Boron Halides as Reagents in Inorganic Syntheses. Part III.[1] Preparation and Characterisation of Halogen- and Pseudohalogen-bridged, Binuclear, Cationic Complexes of Platinum(II)

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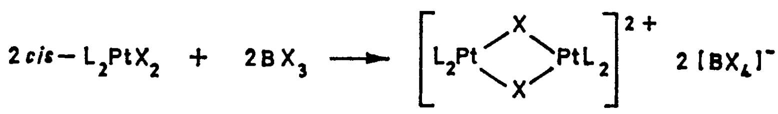
The reactions of boron halides BX_3 (X = F, Cl, or Br) with the square-planar platinum(II) complexes *cis*-L_2PtY_2 (L = Bu^n_3P; Y = Cl, Br, NCO, or N_3) yield halogen-bridged, binuclear, cationic complexes $[L_2PtY]_2^{2+}$ or $[L_2PtX]_2^{2+}$. I.r., ^{11}B n.m.r., ^{31}P n.m.r. spectra, and conductivity measurements serve to identify the cations. The nature of the anions, which is more complicated to define, is also discussed in the light of spectroscopic and analytical data. The cationic complexes afford *cis*-L_2PtY_2 or *cis*-L_2PtX_2, $B(OH)_3$, and HX when treated with cold water.

We have reported, in preliminary form, the synthesis [equation (1)] and characterisation of the first examples of binuclear halogen-bridged platinum(II) cations.[2] Although neutral, dimeric, halogen-bridged species of platinum(II) were well-known,[3] cationic species of this type were unknown. The present paper provides a full account of our data, and forms part of a wider investigation of the interaction of boron trihalides and inorganic substrates.[1,4]



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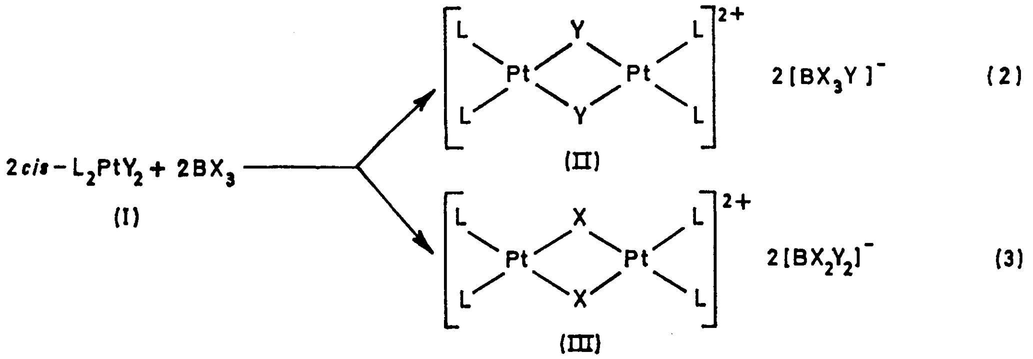
[1] Part II, P. M. Druce and M. F. Lappert, *J. Chem. Soc.* (*A*), 1971, 3595.

[2] P. M. Druce, M. F. Lappert, and P. N. K. Riley, *Chem. Comm.*, 1967, 486.

[3] J. Chatt, *J. Chem. Soc.*, 1951, 652; J. Chatt, N. P. Johnson, and B. L. Shaw, *ibid.*, 1964, 662.

[4] *Cf.* M. F. Lappert and B. Prokai, *J. Chem. Soc.* (*A*), 1967, 129; P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding, and R. C. Srivastava, *ibid.*, 1969, 2106.

The reactions of boron trihalides with the complexes *cis*-L_2PtY_2 may be represented by the general equations (2) and (3) below. The experimental procedure involves the addition of a solution of an excess of the boron trihalide in either benzene or dichloromethane to a solution of the platinum complex in the same solvent. Reaction occurs at room temperature. In the case of benzene, addition of the boron trihalide results in a quantitative precipitation of the product (II) or (III), whereas these compounds are soluble in dichloromethane. Chloro-bridged complexes were obtained for X = Y = Cl and X = F with Y = Cl, bromo-bridged complexes for X = Y = Br and X = Br with Y = Cl, an isocyanato-bridged complex for X = Cl with Y = NCO, and an azido-bridged complex for X = Cl with Y = N_3. Evidence for the structures is based on analyses, i.r. and n.m.r. spectra, and conductivity measurements, and some of these data are shown in the Table.



I.r. and n.m.r. spectral, and conductivity data for some halogen-bridged binuclear complexes

Complex derived from	Bridging group	I.r.[a]	^{11}B N.m.r.[b]	^{31}P N.m.r.[c]	Conductivity[d]
$(Bu^n{}_3P)_2PtCl_2 + BCl_3$	Cl	660s, 692s	−7·2	δ = 117 (126·4) *J* (Pt–P) = 3·58 (3·505)	79
$(Bu^n{}_3P)_2PtBr_2 + BBr_3$	Br	583s, 595s	+23·4	δ = 116·6 (126·2) *J* (Pt–P) = 3·514 (3·477)	68
$(Bu^n{}_3P)_2PtCl_2 + BBr_3$	Br	583s, 595s	+21·43	δ = 117 (126·4) *J* (Pt–P) = 3·522 (3·505)	62·7
$(Bu^n{}_3P)_2PtCl_2 + BF_3$	Cl	See text	+1·2, +0·75	δ = 116·7, 126 (126·4)	86·3

[a] $\nu_{max.}$ 700—400 cm^{-1}. [b] W.r.t. BF_3,OEt_2, δ in p.p.m.; in CH_2Cl_2. [c] W.r.t. $P(OPh)_3$, δ in p.p.m.; *J* in kHz; parentheses values of δ and *J* refer to parent mononuclear complexes. [d] In 10^{-3}M-CH_3CN, mho cm^{-2}.

The molar conductivities (see Table) of some compounds (II) and (III), represent roughly a 100-fold increase over that of (I), and support the assignment for (II) and (III) of ionic structures.

The ^{31}P n.m.r. spectra reveal changes both in the chemical shifts and ^{31}P–^{195}Pt coupling constants compared with those of (I). ^{11}B N.m.r. and i.r. spectra serve to identify the appropriate BX_4^- and related anions.

The i.r. spectra of the products obtained from the reactions of boron trihalides with corresponding (X = Y) complexes (I) show new absorptions, attributed to the tetrahalogenoborate anion. There are no absorptions in the regions where the trihalides absorb. The i.r. spectrum of the product from the reaction of (I; Y = Cl) with boron trichloride [equation (2; X = Y = Cl)] shows new absorptions at 660 and 692 cm^{-1} which are attributed to BCl_4^- by comparison with the spectrum of $Cs^+BCl_4^-$. The corresponding bromo-compounds gave a product having strong absorptions at 583 and 595 cm^{-1} attributed to BBr_4^-, again by comparison with the spectrum of $Cs^+BBr_4^-$ and $pyH^+BBr_4^-$. The far-i.r. spectra of the products (II; X = Cl or Br), obtained from the reactions of BCl_3 with (I; Y = Cl) and of BBr_3 with (I; Y = Br), showed no significant changes in the position of the absorptions believed to be ν(Pt–Hal) in complexes (I). Thus, in (I; X = Y = Cl), Pt–Cl stretching frequencies ν(Pt–Cl) lie at 303 and 280 cm^{-1},[5] whilst in (II; X = Y = Cl) they are at 303 and 279 cm^{-1}. In (I; Y = Br), ν(Pt–Br) lie at 212 and 194 cm^{-1},[5] whilst in (II; X = Y = Br), they are at 209 and 200 cm^{-1}. There was, however, considerable broadening of the doublet in (II) compared with (I). It is supposed that the decrease in frequency expected for a bridged rather than a terminal Pt–Hal bond is counteracted by the increase expected in changing from uncharged to bipositive platinum. In the reaction of (I; Y = Cl) with BBr_3, the far-i.r. spectrum of the product shows the appearance of Pt–Br stretching absorptions and the disappearance of Pt–Cl stretches, confirming that Pt–Hal exchange as well as halide abstraction has taken place. Absorptions at 583 and 595 cm^{-1} are attributed to BBr_4^- or BBr_3Cl^- (these

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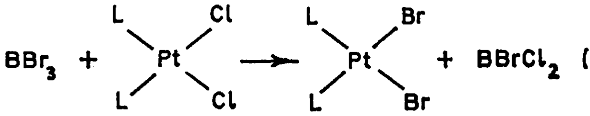
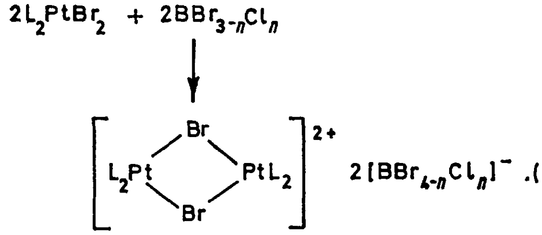
[5] D. M. Adams, J. Chatt, and A. D. Westland, *J. Chem. Soc.*, 1964, 734.

have almost identical characteristics). Formulation of the product as a bromine–bridged cation with the BBr_3Cl^- anion is supported by analysis (C, H only), whereas ^{11}B n.m.r. and i.r. spectra do not provide definitive evidence for either anion. ^{31}P N.m.r. data are essentially identical with those obtained for (II; X = Y = Br) (see Table). The nature of the bromo-bridged cation is thus established. The reaction sequence may involve the steps shown in equations (4)—(6). Reaction (4) is of the general type established earlier,[1,2] whereby most inorganic chlorides are converted into corresponding bromides by treatment with boron tribromide. The redistribution equilibrium (5) is well-known, and distribution of products is not far removed from statistical.[6] Hence, with a large excess of boron tribromide in the reaction mixture, equation (6) with $n = 0$ is clearly of much greater significance than with $n = 1$ to 3. A further complication regarding the nature of the anion, is that halogen-exchange at boron, as in (5) but now for four-co-ordinate boron, is possible. Thus, mixing pyH^+-BCl_4^- with BBr_3 in an n.m.r. tube showed (^{11}B n.m.r.) the presence of BCl_2Br and $BClBr_2$, although no clear evidence for mixed four-co-ordinate species such as BCl_3Br^-. The far-i.r. spectrum of the product from the reaction of (I; Y = Cl) and BF_3 showed absorptions attributable to ν(Pt–Cl) at 304 and 280 cm^{-1}. The ^{31}P n.m.r. signal was too weak to accurately measure $J(^{195}Pt-^{31}P)$. The problem of the nature of the anion is essentially similar to that discussed for Cl/Br exchange discussed above. The i.r. spectrum showed some of the absorptions previously reported and assigned to the BF_3Cl^- anion:[7] ($\nu_{max.}$ in cm^{-1}) 460, 525, 780, 840, 882, 1045, 1060, and 1190. It appears from the analysis and ^{31}P n.m.r. spectra that the samples obtained from the reaction of (I; Y = Cl) and BF_3 were impure. The characteristic stretching frequencies associated with the mononuclear pseudohalides are 2230 (NCO) and 2290 (N_3) cm^{-1}, and with the binuclear pseudohalides at 2060 (NCO) and 2190 (N_3) cm^{-1}. Thus, the absorption associated with the pseudohalide moves to a higher frequency in the bridged product. The situation parallels that found in neutral bridging and terminal selenocyanato–metal complexes,[8] but differs from that obtaining with isothiocyanates.[9] The question of the nature of the anion is again complicated, owing to the possibility not only of exchange but also of polymerisation or decomposition of three-co-ordinate species. Simple isocyanates of boron may polymerise, and azidoboranes tend to be unstable.[10] Thus, although the analysis of the product of the reaction of (I; Y = NCO) and BCl_3 suggests that the composition corresponds to (III; X = Cl, Y = NCO), this may be a mixture, in appropriate stoicheiometry, of $[BCl_4]^-$ and $[B(NCO)_4]^-$, or other combinations of $[BCl_n(NCO)_{4-n}]^-$. The i.r. spectrum of the product shows two important regions of absorption at 660 and 690 cm^{-1}, as found for the BCl_4^- anion, and a series of absorption bands between 1570 and 1800 cm^{-1}, which are absent in (I; Y = NCO).


(4)

$$3BBrCl_2 \rightleftharpoons 2BCl_3 + BBr_3 \qquad (5)$$


.(6)

Boron trichloride failed to react with *trans*-$(Bu^n_3P)_2$-$PtCl_2$ at room temperature. The starting materials were recovered essentially quantitatively. Had the binuclear complex been obtained from this reaction, its hydrolysis to yield the *cis*-mononuclear species would have provided a route for *trans–cis*-interconversion. This still appears to be a feasible proposition under more forcing conditions.

Subsequent to our original communication, Clark *et al.* have synthesised dimeric halogen-bridged platinum(II)[11a] and palladium(II)[12] cations of the type $[M_2X_2(R_3P)_4][BF_4]_2$, using BF_3 with various *cis*-complexes $(R_3P)_2MX_2$, and vibrational spectra have been reported.[13] Such bridged-complexes were cleaved by carbon monoxide to carbonyl cations of the type *trans*-$[PtX(CO)(R_3P)_2]BF_4$:[11b] thus the bridged cationic, binuclear, complexes, like their neutral analogues $[L(X)PtX]_2$,[3] are useful synthetic reagents being susceptible to nucleophilic attack which results in bridge-splitting. Fluoride-bridged complexes of the type $[PtF(PPh_3)_2]_2[ClO_4]_2$ and $[PdF(PPh_3)_2]_2F_2$ have been recently reported resulting from the reactions of $LiClO_4$ with $[PtF(PPh_3)_3][BX_4]$ (X = Ph or F), and of liquid HF with $Pd(PPh_3)_4$, respectively.[14] Beck *et al.* have

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[6] M. F. Lappert, M. R. Litzow, J. B. Pedley, T. R. Spalding, and H. Nöth, *J. Chem. Soc.* (*A*), 1971, 383.

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[8] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Hass, *Inorg. Chem.*, 1962, **1**, 565.

[9] J. Chatt and L. A. Duncanson, *Nature*, 1956, **178**, 997.

[10] *Cf.* M. F. Lappert and H. Pyszora, *Adv. Inorg. Chem. Radiochem.*, 1966, **9**, 133.

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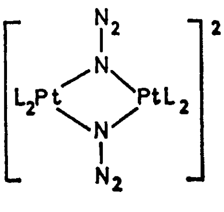
[12] H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, 1969, **91**, 596.

[13] D. M. Adams and P. J. Chandler, *J. Chem. Soc.* (*A*), 1969, 588; D. A. Dudell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545; P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *ibid.*, 1971, 2031.

[14] R. D. W. Kemmitt, R. D. Peacock, and J. Stocks, *J. Chem. Soc.* (*A*), 1971, 846.

described the preparation of salts of azido-bridged platinum(II) and palladium(II) dimeric cations, obtained from interaction of *trans*-$(Ph_3P)_2M(N_3)_2$ and one of BF_3,[15a] nitrosyl- or tetraethylammonium salts, or diethyl sulphate.[15b] The azido-bridge was thought to involve a single nitrogen atom with the complex cation formulated as (IV).



(IV)

EXPERIMENTAL

Manipulations were carried out either *in vacuo*, or in an inert atmosphere of oxygen-free nitrogen. Boron trichloride was condensed at −78°, and sealed into previously dried and weighed ampoules. Boron tribromide was purified by treatment with mercury (to remove any bromine), heating under reflux (to remove hydrogen bromide), and distillation (b.p. 90°). Dichloromethane and benzene were purified and dried by conventional methods. The complexes *cis*- and *trans*-dichlorobis(tri-n-butylphosphine)platinum(II),[16] and caesium, pyridinium, and tetraethylammonium tetrachloro- and tetrabromoborates,[17] were prepared by standard methods. The complexes *cis*-dibromobis(tri-n-butylphosphine)platinum(II), *cis*-di-isocyanatobis(tri-n-butylphosphine)platinum(II), and *cis*-diazidobis(tri-n-butylphosphine)platinum(II) were generous gifts from Dr. A. Pidcock of this laboratory.

I.r. spectra (4000—400 cm^{-1}) were recorded with Perkin-Elmer 237 and 337 spectrophotometers. Far-i.r. spectra were obtained with an R.I.I.C., FS-620 Michelson interferometer calibrated against a built-in test function corresponding to 156·25 cm^{-1}. N.m.r. spectra were measured on a Perkin-Elmer R 10 spectrometer.

Spectroscopic and conductivity data are in the previous section.

Reactions of Boron Trichloride with cis-$(Bu^n_3P)_2PtY_2$.—(a) ($Y = Cl$). Boron trichloride (1·8 g, 15 mmol) in dichloromethane (5 ml) was added to a solution of *cis*-$(Bu^n_3P)_2PtCl_2$ (0·61 g, 1 mmol) in the same solvent (10 ml), and the mixture was set aside for several minutes. Removal of the solvent and excess boron trichloride at 20 °C/0·05 mmHg, afforded *di-μ-chloro-tetrakis(tri-n-butylphosphine)diplatinum*(II) *tetrachloroborate* (0·71 g, 100%) (Found: C, 36·4; H, 7·0; Cl, 21·6; P, 8·2. $C_{48}H_{108}B_2Cl_{10}P_4Pt_2$ requires C, 36·6; H, 6·8; Cl, 22·5; P, 7·8%). When the reaction was carried out in benzene solution, the product was precipitated quantitatively.

(b) ($Y = NCO$). Boron trichloride (1·7 g, 14·5 mmol) in dichloromethane (5 ml) was added to a solution of *cis*-$(Bu^n_3P)_3Pt(NCO)_2$ (0·41 g, 0·6 mmol) in the same solvent (10 ml), and the mixture was set aside for several minutes. Work-up as in (a) afforded *di-μ-isocyanato-tetrakis(tri-n-butylphosphine)diplatinum*(II) *trichloroisocyanatoborate* (0·46 g, 95·6%) (Found: C, 38·5; H, 7·0; Cl, 12·2; P, 7·5. $C_{52}H_{108}B_2Cl_6N_4O_4P_4Pt_2$ requires C, 39·0; H, 6·7; Cl, 13·3; P, 7·7%).

(c) ($Y = N_3$). Boron trichloride (1·5 g, 12 mmol) in dichloromethane (10 ml) was added to a solution of *cis*-$(Bu^n_3P)_2Pt(N_3)_2$ (0·287 g, 0·4 mmol) in the same solvent (10 ml). Work-up as in (a) gave an oily solid tentatively formulated as di-μ-azido-tetrakis(tri-n-butylphosphine)-diplatinum(II) azidotrichloroborate (0·392 g) on the basis of spectral data and comparison with published data on related compounds.[14]

Reactions of Boron Tribromide with cis-$(Bu^n_3P)_2PtY_2$.—(a) ($Y = Br$). Boron tribromide (2·0 g, 8·0 mmol) in dichloromethane (5 ml) was added to a solution of *cis*-$(Bu^n_3P)_2PtBr_2$ (0·52 g, 0·7 mmol) in the same solvent (10 ml). Removal of the solvent and excess boron tribromide at 20 °C/0·05 mmHg, afforded *di-μ-bromo-tetrakis-(tri-n-butylphosphine)diplatinum*(II) *tetrabromoborate* (0·69 g, 100%) (Found: C, 28·1; H, 5·7; Br, 39·1; P, 6·3. $C_{48}H_{108}B_2Br_{10}P_4Pt_2$ requires C, 28·5; H, 5·4; Br, 39·6; P, 6·1%).

(b) ($Y = Cl$). Boron tribromide (3·3 g, 13·0 mmol) in dichloromethane (5 ml) was added to a solution of *cis*-$(Bu^n_3P)_2PtCl_2$ (1·09 g, 1·6 mmol). Work-up as in (a) gave *di-μ-bromo-tetrakis(tri-n-butylphosphine)diplatinum*(II) *tribromochloroborate* (1·63 g) (Found: C, 30·0; H, 5·6. $C_{48}H_{108}B_2Br_8Cl_2P_4Pt_2$ requires C, 29·9; H, 5·6%).

Reaction of Boron Trifluoride with cis-$(Bu^n_3P)_2PtCl_2$.—Boron trifluoride (0·27 g, 4·0 mmol) was bubbled through a solution of *cis*-$(Bu^n_3P)_2PtCl_2$ (0·824 g, 1·2 mmol) in benzene (20 ml). Removal of solvent and excess of boron trifluoride at 20 °C/0·5 mm afforded *di-μ-chloro-tetrakis(tri-n-butylphosphine)diplatinum*(II) *chlorotrifluoroborate* (0·91 g, 100%) (Found: C, 41·1; H, 7·6. $C_{48}H_{108}B_2Cl_4F_6P_4Pt_2$ requires C, 39·0; H, 7·4%).

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