491. *Complexes of Zerovalent Transition Metals with the Ditertiary Phosphine,* $Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2$.

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The ditertiary phosphine, $Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2$, is shown to form complexes of the types $[M(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_3]$ (M = V, Cr, Mo, or W) and $[M(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2]$ (M = Fe or Co) of essentially octahedral planar and tetrahedral configuration, respectively, by reduction of higher-valent complexes with sodium naphthalenide ($NaC_{10}H_8$) in tetrahydrofuran. They are thermally stable but very sensitive to oxidation by air. Their colours range from almost black (vanadium) to pale yellow (tungsten).

TERTIARY phosphines, owing to their capacity to form π-type bonds to transition metals, can stabilise low-valent states.[1] The extent of this effect is under investigation in these laboratories. The preparation of complexes of cobalt(0),[2] nickel(0),[3,4] palladium(0),[3] platinum(0),[5] and molybdenum(0) [6] is now well established, and here we describe the extension of this work to metals from all of the remaining transition-metal Groups with the diphosphine $Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2$. Of the first transition series, only titanium(0) and manganese(0) failed to form thermally stable complexes with this diphosphine. Copper(0) gave only an indefinite result. The part of this work concerning complexes of vanadium(0), chromium(0), molybdenum(0), and tungsten(0) has already been the subject of a preliminary communication.[7]

Types of Compound.—Vanadium and the metals of the chromium group form 6-co-ordinated complexes of the type $[M(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_3]$, iron and cobalt form 4-co-ordinated complexes, $[M(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2]$, of planar and tetrahedral configuration, respectively. The iron compound was prepared by reduction of the dichloride *trans*-$[FeCl_2(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2]$, and the remainder by reduction of the appropriate metal halide in solution in an excess of the diphosphine.

Methods of Reduction.—The compounds of the zerovalent metals with this purely aliphatic diphosphine are destroyed by hydroxylic solvents and were therefore prepared in tetrahydrofuran.

Lithium aluminium hydride was satisfactory for the preparation of the complexes of the zerovalent metals of the chromium group, but its use is restricted to systems where stable metal–hydrogen bonds are not formed, as they are during the reduction of *trans*-$[FeCl_2(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2]$.[8] Sodium naphthalenide is the most versatile reducing agent we have found but even it gave a hydrido-complex, apparently by taking hydrogen

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[1] Chatt, *J. Inorg. Nuclear Chem.*, 1958, **8**, 515.
[2] Chatt, Hart, and Rosevear, *J.*, 1961, 5504.
[3] Chatt, Hart, and Watson, preceding paper.
[4] Chatt and Hart, *J.*, 1960, 1378.
[5] Chatt and Rowe, *Nature*, 1961, **191**, 1191.
[6] Chatt and Watson, *Proc. Chem. Soc.*, 1960, 243.
[7] Chatt and Watson, *Nature*, 1961, **189**, 1003.
[8] Chatt and Hayter, *J.*, 1961, 5507.

from the naphthalene, in the attempted preparation of $[M(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$ (M = Ru or Os). This reaction is still under investigation. The metal halide undergoing reduction is present in tetrahydrofuran solution as a diphosphine complex, as shown by the change of colour on dissolution, but we have not attempted to isolate and characterise it. Addition of the reducing agent to most systems is accompanied by successive colour changes indicating stepwise reduction. For example, the solution of vanadium trichloride is deep green and as reduction proceeds it passes through distinct stages of blue (V^{2+}), pale brown (V^{1+}), and deep brown (V^0).

Choice of $Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2$ *as Ligand.*—In our previous work [3-5] various chelate diphosphines were compared and the aromatic diphosphines were found to give less reactive complexes of zerovalent metals than did the aliphatic one $Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2$. However, because the diphosphines $R_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PR_2$ (R = Et or Ph) and $o\text{-}C_6H_4(PEt_2)_2$ are destroyed by sodium naphthalenide and lithium aluminium hydride, we were unable to prepare their complexes with zerovalent metals by the above method and were compelled to use the otherwise less desirable $Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2$. It reacts only slowly with sodium naphthalenide, reaction being complete after about one hour in absence of the transition-metal halide.

Six-co-ordinate Complexes.—The complexes $[M(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_3]$ (M = V, Cr, Mo, or W) have closely similar physical properties. Those of the chromium group are yellow, paling with increasing molecular weight. Models show the molecules to be extraordinarily compact, and in accord with this the substances have high melting points (*ca.* 250—400°) and are sparingly soluble in benzene and light petroleum, indicating a high lattice energy. They are more soluble in chloroform but are quickly decomposed by it. Nevertheless the molybdenum derivative is sufficiently stable for ebullioscopic measurements and we were able to show that it is monomeric in chloroform.[6] The chromium-group compounds have almost identical infrared spectra and we conclude that they are isostructural. Since they are d^6-complexes an essentially octahedral structure is presumed.

The deep brown vanadium derivative (d^5) is paramagnetic ($\mu_{\text{eff}} = 2{\cdot}10 \pm 0{\cdot}25$ B.M.) and crystallises from benzene in the rare habit of rhombic dodecahedra.

All the above substances oxidise rapidly in air, in the order $V > Cr > Mo \gg W$.

Four-co-ordinate Complexes.—In contrast with the above 6-co-ordinated complexes, the orange crystals of the cobalt(0) compound $[Co(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$ are soft, waxy, and have a low melting point. They dissolve in less than their own weight of benzene and are extremely soluble even in light petroleum. High solubility seems to be a characteristic of cobalt(0) complexes with diphosphines.[2] The compound sublimes at 65° in a high vacuum, and reaction with iodine gives no hydrogen iodide, indicating the absence of hydridic hydrogen. Magnetic measurements were variable, which we attribute to traces of metallic cobalt. However, the solid is isomorphous with the corresponding nickel compound,[3] thus indicating an essentially tetrahedral configuration, exactly analogous to the aromatic analogue $[Co(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$,[2] which, being more tractable, was examined more thoroughly.

The brown iron(0) complex $[Fe(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$ is diamagnetic and being a d^8-complex has presumably a planar configuration, perhaps with metal–metal interaction between the molecules because the crystals are harder, of higher melting point, and much less soluble than those of the corresponding cobalt(0) and nickel(0) derivatives. The alternative tetrahedral configuration would require paramagnetism corresponding to two unpaired electrons. Reaction with iodine gives a complex *trans*-$[FeI_2(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$ with no hydrogen iodide. This is the only 4-co-ordinate planar iron(0) compound to have been described.

Reduction of Other Systems.—Only carbon-free precipitates were isolated from attempts to prepare complexes of titanium(0) and manganese(0). The red titanium tetrachloride–diphosphine solution underwent successive colour changes during reduction, but the manganese chloride solution did not.

EXPERIMENTAL

M. p.s are corrected and were determined in sealed nitrogen-filled tubes. Molecular weights were determined ebullioscopically in benzene. Solvents were dried and de-gassed; tetrahydrofuran was distilled from sodium diphenylketyl and stored under nitrogen in sealed ampoules. All operations were carried out in dry nitrogen.

Preparation of Sodium Naphthalenide Solutions.—Naphthalene was dissolved in tetrahydrofuran (*ca.* 25 c.c. per 1 g. of naphthalene); the addition of sodium chips (in *ca.* 150% excess) caused immediate formation of the deep green colour of the naphthalenide ion. The mixture having been shaken for 3 hr., the solution was decanted from the agglomerated ball of sodium. Titrations indicated that the yield of sodium naphthalenide ($NaC_{10}H_8$) was about 90%.

Tri-(1,2-bisdimethylphosphinoethane)vanadium(0), $[V(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_3]$.—A suspension of vanadium trichloride (1·09 g.) in tetrahydrofuran (25 c.c.) was boiled with the diphosphine (3·27 g., 3·15 mol.) for 15 min. to give a clear apple-green solution. Sodium naphthalenide (naphthalene; 2·92 g., 3·3 mol.) solution was added dropwise to the cooled mixture. The naphthalenide colour was discharged immediately; the solution colour passed through deep lavender-blue to pale brown and was finally deep brown. Sodium chloride separated during the addition. Tetrahydrofuran and naphthalene having been removed at 16 mm. and 0·01 mm., respectively, the residue was extracted with portions of boiling benzene (*ca.* 1000 c.c. total) until the filtered extracts were no longer deep brown. Concentration followed by hot filtration and cooling gave the vanadium(0) *complex* (1·06 g., 38%); this formed black rhombododecahedra, giving a chocolate-brown streak, m. p. 253—254° (decomp.), on further recrystallisation (Found: V, 10·4. $C_{18}H_{48}P_6V$ requires V, 10·2%), μ (solid at 25°) 2·10 ± 0·25 B.M. The compound in air rapidly effloresces to a moist lavender powder. (All the octahedral complexes appear to have low temperature-coefficients of solubility, and were crystallised in the above way, by dissolution in a necessarily large volume of benzene followed by crystallisation from the greatly supersaturated solution.)

Tri-(1,2-bisdimethylphosphinoethane)chromium(0), $[Cr(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_3]$.—Dropwise addition of sodium naphthalenide (naphthalene, 2·26 g., 3·45 mol.) to the deep purple solution of the 1 : 3 solvate of chromic chloride and tetrahydrofuran[9] (1·90 g.) and the diphosphine (2·28 g., 3·0 mol.) in tetrahydrofuran (25 c.c.) caused colour changes through deep green to yellow. Tetrahydrofuran and naphthalene having been removed from the resulting mixture, the residue was extracted with benzene, the concentrated extracts yielding the chromium(0) *complex* (0·62 g., 25%) as bright yellow granules, m. p. *ca.* 293° (decomp.), reversibly becoming red at *ca.* 200° (Found: C, 42·9; H, 9·6; Cr. 10·1. $C_{18}H_{48}CrP_6$ requires C, 43·0; H, 9·6; Cr, 10·35%).

Alternative Method with Lithium Aluminium Hydride.—A solution of chromic chloride–tetrahydrofuran solvate and the diphosphine (3 mol.) was treated with portions of lithium aluminium hydride until hydrogen evolution ceased. Subsequent working-up as above gave the chromium(0) complex (28%), identical with the sample prepared as above.

Tri-(1,2-bisdimethylphosphinoethane)molybdenum(0).—A mixture of molybdenum pentachloride and the diphosphine (4·0 mol.) was reduced as above with lithium aluminium hydride. Removal of solvent and extraction of the residue with benzene, followed by crystallisation, gave the molybdenum(0) derivative (11% yield), identical with the authentic material.[6] The compound can also be prepared by reduction with sodium naphthalenide (the $MoCl_5$ having been treated with two mol. of naphthalenide before the diphosphine is added), but very difficult filtration in the extraction stages makes the method inconvenient.

Tri-(1,2-bisdimethylphosphinoethane)tungsten(0), $[W(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_3]$.—Lithium aluminium hydride was added in small portions to a solution of tungsten hexachloride (1·47 g.) in tetrahydrofuran (50 c.c.) until the solution became very deep brown. The diphosphine (1·75 g., 3·15 mol.) was added to the mixture, which was then heated to boiling and treated with further portions of lithium aluminium hydride until hydrogen evolution ceased. Tetrahydrofuran having been removed, the resulting gum was washed with light petroleum (b. p. 80—100°) and extracted with hot benzene. The extracts, on concentration, yielded the tungsten(0) *derivative* (0·230 g., 10%) as pale yellow granules, m. p. 396° (decomp. after 350°) (Found: C, 34·1; H, 7·7. $C_{18}H_{48}P_6W$ requires C, 34·1; H, 7·6%).

[9] Herwig and Zeiss, *J. Org. Chem.*, 1958, **23**, 1404.

Di-(1,2-*bisdimethylphosphinoethane*)*iron*(0), [Fe($Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2$].—Sodium naphthalenide solution (naphthalene, 1·80 g., 2·2 mol.) was added dropwise to a solution of *trans*-[$FeCl_2\{C_2H_4(PMe_2)_2\}_2$] [8] in tetrahydrofuran (50 c.c.). The green colour of the naphthalenide was discharged immediately. With about half of the solution added, the mixture was yellow-brown and, with addition complete, it was deep red-brown. Tetrahydrofuran and naphthalene having been removed, the residual brown gum was extracted with light petroleum (b. p. 40—60°) (*ca.* 250 c.c.). The extracts, on concentration, gave the *iron*(0) *derivative* (0·774 g., 35%); it recrystallised from light petroleum (b. p. 40—60°) as russet-brown plates, m. p. 205° (prior decomp.) (Found: C, 40·4; H, 9·1%; *M*, in 0·501% solution, 380. $C_{12}H_{32}FeP_4$ requires C, 40·5; H, 9·1%; *M*, 356). The compound is diamagnetic; magnetic measurement of the solid indicated a weak paramagnetism, probably due to traces of iron, but the absence of interference in the nuclear magnetic resonance spectrum of the scrupulously filtered benzene solution indicates lack of paramagnetic behaviour. In air, the solid compound is oxidised rapidly, darkening and evolving the phosphine; its solutions deposit a black sludge immediately.

Oxidation with Iodine.—A solution of iodine (0·142 g., 1 mol.) in benzene (5 c.c.) was added slowly to the complex [Fe($Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2$] (0·199 g.) in benzene (5 c.c.). The iodine colour was discharged immediately, and the brown of the iron(0) compound paled progressively. The pale yellow-brown precipitate was combined with the yellow crystalline residue from the benzene solution (total, 0·314 g., 92%) and on recrystallisation from benzene gave pure trans-*di-iododi-*(1,2-*bisdimethylphosphinoethane*)*iron*(II), yellow-green plates, m. p. 373—380° (prior decomp.) (Found: C, 23·5; H, 5·3. $C_{12}H_{32}FeI_2P_4$ requires C, 23·6; H, 5·3%). A small portion of the initial benzene solution was extracted with (*a*) water and (*b*) sodium hydrogen carbonate solution: extract (*a*) was neutral and (*b*) gave a negative test for the iodide ion. This evidence, together with the absence of bands attributable to ν(Fe–H) in the infrared spectrum, proves that the compound contains no iron–hydrogen bond.

Di-(1,2-*bisdimethylphosphinoethane*)*cobalt*(0), [Co($Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2$].—A mixture of anhydrous cobalt chloride [10] (1·525 g.) and the diphosphine (3·87 g., 2·20 mol.) in cold tetrahydrofuran (50 c.c.) was shaken until a clear blue solution resulted. Sodium naphthalenide solution (naphthalene, 3·30 g., 2·20 mol.) was added dropwise. The naphthalenide colour faded immediately; with about half of the reagent added, the solution was yellow-brown and, with addition complete, was deep brown. Tetrahydrofuran and naphthalene having been removed, the residue was extracted with light petroleum (b. p. 80—100°). With solvent removed from the extract at 20 mm., the residue was distilled at 0·01 mm. The *cobalt*(0) *derivative* (1·105 g., 26%) distilled at 120—125° (bath-temperature) and then sublimed at 65°/0·001 mm. as pale orange needles, m. p. 101—102° (Found: C, 39·7; H, 8·5%; *M*, 1·180% solution, 366. $C_{12}H_{32}CoP_4$ requires C, 40·1; H, 9·0%; *M*, 359). In air the crystals are slowly oxidised, being completely decomposed to a green slime during some hours; but when a crystal is lightly scratched (*e.g.*, on one corner) a black zone speeds across it and it then emits black smoke and inflames. Dilute solutions in air deposit a black sludge immediately: concentrated ones inflame.

Reduction of Titanium Tetrachloride–Diphosphine Mixture.—A solution of titanium tetrachloride and the diphosphine (3·3 mol.) in tetrahydrofuran was cooled to −78° and whilst being stirred was titrated with a solution of sodium naphthalenide (4 mol.). The naphthalenide colour is discharged immediately. Successive colour changes occurred, each stage representing 1 mol. of reagent, and so probably reduction steps are as follows: Initial, red-orange, Ti^{4+}; deep blue-green, Ti^{3+}; deep yellow-brown, Ti^{2+}; deep red-brown, Ti^{+}. The addition of the final mol. of reagent caused deposition of a black carbon-free precipitate, presumably titanium, from a colourless solution.

Reduction of Other Systems.—The anhydrous halides $NbCl_5$, $MnCl_2$, or UCl_4, admixed with an excess of the diphosphine $C_2H_4(PMe_2)_2$ in tetrahydrofuran, were reduced with sodium naphthalenide under conditions corresponding to those described above. In each system a black carbon-free sludge, apparently the metal, was deposited. A similar attempt to prepare a manganese(I) complex also failed.

Various Measurements.—Infrared spectra were recorded from Nujol mulls on a Grubb–Parsons GS2A spectrometer. The spectra of the complexes are simple; those of vanadium(0), chromium(0), molybdenum(0), and tungsten(0) are almost identical. The spectrum of the iron(0) compound shows marked differences from those of the octahedral and tetrahedral series.

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[10] Watt, Gentile, and Helverston, *J. Amer. Chem. Soc.*, 1955, **77**, 2752.

Magnetic measurements were taken with a Faraday-type quartz-microbalance at 25° by Dr. J. F. Gibson. Solids were sealed under nitrogen in Lindemann-glass capillaries which had previously been calibrated for diamagnetic correction.

Dipole moment measurements were made as described previously.[11] The values for *trans*-di-iododi-(1,2-bisdimethylphosphinoethane)iron(II) are: $\Delta^3\omega$, 4·28; $\Delta\varepsilon/\omega$, 0·422; $-\Delta v/\omega$, (0·554); $_{\mathrm{T}}P$, 156*; $_{\mathrm{E}}P$, (126); $_{\mathrm{O}}P$, 11·6*; $\mu = 0{\cdot}75^*$ D.

X-Ray powder photographs were taken with a 6 cm. diameter camera and Cu-K_α radiation. Under nitrogen, ground samples of a complex $[\mathrm{M(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2}]$ (M = Co or Ni) were introduced into Lindemann-glass capillary tubes which were then sealed. The two compounds are isomorphous; we thank Dr. Joan Rowe for this interpretation.

Carbon and hydrogen analyses are by the Microanalytical Department at these laboratories; samples were admixed with potassium dichromate to obtain complete combustion.

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