Halogen Exchange in Platinum(IV) Complexes

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Summary ^{31}P N.m.r. spectra show that addition of an equimolar amount either of bromine to *trans*-[$PtCl_2(PR_3)L$] (R = Et, L = py, 3,5-Me_2-py, 4-Bu^t-py, PEt_3; R = Bu^n, L = py) (py = pyridine) or of *trans*-[$PtCl_4(PEt_3)(py)$] to *trans*-[$PtBr_4(PEt_3)(py)$] results in halogen scrambling and gives an approximately statistical distribution of *trans*-[$PtBr_xCl_{4-x}(PEt_3)L$] (x = 0—4).

Addition of halogens to square-planar platinum(II) complexes has long been known to give the corresponding platinum(IV) complex.[1,2] These reactions generally result in *trans*-addition of halogen and have recently been said to be straightforward and not deserving of further comment.[3] This may be true for reactions of the type (1) but it is not

$$PtX_2L_2 + Y_2 \rightarrow PtX_2Y_2L_2 \qquad (1)$$

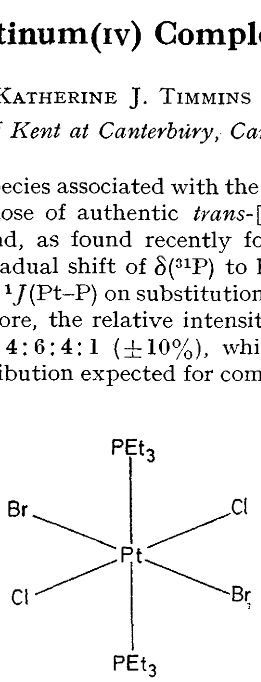
X = Y = Cl or Br; L = tertiary-phosphine or -arsine.

true for reactions when X ≠ Y. In this case, although it has previously been assumed to proceed as shown in equation (1),[2] we find that reaction (2) occurs.

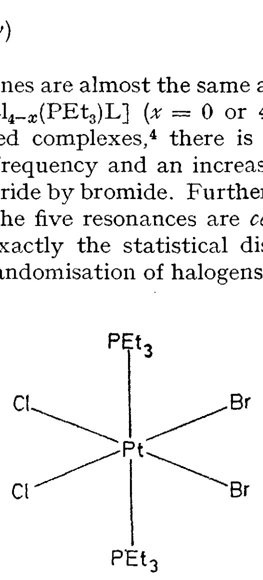
$$trans\text{-}[PtCl_2(PR_3)L] + Br_2 \rightarrow trans\text{-}[PtBr_xCl_{4-x}(PEt_3)L] \qquad (2)$$

R = Et, L = py, 3,5-Me_2-py, 4-Bu^t-py, PEt_3; R = Bu^n, L = py; x = 0—4.

The resulting product, which is crystalline and obtained in high yield, even on repeated recrystallisation gives analytical data consistent with the formulation '$PtBr_2Cl_2(PEt_3)L$'. However, when L ≠ PEt_3, the proton-decoupled ^{31}P n.m.r. spectrum shows five equally spaced resonances (plus ^{195}Pt satellites) which can be attributed to the presence of five species of the type *trans*-[$PtBr_xCl_{4-x}(PEt_3)L$] (x = 0—4). Apart from slight differences, which may be due to the different concentration of solutions used, the chemical shifts and ^{195}Pt–^{31}P coupling constants of the species associated with the outer lines are almost the same as those of authentic *trans*-[$PtBr_xCl_{4-x}(PEt_3)L$] (x = 0 or 4) and, as found recently for related complexes,[4] there is a gradual shift of $\delta(^{31}P)$ to higher frequency and an increase in ^1J(Pt–P) on substitution of chloride by bromide. Furthermore, the relative intensities of the five resonances are *ca.* 1:4:6:4:1 (±10%), which is exactly the statistical distribution expected for complete randomisation of halogens.[5]



(I)



(II)

When L = PEt_3, the ^{31}P n.m.r. spectrum shows a similar pattern except that the central resonance is split into two with relative intensities 2:4; these two resonances are attributed to *trans*- (I) and *cis*-isomers (II), and, if it is assumed that a redistribution, similar to those commonly observed with compounds of the main group elements,[6] has occurred, then the resonances due to [$PtBr_2Cl_2(PEt_3)_2$] with relative intensities 2:4 can be assigned to (I) and (II), respectively. The ^{31}P resonances of the analogous *cis*- and *trans*-isomers of [$PtBr_2Cl_2(PR_3)L$] (L ≠ PEt_3) must be coincident.

Platinum(IV) complexes undergo substitutions which, in the absence of steric effects and readily oxidisable anions, are found to be catalysed by platinum(II) and are generally thought to proceed by way of the bridged species Y——Pt^{II}——X——Pt^{IV}——X, (X,Y = Cl$^-$, Br$^-$ *etc.*).[7,8] Preliminary attempts to elucidate the mechanism of these halogen scrambling reactions in platinum(IV) complexes suggest a mechanism similar to that described above in which Y *is* replaced by a polarised halogen molecule. Thus, on dissolving equimolar amounts of [PtBr$_4$(PEt$_3$)(py)] and [PtCl$_4$(PEt$_3$)(py)] in deuteriochloroform containing bromine ([Br$_2$]:[Pt] = *ca.* 1:20) the ^{31}P n.m.r. spectrum after *ca.* 1 h showed resonances due only to the tetrachloro- and tetrabromo-complexes, whereas on carrying out the same experiment in the absence of bromine the ^{31}P n.m.r. spectrum, after 1 h, showed all five species of the type [PtBr$_x$Cl$_{4-x}$(PEt$_3$)(py)] (x = 0—4) to be present and after *ca.* 24 h, a statistical distribution of the five species had been attained. This supports a mechanism involving platinum(II) catalysis and rules out a mechanism involving a fast reductive elimination–oxidative addition of halogen.

Since an approximately statistical distribution of products is obtained in these halogen scrambling reactions, this suggests that thermodynamic effects are relatively unimportant, and further studies are in progress to see how widespread these reactions are.

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