Influence of Light on the Oxidative Addition of Bromine to *trans*-$[PtCl_2(PEt_3)_2]$: † Crystal Structure of all-*trans*-$[PtBr_2Cl_2(PEt_3)_2]$ ‡

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Addition of bromine to *trans*-$[PtCl_2(PEt_3)_2]$ in chloroform solution gives a single product, all-*trans*-$[PtBr_2Cl_2(PEt_3)_2]$, provided that light is excluded. In the presence of light, halogen scrambling occurs to give a mixture of species $[PtBr_xCl_{4-x}(PEt_3)_2]$, x = 0—4, with *trans* phosphines. Previously, the importance of light to this scrambling reaction had not been realized. In the dark, platinum(II) complexes *trans*-$[PtCl_2(PEt_3)_2]$ or *trans*-$[PtBr_2(PEt_3)_2]$ are poor at promoting halogen scrambling in *trans*-$[PtBr_2Cl_2(PEt_3)_2]$, the structure of which has been determined by *X*-ray diffraction. Crystals are monoclinic with a = 9.414(2), b = 13.146(3), c = 8.656(1) Å, and β = 103.10(2)°. The molecule has a crystallographic centre of symmetry and the structure has been refined to a final R of 0.030 for 1 108 reflections.

We have shown that some iridium and rhodium complexes of type *trans*-$[MCl(CO)(PR_3)_2]$ and $[MCl_3(CO)(PR_3)_2]$ can react with each other or with *trans*-$[PtCl_4(PEt_3)_2]$ to undergo mutual oxidative addition–reductive elimination. It was suggested that such reactions went *via* an inner-sphere two-electron-transfer process involving double chloro-bridged intermediates.[1] This study led us to reinvestigate the action of bromine on *trans*-$[PtCl_2(PEt_3)_2]$.

RESULTS AND DISCUSSION

It was reported by Heaton and Timmins[2] that addition of bromine (1 mol equivalent) to *trans*-$[PtCl_2(PEt_3)_2]$ in chloroform (deuteriochloroform) [3] produced in a remarkable reaction (or sequence of reactions) a mixture of all possible products of type $[PtBr_xCl_{4-x}(PEt_3)_2]$ (x = 0—4) (with *trans* P atoms) in amounts corresponding to the statistical ratio (±10%) of 1 : 4 : 2 : 4 : 4 : 1.[2]

At first when we tried to repeat this work we had variable results, but then we found that light of intensity normally present in a laboratory played an essential part in this redistribution reaction. Thus, we now find that, in the absence of light, addition of bromine (1 mol) to *trans*-$[PtCl_2(PEt_3)_2]$ gives exclusively all-*trans*-$[PtBr_2Cl_2(PEt_3)_2]$. Moreover, a 0.03 mol dm^{-3} solution of this complex in chloroform, when stored in the dark at 20 °C for 17 h, was unchanged, as evidenced by the $^{31}P-\{^1H\}$ n.m.r. spectrum [Figure 1(*a*)]. However, irradiation of the n.m.r. tube using a fluorescent light of the type commonly found in a laboratory caused isomerization–disproportionation to give a mixture of the six species $[PtBr_xCl_{4-x}(PEt_3)_2]$ (x = 0—4). Each species was characterized by its δ(P) and ^1J(PtP) values (Table 1). The $^{31}P-\{^1H\}$ n.m.r. spectra after irradiation for 1, 3, and 9 h are shown in Figure 1(*b*), (*c*), and (*d*) respectively. Further irradiation caused no noticeable change in the $^{31}P-\{^1H\}$ spectra. Not surprisingly, we found that addition of bromine to a solution of *trans*-$[PtCl_2(PEt_3)_2]$, subjected to the level of illumination normally present in our laboratory, gave a mixture of all six species.

We also studied the possibility of a platinum(II) complex catalysing the isomerization–disproportionation of all-*trans*-$[PtBr_2Cl_2(PEt_3)_2]$ as had been suggested previously. However, a 0.05 mol dm^{-3} deuteriochloroform solution of this platinum(IV) complex in the presence of *trans*-$[PtCl_2(PEt_3)_2]$ (10^{-3} mol dm^{-3}) showed only traces of isomerization–disproportionation after 17 h in the dark: at least 90% of the starting complex still remained. Addition of a further quantity of *trans*-$[PtCl_2(PEt_3)_2]$, raising its total concentration to 10^{-2} mol dm^{-3}, followed by storage at *ca.* 20 °C in the dark for a further 2 days, caused *ca.* 20% conversion of the all-*trans* isomer into its *cis* isomer together with traces of the other species. We also found that a deuteriochloroform solution, initially 0.05 mol dm^{-3} in both *trans*-$[PtCl_4(PEt_3)_2]$ and *trans*-$[PtBr_2(PEt_3)_2]$, underwent negligible change after storage for 20 h at 20 °C in the dark (as evidenced by the $^{31}P-\{^1H\}$ n.m.r. spectrum).

TABLE 1

Phosphorus-31 chemical shifts * and ^1J(PtP) coupling constants for complexes of the type $[PtBr_xCl_{4-x}(PEt_3)_2]$

Complex	δ(P)	^1J(PtP)/Hz
$[PtBr_4(PEt_3)_2]$	−9.1	1 479
$[PtBr_3Cl(PEt_3)_2]$	−5.11	1 472
all-*trans*-$[PtBr_2Cl_2(PEt_3)_2]$	−1.5	1 470
$[PtBr_2Cl_2(PEt_3)_2]$	−0.93	1 470
$[PtBrCl_3(PEt_3)_2]$	2.58	1 467
$[PtCl_4(PEt_3)_2]$	6.0	1 460

* In $CDCl_3$.

Complexes of the type *cis*- or *trans*-$[PtX_4(PEt_3)_2]$ (X = Cl or Br) have been extensively studied by i.r. and Raman spectroscopy,[4] as have close analogues,[5,6] and bands due to ν(Pt–X) assigned. Our complex $[PtBr_2Cl_2(PEt_3)_2]$ which we knew to have *trans* phosphines from the n.m.r. spectra showed the following i.r. absorption bands in the region 200—400 cm^{-1}: 222m, 245s, 323m, and 335s cm^{-1}. These bands favoured the all-*trans* configuration but we considered it important to establish the configuration beyond doubt and so the structure was determined by *X*-ray diffraction analysis

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† *trans*-Dichlorobis(triethylphosphine)platinum.

‡ all-*trans*-Dibromodichlorobis(triethylphosphine)platinum.

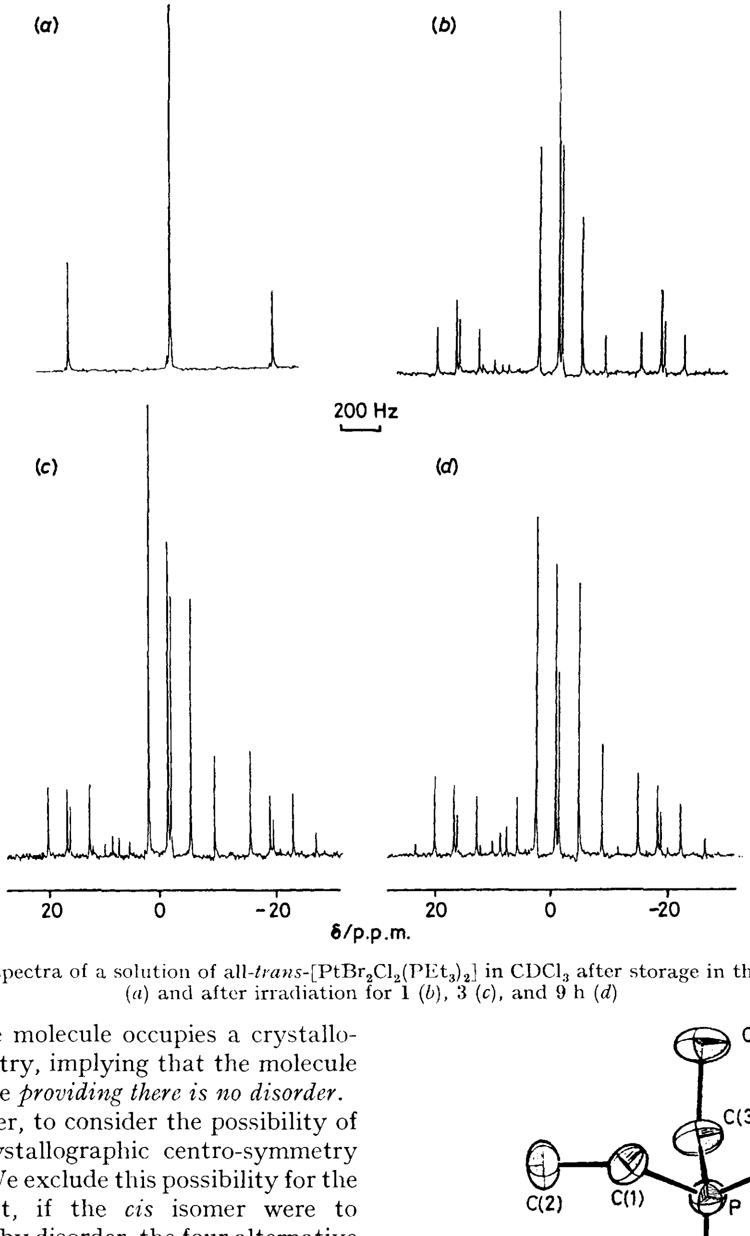

FIGURE 1 ^{31}P-{^{1}H} n.m.r. spectra of a solution of all-*trans*-[$PtBr_2Cl_2(PEt_3)_2$] in $CDCl_3$ after storage in the dark for 17 h at *ca.* 20 °C (*a*) and after irradiation for 1 (*b*), 3 (*c*), and 9 h (*d*)

of a single crystal. The molecule occupies a crystallographic centre of symmetry, implying that the molecule has the all-*trans* structure *providing there is no disorder.*

It is necessary, however, to consider the possibility of a *cis* structure with crystallographic centro-symmetry achieved by disorder. We exclude this possibility for the following reasons. First, if the *cis* isomer were to achieve centrosymmetry by disorder, the four alternative orientations would need to occur with equal probability, and as a result the electron density would be the same in the two halide sites, each corresponding to $\frac{1}{2}$Cl + $\frac{1}{2}$Br. However, the electron-density maps showed a substantial difference enabling the sites to be identified as Cl and Br positions. Secondly, there is a considerable difference in Pt–Cl and Pt–Br bond lengths, whereas a disordered *cis* structure would lead to a bond length between the two values and apparent high thermal parameters due to the difference in Cl and Br positions. Our Pt–Cl and Pt–Br bond lengths of 2.358(2) and 2.469(1) Å are comparable with the 2.323(1) and 2.463(3) Å found in $K_2[PtCl_6]$ (ref. 7) and $K_2[PtBr_6]$ (ref. 8). In [$PtCl_4(PEt_3)_2$] (ref. 9) the Pt–Cl bond length is 2.323(5) Å. In the latter compound the Pt–P bond length is 2.393(5) Å, in reasonable agreement with our value of 2.410(3) Å. Figure 2 shows an

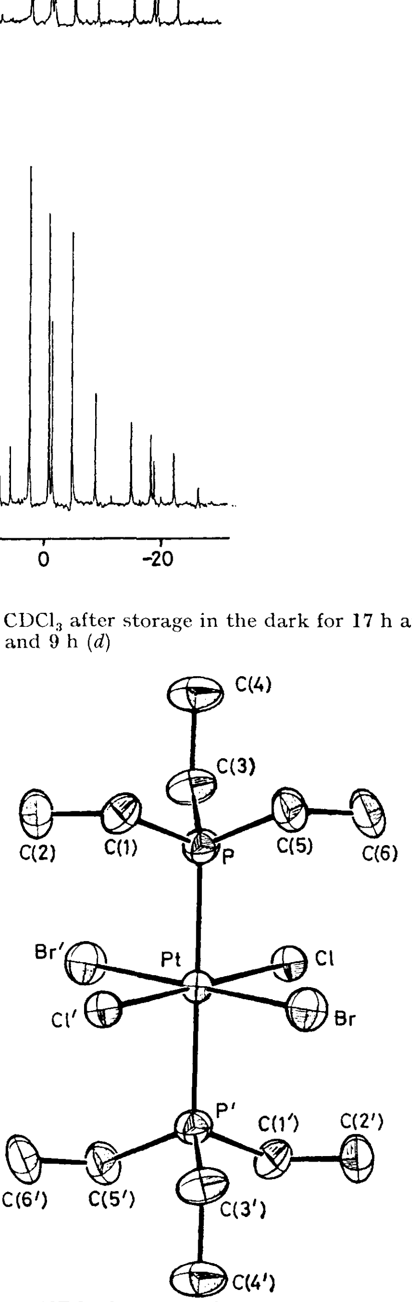

FIGURE 2 ORTEP drawing of the molecular structure of [$PtBr_2Cl_2(PEt_3)_2$], showing 50% probability thermal ellipsoids. The molecule has $\bar{1}$ symmetry

ORTEP drawing of the molecular structure with thermal ellipsoids shown at the 50% probability level. It can be seen that the thermal ellipsoids of the halide ligand are similar and do not show the large values which would result from Cl/Br disorder. In fact, the thermal parameters of Br are *slightly* greater than those of Cl. This, together with the slightly longer Pt–Cl bond length compared with the published values discussed above, may indicate a *small* amount of disorder between two orientations of the *trans* isomer, but is not consistent with the molecule being the *cis* isomer.

EXPERIMENTAL

Phosphorus-31 n.m.r. spectra were recorded on a JEOL FX 100Q spectrometer using an internal deuterium lock and broad-band proton decoupling. Except where otherwise stated, concentrations were 0.05 mol dm^{-3}. Irradiation was performed with a 20-W white fluorescent lamp, length 56 cm: the n.m.r. tube containing the sample was held *ca.* 2 cm from and parallel to the lamp. The platinum complexes were prepared by standard methods and their purity checked by ^{31}P n.m.r. spectroscopy before use.

all-trans-$[PtBr_2Cl_2(PEt_3)_2]$.—All operations were carried out in the dark. A solution of bromine (0.186 g, 1.17 mmol) in dry chloroform (1 cm^3) was added to a solution of *trans*-$[PtCl_2(PEt_3)_2]$ (0.535 g, 106 mmol) in CH_2Cl_2 (10 cm^3). The mixture was then evaporated to dryness, diethyl ether added, and the ether evaporated under reduced pressure. This gave the pure complex (0.646 g, 1.03 mmol, 92%) as orange crystals, m.p. 160—165 °C (Found: C, 21.85; H, 4.6%; *M*, 673. $C_{12}H_{30}Br_2Cl_2P_2Pt$ requires C, 21.75; H, 4.55%; *M*, 662). By halogen estimation, 10.795 mg of the complex was found to be equivalent to 10.875 mg silver nitrate; the calculated value is 11.076 mg.

Crystal Data.—$C_{12}H_{30}Br_2Cl_2P_2Pt$, $M = 662.12$, Monoclinic, $a = 9.414(2)$, $b = 13.146(3)$, $c = 8.656(1)$ Å, $\beta = 103.10(2)^\circ$, $U = 1\,043.3(3)$ Å^3, $Z = 2$, $D_c = 2.107$ g cm^{-3}, $F(000) = 628$, space group $P2_1/n$, molecular symmetry $\bar{1}$, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 109.90$ cm^{-1}.

Structure Determination.—Measurements were made on a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo-K_α radiation. Cell dimensions and their standard deviations were obtained by least-squares fitting of the setting angles of 15 reflections with $35 < 2\theta < 40^\circ$. All independent reflections with $4 < 2\theta < 45^\circ$ were measured in the ω—2θ scan mode and corrected for Lorentz, polarization, and transmission factors. The structure analysis used the 1 108 reflections with $I > 3\sigma(I)$; 260 with $I < 3\sigma(I)$ were excluded as ' unobserved '. Solution of the structure using Patterson and difference syntheses, followed by full-matrix least-squares refinement of co-ordinates and anisotropic thermal parameters of non-hydrogen atoms, gave a final *R* of 0.030 and *R'* of 0.043. A final difference map showed the hydrogen atoms as peaks of 0.4—0.7 e Å^{-3}, but they were not included in the refinement. The atomic co-ordinates and their estimated standard deviations are in Table 2, with bond lengths and angles in Table 3. The thermal parameters and a list of observed and calculated structure factors are in Supplementary Publication No. SUP 23118 (12 pp.).*

TABLE 2

Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt	0	0	0
Br	−0.175 6(1)	0.110 8(1)	0.092 6(1)
P	0.201 1(3)	0.104 3(2)	0.133 4(3)
Cl	0.032 9(3)	−0.097 5(2)	0.234 0(3)
C(1)	0.267 3(13)	0.191 6(9)	−0.002 0(14)
C(2)	0.350 3(15)	0.140 8(11)	−0.114 0(14)
C(3)	0.356 7(13)	0.028 8(9)	0.235 5(16)
C(4)	0.489 0(14)	0.095 9(11)	0.326 0(16)
C(5)	0.160 6(13)	0.194 1(9)	0.279 3(13)
C(6)	0.127 8(16)	0.143 1(11)	0.431 0(14)

TABLE 3

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Pt–Br	2.469(1)	Br–Pt–Cl	90.5(1)
Pt–Cl	2.358(2)	Br–Pt–P	91.1(1)
Pt–P	2.410(3)	Cl–Pt–P	87.8(1)
P–C(1)	1.847(13)	Pt–P–C(1)	113.0(3)
P–C(3)	1.824(12)	Pt–P–C(3)	112.3(4)
P–C(5)	1.831(13)	Pt–P–C(5)	115.7(4)
C(1)–C(2)	1.530(20)	P–C(1)–C(2)	115.2(8)
C(3)–C(4)	1.582(17)	P–C(3)–C(4)	113.1(8)
C(5)–C(6)	1.566(18)	P–C(5)–C(6)	114.5(8)

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.