387. *Metal Carbonyl Compounds. Part III.* Reactions of Monocarbonyl Complexes of Platinum*(II).

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The reaction of neutral monodentate ligands with the dimeric carbonyl halides of platinum gives rise to compounds $\{Pt(CO)LX_2\}$ whose stabilities and configurations are generally dependent on the *trans*-effect of the ligands introduced. Very weakly π-bonding ligands (ammonia or *p*-toluidine) in excess do not easily expel carbon monoxide, but addition of excess of the more strongly bonding ligands (pyridine or phosphorus trichloride) results in immediate evolution of carbon monoxide, even at low temperatures. The introduction of strongly double-bonding bidentate ligands such as *o*-phenylenebisdimethylarsine results in the rapid elimination of carbon monoxide, though the transitory existence of the entity containing both ligands can be demonstrated.

Reaction mechanisms are discussed, on the basis of which the general behaviour of halogen-bridged platinum compounds may be explained.

IT is now generally agreed that "*trans*-effect" in Pt(II) complexes is largely determined by the character of the bond between the ligand and the platinum atom.[1-3] With ligands such as carbon monoxide, ethylene, phosphorus trifluoride, and, perhaps to a smaller extent, phosphorus trichloride, π-bonding (back-co-ordination between the filled *d*-orbitals of platinum and the unfilled *p*- or *d*-orbitals of the co-ordinating atom) accounts for much of the bond strength.[2, 3] In ligands such as mono- or di-tertiary arsines, these π-bonds exist in addition to stronger σ-bonds. The *d*-orbitals responsible for this co-ordination have been qualitatively represented by Chatt and Duncanson.[3] In the case of redistribution of overlap caused by competition for π-character by two ligands *trans* to each other, labilisation of the ligands not stabilised by strong σ-overlap will occur. Accordingly, we may expect arsines and other strong "double-bonding" † ligands to labilise ligands such as carbon monoxide and ethylene, but not to be labilised to any great extent by them.

The purpose of this section of the investigation has been to study the action of ligands possessing varying degrees of "*trans*-effect" on the dimeric carbonyl platinous halides described in Part I. The probable schemes of reaction are outlined below (L = monodentate ligand; L–L = bidentate ligand; X = Cl, Br, or I).

Where L is ammonia, compounds (II), (III), and (IV) have been isolated.[4, 5] The compounds (II; L = *p*-toluidine, pyridine, or methyldiphenylarsine) are relatively stable to heat but sensitive to moisture; of these the *p*-toluidine compound is by far the most stable to heat and moisture, and also in the presence of excess of ligand. Isolation of the salt (III) was not possible in the case of pyridine and methyldiphenylarsine. The action

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* Parts I and II (*J.*, 1956, 1860, 2879) were published under a different general title.

† The term "double-bonding ligand" indicates a ligand which possesses a strong σ-bond and also a strong π-bond. The terms "π-bonding ligand" and "σ-bonding ligand" refer to ligands which form bonds deriving their strength mainly from π-bonds and σ-bonds respectively. This distinction between the σ-bond strengths of ligands possessing π-bonds in addition is important in discussions of stabilities and of directive effects in complex compounds. Thus the "*trans*-directing" properties of the ligands CO, PCl_3, PF_3, C_2H_4, methyldiphenylarsine, and *o*-phenylenebisdimethylarsine ("Diarsine") are all fairly high, but the relative stabilities of platinum(II) compounds involving these ligands differ markedly with respect to heat, moisture, and excess of ligand.

[1] Emeléus and Anderson, "Modern Aspects of Inorganic Chemistry," Routledge and Kegan Paul, London, 1952, pp. 413, 418.

[2] Chatt and Williams, *J.*, 1951, 3061.

[3] Chatt and Duncanson, *J.*, 1953, 2939.

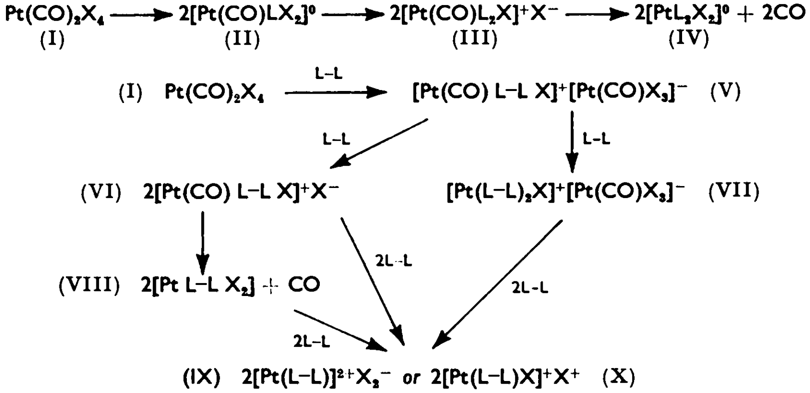
[4] Schutzenberger, *Bull. Soc. chim.*, 1870, **14**, 97.

[5] Gelman, *Ann. Inst. Plat.*, 1945, **18**, 50.

of excess of these ligands on compound (II) immediately liberated carbon monoxide and formed compound (IV) even below −30°.

In view of the foregoing, phosphorus trichloride would also be expected to form a compound of type (II). Emeléus and Anderson [1] reported that the action of two mols. of phosphorus trichloride removed all the carbon monoxide from the dimer. The present work supports this, but by the action of one mol. it is possible to isolate very unstable carbonyl-containing compounds (II), the bromide and iodide being isolated in the pure state. The chloride could not be freed from impurity but a comparison of its infrared spectrum with those of the bromide and iodide strongly supported its identity (see Part I).

The action of phosphorus trichloride was studied conductometrically in dry acetone at 0°. After addition of more than one mol. per platinum atom, carbon monoxide was evolved. No evidence of even transitory salt formation was observed. Pyridine behaved in the same way.



Dipyridyl forms compounds (V) and (VI) which are stable in dry air. In the presence of moisture and excess of ligand, compounds (VIII) and (IX) respectively are formed with the liberation of carbon monoxide. The action of *o*-phenanthroline is analogous.

When *o*-phenylenebisdimethylarsine (" Diarsine ") was used, no carbonyl-containing entities could be isolated but compounds with the 5-covalent cation $[Pt(Diarsine)_2X]^+$ were always obtained, even at −50°. The labilisation of carbon monoxide due to the strong " double-bonding " of the diarsine is such that the intermediate compound (V) must be very unstable. Colour changes during the reaction suggested its formation and this was supported by conductivity titrations. Table 1 shows the C–O stretching frequencies of substances isolated in attempts to prepare diarsine carbonyl compounds. No absorption indicative of carbon monoxide in a co-ordination entity containing diarsine was obtained.

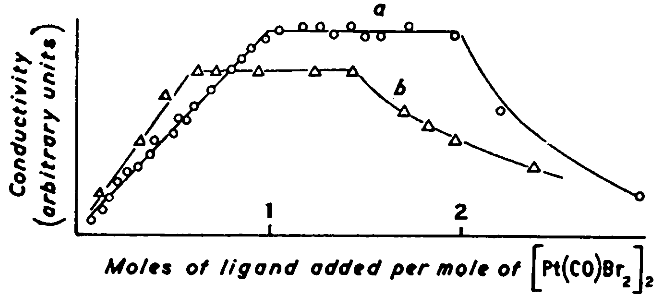
TABLE 1.

Starting material	Frequency (cm.$^{-1}$) of absorption peak after reaction with diarsine	Assignments [a]
$[Pt(CO)Cl_2]_2$	2105	$[Pt(CO)Cl_3]^-$
$[Pt(CO)Br_2]_2$	2092	$[Pt(CO)Br_3]^-$
$[Pt(CO)I_2]_2$	2082	$[Pt(CO)I_3]^-$

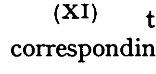
[a] Irving and Magnusson, *J.*, 1956, 1860.

As Diarsine was added to a solution of $(PtCOBr_2)_2$ in dry acetone at 0° (Fig. *a*), the conductivity of the solution increased linearly, reaching a maximum after the addition of one mole of ligand per mole of dimer. This point corresponds to the formation of compound (V). Addition of more ligand resulted in slow evolution of carbon monoxide but did not greatly affect the conductivity until 2 mol. had been added, after which the conductivity slowly decreased. This decrease was accompanied by the further evolution of carbon monoxide and precipitation of the salt (X). At room temperatures, the conductivity curve followed the same trend but the salt (X) began to be precipitated well before 2 equivs. of ligand had been added (Fig. *b*). The sequence (I)-(V)-(VII)-(X) represents a possible course of reactions on the basis of the above evidence. If the initial attack is in the CO-Pt direction rather than along the bridging halogen-Pt bond, carbon monoxide would be given off immediately irrespective of temperature. The compounds (X) were identified with those obtained by Harris, Nyholm, and Stephenson.[6] The short Pt-As bond distance (2·38 Å) noted by these authors, and their postulate of double-bonding, explain the strong labilising properties attributed to Diarsine in the reactions described above. The compounds (VII) are quite stable and may be isolated by the action of Diarsine on (I) or on the ions $[Pt(CO)X]_3^-$. The alternative scheme (I)-(V)-(VI)-X is thus eliminated.

It is well known that addition of potassium cyanide to any platinum carbonyl compound results in the evolution of carbon monoxide with the formation of the tetracyano-complex. Mylius and Foerster [7] reported that the addition of aqueous potassium cyanide to the hydrochloric acid solution of $[Pt(CO)Cl_2]_2$ produced a colour change suggesting the formation of intermediates $Pt(CO)(CN)_2$ or $K[Pt(CO)(CN)_3]$ before formation of $K_2Pt(CN)_4$, but they could not isolate these compounds. We attempted to isolate a carbonyl cyanide compound at temperatures down to −40°, but in all cases evolution of carbon monoxide was immediate and the compound isolated was $K_2Pt(CN)_4$.



Properties of the Derivatives (II).—Physical properties of the co-ordination compounds $[Pt(AsMePh_2)(CO)X_2]$ point to the *cis*-configuration. These compounds are comparatively stable, paler than their *p*-toluidine analogues, and not appreciably soluble in non-polar solvents. Further, their C–O stretching frequencies are not far removed from those of the entities $[Pt(CO)X_3]^-$, whereas C–O frequencies for the *trans*-[Pt(CO) *p*-tolX$_2$] are higher by about 30 cm.$^{-1}$ (X = Cl, Br, and I). Further support for this configuration is supplied by the fact that the C–O stretching frequencies of $[Pt(AsMePh_2)(CO)Cl_2]$ and of the compound believed to be $[Pt(AsMePh_2)_2(CO)Cl]^+Cl^-$ [*trans*-di(methyldiphenylarsine)carbonylchloroplatinum(II) chloride] are almost identical. Chatt and Wilkins [8] have shown that the *cis*-forms of the compounds $PtLL'X_2$ are more stable than the *trans*-forms when both L and L′ have appreciable *trans*-effect, and the instability of the entity (XI) is in agreement with this. *cis*-Planar compounds containing two double-bonding ligands are expected to be more stable than the corresponding *trans*-isomers.[9-11]



(XI)

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[6] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.
[7] Mylius and Foerster, *Ber.*, 1891, **24**, 2426; Foerster, *ibid.*, p. 3751.
[8] Chatt and Wilkins, *J.*, 1952, 273.
[9] Jaffe, *J. Phys. Chem.*, 1954, **58**, 185.
[10] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.
[11] Chatt and Wilkins, *J.*, 1952, 4300.

Phosphorus trichloride has empty 3*d*-orbitals available for π-bonding and should have a similar *trans*-effect to the tertiary arsines and phosphines. It might also be expected to form stable compounds of *cis*-configuration. However, its compounds are very unstable, quite soluble in non-polar solvents, have C–O frequencies 30—40 cm.$^{-1}$ higher than those for compounds with CO *trans*- to halogen {*e.g.*, $[Pt(CO)X_3]^-$ or *cis*-$Pt(CO)LX_2$}, and are more brightly coloured. This suggests *trans*-configuration.

Attempts to prepare the *trans*-arsine compounds $Pt(AsMePh_2)(CO)X_2$ by the action of methyldiphenylarsine on the ion $[Pt(CO)X_3]^-$ were unsuccessful, carbon monoxide being evolved on all occasions. Also, attempted substitution by the arsine in hot acetone solutions of the dimers $[Pt(CO)X_2]_2$ resulted in decomposition, presumably because of dissociation. On the other hand, ligands less strongly *trans*-labilising than the arsine readily form *trans*-compounds in the reaction with the single entity $[Pt(CO)X_3]^-$. This is paralleled by the action of amines on Zeise's salt.[12] Indeed, pyridinium carbonyltri-iodoplatinite [13] forms the compound *trans*-pyridinecarbonyldi-iodoplatinum(II) on storage. It is apparent that a different mechanism is involved in the formation of derivatives by bridge fission of the dimeric compounds from that in the reaction with the ion $[PtLX_3]^-$, at least in the case where the directing ligand L and the entering ligand L′ are both of fairly high *trans*-effect.

Discussion of Mechanisms.—Previous discussions (for references see Chatt [14]) give no detail, and *trans*-bridge fission is the only possibility considered. However, the formation of *cis*- or *trans*-compounds, or equilibrium mixtures of both, from halogen-bridged dimers $[PtLX_2]_2$ by the action of any neutral ligand L′ will probably involve one of the following mechanisms: (i) Initial formation of *trans*-compounds by *trans*-bridge fission, with subsequent possible isomerisation to *cis*. (ii) Direct formation of *trans*- or *cis*-compounds after fission of the *trans*- or *cis*-bridges, respectively. (iii) Formation of intermediates from which the *cis*- or *trans*-products may result, depending on the nature of the orbitals available to the ligands L and L′.

Case (i) probably explains the formation of Rosenheim and Levy's *cis*- and *trans*-compounds,[15] but on this basis the same products would be obtained from the monodentate entity.

Determinations of structure by *X*-ray methods [16, 17] indicate that application of case (ii) must be restricted when the directing ligand L has a high *trans*-effect, owing to the appreciable *trans*-bond weakening in dimeric as well as monomeric compounds.

Case (iii) is more in agreement with recent theories of substitution [6, 18-21] as well as chemical evidence, and involves successive addition of the entering ligands L′ to the " fifth positions " of the configurations. Displacement of the bridge atoms (probably *trans*-displacement for the case where L has a high *trans*-effect) leads to approximately tetrahedral 4-covalent entities from which the *trans*- (normally the more stable) or the *cis*-square planar derivatives (favoured when both L and L′ are π-bonding ligands) may result. The distinction between this mechanism and that of case (i) lies, of course, in the fact that the case (i) rearrangement is the normally slow " isomerisation," whereas that of case (iii) would be expected to be fast. Further, although monomeric substitution will proceed through a somewhat similar initial transition state, the square planar configuration is more nearly retained throughout, resulting in the replacement of the *one* weakly bonded atom,[17] whereas the two weak bridges [16] in the dimer permit the severe

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[12] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.
[13] Irving and Magnusson, *J.*, 1956, 1860.
[14] Chatt, *J.*, 1951, 652.
[15] Rosenheim and Levy, *Z. anorg. Chem.*, 1905, **43**, 35.
[16] Dempsey and Baenziger, *J. Amer. Chem. Soc.*, 1955, **77**, 4984; Holden and Baenziger, *ibid.*, p. 4987.
[17] Mellor and Wunderlich, *Acta Cryst.*, 1954, **7**, 130; 1955, **8**, 57.
[18] Nyholm, *J. Roy. Inst. Chem.*, 1956, **80**, 328.
[19] Chatt, Duncanson, and Venanzi, *Chem. and Ind.*, 1955, 749; *J.*, 1955, 4456.
[20] Cardwell, *Chem. and Ind.*, 1955, 422.
[21] Ingold, *Chem. Soc. Special Publ.* No. 1, 1954, p. 10.

distortion of the entities after bridge fission. Experimentally, for L = CO, all reactions are fast whether *cis*- or *trans*-products result, whereas normal *cis*-substitution is slow. The possibility that the ligands L′ " change places " with the bridging atoms before separation of the entities (*i.e.*, with the halogens occupying the fifth positions), and that the *cis*- or *trans*-products result without deformation of the plane, by the bonding of the ligands to the most favourable sites on either platinum atom, has been suggested, but the scheme is open to criticism.

TABLE 2.

	Reaction with the dimers $[Pt(CO)X_2]_2$			
Ligand	Products	Stability in air	Stability to excess ligand	Reaction with the ions $[Pt(CO)X_3]^-$
p-Toluidine[13]	(II) (*trans*)	Fairly stable	CO slowly evolved	As with the dimers
Aniline[23] *m*-Nitroaniline[23]	(II) *trans*)	,,	,, ,,	As with the dimers
Ammonia[4]	(II) (*trans*)	,,	(III), (IV) easily formed	As with the dimers[24, 4]
Pyridine	(II) (*trans*)	,,	Immediate evolution of CO; $\longrightarrow$ (IV)	As with the dimers[24, 4, 5]
$AsMePh_2$[13]	(II) (*cis*)	,,	Immediate evolution of CO; $\longrightarrow$ (IV)	Immediate evolution of CO
PCl_3	(II) (*trans*)	Very unstable	Immediate evolution of CO; $\longrightarrow$ (IV)	— —
Carbon monoxide[2]	(II) (*cis*)	Unstable	—	—
	$Pt(CO)_2Cl_2$	Stable in very dry conditions		
Ethylene[4]	(II) (*cis*)	Unstable	—	—
Dipyridyl[13] *o*-Phenanthroline	(V), (VI)	Fairly stable	Strong action gives (VIII), (IX)	As with the dimers
$o\text{-}C_6H_4(AsMe_2)_2$	(V), (VII), (X)	Transitory existence only	Almost immediate precipitation of (X)	As with the dimers
Cl^-	$[Pt(CO)Cl_3]^-$	Fairly stable as salt of organic cations Stable in solution only when excess Cl^- present		
Br^-	$[Pt(CO)Br_3]^-$	Ditto		
I^-	$[Pt(CO)I_3]^-$	More stable to moisture, less stable to heat, than above		
CNS^-	$[Pt(CO)(CNS)_3]^- \longrightarrow [Pt(CO)(CNS)_4]^{=}$	Unstable		
CN^-	$K_2Pt(CN)_4$	No carbonyl compounds		

With bidentate ligands there is no doubt of the configuration of the products. Previous discussions of such reactions are summarised by Chatt.[14] Attack must take place in the fifth position with the subsequent formation of 5-covalent intermediates. (It should be noted that dipyridyl, *o*-phenanthroline, Diarsine, and other bidentate ligands cannot co-ordinate through one point alone,[22] and any mechanism involving simultaneous attack of the two platinum atoms by one ligand is untenable because of steric effects, for these three compounds at least.) If L′–L′ is a strongly double-bonding ligand such as Diarsine, the intermediate will be unstable. Reaction of bidentate ligands with the ions $[Pt(CO)X_3]^-$ will obviously produce the same results as with the dimers.

In Table 2 the products of reaction of ligands with the platinum carbonyl halides are tabulated in the approximate order of increasing *trans*-effect of the ligands.

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[22] Quagliano and Schubert, *Chem. Rev.*, 1952, **50**, 201.

EXPERIMENTAL

Attempted Preparation of Carbonyl-containing Diarsine Compounds.—*Chlorine compounds.* *o*-Phenylenebisdimethylarsine ("Diarsine") (0·20 g.) in benzene (30 ml.) was added to dicarbonyldichloro-μμ'-dichlorodiplatinum(II) (0·21 g.) in benzene (100 ml.). An immediate yellow-green precipitate was obtained which quickly changed to a deeper yellow. Metallic platinum was slowly precipitated, indicating that not all the dimer had reacted. When 4 moles of diarsine per platinum atom were used precipitation of the yellow derivative was quantitative, no metallic platinum being obtained after the reaction had occurred. The identical yellow precipitate and accompanying colour change were obtained when pyridinium carbonyltrichloroplatinite was used instead of the dimer. The experiment was repeated several times with both starting materials at temperatures down to $-50°$ in the case of the $[Pt(CO)Cl_3]^-$ ion (dissolved in acetone), but it was not possible to isolate any carbonyl-containing entity for any period of time.

Bromine compounds. Diarsine (0·102 g.) in benzene (30 ml.) was added to dicarbonyldibromo-μμ'-dibromodiplatinum(II) (0·138 g.) in benzene (100 ml.). An immediate yellow-orange precipitate quickly gave off bubbles of carbon monoxide, changing colour slightly. The substance dissolved easily in nitrobenzene, and in a M/1000-solution its conductivity was 30·3 mho (calculated on a molecular weight of 1338 for the compound $[Pt(Diarsine)_2Br]^+[Pt(CO)Br_3]^-$). The infrared spectrum of the compound pointed to the presence of the ion $[Pt(CO)Br_3]^-$, the absorption being at 2092 ± 2 cm.$^{-1}$ for a number of experiments. Addition of two more mols. of Diarsine (0·102 g.) produced the yellow substance later shown to be di-(*o*-phenylenebisdimethylarsine)bromoplatinum(II) bromide. Low-temperature reactions with the dimer and the carbonyltribromoplatinite ion again resulted in slower colour changes, but no compounds could be isolated.

Iodine compounds. Reactions with Diarsine yielded results analogous to those described above. The carbonyl-containing complex (assumed to be $[Pt(Diarsine)_2I]^+[Pt(CO)I_3]^-$) absorbed sharply in the infrared region at 2085 cm.$^{-1}$, and further action on this compound produced the 5-covalent salt described below.

A 1 mm. liquid cell with rock-salt windows, so designed as to be easily filled or flushed with solvent, was half-filled with 2% carbon tetrachloride solutions of the respective halogen-bridged carbonyl dimers and cooled to its freezing point. After the cell had been quickly transferred to the cell-holder in the beam of the infrared spectrometer, a solution of Diarsine was added from the filling micropipette (less than one mole of Diarsine per platinum atom being added), and the region 2200—2000 cm.$^{-1}$ quickly scanned. In several instances weak bands were obtained which disappeared after a short time, but in no case were these considered adequate for any serious attempt at assignment.

Di-(o*-phenylenebisdimethylarsine)chloroplatinum*(II) *Chloride.*—Diarsine in acetone was added to a solution of platinous carbonyl chloride in concentrated hydrochloric acid until the final yellow precipitate ceased to be formed. The compound may also be prepared by addition of Diarsine in benzene to a benzene solution of the platinous carbonyl chloride dimer. In M/1000-nitrobenzene solution the conductivity was 28·3 mho (Found: C, 28·3; H, 3·8; Pt, 23·4. Calc. for $C_{20}H_{32}As_4Cl_2Pt$: C, 28·6; H, 3·85; Pt, 23·3%).

Di-(o*-phenylenebisdimethylarsine)bromoplatinum*(II) *Bromide.*—Diarsine (0·35 g.) in benzene (100 ml.) was added to platinous carbonyl bromide (0·200 g.) in benzene (100 ml.), and the resulting yellow precipitate was filtered off and washed with benzene. In M/1000-nitrobenzene solution the conductivity was 32·0 mhos (Found: C, 25·6; H, 3·3. Calc. for $C_{20}H_{32}As_4Br_2Pt$: C, 25·9; H, 3·5%).

Di-(o*-phenylenebisdimethylarsine)iodoplatinum*(II) *Iodide.*—Diarsine (0·50 g.) in benzene (50 ml.) was added to platinous carbonyl iodide (0·30 g.) in benzene (100 ml.). The yellow precipitate was filtered off, washed with benzene, and dried under vacuum (yield approx. 0·7 g.). In M/1000-nitrobenzene solution the conductivity was 28·2 mhos (Found: C, 23·7; H, 3·3; Pt, 20·1. Calc. for $C_{20}H_{32}As_4I_2Pt$: C, 23·5; H, 3·1; Pt, 19·1%).

Attempted Preparation of (*Trichlorophosphine*)*carbonyldichloroplatinum*(II).—Phosphorus trichloride (0·20 g.) in carbon tetrachloride (50 ml.) was added to platinous carbonyl chloride (0·29 g.) in carbon tetrachloride (100 ml.). No colour change was observed. Evaporation under vacuum merely decomposed the substance. It was not possible to obtain a pure substance but its infrared spectrum exhibited a sharp absorption at 2135 cm.$^{-1}$ and indicated the possibility that carbon monoxide had been co-ordinated in a configuration such as has been represented.

(Trichlorophosphine)carbonyldibromoplatinum(II).—Phosphorus trichloride (0·045 g.) in carbon tetrachloride (50 ml.) was added to platinous carbonyl bromide (0·25 g.) in carbon tetrachloride (100 ml.). On evaporation to about 2 ml. and cooling overnight in dry conditions, brown-orange crystals of *(trichlorophosphine)carbonyldibromoplatinum*(II) were obtained (Found: Pt, 38·0. $COCl_3Br_2PPt$ requires Pt, 37·48%). Decomposition was soon apparent, even when the compound was kept over phosphoric oxide.

(Trichlorophosphine)carbonyldi-iodoplatinum(II).—Phosphorus trichloride (0·043 g.) in benzene (100 ml.) and a little acetone (20 ml.) was added to platinous carbonyl iodide (0·168 g.) in benzene (50 ml.). The colour changed immediately from orange to yellow. On evaporation a red oil was obtained which was crystallised with difficulty. The *compound* was non-conducting in M/1000-nitrobenzene solution (Found: Pt, 32·2. $COCl_3I_2PPt$ requires Pt, 31·78%).

Pyridinecarbonyldi-iodoplatinum(II).—Pyridine (0·23 ml.) was added to platinous carbonyl iodide (1·30 g.) in benzene (150 ml.). The colour of the solution changed from red to orange, and, after concentration on the water-bath, yellow-orange crystals of the *compound* were deposited; it decomposed slowly in air and rather quickly in solutions left open to the atmosphere, and it was non-conducting in M/1000-nitrobenzene solution (Found: C, 13·4; H, 1·03; I, 45·7; Pt, 35·3. $C_6H_5ONI_2Pt$ requires C, 13·0; H, 0·9; I, 45·6; Pt, 35·2%). (C and H values are high because of some decomposition before analysis.)

Dipyridinedi-iodoplatinum(II).—This compound, m. p. 270°, was obtained as bright yellow needles on addition of excess of pyridine to the preceding compound. It was described by S. G. Hedin in 1887 but the publication (*Lunds. Arskr.*) was not available. The compound did not conduct electricity in M/1000-nitrobenzene (Found: Pt, 32·3. Calc. for $C_{10}H_{10}N_2I_2Pt$: Pt, 32·3%).

Di(methyldiphenylarsine)dichloroplatinum(II).—This compound was obtained as yellow-white needles by the action of excess of methyldiphenylarsine on methyldiphenylarsinecarbonyldichloroplatinum(II); it was non-conducting in M/1000-nitrobenzene solution and was probably the *cis*-form described by Nyholm [25] (Found: Pt, 25·5. Calc. for $C_{26}H_{26}Cl_2As_2Pt$: Pt, 25·8%).

Di(methyldiphenylarsine)di-iodoplatinum(II).—This compound was similarly obtained by use of the corresponding di-iodo-analogue; [13] recrystallisation from benzene afforded yellow needles (Found: Pt, 20·8. Calc. for $C_{26}H_{26}I_2As_2Pt$: Pt, 20·8%).

Attempted Preparation of trans-*Di(methyldiphenylarsine)carbonylchloroplatinum*(II) *Chloride*.—Many attempts were made to prepare this compound by the action of molar quantities of methyldiphenylarsine on *cis*-methyldiphenylarsinecarbonyldichloroplatinum(II), and by the action of 4 moles of the arsine on one of the chloride dimer, at temperatures down to −50°. In most cases carbon monoxide was evolved and *trans*-di(methyldiphenylarsine)dichloroplatinum(II) (which isomerises to the *cis*-form [25]) was obtained. In another attempt, *trans*-di(methyldiphenylarsine)dichloroplatinum(II) (*ca.* 1·0 g.) was kept above its m. p. (200—210°) for 45 min., during which carbon monoxide was bubbled through the melt. The resulting substance was ground, and its infrared spectrum examined, a band of medium strength being observed at 2105 cm.$^{-1}$ (as opposed to the C–O frequency of *cis*-methyldiphenylarsinecarbonyldichloroplatinum(II) of 2111 cm.$^{-1}$). The conductivity of the substance in M/1000-nitrobenzene solution (*M* being assumed to be 754) was approx. 10 mhos. It was not possible to separate the compounds present. These results were interpreted as indicating the presence of some *trans*-dimethyldiphenylarsine)carbonylchloroplatinum(II) chloride in the product.

Attempted Preparation of trans-*Methyldiphenylarsinecarbonyldichloroplatinum*(II).—Methyldiphenylarsine (0·18 g.) in benzene (20 ml.) was added to pyridinium carbonyltrichloroplatinite (0·15 g.) in benzene (30 ml.) and dry acetone (20 ml.). An immediate evolution of gas occurred, and the infrared spectrum of the substance obtained on evaporation showed no carbonyl absorption.

Attempted Preparation of trans-*Methyldiphenylarsinecarbonyl-bromo- and -iodo-platinum*(II).—Methyldiphenylarsine (0·12 g.) in benzene (30 ml.) was added to pyridinium carbonyltribromoplatinite (0·17 g.) in benzene (30 ml.) and acetone (10 ml.). That the evolution of carbon monoxide was quantitative was shown by the infrared spectrum, as in the previous case. A similar reaction took place with the analogous iodine compound.

Reactions of Bidentate Ligands with the Ions $[Pt(CO)X_3]^-$.—When dipyridyl and pyridinium carbonyltri-chloro-, -bromo-, and -iodo-platinite respectively in benzene and acetone were mixed in molar proportions, precipitates were obtained which on recrystallisation from acetone yielded compounds identical (infrared spectra and molar conductivities) with those obtained from that ligand with the corresponding carbonyl halide dimers.[13]

Reactions of Hot Acetone Solutions of the Dimers $[Pt(CO)Br_2]_2$ *and* $[Pt(CO)I_2]_2$.—Molar quantities of methyldiphenylarsine reacted with acetone solutions of the platinum carbonyl bromide and iodide dimers, resulting again in the complete evolution of carbon monoxide. No carbon monoxide-containing compounds were obtained from these solutions. Less strongly double-bonding ligands such as aniline and *p*-toluidine formed the usual *trans*-derivatives under these conditions. No attempt was made to perform this reaction with the corresponding chlorine compound, as it is immediately decomposed by acetone.[23]

Potassium Carbonyltrithiocyanatoplatinum(II).—Potassium thiocyanate (3·0 g.) in 5N-hydrochloric acid (50 ml.) was added to $[Pt(CO)Cl_2]_2$ (0·5 g.) in 5N-hydrochloric acid at 0°. On cooling to −30°, the mixture solidified and a precipitate was obtained on subsequent slow warming. This was filtered off at 0°, washed, and dried (Found: Pt, 44·9. Calc. for $C_4ON_3S_3KPt$: Pt, 44·7%).

When potassium thiocyanate was added to $[Pt(CO)Cl_2]_2$ in 5N-hydrochloric acid on a water-bath the solution became orange, then red, finally depositing a red precipitate. This substance was only slightly soluble in nitrobenzene, but its conductivity in dry acetone (60 mhos) indicated the presence of more than two ions (possibly three), though such results must be regarded with caution. The compound contained carbon monoxide and may have been $(NH_4)_2[Pt(CO)(CNS)_4]$ (Found: Pt, 40·4. Calc. for $C_5H_8ON_6S_4Pt$: Pt, 39·7%).

Attempted Preparation of a Cyanide Complex.—Potassium cyanide (6 ml. of a 1% solution was added to $[Pt(CO)Cl_2]_2$ (0·5 g.) in concentrated hydrochloric acid at −40°. There was immediate evolution of carbon monoxide and it was not possible to obtain any intermediate product. The striking colour change noted by Mylius and Foerster[7] was not observed. Potassium tetracyanoplatinite was obtained from the solution.

Conductometric Titrations.—Acetone for use as solvent in these titrations was freshly distilled after being dried ($CaCl_2$) under reflux. Conductivities were measured with a dip-type cell with platinum electrodes coated with platinum-black, and with a cell constant of 1·52 (referred to potassium chloride at 20°). A "Philoscope" conductivity bridge was used. The reaction vessel was immersed in a large beaker, containing acetone–solid carbon dioxide at approximately −5°. Diarsine, phosphorus trichloride, and pyridine were added in an acetone solution of appropriate concentration from a 10 ml. burette.

Infrared measurements were carried out on paraffin mulls of the solid compounds as described in Part I,[13] except where otherwise specified.

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