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Zirconocene [Cp_2Zr] synthon and benzynezirconocene complexes as tools in main group element chemistry

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Contents

Abstract

Interactions between zirconocene or benzyne zirconocene and unsaturated species incorporating main group elements lead to a variety of new metallaheterocycles. Efficient new methodologies of regiospecific syntheses of mono-, bi-, or tricyclic systems incorporating phosphorus, nitrogen, selenium, antimony, germanium or tin are reported. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Benzynezirconocene; Heterocycles; Main group element; Nitrogen; Phosphorus; Zirconocene

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1. Introduction

The organometallic chemistry of zirconium compounds is blossoming, probably because of the new perspectives zirconium reagents bring in a number of areas of research. As an example, properties of cationic zirconium(IV) complexes in catalysis are well known and well documented, while the use of other zirconium species in organic chemistry is expanding. However, studies of interactions between main group elements and zirconium compounds were not so frequently reported. Therefore, this review will focus on such topics with emphasis on the behaviour of zirconocene [Cp_2Zr] towards phosphorus derivatives. The reactivity of benzynezirconocene [$Cp_2ZrC_6H_4$] and related species, mainly towards main group element compounds, will also be described, attention being paid to the results obtained by research groups from Dijon, Toulouse and Lodz during the last five years.

2. Zirconocene chemistry

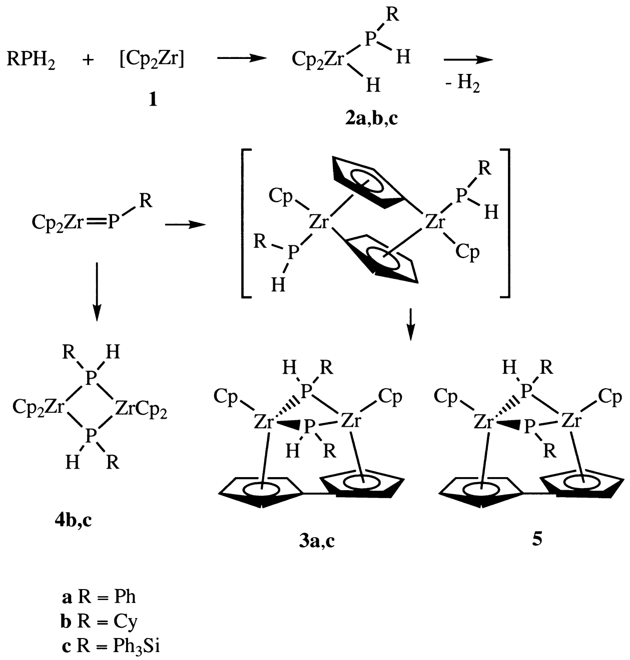
The most straightforward preparation of the [Cp_2Zr] synthon was developed by Negishi and coworkers [1,2] via the reaction of Cp_2ZrCl_2 with 2 equiv. *n*-BuLi at -78 °C in THF. β-hydrogen elimination from the dialkyl intermediate species affords the highly reactive Zr(II)-alkene intermediate which is generally an effective source of zirconocene. Other widely used methods for the [Cp_2Zr] metallocene synthon include, for example, reduction of Cp_2ZrCl_2 [3], thermal decomposition of $Cp_2Zr(CO)_2$ [4], ligand exchange reactions from butadiene [5], PMe_3 [6] and bis(trimethylsilyl)acetylene [7] zirconocene complexes.

Reaction of zirconocene with a series of phosphorus derivatives will be reported, showing the versatile behaviour of zirconocene which allows different types of reaction to take place: mono- and diinsertion into various carbon–carbon or phosphorus–carbon double or triple bonds, P–H and cyclopentadienyl C–H activations, exchange reactions with cleavage of zirconium–carbon bonds, monomer or dimer zirconocene–η^2 phosphabenzyne complex formation, etc. Several features of the reactivity of the unusual resulting complexes will also be presented.

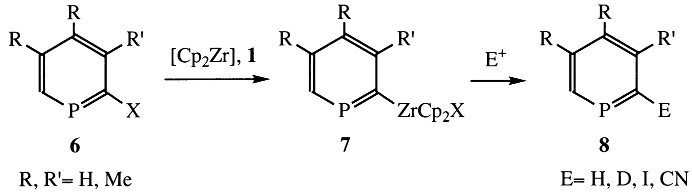
Oxidative addition of P–H bonds to zirconocene [Cp_2Zr] (**1**) has been performed. The resulting zirconocene-phosphide-hydrides are not stable and react further to give a variety of derivatives, the nature of which depends on the electronic and steric properties of the phosphide moiety. For example, generation of **1** in the presence of the primary phosphine $PhPH_2$ results in P–H activation, giving the intermediate $Cp_2Zr(PPhH)H$ **2a**. Cyclopentadienyl C–H activation and subsequent C–C bond formation yield the Zr(III) bridged-diphosphide fulvalenide complex $[CpZr(\mu\text{-}PPhH)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ **3a** (Scheme 1). In similar reaction with $CyPH_2$, the isolated product is **4b** while with Ph_3SiPH_2 three products are isolated: compounds **3c**, **4c** as major products and $[CpZr]_2(\mu\text{-}PHSiPh_3)(\mu\text{-}PSiPh_3)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ **5** as the minor one [8–10].

Insertion of zirconocene **1** into the C–X bond of 2-halophosphinines (X = Cl, Br) **6** takes place between -80 and 20 °C in THF. Protonation, deuteration, halogenation and cyanation of the resulting complexes **7** lead to the expected phosphinines **8** by cleavage of the Zr–C bond (Scheme 2) [11].

Proposed Mechanism for the Formation of Zr(III) Dimers

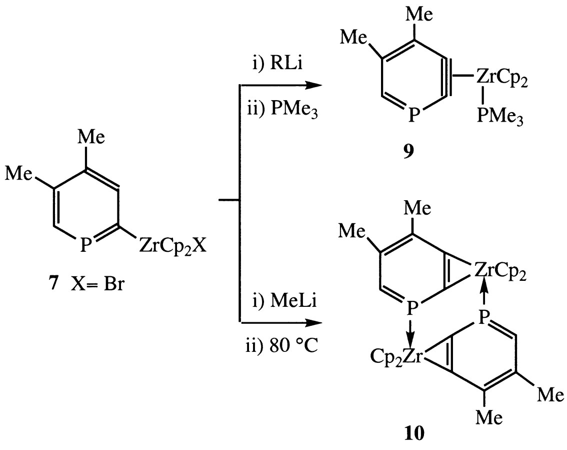


Scheme 1.



Scheme 2.

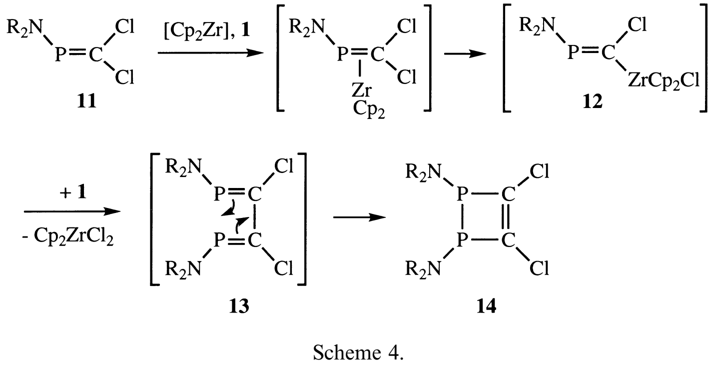
Under the same experimental conditions, **1** does not insert into the C–Br bonds of bromobenzene and 2-bromopyridine, suggesting that the reaction of **1** with phosphinines **6** proceeds first via complexation of the phosphorus lone pair of **6** followed by an intramolecular insertion of the unit into the C–X bonds. Treatment of a THF solution of **7** (X = Br) with MeLi or PhLi at 80 °C followed by warming the resulting solution to 20 °C then addition of PMe_3 leads to the synthesis of an η^2-phosphabenzyne–zirconocene **9** stable enough for in situ characterization by NMR spectroscopy [12] (Scheme 3). In contrast, thermolysis of **7** (X = Me) (80 °C, benzene or THF, 2 h) affords the poorly soluble dimeric species **10** via extrusion of



Scheme 3.

methane. The structure of **10** has been determined by X-ray analysis. Other analogous dimers are prepared and also appear to be thermally stable with strong P–Zr bonds [13].

1 is used as reductive coupling reagent of C-dihalogenated phosphaalkenes $R_2N–P{=}CCl_2$ [R_2N = tetramethylpiperidine (TMP), $(Me_3Si)_2N$] **11** in the straightforward synthesis of the first 3,4-dihalo-1,2-dihydro-1,2-diphosphetes **14** (Scheme 4) [14]. A single crystal X-ray determination of $(TMP\text{-}PCCl)_2$ **14a** reveals an unprecedented stretched phosphorus–phosphorus bond [2.320(4) Å] due to a negative hyperconjugation between the nitrogen lone pairs of the amino groups and the antibonding σ^*PP orbital. The reaction is postulated to proceed by way of an oxidative addition of the metal fragment across a C–Cl bond to give a (phosphaalkenyl)zircona species **12** which reacts further on a second equivalent of **1** to give, after elimination of Cp_2ZrCl_2, the 1,4-diphosphabutadiene **13** which rearranges via cyclization to the more thermodynamically stable diphosphete **14**. Ab initio calculations are consistent



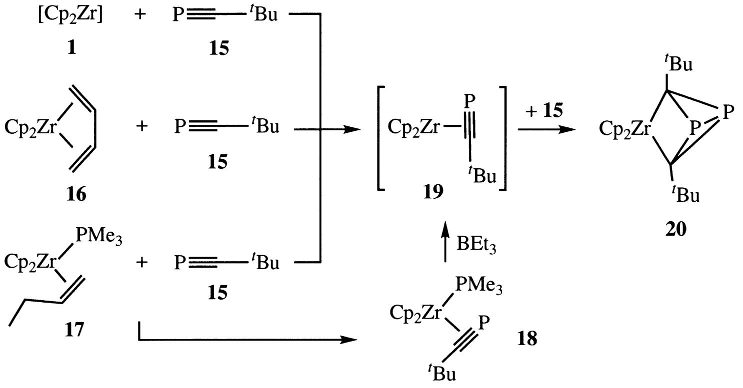
Scheme 4.

with a strong interaction of π-HOMO of **1** and $2a_1$ orbital of the metallocene fragment as the first step in the formation of **14**. Identical reactions can be performed with [$Cp_2Ti(CO)_2$] as the metallocene [Cp_2Ti] source. All these experiments are in marked contrast with previous reactions involving C-dihalogenated phosphaalkenes and leading to phosphaalkynes [15], C-substituted phosphaalkenes (see for example Ref. [16]) or azaphosphiridines [17].

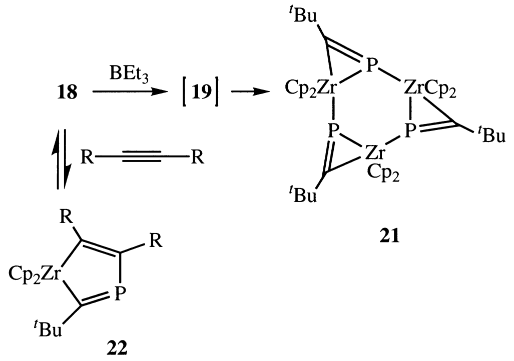
Treatment of [Cp_2ZrCl_2] with n-butyllithium at −78 °C and with the phosphaalkyne P≡C-^{t}Bu **15** at −78 °C to 20 °C or reaction of [Cp_2ZrCl_2] with **15** in the presence of magnesium gave rise to the 1,3-diphosphabicyclo-[1.1.0]-butane-diyl-zirconium complex **20** in about 70% yield [18]. **20** can also be prepared from butadiene or butene zirconocene complexes **16** and **17** [19], thus indicating that a coordinatively unsaturated zirconocene species **19** is an intermediate in all the different syntheses of **20** (Scheme 5). The trimethyl phosphine can be removed from the side-on coordinated phosphaalkyne complex by triethylborane as a Lewis acid. The trigonal metal complex **19** can be trapped with **15** to give **20** (see above). In the absence of **15**, **19** trimerizes to the crystalline compound **21** (Scheme 6) [20]. In the presence of alkynes, **18** reacts with displacement of the trimethylphosphine ligand. This reaction takes place at 0 °C with acetylene itself, whereas warming to 60 °C is necessary with 2-butyne to go to completion. Thermally unstable phosphazirconacyclopentadiene **22** species are thus formed (Scheme 6).

The complex **18** can also react with alkenes: the reaction proceeds via elimination of PMe_3 and coupling of the two unsaturated fragments to give the new complexes **23** and **24** (Scheme 7).

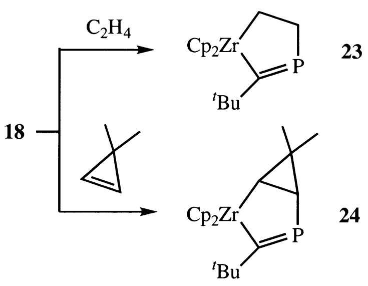
Complex **20** appears to be a reagent of choice for the preparation of a variety of phosphorus heterocycles. Some of the reactions reported from **20** are shown in Scheme 8 (see for example Refs. [20,21]). Emphasis has to be made on the high-yield synthesis of tetraphosphacubanes **25** from **20** and therefore from the phosphaalkyne **15** with an overall yield of 50% [22]. Preparation of tetraphosphatricyclo



Scheme 5.



Scheme 6.



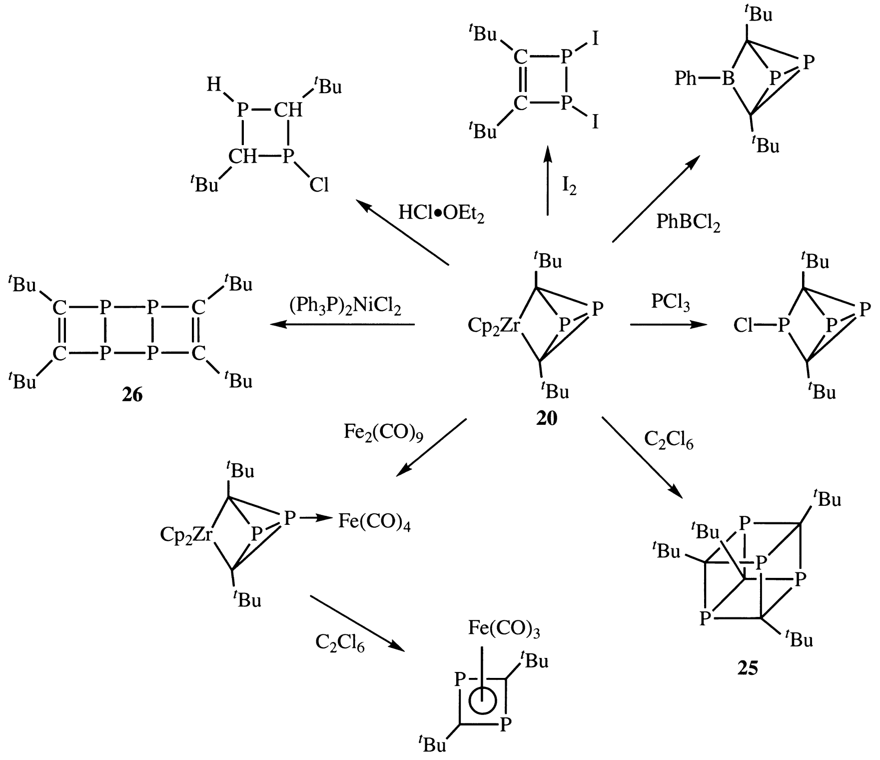
Scheme 7.

[4.2.0.0.2.5] octadienes **26** has also to be outlined as an outstanding piece of work [23].

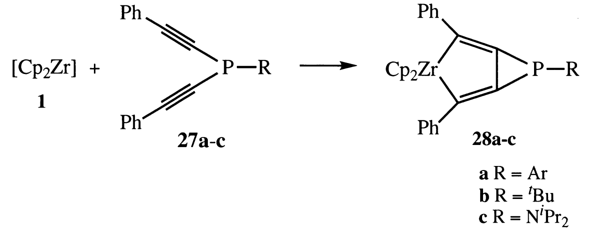
Several recent papers report oxidative alkyne coupling reactions induced by **1**. A number of metallacycles have been prepared using this method (for an overview concerning the reaction of zirconocene with bis(alkynyl) derivatives, see for example Refs. [24–29]). Analogous experiments performed with unsaturated phosphorus species often lead to different reactions and unexpected derivatives.

Treatment of diacetylenic phosphines **27** with **1** in THF at −78 °C affords the zirconacyclopentadiene phosphiranes **28** isolated as powders in 90% average yield (Scheme 9) [30]. The strongly shielded ^{31}P chemical shifts of **28**, from −244.2 to −300.5 ppm, are characteristic for phosphirane type structures.

Addition of $HCl \cdot OEt_2$ to the phosphirane **28b** in THF at −78 °C leads to a mixture of four compounds: the alkenyl–alkynyl phosphanes *E*/*Z*-**29** (35%) in a 1/1 ratio, the phospharadialene **30** (35%) and the secondary phosphane **31** (30%) (Scheme 10). The molecular structure of the sulphide adduct of *E*/*Z*-**29** and of the radialene **30** was established by X-ray crystallography studies. Formation of *E*/*Z*-**29**, **30**, and **31** can easily be explained via the transient generation of the complex **32** resulting from the cleavage of a zirconium–carbon bond and subsequent protona-

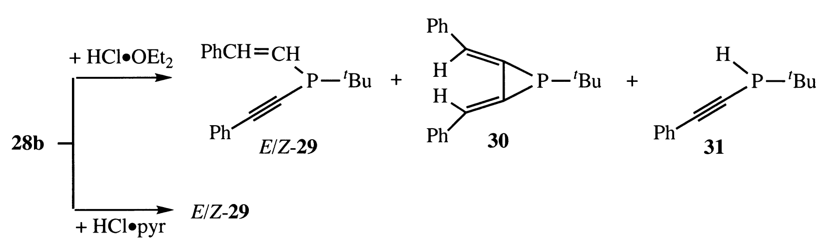


Scheme 8.

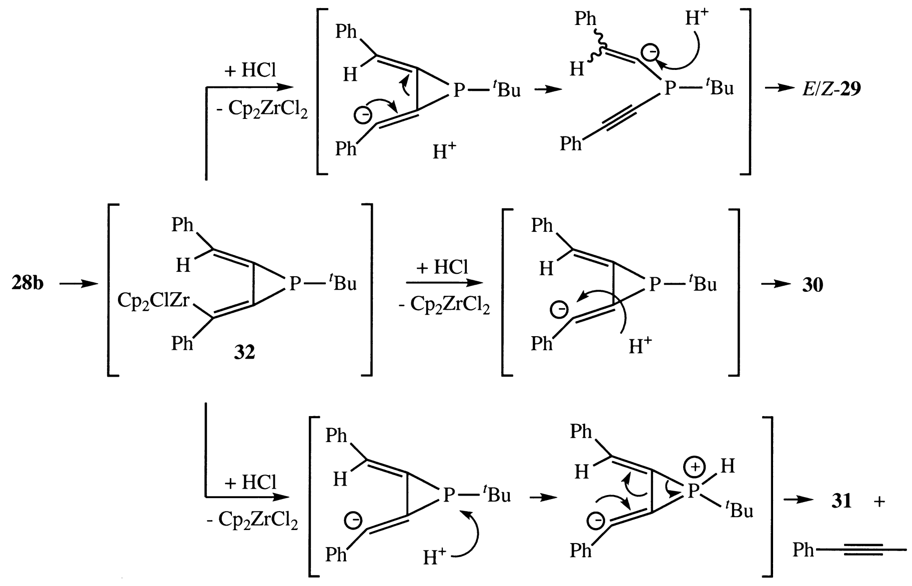


Scheme 9.

tion (Scheme 11). **32** can further react with a second equivalent of HCl to give *E*/*Z*-**29** via phosphirane ring-opening and **30** via substitution of the remaining zirconium fragment. Protonation on the phosphorus atom of **32** followed by concomitant cleavage of the zirconium–carbon bond then ring-opening and phosphorus–carbon bond cleavage can be evoked to explain the formation of the secondary phosphane **31**.

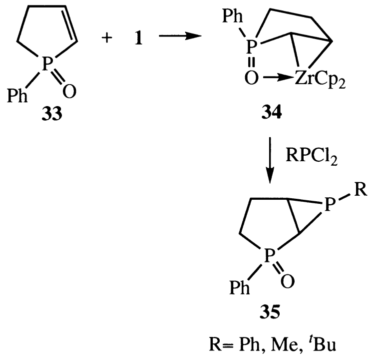


Scheme 10.



Scheme 11.

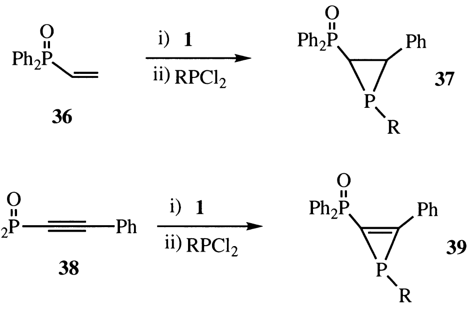
Reaction between a π-component and **1** usually forms the required η^2–π complex. This is observed when the phospholene **33** reacts with **1**: a stable complex **34** is formed. The ^{31}P chemical shift detected for **34** strongly suggests that a dative bond between the phosphoryl group and the zirconium fragment takes place [31]. Exchange reactions involving **34** and various dichlorophosphines occur readily, leading to new bicyclic diphosphines **35** incorporating fused three- and five-membered rings (Scheme 12) [31]. While the role of the phosphorus lone pair of phosphines was many times exemplified in a number of reactions involving zirconium derivatives such as $[Cp_2ZrHCl]_n$ [32], $[Cp_2ZrC_6H_4]$ or Cp_2ZrMe_2 [33], it is the first time that a dramatic effect of the phosphoryl group is illustrated in zirconium chemistry. Such an effect is also found in the reaction of vinyl **36** or acetylenic **38** phosphine oxides with **1**, followed by addition of dichlorophosphines on the resulting mixture: new



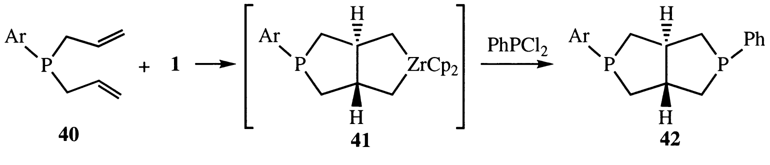
Scheme 12.

unstable C-phosphorylated phosphirenes **37** or **39** were thus obtained [31] (Scheme 13).

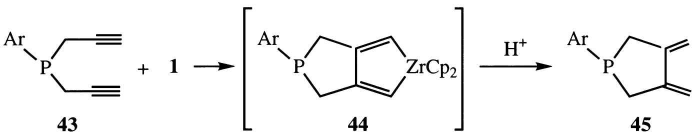
Reactions previously described by Nugent and Taber (see for example Ref. [34]) and Negishi and coworkers (see for example Ref. [35]) for generating metallocenes and forming heterocycles were extended to the synthesis of phosphorus-containing heterocyclopentanes. Indeed, treatment of a bis-allylphosphine **40** with **1** leads to the fused ring **41** which reacts with dichlorophenylphosphine to give **42** (Scheme 14) [36]. Similarly, addition of **1** to the bis-propargylphosphine **43** affords the bicyclic compound **44**. Protonolysis of **44** gives the dienic system **45** (Scheme 15) [36].



Scheme 13.



Scheme 14.



43 **44** **45**

Scheme 15.

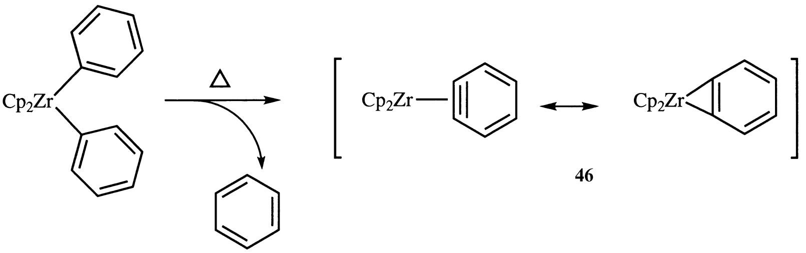
3. Benzynezirconocene chemistry

Photolysis of dialkyl or diarylzirconocenes yields alkane or diaryl compounds respectively, together with a transient zirconocene intermediate which can be trapped with several types of electron-donating ligands including dienes, phosphines and carbon monoxide [37,38].

Thermolysis of diarylzirconocenes is also a good way to generate reactive species like arynezirconocene complexes (Scheme 16). First postulated by Vol'pin and coworkers [39] and Erker [40], benzynezirconocene **46** was well characterized by Buchwald et al. [41] by X-ray crystal structure analysis of its trimethylphosphine complexed adduct.

3.1. Reactions with chalcogens

We have first demonstrated that heating a mixture of selenium powder and diaryl (di-tert-butyl)zirconocene in boiling heptane leads to a diselenophenylenezirconocene **47** in high yield (Scheme 17) [42,43]. In boiling octane starting from $(^tBuCp)_2Zr(p\text{-}MeC_6H_4)_2$, a mixture of *ortho*- and *meta*-substituted complexes is



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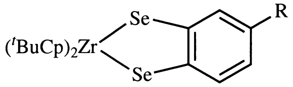
Scheme 16.



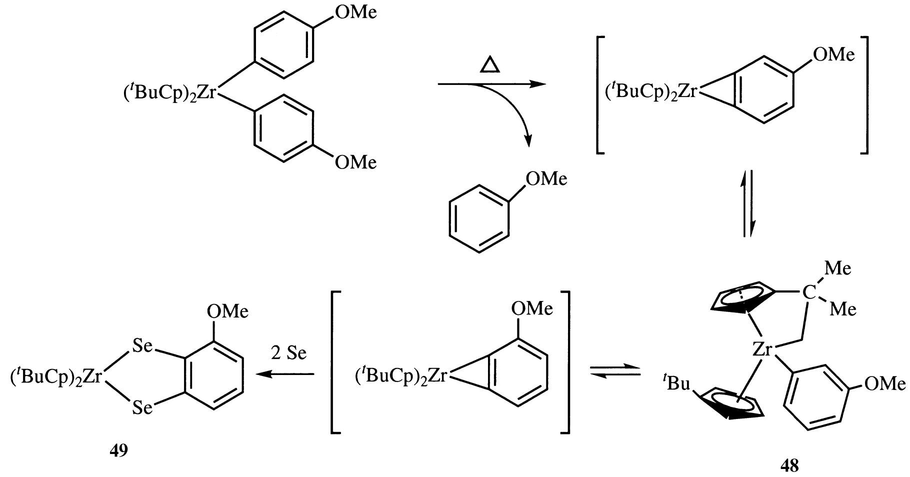
R = H, Me, OMe, Br, NMe_2

47

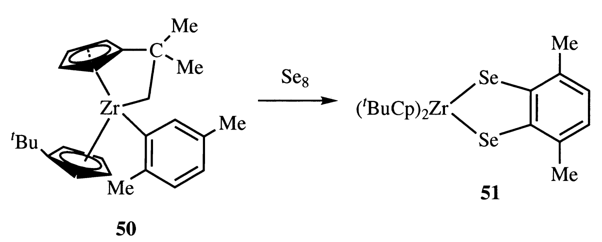
Scheme 17.

obtained. With $(^{t}BuCp)_2Zr(p\text{-}OMeC_6H_4)_2$, the reaction is selective and leads to **49**. The mechanism involves a cyclometalated intermediate **48** via C–H bond activation of a methyl substituent of a tert-butyl group (Scheme 18). If the reaction is done at 100 °C, the equilibrium can be shifted to favour the formation of the *ortho*-substituted benzynezirconocene. The subsequent insertion of selenium affords selectively an *ortho*-substituted compound. As it was not possible to isolate suitable crystals of **48**, a more sterically hindered complex **50** was synthesized and characterized by X-ray diffraction analysis. The cyclometalated product **50** represents a useful precursor for the synthesis of *ortho*-disubstituted diseleno complexes **51** for which the corresponding diarylzirconocenes are not accessible for steric reasons (Scheme 19).

All these diseleno complexes are good synthons for preparing chalcogen-containing heterocyclic molecules. Some years ago, we demonstrated for the first time that diselenophenylenezirconocenes could exchange a zirconium atom with transfer of the organic part to electrophilic reagent [44]. More recently, this methodology has been extended by Fagan starting from zirconacarbocycles [45,46]. Synthesis of



Scheme 18.

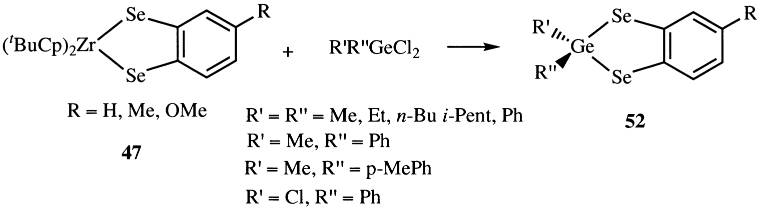


Scheme 19.

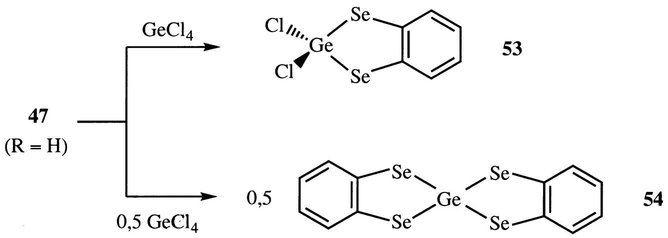
benzodiselenagermoles **52** is carried out from diselenophenylenezirconocenes **47** and different dichloro- or aryltrichlorogermanes (Scheme 20) [47].

Reactions between germanium tetrachloride and diselenophenylenezirconocenes **47** have been especially investigated, and two types of germanium-containing compounds are obtained depending on the stoichiometry used. Dropwise addition of a solution of **47** to an equimolecular solution of $GeCl_4$ leads to the expected dichlorodiselenogermane **53**. In another experiment, addition of 0.5 equiv. $GeCl_4$ on **47** gave the spirobisbenzodiselenagermole **54** in good yield (Scheme 21). ^{77}Se NMR of the whole family demonstrates the very high dependence of the chemical shifts on the nature of the substituents present either on the germanium atom or on the benzenic rings.

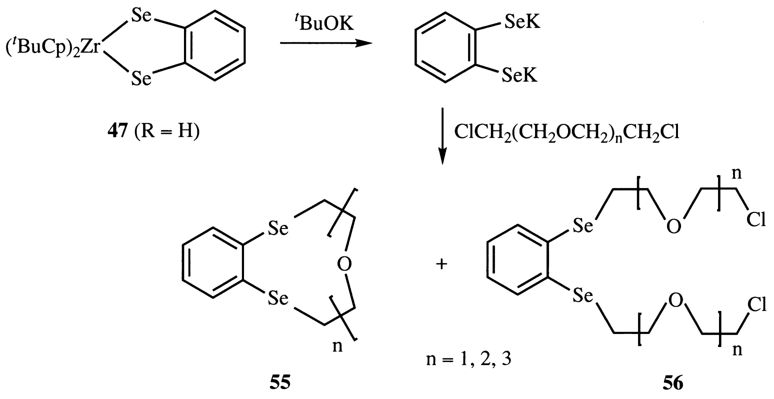
Diselena complex **47** (R = H) is also a good precursor for the preparation of diselena crown ethers **55** via dipotassium benzene-1,2-diselenolate intermediate (Scheme 22) [48]. Reaction of hydrogen chloride with **47** (R = H) is fast, leading quantitatively to the benzene-1,2-diselenol which on treatment with Cs_2CO_3 provides in high yield the caesium salt of the benzene-1,2-diselenolate anion **57**. Further reactions with open diseleno ethers **56** under mild conditions allow cyclization and formation of tetraselena crown ether **58** (Scheme 23). These di- or tetraselena crown ethers are able to complex heavy metals via their selenium atoms as soft sites. The great sensitivity of ^{77}Se chemical shifts to the Se environment was demonstrated in particular by complexation with Hg(II) salts (a large shielding effect of $\Delta\nu =$ 70–80 ppm is observed).



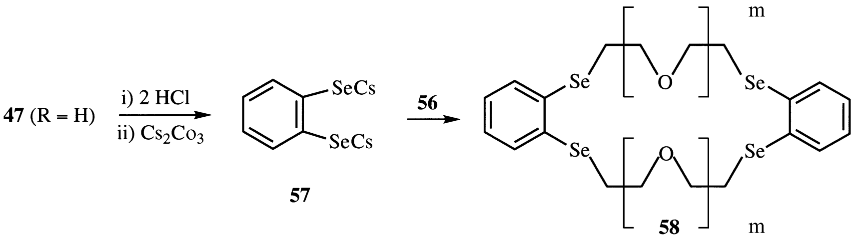
Scheme 20.



Scheme 21.



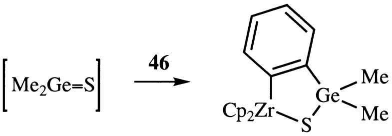
Scheme 22.



Scheme 23.

3.2. Reaction with inorganic fragments

To our knowledge, before our work, there was only one example of insertion of an inorganic fragment into the zirconium–carbon bond of benzynezirconocene. Recently, we described two new types of complex resulting from the reaction of germanium–, sulphur– and phosphorus–nitrogen double bonds with **46**. In boiling heptane, the reaction of $[Me_2GeS]_3$ with $Cp_2ZrMePh$ leads to the dimetallacycle **59** resulting from the insertion of the monomer germanethione $[Me_2Ge{=}S]$ into the zirconium carbon bond of the transient benzynezirconocene (Scheme 24) [49]. More

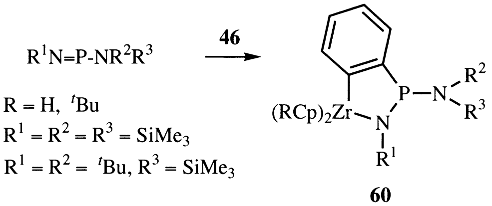


Scheme 24.

recently, the reaction was extended starting from alkynezirconocene and cyclopropenezirconocene [50].

Azaphosphazirconaindan systems **60** are easily synthesized in a regiospecific way, via a benzynezirconocene intermediate by means of thermolysis of $Cp_2ZrMePh$ or $(^tBuCp)_2ZrPh_2$ in the presence of phosphaimines (Scheme 25) [51].

The versatility of the benzynezirconocene reagent was also demonstrated by Buchwald and coworkers during reaction of the transient species with Group 13 (B, Al, Ga) alkoxides affording **61–63** (Scheme 26) [52]. These compounds contain a dative bond from an oxygen lone pair of the methoxy ligand on the zirconium to an acceptor p-orbital on the main group atom. In contrast, the weakly Lewis acidic boron centre in the naphtyl compound **64** does not show a bonding interaction between the alkoxyl ligand on the zirconocene fragment and the boron centre (Scheme 27).



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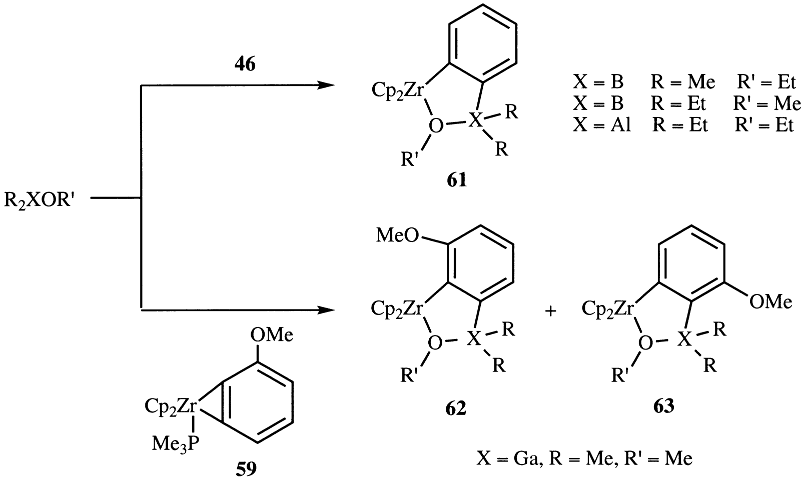
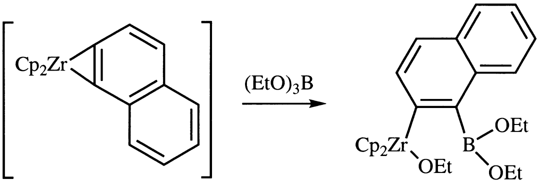
Scheme 25.



61 **59** **62** **63**

Scheme 26.



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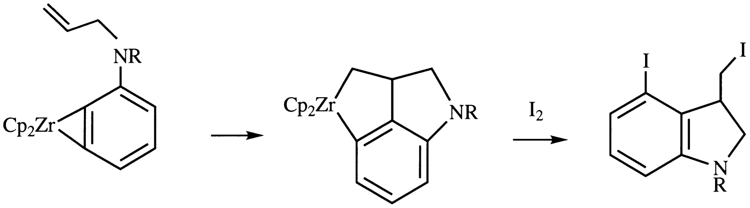
Scheme 27.

3.3. Insertion of alkenes

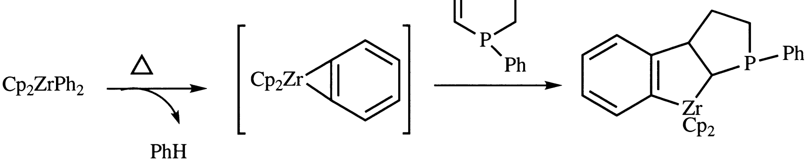
A new method for the regiospecific synthesis of polysubstituted indoles and indolines has been developed by Buchwald et al. The key steps involve the generation of zirconocene-stabilized benzyne complexes and subsequent intramolecular olefin insertion to provide tricyclic indoline zirconacycles **65** (Scheme 28) [53]. Diiodo indolines **66** can be converted to a wide variety of indole and indoline products such as analogues of tryptamine, serotonin or tryptophan.

Insertion reaction of 2,3-dihydrophosphole into the zirconium–carbon bond of in situ generated benzynezirconocene leads to the tricyclic system **67** in a regiospecific way (Scheme 29) [54]. The regiospecific synthesis of **67** could be regarded as the result of a strong interaction between the phosphorus lone pair and zirconium. A clean exchange reaction occurs by reacting **67** with various dichlorophosphines leading to original 1,1-diphosphines, which are isolated as their corresponding disul-



65 **66**

Scheme 28.



67

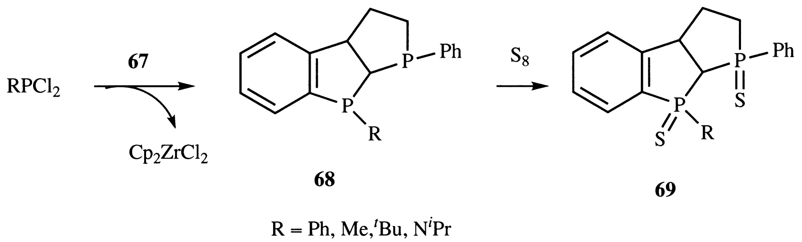
Scheme 29.

phide adducts (Scheme 30). An analogous exchange reaction performed with $PhSbCl_2$ or Me_2SnCl_2 gives stiba or tin phosphorus-containing tricyclic systems in high yield [55]. These compounds are the first examples of fused tricyclic systems incorporating phosphorus and antimony or phosphorus and tin in the cyclic skeleton. All these reactions proceeded with ring-retention.

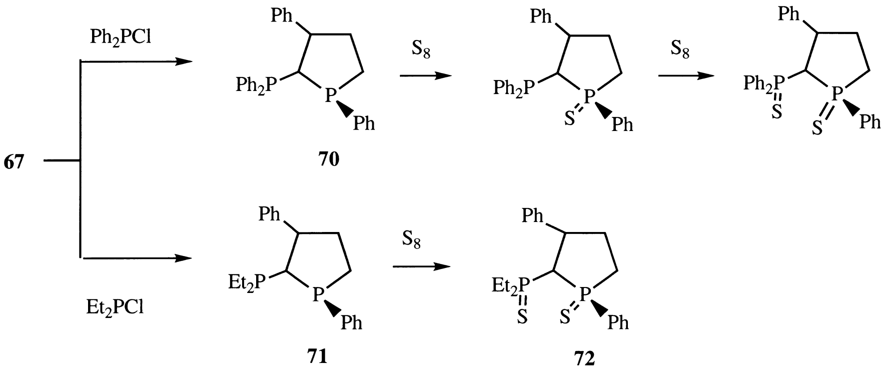
In contrast, an exchange reaction with concomitant ring-opening was observed when **67** was reacted with monochlorophosphane such as Ph_2PCl or Et_2PCl. The 1,1-diphosphane **70** is obtained as two isomers in a 4/1 ratio as shown by ^{31}P NMR spectroscopy. Monosulphurization occurs regioselectively on the intracyclic phosphorus atom. Further addition of sulphur leads to the formation of the corresponding disulphide. A similar ring-opening process is detected by reaction of **67** with Et_2PCl (Scheme 31).

3.4. Insertion of alkynes

It was clearly demonstrated that alkynes could insert into a zirconium–carbon bond of benzynezirconocene affording zirconaindenes. We synthesized various of them in a regioselective way and demonstrate that they are good precursors of



Scheme 30.



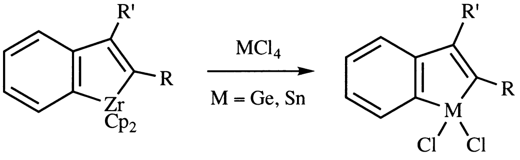
Scheme 31.

germa- or stannaindenes with metal–halogen bonds **73** (Scheme 32). The first X-ray crystal structure determination of a stannole derivative was performed. It was not possible to obtain silaindene derivative by the same direct exchange reaction [56,57].

Takahashi and coworkers demonstrated the remarkable effect of copper chloride on diiodination of zirconacyclopentadienes and obtained spirosila and germa indenes derivatives **74** (Scheme 33) [58].

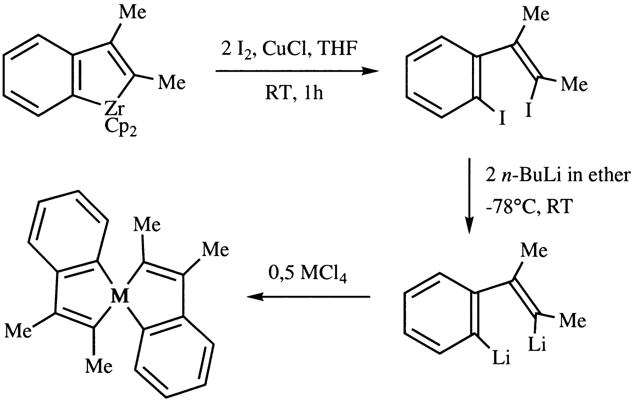
New bis-stiboles are generated by a zirconium antimony exchange reaction starting from zirconacycle **75** (Scheme 34) [59]. Synthesis of **75** was previously described by Buchwald as a double insertion process of alkyne into benzdiyne. Isomer **76a** can be crystallized from the mixture. Once purified, solutions of the isomers are stable with respect to interconversion at temperatures up to 150 °C, at which temperature the compounds begin to decompose.

Starting from diphenylzirconocene, an efficient regio synthesis of 2-phosphinozirconacyclopentadiene and its transformation into 2-phosphinophospholes and 2-phosphinostiboles was developed (Scheme 35) [60]. The regioisomer **77**, where the phosphino substituent is located on the α position of the five-membered zirconacycle, is probably the result of an initial interaction between phosphorus and



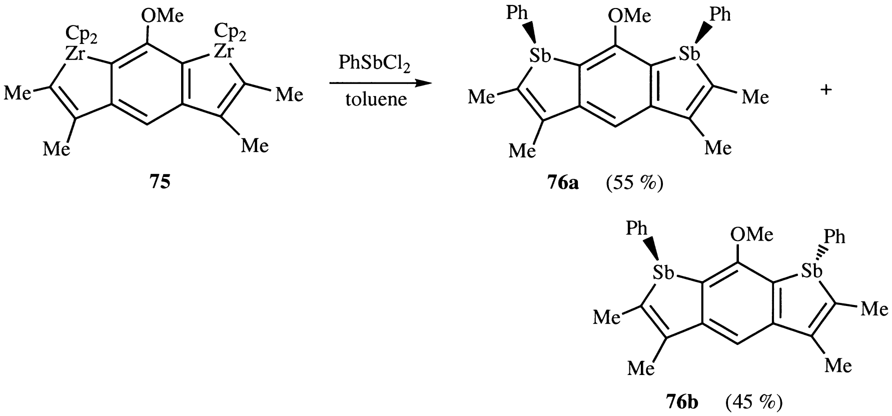
73

Scheme 32.



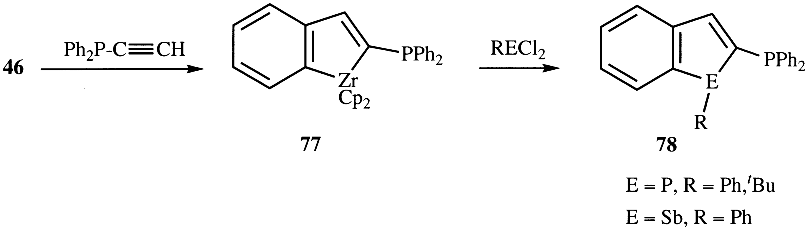
74 M = Si, Ge

Scheme 33.



75 **76a** (55 %) **76b** (45 %)

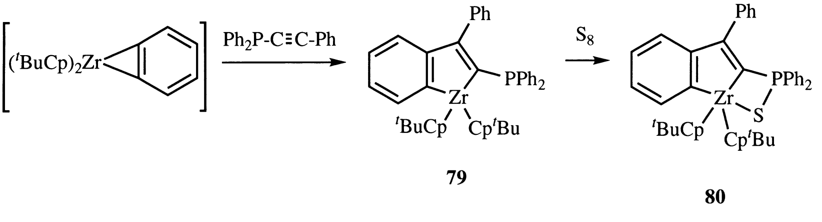
Scheme 34.



46 **77** **78**

Scheme 35.

zirconium. Remarkably, such a stereoselective synthesis occurred with the more hindered diphenyl (di-tert-butyl)zirconocene complex (Scheme 36). Successful X-ray diffraction analysis of **80** reveals an important interaction between zirconium and sulphur. The Zr–S distance [2.797(1) Å] is significantly shorter than the sum of the Zr and S van der Waals radii (Å). As a consequence, the P–S bond length is found slightly larger [2.005(1) Å] than those generally observed for thiophosphoryl groups



79 **80**

Scheme 36.

(1.93–1.95 Å). Indeed, the detected P–S bond length lies between those of a single and a double P–S bond.

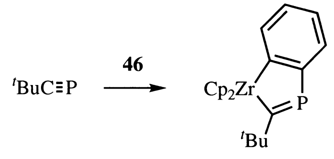
1,1-Bis-(η^5-cyclopentadienyl)-1-3-zircona-3-phosphaindene **81** is obtained in good yield and high regioselectivity by reacting benzynezirconocene and tert-butylphosphaalkyne (Scheme 37) [61].

η^2-Phosphabenzynezirconocene **9** insert alkynes or ketones selectively into the Zr–C bond in the α position relative to phosphorus. Complexes **82** and **85** appear to be useful starting materials to obtain functional phosphinines **84** or **87** (Scheme 38).

An unexpected intramolecular coupling reaction of a dialkynylphosphane and benzynezirconocene provides unusual 1,2-dihydrophosphete-zirconium complexes **88** (Scheme 39) [62]. The structure of **88** was established by X-ray crystallography. All the atoms of the three cycles lie in the same plane. The bond length between the sp^2 ring carbon and phosphorus atoms [1.844(8) Å] is as expected for a C–P single bond (1.85 Å). This is in marked contrast to the values for known dihydrophosphetes [1.902(5)–1.93(1) Å]. More insight on the mechanism of the formation of **88** is found when the cyclometalated complex **89** was reacted with dialkylnylphosphine at room temperature. The first step of the reaction is the insertion of one of the alkynyl groups into a Zr–C bond of benzynezirconocene to form **90**. Heating of **90** generates **91** in good yield (Scheme 40). Treatment of **88** with hydrogen conveniently provides phosphete **92**. The exchange reaction of **88** with PhSbCl$_2$ leads to the corresponding tricyclic compound **93** (Scheme 41).

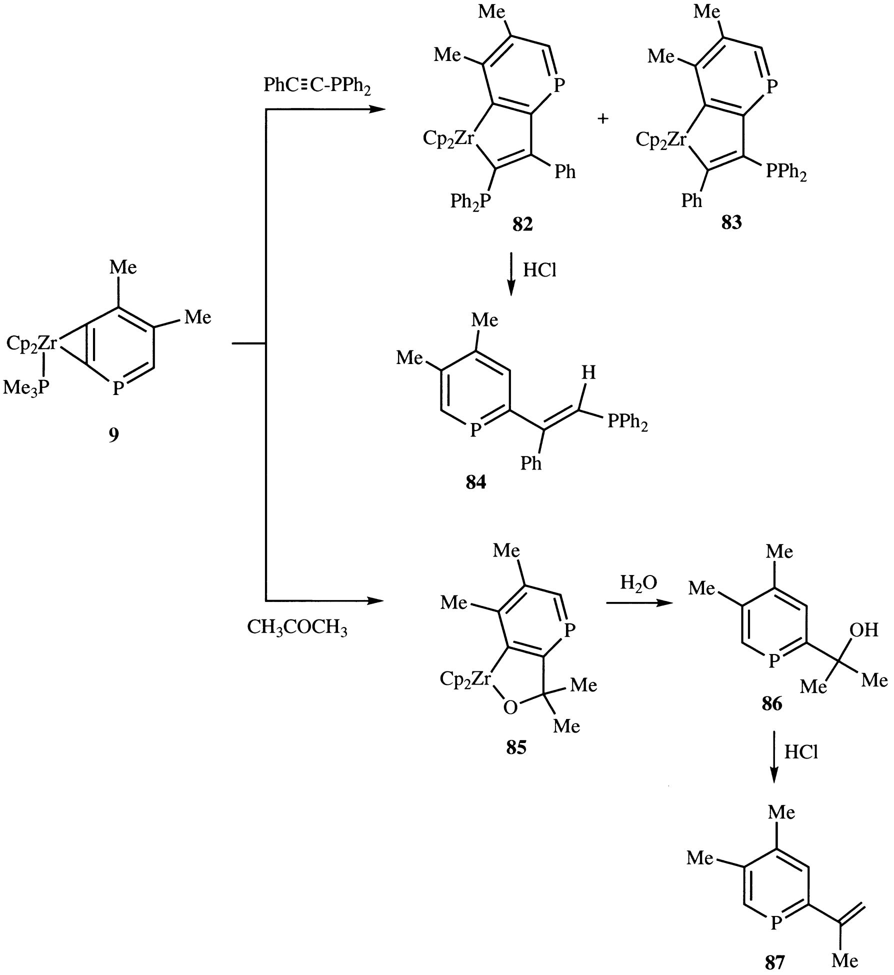
4. Conclusion

Interactions between unsaturated species incorporating main group elements and either zirconocene or benzynezirconocene lead to a variety of new metallaheterocycles, difficult or impossible to obtain via more classical ways. It has been found that the presence of a heteroatom donor (phosphorus, nitrogen, oxygen) dramatically changes the course of the reaction and definitely induces different reactions from those observed when the same zirconium reagents are reacted with pure organic compounds. Thus, efficient new methodologies of regiospecific syntheses of mono-, bi- or tricyclic systems incorporating phosphorus, nitrogen, selenium, antimony, germanium or tin are proposed and should be extended in the near future to

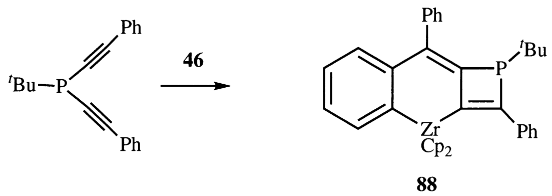


81

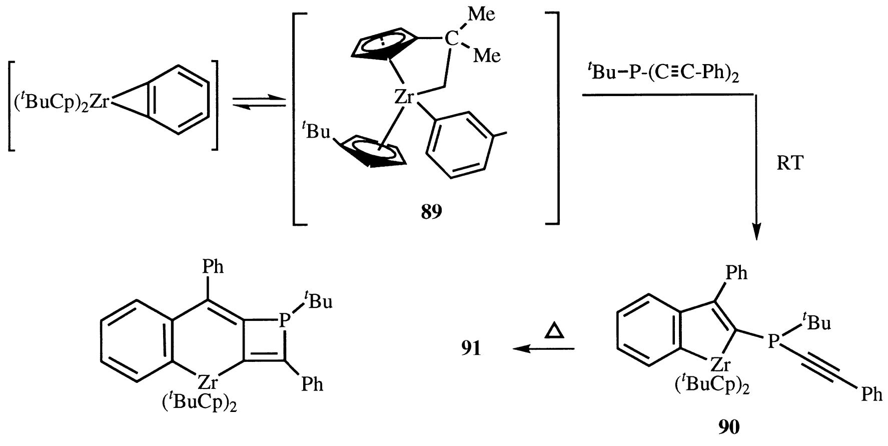
Scheme 37.



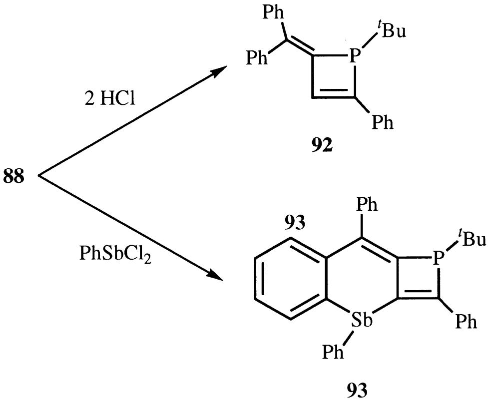
Scheme 38.



Scheme 39.



Scheme 40.



Scheme 41.

other main group elements. Preparation and chemical properties of new η^2-phosphabenzynezirconocene dimers also appear of particular interest for the development of a new chemistry based on phosphinines derivatives.

Acknowledgements

The authors thank all their coworkers whose names appear in the references.

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