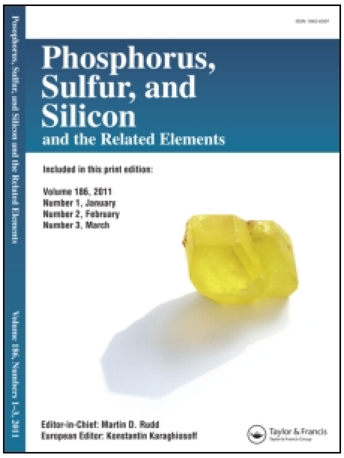

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# Access to New Phosphorus Structures by the Way of the Transient Terminal Phosphinidene Complexes

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# ACCESS TO NEW PHOSPHORUS STRUCTURES BY THE WAY OF THE TRANSIENT TERMINAL PHOSPHINIDENE COMPLEXES

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Abstract The Tungstaphosphirenes, Phosphaalkenes, Phosphahexatrienes, $\eta^4$-phosphabutadiene complexes and 1,2-dihydrophosphete ring have been synthesized by coupling reactions of carbyne or carbene complexes with the transient phenyl phosphinidene pentacarbonyl tungsten [PhP=W(CO)$_5$]. The preparation of other heterocycles such as Dihydrodiphosphetes and Dihydrophosphepines has been realized from the vinylphosphinidene complexes via a 4$\pi$-electrocyclization and a Phospha-Cope rearrangement respectively.

## INTRODUCTION

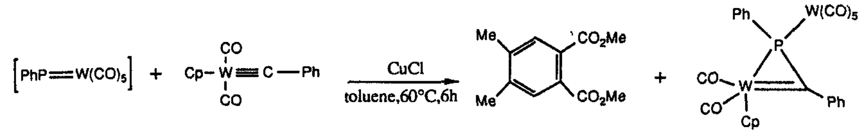
It was shown ten years ago, that transient phosphinidene complexes can be generated from their corresponding phosphanorbornadiene complexes by trapping reactions with organic reagents.[1] But there remains many possibilities to create new phosphorus structures from these transient species.

## CYCLOADDITIONS OF [PhP=W(CO)$_5$]WITH CARBYNE AND CARBENE COMPLEXES

A rich chemistry has been developed with Fischer-Carbene Complexes. Different new phosphorus compounds have been prepared, depending on the carbene ligands.

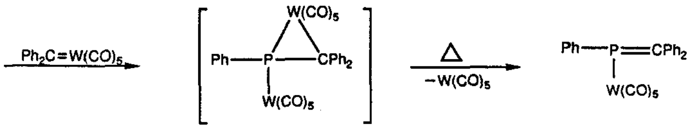
### With Carbyne Cp(CO)$_2$W≡C-Ar

These carbyne complexes behaved as C≡C compounds in reacting with phosphinidene species [PhP=W(CO)$_5$] leading to a 3-membered tungstaphosphirene ring via a formal [2 + 1] cycloaddition.



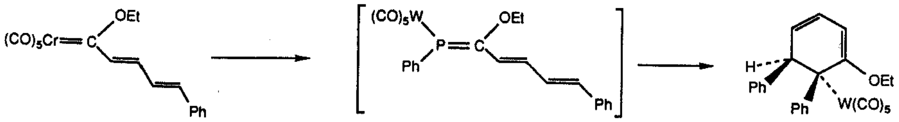
### With Ph$_2$C=W(CO)$_5$ and (Ph)(OEt)C=W(CO)$_5$

In these cases, the 3-membered cycloadducts are not stable. The transient 4$\pi$-electron $\sigma$, $\pi$-phosphaalkene complexes tend to lose the $\pi$-bound metal, thus giving a free P=C double bond.[3]



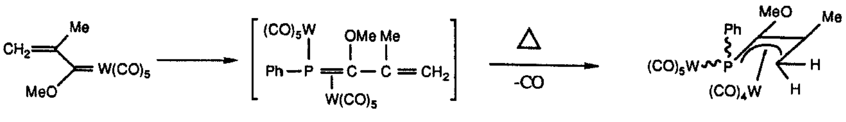
### With $(PhCh{=}CH{-}CH{=}CH)(OEt)C{=}Cr(CO)_5$

The application of the previous coupling to the butadienyl chromium carbene allowed the synthesis of the transient 1-phosphahexatriene. This intermediate spontaneously cyclized to give the corresponding 1,2-dihydrophosphinine complex. It is the first reported 6π-electrocyclization of a 1-phosphahexatriene.[4]



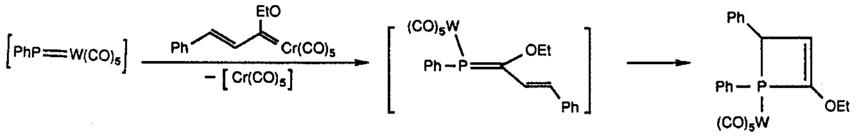
### With $(CH_3{-}C{=}CH_2)(OEt)C{=}W(CO)_5$

When we used the tungsten vinyl carbene as starting material, the resulting transient product loses one CO and yields the first known $\eta^4$-phosphabutadiene complex.[5]



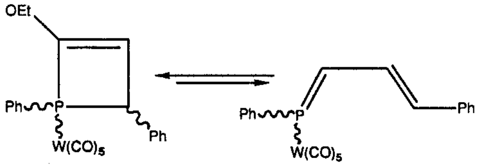
### With $(PHCH{=}CH)(OEt)C{=}Cr(CO)_5$

By changing the metal to Cr instead of W, the free phosphabutadiene unit was transiently produced but immediately underwent a 4π-electrocyclization leading to a new 1,2-dihydrophosphete ring.[6]



### PHOSPHETE RING AS MASKED 1-PHOSPHADIENE

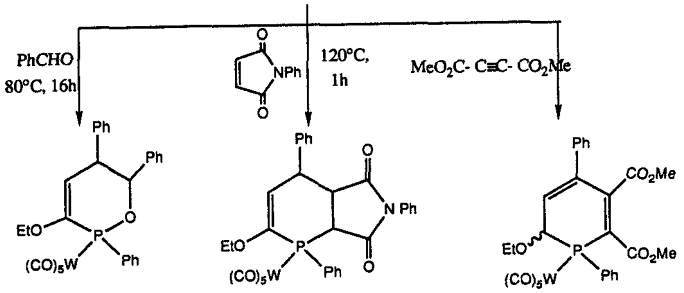
As shown by the X-Ray structure, the dihydrophosphete ring has a long intracyclic bond length P-C (1.902 Å). This suggests the following equilibrium :



Different cycloadditions confirmed this equilibrium and permitted the synthesis of new phosphorus compounds.

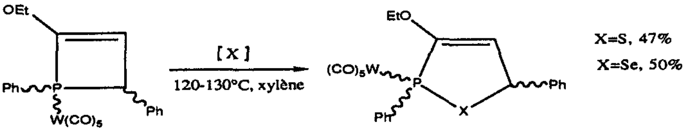
### With Benzaldehyde, N-Phenylmaleimide and Dimethyl acetylene dicarboxylate

At ca 100°C, the 1,2-dihydrophosphete behaved as a phosphabutadiene. We isolated the [4 + 2] cycloadducts in good yield.[7]



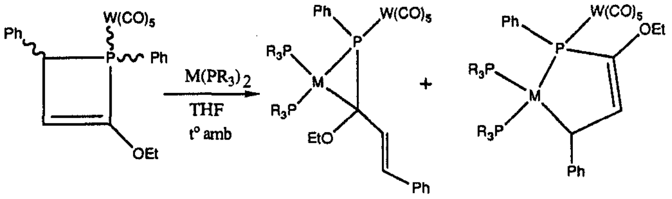
With S, Se

Both S and Se were able to insert into the 1,2-dihydrophosphete ring at ca 120°C. This offers a new access to dihydro 1,2-thiaphospholes and dihydro 1,2-selenaphospholes.[8]



With $Pt(PPh_3)_2$

Platinium fragment gives either the $\lambda^2$-complex of 1-phosphabutadiene or the formal [1 + 4] cycloadduct. This reaction takes place even at room temperature.[9]

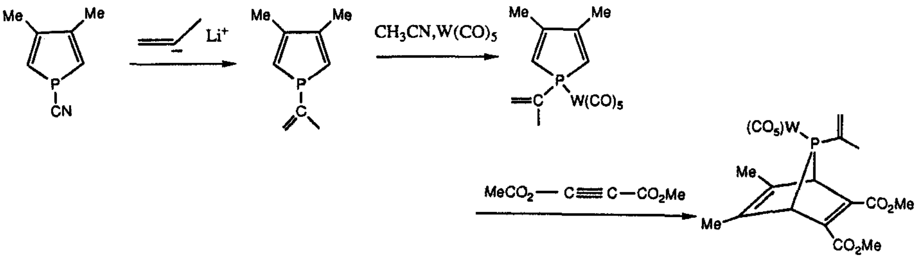


VINYL PHOSPHINIDENE COMPLEX : SYNTHESIS AND REACTIVITY

Phosphinidenes with a functional group such as vinyl give interesting rearrangements leading to new phosphorus structures

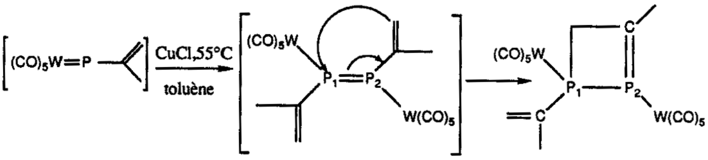
Synthesis

The preparation of the 7-vinyl phosphinidene pentacarbonyl tungsten is showed in the following scheme. This complex proved to be a good precursor of vinylphosphinidene in trapping reactions with organic reagents (tolane and alcohols).



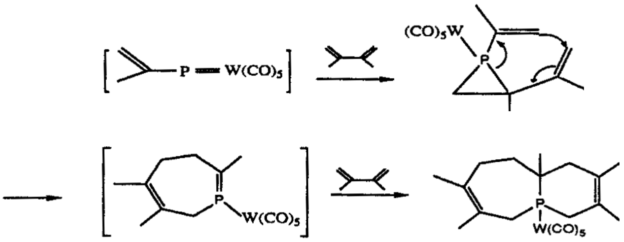
## 4π-Electrocyclization : Synthesis of dihydrodiphosphete

When no trapping reagent is present in the medium, the transient dimer 3,4-diphosphahexatriene was produced and a spontaneous 4π-electrocyclization took place. This leads to a novel dihydrodiphosphete 4-membered unsaturated ring with an intracyclic P=C bond.[10]



## Phospha-Cope rearrangement : Synthesis of transient 2H-dihydrophosphepines

Vinylphosphinidene reacted with cyclopentadiene or 2,3-dimethyl butadiene leading first to divinylphosphirane complexes which underwent a [3,3] Phospha-Cope rearrangement giving 2H-dihydrophosphepine derivatives. These intermediates with a reactive P=C M-bond finally afforded bicyclic phosphine complexes via a [4 + 2] cycloaddition with excess diene.[11]



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