# Sterically Hindered Diphosphines $(Ph_2P)_2C{=}CHR$ (R = Me or Ph) and their Derivatives†

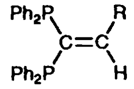
**Jonathan L. Bookham,**[*,a] **Fosca Conti,**[b] **H. Christina E. McFarlane,**[b] **William McFarlane**[*,b] **and Mark Thornton-Pett**[c]
[a] *Department of Chemical and Life Sciences, University of Northumbria at Newcastle, Newcastle upon Tyne, NE1 8ST, UK*
[b] *Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK*
[c] *Department of Chemistry, University of Leeds, Leeds LS2 9JT, UK*

Reactions of $(Ph_2P)_2C{=}CHR$ (R = Me or Ph) with E (E = S or Se) yielded the corresponding mono- and di-chalcogenides and the mixed S/Se derivatives, $^1H$, $^{13}C$ and $^{31}P$ NMR parameters for which are reported. These are rationalized in terms of conformational preferences associated with the relative P–E and phosphorus-lone pair orientations. The complexes $[M(CO)_4\{(Ph_2P)_2C{=}CHR\}]$ (M = Mo or W, R = Me or Ph) have also been prepared and have NMR parameters which can be accounted for similarly. The crystal structure of $(Ph_2P)_2C{=}CHMe$ has been determined by single-crystal X-ray diffraction and shows that the solid-state conformation is similar to that deduced in solution on the foregoing basis.

The 1,1-bis(diphenylphosphino)ethenes **1–3** are of interest in view of the reactivity of their C=C double bonds. In particular the base-catalysed anti-Markownikov addition of species with P–H bonds leads to polyphosphines which have potential as poly- and ambi-dentate ligands in transition-metal complexes. Such complexes can also be made directly by P–H addition to **1–3** in their co-ordinated form.[1–6] The diphosphines **1** and **2** themselves can be made in good (*ca.* 50%) and poor (*ca.* 10%) yields respectively from the reaction of lithium diphenylphosphide with $RHC{=}CCl_2$,[1,6] the difference in reactivity apparently being due to the smaller bulk of hydrogen compared to methyl. Compound **3** has not been successfully made in this way but is available by a different route which involves the reaction of $Li[\{Ph_2P(S)\}_2CH]$ with benzaldehyde and subsequent reduction of the resulting disulfide with $Si_2Cl_6$.[7]

Although methyl is not normally regarded as a 'bulky' group, models indicate that in compound **2** it can interact sufficiently with the phenyl substituents of the phosphorus to which it is *cis* to destabilise conformations with the phosphorus electron lone pair directed away from the methyl group. Similar considerations apply to **3** with respect to the CPh group. This view is strongly supported by measurements of the geminal $^{31}P$–$^{31}P$ coupling constants which are known to be sensitive to conformational effects[8–10] and which have approximate values of 98, 8 and 2 Hz for **1**, **2** and **3** respectively. Furthermore, for the last two compounds these couplings show significant solvent and temperature dependences which are consistent with their being conformationally sensitive.

In earlier studies of such phenomena we have reported[6] the synthesis, NMR spectra and solid-state structures (from X-ray diffraction) of a range of flexible polyphosphines derived from the addition of primary and secondary phosphines to compounds **1** and **2** and have demonstrated the striking effects upon conformational priorities of the presence of the methyl group in polyphosphines derived from **2**. We now report the preparation and characterisation of chalcogenide and Group VI metal carbonyl derivatives of **2** and **3** in which the lower symmetry compared with the corresponding derivatives of **1** permits the more convenient measurement of a wider range of diagnostically important NMR parameters. In addition we report the molecular structure of **2** as determined by single-crystal X-ray diffraction.



R
**1** H
**2** Me
**3** Ph

## Results and Discussion

The 1 : 1 reaction between elemental sulfur and compound **2** in benzene or in dichloromethane gave three species with P=S bonds as shown readily by $^{31}P$ NMR spectroscopy owing to the *ca.* 50 ppm increase in $\delta(^{31}P)$ upon sulfurisation of phosphorus.[11] There was no evidence of cleavage of P–C or C–C bonds, and the species formed are thus **4a**, **4b** and **6**, each being readily identified by its characteristic AX $^{31}P$ NMR spectrum. There is evidence of sulfur-transfer processes following completion of the initial reaction of sulfur, but in benzene after 68 h at room temperature an equilibrium was attained with compounds **2**, **4a**, **4b** and **6** in the approximate proportions 19 : 37 : 25 : 19. (For the assignment of **4a** and **4b** see discussion of NMR parameters.) It was not possible to isolate the monosulfides produced in these reactions, but they were characterised in solution from their $^{31}P$ NMR spectra and from their ability to react with additional chalcogen. The disulfide **6** was obtained in essentially quantitative yield from a 1 : 2 reaction mixture and was isolated as an air-stable white solid. Melting points and elemental analyses for this and other isolated species are in Table 1. Similar ratios of products were obtained when the same reactions were conducted in dichloromethane.

The 1 : 1 reaction of compound **2** with elemental selenium in benzene followed a similar course to that with sulfur. However, it was slower and after 68 h the reaction mixture contained unreacted **2**, the two isomeric monoselenides **8a** and **8b** and the diselenide **10** in an approximate ratio of 28 : 28 : 35 : 9, although it had not yet reached equilibrium. At this stage the type **b** isomer predominated whereas for sulfur type **a** predominated.

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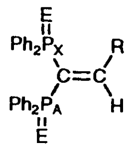
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



| | | E | |
|---|---|---|---|
| | R | $P_A$ | $P_X$ |
| **2** | Me | l.p. | l.p. |
| **3** | Ph | l.p. | l.p. |
| **4a** | Me | l.p. | S |
| **4b** | Me | S | l.p. |
| **5a** | Ph | l.p. | S |
| **5b** | Ph | S | l.p. |
| **6** | Me | S | S |
| **7** | Ph | S | S |
| **8a** | Me | l.p. | Se |
| **8b** | Me | Se | l.p. |
| **9a** | Ph | l.p. | Se |
| **9b** | Ph | Se | l.p. |
| **10** | Me | Se | Se |
| **11** | Ph | Se | Se |
| **12a** | Me | S | Se |
| **12b** | Me | Se | S |

l.p. = Electron lone pair

**Table 1** Elemental analyses and melting points

| | Analysis (%) | | | | |
|---|---|---|---|---|---|
| | Found | | Calc. | | |
| Compound* | C | H | C | H | M.p./°C |
| **2** | 79.0 | 5.9 | 79.0 | 5.9 | 133 |
| **3** | 80.3 | 5.4 | 81.3 | 5.6 | 177 |
| **6** | 67.4 | 4.9 | 68.3 | 5.1 | 201 |
| **7** | 71.4 | 4.7 | 71.6 | 4.9 | 160 |
| **10** | 56.8 | 3.9 | 56.9 | 4.2 | 206 |
| **11** | 60.9 | 4.2 | 60.8 | 4.2 | 176 |
| $[Mo(CO)_4L^1]$ | 58.8 | 3.8 | 60.0 | 3.9 | 170 (decomp.) |
| $[Mo(CO)_4L^2]$ | 62.4 | 3.7 | 63.3 | 3.8 | 190 (decomp.) |
| $[W(CO)_4L^1]$ | 52.4 | 3.3 | 52.7 | 3.4 | 201 (decomp.) |
| $[W(CO)_4L^2]$ | 55.8 | 3.4 | 56.2 | 3.4 | 213 (decomp.) |

* $L^1 = (Ph_2P)_2C{=}CHMe$, $L^2 = (Ph_2P)_2C{=}CHPh$.

Treatment of this mixture with a further equivalent of selenium ultimately afforded the diselenide **10** in virtually quantitative yield and this was isolated as an air-stable white solid. Similar ratios of products were found for the same reaction in dichloromethane. Treatment of **2** with elemental selenium in benzene for 68 h followed by the addition of 1 equivalent of sulfur eventually yielded a mixture of the disulfide **6**, the two mixed sulfide–selenides **12a** and **12b** and the diselenide **10** in an approximate ratio of 34:21:34:12. The similarity of this ratio to that from the reaction with 1 equivalent of selenium alone (the labelling of the mixed isomers **12a** and **12b** is the same as that for the monoselenides **8a** and **8b** with respect to selenium atom positions) suggests that the proportions of the products of this mixed reaction depend to a large extent on the proportions following the initial selenisation reaction and hence that little sulfur–selenium exchange had occurred. In its reactions with sulfur and with selenium **3** behaved similarly to **2** and gave a similar distribution of the corresponding mono- and di-chalcogenides. In this case no attempt was made to prepare the corresponding mixed sulfur–selenium species.

Compounds **2** and **3** reacted smoothly with $[Mo(CO)_4(pip)_2]$ (pip = piperidine) in dichloromethane to yield the complexes $[Mo(CO)_4\{(Ph_2P)_2C{=}CHR\}]$ (R = Me or Ph) and with $[W(CO)_6]$ in refluxing diglyme (2,5,8-trioxanonane) to give the corresponding tungsten derivatives. All the complexes were isolated as air-stable orange crystals. There was no evident effect of the substituent R upon the course or speed of these reactions, which is consistent with the energies of different conformations being quite similar.

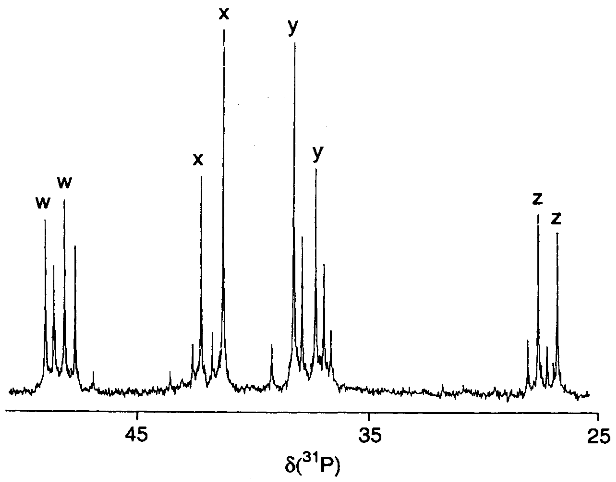
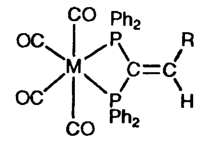


**Fig. 1** Phosphorus(v) region of the $^{31}P$ NMR spectrum at 36.2 MHz of the mixture resulting from successive additions of 1 atomic equivalent of sulfur and 1 atomic equivalent of selenium to compound **2** in dichloromethane. Signals are assigned as follows: w and z, **12a**; x and y, **12b**. Signals are also observed from small amounts of **6** and **10**. The phosphorus(III) region of the spectrum showed no significant signals



| M | R |
|---|---|
| Mo | Me |
| Mo | Ph |
| W | Me |
| W | Ph |

*NMR Parameters*.—Phosphorus-31, carbon-13 and proton NMR data are in Tables 2–5. The signal-to-noise ratios for the $^{13}CO$ resonances of the metal complexes were poor owing to extensive line splitting by the inequivalent phosphorus nuclei and low solubility.

(*a*) $^{31}P$ *Chemical shifts*. Sulfurisation of phosphines of the form $PPh_2R$ is known[11] to cause a *ca.* 50 ppm increase in $\delta(^{31}P)$ and this permits the assignment of the isomers as shown. For compounds **4a**, **4b** and **6** the increases in $\delta(^{31}P)$ upon sulfurisation ($\Delta_s$) are +51.0, +53.5 and +50.9 and +52.5 ppm respectively. The alternative assignment of isomers **a** and **b** leads to the unacceptably wide variation in $\Delta_s$ of +42.0 and +62.5 ppm for the two monosulfides and +41.9 and +61.5 ppm for the disulfide. For **8a** and **8b** values of $\Delta_{Se}$ (41.7–49.4 ppm) are in the expected range,[1] and again the alternative assignment of the **a** and **b** isomers is untenable. Essentially the same considerations apply to the chalcogenides of **3** where the alternative assignment of **5a** and **5b** leads to values of $\Delta_s$ ranging from 39.6 to 63.1 ppm rather than the more acceptable 47.9 and 54.8 ppm for the proposed assignment. The foregoing conclusions are crucially dependent upon the validity of the original assignments of the $^{31}P$ NMR spectrum of **2** which was based on the pattern of $^{31}P$–$^{1}H$ couplings.[6] In the present work we have confirmed their correctness with the aid of selective $^{1}H$-$\{^{31}P\}$ decoupling experiments and a proton ROESY[12] (rotating frame nuclear Overhauser effect spectroscopy) spectrum of **6**. With a spin-locking (mixing) time of 350 ms this gave off-diagonal peaks between the phenyl *o*-protons of $P_A$ and the olefinic H, and between the phenyl *o*-protons of $P_X$ and the methyl protons, but none for $P_A$(*ortho*)/Me or $P_X$(*ortho*)/CH.

Fig. 1 shows a typical $^{31}P$ NMR spectrum of a mixture

**Table 2** Phosphorus-31 NMR data for the compounds

| Compound | Solvent | $\delta(^{31}P_A)^a$ | $\delta(^{31}P_X)^a$ | $^2J(P_AP_X)^b$ | $^1J(MP_A)^{b,c}$ | $^1J(MP_X)^{b,c}$ |
|---|---|---|---|---|---|---|
| **2** | $C_6D_6$ | −5.2 | −14.2 | 6.8 | — | — |
| | $CH_2Cl_2$ | −4.8 | −14.0 | 9.8 | — | — |
| | $CDCl_3$ | −4.6 | −14.0 | 7.9 | — | — |
| **3** | $CH_2Cl_2$ | −3.5 | −11.8 | 1.8 | — | — |
| **4a** | $C_6D_6$ | −0.6 | +36.8 | 85.5 | — | — |
| | $CH_2Cl_2$ | −1.2 | +38.1 | 92.8 | — | — |
| **4b** | $C_6D_6$ | +48.3 | −17.9 | 83.0 | — | — |
| | $CH_2Cl_2$ | +50.1 | −17.9 | 105.0 | — | — |
| **5a** | $CH_2Cl_2$ | −3.1 | +40.7 | 117.2 | — | — |
| **5b** | $CH_2Cl_2$ | +50.6 | −7.9 | 34.2 | — | — |
| **6** | $C_6D_6$ | +47.3 | +36.7 | 32.9 | — | — |
| | $CH_2Cl_2$ | +48.2 | +37.4 | 34.2 | — | — |
| **7** | $CH_2Cl_2$ | +51.3 | +36.1 | 31.7 | — | — |
| **8a** | $C_6D_6$ | −1.0 | +27.5 | 87.9 | — | 747 |
| | $CH_2Cl_2$ | −1.4 | +28.7 | 94.6 | — | *d* |
| **8b** | $C_6D_6$ | +44.2 | −19.7 | 102.5 | 750 | — |
| | $CH_2Cl_2$ | +45.6 | −20.3 | 125.1 | *d* | — |
| **9a** | $CH_2Cl_2$ | −6.4 | +32.6 | 126.9 | — | *d* |
| **9b** | $CH_2Cl_2$ | +44.1 | −9.6 | 58.6 | *d* | — |
| **10** | $C_6D_6$ | +41.6 | +27.5 | 29.3 | 746 | 734 |
| | $CH_2Cl_2$ | +43.4 | +28.8 | 29.3 | 742 | 730 |
| **11** | $CDCl_3$ | +47.0 | +28.4 | 28.8 | 745 | 742 |
| **12a** | $C_6D_6$ | +47.7 | +27.1 | 29.3 | — | 753 |
| | $CH_2Cl_2$ | +48.5 | +27.1 | 30.5 | — | *d* |
| **12b** | $C_6D_6$ | +41.0 | +37.1 | 32.9 | 756 | — |
| | $CH_2Cl_2$ | +41.6 | +37.8 | 34.2 | *d* | — |
| $[Mo(CO)_4L^1]$ | $CDCl_3$ | +24.1 | +23.3 | 85.0 | — | — |
| $[Mo(CO)_4L^2]$ | $CH_2Cl_2$ | +31.8 | +30.2 | 78.2 | — | — |
| $[W(CO)_4L^1]$ | $CDCl_3$ | +3.1 | +2.1 | 94.0 | 209.8 | 209.8 |
| $[W(CO)_4L^2]$ | $CH_2Cl_2$ | +9.0 | +8.6 | 85.6 | 205.2 | 205.2 |

[a] In ppm (±0.2 ppm) relative to external 85% $H_3PO_4$ (δ 0.0). [b] In Hz (±0.5 Hz). [c] $^1J(^{77}Se^{31}P)$ for compounds **8–12**; $^1J(^{183}W^{31}P)$ for tungsten complexes. [d] Not determined due to unfavourable signal overlap and/or intensity.

**Table 3** Carbon-13 NMR data for non-phenyl carbons in the isolated compounds[a]

| Compound | $\delta(^{13}CH_3)^b$ | $^3J(^{31}P^{13}CH_3)^c$ | $\delta(^{13}CH{=})^b$ | $^2J(^{31}P^{13}CH)^c$ | $\delta(^{13}C{=})^b$ | $^1J(^{31}P^{13}C{=})^c$ |
|---|---|---|---|---|---|---|
| **2** | 18.3 | 27.8, 0.9 | 149.1 | 25.9, 0[d] | 134.4 | 43.6, 29.4 |
| **3** | — | — | 153.2 | 29.8, 10.2 | 135.8 | 51.0, 34.0 |
| **6** | 20.1 | 14.4, 10.7 | 158.9 | 4.4, 2.6 | 133.5 | 59.7, 59.7 |
| **7** | — | — | 159.4 | 7.0, 0 | *e* | *e* |
| **10** | 20.3 | 13.9, 10.9 | 158.8 | 2.5, 2.5 | 129.6 | 52.0, 49.5 |
| **11** | — | — | 159.6 | *e* | *e* | *e* |
| $[Mo(CO)_4L^1)$ | 18.2 | 8.4, 8.4 | 147.5 | 3.0, 3.0 | 145.4 | 16.4, 13.8 |
| $[W(CO)_4L^1)$ | 18.0 | 9.2, 9.2 | 149.1 | 6.0, 6.0 | 148.2 | 24.7, 20.0 |

[a] Not observed for $[Mo(CO)_4L^2]$ and $[W(CO)_4L^2]$ due to unfavourable signal overlap and/or intensities. [b] In ppm (±0.1 ppm) relative to $SiMe_4$(δ 0.0). [c] In Hz (±0.2 Hz); where two values are shown these have been placed in order of decreasing magnitude. [d] Listed as $J(P_XC)$, $J(P_AC)$. [e] Not determined due to unfavourable signal overlap and/or intensity.

resulting from the reaction of compound **2** with successive equivalents of sulfur and selenium. Assignments of the peaks are in the caption. Values of $\delta(^{31}P)$ for the mixed species **12a** and **12b** all lie within 0.6 ppm of the values for the corresponding phosphorus nuclei in **6** and/or **10** and this shows that $\delta(^{31}P^V)$ is not significantly affected by a change of sulfur to selenium at a *neighbouring* phosphorus atom. Greater effects (of up to 6 ppm) are observed for the changes in chemical shift of unreacted phosphorus nuclei when a neighbouring phosphorus atom is sulfurised or selenised but these are difficult to quantify. Small solvent effects on $\delta(^{31}P)$ (up to 2 ppm) are observed for the solvent systems used in this study. For the metal complexes it is noteworthy that the chemical shift differences between the two types of phosphorus nuclei are much smaller than for the free phosphine itself and hence it is not possible confidently to assign $P_A$ and $P_X$ simply by consideration of chemical shifts. For these species the mean co-ordination chemical shifts[13,14] $\{[\delta(^{31}P_A)_{coord} - \delta(^{31}P_A)_{free} + \delta(^{31}P_X)_{coord} - \delta(^{31}P_X)_{free}]/2\}$ are 33.0 and 38.7 ppm for the molybdenum complexes (R = Me or Ph), and 11.9 and 16.5 ppm for the corresponding tungsten complexes respectively and these compare well with the values found for analogous complexes of **1** (30.3 and 11.7 ppm).[15] Furthermore, the similarities of $\delta(^{31}P_A)$ and $\delta(^{31}P_X)$ themselves for complexes of **2** and of **3** suggest that the origin of the difference within the parent **2** and within the parent **3** must be conformational in nature (*i.e.* dissimilar lone-pair orientations for $P_A$ and $P_X$) and not electronic, as differences in the latter are likely to remain after co-ordination. Upon chelation to a metal centre the two phosphorus atoms are forced into nearly identical conformational environments and this results in the near equality of $\delta(^{31}P_A)$ and $\delta(^{31}P_X)$ for the complexes.

(*b*) *Coupling constants* $^2J$(PCP). Discussion of $^2J$(PCP) coupling constants has centred mostly on the contributions to the observed values from conformations such as **I**–**III**.[8,9] It has been shown by a combination of X-ray and variable-temperature NMR studies that conformation **I** is associated with high values of $^2J$(PCP) whereas **II** gives rise to low values. Conformer **II** tends to predominate when the remainder of the molecule imposes a degree of steric hindrance on the orientation of the phenyl groups on either of the two phosphorus atoms.

**Table 4** Carbon-13 NMR data for the PPh groups

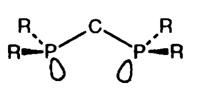
| Compound | δ($C^1$)[a] | $^1J(C^1P)$, $^3J(C^1P)$[b] | δ($C^2$)[a] | $^2J(C^2P)$, $^4J(C^2P)$[b] | δ($C^3$)[a] | $^3J(C^3P)$, $^5J(C^3P)$[b] | δ($C^4$)[a] | $^4J(C^4P)$, $^6J(C^4P)$[b] |
|---|---|---|---|---|---|---|---|---|
| **2** | 136.3 | 13.8, 0 | 134.3 | 20.1, < 1 | 128.2 | 6.3, 0 | 128.5 | 0, 0 |
| | 135.4 | 10.2, 4.7 | 134.2 | 20.1, 0 | 127.9 | 7.5, 0 | 128.5 | 0, 0 |
| **3**[c] | 136.2 | 14.9, 0 | 134.9 | 19.0, 2.0 | 128.2 | 7.0, 0 | 128.6 | 0, 0 |
| | 135.9 | 10.5, 5.5 | 134.0 | 20.0, 0 | 127.8 | 7.0, 0 | 128.5 | 0, 0 |
| **6** | 130.9 | 85.2, < 1 | 133.5 | 11.4, 0 | 128.5 | 12.7, 0 | 131.6 | 2.9, 0 |
| | 130.7 | 85.2, < 1 | 132.4 | 10.7, 0 | 127.5 | 13.2, 0 | 131.1 | 3.1, 0 |
| **7**[d] | 132.2 | 85.0, 0 | 132.8 | 11.0, 0 | 128.1 | 13.0, 0 | 131.2 | 2.5, 0 |
| | 130.8 | 85.0, 2.0 | 132.4 | 11.0, 0 | 127.6 | 13.0, 0 | 130.7 | 3.0, 0 |
| **10** | 129.4 | 76.3, < 1 | 134.3[e] | 11.6, 0 | 128.5[f] | 12.7, 0 | 131.7[f] | 2.9, 0 |
| | 128.9 | 76.5, < 1 | 133.2[f] | 11.0, 0 | 127.5[e] | 13.2, 0 | 131.2[e] | 3.1, 0 |
| **11**[g] | 133.2 | 75.6, 5.5 | 133.6 | 11.1, 0 | 128.0 | 12.6, 0 | 131.1 | < 2, 0 |
| | 131.5 | 75.7, < 1 | 132.8 | 11.5, 0 | 127.4 | 13.8, 0 | 130.9 | < 2, 0 |
| [$Mo(CO)_4L^1$] | 134.9 | 27.7, 8.8 | 132.5 | 13.8, 0 | 128.7 | 9.5, 0 | 130.0 | < 1.5, 0 |
| | 134.1 | 27.7, 10.0 | 131.8 | 13.8, 0 | 128.6 | 9.5, 0 | 129.9 | < 1.5, 0 |
| [$Mo(CO)_4L^2$][h] | *i* | *i* | 132.9 | 13.5, 0 | 128.7 | 10.0, 0 | 130.2 | 1.5, 0 |
| | *i* | *i* | 131.6 | 12.5, 0 | 128.5 | 10.0, 0 | 129.7 | 1.5, 0 |
| [$W(CO)_4L^1$] | 134.3 | 33.0, 10.3 | 132.3 | 12.6, 0 | 128.7 | 9.4, 0 | 130.2 | < 1.5, 0 |
| | 133.4 | 32.1, 11.1 | 131.8 | 12.2, 0 | 128.6 | 9.4, 0 | 130.2 | < 1.5, 0 |
| [$W(CO)_4L^2$][j] | *i* | *i* | 132.8 | 12.6, 0 | 128.7 | 10.1, 0 | 130.4 | 2.0, 0 |
| | *i* | *i* | 131.5 | 11.3, 0 | 128.5 | 10.1, 0 | 130.0 | 2.0, 0 |

[a] $C^1$ refers to the *ipso*-carbon atoms, $C^2$ to *ortho*, $C^3$ to *meta* and $C^4$ to *para*. In ppm (± 0.01 ppm) relative to $SiMe_4$ (δ 0.0). [b] In Hz (± 0.5 Hz). Individual assignments made by comparisons with data taken from related species.[1,15] [c] For CPh: δ($C^1$) 137.3 [dd, $^3J(PC^1)$ 8.5, 5.6], δ($C^2$) 129.6 [d, $^3J(PC^1)$ 8.0, 0 Hz], δ($C^3$) 127.9 (s), δ($C^4$) 128.1 (s). [d] For CPh: δ($C^1$) 134.6 [dd, $^3J(PC^1)$ 25.0, 7.0], δ($C^2$) 130.7 [$^3J(PC^1)$ < 1 Hz], δ($C^3$) 127.4 (s), δ($C^4$) 129.6 (s). [e] $P_XPh$. [f] $P_APh$. [g] For CPh: δ($C^1$) not observed due to low signal intensity, δ($C^2$) 130.7 [$^3J(PC^1)$ < 1, < 1 Hz], δ($C^3$) 127.8 (s), δ($C^4$) 129.7 (s). [h] For CPh: δ($C^1$) not observed due to low signal intensity, δ($C^2$) 130.0 (s), δ($C^3$) 127.6 (s), δ($C^4$) 129.7 (s). [i] Not determined due to unfavourable signal overlap and/or intensity. [j] For CPh: δ($C^1$) not observed due to low signal intensity, δ($C^2$) 130.2 (s), δ($C^3$) 127.7 (s), δ($C^4$) 128.9 (s).

**Table 5** Proton NMR data

| Compound[a] | δ($CH_3$)[b] | $^3J(HH)$[c] | $^4J(PH)$[c] | δ(CH=)[b] | $^3J(PH)$[c] | δ(Ph)[b] |
|---|---|---|---|---|---|---|
| **2** | 1.94 | 6.8 | < 1, < 1 | 6.18 | 21.5, 8.8[d] | 7.0–7.5 |
| **3** | — | — | — | *e* | *e* | 7.0–7.4 |
| **4a**[f] | 1.64 | 7.1 | 3.0, 0 | 6.49 | 40.4, 7.3 | 7.1–8.3 |
| **4b**[f] | 2.09 | 6.8 | 1.2, 0 | 7.61 | 28.1, 13.8 | 7.1–8.3 |
| **6** | 1.84 | 7.3 | 2.8, 2.8 | 6.63 | 37.8, 26.6 | 7.1–8.0 |
| **7** | — | — | — | 7.99 | 38.0, 30.5[d] | 7.0–8.0[g] |
| **10** | 1.93 | 7.3 | 2.9, 2.9 | 6.68 | 38.2, 26.8[d] | 7.1–7.9[h] |
| **11** | — | — | — | 8.13 | 39.8, 29.6[d] | 7.0–8.0[i] |
| [$Mo(CO)_4L^1$] | 1.48 | 7.2 | 1.9, 1.9 | 6.21 | 27.5, 20.2 | 7.1–7.5 |
| [$Mo(CO)_4L^2$] | — | — | — | 6.83 | 28.6, 21.9 | 7.1–7.5 |
| [$W(CO)_4L^1$] | 1.43 | 7.1 | 1.9, 1.9 | 6.06 | 28.7, 20.8 | 7.2–7.5 |
| [$W(CO)_4L^2$] | — | — | — | 6.72 | 29.3, 22.5 | 7.1–7.5 |

[a] As $CDCl_3$ solutions unless otherwise specified. [b] In ppm (± 0.01 ppm) relative to $SiMe_4$ (δ 0.0). [c] In Hz (± 0.2 Hz). [d] Listed as $^3J(P_XH)$, $^3J(P_AH)$. [e] Not observed due to unfavourable signal overlap. [f] As a solution in $C_6D_5CD_3$. [g] For $P_APh$: δ 7.97 ($H_o$), 7.29 ($H_m$), 7.36 ($H_p$). For $P_XPh$: δ 7.75 ($H_o$), 7.04 ($H_m$), 7.14 ($H_p$). For CPh: δ 7.58 ($H_o$), 6.98 ($H_m$), 6.98 ($H_p$). [h] For $P_APh$: δ 7.89 ($H_o$), 7.30 ($H_m$), 7.37 ($H_p$). For $P_XPh$: δ 7.81 ($H_o$), 7.10 ($H_m$), 7.22 ($H_p$). [i] For $P_APh$: δ 8.04 ($H_o$), 7.27 ($H_m$), 7.33 ($H_p$). For $P_XPh$: δ 7.82 ($H_o$), 7.04 ($H_m$), 7.12 ($H_p$). For CPh: δ 7.66 ($H_o$), 6.89 ($H_m$), 6.89 ($H_p$).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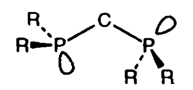
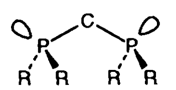

II


III

We have suggested that the small value of $^2J(PCP)$ for compound **2** can be attributed to a dominance of conformation **II** in solution[5] and this is supported by the molecular structure of this species as determined by single-crystal X-ray diffraction (see below).

Important features of the values of $^2J(PP)$ for the monochalcogenides of **2** and **3** are (*a*) their solvent dependence, (*b*) a decrease with temperature of *ca.* 10 Hz between 296 and 168 K in $CH_2Cl_2$, and (*c*) isomeric differences which are significant for the derivatives of **2** and large for those of **3**. These observations are all consistent with the geminal couplings $J(P^{III}P^V)$ being strongly dependent upon conformation. This dependence presumably involves the orientation of the phosphorus lone-pair direction, but it is not clear whether it also involves the P=E direction. In the case of the dichalcogenides, all of the values of $J(P^VP^V)$ are very close indeed, and show essentially no solvent or temperature dependence which perhaps indicates that this factor is not important. In this context it is interesting to compare the effects of replacing methyl by phenyl in the cases of **4a**/**5a** and **4b**/**5b** in which the larger change in $J(P^{III}P^V)$ occurs when the replaced group is *cis* to the phosphorus with the lone pair. At temperatures below 230 K the 202 MHz $^{31}P$ NMR spectra of **4a** and **4b** showed differential line-broadening effects which are probably indicative of restricted rotation, although it was not possible to resolve resonances from individual conformers at any accessible temperature (*i.e.* > 168 K). These effects were found only for the $P_X^{III}$ and $P_X^V$ resonances from phosphorus *cis* to the substituent R.

In the complexes the constraints of the four-membered ring remove the need to take into account differential conformational effects of the foregoing kind and the values of $^2J(PP)$ can be regarded as the sum of metal- and backbone-mediated contributions;[16] they are close to those found for corresponding complexes of **1** (76 and 84 Hz for molybdenum and tungsten respectively).[15]

(*c*) *Proton and* $^{13}C$ *data.* Proton and carbon-13 NMR data are in Tables 3–5. Details of phenyl-proton chemical shifts are

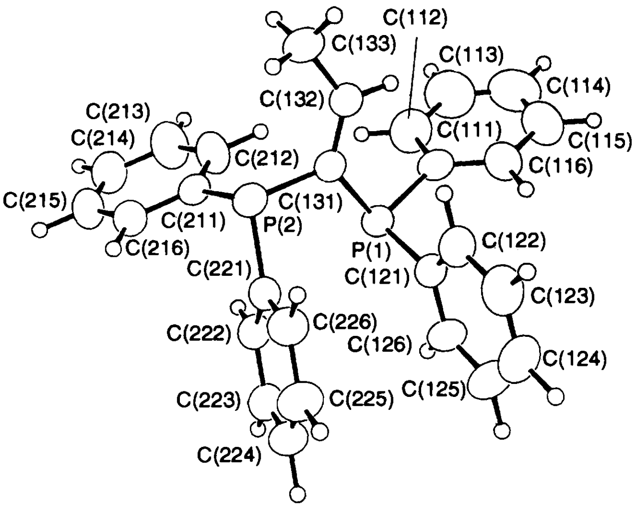


**Fig. 2** An ORTEP[23] representation of the crystal and molecular structure of compound **2**. Hydrogen atoms are shown as circles with a small arbitrary radius. Ellipses for non-hydrogen atoms are at the 50% probability level

**Table 6** Selected interatomic distances (pm), angles between interatomic vectors (°) and dihedral angles (°) for compound **2** with estimated standard deviations (e.s.d.s) in parentheses

| | | | |
|---|---|---|---|
| C(111)–P(1) | 184.1(4) | C(211)–P(2) | 184.2(3) |
| C(121)–P(1) | 183.2(3) | C(221)–P(2) | 183.5(3) |
| C(131)–P(1) | 183.7(4) | C(131)–P(2) | 183.9(5) |
| C(132)–C(131) | 133.5(4) | C(133)–C(132) | 150.0(6) |
| C(121)–P(1)–C(111) | 103.0(2) | C(221)–P(2)–C(211) | 101.8(2) |
| C(131)–P(1)–C(111) | 102.6(2) | C(131)–P(2)–C(211) | 101.6(2) |
| C(131)–P(1)–C(121) | 102.1(2) | C(131)–P(2)–C(221) | 103.0(2) |
| P(2)–C(131)–P(1) | 117.3(2) | C(132)–C(131)–P(1) | 123.4(3) |
| C(132)–C(131)–P(2) | 119.0(3) | C(133)–C(132)–C(131) | 126.5(4) |
| l.p.–P(1)–C(131)–C(132)* | 132.1(2) | | |
| l.p.–P(2)–C(131)–C(132) | −33.5(3) | | |

* l.p. is the position of the lone pair, taken as being the idealised fourth co-ordination vertex of a tetrahedron centred on each phosphorus atom.

given only in cases where a fortuitous combination of chemical shifts and coupling constants permitted a full analysis.

Methyl-proton chemical shifts for compounds **2**, **4a**, **4b**, **6** and **10** bear a close relation to those found for protons in similar environments in other substituted vinyldiphenylphosphines.[17–19] Of interest are the various phosphorus–proton coupling constants involving the olefinic proton. For **2** these are 8.8 and 21.5 Hz which may confidently be assigned as $^3J(P_AH)_{cis}$ and $^3J(P_XH)_{trans}$ respectively using the well established relationship $^3J(PH)_{cis} < {}^3J(PH)_{trans}$ (typically ≈10 and ≈25 Hz) for similar systems.[20] This knowledge also enabled the confirmation of the original assignment of the $^{31}P$ NMR spectrum by means of selective $^1H$-{$^{31}P$} decoupling experiments. The greater magnitude of both the *cis* and *trans* couplings in **6**, **7**, **10** and **11** is as expected[20] for a change in oxidation state from $P^{III}$ to $P^V$.

Table 3 shows backbone-carbon NMR data for the species isolated in this study. Carbon-13 chemical shifts for sp$^2$ carbons in substituted vinylphosphines have received some attention but appear to follow no clear pattern. For **2** the values of $\delta(C^1)$ and $\delta(C^2)$ are 134.4 and 149.1 respectively and at first appear inconsistent with those found for **1** of δ 148.4 and 135.5. However, methyl-group substitution is known to give rise to significant α and β effects on carbon-13 chemical shifts in such systems † and the near interchange of values can be explained as caused by α and β effects of approximately equal magnitude but opposite sign. Sulfurisation or selenisation of phosphorus has also been shown to have similar but opposite α and β effects. For the diselenide of **1** the chemical shifts of $C^1$ and $C^2$ are δ 144.1 and 154.6 and indicate α and β effects of −4.3 and +19.1 ppm respectively (for a double selenisation).[1] Although the analogous values derived from **2** and **10** are consistent in sign but slightly different in magnitude it is clear from the other data[1] that other factors are involved in determining $\delta(^{13}C)$ in such systems; the near identity of the values of $\delta(C^1)$ for *trans*-$Ph_2PCH{=}CHPPh_2$ and its diselenide (δ 142.2 and 142.1 respectively) compared to the difference found for the *cis* isomer and its diselenide (δ 146.7 and 136.6) demonstrate that these parameters must also have some dependence on other factors such as conformation.

One-bond $^{31}P$–$^{13}C$ coupling constants show the expected increase in going from $P^{III}$ to $P^V$. Two-bond couplings are less easy to categorise although the similarity of these and also of $^1J(P^VC)$ within compound **6** and within **10** suggest that these couplings are not greatly affected by conformational variations when the phosphorus atoms are $P^V$. The same cannot be said for the corresponding couplings in **2** which involve $P^{III}$.

The three-bond $P$–$C_{methyl}$ couplings in these compounds might be expected to show clear stereochemical dependences. For **2** the values of $^3J(PC)_{trans}$ and $^3J(PC)_{cis}$ are 0.9 and 27.8 Hz respectively. The value of 27.8 Hz is similar to other values of $^3J(P^{III}C)_{cis}$ for related molecules ‡ and the range 22–28 Hz appears to be typical for this potentially diagnostically important parameter. The values of $^3J(PC)_{trans}$ for this and other related species are more variable but all are significantly less than the lower limit of the range found for the *cis* couplings.

*X-Ray Diffraction Studies.*—Crystals of compound **2** suitable for single-crystal X-ray diffraction analysis were obtained by diffusion of methanol into its solution in benzene. An ORTEP[23] drawing of the molecular structure is shown in Fig. 2. Bond lengths and angles are given in Table 6 and fractional non-hydrogen coordinates in Table 7.

The methyl substituent on the C=C double bond appears to have little effect on bond lengths and angles of the rest of the vinylidene group and these are close to those observed[24] in the unsubstituted diphosphine $(Ph_2P)_2C{=}CH_2$ (vdpp). The carbon atom of the methyl group is in the olefinic plane [defined by P(1), P(2), C(131) and C(132)] and the methyl group interacts with the $PPh_2$ group to which it is *cis* so that the angle C(131)–C(132)–C(133) of 126.5° is larger than normal for an sp$^2$-hybridised carbon. A similar effect was noted for the triphosphine $(Ph_2P)_2C{=}CH(PPh_2)$.[10] Other effects of the methyl substituent upon the vinylidene geometry appear to be minimal.

The relative orientations of the phosphorus lone pairs are shown in Fig. 3. These are similar to those seen in both vdpp and $(Ph_2P)_2C{=}CH(PPh_2)$, *viz.* the lone pair of atom P(1) points towards the inside of the P(1)–C(131)–P(2) angle while that on P(2) points towards the methyl group. The phosphorus–lone pair vectors point out of the olefinic plane on opposite sides, presumably to minimise steric interactions.

## Experimental

Solvents were dried and deaerated by standard procedures prior to use and all manipulations were performed under an

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† For example, *trans*-$Ph_2PC(Me){=}CH(PPh_2)$ exhibits values of $\delta(^{13}C)$ of 151.5 and 137.5 [compared with 142.2 for *trans*-$(Ph_2P)CH{=}CH(PPh_2)$] showing α and β effects of +9.3 and −4.7 ppm respectively.[1,21]

‡ *For example*, *cis*-$(Ph_2P)CH{=}CHMe$, $^3J(CP)_{cis}$ = 22.9 Hz;[17] *trans*-$(Ph_2P)CH{=}C(Me)PPh_2$, $^3J(CP)_{cis}$ = 22.9 Hz; *trans*-$(Ph_2P)CH{=}C(Me)CH_2PPh_2$, $^3J(CP)_{cis}$ = 24.4 Hz;[22] *cis*-$(Ph_2P)CH{=}C(Me)CH_2PPh_2$, $^3J(CP)_{cis}$ = 24.4 Hz.[22]

**Table 7** Non-hydrogen fractional atomic coordinates ($\times 10^4$) for compound **2** with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| P(1) | 6 160(1) | 9 369(1) | 2 603(1) |
| P(2) | 7 367(1) | 6 228(1) | 2 164(1) |
| C(111) | 6 445(2) | 10 732(2) | 1 683(2) |
| C(112) | 7 879(2) | 10 778(2) | 1 467(2) |
| C(113) | 8 170(2) | 11 839(2) | 864(2) |
| C(114) | 7 027(2) | 12 854(2) | 477(2) |
| C(115) | 5 593(2) | 12 808(2) | 692(2) |
| C(116) | 5 302(2) | 11 747(2) | 1 295(2) |
| C(121) | 4 115(2) | 9 777(2) | 2 872(2) |
| C(122) | 3 501(2) | 9 541(2) | 2 049(2) |
| C(123) | 1 929(2) | 9 881(2) | 2 317(2) |
| C(124) | 973(2) | 10 457(2) | 3 408(2) |
| C(125) | 1 587(2) | 10 693(2) | 4 231(2) |
| C(126) | 3 158(2) | 10 353(2) | 3 963(2) |
| C(131) | 7 046(3) | 7 906(3) | 1 566(2) |
| C(132) | 7 592(3) | 7 991(3) | 427(2) |
| C(133) | 8 485(4) | 6 830(3) | −456(3) |
| C(211) | 9 123(2) | 5 841(2) | 2 587(2) |
| C(212) | 10 026(2) | 6 588(2) | 2 245(2) |
| C(213) | 11 393(2) | 6 185(2) | 2 537(2) |
| C(214) | 11 856(2) | 5 035(2) | 3 172(2) |
| C(215) | 10 953(2) | 4 288(2) | 3 514(2) |
| C(216) | 9 587(2) | 4 691(2) | 3 221(2) |
| C(221) | 5 907(2) | 6 618(2) | 3 576(1) |
| C(222) | 6 105(2) | 6 979(2) | 4 853(1) |
| C(223) | 4 936(2) | 7 245(2) | 5 622(1) |
| C(224) | 3 568(2) | 7 149(2) | 5 654(1) |
| C(225) | 3 370(2) | 6 788(2) | 4 646(1) |
| C(226) | 4 539(2) | 6 523(2) | 3 607(1) |

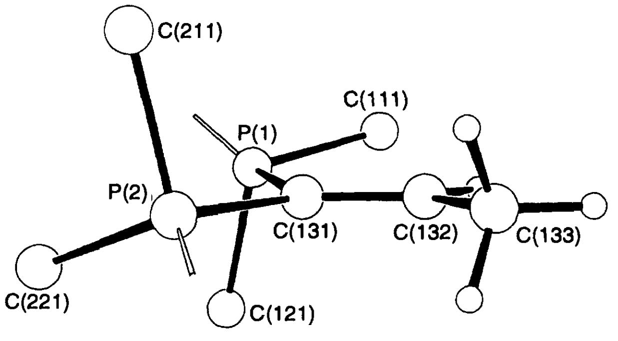

**Fig. 3** Schematic diagram showing the relative orientations of the phosphorus lone pairs. For clarity, atoms of the phenyl groups other than the *ipso*-carbons have been omitted. The lone pairs are represented by open lines

atmosphere of dry dinitrogen. The compounds 1,1-bis(diphenylphosphino)prop-1-ene **2**,[6] 1,1-bis(diphenylphosphino)-2-phenylethene **3**,[7] and [Mo(CO)$_4$(pip)$_2$][25] were prepared by previously published methods.

*Sulfurisation/selenisation Reactions; General Procedure*.—To a benzene solution of the diphosphine (typically 5 mmol in 30 cm$^3$) was added 1 atomic equivalent of chalcogen and the mixture was stirred under an atmosphere of dry dinitrogen for 68 h. The resulting equilibrium mixtures of diphosphine, monochalcogenides and dichalcogenide were characterised in solution by NMR spectroscopy. Dichalcogenides were prepared by the reaction of the diphosphine with 2 equivalents of the chalcogen under similar or modified conditions. The 1:2 reactions with sulfur were essentially complete in 2 h whereas the corresponding reactions with selenium required *ca.* 3 d at room temperature and were therefore accelerated by means of a 2 h reflux period after which the reaction was found to have proceeded virtually quantitatively. Addition of methanol (30 cm$^3$) to the filtered benzene solutions from the 1:2 reactions yielded the dichalcogenides as air-stable white crystals in typical yields of 80–90%.

*Preparation of the Complexes*.—*Molybdenum*. A mixture of [Mo(CO)$_4$(pip)$_2$] (2.5 mmol) and the diphosphine (2.5 mmol) in dichloromethane (30 cm$^3$) was stirred under nitrogen at ambient temperature for 0.5 h. The solution was then filtered and methanol (30 cm$^3$) added to the filtrate. On standing, orange-red crystals were precipitated which were recrystallised from dichloromethane (20 cm$^3$)–methanol (20 cm$^3$) to give the product as air-stable orange crystals; typical yields 70–80%.

*Tungsten*. The corresponding tungsten complexes were prepared by the stoichiometric reaction of the diphosphine with [W(CO)$_6$] in refluxing diglyme according to the method described in ref. 15; typical yields were 60–70%.

*Single-crystal X-Ray Analysis*.—All crystallographic measurements were carried out at ambient temperature on a Nicolet P3/F diffractometer operating in the ω–2θ scan mode using graphite-monochromated Mo-Kα radiation and followed a standard procedure described in detail elsewhere.[26] The data set was corrected for Lorentz and polarisation factors but no absorption correction was applied.

The structure was determined by direct methods and refined by full-matrix least squares using SHELX 76.[27] Anisotropic thermal displacement parameters were applied to all non-hydrogen atoms and phenyl groups were constrained at all times as rigid bodies with idealised geometry (all C–C 139.5 pm, all C–C–C 120°). All hydrogen atoms were included in idealised positions (C–H 96 pm) and were assigned an overall isotropic displacement parameter. The weighting scheme $w = [\sigma^2(F_o) + 0.0003(F_o)^2]^{-\frac{1}{2}}$ was used. The final difference synthesis contained no features of chemical significance (maximum and minimum residual electron density = 0.26 and −0.29 e Å$^{-3}$ respectively).

*Crystal data*. $C_{27}H_{24}P_2$ **2**, $M = 410.44$, 0.8 × 0.6 × 0.2 mm, triclinic, space group $P\bar{1}$, $a = 995.42(13)$, $b = 1208.2(2)$, $c = 1080.3(2)$ pm, $\alpha = 85.670(12)$, $\beta = 73.028(10)$, $\gamma = 66.294(11)°$, $U = 1.1365(3)$ nm$^3$, $Z = 2$, $D_c = 1.199$ g cm$^{-3}$, $\mu = 0.161$ mm$^{-1}$, $F(000) = 432$.

*Data collection*. $4.0 < 2\theta < 45°$, scan widths 2.0° + α-doublet splitting, scan speeds 2.0–29.3° min$^{-1}$. 3046 Data collected, 2879 with $I > 2.0\sigma(I)$ considered observed, $T = 290$ K.

*Structure refinement*. Numbers of parameters = 254, $R = 0.0515$, $R' = 0.0579$, maximum $\Delta/\sigma = 0.07$ [in $U_{11}$ of H(112)].

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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