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Reaction of ketenylidenetriphenylphosphorane, $Ph_3PC{=}C{=}O$, with water: formation of methyltriphenylphosphonium hydrogencarbonate

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Abstract

The reaction of the oxocumulene ylide ketenylidenetriphenylphosphorane, $Ph_3PC{=}C{=}O$ (**1**), with an excess of water in THF yields a white microcrystalline solid, methyltriphenylphosphonium hydrogencarbonate, which contains one molecule of crystallization water, $[Ph_3MeP]CO_3H \cdot H_2O$ (**2**). Compound **2** was characterized by IR, multinuclear NMR and ESI mass spectra. The chemical constitution was confirmed by X-ray crystal analysis. On heating, compound **2** decomposes giving CO_2, H_2O, C_6H_6 and Ph_2MePO. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ketenylidenetriphenylphosphorane; Phosphorus ylides; Hydrolisis; Ketenes; Crystal structure

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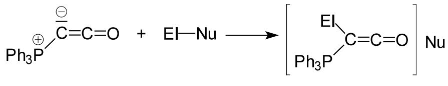
1. Introduction

Since Staudinger's synthesis of the first ketene, $Ph_2C{=}C{=}O$, at the beginning of the 20th century [1], the chemistry of these fascinating molecules has been widely developed and studied [2]. The chemistry of phosphorus ylides, which are important building blocks in several organic syntheses [3], was investigated to an even greater degree at this time. In 1966 ketenylidenetriphenylphosphorane, $Ph_3PC{=}C{=}O$ (**1**), the first molecule containing both ketene and ylide functionalities, was synthesized [4] and since then its organic chemistry has been continually investigated and reviewed [3,5].



Scheme 1.

An important feature of $Ph_3PC{=}C{=}O$ is its π electron system which differs from that of ketenes and is responsible for its particular reactivity, for example the fact that it does not dimerize [5b,6]. Moreover, in reactions with a generic dipolar compound, El–Nu, **1** undergoes electrophilic attack on the ylidic carbon, thus becoming a 'true' ketene (Scheme 1) that can display the reactivity typical of ketenes [5b].

In the case where Nu^- is a strong nucleophile it can attack the carbonyl carbon of the cationic ketene yielding carbonyl stabilized ylides, $Ph_3PC(El)–C(Nu)({=}O)$, as occurs with alcohols, thiols and primary or secondary amines [4,5b,7]. This behavior, at least for the electrophilic attack, was also observed in the reaction of **1** with suitable metal complexes that act as electrophiles without the nucleophilic counterpart, leading to the formation of mono- and bis-η^1-ketenyl derivatives $[L_nM\{\eta^1\text{-}C(PPh_3)CO]_m$ (M = Cr, W, Mo, Mn, Re, Pt,

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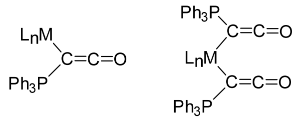
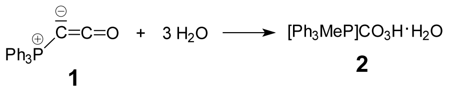


Chart 1.



Scheme 2.

Pd; $m = 1, 2$) [8,9], that can also be considered as metal substituted mono- or bis-ketenes [9e] (Chart 1).

During the study into the reactivity of some of these Pt substituted ketenes we found a quite normal ketene reactivity towards protic nucleophiles such as alcohols or amines, leading to the formation of the corresponding esters or amides derivatives [9c,9d,9e]. On the contrary, when the same compounds were treated with water we observed extensive decomposition leading to formation of CO_2 and unidentified compounds [10]. With the aim of understanding this behavior we started a literature research but, surprisingly, we were unable to find any mention of the interaction of free $Ph_3PC{=}C{=}O$ with water. This is a potentially interesting reaction, since **1** could conceivably undergo at least two different attacks by water to form: (i) an acid ylide, $Ph_3PCHCOOH$ [11]; or (ii) a phosphine oxide and a hydrocarbon, according to the 'classical' hydrolysis of ylides [12].

Here we report the observed results of the treatment, at room temperature, of a THF solution of **1** with an excess of water, that produced, in fairly good yield, a solid phosphonium hydrogen carbonate, containing also one molecule of crystallization water, $[Ph_3MeP]CO_3H{\cdot}H_2O$ (**2**).

2. Results

On treating a THF solution of **1** with an excess of water ($H_2O/\mathbf{1} = 5$) compound **2** formed and precipitated. The molar ratio $H_2O/\mathbf{1} = 5$ produced the best yield, but compound **2** was obtained even with lower molar ratios, with some $Ph_3PC{=}C{=}O$ remaining unreacted. Compound **2**, which analyses as $C_{20}H_{21}O_4P$, is scarcely soluble in most organic solvents, but dissolves easily in water producing a basic solution. The IR spectrum of **2** in KBr shows a broad, strong signal at 1656 cm^{-1} and significant signals related to the presence of OH groups (see Section 4). The ^1H-NMR spectrum of **2** in CD_2Cl_2 exhibits a multiplet (15H) at 7.75 ppm and a doublet (3H) at 3.10 ppm, ($^2J_{PH} = 13.4$ Hz) both of which are typical for $[Ph_3MeP]^+$ ions [13]. A broad signal centered at about 4 ppm (the chemical shift is dependent on the concentration) which integrates for three protons was attributed to hydrogens bonded to oxygen (OH and H_2O) in rapid exchange. $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR spectra (see Section 4) agree with those reported for the $[Ph_3MeP]^+$ ions [14]; moreover, a signal at 160.3 ppm in ^{13}C-NMR spectrum corresponds to CO_3H^- [15]. Positive-ion ESI mass spectrum of **2** in CH_3CN shows a signal at m/z 277 corresponding to $[Ph_3MeP]^+$ ions. Ms/ms measurement on these ions revealed a normal decomposition pattern, with loss of Me and Ph fragments. Negative-ion ESI mass spectrum did not show significant peaks, excluding a weak signal at m/z 44 (CO_2), which is likely to be due to the decomposition of CO_3H^-. The thermal decomposition of **2** was accomplished through a TGA experiment and also by decomposing a macroscopic quantity of solid compound. The TGA experiment (heating rate 8 °C min^{-1}) revealed, between 60 and 120 °C, a weight loss of 38%, corresponding to the release of CO_2, H_2O and C_6H_6, as was confirmed by IR spectrum of evolved gas. A lower heating rate (2 °C min^{-1}) led to the observation of two not well distinguished weight losses, indicating that at least two decomposition processes act almost contemporaneously. The thermal decomposition of a macroscopic quantity of **2**, carried out according to the procedure described in the Section 4, gave same results, besides allowing the identification of the compound remained after prolonged heating at ca. 115–120 °C, as Ph_2MePO. It is noteworthy that Ph_2MePO was also present in the mother liquors obtained in the synthesis of **2** and that solutions of **2** in chlorinated solvents undergo an analogous decomposition, during a 3-day period, as indicated by the disappearance of its typical ^1H-NMR signals and the formation of signals corresponding to C_6H_6 and Ph_2MePO.

All these data corroborate for a formulation for **2** corresponding to methyltriphenylphosphonium hydrogencarbonate containing one molecule of water, $[Ph_3MeP]CO_3H{\cdot}H_2O$, obtained according to the overall process indicated in Scheme 2.

This hypothesis has been confirmed by an X-ray analysis on crystals obtained by rapid evaporation of a saturated solution of **2** in CH_2Cl_2.

2.1. Description of the structure of **2** and comments

The compound **2** crystallizes in the acentric space group $P1$ and the independent structural unit consists of two chiral formula units, whose corresponding cations **a** and **b** are reported in Fig. 1 with the atom scheme numbering; they are arbitrarily oriented with respect to each other in order to show their particular reciprocal relation. Fig. 1 together with the structural parameters (Table 1) indicates that the two cations **a**

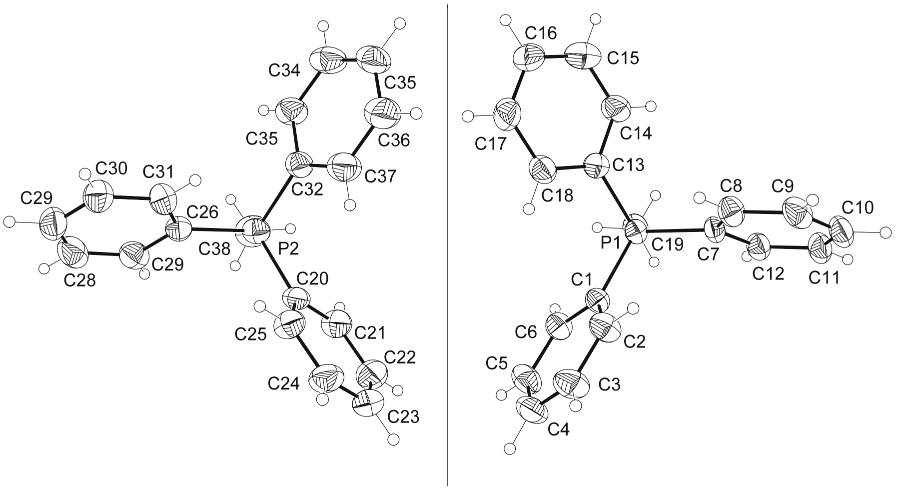


Fig. 1. Structure of the two cations forming the asymmetric unit. The two cations **a** and **b** are viewed down the P(1)–C(19) [P(2)–C(38)] axis and are suitably oriented in order to show their pseudo-mirror symmetry.

and **b** have virtually identical geometrical parameters but are enantiomorphous, having the propeller-shaped $[Ph_3MeP]^+$ groups in opposite configuration. The presence of both enantiomers in the independent structural unit is a rather unusual feature observed in other structures with similar chiral groups Ph_3X (X = P, Sn, Si) [16,17] or with quite different molecules having one center of stereomery [18]. Thus, the crystals in the present structure are racemates in spite of the absence of inversion centers or planes of symmetry [19].

The hydrogencarbonate anions dimerize through hydrogen bonds and undergo subsequent association in rows elongated in the *c* direction, through bridging water molecules (see this structural detail in Fig. 2). The geometrical parameters of the observed hydrogen bonds are reported in Table 2. The location of the hydrogen atoms bonding the two CO_3H anions was partially revealed by difference Fourier syntheses and confirmed by the geometry of the bicarbonate groups having bond lengths and angles distinctly differentiated (see Table 1), yet they were geometrically recalculated but not refined. The water hydrogen atoms were unambiguously located from Fourier syntheses, and refined. From this linear polymeric anion branch out hydrogen bonds with the cation subunits of type CH···O, widely described in the literature [20], with agreeable H···O distances in the range of 2.4–2.7 Å and angles C–H···O in the range of 130–170° (Table 2). A few of them are involved in weak intermolecular bond interactions, suggesting a probable cooperative contribution of the water molecules also to the lattice stability.

3. Discussion and conclusion

The reaction between ketenylidenetriphenylphosphorane (**1**), and water gives rise to the formation, in good yield, of $[Ph_3MeP]CO_3H{\cdot}H_2O$ (**2**). The synthesis of $[Ph_3MeP]CO_3H$ has only been previously reported in four patents [21] in which its catalytic uses were also claimed [22]. In one of these [21a] $[Ph_3MeP]CO_3H$ was obtained through the hydrolysis of the inner salt $Ph_3P^+CH_2COO^-$, whereas in other cases it was prepared by reaction of $[Ph_3MeP]OH$ with CO_2 [21b,21c], or by hydrolysis of $[Ph_3MeP]CO_3Me$ [21d]. No detailed characterization of $[Ph_3MeP]CO_3H$ has been reported in any of these patents.

Table 1
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **2**

Molecule **a**		Molecule **b**	
Bond lengths			
P(1)–C(1)	1.792(5)	P(2)–C(20)	1.789(5)
P(1)–C(7)	1.798(4)	P(2)–C(26)	1.795(5)
P(1)–C(13)	1.788(5)	P(2)–C(32)	1.801(5)
P(1)–C(19)	1.786(5)	P(2)–C(38)	1.798(6)
C(39)–O(1)	1.338(8)	C(40)–O(6)	1.330(7)
C(39)–O(2)	1.247(9)	C(40)–O(4)	1.265(6)
C(39)–O(3)	1.258(6)	C(40)–O(5)	1.239(8)
Bond angles			
C(1)–P(1)–C(13)	109.3(2)	C(32)–P(2)–C(38)	109.6(3)
C(1)–P(1)–C(7)	111.3(2)	C(26)–P(2)–C(38)	108.3(3)
C(7)–P(1)–C(13)	108.7(2)	C(20)–P(2)–C(38)	109.3(3)
C(13)–P(1)–C(19)	109.4(2)	C(20)–P(2)–C(32)	107.6(2)
C(7)–P(1)–C(19)	108.8(2)	C(20)–P(2)–C(26)	111.4(2)
C(1)–P(1)–C(19)	109.3(2)	C(26)–P(2)–C(32)	110.6(2)
O(2)–C(39)–O(3)	125.2(6)	O(4)–C(40)–O(5)	124.4(5)
O(1)–C(39)–O(3)	117.9(6)	O(6)–C(40)–O(5)	117.1(5)
O(1)–C(39)–O(2)	116.9(6)	O(6)–C(40)–O(4)	118.5(5)
Torsion angles			
C(38)–P(2)–C(20)–C(21)	26.0(5)	C(19)–P(1)–C(1)–C(6)	−21.7(5)
C(38)–P(2)–C(26)–C(27)	30.8(5)	C(19)–P(1)–C(7)–C(12)	−21.6(5)
C(38)–P(2)–C(32)–C(33)	38.1(5)	C(19)–P(1)–C(13)–C(18)	−55.6(5)

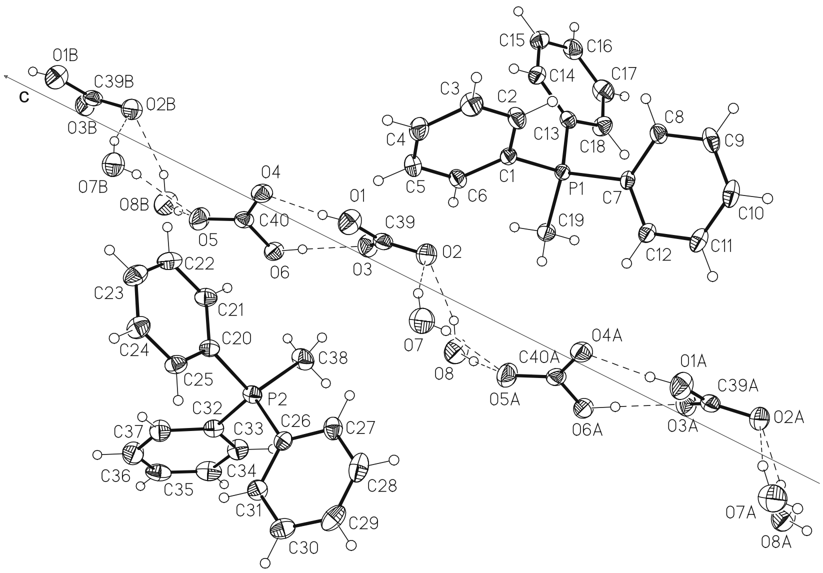


Fig. 2. The whole structural unit with atom numbering. The row along *c* of dimerized anions associated through hydrogen bonds with water of crystallization is evidenced.

The formation of **2** by reacting **1** with water can be interpreted, at least for the first step, in the terms proposed by Bestmann for the reactions of $Ph_3PC{=}C{=}O$ with El–Nu [5b] (Scheme 1). Accordingly, the addition of the electrophilic H^+ to the ylide lone pair of **1** leads to the formation of a cationic ketene having OH^- as anion (**A**) (Scheme 3). Thus, in the presence of an excess of water, three reaction-pathways are conceivable:

1. the migration of OH^- to the positively charged phosphorus, to give the ketene species **B**,
2. the attack of OH^- to the ketene to give, with a rearrangement, the inner salt **C**, or
3. the addition of another molecule of water to the ketene to give compound **D**.

Path (a) is to be excluded, as compound **B** would be extremely reactive and it would not react to form compound **2**. As previously mentioned, $[Ph_3MeP]CO_3H$ has been prepared by hydrolysis of **C** [21a] or by reaction of hydroxide **E** with CO_2 [21b,21c]. For this reason both paths (b) and (c) of Scheme 3 could be possible. In either case, species **D** is formed, which then loses CO_2 which is subsequently trapped by the hydroxide **E** to give **2**, together with another molecule of water.

Water plays a very important role in the formation of compound **2** since it acts not only as reagent in two different steps, but is also strongly bonded to the hydrogencarbonate anions forming rows through association with bridged CO_3H^- units, as indicated by the X-ray structure, which also reveals the presence of intra- and intermolecular CH···O hydrogen bonds. Some of these bonding interactions are also very likely to be present in solution as suggested by the exchange observed in the ^{1}H-NMR spectrum between protons of CO_3H^- and H_2O. Further evidence of a strong interaction between CO_3H^- and H_2O could be inferred by the fact that, if compound **2** is dissolved in

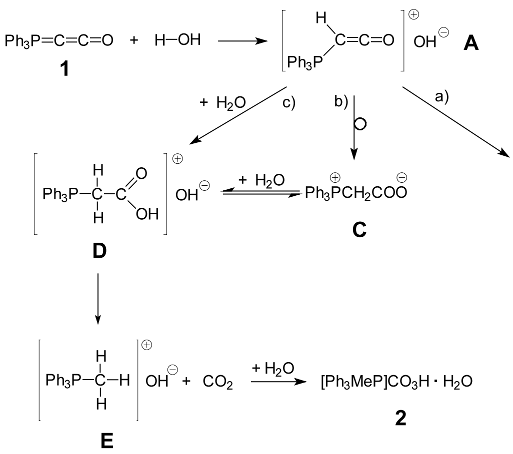
Table 2

Hydrogen bond interactions

O–H···O	H···O (Å)	O···O (Å)	O–H···O (°)	Equivalent position of O
O(1)–H(1)···O(4)	1.81(1)	2.620(7)	172(1)	*x*, *y*, *z*
O(6)–H(60)···O(3)	1.77(1)	2.584(7)	169(1)	*x*, *y*, *z*
O(7)–H(70)···O(5)A	2.14(8)	2.752(9)	159(3)	*x*, *y*, 1+*z*
O(7)–H(71)···O(2)	1.93(8)	2.918(8)	164(7)	*x*, *y*, *z*
O(8)–H(80)···O(5)A	1.98(8)	2.853(7)	170(5)	*x*, *y*, 1+*z*
O(8)–H(81)···O(2)	2.19(6)	2.888(9)	144(5)	*x*, *y*, *z*

Possible hydrogen bonds

C–H···O	H···O (Å)	C···O (Å)	C–H···O (°)	Equivalent position of O
C(19)–H(19b) ···O(2)	2.41	3.26	147	*x*, *y*, *z*
C(6)–H(6)···O(2)	2.36	3.43	170	*x*, *y*, *z*
C(21)–H(21)···O(6)	2.78	3.85	170	*x*, *y*, *z*
C(21)–H(21)···O(4)	2.65	3.44	131	*x*, *y*, *z*
C(21)–H(21)···O(5)	2.87	3.58	126	*x*, *y*, *z*
C(27)–H(27)···O(7)	2.56	3.43	155	*x*, *y*, *z*
C(38)–H(38c)···O(6)	2.70	3.58	152	*x*, *y*, *z*
C(10)–H(10)···O(8)	2.50	3.21	134	1+*x*, *y*, 1+*z*
C(17)–H(17)···O(7)	2.51	3.37	153	*x*, *y*−1, *z*
C(9)–H(9)···O(8)	2.89	3.40	116	*x*+1, *y*, *z*+1
C(30)–H(30)···O(8)	2.78	3.39	118	*x*, *y*+1, *z*
C(31)–H(31)···O(8)	2.76	3.39	119	*x*, *y*+1, *z*



Scheme 3.

dichloromethane and recrystallized or precipitated by addition of *n*-pentane, it retains the molecule of crystallization water.

As for the thermal decomposition of **2**, even though we were unable to observe a clean separation among the processes causing the elimination of CO_2, H_2O and C_6H_6, it is very likely that, on heating, compound **2** first releases CO_2 (and maybe crystallization H_2O) with formation of the corresponding hydroxide. The subsequent decomposition of this species does not deserve particular attention, as it is well known that phosphonium hydroxides decompose, in solution, giving phosphine oxides and hydrocarbons [23], in this case Ph_2MePO and C_6H_6. In our case decomposition occurs in the solid state, (or, maybe in the melt) possibly with a different mechanism with respect to that proposed for the reaction in solution.

Concluding, the reaction with water further confirms the mechanism proposed by Bestmann for the attack of El–Nu to **1** [5b]. The ketene obtained through the attack of H^+ reacts with a further molecule of water and a following decomposition process yields the hydrogen carbonate anion through the capture of CO_2. We are confident that these results will aid understanding of the previously mentioned behavior of Pt(II) η^1-ketenyl derivatives $[L_nPt\{\eta^1\text{-}C(PPh_3)CO\}_m]$, that decompose when treated with water with formation of CO_2 and other unidentified compounds.

4. Experimental

All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. $Ph_3PC{=}C{=}O$ (**1**), was synthesized according to literature methods [24]. IR spectra were recorded on a Perkin–Elmer 983 spectrophotometer. ^1H-, ^{13}C- and ^{31}P-NMR spectra were recorded at 298 K on a Bruker AC 200 spectrometer. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Electrospray Ionization (ESI) mass spectra of **2** were recorded on a LCQ (Finnigan MAT) instrument. TG experiments have been performed on a TA SDT 2960 instrument interfaced through a Nicolet Nexux TGA device to a Nicolet Magna FT/IR AEM spectrophotometer. Elemental analyses were provided by the Microanalysis Laboratory of the CIMA Department of the University of Padova.

*4.1. Synthesis of **2***

Compound **1** (0.690 g, 2.28 mmol) was dissolved in 10 ml of THF and 0.2 ml (11.1 mmol) of H_2O were added at room temperature (r.t.). The resulting solution was stirred, observing an exothermic reaction, and the solution became turbid. After 8 h a white, microcrystalline solid was filtered off, washed with THF and *n*-hexane and dried under vacuum. The solid was purified by dissolution in CH_2Cl_2 and precipitated by addition of *n*-pentane. Yield 0.595 g (73%). Mother liquors were taken to dryness under vacuum obtaining a pitchy solid that was identified by ^1H- and ^{31}P-NMR spectra as impure Ph_2MePO.

2. m.p. 108–110 °C (dec.), Elemental Anal. Calc. for $C_{20}H_{21}O_4P$: C, 67.41; H, 5.94. Found: C, 66.79; H, 5.66%. IR (KBr, cm^{-1}) 3475, 3415, 1656. ^1H-NMR (200 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 3.10$ (d, $^2J_{PH} = 13.4$ Hz, 3H, CH_3), 4.5 (broad, 3H, OH), 7.75 (m, 15H, Ph). $^{31}P\{^1H\}$-NMR (80 MHz, CD_2Cl_2, 25 °C, 85% H_3PO_4): $\delta = 22.15$ (s). $^{13}C\{^1H\}$-NMR (50 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 9.5$ (d, $^1J_{PC} = 57.5$ Hz, CH_3), 119.8 (d, $^1J_{PC} = 89.1$ Hz, Ph C_{ipso}), 130.6 (d, $^2J_{PC} = 12.9$ Hz, Ph C_m), 133.5 (d, $^3J_{PC} = 10.9$ Hz, Ph C_o), 135.2 (d, $^4J_{PC} = 4.8$ Hz, Ph C_p), 160.3 (s, CO_3H). ESI MS (CH_3CN) 277 $[Ph_3MeP^+]$; ms/ms of 277: 262 $[Ph_3P^{+\bullet}]$, 200 $[Ph_2MeP^{+\bullet}]$, 185 $[Ph_2P^{+\bullet}]$, 108 $[PhP^{+\bullet}]$.

*4.2. X-ray crystal structure analysis of **2***

Crystal data were collected using a Philips PW1100 diffractometer [25], with graphite-monochromated Mo–K_α radiation, following the standard procedures. All intensity data were corrected for Lorentz-polarization effects and absorption [26]. The structure was solved by direct methods using SIR-92 [27]. All non-H atoms were located in the subsequent Fourier maps. The structure was refined by full-matrix least-square methods using anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions in their described geometries and during refinement were allowed to ride on the attached carbon atoms with fixed isotropic thermal parameters (1.2 U_{eq} of the parent carbon atom) except for those of the water molecules, which were located from difference maps and refined with isotropic displacement parameters. The Flack parameters [28] have been refined for the structure. The calculations were performed with the SHELXL-97 program [29], using the scattering factors enclosed therein. The program for the ORTEP drawing was taken from [30]. Crystal data are given in Table 3.

4.3. Thermal decomposition of **2**

Compound **2** (0.242 g, 0.68 mmol) was heated for 30 min at 115–120 °C in an evacuated Schlenk tube, connected with a liquid nitrogen trap. The solid decomposed evolving gases and becoming a light-yellow liquid that solidified below 100 °C. This solid was collected (0.155 g) and was identified as impure Ph_2MePO by ^1H-, ^{31}P- and ^{13}C-NMR spectra that were compared with those of an authentic sample. The gases developed during the decomposition were collected in a liquid nitrogen trap which was then allowed to reach r.t. The ^1H-NMR spectrum of the resulting liquid indicated the presence of C_6H_6 and H_2O in 1:1 molar ratio.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 159164 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 3
Crystal data of **2**

Compound	$[Ph_3MeP]CO_3H \cdot H_2O$
Empirical formula	$C_{20}H_{21}O_4P$
Molecular weight	356.4
Temperature (K)	293(2)
Space group	$P1$
Crystal system	Triclinic
Unit cell dimensions	
a (Å)	10.399(3)
b (Å)	10.364(3)
c (Å)	9.497(2)
α (°)	105.16(2)
β (°)	101.90(2)
γ (°)	104.09(2)
Cell volume (Å^3)	917.5(5)
Formula units/unit cell	2
D_{calc} (g cm^{-3})	1.290
Radiation (Mo–K_{α}) (Å)	0.71073
μ (mm^{-1})	0.17
θ_{max}	56
Reflections measured	4699
Reflections observed [$I = 2\sigma(I)$]	4315
Weight	$1/[\sigma^2(F_o^2)+(0.0246P)^2+0.53P]$ [a]
R (on F)	0.055
R_w (on F^2)	0.126
S	1.32

[a] $P = \max(F_o^2 - F_c^2)^{2/3}$.

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