[1,3]-Sigmatropic Rearrangement of 1,3,5-Triphosphabicyclo[2.1.0]pent-2-ene

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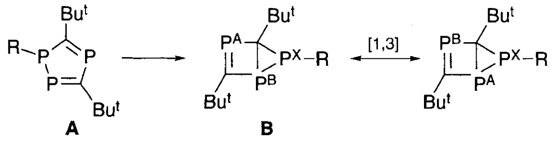
The activation barrier for the [1,3]-phosphorus migration in the title compound is estimated (MP4SDTQ/6–31 G*//MP2/6–31 G* + ZPE) to be 11.62 kcal mol^{-1} (1 cal = 4.184 J), which is considerably smaller than the barrier (31.13 kcal mol^{-1}) for [1,3]-carbon migration in the corresponding hydrocarbon.

Recently, Nixon and coworkers prepared the first example of 1,2,4-triphosphole **A**, [R = $(Me_3Si)_2CH$], which has been characterised by X-ray crystallography.[1] At room temperature **A** slowly rearranges (under the influence of light) to the 1,3,5-triphosphabicyclo[2.1.0]pent-2-ene **B** *via* an electrocyclisation reaction, and the latter has been characterised as its $[W(CO)_5]$ complex **C**. Compound **B** undergoes an interesting insertion and chlorine migration reaction on treatment with $[PtCl_2(PEt_3)]_2$ to give **D** which has been fully structurally characterised by a single crystal X-ray diffraction study.[2]

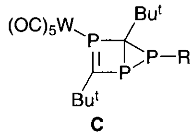
Surprisingly, the ^{31}P NMR of **B** at room temperature shows a triplet and doublet (broad) pattern of relative intensities 1 : 2, which suggest fast interchange of P^A and P^B. The tungsten pentacarbonyl complex shows the expected ABX ^{31}P NMR pattern. Nixon *et al.*[2] proposed a facile [1,3]-sigmatropic shift of P^X from P^A to P^B to explain these results (Scheme 1).

Berson and Nelson's[3] classic experiment conclusively demonstrated [1,3]-sigmatropic shifts of carbon are allowed *via* a suprafacial pathway only with inversion at the migrating carbon. However, the shift occurs at temperatures (>300 °C) well above the conditions observed in Scheme 1. Here we present high level *ab initio* calculations[4] on the parent system (Scheme 2) demonstrating that the [1,3]-shift in the phosphorus system proceeds through a low energy transition structure.

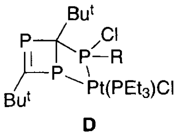
1,3,5-triphosphabicyclo[2.1.0]pent-2-ene can have an *exo* **1x** or *endo* **1n** structure. [1,3]-Sigmatropic migration of the 5 phosphorus can occur *via* cleavage of the P–P bond (**2**) or the C–P bond (**3**). According to orbital symmetry rules,[5] as confirmed by experiment,[3] the migrating group must invert. Therefore, the allowed [1,3]-migration by either path takes **1x** into its mirror image and **1n** into its mirror image. **1x** can convert into **1n** only by inversion through phosphorus **4** or by the unlikely antarafacial [1,3] path. We have optimized the geometry of **1x** and **1n** and the transition structures **2–3** at the MP2/6–31 G* level. To better account for the effects of electron correlation, which can be significant in pericyclic reactions of phosphaalkenes,[6] we obtained energies at MP4SDTQ/6–31 G*//MP2/6–31 G*. All structures were characterized using HF/6–31 G* analytical frequencies. Zero-point energy corrections were scaled by 0.89. The MP2 optimized structures are drawn in Fig. 1. We also examined bicyclo[2.1.0]pent-2-ene **5** and the transition structure for its [1,3]-rearrangement **6**. Relative energies for all structures are listed in Table 1.



Scheme 1



C

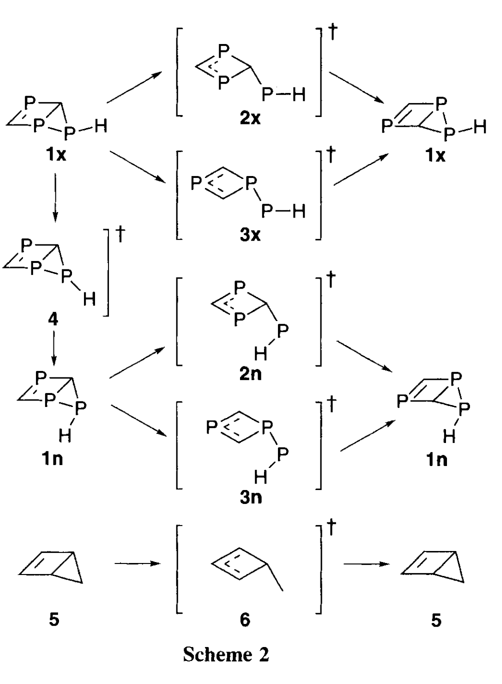


D

The *endo* form of **1** lies 2.73 kcal mol^{-1} above the *exo* isomer. This is probably due to decreased lone pair–lone pair repulsion in **1x**, whereas in **1n** the adjacent phosphorus lone pairs are nearly eclipsed, resulting in a long P–P bond. The other distances in the two isomers differ by less than 0.01 Å. The inversion process converting **1x** into **1n** has a barrier of 54.79 kcal mol^{-1}. This can be compared to the inversion barrier in phosphirane (68.3 kcal mol^{-1}) and dimethylphosphine (38.2 kcal mol^{-1}).[7] The transition structures (**2–3**) for the [1,3]-phosphorus migration from **1x** and **1n** have C_s symmetry, as expected for a suprafacial pathway with inversion at phosphorus. Compound **6** also has C_s symmetry. We were unable to locate a transition structure with retention at P or C (the antarafacial pathway).

The lowest barrier, 11.62 kcal mol^{-1}, is for migration of **1x** through **2x**. This pathway involves cleavage of the P–P bond. The activation barrier for reaction through **3x**, which involves cleavage of the stronger C–P bond, is 28.66 kcal mol^{-1}. The barrier for migration in **1n** is 11.97 kcal mol^{-1} through **2n** and 26.13 kcal mol^{-1} through **3n**. For comparison, the activation energy for the migration in the hydrocarbon (taking **5** through **6**) is 31.13 kcal mol^{-1}. Clearly, migration in the phosphorus compound will be much more facile than in the hydrocarbon, regardless of the pathway, but the lowest barrier for migration in **1** is 20 kcal mol^{-1} less than in **5**.

The geometries of the transition states for migration show many similarities. The allylic C–P distance is about 1.75 Å in all four TSs, between typical C–P and C=P lengths. The C–P_5 distance is shorter in **2** than in **1**, and the P–P_5 distance in **3** is also shorter than in **1**. The same trends are also seen in **6**. On the other hand, the distances between the migrating atoms differs greatly between the *endo*/*exo* isomers. The P···P distance in **2x** is 2.618 Å (a lengthening of 0.39 Å from **1x**) and is 2.811 Å in **2n** (an increase of 0.56 Å). The C···P is 2.511 and 2.768 Å in **3x**



Scheme 2

and **3n**, increases of 0.65 and 0.92 Å, respectively, from **1x** and **1n**.

We utilized the topological electron density method[8] to evaluate the bonding in the TSs. The presence of a bond critical point is indicative of chemical bonding. No such critical points could be found between the making/breaking bonds in **2, 4** or **6**. Thus, the three-membered ring is broken in the transition state, before any new bonding is established. The bond order of C–P and C–C bonds can be estimated using the value of the density at the bond critical point.[9] The bond order of the allylic C–P bonds in **2x** and **2n** are 1.58 and 1.55, respectively, while the bond order for the allylic C–C bonds in **6** is 1.58. However, the bond order for the allylic C–P bonds in **3x** and **3n** is substantially less (1.29 and 1.30) even though the bonds are only slightly longer than the analogous bonds in **2**. The central atom of the allylic fragment in **3** is P, which poorly conjugates, compared with C, leading to the smaller bond orders. The transition states **2** and **6** are very similar in terms of their structure, topology, and electron distribution. The [1,3]-bond migrations in the two systems proceed by similar mechanism namely the orbital symmetry allowed sigmatropic rearrangement with inversion at the migrating atom.

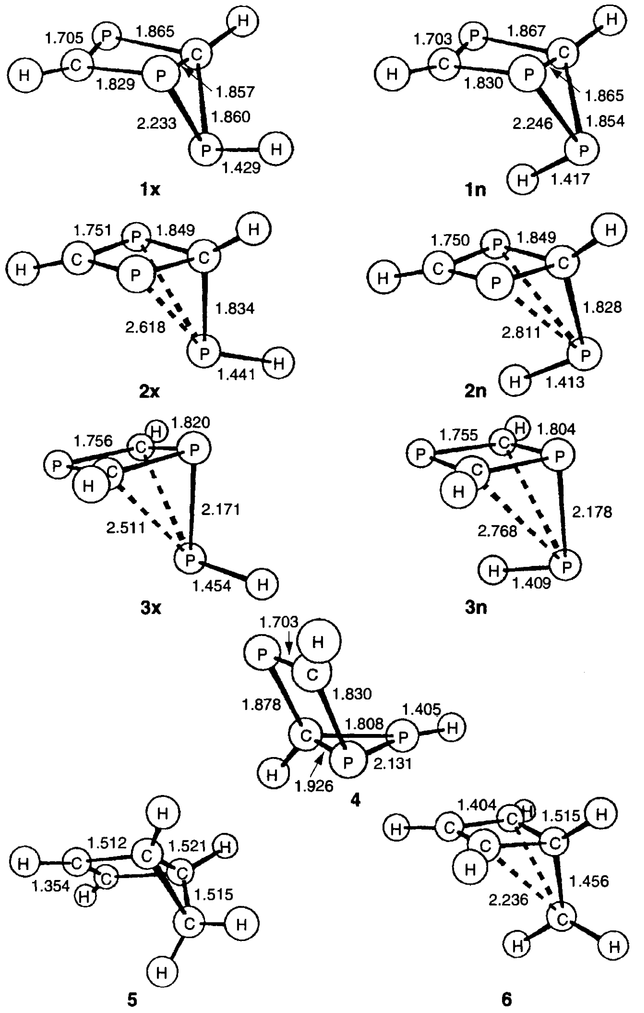


Fig. 1 MP2/6–31 G* Optimized geometries of **1–6**. All distances are in Å.

Table 1 Relative Energies (kcal mol^{-1}) of **1–6** at MP4SDTQ/6–31 G*//MP2/6-31 G* + ZPE(HF/6–31 G*)

Compound	E_{rel}
1x	0.00
1n	2.73
2x	11.62
2n	13.70
3x	28.66
3n	28.84
4	54.79
5	0.00
6	31.13

Migration in the phosphorus system is much more facile than in the hydrocarbon. This can be attributed to two factors, (i) reaction through **2** requires cleavage of the weak P–P bond, compared to cleavage of the C–P bond in **3**, and the strong C–C bond in **6**, (ii) the suprafacial pathway requires the migrating atom to become planar, an easier task for phosphorus than for carbon. The exceptionally small activation energy of 11.62 kcal mol^{-1} for the [1,3]-phosphorus migration in **1** fully supports the proposed reaction of Scheme 1.

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