490. *Complex Compounds of Ditertiary Phosphines and Arsines with Nickel*(0) *and Palladium*(0).

By J. Chatt, F. A. Hart, and H. R. Watson.

A number of nickel(0) and palladium(0) complexes of the types [ML_2], [MLL′], and [ML'_2] have been prepared by the reduction of the corresponding dipositive cationic complexes. In these M is nickel or palladium, L is a chelate ditertiary phosphine, *e.g.*, $Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2$, and L′ is a ditertiary arsine, *e.g.*, *o*-$C_6H_4(AsMe_2)_2$ or a tritertiary phosphine, *e.g.*, $Me{\cdot}C(CH_2{\cdot}PPh_2)_3$. When the ligands L and L′ are predominately aliphatic the complexes tend to be colourless and readily oxidised by air, becoming more orange and less readily oxidised as the aromatic nature of the ligands increases.

The tritertiary phosphine complexes [$M\{Me{\cdot}C(CH_2{\cdot}PPh_2)_3\}_2$] exhibit a novel type of isomerism between an octahedrally co-ordinated form (α-isomer) and a form of lower co-ordination number (β-isomer).

Also, a number of new nickel(II) and palladium(II) complexes derived from the di- and tri-tertiary phosphines have been characterised.

Until 1950 the chemistry of nickel and palladium in their zerovalent states was limited to the tetracarbonyl and substituted carbonyls of nickel,[1] and the complex cyanides of nickel [1] and palladium.[2] Developments have since been fairly rapid; many other four-co-ordinated nickel(0) complexes [1,3] are now known as well as three- and four-co-ordinated palladium(0) complexes having isocyanide groups [4] or phosphorus(III) or arsenic(III) atoms [5] as donors. The four-co-ordinated complexes are presumed to have the tetrahedral co-ordination characteristic of a d^{10}-ion.

Three general methods of preparation have been used: (*a*) direct action of the ligand on the metal; (*b*) displacement of carbon monoxide from nickel carbonyl by the ligand; and (*c*) reduction of complex salts of nickel(II) and palladium(II). In general the products are only moderately stable thermally and are slowly decomposed by air.

We are now reporting the use of a variety of ditertiary and tritertiary phosphines to afford several thermally stable but air-sensitive compounds containing nickel(0) and palladium(0). These were prepared by reducing the corresponding nickel(II) and palladium(II) complexes. The physical properties of the compounds [ML_2], [MLL′], and [ML'_2] thus prepared (M = Ni or Pd; L = ditertiary phosphine, L′ = ditertiary arsine or tritertiary phosphine) are listed in Table 1 together with a triphosphine-monophosphine complex.

Aqueous sodium borohydride is the most convenient reducing agent when L and L′ are aromatic and gives the best yield based on the complex salt undergoing reduction. Reduction is rapid, and the complex of the zerovalent metal is precipitated almost immediately from aqueous alcohol or acetone. A considerable volume of hydrogen is also evolved during the reduction and about 3 mol. of borohydride are consumed for each metal atom. The unsymmetrical compounds [MLL′] were made by similar reduction of a solution prepared from equimolar quantities of [MCl_2L] and the ligand L′. Presumably the intermediates [MLL′]Cl_2 were first formed and then reduced; no attempt was made to isolate them. Reduction by hydrazine in boiling aqueous alcohol gave much poorer yields and the use of metallic sodium in liquid ammonia was complicated by the relative insolubility of the bivalent salts and the products in this medium.

The complexes (II) and (VIII) derived from the aliphatic ligand $C_2H_4(PMe_2)_2$ are

---

[1] For references see Chatt and Hart, *J.*, 1960, 1378.

[2] Burbage and Fernelius, *J. Amer. Chem. Soc.*, 1943, **65**, 1484.

[3] Seel, Ballreich, and Schmutzler, *Chem. Ber.*, 1961, **94**, 1173.

[4] Malatesta and Angoletta, *J.*, 1955, 3924.

[5] Malatesta and Angoletta, *J.*, 1957, 1186.

formed in fair yield by the action of sodium naphthalenide ($NaC_{10}H_8$) on a mixture of the complex $[MCl_2(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)]$ (M = Ni, Pd) and an excess of the diphosphine in tetrahydrofuran.[6] They are decomposed by hydroxylic solvents.

The zerovalent compounds listed in Table 1 and described below could have co-ordination numbers from 3 to 6 and are described in that order.

Diphosphine-monophosphine Complexes.—Attempts to obtain the 3-co-ordinated complex $[Pd\{o\text{-}C_6H_4(PEt_2)_2\}PPh_3]$ by reductions of the dichloride $[Pd\{o\text{-}C_6H_4(PEt_2)_2\}Cl_2]$ in the presence of triphenylphosphine gave tristriphenylphosphinepalladium as the only 3-co-ordinated product. The diphosphine imposes a P–Pd–P angle of about 90° at the metal and presumably this is so far removed from the required angle of 120° that the molecule is unstable and disproportionates to give the observed product.

TABLE 1.

Chelate tertiary phosphine and arsine derivatives of nickel(0) and palladium(0).

Compound		M. p.	Colour	Dipole moment (D)
$[Pd\{PhP(o\text{-}C_6H_4\cdot PEt_2)_2\}\{PPh_3\}]$ *	I	175—178°	Dark red	—
Formula $[ML_2]$ and $[ML'_2]$				
$[Ni\{C_2H_4(PMe_2)_2\}_2]$ *	II	120 †	White	1·65
$[Ni\{o\text{-}C_6H_4(PEt_2)_2\}_2]$	III	240—242	Orange	—
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ *¶	IV	190—196 ‡	Orange	—
$[Ni\{C_2H_4(PPh_2)_2\}_2]$	V	253—256	Orange	1·5
α-$[Ni\{Me\cdot C(CH_2\cdot PPh_2)_3\}_2]$ *	VI	225—229 †‡	Yellow-orange	—
β-$[Ni\{Me\cdot C(CH_2\cdot PPh_2)_3\}_2]$ *	VII	203—210 †§	Bright orange	—
$[Pd\{C_2H_4(PMe_2)_2\}_2]$ *	VIII	182—183 †	White	1·6
$[Pd\{o\text{-}C_6H_4(PEt_2)_2\}_2]$	IX	229—230	Yellow	~0
$[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ *	X	188—189 ‡	Yellow	—
$[Pd\{CH_2(PPh_2)_2\}_2]$ *	XI	195—210 ‡	Scarlet	—
$[Pd\{C_2H_4(PPh_2)_2\}_2]$ *	XII	234	Yellow	1·6
α-$[Pd\{Me\cdot C(CH_2\cdot PPh_2)_3\}_2]$ *	XIII	246—247 †	Dull yellow	~0
β-$[Pd\{Me\cdot C(CH_2\cdot PPh_2)_3\}_2]$ *	XIV	194—195 †§	Bright yellow	2·25
Formula $[PdLL']$				
$[Pd\{o\text{-}C_6H_4(PEt_2)_2\}\{o\text{-}C_6H_4(AsEt_2)_2\}]$ *	XV	184—186	Yellow	0·95
$[Pd\{o\text{-}C_6H_4(PEt_2)_2\}\{o\text{-}C_6H_4(AsMe_2)_2\}]$ *	XVI	141	Orange	—
$[Pd\{o\text{-}C_6H_4(PEt_2)_2\}\{C_2H_4(PPh_2)_2\}]$ *	XVII	207—208	Yellow	2·1
$[Pd\{o\text{-}C_6H_4(PEt_2)_2\}\{Me\cdot C(CH_2\cdot PPh_2)_3\}]$ *	XVIII	200—201 †	Bright yellow	3·1

* New compounds. † In nitrogen-filled tubes. ‡ With decomp. § With isomerisation. ¶ Cf. Rao, quoted by Harris, Nyholm, and Phillips, *J.*, 1960, 4379.

Diphosphine-diphosphine and Diarsine-diarsine Complexes.—These are symmetrical complexes of the general type $[ML_2]$ and are soluble in non-polar solvents. Solubility decreases with rising molecular weight of the ligand and rising atomic weight of the metal; the colours range from white to scarlet in passing from the aliphatic to highly aromatic complexes (Table 1).

We should expect the π-character of the metal–ligand bond to be more developed in the complexes containing aromatic ligands[1] and this should increase the thermal stability and lower the reactivity of the aromatic relative to the aliphatic complexes. The present series accords with this. In solution all the complexes are oxidised rapidly by air. The solid compounds with aromatic ligands are oxidised rather slowly, their complete decomposition being measurable in hours, whereas the aliphatic palladium derivative (VIII) is oxidised immediately. The aliphatic nickel derivative (II) shows a remarkable behaviour in air: on exposure, the crystals undergo no apparent change until gently rubbed, they then darken, evolve black smoke, and inflame. Samples of the compound have retained this property after storage in air for three weeks.

Corresponding ditertiary phosphine and ditertiary arsine complexes have comparable stabilities. The symmetrical nature of the co-ordination at the metal atom is demonstrated

---

[6] Chatt and Watson, *Nature*, 1961, **189**, 1003.

by the low dipole moments of the compounds in benzene solution, and a tetrahedral configuration distorted by the steric requirements of the ligands is presumed.

Diphosphine-diarsine Complexes.—Mixed complexes of the type [MLL′] are formed without difficulty when L is o-$C_6H_4(PEt_2)_2$ and L′ is $C_2H_4(PPh_2)_2$, o-$C_6H_4(AsMe_2)_2$, or o-$C_6H_4(AsEt_2)_2$, but attempts to obtain complexes with $CH_2(PPh_2)_2$ and $C_2H_4(PEt_2)_2$ as the ligand L′ failed.

The diphosphine-diarsine complex (XV), which is symmetrical except for the pairs of different ligand atoms, has a low dipole moment (0·95 D), in accord with the suggested similarity of the electric moments of the Ni–P and Ni–As bonds.[1]

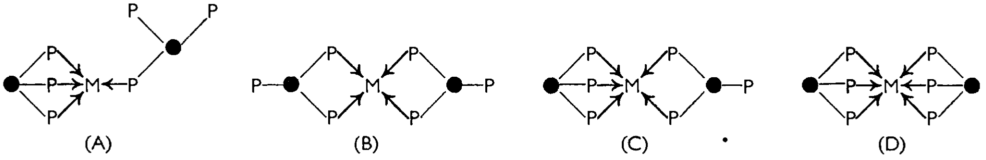
Diphosphine-triphosphine complexes.—The complex $[Pd\{o\text{-}C_6H_4(PEt_2)_2\}\{Me{\cdot}C(CH_2{\cdot}PPh_2)_3\}]$ (XVIII) was obtained by reduction of an alcoholic solution of $[PdCl_2\{o\text{-}C_6H_4(PEt_2)_2\}]$ with sodium borohydride in the presence of the triphosphine. This compound might be 4-co-ordinate with the triphosphine behaving as a bidentate ligand, or 5-co-ordinate. Its dipole moment of 3·1 D is appreciably higher than any of the definitely 4-co-ordinated derivatives listed in Table 1, hence we incline to the view that it is 5-co-ordinate and that its configuration is based on the square pyramid rather than that on the more symmetrical trigonal bipyramid. The moment of 3·1 D is that expected for one P–Ni(0) co-ordinate bond.[1] It would accord nicely with a square pyramidal configuration if the P–Pd(0) bond moment is similar to the P–Ni(0), and we make the reasonable assumption that we may neglect the contribution to the moment from the organic part of the molecule.[1] Nevertheless neither the co-ordination number nor the configuration can be regarded as certain.

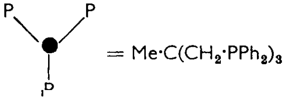
A corresponding nickel compound of almost identical infrared spectrum could not be obtained pure. High carbon values persisted through repeated recrystallisation, which suggests that it disproportionates slightly to the bisdiphosphine- and the less soluble bistriphosphine-nickel(0) complex during recrystallisation.

Triphosphine-triphosphine Complexes.—Compounds of the formula $[M\{Me{\cdot}C(CH_2{\cdot}PPh_2)_3\}_2]$ (M = Ni or Pd) were prepared by reduction, with sodium borohydride, of solutions containing the corresponding dipositive cation. Each exists in two isomeric forms designated α and β. Their individuality is proved by their different colours, solubilities, and melting points. They have similar but different infrared spectra (Nujol mulls) and different *X*-ray powder photographs. The isomers are readily interconvertible; the α-isomers pass into the β-isomers on recrystallisation from benzene–methanol, and the β-isomers pass into the α-isomers when the solid is heated or, better, recrystallised from light petroleum. Interconversion of the isomeric nickel complexes is more rapid, and such compounds are more difficult to obtain pure than their palladium analogues. Both nickel isomers are always present together in solution and attempts to measure their dipole moments gave variable results. The two α-isomers (Ni and Pd) are isomorphous and so are the two β-isomers. Also each isomorphous pair has almost identical infrared spectra (Nujol mulls). The following arguments about the nature of the isomerism were developed from the properties of the less labile palladium complexes.

This is a new type of isomerism in which the isomers differ only in the number of points of attachment of the tridentate ligands. If we admit higher co-ordination numbers than four, possible isomers are the tetrahedrally co-ordinated A and B, 5-co-ordinated C, and octahedrally co-ordinated D.

Since the α-isomer has a zero dipole moment it must have a high symmetry. The related tetrahedral complexes, *e.g.*, $[M(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$ (Table 1) have definite dipole moments of 1—2 D, yet have greater symmetry than A, B, and C. We conclude therefore that the α-isomer has the octahedral configuration D, and the metal is isoelectronic in the valency shell with the octahedral complexes of zinc(II). It is surprising that nickel(0) and palladium(0) can accommodate six donor atoms which give them effective atomic numbers of four beyond the next inert gas. This is much more likely with positively charged ions, *e.g.*, Zn^{2+}, where the higher energy orbitals, lowered by the charge, can more easily accommodate the additional electrons. The ready conversion of the octahedrally co-ordinated α-isomer into a stable isomer of lower co-ordination number accords with the expectation that the binding energy of the sixth, and perhaps fifth, phosphorus atom to the zerovalent metals must be small.* The β-isomer must have a lower co-ordination number, as in A, B, or C, but which of these is uncertain. We think B is most likely because a considerable change in configuration in addition to bond breaking is involved in the conversion of the essentially octahedral D into the essentially tetrahedral B. This could account for the energy barrier between the two isomers, which allows their isolation as pure compounds. A and C are derived from D by simple breaking of weak co-ordinate bonds with little re-arrangement of the triphosphine molecules. Thus, we should expect a labile equilibrium between the isomers if the β-isomer had structure A or C.





Possible isomers of $[M\{Me{\cdot}C(CH_2{\cdot}PPh_2)_3\}_2]$ (M = Ni or Pd).

The properties of the two isomers accord with this explanation of the isomerism. (1) The more polar solvents, which by solvating a free phosphine group would favour the lower co-ordination number, convert the α- into the β-isomer. (2) Both isomers are very sparingly soluble in the lower alcohols and ketones and more soluble in light petroleum and benzene. The more compact octahedral complex should be less soluble than the less symmetrical complex of lower co-ordination number, and in fact the α-isomer is much less soluble than the β-isomer in inert organic solvents.

The dipole moment of the β-isomer (2·25 D) would indicate a tetrahedral configuration, although the spread of values amongst the tetrahedrally co-ordinated complexes (Table 1) is too great to allow complete reliance to be placed on this argument; a 5-co-ordinated structure is not altogether excluded, *e.g.*, compare compound (XVIII) of 3·1 D.

Absence of Hydridic Hydrogen.—Sodium borohydride, as used in these preparations, might give tertiary phosphine complexes containing a metal–hydrogen bond. We have found no evidence of this in any of the compounds listed in Table 1. The infrared spectra of all the compounds have been measured in Nujol mulls, and none exhibits absorption attributable to a metal–hydrogen bond. The nuclear magnetic resonance spectra of compounds (VIII) and (IX), compounds typical of the aliphatic and aromatic classes in the palladium series, show no resonance attributable to a metal–hydrogen bond. Also, in the nickel series, typical compounds (III) and (V) have been prepared by the unequivocal method of displacing carbon monoxide from nickel carbonyl.[1] The reaction of 1 mol. of compound (XI) with 1 mol. of bromine gave a 70% yield of pure dibromobisdiphenylphosphinomethanepalladium which could not have been obtained in this yield had the original compound contained hydridic hydrogen.

Tertiary Phosphine Complexes of Nickel(II) *and Palladium*(II).—New complex compounds of nickel(II) and palladium(II) which were isolated and characterised as a preliminary to the preparation of the corresponding zerovalent compounds are listed with their

---

* We do not intend to imply that two bonds are different from the other four. Since Pd(0) and Ni(0) are d^{10} atoms this is unlikely. Nevertheless two of the bonds may be very much more easily broken than any of the remaining four, just as one of the four equivalent bonds in NH_4^+ is much more readily broken by OH^- than any of the remaining three.

TABLE 2.

Ditertiary phosphine complexes of palladium(II) and nickel(II).

Compound	M. p.	Colour	Conductivity, Λ_M, at 23° (mhos cm.$^{-1}$)
$[Pd\{o\text{-}C_6H_4(PEt_2)_2\}_2]Br_2$	*ca.* 290°	White	198 *
$[Ni\{o\text{-}C_6H_4(PEt_2)_2\}_2](NO_3)_2$	200—220	Yellow	182,* 50·0 †
$[Ni\{C_2H_4(PPh_2)_2\}_2](NO_3)_2$	217—230	Orange	46·3 †
$[Pd\{C_2H_4(PPh_2)_2\}_2]Br_2$	*ca.* 240 ‡	White	(Insol.)
$[Pd\{CH_2(PPh_2)_2\}_2]Br_2$	313—316 ‡	Yellow	(Insol.)
$[Pd\{C_2H_4(PEt_2)_2\}_2](NO_3)_2$	283 ‡	White	193,* 40·5 †
$[PdCl_2o\text{-}C_6H_4(PEt_2)_2]$	350	White	(Insol.)
$[PdClPhP(o\text{-}C_6H_4{\cdot}PEt_2)_2]Cl$	322—330	Cream	26·6 †

* In water (2—3 × 10^{-3} g./c.c.). † In nitrobenzene (1 × 10^{-3} g./c.c.) ‡ With decomp.

properties in Table 2. They were all prepared by allowing two molecular proportions of the diphosphine to react with the bivalent metal salts in aqueous alcohol or aqueous acetone.

EXPERIMENTAL

M. p.s are corrected; those of the zerovalent metal compounds were determined *in vacuo*, unless otherwise stated. Those of the bivalent metal complexes were determined on a Kofler hot-stage. All manipulations involving phosphines or zerovalent metal complexes were carried out in a nitrogen atmosphere. Molecular weights were determined ebullioscopically in benzene.

Di-(1,2-*bisdimethylphosphinoethane*)*nickel* (II).—A solution of sodium naphthalenide, prepared by shaking naphthalene (2·66 g., 2·30 mol.) with an excess of sodium chips in tetrahydrofuran (50 c.c.), was added portionwise to a mixture of dibromo-1,2-dimethylphosphinoethanenickel[7] (3·33 g., 1·00 mol.) and the diphosphine (1·83 g., 1·35 mol.) in dry tetrahydrofuran (40 c.c.). The naphthalenide colour of each portion (*ca.* 5 c.c.) was allowed to fade before the next portion was added, and the suspended dibromo-complex slowly dissolved to give a pale yellow solution. Addition was stopped when the green colour persisted (*ca.* 3 c.c. not added). Tetrahydrofuran was removed from the mixture at 20 mm., and naphthalene at 80°/0·1 mm. The resulting brown residue was extracted with hot light petroleum (b. p. 80—100°) (20 c.c.); the extract, when concentrated and cooled, yielded the *nickel compound* (0·57 g., 17·4%), which was purified by sublimation at 100°/0·001 mm. (Found: C, 40·2; H, 8·8%; *M*, 0·759% solution, 366. $C_{12}H_{32}NiP_4$ requires C, 40·15; H, 9·0%; *M*, 359).

Di-(1,2-*bisdimethylphosphinoethane*)*palladium* (VIII).—As described for the nickel derivative (II), the complex $[PdBr_2C_2H_4(PMe_2)_2]$[8] (1·04 g.) in the presence of the diphosphine (0·67 g., 1·80 mol.) was reduced by sodium naphthalenide (2·00 mol.). Tetrahydrofuran and naphthalene having been removed, the residue was extracted with light petroleum (b. p. 80—100°). Crystallisation from the extract followed by further recrystallisations from light petroleum gave the pure *compound* (0·46 g., 45·5%) as prisms (Found: C, 35·7; H, 8·0%; *M*, 0·690% solution, 430. $C_{12}H_{32}P_4Pd$ requires C, 35·4; H, 7·9%; *M*, 407).

Reductions with Sodium Borohydride.—*General method.* A solution containing the cation $[ML_2]^{2+}$ or $[MLL']^{2+}$, where M = Ni or Pd, was prepared in acetone or ethanol either (*a*) by direct dissolution of the appropriate complex salt (*e.g.*, $[Pd\{o\text{-}C_6H_4(PEt_2)_2\}_2]Br_2$), (*b*) by adding the metal halide or nitrate to the hot solution of the ligand (2 mol.), or (*c*), for complexes [MLL'], by adding the ligand L' (1 mol.) to a suspension of the covalent halide $[MX_2L]$ and shaking the mixture until it became clear. The solutions thus obtained were of approximate concentration 1×10^{-4} to 2×10^{-4} molar, and were diluted with an equal volume of water. To this mixture a solution of sodium borohydride (3 mol.) in a small volume of water was added dropwise at room temperature. Hydrogen was evolved. The complex of the zerovalent metal was precipitated as a finely divided solid, and was separated, washed, and recrystallised from a suitable solvent. The following compounds were prepared in the above manner. Starting materials, reaction solvent, and yield are given in parentheses.

---

[7] Booth and Chatt, unpublished work.

[8] Chatt, Hart, and Rosevear, *J.*, 1961, 5504.

*[Bis-(*o*-diethylphosphinophenyl)phenylphosphine]triphenylphosphinepalladium* (I) ($[PdClPhP(o\text{-}C_6H_4PEt_2)_2]Cl$ and PPh_3 in ethanol) (11%) recrystallised from benzene–methanol (Found: C, 64·1; H, 5·95. $C_{42}H_{48}P_4Pd$ requires C, 64·4; H, 6·2%).

Di-(*o*-phenylenebisdiethylphosphine)nickel (III) ($[Ni\{o\text{-}C_6H_4(PEt_2)_2\}_2](NO_3)_2$ in acetone) (85%) recrystallised from benzene–methanol. [*Alternative method:* The complex nickel nitrate (0·50 g.) was boiled for 16 hr. in water (17 c.c.) and alcohol (3 c.c.) in the presence of hydrazine hydrate (0·6 c.c.). The identical product was filtered off and purified as above (0·14 g.).]

*Di-(*o*-phenylenebisdimethylarsine)nickel* (IV) ($[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2]Cl_2$ in ethanol) (24%) formed prisms from ethanol (Found: C, 37·9; H, 5·2; Ni, 9·3%; *M*, 0·60% solution, 672. $C_{20}H_{32}As_4Ni$ requires C, 38·1; H, 5·1; Ni, 9·3%; *M*, 631).

Di-(1,2-bisdiphenylphosphinoethane)nickel (V) ($[Ni\{C_2H_4(PPh_2)_2\}_2](NO_3)_2$ in acetone) (47%) crystallised from benzene–methanol and was identical with authentic material.

Di-[1,1,1-tris(diphenylphosphinomethyl)ethane]nickel, β-isomer, (VII) [$Ni(NO_3)_2,6H_2O$ and $CH_3{\cdot}C(CH_2{\cdot}PPh_2)_3$ [9] in ethanol]. The collected precipitate was dissolved in the minimum of warm benzene, and the solution was added with stirring to an excess of cold methanol. Repetition of such crystallisations, which caused deposition of minute needles, gave the pure nickel *β-isomer* (VII), m. p. (nitrogen-filled tube; immersion at 190°), 203—210° (Found: C, 75·3; H, 6·3%; *M*, 1·09% solution, 1300; 1·62% solution, 1327. $C_{82}H_{78}NiP_6$ requires C, 75·3; H, 6·0%; *M*, 1308). Heated slowly, the compound shrinks at *ca.* 200° and melts finally at 224—227° with decomposition.

Recrystallisation of the β-isomer from light petroleum (b. p. 80—100°) or from benzene–light petroleum (b. p. 30—40°) gives the pure *α-isomer,* as minute needles, m. p. (nitrogen-filled tube, immersion at 190° or 25°), 225—229° (decomp.) (Found: C, 75·7; H, 6·5%).

Di-(*o*-phenylenebisdiethylphosphine)palladium (IX) [Na_2PdCl_4 and $o\text{-}C_6H_4(PEt_2)_2$ in ethanol] (46%) recrystallised from benzene–ethanol and was identical with an authentic sample.[8] [*Alternative method:* The compound $[Pd\{o\text{-}C_6H_4(PEt_2)_2\}_2]Br_2$ (1·0 g.) in liquid ammonia (20 c.c.) was treated with sodium (0·074 g., 2·2 g.-atoms) in liquid ammonia (10 c.c.). After being stirred for 20 min., the ammonia was allowed to evaporate and the residue was twice crystallised from benzene–ethanol (0·25 g.; identical with authentic material).]

*Di-(*o*-phenylenebisdimethylarsine)palladium* (X) ($[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2]Cl_2$ in acetone) (37%) crystallised as needles from benzene–ethanol (Found: C, 35·6; H, 4·9%; *M*, 0·79% solution, 756; 1·39% solution, 720. $C_{20}H_{32}As_4Pd$ requires C, 35·4; H, 4·8%; *M*, 679).

Di(bisdiphenylphosphinomethane)palladium (XI) [Na_2PdCl_4 and $CH_2(PPh_2)_2$ in ethanol] (43%) recrystallised from benzene–methanol (Found: C, 68·2; H, 5·25%; *M*, 1·17% solution, 933; 1·95% solution, 946. $C_{50}H_{44}P_4Pd$ requires C, 68·5; H, 5·1%; *M*, 857).

Di-(1,2-bisdiphenylphosphinoethane)palladium (XII) ($[Pd\{C_2H_4(PPh_2)_2\}_2]Br_2$ in acetone) (68%) recrystallised from benzene–ethanol (Found: C, 69·3; H, 5·4%; *M*, 0·60% solution, 941; 1·16% solution, 877. $C_{52}H_{48}P_4Pd$ requires C, 69·2; H, 5·4%; *M*, 903).

Di-(1,1,1-trisdiphenylphosphinomethylethane)palladium, β-isomer (XIV) [K_2PdCl_4 in a little water added to $CH_3{\cdot}C(CH_2{\cdot}PPh_2)_3$ in ethanol]. The collected precipitate was dissolved in cold chloroform from which it crystallised as minute needles on the addition of cold methanol. Recrystallisation in this way gave the pure *β-isomer,* m. p. (nitrogen-filled tube; immersion at 191°), 194—195° to a yellow liquid, resolidifying almost immediately and melting finally to a brown liquid at 244—245° (Found: C, 72·5; H, 5·9. $C_{82}H_{78}P_6Pd$ requires C, 72·6; H, 5·8%). Heated slowly, the crystals shrink at 194° but do not melt until 245—246°.

The β-isomer (XIV), on crystallisation from benzene or light petroleum (b. p. 80—100°), yields the *α-isomer,* microcrystals, m. p. (nitrogen-filled tube; immersion at 25° or 191°), 247—248°, unchanged on admixture with isomer (XIV), with temperature of immersion 25° (Found: C, 72·1; H, 6·2%).

The nickel isomers are noticeably more soluble than their palladium analogues. Isomerism in the palladium series is distinct, and from a particular solvent only one isomer is deposited. In the nickel series, isomerism is less distinct, and many solvents give solids which appear from physical properties to be a mixture of α- and β-isomers. Furthermore, dipole moment measurements of either of the nickel isomers gave variable, rather high values (*e.g.*, $\mu = 3{\cdot}4, 3{\cdot}8$ D) suggesting the presence of a 5-co-ordinate complex in benzene solution.

---

[9] Hewertson and Watson, unpublished work.

o-*Phenylenebisdiethylarsine*-o-*phenylenebisdiethylphosphinepalladium* (XV) {[$PdCl_2$*o*-$C_6H_4(PEt_2)_2$] and *o*-$C_6H_4(AsEt_2)_2$ [10] in ethanol} (29%) crystallised from ethanol (Found: C, 48·4; H, 6·9%; *M*, 0·99% solution, 695; 2·00% solution, 653; 2·66% solution, 649. $C_{28}H_{48}As_2P_2Pd$ requires C, 47·8; H, 6·9%; *M*, 703).

o-*Phenylenebisdiethylphosphine*-o-*phenylenebisdimethylarsinepalladium* (XVI) {[$PdCl_2$*o*-$C_6H_4(PEt_2)_2$] and *o*-$C_6H_4(AsMe_2)_2$ in ethanol} crystallised from ethanol (Found: C, 44·7; H, 6·4. $C_{24}H_{40}As_2P_2Pd$ requires C, 44·6; H, 6·2%).

1,2-*Bisdiphenylphosphinoethane*-o-*phenylenebisdiethylphosphinepalladium* (XVII) {[$PdCl_2$*o*-$C_6H_4(PEt_2)_2$] and $C_2H_4(PPh_2)_2$ in ethanol} crystallised from benzene–methanol (Found: C, 63·0; H, 6·35%; *M*, 1·22% solution, 736; 1·60% solution, 739. $C_{40}H_{48}P_4Pd$ requires C, 63·3; H, 6·4%; *M*, 759).

o-*Phenylenebisdiethylphosphine*-1,1,1-*tris*(*diphenylphosphinomethyl*)*ethanepalladium* (XVIII) {[$PdCl_2$*o*-$C_6H_4(PEt_2)_2$] and $CH_3{\cdot}C(CH_2{\cdot}PPh_2)_3$ in ethanol}. The collected precipitate was twice recrystallised from benzene–methanol to give this *complex* as needles (0·51 g., 81%), m. p. 200—201° (nitrogen-filled tube, immersion at 25° or 190°) (Found: C, 67·4; H, 6·5%; *M*, 0·142% solution, 918. $C_{55}H_{63}P_5Pd$ requires C, 67·0; H, 6·4%; *M*, 985). Recrystallisation from benzene–light petroleum (40—60°) or light petroleum (b. p. 80—100°) did not change the m. p.

Reduction of Dichloro-o-*phenylenebisdiethylphosphinepalladium in the Presence of Triphenylphosphine*.—The compound [$PdCl_2$*o*-$C_6H_4(PEt_2)_2$] (0·50 g., 1 mol.) and triphenylphosphine (0·304 g., 1 mol.) were dissolved in hot ethanol (50 c.c.) and water (10 c.c.). The cooled solution was treated with water (10 c.c.), then sodium borohydride (0·132 g., 3 mol.) in water (10 c.c.). The collected precipitate (0·30 g.) was crystallised four times from benzene–methanol, giving yellow crystals of *tristriphenylphosphinepalladium*, m. p. (decomp.) *ca.* 120°, which soon darkened when kept in nitrogen (Found: C, 72·1; H, 5·2. $C_{54}H_{45}P_3Pd$ requires C, 72·6; H, 5·1%).

Action of Bromine on Di(*bisdiphenylphosphinomethane*)*palladium*.—The compound [$Pd\{CH_2(PPh_2)_2\}_2$] (0·77 g.) in ethylene dibromide (20 c.c.) was treated with bromine (0·139 g., 1 mol.) in ethylene dibromide (1·5 c.c.). Solvent having been removed, the residue was dissolved in acetone and this solution immediately deposited *dibromo*(*bisdiphenylphosphinomethane*)-*palladium* (0·40 g., 70%), that recrystallised from dimethylformamide (Found: C, 45·9; H, 3·4. $C_{25}H_{22}Br_2P_2Pd$ requires C, 46·1; H, 3·4%).

Complexes of Nickel(II) *and Palladium*(II).—Some of these compounds, formulated as salts, are probably 6-co-ordinated complexes in the solid state.[11] The degree of dissociation and the co-ordination number in solution will depend on the solvent and, in accord with the usual practice, they are named and formulated as 4-co-ordinate salts.

Di(*bisdiphenylphosphinomethane*)*palladium dibromide*. Sodium chloropalladite (1·47 g.) in alcohol (50 c.c.) was added with swirling to a solution of bisdiphenylphosphinomethane (3·86 g.) in alcohol (150 c.c.) at 70° and the mixture was heated on a steam-bath for 15 min. and then cooled. An excess of concentrated aqueous sodium bromide was added slowly, to precipitate orange crystals (3·80 g.). Repeated recrystallisation from aqueous methanol gave the pure *product*, m. p. 104—106°, as the dihydrate (Found: C, 56·15; H, 4·7. $C_{50}H_{48}Br_2O_2P_4Pd$ requires C, 56·1; H, 4·5%). This compound is very soluble in benzene and acetone, from which dioxan precipitates the yellow crystalline dibromobisdiphenylphosphinomethanepalladium, decomp. 313—316°.

Di-o-*phenylenebisdiethylphosphinepalladium dibromide*, [$Pd\{o\text{-}C_6H_4(PEt_2)_2\}_2]Br_2$. The diphosphine (1·84 g., 2 mol.) and palladium chloride (0·645 g., 1 mol.) were boiled in ethanol (7 c.c.) for 10 min. Excess of aqueous sodium bromide was added carefully to the cooled solution. The resulting precipitate was collected and crystallised from water. The pure *dibromide*, m. p. 320° (appears to lose diphosphine from *ca.* 290°), weighed 1·39 g. (Found: C, 43·7; H, 6·5. $C_{28}H_{48}Br_2P_4Pd$ requires C, 43·4; H, 6·2%).

Di-o-*phenylenebisdiethylphosphinenickel dinitrate*, [$Ni\{o\text{-}C_6H_4(PEt_2)_2\}_2](NO_3)_2$. Nickel nitrate hexahydrate (1·49 g.) in acetone (10 c.c.) was added to the diphosphine (2·6 g., 2 mol.) in acetone (10 c.c.). The precipitated *complex* recrystallised from aqueous acetone as yellow prisms (1·80 g.) (Found: C, 48·3; H, 7·3. $C_{28}H_{48}NiN_2O_6P_4$ requires C, 48·6; H, 7·0%).

Di-(1,2-*bisdiphenylphosphinoethane*)*nickel dinitrate*, [$Ni\{C_2H_4(PPh_2)_2\}_2](NO_3)_2$. The diphosphine (4·0 g., 2 mol.) was shaken with nickel nitrate hexahydrate (1·45 g., 1 mol.) dissolved

---

[10] Cochran, Hart, and Mann, *J.*, 1957, 2816.

[11] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.

in ethanol (50 c.c.) for 1 hr. The product (4·78 g.) was collected and twice crystallised from aqueous alcohol with large loss, giving the pure *dinitrate* (0·57 g.) (Found: C, 63·7; H, 5·0; N, 2·9. $C_{52}H_{48}NiN_2O_6P_4$ requires C, 63·8; H, 4·9; N, 2·9%).

Di-(1,2-*bisdiphenylphosphinoethane*)*palladium dibromide*, $[Pd\{C_2H_4(PPh_2)_2\}_2]Br_2$. The diphosphine (2·0 g., 2 mol.) was boiled under reflux with palladium chloride (0·455 g., 1 mol.) in ethanol (50 c.c.) for 10 min. The cooled solution was added to an excess of aqueous sodium bromide, and the collected product was crystallised from aqueous ethanol, to give the pure *dibromide* (1·30 g.) (Found: C, 58·5; H, 4·6. $C_{52}H_{48}Br_2P_4Pd$ requires C, 58·7; H, 4·55%).

Di-(1,2-*bisdiethylphosphinoethane*)*palladium dinitrate*, $[Pd\{C_2H_4(PEt_2)_2\}_2](NO_3)_2$. The diphosphine (2·39 g., 2 mol.) in acetone (20 c.c.) was treated with palladium nitrate (1·34 g., 1 mol.) in water (4 c.c.). The solvents were removed at 12 mm. and the white residue, when crystallised twice from dimethylformamide–acetone, gave the *dinitrate* (0·80 g.) of apparent decomposition point 283° (Found: C, 37·0; H, 7·6. $C_{20}H_{48}N_2O_6P_4Pd$ requires C, 37·4; H, 7·5%).

The complex, when treated with sodium borohydride or hydrazine under conditions similar to those described for other complexes, showed no evidence of reduction.

*Dichloro-*o-*phenylenebisdiethylphosphinepalladium*, $[PdCl_2o\text{-}C_6H_4(PEt_2)_2]$. The diphosphine (2·01 g., 1 mol.) was shaken with a solution of potassium chloropalladite (2·59 g., 1 mol.) in water (20 c.c.) and ethanol (2 c.c.). The buff precipitate was collected (3·45 g.) and boiled with dimethylformamide (50 c.c.) and concentrated hydrochloric acid (1 c.c.) for 5 min. The resultant solution was filtered and cooled, giving the *dichloro-complex* (1·70 g.), purified by recrystallisation from dimethylformamide (Found: C, 39·15; H, 5·65. $C_{14}H_{24}Cl_2P_2Pd$ requires C, 38·95; H, 5·6%).

Chloro-phenylbis-(o-*diethylphosphinophenyl*)*phosphinepalladium chloride*, $[PdClPhP(o\text{-}C_6H_4{\cdot}PEt_2)_2]Cl$. The triphosphine (0·687 g., 1 mol.) in ethanol (10 c.c.) was treated with sodium chloropalladite (0·47 g., 1 mol.) in dimethylformamide (5 c.c.). The ethanol was removed at 12 mm. and ether was carefully added. The white crystalline *product* was thrice recrystallised from water as white crystals (0·55 g.), which became very pale yellow on drying at 100°/0·01 mm., then having m. p. 322—330° (Found: C, 50·4; H, 5·7. $C_{26}H_{33}Cl_2P_3Pd$ requires C, 50·7; H, 5·4%).

Various Measurements.—Infrared spectra were measured from Nujol mulls with a Grubb–Parsons GS2A spectrometer.

X-Ray powder photographs were taken with a 6 cm. diameter camera and using Cu-K_α radiation. The ground samples were introduced into Lindemann-glass capillary tubes which were then sealed under nitrogen. Each pair of compounds, (III) and (IX), (VI) and (XIII), and (VII) and (XIV), gave powder photographs with very similar line spacings, with the variation in relative line intensities compatible with the difference in atomic number of nickel and palladium, and therefore the compounds of any pair are isomorphous. We thank Dr. Joan Rowe for the above interpretation.

The method of determination and notation for dipole moments (recorded in Table 3) are described in ref. 12.

TABLE 3.

Measurements for dipole-moment determinations.

Compound	$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	Compound	$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$
II	3·690	1·650	—	—	XII	5·059	0·964	—	—
	4·018	1·659	—	(0·36)	XIII	1·578	0·687	—	(0·40)
V	3·700	1·076	—	—	XIV	2·234	1·082	—	—
	4·805	1·000	—	—		7·176	1·091	—	(0·40)
	19·51	—	17·04	—	XV	18·54	0·696	—	—
	22·20	—	17·01	(0·36)		18·74	0·723	—	(0·40)
VIII	3·400	1·235	—	—	XVII	1·747	1·304	—	—
	6·416	1·202	—	(0·40)		3·122	1·259	—	(0·40)
IX	14·91	0·630	—	—	XVIII	4·620	1·738	—	(0·40)
	15·19	0·563	—	(0·40)					

Compound	${}_{T}P$	${}_{E}P$	${}_{O}P$	Compound	${}_{T}P$	${}_{E}P$	${}_{O}P$
II	196	(123)	54	XIII	477	(415)	0
V	368	279	47	XIV	579	(415)	101
VIII	184	(115)	51	XV	250	(202)	18
IX	206	(182)	−3	XVII	352	(227)	91
XII	363	(271)	51	XVIII	542	(299)	198

---

[12] Chatt and Shaw, *J.*, 1959, 705.

Nuclear magnetic resonance spectra of benzene solutions were kindly measured by Dr. N. Sheppard.

Carbon and hydrogen microanalyses were by the Microanalytical Department of these laboratories.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, HEAVY ORGANIC CHEMICALS DIVISION,
AKERS RESEARCH LABORATORIES, THE FRYTHE,
WELWYN, HERTS.

[*Received, November* 16*th*, 1961.]