

From phosphatriafulvenes to phosphabenzenes and stable six-membered phosphallenes*

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Abstract: Phosphatriafulvenes readily react with kinetically stabilized phosphalkynes. Depending on the substituent at the phosphorus atom of the phosphatriafulvene, different six-membered phosphaheterocycles can be isolated. On the one hand, 1,3-diphosphabenzenes are formed, which can be isomerized thermally to diphospha dewarbenzenes or complexed by $\text{Cr}(\text{CO})_3$. On the other hand, 1,3-diphosphaisobenzenes are thus available. They are converted to bicyclic six-membered allenes via 1,3-dipolar cycloaddition to the P/C double bond.

INTRODUCTION

Phosphatriafulvenes **1**, which are known for more than ten years now, constitute a unique class of phosphalkenes with inverse electron density [2]. This was shown chemically by reaction with nucleophiles that attack the three-membered ring [3], whereas the phosphorus atom is nucleophilic [2,4]. Furthermore, the inverse electron distribution is underlined by a single crystal structure analysis of one phosphatriafulvene where the P/C double bond is markedly stretched [5] and by *ab initio* calculations [2].

While reactions of the title compounds **1** with alkynes [3,4] and phosphalkenes [5] are known, the reactivity towards kinetically stabilized phosphalkynes has been much less studied so far [6].

SYNTHESIS OF 1,3-DIPHOSPHABENZENES

Heating the phosphatriafulvene **1a** in the presence of a stoichiometric amount of the phosphalkynes **2** yields the 1,3-diphosphabenzenes **3** (Fig. 1). The latter are isolated as yellow oils in good yield.

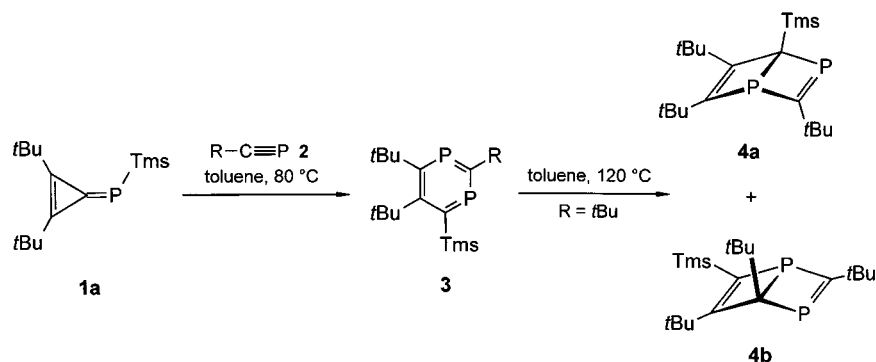


Fig. 1 Synthesis and valence isomerization of the 1,3-diphosphabenzenes **3**.

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For the derivative **3** ($R = tBu$) it is demonstrated that for this substitution pattern the diphosphadewarbenzenes **4** are the thermodynamically more stable valence isomers. The isomeric compounds **4a** and **4b** are obtained as an inseparable mixture (**4a:4b** = 5:2) upon heating the appropriate diphosphabenzene to 120 °C.

COMPLEX BEHAVIOR OF 1,3-DIPHOSPHABENZENES

Complexation of the diphosphabenzene **3** is successful using Kündig's reagent [7], the chromium naphthalene complex **5** (Fig. 2). The resulting complexes **6** are rather stable compounds and can be isolated by column chromatography as black crystals. Whereas a typical high-field shift of the phosphorus and carbon resonances is found in the NMR spectra compared to the starting material **3**, one carbon atom experiences a dramatic low-field shift. This deshielding effect can be explained by a formal positive charge at the carbon atom, leaving the chromium atom formally negatively charged.

A single crystal structure analysis of a derivative of **6** ($R = tBu$) confirms a strongly distorted η^5 complex, with the six-membered ring being in a boat-like conformation. This is not necessarily due to the complexation, as it is well known that arenes bearing sterically demanding substituents also adopt a boat-like conformation [8]. The distance between chromium and the carbon atom bearing the positive charge is extremely lengthened so that hardly any binding interaction can be discussed.

SYNTHESIS AND DIMERIZATION OF THE PHOSPHATRIAFULVENE **1b**

A procedure for the preparation of the triafulvene **1b** bearing three *tert*-butyl groups has been described recently [6]. Whereas the usual Peterson-like olefination reaction for the synthesis of phosphatriafulvenes [2] is unsuccessful, **1b** is easily synthesized starting from cyclopropenone **7** and phosphine **8** in the presence of the Lewis acid boron trifluoride (Fig. 3).

Compliance with the exact protocol is crucial, as **1b** is prone to dimerization. In accord with the polarity of the phosphatriafulvene a formal [3+3] cycloaddition results in the formation of the tricycle **9** (Fig. 3) [9]. The structure of the surprisingly stable double *anti* Bredt compound **9** is confirmed unequivocally by a single crystal structure analysis. Thereby, a highly strained and distorted cyclopropene moiety is found. The C/C double bonds of **9**, which possess a twofold axis of rotation in solution, are still planar. The individual angles around the sp^2 carbon atoms of up to 168° exhibit remarkable deviations from the ideal values.

SYNTHESIS OF PHOSPHACYCLOHEXA-1,2-DIENES

A thermally induced reaction between the phosphatriafulvene **1b** and various phosphalkynes **2** leads to the formation of diphosphaisobenzene **10** (Fig. 4) [6]. Compounds **10** are isolated by bulb-to-bulb distillation as orange-red oil or as a solid ($R = IAd$) and are surprisingly stable in the absence of moisture and air [10].

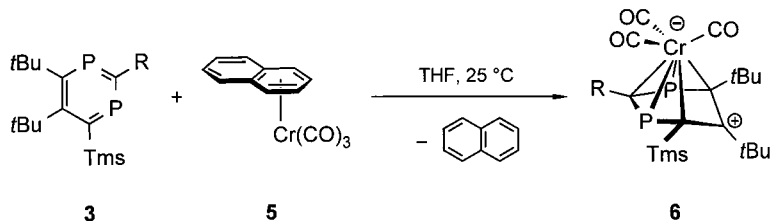


Fig. 2 Complexation of the 1,3-diphosphabenzene **3**.

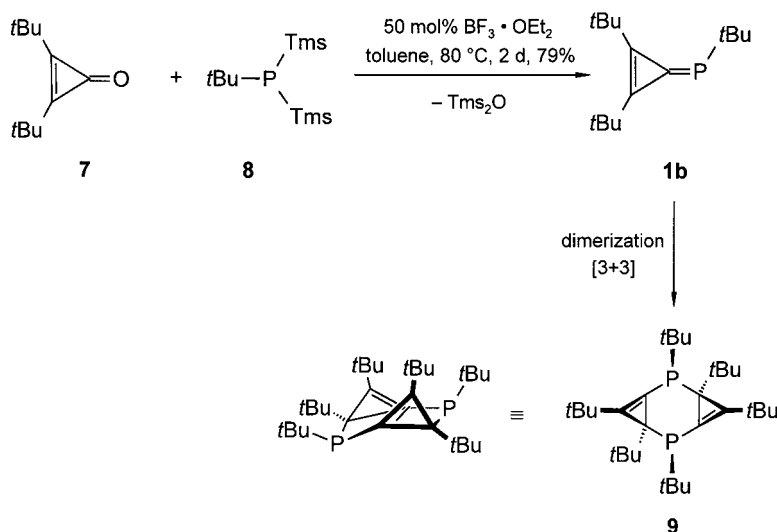


Fig. 3 Synthesis and dimerization of the phosphatriafulvene **1b**.

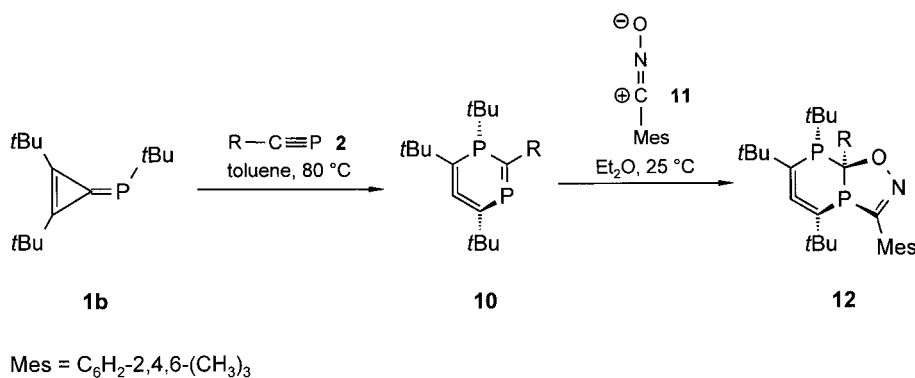


Fig. 4 Synthesis of the six-membered allenes **10** and **12**.

Their constitution can be easily deduced by spectroscopic means. The allene bands in the IR spectra of **10** between 1835 and 1866 cm⁻¹, as well as the ¹³C NMR resonances of the central allene carbons between $\delta = 198$ and 203, are particularly characteristic.

The isobenzenes **10** are converted to bicyclic allenes **12** with mesityl nitrile oxide **11** at room temperature (Fig. 4). The [3+2] cycloaddition exclusively takes place at the more reactive P/C double bond in a highly diastereoselective manner. The strained C/C double bonds seem to be kinetically stabilized very well. The regioselectivity of the reaction is in agreement with that of [3+2] cycloadditions of nitrile oxides onto P/C double and triple bonds [11].

The structure and relative stereochemistry of **12** (R = *t*Bu) was confirmed by single crystal structure analysis, thereby proving that of **10**. The 1,2-diene moiety is significantly bent: the angle of about 156° is markedly smaller than found for the other stable 1,2-dienes [12]. The same holds true for the dihedral angles, which show marked deviations from the ideal value of 90°.

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