Zirconium Species as Tools in Phosphorus Chemistry, 1

$[Cp_2ZrHCl]_n$, a Versatile Reagent

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Received March 28, 1996

Key Words: Hydrozirconation / Ring formation / Ring opening / Ring functionalization / Phosphanes, unsaturated

$[Cp_2ZrHCl]_n$ was found to be a useful reagent for a number of either ring formation or ring opening reactions involving unsaturated phosphorus compounds. Furthermore, treatment of a variety of phosphorus derivatives with $[Cp_2ZrHCl]_n$ allowed the preparation of several linear or cyclic mono-, di-, tri- or polyphosphanes as well as optically active diphosphanes.

The propensity of group-4 elements to form strong bonds with hard donor atoms such as chlorine, fluorine, oxygen or nitrogen is a well-known phenomenon, which has allowed the development of a rich chemistry based on interactions between organic reagents and group-4 metals. The success of organo zirconium reagents in synthesis can also be explained in terms of chemo-, regio-, diastereo-, and enantioselectivity; these compounds are generally able to discriminate between similar functionalities that differ only slightly in their steric and/or electronic environment[1].

Our more recent efforts have been directed to the chemistry of $Cp_2Zr(IV)$ and $Cp_2Zr(II)$ species. This review deals with the reactivity of one of these derivatives, $[Cp_2ZrHCl]_n$, towards unsaturated phosphorus compounds.

$[Cp_2ZrHCl]_n$, first discovered by Wailes and Weigold in 1970[2], was developed by Schwartz[3] then by others[1p] as a useful tool in organic chemistry. For example, hydrozirconation of alkenes and alkynes occurs easily with only a few exceptions. It can be compared to hydroboration (or hydroalumination) as a method of hydrometalation with re-

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0009–2940/96/0808–0879 $ 15.00+.25/0

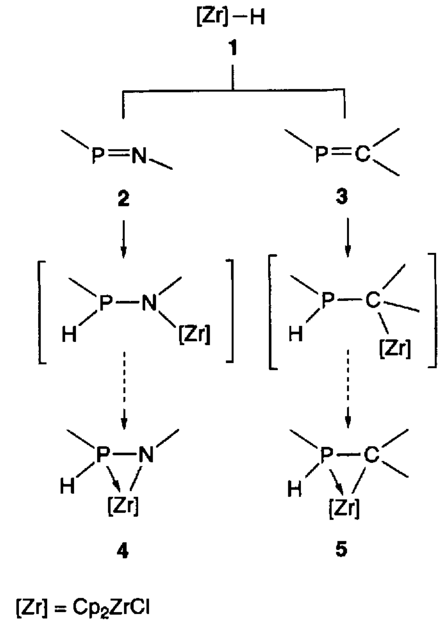
spect to scope and chemoselectivity. However, in the case of the resulting zirconated species, migration of the metal group along the carbon chain is facile; whereas the migration of boron to the terminal position is seldom a clean transformation.

As part of our broad-spectrum project on the interaction between $[Cp_2ZrHCl]_n$ **1** and main group element compounds, we developed new methodologies of ring formation or ring opening as well as new methods of ring substitution and ring functionalization. Synthesis of optically active diphosphanes and of cationic or dicationic phosphorus-zirconium derivatives also resulted from interactions between **1** and various cyclic or acyclic phosphorus ligands.

Ring Formation

Our efforts were first directed to the reactivity of **1** towards unsaturated, low-coordinated, heavier main group element species such as phosphaimines **2** or phosphaalkenes **3**. We anticipated that hydrozirconation should take place to produce metallacyclic compounds. Indeed, addition of the hydride **1** to THF solutions of various phosphaimines afforded zirconaazaphosphiranes **4** in high yield[5], Scheme 1. A 1,2-addition of $[Cp_2ZrHCl]_n$ to the phosphorus-nitrogen double bond of compounds **2** followed by cyclization is a reasonable explanation for the formation of these derivatives; although an insertion of the phosphaimine into a Zr–H bond with transient formation of a metallaiminophosphorane $RP(H)(ZrCp_2Cl){=}N{-}R'$ cannot be totally ruled out[4].

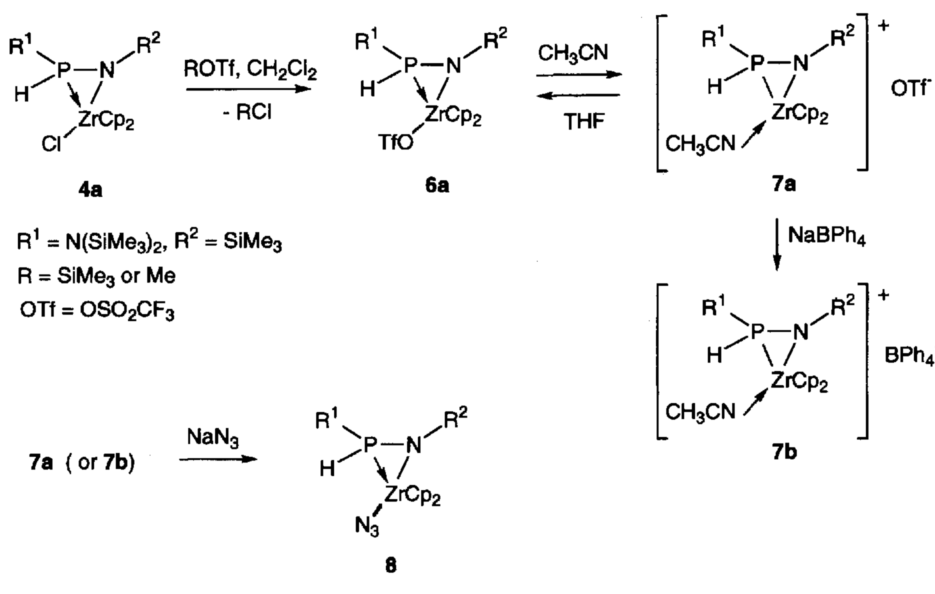
Scheme 1



Ring opening reactions involving **4** and $Fe_2(CO)_9$, S_8 or Se were observed as well as ring retention[6]. For example, addition of trifluoromethanesulfonate or trifluoromethyl methanesulfonate to **4a** in dichloromethane led to the corresponding zirconaazaphosphirane **6a** with a Zr–O covalent bond (Scheme 2). Dissociation of the Zr–O bond occurred when **6a** was solubilized in a more polar solvent, leading to the ionic zirconium ring **7a**. An easy exchange of anion can be performed by reaction of **7a** with $NaBPh_4$ in acetonitrile with the formation of complex **7b**. Surprisingly, preparation of a cyclic zirconium azide **8** could be achieved only by starting from the cationic species **7a**,**b** and NaN_3; **4a** did not react with sodium azide.

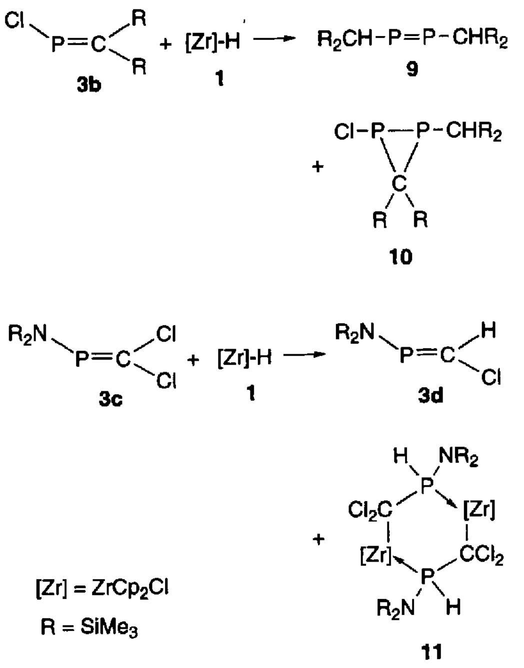
Hydrozirconation of phosphaalkenes **3** gave also metallacycles **5** (Scheme 1). As an example, addition of $[Cp_2ZrHCl]_n$ to a THF solution of the phosphaalkene $(Me_3Si)_2N{-}P{=}C(H)SiMe_3$ **3a** gave **5a** in high yield. The reaction strongly depends on the nature of the substituents at the phosphorus and carbon atom. Indeed, hydrozirconation of the *P*-halogenated phosphaalkene **3b** afforded

Scheme 2



the diphosphene **9** as the major product of the reaction as well as the diphosphirane **10** while hydrozirconation of *C*-halogenated phosphaalkene **3c** furnished the phosphaalkene **3d** and the six-membered ring compound **11**[7] (Scheme 3).

Scheme 3

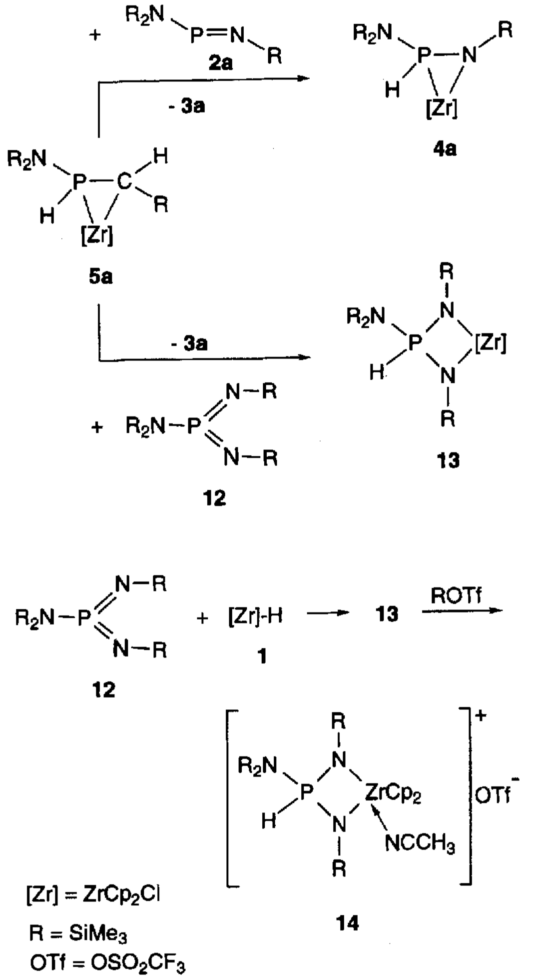


An interesting ligand exchange reaction occurred when a stoichiometric amount of phosphaimine $(Me_3Si)_2$-N$-$P=NSiMe$_3$ **2a** or bis(imino)phosphorane **12** was added to a THF solution of the zirconaphosphirane **5a** at room temperature, which produced the zirconaazaphosphirane **4a** or the four-membered ring compound **13**; in each case **3a** was recovered[7]. The metallacycle **13** can be directly obtained by reaction of the bis(imino)phosphorane **12** with $[Cp_2ZrHCl]_n$ in solution at −20 °C. Treatment of **13** with Me$_3$SiOTf in acetonitrile allowed the preparation of the corresponding cyclic zirconated cation **14** (Scheme 4).

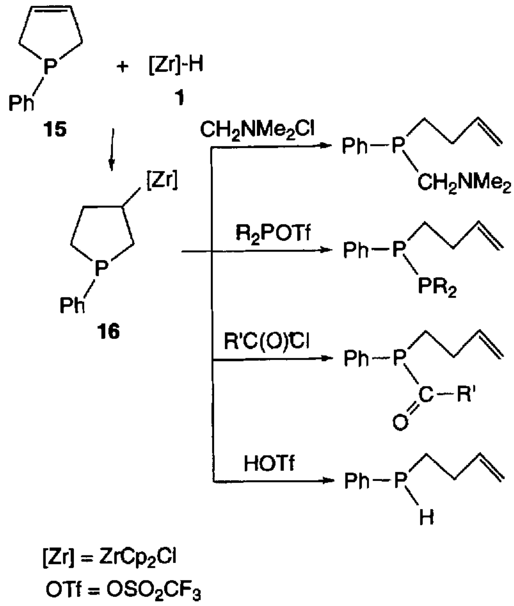
Ring Opening

We initiated our studies in this field by examining the hydrozirconation of the dihydrophosphole **15** by using **1**. Hydrozirconation took place as expected with the formation of the β-zirconated phospholane **16**, which can be treated with a variety of electrophiles EX to give, through elimination of Cp$_2$ZrClX (X = Cl, OSO$_2$CF$_3$), unsymmetrical functionalized acyclic phosphorus derivatives[8] (Scheme 5). No substitution reaction that would have resulted in the formation of β-substituted phospholane was detected. The ring opening is caused by the concomitant attack of the electrophile on the phosphorus atom of the ring and nucleophilic attack of the anion X$^-$ on the Zr center.

Scheme 4

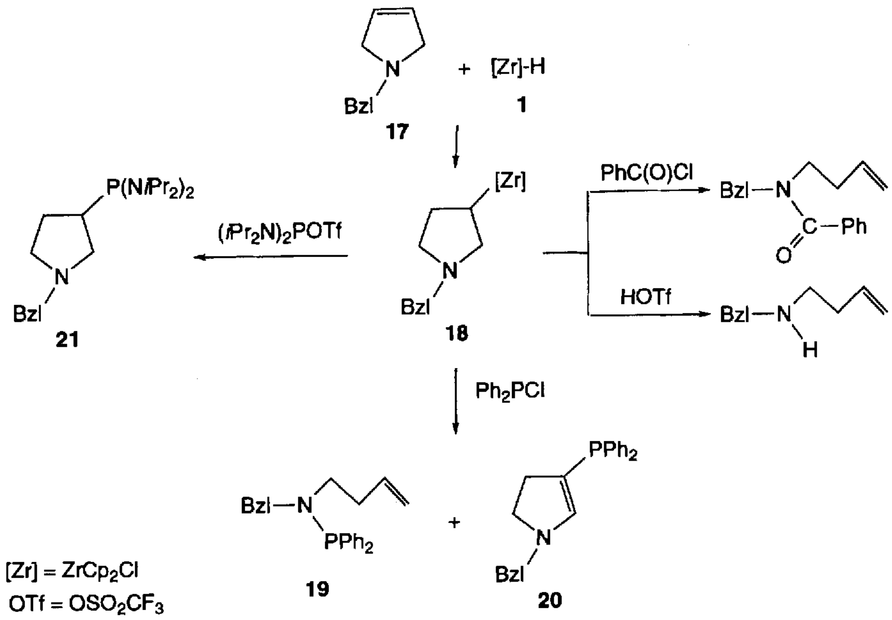


Scheme 5



Such reactions can be extended to the ring cleavage of nitrogen-containing heterocycles such as 1-benzyl-3-pyrroline **17**[9], but these reactions were not so selective. Hydrozirconation of **17** gave the expected β-zirconated five-membered nitrogen heterocycle **18**, which was stable. Ring opening was observed when **18** was treated with triflic acid or benzoyl chloride. Addition of diphenylchlorophosphane to **18** resulted in the formation of the aminophosphane **19** and the ring system **20** (Scheme 6). The formation of **19** can be explained by the same mechanism proposed for the ring opening of phospholane **16**; however, the formation of **20** may involve β-hydride elimination to give 1-benzyl-2-pyrroline followed by electrophilic addition of diphenylchlorophosphane to the enamine and loss of H^+. In marked contrast to the behavior of the β-zirconated phospholane **16**, the β-zirconated nitrogen heterocycle **18** reacted with the electrophile phosphenium salt $(iPr_2N)_2P^+CF_3SO_3^-$ to give compound **21**, which is formed from a direct exchange reaction between $(iPr_2N)_2P^+$ and the $ZrCp_2Cl$ fragment: no ring opening was detected in this case[9] (Scheme 6).

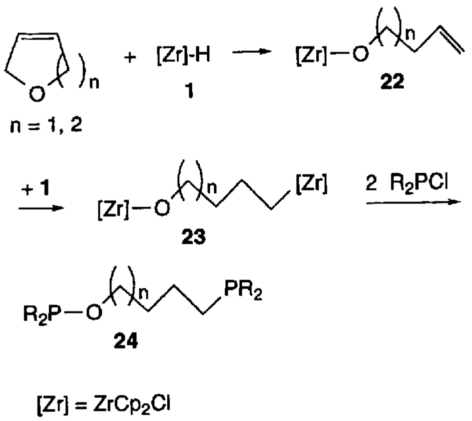
Scheme 6



All these discrepancies between phosphorus and nitrogen heterocycles might be due to the difference in nucleophilicity between phosphorus and nitrogen; reactions are slower with pyrroline derivatives than with phospholane, and this allows competitive reactions to take place.

Ring opening reactions of oxygen heterocycles such as 2,5-dihydrofuran, 2,3-dihydrofuran, 2-methyl-4,5-dihydrofuran and 3,4-dihydro-2*H*-pyran are initiated by the Schwartz reagent and not by addition of electrophiles[9] (Scheme 7). Due to the oxophilicity of zirconium, migration of the Cp_2ZrCl fragment occurred rapidly affording, for example, the linear derivative **22** or **23** if two equivalents of $[Cp_2ZrHCl]_n$ per equivalent of oxygen heterocycle were used. Addition of chlorophosphane led to various phosphinites or phosphanylphosphanes **24**.

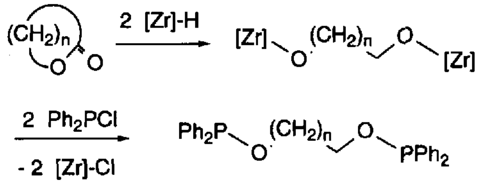
Scheme 7

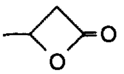
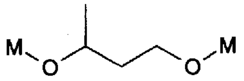
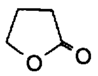
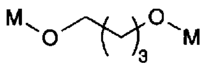
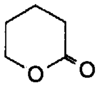
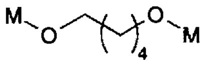
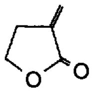
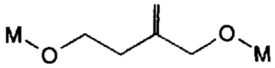


In marked contrast to phosphorus, nitrogen and oxygen heterocycles, no ring opening of sila- or boracyclopentene took place under the same experimental conditions. Indeed, a ring opening process occurred only with four-, five-, six- or seven-membered rings possessing an intracyclic donor heteroatom[9].

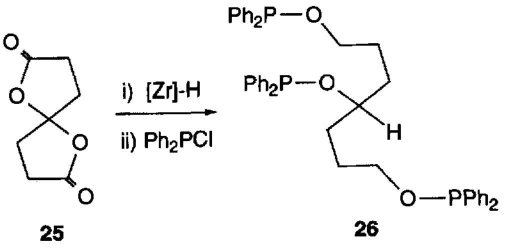
Such a useful ring opening methodology can be extended to various lactones and anhydrides allowing a one-pot synthesis of a number of di-, tri- or tetraphosphinites[10]. β-butyrolactone, γ-butyrolactone, δ-valerolactone or α-methylene-γ-butyrolactone reacted with $[Cp_2ZrHCl]_n$ to give the corresponding acyclic dizirconated species. Treatment of the latter compounds with, for example, diphenylchlorophosphane led to 1,5–1,7- or 1,8-diphosphinites (Table 1). Ring opening of bislactones such as 1,6 dioxaspiro[4,4]nonane-2,7-dione **25** also occurred readily and treatment of the resulting trizirconated species with diphenylchlorophosphane afforded a triphosphinite **26** (Scheme 8).

Table 1



Lactones	Products
	
	
	
	

Scheme 8

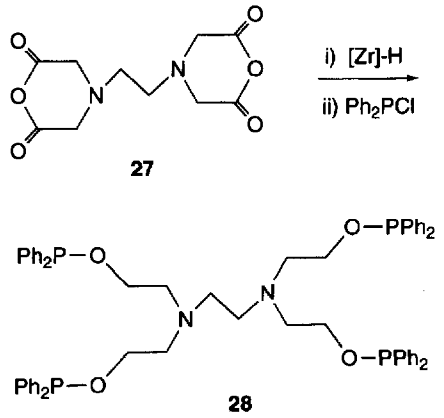


25 **26**

[Zr] = ZrCp$_2$Cl

Similarly, hydrozirconation of succinic anhydride or glutaric anhydride followed by addition of Ph$_2$PCl led to disphosphinites, while a linear hexadentate ligand **28** was obtained from ethylenediaminetetraacetic dianhydride[10] **27** (Scheme 9).

Scheme 9

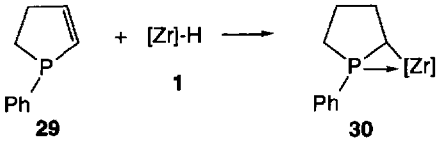


[Zr] = ZrCp$_2$Cl

Ring Retention

While hydrozirconation of the dihydrophosphole **15** led to the β-zirconated phospholane **16**, hydrozirconation of the dihydrophosphole **29** afforded a stable α-substituted phospholane **30** (one diastereoisomer)[11] (Scheme 10).

Scheme 10



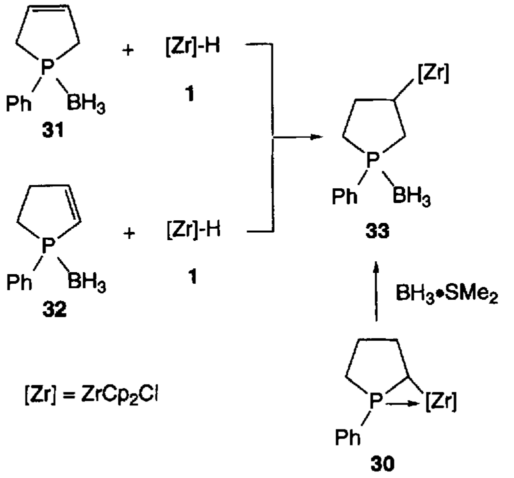
[Zr] = ZrCp$_2$Cl

Therefore, both α- and β-zirconated products can be prepared by direct hydrozirconation of dihydrophospholes in a completely regio- and diastereoselective fashion. The observed reversal of regioselectivity with **29** is most likely due to the coordination of zirconium to the phosphane site, which provides extra stabilization of the α-metalated phospholane. Such a phenomenon was corroborated by the hydrozirconation of the corresponding dihydrophosphole borane adducts **31** and **32**. In both cases exclusive formation of the β-zirconated phospholane **33** was detected (Scheme 11). Moreover, treatment of **30** with BH$_3$·SMe$_2$ at 0°C led to **33** by cleavage of the phosphorus-zirconium bond followed by complexation of the phosphorus lone pair with BH$_3$ and migration of the ZrCp$_2$Cl fragment to the less hindered position of the heterocycle[11].

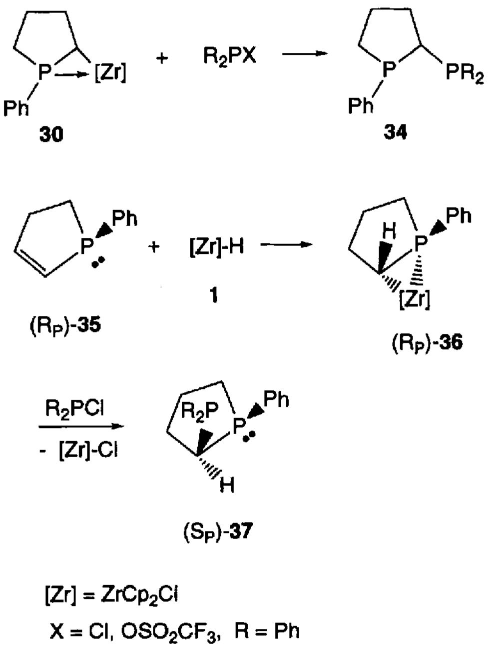
Subsequent treatment of **30** with chlorophosphanes or phosphenium salts led diastereoselectively to new 1,1-diphosphanes **34** by inversion of configuration at the α-substituted phospholane carbon atom (Scheme 12). No traces of compounds arising from ring opening were detected in these cases.

The synthesis of the optically active diphosphane **37** and the corresponding diphosphanyl disulfide **38** by hydrozir-

Scheme 11



Scheme 12

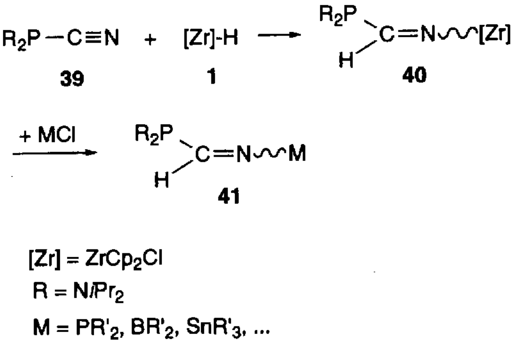


conation of the optically active dihydrophosphole **35** provided additional proof that inversion of configuration at the carbon atom took place during the exchange reaction between the α-zirconated phospholane **30** (or **36**) and chlorophosphanes or phosphenium salts[12] (Scheme 12).

Hydrozirconation of Unsaturated Acyclic Phosphanes

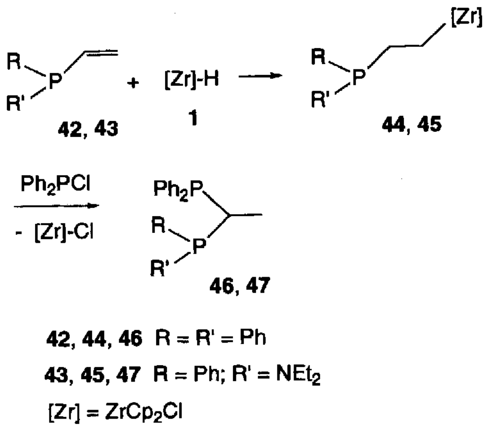
The *N*-zirconaimino species **40** was conveniently prepared in near quantitative yield by reaction of bis(diisopropylamino)cyanophosphane **39** with **1** in THF. Compound **40** is a useful starting compound for the synthesis of a large variety of *C*-phosphanyl-*N*-phosphanyl or *N*-boranylimines **41**[13a] (Scheme 13).

Scheme 13



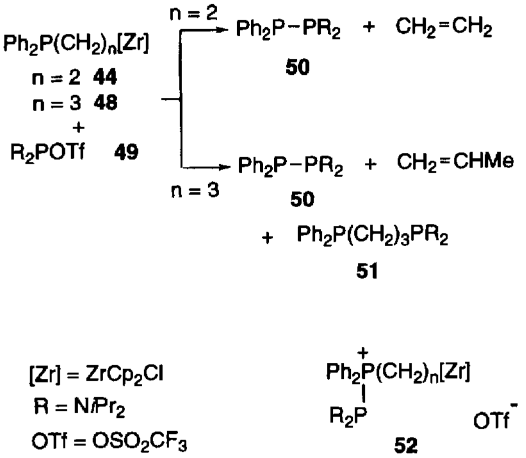
In all these examples, hydrozirconation took place at the more electronegative atom of the double bond, namely the nitrogen[13b,c]. To get an insight into the role of a donor heteroatom in a position α or β to the C=C bond, we performed hydrozirconations on vinyl and allyl phosphanes. Indeed, treatment of a THF solution of a phosphane, such as **42** or **43** with **1**, followed by addition of diphenylchlorophosphane afforded the 1,1-diphosphanylethane **46** or **47** and not the 1,2-diphosphanylethane $Ph_2P(CH_2)_2PPh_2$ or $Ph(Et_2N)P(CH_2)_2\ PPh_2$ (Scheme 14). On the basis of spectral evidence, the structure of the intermediate obtained by reaction of phosphanes **42** or **43** with **1** was found to be fully consistent with a β-zirconated species $Ph(R)P(CH_2)_2ZrCp_2Cl$ **44** or **45**[14]. During the exchange reaction with chlorophosphane, migration of the metal group along the carbon chain from the β to α position can be and is probably facilitated by coordination of the Cp_2ZrCl fragment to phosphorus as in the case of dihydrophosphole.

Scheme 14

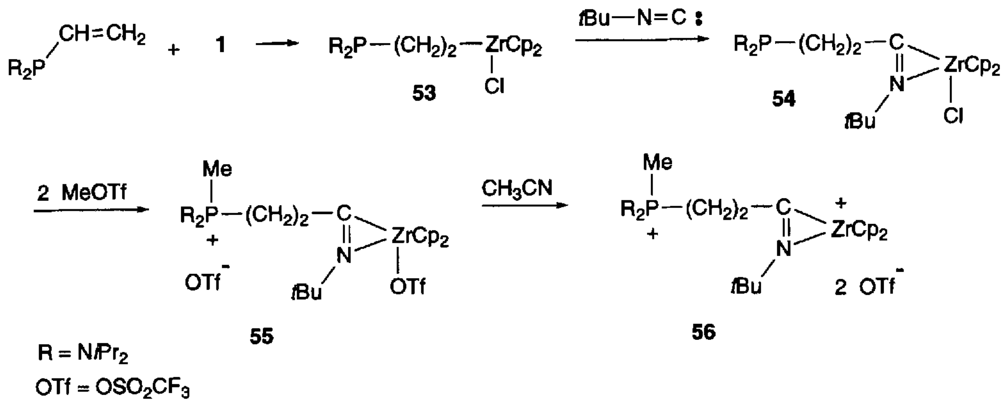


In marked contrast, the closely related hydrozirconation of $Ph_2PCH_2CH{=}CH_2$ gave $Ph_2P(CH_2)_3ZrCp_2Cl$ **48**; addition of Ph_2PCl afforded the expected terminal substi-

Scheme 15



Scheme 16



tution product $Ph_2P(CH_2)_3PPh_2$. β- and γ-zirconated phosphanes **44** and **48** reacted quite differently with the same phosphenium salt $(i\text{Pr}_2\text{N})_2\text{P}^+\text{CF}_3\text{SO}_3^-$ **49**. A transfer reaction easily took place when a THF solution of **48** was added to **49** in dichloromethane at 0 °C. The expected diphosphane **51** (75% yield) as well as the diphosphane $(i\text{Pr}_2\text{N})_2\text{P}-\text{PPh}_2$ **50** and propene were formed. Addition of **49** to **44** under the same conditions led exclusively to **50** and ethylene[15] (Scheme 15). The formation of **50** in these two reactions can be explained by the generation of the transient phosphanylphosphonium salt **52**, which rearranged to **50** with loss of propene or ethylene, respectively.

A series of phosphorus-zirconium salts which are stable either in the solid state or in solution were synthesized in high yield by starting from compound **54** obtained by insertion of an isocyanide such as *t*-BuNC into the zirconium-carbon bond of the β-zirconated phosphane **53**[16] (Scheme 16). Addition of 2 equiv. of trifluoromethyl methanesulfonate to a dichloromethane solution of **54** gave the phosphonium salt **55**. Here two different processes occurred: alkylation of the phosphorus and substitution on zirconium with the formation of a Zr–O bond. Evidence was found by conductimetric measurements of the generation of a dicationic species **56** on dissolution of **55** in acetonitrile[16].

Conclusion

This review points out the usefulness of $[Cp_2ZrHCl]_n$ **1** as a reagent in main group element chemistry and in particular in phosphorus chemistry. Most of the reactions involving **1** and unsaturated phosphorus compounds can be explained by the formation of a dative bond between the phosphorus lone pair and the sixteen-electron species $[Cp_2Zr(Cl)R]$. This bond underwent quite different reactions than those observed for organic reagents, allowing us to propose new methodologies for ring formation, ring opening or ring substitution, as well as new methods of preparation of phosphorus ligands.

The help of many dedicated coworkers and colleagues, whose names are cited in the references, is acknowledged.

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