Journal of Organometallic Chemistry 848 (2017) 232–238

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Complexes of BX_3 with EMe_2 (X = F, Cl, Br, I; E = Se or Te): Synthesis, multinuclear NMR spectroscopic and structural studies

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ARTICLE INFO

Article history:
Received 16 June 2017
Received in revised form
27 July 2017
Accepted 4 August 2017
Available online 8 August 2017

Keywords:
Boron halide
Selenoether
Telluroether
Boron-11 NMR
Crystal structures

ABSTRACT

The $[BX_3(EMe_2)]$ (X = Cl, Br, I; E = Se or Te) have been prepared by reaction of BX_3 with the EMe_2 in hexane under anhydrous conditions. The X-ray crystal structures of $[BX_3(TeMe_2)]$ (X = Cl, Br, I) and $[BX_3(SeMe_2)]$ (X = Cl, Br) have been determined; all are pseudo-tetrahedral monomers and show d(B–E) decreases with halogen, Cl > Br > I. Multinuclear NMR data (^{1}H, ^{11}B, ^{77}Se and ^{125}Te) are reported and compared with data on the corresponding $[BX_3(SMe_2)]$, and the trends discussed. The unstable $[BF_3(SeMe_2)]$, prepared from BF_3 and $SeMe_2$ in the absence of a solvent, has been similarly characterised by multinuclear NMR spectroscopy, and evidence for the existence of unstable $[BF_3(TeMe_2)]$ obtained for the first time, although it could not be obtained pure. The results are discussed in the light of recent theoretical modelling of boron halide adducts.

1. Introduction

The study of boron Lewis acids remains a very active area of research and has been discussed in several recent reviews [1–6]. The boron(III) halides are good Lewis acids whose acidity generally increases $BF_3 < BCl_3 < BBr_3 < BI_3$, which is counter-intuitive on electronegativity grounds, and was for many years attributed to significant X→B π bonding which decreased down Group 17. Much computational work over the past fifteen years has been devoted to exploring the factors involved, almost all focussed on N- or O-donor ligands. The results of the 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 the π-bonding explanation has been discounted [5,7–9]. 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. Due to their innate Lewis acidity, boron(III) halides have found widespread use in organic syntheses and catalysis [6,10]. There is also much current interest in the chemistry of boron-based frustrated Lewis pairs [11], and the use of boron compounds in fluoride sensing and PET imaging [12].

We recently reported a systematic study of the coordination chemistry of the neutral diphosphines, $R_2P(CH_2)_2PR_2$ (R = Me or Et) and *o*-$C_6H_4(PR'_2)_2$ (R' = Me or Ph), and the diarsine, *o*-$C_6H_4(AsMe_2)_2$ towards BX_3 (X = F, Cl, Br and I). The studies revealed that whilst flexible ligands produced $[X_3B(\mu\text{-}L\text{–}L)BX_3]$ complexes, with *o*-phenylene linked diphosphines and diarsines, very rare dihaloboronium cations, $[BX_2\{o\text{-}C_6H_4(EMe_2)_2\}]^+$ (E = P, As) were obtained [13]. In these complexes and in the corresponding $[BX_3(PMe_3)]$ [14] and $[BX_3(AsMe_3)]$ [15] the d(B–P) and d(B–As) bond lengths follow the expected order with X (F > Cl > Br > I), although data on fluoride complexes are rather limited.

Boron trihalide complexes of thio- and seleno-ethers were reported many years ago and are all of type $[BX_3(ER_2)]$ (X = F, Cl, Br or I; E = S or Se, R most often Me, sometimes Et or ^{i}Pr, R_2 = c-$(CH_2)_n$) Typical syntheses involved direct reaction of the BX_3 and ER_2 in the absence of a solvent, whilst others used alkanes, CCl_4, CH_2Cl_2 or CS_2 as solvents [16–25]. Generally, the complexes were characterised by microanalysis, ^{1}H and sometimes ^{11}B NMR and IR spectroscopy. X-Ray structural data are surprisingly rare with only the crystal structures of $[BX_3(tht)]$ (X = Cl, Br or I; tht = tetrahydrothiophene) reported [26]. In these, the d(B–S) bond length increased with halide Br > Cl > I, the anomalous position of the bromide was suggested by the authors to be due either to solid state effects or a

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http://dx.doi.org/10.1016/j.jorganchem.2017.08.004

consequence of the disorder of the tht molecule [26]. The unit cell data for several $[BX_3(EMe_2)]$ (E = S, Se) were reported in a conference paper [27], but the full structures have never appeared. Very much less is known about $TeMe_2$ adducts [22,23], and no complex was reported to form between BF_3 and $TeMe_2$ at ambient temperatures [28].

Here, we report a detailed study of the complexes $[BX_3(EMe_2)]$ (E = Se or Te) focussing on multinuclear NMR data and the X-ray crystal structures of $[BX_3(TeMe_2)]$ (X = Cl, Br, I) and $[BX_3(SeMe_2)]$ (X = Cl, Br). Multinuclear NMR spectroscopic data are also reported for $[BX_3(SMe_2)]$ for comparison. Comparisons between the boron complexes and chalcogenoether complexes with other Group 13 halides are also described.

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}. ^1H, ^{11}B, $^{19}F\{^1H\}$, $^{77}Se\{^1H\}$, and $^{125}Te\{^1H\}$ 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. 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. SMe_2 and $SeMe_2$ (Sigma-Aldrich) were stored over molecular sieves. $TeMe_2$ was made as described [29]. $[BF_3(SMe_2)]$ and $[BCl_3(SMe_2)]$ were commercial samples (Sigma-Aldrich), and $[BX_3(SMe_2)]$ (X = Br, I) were made as described, by reaction of the constituents in n-hexane [23].

2.1. $[BCl_3(TeMe_2)]$

$TeMe_2$ (0.14 g, 0.9 mmol) was dissolved in n-hexane (10 mL), the solution cooled in an ice bath, and a slow stream of BCl_3 passed in, producing a white precipitate. The mixture was stirred for 30 min and then the solid filtered off and dried *in vacuo*. Yield: 0.185 g, 61%. Anal. Required for $C_2H_6BCl_3Te$ (274.8): C, 8.74; H, 2.20%. Found: C, 9.19; H, 2.13%. ^1H NMR ($CDCl_3$, 295 K): δ 2.10 (s). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +4.78 (s), ^{125}Te NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +182.9 (s). IR (Nujol): ν = 721 (br) (BCl) cm^{-1}. Colourless crystals were grown by slow evaporation of a CH_2Cl_2 solution of the product.

2.2. $[BBr_3(TeMe_2)]$

To an n-hexane solution (10 mL) of BBr_3 (0.20 g, 0.8 mmol) in an ice bath, was added dropwise $TeMe_2$ (0.126 g, 0.8 mmol), leading to the formation of an immediate white precipitate. After stirring for 30 min, the white powder was isolated by filtration and dried *in vacuo*. Yield: 0.230 g, 70%. Anal. Required for $C_2H_6BBr_3Te$ (408.2): C, 5.99; H, 1.48%. Found: C, 6.94; H, 1.81%. ^1H NMR ($CDCl_3$, 295 K): δ 2.10 (s). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −20.01 (s), ^{125}Te NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +242.9 (s). IR (Nujol): ν = 622 (s) (BBr) cm^{-1}. Small colourless crystals were grown by slow evaporation of a CH_2Cl_2 solution of the product.

2.3. $[BI_3(TeMe_2)]$

Powdered BI_3 (0.20 g, 0.5 mmol) was added to n-hexane (15 mL) and $TeMe_2$ (0.08 g, 0.5 mmol) was added dropwise to the stirred solution. A pale cream solid formed immediately and after stirring for 20 min the white solid was filtered off and dried *in vacuo*. Yield: 0.19 g, 69%. $C_2H_6BI_3Te$ (549.2): C, 4.37; H, 1.10%. Found: C, 5.14; H, 1.68%. ^1H NMR ($CDCl_3$, 295 K): δ 1.91 (s). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −86.80 (s). ^{125}Te NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +290.2 (q, $^1J_{BTe}$ = 121 Hz). IR (Nujol): ν = 560(m), 543(s) (BI) cm^{-1}.

2.4. $[BCl_3(SeMe_2)]$

SeMe_2 (0.16 g, 1.5 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: 0.120 g, 36%. $C_2H_6BCl_3Se$ (226.2): C, 10.62; H, 2.67%. Found: C, 10.61; H, 2.65%. ^1H NMR ($CDCl_3$, 295 K): δ 2.36 (s). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +7.36 (s). ^{77}Se NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +170.5 (s). IR (Nujol): ν = 765 (m), 723 (s) (BCl) cm^{-1}.

2.5. $[BBr_3(SeMe_2)]$

To a solution of $SeMe_2$ (0.087 g, 0.8 mmol) in n-hexane (8 mL) was added dropwise BBr_3 (0.20 g, 0.8 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: 0.134 g, 47%. $C_2H_6BBr_3Se$ (359.6): C, 6.68; H, 1.68%. Found: C, 6.76; H, 2.60%. ^1H NMR ($CDCl_3$, 295 K): δ 2.33 (s). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −12.94 (s). ^{77}Se NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +194.4 (s). IR (Nujol): ν = 680(m), 640 (s) (BBr) cm^{-1}.

2.6. $[BI_3(SeMe_2)]$

To a n-hexane (10 mL) solution of BI_3 (0.05 g, 0.13 mmol) was added dropwise Me_2Se (0.014 g, 0.13 mmol) leading to the immediate formation of a white precipitate. After stirring the mixture for a further 30 min the white powder was filtered and dried *in vacuo*. Yield: 0.022 g (34%). $C_2H_6BI_3Se$ (500.6): C, 4.80; H, 1.21%. Found: C, 4.87; H, 1.33%. ^1H NMR ($CDCl_3$, 295 K): δ 2.30 (s). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −73.96 (s), ^{77}Se NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +203.7 (q, $^1J_{BSe}$ = 52 Hz). IR (Nujol): ν = 560 (m), 550 (s) (BI) cm^{-1}.

2.7. $[BF_3(SeMe_2)]$

Neat $SeMe_2$ (0.22 g, 2.0 mmol) was cooled in an ice-bath and a slow stream of BF_3 bubbled in for 5 min. The product was a clear straw coloured liquid which fumes in air and is hydrolysed by trace moisture. The liquid was stored under a nitrogen atmosphere and measurements made on freshly prepared samples. The complex has a significant vapour pressure of BF_3 at room temperature and the microanalysis cannot be obtained. ^1H NMR ($CDCl_3$, 295 K): δ 2.04 (s). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +5.31 (s); (183 K): δ +3.25 (s). $^{19}F\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −132.8 (s); (183 K): δ −134.2 (s). ^{77}Se NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +1.03 (s); (183 K): δ +0.53 (s).

2.8. $[BF_3(TeMe_2)]$

Treatment of $TeMe_2$ with BF_3 gas either at ambient temperature or in an ice bath gave a yellow oil with some orange-red solid. Similarly, adding BF_3 gas to a solution of $TeMe_2$ in CH_2Cl_2 gave a yellow solution and some red precipitate. Both the neat liquid and the solution decompose in a few hours at room temperature, turning orange and then dark red. It was not possible to produce a pure sample, and the freshly made yellow CH_2Cl_2 solution was used

for the spectroscopic measurements. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.98 (s); (183 K): 1.86 (s). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +5.31 (s); (183 K): δ −1.52 (s). ^{19}F{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −144.5 (s); (183 K): δ −148.3 (s). ^{125}Te NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −4.80 (s); (183 K): δ −29.2 (s).

After 12 h at room temperature the CH_2Cl_2 solution had become deep orange with much orange-red precipitate and had singlet ^{1}H NMR resonances at 1.92, 2.68 and 5.41, tentatively assigned to free $TeMe_2$ and $[Me_2TeCH_2Cl]^+$ (or $[Me_2Te(CH_2Cl)Cl]$), with corresponding ^{125}Te{^{1}H} resonances at −13 and + 418. The ^{19}F{^{1}H} NMR showed $[BF_4]^-$ as the major species, with some smaller amounts of F^-.

2.9. 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 [30]. 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 $[BCl_3(TeMe_2)]$: CCDC 1554690; $[BBr_3(TeMe_2)]$: CCDC 1554688; $[BI_3(TeMe_2)]$: CCDC 1554689; $[BCl_3(SeMe_2)]$: CCDC 1554686; $[BBr_3(SeMe_2)]$: CCDC 1554687. 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.

3. Results and discussion

3.1. $[BX_3(TeMe_2)]$ (X = Cl, Br, I)

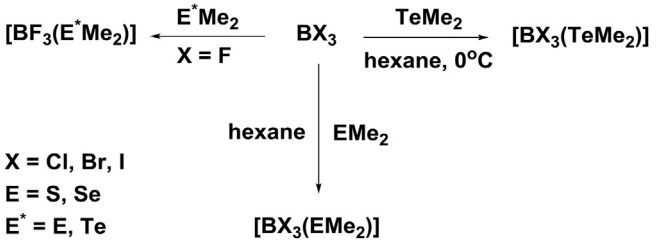
Although $[BX_3(TeMe_2)]$ (X = Cl, Br, I) have been briefly mentioned in larger studies of boron halide complexes [22,23], they lack detailed characterisation. All three complexes were made by reaction of the appropriate BX_3 and $TeMe_2$ in dry n-hexane at 0 °C, when they separated as white powders (Scheme 1).

The same compounds are produced using excess ligand. The solids slowly darken and decompose at room temperature and are significantly decomposed after 24 h in solution in chlorocarbons.

Colourless crystals of $[BX_3(TeMe_2)]$ (X = Cl, Br, I) were grown by evaporation of CH_2Cl_2 solutions in the glove box and the structures are shown in Fig. 1.

The crystals are isomorphous and contain tetrahedrally coordinated boron centres with <X−B−X slightly greater than the idealised tetrahedral angle and one of the <X−B−Te slightly smaller. The d(B−X) (Table 2) are very similar to those in the corresponding PMe_3 or $AsMe_3$ adducts [14,15]. The d(B−E) bonds increase I ~ Br < Cl. The B-X bonds are not significantly affected by the chalcogenoether present. The < C−Te−C angles are ~95°, consistent with a large tellurium p-character in the C−Te bonds [31]. Examination of the packing diagrams shows no Te···X interactions between neighbouring molecules within the sum of the van der Waals radii, and hence no hypervalent interactions at Te.

The ^{11}B NMR resonances (^{11}B, 80%, I = 3/2, Ξ = 32.084 MHz, Q = 3.55 × 10^{-30} m^2, R_c = 754) move to high frequency with halide, I < Br < Cl, the same trend as found with Group 15 donor ligands [13,32]. The ^{11}B chemical shifts of the telluroether complexes are all much lower frequency than those of the parent trihalides, reflecting both the change in coordination number and the different electronic environment at B (Table 3).



Scheme 1. Synthesis of the complexes.

Table 1
X-ray crystallographic data.[a]

Compound	$[BCl_3(TeMe_2)]$	$[BBr_3(TeMe_2)]$	$[BI_3(TeMe_2)]$	$[BCl_3(SeMe_2)]$	$[BBr_3(SeMe_2)]$
Formula	$C_2H_6BCl_3Te$	$C_2H_6BBr_3Te$	$C_2H_6BI_3Te$	$C_2H_6BCl_3Se$	$C_2H_6BBr_3Se$
M	274.85	408.21	549.18	226.19	359.57
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group (No)	$P2_1/m$ (11)	$P2_1/m$ (11)	$P2_1/m$ (11)	$P2_1/m$ (11)	$P2_1/m$ (11)
a [Å]	5.76470(10)	6.08639(17)	6.6604(2)	5.78171(18)	6.1384(3)
b [Å]	10.8546(2)	11.0548(3)	11.3864(9)	10.6641(2)	10.8664(4)
c [Å]	6.5636(2)	6.69386(18)	6.96470(10)	6.4752(3)	6.6455(3)
α °	90	90	90	90	90
β °	104.676(3)	104.876(3)	105.488(2)	107.398(4)	108.280(5)
γ °	90	90	90	90	90
U [Å^3]	397.308(17)	435.29(2)	509.01(4)	380.97(2)	420.90(3)
Z	2	2	2	2	2
μ(Mo Kα) [mm^{-1}]	4.645	17.089	11.938	5.868	18.600
total no. reflns	4289	3420	11377	216	324
unique reflns	822	904	468	8451	9534
R_{int}	0.0163	0.020	0.039	0.035	0.055
no. of params, restraints	38, 0	38, 0	38, 0	38, 0	38, 0
F(000)	252	360	1059	781	876
GOF	1.089	1.074	1.165	1.140	1.104
Largest peak and hole e/Å^3	0.379, −0.235	0.923, −0.623	0.566, −0.741	0.523, −0.249	0.798, −0.498
R_1[b] [$I_o > 2\sigma(I_o)$]	0.010	0.017	0.014	0.016	0.021
R_1 [all data]	0.027	0.044	0.014	0.016	0.023
wR_2[b] [$I_o > 2\sigma(I_o)$]	0.011	0.017	0.035	0.039	0.051
wR_2 [all data]	0.027	0.044	0.035	0.039	0.052

[a] Common items: temperature = 100 K; wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°.
[b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma\, wF_o^4]^{1/2}$.

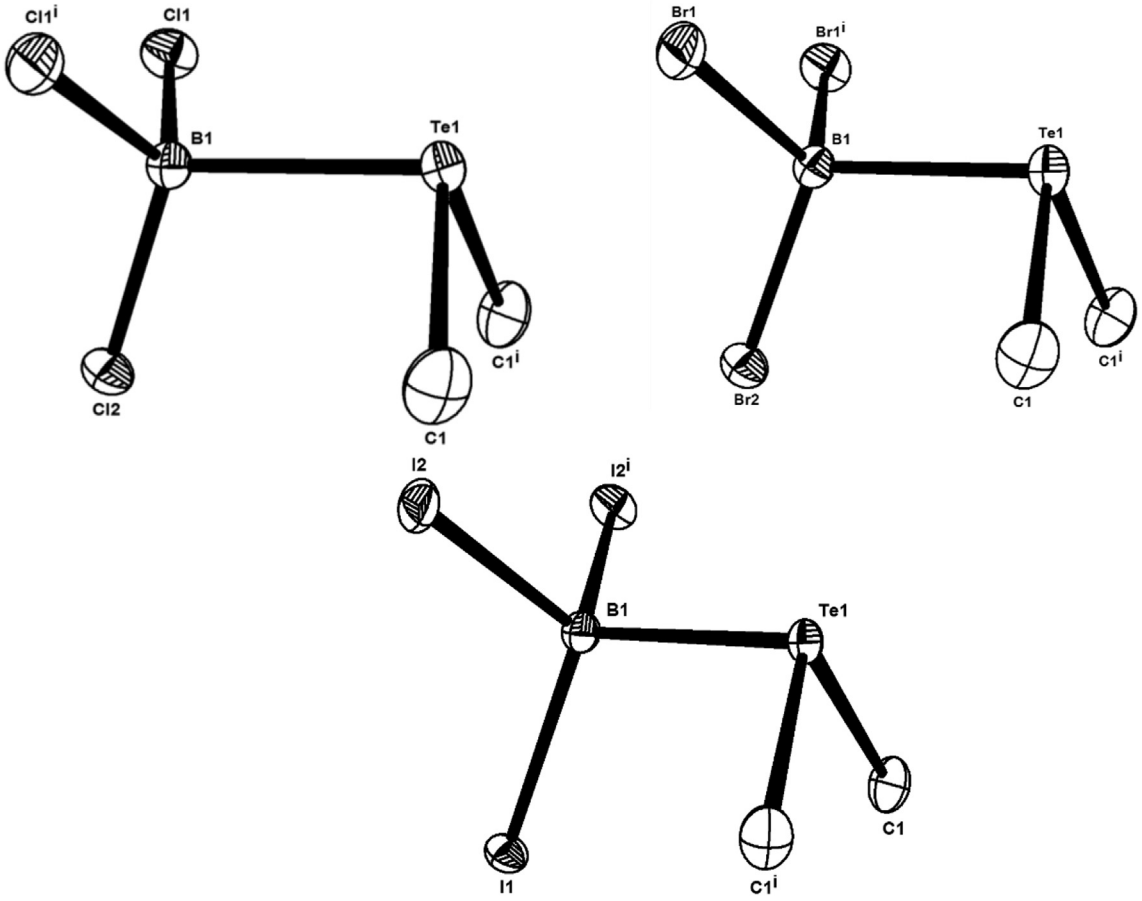


Fig. 1. The structures of $[BX_3(TeMe_2)]$ (X = Cl, Br, I) showing the numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: i = x, ½ -y, z. Selected bond lengths (Å) and angles (°):
X = Cl: Te1–B1 = 2.298(2), Cl1–B1 = 1.8302(13), Cl2–B1 = 1.834(2), C1–Te1–$C1^i$ = 95.00(9), Cl1–B1–Te1 = 106.29(8), Cl2–B1–Te1 = 108.87(10), Cl2–B1–Cl1 = 111.18(8), Cl2–B1–$Cl2^i$ = 112.73(11).
X = Br: Te1–B1 = 2.266(4), Br2–B1 = 1.986(4), Br1–B1 = 1.996(2), C1–Te1–$C1^i$ = 95.08(16), Br2–B1–Te1 = 110.60(17), Br2–B1–Br1 = 110.92(12), Br1–B1–Te1 = 106.29(12), Br1–B1–$Br1^i$ = 111.63(18).
X = I: I1–B1 = 2.215(4), I2–B1 = 2.227(2), Te1–B1 = 2.262(4), C1–Te1–$C1^i$ = 95.84(17), I1–BI–I2 = 111.15(12), I1–B1–Te1 = 111.66(18), I2–B1–$I2^i$ = 111.12(18), I2–B1–Te1 = 105.75(13).

Table 2
Bond length comparisons.

	$[BCl_3(TeMe_2)]$	$[BBr_3(TeMe_2)]$	$[BI_3(TeMe_2)]$	$[BCl_3(SeMe_2)]$	$[BBr_3(SeMe_2)]$
B-E/Å	2.298(2)	2.266(4)	2.262(4)	2.106(3)	2.088(4)
B-X/Å	1.8302(13)	1.986(4)	2.215(4)	1.8287(15)	1.987(5)
	1.834(2)	1.996(2)	2.227(2)	1.825(3)	1.993(3)

The $^{125}Te\{^1H\}$ NMR resonances observed for X = Cl or Br, are singlets with no resolved coupling to ^{11}B; this can be attributed to a combination of fast ligand exchange in solution and quadrupolar relaxation of the ^{11}B in the significant electric field gradients about the boron centre [20,22]. Cooling the samples stepwise down to 190 K resulted in small changes in the line width and small drifts in chemical shifts, but did not resolve couplings. In contrast, the $^{125}Te\{^1H\}$ NMR spectrum of $[BI_3(TeMe_2)]$ at 295 K is a four line pattern with the ^{11}B coupling clearly resolved (Fig. 2). Couplings to the ^{10}B (I = 3, Ξ = 10.75 MHz, Q = 7.4 × 10^{-30} m^2) were not resolved due to its larger quadrupole moment, and account for the broad feature underlying the four line pattern. The coordination shifts are large and increase Cl < Br < I, suggesting increasingly strong B–Te interaction in this order, although care should be taken in interpreting such changes as due to a single effect [32,33].

3.2. $[BX_3(SeMe_2)]$ (X = Cl, Br, I)

The dimethylselenide complexes are white powders and unlike the telluroether analogues (Scheme 1), are stable for many weeks in the solid state and show no decomposition in chlorocarbon solution after several days. X-ray structures were determined for $[BX_3(SeMe_2)]$ (X = Cl or Br) (Fig. 3) and again are isomorphous. The trends in bond length with X and E are as seen in the telluroether complexes.

The ^{11}B NMR chemical shifts occur at slightly higher frequency than those found in the telluroether complexes for common X (Table 3) and the trend to higher frequency Cl > Br > I is observed. The ^{77}Se NMR spectra also show coordination shifts with X (Cl < Br < I). At 295 K the ^{77}Se NMR resonances of $[BX_3(SeMe_2)]$ (X = Cl or Br) are broad singlets, but that of $[BI_3(SeMe_2)]$ (Fig. 4)

Table 3
Multinuclear NMR data on $[BX_3(ER_2)]$.[a,b]

	^{1}H	^{11}B[c]	^{19}F[d]	$^{77}Se/^{125}Te$[e]
$[BF_3(SMe_2)]$	2.25	+3.52	−138.8	–
$[BF_3(SeMe_2)]$	2.01	+5.34	−132.8	+1.04
$[BF_3(TeMe_2)]$	1.93	+1.90	−144.2	−4.8
$[BCl_3(SMe_2)]$	2.49	+8.49	–	–
$[BCl_3(SeMe_2)]$	2.36	+7.36	–	+170.5
$[BCl_3(TeMe_2)]$	2.10	+4.78	–	+182.9
$[BBr_3(SMe_2)]$	2.57	−9.84	–	–
$[BBr_3(SeMe_2)]$	2.33	−12.94	–	+194.4
$[BBr_3(TeMe_2)]$	2.10	−20.01	–	+243.2
$[BI_3(SMe_2)]$	2.56	−67.55	–	–
$[BI_3(SeMe_2)]$	2.30	−73.96	–	+203.7 (q)
$[BI_3(TeMe_2)]$	2.05	−86.80	–	+290.2 (q)

[a] All data from CH_2Cl_2/CD_2Cl_2 solution at 295 K.
[b] 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. [34].
[c] Relative to external $[BF_3(OEt_2)]$.
[d] Relative to external $CFCl_3$.
[e] Relative to neat $SeMe_2$ or $TeMe_2$ singlets except q = four line pattern. Since the zero references are $SeMe_2$ and $TeMe_2$, the coordination shifts (Δ) in these cases are numerically the same as the observed chemical shifts.

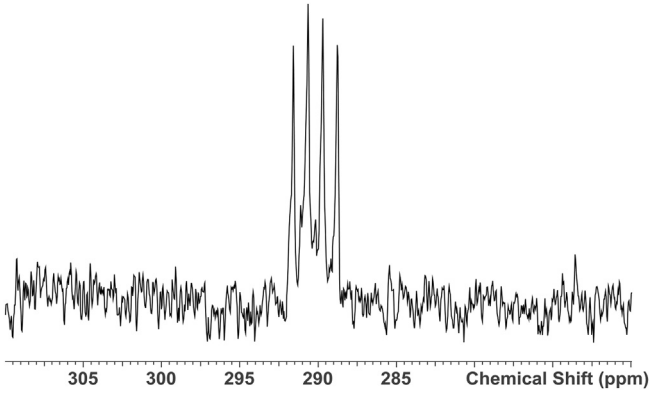


Fig. 2. The ^{125}Te NMR spectrum of $[BI_3(TeMe_2)]$ in CH_2Cl_2 at 295 K showing the $^{11}B-^{125}Te$ coupling, ^{1}J = 120 Hz. The broad feature under the resonance is due to unresolved ^{10}B couplings.

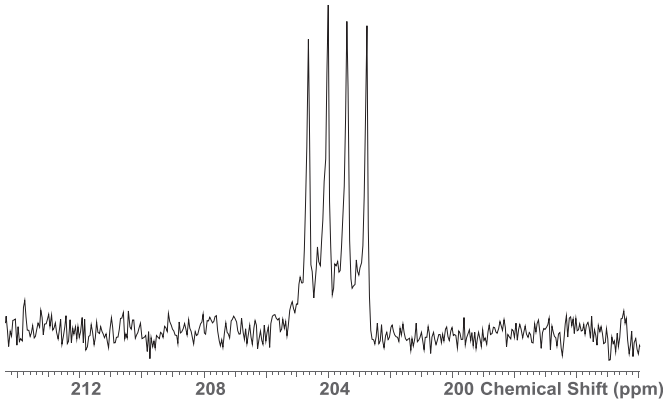


Fig. 4. The ^{77}Se NMR spectrum of $[BI_3(SeMe_2)]$ in CH_2Cl_2 at 295 K showing the $^{11}B-^{77}Se$ coupling, ^{1}J = 52 Hz. The broad feature under the resonance is due to unresolved ^{10}B couplings.

shows a sharp four line pattern due to coupling to ^{11}B, $^{1}J_{BSe} = 52$ Hz. Cooling a CH_2Cl_2 solution of $[BBr_3(SeMe_2)]$ to 183 K caused the singlet resonance to significantly broaden, but even at this temperature $^{11}B-^{77}Se$ coupling was not resolved.

3.3. $[BX_3(SMe_2)]$ (X = Cl, Br, I)

Multinuclear NMR data for these three complexes are given in Table 3. The data are generally in good agreement with literature data [18,21–23] when allowance is made for the use of different solvents and sometimes different boron zero references. The trends in chemical shift with X mirror those described above.

3.4. $[BF_3(EMe_2)]$ (E = Te, Se, S)

The BF_3 adducts are very different to those formed by the other boron halides. The commercially available $[BF_3(SMe_2)]$, which is a convenient source of BF_3 in organic synthesis, is a colourless oil, which fumes in air and has a significant vapour pressure at 298 K [16,18]. The ^{1}H, ^{11}B and ^{19}F NMR data (Table 3) obtained from CH_2Cl_2 solution at 295 K are in good agreement with literature data [20]. Cooling the solution results in small low temperature drifts of the

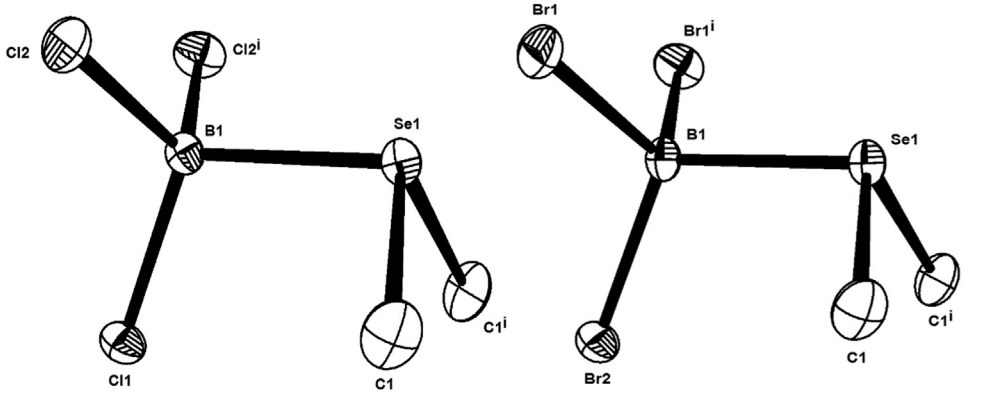


Fig. 3. The structures of $[BX_3(SeMe_2)]$ (X = Cl, Br) showing the numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: i = x, ½ -y, z. Selected bond lengths (Å) and angles (°):
X = Cl: B1–Se1 = 2.106(3), B1–Cl2 = 1.8287(15), B1–Cl1 = 1.825(3), Cl2–B1–Se1 = 105.30(10), Cl2–B1–$Cl2^{i}$ = 112.58(14), Cl1–B1–Se1 = 109.57(13), Cl1–B1–Cl2 = 111.82(10), C1–Se1–$C1^{i}$ 97.93(11).
X = Br: B1–Se1 = 2.088(4), B1–Br2 = 1.987(5), B1–Br1 = 1.993(3), Br2–B1–Se1 = 110.7(2), Br1–B1–$Br1^{i}$ = 112.1(2), Br1–B1–Se1 = 105.14(14), Br1–B1–Br2 = 111.66(14), C1–Se1–$C1^{i}$ 98.3(2).

chemical shifts and below ~200 K the resonances broaden, but even at 183 K, ^{11}B-^{19}F coupling is not resolved. [$BF_3(SeMe_2)$] was obtained as a very pale yellow liquid by saturating neat $SeMe_2$ in an ice-bath with BF_3. It is more volatile and more extensively dissociated than the SMe_2 analogue [16], and has a significant vapour pressure of BF_3 at ambient temperature. The ^1H, ^{11}B and ^{19}F NMR data (Table 3) obtained from CH_2Cl_2 solution at 295 K are similar to those observed for [$BF_3(SMe_2)$]. The ^{77}Se chemical shift of [$BF_3(SeMe_2)$] in CH_2Cl_2 solution is very different to those found with the other three boron halides. At ambient temperatures it is a broad singlet at ~ +1 ppm, which is little changed on cooling the solution to 183 K. It is worth pointing out here that the zero reference is neat $SeMe_2$ ($\delta = 0$), and that $SeMe_2$ in CH_2Cl_2 solution has (δ ~ −7) [34], so the observed value is some ~ 8 ppm to high frequency of the free selenoether in this solvent; nonetheless a very small coordination shift. The most obvious explanation is that the $SeMe_2$ is very weakly bound to the BF_3 centre and fast neutral ligand exchange may be taking place even at the lowest temperatures. The [$BF_3(SeMe_2)$] fumes in air and is very sensitive to moisture which generates $[BF_4]^-$ and a species with δ (^1H) = 2.59 and δ (^{77}Se) = 247, which is tentatively identified as $[Me_3Se]^+$ (lit. δ (^{77}Se) = 253 (H_2O) [34], 259 (acetone) [35]).

The only report [28] found of the reaction of BF_3 with $TeMe_2$ described "immediately upon addition of BF_3 the solution assumed a brilliant red hue and a volatile orange coloured sublimate quickly formed". We observed that on passing BF_3 gas into $TeMe_2$ in an ice bath, a yellow liquid with small amounts of orange-red solid formed. A yellow solution and some red solid formed on conducting the reaction in anhydrous CH_2Cl_2 solution. The amount of red solid increases over time, and both the liquid and the CH_2Cl_2 solution seem extensively decomposed after 12 h at room temperature. The multinuclear NMR data (Table 3) suggest the yellow liquid is [$BF_3(TeMe_2)$], but this has not been obtained pure, always seeming to contain some orange impurity. The ^{11}B and ^{19}F NMR spectra are not dissimilar to those obtained from the SMe_2 and $SeMe_2$ adducts and are little affected by cooling the solution to 183 K. The $^{125}Te\{^1H\}$ NMR spectrum in CH_2Cl_2 at 295 K is a sharp resonance at $\delta = -4.8$, which shifts to $\delta = -29$ at 183 K. Like the case of the selenium analogue discussed above, the chemical shift of free $TeMe_2$ is solvent and temperature sensitive [34] and in CH_2Cl_2 solution at 295 K has $\delta = -15$ relative to the zero reference of neat $TeMe_2$. A CH_2Cl_2 solution which had become deep orange with much orange precipitate after ~20 h at room temperature showed new resonances identified as free $TeMe_2$, $[BF_4]^-$, and possibly $[Me_2Te(CH_2Cl)Cl]$ (see Section 2.9). The $[Me_2Te(CH_2Cl)Cl]$ or possibly$[Me_2Te(CH_2Cl)][BF_4]$ is formed by the quaternisation of the telluroether by the solvent, promoted by the strong Lewis acidic BF_3. We have observed similar Lewis acid promoted quaternisation of chalcogenoether ligands in gallium and aluminium systems [36,37].

4. Comparisons and conclusions

The X-ray crystallographic data described for the $[BX_3(EMe_2)]$ (E = Se or Te; X = Cl, Br, I) above (Table 2) shows systematic trends with d(B–E) falling with X, Cl > Br > I, the same order as found with most other neutral donor systems, and consistent with BI_3 being the strongest Lewis acid [3,5]. Although the X-ray data are less complete, the heavier elements of Group 13 (Al, Ga and In) show the reverse trends, with the metal chloride forming the shortest M–E bonds [37–40]. The multinuclear NMR data (Table 3) also show some consistent trends, for example the ^{11}B chemical shifts for a fixed chalcogenoether move to low frequency Cl → Br → I, whilst for a fixed halide the trend to low frequency is S → Se → Te. For complexes of these three boron halides with $SeMe_2$ the ^{77}Se coordination shifts ($\Delta = \delta_{complex} - \delta_{ligand}$) are also large and positive (to high frequency) with Δ I > Br > Cl. The ^{125}Te coordination shifts follow the same order. In many series of organoselenium and organotellurium compounds the ratio $\delta(Te)/\delta(Se)$ ~ 1.8 is observed [33,34,41], and this empirical observation also holds for some d-block metal complexes in medium oxidation states [33]. However, in low valent organometallic or carbonyl complexes the ratio of the coordination shifts are much larger, $\delta(Te)/\delta(Se) > 2.3$, rationalised as due to greater $R_2Te \rightarrow M$ donation in the soft metal centres and with expanded metal d-orbitals resulting from the low oxidation states providing good orbital overlap with Te centres [33,42–44]. In the case of the boron halide adducts the opposite trend is observed with $\delta(Te)/\delta(Se)$ ~ 1.1–1.4, consistent with the stronger interaction being B–$SeMe_2$.

The chalcogenoether adducts of BF_3 are clearly different to those with the other boron halides, and whilst this work has shown that [$BF_3(TeMe_2)$] does exist, it is unstable and could not be obtained pure. The ^{11}B NMR spectra show the chemical shifts move to low frequency Cl > F > Br > I for a fixed EMe_2, the anomalous position of the fluoride also being observed with Group 15 donor ligands [3,13]. The very small coordination shifts observed in the ^{77}Se and ^{125}Te NMR spectra of the fluoride complexes also suggest weak interactions. Overall the data confirm the trends in Lewis acidity of the boron halides predicted by recent theoretical studies [5–9].

Acknowledgements

C.K.Y.A.O. thanks the Universidad Nacional de Colombia for authorising sabbatical leave. We also thank the EPSRC (EP/L505651/1, EP/K039466/1) and the Newton Fund for support.

Appendix A. Supplementary data

ESI for this work including X-ray crystallographic data, and multinuclear NMR spectra may be found at http://dx.doi.org/10.1016/j.jorganchem.2017.08.004.

References

[1] A. Staubitz, A.P.M. Robertson, I. Manners, Chem. Rev. 110 (2010) 4079.
[2] A. Staubitz, A.P.M. Robertson, M.E. Sloan, I. Manners, Chem. Rev. 110 (2010) 4023.
[3] J. Burt, W. Levason, G. Reid, Coord. Chem. Rev. 260 (2014) 65.
[4] N.A. Young, Coord. Chem. Rev. 257 (2013) 956.
[5] I.B. Sivaev, V.I. Bregadze, Coord. Chem. Rev. 270–271 (2014) 75.
[6] N.S. Hosmane (Ed.), Boron Science: New Technologies and Applications, CRC Press, Florida, 2012.
[7] F. Bessac, G. Frenking, Inorg. Chem. 42 (2003) 7990.
[8] F. Bessac, G. Frenking, Inorg. Chem. 45 (2006) 6956.
[9] J.A. Plumley, J.D. Evanseck, J. Phys. Chem. A 113 (2009) 5985.
[10] A.M. McKinty, C. Lund, D.W. Stephan, Organometallics 32 (2013) 4730.
[11] D.W. Stephen, Nat. Chem. 6 (2014) 952.
[12] K. Chansaenpak, B. Vabre, F.P. Gabbaï, Chem. Soc. Rev. 45 (2016) 954.
[13] J. Burt, J.W. Emsley, W. Levason, G. Reid, I.S. Tinkler, Inorg. Chem. 55 (2016) 8852.
[14] D.L. Black, R.C. Taylor, Acta Cryst. Sect. B 31 (1975) 1116.
[15] R.K. Chadha, J.M. Chehayber, J.E. Drake, J. Cryst. Spectros. Res. 15 (1985) 53.
[16] W.A.G. Graham, F.G.A. Stone, J. Inorg. Nucl. Chem. 3 (1956) 164.
[17] H.L. Morris, N.I. Kulevsky, M. Tamres, S. Searles Jr., Inorg. Chem. 5 (1966) 124.
[18] H.C. Brown, N. Ravindran, Inorg. Chem. 16 (1977) 2938.
[19] K. Kinberger, W. Siebert, Z. Naturforsch. Teil B 30 (1975) 55.
[20] M.J. Bula, J.S. Hartman, J. Chem. Soc. Dalton Trans. (1973) 1047.
[21] H. Fußstetter, H. Nöth, B. Wrackmeyer, W. McFarlane, Chem. Ber. 110 (1977) 3172.
[22] R. Conrady, W. Müller-Warmuth, B. Krebs, G. Schwetlik, M. Wienkenhöver, Ber. Bunsenges. Phys. Chem. 91 (1987) 1322.
[23] M. Schmidt, H.D. Block, Chem. Ber. 103 (1970) 3705.
[24] J. Le Calve, J. Lascombe, Spectrochim. Acta 24A (1968) 737.
[25] P. Labarbe, M.T. Forel, Spectrochim. Acta 31A (1975) 525.
[26] B. Krebs, G. Schwetlik, M. Wienkenhöver, Acta Crystallogr. B45 (1989) 257.
[27] M. Wienkenhover, A. Vahrenhorst, M. Tatermann, B. Krebs, Eur. Cryst. Meet. 9 (1985) 154 (CCDC- codes DIMCEH, DIMCIL, DIMCOR, DIMCAO, DIMBUW).
[28] A.A. Palko, J.S. Drury, J. Chem. Phys. 46 (1967) 2297.
[29] N. Kuhn, P. Faupel, E. Zauder, J. Organomet. Chem. 302 (1986) C4.

[30] G.M. Sheldrick, Acta Crystallogr. Sect. A 64 (2008) 112.
[31] W. Levason, G. Reid, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, vol. 1, Elsevier Oxford, 2004, p. 391.
[32] H. Nöth, B. Wrackmeyer, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, Springer-Verlag, N.Y, 1978.
[33] W. Levason, S.D. Orchard, G. Reid, Coord. Chem. Rev. 235 (2002) 159.
[34] N.P. Luthra, J.D. Odom, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Selenium and Tellurium Compounds, vol. 1, Wiley, NY, 1986 (chapter 6).
[35] W. Levason, L.P. Ollivere, G. Reid, M. Webster, J. Organometal. Chem. 695 (2010) 1346.
[36] K. George, M. Jura, W. Levason, M.E. Light, L.P. Ollivere, G. Reid, Inorg. Chem. 51 (2012) 2231.
[37] K. George, M. Jura, W. Levason, M.E. Light, G. Reid, Dalton Trans. 43 (2014) 3637.
[38] C. Gurnani, W. Levason, R. Ratnani, G. Reid, M. Webster, Dalton Trans. (2008) 6274.
[39] S. Mishra, E. Jeanneau, S. Daniele, Polyhedron 29 (2010) 500.
[40] C. Gurnani, M. Jura, W. Levason, R. Ratnani, G. Reid, M. Webster, Dalton Trans. (2009) 1611.
[41] T. Kemmitt, W. Levason, Organometallics 8 (1989) 1303.
[42] N. Kuhn, H. Schumann, E. Zauder, J. Organometal. Chem. 327 (1987) 17.
[43] A.J. Barton, W. Levason, G. Reid, J. Organometal. Chem. 579 (1999) 235.
[44] W. Levason, S.D. Orchard, G. Reid, J.M. Street, J. Chem. Soc. Dalton Trans. (2000) 2537.