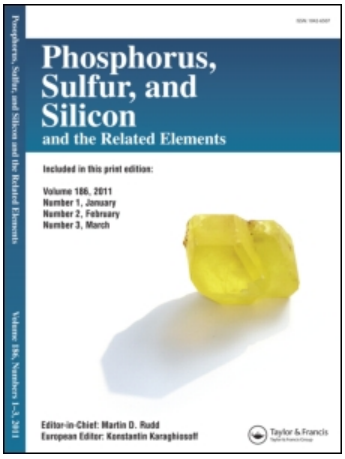

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Cycloaddition Reactions with Metallated Diphosphenes

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CYCLOADDITION REACTIONS WITH METALLATED DIPHOSPHENES.

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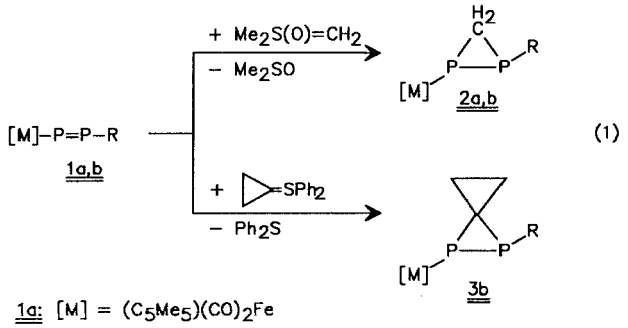
Abstract Several types of cycloaddition reactions performed with metal-functionalized diphosphenes are discussed.

INTRODUCTION

The concepts of the diagonal relationship in the periodic table and isoelectronic compounds emphazise similarities in the chemistry of carbon and phosphorus. Thus olefins and diphosphenes are expected to display closely related patterns of reactivity.

RESULTS

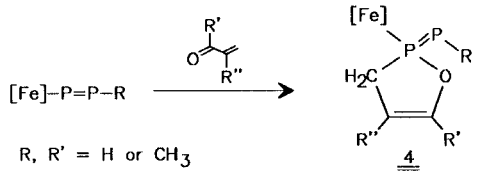
Like activated olefins metal-substituted diphosphenes are converted to three-membered rings by treatment with sulfur ylides. The use of sulfoniocyclopropanides provides a synthetic pathway to 1,2-diphospha[2.2]spiropentanes.[1]



(1)

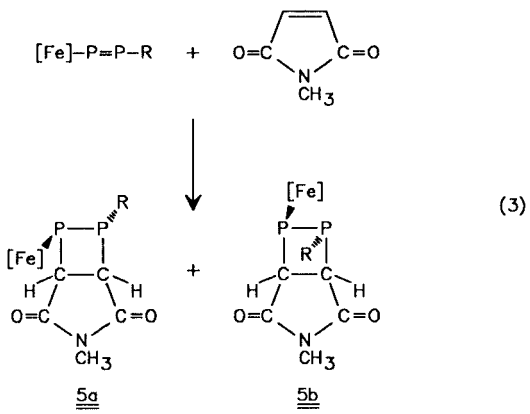
1a: [M] = $(C_5Me_5)(CO)_2Fe$
1b: [M] = $(C_5Me_5)(CO)_2Ru$
R = $2,4,6\text{-}tBu_3C_6H_2$

Usually reactive diphosphenes are conveniently intercepted by 1,3-dienes in the well-known Diels-Alder-reaction.[2] This type of transformation fails in the case of metal-substituted diphosphenes. Heterodienes react with 1a in a cheletropic [1+4] cycloaddition to give oxaphospholene derivatives 4 with exocyclic P=P-bonds.[3]



4 (2)

If the C=C-bond is incorporated in a cyclic system such as N-methyl maleimide the cisoid conformation, which is crucial for the cheletropic cycloaddition, can not be achieved. In this case one observes a [2+2]cycloaddition between equimolar amounts of 1a and the imide. Two diastereoisomers are obtained in 3:1 ratio.[4]

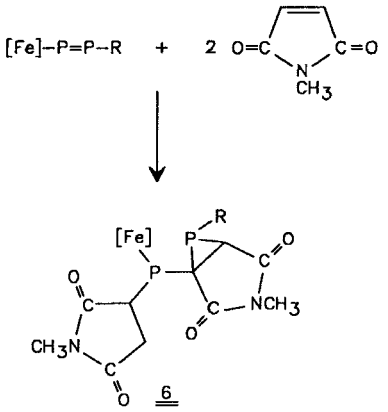


5a 5b (3)

3 : 1

[2+2]-cycloadditions also take place when 1a is allowed to react with fumarodinitrile, dimethyl fumarate and dimethyl maleate.[5]

A different situation is encountered when 1a is treated with a five-fold excess of N-methyl maleimide. Here cleavage of the P=P-bond takes place with the formation of the phosphido iron complex 6.[6]



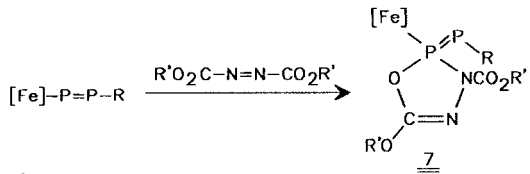
(4)

One substituent at the three-coordinate phosphorus atom is represented by a 3-succinimidyl group whereas the second one can be regarded as a 3-aza-6-phosphabicyclohex-1-yl system.

In contrast to a large variety of 1,3-diaza-2,4-diphosphetidines A [7] the isomeric 1,2-diaza-3,4-diphosphetidines B have not been described in the literature. A [2+2] cycloaddition between 1a and electron-poor azo-compounds should offer a suitable pathway to this class of compounds.

A B

However, the diphosphenyl-complex 1a undergoes cheletropic [1+4] cycloadditions when exposed to the reaction with dialkyl azodicarboxylates.[8]

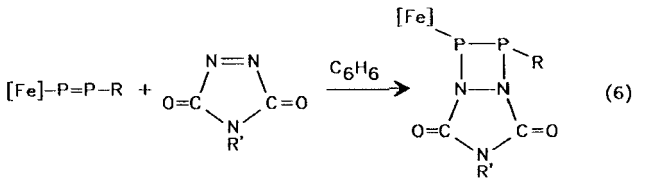


(5)

R' = Et, tBu, CH_2Ph

Again for a successful [2+2] cycloaddition the formation of a cisoid conformation of the heterodiene has to be prevented. This demand is fulfilled in 1,2,4-triazoline-2,5-diones. In keeping with this the reaction of 1a with 1,2,4-triazoline-2,5-diones in benzene furnish the

desired 1,2-diaza-3,4-diphosphetidines B as members of the fused heterocyclic system 8.

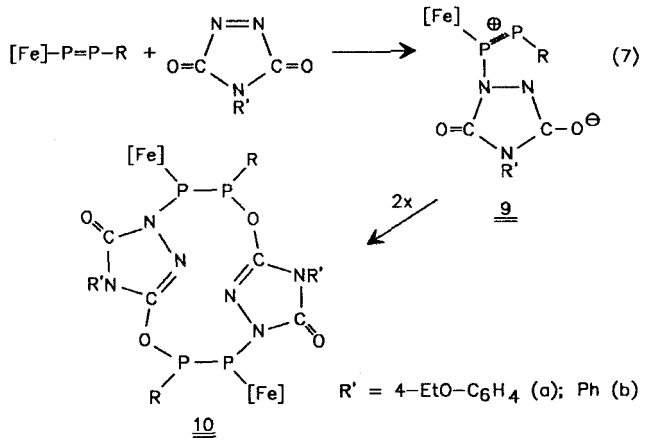


(6)

R' = 4-EtO-C_6H_4 (a); Ph (b)

8

This transformation is highly dependant on the solvents involved. In ether 1a and 1,2,4-triazoline-2,5-diones are converted to the twelve-membered heterocycle 10, which is presumably the result of a [6+6] head-to-tail cyclodimerization of the zwitterionic intermediate 9.



(7)

Moreover compounds 8a and 8b isomerize in ether to afford the macrocycles 10a and 10b.

Constitutions and configurations of the novel complexes are deduced from elemental analyses and spectroscopic data (IR, ^{1}H-, ^{13}C-, ^{31}P-NMR, MS). In addition the molecular structures of one representive of each class of products is elucidated by X-ray diffraction analysis.

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