# Conformational Effects on *P*–N–*P* Coupling Constants in Diphosphinoamines and Related Compounds

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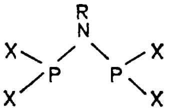
$^1$H-{$^{31}$P} and $^{31}$P n.m.r. measurements on the triphosphazanes $(Ph_2P{\cdot}NR)_2PPh$ show that $J(PNP)$ is +280 Hz when R = Me and 25.1 Hz when R = Et. A similar marked dependence on the R groups has been found for the diphosphinoamines, $Ph_2P{\cdot}NR{\cdot}PPhCl$ (R = Me, Et, Pr$^n$, Pr$^i$, and Bu$^t$) (+334 to −35 Hz), and this may be related to the conformations about the P–N bonds, which are influenced by the stereochemical bulk of R. $^1$H-{$^{31}$P} INDOR experiments on the symmetrical diphosphinoamines, $Ph_2P{\cdot}NR{\cdot}PPh_2$ (R = Me, Et, and Pr$^i$), indicate that $J(PNP)$ is much greater when R = Me than when R = Et or Pr$^i$.

SEVERAL examples of diphosphinoamines, (I), with halogeno-,[1-5] alkyl,[6-8] and aryl[4,9,10] substituents (X) on phosphorus are known and many details of their n.m.r. spectra have been reported. The $^{19}$F n.m.r. spectra of the difluorophosphino-derivatives (I; X = F, R = Me, Et, or aryl) are particularly informative[3,11,12] about the coupling constant $J(PNP)$ which might be expected to reflect details of molecular structure associated with the


(I)

P–N–P skeleton. These coupling constants were particularly large (371—446 Hz)[3] compared to $J(PNP)$ in cyclophosphazenes[13,14] and other phosphorus(v) compounds[15] containing the P–N–P unit (typically <100 Hz). They were relatively insensitive to temperature changes, however. For example, in $F_2P{\cdot}NMe{\cdot}PF_2$, $J(PNP)$ changes[11] by 10 Hz over the range −70 to +30 °C, in which rotation about the P–N bonds is expected to be fast on the n.m.r. time scale. No information on this coupling constant in diphenylphosphino-derivatives (I; X = Ph) was available until very recently because of the symmetrical nature of these molecules.

TABLE 1

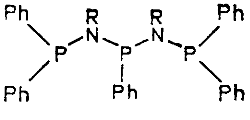
N.m.r. data for triphosphazanes $Ph_2P_B{\cdot}NR{\cdot}P_APh{\cdot}NR{\cdot}P_BPh_2$, (II) [a]

| R | δ(P$_A$) | δ(P$_B$) | $J(PNP)$ | δ(NC$H_n$) | $J(P_A$NC$H)$ | $J(P_B$NC$H)$ [b] |
|---|---|---|---|---|---|---|
| | p.p.m. | | Hz | p.p.m. | Hz | |
| Me | 119.5 | 62.3 | +280 (±3) | 2.73 | 4.5 | 2.9 |
| Et | 104.3 | 52.8 | 25.1 (±0.5) | *ca.* 3.4, 3.2 | | |

[a] In $CH_2Cl_2$ solutions at ambient temperatures. [b] Apparent value.

RESULTS

*Triphosphazanes*, $Ph_2P{\cdot}NR{\cdot}PPh{\cdot}NR{\cdot}PPh_2$.—During the course of examination of the $^{31}$P-{$^1$H} n.m.r. spectra of the


(II)

related triphosphazanes, (II),[16] we were surprised to find an unprecedented decrease in the magnitude of $J(PNP)$ from 280 to 25.1 Hz when R was changed from methyl to ethyl (Table 1). There was no evidence for restricted rotation about the P–N bonds in either of these molecules, since the proton spectra changed little in the range −50 to +140 °C. There were two groups of methylene proton signals in (II; R = Et), but this might be expected in view of the diastereotopic nature of these protons. In (II; R = Me) the *N*-methyl proton signals consisted[16] of a doublet of triplets and their interpretation was ambiguous. Selective $^1$H-{$^{31}$P} double-resonance experiments confirmed the magnitude of $J(PNP)$ and furthermore showed that it had the same sign as $J(PNCH)$, generally assumed to be positive.[17] The ' triplet ' structure is probably a ' virtual-coupling ' effect[18] implying a significant $J(P$–N–P–N–$P)$ coupling constant. The $^1$H spectrum of (II; R = Et) was complex even after complete $^{31}$P decoupling, presumably

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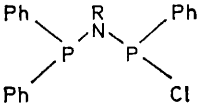
largely due to the diastereotopic nature of the methylene protons, for which a chemical-shift effect was apparent on comparison of 60 and 100 MHz spectra. Attempts to establish the relative signs of *J*(*PNP*) and *J*(*PNCH*) by off-resonance $^1$H-{$^{31}$P} decoupling were unsuccessful.

*Diphosphinoamines*, $Ph_2P{\cdot}NR{\cdot}PPhCl$.—In order to gain some insight into the factors which determine the magnitude of *J*(*PNP*) in compounds (II) we synthesised a series of diphosphinoamines, (III; R = Me, Et, Pr$^n$, Pr$^i$, and Bu$^t$), by routes (1)—(3). In general, the best yields of compounds (III) were obtained by route (3). *J*(*PNP*) Values were obtained directly from the $^{31}$P-{$^1$H} spectra and are listed in Table 2. A large variation in *J*(*PNP*) is again apparent, and the smallest values are associated with the bulkiest R groups. The coupling *J*(*PNP*) was again obtained by $^1$H-{$^{31}$P} double resonance and when R = Me, Et, and Pr$^n$ this coupling constant had the same relative sign as *J*(*PNCH*). In contrast, when R = Pr$^i$, *J*(*PNP*) and *J*(*PNCH*) were of opposite sign. Assuming that *J*(*PNCH*) is again positive, this appears to be the first example of a negative coupling constant involving two tervalent phosphorus atoms in a P–N–P unit. With very few exceptions,[19,20] *J*(*PNP*) is positive [11,14,15,19] irrespective of the oxidation state of phosphorus.



(III)

$$\mathrm{NHR(PPh_2)} + \mathrm{PPhCl_2} \xrightarrow{\mathrm{NEt_3}} \mathrm{(III)} + \mathrm{HCl} \tag{1}$$

$$\mathrm{Ph_2P{\cdot}NR{\cdot}SiMe_3} + \mathrm{PPhCl_2} \longrightarrow \mathrm{(III)} + \mathrm{SiMe_3Cl} \tag{2}$$

$$\mathrm{NHR(PPh_2)} \xrightarrow[\text{(b) PPhCl}_2]{\text{(a) LiBu}^n} \mathrm{(III)} + \mathrm{LiCl} + \mathrm{Bu^nH} \tag{3}$$

TABLE 2

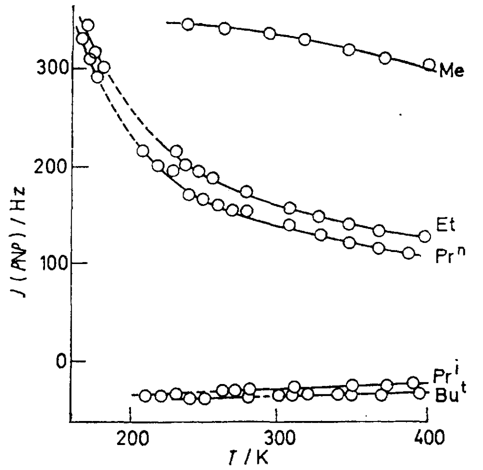
N.m.r. data for (chlorophenylphosphino)(diphenylphosphino)amines $Ph_2P{\cdot}NR{\cdot}PPhCl$ [a]

| R | δ(*P*Ph$_2$) p.p.m. | δ(*P*PhCl) p.p.m. | *J*(*PNP*) Hz | δ(NCH$_n$) p.p.m. | *J*(*PNCH*) Hz |
|---|---|---|---|---|---|
| Me | 67.4 | 141.8 | +333.5 (±1) | 2.46 | +2.4,[b] +4.8[c] |
| Et | 65.1 | 139.9 | +158 (±2) | *ca.* 3.2 | |
| Pr$^n$ | 64.8 | 124.4 | +145 (±2) | *ca.* 2.9 | |
| Pr$^i$ | 42.1 | 132.0 | −29 (±1) | 3.7 | |
| Bu$^t$ | 59.0 | 128.7 | −35 (±1) | | |

[a] In $CH_2Cl_2$ solutions at *ca.* 300 K. [b] *J*($Ph_2$*P*NC*H*). [c] These couplings are 2.2 and 4.5 Hz at 243 K and 2.5 and 4.9 Hz at 378 K in toluene solution.

The temperature-induced variation of *J*(*PNP*) in some of the compounds (III) was much more marked than with the fluoro-derivatives (I; X = F) as shown (Figure). Coalescence phenomena were observed in the $^{31}$P spectra of (III; R = Et or Pr$^n$) at *ca.* 200 K, and of (III; R = Pr$^i$ or Bu$^t$) at, or near, ambient temperatures. The $^1$H-decoupled spectra were of a simple AX or AB type above and below the coalescence region. Phosphorus-31 chemical shifts were only slightly affected by changes in temperature (generally <5 p.p.m. over the range examined). Studies of the $^1$H n.m.r. spectra of aminophosphines [21] suggest that the coalescence phenomena are likely to be associated with slow rotation about the ClPhP–N bond, and the increase in coalescence temperatures with increase in the bulk of R is consistent with this suggestion. There is also the possibility [22] that chloride-ion exchange may become fast on the n.m.r. time scale at elevated temperatures, or in the presence of free chloride ions, but since the spectra were not concentration dependent, or affected by addition of amine hydrochlorides, this is not likely to be the rate process involved.

*Diphosphinoamines*, $Ph_2P{\cdot}NR{\cdot}PPh_2$.—The measurement of *J*(*PNP*) in the symmetrical diphosphinoamines (I; X = Ph) is more difficult. In principle an estimate [18] of *J*(*PNP*) might be made by examination of the *ortho*-proton signals (conveniently separated from the *meta* and *para* signals in benzene [23]) which form the X part of an $X_4AA'X'_4$ spin system, neglecting *meta*-, *para*-, and R-group protons. In practice this is very difficult because of the complexity of the *ortho*-proton signals and the relatively large magnitude of *J*(*PNP*). However, it has recently been shown [24,25] that *J*(P ··· P) can also be determined by $^1$H-{$^{31}$P} double-resonance experiments. When *J*(HH′) is zero, the $^1$H spectrum of an $H_nPP'H'_n$ spin system generally consists of a strong doublet (' N doublet ') enclosing a ' hump ' or multiplet of signals.[18] Furthermore, the transitions which give rise to the ' N doublet ' are connected to two groups of weak outer lines in the $^{31}$P spectrum. The groups of



Variation of *J*(*PNP*) with temperature for the diphosphinoamines (III) (R given). Measurements below 300 K were made on $CH_2Cl_2$ solutions and above 300 K on PhCl solutions. The broken lines represent the coalescence ranges observed in the $^1$H-decoupled $^{31}$P spectra

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lines are separated from the central $^{31}$P multiplet by $J(PNP) + 4[L^2/J(PNP)]$, where $L = J(\mathrm{PH}) - J(\mathrm{PH'})$.[26] By monitoring the *ortho*-proton signals of (I; X = Ph, R = Me) it was possible to find the positions of the outer lines in the $^{31}$P spectrum. The low-frequency proton lines are connected with the low-frequency group of lines in the $^{31}$P spectrum so that $J(PNP)$ (= 273 ± 3 Hz) and $J(PCCH)$ have the same sign. The latter coupling constant is known to be positive in triphenylphosphine.[27] It has recently been shown [28] that a $J(PNP)$ value of +280 ± 10 Hz for (I; X = Ph, R = Me) can be obtained by monitoring the outer components of the *N*-methyl triplet. Unfortunately, it was not possible to find the outer groups of $^{31}$P lines in the spectra of (I; X = Ph, R = Et or Pr$^i$) by monitoring the *ortho*-proton signals or the methylene-proton signals (R = Et), suggesting that $J(PNP)$ is small (< *ca.* 50 Hz) in these cases.

## DISCUSSION

Since changes in the R substituents in (I; X = Ph), (II), and (III) are unlikely to result in large changes in electronic effects, a correlation of $J(PNP)$ with conformational changes about the P–N bonds was sought. It has been accepted for some time that the magnitude of $J(PNCH)$ [21] and $J(PNC)$ [29] in $\mathrm{NMe_2(PPhCl)}$ and other phosphinoamines are related to the positions of the methyl groups relative to the phosphorus lone pair. When rotation about the P–N bonds has stopped at low temperatures, the assumption is that the relatively large and positive couplings apply to the methyl group *cis* to the lone pair on phosphorus, and that relatively small couplings [$J(PNC)$ is negative [29]] apply to the methyl group *trans* to the lone pair on phosphorus. Unambiguous evidence for this assignment is still lacking.

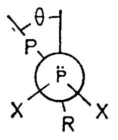
TABLE 3

N.m.r. data for diphenylphosphinoamines [a]

| Compound | $\delta_P$ p.p.m. | $J(PNP)$ Hz | $\delta(\mathrm{NC}H_n)$ p.p.m. | $\delta(\mathrm{NCC}H_3)$ p.p.m. | $J(PNCH)$ Hz |
|---|---|---|---|---|---|
| $\mathrm{NMe(PPh_2)_2}$ | 73.2 | +273 [b](±3) | 2.42 | | 3.2 |
| $\mathrm{NEt(PPh_2)_2}$ | 61.8 | <50 | 3.33 | 1.03 | 9.5 |
| $\mathrm{NPr^i(PPh_2)_2}$ | 48.8 | <50 | 3.80 | 1.10 | |
| $\mathrm{NMeH(PPh_2)}$ | 43.8 | | 2.37 | | 10.5 |
| $\mathrm{NEtH(PPh_2)}$ | 40.4 | | 2.90 | 1.03 | *ca.* 7 |
| $\mathrm{NPr^nH(PPh_2)}$ | 40.9 | | 2.83 | *ca.* 1.4 | 8.8 |
| $\mathrm{NPr^iH(PPh_2)}$ | 33.6 | | 3.22 | 1.01 | |
| $\mathrm{NBu^tH(PPh_2)}$ | 21.7 | | | 1.20 | 0.6 [c] |
| $\mathrm{NMe(PPh_2)(SiMe_3)}$ | 46.4 | | 2.83 | | 5.3 |
| $\mathrm{NEt(PPh_2)(SiMe_3)}$ | 45.8 | | 3.10 | 0.38 | 7.1 |
| $\mathrm{NPr^i(PPh_2)(SiMe_3)}$ | 41.2 | | *ca.* 3.6 | 1.10 | |

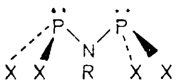
[a] In $\mathrm{CH_2Cl_2}$ solutions at ambient temperatures. [b] Same relative sign as apparent $J(PCCH)$ (*ca.* 7 Hz). [c] $J(PNCCH)$.

It is therefore not unreasonable to assume that $J(PNP)$ will also depend critically on the relation between the lone pair on one phosphorus atom and the position of the second phosphorus atom in the same molecule. This can be defined in terms of a dihedral angle, θ, between the plane bisecting the two non-bridging phosphorus substituents and the plane containing the PNP unit about the P–N bond as shown in (A).

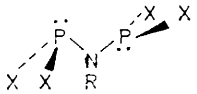


(A)

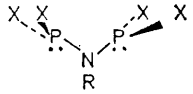
Excluding all conformations in which groups on adjacent phosphorus and nitrogen atoms are eclipsed, and assuming a planar distribution of bonds about nitrogen, conformations (IV)—(VI) and their relation with the stereochemical bulk of R have been considered. This choice is based on the findings that lone pairs of electrons on phosphorus and on nitrogen tend to lie orthogonal to one another,[21,30,31] and on the construction of molecular models. The models suggest that (IV) is likely to be important with R groups of relatively small steric demand, and that conformations (V) and (VI) will assume increasing importance with larger R substituents.



(IV)



(V)



(VI)

Experimental evidence to support these suggestions is sparse, but a recent electron-diffraction study [31] of (I; X = F, R = Me) indicates that it has a conformation analogous to (IV) (both angles θ = 0°) possibly together

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[26] D. J. Mowthorpe and A. C. Chapman, *Spectrochim. Acta*, 1967, **23**, 451.

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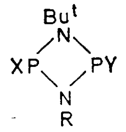
with small quantities of a conformer analogous to (V) (10—15%). In this derivative *J*(*P*N*P*) is relatively large (+437 Hz)[3] and *J*(*P*NC*H*) is small (3.2 Hz), the latter coupling being consistent with the methyl group having a *trans* relation to the lone pairs on the two phosphorus atoms. Although attempts to relate crystal-structure data to solution properties need to be treated with caution, it is worth noting that the monosulphide of (I; X = Ph, R = Me), $Ph_2P{\cdot}NMe{\cdot}PPh_2S$, has a crystal structure[32] in which $\theta = 20°$. The coupling $J(P^{III}NCH)$ is also small (1.7 Hz) in this compound.[33] The bis(difluorophosphino)amine, $F_2P{\cdot}NH{\cdot}PF_2$, has recently been studied.[34] The preferred conformation of this compound is not known with certainty, but there is i.r. evidence that H · · · F hydrogen bonding keeps one fluorine atom on each phosphorus, the two phosphorus atoms, the nitrogen atom, and the hydrogen atom all approximately coplanar; *J*(*P*N*P*) is 154 ± 1 Hz in this case.

If it is assumed that *J*(*P*N*P*) changes in the same way as *J*(*P*NC*H*) and *J*(*P*N*C*), then the weight of evidence is that conformations close to (IV) are important for all the *N*-methyl derivatives of (I)—(III). This being so, increasing temperatures would increase the relative populations of conformers (V) and (VI) paralleling the decrease in *J*(*P*N*P*) (Figure) for (III; R = Me). At the same time, *J*(*P*NC*H*) coupling constants in this derivative increase with increasing temperature (Table 2); although these increases appear small, the relative change is of a similar order to that observed for *J*(*P*N*P*) over the same temperature range. With compounds (III; R = Et or $Pr^n$), conformations analogous to (V) and (VI) could be more populated than when R = Me, resulting in an intermediate value of *J*(*P*N*P*).

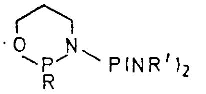
In all probability conformation (IV) is very unfavourable in (III; R = $Pr^i$ or $Bu^t$) even when rotation about the P–N bonds is fast on the n.m.r. time scale. It is striking that the *P*–N–*P* couplings for the latter two compounds change little when measured above and below the coalescence region. The relative sign of *J*(*P*N*P*) for (III; R = $Bu^t$) was not obtained by $^1H$-{$^{31}P$} double resonance, but the properties of the R groups and the similarity of this coupling constant to that for (III; R = $Pr^i$) indicate that it is also negative. The moderate value of *J*(*P*N*P*) measured[34] for $F_2P{\cdot}NH{\cdot}PF_2$, compared to that for $F_2P{\cdot}NMe{\cdot}PF_2$,[3] is compatible with the hydrogen-bonded conformations suggested for this molecule. Presumably, *J*(*P*N*P*) is positive in this case.

Further evidence for the correlation between *J*(*P*–N–*P*) and the conformation adopted about the P–N bonds indicated above was sought from relatively rigid structures containing the P–N–P skeleton. No compounds are available in which phosphorus substituents are strictly comparable with those above, but it is worth considering *J*(*P*N*P*) values in cyclodiphosphazanes, (VII; R = alkyl), and the adamantane-type cage compound $P_4(NMe)_6$. In the cyclodiphosphazanes (VII;



(VII)

X and Y = halogeno or amino) *J*(*P*N*P*) is generally less than 100 Hz,[4,20,35] and positive,[20] which is compatible with θ between 90 and 180°. This dihedral angle is almost certainly *ca.* 180° in $P_4(NMe)_6$[36] where $^1H$-{$^{31}P$} INDOR experiments of the type described for $Ph_2P{\cdot}NMe{\cdot}PPh_2$ suggested that *J*(*P*N*P*) is small (<*ca.* 50 Hz). The coupling *J*(*P*N*P*) was not measurable[37] in the analogous open-cage compound, $P_4Cl_2(NMe)_5$, and again is assumed to be small (<10 Hz). The aminophosphino-derivatives, (VIII), are also interesting in that *J*(*P*N*P*)



(VIII) R = Ph or alkoxy
R′ = Me or Et

is too small to be measured from the $^{31}P$ spectra.[38] The results described above suggest that the conformation adopted in this case does not approximate to (IV).

It should be emphasised that conformations (IV)—(VI) for the acylic P–N–P compounds are idealised, especially for compounds of types (I) and (II), but we feel that they strongly indicate a decrease in the population of (IV) with increase in bulk of the R group. It is difficult to establish the relative proportions of (V) and (VI); assuming that *J*(*P*N*P*) is related to the sum of two dihedral angles θ, then negative *P*–N–*P* coupling constants may be due to a preponderance of (VI) over (V). At present it appears that changes in the electron-supplying power of the phosphorus substituents result in smaller changes in *J*(*P*N*P*) than are effected by conformational changes.

## EXPERIMENTAL

Preparative procedures were as previously described.[33] Literature methods were employed for the preparation of diphenylphosphinoamines $NHR(PPh_2)$ (R = Me, Et, $Pr^n$, and $Pr^i$),[9,39] (diphenylphosphino)(silyl)amines, $NR(PPh_2)$-$(SiMe_3)$ (R = Me, Et, or $Pr^i$),[33] bis(diphenylphosphino)-amines, $Ph_2P{\cdot}NR{\cdot}PPh_2$ (R = Me or Et),[9] the triphosphazanes, $Ph_2P{\cdot}NMe{\cdot}PPh{\cdot}NMe{\cdot}PPh_2$,[16] and the cage compound, $P_4(NMe)_6$.[36]

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Hydrogen-1 and $^{31}P$ n.m.r. spectra were obtained on a JEOL C60HL spectrometer at 60 and 24.3 MHz respectively. Hydrogen-1 spectra for $^{1}H-\{^{31}P\}$ double-resonance experiments (including INDOR) were recorded in the frequency-sweep internal-lock mode and $^{31}P$ spectra in the field-sweep external-lock mode. Charts for the latter spectra were calibrated by observation of the shifts produced by changes in the $^{31}P$ frequencies as measured on a frequency counter. A Schomandl ND100M frequency synthesiser was used as a source of $^{31}P$ irradiation frequencies. Several $^{31}P$ shifts were determined by $^{1}H-\{^{31}P\}$ double resonance using a $\Xi$ value [40] of 40.480 740 MHz for 85% $H_3PO_4$. Literature values for this constant vary between 40.480 720 [15] and 40.480 754 MHz,[41] but direct observation of the $^{31}P$ shift of trimethyl phosphate relative to 85% $H_3PO_4$ (contained in a capillary tube coaxial with the sample tube) gave $\delta$ +2.34 p.p.m., and this was then used, together with the results of $^{1}H-\{^{31}P\}$ experiments on $PO(OMe)_3$, to calculate $\Xi$. The result is identical to that given originally.[40] Mass spectra were obtained on an A.E.I. MS12 spectrometer.

Preparative routes to new compounds are described below.

*Diphenylphosphino-t-butylamine.*—t-Butylamine (15.0 g, 0.206 mol) was added to a stirred solution of chlorodiphenylphosphine (22.1 g, 0.100 mol) in light petroleum (b.p. 60—80 °C) (250 cm$^3$) at ambient temperature. The mixture was stirred (1 h) and the precipitate and solvent removed leaving a colourless oil. This was distilled under reduced pressure to give a colourless liquid (21.2 g, 82%), b.p. 145—150 °C (0.5 mmHg),* which solidified, m.p. 38 °C (Found: C, 74.6; H, 7.5. $C_{16}H_{20}NP$ requires C, 74.7; H, 7.8%).

*Bis(diphenylphosphino)-i-propylamine*, (I; X = Ph, R = $Pr^i$).—Diphenylphosphino-i-propylamine (5.0 g, 0.021 mol) and $PPh_2Cl$ (4.6 g, 0.021 mol) were mixed in a stirred diethyl ether (200 cm$^3$) solution at ambient temperatures. Triethylamine (2.1 g, 0.021 mol) was added and the mixture boiled under reflux (0.5 h). Removal of triethylamine hydrochloride and solvent gave a pale yellow oil which was crystallised from ethanol as white needles (3.2 g, 36%), m.p. 133—134 °C (Found: C, 75.8; H, 6.3%; *m/e*, 427. $C_{27}H_{27}NP_2$ requires C, 75.9; H, 6.3%; *m/e*, 427).

*(Chlorophenylphosphino)(diphenylphosphino)methylamine*, (III; R = Me).—(Diphenylphosphino)methylamine (3.6 g, 0.017 mol) in benzene (50 cm$^3$) was mixed with a solution of n-butyl-lithium (0.017 mol, in hexane) and stirred (1 h). Dichlorophenylphosphine (3.0 g, 0.017 mol) was added and a white precipitate formed immediately. After refluxing (1 h) the precipitate was centrifuged off and the solvent removed to leave a yellow oil. The oil was purified by distillation under reduced pressure to give a very viscous oil (2.9 g, 48%), b.p. 60—78 °C (0.08 mmHg) (Found: C, 64.0; H, 5.6%; *m/e*, 357. $C_{19}H_{18}{}^{35}ClNP_2$ requires C, 63.8; H, 5.0%; *m/e*, 357).

A similar route was employed to obtain the following in yields of 20—40%: *(chlorophenylphosphino)(diphenylphosphino)ethylamine*, (III; R = Et), b.p. 140 °C (0.15 mmHg) (Found: C, 64.6; H, 6.5%; *m/e*, 371. $C_{20}H_{20}{}^{35}ClNP_2$ requires C, 64.6; H, 5.4%; *m/e*, 371); *(chlorophenylphosphino)(diphenylphosphino)-n-propylamine*, (III; R = $Pr^n$), sublimes 80 °C (0.35 mmHg) (Found: C, 63.5; H, 5.9; N, 3.0; *m/e*, 385. $C_{21}H_{22}{}^{35}ClNP_2$ requires C, 65.4; H, 5.7; N, 3.6%; *m/e*, 385); *(chlorophenylphosphino)(diphenylphosphino)-i-propylamine*, (III; R = $Pr^i$), b.p. 162 °C (0.1 mmHg) (Found: C, 64.9; H, 5.9%; *m/e*, 385. $C_{21}H_{22}{}^{35}ClNP_2$ requires C, 65.4; H, 5.7%; *m/e*, 385); and *(chlorophenylphosphino)(diphenylphosphino)-t-butylamine*, (III; R = $Bu^t$), b.p. 150—160 °C (0.1 mmHg) (Found: *m/e*, 399. $C_{22}H_{24}{}^{35}ClNP_2$ requires *m/e*, 399) (satisfactory elemental analyses not obtained).

Compounds (III; R = Me, Et, and $Pr^i$) were also synthesised by (*a*) the condensation of alkyl(diphenylphosphino)amines with dichlorophenylphosphine in the presence of $NEt_3$, and (*b*) by the reaction of (diphenylphosphino)(trimethylsilyl)alkylamines with $PPhCl_2$ (see text). In both cases it was difficult to exclude by-products, especially when R = Et or $Pr^i$. For example, attempts to prepare (III; R = Me) by these methods invariably resulted in the formation of a product tentatively identified ($^1H$ and $^{31}P$ n.m.r.) as $OPh_2P_A{\cdot}NMe{\cdot}P_BPhCl$ [$\delta(P_A)$ 31.2, $\delta(P_B)$ 123.7 p.p.m., *J*(*PNP*) +85 Hz].

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

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