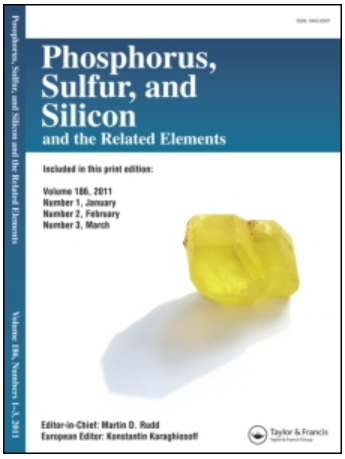

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Low-Coordinated Organophosphorus Compounds

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LOW-COORDINATED ORGANOPHOSPHORUS COMPOUNDS

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*Low-coordinate organophosphorus compounds can be prepared by steric protection. They are diphosphenes, phosphaethenes, phosphaallenes, phosphabutatrienes, phosphaalkynes, and so on, of coordination number **2** and **1**.*

Keywords: Diphosphene; low-coordination states; organophosphorus compounds; phosphaalkene; phosphaalkyne; phosphacumulene

INTRODUCTION

Multiple bonds containing heavier main group elements are unstable because the multiple-bond energies are not large. However, by utilizing a very bulky substituent as a protecting group, such as the 2,4,6-tri-*t*-butylphenyl group (abbreviated Mes*),[1] we have been successful in stabilizing several low-coordinated organophosphorus compounds as stable chemical species. We isolated highly reactive but kinetically stabilized organophosphorus compounds, such as diphosphenes (R–P=P–R), phosphaethenes (R–P=CR_2), phosphaallenes (R–P=C=CR_2), diphosphaallenes (R–P=C=P–R), phosphabutatrienes (R–P=C=C=CR_2), diphosphabutatrienes (R–P=C=C=P–R), phosphaalkynes (R–C≡P), and so on. They are interesting new-type molecules because of their unusual structures and properties.[2,3]

Diphosphenes

A sterically protected diphosphene **1** is prepared as a stable compound by dechlorination reaction of the corresponding phosphonous

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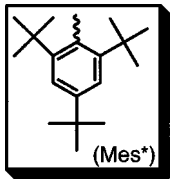
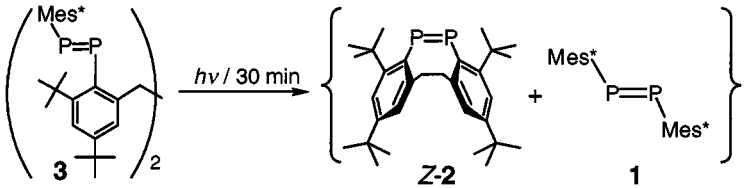


dichloride Mes^*PCl_2 with magnesium metal.[1] There is an alternative method to prepare diphosphenes especially for asymmetrical ones such as $Mes^*P{=}PMes$, starting from the primary phosphine Mes^*PH_2 and mesitylphosphonous dichloride ($MesPCl_2$) in the presence of an organic base, such as triethylamine or DBU (diazabicyclo[5.4.0]undec-7-ene).[4]

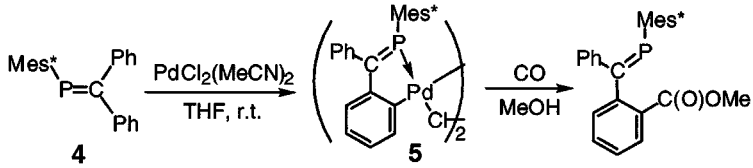
On the other hand, photolysis of diphosphenes often causes reactions of the olefin-metathesis mode. Utilizing 1,2-bis(2-bromo-3,5-di-*t*-butylphenyl)ethane as a protecting group, an internal *cis*-diphosphene ***Z*2** of the *o*-cyclophane type was obtained together with **1** from a bis-diphosphene **3**.[5]



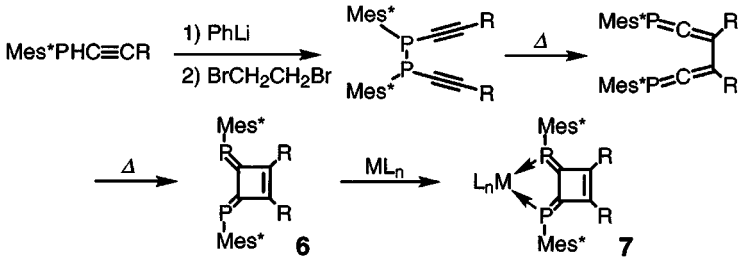
Phosphaalkenes

Various kinds of phosphaalkenes with the Mes^* group as a protecting group, such as compound **4**, are prepared from the corresponding silylphosphide and the ketones or aldehydes by the method of the phospha-Peterson reaction.[6]

Phosphaalkene **4** reacts with $PdCl_2(MeCN)_2$ to give *o*-palladate complex **5**, resulted from a C—H bond activation at the 2-position to form a Pd—C bond.[7] The *o*-palladate complexes of the compound type **5** react with carbon monoxide under high pressure to give the corresponding esters in the presence of alcohols.



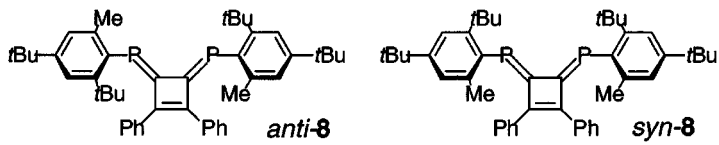
Märkl et al.[8] and Yoshifuji et al.[9] reported the synthesis and structure of diphosphinidenecyclobutene **6**, where R = Tms = trimethylsilyl. The shape of the cyclobutene derivatives indicates that the two phosphorus atoms behave as a bidentate ligand. Recently, bidentate diphosphane ligands with sp^3-type hybridized phosphorus atoms such as 1,2-bis(diphenylphosphino)ethane (dppe) or 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) have been widely used in organic synthesis as well as in coordination chemistry.[10]



In fact, though the phosphinidenecyclobutene **6** takes a rigid configuration, it also acts as a bidentate ligand to the transition metals to give **7**.[3]

A coupling reaction of trimethylsilylacetylene with *p*-bromonitrobenzene of the Heck or Sonogashira type proceeds in THF-Et_2NH in the presence of 1.1 mol% of copper(I) iodide catalyzed by 1.5 mol% of palladium complexes of a diphosphinidenecyclobutene **6** to give the corresponding phenylacetylene in a good yield.[11]

On the other hand, we have developed several protecting groups in addition to than the Mes* group and found that the 2,4-di-*t*-butyl-6-methylphenyl (abbreviated to Dbt) group is useful to stabilize the diphosphinidenecyclobutene system, where conformational isomerism due to the restricted rotation around the two P-Dbt bonds at the edges of the system was observed. Thus **8** consists of two rotamers, *syn*-**8** and *anti*-**8**, according to the ^{31}P NMR studies, indicating that an asymmetric environment can be created in the transition metal complex system.[12]



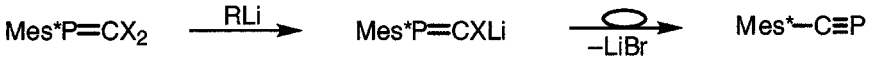
Some palladium complexes turned out to catalyze polymerization of ethylene.[13]

Phosphacumulenes

Phosphacumulenes such as phosphaallenes, diphosphaallenes, phosphabutatrienes, and diphosphabutatrienes also behave as a ligand to the transition metal complexes. For example, 2,2-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene can be prepared by either the Peterson reaction or the phospha-Peterson reaction. 1,3-Diphosphaallene can also be prepared by various methods. Recently we have developed a phosphorus version of the Doering-Moore-Skattebøl reaction for the preparation of low coordinate phosphacumulenes.[14]

Phosphaalkynes

Phosphaalkynes **9**, with coordination number 1, can be prepared from 1-halo-2-phosphaethenyllithiums, plausibly due to a reaction involving the Fritsch-Buttenberg-Wiechell reaction type.[15]



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