590. *Some Complexes of Ditertiary Phosphines with Nickel*(II) *and Nickel*(III)

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Complexes of bivalent nickel of the types [NiX_2(diphosphine)] and [NiX_2(diphosphine)$_2$] (X = Cl, Br, or I) where diphosphine = $Ph_2P{\cdot}CH_2{\cdot}PPh_2$ or $R_2P{\cdot}C_2H_4{\cdot}PR_2$ (R = Me, Et, or Ph) are described. Tervalent nickel is exemplified in the following complexes [$NiBr_3(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)$], [$NiX_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2$]X, and [$NiBr_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2$][$Br_3$].

Several complexes of ditertiary phosphines with nickel halides are known. Chatt and Hart[1] prepared the complexes [$NiCl_2(Et_2P{\cdot}C_2H_4{\cdot}PEt_2)$], [$NiX_2\{o\text{-}C_6H_4(PEt_2)_2\}$] (X = Cl, Br, or I) and [$NiBr_2\{o\text{-}C_6H_4(PEt_2)_2\}_2$] by halogenation of the corresponding nickel(0) complexes, and Wymore and Bailar[2] have described the direct preparation of [$NiX_2(Et_2P{\cdot}C_2H_4{\cdot}PEt_2)$], [$Ni(Et_2P{\cdot}C_2H_4{\cdot}PEt_2)_2$]$(ClO_4)_2$, and [$NiBr_3(Et_2P{\cdot}C_2H_4{\cdot}PEt_2)$]. In this Paper we shall describe a comparative study of the nickel derivatives of four diphosphines, $R_2P{\cdot}C_2H_4{\cdot}PR_2$ (R = Me, Et, or Ph) and $Ph_2P{\cdot}CH_2{\cdot}PPh_2$, and their relation to the nickel complexes of *o*-phenylenebisdimethylarsine (dias).[3-5]

Complexes of Nickel(II).—1,2-Bis(diethylphosphino)ethane, even when used in excess, has previously been reported to form only the complexes [$NiX_2(Et_2P{\cdot}C_2H_4{\cdot}PEt_2)$] through reaction with nickel halides.[2] We now find that [$NiX_2(Et_2P{\cdot}C_2H_4{\cdot}PEt_2)_2$] is first formed, although one molecule of diphosphine readily breaks away, and only where X = I could a stable 2 : 1 complex be isolated. 1,2-Bis(dimethylphosphino)ethane behaves similarly, but the 2 : 1 complexes, [$NiX_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2$], which are formed even with the reactants in equimolecular proportions, are somewhat more stable, perhaps owing to lower steric interaction between the ligand molecules. The order of stability is again X = I > Br > Cl but, in this case, only the chloro-complex was too unstable to be isolated in a pure state. These alcohol-soluble 2 : 1 complexes are readily converted to the corresponding insoluble 1 : 1 complexes on treatment with nickel halide.

1,2-Bis(diphenylphosphino)ethane precipitates [$NiX_2(Ph_2P{\cdot}C_2H_4{\cdot}PPh_2)$] from alcoholic nickel halide solutions. The 2 : 1 complexes are more difficult to prepare and are much less deeply coloured than the analogous complexes from the aliphatic diphosphine. However, the pale yellow [$NiBr_2(Ph_2P{\cdot}C_2H_4{\cdot}PPh_2)_2$] forms red solutions in non-aqueous solvents.

The diphosphines $R_2P{\cdot}C_2H_4{\cdot}PR_2$ thus differ from *o*-phenylenebisdimethylarsine, which only forms stable 2 : 1 complexes [$NiX_2(dias)_2$] with nickel halides,[3] although unstable complexes of the type [NiX_2(dias)] have been prepared by halogenation [5] of [$Ni(CO)_2$(dias)].

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[1] J. Chatt and F. A. Hart, *J.*, 1960, 1378.
[2] C. E. Wymore and J. C. Bailar, *J. Inorg. Nuclear Chem.*, 1960, **14**, 42.
[3] R. S. Nyholm, *J.*, 1950, 2061.
[4] R. S. Nyholm, *J.*, 1951, 2602.
[5] R. S. Nyholm, *J.*, 1952, 2906.

The complexes $[NiX_2(R_2P{\cdot}C_2H_4{\cdot}PR_2)]$ are electrically non-conducting in nitrobenzene. They show anomalous magnetic properties, indicating that in this respect the chelate diphosphine complexes are similar to those of certain monophosphines. Indeed, $[NiCl_2(Ph_2P{\cdot}C_2H_4{\cdot}PPh_2)]$ exists in two distinct crystalline forms, dull orange needles in which the nickel has $\mu_{eff} = 1{\cdot}34$ B.M. and diamagnetic yellow-brown plates. The low magnetic moments of many samples might be explained if the paramagnetic and diamagnetic forms of the molecule crystallised together, cf. $[NiBr_2(PBzPh_2)_2]$,[6] but the magnetic moments of the solids are uncertain quantities and tend to change on storage.

The 2 : 1 complexes $[NiX_2(R_2P{\cdot}C_2H_4{\cdot}PR_2)_2]$ behave as uni-univalent electrolytes in nitrobenzene solutions, when R = Me or Et, but have a somewhat lower conductivity when R = Ph. They are presumably octahedrally co-ordinated in the solid and dissociate in nitrobenzene, as do the complexes [7] $[MX_2(dias)_2]$ (M = Ni, Pd, or Pt).

Bis(diphenylphosphino)methane differs from the other diphosphines described here, since it appears to behave as a monodentate ligand in $[NiX_2(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2]$, so resembling more closely $Ph_2P{\cdot}PPh_2$.[8] However, in complexes where the metal atom has a greater affinity for tertiary phosphines, *e.g.*, palladium and platinum, chelate complexes are obtained from $Ph_2P{\cdot}CH_2{\cdot}PPh_2$.[9,10]

Carbon monoxide did not react with the complexes $[NiX_2(Ph_2P{\cdot}C_2H_4{\cdot}PPh_2)]$ or $[NiX_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)]$ to give carbonyl complexes under conditions where complexes of the type $[NiX_2(PR_3)_2]$ react readily.[11] Nevertheless, the expected products $[Ni(CO)_2(Ph_2P{\cdot}C_2H_4{\cdot}PPh_2)]$ and $[Ni(CO)_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)]$ are readily prepared from nickel carbonyl.[1]

Complexes of Nickel(III).—The complex $[NiBr_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)]$ is readily oxidised with bromine to $[NiBr_3(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)]$. The properties of this complex ($\mu_{eff} =$ 2·12 B.M.; non-conductor in nitrobenzene) are in accord with a five-covalent nickel(III) complex, but it could equally well be an octahedral polymer as suggested for the analogous[2] $[NiBr_3(Et_2P{\cdot}C_2H_4{\cdot}PEt_2)]$. The complex $[NiBr_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2]$ is oxidised by air in the presence of hydrobromic acid to the very stable complex formulated as $[NiBr_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2]Br$ on the basis of its electrical conductivity in nitrobenzene solution and its magnetic properties. 1,2-Bis(dimethylphosphino)ethane thus resembles dias, which readily forms[3] $[NiBr_2(dias)_2]Br$, more closely than 1,2-bis(diphenylphosphino)ethane, since $[NiBr_2(Ph_2P{\cdot}C_2H_4{\cdot}PPh_2)_2]$ is not similarly oxidised.

An attempt to prepare a complex of nickel(IV) analogous to Nyholm's[4] unstable $[NiX_2(dias)_2]X_2$, failed. The action of bromine on $[NiBr_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2]Br$ gave a further tervalent nickel complex, $[NiBr_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2](Br_3)$. This formulation is supported by the electron spin resonance spectrum of the complex, which is very similar to the spectrum of $[NiBr_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2]Br$. Evidently the aliphatic diphosphines do not stabilise the quadrivalent state of nickel in the way that the *o*-phenylene diarsine does.

EXPERIMENTAL

Reactions involving free diphosphines were carried out under nitrogen. Evaporations were carried out at *ca.* 20 mm. pressure. Molar conductivities were determined in nitrobenzene at 23°, the new complexes are non-conducting except where stated.

Dichloro-{1,2-*bis*(*dimethylphosphino*)*ethane*}*nickel*(II), $[NiCl_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)]$.—A solution of hydrated nickel chloride (2·38 g.) in ethanol (20 c.c.) was added to 1,2-bis(dimethylphosphino)ethane (3·06 g.) in ethanol (50 c.c.). The resulting solution was evaporated to low volume, and then acetone (50 c.c.) and benzene (100 c.c.) were added to give orange crystals (3 g.) of the unstable dichlorodi-{1,2-bis(dimethylphosphino)ethane}nickel. This impure 2 : 1 complex

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[6] B. T. Kilbourn, H. M. Powell, and J. A. C. Darbyshire, *Proc. Chem. Soc.*, 1963, 207.
[7] C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J.*, 1960, 4379.
[8] K. Issleib and G. Schwager, *Z. anorg. Chem.*, 1961, **310**, 43.
[9] J. Chatt, F. A. Hart, and H. R. Watson, *J.*, 1962, 2537.
[10] G. Booth and J. Chatt, unpublished work.
[11] G. Booth and J. Chatt, *J.*, 1962, 2099.

(1 g.) and hydrated nickel chloride (1 g.) in ethanol (12 c.c.) were heated under reflux for ½ hr. A bronze solid was precipitated, which redissolved at the boil on addition of further ethanol (600 c.c.). The *product* crystallised as golden yellow plates (0·63 g.) (Found: C, 25·7; H, 5·8. $C_6H_{16}Cl_2NiP_2$ requires C, 25·75; H, 5·75%); μ_{eff} = 1·23 B.M.

Dibromodi-{1,2-*bis*(*dimethylphosphino*)*ethane*}*nickel*(II) [$NiBr_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2$].—The diphosphine (3 g.) was added to a solution of hydrated nickel bromide (2·75 g.) in water (2 c.c.) and ethanol (20 c.c.). The resulting solution was evaporated down to a volume of 10 c.c. to give orange crystals (3·6 g.) of the *complex* (Found: C, 28·0; H, 6·3. $C_{12}H_{32}Br_2NiP_4$ requires C, 27·8; H, 6·2%). Molar conductivity 20·8 ohm^{-1} (5 × 10^{-3}M). A further quantity (1 g.) of less pure 2 : 1 complex was obtained on addition of ether to the ethanol filtrate.

Dibromo-{1,2-*bis*(*dimethylphosphino*)*ethane*}*nickel*(II) [$NiBr_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)$].—The crude 2 : 1 complex (1 g.), precipitated as above, in ethanol (25 c.c.) was heated under reflux (under nitrogen) for 1 hr. The 1 : 1 *complex* crystallised as glistening bronze plates (Found: C, 19·65; H, 4·45. $C_6H_{16}Br_2NiP_2$ requires C, 19·55; H, 4·35%).

Di-iododi-{1,2-*bis*(*dimethylphosphino*)*ethane*}*nickel*(II) [$NiI_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2$].—The 2 : 1 dibromo-complex (0·5 g.) in water (10 c.c.) was treated with potassium iodide (0·5 g.) in water (5 c.c.). Orange-red needles of the 2 : 1-di-iodo-*complex* slowly crystallised (Found: C, 23·85; H, 5·4. $C_{12}H_{32}I_2NiP_4$ requires C, 23·5; H, 5·25%); molar conductivity 26·5 ohm^{-1} (2·4 × 10^{-3}M). On heating the 2 : 1 complex in ethanolic solution (under nitrogen) with nickel iodide, *di-iodo-*{1,2-*bis*(*dimethylphosphine*)*ethane*}*nickel*(II) crystallised as dark brown prisms (Found: C, 15·6; H, 3·5. $C_6H_{16}I_2NiP_2$ requires C, 15·6; H, 3·5%).

Tribromo-{1,2-*bis*(*dimethylphosphino*)*ethane*}*nickel*(III) [$NiBr_3(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)$].—Dibromo-{1,2-bis(dimethylphosphino)ethane}nickel (0·25 g.) in chloroform (240 c.c.) was treated with a solution of bromine (0·055 g.) in chloroform (15 c.c.). The *product* was precipitated as black crystals (Found: C, 15·85; H, 3·6. $C_6H_{16}Br_3NiP_2$ requires C, 16·05; H, 3·6%); μ_{eff} = 2·12 B.M.

Dibromodi-{1,2-*bis*(*dimethylphosphino*)*ethane*}*nickel*(III) *Bromide* [$NiBr_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2$]Br.—A mixture of dibromodi-{1,2-bis(dimethylphosphino)ethane}-nickel (1 g.), ethanol (30 c.c.), and concentrated hydrobromic acid (3 c.c.) was heated under reflux for 4 hr. with a stream of air blowing over the surface. When the solution was cooled the *product* crystallised as dark brown plates (0·95 g.) which were recrystallised from ethanol (Found: C, 23·6; H, 5·35. $C_{12}H_{32}Br_3NiP_4$ requires C, 24·05; H, 5·4%); molar conductivity 24·9 ohm^{-1} (0·65 × 10^{-3}M); μ_{eff} = 2·05 B.M.

Di-iododi-{1,2-*bis*(*dimethylphosphino*)*ethane*}*nickel*(III) *Iodide* [$NiI_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2$]I.—A solution of di-iododi-{1,2-bis(dimethylphosphino)ethane}nickel (0·6 g.) in ethanol (600 c.c.) and hydriodic acid (8 c.c.) was heated under reflux and in a stream of air for 4 hr. When the solution was cooled the *product* crystallised as dark brown prisms (0·4 g.) (Found: C, 18·9; H, 4·3. $C_{12}H_{32}I_3NiP_4$ requires C, 19·45; H, 4·35%); molar conductivity 22·9 ohm^{-1} (3·5 × 10^{-3}M).

Dibromodi-{1,2-*bis*(*dimethylphosphino*)*ethane*}*nickel*(III) *Tribromide* [$NiBr_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)_2$][$Br_3$]—Dibromodi-{1,2-bis(dimethylphosphino)ethane}nickel bromide (0·1 g.) in ethanol (20 c.c.) was treated with a solution of bromine (0·018 g.) in carbon tetrachloride (0·1 c.c.). The *product* was precipitated as small light brown prisms (Found: C, 18·95; H, 4·3; Br, 51·35. $C_{12}H_{32}Br_5NiP_4$ requires C, 19·0; H, 4·25; Br, 52·65%); molar conductivity 23·0 ohm^{-1} (1·5 × 10^{-3}M); μ_{eff} = 2·02 B.M.

Di-iododi-{1,2-*bis*(*diethylphosphino*)*ethane*}*nickel*(II) [$NiI_2(Et_2P{\cdot}C_2H_4{\cdot}PEt_2)_2$].—Dibromo-{1,2-bis(diethylphosphino)ethane}nickel[2] (1 g.) in acetone (50 c.c.) was treated with 1,2-bis-(diethylphosphino)ethane (0·63 g.). On cooling to 0°, orange crystals of the unstable dibromodi-{1,2-bis(diethylphosphino)ethane}nickel separated. These were dissolved in water and the solution treated with aqueous potassium iodide. The resultant precipitate was crystallised from aqueous methanol to give the 2 : 1 *di-iodo-complex* as dark red needles (Found: C, 32·95; H, 6·6. $C_{20}H_{48}I_2NiP_4$ requires C, 33·15; H, 6·65%); molar conductivity 26·3 ohm^{-1} (1·85 × 10^{-3}M).

Dichloro-{1,2-*bis*(*diphenylphosphino*)*ethane*}*nickel*(II) [$NiCl_2(Ph_2P{\cdot}C_2H_4{\cdot}PPh_2)$].—A solution of 1,2-bis(diphenylphosphino)ethane (4 g.) in warm ethanol (400 c.c.) was added to hydrated nickel chloride (2·4 g.) in ethanol (20 c.c.). The *product* crystallised as dull orange feathery needles (Found: C, 59·3; H, 4·8. $C_{26}H_{24}Cl_2NiP_2$ requires C, 59·15; H, 4·6%). The filtrate deposited more of the complex as glistening yellow-brown platelets (Found: C, 59·0; H, 4·8%).

Dibromo-{1,2-bis(diphenylphosphine)ethane}nickel(II) [$NiBr_2(Ph_2P{\cdot}C_2H_4{\cdot}PPh_2)$].—Prepared in a similar way from nickel bromide and the diphosphine the *complex* was obtained as small dull red prisms (Found: C, 50·2; H, 4·15. $C_{26}H_{24}Br_2NiP_2$ requires C, 50·6; H, 3·9%).

Dibromodi-{1,2-bis(diphenylphosphino)ethane}nickel(II) [$NiBr_2(Ph_2P{\cdot}C_2H_4{\cdot}PPh_2)_2$].—Dibromo-{1,2-bis(diphenylphosphino)ethane}nickel (3·1 g.) and 1,2-bis(diphenylphosphino)ethane (2 g.) were dissolved in methylene chloride (100 c.c.). The resulting red solution was evaporated to dryness, the residue was washed with acetone then crystallised from aqueous ethanol (1 : 1) to give the complex as yellow prisms (Found: C, 60·85; H, 4·85. $C_{52}H_{48}Br_2NiP_4$ requires C, 61·5; H, 4·75%); molar conductivity 11·9 ohm^{-1} (2·3 × 10^{-3}M).

Di-iododi-{1,2-bis(diphenylphosphino)ethane}nickel(II) [$NiI_2(Ph_2P{\cdot}C_2H_4{\cdot}PPh_2)_2$].—A solution of the 2 : 1 dibromo-complex (0·5 g.) in 50% aqueous ethanol (30 c.c.) was treated with an aqueous solution of sodium iodide (0·5 g.). An intermediate, pink, gelatinous precipitate rapidly changed to bright yellow prisms (0·46 g.) of the *product* (Found: C, 55·9; H, 4·6. $C_{52}H_{48}I_2NiP_4$ requires C, 56·3; H, 4·35%); molar conductivity 8·7 ohm^{-1} (2 × 10^{-3}M).

Dibromodi{bis(diphenylphosphino)methane}nickel(II) [$NiBr_2(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2$].—Hydrated nickel bromide (1·36 g.) in water (1 c.c.) was added to a solution of bis(diphenylphosphino)-methane (1·92 g.) in ethanol (300 c.c.). The resulting solution was concentrated to 50 c.c. to give the *complex* as dark red plates, m. p. 115—117°, from ethanol (Found: C, 60·6; H, 4·75. $C_{50}H_{44}Br_2NiP_4$ requires C, 60·8; H, 4·5%).

Dicarbonyl{1,2-bis(dimethylphosphino)ethane}nickel(0) [$Ni(CO)_2(Me_2P{\cdot}C_2H_4{\cdot}PMe_2)$].—Nickel carbonyl (3·4 g.) was added during 30 min. to a solution of 1,2-bis(dimethylphosphino)ethane (3 g.) in ether (30 c.c.). Carbon monoxide was evolved and the reaction completed by heating under reflux for 1 hr. The resulting solution was filtered and evaporated to give the *product* as cream prisms, m. p. (evacuated tube) 70—73° (Found: C, 35·4; H, 6·0%; *M*, ebullioscopically in 0·8% benzene solution, 265. $C_8H_{16}O_2P_2Ni$ requires C, 36·25; H, 6·1%; *M*, 265); dipole moment 5·2 D; ν_{CO} (in ethylene dichloride solution) γ_{CO} 1994 and 1929 cm.$^{-1}$. The complex is unstable in air and smells of diphosphine.

Analyses.—Microanalyses were carried out by the Microanalytical Department of these laboratories.

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