Synthesis, Stereochemistry, and Crystal and Molecular Structure of 4-Bromo-1,2,2,3-tetramethyl-1-phenylphosphetanium Bromide

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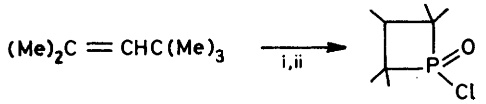
The synthesis of 4-bromo-2,2,3-trimethyl-1-phenylphosphetan 1-oxide was achieved by reaction of 1-bromo-3,3-dimethylbut-1-ene with phenylphonous dichloride in the presence of anhydrous aluminium chloride, followed by the addition of water. The oxide was converted into the title compound by reduction (Cl_3SiH) and then quaternization with methyl bromide. The title compound crystallizes in the monoclinic space group $P2_1/n$, with four molecules in a unit cell of dimensions a = 7.653(1), b = 12.662(3), c = 15.487(3) Å and β = 97.58(2°). The structure was solved by the heavy-atom method and refined to a final R value of 0.065. The four-membered ring is puckered with a dihedral angle of 34.0°. The methyl substituent at C(3) and the phenyl group have a *cis*-relation, whereas the bromo-substituent and phenyl ring are *trans*. All three of these groups occupy equatorial positions with respect to the ring.

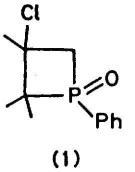
THE synthesis, stereochemistry, and reactions of four-membered rings containing phosphorus as a heteroatom (phosphetans) has received considerable attention in the last decade.[1] The preparations leading to this system are few in number, and are often too specific or give low yields.[2] The most general method to date is patterned after that reported by McBride *et al.*[3] (Scheme 1).



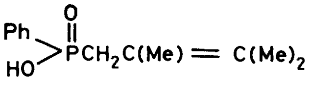
SCHEME 1 Reagents: i, PCl_3–$AlCl_3$; ii, H_2O

Extension of this methodology is limited, since no functionality other than methyl substituents at the ring carbons has been involved;[4] of course, several variations of the P–Cl linkage are possible (P–Ph, P–Me, P–OH). Because of this limitation, our interest in introducing reactive functionality in the ring (such as a double bond or exocyclic ketone group) has prompted us to find a solution to this problem. To date, the direct free radical halogenation of the ring has not been successful. An alternate approach therefore led us back to the useful work of McBride *et al.*[3] By incorporation of a halogen into the starting alkene, we anticipated its 'survival' in the phosphetan, provided it was in a non-allylic position.[5] We have now achieved such a preparation; the structure proof and stereochemistry of the resulting substituted phosphetanium salt has been confirmed by an X-ray study.

Synthesis.—An initial synthesis (using the method of McBride *et al.*) attempted to introduce a chloro-substituent at C(3) as shown in the phosphetan oxide (1). Because of the apparent lability of the chloro-group, we were not able to isolate this compound; however, the isolation of ring-opened products such as the alkene (2) implied the transient existence of a four-membered ring which underwent ring cleavage. Consequently, we turned to placement of the halogen (bromo-group) at C(4). This method of approach did give the desired product and is shown in Scheme 2.



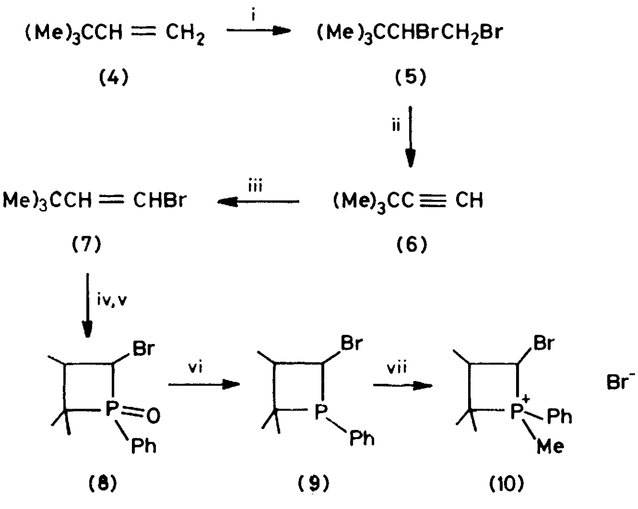
(1)



$$\underset{HO}{\overset{Ph}{}}\!\!>\overset{O}{\overset{\|}{P}}CH_2C(Me) = C(Me)_2$$

(2)

Commercially available 3,3-dimethylbut-1-ene (4) was converted into (7) by a series of modified preparations which have been described in the literature. The reaction of the vinyl bromide (7) with $PhPCl_2$–$AlCl_3$ followed by water treatment led to two isomers of the phosphetan oxide (8), one of which predominated.



SCHEME 2 Reagents: i, Br_2–CCl_4–EtOH; ii, Bu^{t}OK, heat; iii, HBr–Bz_2O_2, 0 °C; iv, $PhPCl_2$–$AlCl_3$; H_2O; vi, Cl_3SiH–C_6H_5; vii, MeBr

Reduction of the 'major' isomer of (8) and subsequent reaction with methyl bromide gave the phosphetanium salt (10); each step was expected to proceed with retention of configuration about the phosphorus atom.[4a,6]

Preliminary Isomer Assignment.—Both ^1H and ^{13}C n.m.r. spectroscopy were used to make tentative stereochemical assignments; a large data base on analogous compounds already exists and has been described in detail.[2,7]

The major isomer of (8), m.p. 154—156 °C, showed ^{13}C absorption at δ 48.53 [J 9.8 Hz, C(3)] * and 12.10 [J 23.1 Hz, C(7)] [crystallographic numbering (Figure 1)]; the minor isomer, m.p. 138—140 °C, showed corresponding peaks at δ 43.29 (J 2.5 Hz) and 12.08 (J 27.5 Hz), respectively. The relative size of the ^{31}P–C coupling constants are stereodependent [7] and permit a *cis*-(diequatorial) relation of the phenyl and methyl [at C(3)] to be assigned to the higher melting isomer and *trans* to the lower melting isomer. Furthermore, in the ^{1}H n.m.r. spectrum, the smaller ^{31}P–C–^{1}H coupling in the major isomer (2.5 Hz) compared to the minor isomer (13.5 Hz) established a *trans*- (diequatorial) relation between the phenyl and bromo-substituents in the major isomer.[2,8]

Reduction of (8), m.p. 154—156 °C, with trichlorosilane is presumed to go with retention of stereochemistry about phosphorus.[6] This is supported by the observed ^{31}P–C–^{1}H coupling constant (6.5 Hz) in the phosphetan (9) (derived from the major oxide); a previously reported Karplus relationship indicates the small magnitude of coupling to be consistent with a *trans*-relation between the phosphorus lone-pair electrons and the adjacent C–H bond.[9] Reduction (Cl_3SiH) of the lower melting oxide initially gave an isomeric phosphetan which rapidly isomerized to the identical phosphetan derived from the major oxide. This behaviour is consistent with unstable phosphetans which isomerize thermally or by acid catalysis to the more stable configuration, which in this case is represented by an equatorial phenyl group.

Because of the tentative nature of the stereochemical assignments, an *X*-ray study was undertaken.

EXPERIMENTAL

General Conditions.—^{13}C N.m.r. spectra were measured with a JEOL FX-60 QD Fourier transform spectrometer and ^{1}H n.m.r. spectra were obtained using a Varian A-60 A spectrometer; chemical shifts are expressed in δ values (tetramethylsilane reference) and were measured in $CDCl_3$ solution unless specified otherwise. M.p.s were determined with a Thomas–Hoover apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Manipulation of air and moisture sensitive compounds was conducted in a glove box under dry nitrogen. The anhydrous $AlCl_3$ was Baker analysed reagent grade.

1,2-*Dibromo*-3,3-*dimethylbutane* (5).—In a 1 l flask equipped with a dropping funnel, drying tube, thermometer, and magnetic stirring bar were placed carbon tetrachloride (300 ml), absolute ethanol (15 ml), and 3,3-dimethylbut-1-ene (115 g, 1.37 mol). The solution was cooled to −20 °C and bromine (192 g, 1.2 mol) in carbon tetrabromide (150 ml) was added dropwise over 2.5 h; the temperature during addition was kept below −10 °C. The mixture was then allowed to warm to ambient temperature and was stirred overnight. The solvent was removed by distillation (atmospheric pressure) and the residue was purified by fractional distillation to give the product (260 g, 89%), b.p. 80—82 °C at 11 mmHg (lit.,[10] 81—83 °C at 12 mmHg).

3,3-*Dimethylbut*-1-*yne* (6).—1,2-Dibromo-3,3-dimethylbutane was converted into the acetylene using the method described by Macomber.[10]

1-*Bromo*-3,3-*dimethylbut*-1-*ene* (7).—To 3,3-dimethylbut-1-*yne* (20 g, 0.24 mol) in a pear-shaped, two-necked flask was added dibenzoyl peroxide (0.5 g). The flask was cooled to 0 °C and HBr gas was bubbled through the mixture at a slow rate. The addition was stopped when an aliquot portion showed that the acetylene was no longer present (monitored by ^{1}H n.m.r. spectroscopy). The mixture was diluted with pentane and washed with water (50 ml), saturated sodium hydrogencarbonate solution, and finally with a saturated solution of sodium chloride. The organic layer was then dried (anhydrous Na_2SO_4) and fractionally distilled to give product (21.5 g, 55%), b.p. 124—125 °C (lit.,[11] 127—128 °C).

4-*Bromo*-2,2,3-*trimethyl*-1-*phenylphosphetan* 1-*Oxide* (8).—Phenylphosphonous dichloride (17.8 g, 0.1 mol) and aluminium chloride (15 g, 0.11 mol) were combined in methylene dichloride (200 ml) (at 0 °C) and the mixture was stirred until it became homogeneous. After cooling the mixture to 5 °C, 1-bromo-3,3-dimethylbut-1-ene (16.3 g, 0.1 mol) in methylene dichloride (50 ml) was added dropwise over 30 min. The solution was stirred at room temperature for 1 h. In certain runs a ^{1}H n.m.r. monitor showed unchanged alkene to be present. In these cases additional aluminium chloride was added until a slight excess was obtained (or until some solid $AlCl_3$ remained undissolved). Stirring was continued until the alkene was consumed. The mixture was then poured onto ice, and the organic layer washed successively with water and saturated sodium hydrogencarbonate solution. The organic layer was dried ($MgSO_4$) and evaporated. The crude, gummy residue was dissolved in boiling cyclohexane; a crude solid precipitated which was recrystallized from cyclohexane or benzene–cyclohexane. Purification was also carried out by sublimation of impure product at 100 °C and 0.05 mmHg. The yields of several runs ranged from 15—20%. A pure *sample* had m.p. 154—156 °C (Found: C, 50.25; H, 5.75. $C_{12}H_{16}BrOP$ requires C, 50.2; H, 5.6%); δ_{H} ($CDCl_3$) 7.2—7.9 (5 H, m, aromatic), 4.48 (1 H, dd, J_{PCH} 2.5, J_{HCCH} 11 Hz), 2.5—3.1 (1 H, m), 1.42 (3 H, d, J_{PCCH} 17.5 Hz), 1.18 (3 H, d, J_{PCCH} 7 Hz), and 0.95 (3 H, d, J_{PCCH} 20.5 Hz).

The mother-liquors from cyclohexane contained an isomeric oxide (one in which the phenyl group and 3-methyl are presumably *trans*) which had m.p. 138—140 °C; δ_{H} ($CDCl_3$) 7.2—8.2 (5 H, m, aromatic), 4.32 (1 H, dd, J_{PCH} 13.5, J_{HCCH} 11 Hz), 2.0—2.5 (1 H, m), 1.40 (3 H, d, J_{PCCH} 17.0 Hz), 1.2 (3 H, d, J_{HCCH} 7 Hz), and 1.07 (3 H, d, J_{HCCH} 19.5 Hz).

4-*Bromo*-2,2,3-*trimethyl*-1-*phenylphosphetan* (9).—The phosphetan 1-oxide, m.p. 154—156 °C (2.87 g, 0.01 mol), was dissolved in dry benzene (100 ml) and treated with trichlorosilane (3.5 g, 0.03 mol). The mixture was heated at reflux overnight, the solution was cooled to 5 °C and cold, 20% aqueous sodium hydroxide solution (100 ml) was added dropwise. The solution was stirred until all the solid dissolved and two clear layers were evident. The organic layer was washed several times with water (50 ml) and then dried (Na_2SO_4). The solvent was evaporated to give the crude phosphetan (2.6 g), δ_{H} ($CDCl_3$) 7.05—7.60 (5 H, m, aromatic), 4.13 (1 H, dd, J_{HCCH} 11, J_{PCH} 6.5 Hz), 2.3—3.1 (1 H, m), 1.35 (3 H, d, J_{PCCH} 18.0 Hz), 1.02 (3 H, d, J_{HCCH} 6.5

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* The ^{31}P–C coupling constant is here in parentheses as well as the carbon assignments.

Hz), and 0.71 (3 H, d, J_{PCCH} 5.5 Hz). To prevent thermal decomposition no attempt was made to distil the phosphetan; it was characterized by conversion into the phosphetanium salt derivative (10).

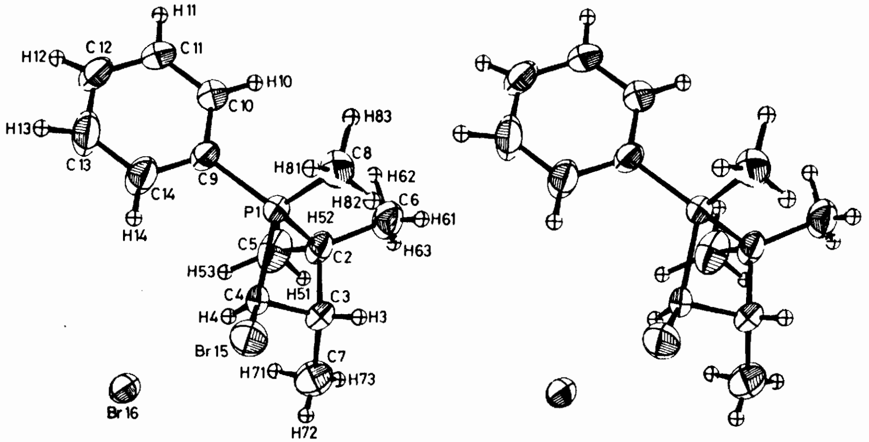

FIGURE 1 Stereopair for 4-bromo-1,2,2,3-tetramethyl-1-phenylphosphetanium bromide

4-Bromo-1,2,2,3-tetramethyl-1-phenylphosphetanium Bromide (10).—To benzene (100 ml) containing the phosphetan (5.7 g, 0.02 mol) was added methyl bromide (10 ml) (liquid was condensed in a cold trap); the mixture was allowed to stand for one week in a securely stoppered flask (thick-walled). The solid powder which formed was filtered and recrystallized from dry acetonitrile to give pure *product* (5.96 g, 78%), m.p. 193—194 °C (decomp.) (Found: C, 42.65; H, 5.25. $C_{13}H_{19}Br_2P$ requires C, 42.7; H, 5.3%), δ_H ($CDCl_3$) 8.3—9.0 (2 H, aromatic), 7.5—7.9 (3 H, aromatic), 6.5 (1 H, dd, J_{HCCH} 7, J_{PCH} 11.5 Hz), 2.5—3.3 (1 H, m), 2.70 (3 H, d, J_{PCH} 13.5 Hz), 1.71 (3 H, d, J_{PCCH} 21 Hz), 1.47 (3 H, d, J_{PCCH} 21 Hz), and 1.44 (3 H, d, J_{HCCH} 7 Hz).

Crystal Data.—$C_{13}H_{19}Br_2P$, $M = 366.1$, monoclinic, $a = 7.653(1)$, $b = 12.662(3)$, $c = 15.487(3)$ Å, $\beta = 97.58(2°)$, $U = 1\,487.5$ Å^3, D_m (by flotation) $= 1.64$, $Z = 4$, $D_c = 1.635$ g cm^{-3}. Space group $P2_1/n$; Mo-K_α radiation, $\lambda = 0.710\,73$ Å, $\mu = 58.5$ cm^{-1}, $F(000) = 728$.

A crystal measuring 0.47 × 0.35 × 0.68 mm was used for data collection. The Enraf–Nonius program SEARCH was used to obtain 25 reflections, which were then used in the program INDEX to obtain approximate cell dimensions. Accurate cell dimensions and their estimated standard deviations were obtained from least-squares refinement of these 25 accurately centred reflections.

The data were collected (to $\theta \leqslant 25°$) on an Enraf–Nonius CAD-4 diffractometer controlled by a PDP8/A computer at a take-off angle of 5° using Mo-K_α radiation from a highly oriented graphite crystal monochromator. The ω–2θ scan technique was used to record the intensities, using the ZIGZAG routine; background counts were taken on each side of the peak. The intensities of three standard reflections, monitored at 100 reflection intervals, showed no significant change during the data collection. 1 833 Reflections having $I > 3\sigma(I)$ were considered observed. Lorentz and polarization corrections were applied; form factors for non-hydrogen atoms were from Cromer and Waber,[12] and those for hydrogens were from Stewart *et al.*[13] Anomalous terms for Br and P were included.

All calculations were carried out on the University of Petroleum and Minerals IBM 370/158 computer using N.R.C. crystallographic programs.[14]

The three-dimensional Patterson map revealed bromine and phosphorus atoms. A Fourier map phased on these atoms revealed all non-hydrogen atoms. Block-diagonal isotropic refinement of these atoms gave R 0.124, and anisotropic refinement reduced R to 0.070. All hydrogen atoms were located from a difference map and further refinement of non-hydrogen atoms anisotropically and hydrogen atoms isotropically reduced final R to 0.065. A Hughes weighting scheme of the form $w = 1$ for $|F_o| \leqslant 20$, $\sqrt{w} = 20/|F_o|$ for $|F_o| > 20$ was used.

RESULTS AND DISCUSSION

Figure 1 is an ORTEP drawing of the molecule illustrating 50% probability ellipsoids and Figure 2 shows the packing of molecules. The atomic co-ordinates of non-hydrogen and hydrogen atoms are given in Tables 1 and 2, respectively. Bond distances and valence angles are listed in Table 3. The structure factors and thermal parameters are listed in Supplementary Publication No. SUP 23071 (7 pp.).*

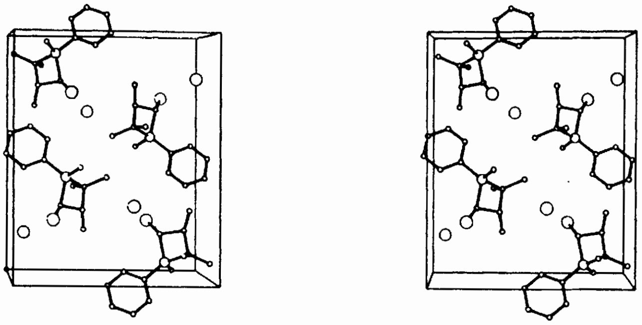

FIGURE 2 Stereopair showing the packing of molecules

The P–C bond length of 1.800(8) Å involving a monosubstituted carbon agrees very well with a value of 1.799(5) Å found in a monosubstituted α-carbon of an asymmetrically substituted phosphetan ring system.[15]

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* See Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1980, Index issue.

The P–C bond length of 1.829(8) Å involving a disubstituted carbon also agrees reasonably well with the values 1.83—1.84 Å previously reported for such a bond.[15-20] The C–C bond lengths in the phosphetan ring of 1.603(11) and 1.543(11) Å are comparable to those found in the other phospetan ring systems.[15-20] The P–C(Ph) distance of 1.774(8) Å is similar to those found in 3,3-dimethyl-1,1-diphenylphosphetanium iodide,[21] *NN*-dimethyldiphenylphosphinamide,[22] and 1-phenyl-1,2,2,3,4,4-hexamethylphosphetanium bromide.[17] The P–C(methyl) distance of 1.767(9) Å is longer than the value of 1.70(1) Å found in 1-phenyl-1,2,2,3,4,4-hexamethylphosphetanium bromide.[17]

The internal angle at the phosphorus is 80.0(4°) with adjacent angles 85.7(5) and 88.5(5°). The internal angle opposite the phosphorus is 95.8(6°). The phosphetan ring is non-planar, P(1) and C(3) are 0.14 and 0.20 Å below and C(2) and C(4) are 0.17 and 0.18 Å above the plane. The angle between the planes C(2)–P(1)–C(4) and C(2)–C(3)–C(4) is 34.0°. There are nine structures determined by *X*-ray analysis [16-21,23] which contain a phosphetan ring system. In eight of these the amount of pucker in the ring is 16.7–29.8° and one of them which has a tetracyclic system is puckered to an angle of 46.6°.[23] The average puckering angle for the five symmetrically substituted compounds is 22.9°. The two asymmetrically substituted structures have puckering angles of 16.9 and 29.8°. The puckering angle of 34.0° is therefore the largest of any monocyclic phosphetan derivative; of the two possible conformations (11a and b), the former is the more appropriate one, at least in the solid state, and probably in solution.[15]

TABLE 1

Fractional atomic co-ordinates ($\times 10^3$) with e.s.d.s in parentheses

Atom	x	y	z
P(1)	8 150(3)	2 634(2)	4 226(1)
C(2)	6 527(11)	3 625(6)	3 796(5)
C(3)	7 334(12)	3 497(7)	2 899(5)
C(4)	8 026(11)	2 363(6)	3 078(5)
C(5)	4 651(13)	3 202(8)	3 765(8)
C(6)	6 752(13)	4 724(7)	4 185(6)
C(7)	6 086(17)	3 636(9)	2 054(7)
C(8)	10 184(12)	3 199(7)	4 666(6)
C(9)	7 586(10)	1 579(6)	4 891(5)
C(10)	7 058(14)	1 770(7)	5 705(5)
C(11)	6 691(14)	936(8)	6 212(5)
C(12)	6 840(13)	−84(7)	5 922(6)
C(13)	7 350(15)	−273(7)	5 122(7)
C(14)	7 708(14)	562(7)	4 599(6)
Br(15)	10 118(1)	1 904(1)	2 613(1)
Br(16)	3 993(1)	725(1)	1 810(1)

TABLE 2

Fractional co-ordinates ($\times 10^3$) and isotropic temperature factors for H atoms, with e.s.d.s in parentheses

Atom	x	y	z	B(Å^2)
H(3)[C(3)]	830(8)	394(5)	290(4)	3.8(11)
H(4)[C(4)]	707(11)	207(7)	285(6)	4.0(10)
H(51)[C(5)]	395(11)	385(7)	340(5)	3.7(11)
H(52)[C(5)]	432(12)	330(7)	436(6)	4.6(10)
H(53)[C(5)]	434(11)	242(8)	348(6)	4.5(12)
H(61)[C(6)]	781(9)	506(5)	419(5)	3.8(11)
H(62)[C(6)]	632(13)	463(8)	480(7)	5.5(13)
H(63)[C(6)]	560(13)	505(9)	391(7)	6.0(12)
H(71)[C(7)]	500(14)	318(10)	212(8)	6.2(10)
H(72)[C(7)]	675(16)	337(11)	159(9)	6.8(13)
H(73)[C(7)]	521(17)	423(11)	201(9)	6.7(10)
H(81)[C(8)]	1 110(11)	262(7)	460(6)	4.2(11)
H(82)[C(8)]	1 061(10)	366(7)	431(5)	3.9(10)
H(83)[C(8)]	1 025(10)	340(10)	528(8)	6.6(14)
H(10)[C(10)]	685(11)	248(8)	591(6)	4.7(13)
H(11)[C(11)]	644(12)	98(8)	676(6)	4.7(12)
H(12)[C(12)]	644(14)	−68(8)	615(8)	6.7(14)
H(13)[C(13)]	776(17)	−101(11)	506(9)	6.6(14)
H(14)[C(14)]	993(12)	41(7)	402(6)	4.3(10)

TABLE 3

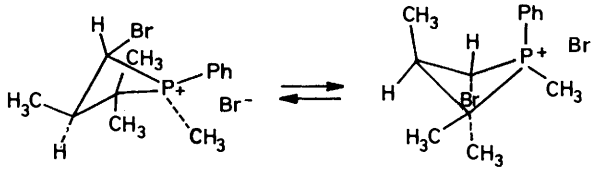
Bond lengths and angles with e.s.d.s in parentheses

(a) Distances (Å)

P(1)–C(2)	1.829(8)	C(7)–H(71)	1.03(12)
P(1)–C(4)	1.800(8)	C(7)–H(72)	1.00(13)
P(1)–C(8)	1.767(9)	C(7)–H(73)	1.00(13)
P(1)–C(9)	1.774(8)	C(8)–H(81)	1.03(9)
C(2)–C(3)	1.603(11)	C(8)–H(82)	0.89(8)
C(2)–C(5)	1.527(13)	C(8)–H(83)	0.98(12)
C(2)–C(6)	1.517(12)	C(9)–C(10)	1.395(12)
C(3)–C(4)	1.543(11)	C(9)–C(14)	1.372(12)
C(3)–C(7)	1.524(14)	C(10)–C(11)	1.367(13)
C(3)–H(3)	0.93(6)	C(10)–H(10)	0.97(10)
C(4)–H(4)	0.86(9)	C(11)–C(12)	1.376(13)
C(4)–Br(15)	1.931(8)	C(11)–H(11)	0.90(9)
C(5)–H(51)	1.09(9)	C(12)–C(13)	1.368(14)
C(5)–H(52)	0.99(10)	C(12)–H(12)	0.90(11)
C(5)–H(53)	1.09(10)	C(13)–C(14)	1.381(13)
C(6)–H(61)	0.92(1)	C(13)–H(13)	0.99(14)
C(6)–H(62)	1.06(10)	C(14)–H(14)	0.95(9)
C(6)–H(63)	1.02(11)		

(b) Angles (°)

C(2)–P(1)–C(4)	80.0(4)	H(61)–C(6)–H(62)	115(7)
C(2)–P(1)–C(8)	112.6(4)	H(61)–C(6)–H(63)	122(8)
C(2)–P(1)–C(9)	121.5(4)	H(62)–C(6)–H(63)	94(8)
C(4)–P(1)–C(8)	112.8(4)	C(3)–C(7)–H(71)	106(7)
C(4)–P(1)–C(9)	116.4(4)	C(3)–C(7)–H(72)	105(8)
C(8)–P(1)–C(9)	110.5(4)	C(3)–C(7)–H(73)	113(8)
P(1)–C(2)–C(3)	85.7(5)	H(71)–C(7)–H(72)	112(10)
P(1)–C(2)–C(5)	111.2(6)	H(71)–C(7)–H(73)	84(10)
P(1)–C(2)–C(6)	116.7(6)	H(72)–C(7)–H(73)	127(11)
C(3)–C(2)–C(5)	113.9(7)	P(1)–C(8)–H(81)	105(5)
C(3)–C(2)–C(6)	113.6(7)	P(1)–C(8)–H(82)	114(5)
C(5)–C(2)–C(6)	113.0(7)	P(1)–C(8)–H(83)	114(7)
C(2)–C(3)–C(4)	95.8(6)	H(81)–C(8)–H(82)	95(7)
C(2)–C(3)–C(7)	117.6(7)	H(81)–C(8)–H(83)	109(9)
C(2)–C(3)–H(3)	109(4)	H(82)–C(8)–H(83)	117(9)
C(4)–C(3)–C(7)	115.1(7)	P(1)–C(9)–C(10)	121.1(6)
C(4)–C(3)–H(3)	108(4)	P(1)–C(9)–C(14)	118.9(6)
C(7)–C(3)–H(3)	110(4)	C(10)–C(9)–C(14)	120.0(8)
P(1)–C(4)–C(3)	88.5(5)	C(9)–C(10)–C(11)	119.5(8)
P(1)–C(4)–Br(15)	119.2(4)	C(9)–C(10)–H(10)	122(6)
P(1)–C(4)–H(4)	115(6)	C(11)–C(10)–H(10)	118(6)
C(3)–C(4)–Br(15)	119.7(5)	C(10)–C(11)–C(12)	120.3(9)
C(3)–C(4)–H(4)	94(6)	C(10)–C(11)–H(11)	126(6)
Br(15)–C(4)–H(4)	115(6)	C(12)–C(11)–H(12)	114(6)
C(2)–C(5)–H(51)	99(4)	C(11)–C(12)–C(13)	120.4(9)
C(2)–C(5)–H(52)	107(6)	C(11)–C(12)–H(12)	127(7)
C(2)–C(5)–H(53)	119(5)	C(13)–C(12)–H(12)	111(7)
H(51)–C(5)–H(52)	102(7)	C(12)–C(13)–C(14)	120.0(9)
H(51)–C(5)–H(53)	114(7)	C(12)–C(13)–H(13)	113(8)
H(52)–C(5)–H(53)	115(7)	C(14)–C(13)–H(13)	125(8)
C(2)–C(6)–H(61)	119(4)	C(9)–C(14)–C(13)	119.9(9)
C(2)–C(6)–H(62)	103(6)	C(9)–C(14)–H(14)	122(6)
C(2)–C(6)–H(63)	100(6)	C(13)–C(14)–H(14)	118(6)



(11a) (11b)

The C(7)–C(9) distance of 5.1 Å from the *X*-ray study agrees well with the distance measured from a molecular model of (11a) but not (11b).

The phenyl ring is planar, the mean C–C distance of 1.376 Å in this ring is not significantly shorter than the standard value 1.395 Å.

The molecular packing in the crystal is shown in Figure 2. There are only five intermolecular contacts <3.6 Å, the shortest being 3.43 Å between C(12) and C(13) at $(1 - x, -y, 1 - z)$.

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