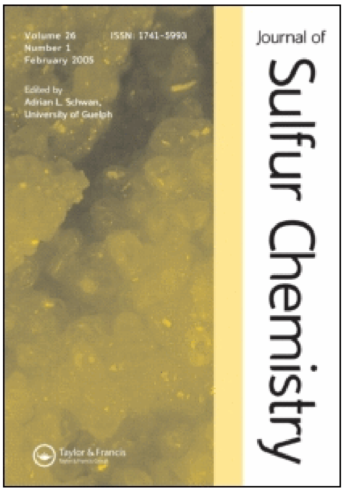

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Addition of thianthrene cation radical to non-conjugated dienes – Part I: Addition to one double bond

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Reaction of thianthrene cation radical tetrafluoroborate and hexafluorophosphate with an excess of 1,4-hexadiene, 1,5-hexadiene, 1,7-octadiene, 1,8-nonadiene and 1,9-decadiene gave, in each case, a mixture of bis- and monoadduct from addition to one of the diene's double bonds. Addition to both double bonds did not occur. The monoadduct of each diene and the bisadduct (**7a**) of 1,5-hexadiene were isolated. All monoadducts and **7a** were characterized with ^{1}H and ^{13}C NMR spectroscopy. By reaction on activated alumina adducts were converted into (*E*)- and (*Z*)-(5-thianthreniumyl)dienes, all of which were characterized with ^{1}H and ^{13}C NMR spectroscopy. The monoadduct (**6a**) of 1,4-hexadiene and the bisadduct **7a** were characterized with X-ray crystallography.

Keywords: Thianthrene cation radical; Adducts of dienes; NMR

1. Introduction

Numerous reactions of the thianthrene cation radical with nucleophiles, electron-rich aromatics, alcohols, azoalkanes, organometallics, ketones, and various derivatives of aldehydes and ketones are to be found, and have been in part reviewed, in the literature [1–14]. Among these reactions, additions to alkenes and cycloalkenes, which were first discovered more than 20 years ago [15, 16], have drawn, recently, further extensive interest [17–20]. Thus, whereas earlier [15–17] it was believed that addition of thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) to alkenes and cycloalkenes gave only bisadducts, it was found more recently that mono- (**2**) and bisadducts (**3**) are formed, in relative amounts depending on the structure of the alkene and cycloalkene [18–20]. Furthermore, it was found in these additions that the configuration of the alkene was retained in both types of adduct. A mechanism of addition was formulated to explain these results [19, 20] and is shown in scheme 1. The scheme shows that stereospecific cycloaddition of $Th^{\bullet+}$ to a double bond forms an intermediate, a cyclic distonic cation radical (**1**). Reaction of that cation radical with a second $Th^{\bullet+}$ can occur in two ways: displacement

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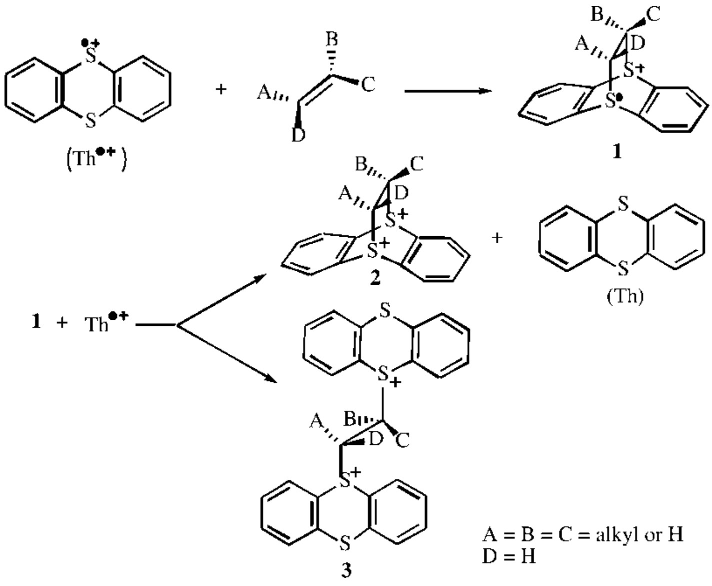
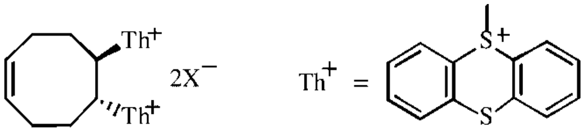
to give a bisadduct (**3**) or oxidation to give a monoadduct (**2**) and thianthrene (Th). In each product, the configuration of the alkene is retained.



SCHEME 1

Only one diene was included in those investigations [18–20], namely 1,5-cyclooctadiene. We were struck at that time [19] that only one of the double bonds of cyclooctadiene underwent addition of Th$^{\bullet+}$. Only a bisadduct (**4**) was formed, which was characterized with NMR spectroscopy and X-ray crystallography. The question arose as to whether both bonds of an acyclic diene might undergo addition, particularly if they were separated by several methylene groups. To answer that question we have carried out reactions of Th$^{\bullet+}$BF$_4^-$ and Th$^{\bullet+}$PF$_6^-$ with 1,4- and 1,5-hexadiene, 1,7-octadiene, 1,8-nonadiene and 1,9-decadiene. We have found (Part I) that addition to only one double bond occurs when a large excess of diene is used. When an excess of cation radical is used, however, additions occur to the two double bonds of the last four dienes. The two-fold additions are reported in Part II (succeeding publication). We have also investigated the behavior of the addition products on activated alumina.



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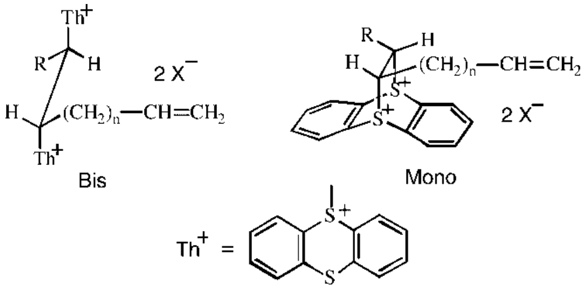
2. Results and discussion

2.1 *Formation of adducts*

The additions to non-conjugated dienes that we describe are distinct from reactions of conjugated dienes with cation radicals, particularly triarylaminium salts. The latter reactions are Diels-Alder cylcoadditions, so-called hole-catalyzed by the cation radical [21, 22]. The additions we describe here are of the cation radical itself to the isolated alkene double bonds of a non-conjugated diene. A bis- and monoadduct were formed by each of the dienes used. They are listed in table 1. The adducts were obtained as mixtures, the composition of which was measured with ^1H NMR spectroscopy. Integration of assignable, unoverlapped signals was used for that purpose. Fractional precipitation and crystallization were used next to separate mono- from bisadducts. Separation of products by column chromatography was pre-empted by the decomposition of the products on such columns. Initially, adducts were made with $Th^{\bullet+}PF_6^-$ and gave us monoadducts **10b** and **12b**. However, separation of tetrafluoroborates proved to be easier than of hexafluorophosphates, so that $Th^{\bullet+}BF_4^-$ was used with the other dienes. A detailed example is given for addition to 1,5-hexadiene in which the initial mixture of adducts contained **7a** (bis) and **8a** (mono) in a ratio of 3:2. Analogous additions were obtained with the other four dienes and the results are given in the Experimental section.

Separation of bis- and monoadducts to obtain pure samples of each was made difficult because of the slow conversion of a bis- into a monoadduct. This made isolation of a bisadduct the more difficult. We have reported this property of bisadducts earlier [19]. In the present work only the bisadduct **7a** has been isolated and we have followed its conversion into the monoadduct **8a** with NMR spectroscopy. Each monoadduct (**6a**, **8a**, **10b**, **12b**, and **14a**) was obtained almost completely free of the corresponding bisadduct, and was characterized with ^1H and ^{13}C NMR spectroscopy, aided with DEPT, COSY, HMQC and HMBC. Signals assignable to a bisadduct were evident in the NMR spectrum of a mixture of bis and monoadducts, but

Table 1. Products of addition of $Th^{\bullet+}$ to one double bond of a diene.



			Products (%)[a]			
n	*R*	*X*	bis	mono	Th[b]	Sum
1	Me	BF_4	**5a**[c]	**6a**[c]		
2	H	BF_4	**7a**, 42	**8a**, 15	33	90
4	H	BF_4	**9a**, 38	**10a**, 19	38	95
4	H	PF_6	**9b**, 29	**10b**, 10	54	93
5	H	BF_4	**11a**, 51	**12a**, 17	34	102
5	H	PF_6	**11b**, 36	**12b**, 13	42	91
6	H	BF_4	**13a**, 43	**14a**, 17	30	90

[a] Based on the Th^+ units in each compound; 50% in a monoadduct would represent complete conversion of $Th^{\bullet+}$ into that adduct and Th; yields of adducts were measured with 300 HMz NMR spectroscopy.

[b] Measured with GC and includes the amount of Th equivalent to the amount of monoadduct. The remainder represents unprecipitated mono- and bisadduct that decomposed in the GC inlet.

[c] Yield not measured.

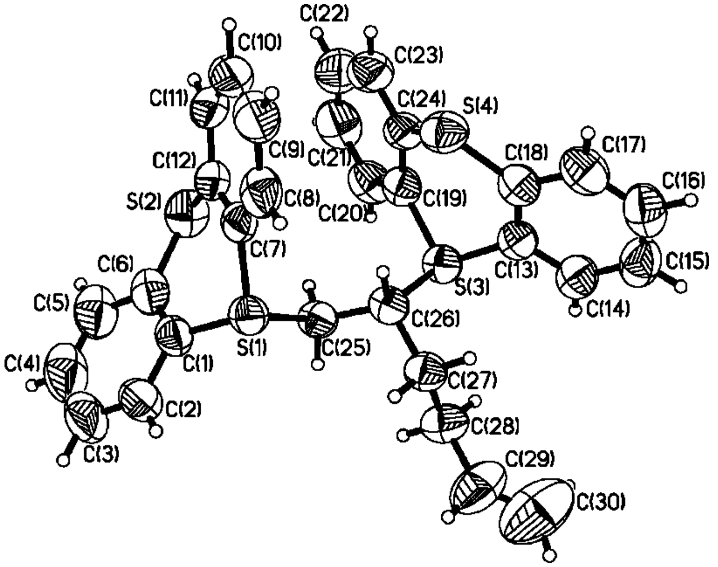


Figure 1. Ortep diagram for 5,6-bis(5-thianthreniumyl)hexene ditetrafluoroborate (**7a**). The counterions and solvent of crystallization are omitted.

extensive overlapping of ^{1}H signals from the two adducts prevented the complete characterization of bisadducts, except for the isolated **7a**. X-ray crystallography confirmed the structure of **7a** (figure 1).

To emphasize the validity of the structures assigned to monoadducts we have tabulated selected pertinent ^{1}H (table 2) and ^{13}C NMR data (table 3) of the adducts of the four terminal dienes. The consistency in chemical shift (δ, ^{1}H and ^{13}C) and coupling constants (J) is evident. Table 2 shows assignments of δ (J) for each remaining double bond (H_a, H_b, H_c) and the three protons of the former double bond (H_d, H_e, H_f). The smaller J (5.0–5.8 Hz) for the *trans* (threo) protons H_d and H_e and the larger J (7.9–8.8 Hz) for the *cis* (erythro) protons H_d and H_f are consistent with data for analogous rigid systems [19, 23–25]. The consistency of δ (^{13}C) for the four adducts (table 3) is notable. In these spectra DEPT was used for designating proton-bearing C atoms. That there are eight aromatic CH carbons (instead of four) and four aromatic quaternary carbons (instead of two) illustrates the absence of symmetry in the thianthrenium portion of each adduct. That is also disclosed by the number of signals (6–7 rather than 4) of the aryl protons listed in the Experimental section.

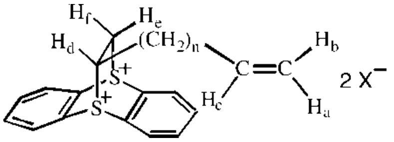
The structure of the fifth monoadduct (**6a**), revealed by its Ortep diagram (figure 2), is supported by its ^{1}H and ^{13}C NMR data (Experimental). Surprisingly, addition of $Th^{\bullet+}$ occurred at the internal rather than the terminal double bond of *trans*-1,4-hexadiene. Apparently, in the electrophilic addition of $Th^{\bullet+}$, the electron donating property of the methyl group was of greater influence than the group's contribution to steric encumbrance.

Finally, thus far, as addition to dienes is concerned, in no case did we find evidence for addition to two double bonds when a 4–5 molar excess of diene was used.

2.2 *Formation of (5-thianthreniumyl)dienes*

Both mono and bisadducts of the 1,5-, 1,7-, 1,8- and 1,9-dienes were converted into 1-(5-thianthreniumyl)dienes on alumina, as is shown in abbreviated form in scheme 2. The monoadducts **8a** ($n = 2$), **10b** ($n = 4$) and **12b** ($n = 5$), each of which contained only a small

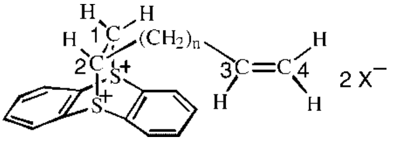
Table 2. Selected[a] ^{1}H NMR Data[b] for monoadducts **8a**, **10b**, **12b**, **14a**.



H	**8a** $n = 2, X = BF_4$	**10b** $n = 4, X = PF_6$	**12b** $n = 5, X = PF_6$	**14a** $n = 6, X = BF_4$
H_c	5.74, ddt (17.3, 10.3, 6.7)	5.81, ddt (17.3, 10.3, 6.7)	5.83, ddt (17.3, 10.3, 6.7)	5.80, ddt (17.3, 10.3, 6.8)
H_b	5.13, dq (17.0, 1.5)	5.02, dq (17.3, 1.7)	5.01, dd (17.0, 2.0)	4.99, dq (17.0, 1.8)
H_a	5.08, dd (10.5, 1.3)	4.98, ddt (11.8, 2.3, 1.1)	4.94, dd (10.0, 1.0)	4.93, ddt (10.5, 2.0, 1.1),
H_d	4.48, dtd (7.5, 7.9, 5.5)	4.50, dtd (8.3, 8.0, 5.8)	4.52, dtd (8.0, 7.9, 5.5)	4.48, dtd (7.8, 7.8, 5.8)
H_f	4.35, ddd (13.5, 8.8, 2.8)	4.36, dd (14.5, 8.5)	4.38, dd (13.8, 8.8)	4.33, dd (13.5, 8.5)
H_e	3.66, dd (13.8, 5.3)	3.65, dd (13.8, 5.3)	3.69, dd (13.9, 5.0)	3.62, dd (13.5, 5.5)

[a] Only data for H_{a-f} are given. Data for all other protons are in the Experimental.
[b] δ (ppm), multiplicity and J (Hz).

Table 3. ^{13}C NMR chemical shifts for monoadducts **8a**, **10b**, **12b**, **14a**.



$^{13}C^a$	**8a** $n = 2, X = BF_4$	**10b** $n = 4, X = PF_6$	**12b** $n = 5, X = PF_6$	**14a** $n = 6, X = BF_4$
C-3	137.61	139.21	139.74	139.99
Th^+CH	137.59	137.62	137.62	137.56
Th^+CH	138.48	137.57	137.54	137.49
Th^+CH	137.15	137.56	137.54	137.47
Th^+CH	137.02	137.18	137.17	137.12
Th^+CH	136.76	137.04	137.04	136.99
Th^+CH	136.66	136.71	136.70	136.70
Th^+CH	136.48	136.63	136.63	136.68
Th^+CH	136.18	136.55	136.53	136.54
Th^+quat	126.99	126.89	126.91	126.94
Th^+quat	126.39	126.18	126.19	126.27
Th^+quat	124.81	124.83	124.84	124.97
Th^+quat	123.01	123.05	123.07	123.14
C-4	118.01	115.53	115.10	114.91
C-2	55.64	56.08	56.10	56.10
C-1	42.02	42.15	42.15	42.18
	32.13	35.60	34.07	34.26
	30.91	32.69	32.80	32.86
		28.49	28.89	29.31
		26.48	28.78	29.13
			26.89	29.10
				26.99

[a] All unassigned shifts are for CH_2 groups.

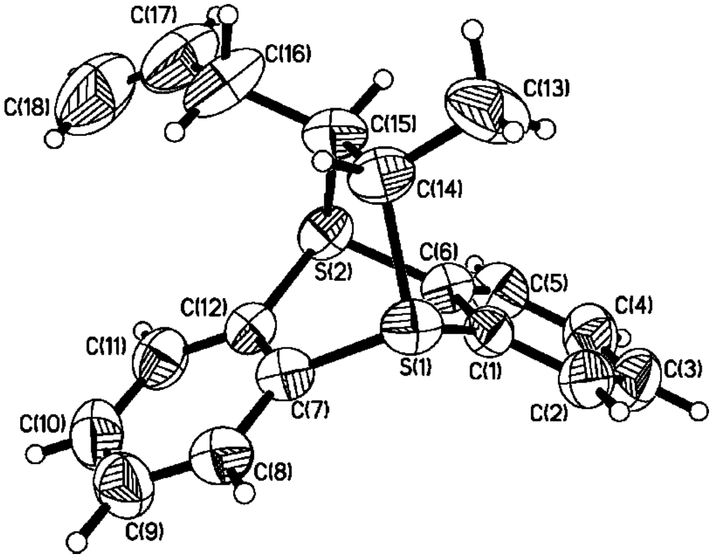
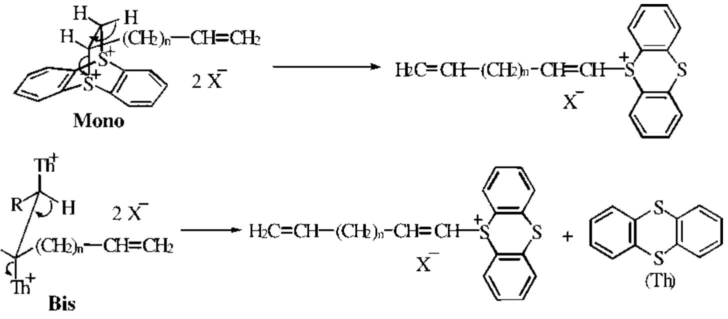


Figure 2. Ortep diagram for 4,5-(5,10-thianthreniumdiyl)hexene ditetrafluoroborate (**6a**). The counterions and solvent of crystallization are omitted.

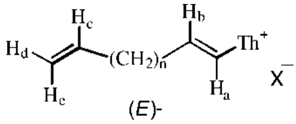
amount of bisadduct (**7a**, **9b**, and **11b**, respectively), gave mainly (*E*)-isomers. That is, **8a** gave **16a**, **10b** gave **18b** and **12b** gave **20b**, allowing for the recording of NMR spectra of (*E*)-isomers unimpeded by the presence of the small signals from the (*Z*)-isomers. To record the spectra of (*Z*)-isomers, we began with the isolated **7a**, which gave a mixture of **15a**, the (*Z*)-isomer, and the already characterized (*E*)-isomer, **16a**, in a ratio of 2:3. This allowed us to assign signals to **15a**. For the NMR spectra of (*Z*)-1-(5-thianthreniumyl)-1,7-octadiene (**17**) and -1,8-nonadiene (**19**), we used mixtures of bis- and monoadduct tetrafluoroborates; that is, a 35:65 mixture of **9a** and **10a** gave **17a**, the (*Z*)-isomer and **18a**, the (*E*)-isomer in a ratio of 23:73 which allowed for characterizing **17a**. Similarly, a 34:66 mixture of **11a** and **12a** gave **19a** and **20a** in a 15:85 ratio, which allowed us to characterize **19a**. A 1:4 mixture of bis- (**13a**) and monoadduct (**14a**) of 1,9-decadiene gave the (*Z*)- and (*E*)-1-(5-thianthreniumyl)decadiene tetrafluoroborates in a 16:84 ratio, which allowed for characterizing both isomers, **21a** (table 5) and **22a** (table 4).



SCHEME 2

Pertinent ^{1}H and ^{13}C NMR data for four (*E*)-isomers are summarized in tables 4 and 6, and the corresponding data for (*Z*)-isomers are in tables 5 and 7. These data show consistency of

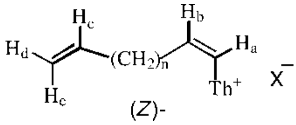
Table 4. Selected[a] ^1H NMR data[b] in (*E*)-1-(5-thianthreniumyl)dienes.



	16a	**18b**	**20b**	**22a**
H	$n = 2, X = BF_4$	$n = 4, X = PF_6$	$n = 5, X = PF_6$	$n = 6, X = BF_4$
H_b	6.86, dt (14.5, 7.1)	6.83, dt (14.5, 7.1)	6.83, dt (15.0, 7.0)	6.86, dt (14.5, 7.1)
H_a	6.55, d, (14.5)	6.50, dt, (14.5, 1.3)	6.49, d, (15.0)	6.50, dt, (15.0, 1.4)
H_c	5.73, ddt (17.3, 10.5, 6.6)	5.75, ddt (17.3, 10.3, 6.7)	5.76, ddt (17.0, 10.5, 6.8)	5.78, ddt (17.0, 10.5, 6.8)
H_e	4.99, dd (17.0, 1.5)	4.95, dq (17.3, 1.8)	4.95, dq (17.3, 1.8)	4.96, dd (17.5, 1.5)
H_d	4.96, dd (9.8, 1.5)	4.90, ddt (10.0, 2.0, 1.0)	4.89, dd (10.0, 1.0)	4.90, ddt (10.3, 1.8, 1.0)

[a] Only data for H_{a-e} are given. Data for all other protons are in the Experimental section.
[b] δ (ppm), multiplicity and *J* (Hz).

Table 5. Selected[a] ^1H NMR data[b] in (*Z*)-1-(5-thianthreniumyl)dienes.



	15a	**17a**	**19a**	**21a**
H	$n = 2, X = BF_4$	$n = 4, X = BF_4$	$n = 5, X = BF_4$	$n = 6, X = BF_4$
H_b	6.79, dt, (8.5, 8.1)	6.82, dt, (8.5, 8.2)	6.82, dt, (8.0, 8.2)	6.82, dt, (9.0, 8.0)
H_a	6.71, dt, (8.5, 1.4)	6.66, dt, (8.5, 1.4)	6.66, dt, (8.5, c)	6.66, dt, (8.5, c)
H_c	5.79, ddt (17.3, 10.3, 6.8)	5.81, ddt (17.0, 10.5, 6.8)	5.85–5.78, ddt (c, 10.5, 7.0)	5.86–5.79, ddt (c, 9.0, 6.8)
H_e	5.06, dd (17.3, 1.7)	5.01, dq (17.3, 1.6)	4.99, dd (17.5, 2.0)	4.99, dq (18.0, 1.2)
H_d	5.01, ddt (10.3, 1.8, 1.0)	d	d	d

[a] Only data for H_{a-e} are given. Data for all other protons are in the Experimental.
[b] δ (ppm), multiplicity and *J* (Hz).
[c] Coupling not measurable with small signal.
[d] Overlapped by (*E*)-isomer.

δ and *J* values for the protons on C-1 and C-2 carbon atoms in each set of four isomers. The relatively large value of *J* (14.5 Hz) for these protons in the (*E*)-isomers as compared with the smaller value (8–9 Hz) in the (*Z*)-isomers is as expected.

The remaining terminal double bond is characterized uniformly in all eight isomers. The symmetry of the Th^+ group is shown in the ^{13}C NMR spectra of the eight isomers by there being only four CH and two quaternary C atoms. Notably, the furthest downfield C atom (*ca.* 156 ppm) is C-2, and corresponding with that is the furthest downfield proton signal, H_b. The data point to delocalization of charge as shown with a (*Z*)-isomer in **23**. In none of these reactions on alumina was evidence found for formation of a 2-(5-thianthreniumyl)diene.

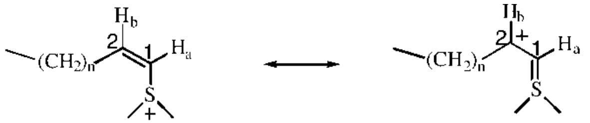


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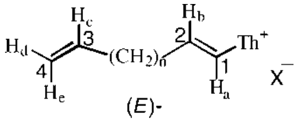
Table 6. ^{13}C NMR chemical shifts for (*E*)-1-(5-thianthreniumyl)dienes.

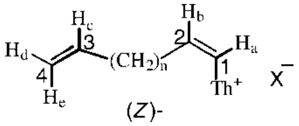


^{13}C^{a}	**16a** $n = 2$, $X = BF_4$	**18b** $n = 4$, $X = PF_6$	**20b** $n = 5$, $X = PF_6$	**22a** $n = 6$, $X = BF_4$
C-2	155.81	156.71	156.84	156.91
C-3	137.51	139.55	139.87	140.04
Th$^+$quat	136.51	136.54	136.53	136.48
Th$^+$CH	135.47	135.48	135.48	135.46
Th$^+$CH	133.97	133.96	133.95	133.99
Th$^+$CH	131.28	131.31	131.31	131.27
Th$^+$CH	130.84	130.85	130.85	130.86
Th$^+$quat	121.18	121.23	121.24	121.25
C-4	116.52	115.15	114.94	114.83
C-1	111.28	110.89	110.80	110.78
	32.67	33.83	34.16	34.26
	31.98	33.34	33.44	33.47
		28.72	29.07	29.40
		27.48	28.88	29.22
			27.80	29.21
				27.90

[a] All unassigned shifts are for CH$_2$ groups.

In contrast with the adducts of the four terminal dienes, the monoadduct (**6a**) of 1,4-hexadiene did give positional isomers from reaction on alumina, namely (*Z*)-4- (**24a**) and (*Z*)-5-(5-thianthreniumyl)-1,4-hexadiene (**25a**) tetrafluoroborates. The (*Z*)-configuration was assigned to these compounds on the basis of our earlier work that showed that (*Z*)-isomers

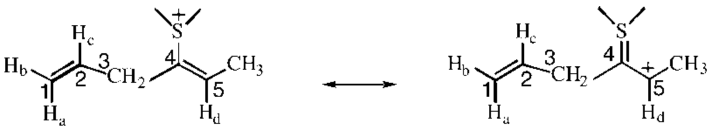
Table 7. ^{13}C NMR chemical shifts for (*Z*)-1-(5-thianthreniumyl)dienes.



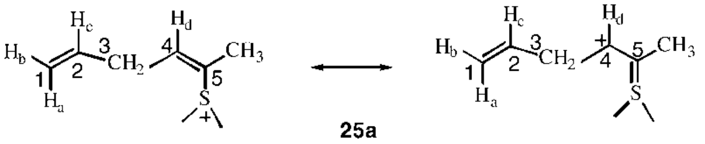
^{13}C^{a}	**15a** $n = 2$, $X = BF_4$	**17a** $n = 4$, $X = BF_4$	**19a** $n = 5$, $X = BF_4$	**21a** $n = 6$, $X = BF_4$
C-2	155.53	156.32	156.49	156.54
C-3	137.31	139.51	139.87	140.04
Th$^+$quat	136.59	136.62	136.58	136.58
Th$^+$CH	135.42	135.40	135.39	135.38
Th$^+$CH	133.47	133.41	133.41	133.41
Th$^+$CH	131.62	131.63	131.61	131.60
Th$^+$CH	130.96	130.97	130.97	130.96
Th$^+$quat	122.08	122.22	122.22	122.24
C-4	117.21	115.30	115.03	114.88
C-1	113.01	112.70	112.61	112.59
	32.46	33.98	34.18	34.29
	30.48	31.07	31.18	31.22
		28.99	29.26	29.56
		28.18	29.22	29.41
			28.52	29.41
				28.62

[a] All unassigned shifts are for CH$_2$ groups.

are formed from adducts of trans alkenes [20]. Notably, δ(6.6 ppm) for H_d in each isomer is much further downfield than for the alkenyl protons H_a, H_b and H_c, and in the ^{13}C spectra the furthest downfield C atoms ($\delta = 147$–148 ppm) are C-5 (**24a**) and C-4 (**25a**). These data result from delocalization of charge as shown.



24a



25a

3. Experimental

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 [18]. All dienes were from commercial sources. A 300 MHz NMR instrument was used for following changes in ^1H NMR spectra over timed periods. A 500 MHz NMR instrument was used for obtaining all ^1H and ^{13}C chemical shifts and coupling data, listed as $\delta(J)$ in ppm and Hertz, for compounds **5–25**. Values of J have been averaged. Most of the NMR data are tabulated in tables 2–7. 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.

3.1 *Preparation of bis- and monoadducts*

A detailed example is given for 5,6-bis(5-thianthreniumyl)hexene ditetrafluoroborate (**7a**) and 5,6-(5,10-thianthreniumdiyl)hexene ditetrafluoroborate (**8a**). To a stirred suspension of 433 mg (1.43 mmol) of $Th^{\bullet+}BF_4^-$ in 8 mL of MeCN was added 0.8 mL (6.74 mmol) of 1,5-hexadiene. After 3 h of stirring, dry ether was added dropwise giving a precipitate, which was filtered, washed with ether and dried to give 308 mg of product. The aromatic portion of the ^1H NMR spectrum showed that the product was a mixture of **7a** and **8a** in the ratio of 58:42. These data show that the total yield of adducts was 72%, namely, 42% of **7a** and 30% of **8a**. GC assay of the filtrate gave 0.469 mmol of Th, of which 0.239 mmol corresponds with the formation of **8a**. Thus the filtrate had an additional 0.230 mmol of Th, attributable to decomposition of unprecipitated adducts in the GC inlet. The recovery of thianthrenium units totaled 1.47 mmol, 96% of the initial $Th^{\bullet+}BF_4^-$. Repeated fractional precipitation of the mixture gave **7a**, mp 124–125 °C (dec) and **8a**, mp 158–159 °C (dec). The NMR spectral data of adducts are given in part in tables 2 and 3 and, when not tabulated, in the Experimental section below.

7a ^1H NMR: 8.12 (8.3, 1.3), dd, 1H, overlapping 8.11 (8.0, 1.0), dd, 1H; 8.07 (8.0, 1.0), dd, 1H; 7.97 (7.8, 1.2), td, 1H; 7.94 (8.3, 1.3), dd, 1H; 7.90 (8.0, 1.0), dd, 2H; 7.88 (8.0, 1.5), dd, 1H; 7.87 (7.3, 1.3), dd, 1H; 7.85-7.79, m, 3H; 7.77–7.01, m, 4H; 5.62 (17.0, 10.5, 6.5), ddt, 1H; 5.05 (10.3, 1.3), dd, 1H; 4.97 (17.0, 1.3), dd, 1H; 4.21 (12.0, 4.0, 2.0), dtd, 1H; 4.03 (13.5, 2.0), dd, 1H; 3.80 (13.8, 10.3), dd, 1H; 2.20–2.06, m, 2H, overlapping solvent water; 2.00–1.86, m, overlapping solvent. ^{13}C NMR: 137.15, 137.11, 136.87, 136.81, 136.79, 136.71, 136.57, 136.51, 136.46, 136.27, 136.17, 136.15, 135.63, 132.19, 132.12, 131.76, 131.75, 131.56, 131.47, 131.23, 131.13, 118.07, 116.49, 115.95, 115.28, 114.39, 47.11, 37.38, 29.68, 29.38.

8a ^{1}H NMR: 8.59–8.57, m, 1H; 8.54–8.53, m, 1H; 8.50-8.49, m, 2H; 8.154 (6.8, 2.8), dd, 1H overlapping 8.147 (7.0, 2.5), dd, 1H; 8.11–8.10, m, 2H; 2.32–2.26, m, 2H; 1.90, m, 1H, overlapping solvent; 1.83–1.75, m, 1H.

Similar reactions were carried out with four other dienes, all of which gave mixtures of bis- and monoadducts. Monoadducts were isolated containing only small amounts of the bisadduct.

6a (from $Th^{\bullet+}BF_4^-$ and 1,4-hexadiene), mp 137–138 °C (dec), ^{1}H NMR: 8.60, m, 1H; 8.55, m, 2H; 8.51 (7.5, 1.5), dd, 1H; 8.16, m, 4H; 5.79 (16.5, 10.7, 8.1, 6.3), dddd, 1H; 5.38 (10.0), d, 1H; 5.30 (15.0, 1.0), dt, 1H; 4.14, m, 1H overlapping 4.13, m, 1H; 2.84 (15.0, 6.5), dt, 1H; 2.40 (15.0, 7.5), dt, 1H; 1.58 (7.0), d, 3H. ^{13}C NMR: 138.15, 137.80, 137.69, 137.66, 137.63, 137.57, 136.96, 136.93, 130.90, 127.07, 126.41, 123.82, 123.33, 121.58, 61.11, 56.35, 36.04, 17.93.

10b (from $Th^{\bullet+}PF_6^-$ and 1,7-octadiene), mp 135–136 °C (dec), ^{1}H NMR: 8.58 (6.5, 2.5), dd, 1H; 8.55 (6.5, 3.0), dd, 1H; 8.52 (6.5, 3.0), dd, 2H; 8.18 (4.5, 3.0), dd, 1H overlapping 8.17 (5.0, 3.0), dd, 1H; 8.13 (6.0, 3.5), dd, 2H; 2.07 (7.0, 7.0), dt, 2H; 1.75 (7.5, 7.8, 2.9), dtd, 2H; 1.54 (7.4), quint, 2H; 1.40, m, 2H.

12b (from $Th^{\bullet+}PF_6^-$ and 1,8-nonadiene), mp 143–144 °C (dec), ^{1}H NMR: 8.56 (6.5, 2.5), dd, 1H; 8.52 (6.3, 2.8), dd, 1H; 8.50 (6.3, 2.8), dd, 1H overlapping 8.49 (6.0, 3.0), dd, 1H; 8.16 (7.0, 2.5), dd, 1H overlapping 8.15 (7.0, 2.5), dd, 1H; 8.11 (6.3, 2.3), dd, 2H; 2.02 (7.2), q, 2H; 1.72 (7.3), quint, 2H; 1.51 (7.3), quint, 2H; 1.36 (7.3), quint, 2H; 1.29 (7.0), q, 2H.

14a (from $Th^{\bullet+}BF_4^-$ and 1,9-decadiene), mp 140–142 °C (dec), ^{1}H NMR: 8.59 (7.3, 2.3), dd, 1H; 8.56 (7.3, 1.8), dd, 1H; 8.53, m, 2H; 8.18 (7.3, 1.8), dd, 1H overlapping 8.17 (7.0, 2.0), dd, 1H and 8.13 (5.5, 3.4), dd, 2H; 2.04 (7.2), q, 2H; 1.74, m, 2H; 1.53, m, 2H; 1.37, m, 2H; 1.30, m, 4H.

3.2 *Preparation of (5-thianthreniumyl)dienes 15–25*

An example is given for (*E*)- (**16a**) and (*Z*)-1-(5-thianthreniumyl)-1,5-hexadiene tetrafluoroborate (**15a**). A solution of 45 mg (0.109 mmol) of **8a** in 6 mL of MeCN was poured onto 40 g of activated 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 27 mg of sticky solid. Assay of a sample with ^{1}H NMR showed it to contain **16a** and **15a** in the ratio of 94:6. The total yield of **15a** and **16a** was 63%. Similar treatment of the bisadduct **7a** gave a mixture of **16a** and **15a** in the ratio of 3:2. NMR spectra were obtained with the use of both products. The NMR spectral data of (5-thianthreniumyl)dienes are given in part in tables 4–7 and, when not tabulated, in the Experimental section below.

16a ^{1}H NMR: 8.15 (8.0), d, 2H; 7.98 (8.0), d, 2H; 7.84 (7.5, 1.0), td, 2H; 7.75 (7.8, 1.0), td, 2H; 2.38 (7.2, 1.0), qd, 2H; 2.19 (7.0), q, 2H.

15a ^{1}H NMR: 8.10 (8.5, 1.5), dd, 2H; 7.96 (8.3, 1.3), dd, 2H; 7.80 (7.6, 1.3), td, 2H; 7.70 (7.8, 1.3), td, 2H; 2.74 (7.3, 1.4), qd, 2H; 2.22 (7.2, 1.3), qt, 2H.

The reactions of all other adducts and mixtures of adducts were carried out in the same way. The following products were isolated: **24a** and **25a**, a mixture in the ratio of 3:2, 77%, from **6a**; **17a** and **18a**, a mixture in the ratio of 1:3 from use of a 65:35 mixture of **10a** and **9a**; **17b** and **18b**, a mixture in the ratio of 8:92, mp 104–105 °C (dec), 87%, from **10b**; **19a** and **20a**, a mixture in the ratio of 15:85, 87%, from a 66:34 mixture of **12a** and **11a**; **19b** and **20b**, a mixture in the ratio of 1:9, mp 92–93 °C, 83%, from **12b**; **21a** and **22a**, a mixture in the ratio of 14:86, 93% from an 81:19 mixture of **14a** and **13a**.

24a ^{1}H NMR: 7.99 (8.0, 1.0), dd, 2H; 7.85 (8.0, 1.5), dd, 2H; 7.79 (7.8, 1.0), td, 2H; 7.67 (7.4, 1.5), td, 2H; 6.60 (6.8, 1.3), qt, 1H; 5.53 (17.0, 10.0, 6.5), ddt, 1H; 4.97 (10.3, 1.3), dq, 1H; 4.91 (17.0, 1.5), dq, 1H; 2.99 (6.5, 1.4), dq, 2H; 2.23 (7.0, 1.5), dt, 3H. ^{13}C NMR: 147.43, 136.79, 135.46, 134.24, 133.34, 130.88, 130.76, 130.18, 119.33, 117.92, 37.67, 16.48.

25a ^{1}H NMR: 7.96 (8.0, 1.0), dd, 2H; 7.86 (8.0, 1.5), dd, 2H; 7.79 (7.8, 1.5), td, 2H; 7.66 (7.8, 1.3), td, 2H; 6.57 (7.5, 1.3), td, 1H; 5.87 (16.5, 10.8, 6.0), ddt, 1H; 5.16 (9.8, 1.5), dq, 1H; 5.15 (17.0, 1.5), dq, 1H; 3.44 (6.3, 1.0), tt, 1H; 1.96 (1.2), q, 3H. ^{13}C NMR: 148.64, 136.59, 135.44, 134.15, 133.90, 130.83, 128.62, 119.20, 117.77, 34.81, 19.96.

17a ^{1}H NMR: 8.10 (8.0), d, 2H; 7.94 (8.3, 0.5), dd, 2H; 7.80 (7.8, 1.0), td, 2H; these signals overlapped those of **18a**; 7.70 (7.8, 1.0), td, 2H; 2.64 (6.8), q, 2H; 2.05 (6.7), q, 2H; 1.39, m, 2H overlapping peak of **18a**; 1.29, m, 2H overlapping peak of **18a**.

18b ^{1}H NMR: 8.09 (8.0, 1.0), dd, 2H; 7.94 (7.5, 1.0), dd, 2H; 7.80 (7.8, 1.3), td, 2H; 7.70 (7.8, 1.0), td, 2H; 2.25 (7.2, 1.8), qd, 2H; 1.97 (7.2), q, 2H; 1.39 (7.3), quint, 2H; 1.29 (7.3), quint, 2H.

19a ^{1}H NMR: 8.11 (8.0, 1.0), dd, 2H; 7.93 (8.0, 1.0), dd, 2H; 7.80 (7.6, 1.2), td, 2H; 7.70 (7.8, 0.8), td, 2H; these signals overlapped those of **20a**; 2.63 (7.0), q, 2H; 2.00 (7.3), q, 2H, overlapping a peak from **20a**.

20b ^{1}H NMR: 8.09 (8.0), d, 2H; 7.94 (8.0), d, 2H; 7.81 (7.8, 1.2), td, 2H; 7.71 (7.8, 1.0), td, 2H; 2.24 (7.3, 1.2), qd, 2H; 1.97 (7.0), q, 2H; 1.39 (7.5), quint, 2H; 1.30 (7.5), quint, 2H; 1.20, m, 2H.

21a ^{1}H NMR: 8.11 (8.0, 1.5), dd, 2H; 7.92 (8.0), d, 2H; 7.79 (7.6, 1.3), td, 2H; 7.70 (7.8, 0.8), td, 2H; these signals overlapped those of **22a**; 2.63 (7.2, 1.0), qd, 2H; 2.01 (7.0), q, 2H; 1.37, m, 2H; 1.28, m, 2H; 1.20, m, 4H; the last three signals overlapped signals from **22a**.

22a ^{1}H NMR: 8.11 (8.0, 1.0), dd, 2H; 7.93 (8.0), d, 2H; 7.79 (7.5), t, 2H; 7.70 (7.8, 0.8), td, 2H; 2.23 (7.3, 1.0), qd, 2H; 1.97 (7.3), q, 2H; 1.37, m, 2H; 1.28, m, 2H; 1.20, m, 4H.

3.3 *Conversion of 7a into 8a; subsequent decomposition of 8a*

A solution of **7a** in CD_3CN was kept in a light-shielded NMR tube and the ^{1}H NMR spectrum was recorded daily, during which time the signals from **7a** decreased and those from **8a** increased. The furthest downfield (8.60–8.48 ppm) aromatic multiplet from **8a** was used to measure the amount of **8a**. After 5 days, the integrated ratio **7a** : **8a** was 2:98. During this time the amount of Th that was formed was also measured by integrating its clearly separated pair of dd at 7.52 and 7.30 ppm. The ratio of **8a** : Th was 1:1 at each measurement. The solution was kept further for monitoring the slow decomposition of **8a** into **15a** and **16a**, the amounts of these isomers being measured by integrating their separated dt at, respectively, 6.7 and 6.5 ppm. After 34, 48, and 69 days the ratio of **8a**:(**15a** + **16a**) was, respectively, 75:25, 63:37, and 38:62, while the ratio **15a**:**16a** was 27:73, 15:85, 10:90.

4. X-ray crystallography and Ortep diagrams

Each single crystal was glued to a glass fiber and mounted on a Bruker Smart 1000 diffractometer equipped with a CCD area detector. Graphite monochromated MoKα radiation ($\lambda = 0.71073$Å) in the ω-2θ scanning mode was used. The data were collected at room temperature and corrected for Lorentz and polarization effects. An absorption correction was applied using the program SADABS. No decay of the crystals was detected during data collection. Heavy atoms in the compounds were located using Patterson methods. The structures were solved using direct methods using the SHELXTL software package and refined by full matrix least-square techniques on F^2. Hydrogen atoms were included in calculated positions and refined using riding model. All thermal ellipsoids are drawn at the 50% probability level.

The CCDC deposition numbers for **6a** and **7a** are 286929 and 286930.

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