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Zirconium species as tools in phosphorus chemistry: II $[Cp_2ZrMe_2]$, a useful reagent

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Abstract

The usefulness of dimethylzirconocene [Cp_2ZrMe_2], **1**, in phosphorus chemistry is illustrated with several examples. Reactions involving methane evolution allow the synthesis of small rings as well as macrocycles. Methyl group transfer from **1** can be performed with phosphenium salts, or can be realized on the surface of metalladendrimers. The carbozirconation reaction on chlorophosphaimine leads to the first P-metalated iminophosphorane which presents a versatile reactivity.

Keywords: Dimethylzirconocene; Phosphorus

1. Introduction

The synthetic chemistry of zirconium derivatives has grown in the last decade. Indeed these compounds play central roles in a number of technologically important processes including for example the Ziegler–Natta type polymerization of olefines. Moreover, the group IV metallocene derivatives have been the target of an extraordinary range of studies directed either to the generation and trapping or the isolation of a large number of significant species in organic and organometallic chemistry. A number of new methodologies in synthesis has been found giving easy access to useful starting materials for elaborated preparations or to sophisticated molecules [1–6]. Interestingly zirconocene derivatives are not so frequently used in main group element chemistry [7] and the studies based on the interactions between zirconium compounds and phosphorus derivatives are flourishing only a few years.

The Schwartz reagent [$Cp_2ZrHCl]_n$ was one of the first species studied in the area of phosphorus chemistry. It allowed the preparation, via hydrozirconation reaction of unsaturated compounds followed by exchange reactions, of numerous new linear or cyclic mono, di- or polyphosphines which appear to be excellent ligands. The formation of a dative bond between the phosphorus lone pair and the 16-electron species [$Cp_2Zr(Cl)R$] underwent quite different reactions than those observed for organic reagents. Indeed new methodologies for ring formation, ring opening or ring substitution were reported [8].

The behavior of the zirconocene like reagent [Cp_2Zr], or the benzene zirconocene [$Cp_2ZrC_6H_4$] and other group 4 metallocene derivatives towards unsaturated phosphorus compounds was also studied in depth in several recent papers [1–6].

On the other hand, a species like [Cp_2ZrMe_2] was not so frequently used, not only in phosphorus chemistry but more generally in organic chemistry, in spite of the possibilities offered by such a derivative. As an example it was found to insert carbon monoxide [9–11] diphenylketene, isocyanate, *p*-tolylcarbodiimide, the important factor determining the insertion being the polarization of the cumulene structure [12]. Evolution of methane when [Cp_2ZrMe_2] is treated with hydrogen-containing species is one of the other expected main reactions [13,14].

[Cp_2ZrMe_2] is easily obtained as a white crystalline product after sublimation in a 73–79% yield by reacting [Cp_2ZrCl_2] with methyllithium.

The survey covers the reactivity of the dimethylzirconocene [Cp_2ZrMe_2], **1**, towards various phosphorus compounds and illustrates how useful **1** can be for the synthesis of a variety of new species difficult or impossible to prepare by other methods.

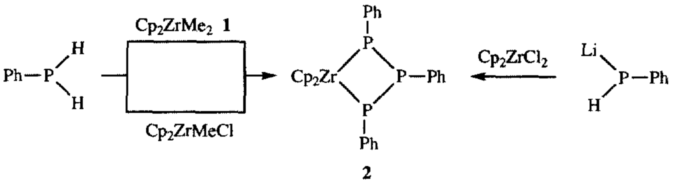
2. Reactions involving methane evolution

The propensity of dimethylzirconocene (**1**) to loose one or two methyl groups when reacted with alcohols, amines, thiols, acidic reactives, etc., is well known. Such a behavior can also be exemplified with a variety of phosphorus derivatives. Indeed the reaction of **1** with phenylphosphine ($PhPH_2$) affords the bis(η^5-cyclopentadienyl)(1,2,3-triphenyltriphosphane-1,3-diyl)zirconium(IV), **2** (Scheme 1) [15]. The same reaction can be performed with $Cp_2ZrMeCl$ instead of **1** or with Cp_2ZrCl_2 and the phosphide Ph_2PLi. Treatment of *o*-phenylenebis(phenylphosphane) **3** with an equimolecular amount of **1** affords the five-membered chelate complex **5**. The P, P′ dilithium salt of **3**, i.e. **4** gives rise also to the complex **5** when treated with Cp_2ZrCl_2 (Scheme 2) [16].

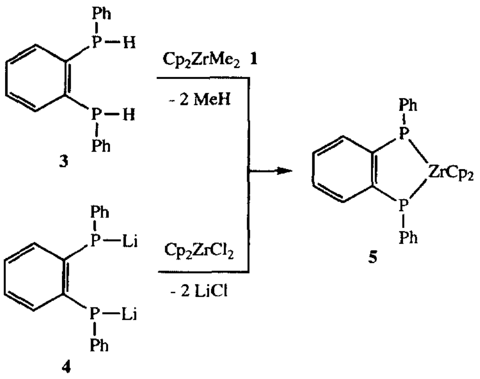
Therefore four and five-membered rings can be easily prepared from **1**. The stability and ability of phosphorus ligands to form complexes prompted us to investigate the possibility of preparing early transition metal bimetallic macrocyclic species possessing numerous electron donors in order to enhance the ability of zirconium (or titanium) macrocycles to bind other metals.

The synthesis of phosphorus zirconium- and phosphorus titanium-containing macrocycles arising from [2 + 2] cyclocondensation reactions was undertaken from *meta*- or *para*phosphodihydrazones **6**, **7** or **8**, **9**, respectively.

In a typical experiment addition of a THF solution of **1** (2 Equiv) to a THF solution of *meta*- or *para*phosphodihydrazones (2 Equiv) was accompanied by rapid evolution of methane with the formation of the [2 + 2] cycloadducts **10**, **11** or **12**, **13** (Scheme 3) [17]. ^{31}P-NMR spectra of the resulting mixture showed, as expected, no $\Delta\delta$ (^{31}P) between the chemical shifts of the starting derivatives and the final



Scheme 1.

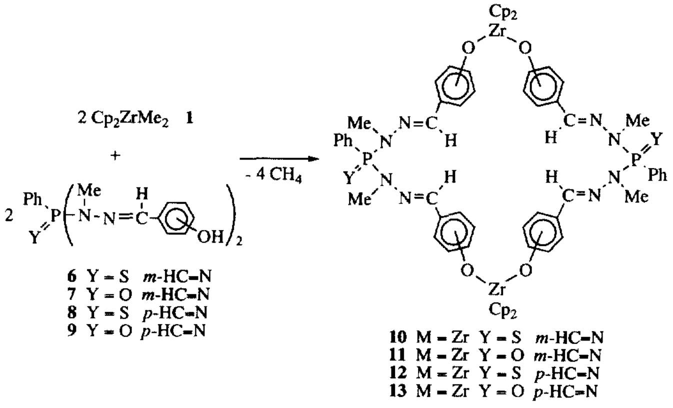


Scheme 2.

compounds but ^{1}H-NMR spectra exhibited a singlet resonance arising from the cyclopentadienyl protons while no signal corresponding to either the OH groups of the linear phosphorus ligands or the methyl groups of **1** was detected. ^{13}C-NMR corroborated such an assignment which was confirmed by FAB mass spectrometry: no peak due to [1 + 1], [3 + 3] or other types of cyclocondensations between **1** and the ligands **6–9** was observed.

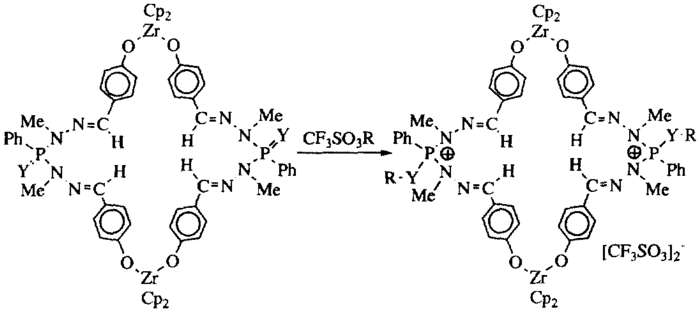
The position of the hydroxyl groups in species **6–9** is of the greatest importance since the reaction is significantly faster with **8,9** (OH in the *para* position) than with **6,7** (OH in the *meta* position). No reaction was observed with phosphodihydrazones **14**, **15** in which the OH groups are in the *ortho* position.

The 32 or 36-membered rings (**10–13**) represent the first examples of phosphorus containing early transition metal macrocycles. The same experiments can be conducted with Cp_2TiMe_2.



Scheme 3.

Macrocyclic salts were obtained by reacting some of these derivatives with either methyl- or trimethylsilyltrifluoromethanesulfonate reagents. Macrocyclic bis phosphonium salts (**16**, **17**) were formed, the ionic character of these species being proved by conductimetric measurements (Scheme 4). Alkylation selectively occurred on the sulfur atom of the thiophosphoryl groups, while silylation took place exclusively on the oxygen atom of the two phosphoryl groups.



12, 13

16 Y = S R = Me
17 Y = O R = SiMe$_3$

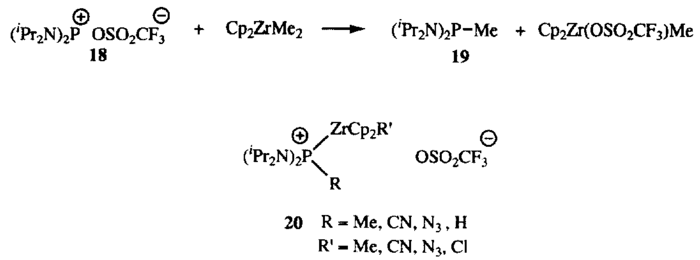
Scheme 4.

3. Methyl transfer reactions

A transfer reaction easily took place when a THF solution of **1** was added dropwise to a solution of the bis(diisopropylamino)phosphanylium salt **18** giving rise to the phosphane (iPr$_2$N)$_2$PMe, **19** (Scheme 5) [18]. Such a transfer, due to the oxophilicity of zirconium appeared to be general since not only methyl but also for example cyano and azide groups as well as hydride can be easily transferred from the corresponding zirconium derivatives Cp$_2$Zr(CN)$_2$, Cp$_2$Zr(N$_3$)$_2$ and [Cp$_2$ZrHCl]$_n$ to the R$_2$P$^+$ moieties, the phosphanes (iPr$_2$N)$_2$PCN, (iPr$_2$N)$_2$PN$_3$ and (iPr$_2$N)$_2$PH were obtained in excellent yield.

The presence of a low-lying vacant orbital and a lone electron pair in **18** confers to this salt the ability to activate C–H and C–C bonds. Indeed a number of reactions involving insertion reactions (oxidative addition) into C–H, C–C or N–N bonds have been reported [19]. Nevertheless, for the reactions described above, phosphonium salts **20** which would result from an insertion into a Zr–R bond were never detected even at low temperatures. If they are eventually formed they would rearrange very quickly to give the corresponding phosphane and Cp$_2$Zr(R)OSO$_2$CF$_3$.

A number of phosphino-terminated dendrimers from generation 1 (six phosphino groups) to generation 10 (3072 phosphino groups) were submitted to react with [AuCl(THT)]. The resulting complexes possess one chlorine atom bonded to each gold atom of the surface [20]. It is well known that [LAu–Cl] complexes



Scheme 5.

display a versatile reactivity. For instance they react easily with RLi or Grignard reagents to afford the corresponding [LAu–R] complexes.

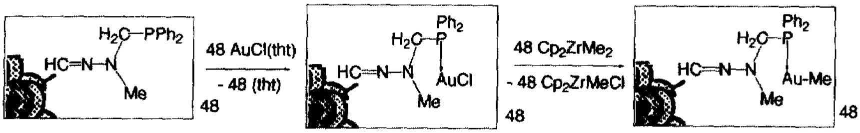
An experiment was carried out between a dendrimer of generation 4 (**22**) and **1** as alkylating agent. The exchange reaction occurred readily at room temperature to afford the dendrimer, **23** (Scheme 6) [21]. The exchange is characterized by the deshielding of the signal corresponding to the PPh$_2$ group (δ^{31}P = 38.2 ppm) and the presence of a doublet for the Me–Au groups in ^{1}H-NMR spectra (δ = 0.4 ppm, $^3J_{HP}$ = 8.1 Hz). Therefore such a reaction allowed to exchange 48 chlorine atoms with 48 methyl groups and corroborated the usefulness of **1** as an alkylating reagent.

On the other hand monomethylation, exclusively, can be clearly performed when the metalladendrimers of generation 1 (six terminal N(CH$_2$PPh$_2$)$_2$PdCl$_2$ moieties), **26**, or generation 3 (24 terminal N(CH$_2$PPh$_2$)$_2$PdCl$_2$ units), **27**, were treated with **1**: the dendritic complexes **28** or **29** were isolated in a 60–70% yield (Scheme 7) [22]. Methylation on the surface metal complexes can be achieved also by using MeMgBr but methylation in this case is accompanied by halogen exchange.

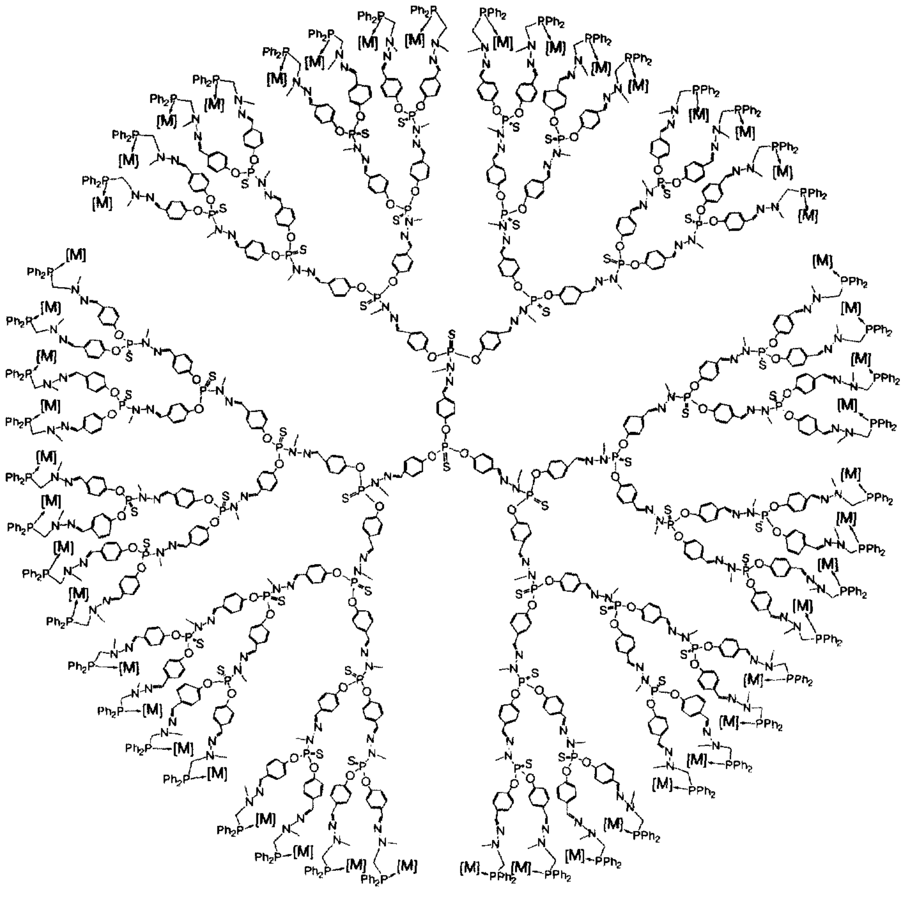
4. Carbozirconation

A few reactions concerning carbozirconation of unsaturated species with **1** are known. Indeed **1** reacts with ketenes, isocyanates, carbodiimides which insert into a Zr–Me bond with concomitant methylation on the sp^2 carbon [23].

Because of the strong polarization of the phosphorus nitrogen double bond of compounds of the type R–P=N–R, i.e. phosphaimines, one might expect that carbozirconation of these derivatives will be facilitated. Indeed treatment of **1** with the phospha-imine (**30**) in THF at −20°C resulted in the quantitative formation of a three-membered ring, namely the zirconaazaphosphirane, **31** (Scheme 8) [24]. A 1–2 addition of **1** to the phosphorus nitrogen double bond of **30** followed by cyclization is a reasonable postulation to explain the formation of **31**. NMR data strongly suggested a cyclic structure for **31**. Thus the ^{1}H-NMR spectrum exhibited two doublets for the Cp groups with phosphorus hydrogen coupling constants (^3JH$_{Cp}$P = 2.1 and 1.4 Hz). Similar coupling constants were detected for the



21 **22** **23**



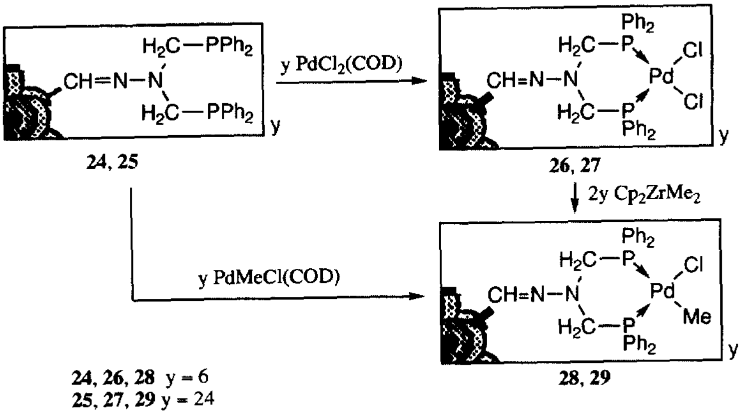
22 M = AuCl

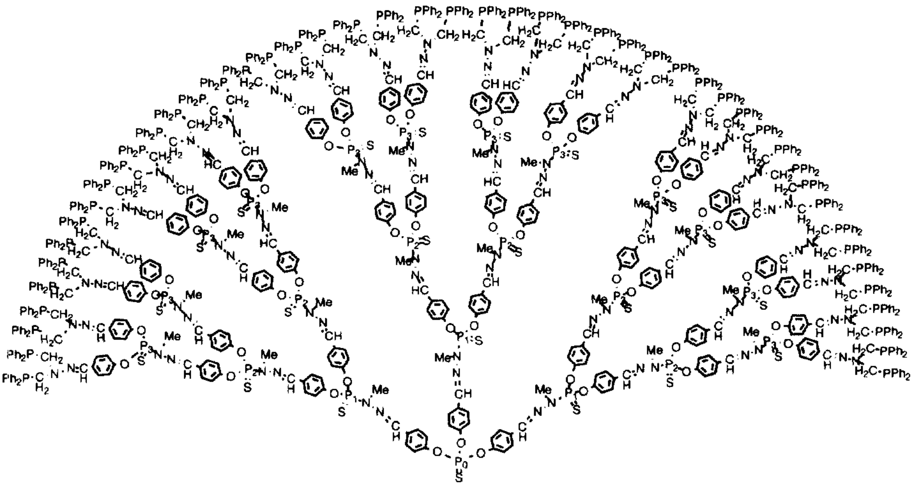
23 M = AuMe

Scheme 6.

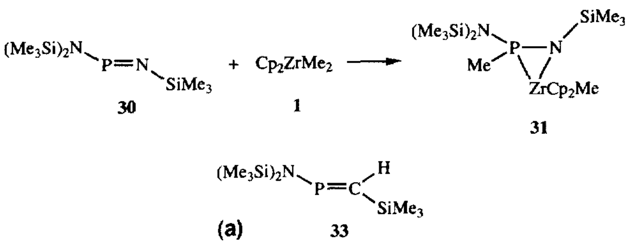
crystallographically characterized zirconaazaphosphirane **32** $(Me_3Si)_2N$-$P(H)N(SiMe_3)ZrCp_2Cl$ [25]. The presence of a methyl group on phosphorus and on zirconium is confirmed by ^{13}C-NMR spectroscopy.

It should be pointed out that no carbozirconation took place when a phos-





Scheme 7.



Scheme 8.

phaalkene such as **33** was reacted with Cp_2ZrMe_2. This is not surprising since the phosphorus carbon double bond is weakly polarized.

4.1. Generation of a P-metalated iminophosphorane

On the other hand, addition of **1** to a pentane solution of the chlorophosphaimine (**34**) at −40°C led to an air and moisture-sensitive powder (**36**) in an 85% yield (Scheme 9) [26]. The ^{31}P-NMR spectrum of **36** revealed the presence of a doublet of septets at −4.3 ppm ($^2J_{PH}$ = 6.3 Hz and $^3J_{PH}$ = 1.4 Hz). The signal for the Cp protons appeared in ^{1}H-NMR as a doublet with the coupling constant $^3J_{HP}$ = 1.4 Hz consistent with a Cp–Zr–P skeleton (see above). The ^{1}H-NMR spectrum also suggested that each of the methyl groups are bound to the phosphorus atom: only one doublet was detected for the two methyl groups ($^2J_{HP}$ = 6.3 Hz). ^{13}C-NMR corroborated this interpretation, only one doublet was observed for the same groups ($^1J_{CP}$ = 11.1 Hz).

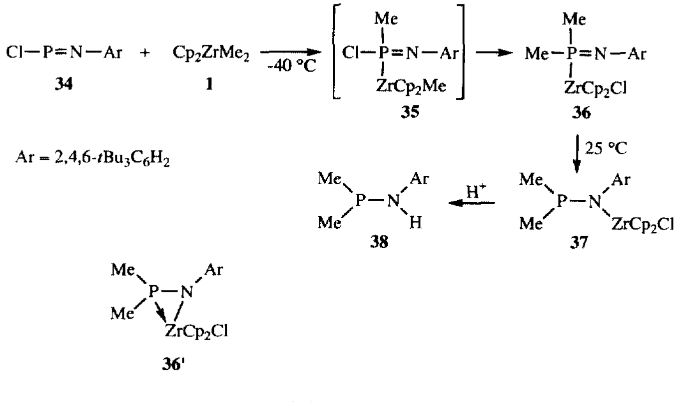
The generation of **36** should involve the transient intermediate **35** (resulting from insertion of the chloroiminophosphane, **34**, on the Zr–C bond of **1**) which rearranges via migration of the chlorine atom from phosphorus to zirconium and of a methyl group from zirconium to phosphorus. In solution at room temperature **36** afforded quantitatively the phosphane (**37**) which is the thermodynamically favored product of the reaction of **1** with **34**. The Zr–N bond in **37** can be easily cleaved in the presence of proton sources to give the phosphane **38**.

The study of the reactivity of **36** corroborated the structure of this derivative which can be described as the first P-metalated iminophosphorane or iminozirconiophosphorane and allowed to exclude a cyclic form (**36′**).

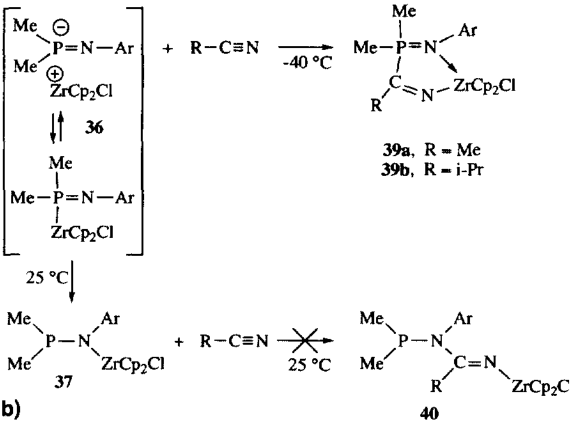
4.2. Reactivity of the P-metalated iminophosphorane (36)

4.2.1. Insertion reactions into the P–Zr bond

Derivative **36** reacted instantaneously with 1 Eq. of CH_3CN at −40°C to give



Scheme 9.

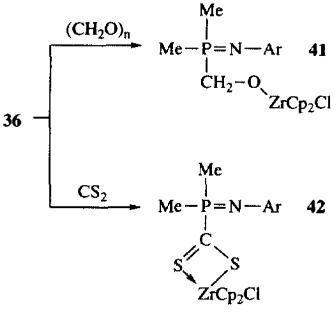


Scheme 10.

39a via insertion of CH_3CN into the P–Zr bond [26] (Scheme 10). NMR data were in favor of a structure such as **39** but did not allow exclusion of the formation of the phosphane **40** which would have resulted from the insertion of CH_3CN into the Zr–N bond of the phosphane **37**. However, the thermodynamic form **37** did not react even in the presence of a large excess of CH_3CN. It can also be noted that the cyclic zirconaazaphosphirane (**31**) did not react with CH_3CN. Addition of iPr–C≡N to **36** similarly afforded the insertion product **39b**.

Two other clear insertion reactions into the P–Zr bond of **36** can be pointed out [24]. The first one consisted of the treatment of **36** with paraformaldehyde at −40°C: the linear iminophosphorane **41** was quantitatively formed (Scheme 11).

The presence of a methylene group directly linked to phosphorus was confirmed by ^{13}C-NMR [δ CH_2: 76.8 (d, $^1J_{CP}$ = 94.5 Hz)] and ^{1}H-NMR. The second insertion reaction into the P–Zr bond of **36** was observed when CS_2 was added to **36** at −40°C: the iminophosphorane **42** was isolated as two isomers (Scheme 11).



Scheme 11.

In marked contrast to these experiments neither the phosphane **37** nor the zirconaazaphosphirane **31** reacted with paraformaldehyde or carbon disulfide.

Therefore all these insertion reactions demonstrated that the reactive species is the P-metalated iminophosphorane **36** and not the thermodynamic form **37**. Indeed **36**, which is stable at −40°C, acts as a masked iminophosphide, a new tricoordinated tetravalent phosphorus anion.

This behavior was corroborated by sets of additional experiments including reactions at phosphorus and formal insertion into the N–Zr bond.

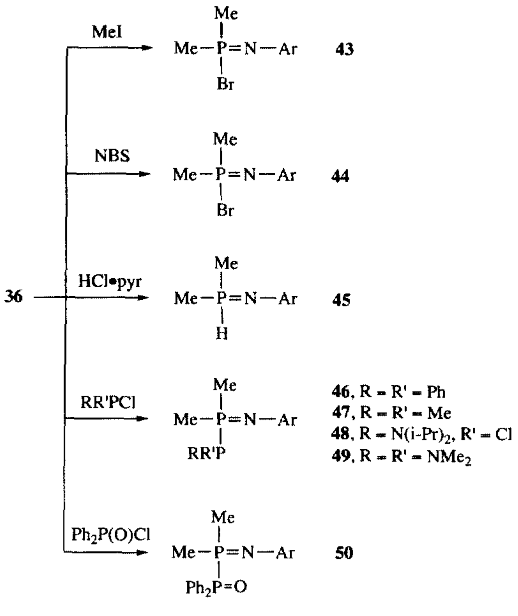
4.2.2. Electrophilic substitution reactions at phosphorus

Substitution reactions on **36** occurred when methyl iodide, *N*-bromosuccinimide or HCl pyridine are added to **36** at −78°C giving rise, respectively, to compounds **43–45** (Scheme 12) [27].

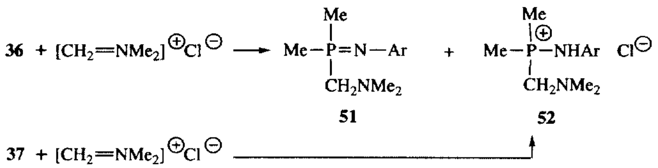
Similar exchange reactions were observed starting from **36** and various chlorophosphanes; however, the resulting phosphanyliminophosphoranes (**46–49**) appeared to be unstable and quickly decomposed into a variety of species.

Nevertheless compound **49** was fully characterized as well as species **50** arising from the treatment of **36** with diphenylchlorophosphane oxide.

In contrast to these reactions, addition of the Eschenmoser salt $[H_2C{=}NMe_2]^+Cl^-$ to **36** at −78°C afforded a mixture of the iminophosphorane **51** and the phosphonium salt **52** (Scheme 13). The formation of **51** can be easily explained via a classical exchange reaction from the P-metalated iminophospho-



Scheme 12.



Scheme 13.

rane form **36**, while the generation of the salt **52** might involve the phosphane **37**. Such an assumption was corroborated by the following experiment: treatment of **37** with $[H_2C{=}NMe_2]^+Cl^-$ gave exclusively the salt **52**.

4.2.3. Formal insertion reactions into the N–Zr bond

Addition of isocyanides Me_3SiCH_2NC or cyclohexyl-NC to **36** at −78°C in toluene led to the phosphanes **53** or **54** (Scheme 14). The X-ray structure determination of **53** clearly confirmed the phosphane structure with coordination of the imino nitrogen atom to the Cp_2ZrCl center [27].

In a first approach one could postulate that **53** (or **54**) arises from insertion of the isocyanide into the nitrogen–zirconium bond and therefore that the reactive species here is not the P-metalated iminophosphorane **36** but rather the phosphane **37**. However, no reaction occurred when **37** is treated directly with these isocyanides. Therefore it appeared that the first step of the reaction involving **36** is the coordination of the isocyanide on the vacant coordination site of the metal moieties to give **55**. Such a coordination could induce the dissociation of the P–Zr bond to afford **55″**. Lastly, electrophilic attack of the metalated carbocation **55″** at the hard nitrogen nucleophilic center of the thermodynamically more stable aminophosphide $Me_2P{-}N{-}Ar^-$ give **53** (or **54**) (Scheme 14).

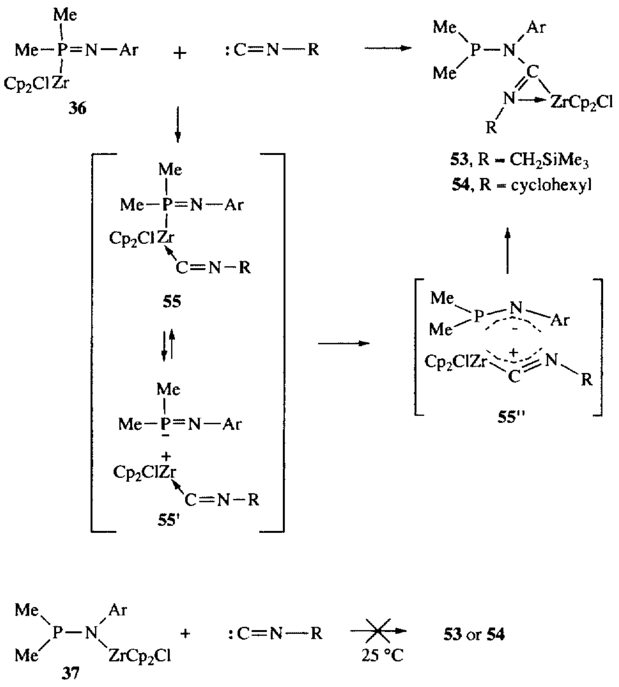
It is of interest to note that derivatives **53** and **54** are formally the first compounds resulting from insertion of isocyanides into a N–Zr bond.

4.2.4. Reaction at nitrogen

Two hypotheses can be formulated to explain the formation of the aminoiminophosphane **56** from **36** and the chloroiminophosphane **34** (Scheme 15). The first one involves the preliminary exchange reaction between **36** and **34** leading to **57** which further rearranges into **56**, while the second one implies a direct exchange with the phosphane form **37**. The 1,2 shift of a phosphorus group from phosphorus to the imino nitrogen has already been observed [28] and indeed cannot be totally ruled out. However, the formation of **57** was never detected in ^{31}P-NMR. Therefore the more realistic mechanism of formation of **56** is the direct grafting of **34** to the nitrogen atom of the phosphane **37**.

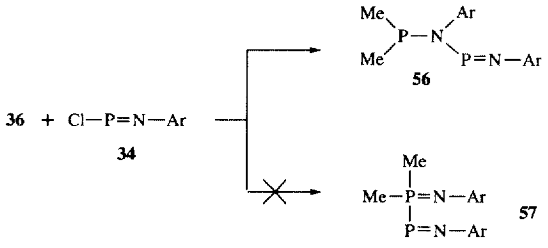
4.2.5. Concluding remarks

Therefore treatment of the chloroiminophosphane **34** with **1** allowed preparation of an unprecedented iminozirconiophosphorane (**36**) which reacts as a masked

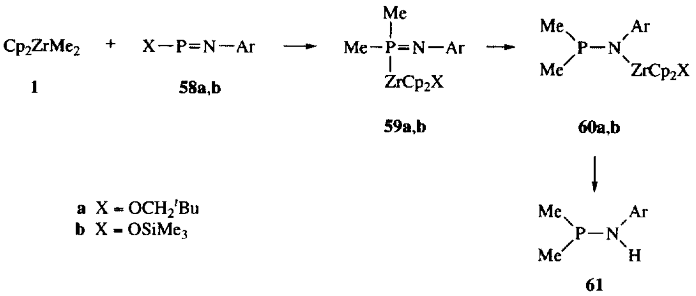


Scheme 14.

iminophosphide $[Me_2P{=}N(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]^-$ $[ZrCp_2Cl]^+$ or as the (zirconioamino)phosphane $Me_2P{-}N\,(ZrCp_2Cl)-2,4,6\text{-}t\text{-}Bu_3C_6H_2$. Up to now only a few reports dealt with the iminophosphide anion, $>P{=}N^-$. Transient generation of such a species was postulated during the treatment of the phosphaimine **30** with MeLi [29]. A single-crystal X-ray crystallography study of $[Li(PhN{-}PPh_2)(OEt_2)]_2$ showed that the lithium cations are ligated by both of the heteroatoms of the $PhN{-}PPh_2^-$ anion. However, the P–N distance (1.672 Å) was found in the range of the P–N single bond lengths [30] and ab initio calculations carried out on the



Scheme 15.



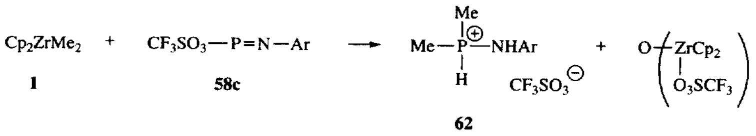
Scheme 16.

parent phosphinoamide/iminophosphide anion H_2PNH^-, suggested that this system is best described as the phosphino amide anion H_2PNH^- with the negative charge mainly located on nitrogen [31]. Therefore no stable linear iminophosphide anion $[R_2P{=}N - R']^-$, as well as no useful precursor of such a species, had been reported before the characterization and the study of the reactivity of **36**. Indeed the high electronegativity of nitrogen appears to be the dominant factor which generally hinders the formation of such anionic species. In the case of **36** the transition metal derivatization of $[R_2P{=}N - R']^-$ considerably affects its reactivity allowing this species to react as a new tricoordinated tetravalent phosphorus anion.

4.3. From phosphaimines to phosphanes via transient imino-zirconiophosphoranes

Carbozirconation of phosphaimines **58a,b** with **1** gave rise to the phosphane **61** [32]. A similar reaction of **1** with the phosphaimine **58c** led to the protonated form of the phosphane **61**, i.e. the phosphonium salt **62** and the zirconium oxide $\{[Cp_2Zr(OSO_2CF_3)]_2O\}$ (Schemes 16 and 17). It was demonstrated that these phosphaimine–phosphane transformations involved an easy transfer of alcoxy, trimethylsiloxy or triflate groups from phosphorus to zirconium via the transient formation of P-metalated iminophosphoranes, i.e. the iminozirconiophosphoranes **59a–c**.

Additional examples of formation of transient iminozirconiophosphoranes were provided from **34** and $Cp_2Zr(CH_2Ph)_2$ or $Cp_2Zr(Me)(OMe)$.



Scheme 17.

5. Conclusion

It is obvious that the studies of interactions between main group elements and more precisely phosphorus compounds and zirconium species such as Cp_2ZrMe_2 and related species are underdeveloped. The chemistry presented in this review clearly demonstrates how useful these studies can be for the preparation of new species which might possess interesting properties in the area of catalysis, macrocyclic chemistry, nanostructures, etc.

Acknowledgements

Authors thank all their co-workers whose names appear in references.

References

[1] For some reviews on zirconium derivatives see for example: Recent Advances in the Chemistry of Zirconocene and Related Compounds, Tetrahedron Symposia-in-Print N°57, in: E.I. Negishi (Ed.), 51 (1995) 4255.
[2] S.A. King, J.B. Miller, A.C.C. Wong, J. Schwartz, Chem. Scr. 29 (1989) 411.
[3] G. Erker, M. Aulbach, M. Mena, R. Pfaff, F. Sosna, Chem. Scr. 29 (1989) 451.
[4] E.I. Negishi, Chem. Scr. 29 (1989) 457.
[5] S.L. Buchwald, R.B. Nielsen, Chem. Rev. 88 (1988) 1047.
[6] E.I. Negishi, T. Takahashi, Synthesis (1988) 1.
[7] E. Hey-Hawkins, Chem. Rev. 94 (1994) 1661.
[8] J.P. Majoral, M. Zablocka, A. Igau, N. Cénac, Chem. Ber. 129 (1996) 879.
[9] G. Erker, F. Rosenfeldt, J. Organometal. Chem. C1 (1980) 188.
[10] G. Erker, Acc. Chem. Res. 17 (1984) 103.
[11] J.W. Lauher, R. Hoffman, J. Am. Chem. Soc. 98 (1976) 1729.
[12] S. Gambarotta, S. Strologo, C. Floriani, A. Chiesi-Villa, C. Guastini, Inorg. Chem. 24 (1985) 654.
[13] D. Stephan, Organometallics 9 (1990) 2718.
[14] D. Stephan, Organometallics 10 (1991) 2037.
[15] E. Hey, S.G. Bott, J.L. Atwood, Chem. Ber. 121 (1988) 561.
[16] H. Köpf, V. Richtering, J. Organomet. Chem. 346 (1988) 355.
[17] D. Colombo-Khater, A.-M. Caminade, B. Delavaux-Nicot, J.-P. Majoral, Organometallics 12 (1993) 2861.
[18] F. Boutonnet, M. Zablocka, A. Igau, J.-P. Majoral, J. Jaud, K.M. Pietrusiewicz, J. Chem. Soc., Chem. Commun. (1993) 1487.
[19] M. Sanchez, M.R. Mazières, L. Lamandé, R. Wolf, in: M. Regitz, O.J. Scherer (Eds.), Multiple Bonds and Low Coordination in Phosphorus Chemistry, Georg Thieme Verlag, Stuttgart 1990, p. 129.
[20] M. Slany, M. Bardaji, M.J. Casanove, A.-M. Caminade, J.-P. Majoral, B. Chaudret, J. Am. Chem. Soc. 117 (1995) 9764.
[21] M. Slany, M. Bardaji, A.-M. Caminade, B. Chaudret, J.-P. Majoral, Inorg. Chem. 36 (1997) 1939.
[22] M. Bardaji, M. Kustos, A.-M. Caminade, J.-P. Majoral, B. Chaudret, Organometallics 16 (1997) 403.
[23] S. Gambarotta, S. Strologo, C. Floriani, A. Chiesa-Villa, C. Guastini, Inorg. Chem. 24 (1985) 654.
[24] N. Dufour, A.-M. Caminade, M. Basso-Bert, A. Igau, J.-P. Majoral, Organometallics 11 (1992) 1131.

[25] N. Dufour, J.-P. Majoral, A.-M. Caminade, R. Choukroun, Y. Dromzee, Organometallics 10 (1991) 45.
[26] A. Igau, N. Dufour, A. Mahieu, J.-P. Majoral, Angew. Chem. Int. Ed. Engl. 1 (1993) 95.
[27] A. Mahieu, A. Igau, J. Jaud, J.-P. Majoral, Organometallics 14 (1995) 944.
[28] Y.G. Gololobov, E.A. Swalova, T.I. Chudakova, Zh. Obshch. Khim. 51 (1981) 1433.
[29] A.H. Cowley, R.A. Kemp, Inorg. Chem. 22 (1983) 547.
[30] M.T. Ashby, Z. Li, Inorg. Chem. 31 (1992) 1321.
[31] G. Trinquier, M.T. Ashby, Inorg. Chem. 33 (1994) 1306.
[32] C. Larré, A. Mahieu, A. Igau, J.-P. Majoral, J. Organomet. Chem. 493 (1995) 133.