

### 352. The Constitution of Complex Metallic Salts. Part XX.<sup>1</sup> The Co-ordinated Derivatives of 2-Phenylisophosphindoline with Cobalt, Rhodium, and Iridium Halides.

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2-Phenylisophosphindoline (I) combines with cobalt dihalides to give covalent compounds of composition  $[(C_{14}H_{13}P)_3CoX_2]$  (X = halogen). These 5-covalent cobalt compounds may have a structure similar to that of the analogous compound  $[(C_{14}H_{13}P)_3PdBr_2]$ , but unlike the latter they do not apparently, in organic solvents, give the isomeric salts  $[(C_{14}H_{13}P)_3CoX]X$ . In hot benzene solution they dissociate to form the normal derivatives of type  $[(C_{14}H_{13}P)_2CoX_2]$ .

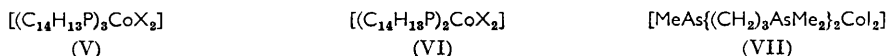
Rhodium trihalides behave normally with this phosphine, to give covalent compounds of type  $[(C_{14}H_{13}P)_3RhX_3]$ . Iridium trichloride and tribromide in boiling ethanol give compounds of type  $[(C_{14}H_{13}P)_3IrHX_2]$ , which with appropriate reagents pass readily into the corresponding compounds  $[(C_{14}H_{13}P)_3IrX_3]$ .

In Part XIX,<sup>1</sup> it was shown that 2-phenylisophosphindoline (I) combined with platinum(II), palladium(II), and nickel dihalides to give normal covalent complexes (II; M = metal, X = halogen) and also tris(phosphine) complexes (III). The nickel compounds (III), although readily isolated, were unstable in solution, and their structures were not investigated. The red palladium bromide compound (III; M = Pd, X = Br) has a covalent square-pyramid structure, with one bromine atom at the apex; in ethanolic solution, however, the compound acts as a salt of type (IV; M = Pd, X = Br). The platinum(II) compounds (III) also appeared to exist in certain solvents as salts (IV).



We have briefly investigated the ability of the phosphine (I) to form complexes with the halides of cobalt, rhodium, and iridium, in which the metal has an unusual valency or co-ordination number.

The phosphine (3 equivalents) readily combined with cobalt dichloride in ethanol to form the greenish-black monohydrated tris(phosphine)dichlorocobalt (V; X = Cl), and similarly with the dibromide and di-iodide to form the solvent-free purple dibromide (V; X = Br) and di-iodide (V; X = I). These compounds are covalent; they dissolve in



benzene, show normal molecular weights in dichloromethane solution at 23°, and their solutions in nitrobenzene are non-conducting. In warm ethanolic solution they gave no perceptible reaction with sodium perchlorate or tetraphenylborate. Although they cannot be readily recrystallised without decomposition, they are apparently more stable than the analogous nickel compounds.<sup>1</sup>

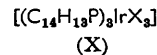
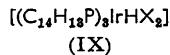
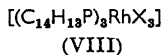
In boiling benzene they gave blue solutions, which on dilution with petroleum deposited the corresponding blue bis(phosphine)dihalogenocobalt (VI), of which the dichloro- and dibromo-members after crystallisation were dihydrated and the di-iodo member monohydrated. These compounds were also covalent, and gave non-conducting solutions in nitrobenzene; solutions of the dichloro- and dibromo-members in dichloromethane slowly decomposed, but the di-iodo-member showed a normal molecular weight.

There is at present no definite evidence for the structure of our tris(phosphine)cobalt

<sup>1</sup> Part XIX, Collier, Mann, D. G. Watson, and H. R. Watson, preceding paper.

compounds of type (V). It is noteworthy that the compound (VII), prepared by Barclay and Nyholm,<sup>2</sup> is the only other 5-co-ordinate cobaltous compound recorded; the corresponding nickel dibromide compound<sup>2,3</sup> has a square-pyramidal structure<sup>4</sup> closely similar to that of the red palladium dibromide compound (III; M = Pd, X = Br).<sup>1</sup> It is not unlikely, therefore, that our cobalt compounds (V) have a similar structure (although the monohydrated dichloride may possibly be a 6-co-ordinate compound). Indirect evidence for the square-pyramidal structure for our cobalt compounds (V) is that their electron spin resonance spectra indicate that they are paramagnetic, like compound (VII), and their infrared spectra show no evidence of a Co-H group.

The addition of the phosphine (3 mol.) to a warm aqueous ethanolic solution of sodium hexachlororhodate,  $\text{Na}_3\text{RhCl}_6$ , gave the bright yellow tris(phosphine)trichlororhodium (VIII; X = Cl). Treatment of the hexachlororhodate solution with sodium bromide or



iodide before addition of the phosphine gave the deep orange tribromide (XIII; X = Br) and the pale brown tri-iodide (XIII; X = I), respectively. These three compounds gave normal molecular weights in dichloromethane, and non-conducting nitrobenzene solutions; their infrared spectra showed no indication of Rh-H groups. The compounds are therefore normal 6-co-ordination derivatives of trivalent rhodium, and no indication of the formation of derivatives of uni- or bi-valent rhodium under our experimental conditions could be detected.

When an aqueous ethanolic solution of sodium chloroiridate,  $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ , and the phosphine (3 mol.) was boiled for 1 hour, working up gave the golden-yellow crystalline tris(phosphine)dichlorohydroiridium (IX; X = Cl), m. p. 188—189°, and treatment of the reaction mixture with sodium bromide before heating similarly gave the dibromohydro-derivative (IX; X = Br), m. p. 195—196°. Both compounds are diamagnetic, give non-conducting nitrobenzene solutions, and show normal molecular weights in dichloromethane. Their infrared spectra show strong Ir-H peaks, at 2080 and 2070  $\text{cm}^{-1}$ , respectively, and in benzene solution they have dipole moments of 5.55 and 5.50 D. In compounds of type  $[\text{L}_3\text{IrHX}_2]$ , where L is a ligand and X a halogen atom, values for  $\epsilon(\text{Ir-H})$  have been recorded: 2114,<sup>5</sup> 2100—2200,<sup>6</sup> 2230  $\text{cm}^{-1}$ .<sup>7</sup>

The dichlorohydro-derivative (IX; X = Cl), when heated with ethylene dichloride, carbon tetrachloride, or n-butyl chloride, or when treated with chlorine or hydrogen chloride, gave the tris(phosphine)trichloroiridium (X; X = Cl), m. p. 286—287°, and with ethylene dibromide gave the analogous bromodichloro-derivative. The dibromohydro-derivative (IX; X = Br), when treated with similar bromo-reagents, gave the tribromoiridium compound (X; X = Br), m. p. 317—318°. All four iridium compounds are diamagnetic.

The phosphine reacted quite differently with iridium tri-iodide. In boiling aqueous ethanolic solution it gave an initial product, orange crystals, m. p. 199—200°, which in boiling 1,2-dibromoethane gave orange crystals, m. p. 319—320°. Both compounds were paramagnetic, had, respectively, magnetic moments 1.8 and 1.7 B.M. and dipole moments 6.7 and 7.6 D, and gave non-conducting nitrobenzene solutions. The infrared spectrum of the first showed a marked peak at 2075  $\text{cm}^{-1}$ , whilst that of the second showed no peak in the 2200—1800  $\text{cm}^{-1}$  region. Although these properties, the analytical carbon and hydrogen values, and the molecular weight values in dichloromethane indicated that the

<sup>2</sup> Barclay and Nyholm, *Chem. and Ind.*, 1953, 378.

<sup>3</sup> Barclay, Nyholm, and Parish, *J.*, 1961, 4433.

<sup>4</sup> Mair, Powell, and Henn, *Proc. Chem. Soc.*, 1960, 415.

<sup>5</sup> Chatt and Shaw, *Chem. and Ind.*, 1960, 931.

<sup>6</sup> Vasca, *J. Amer. Chem. Soc.*, 1961, **83**, 756.

<sup>7</sup> Hayter, *J. Amer. Chem. Soc.*, 1961, **83**, 1259.

compounds were  $(R_3P)_3Ir(CO)I_2$  and  $(R_3P)_3IrI_2$ , respectively, inconsistent analytical values for iridium and iodine were obtained for the products from repeated preparations, and these formulæ cannot be accepted without further investigation. The formation of carbonyl compounds by the interaction of transition-metal complexes with boiling ethanol is however known.<sup>5</sup>

It is noteworthy that all attempts to combine diethylphenylphosphine with cobalt bromide gave only the blue bis(diethylphenylphosphine)dibromocobalt, and compounds of type (V) could not be isolated. Sodium chlororhodate with an excess of the phosphine also gave the normal yellow tris(diethylphenylphosphine)trichlororhodium, the infrared spectrum of which showed no evidence of a Rh-H group.

The tris(diethylphenylphosphine)trichloro (and tribromo)iridium compounds and their conversion into the hydridohalogeno-derivatives have been recorded by Chatt and Shaw.<sup>8</sup> We find that this phosphine in boiling aqueous acetone or methanol gives with iridium trichloride or tribromide the trihalogeno-compound with only a trace of the hydrido-derivative, but in aqueous ethanol gives a mixture of approximately equal quantities of each compound. The tri-iodo-compound can also be readily isolated, and in boiling ethanol gives tris(diethylphenylphosphine)hydridodi-iodoiridium, whose infrared spectrum shows the Ir-H band at  $2100\text{ cm.}^{-1}$ .

#### EXPERIMENTAL

The term "the phosphine" refers to 2-phenylisosphosphindoline unless otherwise stated. The term "petroleum" refers to light petroleum of b. p.  $60\text{--}80^\circ$ . Molecular weight determinations were carried out in dichloromethane solution at  $23^\circ$  by the vapour-pressure thermistor method.

*Tris-(2-phenylisosphosphindoline)dihalogenocobalt (V).*—The dropwise addition of the phosphine (0.32 g., 3 mol.) in ethanol (5 ml.) to cobalt chloride hexahydrate (0.12 g.) in ethanol (10 ml.) gave a deep blue solution, which, when warmed for 5 min. and cooled, deposited the *dichloride monohydrate* (V; X = Cl) as deep greenish-black crystals, m. p.  $183\text{--}184^\circ$  after washing with ethanol and ether (Found: C, 63.7; H, 5.3%; M, 730.  $C_{42}H_{39}Cl_2CoP_3H_2O$  requires C, 64.2; H, 5.2%; M, 784). The *dibromide*, similarly prepared, formed crystals, m. p.  $181\text{--}183^\circ$ , which appeared almost black by reflected light and deep blue-purple by transmitted light (Found: C, 58.6; H, 4.9%; M, 786.  $C_{42}H_{39}Br_2CoP_3$  requires C, 58.9; H, 4.7%; M, 855). The *di-iodide* formed similarly coloured crystals, m. p.  $176\text{--}178^\circ$  (Found: C, 52.4; H, 4.0%; M, 908.  $C_{42}H_{39}CoI_2P_3$  requires C, 53.1; H, 4.2%; M, 949).

*Bis(phosphine)dihalogenocobalt (VI).*—Each member of this type could be obtained from the corresponding member of type (V) by (a) boiling a benzene solution for 1 hr. and diluting with petroleum, when on cooling the compound (VI) crystallised out, or (b) adding methyl iodide to a cold benzene solution, and after *ca.* 30 min. collecting the precipitated mixture of the compound (VI) and the phosphine methiodide,<sup>9</sup> from which the latter was readily extracted with warm ethanol. The compounds (VI) were all recrystallised from acetone-petroleum, giving: the "duck-egg blue" dihydrated *dichloride* (VI; X = Cl), m. p.  $192\text{--}193^\circ$  (Found: C, 57.1; H, 4.8.  $C_{28}H_{26}Cl_2CoP_2 \cdot 2H_2O$  requires C, 57.1; H, 5.0%); the turquoise dihydrated *dibromide*, m. p.  $183\text{--}184^\circ$  (Found: C, 49.6; H, 4.4.  $C_{28}H_{26}Br_2CoP_2 \cdot 2H_2O$  requires C, 49.5; H, 4.7%); the turquoise monohydrated *di-iodide*, m. p.  $176\text{--}178^\circ$  (Found: C, 44.9; H, 4.1%; M, 740.  $C_{28}H_{26}CoI_2P_2 \cdot H_2O$  requires C, 44.5; H, 4.0%; M, 755).

The preparation of the compounds (VI; X = Cl, Br, or I) by the direct union of the appropriate cobalt dihalide and the phosphine (2 mol.) in hot ethanol proved unsatisfactory, a mixture containing mainly the compounds of type (V) and (VI) being obtained.

*Tris-(2-phenylisosphosphindoline)trihalogenorhodium (VIII).*—The three compounds were all recrystallised from aqueous acetone. A solution of the phosphine (0.318 g., 3 mol.) in ethanol (15 ml.), when added to a warm solution of sodium hexachlororhodate dihydrate<sup>10</sup> (0.210 g.) in water (30 ml.) and ethanol (10 ml.), caused the deep red colour to fade to yellow, with precipitation of the bright yellow hygroscopic *trichloride monohydrate* (VIII; X = Cl), m. p.

<sup>8</sup> Chatt and Shaw, *Chem. and Ind.*, 1961, 290; see also Adams, *Proc. Chem. Soc.*, 1961, 431.

<sup>9</sup> Mann, Millar, and Stewart, *J.*, 1954, 2832.

<sup>10</sup> Mann, *J.*, 1933, 412.

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263—264° (Found: C, 58.5; H, 4.9%; M, 782.  $C_{42}H_{39}Cl_3P_3Rh, H_2O$  requires C, 58.4; H, 4.7%; M, 863). Repetition of this experiment, with the addition of sodium bromide or iodide (4 g.) before the phosphine, gave, respectively, the orange *tribromide*, m. p. 278—280° (Found: C, 51.3; H, 4.05%; M, 929.  $C_{42}H_{39}Br_3P_3Rh$  requires C, 51.5; H, 4.0%; M, 978), and the pale brown tri-iodide, m. p. 269—270° (Found: C, 45.6; H, 3.9%; M, 1080.  $C_{42}H_{39}I_3P_3Rh$  requires C, 45.3; H, 3.6%; M, 1119).

*Tris-(2-phenylisosphosphindoline)dihalogenohydrido-iridium* (IX).—The phosphine (0.636 g., 3 mol.) in ethanol (5 ml.) was added to a solution of sodium chloroiridate,  $Na_2IrCl_6, 6H_2O$  (0.560 g.) in water (20 ml.) and ethanol (10 ml.), and boiled under reflux for 1 hr., the colour fading rapidly to green and then to yellow. On cooling, the initial deposit of yellow crystals became contaminated with pink material. The mixed deposit was digested with boiling ethanol or acetone, and the clear solution, when diluted with a small quantity of water and cooled, deposited the *dichlorohydrido-compound* (IX; X = Cl), golden yellow needles, m. p. 188—189° (Found: C, 55.8; H, 4.6%; M, 872.  $C_{42}H_{40}Cl_2IrP_3$  requires C, 56.0; H, 4.3%; M, 900).

Repetition of this experiment, with the addition of sodium bromide (2 g.) before the phosphine, again gave a mixed product which, treated as before, afforded the orange-yellow crystalline *dibromo-hydrido-compound* (IX; X = Br), m. p. 195—196° (Found: C, 50.4; H, 4.2%; M, 992.  $C_{42}H_{40}Br_2IrP_3$  requires C, 50.5; H, 4.0%; M, 989).

*Tris(phosphine)trichloroiridium* (X; X = Cl) was obtained when the compound (IX; X = Cl) was (i) repeatedly recrystallised from chloroform-petroleum, (ii) boiled under reflux with carbon tetrachloride (1 hr.), n-butyl chloride (2 hr.), or 1,2-dichloroethane (8 hr.), (iii) warmed with an aqueous dimethylformamide solution of sodium chloroiridate, (iv) treated in cold ethereal solution with chlorine or hydrogen chloride. The *trichloro-compound* formed bright yellow crystals, m. p. 285—287° (from chloroform-ether) (Found: C, 53.9; H, 4.4; Cl, 11.4; Ir, 20.6%; M, 900.  $C_{42}H_{39}Cl_3IrP_3$  requires C, 53.9; H, 4.3; Cl, 11.6; Ir, 20.8%; M, 935). The compound (IX; X = Cl), when boiled with 1,2-dibromoethane for 8 hr., gave the dark yellow *bromodichloro-compound* (as X), m. p. 306—307° (from aqueous dimethylformamide) (Found: C, 51.3; H, 4.3.  $C_{42}H_{39}BrCl_2IrP_3$  requires C, 51.4; H, 4.0%).

The compound (IX; X = Br), when similarly boiled under reflux with ethyl bromide, n-butyl bromide, or 1,2-dibromoethane, or heated with molten carbon tetrabromide, or treated in ether with bromine or hydrogen bromide, gave the orange-yellow *tribromo-compound* (X; X = Br), m. p. 317—318° (from ethyl bromide-petroleum) (Found: C, 46.8; H, 3.65; Ir, 18.0%; M, 1040.  $C_{42}H_{39}Br_3IrP_3$  requires C, 47.1; H, 3.6; Ir, 17.8%; M, 1068).

*Derivatives of Diethylphenylphosphine*.—The bis(phosphine)dibromocobalt, prepared by the action of the phosphine on hydrated cobalt chloride, both in ethanolic solution, formed turquoise needles, m. p. 80.5—81° (lit.,<sup>11</sup> 80—82°) (Found: C, 43.7; H, 6.9. Calc. for  $C_{20}H_{30}Br_2CoP_2$ : C, 43.5; H, 5.5%). A solution of sodium chlororhodate dihydrate (0.39 g.) in aqueous ethanol (15 ml., 2:1 v/v), when treated with the phosphine (0.5 g., 3 mol.) in ethanol (5 ml.), heated at 100° for 10 min., and cooled, deposited the orange-yellow *tris(phosphine)trichlororhodium*, m. p. 173—174° (from aqueous acetone) (Found: C, 52.1; H, 6.8.  $C_{30}H_{45}Cl_3P_3Rh$  requires C, 52.3; H, 6.7%).

The phosphine (0.6 g., 4 mol.) in ethanol (5 ml.) was added to a solution of sodium chloroiridate hexahydrate (0.56 g.) in aqueous ethanol (25 ml.), boiled under reflux for 20 min., and cooled. The deposited bright yellow crystals, when recrystallised from carbon tetrachloride-petroleum afforded the *tris(phosphine)trichloroiridium*, m. p. 240—241° (decomp.) (lit.,<sup>12</sup> 235—241°) (Found: C, 45.3; H, 5.6. Calc. for  $C_{30}H_{45}Cl_3IrP_3$ : C, 45.2; H, 5.6%). The addition of sodium bromide (2 g.) to the above reaction mixture before boiling, with recrystallisation of the product from n-butyl bromide-petroleum, gave the orange-yellow tribromo-derivative, m. p. 221—222° (decomp.) (lit.,<sup>12</sup> 235—250°) (Found: C, 38.65; H, 4.8. Calc. for  $C_{30}H_{45}Br_3IrP_3$ : C, 38.65; H, 4.8%). (The difference in m. p.s may result from our values being determined in capillary tubes and those in ref. 12 on a Kofler block.) The similar addition of sodium iodide (2 g.), with crystallisation of the product from n-butyl iodide-petroleum, gave the *tris(phosphine)tri-iodoiridium*, m. p. 209—210° (Found: C, 35.4; H, 4.1.  $C_{30}H_{45}I_3IrP_3$  requires C, 35.6; H, 4.2%). An ethanolic solution of this compound when boiled for 1 hr. yielded the *tris(phosphine)hydridodi-iodoiridium*, orange needles, m. p. 164—166° (Found:

<sup>11</sup> Chatt and Shaw, *J.*, 1961, 285.

<sup>12</sup> Chatt, Field, and Shaw, *J.*, 1963, 3371.

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C, 37.9; H, 5.2.  $C_{30}H_{46}I_2IrP_3$  requires C, 38.1; H, 4.9%). The mixed solvents used for recrystallisation (developed before the paper in ref. 12 was available) were found to give the highest yields of the trihalogeno-compounds. All the above metallic derivatives of this phosphine gave non-conducting nitrobenzene solutions.

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