

# Facile syntheses and interconversions between simple phosphiranium and phosphirenium salts

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## Abstract

The first phosphiranium salt, 1-methyl-1-phenylphosphiranium triflate (**1**), has been isolated in 73% yield from the reaction between 1-phenylphosphirane and methyl triflate in benzene. The crystal and molecular structures of **1** have been determined. The phosphiranium ion in **1** undergoes ring opening with water to give ( $\pm$ )-ethylmethylphenylphosphine oxide, and reacts with primary alcohols to give ( $\pm$ )-alkoxyethylmethylphenylphosphonium ions. Treatment of **1** with dimethyl- or methylphenylacetylene in dichloromethane affords over one week the corresponding substituted phosphirenium salts in high yield. Phosphirenium salts can also be prepared in high yields by reacting a chloroalkylaryl- or chlorodiarylphosphine and an alkyne with thallium(I) triflate in dichloromethane. The crystal and molecular structures of 1,2,3-trimethyl-1-phenylphosphirenium triflate have been determined. The reaction of chloromethylphenylphosphine with thallium(I) triflate in the absence of an alkyne leads to an unstable phosphinophosphonium triflate that undergoes rapid chloride exchange and/or pyramidal inversion at phosphorus under ambient conditions, as determined by variable temperature NMR spectroscopy.

**Keywords:** Crystal structure; Alkene; Alkyne; Small ring; Phosphirenium; Phosphiranium

## 1. Introduction

The chemistry of three-membered phosphorus heterocycles is a burgeoning field of considerable interest [1]. Although saturated phosphiranes are accessible by a variety of routes, and tertiary phosphines are readily alkylated to give stable phosphonium ions, the synthesis and characterization of a phosphiranium salt have yet to be reported. In 1969 a phosphiranium or  $\lambda^3$ -phosphirane structure was assigned to the product of the reaction between chlorodiethylphosphine and acrylonitrile on the basis of analytical, IR and  $^1\text{H}$  NMR data [2]. In other work, phosphiranium salts were proposed as products of the reaction between certain 9-phosphabicyclo[6.1.0]-phosphines and trialkyloxonium salts [3]. Phosphiranium cations have also been postulated as reactive intermediates in the solvolysis of (2-chloroethyl)-diphenylphosphine [4], in the reaction of the bis( $\alpha$ -bromobenzyl)-diphenylphosphonium cation with triethylamine [5], in Ramberg-Bäcklund type reactions of phosphonium salts [6], and in eliminations of 1,2-phos-

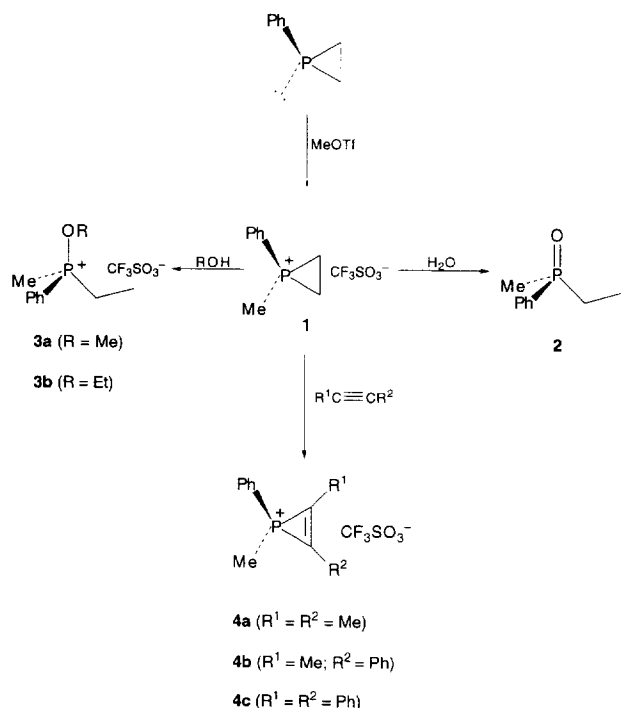
phinoyl alcohols [7]. Theoretical calculations indicate that the phosphiranium ion  $[\text{H}_2\text{PCH}_2\text{CH}_2]^+$  is of lower energy than the primary phosphine  $\text{H}_2\text{PCH}_2\text{CH}_2$  [8]. Here we report that 1-methyl-1-phenylphosphiranium trifluoromethanesulfonate (**1**) can be readily prepared from 1-phenylphosphirane and methyl trifluoromethanesulfonate (methyl triflate), and that the salt is a convenient precursor of substituted phosphirenium salts by reaction with acetylenes. We also describe a new method for the synthesis of phosphirenium salts from chloroalkylaryl- or chlorodiarylphosphines and alkynes in the presence of thallium(I) triflate. A preliminary account of part of this work has been published [9].

## 2. Results and discussion

### 2.1. 1-Methyl-1-phenylphosphiranium triflate (**1**)

Treatment of 1-phenylphosphirane [10] in benzene with methyl triflate at 20°C affords, after maintaining the solution at 5°C for 3 h, colorless crystals of pure **1** in 73% yield having m.p. 75–78°C (decomp., with

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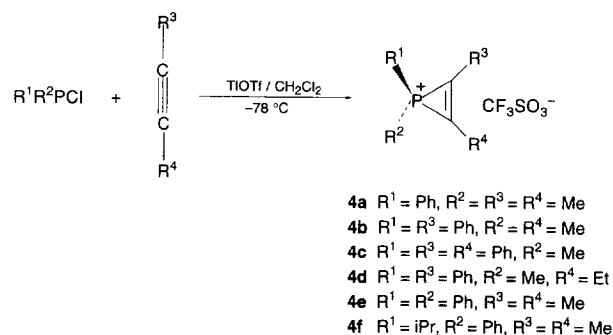


Scheme 1.

evolution of ethylene) (Scheme 1). The salt can be stored for several weeks under argon at room temperature without decomposition. Spectroscopic data for **1**, in particular the high-field shift of the phosphorus resonance at  $\delta -96.79$ , support the proposed structure. Crystals of **1** are moderately stable to the atmosphere, but react with water to give ( $\pm$ )-ethylmethylphenylphosphine oxide **2** [11], and with primary alcohols to form the ( $\pm$ )-alkoxyethylmethylphenylphosphonium triflates **3a** and **3b** (Scheme 1). The phosphirenium salt is moderately stable in dichloromethane, but ethylene was detected in the solution by  $^1\text{H}$  NMR spectroscopy after 5 min. Salt **1** is stable in acetone or acetonitrile for several hours, whereafter decomposition is evident. In neat triflic acid, however, **1** appears to be stable indefinitely.

## 2.2. Phosphirenium triflates (**4a–f**)

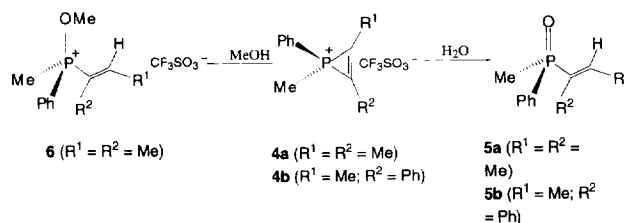
Treatment of **1** with dimethyl- or methylphenylacetylene in dichloromethane affords over one week the corresponding substituted phosphirenium salts **4a** and ( $\pm$ )-**4b** in high yield, thereby effecting the formal transfer of the methylphenylphosphonium ion from ethylene to the alkynes. The reaction with diphenylacetylene is less efficient, giving ca. 50% of the phosphirenium salt **4c** having  $\delta -109.2$  in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum in dichloromethane- $d_2$  (lit. [12]  $\delta -109.9$ ). The phosphirenium triflates can also be generated in high yields from reactions between chloromethylphenylphosphine and thallium(I) triflate in the pres-



Scheme 2.

ence of the alkynes in dichloromethane at  $-78^\circ\text{C}$  (Scheme 2). Phosphirenium salts of the type  $\text{R}^1\text{CIP}^+\text{C}(\text{R}^2)=\text{CR}^3\text{AlCl}_4^-$  had been prepared previously by the reactions of alkynes with phosphonous dichlorides in the presence of aluminium trichloride [13]. After warming to room temperature and removal of the thallium(I) chloride by centrifugation, the phosphirenium salts were obtained in high yields as colorless oils that readily crystallized from dichloromethane–diethyl ether. 1,2,3-Trimethyl-1-phenylphosphirenium triflate (**4a**), m.p.  $59^\circ\text{C}$ , was isolated in 89% yield by this method. The salt was spectroscopically identical to that obtained from the reaction of **1** with 2-butyne over one week. The salts **4b–f** were prepared similarly from the appropriate chlorophosphines and alkynes (Scheme 2). Compound **4b** crystallized as a 0.5-dichloromethane solvate. The attempted synthesis of **4a** with use of various silver salts was less successful: silver(I) triflate or hexafluoroantimonate in conjunction with 2-butyne gave ca. 33% of the respective phosphirenium salt, as indicated by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. In addition to the high-field phosphorus resonances, the  $^1J_{\text{CP}}$  values of ca. 8–13 Hz for the ring carbon atoms of the cations are characteristic of three-membered heterocycles containing four-coordinate phosphorus atoms [1].

The salts **4a–f** hydrolyze within minutes in air. Treatment of **4a** with methanol yields the methoxyphosphonium salt **6**, and with water ( $\pm$ )-methylphenyl[(*E*)-1-methyl-1-propenyl]phosphine oxide was formed (**5a**, Scheme 3). The structure of **5a** was corroborated by the reaction of **4a** with  $\text{D}_2\text{O}$  in dichloromethane, whereupon the signal at  $\delta 6.49$  for the olefinic proton of the phosphine oxide in the  $^1\text{H}$  NMR spectrum was replaced



Scheme 3.

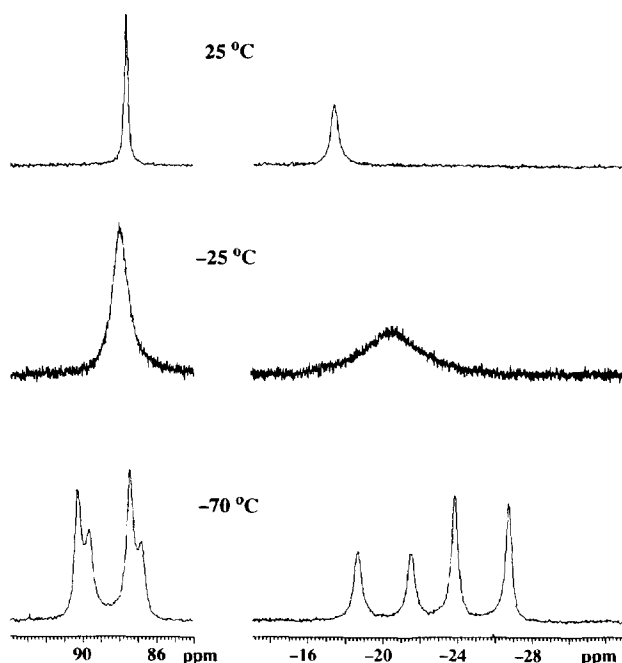


Fig. 1. Variable low-temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of  $(R^*,R^*)/(R^*,S^*)$ -7 in dichloromethane- $d_2$ .

by a singlet at  $\delta$  6.50 in the  $^2\text{H}\{^1\text{H}\}$  NMR spectrum. The coupling constant  $^3J_{\text{HP}} = 20.7$  Hz for the olefinic proton was consistent with the *E*-configuration about the carbon–carbon double bond in **5** [14]. Reaction of **4b** with water gave the oxide **5b**: NMR data indicated ring opening at the ring carbon containing the methyl substituent.

### 2.3. Attempted isolation of methylphenylphosphonium triflate

The reaction of chloromethylphenylphosphine with excess thallium(I) triflate in dichloromethane at  $-78^\circ\text{C}$  in the absence of alkyne led to the isolation of a colorless, non-volatile oil after removal of solvent. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the oil at  $25^\circ\text{C}$  consisted of two singlets of equal intensity at  $\delta$  82 and  $-17$ ; the low-field resonance is coincident with that of chloromethylphenylphosphine. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the oil at low temperatures are shown in Fig. 1. At  $-25^\circ\text{C}$ , the two signals are broadened considerably, but at  $-70^\circ\text{C}$  the spectrum consists of four sets of doublets, consistent with the two diastereomers of **7**. The P–P coupling constant of 351 Hz and behavior of the adduct at low temperatures are similar to those of related phosphinophosphonium salts [15,16]. The collapse of the fine structure in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **7** at elevated temperatures is consistent with dissociation into  $\text{PhMePCl}$  and  $\text{PhMePOTf}$ . Halide exchange in chlorophosphines by dissociation into short-lived phosphonium chlorides has been postulated elsewhere [17].

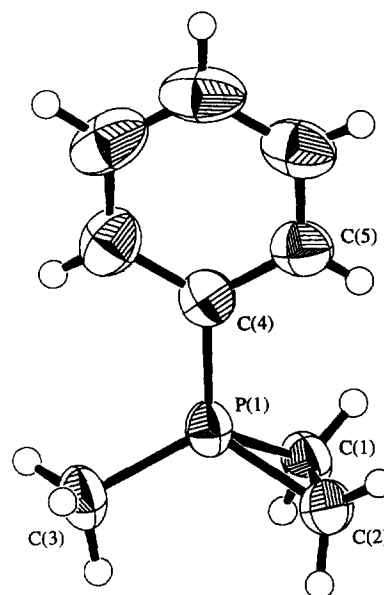
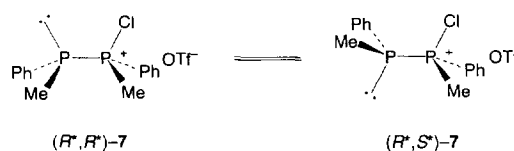


Fig. 2. ORTEP view of **1** showing atom-labelling scheme of selected atoms. Thermal ellipsoids enclose 50% probability levels.

Salt **7** can be considered as a phosphine adduct of a phosphonium ion, i.e.  $\text{MePhP}^+ \leftarrow \text{PClMePh OTf}^-$ : thus, addition of 2-butyne to **7** led to quantitative formation of **4a** and chloromethylphenylphosphine. In the presence of thallium(I) triflate, however, the addition of alkynes to **7** led to quantitative yields of the corresponding phosphirenium triflates. The adduct **7** could not be crystallized and displayed only moderate stability in the neat state or in solution.



### 2.4. Crystal and molecular structures of **1** and **4a**

The molecular structures of **1** and **4a** are depicted in Figs. 2 and 3 respectively. Crystal data for the two compounds are given in Table 1. The most important bond distances and angles for the two compounds are given in Tables 2 and 3 respectively. Atomic coordinates of non-hydrogen atoms for the two compounds are given in Tables 4 and 5 respectively. The phosphorus–carbon bonds in the phosphirenium cation are shorter by ca. 0.06 Å and the carbon–carbon bond is ca. 0.02 Å longer than the corresponding bonds in the neutral complexes *fac*- $[\text{Mo}(\text{CO})_3(\text{PhPCH}_2\text{CH}_2)_3]$  [10] and  $[\text{W}(\text{CO})_5(\text{PhPCH}_2\text{CH}_2)]$  [18]. The C(1)–P–C(2) angle

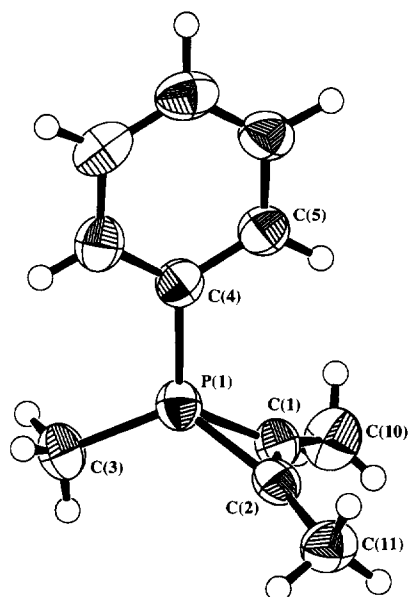


Fig. 3. ORTEP view of **4a** showing atom-labelling scheme of selected atoms. Thermal ellipsoids enclose 50% probability levels.

Table 1  
Crystallographic data for **1** and **4a**

	$C_{10}H_{12}F_3O_3PS$ ( <b>1</b> )	$C_{12}H_{14}F_3O_3PS$ ( <b>4a</b> )
Formula	$C_{10}H_{12}F_3O_3PS$ ( <b>1</b> )	$C_{12}H_{14}F_3O_3PS$ ( <b>4a</b> )
FW	300.23	326.27
Crystal system	monoclinic	monoclinic
Space group	$P21/c$	$P21/n$
$a$ (Å)	6.675(3)	9.123(2)
$b$ (Å)	27.585(9)	13.066(5)
$c$ (Å)	7.271(3)	13.061(2)
$\beta$ (°)	104.88(4)	104.72(2)
$V$ (Å <sup>3</sup> )	1294.0(9)	1505.8(7)
$Z$	4	4
Crystal dimensions (mm <sup>3</sup> )	0.20 × 0.08 × 0.10	0.28 × 0.16 × 0.20 and 0.24 × 0.38 × 0.16
$D_{calc}$ (g cm <sup>-3</sup> )	1.541	1.439
$\mu$ (cm <sup>-1</sup> )	32.62	32.81
Radiation	Cu K $\alpha$	Cu K $\alpha$
	( $\lambda = 1.54178$ Å)	( $\lambda = 1.54178$ Å)
Diffractometer	Rigaku AFC6R	Rigaku AFC6R
$T$ (°C)	-60.0	-60.0
No. of unique data	1995	2510
No. of data used	1412	1702
No. of variables	211	238
$R$ , $R_w$ <sup>a,b</sup>	0.043, 0.045	0.054, 0.057
GOF	2.16	2.85
$F(000)$	616.00	672.00

$$^a R = \sum(|F_o| - |F_c|) / \sum|F_o|$$

$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

Table 2  
Selected bond distances (Å) and angles (°) for **1**

P–C(1)	1.761(4)	P–C(2)	1.756(5)
P–C(3)	1.779(5)	P–C(4)	1.763(4)
C(1)–C(2)	1.533(6)	P–C(1)–C(2)	64.0(3)
C(1)–C(2)–P	64.3(3)	C(1)–P–C(2)	51.7(2)
C(1)–P–C(3)	118.8(3)	C(2)–P–C(3)	117.6(3)
C(1)–P–C(4)	119.1(2)	C(2)–P–C(4)	119.1(2)

Table 3  
Selected bond distances (Å) and angles (°) for **4a**

P–C(1)	1.730(5)	P–C(2)	1.727(5)
P–C(3)	1.776(6)	P–C(4)	1.789(5)
C(1)–C(2)	1.305(7)	C(1)–C(10)	1.479(8)
C(2)–C(11)	1.489(7)	P–C(1)–C(2)	67.7(3)
C(1)–C(2)–P	67.9(3)	C(1)–P–C(2)	44.4(2)
C(1)–P–C(3)	122.1(3)	C(2)–P–C(3)	121.5(3)
C(1)–P–C(4)	117.3(2)	C(2)–P–C(4)	121.5(2)

Table 4  
Atomic coordinates and isotropic displacement parameters for **1**

Atom	$x$	$y$	$z$	$B_{eq}$ <sup>a</sup>
S	0.7828(2)	0.09288(4)	0.2193(2)	3.90(3)
P	0.2384(2)	0.07609(4)	0.7618(1)	3.41(3)
F(1)	0.7357(6)	0.1861(1)	0.1736(5)	8.1(1)
F(2)	0.4752(4)	0.1504(1)	0.2264(4)	6.22(8)
F(3)	0.7415(5)	0.1619(1)	0.4533(4)	8.14(10)
O(1)	1.0017(5)	0.0991(1)	0.2838(5)	6.5(1)
O(2)	0.7044(4)	0.0886(1)	0.0154(4)	4.33(7)
O(3)	0.6935(6)	0.0590(1)	0.3252(5)	7.0(1)
C(1)	0.2160(8)	0.0402(2)	0.9558(7)	4.0(1)
C(2)	0.0279(7)	0.0402(2)	0.7825(7)	4.0(1)
C(3)	0.3922(8)	0.0545(2)	0.6122(7)	4.3(1)
C(4)	0.2207(7)	0.1396(2)	0.7776(5)	3.7(1)
C(5)	0.0613(9)	0.1615(2)	0.8402(6)	4.4(1)
C(6)	0.050(1)	0.2104(2)	0.8507(7)	5.5(2)
C(7)	0.192(1)	0.2394(2)	0.7982(8)	6.1(2)
C(8)	0.351(1)	0.2184(2)	0.7380(8)	6.2(2)
C(9)	0.3664(9)	0.1691(2)	0.7272(7)	5.2(1)
C(10)	0.6800(8)	0.1505(2)	0.2707(7)	4.6(1)

$$^a B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

Table 5  
Atomic coordinates and isotropic displacement parameters for **4a**

Atom	$x$	$y$	$z$	$B_{eq}$ <sup>a</sup>
S	0.8136(1)	0.2886(1)	0.0873(1)	3.96(3)
P	0.6447(2)	0.1027(1)	0.3390(1)	3.67(3)
F(1)	0.5716(4)	0.2742(3)	-0.0702(3)	8.2(1)
F(2)	0.5348(5)	0.3320(6)	0.0727(4)	14.5(2)
F(3)	0.5743(5)	0.1744(5)	0.0543(4)	11.8(2)
O(1)	0.8810(4)	0.2136(3)	0.0357(3)	6.5(1)
O(2)	0.8345(5)	0.2751(3)	0.1980(3)	6.6(1)
O(3)	0.8340(5)	0.3912(3)	0.0566(3)	5.8(1)
C(1)	0.6783(5)	0.2168(4)	0.4082(4)	3.7(1)
C(2)	0.6873(5)	0.1379(4)	0.4707(4)	3.6(1)
C(3)	0.7823(8)	0.0452(6)	0.2825(5)	4.6(2)
C(4)	0.4541(6)	0.0772(4)	0.2661(4)	3.6(1)
C(5)	0.3407(6)	0.1406(4)	0.2816(4)	4.1(1)
C(6)	0.1911(7)	0.1239(5)	0.2252(4)	4.5(1)
C(7)	0.1574(7)	0.0424(5)	0.1576(4)	5.0(2)
C(8)	0.2695(8)	-0.0236(5)	0.1432(5)	5.1(2)
C(9)	0.4196(7)	-0.0070(5)	0.1990(4)	4.4(1)
C(10)	0.6895(10)	0.3297(5)	0.4061(6)	5.3(2)
C(11)	0.7132(8)	0.1036(6)	0.5826(5)	4.7(2)
C(12)	0.6140(7)	0.2686(6)	0.0331(5)	6.0(2)

$$^a B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

in **1** of  $51.7(2)^\circ$  compares with the angles of  $48.88(16)^\circ$  and  $48.6(7)^\circ$  in the molybdenum and tungsten complexes respectively. The ring phosphorus–carbon distances in **4a** are similar to those reported for the only other structurally characterized phosphirenium salt, 1-di-isopropylamino-2,3-diphenyl-1-(2-chloro-1,2-diphenylvinyl)phosphirenium tetrachloroaluminate [19], but are ca.  $0.06 \text{ \AA}$  shorter than those in the complex  $[\text{W}(\text{CO})_5(\text{PhPC}(\text{Ph})\text{C}(\text{Ph}))]$  [20]. The phosphorus–carbon distances in **1** are also shorter than those in the four-membered 1,1-di-*tert*-butylphosphetanium ion, i.e.  $1.81 \text{ \AA}$  (av.) [21]. The carbon–carbon bond in the ring of **4a** is ca.  $0.06 \text{ \AA}$  shorter than the same bond in the above tetrachloroaluminate, and the C(1)–P–C(2) angle of  $44.4(2)^\circ$  for **4a** compares with the angle of  $46.1(5)^\circ$  in the tetrachloroaluminate.

### 3. Conclusion

The first phosphiranium salt to be isolated, 1-methyl-1-phenylphosphiranium triflate, has been obtained in high yield from the reaction of 1-phenylphosphirane with methyl triflate in benzene. The salt reacts with acetylenes to form the corresponding phosphirenium salts, thereby effecting the formal transfer of the methylphenylphosphirenium ion from ethylene to the alkynes. Phosphirenium salts can also be synthesized in high yield by reacting chloroalkylaryl- or chlorodiarylphosphines with alkynes in the presence of thallium(I) triflate.

### 4. Experimental details

Manipulations involving air-sensitive compounds were performed under argon with use of the Schlenk technique. Solvents were purified by conventional methods and stored under argon. Chloromethylphenylphosphine and chlorophenylisopropylphosphine [22] and 1-phenylphosphirane [10] were prepared according to published procedures.  $^1\text{H}$ ,  $^2\text{H}\{^1\text{H}\}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded in dichloromethane- $d_2$  at  $23^\circ\text{C}$  on Varian XL 200E or Varian VXR 300S spectrometers at the frequencies specified, with reference to  $\text{Me}_4\text{Si}$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ),  $\text{CD}_2\text{Cl}_2$  ( $^2\text{H}$ ), or external 85% aqueous  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) with downfield shifts being positive and quoted in parts per million. Mass spectra were recorded on a VG Micromass 7070F double-focussing mass spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a VG Analytical ZAB-2SEQ mass spectrometer (ionization:  $30 \text{ keV Cs}^+$  ions) in a matrix of 3-nitrobenzyl alcohol. Elemental analyses were carried out by staff within the Research School of Chemistry.

#### 4.1. 1-Methyl-1-phenylphosphiranium triflate (**1**)

A solution of 1-phenylphosphirane (1.14 g, 8.37 mmol) was dissolved in benzene (30 ml) and treated with methyl triflate (2.75 g, 16.80 mmol) at room temperature. After 1 h at this temperature the mixture was cooled to  $5^\circ\text{C}$  for 2 h. The colorless, crystalline product that separated was collected by centrifugation, washed with benzene, and dried in vacuo: yield 1.41 g (73%); m.p.  $75\text{--}78^\circ\text{C}$  (decomp., with evolution of ethylene). Anal. Found: C, 40.2; H, 3.9.  $\text{C}_{10}\text{H}_{12}\text{F}_3\text{O}_3\text{PS}$  Calc.: C, 40.0; H, 4.0%.  $^1\text{H}$  NMR (299.9 MHz):  $\delta$  2.45 (d,  $^2J_{\text{HP}} = 18.3 \text{ Hz}$ , 3H,  $\text{CH}_3$ ), 2.36–2.57 (m, 4H,  $\text{CH}_2$ ), 7.61–7.90 (m, 5H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.4 MHz):  $\delta$  3.10 (d,  $^1J_{\text{CP}} = 51.6 \text{ Hz}$ ,  $\text{CH}_3$ ), 7.82 (d,  $^1J_{\text{CP}} = 6.6 \text{ Hz}$ ,  $\text{CH}_2$ ), 113.69 (d,  $^1J_{\text{CP}} = 90.0 \text{ Hz}$ , 1-ArC), 130.53 (d,  $^2J_{\text{CP}} = 16.4 \text{ Hz}$ , 2-ArC), 133.16 (d,  $^3J_{\text{CP}} = 12.1 \text{ Hz}$ , 3-ArC), 135.65 (d,  $^4J_{\text{CP}} = 4.4 \text{ Hz}$ , 4-ArC).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.4 MHz):  $\delta$   $-96.79$  (s). FAB MS:  $m/e$  151 amu ( $[\text{M} - \text{OTf}]^+$ ). The gas that evolved at the melting point was identified by heating a sample of the salt in 1,2-xylene- $d_{10}$  at  $100^\circ\text{C}$  for 10 min; the  $^1\text{H}$  NMR spectrum of the solution contained a signal at  $\delta$  5.53 due to ethylene.

#### 4.2. ( $\pm$ )-Ethylmethylphenylphosphine oxide (**2**)

A solution of **1** (0.25 g, 0.83 mmol) in dichloromethane (2 ml) was stirred with water (2 ml) at room temperature. After 1 h, the organic phase was separated and dried ( $\text{MgSO}_4$ ). Filtration, followed by removal of solvent in vacuo, gave the product as a colorless oil: yield 0.27 g (99%).  $^1\text{H}$  NMR (299.9 MHz):  $\delta$  1.04 (d of t,  $^3J_{\text{HP}} = 17.4 \text{ Hz}$ ,  $^3J_{\text{HH}} = 7.5 \text{ Hz}$ , 3H,  $\text{PCH}_2\text{CH}_3$ ), 1.62 (d,  $^2J_{\text{HP}} = 12.6 \text{ Hz}$ , 3H,  $\text{PCH}_3$ ), 1.82–1.97 (m, 2H,  $\text{PCH}_2\text{CH}_3$ ), 7.48–7.73 (m, 5H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.4 MHz):  $\delta$  5.83 (d,  $^2J_{\text{CP}} = 4.4 \text{ Hz}$ ,  $\text{PCH}_2\text{CH}_3$ ), 15.10 (d,  $^1J_{\text{CP}} = 75.9 \text{ Hz}$ ,  $\text{PCH}_3$ ), 24.45 (d,  $^1J_{\text{CP}} = 70.9 \text{ Hz}$ ,  $\text{PCH}_2\text{CH}_3$ ), 128.83 (d,  $^2J_{\text{CP}} = 11.3 \text{ Hz}$ , 1-ArC), 130.39 (d,  $^3J_{\text{CP}} = 8.7 \text{ Hz}$ , 2-ArC), 131.76 (d,  $^4J_{\text{CP}} = 3.3 \text{ Hz}$ , 4-ArC), 133.67 (d,  $^1J_{\text{CP}} = 94.3 \text{ Hz}$ , 1-ArC).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.4 MHz):  $\delta$  37.98 (s).

#### 4.3. ( $\pm$ )-Ethylmethoxymethylphenylphosphonium triflate (**3a**)

A solution of **1** (0.39 g, 1.30 mmol) in dichloromethane (2 ml) was treated with methanol (2 ml) and the solution was stirred for 1 h at room temperature. Removal of the solvents in vacuo gave the product as a colorless oil: yield 0.43 g (99%).  $^1\text{H}$  NMR (299.9 MHz):  $\delta$  1.26 (d of t,  $^3J_{\text{HP}} = 20.4 \text{ Hz}$ ,  $^3J_{\text{HH}} = 7.8 \text{ Hz}$ , 3H,  $\text{PCH}_2\text{CH}_3$ ), 2.44 (d,  $^2J_{\text{HP}} = 12.6 \text{ Hz}$ , 3H,  $\text{PCH}_3$ ), 2.60–2.82 (m, 2H,  $\text{PCH}_2\text{CH}_3$ ), 3.93 (d,  $^3J_{\text{HP}} = 12.3 \text{ Hz}$ , 3H,

POCH<sub>3</sub>), 7.60–7.95 (m, 5H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz): δ 5.12 (d, <sup>2</sup>J<sub>CP</sub> = 4.4 Hz, PCH<sub>2</sub>CH<sub>3</sub>), 8.09 (d, <sup>1</sup>J<sub>CP</sub> = 63.6 Hz, PCH<sub>3</sub>), 19.18 (d, <sup>1</sup>J<sub>CP</sub> = 67.0 Hz, PCH<sub>2</sub>CH<sub>3</sub>), 57.06 (d, <sup>2</sup>J<sub>CP</sub> = 7.7 Hz, POCH<sub>3</sub>), 118.83 (d, <sup>1</sup>J<sub>CP</sub> = 98.8 Hz, 1-ArC), 130.62 (d, <sup>2</sup>J<sub>CP</sub> = 13.1 Hz, 2-ArC), 131.74 (d, <sup>3</sup>J<sub>CP</sub> = 11.0 Hz, 3-ArC), 136.37 (d, <sup>4</sup>J<sub>CP</sub> = 3.2 Hz, 4-ArC). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz): δ 89.63 (s). FAB MS: *m/e* 183 amu ([M – OTf]<sup>+</sup>).

#### 4.4. General synthesis of phosphirenium salts

The chloroalkylaryl- or chlorodiarylphosphine (ca. 2 g) in dichloromethane (5 ml) was added to a suspension of thallium(I) triflate (ca. 5 g, recrystallized from acetonitrile) in dichloromethane (15 ml) at –78 °C, followed by the alkyne (2 ml). After stirring for 5 min at –78 °C, the reaction mixtures were warmed to room temperature and stirred for 1 h (except for **4c**, which required stirring for 15 h); dichloromethane (50 ml) was then added and the thallium(I) chloride in each case was separated by centrifugation. Removal of the solvent from the filtrates in vacuo, followed by recrystallization of the residues from dichloromethane–diethyl ether, afforded the colorless, crystalline products. The following salts were prepared by this method.

##### 4.4.1. 1,2,3-Trimethyl-1-phenylphosphirenium triflate (**4a**)

Thallium(I) triflate (5.15 g, 14.57 mmol), chloromethylphenylphosphine (2.08 g, 13.13 mmol), 2-butyne (2 ml): yield 3.85 g (89%); m.p. 59 °C. Anal. Found: C, 43.4; H, 4.4. C<sub>12</sub>H<sub>14</sub>F<sub>3</sub>O<sub>3</sub>PS Calc.: C, 44.2; H, 4.3%. <sup>1</sup>H NMR (299.9 MHz): δ 2.38 (d, <sup>2</sup>J<sub>HP</sub> = 17.1 Hz, 3H, PCH<sub>3</sub>), 2.42 (d, <sup>3</sup>J<sub>HP</sub> = 16.2 Hz, 6H, CCH<sub>3</sub>), 7.58–7.73 (m, 5H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz): δ 7.33 (d, <sup>1</sup>J<sub>CP</sub> = 54.9 Hz, PCH<sub>3</sub>), 10.52 (d, <sup>2</sup>J<sub>CP</sub> = 2.2 Hz, CCH<sub>3</sub>), 120.58 (d, <sup>1</sup>J<sub>CP</sub> = 91.1 Hz, 1-ArC), 129.95 (d, <sup>2</sup>J<sub>CP</sub> = 15.4 Hz, 2-ArC), 132.60 (d, <sup>1</sup>J<sub>CP</sub> = 13.1 Hz, CCH<sub>3</sub>), 132.70 (d, <sup>3</sup>J<sub>CP</sub> = 13.1 Hz, 3-ArC), 134.72 (d, <sup>4</sup>J<sub>CP</sub> = 4.4 Hz, 4-ArC). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz): δ –103.75 (s). FAB MS: *m/e* 177 amu ([M – OTf]<sup>+</sup>).

##### 4.4.2. 1,2,3-Dimethyl-1,2-diphenylphosphirenium triflate–0.5-dichloromethane (**4b**)

Thallium(I) triflate (2.32 g, 6.56 mmol), chloromethylphenylphosphine (0.95 g, 6.00 mmol), 1-phenyl-1-propyne (2 ml): yield 1.25 g (54%); m.p. 63 °C. Anal. Found: C, 49.2; H, 4.1. C<sub>17.5</sub>H<sub>17</sub>ClF<sub>3</sub>O<sub>3</sub>PS Calc.: C, 48.8; H, 4.0%. <sup>1</sup>H NMR (200.05 MHz): δ 2.55 (d, <sup>2</sup>J<sub>HP</sub> = 17.0 Hz, 3H, PCH<sub>3</sub>), 2.71 (d, <sup>3</sup>J<sub>HP</sub> = 17.2 Hz, 3H, PCCH<sub>3</sub>), 7.57–7.84 (m, 10H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz): δ 7.50 (d, <sup>1</sup>J<sub>CP</sub> = 55.1 Hz, PCH<sub>3</sub>), 11.80 (s, PCCH<sub>3</sub>), 130.07–135.16 (ArC). (The presence of 0.5-CH<sub>2</sub>Cl<sub>2</sub> in the salt was confirmed by recording the <sup>1</sup>H and <sup>13</sup>C NMR spectra in chloroform-*d*<sub>1</sub>.) <sup>31</sup>P{<sup>1</sup>H}

NMR (81.0 MHz): δ –104.85 (s). FAB MS: *m/e* 239 amu ([M – OTf]<sup>+</sup>).

##### 4.4.3. 1-Methyl-1,2,3-triphenylphosphirenium triflate (**4c**)

Thallium(I) triflate (7.70 g, 21.78 mmol), chloromethylphenylphosphine (2.54 g, 16.03 mmol), diphenylacetylene (4.00 g, 22.44 mmol): yield 4.63 g (96%); m.p. 160 °C. Anal. Found: C, 58.6; H, 3.7. C<sub>22</sub>H<sub>18</sub>F<sub>3</sub>O<sub>3</sub>PS Calc.: C, 58.7; H, 4.0%. <sup>1</sup>H NMR (299.9 MHz): δ 2.80 (d, <sup>2</sup>J<sub>HP</sub> = 16.8 Hz, 3H, CH<sub>3</sub>), 7.62–8.08 (m, 15H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz): δ 7.23 (d, <sup>1</sup>J<sub>CP</sub> = 53.8 Hz, CH<sub>3</sub>), 126.32–135.59 (ArC). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz): δ –109.15 (s). FAB MS: *m/e* 301 amu ([M – OTf]<sup>+</sup>).

##### 4.4.4. 3-Ethyl-1-methyl-1,2-diphenylphosphirenium triflate (**4d**)

Thallium(I) triflate (2.52 g, 7.13 mmol), chloromethylphenylphosphine (0.94 g, 5.93 mmol), 1-phenyl-1-butyne (2 ml): yield 1.39 g (58%); m.p. 110 °C. Anal. Found: C, 53.9; H, 4.7. C<sub>18</sub>H<sub>18</sub>F<sub>3</sub>O<sub>3</sub>PS Calc.: C, 53.7; H, 4.5%. <sup>1</sup>H NMR (200.05 MHz): δ 1.42 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 3H, PCH<sub>2</sub>CH<sub>3</sub>), 2.59 (d, <sup>2</sup>J<sub>HP</sub> = 17.0 Hz, 3H, PCH<sub>3</sub>), 3.07–3.28 (m, 2H, PCCH<sub>2</sub>CH<sub>3</sub>), 7.55–7.84 (m, 10H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz): δ 7.35 (d, <sup>1</sup>J<sub>CP</sub> = 54.8 Hz, PCH<sub>3</sub>), 12.21 (d, <sup>2</sup>J<sub>CP</sub> = 5.7 Hz, PCH<sub>2</sub>CH<sub>3</sub>), 20.48 (s, PCH<sub>2</sub>CH<sub>3</sub>), 130.04–133.20 (ArC). <sup>31</sup>P{<sup>1</sup>H} NMR (81.0 MHz): δ –107.03 (s). FAB MS: *m/e* 253 amu ([M – OTf]<sup>+</sup>).

##### 4.4.5. 2,3-Dimethyl-1,1-diphenylphosphirenium triflate (**4e**)

Thallium(I) triflate (2.07 g, 5.86 mmol), chlorodiphenylphosphine (1.07 g, 4.85 mmol), 2-butyne (2 ml): yield 0.98 g (52%); m.p. 125 °C. Anal. Found: C, 52.2; H, 4.0. C<sub>17</sub>H<sub>16</sub>F<sub>3</sub>O<sub>3</sub>PS Calc.: C, 52.6; H, 4.2%. <sup>1</sup>H NMR (299.9 MHz): δ 2.59 (d, <sup>3</sup>J<sub>HP</sub> = 16.5 Hz, 6H, PCCH<sub>3</sub>), 7.66–7.82 (m, 10H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz): δ 11.22 (s, PCCH<sub>3</sub>), 117.44 (d, <sup>1</sup>J<sub>CP</sub> = 93.5 Hz, 1-ArC), 130.45 (d, <sup>2</sup>J<sub>CP</sub> = 16.4 Hz, 2-ArC), 133.00 (d, <sup>1</sup>J<sub>CP</sub> = 11.0 Hz, CCH<sub>3</sub>), 134.35 (d, <sup>3</sup>J<sub>CP</sub> = 13.1 Hz, 3-ArC), 135.69 (d, <sup>4</sup>J<sub>CP</sub> = 3.3 Hz, 4-ArC). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz): δ –102.93 (s). FAB MS: *m/e* 239 amu ([M – OTf]<sup>+</sup>).

##### 4.4.6. 2,3-Dimethyl-1-phenyl-1-isopropylphosphirenium triflate (**4f**)

Thallium(I) triflate (4.47 g, 12.65 mmol), chlorophenylisopropylphosphine (2.11 g, 11.31 mmol), 2-butyne (2 ml): yield 3.13 g (78%); m.p. 87 °C. Anal. Found: C, 47.5; H, 5.5. C<sub>14</sub>H<sub>18</sub>F<sub>3</sub>O<sub>3</sub>PS Calc.: C, 47.5; H, 5.1%. <sup>1</sup>H NMR (299.9 MHz): δ 1.25 (d of d, <sup>3</sup>J<sub>HP</sub> = 24.6 Hz, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 3H, PCHCH<sub>3</sub>), 2.46 (d, <sup>3</sup>J<sub>HP</sub> = 15.3 Hz, 3H, PCCH<sub>3</sub>), 3.59–3.74 (m, 1H,

PCCHCH<sub>3</sub>), 7.57–7.77 (m, 5H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz): δ 9.11 (d, <sup>2</sup>J<sub>CP</sub> = 2.2 Hz, PCCH<sub>3</sub>), 15.78 (d, <sup>2</sup>J<sub>CP</sub> = 3.2 Hz, PCHCH<sub>3</sub>), 22.05 (d, <sup>1</sup>J<sub>CP</sub> = 46.1 Hz, PCHCH<sub>3</sub>), 116.97 (d, <sup>1</sup>J<sub>CP</sub> = 76.8 Hz, 1-ArC), 128.27 (d, <sup>2</sup>J<sub>CP</sub> = 14.3 Hz, 2-ArC), 128.86 (d, <sup>1</sup>J<sub>CP</sub> = 8.7 Hz, PCCH<sub>3</sub>), 131.53 (d, <sup>3</sup>J<sub>CP</sub> = 12.1 Hz, 3-ArC), 132.94 (d, <sup>4</sup>J<sub>CP</sub> = 4.4 Hz, 4-ArC). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz): δ -86.71 (s). FAB MS: *m/e* 205 amu ([M - OTf]<sup>+</sup>).

The phosphirenium triflates **4a–f** (but not **4c**) can also be prepared in high yields by the reaction of **1** with the appropriate alkyne in dichloromethane for ca. one week, as determined by the disappearance of the peak at δ -96.79 for the phosphiranium salt and the appearance of new peaks for the phosphirenium salts in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the reaction mixtures in dichloromethane-*d*<sub>2</sub>. No phosphorus-containing by-products were obtained in these reactions.

#### 4.5. (±)-Methyl[(E)-1-methyl-1-propenyl]phenylphosphine oxide (**5a**)

A solution of **4a** (0.57 g, 1.75 mmol) in dichloromethane (2 ml) was treated with water (2 ml) and the mixture was stirred for 1 h at room temperature. The organic layer was separated, dried (MgSO<sub>4</sub>), and the solvent was removed in vacuo, affording the product as a colorless solid: yield 0.30 g (88%); m.p. 88 °C. <sup>1</sup>H NMR (299.9 MHz): δ 1.67 (d of m, <sup>3</sup>J<sub>HP</sub> = 12.9 Hz, 3H, PCCH<sub>3</sub>), 1.70 (d, <sup>2</sup>J<sub>HP</sub> = 13.2 Hz, 3H, PCH<sub>3</sub>), 1.78 (d of m, <sup>4</sup>J<sub>HP</sub> = 6.9 Hz, 3H, PCCHCH<sub>3</sub>), 6.49 (d of q of q, <sup>3</sup>J<sub>HP</sub> = 20.7 Hz, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H, PCCHCH<sub>3</sub>), 7.42–7.70 (m, 5H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz): δ 12.11 (d, <sup>3</sup>J<sub>CP</sub> = 12.1 Hz, PCCHCH<sub>3</sub>), 13.87 (d, <sup>1</sup>J<sub>CP</sub> = 73.5 Hz, PCH<sub>3</sub>), 14.37 (d, <sup>2</sup>J<sub>CP</sub> = 15.4 Hz, PCCH<sub>3</sub>), 128.75 (d, <sup>2</sup>J<sub>CP</sub> = 11.0 Hz, 2-ArC), 130.58 (d, <sup>3</sup>J<sub>CP</sub> = 9.9 Hz, 3-ArC), 131.62 (d, <sup>4</sup>J<sub>CP</sub> = 3.2 Hz, 4-ArC), 132.78 (d, <sup>1</sup>J<sub>CP</sub> = 10.7 Hz, PCCHCH<sub>3</sub>), 133.73 (d, <sup>1</sup>J<sub>CP</sub> = 97.6 Hz, 1-ArC), 138.27 (d, <sup>2</sup>J<sub>CP</sub> = 8.7 Hz, PCCHCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz): δ 31.22 (s). EI MS: *m/e* 194 amu (M<sup>+</sup>). The (*E*)-2-deuterio-1-methyl-1-propenyl isotopomer was prepared under similar conditions with use of D<sub>2</sub>O and gave the following spectroscopic data. <sup>1</sup>H NMR (299.9 MHz): δ 1.68 (d of m, <sup>3</sup>J<sub>HP</sub> = 13.2 Hz, 3H, PCCH<sub>3</sub>), 1.71 (d, <sup>2</sup>J<sub>HP</sub> = 12.9 Hz, 3H, PCH<sub>3</sub>), 1.80–1.83 (br m, 3H, PCDCCH<sub>3</sub>), 7.47–7.71 (m, 5H, Ph). <sup>2</sup>H{<sup>1</sup>H} NMR (46.04 MHz, CH<sub>2</sub>Cl<sub>2</sub>): δ 6.50 (s, PCCDCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz): δ 12.08 (d, <sup>3</sup>J<sub>CP</sub> = 13.2 Hz, PCDCCH<sub>3</sub>), 13.89 (d, <sup>1</sup>J<sub>CP</sub> = 72.5 Hz, PCH<sub>3</sub>), 14.26 (d, <sup>2</sup>J<sub>CP</sub> = 16.4 Hz, PCCH<sub>3</sub>), 128.78 (d, <sup>2</sup>J<sub>CP</sub> = 12.1 Hz, 2-ArC), 130.61 (d, <sup>3</sup>J<sub>CP</sub> = 9.9 Hz, 3-ArC), 131.66 (d, <sup>4</sup>J<sub>CP</sub> = 3.3 Hz, 4-ArC), 132.65 (d, <sup>1</sup>J<sub>CP</sub> = 10.9 Hz, PCCHCH<sub>3</sub>), 133.66 (d, <sup>1</sup>J<sub>CP</sub> = 99.5 Hz, 1-ArC), 138.07 (t of d, <sup>1</sup>J<sub>CD</sub> = 24.1 Hz, <sup>2</sup>J<sub>CP</sub> = 8.8 Hz, PCCDCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz): δ 31.57 (s). EI MS: *m/e* 195 amu (M<sup>+</sup>).

#### 4.6. (±)-Methoxyphenyl[(E)-1-phenyl-1-propenyl]phosphine oxide (**5b**)

A solution of **4b** (0.27 g, 0.70 mmol) in dichloromethane (2 ml) was treated with water (2 ml) and the mixture was stirred for 1 h at room temperature. The organic layer was separated, dried (MgSO<sub>4</sub>), and the solvent removed in vacuo, affording the product as a colorless solid: yield 0.14 g (79%); m.p. 112 °C. <sup>1</sup>H NMR (299.9 MHz): δ 1.83 (d, <sup>2</sup>J<sub>HP</sub> = 13.2 Hz, 3H, PCH<sub>3</sub>), 1.93 (d of d, <sup>4</sup>J<sub>HP</sub> = 14.1 Hz, <sup>3</sup>J<sub>HH</sub> = 0.5 Hz, 3H, PCCHCH<sub>3</sub>), 7.37–7.77 (m, 11H, Ph and PCCH). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz): δ 13.64 (d, <sup>1</sup>J<sub>CP</sub> = 73.5 Hz, PCH<sub>3</sub>), 14.35 (d, <sup>3</sup>J<sub>CP</sub> = 12.1 Hz, PCCHCH<sub>3</sub>), 128.47–131.88 (ArC), 136.32 (d, <sup>1</sup>J<sub>CP</sub> = 18.6 Hz, PCCHCH<sub>3</sub>), 140.15 (d, <sup>2</sup>J<sub>CP</sub> = 8.7 Hz, PCCHCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz): δ 32.05 (s). EI MS: *m/e* 255 amu (M<sup>+</sup>).

#### 4.7. (±)-Methoxymethyl[(E)-1-methyl-1-propenyl]phenylphosphonium triflate (**6**)

A solution of **4a** (1.21 g, 3.71 mmol) in dichloromethane (2 ml) was treated with methanol (2 ml) and the mixture was stirred for 1 h at room temperature, after which time the solvents were removed in vacuo. The product was thus isolated as a colorless oil: yield 1.21 g (99%). <sup>1</sup>H NMR (200 MHz): δ 1.86 (d of m, <sup>3</sup>J<sub>HP</sub> = 14.8 Hz, 3H, PCCH<sub>3</sub>), 2.03 (d of m, <sup>4</sup>J<sub>HP</sub> = 6.8 Hz, 3H, PCCHCH<sub>3</sub>), 2.44 (d, <sup>2</sup>J<sub>HP</sub> = 12.8 Hz, 3H, PCH<sub>3</sub>), 3.93 (d, <sup>3</sup>J<sub>HP</sub> = 12.2 Hz, 3H, POCH<sub>3</sub>), 6.91 (d of q of q, <sup>3</sup>J<sub>HP</sub> = 24.0 Hz, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, <sup>4</sup>J<sub>HH</sub> = 1.6 Hz, 1H, PCCCHCH<sub>3</sub>), 7.67–7.91 (m, 5H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz): δ 7.88 (d, <sup>1</sup>J<sub>CP</sub> = 65.9 Hz, PCH<sub>3</sub>), 11.71 (d, <sup>3</sup>J<sub>CP</sub> = 14.5 Hz, PCCHCH<sub>3</sub>), 15.84 (d, <sup>2</sup>J<sub>CP</sub> = 17.8 Hz, PCCH<sub>3</sub>), 56.93 (d, <sup>2</sup>J<sub>CP</sub> = 7.1 Hz, POCH<sub>3</sub>), 130.44 (d, <sup>2</sup>J<sub>CP</sub> = 13.7 Hz, 2-ArC), 132.09 (d, <sup>3</sup>J<sub>CP</sub> = 11.7 Hz, 3-ArC), 136.08 (d, <sup>4</sup>J<sub>CP</sub> = 2.8 Hz, 4-ArC), 152.99 (d, <sup>2</sup>J<sub>CP</sub> = 13.0 Hz, PCCHCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (81.0 MHz): δ 76.65 (s). FAB MS: *m/e* 209 amu ([M - OTf]<sup>+</sup>).

#### 4.8. Crystal structure analyses

Crystal data for **1** and **4a** are given in Table 1. For **1**, the data were collected at -60 ± 1 °C using the ω-2θ scan technique to a maximum 2θ value of 120.1°. Scans of (1.42 + 0.30 tan θ)° were made at a speed of 16.0° min<sup>-1</sup> in ω. For **4a**, owing to crystal instability at -60 ± 1 °C, data were collected on two separate crystals and merged with independent scale factors. The first data set comprised a complete 80° sphere, plus a partial 80–120° set. The second data set completed the outer shell. Scans of (1.10 + 0.30 tan θ)° were made at a speed of 32.0° min<sup>-1</sup> in ω. In both **1** and **4a** stationary background counts were recorded on each side of every reflection. The intensities of three representative

reflections were measured periodically. A decay correction of 8.8% was applied to **1**. Whilst no crystal decay was evident in either crystal of **4a**, both crystals appeared to change phase at some transition point after exposure to the X-ray beam. Attempts to index the new peak locations, some of which were broad and split, were unsuccessful, despite prolonged further exposure to the X-rays. Data were also corrected for absorption [23] (transmission ranges 0.78 to 1.00 for **1** and 0.83 to 1.00 and 0.78 to 1.00 for the two crystals of **4a**) and for Lorentz and polarization effects. The structures were solved by heavy-atom Patterson methods and expanded using Fourier techniques [24]. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.29 and  $-0.26 \text{ e } \text{\AA}^{-3}$  for **1** and to 0.33 and  $-0.28 \text{ e } \text{\AA}^{-3}$  for **4a**. All calculations were performed using teXsan [25]. Atomic scattering factors for neutral atoms were taken from Ref. [26], and real and imaginary dispersion terms from Ref. [27]. Tables of anisotropic displacement factors, interatomic distances and angles involving non-hydrogen and hydrogen atoms, torsion angles involving non-hydrogen atoms, and non-bonded contacts out to 3.60 Å have been deposited at the Cambridge Crystallographic Data Centre.

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