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Phosphorus, Sulfur, and Silicon and the Related Elements

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PHOSPHORUS AND ZIRCONIUM: A FRUITFUL RENDEZ-VOUS

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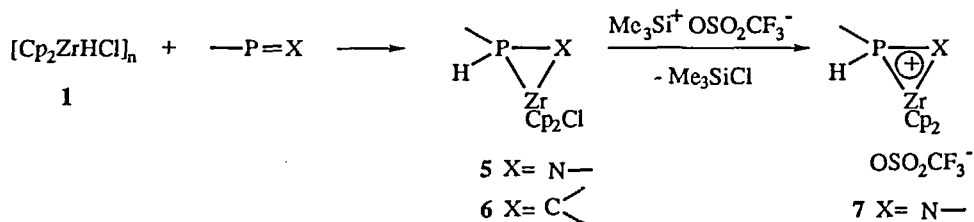
Abstract Zirconium reagents such as $[\text{Cp}_2\text{ZrHCl}]_n$, Cp_2ZrMe_2 , $[\text{Cp}_2\text{Zr}]$... were found to be useful tools for the regio and diastereospecific synthesis of diphosphines including optically active diphosphines as well as for the generation of masked iminophosphide anions, metalated phosphorus containing macrocycles, phosphirane zirconacyclopentadienes or zirconacycloprenes.

INTRODUCTION

Zirconium derivatives were found to be useful tools in organic and organometallic syntheses.¹ In contrast a few reactions were concerned with the interactions between main group elements, and more precisely phosphorus compounds with zirconium species. We describe here our efforts to develop new methodologies of synthesis of linear or cyclic, neutral or cationic phosphorus derivatives from easily available zirconium compounds such as $[\text{Cp}_2\text{ZrHCl}]_n$ **1**, Cp_2ZrMe_2 **2**, $[\text{Cp}_2\text{Zr}]$ **3** or Cp_2ZrCl_2 **4**.

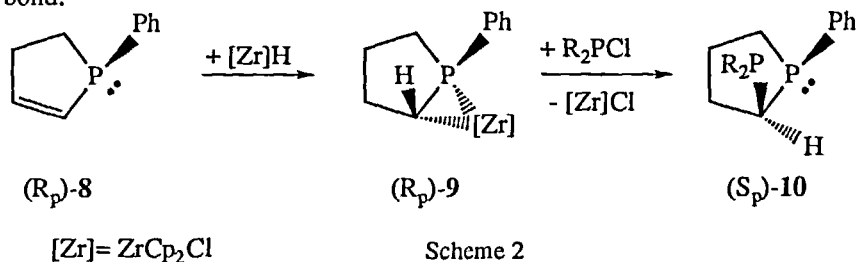
Reactions from $[\text{Cp}_2\text{ZrHCl}]_n$ **1**

Addition of **1** to various phosphamines or phosphalkenes led to the metalated three membered ring **5** ($\text{X} = \text{N}-$) or **6** ($\text{X} = \text{C} <$). Abstraction of chlorine allowed the synthesis of the first cyclic zirconium phosphorus cations **7** (Scheme 1).²



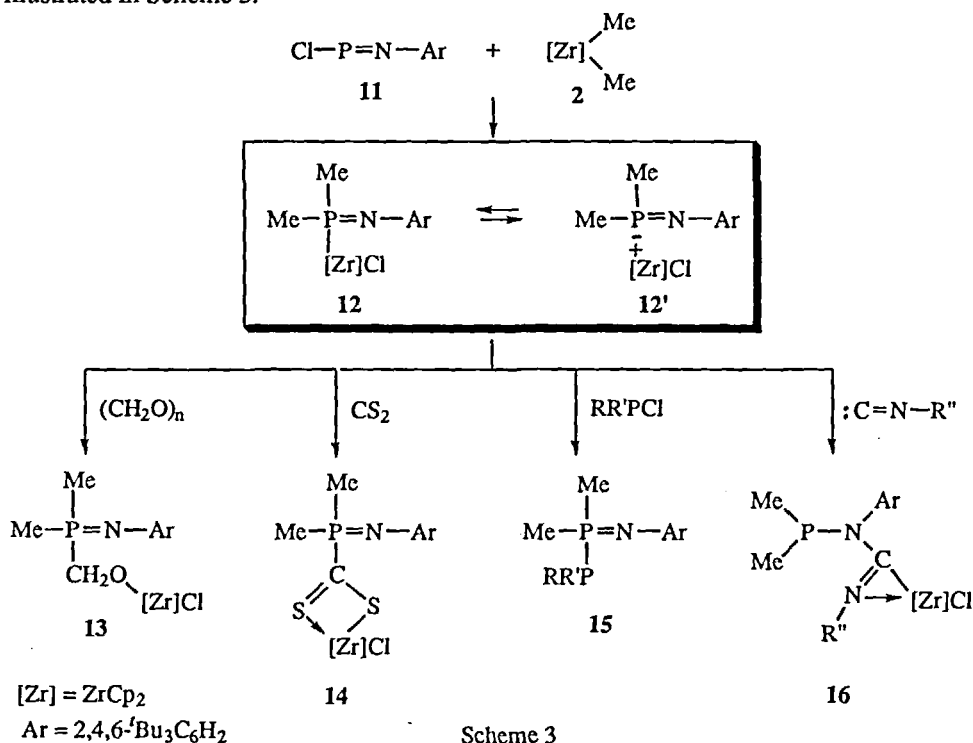
Scheme 1

A regio and diastereospecific way to new diphosphines can be proposed from hydrosilyrconation of dihydrophosphole $\text{Ph-P-CH=CH-CH}_2\text{-CH}_2$ **8** followed by treatment of the resulting unexpected α -zirconated phospholane $\text{Ph-P-CH(ZrCp}_2\text{Cl)(CH}_2)_2\text{CH}_2$ **9** with various chlorophosphines.³ Such a methodology can be applied to the synthesis of an optically active diphosphine **10** (Scheme 2) and allowed to point out an unprecedented inversion of configuration at carbon in the electrophilic cleavage of the carbon-zirconium (IV) bond.⁴

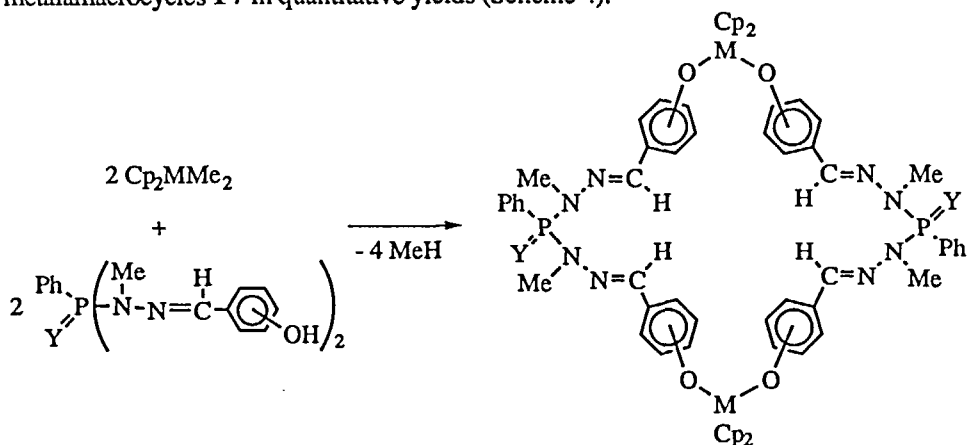


Reactions from Cp_2ZrMe_2 2

Treatment of the chlorophosphimine **11** with **2** led to the iminozirconophosphorane **12**, the first P-metalated iminophosphorane. This compound can be considered as a masked iminophosphide anion **12'** which has presented a versatile behaviour. Insertion reactions into the Zr-P bond, formal insertion into the N-Zr bond and reactions at phosphorus are illustrated in Scheme 3.⁵



Cp_2MMe_2 ($\text{M} = \text{Zr}, \text{Ti}$) can be reacted with phosphodihydrazones to give metalamacrocycles **17** in quantitative yields (Scheme 4).⁶

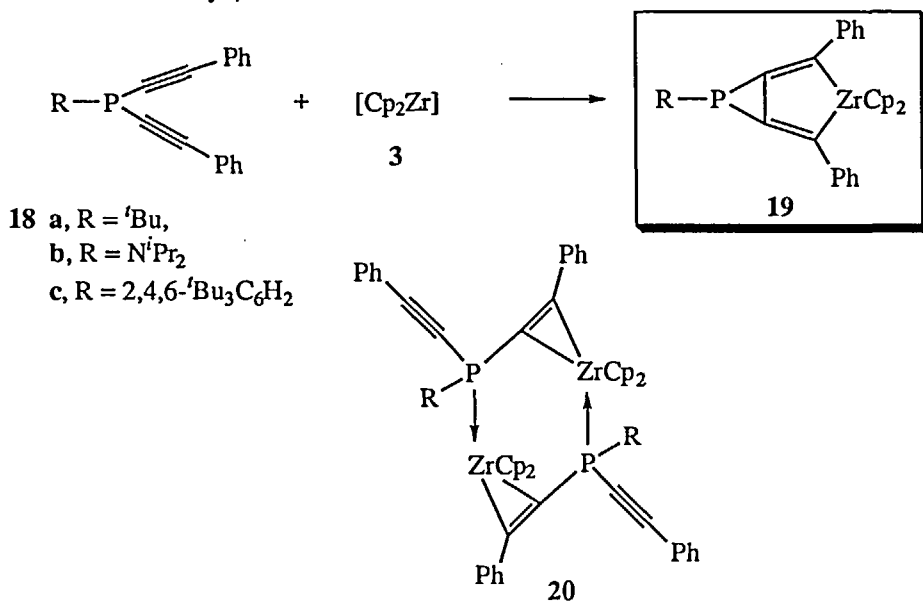


Scheme 4

17 $\text{M} = \text{Zr}, \text{Ti}$

Reactions from $[\text{Cp}_2\text{Zr}]$ 3

A clean synthesis of metalated cyclic derivatives such as phosphirane-zirconacyclopentadienes **19** can be proposed from the addition of diacetylenic phosphines **18** to **3**. These bicyclic systems reacted as zirconacyclopropenes **20** towards a variety of reagents (H_2O , HCl , PhPCl_2 , PCl_3 , etc...) (Scheme 5). The zirconacyclopropene **20c** was isolated and fully characterized.



Scheme 5

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