

Article

# Oxo-Stabilised Phosphonium Ylides as Hydrogen Bond Acceptors

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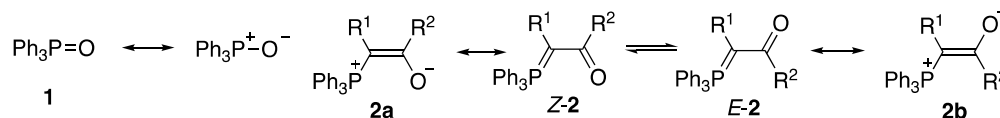
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**Abstract:** Oxo-stabilised phosphonium ylides are found to form crystalline hydrogen-bonded adducts with aromatic carboxylic acids, as confirmed by X-ray diffraction. There is also strong hydrogen bonding in solution as indicated by  $^{13}\text{C}$  NMR spectroscopy and this confirmed adduct formation with acetic acid, benzamide, thiobenzamide, benzyl alcohol, benzenesulfinic acid and diphenylphosphinic acid. The X-ray structure of the benzamide adduct was also determined, showing a hydrogen-bonded dimeric structure. A bis(stabilised ylide) was also prepared and is found to form a complex hydrogen-bonded adduct with benzoic acid, ethanol and water.

**Keywords:** hydrogen bond; phosphonium ylide; carboxylic acid; X-ray structure

## 1. Introduction

The ability of triphenylphosphine oxide **1** (Figure 1) to act as a hydrogen bonding acceptor is well known, with crystalline complexes being reported with hydroquinone and chlorinated analogues as early as 1959 [1]. More recently,  $\text{Ph}_3\text{PO}$  has been used as a “crystallisation aid” for compounds containing a range of hydrogen bond donor functions, including *N*-acylsulfonamides, phenols, alcohols, amides [2] and acyclic imides [3]. Crystalline hydrogen-bonded adducts have also been characterised between **1** and a wide range of carboxylic acids including oxalic [4], adamantanecarboxylic, terephthalic and phthalic [5], dimethylmalonic [6], trichloroacetic [7], 3-chlorobenzoic acids [8] and agrochemically important phenoxyacetic acid derivatives such as 4-chloro-2-methylphenoxyacetic acid (MCPA) [9]. Adducts with diphenylmethanol [10] and triphenylmethanol [11] have also been reported. In contrast, the hydrogen bonding acceptor ability of the formally vinylogous oxo-stabilised phosphonium ylides **2** has hardly been examined.



**Figure 1.** Structures of  $\text{Ph}_3\text{PO}$  **1** and vinylogous oxo-stabilised ylides **2**.

We have previously surveyed the known X-ray structures of such ylides [12,13], and while this revealed a well-defined pattern of *E* vs. *Z* relative arrangement of the phosphorus and oxygen atoms depending upon the nature of  $\text{R}^1$  and  $\text{R}^2$  (i.e., forms **2a** and **2b**, Figure 1), we are only aware of two previous cases of hydrogen bonding in such ylides, both intramolecular. The first involves the acetyl(phenylamido)arsonium ylide **3** (Figure 2) [14,15], where there is an *S*(6) [16] interaction between the NH and acetyl  $\text{C}=\text{O}$ , and the second is the biphenylcarboxylic acid containing phosphonium ylide **4** where there is an *S*(9) interaction between the carboxylic acid hydrogen and the ylide-conjugated carbonyl [17]. There seems to be no good reason why a similar interaction should not be possible in an intermolecular mode.



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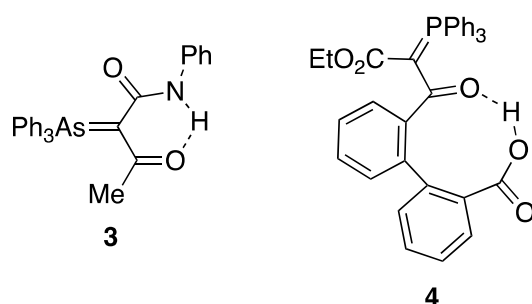
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**Figure 2.** Previously reported intramolecular hydrogen-bonded structures.

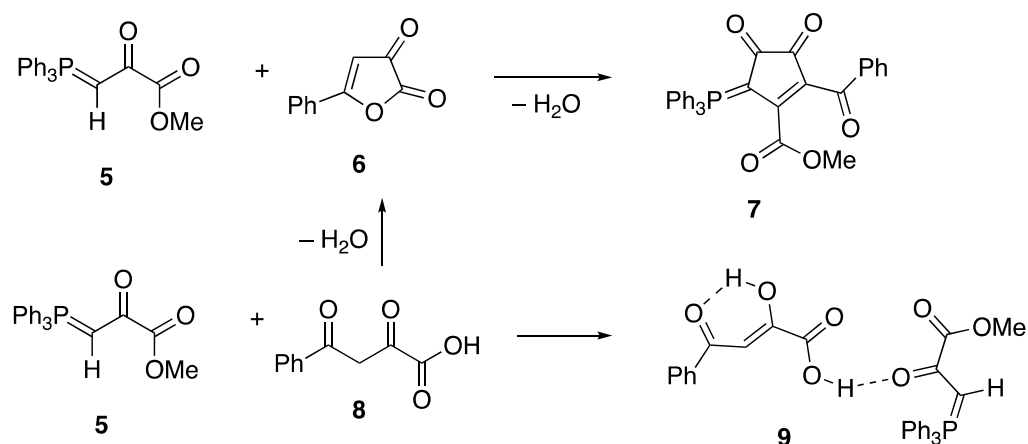
Although the behaviour of oxo-stabilised ylides **2** as intermolecular hydrogen-bond acceptors is essentially unexplored until now, such compounds do exhibit a rich coordination chemistry, acting as ligands binding through C or O or both atoms with a range of transition metals [18,19]. Crystalline adducts have also been formed with main group Lewis acidic halides such as HgCl<sub>2</sub>, HgBr<sub>2</sub> and HgI<sub>2</sub> [20], Me<sub>3</sub>SnCl [21] and TiCl<sub>4</sub>, ZrCl<sub>4</sub> and HfCl<sub>4</sub> [22]. The formation of complexes between bis(oxo-stabilised ylides) and organotin chlorides Me<sub>3</sub>SnCl, Me<sub>2</sub>SnCl<sub>2</sub>, Ph<sub>3</sub>SnCl and PhSnCl<sub>3</sub> [23] as well as HgCl<sub>2</sub> and PdCl<sub>2</sub> [24] has also been reported.

In this paper, we describe for the first time the formation and characterisation, both in solution and in the solid state, of hydrogen-bonded adducts between oxo-stabilised phosphonium ylides of type **2** and carboxylic acids, benzamide, thiobenzamide, benzyl alcohol, a sulfinic acid and a phosphinic acid.

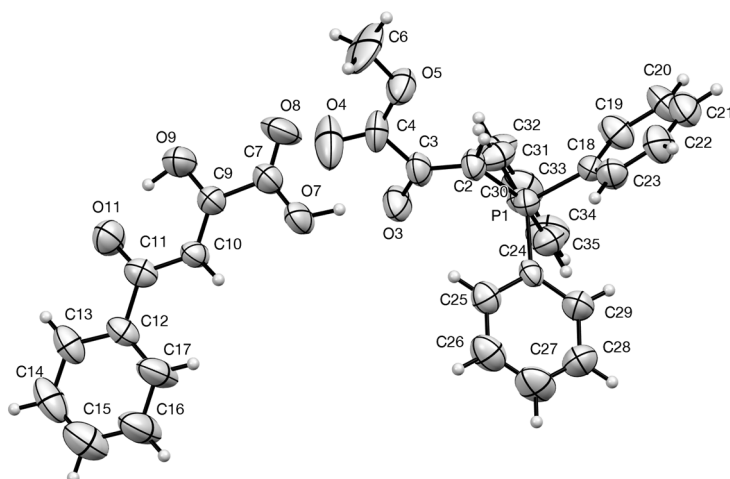
## 2. Results and Discussion

### 2.1. Initial Discovery

Some time ago, we described the formation and structure of the highly delocalised 3-triphenylphosphoranylidene-cyclopentene-1,2-dione **7** in a condensation reaction between methyl triphenylphosphoranylidene-pyruvate **5** and the furan-2,3-dione **6** (Scheme 1) [25]. The latter was prepared by dehydration of benzoylpyruvic acid **8**, but on one occasion, this dehydration failed, and we unwittingly heated a mixture of **5** and **8** in toluene to give, upon evaporation, a new crystalline material. This was initially suspected to be the ionic salt formed by protonation of the ylide function by the carboxylic acid. However, the structure, as determined by X-ray diffraction, showed it to be a hydrogen-bonded 1:1 adduct with both intra- and intermolecular O–H...O=C hydrogen bonds (Figure 3).

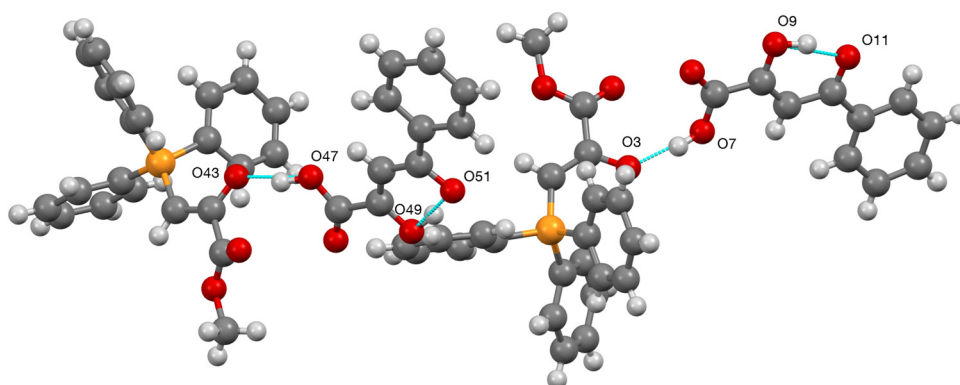


**Scheme 1.** Discovery of hydrogen bonded adduct **9**.



**Figure 3.** Molecular structure of **9** with anisotropic displacement ellipsoids drawn at the 50% probability level and the numbering system used.

In fact, the crystal structure consists of two independent but closely similar hydrogen-bonded adducts (Figure 4) and the hydrogen bonding parameters for each fall within the normal ranges (Table 1).



**Figure 4.** Hydrogen bonding interactions in the crystal structure of **9**.

**Table 1.** Hydrogen bonding parameters for ylide adducts (Å, °).

Compound	D–H...A	D–H	H...A	D...A	D–H...A
<b>9</b>	O(7)–H(7)...O(3)	0.98(8)	1.62(9)	2.490(9)	145(6)
<b>9</b>	O(9)–H(9)...O(11)	0.98(6)	1.59(6)	2.501(8)	153(6)
<b>9</b>	O(47)–H(47)...O(43)	0.98(4)	1.51(2)	2.471(8)	165(7)
<b>9</b>	O(49)–H(49)...O(51)	0.98(9)	1.58(8)	2.507(9)	156(8)
<b>11</b>	O(6)–H(6)...O(3)	0.93(5)	1.53(5)	2.501(6)	173(6)
<b>11</b>	O(36)–H(36)...O(33)	0.98(5)	1.53(5)	2.506(6)	171(6)
<b>21</b>	N(5)–H(5A)...O(3)	0.86(3)	2.04(3)	2.889(3)	169(2)
<b>21</b>	N(5)–H(5B)...O(6)	0.94(3)	1.97(3)	2.901(4)	173(3)
<b>27</b>	O(102)–H(10B)...O(2)	0.980(4)	1.639(3)	2.555(5)	153.83(19)
<b>27</b>	O(108)–H(10M)...O(52)	0.980(3)	1.803(3)	2.783(4)	177.8(2)

The structure of benzoylpyruvic acid within adduct **9** is in good agreement with that of the pure acid [26], which also exists as an intramolecularly hydrogen-bonded enol. The structure of the ylide within adduct **9** also compares well with that of the corresponding ethoxycarbonyl ylide [13].

## 2.2. Scope of the Stabilised Ylide—Carboxylic Acid Interaction

Although discovered fortuitously in the case of **9**, it seemed likely that the formation of hydrogen-bonded adducts could be more general, and indeed, this proved to be the case with ylide **5** forming a 1:1 adduct **10** with benzoic acid, and the much simpler ylide triphenylphosphoranylideneacetone also forming a benzoic acid adduct **11** (Figure 5) whose structure could again be confirmed by X-ray diffraction (Figures 6 and 7, Table 1). Again, in this case, we have two independent but closely similar adducts in the crystal.

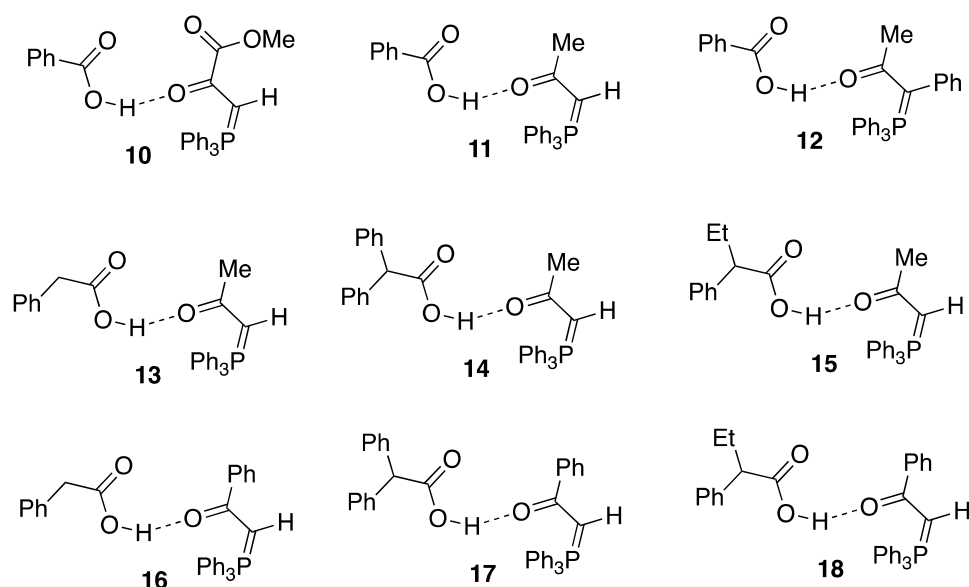


Figure 5. Ylide—carboxylic acid adducts formed.

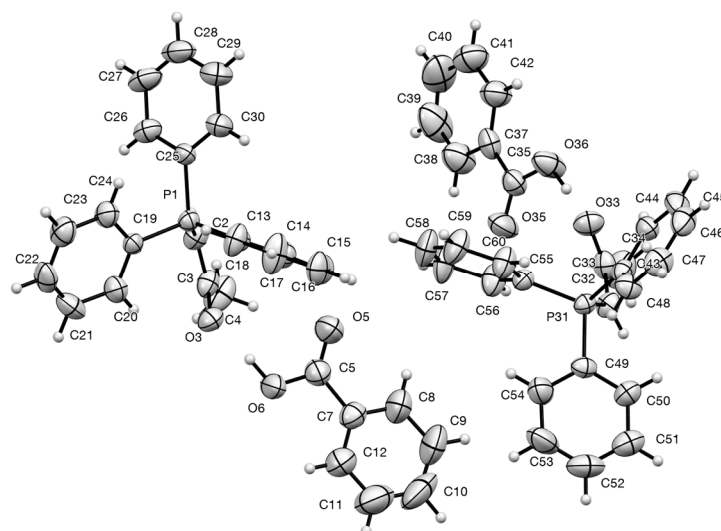


Figure 6. Molecular structure of **11** with anisotropic displacement ellipsoids drawn at the 50% probability level and the numbering system used.

Comparison of the molecular dimensions of the ylide in adduct **11** with those of the ylide on its own [13,27], as well as its adducts with  $\text{Me}_3\text{SnCl}$  [21] and  $\text{TiCl}_4$  [22] (Figure 8), shows that complexation results in lengthening of  $\text{P}=\text{C}$  and  $\text{C}=\text{O}$  with concomitant shortening of the intervening  $\text{C}-\text{C}$  bond and the effect increases along the series with hydrogen bonding to benzoic acid having less of an effect than bonding to  $\text{Me}_3\text{SnCl}$  which in turn is less than to  $\text{TiCl}_4$ .

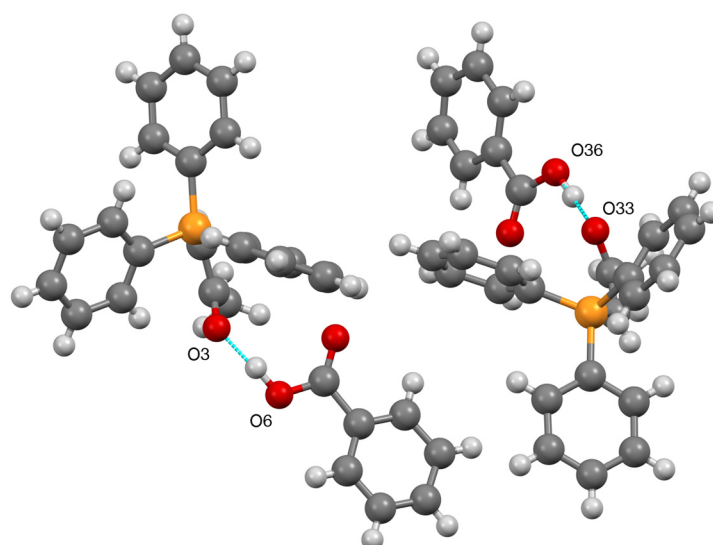


Figure 7. Hydrogen bonding interactions in the crystal structure of 11.

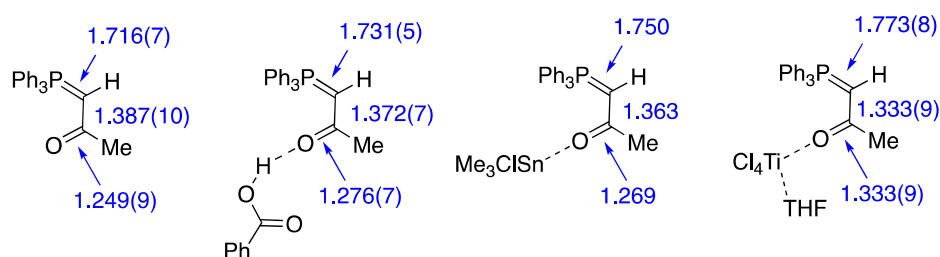


Figure 8. Bond lengths (Å) in triphenylphosphoranylideneacetone and its adducts as determined by X-ray diffraction.

Although it was initially expected that such adducts would exist only in the solid state and that they would dissociate upon dissolving, careful analysis of the NMR spectra showed that this was not the case. When the  $^{13}\text{C}$  NMR data obtained by dissolving an adduct such as **10** or **11** in  $\text{CDCl}_3$  were compared with those of the individual components, significant differences were noted in the signals due to nuclei around the site of hydrogen bonding (see Supplementary Materials). Specifically, the signal for  $\text{C}=\text{O}$  of the carboxylic acid in the adducts came at 2–4 ppm lower chemical shift than for the pure acid, while the  $\text{P}=\text{C}$  ylide signal came at 2–5 ppm higher chemical shift in the adducts as compared to the pure ylides. This then allowed rapid screening of a range of simple ylides and aromatic carboxylic acids with adducts **12**–**18** (Figure 5) being obtained. The data are summarised in Table 2.

Table 2. Changes observed in key  $^{13}\text{C}$  NMR shifts upon adduct formation (ppm).

Adduct	$\text{CO}_2\text{H}$ ( $\delta$ )			$\text{P}=\text{C}$ ( $\delta$ )		
	Adduct	Free Acid	$\Delta\delta$	Adduct	Free Ylide	$\Delta\delta$
<b>10</b>	170.2	172.6	−2.4	58.8	57.0	+1.8
<b>11</b>	169.6	172.6	−3.0	56.3	51.5	+4.8
<b>12</b>	169.7	172.6	−2.9	75.1	71.0	+4.1
<b>13</b>	174.6	178.2	−3.6	56.1	51.5	+4.6
<b>14</b>	175.2	179.0	−3.8	56.0	51.5	+4.5
<b>15</b>	177.0	180.5	−3.5	55.4	51.5	+3.9
<b>16</b>	174.5	178.2	−3.7	52.7	50.6	+2.1
<b>17</b>	174.9	179.0	−4.1	52.5	50.6	+1.9
<b>18</b>	177.7	180.5	−2.8	53.5	50.6	+2.9

In most of these cases, well-defined crystalline adducts were formed by heating equimolar amounts of the components in toluene under reflux for 5 min, evaporation and recrystallisation of the residue from ethanol, and the NMR data were obtained by dissolving these in  $\text{CDCl}_3$ . For adducts **12**, **16**, and **18** only, we were unable to isolate the pure adduct in crystalline form, but the solution interaction could still be observed by directly preparing a 0.1 M solution of the two components in  $\text{CDCl}_3$ .

It was of interest to examine the solvent dependence of the solution interaction, and this was done in the case of **11** by running  $^{13}\text{C}$  NMR spectra of the two components together and individually in a range of solvents. The results (Table 3) show that the shift in the ylide carbon drops off steadily with increasing solvent polarity indicating a progressive weakening of the interaction, while the carboxylic acid shifts do not show any meaningful trend.

**Table 3.** Solvent effect on the key  $^{13}\text{C}$  NMR shifts upon adduct formation for **11** (ppm).

Solvent	$\text{CO}_2\text{H}$ ( $\delta$ )			$\text{P}=\text{C}$ ( $\delta$ )		
	Adduct	Free Acid	$\Delta\delta$	Adduct	Free Ylide	$\Delta\delta$
$\text{C}_6\text{D}_6$	168.8	168.9	−0.1	55.9	50.2	+5.7
$\text{CDCl}_3$	169.6	172.6	−3.0	56.3	51.5	+4.8
$\text{CD}_3\text{COCD}_3$	168.1	168.0	+0.1	54.4	51.7	+2.7
$\text{CD}_3\text{OD}$	170.7	169.8	+0.9	54.1	51.8	+2.3
$\text{CD}_3\text{SOCD}_3$	167.4	167.3	+0.1	50.2	49.7	+0.5

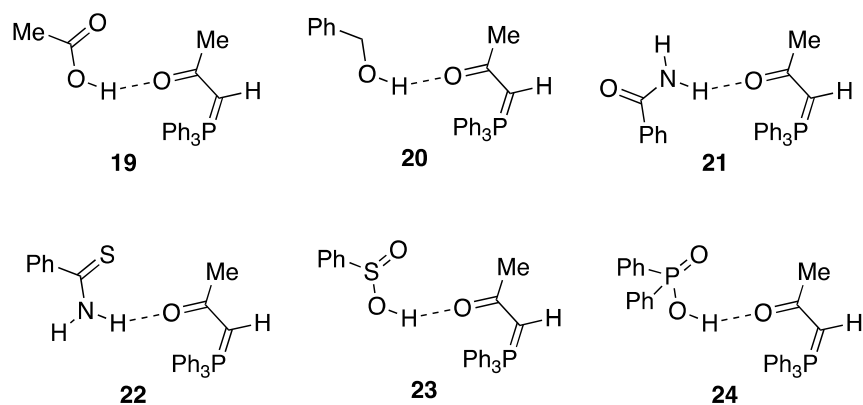
### 2.3. Expanding the Range of Hydrogen Bond Donors

Using the  $^{13}\text{C}$  chemical shift of the ylide carbon as a diagnostic parameter, the solution interaction of triphenylphosphoranylideneacetone with a range of potential hydrogen bond donors was investigated by preparing 0.1 M solutions of the two components in  $\text{CDCl}_3$ . The results (Table 4) show clear evidence of adduct formation for acetic acid, benzyl alcohol, benzamide, thiobenzamide, benzenesulfinic acid, and diphenylphosphinic acid with the suggested structures **19**–**24** shown in Figure 9. For benzylamine the minimal change in  $\delta_{\text{C}}$  indicated no adduct formation while for benzenesulfonic acid proton transfer occurred to give the ionic salt: a phosphonium sulfonate.

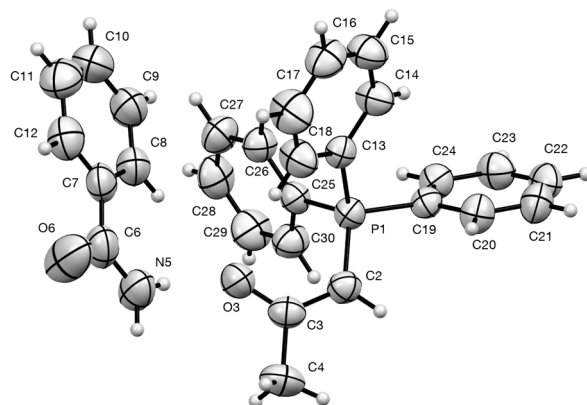
**Table 4.** Formation of adducts with other types of donor in  $\text{CDCl}_3$ .

Adduct	Donor	$\delta_{\text{C}}$ Adduct	$\delta_{\text{C}}$ Free Ylide	$\Delta\delta$
<b>19</b>	$\text{MeCO}_2\text{H}$	56.5	51.5	+5.0
<b>20</b>	$\text{PhCH}_2\text{OH}$	58.0	51.5	+6.5
<b>21</b>	$\text{PhCONH}_2$	56.2	51.5	+4.7
<b>22</b>	$\text{PhCSNH}_2$	54.5	51.5	+3.0
<b>23</b>	$\text{PhSO}_2\text{H}$	57.2	51.5	+5.7
<b>24</b>	$\text{Ph}_2\text{P}(=\text{O})\text{OH}$	59.1	51.5	+7.6
-	$\text{PhCH}_2\text{NH}_2$	51.8	51.5	+0.3
-	$\text{PhSO}_3\text{H}$	-	51.5	-

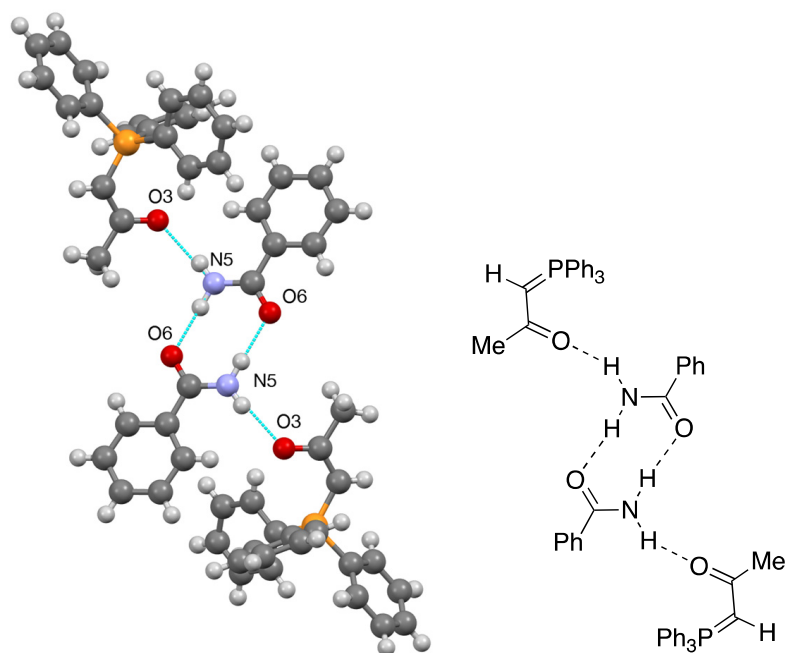
In the case of benzamide and thiobenzamide, the adducts **21** and **22** could be isolated in crystalline form by following the same procedure as used for aromatic carboxylic acid adducts. These gave the expected analytical and spectroscopic data and for **21** the structure was confirmed by X-ray diffraction (Figures 10 and 11, Table 1). As shown, the crystal structure involves  $\text{C}=\text{O} \dots \text{NH}$  hydrogen bonded pairs of benzamide molecules which are then each bonded by the remaining NH to  $\text{C}=\text{O}$  of the ylide (Figure 11). The hydrogen bonding parameters given in Table 1 are within the expected range.



**Figure 9.** Formation of adducts with other donor types.



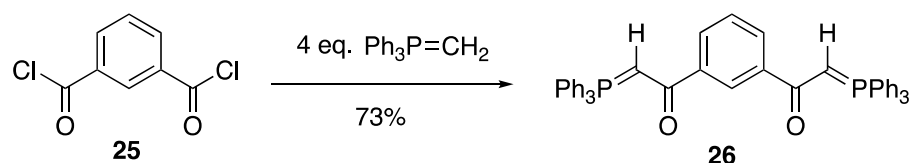
**Figure 10.** Molecular structure of **21** with anisotropic displacement ellipsoids drawn at the 50% probability level and the numbering system used.



**Figure 11.** Hydrogen bonding interactions in the crystal structure of **21** and schematic representation.

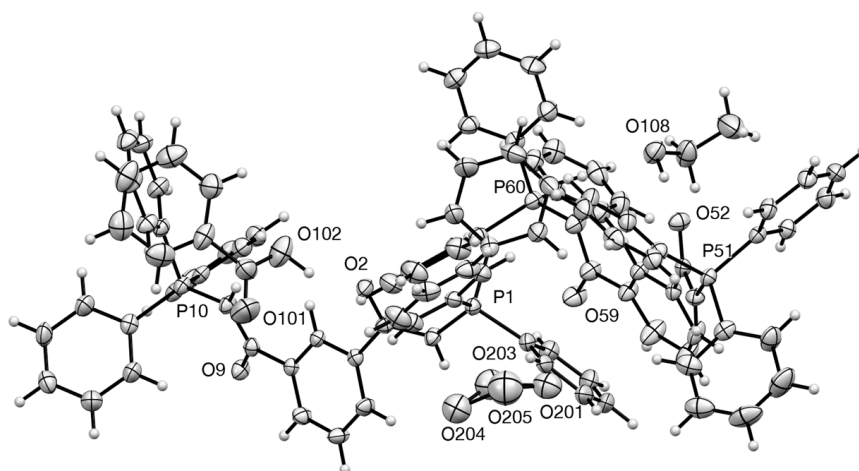
#### 2.4. Synthesis and Properties of a Bis(Stabilised Ylide)

It occurred to us that the hydrogen bonding interactions revealed by these studies could form the basis of molecular recognition and for this a bis(ylide) with carbonyl acceptor groups at a fixed distance apart and orientation would be ideal. We therefore prepared the *meta*-isomer **26** by reaction of benzene-1,3-dicarbonyl chloride **25** with 4 equiv. of  $\text{Ph}_3\text{P}=\text{CH}_2$  (Scheme 2). This was obtained as a high melting point solid from which it was difficult to remove the last traces of solvent, but the NMR data were in full agreement with the expected values. It might be noted that we prepared the *para* isomer of **26** some years ago and confirmed its structure by X-ray diffraction, while attempts to form the corresponding *ortho* isomer resulted in an unexpected rearrangement [28].



**Scheme 2.** Synthesis of bis(ylide) **26**.

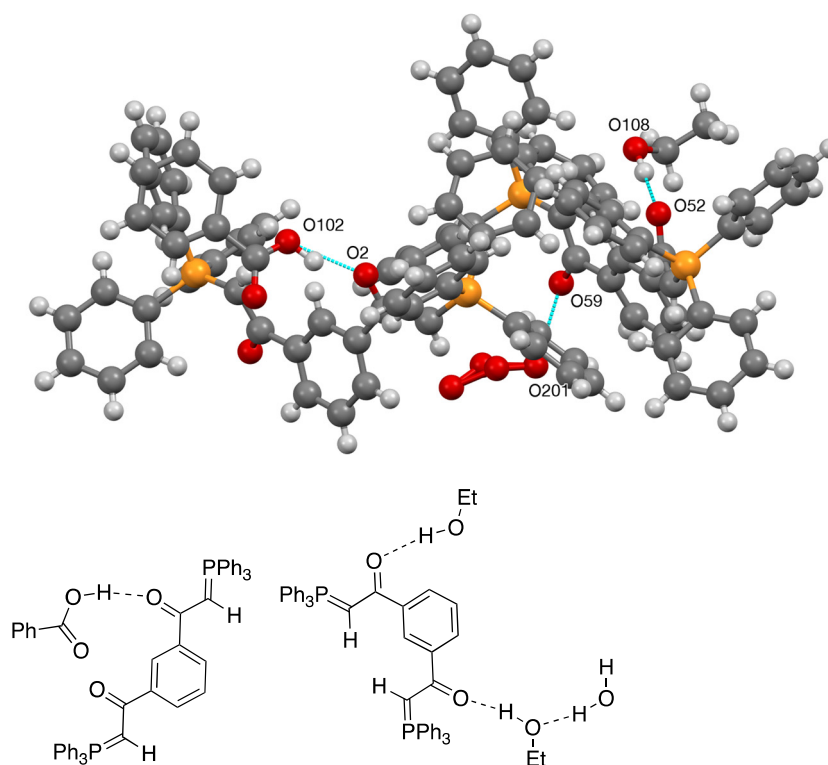
Treating a solution of **26** with benzoic acid in ethanol led to the deposition of crystals **27**, whose composition could only be determined by X-ray diffraction as containing two molecules of **26**, one of them bonded to a single benzoic acid and the other to two molecules of ethanol and one of water with disorder in the region of one EtOH/ $\text{H}_2\text{O}$  (Figures 12 and 13, Table 1).



**Figure 12.** Molecular structure of **27** with anisotropic displacement ellipsoids drawn at the 50% probability level and the numbering system used for non-C,H atoms.

The ready formation of this unexpectedly complex adduct shows that while bis(ylides) such as **26** have significant hydrogen bond acceptor properties, these can be difficult to control, and the practical use of such compounds for molecular recognition will require further detailed studies.





**Figure 13.** Hydrogen bonding interactions in the crystal structure of **27** and schematic representation.

### 3. Experimental Section

#### 3.1. General Experimental Details

NMR spectra were recorded on solutions in  $\text{CDCl}_3$  unless otherwise stated using a Varian Gemini 2000 instrument and chemical shifts are given in ppm to high frequency from  $\text{Me}_4\text{Si}$  (H, C) or  $\text{H}_3\text{PO}_4$  (P) with coupling constants  $J$  in Hz. IR spectra were recorded using the ATR technique on a Shimadzu IRAffinity 1S instrument. Melting points were recorded on a Gallenkamp 50W melting point apparatus or a Reichert hot-stage microscope. Elemental analysis was performed using a Carlo-Erba 1106 elemental analyser.

Methyl triphenylphosphoranylidenepyruvate **5** [29], benzoylpyruvic acid **8** [30], triphenylphosphoranylideneacetone [31], 1-phenyl-1-triphenylphosphoranylidenepropan-2-one [32], and triphenylphosphoranylideneacetophenone [31] were prepared by literature methods.

#### 3.2. Preparation of Adducts with Methyl Triphenylphosphoranylidenepyruvate

##### 3.2.1. Methyl Triphenylphosphoranylidenepyruvate—Benzoylpyruvic Acid Adduct **9**

A solution of methyl triphenylphosphoranylidenepyruvate **5** (0.72 g, 2 mmol) and benzoylpyruvic acid **8** (0.42 g, 2 mmol) in toluene (40 mL) was heated under reflux for 5 min and then evaporated. Recrystallisation of the residue from ethanol gave colourless crystals (0.74 g, 65%), mp 140–141 °C.

##### 3.2.2. Methyl Triphenylphosphoranylidenepyruvate—Benzoic Acid Adduct **10**

A solution of methyl triphenylphosphoranylidenepyruvate **5** (0.72 g, 2 mmol) and benzoic acid (0.24 g, 2 mmol) in toluene (40 mL) was heated under reflux for 5 min and then evaporated. Recrystallisation of the residue from ethanol gave yellow crystals (0.21 g, 21%), mp 139–140 °C. Found: C, 72.6; H, 4.7.  $\text{C}_{29}\text{H}_{25}\text{O}_5\text{P}$  requires C, 71.9; H, 5.2%. IR ( $\text{cm}^{-1}$ ): 1721, 1681, 1582, 1534, 1438, 1313, 1237, 1107, 851, 753, 722, 648.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.12 (2H, d,  $J$  9), 7.83–7.25 (18H, m), 4.93 (1H, d,  $J_{\text{H-P}}$  23), 3.81 (3H, s).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4 (d,  $J$  5, P=CHCO), 170.2 (CO<sub>2</sub>H), 165.9 (d,  $J$  22, CO<sub>2</sub>Me), 133.1 (d,  $J$  11, PPh C-2), 132.9 (PhCO<sub>2</sub>H C-4), 132.6 (d,  $J$  2, PPh C-4), 130.3 (PhCO<sub>2</sub>H C-1), 129.9 (2CH,

PhCO<sub>2</sub>H), 129.0 (d, *J* 13, PPh C-3), 128.1 (2CH, PhCO<sub>2</sub>H), 124.7 (d, *J* 92, PPh C-1), 58.8 (d, *J* 107, P=CH), 52.2 (OMe). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ + 17.3.

### 3.3. Preparation of Adducts with Triphenylphosphoranylideneacetone

#### 3.3.1. Triphenylphosphoranylideneacetone—Benzoic Acid Adduct 11

A solution of triphenylphosphoranylideneacetone (0.63 g, 2 mmol) and benzoic acid (0.24 g, 2 mmol) in toluene (40 mL) was heated under reflux for 5 min and then evaporated. Recrystallisation of the residue from ethanol gave colourless crystals (0.38 g, 44%), mp 132–133 °C. Found: C, 76.4; H, 5.7. C<sub>28</sub>H<sub>25</sub>O<sub>3</sub>P requires C, 76.4; H, 5.7%. IR (cm<sup>-1</sup>): 1701, 1437, 1107, 856, 798, 746, 715, 692. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.06 (2H, m), 7.75–7.16 (18H, m), 6.00 (1H, br s), 2.19 (3H, d, *J* 2, COMe). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 190.4 (COMe), 169.6 (CO<sub>2</sub>H), 133.8 (PhCO<sub>2</sub>H C-4), 133.2 (d, *J* 10, PPh C-2), 132.4 (d, *J* 2, PPh C-4), 129.7 (2CH, PhCO<sub>2</sub>H), 129.2 (PhCO<sub>2</sub>H C-1), 129.0 (d, *J* 12, PPh C-3), 127.9 (2CH, PhCO<sub>2</sub>H), 125.8 (d, *J* 91, PPh C-1), 56.3 (d, *J* 105, P=CH), 28.0 (d, *J* 14, Me). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ + 14.8.

#### 3.3.2. Triphenylphosphoranylideneacetone—Phenylacetic Acid Adduct 13

A solution of triphenylphosphoranylideneacetone (0.63 g, 2 mmol) and phenylacetic acid (0.27 g, 2 mmol) in toluene (40 mL) was heated under reflux for 5 min and then evaporated. Recrystallisation of the residue from ethanol gave yellow crystals (0.69 g, 77%), mp 98–100 °C. Found: C, 76.4; H, 6.3. C<sub>29</sub>H<sub>27</sub>O<sub>3</sub>P requires C, 76.6; H, 6.0%. IR (cm<sup>-1</sup>): 1700, 1315, 1231, 1105, 996, 857, 749, 692. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.65 (1H, br s), 7.73–7.15 (20H, m), 3.48 (2H, s), 2.15 (3H, d, *J* 2, COMe). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 190.2 (COMe), 174.6 (CO<sub>2</sub>H), 135.7 (PhCH<sub>2</sub>CO<sub>2</sub>H C-1), 133.0 (d, *J* 10, PPh C-2), 132.5 (d, *J* 2, PPh C-4), 129.3 (2CH, PhCH<sub>2</sub>CO<sub>2</sub>H), 129.0 (d, *J* 12, PPh C-3), 128.1 (2CH, PhCH<sub>2</sub>CO<sub>2</sub>H), 126.2 (PhCH<sub>2</sub>CO<sub>2</sub>H C-4), 125.3 (d, *J* 91, PPh C-1), 56.1 (d, *J* 103, P=CH), 42.3 (CH<sub>2</sub>), 26.8 (d, *J* 14, Me). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ + 15.0.

#### 3.3.3. Triphenylphosphoranylideneacetone—Diphenylacetic Acid Adduct 14

A solution of triphenylphosphoranylideneacetone (0.63 g, 2 mmol) and diphenylacetic acid (0.42 g, 2 mmol) in toluene (40 mL) was heated under reflux for 5 min and then evaporated. Recrystallisation of the residue from ethanol gave colourless crystals (0.88 g, 84%), mp 99–100 °C. Found: C, 79.2; H, 5.8. C<sub>35</sub>H<sub>31</sub>O<sub>3</sub>P requires C, 79.2; H, 5.9%. IR (cm<sup>-1</sup>): 1698, 1112, 996, 746, 716. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.10 (1H, br s), 7.75–7.11 (25H, m), 4.93 (1H, s), 2.14 (3H, s, COMe). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 190.5 (COMe), 175.2 (CO<sub>2</sub>H), 140.2 (Ph<sub>2</sub>CHCO<sub>2</sub>H C-1), 133.2 (d, *J* 10, PPh C-2), 132.5 (d, *J* 2, PPh C-4), 129.0 (d, *J* 12, PPh C-3), 128.9 (4CH, Ph<sub>2</sub>CHCO<sub>2</sub>H), 128.2 (4CH, Ph<sub>2</sub>CHCO<sub>2</sub>H), 126.5 (Ph<sub>2</sub>CHCO<sub>2</sub>H C-4), 125.3 (d, *J* 91, PPh C-1), 58.2 (Ph<sub>2</sub>CH), 56.0 (d, *J* 100, P=CH), 26.8 (d, *J* 15, Me). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ + 15.0.

#### 3.3.4. Triphenylphosphoranylideneacetone—2-Phenylbutyric Acid Adduct 15

A solution of triphenylphosphoranylideneacetone (0.63 g, 2 mmol) and 2-phenylbutyric acid (0.33 g, 2 mmol) in toluene (40 mL) was heated under reflux for 5 min and then evaporated. Recrystallisation of the residue from ethanol gave colourless crystals (0.47 g, 49%), mp 113–114 °C. Found: C, 77.1; H, 6.2. C<sub>31</sub>H<sub>31</sub>O<sub>3</sub>P requires C, 77.2; H, 6.5%. IR (cm<sup>-1</sup>): 1708, 1575, 1106, 860, 719, 699. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.78–7.20 (21H, m), 3.36 (1H, t, *J* 7), 2.10 (3H, s), 2.08 (1H, m), 1.72 (1H, m), 0.85 (3H, t, *J* 7). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 190.6 (COMe), 177.0 (CO<sub>2</sub>H), 140.2 (PhCH(Et)CO<sub>2</sub>H C-1), 133.1 (d, *J* 10, PPh C-2), 132.4 (d, *J* 2, PPh C-4), 129.0 (d, *J* 12, PPh C-3), 128.20 (2CH, PhCH(Et)CO<sub>2</sub>H), 128.16 (2CH, PhCH(Et)CO<sub>2</sub>H), 126.6 (PhCH(Et)CO<sub>2</sub>H C-4), 125.9 (d, *J* 91, PPh C-1), 55.4 (d, *J* 105, P=CH), 54.0 (CH-CO<sub>2</sub>H), 27.1 (d, *J* 15, Me), 26.8 (CH<sub>2</sub>), 12.3 (CH<sub>3</sub>). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ + 14.9.

### 3.4. Preparation of Adducts with Triphenylphosphoranylideneacetophenone

#### Triphenylphosphoranylideneacetophenone—Diphenylacetic Acid Adduct 17

A solution of triphenylphosphoranylideneacetophenone (0.70 g, 2 mmol) and diphenylacetic acid (0.42 g, 2 mmol) in toluene (40 mL) was heated under reflux for 5 min and then evaporated. Recrystallisation of the residue from ethanol gave orange crystals (0.87 g, 77%), mp 123–124 °C. Found: C, 80.8; H, 5.5.  $C_{40}H_{33}O_3P$  requires C, 81.1; H, 5.6%. IR ( $cm^{-1}$ ): 1746, 1587, 1437, 1205, 1200, 881, 745, 697, 634.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  8.02–7.18 (31H, m), 4.95 (1H, s).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  185.8 (COPh), 174.9 ( $CO_2H$ ), 140.1 (d,  $J$  10, COPh C-1), 139.6 ( $Ph_2CHCO_2H$  C-1), 133.2 (d,  $J$  10, PPh C-2), 132.4 (PPh C-4), 129.9 (COPh C-4), 128.9 (d,  $J$  12, PPh C-3), 128.8 (4CH,  $Ph_2CHCO_2H$ ), 128.1 (4CH,  $Ph_2CHCO_2H$ ), 127.8 (COPh C-2), 127.3 (COPh C-3), 126.5 ( $Ph_2CHCO_2H$  C-4), 125.5 (d,  $J$  91, PPh C-1), 57.6 ( $Ph_2CH$ ), 52.5 (d,  $J$  106, P=CH).  $^{31}P$  NMR (121 MHz,  $CDCl_3$ )  $\delta$  + 18.0.

### 3.5. Preparation of Adducts with 1-Phenyl-1-triphenylphosphoranylidenepropan-2-One

#### 1-Phenyl-1-triphenylphosphoranylidenepropan-2-One—Benzoic Acid Adduct 12

A solution of 1-phenyl-1-triphenylphosphoranylidenepropan-2-one (39 mg, 0.1 mmol) and benzoic acid (12.2 mg, 0.1 mmol) in  $CDCl_3$  was analysed by  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  187.0 (COPh), 169.7 ( $CO_2H$ ), 137.8 (d,  $J$  13, P=C-Ph C-1), 134.4 (d,  $J$  5, P=C-Ph C-2,6), 133.7 (d,  $J$  9, PPh C-2), 132.2 ( $PhCO_2H$  C-4), 132.0 (PPh C-4), 131.8 (2C,  $PhCO_2H$ ), 129.8 ( $PhCO_2H$  C-1), 128.6 (d,  $J$  13, PPh C-3), 127.9 (2CH,  $PhCO_2H$ ), 127.7 (2C, P=C-Ph), 125.7 (d,  $J$  91, PPh C-1), 125.7 (P=C-Ph C-4), 75.1 (d,  $J$  118, P=C), 24.3 (Me). All signals are within  $\pm 2$  ppm of those for the separate components except 169.7 (free acid 172.6) and 75.1 (free ylide 71.0).

### 3.6. Formation of Solution Adducts with Triphenylphosphoranylideneacetone

For this, 0.1 M solutions of triphenylphosphoranylideneacetone and the potential donor in  $CDCl_3$  were prepared, and  $^{13}C$  NMR spectra were obtained. All signals for the ylide carbons in the mixture were within  $\pm 2$  ppm of those for the pure ylide except those for P=C, which were shifted as shown in Table 4. This provided evidence for the formation of adducts between the ylide and acetic acid **19**, benzyl alcohol **20**, benzamide **21**, thiobenzamide **22**, benzenesulfinic acid **23**, and diphenylphosphinic acid **24**

### 3.7. Preparation of Adducts with Triphenylphosphoranylideneacetone

#### 3.7.1. Triphenylphosphoranylideneacetone—Benzamide Adduct 21

A solution of triphenylphosphoranylideneacetone (0.79 g, 2.5 mmol) and benzamide (0.30 g, 2.5 mmol) in ethanol (5 mL) was heated to the boil for 5 min and allowed to cool. After 18 h, the solid that had formed was filtered off to give **21** (0.82 g, 75%) as colourless crystals, mp 151–153 °C. Found: C, 76.5; H, 6.0; N, 3.2.  $C_{28}H_{26}NO_2P$  requires C, 76.5; H, 6.0; N, 3.2%. IR ( $cm^{-1}$ ) 1686, 1629, 1576, 1508, 1153, 1110, 986, 869, 752, 722, 694, 637.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.90–7.80 (2H, m), 7.70–7.35 (18H, m), 6.65 (1H, br s), 5.72 (1H, br s), 3.73 (1H, br d,  $J$  23), 2.09 (3H, d,  $J$  2).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  190.7 (CO), 169.4 ( $CONH_2$ ), 133.4 (C), 132.9 (d,  $J$  10, PPh C-2), 131.9 (d,  $J$  3, PPh C-4), 131.5 (CH), 128.7 (d,  $J$  12, PPh C-3), 128.2 (2CH), 127.5 (2CH), 126.9 (d,  $J$  90, PPh C-1), 52.2 (d,  $J$  107, P=CH), 28.3 (d,  $J$  16,  $CH_3$ ).  $^{31}P$  NMR (121 MHz,  $CDCl_3$ )  $\delta$  + 15.5.

#### 3.7.2. Triphenylphosphoranylideneacetone—Thiobenzamide Adduct 22

A solution of triphenylphosphoranylideneacetone (0.79 g, 2.5 mmol) and thiobenzamide (0.34 g, 2.5 mmol) in ethanol (2 mL) was heated to the boil for 5 min and allowed to cool. After 10 days, the solid that had formed was filtered off to give **22** (0.73 g, 65%) as colourless crystals, mp 140–141 °C. Found: C, 73.6; H, 5.8; N, 3.0.  $C_{28}H_{26}NOPS$  requires C, 73.8; H, 5.8; N, 3.1%. IR ( $cm^{-1}$ ) 1508, 1437, 1396, 1110, 866, 750, 717, 692.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  8.40 (1H, br s), 7.90–7.80 (2H, m), 7.72 (1H, br s), 7.70–7.35 (18H, m), 3.80 (1H, br d,  $J$  23), 2.09 (3H, d,  $J$  2).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  201.7 (CS), 190.3 (CO), 138.7 (C), 132.8 (d,  $J$  10, PPh C-2), 132.1 (d,  $J$  3, PPh C-4), 131.3 (CH), 128.8 (d,  $J$  12, PPh C-3),

127.8 (2CH), 127.5 (2CH), 126.4 (d, *J* 90, PPh C-1), 53.6 (d, *J* 108, P=CH), 28.0 (d, *J* 16, CH<sub>3</sub>). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ + 15.5.

### 3.8. Preparation of Adducts with 1,3-Bis(triphenylphosphoranylideneacetyl)benzene **26**

#### 3.8.1. 1,3-Bis(triphenylphosphoranylideneacetyl)benzene **26**

A suspension of methyltriphenylphosphonium bromide (17.6 g, 50 mmol) in dry THF (150 mL) was stirred under nitrogen while *n*-butyllithium (2.5M in hexane, 20 mL, 50 mmol) was added slowly. The mixture was stirred for 20 min, and then a solution of isophthaloyl dichloride **25** (2.5 g, 12.5 mmol) in THF (20 mL) was added. After stirring for 18 h, the mixture was poured into water and extracted with ethyl acetate (3 × 50 mL). Drying and evaporation followed by recrystallisation from EtOAc/CH<sub>2</sub>Cl<sub>2</sub> gave the product **26** (6.2 g, 73%) as pale-yellow crystals, mp > 300 °C. Found: C, 79.8; H, 4.8. C<sub>46</sub>H<sub>36</sub>O<sub>2</sub>P<sub>2</sub> requires C, 80.9; H, 5.3%. IR (cm<sup>-1</sup>) 1585, 1508, 1466, 1436, 1107, 870, 750, 732, 693. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.60 (1H, t, *J* 1.6), 8.01 (2H, dt, *J* 7.5, 1.6), 7.75–7.68 (12H, m), 7.60–7.40 (18H, m), 7.35 (1H, t, *J* 7.5), 4.56 (2H, br s). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 184.8 (CO), 140.5 (d, *J* 15, 2 C–CO), 133.2 (d, *J* 10, PPh C-2), 131.9 (PPh C-4), 128.8 (d, *J* 12, PPh C-3), 128.1 (2CH), 127.2 (CH), 127.1 (d, *J* 91, PPh C-1), 125.4 (C), 50.8 (d, *J* 110, P=C). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ + 17.8.

#### 3.8.2. 1,3-Bis(triphenylphosphoranylideneacetyl)benzene—Benzoic Acid Adduct **27**

The bis(ylide) **26** (0.34 g, 0.5 mmol) and benzoic acid (0.12 g, 1.0 mmol) were dissolved with warming in ethanol (2 mL), and the mixture was allowed to cool and stored at RT until an adduct (0.29 g, 72%) was obtained as colourless crystals, mp 154–156 °C. These were found by X-ray diffraction to be an adduct of formula (26)<sub>2</sub>•PhCO<sub>2</sub>H•(EtOH)<sub>2</sub>•H<sub>2</sub>O. Found: C, 77.4; H, 5.9. C<sub>103</sub>H<sub>92</sub>O<sub>9</sub>P<sub>4</sub> requires C, 77.4; H, 5.8%.

### 3.9. X-ray Structure Determination of Adducts

Data were collected using graphite monochromated Mo Kα radiation λ = 0.71073 Å. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/getstructures>. The structure was solved by direct methods and refined by full-matrix least-squares against F<sup>2</sup> (SHELXL, Version 2018/3 [33]).

#### 3.9.1. Methyl Triphenylphosphoranylideneacetylpyruvate—Benzoylpyruvic Acid Adduct **9**

Crystal data for C<sub>32</sub>H<sub>27</sub>O<sub>7</sub>P, *M* = 554.51 g mol<sup>-1</sup>, colourless prism, crystal dimensions 0.19 × 0.10 × 0.10 mm, triclinic, space group P-1 (No. 2), *a* = 10.4270(10), *b* = 10.4963(10), *c* = 29.347(3) Å, α = 80.680(2), β = 88.251(2), γ = 63.914(2)°, *V* = 2843.6(5) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.295 g cm<sup>-3</sup>, *T* = 293 K, *R*<sub>1</sub> = 0.0645, *R*<sub>w</sub>2 = 0.1166 for 2698 reflections with *I* > 2σ(*I*), and 738 variables. Data were deposited at the Cambridge Crystallographic Data Centre as CCDC 2169369.

#### 3.9.2. Triphenylphosphoranylideneacetone—Benzoic Acid Adduct **11**

Crystal data for C<sub>28</sub>H<sub>25</sub>O<sub>3</sub>P, *M* = 440.45 g mol<sup>-1</sup>, colourless prism, crystal dimensions 0.10 × 0.10 × 0.10 mm, orthorhombic, space group Pna2<sub>1</sub> (No. 33), *a* = 17.924(4), *b* = 9.364(2), *c* = 28.710(6) Å, *V* = 4819.1(17) Å<sup>3</sup>, *Z* = 8, *D*<sub>calc</sub> = 1.214 g cm<sup>-3</sup>, *T* = 293 K, *R*<sub>1</sub> = 0.0794, *R*<sub>w</sub>2 = 0.1556 for 8656 reflections with *I* > 2σ(*I*), and 586 variables. Data were deposited at the Cambridge Crystallographic Data Centre as CCDC 2169371.

#### 3.9.3. Triphenylphosphoranylideneacetone—Benzamide Adduct **21**

Crystal data for C<sub>28</sub>H<sub>26</sub>NO<sub>2</sub>P, *M* = 439.47 g mol<sup>-1</sup>, colourless prism, crystal dimensions 0.15 × 0.10 × 0.10 mm, monoclinic, space group P2<sub>1</sub>/n (No. 14), *a* = 10.9414(3), *b* = 15.8906(6), *c* = 14.1127(3) Å, β = 100.9000(10)°, *V* = 2409.44(12) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.211 g cm<sup>-3</sup>, *T* = 293 K, *R*<sub>1</sub> = 0.0384, *R*<sub>w</sub>2 = 0.0937 for 2370 reflections with *I* > 2σ(*I*), and 298 variables. Data were deposited at the Cambridge Crystallographic Data Centre as CCDC 2169368.

### 3.9.4. 1,3-Bis(triphenylphosphoranylideneacetyl)benzene—Benzoic Acid Adduct 27

Crystal data for  $C_{101}H_{88}O_9P_4$ ,  $M = 1569.70 \text{ g mol}^{-1}$ , colourless prism, crystal dimensions  $0.14 \times 0.10 \times 0.03 \text{ mm}$ , triclinic, space group P-1 (No. 2),  $a = 15.212(2)$ ,  $b = 17.837(2)$ ,  $c = 18.156(2) \text{ \AA}$ ,  $\alpha = 100.322(2)$ ,  $\beta = 107.860(2)$ ,  $\gamma = 110.549(2)^\circ$ ,  $V = 4157.0(9) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.254 \text{ g cm}^{-3}$ ,  $T = 125 \text{ K}$ ,  $R1 = 0.060$ ,  $Rw2 = 0.1578$  for 9039 reflections with  $I > 2\sigma(I)$ , and 1056 variables. Data were deposited at the Cambridge Crystallographic Data Centre as CCDC 2169370.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics11020050/s1>, Figures S1–S16: selected NMR spectra; cif and check-cif files for 9, 11, 21 and 27.

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