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π-Ligand Exchange on Phosphenium Ions: Reversible Exchange between Free and Coordinated Alkynes in Phosphirenium Salts

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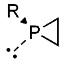
Summary: The rate of reversible alkyne exchange between 1-methyl-1,2,3-triphenylphosphirenium triflate and ethylphenylacetylene, and that of the reverse reaction between 2-ethyl-1-methyl-1,3-diphenylphosphirenium triflate and diphenylacetylene, are independent of alkyne concentration, which suggests a mechanism that involves rate-determining elimination of alkyne from the phosphirenium triflate to give a transient phosphenium triflate. The mechanism is supported by the observation of crossover products upon mixing phosphirenium triflates containing different substituents.

Introduction

The cyclic strain at phosphorus in phosphiranes (**1**) and phosphirenes (**2**) induces a wide range of dissociation, ring-opening, and expansion reactions,[1] among which is the exchange at phosphorus of ethylene for alkenes and alkynes in transition metal derivatives[2] and free phosphiranes.[3] Thus, the thermal decomposition of the neutral phosphirane−metal complexes **4** (e.g., R = NEt_2) in the presence of an alkyne affords the corresponding phosphirene−metal complexes **5** (R′ = H, Ph)[2b] via the phosphinidene complexes $(OC)_5W{=}PR$ (eq 1), which (for R = NEt_2, Me, Ph) also react with olefins to give the expected phosphirane complexes.[2] The free phosphirane **1** (R = MeS), when photochemically decomposed in the presence of EtCCEt, gives **3** in a reaction that is in accord with the free phosphinidene PMes being present as a reactive intermediate.[3a] Triplet PMes has been identified in a frozen matrix by ESR.[3b] Recently, we have shown that the phosphiranium salt **6**, the only phosphiranium salt to be isolated and structurally characterized, behaves similarly and undergoes elimination of ethylene under mild conditions in the presence of MeCCMe or MeCCPh to give quantitative yields of the corresponding phosphirenium salts **7** (R = Me, Ph) (eq 2).[4] We now report that simple phosphirenium salts of this type undergo *reversible* alkyne exchange with free alkynes, as well as alkyne group redistribution reactions, by a dissociative mechanism that implies phosphenium salts as intermediates.



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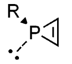

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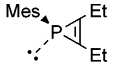

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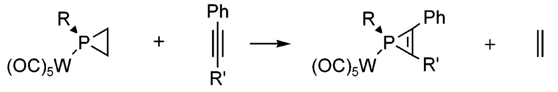
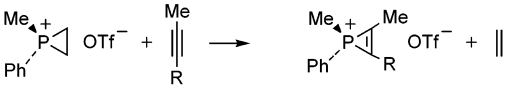


4 **5** (1)



6 **7** (2)

The formal transfer of the methylphenylphosphenium ion, $MePhP^+$, from one unsaturated hydrocarbon to another is reminiscent of π-ligand exchange in transition metal organometallic chemistry, and it is tempting to consider **6** and **7** as π-ethylene and π-alkyne complexes of the six-electron phosphenium ion. Indeed, G2 ab initio calculations[5] show that although the charge densities at the C−P bond critical points[6] in the saturated parent ion **8** are typical of normal covalent linkages, the interaction between AsH_2^+ and ethylene can be roughly described as **9**. For the unsaturated phosphirenium ion **10**, calculations show a stabilizing interaction between a p-type σ^*-orbital on the phosphorus, which is antibonding to the exocyclic P-substituents, and the double bond.[7] This stabilization, termed σ^*-aromaticity, influences the geometries of phosphirenium ions and depends on the substituents' electronegativities. Thus, the bond separation energy for the 1,1-dimethylphosphirenium ion, which is correlated to relief

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[1] (a) Mathey, F. *Chem. Rev.* **1990**, *90*, 997−1025. (b) Mathey, F.; Regitz, M. In *Phosphorus−Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Mathey, F., Ed.; Pergamon: Oxford, 2001; Chapter 2.

[2] (a) Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134−2138. (b) Mercier, F.; Deschamps, B.; Mathey, F. *J. Am. Chem. Soc.* **1989**, *111*, 9098−9100. (c) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456−461. (d) Lammertsma, K.; Chand, P.; Yang, S.-W.; Hung, J.-T. *Organometallics* **1988**, *7*, 1875−1876. (e) Hung, J.-T.; Lammertsma, K. *Organometallics* **1992**, *11*, 4365−4366. (f) Lammertsma, K.; Hung, J.-T.; Chand, P.; Gray, G. M. *J. Org. Chem.* **1992**, *57*, 6557−6560. (g) Hung, J.-T.; Yang, S.-W.; Gray, G. M.; Lammertsma, K. *J. Org. Chem.* **1993**, *58*, 6786−6790. (h) Hung, J.-T.; Yang, S.-W.; Chand, P.; Gray, G. M.; Lammerstma, K. *J. Am. Chem. Soc.* **1994**, *116*, 10966−10971.

[3] (a) Li, X.; Lei, D.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 8526−8531. (b) Li, X.; Weissman, S. I.; Lin, T.-S.; Gaspar, P. P.; Cowley, A. H.; Smirnov, A. I. *J. Am. Chem. Soc.* **1994**, *116*, 7899−7900.

[4] (a) Hockless, D. C. R.; McDonald, M. A.; Pabel, M.; Wild, S. B. *J. Chem. Soc., Chem. Commun.* **1995**, 257−258. (b) Hockless, D. C. R.; McDonald, M. A.; Pabel, M.; Wild, S. B. *J. Organomet. Chem.* **1997**, *529*, 189−196.

[5] Mó, O.; Yáñez, M.; Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Guillemin, J.-C. *J. Am. Chem. Soc.* **1999**, *121*, 4653−4663.

[6] Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: Oxford, 1990.

[7] Göller, A.; Heydt, H.; Clark, T. *J. Org. Chem.* **1996**, *61*, 5840−5846.

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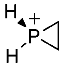
of ring strain, is only 7.14 kcal mol^{-1} more exothermic than that for the saturated analogue, as opposed to a corresponding exothermicity difference of 23.64 kcal mol^{-1} for cyclopropene and cyclopropane.[7] This is consistent with the experimental observation of facile replacement of ethylene by alkynes on the MePhP$^+$ ion.[4]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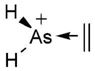
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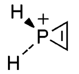
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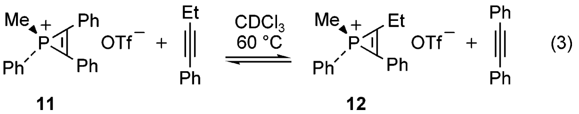
Ab initio calculations at the G2 level show that π-ethylene and π-acetylene exchange on PH$_2{}^+$ can occur by an associative pathway through a spirocyclic transition state of C_{2v} symmetry with barriers of 3.6 and 39.4 kJ mol^{-1}, respectively.[8] These values are much smaller than those calculated for the corresponding insertion reactions that lead to the thermodynamically preferred five-membered heterocycles (234.0 and 216.9 kJ mol^{-1}, respectively).[8] 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** ⇌ **12** (eq 3). This *reversible* alkyne exchange is unprecedented in main group heterocyclic chemistry.



(3)

Results and Discussion

Synthesis of Phosphirenium Triflates. Phosphirenium triflates **11** and **12** were prepared by treating PhMePCl with trimethylsilyl triflate (1 equiv) in CH$_2$Cl$_2$ 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,[4b] 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$_3$ were investigated by ^{1}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.

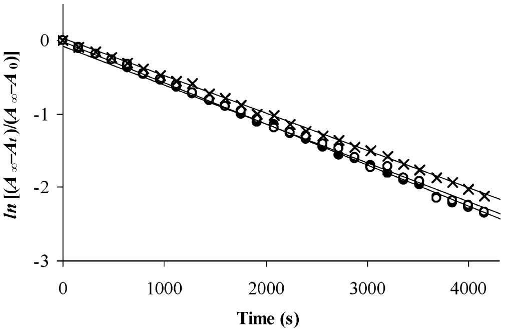


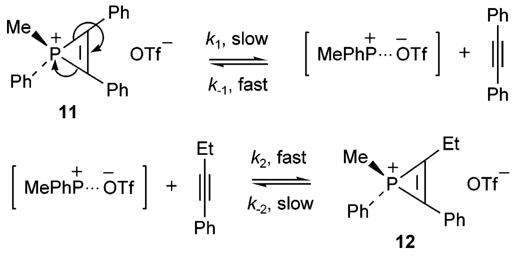
Figure 1. Kinetic plots showing the decrease in [**11**] with time for the reaction of **11** (0.0143 M) with EtCCPh at concentrations of 0.143 M (●), 0.715 M (×), and 1.43 M (○) in the presence of PhCCPh (0.143 M) at 60 °C in CDCl$_3$. Abbreviations are as defined in the Experimental Section.

Table 1. Observed Pseudo-First-Order Rate Constants[a] for (A) Reaction of 11 with EtCCPh[b] and (B) Reaction of 12 with PhCCPh[c] at 60 °C in CDCl$_3$

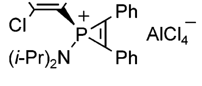
	$10^4 \times k_{obs}$/s^{-1}	
[alkyne]/M	A	B
0.143	5.6 ± 0.3	5.3 ± 1.0
0.286	4.9 ± 0.3	5.7 ± 1.5
0.714	5.1 ± 0.2	5.4 ± 0.8
1.07	5.2 ± 0.2	5.6 ± 0.4
1.43	5.2 ± 0.6	6.2 ± 0.8

[a] Average of two experiments. [b] [**11**]$_0$ = 0.0143 M, [PhCCPh]$_0$ = 0.143 M. [c] [**12**]$_0$ = 0.0143 M, [EtCCPh]$_0$ = 0.143 M.

Scheme 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 angles in **7** (R = Me) [44.4(2)°][4b] and **13** [46.1(5)°][9] (the only examples that have been structurally characterized) are much smaller than the corresponding angle in the phosphiranium salt **6** [51.7(2)°],[4] 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 phosphenium triflate intermediate (not detected) that rapidly adds to the incoming alkyne to give the new phosphirenium salt (Scheme 1).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Application of the steady-state approximation to the mechanism shown in Scheme 1 gives the following

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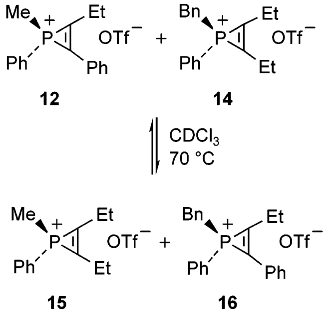
(8) Sølling, T. I.; McDonald, M. A.; Wild, S. B.; Radom, L. *J. Am. Chem. Soc.* **1998**, *120*, 7063−7068.

(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: $k_{obs} = \{k_1k_2[B] + k_{-1}k_{-2}[A]\}/\{k_2[B] + k_{-1}[A]\}$, where [A] and [B] are the PhCCPh and EtCCPh concentrations, respectively.[10] In this model, when [B]/[A] = 0, k_{obs} is equal to k_{-2}, but as [B]/[A] becomes large, k_{obs} approaches k_1. The data for the forward direction (column A in Table 1) fall in the latter regime, giving $k_1 = (5.2 \pm 0.3) \times 10^{-4}$ s^{-1}. Analysis of data for the reverse reaction (column B) gives $k_{-2} = (5.6 \pm 0.9) \times 10^{-4}$ s^{-1}. In principle, the variation in k_{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, $K = k_1k_2/k_{-1}k_{-2}$: we determine K to be 11 ± 2, and thus k_{-1}/k_2 is 0.08.

In phosphenium salts, $R_2P^+X^-$, one or two electron-rich amido or sulfido substituents are usually required to confer isolability.[11] The only phosphenium salt to have been isolated that contains a P–C bond is [P(Mes)(N^{i}Pr$_2$)]AlCl$_4$, and, while this is ionic or loosely ion-paired in CD$_2$Cl$_2$ (δ_P 500 ppm), the corresponding triflate is covalent (δ_P 185 ppm, C$_6$D$_6$).[12] A cyclic bis(amido)-substituted phosphenium triflate has also shown a P···O interaction in dichloromethane that was intermediate between ionic and covalent.[13] The importance of ion-pairing to the stability of phosphenium salts was further evidenced by the reaction of [P(N^{i}Pr$_2$)$_2$]BPh$_4$ with CH$_2$Cl$_2$ to give [P(CH$_2$Cl)Cl(N^{i}Pr$_2$)$_2$]BPh$_4$, in contrast with the corresponding GaCl$_4^-$ salt, which gave no such reaction.[14] The reaction rates of stable carbenium ions with neutral nucleophiles in aprotic solvents vary little with the nature of the solvent,[15] and, furthermore, spectroscopic investigations have shown that the trityl cation does not form an adduct with chloroform.[16] We believe, therefore, that the stability of the intermediate MePhP$^+$ 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[17] have shown that, while an associative mechanism is favored in the gas phase when solvation and ion-pairing are not taken into account,[8] 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 ^{31}P{^{1}H} NMR spectrum of an equimolar mixture of **12** and **14** in CDCl$_3$ 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 phosphenium salts with alkynes is a known synthetic route to phosphirenium salts;[9] indeed, the standard synthetic route—treatment of a chlorophosphine with a Lewis acid in the presence of an alkyne—implies the participation of a phosphenium ion.[11a] 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)$_5$W=PR], which are isolobal with phosphenium ions. The initial ring-cleavage represents the microscopic reverse of this cycloaddition.



(4)

Experimental Section

General Comments. Manipulations of air-sensitive compounds were performed under nitrogen or argon with use of the Schlenk technique. CDCl$_3$ was dried over 3 Å molecular sieves and Mg(ClO$_4$)$_2$·2H$_2$O. Other solvents were purified by conventional methods and stored under nitrogen.[18] PhMePCl and PhBnPCl were prepared according to published procedures.[19] 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 (^{1}H and ^{13}C{^{1}H} spectra) or to external 85% aqueous H$_3$PO$_4$ (^{31}P{^{1}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$_3$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$_{20}$H$_{22}$F$_3$O$_3$PS: C 55.81, H 5.15. Found: C 55.56, H 4.86. ^{1}H NMR (299.9 MHz, CD$_2$Cl$_2$): δ 1.15 (t, J = 7.6 Hz, 6H, CH$_2$CH_3), 2.69–2.78 (m, 4H, CH_2CH$_3$), 4.54 (d, J = 15.6 Hz, 2H, CH_2Ph), 7.32–7.41 (m, 5H, ArH), 7.65–7.82 (m, 5H, ArH). ^{13}C{^{1}H} NMR (75.4 MHz, CD$_2$Cl$_2$): δ 12.1 (br s, CH$_2$CH$_3$), 19.7 (s, CH$_2$CH$_3$), 28.8 (d, J = 43.8 Hz, CH$_2$Ph), 119–134 (ArC). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$): δ −93.9 (s). FABMS: m/z 281 (100%), [(M − OTf)]$^+$.

Kinetic Investigation. Kinetic measurements were conducted in CDCl$_3$, 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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(10) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill: New York, 1995; Chapter 4.

(11) (a) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367–382. (b) Burford, N.; Ragogna, P. J. *J. Chem. Soc., Dalton Trans.* **2002**, 4307–4315.

(12) Reed, R. W.; Xie, Z.; Reed, C. A. *Organometallics* **1995**, *14*, 5002–5004.

(13) Jones, V. A.; Sriprang, S.; Thornton-Pett, M.; Kee, T. P. *J. Organomet. Chem.* **1998**, *567*, 199–218.

(14) (a) Burford, N.; Losier, P.; Bakshi, P. K.; Cameron, T. S. *J. Chem. Soc., Dalton Trans.* **1993**, 201–202. (b) Burford, N.; Losier, P.; Macdonald, C.; Kyrimis, V.; Bakshi, P. K.; Cameron, T. S. *Inorg. Chem.* **1994**, *33*, 1434–1439.

(15) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938–957.

(16) Gatzke, A. L.; Stewart, R. *Can. J. Chem.* **1961**, *39*, 1849–1853.

(17) Radom, L.; Sølling, T. I., personal communication, 2003.

(18) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, 1996; Chapter 3.

(19) Fild, M.; Schmutzler, R. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 4, pp 90–91.

M. The sample was inserted into the spectrometer probe, which had been preheated to 60.4 (±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** (δ 2.97, d, $J = 16.5$ Hz) and the methylene signal for **12** (δ 3.35, dq, $J = 17.9, 7.6$ Hz) and fitted with the program Microcal Origin 3.5 to the equation

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

(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_{obs} = observed pseudo-first-order rate constant). Good agreement was obtained between the k_{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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