Synthetic, Nuclear Magnetic Resonance and X-Ray Crystallographic Studies of Conformations of Polyorganophosphorus Compounds†

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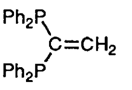
Addition reactions between ERH_2 (E = P or As; R = Ph, CH_2CH_2CN, Bu or $C_6H_2Bu^t_3$-2,4,6) and $(Ph_2P)_2C{=}CH_2$ or $(Ph_2P)_2C{=}CHR'$ (R' = H or Me) yield the triphosphines $(Ph_2P)_2CHCHR'ERH$ and the pentaphosphines $[(Ph_2P)_2CHCH_2]_2ER$ and $(Ph_2P)_2CHCH(Me)P(Ph)CH_2CH(PPh_2)_2$. The two- and three-bond $^{31}P-^{31}P$ nuclear spin-spin coupling constants in these vary substantially with the bulk of substituents on or near phosphorus, probably as a result of conformational differences. The structures of $(Ph_2P)_2CHCH_2PHPh$, $(Ph_2P)_2PCHCH_2PH(C_6H_2Bu^t_3$-2,4,6) and $[(Ph_2P)_2CHCH_2]_2PPh$ have been determined by X-ray diffraction and suggest that each of these species adopts a conformation in solution that is very similar to that found in the solid state.

It is well established that many indirect (J) nuclear spin-spin coupling constants are affected by molecular conformation, the dependence often taking the form of a Karplus relationship[1] (*i.e.* a proportionality to $\cos^2\theta$, where θ is a dihedral angle between chemical bonds). In the case of ^{31}P ($I = \frac{1}{2}$, natural abundance = 100%) it may also be necessary to take into account phosphorus lone-pair directions, and the couplings $^2J(^{31}PH)$, $^3J(^{31}PH)$, $^2J(^{31}P^{13}C)$ and $^3J(^{31}P^{13}C)$ are known to be sensitive to this factor.[2–5] There is now evidence that similar factors can also influence $^nJ(^{31}P^{31}P)$ [n = 1,2,3]. Thus in R_2PPR_2 (R = alkyl or aryl) $^1J(^{31}P^{31}P)$ is smaller (*i.e.* is less negative) when R is bulky;[6] in $X_2PN(R)PX_2$ (X = halide) bulky groups R destabilise conformations in which the two phosphorus lone pairs can come into close proximity and this reduces $^2J(^{31}PN^{31}P)$;[7] $^2J(^{31}PC^{31}P)$ is large and independent of temperature in $(Ph_2P)_2CH_2$ and in 1,1-bis(diphenylphosphino)ethene[8] **1**, but is small in 1,1-bis(diphenylphosphino)prop-1-ene[9] **2** (7 Hz) and tris(diphenylphosphino)ethene[10] **3** (1.5 Hz) where R can interact with the phenyl groups of the phosphorus to which it is *cis*; and in substituted benzenes $(Ph_2P)_nC_6H_{6-n}$ $^3J(^{31}P^{31}P)$ is substantially reduced when crowding forces the phosphorus electron lone pairs into non-proximate orientations.[11] Additionally, in many polycyclic systems $^nJ(^{31}P^{31}P)$ is stereochemically dependent, but here the interpretation is complicated by often severe deformation of interbond angles and by the availability of multiple coupling pathways.

An understanding of this behaviour is of value in the interpretation and assignment of the ^{31}P NMR spectra of polyorganophosphines; these are of considerable interest as ligands but their study has been somewhat restricted by difficulties of characterisation and identification of diastereomers resulting from the stereochemical rigidity of phosphorus(III). Recently, we have shown[12–14] how additions of primary and secondary phosphines to **1** and **2** can lead to polyorganophosphines with up to seven phosphorus atoms and we have used ^{31}P NMR spectroscopy (including two-dimensional experiments)[15,16] to identify the products of these reactions. In addition to their value as poly and/or ambidentate ligands these species display a wide range of phosphorus-31 chemical shifts and coupling constants whose variation appears to be substantially dependent upon conformation.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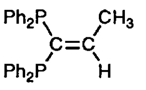
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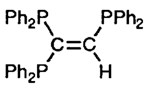
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In this paper we report the synthesis of a new range of such molecules which permit the exploration of the relationship of conformation to $\delta(^{31}P)$ and $^{2/3}J(^{31}P^{31}P)$ in circumstances where the presence of bulky substituents on or near phosphorus provides conformational constraint, but where the differences in electronic factors should be of minor importance. The NMR measurements have been supplemented by X-ray diffraction determinations of the structures of three selected compounds which suggest that their solid-state structures are closely similar to their conformations in solution.

Results and Discussion

(*a*) *General.*—The base-catalysed addition at room temperature of phenylphosphine to **1** in tetrahydrofuran (thf) gave the expected[12] anti-Markovnikov product **4** as air-stable colourless needles, soluble in most organic solvents apart from alcohols. Other primary phosphines reacted similarly to give the related triphosphines **5**–**7** (see Scheme 1 and Table 1) which were identified in solution by ^{31}P NMR spectroscopy, although only **7** could be successfully crystallised and was obtained as air-stable colourless crystals. In general species derived from n-butylphosphine and 2-cyanoethylphosphine could not be crystallised and were found to be considerably more air-sensitive than their aryl counterparts. These triphosphines contain a secondary phosphine moiety and compounds **4**–**6** were found to add smoothly under the same conditions to a second equivalent of **1** to yield the pentaphosphines **9**–**11**, the first of which we have previously characterised and reported.[15] However, **7** would not add to **1**, even under reflux in thf and this lower reactivity is presumably due to the bulk of the tri-*tert*-butylphenyl group on P_x, a feature which also affects the NMR parameters as discussed below.

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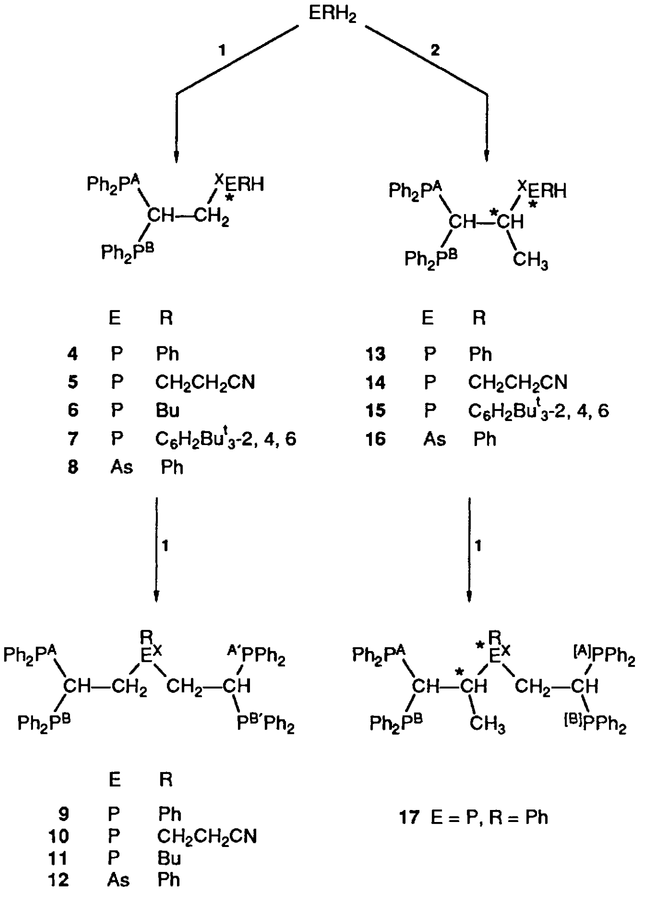
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Phosphorus-31 NMR parameters[a]

Compound	E	R	$\delta(^{31}P_A)$	$\delta(^{31}P_B)$	$\delta(^{31}P_X)$	$^2J(^{31}P_A{}^{31}P_B)$	$^3J(^{31}P_A{}^{31}P_X)$	$^3J(^{31}P_B{}^{31}P_X)$
4	P	Ph	−4.0	−5.7	−54.8	112.3	15.9	17.1
5	P	CH_2CH_2CN	−3.8	−5.7	−70.1	124.5	19.6	20.1
6	P	Bu^n	−3.4	−5.8	−65.3	125.7	15.9	17.7
7	P	$C_6H_2Bu^t{}_3$-2,4,6	−3.7	−4.4	−69.0	58.6	29.3	28.1
8	As	Ph	−4.9[b]	−4.9[b]	—	[c]	—	—
9	P	Ph	−2.9	−4.8	−29.7	100.7	28.6	17.0
10	P	CH_2CH_2CN	−2.5	−4.0	−26.6	110.5	19.5	19.5
11	P	Bu^n	−2.7	−3.3	−27.7	101.3	20.1	19.5
12	As	Ph	−3.2	−4.6	—	96.2	—	—
13a[d]	P	Ph	−10.8	−14.0	−42.0	37.8	32.3	32.3
13b[d]	P	Ph	−8.7	−14.1	−25.3	55.5	39.7	62.3
14a[d]	P	CH_2CH_2CN	−11.7	−12.7	−59.0	55.0	49.4	42.7
14b[d]	P	CH_2CH_2CN	−9.3	−13.7	−44.3	55.5	51.3	61.0
15a[e]	P	$C_6H_2Bu^t{}_3$-2,4,6	−8.9	−12.9	−42.8	31.7	8.5	34.2
16a[d]	As	Ph	−8.5	−12.9	—	56.6	—	—
16b[d]	As	Ph	−9.4	−13.0	—	47.4	—	—
18	P	Ph	−10.0	−11.7	−8.4	25.7	80.6	2.8
17a[e]	P	Ph	−9.2	−12.6	−17.4	29.7	82.8	3.1
			−1.7[f]	−3.8[g]		123.5[h]	30.8[i]	9.3[j]

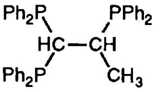
[a] Chemical shifts δ are in ppm (±0.1 ppm) to high frequency of external 85% H_3PO_4; coupling constants are in Hz (±0.1 Hz). [b] Mean of $\delta(^{31}P_A)$ and $\delta(^{31}P_B)$. [c] Tightly coupled AB system with outer lines unobserved. [d] Diastereomers. [e] Only one diastereomer observed. [f] $\delta(P_{[A]})$. [g] $\delta(P_{[B]})$. [h] $^2J(^{31}P_{[A]}{}^{31}P_{[B]})$. [i] $^3J(^{31}P_{[A]}P_X)$. [j] $^3J(^{31}P_{[B]}P_X)$.



Scheme 1

Primary phosphines were also found to add analogously to the carbon–carbon double bond of **2** to give the new triphosphines **13**–**15**. Each of these reactions has the potential to yield two diastereomeric products owing to the presence of two chiral centres (marked *). With **13** and **14** both diastereomers were indeed formed (in a *ca.* 1:1 ratio from ^{31}P NMR spectroscopy) but in the case of **15** only one isomer was detected. Further addition of these secondary phosphine species to extra **2** did not occur, again presumably as a consequence of steric hindrance, but **13** did add to **1** to yield the pentaphosphine **17** as an air-stable white solid. Pentaphosphine **17** should also exhibit diastereoisomerism, but only one isomer was actually formed in this reaction, even though the initial reagent, **13**, was a 1:1 mixture of diastereomers. This confirms that these addition reactions of species with P–H bonds occur without retention of configuration at phosphorus under these conditions.

Phenylarsine was found to add to **1** in an analogous manner to give first **8** and then the tetraphosphinoarsine **12** which was isolated as air-stable colourless crystals, and to **2** to give two diastereomers of **16**. Addition of diphenylphosphine to **2** under these conditions proceeded similarly to its addition to **1** and gave the new tritertiary phosphine **18** which was isolated as an air-stable white powder.



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(*b*) *NMR.*—The presence of the chiral centre at P_X in compounds **4**–**7** renders the geminally related phosphorus nuclei P_A and P_B chemically inequivalent so that the ^{31}P spin system is ABX in which the secondary phosphine X resonances were readily assigned from their characteristic negative chemical shifts and values of $^1J(^{31}PH)$ of *ca.* 200 Hz. In compound **8** chirality at arsenic leads to an AB pattern for the geminal phosphorus nuclei. In **13**–**15** the geminal phosphorus nuclei are again inequivalent in each diastereomer, as they are in **9**–**12** owing to prochirality at the central phosphorus or arsenic atom. Strictly, the ^{31}P NMR spectra of **9**–**11** arise from AA′BB′X spin systems, but since $^6J(^{31}P^{31}P)$ is negligible it is convenient to regard them as $(AB)_2X$, and similarly to treat **12** as containing two identical AB spin systems. In **17** all five phosphorus nuclei are inequivalent, but in the absence of long-range coupling the geminal ^{31}P nuclei can be regarded as being part of two separate ABX systems with a common X.

Hence in all cases it was possible to obtain the ^{31}P–^{31}P coupling constants and ^{31}P chemical shifts by direct analysis of the spectra. When appropriate the raw parameters thus derived

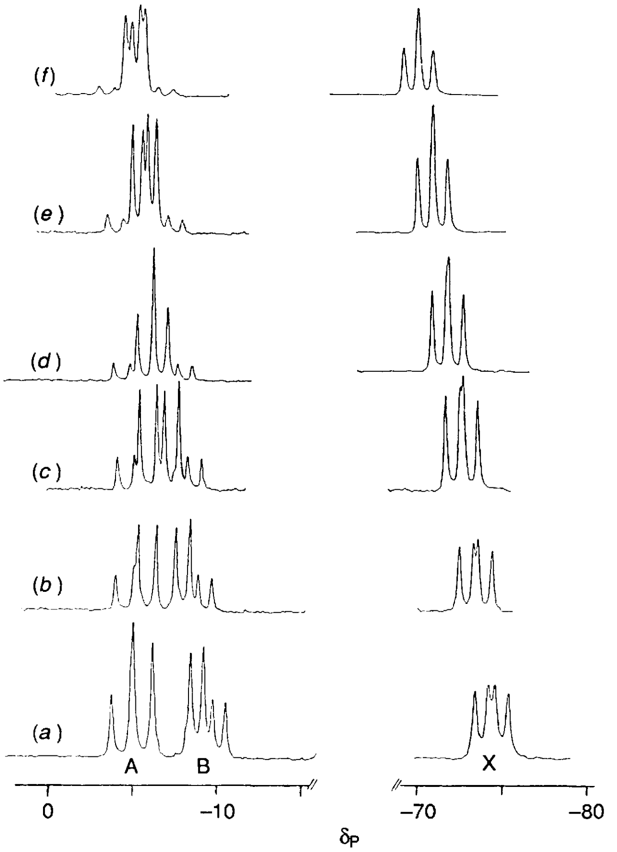
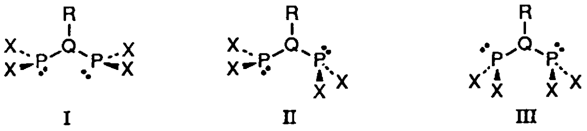


Fig. 1 ^{31}P NMR spectra at 36.2 MHz of **7** at different temperatures, with values of the three ^{31}P–^{31}P coupling constants. *T*/K; $^2J(P_AP_B)$, $^3J(P_AP_X)$, $^3J(P_BP_X)$/Hz: (*a*) 173; 46.4, 41.5, 28.1: (*b*) 193; 47.6, 39.1, 29.3: (*c*) 213; 48.8, 36.6, 30.5: (*d*) 233; 51.3, 35.3, 29.4: (*e*) 253; 53.7, 33.0, 29.3: (*f*) 273; 56.2, 31.7, 28.1

were refined by computer analysis using a program based upon LAOCOON.[17] The data are in Table 1, and for the pairs of geminally related Ph_2P groups the arbitrary spectral assignment $\delta(^{31}P_A) > \delta(^{31}P_B)$ is made, although this implies no stereochemical assignment.

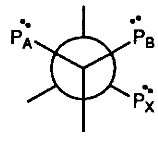
(*i*) *Phosphorus*-31 *chemical shifts*. For the geminally related nuclei P_A and P_B the phosphorus chemical shifts are clustered in the range δ −5.8 to −1.7 in **4**–**12** where there is no methyl group in the position β to P_A and P_B, and in the range δ −14.1 to −8.7 for **13**–**18** where there is such a methyl group. The difference of *ca.* 7 ppm between the two groups is somewhat greater than predicted by group contribution theory,[18] and may reflect significant conformational effects. For P_X the same substitution of a methyl group corresponds to an α-substitution, and for this an increase in $\delta(^{31}P)$ of *ca.* 18 ppm is predicted by the group contribution theory. In fact, the mean $\delta(^{31}P_X)$ for **13a** and **13b** is −33.7, *i.e.* a change from **4** of +21 ppm and the corresponding mean figure for **14a** and **14b** is +18 ppm in apparent conformity with the prediction. However, these diastereomeric averages conceal wide individual differences of some 15 ppm that cannot be accommodated by group contribution theory which takes no account of conformational preferences. It seems likely that in our species there are present groups sufficiently bulky to produce substantial imbalances in conformer populations, whereas this was not the case for the molecules from which group contribution theory was originally derived. Furthermore these imbalances apparently lead to contributions of opposite but approximately equal magnitude for diastereomeric pairs and thus have no observable effect in molecules of higher effective symmetry.

(*ii*) ^{31}P–^{31}P *Coupling constants*. It has been found for species of the type $X_2PQ(R)PX_2$ (X = Cl or Ph, Q = N or CH) that the bulk of R determines which of the idealised conformations **I**, **II** or **III** predominates and hence also controls the value of $^2J(^{31}P^{31}P)$.[19–21] Large values occur for conformation **I**, moderate for **II** and small for **III**. Our present results conform to this pattern, although the changes arise from the bulk of the substituent on C^2 rather than C^1. Thus in the species **4**–**6** and **9**–**12** with no methyl substituent on C^2, $^2J(^{31}P_A{}^{31}P_B)$ is in the range 100.7–125.7 Hz and is comparable with its value in $(Ph_2P)_2CH_2$ (125.0 Hz). Introduction of a methyl group at C^2 however dramatically reduces the coupling to the range of 29.7–55.5 Hz, a feature most clearly demonstrated in **17a** which has each type of geminal phosphorus environment and corresponding two greatly different values of $^2J(^{31}P^{31}P)$ (123.5 and 29.7 Hz). In **7** the effect is due to the exceptional bulk of the substituent on E, while in **9** and **12** E has two substituents of moderate size and there is a small decrease in $^2J(^{31}P_A{}^{31}P_B)$, corresponding to a reduction in the population of conformation **I**. In conformity with this, the couplings in **7** were found to be temperature dependent (see Fig. 1), and $^2J(^{31}P_A{}^{31}P_B)$ varied from 46.4 Hz at 173 K to 56.2 Hz at 273 K, as the proportion of conformation **I** rose at higher temperature. Furthermore, in **13** and **16** with two asymmetric centres there are significant differences in $^2J(^{31}P_A{}^{31}P_B)$ for the diastereomers, and this confirms the importance of conformational rather than electronic factors.

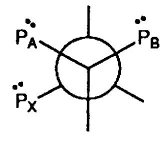


The vicinal ^{31}P–^{31}P couplings in these species can be expected to depend upon rotation about the C^1–C^2 bond and upon the phosphorus electron lone-pair directions, and thus present a multi-dimensional problem. It can be simplified by the use of the following reasonable assumptions: (*a*) only staggered conformers need to be considered; (*b*) conformers with P_X *gauche* to P_A *and* P_B are sterically excluded; (*c*) $^3J(^{31}P^{31}P)$ is large when the phosphorus electron lone pairs are directed towards each other and small when their directions are opposed. Conformations **I′**–**VIII′** are idealised conformations that should arise on this basis. In species with large $^2J(^{31}P_A{}^{31}P_B)$ (**4**–**6** and **9**–**11**) conformations **I′** and **II′** predominate so that $^3J(^{31}P^{31}P)$ is small for both P_A and P_B. With a bulky substituent on P_X (as in **7**) there is interference with the phenyl groups of P_A or P_B and **I′** and **II′** are no longer the predominant conformations. Hence there is the concomitant decrease in $^2J(^{31}P_A{}^{31}P_B)$ already referred to, and there are also increases in $^3J(^{31}P_A{}^{31}P_X)$ and $^3J(^{31}P_B{}^{31}P_X)$ as indeed observed. Owing to the chirality at P_X the conformers **III′** and **VIII′** are a diastereomeric (rather than an enantiomeric) pair and so will be unequally populated, the size of the imbalance depending upon the bulk of the substituents of P_X. The same considerations apply to the pairs **V′**/**VI′** and **IV′**/**VII′**. It is therefore perhaps surprising that the two vicinal couplings in **7** are so similar. However, this near equality is probably fortuitous, as the temperature dependence study of Fig. 1 shows. In these circumstances the proportion of conformers **I′**/**II′** will increase with rising temperature [as shown by an increase in $^2J(^{31}P_A{}^{31}P_B)$ so $^3J(^{31}P_A{}^{31}P_X)$ decreases while $^3J(^{31}P_B{}^{31}P_X)$ remains essentially constant. This may indicate that conformations such as **IV′** and **VIII′** are more important than **V′** and **VII′**.

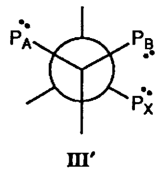
With a bulky substituent on C^2 the change in conformer populations is greater and the effects on all three couplings become more pronounced. In particular the greatest reductions in $^2J(^{31}P_A{}^{31}P_B)$ (in **17a** and **18**) are associated with the largest differences between $^3J(^{31}P_A{}^{31}P_X)$ and $^3J(^{31}P_B{}^{31}P_X)$ and also with the presence of especially bulky substituents on C^2.



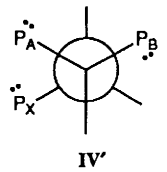
I′



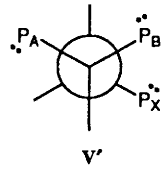
II′



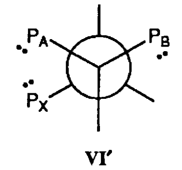
III′



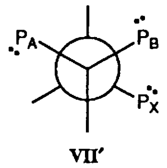
IV′



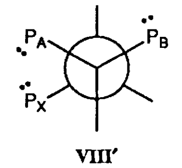
V′



VI′



VII′



VIII′

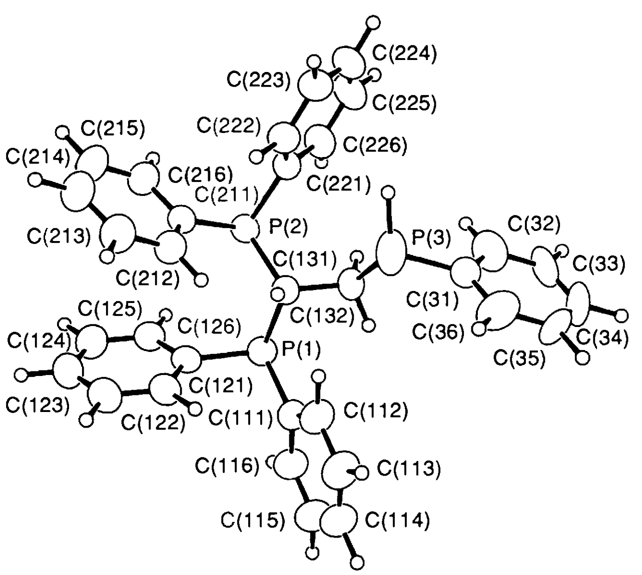


Fig. 2 An ORTEP[22] diagram of the molecular structure of compound **4**

(*c*) *X-Ray Structures*.—The crystal structures of the triphosphines **4** and **7** have been determined, together with that of the pentaphosphine **9**, and these are shown in Figs. 2, 3 and 4 respectively. Selected bond lengths and angles are given for each compound in Tables 2, 3 and 4, and fractional atomic coordinates are given in Tables 5, 6 and 7. None of the structures shows any unexpected features although the *para*-*tert*-butyl substituent of the phenyl group in **7** was found to be disordered—see Experimental section for more detail. The bond lengths and angles of all three therefore fall in expected ranges and compare well with those of other organophosphines whose structures have been determined.[10,23]

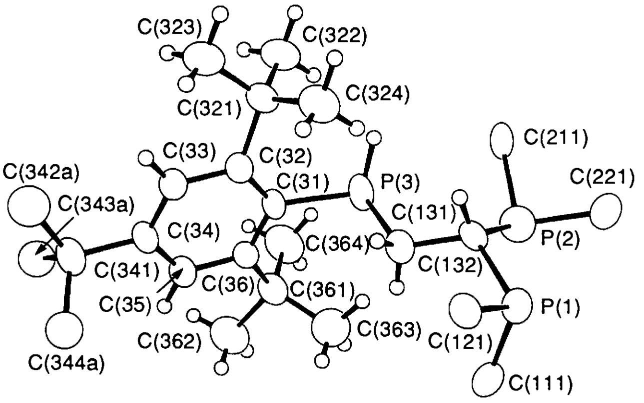


Fig. 3 An ORTEP diagram of the molecular structure of compound **7**. For clarity, only the *ipso* carbon atoms of the phenyl groups of the geminally related phosphorus atoms are shown, and only one position of the rotationally disordered *tert*-butyl group is shown

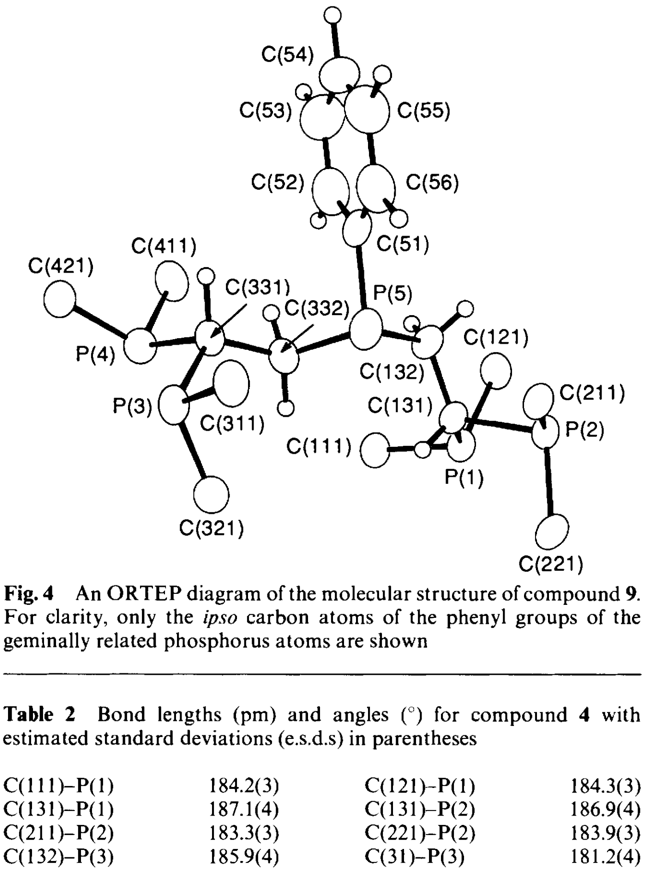


Fig. 4 An ORTEP diagram of the molecular structure of compound **9**. For clarity, only the *ipso* carbon atoms of the phenyl groups of the geminally related phosphorus atoms are shown

Table 2 Bond lengths (pm) and angles (°) for compound **4** with estimated standard deviations (e.s.d.s) in parentheses

C(111)–P(1)	184.2(3)	C(121)–P(1)	184.3(3)
C(131)–P(1)	187.1(4)	C(131)–P(2)	186.9(4)
C(211)–P(2)	183.3(3)	C(221)–P(2)	183.9(3)
C(132)–P(3)	185.9(4)	C(31)–P(3)	181.2(4)
C(132)–C(131)	155.8(5)		
C(121)–P(1)–C(111)	100.6(2)	C(131)–P(1)–C(111)	103.3(2)
C(131)–P(1)–C(121)	102.9(2)	C(211)–P(2)–C(131)	105.0(2)
C(221)–P(2)–C(131)	104.4(2)	C(221)–P(2)–C(211)	98.8(2)
C(31)–P(3)–C(132)			
P(2)–C(131)–P(1)	105.1(2)	C(132)–C(131)–P(1)	106.6(3)
C(132)–C(131)–P(2)	112.1(3)	C(131)–C(132)–P(3)	112.4(3)

Of special interest here are the relative orientations of the electron lone pairs of the geminally related phosphorus atoms. There are no significant distortions of the interbond angles at any of these phosphorus atoms and it can therefore be assumed that the phosphorus-lone pair vector forms equal angles with each phosphorus-bond vector. This makes it possible to determine the positions of the phosphorus-lone pair vectors and

Table 3 Selected bond lengths (pm) and angles (°) for compound **7** with e.s.d.s in parentheses

C(111)–P(1)	183.8(5)	C(121)–P(1)	185.0(5)
C(131)–P(1)	188.5(7)	C(131)–P(2)	183.4(8)
C(211)–P(2)	186.0(5)	C(221)–P(2)	185.4(6)
C(132)–P(3)	187.3(8)	C(31)–P(3)	188.3(5)
C(132)–C(131)	152.7(9)		
C(321)–C(32)	158.5(7)	C(341)–C(34)	156.5(8)
C(361)–C(36)	157.4(8)	C(322)–C(321)	152.8(9)
C(323)–C(321)	155.6(10)	C(324)–C(321)	154.5(9)
C(342a)–C(341)	155.9(16)	C(342b)–C(341)	151.5(24)
C(342s)–C(341)	162.9(34)	C(342d)–C(341)	172.4(37)
C(343a)–C(341)	157.0(16)	C(343b)–C(341)	155.2(20)
C(343c)–C(341)	164.6(30)	C(343d)–C(341)	171.1(28)
C(344a)–C(341)	156.7(14)	C(344b)–C(341)	155.6(22)
C(362)–C(361)	154.6(9)	C(363)–C(361)	156.6(10)
C(364)–C(361)	153.3(9)		
C(121)–P(1)–C(111)	104.3(3)	C(131)–P(1)–C(111)	100.9(3)
C(131)–P(1)–C(121)	103.3(3)	C(211)–P(2)–C(131)	104.1(3)
C(221)–P(2)–C(131)	104.8(3)	C(221)–P(2)–C(211)	95.0(3)
C(31)–P(3)–C(132)	101.6(3)		
P(2)–C(131)–P(1)	109.4(4)	C(132)–C(131)–P(2)	113.8(5)
C(132)–C(131)–P(1)	113.1(4)	C(131)–C(132)–P(3)	116.5(5)
C(32)–C(31)–P(3)	120.8(2)	C(36)–C(31)–P(3)	118.5(2)
C(341)–C(34)–C(33)	119.2(3)	C(341)–C(34)–C(35)	120.8(3)
C(361)–C(36)–C(31)	125.5(3)	C(361)–C(36)–C(35)	113.8(3)
C(322)–C(321)–C(32)	110.5(5)	C(323)–C(321)–C(32)	112.1(5)
C(323)–C(321)–C(322)	104.5(6)	C(324)–C(321)–C(32)	111.8(5)
C(324)–C(321)–C(322)	113.6(6)	C(324)–C(321)–C(323)	104.0(6)
C(362)–C(361)–C(36)	112.5(5)	C(363)–C(361)–C(36)	113.1(5)
C(363)–C(361)–C(362)	104.2(6)	C(364)–C(361)–C(36)	109.5(5)
C(364)–C(361)–C(362)	105.8(6)	C(364)–C(361)–C(363)	111.4(6)

Table 4 Bond lengths (pm) and angles (°) for compound **9** with e.s.d.s in parentheses

C(111)–P(1)	183.1(5)	C(121)–P(1)	182.4(5)
C(131)–P(1)	187.1(7)	C(131)–P(2)	185.9(7)
C(211)–P(2)	182.2(5)	C(221)–P(2)	183.0(5)
C(311)–P(3)	182.3(5)	C(321)–P(3)	181.9(5)
C(331)–P(3)	187.1(7)	C(331)–P(4)	187.3(7)
C(411)–P(4)	182.5(5)	C(421)–P(4)	182.4(5)
C(132)–P(5)	186.2(7)	C(332)–P(5)	180.6(8)
C(51)–P(5)	184.7(5)		
C(132)–C(131)	152.3(9)	C(332)–C(331)	151.5(9)
C(121)–P(1)–C(111)	106.0(3)	C(131)–P(1)–C(111)	104.7(3)
C(131)–P(1)–C(121)	102.6(3)	C(211)–P(2)–C(131)	101.8(3)
C(221)–P(2)–C(131)	103.9(3)	C(221)–P(2)–C(211)	99.5(3)
C(321)–P(3)–C(311)	104.0(3)	C(331)–P(3)–C(311)	105.1(3)
C(331)–P(3)–C(321)	102.7(3)	C(411)–P(4)–C(331)	101.6(3)
C(421)–P(4)–C(331)	103.2(3)	C(421)–P(4)–C(411)	100.1(3)
C(332)–P(5)–C(132)	98.7(4)	C(51)–P(5)–C(132)	99.8(3)
C(51)–P(5)–C(332)	100.5(3)		
P(2)–C(131)–P(1)	103.7(3)	C(132)–C(131)–P(1)	116.1(4)
C(132)–C(131)–P(2)	111.2(5)	C(131)–C(132)–P(5)	112.7(4)
P(4)–C(331)–P(3)	103.4(3)	C(332)–C(331)–P(3)	117.2(5)
C(332)–C(331)–P(4)	108.5(5)	C(331)–C(332)–P(5)	118.1(5)

hence to specify their relative orientations in terms of the dihedral angle about a notional P–P link. These dihedral angles are 111° in **7**, 25° in **4** and 83 and 86° for the two geminal phosphorus pairs of **9**. As there are no abnormally close intermolecular contacts in any of these structures it is probable that these dihedral angles are primarily determined by the bulk of the substituents on P_X so that in **7** with the very bulky tri-*tert*-butylphenyl group the lone-pair directions are essentially opposed whereas in **4** they point more or less towards each other. The similarity of the two dihedral angles of intermediate size in **9** also supports this view.

Table 5 Fractional atom coordinates (× 10^4) for compound **4**

Atom	*x*	*y*	*z*
P(1)	1 374(1)	131.6(3)	8 048.2(3)
P(2)	1 448(1)	1 128.0(3)	7 076.5(3)
P(3)	−1 932(2)	1 937.7(5)	8 377.7(4)
C(111)	−427(2)	−167(1)	8 658(1)
C(112)	−2 524(2)	65(1)	8 778(1)
C(113)	−3 730(2)	−192(1)	9 260(1)
C(114)	−2 839(2)	−682(1)	9 622(1)
C(115)	−742(2)	−914(1)	9 502(1)
C(116)	464(2)	−657(1)	9 020(1)
C(121)	652(2)	−410(1)	7 399(1)
C(122)	−1 380(2)	−718(1)	7 343(1)
C(123)	−1 796(2)	−1 136(1)	6 849(1)
C(124)	−182(2)	−1 246(1)	6 413(1)
C(125)	1 849(2)	−938(1)	6 469(1)
C(126)	2 266(2)	−520(1)	6 963(1)
C(131)	−7(4)	880(1)	7 793(1)
C(132)	349(4)	1 356(1)	8 342(1)
C(211)	−308(2)	847(1)	6 418(1)
C(212)	−2 425(2)	595(1)	6 455(1)
C(213)	−3 610(2)	423(1)	5 909(1)
C(214)	−2 677(2)	503(1)	5 327(1)
C(215)	−560(2)	756(1)	5 290(1)
C(216)	625(2)	928(1)	5 835(1)
C(221)	865(2)	1 974(1)	7 007(1)
C(222)	−1 114(2)	2 215(1)	6 754(1)
C(223)	−1 382(2)	2 862(1)	6 685(1)
C(224)	329(2)	3 268(1)	6 869(1)
C(225)	2 307(2)	3 027(1)	7 122(1)
C(226)	2 576(2)	2 380(1)	7 191(1)
C(31)	−1 498(3)	2 235(1)	9 168(1)
C(32)	418(3)	2 562(1)	9 347(1)
C(33)	691(3)	2 790(1)	9 957(1)
C(34)	−954(3)	2 692(1)	10 388(1)
C(35)	−2 870(3)	2 365(1)	10 208(1)
C(36)	−3 142(3)	2 136(1)	9 599(1)

It is striking that for species **4**, **7** and **9** the pattern of values of $^2J(^{31}P^{31}P)$ in solution (112.3, 58.6 and 100.7 Hz respectively) closely follows that of the corresponding lone-pair/lone-pair dihedral angles in the solid state. This strongly suggests that the solid and solution conformations of these species are very similar and are probably determined by the bulk of the substituent on P_X. It is also noteworthy that in the other species, $^2J(^{31}P^{31}P)$ is invariably of the size to be expected from consideration of the bulk of neighbouring substituents, thus confirming that this parameter is a useful guide to the conformations of polyorganophosphines.

Experimental

All solvents were dried and deaerated by standard procedures immediately prior to use. All manipulations were conducted under an atmosphere of dry nitrogen. 1,1-bis(diphenylphosphino)ethene **1**, diphenylphosphine and tri-*tert*-butylphenylphosphine were prepared by literature methods. Phenylphosphine, 2-cyanoethylphosphine, and *n*-butylphosphine were purchased from Strem Chemicals and used without further purification. Proton, ^{13}C and ^{31}P NMR spectra were measured on solutions in $CDCl_3$ in 10 mm o.d. spinning tubes using a JEOL FX 90Q pulsed Fourier transform spectrometer. Carbon-13 and ^{31}P NMR data quoted were obtained under conditions of broad-band proton decoupling, and ^1H-{^{31}P} and ^{13}C-{^{31}P} selective decoupling experiments and spectral editing techniques were used to confirm assignments.

1,1-*Bis(diphenylphosphino)prop*-1-*ene* **2**.—Triphenylphosphine (86.8 g, 0.33 mol) and lithium (4.6 g, 0.66 mol) in thf (750 cm^3) were stirred overnight. The resulting solution was treated with 2-chloro-2-methylpropane (36.5 cm^3, 0.33 mol)

Table 6 Fractional atom coordinates (× 10^4) for compound **7**

Atom	x	y	z
P(1)	6 592(2)	4 583(1)	3 078(1)
P(2)	3 881(2)	4 350(1)	1 922(1)
P(3)	4 918(2)	3 165(1)	1 428(1)
C(111)	7 302(3)	4 786(1)	2 122(2)
C(112)	8 451(3)	4 573(1)	1 879(2)
C(113)	8 878(3)	4 748(1)	1 124(2)
C(114)	8 155(3)	5 136(1)	614(2)
C(115)	7 005(3)	5 349(1)	858(2)
C(116)	6 579(3)	5 174(1)	1 612(2)
C(121)	7 983(3)	4 221(1)	3 769(2)
C(122)	7 769(3)	3 743(1)	4 142(2)
C(123)	8 811(3)	3 509(1)	4 732(2)
C(124)	10 066(3)	3 753(1)	4 949(2)
C(125)	10 280(3)	4 230(1)	4 576(2)
C(126)	9 239(3)	4 465(1)	3 986(2)
C(131)	5 395(5)	4 056(2)	2 581(4)
C(132)	6 067(5)	3 649(2)	2 089(4)
C(211)	2 524(3)	3 865(1)	1 961(3)
C(212)	2 152(3)	3 689(1)	2 732(3)
C(213)	1 027(3)	3 368(1)	2 692(3)
C(214)	275(3)	3 222(1)	1 881(3)
C(215)	646(3)	3 398(1)	1 110(3)
C(216)	1 771(3)	3 720(1)	1 150(3)
C(221)	3 274(3)	4 816(1)	2 671(3)
C(222)	3 542(3)	4 801(1)	3 585(3)
C(223)	2 902(3)	5 150(1)	4 061(3)
C(224)	1 996(3)	5 514(1)	3 623(3)
C(225)	1 728(3)	5 529(1)	2 709(3)
C(226)	2 367(3)	5 180(1)	2 233(3)
C(31)	6 147(2)	2 643(1)	1 251(2)
C(32)	6 527(2)	2 257(1)	1 877(2)
C(33)	7 586(2)	1 921(1)	1 802(2)
C(34)	8 266(2)	1 972(1)	1 101(2)
C(35)	7 887(2)	2 358(1)	475(2)
C(36)	6 827(2)	2 694(1)	550(2)
C(321)	5 693(5)	2 096(2)	2 607(4)
C(322)	4 220(5)	1 985(3)	2 196(4)
C(323)	6 214(6)	1 580(2)	3 069(4)
C(324)	5 857(6)	2 495(2)	3 362(4)
C(341)	9 469(5)	1 598(2)	1 038(4)
C(342a)*	9 237(11)	1 341(5)	113(8)
C(342b)*	8 867(16)	1 069(9)	785(14)
C(342c)*	8 874(21)	1 171(14)	293(19)
C(342d)*	8 925(21)	994(14)	1 322(19)
C(343a)*	9 663(12)	1 157(5)	1 747(9)
C(343b)*	10 502(16)	1 617(9)	1 914(12)
C(343c)*	10 121(21)	1 365(14)	2 011(18)
C(343d)*	10 831(21)	1 903(14)	1 655(19)
C(344a)*	10 816(11)	1 912(5)	1 094(8)
C(344b)*	10 291(17)	1 749(9)	319(13)
C(344c)*	10 696(21)	2 001(14)	571(19)
C(344d)*	9 582(22)	1 545(15)	−51(19)
C(361)	6 378(5)	3 051(2)	−275(4)
C(362)	7 274(6)	2 978(3)	−974(4)
C(363)	6 495(7)	3 643(2)	−52(4)
C(364)	4 940(5)	2 906(3)	−726(4)

* Atom refined with an occupancy factor of 0.25.

Table 7 Fractional atom coordinates (× 10^4) for compound **9**

Atom	x	y	z
P(1)	2655.3(7)	5703.6(10)	3003.1(4)
P(2)	2749.2(7)	7546.8(9)	3415.7(4)
P(3)	5817.2(7)	4809.4(10)	3988.4(4)
P(4)	5137.9(7)	2836.5(10)	3831.5(4)
P(5)	3811.7(7)	5639.1(11)	3992.2(4)
C(111)	3151(2)	4526(2)	2914(1)
C(112)	2783(2)	3693(2)	2776(1)
C(113)	3176(2)	2851(2)	2665(1)
C(114)	3937(2)	2843(2)	2692(1)
C(115)	4305(2)	3676(2)	2830(1)
C(116)	3912(2)	4518(2)	2941(1)
C(121)	1764(1)	5314(2)	3157(1)
C(122)	1609(1)	4393(2)	3314(1)
C(123)	895(1)	4170(2)	3407(1)
C(124)	336(1)	4868(2)	3343(1)
C(125)	491(1)	5790(2)	3186(1)
C(126)	1205(1)	6012(2)	3093(1)
C(131)	3113(3)	6229(3)	3388(1)
C(132)	2991(3)	5644(4)	3711(1)
C(211)	3206(2)	8014(2)	3794(1)
C(212)	3946(2)	8267(2)	3804(1)
C(213)	4274(2)	8586(2)	4103(1)
C(214)	3861(2)	8652(2)	4393(1)
C(215)	3120(2)	8399(2)	4384(1)
C(216)	2792(2)	8081(2)	4084(1)
C(221)	3263(2)	8249(2)	3101(1)
C(222)	3175(2)	9303(2)	3113(1)
C(223)	3529(2)	9920(2)	2882(1)
C(224)	3970(2)	9484(2)	2639(1)
C(225)	4057(2)	8430(2)	2627(1)
C(226)	3704(2)	7813(2)	2858(1)
C(311)	5703(2)	5937(2)	4249(1)
C(312)	5327(2)	5875(2)	4549(1)
C(313)	5335(2)	6696(2)	4770(1)
C(314)	5720(2)	7578(2)	4691(1)
C(315)	6096(2)	7640(2)	4391(1)
C(316)	6088(2)	6819(2)	4169(1)
C(321)	5808(2)	5303(3)	3563(1)
C(322)	5444(2)	6185(3)	3461(1)
C(323)	5467(2)	6492(3)	3127(1)
C(324)	5854(2)	5917(3)	2895(1)
C(325)	6218(2)	5035(3)	2998(1)
C(326)	6195(2)	4728(3)	3332(1)
C(331)	4925(3)	4119(4)	4010(1)
C(332)	4284(3)	4565(4)	3814(2)
C(411)	4279(2)	2161(3)	3895(1)
C(412)	4098(2)	1723(3)	4201(1)
C(413)	3438(2)	1203(3)	4233(1)
C(414)	2960(2)	1120(3)	3959(1)
C(415)	3140(2)	1558(3)	3654(1)
C(416)	3800(2)	2078(3)	3621(1)
C(421)	5704(2)	2249(2)	4158(1)
C(422)	5970(2)	1287(2)	4075(1)
C(423)	6377(2)	732(2)	4310(1)
C(424)	6519(2)	1138(2)	4627(1)
C(425)	6254(2)	2100(2)	4709(1)
C(426)	5846(2)	2655(2)	4475(1)
C(51)	3417(2)	5041(3)	4367(1)
C(52)	3110(2)	4071(3)	4373(1)
C(53)	2866(2)	3664(3)	4674(1)
C(54)	2930(2)	4228(3)	4969(1)
C(55)	3238(2)	5199(3)	4963(1)
C(56)	3481(2)	5606(3)	4662(1)

and then decanted into a large dropping funnel. The red solution was added dropwise to 1,1-dichloroprop-1-ene (15.7 cm^3, 0.165 mol) in thf (50 cm^3). When the addition was complete water (200 cm^3) was added and most of the thf was removed by rotary evaporation. Extraction of the crude product into diethyl ether (2 × 200 cm^3) followed by removal of the solvent at the pump yielded an oil to which ethanol (300 cm^3) was added. Overnight the solution deposited colourless crystals which were

Table 8 Crystallographic data for compounds **4**, **7** and **9**[a]

Compound	**4**	**7**	**9**
Crystal data			
Formula	$C_{32}H_{39}P_3$	$C_{44}H_{53}P_3$	$C_{58}H_{51}P_5$
M	506.50	674.83	902.91
Crystal dimensions/mm	0.8 × 0.4 × 0.2	0.9 × 0.5 × 0.2	0.8 × 0.6 × 0.5
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
a/pm	605.6(1)	1006.1(2)	1836.2(3)
b/pm	2128.8(4)	2580.0(6)	1321.4(4)
c/pm	2135.4(3)	1552.6(3)	40 009.2(8)
β/°	92.05(1)	100.69(2)	90.80(2)
U/nm^3	2.7512(7)	3.960(1)	9.727(4)
Z	4	4	8
D_c/g cm^{-3}	1.22	1.13	1.23
F(000)	1064	1448	3472
μ/cm^{-1}	1.92	1.41	1.82
Data collection			
No. of data collected	5145	5482	9220
No. of data observed[b]	4165	4165	5771
Refinement			
ρ_{max},ρ_{min}/e Å^{-3}	0.41, −0.43	0.71, −0.54	0.35, −0.62
Δ/σ_{max}	0.08	0.11	0.19
R[c]	0.0549	0.0859	0.0742
R'[d]	0.0698	0.0769	0.0722
Weighting parameter g[e]	0.0001	0.0	0.0001
No. of parameters	260	425.	479

[a] Common to all three complexes: scan mode ω–2θ, scan widths 2.0° + α-doublet splitting, scan speeds 2.0–29.3° min^{-1}, $4.0 < 2\theta < 50°$. [b] Criterion for observed reflection, $|F_o| > 4.0\sigma(|F_o|)$. [c] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [d] $R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$. [e] $w = [\sigma^2(|F_o) + g(|F_o|)^2]^{-1}$.

recrystallised from dichloromethane (50 cm^3)–methanol (100 cm^3) to give the product as air-stable colourless crystals; yield 8.5 g (12.6%), m.p. 133 °C (Found: C, 79.0; H, 5.9; P, 15.1. $C_{27}H_{24}P_2$ requires C, 79.0; H, 5.9; P, 15.1%). NMR: ^{1}H, δ 1.94 [d, ^3J(HH) 6.8, ^4J(PH) 0, CH$_3$], 6.18 [m, ^3J(HH) 6.8, ^3J(P$_A$H) 8.8, ^3J(P$_B$H) 21.5 Hz, CH] and 7.0–7.3 (complex, C$_6$H$_5$ groups); ^{13}C, δ 18.4 [dd, J(P$_A$C) 0.9, J(P$_B$C) 27.8, CH$_3$], 135.2 [dd, J(P$_A$C) 10.4, J(P$_B$C) 4.9, *ipso*-C], 149.1 [d, J(PC) 25.9, CH], 134.2 [d, J(P$_A$C) 20.7, *ortho*-CH(P$_A$)], 134.1 [d, ^1J(P$_B$C) 20.1, *ortho*-CH(P$_B$)], 128.0 [d, J(P$_A$C) 6.7, *meta*-CH(P$_A$)], 127.7 [d, J(P$_B$C) 7.0, *meta*-CH(P$_B$)] and 128.3 [br, s, *para*-CH (P$_A$ and P$_B$)]; ^{31}P, δ(P$_A$) −4.6, δ(P$_B$) −14.0, ^2J(PP) 7.0 Hz.

[2,2-*Bis*(*diphenylphosphino*)*ethyl*]*phenylphosphine* **4**.—A solution of **1** (10.8 g, 27.3 mmol) in dry thf (40 cm^3) was added in a dropwise manner to a stirred solution of phenylphosphine (3 g, 27.3 mmol) in dry thf (50 cm^3) containing a catalytic amount of potassium *tert*-butoxide. When addition was complete the solvent was removed at the pump to yield an oily residue which on addition of methanol (50 cm^3) deposited a powdery white solid. Recrystallisation from dichloromethane (50 cm^3)–methanol (150 cm^3) gave the product as air-stable colourless needles. Yield 11.05 g (85%), m.p. 110 °C (Found: C, 75.8; H, 5.8; P, 18.5. $C_{32}H_{29}P_3$ requires C, 75.8; H, 5.8; P, 18.4%). NMR: δ 3.48 [m, ^2J(P$_A$H) 0, ^2J(P$_B$H) 0, ^3J(P$_X$H) 12.2, ^3J(HH) 6.1, CH], 2.0–2.4 (complex overlapping, CH$_2$), 3.97 [m, ^1J(PH) 211.4, ^3J(HH) 7.8, Hz, PH], 6.9–7.1 and 7.4–7.6 (complex m, C$_6$H$_5$ groups); ^{13}C, δ 31.2 [m, ^1J(P$_A$C) 28.7, ^1J(P$_B$C) 28.7, CH], 24.6 [m, ^2J(P$_A$C) 10.4, ^2J(P$_B$C) 10.4, ^1J(P$_X$C) 16.5 Hz, CH$_2$] and 127.5–137.5 (complex overlapping m, C$_6$H$_5$ groups).

[2,2-*Bis*(*diphenylphosphino*)*ethyl*]*tri*-tert-*butylphenyl*)*phosphine* **7**.—This compound was prepared in an analogous manner to **4** from tri-*tert*-butylphenylphosphine[24] (2.1 g, 7.4 mmol) and **1** (2.9 g, 7.4 mmol) to give the product as air-stable colourless crystals. Yield, 3.7 g (74%); m.p. 150 °C (Found: C, 78.5; H, 7.9; P, 13.7. $C_{44}H_{53}P_3$ requires C, 78.5; H, 7.9; P, 13.8%). NMR: ^{1}H, δ 3.49 [m, ^2J(P$_A$H) 0, ^2J(P$_B$H) 0, ^3J(P$_X$H) 8.2, ^3J(HH) 7.8, CH], 2.0–2.3 (complex overlapping m, CH$_2$), 5.13 [m, ^4J(P$_A$H), ^4J(P$_B$H) 0, J(P$_X$H) 227.4, ^3J(HH) 6.3, 9.8 Hz, PH], 6.8–7.7 (complex m, C$_6$H$_5$ groups); 1.23 (s, *para*-CMe$_3$) and 1.51 (s, *ortho*-C$_4$H$_9$ groups); ^{13}C, δ 33.5 [m, J(P$_A$C) 32.3, ^1J(P$_B$C) 32.3, ^2J(PC) 9.5, CH], 29.6 [m, ^2J(P$_A$C) 10.7, ^2J(P$_B$C) 10.7, ^2J(P$_X$C) 18.6, CH$_2$], 33.9 [d, J(P$_X$C) 7.3, *ortho*-C groups], 31.5 (s, *para*-CMe$_3$), 3.85 (s, *ortho*-*C*Me$_3$ groups), 35.4 (s, *para*-*C*Me$_3$), 127.8–137.7 (complex overlapping m, C$_6$H$_5$), 122.5 [d, J(P$_X$C) 3.3, *meta*-CH of $\mathrm{C_6H_2Bu^t_3}$], 149.4 (s, *para*-C of $\mathrm{C_6H_2Bu^t_3}$) and 154.9 [d, J(P$_X$) 7.7 Hz, *ortho*-C of $\mathrm{C_6H_2Bu^t_3}$].

1,1,2-*Tris*(*diphenylphosphino*)*propane* **18**.—A solution of **1** (2.0 g, 5 mmol) and diphenylphosphine (0.9 g, 5 mmol) in dry thf (30 cm^3) containing a catalytic amount of potassium *tert*-butoxide was stirred under nitrogen for 24 h. The solvent was then removed at the pump and methanol (50 cm^3) was added to the resulting oily residue. The mixture was shaken vigorously until a white powdery solid was evident. Filtration followed by recrystallisation from dichloromethane (10 cm^3)–methanol (40 cm^3) at *ca.* −20 °C yielded the product as an air-stable white powdery solid. Yield 1.3 g (45%), m.p. 112 °C (Found: C, 78.4; H, 5.8. $C_{39}H_{35}P_3$ requires C, 78.5; H, 5.9%). NMR: ^{1}H, δ 1.34 [dd, ^3J(HH) 6.8, J(PH) 13.3, CH$_3$], 2.82 (m) and 3.35 [dd, ^3J(HH) 2.0, ^3J(PH) 8.7 Hz, C*H*(PPh$_2$)$_2$]; ^{13}C, δ 14.2 [m, ^nJ(PC) 11.1, 15.0, 16.6, CH$_3$], 32.1 [m, ^nJ(PC) 7.2, 22.2, *C*H(Me)] and 33.8 [m, ^nJ(PC) 8.9, 27.7, 39.6 Hz, *C*H(PPh$_2$)$_2$].

Bis[2,2-*bis*(*diphenylphosphino*)*ethyl*]*phenylarsine* **12**.—A solution of phenylarsine (0.82 g, 5.3 mmol), **1** (4.2 g, 10.6 mmol) and a catalytic amount of potassium *tert*-butoxide in thf (50 cm^3) was stirred for 18 h and then refluxed for 0.5 h. The solvent was removed under vacuum and methanol (50 cm^3) was added to the residue to give a white precipitate. Recrystallisation of the precipitate from dichloromethane (25 cm^3)–methanol (75 cm^3) gave the product as air-stable white crystals. Yield 3.4 g (68%), m.p. 148 °C (Found: C, 72.7; H, 5.4. $C_{58}H_{51}AsP_4$ requires C, 73.6; H, 5.4%). NMR: ^{1}H, δ 3.25 [t, ^3J(HH) 7.3, 7.3, CH], 1.7–2.0

(complex overlapping m, CH_2) and 6.9–7.7 (complex overlapping m, C_6H_5 groups); ^{13}C, δ 26.6 (s, CH), 43.5 [t, J(PC) 39.3, 39.3 Hz, CH_2] and 127.5–134.0 (complex m, C_6H_5 groups).

All the remaining compounds were prepared by mixing equimolar amounts of the two starting reagents in thf in the presence of a catalytic amount of potassium *tert*-butoxide as shown in Scheme 1. These compounds were examined in solution only, owing to difficulties of crystallisation and their air sensitivity.

X-Ray Diffraction Analysis.—All diffraction measurements were made at 290 K on a Nicolet P3/F diffractometer operating in the ω–2θ scan mode using graphite-monochromated radiation. Crystallographic data are listed in Table 8 together with details of data collection and structure refinement. The data sets were corrected for Lorentz and polarisation factors but not for absorption.

The structures of all three compounds (**4**, **7** and **9**) were solved by direct methods using SHELXS 86.[25] All were refined by full-matrix least squares using the SHELX 76 program system.[26] In all three cases all non-hydrogen atoms were refined with anistropic thermal parameters, with the exception of a *tert*-butyl group in the *p*-phenyl position of **7** which was found to be rotationally disordered over four positions. Each methyl carbon atom position of this group was refined with an occupancy factor of 0.25 and an isotropic thermal parameter. The phenyl groups of all three complexes were treated as rigid bodies with idealised geometry (C–C 139.5 pm). In all three cases the phenyl hydrogen atoms were included in calculated positions (C–H 96 pm) whilst the methine and methylene hydrogen atoms were located in Fourier difference syntheses. All hydrogen atoms of each structure were refined with an overall isotropic thermal parameter. The weighting scheme $w^{-1} = \sigma^2(F) + g(F)^2$ was used for all three complexes where g is a parameter which was adjusted so as to give a flat analysis of variance with increasing sinθ and $[F/F_{\max}]^{\frac{1}{2}}$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H atom coordinates, thermal parameters and remaining bond lengths and angles.

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