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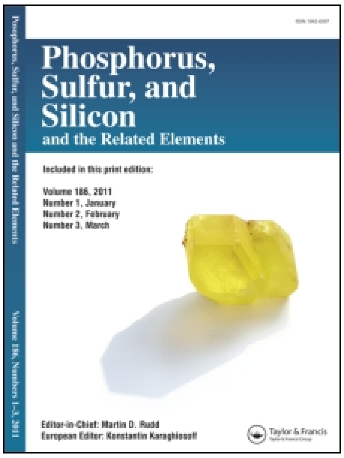

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Phosphorus Compounds for the Formation of Unprecedented Anionic Zirconium Complexes

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Using the nucleophilic ability of tertiary phosphines we have been able to prepare a large variety of unprecedented stable phosphonium anionic zirconocene(IV) complexes.

Keywords: phosphines; zirconocenes; nucleophilic addition; zwitterion; anionic complexes

INTRODUCTION

Neutral and cationic zirconocene(IV) complexes have found to be important classes of compounds respectively due to their synthetic applications in organic and organometallic chemistry and in the catalytic polymerization process of olefins.[1] Little is known about the interaction of zirconocene(IV) complexes with main group elements. Very recently we focused our attention on the study of the interaction of phosphine derivatives with neutral zirconocene(IV) complexes with the aim to stabilize and prepare new highly reactive species.

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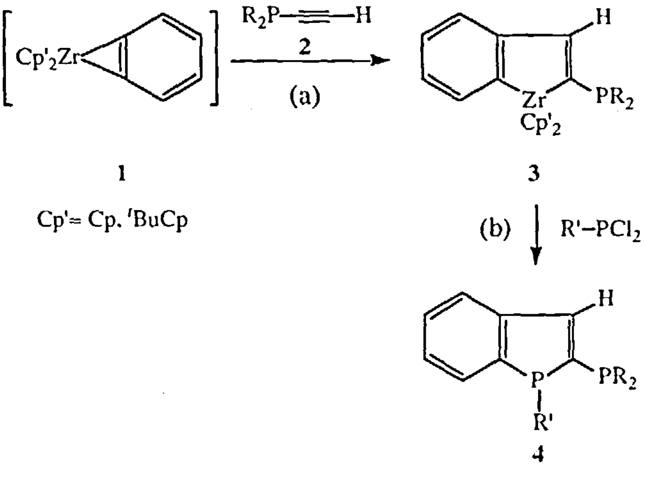
RESULTS AND DISCUSSION

We have demonstrated in our group that phosphine derivatives in the close environnement of zirconocene complexes could have a dramatic effect on (i) the stereochemical consequence at carbon during the cleavage process of the carbon-zirconium bond,[2] and (ii) the course of the carbon-zirconium substitution reaction.[3] Using the strength of the electrophiles, the ability of the counteranion to form strong bond with the metal and the nucleophilicity of the heteroelement we have developped new synthetic pathways - ring closure and opening reactions - for the preparation of linear and cyclic phosphorus compounds.[4] As an example, the two steps preparation of the new ligands, α-phosphino-P(III)-phosphaindenes **4**, illustrates the biphilic ability - electrophilic and nucleophilic - of phosphorus(III) we have exploited in zirconocene complexes chemistry: (a) regioselective insertion reaction of phosphaalkynes **2** in the Zr-C bond of the benzyne-zirconocene **1** to give **3**, (b) exchange reaction of the metallic fragment in **3** with dichlorophosphines $R'\text{-}PCl_2$.[5]



1

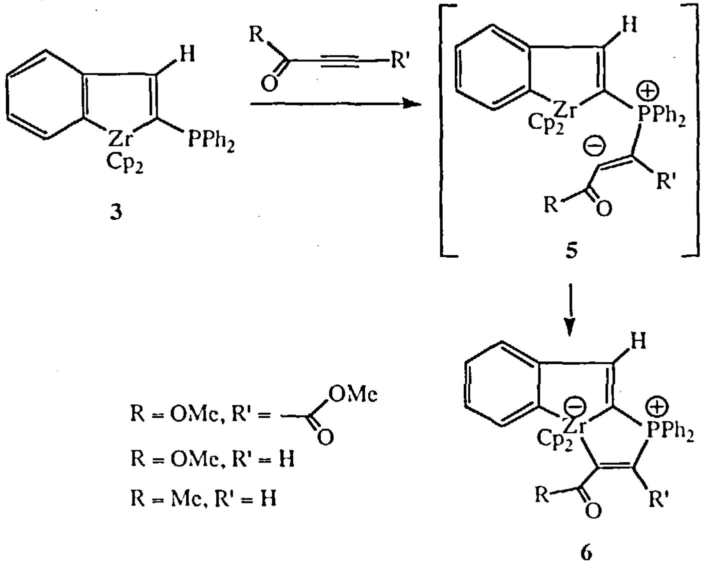
Cp'= Cp, ^{t}BuCp

3

4

R = H, Ph R'= Ph, Et

Nucleophilic attack by tertiary phosphines on activated acetylenic reagents leads to an increase in coordination number on phosphorus atom to four and to the formation of transient betaïne species which have been up to now intercept by organic trapping reagents.[6] Surprisingly to the best of our knowledge the reactivity of these betaïne species has not been exploited in organometallic chemistry. It is known however that organometallic reagents having Lewis acidity vacant orbital react with anionic species to generate the corresponding metallic anionic complexes. Nucleophilic addition of the phosphine in 3 on activated acetylenic systems to give 5 as a transient species followed by a cyclization reaction on the coordinatively unsaturated metal fragment allowed us to prepare and isolate unprecedented stable 18-electron phosphonium anionic zirconocene complexes 6.[7]



This method of preparation of these unknown anionic species has been extended to the nucleophilic attack of 3 at aldehydes, heterocumulenes (*i.e.* carbon dioxide, carbon disulfide, isocyanates and isothiocyanates), and azo-reagents. The reaction is regio- and chemioselective. The X-ray crystal structures of most of these anionic complexes clearly show the presence of the phosphonium center and the five coordinated zirconium atom which confirm the zwitterionic form of these complexes. Thus we have been able to synthesize not only the first anionic five coordinated zirconocene(IV) complexes in which all the atoms linked to the zirconium

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atom are carbons but also zwitterionic zirconocene(IV) complexes in which one of the carbon atoms linked to Zr has been replaced by an heteroelement as oxygen, nitrogen, and sulfur.

Using this method we have prepared new phosphonium-zwitterionic zirconocene complexes starting from different Cp_2Zr/phosphine systems. We are now investigating the reactivity of these species in different areas as for example the preparation of new ligands for the coordination chemistry, and in homogeneous catalysis as it has been demonstrated that the stereospecific polymerization of α-olefins involves in the transition state a five-coordinate geometry around zirconium atom for chain propagation.

ACKNOWLEDGEMENTS

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