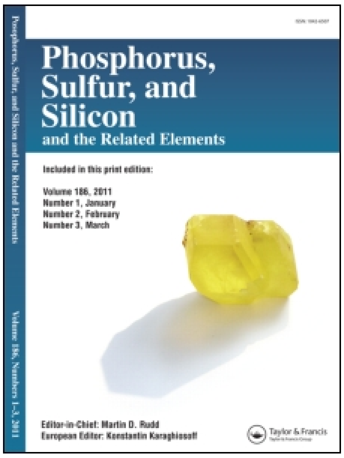

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SYNTHESIS AND CHARACTERIZATION OF KINETICALLY STABILIZED 1,3-DIPHOSPHACYCLOBUTENE DERIVATIVES

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SYNTHESIS AND CHARACTERIZATION OF KINETICALLY STABILIZED 1,3-DIPHOSPHACYCLOBUTENE DERIVATIVES

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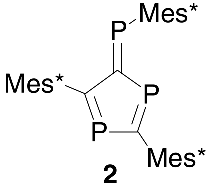
*1-(2,4,6-Tri-*tert*-butylphenyl)-2-phosphaethyne (**1**) was allowed to react with 0.5 equiv of an alkyllithium and subsequently with an alcohol to afford a bulky 1,3-diphosphacyclobutene, and its structure and coordination properties on transition metals were investigated. On the other hand, **1** was allowed to react with an alkyllithium and iodomethane to form a stable biradical, 1,3-diphosphacyclobutane-2,4-diyl.*

Keywords: 1,3-Diphosphacyclobutene; biradical; kinetic stabilization; phosphaalkyne; phosphorus

Compounds bearing the phosphorus-carbon triple bond have been used for synthesis of a number of heterocyclic compounds including unsaturated phosphorus atoms.[1,2] By using phosphaalkyne **1** intermediarily generated from the corresponding phosphanylidenecarbenoid,[3] we prepared and isolated a sterically protected 1,3,6-triphosphafulvene (**2**).[4] In spite of the steric encumbrance of the Mes* (= 2,4,6-tri-*tert*-butylphenyl) group, **1** reacts with nucleophiles to generate the corresponding phosphaethene derivatives.[3,5,6] Here we report preparation of several 1,3-diphosphacyclobutenes[7] and 1,3-diphosphacyclobutane-2,4-diyl[8] from **1**.

$\text{Mes}^{*}{-}\text{C}{\equiv}\text{P}$

1



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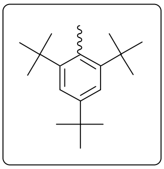

Mes*

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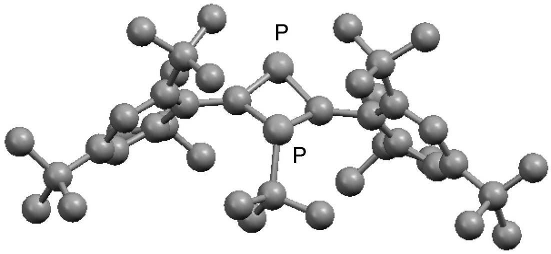
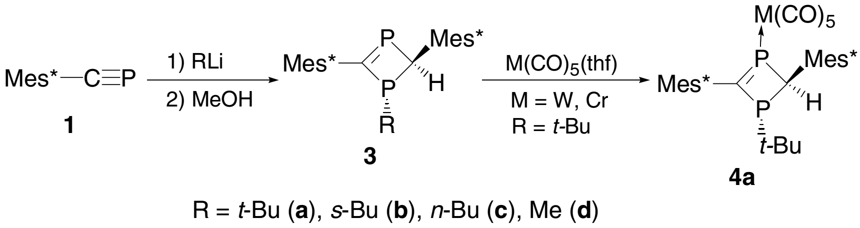


FIGURE 1 Molecular structure of **3a**. H atoms are omitted.

RESULTS AND DISCUSSION

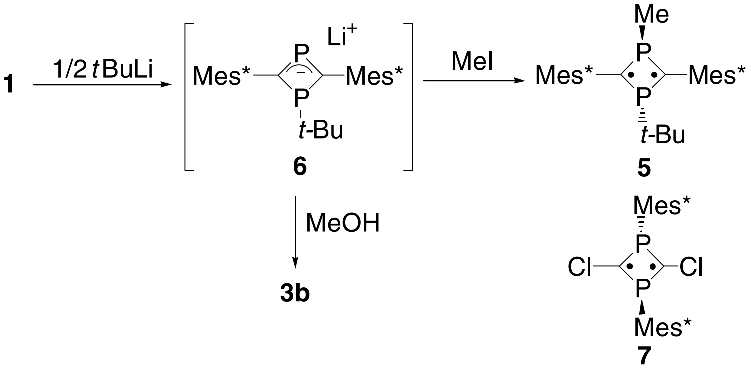
Phosphaalkyne **1**, prepared by the nickel-mediated [1,2]-rearrangement reaction as described in the literature,[3,8] was allowed to react with 0.5 equiv. of alkyllithiums followed by quenching with methanol to afford the corresponding 1,3-diphosphacyclobutenes **3** (Scheme 1). Compounds **3** were characterized by the spectroscopic analyses and as for **3a** (R = *t*-Bu) the structure was unambiguously determined by x-ray crystallography (Figure 1). The *tert*-butyl group on the phosphorus atom is *trans* to the Mes* group at the 4 position probably to minimize the steric congestion. Compound **3** seemed to be formed by cyclization of the intermediate including the 1,3-diphosphabuta-1,3-diene skeleton, which was predicted by theoretical calculation,[9,10] and might be formed from phosphaethenyllithium [Mes*C(Li)=PR] and **1**. No ring-opening reaction of the 1,3-diphosphacyclobutene skeleton giving the corresponding 1,3-diphosphabuta-1,3-diene was observed. The methyl derivative **3d** was unstable and was not be isolated, probably due to its poor steric protection. Compound **3a** was allowed to react with $M(CO)_5(thf)$ (M = W, Cr) to afford the corresponding complex **4a** revealing dominant coordination of the sp^2 phosphorus atom (Scheme 1). The steric congestion around the position 3 might hinder the coordination of the phosphorus atom on transition metals,



SCHEME 1

although the basicity of sp^3 phosphorus atom is superior to that of sp^2 phosphorus atom.[11]

When **1** reacted with 0.5 equiv. of *tert*-butyllithium and subsequently with iodomethane, we obtained 1,3-diphosphacyclobutane-2,4-diyl **5** as a deep blue-violet crystals. No 1,3-diphosphacyclobutene derivative was obtained. As shown in Scheme 2, the anion intermediate **6** shows a formally ambident nature of the PCP anion system,[13,14] although the ^{31}P NMR data of **6** suggests a 1,3-diphosphacyclobutene structure [$\delta_P = 268.5$ (P=C), 87.6 (*t*-BuP), $^2J_{PP} = 86.8$ Hz]. In ^{13}C NMR spectrum, the radical sp^2 carbon in **5** was observed at δ_C 111.3, which is similar to that of the Niecke's biradical **7** (δ_C 98.8).[15] In ^{31}P NMR spectrum, two kinds of phosphorus nuclei were observed at δ_P 55.9 (*t*BuP) and −11.3 (MeP) with a large J_{PP} coupling constant (362.8 Hz). In UV-Vis spectrum of **5** (hexanes), the absorption maximum was observed at 612 nm. Biradical **5** does not decompose at room temperature and even in air within several minutes, indicating rational stabilization by the electronic effect of phosphorus and bulky substituents. The structure of **5** was unambiguously determined by x-ray crystallography (Figure 2).



SCHEME 2

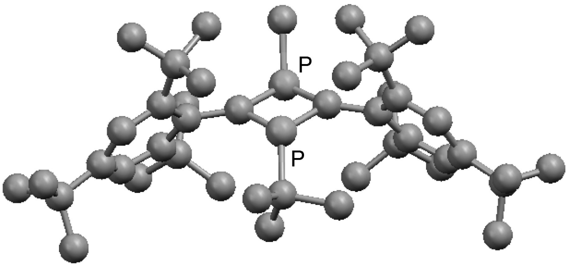


FIGURE 2 Molecular structure of **5**. H atoms are omitted.

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