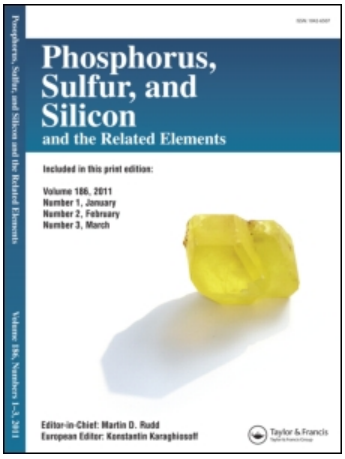

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Synthesis and Reactivity of Cyclic (R_3 P-PR_3) Dications

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SYNTHESIS AND REACTIVITY OF CYCLIC $(R_3P\text{-}PR_3)^{++}$ DICATIONS

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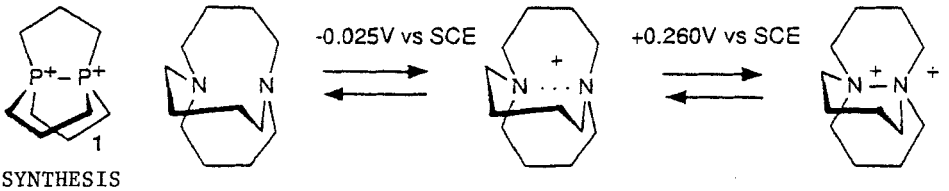
Abstract The synthesis and reactivity of a novel bicyclic system containing directly bonded phosphonium centres is discussed.

INTRODUCTION

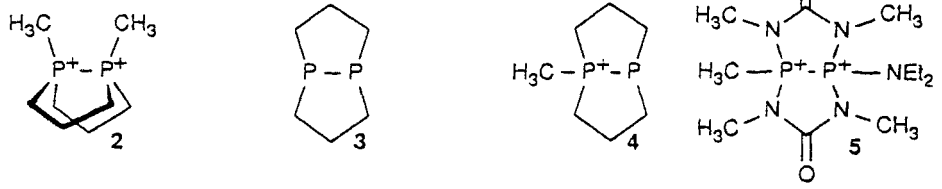
1,5-Diphospha[3.3.3]propellane dication salts, 1, and related species, may have a rich redox chemistry comparable to that observed for related nitrogen species.[1]



1

SYNTHESIS

Alkylation of diphosphine 3[2] to the known monomethylated ion 4[2] followed by second alkylation with methyl trifluoromethanesulphonate, or direct dialkylation of 3 with methyl trifluoromethanesulphonate, gives 2 in quantitative yield. Attempts to prepare 1 by cycloalkylation of 3 have so far failed.

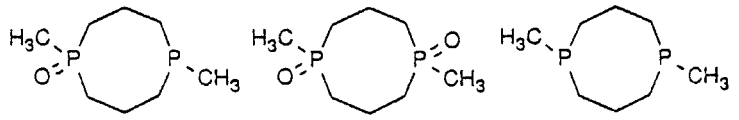


2 3 4 5

The synthesis and properties of 2 may be compared with those of 5,[3] the only compound with directly bonded phosphonium centres previously reported.

Reactivity of 2

Compound 2 is exceptionally sensitive to water. Hydrolysis cleaves the P-P bond and gives the diphosphine mono-oxide 6. Compound 6 can be converted into 7 or 8.



6 7 8

High field ^{1}H-NMR studies carried out on diphosphine 8 show that the methyl groups take up a transconformation, which indicates that the hydrolysis of dication 2 must proceed via apical attack of water.

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