Adducts of Co-ordination Compounds. Part XI.[1] Isomerism and Solvation of Dichlorobis(triphenylphosphine)platinum(II)

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The complex *cis*-[$Pt(PPh_3)_2Cl_2$] forms distinct adducts with chloroform and *NN*-dimethylformamide. The existence of these adducts, for which *X*-ray powder results are given, accounts for several discrepancies in the literature. In particular, the product (recrystallised from chloroform–hexane) of reaction of carbon tetrachloride with tetrakis(triphenylphosphine)platinum(0), previously incorrectly formulated as [$Pt(PPh_3)_2(CCl_3)Cl$], is in fact a partly desolvated sample of the chloroform adduct of the *cis*-dichloro-complex. In solution, *cis–trans*-isomerisation is easily set up providing access to the *trans*-isomer. Two further methods, which give much better yields of the *trans*-isomer, are described.

COMPLEXES of the type [ML_2X_2] (M = Pd or Pt; L = phosphine or arsine; X = Cl, Br, or I) are well known.[2] [$Pt(PPh_3)_2Cl_2$], first made[3] by Jensen, is among the best known. However, its reported properties (such as solubility and m.p.) are distinctly variable, *e.g.* quoted m.p.s range from 287 to 312 °C. Further, until recently, only one isomer (white *cis* †) was known. This isomer has been obtained in a number of ways, which divide into two general classes: (*a*) substitution at platinum(II) and (*b*) oxidative addition to platinum(0). Under (*a*), routes include: (*i*) Jensen's original method[3] (reaction in an aqueous medium of $K_2[PtCl_4]$ and the phosphine), developments including heating[4] and boiling;[10] (*ii*) interaction of the same reactants under reflux in xylene;[11] (*iii*) reaction of platinum(II) chloride in molten triphenylphosphine;[12] and (*iv*) substitution[6] by phosphine of sulphur ligands (L) in [PtL_2Cl_2] and the presumably related formation[13] on adding phosphine to a hot *NN*-dimethylformamide–xylene solution of hexachloroplatinic(IV) acid. Under the heading (*b*), (*i*) numerous halogenated reactants (*e.g.*[8] C_2Cl_6, *cis*- or *trans*-$C_2H_2Cl_2$, C_3Cl_6, $CHCl_3$, and HCl[14]) have been employed to give *cis*-[$Pt(PPh_3)_2Cl_2$] from [$Pt(PPh_3)_4$]; (*ii*) presumably related is the reaction[15] of η-allylplatinum(II) species with dihydrogen in chloroform. The usual solvents for recrystallisation have been chloroform and dichloromethane.

The yellow *trans*-isomer has been obtained recently in several ways, *e.g.* (*i*) by interaction of *trans*-[$Pt(PPh_3)_2(H)Cl$] with $HgCl_2$[9a] or of [$Pt(PPh_3)_2(SnPh_3)Cl$] with HCl[9b] and (*ii*) by photochemical isomerisation[7] in chloroform of the *cis*-isomer. Its properties are agreed: m.p. 306—309,[7] 307—310,[9] 300 °C;[16] ν(Pt-Cl) at 344[7] and 345 cm^{-1};[9] dipole moment ≃ 0;[9] its electronic spectrum[16] differs quantitatively from that of the *cis*-isomer.

In syntheses of *trans*-[$Pt(PPh_3)_2(H)Cl$][17] from various samples of *cis*-[$Pt(PPh_3)_2Cl_2$] we observed that the crude product of Jensen's reaction[3] reacts markedly more slowly with ethanolic hydrazine than do samples recrystallised from chloroform. Since complexes containing triaryl-phosphines and -arsines are well known to be prone to polymorphism and solvation {as exemplified by *trans*-[$Pt(PPh_3)_2(H)Cl$] itself, which has recently been shown[18] to exist in at least three unsolvated modifications in addition to yielding numerous adducts}, it seemed possible that the variance in the properties of *cis*-[$Pt(PPh_3)_2Cl_2$] might be due to similar phenomena. We have therefore made a detailed investigation of the properties (including *X*-ray diffraction of powders) of samples of *cis*-[$Pt(PPh_3)_2Cl_2$] prepared by different methods. This paper presents our results, which show the existence of distinct adducts of the complex with chloroform and *NN*-dimethylformamide (dmf). The work has also led to the development of convenient preparations of the *trans*-isomer. We further find that the product of the reaction of carbon tetrachloride with [$Pt(PPh_3)_4$] is *cis*-[$Pt(PPh_3)_2Cl_2$].‡ This product, recrystallised[8] from chloroform–hexane, has been incorrectly formulated as [$Pt(PPh_3)_2(CCl_3)Cl$]. It is in fact

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† The assignment of the *cis*-configuration to Jensen's compound (Registry No. 15604-36-1) rests on chemical evidence[4] and the Pt-Cl vibrations [$\bar{\nu}$/cm^{-1}]: 321 and 295;[5] 317 and 293;[6] 316 and 293 with Raman bands at 323 and 299;[7] and 316 and 291[8]. Statements (*e.g.* in ref. 9*a*) that Jensen found[3] a high dipole moment are erroneous; he was unable to measure it.

‡ The complexes [$Pt(PPh_3)_{3\text{ or }4}$] have already been said[19] to react with CCl_4 giving *cis*-[$Pt(PPh_3)_2Cl_2$], although the reference given for the statement is not correct.

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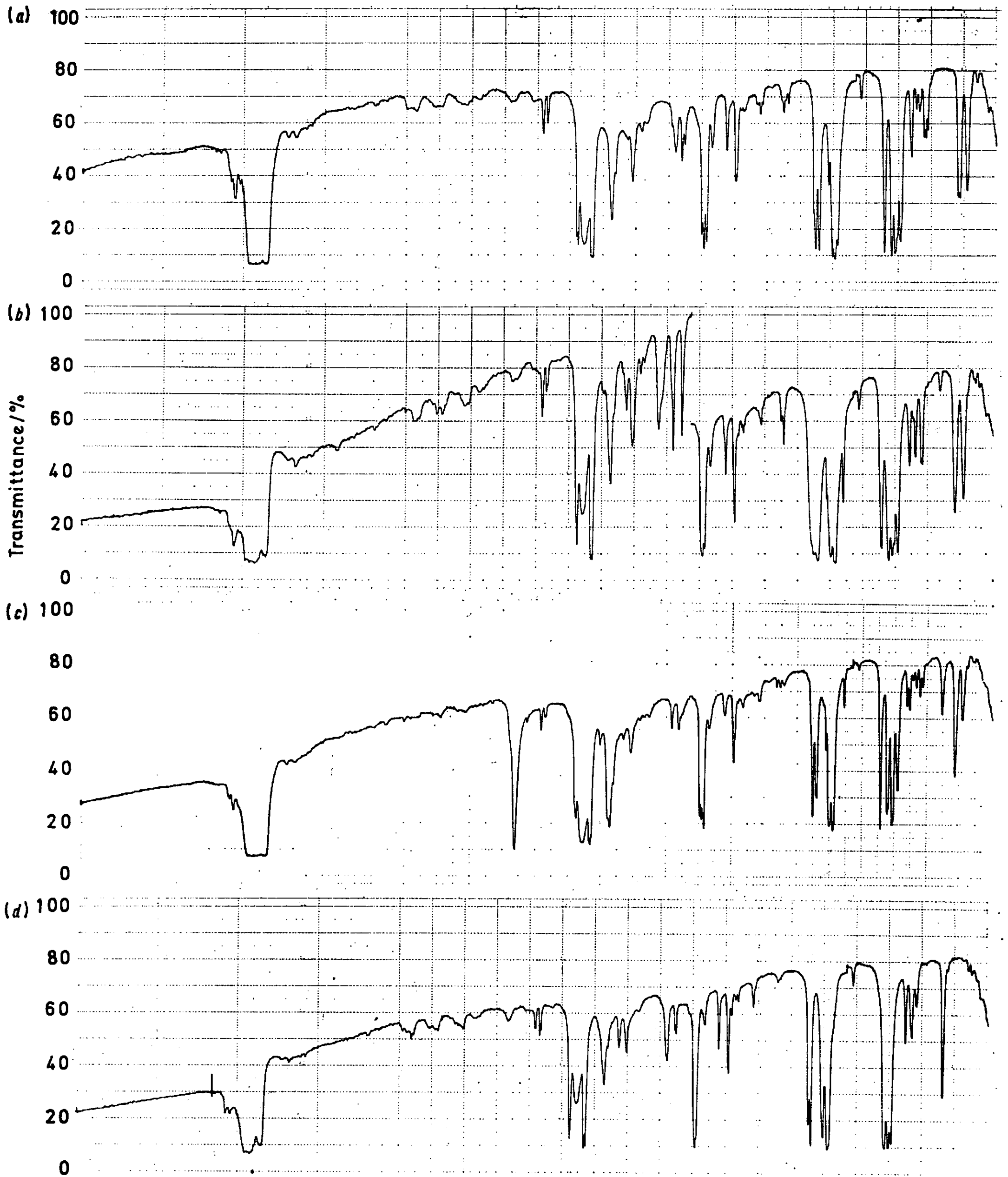
a partly desolvated sample of the chloroform adduct of *cis*-[$Pt(PPh_3)_2Cl_2$].

RESULTS

Adducts of cis-[$Pt(PPh_3)_2Cl_2$].—Several recipes gave samples of *cis*-[$Pt(PPh_3)_2Cl_2$] in the same unsolvated form. These (as given in the Introduction section) are (*a*) (*i*),[3] (*a*) (*ii*),[11] (*a*) (*ii*),[12] and (*b*) (*i*) (which uses[8] CCl_4 as a medium). Any sample recrystallised from $CHCl_3$ gave the chloroform adduct [$Pt(PPh_3)_2Cl_2$],$CHCl_3$. Preparation (*a*) (*iv*) (in dmf as medium[13]) gave the adduct 2[$Pt(PPh_3)_2Cl_2$],dmf. Recrystallisation of any sample from dmf gave this adduct, whereas recrystallisation of any sample from CH_2Cl_2 gave the unsolvated form.

All three forms had ν(Pt–Cl) at 293 and 315 cm^{-1}, indicating that the *cis*-geometry persists. The i.r. spectra of the unsolvated *cis*- and *trans*-isomers, and of the adducts with $CHCl_3$ and dmf are reproduced in the Figure. The i.r. spectra of the adducts contained extra bands due to vibrations of the solvent. Thus, *cis*-[$Pt(PPh_3)_2Cl_2$],$CHCl_3$ had extra bands (in cm^{-1}) at 2 420w, 1 220ms, 760s, 670ms, 630vw, and 360wm which correspond to the strongest bands



I.r. spectra (Nujol mulls) of: (*a*) *cis*-[$Pt(PPh_3)_2Cl_2$]; (*b*) *cis*-[$Pt(PPh_3)_2Cl_2$],$CHCl_3$; (*c*)2 *cis*-[$Pt(PPh_3)_2Cl_2$],dmf; and (*d*) *trans*-[$Pt(PPh_3)_2Cl_2$]

in pure chloroform. The adduct 2 *cis*-[Pt(PPh_3)$_2$$Cl_2$],dmf had extra bands arising from solvating dmf at 1 670vs, 1 500vw, 1 400w, 1 255w, 1 090s, 865vw, 660m, and 350s cm^{-1}. Final confirmation of the presence of chloroform in the lattice of *cis*-[Pt(PPh_3)$_2$$Cl_2$],$CHCl_3$ was obtained by recrystallising the unsolvated complex from deuteriochloroform: the product had extra bands due to $CDCl_3$ at 2 215m, 910m, 750m, 640w, and 360wm cm^{-1}.

X-Ray powder photographs confirmed the i.r. evidence for the existence of three forms of the *cis*-isomer, as indicated by the *d* spacings and relative intensities of the powder lines given in Table 1. The powder lines for the *trans*-isomer are also given. Further, heating either adduct at 180 °C for 7 h gave the unsolvated complex in both cases. This desolvation has already been noticed (at least implicitly) by Volger and Vrieze,[15] who used a vacuum at 100 °C to remove chloroform from the precipitated *cis*-isomer; we repeated this experiment and the volatile material evolved from complexes crystallised from chloroform was indeed chloroform (i.r. spectrum). At 25 °C, loss of chloroform occurred only very slowly.

TABLE 1

X-Ray powder results *

cis-[Pt(PPh_3)$_2$Pt]		*cis*-[Pt(PPh_3)$_2$$Cl_2$],$CHCl_3$		2 *cis*-[Pt(PPh_3)$_2$$Cl_2$],dmf		*trans*-[Pt(PPh_3)$_2$$Cl_2$]	
d/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*
		13·00	s				
		12·14	w—m				
		10·27	m				
				9·61	m—s	9·82	s
9·40	w	9·41	m				
9·21	w						
8·67	s	8·50	m	8·50	w	8·51	s
8·19	s			8·11	s	7·76	s
7·76	m	7·76	w—m	7·50	w—m	7·62	m
7·56	m	7·38	m—s	7·38	m—s	6·71	m—s
7·02	w—m	7·25	m—s	6·47	w	6·15	w
6·71	w	7·13	w	5·68	vw	5·09	w
6·07	w	6·71	m	5·47	w	4·98	vw
5·82	w	6·61	w—m	5·10	vw	4·53	s
5·40	w	6·03	s	4·79	w—m	4·44	w—m
5·28	w—m	5·65	w	4·67	w	4·23	w—m
4·67	w	5·01	vw	4·50	w	4·13	w
4·53	w	4·82	vw	4·35	w—m	4·04	w—m
4·31	m	4·75	w	4·31	m	3·95	vw
4·15	w—m			4·19	vw	3·87	vw
				4·11	vw	3·80	w—m

* Cu-K_a Radiation.

The extra vibrations found here in the chloroform adduct of *cis*-[Pt(PPh_3)$_2$$Cl_2$] are remarkably similar to those observed by Bland and Kemmitt [8] in the substance which they obtained by reaction of carbon tetrachloride with [Pt(PPh_3)$_4$] and subsequently recrystallised from chloroform–hexane. It was said to be a mixture of *cis*- and *trans*-[Pt(PPh_3)$_2$(CCl_3)Cl]. We repeated this experiment and found that the crude product obtained on mixing the reactants was the unsolvated form of *cis*-[Pt(PPh_3)$_2$$Cl_2$], as indicated by its i.r. spectrum and *X*-ray powder picture; recrystallisation from chloroform gave, as expected, the adduct. As can be seen from our i.r. results, this formulation is fully consistent with the i.r. data given previously [8] {extra bands relative to *cis*-[Pt(PPh_3)$_2$$Cl_2$] at 847, 664, and 642 cm^{-1}, with ν(Pt–Cl) at 316 and 291 cm^{-1}}. It is surprising that no special reference was made [8] to the strongest chloroform peak at 1 220 cm^{-1}, since it is listed in the experimental section. The analytical results reported [8] for this substance are equally consistent with our formulation: as we have noted above, under the conditions which were used (vacuum for 4 d), chloroform loss is slow. The reported analyses [8] are quite consistent with the sample's being a partly (63%) desolvated chloroform adduct of *cis*-[Pt(PPh_3)$_2$$Cl_2$].

The existence of a chloroform adduct of *cis*-[Pt(PPh_3)$_2$$Cl_2$] explains the difference in solubilities of different samples. Thus, whenever the compound was dissolved in chloroform, the crystallised product redissolved more readily in $CHCl_3$ or CH_2Cl_2 (and also in ethanol–hydrazine) than material which had never been exposed to chloroform. A reasonable explanation of this dissolution behaviour is afforded by comparison of the *X*-ray results for the unsolvated and solvated forms. From Table 1, assuming that the *hkl* values of the first reflections in both powder patterns are of the same order of magnitude, the cell constants for the solvated species are much larger than those for the unsolvated material, *i.e.* breakdown of the crystal lattice of the adduct by solvent is easier than in the case of the more closely packed unsolvated form.

The above results also allow the discrepancies in reported m.p.s for *cis*-[Pt(PPh_3)$_2$$Cl_2$] to be rationalised [†] to some degree. The 'normal' m.p. (310—312 °C) is that of the unsolvated form. Variance from this value arose for initially solvated material. This lost chloroform as the temperature rose and underwent a phase transition, the exact rate of which was a property of the crystal chosen. Melting of solvated samples therefore refers to the complicated situation of phase change accompanying state change. The reported range of m.p.s for *cis*-[Pt(PPh_3)$_2$$Cl_2$] recrystallised from chloroform is therefore not too surprising.

cis–trans-*Isomerisation*.—It was known that (*a*) in chloroform isomerisation of yellow *trans*-[Pt(PPh_3)$_2$$Cl_2$] to its white *cis*-isomer is catalysed by triphenylphosphine [9a] and (*b*) irradiation of a solution of the *cis*-isomer in chloroform gives a mixture of *ca.* 40% *cis*: 60% *trans*.[7] As predicted from (*a*) and (*b*) we found that a solution of the *cis*-isomer in chloro-

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[*] An additional complication in the melting behaviour was indicated by differential thermal analyses: the onset of decomposition was in all samples at *ca.* 285 °C, although this was not usually observed in m.p. measurements. (In some samples, slight darkening occurred at this temperature.) Thus the material which actually melts is partly decomposed.

form when treated with triphenylphosphine became yellow as isomerisation proceeded. The electronic spectra of solutions at equilibrium gave $K \simeq 0{\cdot}1$ at 25 °C. Electronic

$$cis + PPh_3 \rightleftharpoons trans + PPh_3 \qquad (1)$$

absorptions for the pure *cis*- and *trans*-isomers are given in Table 2, together with those reported earlier by Collamati and Furlani.[16]

TABLE 2

Electronic spectra of isomers of $[Pt(PPh_3)_2Cl_2]$

	This work		Ref. 16	
	λ/ nm	ε/ l mol^{-1} cm^{-1}	λ/ nm	ε/ l mol^{-1} cm^{-1}
cis	330	560	328	535
	277 (sh)	8 980	275 (sh)	8 750
	269 (sh)	11 000	267 (sh)	10 100
	259	14 030		
trans	320 (sh)	1 100	320 (sh)	1 600
	284	27 500	283	27 600
	262	1 550	260	1 660

Preparation of trans-$[Pt(PPh_3)_2Cl_2]$.—Such catalysed isomerisations as the above were first used preparatively by Chatt and Wilkins.[20] On concentration of the isomerised yellow solution, without removal of triphenylphosphine catalyst, the less-soluble *cis*-isomer crystallised pure (at least in chloroform, dichloromethane,* and benzene). The equilibrium could however be quenched by removal of the excess of phosphine, as in parallel cases,[20] by addition of the dimer *trans*-$[(Ph_3P)ClPt(\mu\text{-}Cl)_2PtCl(PPh_3)]$,[21] and the *cis*- and *trans*-isomers separated by known methods (see Experimental section) to give a low yield of the *trans*-isomer.

In some of our samples of *cis*-$[Pt(PPh_3)_2Cl_2]$, made by methods (*a*) (*i*) [3] and (*iii*) [12] the presence of small quantities of *trans*-isomer were indicated by a ν(Pt–Cl) band at 345 cm^{-1}. This suggests either that some isomerisation occurs in ethanol–water (although the solubility in this solvent was very low indeed) or that both *cis*- and *trans*-isomers are formed in the reaction. Similarly, by careful working-up of the product of the fusion of triphenylphosphine with platinum(II) chloride, we isolated up to 20% of pure *trans*-isomer.

Since the quenching of the *cis–trans*-equilibrium occurs because of bridge fission, $2PPh_3 + [(Ph_3P)ClPt(\mu\text{-}Cl)_2PtCl(PPh_3)] \longrightarrow 2[Pt(PPh_3)_2Cl_2]$, the question arises: which isomer, *cis* or *trans*, is formed as product? The reaction of the *trans*-dimer with *p*-toluidine gave a *trans*-monomer,[21] while with carbon monoxide the product was *cis*.[22] We found that direct reaction between stoicheiometric quantities of PPh_3 and *trans*-$[(Ph_3P)ClPt(\mu\text{-}Cl)_2PtCl(PPh_3)]$ in benzene gave *trans*-$[Pt(PPh_3)_2Cl_2]$ in 100% yield.

DISCUSSION

Complexes containing triaryl-phosphines and -arsines are distinctly prone to polymorphism and solvation. Presumably, because of the phenyl groups, a number of almost isoenergetic lattices exist distinguished only by the detailed features of the intermolecular packing. Taking *cis*-$[Pt(PPh_3)_2I_2]$ as an example, Malatesta and Cariello obtained [11] a red form from hot xylene but a yellow-orange form (m.p. 285 °C) from colder xylene. Haake and Masten crystallised [7] the same complex from chloroform, obtaining a yellow powder (m.p. 303—304 °C) and, from the filtrate, orange prisms (m.p. 314—316 °C). These forms are presumably polymorphs or adducts. Similarly, as referred to in the Introduction, the remarkable *trans*-$[Pt(PPh_3)_2(H)Cl]$ exists [18] in at least three unsolvated forms and also yields numerous adducts. The present work simply places *cis*-$[Pt(PPh_3)_2Cl_2]$, already known [15] to give an adduct from its solution in sulphur dioxide, in this context.

Such polymorphism or solvation may also be responsible for discrepant descriptions of other similar compounds. Recorded m.p.s for *cis*-$[Pt(PPh_3)_2Br_2]$ have a wide range: (*i*) from [8] $[(Ph_3P)_2Pt(C_2Cl_4)] + Br_2$ in benzene–hexane, 294 °C (decomp.); (*ii*) from [11] $[Pt(PPh_3)_4] + Br_2$, 300 °C (decomp.); and (*iii*) $[Pt(PPh_3)_4] + CBrCl_3$, recrystallised from CH_2Cl_2–MeOH, 308 °C (decomp.).[8] Similarly, for $[Pt(AsPh_3)_2Cl_2]$; (*i*) from [11] $K_2[PtCl_4] + AsPh_3$ heated under reflux in xylene, 278 °C (this product was soluble in benzene and chloroform); (*ii*) from [12a] $PtCl_2$ + molten $AsPh_3$, 292 °C; and (*iii*) when Jensen first made this complex he described [3] a benzene-insoluble unsolvated *cis*-complex (decomp. *ca.* 300 °C), which on boiling with chloroform gave chloroform-containing crystals (soluble in benzene) said to contain the *trans*-isomer (decomp. *ca.* 300 °C). The vibrational spectrum of the *cis*-isomer only has been reported [23] [ν(Pt–Cl) at 320 and 292 cm^{-1}].

Clearly, a full account of the properties of these complexes $[ML_2X_2]$ requires that the possibility of solvation and/or polymorphism be considered. Since the i.r. spectra are basically that of co-ordinated triphenylphosphine or -arsine, they usually show little variation with crystal form, and the best fingerprint may be the *X*-ray powder picture (*cf.* Table 1 and the Figure). The present work, besides giving a convenient and quantitative method of preparation of *trans*-$[Pt(PPh_3)_2Cl_2]$, also brings the reaction of carbon tetrachloride with tetrakis(triphenylphosphine)platinum(0) back into line with most other reactions of perchloroalkanes and reduced complexes of metals, amongst which are (2)—(4). While

$$[Pt(PPh_3)_4] + C_2Cl_6 \longrightarrow [Pt(PPh_3)_2Cl_2] \text{ (ref. 8)} \qquad (2)$$

$$[(Et_3P)_2Rh(CO)Cl] + CCl_4 \longrightarrow [(Et_3P)_2Rh(CO)Cl_3] \text{ (ref. 24)} \qquad (3)$$

$$[(Et_3P)_2Pt(H)Cl] + CCl_4 \longrightarrow [(Et_3P)_2PtCl_2] \text{ (ref. 17)} \qquad (4)$$

the trichloromethyl ligand is certainly well known, as in $[Hg(CCl_3)_2]$,[25] it seems that platinum(II) complexes with it remain to be synthesised.

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* Although the *trans*-isomer dissolved only slowly in dichloromethane, it is the *cis*-isomer which is obtained by crystallisation from the equilibrium solution.

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EXPERIMENTAL

M.p.s were recorded using m.p. tubes in a heated metal block. I.r. spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer as Nujol mulls between caesium iodide plates. Electronic spectra were recorded on a Beckman DK-2 ratio recording spectrophotometer in 1 cm quartz cells. *X*-Ray powder photographs were taken with a Guinier–de Wolff camera using Cu-K_α radiation.

The complexes $K_2[PtCl_4]$ and $PtCl_2$ were supplied by Heraeus GMBH (Hanau). All solvents used in preparations were analytically pure reagent grade (E. Merck) and were used as supplied with the exception of *NN*-dimethylformamide (dmf) which was freshly distilled. For the measurement of electronic spectra, spectroscopic-grade chloroform was used. Triphenylphosphine (Merck) was freshly crystallised from benzene. Tetrakis(triphenylphosphine)platinum(0) was prepared by the method of Ugo *et al.*[19]

Di-μ-chloro-bis[chloro(triphenylphosphine)platinum(II)] was prepared by the method of Smithies *et al.*[21]

cis-*Dichlorobis(triphenylphosphine)platinum*(II).— The letters for the various preparations are used as a code in the Introduction.

(1) Unsolvated form: (*a*) (*i*) Jensen's method.[3] The complex $K_2[PtCl_4]$ (0·7 g) in water (10 cm^3) and PPh_3 (0·15 g) in ethanol (10 cm^3) were shaken at room temperature for 24 h and the precipitated white product collected and washed with cold water, ethanol, and diethyl ether. Alternatively, the same reagents were boiled for 1 h and the filtered product washed with the hot solvents.[10]

(*a*) (*ii*) *Malatesta's method.*[10] The complex $K_2[PtCl_4]$ (0·275 g) and PPh_3 (0·5 g) were heated under reflux in xylene (25 cm^3) for 6 h and the precipitated product filtered off and washed with hexane and diethyl ether.

(*a*) (*iii*) *Melt method.*[12] $PtCl_2$ (0·36 g) Was stirred with molten PPh_3 (2·0 g) at 85—90 °C for 15 min. After cooling, the resulting solid mass was extracted with dichloromethane. Addition of diethyl ether to the CH_2Cl_2 solution resulted in a white precipitate which was filtered off and washed with diethyl ether.

(*b*) (*i*) *From tetrakis(triphenylphosphine)platinum*(0).[8] Carbon tetrachloride (1·6 cm^3) was added to $[Pt(PPh_3)_4]$ (0·4 cm^3) in benzene (8 cm^3). The resulting white precipitate was stirred overnight in the mother liquor, and then filtered off and washed with hexane and diethyl ether.

The product from all the above reactions was the unsolvated *cis*-$[Pt(PPh_3)_2Cl_2]$, as was found on recrystallisation of all samples from CH_2Cl_2, m.p. 310—312 °C (Found: C, 54·5; H, 4·1. Calc. for $C_{36}H_{30}Cl_2P_2Pt$: C, 54·7; H, 3·8%).

(2) *Chloroform adduct.* Recrystallisation of all samples from $CHCl_3$ gave *cis*-$[Pt(PPh_3)_2Cl_2],CHCl_3$. Samples were washed with hexane and diethyl ether (Found: C, 48·3; H, 3·6. Calc. for $C_{37}H_{31}Cl_5P_2Pt$: C, 48·8; H, 3·4%).

(d) *dmf Adduct:* (*a*) (*iv*).[13] Following a report [13] that a heated solution in dmf of hexachloroplatinic(IV) acid reacts with triphenylphosphine to give *cis*-dichlorobis(triphenylphosphine)platinum(II), $H_2PtCl_6,6H_2O$ (1·0 g) was heated under reflux in dmf (15 cm^3); after 5 min a substantial quantity of platinum metal had deposited. This was removed after 20 min under reflux and an excess of triphenylphosphine added which resulted in gas evolution and precipitation of a white product. The latter was collected and washed with methanol and diethyl ether.

The adduct 2 *cis*-$[Pt(PPh_3)_2Cl_2]$,dmf was also formed on recrystallisation of all forms from dmf, m.p. 303—304 °C (Found: C, 54·15; H, 4·40; N, 0·85. Calc. for $C_{75}H_{67}Cl_4NOP_4Pt_2$: C, 54·45; H, 4·05; N, 0·85%).

trans-*Dichlorobis(triphenylphosphine)platinum*(II).— (1) *From* cis–trans-*equilibrium mixture.* The compound *cis*-$[Pt(PPh_3)_2Cl_2]$ (9·22 g) was dissolved in $CHCl_3$ (50 cm^3) and PPh_3 (0·01 g) added. The reaction mixture was boiled for 1·5 h and $[(Ph_3P)ClPt(\mu\text{-}Cl)_2PtCl(PPh_3)]$ (0·03 g) added to absorb the phosphine. After being heated under reflux for a further 1·5 h, the reaction mixture was filtered and evaporated to dryness under reduced pressure. The solid residue was extracted with benzene to give a yellow solution and a white solid (*cis*-isomer) remained. After addition of methanol to the benzene solution, 5% of the pure *trans*-isomer was isolated.

(2) *Adaptation of the melt method* [(*a*) (*iii*)] *above.* $PtCl_2$ (0·36 g) Was stirred with molten PPh_3 (2·0 g) at 85—90 °C for 15 min. After cooling, ice-cold CH_2Cl_2 (10 cm^3) was added and the mixture vigorously stirred for 2 min. The so-formed cream-yellow suspension was decanted free of unreacted $PtCl_2$, filtered off, and washed with cold CH_2Cl_2 (4 × 10 cm^3) to remove the *cis*-isomer and excess of phosphine. After drying at the pump, the cream-yellow solid was recrystallised from benzene to give bright yellow crystals of the pure *trans*-isomer in 20% yield. (Addition of diethyl ether to the CH_2Cl_2 filtrate and washings gave 70% of the white *cis*-isomer.) Attempts to obtain the product from the resolidified melt by adding other reagents, *e.g.* benzene, diethyl ether, ethanol, or chloroform, were unsuccessful.

(d) *From the dimer.* The complex *trans*-$[(Ph_3P)ClPt(\mu\text{-}Cl)_2(PPh_3)]$ (0·2 mmol) was suspended in benzene (*ca.* 20 cm^3) and a solution of PPh_3 (0·2 mmol) in benzene (*ca.* 10 cm^3) was added dropwise over *ca.* 3 h with stirring. During the course of addition, the suspended dimer was slowly consumed to give a clear yellow solution. Addition of methanol gave a quantitative yield of yellow *trans*-$[Pt(PPh_3)_2Cl_2]$, m.p. 306—308 °C (Found: C, 54·2; H, 4·3. Calc. for $C_{36}H_{30}Cl_2P_2Pt$: C, 54·7; H, 3·8%).

Desolvation.—(1) Samples of *cis*-$[Pt(PPh_3)_2Cl_2]$, *cis*-$[Pt(PPh_3)_2Cl_2],CHCl_3$, and 2 *cis*-$[Pt(PPh_3)_2Cl_2]$,dmf were heated in a drying oven at 180 °C for 7 h. The products, as identified by i.r. spectra and *X*-ray powder patterns, were in all cases the unsolvated complex.

(2) The complex *cis*-$[Pt(PPh_3)_2Cl_2],CHCl_3$ (70 mg) was heated in an oil-bath at 100—120 °C for 15 min under vacuum (10^{-4} mmHg). Volatile products were collected in a gas i.r. cell (NaCl windows). The cooled solid residue was identified by its *X*-ray powder pattern as the unsolvated form. The i.r. spectrum of the collected gas showed it to be $CHCl_3$.

(3) The complex *cis*-$[Pt(PPh_3)_2Cl_2],CHCl_3$ (7 mg) was pumped at 25 °C in a 10^{-4} mmHg vacuum. After 12 h only 10% of the theoretical chloroform quantity had been lost and the i.r. spectrum and *X*-ray powder pattern showed the remaining solid to be unchanged adduct.

cis–trans-*Equilibrium.*—Equal quantities (22 mg) of the pure *cis*- and *trans*-isomers were each dissolved in $CHCl_3$ (50 cm^3) and PPh_3 (0·26 mg) was added to each solution. [At the concentrations used to measure the electronic spectra, this quantity of PPh_3 afforded no measurable absorption at the wavelength (280 nm) used.] The two solutions were heated on a water-bath and allowed to cool and remade up to 50 cm^3 with $CHCl_3$ every 0·5 h when u.v. spectra of 1 cm^3 aliquot portions (diluted 10 times) were run. After 2·5 h, the spectra of both solutions were the same (and remained unaffected by further heating), giving a *cis* : *trans* ratio of *ca.* 8 : 1. [The error in the equilibrium constant ($K = 1{\cdot}1 \pm 0{\cdot}2$) is attributed to the inaccuracy in maintaining the concentrations due to the repeated necessity of remaking the solution up to 50 cm^3.]

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