# Unexpected Rearrangement Leading to Formation of a 1,3-Bis(triphenylphosphonio)prop-1-en-3-idyl Carboxylate

## R. Alan Aitken,\*<sup>[a]</sup> Lee P. Cleghorn,<sup>[a]</sup> Rebecca M. Leitch,<sup>[a]</sup> Louis C. Morrill,<sup>[a]</sup> and Alexandra M. Z. Slawin<sup>[a]</sup>

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Whereas biphenyl-4,4'-dicarbonyl dichloride reacts with methylenetriphenylphosphorane to give the expected bis-(acylylide) **1**, the same reaction of biphenyl-2,2'-dicarbonyl dichloride results in a multistep rearrangement leading to the

### Introduction

Delocalisation of the negative charge associated with a phosphonium ylide results in considerable stabilisation, and we have previously reported the isolation of a variety of such compounds as stable solids and their X-ray structure determination.<sup>[1]</sup> Some time ago, we described the synthesis of stable bis(keto ylides) by treatment of diacyl dichlorides with simpler ylides,  $Ph_3P=CHR$ .<sup>[2]</sup> In a continuation of this study, we now report that, whereas biphenyl-4,4'-dicarbonyl dichloride reacts with  $Ph_3P=CH_2$  in the expected way to give the bis(keto ylide), the corresponding reaction of the isomeric biphenyl-2,2'-dicarbonyl dichloride leads by an unprecedented rearrangement to a stable zwitterionic compound containing the rare 1,3-bis(triphenylphosphonio)-allyl anion function.

### **Results and Discussion**

In connection with a study of the keto ylide function,  $Ph_3P=CH-C(=O)$ , as a hydrogen-bond acceptor, we were interested to prepare a series of compounds with two such groups separated by a spacer of defined length and geometry. Reaction of biphenyl-4,4'-dicarbonyl dichloride with 4 equiv. of methylenetriphenylphosphorane in THF proceeded with transylidation<sup>[3]</sup> to give a moderate yield of the expected bis(keto ylide) **1** (Scheme 1). This was obtained as a high-melting solid, which gave the expected spectroscopic data, including a single <sup>31</sup>P NMR signal at  $\delta = +17.8$  ppm. Slow concentration of a dilute solution in CH<sub>2</sub>Cl<sub>2</sub> yielded crystals suitable for X-ray diffraction, and the resulting structure is shown in Figure 1. The only previous structural

zwitterionic 2-[1,3-bis(triphenylphosphonio)prop-1-en-3-id-2-yl]biphenyl-2'-carboxylate **2**. X-ray crystal structures of both **1** and **2** are reported.

study of bis(keto ylides) involved compounds with two carbonyl groups between the ylide functions, thus allowing significant interaction between them.<sup>[4]</sup> Here, in contrast, the keto ylide functions are well separated and show the structural features characteristic of isolated keto ylides, including substantial delocalisation equivalent to a significant contribution from the (*Z*)-aligned coplanar  $P^+-C=C-O^-$  form.<sup>[4]</sup>



Scheme 1.

In an attempt to generate a bis(keto ylide) with the two functions closer together, the isomeric biphenyl-2,2'-dicarbonyl dichloride was subjected to identical reaction conditions. Again a yellow crystalline solid was obtained, which had the correct molecular weight for the expected bis(keto ylide) and gave elemental analysis results consistent with the expected formula as a trihydrate. However, its spectroscopic properties revealed a radically different structure. The <sup>31</sup>P NMR spectrum contained two signals of equal intensity at  $\delta = +9.2$  and +6.5 ppm, neither in the range expected for a keto ylide. The <sup>13</sup>C NMR spectrum contained signals for a carboxyl carbon atom not coupled to a phosphorus atom ( $\delta = 170.8$  ppm) and a series of three carbon atoms all coupled to two phosphorus nuclei [ $\delta$  = 169.3 (dd, J = 7, 6 Hz), 61.6 (dd, J = 99, 16 Hz), 57.3 (dd, J = 123, 8 Hz)] in which both the chemical shifts and coupling constants were consistent with the presence of  $Ph_3P^+$ -CH=C-CH=PPh<sub>3</sub>. This was confirmed by a single-crystal X-ray

 <sup>[</sup>a] EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST, UK Fax: +44-1334-463808
 E-mail: raa@st-and.ac.uk

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Figure 1. X-ray structure of compound 1. Selected bond lengths [Å], angles and torsion angles [°]; P(1)–C(19) 1.718(2), C(19)–C(20) 1.399(3), C(20)–O(20) 1.266(3); P(1)–C(19)–C(20) 116.79(18), C(19)–C(20)–O(20) 121.8(2), P(1)–C(19)–C(20)–O(20) 7.0(3).

diffraction study, which showed the zwitterionic structure **2** with a carboxylate anion on one ring of the biphenyl and the 1,3-bis(triphenylphosphonio)allyl anion group on the other (Figure 2).



Figure 2. X-ray structure of compound **2**. Selected bond lengths [Å], angles and torsion angles [°]; P(1)–C(19) 1.725(3), C(19)–C(20) 1.391(3), C(20)–C(21) 1.394(4), C(21)–P(21) 1.720(3); P(1)–C(19)–C(20) 126.0(2), C(19)–C(20)–C(21) 125.0(2), C(19)–C(20)–C(40) 112.9(2), C(40)–C(20)–C(21) 122.0(2), C(20)–C(21)–P(21) 133.0(2), C(40)–C(20)–C(19)–P(1) 175.27(19), C(40)–C(20)–C(21)–P(21) 11.0(4).

Whereas the bond lengths are consistent with a fully delocalised allyl anion structure in the solid state, the spectroscopic data, particularly the magnitude of the P–C coupling constants, point to a greater contribution from the more localised structure **2A** with two clearly distinct phosphorus atoms in solution (Scheme 2). Very few compounds containing this type of structure have been reported before, and their syntheses involve several steps, but the data obtained here are in excellent agreement with these previous examples. Schmidbaur and co-workers obtained the salt **3** and determined its X-ray structure.<sup>[5]</sup> This showed a delocalised allyl anion with essentially equal C(1)–C(2) and C(2)–C(3) bond lengths, but the <sup>13</sup>C NMR spectroscopic data were more consistent with the localised structure (Table 1). A short time later, Bestmann and Kisielowski reported addition of  $Ph_3P=CH_2$  to alkynylphosphonium salts to give compounds  $4^{[6]}$  whose spectroscopic data also show the same patterns as observed for **2** (Table 1 and Scheme 3).



Scheme 2.

Table 1. Selected NMR spectroscopic data for 2 and similar compounds 3 and 4.

Compound	$\delta(^{31}P)$ [ppm]	$\delta$ <sup>(13</sup> C) [ppm] ( $J_{CP}$ [Hz])		
1	( ) <b>u</b> 1 J	C-1	C-2	C-3
2A	6.5, 9.2	57.3 (123, 8)	169.3 (7, 6)	61.6 (99, 16)
3	5.5, 6.1	56.7 (119, 9)	167.6 (7, 5)	58.5 (106, 18)
4a	9.9, 11.1	59.5 (122, 6)	177.1 (8, 5)	61.0 (102, 16)
4b	11.4, 11.5	58.4 (124, 6)	167.4 (8, 6)	56.3 (108, 15)
<b>4b</b> <sup>[a]</sup>	10.3, 11.4	59.4 (121, 7)	171.0 (7, 7)	60.9 (102, 17)

[a] Slightly different data later reported by Schmidpeter and co-workers.<sup>[7]</sup>



Scheme 3. Similar structures reported previously.

Further evidence for the structure of **2** was obtained by dissolving a sample in DCl/D<sub>2</sub>O (Scheme 4). The resulting solution gave a  ${}^{31}$ P NMR spectrum consisting of doublets



at  $\delta = +11.1$  and +21.0 ppm with a four-bond coupling constant of 7.4 Hz. This behaviour, and particularly the appearance of P-P coupling (absent in the non-protonated species), is exactly analogous to that observed for 4b, which, upon protonation with HBr, gave  ${}^{31}$ P NMR signals at  $\delta$ = +12.6 and +20.4 ppm ( ${}^{4}J_{P,P}$  = 4.6 Hz).<sup>[6]</sup> The <sup>1</sup>H NMR spectrum showed a broad doublet at  $\delta = 6.30$  ppm (J = 8 Hz) attributed to the newly formed CHD-P<sup>+</sup> function, whereas the <sup>13</sup>C NMR spectrum showed a signal for CO<sub>2</sub>H at  $\delta = 167.8$  ppm and a marked lowering of the chemical shift of the doublets due to C-1 of PPh to  $\delta = 121.3$  (J = 91 Hz) and 120.2 (J = 87 Hz) ppm. Slow concentration of this solution led to deposition of small colourless crystals. X-ray diffraction studies of these failed to give data of suitable quality for publication, but key features of the preliminary structure obtained were in agreement with those expected for 5. Thus, whereas the central carbon atom, PCCCP, was still planar (angle sum 359.9°), bond lengths and angles clearly indicated one singly bonded C-CH<sub>2</sub>PPh<sub>3</sub><sup>+</sup> [C–C 1.58(2), C–P 1.746(15) Å, C–C–P 117.6(9)°] and one doubly bonded  $C=CHPPh_3^+$  [C-C 1.386(18), C–P 1.790(13) Å, C–C–P 123.2(10)°].





We propose that the formation of compound  $2 \mod 2$  most likely proceeds according to the mechanism shown in Scheme 5. In this, the acylation of one molecule of ylide



Scheme 5.

 $Ph_3P=CH_2$  by an acyl chloride is followed not by the normal deprotonation, but, at least in a small equilibrium concentration, by nucleophilic attack of a second ylide molecule generating an alkoxide function. This is ideally placed to interact with the second acyl chloride producing a sevenmembered ring lactone. A series of two deprotonations by the remaining molecules of  $Ph_3P=CH_2$  then causes ringopening to give the carboxylate and formation of the diphosphonioallyl anion function.

#### Conclusions

The unexpected rearrangement reported here makes available a compound containing the unusual bis(triphenylphosphonio)allyl anion function in two simple steps from commercially available starting materials, and should facilitate further studies on the structure and reactivity of such systems.

## **Experimental Section**

**General:** M.p.: Reichert hot-stage microscope, uncorrected values. NMR: Bruker AM300 (300 MHz for <sup>1</sup>H, 75 MHz for <sup>13</sup>C, 121 MHz for <sup>31</sup>P); internal TMS as reference for <sup>1</sup>H and <sup>13</sup>C and external 85% H<sub>3</sub>PO<sub>4</sub> as reference for <sup>31</sup>P. MS: Micromass LCT by using electrospray ionization.

Biphenyl-4,4'-bis(2-triphenylphosphoranylideneethanone) (1): A suspension of methyltriphenylphosphonium bromide (17.9 g, 50 mmol) in dry THF (100 cm<sup>3</sup>) was stirred under nitrogen, while butyllithum in hexane (2.5 M, 20 cm<sup>3</sup>, 50 mmol) was added slowly. After 30 min, a solution of biphenyl-4,4'-dicarbonyl dichloride<sup>[8]</sup> (3.49 g, 12.5 mmol) in dry THF (50 cm<sup>3</sup>) was added dropwise, and the mixture was stirred for 18 h. The mixture was added to water and extracted with ethyl acetate. The ethyl acetate extracts were washed thoroughly with water to remove Ph3PMe+Cl-, dried and concentrated to give the product 1 (5.1 g, 54%) as pale yellow crystals, m.p. 256–262 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.00 (d, J = 6 Hz, 4 H), 7.75-7.40 (m, 34 H), 4.45 (br. s, 2 H, CH=P) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 184.3 (CO), 141.8 (C-1, C-1'), 140.0 (d, J = 15 Hz, C-4, C-4'), 133.1 (d, J = 9 Hz, C-2 of PPh), 132.0 (C-4 of PPh), 128.8 (d, J = 13 Hz, C-3 of PPh), 127.3 (4 CH), 126.4 (4 CH), 127.0 (d, J = 91 Hz, C-1 of PPh), 51.0 (d, J = 111 Hz, C=P) ppm. <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta = +17.8$  ppm. MS (ES<sup>+</sup>): m/z = 781 [M + Na<sup>+</sup>], 759  $[M + H^+]$ . C<sub>52</sub>H<sub>40</sub>O<sub>2</sub>P<sub>2</sub> (758.8): calcd. C 82.31, H 5.31; found C 82.44, H 5.70.

**2'-[1-(Triphenylphosphonio)-3-(triphenylphosphoranylidene)prop-1en-2-yl]biphenyl-2-carboxylate Trihydrate (2):** The same procedure as above, but using biphenyl-2,2'-dicarbonyl dichloride<sup>[9]</sup> gave the product **2** (1.89 g, 20%) as yellow prisms, m.p. 214–218 °C. <sup>1</sup>H NMR (CD<sub>3</sub>SOCD<sub>3</sub>):  $\delta$  = 7.77–7.72 (m, 3 H), 7.65–7.54 (m, 17 H), 7.43 (td, *J* = 8, 3 Hz, 6 H), 7.37–7.32 (m, 1 H), 7.17–7.09 (m, 2 H), 6.95 (dd, *J* = 12, 7 Hz, 6 H), 6.89 (d, *J* = 8 Hz, 1 H), 6.78–6.76 (m, 2 H), 5.56 (d, *J* = 8 Hz, 1 H, CH-P), 3.14 (d, *J* = 14 Hz, 1 H, CH=P) ppm. <sup>13</sup>C NMR (CD<sub>3</sub>SOCD<sub>3</sub>):  $\delta$  = 170.8 (CO), 169.3 (dd, *J* = 7, 6 Hz, PCCCP), 142.0 (C), 140.3 (d, *J* = 5 Hz, 1 C), 140.1 (d, *J* = 5 Hz, 1 C), 138.1 (C), 133.3 (d, *J* = 3 Hz, C-4 of PPh), 132.8 (d, *J* = 10 Hz, C-2 of PPh), 130.6 (CH), 129.8 (d, *J* = 12 Hz, C-3 of PPh), 129.4 (d, *J* = 12 Hz, C-3 of PPh), 127.7 (CH), 127.6 (CH), 127.5 (CH), 127.0 (CH), 126.2 (d, *J* = 90 Hz, C-1 of PPh),

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126.1 (CH), 125.3 (CH), 124.8 (CH), 123.5 (d, J = 87 Hz, C-1 of PPh), 61.6 (dd, J = 99, 16 Hz, P-C), 57.3 (dd, J = 123, 8 Hz, P=C) ppm. <sup>31</sup>P NMR (CD<sub>3</sub>SOCD<sub>3</sub>):  $\delta = +9.2$ , +6.5 ppm. MS (ES<sup>+</sup>): m/z = 781 [M + Na], 759 [M + H]. C<sub>52</sub>H<sub>40</sub>O<sub>2</sub>P<sub>2</sub>·3H<sub>2</sub>O (812.9): calcd. C 76.83, H 5.70; found C 76.83, H 5.75.

**Crystal Data for 1:**  $C_{52}H_{40}O_2P_2$ ·4C $H_2Cl_2$ , M = 1098.48, colourless prism, crystal dimensions  $0.10 \times 0.10 \times 0.10$  mm, triclinic, space group  $P\bar{1}$ , a = 9.0123(16), b = 11.924(2), c = 14.115(2) Å, a = 112.396(11),  $\beta = 99.650(12)$ ,  $\gamma = 103.341(12)^\circ$ , V = 1308.4(4) Å<sup>3</sup>, Z = 1,  $D_c = 1.394$  Mg m<sup>-3</sup>, T = 93(2) K, 13040 reflections, 4746 of which unique ( $R_{int} = 0.055$ ),  $R_1 = 0.0543$ ,  $wR_2 = 0.1392$  for 4160 reflections with  $I > 2\sigma(I)$  and 307 variables. Data were recorded by using a Rigaku MM007, Mo- $K_a$  radiation (confocal optic,  $\lambda = 0.71073$  Å) and Saturn detector. The structure was solved by direct methods and refined by using full-matrix least-squares methods.

**Crystal Data for 2:**  $C_{52}H_{40}O_2P_2 \cdot 3H_2O$ , M = 812.83, yellow prism, crystal dimensions  $0.15 \times 0.15 \times 0.10$  mm, triclinic, space group  $P\bar{1}$ , a = 11.616(3), b = 12.001(3), c = 16.208(5) Å, a = 103.506(8),  $\beta = 107.254(5)$ ,  $\gamma = 90.610(8)^\circ$ , V = 2090.3(11) Å<sup>3</sup>, Z = 2,  $D_c = 1.291$  Mgm<sup>-3</sup>, T = 93(2) K, 13388 reflections, 7398 of which unique  $(R_{int} = 0.056)$ ,  $R_1 = 0.0579$ ,  $wR_2 = 0.1457$  for 5632 reflections with  $I > 2\sigma(I)$  and 551 variables. Data were recorded by using a Rigaku MM007, Mo- $K_a$  radiation (confocal optic,  $\lambda = 0.71073$  Å) and Mercury detector. The structure was solved by direct methods and refined by using full-matrix least-squares methods.

CCDC-760279 (1) and -760280 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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