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CHEMISTRY OF STERICALLY PROTECTED BIS(PHOSPHINIDENE)-CYCLOBUTENES

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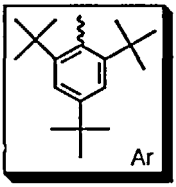
Abstract: Sterically protected low-coordinated phosphorus-containing cyclobutenes were prepared and characterized as well as [4]radialenes. The reactions were studied involving *E*/*Z* isomerization, transition-metal complex formation, and coupling reactions catalyzed by some palladium complex ligated with diphosphacyclobutenes.

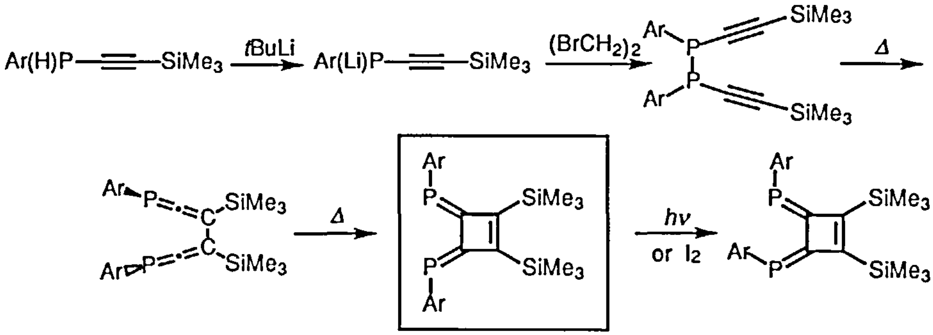
INTRODUCTION

By utilizing a sterically bulky group such as the 2,4,6-tri-*t*-butylphenyl group (abbreviated to Ar), we have been successful in isolation and characterization of organophosphorus compounds in low-coordination states, including diphosphenes (–P=P–),[1a] diphosphaallenes (–P=C=P–),[1b] and phospha-alkynes (–C≡P).[1c,d] Here we report on the sterically protected cyclobutenes and the related low-coordinated phosphorus compounds.

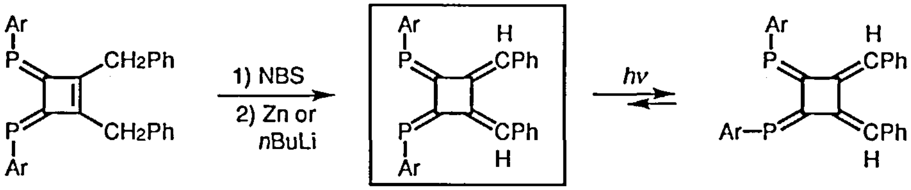


RESULTS

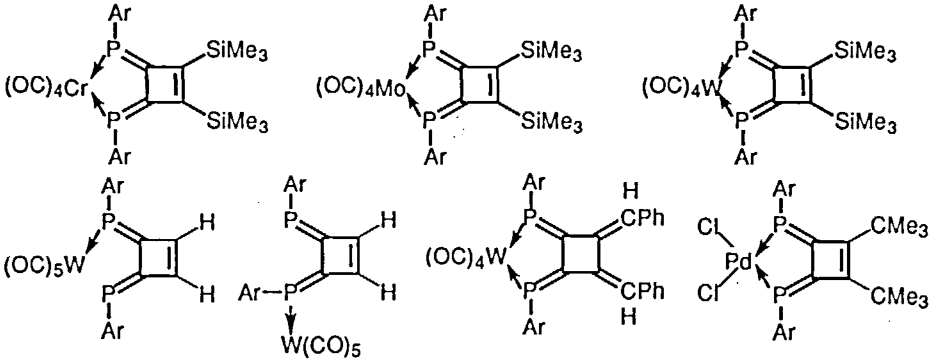
Starting from ArP(H)C≡CR, where R = H, Ph, CH_2Ph, *t*-Bu, Me, Tms, and CH_2Tms, 3,4-diphosphinidenecyclobutenes[2] were obtained by the phosphorus-Cope reactions via dialkynyldiphosphanes and bisphosphaallene compounds. A typical example is shown for R = Tms as follows.[2b] The system of diphosphinidenecyclobutene is of interest because it is a phosphorus analog of methylenecyclobutene involving either the 1,4-diphospha-1,3-butadiene or 1,6-diphospha-1,3,5-hexatriene system. Some of the crystal structures of diphosphinidenecyclobutenes were analyzed by X-ray crystallography indicating the planarity of the π-system.

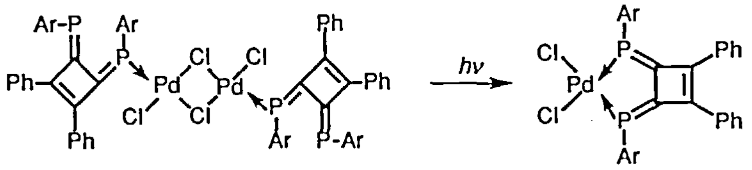


Very similarly, diphospha[4]radialenes were obtained using the benzyl derivative through bromination and debromination as shown below.[3] The *E*/*Z* isomerization was also accomplished with photoirradiation. The structure of the *E*,*E*-isomer was analyzed by X-ray crystallography, indicating that the [4]radialene system is almost planar with tilted Ar and Ph groups. UV-vis spectrum of the radialene indicated that the absorption shows a red shift compared to that of the phosphinidenecyclobutene indicating a very extended π-electron system of the radialene.

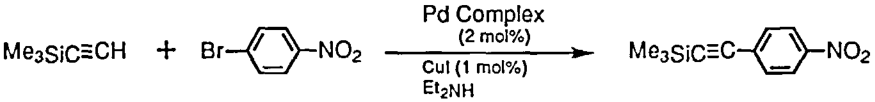


Several transition-metal end-on complexes including Cr(0), Mo(0), W(0), and Pd(II), having such cyclobutene ligands, were prepared as depicted below and some of those were analyzed by X-ray crystallography.[2f]

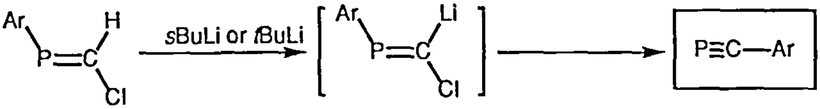




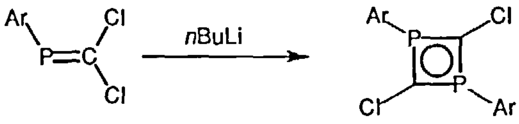
Among those transition-metal complexes, palladium(II) complexes thus obtained worked as efficient catalysts (2 mol%) for some of the coupling reactions of aromatic halides with acetylenes in diethylamine in the presence of copper(I) iodide as shown below.[2e]

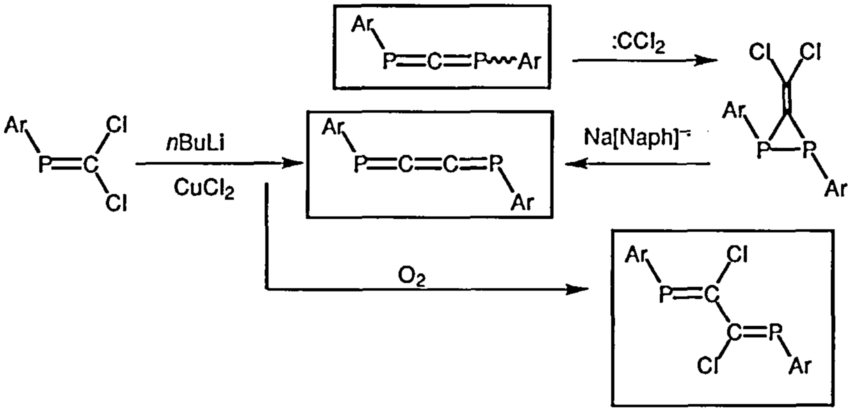


We have found a phosphorus version of the Fritsch-Buttenberg-Wiechel reaction as follows to give phosphaalkynes starting from *E*-2-chloro-1-phosphaethenes.[1d] The reaction might involve a carbene or carbenoid intermediate. On the other hand, the reaction from the corresponding Z-derivative did not take place, while the reaction either from *E*- or Z-phosphaethene in the presence of copper salts gave a phosphaalkyne.



Furthermore, the corresponding dichlorophosphaethene in the presence of a copper salt gave 1,4-diphosphabuta-1,2,3-triene,[4] which we had prepared from a methylenediphosphirane and a SET reagent.[4b] It should be noted that the reaction gave 1,4-diphospha-1,3-butadiene when oxygen gas was bubbled through a reaction mixture at low temperature.[5] The structure of (Z,Z)-2,3-dichloro-1,4-diphospha-1,3-butadiene was confirmed by X-ray crystallography. Although the reaction mechanism for giving either butatriene or butadiene depending upon the introduction of oxygen, our results are of interestt in contrast to the recent results reported by Niecke et al.[5b] on the formation and structural determination of diphosphacyclobutanediyl which was obtained under very similar reaction conditions without any copper salts.





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