

Recent developments in the chemistry of low-coordinated organophosphorus compounds*

Masaaki Yoshifuji[‡]

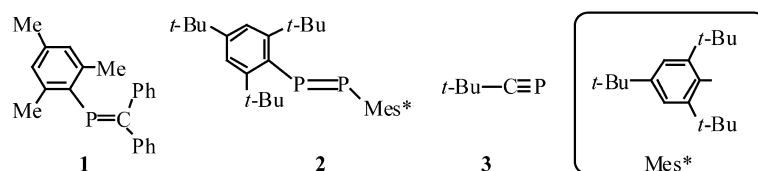
Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Abstract: Sterically protected organophosphorus compounds are described, involving diphosphenes, phosphathenes, diphosphinidenecyclobutenes (DPCBs), phosphalkynes, phosphquinones, diphosphathienoquinones, and so on of coordination number 2 or 1. Application of the DPCBs as well as phosphinophosphathenes as a ligand of transition-metal catalysts for several organic coupling reactions has been investigated.

Keywords: Organophosphorus; diphosphenes; phosphathenes; diphosphinidenecyclobutenes; phosphalkynes; phosphquinones; diphosphathienoquinones; transition-metal catalysts; coupling reactions.

INTRODUCTION

Multiple bonds containing heavier main-group elements are unstable, because the multiple-bond energies are not large [1]. However, by utilizing a very bulky substituent as a protecting group, such as the 2,4,6-tri-*t*-butylphenyl group (abbreviated as Mes*), we have been successful in the stabilization of various low-coordinated organophosphorus compounds as stable chemical species. In 1978, Bickelhaupt and coworkers reported the first kinetically stabilized phosphorus–carbon double bond **1** (phosphathene) [2], and in 1981 we reported the first stable phosphorus–phosphorus double bond **2** (diphosphene) [3]. Moreover, Becker and coworkers reported the first stable phosphorus–carbon triple bond (phosphalkyne) **3** [4]. For research of such low-coordinated phosphorus compounds, we require bulky substituents such as Mes* or the *t*-butyl group, which play an important role in stabilizing unsaturated phosphorus atoms [5] (Scheme 1).



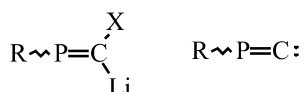
Scheme 1

*Paper based on a presentation at the 7th IUPAC International Conference on Heteroatom Chemistry (ICHAC-7), Shanghai, China, 21–25 August 2004. Other presentations are published in this issue, pp. 1985–2132.

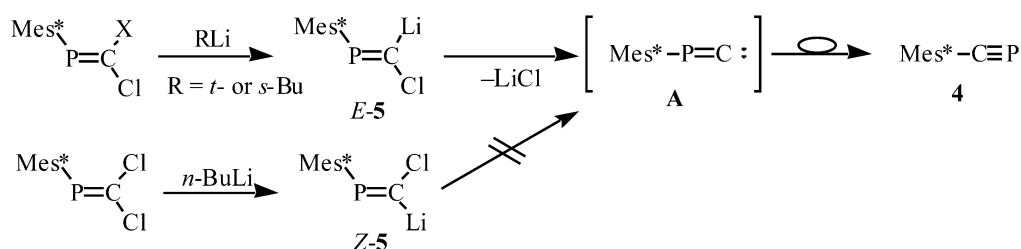
[‡]Current address: Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487-0336, USA

REACTIVITY OF PHOSPHANYLIDENE CARBENOIDS

Phosphanylidene carbenoids are expected to show a variety of reactivity as nucleophiles and carbenes (Scheme 2). In addition, there are configurational isomers in the phosphinyldene carbenoids. We have been interested in such unusual reactivity of halo lithium derivatives protected by Mes* [6]. At $-78\text{ }^{\circ}\text{C}$, the carbenoids behaved as a nucleophile to give alkylation products with alkyl halides with retention of configuration. On the other hand, at room temperature in some cases, the carbenoids showed interesting 1,2-rearrangement of Mes* to give phosphalkyne **4** [7] (Scheme 3).



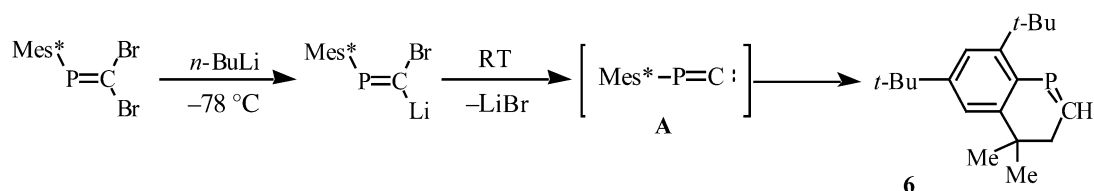
Scheme 2



Scheme 3

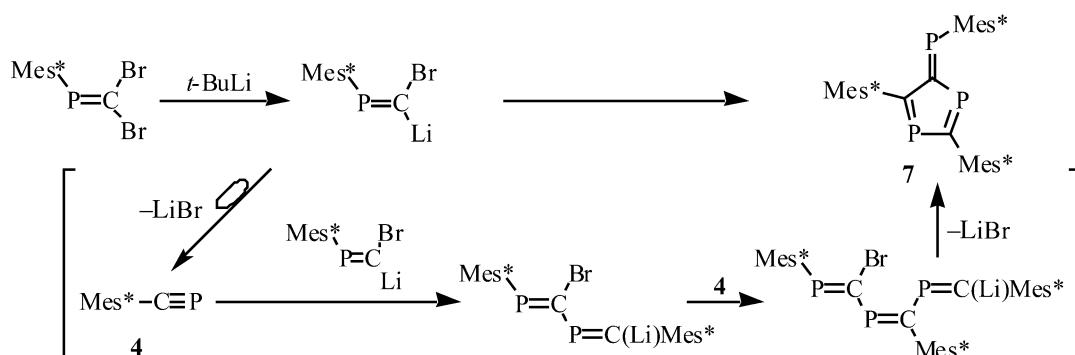
The 1,2-shift of Mes* is similar to the regioselective reaction of the Fritsch–Buttenberg–Wiechell rearrangement with lithium alkylidene carbenoids [8] (see the difference between *E*-**5** and *Z*-**5**). Very recently, we found a NiBr₂/Zn-catalyzed preparation of phosphalkyne from 2,2-dibromo-1-phosphaethene [9].

It is interesting to note that the 2,2-dibromophosphaethene gave a 1-phosphaindene derivative **6** in the reaction with *n*-butyllithium at $-78\text{ }^{\circ}\text{C}$, indicating the generation of a true carbene **A** on warming to room temperature, which inserted into a C–H bond of one of the *o*-*t*-butyl groups to form the six-membered ring compound as shown in Scheme 4 [10].



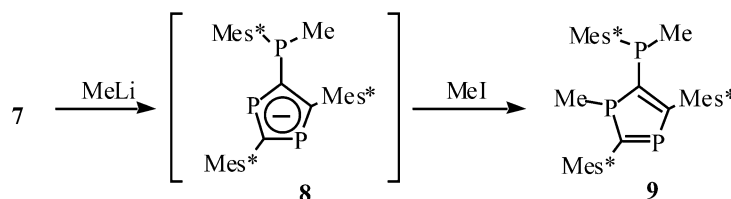
Scheme 4

It is also worth mentioning that a 1,3,6-triphosphafulvene derivative **7** was obtained in the reaction of the dibromophosphaethene with 2 equiv of *t*-butyllithium at $-78\text{ }^{\circ}\text{C}$. The formation of the triphosphafulvene indicates that the phosphanylidene carbenoid reacts with 2 equiv of phosphalkyne **4**, which was generated in situ during the reaction as shown in Scheme 5. The structure of 1,3,6-triphosphafulvene was unambiguously confirmed by X-ray analysis of the pentacarbonyltungsten complex [9]. The total energy of the parent compound (H instead of Mes*) was calculated on the RHF 6-31G* level and compared with that of 1,3,5-triphospha benzene, indicating that the former isomer is less stable by 20.9 kcal/mol. Thanks to the bulky Mes* group, we were able to isolate **7** as a stable compound.



Scheme 5

We have recently found that triphosphafulvene reacted with methyllithium to give a phosphide anion **8**, which gave a dimethyl-substituted phosphinodiphosphole **9** as shown in Scheme 6. The reactivity of the triphosphafulvene has been discussed based on cyclic voltammetry (CV) as well as the lowest unoccupied molecular orbital (LUMO) studies consistent with the strong electrophilicity of the *exo*-phosphorus [11].

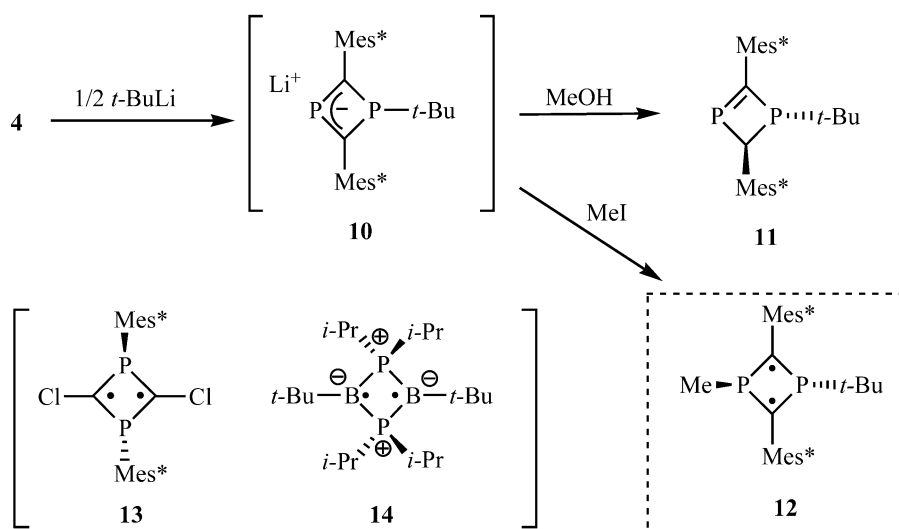


Scheme 6

CYCLIZATION REACTION OF PHOSPHAALKYNE

Phosphaalkyne **4** [12] showed an interesting reactivity toward nucleophiles such as alkylolithium reagents. When 0.5 equiv of *t*-butyllithium was allowed to react with **4**, we observed ^{31}P NMR peaks due to a phosphide anion **10**. The intermediate **10** was then quenched with methanol to give a 1,3-diphosphacyclobutene **11**, the structure of which was characterized by X-ray analysis [13]. A plausible reaction mechanism has been proposed which involves a nucleophilic attack at the terminal phosphorus to lead to a carbanion, which then reacts similarly with another phosphaalkyne to give a new dimeric carbanion. At that stage, cyclization occurs to give a cyclic anion **10** (Scheme 7). The quench with a proton source occurs at the carbon to give the final product **11**. It should be noted that an isodesmic reaction of phosphaalkyne with hydride occurs at carbon rather than phosphorus [14].

On the other hand, when anion **10** was quenched with methyl iodide, alkylation occurred at the phosphorus to give an unusual phosphorus compound, 1,3-diphosphacyclobutane-2,4-diyl of a diradical structure **12** [15] (Scheme 7). The structure of **12** was analyzed by X-ray crystallography, indicating that the four-membered ring is almost flat and that the two carbon atoms are planar with sp^2 configuration while the two phosphorus atoms are not planar. No visible bond is observed between the two carbon atoms because the distance between them is 2.50 Å. Attempts to obtain electron spin resonance (ESR) signals have failed so far, strongly suggesting the compound is a singlet diradical. The compound thus obtained is unusually stable in air at room temperature. Niecke reported the formation of 2,4-dichloro derivative **13** in 1996 [16] starting from chlorophosphanilidene carbenoid. A similar diyl compound **14** of the B₂P₂ system has recently been reported by Bertrand [17]. The 1,3-diphospha-

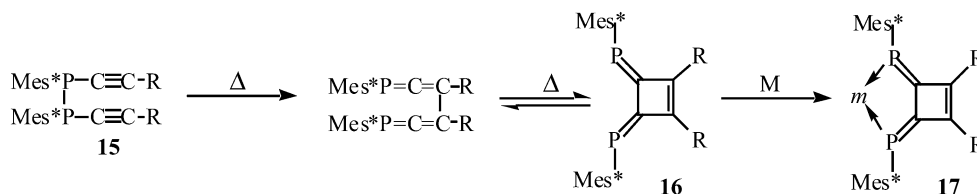


Scheme 7

cyclobutane-2,4-diyl system is now providing a new class of unusual phosphorus compound full of physicochemical interest.

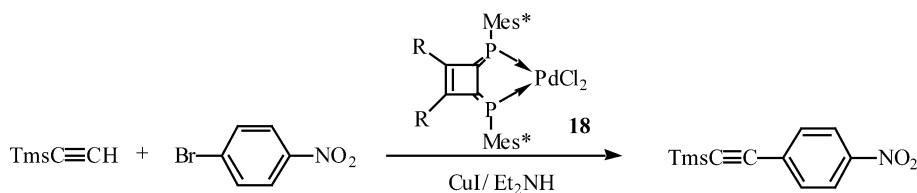
DIPHOSPHINIDENECYCLOBUTENE AS LIGAND FOR TRANSITION-METAL COMPLEXES

Bidentate diphosphane ligands with sp^3 -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 [18]. Märkl [19], Appel [20], and we [21] reported the synthesis and structure of diphosphinidene cyclobutene (DPCB) with two low-coordinated phosphorus atoms in the system which can be prepared from dialkynyldiphosphanes **15** via a kind of phospho-Cope rearrangement followed by rearrangement to **16** (Scheme 8). In fact, the phosphinidene cyclobutene **16** is configurationally stable and also acts as a bidentate ligand to ligate the transition metal to give **17** [22]. The application of transition-metal complexes ligated with DPCB is quite interesting [23].



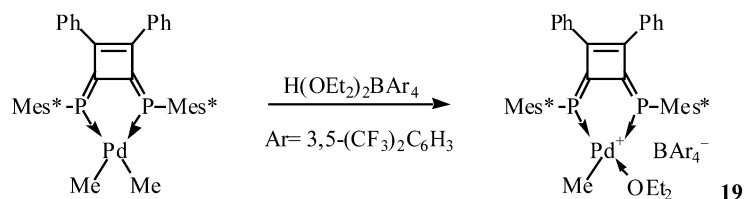
Scheme 8

As shown in Scheme 9, a coupling reaction of trimethylsilylacetylene with *p*-bromonitrobenzene of the Sonogashira type proceeded in THF–Et₂NH in the presence of 1.1 mol % of copper(I) iodide catalyzed by 1.5 mol % of palladium complexes of DPCB **18** to give cross-coupling reaction product in good yields (trimethylsilyl is abbreviated as Tms) [24].



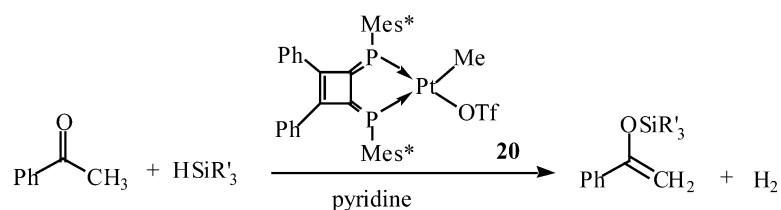
Scheme 9

We have found that the palladium complexes **19** act as a polymerization catalyst of ethylene (Scheme 10). Although the activity is not satisfactory for industry use so far, our new DPCB catalysts are stable toward heat up to 100 °C [25].



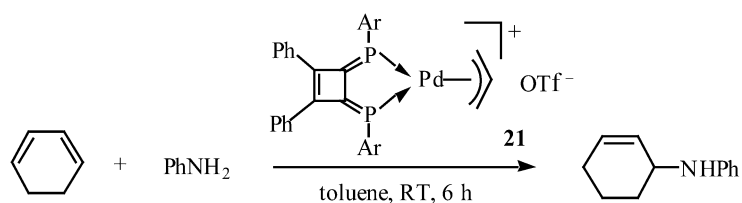
Scheme 10

As for the dehydrogenative silylation, we have noticed the platinum complexes are better than other known catalysts in terms of lower reaction temperature and better selectivity as well. It should be noted that the reaction can be done without solvent. For example, a reaction proceeded starting from acetophenone and dimethylphenylsilane in the presence of 3 mol % of platinum(II) complex with DPCB ligand **20** as catalyst and 3 mol % of pyridine at 50 °C for 4.5 h to give the corresponding silyl enol ether almost quantitatively without any by-product except hydrogen gas as shown in Scheme 11 [26]. It should be noted the reaction can be carried out without solvent with better results. This dehydrogenative silylation can be explained by formation of platinum(II) dihydride in this catalytic system.



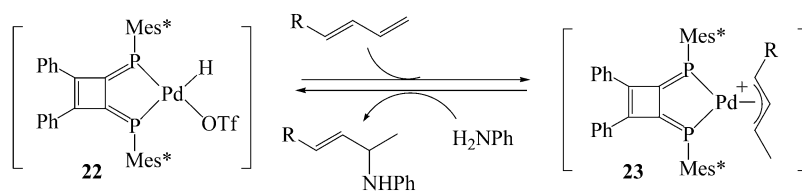
Scheme 11

The (π -allyl)palladium complexes with the DPCB ligand **21** for use in catalytic reactions were prepared from [Pd(π -allyl)Cl]₂ followed by addition of silver triflate in dichloromethane at room temperature as stable compounds. The X-ray analysis indicates that the DPCB plane and π -allyl moiety are perpendicular to each other [27]. The (π -allyl)palladium complexes reacted with cyclohexa-1,3-diene with aniline to give *N*-cyclohex-2-enylaniline as shown in Scheme 12.



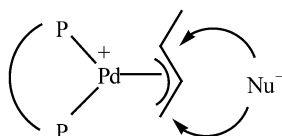
Scheme 12

Moreover, this π -allylpalladium complex **21** turned out to catalyze the reaction of amines with 1,3-dienes quite efficiently at room temperature to give the corresponding amination products: an intermediate **22** appears to be formed during this process and reacts with 1,3-dienes to give (π -allyl)palladium complexes **23**, and the complexes **23** thus formed react with amine to give the amination product and regenerates **22** as shown in Scheme 13 [28].



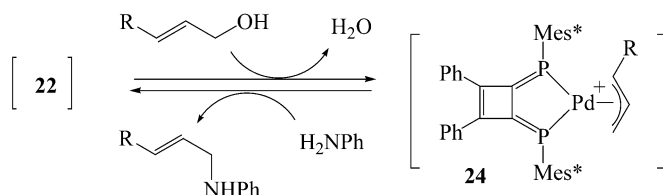
Scheme 13

Regioselectivity can be explained by taking Scheme 14 into account, based on the experimental results, since starting from either allylic alcohol, primary (but-2-en-1-ol) or secondary (but-2-en-2-ol), the same reaction product ratio for *N*-(but-2-enyl)aniline and *N*-(1-methylallyl)aniline (86:14) was observed in the same 95 % yield.



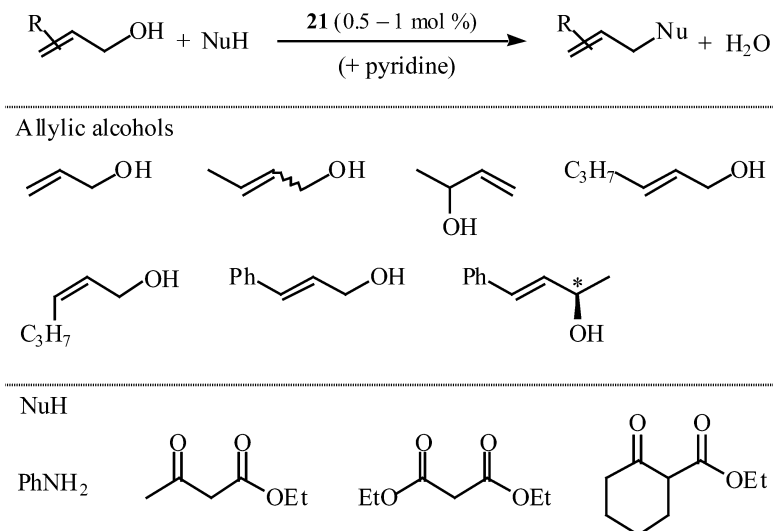
Scheme 14

More interestingly, as described in Scheme 15, even allylic alcohols reacted with aniline catalyzed by **21** to give amination product via the formation of π -allylpalladium complexes **24** and hydride **22** indicating direct amination of allylic alcohols with formal elimination of water in catalytic manner. These reactions can be carried out without solvent [29].



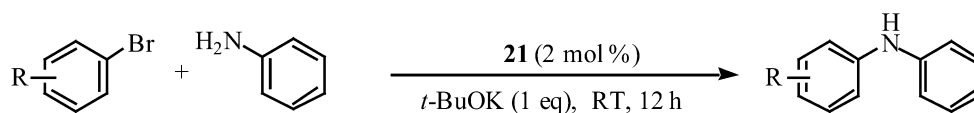
Scheme 15

Interestingly, direct alkylation of allylic alcohols can be achieved catalytically by DPCB complexes **21** at 50 °C. Carbanions from active methylene compounds such as acetylacettes can formally substitute the OH group of the allylic alcohols as described to give alkylation products in good yield. The reaction was rather general as listed in Scheme 16 from various kinds of allylic alcohols and active methylene compounds as nucleophiles with elimination of water [29].



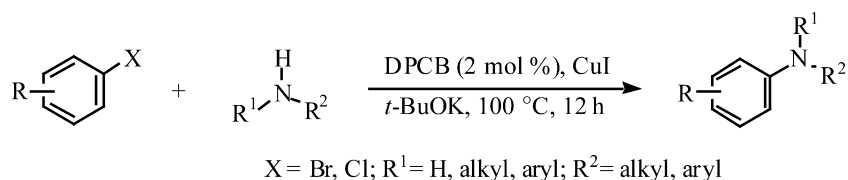
Scheme 16

We have recently found that the DPCB π -allyl complexes **21** facilitate the amination reaction of aromatic bromides at room temperature without solvent as shown in Scheme 17 [30].



Scheme 17

Furthermore, we have found the solvent-free DPCB-catalyzed Ullmann-type coupling reactions as shown in Scheme 18, where X is Br or Cl. It should be noted that even intramolecular cyclization occurs to give an indoline derivative. If we start from iodide, we can prepare tertiary amines from primary amines [31].

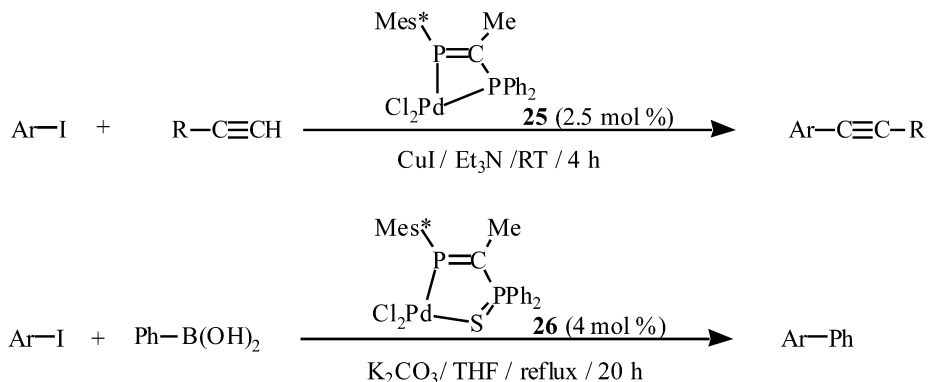


Scheme 18

The transition-metal complexes of DPCBs are promising catalysts for synthetic reactions probably due to the high coordination ability of the ligand owing to σ -donation/ π -back donation interactions

and the strong π -acceptor properties owing to the low-lying LUMO (π^*). In addition, most of the complexes are stable toward air and easy to handle.

Besides the DPCB ligands, we have recently found that phosphinophosphaethene-palladium(II) complexes **25** act as a good catalyst for the Sonogashira as well as Suzuki coupling reactions under mild conditions [32] as shown in Scheme 19. The monosulfide gave palladium(II) complex **26** and behaved like DPCB. This type of unsymmetrical ligand system will provide us a new catalyst for synthetic organic reactions.



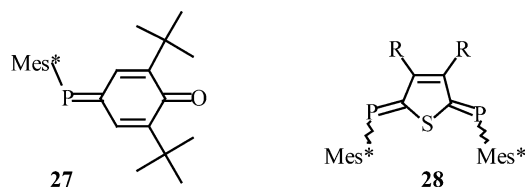
Scheme 19

In summary, the DPCB ligands as well as phosphinophosphaethene and its monosulfide have several advantageous characteristics over the conventional catalysts. The DPCB ligands show appropriate capability to coordinate to palladium, platinum, or even copper.

Environmentally friendly catalytic reactions are to be considered these days, and the DPCB ligands are expected to serve as a good catalyst for that purpose.

MISCELLANEOUS

As new redox systems containing low-coordinated phosphorus, we have been interested in benzoquinone and thiophene derivatives (**27** and **28**) as shown in Scheme 20 and X-ray, CV, and ESR studies have been made [33], suggesting that these compounds will provide a new class of quinoids for construction of new materials.



Scheme 20

ACKNOWLEDGMENTS

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NOTE ADDED IN PROOF

Added in proof related to [30] and [31], for catalytic Stille reactions: A. S. Gajare, R. S. Jensen, K. Toyota, M. Yoshifuji, F. Ozawa. *Synlett.* 144 (2005).