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Review

Recent developments in the chemistry of metallophosphaalkenes

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Contents

Abstract

The chemistry of low-valent organophosphorus compounds such as phosphaalkenes has undergone rapid development in the last three decades. These developments also include the organometallic and coordination chemistry of such species. Metallophosphaalkenes are compounds in which one or more of the organic substituents on the P=C unit are replaced by metal fragments. *P*- and *C*-metallophosphaalkenes have emerged from laboratory curiosities to versatile and useful synthons in organoelement chemistry. Particular examples are *C*-lithiophosphaalkenes and *C*-magnesiophosphaalkenes (phospha-Grignard reagents).

Keywords: Metallophosphaalkenes; Lithiophosphaalkenes; Phospha-Grignard reagents; Organoelement derivatives

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1. Introduction

The chemistry of compounds with low-coodinate phosphorus atoms involved in phosphorus–carbon multiple bonding has been rapidly developed since the discovery of thermolabile HC≡P by Gier in 1961 [1,2]. Shortly after, cationic phosphamethyne cyanines were synthesized by Dimroth and Hofmann [3], while Märkl [4] reported on the first representative of phosphabenzene. In the latter species, the P=C multiple bonds are stabilized by extensive π-delocalization (Scheme 1).

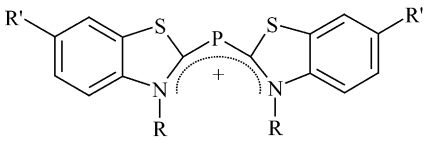
The formal replacement of one methylene group in alkenes $R^2R^3C{=}CR^4R^5$ by the phosphanediyl unit R^1P leads to the class of phosphaalkenes $R^1P{=}CR^2R^3$, the first representatives of which were presented by Becker in 1976. Numerous papers on phosphaalkenes have highlighted the remarkable ability of phosphorus to mimic the chemistry of carbon [2].

The rapid development of phosphaalkene chemistry during the last three decades also includes their coordination chemistry. Five types of complexes are now known featuring phosphaalkene ligands (**A**–**E**) (Scheme 2).

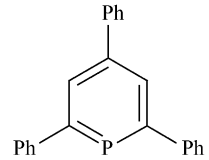
In metallophosphaalkenes, one or more of the substituents R at the P=C backbone are replaced by transition metal complex fragments or main group metals; thus five basically different types of compound (**I**–**V**) can be differentiated (Scheme 3).

The first metallophosphaalkenes of the types **I** and **II** were synthesized in 1985 by our group [5]. In 1996, a review article gave an account on synthesis, structure, bonding and reactivity of the various classes of phosphaalkenes **I**–**IV** [6]. It is now evident that the vast majority of metallophosphaalkenes belong to the classes **I** and **II**, whereas representatives of type **V** still remain elusive. First investigations on their reactivity disclosed metallophosphaalkenes as valuable and versatile starting materials for a wide range of chemical transformations.

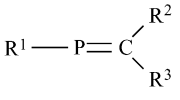
Whereas the previous review provided an overview of metal-functionalized P=C systems with particular emphasis placed on synthetic and structural aspects, this report highlights the remarkable richness of the chemistry exhibited by such species and covers the literature of the years 1996–2003. Almost all papers published in that period of time are restricted to metallophosphaalkenes of the types **I** and **II.**



phosphamethyne cyanine cations

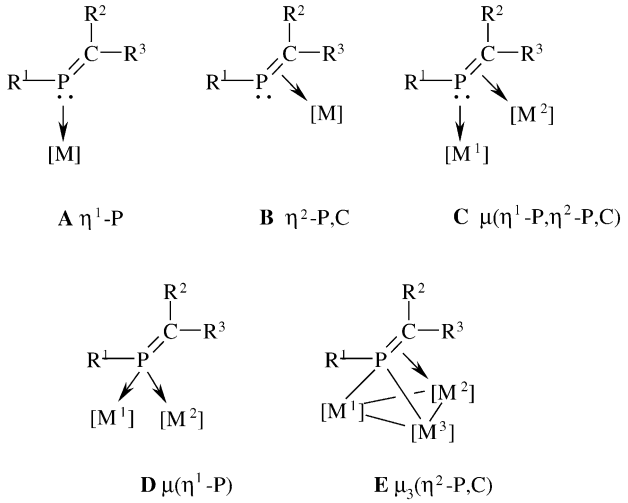


2,4,6-triphenylphosphabenzene

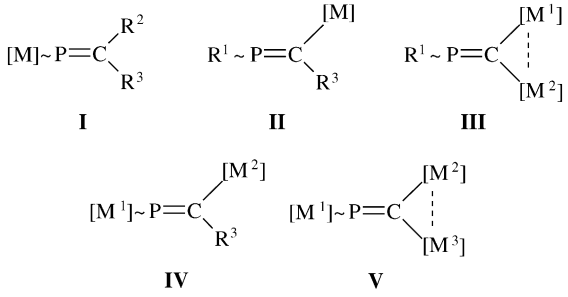


phosphaalkenes

Scheme 1. Molecules featuring P=C multiple bonding.



Scheme 2. Basic types of phosphaalkene transition metal complexes.



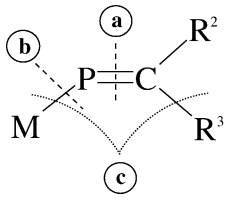
Scheme 3. Basic types of metal-functionalized phosphaalkenes (metallophosphaalkenes).

2. Synthetic methods

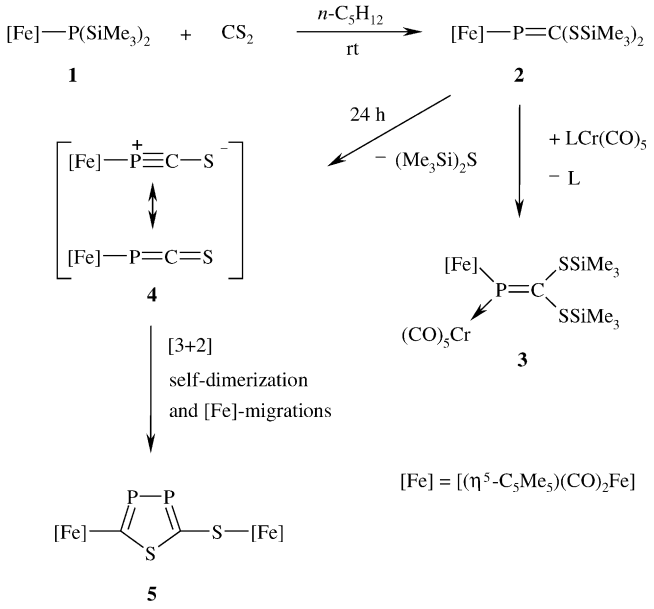
2.1. *P*-Metallophosphaalkenes

For the synthesis of *P*-metallophosphaalkenes, three general principles (a–c) are discernable (Scheme 4).

In syntheses following route (a), the P=C bond is constructed from precursors such as metallophosphanes. In route (b), a metal–phosphorus bond is formed between a *P*-



Scheme 4. Routes to metallophosphaalkenes of type **I**.



Scheme 5. Reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3)_2]$ with CS_2.

functionalized phosphaalkene and an appropriate metal complex and in route (c), phosphaalkynes are reduced within the coordination sphere of a transition metal complex.

2.1.1. Synthesis by route a

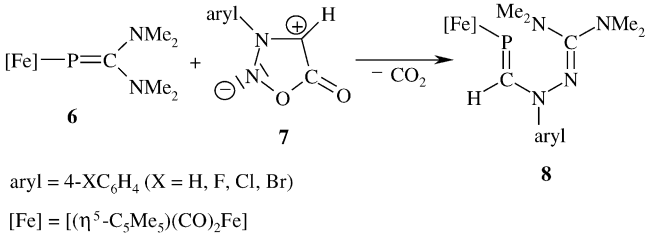
Reaction of iron phosphanide $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}P(SiMe_3)_2]$ (**1**) with an equimolar amount of carbon disulfide in *n*-pentane at 20 °C produced ferriophosphaalkene **2** as indicated by a singlet at δ = 509 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Compound **2** could not be isolated without decomposition. The metallophosphaalkene, however, was intercepted successfully as a stable pentacarbonylchromium complex **3** by treating the reaction mixture with [{(*Z*)-cyclooctene}$Cr(CO)_5$]. (Scheme 5).

Metallophosphaalkene complexation **2** → **3** was accompanied by a small high-field shift of 43.3 ppm. After stirring a mixture of **1** and CS_2 for 24 h at ambient temperature the singlet of metallophosphaalkene **2** had disappeared and 1,3,4-thiadiphosphole **5** was obtained as a red powder [7].

Electron-rich and inversely polarized metallophosphaalkenes are good precursors for novel metallophosphaalkenes when treated with mesoionic compounds or Fischer-type carbene complexes.

Metallophosphaalkene $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(NMe_2)_2]$ (**6**) reacted smoothly with equimolar amounts of the sydnones 3-aryl-NNOC(O)CH (**7**) (aryl = Ph, 4-FC_6H_4, 4-Cl-C_6H_4, 4-BrC_6H_4) in an ether/dichloromethane mixture (0–10 °C) to afford the red–brown microcrystalline ferriophosphaalkene $[(E)\text{-}(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}CHN(aryl)N{=}C(NMe_2)_2]$ (**8**) in good yields (61–72%) [8] (Scheme 6).

In contrast, the reaction of **6** with the more electron-rich 3-methylsydnone or 3-(*p*-methoxyphenyl)sydnone led to de-



Scheme 6. Reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}P{=}C(NMe_2)_2]$ with 3-arylsydnones.

composition. When compound **6** was allowed to react with two molar equivalents of carbene complexes **9a** and **9b** in diethyl ether the novel ferriophosphaalkene complexes **10a,b** and β-aminoalkenyl(ethoxy)carbene complexes **11a,b** were produced [9] (Scheme 7).

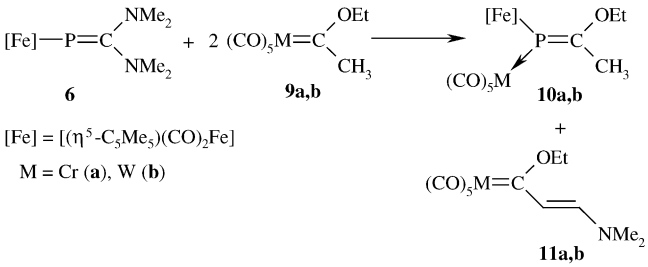
From a formal point of view, the formation of **10a,b** can be regarded as a metathesis process. This protocol for novel phosphaalkenes, however, suffers from severe limitations. No metathesis products were obtained from treatment of **6** with $[(CO)_5W{=}C(OEt)R]$ (R = Ph, $CH{=}CH_2$, C≡CH). In contrast to this, metal-free inversely-polarized phosphaalkenes $R'P{=}C(NMe_2)_2$ (R′ = H, *t*Bu, Me_3Si) and selected aryl(ethoxy)carbene complexes afforded the expected novel phosphaalkenes R′P=C(OEt)aryl η^1-ligated to the $W(CO)_5$-fragment (aryl = C_6H_5, 2-MeC_6H_4, 2-$MeOC_6H_4$) [10].

2.1.2. Synthesis by route b

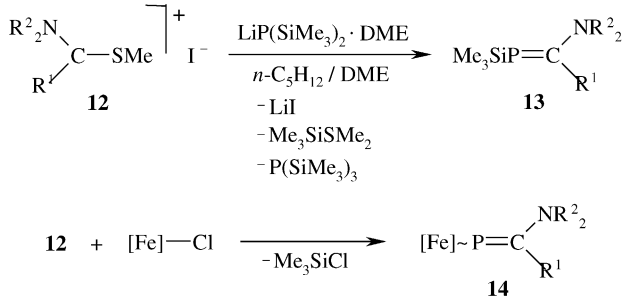
A particularly efficient method for the preparation of metallophosphaalkenes with amino substituents utilizes the reaction of trimethylsilyl(aminomethylene)phosphanes $Me_3SiP = C(NR^1{}_2)R_2$ (**13a–d**) with complex $[(\eta^5\text{-}C_5Me_5)(CO)_2FeCl]$ in a mixture of DME and *n*-pentane. Stable crystalline ferriophosphaalkenes **14a–d** were isolated in moderate yields (34–67%). The required precursors **13a–d** were synthesized as thermolabile orange oils from carbenium iodides $[R^1(R^2{}_2N)(MeS)C]I$ (**12a–d**) and $LiP(SiMe_3)_2{\cdot}DME$ in the same solvent mixture (38–62%) yield [11] (Scheme 8).

2.1.3. Syntheses by route c

A very prominent access to *P*-metallophosphaalkenes is based upon the 1,2-addition of suitable transition metal complexes across the PC triple bond of phosphaalkynes. During the reaction of the hydridoruthe-



Scheme 7. Reaction of **6** with Fischer carbene complexes.



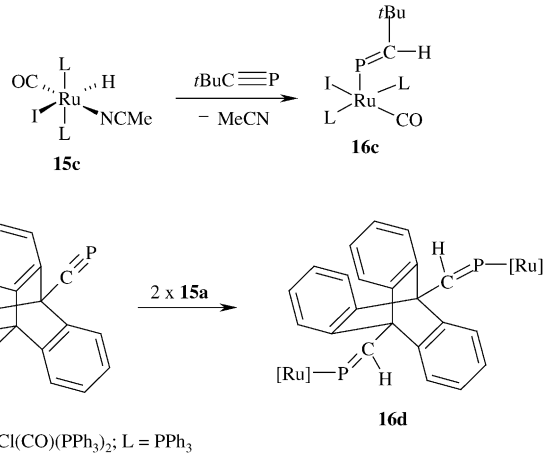
12 - 14	R^1	NR^2_2
a	Ph	NMe_2
b	*t*Bu	NMe_2
c	$(3,4,5\text{-}MeO)_3C_6H_2$	NMe_2
d	Ph	NC_5H_{10}

Scheme 8. Synthesis of phosphaalkenes **13a–d** and **14a–d**.

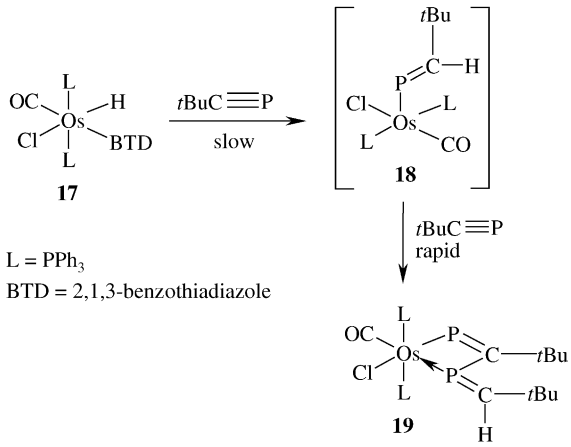
nium complex **15a** with *t*BuC≡ P in CH_2Cl_2 solution orange-red rutheniophosphaalkene **16a** is smoothly formed in 92% yield. Similarly hydrometalation of the phosphaalkyne with $[RuHCl(CS)(PPh_3)_3]$ (**15b**) provided the orange crystalline thiocarbonyl analogue **16b** in 89% yield (Scheme 9) [12]. Both processes are regioselective *cis*-additions.

Rutheniophosphaalkene **16a** is also available by reacting a 2,1,3-benzothiadiazole ruthenium complex analogous to **15a** with an excess of the phosphaalkyne. Reaction of the acetonitrile ruthenium complex **15c** with *t*BuC≡ P gave the same pattern providing the new phosphaalkenyl complex **16c** (Scheme 10) [13]. Similarly, the triptycene derived diphosphaalkyne was converted into the bis-rutheniophosphaalkene **16d** by treatment with **15a** (Scheme 10) [14].

Contrasting the chemistry of the ruthenium complexes **15a** and **15b**, treatment of $[OsHCl(CO)(PPh_3)_3]$ with an excess of *t*BuC≡ P failed to result in any appreciable reaction, which was attributed to the lack of phosphine lability under mild conditions. However, prior conversion of $OsHCl(CO)(PPh_3)_3$ to the more reactive compound **17** provides the conditions where the *cis*-1.2-hydroosmiation of the PC triple bond occured. Instead of the anticipated osmiophosphaalkene $[Os(P{=}CH\textit{t}Bu)Cl(CO)(PPh_3)_2]$ **18** the final product was found to incorporate two equivalents of the phosphaalkyne. Obviously, the putative initial product **18** was added across the P≡ C bond of a second molecule of phosphaalkyne via its Os–P bond (Scheme 11) [13].



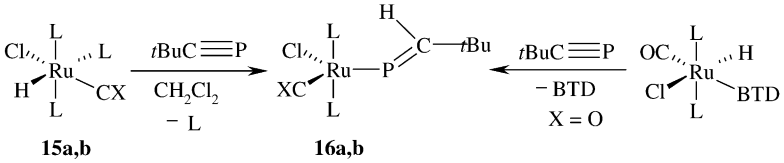
Scheme 10. Formation of **16c** and **16d**.



Scheme 11. Formation of phosphaalkenyl–phosphaalkene complex **19**.

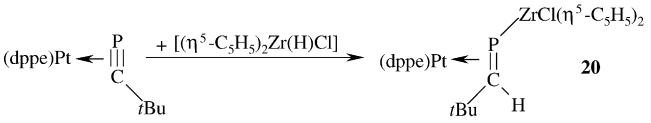
Hydrozirconation of an η^2-coordinated phosphaalkyne by Schwarz's reagent gave rise to the quantitative formation of the synthetically useful *P*-zirconated phosphaalkene complex **20**, which was formed as a single isomer (Scheme 12) [15].

Treatment of $[(\eta^5\text{-}C_5Me_5)_2Zr(py)(=S)]$ (**21a**) with one equivalent of *t*BuC≡ P in toluene led to the ready elimination of pyridine, affording the red crystalline [2 + 2] cycloaddition product (**22a**) in 61% yield. Similarly, red crystalline **22b** was formed in 47% yield from $[(\eta^5\text{-}C_5Me_5)_2Zr(py)(=Se)]$ (**21b**)

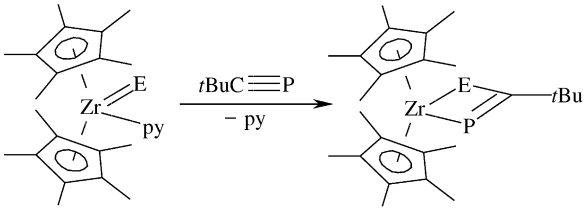


(**a**): X = O; (**b**): X = S; L = PPh_3, BTD = 2,1,3-benzothiadiazole

Scheme 9. Formation of the rutheniophosphaalkenes **16a,b**.



Scheme 12. Hydrozirconation of η^2-ligated *t*BuC≡P.



E = S (**a**), Se (**b**)

Scheme 13. [2 + 2] Cycloaddition of chalcogenidozirconium complexes with *t*BuC≡P.

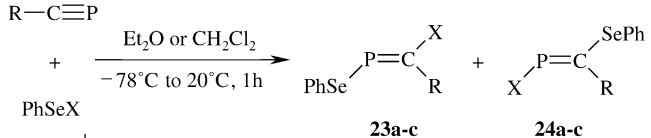
and an equimolar amount of the phosphaalkyne (Scheme 13) [16].

The generation of *P*-metallophosphaalkenes from phosphaalkynes via addition reactions is not restricted to d-block metals. Addition of PhSeX (X = Cl, Br) to RC≡ P (R = *t*Bu, 1-adamantyl) at −78 °C in diethylether or dichloromethane followed by slow warming to room temperature furnished the *P*-selenophosphaalkenes **23a–c** in moderate to high yields (Scheme 14).

In each reaction, a small amount of the *P*-halogenated phosphaalkenes **24a** (8%), **24b** (2%) and **24c** (12%) were produced by reverse addition [17]. Products **23** and **24** could not be separated on a preparative scale.

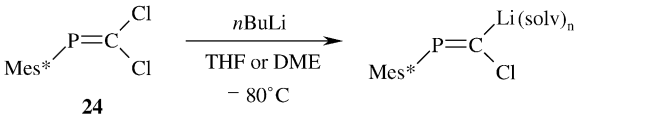
2.2. C-Metallophosphaalkenes

Synthetic methods for *C*-lithio- and *C*-magnesiophosphaalkenes and transmetalation processes thereof are discussed in this section. The latter transformations constitute prominent routes to other main-group metal functionalized phosphaalkenes. One approach to *C*-lithiophosphaalkenes is based upon the lithium/halogen exchange of *C*-halogenated phosphaalkenes by means of alkyllithium reagents. Treatment of THF or DME solutions of the



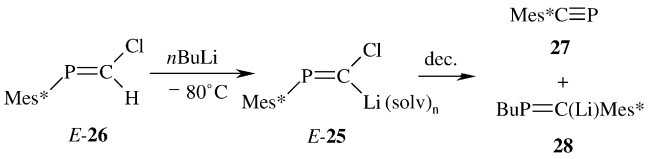
23,24	R	X	23:24
a	*t*Bu	Cl	92:8
b	*t*Bu	Br	98:2
c	Ad	Cl	88:12

Scheme 14. Formation of *P*-selenophosphaalkenes.



Z-**25a**: solv. = DME with n = 2
Z-**25b**: solv. = THF with unknown n

Scheme 15. Lithiation of Mes*P=CCl_2.



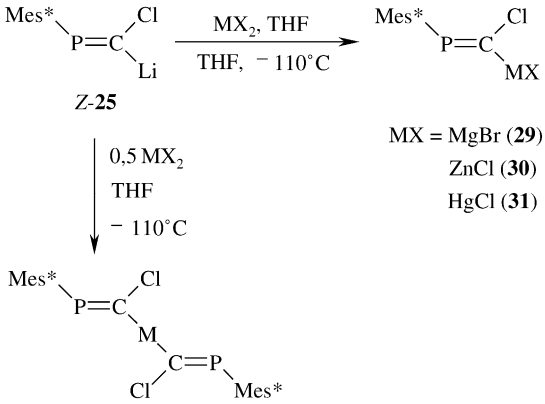
Scheme 16. Formation and decomposition of *E*-**25**.

aryl(dichloromethylene)phosphane (**24**) with an excess of *n*-butyllithium at −80 °C cleanly afforded the *Z*-configurated lithiophosphaalkenes **25a** and **25b** (Scheme 15) [19].

Single crystals of the DME solvate **25a** were grown at −60 °C, and were subjected to an X-ray diffraction study at −150 °C (see below). Interestingly, the *E*-isomer *E*-**25**, generated by metalation of (*E*)-Mes*P=C(H)Cl (**26**) with an excess of *n*-butyllithium under analogous conditions was found to be unstable and decomposed to give Mes*C≡ P (**27**) and *n*BuP=C(Li)Mes* (**28**) as the main products [18,19] (Scheme 16).

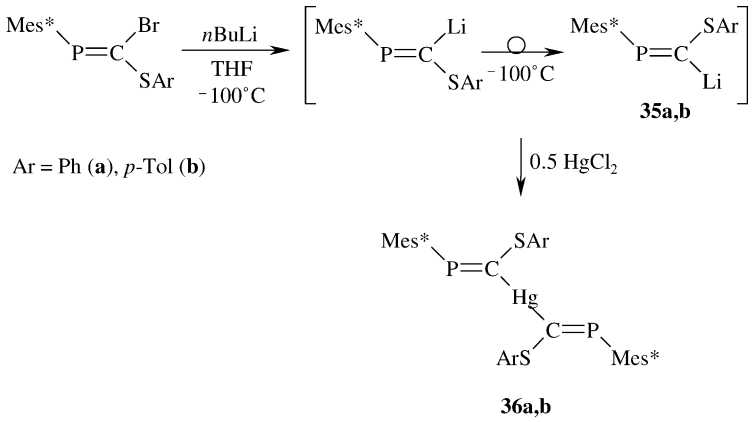
C-Lithiophosphaalkenes were usually generated at low temperature and subsequently subjected to further transformations. At this point, it seems reasonable to also discuss transmetalation processes of *C*-lithiophosphaalkenes which lead to a series of novel phosphaalkenes functionalized by main group metals (Scheme 17).

The magnesium-, zinc- and mercury-derivatives **29**–**31**, which may be also considered as carbenoids, were quantitatively prepared by transmetalation reactions of (*Z*)-**25** with 1 equiv. of magnesium bromide, zinc chloride or mercury(II)chloride in the temperature range of −110 to 15 °C



M = Mg (**32**), Zn (**33**), Hg (**34**)

Scheme 17. Preparation of compounds **29**–**34** by transmetalation of (*Z*)-**25**.



Scheme 18. Preparation of **36a,b**.

(**29**) or at room temperature (**30**, **31**). Analogously, the addition of 0.5 equivalents of the metal halide furnished a solution of the bis(phosphaalkenyl) metal species **32**–**34** (Scheme 17) [20]. Similarily, Ito and Yoshifuji [21] succeeded in the preparation of *C*-lithio-*C*-arylthiophosphaalkenes (**35**) at −100 °C and their subsequent transformation into mercury derivatives **36a,b** by treatment with 0.5 equiv. $HgCl_2$ (Scheme 18).

According to a previously published procedure for the synthesis of Mes*P=C(Cl)MMe_3 (M = Si, Ge, Sn) from (*Z*)-**25** and the chlorotrimethyl derivatives of group 14, lithiophosphaalkene **38** was generated from the dibromophosphaalkene **37** and *n*-butyllithium in diethyl ether at −100 °C, and then quenched with dimesityldifluorogermane at −120 °C. White crystals of germanium-functionalized phosphaalkene **39** were isolated in 35% yield. Analogously Mes*P=CHI was lithiated by *n*-butyllithium in diethyl ether at −90 °C to give Mes*P=CHLi, which was trapped with Mes_2GeF_2 to afford germylated phosphaalkene **40** (Scheme 19) [22].

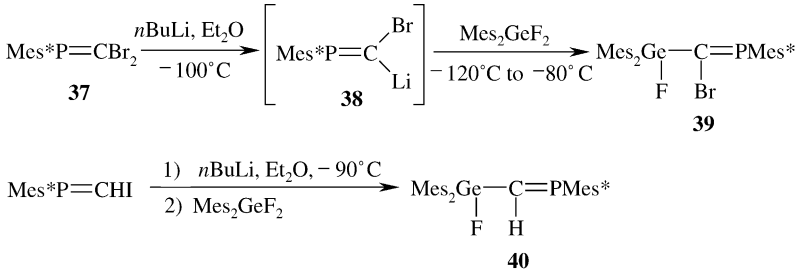
In addition to organolithiums, Grignard reagents also play an important and sometimes complementary role in organic synthesis. Phosphavinyl-Grignard reagents, which may also be regarded as *C*-magnesiophosphaalkenes, are emerging valuable synthetic reagents in organophosphorus chemistry as well. There are generally three synthetic approaches to those species, two of which are based upon modification of the substitution pattern at the P=C moiety of a phosphaalkene and the youngest, and possibly most powerful method, involves 1,2-addition of Grignard reagents to the PC triple bonds of stable phosphaalkynes. All of these approaches suffer to some extent from the limitation, that bulky substituents must be present in the precursors to provide sufficient stability.

In the first method (as depicted in Scheme 17), transmetalation of lithium derivative (*Z*)-**25** depends on the availability of the organolithium compound or of its precursor, namely suitably halogenated phosphaalkenes. In these starting materials, the substituent at the phosphorus atom is almost always the supermesityl group.

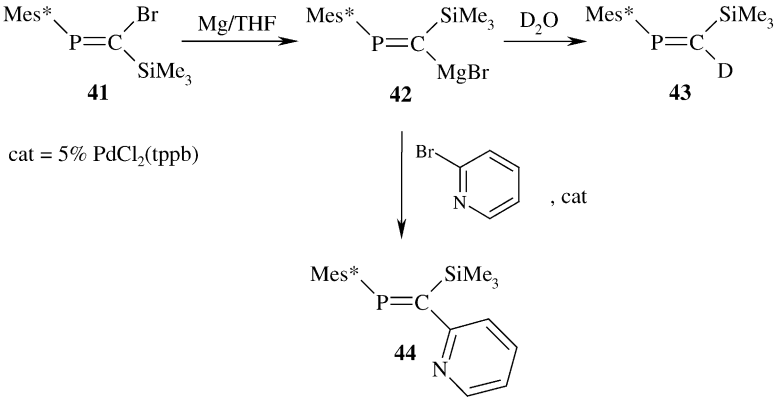
Similar restrictions are valid for the second method which parallels the classical synthesis of Grignard reagents, namely the reaction of phosphavinyl halide **41** with magnesium metal in an ether solvent. Here, the resulting phosphavinyl-Grignard compound **42** was not isolated, but rather quenched with an appropriate electrophile (Scheme 20) [23].

Isomerically pure (*E*)-Mes*P=C(H)$SnMe_3$ (**45**) was prepared by the reaction of (*E*)-Mes*P=C(H)Br with magnesium metal and trimethylchlorostannane under Barbier conditions. It is conceivable that a magnesium functionalized phosphaalkene serves as an intermediate in this process (Scheme 21) [23].

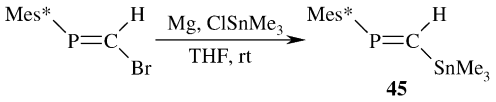
A general, very elegant and efficient pathway to phospha-Grignard reagents is based upon the regio- and stereoselective addition of organomagnesium halides to the PC triple bond of *t*BuC≡ P [24,25]. Under the reaction conditions employed the products are stable to further transforma-



Scheme 19. Synthesis of C-germaniophosphaalkenes **39** and **40**.



Scheme 20. Synthesis and quenching of *C*-magnesiophosphaalkene **42**.

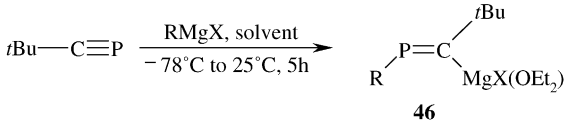


Scheme 21. Synthesis of *C*-stanniophosphaalkene **45**.

tions and can be isolated in the solid state in excellent yields (Scheme 22).

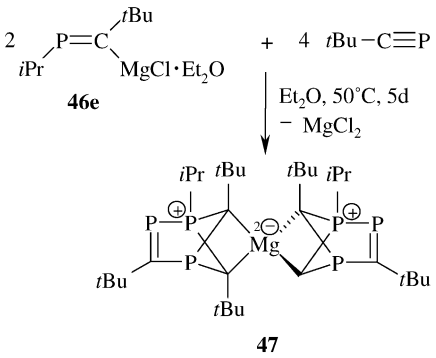
Treating **46a,b,d** with a further equivalent of the respective Grignard reagent did not lead to a second addition across the PC double bond. In the presence of at least two equivalents of *t*BuC≡ P, however, **46e** underwent further reaction even at room temperature. At 50 °C, the reaction took 5 days and afforded the red crystalline organomagnesium complex **47** by the incorporation of two equiv. of the phosphaalkyne (72 % yield) (Scheme 23) [25].

In contrast to the phosphavinyl compounds Mes*P=C(R)MgBr (R = halide, Me_3Si), the substituent R at the P atoms in **46a**–**f** is derived from the organomagnesium halide employed and thus may be varied largely [24,25]. Other kinetically stabilized phosphaalkynes are also amenable to this reaction [25].



46	R	X	solvent
a	cC_6H_{11}	Cl	Et_2O
b	cC_5H_9	Cl	Et_2O
c	Et	Br	Et_2O
d	Mes	Br	Et_2O
e	*i*Pr	Cl	Et_2O
f	*t*Bu	Br	THF

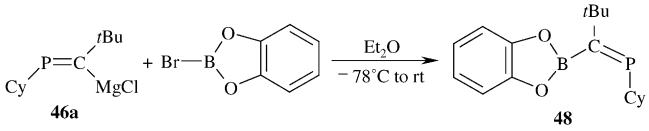
Scheme 22. Addition of Grignard reagents to phosphaalkynes.



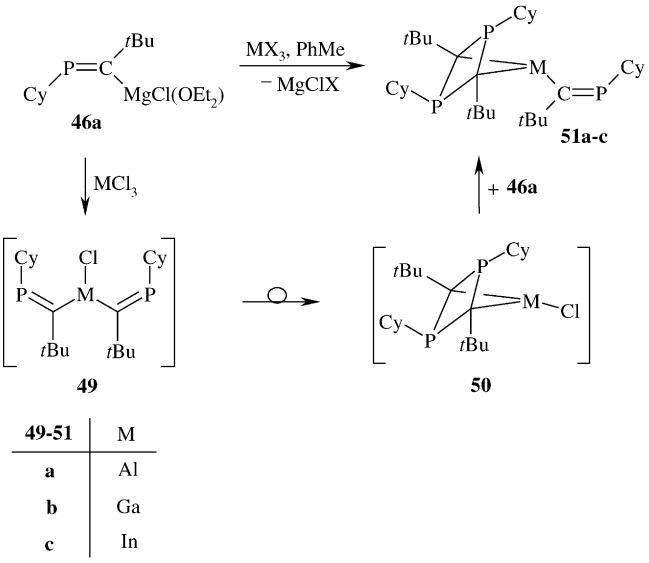
Scheme 23. Formation of **47**.

Magnesiophosphaalkenes **46a**–**f** are excellent precursors for a series of novel group 13 and group 14 metallophosphaalkenes via transmetalation processes. The use of vinyl boronic-acids and -esters in transition metal catalyzed C–C bond forming reactions, such as the Suzuki cross coupling, is well established. It was obvious to envisage the preparation of phosphavinyl equivalents as building blocks in organophosphorus synthesis. Thus, treatment of bromocatecholborane with one equivalent of CyP=C(*t*Bu)MgCl (**46a**) cleanly afforded compound **48** as a waxy solid. Analytically pure samples of the borylated phosphaalkene were obtained by sublimation (Scheme 24) [26].

The preparation of a series of homoleptic triphosphavinyl-group 13 compounds was attempted by reaction of three equivalents of **46a** with the appropriate group 13 halide (Scheme 25) [27]. Unexpectedly, the reactions afforded the novel diphospha-metallobicyclo[1.1.1]pentane derivatives **51a**–**c** in low to moderate yields.

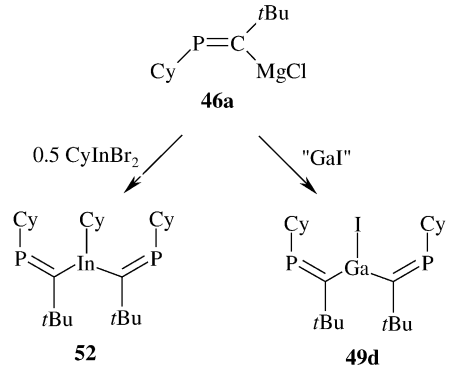


Scheme 24. Formation of borylated phosphaalkene.



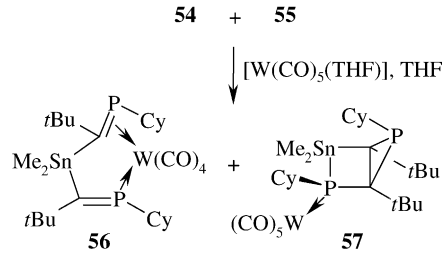
49-51	M
a	Al
b	Ga
c	In

Scheme 25.



Scheme 26. Preparation of compounds **49d** and **52**.

Although there was no spectroscopic evidence for any intermediate, it was believed that the metal halide initially reacted with two equivalents of **46a** to yield intermediate **49**, which subsequently underwent an intramolecular phosphavinyl coupling reaction to give **50**. Reaction of **50** with a third equivalent of the phospha-Grignard reagent furnished the final products **51a–c**. Molecules featuring the structural motif of **49** were synthesized independently. Treatment of two

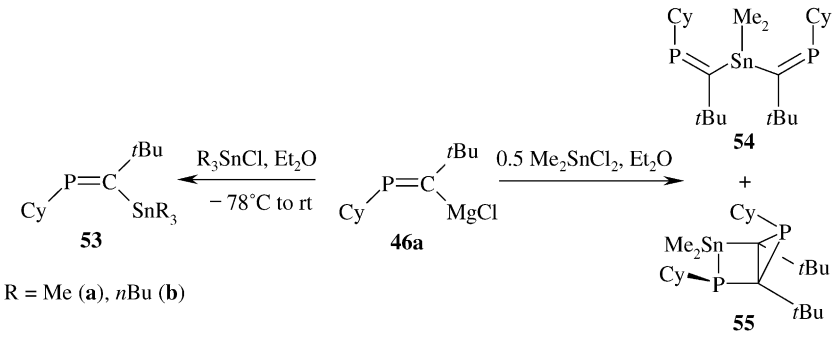


Scheme 28. Carbonyl tungsten complexes of **54** and **55**.

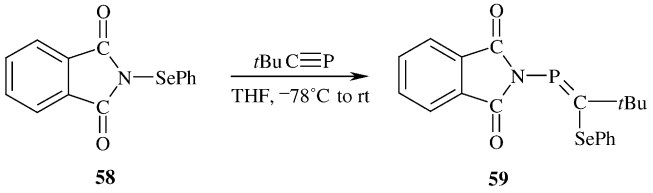
equivalents of **46a** with in situ generated $CyInBr_2$ in toluene afforded the bis(phosphaalkenyl)indium derivative **52** as a thermally stable compound in 40% yield. It was assumed that the bulky cyclohexyl groups prevented the compound from the type of cyclization, encountered with **49a–c** [27].

An iodo analogue of **49b** resulted when **46a** was allowed to react with an equimolar amount of the so-called galliummonoiodide. This was freshly formed via the sonication of gallium metal and half an equivalent of I_2 in toluene (Scheme 26). During the course of this transformation gallium metal was deposited indicating that redistribution and disproportion reactions of the postulated initial product Ga{C(*t*Bu)=PCy} occurred. The corresponding monohalides InCl and TlCl did not exhibit such a behavior. In both cases, the reaction with **46a** led to metal deposition and high yield formation of 2,4-diphosphabicyclobutane $Cy_2P_2C_2tBu_2$. Clearly, this synthetic principle of transmetalating *C*-magnesio-phosphaalkenes has limits. It is interesting to note that iodine derivative **49d** resists reaction with **46a** to give **51b** [26].

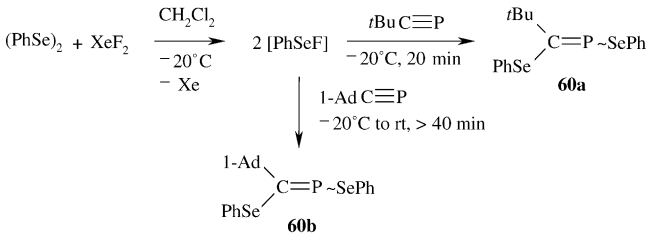
Treatment of **46a** with trimethyl- or tributyl-chlorostannane in diethyl ether at −78 °C led to the straightforward formation of the stannylated phosphaalkenes **53** (Scheme 27) [26]. Reaction of $SnMe_2Cl_2$ with two equivalents of **46a** in diethyl ether yielded an inseparable mixture of products **54** and **55**. Reaction of this mixture with an excess of $[W(CO)_5THF]$ in THF and chromatography of the products led to the isolation of orange crystalline bis(phosphavinyl)tin derivative **56** and the yellow crystalline complex **57** of the stannadiphosphabicyclo[2.1.0]pentane in moderate yields (Scheme 28) [28].



Scheme 27.



Scheme 29. Preparation of phosphaalkenyl selenium compound **59**.



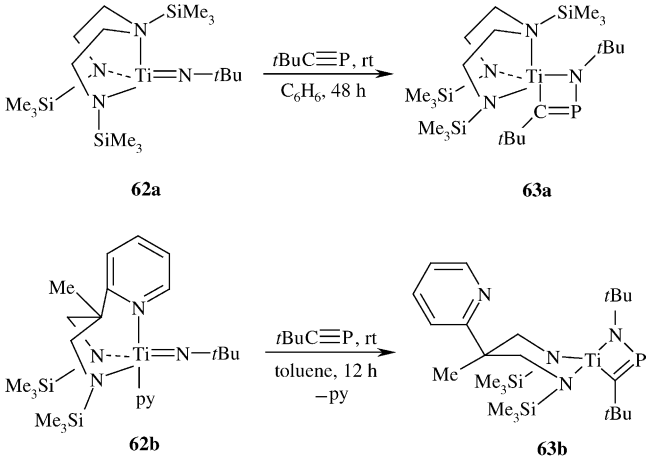
Scheme 30. Synthesis of **60a,b**.

The 1,2-addition of organometallics to the PC triple bond as a synthetic principle for *C*-metallophosphaalkenes was extended to selenium chemistry. A 62% yield of the yellow crystalline phosphaalkenyl selenium derivative **59** was obtained by treatment of *t*BuC≡P with an equimolar amount of *N*-phenylselenylphthalimide **58** in THF in the temperature range –78 ° to 20 °C (Scheme 29) [26].

The phosphaalkene **60a** was observed within 20 min when a solution of equimolar amounts of diphenyl diselenide and xenondifluoride in dichloromethane was treated at −20 °C with two equivalents of *t*BuC≡ P. The corresponding reaction with the sterically more crowded adamantylphosphaethyne was considerably slower. After warming to 20 °C and stirring for 40 min, the conversion to **60b** was only 75%. Due to the thermolability of these products, their characterization was limited to spectroscopic evidence (Scheme 30) [29].

As already discussed in Scheme 14, *C*-selenated phosphaalkenes were formed as minor products during the reaction of phosphaalkynes with phenylselenyl halides, the main products being the *P*-selenated isomers. Interestingly *P*-selenated phosphaalkene **23a** was converted into the *C*-selenated derivative **61** by reaction with *t*BuLi. This transformation was rationalized by the initial replacement of phenyl selenide and the intermediacy of LiSePh and *t*BuP=C(Cl)*t*Bu [17] (Scheme 31).

[2 + 2]-Cycloaddition reactions of bulky titanium imides **62a,b** and *t*BuC≡ P gave rise to the formation of four-membered heterocycles **63a,b** with the structural features of *C*-titaniophosphaalkenes (Scheme 32) [30,31].



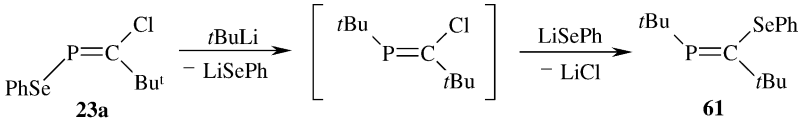
Scheme 32. Synthesis of *C*-titaniophosphaalkenes **63a** and **63b**.

Similarly, the co-thermolysis of zirconium amido complex **64** and *t*BuC≡ P in toluene at 100 °C afforded the *C*-zirconiophosphaalkene **66** as orange crystals in 45% yield. This process invoked the intermediacy of the highly reactive zirconium imide **65** (Scheme 33) [30].

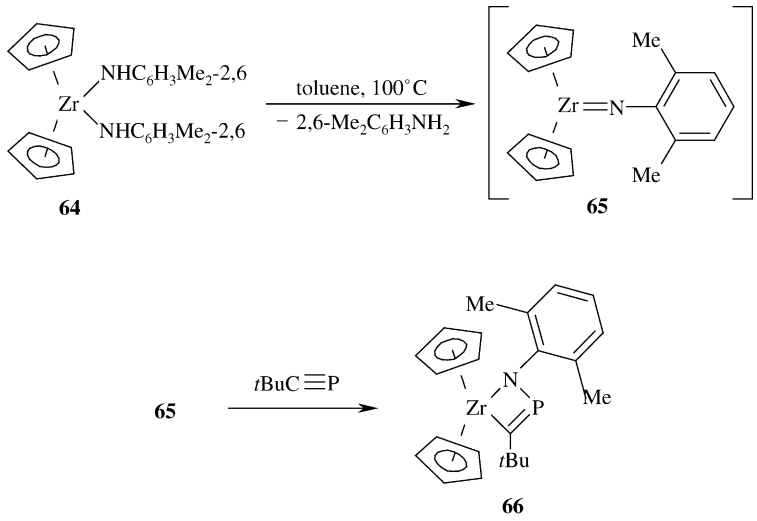
In contrast to the analogous sulfido- and selenido-zirconium complexes (Scheme 13), the reaction of [Cp^*_2Zr(Te)(py)] (**21c**) with *t*BuC≡ P in toluene produced the heterocycle **67** featuring a Zr–C bond instead of the Zr–P linkage observed in phosphaalkenes **22a** (E = S) and **22b** (E = Se) (Scheme 34) [16].

Reactions of equimolar amounts of a phosphaalkyne R–C≡ P (**68**) with *t*butylimido-vanadium(V)trichloride proceeded through [2 + 2] cycloaddition of the P≡ C triple bond to the metal–nitrogen multiple bond to give the 1,2,4-azaphosphavanada(V)cyclobutenes **69a**–**e**, which are stable at room temperature (Scheme 35) [32].

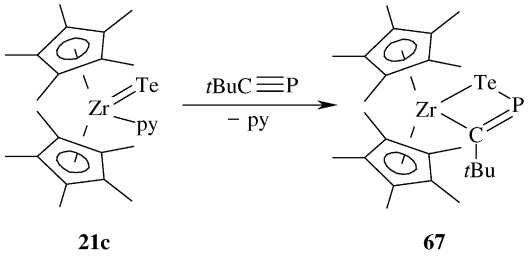
The success of this protocol is dependent on the substituents at the nitrogen atom of the imido compound and on the stoichiometry. Thus, the complexes $R^2N = VCl_3$ with tertiary alkyl groups on the N atom form stable addition products with the phosphaalkynes, whereas with primary and secondary substituents they initially formed four membered rings, analoguous to **69**. Then, they underwent decomposition to afford 1*H*-1,2,4-azadiphospholes. Cyclization reactions can also be applied to the easily accessible bis(*tert*-butylimido)chromium(VI)dichloride **70**. Treatment of **70** with an equimolar amount of *t*BuC≡ P resulted in the quantitative formation of metallocycle **71**. In contrast to the related vanadium chemistry, neither the reaction temperature nor the stoichiometry has a signifi-



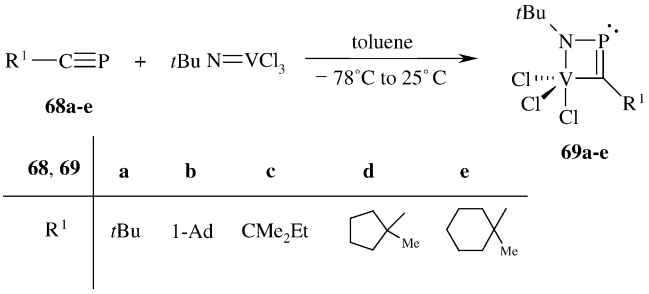
Scheme 31. Synthesis of **61**.



Scheme 33. Preparation of *C*-zirconiophosphaalkene **66**.

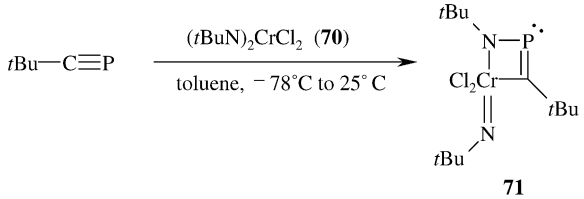


Scheme 34. Preparation of *C*-zirconiophosphaalkene **67**.



Scheme 35. Synthesis of cyclic *C*-vanadiophosphaalkenes.

cant effect. The possible second addition to the remaining multiple bond in **71** was not observed, even in the presence of a large excess of *t*BuC≡ P (Scheme 36) [32].



Scheme 36. Preparation of a cyclic *C*-chromiophosphaalkene.

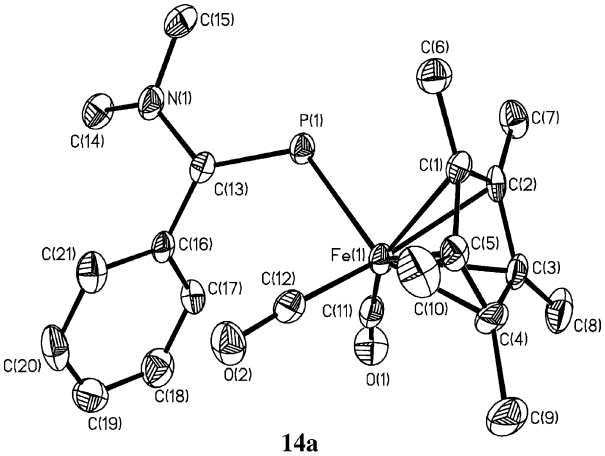
3. Structures and bonding properties

3.1. Molecular structures of metallophosphaalkenes

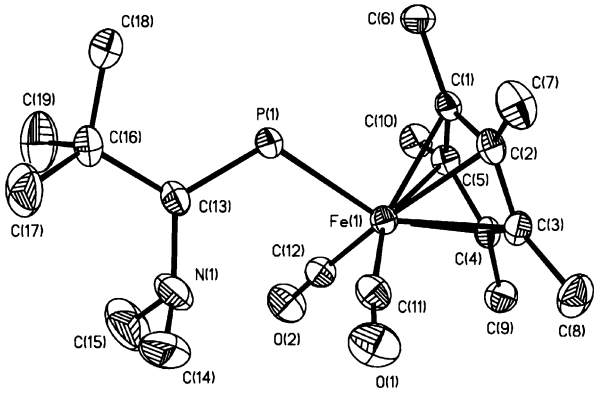
As previously discussed, the most noticeable structural change that a classical phosphaalkene undergoes on exchanging an organic substituent on the phosphorus atom for a transition metal complex fragment is the opening of the valence angle on the phosphorus atom [6].

In $HP{=}CH_2$, the calculated value for the angle H–P–C is 97.4° [33], whereas in *P*-metallophosphaalkenes the angle M–P–C varies from 113.8(2)° in [(*Z*)-$Cp(CO)_2FeP{=}C(OSiMe_3)(tBu)$] [34] to 126.2(3)° in the complex [$Cp^*(CO)_2FeP{=}C(SiMe_3)_2$] [35]. This region includes the angles Fe–P–C13 in **14a** [118.9(1)°] and in **14b** [117.0(1)°] [11]. For comparison in phosphaalkenes with organic substituents, this angle usually varies between 100° and 114° depending on the steric demand of the substituents [36]. In the *C*-lithiophosphaalkene (*Z*)-**25e** [18] and in the *C*-magnesiophosphaalkene **46a** [24] C–P–C angles of 115.36(7)° and 106.49(8)°, respectively, have been measured (Fig. 1).

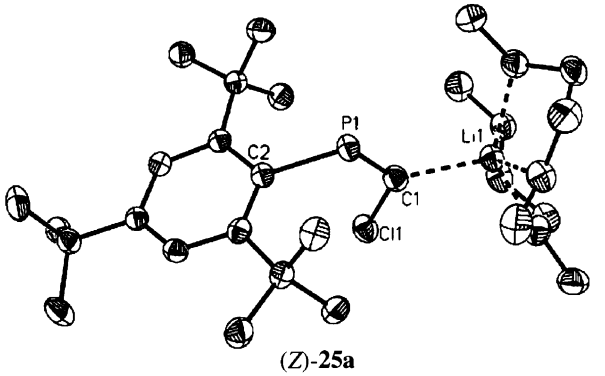
Ferriophosphaalkenes **14a** and **14b** differ significantly about the geometry at the P=C double bond. In **14a**, a trigonal planar dimethylamino group is located in *trans*-disposition to the iron atom, which allows efficient π-conjugation of the lone pair of the electrons at the N-atom and the double bond. This leads to an elongated PC bond length of 1.717(4) Å, when compared with the calculated bond length in $HP{=}CH_2$ (1.673 Å) and the corresponding value in [(*E*)-$Cp^*(CO)_2FeP{=}C(SiMe_3)Ph$] [1.665(6) Å] [11]. Transfer of electron density onto the P-atom of **14a** causes a repulsion between the electron abundant atoms P and Fe which is evident by a lengthened Fe–P bond [2.316(1) Å] in comparison to that in [(*E*)-$Cp^*(CO)_2FeP{=}C(SiMe_3)Ph$] [2.269(2) Å]. In contrast, the sterically demanding substituents at the P=C–bond in **14b** are in trans-disposition. This prevents



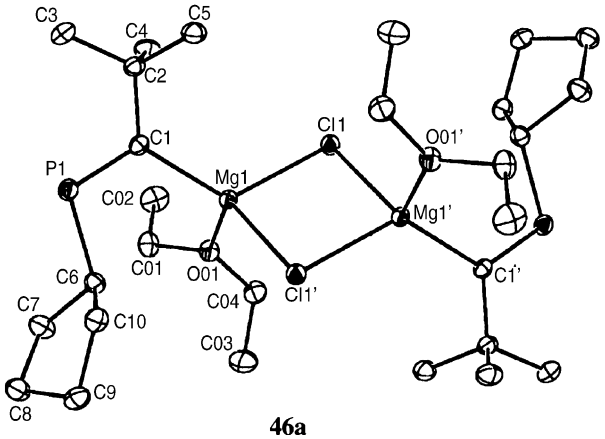
14a



14b



(*Z*)-**25a**



46a

the amino group from attaining a coplanar arangement with the P=C bond and from π-conjugation. Accordingly, the P=C bond in **14b** [1.697(3) Å] is shorter. Due to the lack of additional electron density on the P atom the bond length Fe–P in **14b** [2.276(1) Å] is significantly shorter than in **14a** and is similar to that in [(*E*)-Cp*$(CO)_2$Fe–P=C($SiMe_3$)Ph]. The P–C1 and C1–Cl separations in (*Z*)-**25a** [1.6769(15) and 1.778(2) Å] compare to the corresponding bond lengths in the phosphaalkene Mes*–P=C(Cl)PCl_2, which exhibits the same *Z*-configured C_{aryl}–P=C–Cl skeleton as that of (*Z*)-**25a**. The bulky aryl substituent and the Li-atom occupy *trans*-positions. The Li atom is further ligated by two DME molecules whose four oxygen atoms are located at the basal positions of a square pyramid. The apical C1–Li bond length of 2.128(3) Å matches with the corresponding distances in structurally comparable lithium organyls and suggests a weakly bonding interaction between these atoms. The molecule was interpreted as a donor–acceptor complex between a phosphavinylidene anion and the lithium ion [19].

Magnesiophosphaalkene **46a** is dimeric through symmetrical Mg–Cl–Mg bridges and crystallizes as its (*Z*)-isomer. The P–C1 bond length [1.6725(19) Å] is in the normal range for fully localized P=C double bonds and close to that seen in (*Z*)-**25a**. The Mg–C bond lengths in **46a** [2.1126(19) Å] compare to that in the structurally characterized Grignard compound [{Mg(Et)(*i*Pr_2O)Br}$_2$] [2.094(11) Å] [37].

3.2. NMR spectra

Characteristic ^{31}P and ^{13}C NMR spectra for selected compounds are summarized in Table 1.

Generally, the ^{31}P NMR chemical shifts of phosphaalkenes vary in the wide range between $\delta = -99.9$ ppm for (*Z*)-HP=C(F)NMe_2 [38] and $\delta = 740.5$ ppm for the nickel compound [Cp*(PEt_3)Ni–P=C($SiMe_3$)$_2$] [35]. The ^{31}P NMR data of compounds featuring low-coordinate phosphorus are compiled in several reviews [2d,6,39,40]. In spite of the problems associated with the theoretical collation and interpretation of these large differences in shift, some trends can be discerned for phosphaalkenes in general and for such representatives with metal-substituents in particular. Basically, there are two major contributions to the ^{31}P chemical shift, namely a diamagnetic contribution reflecting the electron density associated with the low-coordinate P-atom and another contribution, which is deter-

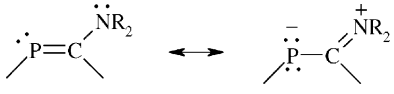
Fig. 1. Crystal structures of the metallophosphaalkenes **14a**, **14b**, (*Z*)-**25a** and **46a**. Selected bond lengths [Å] and angles [°]: **14a**: P–C13 1.717(4), Fe–P 2.316(1), N–C13 1.399(4), Fe–P–C13 118.9(1); **14b**: P–C13 1.697(3), Fe–P 2.276(1), N–C13 1.448(4), Fe–P–C13 117.0(1); (*Z*)-**25a**: P–C1 1.6769(15), C1–Cl1 1.7779(15), C1–Li 2.128(3), P–C2 1.8723(14), C1–P1–C2 115.36(7), P1–C1–Cl 120.52(8), P1–C1–Li 122.44(10), Cl–C1–Li 117.01(10); **46a**: P–C1 1.6725(19), C1–Mg 2.1126(19), P–C(6) 1.861(2), Mg–Cl1 2.4177(18), Mg–Cl1′ 2.4132(14), C1–P–C6 106.49(8).

Table 1
^{13}C and ^{31}P NMR spectroscopic data of selected metallophosphaalkenes

Compound		$\delta^{31}P$	$\delta^{13}C$	$^{1}J_{P,C}$ (Hz)	Reference
[Fe]–P=C(SSiMe$_3$)$_2$	**(2)**	509	n.d.		[7]
(*E*)-[Fe]–P=CH–N(Ph)N=C(NMe$_2$)$_2$	**(8)**	204.9	176.0	69.2	[8]
[Fe]–P=C(NMe$_2$)$_2$	**(6a)**	135.5	199.5	99.4	[41]
[Ru]–P=C(NMe$_2$)$_2$	**(6b)**	121.2	201.4	92.6	[41]
(*E*)–[Fe]–P=C(Ph)NMe$_2$	**(14a)**	232.0	199.8	84.3	[11]
(*Z*)–[Fe]–P=C(*t*Bu)NMe$_2$	**(14b)**	409.0	217.3	75.3	[11]
(*E*)–[Fe]–P=C(Ph)NC$_5$H$_{10}$	**(14d)**	256.4	201.3	82.9	[11]
[Ru(P=CH*t*Bu)Cl(CO)(PPh$_3$)$_2$]	**(16a)**	450.4	184.9	58.9	[12]
[Ru(=CH*t*Bu)Cl(CS)(PPh$_3$)$_2$]	**(16b)**	445.2	183.2	57.1	[12]
[Ru(P=CH*t*Bu)I(CO)(PPh$_3$)$_2$]	**(16c)**	462.7	n.d.	n.d.	[13]
[{Ru*]}$_2${μ–P=CH–C(C$_6$H$_4$)$_3$CC(H)=P}]	**(16d)**	516.7	n.d.		[14]
[Ru(P=CH*t*Bu)Cl(CO)$_2$(PPh$_3$)$_2$]	**(16e)**	369.5	196.8	62.5	[12]
[Ru(P=CH*t*Bu)Cl(CNCMe$_3$)(CO)(PPh$_3$)$_2$]	**(16f)**	389.8	n.d.	n.d.	[12]
[Ru(P=CH*t*Bu)Cl(CNC$_6$H$_3$Me$_2$-2,6)(CO)(PPh$_3$)$_2$]	**(16g)**	391.0	195.1	64.2	[13]
[Ru(P=CH*t*Bu)(CNCMe$_3$)$_2$(CO)(PPh$_3$)$_2$]Cl	**(16h)**	336.8	n.d.	n.d.	[12]
[Ru(P=CH*t*Bu)(CO)(PPh$_3$)([9]aneS$_3$)]Cl	**(16i)**	357.7	204.5	64.3	[12]
[Ru(P=CH*t*Bu)(S$_2$CNEt$_2$)(CS)(PPh$_3$)$_2$]	**(16j)**	387.6	190.0	62.5	[12]
[Ru(P=CH*t*Bu)(O$_2$CH)(CO)(PPh$_3$)$_2$]	**(16k)**	426.5	187.4	59.2	[12]
[Cp*$_2$Zr–P=C(S)*t*Bu]	**(22a)**	380	191	104	[16]
[Cp*$_2$Zr–P=C(Se)*t*Bu]	**(22b)**	388	184.3	110	[16]
(*E*)-PhSeP=C(Cl)*t*Bu	**(23a)**	180.5	192.6	94.3	[17]
[(*Z*)-Mes*P=C(Cl){Li(dme)$_2$}]	**((*Z*)-25a)**	240.3	257.4	99.2	[19]
(*E*)-Mes*P=C(Cl)(HgCl)	**(31)**	281	178.6	98.1	[20]
{(*E*,*E*)-Mes*P=C(Cl)}$_2$Hg	**(34)**	277	197.1	91.7	[20]
{(*E*,*E*)-Mes*P=C(SPh)}$_2$Hg	**(36a)**	231.2	211.1	84.3	[21]
(*E*)-Mes*P=CH–Ge(F)Mes$_2$	**(40)**	334.7	169.9	86.6	[22]
[(*Z*)-*c*C$_5$H$_9$P=C(*t*Bu)MgCl(OEt$_2$)]$_2$	**(46b)**	328	198.4	43	[24]
[MesP=C(*t*Bu)MgBr(OEt$_2$)]$_2$	**(46d)**	309	203.9	44	[24]
[*i*PrP=C(*t*Bu)MgCl(OEt$_2$)]$_2$	**(46e)**	339.4	262.1	72.1	[25]
[*t*BuP=C(*t*Bu)MgBr(OEt$_2$)]$_2$	**(46f)**	355.1	258.9	69.6	[25]
[*c*C$_6$H$_{11}$P=C(*t*Bu)Bcat]	**(48)**	322.3	198.3	45.0	[26]
(*c*C$_6$H$_{11}$P)$_2$(*t*BuC)$_2$Al–C(*t*Bu) = P*c*C$_6$H$_{11}$	**(49a)**	353	n.d.	n.d.	[27]
(*c*C$_6$H$_{11}$P)$_2$(*t*BuC)$_2$Ga–C(*t*Bu) = P*c*C$_6$H$_{11}$	**(49b)**	333	n.d.	n.d.	[27]
(*c*C$_6$H$_{11}$P)$_2$(*t*BuC)$_2$In–C(*t*Bu) = P*c*C$_6$H$_{11}$	**(49c)**	329	n.d.	n.d.	[27]
{*c*C$_6$H$_{11}$P=C(*t*Bu)}$_2$GaI	**(49d)**	307.2	226.0	64.6	[26]
{*c*C$_6$H$_{11}$P=C(*t*Bu)}$_2$In–*c*C$_6$H$_{11}$	**(52)**	329	n.d.	n.d.	[27]
*c*C$_6$H$_{11}$P=C(*t*Bu)SnMe$_3$	**(53a)**	325.2	219.5	68.1	[26]
{*c*C$_6$H$_{11}$P=C(*t*Bu)}$_2$SnMe$_2$	**(54)**	299	n.d.	n.d.	[26]
(*Z*)-N-phthalimido–P=C(*t*Bu)(SePh)	**(59)**	237.7	166.0	64.2	[26]
*t*BuP=C(*t*Bu)(SePh)	**(61)**	360.5	191.9	79.3	[17]
Cl$_3$V–N(*t*Bu)P=C(*t*Bu)	**(69a)**	−73.0	314.2		[32]

[Fe] = [(η^5-C$_5$Me$_5$)(CO)$_2$Fe]; [Ru] = [(η^5-C$_5$Me$_5$)(CO)$_2$Ru]; [Ru*] = [RuHCl(CO)(PPh$_3$)$_2$]; n.d. not determined, [9]aneS$_3$ = 1,4,7-trithiacyclononane.

mined by the HOMO–LUMO gap of the molecule. Small HOMO–LUMO gaps in *P*-metallophosphaalkenes, such as in the previously mentioned nickel complex or the complex [Cp*(CO)$_2$FeP=C(SiMe$_3$)Ph] (δ = 520.7 ppm) [35b], give rise to significant low-field shifts. The large valence angle at phosphorus [119.3(2)°] in the latter compound indicates that the energy of the non-bonding orbital as the HOMO is raised by sp^{2-} hybridization, whereas the energy of the LUMO, the π* orbital, remains essentially unaffected. A second component to the ^{31}P NMR shift has to be considered in amino- and bis(amino)-functionalized representatives where π-conjugation of the nitrogen lone pair with the P=C double bond operates in addition to the paramagnetic contribution. As a consequence of the three-center four-π-electron system, the phosphorus atom β to the nitrogen atom experiences additional negative charge, which causes a pronounced shielding.



This is evident in compounds [Cp*(CO)$_2$FeP=C(NMe$_2$)$_2$] (**6a**) (δ^{31}P = 135.5 ppm), (*E*)-[Cp*(CO)$_2$FeP=C(Ph)NMe$_2$] (**14a**) (δ^{31}P = 232.0 ppm) and [(*E*)-Cp*(CO)$_2$Fe–P=C(Ph)NC$_5$H$_{10}$] (**14d**) (δ^{31}P = 256.4 ppm), where planar three-

center four-π-electron systems are given. It is also obvious that replacement of one amino group with a phenyl substituent is accompanied by a low-field shift of $\Delta\delta$ = 96.5 ppm. Deshielding of the ^{31}P NMR signal by $\Delta\delta$ = 24.4 is observed in going from a dimethylamino group (**14a**) to the related species (**14d**) featuring a piperidyl ring further. For steric reasons, such a π-conjugation between the amino group and the P=C bond is absent in [(*Z*)-Cp*(CO)$_2$FeP=C(*t*Bu)NMe$_2$] (**14b**) (δ^{31}P = 409.0 ppm), resulting in a significant low-field shift of the ^{31}P resonance, in comparison to **14a** ($\Delta\delta^{31}$P = 177 ppm). π-Conjugation between lone pairs of electrons of the sulfur atoms and the P=C bond in **2** seems ineffective and leads to a low-field resonance at δ^{31}P = 509 ppm.

The influence of the substituent at phosphorus on the ^{31}P chemical shift is obvious in the homologous compounds [Cp*(CO)$_2$Fe–P=C(NMe$_2$)$_2$] (**6a**) (δ^{31}P = 135.5 ppm) and [Cp*(CO)$_2$Ru–P=C(NMe$_2$)$_2$] (**6b**) (δ^{31}P = 121.2 ppm). Such a shielding in going from 3d via 4d to 5d-metallophosphaalkenes was already described in a previous review.

Particularly interesting is the role of the coordination number at the ruthenium atom in rutheniophosphaalkenes **16** plays with respect to the ^{31}P chemical shift. Complexes [Ru(P=CH*t*Bu)Cl(CO)(PPh$_3$)$_2$] (**16a**) (δ^{31}P = 450.4 ppm), [Ru(P=CH*t*Bu)Cl(CS)(PPh$_3$)$_2$] (**16b**) (δ^{31}P = 445.2 ppm), [Ru(P=CH*t*Bu)-I(CO)(PPh$_3$)$_2$] (**16c**) (δ^{31}P = 462.7 ppm) and [{(Ph$_3$P)$_2$(CO)ClRu}$_2${μ-P=C(H)C(C$_6$H$_4$)CC(H)=P} (**16d**) (δ^{31}P = 516.7 ppm) with five-coordinate Ru-atoms in a square-pyramidal environment give rise to ^{31}P NMR signals for the P=C unit at much lower field than in related molecules with six-coordinate ruthenium, such as [Ru(P=CH*t*Bu)Cl(CO)$_2$(PPh$_3$)$_2$] (**16e**) (δ^{31}P =369.5 ppm), [Ru(P=CH*t*Bu)Cl(CNCMe$_3$)(CO)(PPh$_3$)$_2$] (**16f**) (δ^{31}P = 389.8 ppm) and [Ru(P=CH*t*Bu)(S$_2$CNEt$_2$) (CS)(PPh$_3$)$_2$] (**16j**) (δ^{31}P = 387.6 ppm).

The unipositive charge on six coordinate rutheniophosphaalkenes such as [Ru(P=CH*t*Bu)(CNCMe$_3$)$_2$(CO)(PPh$_3$)$_2$]$^+$Cl$^-$ (**16h**) (δ^{31}P = 336.8 ppm) gives rise to an additional high field shift of $\Delta\delta$ = 53 ppm. In *C*-metallated phosphaalkenes, ^{31}P NMR chemical shifts range from δ^{31}P = 231.2 ppm in {(*E*/*E*)-Mes*P=C(SPh)}$_2$Hg (**36a**) to δ^{31}P = 360.5 ppm in *t*BuP=C(*t*Bu)SePh (**61**). Interestingly, in the cyclic *C*-vanadiophosphaalkene a ^{31}P NMR signal at δ = −73.0 ppm indicates a considerable accumulation of negative charge at the phosphorus atom and a positive charge on the ring carbon atom (δ^{13}C = 314.2 ppm) as it is familiar in phosphaalkenes with an inverse distribution of electron density about the P=C bond. Generally, the ^{13}C NMR spectra of metallophosphaalkenes show characteristic doublets for the tricoordinate carbon atom of the PC double bond ranging from δ^{13}C = 176.0 ppm in [Cp*(CO)$_2$FeP=CHN(Ph)N=C(NMe$_2$)$_2$] (**8**) to 262.1 in [*i*PrP=C(*t*Bu)MgCl(OEt$_2$)]$_2$ (**46a**). $^1J_{P,C}$-coupling constants vary from 43 Hz in [*c*C$_5$H$_9$P=C(*t*Bu)MgCl(OEt$_2$)]$_2$ (**46b**) to 110 Hz in Cp*$_2$Zr–P=C(Se)*t*Bu (**22b**).

4. Reactivity

Metallophosphaalkenes of the types **I** and **II** are polyfunctional molecules featuring a number of reactive sites for chemical transformations.

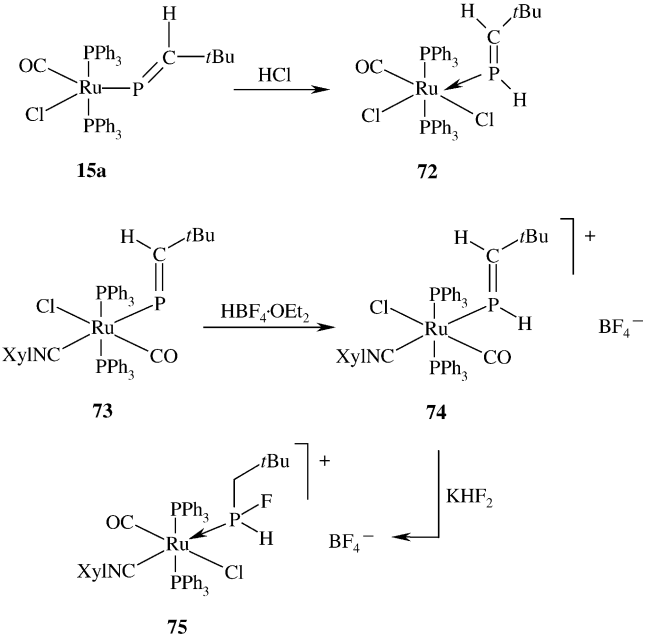
4.1. Reactivity of P-metallophosphaalkenes

4.1.1. Protic reagents

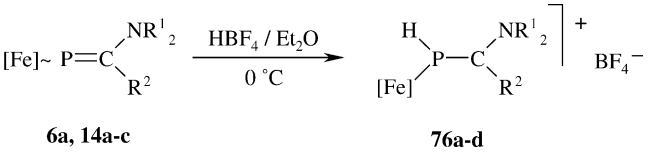
The nucleophilicity of the phosphaalkenyl ligand of the complex **15a** has been demonstrated in its reactivity with HCl to provide the phosphaalkene complex **72** (Scheme 37) [12].

The coordinatively saturated rutheniophosphaalkene **73** is protonated by ethereal HBF$_4$ to afford the cationic phosphaalkene complex **74** [12]. Treatment of **74** with KHF$_2$ lead to the addition of HF across the P=C double bond resulting in the formation of phosphane complex **75** [42] (Scheme 37).

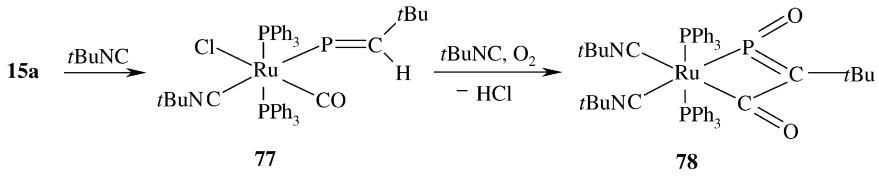
The reaction of equimolar amounts of [(η^5-C$_5$Me$_5$)(CO)$_2$Fe–P=C(NR$^1{}_2$)R^2] (**6a**, **14a–c**) and ethereal HBF$_4$ gave rise to the formation of [(η^5-C$_5$Me$_5$)(CO)$_2$FeP(H)C(NR$^1{}_2$)R^2]BF$_4$ (**76a–d**), which were isolated as light red powders (59-76%) (Scheme 38) [43a,b].



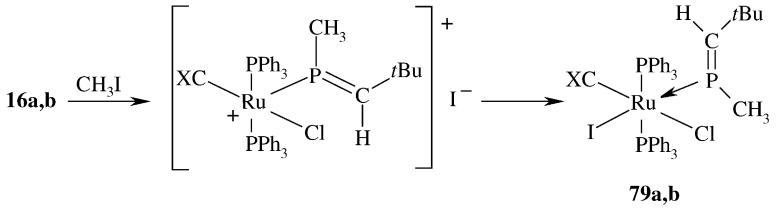
Scheme 37. Protonation of rutheniophosphaalkenes (Xyl = 2,6-Me$_2$C$_6$H$_3$).



Scheme 38. Protonation of ferriophosphaalkenes **6a** = (NR$^1{}_2$ = R^2 = NMe$_2$), **14a** (R^1 = Me, R^2 = Ph), **14b** (R^1 = Me, R^2 = *t*Bu), **14c** (NR$^1{}_2$ = NC$_5$H$_{10}$, R^2 = Ph).



Scheme 39. Formation of **78**.



Scheme 40. Reaction of **16a,b** with methyl iodide (X = O, S).

4.1.2. Chalcogens

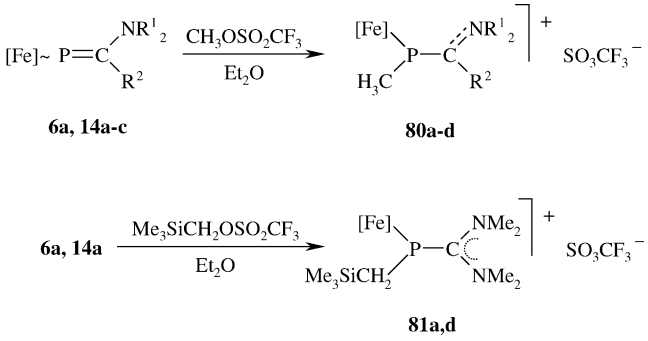
Reaction of the rutheniophosphaalkenes **15a** or [{Ru(P=CH*t*Bu)Cl(CN*t*Bu)(CO)(PPh_3)$_2$] (**77**) with an excess of *tert*-butylisocyanide under aerobic conditions afforded the novel λ^5-phosphaalkenyl complex **78** (Scheme 39). Notably the conversion of **15a** to **78** is accelerated by addition of a non-nucleophilic base such as DBU [44].

4.1.3. Alkylations

Complex **79a,b** featuring a η^1-phosphaalkene ligand was obtained by alkylating rutheniophosphaalkenes **16a** and **16b** with methyl iodide. Obviously, methylation occurred at phosphorus resulting in a transient complex cation which subsequently adds the iodide ion (Scheme 40) [45].

Alkylation of [(η^5-C_5Me_5)$(CO)_2$FeP=C(NR^1_2)R^2] (**6a**, **14a–c**) to afford salts **80a–d** was achieved by reaction with methyl trifluoromethanesulfonate. Similarly, **6a** and **14a–c** were converted to compound **81** by treatment with $Me_3SiCH_2OSO_2CF_3$ (Scheme 41) [43a,b].

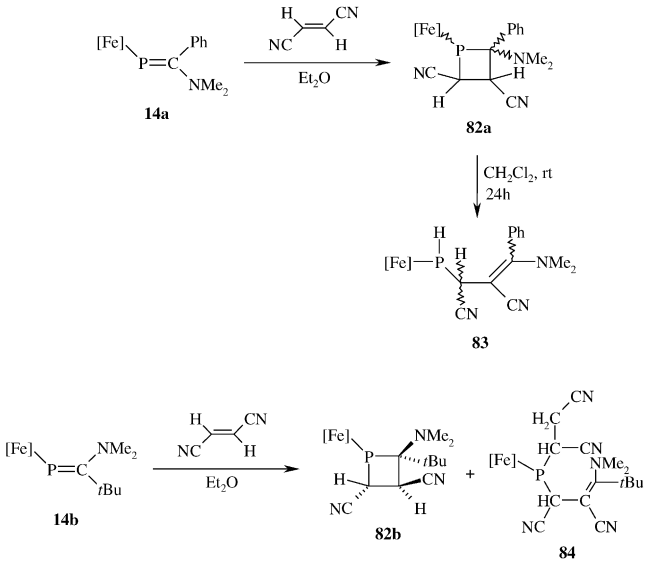
In contrast to alkylation product **79a** with the trigonal planar coordinated P-atom in salts **80** and **81**, the phosphorus adopts a trigonal–pyramidal configuration. Whereas in **79a** a genuine P=C double bond is present, in **80** and **81** the P–C distances have a bond order of unity.



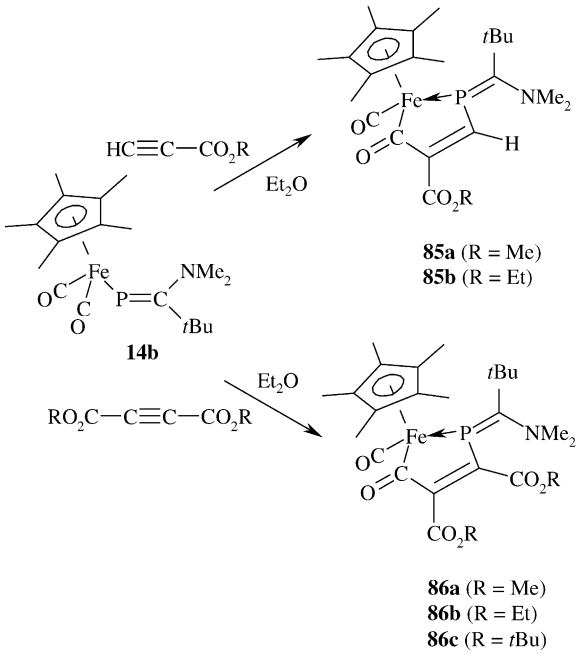
Scheme 41. Alkylation of ferriophosphaalkenes **6a** and **14a–c**.

4.1.4. Alkenes

Reaction of equimolar amounts of the ferriophosphaalkene [Cp*$(CO)_2$FeP=C(Ph)NMe_2] (**14a**) and fumarodinitrile in diethyl ether afforded the ferriophosphetane **82a** (77% yield). Analogously, [Cp*$(CO)_2$FeP=C(*t*Bu)NMe_2] (**14b**) was converted into **82b** (53% yield). Whereas the phosphetane ring of **82b** is retained in solution, in CH_2Cl_2 solution **82a** quantitatively isomerized to give the acyclic secondary ferriophosphane [Cp*$(CO)_2$FeP(H)–CH(CN)–C(CN)=C(Ph)NMe_2] (**83**) as a mixture of isomers. The ferriophosphane **84** was isolated in less than 1% yield from the reaction of **14b** and the alkene (Scheme 42) [46]. The formation of **84** invokes an interme-



Scheme 42. Reaction of **14a,b** with fumarodinitrile.



Scheme 43. Reaction of **14b** with alkyne esters.

diate analogous to **83** the PH bond of which adds across the C=C bond of a second molecule of fumarodinitrile.

4.1.5. Alkynes

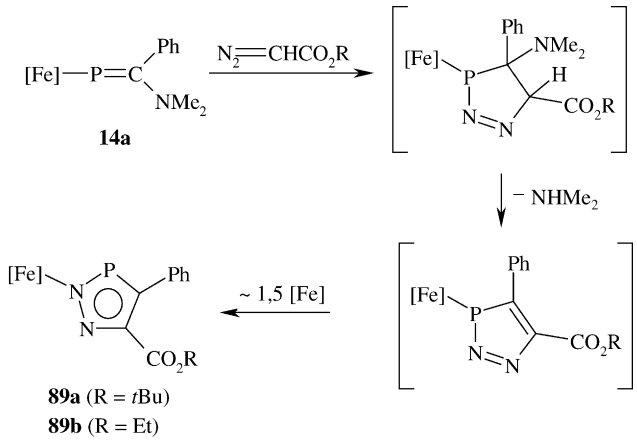
Compound **14b** was smoothly converted to the metallaheterocycles **85a,b** by treatment with propiolates H–C≡C–CO_2R (**a**: R = Me, 56%; R = Et, 72%) in diethyl ether. Similarly, complexes **86a–c** result from the phosphaalkene and acetylene dicarboxylates (66–85% yield) (Scheme 43) [47].

4.1.6. Azo and diazo compounds

From the reaction of equimolar amounts of **14a** and diethyl azodicarboxylate complex

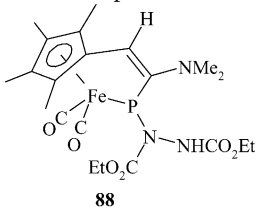
$[(C_5Me_4CH_2)(CO)_2FeP\{CHP(Ph)NMe_2\}N–(CO_2Et)N=C(CO_2Et)O]$

(**87**) was isolated as the result of a cheletropic [1 + 4] cycloaddition with subsequent transprotonation (Scheme 44) [48].



Scheme 45. Reaction of **14a** with diazoacetates.

This finding clearly contrasts the reaction of the azo compound with **6a** reported previously, which furnished the condensation product



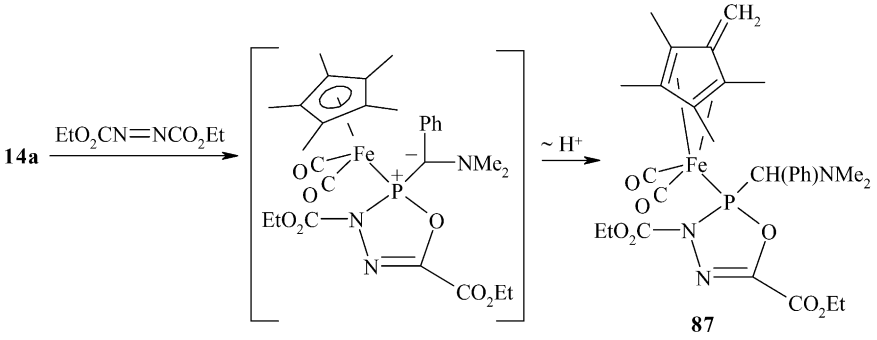
88 [49].

The diazoacetates N_2=$CHCO_2R$ (R = *t*Bu, Et) and **14a** gave rise to the formation of the N-metallated 1,2,3-diazaphospholes **89a,b** (Scheme 45) [48].

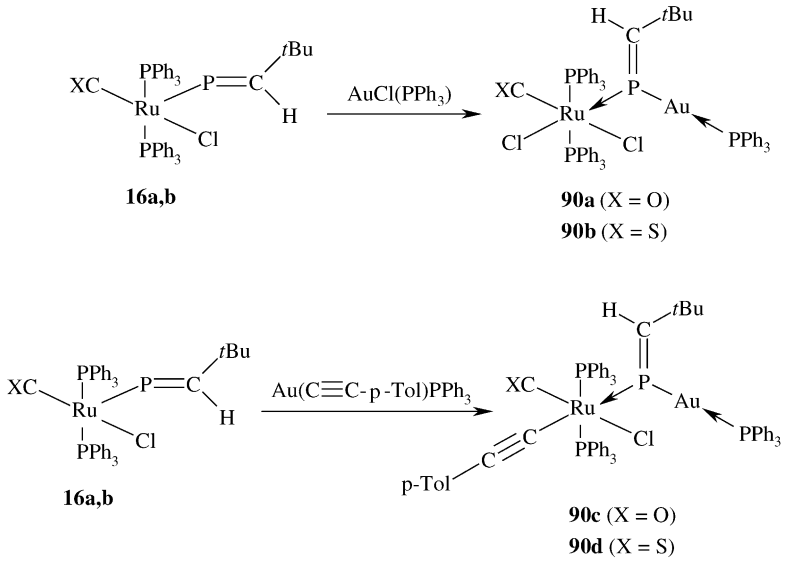
It is conceivable that the generation of products **89a,b** was initiated by a [3 + 2] cycloaddition, which was followed by amine elimination and a 1,5-shift of the complex iron fragment to form a 6π-electron system.

4.1.7. Metallations

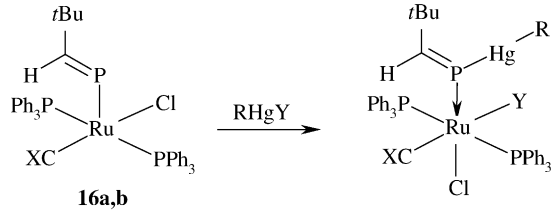
The nucleophilicity of the phosphaalkenyl ligand in the complex Ru(P=CH*t*Bu)Cl(CO)$(PPh_3)_2$ **16a** has been demonstrated in its reactivity towards HCl and methyl iodide. In terms of isolobal considerations, the fragment $AuPPh_3^+$ has come to be viewed as the organometal-



Scheme 44. Reaction of **14a** with diethyl azodicarboxylate.



Scheme 46. Auration of **16a,b**.



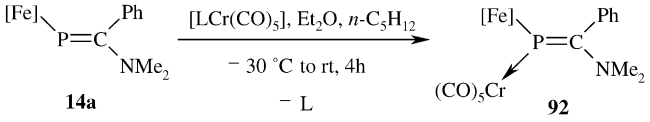
91	X	Y	R
a	O	Cl	Cl
b	S	Cl	Cl
c	O	I	Me
d	O	Cl	Ph
e	S	Cl	Ph
f	O	Cl	C_5H_4FeCp
g	S	Cl	C_5H_4FeCp

Scheme 47. Reaction of **15a,b** with mercury derivatives.

lic chemist's proton. In keeping with this, the reaction of **16a** and **16b** with AuY(PPh_3) (Y = Cl, C≡ C–*p*Tol) leads to the heterodinuclear phosphaalkene complexes [Ru{P(AuPPh_3)=CH*t*Bu}ClY(CX)(PPh_3)$_2$] **90a** (X = O, Y = Cl), **90b** (X = S, Y = Cl), **90c** (X = O, Y = C≡ C–*p*Tol), **90d** (X = S, Y = C≡ C–*p*Tol) via addition of the Au–Y bonds across the Ru–P linkage (Scheme 46) [50].

P-Mercuriophosphaalkenes **91** are available in high yield by the reaction of **16a,b** with mercury derivatives of the type R–Hg–Y (Scheme 47) [50,51].

The black complex [(η^5-C_5Me_5)$(CO)_2$FeP{Cr$(CO)_5$}C(NMe_2)Ph] **92** resulted from the combination of **14a** with [{(*Z*)-cyclooctene} Cr$(CO)_5$] (81% yield) (Scheme 48) [43a].



Scheme 48. Formation of complex **92**; [Fe] = Cp*$(CO)_2$Fe, L = cyclooctene.

4.2. Reactivity of C-metallophosphaalkenes

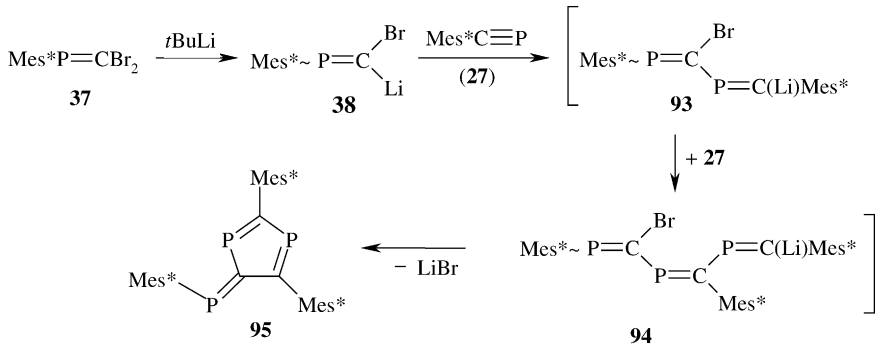
4.2.1. C-Lithiophosphaalkenes

Reaction of the dibromophosphaethene Mes*P=CBr_2 (**37**) with two equivalents of *tert*-butyllithium at −78 °C provided the lithium derivative **38**. Warming the reaction mixture to ambient temperature led to the formation of 1,3,6-triphosphafulvene **95** as the main product in 18% yield (Scheme 49) [52].

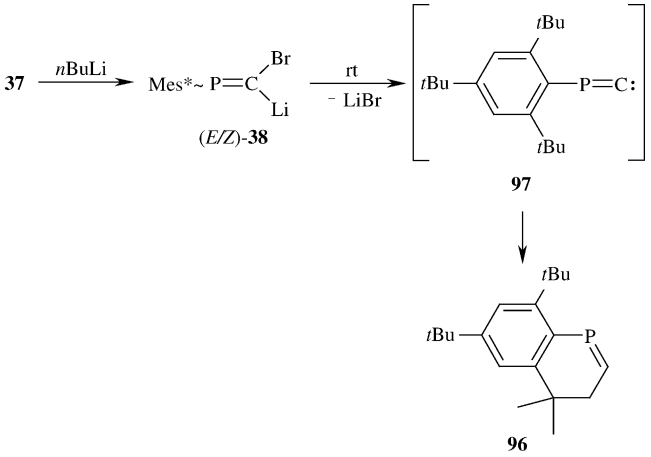
This result was rationalized by the initial formation of Mes*C≡ P (**27**) from intermediate **38** by a Fritsch–Buttenberg–Wiechell type rearrangement and the addition of two equivalents of **27** to **38** to give the transient lithio-1,3-5-triphosphahexatriene **94**. Cyclocondensation of **94** with extrusion of LiBr yields the observed product **95**.

This reaction was accompanied by the formation of trace amounts of 6,8-di-*tert*-butyl-4,4-dimethyl-1-phospha-3,4-dihydronaphthalene **96**. This compound was isolated in a separate experiment where a (*E*/*Z*)-mixture of **38** (1:5) was first generated from **37** by reaction with *n*-butyllithium in THF at −78 °C. When the mixed solution of (*E*)- and (*Z*)-**38** was warmed to ambient temperature, it turned violet and derivative **96** was isolated in 17% yield by silica-gel column chromatography (Scheme 50) [53].

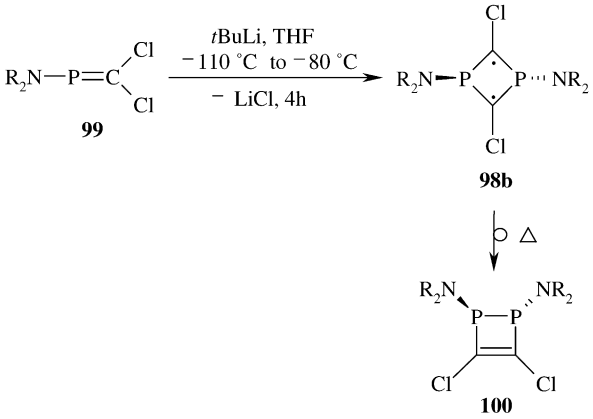
The initial formation of transient isophosphaalkyne **97** and insertion of the one-coordinate C-atom into CH-bond of a *tert*-butyl group was invoked to rationalize this result.



Scheme 49. Synthesis of 1,3,6-triphosphafulvene **93**.



Scheme 50. Synthesis of **96**.



Scheme 52. Synthesis of **98b** and rearrangement to 1,2-dihydro-1,2-diphosphete **100** NR_2 = 2,2,6,6-$Me_4C_5H_6N$.

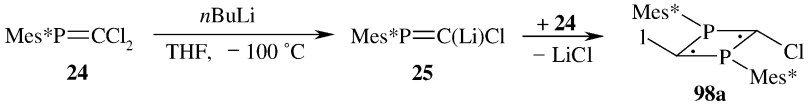
A different type of coupling was observed by Niecke et al. who treated a solution of the dichlorophosphaalkene **24** in THF at −100 °C with half an equivalent of *n*-butyllithium. Upon slow warming to room temperature, the color of the solution changed from yellow to dark red. 1,3-Diphosphacyclobutane-2,4-diyl **98a** was isolated from *n*-pentane as dark red crystals in 63% yield (Scheme 51) [54].

The corresponding reaction of phosphaalkene **99** with *tert*-butyllithium at −110 °C to −80 °C lead to the generation of dark violet **98b**, which was isolated in 70% yield at −80 °C. Attempted recrystallization from toluene at −30 °C afforded the isomeric 1,2-dihydro-1,2-diphosphete **100** (Scheme 52) [55].

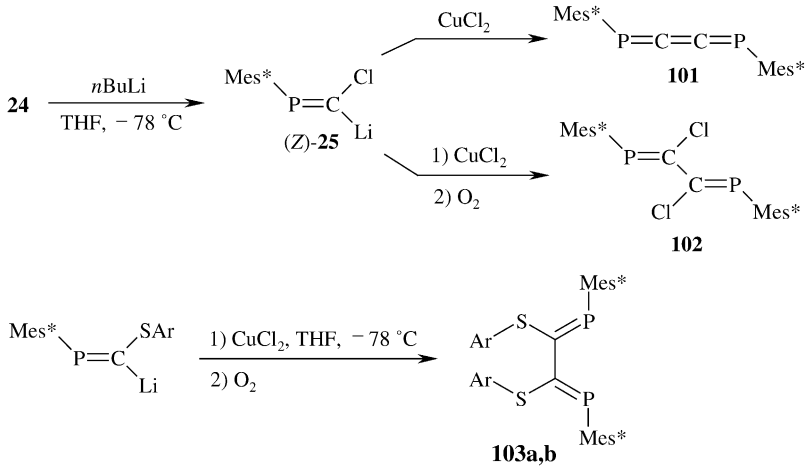
As discussed before, *C*-lithiophosphaalkenes are excellent candidates for transmetallations. However, transmetallation failed with $CuCl_2$ and coupling of two phosphaalkene units was observed instead. Thus, when 0.5 equivalents of copper(II)chloride was added to a freshly prepared THF solution of (*Z*)-**25** at −78 °C and the mixture was subsequently warmed up to room temperature, 1,4-diphospha-1,2,3-butatriene **101** was formed in 63% yield. If, however, oxygen gas was bubbled through the mixture of (*Z*)-**25** and 0.5 equivalents $CuCl_2$ at −78 °C 2,3-dichloro-1,4-diphospha-1,3-butadiene **102** was obtained instead (23% yield) (Scheme 53) [56].

The same reaction sequence was utilized in the generation of the arylthiosubstituted 1,4-diphosphabutadienes **103a** (Ar = Ph, 84% yield) and **103b** (Ar = *o*-Tol, 38 %) [21,57] (Scheme 53). The precursors Mes*P=C(Br)SAr were obtained by reacting **38** with diaryldisulfides [57].

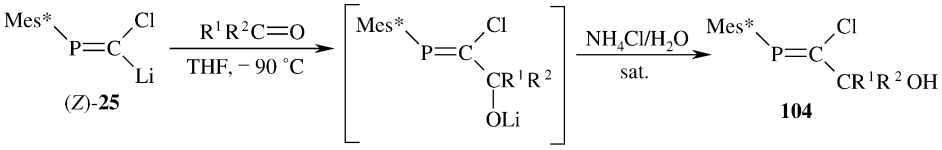
Lithium derivatives **25** and **38** have been reacted with a series of carbonyl compounds. Thus, treatment of **25** in a THF solution at −90 °C with aldehydes and ketones afforded the phosphaallylic alcohols **104** after an aqueous workup. The reaction of (*Z*)-**25** with acetophenone failed and protonation of the metallophosphaalkene was observed instead [20,58] (Scheme 54).



Scheme 51. Synthesis of diradical **98a**.

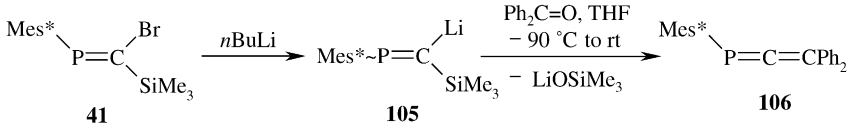


Scheme 53. Copper(II) mediated couplings of *C*-lithiophosphaalkenes.



104	carbonyl compound	yield
a	PhCHO	94
b	Ph_2CO	95
c	MeHC=CH-CHO	77
d	$(CH_2)_5CO$	29

Scheme 54. Reaction of (*Z*)-**25** with aldehydes and ketones.

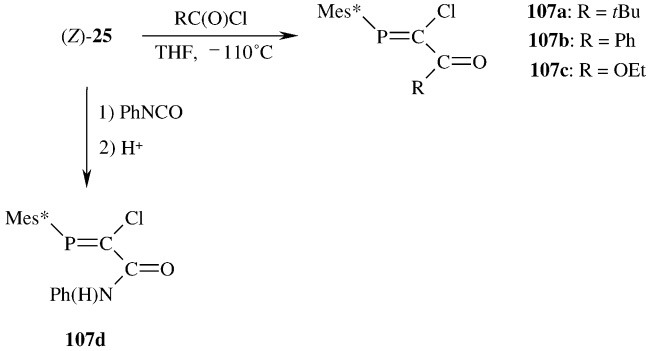


Scheme 55. Preparation of **106**.

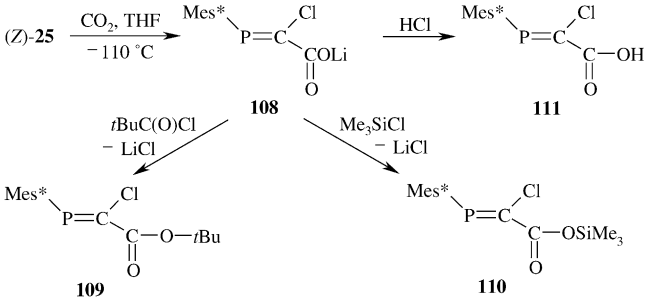
Condensation of lithium derivative **105** with benzophenone under comparable conditions yielded phosphaallene **106** (95%) in a Peterson-type olefination (Scheme 55) [20].

β-Phosphaenones **107a–d** are accessible by reacting (*Z*)-**25** with pivaloyl chloride, benzoyl chloride, ethyl chloroformate and phenyl isocyanate (74–81% yield) (Scheme 56) [58,59].

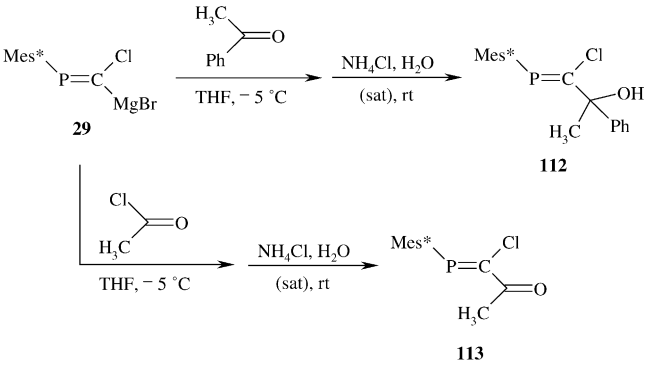
When carbon dioxide was sublimed into the reaction mixture containing (*Z*)-**25**, the novel β-phosphaacrylate anion **108** was formed. Addition of pivaloyl chloride to the reaction mixture containing **108** furnished the anhydride **109** as the only product in 76% yield. Addition of trimethylsilyl chloride gave the silylester **110** (82% yield). Acidification of **108** to yield acid **111** (85%) was achieved by addition of water, chloroform and HCl (Scheme 57) [59].



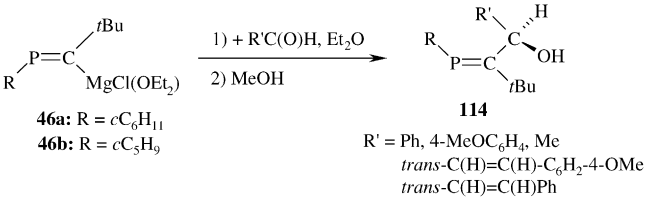
Scheme 56. Synthesis of β-phosphaenones **107a–d**.



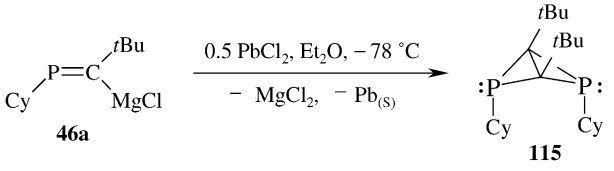
Scheme 57. Syntheses of phosphaacrylic acid derivatives from (*Z*)-**25**.



Scheme 58. Synthesis of **112** and **113** from **29**.



Scheme 59.



Scheme 60. Synthesis of **115**.

4.2.2. *C*-Magnesiophosphaalkenes

As discussed in Section 2.2, *C*-magnesiophosphaalkenes have turned out to be valuable and versatile synthons in the design of novel *C*-metallophosphaalkenes. Here, the reaction behavior of such species towards a series of electrophiles that do not furnish *C*-metallophosphaalkenes as discussed before, is described.

In contrast to lithium derivative (*Z*)-**25**, addition of acetophenone to the less basic *C*-magnesiophosphaalkene **29** gave the expected alcohol **112** in 75% yield. Similarly, **29** was smoothly converted into **113** by reaction with acetyl chloride (60% yield) (Scheme 58) [20].

In a more recent paper, phosphavinyl-Grignards **46a** and **46b** were reacted with a series of aryl- and alkyl-aldehydes to afford the expected β-phophaallylic alcohols **114** in moderate to good yields after quenching with methanol (Scheme 59) [60].

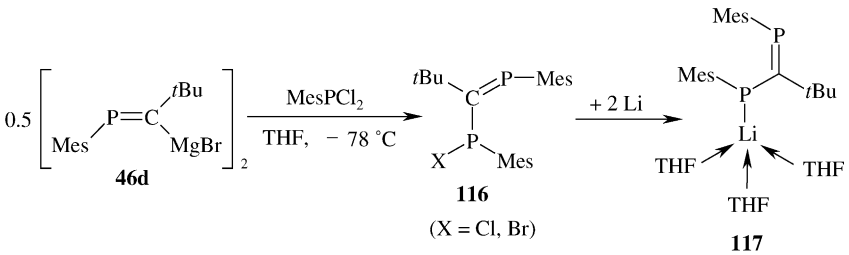
The reaction of $PbCl_2$ with (*Z*)-CyP=C(*t*Bu)MgCl(OEt_2) (**46a**) afforded the first example of an endo:endo-2,4-diphosphabicyclo[1.1.0]butane **115** instead of the anticipated transmetallation products (Scheme 60) [61].

Treatment of the phosphavinyl-Grignard reagent **46d** with $MesPCl_2$ quantitatively affords the corresponding 1,3-diphosphapropene **116**. Subsequent reduction with two equivalents of elemental lithium in THF gives rise to the formation of the 1,3-diphosphaallyl lithium complex **117**, which contains an η^1-1,3-diphosphaallyl ligand (Scheme 61) [62].

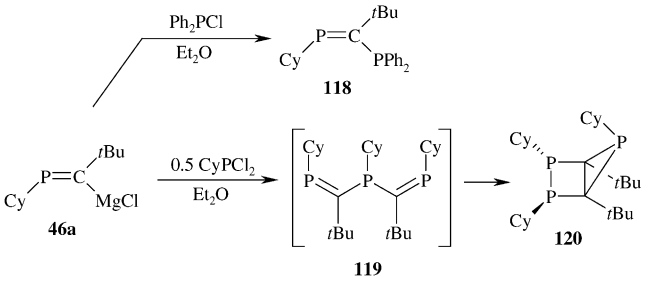
Magnesium derivative **46a** reacts with Ph_2PCl to give the expected 1,3-diphosphapropene **118** in high yield (75%) and with retention of the stereochemistry of the phosphavinyl fragment. In the reaction of **46a** with in situ generated $CyPCl_2$, a phosphavinyl coupling occurred giving the triphosphabicyclo[2.1.0]pentane derivative **120** (Scheme 62) [63]. Detection of the conceivable intermediate **118** by ^{31}P NMR spectroscopy at low temperature failed.

Reaction of 3 equivalents of **46a** with PCl_3 and $AsCl_3$ in diethyl ether led to the formation of the triphospha- and arsa-diphosphabicyclo[1.1.1]pentanes **122** and **123** in moderate yields. Presumably these species were formed via the bisphosphavinyl phosphorus or arsenic intermediates **121** (Scheme 63) [63].

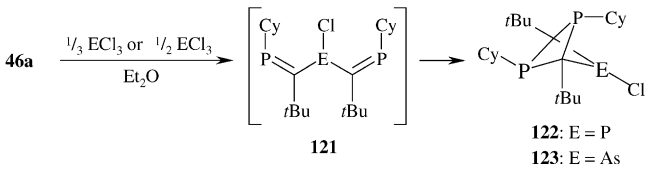
The reaction of **46a** with an equimolar amount of PCl_3 afforded tetraphospha-bicyclo[2.1.1]hexane **125** (15% yield) and the phosphino substituted ylide **126** (5% yield) as major products. These results were rationalized by invok-



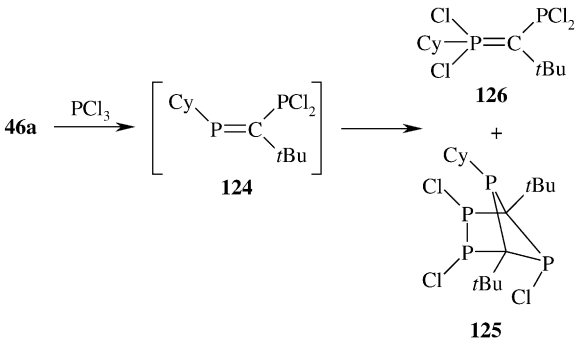
Scheme 61. Synthesis of **116** and **117**.



Scheme 62. Reaction of **46a** with Ph_2PCl and $CyPCl_2$.



Scheme 63. Formation of compounds **122** and **123**.



Scheme 64. Reaction of **46a** and PCl_3 (1:1).

ing phosphaalkene **124** as an intermediate (Scheme 64) [63].

The reactions of **46a** with either one equivalent of $AsCl_3$ or $BiCl_3$ were not clean and gave inseparable mixtures of products. The corresponding 1:1 reaction of **46a** with $SbCl_3$, however, was very clean and furnished heterocycle **127** in 66% yield. In the solid state, the compound was moderately thermally stable. However, in toluene solution it quantitatively decomposed to the diphosphete **128** over 2 days, extruding elemental antimony and $SbCl_3$ (Scheme 65) [63].

The 1:1 reaction of **46a** with PhSeCl in diethyl ether afforded a high yield of the 1,3-λ^5,λ^5-diphosphete **129** instead of the anticipated (*Z*)-phosphaalkenyl compound (*Z*)-PhSe{C(*t*Bu) = PCy **130**. The transient formation of **130** was evidenced in the ^{31}P NMR spectrum of the fresh reaction mixture by a signal at low field (δ = 320 ppm). A 1,2-selenyl shift to give a short lived λ^5-phosphaalkyne Cy(PhSe)P≡ C–*t*Bu, which underwent a spontaneous [2 + 2] cycloaddition, may explain the formation of **129** [26] (Scheme 66).

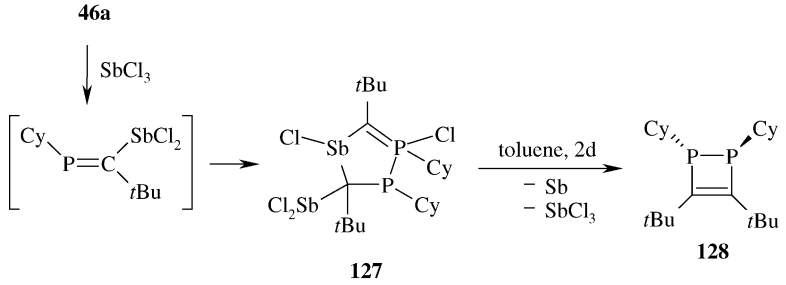
Treatment of a toluene slurry of Cp^*TaCl_4 with 2 equivalents of **46a** resulted in a deep blue–green solution, which changed to a brown color on warming to room temperature and stirring overnight. Bicyclic **115** was then isolated as the product of a coupling process. Blue–green crystals of complex **132** were obtained by placing the reaction solution at −30 °C without allowing it to warm to room temperature (Scheme 67).

It was assumed that *C*-metallophosphaalkene **131** is formed as an initial product. A series of redox reactions and rearrangements to give radical $[Cp^*TaCl_2(=C(tBu)–P–Cy]\cdot$, which eventually dimerized, was proposed for a reaction mechanism (Scheme 67) [64]. The analogous reaction of 2 equivalents of **46a** with Cp^*NbCl_4 led to the formation of the coupling products **115** and **128** without evidence of any tractable organometallic intermediate [64].

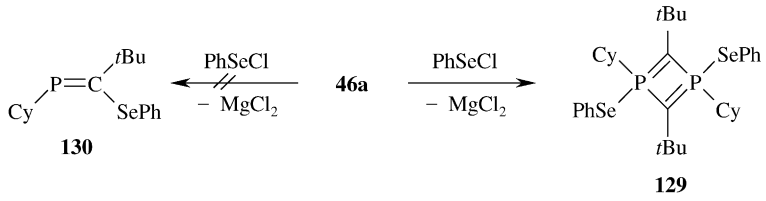
Another η^2-phosphidocarbene complex **133** resulted from treatment of $[IrCl(CO)(PPh_3)_2]$ with one equivalent of **46a** in toluene. Passing CO gas through a toluene solution of **133** rapidly lead to the quantitative displacement of one PPh_3 ligand and the formation of **134**. In toluene or ethereal solution, compound **134** decomposed over several hours to give many phosphorus containing products, one of which was isolated in very low yield (<1%) and identified as dinuclear complex **135** by X-ray analysis (Scheme 68) [65].

4.2.3. *C*-Vanadiophosphaalkenes

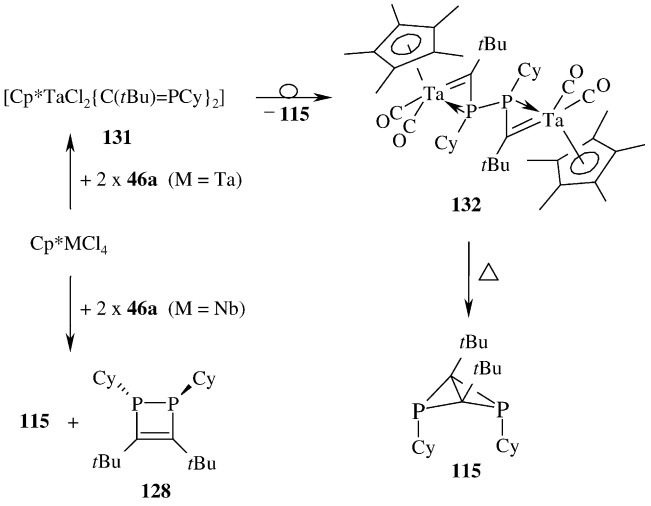
When vanadiophosphaalkene **69a** was allowed to react with two or three equivalents of phosphaalkyne *t*BuC≡ P (**68a**), the formation of triphosphabenzene **136a** was observed (68% yield). Alternatively, synthesis of **136a** was achieved by combination of four equivalents of phosphaalkyne **68a** with *t*BuNVCl$_3$ in toluene solution in the



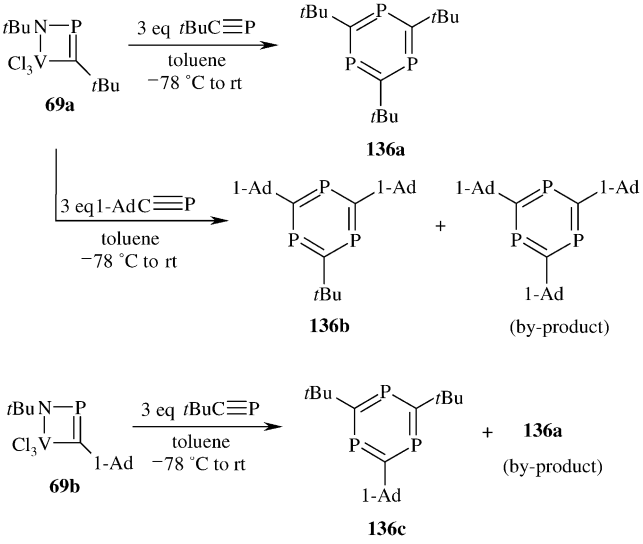
Scheme 65. Reaction of **46a** with $SbCl_3$ (1:1).



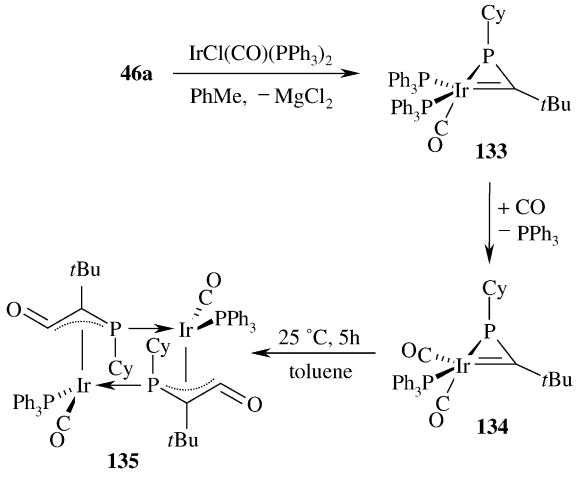
Scheme 66. Synthesis of **129**.



Scheme 67. Reaction of **46a** with Cp^*MCl_4 (M = Nb, Ta).



Scheme 69. Conversion of **69a,b** into 1,3,5-triphosphabenzenes **136**.



Scheme 68. Reaction of **46a** with $[IrCl(CO)(PPh_3)_2]$.

temperature range −78–20 °C. Similarly, phosphaalkynes **68b–e** were converted to the respective triphosphabenzenes. Triphosphabenzene **136b** was produced if vanadiophosphaalkene **69a** was reacted with 3 equivalents of 1Ad–C≡P (**68b**). Analogously, vanadocycle **69b** and 3 equivalents of *t*BuC≡P furnished triphosphabenzene **136c** (Scheme 69) [32].

5. Conclusions and perspectives

It is obvious that the chemistry of metal-functionalized phosphaalkenes has developed rapidly in the recent years. In the beginning, the interest mainly focussed on the synthesis and structural elucidation of such complexes. Ever increasingly it has shifted towards the reactivity of these compounds, and particularly to main group derivatives, which are to be encountered at the interface of organophosphorus, organometallic, and complex chemistry.

The combination of electrophilic and nucleophilic centers on the P=C unit as well as on the organometallic fragment renders metallophosphaalkenes as versatile synthons, and the exploration of their rich chemistry is by no means exhausted. Even phosphaalkynes, which are nowadays well-familiar species, serve further as a valuable source for the synthesis of metallophosphaalkenes as impressively demonstrated with phospha-Grignard reagents. Metallophosphaalkenes play a key role as intermediates in the metal-mediated oligomerization of phosphaalkenes to phosphorus carbon heterocycles and cages.

In future, along with purely preparative considerations, physico-chemical investigations still await realization. Application-oriented aspects such as polymerization and copolymerization of suitably substituted derivatives are also waiting to be discovered.

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