468. *Platinum*(0) *Compounds with Triarylphosphines and Analogous Ligands.*

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Some new derivatives of platinum in a zero oxidation state with triarylphosphines and -arsines and triaryl phosphites are described. Some of these compounds are co-ordinatively saturated, *i.e.*, of the type $Pt^0(PAr_3)_4$; others are unsaturated, of the type $Pt^0(PAr_3)_3$.

The phosphine derivatives react with carbon monoxide giving mixed carbonyl phosphine derivatives of the type $Pt(CO)(PAr_3)_3$ and $Pt(CO)(PAr_3)_2$.

Since there is a close analogy between the complex compounds of palladium and platinum in the same oxidation state it seemed likely, after the discovery of stable palladium(0) complexes,[1] that similar complexes of platinum(0) should exist. However, we have been unable to obtain $Pt(CNR)_2$ analogous to $Pd(CNR)_2$, the first palladium(0) compound to be reported, nor any other individual compound from the reduction of either isomer of $Pt(CNR)_2X_2$ (X = Cl, Br, I).[2] Nevertheless, we have now obtained platinum(0) complexes with tervalent phosphorus as ligand atom.[3]

Triarylphosphine Derivatives of Platinum(0).—The dihalogenobis(triphenylphosphine)-platinum(II), in the presence of an excess of triphenylphosphine, can be reduced quantitatively to platinum(0) compounds with anhydrous hydrazine, which reacts as follows:

$$PtI_2(PPh_3)_2 + 2{\cdot}5H_2N{\cdot}NH_2 + 2PPh_3 = Pt(PPh_3)_4 + 0{\cdot}5N_2 + 2H_2N{\cdot}NH_3I$$

Tetrakis(triphenylphosphine)platinum(0) can also be obtained, as in the case of palladium, either from dihalogenobis(triphenylphosphine)platinum(II), triphenylphosphine and ethanolic potassium hydroxide, or from chloroplatinate(II), triphenylphosphine, and ethanolic potassium hydroxide.

The reducing agent could be either phosphine:

$$PtX_2(PPh_3)_2 + 3PPh_3 + 2KOH = Pt(PPh_3)_4 + O{:}PPh_3 + 2KX + H_2O$$

$$K_2PtCl_4 + 2KOH + 5PPh_3 = Pt(PPh_3)_4 + O{:}PPh_3 + 4KCl + H_2O$$

or the potassium ethoxide.

Tetrakis(triphenylphosphine)platinum(0) is yellow, crystalline, soluble in benzene and chloroform, almost insoluble in ethanol, and stable to air for many hours. Cryoscopy in benzene shows a dissociation which increases with time, possibly due to replacement of part of the phosphine by the solvent.

Platinum appears to form these zero-valent compounds even more readily than palladium, since, while the dihalogenobis(triphenylphosphine)palladium(II) reacts with hydrazine (without excess of ligand) giving metallic palladium, yet the dihalogenobis(triphenylphosphine)platinum(II) under the same conditions disproportionates forming unsaturated platinum(0) compounds:

$$4PtI_2(PPh_3)_2 + 3H_2N{\cdot}NH_2 = 2Pt(PPh_3)_3 + Pt_2I_4(NH_2{\cdot}NH_2)_2(PPh_3)_2 + N_2 + 4HI$$

Tris(triphenylphosphine)platinum(0) is yellow, crystalline, stable to air, and soluble in benzene in which it dissociates. The product written as $Pt_2I_4(NH_2{\cdot}NH_2)_2(PPh_3)_2$ will be discussed elsewhere.

When tri-*p*-chlorophenylphosphine instead of triphenylphosphine complexes are reduced only the trico-ordinate Pt^0 derivative $Pt[P(p\text{-}Cl{\cdot}C_6H_4)_3]_3$ is obtained, as happened with palladium.[1]

Triarylarsine Derivatives of Platinum(0).—Platinum(0) compounds with triarylarsines are analogous to the saturated ones with triarylphosphines. They could be obtained only

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[1] Malatesta, *J.*, 1956, 3924; Malatesta and Angoletta, *J.*, 1957, 1186.

[2] Tschugaev and Teearu, *Ber.*, 1914, **47**, 568.

[3] Malatesta and Angoletta, *Atti Accad. naz. Lincei, Rend. Classe Sci. Fis. Mat.*, 1955, **19**, 43.

by reduction of the dihalogenobis(triarylarsine)platinum(II) with hydrazine and an excess of ligand. They are very similar to, but much less stable than, the phosphine compounds of the same series.

Triaryl Phosphite Derivatives of Platinum(0).—Reaction of dihalogenobis(triphenyl phosphite)platinum(II) with ethanolic hydrazine and excess of triphenyl phosphite gives tetrakis(triphenyl phosphite)platinum(0). This is a white crystalline product, stable to air, and very soluble in benzene and chloroform, in which it largely dissociates. Tri-*p*-chlorophenyl phosphite behaves analogously. The same reaction, without excess of the phosphite, gives, analogously to the phosphines, the trico-ordinated compound $\mathrm{Pt[P(OPh_3)]_3}$ which is white, crystalline, stable to air, and dissociated in benzene.

The tetrakis(triphenyl phosphite) derivatives can also be obtained from the triphenylphosphineplatinum(0) derivatives and triphenyl phosphite by ligand exchange:

$$\mathrm{Pt(PPh_3)_4 + 4P(OPh)_3 = Pt[P(OPh)_3]_4 + 4PPh_3}$$

On the other hand tris(tri-*p*-chlorophenylphosphine)platinum(0), even in the presence of a large excess of triphenyl phosphite, gives a tetraco-ordinated platinum(0) compound with three molecules of phosphite and a molecule of phosphine. With the triphenylphosphine complex, mixed products can be prepared only by reaction of the platinum-phosphine derivative with the stoicheiometric amount, *i.e.*, 3 moles, of the phosphite.

List of the Pt(0) *compounds prepared.*

Compound	Colour	M. p. or decomp. pt.
$\mathrm{Pt^0(PPh_3)_4}$	Ivory-yellow	118°
$\mathrm{Pt^0(PPh_3)_3}$	Yellow	125—130
$\mathrm{Pt^0[P(}p\mathrm{\text{-}Cl{\cdot}C_6H_4)_3]_3}$	Golden-yellow	186
$\mathrm{Pt^0(AsPh_3)_4}$	Colourlesss	183
$\mathrm{Pt^0[As(}p\mathrm{\text{-}Cl{\cdot}C_6H_4)_3]_4}$	,,	178
$\mathrm{Pt^0[P(O{\cdot}Ph)_3]_4}$	,,	145
$\mathrm{Pt^0[P(O{\cdot}Ph)_3]_3}$	Ivory-yellow	120—124
$\mathrm{Pt^0[P(O{\cdot}C_6H_4{\cdot}Cl\text{-}}p\mathrm{)_3]_4}$	Colourless	163
$\mathrm{Pt^0(}p\mathrm{\text{-}Cl{\cdot}C_6H_4)_3[P(O{\cdot}Ph)_3]_3}$	,,	157
$\mathrm{Pt^0P(PPh_3)_3[P(O{\cdot}C_6H_4{\cdot}Cl\text{-}}p\mathrm{)_3]_3}$	,,	141
$\mathrm{Pt^0(CO)_2(PPh_3)_2}$	,,	118 *
$\mathrm{Pt^0(CO)(PPh_3)_3}$	Orange	130
$\mathrm{Pt^0(CO)_2[P(}p\mathrm{\text{-}Cl{\cdot}C_6H_4)_3]_2}$	Colourless	—
$\mathrm{Pt^0(CO)[P(}p\mathrm{\text{-}Cl{\cdot}C_6H_4)_3]_2}$	Orange	141

* Mixed with $\mathrm{2PPh_3}$.

Carbonylphosphine Derivatives of Platinum(0).—The platinum(0) derivatives were treated with carbon monoxide under pressure in an attempt to prepare platinum(0) derivatives analogous to those of nickel, which had been obtained by action of phosphines and phosphites on nickel tetracarbonyl.[4] Carbon monoxide does not react with the phosphite compounds, and gives dicarbonyl derivatives with the phosphine compounds.

As the co-ordination number of platinum(0) is unlikely to exceed four, one must assume that the following reactions have taken place:

$$\mathrm{Pt(PPh_3)_4 + 2CO = Pt(CO)_2(PPh_3)_2 + 2PPh_3}$$

$$\mathrm{Pt(PPh_3)_3 + 2CO = Pt(CO)_2(PPh_3)_2 + PPh_3}$$

The phosphine displaced by the carbon monoxide cannot be removed from the reaction mixture because, if one tries to dissolve it in a solvent, it reacts with the product, substituting one of the two carbon monoxide molecules:

$$\mathrm{Pt(CO)_2(PPh_3)_2 + PPh_3 = Pt(CO)(PPh_3)_3 + CO}$$

When the reaction product of tris-(*p*-chlorophenylphosphine)platinum(0) with carbon monoxide is dissolved in diethyl ether it gives the co-ordinatively unsaturated compound

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[4] Malatesta and Sacco, *Ann. Chim.*, 1954, **44**, 134.

$Pt(CO)[(p\text{-}Cl{\cdot}C_6H_4)_3P]_2$. This may be formed either by the action of the solvent on a primary co-ordinatively saturated compound:

$$Pt(CO)_2[(p\text{-}Cl{\cdot}C_6H_4)_3P]_2 = Pt(CO)[(p\text{-}Cl{\cdot}C_6H_4)_3P]_2 + CO$$

or by reaction of a co-ordinatively unsaturated, primary compound with the displaced phosphine:

$$Pt(CO)_2(p\text{-}Cl{\cdot}C_6H_4)_3P + (p\text{-}Cl{\cdot}C_6H_4)_3P = Pt(CO)[(p\text{-}Cl{\cdot}C_6H_4)_3P]_2 + CO$$

The primary reaction mixtures of the dicarbonyl derivatives and phosphine are crystalline and light yellow. They slowly lose carbon monoxide and melt at the same temperature as the original phosphine derivatives. The monocarbonyl derivatives are orange-yellow; they can be recrystallized, and melt without decomposition.

EXPERIMENTAL

(A) *Intermediates.*—(I) *Di-iodobis(triphenylphosphine)platinum*(II), $PtI_2(PPh_3)_2$. A saturated xylene solution of triphenylphosphine (7·8 g., 3 mmoles) and platinous iodide (4·5 g., 1 mmole) were refluxed for about 6 hr. The warm solution was filtered and concentrated to half its original volume. On cooling, orange-yellow crystals soluble in benzene and chloroform, insoluble in hexane and ethanol, were obtained; m. p. 285° (Found: Pt, 20·0; P, 6·2; I, 26·3. $C_{36}H_{30}I_2P_2Pt$ requires Pt, 20·0; P, 6·1; I, 26·1%). This *complex* exists also in a high-temperature form, which can be obtained as brick-red crystals by rapidly cooling the xylene solution.

Analogously prepared were:

(II) *Di-bromobis(triphenylphosphine)platinum*(II), orange crystals, decomp. at 300°. The same product was obtained by treating the tetrakis(triphenylphosphine)platinum(0) compound with calculated amount of bromine: $Pt(PPh_3)_4 + Br_2 = PtBr_2(PPh_2)_2 + 2PPh_3$ (Found: Pt, 24·2; P, 7·5; Br, 19·7. $C_{36}H_{30}P_2Pt$ requires Pt, 24·7; P, 7·7; Br, 20·0%).

(III) *Di-chlorobis(triphenylphosphine)platinum*(II) [from K_2PtCl_4 (2·2 g., 1 mmole) and triphenylphosphine (3·9 g., 3 mmoles)], white crystals, which blacken above 300° without melting; soluble in chloroform and benzene, insoluble in ethanol and diethyl ether (Found: Pt, 24·1; P, 8·0; Cl, 8·9. $C_{36}H_{30}Cl_2P_2Pt$ requires Pt, 24·4; P, 7·8; Cl, 8·9%).

(IV) *Di-iodobis(tri-*p*-chlorophenylphosphine)platinum*(II), very similar to (I); orange crystals, m. p. 288° (Found: Pt, 16·6; P, 5·1; I, 22·0. $C_{36}H_{24}Cl_6I_2P_2Pt$ requires Pt, 16·5; P, 5·2; I, 21·5%).

(V) *Di-iodobis(tri-*p*-methoxyphenylphosphine)platinum*(II), pale yellow crystals, decomp. 250—255° (Found: Pt, 16·7; P, 5·2; I, 21·7. $C_{42}H_{42}O_6I_2P_2Pt$ requires Pt, 16·9; P, 5·4; I, 22·0%).

(VI) *Di-iodobis(tri-*p*-tolylphosphine)platinum*(II), pale yellow crystals, m. p. 263° (Found: Pt, 18·2; P, 5·7; I, 23·6. $C_{42}H_{42}I_2P_2Pt$ requires Pt, 18·5; P, 5·9; I, 23·9%).

(VII) *Di-iodobis(triphenylphosphine)platinum*(II). From Chatt's work[5] this *compound* must be considered dimeric with two iodo-bridges, *i.e.*, di-μ-iodobis[iodo(triphenylphosphine)-platinum(II)]. It was prepared by refluxing compound (I) and an excess of platinous iodide in xylene for several hours; it was then extracted with, and crystallized from, chloroform; dark-red crystals, decomp. >300° without melting (Found: Pt, 26·6; I, 35·2; P, 4·4. $C_{18}H_{15}I_2PPt$ requires Pt, 27·4; I, 35·7; P, 4·5%).

(VIII) *Di-iodobis(triphenyl phosphite)platinum*(II). This was prepared by refluxing for a few minutes platinous iodide (2·2 g., 1 mmole) and triphenyl phosphite (3·8 g., 2·5 mmoles) in xylene (about 20 ml.). The hot solution was then filtered, and 3 vols. of ethanol added. The *compound* crystallized as pale yellow tablets, insoluble in ethanol and hexane. On warming it turns red (perhaps giving the isomeric form) and melts at 201° (Found: Pt, 18·8; P, 5·8; I, 23·9%; *M*, cryoscopic in 2% benzene solution, 1020. $C_{36}H_{30}O_6I_2P_2Pt$ requires Pt, 18·3; P, 5·8; I, 23·7%; *M*, 1068).

(IX) *Di-iodobis(tri-*p*-chlorophenyl phosphite)platinum*(II), prepared as for the previous compound and having similar properties; m. p. 215—220° (Found: Pt, 15·5; P, 4·9. $C_{36}H_{24}O_6Cl_6I_2P_2Pt$ requires Pt, 15·3; P, 4·9%).

(X) *Di-iodobis(triphenylarsine)platinum*(II). This was prepared by refluxing platinous

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[5] Chatt and Venanzi, *J.*, 1955, 2787.

iodide (2·2 g., 1 mmole) and triphenylarsine (4·5 g., 3 mmoles) in xylene for several hours. The hot solution was filtered and, on cooling, crystals of apricot-like colour were obtained. It is soluble in benzene, chloroform, and hot ethanol; m. p. 276° (Found: Pt, 18·1; As, 14·4; I, 23·4. $C_{36}H_{30}I_2As_2Pt$ requires Pt, 18·4; As, 14·2; I, 23·9%).

Similarly prepared were: (XI) *Dichlorobis(triphenylarsine)platinum*(II) [from K_2PtCl_4 (4·3 g., 1 mmole) and triphenylarsine (9·2 g., 2·5 mmoles)], pale-yellow crystals, m. p. 278°, soluble in benzene and chloroform, almost insoluble in alcohol and hexane (Found: Pt, 21·7; As, 17·2. $C_{36}H_{30}Cl_2As_2P$ requires Pt, 22·2; As, 17·1%). (XII) *Di-iodobis(tri-*p*-chlorophenylarsine)platinum*(II), pink crystals, m. p. 285° (Found: Pt, 15·6; Cl, 16·6; I, 20·1; As, 11·0. $C_{36}H_{24}Cl_6I_2As_2Pt$ requires Pt, 15·4; Cl, 16·8; I, 20·0; As, 11·8%). (XIII) *Dichlorobis(tri-*p*-chlorophenylarsine)platinum*(II), lemon-yellow crystals, m. p. 279° (Found: Pt, 19·6; As, 13·8. $C_{36}H_{24}Cl_2As_2Pt$ requires Pt, 19·0; As, 13·8%). (XIV) *Dichlorobis(tri-*p*-tolylarsine)platinum*(II), m. p. 289° (Found: Pt, 20·1; As, 16·4. $C_{42}H_{42}Cl_2As_2Pt$ requires Pt, 20·4; As, 16·0%). (XV) *Dichlorobis(tri-*p*-methoxyphenylarsine)platinum*(II), green-yellow crystals, m. p. 248° (Found: Pt, 18·1; As, 13·9; Cl, 6·5. $C_{42}H_{42}O_6Cl_2As_2Pt$ requires Pt, 18·4; As, 14·2; Cl, 6·7%).

(B) *Platinum*(0) *Compounds with Arylphosphines as Ligands.*—(XVI) *Tetrakis(triphenylphosphine)platinum*(0). (*a*) From K_2PtCl_4, PPh_3, and KOH: A saturated aqueous solution of K_2PtCl_4 (2·2 g., 1 mmole) was slowly added, with vigorous stirring, to a warm (50—60°) saturated ethanolic solution of triphenylphosphine (6·5 g., 5 mmoles) containing potassium hydroxide (0·6 g., 2·5 mmoles). Yellow crystals separated almost immediately. The solution was kept for a few minutes on the water-bath and then filtered. The precipitate was washed first with warm ethanol, then with cold water, and finally with ethanol, and dried in a vacuum.

(*b*) From $PtCl_2(PPh_3)_2$, $H_2N{\cdot}NH_2$, and excess of PPh_3: $PtCl_2(PPh_3)_2$ (4·0 g., 1 mmole) and triphenylphosphine (4 g., 3 mmoles) suspended in ethanol (20 ml.) were warmed to 70—80° and then treated slowly with 10 ml. of 10% ethanolic anhydrous hydrazine. The suspended platinum(II) derivative dissolved slowly with a brisk evolution of gas. After a few minutes the crystalline platinum(0) compound started to separate. It was filtered off, washed, and dried as described previously. The same product can be obtained from the bromo-derivative (II) and the iodo-derivative (I). It was recrystallized by addition of hexane to a cold saturated benzene solution (Found: Pt, 15·6; P, 9·9%; *M*, cryoscopic in 2·2% benzene solution, 400. $C_{72}H_{60}P_4Pt$ requires Pt, 15·7; P, 10·0%; *M*, 1178). Recrystallization from chloroform gave a compound which contained less phosphine and some solvent of crystallization (Found: Pt, 16·2; P, 9·8; Cl, 2·5%). *Tetrakis(triphenylphosphine)platinum*(0) is soluble in benzene and chloroform and almost insoluble in ethanol and hexane. It is stable in air for some hours, and completely stable in nitrogen. It reacts with bromine in chloroform solution, giving the dibromide (II).

(XVII) *Tris(triphenylphosphine)platinum*(0). By proceeding as for compound (XVI, *b*), from the iodide (III) but without free phosphine, a yellow crystalline *product* was obtained (Found: Pt, 19·9; P, 9·4%; *M*, cryoscopic in 2·5% benzene solution, 450. $C_{54}H_{45}P_3Pt$ requires Pt, 19·9; P, 9·5%; *M*, 981). On concentrating the filtrate under reduced pressure, white crystals separated, which decomposed on standing with separation of metallic platinum. These contained Pt : PPh_3 : N : I $\sim$ 1 : 1 : 1 : 2 but were not further investigated.

(XVIII) *Tris(tri-*p*-chlorophosphine)platinum*(0). Prepared as for (XVI) and (XVII), but with tri-*p*-chlorophosphine, this *complex* formed golden-yellow leaflets, indefinitely stable in air, soluble in benzene and chloroform (Found: Pt, 15·4; P, 7·2; Cl, 24·8. $C_{54}H_{36}Cl_9P_3Pt$ requires Pt, 15·1; P, 7·2; Cl, 24·7%).

(C) *Platinum*(0) *Compounds with Arylarsines as Ligands.*—(XIX) *Tetrakis(triphenylarsine)platinum*(0). A 10% solution of anhydrous hydrazine in butanol (5 ml.) was slowly added to a suspension of compound (XI) (4·4 g., 1 mmole) and triphenylarsine (4·6 g., 3 mmoles). A brisk evolution of nitrogen took place and the suspended yellow crystals turned pearly white. (Prolonged heating is apt to cause formation of metallic platinum.) The crystals were washed with warm ethanol and dried under reduced pressure. The *complex* is soluble in benzene and chloroform with partial decomposition, insoluble in ethanol and hexane (Found: Pt, 13·6; As, 21·0. $C_{72}H_{60}As_4Pt$ requires Pt, 13·7; As, 21·1%).

(XX) *Tetrakis(tri-*p*-chlorophenylarsine)platinum*(0), prepared from (XIII) analogously to the previous compound, in ethanol, formed golden-yellow crystals (Found: Pt, 10·7; As, 16·5; Cl, 23·1. $C_{72}H_{48}Cl_{12}As_4Pt$ requires Pt, 10·7; As, 16·5; Cl, 23·4%).

(D) *Platinum*(0) *Compounds with Triaryl Phosphites as Ligands.*—(XXI) *Tetrakis(triphenyl* *phosphite)platinum*(0). The compound (VIII) (5·4 g., 1 mmole) and triphenyl phosphite (3·9 g., 2·5 mmoles), suspended in ethanol (20 ml.), were treated slowly at 70—80° with a 10% ethanolic solution of anhydrous hydrazine, until the crystals wholly disappeared. After filtering and cooling, the *product* separated as white crystals, soluble in cold benzene and chloroform and in warm ethanol and stable to dry air (Found: Pt, 13·3; P, 8·65. $C_{72}H_{60}O_{12}P_4Pt$ requires Pt, 13·6; P, 8·65%).

(XXII) *Tris(triphenyl phosphite)platinum*(0), prepared as above but without addition of triphenyl phosphite, is very similar to compound (XXI) (Found: Pt, 17·1; P, 8·4. $C_{54}H_{45}P_3Pt$ requires Pt, 17·3; P, 8·3%).

(XXIII) *Tetrakis(tri-*p*-chlorophenyl phosphite)platinum*(0) was prepared as for compound (XXI), from $PtCl_2[P(O{\cdot}C_6H_4{\cdot}Cl\text{-}p)_3]_2$ (5·5 g., 1 mmole), $P(O{\cdot}C_6H_4{\cdot}Cl\text{-}p)_3$ (5·1 g., 2·5 mmoles), and hydrazine (Found: Pt, 10·6; P, 6·9; Cl, 22·6. $C_{72}H_{48}O_{12}Cl_{12}P_4Pt$ requires Pt, 10·6; P, 6·7; Cl, 23·0%).

(E) *Reactions between the Tris- and Tetrakis-(triarylphosphine)platinum*(0) *and the Triaryl Phosphites.*—Both tris- and tetrakis-(triphenylphosphine)platinum(0) reacted with a slight excess of triphenyl phosphite in warm ethanolic solution, yielding $Pt[P(OPh)_3]_4$ as pure crystals. The m. p. of the compound prepared by ligand exchange was 146°, mixed m. p. with (XXI) 145·5°.

Tetrakis(triphenylphosphine)platinum(0) (3·1 g., 1 mmole) in ethanolic suspension (20 ml.), and triphenyl phosphite (4·6 g., 4·5 mmoles) were warmed on a water-bath to complete dissolution. On cooling, the tetrakis-ester crystallised. It was purified by recrystallization from benzene–hexane. Similarly, from tetrakis(triphenylphosphine)platinum and tri-(*p*-chlorophenyl phosphite)platinum, the compound $Pt[P(O{\cdot}C_6H_4{\cdot}Cl\text{-}p)_3]_4$, m. p. 165°, was obtained; mixed m. p. with (XXIII), 163°.

(XXIV) *Mono(tri-*p*-chlorophenylphosphine)tris(triphenyl phosphite)platinum*(0), $PtP(O{\cdot}C_6H_4{\cdot}Cl\text{-}p)_3[P(OPh)_3]_3$. $Pt[P(C_6H_4{\cdot}Cl\text{-}p)_3]_4$ (3·2 g., 1 mmole) and triphenyl phosphite (3·5 g., 4·5 mmoles) in ethanol (50 ml.) were kept on a water-bath until solution was complete. From the filtered solution, the pale yellow crystalline *complex* was obtained on cooling. It is very soluble in benzene and chloroform, much less soluble in ethanol (Found: Pt, 13·5; Cl, 7·2; P, 7·3. $C_{72}H_{57}O_9Cl_3P_4Pt$ requires Pt, 13·1; Cl, 7·1; P, 8·3%).

(XXV) *Mono(triphenylphosphine)tris(tri-*p*-chlorophenyl phosphite)platinum*(0). $Pt[P(C_6H_5)_3]_4$ (3·1 g., 1 mmole) and tri-*p*-chlorophenyl phosphite (3·1 g., 3 mmoles) in ethanol (50 ml.) were kept on a water-bath for about 1 hr. From the filtered solution the *compound* separated on cooling, as crystalline leaflets, soluble in cold benzene or chloroform and in warm ethanol (Found: Pt, 11·7; Cl, 18·6; P, 7·1. $C_{72}H_{51}O_9Cl_9P_4Pt$ requires Pt, 11·5; Cl, 18·7; P, 7·3%).

(F) *Reaction of Carbon Monoxide on the Compounds of Tetrakisarylphosphineplatinum*(0).—(XXVI) *Dicarbonylbis(triphenylphosphine)platinum*(0), $Pt(CO)_2(PPh_3)_2$. (*a*) This compound was obtained (mixed with 2 mol. of triphenylphosphine) when $Pt(PPh_3)_4$ was treated with carbon monoxide at 300 atm. The temperature has no effect in the range 20—90°, and the reaction at 20° is complete in about 12 hr. The product loses carbon monoxide slowly, becoming yellow. With all the solvents which dissolve the phosphine, evolution of carbon monoxide takes place. The mixture melted at 118° with gas evolution [same m. p. as that of $Pt(PPh_3)_4$] {Found: CO, 4·50. $Pt(CO)_2[PPh_3]_2,2PPh_3$ requires CO, 4·3%}.

(*b*) From $Pt(PPh_3)_3$ and CO under the same conditions a *product* (m. p. 130°) was obtained which gave 5·35% of CO on heating with phenyl *iso*cyanide [$Pt(CO)_2(PPh_3)_2,PPh_3$ requires CO, 5·37%].

(XXVII) *Monocarbonyltris(triphenylphosphine)platinum*(0). When the mixture obtained as (XXVI, *b*) was dissolved in 10 parts of diethyl ether a brisk evolution of gas took place; on precipitation with 20 parts of ethanol orange-red crystals were obtained; m. p. 130° [Found: Pt, 19·9; CO, 2·7; P, 9·0. $C_{54}H_{45}P_3Pt(CO)$ requires Pt, 19·5; CO, 2·8; P, 9·3%].

(XXVIII) *Dicarbonylbis(tri-*p*-chlorophosphine)platinum*(0), prepared similarly to (XXVI, *b*) from $Pt[P(C_6H_4{\cdot}Cl\text{-}p)_3]_3$ (XVIII), is a crystalline powder which slowly loses carbon monoxide, turning red. It dissolves in diethyl ether, giving off half of its carbon monoxide {Found (in the mixture): CO, 3·9. $Pt(CO)_2[P(C_6H_4{\cdot}Cl\text{-}p)_3]_2,P(C_6H_4Cl\text{-}p)_3$ requires CO, 4·2%}.

(XXIX) *Monocarbonylbis(tri-*p*-chlorophenylphosphine)platinum*(0). This *compound* was formed slowly from (XXVIII) (admixed with tri-*p*-chlorophenylphosphine) by loss of carbon monoxide. In fact, (XXVIII), a few days after being prepared, dissolves in diethyl ether without effervescence. By concentration of this solution, $Pt(CO)(PPh_3)_2$ was obtained as golden-yellow crystals, m. p. 141°. The same *compound* was obtained by dissolution of the freshly prepared compound (XXVIII) in diethyl ether, in this case with evolution of carbon monoxide [Found : Pt, 20·9; CO, 2·9; P, 7·0. $C_{36}H_{24}Cl_6P_2Pt(CO)$ requires Pt, 20·5 ; CO, 2·9 ; P, 6·9%]

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