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LETTER

# A convenient synthesis of carbamoylmethylphosphines. X-ray structure of (diphenylphosphino)-*N*,*N*-diphenylacetamide

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In the last twenty years considerable efforts have been made to elaborate a wide variety of functionalized phosphines [1]. Most developments in this field are motivated by the needs of synthesizing tailor made transition metal ligands and, in particular, ligands suitable for the preparation of efficient homogeneous catalysts [2]. It is noteworthy that there is also a growing interest in the biochemistry of organophosphines, largely owing to the prospect of finding molecules with pharmacological activity [3].

Although organic amides display an extremely rich chemistry, phosphines which incorporate a carbamoyl group (–C(O)$NR_2$) have only scarcely been studied [4]. Recent promising reports on phosphine amides [5], demonstrating *inter alia* the relevance of such ligands for catalytic homogeneous hydrogenations as well as their use for the preparation of new molecular electronic devices, encouraged our efforts to develop strategies for the synthesis of this class of ligands. In this letter we describe three examples of a new and convenient synthesis of carbamoylmethylphosphines of the type $Ph_2PCH_2C(O)NRR'$. The X-ray structure of such a hybrid phosphine amide, $Ph_2PCH_2C(O)NPh_2$ (**1**), is also described. Due to the relative positions of the two functional groups, these compounds are potential candidates for the formation of five-membered P,O metallacycles.

## Experimental

The preparation of the title compound was performed using standard vacuum techniques. Tetrahydrofuran (THF) was distilled over sodium benzophenone and stored under dry nitrogen. Pentane and toluene were dried and distilled over sodium. IR spectra were recorded on an FT-IR Bruker IFS-66 instrument. NMR spectra were measured on a Bruker WP 200 spectrometer.

### *Preparation of $Ph_2PCH_2C(O)NPh_2$ (1)*

A 1.6 M hexane solution of n-BuLi (17.8 ml, 28.4 mmol) was dropwise added to a solution of diisopropylamine (2.874 g, 28.4 mmol) in THF (100 ml) at −78 °C. After the mixture had been stirred for 2 h, a solution of *N*,*N*-diphenylacetamide (6.023 g, 28.4 mmol) in THF (50 ml) was added slowly within 5 min. The mixture was stirred for 2 h at −78 °C and then transferred into a Schlenk flask containing $Ph_2PCl$ (6.266 g, 28.4 mmol) in THF (50 ml). After stirring for 15 h at room temperature, the solvent was removed *in vacuo*. The residue was treated with hot toluene (100 ml), and the resulting suspension filtered through a glass frit. The pale yellow filtrate was then concentrated and precipitated with pentane. The white precipitate thus obtained was recrystallized from degassed ethanol (colorless crystals, 10.440 g, 26.40 mmol, 93%). F: 132–133 °C. $^{1}H$ NMR ($CDCl_3$): $\delta$ 7.45–7.14 (20H, aromatic H), 3.20 (s, 2H, $PCH_2$, $^{2}J(PH)=0$ Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ 169.90 (d, CO, $^{2}J(PC)=9$ Hz), 142.72–126.35 (aromatic C), 36.39 (d, $PCH_2$, $J(PC)=20$ Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ −13.5 (s). IR (KBr): 1658s ($\nu$(C=O)) $cm^{-1}$. *Anal.* Calc. for $C_{26}H_{22}NOP$ ($M_r=395.44$): C, 78.97; H, 5.61; N, 3.54. Found: C, 78.90; H, 5.48; N, 3.42%.

The phosphines $Ph_2PCH_2C(O)NMe_2$ (**2**) and $Ph_2PCH_2C(O)NMePh$ (**3**) were prepared according to a procedure similar to that described above for **1**, using $MeC(O)NMe_2$ and $MeC(O)NMePh$, respectively, as starting material.

### *$Ph_2PCH_2C(O)NMe_2$ (2)*

Yield 90%, white product. F: 97–98 °C. $^{1}H$ NMR ($CDCl_3$): $\delta$ 7.51–7.26 (10H, aromatic H), 3.17 (s, 2H, $PCH_2$, $^{2}J(PH)=0$ Hz), 2.95 (s, 3H, NMe), 2.89 (s, 3H, NMe). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ −18.4 (s). IR (KBr): 1632s ($\nu$(C=O)) $cm^{-1}$. *Anal.* Calc. for $C_{16}H_{18}NOP$

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($M_r = 271.18$): C, 70.84; H, 6.64; N, 5.16. Found: C, 71.28; H, 6.79; N, 5.04%.

*$Ph_2PCH_2C(O)NMePh$ (3)*

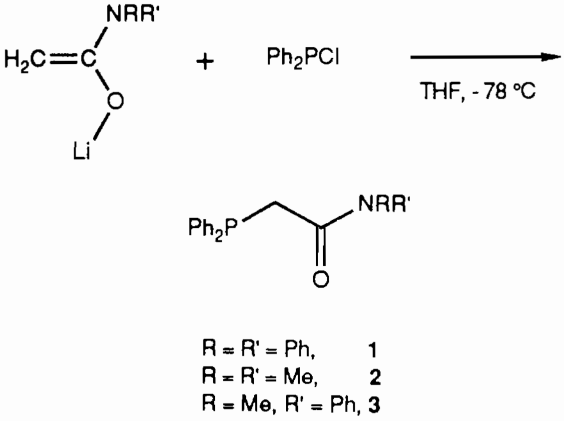
Yield 90%, white. F: 131–145 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 7.81–6.99 (15H, aromatic H), 3.37 (d, 2H, $PCH_2$, $^2J(PH) = 15.5$ Hz), 3.17 (s, 3H, NMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 29.3(s). IR (KBr): 1654s ($\nu$(C=O)), 1192s ($\nu$(P=O)) $cm^{-1}$. *Anal.* Calc. for $C_{21}H_{20}NO_2P$ ($M_r = 349.12$): C, 72.20; H, 5.77; N, 4.01. Found: C, 72.33; H, 5.75; N, 3.98%.

*Crystallographic data collection and structure determination of 1*

Crystal data: $C_{26}H_{22}NOP$, space group $P2_12_12_1$, $a = 8.939(2)$, $b = 10.838(2)$, $c = 21.759(8)$ Å, $V = 2108(1)$ Å$^3$, $Z = 4$, $D_{calc} = 1.246$ g $cm^{-3}$, $\mu$(Mo K$\alpha$) = 1.413 $cm^{-1}$. Crystal dimensions: 0.25 × 0.20 × 0.10 mm. Suitable single crystals of **1** were obtained according to the procedure described above. Two standard reflections measured every hour during the entire data collection period showed no significant decay. Intensity data ($0 \leqslant h \leqslant 10$; $0 \leqslant k \leqslant 12$; $0 \leqslant l \leqslant 25$; 2129 unique reflections; $2 < 2\theta < 50°$) were recorded on an Enraf-Nonius diffractometer equipped with a graphite crystal monochromatized Mo K$\alpha$ radiation. The intensities were collected by $\theta$–$2\theta$ scans at 23 °C. The structure was solved using direct methods (MULTAN 84 [6]) and successive Fourier difference syntheses and was refined by full-matrix least-squares calculations with isotropic displacement parameters for non-hydrogen atoms, due to the limited number of observed data. After refinement of positional and isotropic displacement parameters for all non-hydrogen atoms, the H atoms were observed from Fourier difference synthesis except the positions of the atoms H(4), H(5), H(23), H(24), H(25), H(26) which were computed ($d$(C–H) = 0.95 Å; $B_{eq} = 4$ Å). All hydrogen atoms are included as a fixed contribution to $F_c$ scattering factors and corrections for anomalous dispersion were taken from the literature [7]. The calculations converged at $R = 0.055$ ($R_w = 0.061$, $GOF = 1.51$) over 763 reflections with $I > 3\sigma(I)$. The largest remaining difference peak was 0.251 e Å$^{-3}$. The molecular and crystal structure illustration was drawn with ORTEP. All calculations were performed on a Microwax 3100 computer using the SDP programs described by Frenz [8].

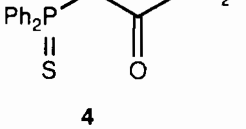
## Results and discussion

Phosphines **1–3** were prepared in high yield by reacting chlorodiphenylphosphine with the enolates derived from the corresponding acetamides ($CH_2{=}C(OLi)NRR'$) at −78 °C in THF (eqn.(1)). This novel synthesis of carbamoylmethylphosphines of the type $Ph_2PCH_2C(O)NRR'$ allowed preparations of **1–3** on a 10 g scale. Carbamoylmethylphosphines of this type have previously been obtained by reaction of phosphino-carboxylic acids with amines [4d]. The products were unambiguously characterized by analytical data and $^1H$, $^{31}P$, $^{13}C$ and IR spectroscopy. Noteworthy is the strong C=O band near 1650 $cm^{-1}$, typical for substituted amides [9]. The $^2J(PH)$ coupling constant is zero for all three phosphines. This observation is likely to correspond to a particular angular relationship of the phosphorus lone pair and the methylene CH bonds. A zero $^2J(PH)$ coupling constant may be anticipated, for phosphines of the $R^1R^2PCH_2R^3$ type, when the dihedral HCP$x$ angle ($x$ being the fourth axis defined by the phosphorus centre assumed to have a regular pyramidal geometry) is close to *c.* 180 or 80° [10]. Interestingly in the solid state structure of **1** (see below) the two PCH$x$ dihedral angles are close to these values (170 and 74°).

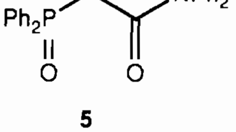


(1)

The quantitative conversion of **1** into the corresponding sulfide **4** was performed by treating a solution of **1** with $S_8$ in toluene. Oxidation of **3** with $H_2O_2$ in dichloromethane gave the phosphine oxide **5**. Characterizing data of **1–5** are given in Table 1.



**4**



**5**

An X-ray analysis was carried out to determine the exact structure of phosphine **1**. Atomic positional and equivalent isotropic thermal parameters of **1** are given in Table 2. The values of selected interatomic distances and angles are listed in Table 3. A diagram of the molecular structure of **1** showing the atomic numbering scheme is shown in Fig. 1.

TABLE 1. Properties of compounds **1–5**

| Compound | Melting point (°C) | IR[a] ($cm^{-1}$) | $^1H$ NMR[b] $\delta PCH_2$ ($^2J_{PH}$) | $^{31}P\{^1H\}$ NMR[b] $\delta P$ |
|---|---|---|---|---|
| **1** | 132–133 | 1658 | 3.20 (0) | −13.5 |
| **2** | 97–98 | 1632 | 3.17 (0) | −18.4 |
| **3** | 50–51 | 1645 | 2.97 (0) | −14.7 |
| **4** | 197–198 | 1665 | 3.74 (14) | 41.0 |
| **5** | 131–145 | 1654 | 3.37 (15) | 29.3 |

[a] In KBr disk; stretching frequency for the C=O bond. [b] In $CDCl_3$; $\delta$ in ppm, $J$ in Hz.

TABLE 2. Positional parameters and equivalent isotropic temperature factors with e.s.d.s in parentheses

| Atom | $x$ | $y$ | $z$ | $B_{iso}$ ($Å^2$) |
|---|---|---|---|---|
| P1 | 1.0129(3) | 0.2340(2) | 0.7022(1) | 3.18(5) |
| O1 | 1.0781(7) | 0.2396(6) | 0.5732(3) | 4.2(2) |
| N1 | 0.9523(8) | 0.4068(6) | 0.5394(3) | 2.9(2) |
| C1 | 0.919(1) | 0.2813(9) | 0.7731(4) | 2.8(2) |
| C2 | 0.836(1) | 0.1922(9) | 0.8046(5) | 3.7(2) |
| C3 | 0.764(1) | 0.2203(9) | 0.8604(5) | 3.6(2) |
| C4 | 0.780(1) | 0.3371(9) | 0.8842(5) | 3.9(2) |
| C5 | 0.865(1) | 0.4238(9) | 0.8535(5) | 3.9(3) |
| C6 | 0.931(1) | 0.3946(9) | 0.7995(5) | 3.4(2) |
| C7 | 1.198(1) | 0.2945(9) | 0.7173(4) | 3.4(2) |
| C8 | 1.276(1) | 0.378(1) | 0.6796(5) | 3.8(3) |
| C9 | 1.422(1) | 0.416(1) | 0.6932(5) | 5.2(3) |
| C10 | 1.493(2) | 0.368(1) | 0.7423(5) | 5.5(3) |
| C11 | 1.421(1) | 0.290(1) | 0.7803(5) | 5.8(3) |
| C12 | 1.277(1) | 0.247(1) | 0.7685(5) | 4.9(3) |
| C13 | 0.935(1) | 0.3487(8) | 0.6497(4) | 3.1(2) |
| C14 | 0.988(1) | 0.3265(8) | 0.5841(4) | 3.4(2) |
| C15 | 1.026(1) | 0.4028(8) | 0.4803(4) | 2.7(2) |
| C16 | 0.942(1) | 0.3807(9) | 0.4284(5) | 4.4(3) |
| C17 | 1.011(1) | 0.3873(9) | 0.3701(5) | 4.7(3) |
| C18 | 1.161(1) | 0.413(1) | 0.3664(5) | 5.3(3) |
| C19 | 1.244(1) | 0.431(1) | 0.4173(5) | 5.5(3) |
| C20 | 1.177(1) | 0.426(1) | 0.4754(5) | 4.5(3) |
| C21 | 0.840(1) | 0.5001(9) | 0.5481(4) | 2.9(2) |
| C22 | 0.890(1) | 0.6223(9) | 0.5580(5) | 3.9(3) |
| C23 | 0.780(1) | 0.712(1) | 0.5637(5) | 5.0(3) |
| C24 | 0.636(1) | 0.685(1) | 0.5571(5) | 5.1(3) |
| C25 | 0.588(1) | 0.569(1) | 0.5452(5) | 5.3(3) |
| C26 | 0.692(1) | 0.4731(9) | 0.5411(5) | 4.2(3) |

$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

The structure of **1** reveals the expected pyramidal geometry about the P(III) atom. The bond angles around this atom are significantly smaller than the ideal value of 109.5° (99.4(4); 99.4(4); 102.5(5)°); this 'compression' is not unusual for phosphines and has been rationalized by Walsh correlation diagram analysis [11]. The individual P–C bond lengths (see Table 3) are not significantly different (mean value 1.82 Å) and may be compared with that found in $PPh_3$ (mean value: 1.831(2) Å [12]).

TABLE 3. Selected bond lengths (Å), bond angles (°) and torsion angles (°)

| | | | |
|---|---|---|---|
| Distances | | | |
| P(1)–C(1) | 1.827(9) | N(1)–C(15) | 1.45(1) |
| P(1)–C(7) | 1.81(1) | N(1)–C(21) | 1.44(1) |
| P(1)–C(13) | 1.83(1) | C(14)–O(1) | 1.26(1) |
| C(13)–C(14) | 1.52(1) | H(20)–O(1) | 2.83(1) |
| C(14)–N(1) | 1.34(1) | H(8)–O(1) | 2.72(1) |
| Bond angles | | | |
| C(1)–P(1)–C(13) | 99.4(4) | O(1)–C(14)–N(1) | 120.0(8) |
| C(7)–P(1)–C(13) | 102.5(5) | C(14)–N(1)–C(21) | 121.9(8) |
| C(1)–P(1)–C(7) | 99.4(4) | C(14)–N(1)–C(15) | 121.7(7) |
| P(1)–C(13)–C(14) | 111.1(7) | N(1)–C(15)–C(20) | 120.6(8) |
| C(13–C(14)–O(1) | 119.6(8) | N(1)–C(15)–C(16) | 119.1(8) |
| Torsion angles | | | |
| P(1)–C(13)–C(14)–O(1) | −2(1) | | |
| O(1)–C(14)–N(1)–C(15) | −6(2) | | |
| C(21)–N(1)–C(14)–O(1) | 174(1) | | |
| C(13)–C(14)–N(1)–C(21) | −13(2) | | |
| C(13)–C(14)–N(1)–C(15) | 167(1) | | |

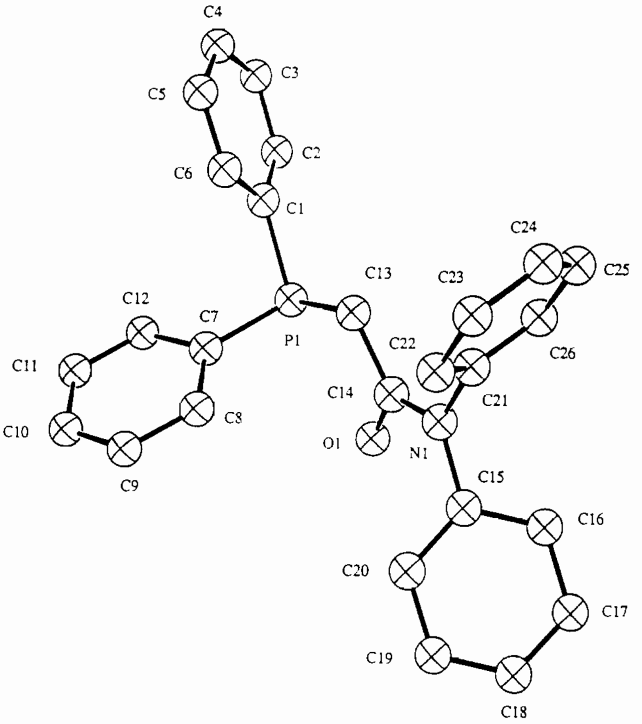
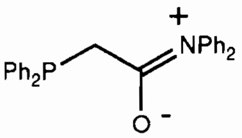


Fig. 1. An ORTEP diagram of **1**. Hydrogen atoms are omitted.

The $PPh_2$ and carbonyl groups are in a *syn* conformation (the P–C(13)–C(14)–O1 torsion angle is −2(1)°). This situation obviously minimizes the steric repulsions between the sterically demanding diphenylamino and diphenylphosphino groups. The amide function is characterized by an almost planar geometry of the N atom and a N(1)–C(14) bond with partial double bond character (1.34(1) Å), in agreement with a zwitterionic contribution of the type:



The expected limited degree of rotation around the N(1)–C(14) bond was confirmed by an NMR study of the related compound **2**: indeed, the room temperature spectrum of this latter phosphine displays two distinct methyl signals ($\delta$ 2.95 and 2.89 ppm, $CDCl_3$).

A weak intramolecular interaction is to be found between the oxygen atom and the aromatic H atom attached to C(8) (O(1)–H(8) = 2.72(1) Å). This results in a slight distortion of the carbonyl plane, the C(13) atom lying 0.168 Å out of the N(1)–C(14)–O(1) plane. The angle between the two planes of the phosphorus bonded phenyl rings is 103.8(3)°, whereas that between the two N-phenyl rings is 78.6(4)°.

Further studies, including coordination properties, on phosphines **1–3** as well as other hybrid phosphines obtained from acetamides are now in progress and will be reported in subsequent publications.

## Supplementary material

The following Tables are available from the authors or from the Cambridge Crystallographic Data Centre: least-squares planes (Table S1), hydrogen atoms positional parameters (Table S2), a complete set of bond distances (Table S3), a complete set of bond angles (Table S4), observed and calculated structure factors amplitudes for all observed reflections (Table S5).

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