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PAPER

A bipyridyl thorium metallocene: synthesis, structure and reactivity†‡

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The synthesis, structure and reactivity of a new bipy thorium metallocene have been studied. The reduction of the thorium chloride metallocene [η^5-1,3-$(Me_3C)_2C_5H_3]_2ThCl_2$ (**1**) with potassium graphite in the presence of 2,2′-bipyridine gives the purple bipy metallocene [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**) in good yield. Complex **2** has been fully characterized by various spectroscopic techniques, elemental analysis and X-ray diffraction analysis. Complex **2** reacts cleanly with trityl chloride, silver halides and diphenyl diselenide, leading to the halide metallocenes [η^5-1,3-$(Me_3C)_2C_5H_3]_2ThX_2$ (X = Cl (**1**), Br (**3**), I (**4**)) and [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(F)(μ-F)$_3$Th[η^5-1,3-$(Me_3C)_2C_5H_3$](F)(bipy) (**5**), and selenido metallocene [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(SePh)$_2$ (**6**), in good conversions. In addition, **2** cleaves the C═S bond of CS_2 to give the sulfido complex, [η^5-1,3-$(Me_3C)_2C_5H_3]_2$ThS (**7**), which further undergoes an irreversible dimerization or nucleophilic addition with CS_2, leading to the dimeric sulfido complex {[η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th}(μ-S)$_2$ (**8**) and dimeric trithiocarbonate complex {[η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th}(μ-CS_3)$_2$ (**10**) in good yields, respectively.

Introduction

Low-valent actinide chemistry has attracted significant attention over the years,[1–7] most notably considering the expanding series of divalent lanthanide complexes and their ability to activate small molecules such as dinitrogen.[8] In contrast, low-valent thorium complexes are not readily accessible due to the highly unfavorable redox-potentials[9] and only a few thorium(III) complexes have been thoroughly characterized.[6] However, the high reactivity of low-valent thorium complexes has previously been demonstrated by *in situ* reduction of appropriate Th(IV) precursors.[7] Therefore, organometallic complexes that can act as synthons for these otherwise difficult to access or even inaccessible oxidation states are a desirable synthetic goal. In general, this challenge can be met by redox non-innocent ligands such as 2,2′-bipyridine,[10] 1,4-diazabutadiene,[5b,11] pyridine diimine[12] and arenes.[13] Some of these metal complexes with redox active ligands show fascinating properties in small molecule activation and catalysis[14] and/or unusual physical and magnetic properties due to electron exchange coupling between the metal and ligand electrons.[11d,15] In the area of thorium chemistry Gambarotta has used naphthalene as a redox-active ligand to synthesize well-characterized thorium arene complexes which act as synthons for low-valent thorium and show a rich reaction chemistry.[13c,d] We have chosen a different approach and have focused on diimine ligands such as 2,2′-bipyridine (bipy). The bipy thorium metallocene, [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$Th(bipy), has been shown to be a useful low-valent thorium synthon for a wide range of transformations.[16] Encouraged by the interesting chemistry of this bipy thorium metallocene, we have recently extended our research work from 1,2,4-$(Me_3C)_3C_5H_2$ to the less sterically demanding 1,3-di-*tert*-butylcyclopentadienyl ligand, 1,3-$(Me_3C)_2C_5H_3$,[17] in order to evaluate the consequences of the reduced steric demand on the reactivity. Herein, we report on some observations concerning the chemistry of the new bipy organothorium complex, [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**).

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. 2,2′-Bipyridine was purified by sublimation prior to use. KC_8,[18] and [η^5-1,3-$(Me_3C)_2C_5H_3]_2ThCl_2$ (**1**)[19] were prepared according to literature methods. All other chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. used as received unless otherwise noted. Infrared spectra were obtained

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† Dedicated to Professor Richard A. Andersen on the occasion of his 70th birthday.

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from KBr pellets on an Avatar 360 Fourier transform spectrometer. UV-Vis spectra were recorded at 294 K in toluene solution on a TU-1901 spectrophotometer. ^{1}H and ^{13}C 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 are 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^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (2). KC_8 (1.22 g, 9.0 mmol) was added to a cyclohexane (20 mL) solution of [η^5-1,3-$(Me_3C)_2C_5H_3]_2ThCl_2$ (**1**; 2.00 g, 3.0 mmol) and 2,2′-bipyridine (bipy; 0.47 g, 3.0 mmol) with stirring at room temperature. After this solution was stirred at 65 °C overnight the solvent was removed. The residue was extracted with n-hexane (10 mL × 3) and filtered. The volume of the filtrate was reduced to 10 mL, purple crystals of **2** were isolated when this solution was kept at room temperature for two days. Yield: 1.76 g (79%) (Found: C, 58.17; H, 6.82; N, 3.65. $C_{36}H_{50}N_2Th$ requires C, 58.21; H, 6.78; N, 3.77%). M.p.: 95–97 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.28 (d, J = 6.4 Hz, 2H, bipy), 6.89 (d, J = 9.6 Hz, 2H, bipy), 6.20 (d, J = 2.4 Hz, 4H, ring C*H*), 6.14 (m, 2H, bipy), 5.95 (t, J = 2.4 Hz, 2H, ring C*H*), 5.30 (t, J = 6.0 Hz, 2H, bipy), 1.22 (s, 36H, $(CH_3)_3C$). ^{13}C{^{1}H} NMR (C_6D_6): δ 146.3, 144.1, 122.5, 121.0, 111.6, 111.5, 110.9, 102.0, 32.9, 31.9. IR (KBr, cm^{-1}): ν 2961 (s), 2858 (m), 1594 (s), 1455 (m), 1359 (s), 1260 (s), 1091 (s), 1019 (s), 799 (s). UV (toluene): λ_{max}/nm 375 (ε/M^{-1} cm^{-1} 2.70 × 10^3), 528 (1.66 × 10^3).

Reaction of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (2) with Ph_3CCl. NMR Scale. Ph_3CCl (11 mg; 0.04 mmol) was added to a J. Young NMR tube charged with [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL). The color of the solution immediately changed from purple to colorless, and resonances due to **1** along with those of $Ph_3CCH(C_2H_2)_2C{=}CPh_2$ (^{1}H NMR (C_6D_6): δ 7.29 (m, 3H, phenyl), 7.00 (m, 22H, phenyl), 6.43 (d, J = 9.8 Hz, 2H, C*H*), 5.92 (t, J = 9.8 Hz, 2H, C*H*), 4.92 (s, 1H, C*H*))[20] and 2,2′-bipyridine (^{1}H NMR (C_6D_6): δ 8.72 (d, J = 8.0 Hz, 2H), 8.53 (d, J = 4.0 Hz, 2H), 7.22 (t, J = 1.8 Hz, 2H), 6.68 (m, 2H))[16] were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (2) with AgCl. NMR Scale. AgCl (5.8 mg, 0.04 mmol) was added to a J. Young NMR tube charged with [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**; 14 mg, 0.02 mmol) and C_6D_6 (0.5 mL). The color of the solution immediately changed from purple to colorless, and resonances due to [η^5-1,3-$(Me_3C)_2C_5H_3]_2ThCl_2$ (**1**) (^{1}H NMR (C_6D_6): δ 6.67 (t, J = 2.8 Hz, 2H, ring C*H*), 6.23 (d, J = 2.8 Hz, 4H, ring C*H*), 1.35 (s, 36H, $(CH_3)_3C$))[19] along with those of 2,2′-bipyridine were observed by ^{1}H NMR spectroscopy (100% conversion).

Preparation of [η^5-1,3-$(Me_3C)_2C_5H_3]_2ThBr_2$ (3). Method A. AgBr (0.75 g, 4.0 mmol) was added to a toluene (20 mL) solution of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**; 1.11 g, 1.5 mmol) with stirring at room temperature. During the course of the reaction, the color of the solution changed from purple to colorless. After the solution was stirred at room temperature for 4 h, the solvent was removed. The residue was extracted with n-hexane (10 mL × 3) and filtered. The volume of the filtrate was reduced to 5 mL and cooled to −20 °C, yielding colorless crystals of **3**, which were isolated by filtration. Yield: 1.01 g (90%) (Found: C, 41.84; H, 5.73. $C_{26}H_{42}Br_2Th$ requires C, 41.83; H, 5.67%). M. p.: 167–169 °C. ^{1}H NMR (C_6D_6): δ 6.81 (t, J = 2.8 Hz, 2H, ring C*H*), 6.22 (d, J = 2.8 Hz, 4H, ring C*H*), 1.36 (s, 36H, $(CH_3)_3C$). ^{13}C{^{1}H} NMR (C_6D_6): δ 151.7, 120.6, 113.3, 33.4, 31.6. IR (KBr, cm^{-1}): ν 2960 (s), 2853 (m), 1597 (m), 1460 (s), 1358 (s), 1260 (s), 1090 (s), 1018 (s), 799 (s).

Method B. NMR Scale. AgBr (7.6 mg, 0.04 mmol) was added to a J. Young NMR tube charged with [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**; 14 mg, 0.02 mmol) and C_6D_6 (0.5 mL). The color of the solution immediately changed from purple to colorless, and resonances due to **2** along with those of 2,2′-bipyridine were observed by ^{1}H NMR spectroscopy (100% conversion).

Preparation of [η^5-1,3-$(Me_3C)_2C_5H_3]_2ThI_2$ (4). Method A. This compound was prepared as colorless crystals from the reaction of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**; 1.11 g, 1.5 mmol) and AgI (0.94 g, 4.0 mmol) in toluene (20 mL) and recrystallization from an n-hexane solution by a similar procedure as in the synthesis of **3**. Yield: 1.17 g (93%) (Found: C, 37.23; H, 4.97. $C_{26}H_{42}I_2Th$ requires C, 37.16; H, 5.04%). M.p.: 200–202 °C. ^{1}H NMR (C_6D_6): δ 7.06 (t, J = 2.8 Hz, 2H, ring C*H*), 6.20 (d, J = 2.8 Hz, 4H, ring C*H*), 1.37 (s, 36H, $(CH_3)_3C$). ^{13}C{^{1}H} NMR (C_6D_6): δ 152.4, 121.4, 113.2, 33.5, 31.8. IR (KBr, cm^{-1}): ν 2961 (s), 2856 (s), 1580 (m), 1459 (s), 1385 (s), 1358 (s), 1260 (s), 1089 (s), 1019 (s), 800 (s).

Method B. NMR Scale. AgI (9.4 mg, 0.04 mmol) was added to a J. Young NMR tube charged with [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**; 14 mg, 0.02 mmol) and C_6D_6 (0.5 mL). The color of the solution immediately changed from purple to colorless, and resonances due to **4** along with those of 2,2′-bipyridine were observed by ^{1}H NMR spectroscopy (100% conversion).

Preparation of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(F)(μ-F)$_3$Th[η^5-1,3-$(Me_3C)_2C_5H_3$](F)(bipy) (5). AgF (0.38 g, 3.0 mmol) was added to a benzene (20 mL) solution of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**; 1.11 g, 1.5 mmol) with stirring at room temperature. After the solution was stirred at room temperature overnight, the solvent was removed. The residue was extracted with n-hexane (10 mL × 3) and filtered. The volume of the filtrate was reduced to 5 mL and cooled to −20 °C, yielding colorless crystals of **5**, which were isolated by filtration. Yield: 0.60 g (64% based on Th) (Found: C, 47.23; H, 5.78; N, 2.19. $C_{49}H_{71}F_5N_2Th_2$ requires C, 47.19; H, 5.74; N, 2.25%). M.p.: > 300 °C. ^{1}H NMR (C_6D_6): δ 9.44 (s, 1H, bipy), 6.97 (m, 4H, bipy), 6.67 (m, 1H, bipy), 6.58 (m, 1H, bipy), 6.42 (s, 4H, ring C*H*), 6.29 (m, 1H, bipy), 6.21 (s, 1H, ring C*H*), 6.13 (s, 1H, ring C*H*), 6.08 (s, 1H, ring C*H*), 5.63 (s, 2H, ring C*H*), 1.55 (s, 18H, $(CH_3)_3C$), 1.42 (s, 36H, $(CH_3)_3C$). ^{13}C{^{1}H} NMR (C_6D_6): δ 154.3, 152.4, 149.3, 146.7, 144.8, 139.6, 136.4, 124.9, 123.4, 121.3, 120.9, 112.7, 111.5, 111.4, 110.3, 110.2, 33.4, 33.1, 31.8, 31.7. IR (KBr,

cm^{-1}): ν 2961 (s), 2917 (s), 1560 (s), 1458 (s), 1260 (s), 1090 (s), 1021(s), 799 (s).

Preparation of [η^5-1,3-$(Me_3C)_3C_5H_2]_2Th(SePh)_2$ (6). Method A. A benzene (10 mL) solution of PhSeSePh (0.47 g, 1.5 mmol) was added to a benzene (20 mL) solution of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**; 1.11 g, 1.5 mmol) with stirring at room temperature. During the course of the reaction, the color of the solution changed from purple to yellow. After the solution was stirred at room temperature for 0.5 h, solvent was removed and the yellow residue was extracted with n-hexane (10 mL × 3) and filtered. The volume of the filtrate was reduced to 5 mL and cooled to −20 °C, yielding yellow crystals of **6**, which were isolated by filtration. Yield: 1.10 g (82%) (Found: C, 50.72; H, 5.88. $C_{38}H_{52}Se_2Th$ requires C, 50.78; H, 5.83%). M.p.: 150–152 °C. ^{1}H NMR (C_6D_6): δ 8.00 (m, 4H, phenyl), 7.08 (m, 4H, phenyl), 6.98 (m, 2H, phenyl), 6.18 (br s, 6H, ring C*H*), 1.33 (s, 36H, $(CH_3)_3C$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.0, 136.5, 135.2, 128.8, 125.5, 115.9, 113.4, 33.9, 32.2. IR (KBr, cm^{-1}): ν 2962 (s), 2844 (m), 1571 (s), 1451 (s), 1392 (s), 1262 (s), 1091 (s), 1019 (s), 799 (s).

Method B. NMR Scale. PhSeSePh (6 mg; 0.02 mmol) was added to a J. Young NMR tube charged with [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**; 14 mg, 0.02 mmol) and C_6D_6 (0.5 mL). The color of the solution immediately changed from purple to yellow, and resonances due to **6** along with those of 2,2′-bipyridine were observed by ^{1}H NMR spectroscopy (100% conversion).

Preparation of {[η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th}(μ-S)$_2$ (8). Method A. A benzene (10 mL) solution of CS_2 (0.11 g, 1.5 mmol) was added to a benzene (20 mL) solution of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**; 1.11 g, 1.5 mmol) with stirring at room temperature. After the solution was stirred at room temperature overnight, solvent was removed and the residue was extracted with n-hexane (10 mL × 3) and filtered. The volume of the filtrate was reduced to 5 mL, colorless microcrystals of **8** were isolated when this solution was kept at room temperature for two days. Yield: 0.77 g (83%) (Found: C, 50.38; H, 6.87. $C_{52}H_{84}S_2Th_2$ requires C, 50.47; H, 6.84%). M.p.: > 300 °C (dec.). ^{1}H NMR (C_6D_6): δ 6.44 (br s, 2H, ring C*H*), 6.39 (br s, 8H, ring C*H*), 6.32 (br s, 2H, ring C*H*), 1.43 (s, 36H, $(CH_3)_3C$), 1.37 (s, 36H, $(CH_3)_3C$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 150.2, 148.0, 124.0, 123.6, 112.8, 111.2, 33.5, 33.1, 32.6, 32.2. IR (KBr, cm^{-1}): ν 2961 (s), 1534 (s), 1451 (s), 1388 (s), 1260 (s), 1089 (s), 1020 (s), 798 (s).

Method B. NMR Scale. A C_6D_6 (0.3 mL) solution of CS_2 (1.5 mg; 0.02 mmol) was added to a J. Young NMR tube charged with [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**; 14 mg, 0.02 mmol) and C_6D_6 (0.2 mL). The color of the solution immediately changed from purple to colorless, and resonances due to **8** along with those of 2,2′-bipyridine were observed by ^{1}H NMR spectroscopy (100% conversion).

Preparation of {[η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th}(μ-CS_3)$_2$ (10). A benzene (20 mL) solution of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**; 1.11 g, 1.5 mmol) was added to a benzene (10 mL) solution of CS_2 (2.00 g, 26.3 mmol) with stirring at room temperature. After the solution was stirred at room temperature overnight, the solution was filtered. The volume of the filtrate was reduced to 5 mL, colorless crystals of **10** were isolated when this solution was kept at room temperature for one week. Yield: 0.65 g (62%) (Found: C, 46.72; H, 6.07. $C_{54}H_{84}S_6Th_2$ requires C, 46.67; H, 6.09%). M.p.: > 300 °C (dec.). ^{1}H NMR (C_6D_6): δ 6.52 (br s, 2H, ring C*H*), 6.45 (br s, 2H, ring C*H*), 6.39 (br s, 4H, ring C*H*), 6.05 (br s, 2H, ring C*H*), 6.00 (br s, 2H, ring C*H*), 1.47 (s, 18H, $(CH_3)_3C$), 1.44 (s, 18H, $(CH_3)_3C$), 1.37 (s, 18H, $(CH_3)_3C$), 1.34 (s, 18H, $(CH_3)_3C$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 264.3, 150.6, 150.0, 114.8, 113.4, 112.8, 111.2, 110.3, 34.7, 34.1, 33.5, 33.1, 32.6, 32.2, 31.8, 31.7. IR (KBr, cm^{-1}): ν 2961 (s), 2856 (m), 1458 (m), 1354 (m), 1260 (s), 1090 (s), 1017 (s), 931 (s), 798 (s).

X-Ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart APEX II CCD diffractometer at 110(2) K or on a Rigaku Saturn CCD diffractometer at 113(2) K using graphite monochromated Mo Kα radiation (λ = 0.71070 Å). An empirical absorption correction was applied using the SADABS program.[21] All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package.[22] All the hydrogen atoms were geometrically fixed using the riding model. Disordered solvents in the voids of **5** and **10** were modelled or removed by using the SQUEEZE program.[23] Crystal data and experimental data for **2–6** and **10** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Results and discussion

Synthesis of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (2)

Treatment of an excess of KC_8 with a 1 : 1 mixture of 2,2′-bipyridine and [η^5-1,3-$(Me_3C)_3C_5H_2]_2ThCl_2$ (**1**) in cyclohexane solution gives the purple bipy metallocene, [η^5-1,3-$(Me_3C)_3C_5H_2]_2$Th(bipy) (**2**) in 79% yield (Scheme 1). Complex **2** is soluble in and readily recrystallized from an n-hexane solution. It is stable in dry nitrogen atmosphere, while it is very sensitive to air and moisture. It has been characterized by various spectroscopic techniques, elemental analysis and X-ray diffraction analysis. Complex **2** has narrow resonances with chemical shifts in the range of 0–10 ppm and well-resolved coupling patterns in its ^{1}H NMR spectrum. The four resonances assigned to the bipy ligand are significantly shifted to the high field in comparison with those in free bipy, and the ratio of bipy to Cp-ligand is 1 : 2.[24] The UV-vis spectrum shows two absorptions at λ_{max} = 528 nm (ε = 1.66 × 10^3 M^{-1} cm^{-1}) and 375 nm (ε = 2.70 × 10^3 M^{-1} cm^{-1}).[24]

The ORTEP representation of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$Th(bipy) (**2**) is shown in Fig. 1. The average Th–C(ring) distance is 2.837 (8) Å. The bulky Me_3C-groups are nearly eclipsed with the Cp-ligands pointing toward the front of the metallocene wedge. As expected, the acceptance of electrons into the lowest unoccupied molecular orbital of neutral bipy results in shortening of the C(5)–C(6) bond and in flattening of the bipyridyl ligand. The bending angle[16] of the bipy in **2** is 139° and the C(5)–C(6) distance is 1.396(12) Å. These structural data are close to those

Table 1 Crystal data and experimental parameters for compounds **2–6** and **10**

Compound	**2**	**3**	**4**	**5**	**6**	**10**
Formula	$C_{36}H_{50}N_2Th$	$C_{26}H_{42}Br_2Th$	$C_{26}H_{42}I_2Th$	$C_{49}H_{71}F_5N_2Th_2$	$C_{38}H_{52}Se_2Th$	$C_{54}H_{84}S_6Th_2$
Fw	742.82	746.46	840.44	1247.16	898.76	1389.65
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	Pc	$P\bar{1}$
a (Å)	11.701(2)	19.672(3)	19.495(2)	12.145(1)	12.033(2)	13.078(1)
b (Å)	17.020(2)	16.500(2)	16.731(2)	13.749(1)	16.165(2)	14.466(1)
c (Å)	16.704(2)	8.672(1)	8.895(1)	17.283(2)	19.461(3)	17.689(2)
α (°)	90	90	90	102.73(1)	90	82.53(1)
β (°)	97.88(1)	98.20(1)	97.32(1)	96.15(1)	104.18(1)	83.11(1)
γ (°)	90	90	90	91.44(1)	90	70.64(1)
V (Å^3)	3295.4(7)	2786.2(6)	2877.8(6)	2795.3(5)	3670.2(9)	3119.9(4)
Z	4	4	4	2	4	2
D_{calc} (g cm^{-3})	1.497	1.780	1.940	1.482	1.627	1.479
μ(Mo Kα)$_{calc}$ (cm^{-1})	4.550	8.230	7.337	5.359	6.069	4.992
Size (mm)	0.27 × 0.24 × 0.17	0.30 × 0.11 × 0.08	0.20 × 0.19 × 0.12	0.24 × 0.20 × 0.18	0.35 × 0.26 × 0.22	0.26 × 0.20 × 0.18
F(000)	1480	1432	1576	1208	1752	1896
2θ range (°)	4.00 to 55.30	4.18 to 50.50	3.22 to 55.08	3.38 to 55.86	4.32 to 50.50	2.32 to 67.50
No. of reflns, collected	19 214	14 047	17 049	35 795	17 883	54 435
No. of unique reflns	7514 (R_{int} = 0.0444)	5020 (R_{int} = 0.0750)	6580 (R_{int} = 0.0658)	13 245 (R_{int} = 0.0466)	9247 (R_{int} = 0.0408)	24 512 (R_{int} = 0.0384)
No of obsd reflns	5281	3568	4692	9449	7973	20 747
No of variables	364	279	274	542	762	583
Abscorr (T_{max}, T_{min})	0.51, 0.37	0.56, 0.19	0.47, 0.32	0.45, 0.36	0.35, 0.23	0.47, 0.36
R	0.055	0.043	0.044	0.031	0.043	0.028
R_w	0.111	0.074	0.082	0.057	0.091	0.057
R_{all}	0.087	0.072	0.071	0.044	0.054	0.035
Gof	1.08	0.98	0.99	0.97	1.02	1.00
CCDC	860416	860417	860418	860419	860420	869908

found in [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$Th(bipy) with the bending angle of 141° and a distance of 1.382(8) Å.[16]

Reactivity of [η^5-1,3-($Me_3C)_2C_5H_3]_2$Th(bipy) (2)

As expected, the bipy thorium complex **2** is very reactive. For example, reaction of complex **2** with trityl chloride quantitatively gives the chloride complex **1**, along with the byproducts neutral bipy and Gomberg's dimer $Ph_3CCH(C_2H_2)_2C{=}CPh_2$[20] (Scheme 1). The formation of Gomberg's dimer, neutral bipy and complex **1** implies that the free radical $Ph_3C^{\cdot}$ is formed by the oxidation of **2** by Ph_3C^+. Likewise, the treatment of **2** with silver chloride, bromide or iodide results in the halide metallocenes [η^5-1,3-($Me_3C)_2C_5H_3]_2ThX_2$ (X = Cl (**1**), Br (**3**), I (**4**)) in quantitative conversion (Scheme 1). The conversions are measured by integration of the NMR resonances against an internal standard. The pure halide complexes may be readily separated from free bipy, which is the only organic byproduct, by recrystallization from an n-hexane solution, and the isolated preparative scale yields are 90% for **3**, and 93% for **4**, respectively. However, under similar reaction conditions, treatment of **2** with 2 equiv of silver fluoride does not give the desired difluoride metallocene [η^5-1,3-($Me_3C)_2C_5H_3]_2ThF_2$, instead, a binuclear thorium complex [η^5-1,3-($Me_3C)_2C_5H_3]_2$Th(F)(μ-F)$_3$Th[η^5-1,3-($Me_3C)_2C_5H_3$](F)(bipy) (**5**) has been isolated in 64% yield (Scheme 1), presumably due to the small size of the fluorine anion and its strong nucleophilicity. Complex **2** cleaves Se–Se bonds to give diselenido complexes. For example, reaction of **2** with 1 equiv of PhSeSePh results in Se–Se bond cleavage to yield diselenido metallocene [η^5-1,3-($Me_3C)_2C_5H_3]_2$Th(SePh)$_2$ (**6**) in quantitative conversion (Scheme 1).

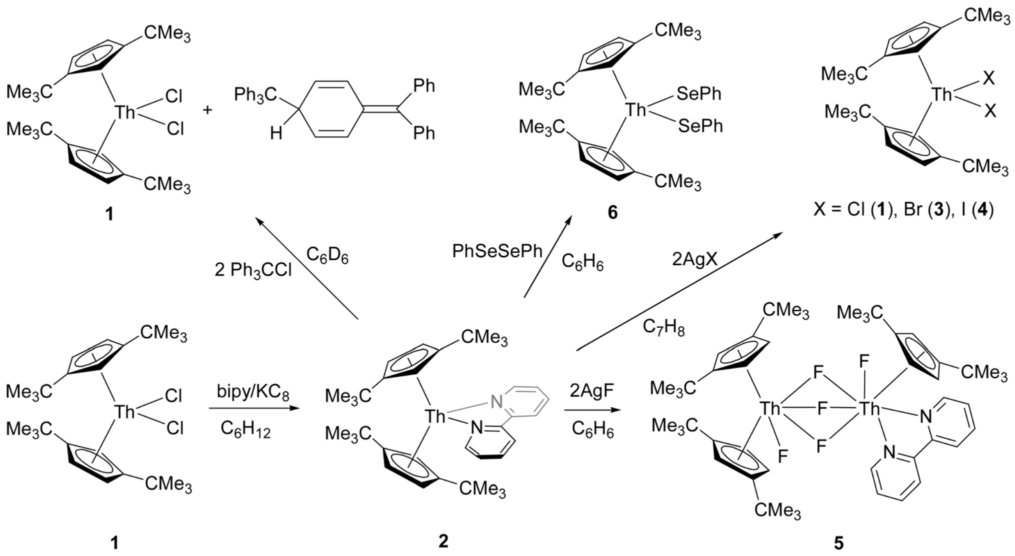
Under similar reaction conditions, treatment of **2** with 1 equiv of CS_2 at room temperature irreversibly gives dimeric sulfido complex {[η^5-1,3-($Me_3C)_2C_5H_3]_2$Th}(μ-S)$_2$ (**8**) in 83% yield (Scheme 2). While reaction of **2** with an excess of CS_2 at room temperature forms the dimeric trithiocarbonate complex {[η^5-1,3-($Me_3C)_2C_5H_3]_2$Th}(μ-$CS_3)_2$ (**10**) in 62% yield (Scheme 2). These observations suggest that **2** cleaves the C═S bond of CS_2 to form the sulfido metallocene [η^5-1,3-($Me_3C)_2C_5H_3]_2$ThS (**7**) and carbon monosulfide CS. Monomeric sulfido **7** is unstable and undergoes an irreversible dimerization or nucleophilic addition resembling that of the thorium sulfido [η^5-1,2,4-($Me_3C)_3C_5H_2]_2$ThS.[25] To the best of our knowledge, this is the first example that a sulfido thorium complex was prepared by reductive cleavage of CS_2 with a low-valent thorium synthon. Although carbon monosulfide is known to be very unstable,[26] there have been instances where CS was trapped *in situ* during reductive disproportionation processes of CS_2.[27] In contrast to uranium μ-sulfido complex [((1-O-4-Me-6-AdC_6H_2-2-$CH_2)_3$N)-U]$_2$(μ-S),[2g] no reaction between thorium μ-sulfido **8** and CS_2 occurs even heated at 65 °C for one week.

The complexes **3–6**, **8** and **10** are stable in dry nitrogen atmosphere, but they are very moisture sensitive. They have been characterized by various spectroscopic techniques and elemental analyses. ^{1}H and ^{13}C NMR spectra indicate that complexes **3**, **4**, **6**, **8** and **10** are symmetrical on the NMR spectroscopic timescale, which are consistent with their C_2 or C_{2v}-symmetric structures. Complexes **3–6** and **10** have been further confirmed by X-ray diffraction analyses. The ORTEP diagrams of [η^5-1,3-

Table 2 Selected distances (Å) and angles (°) for compounds **2–6** and **10**[a]

Compound	C(Cp)–Th (ave)	C(Cp)–Th (range)	Cp(cent)–Th (ave)	Th–X (ave)	Cp(cent)–Th–Cp(cent)	X–Th–X
2	2.837(8)	2.771(8) to 2.882(7)	2.570(8)	2.326(7)	124.1(8)	74.1(2)
3	2.789(8)	2.722(8) to 2.838(8)	2.512(8)	2.794(1)	127.3(8)	98.2(1)
4	2.787(8)	2.719(7) to 2.848(8)	2.514(8)	3.035(1)	127.8(7)	102.4(1)
5	Th(1) 2.865(4) Th(2) 2.855(5)	Th(1) 2.796(4) to 2.926(4) Th(2) 2.813(5) to 2.922(5)	Th(1) 2.603 (4) Th(2) 2.590(5)	Th(1)–F 2.378(2) Th(2)–F 2.292(2) Th(2)–N 2.677(4)	Cp–Th(1)–Cp 112.8(2)	
6	2.796(12)	2.723(12) to 2.863(11)	2.527(8)	2.877(1)	126.4(8)	105.1(1)
10	2.837(2)	2.770(2) to 2.902(2)	2.587(2)	2.988(1)	117.5(1)	S(1)–Th(1)–S(2) 59.4(1)

[a] Cp = cyclopentadienyl ring.



Scheme 1 Synthesis of complexes **2–6**.

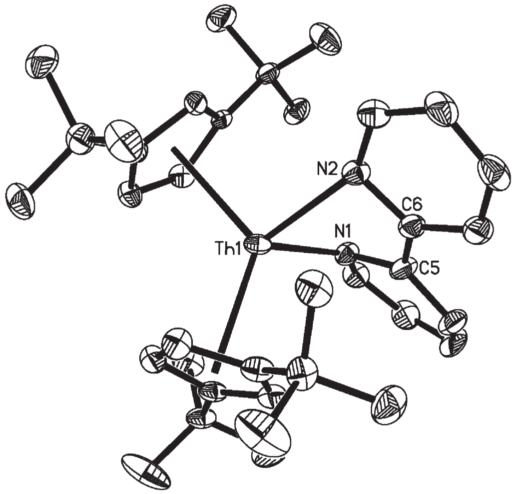
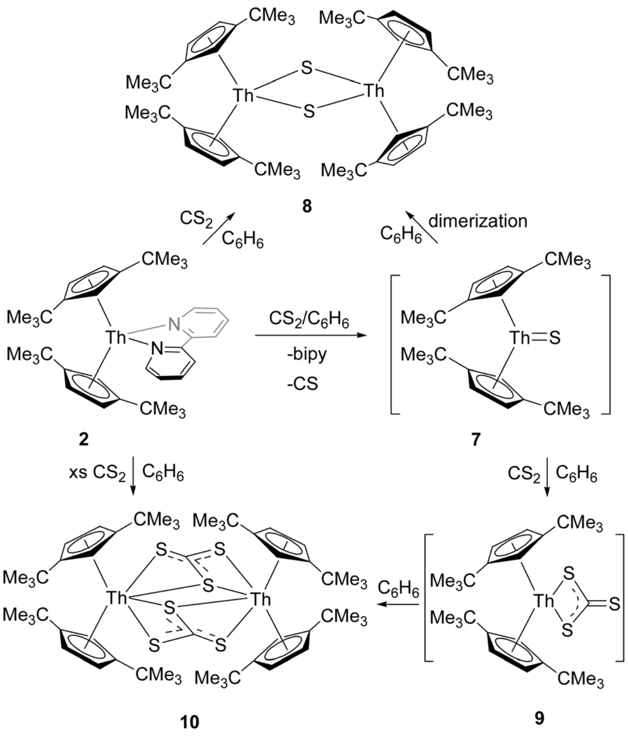


Fig. 1 Molecular structure of **2** (thermal ellipsoids drawn at the 35% probability level).

(Me$_3$C)$_2$C$_5$H$_3$]$_2$ThBr$_2$ (**3**) and [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$ThI$_2$ (**4**) are shown in Fig. 2 and 3. The average Th–C(ring) distance is 2.789(8) Å for **3**, and 2.787(8) Å for **4**, respectively. In the solid state, **3** and **4** have crystallographic C_2 symmetry with staggered



Scheme 2 Synthesis of compounds **8** and **10**.

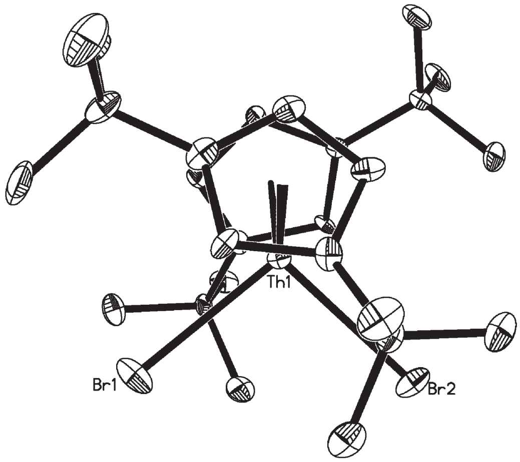


Fig. 2 Molecular structure of **3** (thermal ellipsoids drawn at the 35% probability level).

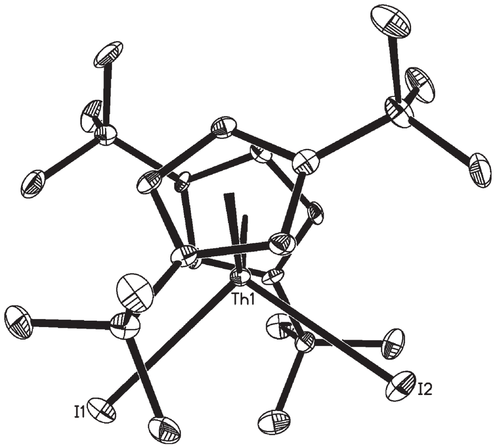


Fig. 3 Molecular structure of **4** (thermal ellipsoids drawn at the 35% probability level).

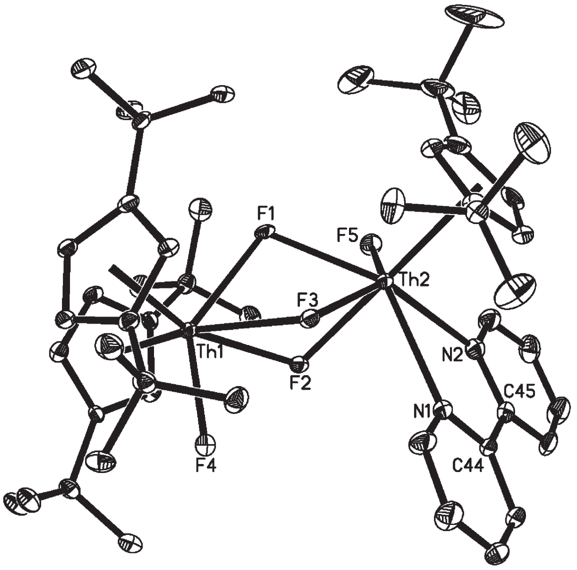


Fig. 4 Molecular structure of **5** (thermal ellipsoids drawn at the 35% probability level).

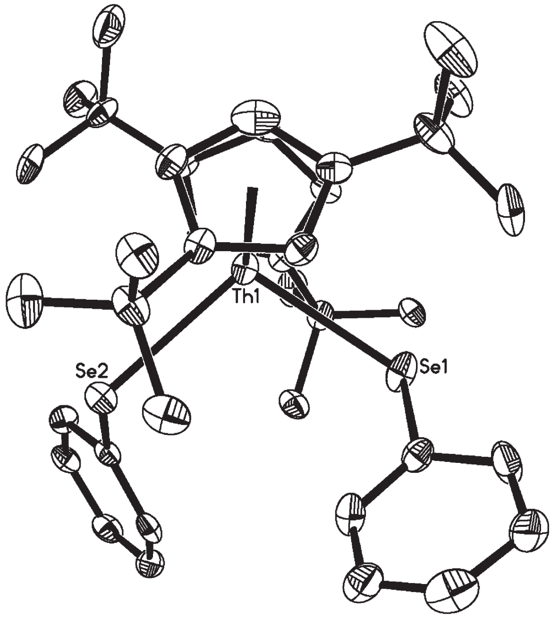


Fig. 5 Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level).

cyclopentadienyl ligands such as those in [η^5-1,3-$(Me_3C)_2C_5H_3]_2ThCl_2$.[19] Complexes **3** and **4** have similar X–Th–X angles (Table 2). In complex **3**, the average Th–Br distance is 2.794(1) Å, which is close to those found in (η^5-$C_5Me_5)_2ThBr_2$ (2.800(2) Å)[28] and [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2ThBr_2$ (2.785(1) Å).[16] In complex **4**, the average Th–I distance is 3.035(1) Å, close to that (2.986(2) Å) found in (η^5-$C_5Me_5)_2ThI_2$.[29]

The molecular structure of **5** is shown in Fig. 4. Coordination of three Cp-ligands and five fluorine atoms and one bipy group around two Th^{4+} ions results in the formation of the dinuclear complex [η^5-1,3-$(Me_3C)_2C_5H_3]_2Th(F)(\mu$-$F)_3Th[\eta^5$-1,3-$(Me_3C)_2C_5H_3](F)$(bipy). One Th^{4+} ion is η^5-bond to two Cp-rings and σ-bound to one terminal fluorine atom and three doubly bridging fluorine atoms in a distorted-octahedral geometry with an average Th–C(ring) distance of 2.865(4) Å. The angle of Cp–Th(1)–Cp is 112.8(2)°. The average Th(1)–F distance is 2.378(2) Å, and slightly longer than that (2.126(5) Å) found in [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2ThF_2$.[16] The other Th^{4+} ion is η^5-bond to one Cp-ring and σ-bound to one terminal fluorine atom, three doubly bridging fluorine atoms and two nitrogen atoms from a bipy group in a distorted-pentagonal-bipyramidal geometry with an average Th–C(ring) distance of 2.855(5) Å. The average Th(2)–F distance is 2.292(2) Å, slightly longer than that (2.126(5) Å) found in [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2ThF_2$,[16] while slightly shorter than that (2.378(2) Å) of Th(1)–F. The distance C(44)–C(45) is 1.467(6), which is comparable to those found in [η^5-1,2,4-$(Me_3C)_3C_5H_2]Th(SePh)_3$(bipy) (1.484(9) Å),[16] and **2** (1.396(12) Å).

The single-crystal X-ray diffraction analysis shows that there are two molecules [η^5-1,3-$(Me_3C)_2C_5H_3]_2Th(SePh)_2$ (**6**) in the lattice. An ORTEP diagram of **6** is shown in Fig. 5, and shows

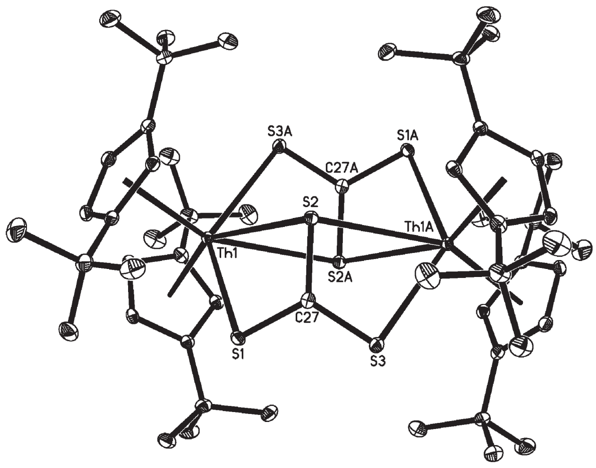


Fig. 6 Molecular structures of **10** (thermal ellipsoids drawn at the 35% probability level).

crystallographic C_2 symmetry with staggered cyclopentadienyl ligands such as those in **3** and **4**. The average Th–C(ring) distance is 2.796(12) Å, while the angle of Cp–Th(1)–Cp is 126.4(8)°, and the angle of Se–Th–Se is 105.1(1)°. The average Th–Se distance is 2.877(1) Å, which is slightly shorter than that (2.938(8) Å) found in [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]Th(SePh)$_3$(bipy).[16]

The single-crystal X-ray diffraction analysis shows that in the solid state **10** has crystallographic C_2 symmetry, but the Th^{4+} ion has a distorted octahedral coordination environment (Fig. 6) with an average Th–C(ring) distance of 2.837(2) Å and the Cp(cent)–Th–Cp(cent) angle of 117.5(1)°. The orientation of the cyclopentadienyl rings is nearly eclipsed. The small differences in the C–S distances (0.006, 0.006 and 0.012 Å) suggest that the negative charge is delocalized over the CS$_3^{2-}$ fragment. The average Th–S distance of 2.988(1) Å is comparable to those found in {[η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(S)[(μ-S)$_2$C]}$_6$ (2.852(2) Å),[25] and [(Ph$_2$PS)$_2$C]$_2$Th(DME) (2.931(2) Å).[30]

Conclusions

In conclusion, a new bipy thorium metallocene [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th(bipy) (**2**) has been prepared and structurally characterized. It cleanly reacts with oxidizing reagents such as trityl chloride, silver halides and diphenyl diselenide, yielding halido- and selenido-complexes. Furthermore, CS$_2$ is activated by a low-valent thorium synthon to give a sulfido thorium complex.

In addition, replacing 1,2,4-tri-*tert*-butylcyclopentadienyl ligand for 1,3-di-*tert*-butylcyclopentadienyl ligand, the different reactivity patterns have been observed between bipy thorium complexes [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(bipy) and [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th(bipy) (**2**). For example, reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(bipy) with 2 equiv of AgF cleanly yields the difluoride complex [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$ThF$_2$,[16] while **2** affords a binuclear complex [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th(F)-(μ-F)$_3$Th[η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$](F)(bipy) (**5**), which is most likely due to the different steric demand of both ligands. Mixing [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(bipy) with 1 equiv of PhSeSePh gives a mixture of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]Th(SePh)$_3$(bipy) and [1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_3$Th(SePh),[16] whereas **2** cleanly affords a diselenido complex [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$Th(SePh)$_2$ (**6**). Further efforts are currently focused on the reactivity and the exploration of the actinide bipy complexes towards other types of transformations.

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