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Reaction of Thianthrene and Phenoxathiin Cation Radicals with 2,3-Dimethyl-2-butene. Chemical and Electrochemical Studies

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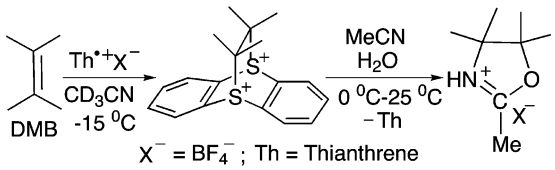
Received January 11, 2006



Thianthrene cation radical tetrafluoroborate ($Th^{\bullet+}BF_4^-$) has been found to add to 2,3-dimethyl-2-butene (DMB) at 0 °C and −15 °C. The adduct, 2,3-dimethyl-2,3-(5,10-thianthreniumdiyl)butane ditetrafluoroborate (**12**), was isolated at −15 °C, and its ^{1}H NMR spectrum was recorded at that temperature. The adduct was stable in CD_3CN solution at −15 °C but decomposed slowly at 0 °C and quickly at 23 °C, forming the salt of 2,4,4,5,5-pentamethyl-2-oxazoline (**8**) with loss of thianthrene (Th). These results explain why earlier attempts to prepare **12** and detect its formation at room temperature with NMR spectroscopy were not successful. Reaction of $Th^{\bullet+}$ with DMB was followed with cyclic voltammetry and was found to exhibit redox catalysis in which Th was regenerated. With the faster scanning techniques of cyclic voltammetry, the formation of **12** was detectable, with a reduction potential of about −1.0 V at 25 °C and 3 °C. The observed reduction potential was in harmony with reduction potentials of a number of other, stable monoadducts. Thus, the redox catalysis involved the rapid formation of **12** and its rapid decomposition into **8** and Th, the newly formed Th being responsible for the observed enhanced oxidation currents. In contrast, **8** appears to be formed directly by oxidation of DMB by $PO^{\bullet+}PF_6^-$.

Introduction

The thianthrene cation radical ($Th^{\bullet+}$) undergoes reactions with a variety of nucleophiles, electron-rich aromatics, ketones, alcohols, azoalkanes, organometallics, and strong bases. These reactions have been well documented in early and more recent literature.[1−9] To some extent, similar reactions of the phenoxathiin cation radical ($PO^{\bullet+}$) are recorded, too. During recent years, research in one of our laboratories has been focused on the additions of these two cation radicals to alkenes, cycloalkenes, and alkynes. Insofar as alkenes and cycloalkenes are concerned, additions of $Th^{\bullet+}$ gave rise to both mono- (**1**) and bisadducts (**2**), in which the configuration of the alkene was retained in both (Scheme 1).[10−13] Additions of $PO^{\bullet+}$, on the other hand, gave only bisadducts, analogous to **2**.[11,14] The addition reactions were carried out in acetonitrile (MeCN) solution at room temperature. The reactions occurred quickly as judged by the disappearance of the deep color of the cation radical. We were struck at the time by the behavior of a number of branched alkenes which reacted quickly with $Th^{\bullet+}$ but did

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10.1021/jo060067q CCC: $33.50
Published on Web 04/13/2006

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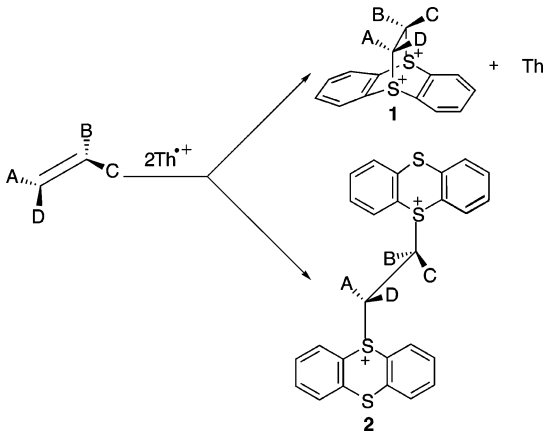

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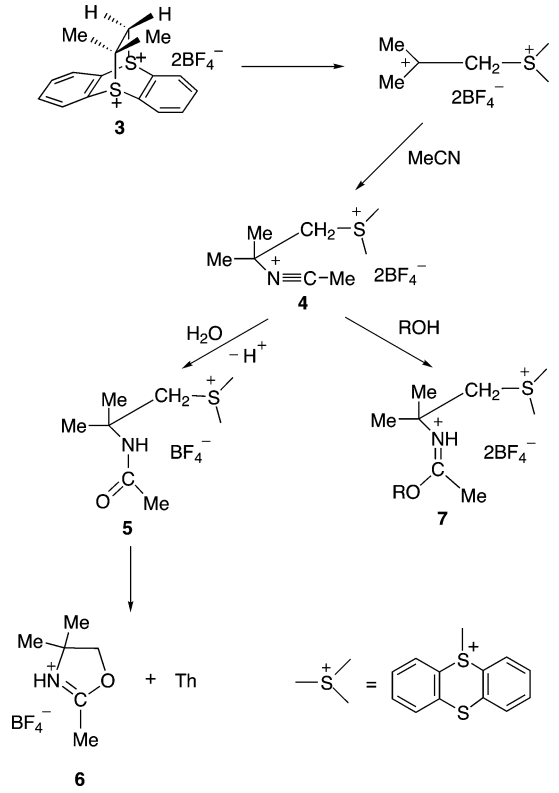

not suffer addition. Instead, the $Th^{\bullet+}$ was reduced to thianthrene (Th). We could, then, find no evidence for the oxidation of the alkenes. Among these alkenes were (*E*)- and (*Z*)-3-methyl-2-pentene and 2,3-dimethyl-2-butene (DMB).[11] Following the discoveries of adduct formation,[10,11] it was found that the monoadducts of some moderately branched alkenes, e. g., isobutene, decomposed spontaneously if kept in solutions of nitriles, with the formation of 2-oxazolines.[12] Thus, the adduct (**3**) of isobutene formed the salt of 2,4,4-trimethyl-2-oxazoline (**6**, Scheme 2). If decomposition occurred in the presence of an alcohol (ROH), oxazoline formation was interrupted and, instead, an (alkoxyalkyl)ammonium salt (**7**) was formed. In these reactions, the water needed for producing **5** and **6** was the residual water in the incompletely dried solvent. The result of forming **6** is the reduction of the thianthrenium unit in **3** to Th. These later findings suggested that alkenes which failed to form adducts but nevertheless appeared to reduce $Th^{\bullet+}$ to Th may

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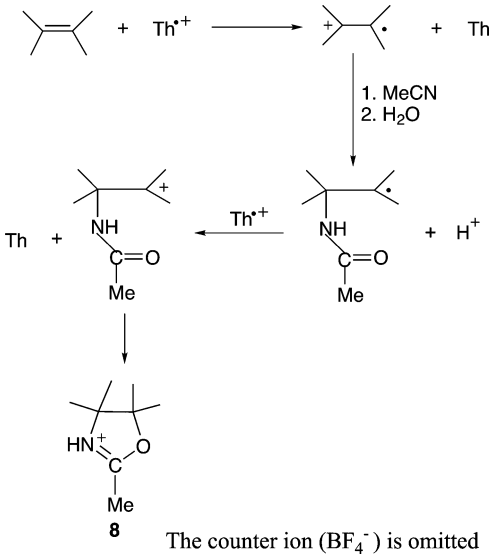

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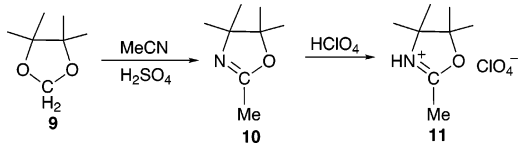


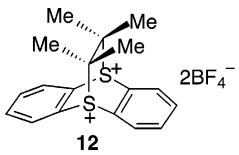
have formed an oxazoline instead. We chose, therefore, to study the behavior of one of these alkenes (DMB) in detail. We have found that, in reaction with $Th^{\bullet+}BF_4^-$, protonated 2,4,4,5,5-pentamethyl-2-oxazoline (**8**) is, indeed, formed. The fact that an adduct could not be found initially suggested that DMB was oxidized by $Th^{\bullet+}$ (Scheme 3) rather than undergoing addition. We set out to investigate that possibility chemically and electrochemically. Furthermore, because $PO^{\bullet+}$ does not form monoadducts with alkenes,[11,14] and thus could not participate as in Scheme 2, we set out to study the reaction of that cation radical with DMB as well.

Results and Discussion

Chemical Investigations. Authentic 2,4,4,5,5-pentamethyl-2-oxazoline (**10**) was prepared from 4,4,5,5-tetramethyl-1,3-dioxolane (**9**), and the perchlorate salt (**11**) of **10** was prepared (Scheme 4) so that the ^1H and ^{13}C NMR characteristics of **8** could be recorded. These characteristics were used in searching with NMR spectroscopy for the formation of **8** in reactions of DMB with $Th^{\bullet+}BF_4^-$.

Reactions of DMB were carried out initially with $Th^{\bullet+}ClO_4^-$ in MeCN at room temperature. Following the usual conditions for preparing adducts, a large excess of DMB was used; the only product detected with GC after workup was Th. In the present work, reactions were carried out first in CD_3CN and with $Th^{\bullet+}BF_4^-$ at 0 °C and a reactant ratio of 1:1. The reactants were mixed after being cooled in an ice bath; as judged by the loss of the color of $Th^{\bullet+}$, the reactions were rapid and led to a large amount of precipitate, assumed to be Th. The ^1H NMR spectrum of the supernatant liquid, withdrawn by syringe into a cold NMR tube, was recorded in an NMR probe that was at room temperature and showed the 4,4,5,5-methyl signals characteristic of **8** (δ: 1.51, s, 6H; 1.40, s, 6H) accompanied by aromatic signals that could be attributed only to a monoad-

duct, i.e., **12**. The intensity of the signals from **12** decreased



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rapidly with time, becoming too small to record after 30 min. The signals of **8** increased correspondingly. Thus, it was evident that DMB could indeed form an adduct at low temperature and that the adduct was converted into a 2-oxazoline quickly at room temperature. Our failure to find an adduct in earlier reactions carried out at room temperature was now understandable.

Further reactions between DMB and $Th^{\bullet+}$ were carried out in an ice/salt bath (−15 °C). Again, the reaction was fast. Transfer of supernatant solution into an NMR tube at −15 °C and thence to an NMR probe precooled to −15 °C revealed the signals of **12** and of a small amount of **8**. The ^{1}H aromatic signals of **12** were clearly those of the monoadduct of a symmetrical alkene,[13] namely, two dd's each of 4H at $\delta = 8.62$ ($J = 5.5$, 3.5 Hz) and 8.21 ($J = 5.8$, 3.3 Hz). The chemical shift of the methyl groups' singlet was at 1.61 ppm. The ratio of **12/8** 6 min after insertion into the probe was 95:5 and remained unchanged during 1 h in the probe at −15 °C. When the temperature of the probe was raised to 0 °C, the ratio of **12/8** changed to 85:15 (77 min) and 55:45 (142 min). After the probe was warmed to 23 °C, the intensity of the signals from **12** decreased rapidly and were no longer visible 165 min after placing the solution in the probe.

The adduct **12** was isolated from a similar experiment at −15 °C by treating the mixture after reaction with cold ether (to dissolve Th), washing the product with cold ether by decantation, and drying with a current of argon while at −15 °C. The **12** obtained in this way in 60% yield had the anticipated NMR spectrum. When recorded at room temperature as quickly as possible after isolation of **12**, the spectrum showed also the presence of **8**, the ratio of **12/8** being 2:1. Within 20 min, the signals from **12** were no longer visible and the spectrum was showing the presence of Th, **8**, and an unknown compound. We have been unable to identify that compound. Attempts to isolate $\mathbf{8BF_4^-}$ from these experiments were unsuccessful.

These experiments show that $Th^{\bullet+}$ does add to DMB and, in fact, rapidly. The adduct is stable in solution at low temperatures but decomposes quickly at room temperature to form **8** and Th. It does not appear that $Th^{\bullet+}$ oxidizes DMB under these conditions. Carrying out reactions between $Th^{\bullet+}$ and DMB at room temperature and seeking an adduct within the usual time frame, conditions that were successful with a number of other adducts, could not succeed.

Reactions with $\mathbf{PO^{\bullet+}PF_6^-}$. Equimolar amounts of $PO^{\bullet+}PF_6^-$ and DMB were allowed to react at −15 °C. Reaction was complete after 15 min and was accompanied by heavy precipitation of solid, assumed to be phenoxathiin (PO). A sample of the colorless supernatant solution was transferred to an NMR probe at −15 °C as described, and the ^{1}H NMR spectrum was again recorded at timed intervals and controlled temperatures. The first NMR scan after 7 min in the probe showed that **8** was present as the major component. Aromatic ^{1}H signals were present and were assignable to PO and also, we propose, to a bisadduct (**13**). The ratio of **8/13** was calculated from integrations of the methyl groups of **8** and the aromatic signals of **13**. The ratio changed with time in the probe and temperature of

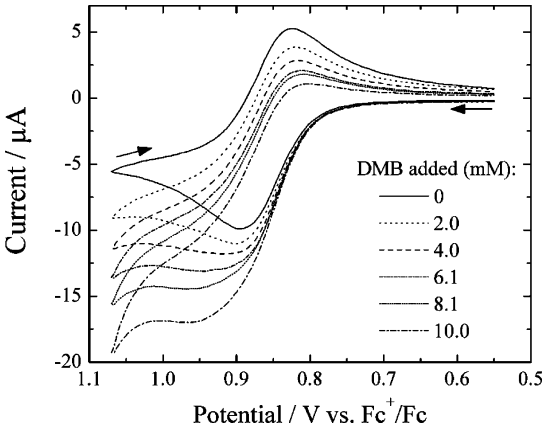
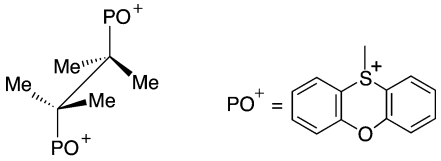


FIGURE 1. Voltammograms of 0.99 mM thianthrene in the presence of the indicated concentrations of 2,3-dimethyl-2-butene (DMB) at 0.100 V/s, 25 °C.

the solution as follows: 80:20 (7 min, at −15 °C), 83:17 (65 min, at −15 °C), 85:15 (after 81 min, probe raised to 0 °C), 90:10 (143 min, at 0 °C), 93:7 (167 min, probe raised to 23 °C). The signals from **13** were no longer visible 228 min after the solution had been placed in the probe and, thus, after 60 min at 23 °C.



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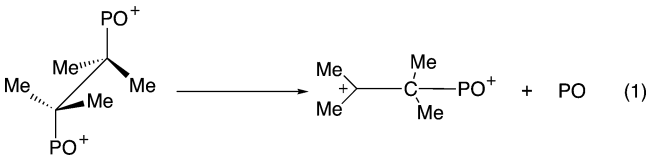
It is evident that, in contrast with reactions of DMB with $Th^{\bullet+}$ in which **12** was the dominant product at −15 °C, the initial dominant product from the reaction with $PO^{\bullet+}$ was **8**. Furthermore, the decomposition of **13** was relatively so slow, as compared with that of **12** even at 0 °C, that it is unlikely that this decomposition could have been the source of **8** at −15 °C. That is, the dominant formation of **8** appears to have been independent of the formation of **13** and to have originated from the oxidation of DMB as shown (with $Th^{\bullet+}$) in Scheme 3. The success of that route to **8** in oxidation of DMB by $PO^{\bullet+}$ must lie in the rapidity of the reactions that follow the formation of $DMB^{\bullet+}$.

The decomposition of **13** is thought to begin with the breaking of a bond to one of the sulfonium sulfur atoms as shown in eq 1, analogously to the route for monoadducts (Scheme 2).



Electrochemical Investigations. Cyclic voltammograms for 0.99 mM Th in MeCN containing 0.10 M Bu_4NPF_6 are shown in Figure 1. They show the reversible oxidation of Th in the absence of added DMB and the continued reversible oxidation but with greater current in the presence of DMB. The voltammograms show that the greater the concentration of added DMB the greater the oxidation current of Th. This is an example of

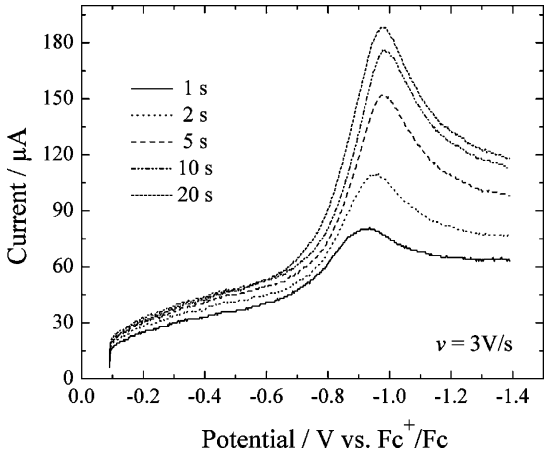


FIGURE 2. Step-and-sweep voltammograms obtained with 1.00 mM thianthrene and 4.00 mM 2,3-dimethyl-2-butene. Potential was held at +1.0 V for the indicated times followed immediately by potential sweep from −0.10 to −1.40 V at 3.00 V/s, 25 °C.

homogeneous redox catalysis[15a,b] in which the Th/Th$^{\bullet+}$ couple is the redox catalyst of a transformation of DMB, a transformation that regenerates Th.

A solution of 1 mM Th and 4 mM DMB was studied at 1 V/s at 25 °C. The negative-going sweep of the voltammogram was extended to −1.4 V, and a small reduction peak was observed at approximately −1.0 V that was not observed in the absence of DMB. The magnitude of this peak was enhanced with step-and-sweep treatment. That is, using the same conditions, the potential was first maintained for variable times (called holding times) at +1.0 V, where Th is oxidized. Thereafter, a linear sweep was applied from −0.1 to −1.4 V (Figure 2). A peak appeared in the region of −1.0 V, and its height increased with increasing holding times, indicating that the concentration of **12** (see below) builds up during the holding time and some **12** can be detected on the subsequent negative-going scan. For holding times greater than 20−30 s, there is very little further increase in the height of the reduction peak for **12** suggesting that its concentration reaches a steady state, with the rate of its electrochemical formation being roughly equal to its conversion to **8** by way of reaction 5. The species responsible for the peak near −1.0 V cannot be **8** because **8**ClO_4^- (i.e., **11**) was found to be reduced at −1.9 to −2.0 V. The product reduced near −1.0 V is believed to be **12** on the basis of its isolation and NMR data at low temperatures and on the basis of the data for the cathodic reduction of a number of authentic monoadducts (Table 1). Table 1 shows that four monoadducts[10,11] have reduction peaks at almost −1.0 V. One bisadduct is included in Table 1, having a reduction potential of about −0.9 V. That potential is in harmony with the reduction potential (−0.93 V vs Fc) reported by Houmam for the bisadduct of cyclohexene.[16]

The electrochemical findings can be summarized with eqs 2−5, in which eq 5 represents several steps (Scheme 2). The detailed stoichiometry of reactions 3−5 differs from the cases considered in the literature,[15a,b] so we resorted to simulation for analysis of the voltammograms in Figure 1.

TABLE 1. Electrochemical Data for Mono- and Bisadducts[a]

alkene	adduct	anion	E_p/V	$E_{p/2} - E_p$/mV	i_p/μA
trans-5-decene	mono	ClO_4^-	−0.98	62	90
trans-3-octene	mono	BF_4^-	−0.99	68	84
cyclooctene	mono	PF_6^-	−0.98	110	42
trans-3-hexene	mono	BF_4^-	−0.98	65	83
cis-2-butene	bis	BF_4^-	−0.88	92	48

[a] Data obtained at 1 V/s with 1 mM reactant. Under the same conditions, 1 mM Th (reversible one-electron oxidation) shows a peak current of 35 μA.

$$\mathrm{Th} \rightleftharpoons \mathrm{Th}^{\bullet+} + \mathrm{e}^- \quad (2)$$

$$\mathrm{Th}^{\bullet+} + \mathrm{DMB} \rightarrow \mathrm{DMB/Th}^{\bullet+} \quad (3)$$

$$\mathrm{DMB/Th}^{\bullet+} + \mathrm{Th}^{\bullet+} \rightarrow \mathbf{12} + \mathrm{Th} \quad (4)$$

$$\mathbf{12} + \mathrm{MeCN} + \mathrm{H_2O} \rightarrow \mathbf{8} + \mathrm{H}^+ + \mathrm{Th} \quad (5)$$

We have simulated the reaction scheme (eqs 2−5) assuming that reaction 3 is rate determining and reactions 4 and 5 (several steps) are fast. We first simulated the voltammograms of Th in the absence of DMB and found that reaction 2 is a simple, reversible electron transfer with a standard potential of 0.85 V (vs Fc). In addition to the data in Figure 1 (0.1 V/s; 1, 2, 4, and 10 mM DMB), data for the same DMB concentrations and scan rates of 0.3, 0.5, and 1.0 V/s were simulated. The rate constant for reaction 3 that provided the best agreement between simulation and experiment was 150 M^{-1} s^{-1}.

Under the time constraints of the NMR study of the reaction of Th$^{\bullet+}$ with DMB at room temperature, **12** could not be detected. It was detected electrochemically, however, by its reduction near −1.0 V. This is shown in Figure 2, and it means that the overall reaction 5 does not go quite to completion at 25 °C in the 0.3 s required to scan from −0.1 V to the reduction peak (near −1.0 V) of **12**.

The peak for **12** near −1.0 V was also seen when the reaction between Th$^{\bullet+}$ and DMB was carried out chemically, and voltammetry was used to monitor the reaction. For example, immediately after mixing solutions of 5.2 mM Th$^{\bullet+}BF_4^-$ and 4.4 mM DMB at 3 °C, the color of Th$^{\bullet+}$ faded and a reduction peak was seen at −1.02 V. This peak was monitored at 3 °C and was found to decline until it was virtually undetectable after 80 min.

The peak heights for the monoadducts (Table 1) are consistent with a two-electron reduction forming Th and alkene, with the exception of the cyclooctene monoadduct whose reduction peak was drawn out and shorter than the others. The reduction peak of the monoadduct of *trans*-5-decene was simulated as a two-electron process with a reasonable diffusion coefficient of the monoadduct (1.6×10^{-5} cm^2/s). On the return sweep, a reversible set of peaks, also adequately simulated, was seen for the Th$^{\bullet+}$/Th couple.

Reactions of Th$^{\bullet+}$ with Other Alkenes. A series of other alkenes was studied by electrochemistry to determine the features needed to see the enhanced anodic currents that were observed in the electrochemistry of Th in the presence of DMB. The results are summarized in Table 2. As can be readily seen, only three alkenes, including DMB, showed significant enhancements of the Th oxidation peak. These three alkenes were the most electron rich of those studied as indicated by oxidation potentials ≤+1.33 V. A very small enhancement was seen for 2-methyl-2-butene. The other alkenes, all with oxidation

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TABLE 2. Reactivity of Electrogenerated $Th^{\bullet+}$ with Alkenes and Anodic Peak Potentials

alkene	E_{pa}/V[a]	reactivity:[b] k_3/M^{-1} s^{-1}
2,3-dimethyl-2-butene	1.21 (2.11)	150
2,3,4-trimethyl-2-pentene	1.24 (1.90)	100
1,2-dimethylcyclohexene	1.33 (1.77)	80−120
2-methyl-2-butene	1.44	barely detectable
trans-3-hexene	1.77	none
cis-4-methyl-2-pentene	1.76	none
cis-2-heptene	1.74	none
cis-2-hexene	1.75	none
trans-3-octene	1.77	none
trans-5-decene	1.77−1.86[c]	none
cyclooctene	1.67−1.73[c]	none
trans-4-methyl-2-pentene	1.80	none
trans-2-pentene	1.89	none
2-ethyl-1-butene	1.86	none

[a] Determined at 1.00 V/s with ca. 1 mM alkene. Second entry in parentheses is for a second, irreversible anodic peak. [b] Rate constants evaluated by digital simulation. Estimated error ±10%. [c] Broad, irreversible oxidation peak over this potential range.

potentials more positive than 1.7 V, did not cause an enhancement of the anodic peak current of Th. This means that any reaction of these alkenes that produces Th was too slow to be detected by cyclic voltammetry even at the smallest scan rates that were practical. Nevertheless, on a preparative, chemical time scale, the alkenes with the larger oxidation potentials in Table 2 gave isolable adducts.

The rate of reaction 3 is significant only for the three alkenes with the least positive oxidation potential. They bear four alkyl groups attached to the central ethylene unit, and accordingly, they are the most electron-rich alkenes. It seems reasonable that addition of $Th^{\bullet+}$ to the alkene, as in reaction 3, will be fastest for the most electron-rich alkenes in agreement with our observations. The oxidation of phenoxathiin ($E^\circ = 0.81$ V) was studied in the presence of DMB, but only a very slight enhancement of the anodic peak current was detected.

The data in Table 2 may suggest that what we show in Figure 1 is redox catalysis associated with oxidation of DMB. However, the formation and detection of **12** in the rapid voltammetric sweeps is persuasive that the electrochemical data are consistent with the formation of **12** and its rapid decomposition leading to **8**.

Conclusions

Instead of being inhibited to addition of $Th^{\bullet+}$ by its four attached methyl groups, the double bond of DMB is very receptive to addition, even at −15 °C. At that temperature, a stable monoadduct (**12**) is formed. The adduct, however, is quite unstable in MeCN solution at room temperature. It appears that the electron-donating character of the four methyl groups not only enhances addition to the double bond but also promotes spontaneous decomposition of the adduct in solution at room temperature. Decomposition leads to the formation of the pentamethyl-2-oxazoline salt (**8**) and thus accounts for the finding in the reactions of DMB with $Th^{\bullet+}$ at room temperature that **8** and Th were formed rather than **12**. DMB has thus served as a model of what may be expected of reactions of similarly branched alkenes with $Th^{\bullet+}$. The formation of **8** also occurs in reactions of DMB with $PO^{\bullet+}$. However, in this case, the intervention of an adduct (**13**) is not observed. The difference in pathways to **8** may be attributable to the ways in which these cation radicals add to alkenes. That is, with $Th^{\bullet+}$, stereospecific cycloaddition can lead to monoadducts such as **12**, but $PO^{\bullet+}$ appears unable to do that.

Experimental Section

Thianthrene cation radical tetrafluoroborate ($Th^{\bullet+}BF_4^-$) and perchlorate ($Th^{\bullet+}ClO_4^-$) were prepared as described previously;[12] phenoxathiin cation radical hexafluorophosphate ($PO^{\bullet+}PF_6^-$) was prepared in a similar way. $Th^{\bullet+}ClO_4^-$ was used early in this work, but because of its potential explosiveness, its use has now been abandoned. A 300 MHz NMR instrument was used for following changes in ^{1}H NMR spectra over timed periods. A 500 MHz NMR instrument was used to obtain ^{1}H NMR spectra at timed intervals and controlled temperatures. CD_3CN was used as the NMR solvent unless otherwise stated.

4,4,5,5-Tetramethyl-1,3-dioxolane (9) was prepared in 65% yield as described for other 1,3-dioxolanes.[17] ^{1}H NMR, 300 HMz, δ: 5.01 (s, 2H); 1.22 (s, 12H).

2,4,4,5,5-Pentamethyl-2-oxazoline (10) was prepared as described[18] from **9** in 20% yield. ^{1}H NMR ($CDCl_3$), 300 MHz, δ: 1.85 (s, 3H); 1.23 (s, 6H); 1.09 (s, 6H). Lit.,[19] ^{1}H NMR, ($CDCl_3$), 100 MHz, δ: 1.79 (s, 3H); 1.20 (s, 6H); 1.05 (s, 6H). ^{1}H NMR (CD_3CN), 300 MHz, δ: 1.77 (s, 3H); 1.22 (s, 6H); 1.06 (s, 6H).

Preparation of 11. Perchloric acid (70%, 0.17 mL, 1.97 mmol) was added dropwise to **10** (268 mg, 1.89 mmol). The mixture was allowed to stand at room temperature. Crystals precipitated and were filtered and washed with ether to give 93 mg (0.39 mmol, 20%) of white product. Mp 111−114 °C. ^{1}H NMR, δ: 10.62 (br s, 1H); 2.32 (s, 3H); 1.52 (s, 6H); 1.40 (s, 6H). ^{13}C NMR, δ: 176.5 (−C═N), 100.3 (quat), 67.4 (quat), 23.1 (CH_3), 22.9 ($2CH_3$), 14.9 ($2CH_3$).

Reaction of DMB with $Th^{\bullet+}X^-$. A. At Room Temperature. To a suspension of 319 mg (1.02 mmol) of $Th^{\bullet+}ClO_4^-$ in 8 mL of acetonitrile was added 1.2 mL (10 mmol) of DMB. The deep color of $Th^{\bullet+}$ discharged very quickly, accompanied by the deposit of a white solid. Addition of 50 mL of ether caused the solid to dissolve, indicating that it was thianthrene (Th). GC assay of the solution showed the presence of 1.17 mmol (114%) of Th.

B. At 0 °C. A suspension of 409 mg (1.35 mmol) of $Th^{\bullet+}BF_4^-$ in 4 g of CD_3CN was cooled in ice, and 0.16 mL (1.35 mmol) of DMB was injected. The deep color of $Th^{\bullet+}$ disappeared very quickly with the precipitation of a white solid. After 10 min of stirring, the ^{1}H NMR spectrum was recorded at 300 MHz, showing two major 6H peaks at 1.51 and 1.40 ppm and the methyl peaks of unreacted DMB. The solution was allowed to warm to room temperature and was stirred overnight. The solvent was removed under vacuum, and the residue was washed with ether to remove Th, leaving a sticky solid whose NMR spectra, including DEPT, HMQC, and HMBC, were consistent with the formation of protonated 2-CD_3-4,4,5,5-tetramethyl-2-oxazoline. ^{1}H NMR, δ: 1.51 (s, 6H); 1.40 (s, 6H). ^{13}C NMR, δ: 176.7 (−C═N), 100.4 (quat), 67.4 (quat), 23.1 (CH_3), 22.9 (2 CH_3), 14.9 (2 CH_3).

C. At −15 °C. Formation of Monoadduct 12. $Th^{\bullet+}BF_4^-$ (379 mg, 1.31 mmol) and 4.5 mL of MeCN were placed in a septum-capped flask that had been flushed with argon. The flask was cooled in an ice-salt bath (−15 °C), and into it was injected a cold solution (−15 °C) of 0.16 mL (1.31 mmol) of DMB in 0.5 mL of MeCN. During the addition of DMB, the color of $Th^{\bullet+}$ disappeared very quickly with precipitation of a white solid. Cold ether (0 °C) was added dropwise into the flask to dissolve Th, and the supernatant liquid was decanted. The residue was washed similarly with ether twice. The remaining white solid was dried with a current of argon

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while in the ice-salt bath, giving 188 mg (0.396 mmol) of white solid shown to be **12** in 60% yield. A sample of the cold solid was taken into an NMR tube containing CD_3CN at −15 °C, and the ^1H NMR spectrum was recorded in a 300 MHz NMR probe that was at room temperature. The spectrum showed the peaks of monoadduct **12** and of protonated 2-CD_3-4,4,5,5-tetramethyl-2-oxazoline (**8**) in a ratio of 2:1. Within 20 min, the peaks of **12** were no longer visible. **12**: mp 138−140 °C (dec). ^1H NMR, 500 MHz, δ (*J*): 8.62 (5.5, 3.5, dd, 4H); 8.22 (5.8, 3.3, dd, 4H); 1.62 (s, 12H).

D. Conversion of Monoadduct 12. As described above (**C**), a cold solution of 0.147 mL (1.24 mmol) of DMB in 0.5 mL of CD_3CN was added to a solution of 374 mg (1.24 mmol) of $Th^{\bullet+}BF_4^-$ at −15 °C. A sample of the supernatant solution was removed into an NMR tube at −15 °C and thence to a 500 MHz NMR probe precooled to −15 °C. The ^1H NMR spectrum was recorded at timed intervals and controlled temperatures. The ratio of peaks of **(2-CD_3-8)BF_4^-/12** increased with time in the probe and temperature of the solution as follows: 5:95 (7 min, at −15 °C), 7:93 (62 min, at −15 °C), 15:85 (77 min, at 0 °C), 45:55 (142 min, at 0 °C). After the probe had been warmed to 23 °C, the signals of **12** were no longer visible.

The remaining solution was stirred 0.5 h at −15 °C, and the same workup as described in (**C**) gave white monoadduct **12** at −15 °C, which was dissolved directly in 7 mL of CH_3CN at −15 °C. During the course of the stirring, the solution turned pink. After 1.5 h of stirring at low temperature (in the range of −15 °C to 0 °C), the solution was allowed to warm to room temperature and continued to be stirred until the pink color of the solution disappeared. Ether was added into the flask, causing precipitation of a sticky solid. After the decantation of the solvent, the sticky solid was dried with a current of air. The ^1H NMR (300 MHz) spectrum showed it to be mainly **8BF_4^-** with δ: 2.31 (s, 3H); 1.51 (s, 6H); 1.40 (s, 6H).

Reaction of DMB with $PO^{\bullet+}PF_6^-$. A. A similar experiment with 497 mg (1.44 mmol) of $PO^{\bullet+}PF_6^-$ and 0.17 mL (1.44 mmol) of DMB in CH_3CN was carried out at −15 °C. Reaction was complete in 15 min and was accompanied by heavy precipitation of solid. The same workup procedure as that with $Th^{\bullet+}BF_4^-$ yielded a white solid at −15 °C. A small amount of solid was removed into an NMR tube containing CD_3CN at −15 °C, and the ^1H NMR spectrum was run in a 300 MHz probe that was at room temperature. Only the following peaks were seen: 2.30 (s, 3H); 1.52 (s, 6H); 1.40 (s, 6H). The data are consistent with the formation **8**.

B. A second, similar experiment with 412 mg (1.19 mmol) of $PO^{\bullet+}PF_6^-$ and 0.14 mL (1.19 mmol) of DMB in 5 g of CD_3CN was carried out at −15 °C. After 25 min of stirring, the colorless supernatant solution was transferred into an NMR tube at −15 °C and thence to a 500 MHz NMR probe precooled to −15 °C. The ^1H NMR spectrum was again recorded at timed intervals and controlled temperatures. The initial ^1H NMR spectrum, completed at 7 min after insertion into the probe at −15 °C, showed the peaks of protonated **2-(CD_3)-8** as the major product, accompanied by peaks of PO and a small number of signals ascribed to bisadduct **13** of DMB. ^1H NMR δ: 7.95 (7.0, 2.0, dd) and 7.93 (8.5, d, 8H); 7.65 (8.5, d) and 7.61 (7.5, 8.0, t, 8H); 1.58 (s, 12H). The ratio of **8**/**13** was calculated from integrations of the methyl groups of **8** and the aromatic signals of **13**. The ratio changed with time in the probe and temperature of the solution as follows: 80:20 (7 min, at −15 °C), 83:17 (65 min, at −15 °C), 85:15 (81 min, at 0 °C), 90:10 (143 min, at 0 °C), 93:7 (163 min, at 23 °C). After 228 min and at 23 °C, the signals from **13** were no longer visible.

Electrochemistry. The source and treatment of solvent and electrolyte and the cell and potentiostat that were used are described elsewhere.[20] Except as noted, the experiments were conducted at 25 °C. The working electrode was a glassy carbon disk whose area was 0.0814 cm^2. The silver reference electrode (AgRE) was a silver wire in contact with a solution of 0.010 M $AgNO_3$ and 0.10 M Bu_4NPF_6 in acetonitrile. The potential of the AgRE was frequently calibrated with respect to the potential of the ferrocene/ferrocenium couple, and all potentials are reported vs ferrocene (Fc). The nominally anhydrous acetonitrile contained up to 5 mM water after solution preparation and transfer to the cell.[21] The electrolyte was 0.10 M Bu_4NPF_6. Digital simulations were carried out with DigiSim, version 3.03 (Bioanalytical Systems). The simulations employed potential steps of 1−5 mV, planar diffusion, and an expanding space-grid factor of 0.5. The accuracy of the simulation program has been confirmed by simulations of various mechanisms for which theoretical results are available and by the comparison of the simulations with theory (e.g., reversible and irreversible electron-transfer reactions, chemical reaction preceding electron transfer, chemical reaction following electron transfer,[22] chemical reaction interposed between two electron transfers,[23] and redox catalysis[15a]). Excellent agreement between simulation and theory was always found.

Acknowledgment. D.H.E. thanks the National Science Foundation, Grant CHE-0347471, and H.J.S. thanks the Welch Foundation, Grant D-0028, for support.

JO060067Q

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