Synthesis of Polytertiary Phosphines and ' Mixed ' Phosphorus–Sulphur and ' Mixed ' Phosphorus–Nitrogen Polydentate Ligands *via* Free-radical Catalysis

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In the presence of free radicals, phosphorus–hydrogen and sulphur–hydrogen bonds cleanly and readily add to the carbon–carbon double bonds of vinyl derivatives to produce organic compounds that are useful as polydentate chelating ligands. The generality and mild conditions of the reaction are demonstrated by the synthesis of di-, tri-, and tetra-(tertiary phosphines) and of compounds that contain both phosphorus and sulphur or phosphorus and nitrogen donor groups. This free-radical-catalysed addition of molecules containing P–H and S–H bonds to vinyl compounds provides a general valuable alternative to the base-catalysed addition method.

In recent years many of the investigations of organometallic chemistry and transition-metal complexes have utilised chelating phosphines as ligands. Particularly, investigations of five-co-ordinate complexes have shown that the stability, stereochemistry, and magnetic properties depend on a subtle blend of electronic and steric effects.[1-5] Consequently, further development of the co-ordination chemistry of tertiary phosphines is highly dependent on the concurrent development of synthetic phosphorus chemistry.

Until 1971 most polytertiary phosphines were prepared by reactions of organic polyhalides with alkali-metal dialkyl- or diaryl-phosphides (*e.g.*, the relatively easy preparation of $Ph_2PCH_2CH_2PPh_2$[6]). However, utilisation of this method for more complicated tri- and tetra-phosphines is severely limited by difficulties either in obtaining the appropriate organic polyhalide or in obtaining complete reaction with the phosphide reagent.[7] The variety of poly(tertiary phosphines) containing PCH_2CH_2P units was greatly increased by King *et al.*[8] by the base-catalysed additions of phosphorus–hydrogen bonds to the carbon–carbon double bonds in various vinylphosphine derivatives.† Even this synthetic method is limited to PCH_2CH_2P connecting linkages and to available vinylphosphines. Our need for a series of flexible polydentate ligands containing either $-CH_2CH_2-$ or $-CH_2CH_2CH_2-$ units and different types of donor groups led us to investigate alternative routes for ligand synthesis.

We have found that the free-radical-catalysed addition of phosphorus–hydrogen and sulphur–hydrogen bonds to the carbon–carbon double-bonds of vinyl derivatives is a high-yield general reaction. Also, the free-radical-catalysed addition of the P–H bond to the C=C bond of certain allylic compounds proceeds well.[10,11] This preparative route represents a valuable alternative to the base-catalysed reactions of vinyl compounds and the Grignard reactions of 3-halogenotrimethylene derivatives for the synthesis of polydentate ligands containing ethylene and trimethylene units, respectively.

EXPERIMENTAL

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, or by M.H.W. Laboratories, Garden City, MI, and are reported in Table 1. I.r. spectra were recorded on a Perkin-Elmer model 337 or a Beckman IR-9 spectrometer. Proton n.m.r. spectra were recorded on a Varian A60-A (60 MHz) or a Jeolco MH-100 (100 MHz) spectrometer using deuteriochloroform as a solvent and are reported in Table 2. Fourier-mode proton-noise-decoupled ^{31}P n.m.r. spectra were obtained on a Bruker HX-90 (36·43 MHz) spectrometer using deuteriochloroform as a solvent in 10 mm diameter tubes. The solvent provided a deuterium lock. The ^{31}P n.m.r. spectra are reported in Table 3. Mass spectra were taken at 70 eV on an A.E.I. MS-902 mass spectrometer using an injection temperature of 150 °C. Melting points were taken of samples enclosed in sealed capillaries and are uncorrected. A nitrogen atmosphere was maintained during the reactions and for all subsequent work-up procedures.

Materials.—Organic solvents were reagent grade and were thoroughly degassed and dried prior to use. Diphenylphosphine, diphenylvinylphosphine, and phenyldivinylphosphine were obtained from Pressure Chemical Company, Pittsburgh, PA, and were used as obtained. The authentic nature of these reagents was checked by i.r. and n.m.r. spectroscopy; significantly, the i.r. spectra in the region for phosphorus–oxygen stretching (*ca.* 1200 cm^{-1}) were devoid of the strong characteristic peak for P=O bonds.[12] Isopropyl phenylvinylphosphinate was prepared by the method described by King [8a] and gave spectra in agreement with those reported. Thiophenol was obtained from Eastman Chemical Company and was used as obtained. The free-radical initiator, 2,2′-azobis(isobutyronitrile) (AIBN) was

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† The precedent for these reactions was the addition of P–H bonds of secondary phosphine oxides and secondary phosphine sulphides to olefins to prepare tertiary phosphine oxides and sulphides.[9]

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[6] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378.

[7] D. Berglund and D. W. Meek, *Inorg. Chem.*, 1969, **8**, 2602.

[8] (*a*) R. B. Kingand P. N. Kapoor, *J. Amer. Chem. Soc.*, 1971, **93**, 4158; (*b*) R. B. King, *Accounts Chem. Res.*, 1972, **5**, 177; (*c*) R. B. King, J. C. Cloyd, jun., and P. N. Kapoor, *J.C.S. Perkin I*, 1973, 2226.

[9] L. Maier, U.S.P. 3,518,312 (*Chem. Abs.*, 1970, **73**, 88015Z); L. Maier, U.S.P. 3,578,311 (*Chem. Abs.*, 1970, **73**, 88018C); H. J. Kleiner, G.P. 1,902,444 (*Chem. Abs.*, 1970, **73**, 88023A).

[10] J. R. Nappier, Ph.D. Thesis, The Ohio State University, 1973.

[11] J. Tiethof and D. W. Meek, unpublished data.

[12] D. E. C. Corbridge, *Topics in Phosphorus Chem.*, 1969, **6**, 235.

used as obtained from Matheson, Coleman, and Bell. The synthesis of 3-phenylphosphinopropylphenylphosphine was accomplished by a modification of the method used by Issleib and Weichmann[13] for the preparation of 2-phenylphosphinoethylphosphine. The i.r. and n.m.r. spectra of the material were consistent with the formulation, and it had a b.p. of 136—140 °C at 1 Torr.

TABLE 1

Elemental analyses

Compound	% C Calc.	% C Found	% H Calc.	% H Found	% P Calc.	% P Found
$CH_2[CH_2P(Ph)CH_2CH_2PPh_2]_2$	75·43	75·55	6·48	6·45	18·09	18·25
$CH_2[CH_2P(Ph)(S)CH_2CH_2P(S)Ph_2]_2$ [a]	63·53	63·8	5·46	5·3	15·24	15·4
$Ph_2PCH_2CH_2P(O)[OCH(CH_3)_2]Ph$	69·69	69·45	6·61	6·6	15·63	15·8
$Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2PPh_2$	76·63	76·65	6·43	6·2	16·94	17·15
$Ph_2PCH_2CH_2SPh$	74·49	74·6	5·94	6·1	9·61	9·45
$PhP(CH_2CH_2SPh)_2$	69·08	69·3	6·06	5·95	8·10	8·0
$PhSCH_2CH_2P(O)[OCH(CH_3)_2]Ph$	63·73	63·35	6·61	7·0	9·67	9·85
$Ph_2PCH_2CH_2C(O)NH_2$ [b]	70·03	69·85	6·27	6·15		

[a] Sulphur: Calc. 15·77; Found 16·0. [b] Nitrogen: Calc. 5·44; Found 5·3.

TABLE 2

Proton n.m.r. spectral data [a,b]

Compound	Chemical shift, τ C_6H_5 [c]	CH_2	CH_3	CH
$Ph_2PCH_2CH_2PPh_2$	2·80	7·93 (t, 4)		
$PhP(CH_2CH_2PPh_2)_2$	2·78, 2·81	7·8—8·6 (m)		
$CH_2[CH_2P(Ph)CH_2CH_2PPh_2]_2$	2·73, 2·77	7·75—8·95 (m)		
$Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2PPh_2$	2·75	7·8—8·7 (m)		
$CH_2[CH_2P(Ph)(S)CH_2CH_2P(S)Ph_2]_2$	2·2, 2·5	7·8—8·4 (m)		
$Ph_2CH_2CH_2P(O)[OCH(CH_3)_2]Ph$ [d]	2·25, 2·48, 2·68	7·5—8·5 (m)	8·65 (d, 6) 8·87 (d, 6)	5·45 (m)
$Ph_2PCH_2CH_2SPh$	2·63, 2·74	6·8—7·2 (m) (adj. to S) [e] 7·5—7·7 (m) (adj. to P)		
$PhP(CH_2CH_2SPh)_2$	2·73, 2·88	7·0—7·4 (m) (adj. to S) [e] 7·9—8·2 (m) (adj. to P)		
$PhSCH_2CH_2P(O)[OCH(CH_3)_2]Ph$ [d]	2·15, 2·42, 2·68	6·88 (m) (adj. to S) [e] 7·75 (m) (adj. to P)	8·59 (d, 6) 8·80 (d, 6)	5·40 (m)

[a] Spectra recorded in $CDCl_3$ solution. [b] Abbreviations used: Ph = phenyl, s = singlet, d = doublet, t = triplet, m = multiplet. Separation (Hz) for doublets and triplets is given in parentheses. [c] Phenyl resonances were unusually broad and asymmetric. The positions of major peaks are given. [d] Comparison of 60 and 100 MHz spectra show that the methyl groups are nonequivalent rather than split by ^{31}P. The pattern (a pair of doublets) shows the same coupling constant to the CH proton (6 Hz) and the same separation (0·21 p.p.m.) at both frequencies. [e] Assignments in these cases were made by analogy to the corresponding phosphine compound.

TABLE 3

^{31}P N.m.r. spectral data [a]

Compound	Chemical shift, δ [b,c]	Group assignment	Coupling constant (J/Hz)
$PhP(CH_2CH_2PPh_2)_2$ [d]	+12·8 (d) } AB$_2$	Ph_2P	29·1 ± 0·5
	+16·6 (t) } δ_{AB} = 136 Hz	PhP	
$PhP(CH_2CH_2CH_2PPh_2)_2$	18·2 (d)	Ph_2P	0·9 ± 0·3
	28·8 (t)	PhP	
$Ph_2PCH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$	13·2 } AMX	$Ph_2PCH_2CH_2$ (A)	J_{AM} = 28·8 ± 0·4
	18·1 } δ_{AM} = 335 Hz	$Ph_2PCH_2CH_2CH_2$ (X)	J_{AX} = 0·0 ± 0·3
	22·4	PhP (M)	J_{MX} = 0·9 ± 0·3
$Ph_2PCH_2CH_2SPh$	+20·6 (s)	Ph_2P	
$PhP(CH_2CH_2SPh)_2$	+29·9 (s)	PhP	
$PhSCH_2CH_2P(O)[OCH(CH_3)_2]Ph$	−79·2 (s)	PhP(O)	
$Ph_2PCH_2CH_2C(O)NH_2$	+15·6 (s)	Ph_2P	

[a] Spectra recorded in $CDCl_3$ solution. [b] External H_3PO_4 used as reference; δ is given in p.p.m. from the external H_3PO_4 standard, where positive is upfield. [c] Abbreviations used: Ph = phenyl, s = singlet, d = doublet, t = triplet. [d] Some second-order splitting observed in this spectrum; discussed in text.

Preparation of Polydentate Phosphine Ligands and Intermediates.—(a) *1,2-Bis(diphenylphosphino)ethane.*—Diphenylphosphine (2·06 g, 11·1 mmol) and diphenylvinylphosphine (2·41 g, 11·4 mmol) were syringed into a 3-necked 100-ml reaction flask under N_2. The flask was immersed in an oil-bath at 110 °C and allowed to warm for 2 min before addition of AIBN (0·03 g). After 15 min a white solid began to form, and after 30 min the flask was evacuated (*ca.* 1 Torr) at 140—150 °C for 2 h to remove volatile materials. After cooling, the resultant white solid was dissolved in a mixture of acetone (50 ml) and benzene (20 ml). Methanol (10 ml) was added, and the volume was reduced *in vacuo* to 5—10 ml. The resultant crystals were collected on a filter; yield 3·88 g (88%), m.p. 140—142 °C. Recrystallisation from benzene–heptane gave a 62% recovery (2·45 g) with m.p. 142—143 °C (lit.,[6] 143—144 °C).

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[13] K. Issleib and H. Weichmann, *Chem. Ber.*, 1968, **101**, 2197.

(b) *Bis*(2-*diphenylphosphinoethyl*)*phenylphosphine*. Phenyldivinylphosphine (1·74 g, 10·7 mmol) and diphenylphosphine (4·00 g, 21·5 mmol) were added to a 3-necked 100-ml reaction flask under N_2, and the flask was immersed in an oil-bath at 110 °C. After warming for 2 min, AIBN (0·02 g) was added; additional 0·02 g portions of AIBN were added after ½ and 1 h. The material in the flask solidified after 1¼ h, and after a total of 1½ h the reaction vessel was evacuated (*ca.* 1 Torr) for 2 h at 140—150 °C. The resultant white solid was dissolved in 1 : 1 benzene–acetone (60 ml). Methanol (15 ml) was then added, and the volume was reduced to *ca.* 8 ml *in vacuo*. The resulting white crystals were collected on a filter and dried; yield 5·20 g (91%), m.p. 126—129 °C. Recrystallisation from benzene–methanol gave 64% recovery (3·63 g), m.p. 126—128 °C (lit.,[14] 129—130 °C).

(c) 1,1,4,8,11,11-*Hexaphenyl*-1,4,8,11-*tetraphosphaundecane*. Diphenylvinylphosphine (17·23 g, 81·3 mmol) and 1,3-bis(phenylphosphino)propane (10·55 g, 40·6 mmol) were added to a reaction flask under N_2, and the flask was immersed in an oil-bath at 100 °C. Over a 2 h period AIBN (0·09 g) was added in portions. The flask was then evacuated (*ca.* 1 Torr) for 12 h at 120 °C. Upon cooling of the reaction flask, a viscous yellow oil was obtained; yield 27·29 g (98%). A white solid was obtained in 40% yield by dissolving the oil in acetone, adding methanol to the point of cloudiness, and cooling.

(d) 1,1,4,8,11,11-*Hexaphenyl*-1,4,8,11-*tetraphosphaundecanetetra*-P-*sulphides*. The above oil (1·31 g, 1·92 mmol) was dissolved in 30 ml of benzene, and sulphur (0·246 g, 7·79 mmol) was added. The reaction was refluxed for 1 h, the solvent was removed on a rotary evaporator, and the resultant white solid was purified by column chromatography using silica gel and a 5 : 95 (v/v) mixture of acetone and dichloromethane as the eluant. The eluted product was crystallised from acetone to give a white solid; yield 0·340 g (26%), m.p. 175—181 °C; $\nu_{P=S}$ 585, 595, 607, and 617 cm^{-1}.

(e) *Isopropyl* (2-*diphenylphosphinoethyl*)*phenylphosphinate*. Diphenylphosphine (2·24 g, 12·1 mmol) and isopropyl phenylvinylphosphinate (2·56 g, 11·3 mmol) were added to a reaction flask under N_2, and the flask was immersed in an oil-bath at 110 °C. After 2 min AIBN (0·02 g) was added; additional AIBN (0·04 g) was added in portions at ½ h intervals during a 3 h period. Some volatile materials were removed by heating the reaction mixture to 135 °C *in vacuo*. The resultant product was a yellowish oil which crystallised when the flask was scratched. The material was recrystallised by dissolution in ether and slow evaporation of the latter under N_2; yield 3·33 g (70%), m.p. 162·5—165 °C; $\nu_{P=O}$ 1175 and 1217 cm^{-1}.

(f) (2-*Diphenylphosphinoethyl*)(3-*diphenylphosphinopropyl*)*phenylphosphine*. (3-Diphenylphosphinopropyl)phenylphosphine (2·75 g, 8·17 mmol) was placed in a 25-ml, 3-necked, round-bottom flask under N_2. The AIBN initiator (0·03 g) was added and the flask was lowered into an oil-bath maintained at 105 °C. Diphenylvinylphosphine (1·71 g, 8·10 mmol) was added and the solution was stirred and heated at 105 °C for 1½ h; the thick reaction mixture was then heated at 100 °C *in vacuo* for 3 h. When cool, the compound was a thick oil; yield 4·00 g (91%).

Preparation of 'Mixed' Polydentate Phosphine–Sulphide Ligands and Intermediates.—(a) 2-*Phenylthioethyldiphenylphosphine*. To a flask containing diphenylvinylphosphine (3·50 g, 16·5 mmol) under N_2, preheated to 110 °C in an oil-bath, was added in sequence thiophenol (2·0 ml, 19 mmol) and AIBN (0·03 g). After the mixture had been heated 1 h, further AIBN (0·03 g) was added; after heating for an additional hour, the volatile materials were removed by heating of the reaction mixture to 80 °C at *ca.* 1 Torr for 8 h. When cool the weight of the resulting white solid corresponded to 99% of the expected yield. Recrystallisation was accomplished by dissolution of the solid in ether and reduction of the volume of the latter under N_2; yield 4·14 g (78%), m.p. 82·5—83·5 °C.

(b) *Bis*(2-*phenylthioethyl*)*phenylphosphine*. To a flask containing thiophenol (3·2 ml, 31 mmol) under N_2, preheated to 110 °C in an oil-bath, was added phenyldivinylphosphine (2·14 g, 13·2 mmol); after 2 min 0·02 g of AIBN was added. Additional 0·02 g portions of AIBN were added after ½ and 1 h. The reaction mixture was heated for a total of 1½ h, and then the flask was evacuated (*ca.* 1 Torr) at 110 °C for 2 h to remove volatile materials. A white solid formed when the reaction flask was cooled; this solid was dissolved in 10 ml of ether and 5 ml of heptane was added. The solution volume was reduced *in vacuo* to 3 ml, producing a white crystalline material, which was collected on a filter and washed with 2 ml of heptane; yield 4·91 g (97%); m.p. 55—65 °C. Recrystallisation from acetone–methanol gave a 78% recovery of a white solid; m.p. 61·5—63·5 °C.

(c) *Isopropyl* (2-*phenylthioethyl*)*phenylphosphinate*. To a flask containing thiophenol (2·8 ml, 27 mmol) under N_2, preheated to 110 °C in an oil-bath, was added isopropyl vinylphenylphosphinate (4·99 g, 23·8 mmol) and AIBN (0·02 g). Additional 0·02 g portions of AIBN were added at ½ h intervals for 2 h, and then the unchanged starting materials were removed and collected by vacuum distillation. An oil, which crystallised when set aside overnight in a refrigerator, remained in the reaction flask; yield 3·79 g (49·7%). Recrystallisation from cyclohexane gave a recovery of 1·96 g (26%), m.p. 63·5—65·5 °C; $\nu_{P=O}$, 1209 and 1223 cm^{-1}.

Preparation of the 'Mixed' Phosphorus–Nitrogen Compound 3-*Diphenylphosphinopropionamide*.—To a 50-ml 3-necked flask in an oil-bath at 100 °C was added in sequence diphenylphosphine (2·38 g, 12·8 mmol), AIBN (0·05 g), and acrylamide (0·89 g, 12·7 mmol). The reaction mixture was maintained at 100 °C for 10 min and then evacuated (*ca.* 1 Torr) for 24 h at 100 °C; the resultant viscous oil solidified to a very hard colourless glass. The i.r. spectrum showed strong ν_{NH} absorptions at *ca.* 3200 and *ca.* 3350 cm^{-1} and a strong ν_{CO} band at 1670 cm^{-1}; it had very weak absorptions at 2330 (P–H) and 1180 (P=O) cm^{-1} due to an impurity; yield 95%.

RESULTS AND DISCUSSION

Free-radical-catalysed addition of phosphorus–hydrogen or sulphur–hydrogen bonds across carbon–carbon double-bonds in vinylphosphines has been found to be a useful method for the preparation both of poly(tertiary phosphines), of 'mixed' phosphorus–sulphur and 'mixed' phosphorus–nitrogen compounds. The general reactions can be summarised as in equations (1)—(3).

$$>\!P{-}H + CH_2{=}CH{-}P\!< \longrightarrow\ >\!PCH_2CH_2P\!< \qquad (1)$$

$$-S{-}H + CH_2{=}CH{-}P\!< \longrightarrow -SCH_2CH_2P\!< \qquad (2)$$

$$>\!P{-}H + CH_2{=}CH{-}C(O)NH_2 \longrightarrow\ >\!PCH_2CH_2C(O)NH_2 \qquad (3)$$

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[14] W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1962, 1490.

In all cases the absence of P–H or S–H stretching frequencies in the i.r. spectra and the absence of vinylic signals from the proton n.m.r. spectra of the products indicated that the reactions had occurred. Clearly, better evidence was the location of peaks and agreement of integral ratios in the proton n.m.r. spectra of the products, as well as the presence of a parent peak in the mass spectrum of each of the poly(tertiary phosphines). Additionally, good elemental analyses were obtained for the recrystallised products.

The only exception to essentially quantitative reactions was the preparation of isopropyl (2-phenylthioethyl)-phenylphosphinate, where both thiophenol and isopropyl phenylvinylphosphinate were recovered by distillation following the usual reaction conditions. All of the compounds prepared in this study are air stable at room temperature, as evidenced by the absence of the strong P=O stretching vibration [12] in the i.r. spectra after exposure for *ca.* 2 weeks to air. The phosphinates were hygroscopic, however, and the sulphur-containing compounds have their usual ' distinctive ' odour.

The free-radical-catalysed reactions to produce 1,2-bis(diphenylphosphino)ethane (diphos) and bis(2-diphenylphosphinoethyl)phenylphosphine (triphos) yielded products with spectral characteristics virtually identical to those of authentic materials. The yields for both these materials were better than those reported [8a] for the base-catalysed process: 88% *vs.* 80% for diphos and 91% *vs.* 50% for triphos. Yields for the other compounds prepared in this study were equally impressive. It is interesting to note that a P–P coupling of 29 Hz was observed in the ^{31}P n.m.r. spectrum of triphos while in the spectrum of an analogous compound, bis(3-diphenylphosphinopropyl)phenylphosphine,[15] P–P coupling of less than 1 Hz was observed [δ(PhP) = +28·8 p.p.m., $\delta(Ph_2P)$ = +18·2 p.p.m.]. It has been reported [16] that P–P coupling is not observed when the phosphorus atoms are separated by four bonds, and these spectra would appear to support this observation.

The new quadridentate phosphine ligand $[Ph_2PCH_2CH_2P(Ph)CH_2]_2CH_2$ was characterised by elemental analysis and by the agreement of integral ratios in the proton n.m.r. spectrum (Ph : CH_2, calc. 30 : 14; obs. 30 : 13). The absence of vinylic protons in the proton n.m.r. spectrum and the absence of a P–H stretching vibration in the i.r. spectrum furnished additional evidence that the reaction was essentially quantitative. The tetrasulphide derivative of this ligand also had a consistent proton n.m.r. spectrum and good elemental analysis. Additionally, the mass spectrum of the tetrasulphide derivative showed a parent peak at m/e = 812.

It is interesting that the addition of one more methylene group in the central unit of our tetraphos ligand, $[Ph_2PCH_2CH_2P(Ph)CH_2]_2CH_2$ (2–3–2 connecting chains), causes the ^{31}P n.m.r. spectrum to appear much simpler than that of King's similar tetraphos ligand $[Ph_2CH_2CH_2P(Ph)CH_2]_2$ (2–2–2 connecting chains). Both ligands would correspond to an AA′XX′ spin system. The 2–3–2 ligand has essentially no P–P coupling (less than 3 Hz) between the two inner phosphorus atoms, whereas the 2–2–2 ligand exhibits strong coupling (24 Hz). Analysis of the observed ^{31}P n.m.r. spectra of both ligands as AA′XX′ systems gives the following parameters: for the 2–2–2 ligand, 12 of the 20 expected lines are observed, from which $\delta_X = \delta_{PPh} = 16{\cdot}7$ p.p.m., $\delta_A = \delta_{PPh_2} = 12{\cdot}8$ p.p.m., and $J_A = 0{\cdot}1$, $J_{AX} = 28{\cdot}9$, $J_{AX'} = 0{\cdot}3$, and $J_X = 24{\cdot}0$ Hz, $\delta_{AX} = 138{\cdot}5$ Hz; for the 2–3–2 ligand, 4 lines are observed from which $\delta_{PPh} = 22{\cdot}8$ p.p.m., $\delta_{PPh_2} = 13{\cdot}6$ p.p.m., and $J_A \cong 0$, $J_X \cong 0$, $J_{AX} \cong 28{\cdot}0$, and $J_{AX'} \cong 0$, $\delta_{AX} = 336$ Hz.*

The unsymmetrical triphosphine compound $Ph_2PCH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$ was prepared in 91% yield by condensing $Ph_2PCH_2CH_2CH_2PHPh$ with vinyldiphenylphosphine in the presence of AIBN. This reaction illustrates that many different polyphosphine ligands containing ' mixed ' ethylene and trimethylene connecting units can now be synthesised simply by choosing the appropriate secondary phosphine and vinylphosphine.

Isopropyl (2-diphenylphosphinoethyl)phenylphosphinate was prepared by King [8c] *via* the base-catalysed process. The material prepared in this work showed a proton n.m.r. spectrum nearly identical to that reported by King assuming the assignment for the methylene protons to be $\tau = 8{\cdot}0$ rather than the reported $\tau = 2{\cdot}0$.[8c,†]

The extension of the free-radical-catalysed process to the preparation of ' mixed ' P and S (and P and N) containing ligands is especially noteworthy, as it represents an easy route to such potentially useful ligands. The two P–S compounds prepared in this work are formally analogous to the ligands diphos and triphos, in which one and two PPh_2 groups, respectively, are replaced by SPh groups. Although the reaction to produce a thio-analogue of isopropyl (2-diphenylphosphinoethyl)-phenylphosphinate did not go to completion, the fact that it did proceed to a significant extent will allow that reaction (and similar ones) to be exploited for the synthesis of much more complicated ' mixed ' ligands. For example, the reduction of the $\rangle$P(O)OR group to a secondary phosphine then provides the capability for additional reactions.

The chief advantages of the free-radical-catalysed method are: (i) the flexibility of designing several different related polydentate ligands that contain different donor groups and either $-CH_2CH_2-$ or $-CH_2CH_2CH_2-$ connecting units by simply choosing the appropriate P–H, S–H, and vinyl derivatives; (ii) the experimental simplicity of the one-pot reaction; (iii) the faster reaction times than the base-catalysed addition to vinylphosphines; (iv) the fact that in most cases the impurities or by-products present after reaction are

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* Error estimates on the computer-fitted parameters are ±0·8 Hz and ±0·1 p.p.m.

† Dr. John Cloyd, jun., subsequently confirmed that the value should be $\tau = 8{\cdot}0$.

[15] T. E. Nappier, jun., D. W. Meek, R. M. Kirchner, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 4194.

[16] S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman, and J. P. Jesson, *Inorg. Chem.*, 1974, **13**, 1095.

removed easily *in vacuo* during the initial work-up leaving a crude material that is sufficiently pure for use as a ligand in subsequent preparations of complexes; and (v) the method routinely gives yields in the range 85—99%. All the solutions involved in the reaction are homogeneous and easily handled. The work-up is simple and fast, and the reaction conditions are relatively mild.

An attempt was made to prepare the quadridentate compound $(Ph_2PCH_2CH_2SCH_2)_2CH_2$ by the free-radical-catalysed reaction between diphenylvinylphosphine and propane-1,3-dithiol; however, the product appeared to be a mixture of compounds, as indicated by its proton n.m.r. spectrum. Also, strong P=S absorptions were observed in the i.r. spectrum (620 and 610 cm^{-1}). Apparently ' β-scission '[17] occurred to a large extent, rather than the desired free-radical addition to the carbon–carbon double-bond.

Numerous attempts were made to extend this general reaction to allylic systems, but the reaction is not as general as for vinyl compounds. On the positive side, the preparations of $PhP(CH_2CH_2CH_2NH_2)_2$[10] and $PhP(CH_2CH_2CH_2OH)_2$[11] were nearly quantitative using phenylphosphine and allylamine and allyl alcohol, respectively. In contrast, use of allyl chloride gave only monoalkylation of phenylphosphine to produce $PhHPCH_2CH_2CH_2Cl$ in good yield. Our qualitative results suggest that the best types of reagents to use for phosphorus–hydrogen addition to the allyl carbon–carbon double bond are allyl derivatives of first-row elements (*e.g.* C, N, O, or F) in combination with quinquevalent phosphorus–hydrogen compounds [*e.g.* $R_2P(O)H$ and $R_2P(S)H$]. These observations are consistent with the patent reports where secondary phosphine oxides and sulphides were added to terminal olefins.[9]

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