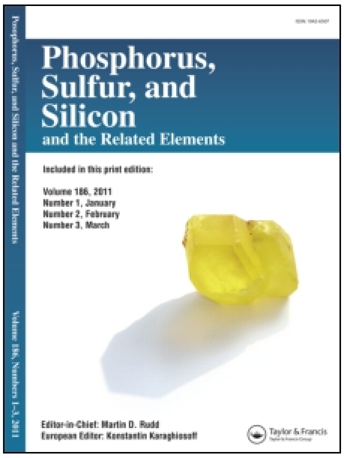

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Metallophosphaalkenes and Metallodiphosphenes as Synthons in Organometallic Chemistry

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METALLOPHOSPHAALKENES AND METALLODIPHOSPHENES AS SYNTHONS IN ORGANOMETALLIC CHEMISTRY

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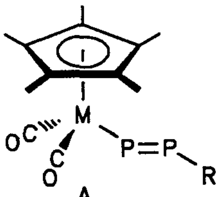
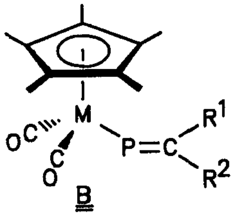
Abstract Cycloaddition reactions of metallodiphosphenes such as $(C_5Me_5)(CO)_2Fe\text{-}P{=}PR$ (R=Mes*, $C(SiMe_3)_3$) are performed with sulfur ylides, CH_2N_2, isocyanides, electron-poor alkenes and heteroalkenes. η^3-Phosphaallyl and η^1-diphosphaallyl complexes are rearranged by transition metal carbonyls to metallophosphaalkenes and η^3-ferra-diphosphaallyl complexes respectively.

Metallodiphosphenes A[1] and metallophosphaalkenes B[2] are polyfunctional molecules with a number of reactive sites.

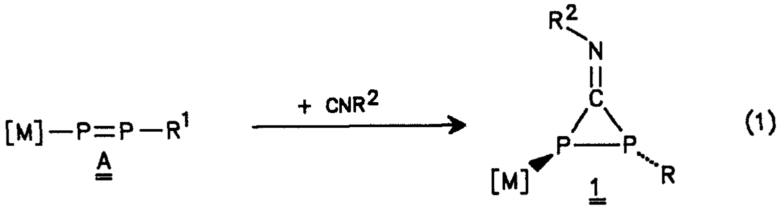


A



B

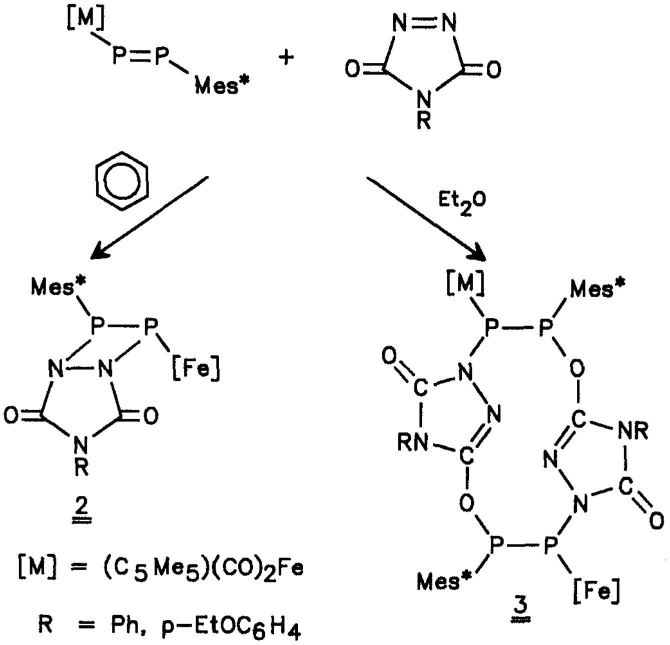
According to the concepts of diagonal relationships in the periodic table and isoelectronic compounds olefins, phosphaalkenes and diphosphenes should display comparable chemical properties.
In keeping with this molecules of the type A undergo (2+1) cycloadditions with sulfur ylides[3], diazomethane[3], and isocyanides with the result of the diphosphiranes 1 (eq.1).
When metallodiphosphenes A are exposed to equimolar amounts of maleimides[4], fumorodinitril[5] or dimethyl fumarate[5] (2+2) cycloadditions with the formation of 1,2-diphosphetanes are observed.



(1)

R^1= Mes*, $C(SiMe_3)_3$; R^2= CF_3,t-Bu; [M] = Cp*Fe(CO)$_2$

The reaction of 1,2,4-triazoline-3,5-diones with A in benzene affords the novel 1,2-diaza-3,4-diphosphetidines 2 as the products of a (2+2) cycloaddition. In ether, however, the twelve-membered macrocycle 3 is generated (eq.2).

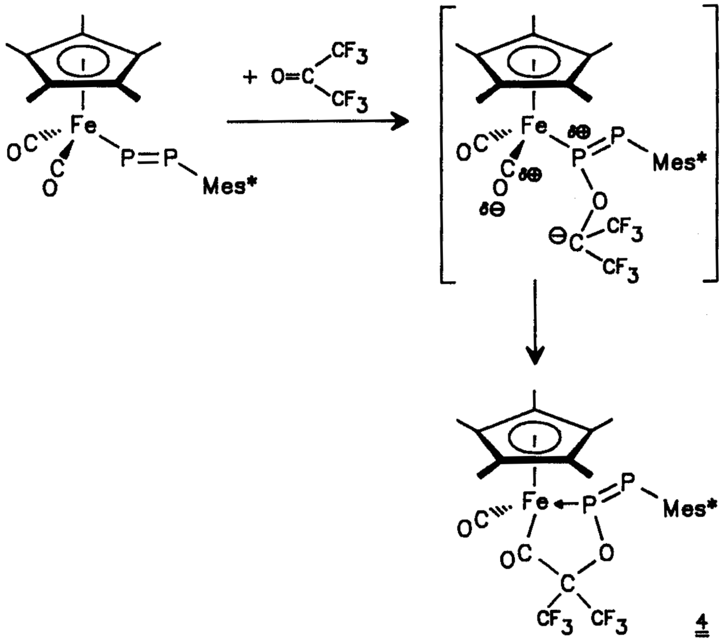


[M] = $(C_5Me_5)(CO)_2Fe$

R = Ph, p-$EtOC_6H_4$

(2)

The C=O bond in anhydrous hexafluoroacetone gives rise to a dipolar (3+2)-cycloaddition. Here the metalloheterocycle 4 is isolated[7] (eq.3). The Fe-P contact in 4 of 2.084(4) Å is the shortest Fe-P bond distance reported in the literature to date and may reflect multiple bond character.

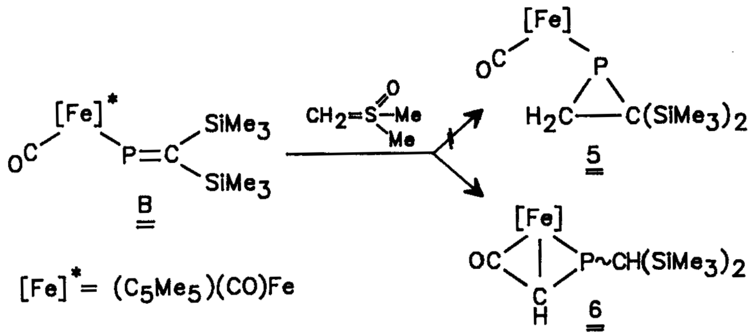


4

(3)

According to our experiences metallophosphaalkenes B should be converted to phosphiranes such as 5 by reaction with sulfur ylides. In contrast to this η^3-phosphaallyl complexes 6 are isolated from B and $Me_2S(O)CH_2$ (eq.4).

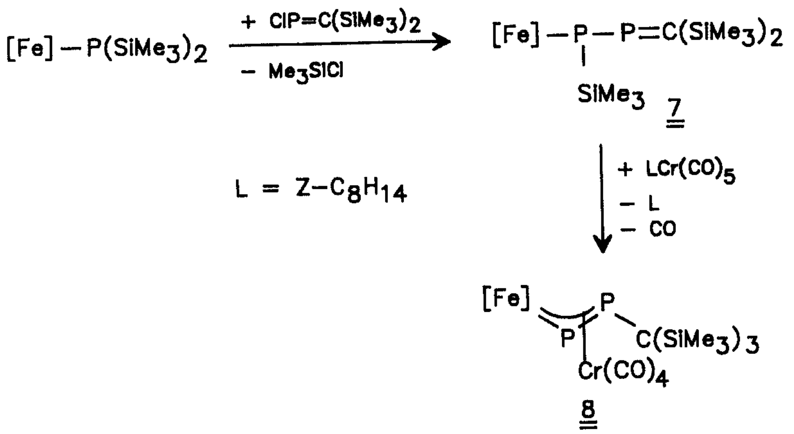
Compounds 6 react with iron and chromium carbonyls to metallophosphaalkenes $(Cp^*(CO)_2Fe\text{-}CH{=}P[M(CO)_n]CH(SiMe_3)_2$.



[Fe]* = $(C_5Me_5)(CO)Fe$

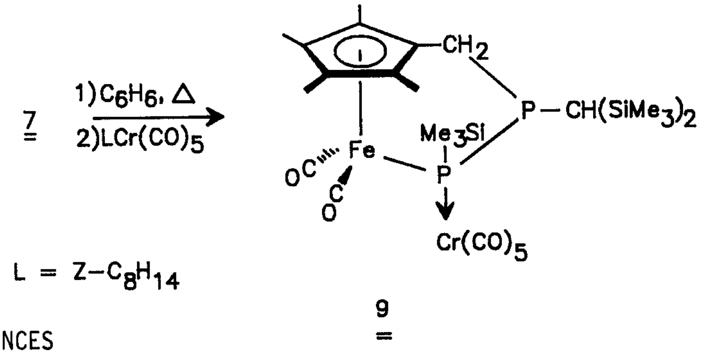
(4)

We then focussed our interest on the coordination chemistry of η^1-diphosphaallyl complexes such as 7. The treatment of 7 with $(Z\text{-}C_8H_{14})Cr(CO)_5$ leads to complex 8 with an η^3-ferradiphosphaallyl ligand. (eq.5).



(5)

Heating 7 in benzene gives rise to the insertion of the P=C functionality into a CH bond of a methyl substituent of the ring ligand. The product is trapped as $Cr(CO)_5$ adduct 9 (eq.6).



(6)

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