231. *Palladium*(0) *Compounds. Part II.*[1] *Compounds with Triarylphosphines, Triaryl Phosphites, and Triarylarsines.*

By L. MALATESTA and (MISS) M. ANGOLETTA.

The preparation of a number of complex compounds of zero-valent palladium with phosphorus donors is described. They can be prepared from $Pd(R{\cdot}NC)_2$ and donor, or by reduction of palladium(II) compounds in the presence of excess of donor.

Three types of complexes have been isolated: $(R{\cdot}NC)(L)_3Pd$, PdL_4, and PdL_3 (L = triarylphosphines and triaryl phosphites). The compounds PdL_4 are largely dissociated in solution.

The triphenylarsine complex $(Ph_3As)_4Pd$ has also been obtained.

PREVIOUSLY we mentioned [1] the reaction between di*iso*cyanopalladium(0) and tri-*p*-chlorophenyl phosphite which yielded a mixed phosphite–*iso*cyanide complex. This is a general reaction, and is shown by triaryl phosphites, triarylphosphines, and triarylarsines. Its course, however, varies with the *iso*cyanide which forms complexes with palladium(0) and the substituting ligand (*e.g.*, phosphines, arsines, and various *para*-substituted triphenyl phosphites). The resulting products, all derivatives of palladium(0), can be classed into three groups.

(1) iso*Cyano–Triphosphite–Palladium*(0) *Compounds*.—The reaction described previously [1] belongs to this class:

$$(p\text{-}CH_3{\cdot}C_6H_4{\cdot}NC)_2Pd + 3(p\text{-}Cl{\cdot}C_6H_4{\cdot}O)_3P = (p\text{-}CH_3{\cdot}C_6H_4{\cdot}NC)[(p\text{-}Cl{\cdot}C_6H_4{\cdot}O)_3P]_3Pd$$

A similar product is also obtained from triphenyl phosphite with di-*p*-methoxyphenyl*iso*cyanopalladium. These products, in view of the similarity in behaviour of *iso*cyanides and carbon monoxide, can be considered analogous to the carbonyltristriaryl phosphite-nickel(0) compounds already described,[2] *e.g.*, $(CO)[(C_6H_5O)_3P]_3Ni$.

(2) *Symmetrical Tetrasubstituted Palladium*(0) *Compounds*.—The action of triphenyl phosphite on di-*p*-tolyl*iso*cyanopalladium(0) and that of triphenylphosphine and triphenylarsine on di-*p*-methoxyphenyl*iso*cyanopalladium(0) lead to the complete loss of *iso*cyanide with the formation of a symmetrically tetrasubstituted compound in which the metal is co-ordinatively saturated:

$$(p\text{-}CH_3{\cdot}C_6H_4{\cdot}NC)_2Pd + 4(C_6H_5O)_3P = [(C_6H_5O)_3P]_4Pd + 2p\text{-}CH_3{\cdot}C_6H_4{\cdot}NC$$

However, reactions of triarylphosphines and triaryl phosphites with nickel carbonyl do not give the analogous symmetrically tetrasubstituted compounds of nickel.

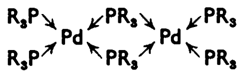
Tetrasubstitution occurs only with the chloro-derivatives of phosphorus(III), *e.g.*, $(C_6H_5{\cdot}PCl_2)_4Ni$, $(C_6H_5O{\cdot}PCl_2)_4Ni$,[2] and $(PCl_3)_4Ni$.[3] It is noteworthy that $Ni(PF_3)_4$, which resembles $Ni(CO)_4$, cannot be obtained by direct replacement of the carbon monoxide from the carbonyl itself; the substitution stops after the introduction of three PF_3 molecules, and the tetrakistrifluorophosphorus(III) compound has to be prepared by fluorination of $Ni(PCl_3)_4$.[3]

(3) *Symmetrically Trisubstituted Palladium*(0) *Compounds*.—When tri-*p*-chlorophenylphosphine reacts with di-*p*-tolyl*iso*cyanopalladium(0) both *iso*cyanide molecules are eliminated with formation of a trisubstituted compound which is co-ordinatively unsaturated * and has no equivalent in the series of nickel complexes:

$$(p\text{-}CH_3{\cdot}C_6H_4{\cdot}NC)_2Pd + 3(p\text{-}Cl{\cdot}C_6H_4)_3P = [(p\text{-}Cl{\cdot}C_6H_4)_3P]_3Pd + 2p\text{-}CH_3{\cdot}C_6H_4{\cdot}NC$$

---

* A referee suggests that the compounds of the type $(PR_3)_3Pd$ could be dimeric and formulated as:



In our opinion this is very unlikely. Lately, compounds of zero-valent platinum $(PR_3)_2Pt$, have been prepared by one of us, in which platinum is certainly not quadricovalent, and this may be taken as an indirect proof for our formulation.

[1] Part I, Malatesta, *J.*, 1955, 3924.

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

[3] Wilkinson, *J. Amer. Chem. Soc.*, 1951, **73**, 5501.

The formation of stable co-ordinatively unsaturated compounds of palladium(0) had already been observed, *e.g.*, with *iso*cyanides as ligands, and could be foreseen from a consideration of the different behaviour of Pd(II) and Ag(I) [which is isolectronic with Pd(0)]. Trico-ordination with uncharged ligands is uncommon but has been recently observed in phosphine complexes of Ag(I).[4]

This tendency to co-ordinative unsaturation is also supported by the fact that the tetraco-ordinated complexes, *e.g.*, $(Ph_3P)_4Pd$, are largely dissociated in benzene.*

Three other methods of preparation of the compounds of classes (2) and (3), *i.e.*, those not containing *iso*cyanides, have been developed. These start from derivatives of palladium(II) and (with only one exception) give exclusively tetraco-ordinated palladium(0) compounds—the exception is the complex of tri-*p*-tolylphosphine which is trico-ordinated: $[(p\text{-}CH_3\cdot C_6H_4)_3P]_3Pd$. These methods are: (i) The action of hydrazine on an alcoholic suspension of bistriarylphosphinedihalogenopalladium in the presence of excess of phosphine, *e.g.*,

$$2(Ph_3P)_2PdCl_2 + 4R_3P + 5H_2N\cdot NH_2 = 2(R_3P)_4Pd + 4H_2N\cdot NH_2,HCl + N_2$$

This reaction is of fairly general application and has given positive results in some cases where methods (ii) and (iii) failed.

(ii) The action of excess of triarylphosphine or triaryl phosphite, in concentrated alcoholic solution, on freshly precipitated palladium oxide:

$$PdO + 5(RO)_3P = [(RO)_3P]_4Pd + (RO)_3PO$$

This reaction gives good results with triphenylphosphine and triphenyl phosphite, but with tri-*p*-tolylphosphine and tri-*p*-chlorophenyl phosphite there is direct reduction of palladium oxide to the metal.

(iii) The reaction of excess of triphenylphosphine or triphenyl phosphite with a hot, concentrated solution of palladium(II) nitrate:

$$Pd(NO_3)_2 + 9R_3P = (R_3P)_4Pd + N_2O + 5R_3PO$$

This method has approximately the same applicability as method (ii), but requires a larger excess of ligand.

It is noteworthy that the autoreduction of palladium(II) to palladium(0) in palladous oxide and nitrate can be correlated with the well-known fact that phosphines, phosphites, and arsines can form complexes with almost comparable stabilities with metals in different oxidation states [Ni(IV),[5] Ni(III),[6] Ni(II), Ni(0), Pd(II), Pd(0), etc.] but only rarely give co-ordination compounds with highly charged cations. In the above reaction one can assume that the hypothetical cation $(Pr_3P)_4Pd^{2+}$, which cannot be isolated, easily forms the uncharged complex with the metal in a formally zero-valent state. The complex with triphenylarsine could be obtained only by the action of this ligand on the di*iso*cyanopalladium(0) compound. It is reasonably stable to aerial oxidation, but we could not purify the complex because the solvents that dissolve it cause decomposition.

The compounds prepared, their decomposition temperature, and colour are given in the Table.

---

* From molecular-weight determination in this solvent it appears to be largely dissociated, and to account for the very low figures obtained one must assume that a dico-ordinated complex is present in solution:

$$(Ph_3P)_4Pd \longrightarrow (Ph_3)_3Pd + Ph_3P$$
$$(Ph_3P)_3Pd \longrightarrow (Ph_3)_2Pd + Ph_3P$$

[4] Cass, Coates, and Hayter, *J.*, 1955, 4007.

[5] Nyholm, *J.*, 1951, 2602.

[6] Jensen, *Z. anorg. Chem.*, 1936, **229**, 265.

Complex	Decompn. temp.	Colour
$(p\text{-MeO}\cdot C_6H_4\cdot NC)[(p\text{-Cl}\cdot C_6H_4)_3P]_3Pd$	90—100°	colourless
$(p\text{-MeO}\cdot C_6H_4\cdot NC)[(p\text{-Cl}\cdot C_6H_4\cdot O)_3P]_3Pd$	100—105	colourless
$(p\text{-MeO}\cdot C_6H_4\cdot NC)[(PhO)_3P]_3Pd$	105—110	colourless
$(Ph_3P)_4Pd$	100—105	yellow
$[(p\text{-Cl}\cdot C_6H_4)_3P]_4Pd$	120—160	lemon-yellow
$[(Ph\cdot O)_3P]_4Pd$	120—130	colourless
$(Ph_3As)_4Pd$	80—100	colourless
$[(p\text{-Cl}\cdot C_6H_4)_3P]_3Pd$	90—100	yellow
$[(p\text{-CH}_3\cdot C_6H_4)_3P]_3Pd$	110	golden-yellow

EXPERIMENTAL

p-*Methoxyphenyl*iso*cyanotristri*-p-*chlorophenylphosphinepalladium.*—Di-*p*-methoxyphenyl*iso*cyanopalladium (0·74 g.; 2 mmoles) and tri-*p*-chlorophenylphosphine (2·92 g.; 8 mmoles) were heated in benzene (8—10 c.c.). The solution was filtered from the solid residue and anhydrous ethanol added. The product thus precipitated cannot be purified (Found: Pd, 8·3; P, 7·3; Cl, 25·6; N, 1·2. Calc. for $C_{62}H_{43}ONCl_9P_3Pd$: Pd, 7·95; P, 7·0; Cl, 23·9; N, 1·05%).

p-*Methoxyphenyl*iso*cyanotris*(*tri*-p-*chlorophenyl phosphite*)*palladium* was prepared analogously, and purified by recrystallization from ethanol (Found: Pd, 7·05; P, 6·5; N, 1·0. $C_{62}H_{43}O_{10}NCl_9P_3Pd$ requires Pd, 7·2; P, 6·3; N, 0·95%).

p-*Methoxyphenyl*iso*cyanotris*(*triphenyl phosphite*)*palladium* was prepared and purified analogously (Found: Pd, 9·2; P, 8·1; N, 1·3. $C_{62}H_{52}O_{10}NP_3Pd$ requires Pd, 9·1; P, 7·9; N, 1·2%).

Tetrakistriphenylphosphinepalladium.—Powdered palladium nitrate (2 mmoles) was treated with triphenylphosphine (approx. 20 mmoles) in hot benzene (10 c.c.). After a vigorous reaction with the evolution of much nitrous oxide a solid mass was obtained on cooling. The crude *product* was recrystallized from ethanol. It is stable to air for only a short time and on prolonged exposure turns from yellow to orange [Found: Pd, 9·2; C, 75·1; H, 5·2; P, 10·4%; *M*, cryoscopic in benzene (0·601 g./20 c.c.), 355. $C_{72}H_{60}P_4Pd$ requires Pd, 9·1; C, 74·9; H, 5·2; P, 10·5%; *M*, 1156). From the mother-liquor of the recrystallization Ph_3PO, m. p. 154° (1·5 g. from 5 g. of Ph_3P), was recovered.

Tetrakistri-p-*chlorophenylphosphinepalladium.*—Finely powdered bistri-*p*-chlorophenylphosphinedichloropalladium (2 g.; 2·5 mmoles) (obtained by treating an alcoholic solution of H_2PdCl_4 with the phosphine) and tri-*p*-chlorophenylphosphine (1·8 g.; 5 mmoles) were suspended in anhydrous ethanol and a 10% alcoholic solution of hydrazine hydrate added dropwise. The yellow crystalline *product* was repeatedly washed with hot chloroform (10—15 c.c.) and the filtrate collected in cold anhydrous ethanol (100 c.c.); the solid formed was filtered off and dried. It is insoluble in alcohol and soluble in chloroform and benzene (Found: Pd, 6·6; P, 8·1; Cl, 26·9. $C_{72}H_{48}Cl_{12}P_4Pd$ requires Pd, 6·8; P, 7·9; Cl, 27·2%).

Tetrakis(*triphenyl phosphite*)*palladium.*—Di-*p*-tolyl*iso*cyanopalladium (0·68 g.; 2 mmoles), triphenyl phosphite (2·48 g.; 8 mmoles), and benzene (10—15 c.c.) were heated for a few minutes, the benzene was evaporated under reduced pressure, and the residue washed with alcohol, then recrystallized from this solvent, from which it was obtained as white *needles* [Found: Pd, 7·85; P, 9·4%; *M*, cryoscopic in benzene (0·731 g./20 c.c.), 380. $C_{72}H_{60}O_{12}P_4Pd$ requires Pd, 7·9; P, 9·2%; *M*, 1347].

Tetrakistriphenylarsinepalladium.—Di-*p*-tolyl*iso*cyanopalladium (0·36 g.; 1 mmole), triphenylarsine (1·84 g.; 6 mmoles), and ethanol (*ca.* 10 c.c.) were warmed on a water-bath for 15—20 min. After cooling, the crystalline precipitate was filtered off and washed on the filter with light petroleum. It could not be further purified, but the crude *product* does not contain nitrogen (Found: Pd, 7·6; As, 21·3. $C_{72}H_{60}As_4Pd$ requires Pd, 8·0; As, 22·5%).

Tristri-p-*chlorophenylphosphinepalladium.*—Di-*p*-tolyl*iso*cyanopalladium (0·67 g.; 2 mmoles), tri-*p*-chlorophenylphosphine (4·36 g.; 12 mmoles), and toluene (5—6 c.c.) were heated for 10—15 min. The *product* was purified by dissolving it in benzene and reprecipitating with ethanol (Found: Pd, 8·7; P, 7·8. $C_{54}H_{36}Cl_9P_3Pd$ requires Pd, 8·85; P, 7·7%).

Tristri-p-*tolylphosphinepalladium* was prepared analogously from $[(p\text{-CH}_3\cdot C_6H_4)_3P]_2PdI_2$ (1·5 g.; 1·55 mmoles), tri-*p*-tolylphosphine (1·52 g.; 5 mmoles), and hydrazine hydrate. It turns brown on exposure to air (Found: Pd, 10·0; P, 9·3. $C_{63}H_{63}P_3Pd$ requires Pd, 10·5; P, 9·1%).

The authors are indebted to the Italian Research Council for a grant.

ISTITUTO DI CHIMICA GENERALE DELL'UNIVERSITÀ DI MILANO. [*Received, September 27th,* 1956.]