

1*H*-Phosphiranes and -enes invert at phosphorus *via* a turnstile rotation†

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Ab initio (CCSD(T)/6-31+G*) calculations suggest that 1*H*-phosphiranes and 1*H*-phosphirenes invert their configuration at phosphorus by a rotation of the PX group (X = H, F, Cl, Br) above the C₂ moiety, rather than the more usual planar trigonal inversion pathway *via* a C_{2v} transition state.

Because of the high inherent barrier to inversion at three-coordinate phosphorus, phosphanes can be isolated as pure enantiomers.¹ The additional effect of inclusion in a three-membered ring increases inversion barriers further,² so that 1*H*-phosphiranes and, even more so, 1*H*-phosphirenes should have particularly high inversion barriers. However, our recent studies on σ*-aromatic 1*H*-phosphirenium ions³ have revealed unusual bonding effects and so we have investigated the inversion process in 1*H*-phosphiranes⁴ and 1*H*-phosphirenes.⁵ Our studies reveal an unusual inversion mechanism caused by the avoidance of large bond angles at phosphorus and, in the unsaturated systems, by the potential antiaromaticity of the trigonal inversion transition states.^{2,6} This mechanism is analogous to that for PF₃ inversion *via* a T-shaped transition state,⁷ but is favoured by additional ring strain and conjugation effects.

1*H*-phosphiranes **1** and 1*H*-phosphirenes **2** can undergo inversion at phosphorus by two distinct mechanisms (absolute energies and geometries are given in Tables 1 and 2 of the Supplementary material,† respectively). The first is *via* the C_{2v} structures **3** and **4** for the saturated and unsaturated systems, respectively, as described by Bachrach.^{2,8} The structures **3** are found to be real transition states (one calculated imaginary frequency), but **4** is found to be a second-order saddle point (hilltop) for all ligands X except hydrogen, for which **4** is also a transition state. *Ab initio*^{9a} [CCSD(T)¹⁰/6-31+G*¹¹/(MP2¹²/6-31+G*)] calculations performed with GAUSSIAN 94^{9b} give energy differences between **1** and **3** at 0 K of 66.5 kcal mol⁻¹ (1 cal = 4.184 J) (X = H), 99.9 kcal mol⁻¹ (X = F), 86.0

kcal mol⁻¹ (X = Cl), and 82.3 kcal mol⁻¹ (X = Br) and those between **2** and **4** of 85.4 kcal mol⁻¹ (X = H), 45.5 kcal mol⁻¹ (X = F), 55.4 kcal mol⁻¹ (X = Cl), and 50.9 kcal mol⁻¹ (X = Br) (see Table 3 of Supplementary material). For the π-donor halogen ligands, the barrier to trigonal inversion is unexpectedly lower for the 1*H*-phosphirenes **2** than for the 1*H*-phosphiranes **1**. This is the result of the partial dissociation of **4** into an aromatic phosphirenium cation–halide ion pair. This dissociation is analogous to that found for the fluoromethyl anion,¹³ which can be regarded as a carbene–fluoride complex. Note that all the above barriers are considerably lower than the 120–130 kcal mol⁻¹ found⁷ for the 8π-electron PF₃.

The second route is the simple rotation of the PX group roughly around an axis through the phosphorus atom and the centre of the C–C bond. This process occurs for the phosphiranes **1** *via* transition state **5** and is found to be more favourable than trigonal inversion for all ligands except hydrogen. The calculated barriers at 0 K are 77.1 kcal mol⁻¹ (X = F), 70.6 kcal mol⁻¹ (X = Cl) and 65.2 kcal mol⁻¹ (X = Br). For X = H, **5** collapses to **3** on geometry optimisation, so that in this

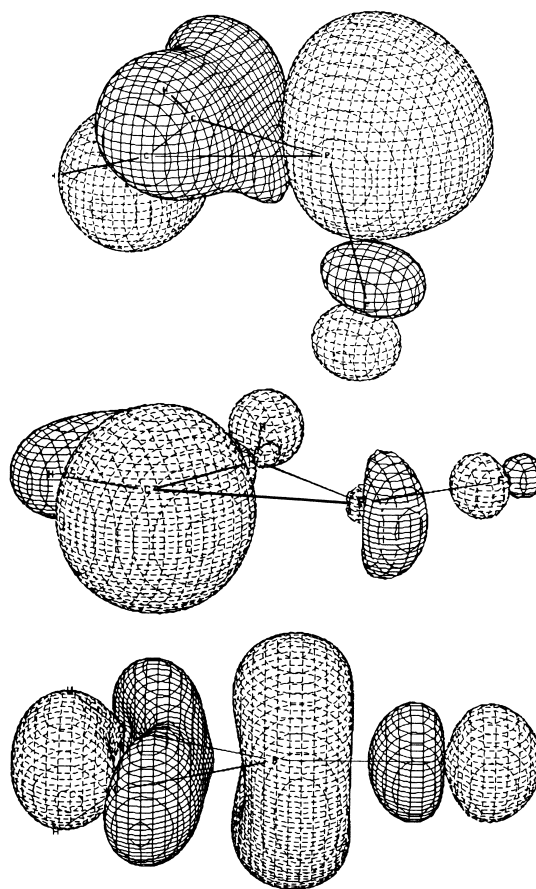
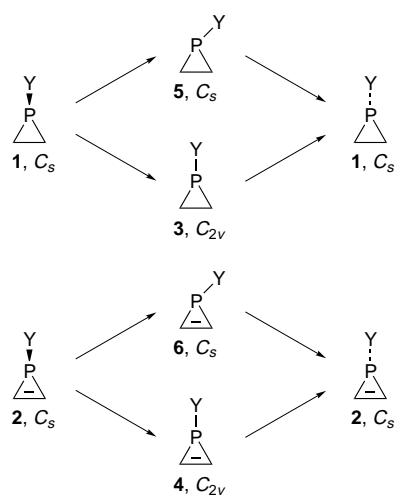


Fig. 1 MO plots of the 'phosphorus lone pair' for the 1-fluoro-1*H*-phosphirene ground state (top), turnstile transition state (middle) and trigonal inversion transition state (bottom)

case the trigonal inversion mechanism applies. The C_s structures **5** are found to be transition states for the halogen ligands. Thus, for electronegative ligands on phosphorus, the 1*H*-phosphiranes **1** show a 10–20 kcal mol⁻¹ preference for the ‘turnstile’ inversion process *via* transition states **5**.

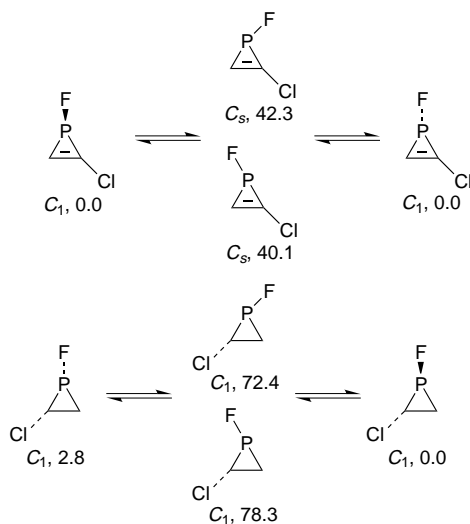
The situation is, however, made even clearer in the 1*H*-phosphirenes **2** by the potential antiaromaticity of **2** and **3**. Because of the unfavourable 4π interaction in these species, **2** strongly prefers the turnstile inversion. By rotating, rather than inverting, the PX group, the 4π-antiaromatic interaction can be avoided completely in the transition state. Furthermore, the antiaromatic destabilisation decreases on going from **2** to **6**, thus favouring the turnstile mechanism. The C–P bond *trans* to the ligand X is lengthened by negative hyperconjugation¹⁴ with the phosphorus lone pair in the transition states **6**, even to the extent that for X = H the transition state is essentially ring-opened. The calculated barrier at 0 K are 52.2 kcal mol⁻¹ (X = H), 38.4 kcal mol⁻¹ (X = F), 43.4 kcal mol⁻¹ (X = Cl) and 40.2 kcal mol⁻¹ (X = Br).

Fig. 1 shows the HOMOs of **2**, **4** and **6** (X = F) and illustrates the partial dissociation of the P–F bond in **4**. The turnstile rotation (**2** to **6**) involves a simple rotation of the PF-group orbitals with strong negative hyperconjugation into the *anti* C–P bond. **4** avoids antiaromaticity by rotating the F lone-pair component into a σ* orientation relative to phosphorus, rather than forming an extra occupied π orbital. The plots were generated with PSI 88.¹⁵

The turnstile mechanism of inversion at phosphorus also means that there are two non-equivalent transition states to inversion of 2-substituted phosphirenes and phosphiranes.

This is shown for chlorine-substituted **1** and **2**. As expected, the transition state in which the lone pair can conjugate with the chlorine-substituted P–C bond (F and Cl *anti*) is favoured. Donor substituents should show the opposite trend.

Thus, our results indicate that inversion of configuration at phosphorus in **1** and **2** is an easier process than might have been expected and that it occurs *via* an unusual turnstile mechanism. A strong experimental indication of the proposed mechanism would be the cumulative effect of ring substituents on inversion barriers.



Scheme 2

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Footnotes

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† This ChemComm (and Supplementary material) is also available in enhanced multi-media format *via* the World Wide Web: <http://chemistry.rsc.org/rsc/cccenha.htm>

‡ Available on request from the authors.

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