Boron Halides as Reagents in Inorganic Chemistry; Synthesis of Anhydrous Metal Bromides and Binuclear Halogen-bridged Platinum(II) Cations

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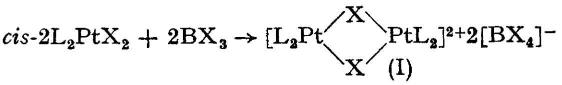
ANHYDROUS metal bromides are often difficult to obtain by methods similar to those available for corresponding chlorides.[1] Furthermore, when the metals are in their highest oxidation states, bromides are frequently less stable with respect to dissociation than related chlorides.

We now report a general method for preparing anhydrous bromides by an exchange reaction with boron tribromide.

$$3MCl_n + nBBr_3 \rightarrow 3MBr_n + nBCl_3$$

The experimental procedure is simple. Thus, boron tribromide was slowly added to the metal chloride at or below room temperature. Almost invariably mixing was accompanied by evolution of heat. The reactions are essentially quantitative, and products were obtained pure, since boron trichloride (b.p. ~12°/760 mm.) is readily eliminated. In this way, the following anhydrous metal bromides have been obtained to date: $HgBr_2$, $AlBr_3$, $SnBr_4$, $PhPBr_2$, $AsBr_3$, $SbBr_3$, $BiBr_3$, $SOBr_2$, $TiBr_4$, $ZrBr_4$, $NbBr_5$, WBr_6, $FeBr_3$, $PtBr_4$, and $CuBr_2$. In two cases ($SbCl_5 \rightarrow SbBr_3 + Br_2$; $MoCl_5 \rightarrow MoBr_3 + Br_2$), reduction accompanied halogen-exchange. Lack of reaction was observed with $SiCl_4$ (even at 300° under pressure), and (upon prolonged reflux) with severally Me_3SiCl, $(n\text{-}C_3H_7BNCl)_3$, $GeCl_4$, or $(PNCl_2)_3$. Boron trichloride failed to react with Me_3SiBr under reflux. The exchange reaction is probably also suitable for obtaining metal iodides; thus, titanium(IV) chloride was converted quantitatively into the iodide, using boron tri-iodide.

Mechanistically, we regard the above reactions as involving reversible halide-ion abstraction by BX_3, with halogenoborate anion intermediates. This is further illustrated by the following experiments ($L = Bu^n{}_3P$; $X = Cl$ or Br), in which such intermediates (I), are isolated. Bromide-bridged complexes were obtained from BBr_3 and not only *cis*-L_2PtBr_2 but also *cis*-L_2PtCl_2.



$$\textit{cis}\text{-}2L_2PtX_2 + 2BX_3 \rightarrow [L_2Pt\genfrac{}{}{0pt}{}{X}{X}PtL_2]^{2+}2[BX_4]^-$$

(I)

Reactions leading to (I) proceeded instantly at room temperature in an anhydrous solvent and under an inert atmosphere. Compounds (I) may be obtained in solution (CH_2Cl_2) or as crystals (from C_6H_6). They afforded *cis*-L_2PtX_2, $B(OH)_3$, and HX when treated with cold water.

Evidence for structures (I) rests on elemental analyses, conductivity, and spectral data. The molar conductivities (in CH_3CN) of the chloro- and bromo-compounds (I) ($X = Cl$ or Br) are 79 and 68 mho. cm.$^{-2}$, respectively, which is almost a hundredfold increase over that of *cis*-L_2PtX_2. Infrared (i.r.) and ^{11}B nuclear magnetic resonance spectra serve to identify the appropriate BX_4^- anion. The ^{31}P n.m.r. spectra reveal changes both in chemical shifts and in ^{31}P–^{195}Pt coupling constants compared with *cis*-L_2PtX_2. Far i.r. spectra have not been particularly helpful, as the decrease in frequency expected for a bridged rather than a terminal Pt–Cl bond seems to be counterbalanced by the increase in changing from uncharged to bipositive platinum.

Compounds (I) are also of interest as providing the first examples of halogen-bridged Pt^{II} cations. Indeed, the only binuclear Pt^{II} cation known to us is a sulphide-bridged species.[2]

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Cf., M. F. Lappert and B. Prokai, *J. Chem. Soc.* (*A*), 1967, 129.

[2] S. E. Livingstone, *J. Chem. Soc.*, 1956, 1994.