Phosphaalkenes with Inverse Electron Density

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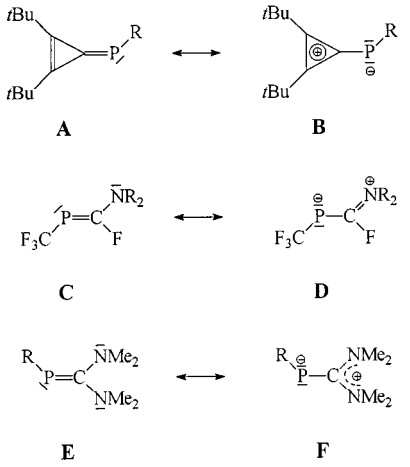
This review gives an account of the syntheses, structures, and properties of phosphaalkenes $R^1P{=}CR^2R^3$ with an inverse electron distribution at the P–C double bond ($P^{\delta-}C^{\delta+}$). The chemical reactivity of compounds of this type is novel and quite surprising compared to the chemistry of "classically polarized" phosphaalkenes ($P^{\delta+}C^{\delta-}$).

1. Introduction

The chemistry of compounds with low-coordinate phosphorus atoms involved in phosphorus−carbon multiple bonding has rapidly developed since the discovery of HC≡P by Gier in 1961.[1,2] The formal replacement of one methylene group in alkenes $R^2R^3C{=}CR^4R^5$ by the phosphanediyl unit R^1P affords the class of phosphaalkenes $R^1P{=}CR^2R^3$. Numerous papers on phosphaalkenes have highlighted the remarkable ability of phosphorus to mimic the chemistry of carbon.[3] The vast majority of phosphaalkenes feature an electron distribution $P^{\delta+}C^{\delta-}$ at the P−C double bond, as would be anticipated from the different electronegativities of carbon (2.5) and phosphorus (2.1).

About ten years ago inversely polarized phosphaalkenes were independently discovered by several research groups. Regitz et al. synthesized the first 2,3-di-*tert*-butylcyclopropylidene phosphanes and pointed out that these phosphatriafulvenes have an inverse π-electron distribution at the exocyclic P=C double bond, as depicted in the zwitterionic limiting structure **B**.[4]

A similar polarization of the π-bond was inferred from the ^{31}P NMR spectra of phosphaalkenes such as $F_3CP{=}C(F)NR_2$ (R = Me, Et, *i*Pr; NR_2 = pyrrolidino, piperidino, 2-methylpiperidino, 3-methylpiperidino, *N*-methylanilino),[5] $F_3CP{=}C(OR)NR'_2$ (R, R′ = Me, Et),[6] or $HP{=}C(Me)NMe_2$[7] where unusual high-field resonances for the dicoordinate phosphorus atom were observed (Scheme 1).



Scheme 1. Resonance structures of phosphaalkenes with an inverse π-electron density

This polarization is even more pronounced in phosphaalkenes with two amino substituents at the carbon atom of the double bond, such as $RP{=}C(NMe_2)_2$ (R = H,[8] Me_3Si,[9] alkyl,[7] aryl[10]) (Scheme 1).

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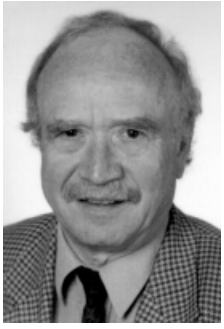

Lothar Weber was born in 1944 in Langenöls in Schlesien. He studied at the Universität Marburg and received his doctorate there under the direction of Professor Günter Schmid in 1973. Afterwards, he carried out post-doctoral studies with Professor Barry M. Trost at the University of Wisconsin in Madison,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

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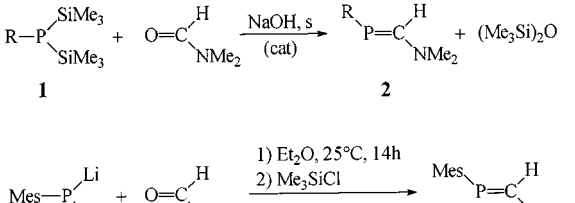
2. Syntheses

Basically, phosphaalkenes with an inverse π-electron density are available by the same synthetic methods which have been developed for phosphaalkenes with a normal π-electron distribution ($P^{\delta+}C^{\delta-}$). The most useful approaches to inversely polarized phosphaalkenes, however, involve condensations or substitution reactions at the P=C skeleton of appropriate precursors.

2.1. Condensation

Among condensation processes the Peterson olefination plays a prominent role in the construction of P=C double bonds.

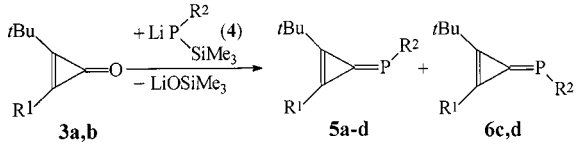
Thus, condensation of neat organobis(trimethylsilyl)phosphanes $RP(SiMe_3)_2$ (**1a**: R = Mes; **b**: Ph; **c**: *t*Bu) with excess *N*,*N*-dimethylformamide to afford the yellow phosphaalkenes $RP{=}C(H)NMe_2$ (**2a–c**, Scheme 2) was achieved in the presence of catalytic amounts of solid sodium hydroxide.[11] Without the catalyst, the reaction takes several weeks for completion.[12] An alternative high-yield synthesis of $MesP{=}C(H)NMe_2$ makes use of lithium phosphanide $LiP(Mes)(SiMe_3)$ as a starting material. Here the $LiOSiMe_3$ byproduct must be treated with Me_3SiCl prior to work up.[11]



1, 2	a	b	c
R	Mes	Ph	*t*Bu

Scheme 2. Synthesis of *C*-(dimethylamino)phosphaalkenes **2a–c**

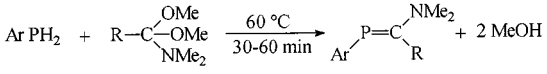
Analogously, treatment of cyclopropenones **3a**,**b** with lithium (trimethylsilyl)phosphanides **4** led to the formation of the cyclopropanylidene phosphanes **5a–d** and **6c**,**d** (Scheme 3).[4]



5, 6	R1	R2
a	*t*Bu	Me_3Si
b	*t*Bu	Mes
c	1-Ad	Me_3Si
d	1-Ad	Mes

Scheme 3. Synthesis of cyclopropenylidenephosphanes **5** and **6**

Another effective route to the *P*-arylated phosphaalkenes **2a**,**b**,**d–f** makes use of the ready condensation of carboxylic amide acetals with primary arylphosphanes at 60 °C. The products were isolated as dark yellow oils, which in some cases solidified to give light yellow crystals (Scheme 4).

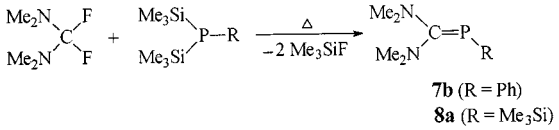


	2a	2b	2d	2e	2f
Ar	Mes	Ph	Ph	Mes*	Mes*
R	H	H	Me	H	Me

Scheme 4. Reaction of carboxylic amide acetals with arylphosphanes

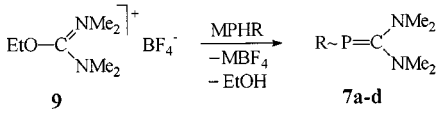
It is worth mentioning that primary alkylphosphanes do not react with these acetals.

Geminal difluorides are useful precursors for the preparation of *C*-amino-functionalized phosphaalkenes. Thus, [bis(dimethylamino)methylene](phenyl)phosphane (**7b**) and [bis(dimethylamino)methylene](trimethylsilyl)phosphane (**8a**) were obtained by gentle heating of an equimolar mixture of 1,1-difluoro-*N*,*N*,*N*′,*N*′-tetramethyldiaminomethane and either $PhP(SiMe_3)_2$ or $(Me_3Si)_3P$, respectively (Scheme 5).[9]



Scheme 5. Synthesis of **7b** and **8a**

Aryl bis(dimethylamino)methylene phosphanes such as $RP{=}C(NMe_2)_2$ [R = Mes (**7a**), Ph (**7b**)] are also conveniently accessible by combination of the carbenium salt $[EtOC(NMe_2)_2]^+BF_4^-$ (**9**) with the respective alkali metal arylphosphanide in diethyl ether[10] (Scheme 6).



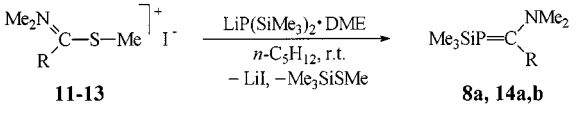
7	a	b	c	d
R	Mes	Ph	*t*Bu	H
M	Li	Na	Li	K

Scheme 6. Reaction of carbenium salts with alkali metal phosphanides

This approach, however, is of only limited value, and usually fails with the more basic alkali metal alkylphosphanides. Only $tBuP{=}C(NMe_2)_2$ (**7c**) could be prepared in 30% yield from lithium *tert*-butylphosphanide and **9**.[7] A comparable yield of the phosphaalkene **7d** was achieved when the carbenium salt **9** was allowed to react with KPH_2 in THF at ambient temperature.[7]

Spontaneous condensation occurred upon mixing of lithium bis(trimethylsilyl)phosphanide · DME with the methylthiocarbenium iodides **11–13** in *n*-pentane. The

phosphaalkenes **8**, **14a**, and **14b** were formed as orange-yellow oils in moderate to good yields (Scheme 7).[15,16]



11-13 **8a, 14a,b**

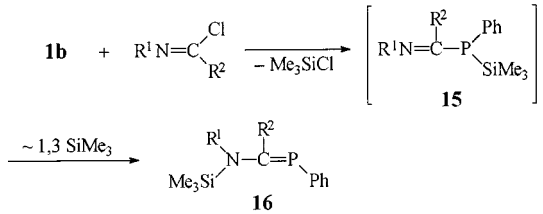
	R
8a, 11	NMe_2
12, 14a	Ph
13, 14b	*t*Bu

Scheme 7. Synthesis of *P*-silylphosphaalkenes **8a** (R = NMe_2), **14a** (R = Ph), and **14b** (R = *t*Bu)

2.2. Condensation and 1,3-Trimethylsilyl Migration

The transformation of organodisilylphosphanes to amino-substituted phosphaalkenes such as **16** with imidoyl chlorides formally parallels the synthesis of the oxygen-functionalized analogues $R^1P{=}C(OSiMe_3)R^2$. Thus, heating a 1:1 mixture of phenylbis(trimethylsilyl)phosphane **1b** with imidoyl chlorides at 150−160 °C led to compounds **16a−k** in 23−85% yield. Intermediates of the type **15** could not be detected by ^{31}P NMR spectroscopy.[17]

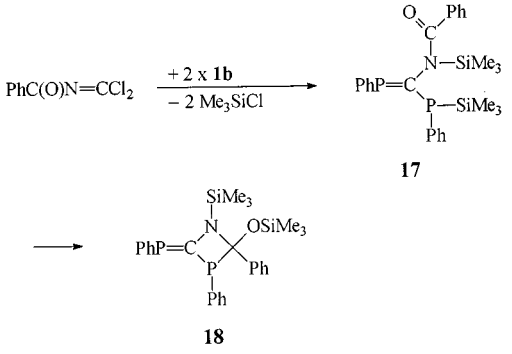
The content of Scheme 8 has to be regarded critically, as not all the phosphaalkenes **16** exhibit an inverse π-electron distribution, and in line with this, significantly shielded ^{31}P NMR absorptions. In keeping with Scheme 1, only those species where the limiting structure **D** is possible are regarded as inverse phosphaalkenes. Whenever, for steric reasons, the amino group and the C−C=P−C skeleton cannot be accommodated in the same plane, π-conjugation between the lone pair of electrons and the P=C-π bond will be precluded and the molecule will behave as a normally polarized phosphaalkene. This point will be discussed in more detail in Chapter 3 of this account.



15, 16	R^2	R^1
a	Ph	Ph
b	*t*Bu	Ph
c	Ph	Me
d	Mes	Ph
e	Ph	2,6-$Et_2C_6H_3$
f	Ph	*c*-C_6H_{11}
g	*p*-ClC_6H_4	Ph
h	*p*-$MeOC_6H_4$	Ph
i	Ph	*p*-ClC_6H_4
k	Ph	*p*-$MeOC_6H_4$

Scheme 8. Synthesis of phosphaalkenes **16** from imidoyl chlorides

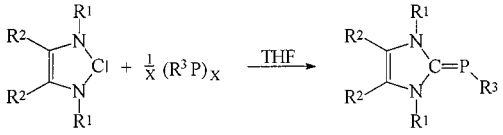
Condensation with subsequent silatropy was also effected with *N*-(dichloromethylene)amides. Consistently, interaction of **1b** with *N*-(dichloromethylene)benzamide afforded phosphaalkene **17**, which in polar solvents at elevated temperatures underwent a rapid intramolecular insertion of the carbonyl unit into the P−Si bond with the formation of **18** (Scheme 9).[18]



Scheme 9. Reaction of *N*-(dichloromethylene)benzamide with $PhP(SiMe_3)_2$

2.3. Carbene Addition

Adducts **20** formed between imidazol-2-ylidenes **19** and phenylphosphinidene or (trifluoromethyl)phosphinidine also exhibit the structural features of phosphaalkenes with an inverse π-electron distribution (Scheme 10). They were easily synthesized from suitable stable carbenes and pentaphenylcyclopentaphosphane, or tetrakis(trifluoromethyl)cyclotetraphosphane as the sources of the phosphinidene fragments.[19,20]



19a-c **20a-c**

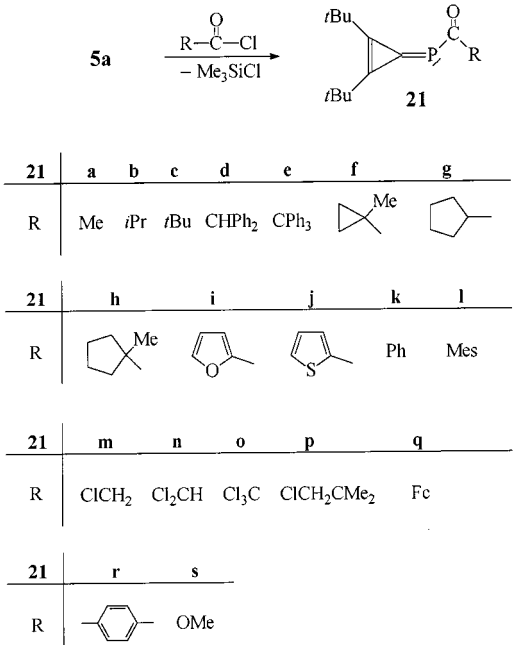
20	R^1	R^2	R^3
a	Me	Me	Ph
b	Mes	H	Ph
c	Mes	H	CF_3

Scheme 10. Synthesis of **20a−c** by carbene addition to phosphinidenes

2.4. Substitution

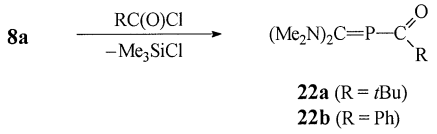
Substitution reactions at the P=C skeleton of inversely polarized phosphaalkenes represent a valuable approach to many of the compounds under discussion. In particular, *P*-silylated phosphaalkenes proved to be appropriate targets for further functionalization.

The reaction of phosphatriafulvene **5a** with carboxylic chlorides in diethyl ether afforded the *P*-acylphosphatriafulvenes **21** in yields of 40−87% (Scheme 11).[4b]



Scheme 11. Acylation of **5a**

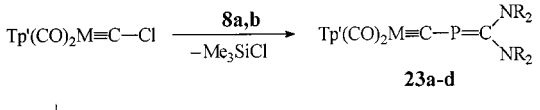
Similarly $Me_3SiP{=}C(NMe_2)_2$ (**8**) was transformed into the *P*-acyl derivatives **22a** and **22b** when allowed to react with an equimolar amount of pivaloyl or benzoyl chloride, respectively (Scheme 12).[21]



22a (R = *t*Bu)
22b (R = Ph)

Scheme 12. Acylation of **8a** by *t*BuC(O)Cl and PhC(O)Cl

Reaction of the chlorocarbyne complexes $Tp'(CO)_2M{\equiv}C{-}Cl$ [M = Mo, W; Tp′ = HB(3,5-$Me_2C_3HN_2)_3$] with two molar equivalents of **8a** in CH_2Cl_2 led to the precipitation of the red carbyne complex functionalized phosphaalkenes **23a**,**b** within 2 h (Scheme 13). The analogous conversion of the chlorocarbyne complexes into **23c**,**d** by treatment with $Me_3SiP{=}C(NEt_2)_2$ (**8b**) required 15−18 h to reach completion.[22]



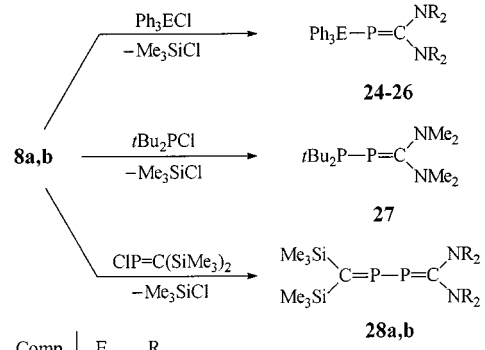
23a-d

23	a	b	c	d
M	Mo	W	Mo	W
R	Me	Me	Et	Et

Scheme 13. Condensation of chlorocarbyne complexes with **8a** and **8b**

Bis(amino)methylene(trimethylsilyl)phosphane **8a** underwent transsilylation when treated with equimolar amounts of chlorotriphenylsilane in benzene at 20 °C for 3 h.[23]

In contrast to this, the reactions of the phosphaalkenes with trialkylchlorosilanes were reversible as indicated by the action of $(Et_2N)_2C{=}PSiMe_3$ (**8b**) with 1.2 equiv. of $Me_2EtSiCl$ at 20 °C, which led to an 1:2 equilibrium mixture of starting material and $(Et_2N)_2C{=}PSiMe_2Et$. Treatment of **8b** with equimolar amounts of Ph_3GeCl and Ph_3SnCl in benzene at 40 °C irreversibly afforded $Ph_3GeP{=}C(NEt_2)_2$ (**25**) and $Ph_3SnP{=}C(NEt_2)_2$ (**26**), respectively (Scheme 14).[23] The replacement of the silyl function in **8a** by a di-*tert*-butylphosphanyl group with formation of $tBu_2P{-}P{=}C(NMe_2)_2$ (**27**) was effected with an equimolar amount of tBu_2PCl in diethyl ether.[9b]

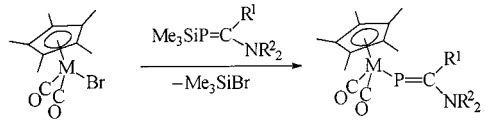


Comp.	E	R
24	Si	Me
25	Ge	Et
26	Sn	Et
28a		Me
28b		Et

Scheme 14. Reaction of **8a**,**b** with Ph_3ECl (E = Si, Ge, Sn), tBu_2PCl, and $ClP{=}C(SiMe_3)_2$

Reactions of *P*-silylphosphaalkenes **8a**,**b** with *P*-chlorophosphaalkenes are a valuable route to compounds **28a**,**b** with a diphosphadiene system (92−93% yield)[24] (Scheme 14).

The transition metal functionalized phosphaalkenes **29a−e** were obtained as crystalline products from the condensation of *P*-silylphosphaalkenes with $[(\eta^5\text{-}C_5Me_5)(CO)_2FeBr]$ and $[(\eta^5\text{-}C_5Me_5)(CO)_2RuBr]$[16,25] (Scheme 15).



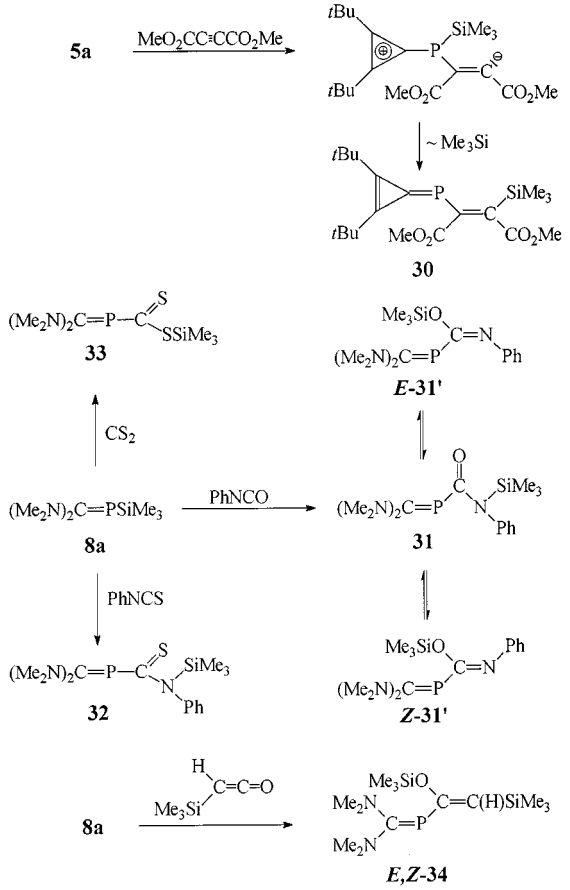
29a-e

29	M	R1	R2
a	Fe	NMe_2	Me
b	Fe	NEt_2	Et
c	Fe	Ph	Me
d	Fe	*t*Bu	Me
e	Ru	NMe_2	Me

Scheme 15. Synthesis of metallophosphaalkenes **29a−e**

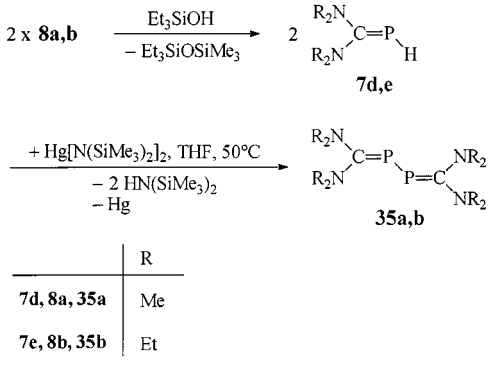
The P−Si bond of **5a** and **8a**,**b** tends to undergo 1,2 addition to the multiple bonds in alkynes and heterocumulenes

to yield compounds **30**−**34** as yellow to red crystalline solids[4,21,26] (Scheme 16).



Scheme 16. Reaction of **5a** and **8a** with $MeO_2C-C{\equiv}C-CO_2Me$ and heterocumulenes

Triethylsilanol selectively cleaved the P−Si bond in *P*-silylphosphaalkenes **8a**,**b** without affecting the P=C bond. This transformation constitutes a convenient method for the preparation of **7d** and **7e**,[27] which can be further transformed into the yellow liquid 2,3-diphosphabutadienes **35a**,**b** by treatment with $Hg[N(SiMe_3)_2]_2$ (Scheme 17).[28]

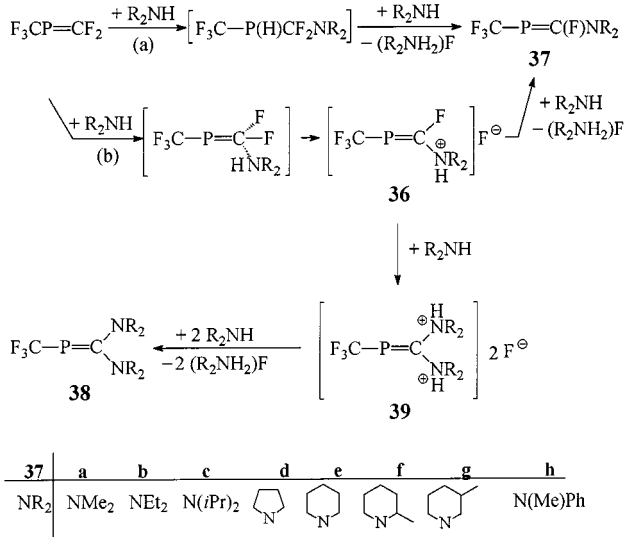


Scheme 17. Preparation of 2,3-diphosphabutadienes from **7d**,**e**

It is also possible to synthesize *C*-amino-functionalized phosphaalkenes by replacement of a fluorine substituent in phosphaalkenes such as $F_3CP{=}CF_2$ or $HP{=}CF_2$.

Perfluoro-2-phosphapropene reacted quantitatively with secondary amines in the molar ratio 1:2 at low temperature to yield the (*Z*)-configured phosphaalkenes $F_3CP{=}C(F)NR_2$ **37a**−**h**.[5]

Two possible mechanisms were discussed in rationalizing this result. In path (a) the addition of the NH function to the P=C bond was rapidly followed by the base-assisted 1,2-elimination of HF. In route (b) one molar equivalent of amine was added to the positively polarized carbon atom of the P=C bond prior to fluoride extrusion to give intermediate **36**, which was subsequently deprotonated by a second equivalent of amine (Scheme 18). During the course of this reaction small amounts of the disubstituted products $F_3CP{=}C(NR_2)_2$ (**38**) were also generated, which was explained by a second competing fluoride displacement from intermediate **36** by amine and a twofold deprotonation of the resulting dication **39**.



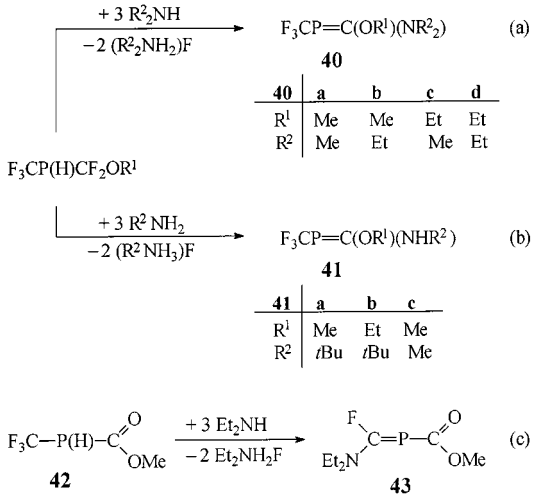
Scheme 18. Preparation of $F_3CP{=}C(F)NR_2$ and $F_3CP{=}C(NR_2)_2$ from $F_3C-P{=}CF_2$

Alternatively, the monoamino products **37** were accessible by treatment of bis(trifluoromethyl)phosphane with the secondary amine in a molar ratio of 1:3 at −40 °C via transient $F_3CP{=}CF_2$. This approach has the advantages of a one-pot reaction and the easy availability of the precursor $(CF_3)_2PH$.[5]

This synthetic principle was extended to the preparation of the yellow liquid phosphaalkenes $HP{=}C(F)NR_2$ [R = Me (**a**), Et (**b**), *i*Pr (**c**)] by the utilization of CF_3PH_2 as a starting material.[29]

Similarly, compounds $F_3CP{=}C(F)(OR^1)$ were subjected to reaction with secondary amines to yield the stable inversely polarized phosphaalkenes $F_3CP{=}C(NR^2_2)(OR^1)$ (**40a**−**d**).[6] Again it was advantageous to generate the phosphaalkene precursors $F_3CP{=}C(F)(OR^1)$ in situ from PH-functionalized phosphanes $F_3CP(H)CF_2OR^1$ by amine-induced HF elimination[6] [Scheme 19 (a)].

The employment of primary amines gave rise to the thermolabile compounds **41a**−**c**, which in CH_2Cl_2 solution at 20 °C completely decomposed within a few hours[30] [Scheme 19, (b)].



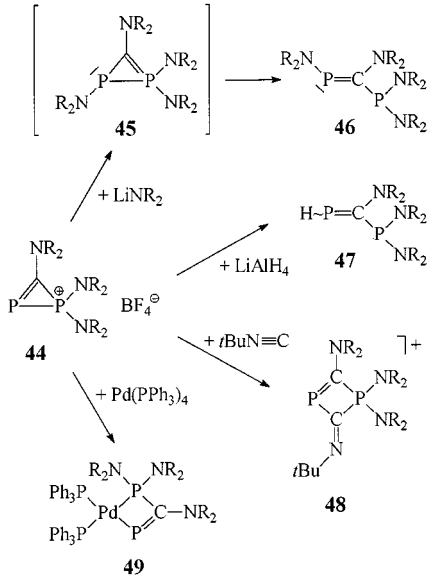
Scheme 19. Preparation of $F_3CP{=}C(OR^1)(NR^2_2)$, $F_3CP{=}C(OR^1)(NHR^2)$ and **43**

The very interesting *P*-methoxycarbonyl-functionalized phosphaalkene **43** resulted as a final product from the combination of phosphane **42** with an excess of diethylamine at −40 °C by a sequence of elimination and addition steps [Scheme 19, (c)].

The product was isolated as a yellow thermally stable oil in 65% yield.[30]

2.5. Miscellaneous

Ring opening reactions occurred when the readily available diphosphirenium salt **44** was treated with nucleophiles. After combination of a THF solution of **44** with a stoichiometric amount of lithium diisopropylamide at −78 °C, phosphaalkene **46** was isolated in 85% yield. The formation of **46** was explained by the nucleophilic attack of the lithium salt at the dicoordinate phosphorus atom of **44**, leading to a transient $\lambda^3\sigma^3,\lambda^5\sigma^4$-diphosphirene **45**, which was stabilized by ring opening[31] (Scheme 20). In a similar manner, addition of one equivalent of lithium aluminium hydride to a THF solution of **44** afforded the corresponding *P*-hydrophosphaalkene **47** as a 50:50 mixture of (*Z*) and (*E*) isomers.[32] Ring expansion of **44** was achieved by the addition of *tert*-butyl isocyanide[31] or $Pd(PPh_3)_4$[32c] to the cation. In both cases diphosphacyclobutenes with the structural features of inversely polarized phosphaalkenes were obtained.

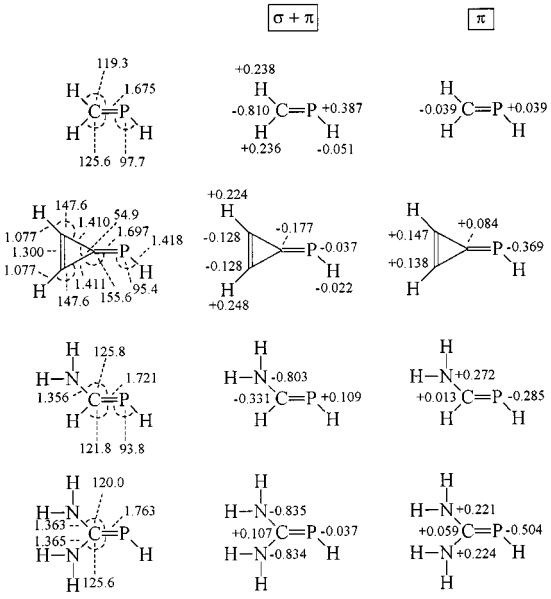


Scheme 20. Nucleophilic ring opening and ring expansion of **44**

3. Structure and Bonding

3.1. Theoretical Studies

Quantum chemical calculations were performed on the parent methylenephosphane and its amino-substituted derivatives (B3LYP/6-31g* level)[33] to substantiate the presence of an inverse π-electron density in the molecules (Scheme 21). The parent compound $HP{=}CH_2$ has a σ+π NBO charge of +0.387 e at the phosphorus and of −0.810 e at the carbon atom, whereas its P−C π-bond is essentially nonpolar (+0.030 e at P; −0.039 e at C). This agrees well with previous ab initio calculations based on Mulliken charges and a different basis set.[34a] By comparison, in the cyclopropylidenephosphane a σ+π Mulliken charge of −0.037 e at the phosphorus and of −0.177 e at the carbon atom of the exocyclic double bond were calculated (at the RHF approximation utilizing an ab initio wavefunction with a double-zeta basis set).[4] Here the P−C π-bond is clearly polarized towards the phosphorus atom as the negative end of the dipole with an excess of 0.369 e at the P atom and a deficiency of 0.084 electron at the C atom. The positive charge is stabilized by incorporation into the Hückel aromatic cyclopropenium unit. Quantum chemical calculations on the *C*-amino-substituted phosphaalkenes (B3LYP/6-31g*) predict a strong polarization of the π-bond. Only one, and to a greater extent, two amino



Scheme 21. Geometric parameters and charge distribution of $HP{=}CH_2$, cyclopropylidenephosphane, $HP{=}C(NH_2)H$ and $HP{=}C(NH_2)_2$

groups at the carbon atom induce an inverse electron density distribution at the π-bond, the charge at the phosphorus is increased in comparison to parent methylenephosphane. Alternatively, an amino group at the phosphorus atom has an opposite effect; it enhances the π-electron density at the methylene carbon atom. One may note that polarization of the P−C π-bond by amino substituents had been proposed some time ago.[34b] The quantum chemical investigations are based on the results of C_s symmetry imposed structures.[33] The calculations reveal that this holds true for the monoamino-substituted derivatives but for the *C*,*C*-diamino-substituted methylenephosphane, weak pyramidalization at the nitrogen atoms is predicted which causes a structural relaxation by 2.5 kcal/mol. However, the principal result of polarization of the P−C π-bond by the amino groups is retained.

Rotation of the amino groups lifts the π-conjugation ability of the amino group and causes a shrinking of the P−C bond. In other words the bonding features resemble more closely those of the parent methylenephosphane. Actually, the following structural parameters were obtained for the geometries with one orthogonal amino group (B3LYP/6-31g*) level:[34c] *cis*-(*trans*-)*C*-aminomethylenephosphane, P−C = 1.686 (1.686), C−N = 1.439 (1.441) Å.

3.2. Molecular Structures

Elongation of the P=C bond is the most noticeable structural change that classical phosphaalkenes undergo on replacement of one or two organic substituents at the tricoordinate carbon atom of the P=C double bond by one or two functionalities which are capable of π-donation. The P=C double bond length in nonconjugated phosphaalkenes ranges from 1.65−1.67 Å[2] whereas in *C*-amino-functionalized phosphaalkenes P−C distances of 1.70−1.76 Å are frequently measured[8] as is illustrated in **29a** [1.709(5) Å],[25] **29c** [1.717(4) Å] [Figure 1, (c)],[16] **7d** [1.740(1) Å],[5b] and **37a** [1.744(2) Å][21] [Figure 1, (a)]. A prerequisite for this bond lengthening is an effective π-interaction with (nearly) coplanar dialkylamino groups. In keeping with this, the atomic distances between the trigonal planar carbon atom and the nitrogen atoms are significantly shorter than the standard value for the C(sp^2)−N(sp^2) single bond (1.45 Å). Compound **29d**[16] represents a good example where, presumably for steric reasons, such a heteroallylic π-electron delocalization does not occur [Figure 1, (d)]. Here the P=C bond length of 1.697(3) Å is smaller and resembles that of the "classical" phosphaalkenes $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{=}C(SiMe_3)Ph$ [1.665(6) Å][16] and $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(SiMe_3)_2$ [1.680(9) Å].[35] The atomic distance between the planar atom C(13) and the slightly pyramidalized nitrogen atom N(1) of 1.448(4) Å is clearly that of a single bond. The ferriophosphaalkenes with an inverse π-electron density about the P=C bond **29a** and **29c** feature significantly longer Fe−P bonds [2.325(2) and 2.316(1) Å] than **29d** [2.276(1) Å]. The latter value compares well with that of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(SiMe_3)_2$ [2.269(2) Å] or (η^5-

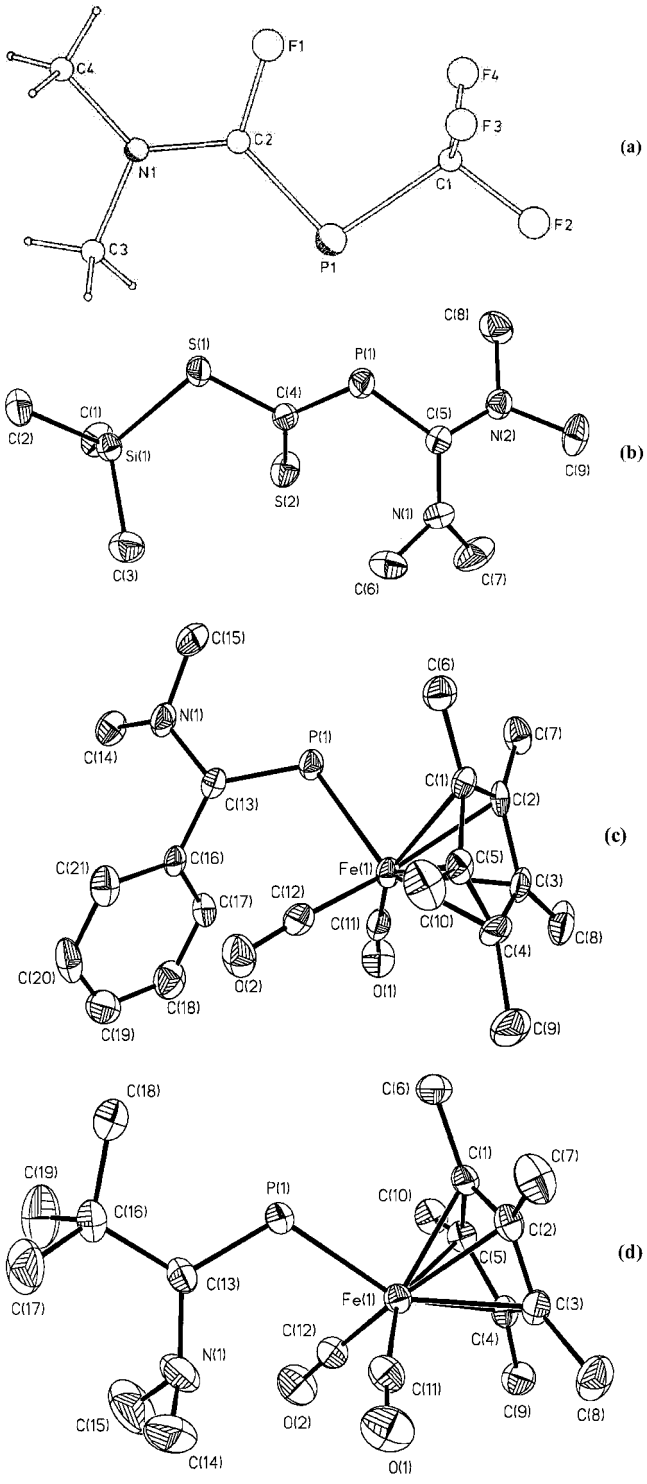


Figure 1. Molecular structures in the crystal of the phosphaalkenes **37a**, **33**, **29c**, and **29d**; selected bond lengths [Å] and angles [°]: (a) **37a**: P(1)−C(1) 1.862(2), P(1)−C(2) 1.744(2), C(2)−N(1) 1.311(2), C(1)−P(1)−C(2) 97.0(1), ΣN(1) 359.3(1); (b) **33**: P(1)−C(4) 1.748(2), P(1)−C(5) 1.826(2), C(4)−S(1) 1.801(2), C(4)−S(2) 1.673(2), C(5)−N(1) 1.341(2), C(5)−N(2) 1.338(2), N(1)−C(6) 1.458(2), C(4)−P(1)−C(5) 101.89(7), ΣN(1) 358.81(15), ΣN(2) 359.18(14); (c) **29c**: P(1)−C(13) 1.717(4), P(1)−Fe(1) 2.316(1), C(13)−N(1) 1.399(4), N(1)−C(14) 1.452(5), Fe(1)−P(1)−C(13) 118.9(1), ΣN(1) 352.6(3); (d) **29d**: P(1)−C(13) 1.697(3), Fe(1)−P(1) 2.276(1), C(13)−N(1) 1.448(4), N(1)−C(14) 1.447(5), Fe(1)−P(1)−C(13) 117.0(1), ΣN(1) 348.2(3)

$C_5Me_5)(CO)_2FeP{=}C(SiMe_3)_2$ [2.256(2) Å]. The bond lengthening in **29a** and **29c** presumably results from an electronic repulsion between the electron-rich iron atom and the negatively polarized P atom of the P=C bond. In the light of these observations the ferriophosphaalkenes **29a** and **29c** have to be considered as inversely polarized phosphaalkenes, whereas compound **29d** displays the characteristics of a normally polarized P=C bond. The molecular structure of **33** is particularly interesting [Figure 1, (b)]. Here a dithiocarboxy function successfully competes for the negative charge accumulated at the P atom of an inversely polarized phosphaalkene. Charge delocalization into the C−S double bond is evident by the bond shortening of P(1)−C(4) to 1.748(2) Å and concomitant elongation of the C=S bond to 1.673(2) Å. By comparison, a P−C single bond and a localized C=S double bond show bond lengths of 1.85 and 1.62 Å, respectively. Consistent with this, the former P−C double bond P(1)−C(5) is lengthened to 1.826(2) Å and the nearly planar nitrogen atoms N(1) and N(2) provide multiple bonding to carbon atom C(5) [N(1)−C(5) = 1.341(2) Å, N(2)−C(5) = 1.338(2) Å]. The bond angles at the P atom in **37a** [97.0(1)°], **7d** [103(1)°], and **33** [101.89(7)°] are comparable to that of the parent molecule $HP{=}CH_2$ (97.4°),[36] whereas steric congestion in **29a**, **29b**, and **29d** accounts for the more obtuse angle of ca. 118°. Thus, the valence angle at the P atom of phosphaalkenes does not reflect the polarity of the P=C π-bond.

3.3. Spectra

3.3.1. NMR Spectra

The characteristic ^{31}P and ^{13}C NMR shifts for selected compounds are summarized in Table 1. Generally, the ^{31}P NMR chemical shifts of phosphaalkenes vary in the wide range between δ = −99.9 for (*Z*)-H−P=C(F)NMe_2[29] and δ = 740.5 in the nickel complex [Cp*(PEt_3)Ni−P=$C(SiMe_3)_2$].[37] The ^{31}P NMR data of compounds containing low-coordinate phosphorus are compiled in several reviews.[2d,38,39] In spite 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 phosphaalkenes in general and for such representatives with an inverse π-electron density 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 determined by the HOMO−LUMO gap of the molecule. Small HOMO−LUMO gaps in *P*-metallophosphaalkenes such as the aforementioned nickel compound or the complex [Cp*$(CO)_2FeP{=}C(SiMe_3)_2$] (δ = 641.5)[37] give rise to significant low-field shifts. The large valence angle at phosphorus [126.2(6)°] in the iron complex indicates that the energy of the nonbonding orbital as the HOMO is raised by sp^2-hy-

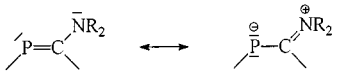
Table 1. ^{13}C and ^{31}P NMR spectroscopic data of selected phosphaalkenes with an inverse π-electron distribution

Compound		$\delta^{31}P$	$^1J_{P,H}$/Hz	$\delta^{13}C$	$^1J_{P,C}$/Hz	Ref.
(*E*)−Mes−P=C(H)NMe_2	**2a**	58.8		187.4	49.0	[11]
(*E*)−*t*Bu−P=C(H)NMe_2	**2c**	119.0		187.5	48.0	[11]
$Me_3Si-P=C^a-C^b(tBu){=}C^c(tBu)(C^a-C^c)$	**5a**	−74.1		174.6	102.5	[4b]
$Mes-P=C^a-C^b(tBu){=}C^c(tBu)(C^a-C^c)$	**5b**	−23.2		163.7	85.6	[4b]
Ph−P=$C(NMe_2)_2$	**7b**	28.4		198.8	67.1	[10]
*t*Bu−P=$C(NMe_2)_2$	**7c**	91.9		199.0	72.7	[7]
H−P=$C(NMe_2)_2$	**7d**	−62.6	158.7	207.5	70.6	[7]
$Me_3Si-P=C(NMe_2)_2$	**8a**	−47.1		204.0	85.0	[9b]
$Ph_3Si-P=C(NMe_2)_2$	**24a**	−85.1				[23]
[Cp*$(CO)_2Fe-P=C(NMe_2)_2$]	**29a**	135.5		202.4	97.0	[25]
(*E*)−$Me_3SiP{=}C(Ph)NMe_2$	**14a**	54.3		204.7	65.2	[16]
(*Z*)−$Me_3SiP{=}C(tBu)NMe_2$	**14b**	68.7		219.7	94.1	[16]
(*E*)−Ph−P=C(Ph)N(Ph)$SiMe_3$	(*E*)-**16a**	144		205	50	[17]
(*Z*)−Ph−P=C(Ph)N(Ph)$SiMe_3$	(*Z*)-**16a**	225		193	47	[17]
$Ph-P^a{=}C^a-N(SiMe_3)C(OSiMe_3)(Ph)P^bPh(C^a-P^b)$	**18**	112.7		197.3	60.6	[18]
$PhP{=}C^aN^a(Me)C(Me){=}C(Me)N^b(Me)(C^a-N^b)$	**20a**	−53.5		169	97.6	[19]
$tBuC(O)-P=C^a-C^b(tBu){=}C^c(tBu)(C^a-C^c)$	**21c**	9.7		174.7	89.2	[4b]
$Tp'(CO)_2Mo{\equiv}C-P=C(NMe_2)_2$	**23a**	62.3		202.7	89.0	[22]
$(Me_3Si)_2C^2{=}P^2-P^1{=}C^1(NMe_2)_2$	**27a**	P^1: 99.7 P^2: 455.4[a]		C^1: 201.2 C^2: 172.0	86.8 87.7	[24]
[(*E*)-Cp*$(CO)_2Fe-P=C(Ph)NMe_2$]	**29c**	232.0		199.8	84.3	[16]
[(*Z*)-Cp*$(CO)_2Fe-P=C(tBu)NMe_2$]	**29d**	409.0		217.3	75.3	[16]
$(Me_2N)_2C=P-C(S)N(Ph)SiMe_3$	**32**	82.8		198.1	72.1	[21]
$(Me_2N)_2C=P-C(S)SSiMe_3$	**33**	145		193.7	87.2	[21]
$F_3C-P=C(F)NMe_2$	**37a**	−9.0		200.5	94.0	[5]
(*E,Z*)−H~P=C(F)NMe_2	(*E,Z*)-**39a**	(*E*): −99.0 (*Z*): −99.9	166.0 178.0	200.6 199.6	65.1 87.7	[29]
(*Z*)−$F_3C-P=C(OMe)NMe_2$	**40a**	17.3		205.8	77.3	[6]
$MeO_2C-P=C(F)NMe_2$	**43**	−23.4		198.7	100.8	[30]

[a] $J_{P1,P2}$ = 403 Hz.

bridization, whereas the energy of the LUMO, which is the π* orbital, remains roughly unaffected. The electronic nature of the substituent at the phosphorus atom also markedly influences the chemical shift. In η^1-Cp*P=$C(SiMe_3)_2$[40] the valence angle at phosphorus was determined to be 118.7(2)°, which also agrees with sp^2-hybridization, but the ^{31}P NMR resonance appears at only δ = 370.6. The substituents at the C atom of the P=C bond in "normal" phosphaalkenes also determine the ^{31}P NMR chemical shift as evident in ClP=C(Ph)$SiMe_3$ (δ = 273) and ClP=$C(SiMe_3)_2$ (δ = 342).[2d]

In several amino- and bis(amino)-substituted representatives where π-conjugation of the nitrogen lone pair with the P=C double bond operates in addition to the paramagnetic contribution, a second component to the ^{31}P NMR shift has to be considered. 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 high-field shift.



This is evident in compounds (*E*)-**16a** ($\delta^{31}P$ = 144) and (*Z*)-**16a** ($\delta^{31}P$ = 225), where presumably for steric reasons only the (*E*) isomer achieves the planar geometry required for a three-center four-electron arrangement in an inversely polarized phosphaalkene.[17]

The influence of the substituent at phosphorus on the ^{31}P chemical shift may be studied in molecules of the type X−P=$C(NMe_2)_2$. Here the compound with the highest degree of shielding at phosphorus is $Ph_3SiP=C(NMe_2)_2$ (δ = −85.1).[23] An increasing low-field shift as a function of X is observed as follows: **7d** (X = H; $\delta^{31}P$ = −62.6) > **8a** (Me_3Si; −47.1) > **23a** [Tp′$(CO)_2$Mo≡C; 62.3] > **7c** (*t*Bu; 91.9) > **29a** [Cp*$(CO)_2$Fe; 135.5]. Particularly interesting is the replacement of the hydrogen atom at phosphorus by functional groups, which are able to withdraw electron density from phosphorus by π-delocalization as observed in $MeO_2CP=C(F)NMe_2$ (**43**) ($\delta^{31}P$ = −23.4)[30] vs. (*E*,*Z*)-HP=$C(F)NMe_2$ (**39a**) ($\delta^{31}P$ = −90.0 and −99.9)[29] or in $(Me_2N)C=P-C(S)SSiMe_3$ (**32**) ($\delta^{31}P$ = 145)[21] vs. **7d**.

The introduction of a bulky and electron-releasing substituent at the phosphorus atom, such as the [Cp*$(CO)_2$Fe] group in **29a**, causes a strong low-field shift which may be due to the small HOMO−LUMO gap discussed above. Further deshielding was achieved by replacing one amino group by a phenyl ring in **29c** ($\delta^{31}P$ = 232.0), which is oriented orthogonally to the NCP four-π-electron unit. In contrast to (*E*)-**29c** in complex (*Z*)-**29d** a planar three-center four-electron arrangement is not possible for steric reasons, and consequently this compound behaves as a normal phosphaalkene with a low-field ^{31}P NMR signal at δ = 409.0.[16]

The ^{13}C NMR spectra of phosphaalkenes show characteristic doublets for the tricoordinate carbon atom of the P−C double bond at δ = 160−220. The cyclopropenylidenephosphanes are found at the lower range ranging from $\delta^{13}C$ = 163.7 (d, $^1J_{P,C}$ = 85.6 Hz) in **5b** to $\delta^{13}C$ = 178.5 (d, $^1J_{P,C}$ = 96.1 Hz) for $Cl_3C-C(O)-P=C^a-C^b(tBu)=C^c(tBu)$($C^a-C^c$) (**21o**). These values are quite typical for the cyclopropenylium system. In the cyclopropenium cation the corresponding resonances appear at δ = 176.8 whereas in the dipolar di-*tert*-butylcyclopropenone a chemical shift of δ = 159.4 was determined for the heteroatom-substituted ring carbon atom.[41] For the methylene carbon atoms of bis(amino)phosphaalkenes $XP=C(NMe_2)_2$ doublets were observed between δ = 197.0 (d, $^1J_{P,C}$ = 68.4 Hz) in **7a** (X = Mes)[10] and δ = 207.5 (d, $^1J_{P,C}$ = 70.6 Hz) in **7d** (X = H).[7] The signals of the monoamino-functionalized inverse phosphaalkenes $XP=C(R)NMe_2$ range from δ = 184.0 (d, $^1J_{P,C}$ = 54.5 Hz) for the P−C carbon atom in **2c** (X = *t*Bu; R = H) to δ = 219.7 (d, $^1J_{P,C}$ = 94.1 Hz) in **14b** (X = Me_3Si; R = *t*Bu).

3.3.2. IR Spectra

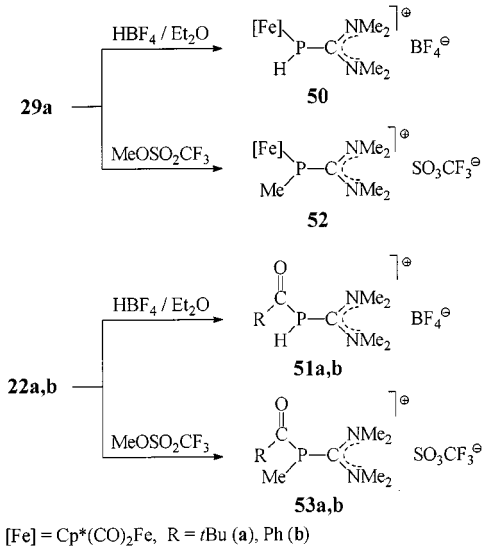
Valuable information about the polarity of the P=C bond in *P*-acylated phosphaalkenes is provided by IR spectroscopy. In *t*BuC(O)P=$C(OSiMe_3)$*t*Bu an intense band at $\tilde{\nu}$ = 1663 cm^{-1} was assigned to the IR stretching mode.[42] This value falls within the 1630−1690 cm^{-1} range usually encountered in acylphosphanes, where no electron delocalization from the phosphorus lone pair into the CO group is present. In the IR spectra of the inversely polarized phosphaalkenes **22a** and **22b**, strong bands at $\tilde{\nu}$ = 1563 and 1546 cm^{-1} respectively, indicate pronounced π-delocalization of electron density into the carbonyl group.[21] In $MeO_2C-P=C(F)NMe_2$ the ν(CO) vibration is observed at $\tilde{\nu}$ = 1685 cm^{-1} and thus at a lower wavenumber than in $MeO_2CP(H)CF_3$ [ν(CO) = 1738 cm^{-1}].[30] The CO frequencies of **21** are also bathochromically shifted (1590−1640 cm^{-1}) in comparison with monoacylated phosphanes.[4b]

4. Reactivity of Inversely Polarized Phosphaalkenes

4.1. Protonation

The ferriophosphaalkene **29a** was protonated at the P atom by ethereal HBF_4 (54%) in diethyl ether at −50 to 20 °C to afford the yellow salt **50** in high yield.[43] Similarly, the reaction of the *P*-acylphosphaalkenes **22a** and **22b** with equimolar amounts of ethereal HBF_4 at −50 °C led to the formation of the phosphanyl carbenium salts $[RC(O)P(H)C(NMe_2)_2]BF_4$ **51a** (R = *t*Bu) and **51b** (R = Ph)[33] (Scheme 22).

Upon protonation, the ^{31}P NMR signal of **29a** (δ = 135.5 in C_6D_6) was shifted upfield and appeared in **50** as a broad singlet at δ = −78.4. In the ^1H NMR spectrum of **50** a doublet at δ = 2.82 ($^1J_{P,H}$ = 205.0 Hz) was attributed to the PH functionality. Interestingly, protonation of the normally polarized phosphaalkene $Cp(CO)_3W-P=C(SiMe_3)_2$ ($\delta^{31}P$ = 505.2) to give $[Cp(CO)_3WP(H)C(SiMe_3)_2]^+$ ($\delta^{31}P$ = 187.0) resulted in even stronger shielding and a much larger PH coupling ($^1J_{P,H}$ = 367 Hz),[44] which agrees with a tri-



Scheme 22. Reaction of **22a**,**b** and **29a** with HBF_4 and $MeOSO_2CF_3$

gonal-planar P atom in this cation. By analogy with the structures of the alkylated products (vide infra) it is clear that the P atom in **50** has a trigonal-pyramidal geometry. In the ^{31}P NMR spectrum, the protonated products **51a**,**b** display doublets at $\delta = -53.7$ ($^1J_{P,H} = 245$ Hz) and $\delta = -46.6$ ($^1J_{P,H} = 257.7$ Hz) which are significantly shifted to high field with respect to the corresponding signals in **22a** ($\delta = 26.4$) and **22b** ($\delta = 31.3$). In the ^1H NMR spectrum a doublet at $\delta = 6.02$ ($^1J_{P,H} = 245$ Hz) (**51a**) and at $\delta = 6.23$ ($^1J_{P,H} = 257.7$ Hz) (**51b**) accounts for the PH unit.[34]

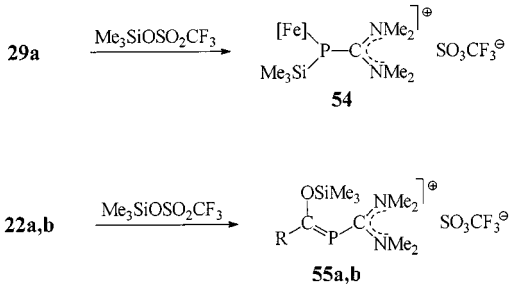
4.2. Alkylation

Alkylation of **29a** and **22a**,**b** was achieved by treatment with equimolar amounts of methyl trifluoromethanesulfonate (triflate) in diethyl ether at −60 °C. Compounds **52** and **53a**,**b** spontaneously precipitated and were isolated in good yield as orange or yellow powders[43,33] (Scheme 22).

Methylation at the phosphorus center of **22a**,**b** and **29a** was accompanied by marked shifts of the P NMR resonances to high field (**52**: $\delta = -26.4$ s; **53a**: −3.8 s; **53b**: −2.3 s). An X-ray structure analysis of the cation $[Cp^*(CO)_2FeAs(Me)C(NMe_2)_2]^+$ displayed a trigonal-pyramidal arsenic atom, analogously to **52**. From the analogous analytical and spectroscopic data it was inferred that **52** also contains a pyramidal pnicogen center.

4.3. Silylation

Reaction of **29a** with trimethylsilyl triflate in diethyl ether at −70 °C caused the precipitation of **54** as a yellow solid in 92% yield (Scheme 23). In the ^{31}P NMR spectrum of **54** a singlet was observed at $\delta = -78.4$. Here it seems appropriate to describe the cation as a η^1-complex of the phosphaalkene $Me_3SiP{=}C(NMe_2)_2$ (**8a**) ($\delta^{31}P = -47.1$) with the 16VE fragment $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe]^+$. Coordination of **8a** caused a high field shift of its ^{31}P NMR signal, which in fact has been frequently encountered in the coordination chemistry of inversely polarized phosphaalkenes (vide infra).

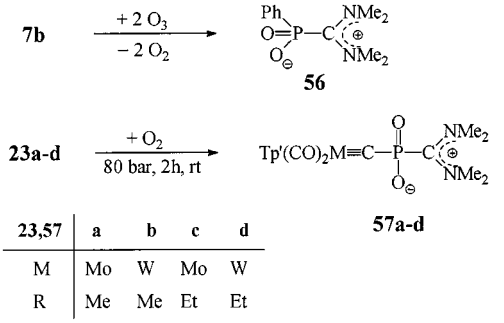


Scheme 23. Silylation of **22a**,**b** and **29a**

The silylation of **22a**,**b** with trimethylsilyl triflate in diethyl ether gave the extremely air- and moisture-sensitive salts **55a**,**b**. Here, in contrast to the protonation and methylation of **22a**,**b**, deshielding of the ^{31}P NMR resonances [$\delta = 109.2$ (**55a**) and $\delta = 101.0$ (**55b**)] was observed. This situation is best explained by an attack of the hard acid "Me_3Si" at the hard oxygen center of the carbonyl group with the generation of Si−O and P=C bonds. The products can be described as salts with unsymmetrical phosphaallyl cations or, alternatively, as phosphaalkenyl-functionalized carbocations.[45] Thus, the main spectroscopic evidence for an electrophilic attack at the P or O atom of *P*-acylphosphaalkenes with inverse electron density is from the direction in which the ^{31}P NMR resonances of the product are shifted.

4.4. Reaction with Chalcogens

Phosphaalkene **7b** reacted directly with ozone at ambient temperature with formation of the amidiniophosphinate **56** (Scheme 24). Compound **7b** always incorporates two atoms of oxygen. Intermediates in this process could not be detected. Product **56** appears to be inert towards excess O_3.[46]



23,57	a	b	c	d
M	Mo	W	Mo	W
R	Me	Me	Et	Et

Scheme 24. Oxidation of **7b** and **23a−d**

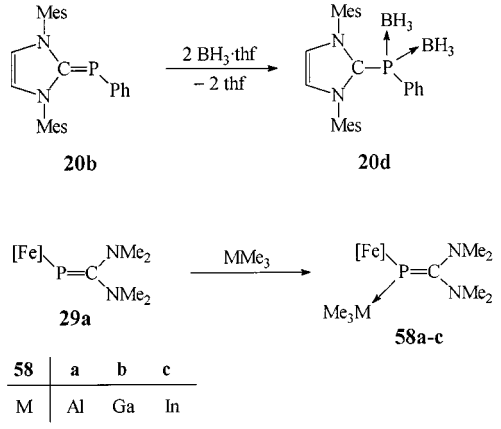
The related carbyne complex functionalized α-carbenium phosphinates **57** were obtained when crystalline samples of the complexes **23c** and **23d** (R = Et) were exposed to air for two weeks, whereupon a color change from deep red to orange-red occurred.

Similarly, compounds **23a** and **23b** (R = Me) were rapidly oxidized under O_2 pressure, whereas in air complete oxidation took about three weeks.[47]

4.5. Reaction with Group 13 Electrophiles

Treatment of carbene **20b** with $BH_3 \cdot THF$ in toluene resulted in exclusive formation of the bis(borane) adduct **20g**.[20b] The ^{31}P NMR signal is shifted from $\delta = -23.0$ to $\delta = 4$. The P−C bond in **20b** [1.763(6) Å] lengthens to 1.856(2) Å in the adduct.[20b]

Combination of **29a** with equimolar amounts of $AlMe_3$, $GaMe_3$, and $InMe_3$ in *n*-pentane in the temperature range −78 °C to 20 °C afforded the trimethylmetal adducts **58a−c** as air- and moisture-sensitive solids, whereas the phosphaalkene appeared to be inert towards $Al\textit{i}Pr_3$[48] (Scheme 25).



Scheme 25. Reaction of **20b** with $BH_3 \cdot THF$, and of **29a** with $AlMe_3$, $GaMe_3$ and $InMe_3$

The ^{31}P NMR spectra of the adducts **58a−c** are characterized by singlets at $\delta = -12.1$, 14.5, and 22.2, which are strongly deshielded with respect to **29a** ($\delta = 135.5$).

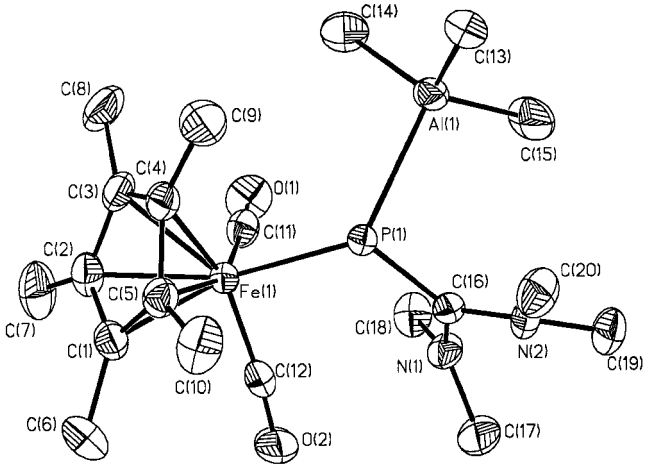
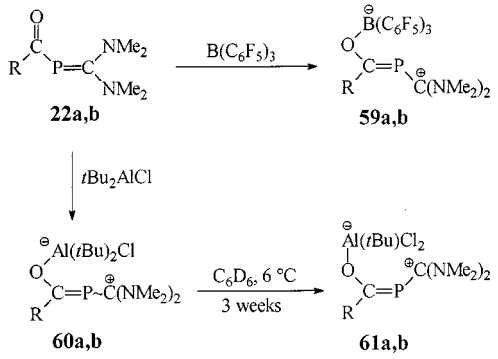


Figure 2. Molecular structure of **58a** in the crystal; selected bond lengths [Å] and angles [°]: Fe(1)−P(1) 2.317(1), Al(1)−P(1) 2.508(1), P(1)−C(16) 1.779(3), Fe(1)−P(1)−Al(1) 124.13(4), Al(1)−P(1)−C(16) 99.4(1), Fe(1)−P(1)−C(16) 116.5(1)

The X-ray structural analysis of **58a** (Figure 2) shows that coordination of **29a** to trimethylaluminium through the phosphorus lone pair results in significant distortion of the organophosphorus ligand. The P atom is now coordinated in a trigonal-pyramidal fashion (sum of angles 340.0°) and forms single bonds to the atoms Fe, Al, and C(16).

In comparison with **29a** the P−C bond is elongated from 1.709(5) to 1.779(3) Å. As in precursor **29a** the methylene carbon atom C(16) is trigonal planar.

In view of the electrophilic attack of Me_3Si at the carbonyl oxygen atom of **22a**,**b** we focused our interest on the reactivity of the phosphaalkene towards the hard Lewis acids $B(C_6F_5)_3$, $t\text{Bu}_2\text{AlCl}$, and $(AlMe_3)_2$. Combination of **22a** or **22b** with tris(pentafluorophenyl)borane in toluene solution at 20 °C gave the adducts **59a** and **59b** as yellow solids (Scheme 26). Low-field shifted singlets in the $^{31}P\{^1H\}$ NMR spectra at $\delta = 68.3$ (**59a**) ($\Delta\delta = 41.9$) and 72.6 (**59b**) ($\Delta\delta = 41.5$), and the absence of ν(C=O) bands in the IR spectra of the adducts agree with the phosphaalkenes attaching to the electron-deficient boron center via the oxygen atom.[34]



Scheme 26. Reaction of **22a**,**b** with $B(C_6F_5)_3$ and $t\text{Bu}_2\text{AlCl}$

The X-ray structural analysis of **59b** confirmed the presence of a tetracoordinate boron atom, which is linked to the carbonyl group via a B−O single bond of 1.506(3) Å (Figure 3). Delocalization of the negative charge into the C=O bond is clear by its elongation from 1.240(2) Å (as measured in **22b**)[49] to 1.315(3) Å, and by the bond length P(1)−C(1) of 1.735(2) Å, which is similar to the P=C bond length in $HP{=}C(NMe_2)_2$ (**7d**) [1.740(1) Å]. The PC(N) bond in **22b** [1.800(1) Å] is lengthened to 1.838(3) Å in **59b**. The very bulky $B(C_6F_5)_3$ moiety is directed towards the P atom of the P−C multiple bond, giving rise to torsion angles B(1)−O(1)−C(1)−P(1) and B(1)−O(1)−C(1)−C(41) of 2.5° and −179.4°, respectively.

Di-*tert*-butylaluminium chloride reacted smoothly with equimolar amounts of **22a** or **22b** in toluene at −30 C° to yield the adducts **60a**,**b** as extremely moisture-sensitive orange solids. Attempts to grow crystals of **60a** and **60b** from C_6D_6 solutions at 6 C over a period of 3 weeks led to the formation of crystals of the dismutation products **61a** and **61b** instead. The $^{31}P\{^1H\}$ NMR resonances of both adducts, which appeared at lower field (**60a**: $\delta = 72.9$ s; **60b**: $\delta = 78.2$ s) than in the precursors are diagnostic for the mode of coordination, and the presence of dative Al−O bonds in the products was inferred.

The X-ray structural analysis of the dismutation product **61b** showed a (*Z*)-configured phosphaalkene with a P=C double bond of 1.728(2) Å between the phosphorus atom and the carbonyl carbon atom. The carbonyl bond is lengthened to 1.309(2) Å. The trigonal-planar amino-sub-

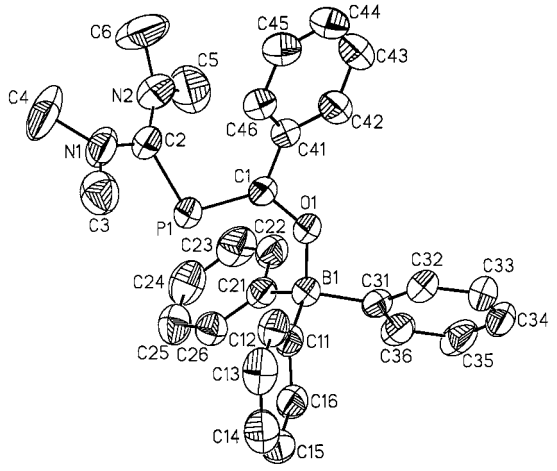
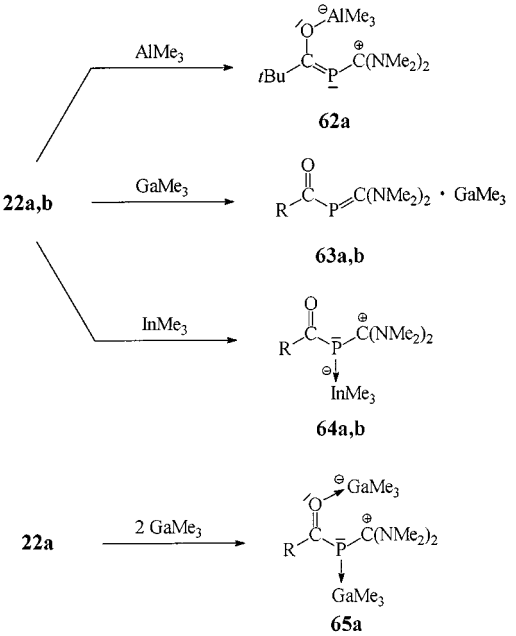


Figure 3. Molecular structure of **59b** in the crystal (fluorine atoms at the borane unit are omitted for clarity); selected bond lengths [Å] and angles [°]: P(1)−C(1) 1.735(2), P(1)−C(2) 1.838(3), O(1)−C(1) 1.315(3), O(1)−B(1) 1.506(3), C(1)−P(1)−C(2) 102.3(1), C(1)−O(1)−B(1) 130.2(2)

stituted carbon atom forms a single bond of 1.844(2) Å with the P atom.

Reaction of equimolar amounts of **22a** and trimethylaluminium in *n*-pentane yielded adduct **62a** as a pale yellow moisture-sensitive oil. The $^{31}P\{^{1}H\}$ NMR spectrum of the product displayed a singlet at $\delta = 62.7$, which is deshielded by $\Delta\delta = 36.3$ with respect to free **22a**. Thus, the aluminium atom is attached to the oxygen atom of the carbonyl group, as it is in the case of the adducts **60** and **61**.

Under analogous conditions one equivalent of trimethylgallium was added to **22a** and **22b** with formation of yellow **63a** and **63b**[34] (Scheme 27).



Scheme 27. Reaction of **22a**,**b** with $AlMe_3$, $GaMe_3$, and $InMe_3$

Broad singlets in the $^{31}P\{^{1}H\}$ NMR spectra at $\delta = 38.7$ (**63a**) or $\delta = 48.1$ (**63b**) did not allow for an unambiguous assignment of the structure, and crystals suitable for an X-ray study were not available. However, it was possible to grow yellow crystals of the 1:2 adduct **65a** from a concentrated mixture of **22a** and excess $GaMe_3$ in *n*-pentane at −30 °C. The NMR spectra of **65a** did not differ significantly from those determined for **63a**. All the three adducts **63a**,**b** and **65a** easily lose the ligated $GaMe_3$ in vacuo.

The crystal structure analysis of **65a** sheds some light in the nature of the 1:2 adduct (Figure 4). The backbone of the molecule is constituted by a *P*-acyl unit with a trigonal-pyramidal P atom (sum of angles 333.26°), which is connected to the atoms C(4), C(12), and Ga(2) via single bonds. The bond length P(1)−C(4) [1.784(3) Å] is shorter than P(1)−C(12) [1.831(3) Å]. The latter bond length was determined to be 1.800(1) Å in **22b**. A pronounced strengthening of the $P-C_{(CO)}$ bond, as observed in **59b** and **61b**, did not occur. The C−O bond length of the carbonyl group [1.249(3) Å] is similar to that of the *P*-acyl function in **2b** [1.240(2) Å]. Both $GaMe_3$ units are only weakly attached to the organophosphorus ligand as is evident from the long atomic distances Ga(2)−P [2.635(2) Å] and Ga(1)−O(1) [2.109(2) Å].

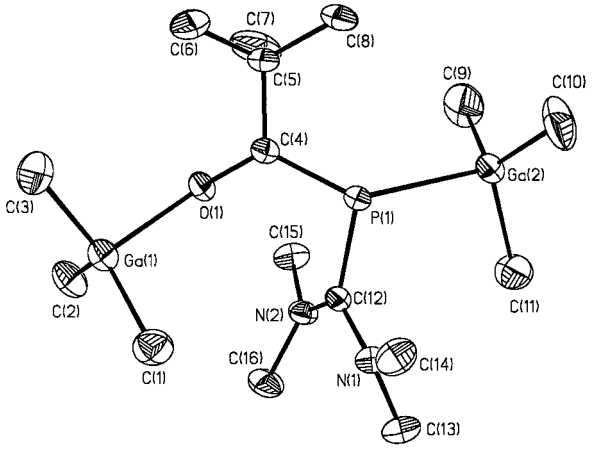


Figure 4. Molecular structure of **65a** in the crystal; selected bond lengths [Å] and angles [°]: P(1)−C(4) 1.784(3), P(1)−C(12) 1.831(3), P(1)−Ga(2) 2.635(2), O(1)−C(4) 1.249(3), O(1)−Ga(1) 2.109(2), C(4)−P(1)−C(12) 102.9(1), C(4)−P(1)−Ga(2) 127.7(1), Ga(2)−P(1)−C(12) 102.6(1)

The coordination chemistry of **22a** and **22b** towards the "soft" acid $InMe_3$ is more straightforward (Scheme 27). The adducts **64a** and **64b** display singlets in their $^{31}P\{^{1}H\}$ NMR spectra at $\delta = 15.6$ and 36.8. A high-field coordination shift of $\Delta\delta = 10.8$ for **64a**, and a low-field shift of $\Delta\delta = 5.5$ are consistent with In−P contact rather than with the alternative In−O ligation. In the IR spectrum of **64a** strong ν(CO) bands appear at $\tilde{\nu} = 1594$ and 1546 cm^{-1}, and in the spectrum of **64b** a ν(CO) band of medium intensity at 1540 cm^{-1} with a shoulder at 1597 cm^{-1} was observed.

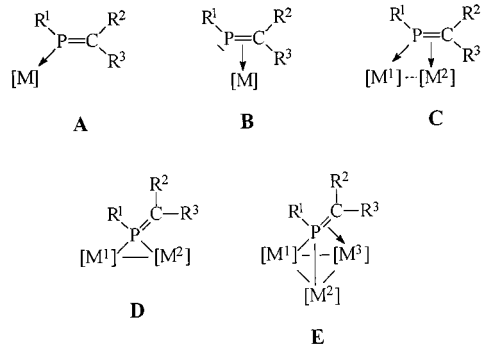
The X-ray structural analysis of **64a** features a *P*-acylphosphaalkene with a trigonal-pyramidal P atom, which is coordinated to the indium atom by a single bond of 2.774(4) Å.

The environment around the carbonyl carbon atom is trigonal-planar; a C=O double bond [1.238(10) Å] and a

single bond to the P atom [1.851(9) Å] clearly exclude π-conjugation of the carbonyl group with the lone pair on phosphorus in **64a**. The bond between the phosphorus atom and the amino-substituted carbon atom of 1.823(8) Å is elongated with respect to the precursor.[34]

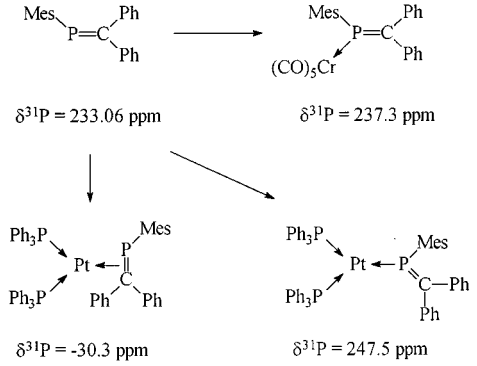
4.6. Transition Metal Complexes

Normally polarized phosphaalkenes are versatile ligands in transition metal coordination chemistry. At least five different fundamental modes of coordination of phosphaalkene ligands are known to date (Scheme 28).



Scheme 28. Modes of coordination in phosphaalkene complexes

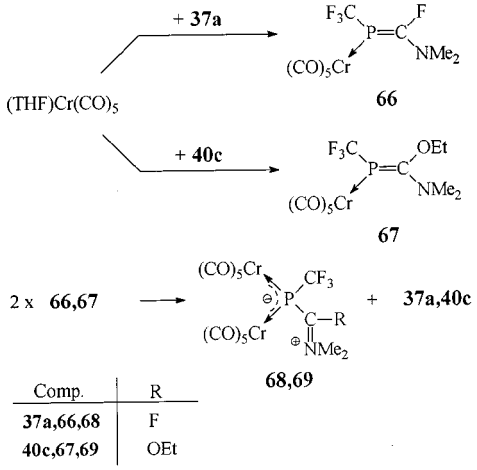
The most frequently observed types are η^1-coordination via the lone pair at phosphorus (**A**) and η^2-ligation **B**, which resembles that of alkenes in their transition metal π-complexes. In all of these complexes **A**−**E** the structural integrity of the phosphaalkene ligand is generally preserved. This particularly applies in case **A**. Here the P atom has a trigonal-planar geometry with a nearly unchanged P=C bond length with respect to the free ligand.[50] In η^2-complexes of the type **B** the P−C bond is usually elongated beyond 1.80 Å. While in η^1-complexes the ^{31}P NMR signals usually exert small coordination shifts (mostly to low field), in η^2-complexes strong high-field shifts are observed[50−52] (Scheme 29).



Scheme 29. Coordination shifts in phosphaalkene complexes

The coordination chemistry of inversely polarized phosphaalkenes is somewhat different. Pentacarbonylchromium complexes of the phosphaalkenes $CF_3P{=}C(F)NMe_2$ (**37a**)[5b] and $CF_3P{=}C(OEt)NMe_2$ (**40c**)[6] are available by treatment with equimolar amounts of $(THF)Cr(CO)_5$ in THF.

In organic solvents ($CDCl_3$, [D_8]toluene) complexes **66** and **67** were dismutated into to the binuclear complexes **68** and **69** and the free ligands **37** and **40c**, respectively (Scheme 30).

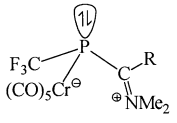


Scheme 30. Formation of the complexes **66**, **67**, **68**, and **69**

The coordination of **37a** ($\delta^{31}P = -9.0$) to one or two $[Cr(CO)_5]$ fragments via the phosphorus atom was accompanied by deshielding of the ^{31}P NMR signal to δ = 3.94 (**66**) and δ = 98.8 (**68**). On going from $CF_3P{=}C(OEt)NMe_2$ to **67** and **69** the ^{31}P NMR resonance is shifted to δ = 13.4 (**67**) and δ = 89.9 (**69**).

The molecular structures of **66**[5b] and **68**[53] are particularly interesting (Figure 5). The P=C bond length is markedly elongated from 1.744(2) Å in **37a** to 1.805(3) Å in **66** and 1.859(5) Å in **68**.

Those atomic distances are close to the average value of 1.85 Å for a P−C single bond. At the same time, the C−N separation in **66** [1.288(3) Å] and **68** [1.278(6) Å] indicates multiple bonding. In contrast with the situation in $[(CO)_5Cr]$ complexes of normally polarized phosphaalkenes having trigonal-planar P atoms, a trigonal-pyramidal phosphorus atom is observed in **66** (sum of angles: 304.8°). These observations favor a zwitterionic description of the complexes and rationalize the binding of a second $[Cr(CO)_5]$ unit at the phosphorus center.



The transfer of negative charge onto the $[Cr(CO)_5]$ building block is also reflected in bathochromically shifted CO stretching bands [**66**: $\tilde{\nu}$ = 2055 w, 1985 w, 1940 vs, 1930 s, 1912 s cm^{-1}] relative to $[(CO)_5Cr\{P(Mes){=}CPh_2\}]$ [ν(CO) ($CHCl_3$): 2068, 1955 cm^{-1}].[50a] The mode of coordination in **68** is unprecedented. Reaction of ferriophosphaalkene **29a** with an excess of $[Ni(CO)_4]$ led to the tricarbonylnickel adduct **70**.[54] This process was accompanied by a strong high-field shift of the $^{31}P\{^1H\}$ NMR signals from δ = 135.5 in **29** to δ = 15.0. A similar observation was made during the preparation of complex **71** from **29a** and [(*Z*)-

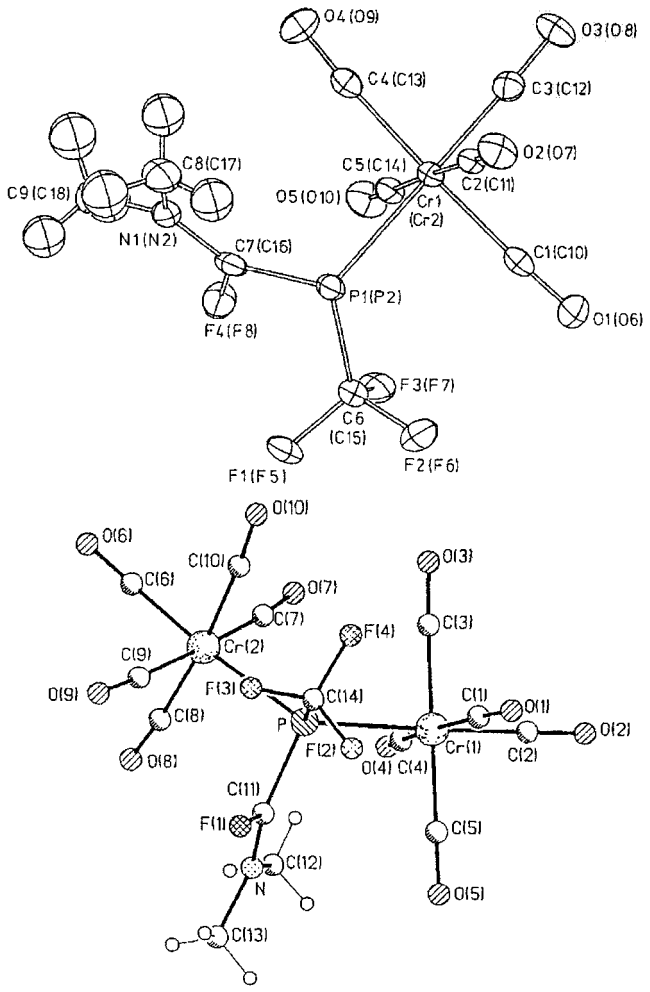
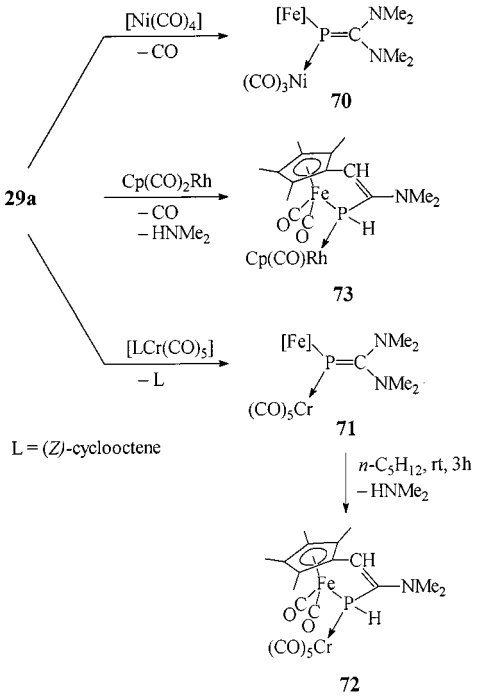


Figure 5. Molecular structures in the crystal of **66** (top) and **68** (bottom); selected bond lengths [Å] and angles[°]: **66**: Cr(1)−P(1) 2.454(1), P(1)−C(7) 1.805(1), N(1)−C(7) 1.288(3); Cr(1)−P(1)−C(6) 108.3(1), Cr(1)−P(1)−C(7) 102.4(1), C(6)−P(1)−C(7) 94.1(1); **68**: Cr(1)−P 2.459(2), Cr(2)−P 2.457(2), P−C(11) 1.859(5), C(11)−N 1.278(6); Cr(1)−P−Cr(2) 127.5(1)

cyclooctene]$Cr(CO)_5$ in *n*-pentane. The dark violet complex ($\delta^{31}P = -1.0$) was, however, not stable. Upon prolonged stirring of the slurry in *n*-pentane it underwent condensation to give **72** and free dimethylamine.[54] A condensation product analogous to **72** resulted from the treatment of **29a** with [η^5-$Cp(CO)_2Rh$][55] in *n*-pentane. No intermediates in this transformation could be detected (Scheme 31).

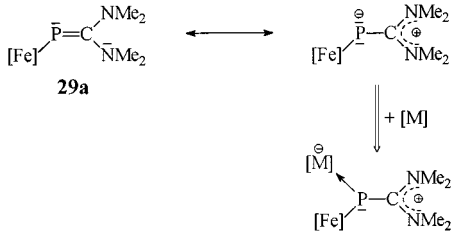
The formation of **72** and **73** is remarkable as one of the five methyl groups of the C_5Me_5 ligand behaves as a CH-acidic species which is involved in a Knoevenagel-type condensation. Usually Cp* ligands are ideal spectator ligands and insertions of metal atoms in one or more C−H bonds of methyl substituents are only observed with coordinatively and electronically unsaturated complexes.

The IR spectra of **70** and **71** display carbonyl stretching bands at remarkably low wavenumbers [e.g. **70**: ν(CO) = 2034, 1957, 1950 cm^{-1}] in comparison with [Mes*P=C=Ph_2]$Ni(CO)_3$ [ν(CO) = 2080, 2020, 1990 cm^{-1}],[56] indicating a considerable transfer of charge from the ligand onto the $[Ni(CO)_3]$ unit.



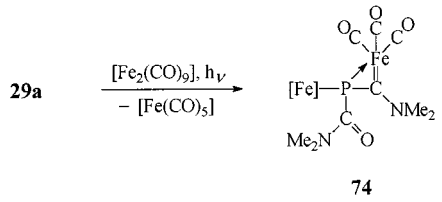
Scheme 31. Conversion of **29a** into the complexes **70**, **71**, **72**, and **73**

According to X-ray diffraction studies, the complexation of **29a** to an $[Ni(CO)_3]$ or $[Cr(CO)_5]$ fragment[57] leads to a severe distortion of the metallophosphaalkene skeleton (Scheme 32). Whereas the Fe(1)−P(1) distance in **70** and **71** [2.329(2) and 2.325(2) Å] remains nearly unaffected when compared with **29a** [Fe(1)−P(1) = 2.325(2) Å] the P−C bond in both complexes is significantly lengthened [**70**: 1.770(5); **71**: 1.793(5) Å. The P atoms have trigonal-pyramidal geometries with sum of angles of 335.9° (**70**) and 346.1° (**71**). In contrast to this, the carbon atom of the former P=C bond is trigonal-planar with relatively short C−N bonds [1.352(6) − 1.373(6) Å]. The electronic ground state of **29a** may be expressed by means of two canonical formulae, the which the zwitterionic form is obviously stabilized by coordination to metal fragments.



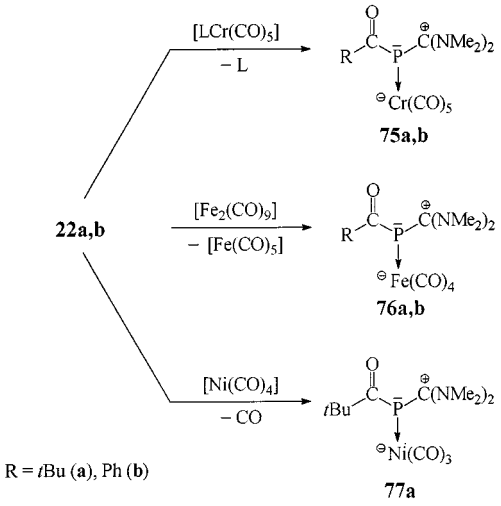
Scheme 32. Resonance structures of **29a** and its complexes

The photochemical reaction of **29a** with $[Fe_2(CO)_9]$ in *n*-pentane took a completely different course. Instead of the anticipated $[Fe(CO)_4]$ adduct, the phosphanylcarbene complex **74** was isolated as black crystals (Scheme 33).



Scheme 33. Formation of **74**

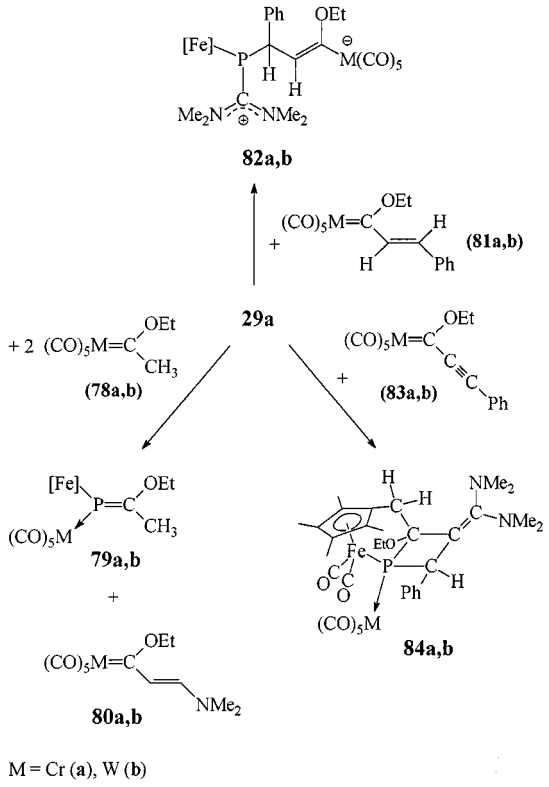
The reaction of **22a** and **22b** with carbonyl compounds of transition metals would be expected to lead to coordination compounds with metal−phosphorus bonds by the hard-soft acid-base concept (Scheme 34).



Scheme 34. Syntheses of complexes **75a**,**b**, **76a**,**b**, and **77a**

The high-field shifts of the $^{31}P\{^{1}H\}$ NMR singlets of complexes **75a**,**b**, **76a**,**b** and **77a**, in the range $\delta = -26.4$ to 1.9, agree with metal−phosphorus ligation. The X-ray structural analysis of **75a** unambiguously confirms coordination to $[Cr(CO)_5]$ of the trigonal-pyramidal phosphorus atom (sum of angles = 332.9°) with a P−Cr bond of 2.516(1) Å, which is at the upper end of P−Cr single bonds in low-valent carbonylchromium−phosphorus systems. The phosphorus−carbon distances [1.848(2) and 1.833(2) Å] are indicative of single bonds. Within the organophosphorus ligand, a localized C−O double bond of 1.225(2) Å was found.[34]

Having obtained some insight into the coordination behavior of inversely polarized phosphaalkenes toward trialkyl- and carbonylmetal compounds, the question of its reactivity towards Fischer carbene complexes became relevant. Compound **29a** was allowed to react with two molar equivalents of carbene complexes **78a** and **78b** in ether, forming the novel ferriophosphaalkene complexes **79a**,**b** and β-aminoalkenyl(ethoxy)carbene complexes **80a**,**b**[58] (Scheme 35).



Scheme 35. Reaction of **29a** with Fischer carbene complexes

The X-ray structural analysis of **79b** (Figure 6) shows an (*E*)-configured, classically polarized phosphaalkene, which is η^1-coordinated to the $[W(CO)_5]$ fragment via a remarkably long W−P bond [2.567(3) Å].[59] The P−C bond of 1.689(10) Å is typical for a P=C bond with an oxygen substituent, and the coordination geometry about P(1) and C(1) is trigonal planar. Interestingly the Fe(1)−P(1) dis-

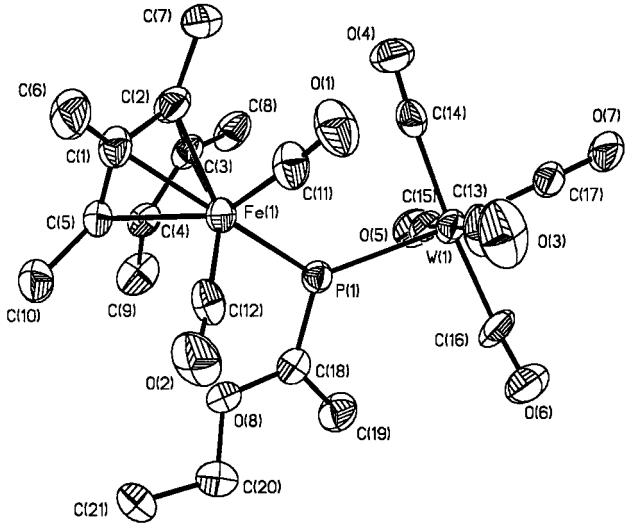


Figure 6. Molecular structure of **79b** in the crystal; selected bond lengths [Å] and angles [°]: W(1)−P(1) 2.567(3), Fe(1)−P(1) 2.262(3), P(1)−C(18) 1.689(10); Fe(1)−P(1)−C(18) 112.8(3)

tance of 2.262(3) Å is significantly shorter than in the carbonylmetal complexes of **29a**.

Combination of **29a** and the alkenylcarbene complexes **81a**,**b** in a mixture of *n*-pentane diethyl ether at −30 °C led to the precipitation of the orange zwitterionic Michael-type adducts **82a**,**b** (Scheme 35).

In sharp contrast to the synthesis of **79a**,**b** and **82a**,**b**, treatment of **29a** with an equimolar amount of the ethynyl(phenyl)carbene complexes **83a**,**b** in *n*-pentane at −60 °C afforded the yellow pentacarbonylmetal adducts **84a**,**b** of a 1-ferriophosphetane as the only tractable phosphorus-containing products (ca. 20% yield). (Scheme 35)

From the diversity of the product patterns the reactions of inversely polarized phosphaalkenes with carbene complexes display, it is clear that exploration of this fruitful area is only just beginning.

5. Conclusions and Perspectives

The "peculiarities" in the chemistry of *C*-amino-substituted phosphaalkenes, as discussed by Markovskii et al.[8] can be explained by their inverse distribution of π-electron density ($P^{\delta-}C^{\delta+}$) in comparison to the normal polarization ($C^{\delta-}P^{\delta+}$) in classical phosphaalkenes. Considering a growing body of evidence, the inverse π-electron density in a phosphaalkene may be detected from the following experimental features:

- The ^{31}P NMR signals of such molecules occur at unusually high field, whereas in normally polarized phosphaalkenes low-field ^{31}P NMR resonances are typical.
- These ^{31}P NMR signals may even be more shielded in transition metal complexes having inversely polarized η^1-phosphaalkene ligands. In η^1-complexes of normally polarized phosphaalkenes, coordination shifts to low field are usually observed.
- In η^1-complexes with inversely polarized phosphaalkene ligands, the phosphorus atom is pyramidal and the P−C bond is significantly elongated, in some cases attaining a bond order of unity, whereas in complexes with normally polarized phosphaalkenes the bond length between the trigonal planar atoms P and C is nearly unaffected upon coordination.
- The introduction of electron-withdrawing substituents at the P atom of inversely polarized phosphaalkenes results in delocalization of negative charge from the P−C unit into the substituent.

It is clear that classically and inversely polarized phosphaalkenes differ in their chemical reactivity. The latter are pronounced nucleophiles via their P atom and the systematic investigation of their synthetic potentials has just commenced. An interesting question still to be answered concerns Wittig-type reactivity of inversely polarized phosphaalkenes with organic carbonyl compounds. Little information is available on transformations with compounds which tend to liberate electron-sextet species, such as organic azides, diazoalkanes, carbenoid species etc.

The electronic situation present in inversely polarized phosphaalkenes should also be studied by electrochemical methods.

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