Metallophosphaalkenes—from Exotics to Versatile Building Blocks in Preparative Chemistry

Lothar Weber

The chemistry of low-valent organophosphorus compounds such as phosphaalkenes and phosphaalkynes has undergone rapid development in the last two decades. This development also includes the coordination chemistry of these species, which can act as versatile ligands in metal complexes. Metallophosphaalkenes are compounds in which one or more of the organic substituents on the P=C unit is replaced by a transition metal complex fragment. Metallophosphaalkenes have emerged from an existence as laboratory curiosities to become a link between main group and organometallic complex chemistry. The great richness of their chemistry not only mirrors the specific properties of the individual building block, but also shows novel and individual traits. Particular examples are cycloadditions of these electron-rich heteroalkenes with electron-deficient alkenes, alkynes, azo, and diazo compounds. These often lead to novel types of reaction and compounds. Metallophosphaalkenes are also important as intermediates in all metal-assisted cyclooligomerizations of phosphaalkynes.

Keywords: metallophosphaalkenes • phosphaalkenes • transition metal compounds

1. Introduction

The rapid development in the chemistry of low-valent phosphorus compounds during the last twenty years includes their coordination chemistry.^[1, 2] There are now five types of complexes known containing phosphaalkene ligands (A-E) (Scheme 1).^[2] The structural integrity of the phosphaalkene ligand is largely retained in complexes A-E. In metallophosphaalkenes, on the other hand, one or more of the substituents



Scheme 1. Basic types of phosphaalkene transition metal complexes,

R on the phosphaalkene is replaced by a transition metal complex fragment; thus five basically different types of compound (I-V) can be differentiated (Scheme 2). Like phosphaalkenes with purely organo substituents, the phosphorus atom as well as the P=C- π bond in compounds of type I-V are capable of acting as donors and are therefore, in principle, in the position to interact further as ligands with other metal centers. Moreover, since metallophosphaalkenes are polyfunctional molecules, they are valuable starting materials for a wide range of chemical transformations with both organic and inorganic partners.



Scheme 2. Basic types of metal-functionalized phosphaalkenes (metallophosphaalkenes).

This review provides an overview of metal-functionalized P=C systems with particular emphasis placed on the preparative and structural aspects of this chemistry.

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2. Synthetic Methods

2.1. P-Metallophosphaalkenes (Type I)

P-Metallophosphaalkenes $[M]-P=R^2R^3$ are now available by several synthetic routes; however, three general principles, a-c, are discernable (Scheme 3). In syntheses following route (a), the P=C bond is constructed from starting materials with

(
©_ _✓ P:	<u>+c</u> ©
[M]	R ³
Scheme 3.	Routes to

metallophosphaal-

kenes of type I.

[M]-P bonds such as metallophosphanes, in route (b), a M-P bond is formed between a P-functionalized phosphaalkene and a metal complex, and in route (c), phosphaalkynes are reduced within the coordination sphere of transition metal complexes.

2.1.1. Syntheses by Route a

The first *P*-metallophosphaalkenes were obtained from the reaction of metallodisilylphosphane **1** with acid chlorides **2** (Scheme 4).^[3] The reaction sequence of condensation and silyl migration resembles the synthesis of phosphaalkenes from acid chlorides and organodisilylphosphanes,^[4] in which, in contrast to transient **3**, the primarily formed acyl(silyl)phosphanes were detectable by ³¹P NMR spectroscopy.

The principle of the synthesis outlined in Scheme 4 cannot be subjected to unlimited generalization (Scheme 5). Thus, the reaction of pentamethylcyclopentadienyl (Cp*) derivatives $[Cp^*(CO)_2M-P(SiMe_3)_2]$ of iron (5)^[5] and ruthenium (6)^[6] with mesitoyl chloride (2a) leads cleanly to the metallophos-



Scheme 4. Syntheses of the metallophosphaalkenes 4. R = mesityl (Mes) (a), Ph (b), *t*Bu (c).



Scheme 5. Reaction of $[Cp^*(CO)_2M - P(SiMe_3)_2]$ with acid chlorides. M = Fe: 5, 8, 11; Ru: 6, 9, 12; Os: 7, 10, 13; R = Mes (a), Ph (b), tBu (c).

phaalkenes **8a** and **9a**, respectively, whilst treatment with benzoyl chloride (**2b**) leads to mixtures of **8b** and **9b**, respectively, together with the dibenzoylphosphido complexes **11b** and **12b**, respectively. With pivaloyl chloride (**2c**) only the diacylphosphido complexes **11c** and **12c**, respectively, are formed. These limitations are even more valid for the osmium complex **7**, which, even with **2a**, produces mixtures of the osmiophosphaalkene **10a** and the dimesitoylphosphido complex **13a**.^[7]

Another successful synthesis of ferriophosphaalkenes (such as 8) following route (a) is based on the lithiation of the acyl(metallo)phosphanes 14a-c and the subsequent treatment of the enolates 15a-c with chlorotrimethylsilane. Compound 8c is also accessible by this route (Scheme 6).



Scheme 6. Ferriophosphaalkenes from acylferriophosphanes. [Fe] = $Cp^*(CO)_2Fe$; R = Mes (a), Ph (b), /Bu (c).



Lothar Weber was born in 1944 in Langenöls in Schlesien. He studied at the Universität Marburg and received his doctorate there under the supervision of Professor Günter Schmid in 1973. Thereafter, he carried out post-doctoral studies with Professor Barry M. Trost at the University of Wisconsin in Madison, USA. On his return to Marburg, he began the experimental work towards his Habilitation, which was completed in 1982 at the Universität Essen. His work centered on the coordination chemical aspects of sulfur ylides. In 1985, he became a C2 Professor, before he received the call to the Fakultät für Chemie der Universität Bielefeld. His research interests also include the chemistry of compounds with low-coordinate elements of the fifth main group, the synthesis of small homo- and heterocycles with heavy elements as well as metal complex catalyzed reactions of multiply bonded systems.

2.1.2. Syntheses by Route b

A particularly efficient method for the synthesis of the metallophosphaalkenes 16-27 utilizes the reaction of halogeno-(methylene)phosphanes XP=C(R)(SiMe₃) with carbonylmetalate ions. The products, with the exceptions of 16 and 20, are obtained as stable solids in good yield (Scheme 7).^[8-10]

	x P=c R	ез	[M] ->	$[M] \xrightarrow{[M]}{x} [M] \sim P = C < R$					
				16-27					
	[M]	R				[M]	R		
16	[Cp(CO)3Mo]	MezSi			22	[Cp(CO)3Mo]	Ph		
17	[Cp*(CO)3Mo]	MezSi			23	[Cp*(CO)3Mo]	Ph		
18	[Cp(CO)3W]	MezSi			24	[Cp(CO)3W]	Ph		
19	[Cp*(CO)3W]	Me3SI			25	[Cp*(CO)3W]	Ph		
20	[Cp(CO) ₂ Fe]	MeʒSi			25	[Cp(CO) ₂ Fe]	Ph		
21	[Cp*(CO) ₂ Fe]	MezSi		Ì	27	[Cp*(CO) ₂ Fe]	Ph		

Scheme 7. Metallophosphaalkenes from carbonylmetalates and halogenophosphaalkenes. $X=\mbox{Cl},\,\mbox{Br}.$

The thermal stability of these metallophosphaalkenes decreases with increasing electron density on the metal $(Mo(d^4) < Fe(d^6))$ as well as with decreasing steric demand of the π ligand $(C_3H_5 < Cp < Cp^*)$. Thus, the thermolabile complexes **20** and $[(\eta^3-C_3H_5)(CO)_2FeP=C(SiMe_3)_2]$ readily undergo further reaction to **28** and **29**, respectively (Scheme 8).^[11]



Scheme 8. Subsequent reactions of unstable metallophosphaalkenes 20 and $[(\eta^3-C_3H_5)(CO)_3Fe-P=CR_2]$. R = Me₃Si. DME = 1.2-dimethoxyethane. THF = tetrahydrofuran.

There have been some reports on the oxidative addition of P-halogenophosphaalkenes to low-valent nickel and platinum centers (Scheme 9). Whilst the platinum complex **30**, a cream-colored solid, is stable, the nickel compounds **31a** and **31b** rapid-ly decompose in solution.^[12]



Scheme 9. P-Nickelio- and P-platiniophosphaalkenes by oxidative addition. X = Cl(a), l(b), cod = 1.5-cyclooctadiene.

Oxidative addition takes place in competition with η^1 and η^2 coordination of the halogenophosphaalkenes and is particularly favored for the reactive P–I bond (184 kJ mol⁻¹). In contrast, the phosphaalkene F–P=C(SiMe₃)₂ has a strong P–F bond (490 kJ mol⁻¹) and has only been observed so far as a η^1 and η^2 ligand for example in *trans*-[Rh(PPh₃)₂(Cl){ η^1 -P(F)=C-(SiMe₃)₂}] or [Ni(PnBu₃)₂{ η^2 -P(F)=C(SiMe₃)₂}].^[13] The nature of the transition metal complex fragment clearly influences the reaction behavior of the corresponding chlorophosphaalkene [dissociation energy (P–Cl) = 319 kJ mol⁻¹]. Here, along with **31a**, η^1 complexes are known such as *trans*-[RhCl(P-Ph₃)₂{ η^1 -P(Cl)=C(SiMe₃)₂}].^[13] and η^2 complexes such as [Pt(PPh₃)₂{ η^2 -P(Cl)=C(SiMe₃)₂}].^[12]

As an alternative to the methods described in Scheme 7, the pentamethylcyclopentadienyl metal derivatives 17 and 19 can be obtained from $Cp^*P=C(SiMe_3)_2$ and the kinetically labile complexes $[M(MeCN)_3(CO)_3]$ (M = Mo, W). Here, the metal complex fragment is inserted into the labile P-C(Cp*) bond (1.931(4) Å^[14]) (Scheme 10).



Scheme 10. Oxidative additions with Cp*P=C(SiMe_3)_2. M = Mo (17), W (19), Cr (32); R = Ph (a), Et (b), nBu (c).

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Complexes 17 and 19 are synthesized photochemically; however, the analogous chromiophosphaalkene 32 is produced by thermolysis. Formation of 21 from $Cp^*P=C(SiMe_3)_2$ and $[Fe_2(CO)_9]$ proceeds by the photolysis of the isolable complex $[\{\eta^1-Cp^*P=C(SiMe_3)_2\}Fe(CO)_4]$. The synthesis approach for 17, 19, and 21 based on $Cp^*P=C(SiMe_3)_2$ does not show any advantages over the method given in Scheme 7 (which generates greater yields), because the organophosphorus starting material has to be prepared from $Cl-P=C(SiMe_3)_2$ beforehand. No alternatives, however, exist for the synthesis of the chromium complex 32 and the nickeliophosphaalkenes 34a-c.^[10]

The particularly electron-rich metallophosphaalkenes **35** and **36** are obtained by condensation of the bromo complexes $[MCp^*(CO)_2Br]$ (M = Fe, Ru) with $Me_3Si-P=C(NMe_2)_2$ (Scheme 11).^[15]



Scheme 11. Metallophosphaalkenes from $Me_3SiP=C(NMe_2)_2$ by condensation. M = Fe (35), Ru (36).

2.1.3. Syntheses by Route c

Phosphaalkynes oligomerize within the coordination sphere of transition metals to furnish a wide range of new compounds^[1f, 2] some of which display the structural characteristics of *P*-metallophosphaalkenes. Thus, cyclotrimerization of $tBuC\equiv P$ or 1-AdC $\equiv P$ on the [CpRu]⁺ fragment of 37 yields complexes 38a and 38b, respectively, in which all the acetonitrile ligands have been displaced by the phosphaalkyne. The fluorine atom in the products originates from the hexafluorophosphate ion (Scheme 12).^[16]



Scheme 12. Synthesis of a *P*-rutheniophosphaalkene by cyclotrimerization of phosphaalkynes; R = tBu (a), 1-adamantyl (1-Ad) (b).

Treatment of $[Rh(C_2H_4)_2Cl]_2$ with trimethylphosphane and *tert*-butylphosphaacetylene in the molar ratio of 1:4:4 produces a 1:2 mixture of the 1,4-diphospha-2-rhodacyclopentadiene **39** and the 1,3-diphosphacyclobutadiene derivative **40**. Reaction of **40** with indenyllithium cleanly yields the sandwich complex **41** (Scheme 13).^[17] Rhodiophosphaalkene **39** is a model complex for an important intermediate product in metal-induced cyclooligomerizations of phosphaalkynes. On cobalt, rhodium,^[16] and iron^[18] centers this usually leads to η^4 -ligated 1,3-diphosphacyclobutadienes. On the other hand, cyclodimerization of *t*BuC \equiv P on [Cp₂Zr] and [Cp₂Hf] fragments yields complexes with 1,3-diphosphabicyclo[1.1.0]butanediyl ligands.^[19] A highly efficient cyclotetramerization of the phosphaalkyne occurs on



Scheme 13. Synthesis of cyclic rhodiophosphaalkenes. Ind = indenyl.

the $(\eta^{8}$ -cyclooctatetraene)zirconium fragment to give a $(\eta^{4}-1,3,5,7$ -tetraphosphabarralene)zirconium complex, and here reactive metallophosphaalkynes are also postulated as intermediates.^[20]

The tolanrhodium complex $[Rh(PiPr_3)_2(Cl)(\eta^2-PhC\equiv CPh]]$ reacts with two equivalents of $tBuC\equiv P$, undergoing a cyclodimerization to yield **42**. One molecule of phosphaalkyne adds to the alkyne to generate a η^3 -phosphacyclobutenyl ligand. The second molecule of phosphaalkyne bridges the P atom of the four-membered ring to the metal center, thus producing a rhodiophosphaalkene (Scheme 13).^[21]

The cyclo-cooligomerization of alkynes with phosphaalkynes is sensitively dependent on the nature of the other ligands on the metal center. Thus, in the reaction of $[RhCp(PiPr_3)(\eta^2 - PhC \equiv CPh)]$ with $tBuC \equiv P$ only one molecule of the phosphaalkyne is incorporated to give the η^4 -phosphacyclobutadienerhodium complex $[CpRh(\eta^4 - PC(Ph)C(Ph)CtBu)]$.^[21]

Another type of [2+2]cycloaddition occurs between the vinylidene complex $[(PiPr_3)_2(Cl)Rh=C=CH_2]$ and $tBuC\equiv P$. Here, the cyclic rhodiophosphaalkene **43** is produced, which subsequently reacts smoothly with cyclopentadienyllithium to yield **44** (Scheme 13).^[21]

2.2. C-Metallophosphaalkenes (Type II)

2.2.1. From Lithiosilylphosphanes and Carbonylmetal Cations

The syntheses of the first C-metallophosphaalkenes 46a-cwere contrived by the addition of lithiosilylphosphanes to the carbonylrhenium cation $[Cp^*Re(CO)_2(NO)]^+$ in ether at

 -80° C (Scheme 14). The initially formed complexes 45a - c can be detected by ³¹P NMR spectroscopy, they rearrange above -40° C to the products 46a - c. Analogously, the extremely sensitive compound [Cp(CO)(NO)Re-C(OSiMe₃)=PtBu] is obtained from the reaction of [CpRe(CO)₂(NO)]BF₄ with LiP(tBu)(SiMe₃).^[22]



Scheme 14. Synthesis of C-rheniophosphaalkenes. $R = Me_3Si(a)$. tBu (b). Ph (c).

This type of synthesis, however, has only a limited range of application. Thus, treatment of the manganese complex cation $[Cp*Mn(CO)_2(NO)]^+$ with LiP(SiMe₃)₂ produces the complex $[Cp*(CO)_2Mn-P(SiMe_3)_2]$ instead of a *C*-manganiophosphaalkene.^[23]

The tendency of formation and stability of *C*-metallophosphaalkenes are also sensitively influenced by the spatial requirements of the other ligands in the complex and by the substituents on the P atom. This is particularly valid for the corresponding iron and ruthenium compounds. The cation $[CpFe(CO)_3]^+$ is attacked at the cyclopentadienyl ligand by $LiP(R)(SiMe_3)$ ($R = SiMe_3$, tBu) at -78 °C in ether. The *exo*phosphinocyclopentadiene complexes **47** thus formed rearrange at room temperature to the metallophosphanes $[Cp(CO)_2-Fe-P(R)(SiMe_3)]$ (Scheme 15).^[24]



Scheme 15. Reaction of $[FeCp(CO)_3]^*$ with lithiosilylphosphanes. $R = Me_3Si(a)$, *iBu* (b).

If the analogous pentamethylcyclopentadienyl cation $[Cp^*(CO)_3Fe]^+$ is used, the attack by the phosphide on the ring ligand does not occur, however, the desired *C*-metallophosphaalkene **49** is only produced in the case of the bulky supermesityl group (Mes^{*} = 2,4,6-tBu₃C₆H₂) on the P atom (Scheme 16).^[25] For R = SiMe₃ and tBu the 1,3-silyl migration does not occur, and the phosphinocarbonyl complexes **48a** and **48b**, respectively, are isolated as the final products (Scheme 16).^[26] Similar results are obtained in the chemistry of the ruthenium derivative $[Cp^*Ru(CO)_3]^+$.^[25, 27]



Scheme 16. Synthesis of (phosphino)carbonyl complexes 48a - c and a C-ferrio-phosphaalkene 49. $R = Me_3Si(a)$, *iBu*(b). Mes* (c).

2.2.2. From C-Functionalized Phosphaalkenes

Two research groups have succeeded in synthesizing *C*-metallophosphaalkenes from phosphaalkenes that have halogen functions on the methylene carbon atom.^[28, 30] The *trans*-configured compounds **50a** and **51** result from the oxidative addition of equimolar amounts of $Cl_2C=PMes^*$ and $[M(PEt_3)_4]$ in benzene or hexane at 20 °C (Scheme 17). Similarly, the bromoplatinum derivative **50b** is obtained from $[Pt(PEt_3)_4]$ and $Br_2C=PMes^*$. The analogous bromopalladium compound could not be isolated due to decomposition to *trans*- $[Pd(PEt_3)_2Br_2]$ and $Mes^*C\equiv P.^{[28a, c]}$



Scheme 17. Synthesis of C-palladio- and C-platiniophosphaalkenes; M = Pt, X = Cl (50a), X = Br (50b); M = Pd, X = Cl (51).

The *cis* isomer corresponding to **50a** is formed from $Cl_2C=PMes^*$ and $[Pt(PEt_3)_4]$ in hexane at $-50\ ^\circ C$ and can be isolated as analytically pure crystals at this temperature. However, in solution *cis*-[(Et_3P)_2(Cl)Pt{C(Cl)=PMes^*}] rearranges in the presence of PEt₃ and above $-30\ ^\circ C$ to the *trans* isomer.^[28e] An alternative synthesis of **50a** utilizes a ligand exchange reaction between *trans*-[Pt(PEt_3)_2Cl_2] and LiC-(Cl)=PMes*.^[28e]

The principle of synthesis outlined in Scheme 17 is also subject to narrow limits: 1. To date there are only a few *C*-halogenomethylenephosphanes known, and these carry, with the exception of the 2,2,6,6-tetramethylpiperidino and bis-(trimethylsilyl)amino substituents, the supermesityl group on phosphorus. 2. The stability of the products discussed here is as follows: Pt > Pd; Cl > Br; $PEt_3 > PPh_3$.

In agreement with this, the reaction of $[Pt(\eta^2-C_2H_4)-(PPh_3)_2]^{[28c]}$ or $[Pd(PPh_3)_4]^{[29]}$ with $Cl_2C=PMes^*$ does not lead to stable *C*-metallophosphaalkenes, but only to the phosphaalkyne Mes*C=P and to *cis*-[Pt(PPh_3)_2Cl_2] and *trans*-[Pd-(PPh_3)_2Cl_2], respectively.

The organolithium compound (Z)-Mes*P=CHLi reacts with one equivalent of HgCl₂ to give the mercuriophosphaalkene (Z)-52, whilst treatment with only 0.5 equiv of HgCl₂ generates the bis(phosphaalkenyl)mercury derivative (Z/Z)-53 (Scheme 18).^[30] If, instead of the single isomer of the lithium compound, the mixture (E/Z)-Mes*P=CHLi is used, as is produced from the lithiation of the phosphaalkene mixture (E/Z)-Mes*P=CHI (80:20), the mercury compound is also obtained as a mixture of (E/E)-53 and (Z/Z)-53. The isomers can be separated by crystallization.^[30]



Scheme 18. Synthesis of C-mercuriophosphaalkenes 52 and 53.

2.2.3. From Phosphaalkynes or η^2 -Phosphaalkyne Complexes

Cyclo-codimerizations of $tBuC \equiv P$ with alkenes and alkynes within the coordination sphere of titanocenes and zirconocenes lead to metallaheterocycles with structural features of *C*-metallophosphaalkenes. If, for example, a solution of **54** in *n*-heptane is heated with the phosphaalkyne for several hours at 80 °C, the zirconiophosphaalkene **55** is obtained as a red powder and a η^2 -dehydrobenzene complex is postulated as an intermediate (Scheme 19). A titanium derivative analogous to **55** has also been reported.^[31]

The C-metallophosphaalkenes 57a-d are readily accessible from the phosphaalkyne complex 56 by reaction with the alkynes HC=CH, MeC=CMe, PhC=CPh, and PhC=CH, respec-



Scheme 19. C-Zirconiophosphaalkenes from alkyne, phosphaalkyne, and zirconocene building blocks. $R^1 = R^2 = H(a)$, Me (b), Ph (c); $R^1 = H$, $R^2 = Ph(d)$.

tively, if the released phosphane is removed from the equilibrium by adduct formation with triethylborane (Scheme 19). However, codimerization fails with silvlated alkynes such as $HC \equiv CSiMe_3$, $PhC \equiv CSiMe_3$, $Me_3SiC \equiv CSiMe_3$ as well as with dimethyl acetylenedicarboxylate. In the absence of trapping agents the coordinatively unsaturated complex 58, formed from 56 by abstraction of phosphane, trimerizes to 59.^[32] The cyclic C-metallophosphaalkenes 55 and 57 are the first stable representatives of a class of compounds which are most probably intermediates playing an important role in all metal-induced cyclo-cooligomerizations, but which have, to date, evaded detection. This is true not only for the formation of $(\eta^4$ -phosphacyclobutadiene)cobalt^[33] and -rhodium^[21] complexes but also for the synthesis of (1,3-diphosphinine)iron compounds.[18] A highly reactive nickeliophosphaalkene has been proposed as an intermediate in the synthesis of a tetraphosphatricyclooctadiene.[34]

The 1-phospha-3-zirconia[3.1.0]bicyclohex-1-enes 60a - e can be synthesized from **58** and cyclopropene derivatives. If **58**, generated in situ, is treated with acetone, benzophenone, benzaldehyde, or isobutyraldehyde, metallaheterocycles **61** are obtained. Treatment of 1,1-dimethylallene or triphenylketeneimine with **58** produces complexes **62** and **63**, respectively (Scheme 20).^[32] The titanium derivatives analogous to **60a**-**c** and **61c,d** have also been prepared.^[32]

The insertion of a methylene group into the metal-phosphorus bond can be achieved when **56** or the trimer **59** is treated with the ylides $Ph_3P=CH_2$ or $Me_3P=CH_2$ as well as with the adduct $Ph_3P=CH_2 \cdot BEt_3$ (Scheme 21).^[32]



Scheme 20. Synthesis of cyclic C-zirconiophosphaalkenes



Scheme 21. Reaction of (η^2 -phosphaalkyne)zirconocene complexes with ylides and diazo compounds. R = Me, Ph.

The reaction of **56** or **59** with diazo compounds does not lead to the expected loss of N₂ and insertion of the carbene fragment into the Zr–P bond. Instead, a cycloaddition reaction yields the 2-aza-1-phospha-3-zirconiacyclobut-4-enes **65** and **66**, respectively, which, like **64**, have the structural motif of a C-metallophosphaalkene in the heterocycle (Scheme 21).^[32]

2.3. C,C-Dimetallophosphaalkenes (Type III)

For compounds of this type, which can also be regarded as μ -isophosphaalkyne or phosphoisonitrile complexes, there are two methods of synthesis available so far. These complexes deserve particular attention, as the ligated isophosphaalkynes $C \equiv P(aryl)$ are unknown as the free species, and all attempts to synthesize them up to now afforded only the already well known phosphaalkyne isomers $(aryl)C \equiv P$. The first complexes of this type, **68** (Scheme 22), are obtained by the oxidative addition of



Scheme 22. Synthesis of C,C-diplatiniophosphaalkenes. X = Cl (a), Br (b); L = PEt_3.

one equivalent of $[Pt(PEt_3)_4]$ to the *C*-metallophosphaalkenes **50**; the dinuclear complexes **67** are assumed to be the primary products.^[28a-d]

Experiments to produce heterodimetallic complexes of type 68 with Pt and Pd proceed by a different route:^[28d] The complexes 70 and 71 are the only organometallic products detectable

following the reaction of **50** with $[Pd(PEt_3)_4]$ for 24 h; however, the metallophosphaalkynes **70** could not be isolated. Their subsequent treatment with $[Pt(PEt_3)_4]$ leads to **72** with the novel $\mu(\eta^1:\eta^2)$ -phosphaethynyl ligand (Scheme 23).^[28d]



Scheme 23. Synthesis of $\mu(\eta^1; \eta^2)$ -phosphaethynyl complexes. X = Cl (a), Br (b); L = PEt₃.

An alternative method for the synthesis of C,C-dimetallophosphaalkenes employs base-induced condensation of aryl(silyl)phosphanes 74a-d with the μ -carbynediiron complex 73 (Scheme 24).^{(35, 36]} Compounds 75a-c are obtained by column chromatography as dark red, air-stable, crystalline substances, whereas 75d has not yet been isolated undecomposed. On the basis of findings to date, the condensation described above is limited to bulky aryl(silyl)phosphanes.



Scheme 24. Synthesis of C,C-diferriophosphaalkenes. Aryl = Mes (a), 2.4.6- $iPr_3C_6H_2$ (b), Mes* (c), 2.4.6-(CF₃)₃C₆H₂ (d); DBU = diazabicycloundecene.

2.4. C, P-Dimetallophosphaalkenes (Type IV)

The only compound with this type of structure known so far, 77, is obtained by the addition of $tBuC\equiv P$ to the Pt-Pt fragment of the diplatinum complex 76 (Scheme 25).^[37]



Scheme 25. Synthesis of a C,P-diplatiniophosphaalkene.

3. Structures and Bonding Properties

3.1. Molecular Structures of Metallophosphaalkenes

The most noticeable structural change that a classical phosphalkene 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. The









Fig. 1. Crystal structures of the metallophosphaalkenes **21**, **46b**, and **75a**. Selected bond lengths [Å] and angles []: **21**: P-C13 1.680(9), Fe-P 2.256(2); Fe-P-C13 126.2(3); **46b**: P1-C1 1.704(4), Re1-C1 2.138(4), C1-O1 1.399(5); C1-P1-C2 112.3(2); **75a**: P1-C13 1.683(12), C13-Fe1 1.903(16), C13-Fe2 1.927(16); C13-P1-C20 104.5(7).

angle M-P-C varies from 113.8(2)° in the [CpFe] complex 4c (see Scheme 4)^[3] to $126.2(3)^{\circ}$ in the [Cp*Fe] complex 21^[9] (Fig. 1). In the parent compound HP=CH₂ the calculated value for the angle H-P-C is 97.4°, [38. 39] whilst in phosphaalkenes with organic substituents the value for this angle usually varies between 100-114° depending on the spatial requirements of the substituents.^[40] The unusually large valence angle N-P-C in $Mes^*(Me_3Si)N-P=C(SiMe_3)_2$ (121.38(6)°) undoubtedly results from steric repulsion within the molecule.^[41] The opening of the angle in metallophosphaalkenes is due not only to steric but also to electronic effects which arise from the low electronegativity of the metal substituent. In the parent compound, the orbital of the lone pair on the phosphorus has mainly 3s character. This changes in the metallophosphaalkenes: the p character of the lone pair increases. This causes an opening of the angle on phosphorus and a decrease in the ionization energy of the n orbital. In metallophosphaalkenes, this orbital then becomes energetically the HOMO, whilst the π orbital becomes HOMO -1. All in all, the energy difference HOMO-LUMO (the latter is a π^* -orbital) is smaller than that in HP=CH,.[38, 39]

In the C-rheniophosphaalkene **46b**^[22] and in the C,C-diferriophosphaalkene **75a**,^[35] C-P-C bond angles of $112.3(2)^{\circ}$ and $104.5(7)^{\circ}$, respectively, have been measured (Fig. 1).

The molybdeniophosphaalkene **16** (see Scheme 7) has the shortest P=C distance observed to date for a *P*-metallophosphaalkene (1.665(3) Å;^[8] calc.: 1.673 Å^[38]). π -Conjugation with the lone pairs on oxygen or nitrogen atoms of heterosubstituents generally leads to a small elongation of the P=C bond (e.g. 1.701(4) Å in *t*Bu(OSiMe₃)C=P complex $4c^{[3]}$ or 1.709 Å in the (NMe₂)₂C=P complex $35^{[15]}$). The same is true of the P=C bond lengths in 46b (1.704(4) Å) and 75a (1.683(17) Å). The metal-phosphorus distances in *P*-metallophosphaalkenes are in agreement with single bonds with negligible π -bond contributions.

3.2. NMR Spectra

The characteristic ³¹P and ¹³C NMR shifts for selected compounds are summarized in Table 1.

The ³¹P NMR chemical shifts of phosphaalkenes vary in the wide range between $\delta = -62.0$ for $(Me_2N)C=PH^{[42]}$ to $\delta = 740.5$ in the nickel complex **34b**.^[9,10] The ³¹P NMR data of compounds containing low-coordinate phosphorus published up to 1987 are summarized in a review.^[43] Inspite of the large problems associated with the theoretical collation and interpretation of these large differences in shift, which generally occur for compounds containing two-coordinate phosphorus, some trends can be discerned for metallophosphaalkenes.

In metallophosphaalkenes strong downfield shifts of the ³¹P resonances relative to the signals of the analogous, purely organo-substituted compounds are typical, this points to a small HOMO-LUMO gap. The effect can be correlated to the σ -donor effect of the complex fragment which is dependent not only on the donor strength of the 3d metal (Cr in 32 ($\delta = 605.4$) < Fe in 21 ($\delta = 641.5$) < Ni in 34b ($\delta = 740.5$)), but also on the ring ligand. Thus, the exchange of a Cp for a Cp* ligand causes a deshielding of $\Delta \delta$ (³¹P) of 42.9 to 60.3.

Table 1, $^{13}\mathrm{C}$ and $^{34}\mathrm{P}$ NMR data of selected P-metallophosphaalkenes and phosphaalkenes $^{\mathrm{Ial}}$

Compound		δ(³¹ Ρ)	δ(¹³ C)	¹ <i>J</i> (P,C)/ Hz	Ref.
$(Z)-tBu-P=C(OSiMe_3)(tBu)$		176.0	213.0	76.5	[44]
(Z)-[Cp(CO) ₂ Fe-P=C(OSiMe ₃)(tBu)]	4c	215.2	213.5	95.7	[3]
(Z)-[Cp*(CO) ₂ Fe-P=C(OSiMe ₃)(tBu)]	8c	258.1	211.2	87.7	[5]
$(Z)-tBu-P=C(OSiMe_3)(Ph)$		188.0	199.6	59.0	[45]
(Z)-[Cp(CO) ₂ Fe-P=C(OSiMe ₃)(Ph)]	4b	237.7	202.1	78.2	[3]
(Z)-[Cp*(CO) ₂ Fe - P=C(OSiMe ₃)(Ph)]	8b	287.1	199.7	72.6	[5]
(Z)-[Cp*(CO) ₂ Ru-P=C(OSiMe ₃)(Ph)]	9b	264.1	196.7	72.6	[6]
(Z)-[Cp*(CO) ₂ Os - P=C(OSiMe ₃)(Ph)]	10b	225.7			[7]
(Z)-[Cp(CO) ₂ Fe-P=C(OSiMe ₃)(Mes)]	4a	208.2	198.6	71.8	[3]
(Z)-[Cp*(CO) ₂ Fe-P=C(OSiMe ₃)(Mes)]	8 a	251.9	196.1	65.4	[5]
(E)-[Cp*(CO) ₂ Ru - P=C(OSiMe ₃)(Mes)]	(E)- 9 a	254.8			[6]
(Z)-[Cp*(CO) ₂ Ru-P=C(OSiMe ₃)(Mes)]	(Z)-9a	230.0	192.6	64.3	[6]
(Z)-[Cp*(CO) ₂ Os-P=C(OSiMe ₃)(Mes)]	(Z)-10 a	193.7	189.8	58.8	[7]
$tBu - P = C(SiMe_3)_2$		438.7	194.4	94.3	[46]
$[Cp(CO)_2Fe-P=C(SiMe_3)_2]$	20	593.2	211.2	110.9	[10]
$[Cp^*(CO)_2Fe \cdot P = C(SiMe_3)_2]$	21	641.5	208.9	106.1	[10]
$[Cp(CO)_3Mo-P=C(SiMe_3)_2]$	16	528.5	213.6	109.5	[10]
$[Cp(CO)_3W - P = C(SiMe_3)_2]$	18	505.2	210.1	106.4	[10]
$[Cp^*(CO)_3Cr - P = C(SiMe_3)_2]$	32	605.4	222.2	107.6	[10]
$[Cp^*(CO)_3Mo - P = C(SiMe_3)_2]$	17	588.8	218.0	106.9	[10]
$[Cp^*(CO)_3W - P = C(SiMe_3)_2]$	19	564.3	210.6	105.0	[10]
$[Cp^*(PEt_3)Ni - P = C(SiMe_3)_2]$	34 b	740.5	202.6	94.7	[10]
trans-[$(Bu_3P)_2(Cl)Ni - P = C(SiMe_3)_2$]	31 a	633.4			[12]
trans-[$(Bu_3P)_2(I)Ni - P = C(SiMe_3)_2$]	31 b	645.4			[12]
trans-[$(Ph_3P)_2(I)Pt - P = C(SiMe_3)_2$]	30	585.0			[12]
$Mes-P=C(NMe_2)_2$		8.05	197.8	72.5	[47]
$[Cp^*(CO)_2Fe - P = C(NMe_2)_2]$	35	135.5	202.4	97.0	[15]
$[Cp^{*}(CO)_{2}Ru - P = C(NMe_{2})_{2}]$	36	121.2	201.4	92.6	[15]

[a] In $C_6 D_6$; 85% H₃PO₄ as external standard for the ³¹P NMR signals.

In contrast, the exchange of iron in **8b** for the heavier homologues Ru and Os causes upfield shifts $(\Delta\delta(^{31}P) = -23.0 \text{ and} -38.4, respectively})$. Similar results are observed in the CpMo and CpW complexes **16** and **18** $(\Delta\delta^{31}P = -23.2)$ as well as in the Cp*Cr, Cp*Mo, and Cp*W complexes **32**, **17**, and **19** $(\Delta\delta^{31}P = -16.6 \text{ and} -24.5, respectively})$. As in nonmetalated phosphaalkenes, substituents on the heteroatom lead to an increased shielding of the phosphorus nucleus by conjugation of a lone pair with the P=C bond.

Up to now there are only a few examples known of (E/Z) isomerism of *P*-metallophosphaalkenes. In these compounds the more strongly sterically hindered (*E*) isomers absorb at somewhat lower field than the (*Z*) isomers (e.g. $\delta((E)$ -(9a)) $-\delta((Z)$ -(9a)) = 24.8^[6]).

Downfield shifts of the ³¹P NMR signal are also observed for *C*-metallophosphaalkenes of type [RP=C[M](OSiMe₃)] when a *tert*-butyl group on the methylene carbon atom is exchanged for a carbonylcyclopentadienyl metal complex fragment. This is attributed essentially to changes in the paramagnetic shift contribution. Thus, the singlet in (*E*)-[Cp*(CO)(NO)Re-C-(OSiMe₃)=PPh] ((*E*)-**46b**)^[22] observed at $\delta = 194.4$ is shifted downfield relative to that in (*E*)-PhP=C(OSiMe₃)(*t*Bu) ($\delta = 135.0^{1441}$) by $\Delta \delta = 59.4$. For the pair of compounds (*E*)-[Cp*(CO)(NO)ReC(OSiMe₃)=PSiMe₃] ((*E*)-**46a**) ($\delta = 214.4^{1221}$) and (*E*)-Me₃SiP=C(OSiMe₃)(*t*Bu)^[48] the corresponding downfield shift is $\Delta \delta = 99.4$. The *P*-aryl-*C*,*C*-dimetallophosphaalkenes **68a**^[28] and **75c**^[35] give singlets at δ (³¹P) = 151.3 and 258.0, respectively.

The ¹³C NMR spectra of phosphaalkenes show characteristic doublets for methylene carbon atoms at $\delta = 170-210$; the *P*-metallophosphaalkenes are found in the upper region of the

range. As the electron density on the metal atom increases, the ¹³C NMR chemical shift decreases. This also applies when the substitution pattern on the phosphaalkenyl fragment remains the same within a triad ((d⁴): Cr > Mo > W; (d⁶): Fe > Ru > Os) as well as for 3d metals with increasing atomic number ($Cr(d^4) > Fe(d^6) > Ni(d^8)$).

In *C*-metallophosphaalkenes **46**^[22] and **49**,^[25] the ¹³C NMR resonances lie at noticeably lower field ($\delta = 210.0-252.5$ (d), ¹*J*_{C,P} = 80.7–113.5 Hz). The corresponding signals in the ¹³C NMR spectra of the *C*,*C*-dimetallophosphaalkenes **75a**–c are doublets at even lower field ($\delta = 338.8-345.8$ (d), ¹*J*_{P,C} = 92–97 Hz)^[35] and therefore within the range of signals observed for carbenium ions.^[49]

4. Reactivity

Metallophosphaalkenes of types I-IV are polyfunctional molecules with various reactive centers that can undergo chemical transformations. The reactivity of *P*-metallophosphaalkenes (type I) has been the most extensively investigated to date. These species react readily with electrophiles, and several types of reaction and products are often observed. The initial step is frequently a Lewis acid-base interaction, in which the phosphaalkene plays the part of the Lewis base through the lone pair of electrons on phosphorus. Therefore, it seems reasonable to organize this section according to the nature of the reaction partner. The subdivision of the metallophosphaalkenes, types I-IV, remains unchanged.

4.1. Reactivity of the P-Metallophosphaalkenes (Type I)

4.1.1. Protic Reagents

The tungstiophosphaalkene **18** is protonated at the P atom by trifluoromethanesulfonic acid in CH_2Cl_2 at -78 °C to afford the cationic η^1 -phosphaalkene complex **78** (Scheme 26).^[8]

Equimolar amounts of **21** and 1,1,1,3,3,3-hexafluoropropane-2,2-diol dihydrate (hexafluoroacetone trihydrate) react in benzene to give the ferriophosphane oxide **79**, which can be isolated as pale yellow crystals in 30% yield.^[50] The hydration is catalyzed by the fluoroorganic compound, a weak protic acid ($pK_a = 6.58$).^[51]



Scheme 26. Reaction of metallophosphaalkenes 18 and 21 with protic reagents. $R = Me_3Si$.

4.1.2. Chalcogens

Reactions of 18 and 24 with sulfur and selenium follow an unexpected course. Instead of the anticipated oxidation to products of type 80, the chalcogen is inserted into the phosphorusmetal bond to produce complexes 81 and 83, respectively (Scheme 27). Double sulfurization of 24 gives the $1,2\lambda^5$ -thiaphosphirane 82 with preservation of the P–W bond. Compounds 80a and 80b, respectively, are postulated as intermediates.⁽¹⁰⁾



Scheme 27. Chalcogenation of tungstiophosphaalkenes; $[W] = Cp(CO)_3W$; E = S (a), Se (b); $R = Me_3Si$.

4.1.3. C₁ Building Blocks

4.1.3.1. Alkylating Agents

The cationic η^1 -[bis(trimethylsilyl)methylene]methylphosphane complex **84** can be prepared by the alkylation of **18** with methyl trifluoromethanesulfonate (Scheme 28).^[10]



Scheme 28. Methylation of $[Cp(CO)_3W-P=C(SiMe_3)_2]$ 18.

4.1.3.2. Diazoalkanes

Diphosphenes react smoothly with diazoalkanes with the loss of N₂ to produce diphosphiranes.^[1h] As yet there are no reports of a similar phosphirane synthesis from phosphaalkenes and diazo compounds. The first 1,2,3-diazaphospholes with metal functions on nitrogen (**86a,b**), are obtained unexpectedly from the treatment of **35** with equimolar amounts of diazoacetates (Scheme 29).^[52] The reaction proceeds by a 1,3-dipolar cycloaddition, in which the P atom of **35** is negatively polarized.^[52] 1,3-Dipolar cycloadditions between acyldiazoalkanes and phosphaalkenes such as Me₃SiP=C(R)(OSiMe₃) or CIP=C(R)-(SiMe₃), which contain positively polarized phosphorus centers, usually lead to 1,2,4-diazaphospholes.^[53] Intermediates such as **85** were not detectable.



Scheme 29. [3+2]Cycloaddition between 35 and diazoacetates. $[Fe] = Cp^*(CO)_2Fe$, R = Et (a), *t*Bu (b).

Evidently, after cycloaddition of the starting materials to produce **85**, there is a subsequent rapid elimination of dimethylamine and a 1,2-metal migration (Scheme 29). Compound **35** and trimethylsilyldiazomethane do not react with one another.

4.1.3.3. Sulfur Ylides

Sulfur ylides are known to be excellent alkylidene transfer reagents that readily convert diphosphenes to diphosphiranes.^[1h] The reaction of **21** with Me₂S(O)=CH₂ or Me(Me₂N)-S(O)=CH₂, however, does not lead to the expected *P*-metallophosphirane, but to the "butterfly" complex **87** (Scheme 30).^[54]

21
$$\xrightarrow{+ Me(R)S(0)=CH_2}_{- Me(R)S=0}$$

Scheme 30. Reaction of 21 with sulfur ylides. R = Me, Me_2N .

4.1.3.4. Isocyanides

The red, crystalline 2-imino-*P*-metallophosphiranes 88a - c result from a formal [2 + 1]cycloaddition of aryl isocyanides to **21** (Scheme 31).^[55] A striking feature in the molecular structure of **88a** (Fig. 2) is the P(1)-C(14) bond which is markedly elongated relative to the P(1)-C(13) bond. The endocyclic angle on the phosphorus atom [45.3(3)°] is strongly compressed com-



Scheme 31. Reaction of **21** with aryl isocyanides. $Aryl = Ph(\mathbf{a}), o-MeC_6H_4(\mathbf{b}), 2.6-Me_2C_6H_3(\mathbf{c}); [Fe] = Cp^*(CO)_2Fe.$



Fig. 2. Crystal Structure of **88a**. Selected bond lengths [Å] and angles [°]: Fe1-P1 2.279(2), P1-C13 1.799(7), P1-C14 1.990(7), C13-C14 1.469(8), N1-C13 1.273(7); C13-P1-C14 45.3(3), P1-C14-C13 60.9(3), P1-C13-C14 74.3(4).

pared to that on the ring carbon atoms C(13) [74.3(4)°] and C(14) [60.5(3)°].^[55]

In contrast, the ferriophosphaalkene **35** is not attacked by isocyanides on the P–C double bond under similar conditions, but reacts with CO substitution to afford $[Cp^*(CO)(RNC)-Fe-P=C(NMe_2)]$ (R = tBu, cC_6H_{11} , 2,6-Me₂ C_6H_3).^[56a]

4.1.4. C₂ Building Blocks

4.1.4.1. Alkenes

Since α,β -unsaturated carboxylic acid esters and nitriles are electrophilic, they are suitable partners for reaction with electron-rich metallophosphaalkenes. As a result of a two-step [2 + 2]cycloaddition, *P*-metallophosphetanes of type **89** are, a priori, the expected products (Scheme 32). However, treatment of **35** with fumarodinitrile and dimethyl fumarate lead instead to the *P*-metallo-1,2-dihydrophosphetes **90**; the initial products **89a,b** were not detectable by spectroscopy.^[15] The reaction of ferriophosphaalkene **21** with fumarodinitrile proceeds completely differently and leads to the insertion product **91**. X-ray structure analysis of the deep violet phosphido complex **91** reveals that the two cyano groups occupy *cis* positions at the C=C bond (Scheme 32).^[56b]

 $[Fe] \xrightarrow{NMe_2} \underbrace{E-CH=CH-E}_{NMe_2} \xrightarrow{[Fe]} \xrightarrow{NMe_2}_{H-C-C-E} \xrightarrow{[Fe]} \xrightarrow{P-C-NMe_2}_{H-C-C-E}$ goa, b $[Fe] \xrightarrow{P=C} \underbrace{SiMe_3}_{SiMe_3} \xrightarrow{NC} \underbrace{Fe]}_{H-C-C} \xrightarrow{Fe}_{NC} \xrightarrow{Fe}_{NC} \xrightarrow{Fe}_{NC} \xrightarrow{Fe}_{NC}$

Scheme 32. Reactivity of ferriophosphaalkenes towards electron-deficient alkenes. $[Fe] = Cp^*(CO)_2Fe; E = CO_2Me (a), CN (b).$

The reactivity of metallophosphaalkenes towards carbonylactivated alkynes is determined largely by the substituents on the reaction partners concerned, as well as by the solvent and by the stoichiometry of the starting materials. There have been no cases of the isolation of *P*-metallo-1.2-dihydrophosphetes, which should result from a formal [2+2]cycloaddition. Thus, the reaction of *C*-silylated metallophosphaalkenes **21** or **27** with one equivalent of dimethyl acetylenedicarboxylate **92a** produced the [3+2]cycloadducts **93** and **94**, respectively (Scheme 33). In this case, the role of the 1,3-dipole is played by the OC-Fe-P fragment which is polarized negatively on the P atom and positively on the carbonyl carbon atom.^[57]



Scheme 33. Reaction of the ferriophosphaalkenes 21 and 27 with dimethyl acetylenedicarboxylate; $E = CO_2Me$; R = Ph: 27, 94; $R = Me_3Si$: 21. 93.

The metallaheterocycle **95a**, which is analogous to **93** and **94**, however, is only a minor product of the reaction between **35** and **92a**. The main product is the 1-metallo-1-phospha-1,3-butadiene **97a**, which is isolated as a stable, red-brown solid (Scheme 34).^[58] The synthesis of **97a** from **35** and the alkyne is plausible if it is assumed that the initial reaction step is a non-concerted [2+2]cycloaddition to give 1,2-dihydrophosphete **96a**. The four-membered ring evades spectroscopic detection by spontaneous [2+2]cycloreversion to **97a** (Scheme 34).^[58] This result is unusual because, as a rule, heterobutadienes with phosphorus fragments can only be isolated if the P=C bond is kinet-



Scheme 34. Reaction of 35 with dimethyl acetylenedicarboxylate. [Fe] = $Cp^*(CO)_2Fe$; E = CO_2Me .

ically stabilized by bulky substituents.^[1a, 59] If there is insufficient steric shielding, the 1-phosphabutadienes spontaneously cyclize to 1,2-dihydrophosphetes. Mathey et al. postulate an equilibrium between 1,2-dihydrophosphetes and 1-phospha-



Scheme 35. Equilibrium between 1phosphabutadienes and 1.2-dihydrophosphetes.

butadienes (Scheme 35). At high temperatures this equilibrium shifts towards the heterodiene, which can be detected by trapping reactions.^[60]

In the synthesis of 97a, however, the reverse reac-

tion from a ring to an acyclic compound was accomplished for the first time, without the resulting heterodiene having particularly bulky substituents.

According to the X-ray structure analysis of **97a** (Fig. 3), the molecule has a cisoid conformation with a localized P=C bond. The C4–C5 and C4–C8 distances are similar and provide evidence for the pronounced delocalization of the C=C bond in the diene moiety of the molecule.



Fig. 3. Crystal Structure of **97a**. Selected bond lengths [Å] and angles []: Fe-P 2.259(2), P-C3 1.688(7), C3-C4 1.451(9), C4-C5 1.427(10), C3-C6 1.513(11), C4-C8 1.428(10); Fe-P-C3 119.3(3).

The ferriophosphaalkenes 21 and 27 are not attacked by methyl 2-butynoate (92b); however, if equimolar amounts of 35 and 92b are allowed to react in *n*-pentane, the 1-phosphabutadiene 97b precipitates as a red-brown solid (42% yield) (Scheme 36). Approximately equal amounts of 95b and the 2-methylene-1,2-dihydrophosphete 98 can be detected in the mother liquor. In ether or benzene, 97b cyclizes rapidly to 98 with release of dimethylamine. In keeping with this, treatment of 35 with the alkyne 92b in ether leads directly to orange microcrystalline 98 as the main product (41% yield).^[58]

On the other hand, alkyl propiolates $HC \equiv CCO_2R$ behave completely differently towards ferriophosphaalkenes. Compound **21** adds two equivalents of the alkyne in pentane to form the bicyclic, red, crystalline *P*-metallo-ylide **99** (Scheme 37); no intermediates were detected by ³¹P NMR spectroscopy.^[61] For-



Scheme 36. Reaction of 35 with methyl 2-butynoate. $E = CO_2Me$. $[Fe] = Cp*Fe(CO)_2$.



Scheme 37. Reaction of 21 with propiolates. R = Me(92c), Et (92d).

mation of the product is evidently preceded by the addition of two equivalents of the ester onto the P atom of **21** and a proton transfer from the ring methyl group to the end of the diene chain.^[61]

Equimolar amounts of 35 and methyl propriolate (92c) react in *n*-pentane to a furnish a mixture of the metallaheterocycle 95cand the 1-phosphabutadiene 97c (Scheme 38). The reaction between the ferriophosphaalkene and three molar equivalents of alkyne is more straightforward, here the bicyclic compound 100



Scheme 38. Reactions of 35 with methyl propiolate. $E = CO_2Me$; [Fe] = $Cp^*(CO)_2Fe$.

is obtained as the sole product in good yield. It is conceivable that **97c** forms a reactive [4+2]cycloadduct with the second equivalent of **92c** and is then rapidly converted to the final product by the third equivalent of alkyne.^[61]

4.1.5. Azo Compounds

Azodicarboxylates E-N=N-E induce the intramolecular condensation of a ring-methyl group with the P=C function in the metallophosphaalkene **35** to afford complexes **101a**-c in 48-54% yield (Scheme 39). This reaction is important because this was the first such condensation involving the η^{5} -C₅Me₅ ligand. An essential advantage of this ring ligand in its complexes, along with its donating ability and bulk, is its pronounced reluctance to chemical transformations.^[62]



101a-c

Scheme 39. Treatment of 35 with azodicarboxylates. $E=CO_2Et$ (a), CO_2tBu (b), CO_2CH_2Ph (c).

The X-ray structure analysis of **101b** (Fig. 4) reveals that the η^5 -ring ligand is additionally bonded to the metal atom by a



Fig. 4. Crystal Structure of **101b**. Selected bond lengths [Å] and angles []: Fe-P 2.307(2), P-C3 1.843(5), P-N2 1.781(5), C3-C4 1.338(9); Fe-P-C3 102.1(2), P-C3-C4 113.3(4), P-C3-N1 121.4(5), N1-C3-C4 124.7(5).

C=C-P chain. The C3-C4 distance of 1.338(9) Å corresponds to a double bond. The trigonal pyramidally surrounded phosphorus atom also bears a hydrazido substituent (N2-N3 1.399(6) Å).^[62]

4.2. Reactivity of the Metallophosphaalkenes of Type II and III

4.2.1. Rearrangement of Phosphametallabicyclohexenes

If the phosphazirconiabicyclic compounds 60a - c are heated in toluene to $60 \,^{\circ}$ C, they undergo ring opening to generate unstable vinylcarbene complexes. Subsequent "dimerization" of the carbene-metal fragment with the phosphaalkyne ligand produces four-membered rings of the type in compound 102, which also show structural properties of C-metallophosphaalkenes (Scheme 40). The corresponding titanium derivatives are also accessible.^[32]



Scheme 40. Thermal rearrangement of the bicyclic compounds 60a-c. [Zr] = Cp_2Zr ; **a**: $R^1 = R^2 = Me$ (89%), **b**: $R^1 = R^2 = Ph$ (97%), **c**: $R^1 = Me$, $R^2 = Ph$ (64%).

4.2.2. Thermolysis of the Phosphazirconiacyclopentadiene 57a

On warming a yellow solution of **57a** in toluene to 60 °C, it changes color to deep red over a period of 72 h with formation of the 1,4-diphosphinine complex **103** (92% yield) (Scheme 41).^[32] The same product arises almost quantitatively from an equimolar mixture of **57a**, **56**, and BEt₃ on warming from -78 °C to 20 °C.^[32]



Scheme 41. Synthesis of a (1,4-diphosphinine)dizirconium complex. $[Zr] = Cp_2 Zr_2$.

4.2.3. Thermolysis of C-Platiniophosphaalkenes

The metallophosphaalkenes **50a**,**b** rearrange at 20 °C in dichloromethane within 24 h to the bicyclic compounds **104a**,**b** which can be isolated without decomposition from the polar solvent (Scheme 42). In *n*-hexane, however, the products rapidly decompose to Mes*C \equiv P and *trans*-[Pt(PEt₃)₂X₂].^[28c]



Scheme 42. Intramolecular cyclization of C-platiniophosphaalkenes 50a,b. $L = PEt_3$; X = Cl(a), Br (b).

5. Coordination Chemistry of Metallophosphaalkenes

5.1. P-Metallophosphaalkenes as Ligands

Akin to their organo-substituted prototypes, the metallophosphaalkenes $L_nMP=CR^2R^3$ (type I) can also act as ligands in transition metal complexes. In principle, the coordination modes G-K are conceivable. (Scheme 43).



Scheme 43. Coordination modes of metallophosphaalkenes in transition metal complexes.

The metallophosphaalkenes of the four other structural types (II-V) should show comparable ligand properties. In contrast to the coordination behavior of conventional phosphaalkenes, it is possible for the lone pair of electrons on the phosphorus atom in *P*-metallophosphaalkenes to displace a loosely bound two-electron donor (2e donor) intramolecularly from the metal, so that the organophosphorus fragment becomes a 3e ligand. Similar behavior is known from phosphido and phosphenium ligands PR_2 ,^[63] and, of course, from NO ligands. In the case discussed here, phosphavinylidene complexes **F** are formed.

5.1.1. Phosphavinylidene Complexes (Type F)

This type of complex is known with molybdenum, tungsten and nickel; the first, the complex **105a**, was obtained from the reaction of K[Mo(CO)₃Cp] with $ClP=C(SiMe_3)_2$ in THF (Scheme 44).^[64]





Scheme 44. Syntheses of phosphavinylidene complexes of molybdenum and tungsten. a: M = Mo, R = H; b: Mo, Me; c: W, H; d: W, Me.

The metallophosphaalkenes 16-19 undergo thermal decarbonylation in solution to give the phosphavinylidene complexes 105a-d (Scheme 44). The reaction conditions required for the cleavage of the CO ligand depend on the stability of the metal-CO bond as well as on the substituents on the phosphaalkenyl fragment. Accordingly, cleavage of CO from the molybdenio-phosphaalkenes 16 and 17 in nonpolar solvents commences at room temperature, whilst the formation of the tungsten derivatives 105c,d requires several hours reflux in benzene. For the ferriophosphaalkenes 21 as well as for the phenyl-substituted metallophosphaalkenes 22-27, elimination of CO to form phosphavinylidene complexes is not observed under thermal nor under photochemical conditions.^[10]

Abstraction of CO can also be carried out chemically. Thus, the adduct obtained from **18** and nickel tetracarbonyl at low temperatures rapidly decomposes in solution at 20 °C to afford **105c** and $[Ni(CO)_4]$ (Scheme 44).^[10]

An interesting route to the (phosphavinylidene)nickel cation **107** is based on the treatment of $[Ni(PPh_3)_2(cod)]$ with triphenyl(phosphaalkenyl)phosphonium ion **106** (Scheme 45). No intermediates were detected by spectroscopy.^[65]



Scheme 45. Synthesis of a (phosphavinylidene)nickel complex. L = 1,5-cyclo-octadiene, R = Me_3Si, X = AlCl_4.

5.1.2. Metallophosphaalkenes as η^1 Ligands (Type G)

Transition metal complexes with η^1 -metallophosphaalkene ligands of type G are formally divided into those without metal – metal interactions (e.g. 108 and 109) and those with M-M bonding (e.g. 110 and 112). The former usually arise from the treatment of metallophosphaalkenes, for example **24**, with transition metal complexes containing labile ligands (Scheme 46).^[10]



Scheme 46. *P*-Metallophosphaalkenes as η^{4} -ligands without M-M bonds.

The preparation of the dinuclear complex **110** with an Fe–Fe bond was carried out by the reaction of $ClP=C(SiMe_3)_2$ with excess $[Na_2Fe(CO)_4]\cdot 1.5$ dioxane in the presence of diazabicy-cloundecene (Scheme 47).^[66]



Scheme 47. P-Metallophosphaalkenes as η^1 -ligands with M-M bonds. **a**: R¹ = R² = c-C₀H₁₁; **b**: tBu; **c**: Me₃Si; **d**: R¹ = tBu, R² = Me₃Si.

Dinuclear carbonylnickel complexes 112a-d with μ -phosphaalkenyl and μ -phosphido ligands result from the treatment of 1,2-diphosphapropenes 111a-d with two molar equivalents of [Ni(CO)₄] (Scheme 47). If a larger excess of nickel carbonyl is added, the trinuclear species 113a-d are formed in which the P=C bond also acts as a π donor. Compounds 112a-d also react directly with [Ni(CO)₄] to give 113a-d.^[67] Derivatives of type 112 are also known with iron and molybdenum centers.^[67]

5.1.3. P-Metallophosphaalkenes as η^2 Ligands (Type H)

Compounds containing a metallophosphaalkene with this mode of coordination usually arise from peripheral reactions of phosphaalkynes with transition metal complexes. For example, the reaction of $[Cp_2^*(CO)_2Rh_2]$ or $[Cp_2^*(CO)_2CoRh]$ with $tBuC\equiv P$ readily affords the complexes 114 (Scheme 48).^[68, 69] Complex 115a is formed as a side-product and can be regarded as a metallodiphosphadiene which is additionally π -bound through both C=P functions to a Cp*Rh fragment. The reaction of $[Cp_2^*(CO)_2Rh_2]$ with AdC $\equiv P$ proceeds similarly.





Scheme 48. Metallophosphaalkenes as η^2 ligands; **a**: $M^1 = M^2 = Rh$, R = tBu; **b**: $M^1 = M^2 = Rh$, R = 1-adamantyl; **c**: $M^1 = Rh$, $M^2 = Co$, R = tBu; **d**: $M^1 = Co$, $M^2 = Rh$, R = tBu.

A mode of coordination similar to that present in 114 is encountered in the dinuclear iron complex 117, which is produced by the photolysis of 116 in the presence of $tBuC\equiv P$ (Scheme 48).^[70]

5.1.4. Metallophosphaalkenes as $\eta^1:\eta^2$ Ligands (Type I)

It appeared reasonable to extend the principle of synthesis for C,C-dimetallophosphaalkenes, outlined in Scheme 24, to the preparation of C,C,P-trimetallophosphaalkenes [[M¹]—P=C-([M²])[M³]] (type V, Scheme 2). Condensation of the cation **73** with metallodisilylphosphanes **5** or **6** gave, instead of the expected threefold functionalized phosphaalkenes, the trinuclear complexes **118a** and **118b**, respectively, in which the $\eta^1:\eta^2$ -metallophosphaalkene ligand bridges the [Fe₂Cp₂(CO)(μ -CO)] skeleton (Scheme 49). Compound **118a** can also be obtained from the reaction of [FeCp*(CO)₂(PH₂)] and **73** under analogous conditions.^[71]



Scheme 49. Synthesis of complexes with $\eta^1:\eta^2$ -metallophosphaalkene ligands; **a**: $[M] = Cp^*(CO)_2Fe$; **b**: $[M] = Cp^*(CO)_2Ru$.

5.2. Miscellaneous

Metallophosphaalkenes of type II and IV (Scheme 2) can also function as ligands in transition metal complexes. For example, the η^1 complexes **119** containing a *C*-metallophosphaalkene ligand are obtained from the action of thermolabile carbonylmetal complexes such as [Cr(cyclooctene)(CO)₅]^[72] or [Fe₂(CO)₉]^[73] on compound **87** (Scheme 50). However, if **87** or **119b** is treated with excess [Fe₂(CO)₉], the trinuclear complex **120** is isolated, which has a formal μ_3 -1-oxa-4-phosphabutadiene ligand.^[73]



Scheme 50. Reaction of 87 with carbonylmetal complexes. $R = Me_3Si$; a: L = cyclooctene, $M(CO)_n = Cr(CO)_5$; b: L = Fe(CO)₅, $M(CO)_n = Fe(CO)_4$.

The coordination mode which the dimetallophosphaalkene **75a** displays towards transition metal fragments is controlled by the nature of the complex building unit. The reaction with equimolar amounts of $[Cr\{(Z)\text{-cyclooctene}\}(CO)_5]$ or $[Fe_2-(CO)_9]$ leads to the black-brown microcrystalline compounds **121** and **122**, respectively (Scheme 51). In complex **123**, obtained from the treatment of **75a** with $[Pt(PPh_3)_2(\eta^2-C_2H_4)]$, the dimetallophosphaalkene can be described as a η^3 -1-phospha-3-ferraallyl ligand bound to a $[Pt(PPh_3)]$ fragment.

The X-ray crystal structure analysis of **123** (Fig. 5) reveals that the molecular framework of **75a** has remained largely intact. The trigonal-planar surrounded donor site C(12) (sum of angles = 359.2°) symmetrically bridges the iron atoms. The P=C bond is elongated to 1.737(10) Å on account of π coordination to the Pt atom. In order to saturate its coordination, the platinum atom also bonds to Fe(1) and C(13). Alternatively, the framework can be regarded as an *arachno* cluster of atoms Pt(1), P(2), C(12), Fe(1), and C(13).^[36]

The complex anions 125a-d, which arise from the reaction of carbonylhydridometalates 124a-d with equimolar amounts of $tBuC \equiv P$ (Scheme 52), contain a $\mu_3 - \eta^2$ -phosphaalkyne ligand,



Scheme 51. The C,C-Diferriophosphaalkene **75a** as a ligand in Cr, Fe, and Pt complexes. **121**: $M(CO)_n = Cr(CO)_5$, L = cyclooctene; **122**: $M(CO)_n = Fe(CO)_4$, L = Fe(CO)₅.



Fig. 5. Crystal Structure of **123**. Selected bond lengths [Å] and angles [°]: Pt1-Fe1 2.577(2), Pt1-P1 2.240(2), Pt1-P2 2.471(2), Pt1-C12 2.162(9), Pt1-C13 1.997(2), Fe1-C13 1.951(9), P2-C12 1.737(10), Fe1-Fe2 2.518(4); Fe1-C12-P2 130.6(5), Fe2-C12-P2 146.5(5), Fe1-C12-Fe2 82.1(4).



Scheme 52. Complex anions with a C,P-dimetallophosphaalkene as a η^2 -ligand. a: $M^1 = PPh_4$, $M^2 = Fe$; b: $M^1 = (Ph_3P)_2N$, $M^2 = Ru$; c: $M^1 = Na$, $M^2 = Ru$; d: $M^1 = NEt_4$, $M^2 = Ru$.

which unsymmetrically spans the metal triangle. Alternatively, these anions may also be regarded as C,P-dimetallophosphaalkenes in which the C=P bond maintains a π interaction with a third metal atom.^[74]

6. Chemical Properties of Phosphavinylidene Complexes

In agreement with the polarization $P^{\delta^+} - C^{\delta^-}$ of the P=C bond in the molybdenumphosphavinylidene complex **105a**, protic substances, HX, add regioselectively to the double bond to form the phosphenium complexes **126** (Scheme 53).^[44b] The



Scheme 53. Reactions of 105a with proton and hydride donors. $R = Me_3Si$; X = EtO, Me_2N , C_6F_5S .

behavior of **105a** towards the hydride donor $\text{Li}(\text{BHEt}_3)$ is explained similarly. If a solution of the phosphavinylidene complex is treated with one equivalent of $\text{Li}(\text{HBEt}_3)$ and subsequently with excess methyl iodide, heterocycles with three-membered rings, **127** and **128**, are produced. Here, hydride attack on the phosphorus atom of **105a** plays the key role.^[75]

Equimolar amounts of the phosphavinylidene complexes **105a** or **105c** and the sulfur ylide $Me_2S(O)=CH_2$ in ether react to form the phosphenium complexes **129** (Scheme 54), which



Scheme 54. Reaction of phosphavinylidene complexes of molybdenum and tungsten with $Me_2S(O)=CH_2$. M = Mo, W.

are isolated as brick red solids in yields of about 70%. Evidently, the addition of the carbanionic ylide center onto the P atom is accompanied by a rapid transylidation. A second ylide molecule subsequently "cyclopropanizes" the M=P bond to yield the metallaheterocycle **130**.^[76]

7. Summary and Future Prospects

This review demonstrates that the chemistry of metal-functionalized phosphaalkenes has developed rapidly in recent years. In the beginning the interest focused on the synthesis and structural elucidation of such complexes. Ever increasingly it has shifted towards the reactivity of these compounds which are to be found in the border regions 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 makes metallophosphaalkenes versatile reaction partners, and we have only just begun to explore the great richness of their chemistry.

The possibilities for the synthesis of metallophosphaalkenes with their structural variations are by no means exhausted. Novel reactive compounds, such as the recently discovered phosphanestabilized methylenediylphosphenium salts ($(Ph_3P-P=CR_2)X$) continually lead to novel metallophosphaalkenes. Even phosphaalkynes, which are in the meantime so well-known, serve further as a valuable source for the synthesis of metallophosphaalkenes. Metallophosphaalkenes play a key role as intermediates in the metal-mediated oligomerization of phosphaalkynes to phosphorus-carbon heterocycles and cages. The understanding of the chemical properties of metallophosphaalkenes not only casts light onto such oligomerization processes, but also should be an aid in the planning of efficient syntheses.

In future, along with purely preparative considerations, physico-chemical investigations will make an important contribution to this field, in particular, electrochemical, kinetic, and mechanistic studies, as well as theoretical calculations. Application-orientated aspects such as polymerization and copolymerization of suitably substituted derivatives are also waiting to be discovered.

I would like to thank all my coworkers who have contributed with great commitment to the development of this field. Their names can be found in the literature citations. I owe many thanks to Professors E. Niecke (Bonn) and W. W. Schoeller (Bielefeld) for helpful discussions. I thank Mrs M. Schimmel for writing up the manuscript. Much of the cited work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the companies BASF AG, Ludwigshafen, and DE-GUSSA AG, Hanau.

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