

# Addition of Thianthrene Cation Radical to Cycloalkenes. An Unexpected Monoadduct

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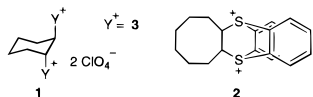
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Whereas the addition of thianthrene cation radical perchlorate ( $\text{Th}^+\text{ClO}_4^-$ ) to cyclohexene gives a bisadduct, namely, *trans*-1,2-bis(5-thianthreniumyl)cyclohexane diperchlorate (**1**), and addition to other alkenes and alkynes also gives *trans*-bisadducts, addition to cyclooctene gave only a *cis*-monoadduct, namely, 1,2-(5,10-thianthreniumdiyl)cyclooctane diperchlorate (**2a**). Similar monoadducts **2b–d** were obtained from the addition of  $\text{Th}^+\text{BF}_4^-$ ,  $\text{Th}^+\text{SbF}_6^-$ , and  $\text{Th}^+\text{PF}_6^-$  to cyclooctene. The structure of the monoadduct was deduced from its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, from the stoichiometry of its formation, and from the stoichiometry of its reaction with NaSPh, which gave equimolar amounts of cyclooctene, thianthrene, and diphenyl disulfide. The structure was confirmed with X-ray crystallography. Addition of  $\text{Th}^+$  salts to cyclopentene and cycloheptene gave mixtures of mono- and bisadducts. The bisadduct of  $\text{Th}^+\text{SbF}_6^-$  to cyclopentene, separated from the small amount of monoadduct by crystallization, was shown with X-ray crystallography to have the *trans* configuration.

## Introduction

Twenty years ago, it was reported from this laboratory that thianthrene cation radical perchlorate ( $\text{Th}^+\text{ClO}_4^-$ ) and phenoxathiin cation radical perchlorate added readily to alkenes, cycloalkenes, and alkynes.<sup>1</sup> In each case, a bisadduct salt was formed, that is, a salt containing two units of cation radical perchlorate. For example, addition of  $\text{Th}^+\text{ClO}_4^-$  to cyclohexene gave 1,2-bis(5-thianthreniumyl)cyclohexane diperchlorate (**1**), and addition to butyne gave 1,2-bis(5-thianthreniumyl)-1-butene diperchlorate. From reactions with nucleophiles, it was deduced that **1** had the *trans*-diaxial configuration.<sup>2</sup> More recently, Wayner and co-workers have reported that addition of  $\text{Th}^+\text{ClO}_4^-$  to alkenes can be achieved by the anodic oxidation of thianthrene (Th) in acetonitrile (MeCN) containing the alkene and tetrabutylammonium perchlorate as electrolyte. Furthermore, the *trans*-diaxial configuration of **1** prepared in that way was demonstrated with single-crystal X-ray crystallography.<sup>3</sup>



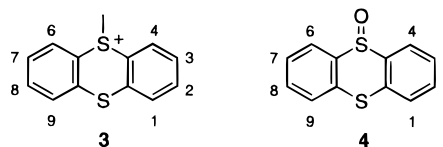
In continuing our work with these additions to other cycloalkenes, we have found that bisaddition is by no means the rule. Addition of  $\text{Th}^+\text{ClO}_4^-$  to cyclooctene, in fact, gave only a monoadduct, 1,2-(5,10-thianthreniumdiyl)cyclooctane diperchlorate (**2a**). Characterization of the adduct and validation of its formation are documented below. Addition of  $\text{Th}^+\text{ClO}_4^-$  to cyclopentene and

cycloheptene gave mixtures of mono- and bisadducts, the monoadduct to a small extent (17%) in the former and a large extent (50%) in the latter. Thus, there was a progression in the extent of monoadduct formation in going from cyclopentene (small) to cycloheptene (large) to cyclooctene (exclusive).

## Results and Discussion

**Reaction of  $\text{Th}^+\text{ClO}_4^-$  with Cyclooctene. Formation and Structure of **2a**.** The structure of **2a** was deduced first from its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, second from the stoichiometry of its formation, and third from the stoichiometry of its reaction with thiophenoxide ion. Its structure was confirmed with single-crystal X-ray crystallography of the analogous bis(hexafluorophosphate) **2d**.

The  $^1\text{H}$  NMR spectrum of a 5-substituted thianthrenium ion (**3**) consists, ideally, of a dd for H-4,6, a dd for H-1,9, and two tds for the pairs H-2,8 and H-3,7. The  $^{13}\text{C}$  NMR spectrum, ideally, also has six distinct signals. The spectra, in fact, are like those of 5-thianthrene oxide (ThO, **4**). We have reported data of this kind for numer-



ous examples of 5-(alkoxy)thianthrenium perchlorates.<sup>4</sup> This, too, is the nature of the NMR spectra of a 1,2-bis(5-thianthreniumyl) adduct, provided that the two thianthrenium units are magnetically equivalent, as has been shown nicely by Wayner and co-workers for **1**.<sup>3</sup> The  $^1\text{H}$  NMR spectrum of the adduct **2a**, however, is strikingly

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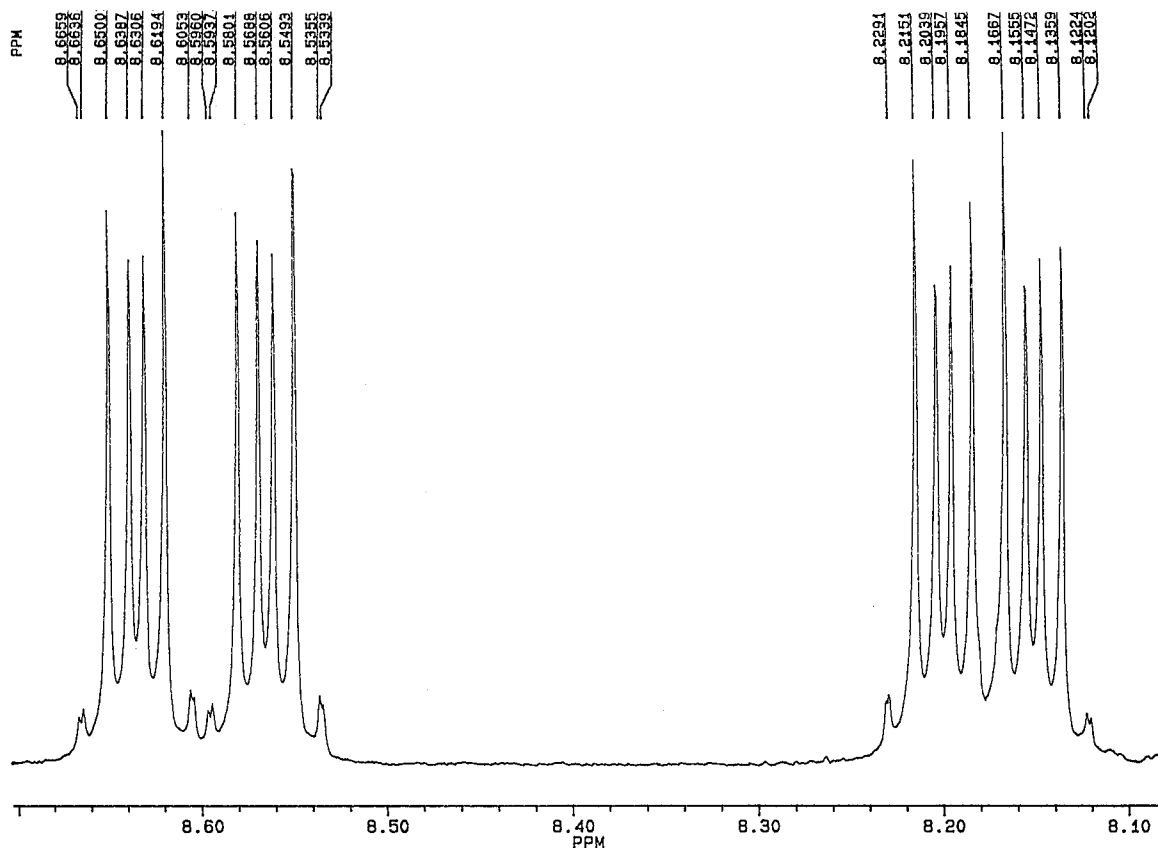
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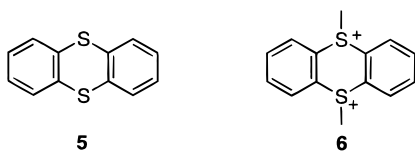
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**Figure 1.**  $^1\text{H}$  NMR spectrum (aromatic region) of the monoadduct **2a** of  $\text{Th}^+\text{ClO}_4^-$  to cyclooctene.

different. It has in its aromatic region the character of the  $^1\text{H}$  NMR spectrum of thianthrene (Th, **5**). The spectrum of **5** consists of two sets of dd's. The downfield set,  $\delta = 7.579$  ( $J = 5.77, 3.47$ ), is for the four equivalent protons H-1,4,6,9, while the upfield set,  $\delta = 7.317$  ( $J = 5.75, 3.41$ ), is for the four equivalent protons H-2,3,7,8. The  $^{13}\text{C}$  spectrum of **5** has three signals. The  $^1\text{H}$  spectrum of **2a** has two downfield dd's and two upfield dd's (Figure 1). The downfield pair of dd's are at  $\delta = 8.635$  ( $J = 5.81, 3.37$ ) and  $\delta = 8.565$  ( $J = 5.81, 3.37$ ). The upfield pair of dd's are at  $\delta = 8.200$  ( $J = 5.82, 3.37$ ) and  $\delta = 8.151$  ( $J = 5.87, 3.38$ ). Thus, the chemical shifts are about 1 ppm downfield from those of **5**. These signals cannot come from a thianthrenium substituent such as **3**. They are attributable to a 5,10-thianthrenium dication akin to **6**.



Like the rings in **5**, the rings in **2a** are equivalent, but unlike the protons of **5**, those of **2a** are not symmetrically equivalent. The downfield pair of dd's are from H-1,9 and H-4,6, while the upfield pair of dd's are from H-2,8 and H-3,7. The inequivalence of the sets of protons arises, presumably, from the twisted shape of the cyclooctane ring. In harmony with this assignment, **2a** has six aromatic  $^{13}\text{C}$  signals, while the  $\text{C}_8$  ring has four; the *cis*-substituted ring of cyclooctene oxide is like that, too. These NMR spectral characteristics are not unique to **2a**, the diperchlorate, but are found also in three other  $\text{Th}^+$  adducts of cyclooctene which we have made containing

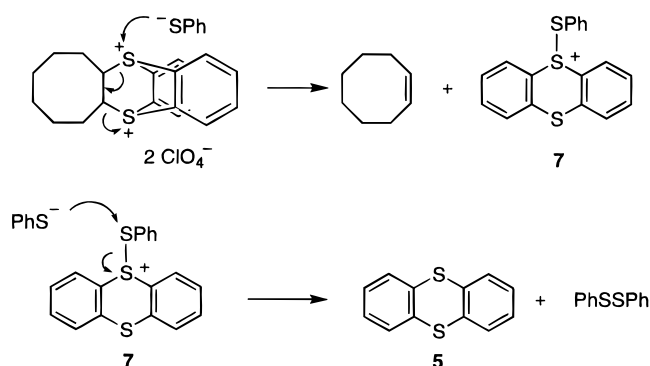
different anions, namely, **2b** ( $2\text{BF}_4^-$ ), **2c** ( $2\text{SbF}_6^-$ ), and **2d** ( $2\text{PF}_6^-$ ).

The structure of **2a** was deduced also from the stoichiometry of its formation and of its reaction with  $\text{PhS}^-$ . We measured the amounts of cyclooctene used and recovered, and the amounts of **2a** and Th obtained in the reaction of cyclooctene with  $\text{Th}^+\text{ClO}_4^-$ . These amounts correspond with eq 1. The stoichiometry of bisadduct (e.g., **1**) formation would be as in eq 2. Thus, whereas both



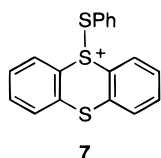
units of  $\text{Th}^+$  add to cyclohexene, one  $\text{Th}^+$  unit adds to cyclooctene and the other serves as the oxidant for dication formation. In this respect, the reaction of  $\text{Th}^+$  with cyclooctene does not fit the rationale that has been proposed by Wayner and co-workers to distinguish the reaction of  $\text{Th}^+$  with alkenes from reaction with the enolic form of ketones. In the examples chosen to illustrate this difference, reaction with acetophenone and cyclohexene,<sup>3</sup> a distonic cation radical is formed in each case from the initial addition of  $\text{Th}^+$ . With acetophenone, the distonic cation radical is easily oxidized by another  $\text{Th}^+$ , which is followed by proton loss to give a monoadduct containing one  $\text{Th}^+$  unit of type **3**. With cyclohexene, oxidation of the distonic cation radical is thought to be exergonic, so that the second  $\text{Th}^+$  adds to rather than oxidizes the cyclohexyl-radical moiety. This exergonic control may be the case with addition to cyclohexene, but does not appear to be the case with cyclooctene and to some extent, as shown below, with cyclopentene and cycloheptene. We do not know the reason a monoadduct

Scheme 1



is formed solely from cyclooctene and in part from cyclopentene and cycloheptene, but not at all from cyclohexene. It may be that a role in these additions is played by the conformations of the dicationic cation radicals, allowing in some for intramolecular reaction with the second sulfur atom of the already present Th<sup>+</sup> unit, but whether the intramolecular reaction precedes or follows oxidation by the second Th<sup>+</sup> is yet to be found.

The reaction of **2a** with PhS<sup>-</sup> gave equimolar amounts of cyclooctene, Th, and diphenyl disulfide (DPDS). The path of reaction is shown in Scheme 1, in which the involvement of intermediate **7** is proposed. Our proposal



for this sequence of reactions is based on the recognized thiophilicity of PhS<sup>-</sup> toward a sulfonium sulfur atom, particularly one that carries an easily displaced group,<sup>5,6</sup> and the extraordinary reactivity of nucleophiles toward sulfonyl sulfur in alkyl- and arylthiosulfonium groups such as shown in **7**.<sup>5,7-9</sup> The attack of the first PhS<sup>-</sup> ion on **2a** sets in motion the elimination of cyclooctene, forming **7**, and the latter is now open to attack at its sulfonyl sulfur atom by the second PhS<sup>-</sup>.

**X-ray Crystallography of 2d.** It was possible to grow single crystals of all of the monoadducts **2a-d**. However, except in the case of the bis(hexafluorophosphate) **2d**, the crystals were too slender to give enough reflections for a crystal pattern. The Ortep diagram for **2d** is shown in Figure 2. There, it can be seen that the cyclooctyl ring has a boat-chair conformation. Calculations of strain energies have shown that this has the lowest total strain energy among conformations of cyclooctane, itself.<sup>10</sup> The thianthrenium portion of **2d** is shown to have the familiar butterfly configuration,<sup>3,4</sup> and to be clearly a *cis* attachment to the cycloalkane.

**Reaction of Th<sup>+</sup>ClO<sub>4</sub><sup>-</sup> with Cyclopentene and Cycloheptene.** The NMR spectra of the products of these reactions showed that in each case a mixture of mono- and bisadduct had been formed. Each monoadduct was easily discernible because its two downfield dd

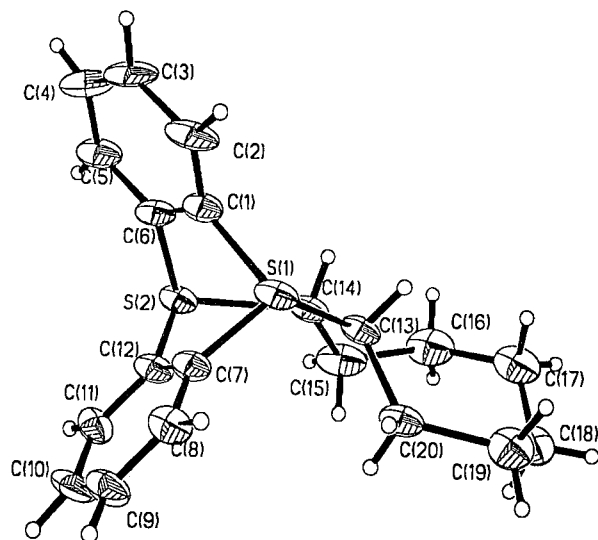


Figure 2. Ortep diagram of the monoadduct C<sub>20</sub>H<sub>22</sub>S<sub>2</sub>P<sub>2</sub>F<sub>12</sub> (**2d**) of Th<sup>+</sup>PF<sub>6</sub><sup>-</sup> to cyclooctene. The counterions are not shown.

were at much lower fields than the signals from the bisadduct. For example, the monoadduct **8** of cyclopentene (Figure 3 in the Supporting Information) had dd's at  $\delta = 8.661$  ( $J = 5.77, 3.41$ ) and  $\delta = 8.585$  ( $J = 5.82, 3.36$ ), whereas the bisadduct **9**'s lowest-field signals were at  $\delta = 8.235$  ( $J = 7.34, 1.93$ ) and  $\delta = 8.125$  ( $J = 7.54, 1.02$ ). The upfield pair of dd's of **8** overlapped with these signals from **9**. The aromatic <sup>1</sup>H NMR spectrum of **9**, furthermore, did not have the simplicity of that of **1**. Rather, the spectrum consisted of sets of dd's and overlapping td's, representing a total of 16 H, meaning that, unlike the situation in **1**, the two thianthrenium units in **9** are not equivalent. Because of the separation of the upfield signals of **9** from the downfield signals of **8**, it was possible to compute from integrated signals that the product contained 0.17 mmol of **8**/mmol of **9**. Fifteen aromatic <sup>13</sup>C signals were obtained with a freshly prepared mixture of **8** and **9**. Reprecipitation gave a product in which the NMR pattern of **8** was no longer discernible. This product had an 11-peak <sup>13</sup>C NMR spectrum, and from the two spectra it was possible to assign 4 peaks to **8** and 11 peaks to **9** in the 15-peak spectrum of the mixture.

Similarly, the <sup>1</sup>H NMR spectrum of the product of reaction of Th<sup>+</sup>ClO<sub>4</sub><sup>-</sup> with cycloheptene showed the monoadduct **10** at  $\delta = 8.643$  ( $J = 5.81, 3.38$ ) and  $\delta = 8.597$  ( $J = 5.86, 3.38$ ), Figure 4 in the Supporting Information. Overlapping of the pair of upfield dd's with signals of the bisadduct **11** occurred in the region  $\delta = 8.12-8.22$ . Integrated intensities of unoverlapped signals showed that equal amounts of **10** and **11** were present. In harmony with this and the inequivalence of the aromatic rings in **11**, 18 aromatic <sup>13</sup>C signals were obtained, which we attribute to **10** (6) and **11** (12). Attempts to separate **10** and **11** failed.

**Crystal Structure of a Cyclopentene Bisadduct.** The reaction of cyclopentene with Th<sup>+</sup>SbF<sub>6</sub><sup>-</sup> also gave a mixture of a bisadduct and a small amount of a monoadduct. In this case, it was possible to separate the bisadduct for X-ray crystallography by slow crystallization from MeCN-ether. The structure of the adduct is shown in the Ortep diagram of Figure 5 in the Supporting Information, in which the *trans* disposition of the two thianthrenium groups is evident.

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### Summary

It is striking, in summary, that monoadducts can be obtained from these three cycloalkenes. In contrast with cyclooctene, cyclooctadiene reacted with  $\text{Th}^+\text{ClO}_4^-$  to give a bisadduct (details of which will be reported later), containing only a very small amount of monoadduct, and this was removable by reprecipitation of the product.

Not many additions to alkenes that result in bissulfonium salts, as described here and earlier, are to be found in the literature. Very recently, Nenajdenko and co-workers<sup>11</sup> reported the reaction of  $\text{Me}_2\text{S}^+-\text{S}^+\text{Me}_2$ , and the analogous tetrahydrothiophene dication, with a number of alkenes and dienes. Addition to alkenes containing an attached aromatic center gave bissulfonium adducts. Reaction with simpler alkenes, such as hexene and cyclohexene, gave a complex mixture of unidentified sulfonium salts, believed to derive from the propensity of the adducts to form products of elimination.

### Experimental Section

Solvent acetonitrile was dried by distillation from  $\text{P}_2\text{O}_5$  followed by distillation from  $\text{CaH}_2$ . Dimethyl sulfoxide (DMSO) was dried by boiling over  $\text{CaH}_2$  for 4 h and distilling under reduced pressure. Cyclopentene, cycloheptene, and cyclooctene were from commercial sources. The GC column used was 10% OV-101 on 80–100 mesh Chrom-WHP, 4 ft stainless steel. It was held at 50 °C for 2 min and ramped to 250 °C at 12 deg/min. NMR spectra were recorded at 300 MHz and in the mixed solvent  $\text{CD}_3\text{CN}/\text{CDCl}_3$ , approximately 1:1.

**Preparation of Thianthrene Cation Radical Salts ( $\text{Th}^+\text{X}^-$ ).**  $\text{Th}^+\text{ClO}_4^-$  was prepared as described earlier.<sup>12</sup> Note the warning about explosiveness.  $\text{Th}^+\text{BF}_4^-$ ,  $\text{Th}^+\text{SbF}_6^-$ , and  $\text{Th}^+\text{PF}_6^-$  were prepared by oxidation of Th with the appropriate nitrosonium salt (Aldrich Chemical Co., Strem Chemicals), as follows. Thianthrene (1.03 g, 4.77 mmol) and  $\text{NOBF}_4$  (580 mg, 4.96 mmol) were placed side by side in a three-necked flask, which was flushed with argon while 80 mL of MeCN was added. The mixture became dark blue very quickly and was stirred under argon for 1 h, after which 250 mL of dry ether was added with continued stirring. The dark blue-black precipitate was filtered, washed with dry ether, and dried under vacuum for 2 h to give 670 mg (2.21 mmol, 46%) of  $\text{Th}^+\text{BF}_4^-$ .  $\text{Th}^+\text{SbF}_6^-$  (44%) and  $\text{Th}^+\text{PF}_6^-$  (57%) were prepared similarly.

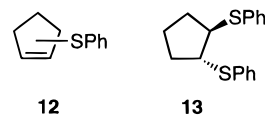
**Preparation of 2a.** A solution of 2.38 g (21.3 mmol) of cyclooctene in 10 mL of MeCN was added to a solution of 846 mg (2.68 mmol) of  $\text{Th}^+\text{ClO}_4^-$  in 10 mL of MeCN. The color of the solution turned from purple to light yellow in 15 min. There was a small amount of white precipitate (possibly Th). After overnight stirring, the now, light pink solution was poured into 60 mL of dry ether. The white precipitate that formed was filtered, washed with dry ether, and crystallized from hot MeCN–ether solution. Drying under vacuum gave 250 mg (0.474 mmol, 35.4%) of **2a**, mp 125–128 °C dec. <sup>1</sup>H NMR:  $\delta$  (J) 8.635 (5.81, 3.37), dd, 2H; 8.565 (5.81, 3.37), dd, 2H; 8.200 (5.82, 3.37), dd, 2H; 8.151 (5.87, 3.38), dd, 2H; 4.598, m, 2H; 2.462, m, 2H; 1.735, m, 2H; 1.623, m, 4H; 1.344, m, 4H. <sup>13</sup>C NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  137.634, 137.333, 137.065, 136.102, 126.848, 123.921, 58.217, 29.938, 28.174, 25.289. Anal. Calcd for  $\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{O}_8\text{S}_2$ : C, 45.7; H, 4.22; Cl, 13.5; S, 12.2. Found (Desert Analytics): C, 45.2; H, 4.16; Cl, 13.2; S, 11.7.

The adducts  $\text{C}_8\text{H}_{14}\text{Th}^{2+}2\text{BF}_4^-$  (**2b**), mp 118–121 °C dec,  $\text{C}_8\text{H}_{14}\text{Th}^{2+}2\text{SbF}_6^-$  (**2c**), mp 120–125 °C dec, and  $\text{C}_8\text{H}_{14}\text{Th}^{2+}2\text{PF}_6^-$  (**2d**), mp 125–128 °C dec were prepared in the same way, with the use of the appropriate cation radical salt. Each had <sup>1</sup>H and <sup>13</sup>C NMR spectral data similar to those listed for **2a**.

**Material Balance in the Preparation of 2a.** A solution of 2.48 g (22.1 mmol) of cyclooctene in 10 mL of MeCN was added to a stirred solution of 1.03 g (3.26 mmol) of  $\text{Th}^+\text{ClO}_4^-$  in 10 mL of MeCN. After overnight stirring, volatile components of the solution were pumped off at room temperature and collected in a trap cooled in liquid nitrogen. GC assay of the trapped solution, with biphenyl as internal standard, gave 13.9 mmol (63%) of cyclooctene. The residue of solid and remaining liquid was dissolved in MeCN, and dry ether was added to precipitate **2a**, which was washed with dry ether and dried to give 830 mg (1.58 mmol) of **2a**. The filtrate was assayed by GC for Th (1.94 mmol, 59.5%) and cyclooctene (3.59 mmol, 16.2%). Thus, this procedure accounted for 19.1 mmol (86.4%) of the cyclooctyl units and 3.52 mmol (108%) of Th units.

**Stoichiometry of Reaction of 2a with Sodium Thiophenoxide.** **2a** (33.7 mg, 0.064 mmol) and PhSNa (38.7 mg, 0.293 mmol) were placed in a septum-capped flask into which 10 mL of MeCN was injected. The mixture was stirred overnight and assayed by GC, with biphenyl as internal standard, giving 0.062 mmol (97%) of cyclooctene, 0.068 mmol (106%) of Th, and 0.099 mmol (155%, based on **2a**) of DPDS. Following GC analysis, the solution was poured into 50 mL of 2 M NaOH solution, which was extracted with 3 × 25 mL of ether. Workup of the ether solution gave a solid residue which was placed on a column of silica gel from which a mixture of biphenyl, Th, and DPDS was eluted with petroleum ether. This mixture was recovered and dissolved in 5 mL of MeCN. GC assay gave 0.058 mmol (91%) of DPDS.

**Preparation of Adducts 8 and 9 of Cyclopentene.** As described for **2a**, a solution of 1.27 g (18.7 mmol) of cyclopentene and a solution of 760 mg (2.41 mmol) of  $\text{Th}^+\text{ClO}_4^-$  were used. The stirred mixture retained a light violet color after being stirred overnight, and on being poured into ether gave a light-violet precipitate, mp 146–150 °C dec, a small amount of which did not dissolve in the NMR solvent. <sup>1</sup>H NMR:  $\delta$  (J) 8.661 (5.77, 3.41), dd, 2H; 8.585 (5.82, 3.36), dd, 2H; 8.235 (7.34, 1.93), dd, 2H; 8.201 (–, 3.37), part of dd, 2H; 8.125 (7.54, 1.02), dd, 2H; 8.105 (–, 3.42), part of dd, 2H; 7.913–7.696, overlapping sets of dd's and td's, 10H; 7.535 (7.29, 1.86) dd, 2H; 4.963, m, 2H; 2.439, m, 2H; 1.949, m, 2H; the remaining C<sub>5</sub> ring multiplet overlapped solvent peaks. <sup>13</sup>C NMR attributable to **8**:  $\delta$  138.376, 138.030, 137.120, 129.071, 58.674, 29.526, 26.551. <sup>13</sup>C attributable to **9**:  $\delta$  137.024, 136.744, 136.613, 136.303, 136.218, 132.461, 131.453, 131.392, 131.064, 116.322, 115.456, 53.953, 30.044, 24.814. A sample (88 mg) of this mixture containing 0.019 mmol of **8** and 0.112 mmol of **9** (from NMR data) reacted with 55 mg (0.417 mmol) of PhSNa in 10 mL of DMSO. GC analysis gave 0.025 mmol (19%) of cyclopentene, 0.243 mmol (100%) of Th, and 0.025 mmol of DPDS. Two other products were obtained, which from GC/MS data appeared to be either 1- or 3-(phenylthio)cyclopentene (**12**) and 1,2-bis(phenylthio)cyclopentane (**13**). In the absence of au-



thentic samples of these compounds, their yields were estimated by comparing GC peak areas with that of the Th that was formed, giving 0.038 mmol (29%) of **12** and 0.087 mmol (78%) of **13**. The collective data correspond to a recovery of 114% of the cyclopentyl units.

**Preparation of the Adducts 10 and 11 of Cycloheptene.** Reaction between 1.41 g (14.7 mmol) of cycloheptene and 660 mg (2.09 mmol) of  $\text{Th}^+\text{ClO}_4^-$  occurred quickly. The pale yellow solution from overnight stirring gave 550 mg of a 1:1 mixture (from <sup>1</sup>H NMR data) of **10** and **11**, mp 141–143 °C dec. <sup>1</sup>H NMR:  $\delta$  (J) 8.643 (5.81, 3.38), dd, 2H; 8.597 (5.86, 3.38), dd, 2H; 8.204 (5.86, 3.34), dd, 2H; 8.143 (5.84, 3.35), dd, 2H; 8.220–8.127, overlapping sets of dd's and td's, 6H; 7.747–7.699, overlapping dd and dd, 2H; 7.632 (7.82, 1.27), dd, 2H; 4.740, m, 2H; 2.621, m, 1H; 1.261, m, 3H; the remaining C<sub>7</sub>

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ring multiplets overlapped solvent peaks.  $^{13}\text{C}$  NMR:  $\delta$  136.868, 136.483, 136.456, 136.337, 136.146, 136.088, 136.027, 135.954, 135.894, 131.535, 131.492, 131.451, 131.043, 130.996, 114.940, 114.893, 114.524, 114.364, 48.416, 47.515, 30.094, 28.178, 27.038, 23.048, 21.234.

**Growth of Single Crystals.** An open wide-mouthed vial containing a solution of an adduct in MeCN was placed in a beaker containing a pool of ether in a closed desiccator. Slow adsorption of ether vapor by the MeCN solution caused slow crystal growth. The crystals were not filtered, unless for elemental analysis, and one was selected with a probe for crystallography.

**X-ray Crystallography.** All crystals were mounted with epoxy cement on the tip of a glass fiber. The data were collected using the TEXSAN<sup>13</sup> automatic data collection series on a Rigaku AFC5S diffractometer using Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å). The crystallographic data collection parameters for each compound are summarized in the Supporting Information. The data were collected at 223 K for  $\text{C}_{20}\text{H}_{22}\text{F}_{12}\text{P}_2\text{S}_2$  (**2d**) and at 298 K for  $\text{C}_{29}\text{H}_{24}\text{F}_{12}\text{Sb}_2\text{S}_4$ . Both sets of data were corrected for Lorentz and polarization effects and for absorption correction using  $\psi$  scans. Crystal and instrument stabilities were checked by measuring 3 standard reflections every 150 observations. Structures were solved using SHELXS-97<sup>14</sup> on a PC. Weighted  $R$  factors ( $R_w$ ) and all goodness of fit values ( $S$ ) are based on  $F^2$ ; conventional  $R$  factors are based on  $F$ . H-atom positions were refined using a riding model.

**Supporting Information Available:** Figures 3 and 4, aromatic NMR spectra of mixtures of **8** and **9** and of **10** and **11**, respectively; Figure 5, Ortep diagram of the bisadduct of cyclopentene ( $\text{C}_{29}\text{H}_{24}\text{S}_4\text{Sb}_2\text{F}_{12}$ ); and tables giving X-ray crystallographic data for **2d** and for the bisadduct to cyclopentene. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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**Note added in proof:** Continued investigation of addition to cyclohexene has shown that a small amount of a monoadduct (about 5% by NMR) appears to be formed along with **2a**.

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