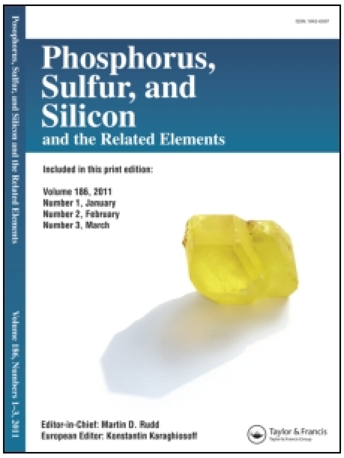

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Sterically Protected Unusual Phosphorus Compounds in Lower Coordination States: Diphosphenes, Phosphaethylenes, and 1-Phospha- and 1,3-Diphosphaallenes

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STERICALLY PROTECTED UNUSUAL PHOSPHORUS COMPOUNDS IN LOWER COORDINATION STATES: DIPHOSPHENES, PHOSPHAETHYLENES, AND 1-PHOSPHA- AND 1,3-DIPHOSPHAALLENES

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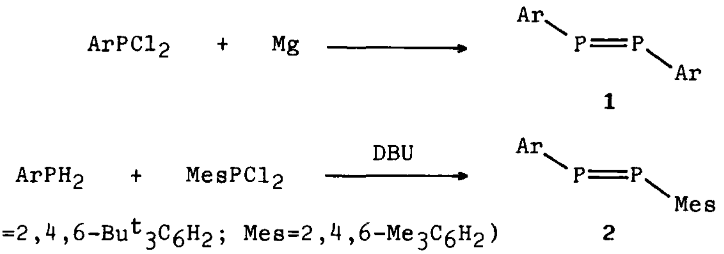
Abstract Physicochemical properties and chemical reactivities of some sterically protected unusual phosphorus compounds in lower coordination states are discussed such as diphosphenes, phosphaethylenes, and 1-phospha- and 1,3-diphosphaallenes.

We have reported the preparation and characterization of several diphosphenes such as **1** and **2** as stable compounds by utilizing 2,4,6-tri-t-butylphenyl moiety as a protecting group.[1,2]



(Ar=2,4,6-$Bu^t{}_3C_6H_2$; Mes=2,4,6-$Me_3C_6H_2$)

Attempts to prepare a P-coordinated chromium complex of **1** failed probably because the aryl groups are too bulky to permit the reaction of **1** with $(THF)Cr(CO)_5$. On the other hand, the thermal reaction of **1** with hexacarbonylchromium(0) gave mono- (**3**) and bis- (**4**) arene metal complexes.[3]

$$\mathbf{1} + Cr(CO)_6 \longrightarrow \underset{\mathbf{3}}{(ArP{=}PAr)Cr(CO)_3} + \underset{\mathbf{4}}{(ArP{=}PAr)[Cr(CO)_3]_2}$$

Indeed, when the less bulky diphosphene (2) was employed, the corresponding P-coordinated complex (5: M=Cr) was obtained.[4] Similarly molybdenum and tungsten complexes at the phosphorus were prepared.

5

The complexes 5 were also prepared by an alternative method from ($ArPH_2$)pentacarbonylmetals(0) (6) of Group VI and mesitylphosphonous dichloride in the presence of a base as follows.

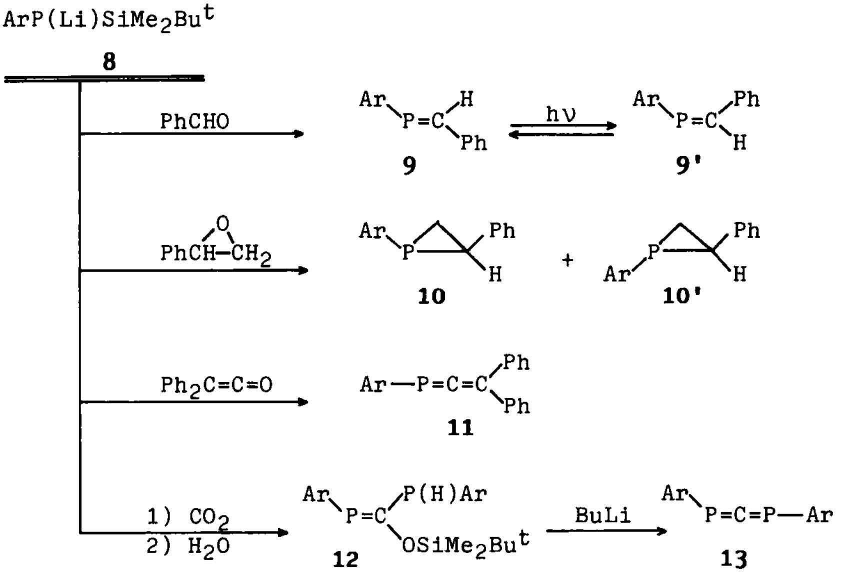
$$\underset{\mathbf{6}}{(ArPH_2)M(CO)_5} + MesPCl_2 \xrightarrow{DBU} \mathbf{5}$$

Interestingly, the complexes 5, were photo-isomerized to the corresponding (Z-diphosphene)-transition metal complexes (7).[5]

7

Similar isomerization reaction of benzylidenephosphine **9** itself to **9'** (the phosphaethylene **9** was prepared from silylphosphide **8** and benzaldehyde) was observed on irradiation.[6] The phosphide **8** reacted with styrene oxide to afford phosphiranes (**10** and **10'**)[7] and with diphenylketene to give 1-phosphaallene **11**.[8] More interestingly, **8** reacted with carbon dioxide, followed by the addition of butyllithium to **12**, to afford 1,3-diphosphaallene **13**,[9] probably via a phosphaketene (ArP=C=O).

The reactions of **9**, **9'**, **11**, and **13** including sulfurization, reduction, thermolysis, and coordination with Group VI metal pentacarbonyls have been studied. The structures in solution and in solid have been discussed in terms of ^{31}P-NMR data and X-ray analyses. We have also found a good correlation among the ^{31}P-NMR chemical shifts of the transition metal complexes and the



coordination sites have been assigned from the NMR data.[10] Furthermore, photoisomerization reaction of **13** was monitored by a method using a chiral HPLC column, (+)-PTrMA.

Finally, we have confirmed that the steric protection plays an important role in obtaining such unusual compounds containing phosphorus atoms in lower coordination states by ab initio calculation.[11]

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