Bonding in the PCP Moiety. Crystal Structures of [(Triphenylphosphoranylidene)methyl]triphenylphosphonium Bromide, and Bis(diphenylphosphinoselenoyl)methane

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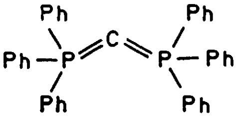
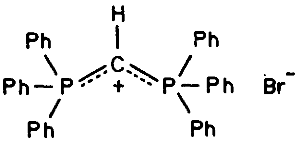
In conjunction with molecular orbital studies of molecules containing the PCP moiety, the structures of the title compounds have been determined. Crystals of both compounds are monoclinic, space group $P2_1/c$. The unit cell of $[Ph_3P{\cdot}CH{\cdot}PPh_3]Br$ is a = 9.666(3), b = 19.187(6), c = 17.116(4) Å, β = 102.675(7)°, with Z = 4; the cell for $Ph_2P(Se){\cdot}CH_2{\cdot}P(Se)Ph_2$ is a = 9.672(1), b = 10.875(1), c = 23.067(7) Å, β = 105.14(1)°, with Z = 4. The PCP bond angles and mean P–C distances for the two compounds were found to be 128.2(3)°, 1.703(11) Å and 117.9(6)°, 1.843(14) Å, respectively. The results are compared with those observed for $Ph_3P{:}C{:}PPh_3$, and some preliminary molecular orbital calculations involving the PCP moiety are discussed.


(1)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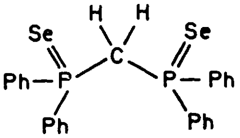
(3)

CONVENTIONAL bonding schemes generally require that systems possessing adjacent double bonds, such as the C=C=C group in allene, have linear conformations in their ground states. This requirement seems to be valid for elements of the first short period, but when a cumulative system contains one or more of the heavier elements such as phosphorus, the deviations from linearity can be considerable. The bond angle of the $P{=}\overset{+}{N}{=}P$ group, which has been studied in several compounds,[1] is usually near 140°, although linear examples have been reported. The P=C=P bond angles in bis(triphenylphosphoranylidene)methane, (1), have been found to be 130.1 and 143.8°, the two values arising from the two independent molecules in the asymmetric unit.[2] The P=C bond distances are extremely short (1.629 and 1.633 Å), in agreement with their assignment as double bonds. The non-linearity of the bond angles in these compounds cannot be attributed to steric factors, since interatomic repulsions would be expected to increase with a deviation in bond angle from 180°.

In cases such as this, where bonding is difficult to rationalize in terms of the traditional valence-bond rules, it is common to invoke the virtual *d* orbitals of phosphorus. It is quite difficult to do this with any reliability in molecular orbital calculations, and in many instances the *d* orbitals are treated merely as fitting parameters. By investigating series of similar molecules containing the P–C–P group, we hope to establish whether *d*-orbital functions are essential to the understanding of bonding in these systems.

In order to obtain molecular parameters for the PCP moiety in a variety of circumstances, we have determined the crystal and molecular structures of two compounds. The first of these, (2), has formal P–C bond orders of 1.5; the other, (3), has formal P–C bond orders of 1. We were unable to obtain suitable crystals of $[Ph_3P{\cdot}CH_2{\cdot}PPh_3]Br_2$, our first choice for an example having a bond order of 1. Preliminary reports of these structures have appeared.[3]

EXPERIMENTAL

Compounds (2) and (3) were prepared by reported methods.[4,5] The space group and approximate cell constants for each compound were determined from Weissenberg and precession photographs. Accurate cell dimensions were obtained from least-squares fits of 2θ values measured on the diffractometer. Intensity data were obtained on a General Electric XRD-6 diffractometer, using the θ—2θ scan method with a scan rate of 2° min^{-1}. Background counts of 20 s each were taken at the extremes of each scan. Nickel-filtered Cu-K_α radiation was used for (2) and zirconium-filtered Mo-K_α radiation was used for (3). In both cases, the intensities were put on a common scale by reference to the intensity of a standard reflection which was measured periodically. Over the period of data collection, the standard reflections underwent intensity losses of 9% for crystal (2) and 11% for crystal (3). The variance of the intensity, $r^2(I)$, was determined from the expression $S + B + (pI)^2$ where S is the scan count, B the background count, and p a factor to account for instrument instability, set equal to 0.04 for both studies. Structure-factor amplitudes were derived in the usual manner, but no absorption corrections were applied. The crystallographic data are in Table 1.

Structure Analysis.—Compound (2). A three-dimensional Patterson map yielded the positions of the Br and P atoms. With the use of a Fourier map based on the phases of these atoms, the remaining non-hydrogen atoms were located. A structure-factor calculation using the unrefined positional parameters of these atoms gave R 0.201 and R' 0.205.

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[1] L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 7312, 7327; J. K. Ruff, R. P. White, and L. F. Dahl, *ibid.*, 1971, **93**, 2159; M. B. Smith and R. Bau, *ibid.*, 1973, **95**, 2388; S. A. Goldfield and K. N. Raymond, *Inorg. Chem.*, 1974, **13**, 770; H. B. Chin, M. B. Smith, R. D. Wilson, and R. Bau, *J. Amer. Chem. Soc.*, 1974, **96**, 5285, 7601.

[2] A. T. Vincent and P. J. Wheatley, *Chem. Comm.*, 1971, 582; *J.C.S. Dalton*, 1972, 617.

[3] P. J. Carroll and D. D. Titus, *Cryst. Struct. Comm.*, 1974, **3**, 433; 1976, **5**, 363.

[4] J. S. Driscoll, D. W. Grisley, J. V. Pustinger, J. E. Harris, and C. N. Matthews, *J. Org. Chem.*, 1964, **29**, 2427.

[5] W. E. Slinkard and D. W. Meek, *J.C.S. Dalton*, 1973, 1024.

Atomic scattering factors[6] were corrected in the cases of P and Br for the real and imaginary parts of anomalous dispersion.[7]

Table 1

Crystallographic data (distances in Å, angles in °) with estimated standard deviations in parentheses

Compound	(2)	(3)
Space group	$P2_1/c$	$P2_1/c$
a	9.666(3)	9.672(1)
b	19.187(6)	10.875(1)
c	17.116(4)	23.067(7)
β	102.675(7)	105.14(1)
M	617.5	542.3
Z	4	4
U/Å^3	3.097.0	2 342.0
D_m/g cm^{-3}	1.31	1.52
D_c/g cm^{-3}	1.32	1.54
μ/cm^{-1}	24.0 (Cu-K_α)	21.2 (Mo-K_α)
Crystal dimensions/mm	0.05 × 0.09 × 0.77	0.11 × 0.12 × 0.27
No. of reflections measured	2 850 ($4 < 2\theta < 90°$)	2 165 ($4 < 2\theta < 40°$)
No. used in refinement	2 381	1 625
Acceptance criterion	$I_o > 3\sigma(I_o)$	$F_o < 1.5\sigma(F_o)$
Weighting function	$w = 0.47F_o/\sigma^2(F_o)$	$w = 0.36F_o/\sigma^2(F_o)$
R[a]	0.036	0.044
R'[a]	0.043	0.047
$[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m - n)]^{\frac{1}{2}}$	0.97	1.04[b]

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.
[b] From the final refinement of non-hydrogen atoms.

Table 2

Fractional co-ordinates for compound (2) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Br	190.8(5)	3 815.1(3)	6 924.4(3)
P(1)	4 968(1)	3 308.0(5)	6 242.0(6)
P(2)	6 622(1)	2 289.0(5)	5 414.1(6)
C(01)	6 478(5)	2 943(2)	6 057(2)
C(11)	3 737(4)	2 662(2)	6 453(2)
C(12)	2 385(5)	2 583(2)	5 998(3)
C(13)	1 524(6)	2 065(3)	6 194(4)
C(14)	2 001(7)	1 638(3)	6 828(4)
C(15)	3 357(7)	1 707(3)	7 279(3)
C(16)	4 229(5)	2 220(2)	7 098(3)
C(17)	4 011(4)	3 887(2)	5 475(2)
C(18)	4 555(5)	4 027(2)	4 804(2)
C(19)	3 868(6)	4 492(3)	4 221(3)
C(110)	2 642(6)	4 812(3)	4 313(3)
C(111)	2 117(5)	4 689(3)	4 988(3)
C(112)	2 787(5)	4 225(2)	5 570(2)
C(113)	5 421(4)	3 848(2)	7 126(2)
C(114)	4 373(5)	4 010(2)	7 542(3)
C(115)	4 669(5)	4 467(3)	8 177(3)
C(116)	5 992(6)	4 768(3)	8 401(3)
C(117)	7 038(5)	4 606(2)	7 995(3)
C(118)	6 763(4)	4 149(2)	7 359(2)
C(21)	7 568(4)	1 541(2)	5 924(2)
C(22)	7 634(5)	1 443(3)	6 725(3)
C(23)	8 267(6)	846(3)	7 108(3)
C(24)	8 854(5)	360(2)	6 706(3)
C(25)	8 827(5)	461(2)	5 912(3)
C(26)	8 192(5)	1 043(2)	5 517(3)
C(27)	7 596(4)	2 542(2)	4 672(2)
C(28)	7 510(5)	2 164(2)	3 971(2)
C(29)	8 384(5)	2 325(3)	3 456(3)
C(210)	9 329(5)	2 873(3)	3 631(3)
C(211)	9 407(5)	3 254(3)	4 315(3)
C(212)	8 542(5)	3 091(2)	4 847(2)
C(213)	4 920(4)	1 963(2)	4 894(2)
C(214)	4 167(5)	2 290(2)	4 212(2)
C(215)	2 837(5)	2 049(2)	3 830(3)
C(216)	2 262(5)	1 485(3)	4 140(3)
C(217)	2 992(6)	1 156(3)	4 818(3)
C(218)	4 335(5)	1 385(2)	5 196(3)
H(01)	7 285(55)	3 102(27)	6 347(30)

Full-matrix least-squares techniques were employed to refine the model, with anisotropic thermal parameters for all non-hydrogen atoms. The function minimized was $w(|F_o| - |F_c|)^2$. The phenyl hydrogen atoms were located from a difference-Fourier map, but because of the large number of carbon atoms and the small number of reflections the phenyl hydrogen-atom parameters were not refined. They were included as fixed contributions to the structure factors, assuming a C–H bond distance of 0.95 Å and isotropic thermal parameters equal to 6.0 Å^2.

Table 3

Fractional co-ordinates for compound (3) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Se(1)	575(1)	10 333(1)	2 078(1)
Se(2)	2 711(2)	8 363(1)	749(1)
P(1)	2 324(3)	9 124(3)	2 341(1)
P(2)	1 420(3)	7 362(3)	1 218(1)
C(01)	1 947(12)	7 547(9)	2 036(4)
C(11)	2 851(11)	8 878(10)	3 139(5)
C(12)	1 999(13)	8 163(11)	3 423(6)
C(13)	2 357(15)	8 016(13)	4 044(5)
C(14)	3 580(16)	8 534(14)	4 373(6)
C(15)	4 461(14)	9 236(14)	4 128(5)
C(16)	4 081(14)	9 394(12)	3 515(6)
C(17)	3 925(12)	9 599(10)	2 133(5)
C(18)	3 914(13)	10 688(10)	1 834(6)
C(19)	5 119(16)	10 966(12)	1 627(7)
C(110)	6 269(15)	10 229(14)	1 729(6)
C(111)	6 300(13)	9 187(14)	2 036(6)
C(112)	5 134(13)	8 828(11)	2 253(6)
C(21)	−466(13)	7 756(10)	958(5)
C(22)	−1 480(13)	7 111(12)	1 173(5)
C(23)	−2 933(14)	7 422(14)	924(7)
C(24)	−3 372(17)	8 334(14)	506(7)
C(25)	−2 315(19)	8 941(14)	329(6)
C(26)	−885(15)	8 692(11)	537(6)
C(27)	1 473(11)	5 701(10)	1 129(5)
C(28)	1 597(13)	5 271(12)	562(5)
C(29)	1 630(14)	3 995(13)	477(6)
C(210)	1 578(15)	3 155(11)	913(6)
C(211)	1 463(14)	3 596(11)	1 452(6)
C(212)	1 425(13)	4 879(10)	1 577(5)
H(01)	2 586(134)	7 035(117)	2 062(56)
H(02)	1 363(134)	7 288(122)	2 307(55)

After three cycles of least-squares refinement, a difference-Fourier map was calculated, the most prominent feature of which was the hydrogen atom attached to the central carbon. The positional parameters of this hydrogen atom were included in the remaining cycles. The refinement was assumed to have converged when no parameter was shifted more than 0.1σ. The final residual indices were R 0.036 and R' 0.043. A difference-Fourier map was calculated, omitting from the input data the parameters of the central hydrogen atom. The largest peak on this map (0.45 eÅ^{-3}) was found at a position 0.008 Å from the least-squares-refined position of the central hydrogen atom.

Compound (3). The position of one of the two selenium atoms, Se(1), was determined from a three-dimensional Patterson map. The locations of the other non-hydrogen atoms were established by successive structure-factor and Fourier calculations. A structure-factor calculation based on the unrefined atom parameters gave R 0.240 and R' 0.388. The model was refined in the same manner as (2), with the phenyl hydrogen atoms again included as fixed

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[6] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[7] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

contributions to the structure factors. The atomic scattering factors of P and Se were corrected for the real and imaginary parts of anomalous dispersion.[7] The refinement converged to R 0.044 and R' 0.047. The methylene hydrogen atoms were located on a difference-Fourier map as peaks of 0.4 eÅ^{-3}. Their positional parameters were refined in three cycles, with all other parameters held constant. A final difference-Fourier map revealed two peaks having electron densities of 0.5 eÅ^{-3}, each of which was < 1 Å from a selenium atom. These peaks probably resulted from inadequacies in the model for thermal motion of the selenium atoms.

The final positional parameters are given in Tables 2 and 3. Measured and calculated structure factor amplitudes together with the thermal parameters are listed in Supplementary Publication No. 21927 (32 pp., 1 microfiche).*

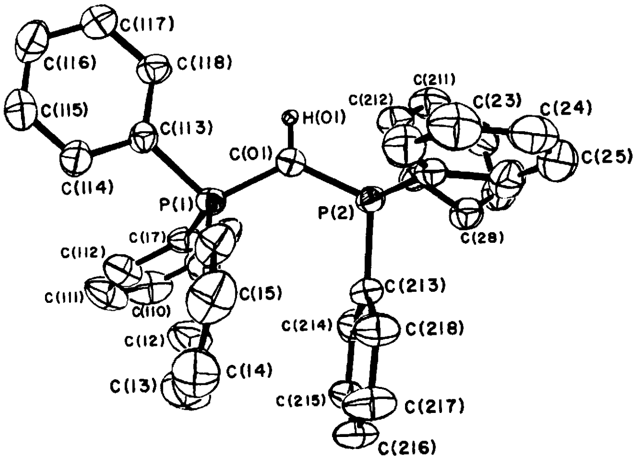

FIGURE 1 Perspective drawing of $[\mathrm{Ph_3P{\cdot}CH{\cdot}PPh_3}]^+$

RESULTS

Both compounds exist as discrete monomeric units, with no significant intermolecular interactions. The bromide ion in (2) is well removed from the cation.

Structure of (2).—Table 4 lists selected interatomic distances and angles; a perspective drawing of the cation is given in Figure 1. The phenyl carbon atoms are numbered in sequence around each ring, with the first digit of each identifier indicating the phosphorus atom to which the phenyl ring is bonded.

The most striking feature of (2) is the P(1)–C(01)–P(2) bond angle, 128.2(3)°, which is only slightly smaller than one of the analogous angles in (1), 130.1(6)°.[2] The P–C(01) bond distances, as expected, are longer than in (1), averaging 1.703(11) Å. The P(1)–C(01)–P(2) angle and P–C(01) bond distances are essentially identical to those reported for $[\mathrm{W(CO)_5\{PO(Ph){\cdot}CH{:}PPh_3\}}]$, 127.9(6)°, and 1.701(11) and 1.681(11) Å.[8] The P–C(Ph) distances, which average 1.808(6) Å, are the same as those observed for the tungsten complex, 1.802(8) Å.[8] This average is smaller than the corresponding value found for (1), 1.834(9) Å,[2] and at the upper end of the range of values observed in various structures containing the $[\mathrm{Ph_3PNPPh_3}]^+$ ion, 1.78—1.81 Å.[1] The central hydrogen atom, H(01), lies in the PCP plane, only slightly removed from the axis bisecting the P(1)–C(01)–P(2) angle. The

TABLE 4

Distances (Å) and angles (°) for (2), with estimated standard deviations in parentheses

(*a*) Basic structure

P(1)–P(2)	3.063(2)	C(11)–P(1)–C(113)	106.0(2)
P(1)–C(01)	1.710(5)	C(17)–P(1)–C(113)	104.3(2)
P(1)–C(11)	1.808(5)	C(01)–P(2)–C(21)	112.1(2)
P(1)–C(17)	1.810(4)	C(01)–P(2)–C(27)	112.8(2)
P(1)–C(113)	1.806(4)	C(01)–P(2)–C(213)	112.5(2)
P(2)–C(01)	1.695(5)	C(21)–P(2)–C(27)	105.3(2)
P(2)–C(21)	1.818(4)	C(21)–P(2)–C(213)	105.8(2)
P(2)–C(27)	1.806(5)	C(27)–P(2)–C(213)	107.8(2)
P(2)–C(213)	1.802(4)	P(1)–C(11)–C(12)	123.2(4)
C(01)–H(01)	0.88(5)	P(1)–C(11)–C(16)	116.8(3)
H(01)–Br	3.09(5)	P(1)–C(17)–C(18)	119.5(3)
		P(1)–C(17)–C(112)	121.0(4)
		P(1)–C(113)–C(114)	119.1(3)
P(1)–C(01)–P(2)	128.2(3)	P(1)–C(113)–C(118)	121.1(3)
P(1)–C(01)–H(01)	116(4)	P(2)–C(21)–C(22)	119.8(4)
P(2)–C(01)–H(01)	116(4)	P(2)–C(21)–C(26)	121.9(3)
C(01)–P(1)–C(11)	112.4(2)	P(2)–C(27)–C(28)	121.8(3)
C(01)–P(1)–C(17)	116.0(2)	P(2)–C(27)–C(212)	118.2(3)
C(01)–P(1)–C(113)	109.3(2)	P(2)–C(213)–C(214)	120.9(3)
C(11)–P(1)–C(17)	108.1(2)	P(2)–C(213)–C(218)	119.6(3)

(*b*) Phenyl groups

	C–C distance	C–C–C angle
mean	1.382(11)	120.0(6)
minimum	1.355(8) [C(23)–C(24)]	118.3(4) [C(22)–C(21)–C(26)]
maximum	1.399(8) [C(211)–C(212)]	121.0(5) [C(22)–C(23)–C(24)]

TABLE 5

Equations of least-squares planes for (2). Deviations (Å) of atoms from the planes are listed in parentheses. The equations are in the form $AX + BY + CZ = D$, where X, Y, and Z represent fractional co-ordinates in the crystal system

Plane (1): $1.557X - 12.85Y + 12.71Z = -2.908$

[P(1) 0.000, P(2) 0.000, C(01) −0.001, H(01) 0.041]

Plane (2): $4.662X - 12.21Y - 11.87Z = 9.163$

[C(11) −0.003, C(12) 0.003, C(13) 0.001, C(14) −0.007, C(15) 0.005, C(16) 0.000, P(1) * 0.033]

Plane (3): $4.378X + 14.39Y + 6.354Z = -10.83$

[C(17) −0.008, C(18) 0.006, C(19) 0.004, C(110) −0.014, C(111) 0.009, C(112) 0.004, P(1) * 0.066]

Plane (4): $1.604X - 14.63Y + 9.817Z = -2.237$

[C(113) −0.002, C(114) 0.001, C(115) 0.003, C(116) −0.005, C(117) 0.002, C(118) 0.001, P(1) * −0.153]

Plane (5): $8.138X - 9.338Y + 0.7355Z = -0.842$

[C(21) −0.009, C(22) 0.012, C(23) −0.002, C(24) −0.008, C(25) 0.006, C(26) 0.004, P(2) * −0.118]

Plane (6): $5.849X - 12.03Y + 5.924Z = -4.149$

[C(27) 0.004, C(28) −0.007, C(29) 0.005, C(210) 0.002, C(211) −0.004, C(212) 0.000, P(2) * 0.178]

Plane (7): $5.368X - 11.68Y - 11.55Z = 5.299$

[C(213) −0.003, C(214) −0.003, C(215) 0.006, C(216) −0.002, C(217) −0.009, C(218) 0.010, P(2) * −0.072]

Dihedral angles between planes (°)

(1)–(2)	95.1	(1)–(7)	95.3
(1)–(3)	103.4	(2)–(7)	4.9
(1)–(4)	20.4	(3)–(5)	30.8
(1)–(5)	107.0	(4)–(6)	27.7
(1)–(6)	47.3		

* Atoms excluded from the calculation of the least-squares plane.

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* For details, see Notices to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue.

[8] S. Z. Goldberg and K. N. Raymond, *Inorg. Chem.*, 1973, **12**, 2923.

bromide ion is also located near the axis, 3.09(5) Å from H(01). Selected least-squares planes are given in Table 5.

A stereoscopic view of the unit cell is depicted in Figure 2. There is no indication that packing forces play an important role in determining the molecular geometry.

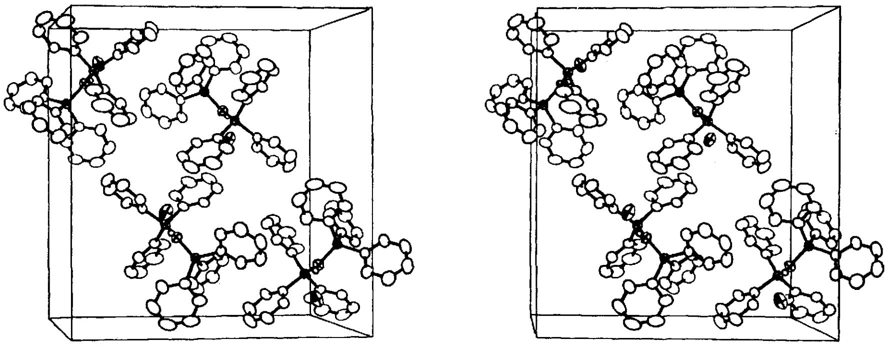

FIGURE 2 Stereoview of the unit cell of (2)

Structure of (3).—Selected interatomic distances and angles are listed in Table 6. The carbon atoms are numbered in the same manner as for (2). The molecule possesses a pseudo-two-fold rotation axis; a stereoscopic view down this axis is depicted in Figure 3. The P(1)–C(01)–P(2) angle is 117.9(6)° and the P–C(01) distances average 1.843(14) Å. The P–Se distances average 2.100(4) Å, compared to 1.96(2) Å in Et_3PSe [9] and 2.12(1) Å in $(o\text{-}MeC_6H_4)_3PSe$.[10] The average of the six C–P–C angles is 104.8(18)°, significantly smaller than the average of the Se–P–C angles, 113.7(16)°. The Se(1)–Se(2) distance is 4.696(2) Å, and the torsional angle Se(1)–P(1)–P(2)–Se(2) is 95.4(1)°. This molecule has been reported to act as a chelating ligand,[5,11] presumably through the selenium atoms. If it is assumed that bond distances in the complexed ligand are nearly the same as those reported here, that the P–C–P angle does not deviate greatly from 118°, and that the typical metal–selenium bond distance is 2.4 Å,[12] the torsional angle in a square-planar complex would be *ca.* 50°. In a tetrahedral complex, which requires that the Se–metal–Se angle open to *ca.* 109°, the torsional angle should be near 80°. Rotation about the P–C(01) bonds should allow the formation of both types of complexes, but steric hindrance from the phenyl groups would probably rule out metal co-ordination numbers higher than four.

TABLE 6

Distances (Å) and angles (°) for (3), with estimated standard deviations in parentheses

(*a*) Basic structure

Se(1)–Se(2)	4.696(2)	Se(1)–P(1)–C(01)	113.9(3)
P(1)–P(2)	3.157(4)	Se(1)–P(1)–C(11)	112.3(4)
P(1)–Se(1)	2.103(3)	Se(1)–P(1)–C(17)	115.1(4)
P(1)–C(01)	1.853(11)	C(01)–P(1)–C(11)	103.1(5)
P(1)–C(11)	1.796(11)	C(01)–P(1)–C(17)	105.1(5)
P(1)–C(17)	1.812(13)	C(11)–P(1)–C(17)	106.3(5)
P(2)–Se(2)	2.097(4)	Se(2)–P(2)–C(01)	115.9(4)
P(2)–C(01)	1.833(10)	Se(2)–P(2)–C(21)	113.6(4)
P(2)–C(21)	1.816(12)	Se(2)–P(2)–C(27)	111.5(4)
P(2)–C(27)	1.819(11)	C(01)–P(2)–C(21)	107.4(5)
C(01)–H(01)	0.82(13)	C(01)–P(2)–C(27)	102.6(5)
C(01)–H(02)	0.99(14)	C(21)–P(2)–C(27)	104.6(5)
		P(1)–C(11)–C(12)	121.0(8)
		P(1)–C(11)–C(16)	123.0(10)
P(1)–C(01)–P(2)	117.9(6)	P(1)–C(17)–C(18)	119.2(9)
P(1)–C(01)–H(01)	122(8)	P(1)–C(17)–C(112)	120.2(9)
P(1)–C(01)–H(02)	96(8)	P(2)–C(21)–C(22)	120.1(8)
P(2)–C(01)–H(01)	90(9)	P(2)–C(21)–C(26)	119.2(10)
P(2)–C(01)–H(02)	125(7)	P(2)–C(27)–C(28)	116.3(9)
H(01)–C(01)–H(02)	107(12)	P(2)–C(27)–C(212)	123.5(9)

(*b*) Phenyl groups

	C–C distance	C–C–C angle
mean	1.384(25)	120.0(26)
minimum	1.332(21) [C(110)–C(111)]	116.0(11) [C(24)–C(25)–C(26)]
maximum	1.427(16) [C(211)–C(212)]	124.6(13) [C(12)–C(11)–C(16)]

Since the geometry of the PCP moiety is of primary interest in this work, the effect of the selenium atoms on this geometry is of some concern. The P–C(01) bond lengths appear not to be significantly affected; the mean distance is 1.843(14) Å, only slightly longer than the mean P–C(Ph) distance of 1.811(10) Å. The P–C-(methylene) distances in *cis*-$[PtPh_2(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2]$ are even greater, 1.86(2) Å, probably because of the reduction of the P–C–P angle to 95° by the constraints of the chelate ring.[13] The selenium atoms undoubtedly have an effect on the P–C–P bond angle, but it does not seem likely that the angle observed here is more than a few degrees different from the value which would be found for $[Ph_3P{\cdot}CH_2{\cdot}PPh_3]Br_2$. A list of selected least-squares planes is given in Table 7; a stereoscopic view of the unit cell is depicted in Figure 4.

DISCUSSION

Figure 5 depicts the PCP moieties of molecules (1),[2] (2), and (3) drawn to the same scale, and employing 50% probability thermal ellipsoids. The range of P–C–P angles (<15°) is quite small when the large range of P–C bond lengths (nearly 0.22 Å) is considered. Another

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molecule of (1), not pictured in Figure 5, has a P–C–P angle of 143.8(6)°,[2] which deviates from the pictured angle by a greater amount than do (2) and (3). The decrease in the P–C bond distance is in agreement with the increase in the formal P–C bond orders. The unusual bond angles in (1), however, prohibit a simple bonding description in terms of *sp* hybridization at carbon.

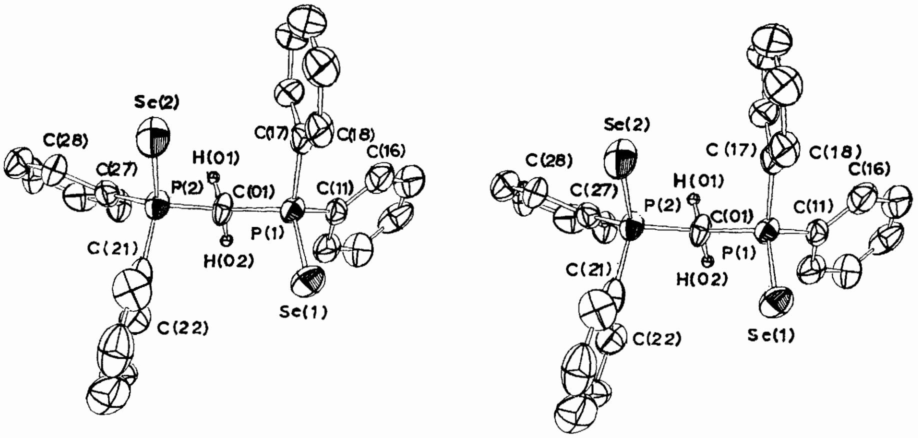

FIGURE 3 Stereoview of (3), looking down the pseudo-two-fold axis

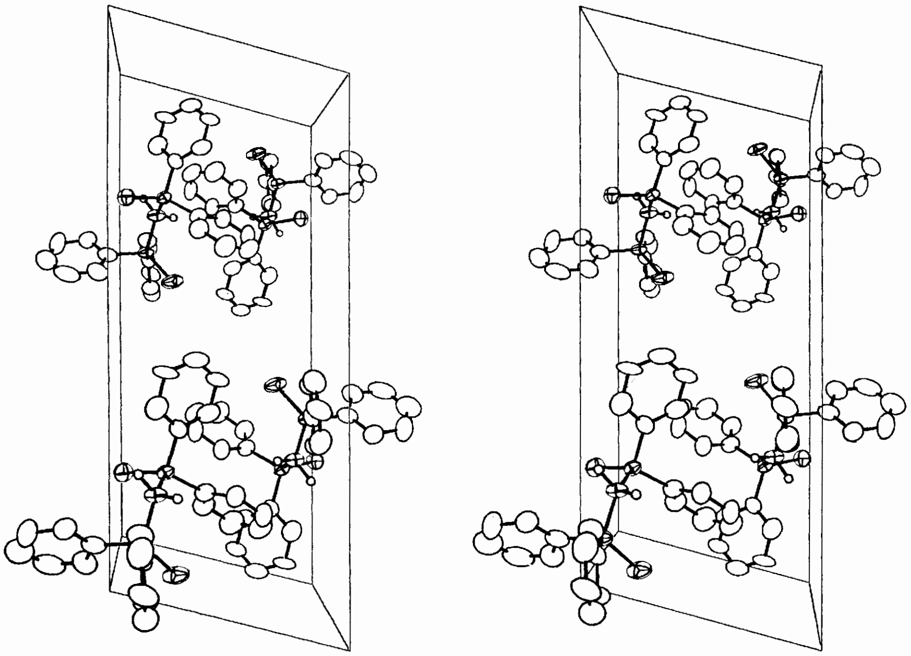

FIGURE 4 Stereoview of the unit cell of (3)

Preliminary INDO calculations for $H_3P{:}C{:}PH_3$, using D. R. Truax's ODIN[14] with a minimum basis set of Slater-type *s* and *p* orbitals, indicate that the energy of the molecule is lowest when the P–C–P bond angle is near 130°. The calculated energy is *ca.* 12 kcal mol^{-1} higher * at 120 or 140°, but *ca.* 100 kcal mol^{-1} higher at 100 or 180°. A broader minimum in energy would be expected in view of the two angles observed for (1). For the molecule having the bond angle equal to 130°, the highest occupied molecular orbital is a non-bonding carbon $2p_x$ orbital (where x is an axis parallel to P ··· P) of b_2 symmetry (with the PCP group in the xz plane; C_{2v} point-group symmetry). A population analysis indicates partial positive charges on the phosphorus atoms and a partial negative charge on the carbon atom. The molecular-orbital picture is thus in qualitative agreement with the charged-atom resonance structures which are often used to represent the bonding in (1).[15] In the model having a P–C–P angle of 180°, a degenerate pair of orbitals p_y, p_z (e' in a molecular symmetry of D_{3h}) serve as the highest filled level. Both orbitals are essentially pure (99%) carbon $2p$ orbitals. The higher total

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* 1 cal = 4.184 J.

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energy of the 180° model appears to arise from the addition of the second non-bonding $2p$ orbital which, in effect, decreases the number of bonding orbitals. These results imply that in the PCP system the carbon $2p$ orbitals are not capable of significant π-like interactions with the phosphorus $3p$ orbitals. However, non-linearity in the PCP system makes it possible for two of the $2p$ orbitals to take part in σ-type interactions, thus lowering the molecular energy. The addition of the large phosphorus d orbitals to the basis set might be expected to improve the chances for π-like bonding to the carbon $2p$ orbitals, leading to an energy minimum at an angle closer to 180°. This is rather ironic, since the d orbitals have been considered responsible for the bending of the PCP group in (1).[2] Subsequent calculations with the same basis but with better convergence give the same qualitative results. The energy difference between the 180 and 130° forms is reduced to a more realistic 45 kcal mol^{-1}. As expected, the corresponding difference in $H_3P{=}\overset{+}{N}{=}PH_3$ is much less, only 18 kcal mol^{-1}. In all cases attempted thus far, inclusion of d-orbital functions has shifted the minimum energy to the linear form.

TABLE 7

Equations of least-squares planes for (3). Deviations (Å) of atoms from the planes are listed in parentheses. The equations are in the form $AX + BY + CZ = D$, where X, Y, and Z represent fractional co-ordinates in the crystal system

Plane (1): $9.655X - 0.1430Y - 7.309Z = -0.3881$

[P(1) 0.014, P(2) −0.013, C(01) −0.105, C(11) −0.057, C(27) 0.128, Se(1) * −1.500, Se(2) * 1.564]

Plane (2): $5.461X - 8.909Y - 5.628Z = 8.117$

[C(11) −0.002, C(12) 0.008, C(13) −0.013, C(14) 0.008, C(15) 0.001, C(16) −0.002, P(1) * −0.060]

Plane (3): $1.728X + 5.236Y + 18.03Z = -9.564$

[C(17) −0.013, C(18) 0.015, C(19) −0.004, C(110) −0.008, C(111) 0.005, C(112) 0.009, P(1) * −0.164, Se(1) * −0.307]

Plane (4): $-1.227X + 7.275Y + 17.07Z = -7.345$

[C(21) −0.010, C(22) 0.013, C(23) −0.009, C(24) −0.004, C(25) 0.006, C(26) 0.004, P(2) * −0.084, Se(2) * −0.388]

Plane (5): $9.133X + 0.2029Y + 1.631Z = -1.651$

[C(27) −0.005, C(28) 0.006, C(29) −0.004, C(210) 0.003, C(211) −0.004, C(212) 0.006, P(2) * −0.006]

Dihedral angles between planes (°)

(1)–(2)	54.5	(1)–(5)	22.6
(1)–(3)	83.0	(2)–(5)	61.0
(1)–(4)	100.3	(3)–(4)	21.9

* Atoms excluded from the calculation of the least-squares plane.

To test the reliability of the calculation procedures, we are currently studying, in addition to H_3PCPH_3, model systems for (2) and (3). Several basis sets are being tested, employing both single- and double-zeta formulations, and the effect of the inclusion of phosphorus-$3d$ virtual orbitals is being investigated.

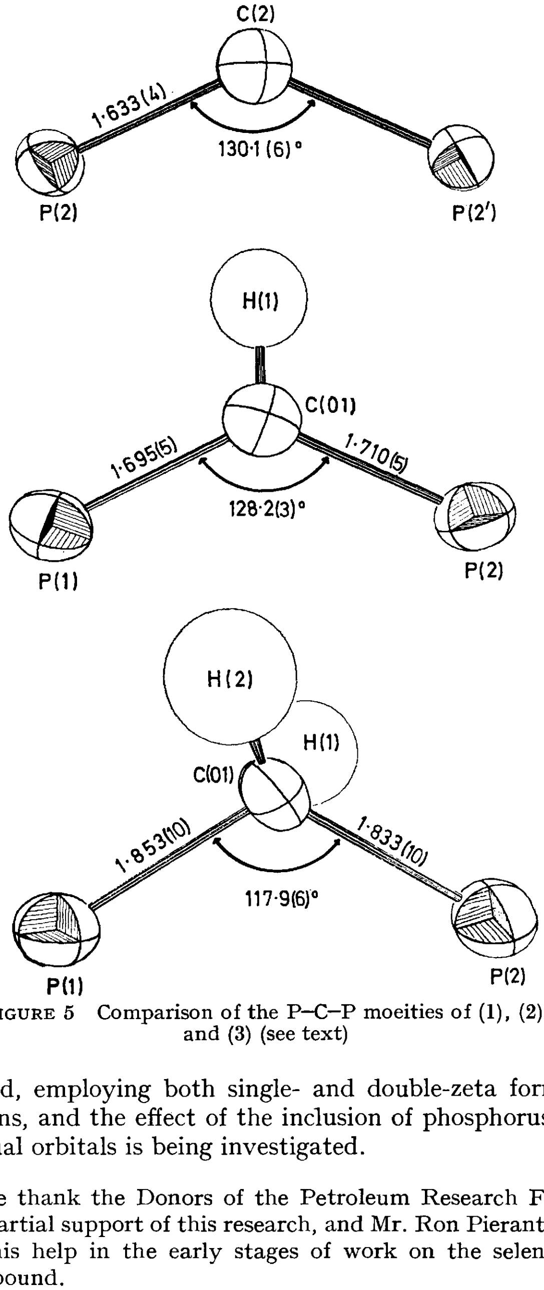

FIGURE 5 Comparison of the P–C–P moeities of (1), (2), and (3) (see text)

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