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Is the bipyridyl thorium metallocene a low-valent thorium complex? A combined experimental and computational study[†]

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Bipyridyl thorium metallocenes [η^5 -1,2,4-(Me₃C)₃C₅H₂]₂Th(bipy) (**1**) and [η^5 -1,3-(Me₃C)₂C₅H₃]₂Th(bipy) (**2**) have been investigated by magnetic susceptibility and computational studies. The magnetic susceptibility data reveal that **1** and **2** are not diamagnetic, but they behave as temperature independent paramagnets (TIPs). To rationalize this observation, density functional theory (DFT) and complete active space SCF (CASSCF) calculations have been undertaken, which indicated that Cp²Th(bipy) has indeed a Th(IV)(bipy²⁻) ground state ($f^0d^0\pi^*2$, $S = 0$), but the open-shell singlet ($f^0d^1\pi^*1$, $S = 0$) (almost degenerate with its triplet congener) is lying only 9.2 kcal/mol higher in energy. Complexes **1** and **2** react cleanly with Ph₂CS to give [η^5 -1,2,4-(Me₃C)₃C₅H₂]₂Th[(bipy)(SCPh₂)] (**3**) and [η^5 -1,3-(Me₃C)₂C₅H₃]₂Th[(bipy)(SCPh₂)] (**4**), respectively, in quantitative conversions. Since no intermediates were observed experimentally, this reaction was also studied computationally. Coordination of Ph₂CS to **2** in its $S = 0$ ground state is not possible, but Ph₂CS can coordinate to **2** in its triplet state ($S = 1$) upon which a single electron transfer (SET) from the (bipy²⁻) fragment to Ph₂CS followed by C-C coupling takes place.

Introduction

In contrast to uranium chemistry, low-valent thorium complexes are not readily accessible due to the highly unfavourable redox-potentials.¹ Consequently, only a few thorium(III) complexes have been thoroughly characterized,² and these studies have revealed that Th(III) has a 6d¹ rather than a 5f¹ ground state.^{2d} Low-valent thorium complexes have also been prepared by *in situ* reduction of appropriate Th(IV) precursors, but the formed species are exceedingly reactive and do not necessarily react in a controlled manner.³ Therefore, well-characterized organometallic complexes that can act as synthons for these otherwise difficult to access or even inaccessible oxidation states are desirable synthetic goals. In principle, this challenge can be met by non-innocent, redox-active ligands such as 2,2'-bipyridine, 1,4-diazabutadiene, pyridine diimine and arenes.⁴ For example, we have used 2,2'-bipyridine to synthesize well-behaved thorium bipy complexes, [η^5 -1,2,4-(Me₃C)₃C₅H₂]₂Th(bipy) (**1**) and [η^5 -1,3-(Me₃C)₂C₅H₃]₂Th(bipy) (**2**), which act as synthons for low-valent thorium and show a rich reaction chemistry.⁵ The narrow resonances with chemical shifts in the range of 0–10 ppm and well-resolved coupling patterns in their ¹H NMR spectra coupled with the absence of absorptions at 800 nm in their UV-vis spectra suggested a Th(IV)(bipy²⁻) ($f^0d^0\pi^*2$, $S = 0$) ground state for these molecules.⁵ This ground state description is consistent with previous density functional theory (DFT) studies on [η^5 -C₅H₅]₂Zr(bipy).⁶ However, the electronic structure of metal complexes involving redox non-innocent ligands can be much more complicated than originally anticipated, and magnetic susceptibility and more elaborate computational studies are crucial for the understanding of the electronic structure.⁷ Herein, we report on some observations concerning the electronic structure and structure-reactivity relationship of the thorium bipy metallocenes **1** and **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. [η^5 -1,2,4-(Me₃C)₃C₅H₂]₂Th(bipy) (**1**),^{5a} [η^5 -1,3-(Me₃C)₂C₅H₃]₂Th(bipy) (**2**)^{5b} and Ph₂CS⁸ were prepared according to literature methods. All other chemicals were purchased from Aldrich Chemical Co. or Beijing Chemical Co. and were used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. ¹H and ¹³C 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 the internal standards, for proton and carbon chemical shifts. The magnetic susceptibility data were recorded on a Quantum Design MPMS XL5 SQUID magnetometer. The samples for magnetic susceptibility measurements (83 mg and 61 mg of **1** and **2**, respectively) were sealed in quartz tubes according to literature procedures.⁹ The magnetic susceptibilities were corrected for diamagnetism using Pascal's constants¹⁰ for all the constituent atoms. 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-(Me₃C)₃C₅H₂]₂Th[(bipy)(SCPh₂)]·2C₆H₆ (3**·2C₆H₆).** Method A. A benzene (10 mL) solution of Ph₂CS (0.30 g, 1.5 mmol) was added to a benzene (20 mL) solution of [η^5 -1,2,4-(Me₃C)₃C₅H₂]₂Th(bipy) (**1**; 1.28 g, 1.5 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, purple crystals of **3**·2C₆H₆ were isolated when this solution was kept at room temperature for two days. Yield: 1.56 g (86%) (Found: C, 68.55; H, 7.31; N, 2.30. C₆₉H₈₈N₂STh requires C, 68.52; H, 7.33; N, 2.32%). M.p.: 85-87 °C. ¹H NMR (C₆D₆): δ 8.81 (d, *J* = 5.2 Hz, 1H, bipy), 8.19 (d, *J* = 7.2 Hz, 4H, bipy), 7.27 (m, 6H, phenyl), 7.15 (s, 12H, C₆H₆), 7.07 (m, 2H, phenyl), 6.71 (m, 2H, phenyl), 6.62 (d, *J* = 2.9 Hz, 1H, ring *CH*), 6.48 (s, 1H, ring *CH*), 6.44 (t, *J* = 6.4 Hz, 1H, bipy), 5.98 (s, 1H, ring *CH*), 5.93 (m, 1H, bipy), 5.25 (m, 1H, ring *CH*), 5.18 (d, *J* = 6.4 Hz, 1H, bipy), 1.81 (s, 9H, (CH₃)₃C), 1.67 (s, 9H, (CH₃)₃C), 1.40 (s, 18H, (CH₃)₃C), 1.36 (s, 9H, (CH₃)₃C), 0.66 (s, 9H, (CH₃)₃C). ¹³C{¹H} NMR (C₆D₆): δ 162.8, 153.2, 151.2, 148.6, 147.4, 146.5, 142.6, 141.0, 139.4, 137.1, 131.4, 128.3, 128.0 (C₆H₆), 127.6, 127.0, 126.7, 125.9, 125.4, 125.1, 123.2, 122.9, 120.4, 118.9, 117.9, 117.4, 113.6, 98.4, 83.1, 79.4, 67.6, 37.2, 36.0, 35.6, 35.1, 34.6, 34.3, 34.1, 33.5, 33.4, 33.2, 32.2, 31.7. IR (KBr, cm⁻¹): ν 2962 (s), 2850 (m), 1618 (m), 1442 (m), 1411 (m), 1379 (m), 1260 (s), 1091 (s), 1019 (s), 798 (s).

Method B. NMR Scale. Ph₂CS (4 mg; 0.02 mmol) was added to a J. Young NMR tube charged with [η^5 -1,2,4-(Me₃C)₃C₅H₂]₂Th(bipy) (**1**; 17 mg, 0.02 mmol) and C₆D₆ (0.5 mL). The resonances due to **3** were observed by ¹H NMR spectroscopy (100% conversion).

Preparation of [η^5 -1,3-(Me₃C)₂C₅H₃]₂Th[(bipy)(SCPh₂)] (**4**).

Method A. This compound was prepared as purple crystals from the reaction of [η^5 -1,3-(Me₃C)₂C₅H₃]₂Th(bipy) (**2**; 1.11 g, 1.5 mmol) and Ph₂CS (0.30 g, 1.5 mmol) in benzene (20 mL) and recrystallization from a benzene solution by a similar procedure as in the synthesis of **3**. Yield: 1.17 g (83%) (Found: C, 62.55; H, 6.38; N, 2.96. C₄₉H₆₀N₂STh requires C, 62.53; H, 6.43; N, 2.98%). M.p.: 132-134 °C. ¹H NMR (C₆D₆): δ 8.64 (s, 1H, bipy), 8.26 (d, *J* = 4.0 Hz, 2H, bipy), 8.13 (d, *J* = 3.4 Hz, 2H, bipy), 7.26 (m, 4H, phenyl), 7.07 (m, 4H, phenyl), 6.78 (m, 2H, phenyl), 6.65 (s, 1H, ring *CH*), 6.43 (m, 2H, bipy), 6.20 (s, 1H, ring *CH*), 6.01 (s, 1H, ring *CH*), 5.86 (s, 2H, ring *CH*), 5.35 (s, 1H, ring *CH*), 5.15 (s, 1H, bipy), 1.70 (s, 9H, (CH₃)₃C), 1.42 (s, 9H, (CH₃)₃C), 1.00 (s, 9H, (CH₃)₃C), 0.74 (s, 9H, (CH₃)₃C). ¹³C{¹H} NMR (C₆D₆): δ 162.6, 151.9, 150.4, 149.1, 147.1, 147.0, 143.4, 137.0, 131.3, 131.2, 128.3, 127.8, 127.6, 127.1, 126.9, 125.8, 125.2, 123.8, 123.5, 122.6, 119.0, 115.7, 112.6, 111.7, 110.8, 98.2, 78.9, 33.9, 33.8, 33.7, 33.0, 32.5, 32.4, 31.1, 31.0; the other carbon atoms overlapped. IR (KBr, cm⁻¹): ν 2962 (s), 2850 (m), 1599 (s), 1439 (s), 1260 (s), 1084 (s), 1020 (s), 799 (s).

Method B. NMR Scale. Ph₂CS (4 mg; 0.02 mmol) was added to a J. Young NMR tube charged with [η^5 -1,3-(Me₃C)₂C₅H₃]₂Th(bipy) (**2**; 15 mg, 0.02 mmol) and C₆D₆ (0.5 mL). The resonances due to **4** were observed by ¹H NMR spectroscopy (100% conversion).

X-Ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart APEX II CCD diffractometer at 110(2) K using graphite monochromated Mo K α radiation (λ = 0.71070 Å). An empirical absorption correction was applied using the SADABS program.¹¹ All structures were solved by direct

methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package.¹² All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **3** and **4** are summarized in Table 1 and selected bond lengths and angles are listed in Table 2.

<Tables 1 and 2 here>

Computational Methods

All calculations were carried out with the Gaussian 09 program (G09),¹³ employing the B3PW91 functional with standard 6-31G(d,p) basis set for S, C, H and N elements and Stuttgart RLC ECP from EMSL basis set exchange (<https://bse.pnl.gov/bse/portal>) for Th element,¹⁴ to fully optimize the geometries of the complexes (with no symmetry restrictions imposed (*C*₁)). All resultant stationary points were subsequently characterized by vibrational analyses, from which their respective Gibbs Free Energies (ΔG) were extracted and used in the relative energy determinations. Two spins (*S* = 0 and 1) were considered for **1** and **2**, respectively, and CASSCF calculations were also carried out to determine the nature of the two lowest singlet and the lowest triplet state.

Results and discussion

Solid state magnetic susceptibility studies (SQUID)

The variable-temperature magnetic susceptibilities (χ) of **1** and **2** have initially been measured in the range of 5–300 K at 1000 G (see ESI for details). The samples were sealed in quartz tubes and the measurements were repeated on independently prepared samples. In all these cases a temperature-independent paramagnetism (TIP) was observed, but the values varied (slightly) from run to run, which suggested the presence of small amounts of magnetic impurities (presumably ferromagnetic ferrites from stainless steel equipment). It should be noted that the measurement of magnetic susceptibility data on air and moisture sensitive samples with low magnetic moments requires extreme care and attention to detail. To overcome the impurity problems we recorded the magnetic susceptibility at three different temperatures (200, 250 and 300 K) and varied the applied magnetic field (*H*) between 0 and 70 kG. The magnetization (*M*_{tot}) vs. *H* curves were plotted for both molecules (see ESI for details). The recorded magnetization is the sum of the magnetization of the sample components including the (ferromagnetic) impurities (*M*_{impurity}) and the magnetization is described by the formula $M_{tot} = \chi H + M_{impurity}$. In our study χ is negative because the diamagnetism of the atoms in the compound is larger than the actual TIP. In addition, these field sweeps reveal that we have a small amount of a ferromagnetic impurity in our SQUID samples. At relatively low magnetic fields (~ 0.5 T) the magnetization of this impurity is saturated, so above 1T the magnetization becomes field independent, $M_{impurity} = M_{ferro}$, where *M*_{ferro} is the saturation magnetism. Hence, at high fields, the magnetization of the sample can be expressed by

$$M_{tot} = \chi H + M_{ferro} \quad (\text{eq1})$$

At lower fields the curvature in the *M*_{tot} vs. *H* curves is caused by the fact that the ferromagnetism of the sample is not saturated, but still larger than the TIP. However, at fields *H* > 1T, the *M*_{tot} vs.

H plots are linear and can be fit to eq.1 to determine χ and M_{ferro} (see ESI for details). The χ values obtained from these analyses at three different temperatures were corrected for Pascal's constants to yield a temperature independent χ_{TIP} . For **1** and **2** we find small, but positive values of $9.3(3) \times 10^{-5}$ and $8.36(4) \times 10^{-5}$ emu/mol, respectively. The TIP is presumably van Vleck paramagnetism, which arises from excited states coupling to the ground state. (ref J.H. van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press: London, 1932.)

Reactivity

As expected from previous studies on bipy uranium complexes,¹⁵ the bipy thorium derivatives react with aldehydes, ketones or thio-ketones. For example, treatment of **1** with 1 equiv of Ph_2CS at room temperature results in the formation of the metallocene $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{Th}[(\text{bipy})(\text{SCPh}_2)]$ (**3**) in quantitative yield (Scheme 1), where the dianion $[(\text{bipy})(\text{SCPh}_2)]^{2-}$ may be formed by two alternative pathways. On the top of the scheme a nucleophilic attack of the dianionic $[\text{bipy}]^{2-}$ on Ph_2CS is shown, whereas on the bottom of the scheme, the substrate Ph_2CS coordinates to **1** via the sulfur atom, then a single electron transfer process occurs the C^+-S^- bond forming two radicals ($[\text{bipy}]^-$ and $[\text{Ph}_2\text{CS}]^-$) that hetero-couple to **3** (Scheme 1). The latter pathway was originally proposed by Bart and co-workers for the reaction between uranium(III) bipy metallocene, $[\eta^5\text{-C}_5\text{Me}_5]_2\text{U}(\text{bipy})$, and aldehydes or ketones,¹⁵ which is adapted for **1**. Under similar reaction conditions, $[\eta^5\text{-}1,3\text{-(Me}_3\text{C)}_2\text{C}_5\text{H}_3\text{]}_2\text{Th}(\text{bipy})$ (**2**) reacts with 1 equiv of Ph_2CS to give $[\eta^5\text{-}1,3\text{-(Me}_3\text{C)}_2\text{C}_5\text{H}_3\text{]}_2\text{Th}[(\text{bipy})(\text{SCPh}_2)]$ (**4**) in quantitative yield (Scheme 2). The NMR experiments confirm a clean and fast reaction, and no intermediates have been detected.

<Schemes 1 and 2 here>

Complexes **3** and **4** are stable in dry nitrogen atmosphere, but they are very moisture sensitive. They have been characterized by various spectroscopic techniques, elemental analyses and X-ray diffraction analyses. The ORTEP diagrams of $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{Th}[(\text{bipy})(\text{SCPh}_2)]$ (**3**) and $[\eta^5\text{-}1,3\text{-(Me}_3\text{C)}_2\text{C}_5\text{H}_3\text{]}_2\text{Th}[(\text{bipy})(\text{SCPh}_2)]$ (**4**) are shown in Fig. 1 and 2. The average Th-C(ring) distance for **3** and **4** is 2.936(3) Å and 2.860(17) Å, respectively (Table 2). The Cp(cent)-Th-Cp(cent) angle is 128.1(3)° for **3** and 123.8(8)° for **4**. The relatively long Th-N(1) distances of 2.564 Å and 2.556(13) Å for **3** and **4**, respectively, are indicative of a datively coordinated nitrogen and are close to that (2.587(5) Å) found in $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{ThO}(4\text{-Me}_2\text{NC}_5\text{H}_4\text{N})$.¹⁶ The Th-N(2) distances of for 2.435 Å **3** and 2.395(12) Å for **4** are shorter than the distance of Th-N(1) (2.564 Å for **3** and 2.556(13) Å for **4**), while they are slightly longer than those found in the metallocene amides $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{Th}(\text{NHMe})_2$ (2.255(4) and 2.227(4) Å) and $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{Th}(\text{NH-}p\text{-tolyl})_2$ (2.279(3) and 2.286(3) Å).¹⁷ The Th-S distances of 2.754 Å and 2.759(4) Å for **3** and **4**, respectively, can be compared to those found in the metallocenes $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{Th}[(p\text{-tolyl})\text{C}(\text{S})\text{-S}]$ (2.704(2) Å),¹⁶ $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{Th}[(p\text{-tolyl})\text{C}(\text{NPh})\text{-S}]$ (2.709(1) Å),¹⁶ $[\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2\text{]}_2\text{Th}[(p\text{-tolyl})\text{C}(\text{SSiMe}_3)\text{-S}]$ (2.890(3) Å),¹⁶ and $[(\text{Ph}_2\text{PS})_2\text{C}]_2\text{Th}(\text{DME})$ (2.875(2), 2.909(2), 2.931(2)

and 3.007(2) Å).¹⁸ In **3**, the angles around the C(44) and C(45) atoms are in the range of 104-118° and the distances of C(43)-C(44) and C(44)-C(45) are 1.519(5) and 1.572(5) Å, respectively, supporting that the C(44) and C(45) are indeed sp^3 -hybridized carbon atoms.¹⁵ Similar metric parameters are also observed in **4**, in which the angles around C(10) and C(11) range from 104-116° and the distances of C(9)-C(10) and C(10)-C(11) are 1.53(2) and 1.59(2) Å, respectively.

<Fig. 1 and 2 here>

Computational study

1 and **2** are TIPs but exhibit similar reactivity to the bipy uranium system $[\eta^5\text{-C}_5\text{Me}_5]_2\text{U}(\text{bipy})$.¹⁵ Interestingly the bipy thorium and uranium have different electronic ground states of Th(IV)(bipy^{2-}) vs. U(III)(bipy^-), respectively. Computational studies might shed some light on the structure-reactivity relationship in thorium systems and help to differentiate between the two alternative reaction pathways discussed above. First of all, two different geometry optimizations were carried out for **2** at the DFT level (B3PW91) imposing two different spin states, namely a singlet ($S = 0$) and a triplet ($S = 1$). The nature of the optimized geometries differ strongly (Fig. 3) and only the singlet state geometry (with idealized C_s symmetry) is in good agreement with the experimental structure. In particular, the interaction of the bipyridine ring with the thorium center differs significantly between both spin states. However, the precise nature of the electronic ground state configuration cannot be ascertained at the DFT level since this method has the tendency to favour the closed-shell configuration. Thus, CASSCF calculations, as already used in computational studies on bipy ytterbocene adducts,^{7b,c} were carried out in order to determine the electronic configuration of the ground state. Interestingly, a closed-shell singlet (best describe as $f^0d^0\pi^{*2}$) is found to be the lowest state but an open-shell singlet (almost degenerate with its triplet congener) is only 9.2 kcal/mol higher in energy (Fig. 4). This open-shell singlet has a $f^0d^1\pi^{*1}$ electronic configuration and can be populated thermally. Thus, the geometry of **2** is clearly associated with a doubly-reduced bipyridine, as found at the DFT level, and the CASSCF results justify the use of DFT methods for further investigation of the reaction mechanism.

<Fig. 3 and Fig. 4 here>

The coordination of Ph_2CS to **2** has thus been theoretically investigated at the DFT level. The coordination was investigated on both the singlet and triplet state. Interestingly, the coordination is not possible on the singlet state geometry (the Ph_2CS molecule dissociates from **2**). It is noteworthy that the singlet corresponds to the closed-shell singlet, which is the ground state of **2**. However, Ph_2CS remains coordinated at the triplet state (Fig. 5).

<Fig. 5 here>

The adduct **2-SCPh₂** in the triplet state is 17.0 kcal/mol lower in energy than the corresponding adduct in the singlet state, indicating an extremely strong interaction. Although the triplet state was *ca.* 10 kcal/mol higher in energy than the closed-shell

singlet in **2**, it is now 17 kcal/mol lower in energy. In the triplet state, the unpaired spins are mainly located on the bipyridine and Ph₂CS ligands (1.89) and only marginally on Th (only 0.11). Thus, the coupling between the two ligands occurs on the triplet state surface and certainly without any activation barrier (despite our effort it has not been possible to locate any transition state for this coupling). The surface crossing can be estimated to be the roughly 25 kcal/mol (that corresponds to the sum of the energy difference between the singlet and the triplet on complex **2** and the loss of entropy upon coordination)¹⁹ and is a good estimate of the overall barrier for the reaction. This value is in line with the experimental observation. The reaction product is 12.4 kcal/mol more stable than the triplet adduct (Fig. 4), indicating an overall energetically favourable reaction.

Conclusions

In conclusion, both experimental and computational studies reveal that the ground state of the bipy thorium metallocene is best described as Th(IV)(bipy²⁻) (*S* = 0). However, the open-shell singlet and triplet excited states are not too far away in energy, so that they become relevant in the magnetism and the reaction chemistry of these systems. As demonstrated for the reactivity of [η⁵-1,2,4-(Me₃C)₃C₅H₂]₂Th(bipy) (**1**) and [η⁵-1,3-(Me₃C)₂C₅H₃]₂Th(bipy) (**2**) with Ph₂CS, coordination of Ph₂CS to **1** and **2** in their ground state (*S* = 0) is not possible. However, when this Ph₂CS coordinates to the triplet state (*S* = 1) a single electron transfer (SET) occurs from the [bipy]²⁻ to form [bipy]⁻ and [Ph₂CS]⁻. These two organic radicals readily undergo C-C coupling to form **3** and **4**, respectively. This reaction represents the first example of a heterocoupling reaction mediated by a low-valent thorium synthon. Further efforts are currently focused on the reactivity and the exploration of actinide bipy complexes towards other types of transformations.

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Notes and references

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Table 1 Crystal Data and Experimental Parameters for Compounds 3 and 4

Compound	3·2C ₆ H ₆	4
Formula	C ₆₉ H ₈₈ N ₂ STh	C ₄₉ H ₆₀ N ₂ STh
Fw	1209.51	941.09
crystal system	monoclinic	triclinic
space group	<i>C2/c</i>	<i>P(-1)</i>
<i>a</i> (Å)	43.489(3)	11.025(3)
<i>b</i> (Å)	11.082(1)	20.974(5)
<i>c</i> (Å)	25.359(2)	21.352(5)
α (deg)	90	115.26(1)
β (deg)	98.79(1)	90.45(1)
γ (deg)	90	99.12(1)
<i>V</i> (Å ³)	12078.0(15)	4393.3(17)
<i>Z</i>	8	4
<i>D</i> _{calc} (g/cm ³)	1.330	1.423
μ (Mo/K α) _{calc} (cm ⁻¹)	2.545	3.476
size (mm)	0.60 × 0.44 × 0.35	0.08 × 0.06 × 0.02
<i>F</i> (000)	4976	1896
2 θ range (deg)	3.80 to 55.38	3.76 to 50.10
no. of reflns, collected	34309	21622
no. of unique reflns	13896 (<i>R</i> _{int} = 0.0426)	15324 (<i>R</i> _{int} = 0.1052)
no of obsd reflns	11172	7406
no of variables	667	979
abs corr (<i>T</i> _{max} , <i>T</i> _{min})	0.47, 0.31	0.93, 0.77
<i>R</i>	0.033	0.079
<i>R</i> _w	0.072	0.133
<i>R</i> _{all}	0.048	0.183
Gof	1.03	0.95
CCDC	860422	860421

Table 2 Selected Distances (Å) and Angles (deg) for Compounds 3 and 4^a

compound	3	4
C(Cp)-Th (ave)	2.936(3)	2.860(17)
C(Cp)-Th (range)	2.815(3) to 3.055(3)	2.741(16) to 2.988(17)
Cp(cent)-Th (ave)	2.676(3)	2.600(8)
Th-N	Th-N(1) 2.564 Th-N(2) 2.435	Th-N(1) 2.556(13) Th-N(2) 2.395(12)
Th-S	Th-S 2.754	Th-S 2.759(4)
Cp(cent)-Th-Cp(cent)	128.1(3)	123.8(8)
X-Th-X	N-Th-N 64.2	N-Th-N 64.5(4)
N-Th-S	128.5 and 69.9	133.0(3) and 71.9(3)

^a Cp = cyclopentadienyl ring.

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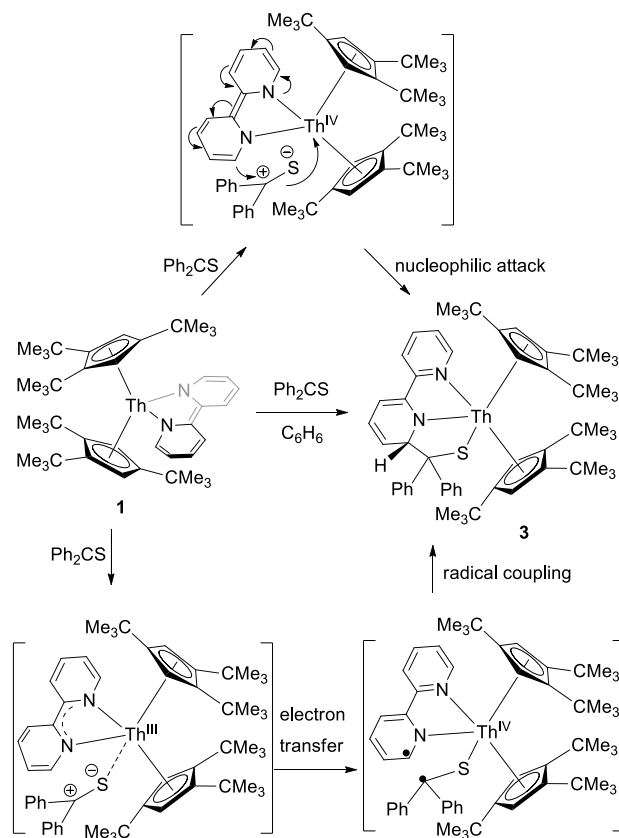
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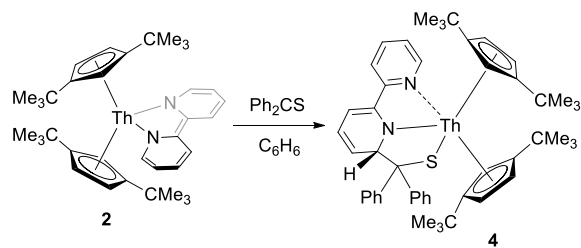
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Scheme 1 Synthesis of complex 3.

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Scheme 2 Synthesis of complex 4.

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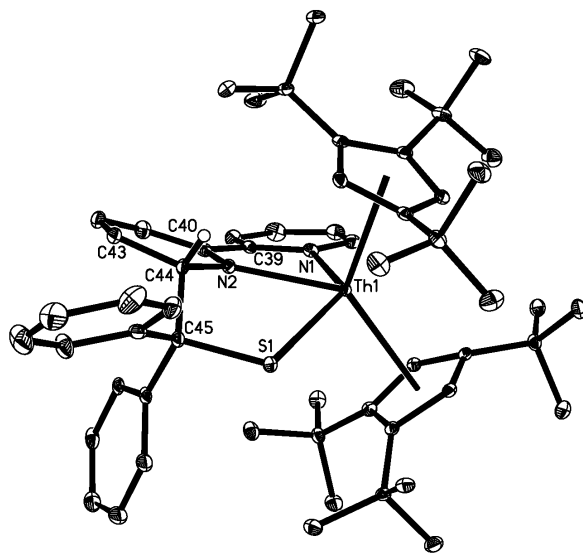


Fig. 1 Molecular structure of **3** (thermal ellipsoids drawn at the 35% probability level).

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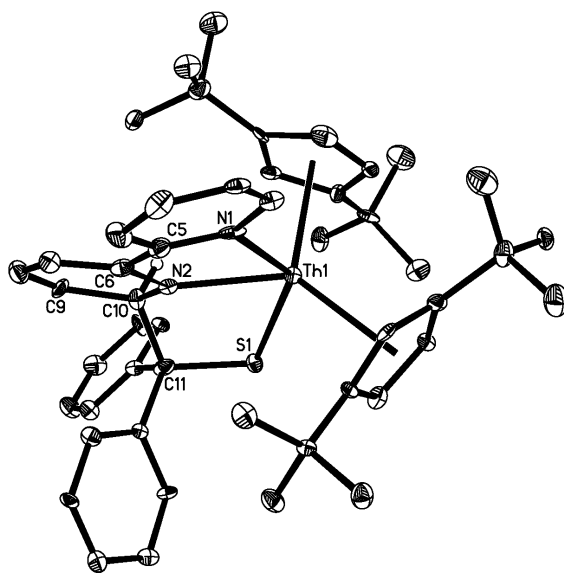


Fig. 2 Molecular structures of **4** (thermal ellipsoids drawn at the 35% probability level).

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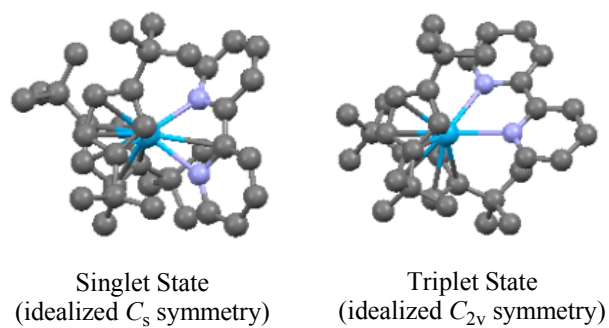


Fig. 3. Optimized structures of complex 2.

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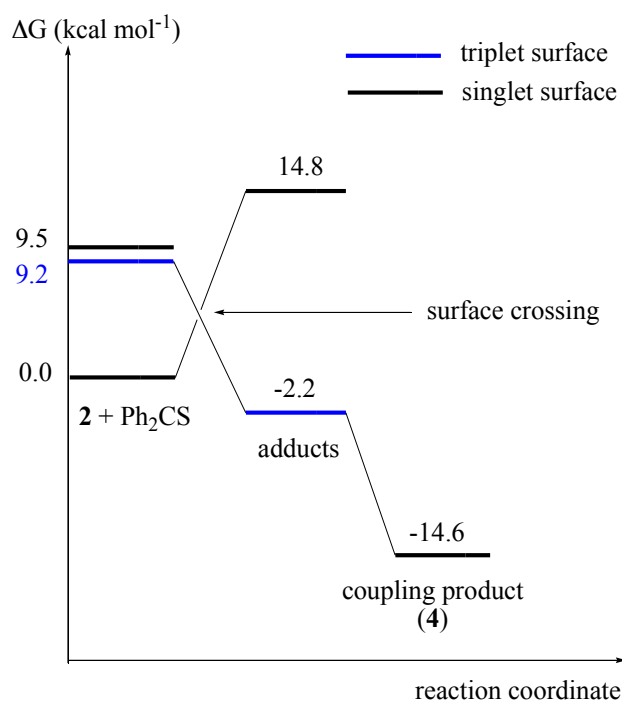


Fig. 4. Energy profile [kcal mol^{-1}] for 2 and its reactivity with Ph₂CS.

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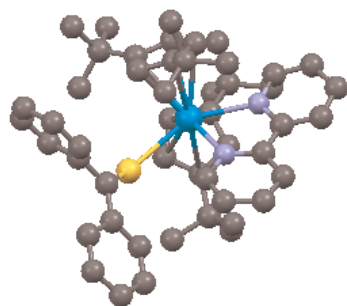


Fig. 5. Optimized structure of the adduct 2·SCPh₂.

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