Summary: The rate of reversible alkyne exchange between 1-methyl-1,2,3-triphosphinidene 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 phosphonium 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 phosphirenium salts (2) induces a wide range of dissociation, ring-opening, and expansion reactions,1 among which is the exchange at phosphorus of ethylene for alkynes and alkynes in transition metal derivatives2 and free phosphiranes.3 Thus, the thermal decomposition of the neutral phosphirane–metal complexes 4 (eq. R = NET2) in the presence of an alkyne affords the corresponding phosphirane–metal complexes 5 (R′ = H, Ph)2b via the phosphinidene complexes (OC)2W=PR (eq 1), which for R = NET2, 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.3b Triplet PMes has been identified in a frozen matrix by ESR.3b Recently, we have shown that the phosphirane salt 6, the only phosphirane 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 phosphonium salts as intermediates.

The formal transfer of the methylphenylphosphonium 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 3-alkyne complexes of the six-electron phosphonium ion. Indeed, G2 ab initio calculations5 show that although the charge densities at the C–P bond critical points6 in the saturated parent ion 8 are typical of normal covalent linkages, the interaction between AsH2 and ethylene can be roughly described as 9. For the unsaturated phosphonium ion 10, calculations show a stabilizing interaction between a π-type π*-orbital on the phosphorus, which is antibonding to the exocyclic P-substituents, and the double bond.7 This stabilization, termed π*-aromaticity, influences the geometries of phosphirenium ions and depends on the substituents’ electronegativities. Thus, the bond separation energy for the 1,1-dimethylphosphonium ion, which is correlated to relief
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 cyclopropane.\(^7\) This is consistent with the experimental observation of facile replacement of ethylene by alkynes on the MePhP\(^+\) ion.\(^4\)

Ab initio calculations at the G2 level show that \(\pi\)-ethylene and \(\pi\)-acetylene exchange on PH\(_2\)^+ can occur by an associative pathway through a spirocyclic transition state of C\(_2\)v 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 \(\rightleftharpoons\) 12 (eq 3). This reversible alkyne exchange is unprecedented in main group heterocyclic chemistry.

\[
\begin{align*}
11 & \quad \text{MePh}^+ + \text{PhCCPh} \quad \text{EtCCPh} + \text{Ph}^- + \text{OTF}^- \\
12 & \quad \text{MePh}^+ + \text{EtCCPh} \quad \text{PhCCPh} + \text{Ph}^- + \text{OTF}^- 
\end{align*}
\]

\(\text{MePh}^+\) and \(\text{PhCCPh}\) at 60 °C in CDCl\(_3\) were prepared by treating PhMePCl with trimethylsilyl triflate (1 equiv) in CH\(_2\)Cl\(_2\) in the presence of PhCCPh (0.143 M) at 60 °C in CDCl\(_3\). 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 the EtCCPh 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\(_3\)

<table>
<thead>
<tr>
<th>[alkyne]/M</th>
<th>(10^4 \times k_{obs}/s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>0.143</td>
<td>5.6 ± 0.3</td>
</tr>
<tr>
<td>0.286</td>
<td>4.9 ± 0.3</td>
</tr>
<tr>
<td>0.714</td>
<td>5.1 ± 0.2</td>
</tr>
<tr>
<td>1.07</td>
<td>5.2 ± 0.2</td>
</tr>
<tr>
<td>1.43</td>
<td>5.6 ± 0.6</td>
</tr>
</tbody>
</table>

\(^a\) Average of two experiments. \(^b\) [11] = 0.0143 M, [PtCCPh] = 0.143 M. \(^c\) [12] = 0.0143 M, [EtCCPh] = 0.143 M.

## Results and Discussion

**Synthesis of Phosphireniurn Triflates.** Phosphireniurn triflates 11 and 12 were prepared by treating PhMePCI with trimethylsilyl triflate (1 equiv) in CH\(_2\)Cl\(_2\) to form the appropriate alkyne and were isolated as colorless, moisture-sensitive, crystalline solids. This method represents an improvement on the previously reported method,\(^4\) 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.

These findings suggest that the exchange follows a mechanism in which the addition of the incoming alkyne takes place rapidly after the slow, alkylene-independent deavage of the three-membered ring. Phosphireniurn rings are highly strained entities. The intracyclic C–P–C angles in 7 (R = Me) [44.4(2)°] and 13 [46.1(5)°] (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 [av 1.759(6) Å]. We propose that the reactivity of phosphireniurn 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 phosphireniurn triflate intermediate (not detected) that rapidly adds to the incoming alkyne to give the new phosphireniurn salt (Scheme 1).

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

---


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 confer isolability.\(^{11a}\) The stability of the trityl cation does not form an adduct with chloro-

In this model, when \([B]/[A]\) becomes large, \( k_{-2} \) 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 \([B]/[A]\) are not distinguishable within experimental error, no hyperbolic behavior was seen. The ratio \( k_-1 \) \( k_2 \) may, however, be estimated from the equilibrium constant, \( K = k_{1}k_{-2}/k_{2}k_{-1} \): we determine \( K \) to be 11 \( \pm \) 2, and thus \( k_{-1}/k_2 \) is 0.08.

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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

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

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