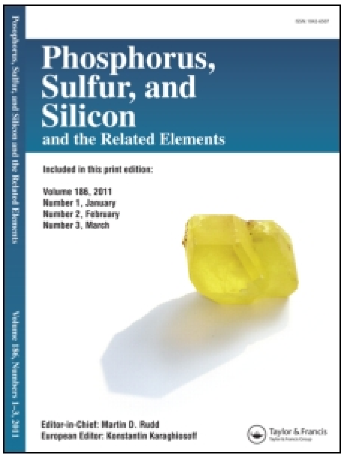

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Huy, Ngoc Hoa Tran and Mathey, François(2001) 'Some Synthetic Applications of 1-Metalla-2-Phospha-Cyclobutane and -Cyclobutene Complexes', Phosphorus, Sulfur, and Silicon and the Related Elements, 169: 1, 85 — 88

To link to this Article: DOI: 10.1080/10426500108546596

URL: http://dx.doi.org/10.1080/10426500108546596

Phosphorus, Sulfur and Silicon, 2001, Vol. 169, pp. 85-88
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Some Synthetic Applications of 1-Metalla-2-Phospha-Cyclobutane and -Cyclobutene Complexes

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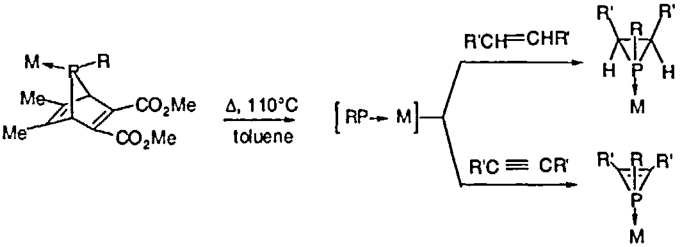
INTRODUCTION :



Phosphirene and phosphirane complexes are interesting strained three-membered rings which have a rich and versatile chemistry. The most efficient way to prepare them involves the [2+1] cycloaddition between a phosphinidene unit and a alkyne or an alkene[1]. The phosphinidene precursors can be obtained on a large scale, so we are interested to investigate the synthetic potential of these three -membered rings. Here we present some metal- initiated ring openings and dimerisations.

SYNTHETIC APPLICATIONS :

The insertion reaction of Pd(0) and Pt(0) into the P-C bonds of three membered rings is known to lead to 1-metalla-2-phospha-cyclobutene, or –cyclobutane rings[2,3]. By choosing suitable ring substituents, these four- membered ring products can be used as synthetic tools to prepare new phosphorus derivatives. Hereafter we give two examples :

I- New route to vinyl phosphorus derivatives [4]:

When a chlorine substituent is present on the phosphirane ring, a metal- induced concerted migration of chlorine from carbon to phosphorus occurs. A favourable overlap between a chlorine lone pair orbital and a low-lying empty orbital at phosphorus could provide the drive

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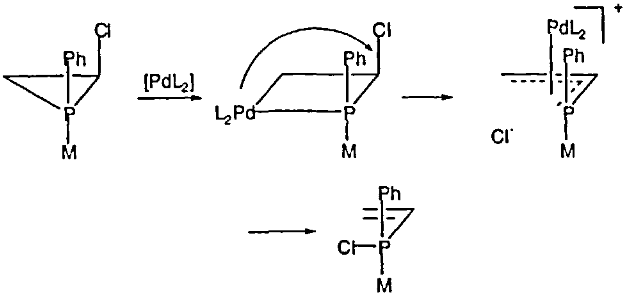
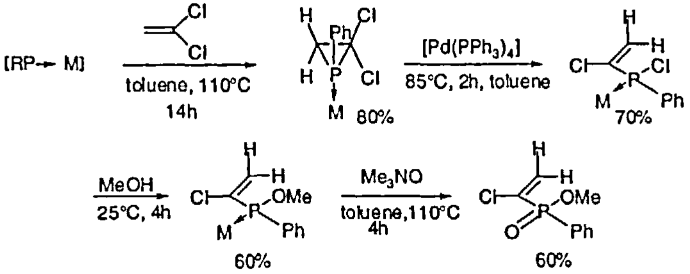
for this process. The complexation of phosphorus by the metal probably lowers the energy of the acceptor orbitals and prevents repulsions between the lone pairs at P and Cl.



The phosphirane complex which is formed through the cycloaddition of 1'1-dichloroethylene and complexed phenylphosphinidene undergoes a palladium- catalysed ring opening. The chloro(vinyl)phosphine product was trapped by reaction with methanol and the product phosphinite complex was subjected to oxidative decomplexation with trimethylamine oxide.

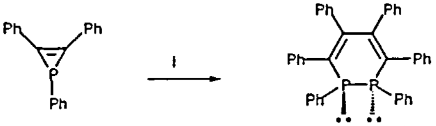


Vinyl phosphorus derivatives play a key role in organic synthesis, organophosphorus, and coordination chemistry. This methodology allows a simple access from readily available chloroalkenes and tolerates a wide variety of functional groups. It shows considerable promise.

II- Synthesis of 1,2-dihydro-1,2-diphosphinines from the unexpected head-to-head dimerisation of phosphirenes[5].

The dimerisation of borirenes to 1,4-diboracyclohexadienes is well-documented [6]. Similiarly,silirenes readily give 1,4-dicyclohexadienes in the presence of a palladium catalyst[7], probably through1-metalla-2-sila cyclobutene intermediates[8]. We describe hereafter the behaviour of some phosphirenes towards Pd or Ni as catalysts.

1) With 1,2,3-Triphenylphosphirene



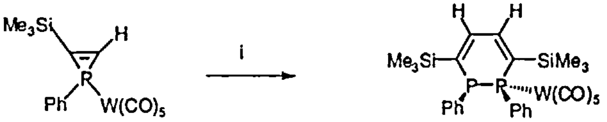
1 2

Reagents and conditions: (i) 150mg of 1, 10mg of $NiCl_2(Ph_2PCH_2CH_2PPh_2)$, CH_3CN, 25°C, 2d., 70% yield

Crystal structure analysis of 2 shows a head-to-head dimer. The highly distorted ring has two *trans*- phosphorus lone pairs and seems somewhat strained, as indicated by the rather small P-P-C(ring) angles of 91.09 and 91.27°. The P-P bond is short for a single bond at 2.193Å. It displays surprising instability. To prepare more stable derivatives, we decided to investigate the dimerisation of the coresponding phosphirene-P-W(CO)$_5$ complexes. However, the complex of 1 proved rather inert.

2) With (1-phenyl-2-trimethylsilylphosphirene)W(CO)$_5$

We decided to prepare the 1,2-disubstituted precursors such as 1-phenyl-2-trimethylsilyl phosphirene pentacarbonyltungsten 3. After one night at 85°C in the presence of catalytic quantities of $[Pd(Ph_3P)_4]$, we isolated the head- to-head dimer 4.



3 4

Reagents and conditions: (i) 530mg of 3, 30mg of $[Pd(PPh_3)_4]$, toluene, 85°C, 16h.

The dimerisation is regio- and stereo-selective. The regioselectivity can be easily explained by the preferential insertion of Pd(0) into the less-hindered P-CH intracyclic bond. The ring is only slightly distorted. The intracyclic angles at phosphorus are normal at 101.35° P(III) and 105.7°(PW). The P-P bond is also in the normal range at 2.227Å. Compound 4, which differs from 2 in showing a *cis*- stereochemistry at the phosphorus atoms, is quite stable. At present, the only arguments which we can offer for this unexpected head-to-head dimerisation present, the only arguments which we can offer for this unexpected head-to-head dimerisation have a thermodynamic basis. The building of one P-P and one C-C bonds is more energetically favourable than building two P-C bonds : 61+88 > 2x65 $\mathrm{kcalmol^{-1}}$.

This head-to-head dimerisation of phosphirenes provides a direct access to the almost unknown 1,2-dihydro-1,2-diphosphinine ring, whose chemistry is now open for investigation.

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