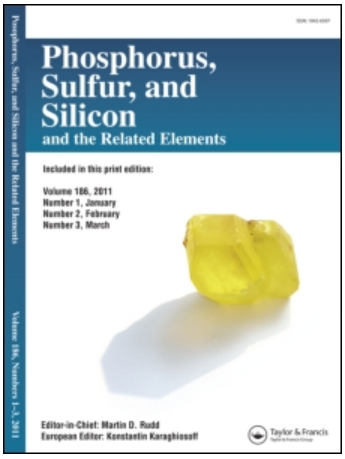


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# THE STUDY OF THE REACTION BETWEEN THIOPHOSPHORYL ESTERS AND BORON TRIBROMIDE. THE SYNTHESIS OF OXATHIAPHOSPHABORETANES

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# THE STUDY OF THE REACTION BETWEEN THIOPHOSPHORYL ESTERS AND BORON TRIBROMIDE. THE SYNTHESIS OF OXATHIAPHOSPHABORETANES

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Reactions between three thiophosphoryl esters and boron tribromide are reported. O,O,O-triethyl phosphorothionate (**1**) and O,O-diethyl methanephosphonothionate (**5**) gave substituted oxathiaphosphaboretanes **4** and **7** respectively. O-methyl diphenyl-phosphinothionate (**9**) led to the complex **11** and the corresponding oxathiaphosphaboretane **12**. In order to establish the mechanism, reactions were monitored by the multinuclear NMR spectroscopy.

*Keywords:* Thiophosphoryl compounds; boron tribromide; oxathiaphosphaboretanes; NMR studies; mechanism

## INTRODUCTION

Recently, there have been published the intriguing results of reactions between phosphates or alkylphosphonates and alkylboron halides[1,2]. Authors found that the products have cubanoide-like structures. Similar structures were obtained and described by Diemert *et al.*[3] and Bontchev *et al.*[4]. But studies on this topic started 40 years ago, commenced by Gerrard *et al.*,[5,6] who explored this kind of reactions, reporting the preparation of the famous boron phosphate $[PBO_4]_n$ after the prolonged heating of trimethyl phosphate with boron tribromide.

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Since this date some interesting works have been published, presenting different approaches to this topic. Bravo and Laurent[7] presented reactions of boron trichloride with trialkyl phosphates and dialkyl alkanephosphonates giving bicyclic compounds bearing tetracoordinated phosphorus and boron atoms. Kastromina *et al.*[8] published the synthesis of various binuclear complexes of boron with hydroxyethylidenediphosphonic acids. Washio *et al.*[9] patented the synthesis and the application of tetrakis(dibutylphosphato)borate.

However, only a few papers were published about reactions of thiophosphoroorganic esters with boron Lewis acids. Palmtag and Binder[10] performed the reaction of tris-(diethylphosphito)-borate with sulfur leading to tris-(diethylthiophosphato) borate. Singh *et al.*[11] presented the study on reaction of B-chlorodioxaborolanes and -borinanes with dithiophosphates and Chaturvedi *et al.*[12] investigated the reaction of trimethylaminoborane with O,O-dialkyl dithiophosphates. Very recently, Brusilovets *et al.*[13] published their study on the conversions of phosphan-imidothioic amides in reaction with boron trichloride and Nizamov *et al.*[14] treated trialkyl borates with phosphorus pentasulfide.



All these papers are confined to the formation of compounds containing tricoordinated boron. It seemed to us interesting to examine the reactions leading to tetracoordinated boron and phosphorus containing compounds. Simultaneously, we wanted to investigate the behaviour of thiophosphororganic esters in reactions with boron Lewis acids (such as boron trihalides) in comparison with non-sulfurated phosphates and phosphonates.

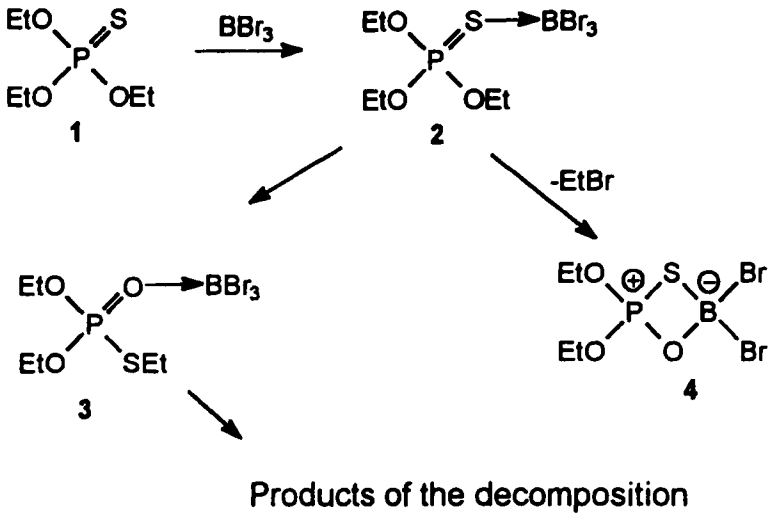
In this paper, we wish to present reactions of thio-analogues of phosphates, phosphonates and phosphinates with boron tribromide.

## RESULTS AND DISCUSSION

The reactions of three thiophosphororganic esters: O,O,O-triethyl phosphorothionate **1**, O,O-diethyl methanephosphonothionate **6** and O-methyl diphenylphosphinothionate **11** with boron tribromide were performed.

The reaction with thiophosphate **1** led to the oxathiaphosphaboretane derivative **4** – B,B-dibromo-P,P-diethoxy-1,2,3,4-oxathiaphosphaboretane (**4**), which was isolated from the post-reaction mixture and was char-

acterised by the NMR spectroscopy and the mass spectrometry. This compound was found to be extremely moisture sensitive, (Scheme 1).

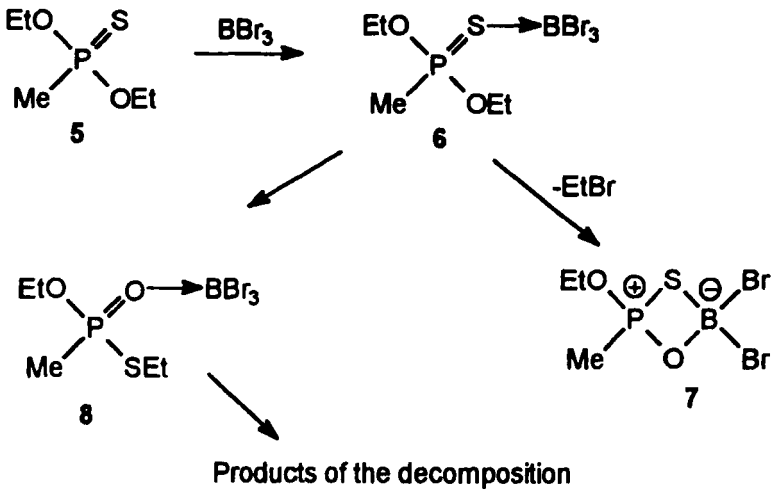



SCHEME 1

The second product of this reaction was insoluble in most of common solvents, it was then difficult to perform NMR study. But when the reaction was carried out in a diluted solution of reagents, a clear gel was formed, which was possible to analyze by NMR spectroscopy. $^{1}H$ and $^{13}C$ NMR measurements showed ethyl groups linked to sulfur ($\delta_H$=3.1; $\delta_C$=31.4 ppm for S-$CH_2$- group). $^{11}B$ and $^{31}P$ NMR – the formation of tetracoordinated phosphorus and boron ($\delta_B$=-4.4; −7.3. $\delta_P$=31.8; 21.8 ppm) atoms. The EI-MS did not give the significant peak until the apparatus temperature limit (365°C) and the FAB-MS could not be used, because the product reacted with a polyol matrix. Thus, the structure of the second product remained unresolved.

The reaction between thiophosphonate **5** and boron tribromide resulted in the formation of the cyclic compound **7** bearing POEt groups and a second product with tar consistence. *(Scheme 2)* The first product – B,B-dibromo-P-ethoxy-P-methyl-1,2,3,4-oxathiaphosphaboretane **7** was isolated from the post-reaction mixture and characterised by the NMR

spectroscopy and the mass spectrometry. The compound **7** was also found to be moisture sensitive.



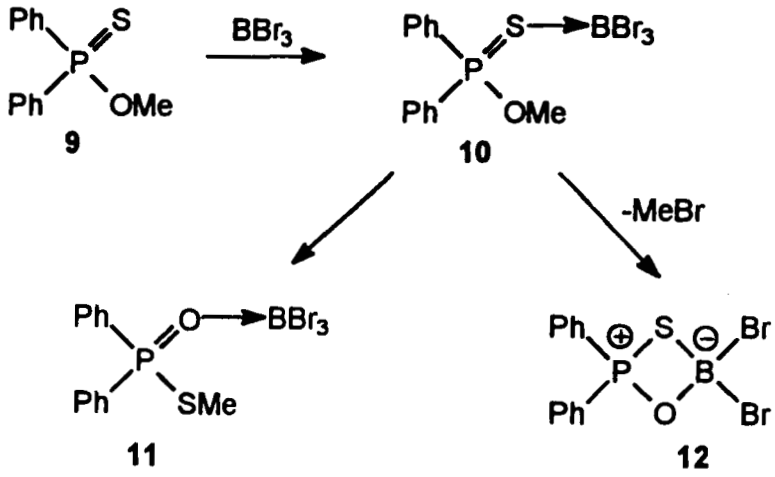

SCHEME 2

The second product was found to be insoluble in the majority of solvents, so its NMR studies were performed as in the previous case. NMR studies showed the occurrence of SEt group ($\delta_H$=3.05; $\delta_C$=31.40 for for S-$CH_2$- group) and tetracoordinated boron and phosphorus ($\delta_B$=-3.5, −17.4 and − 24.3; $\delta_P$= 93.0, 77.4 and 73.8).

The Electron Impact Mass Spectrometry gave no significant high-mass peak until 365°C. As in the previous case, the structure of this product remained unresolved.

The reaction between thiophosphinate **9** with boron tribromide lead to the formation of the complex **11** bearing the P=O→B bond and B,B-dibromo-P,P-diethoxy-1,2,3,4-oxathiaphosphaboretane **12** in a 1:1 ratio. *(Scheme 3)* The separation of the products **11** and **12** failed due to their extreme sensitivity. However, the NMR spectroscopy together with the mass spectrometry allowed to establish their structures.

NMR studies showed clearly that the complex **11** contained the SMe group ($\delta_H$=2.70; $\delta_C$=16.75; $\delta_P$=66.6; $\delta_B$=-6.6 ppm) and that the compound **12** is the product of an intramolecular condensation as no signals of the




SCHEME 3

methoxy or thiomethyl group was detected ($\delta_P$=80.5; $\delta_B$=-6.6 ppm). The EI-MS of the mixture showed two molecular peaks m/z [$M^+$]=404 corresponding to the cyclic product **12** and m/z [$M^+$]=499 corresponding to the complex **11**.

## NMR monitoring of the reactions

The first step to establish the mechanism of the reaction was to monitor them by NMR. To do this, the reactions were carried out in the NMR apparatus tube and stored for several days at room temperature.

Reaction between the thiophosphate **1** and boron tribromide occurred immediately leading to the clear formation of the complex **2**. The $^{31}P$ NMR signal occurred at 45.7 ppm, more than 20 ppm upfield of the starting thiophosphate ($\delta_P$=68.27 ppm), the $^{11}B$ NMR signal occurred at −12.9 ppm – about 50 ppm upfield of the starting tribromide ($\delta_B$=39.2 ppm). $^1H$ NMR signals shifted about 0.5 ppm downfield. As it is visible, boron became tetracoordinated and the thiophosphoryl group formed a coordinative bond.

After one hour, the transformation of the complex **2** was observed. The evolving of bromoethane was detected ($\delta_H$=3.34 and 1.57; $\delta_C$=28.41 and

19.53 ppm) and two new phosphorus resonance signals occurred ($\delta_P$=47.1 and 51.3 ppm). Their intensities increased within the next 8 hours. The $^1H$ and $^{13}C$ NMR spectra showed the presence of the compound bearing ethoxy and thioethyl groups ($\delta_H$=4.38 and 3.34; $\delta_C$=67.83 and 32.44 ppm for -$CH_2$-). Based on relative intensities and decoupling (H from P) experiments, the $^{31}P$ NMR signal at 47.1 ppm was assigned to the compound bearing only ethoxy groups of the postulated structure **3** - a product of an intramolecular rearrangement. The other signal ($\delta_P$=51.3) was assigned to the cyclic compound **4** - the product of an intramolecular cyclisation. Both compounds (**3** and **4**) gave $^{11}B$ NMR signals at −10.3 and −13.7 ppm, respectively.

During the next 10 hours a further reaction occurred. A slow disappearance of the signals of the compounds **2** and **3** and the occurrence of new broad signals of the second product ($\delta_P$=61.9, 34.6, 31.7, 21.7 and 13.3; $\delta_B$=-2.4, −4.4, −7.3 and −23.1) demonstrated clearly the decomposition of the complex **3**.

Within a day the reaction was completed and the measurements recorded within the next 3 days showed no changes. NMR studies showed that the post-reactior mixture contained exclusively the end products: the cyclic oxathiaphosphaboretane **4** and the secondary product.

All these data seemed to suggest the following mechanism *(Scheme 1)*. Thiophosphate **1**, reacts with boron tribromide to form the complex **2**, which undergoes the intramolecular rearrangement to yield complex **3**, which decomposes to give the substance of the unresolved structure. The complex **2** parallelly undergoes the intramolecular condensation to give the cyclic compound – oxathiaphosphaboretane **4**.

The reaction between the thiophosphonate **5** and boron tribromide occurred also immediately to give the complex **6**. The $^{31}P$ NMR signal occurred at 90.32 ppm, about 4.5 ppm upfield of the starting thiophosphonate ($\delta_P$=94.7 ppm) and the $^{11}B$ NMR signal occurred at −10.9 ppm, which is about 50 ppm upfield of the starting tribromide. $^1H$ NMR signals were shifted 0.5 ppm downfield of the starting compound **5**. As previously, we observed a strong shielding of boron and a weaker but significant shielding of phosphorus. Protons and carbons were deshielded, which suggests a stronger electron-withdrawing character of the P-S bond.

About 6 hours later, the transformation of the complex **6** was observed. The progress of the reaction was visible after the next 48 hours, where the formation of the cyclic compound **7** was detected by the NMR spectros-

copy ($\delta_H$=4.10, 2.45 and 1.35 ppm; $\delta_C$=64.1, 32.2 and 15.5 ppm; $\delta_B$=-12.9 ppm; $\delta_P$=81.5 ppm). The evolution of bromoethane was also detected. Simultaneously, the rearrangement of the ethyl group occurred, leading to the complex **8** containing PSEt groups ($\delta_H$=3.15 ppm; $\delta_C$=30.32 ppm for $CH_2$-S-P group).

After the next 10 hours, the decomposition of the complex **8** was observed; its signals disappeared and broad signals occurred instead. Within the next **8** hours the reaction was completed and the NMR analysis showed the presence of the end products of the reaction: the cyclic oxathiaphosphaboretane **7** and the broad signals of the secondary product.

These data suggest the following mechanism of this reaction *(Scheme 2)*: the thiophosphonate **5** reacts with boron tribromide to form the complex **6**, which undergoes an intramolecular condensation to form the cyclic compound **7**. The complex **6** undergoes the parallel intramolecular rearrangement to give the complex **8**, which decomposes resulting in a tar substance of an unresolved structure.



The reaction between the thiophosphinate **9** and boron tribromide *(Scheme 3)* occurred also immediately to form the complex **10**. The $^{31}P$ NMR signal occurred at 78.1 ppm, about 7 ppm upfield of the starting thiophosphinate ($\delta_P$=84.79 ppm), the $^{11}B$ NMR signal occurred at −3.4 ppm, which is about 45 ppm upfield of the starting tribromide. $^1H$ NMR signals were shifted 0.4 ppm downfield compared to the starting compound **9**. As previously, we observed the same phenomena confirming clearly the formation of the P=S→B coordinative bond.

One hour later the simultaneous formation of compounds **11** and **12** was observed. Both $^1H$ and $^{13}C$ NMR spectra showed the evolution of bromomethane ($\delta_H$=2.65 ppm; $\delta_C$=10.48 ppm) and the formation of a SMe group ($\delta_H$=2.71 ppm; $\delta_C$=16.47 ppm). The signals in the $^{31}P$ NMR spectrum occurred at 66.8 and 80.2 ppm and in the $^{11}B$ NMR spectrum at −6.6 ppm as a broad signal. After 3 hours, the reaction was completed giving two exclusive end products in a 1:1 ratio: the complex **11** bearing the P=O→B coordinative bond and the cyclic compound **12** – the product of intramolecular cyclisation of the complex **10**.

These data suggest that the thiophosphinate reacts with boron tribromide to give the complex **10**, which undergoes two parallel reactions: the intramolecular rearrangement to give the complex **11** and the intramolecular cyclisation leading to the cyclic product **12**. *(Scheme 3)*.

## CONCLUSIONS

The reaction of boron tribromide with thio-analogues of organophosphorus esters leads in each case to oxathiaphosphaboretanes. accompanied by the product of the complexes **3** or **8** or, in the case of the thiophosphinate **9**, by the complex **11**.

We have demonstrated that the P=S→B complexes formed and underwent subsequently two parallel reactions – the rearrangement to the P=O→B complexes and the cyclisation to oxathiaphosphaboretanes.

We cannot explain why the complexes **3** and **8** decompose while the complex **11** does not. But considering the fact that the complexes **3** and **8** bear alkoxy groups, while the complex **11** does not, we can suppose that the condensation between the P-OEt and the Br-B groups occurs leading to the formation of P-O-B bonds. That is why the complex **11** remained intact. Apparently, alkoxy groups react more readily than thioalkyl with the B-Br group.

It is unclear why the rearrangement occurs, but we can look for the answer in the "thionate – thiolate" tautomerism. Hudson[15] stated that in solution, the equilibrium is shifted mostly towards the thiolate form. Possibly, in the case of P=S→B complexes the similar situation takes place – the P=O→B complex is more stable and its formation is much more preferred.

Due to the decomposition of complexes **3** and **8**, it was practically impossible to state whether this is an equilibrium or a non-reversible reaction. But analysing the case of the thiophosphinate, where polymerisation does not occur, it was found that it was an irreversible rearrangement as no trace of a P=S→B complex was detected in the post reaction mixture. *Per analogia* one can expect that in other cases this is also an irreversible reaction not an equilibrium, especially since the mechanisms are similar.

But this problem is still an object of further studies.

## EXPERIMENTAL

All solvents and reagents (Prolabo, Aldrich) were routinely distilled and dried prior to use. Boron tribromide, triethyl phosphite, O,O-diethyl methanephosphonothionate and methyl diphenylphosphinite (ALDRICH) were

used as received. All reactions were carried out under nitrogen. NMR spectra were recorded on a Brucker AC 300 spectrometer, EI-MS were recorded on a Varian MAT 311 spectrometer.

**CAUTION**!! All products of these reactions are extremely toxic. The reactions must be carried out under the very efficient hood and **in a well-ventilated** room.

### Synthesis of O,O,O-triethyl phosphorothionate (1)

To a solution of triethyl phosphite (0.1 mol, 16.6 g, 17.1 mL) in toluene (60 mL), sulfur powder (0.11 mol, 3.5 g) was added portionwise. Exothermic reaction occurred accompanied by an immediate dissolution of sulfur. The mixture was refluxed for 3 hours. The reaction was monitored by $^{31}P$ NMR (disappearance of the signal at 138.34 ppm corresponding to triethyl phosphite. Then it was filtrated, solid residue discarded and the filtrate was evaporated and dried in the vacuum to obtain 20 g of product in quantitative yield. The product was distilled in the vacuum, $bp_{10}$ = 91–92°C, lit[16] $bp_{17}$= 99–101°C. $^1H$ NMR (300 MHz, $CDCl_3$): δ 4.13 (dq, $^3J_{HH}$ = 7.1 Hz and $^3J_{PH}$ = 9.5 Hz, $CH_2CH_3$, 6H); 1.33 (dt, $^3J_{HH}$ = 7.1 Hz and $^4J_{PH}$ = 0.6 Hz, $CH_2CH_3$, 9H). $^{31}P$ NMR (121 MHz, $CDCl_3$): δ 68.27

### *O,O-diethyl methanephosphonothionate (6)*

$^1H$ NMR (300 MHz, $CDCl_3$): δ 4.11 (dq, $^3J_{HH}$ = 7.1 Hz and $^3J_{PH}$= 10.1 Hz, $CH_2CH_3$, 6H); 1.81 (d, $^3J_{PH}$ = 15.6 Hz, $CH_3$, 3H); 1.32 (dt, $^3J_{HH}$ = 7.1 Hz and $^4J_{PH}$ = 0.6 Hz, $CH_2CH_3$, 9H). $^{31}P$ NMR (121 MHz, $CDCl_3$): δ 94.73.

### Synthesis of O-methyl diphenylthiophosphinate (9)

To a solution of O-methyl diphenylphosphinite (10 mmol, 2.16 g, 2 mL) in toluene (30 mL), sulfur powder (11 mmol, 0.35 g) was added portionwise. Exothermic reaction occurred accompanied by immediate dissolution of sulfur. When the whole amount of sulfur was added, the mixture was refluxed for 3 hours. The reaction was monitored by $^{31}P$ NMR (disappearance of signal at 117.69 ppm corresponding to O-methyl diphenylphosphinite). Then it was filtrated, the solid residue discarded and the filtrate was evaporated and dried in the vacuum to obtain 2.4 g (97%) of a light yellow

solid which was recrystallised from methanol. Mp = 88–90°C, lit[17] = 87–88°C. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.87 (ddd, $^2J_{PH}$ = 13.7 Hz and $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.6 Hz); 7.41 (m, ArH, 6H); 3.69 (d, $^2J_{PH}$ = 13.8 Hz, $CH_3$, 3H). $^{31}$P NMR (121 MHz, $CDCl_3$): δ 87.79

## The reaction of O,O,O-triethyl phosphorothionate (1) with boron tribromide

To a previously prepared solution of boron tribromide (3.79 mmol, 0.9 g) in chloroform (30 mL) cooled to −15°C, triethyl thiophosphate (0.75 g, 3.79 mmol) was added. The mixture was allowed to worm up to room temperature, then it was refluxed for 14 hrs. Then, the mixture was evaporated and the dark yellow residue was treated with chloroform, the solid residue was filtered off and the filtrate was evaporated to give 0.64 g of **4** as a white powder.



## The reaction of O,O-diethyl methanethiophosphonate (5) with boron tribromide

To a solution of boron tribromide (3.2 mmol, 0.8 g) in chloroform cooled to −15°C, O,O-diethyl methanethiophosphonate (3.2 mmol, 0.5 g) was added. The mixture was allowed to worm up to room temperature and then it was refluxed for 14 hrs. Then, the mixture was evaporated and the dark yellow residue was treated with chloroform, the solid residue was filtered off and the filtrate was evaporated to give 0.50 g of the cyclic product **7**.

## Reaction of O-methyl diphenylthiophosphinate (9) with boron tribromide

To a solution of boron tribromide (1.6 mmol, 0.4 g) in chloroform cooled to −15°C, O-methyl diphenyl thiophosphinate (1.6 mmol, 0.4 g) was added. The mixture was allowed to worm up to room temperature, then it was refluxed for 14 hrs. Then, the mixture was evaporated and the dark yellow residue was dissolved in chloroform. The solution was filtrated and the filtrate was evaporated in the vacuum to give 0.7 g of the mixture of compounds **11** and **12** as a white powder.

### NMR monitoring of the reaction

In a NMR tube with deuterochloroform (0.4 mL) boron tribromide (0.379 mmol, 0.09 g) was dissolved. The tube was cooled to −15°C then the thiophosphoryl reagent (0.379 mmol) was added. The tube was stored at room temperature for several days and NMR spectra were recorded in 3 or 8 hour intervals.

### Complex of O,O,O-triethyl phosphorothionate with boron tribromide (2)

$^1$H NMR (300 MHz, $CDCl_3$): δ 4.41 ($dq_D$, $^3J_{HH}$ = 7.1 Hz and $^3J_{PH}$= 8.3 Hz, $CH_2CH_3$, 6H); 1.38 (dt, $^3J_{HH}$ = 7.1 Hz and $^3J_{PH}$ = 1.4 Hz, $CH_2\underline{CH}_3$, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 66.81 (d, $^2J_{PC}$= 7.8 Hz, $\underline{C}H_2CH_3$); 16.76 (d, $^3J_{PC}$ = 7.4 Hz, $CH_2\underline{C}H_3$). $^{31}$P NMR (121 MHz, $CDCl_3$): δ 45.7. $^{11}$B NMR (96 MHz, $CDCl_3$): δ −12.9

### Complex of S,O,O-triethyl phosphorothiolate with boron tribromide (3)

$^1$H NMR (300 MHz, $CDCl_3$): δ 4.38 ($dq_D$, $^3J_{HH}$ = 7.1 Hz and $^3J_{PH}$= 8.3 Hz, $CH_2CH_3$); 3.34 ($dq_D$, $^3J_{HH}$ = 7.1 Hz and $^3J_{PH}$= 7.8 Hz, $SCH_2CH_3$); 1.57 (dt, $^3J_{HH}$ = 7.1 Hz and $^4J_{PH}$= 1.3 Hz, $SCH_2\underline{CH}_3$); 1.38 (dt, $^3J_{HH}$ = 7.1 Hz and $^4J_{PH}$ = 1.3 Hz, $CH_2\underline{CH}_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 67.83 (d, $^2J_{PC}$= 8.7 Hz, $O\underline{C}H_2CH_3$); 32.45 (d, $^2J_{PC}$ = 7.6 Hz, $S\underline{C}H_2CH_3$); 15.91 (d, $^3J_{PC}$ = 7.4 Hz, $CH_2\underline{C}H_3$); 15.60 (d, $^3J_{PC}$ = 8.25 Hz, $CH_2\underline{C}H_3$). $^{31}$P NMR (121 MHz, $CDCl_3$): δ 47.09. $^{11}$B NMR (96 MHz, $CDCl_3$): δ − 10.3

### P,P-diethoxy-B,B-dibromooxathiaphosphaboretane (4)

$^1$H NMR (300 MHz, $CDCl_3$): δ 4.53 (dq, $dq_D$, $^3J_{HH}$ = 6.8 Hz and $^3J_{PH}$ = 8.8 Hz, $CH_2CH_3$); 1.48 (dt, $^3J_{HH}$ = 6.8 Hz and $^4J_{PH}$= 1.2 Hz, $CH_2\underline{CH}_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 72.44 (d, $^2J_{PC}$ = 8.4 Hz, $\underline{C}H_2CH_3$); 16.13 (d, $^3J_{PC}$ = 7.4 Hz, $CH_2\underline{C}H_3$). $^{31}$P NMR (121 MHz, $CDCl_3$): δ 51.49. $^{11}$B NMR (96 MHz, $CDCl_3$): δ −13.7. EI-MS: m/e $[M^+]$ = 340

*Elem. anal.* Found: C-14.72; H-3.12; B-3.32; P-9.45; S-9.56; Br-46.84. Calctd. for $\mathbf{C_4H_{10}O_3Br_2BPS}$: C-14.14; H-2.97; B-3.18; P-9.12; S-9.44; Br-47.03.

**Complex of O,O-diethyl methanephosphonothionate with boron tribromide (6)**

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 4.47–4.20 (m, $\underline{CH_2}CH_3$, 4H); 2.33 (d, $^{2}J_{PH}$=15.3 Hz, $CH_3$, 3H); 1.93 (dt, $^{4}J_{PH}$=0.6 Hz and $^{3}J_{HH}$=7.0 Hz, $CH_2\underline{CH_3}$, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 67.86 (d, $^{2}J_{CP}$=8.7 Hz, $\underline{CH_2}CH_3$); 16.90 (d, $^{1}J_{CP}$=99.6 Hz, $CH_3$); 16.07 (d, $^{3}J_{CP}$=7.2 Hz, $CH_2\underline{CH_3}$). $^{31}$P NMR (121 MHz, $CDCl_3$): δ 90.33. $^{11}$B NMR (96 MHz, $CDCl_3$): δ −10.9 (s).

**P-ethoxy-P-methyl-B,B-dibromo-oxathiaphosphaboretane (7)**

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 4.21–4.05 (m, $O\underline{CH_2}CH_3$, 4H); 2.45 (d, $^{2}J_{PH}$=14.9 Hz, $CH_3$, 3H); 1.35 (dt, $^{4}J_{PH}$=0.4 Hz and $^{3}J_{HH}$=6.8 Hz, $CH_2\underline{CH_3}$, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 64.13 (d, $^{2}J_{CP}$=8.8 Hz, $\underline{CH_2}CH_3$); 32.18 (d, $^{1}J_{CP}$=92.1 Hz, $CH_3$); 15.52 (d, $^{3}J_{CP}$=8.7 Hz, $CH_2\underline{CH_3}$). $^{31}$P NMR (121 MHz, $CDCl_3$): δ 81.51. $^{11}$B NMR (96 MHz, $CDCl_3$): δ −12.9. EI-MS: m/e [$M^+$] = 310 *Elem. anal.* Found: C-11.72; H-2.22; B-3.26; P-9.85; S-9.96; Br-51.84. Calctd. for **$C_3H_8O_3Br_2BPS$**: C-11.63; H-2.60; B-3.49; P-10.00; S-10.35; Br-51.59.

**Complex of S,O,O-triethyl phosphorothiolate with boron tribromide (8)**

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 4.59–4.48 (m, $O\underline{CH_2}CH_3$, 4H); 3.25–3.05 (m, $S\underline{CH_2}CH_3$, 4H); 3.03 (d, $^{2}J_{PH}$=12.9 Hz, $CH_3$, 3H); 1.55–1.40 (m, $OCH_2\underline{CH_3}$, $SCH_2\underline{CH_3}$, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 70.39 (d, $^{2}J_{CP}$=8.7 Hz, $O\underline{CH_2}CH_3$); 30.32 (d, $^{2}J_{CP}$=4.4 Hz, $S\underline{CH_2}CH_3$); 16.24 (d, $^{3}J_{CP}$=5.5 Hz, $SCH_2\underline{CH_3}$); 15.85 (d, $^{1}J_{CP}$=97.1 Hz, $CH_3$); 15.35 (d, $^{3}J_{CP}$=7.6 Hz, $OCH_2\underline{CH_3}$). $^{31}$P NMR (121 MHz, $CDCl_3$): δ 91.21. $^{11}$B NMR (96 MHz, $CDCl_3$): δ −13.6.

**Complex of O-methyl diphenylphosphinothionate with boron tribromide (10)**

$^{1}$H NMR (200 MHz, $CDCl_3$): δ 7.99–7.58 (m, 10H, ArH); 4.07 (d, $^{3}J_{PH}$ = 14.1 Hz, 3H, $OCH_3$). $^{13}$C NMR (50 MHz, $CDCl_3$): δ 134.97 (d, $^{4}J_{PC}$ = 3.0 Hz, $C_{para}$); 132.45 (d, $^{3}J_{PC}$ = 11.3 Hz, $C_{meta}$); 129.50 (d, $^{2}J_{PC}$ = 14.3 Hz, $C_{ortho}$); 124.46 (d, $^{1}J_{PC}$ = 111.2 Hz, $C_{ipso}$); 55.50 (d,

$^{2}J_{PC}$ = 7.4 Hz, $OCH_3$). $^{31}P$ NMR (121 MHz, $CDCl_3$): δ 78.14. $^{11}B$ NMR (96 MHz, $CDCl_3$): δ −3.4

### Complex of S-methyl diphenylphosphinothiolate with boron tribromide (11)

$^{1}H$ NMR (300 MHz, $CDCl_3$): δ 7.97–7.55 (m, 10H, ArH); 2.70 (d, $^{3}J_{PH}$ = 19.2 Hz, 3H, $SCH_3$). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 137.67 (d, $^{4}J_{PC}$ = 3.5 Hz, $C_{para}$); 132.89 (d, $^{3}J_{PC}$ = 13.5 Hz, $C_{meta}$); 131.30 (d, $^{2}J_{PC}$ = 15.5 Hz, $C_{ortho}$); 127.41 (d, $^{1}J_{PC}$ = 85.5 Hz, $C_{ipso}$); 16.47 (d, $^{2}J_{PC}$ = 4.7 Hz, $SCH_3$). $^{31}P$ NMR (121 MHz, $CDCl_3$): δ 66.55. $^{11}B$ NMR (96 MHz, $CDCl_3$): δ −6.6 (v. large s). EI-MS: m/e [$M^+$] = 499

### P,P-diphenyl-B,B-dibromodibromooxaborathiaphosphetane (12)

$^{1}H$ NMR (300 MHz, $CDCl_3$): δ 8.0–7.5 (m, ArH). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 135.02 (d, $^{4}J_{PC}$ = 3.4 Hz, $C_{para}$); 132.53 (d, $^{3}J_{PC}$ = 13.1 Hz, $C_{meta}$); 129.60 (d, $^{2}J_{PC}$ = 15.5 Hz, $C_{ortho}$); 120.14 (d, $^{1}J_{PC}$ = 84.4 Hz, $C_{ipso}$). $^{31}P$ NMR (121 MHz, $CDCl_3$): δ 80.47. $^{11}B$ NMR (96 MHz, $CDCl_3$): δ −6.6 (v. large s). EI-MS: m/e [$M^+$] = 404



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