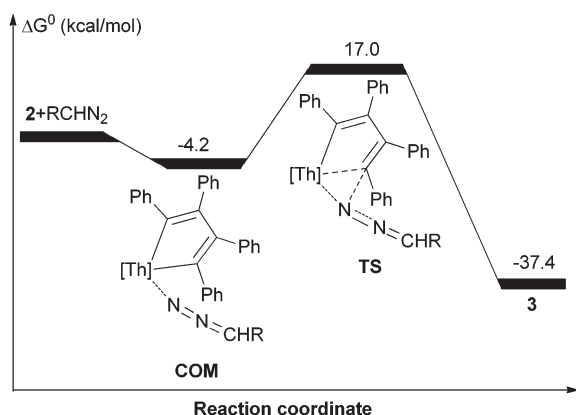


Fig. 2 Plots of MOs for **2** (the hydrogen atoms have been omitted for clarity).





Scheme 3 Synthesis of compounds 3–5.

Fig. 3 Free energy profile (kcal mol⁻¹) for the reactions of 2 + Me₃SiCHN₂. [Th] = (η⁵-C₅Me₅)₂Th. R = Me₃Si.

Furthermore, in contrast with the thorium metallacyclopentadiene [η⁵-1,2,4-(Me₃C)₃C₅H₂]₂Th(η²-C₂Ph₂),⁹ complex 2 reacts with organic azides such as *p*-tolylN₃ to the bis(triazenido) complex (η⁵-C₅Me₅)₂Th[N(N=N(*p*-tolyl))(C₄Ph₄)N(N=N(*p*-tolyl))] (5) (Scheme 3). Double insertion of *p*-tolylN₃ into the Th–C σ-bonds appears to be more favorable in this case, since the bis(triazenido) moiety [N(N=N(*p*-tolyl))(C₄Ph₄)N(N=N(*p*-tolyl))] is formed irrespectively of the amount of *p*-tolylN₃ employed.

Complexes 3–5 are air and moisture sensitive and they could be characterized by various spectroscopic techniques, elemental analyses and single crystal X-ray diffraction analyses. The solid state molecular structures of (η⁵-C₅Me₅)₂Th[N(N=CHSiMe₃)(C₄Ph₄)] (3) and (η⁵-C₅Me₅)₂Th[N(N=C(C₁₂H₈))(C₄Ph₄)] (4) are shown in Fig. 4 and 5. The average Th–C(Cp) distances in 3 and 4 are virtually identical with 2.859(4) Å and 2.850(4) Å, respectively, whereas the angle Cp(cent)–Th–Cp(cent) in 3 with 138.9(1)° is slightly larger than that in 4 with

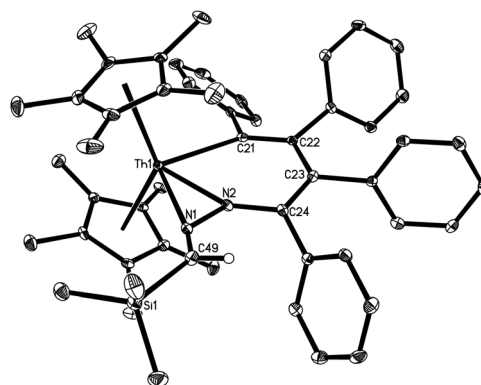


Fig. 4 Molecular structure of 3 (thermal ellipsoids drawn at the 35% probability level).

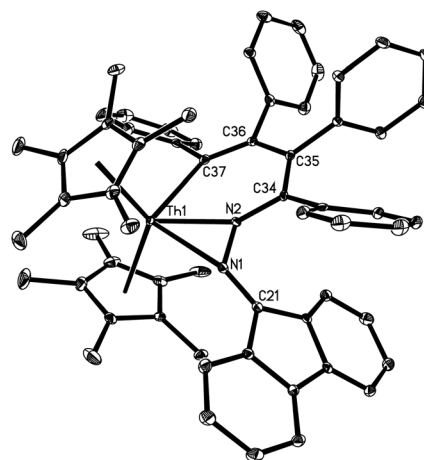


Fig. 5 Molecular structure of 4 (thermal ellipsoids drawn at the 35% probability level).

133.3(1)°. Furthermore, Th–C (C(21) for 3 and C(37) for 4) distances of 2.545(3) Å and 2.537(3) Å, respectively, are elongated compared to those found in 2 (2.465(2) Å). The N(1)–N(2) distances of 1.381(4) Å and 1.367(3) Å for 3 and 4, respectively, are comparable to that found in [η⁵-1,2,4-(Me₃C)₃C₅H₂][η⁵-σ-1,2-(Me₃C)₂-4-CMe₂(CH₂NN=CHSiMe₃)C₅H₂][Th[NH(*p*-tolyl)]] (1.366(8) Å).⁸ The Th–N(1) distances of 2.528(3) Å and 2.568(2) Å in 3 and 4, respectively, are relatively long and indicative of datively coordinated nitrogen atoms and in the same range as those found in [η⁵-1,2,4-(Me₃C)₃C₅H₂]₂ThO(4-Me₂NC₅H₄N) (2.587(5) Å)¹⁰ and [η⁵-1,2,4-(Me₃C)₃C₅H₂]₂Th[(bipy)(SCPh₂)] (2.564(1) Å).²¹ In contrast, the Th–N(2) distances of 2.298(3) Å and 2.304(2) Å for 3 and 4, respectively, are significantly shorter and can be compared to those found in [η⁵-1,2,4-(Me₃C)₃C₅H₂]₂Th(NH*p*-tolyl)₂ (2.279(3) and 2.286(3) Å),⁶ [η⁵-1,2,4-(Me₃C)₃C₅H₂]₂Th[N(*p*-tolyl)C(S)–S] (2.347(6) Å),⁸ [η⁵-1,2,4-(Me₃C)₃C₅H₂]₂Th[N(*p*-tolyl)C(NPh)–S] (2.328(3) Å),⁵ and [η⁵-1,2,4-(Me₃C)₃C₅H₂]₂Th[N(*p*-tolyl)N=NN(*p*-tolyl)] (2.366(3) and 2.354(3) Å),⁸ [η⁵-1,2,4-(Me₃C)₃C₅H₂]₂Th(bipy) (2.325(5) and



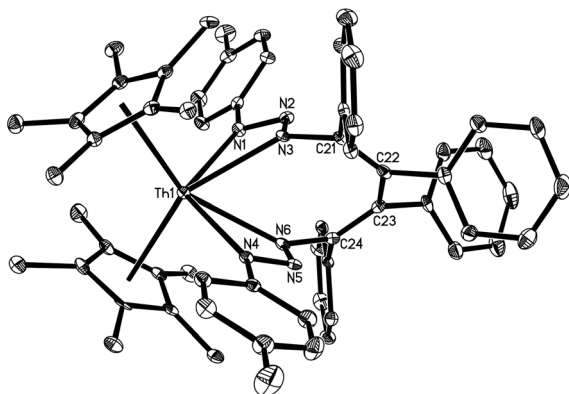


Fig. 6 Molecular structure of **5** (thermal ellipsoids drawn at the 35% probability level).

2.363(4) Å,²² and $[\eta^5\text{-}1,3\text{-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{Th}(\text{bipy})$ (2.326(7) and 2.325(7) Å).²³

Fig. 6 depicts the molecular structure of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}[\text{N}(\text{N}=\text{N}(p\text{-tolyl}))(\text{C}_4\text{Ph}_4)\text{N}(\text{N}=\text{N}(p\text{-tolyl}))]$ (**5**). The N–N distances of 1.335(4) Å for N(1)–N(2), 1.310(4) Å for N(2)–N(3), 1.318(4) Å for N(4)–N(5), and 1.309(4) Å for N(5)–N(6), are nearly identical and consistent with a delocalization of the negative charge within the triazene fragments N(1)–N(2)–N(3) and N(4)–N(5)–N(6). Hence the Th–N distances of 2.537(3) Å for Th–N(1), 2.623(3) Å for Th–N(3), 2.565(3) Å for Th–N(4), and 2.594(3) Å for N(6)–Th(1) are much longer than those found in **3** (2.298(3) Å), **4** (2.304(2) Å), $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\text{NH}p\text{-tolyl})_2$ (2.279(3) and 2.286(3) Å),⁶ $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}[\text{N}(p\text{-tolyl})\text{C}(\text{S})\text{-S}]$ (2.347(6) Å),⁵ $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}[\text{N}(p\text{-tolyl})\text{C}(\text{NPh})\text{-S}]$ (2.328(3) Å),⁵ and $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}[\text{N}(p\text{-tolyl})\text{N}=\text{NN}(p\text{-tolyl})]$ (2.366(3) and 2.354(3) Å),⁸ $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}(\text{bipy})$ (2.325(5) and 2.363(4) Å),²² and $[\eta^5\text{-}1,3\text{-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{Th}(\text{bipy})$ (2.326(7) and 2.325(7) Å).²³

Conclusions

In conclusion, the first thorium metallacyclopentadiene complex, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Th}(\eta^2\text{-C}_4\text{Ph}_4)$ (**2**), was comprehensively studied. Similar to thorium metallacyclopentadiene,⁹ density functional theory (DFT) studies reveals that 5f orbitals contribute to the Th–C σ -bonds of the Th–($\eta^2\text{-C}=\text{C}=\text{C}$) moiety, and that the σ -bonds between the $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{Th}^{2+}$ and the $[\text{C}_4\text{Ph}_4]^{2-}$ fragments are very polarized, which makes the insertion of unsaturated substrates favorable. However, when the steric strain of the metallacycle is reduced, the reaction chemistry changes, as illustrated by their reaction with organic azides and diazoalkanes. While the thorium metallacyclopentadiene yields rearranged products,⁹ the thorium metallacyclopentadiene shows mono- and double insertion of diazoalkanes and organic azides into the Th–C bond to yield hydrazido and bis(triazenido) ligands, respectively. Further studies on the intrinsic reactivity of actinide metallacycles are in progress and will be reported in due course.

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