

Exocyclic P–C vs. Endocyclic P–P Bond Cleavage in 1,2-Diphosphetes. A Competition between Cyclic Delocalization and Cyclic Strain Controlled by the Substitution Pattern

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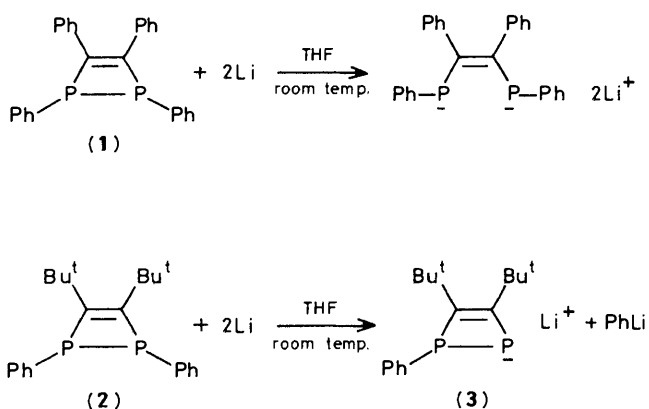
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Attack by lithium on 1,2-diphenyl-3,4-di-R-substituted-1,2-diphosphetes takes place on the endocyclic P–P bond when R = Ph whereas it takes place on the exocyclic P–Ph bond when R = Bu[†]; in this latter case, a 1,2-diphosphet-1-yl anion is obtained which is probably stabilized by cyclic delocalization.

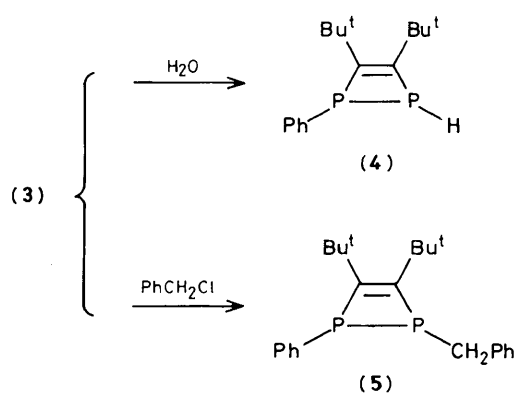
In a previous paper¹ we demonstrated on the basis of *X*-ray structural data that the stability, and hence very probably the chemistry, of the 1,2-diphosphete ring are controlled by the substituents on the double bond subunit. *C*-Unsubstituted 1,2-diphosphetes are unknown and probably very unstable whereas the stability sharply increases with bulky substituents on the ring carbon atoms. Therefore, we were interested in

comparing the chemistries of the readily available 1,2,3,4-tetraphenyldiphosphete^{1,2} (**1**) with that of the more bulkily substituted, and hence more stable, 1,2-diphenyl-3,4-di-*t*-butyldiphosphete¹ (**2**). *X*-Ray crystal structure analysis of (**2**)[†]

[†] A full description of the structure of (**2**) will be published later.



Scheme 1



Scheme 2

has shown significant differences from the structure of (1).¹ The endocyclic P–P bond length decreases from 2.248(1) Å in (1)¹ to 2.214(4) Å in (2) whereas, at the same time, the exocyclic P–C bond length increases from 1.814(4) Å in (1) to 1.848(4) Å in (2). A spectacular difference between the chemistry of (1) and (2) was evident in their reactions with lithium in tetrahydrofuran (THF). Whereas classical P–P bond cleavage is observed in the case of (1),¹ exocyclic P–C bond cleavage is surprisingly observed in the case of (2) (Scheme 1).

The ³¹P n.m.r. spectrum of the crude red anion (3) in THF shows two resonances at δ –53.2 and –18.4 p.p.m. (+ve for downfield shifts, 85% H₃PO₄ as external reference) with a ¹J(P–P) coupling constant of 80 Hz. It readily reacts with water and benzyl chloride to give the expected unsymmetrical diphosphetes (4) [δ(³¹P) –83.5 (PPh) and –116.0 (PH) p.p.m.; ¹J(P–P) 29.3 Hz and ¹J(P–H) 161 Hz] and (5) [δ(³¹P) –42.7 and –65 p.p.m.; ¹J(P–P) 53.7 Hz] (Scheme 2).

The very low ¹J(P–P) coupling constants appear to be a general characteristic of the 1,2-diphosphete ring. The only

way to rationalize this preferential exocyclic P–C vs. endocyclic P–P bond cleavage in (2) is to assume that some stabilization by cyclic delocalization is operative in (3). Indeed, whereas the two phosphorus lone pairs are *trans* in (2) and thus preclude any cyclic delocalization, one of the two lone pairs on the anionic phosphorus atom in (3) is necessarily *cis* to the lone pair of the other phosphorus and some Hückel aromaticity may result. Besides, it is thought that the shorter P–P bond length of (2) reflects a larger stability of the ring which prevents its opening by the lithium attack. In any case, this result offers many interesting synthetic opportunities that we are currently exploring.

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References

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