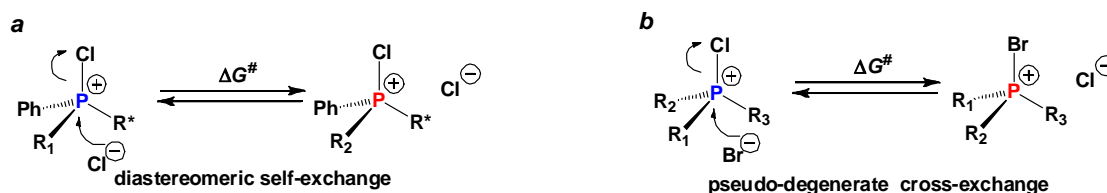


# Phosphorus and Carbon: a Tetrahedral Connection

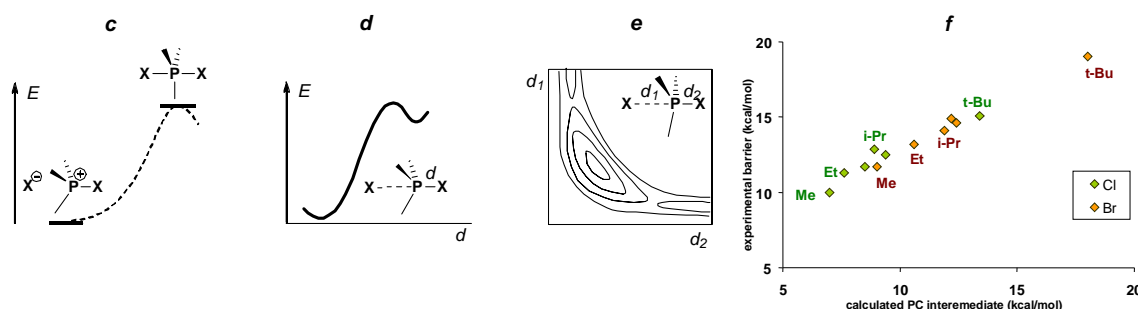
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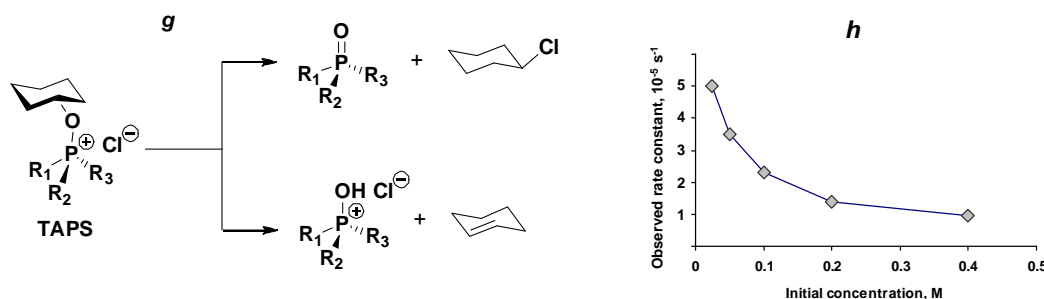
The solution dynamics of tetrahedral halophosphonium salts (XPS) were studied by variable temperature <sup>31</sup>P NMR in both diastereomeric series (a) and the cross-exchange series (b) which showed that this is a rapid reaction controlled sterically:



We have identified possible computational approaches to estimate the energy barriers to Walden-type epimerisation of XPS: single point method (c); single constrained method (d); and the three-dimensional PES approach (e). The computations were extended to the experimental systems and a good correlation (f) of calculated and experimentally determined reaction barriers was observed.<sup>1</sup>



Formation<sup>2</sup> and thermal collapse of tetrahedral alkoxyphosphonium salts (TAPS, g) demonstrate unexpected effects of acids, bases and overall negative kinetic order (h). This is consistent with the presence of HCl<sub>2</sub> anions in the structure of TAPS.



1. Jennings, E.; Nikitin, K.; Ortin, Y.; Gilheany, D.G. *J. Am. Chem. Soc.*, **2014**, 136, 16217–16226. 2. Nikitin, K.; Rajendran, K.; Müller-Bunz, H.; Gilheany, D.G. *Angew. Chem. Int. Ed.* **2014**, 53, 1906–1909.