

# Approach to the Synthesis of Five-Membered Organophosphorus Compounds via Alumoles and Alumolanes <sup>†</sup>

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**Abstract:** This work summarizes the results of a new approach to the synthesis of previously undescribed, hard to obtain five-membered cyclic organophosphorus compounds—3-alkyl(aryl)-substituted phospholanes,  $\alpha,\omega$ -bisphospholanes, polycyclic phospholanes, 4,5-dialkyl(diaryl)-disubstituted 2,3-dihydrophospholes, as well as their oxides and sulfides. Alumoles and alumolanes synthesized by the reaction of cycloaluminumation of available unsaturated compounds (terminal alkenes,  $\alpha,\omega$ -alkadienes, norbornene derivatives, symmetrical internal alkynes) with Et<sub>3</sub>Al in the presence of a Cp<sub>2</sub>ZrCl<sub>2</sub> catalyst were used as precursors. The substitution of aluminum atoms in cyclic organoaluminum compounds for phosphorus atoms takes place using alkyl(aryl)phosphorus (III) dichlorides. The developed one-pot method gives the high yields of products under mild conditions.

**Keywords:** phospholanes; phospholes; alumolane; alumole; cycloaluminumation; zirconocene dichloride; metal complex catalysis

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## 1. Introduction

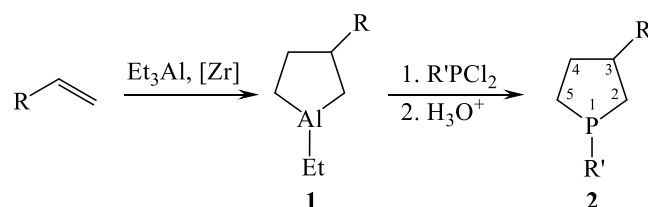
Phosphorus-containing heterocycles, due to their unique properties, are widely used as intermediates, ligands for organometallic chemistry and catalysis, monomers for electronics, and effective drugs for medicine and agriculture [1–6]. Therefore, the development of original methods for obtaining hard to obtain and previously undescribed five-membered organophosphorus compounds (OPCs) is a demanded, relevant task and is of great practical importance.

A number of fairly effective approaches to the synthesis of cyclic OPCs include methods based on the direct conversion of five-membered metallocarboranes based on transition metals into phosphocarboranes using phosphorus dihalides. A few examples of the synthesis of phospholanes and phospholes from zirconacyclopentenes [7,8], zirconacyclopentadienes [9–11], and titanacyclopentadienes [12] are known in the literature. The direct conversion of aluminacarboranes into cyclic OPCs has not been practically studied. We assumed that the replacement of the aluminum atom in aluminacarboranes by a phosphorus atom using organic phosphorus dihalides would allow us to develop promising methods for practical application to obtain a wide range of previously inaccessible and new classes of cyclic and acyclic organophosphorus compounds of a given structure.

## 2. Results and Discussion

Presently, we have developed effective one-pot methods for the synthesis of phospholanes and phospholes of various structures, based on the reaction of catalytic cycloaluminumation of unsaturated compounds (alkenes, alkynes,  $\alpha,\omega$ -diolefins, norbornenes) through the formation of alumoles (aluminacyclopentadienes) and alumolanes (aluminacyclopentanes). The alumoles and alumolanes obtained in situ were involved in the substitution of aluminum atoms in substituted alumolanes for phosphorus atoms with alkyl(aryl)phosphorus dichlorides.

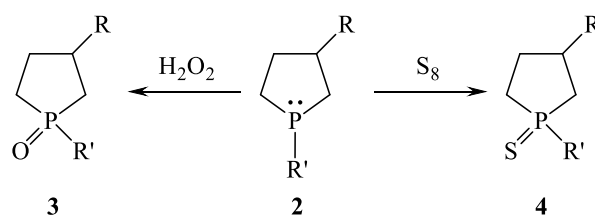
In 2012, 3-substituted phospholanes were obtained [13,14]. It was found that aluminocyclopentanes **1** obtained by the reaction of alkenes with  $\text{Et}_3\text{Al}$  in the presence of 5 mol. %  $\text{Cp}_2\text{ZrCl}_2$  (20 °C, 6–8 h), react in situ with  $\text{R}'\text{PCl}_2$  ( $\text{R}' = \text{Me, Bu, Ph}$ ) in toluene for 30 min with the replacement of the Al atom by the P atom to form the corresponding phospholanes **2** in yields 79–84% (Scheme 1). Compounds **2** are mixtures of diastereomers 3:2, formed due to the presence in the molecule of two centers of asymmetry at C-3 and P-1. The latter exists due to the high configuration inversion barrier at the phosphorus atom [15].



[Zr] =  $\text{Cp}_2\text{ZrCl}_2$ ;  
 $\text{R} = \text{Bu, Hex, Oct, cyclohexyl, cyclohexen-3-yl, Bn}$ ;  
 $\text{R}' = \text{Me, Bu, Ph}$ .

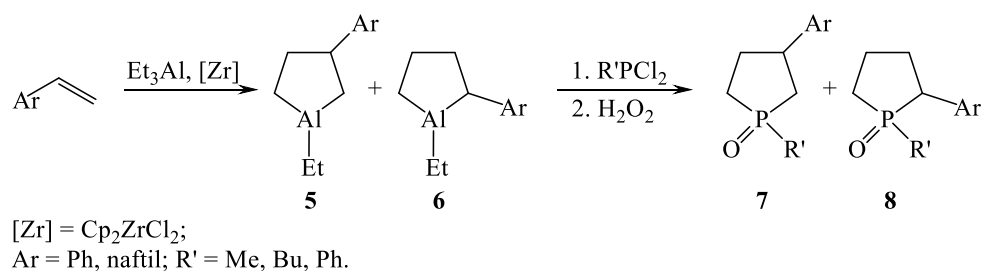
**Scheme 1.** Synthesis of 3-substituted phospholanes **2**.

Phospholanes **2** easily react with  $\text{H}_2\text{O}_2$  in chloroform due to the presence of a lone electron pair in phosphorus with quantitative yields of phospholane 1-oxides **3**. The reaction of **2** with  $\text{S}_8$  leads to phospholane-1-sulfides **4** also in quantitative yields (Scheme 2).



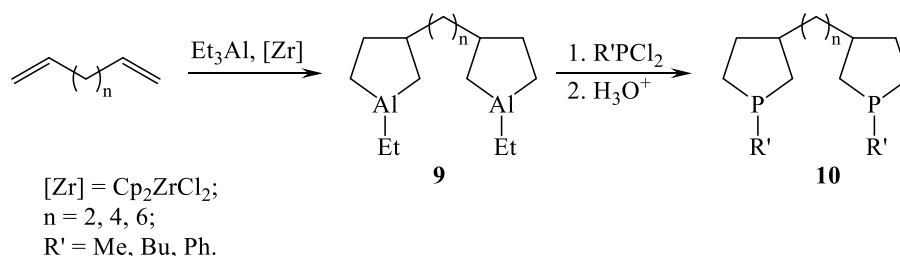
**Scheme 2.** Synthesis of 3-substituted phospholane 1-oxides and 1-sulfides.

In the reaction of styrene or 2-vinylnaphthalene with  $\text{AlEt}_3$  in the presence of  $\text{Cp}_2\text{ZrCl}_2$ , in addition to 3-phenyl(naphthyl)-1-ethylaluminumcyclopentanes **5**, the reaction mixture contains 2-phenyl(naphthyl)-1-ethylaluminumcyclopentane **6** [14]. Both regioisomers react in situ with phosphorus dihalides and hydrogen peroxide to form 1-phenyl(alkyl)-3-arylphospholane oxides **7** and 1-phenyl(alkyl)-2-arylphospholane oxides **8** in a 1:2 ratio with a total yield of 87% (Scheme 3).



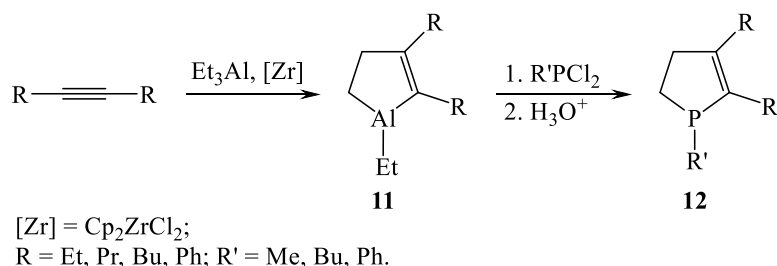
**Scheme 3.** Synthesis of 3-substituted **7** and 2-substituted **8** phospholan oxides.

Next, we thought it expedient to apply our method to obtain  $\alpha,\omega$ -bisphospholane compounds by the interaction of phosphorus dihalides with bisaluminacyclopentanes. It was established that, under the developed conditions, bisaluminacyclopentanes **9**, obtained by catalytic cycloaluminum of 1,5-hexadiene, 1,7-octadiene, and 1,9-decadiene, react with phosphorus dihalides to form bisphospholanes **10** as a mixture of isomers with a total yield of 84–85% (scheme 4) [16].



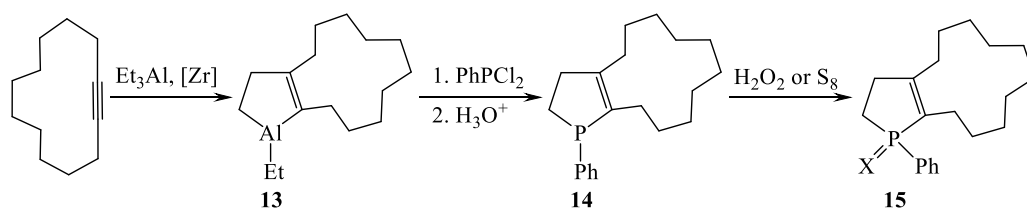
**Scheme 4.** Synthesis of bisphospholanes **10**.

The reaction of substitution of the Al atom for the P atom in 4,5-disubstituted 2,3-dihydroaluminum was studied for the first time [17]. It was established that 4,5-disubstituted 2,3-dihydroaluminum **11**, synthesized by catalytic cycloaluminum of symmetrical acetylenes with AlEt<sub>3</sub> under the action of a Cp<sub>2</sub>ZrCl<sub>2</sub> catalyst, enter into the reaction of substitution of an aluminum atom for a phosphorus atom with phenyl- and alkyl-dichlorophosphines (~20 °C, 30 min) with the formation 4,5-disubstituted 2,3-dihydrophospholes **12** in 84–92% yields (Scheme 5).



**Scheme 5.** Synthesis of 4,5-disubstituted 2,3-dihydrophospholes **12**.

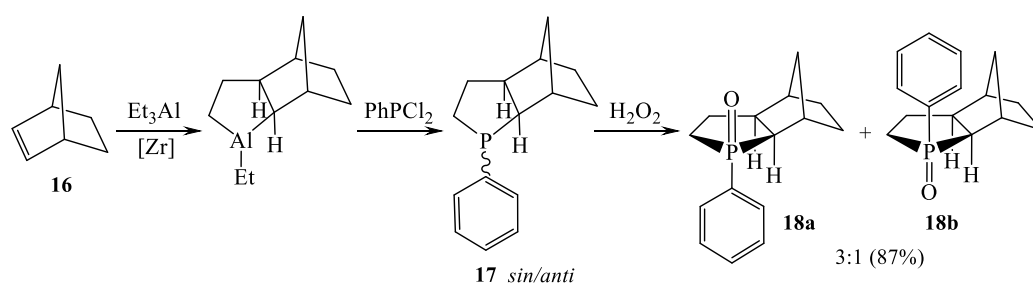
The interaction of in situ generated bicyclic organoaluminum compound **13** with PhPCl<sub>2</sub> yielded phospholene **14** with an annelated cyclic fragment in 81% yield (Scheme 6) [17]. Derivatization of bicyclic phospholene **14** gave rise to 2,3-dihydrophosphol-1-oxide **15a** and 2,3-dihydrophosphol-1-sulfide **15b** in quantitative yields.



[Zr] = Cp<sub>2</sub>ZrCl<sub>2</sub>; X = O (a), S (b).

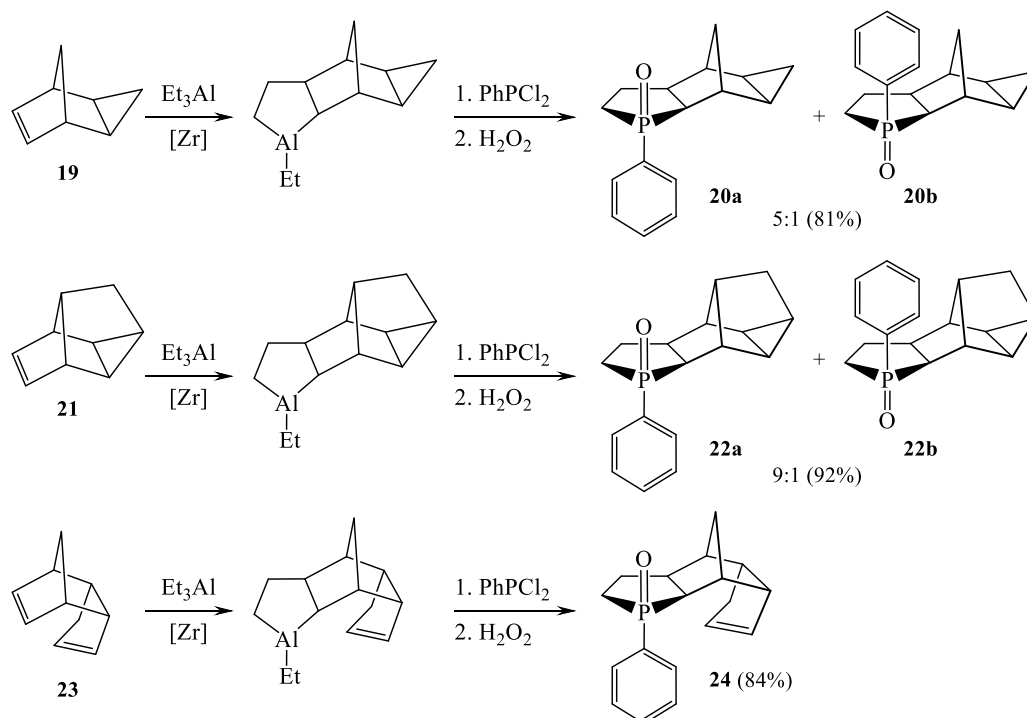
**Scheme 6.** Synthesis of 13-phenyl-13-phosfabicyclo[1.0.3.0]pentadec-1(12)-ene **14**.

An efficient one-pot method was developed for the synthesis of polycyclic phospholane oxides **18**, **20**, **22**, and **24** by the in situ reaction of dichlorophosphines with norbornane-annulated aluminacyclopentanes obtained by the catalytic cycloaluminum of norbornenes in 81–92% yields (Schemes 7 and 8) [18].



**Scheme 7.** Synthesis of the 3-Phenyl-3-phosatricyclo[5.2.1.0<sup>2,6</sup>]decane 3-Oxide.

It was found that compounds with a bulkier hydrocarbon framework, such as **19** and **21**, predominantly form *syn*-phenyl-substituted phospholane 3-oxides **20a** and **22a**; the proportion of *anti*-isomers in these experiments does not exceed 15% and 10%, respectively. In the case of **23**, the formation of a single *syn*-isomer **24** is observed (Scheme 8). Thus, the ratio of polycyclic *syn*- and *anti*-3-phenyl-phospholane 3-oxides depends on the structure of the polycyclic hydrocarbon substituent annulated to aluminacyclopentane.



**Scheme 8.** Synthesis of the Polycyclic Phospholane 3-Oxides **20**, **22**, and **24**.

### 3. Conclusions

Thus, in our research, we have developed efficient one-pot methods for the synthesis of a wide range of previously undescribed and hard to obtain five-membered cyclic organic molecules containing a phosphorus atom. The studied reaction of replacement of an aluminum atom by a phosphorus atom in five-membered aluminacarbocycles—aluminumanes and alumols—is an effective tool for designing cyclic organophosphorus compounds in one preparative step.

**Author Contributions:** Conceptualization, U.M.D. and A.L.M.; methodology, validation, and execution of chemistry experiments, A.L.M. and T.V.T.; manuscript preparation, A.L.M. and T.V.T. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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