Boron Halides as Reagents in Inorganic Syntheses. Part II.[1] A Further General Method for the Preparation of Anhydrous Bromides and Iodides: Halogen Exchange Reactions

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Metathetical exchange reactions of (i) boron tribromide with anhydrous chlorides of Al^{III}, Tl^{I}, Sn^{IV}, As^{III}, Sb^{III}, Sb^{V}, Bi^{III}, Ti^{III}, Ti^{IV}, Zr^{IV}, Hf^{IV}, V^{III}, Nb^{V}, Ta^{V}, Mo^{V}, W^{VI}, Fe^{III}, Co^{II}, Ni^{II}, Pt^{IV}, Cu^{II}, and Cd^{II}; (ii) BBr_3 and oxychlorides of S^{VI} and V^{V}; and (iii) BI_3 with anhydrous chlorides of Sn^{IV}, Sb^{III}, and Ti^{IV}, provide a general method of synthesising anhydrous bromides and iodides. Boron tribromide reacts with the cluster chloride Pt_6Cl_{12} forming the new mixed halide $(PtBrCl)_n$. The exchange reactions are essentially quantitative, and separation of pure products is readily achieved.

The general reaction between boron tribromide and metal, metalloid, and non-metal oxides for preparing anhydrous bromides and oxybromides has been extended. Thus the reactions of BBr_3 with oxides of Ga^{III}, In^{III}, Tl^{III}, Sn^{IV}, Bi^{III}, Te^{IV}, Zr^{IV}, Nb^{V}, Ta^{V}, Mo^{IV}, Mo^{VI}, Fe^{III}, La^{III}, U^{IV}, Zn^{II}, Hg^{I}, and Hg^{II}, and of BI_3 with oxides of Sn^{IV} and Ta^{V}, are reported.

Vibrational spectra for the halides $NbOBr_3$, $NbBr_5$, $TaBr_5$, and $Pt_6Br_6Cl_6$ are described.

ALTHOUGH a few isolated examples of exchange reactions of boron tribromide and tri-iodide have been reported, no systematic investigation of the reactions of these compounds with anhydrous metal chlorides has been carried out. Boron tribromide had been observed to exchange halogen with, for example, SbF_3,[2] UF_6,[3a] ReF_6,[3b] and GeH_3Cl.[4] Boron tri-iodide reacts with AgF,[5] whilst the trichloride has been reported to exchange halogen with

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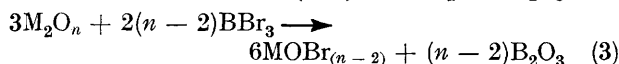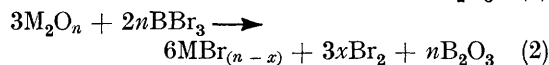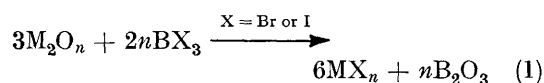
XeF_4,[6] SF_4,[7] and several transition-metal fluorides.[3] The chemistry of the boron halides has been comprehensively surveyed.[8]

We now present results on (i) further reactions (see ref. 1) of boron tribromide and tri-iodide with metal oxides, and (ii) the metathetical exchanges of these trihalides with a variety of anhydrous metal chlorides. From (ii) it is clear that a convenient general route for the synthesis of anhydrous bromides and iodides has become available. A preliminary account has been published,[9] and the reactions of boron trihalides with the Group IVA metallocene halides $(\pi\text{-}C_5H_5)_2MCl_2$ (M = Ti, Zr, and Hf), have been described.[10]

For systems (i), the three types of reaction encountered are summarised by equations (1)—(3). The results are shown in Table 1. The general procedure involved a

$$3M_2O_n + 2nBX_3 \xrightarrow{X = Br \text{ or } I} 6MX_n + nB_2O_3 \quad (1)$$

$$3M_2O_n + 2nBBr_3 \longrightarrow 6MBr_{(n-x)} + 3xBr_2 + nB_2O_3 \quad (2)$$

$$3M_2O_n + 2(n-2)BBr_3 \longrightarrow 6MOBr_{(n-2)} + (n-2)B_2O_3 \quad (3)$$

slow addition of excess of boron trihalide (Br, I) to the oxide; in many cases the reaction was noticeably exothermic. Oxybromides were prepared by adding a stoicheiometric amount of boron tribromide. For several oxides it was necessary to use more forcing conditions to effect a reaction. This involved heating the oxide and the trihalide in an evacuated sealed tube laid horizontally in a furnace; the temperatures quoted represent upper limits. An interesting feature of the sealed-tube reactions was that beautifully crystalline, sublimed products were obtained, notably for $NbOBr_3$ and $NbBr_5$. This phenomenon is probably related to the 'transport' experiments of Schäfer.[11] Volatile products were distilled or sublimed out of the reaction vessel, leaving boric oxide as a residue. Where the product was involatile, for example $LaBr_3$ and TlBr, it was obtained by extracting the boric oxide with tri-n-butoxyborane (thus the orthoboric ester is converted into metaboric ester).[12] The compounds $NbBr_5$ and $GaBr_3$ were readily obtained either by extraction with hot carbon tetrachloride or by sublimation, but the latter is the preferred method.

The mechanism for these reactions is uncertain, not least because of the often complex oxide crystal structures. However, the considerable Lewis acidity of the boron halides and the high B–O bond strength are obviously important factors. It is likely that oxybromides are intermediates in the metal oxide–metal halide transformation.

The far-i.r. and Raman spectra of the halides MBr_5 (M = Nb, Ta) and $NbOBr_3$ were recorded in order to carry out full co-ordinate analyses of the vibrational modes; this has since been done by others, but our experimental results are in reasonable agreement.[13] $TaBr_5$: I.r. ($\nu_{max.}$ in cm^{-1}), 260, 250, 218, 162, 148, 128, 113, 102, 90; Raman, 266, 250, 235, 224, 170, 128, 112, and 86. $NbOBr_3$: I.r., 750, 342, 308, 297, 284, 264, 196, 157, 132, and 96; Raman, 748, 325, 286, 268, 197, and 134. The spectra of $NbBr_5$ are essentially identical with those of $TaBr_5$, except that the three
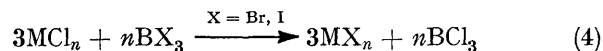
TABLE 1

Products of reactions of M_2O_n with BBr_3 and BI_3

M_2O_n	Product	Yield/% [a]	Reaction type (equation)	Conditions
Ga_2O_3	$GaBr_2$	86	1	90—110°/3 h [b]
In_2O_3	$InBr_3$	94	1	90—100°/ 3h [b]
Tl_2O_3	TlBr	81	2	90—110°/3 h [b]
SnO_2	$SnBr_4$	93	1	290—310°/12 h [c]
Bi_2O_3	$BiBr_3$	76	1	90—100°/3 h [b]
TeO_2	$TeBr_4$	91	1	110—120°/5 h [b]
ZrO_2	$ZrBr_4$	92	1	280—300°/12 h [c]
Nb_2O_5	$NbOBr_3$	87	3	280°/12 h [c]
Nb_2O_5	$NbBr_5$	94	1	280°/12 h [c]
Ta_2O_5	$TaBr_5$	92	1	280°/12 h [c]
MoO_2	$MoBr_4$	65	1	280—300°/12 h [c]
MoO_3	MoO_2Br_2 (+ other products)		3	[b]
Fe_2O_3	$FeBr_3$	62	1	90—100°/4 h [b]
La_2O_3	$LaBr_3$	72	1	300—330°/12 h [c]
UO_2	UBr_4	51	1	300—330°/12 h [c]
ZnO	$ZnBr_2$	70	1	90—100°/2 h [b]
Hg_2O	Hg_2Br_2	80	1	110—120°/4 h [b]
HgO	$HgBr_2$	84	1	110—120°/4 h [b]
SnO_2	SnI_4	78	1	280—300°/12 h [c]
Ta_2O_5	TaI_5	89	1	280—300°/12 h [c]

[a] These represent percentage yields of purified product; conversion is therefore substantially quantitative. [b] Exothermic reaction at room temperature. [c] Evacuated, sealed tube.

bands at highest wavenumber are displaced by ca. 20 cm^{-1} to higher energy.

Reactions of type (ii) may be generalised as in equations (4) and (5). The results are summarised in Table 2.

$$3MCl_n + nBX_3 \xrightarrow{X = Br, I} 3MX_n + nBCl_3 \quad (4)$$

$$3MCl_n + nBBr_3 \longrightarrow 3MBr_{n-2} + nBCl_3 + 3Br_2 \quad (5)$$

The experimental procedure, in the case of bromides, involved the slow addition, often exothermic, of boron tribromide, normally in excess, to the pure anhydrous chloride. In most cases, the mixture was then heated to ensure completeness of the usually heterogeneous reaction. Boron trichloride was readily eliminated from the system, in view of its low b.p., leaving the essentially pure metal bromide which, in many cases, was further

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[11] H. Schäfer, 'Chemical Transport Reactions,' Academic Press, New York, 1964.
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purified, usually by sublimation. In certain reactions, a solvent was used for dissolution of the chloride. For the synthesis of iodides, the procedure was to add a stoicheiometric amount of chloride (in the case of a liquid) to BI_3,
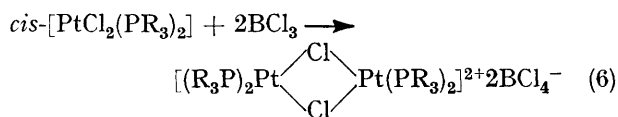
TABLE 2

Products of reactions of MCl_n with BBr_3 and BI_3

MCl_n	Product	Yield/ % [a]	Reaction type (equation)	Conditions
$AlCl_3$	$AlBr_3$	91	4	$90°/2$ h
$TlCl$	$TlBr$	99	4	$90-100°/3$ h
$SnCl_4$	$SnBr_4$	99	4	b
$PhPCl_2$	$PhPBr_2$	100	4	b
$AsCl_3$	$AsBr_3$	93	4	b
$SbCl_3$	$SbBr_3$	92	4	$100-120°/3$ h ^{b}
$SbCl_5$	$SbBr_3$	95	5	b
$BiCl_3$	$BiBr_3$	90	4	$90-120°/3h$ ^{b}
$SOCl_2$	$SOBr_2$	95	4	b
$TiCl_3$	$TiBr_3$	97	4	$90-100°/7$ h
$TiCl_4$	$TiBr_4$	96	4	b
$ZrCl_4$	$ZrBr_4$	93	4	$90-110°/4$ h
$HfCl_4$	$HfBr_4$	87	4	$90-110°/4$ h
VCl_3	VBr_3	98	4	$90-100°/7$ h
$VOCl_3$	$VOBr_2$	92	5	b
$NbCl_5$	$NbBr_5$	88	4	$90-100°/12$ h
$TaCl_5$	$TaBr_5$	98	4	$90-100°/12$ h
$MoCl_5$	$MoBr_3$	94	5	$90-120°/4$ h
WCl_6	WBr_6	88	4	CS_2
$FeCl_3$	$FeBr_3$	98	4	$95-100°/12$ h ^{b}
$CoCl_2$	$CoBr_2$	99	4	$90-100°/3$ h
$NiCl_2$	$NiBr_2$	84	4	$90-100°/3$ h
$PtCl_4$	$PtBr_4$	97	4	$90-100°/3$ h
$CuCl_2$	$CuBr_2$	94	4	$90-100°/3$ h ^{b}
$CdCl_2$	$CdBr_2$	91	4	$90-100°/3$ h ^{b}
$SnCl_4$	SnI_4	99	4	b
$SbCl_3$	SbI_3	100	4	CS_2 ^{b}
$TiCl_4$	TiI_4	100	4	b

^{a} These represent percentage yields of pure product. ^{b} Exothermic reaction at room temperature.

or to mix the reactants in the solvent (in the case of a solid chloride).

Reactions of boron trihalides with metal halides may lead to, apart from halogen-exchanged products, three other types of complex. These are (a) a Lewis acid–Lewis base adduct; (b) a salt, with a tetrahalogenoborate anion; and (c) a halide-bridged cationic complex. Examples of (a) are the adducts of Group VB halides with the boron halides.[14] Situation (b) is exemplified by the adduct SF_4,BF_3[7] which has the structure $SF_3^+BF_4^-$ (however, whilst SF_4 and BCl_3 exchange halogens, an intermediate has not been isolated). Evidence for (c) is found in the formation of halide-bridged binuclear cationic platinum(II) complexes; e.g., reaction (6).[15]

$$cis\text{-}[PtCl_2(PR_3)_2] + 2BCl_3 \longrightarrow$$

$$[(R_3P)_2Pt\underset{Cl}{\overset{Cl}{<>}}Pt(PR_3)_2]^{2+}2BCl_4^- \quad (6)$$

Features favouring the exchange process include the

greater volatility of BCl_3 than BBr_3, the higher Lewis acidity of BBr_3 than BCl_3, and the possible favourable enthalpy change [i.e., in simplified form, that $\bar{E}(M-Br) + \bar{E}(B-Cl) > \bar{E}(M-Cl) + \bar{E}(B-Br)$]. Lack of reaction [an attempt to isolate complexes of types (a)—(c)] was observed (upon reflux) between BCl_3 and severally $TiCl_4$, WCl_6, and K_2PtCl_4. Similarly, BBr_3 failed to react with severally $SiCl_4$ ($300°/12$ h), $GeCl_4$, $(Pr^nBNCl)_3$, $(PNCl_2)_3$, Me_3SiCl, $PSCl_3$, and K_2PtCl_4. This may be because for these reactions there is no particular thermodynamic gain. Thus, for example (data from ref. 16): $\bar{E}(Si-Br) + \bar{E}(B-Cl) = 180$ kcal mol^{-1}, whereas $\bar{E}(Si-Cl) + \bar{E}(B-Br) = 179$ kcal mol^{-1}. The behaviour of $SiCl_4$ and $GeCl_4$ is in contrast to other tetrahalides of Group IV, CCl_4, and $SnCl_4$, which undergo exchange with boron trihalides.[17] $GeCl_4$, $GeBr_4$, $SnBr_4$, and SnI_4 had previously been shown not to form adducts with BBr_3.[18] That $PSCl_3$ failed to react with BBr_3, while BX_3-POX_3 1:1 adducts are well known,[14] is consistent with the view [14] that in the latter oxygen is the donor site. It had previously been observed that $PSCl_3$ does not react with BCl_3,[19] although the exchange occurs with $AlBr_3$.[20]

Attempts to prepare the unknown bromides $MoBr_5$ and $SbBr_5$ resulted in the formation of the lower bromides and bromine.

Platinum(II) chloride is known[21] to have a structure based on an octahedral cluster of metal atoms with bridging chlorine atoms. The reaction between Pt_6Cl_{12} and BBr_3 in stoicheiometric amounts resulted in the formation of the light-brown mixed halide $(PtBrCl)_n$ presumed to be $Pt_6Br_6Cl_6$. The far-i.r. spectrum of the mixed halide was recorded as follows: (ν_{max} in cm^{-1}: 358m, 310s, 231s, 196vw, 137vw, + weaker features). By comparison with the known spectrum[22] of Pt_6X_{12} (X = Cl, Br), it is clear that our product is not a mixture of the binary halides and that the bands at 310 and 231 cm^{-1} in $Pt_6Br_6Cl_6$ are due to essentially pure Pt–Cl and Pt–Br stretching modes, respectively. With a large excess of BBr_3 and prolonged heating it was possible to replace more than 6 chloride ligands of Pt_6Cl_{12}, but complete halide exchange was not achieved. The reactivity of the bridging chloride ligands in the platinum cluster contrasts with their total unreactivity in Re_3Cl_9 (in contrast to the 6 terminal chlorides).[23]

It appears that exchange reactions of metal halides with boron tribromide and tri-iodide provide a convenient general method for the syntheses of anhydrous bromides and iodides, possibly the most widely useful of those currently available. By comparison with the oxide–BX_3 method (see also ref. 1), yields are usually higher, a solvent may be employed, and the immediate

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[15] Part III, P. M. Druce, M. F. Lappert, and P. N. K. Riley, J. C. S., Dalton, submitted for publication.

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product is often very pure without the necessity of further elaborate treatment. The last feature is particularly important for halides which are susceptible to decomposition during sublimation, *e.g.*, FeBr₃. Further, reaction conditions are mild, pure starting materials are readily accessible, simple apparatus can be used, and separation of the boron by-product is not difficult. The method has been used by others in the actinide series,[24] and it is noteworthy that halogen exchange there is invariably more effective with boron trihalides than with silicon halides.[24] Likewise, BCl_3 was regarded as a more effective reagent than either CCl_4 or PCl_3 for the transformation $ReF_6 \longrightarrow ReCl_6$;[3b] boron tribromide and ReF_6 afforded $ReBr_5$.

Other methods for the preparation of bromides and iodides, *e.g.*, using CX_4, HX, SiX_4 (X = Br or I) as halogenating agents, or the reaction between metal and halogen, generally require vigorous reaction conditions.[25]

EXPERIMENTAL

All reactions were performed in an atmosphere of nitrogen or *in vacuo*. Halogen was estimated by the Volhard method, whilst in the case of mixed chloro-bromo-compounds, the halogen was estimated potentiometrically. Boron was estimated by Thomas's method.[26] Boron tribromide was purified by treatment with mercury, heating under reflux, and distillation. Boron tri-iodide was dissolved in CS_2 and shaken with mercury. After filtration, CS_2 was removed *in vacuo*, leaving almost white crystals of the tri-iodide. Hydrated chlorides were dehydrated by refluxing with thionyl chloride. Carbon disulphide was dried over P_2O_5 and distilled therefrom.

Far-i.r. spectra were recorded with an R.I.I.C. FS-620 Michelson interferometer calibrated against a built-in test function corresponding to 156·25 cm⁻¹, and with samples dispersed in Polythene discs. Raman spectra were measured with a Coderg laser-Raman instrument having He–Ne excitation.

High-temperature sublimations were carried out with a Wood's-metal bath, and temperatures quoted refer to those of the bath. Literature references (m.p. and b.p.) are quoted from 'The Handbook of Chemistry and Physics' (49th edn., 1968).

Typical reactions only are described.

Reactions of Boron Tribromide with Metal Oxides.—(a) *Gallium*(III) *oxide.* Boron tribromide (3·91 g, 7·8 mmol) was added to the oxide (1·0 g, 5·3 mmol) and an exothermic reaction ensued. The mixture was heated (90—110 °C) (3 h). Excess of boron tribromide was removed (20 °C/0·1 mmHg), and sublimation (60—70 °C/0·01 mmHg) of the remaining solid yielded gallium(III) bromide (2·83 g, 85·6%), m.p. 120—121° (lit., 121—122°) (Found: Br, 77·1. Calc. for Br_3Ga: Br, 77·5%).

(b) *Tin*(IV) *oxide.* Boron tribromide (9·55 g, 38 mmol) and the oxide (4·05 g, 16 mmol) were heated together in an evacuated sealed tube (290—310°) (12 h). Excess of boron tribromide was removed (20 °C/0·1 mmHg), and distillation of the remaining solid afforded white crystals of tin(IV) bromide (11·01 g, 93·4%), b.p. 108—110 °C/10 mm., m.p.

30° (lit., 31°) (Found: Br, 72·8. Calc. for Br_4Sn: Br, 72·9%). The residue was boric oxide (1·2 g, 96·2%) (Found: B, 30·9. Calc. for B_2O_3: B, 31·0%).

(c) *Niobium*(V) *oxide.* Boron tribromide (6·13 g, 24 mmol) and the oxide (3·34 g, 12·6 mmol) were heated in an evacuated sealed tube (280°) (12 h). On cooling, large yellow needles were observed in the tube. Sublimation (190 °C/0·05 mmHg) of the solid afforded yellow crystals of niobium oxytribromide (7·32 g, 87·2%) (Found: Br, 68·5. Calc. for Br_3ONb: Br, 68·8%).

Boron tribromide (11·45 g, 46 mmol) and the oxide (3·14 g, 12 mmol) were treated as above. On cooling, deep red crystals were observed in the tube. Sublimation (200—220 °C/0·02 mmHg) of the solid afforded niobium(V) bromide (10·94 g, 93·9%), m.p. 264—265° (lit., 265°) (Found: Br, 80·9. Calc. for Br_5Nb: Br, 81·1%). In a further experiment, the solid product was extracted with hot CCl_4 (15 ml) (7 h) in a nitrogen atmosphere. Removal of the solvent (20 °C/0·1 mmHg) afforded purple crystals of niobium(V) bromide (95·9%), m.p. 265°.

(d) *Mercury*(I) *oxide.* Boron tribromide (4·1 g, 16·4 mmol) was slowly added to the oxide (9·5 g, 7·6 mmol) and an exothermic reaction ensued. The mixture was heated (110—120°) (4 h). Excess of boron tribromide was removed (20 °C/0·1 mmHg), and sublimation (220—240 °C/0·01 mmHg) of the remaining solid gave white crystals of mercury(I) bromide (10·2 g, 79·7%) (Found: Br, 28·3. Calc. for Br_2Hg_2: Br, 28·5%).

Reaction of Boron Tri-iodide with Metal Oxides.—*Tin*(IV) *oxide.* Boron tri-iodide (6·4 g, 16·3 mmol) and the oxide (1·8 g, 11·9 mmol) were heated in an evacuated sealed tube (280—300°) (12 h). Removal of excess of boron tri-iodide (20 °C/0·01 mmHg) and sublimation (200—220 °C/0·01 mmHg) of the remaining solid afforded orange crystals of tin(IV) iodide (7·49 g, 78·5%), m.p. 142—144° (lit., 144°) (Found: I, 81·1. Calc. for I_4Sn: I, 81·1%).

Reactions of Boron Tribromide with Anhydrous Metal Chlorides.—(a) *Tin*(IV) *chloride.* Boron tribromide (4·81 g, 19 mmol) was slowly added to the chloride (2·44 g, 12·8 mmol) and an exothermic reaction ensued. Boron trichloride (2·06 g, 99·8%) (authentic i.r.) was obtained in a trap at −78 °C. Excess of boron tribromide was removed (20 °C/0·1 mmHg), and distillation of the remaining solid afforded white crystals of tin(IV) bromide (4·7 g, 99·4%), b.p. 108—110 °C/10 mmHg. m.p. 30° (lit., 31°) (Found: Br, 72·2. Calc. for Br_4Sn: Br, 72·9%).

(b) *Antimony*(V) *chloride.* Boron tribromide (8·95 g, 28·3 mmol) and the chloride (5·95 g, 19·9 mmol), when mixed as in (a) above, afforded boron trichloride (3·78 g, 92·7%), bromine (3·1 g, 97·6%), b.p. 58° (lit., 58·8°), and antimony-(III) bromide (6·8 g, 94·6%), b.p. 130—132 °C/2 mmHg, m.p. 96—97° (lit., 96·6°) (Found: Br, 66·2. Calc. for Br_3Sb: Br, 66·3%).

(c) *Thionyl chloride.* Boron tribromide (4·51 g, 18 mmol) and the chloride (3·20 g, 27 mmol), when mixed at 0 °C afforded boron trichloride (1·92 g, 91·2%) and thionyl bromide (5·28 g, 94·5%), b.p. 50—52 °C/20 mmHg (lit., 68 °C/40 mmHg) (Found: Br, 76·3. Calc. for Br_2OS: Br, 76·9%).

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[26] L. H. Thomas, *J. Chem. Soc.*, 1946, 820.

(d) *Zirconium*(IV) *chloride.* Boron tribromide (5·4 g, 21·5 mmol) and the chloride (3·01 g, 12·9 mmol), when mixed as in (a) above and heated (90—110 °C) (4 h), afforded boron trichloride (1·86 g, 92·1%) and white crystals of zirconium(IV) bromide (4·95 g, 93·2%), subl. >360 °C/0·01 mmHg (Found: Br, 77·6. Calc. for Br_4Zr: Br, 77·8%).

(e) *Niobium*(V) *chloride.* Boron tribromide (7·35 g, 29·3 mmol) and the chloride (4·37 g, 16·2 mmol), when mixed as in (a) above and heated (90—100°) (12 h), afforded boron trichloride (2·9 g, 91·8%), and deep-red niobium(V) bromide (7·07 g, 88·7%), m.p. 258—263° (lit., 265°) (Found: Br, 81·7. Calc. for Br_5Nb: Br, 81·1%).

(f) *Platinum*(II) *chloride.* Boron tribromide (0·35 g, 1·4 mmol) was added to the chloride (1·01 g, 0·6 mmol) and the mixture was heated in an evacuated sealed tube (300°) (36 h). Work-up of the light-brown product afforded a compound analysing as Br_6Cl_6Pt (Found: Br, 26·0; Cl, 11·6. Calc. for Br_6Cl_6Pt: Br, 25·8; Cl, 11·4%).

Platinum(II) chloride (0·86 g, 0·5 mmol) and boron tribromide (3·4 g, 10 mmol), when treated similarly, afforded a brown solid (1·02 g) (Found: Br, 38·8; Cl, 1·1. Calc. for $Br_{12}Pt_6$: Br, 45·0%).

Reactions of Boron Tri-iodide with Anhydrous Metal Chlorides.—(a) *Antimony*(III) *chloride.* Boron tri-iodide (2·3 g, 5·9 mmol) in carbon disulphide (7 ml) was slowly added to the chloride (0·83 g, 3·6 mmol) in the same solvent (10 ml); an exothermic reaction ensued. The solvent and excess of boron tri-iodide were removed (20 °C/0·1 mmHg), and the remaining red crystalline solid was identified as antimony(III) iodide (1·82 g, 100%), m.p. 170° (lit., 170°) (Found: I, 64·0. Calc. for I_3Sb: I, 64·6%).

(b) *Titanium*(IV) *chloride.* The chloride (1·94 g, 12 mmol) was slowly added to boron tri-iodide (4·84 g, 14·9 mmol); an exothermic reaction ensued and the mixture was warmed (60°) ($\frac{1}{4}$ h). Boron trichloride (1·42 g, 98%) was obtained in a trap at −78°, and the remaining red solid was identified as titanium(IV) iodide (5·15 g, 100%), m.p. 148—150° (lit., 150°) (Found: I, 96·0. Calc. for I_4Ti: I, 96·4%).