

1078. *The Reaction of Metals with o-Phenylenebis(diethylphosphine).*

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o-Phenylenebisdiethylphosphine reacts with finely divided cobalt, nickel, and palladium at about 200° to form zerovalent complexes of type $[M\{o-C_6H_4(PEt_2)_2\}_2]$. It does not react with metals neighbouring on these in Group VIII except in the presence of hydrogen. Then it reacts with iron to form a dihydride *trans*- $[FeH_2\{o-C_6H_4(PEt_2)_2\}_2]$ and with rhodium to form a salt of uncertain structure.

THE direct combination of uncharged ligands and metals to form complexes of the metals in their zerovalent states is rare. Until recently the only examples were the combination of carbon monoxide with nickel, iron, and (with difficulty) cobalt, molybdenum, tungsten, rhodium, and ruthenium, to form the metal carbonyls;¹ and of methylchlorophosphine with metallic nickel to form $[Ni(PMeCl_2)_4]$.² The recent discovery³ that *o*-phenylenebis(diethylphosphine)⁴ combines with metallic nickel to form $[Ni\{o-C_6H_4(PEt_2)_2\}_2]$ has led us to examine its reaction with neighbouring metals in Group VIII.

We have found that the diphosphine dissolves finely divided cobalt and palladium at

¹ Mattern and Gill in "The Chemistry of the Co-ordination Compounds," ed. J. C. Bailar, Jr., Chapman and Hall, Ltd., London 1956, p. 511, and references therein.

² Quin, *J. Amer. Chem. Soc.*, 1957, **79**, 3681.

³ Chatt and Hart, *J.*, 1960, 1378.

⁴ Hart, *J.*, 1960, 3324.

about 200° under nitrogen to form complexes of the formula $[M\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_2]$ ($M = \text{Co}$ or Pd) but does not react with finely divided iron, ruthenium, rhodium, or platinum. Under hydrogen reaction occurs with iron to form a dihydride *trans*- $[\text{FeH}_2\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_2]$, and with rhodium to form a complex which was obtained in such poor yield that its composition is still uncertain. Cobalt does not form $[\text{CoH}\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_2]$ under hydrogen but yields the same product as is formed under nitrogen. Neither ruthenium nor platinum reacts under hydrogen.

The permanganate-coloured cobalt compound, $[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_2]$, is obtained only in poor yield. It sublimes at 160°/0.01 mm. and is so soluble in all organic solvents which do not react with it that it could not be freed entirely from metallic cobalt by recrystallisation. It reacts with hydroxylic solvents and is immediately destroyed by air. We therefore made a more thorough study of the analogous complex $[\text{Co}(\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2)_2]$ which is easier to manipulate and is obtained by reduction of $\text{CoBr}_2(\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2)_2$ with sodium borohydride. This is monomeric in benzene solution, has a magnetic moment of 1.36 B.M., and is isomorphous with the corresponding nickel³ and palladium⁵ complexes.

By analogy with $\text{Ni}(\text{CO})_4$ and other 4-co-ordinated d^{10} -complexes we should expect these complex compounds of nickel(0) and palladium(0) to have essentially tetrahedral configurations. We therefore presume that the isomorphous cobalt d^9 complex has a tetrahedral rather than the alternative planar configuration. Molecular models indicate that a dimeric diamagnetic structure with a Co-Co bond would be very unfavourable sterically. Thus this paramagnetic cobalt(0) complex occupies the same position amongst tetrahedral complexes as do the paramagnetic $[\text{V}(\text{CO})_6]$ ⁶ and $[\text{V}(\text{Me}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PMe}_2)_3]$ ⁷ amongst octahedral complexes of zerovalent metals.

The complex $[\text{Pd}\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_2]$ is the only palladium(0) complex to have been obtained directly from metallic palladium and a ligand. It is formed rather more slowly than the analogous nickel(0) complex³ and has an almost identical infrared spectrum over the range 4000—450 cm^{-1} . It is a paler orange and is rather less sensitive to air. We presume that it has a tetrahedral configuration.

The dihydridoiron complex *trans*- $[\text{FeH}_2\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_2]$ was formed in only 7% yield by the direct action of finely divided (pyrophoric) iron on the diphosphine under hydrogen at 200° for 60 hr. In the presence of mercury the yield was increased to 25%. The hydridic proton had a magnetic resonance at $\tau = 23.1$. This resonance should be split into five bands by the four equivalent phosphorus nuclei, but only the three strong centre bands were observed. The *trans*-arrangement was confirmed by the low electric dipole moment, which was, however, not measured accurately because in benzene solution the substance is readily oxidised to highly dipolar products. The corresponding dideuteride, prepared under deuterium, was contaminated with hydride because of hydrogen exchange with the ligand. In the infrared spectra $\nu_{\text{Fe-H}}$ occurs at 1726 cm^{-1} , and $\nu_{\text{Fe-D}}$ at 1259 cm^{-1} in the dihydride and dideuteride, respectively.

The orange-yellow rhodium complex had the composition $\text{Rh}_n\text{H}_n\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_3$, where n is unknown and may be zero because the infrared spectrum gives no evidence of hydridic hydrogen. It was obtained in too small a quantity to establish its exact nature, but it is an electrolyte in acetone solution and has a magnetic moment μ_{eff} of 1.8 B.M. It may be a complex hydride of general formula, $[\text{RhH}_r\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_n][\text{RhH}_y\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_{3-n}]$ ($n \leq 3$), related to Farr's "rhodium hydryls."⁸

Preliminary studies show that $\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2$ has similar power to dissolve metals.

⁵ Chatt, Hart, and Watson, unpublished results.

⁶ Natta, Ercoli, Calderazzo, Alberola, Corradini, and Allegra, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1959, **27**, 107.

⁷ Chatt and Watson, *Nature*, 1961, **189**, 1003.

⁸ Farr, *J. Inorg. Nucl. Chem.*, 1960, **14**, 202.

EXPERIMENTAL

In this work a nitrogen-filled glove-box was used. Samples for determination of m. p. were contained in evacuated tubes.

Di-o-phenylenebisdiethylphosphinepalladium, $[\text{Pd}\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_2]$.—The diphosphine (1.43 g.) and palladium black (0.90 g.), obtained by magnesium reduction of ammonium chloropalladate(II) in aqueous hydrochloric acid, were heated under nitrogen at 200° for 3 hr. The cooled product was extracted with boiling benzene (25 c.c.), and the cold extract filtered and then evaporated to smaller bulk. Addition of methanol gave orange crystals (0.10 g.) of the *complex*, m. p. 229–230° after two crystallisations from benzene–methanol (Found: C, 54.4; H, 8.0%; *M*, ebullioscopically in 1.17% benzene solution, 564; in 2.09% solution, 632. $\text{C}_{28}\text{H}_{48}\text{P}_4\text{Pd}$ requires C, 54.7; H, 7.9%; *M*, 615).

Di-o-phenylenebisdiethylphosphinecobalt, $[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_2]$.—Cobalt (1.66 g.) (obtained by heating cobalt oxalate at 20 mm.) was heated at 200° with the diphosphine (1.23 g.) for 65 hr. The product was extracted with benzene, the extract filtered, and the solvent removed in a stream of nitrogen, leaving a red-black powder (0.16 g.). Sublimation at 160°/0.01 mm. resulted in some decomposition but also gave 0.015 g. of permanganate-coloured *complex* (Found: C, 58.7; H, 8.65. $\text{C}_{28}\text{H}_{48}\text{CoP}_4$ requires C, 59.25; H, 8.6%). The substance is very soluble in most organic solvents, except alcohols, which appear to decompose it, and it is instantly decomposed by air.

Dibromodi-1,2-bisdiphenylphosphinoethanecobalt, $\text{CoBr}_2\{\text{C}_2\text{H}_4(\text{PPh}_2)_2\}_2$.—A solution of cobalt bromide (1.20 g.) in methanol (10 c.c.) was added to a stirred suspension of the diphosphine (3.0 g., 2 mols.) in methanol (50 c.c.). The resulting solution was evaporated to dryness at 12 mm. and the residue, after crystallisation from 3 : 1 ethanol–water (20 c.c.), gave the *complex* as pleochroic black crystals (2.53 g.), decomp. 120–125°, having a green streak (Found: C, 61.9; H, 5.2. $\text{C}_{52}\text{H}_{48}\text{Br}_2\text{CoP}_4$ requires C, 61.5; H, 4.8%). This complex ionised in nitrobenzene ($\Lambda_m = 14.0$ at 26°) to a smaller extent than a uni-univalent electrolyte. Addition of water to its ethanolic solution caused decomposition with precipitation of the diphosphine.

Di-1,2-bisdiphenylphosphinoethanecobalt, $[\text{Co}\{\text{C}_2\text{H}_4(\text{PPh}_2)_2\}_2]$.—A solution of the dibromocompound described above (1.48 g.) in ethanol (75 c.c.) and water (25 c.c.) was treated with a solution of sodium borohydride (0.166 g., 3 mol.) in water (2 c.c.). The resulting orange precipitate was collected, dried (1.07 g.), and crystallised from benzene–methanol and then from dimethylformamide, giving red crystals of the *complex*, m. p. 280° (decomp.) (Found: C, 72.7; H, 5.9%; *M*, in 1.17% benzene solution, 844; in 1.35% solution, 849. $\text{C}_{52}\text{H}_{48}\text{CoP}_4$ requires C, 73.0; H, 5.65%; *M*, 856). After exposure to hydrogen at 200° for 30 min. the *complex* showed no evidence of a Co–H stretching band in the infrared spectrum.

Dihydrodi-o-phenylenebisdiethylphosphineiron, $[\text{FeH}_2\{o\text{-C}_6\text{H}_4(\text{PET}_2)_2\}_2]$.—Iron powder (1.57 g.) (obtained by heating ferrous oxalate at 20 mm.) was heated with the diphosphine (2.07 g.) and mercury (2 c.c.) under hydrogen at 200° for 88 hr. The product was extracted with benzene, and the extract filtered and evaporated to dryness. Trituration with cold acetone left orange crystals (0.58 g.) which after crystallisation from light petroleum (b. p. 80–100°) gave the pure *product* (0.35 g.), m. p. 248–249.5°; the approximate dipole moment was 1.8 D (Found: C, 59.3; H, 9.0%; *M*, ebullioscopically in 0.753% benzene solution, 557; in 1.879% solution, 565. $\text{C}_{28}\text{H}_{50}\text{FeP}_4$ requires C, 59.4; H, 8.9%; *M*, 566). The dideuteride was prepared similarly, but at 150° to minimise hydrogen–deuterium exchange: the presence of deuterium in the ligand was shown by the infrared spectrum of the product prepared at higher temperatures.

Action of o-Phenylenebisdiethylphosphine on Rhodium.—The diphosphine (1.91 g.) was heated with rhodium powder (0.91 g.) at 200° for 4 days under hydrogen. The acetone extract, on addition of light petroleum (b. p. 60–80°), gave a product which was redissolved in acetone and reprecipitated with benzene as orange crystals (0.2 g.), m. p. 360–362° (Found: C, 52.35; H, 7.8%). No reaction was observed when rhodium and the diphosphine were heated in an evacuated and sealed tube.

Action of o-Phenylenebisdiethylphosphine on Other Metals.—The diphosphine (1.0 g.) was heated with (a) platinum black (1.3 g.) at 250° for 4½ hr. under carbon dioxide and (b) with ruthenium black (0.50 g.) at 200° for 21 hr. under hydrogen. In neither case was a solid product detected.

The dipole moments were determined as described in ref. 9 and the nuclear magnetic resonance and infrared spectra as in ref. 10.

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⁹ Chatt and Shaw, *J.*, 1960, 1718.

¹⁰ Chatt and Hayter, *J.*, 1961, 2605.
