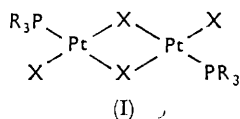


### 327. *The Fission of Halogeno-bridged Binuclear Platinum(II)-Tertiary Phosphine Complexes by Carbon Monoxide and Olefins.*

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Halogen-bridged compounds of the type (I; R = Et, Pr, and Bu; X = halogen) are shown to react slowly with carbon monoxide or simple mono-olefins (ethylene, propylene, allyl alcohol) to give mononuclear complexes of the type *cis*-[PtX<sub>2</sub>L(PR<sub>3</sub>)] (L = carbon monoxide or olefin). Binuclear butadiene bridged complexes [Pt<sub>2</sub>Cl<sub>4</sub>(C<sub>4</sub>H<sub>6</sub>)(PR<sub>3</sub>)<sub>2</sub>] were also prepared. The carbonyl complexes are more stable than the olefin complexes both towards heat and to metathetical halogen replacement reactions. Dipole moment and infrared data are given.

CHLORO-BRIDGED platinum(II) complexes of the type [Pt<sub>2</sub>Cl<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub>] (I; R = Et, Pr, Bu, X = Cl) react rapidly with a variety of amines (am) to give mononuclear complexes [PtCl<sub>2</sub>am(PR<sub>3</sub>)], which invariably have the *trans*-configuration<sup>1</sup>



owing to the high *trans*-effect of the tertiary phosphine ligands<sup>2,3</sup> which directs the amine into the *trans*-position, and the low *trans*-effect of the amine which makes for stability of the *trans*-product.

We now describe the results of a study of the action of (1) carbon monoxide and (2) olefins, both of high *trans*-effects, on halogeno-bridged complexes of this type.

*Carbon Monoxide.*—When benzene suspensions of the orange chloro-bridged complexes [Pt<sub>2</sub>Cl<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub>] (R = Et, Pr, or Bu) are shaken with carbon monoxide at 20°/1 atm., colourless crystals of the mononuclear carbonyl complexes *cis*-[PtCl<sub>2</sub>(CO)(PR<sub>3</sub>)] were formed in 70—90% yield after about 2 hours. Their *cis*-configurations were shown by high dipole moments (~10 D) and were to be expected, since both carbon monoxide (especially) and the phosphine are strongly double-bonding ligands. They would form the strongest bonds to the metal when they are in mutual *cis*-positions and in *trans*-positions to the weakly double-bonding chlorine atoms.<sup>4</sup> Thus the *cis* are expected to be thermodynamically more stable than the *trans*-isomers. It is very probable that rapid substitution by carbon monoxide also takes place *trans* to the highly *trans*-directing phosphine, setting up an equilibrium which would favour the binuclear complex [Pt<sub>2</sub>Cl<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub>] rather than the unstable mononuclear complex, *trans*-[PtCl<sub>2</sub>(CO)(PR<sub>3</sub>)]. Since chlorine has a relatively small *trans*-effect, slow *cis*-substitution will also take place to give the thermodynamically more stable *cis*-isomers [PtCl<sub>2</sub>(CO)(PR<sub>3</sub>)] until all the bridged complex has been converted into the *cis*-product. These fission reactions of carbon monoxide are summarised below.

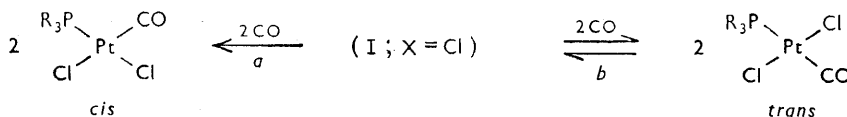
The carbonyl complexes *cis*-[PtCl<sub>2</sub>(CO)PR<sub>3</sub>] (R = Et, Pr, and Bu) all melted sharply without decomposition, and molten *cis*-[PtCl<sub>2</sub>(CO)(PEt<sub>3</sub>)] was recovered unchanged even

<sup>1</sup> Chatt and Venanzi, *J.*, 1955, 3858.

<sup>2</sup> Quagliano and Schubert, *Chem. Rev.*, 1952, 50, 201

<sup>3</sup> Chatt, Duncanson, and Venanzi, *J.*, 1955, 4456.

<sup>4</sup> Chatt and Wilkins, *J.*, 1952, 4300.



(a) Slow, but goes essentially to completion.

(b) Equilibrium favours left-hand side.

after being heated at 130°/0.001 mm. for 1 hour. A colourless bromo-complex, *cis*-[PtBr<sub>2</sub>(CO)(PEt<sub>3</sub>)], was prepared from the corresponding chloro-complex by treatment with an acetone solution of lithium bromide, and its yellow iodo-analogue was prepared by fission of the iodo-bridged complex [Pt<sub>2</sub>I<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>] with carbon monoxide. This iodo-carbonyl complex lost carbon monoxide on melting (at 104–108°) and was thermally less stable than the corresponding chloro- and bromo-complexes. This was probably due to the higher *trans*-effect of iodine over chlorine or bromine, which would labilise the carbon monoxide ligand in a *trans*-position.

These carbonyl complexes showed a very strong sharp infrared absorption band at *ca.* 2100 cm.<sup>-1</sup>, due to the C≡O stretching mode of vibration. The values of these stretching frequencies are given in Table I. In the series *cis*-[PtX<sub>2</sub>(CO)(PEt<sub>3</sub>)] (X = Cl, Br, and I) the C≡O stretching frequency,  $\nu$  (C≡O), falls slightly in passing from chloride to iodide. This

TABLE I.

Carbonyl stretching frequencies of some carbonylplatinum(II) complexes.

Complex	$\nu$ (C≡O) (cm. <sup>-1</sup> )		Complex	$\nu$ (C≡O) (cm. <sup>-1</sup> )	
	Nujol	CHCl <sub>3</sub>		Nujol	CHCl <sub>3</sub>
<i>cis</i> -[PtCl <sub>2</sub> (CO)(PEt <sub>3</sub> )].....	2100	2100	<i>cis</i> -[PtBr <sub>2</sub> (CO)(PEt <sub>3</sub> )] ...	2095 } 2049 J	2094
<i>cis</i> -[PtCl <sub>2</sub> (CO)(PEt <sub>3</sub> )].....	2100	2096	<i>cis</i> -[PtI <sub>2</sub> (CO)(PEt <sub>3</sub> )] .....	2087 } 2033sh }	2085
<i>cis</i> -[PtCl <sub>2</sub> (CO)(PBu <sub>3</sub> )] ...	2087	2101			

sh = shoulder.

order can be explained if one supposes that the inductive effects of the halogens (Cl > Br > I) outweigh effects of mesomeric electron withdrawal of electrons from the filled non-bonding *d*-orbitals of the metal into the *d*-orbitals of the halogen, which is believed to decrease along the series I > Br > Cl. This seems likely as there can be very little mesomeric withdrawal by the halogens in competition with the strongly double-bonding carbon monoxide; there might even be electron release from the halogen *p*-orbitals. A similar order of  $\nu$  (C≡O) was observed in the series *cis*-[PtX<sub>2</sub>(CO)AsMePh<sub>2</sub>] and was explained similarly.<sup>5</sup>

*Olefins.*—When benzene or acetone suspensions of the chloro-bridged complexes [Pt<sub>2</sub>Cl<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub>] were shaken for several days in an atmosphere of an olefin (ethylene, propene, or but-1-ene) at 20°, mononuclear olefin complexes of the type *cis*-[PtCl<sub>2</sub>(olefin)(PR<sub>3</sub>)] were formed in 70–96% yield. These reactions were much slower than those with carbon monoxide. Above 100° these complexes lost olefin and reverted to the halogeno-bridged complexes, in marked contrast to the corresponding carbonyl complexes. Moreover attempts to prepare bromo- and iodo-complexes [PtX<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(PR<sub>3</sub>)] (X = Br and I) from the chloro-complexes by treatment with lithium bromide or sodium iodide in acetone at 20° gave only the bromo- or iodo-bridged complexes [Pt<sub>2</sub>X<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub>], with loss of ethylene. Nevertheless the bromo-bridged complex [Pt<sub>2</sub>Br<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>] reacted with ethylene, and readily gave *cis*-[PtBr<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(PEt<sub>3</sub>)] in 85% yield.

With butadiene the chloro-bridged complexes gave very insoluble products [Pt<sub>2</sub>Cl<sub>4</sub>(C<sub>4</sub>H<sub>6</sub>)(PR<sub>3</sub>)<sub>2</sub>]. We suggest that these are binuclear with butadiene bridging the two platinum atoms. Their insolubility is more consistent with a tightly packed symmetrical bridge of the type suggested for the [Cl<sub>3</sub>Pt(C<sub>4</sub>H<sub>6</sub>)PtCl<sub>3</sub>]<sup>2-</sup> ion<sup>6</sup> than that each

<sup>5</sup> Irving and Magnusson, *J.*, 1958, 2283.<sup>6</sup> Chatt, *Chimica Inorganica, Accad. Naz. Lincei*, 1961, 155.

double bond interacts independently, stringing the two platinum atoms together, with free rotation about the centre C-C bond. A similar compound  $[\text{Pt}_2\text{Cl}_4(\text{C}_4\text{H}_6)(\text{NH}_3)_2]$  but probably of *trans*-configuration is also known.<sup>7</sup> Our butadiene complexes were too insoluble for molecular-weight or dipole-moment determinations and we can only speculate about their configuration by analogy with their corresponding mono-olefin complexes.

Treatment of the bridged compound  $[\text{Pt}_2\text{Cl}_4(\text{PEt}_3)_2]$  with allyl alcohol gave the complex  $[\text{PtCl}_2(\text{C}_3\text{H}_5\cdot\text{OH})(\text{PEt}_3)]$  in which the double bond is attached to the platinum, since  $\nu(\text{C}=\text{C})$  was lowered by some  $140\text{ cm}^{-1}$  on co-ordination.

#### EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and corrected.

*Preparation of Carbonyl Complexes.*—Three compounds of formula *cis*-dichloro(carbonyl)-(trialkylphosphine)platinum(II) were prepared by shaking a benzene solution or suspension of the appropriate halogeno-bridged compound, di- $\mu$ -chloro-dichlorobis(trialkylphosphine)diplatinum(II), with carbon monoxide at room temperature and atmospheric pressure. When absorption was complete the white product was filtered off and recrystallised from ethanol. Evaporation of the benzene mother-liquors and recrystallisation of the residue from ethanol gave a further quantity of product.

*cis*-Dichloro(carbonyl)(triethylphosphine)platinum(II),  $[\text{PtCl}_2(\text{CO})\text{PEt}_3]$ , was obtained after 1 hr. as white prisms, m. p.  $134\text{--}136^\circ$ , in 90% yield (Found: C, 20.55; H, 3.7.  $\text{C}_7\text{H}_{16}\text{Cl}_2\text{OPPt}$  requires C, 20.4; H, 3.65%). *cis*-Dichloro(carbonyl)(tripropylphosphine)platinum(II),  $[\text{PtCl}_2(\text{CO})\text{PPr}_3]$ , was obtained after 18 hr. as white needles, m. p.  $105\text{--}107^\circ$  in 70% yield (Found: C, 26.55; H, 4.7%; *M*, cryoscopic in 0.72% benzene solution, 455.  $\text{C}_{10}\text{H}_{21}\text{Cl}_2\text{OPPt}$  requires C, 26.45; H, 4.65%; *M*, 454). *cis*-Dichloro(carbonyl)(tributylphosphine)platinum(II),  $[\text{PtCl}_2(\text{CO})\text{PBu}_3]$ , was obtained after 24 hr. as white needles, m. p.  $114\text{--}116^\circ$  in 86% yield (Found: C, 31.6; H, 5.55.  $\text{C}_{13}\text{H}_{27}\text{Cl}_2\text{OPPt}$  requires C, 31.45; H, 5.5%). *cis*-Di-iodo(carbonyl)-(triethylphosphine)platinum(II),  $[\text{PtI}_2(\text{CO})\text{PEt}_3]$ , was similarly prepared as yellow microcrystals, m. p.  $104\text{--}108^\circ$  (decomp.), in 92% yield by shaking di- $\mu$ -iodo-di-iodobis(triethylphosphine)diplatinum(II) in benzene solution with carbon monoxide for 2 hr. The benzene was evaporated and the yellow residue recrystallised from methanol (Found: C, 14.3; H, 2.6.  $\text{C}_7\text{H}_{15}\text{I}_2\text{OPPt}$  requires C, 14.15; H, 2.55%).

*cis*-Dibromo(carbonyl)(triethylphosphine)platinum(II),  $[\text{PtBr}_2(\text{CO})\text{PEt}_3]$ . A solution of *cis*- $[\text{PtCl}_2(\text{CO})\text{PEt}_3]$  (0.75 g.) and lithium bromide (4.5 g.) in acetone (100 c.c.) was put aside at  $20^\circ$  for 24 hr. The mixture was then evaporated to dryness and the residue washed with water and crystallised from ethanol to give *cis*-dibromo(carbonyl)(triethylphosphine)platinum(II) as needles (0.87 g.), m. p.  $118\text{--}120^\circ$  (Found: C, 16.9; H, 3.05.  $\text{C}_7\text{H}_{15}\text{Br}_2\text{OPPt}$  requires C, 16.8; H, 3.0%).

*Preparation of Olefin Complexes.*—The following nine olefin complexes were prepared in a similar way to the carbonyl complexes by shaking the corresponding bridged compound in benzene or acetone in one atmosphere of the olefin at  $20^\circ$ . The product was isolated by filtration and/or evaporation of the solvent. Five compounds decomposed on attempted recrystallisation, but were obtained analytically pure from the reaction mixture, the remainder were purified by recrystallisation.

*cis*-Dichloro(ethylene)(triethylphosphine)platinum(II),  $[\text{PtCl}_2(\text{C}_2\text{H}_4)\text{PEt}_3]$ , was obtained in benzene solution, after 10 days, in 96% yield and formed prisms from chloroform-light petroleum (b. p.  $40\text{--}60^\circ$ ) (Found: C, 23.4; H, 4.65.  $\text{C}_8\text{H}_{16}\text{Cl}_2\text{PPt}$  requires C, 23.3; H, 4.65%). *cis*-Dichloro(ethylene)(tripropylphosphine)platinum(II),  $[\text{PtCl}_2(\text{C}_2\text{H}_4)\text{PPr}_3]$ , was obtained in acetone after 4 days, in 80% yield and formed needles, m. p.  $138\text{--}141^\circ$  (decomp.), from methanol (Found: C, 29.15; H, 5.6.  $\text{C}_{11}\text{H}_{25}\text{Cl}_2\text{PPt}$  requires C, 29.1; H, 5.55%). *cis*-Dichloro(ethylene)-(tributylphosphine)platinum(II),  $[\text{PtCl}_2(\text{C}_2\text{H}_4)\text{PBu}_3]$ , was obtained in acetone after 6 days in 76% yield and formed needles, m. p.  $110\text{--}112^\circ$  (decomp.), from methanol-water (Found: C, 33.9; H, 6.3%; *M*, cryoscopically in 1.05% benzene solution, 522.  $\text{C}_{14}\text{H}_{31}\text{Cl}_2\text{PPt}$  requires C, 33.9; H, 6.25%; *M*, 496). *cis*-Dibromo(ethylene)(triethylphosphine)platinum(II),  $[\text{PtBr}_2(\text{C}_2\text{H}_4)\text{PEt}_3]$ , obtained in benzene after 24 hr. in 85% yield and formed needles, m. p.  $110\text{--}112^\circ$  (decomp.), from the mixture (Found: C, 19.25; H, 3.85.  $\text{C}_8\text{H}_{16}\text{Br}_2\text{PPt}$  requires

<sup>7</sup> Gelman, *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **23**, 532.

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C, 19.2; H, 3.8%). *cis*-Dichloro(propene)(triethylphosphine)platinum(II), [PtCl<sub>2</sub>(C<sub>3</sub>H<sub>6</sub>)PEt<sub>3</sub>], was obtained in acetone after 11 days in 79% yield and formed needles from methanol (Found: C, 25.4; H, 4.95. C<sub>9</sub>H<sub>21</sub>Cl<sub>2</sub>PPt requires C, 25.3; H, 5.2%); i.r. (Nujol mull) weak band at 1506 cm.<sup>-1</sup> (C=C stretch). *cis*-Dichloro(but-1-ene)(triethylphosphine)platinum(II), [PtCl<sub>2</sub>(C<sub>4</sub>H<sub>8</sub>)PEt<sub>3</sub>], was obtained in benzene after 18 days in 79% yield and formed needles from the mixture (Found: C, 27.45; H, 5.25. C<sub>11</sub>H<sub>23</sub>Cl<sub>2</sub>PPt requires C, 27.3; H, 5.25%), i.r. (Nujol mull) weak band at 1504 cm.<sup>-1</sup> (C=C stretch). Tetrachloro(butadiene)bis(triethylphosphine)diplatinum(II), [Pt<sub>2</sub>Cl<sub>4</sub>(C<sub>4</sub>H<sub>6</sub>)(PEt<sub>3</sub>)<sub>2</sub>], was obtained in acetone after 4 days in 41% yield and formed pale yellow microcrystals from the mixture (Found: C, 23.45; H, 4.45. C<sub>16</sub>H<sub>36</sub>Cl<sub>4</sub>P<sub>2</sub>Pt<sub>2</sub> requires C, 23.4; H, 4.4%), i.r. (Nujol mull), medium band at 1479 cm.<sup>-1</sup> (C=C stretch). Tetrachloro(butadiene)bis(triisopropylphosphine)diplatinum(II), [Pt<sub>2</sub>Cl<sub>4</sub>(C<sub>4</sub>H<sub>6</sub>)(PPr<sub>3</sub>)<sub>2</sub>], was obtained in acetone after 3 days in 77% yield and formed pale yellow microcrystals from the mixture (Found: C, 29.15; H, 5.35. C<sub>22</sub>H<sub>48</sub>Cl<sub>4</sub>P<sub>2</sub>Pt<sub>2</sub> requires C, 29.15; H, 5.35%), i.r. (Nujol mull), medium band at 1478 cm.<sup>-1</sup> (C=C stretch). Tetrachloro(butadiene)bis(tributylphosphine)diplatinum(II), [Pt<sub>2</sub>Cl<sub>4</sub>(C<sub>4</sub>H<sub>6</sub>)(PBu<sub>3</sub>)<sub>2</sub>], was obtained in acetone after 13 days in 68% yield and formed pale yellow microcrystals from the mixture (Found: C, 33.85; H, 6.0. C<sub>28</sub>H<sub>60</sub>Cl<sub>4</sub>P<sub>2</sub>Pt<sub>2</sub> requires C, 33.95; H, 6.1%), i.r. (Nujol mull) medium band at 1480 cm.<sup>-1</sup> (C=C stretch).

TABLE 2.

Dipole moments of some carbonyl and olefin complexes of platinum(II) in benzene at 25°.

10 <sup>3</sup> ω	Δε/ω	-Δν/ω	<i>τ</i> P	<i>ε</i> P	<i>o</i> P	μ (D)
<i>cis</i> -[PtCl <sub>2</sub> (CO)PEt <sub>3</sub> ]						
0	26.18	—	—	—	—	—
1.546	24.86	—	—	—	—	—
2.568	24.26	—	—	—	—	—
3.207	23.66	—	—	—	—	—
3.951	23.32	—	—	—	—	—
4.140	23.24	—	—	—	—	—
6.053	22.29	—	—	—	—	—
7.161	21.85	(0.53)	2109 *	(62)	2037 *	10.0 *
<i>cis</i> -[PtCl <sub>2</sub> (CO)PPr <sub>3</sub> ]						
0	24.70	—	—	—	—	—
1.115	23.61	—	—	—	—	—
1.474	23.75	—	—	—	—	—
2.461	22.87	—	—	—	—	—
3.778	22.32	—	—	—	—	—
5.803	21.70	—	—	—	—	—
7.464	21.27	(0.53)	2197 *	(74)	2113 *	10.15 *
<i>cis</i> -[PtCl <sub>2</sub> (CO)PBu <sub>3</sub> ]						
0	22.70	—	—	—	—	—
1.339	21.94	—	—	—	—	—
2.571	21.17	—	—	—	—	—
3.048	21.05	—	—	—	—	—
4.220	20.69	—	—	—	—	—
4.525	20.62	—	—	—	—	—
5.580	20.37	—	—	—	—	—
7.791	19.98	(0.53)	2214 *	(90)	2111 *	10.15 *
<i>cis</i> -[PtBr <sub>2</sub> (CO)PEt <sub>3</sub> ]						
0	20.92	—	—	—	—	—
1.937	20.28	—	—	—	—	—
2.271	20.29	—	—	—	—	—
3.374	19.92	(0.58)	2060 *	(68)	1981 *	9.85 *
<i>cis</i> -[PtCl <sub>2</sub> (ethylene)PPr <sub>3</sub> ]						
0	25.20	—	—	—	—	—
1.151	24.46	—	—	—	—	—
2.928	23.60	—	—	—	—	—
4.178	23.11	—	—	—	—	—
5.510	22.73	(0.53)	2240 *	(80)	2148 *	10.25 *
<i>cis</i> -[PtCl <sub>2</sub> (but-1-ene)PEt <sub>3</sub> ]						
0	26.30	—	—	—	—	—
1.006	25.42	—	—	—	—	—
1.643	24.84	(0.53)	2262 *	(78)	2173 *	10.3 *

*cis*-Dichloro(allyl alcohol)(triethylphosphine)platinum(II). Di- $\mu$ -chloro-dichlorobis(triethylphosphine)diplatinum (0.5 g.) was dissolved in hot allyl alcohol (15 c.c.), and the solution set aside for 2½ hr. The required compound formed *prisms* (0.30 g.) (Found: C, 24.7; H, 4.8. C<sub>9</sub>H<sub>21</sub>Cl<sub>2</sub>OPPt requires C, 24.45; H, 4.8%), i.r. (Nujol mull) strong band at 3378 cm.<sup>-1</sup> (OH stretch) and a weak one at 1504 cm.<sup>-1</sup> (C=C stretch). The compound decomposed when heated, to give the starting bridged compound.

*Action of Lithium Bromide on cis-Dichloro(ethylene)(triethylphosphine)platinum(II)*.—A solution of *cis*-[PtCl<sub>2</sub>(ethylene)PEt<sub>3</sub>] (0.50 g.) and lithium bromide (3.0 g.) in acetone (25 c.c.) was put aside at 20° for 24 hr. The mixture was then evaporated to dryness and the residue washed with water and crystallised from acetone to give di- $\mu$ -bromo-dibromobis(triethylphosphine)-diplatinum(II) as orange prisms, (0.41 g.), m. p. 202—204° (Found: C, 15.3; H, 3.2. Calc. for C<sub>12</sub>H<sub>30</sub>Br<sub>4</sub>P<sub>2</sub>Pt<sub>2</sub>: C, 15.25; H, 3.2%).

*Action of Sodium Iodide on cis-Dichloro(ethylene)(triethylphosphine)platinum(II)*. A solution of *cis*-[PtCl<sub>2</sub>(ethylene)PEt<sub>3</sub>] (0.50 g.) and sodium iodide (4.0 g.) in acetone (25 c.c.) was put aside at 20° for 24 hr. The mixture was then evaporated to dryness and the residue washed with water and crystallised from acetone to give di- $\mu$ -iodo-di-iodobis(triethylphosphine)-diplatinum(II) as red prisms, (0.52 g.), m. p. 211—213° (Found: C, 12.8; H, 2.65. Calc. for C<sub>12</sub>H<sub>30</sub>I<sub>4</sub>P<sub>2</sub>Pt<sub>2</sub>: C, 12.7; H, 2.65%).

*Action of Heat on cis-Dichloro(ethylene)(tripropylphosphine)platinum(II)*.—When *cis*-[PtCl<sub>2</sub>(ethylene)PPr<sub>3</sub>] at 132°/1 mm. was heated for 1 hr. it became yellow. The infrared spectrum of the product was identical with that of an authentic sample of di- $\mu$ -chloro-dichloro-(tripropylphosphine)platinum(II).

*Action of Heat on cis-Dichloro(carbonyl)(triethylphosphine)platinum(II)*.—When *cis*-[PtCl<sub>2</sub>(CO)PEt<sub>3</sub>] was heated at 132°/0.001 mm. for 1 hr. it melted, but resolidified on cooling. The infrared spectrum of the product was identical with that of the starting material.

*Determination of Dipole Moments*.—The method of determination and the meanings of the symbols were as described previously<sup>8</sup> except that values of  $\Delta\epsilon/\omega$  were plotted against values of  $\omega$  and the limiting value of  $\Delta\epsilon/\omega$  for zero  $\omega$  obtained graphically. This limiting value (shown in Table 2) was used in calculating the dipole moment.

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<sup>8</sup> Chatt and Shaw, *J.*, 1959, 705, 4020.