



Preparation of 2-phosfolene derivatives from zirconacyclopentenes

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This Letter is dedicated to the memory of
Professor Pascal Le Floch

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ABSTRACT

Zirconacyclopentenes, which are easily prepared from alkynes, alkenes, and zirconocene compounds, reacted with dichlorophenylphosphine to give 2-phosfolene in high yields. The reaction was performed conveniently in one-pot from an alkyne, alkene, dichlorophosphine, and zirconocene compounds.

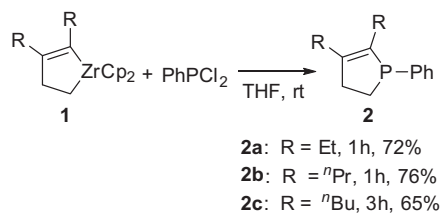
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P-heterocycles are of current interest due to their rich chemistry and applications.^{1–3} For example, the phosfolenes including the 3-phosfolenes and 2-phosfolenes are extremely versatile reactive intermediates in organic synthesis² and excellent ligands in organometallic chemistry.^{1,3} Consequently, there is a significant interest in the development of new synthetic methodologies to access phosfolenes. Although a number of synthetic methods affording phosfolenes have been reported,⁴ the most attractive one seems to be the direct transformation of metallacyclopentenes to phosfolenes. In this regard especially attractive are zirconacyclopentenes, which can be easily prepared by the reaction of an alkyne with zirconocene ethylene complex Cp₂Zr(CH₂=CH₂) or zirconacyclopentane.⁵ Fagan, Nugent, and co-workers have reported a single example for the preparation of 3-phosfolene from zirconacyclopenta-3-ene.⁶ In this Letter we would like to report a convenient method for the preparation of 2-phosfolene derivatives from zirconacyclopenta-2-enes.

Typical procedure is as follows. To the THF solution of zirconacyclopentene **1a** (1 mmol), prepared in situ from Cp₂ZrEt₂ (1 mmol) and 3-hexyne (1 mmol),^{5c} was added dichlorophenylphosphine (1 mmol, 145 μL) at room temperature. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed under reduced pressure. The residue was extracted with diethyl ether and filtered. The solvent was evaporated in vacuo and the residue was purified by column chromatography on alumina to

afford the desired product **2a** (72% isolated yield) (Scheme 1). Other zirconacyclopentenes **1b** and **1c** showed a similar reactivity, and **2b** and **2c** were isolated in 76% and 65% yield, respectively.

Since trivalent phosphines **2** were sensitive to oxygen, the products were isolated as phosphine sulfides **3** after treatment of the reaction mixture with elemental sulfur. To extend the reaction, we tried out various substituted monocyclic as well as bicyclic zirconacyclopentenes bearing alkyl, aryl, and TMS groups. The representative results are summarized in Table 1. In all cases, the corresponding products were formed in high yields. When unsymmetrical alkynes were used, two regioisomers were observed (entries 5–8). The ratio of the two isomers depended on the selectivity of the formation of zirconacyclopentenes.⁵ The reaction of bicyclic zirconacyclopentene **1i**⁷ with PhPCl₂ formed cyclopenta[*c*]phosfolene **3i** (entry 9). To our delight, the crystal of **3i** was suitable for single crystal analysis, and its structure was fully characterized by the X-ray diffraction analysis (Fig. 1).⁸ The zirconacycle compound **1j** prepared from benzyne and styrene with Zr(II)⁹ reacted



Scheme 1.

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8. Compound **3j**: C₁₉H₁₉PS, crystal size (mm): 0.35 × 0.33 × 0.23, colorless, crystallized in monoclinic, space group P2(1)/n with cell parameters: $a = 9.6574(19)$, $b = 15.921(3)$, $c = 10.442(2)$ Å³, $\beta = 90.96(3)^\circ$, $V = 1605.2(6)$ Å³, $D_c = 1.284$ g/cm³, $Z = 4$. Temperature (K): 173(2). CCDC 785906.
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