Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2'-(Diphenylphosphino)propiophenone, a Functionalized Tertiary Phosphine

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Abstract

The structure of the title compound, $Ph_2P(o\text{-}C_6H_4\text{---}CO\text{---}C_2H_5)$, shows significant distortions from tetrahedral geometry around the P atom; the C21—P1—C31 angle between the two unsubstituted rings [99.69 (9)°] is smaller than the other two C—P—C angles [104.37 (9)

and 102.24 (9)°]. The P—C distances are 1.828 (2), 1.846 (2) and 1.851 (2) Å. The C=O group does not lie in the plane of the ring to which it is bonded but is rotated −11.2 (2)° out of the ring plane; the P···O intramolecular distance is 2.669 (3) Å. The dihedral angles which define the rotations of the phenyl ring planes relative to the lone-pair direction on the P atom are 49.3 (1), 37.7 (1) and 34.9 (1)°, and are closer to those of a regular propeller conformation than was found in triphenylphosphine.

Comment

Functionalized tertiary phosphines play an important role in the chemistry of transition metal coordination complexes. A recent review on so-called 'hemilabile' phosphorus–oxygen ligands (Bader & Lindner, 1991) describes how an oxygen-containing functional group in a tertiary phosphine ligand can influence the catalytic chemistry of the phosphine complex. As a part of a research program directed toward the study of transition-metal–enolate complexes, we were interested in the preparation of ligands in which one of the donor moieties is an enolizable carbonyl group. Although 2-formylphenyl- and 2-acylphenyldiphenylphosphine have been prepared (Schiemenz & Kaack, 1973), to our knowledge there have been no structural studies of the free ligands or of any structurally related molecules. We have thus prepared the title compound, (1), in 56% yield by the addition of ethylmagnesium bromide (Cannone, Foscolos & Caron, 1982) to (2-cyanophenyl)diphenylphosphine (Ravindar, Hemling, Schumann & Blum, 1992). Although (1) was fully characterized by IR and ^1H and ^{13}C NMR spectroscopy (Rasley & Kulawiec, 1994), the crystal structure analysis was performed in order to establish the geometry of the uncomplexed ligand for use in future studies of the geometric deformations in its transition metal complexes.

(1)
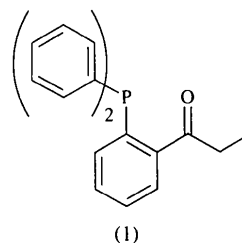
The compound consists of discrete molecules; a perspective view showing the atomic labelling scheme is shown in Fig. 1. The labelling scheme is similar to that used for the low-temperature structure of triphenylphosphine (Dunne & Orpen, 1991) and atoms C11–C16 will be referred to as ring 1, C21–C26 as ring 2, and C31–C36 as ring 3. A comparison of these two structures

shows that (1) has much bigger distortions from tetrahedral geometry around the P atom as a result of the presence of a bulky group in the *ortho* position of one phenyl ring. The P1—C21 distance [1.828 (2) Å] is significantly shorter than the other two P—C distances [1.846 (2) and 1.851 (2) Å] and the C21—P1—C31 angle [99.69 (9)°] is smaller than the other two [104.37 (9) and 102.24 (9)°]. The internal geometries of rings 2 and 3 are similar to those of triphenylphosphine but in ring 1 the C11—C12 distance is 0.036 Å longer than the average of the remaining 17 aromatic C—C distances [1.386 (7) Å]. Deviations from the least-squares planes defined by rings 1, 2 and 3 show that the P atom is −0.224 (3) Å from ring 1, 0.088 (4) Å from ring 2 and −0.219 (3) Å from ring 3. The C=O bond does not lie in the plane of ring 1 but has the O1 atom 0.161 (4) Å above the plane as a result of rotation about the C3—C12 bond [torsion angle O1—C3—C12—C11 −11.2 (2)°] leading to an intramolecular P1···O1 separation of 2.669 (3) Å. Following the same convention used by Dunne & Orpen (1991), the vector normal to the $(C_{ipso})_3$ plane may be used to define a lone-pair 'direction' to which the dihedral angles defining the extent of the phenyl ring rotation may be referred. The angles are 49.3 (1), 37.7 (1) and 34.9 (1)° for rings 1, 2 and 3, respectively, and are closer to those of a regular propeller conformation than was found in triphenylphosphine (25.0, 26.6 and 59.4°).
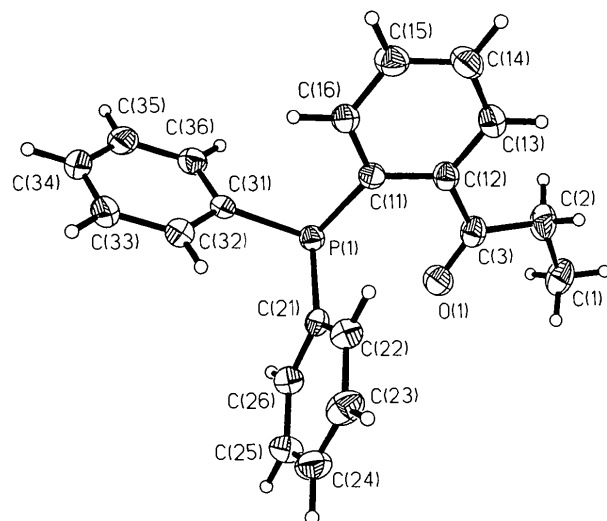

Fig. 1. Molecular structure of (1) showing 50% probability displacement ellipsoids.

Experimental

A solution of (2-cyanophenyl)diphenylphosphine (1.46 mmol) in 1:1 mixture of thf and benzene (15 ml) was treated with ethylmagnesium bromide (1.74 mmol) at 273 K, and allowed to warm to room temperature, with stirring, overnight.

The reaction mixture was hydrolyzed with saturated aqueous NaHSO₄; the organic layer was separated, washed with brine and dried. The solvent was evaporated, and the residue was redissolved in 6:1 hexane–ethyl acetate and filtered through silica gel. Recrystallization from methanol yielded bright yellow crystals.

Crystal data

$C_{21}H_{19}OP$	Mo $K\alpha$ radiation
$M_r = 318.33$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 11.484$ (3) Å	$\theta = 6–17°$
$b = 15.913$ (4) Å	$\mu = 0.159$ mm^{-1}
$c = 9.407$ (3) Å	$T = 293$ (2) K
$\beta = 101.46$ (1)°	Rod-like
$V = 1684.8$ (8) Å^3	0.4 × 0.3 × 0.3 mm
$Z = 4$	Yellow
$D_x = 1.255$ Mg m^{-3}	

Data collection

Siemens *P4/RA* four-circle diffractometer	$R_{int} = 0.0242$
	$\theta_{max} = 25°$
$\omega–2\theta$ scans	$h = -13 \rightarrow 13$
Absorption correction: none	$k = -18 \rightarrow 1$
	$l = -1 \rightarrow 11$
3786 measured reflections	3 standard reflections
2935 independent reflections	monitored every 97
2336 observed reflections	reflections
$[I > 2\sigma(I)]$	intensity decay: 1%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = -0.001$
$R[F^2 > 2\sigma(F^2)] = 0.0400$	$\Delta\rho_{max} = 0.266$ e Å^{-3}
$wR(F^2) = 0.0944$	$\Delta\rho_{min} = -0.216$ e Å^{-3}
$S = 1.070$	Extinction correction: none
2934 reflections	Atomic scattering factors
208 parameters	from *International Tables*
H atoms riding: C—H	*for Crystallography* (1992,
0.96 Å	Vol. C, Tables 4.2.6.8 and
$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 0.6022P]$	6.1.1.4)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P1	0.17508 (4)	0.97209 (3)	0.20711 (6)	0.0250 (2)
O1	0.12619 (14)	0.82377 (9)	0.3141 (2)	0.0401 (4)
C1	0.0559 (2)	0.65826 (14)	0.3187 (3)	0.0438 (6)
C2	0.1532 (2)	0.68328 (13)	0.2399 (3)	0.0415 (6)
C3	0.1797 (2)	0.77664 (13)	0.2489 (2)	0.0306 (5)
C11	0.2841 (2)	0.89857 (12)	0.1559 (2)	0.0244 (4)
C12	0.2725 (2)	0.81041 (12)	0.1736 (2)	0.0270 (4)
C13	0.3467 (2)	0.75547 (13)	0.1166 (2)	0.0352 (5)
C14	0.4320 (2)	0.78526 (14)	0.0446 (2)	0.0379 (5)
C15	0.4448 (2)	0.87052 (14)	0.0281 (2)	0.0366 (5)
C16	0.3713 (2)	0.92603 (13)	0.0823 (2)	0.0299 (5)
C21	0.2271 (2)	0.98849 (12)	0.4017 (2)	0.0258 (4)
C22	0.3390 (2)	0.96681 (14)	0.4802 (2)	0.0326 (5)
C23	0.3709 (2)	0.9858 (2)	0.6264 (2)	0.0416 (6)
C24	0.2924 (2)	1.0263 (2)	0.6963 (2)	0.0429 (6)

C25	0.1804 (2)	1.04731 (15)	0.6204 (2)	0.0416 (6)
C26	0.1482 (2)	1.02818 (13)	0.4750 (2)	0.0339 (5)
C31	0.2198 (2)	1.07360 (12)	0.1381 (2)	0.0249 (4)
C32	0.2996 (2)	1.13061 (13)	0.2166 (2)	0.0299 (5)
C33	0.3152 (2)	1.20978 (14)	0.1616 (2)	0.0377 (5)
C34	0.2521 (2)	1.23238 (14)	0.0263 (3)	0.0405 (6)
C35	0.1743 (2)	1.17634 (14)	−0.0540 (2)	0.0395 (6)
C36	0.1574 (2)	1.09760 (14)	0.0019 (2)	0.0331 (5)

Table 2. *Selected geometric parameters (Å, °)*

P1—C21	1.828 (2)	C11—C16	1.396 (3)
P1—C11	1.846 (2)	C11—C12	1.422 (3)
P1—C31	1.851 (2)	C12—C13	1.400 (3)
O1—C3	1.211 (2)	C13—C14	1.381 (3)
C1—C2	1.511 (3)	C14—C15	1.377 (3)
C2—C3	1.516 (3)	C15—C16	1.387 (3)
C3—C12	1.492 (3)		
C21—P1—C11	104.37 (9)	C13—C12—C3	120.2 (2)
C21—P1—C31	99.69 (9)	C11—C12—C3	120.2 (2)
C11—P1—C31	102.24 (9)	C14—C13—C12	121.3 (2)
C1—C2—C3	113.0 (2)	C15—C14—C13	119.7 (2)
O1—C3—C12	120.0 (2)	C14—C15—C16	120.0 (2)
O1—C3—C2	121.3 (2)	C15—C16—C11	122.1 (2)
C12—C3—C2	118.8 (2)	C22—C21—P1	125.4 (2)
C16—C11—C12	117.4 (2)	C26—C21—P1	116.4 (2)
C16—C11—P1	121.43 (15)	C36—C31—P1	115.8 (2)
C12—C11—P1	120.70 (14)	C32—C31—P1	125.6 (2)
C13—C12—C11	119.5 (2)		
O1—C3—C12—C11	−11.2 (2)	C1—C2—C3—O1	0.3 (2)

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1987). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1009). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,6-Diphenyl-3-vinylpyridine

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Abstract

In the structure of $C_{19}H_{15}N$, steric interactions force all three substituents (one vinyl and two phenyl groups) out of coplanarity with the central pyridine ring. Individual torsion angles around the relevant bonds are in the ranges 33.2 (3)–36.1 (3), 38.9 (3)–41.8 (3) and 29.6 (3)–31.1 (3)°.

Comment

In connection with an investigation of the chemistry of 5,6-dihydro-4*H*-1,2-oxazines (Ellames, Hewkin, Jackson, Smith & Standen, 1989), we treated 3-phenyl-5,6-dihydro-4*H*-1,2-oxazine, (1), with potassium *t*-amyloxide (6 equivalents) in *t*-amyl alcohol at reflux for 4 h. Flash chromatography allowed the isolation of the title compound (2) (13% yield) and the structure was determined by X-ray crystallography. This structure is consistent with the spectroscopic data obtained.

(1)   (2)   (3)
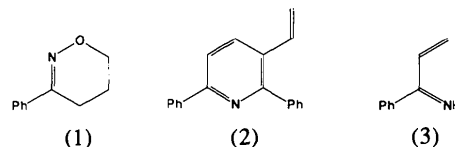
We believe that the title compound arises as a result of a Diels–Alder cycloaddition reaction between the imine (3) [which we have already postulated as an intermediate in the base-induced reactions of oxazine (1)] and 1-phenylbuta-1,3-diene, also derived from oxazine (1) by base-induced double-bond migration and a retro-Diels–Alder reaction. A final air oxidation would then lead to the aromatic title compound (2).

Although a number of copper and nickel complexes of 2-vinylpyridine have been structurally characterized (Engelhardt, Healy, Kildea & White, 1989; Hoberg, Guhl & Betz, 1990; Munakata, Kitagawa, Simono, Emori & Masuda, 1987), this appears to be the first report of the crystal structure of a 3-vinylpyridine, or indeed of any vinylpyridine not complexed to a metal. The three aromatic rings are essentially planar (r.m.s. deviations of 0.004, 0.003 and 0.004 Å), but the two phenyl and one vinyl substituent are twisted markedly