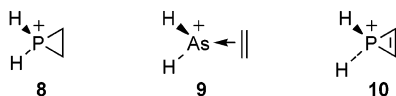
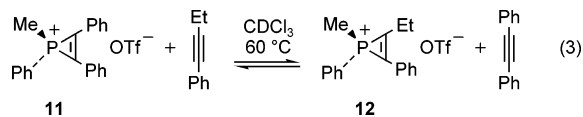




of ring strain, is only 7.14 kcal mol<sup>-1</sup> more exothermic than that for the saturated analogue, as opposed to a corresponding exothermicity difference of 23.64 kcal mol<sup>-1</sup> for cyclopropene and cyclopropane.<sup>7</sup> This is consistent with the experimental observation of facile replacement of ethylene by alkynes on the MePhP<sup>+</sup> ion.<sup>4</sup>



Ab initio calculations at the G2 level show that  $\pi$ -ethylene and  $\pi$ -acetylene exchange on Ph<sub>2</sub>P<sup>+</sup> can occur by an associative pathway through a spirocyclic transition state of C<sub>2v</sub> symmetry with barriers of 3.6 and 39.4 kJ mol<sup>-1</sup>, respectively.<sup>8</sup> These values are much smaller than those calculated for the corresponding insertion reactions that lead to the thermodynamically preferred five-membered heterocycles (234.0 and 216.9 kJ mol<sup>-1</sup>, respectively).<sup>8</sup> We have now investigated experimentally the alkyne exchange in solution and report here kinetic results concerning the exchange of PhCCPh with EtCCPh in the system **11**  $\rightleftharpoons$  **12** (eq 3). This reversible alkyne exchange is unprecedented in main group heterocyclic chemistry.

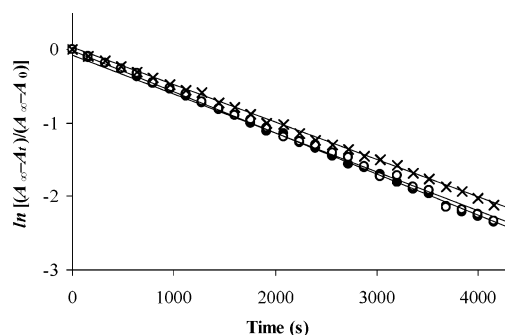


## Results and Discussion

**Synthesis of Phosphirenium Triflates.** Phosphirenium triflates **11** and **12** were prepared by treating PhMeP<sup>+</sup>Cl<sup>-</sup> with trimethylsilyl triflate (1 equiv) in CH<sub>2</sub>-Cl<sub>2</sub> in the presence of the appropriate alkyne and were isolated as colorless, moisture-sensitive, crystalline solids. This method represents an improvement on the previously reported method,<sup>4b</sup> which involved the use of thallium(I) triflate.

**Kinetics of Alkyne Exchange.** The kinetics of the reaction of **11** (0.0143 M) with EtCCPh (0.143–1.43 M) to give **12** and PhCCPh at 60 °C in CDCl<sub>3</sub> were investigated by <sup>1</sup>H NMR spectroscopy, by monitoring the increase in intensity of the methylene signal for **12** and the decrease in intensity of the methyl signal for **11**. Pseudo-first-order conditions in both the forward and reverse directions were achieved by ensuring that the concentrations of the alkynes were at least 10 times greater than that of **11**. No intermediates or side-products were identified. The rate of exchange is independent of the EtCCPh concentration over the range studied (Figure 1). The reverse reaction, in which **12** reacts with PhCCPh, is likewise independent of PhCCPh concentration. Observed rate constants for both directions are given in Table 1.

These findings suggest that the exchange follows a mechanism in which the addition of the incoming alkyne takes place rapidly after the slow, alkyne-independent cleavage of the three-membered ring. Phosphirenium rings are highly strained entities. The intracyclic C–P–C



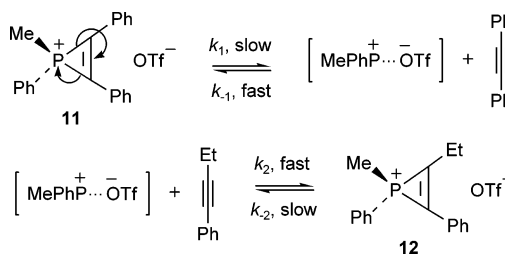
**Figure 1.** Kinetic plots showing the decrease in **[11]** with time for the reaction of **11** (0.0143 M) with EtCCPh at concentrations of 0.143 M (●), 0.715 M (×), and 1.43 M (○) in the presence of PhCCPh (0.143 M) at 60 °C in CDCl<sub>3</sub>. Abbreviations are as defined in the Experimental Section.

**Table 1.** Observed Pseudo-First-Order Rate Constants<sup>a</sup> for (A) Reaction of **11** with EtCCPh<sup>b</sup> and (B) Reaction of **12** with PhCCPh<sup>c</sup> at 60 °C in CDCl<sub>3</sub>

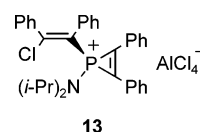
[alkyne]/M	10 <sup>4</sup> × k <sub>obs</sub> /s <sup>-1</sup>	
	A	B
0.143	5.6 ± 0.3	5.3 ± 1.0
0.286	4.9 ± 0.3	5.7 ± 1.5
0.714	5.1 ± 0.2	5.4 ± 0.8
1.07	5.2 ± 0.2	5.6 ± 0.4
1.43	5.2 ± 0.6	6.2 ± 0.8

<sup>a</sup> Average of two experiments. <sup>b</sup> **[11]**<sub>0</sub> = 0.0143 M, **[PhCCPh]**<sub>0</sub> = 0.143 M. <sup>c</sup> **[12]**<sub>0</sub> = 0.0143 M, **[EtCCPh]**<sub>0</sub> = 0.143 M.

## Scheme 1



angles in **7** (R = Me) [44.4(2)<sup>o</sup>]<sup>4b</sup> and **13** [46.1(5)<sup>o</sup>]<sup>9</sup> (the only examples that have been structurally characterized) are much smaller than the corresponding angle in the phosphiranium salt **6** [51.7(2)<sup>o</sup>],<sup>4</sup> although the P–C distances in **7** (R = Me) [av 1.729(7) Å] and **13** [av 1.731(12) Å] are only ca. 0.03 Å shorter than those in **6** [1.759(6) Å]. We propose that the reactivity of phosphirenium salts toward alkynes reflects this ring strain and involves, as the rate-determining step, the concerted cleavage of both intracyclic P–C bonds. This generates a phosphirenium triflate intermediate (not detected) that rapidly adds to the incoming alkyne to give the new phosphirenium salt (Scheme 1).



**13**

Application of the steady-state approximation to the mechanism shown in Scheme 1 gives the following

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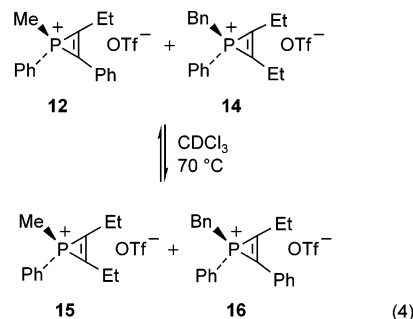
(9) Vural, J. M.; Weissman, S. A.; Baxter, S. G.; Cowley, A. H.; Nunn, C. M. *J. Chem. Soc., Chem. Commun.* **1988**, 462–463.

expression for the observed rate constant:  $k_{\text{obs}} = \{k_1 k_2 [B] + k_{-1} k_{-2} [A]\} / \{k_2 [B] + k_{-1} [A]\}$ , where [A] and [B] are the PhCCPh and EtCCPh concentrations, respectively.<sup>10</sup> In this model, when [B]/[A] = 0,  $k_{\text{obs}}$  is equal to  $k_{-2}$ , but as [B]/[A] becomes large,  $k_{\text{obs}}$  approaches  $k_1$ . The data for the forward direction (column A in Table 1) fall in the latter regime, giving  $k_1 = (5.2 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$ . Analysis of data for the reverse reaction (column B) gives  $k_{-2} = (5.6 \pm 0.9) \times 10^{-4} \text{ s}^{-1}$ . In principle, the variation in  $k_{\text{obs}}$  with [B]/[A] between the two extremes is a hyperbolic function of the ratio  $k_{-1}/k_2$ , but because  $k_1$  and  $k_{-2}$  are indistinguishable within experimental error, no hyperbolic behavior was seen. The ratio  $k_{-1}/k_2$  may, however, be estimated from the equilibrium constant,  $K = k_1 k_2 / k_{-1} k_{-2}$ : we determine  $K$  to be  $11 \pm 2$ , and thus  $k_{-1}/k_2$  is 0.08.

In phosphonium salts,  $R_2P^+X^-$ , one or two electron-rich amido or sulfido substituents are usually required to confer isolability.<sup>11</sup> The only phosphonium salt to have been isolated that contains a P–C bond is [P(Mes)(N<sup>i</sup>Pr<sub>2</sub>)]AlCl<sub>4</sub>, and, while this is ionic or loosely ion-paired in CD<sub>2</sub>Cl<sub>2</sub> ( $\delta_P$  500 ppm), the corresponding triflate is covalent ( $\delta_P$  185 ppm, C<sub>6</sub>D<sub>6</sub>).<sup>12</sup> A cyclic bis-(amido)-substituted phosphonium triflate has also shown a P...O interaction in dichloromethane that was intermediate between ionic and covalent.<sup>13</sup> The importance of ion-pairing to the stability of phosphonium salts was further evidenced by the reaction of [P(N<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>]BPh<sub>4</sub> with CH<sub>2</sub>Cl<sub>2</sub> to give [P(CH<sub>2</sub>Cl)Cl(N<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>]BPh<sub>4</sub>, in contrast with the corresponding GaCl<sub>4</sub><sup>-</sup> salt, which gave no such reaction.<sup>14</sup> The reaction rates of stable carbenium ions with neutral nucleophiles in aprotic solvents vary little with the nature of the solvent,<sup>15</sup> and, furthermore, spectroscopic investigations have shown that the trityl cation does not form an adduct with chloroform.<sup>16</sup> We believe, therefore, that the stability of the intermediate MePhP<sup>+</sup> ion in the present system arises principally from an intimate interaction with the triflate, with solvation (in the sense of solvent-separated ion pairs) playing a lesser role. Preliminary calculations<sup>17</sup> have shown that, while an associative mechanism is favored in the gas phase when solvation and ion-pairing are not taken into account,<sup>8</sup> the magnitude of interactions such as these could well be sufficient to favor a dissociative mechanism in solution.

A dissociative alkyne-exchange mechanism is supported by the crossover experiment shown in eq 4. After 2 h at 70 °C, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of an equimolar mixture of **12** and **14** in CDCl<sub>3</sub> showed signals of equal intensity for the crossover products **15** and **16**. That such an exchange can occur in the absence of added

alkyne implies that the alkynes are liberated in situ by dissociation of the phosphirenium ions. The treatment of stabilized phosphirenium salts with alkynes is a known synthetic route to phosphirenium salts;<sup>9</sup> indeed, the standard synthetic route—treatment of a chlorophosphine with a Lewis acid in the presence of an alkyne—implies the participation of a phosphirenium ion.<sup>11a</sup> The cyclization is believed to follow a concerted path akin to the known behavior of singlet carbenes and their analogues [including the terminal phosphinidene complexes (OC)<sub>5</sub>W=PR], which are isolobal with phosphirenium ions. The initial ring-cleavage represents the microscopic reverse of this cycloaddition.



## Experimental Section

**General Comments.** Manipulations of air-sensitive compounds were performed under nitrogen or argon with use of the Schlenk technique. CDCl<sub>3</sub> was dried over 3 Å molecular sieves and Mg(ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O. Other solvents were purified by conventional methods and stored under nitrogen.<sup>18</sup> PhMePCL and PhBnPCL were prepared according to published procedures.<sup>19</sup> Trimethylsilyl triflate (Lancaster) was distilled under vacuum. PhCCPh (Lancaster) was recrystallized from ethanol and dried under vacuum. EtCCPh (Aldrich) was dried over sodium and distilled under vacuum. EtCCEt (Aldrich) was dried over sodium and distilled under nitrogen. NMR data are referenced to internal tetramethylsilane (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra) or to external 85% aqueous H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P{<sup>1</sup>H} spectra).

**Synthesis of Phosphirenium Triflates.** In a typical preparation, a solution of PhMePCL or PhBnPCL (2.6–4.4 mmol) and the alkyne (1 equiv) in dichloromethane was treated with trimethylsilyl triflate (1 equiv) and stirred at room temperature for 1 h. After removal of solvent and Me<sub>3</sub>SiCl under vacuum, the product was recrystallized from dichloromethane–diethyl ether (yields 69–82%). **11** and **12**: Analytical and spectroscopic data were in agreement with those given in ref 4b. **14**: Anal. Calcd for C<sub>20</sub>H<sub>22</sub>F<sub>3</sub>O<sub>3</sub>PS: C 55.81, H 5.15. Found: C 55.56, H 4.86. <sup>1</sup>H NMR (299.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.15 (t,  $J = 7.6$  Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>), 2.69–2.78 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 4.54 (d,  $J = 15.6$  Hz, 2H, CH<sub>2</sub>Ph), 7.32–7.41 (m, 5H, ArH), 7.65–7.82 (m, 5H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  12.1 (br s, CH<sub>2</sub>CH<sub>3</sub>), 19.7 (s, CH<sub>2</sub>CH<sub>3</sub>), 28.8 (d,  $J = 43.8$  Hz, CH<sub>2</sub>-Ph), 119–134 (ArC). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -93.9 (s). FABMS:  $m/z$  281 (100%), [(M - OTf)]<sup>+</sup>.

**Kinetic Investigation.** Kinetic measurements were conducted in CDCl<sub>3</sub>, under argon, using a 500 MHz NMR spectrometer. A solution of the starting phosphirenium triflate in a pressure NMR tube was mixed with appropriate amounts of EtCCPh and of a solution of PhCCPh, so that the initial concentration of starting phosphirenium triflate was 0.0143

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M. The sample was inserted into the spectrometer probe, which had been preheated to 60.4 ( $\pm 0.6$ ) °C, and left for at least 10 min for thermal equilibration. Quantitative spectra were then acquired over a period exceeding six half-lives. Concentrations were monitored by integrating the methyl signal for **11** ( $\delta$  2.97, d,  $J = 16.5$  Hz) and the methylene signal for **12** ( $\delta$  3.35, dq,  $J = 17.9, 7.6$  Hz) and fitted with the program Microcal Origin 3.5 to the equation

$$A_t = A_e + (A_0 - A_e) \exp(-k_{\text{obs}}t)$$

(where  $A_t$  = signal intensity at time  $t$  (s);  $A_e$  = signal intensity

at equilibrium (taken as 9200 s);  $A_0$  = signal intensity at time 0 s; and  $k_{\text{obs}}$  = observed pseudo-first-order rate constant). Good agreement was obtained between the  $k_{\text{obs}}$  values for the two peaks.

**Supporting Information Available:** Kinetic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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