

306. *Tervalent Phosphorus-Nitrogen Chemistry. Part II.*¹ *Mono- and Bis-(diphenylphosphino)alkylamines.*

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Methyl, ethyl, and n-propyl mono- and bis-(diphenylphosphino)alkylamines have been prepared. The bis(diphenylphosphino)alkylamines can be converted into the corresponding dioxides and disulphides; 1:1 alkyl iodide adducts and 1:1 complexes with nickel(II) and palladium(II) salts are formed.

THE reaction of chlorodiphenylphosphine with secondary alkylamines has been reported,^{1,2} Primary alkylamines similarly led to compounds with either >P-NHR or >P-NR-P< skeletons ($\text{R} = \text{Me, Et, or Pr}^n$). The isolation of the >P-NHR compounds is complicated, in the examples studied, by the elimination of amine and the consequent formation of >P-NR-P< compounds. This reaction appears to proceed most readily with the methyl analogue, as with the corresponding Si-NHR compounds.³ The conversion of >P-NHR into >P-NR-P< is accelerated by refluxing under reduced pressure, the nitrogen-bridged compound being readily isolated by crystallisation. Yields of only up to 60% of the >P-NR-P< have been obtained; the occurrence of side-reactions, leading to yields below the theoretical value, is currently under investigation.

The methyl-, ethyl-, and n-propyl-bis(diphenylphosphino)alkylamines behave as diphosphines in many of their reactions. Oxidation with ozone,⁴ or with activated manganese dioxide,² gives the corresponding dioxides. The phosphinoalkylamines show no great tendency to oxidation, although prolonged storage leads to the formation of a small amount of phosphoryl impurity [detected by the appearance of a band at 1200 cm.^{-1} in the infrared (i.r.) spectrum].

Addition of sulphur to the bis(diphenylphosphino)alkylamines occurs readily to give the corresponding disulphides. With alkyl iodides only the 1:1 adducts have been

¹ Part I is considered to be: Ewart, Payne, Porte, and (in part) Lane, *J.*, 1962, 3984.

² Sisler and Smith, *J. Org. Chem.*, 1961, **26**, 611, 4733, 5145.

³ Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p. 341.

⁴ Berlin and Butler, *Chem. Rev.*, 1960, **60**, 243.

prepared, this being in line with the tetra-alkyldiphosphines⁵ in which only one of the phosphorus atoms appears able to undergo quaternisation. Tetraphenyldiphosphine undergoes scission with methyl iodide to give dimethyldiphenylphosphonium iodide.⁶ In certain of the quaternary salts of the bis(diphenylphosphino)alkylamines, the yields have been low, and any attempt to obtain further material by evaporation of the solvent has led to products which have not so far been identified, but which may be the result of such a scission. In one preparation of the n-propyl iodide adduct of the propyl compound, the initial product from the ethereal solution was contaminated with a compound of higher iodide and nitrogen content, which was not the 1 : 2 adduct, since its nitrogen value was too high. Owing to its hygroscopic nature, this compound was not investigated further.

The reaction between methyl iodide and the bis(diphenylphosphino)alkylamines proceeded smoothly, with the evolution of heat, to give the 1 : 1 adducts in ~100% yield; with ethyl and with n-propyl iodide, the reactions were much slower and the yields less than quantitative. The individual character of the pairs methyl iodide-bis(diphenylphosphino)ethylamine and ethyl iodide-bis(diphenylphosphino)methylamine, ethyl iodide-bis(diphenylphosphino)-n-propylamine and n-propyl iodide-bis(diphenylphosphino)ethylamine, and methyl iodide-bis(diphenylphosphino)-n-propylamine and n-propyl iodide-bis(diphenylphosphino)methylamine, as shown by their i.r. spectra, demonstrates that the phosphorus is the quaternary centre and hence that these compounds must be regarded as phosphonium salts. The separation of the two phosphorus atoms by the *N*-alkyl group does not permit them to react independently and hence dipositive phosphonium salts are not formed. In contrast, separation by a methylene group, such as occurs in bis(diphenylphosphino)methane, permits the formation of a dimethiodide.⁷ The quaternary centres are thus found only when separated by a saturated carbon atom, not when separated by a nitrogen atom. This lends further support to the postulate made previously^{1,8} that there is considerable delocalisation in the trivalent phosphorus-nitrogen system, arising from $p_{\pi}-d_{\pi}$ bonding.

Scission of the P-N bond occurs with dry gaseous hydrogen chloride, giving the corresponding alkylamine hydrochloride and chlorodiphenylphosphine in quantitative yield. Dilute aqueous hydrochloric acid hydrolyses the P-N bond to give the corresponding alkylammonium ion and diphenylphosphinous acid, which is not isolated since it undergoes disproportionation and oxidation to diphenylphosphinic acid. With concentrated aqueous hydrochloric acid, bis(diphenylphosphino)alkylamines dissolve without undergoing hydrolysis. The products appear to be hydrochlorides, similar to the compound formed with triphenylphosphine under similar conditions.⁹ Investigation of this presumed salt formation is in progress.

Complexes of nickel(II) and palladium(II) with bis(diphenylphosphino)ethylamine are of the form LMX_2 , the phosphine being clearly bidentate. The nickel complexes are all of the low-spin type and this is confirmed by reference to the absorption spectra which show a broad band at 20,000—21,000 cm^{-1} (ϵ 10^{-2}) and no absorption at 14,000—15,000 cm^{-1} or below.

The corresponding triphenylphosphine complexes are high-spin tetrahedral complexes showing characteristic peaks¹⁰ at 15,000 and 7000—8000 cm^{-1} . Preliminary work on the X-ray structure determination¹¹ of the palladium complex confirms the presence of a four-membered ring, corresponding to the bidentate function of the phosphine.

The i.r. spectra of the mono- and bis-(diphenylphosphino)alkylamines show the

⁵ Kuchen and Buchwald, *Chem. Ber.*, 1958, **91**, 2871.

⁶ Issleib and Tyschach, *Chem. Ber.*, 1959, **92**, 1397.

⁷ Hewertson and Watson, *J.*, 1962, 1490.

⁸ Lane and Payne, *J.*, 1963, 4004.

⁹ Sheldon and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 2117.

¹⁰ Venanzi, *J.*, 1958, 719; Coussmaker, Hutchinson, Mellor, Sutton, and Venanzi, *J.*, 1961, 2705; Browning, Davies, Morgan, Sutton, and Venanzi, *J.*, 1961, 4816; Browning, Mellor, Morgan, Pratt, Sutton, and Venanzi, *J.*, 1962, 693.

¹¹ Mokuolu and Speakman, unpublished work.

characteristic frequencies of 1440 and 1000 cm^{-1} assigned to Ph-P, and 750 and 695 cm^{-1} characteristic of a monosubstituted benzene ring. The phosphoryl frequency in the bis(diphenylphosphinyl)alkylamines is near 1200 cm^{-1} . There is little shift in frequency from the 1190 cm^{-1} observed in triphenylphosphine oxide; ¹² the P=O linkage is thus little affected by the substitution, and the alkyl-nitrogen bridge seems to transmit the electronic effect of the diphenylphosphinyl group, which is equivalent to that of a phenyl group. The existence of a certain amount of π -bonding in the P-N-P skeleton, as has been suggested for other systems,⁸ is again supported. The P=S frequency has been assigned by Thomas and Chittenden ¹³ between 713 and 835 cm^{-1} and of variable intensity. Recently Zingaro ¹⁴ examined the assignment, and favours a value of $610 \pm 20 \text{ cm}^{-1}$ for the absorption in trialkyl- or triaryl-phosphine sulphides. Examination of the i.r. spectra of the bis-(diphenylphosphinothiyl)alkylamines showed a very strong absorption at $642 \pm 1 \text{ cm}^{-1}$ and a medium absorption at 612 cm^{-1} in each of the three compounds examined, these bands being absent from both the parent phosphine and the corresponding phosphinyl compounds.

Whilst the assignment of a range of frequencies to the P=N bond in phosphazenes is reasonably well founded,¹⁵ the corresponding information for the P-N bond in phosphazanes (*i.e.*, compounds with tervalent phosphorus), is difficult to obtain because of the relatively small number of compounds so far examined. Holmsted and Larson,¹⁶ Mayhood and Harvey,¹⁷ and McIvor and Hubley ¹⁸ have discussed the assignments to P-N bonds in phosphorus(v) compounds. However, no general conclusions can be drawn, the assignments which have been made being for specific groups such as PNMe_2 , PNet_2 , etc. It is clear, however, that the P-N vibration in this type of compound is to be found near 1000 cm^{-1} . The i.r. spectrum of the dimeric compound $(\text{MeNPCl}_2)_2$ shows ¹⁹ a strong peak at 847 cm^{-1} . Sisler and Smith ² prepared a number of similar phosphazanes and we have examined their i.r. spectra together with those of our compounds. No definite assignment to the P-N bond in this class of compound appears possible. It seems likely that the coupling between the P-N bond and the adjacent groups causes the frequencies to be variable in position and intensity, particularly where the group is involved with a further P-N bond. The i.r. spectra of the PdCl_2 , NiCl_2 , NiBr_2 , NiI_2 , and $\text{Ni}(\text{SCN})_2$ complexes of bis(diphenylphosphino)ethylamine show a shift of the bands at 1092s and 1070s cm^{-1} to higher frequencies. The intensities are little changed and the amount of the shift is small, 40–60 cm^{-1} , and varies from complex to complex. The spectra of bis(diphenylphosphino)alkylamines and related compounds (with certain exceptions) have characteristic bands near 880 cm^{-1} which are unaffected by complex formation. In the complexes mentioned, the medium band at 930 cm^{-1} in the original ligand disappears, and there are other less significant changes in this region.

The i.r. spectra of the compounds investigated are recorded on D.M.S. cards No. 11,944, *et. seq.*

EXPERIMENTAL

Chlorodiphenylphosphine was obtained commercially and was used without purification. The amines were thoroughly dried before use.

Diphenylphosphinomethylamine.—Chlorodiphenylphosphine (22.0 g., 0.100 mole) was added to methylamine at -50° under nitrogen. The excess of amine was removed and the residue extracted with ether. Methylamine hydrochloride filtered off, and the solvent removed to give 20.5 g. of crude product (theoretical yield of diphenylphosphinomethylamine, 21.5 g.; bis(diphenylphosphino)methylamine, 19.9 g.), which on distillation gave two fractions, b. p.

¹² Daasch and Smith, *Analyt. Chem.*, 1951, **23**, 853.

¹³ Thomas and Chittenden, *Chem. and Ind.*, 1961, 1913.

¹⁴ Zingaro, *Inorg. Chem.*, 1963, **2**, 192.

¹⁵ Shaw, Fitzsimmons, and Smith, *Chem. Rev.*, 1962, **62**, 247.

¹⁶ Holmsted and Larsson, *Acta Chem. Scand.*, 1951, **5**, 1179.

¹⁷ Mayhood and Harvey, *Canad. J. Chem.*, 1955, **33**, 1552.

¹⁸ McIvor and Hubley, *Canad. J. Chem.*, 1959, **57**, 869.

¹⁹ Chapman, Holmes, Paddock, and Searle, *J.*, 1961, 1825.

93—102° (0.2 g.) and 114—118°/0.1 mm. (4.7 g.), and a residue. The i.r. spectra of both fractions showed strong NH bands. The latter fraction could not be purified, since methylamine was lost and a higher-boiling material produced. The nitrogen analysis of this fraction was ~4.5%, well below that required for diphenylphosphinomethylamine (6.5%). Addition of methyl iodide to an ethereal solution of the higher-boiling fraction gave a white crystalline *methiodide*, m. p. 108—110° (Found: N, 4.0. $C_{14}H_{17}INP$ requires N, 3.9%).

Bis(diphenylphosphino)methylamine.—The residue obtained in the previous preparation was soluble in hot ethanol, and on cooling the solution a white crystalline product, m. p. 112—115°, was obtained. Repetition of the experiment led to two further fractions, b. p. 206—218°/0.1 mm. (6.4 g.) and 218°/0.1 mm. (3.4 g.). These were combined, and solidified slowly on standing. Recrystallisation from ethanol gave a white *solid*, m. p. 116—118° [Found: C, 75.4; H, 5.7; N, 3.6; P, 15.3%; *M* (cryoscopic in benzene), 385. $C_{25}H_{23}NP_2$ requires C, 75.2; H, 5.8; N, 3.5; P, 15.5%; *M*, 399.] *Bis(diphenylphosphino)methylamine* (0.978 g., 2.45 mmoles) reacted vigorously with methyl iodide (0.44 ml., 4.75 mmoles) in ether (15 ml.) to give a white *methiodide* (1.279 g., 99%), m. p. 170° (decomp.) (Found: I, 22.8. $C_{26}H_{26}INP_2$ requires I, 23.5%). Similarly, ethyl iodide (0.58 ml., 5.65 mmoles) gave a white *ethiodide* (0.957 g., 70%) (Found: I, 22.3. $C_{27}H_{28}INP_2$ requires I, 22.9%), and *n*-propyl iodide (0.96 ml., 6.1 mmoles) gave a white *n-propiodide* (0.499 g., 36%) (Found: I, 21.9. $C_{28}H_{30}INP_2$ requires I, 22.3%) with 0.990 g. (2.48 mmoles) and 0.980 g. (2.46 mmoles), respectively, of the amine.

Bis(diphenylphosphinyl)methylamine.—This was obtained by refluxing bis(diphenylphosphino)methylamine (0.692 g., 1.73 mmoles) in benzene (25 ml.) with activated manganese dioxide (0.8 g., 10 mmoles) for 2 hr. The filtrate from the reaction mixture gave a white solid, m. p. 220—222° (from aqueous acetone) (Found: C, 69.1; H, 5.5; N, 3.4; P, 14.4. $C_{25}H_{23}NO_2P_2$ requires C, 69.6; H, 5.3; N, 3.3; P, 14.4%).

The diphenylphosphino-compound (1.509 g., 3.79 mmoles) was refluxed with sulphur (0.253 g., 7.91 mmoles) in sodium-dried benzene (25 ml.). After removal of the excess of sulphur, the solution was evaporated, to give *bis(diphenylphosphinothiyl)methylamine*, which formed long white needles (from absolute alcohol), m. p. 168—170° (Found: C, 64.8; H, 5.0; N, 3.0; P, 13.1. $C_{25}H_{23}NP_2S_2$ requires C, 64.8; H, 5.0; N, 3.0; P, 13.4%).

Diphenylphosphinoethylamine.—The method described for the methyl analogue was employed. Difficulty was experienced in obtaining a pure sample by fractionation, because of the continuous elimination of ethylamine. The reaction was repeated with benzene as solvent at room temperature; chlorodiphenylphosphine (61.5 g., 0.28 mole) in benzene (200 ml.) was added to ethylamine (30 g., 0.66 mole) in benzene (100 ml.). Filtration and evaporation gave 61.6 g. of crude product (theoretical yield of diphenylphosphinoethylamine, 64.2 g.; bis(diphenylphosphino)ethylamine, 57.9 g.). Distillation gave the following fractions: b. p. (i) <190°/0.1 mm. (6.3 g.); (ii) 190—192°/0.1 mm. (12.5 g.); (iii) 200—203°/0.1 mm. (12.8 g.). Redistillation of fraction (i) gave a *liquid*, b. p. 195°/0.1 mm. (Found: N, 5.9. $C_{14}H_{16}NP$ requires N, 6.1%). *Diphenylphosphinoethylamine methiodide* was obtained from the reaction of diphenylphosphinoethylamine with an excess of methyl iodide in ether. The product, initially an oil, was a white solid (Found: N, 3.8. $C_{15}H_{16}INP$ requires N, 3.8%).

Bis(diphenylphosphino)ethylamine.—Chlorodiphenylphosphine (22.0 g., 0.100 mole) was added dropwise to ethylamine (50 ml., 0.78 mole) at -10° under dry nitrogen. The reactants were stirred for 2 hr., sodium-dried ether (100 ml.) was added, and the solution was filtered. Removal of the ether gave an oil (28.7 g.) containing much ethylamine, but this was removed in the course of the fractional distillation, which gave crude diphenylphosphinoethylamine (10.2 g.) and a residue (7.8 g.). The residue, on standing, gave a *solid*, m. p. 99° (from aqueous ethanol) [Found: C, 75.8; H, 6.0; N, 3.5; P, 14.9%; *M* (cryoscopic in benzene), 421. $C_{26}H_{25}NP_2$ requires C, 75.5; H, 6.05; N, 3.4; P, 15.0%; *M*, 413]. The above reaction, repeated without the exclusion of oxygen or moisture, led to a solid shown to be a mixture of tetraphenyldiphosphine, tetraphenyldiphosphine dioxide, and diphenylphosphinic acid. *Bis(diphenylphosphino)ethylamine* (0.980 g., 2.37 mmoles), with an excess of methyl iodide (0.45 ml., 4.8 mmoles) in ether (15 ml.), gave *bis(diphenylphosphino)ethylamine methiodide* (1.317 g., 95%) as a white solid, m. p. 145° (decomp.) (Found: I, 22.6. $C_{27}H_{28}INP_2$ requires I, 22.9%), and with ethyl iodide (0.58 ml., 5.65 mmoles), the amine (0.974 g., 2.36 mmoles) gave a white *ethiodide* (0.533 g.; 40%) (Found: I, 23.2. $C_{28}H_{30}INP_2$ requires I, 22.2%). *Bis(diphenylphosphino)ethylamine* (0.414 g., 1.00 mmole), with mercury(II) iodide (0.455 g., 1.00 mmole) in ethanol, gave 0.77 g. of a white solid, *di-iodobis(diphenylphosphino)ethylaminemercury(II)*, m. p. 195—200° [Found:

I, 29.2%; *M* (cryoscopic in nitrobenzene), 604, falling to 529 after 2 hr. $C_{26}H_{25}HgI_2NP_2$ requires I, 29.3%; *M*, 867].

Bis(diphenylphosphinyl)ethylamine.—This was obtained by the oxidation of bis(diphenylphosphino)ethylamine (0.943 g., 2.28 mmoles) with activated manganese dioxide (1.162 g., 13.4 mmoles) in benzene (35 ml.) under reflux for 2 hr. After filtration and repeated extraction of the residual dioxide with acetone, a white solid (0.503 g., 47%), m. p. 171–172°, was recovered. Bis(diphenylphosphino)ethylamine (0.995 g., 2.30 mmoles) was dissolved in methylene chloride (25 ml.), cooled to 0°, and treated with ozonised oxygen (equivalent to 9 mmoles of ozone). Removal of the solvent gave a white solid (1.002 g., 89%) which crystallised from acetone, m. p. 174–175° (Found: C, 69.9; H, 5.6; N, 3.2; P, 14.0. $C_{26}H_{25}NO_2P_2$ requires C, 70.1; H, 5.6; N, 3.1; P, 13.9%).

Bis(diphenylphosphinothiyl)ethylamine.—This was obtained by reaction of the diphenylphosphino-compound (1.496 g., 3.62 mmoles) with an excess of sulphur in boiling benzene, as a white solid (1.692 g., 98%), m. p. 173–174° (from ethanol) (Found: C, 65.3; H, 5.0; N, 3.0; P, 13.3; S, 13.6. $C_{26}H_{25}NP_2S_2$ requires C, 65.4; H, 5.2; N, 2.9; P, 13.0; S, 13.4%).

Dichlorobis(diphenylphosphino)ethylaminenickel(II).—Bis(diphenylphosphino)ethylamine (0.394 g., 0.955 mmole) in boiling ethanol (10 ml.) was added to nickel chloride hexahydrate (0.251 g., 1.73 mmoles) in ethanol. The resulting red solution, on standing, yielded a red crystalline product (0.303 g., 59%), m. p. 269–270° (from nitromethane) (Found: N, 2.6; Cl, 12.9. $C_{26}H_{25}Cl_2NNiP_2$ requires N, 2.6; Cl, 13.1%).

The complexes with nickel bromide, iodide, and thiocyanate were prepared by the above method. $[(Ph_2P)_2N\text{Et}]NiBr_2$ (81.9%), deep red, m. p. 289–291° (Found: Br, 25.3; N, 2.4. Reqd.: Br, 25.5; N, 2.2%); $[(Ph_2P)_2N\text{Et}]NiI_2$ (83.5%), purple, m. p. 285–286° (Found: I, 35.0; N, 2.0. Reqd.: I, 34.7; N, 1.9%); $[(Ph_2P)_2N\text{Et}]Ni(SCN)_2$ (85.6%), orange, m. p. 252–253° (Found: N, 7.2; S, 10.9. Requires: N, 7.2; S, 10.7%).

Dinitratobis(diphenylphosphino)ethylaminenickel(II).—Bis(diphenylphosphino)ethylamine (0.576 g., 1.39 mmoles) in cold 2-methylpropanol (10 ml.) was added to nickel nitrate hexahydrate (0.434 g., 1.49 mmoles) in 2-methylpropanol. The resulting deep red solution, on standing, yielded a yellow crystalline solid (0.536 g.) (65%), m. p. 160–163° (Found: N, 7.1; C, 56.0; H, 5.1. $C_{26}H_{25}N_4NiO_6P_2$ requires N, 7.0; C, 52.4; H, 4.7%).

Dichlorobis(diphenylphosphino)ethylaminepalladium(II).—Bis(diphenylphosphino)ethylamine (8.268 g., 0.0200 mole) in warm acetone (120 ml.) and water (3 ml.) was added dropwise to potassium tetrachloropalladate(II) (3.265 g., 0.010 mole) in water (100 ml.) and acetone (4 ml.), and on standing, gave a yellow crystalline solid (6.081 g., 67%), m. p. 276–278° (from alcohol) [Found: C, 53.1; H, 4.3; Cl, 10.8; N, 2.7; P, 10.2%; *M* (from unit-cell and density measurements), 590. $C_{26}H_{25}Cl_2NP_2Pd$ requires C, 52.8; H, 4.3; Cl, 12.0; N, 2.4; P, 10.5%; *M*, 591].

Diphenylphosphino-n-propylamine.—This was a colourless liquid, b. p. 106°/0.1 mm. (Found: N, 5.9. $C_{15}H_{18}NP$ requires N, 5.8%). It and *bis(diphenylphosphino)-n-propylamine*, white solid, m. p. 85–86° (from ethanol) [Found: C, 75.75; H, 6.3; N, 3.4; P, 14.3%; *M* (cryoscopic in benzene), 430. $C_{27}H_{27}NP_2$ requires C, 75.9; H, 6.3; N, 3.3; P, 14.5%; *M*, 427], were prepared as described for the ethyl analogues. Bis(diphenylphosphino)-n-propylamine (0.982 g., 2.29 mmoles) with methyl iodide (0.44 ml., 0.47 mmoles) gave a white *methiodide* (1.306 g., 100%) (Found: I, 21.7. $C_{28}H_{30}INP_2$ requires I, 22.3%). Similarly, 0.979 g. (2.28 mmoles) of the amine, with ethyl iodide (0.58 ml., 5.65 mmoles), gave a white *ethiodide* (0.551 g., 41%) (Found: I, 22.3. $C_{29}H_{32}INP_2$ requires I, 21.8%), and 0.962 g. (2.24 mmoles) of the amine with n-propyl iodide (0.70 ml., 6.2 mmoles), gave a white *n-propiodide* (Found: I, 21.9. $C_{30}H_{34}INP_2$ requires I, 21.3%). Oxidation of bis(diphenylphosphino)-n-propylamine (0.589 g., 1.38 mmoles) with activated manganese dioxide gave a small yield (~8%) of a white solid, m. p. 141–143° (from acetone-water) (Found: C, 70.3; H, 6.0; N, 3.1; P, 13.4. $C_{27}H_{27}NO_2P_2$ requires C, 70.6; H, 5.9; N, 3.1; P, 13.5%).

Bis(diphenylphosphinothiyl)-n-propylamine. This was obtained from the reaction bis(diphenylphosphino)-n-propylamine (1.592 g., 3.73 mmoles) with an excess of sulphur in boiling benzene solution, as a white solid (1.614 g., 88%), m. p. 180–182° (from ethanol) (Found: C, 66.3; H, 5.6; N, 2.9; P, 12.6. $C_{27}H_{27}NP_2S_2$ requires C, 66.0; H, 5.5; N, 2.9; P, 12.6%).

We thank Mr. J. M. Cameron, B.Sc., and his assistants for nitrogen determinations, and Mr. M. J. Kennedy and Mr. J. Mokuolu, who have helped in part of this work.