

Dynamic diphosphanes

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Dynamic and reversible chemical reactions have garnered increasing attention in medicine and biology, supramolecular chemistry and materials science, and they are key to the rapidly growing field of dynamic combinatorial chemistry (DCC). One of the most widely studied of such systems is disulfide metathesis, which by virtue of the weak (~260 kJ/mol) and reactive S–S bond, are capable of various exchange mechanisms both in solution and polymer melts.^[1]

Amongst the main group E–E bonds not explored in DCC, the P–P bond of diphosphanes is a potentially interesting candidate because of its relative weakness (~220 kJ/mol). Moreover, diphosphanes undergo many reactions that involve P–P scission,^[2] including “diphosphane scrambling”.^[3]

In this study, through a combination of experimental and computational techniques, new insights into the metathesis of tetra-aryldiphosphanes (see Figure 1 for an example) have emerged, revealing parallels with radical-mediated disulfide exchange.^[4]

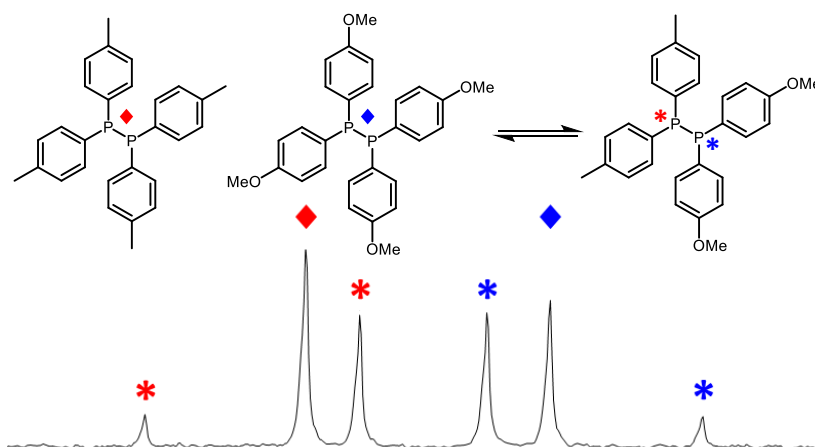


Figure 1: ³¹P{¹H} NMR spectrum of the equilibrium mixture obtained from (p-Tol)₂P–P(p-Tol)₂ and (p-Anisyl)₂P–P(p-Anisyl)₂.

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