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The synthesis, nuclear magnetic resonance spectra, crystal structure, and solid-state and solution conformations of tris(diphenylphosphino)ethene (tppee)

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Abstract

The synthesis of tris(diphenylphosphino)ethene (tppee) by addition of Ph_2PH to $Ph_2PC{\equiv}CPPh_2$, or by the reaction of Ph_2PCl with $Ph_2PCLi:CHPPh_2$, and its crystal structure are described. Crystals of tppee are monoclinic, space group $C2/c$ with a 3553.0(4), b 1044.1(1), c 1855.7(2) pm, β 93.40(1)°, and $Z = 8$; final $R = 0.0597$ for 4585 observed reflections. The proton, ^{13}C and ^{31}P NMR parameters are reported, and the P–P and P–C coupling constants suggest a solution conformation that is close to that found by X-ray diffraction on the solid; that is, a close approach of the electron lone pairs of the *cis*-vicinal phosphorus atoms, and opposition of those on the geminal phosphorus atoms.

Introduction

Of the many known organo-phosphine ligands [1] comparatively few have an unsaturated aliphatic carbon–carbon bond adjacent to a phosphorus atom, notable exceptions being $Ph_2PC{\equiv}CH$ [2], $Ph_2PC{\equiv}CPPh_2$ [3], and the first four members of the series of diphenylphosphino-substituted ethenes, $Ph_2PCH{=}CH_2$ [4], $(Ph_2P)_2C{=}CH_2$ [5], and *cis*- and *trans*-$Ph_2PCH{=}CHPPh_2$ [6]. These species are of special interest for two main reasons: (a) the degree of rigidity conferred by the multiple bond can be used to control the types of complex that can be formed, and (b) it is often possible to perform addition reactions [7] to the multiple bond in both

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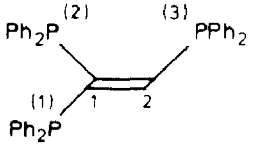
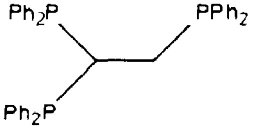
the free ligands [8–10] and in their complexes [9,11,12] so as to generate new species. In this paper we report the preparation by two different routes of the next member of the series of substituted ethenes, tris(diphenylphosphino)ethene (tppee),



tppee

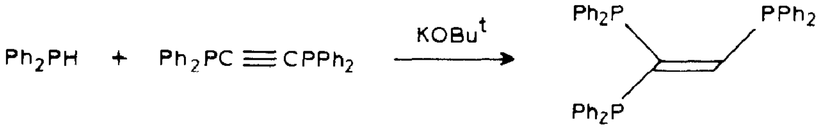


tppe

together with its proton, carbon-13 and phosphorus-31 NMR spectra, and its crystal structure. Note that tppe is 1,1,2-tris(diphenylphosphino)ethane [9]. As a ligand, tppee can be expected to be unable to use all three phosphorus atoms in coordination to the same metal atom whereas it is known that tppe can do this [9]. However, it may well be possible for all three phosphorus atoms of tppee to be coordinated to different metal atoms in the same cluster.

Results and discussion

The base-catalysed (KOBu^t) addition of Ph_2PH to $Ph_2PC{\equiv}CPPh_2$ in thf at room temperature gives tppee as air stable white crystals in 51% yield, according to reaction 1.



(1)

A correct elemental analysis and an ABX type of ^{31}P NMR spectrum (Fig. 1) in conjunction with the route of preparation support the proposed structure. It is also

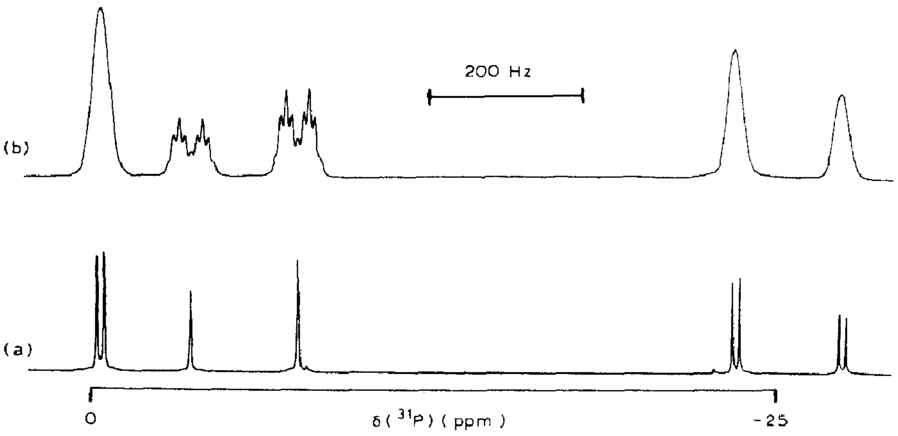


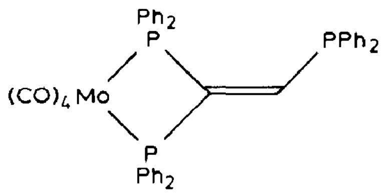
Fig. 1. ^{31}P NMR spectrum at 36.2 MHz of tppee. (a) With full proton decoupling. (b) Without proton decoupling showing resolved splitting of the P(2) resonance by the olefinic (*J* 30.8 Hz) and *o*-phenyl protons.

possible to make tppee by route 2, which gives a ca. 20% yield of an identical product,

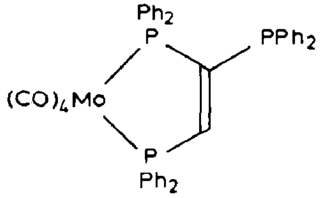
$$\textit{cis-}\text{ or }\textit{trans-}Ph_2PCH{=}CHPPh_2 \xrightarrow{BuLi} Ph_2PCLiCHPPh_2 \xrightarrow{Ph_2PCl} (Ph_2P)_2C{=}CHPPh_2 \qquad (2)$$

In this case the preparative route does not provide compelling evidence for the structure of the product since treatment of $Ph_2PCH{=}CHPPh_2$ with BuLi might remove an *ortho*-proton of a phenyl group and lead to $Ph_2PCH{=}CHP(Ph)C_6H_4PPh_2$ as the final product. This would also have an ABX or AMX type of ^{31}P NMR spectrum, with coupling constants and chemical shifts which might be similar to those actually found in tppee itself. Attempts to make tppee directly from trichloroethene were unsuccessful.

In its reactions with metal substrates tppee tends to yield complex mixtures of products, some of which can be identified by ^{31}P NMR on the basis of known trends in chemical shifts and coupling constants for different metals and chelate ring sizes [9,13]. For example, the products of the reaction with Mo-(piperidine)$_2$(CO)$_4$ included **1** and **2**, and although these have not yet been isolated in pure form their ^{31}P NMR parameters are given in Table 2. Support for the assignments is provided by very similar values of ^2J(PMP) found in the analogous complexes $(CO)_4Mo[(Ph_2P)_2C{=}CH_2]$ (76 Hz) [14] and $(CO)_4)Mo[$*cis*-$Ph_2PCH{=}CHPPh_2]$ (8.7 Hz) [14], and these in turn support our assignments in the parent tppee.



(**1**)



(**2**)

NMR spectra: As indicated above, tppee has an ABX ^{31}P NMR spectrum, and the chemical shifts and coupling constants are given in Table 1 together with our proposed assignment. This is based upon the following considerations. The geminal pair of phosphorus nuclei can be expected [9,13] to experience similar changes in chemical shift upon coordination to a metal, that is, they should have similar "coordination chemical shifts" [15], and hence they should maintain a constant relative shielding difference in tppee itself and in the complex **1**. In **1** the uncoordinated (non-geminal) Ph_2P group can be identified immediately by its chemical shift of -30.8 ppm (see Table 2) and thus there is a difference of 3.4 ppm between the chemical shifts of the coordinated geminal phosphorus nuclei which should therefore also be found in tppee itself. Our assignment of $\delta(P(3))$ -25.7 ppm in tppee leads to a geminal shielding difference of 4.5 ppm between P(1) and P(2) in excellent agreement with the foregoing considerations, whereas other assignments of P(3) would lead to the unacceptable values of 20.3 or 24.8 ppm for this difference. Furthermore, on our assignment the change in chemical shift of P(3) when the geminal phosphorus atoms become coordinated is small, as would be expected. Similar reasoning based on the ^{31}P chemical shifts in **2** leads to the same conclusions.

Table 1

^{31}P NMR data for tppee [a]

Parameter (unit)	Phosphorus nucleus P(i)		
	P(1)	P(2)	P(3)
$\delta(^{31}P(i)$ (ppm)[b]	-0.9	-5.4	-25.7
$J(P(1)P(i))$ (Hz) [c]	–	$(+1.5)$	$[-9.8]$
$J(P(2)P(i))$ (Hz) [c]	$(+1.5)$	–	$[+142.8]$
$J(P(3)P(i))$ (Hz) [c]	-9.8	$[+142.8]$	–
$J(P(i)C(1))$ (Hz) [c]	-55.0	-31.2	$(+19.7)$
$J(P(i)C(2))$ (Hz) [c]	(-3.1)	$(+31.1)$	-17.5
$J(P(i)H)$ (Hz) [c,d]	$[+8.7]$	$[+30.8]$	(0.6)

[a] In CH_2Cl_2 at 295 K. [b] To high frequency of external 85% H_3PO_4, ±0.1 ppm. [c] ±0.1 Hz. [d] Olefinic proton, from 2D $^{13}C/H$ spectrum. [e] One-bond couplings are unbracketed, two-bond couplings are in round brackets, three-bond couplings are in square brackets.

With P(3) assigned, its couplings to P(1) and P(2) can be used to assign these also, since in $Ph_2PCH{=}CHPPh_2$ $^3J(PP)$ is large (+105.5 Hz) for the *cis* and small (+13.4 Hz) for the *trans* relationship [5], and in tppee $^3J(P(2)P(3))$ is therefore assigned to the former. It will be noticed that our assignment gives a small value for $^2J(P(1)P(2))$ whereas in $(Ph_2P)_2C{=}CH_2$ this coupling is +98 Hz [5]. However, we have evidence [16] that in $(Ph_2P)_2C{=}CHR$ $^2J(PP)$ is very sensitive to the size of R and can fall as low as 3 Hz even for R = Me. By contrast, *cis* $^3J(PP)$ in $Ph_2PCH{=}C(R)PPh_2$ is much less sensitive to the size of R [17].

The ^1H and ^{13}C parameters of the olefinic part of tppee are also given in Table 1 and are consistent with the above assignment. C(1) and C(2) were assigned by a gated-decoupler spin-echo experiment, and a series of $^{13}C\text{-}\{^{31}P\}$ selective decoupling and spin-tickling experiments (under conditions of full proton decoupling) was used to assign the $^{31}P\text{-}^{13}C$ coupling constants and to compare their signs with those of the $^{31}P\text{-}^{31}P$ couplings. A typical set of experiments is illustrated in Fig. 2. Homonuclear ^{31}P spin-tickling was used to determine the relative signs of the three $^{31}P\text{-}^{31}P$ coupling constans. A two-dimensional $^{13}C/^1H$ chemical shift correlation experiment illustrated in Fig. 3 was used to determine the positions of the olefinic proton resonances since these were hidden by the phenyl signals. The slopes, positive or negative, of the broken lines in Fig. 3 also gave the relative signs [18] of the $^{31}P\text{-}^1H$ and $^{31}P\text{-}^{13}C(2)$ coupling constants as follows: $^3J(P(1)H)/^2J(P(1)C) < 0$; $^2J(P(3)H)/^1J(P(3)C) < 0$; $^3J(P(2)H)/^2J(P(2)C) > 0$.

Table 2

^{31}P NMR data for complexes **1** and **2** [a]

Parameter (unit)	**1**	**2**
$\delta(^{31}P(1))$ (ppm) [b]	$+34.0$	-11.3
$\delta(^{31}P(2))$ (ppm) [b]	$+30.6$	$+71.1$
$\delta(^{31}P(3))$ (ppm)[b]	-30.8	$+53.7$
$J(P(1)P(2))$ (Hz) [c]	83.6	25.3
$J(P(1)P(3))$ (Hz) [c]	10.7	4.2
$J(P(2)P(3))$ (Hz) [c]	9.5	9.5

[a] In CH_2Cl_2. [b] To high frequency of external 85% H_3PO_4, ±0.1 ppm. [c] ±0.1 Hz.

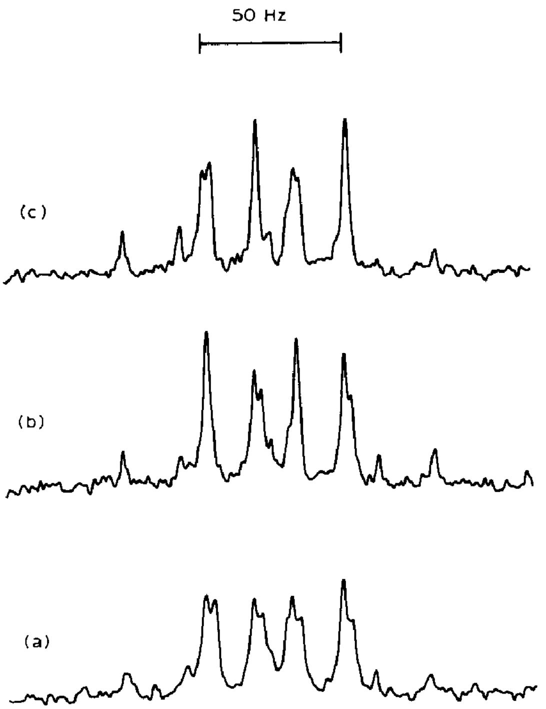


Fig. 2. ^{13}C NMR spectrum at 22.5 MHz of C(2) in $(Ph_2P(_2C{=}CHPPh_2$ with signal from the non-protonated C(1) suppressed by suitable pulse timing. (a) Normal spectrum. (b) With selective ^{31}P decoupling centred on high frequency component of P(1). (c) With selective ^{31}P decoupling centred on low frequency component of P(1).

Finally, a ^{13}C-{^{31}P} selective decoupling experiment (without proton irradiation) was used to place these signs on an absolute basis by showing that ^3J(P(2)H) is of the same sign as ^1J(C(2)H), i.e. positive.

The parameters in Table 2 were determined at 295 K; within the range 190 to 375 K in toluene ^2J(P(1)P(2)) varied from 0 to 3.7 Hz, ^3J(P(2)P(3)) varied from 143.4 to 140.8 Hz, and ^3J(P(1)P(3)) was unchanged. We attribute this to a dependence on relative lone pair orientation of the geminal and *cis*-vicinal, but not the *trans*-vicinal, coupling constants. Small variation (< 1 ppm) in the ^{31}P chemical shifts also occurred.

Molecular structure. Crystals (of the benzene demisolvate) suitable for single-crystal X-ray diffraction analysis were obtained from benzene/methanol. An ORTEP drawing of the molecular structure obtained by this analysis is shown in Fig. 4, interatomic distances and angles are given in Table 3, and fractional non-hydrogen atomic coordinates are in Table 4.

It is surprising to note that the presence of the third PPh_2 group on atom C(132) (i.e. C(2) does not greatly affect the bond distances and angles about the rest of the vinylidene group as these are close to those observed [19] in the diphosphine $(PPh_2)_2C{=}CH_2$. Furthermore, the atom P(3) is not significantly out of the olefinic plane defined by atoms P(1), P(2), C(131) and C(132). However, there does appear to be some interaction between the two *cis*-PPh_2 groups as the angle C(131)–C(132)–P(3) has increased slightly to 124.6(4)°.

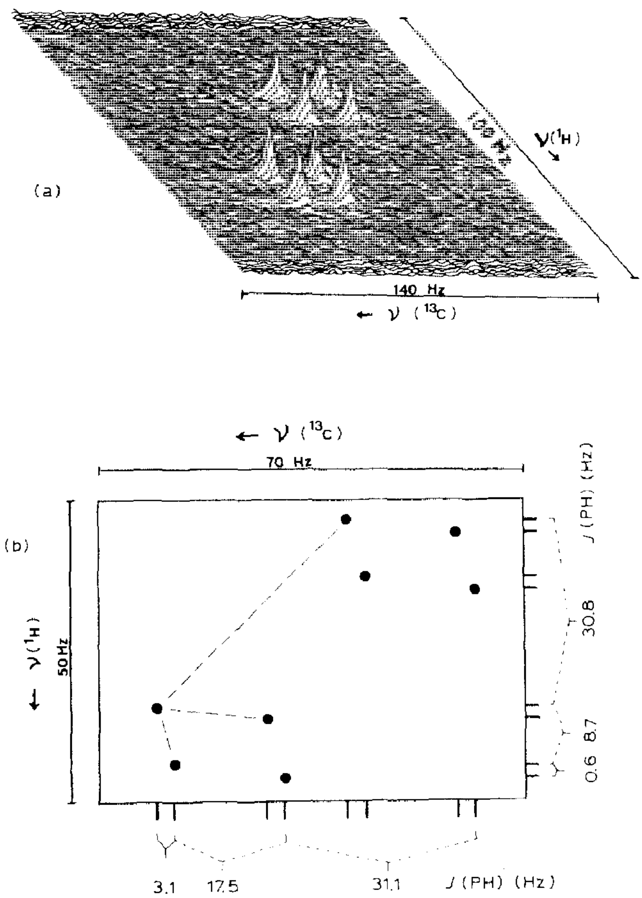


Fig. 3. $^{13}C/^{1}H$ 2D chemical shift correlation spectrum of C(2) region of tppee measured at 22.5 MHz. (a) Full plot. (b) Schematic contour plot with projections onto the two axes giving the corresponding 1D spectra of C(2) and the olefinic H, showing three different splittings by ^{31}P in each.

The relative phosphorus lone pair orientations are shown in Fig. 5. It can be readily seen that the relative orientation of the lone pairs of the two geminal phosphorus atoms is similar to that observed [19] for $(PPh_2)_2C{=}CH_2$, viz. the lone pair on P(1) points approximately towards the inside of the P–C–P angle (the dihedral angle defined by lone pair/P(1)/C(131)/C(132) being −127.5°) while the lone pair on atom P(2) (i.e. *cis* to P(3)) is directed outwards (the dihedral angle defined by lone pair/P(2)/C(131)/C(132) being −43.1°). Note that the lone pairs on P(1) and P(2) are directed to opposite sides of the olefinic plane. The lone pairs on the *cis* phosphorus atoms P(2) and P(3) are oriented approximately towards one another.

The P–C bond lengths and interbond angles at phosphorus in Table 3 are all as expected for triorganophosphines with substituents of moderate bulk, and indicate that the phosphorus hybridization can be regarded as "normal", a feature that can be expected to persist in solution. However, the various dihedral angles may depend significantly upon crystal packing forces and might be different in solution. This is an important factor in connection with the ^{31}P–^{13}C, ^{31}P–H and ^{31}P–^{31}P coupling constants which are known [20,21] to depend upon lone-pair relationships. On the

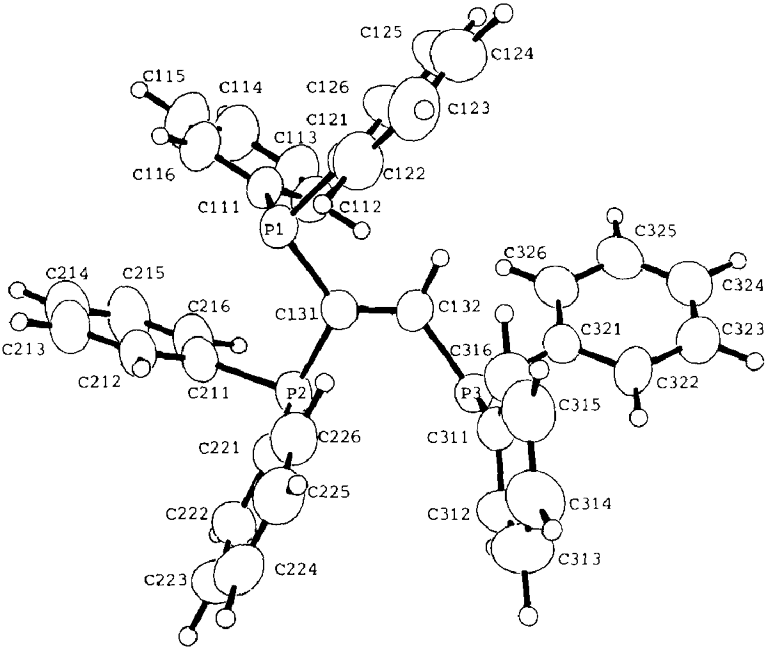


Fig. 4. ORTEP drawing of the crystallographically determined molecular structure of $(Ph_2P)_2C{=}CHPPh_2$.

basis that the lone pair direction makes equal angles with the three actual bonds to phosphorus, the lone pair/lone pair dihedral angles (about notional P–P links) in the crystal are 166, 76, and 21° for P(1)/P(2), P(1)/P(3) and P(2)/P(3) respectively. Large (ca. 100 Hz or more) geminal $^{31}\mathrm{P}^{\mathrm{III}}$–$^{31}\mathrm{P}^{\mathrm{III}}$ couplings have been [21,22] associated with small inter-lone pair dihedral angles (i.e. lone pairs pointing approximatetly towards each other) and small couplings with dihedral angles near 180°. Thus the P(1)P(2) dihedral angle of 166° and associated small coupling

Table 3

Interatomic bond lengths (pm) and angles (deg.)

C(111)-P(1)	183.6(4)	C(121)-P(1)	183.1(4)
C(131)-P(1)	183.9(5)		
C(131)-P(2)	183.5(5)	C(211)-P(2)	184.4(4)
C(221)-P(2)	184.1(4)		
C(132)-P(3)	181.1(5)	C(311)-P(3)	183.3(4)
C(321)-P(3)	184.6(4)		
C(132)-C(131)	134.8(5)	H(132)-C(132)	100.5(38)
C(121)-P(1)-C(111)	103.0(2)	C(131)-P(1)-C(111)	102.0(2)
C(131)-P(1)-C(121)			
C(211)-P(2)-C(131)	103.5(2)	C(221)-P(2)-C(131)	102.4(2)
C(221)-P(2)-C(211)	101.1(2)		
C(311)-P(3)-C(132)	101.5(2)	C(231)-P(3)-C(132)	99.1(2)
C(321)-P(3)-C(311)	101.0(2)		
P(2)-C(131)-P(1)	118.8(3)	C(132)-C(131)-P(1)	122.1(3)
C(132)-C(131)-P(2)	119.0(3)	C(131)-C(132)-P(3)	124.6(4)
H(132)-C(132)-P(3)	108.9(21)	H(132)-C(132)-C(131)	126.4(21)

Table 4

Atom coordinates ($\times 10^4$)

	x	y	z
P(1)	1001.2(2)	5253(1)	3826.9(4)
P(2)	1197.5(2)	8163(1)	3560(5)
P(3)	2070.0(4)	7351(1)	3322.6(5)
C(111)	931(1)	5471(2)	4792(1)
C(112)	1201	6013	5277
C(113)	1121	6181	5998
C(114)	772	5808	6234
C(115)	503	5266	5748
C(116)	582	5098	5027
C(121)	1281(1)	3782(2)	3811(1)
C(122)	1296	3201	3137
C(123)	1505	2082	3063
C(124)	1700	1546	3664
C(125)	1685	2128	4339
C(126)	1476	3246	4412
C(131)	1353(1)	6496(3)	3662(2)
C(132)	1717(1)	6206(3)	3574(2)
C(211)	717(1)	8139(2)	3879(1)
C(212)	399	7730	3461
C(213)	45	7743	3749
C(214)	8	8166	4455
C(215)	325	8575	4872
C(216)	679	8561	4584
C(221)	1099(1)	8301(2)	2579(1)
C(222)	962	9486	2335
C(223)	903	9715	1596
C(224)	981	8758	1101
C(225)	1118	7573	1345
C(226)	1177	7344	2084
C(311)	2131(1)	6900(2)	2382(1)
C(312)	2199	7903	1910
C(313)	2245	7649	1183
C(314)	2224	6393	927
C(315)	2156	5390	1399
C(316)	2109	5644	2127
C(321)	2491(1)	6609(2)	3780(1)
C(322)	2833	6580	3447
C(323)	3160	6176	3834
C(324)	3145	5801	4554
C(325)	2803	5830	4886
C(326)	2476	6234	4499

suggest that the solution and solid state conformations of this part of the molecule may well be similar. It also appears that the solution and solid state conformations of $(Ph_2P)_2C{=}CH_2$ must differ significantly since in this molecule $^2J(PP)$ is large at 98 Hz [5]. Rather little is known about the dependence on dihedral angle of vicinal $^{31}P-^{31}P$ couplings, but on the assumption that proximity of the lone pairs leads to a large coupling it would also appear that the P(3) moiety has the same conformation in both phases since the P(1)P(3) dihedral angle is small, and *cis*-$^3J(P(1)P(3))$ is

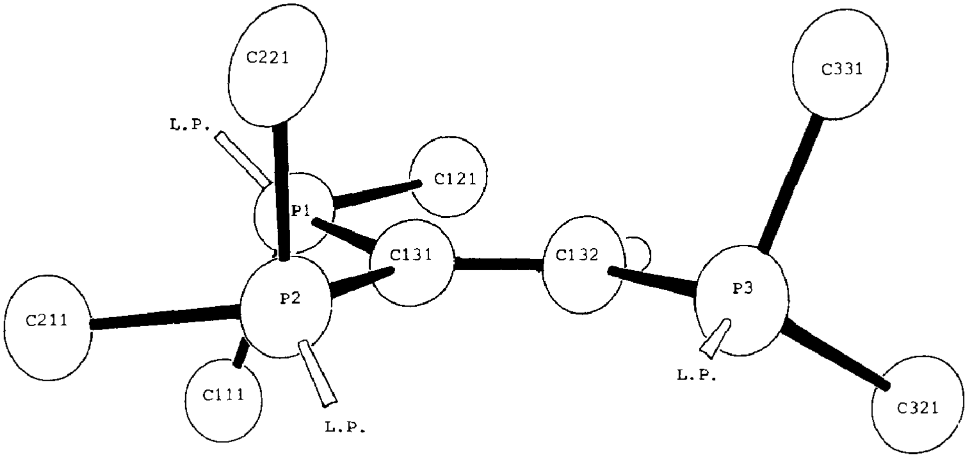


Fig. 5. Molecular structure of $(Ph_2P)_2C{=}CHPPh_2$ showing the relative orientations of the phosphorus electron lone pairs. The lone pairs are represented by open lines, and for clarity only the *ipso* carbon atoms of the phenyl groups are shown.

large. Thus the molecule appears to adopt the same overall conformation in the solid and in solution.

The one-bond phosphorus-carbon couplings are all negative as is common for P^{III}, and of large magnitude which may be attributed in part to the sp^2 hybridization of carbon. However, the large differences among these three couplings must be primarily due to variations in the lone pair orientations since the interbond angles at phosphorus are almost identical for all three atoms, implying closely similar hybridizations. There is evidence that ^1J(PP) is sensitive to rotation about the P–P single bond [23,24], but the corresponding effect of rotation about a P–C single bond so as to influence ^1J(PC) does not seem to be established. In the present case the double bond to the other carbon atom provides a convenient way of defining this rotation in terms of the lone pair/phosphorus/carbon/double bond dihedral angle. It appears that when this is large (i.e. approximating to a *trans* relationship) then the magnitude of ^1J(PC) is also large as with P(1)C(1): 127°, −55 Hz. For an approximation to a *cis* relationship the corresponding one-bond P–C coupling is smaller as with P(2)C(1): 43°, −31 Hz, and P(3)C(2): 23°, −17.5 Hz.

In general, large positive $^2J(P^{III}C)$ couplings imply relative proximity of the phosphorus lone pair and the coupled carbon, whereas small (even negative) couplings imply a substantial spatial separation [25]. In conformity with this ^2J(P(2)C(2)) and ^2J(P(3)C(1)) are large positive while ^2J(P(1)C(2)) is small and negative, thus confirming the similarity of the solid and solution state conformations. Similarly, ^2J(P(3)H) is close to zero as expected [20,26] from its lone pair/P/C/H dihedral angle of 161°, and $^3J(PH)_{trans}$ is larger than $^3J(PH)_{cis}$, also as expected [20].

Experimental

^{31}P, ^{13}C and ^1H NMR spectra were measured on a JEOL FX 900 spectrometer at measuring frequencies of 36.2, 22.5 and 89.6 MHz respectively. For the $^{13}C\text{-}\{^{31}P\}$ multiple resonance experiments radiofrequency power at 36.2 MHz was supplied to the proton decoupler coils via a tuned amplifier and matching network. Time-sharing with the receiver was used to avoid electronic interference. The $^{13}C/H$ 2D correlation experiment used JEOL software for manipulation of the data which were acquired as a 1024 × 256 matrix.

X-ray crystallography

All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω scan mode using graphite monochromatised Mo-K_α radiation (λ 71.069 pm) following a standard procedure described in detail elsewhere [27]. The data set was corrected for absorption empirically once the structure had been determined [28]. The structure was solved by direct methods and refined by full-matrix least-squares using the SHELX program system [29]. All non-hydrogen atoms were refined with anisotropic thermal parameters except for a benzene molecule (which was slightly disordered about a crystallographic C_2 axis) which was refined with isotropic thermal parameters. The phenyl groups were treated as rigid bodies with idealised hexagonal symmetry (C–C 139.5 pm). The phenyl and methyl hydrogen atoms were included in calculated positions (C–H 108 pm) and were assigned to an overall isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F_0) + g(F_0)^2]^{-1}$ was used at the end of refinement in which the parameter g was included in refinement in order to obtain satisfactory agreement analyses.

Crystal data for $C_{38}H_{31}P_3 \cdot 0.5C_6H_6$, $M = 619.64$, monoclinic, space group $C2/c$, a 3553.0(4), b 1044.1(1), c 1855.7(2) pm, β 93.40(1)°, U 6.872(4) nm^3, $Z = 8$, μ 1.60 cm^{-1}, $F(000) = 2600$.

Data collection. Scan widths 1.0° + α-doublet splitting, scan speeds 2.0–29.3° min^{-1} and $4.0 < 2\theta < 50.0°$. Total data collected 6554, no. observed 4585 ($I > 2.0\sigma(I)$).

Structure refinement. Number of parameters 352, weighting factor $g = 0.0006$, $R = 0.0597$, $R_w = 0.0656$. Atom H(132) was included in the least squares refinement. Lists of thermal parameters and observed and calculated structure factors are available from the authors.

Tris(diphenylphosphino)ethene, tppee (Route 1)

A solution of bis(diphenylphosphino)ethyne [3] (10 g, 25.4 mmol) and diphenylphosphine (4.7 g, 25.4 mmol) in dry thf (150 cm^3) was stirred under nitrogen at room temperature in the presence of KOBu^t (catalytic amount) for 18 h. The solvent was then removed under vacuum and the red oily residue was shaken with methanol (200 cm^3) to give a white powder, which was recrystallized twice from C_6H_6/MeOH to give the product as white crystals, yield 51% containing 0.5 mole of C_6H_6 of crystallization. Found: C, 79.5; H, 5.69; P, 15.0. $C_{41}H_{34}P_3$ calcd.: C, 79.5; H, 5.53; P, 15.0%. Benzene-free material was obtained as white crystals m.p. 151°C by maintaining this product at 100°C/0.01 torr for 2 h. Found: C, 78.4; H, 5.43; P, 15.5. $C_{38}H_{31}P_3$ calcd.: C, 78.6; H, 5.38; P, 16.0%.

Tris(diphenylphosphino)ethene (Route 2)

Cis- or *trans*-bis(diphenylphosphino)ethene [6] (7.92 g, 20 mmole) and butyllithium (12.5 cm^3 of 1.6 *M* solution in hexane, 20 mmol) were stirred under nitrogen in dry thf (100 m^3) at room temperature for 1 h. Diphenylchlorophosphine (4.41 g, 20 mmol) in thf (25 cm^3) was then added during 0.5 h and the mixture was stirred for a further 0.5 h. Volatile material was removed under vacuum and the resulting oil was treated with methanol (2×50 cm^3) to give the product as white crystals, yield 2.2 g, 20%. ^{1}H NMR δ 7.0–7.4, complex multiplets, Ph groups; δ 7.09, octet (from ^{13}C/H 2D experiment), $^1J(^{13}$C–H) 159.0 Hz, olefinic H. ^{13}C NMR: δ 127–130 ppm, multiplet, *m*- and *p*-phenyl carbons; δ 132–138 ppm, multiplet, *o*-phenyl carbons; δ 139.5–140.5, multiplet, *ipso*-carbons; δ 154.9, octet, C(1); δ 155.0, octet C(2). Other NMR data including couplings to ^{31}P are in Table 1.

The mass spectrum showed the molecular ion at *m/e* 580, and a fragment resulting from the loss of one Ph_2P group at *m/e* 395.

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