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Systematics of boron halide complexes with dichalcogenoether ligands – Synthesis, structures and reaction chemistry

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The complexes $[BX_3(\mu\text{-}L\text{–}L)BX_3]$ ($X = Cl, Br, I$; $L\text{–}L = EtS(CH_2)_2SEt, MeSe(CH_2)_2SeMe$), $[BX'_3\{o\text{-}C_6H_4(SMe)_2\}]$ ($X' = Cl, I$), $[(BBr_3)_2\{o\text{-}C_6H_4(SMe)_2\}]$, $[(BBr_3)_2\{o\text{-}C_6H_4(SeMe)_2\}]$ and $[BI_3\{o\text{-}C_6H_4(SeMe)_2\}]$ have been prepared as moisture-sensitive pale solids by reaction of the appropriate BX_3 with the dichalcogenoether in anhydrous n-hexane solution, and characterised by microanalysis, IR and multinuclear (^1H, ^{11}B, $^{77}Se\{^1H\}$) NMR spectroscopy. In contrast, the $[BF_3(\mu\text{-}L\text{–}L)BF_3]$, $[(BF_3)_2\{o\text{-}C_6H_4(SMe)_2\}]$ and $[(BF_3)_2\{o\text{-}C_6H_4(SeMe)_2\}]$, made from BF_3 and the neat ligands, are viscous oils which have a significant vapour pressure of BF_3 at ambient temperatures. X-ray crystal structures are reported for $[BX_3\{\mu\text{-}EtS(CH_2)_2SEt\}BX_3]$ ($X = Cl, Br, I$), $[BBr_3\{\mu\text{-}MeSe(CH_2)_2SeMe\}BBr_3]$, $[BCl_3\{o\text{-}C_6H_4(SMe)_2\}]$ and $[(BBr_3)_2\{\mu\text{-}o\text{-}C_6H_4(SeMe)_2\}]$. The complexes $[(BX_3)_2\{MeTe(CH_2)_3TeMe\}]$ ($X = F, Cl, Br$) have been identified in solution by multinuclear NMR spectroscopy, but decompose rapidly, whilst $o\text{-}C_6H_4(TeMe)_2$ decomposes immediately on contact with BBr_3 or BCl_3. Dealkylation of some of the chalcogenoether ligands at room temperature by BI_3, to yield complexes including $[BI_2\{o\text{-}C_6H_4S(SMe)\}]$ and $[BI_2\{o\text{-}C_6H_4Se(SeMe)\}]$, has been identified and the X-ray structure of $[BI_2\{o\text{-}C_6H_4Se(SeMe)\}]$ determined. The trends in behaviour along the series of boron halides and with the various chalcogenoethers are described and compared with the behaviour of BX_3 with neutral phosphorus and arsenic donor ligands (Burt et al., *Inorg. Chem*., 2016, **55**, 8852) and with $[BX_3(EMe_2)]$ ($E = S, Se, Te$) (Okio et al., *J. Organometal. Chem*., 2017, **848**, 232).

1. Introduction

Almost 100 years ago, G. N. Lewis proposed the concept of (Lewis) acids and bases as electron pair acceptors and electron pair donors respectively [1], and this concept has become a classification widely used in much p-block chemistry. Boron and aluminium trihalides are textbook examples of Lewis acids. Study of boron derivatives BY_3, where $Y =$ halide, H, substituted aryl, remains an active area of research both in terms of fundamental chemistry [2–5], and their many applications in organic synthesis [6,7]. Trends in Lewis acidity with Y are commonly quoted in textbooks, for example with halide, $F < Cl < Br < I$, which was originally ascribed to π-bonding between the halogen lone pairs and the empty boron p-orbital, which decreased down Group 13, hence reducing the Lewis acidity of the boron centre. More detailed studies show that the order can vary with the Lewis base involved. For example, Et_2O forms stronger bonds with BF_3 than BH_3, but for SMe_2 the reverse order is found [8]. Much computational work over the past fifteen years has been devoted to exploring the factors involved, almost all has focussed on complexes with N- or O-donor ligands. The results of the different DFT calculations may differ in fine details, however, it is generally agreed that the order of Lewis acidity results from the varying strength of the σ-interactions, and in some cases a steric component, with the π-bonding explanation now discounted [2,9–11]. It is important to note that the properties of both the Lewis acid and Lewis base in a complex must be taken in consideration, and that calculations deal with gas phase species, meaning solvation or solid state effects may mask Lewis acidity trends in solution or in the solid state. As noted above, detailed studies of N- and O-donor ligand complexes have been carried out [2–5], but data on neutral heavier donor ligand complexes are much less common [12].

We recently reported full X-ray crystallographic and multinuclear NMR studies of chalcogenoether complexes $[BX_3(EMe_2)]$ (EMe_2, $E = S$, Se and Te) of all four boron halides [13]. This work included the structures of $[BX_3(EMe_2)]$ ($X = Cl, Br, I$; $E =$ Te and

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X = Cl, Br; E = Se) which, along with the tetrahydrothiophene adducts, $[BX_3(tht)]$ [14], are the only chalogenoether adducts of BX_3 for which structural parameters have been determined. The B–E bond lengths decrease with halide Cl > Br > I, consistent with the increasing Lewis acidity in this order. The adducts $[BF_3(EMe_2)]$ are less stable oils, with significant vapour pressure of BF_3 at ambient temperatures [13,15], and whilst multinuclear NMR data (^{19}F, ^{11}B, ^{125}Te) identified $[BF_3(TeMe_2)]$ for the first time, this was very unstable and not obtained as a pure species [13]. We have also reported [16] a systematic study of complexes of the boron halides with diphosphine and diarsine ligands, which established that, whilst flexible bidentates, $R_2P(CH_2)_2PR_2$ (R = Et or Me), formed ligand bridged dimers only, i.e. $[X_3B\{\mu\text{-}R_2P(CH_2)_2PR_2\}BX_3]$, the *o*-phenylene-backboned *o*-$C_6H_4(EMe_2)_2$ (E = P or As), which are preorganised for chelation, produced the first examples of dihaloboronium cations, $[BX_2\{o\text{-}C_6H_4(EMe_2)_2\}]^+$ with P- or As-donors. Surprisingly, no exploration of the coordination chemistry of boron halides with bi- or poly-chalcogenoethers has been reported, and hence we describe here a systematic investigation into the synthesis, spectroscopic and structural properties of such complexes and some reaction chemistry thereof. Cleavage of ^{i}Pr–S bonds in substituted *o*-$C_6H_3R(S^iPr)_2$ by prolonged heating with BBr_3 to yield dithiaboroles, *o*-$C_6H_3RS_2BBr$, has been reported very recently [17].

2. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm^{-1}. ^{1}H, ^{11}B, ^{19}F{^{1}H},^{77}Se{^{1}H}, and ^{125}Te{^{1}H} NMR spectra were recorded from CH_2Cl_2/CD_2Cl_2 solutions using a Bruker AV400 spectrometer and referenced to the residual solvent resonance, external $[BF_3(OEt_2)]$, $CFCl_3$, neat $SeMe_2$ and neat $TeMe_2$ respectively. Microanalyses were undertaken by Medac Ltd. n-Hexane was dried prior to use by distillation from sodium and CH_2Cl_2 from CaH_2, and all preparations were carried out under rigorously anhydrous conditions via a dry dinitrogen atmosphere and standard Schlenk and glovebox techniques. Boron trifluoride was obtained from Fluorochem. Other boron trihalides were obtained from Sigma-Aldrich and used as received. The chalcogenoethers $EtS(CH_2)_2SEt$, $MeSe(CH_2)_2SeMe$, $MeTe(CH_2)_3TeMe$, o-$C_6H_4(SMe)_2$, o-$C_6H_4(SeMe)_2$, o-$C_6H_4(TeMe)_2$ and $C(CH_2SMe)_4$, were made by literature methods or minor modifications thereof [18–22].

$[(BF_3)_2\{EtS(CH_2)_2SEt\}]$: Neat $EtS(CH_2)_2SEt$ (0.20 g, 1.33 mmol) was treated with a slow stream of BF_3 for 5 min leading to a yellowish oil. The complex has a significant vapour pressure of BF_3 at ambient temperatures and attempts to obtain combustion analyses failed to give reproducible results. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.27 (s, [6H], CH_3), 2.59 (s, [4H], CH_2), 2.74 (s, [4H], CH_2). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +2.43 (s). ^{19}F{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −144.3(s). IR (Nujol/cm^{-1}): ν = 1068 (vs, br), 847 (s) (BF).

$[(BCl_3)_2\{EtS(CH_2)_2SEt\}]$: $EtS(CH_2)_2SEt$ (0.17 g, 1.13 mmol) was dispersed in stirring n-hexane (15 mL), and BCl_3 gas slowly bubbled into the solution for 5 min, resulting in the rapid formation of a white powdery precipitate. The BCl_3 addition was stopped, and the mixture stirred for 30 min, after which the white precipitate was isolated by filtration and dried to a white powder *in vacuo*. Yield: 0.38 g (86%). Anal. Calcd for $C_6H_{14}B_2Cl_6S_2\cdot0.15C_6H_{14}$: C, 20.9; H, 4.1. Found: C, 21.1; H, 4.0%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.43 (t, $^3J_{HH}$ = 8 Hz, [6H], CH_3), 3.05 (q, $^3J_{HH}$ = 8 Hz, [4H], CH_2), 3.32 (s, [4H], CH_2), 0.89 (m), 1.26 (m) C_6H_{14}. ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +10.53 (s). IR (Nujol/cm^{-1}): ν = 761 (vs), 741 (vs) (BCl). Small colourless crystals were grown from slow evaporation of a CH_2Cl_2 solution of the product.

$[(BBr_3)_2\{EtS(CH_2)_2SEt\}]$: To a solution of $EtS(CH_2)_2SEt$ (0.06 g, 0.40 mmol) in n-hexane (15 mL) was added dropwise BBr_3 (0.20 g, 0.80 mmol) which immediately led to the precipitation of a white solid. The reaction was stirred for 30 min, after which the white powder was isolated by filtration and dried *in vacuo*. Yield: 0.23 g (88%). Anal. Calcd for $C_6H_{14}B_2Br_6S_2$: C, 11.1; H, 2.2. Found: C, 11.0; H, 2.0%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.58 (t, $^3J_{HH}$ = 8 Hz, [6H], CH_3), 3.20 (br, [4H], CH_2), 3.56 (s, [4H], CH_2). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −10.58 (s). IR (Nujol/cm^{-1}): ν = 663 (s), 612 (m) (BBr). Small colourless crystals were grown from slow evaporation of a CH_2Cl_2 solution.

$[(BI_3)_2\{EtS(CH_2)_2SEt\}]$: $EtS(CH_2)_2SEt$ (0.019 g, 0.13 mmol) in n-hexane (8 mL) was added to an n-hexane solution (25 mL) of BI_3 (0.10 g, 0.026 mmol), leading to an immediate white precipitate. The mixture was stirred for 1 h, and the precipitate isolated by filtration, and dried *in vacuo*. Yield: 0.03 g, 25%. Anal. Calcd for $C_6H_{14}B_2I_6S_2$: C, 7.7; H, 1.5. Found: C, 7.6; H, 1.4%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.25 (t, $^3J_{HH}$ = 8 Hz, [6H], CH_3), 2.57 (br, [4H], CH_2), 2.72 (s, [4H], CH_2). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −70.78 (s). IR (Nujol/cm^{-1}): ν = 602(s), 569 (m) (BI). Small colourless crystals were grown from slow evaporation of a CH_2Cl_2 solution.

$[(BF_3)_2\{MeSe(CH_2)_2SeMe\}]$: Neat $MeSe(CH_2)_2SeMe$ (0.21 g, 1.0 mmol) was cooled in an ice bath and a slow stream of BF_3 bubbled in for 5 min, leading to formation of a pale yellow oil. This decomposed rapidly at room temperature, depositing a white solid and hence microanalytical data were not obtained. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.03 (s, [6H], CH_3), 2.83 (s, [4H], CH_2). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +5.55 (s). ^{77}Se{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +121.3 (s). ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): δ −141.4 (s).

$[(BCl_3)_2\{MeSe(CH_2)_2SeMe\}]$: $MeSe(CH_2)_2SeMe$ (0.19 g, 0.88 mmol) was dispersed in stirred n-hexane (15 mL), and BCl_3 gas slowly bubbled into the solution for 5 min, resulting in the rapid formation of a yellow powdery precipitate. The BCl_3 was stopped, and the mixture stirred for 30 min, after which the precipitate was isolated by filtration, and dried to a yellowish powder *in vacuo*. Yield: 0.28 g (71%). Anal. Calcd for $C_4H_{10}B_2Cl_6Se_2$: C, 10.7; H, 2.2. Found: C, 11.2; H, 2.2%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.26 (s, [6H], CH_3), 3.12 (s, [4H], CH_2). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +14.85 (s). ^{77}Se{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +191.9 (four lines, $^1J_{BSe}$ = 29 Hz). IR (Nujol/cm^{-1}): ν = 762 (s), 745 (s) (BCl).

$[(BBr_3)_2\{MeSe(CH_2)_2SeMe\}]$: To a solution of $MeSe(CH_2)_2SeMe$ (0.09 g, 0.40 mmol) in n-hexane (20 mL) was added dropwise BBr_3 (0.200 g, 0.80 mmol), which immediately led to the precipitation of a reddish solid. The reaction was stirred for 30 min, and then the pale red powder was isolated by filtration and dried *in vacuo*. Yield: 0.17 g (61%). Anal. Calcd for $C_4H_{10}B_2Br_6Se_2$: C, 6.7; H, 1.4. Found: C, 7.1; H, 1.3%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.37 (s, [6H], CH_3), 3.32 (s, [4H], CH_2). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −12.72 (s). ^{77}Se{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +254.0 (s). IR (Nujol/cm^{-1}): ν = 649 (s) (BBr). Small red crystals were grown from slow evaporation of a CH_2Cl_2 solution of the product.

$[(BI_3)_2\{MeSe(CH_2)_2SeMe\}]$: A suspension of BI_3 (0.10 g, 0.013 mmol) in n-hexane (10 mL) was treated with a solution of $MeSe(CH_2)_2SeMe$ (0.015 g, 0.007 mmol) in n-hexane (5 mL). Initially a cream powder precipitated, but this darkened rapidly and after ~20 min had become dark brown. NMR data were collected from a freshly prepared solution of BI_3 and $MeSe(CH_2)_2SeMe$ in a 2:1 ratio in CH_2Cl_2/CD_2Cl_2 immediately after mixing. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.18 (s, [6H], CH_3), 3.05 (s, [4H], CH_2). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −75.32 (s). ^{77}Se{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +257.8 (q, *J* = 50 Hz).

$[(BF_3)_2\{MeTe(CH_2)_3TeMe\}]$: A slow stream of BF_3 gas was bubbled into a solution of $MeTe(CH_2)_3TeMe$ (0.2 mL) in anhydrous CH_2Cl_2 (3 mL) producing a deep yellow solution with some orange precipitate. More orange solid separates over time and a pure sample of the complex was not obtained. The freshly made yellow solution was used for NMR studies. ^{1}H NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ 1.92 (s, [6H], CH_3), 2.13 (m, [2H], CH_2), 2.70 (m, [4H] CH_2). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +0.17 (s). ^{125}Te{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +111.3 (s). ^{19}F{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −143.4 (s).

[$(BX_3)_2${$MeTe(CH_2)_3TeMe$}] (X = Cl or Br): Solutions of $MeTe(CH_2)_3TeMe$ in n-hexane treated with n-hexane solutions of the appropriate BX_3 gave pale orange-yellow solutions and sticky orange-yellow materials deposited immediately. On standing, the solutions darkened and the solids became orange-brown and then finally after a few hours, black. It was possible to obtain *in situ* NMR data in CH_2Cl_2/CD_2Cl_2 solutions of the constituents run *immediately* after mixing. After ~1 h these solutions exhibited new significant resonances (unidentified) indicative of decomposition, and after ~ 6 h the initial resonances had all been lost.

(X = Cl): *in situ NMR.* ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.92 (s, [6H], CH_3), 2.14 (m, [2H], CH_2), 2.71 (m, [4H] CH_2). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +4.19 (s). ^{125}Te{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +189.3 (s).

(X = Br): *in situ NMR.* ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.15 (s, [6H], CH_3), 2.50 (m, [2H], CH_2), 2.91 (m, [4H] CH_2). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −18.53 (s). ^{125}Te{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +303.0 (s).

[$(BF_3)_2${*o*-$C_6H_4(SMe)_2$}]: *o*-$C_6H_4(SMe)_2$ (0.10 g, 0.59 mmol) was saturated with BF_3 gas, producing a viscous pale pink oil. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.47 (s, [6H], CH_3), 7.19 (m, [2H], C_6H_4), 7.23 (m, [2H], C_6H_4). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +0.54 (s). ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): −148.8 (s). IR (Nujol/cm^{-1}): $\nu = 1030$ (s), 806 (m) (BF).

[BCl_3{*o*-$C_6H_4(SMe)_2$}]: *o*-$C_6H_4(SMe)_2$ (0.15 g, 0.88 mmol) was dispersed in stirred n-hexane (15 mL), and BCl_3 gas slowly bubbled into the solution for 5 min, resulting in the rapid formation of a white powdery precipitate. The BCl_3 was stopped, and the mixture stirred for 30 min, after which the white precipitate was isolated by filtration and dried to a white powder *in vacuo*. Yield: 0.24 g (93%). Anal. Calcd for $C_8H_{10}BCl_3S_2$: C, 36.9 H, 4.4. Found: C, 36.8; H, 4.2%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.67 (s, [6H], CH_3), 7.39 (m, [2H], C_6H_4), 7.50 (m, [2H], C_6H_4); (183 K): δ 2.55 (s, [3H], CH_3), 2.88 (s, [3H], CH_3), 7.34 (m, [2H], C_6H_4), 7.62 (m, [2H], C_6H_4); ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +24.93 (s). IR (Nujol/cm^{-1}): $\nu = 748$ (m) (BCl). Small colourless crystals were grown from slow evaporation of a CH_2Cl_2 solution of the product.

***In situ* [BCl_3{o-$C_6H_4(SMe)_2$}] + excess BCl_3**: ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.75 (s, [6H], CH_3), 7.51 (m, [2H], C_6H_4), 7.66 (m, [2H], C_6H_4); (183 K): δ 2.95 (s, [6H], CH_3), 7.87 (m, [4H], C_6H_4); ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ 33.21 (s), 45.0 (BCl_3).

[$(BBr_3)_2${*o*-$C_6H_4(SMe)_2$}]: To a solution of *o*-$C_6H_4(SMe)_2$ (0.07 g, 0.41 mmol) in n-hexane (15 mL) was added dropwise BBr_3 (0.20 g, 0.80 mmol), which immediately led to the precipitation of a white solid. The reaction was stirred for 30 min, and then the white powder was isolated by filtration and dried *in vacuo*. Yield: 0.20 g (71%). Anal. Calcd for $C_8H_{10}B_2Br_6S_2$: C, 14.3; H, 1.5. Found: C, 14.4; H, 1.4%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.98 (s, [6H], CH_3), 7.75 (m, [2H], C_6H_4), 8.07 (m, [2H], C_6H_4). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −5.70 (s). IR (Nujol/cm^{-1}): $\nu = 663$ (m) (BBr).

[BI_3{*o*-$C_6H_4(SMe)_2$}]: An n-hexane (5 mL) solution of *o*-$C_6H_4(SMe)_2$ (0.04 g, 0.25 mmol) was added dropwise to a suspension of BI_3 (0.20 g, 0.51 mmol) in n-hexane (20 mL). A yellowish precipitate was obtained, which was then filtered off after 10 min, and dried *in vacuo.* Yield: 0.17 g (70%). Anal. Calcd for $C_8H_{10}BI_3S_2$: C, 17.1; H, 1.8. Found: C, 16.6; H, 1.7%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.62 (s, [6H], CH_3), 7.24–7.46 (m, [4H], C_6H_4)); (223 K): δ 2.47 (s, [3H], CH_3), 2.57 (s, [3H], CH_3), 7.14–7.64 (m, [4H], C_6H_4). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −69.49 (s). IR (Nujol/cm^{-1}): $\nu = 588$ (m), 547 (w) (BI).

[$(BF_3)_2${*o*-$C_6H_4(SeMe)_2$}]: *o*-$C_6H_4(SeMe)_2$ (0.26 g, 1.0 mmol) was cooled in an ice-bath and saturated with BF_3 for 5 min, producing a viscous pink oil. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.32 (s, [6H], CH_3), 7.18 (m, [2H], C_6H_4), 7.33 (m, [2H]; (183 K): δ 2.27 (s, [6H], CH_3), 7.14 (m, [2H], C_6H_4) 7.27 (m, [2H], C_6H_4); ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +2.40 (s); (183 K): +0.74 (s). ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): −148.8 (s); (183 K): −147.7. ^{77}Se{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +199.9 (s); (183 K): +191.5 (s). IR (Nujol/cm^{-1}): $\nu = 1035$ (s), 810 (m) (BF).

[$(BBr_3)_2${*o*-$C_6H_4(SeMe)_2$}]: To a solution of *o*-$C_6H_4(SeMe)_2$ (0.05 g, 0.19 mmol) in n-hexane (15 mL) was added dropwise BBr_3 (0.095 g, 0.38 mmol), which immediately led to the precipitation of a yellowish solid. The reaction was stirred for 30 min, and then the yellow powder was isolated by filtration and dried *in vacuo*. Yield: 0.07 g (49%). Anal. Calcd for $C_8H_{10}B_2Br_6Se_2\cdot0.3C_6H_{14}$: C, 15.1; H, 1.9. Found: C, 14.6; H, 2.2%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.69 (s, [6H], CH_3), 7.58 (m, [2H], C_6H_4), 7.76 (m, [2H], C_6H_4), 0.89 (m), 1.26 (m) C_6H_{14}. ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ + 0.95 (s). ^{77}Se{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +263.3. IR (Nujol/cm^{-1}): $\nu = 653$ (m) (BBr). Small yellowish crystals were grown from slow evaporation of a CH_2Cl_2 solution of the product.

[BI_3{*o*-$C_6H_4(SeMe)_2$}]: A solution of *o*-$C_6H_4(SeMe)_2$ (0.04 g, 0.15 mmol) in n-hexane (15 mL) was added slowly to a n-hexane solution (15 mL) of BI_3 (0.12 g, 0.31 mmol), which immediately led to the precipitation of a white solid. The reaction was stirred for 1 h and then the white powder was isolated by filtration and dried *in vacuo*. Yield: 0.06 g (59%). Anal. Calcd for $C_8H_{10}BI_3Se_2$: C, 14.6; H, 1.5. Found: C, 14.2; H, 1.3%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.52 (s, [6H], CH_3), 7.42 (m, [2H], C_6H_4), 7.64 (m, [2H], C_6H_4); (253 K): δ 2.43 (s, [3H], CH_3), 2.72 (s, [3H], CH_3), 7.52–7.70 m, [4H], C_6H_4). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −74.00 (s). ^{77}Se{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 253 K): δ + 222.8, +290.7. IR (Nujol/cm^{-1}): $\nu = 571$ (m), 515 (w) (BI).

[BI_2{*o*-$C_6H_4Se(SeMe)$}]: This was generated by allowing a solution of [BI_3{*o*-$C_6H_4(SeMe)_2$}] in CH_2Cl_2 to stand for 48 h, and isolated as a fawn solid. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.56 (s, [3H], CH_3), 7.20–7.60 (m, [4H], C_6H_4). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −43.85; (183 K): δ −43.09. ^{77}Se{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +406.3 (q, J = 43 Hz, Se), +360.4 (q, J = 64 Hz, SeMe); (183 K): δ +402.9, +345.5.

2.1. X-ray experimental

Crystals of the complexes were grown from CH_2Cl_2 solutions of the complexes allowed to evaporate slowly in the glove box. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724 + detector mounted at the window of an FR-E + SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K. Structure solution and refinement were performed using SHELX(S/L)97, SHELX-2013 or SHELX-2014/7 [23]. H atoms bonded to C were placed in calculated positions using the default C−H distance, and refined using a riding model. Details of the crystallographic parameters are given in Table 1. CCDC reference numbers in cif format are [$(BBr_3)_2${$EtS(CH_2)_2SEt$}]: 1569688; [$(BCl_3)_2${$EtS(CH_2)_2SEt$}]: 1569689; [$(BI_3)_2${$EtS(CH_2)_2SEt$}]: 1569690; [$(BBr_3)_2${$MeSe(CH_2)_2SeMe$}]: 1569691; [BCl_3{*o*-$C_6H_4(SeMe)_2$}]: 1569692; [$(BBr_3)_2${*o*-$C_6H_4(SeMe)_2$}]: 1569693; [BI_2{*o*-$C_6H_4Se(SeMe)$}]: 1569694; [{*o*-$C_6H_4S_2B$}$_2$O]: 1569695; [$(BBr_3)_2C(CH_2SMe)_4$]: 1569696. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Table 1
X-ray crystallographic data.[a]

Compound	$[(BBr_3)_2\{EtS(CH_2)_2SEt\}]$	$[(BCl_3)_2\{EtS(CH_2)_2SEt\}]$	$[(BI_3)_2\{EtS(CH_2)_2SEt\}]$
Formula	$C_6H_{14}B_2Br_6S_2$	$C_6H_{14}B_2Cl_6S_2$	$C_6H_{14}B_2I_6S_2$
M	651.37	384.61	933.39
Crystal system	monoclinic	triclinic	monoclinic
Space group (no.)	$P2_1/n$ (14)	P-1 (2)	$P2_1/n$ (14)
a/Å	6.7904(2)	5.9539(4)	7.1896(3)
b/Å	11.8825(3)	6.6345(3)	12.2646(4)
c/Å	10.6434(4)	10.8330(6)	11.3844(5)
α/°	90	98.689(4)	90
β/°	93.712(3)	94.987(5)	92.131(4)
γ/°	90	113.172(5)	90
U/Å^3	856.99(5)	383.80(4)	1003.15(7)
Z	2	1	2
μ(Mo-K_α)/mm^{-1}	14.272	1.361	9.477
F(000)	604	194	816
Total number reflns	6316	4118	35834
R_{int}	0.031	0.034	0.087
Unique reflns	1684	1506	2303
No. of params, restraints	74, 0	74, 0	74, 10
GOF	1.070	1.251	1.0238
Largest peak and hole e/Å^3	1.797, −0.795	0.683, −0.723	7.4164,-2.3088
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.026, 0.066	0.027, 0.078	0.058, 0.151
R_1, wR_2 (all data)	0.027, 0.066	0.036, 0.127	0.061, 0.154

Compound	$[(BBr_3)_2\{MeSe(CH_2)_2SeMe\}]$	$[BCl_3\{o\text{-}C_6H_4(SMe)_2\}]$	$[(BBr_3)_2\{o\text{-}C_6H_4(SeMe)_2\}]$
Formula	$C_4H_{10}B_2Br_6Se_2$	$C_8H_{10}BCl_3S_2$	$C_8H_{10}B_2Br_6Se_2$
M	717.11	287.44	765.16
Crystal system	monoclinic	monoclinic	monoclinic
Space group (no.)	$P2_1/c$ (14)	Cc (9)	I2/a (15)
a/Å	6.4418(2)	17.9902(4)	7.5155(3)
b/Å	11.3158(3)	11.8673(3)	11.7391(4)
c/Å	11.7385(4)	11.7862(3)	20.0488(10)
α/°	90	90	90
β/°	116.721(3)	101.782(2)	99.567(4)
γ/°	90	90	90
U/Å^3	764.29(4)	2463.29(10)	1744.20(13)
Z	2	8	4
μ(Mo-K_α)/mm^{-1}	20.484	1.040	17.964
F(000)	641	1168	1384
Total number reflns	7202	15425	6969
R_{int}	0.024	0.025	0.025
Unique reflns	1489	4771	1723
No. of params, restraints	65, 7	257, 2	83, 0
GOF	1.0365	1.082	1.045
Largest peak and hole e/Å^3	0.7985, −0.8298	0.237, −0.200	0.623,-0.472
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.023, 0.058	0.021, 0.047	0.019, 0.046
R_1, wR_2 (all data)	0.024, 0.058	0.021, 0.047	0.022, 0.048

Compound	$[BI_2\{o\text{-}C_6H_4Se(SeMe)\}]$	$[\{o\text{-}C_6H_4S_2B\}_2O]$
Formula	$C_7H_7BI_2Se_2$	$C_{12}H_8B_2OS_4$
M	513.66	318.11
Crystal system	orthorhombic	orthorhombic
Space group (no.)	Pbca (61)	Pbcn (60)
a/Å	7.2963(3)	11.9283(5)
b/Å	14.7899(6)	13.8287(7)
c/Å	21.6844(9)	16.4039(7)
α/°	90	90
β/°	90	90
γ/°	90	90
U/Å^3	2340.00(17)	2705.9(2)
Z	8	8
μ(Mo-K_α)/mm^{-1}	11.546	0.685
F(000)	1824	1300
Total number reflns	13982	27109
R_{int}	0.033	0.146
Unique reflns	2674	2667
No. of params, restraints	110, 0	172, 16
GOF	0.9782	1.0437
Largest peak and hole e/Å^3	1.0826,-1.0697	0.7265, −0.7431
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.024, 0.039	0.049, 0.084
R_1, wR_2 (all data)	0.036, 0.042	0.081, 0.093

[a] Common items: T = 293 K; wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°.

[b] $R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR_2 = [\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo^4]^{1/2}$.

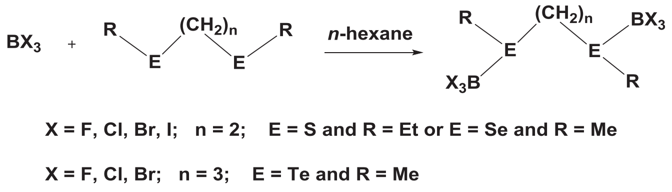
3. Results and discussion

[$(BX_3)_2${μ-EtS$(CH_2)_2$SEt }] (X = Cl, Br or I): The addition of BBr_3 to a solution of EtS$(CH_2)_2$SEt in anhydrous n-hexane in a ≥2: 1 M ratio resulted in the immediate precipitation of a white moisture sensitive powder, identified by microanalysis as [$(BBr_3)_2${EtS$(CH_2)_2$SEt}]. Similarly, bubbling excess BCl_3 into an n-hexane solution of EtS$(CH_2)_2$SEt produced white [$(BCl_3)_2${EtS$(CH_2)_2$SEt}] (Scheme 1).

The corresponding reaction of dilute n-hexane solutions of BI_3 and EtS$(CH_2)_2$SEt gave [$(BI_3)_2${EtS$(CH_2)_2$SEt}], but if concentrated solutions were used, a mixture of [$(BI_3)_2${EtS$(CH_2)_2$SEt}] and a second product, identified as [BI_3{κ^1-EtS$(CH_2)_2$SEt}], precipitated. Attempts to isolate a pure solid sample of [BI_3{κ^1-EtS$(CH_2)_2$SEt}] using an excess of the dithioether were unsuccessful, mixtures of the 1:1 and 2:1 complexes being obtained, although the ^{11}B NMR spectrum showed the 1:1 to be the major species in such solutions. The complexes are moisture sensitive, particularly in solution, but are indefinitely stable in sealed containers at ambient temperature. Crystals of all three [$(BX_3)_2${EtS$(CH_2)_2$SEt}] suitable for X-ray crystallographic studies were obtained by allowing CH_2Cl_2 solutions to evaporate under a dinitrogen atmosphere. The structures Fig. 1–3 confirm the presence of tetrahedrally-coordinated boron and the bridging dithioether. The crystals of the triiodide complex were identified as non-merohedral twins, and hence comparisons with this structure need to be made with care. However the d(B–S) decrease with halide Cl > Br ≥ I, the trend identified previously in systems with tetrahydrothiophene [24], and in related $SeMe_2$ and $TeMe_2$ complexes [13].

The ^{1}H spectra obtained in CD_2Cl_2 solution, show simple patterns consistent with the solid state structures, and the ^{11}B NMR spectra (Table 2) show singlet resonances at similar frequencies to those reported in the corresponding [$BX_3(SMe_2)$] [13]. As noted above, a [BI_3{κ^1-EtS$(CH_2)_2$SEt}] complex was also identified; the ^{11}B NMR resonance of this was only ~ 1 ppm different to that of [$(BI_3)_2${EtS$(CH_2)_2$SEt}] (Table 2), showing there is little communication between the chalcogen donors in this ligand.

[$(BX_3)_2${μ-MeSe$(CH_2)_2$SeMe}] (X = Cl, Br or I): The complexes with X = Cl or Br precipitate as pale yellow powders from n-hexane solutions of BX_3 and the diselenoether. The reaction of BI_3 with MeSe$(CH_2)_2$SeMe in either n-hexane or CH_2Cl_2 initially produces a yellow powder, which rapidly darkens, becoming red-brown after ~ 20 min in contact with the solution. Multinuclear NMR data obtained immediately on mixing dilute dichloromethane solutions of the constituents (which also darkened over time), identified the formation of [$(BI_3)_2${μ-MeSe$(CH_2)_2$SeMe}] which typically constitutes ~ 90% of the initial product. However, there is also a second species present which grows quite rapidly in solution in CH_2Cl_2 and which was tentatively identified by multinuclear NMR spectroscopy as containing a selenoether-selenide ligand resulting from dealkylation at Se, probably [BI_2{MeSe$(CH_2)_2$Se)], although the data do not establish it is monomeric. In particular, the ^{77}Se{^{1}H} NMR spectrum shows resonances at δ = 135.6 and 267.3 with 1:1 intensities, which may be assigned to the MeSe and Se^- groups, respectively, whilst the ^{11}B NMR spectrum has a new singlet at



Scheme 1. Reactions of the boron halides with dichalcogenoalkanes.

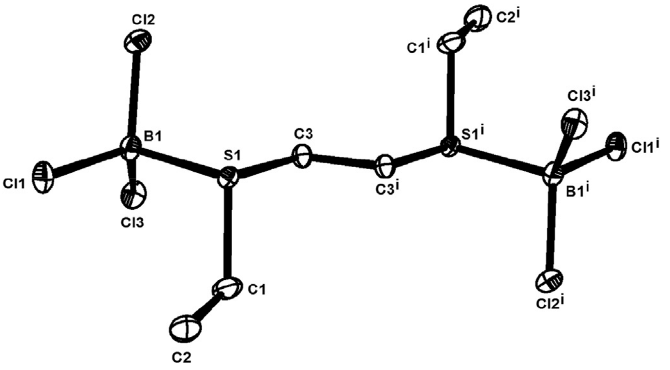


Fig. 1. The structure of [$(BCl_3)_2${EtS$(CH_2)_2$SEt}] showing the numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: i = 1-x, -y, 2-z. Selected bond lengths (Å) and angles (°): S1–B1 = 1.985(3), Cl2–B1 = 1.836(3), Cl1–B1 = 1.813(3), Cl3–B1 = 1.811(3), Cl2–B1–S1 = 104.78(14), Cl1–B1–S1 = 105.03(13), Cl1–B1–Cl2 = 112.37(15), Cl3–B1–S1 = 109.62(14), Cl3–B1–Cl2 = 111.26(14), Cl3–B1–Cl1 = 113.22(16).

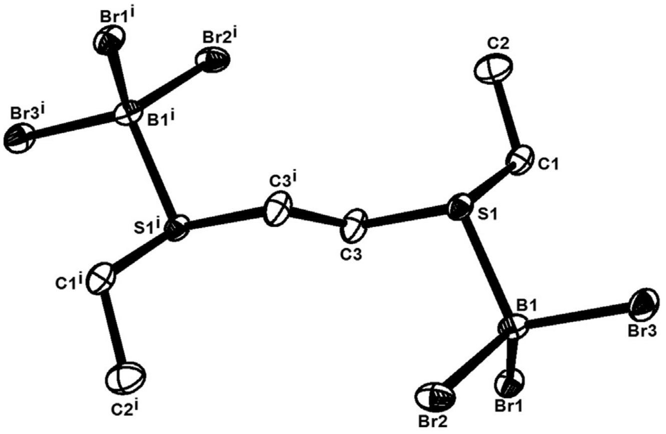


Fig. 2. The structure of [$(BBr_3)_2${EtS$(CH_2)_2$SEt}] showing the numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: i = 1-x, 1-y, 1-z. Selected bond lengths (Å) and angles (°): Br1–B1 = 1.993(4), Br3–B1 = 1.991(4), Br2–B1 = 1.995(4), S1–B1 = 1.961(4), Br1–B1–Br2 = 110.89(19), Br3–B1–Br1 = 112.48(19), Br3–B1–Br2 = 113.2(2), S1–B1–Br1 = 111.1(2), S1–B1–Br3 = 103.89(18), S1–B1–Br2 = 104.77(18).

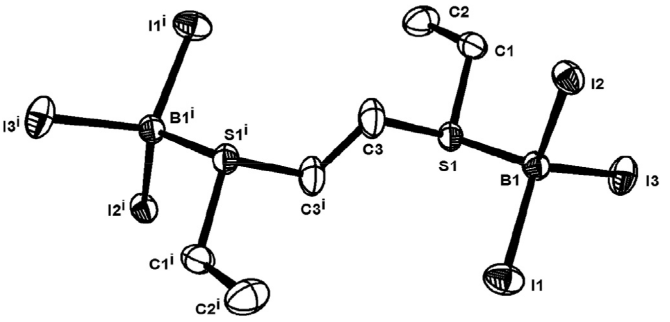


Fig. 3. The structure of [$(BI_3)_2${EtS$(CH_2)_2$SEt}] showing the numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: i = 1-x, 1-y, 1-z. Selected bond lengths (Å) and angles (°): S1–B1 = 1.950(11), B1–I2 = 2.215(11), B1–I3 = 2.226(11), B1–I1 = 2.211(11), I2–B1–S1 = 112.6(5), I3–B1–S1 = 102.8(5), I3–B1–I2 = 112.0(4), I1–B1–S1 = 105.5(5), I1–B1–I2 = 110.4(5), I1–B1–I3 = 113.2(5).

Table 2
NMR spectroscopic data for BX_3 complexes with bidentate ligands[a] (all NMR data were recorded in CH_2Cl_2/CD_2Cl_2 solution at 295 K).

	^{11}B	^{19}F	$^{77}Se/^{125}Te$	Δ(Se/Te)
$[(BF_3)_2\{EtS(CH_2)_2SEt\}]$	+2.43	−144.3		
$[(BCl_3)_2\{EtS(CH_2)_2SEt\}]$	+10.53			
$[(BBr_3)_2\{EtS(CH_2)_2SEt\}]$	−10.58			
$[(BI_3)_2\{EtS(CH_2)_2SEt\}]$	−70.78			
$[BI_3\{\kappa^1\text{-}EtS(CH_2)_2SEt\}]$ (*in situ*)	−69.80			
$[(BF_3)_2\{MeSe(CH_2)_2SeMe\}]$	+5.56	−141.4	+121.3	~0
$[(BCl_3)_2\{MeSe(CH_2)_2SeMe\}]$	+14.85		+191.9 (J = 29 Hz)	62
$[(BBr_3)_2\{MeSe(CH_2)_2SeMe\}]$	−12.72		+254.0	127
$[(BI_3)_2\{MeSe(CH_2)_2SeMe\}]$(*in situ*)	−75.32		+257.8 (J = 50 Hz)	137
$[(BF_3)_2\{MeTe(CH_2)_3TeMe\}]$	+0.17	−143.4	+111.3	~7
$[(BCl_3)_2\{MeTe(CH_2)_3TeMe\}]$ (*in situ*)	+4.19		+189.3	85
$[(BBr_3)_2\{MeTe(CH_2)_3TeMe\}]$ (*in situ*)	−18.53		+303.0	199
$[(BF_3)_2\{o\text{-}C_6H_4(SMe)_2\}]$	+0.54	−148.8		
$[BCl_3\{o\text{-}C_6H_4(SMe)_2\}]$	+24.93			
$[(BCl_3)_2\{o\text{-}C_6H_4(SMe)_2\}]$ (*in situ*)	+33.21			
$[(BBr_3)_2\{o\text{-}C_6H_4(SMe)_2\}]$	−5.70			
$[BI_3\{o\text{-}C_6H_4(SMe)_2\}]$	−69.49			
$[(BF_3)_2\{o\text{-}C_6H_4(SeMe)_2\}]$	+2.4	−148.8	+199.9	~0
$[(BBr_3)_2\{o\text{-}C_6H_4(SeMe)_2\}]$	+0.95		+263.3	63.4
$[BI_3\{o\text{-}C_6H_4(SeMe)_2\}]$	−74.00		+222.8, +290.7	91
$[BI_2\{o\text{-}C_6H_4Se(SeMe)\}]$	−43.85		+406.3 (J = 43 Hz)	
			+360.4 (J = 64 Hz)	160

[a] For comparison, NMR data on the parent BX_3 species are: BF_3: ^{19}F NMR (CD_2Cl_2): −127.8; ^{11}B NMR (CD_2Cl_2): BF_3 +11.03; BCl_3 +41.9, BBr_3 +39.5, BI_3 −5.5 (from Ref. [26]).

$\delta = -41.5$. Although it was not isolated, support for this identification comes from comparison with the data presented below on the $o\text{-}C_6H_4(SeMe)_2/BI_3$ reaction. It does not appear to be possible to isolate a pure solid sample of $[(BI_3)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$ due to the rapid decomposition. Crystals of $[(BBr_3)_2\{MeSe(CH_2)_2SeMe\}]$ were obtained easily from CH_2Cl_2 solution and the structure (Fig. 4) shows that the d(B–Br) are not significantly different from those in the dithioether complex or in $[BBr_3(SeMe_2)]$ [13]. In contrast to the rapid decomposition of $[(BI_3)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$, the analogous chloride and bromide complexes appear to be stable solids if protected from moisture.

The ^{11}B NMR spectra of the three $[(BX_3)_2\{MeSe(CH_2)_2SeMe\}]$ are singlets, showing the same trends in δ_B to the corresponding $[(BX_3)_2\{EtS(CH_2)_2SEt\}]$ (Table 2). The $^{77}Se\{^1H\}$ NMR spectra show chemical shifts to high frequency of $MeSe(CH_2)_2SeMe$ ($\delta = 121$) [19] with coordination shifts (Δ) of +62 (Cl), +127 (Br) and +137 (I). Notably, whilst the resonance in the bromo-complex is a very broad singlet, that of $[(BCl_3)_2\{MeSe(CH_2)_2SeMe\}]$ shows a distorted four line pattern (Fig. 5) due to partially resolved coupling to ^{11}B (^{11}B, 80%, $I = 3/2$, $\Xi = 32.084$ MHz, $Q = 3.55 \times 10^{-30}$ m^2, $R_c = 754$). Resolved coupling to the ^{10}B ($I = 3$, $\Xi = 10.75$ MHz, $Q = 7.4 \times 10^{-30}$ m^2) is not expected due to its larger quadrupole moment. The $[(BI_3)_2\{MeSe(CH_2)_2SeMe\}]$ also shows a four line coupling pattern on the ^{77}Se resonance ($J = 50$ Hz). In most of the boron halide-selenoether complexes, ^{11}B coupling was not observed; this can be attributed to a combination of ligand exchange in solution and quadrupolar relaxation of the ^{11}B in the significant electric field gradients about the boron centre [13,14,26].

$[BX_3\{MeTe(CH_2)_3TeMe\}]$ (X = Cl or Br): Since $RTe(CH_2)_2TeR$ ligands are unknown, all attempts to prepare them resulting in formation of R_2Te_2 and $CH_2{=}CH_2$ [21], $MeTe(CH_2)_3TeMe$ was used as a representative alkyl ditelluroether.

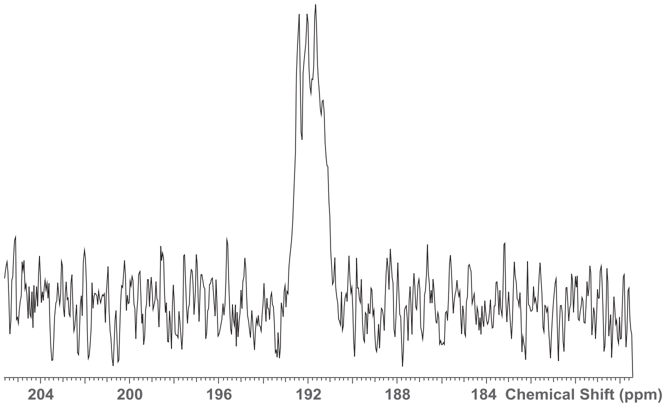


Fig. 5. $^{77}Se\{^1H\}$ NMR spectrum of $[(BCl_3)_2\{MeSe(CH_2)_2SeMe\}]$ in CH_2Cl_2 at 295 K.

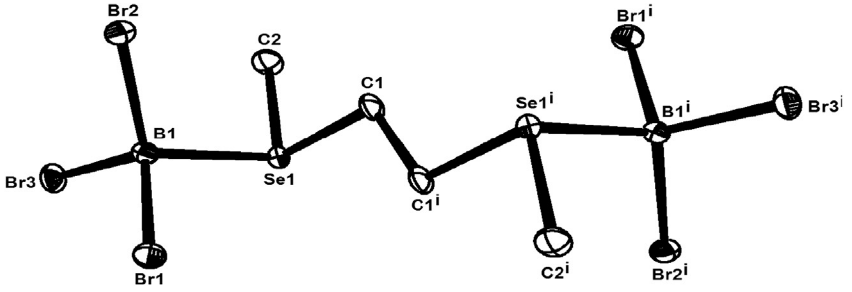


Fig. 4. The structure of $[(BBr_3)_2\{MeSe(CH_2)_2SeMe\}]$ showing the numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: i = 2-x, 1-y, 2-z. Selected bond lengths (Å) and angles (°): Br1–B1 = 1.999(4), Br2–B1 = 1.992(4), Br3–B1 = 1.989(4), Se1–B1 = 2.092(4), Br2–B1–Br1 = 111.99(17), Br3–B1–Br1 = 111.65(17), Br3–B1–Br2 = 113.3(2), Se1–B1–Br1 = 104.41(18), Se1–B1–Br2 = 104.35(16), Se1–B1–Br3 = 110.55(16).

Addition of BX_3 (X = Cl or Br) to n-hexane solutions of $MeTe(CH_2)_3TeMe$ gave yellow-brown solutions and sticky orange-yellow precipitates. On standing, the solutions quickly darkened and the precipitates became brown and then finally after a few hours, black. It was possible to obtain *in situ* NMR data in CH_2Cl_2/CD_2Cl_2 solutions of the constituents run *immediately* after mixing. After ~1 h these solutions exhibited new resonances (unidentified) indicative of decomposition, and after ~ 6 h the resonances of the telluroether complexes had been completely lost. The addition of $MeTe(CH_2)_3TeMe$ to BI_3 in CH_2Cl_2 solution produced an immediate orange-brown precipitate and the proton NMR spectrum of the yellow supernatant solution showed multiple resonances, whilst there were no significant ^{11}B or $^{125}Te\{^1H\}$ resonances observed. It was concluded that BI_3 decomposed the ditelluroether upon contact.

$[(BF_3)_2(L{-}L)]$ (L–L = $EtS(CH_2)_2SEt$, $MeSe(CH_2)_2SeMe$, $MeTe(CH_2)_3TeMe$, *o*-$C_6H_4(SMe)_2$, *o*-$C_6H_4(SeMe)_2$): The chalcogenoether adducts of BF_3 are quite different to those formed by the other three halides (*cf.* ref 13, 25). Saturation of neat $EtS(CH_2)_2SEt$ or $MeSe(CH_2)_2SeMe$ with BF_3 gas at 0 °C produced viscous pale yellow liquids. The $[(BF_3)_2\{o\text{-}C_6H_4(EMe)_2\}]$ (E = S, Se) were obtained similarly as very pale pink oils. The oils are very moisture sensitive, fume in air and have a significant positive pressure of BF_3 over them at room temperature, thus resembling the commercially available BF_3 reagent, $[BF_3(SMe_2)]$ [15]. Attempts to obtain microanalyses failed to give reproducible results, most likely due to the loss of BF_3 in handling as previously established with the monodentate chalcogenoether analogues $[BF_3(EMe_2)]$ (E = S or Se) [13,15,25]. In contrast to the diphosphine complexes [16], the ^{11}B and ^{19}F NMR spectra (Table 2) are broad singlets with no resolved couplings, attributed to fast dissociative neutral ligand exchange in solution. However, it should be noted that the ^{11}B and ^{19}F chemical shifts are very different to those of BF_3 in CH_2Cl_2 solution (Table 2) [26]. The $^{77}Se\{^1H\}$ resonance of $[(BF_3)_2\{MeSe(CH_2)_2SeMe\}]$ is a singlet with a chemical shift little different to that of free $MeSe(CH_2)_2SeMe$ [19], identical behaviour was observed in $[BF_3(SeMe_2)]$ [13], and explained similarly as due to weak B–Se bonding resulting in fast ligand exchange. The NMR spectra are essentially the same at 183 K. Although coordination shifts in d-block metal selenoether complexes are typically large and positive, there are examples of low frequency coordination shifts in some p-block systems, including those of AlX_3 and GaX_3 [27–29], so it is possible that in the BF_3 complexes the coordination shifts are inherently very small, in addition to the effects of ligand exchange. The complex $[(BF_3)_2\{EtS(CH_2)_2SEt\}]$ appears to be stable in a sealed container at room temperature, but $[(BF_3)_2\{MeSe(CH_2)_2SeMe\}]$ decomposes in hours as a neat oil, and faster in CH_2Cl_2 solution, depositing a white solid. Multinuclear NMR spectroscopic data show the decomposition generates $[BF_4]^-$ (and a weak resonance assigned to $[SiF_5]^-$, probably due to attack on the glass). A number of new resonances appear in the ^1H NMR spectrum, the major one having $\delta = 2.55$ is tentatively assigned to $[Me_3Se]^+$, since there appear to be no associated CH_2 resonance(s), whilst the ^{77}Se NMR shows a new resonance at $\delta \sim +264$ which increases in intensity relative to that of the initial complex over time. The chemical shift of $[Me_3Se]^+$ is solvent and anion sensitive, but lies in the range $\delta \sim$ 245–265 [13,30,31]. Dimethylene linkages in diselenoethers have been found to eliminate $CH_2{=}CH_2$ and form RSeSeR in the presence of some d-block Lewis acids, including $TiCl_4$ or $ZrCl_4$ [32,33], but the reaction here with BF_3 is more complex, and also involves alkylation of the selenium.

The oils $[(BF_3)_2\{o\text{-}C_6H_4(EMe)_2\}]$ (E = S, Se) appear reasonably stable at ambient temperatures, although very moisture sensitive, and their spectroscopic properties (Table 2) are unexceptional. Bubbling BF_3 into a solution of $MeTe(CH_2)_3TeMe$ produced a deep yellow solution with some orange solid. The NMR spectroscopic data (Table 2 and Experimental Section) of the yellow solution are consistent with the formation of $[(BF_3)_2\{MeTe(CH_2)_3TeMe\}]$ as the major product, although some $[BF_4]^-$ and an unidentified species with $\delta_{Te} = +234$ are also present. The solution decomposes over time, producing more insoluble orange-red materials (*cf.* $[BF_3(TeMe_2)]$ [13]) and it was not obtained pure.

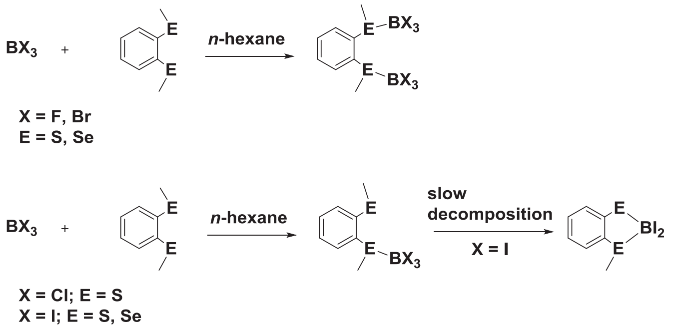
$[(BX_3)_n\{o\text{-}C_6H_4(EMe)_2\}]$ (X = Cl, Br or I, E = S or Se): The *o*-phenylene linked diphosphine or diarsine *o*-$C_6H_4(E'Me_2)_2$ (E' = P or As) ligands gave [14] the first P or As ligand examples of dihaloboronium cations, $[BX_2\{o\text{-}C_6H_4(E'Me_2)_2\}]^+$, and thus the corresponding *o*-phenylene linked chalcogenoethers were explored to see if they supported similar cations. In fact, as discussed below, no dihaloboronium cations were found, but examples of κ^1-and μ^2-coordination and also E-dealkylation were identified (Scheme 2).

The reaction of the appropriate BX_3 with *o*-$C_6H_4(EMe)_2$ (E = S or Se) in a 2:1 M ratio in n-hexane precipitated powders identified by microanalysis as $[(BBr_3)_2\{o\text{-}C_6H_4(EMe)_2\}]$, $[BI_3\{o\text{-}C_6H_4(EMe)_2\}]$ and $[BCl_3\{o\text{-}C_6H_4(SMe)_2\}]$. Repeated attempts to isolate a pure sample from the BCl_3/*o*-$C_6H_4(SeMe)_2$ system were unsuccesful. The isolation of 1:1 complexes in the chloride and iodide cases is probably a result of their low solubility, since *in situ* NMR evidence (below) showed that in the presence of excess BX_3 the 1:2 complexes formed in solution.

The structures of $[BCl_3\{o\text{-}C_6H_4(SMe)_2\}]$ and $[(BBr_3)_2\{o\text{-}C_6H_4(SeMe)_2\}]$ (Figs. 6 and 7) provide confirmation of the two complex types. In the latter, the BBr_3 groups are arranged *anti*, possibly to minimise steric crowding.

The ^1H NMR spectrum of $[BCl_3\{\kappa^1\text{-}o\text{-}C_6H_4(SMe)_2\}]$ in CD_2Cl_2 at 295 K shows a singlet δ(Me) resonance, but on cooling the solution this broadens and then splits into two resonances with 1:1 intensity ratio, the effects reversing on warming the solution back to ambient temperatures. This shows that the κ^1-coordination is present in solution with the BCl_3 exchanging between the two thioether groups at ambient temperatures, but exchange slows on cooling the solution and separate resonances are resolved for the $-S(Me)BCl_3$ and the uncoordinated $-SMe$ group. On bubbling excess BCl_3 into the solution, the ^1H chemical shifts change and a singlet methyl resonance is present at all temperatures, whilst the ^{11}B NMR shows a resonance at $\delta = +45$ (excess BCl_3) and a new resonance at $\delta = +33$, which is assigned to $[(BCl_3)_2\{o\text{-}C_6H_4(SMe)_2\}]$. In contrast, the ^1H and ^{11}B NMR spectra of $[(BBr_3)_2\{o\text{-}C_6H_4(SMe)_2\}]$ (Table 2) are simple and invariant with temperature, as expected for the 2:1 adduct. The spectroscopic data for $[(BBr_3)_2\{o\text{-}C_6H_4(SeMe)_2\}]$ (Table 2 and Experimental Section) are straightforward, and the complex shows a broad ^{77}Se NMR resonance at $\delta = +263.4$ ($\Delta = 63.4$), but attempts to resolve ^{11}B coupling were unsuccessful over the temperature range 295–190 K.

The room temperature ^1H NMR spectrum of a freshly prepared



Scheme 2. Reactions of boron halides with *o*-phenylene dichalcogenoethers.

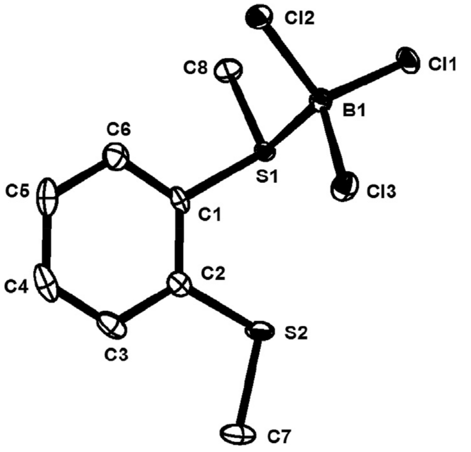


Fig. 6. The structure of one independent molecule of [$BCl_3\{o\text{-}C_6H_4(SMe)_2\}$] showing the numbering scheme, the second molecule in the asymmetric unit is very similar. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cl1–B1 = 1.834(3), S1–B1 = 1.994(3), Cl2–B1 = 1.821(3), Cl3–B1 = 1.824(3), Cl1–B1–S1 = 101.36(14), Cl2–B1–Cl1 = 112.06(16), Cl2–B1–S1 = 111.27(16), Cl2–B1–Cl3 = 112.66(16), Cl3–B1–Cl1 = 113.28(17), Cl3–B1–S1 = 105.42(15).

CD_2Cl_2 solution of [$BI_3\{o\text{-}C_6H_4(SMe)_2\}$] shows a singlet δ(Me) resonance, but on cooling to ~ 223 K, this splits into two with a 1:1 intensity ratio, similar behaviour to that described for [$BCl_3\{\kappa^1\text{-}o\text{-}C_6H_4(SMe)_2\}$] above, although the exchange slows at a higher temperature, consistent with the expected stronger bonding of the thioether to BI_3; the resonances coalesce on warming. However, over a few hours in solution at ambient temperature a new resonance appears at δ = 2.95, which is to high frequency of the coordinated dithioether resonance (and is not involved in exchange processes), and is associated with growing complexity of the aromatic region. The initial spectrum has an ^{11}B resonance at δ = −69.49, typical of a I_3S donor set [13], but after some hours a new resonance at δ = −32.40 has appeared and this grows in relative intensity over time. The new complex is identified as [$BI_2\{o\text{-}C_6H_4S(SMe)\}$] (*cf.* the seleno-analogue below). S-dealkylation of *o*-phenylene dithioethers by refluxing with BBr_3 has been reported very recently [17]. There are a small number of d-block metal complexes of the thioether-thiolate, *o*-$C_6H_4S(SMe)^-$, known, e.g. [$Ni\{o\text{-}C_6H_4S(SMe)\}_2PMe_3$] [34], whilst dithiaboroles [(*o*-$C_6H_4S_2$)BX] are well established [17,35]. The latter typically have ^{11}B NMR resonances some 30–60 ppm to high frequency of the corresponding thioether-BX_3 adducts. A few crystals of [$(o\text{-}C_6H_4S_2B)_2O$] (Fig. 8) were obtained from a solution of [$BI_3\{o\text{-}C_6H_4(SMe)_2\}$] in CH_2Cl_2 allowed to evaporate slowly over several days, and clearly result from cleavage of the S–Me linkages, followed by hydrolysis with trace moisture of the remaining B–I bonds.

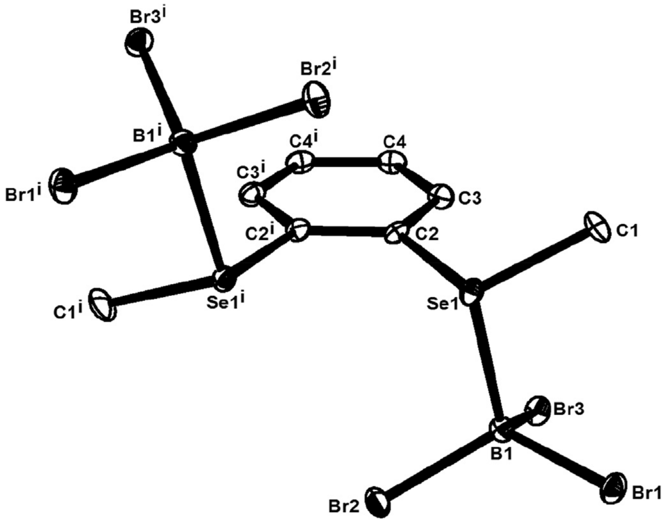


Fig. 7. The structure of [$(BBr_3)_2\{o\text{-}C_6H_4(SeMe)_2\}$] showing the numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: i = -x+1/2, y, -z. Selected bond lengths (Å) and angles (°): Se1–B1 = 2.116(3), Br2–B1 = 1.993(3), Br1–B1 = 1.980(3), Br3–B1 = 1.978(3), Br2–B1–Se1 = 103.64(15), Br1–B1–Se1 = 103.38(14), Br1–B1–Br2 = 112.81(15), Br3–B1–Se1 = 111.64(15), Br3–B1–Br2 = 112.54(15), Br3–B1–Br1 = 112.13(16).

The spectroscopic properties of [$BI_3\{o\text{-}C_6H_4(SeMe)_2\}$] are similar to those of the thioether analogue, and it is identified as containing κ^1-coordinated selenoether. The ^{11}B NMR spectrum is a singlet at δ = −74.00 (s). It does not exhibit a ^{77}Se NMR spectrum at 295 K, but on cooling the solution to 253 K, two resonances of equal intensity are present at δ +222.8, +290.7, which are assigned to the “free” and coordinated –SeMe groups respectively. The high frequency shift of the uncoordinated –SeMe group from the value in the parent ligand is ascribed to inductive effects transmitted *via* the aromatic ring from the –SeMe(BI_3). On allowing the solution to stand for several hours, new resonances appear, including an ^{11}B resonance at δ = −43.85, which is assigned to complex with a dealkylated selenide group, and a ^1H resonance at δ = 2.18 (CH_3I). The corresponding $^{77}Se\{^1H\}$ NMR spectrum shows two new resonances of similar intensity, both showing distorted four line patterns due to ^{11}B coupling, at δ = +406.3 (q, J = 43 Hz) (Se) +360.4 (q, J = 64 Hz) (SeMe). After 48 h the original complex has been consumed, and the major species present is [$BI_2\{o\text{-}C_6H_4Se(SeMe)\}$]. The identity of the decomposition product as [$BI_2\{o\text{-}C_6H_4Se(SeMe)\}$] (Fig. 9) was confirmed by the X-ray crystal structure obtained from crystals isolated by slow evaporation. The complex has a distorted tetrahedral geometry with d(B–I) not significantly different to those in BI_3-chalcogenoether complexes [13 and above]. The d(B–Se) of the selenido group is shorter (2.007(4) Å) than that of the B–SeMe group (2.088(4) Å) by ~ 0.08 Å.

BX_3 (X = Cl or Br)/*o*-$C_6H_4(TeMe)_2$: Addition of BBr_3 or BCl_3 to solutions of the ditelluroether in either n-hexane or CH_2Cl_2 immediately formed much red-brown precipitate which was mostly insoluble in CH_2Cl_2. The ^1H NMR spectra of the yellow-brown supernatant solutions showed multiple resonances, whilst the ^{11}B and ^{125}Te showed several weak features, none in the chemical shift range where BX_3-telluroether groups would be expected [13]. The ditelluroether clearly undergoes very rapid Te–C cleavage and these reactions were not pursued further.

[$(BBr_3)_n\{C(CH_2SMe)_4\}$]: Given that all the chalcogenoether

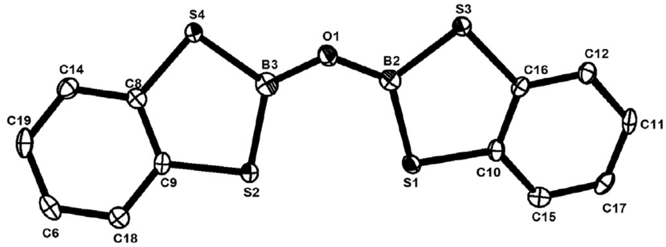


Fig. 8. The structure of [$(o\text{-}C_6H_4S_2B)_2(\mu\text{-}O)$] showing the numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): S1–B2 = 1.817(4), S2–B3 = 1.814(4), S3–B2 = 1.808(4), S4–B3 = 1.804(4), B2–O1 = 1.355(4), B3–O1 = 1.359(4), S3–B2–S1 113.7(2), O1–B2–S1 = 125.9(3), O1–B2–S3 = 120.4(3), S4–B3–S2 = 114.1(2), O1–B3–S2 = 126.3(3), O1–B3–S4 = 119.6(3), B3–O–1B2 = 133.3(3).

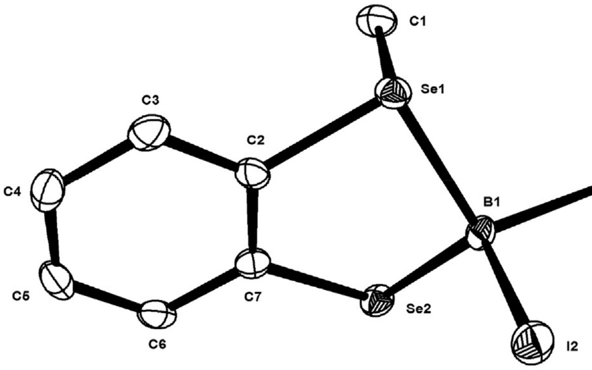


Fig. 9. The structure of $[BI_2\{o\text{-}C_6H_4Se(SeMe)\}]$ showing the numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): I1–B1 = 2.219(4), I2–B1 = 2.250(4), Se1–B1 = 2.088(4), Se2–B1 = 2.007(4), Se2–B1–Se1 = 104.37(17), Se2–B1–I1 = 113.12(19), Se1–B1–I1 = 109.61(17), Se2– B1–I2 = 114.79(19), Se1–B1–I2 = 102.70(17), I1–B1–I2 = 111.28(17).

complexes described above coordinated only a single donor group to each BX_3 unit, it seemed unlikely that polydentate ligands would produce new motifs. In fact, reaction of excess BBr_3 with the spirocyclic $C(CH_2SMe)_4$ in n-hexane precipitated a cream solid. Microanalysis and the ^1H VTNMR spectra suggested a mixture of complexes, $[(BBr_3)_n\{C(CH_2SMe)_4\}]$ (n = 1,2), and attempts to separate these were not pursued. However, a few crystals deposited from a CH_2Cl_2 solution were found to be $[(BBr_3)_2\{\kappa^2\text{-}C(CH_2SMe)_4\}]$ see ESI.

4. Conclusions

A series of dichalcogenoether complexes of the four boron trihalides have been prepared and characterised in detail. All contain tetrahedral coordination at boron and the detailed spectroscopic and structural data provided are consistent with increasing Lewis acidity $BI_3 > BBr_3 > BCl_3$ and with the affinity of the dichalcogenoethers for BX_3 decreasing down Group 16. The fluoride complexes are anomalous and in these the Group 16 ligands are weakly bound to the boron centre, as shown by their ready loss of BF_3 and by the solution spectroscopic data. The $[BX_3(ER_2)]$ [13] show similar stability trends, and as is usually observed in p-block complexes [12,16,36] the phosphine and arsine analogues are much less dissociated than those with Group 16 donor ligands. The complex formation occurs immediately on mixing the reagents, but in some systems this is followed by C–E cleavage reactions, which are greater in the order S < Se ≪ Te, as might be expected from the decreasing C–E bond energies in this order. The dichalcogenoethers display more complicated chemistry than the $[BX_3(ER_2)]$ [13] since they have more coordination modes available, and a wider range of decomposition routes possible. Thus, the instability of $[(BF_3)_2\{MeSe(CH_2)_2SeMe\}]$ compared to $[BF_3(SeMe_2))]$ is due to the fragile dimethylene linkage, which is eliminated in the presence of the strong Lewis acid, behaviour observed in other systems with 1,2-diselenoethanes [32,33]. Similarly, the decreased stability of $[(BX_3)_2\{MeTe(CH_2)_3TeMe\}]$ compared to $[BX_3(TeMe_2)]$ [13] is no doubt due to different C–Te cleavage routes possible for the ditelluroether, and similar differences have been seen with other Lewis acids, including Al, Ga and In systems [27,28,37,38]. The specific C–E dealkylations are observed most readily with BI_3 and $o\text{-}C_6H_4(EMe)_2$ (E = S, Se), (for E = Te, complete decomposition occurs on mixing the ditelluroether with BI_3), and whilst the initial complexation occurs very rapidly, this dealkylation occurs more slowly in solution. Mechanistically, it is likely that the complexation polarises the C–E bond, and then bond cleavage to eliminate CH_3I occurs (CH_3I was identified in the ^1H NMR spectra). The cleavage of C–S bonds in $o\text{-}C_6H_3R(S^iPr)_2$ by refluxing BBr_3 [17] compared to the room temperature cleavage by BI_3 in CH_2Cl_2 solution, is consistent with the mechanism proposed; BI_3 is the stronger Lewis acid, so will provide greater polarisation of the C–S bond, whilst the B–I bond is weaker than B–Br, facilitating easier cleavage.

The failure of the o-phenylene-dichalcogenoethers to produce dihaloboronium cations, $[BX_2\{o\text{-}C_6H_4(EMe_2)_2\}][BX_4]$, as found with P or As analogues, is probably traceable to the weaker B–E bonds compared to B–P(As), which are unable to displace a B–X group, even with excess Lewis acid (BX_3) present to aid the reaction (by forming the corresponding $[BX_4]^-$) [16].

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Appendix A. Supplementary data

ESI for this work including X-ray crystallographic data, the X-ray structure of $[(BBr_3)_2\{C(CH_2SMe)_4\}]$ and multinuclear NMR spectra may be found at https://doi.org/10.1016/j.jorganchem.2017.11.018.

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