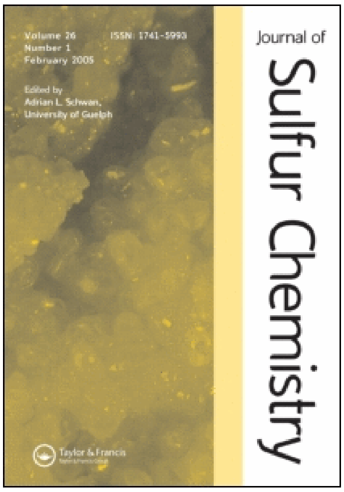


Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

Addition of thianthrene cation radical to non-conjugated dienes—Part II: Addition to two double bonds

Bing-Jun Zhao[a]; Henry J. Shine[a]; John N. Marx[a]; Anna T. Kelly[b]; Cristina Hofmann[b]; Teyeb Ould-Ely[b]; Kenton H. Whitmire[b]
[a] Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas, USA [b] Department of Chemistry, Rice University, Houston, Texas, USA

To cite this Article Zhao, Bing-Jun , Shine, Henry J. , Marx, John N. , Kelly, Anna T. , Hofmann, Cristina , Ould-Ely, Teyeb and Whitmire, Kenton H.(2006) 'Addition of thianthrene cation radical to non-conjugated dienes—Part II: Addition to two double bonds', Journal of Sulfur Chemistry, 27: 2, 139 — 147
To link to this Article: DOI: 10.1080/17415990600578467
URL: http://dx.doi.org/10.1080/17415990600578467

Journal of Sulfur Chemistry
Vol. 27, No. 2, April 2006, 139–147

Taylor & Francis
Taylor & Francis Group

Addition of thianthrene cation radical to non-conjugated dienes – Part II: Addition to two double bonds

BING-JUN ZHAO†, HENRY J. SHINE*†, JOHN N. MARX†, ANNA T. KELLY‡, CRISTINA HOFMANN‡, TEYEB OULD-ELY‡ and KENTON H. WHITMIRE‡

†Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, USA
‡Department of Chemistry, Rice University, Houston, Texas 77005, USA

(Received 17 October 2005; in final form 9 January 2006)

Reaction of thianthrene cation radical tetrafluoroborate with 1,5-hexadiene, 1,7-octadiene, 1,8-nonadiene and 1,9-decadiene in the molar ratio 4:1 caused addition to occur to one and both of each diene's double bonds. A mixture of four adducts was thus obtained, namely a bisadduct (**12a**–**d**), a monoadduct (**13a**–**d**), a di(bis)adduct (**14a**–**d**) and a di(mono)adduct (**15a**–**d**). The di(mono)adducts (**15b**–**d**) were isolated and characterized with ^{1}H and ^{13}C NMR spectroscopy. Under the same condition of excess of cation radical, addition occurred to only one double bond of 1,4-cyclohexadiene and 1,5-cyclooctadiene. Addition to both double bonds was not observed. The bisadduct (**16**) of 1,4-cyclohexadiene was characterized with ^{1}H and ^{13}C NMR spectroscopy and X-ray crystallography. On activated alumina, **15b**–**d** underwent fast opening of dicationic rings to form mixtures of (*E*, *E*)- (**17b**–**d**) and (*E*, *Z*)-di(5-thianthreniumyl)diene (**18b**–**d**) in which the (*E*, *E*)-isomer was dominant and was characterized with ^{1}H and ^{13}C NMR spectroscopy.

Keywords: Thianthrene cation radical; Adducts of dienes; NMR

1. Introduction

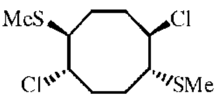
In the preceding publication (Part I) [1], we have described the addition of thianthrene cation radical (Th$^{\bullet+}$) to one of the double bonds of some non-conjugated dienes. Under the conditions of reaction, namely, a large molar excess of diene over Th$^{\bullet+}$ or even a molar ratio diene: Th$^{\bullet+}$ of 1:2, addition occurred to only one of the diene's double bonds. That is, the diene behaved as an alkene and addition of Th$^{\bullet+}$ gave the now well-documented mixture of bis- and monoadduct [2–4]. The mechanism of the formation of these two adducts has been laid out in Part I. It was pointed out that hitherto only one diene, 1,5-cyclooctadiene, had been used in reactions with Th$^{\bullet+}$ and that one of that diene's double bonds had suffered addition, to give a bisadduct [3]. As a continuation of the work described in Part I, we set out to find if, in reactions with a large excess of Th$^{\bullet+}$, both of the double bonds of acyclic and cyclic non-conjugated dienes would participate in additions.

---

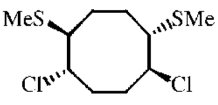
*Corresponding author. Email: henry.shine@ttu.edu

Journal of Sulfur Chemistry
ISSN 1741-5993 print/ISSN 1741-6000 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/17415990600578467

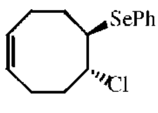
We have been unable to find in the literature additions of cation radicals to non-conjugated dienes other than those we have reported. 1,5-Cyclooctadiene and 1,4-cyclohexadiene have often been used as models for radical and electrophilic additions to non-conjugated dienes [5]. Insofar as additions of sulfur (and selenium) compounds are concerned, reactions with 1,5-cyclooctadiene may lead to addition to one or both double bonds, and even to bridging [5]. Thus, addition of methanesulfenyl chloride to 1,5-cyclooctadiene gave the geometric isomers **1** and **2** [6]. Addition of benzeneselenyl chloride, on the other hand, gave only **3** [7]. Addition of PhSeCl to 1,4-cyclohexadiene gave, similarly, **4** [7]. In contrast, reaction of sulfur dichloride with each cyclic diene gave a bicycloalkane, **5** and **6** [8]. Addition of *p*-toluenesulfonyl halides to 1,5-cyclooctadiene, under radical-forming conditions, gave a 1,2-adduct (**7**) and also a bridged bicycloalkane (**8**) [9]. Among the acyclic dienes of interest to us, 1,5-hexadiene underwent interesting cyclization reactions with PhSeCN (in aqueous MeCN containing $CuCl_2$), giving **9** and **10** [10] and with $TsNH_2/Hg(NO_3)_2$, giving **11** [11]. These are a few examples of the complexity that may occur in additions of sulfur and selenium reagents to non-conjugated dienes.



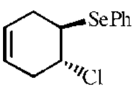
1



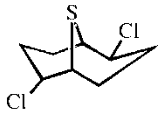
2



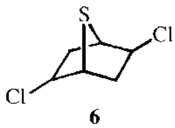
3



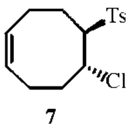
4



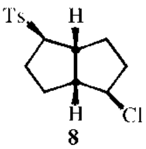
5



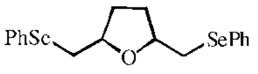
6



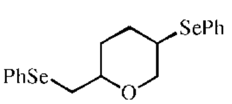
7



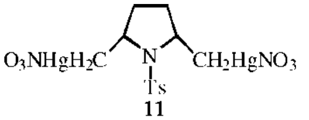
8



9



10



11

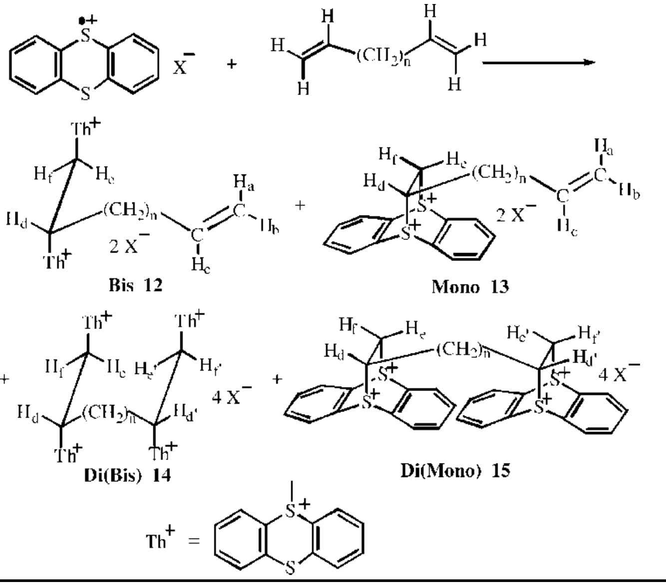
In this context, the additions to only one of a diene's double bonds which we report in Part I [1] are comparatively simple. The additions we report now in Part II, in which a molar excess of $Th^{\bullet +}$ was used, show that comparatively still uncomplicated additions occur to both double bonds of the α, ω-acyclic but not to the cyclic dienes. No NMR evidence suggesting the formation of bridged or bicyclic adducts was seen.

2. Results and discussions

2.1 *Formation of four adducts*

The product of reaction of $Th^{\bullet +}$ with each of 1,5-hexadiene, 1,7-octadiene, 1,8-nonadiene and 1,9-decadiene in the 4:1 ratio was a mixture with a complex ^1H NMR spectrum. It was

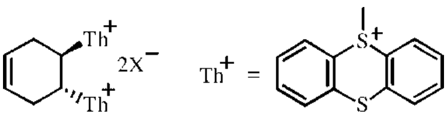
Table 1. Products of addition of $Th^{\bullet+}$ X^- to non-conjugated diene.[a]



		Product				
n	*X*	Bis **12**	Mono **13**	Di(bis) **14**	Di(mono) **15**	(**12**+**13**):(**14**+**15**)
2	BF_4	**12a**	**13a**	**14a**	**15a**	75:25
4	BF_4	**12b**	**13b**	**14b**	**15b**	70:30
5	BF_4	**12c**	**13c**	**14c**	**15c**	40:60
6	BF_4	**12d**	**13d**	**14d**	**15d**	40:60

[a] The molar ratio $Th^{\bullet+}$ X^- to diene was 4: 1.

possible to deduce from each 300 MHz NMR spectrum, however, that the mixture contained four adducts which we call bis, (**12a–d**); mono, (**13a–d**); di(bis), (**14a–d**); and di(mono), (**15a–d**). The structures are shown in table 1. Deductions about the NMR spectra were made with the aid of data from isolated products (Part I). The presence of **12** and **13** in a mixture was shown by overlapping sets of ddt (H_c) and sets of dd (H_a, H_b) in the expected alkenyl proton region, 6.0–5.0 ppm. These NMR signals, showing the presence of **12** and **13** in solution, had to be accompanied in the appropriate region by signals from H_d, H_e, and H_f in both **12** and **13**. Again, we were helped in this understanding by the spectra of earlier isolated examples of **12** and **13** (Part I), with peaks distributed in the region 5.0–3.5 ppm. These signals and their integrations indicated the presence of two-fold addition products, namely **14a–d** and **15a–d**. We were successful in isolating three of the di(mono)adducts, **15b–d**, and recording their 500 MHz NMR spectra, thus confirming the indications of the 300 MHz spectra. We used integrations of peaks H_a, H_b, H_c and H_d, H_e, H_f in the 300 MHz spectra to calculate the ratio of adducts (**12**+**13**):(**14**+**15**) and the results are in table 1. It was not possible to calculate the proportions of individual components in the four-component mixture.



16

Reaction of a large excess of $Th^{\bullet +}$ with 1,4-cyclohexadiene and 1,5-cyclooctadiene failed to give addition to more than one double bond. From each of these dienes, only a bisadduct was obtained, one of which (of 1,5-cyclooctadiene) has been reported earlier [3], too. The bisadduct dihexafluorophosphate (**16**) of 1,4-cyclohexadiene was characterized with NMR spectroscopy and X-ray crystallography; and its Ortep diagram is shown in figure 1. Figure 1 shows the trans relationship of the two thianthreniumyl groups in **16**, a feature that was seen earlier with the bisadduct of 1,5-cyclooctadiene [3]. There was no evidence for formation of a monoadduct (with structure such as that in **13**) from these two cyclic dienes.

2.2 *NMR spectra of 15b–d*

The adducts **15a–d** were isolated with fractional precipitation and recrystallization, allowing for ^1H and ^{13}C NMR characterization. However, **15a** was too labile in solution to give reliable 500 MHz spectra. At the time of recording the 500 MHz spectra of each of the other three adducts, each NMR solution showed the presence of small amounts of di(5-thianthreniumyl)diene, attributable to the slow opening of the rings of the adducts. The small amount of impurity, however, did not detract from the clarity of the NMR spectra of the adducts. The NMR data are tabulated (tables 2 and 3) to emphasize the uniformity in the spectra and thus provide support for the assignment of structure. The aromatic ^1H signals of **15b–d** were multiplets of 16H made complex by overlapping peaks. This situation indicates that the heterocyclic rings were not symmetrically placed. That is also evident from the aromatic ^{13}C spectra in which numerous CH and quaternary C peaks were evident (table 3). If the two thianthreniumdiyl rings were identical and symmetrically placed, the ^{13}C spectrum would have four aromatic CH signals representing 16 CH atoms and two quaternary C signals

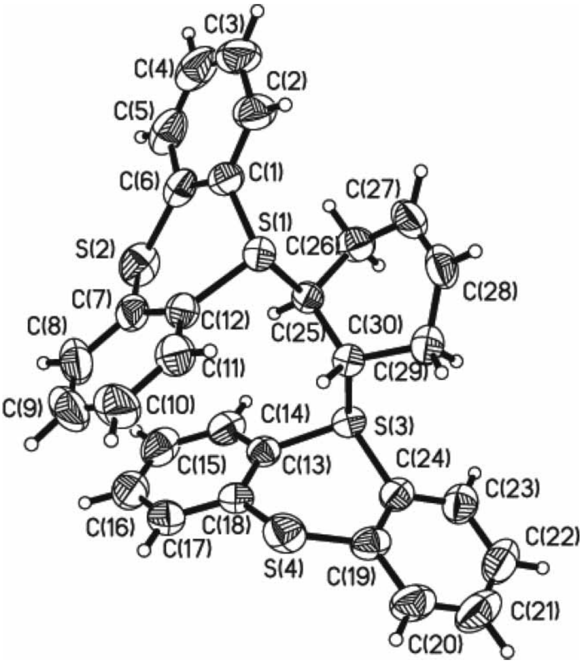
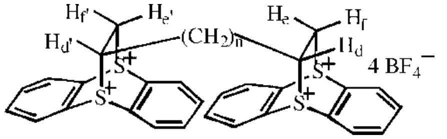


Figure 1. Ortep diagram for 4,5-bis(5-thianthreniumyl)cyclohexene dihexafluorophosphate (**16**). The counterions and solvent of crystallization are omitted.

Table 2. ^{1}H NMR data[a] for di(mono)adducts **15b**, **15c**, **15d**.



^{1}H[b]	$n = 4$, **15b**	$n = 5$, **15c**	$n = 6$, **15d**
	8.60–8.50, m, 8H	8.60–8.50, m, 8H	8.59–8.50, m, 8H
	8.17–8.09, m, 8H	8.17–8.09, m, 8H	8.17–8.09, m, 8H
H_d, $H_{d'}$	4.48, m, 2H	4.502, dtd, 1H (8.0, 7.6, 6.0) 4.500, dtd, 1H (8.3, 7.8, 6.3)	4.51, dtd, 2H (7.9,7.5, 5.5)
H_f, $H_{f'}$	4.38, dd, 1H (13.8, 6.8) 4.37, dd, 1H (14.3, 7.8)	4.380, dd, 1H (13.5, 8.5) 4.377, dd, 1H (13.8, 8.8)	4.38, dd, 2H (13.5, 8.5)
H_e, $H_{e'}$	3.68, dd, 2H (13.5, 5.0)	3.69, dd, 2H (13.8, 5.3)	3.69, dd, 2H (13.5, 5.0)
CH_2	1.79–1.73, m, 2H	1.76–1.62, m, 4H	1.75–1.62, m, 4H
CH_2	1.70–1.62, m, 2H	1.54–1.44, m, 4H	1.54–1.42, m, 4H
CH_2	1.58–1.42, m, 4H	1.26, quint, 2H, (7.3)	1.30–1.22, m, 4H

[a] δ (ppm), multiplicity and J (Hz).

[b] All unassigned shifts are for aromatic protons.

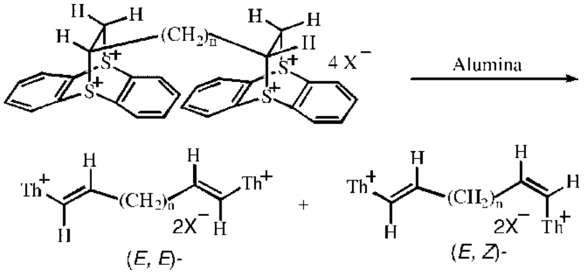
Table 3. ^{13}C NMR chemical shifts for di(mono)adducts **15b**, **15c**, **15d**.

^{13}C	$n = 4$, **15b**	$n = 5$, **15c**	$n = 6$, **15d**
Th$^+$CH	137.60, 2[a]	137.55, 4[a]	137.54, 2[a]
Th$^+$CH	137.57, 2	137.43, 2	137.50, 2
Th$^+$CH	137.44, 2	137.10, 2	137.43, 2
Th$^+$CH	137.13, 2	136.97, 2	137.10, 2
Th$^+$CH	136.98, 2	136.68, 4	136.97, 2
Th$^+$CH	136.70, 2	136.56, 2	136.69, 2
Th$^+$CH	136.69, 1		136.68, 2
Th$^+$CH	136.66, 1		136.54, 2
Th$^+$CH	136.57, 1		
Th$^+$CH	136.54, 1		
Th$^+$quat	126.94, 2C	126.98, 1C	126.98, 1C
Th$^+$quat	126.27, 2C	126.96, 1C	126.97, 1C
Th$^+$quat	124.91, 2C	126.28, 1C	126.28, 2C
Th$^+$quat	122.96, 2C	126.26, 1C	124.98, 2C
Th$^+$quat		124.99, 1C	123.13, 2C
Th$^+$quat		124.96, 1C	
Th$^+$quat		123.07, 2C	
CH	55.73	55.90, 2	55.98, 2
CH	55.68		
CH_2[b]	42.11	42.15	42.15, 2
CH_2[b]	42.06	42.13	

[a] These are the number of carbon atoms represented by the chemical shift.

[b] Terminal CH_2. The remaining signals were: for **15b**, 32.24, 32.21, 26.14, 26.06; for **15c**, 32.57, 32.54, 28.26, 28.22, 26.35; for **15d**, 32.75, 32.73, 28.57, 28.55, 26.69, 26.67.

Table 4. Products of ring-opening of di(mono)adducts on alumina.



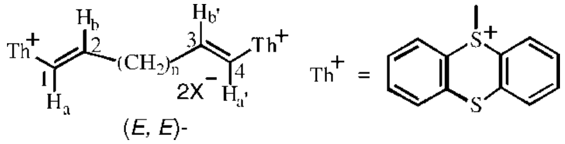
n	*X*	Product Di(mono)	 (*E*, *E*)-	 (*E*, *Z*)-	 (*E*, *E*):(*E*, *Z*)
4	BF_4	**15b**	**17b**	**18b**	85:15
5	BF_4	**15c**	**17c**	**18c**	85:15
6	BF_4	**15d**	**17d**	**18d**	90:10

representing eight quaternary C atoms. If symmetry remained in each of the two thianthreniumdiyl rings but they were not identical, we should expect to see eight aromatic CH and four quaternary C signals. Similarly revealing of structures of **15b–d** are the data for the protons $H_{d,d'}$, $H_{e,e'}$ and $H_{f,f'}$. They exhibit the coupling patterns expected of them and their chemical shifts mimic those of analogous protons (H_d, H_e, H_f) in the alkenyl monoadducts isolated and reported (as **8a**, **10b**, **12b**, **14a**) in Part I.

2.3 *Formation of di(5-thianthreniumyl)dienes from 15b–d*

When a solution of each of **15b–d** in CH_3CN was poured onto activated basic alumina, deprotonation occurred, accompanied by opening of the dicationic thianthreniumdiyl rings. A mixture of (*E*, *E*)- and (*E*, *Z*)-di(5-thianthreniumyl)diene salts was formed, as shown in table 4. The nature of the products was deduced with NMR spectroscopy and from experience

Table 5. ^1H NMR data[a] for (*E*, *E*)-di(5-thianthreniumyl)-dienes.

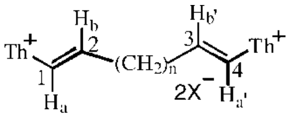


$^1H^b$	*n* = 4, **17b**	*n* = 5, **17c**	*n* = 6, **17d**
	8.09(8.0), d, 4H,	8.10(7.8, 1.3), dd, 4H	8.10(8.0, 1.0), dd, 4H
	7.93(8.0, 1.0), dd, 4H	7.93(8.0, 1.0), dd, 4H	7.93(8.0, 1.5), dd, 4H
	7.80(7.8, 1.3), td, 4H	7.80(7.6, 1.3), td. 4H	7.80(7.8, 1.3), td, 4H
	7.70(7.8, 1.3), td, 4H	7.70(7.6, 1.0), td, 4H	7.70(7.8, 1.3), td, 4H
H_b, $H_{b'}$	6.753(15.0, 7.3), dt, 1H	6.81(15.0, 7.3), dt, 2H	6.82(14.5, 7.3), dt, 2H
	6.750(14.5, 7.1), dt, 1H		
H_a, $H_{a'}$	6.44(15.0, 1.0), dd, 2H	6.47(15.0, 1.4), dt, 2H	6.47(14.5, 1.4), dt, 2H
CH_2	2.17(6.0), q, 4H	2.17(7.3, 1.2), qd, 4H	2.17(7.3, 1.2), qd, 4H
CH_2	1.29, m, 4H	1.31(7.5), quint, 4H	1.32-1.26, m, 4H
CH_2		1.13(7.4), quint, 2H	1.15-1.12, m, 4H

[a] δ (ppm),multiplicity and *J* (Hz).

[b] All unassigned shifts are for aromatic protons.

Table 6. ^{13}C NMR chemical shifts for (E, E)-di (thianthreniumyl)-dienes.



(*E, E*)-

^{13}C	$n = 4$, **17b**	$n = 5$, **17c**	$n = 6$, **17d**
C-2, C-3	155.99	156.53	156.69
Th^+quat[a]	136.55	136.51	136.52
Th^+CH[b]	135.52	135.49	135.49
Th^+CH[b]	134.08	134.01	134.01
Th^+CH[b]	131.31	131.29	131.29
Th^+CH[b]	130.87	130.86	130.86
Th^+quat[a]	121.11	121.21	121.22
C-1, C-4	111.09	110.85	110.81
CH_2^c	33.01	33.30	33.40
CH_2	27.21[c]	28.73[d]	28.95[c]
CH_2^c		27.51	27.78

[a] Representing 4 quat C; [b] representing 4 CH; [c] representing 2 CH_2; [d] representing 1 CH_2.

with similar results from monoadducts (Part I). The two isomers could not be separated but their presence and relative amounts in solution were readily identifiable with their cleanly separated ^{1}H alkenyl NMR spectra. Thus, the trans-configuration of H_a, H_b and $H_{a'}$, $H_{b'}$ in both double bonds was identifiable in the (*E*, *E*)-isomers by the dt (J ≈ 15, 7 Hz) for H_b, $H_{b'}$ and dt (J ≈ 15, 1.5 Hz) for H_a, $H_{a'}$. In contrast, the two smaller multiplets of an (*E*, *Z*)-isomer had J ≈ 15 and ≈ 8.5 Hz, diagnostic of one pair of *trans*- and another of *cis*-related protons. The NMR data of the major component of each mixture, the (*E*, *E*)-isomer, are tabulated for clarity in tables 5 and 6. Although the (*E*, *Z*)-isomers were discernable from peaks of their NMR spectra, their small ^{1}H NMR signals were often buried by the large signals of the (*E*, *E*)-isomers. Therefore, complete data for the (*E*, *Z*)-isomers were not recoverable.

The ^{1}H and ^{13}C NMR data show uniformity consistent with the assigned structures. The symmetry of each structure is revealed by the uniform pattern of the aromatic ^{1}H and ^{13}C data. In particular, the ^{13}C data of four CH and two quaternary carbon peaks representing 16 CH and 8 quaternary carbon atoms are strikingly diagnostic of symmetrical structures.

3. Conclusion

Addition of $Th^{\bullet +}$ to both double bonds of a linear non-conjugated α, ω-diene does occur if an excessive amount of $Th^{\bullet +}$ is used. In contrast, double addition to the cyclic dienes 1,4-cyclohexadiene and 1,5-cyclooctadiene was not achieved. It appears that proximity of the remaining double bond to the two thianthreniumyl groups in the cyclic bisadducts (e.g., **16**) inhibits further addition. The NMR data offered no evidence for cyclization or bridging products.

4. Experimental

The preparation of thianthrene cation radical tetrafluoroborate ($Th^{\bullet +}BF_4^-$) and hexafluorophosphate ($Th^{\bullet +}PF_6^-$) and the procedure for drying solvent MeCN have been described earlier [2, 4]. All dienes were from commercial sources. Activated, basic alumima was from the Aluminum Company of America. A 300 MHz NMR instrument was used for assaying the composition of product mixtures with their ^{1}H NMR spectra. A 500 MHz NMR instrument was used for obtaining all ^{1}H and ^{13}C chemical shifts and coupling data, listed as $\delta(J)$ in ppm and Hz. Values of J have been averaged. Most of the NMR data are tabulated in tables 2, 3, 5 and 6. Data that are not included in the tables are given in the relevant Experimental section. CD_3CN was used as NMR solvent in all cases.

4.1 *Preparation of di(mono)adducts*

A detailed example is given for 1,2-8,9-di(5,10-thianthreniumdiyl)nonane tetrafluoroborate (**15c**). To a stirred suspension of 894 mg (2.95 mmol) of $Th^{\bullet+}BF_4^-$ in 8 mL of MeCN was added 0.125 mL (0.74 mmol) of 1,8-nonadiene. The mixture was stirred until the color of $Th^{\bullet+}$ had disappeared. The dropwise addition of dry ether gave a precipitate, which was removed, washed with ether and dried to give 623 mg of a mixture of products. The ^{1}H NMR spectrum showed that the product was a mixture of **12c, 13c, 14c** and **15c** and the ratio of (**14c**+**15c**): (**12c**+**13c**) 60:40. GC assay of the filtrate gave 1.42 mmol of thianthrene (48%), and 0.19 mmol of thianthrene 5-oxide (6%). Repeated fractional precipitation of the mixture from acetonitrile and ether gave 186 mg (28%) of **15c**, mp 169–171 °C (dec).

Similar reactions were carried out with 1,5-, 1,7- and 1,9-dienes, each of which gave mixtures of bis- and monoadduct, di(bis)- and di(mono)adduct. **15b** (from $Th^{\bullet+}BF_4^-$ and 1,7-octadiene), mp 183–184 °C (dec), 12% isolated yield; **15d** (from $Th^{\bullet+}BF_4^-$ and 1,9-decadiene), mp 180–182 °C (dec), 37% isolated yield. Similar reactions were carried out with 1,4-cyclohexadiene and 1,5-cyclooctadiene, each of which gave only a bisadduct. **16** ($X = PF_6^-$) (from $Th^{\bullet+}PF_6^-$ and 1,4-cyclohexadiene in a ratio of 4:1 or from $Th^{\bullet+}PF_6^-$ with excess of 1,4-cyclohexadiene), mp 135–136 °C (dec); ^{1}H NMR: 8.04 (7.5), d, 2H; 8.01 (8.0, 1.5), dd, 2H; 7.97 (8.0, 1.0), dd, overlapping 7.96 (7.8, 0.8), dd, 2H; 7.89-7.86, m, 6H; 7.74 (7.9, 1.3), td, 2H; 7.73 (8.3, 1.0), td, 2H; 5.99 (2.5), d, 2H; 4.26 (5.0), d, 2H; 2.75 (19.0, 5.0), dd, 2H; 2.04 (20.5), d, 2H. ^{13}C NMR: 137.15, 136.83, 136.79, 136.64, 136.47, 136.15, 131.83, 131.76, 131.56, 131.23, 123.40, 115.07, 114.64, 45.29, 22.07.

4.2 *Preparation of di(5-thianthreniumyl)dienes*

An example is given for (*E, E*)- (**17b**) and (*E*, *Z*)-1,8-di(5-thianthreniumyl)-1,7-octadiene ditetrafluoroborate (**18b**). A solution of 115 mg (0.129 mmol) of **15b** in 6 mL of MeCN was poured onto 40 g of alumina held in a fritted glass funnel and was allowed to stand for 1 h. The mixture was washed with MeCN and the filtrate was evaporated to give a sticky solid. This was washed three times with ether to remove Th, leaving 68 mg (0.095 mmol) of sticky solid. Assay of a sample with ^{1}H NMR showed it to contain **17b** and **18b** in the ratio of 85:15. The total yield of **17b** and **18b** was 73%. Similar treatment of the di(mono)adduct from the reaction of $Th^{\bullet+}PF_6^-$ with 1,7-octadiene gave a similar mixture of **17b** and **18b** in the ratio of 85:15, mp: 105–106 °C; Anal. Calcd for $C_{32}H_{28}S_4P_2F_{12}\cdot H_2O$: C, 45.3; H, 3.56; S, 15.1. Found: C, 45.2; H, 3.48; S, 14.9.

The reactions of **15c** and **15d** were carried out in the same way. The following products were isolated: **17c** and **18c**, a mixture in the ratio of 85:15, 83%, from **15c**; **17d** and **18d**, a mixture in the ratio of 90:10, 90%, from **15d**.

4.3 *The ratio monoadducts: Bisadducts in a mixture*

The relative amount of **12**+**13** in a mixture was given simply by integration of overlapping alkenyl protons; we shall call this a. This integration was, of necessity equal to that of the protons H_d, H_e, and H_f in **12**+**13**, but that integration was a composite with similar protons in **14**, which we call b, and **15**, which we call c. The molar amount of **14**+**15** in a mixture is therefore represented by (b+c–a)/2, since there are six of the pertinent protons in each of **14** and **15**, but only three each in **12** and **13**. Therefore the ratio of (**12**+**13**):(**14**+**15**) is given by the integration 2a:(b+c–a). It was not possible to measure the amount of the four compounds individually.

X-Ray crystallography was performed as described in Part I [1]. The CCDC deposition number for **16** is 286931.

Acknowledgements

H. J. S. thanks the Welch Foundation for support (Grant D-0028). K. H. W. thanks the Welch Foundation for support (Grant C-0976) and for the purchase of the CCD, and the National Science Foundation for support (Grant CHE-9983352). We thank Mr. David Purkiss (TTU) for the 500 MHz NMR spectroscopy.

References

[1] B.-J. Zhao, H.J. Shine, J.N. Marx, A.T. Kelly, C. Hofmann, K.H. Whitmire. *J. Sulfur. Chem.*, **27**, 127 (2006).
[2] W.K. Lee, B. Liu, C.W. Park, H.J. Shine, I.Y. Guzman-Jimenez, K.H. Whitmire. *J. Org. Chem.*, **64**, 9206 (1999).
[3] D.-Q. Qian, H.J. Shine, I.Y. Guzman-Jimenez, J.H. Thurston, K.H. Whitmire. *J. Org. Chem.*, **67**, 4030 (2002).
[4] H.J. Shine, B.-J. Zhao, J.N. Marx, T. Ould-Ely, K.H. Whitmire. *J. Org. Chem.*, **69**, 9255 (2004).
[5] C. Chiappe, M.-F. Ruasse. In *The chemistry of dienes and polyenes*, vol. 2. Z. Rapaport (Ed.), pp. 545–643, John Wiley, Chichester, UK (2000).
[6] W.H. Mueller. *J. Am. Chem. Soc.*, **91**, 1223 (1969).
[7] D.G. Garratt, A. Kabo. *Can. J. Chem.*, **58**, 1030 (1980).
[8] E.J. Corey, E. Block. *J. Org. Chem.*, **31**, 1663 (1966).
[9] I. De Riggi, J.-M. Surzur, M.P. Bertrand. *Tetrahedron*, **44**, 7119 (1988).
[10] A. Toshimitsu, T. Aoai, S. Uemura, M. Okano. *J. Org. Chem.*, **46**, 3021 (1981).
[11] J. Barluenga, C. Jiménez, C. Nájera, M. Yus. *J. Chem. Soc. Perkin I*, 721 (1984).