Structural Studies in Main-group Chemistry. Part IX.[1] Crystal Structure of Chlorotrimethyl(triphenylphosphoranylideneacetone)tin(IV)

By **John Buckle, Philip G. Harrison,* Trevor J. King,** and **John A. Richards,** Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD

The crystal structure of the title compound has been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are monoclinic, space group $P2_1/c$ with $a = 9.303(2)$, $b = 10.221(2)$, $c = 26.338(4)$ Å, $\beta = 102.43(1)°$, $Z = 4$. The tin atom possesses a trigonal bipyramidal configuration with the three methyl groups occupying equatorial positions [mean r(Sn–C) 2.133 Å] in a planar arrangement. The two axial sites are occupied by the chlorine atom [r(Sn–Cl) 2.56 Å] and the phosphorus ylide residue which functions as a unidentate oxygen-donor ligand [r(Sn–O) 2.332 Å]. The structural parameters of the ylide skeleton indicate strong electron-withdrawal from the P:C bond towards the acetyl group.

RECENTLY, much attention has been directed towards understanding the stability conferred on metal–carbon bonds by the substitution of a heteroatom at the β-position of the organic ligand. The stabilizing ability of the (trimethylsilyl)methyl group has been known for several years, and more recently the properties of the isoelectronic triorganophosphinemethylenes and other ylidic species have come under investigation. Unlike (organosilyl)methyl–metal derivatives, for which a relatively large amount of structural data are available, the structures of only two ylide–metal complexes, $[(C_6H_{11})_3P{:}CHMe]\cdot Ni(CO)_3$,[2] and $[(C_5H_{11})_2SMe]^+[(C_5H_{11})_2SCH_2ZnI_3]^-$,[3] have been determined. In both complexes, the geometry at the ylidic carbanion shows unequivocally the change from trigonal sp^2 to tetrahedral sp^3 hybridisation on complex formation, giving metal–carbon bonds of essentially σ character.

With carbonyl-stabilised ylides, the ability to delocalise electric charge on the carbonyl oxygen *via* the additional canonical representation (III) permits the possibility of ambidentate bonding towards Lewis acids for these compounds. Thus, towards a metallic centre, a carbonyl-stabilised ylide may bond *via* either the carbanionic carbon (IV), the carbonyl oxygen (V), or both (VI), depending on the nature of R^1, R^2, X, and M. From spectroscopic data, Nesmeyanov *et al.*[4] have suggested the *C*-bonded structure for a number of carbonyl-stabilised triphenylphosphine ylide complexes of mercury(II) halides, whilst the bidentate formulation (VI) was preferred by Ishii *et al.* for similar phosphine and sulphur ylide complexes of triorganotin halides.[5,6]

As part of our investigations into factors controlling the mode of interaction between ylides and (organo)tin and lead halides, we now report the *X*-ray crystal

---

[1] Part VIII, P. G. Harrison, T. J. King, and J. A. Richards, *J.C.S. Dalton*, 1975, 826.

[2] B. L. Barnett and C. Krüger, *J. Cryst. Mol. Struct.*, 1972, **2**, 271.

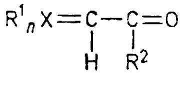
[3] B. T. Kilbourn and D. Felix, *J. Chem. Soc.* (*A*), 1969, 163.

[4] N. Nesmeyanov, V. M. Novikova, and O. A. Reutov, *J. Organometallic Chem.*, 1965, **4**, 202.

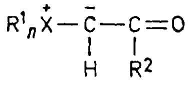
[5] S. Kato, T. Kato, M. Mizuta, K. Itoh, and Y. Ishii, *J. Organometallic Chem.*, 1973, **51**, 167.

[6] K. Itoh, S. Kato, and Y. Ishii, *J. Organometallic Chem.*, 1972, **34**, 293.

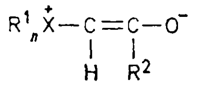
structure of the trimethyltin chloride complex of triphenylphosphosphoranylideneacetone.


$R^1{}_nX{=}\underset{H}{C}{-}\underset{R^2}{C}{=}O$

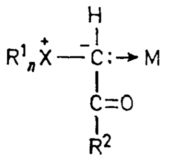
(I)

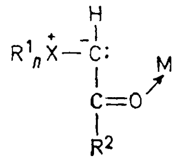

$R^1{}_n\overset{+}{X}{-}\underset{H}{\overset{-}{C}}{-}\underset{R^2}{C}{=}O$

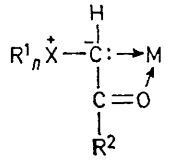
(II)


$R^1{}_n\overset{+}{X}{-}\underset{H}{C}{=}\underset{R^2}{C}{-}O^-$

(III)


(IV)


(V)


(VI)

EXPERIMENTAL

Prismatic monoclinic crystals are air stable, and a suitable specimen of dimensions 0.4 × 0.35 × 0.7 mm was mounted directly on a glass fibre with shellac.

Crystal Data.—$C_{24}H_{28}ClOPSn$, $M = 517.60$, $a = 9.303(2)$, $b = 10.221(2)$, $c = 26.338(4)$ Å, $\beta = 102.43(1)°$, $U = 2445.67$ Å^3, $D_m = 1.43$, $Z = 4$, $D_c = 1.416$, $F(000) = 1048$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) $= 12.36$ cm^{-1}. Space group $P2_1/c$ by systematic absences ($h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$).

The space group and initial cell parameters were determined from oscillation, and from zero- and first-layer Weissenberg photographs obtained on a Leeds equi-inclination Weissenberg camera. Cell parameters were further refined and relative intensities collected with Mo-K_α radiation on a Hilger and Watts single-crystal computer-controlled four-circle diffractometer, Y 290. Individual reflections were counted for 30 s each and the associated two background counts for 10 s; data were collected up to θ 30°. Reference reflections were recorded every 100, and the diffractometer orientation references every 200 reflections. All reflections were brought to the same relative intensities and 2 997 with a corrected count of $<3\sigma(I)$ were considered observed and used in the subsequent refinement. Intensities were corrected for Lorentz and polarization effects, but not for absorption.

Structure Determination and Refinement.—A Patterson synthesis gave the positional co-ordinates of the tin atom. A subsequent structure-factor calculation phased on these co-ordinates and a Fourier synthesis revealed 32 significant peaks, which with the aid of a model enabled location of the other non-hydrogen light atoms. Four cycles of isotropic full-matrix least-squares refinement reduced R to 0.0726. A further cycle of isotropic and three cycles of anisotropic full-matrix refinement further reduced R to 0.0501. The weighting scheme: $w = 1/[1 + (F_o - 37.5)/18.7]^2$ was then applied. After a further two cycles of full-matrix anisotropic least-squares refinement, the calculation was terminated when R was 0.0495. Scattering factors for neutral atoms and chlorine anion were taken from ref. 7.

TABLE 1

Fractional atomic co-ordinates

Atom	x/a	y/b	z/c
Sn(1)	0.53328(6)	0.72186(6)	0.29751(2)
Cl(1)	0.3409(3)	0.7927(3)	0.2171(1)
P(1)	1.0210(2)	0.7059(2)	0.4323(1)
O(1)	0.7135(6)	0.6645(7)	0.3702(2)
C(1)	1.0119(8)	0.8255(8)	0.3818(3)
C(2)	1.3547(12)	0.8962(11)	0.5326(5)
C(3)	0.8560(9)	0.6934(8)	0.4537(3)
C(4)	1.1758(11)	0.6791(10)	0.5323(3)
C(5)	0.5834(10)	0.6652(13)	0.4406(4)
C(6)	1.2812(11)	0.7122(11)	0.5777(3)
C(7)	0.7259(9)	0.6763(9)	0.4189(3)
C(9)	0.9221(11)	0.9347(9)	0.3814(4)
C(10)	0.9105(11)	1.0284(9)	0.3421(4)
C(11)	0.5109(11)	0.9052(9)	0.3345(4)
C(12)	0.7036(10)	0.6994(10)	0.2559(4)
C(13)	1.0835(11)	0.9060(10)	0.3046(3)
C(14)	0.4041(10)	0.5564(9)	0.3085(4)
C(15)	1.0381(11)	0.3717(10)	0.3509(4)
C(16)	1.0932(10)	0.8114(8)	0.3428(3)
C(17)	1.1762(11)	0.3184(9)	0.3723(4)
C(18)	1.0860(8)	0.5544(7)	0.4090(3)
C(19)	1.2698(11)	0.3861(9)	0.4124(3)
C(20)	1.2243(8)	0.5047(8)	0.4310(3)
C(21)	1.1594(8)	0.7547(7)	0.4885(3)
C(22)	1.2485(11)	0.8637(10)	0.4877(4)
C(23)	0.9909(10)	0.4884(9)	0.3682(3)
C(24)	0.9898(11)	1.0122(10)	0.3040(4)
C(25)	1.3686(12)	0.8209(12)	0.5764(4)

TABLE 2

Bond lengths (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances

Sn(1)–Cl(1)	2.565(2)	C(24)–C(13)	1.390(14)
Sn(1)–O(1)	2.332(6)	C(13)–C(16)	1.385(12)
Sn(1)–C(11)	2.143(9)	C(16)–C(1)	1.408(12)
Sn(1)–C(12)	2.125(10)	C(18)–C(20)	1.389(11)
Sn(1)–C(14)	2.130(9)	C(20)–C(19)	1.406(13)
P(1)–C(1)	1.795(8)	C(19)–C(17)	1.399(13)
P(1)–C(18)	1.816(7)	C(17)–C(15)	1.397(14)
P(1)–C(21)	1.810(8)	C(15)–C(23)	1.381(13)
P(1)–C(3)	1.750(8)	C(23)–C(18)	1.408(11)
C(3)–C(7)	1.634(12)	C(21)–C(4)	1.392(12)
C(7)–O(1)	1.268(10)	C(4)–C(6)	1.396(13)
C(7)–C(5)	1.557(13)	C(6)–C(25)	1.381(16)
C(1)–C(9)	1.393(12)	C(25)–C(2)	1.370(16)
C(9)–C(10)	1.397(14)	C(2)–C(22)	1.408(16)
C(10)–C(24)	1.378(14)	C(22)–C(21)	1.391(13)

(*b*) Angles

C(11)–Sn(1)–C(12)	119.0(4)	C(9)–C(1)–C(16)	119.5(8)
C(12)–Sn(1)–C(14)	119.3(4)	C(1)–C(9)–C(10)	120.3(9)
C(11)–Sn(1)–C(14)	121.3(4)	C(9)–C(10)–C(24)	119.3(9)
C(12)–Sn(1)–Cl(1)	94.0(3)	C(10)–C(24)–C(13)	121.3(9)
C(11)–Sn(1)–Cl(1)	90.6(3)	C(24)–C(13)–C(16)	119.7(9)
C(14)–Sn(1)–Cl(1)	91.3(3)	C(13)–C(16)–C(1)	119.9(8)
C(11)–Sn(1)–O(1)	88.3(3)	P(1)–C(18)–C(20)	121.1(6)
C(12)–Sn(1)–O(1)	85.0(3)	P(1)–C(18)–C(23)	117.8(6)
C(14)–Sn(1)–O(1)	90.9(3)	C(20)–C(18)–C(23)	121.7(7)
O(1)–Sn(1)–Cl(1)	177·8(2)	C(18)–C(20)–C(19)	119·4(8)
C(1)–P(1)–C(18)	107·2(4)	C(20)–C(19)–C(17)	120·3(8)
C(18)–P(1)–C(21)	106·4(3)	C(19)–C(17)–C(15)	118·7(9)
C(1)–P(1)–C(21)	109·2(4)	C(17)–C(15)–C(23)	122.3(9)
C(3)–P(1)–C(1)	112.6(4)	C(18)–C(23)–C(15)	118.2(8)
C(3)–P(1)–C(18)	115.2(4)	P(1)–C(21)–C(4)	118.0(6)
C(3)–P(1)–C(21)	106.0(4)	P(1)–C(21)–C(22)	122.0(6)
P(1)–C(3)–C(7)	120.3(6)	C(4)–C(21)–C(22)	120.0(8)
C(3)–C(7)–O(1)	124.6(8)	C(21)–C(4)–C(6)	120.3(9)
C(3)–C(7)–C(5)	117.7(8)	C(4)–C(6)–C(25)	119.1(10)
C(5)–C(7)–O(1)	117.7(8)	C(6)–C(25)–C(2)	121.5(10)
Sn(1)–O(1)–C(7)	134.3(5)	C(25)–C(2)–C(22)	119.8(10)
P(1)–C(1)–C(9)	118.9(6)	C(2)–C(22)–C(21)	119.3(9)
P(1)–C(1)–C(16)	121.6(6)		

---

[7] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

All calculations were performed by use of the ' *X*-ray '70 ' suite of programmes.

Final atomic positions and intramolecular bond distances and angles are listed in Tables 1 and 2, deviations of atoms from least-squares planes and dihedral angles between planes in Table 3, and principal intermolecular contacts in Table 4. Calculated and observed structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21285 (15 pp., 1 microfiche).*

TABLE 3

Equations of least-squares planes, and, in square brackets, deviations (Å) of atoms from these planes *

Plane (1): P(1), C(2), C(4), C(6), C(21), C(22), C(25)
$-0.7583x' + 0.5714y' + 0.3139z' - 2.2699 = 0$

[P(1) −0.0011, C(2) −0.0024, C(4) −0.0006, C(6) −0.0011, C(21) 0.0027, C(22) 0.0006, C(25) 0.0019]

Plane (2): P(1), C(15), C(17)—(20), C(23)
$-0.5457x' - 0.5059y' + 0.6680z' + 0.0804 = 0$

[P(1) 0.0120, C(15) 0.0027, C(17) 0.0108, C(18) −0.0077, C(19) −0.0017, C(20) −0.0062, C(23) −0.0105]

Plane (3): P(1), C(1), C(9), C(10), C(13), C(16), C(24)
$0.6529x' + 0.5030y' + 0.5663z' - 14.5361 = 0$

[P(1) −0.0095, C(1) 0.0025, C(9) 0.0142, C(10) −0.0020, C(13) 0.0115, C(16) 0.0002, C(24) −0.0170]

Plane (4): Sn(1), P(1), Cl(1), O(1), C(3), C(5), C(7), C(12), C(21)
$-0.0744x' + 0.9762y' + 0.2035z' - 8.6666 = 0$

[Sn(1) −0.1497, P(1) 0.1157, Cl(1) 0.2351, O(1) −0.4356, C(3) 0.2267, C(5) 0.0590, C(7) 0.0512, C(12) −0.7269, C(21) 0.8250]

Plane (5): Sn(1), C(11), C(12), C(14)
$0.4917x' - 0.2721y' + 0.8272z' - 5.986 = 0$

[Sn(1) −0.0541, C(11) 0.0181, C(12) 0.0178, C(14) 0.0182]

* Defined in terms of the orthogonal axes: $x' = x + z \cos \beta$; $y' = y$; $z' = z \sin \beta$.

Dihedral angles (°)

(1)–(2)	70.46	(2)–(4)	71.50
(1)–(3)	88.28	(2)–(5)	65.05
(1)–(4)	47.30	(3)–(4)	56.10
(1)–(5)	74.41	(3)–(5)	49.26
(2)–(3)	76.55	(4)–(5)	82.31

DISCUSSION

Crystals of the title complex are made up of discrete, non-interacting, molecules (Figure 1), arranged in parallel chains (Figure 2). The shortest intermolecular contacts are ⩾3.59 Å (Table 4).

Figure 3 shows that the phosphorus ylide residue is attached to the tin solely by the carbonyl oxygen atom. Contrary to the conclusions of Ishii *et al.*[5] the carbanionic carbon atom takes no part in co-ordination.

The Geometry at Tin.—The geometry about the tin is that of a trigonal bipyramid with the three methyl groups occupying equatorial positions in a planar arrangement, and the two electronegative atoms occupying the axial sites. The mean tin–carbon bond distance (2.133 Å) is within the range of distances measured for model compounds of similar structure (Table 4). The tin–chlorine bond distance (2.565 Å) is considerably longer than that in the analogous pyridine complex (2.42 Å),[8] probably reflecting the greater donor ability of the carbonyl oxygen in the present case. Consistent with this is the short length of the co-ordinate tin–oxygen bond (2.332 Å) compared with the tin–oxygen(water) distance[9] (2.47 Å) in $Me_3SnNO_3\cdot H_2O$ and the inter-

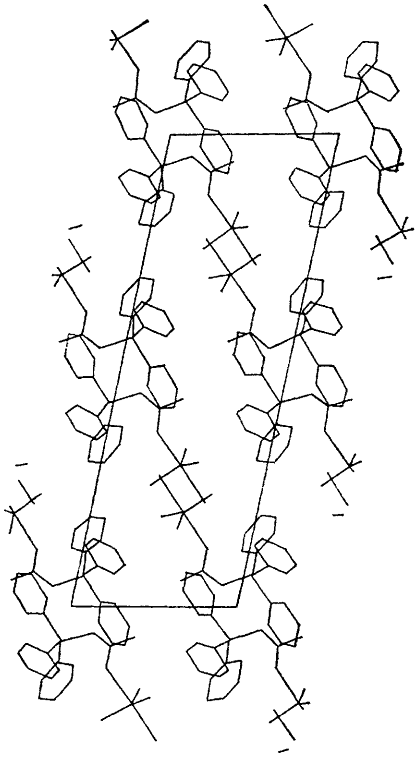


FIGURE 1 Projection on the *bc* plane

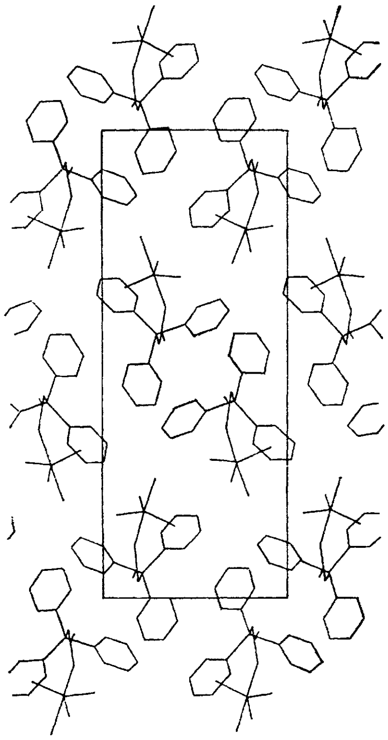


FIGURE 2 Projection on the *ac* plane

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[8] R. Holme, *J. Chem. Soc.*, 1963, 1524.

[9] R. E. Drew and F. W. B. Einstein, *Acta Cryst.*, 1972, **B28**, 345.

molecular tin–oxygen distance (2.65 Å) in tribenzyltin acetate,[10] in which carboxylate groups bridge tribenzyltin moieties to form a co-ordinate chain polymer. The co-ordinate tin–oxygen bond distance in triphenyltin *N*-benzoyl-*N*-phenylhydroxamate, however, is even shorter (2.31 Å).[11]

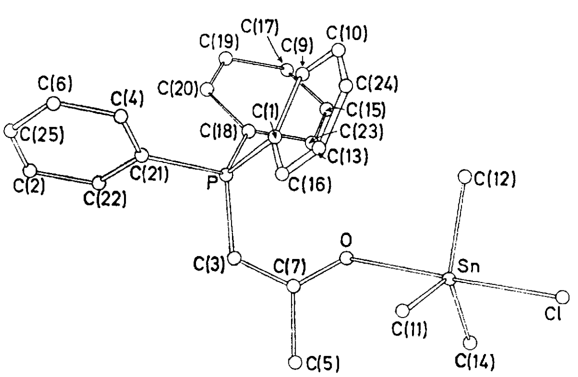


FIGURE 3 Atomic numbering

TABLE 4

Principal intermolecular contacts (Å), with estimated standard deviations in parentheses

C(3) · · · C(20)	3.85(1)	C(14) · · · C(17)	3.84(1)
C(4) · · · C(23)	3.74(1)	C(14) · · · C(19)	3.68(1)
C(4) · · · C(7)	3.90(1)	C(15) · · · C(24)	3.87(1)
C(5) · · · C(20)	3.68(1)	C(12) · · · C(17)	3.97(2)
C(5) · · · C(19)	3.85(1)	Cl · · · C(6)	3.59(1)
C(6) · · · C(7)	3.97(1)	Cl · · · C(10)	3.69(1)
C(6) · · · C(15)	3.94(1)	Cl · · · C(13)	3.84(1)
C(10) · · · C(15)	3.70(1)	Cl · · · C(15)	3.68(1)
C(10) · · · C(17)	3.83(1)	Cl · · · C(23)	3.95(1)
C(11) · · · C(25)	3.67(1)	Cl · · · C(25)	3.94(1)

The $Ph_3P{:}CH{\cdot}C({:}O)Me$ *Residue*.—The structural parameters of the ylide residue are indicative of substantial delocalisation of the carbanionic lone pair into the acetyl substituent. The bond angle at the carbanionic carbon (120.3°) is consistent with the retention of sp^2 hybridisation for carbon as in the unsubstituted ylide, $Ph_3P{:}CH_2$.[12] The (P:)C–C(:O) bond distance is substantially shorter (1.364 Å) than that usually found for C–C(:O) bonds in simple aldehydes or ketones (1.516 Å),[13] though not as short as the C=C bond distance in alkenes (1.337 Å).[13] In addition, the carbonyl bond distance is increased from that in simple carbonyl compounds (1.23 Å)[13] to 1.268 Å, a value marginally longer than that found in zwitterionic amino-acids (1.26 Å).[13] Similar behaviour has also been observed for the carbonyl-stabilised ylides $Ph_3P{:}CH{\cdot}CO{\cdot}OMe$,[14] and $Ph_3P{:}CX{\cdot}COMe$ (X = Cl or I).[15] In the ketenyl and thioketenyl ylides, $Ph_3P{:}C{:}C{:}X$ (X = O or S), the C:C bond distance is further reduced to 1.21 Å owing to the partial triple-bond character of the bond.[16]

TABLE 5

Comparison of tin–ligand bond distances (Å) in $[Ph_3P{\cdot}CH{\cdot}C({:}O)Me]Me_3SnCl$ with those in related compounds

Molecule	Geometry	Distance
(*a*) Sn–C		
$[Ph_3P{:}CH{\cdot}C(O)Me]Me_3SnCl$ [a]	Trig. bipyr.	2.133(9)
Me_3SnCN [b]	Trig. bipyr.	2.16(3)
$[Me_3SnCl_2]^-$ [c]	Trig. bipyr.	2.12(1)
$Me_3Sn(NCS)$ [d]	Trig. bipyr.	2.13(5)
$Me_3Sn(NO_3){\cdot}H_2O$ [e]	Trig. bipyr.	2.11(2)
Me_3SnF [f]	Dist. trig. bipyr.	2.11
$Me_3Sn(S_2CNMe_2)$ [g]	Dist. tet.	2.21(3)
$Me_2Sn(O_2C_5H_7)_2$ [h]	Oct.	2.14(2)
(*b*) Sn–O		
$[Ph_3P{\cdot}CH{\cdot}C(O)Me]Mc_3$-SnCl [a]	Trig. bipyr.	2.332(6)
$Me_3Sn(NO_3){\cdot}H_2O$ [e]	Trig. bipyr.	2.22(3) (NO_3), 2.47(2) (H_2O)
$Ph_3Sn(O{\cdot}NPh{\cdot}CO{\cdot}Ph)$ [i]	Dist. trig. bipyr.	2.091(5) (cov.), 2.308(4) (co-ord.)
$(PhCH_2)_3Sn(O_2CMe)$ [j]	Dist. trig. bipyr.	2.14(2), 2.65(2)
$(C_6H_{11})_3Sn(O_2CMe)$ [k]	Dist. tet.	2.12(3)
(*c*) Sn–Cl		
$[Ph_3P{:}CH{\cdot}C(O)Me]Me_3$-SnCl [a]	Trig. bipyr.	2.565(2)
$Me_3SnCl{\cdot}C_5H_5N$ [l]	Trig. bipyr.	2.42(4)
Me_3SnCl [m]	Tet.	2.106(6)
Ph_3SnCl [n]	Tet.	2.122(22)
$[SnCl_5]^-$ [p]	Trig. bipyr.	2.38 (ax.); 2.30, 2.38, 2.40 (eq.)
$[Me_3SnCl_2]^-$ [c]	Trig. bipyr.	2.572(4), 2.696(3)
$[Me_2SnCl_3]^-$ [q]	Dist. trig. bipyr.	2.54(2) (ax.), 2.32(1) (eq).

[a] This work. [b] E. O. Schlemper and D. Britton, *Inorg. Chem.*, 1966, **5**, 507. [c] P. J. Vergamini, H. Vahrenkamo, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 6237. [d] R. A. Forder and G. M. Sheldrick, *J. Organometallic Chem.*, 1970, **21**, 115. [e] Ref. 9. [f] H. C. Clark, R. J. O'Brien, and J. Trotter, *J. Chem. Soc.*, 1964, 2332. [g] G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc.* (*A*), 1970, 490, 493. [h] G. A. Miller and E. O. Schlemper, *Inorg. Chem.*, 1973, **12**, 677. [i] Ref. 11. [j] Ref. 10. [k] N. W. Alcock and R. E. Timms, *J. Chem. Soc.* (*A*), 1968, 1876. [l] Ref. 8. [m] K. McAloon, quoted in H. Fujii and M. Kimura, *Bull. Chem. Soc. Japan*, 1971, **44**, 2643. [n] N. G. Bokii, G. N. Zahkarova, and Yu. T. Struchkov, *J. Struct. Chem.*, 1970, **11**, 828. [p] R. F. Bryan, *J. Amer. Chem. Soc.*, 1964, **86**, 733. [q] F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc.* (*A*), 1968, 3019. Trig. bipyr. = trigonal bipyramid, dist. = distorted, tet. = tetrahedral, oct. = octahedral, ax. = axial, eq. = equatorial, cov. = covalent, co-ord. = co-ordinate.

Not unexpectedly, delocalisation of the lone pair into the acetyl substituent affects the geometry at phosphorus compared with that in $Ph_3P{:}CH_2$. In the unsubstituted ylide, the $P{:}CH_2$ bond is shortened to 1.661 Å relative to the mean P–C(Ph) distance (1.823 Å) *via* the small but significant * [P(*d*)-C(*p*$_z$)] π overlap. As a result, the three phenyl groups are folded back, as indicated by the C(Ph)–P–C(Ph) bond angles which are less than the tetrahedral value (105.0°) and the $C(Ph){-}P{-}CH_2$ angles which are concomitantly greater (113.5°).[12] The introduction

---

* The bond order of the P:S bond in $Ph_3P{:}CH_2$ has been estimated as 1.3 from force-constant data [17] and 1.1 from ^{31}P n.m.r. and structural data.[18]

[10] N. W. Alcock and R. E. Timms, *J. Chem. Soc.* (*A*), 1968, 1873.

[11] P. G. Harrison and T. J. King, *J.C.S. Dalton*, 1974, 2298.

[12] J. C. J. Bart, *J. Chem. Soc.* (*B*), 1969, 350.

[13] 'Molecular Structures and Dimensions,' vol. AI, eds. O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. C. Petersen, and W. G. Town, N. V. A. Oosthoek's Vitgevers Mig, Utrecht, 1972.

[14] V. D. Cherepinskii-Malov, G. G. Aleksandrov, A. I. Gusev, and Yu. T. Struchkov, *J. Struct. Chem.*, 1971, **13**, 273.

[15] F. S. Stephens, *J. Chem. Soc.*, 1965, pp. 5640, 5658.

[16] J. J. Daly and P. J. Wheatley, *J. Chem. Soc.* (*A*), 1966, 1703; J. J. Daly, *J. Chem. Soc.* (*A*), 1967, 1913.

[17] W. Lüttke and K. Wilhelm, *Angew. Chem.*, 1965, **77**, 867.

[18] J. H. Letcher, J. R. Van Wazer, J. R. Van Wazer, and J. H. Letcher in 'Topics in Phosphorus Chemistry,' vol. V, Interscience, New York, 1967.

TABLE 6

Comparison of bond distances (Å) and angles (°) of the phosphorus ylide residue with those in related compounds

Compound	r(P=C)	r[P–C(Ph)]	Mean r[P–C(Ph)]	Mean C(Ph)–P–C(Ph)
$Ph_3P{:}C{:}PPh_3$ [a]	1.631(4)	1.823—1.845(6)	1.834	103.8(3)
$Ph_3P{:}C{:}C{:}O$ [b]	1.648(7)	1.793—1.815(6)	1.805	107.3(3)
$Ph_3P{:}CH_2$ [c]	1.661(8)	1.811—1.839(15)	1.823	105.0(2)
$Ph_3P{:}C{:}C{:}S$ [d]	1.677(8)	1.783—1.804(7)	1.795	108.1(3)
$Ph_3P{:}CH{\cdot}CO{\cdot}OMe$ [e]	1.69(3)		1.81	107
$Ph_3P{:}CH{\cdot}SO_2{\cdot}C_6H_4Me$-$p$ [f]	1.709(19)	1.777—1.832(17)	1.808	106.8(8)
$Ph_3P{:}CCl{\cdot}COPh$ [g]	1.736(14)	1.798—1.822(13)	1.807	106.9(6)
$[Ph_3P{:}CH{\cdot}C(O)Me]Me_3SnCl$ [h]	1.750(8)	1.795—1.816(8)	1.807	107.6(4)
$(Ph_3P)(MeO_2C)CC(CO_2Me)[N(C_6H_4Cl)(NCN)]$ [j]	1.753	1.796—1.825	1.809	108.0
$2[Ph_3PMe^+][Zn(B_{10}H_{12})_2{}^{2-}]$ [k]	1.781(10)	1.766—1.781(9)	1.771	109.2(4)

Compound	C(Ph)–P=C	r[C–C(O)]	r(C=O)	P=C–C	(P=)C–C=O
$Ph_3P{:}C{:}PPh_3$ [a]	114.7(4)				
$Ph_3P{:}C{:}C{:}O$ [b]	111.5(4)	1.210(10)		145.1(7)	1.756(8)
$Ph_3P{:}CH_2$ [c]	113.5(3)				
$Ph_3P{:}C{:}C{:}S$ [d]	110.8(4)	1.209(11)		1.680(7)	
$Ph_3P{:}CH{\cdot}CO{\cdot}OMe$ [e]	111	1.37(3)	1.33(2)	116(1)	134(2)
$Ph_3P{:}CH{\cdot}SO_2{\cdot}C_6H_4Me$-$p$ [f]	112.0(8)				
$Ph_3P{:}CCl{\cdot}COPh$ [g]	111.9(6)	1.361(20)	1.301(19)	120.2(11)	116.6(13)
$[Ph_3P{:}CH{\cdot}C(O)Me]Me_3SnCl$ [h]	111.3(4)	1.364(12)	1.268(10)	120.3(6)	124.6(8)
$(Ph_3P)(MeO_2C)CC(CO_2Me)[N(C_6H_4Cl)(NCN)]$ [j]	110.7				
$2[Ph_3PMe^+][Zn(B_{10}H_{12})_2{}^{2-}]$ [k]	109.7(5)				

[a] A. T. Vincent and P. J. Wheatley, *Chem. Comm.*, 1971, 582. [b] Ref. 16. [c] Ref. 12. [d] Ref. 16. [e] Ref. 14. [f] P. J. Wheatley, *J. Chem. Soc.*, 1965, 5785. [g] Ref. 15. [h] This work. [j] R. D. Gilardi and I. L. Karle, *Acta Cryst.*, 1972, **B28**, 3420. [k] N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J. Chem. Soc.*, (*A*) 1971, 809.

of substituents at the carbanionic carbon atom causes competition for the carbon lone-pair. As the lone-pair density is removed from phosphorus to the substituent, the C(Ph)–P–C(Ph) angles increase and the C(Ph)–P=C angles decrease to the tetrahedral value, and the P:C bond distance increases to the normal P–C single-bond value, indicating that the environment at phosphorus has become more phosphonium in character (Table 5). In the present case, the P:C bond distance (1.750 Å) is the longest such distance of any ylide species yet examined, being slightly shorter than the mean P–C(Ph) distance (1.807 Å), and the mean bond angles at phosphorus deviate by less than 2° from the tetrahedral value. In the $[Ph_3\overset{+}{P}Me]$ cation, the phosphorus–phenyl and –methyl bond distances are very nearly equal (1.771 and 1.781 Å, respectively), and the bond angles at phosphorus are tetrahedral. Hence, the observed structural data are indicative of a large contribution of the canonical resonance form (III) to the electronic distribution, whilst structures (I) and (II) are of only minor importance.

We thank the S.R.C. for the award of studentships (to J. B. and J. A. R.).

[4/2122 *Received*, 14*th October*, 1974]