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The Chemistry of Diphosphenes and Their Heavy Congeners: Synthesis, Structure, and Reactivity

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I. Introduction

According to the so-called "classical double-bond rule"[1] stable molecules featuring multiple bonding should only be possible with elements of the first long period. This statement was rationalized by long bond distances and concomitantly inefficient π-bonding. Obviously this rule was a result of numerous thwarted

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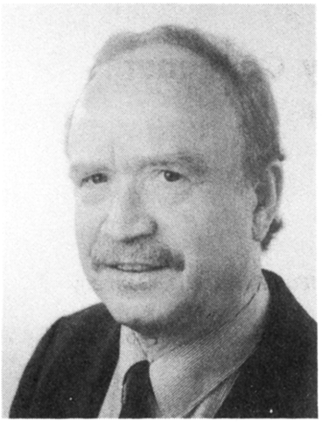
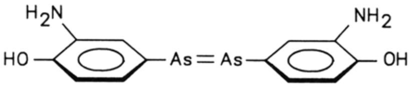


Lothar Weber was born in Langenöls/Silesia in 1944. He studied chemistry at the Philipps Universität in Marburg, where he received his "Doctor Rerum Naturalium" in 1973. For the year 1974 to 1975, he carried out postdoctoral studies with Prof. B. M. Trost in Madison/Wisconsin. In 1982 he accomplished his "Habilitation" at the University of Essen, where he became a C2-professor in 1985. Since 1988 he has been professor of Inorganic Chemistry at the University of Bielefeld. His research interests include the organometallic chemistry of sulfur ylides as well as synthetic and structural aspects of low-coordinated heavier main group elements' chemistry. Emphasis is also made on the synthesis and ligation properties of phosphorus homo- and heterocycles and cage compounds.

attempts to prepare compounds with double bonds between two phosphorus atoms, two silicon centers, etc.

Early reports by Köhler and Michaelis (1877) on phosphobenzene "Ph—P=P—Ph",[2] which was claimed to result from the condensation reaction of $PhPCl_2$ and $PhPH_2$, later turned out to be wrong. Kuchen showed in 1958 that the condensation product was a mixture of oligomers of "phosphobenzene".[3] This was confirmed a little later by X-ray structure analyses[4,5] of pentaphenylcyclopentaphosphane [$(PhP)_5$] and hexaphenylcyclohexaphosphane [$(PhP)_6$].

A similar correction was necessary for the molecular structure of the medicament "Salvarsan",[6] which was first described by Ehrlich as



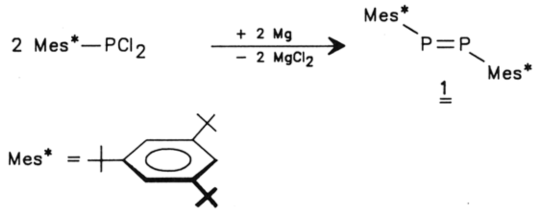
Later X-ray crystallographic work on compounds of the empirical composition C_6H_5As revealed their oligomeric character.[7]

The idea of kinetic stabilization of reactive multiple bonds by very bulky substituents provided an efficient breakthrough to molecules with P=P, P=As, and As=As double bonds. In 1981 the first diphosphene was reported by Yoshifuji, who introduced the voluminous 2,4,6-tri-*tert*-butylphenyl (supermesityl, Mes*) group as a substituent into phosphorus chemistry.[8]

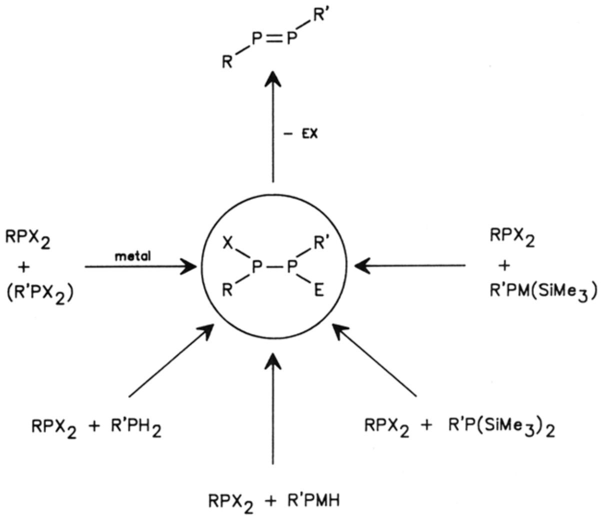
The reduction of (2,4,6-tri-*tert*-butylphenyl)dichlorophosphane with elemental magnesium in THF led to the orange-red crystalline diphosphene 1 (Scheme 1).

His account was the initiative of a very dynamic and intense development in the chemistry under discussion which furnished a great number of novel compounds. This is reflected in several review articles[9-13] on diphosphenes which have to be considered as a completely new class of compounds of great current interest.

Scheme 1



Scheme 2



In this article the chemistry of heteroarenes with PP multiple bonding is not considered.

The following abbreviations will be used all along this review: nBu (*n*-butyl), tBu (*tert*-butyl), Cp (cyclopentadienyl), Cp* (pentamethylcyclopentadienyl), Cy (cyclohexyl), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), Et (ethyl), Is (isityl = 2,4,6-triisopropylphenyl), Me (methyl), Ment (menthyl), Mes (mesityl), Mes* (supermesityl = 2,4,6-tri-*tert*-butylphenyl), Ph (phenyl), iPr (isopropyl), tPn (*tert*-pentyl), THF (tetrahydrofuran), TMEDA (*N*,*N*,*N'*,*N'*-tetramethylethylenediamine), and TMP (2,2,6,6-tetramethylpiperidyl).

II. Preparations of Diphosphenes

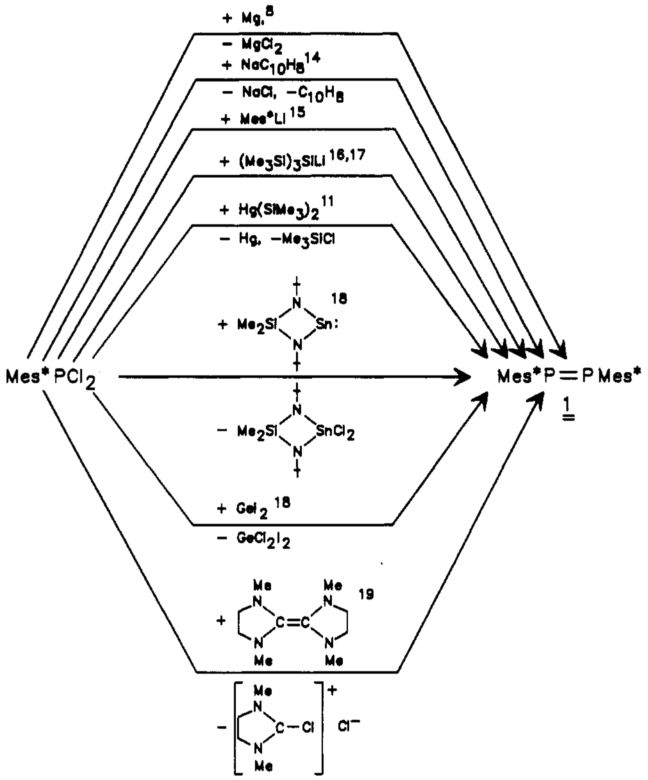
A. Eliminations and/or Condensations

The close chemical relation of C=C, C=P, and P=P double bonds as invoked by the concept of diagonal relationship in the periodic table of elements and by the concept of isoelectronic molecules parallels in the formation of multiple bonds within these three classes of compounds. Consequently one should expect base induced 1,2-hydrogen halide elimination from halogenated diphosphanes RPX-PHR' to give diphosphenes (Scheme 2).

Alternatively the elimination of salts or trimethylsilyl halides is conceivable. Moreover 1,2-dihalogen eliminations similar to the well-known zinc dust elimination of bromine from vicinal organodibromides should provide an additional tool for diphosphene synthesis.

In contrast to the organic precursors, which in most cases already possess a C–C single bond between the two centers of interest, in phosphorus chemistry the respective educts for the elimination process, the functionalized diphosphanes, are often not easily available as stable compounds, but have to be prepared by

Scheme 3



the formation of the P–P single bond in advance to the elimination. Wurtz-type couplings of dihalophosphanes by means of metals or condensation reactions utilizing halophosphanes, primary phosphanes, silylphosphanes, and the corresponding phosphides provide viable routes to these targets.

According to the opinion of the author the idea of phosphinidene generation and their subsequent dimerization should be regarded with care especially with respect to the high reactivity of free phosphinidenes and the lack of unambigious proof of their transient occurrence in the vast majority of the cases.

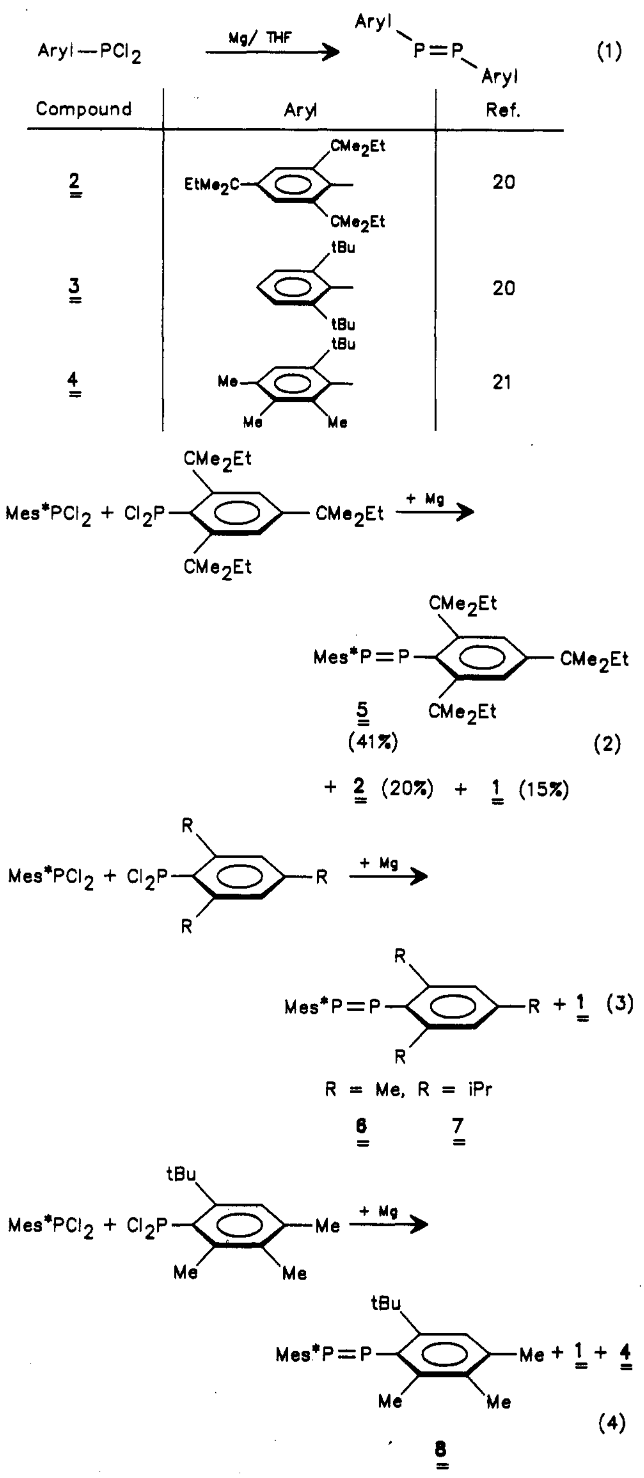
The conversion of organodichlorophosphanes such as Mes*PCl_2 to diphosphenes was accomplished by a number of reducing agents, such as magnesium metal, sodium naphthalenide, organolithium species, bis(trimethylsilyl)mercury, two-valent germanium and tin compounds, or electron-rich olefins. In the latter reactions the occurrence of the corresponding dichlorodiphosphane was unambigiously shown by ^{31}P NMR spectroscopy.

The reductive coupling of aryldichlorophosphanes by magnesium metal was utilized to furnish other symmetrically[20,21] and unsymmetrically substituted diphosphenes[21] (Schemes 3 and 4).

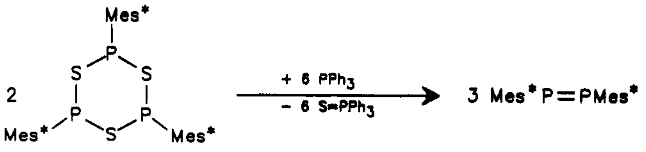
Diphosphene **1** is also available from the reduction of a 1,3,5-trithia-2,4,6-triphosphinane with triphenylphosphane[15] (Scheme 5).

The first dialkyldiphosphene $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**9**) was obtained from the reaction of dichlorophosphane $(Me_3Si)_3CPCl_2$ with sodium naphthalenide.[14,22] Alternative syntheses of **9** made use of organolithium reagents such as $(Me_3Si)_3CLi$,[14] tBuLi,[23] as well as lithium metal[24] or $Hg(SiMe_3)_2$[11] as reducing agents (Scheme 6).

Scheme 4



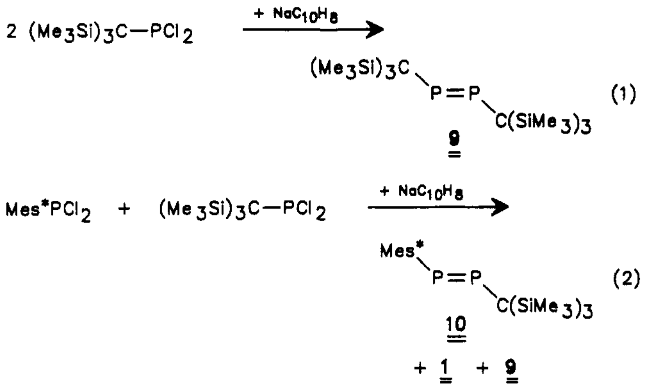
Scheme 5



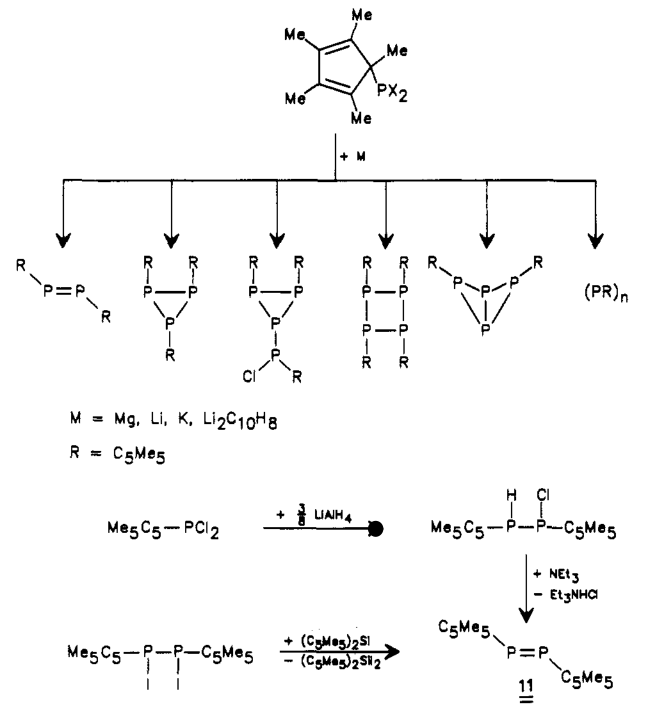
When the sodium naphthalenide reduction was carried out with equimolar amounts of Mes*PCl_2 and $(Me_3Si)_3CPCl_2$ the predominant formation of the symmetrical diphosphenes **1** and **9** was observed. In addition the unsymmetrical diphosphene **10** was produced in 20% yield.[25]

Bis(pentamethylcyclopentadienyl)diphosphene (**11**) was detected among a number of products when $(C_5Me_5)PCl_2$ was reduced by metals such as Mg, Li, and

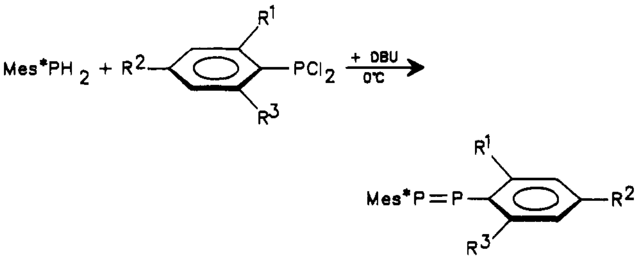
Scheme 6



Scheme 7

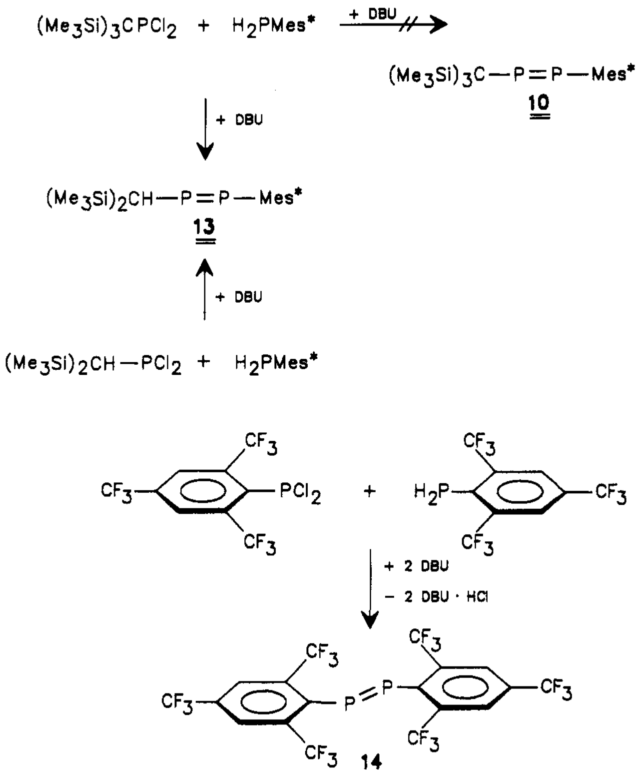


Scheme 8



Compound	R^1	R^2	R^3	yield
1	tBu	tBu	tBu	–
6	Me	Me	Me	76%
12a	tBu	tBu	Me	31%
12b	H	H	H	–

Scheme 9



K or alternatively dilithium naphthalenediide.[26] The dehalogenation of $[(C_5Me_2)PI]_2$ with decamethylsilicocene also afforded 11.[27] A more convenient and straightforward synthesis of 11 was accomplished by the reduction of $(C_5Me_5)PCl_2$ with $LiAlH_4$ and the subsequent elimination of hydrogen chloride from the chlorodiphosphane by means of triethylamine[28] (Scheme 7).

It is conceivable that the intermediate diphosphane resulted from the coupling of $(C_5Me_5)PCl_2$ with $(C_5Me_5)PH_2$.

In keeping with this the reaction of Mes^*PH_2 with aryldichlorophosphanes in the presence of diazabicycloundecene (DBU) provided a clean approach to symmetrical and unsymmetrical diphosphenes[29] (Scheme 8).

It was pointed out by Yoshifuji et al. that phenylsupermesityldiphosphene (**12b**) although observed in the ^{31}P NMR spectrum, could not be isolated without decomposition.[29]

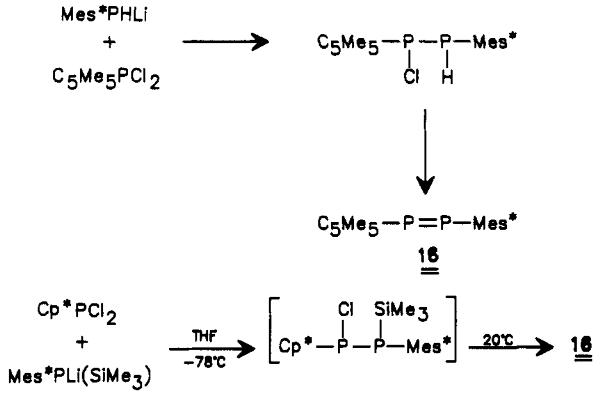
Surprisingly the attempted condensation of $(Me_3Si)_3CPCl_2$ with Mes^*PH_2 in the presence of DBU did not afford the expected diphosphene **10**. Instead the unsymmetrical diphosphene $(Me_3Si)_2CHP{=}PMes^*$ (**13**) was obtained.[30] Presumably one Me_3Si group at the trisilylmethyl substituent was removed by the nucleophilic attack of chloride during the course of the reaction. A more straightforward access to **13** was realized by the reaction of $(Me_3Si)_2CHPCl_2$ with Mes^*PH_2 under similar conditions[30] (Scheme 9a).

The application of the same strategy to fluorinated arylphosphanes led to the stable bis(nonafluoromesityl)diphosphene (**14**), which was isolated as a pale yellow solid[31] (Scheme 9b).

A mixture of $2,4,6\text{-}(CF_3)_3C_6H_2PCl_2$ and Mes^*PH_2 was dehydrochlorinated to give the unsymmetrical thermolabile diphosphene $2,4,6\text{-}(CF_3)_3C_6H_2P{=}PMes^*$ (**15**).[32] Instead of primary phosphanes the respective phosphides or organosilylphosphides were also successfully employed for diphosphene syntheses (Scheme 10). The intermediate diphosphane $Cp^*P(Cl)\text{–}P(H)Mes^*$ was not identified.[33]

An efficient synthesis of $(Me_3Si)_2CHP{=}PCH(SiMe_3)_2$ made use of HX or Me_3SiX eliminations from diphos-

Scheme 10



phanes as the crucial step of the process[34] (Scheme 11).

The cyclotetraphosphane stemmed from the [2 + 2] self-dimerization of **17**. This reaction possesses a half-life time of one week at ambient temperature. Obviously diphosphene **17** is at the borderline of kinetic stability.

Base-induced HCl elimination from a diphosphane provided an entry into the class of diphosphenes with amino substituents. Thus the corresponding chlorodiphosphane underwent 1,2-elimination when treated with an equimolar amount of LiN(tBu)SiMe$_3$ to give diphosphene **18a**[35] (Scheme 12, eq 1).

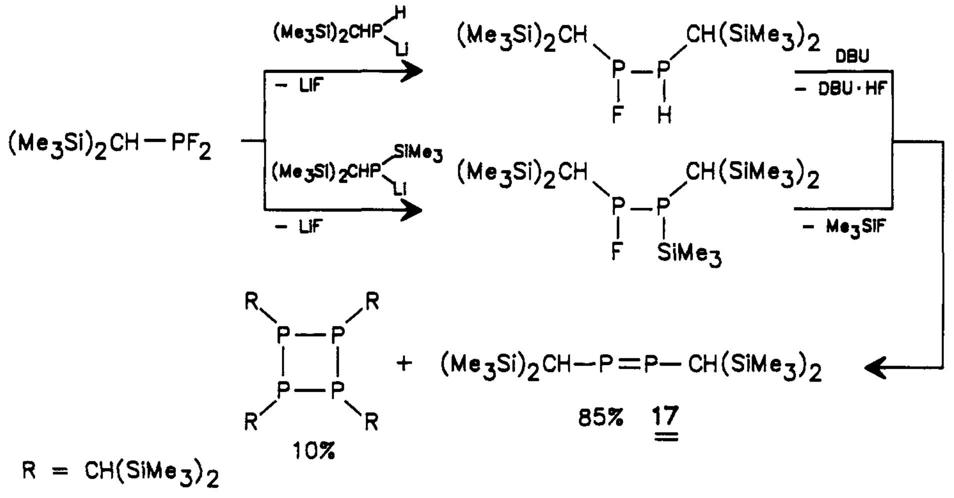
Compound **18a** was a ruby red liquid which dimerized to a cyclotetraphosphane within a few hours. The syntheses of similar diaminodiphosphenes were performed in a one-pot reaction involving the subsequent treatment of the lithium amides LiNR(SiMe$_3$) with PCl$_3$, LiAlH$_4$, and NEt$_3$[36] (Scheme 12, eq 2).

If a mixture of the amides LiN(SiMe$_3$)$_2$ and LiN(tBu)(SiMe$_3$) was employed the unsymmetrical diaminodiphosphene **19** was formed in addition to **18a** and **18b**. Their stabilities with respect to dimerization increase in the order **18a** < **19** < **18b**, reflecting the influence of steric congestion.[36]

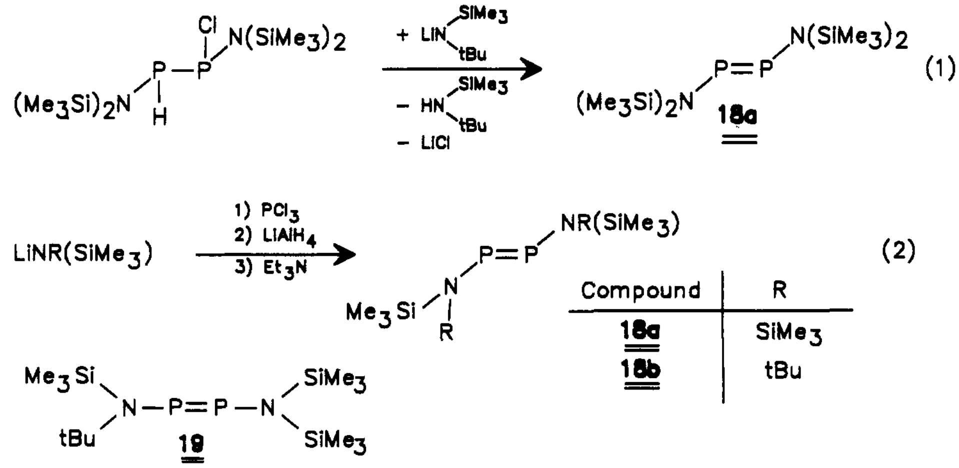
Other synthetic approaches discussed earlier were also operating well in the generation of symmetrical aminodiphosphenes. Thus the sterically well protected diphosphene **21a** was available by the reductive coupling of **20a** with lithium metal,[36] *tert*-butyllithium,[36] or Hg(SiMe$_3$)$_2$[11] (Scheme 13). The latter reagent is obviously of general use in the transformation of bulky aminodichlorophosphanes of the type **20** into the corresponding diaminodiphosphenes **18a** and **21**[11,37] (Scheme 14).

The scope of 1,2-elimination processes can be extended to the synthesis of the amino–aryl substituted diphosphenes **22**. The generation of the precursor diphosphanes was made feasible by treatment of the respective aminodichlorophosphanes with either

Scheme 11

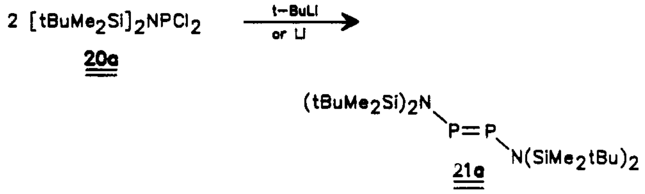


Scheme 12

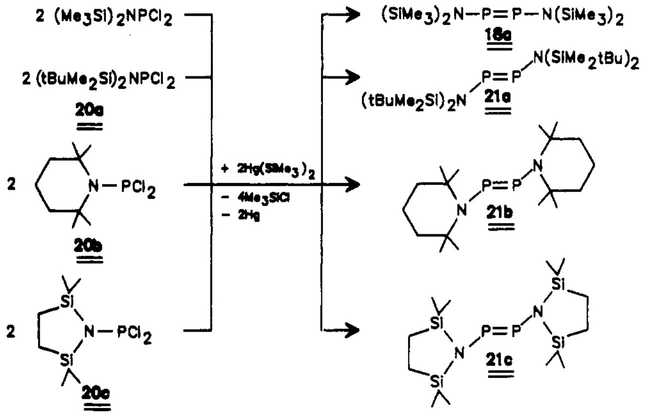


Compound	R
18a	SiMe$_3$
18b	tBu

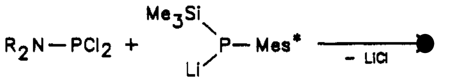
Scheme 13



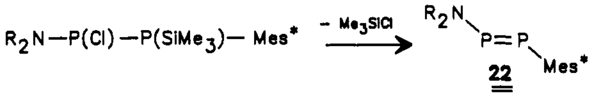
Scheme 14



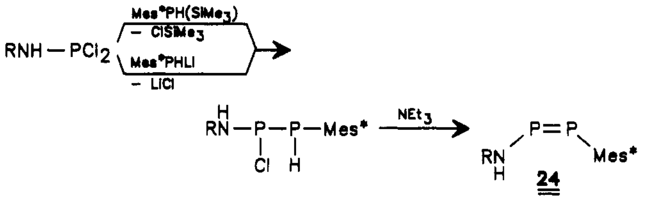
Scheme 15



22	R2N
a	$(Me_3Si)_2N$
b	$(tBuMe_2Si)_2N$
c	iPr_2N
d	TMP



Scheme 16



24	R
a	tBu
b	adamantyl
c	CEt_3
d	$C_6H_2iPr_3$ (2,4,6)

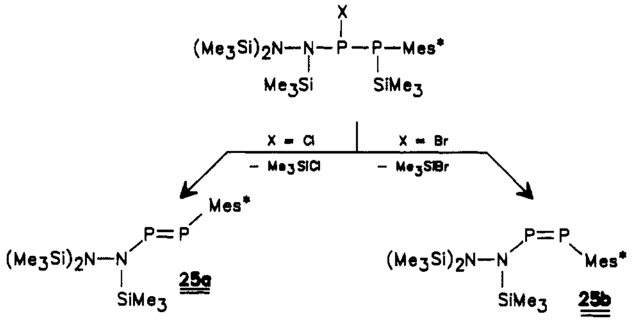
$Mes^*PLi(SiMe_3)$, $Mes^*PH(SiMe_3)$, or Mes^*PHLi[11,38] (Scheme 15).

A similar reaction between aminodichlorophosphane **20b** and LiP(tBu)($SiMe_3$) furnished thermolabile TMPP=PtBu (**23**).[37b]

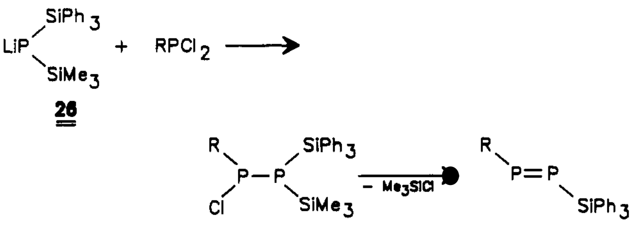
The presence of a primary amino substituent led to the rare class of the *Z*-configurated diphosphenes **24**[39] (Scheme 16).

Recently Niecke reported for the first time on both stereoisomers of an amino-substituted diphosphene

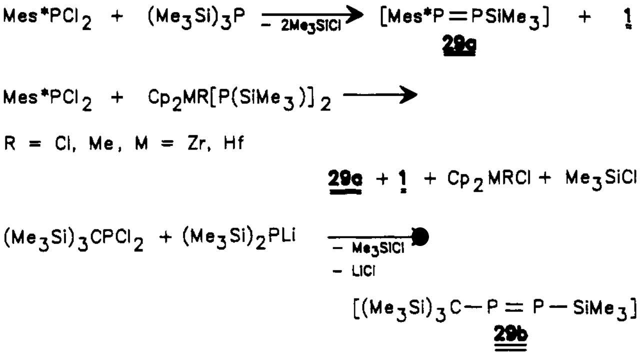
Scheme 17



Scheme 18



27: R = Mes*
28: R = $(Me_3Si)_3C$

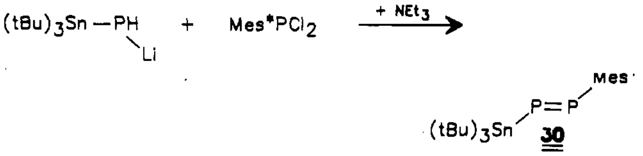


which were stable and could be synthesized selectively.[40a,b] Thus (*E*)-$(Me_3Si)_2NN(SiMe_3)P{=}PMes^*$ (**25a**) was obtained as the only product after elimination of Me_3SiCl from a functionalized 1-chlorodiphosphane, whereas the analogous reaction of the bromo derivative cleanly afforded the *Z*-isomer **25b** (Scheme 17). In solution both isomers equilibrated to a mixture **25a**/**25b** = 11:6. The free enthalpies of activation of the reversible transformation **25a** ⇌ **25b** were determined to $\Delta G_{(293)E/Z}$ = 25.5 (5) and $\Delta G_{(293)Z/E}$ = 25.4 (5) kcal/mol. These enthalpies are significantly lower than the calculated barrier of rotation for HP=PH (34.0 kcal/mol), but on the other hand significantly higher than for the conversion *E*-1 ⇌ *Z*-1 ($\Delta G_{(293)Z/E}$ = 20.3 kcal/mol). In keeping with this *Z*-1 could not be isolated.

Not only carbon and nitrogen substituents are capable of stabilizing the P=P double bond in diphosphenes. Silyl- and stannyl-substituted diphosphenes are also isolable compounds provided that bulky groups guarantee sufficient kinetic stabilization. Treatment of the lithium disilylphosphide **26** with equimolar quantities of Mes^*PCl_2 or $(Me_3Si)_3CPCl_2$ in ether solution afforded the diphosphenes **27** and **28** quantitatively. In both cases the intermediate functionalized diphosphanes were detected by ^{31}P NMR spectroscopy[41] (Scheme 18a).

Compound **28** appeared to be stable for extended periods both in solution and in the solid phase, whereas

Scheme 19



27 easily dimerized, especially in solution. The crucial influence of steric requirements was further demonstrated in the thermolability of the diphosphenes **29a,b** with a Me_3Si substituent instead of the more bulky $SiPh_3$ group.

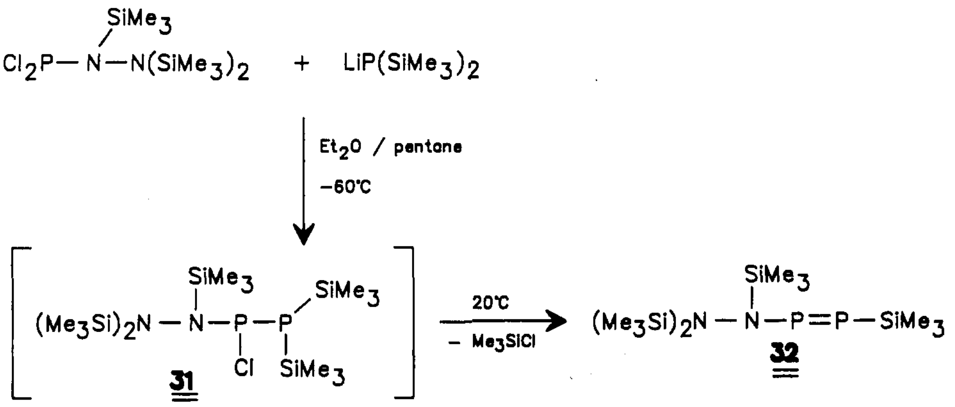
When Mes^*PCl_2 and $P(SiMe_3)_3$ were heated in $CDCl_3$ the formation of $Mes^*P{=}PMes^*$ (1) took place. The unsymmetrical and thermolabile diphosphene **29a** was observed as byproduct by ^{31}P NMR techniques.[21] A similar result was obtained when Mes^*PCl_2 was treated with bis(trimethylsilyl)phosphido complexes of zirconium and hafnium[42] (Scheme 18b).

The formation of 1 was rationalized by a rapid Me_3Si/Cl exchange between the educts. **29b** was produced by coupling $(Me_3Si)_3CPCl_2$ with $LiP(SiMe_3)_2$. It decomposed to a bicyclic tetraphosphane (see section IV.C.2).

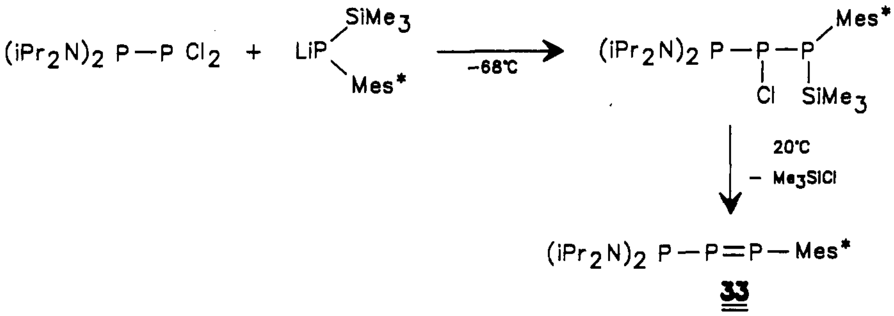
The synthesis of the first stable stannyl-substituted diphosphene **30** was also based on condensation and 1,2-elimination processes[43] (Scheme 19). Violet crystalline **30** was isolated in 62% yield.

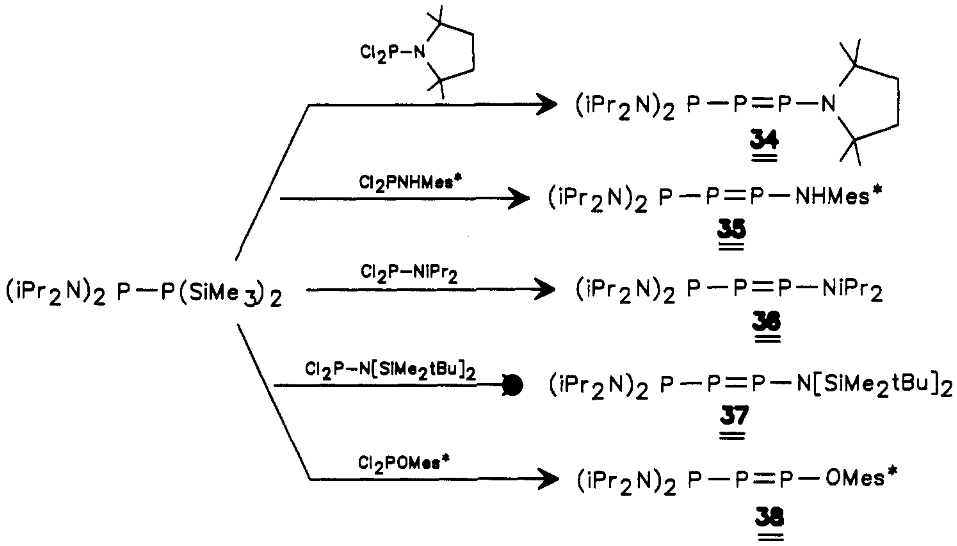
When a solution of $Cl_2PN(SiMe_3)N(SiMe_3)_2$ in pentane was reacted at -60 °C with a solution of $LiP(SiMe_3)_2$ in ether and the resulting solution was stirred for 3 h at room temperature the intermediate diphosphane **31**

Scheme 20

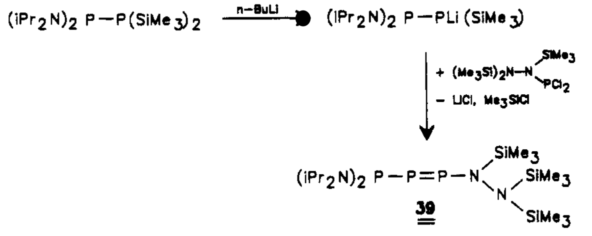


Scheme 21





Scheme 22



was completely converted into diphosphene **32** with amino and silyl ligands[44a] (Scheme 20). Following similar synthetic approaches Niecke succeeded in the synthesis of a number of stable unsymmetrical diphosphenes **33**–**38** containing substituents derived from phosphorus, nitrogen, and oxygen atoms[44b] (Scheme 21).

The transformation of the 1,1-disilyldiphosphane $(iPr_2N)_2P$–$P(SiMe_3)_2$ into a lithium derivative previous to the reaction with the hydrazidodichlorophosphane $(Me_3Si)_3N_2PCl_2$ furnished diphosphene **39** (Scheme 22).

The diphosphenes **33**, **34**, **37**, and **38** are orange to red crystalline solids, while **35**, **36**, and **39** were isolated as orange to red oils. Only diphosphene **36** lacks sufficient kinetic stability as it was indicated by its complete dimerization within a few hours at ambient temperature.

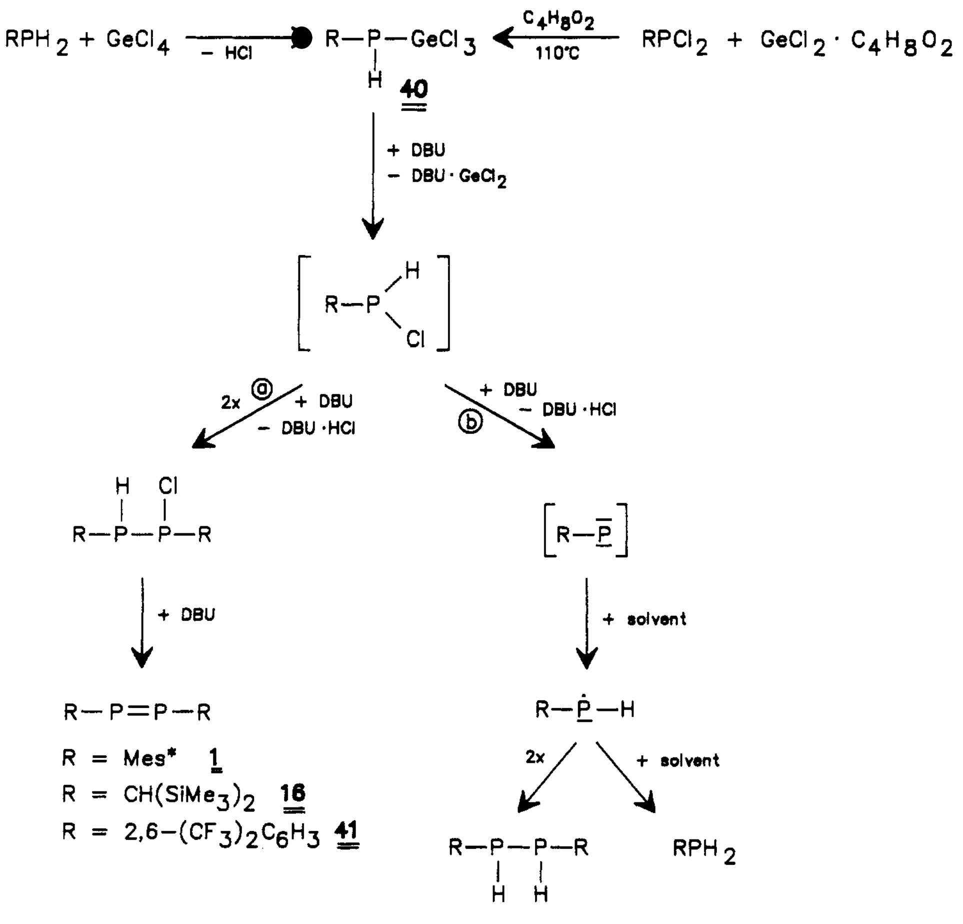
Another interesting elimination reaction for the synthesis of diphosphenes was claimed to be of general applicability. Satgé observed that the chlorophosphane Mes*PHCl was transformed almost quantitatively into diphosphene **1** upon reaction with DBU.[45] Chlorophosphanes are only sufficiently stable with bulky substituents. However the easily available (trichlorogermyl)phosphanes **40** can be utilized as in situ reagents for these reactive species. They are conveniently accessible by the treatment of a primary phosphane with $GeCl_4$ and the subsequent removal of $GeCl_2$ by means of DBU.[45] Surprisingly (trichlorogermyl)phosphanes of the type **40** were also the products of the reaction of the germanium dichloride–dioxane complex with organodichlorophosphanes in refluxing dioxane[45] (Scheme 23).

There are two mechanisms invoked to account for diphosphene formation as well as for the occurrence of RPH_2 and RPH–PHR [R = $(Me_3Si)_2CH$] as byproducts. Route a leads to the expected diphosphene via the intermolecular dehydrochlorination of RPHCl with formation of an intermediate chlorodiphosphane. Route b pronounces the intramolecular dehydrochlorination to yield a phosphinidene, which was believed to be converted into phosphanes RPH_2 and diphosphanes RPH–PHR via radical intermediates. When the DBU-induced elimination was carried out with a mixture of $Mes^*P(H)GeCl_3$ and $2,6\text{-}(CF_3)_2C_6H_3P(H)GeCl_3$ a 60% yield of the unsymmetrical diphosphene **42** was obtained. The symmetrical diphosphenes **1** and **41** were also observed in 30% and 10% yields respectively[45d] (Scheme 24).

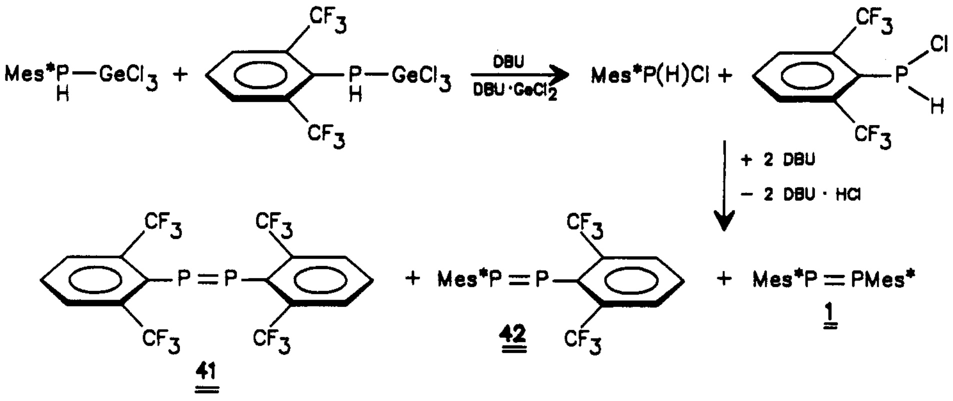
B. Rearrangement Reactions

1,3-Shift reactions of silyl substituents are of great importance for the synthesis of phosphaalkenes,[46] but there are only a few examples for the formation of P=P

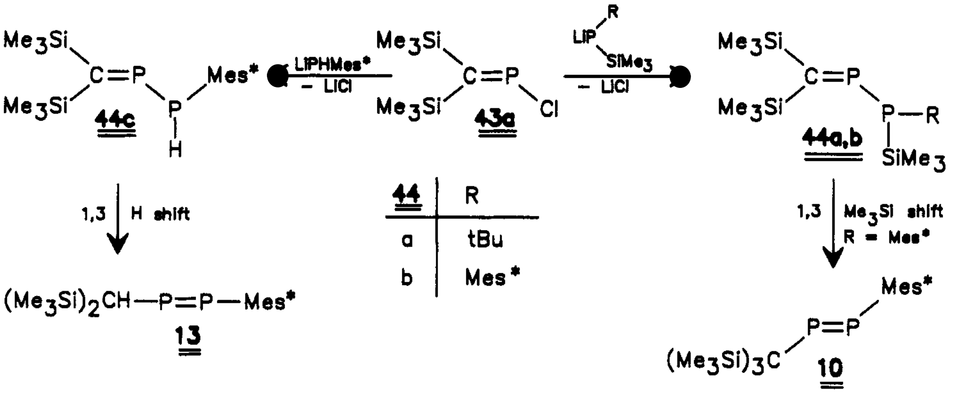
Scheme 23



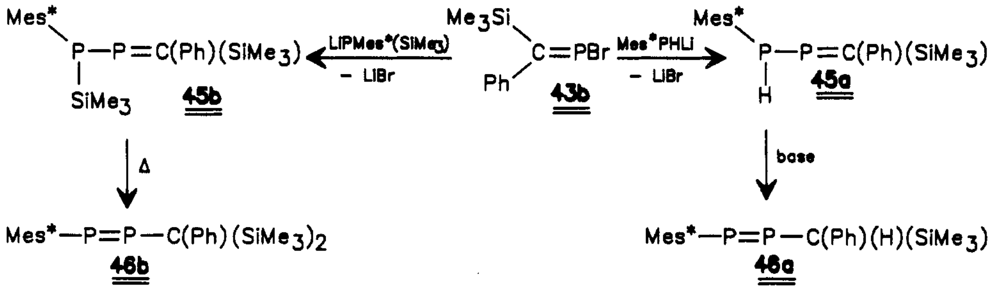
Scheme 24



Scheme 25



Scheme 26



bonds via this route. *P*-chloro[bis(trimethylsilyl)methylene]phosphane (**43a**) reacts with lithium (trimethylsilyl)-*tert*-butylphosphide to give the *P*-phosphinomethylenephosphane **44a**, which resisted isomerization in boiling benzene solution or when irradiated with UV light.[47] However, a different situation was met when the more bulky supermesityl substituent was present in the lithium silylphosphide. In this case the expected *P*-phosphinomethylenephosphane **44b** could not be detected even at −78 °C. Instead diphosphene **10** was quantitatively isolated as the result of an 1,3-Me_3Si shift[47] (Scheme 25).

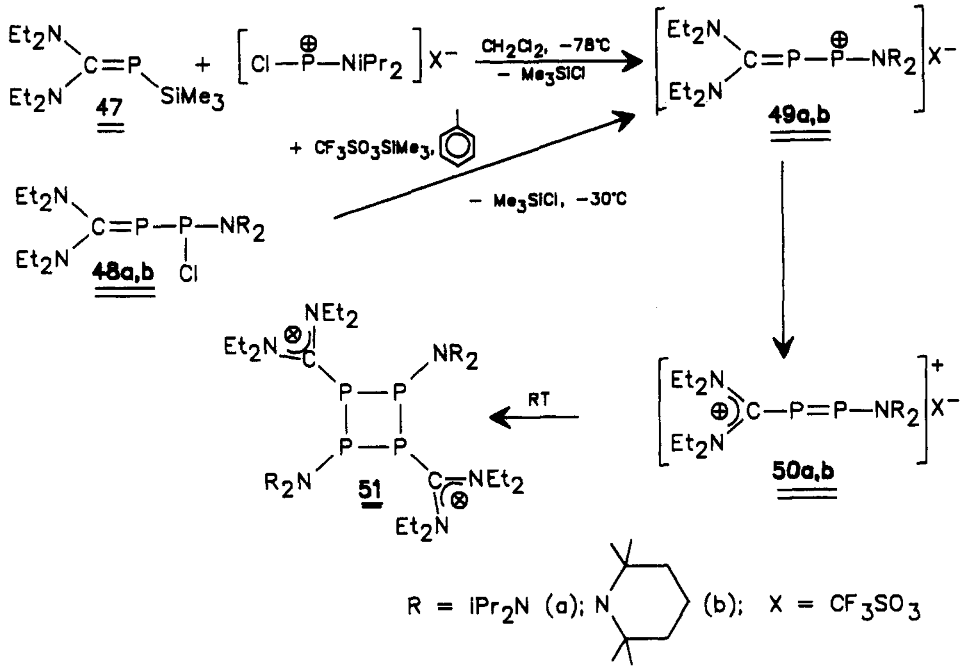
The phosphino-substituted phosphaalkene **44c**, which was formed from **43a** and LiHPMes*, suffered from a 1,3-proton shift to furnish diphosphene **13**. In THF solution at ambient temperature this isomerization takes 7–9 days to reach completion.

Diphosphenes **46a,b** were synthesized similarly from the *P*-bromomethylenephosphane **43b** and the respective lithium phosphides via the phosphaalkenes **45a** and **45b**[50c] (Scheme 26).

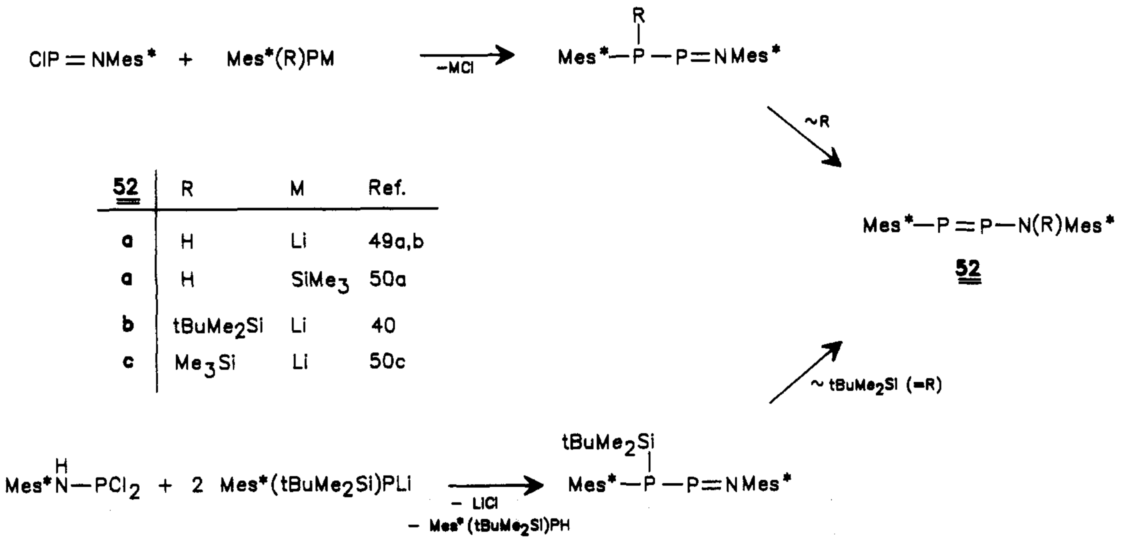
The phosphenium ions **49a,b** could neither be detected in the coupling reaction of $(Et_2N)_2C{=}PSiMe_3$ (**47**) with the phosphenium moiety $[ClPN(iPr)_2]^+$-$SO_3CF_3^-$ nor in the halide abstraction process from $(Et_2N)_2C{=}P{-}P(Cl)NR_2$ (**48a,b**). Instead at −78 °C the carbenium ion-substituted diphosphenes **50a,b** were observed by ^{31}P NMR (**50a**, δ = 493.5 d, 200.0 d, $^1J_{PP}$ = 520 Hz; **50b**, δ = 465 d, 210 d, J_{PP} = 525 Hz). It was obvious that the formation of the diphosphenes **50a,b** was due to the extremely fast isomerization **49** → **50**, favored by the higher stability of **50a,b** in comparison to the phosphenium ions **49a,b**. The delocalization of the positive charge on the $(Et_2N)_2C$ moiety of **50a,b** contributed to this stabilization. The ions **50a,b** could not be isolated from the solution. At room temperature they dimerized to the dicationic cyclotetraphosphanes **51**[48] (Scheme 27). There are two research groups reporting on structural isomerizations of phosphino-substituted iminophosphanes to diphosphenes.[40,49,50b,c]

Coupling of the *P*-chloroiminophosphane $ClP{=}NMes^*$ with lithium phosphides of the type Mes*RPLi led to novel iminophosphanes which underwent 1,3-hydrogen or 1,3-trimethylsilyl shifts from phosphorus to nitrogen to afford the amino-functionalized diphosphenes **52** (Scheme 28). Alternatively the

Scheme 27



Scheme 28



52	R	M	Ref.
a	H	Li	49a,b
a	H	$SiMe_3$	50a
b	$tBuMe_2Si$	Li	40
c	Me_3Si	Li	50c

iminophosphane which served as precursor for **52b** was synthesized by an addition elimination process as also depicted in Scheme 28.[50b]

C. Substitution Reactions

Diphosphenes XP=PR′ which are functionalized by the leaving group X^- undergo substitution reactions with nucleophiles more powerful than X^-. This was first exemplified by the reaction of the amino-substituted diphosphene **22a** with organolithium reagents as well as lithium diisopropylamide[51] (Scheme 29).

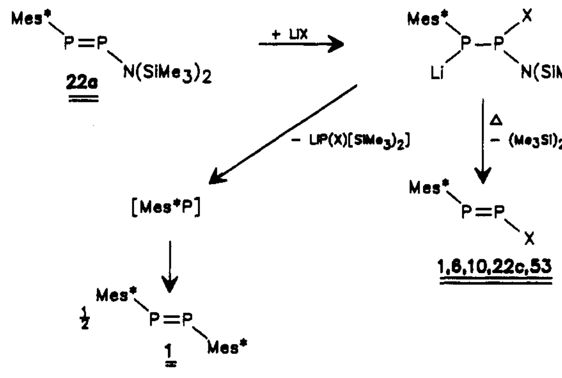
The diphosphenes were generated in 80–95% yield in addition to small amounts of **1**. The scope of substitution reactions was considerably increased by the availability of diphosphene **54** possessing a chloro substituent. Treatment of **54** with nucleophiles rendered accessible a variety of other diphosphenes displaying aryl, silyl, amino, phosphino, alkoxy, and thioxy groups bound in Mes*P=PNu. Diphosphene **54**, which is stable in solution up to −30 °C, was conveniently synthesized by the exposure of **22c** to an excess of gaseous HCl in ether solution at −78 °C[52] (Scheme 30).

The tendency of the diphosphene Cp*P=PCp* (**11**) to undergo facile substitution reactions could be inferred from the remarkably long P—C bonds, which were evident in the X-ray structure analysis of the molecule. The reaction of **11** with bulky lithium amides or lithium alkyls led to the stepwise replacement of the Cp* ligands. The unsymmetrical intermediates **56** were identified by ^{31}P NMR spectroscopy, their isolation however failed[28] (Scheme 31).

D. Miscellaneous Methods

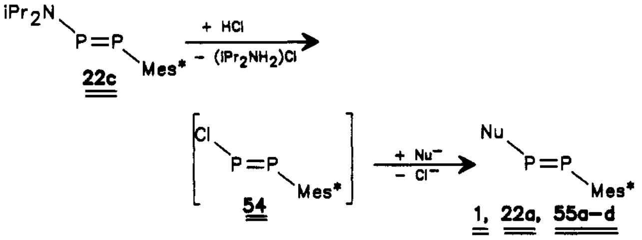
The phosphorus–phosphorus double bond in the first 1,2,4-triphospha-1,3-butadiene **58** resulted from a base-induced trimethylsilyl chloride elimination with concomitant CO extrusion of the intermediate 1,3,5-triphospha-1,4-pentadiene **57**[53] (Scheme 32).

Scheme 29



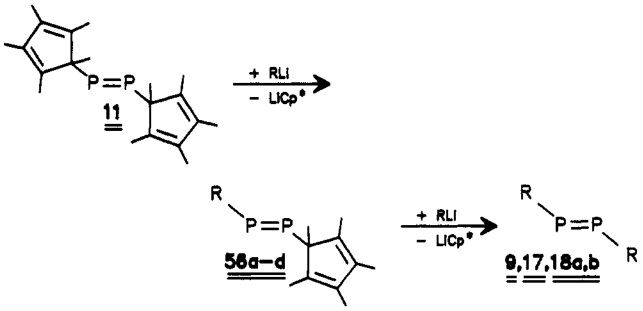
	X
1	Mes*
6	Mes
10	C(SiMe3)3
22c	iPr2N
53	tBu

Scheme 30



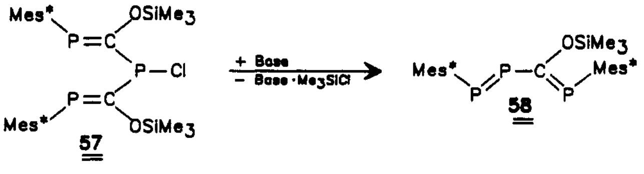
	1	22a	55a	55b	55c	55d
Nu	Mes*	N(SiMe3)2	Si(SiMe3)3	OtBu	P(tBu)2	S(tBu)

Scheme 31



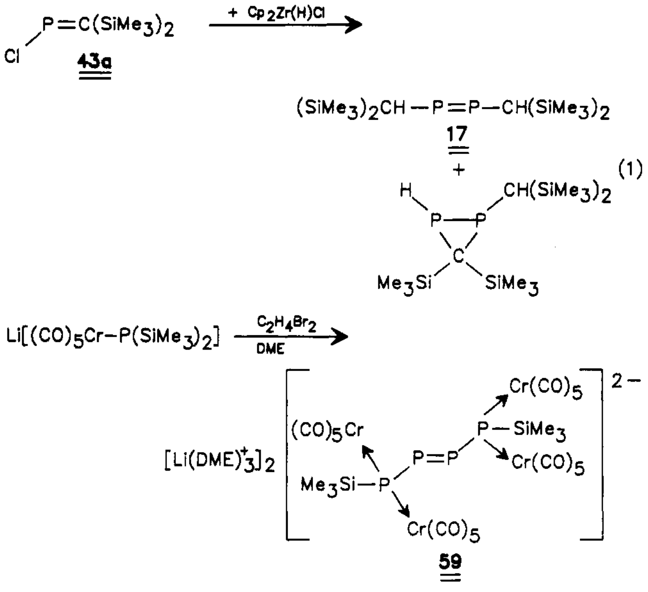
	R
9,56a	C(SiMe3)3
17,56b	CH(SiMe3)2
18a,56c	N(SiMe3)2
18b,56d	N(tBu)(SiMe3)

Scheme 32



The hydrozirconation reagent $Cp_2Z(H)Cl$ reduces the phosphaalkene **43a** to give a mixture of diphosphene **17** and diphosphirane $\overline{PH\text{-}P[CH(SiMe_3)_2]C}(SiMe_3)_2$[54a] (Scheme 33).

Scheme 33



Unexpectedly the reaction of the anionic phosphido complex $Li[(CO)_5Cr\text{-}P(SiMe_3)_2]$ with 1,2-dibromoethane furnished the novel tetraphosphene dianion **59** which is ligated at each terminal phosphorus center by the two bulky $Cr(CO)_5$ groups.[54c]

III. Structure and Bonding

A. Theoretical Studies

Several theoretical studies on diphosphenes have been reported in the literature.[9b,44,55–69] For the parent diphosphene HP=PH ab initio calculations revealed that the *E*-isomer is stabilized by 3.5 kcal/mol with respect to (*Z*)-HP=PH. The P=P π-bond strength, represented by the rotational barrier for the *E*/*Z* isomerization was found to 34 kcal/mol. For an inversion process 66 kcal/mol were necessary.[66] An experimental study by laser irridiation of Mes*P=PMes* (**1**) showed that the free activation energy for the *Z*/*E* conversion is only 20.3 kcal/mol at 0 °C.[70] In comparison to this the P–P σ-bond strength in P_2H_4 amounts to 49 kcal/mol.[68]

The P=P bond distance in (*E*)-HP=PH was calculated to 2.004 Å and the valence angle HPP to 96.0°.[66] As a consequence of orbital nonhybridization the valence angle at phosphorus is strongly decreased in order to accumulate s-character to the nonbonding lone pair at the phosphorus atoms.

Recently it has been demonstrated that σ-push–pull substitution effects a distortion of the usual *E* geometry.[44,71] Thus for diphosphene HP=PF a bridged structure was calculated with a valence angle P=P—H of only 88.0°, while the angle P=P—F was found to be opened to 103.5°. These theoretical findings were supported by X-ray crystal structure determinations of appropriate push–pull-substituted diphosphenes such as TMP—P=P—P[N(iPr$_2$)$_2$] **34**. Here valence angles PPP of 89.4° and NPP of 114.8° were encountered.

The frontier orbitals of (*E*)-HP=PH are also of interest. Molecular orbital calculations (SCF method) showed that this diphosphene possesses a low-lying lowest unoccupied molecular orbital (LUMO) ($2b_g$) which essentially is the antibonding (P=P) π^* orbital. The two highest occupied MO's, which are the bonding (P=P) π-orbital ($2a_u$) and n_+-orbital, a symmetrical lone pair combination ($7a_g$), are closely spaced. The exact orbital sequence and the ionization energies are very sensitive to the method of calculation. The SCF orbital energies of the valence electrons are the highest for the π-orbital $2a_u$ (−9.69 eV) followed by the energy of the n_+ combination (−9.86 eV).

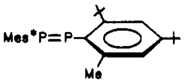
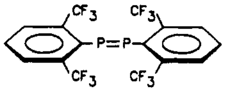
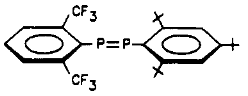
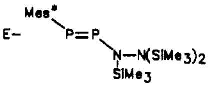
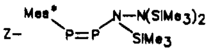
A study of the vertical ionization energies, affording the $H_2P_2^+$ cation, was also performed to get further insight into the relative energies of the π and n_+ MO's. When an electron is removed from the $2a_u$ (π) MO to form the cation in an ^2A_u state then the SCF (self-consistent field method), CI (configuration interaction), and Davidson-corrected ionization energies are 9.03, 9.72, and 9.88 eV, respectively.[66] The corresponding energies for removal of an electron from the $7a_g$ (n_+) MO, to form the cation in an ^2A_g state, are 9.29, 9.38, and 9.35 eV. Thus the π-MO is the HOMO according to both the SCF ionization energies and the SCF orbital energies, whearas the n_+ MO is the HOMO according to the presumably more accurate CI and Davidson-corrected energies.[66] The latter conclusion in an accord with the results of X_α studies on trans HP=PH.[9b,63]

B. Electric and Electron-Spectroscopic Studies

The presence of a low-lying unoccupied (P=P) π^* MO is reflected in the facile reduction of the diphosphenes **1** and **9** resulting in radical anions via population of the π^* orbital. Thus cyclic voltammetry at a Pt electrode in acetonitrile using $(nBu_4N)BF_4$ as a supporting salt revealed a reversible reduction of **1** at −1.74 V vs a saturated calomel electrode (sce).[15] Under slightly different conditions a reduction potential of −1.93 V was measured (THF, $NnBu_4BF_4$, 25 °C). Bulk electrolysis gave THF solutions of $[Mes^*P\text{-}PMes^*]^-$ which were stable for several days under an inert gas atmosphere.[72]

The triplet appearance of the ESR spectrum of the radical anion $(\mathbf{1})^-$ [$a(^{31}P)$ = 55G, g = 2.013] demonstrated that the unpaired electron resides in the P=P* orbital.[72] Similar findings were reported for diphosphene **9** where reversible reduction was apparent at −1.84 V (THF, $(NnBu_4)BF_4$, 25 °C).[72] At a mercury-coated platinum electrode in acetonitrile the reduction of **9** was observed at −1.73 V.[73] The bulk coulometry experiment with **9** resulted in the production of a purple radical anion, which was stable in THF solution for several days. In the ESR spectrum a triplet was observed [$a(^{31}P)$ = 43G, g = 2.018]. The production of the radical anions $(\mathbf{1})^-$ [74] and $(\mathbf{9})^-$ [73] could also be realized chemically by means of sodium naphthalenide. The radical anion of **1** was also detected in the reaction of Mes^*PCl_2 with magnesium.[15] In contrast to this the oxidation of **9** at a Pt electrode in acetonitrile [$(nBu_4N)PF_6$, 25 °C] proceeded irreversibly at +1.14 V (vs sce).[73] However at −75 °C a CH_2Cl_2 solution of **1** showed a reversible one-electron wave at +1.6 V (vs sce).[72] The two low-lying occupied molecular orbitals (n_+ and π) were evidenced by the He 1-photoelectron spectrum of **1** which displayed two bands at 7.24 and 8.05 eV.[15]

Table 1. UV/Vis Data of Selected Diphosphenes

compound	λ_{max}, nm	ref(s)
$Mes^*P{=}PMes^*$ **1**	460 (ϵ = 1 360) 340 (ϵ = 7 690) 284 (ϵ = 15 660)	8,15,16,18,22
$(Me_3Si)_3CP{=}PC(SiMe_3)_3$ **9**	484 (ϵ = 63) 353 (ϵ = 9 474) 241 (ϵ = 8 532)	22,23
$Mes^*P{=}PCH(SiMe_3)_2$ **13**	427 (ϵ = 370) 325 (ϵ = 13 000) 261 (ϵ = 15 500)	14,30
 **12a**	481 (ϵ = 468) 330 (ϵ = 5 080) 279 (ϵ = 13 800)	29
$Mes^*P{=}PMes$ **6**	456 (ϵ = 220) 326 (ϵ = 2 500) 273 (ϵ = 9 830)	29
 **41**	394 (ϵ = 197) 277 (ϵ = 11 840)	45d
 **42**	437 (ϵ = 880) 298 (ϵ = 23 950) 248 (ϵ = 21 000)	45d
 **25a**	318 355	40b
 **25b**	319 365	40b

As shown in Table 1 each diphosphene exhibits two electronic absorptions in the range of 300 to 500 nm. These absorptions were assigned to the $n_+ \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the P=P chromophore and are responsible for the characteristic orange-red color of diphosphenes. The absorption of the band with the longer wavelength is markedly less intense than the other one.

On the basis of this observation the longer wavelength absorption seemed to be symmetry forbidden and therefore was assigned to the $n_+ \rightarrow \pi^*_{PP}$, which implied that the n_+MO is the HOMO of **1**. In contrast to that the $\pi_{PP} \rightarrow \pi^*_{PP}$ transition is symmetry allowed. A comparison of the λ_{max} values of **1** and **9** indicated that there is little conjugation between aryl groups and the P=P unit.[10]

C. Molecular Structures

The molecular structures of several diphosphenes have been elucidated by X-ray crystallography, and their selected structural data are collected in Table 2. Their most conspicuous feature was the shortness of the phosphorus–phosphorus double bond, which ranged from 2.001 (3) in **9**[14,75] to 2.049 (1) Å in **22c**.[11] In most of the cases the *E* configuration of the ligands at the double bond is favored. Theoretical calculations on P_2H_2 predict a P–P bond length of 2.004 Å,[66] which is in good agreement with the sum of the double bond covalent radii 2.00 Å.[76]

The P–P bond distances of diphosphenes relative to those in diphosphanes (ca. 2.22 Å)[77] merit a comment. Generally it is accepted that a double bond in main group compounds involves a σ- and a π-bond. The difference in length between double and single bonds is due to π-overlap and to a change in hybridization in the σ-bonding orbitals. For carbon–carbon double

Table 2. Selected Structural Data of Diphosphenes (in Å and deg)

compound	d(P = P)	d(P–X)	d(P–Y)	∠X–P–P	∠P–P–Y	∠X–P–P–Y	ref(s)
trans-Diphosphenes							
Mes*P = PMes* (**1**)	2.034 (2)	1.862 (2)		102.8 (1)		172.2 (1)	8
$(Me_3Si)_3CP = PC(SiMe_3)_3$ (**9**)	2.003 (3)	1.866 (5)		108.1 (2)		180.0	14,75
	2.001 (3)	1.855 (5)		108.9 (2)		180.0	
Cp*P = PCp* (**11**)	2.031 (3)	1.893 (7)	1.883 (7)	103.4	103.9		28
$(tBuMe_2Si)_2NP = PN(SiMe_2tBu)_2$ (**21a**)	2.034 (2)	1.769		102.2			36
MesP = P-$NiPr_2$ (**22c**)	2.049 (1)	1.863 (3)[a]	1.666 (3)[a]	92.0 (1)[a]	108.1 (1)[a]		11
Mes*P = PTMP (**22d**)[b]	2.033 (2)	1.869 (5)[a]	1.685 (4)[a]	89.4 (3)[a]	115.1 (3)[a]		11
Mes*P = $PN_2(SiMe_3)_3$ (**25a**)	2.037 (2)	1.864 (4)[a]	1.700 (3)[a]	97.6 (1)[a]	106.1 (1)[a]	179.4 (2)	40b
$(Me_3Si)_3CP = PSiPh_3$ (**28**)	2.005 (2)	1.868 (6)[c]	2.269 (2)[c]	110.5 (1)[c]	98.65 (8)[c]	0.21	41
Mes*P = $PSntBu_3$ (**30**)	2.033 (3)	1.871 (7)[d]	2.546 (2)[d]	102.2 (2)[d]	100.6 (1)[d]	179.1 (2)	43
$(iPr_2N)_2PP$ = PMes* (**33**)	2.018 (1)	1.859 (2)[f]	2.242 (1)[f]	101.2 (1)[f]	92.3 (<0.1)[f]	175.3 (1)	44b
$(iPr_2N)_2PP$ = PTMP (**34**)[b]	2.029 (2)	1.691 (4)[g]	2.233 (2)[g]	114.8 (1)[g]	89.4 (1)[g]	177.7 (2)	44b
$(iPr_2N)_2PP = PN[SiMe_2tBu]_2$ (**37**)	2.011 (2)	1.736 (4)[g]	2.228 (1)[g]	110.5 (1)[g]	89.8 (<0.1)[g]	−179.8 (1)	44b
$(LiL_3)_2\{[M]_2RPP + PPR[M]_2\}$ (**59**)[h]	2.025 (3)	2.219 (2)		105.9 (1)			54c
cis-Diphosphenes							
Mes*P = P-NHtBu (**24a**)	2.038 (2)	1.862 (4)[a]	1.645 (4)[a]	102.0 (2)[a]	109.9 (2)[a]	0.6 (2)	39
Mes*P = PNH(1-Ad) (**24b**)[e]	2.044 (2)	1.855 (3)[a]	1.652 (5)[a]	102.2 (2)[a]	109.2 (2)[a]	0.5 (2)	39
Mes*P = $PN_2(SiMe_3)_3$ (**25b**)	2.027 (3)	1.878 (9)[a]	1.686 (7)[a]	121.4 (3)[a]	126.3 (3)[a]	1.5 (6)	40b

[a] X = C, Y = N. [b] TMP = 2,2,6,6-tetramethylpiperidino. [c] X = C, Y = Si. [d] X = C, Y = Sn. [e] 1-Ad = 1-adamantyl. [f] X = C, Y = P. [g] X = N, Y = P. [h] L = DME, [M] = $Cr(CO)_5$; R = Me_3Si.

bonds the shortening due to (p–p) π-overlap amounts to 70–75%, whereas 25–30% can be accounted for the change in hybridization from sp^3 to sp^2. In an elegant study Power et al. showed that in the case of diphosphenes the bond shortening is about equally divided between (p–p) π-overlap and rehybridization of the σ-orbitals.[78] Thus in diphosphenes with organic substituents the valence angles at the phosphorus centers vary from 90 to 110°. In the boryl-substituted diphosphanes $[Mes_2B(R)P]_2$ (R = 1-Ad, Mes) the phosphorus atoms possess a planar geometry and the P–P bond distance amounts to only ca. 2.11 Å. Inspite of this the P–P bonds have a bond order of unity. From calculations a valence angle of 96.1° is inferred for the parent diphosphene P_2H_2. In the symmetrical diphosphenes the bond angles range from 102.2 (1)° in $(tBuMe_2Si)_2NP{=}PN(SiMe_2tBu)_2$ (**21a**), to 108.9 (2)° in **9**, reflecting the steric demands of the bulky ligands at the P=P moiety. In unsymmetrical diphosphenes the bond angles may differ markedly which is rationalized by a push–pull effect imposed by ligands of different electronegativity[44b] or by steric interactions. Thus in Mes*P=PTMP **22d** an obtuse angle NP=P of 115.1 (3)° has to be compared to the angle P=PC of only 89.4 (3)°.[11]

In $(Me_3Si)_3CP{=}PSiPh_3$ (**28**) the difference between the angles SiPP = 98.65 (8)° and CPP = 110.5 (1)° considerably decrease,[41] while in Mes*P=$PSntBu_3$ the bond angles Sn–P–P = 100.6 (1)° and P–P–C = 102.2 (2)° are no longer essentially different.[43] In all the *E*-configurated diphosphenes yet analyzed by X-ray diffraction the atoms directly attached the P=P unit are located in the same plane. This was inferred from torsion angles X–PP–Y ranging from 172.2 (1)° to 180.0°. In *E* diphosphenes with supermesityl-substituents the aryl rings are usually in an orthogonal orientation to the plane defined by the atoms X,P,[1] P,[2] and Y. A similar observation was made in the bisaminodiphosphene **21a**[36] where the lone pairs at nitrogen are directed perpendicularily to the π-bond. The same holds for diphosphene $(iPr_2N)_2PP{=}PN(SiMe_2tBu)_2$ (**37**)[44b] and is in sharp contrast to $(iPr_2N)_2PP{=}PTMP$ (**34**),[44b] Mes*P=$PN(iPr)_2$ (**22c**),[11] and **22d**,[11] where the lone pair at the nitrogen atom is in conjugation with P=P double bond, thus establishing a three-center, four-electron system as it is well known from the allylic anion. In accord with this the diphosphenes **22c**,[11] **22d**,[11] and **34**[44b] display PN bonds [1.666 (3); 1.685 (4); and 1.691 (4) Å, respectively] which are significantly shortened in comparison to the corresponding distances in **21a** (1.769 Å)[39] and **37** [1.736 (2) Å].[44]

In the two *Z*-configurated diphosphenes **24a** and **24b**,[39] fully characterized by X-ray analyses, the atoms N, P(1), and P(2) and the ipso carbon atom of the aryl substituent are located in the same plane. The aryl ring is directed orthogonally to the plane defined by N, P(1), P(2) and the ipso C atom, thus rendering it possible that the hydrogen atom of the amino group points to the center of the arene ring. The attractive interaction resulting from this was invoked to explain the stability of the rare *Z* arrangement. The P=P bonds in **24a** and **24b** are 2.038 (2) and 2.044 (2) Å, respectively, whereas the PN separations are shortened [1.645 (4) and 1.652 (5) Å, respectively] due to π-conjugation. The bond angles N–P–P amount to 109.9 (2) and 109.2 (2)°, while the angles P–P–C were conspicuously more acute [102.0 (2) and 102.2 (1)°, respectively].

The molecular structures of the compounds (*E*)- and *Z*)-Mes*P=$PN(SiMe_3)N(SiMe_3)_2$ (**24a,b**) provide insight in structural differences between the *E*- and *Z*-isomers of the same diphosphene. In both species the planar-coordinated N atoms of the hydrazino substituents and the P atoms of the double-bond system are located in one plane (three-center, four π-electron system), which give rise to a more obtuse angle N–P–P in **25a** (106°) and **25b** (126°) in comparison to the valence angles C–P–P in both species 98° (**25a**) and 121° (**25b**), respectively (Figure 1). The P–P bond distance in the *Z*-isomer is found slightly shorter [2.027 (3) Å] than that in the *E*-configurated **25a** [2.037 (2) Å]. Despite the fact that this difference is not significant an explanation was given, which invoked an increased participation of 3s electron density in the P–P bond of **25b**.[40b]

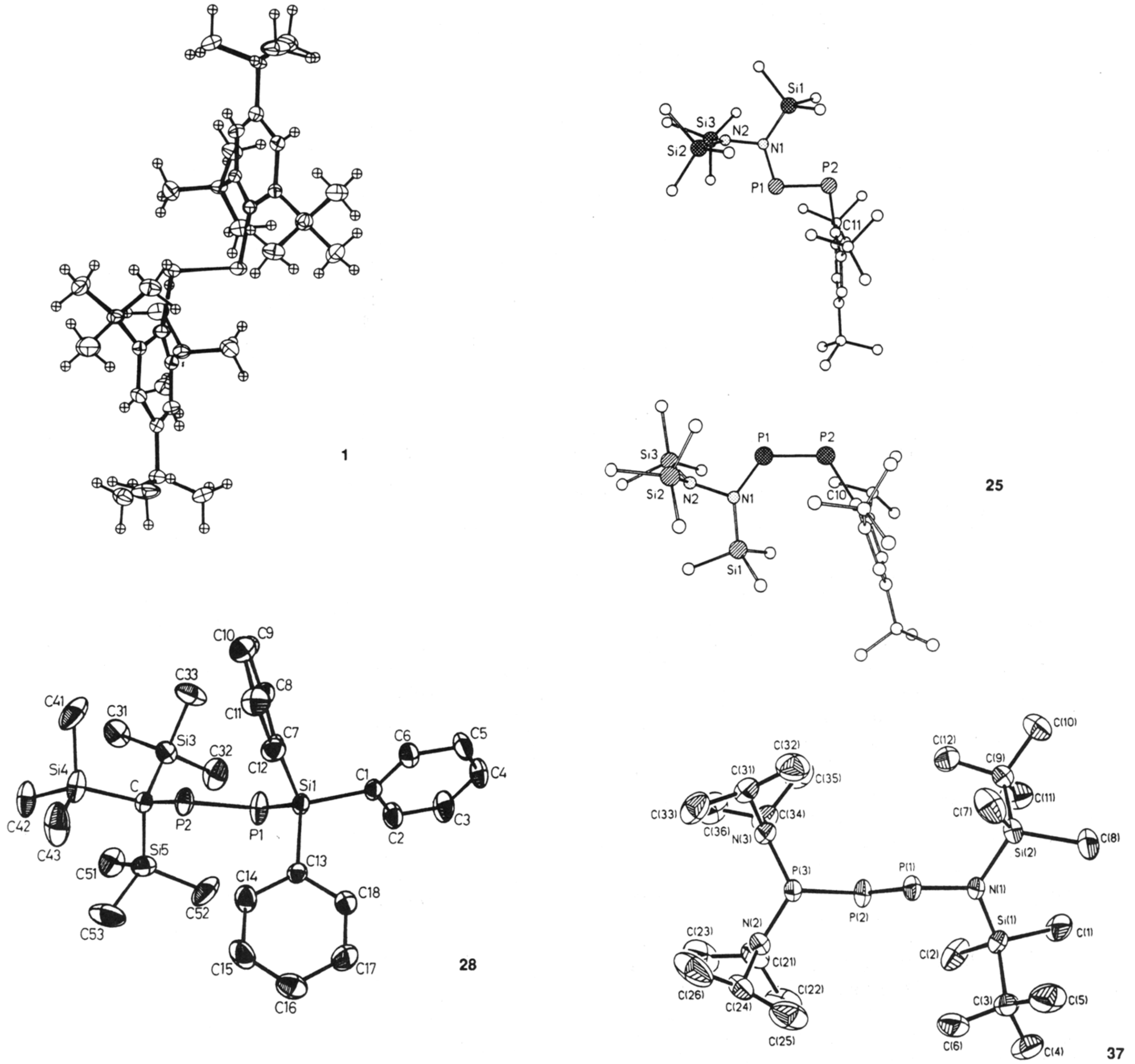


Figure 1. Molecular structures of Mes*P=PMes* (**1**), Mes*P=PSiPh$_3$ (**28**), (iPr$_2$N)$_2$PP=PN[SiMe$_2$tBu]$_2$ (**37**), and (*E*)- and (*Z*)-Mes*P=PN$_2$(SiMe$_3$)$_3$ (**25a,b**). Reprinted from refs 8 (**1**), 41 (**28**), and 44b (**37**). Copyrights 1981, 1989, and 1989, respectively, American Chemical Society. Reprinted from ref 40b (**25**). Copyright 1991 VCH (Weinheim).

D. ^{31}P NMR Spectroscopic Studies

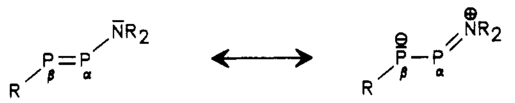
Generally ^{31}P NMR spectra comprise a range from $\delta = -530$ ppm for white phosphorus P$_4$[79] to $\delta = +1362$ ppm in the phosphinidene complex tBuP[Cr(CO)$_5$]$_2$.[80] The P atom in the latter species is tricoordinate. An explanation for the high-field resonance in P$_4$ invokes the fact that the lone pairs at the phosphorus atoms in this strained molecule are mainly 3s in character, providing a high degree of diamagnetic shielding. On the other hand the reason for the low-field ^{31}P NMR chemical shift in phosphinidene complexes is assumed to be due to a significant increase in the paramagnetic shielding term σ_P, which dominates the overall shielding in multiple-bonded compounds. This paramagnetic shielding term is reverse proportional to the size of the HOMO–LUMO gap ΔE. This gap is quite small in these three-center, four π-electron systems as indicated by the intense color of phosphinidene complexes. Indeed Huttner succeeded in finding a linear correlation between the absorbance in the UV/vis spectra λ_{max} and the chemical shifts δ ^{31}P of a series of phosphinidene complexes.[81] The situation, however, is more complicated in the case of *E*-configurated diphosphenes with a coordination number of two at both phosphorus centers. The chemical shifts for diphosphenes are among the lowest field shifts known in ^{31}P NMR spectroscopy. They essentially range from 500 to 670 ppm. Here again it is obvious to correlate the ^{31}P chemical shifts with λ_{max} values from UV/vis experiments in order to determine whether the paramagnetic term is governed by the $n_+ \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transition of the diphosphene. However, no such simple relationship was found.[10,14] The ^{31}P nuclei in **1** give rise to a resonance at $\delta = 492.4$, whereas in **9** the corresponding absorbance is significantly low field shifted ($\delta = 599.6$). One might argue that in **9** the valence angles P–P–C

[108.1 (2) or 108.9 (2) respectively] is widened as compared to the corresponding angle in 1 [102.8 (1)°]. The decreased s-character of the lone pair in **9** might result in a destabilization of the n_+-MO with a concomitant decrease of the HOMO–LUMO gap ΔE. On the other hand in the unsymmetrical diphosphene $Mes^*P{=}PC(SiMe_3)_3$ (**10**) no such effect is apparent as indicated by an AB-type spectrum at $\delta_A = 530.0$ and $\delta_B = 533.1$ ppm.

A significant deshielding of a phosphorus atom is effected by the substitution with less electronegative substituents such as $SiMe_3$ or $SiPh_3$ groups as realized in $(Me_3Si)_3CP^A{=}P^BSiMe_3$ (**29b**)[41] ($\delta_A = 544.1, \delta_B = 686.9$, $^1J_{PP} = 633.2$ Hz) or $(Me_3Si)_3CP^A{=}P^BSiPh_3$ (**28**)[41] ($\delta_A = 511.8$, $\delta_B = 711.4$, $^1J_{PP} = 633.1$ Hz). Here one might argue that the energy of the n_+-MO is raised by the electropositive and electron-donating substituent.

A similar argument might be helpful to provide an understanding for the significant low-field absorptions of the metalated P atoms in diphosphenyl complexes such as: $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)FeP^A{=}P^BAryl_F$ ($Aryl_F$ = 2,4,6-$(CF_3)_3C_6H_2$), ($\delta_A = 877.9$d, $\delta_B = 487.0$d; $^1J_{PP} = 615$ Hz) (see section VII.A).

The opposite situation, a high-field shift of the ^{31}P resonance, was observed in several nitrogen substituted representatives such as $Mes^*P{=}PN(iPr)_2$ (**22c**), $Mes^*P{=}PTMP$ (**22d**), or $(iPr_2N)_2PP{=}PTMP$ (**34**), where π-conjugation of the nitrogen lone pair with the P=P double bond is operating. As a consequence of this three-center, four π-electron system



the phosphorus atom in β position to the nitrogen atom experiences an additional negative charge, which causes a high-field shift. In **22c** the ^{31}P absorbances are registered at $\delta_{P\alpha} = 446.9$ and $\delta_{P\beta} = 276.4$ ($^1J_{PP} = 537$ Hz). For comparison in $Mes^*P{=}PN(SiMe_3)_2$, where such a three-center, four π-electron situation is absent, the ^{31}P NMR spectrum comprises two doublets at $\delta_\alpha = 409.3$ and $\delta_\beta = 501.5$ ppm ($^1J_{PP} = 584.2$ Hz).

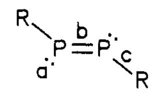
In sharp contrast to their *E*-isomers *Z*-configurated diphosphenes give rise to ^{31}P resonances at significantly higher fields. Thus for *Z*-1 a singlet was observed at $\delta = 368$ which is about 124 ppm upfield from the corresponding signal in *E*-1. In (*Z*)-$Mes^*P{=}PNH(tBu)$ (**24a**) two doublets are registered at $\delta = 214$ and 377 ppm ($^1J_{PP} = 526.0$ Hz).

Especially interesting is the comparison of the spectra of (*E*)- and (*Z*)-$Mes^*P{=}PN(SiMe_3)N(SiMe_3)_2$ **25a** and **25b**, respectively. The spectrum of **25a** features doublets at $\delta = 311$ (P_β) and $\delta = 481$ (P_α) ($J_{PP} = 554$ Hz) which agrees with the precence of the already mentioned three-center, four π-electron system. The same is true for the *Z*-isomer **25b**, where ^{31}P resonances were observed at considerably higher fields [$\delta = 190$ (P_β) and $\delta = 358$ (P_α), $J_{PP} = 516$ Hz]. The differences in chemical shifts between the *E*- and *Z*-isomers amount to $\Delta\delta_{P\alpha} = 123$ ppm and $\Delta\delta_{P\beta} = 121$ ppm.

The values of $^1J_{PP}$ obtained directly from the spectra of unsymmetrical diphosphenes merit a special comment. Generally these couplings are large and vary from 510 to 670 Hz. These remarkable $^1J_{PP}$ values for P=P′ systems originate from increases in the Fermi contact term, which reflects changes in the valence character of the phosphorus atoms.[10] In Table 3 ^{31}P NMR parameters of diphosphenes are compiled.

IV. Reactivity of Diphosphenes

Diphosphenes are polyfunctional molecules where chemical reactions are conceivable at (a) the P atom, (b) the P=P bond, and (c) the P–R bond:



The presence of low-lying frontier orbitals makes diphosphenes to suitable candidates for redox processes and for reactions with electrophiles as well as nucleophiles. Moreover the diagonal relationship in the periodic table between the elements carbon and phosphorus makes cycloadditions to the P=P double bond according to the respective organic model obvious.

Reactions at the P–R bond (c) involve substitutions with retainment of the P=P bond and are already included in the chapter on the synthesis of diphosphenes. Ligating properties of diphosphenes in transition metal complexes are discussed separately (section V).

A. Reactions with Electrophiles

1. Oxidations

In the solid state heavily substituted diphosphenes such as 1 or 9 were not affected by triplet oxygen at ambient temperature. However heating a toluene solution of 1 for 3 days at 80 °C in the presence of oxygen led to the formation of the decomposition products **60**–**62**.[83]

A possible mechanism invoked the generation of a phosphinidene which might have abstracted hydrogen from the solvent or undergone an intramolecular insertion into a C-H bond of an *o-tert*-butyl group of the aryl ring prior to oxidation. Product **62** involved oxidation of the phosphinidene to a dioxophosphorane with subsequent insertion of the P=O functionality into the C–H bond (Scheme 34).

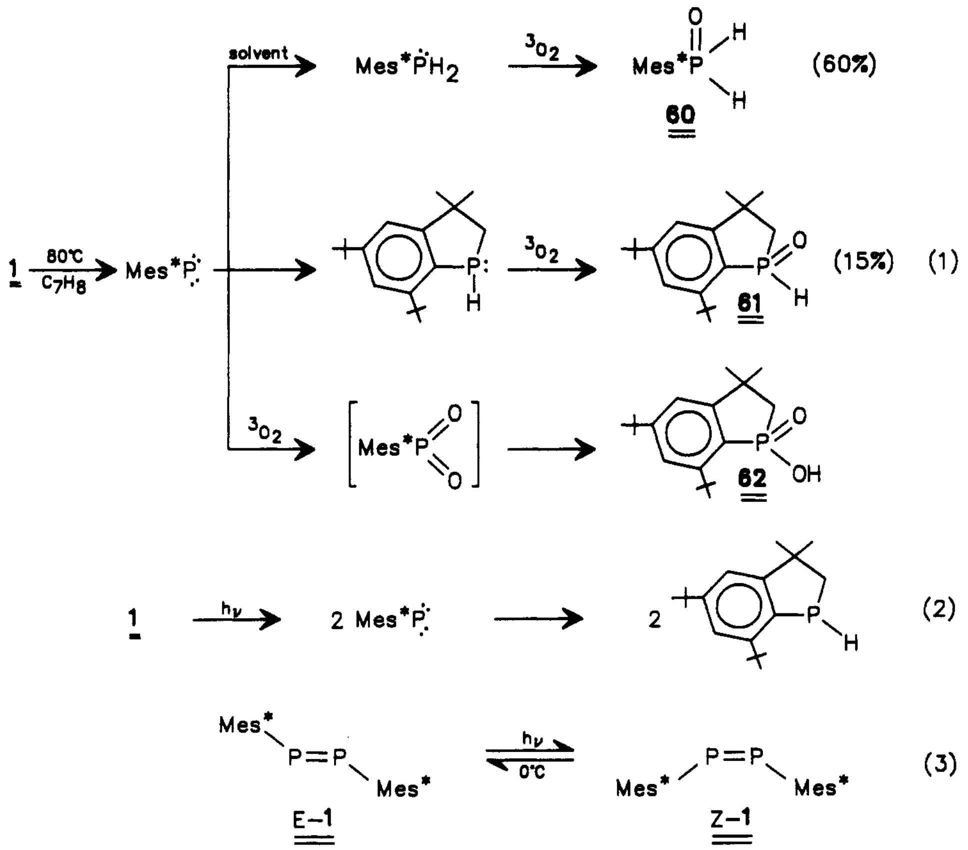
This assumption was supported by the thermal decomposition of 1 in a THF/C_6H_6 mixture at +120 °C which eventually afforded Mes^*PH_2.[16] Photoirradiation of 1 with a medium-pressure mercury lamp without a pyrex filter gave a phosphaindan derivative via the believed intermediacy of a phosphinidene.[84] If, however, the same irradiation was carried out at low temperature in the presence of a pyrex filter an *E*/*Z* isomerization of 1 took place.[84] A similar process was observed when 1 was exposed to the light of an argon laser (514.5 nm) at −78 °C.[70,83]

In contrast to triplet oxygen, singlet oxygen is reactive to diphosphenes even at low temperatures.[83] At room temperature the reaction of singlet oxygen which was generated chemically from a number of trioxophosphetanes (phosphorus ozonides) **63** led to the formation

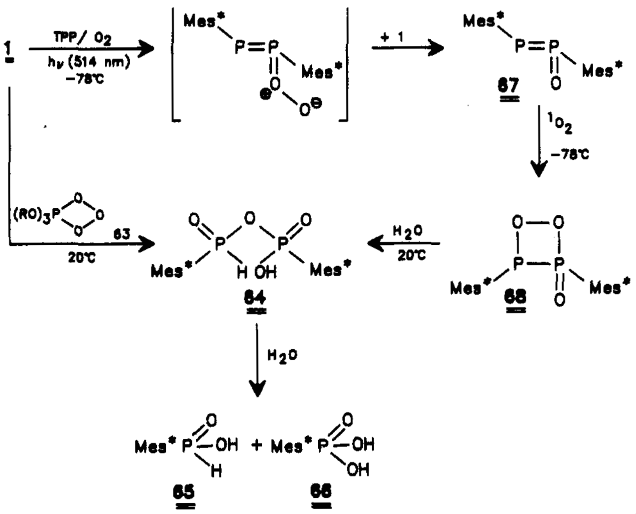
Table 3. ^{31}P NMR Data of Diphosphenes R^{1}P^1=P^{2}R^2

compd	R^1	R^2	^{31}P NMR: δ, ppm	$^1J_{PP}$, Hz	ref(s)
Z-1	Mes*	Mes*	368		70
E-1	Mes*	Mes* (1)	492.4		82
2	2,4,6-tPn$_3$C$_6$H$_2$	2,4,6-tPn$_3$C$_6$H$_2$	490.8		20b
3	2,6-tBu$_2$C$_6$H$_3$	2,6-tBu$_2$C$_6$H$_3$	488.7		20a
4	2-tBu-4,5,6-Me$_3$C$_6$H	2-tBu-4,5,6-Me$_3$C$_6$H	509.8		21
5	Mes*	2,4,6-tPn$_3$C$_6$H$_2$	489.9; 491.2	582.9	20b
6	Mes*	Mes	467.6; 540.4	573.7	29
7	Mes*	2,4,6-iPr$_3$C$_6$H$_2$	470, 535	572	21
8	Mes*	2-tBu-4,5,6-Me$_3$C$_6$H	478, 512	580	21
9	(Me$_3$Si)$_3$C	(Me$_3$Si)$_3$C	599.6 [598.6]		14, 22 [23]
10	Mes*	(Me$_3$Si)$_3$C	530.0; 533.1	619.7	25
11	C$_5$Me$_5$	C$_5$Me$_5$	504.0		28
12a	Mes*	2,4-tBu$_2$-6-MeC$_6$H$_2$	480.1; 517.0	583.5	29
12b	Mes*	Ph	455.5; 525.5	548.7	29
13	Mes*	CH(SiMe$_3$)$_2$	493.0; 513.0	577.5	30
14	2,4,6-(CF$_3$)$_3$C$_6$H$_2$	2,4,6-(CF$_3$)$_3$C$_6$H$_2$	474		31
15	2,4,6-(CF$_3$)$_3$C$_6$H$_2$	Mes*	416.8; 537.6	572	32
16	Mes*	C$_5$Me$_5$	484.6; 491.1	584	33
17	(Me$_3$Si)$_2$CH	(Me$_3$Si)$_2$CH	517		34
18a	(Me$_3$Si)$_2$N	(Me$_3$Si)$_2$N	572		35
18b	(Me$_3$Si)(tBu)N	(Me$_3$Si)(tBu)N	499		36
19	(Me$_3$Si)(tBu)N	(Me$_3$Si)$_2$N	507; 544	670	36
21a	(tBuMe$_2$Si)$_2$N	(tBuMe$_2$Si)$_2$N	561		36
21b	TMP	TMP	471.1		37a
22a	Mes*	(Me$_3$Si)$_2$N	409.3; 501.5	584.2	38
22b	Mes*	(tBuMe$_2$Si)$_2$N	389.6; 501.2	537.1	11
22c	Mes*	iPr$_2$N	276.4; 446.9	537	52a
22d	Mes*	TMP	336.1; 460.7	579.9	38
23	tBu	TMP	383; 508	611	37b
Z-24a	Mes*	tBuNH	214; 377	526	39
Z-24b	Mes*	1-AdNH	213; 375	524.5	39
Z-24c	Mes*	Et$_3$CNH	212.3; 379.0	527.2	39
Z-24d	Mes*	2,4,6-iPr$_3$C$_6$H$_2$NH	209.3; 379.7	523	39
E-25a	Mes*	(Me$_3$Si)$_3$N$_2$	311, 481	554	40b
Z-25b	Mes*	(Me$_3$Si)$_3$N$_2$	190; 358	516	40b
27	Mes*	SiPh$_3$	457.7; 641.9	588.7	41
28	(Me$_3$Si)$_3$C	SiPh$_3$	511.8; 711.4	633.1	41
29a	Mes*	SiMe$_3$	490.8; 632.3	584	42
			486.8; 628.2	575	21
29b	(Me$_3$Si)$_3$C	SiMe$_3$	544.1; 686.9	633.2	41
30	Mes*	SntBu$_3$	446.57; 465.71	607.9	43
32	(Me$_3$Si)$_3$N$_2$	SiMe$_3$	210.3; 542	540	44a
33	Mes*	P(NiPr$_2$)$_2$	502.7; 554.0	574	44b
34	TMP	P(NiPr$_2$)$_2$	320.1; 496.5	574	44b
35	NHMes*	P(NiPr$_2$)$_2$	407.4; 544.0	570	44b
36	N-iPr$_2$	P(NiPr$_2$)$_2$	245.7; 483.9	534	44b
37	N(SiMe$_2$tBu)$_2$	P(NiPr$_2$)$_2$	442.9; 577.6	602	44b
38	OMes*	P(NiPr$_2$)$_2$	386.2; 590.2	564	44b
39	(Me$_3$Si)$_3$N$_2$	P(NiPr$_2$)$_2$	298.7; 522.3	522	44b
41	2,6-(CF$_3$)$_2$C$_6$H$_3$	2,6-(CF$_3$)$_2$C$_6$H$_3$	477.1		45d
42	Mes*	2,6-(CF$_3$)$_2$C$_6$H$_3$	422.1; 533.0	574.3	45d
46a	Mes*	C(Ph)(H)(SiMe$_3$)	486.6; 522.8	569.9	50c
46b	Mes*	CPh(SiMe$_3$)$_2$	510.8; 530.1	598.0	50c
50a	(Et$_2$N)$_2$C$^+$	N(iPr)$_2$	200; 493.5	520	48
50b	(Et$_2$N)$_2$C$^+$	TMP	210; 465	525	48
52a	Mes*	NHMes*	314; 455	537	49a
			316.2; 450	532	50a
52b	Mes*	N[SiMe$_2$(tBu)]Mes*	350.1; 480.8	578.2	50c
52c	Mes*	N(SiMe$_3$)Mes*	343.1; 483.2	571.4	50c
53	Mes*	tBu	524.7; 531.9	576.6	51, 11
54	Mes*	Cl	473.4; 522.8	598	52a
55a	Mes*	Si(SiMe$_3$)$_3$	501.2; 610.6	598	52a
55b	Mes*	OtBu	397.6; 524.3	573.7	52a
55c	Mes*	P(tBu)$_2$	487.1; 600.9	586	52a
55d	Mes*	StBu	448.1; 468.0	549.3	52a
56a	C$_5$Me$_5$	C(SiMe$_3$)$_3$	522.2; 545.8	635	28
56b	C$_5$Me$_5$	CH(SiMe$_3$)$_2$	492.6; 522.8	599	28
56c	C$_5$Me$_5$	N(SiMe$_3$)$_2$	478.3; 546.2	632	28
56d	C$_5$Me$_5$	N(tBu)(SiMe$_3$)	529.1; 440.1	640	28
58	Mes*	C(OSiMe$_3$) = PMes*	414.6; 394.3	510	53
59	[(CO)$_5$Cr]$_2$(Me$_3$Si)P	[(CO)$_5$Cr]$_2$(Me$_3$Si)P	552	640	54c
98	Mes*	PHMes*	500; 552	571	98a
99	Mes*	PMeMes*	473; 493	558	98a
140	(Me$_3$Si)$_3$N$_2$	N$_2$(SiMe$_3$)$_3$	325		40b, 112

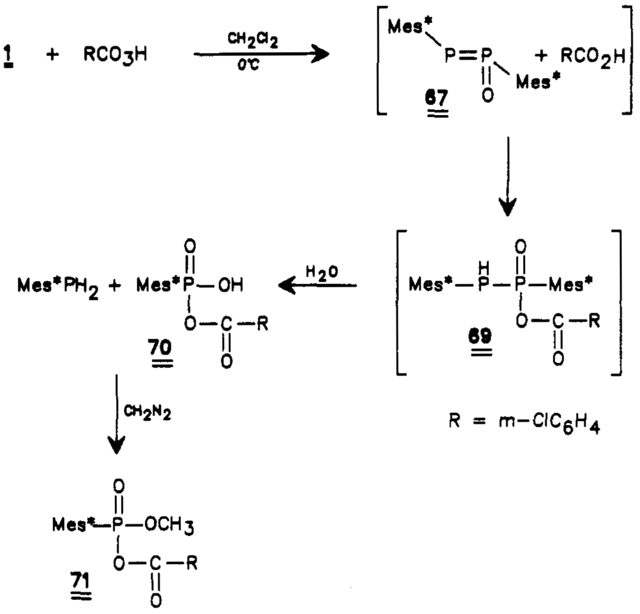
Scheme 34



Scheme 35



Scheme 36



Scheme 37

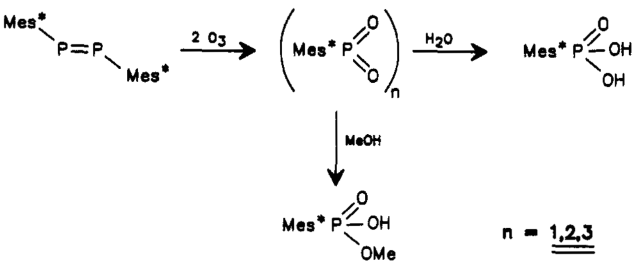
of anhydride 64. Compound 64 was easily hydrolyzed to a mixture of phosphinic acid 65 and phosphonic acid 66.[83,85]

Photochemically produced $^1O_2$ (sensitizer, tetraphenylporphine TPP 514 nm) reacted with 1 at −78 °C to give a mixture of the diphosphene oxide 67 and the dioxodiphosphetane 68. Compound 68 was stable for several days at −78 °C. At 20 °C, however, it experienced decomposition and easy hydrolysis to 65 and 66[83,85] (Scheme 35).

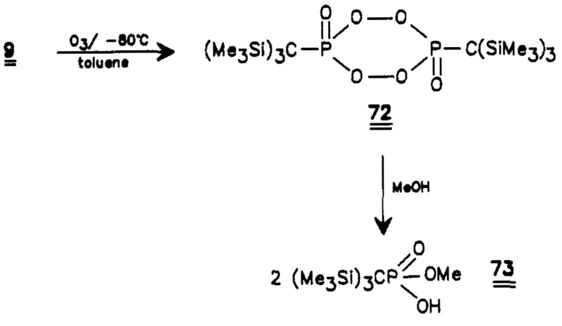
The transient production of diphosphene oxide 67 was also invoked in the reaction of 1 with *m*-chloroperbenzoic acid in CH_2Cl_2 and subsequent treatment of the reaction mixture with ethereal diazomethane. The mixed ester anhydride 71 was obtained in 58% yield[86] (Scheme 36).

Compound 67 was available as a stable product (71%) from the ultrasonic irradiation of a mixture of supermesityl phosphonic dichloride and magnesium at 0 °C[86] (Scheme 37).

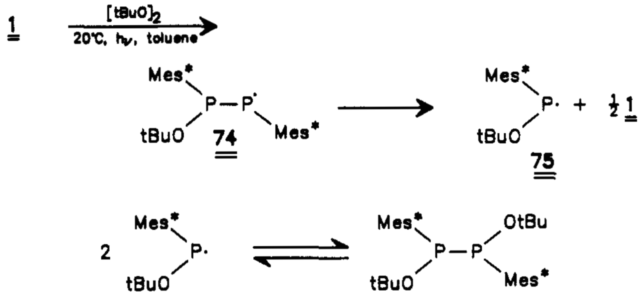
Scheme 38



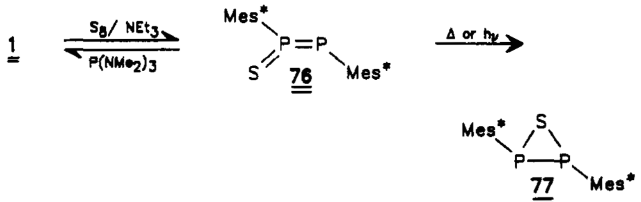
Scheme 39



Scheme 40



Scheme 41



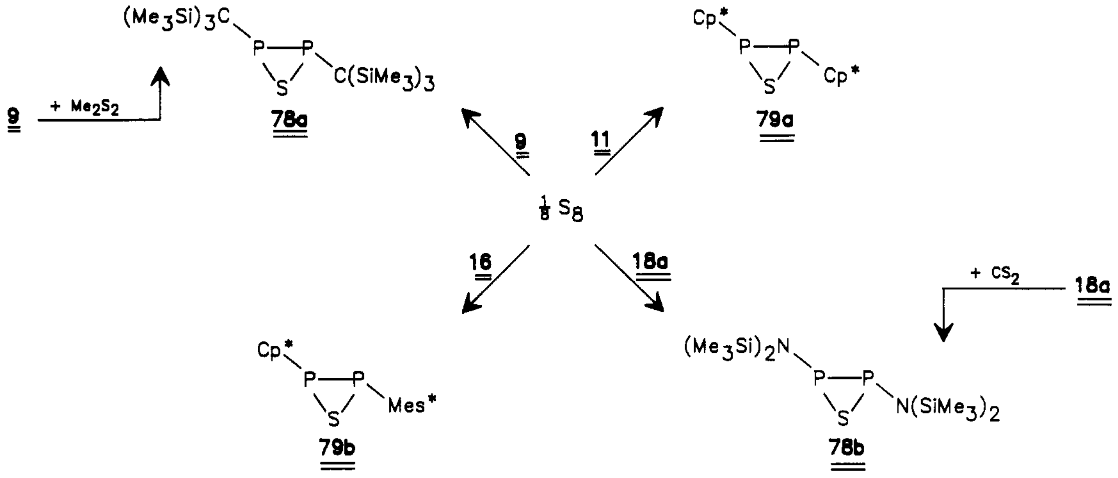
In the ^{31}P NMR spectrum compound 67 exhibited an AB pattern centered at $\delta = 206.5$ (Mes*P=) and 69.8 (Mes*P(O)=) with a large coupling constant $^1J_{PP} = 638.6$ Hz.

Ozonolysis of 1 in CH_2Cl_2 or toluene at −96 °C produced the monomer, dimer, and trimer of Mes*PO_2 (^{31}P NMR control) which reacted with methanol or water to the methyl ester and the acid respectively[87] (Scheme 38).

The ozonolysis of 9 in toluene at −70 °C yielded the cyclic diperoxide 72, characterized by a ^{31}P NMR signal at $\delta = 33$. 72 was solvolyzed by methanol to give the phosphonic ester 73[88] (Scheme 39).

tert-Butoxide radicals, which were photochemically freed from di-*tert*-butyl peroxide, attacked diphosphene 1 with the formation of the phosphorus-based radicals 74 and 75, which were characterized by ESR spectroscopy[74] (Scheme 40).

Scheme 42



2. Reactions with Sulfur and Selenium

Diphosphene 1 was easily transformed into the diphosphene monosulfide 76 by treatment with elemental sulfur in triethylamine (Scheme 41).

The ^{31}P NMR spectrum of 76 comprised an AB signal at δ = 247.8 and 255.8. The large coupling constant $^1J_{PP}$ = 629.9 Hz agrees with the presence of a P=P double bond.[89]

This conclusion was fully confirmed by a single-crystal X-ray structure analysis. The molecule features the situation of an *E*-configurated diphosphene with a P=P double bond of 2.054 (2) Å. The sulfur atom is attached to a trigonal-planarily configurated phosphorus atom via a P=S double bond [1.931 (2) Å]. Desulfurization of 76 was achieved by P(NMe$_2$)$_3$.[89] Heating 76 in boiling toluene or its photoirradation with a mercury lamp led to thiadiphosphirane 77. This species was also accessible by the reduction of Mes*P(S)Cl$_2$ with magnesium metal.[89]

Similarly some unsymmetrically substituted diphosphenes were converted into thiadiphosphiranes via diphosphene monosulfides.[90]

Thiadiphosphiranes **78a,b** and **79a,b** were synthesized from the diphosphenes **9**,[23b] **18a**,[35,91a] **11**,[91b] and **16**[91b] by treatment with elemental sulfur, dimethyl disulfide, or CS$_2$ (Scheme 42).

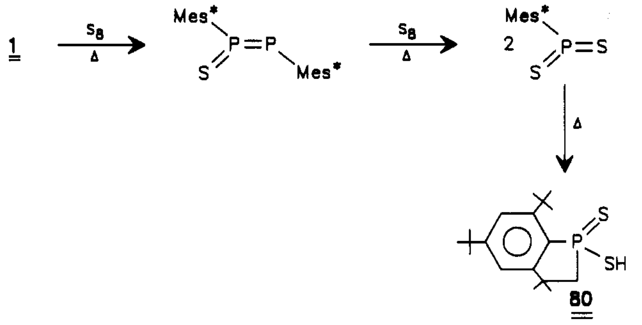
When 1 was reacted with sulfur and DBU in refluxing toluene the P=P bond was broken and the dithiophosphinic acid **80** was obtained. **80** was believed to be the product of a P=S insertion of transient Mes*PS$_2$ into the CH bond of an *o-tert*-butyl group.[92a–c] This assumption was underlined independently by the thermal decomposition of isolated Mes*PS$_2$[92d,e] (Scheme 43).

The synthesis of selenadiphosphiranes **81–83** was achieved by the reaction of the diphosphenes **1**, **6**, or **17** with gray selenium. The formation of **81** was accompanied by the appearance of Mes*P(Se)$_2$. The ^{31}P NMR spectrum of **81** diplayed a singlet at δ^{31}P = −47.4 with a selenium coupling of $^1J(^{31}P^{77}Se)$ = 131.8 Hz.[93] The large P–Se coupling of 854.5 Hz in the ^{31}P NMR spectrum of Mes*P(Se)$_2$ (δ = 273.0) is indicative of P=Se double bonds (Scheme 44).

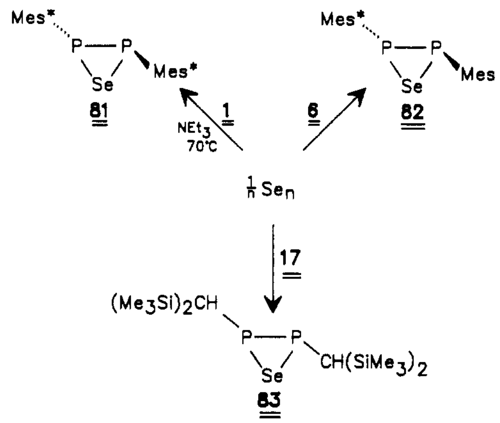
3. Halogenations

The 1,2-dichlorodiphosphane **84** was produced in the reaction of **9** with equimolar amounts of chlorine in CCl$_4$ at ambient temperature. An excess of the halogen furnished the alkyl phosphorus tetrachloride **85**[23b] (Scheme 45).

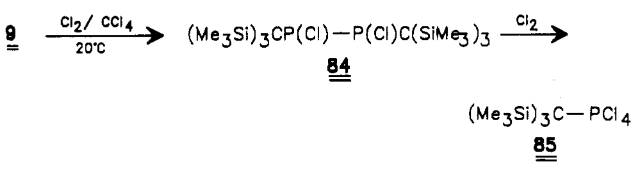
Scheme 43



Scheme 44



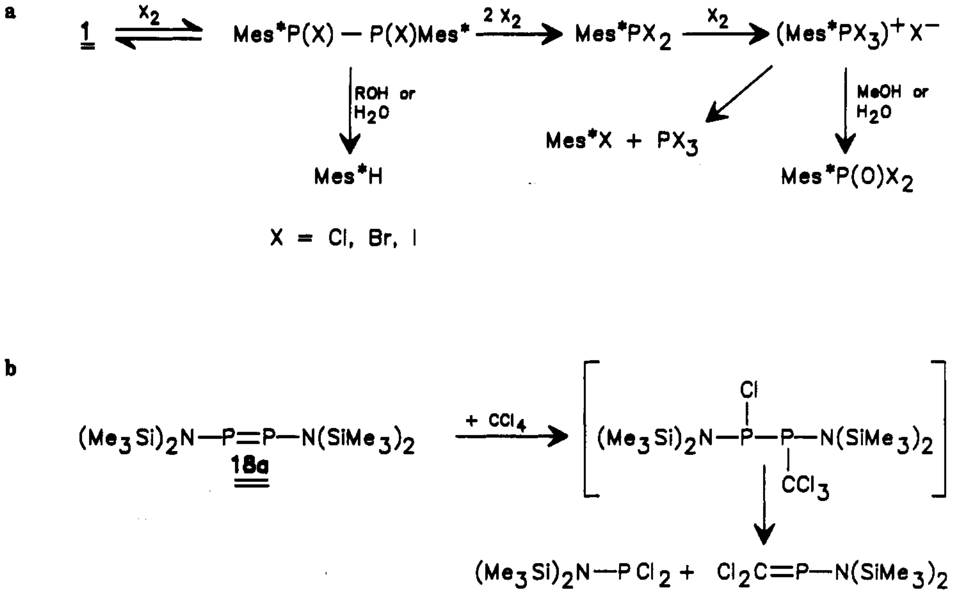
Scheme 45



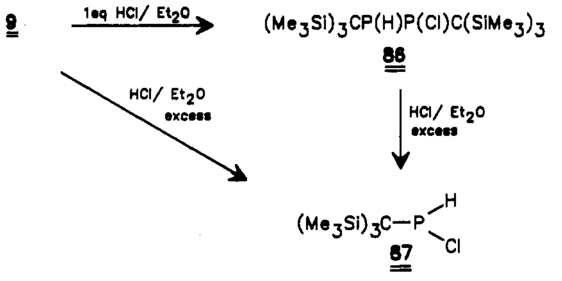
Diphosphene 1 was attacked by various halogens to give products such as phosphinic dihalides, phosphorus trihalides, haloarenes, and supermesitylene dependent upon the nature of the halogen and the reaction conditions. The Scheme 46a gives a rationale for the observed pattern of products.

When diphosphene **18a** was exposed to tetrachloromethane, the rupture of the P–P bond occurred with

Scheme 46



Scheme 47



formation of bis[(trimethylsilyl)amino](dichloromethylene)phosphane and bis[(trimethylsilyl)amino]dichlorophosphane.[91a] A 1-chloro-2-(trichloromethyl)diphosphane was suggested as a possible intermediate in this transformation (Scheme 46b).

4. Reactions with Protic Reagents

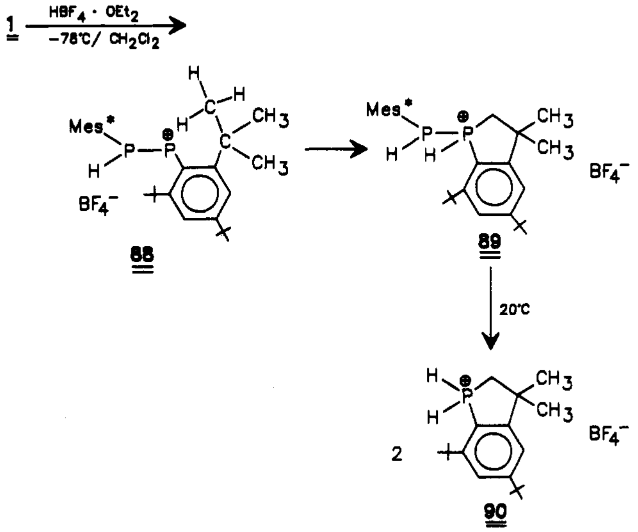
An equimolar amount of hydrogen chloride was cleanly added to diphosphene **9** with the result being a diastereomeric mixture of chlorodiphosphanes **86**[23b,92b,c] (Scheme 47).

9 and **86** suffered from cleavage of the P–P bond when an excess of ethereal HCl was employed in the reaction. Compound **87** is a representative of the rare class of organochlorophosphanes RP(H)Cl.[23b,92b] The P=P double bond of **9** was also cleaved by an excess of ethereal HBF_4 in CH_2Cl_2 solution at −78 °C. Phosphonium salt $[(Me_3Si)_3CPH_3]^+BF_4^-$ was the sole product. The protonation of **1** by an excess of $HBF_4{\cdot}OEt_2$ at −78 °C took a different course. The intermediate phosphenium ion **88** underwent an intramolecular CH insertion to yield cation **89**, which eventually decomposed at room temperature to give the cyclic phosphonium ion **90**[92b] (Scheme 48).

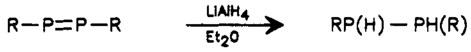
B. Reactions with Nucleophiles

1. Hydrogenations

Scheme 48



Scheme 49



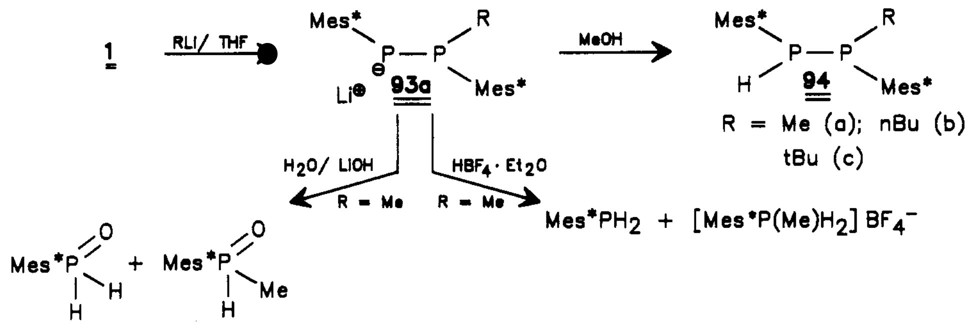
	9,91	**17,92**
R	$(Me_3Si)_3C$	$(Me_3Si)_2CH$

The one-electron reduction of **1** and **9** by sodium naphthalenide[73,74] or alternatively in electrochemical experiments has already been mentioned.[73,74] The synthesis of **1** from Mes^*PCl_2 and an excess of magnesium in THF was accompanied by a considerable amount of the diphosphane Mes*P(H)P(H)Mes*, which might result from the reduction of **1** with subsequent proton abstraction.[22] A clean reduction of **1** to give a mixture of *dl*- and *meso*-diphosphanes was accomplished by treatment with $LiAlH_4$[95] or $K[sBu_3BH]$.[92b,96] $LiAlH_4$ reduction of the diphosphenes **9** and **17** also led to diastereomeric mixtures of the corresponding diphosphanes **91**[23b] and **92**[45c] (Scheme 49).

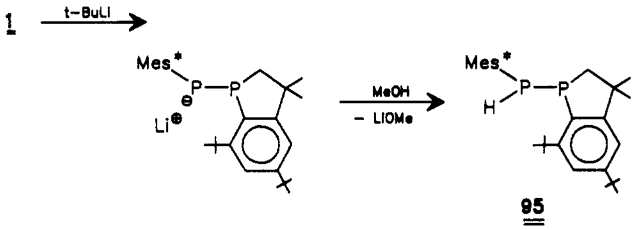
2. Reactions with Lithium Alkyls

Independently Cowley[92b,96] and Yoshifuji[97] reported on the nucleophilic addition of lithium alkyls to **1** and the subsequent quench of the obtained anions by protons or alkyl halides (Scheme 50).

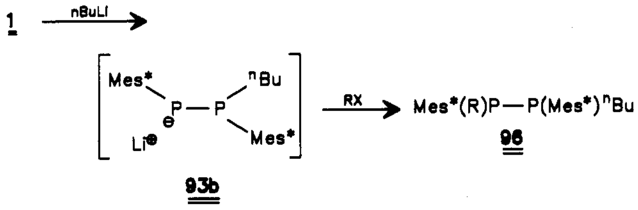
Scheme 50



Scheme 51



Scheme 52



R = Me, Et, nPr, nBu, nOct, $PhCH_2$, $PhCH_2CH_2$, $tBuCH_2$

While treatment of the anions **93a–c** with methanol afforded the diphosphanes **94a–c**, the P–P bond in **93a** (R = Me) was cleaved by hydrolysis to $Mes^*P(O)H_2$ and $Mes^*P(O)(H)Me$, or alternatively by ethereal HBF_4 to produce Mes^*PH_2 and $[MesP(Me)H_2]^+BF_4^-$. In the reaction of **1** with tBuLi the phosphaindan derivative **95** was detected as a byproduct (Scheme 51). Obviously one of the *o-tert*-butyl groups at the aryl ring was deprotonated prior to the nucleophilic attack at the adjacent phosphorus center.

Anion **93b** was shown to be an appropriate candidate to alkylation by alkyl halides with generation of unsymmetrical diphosphanes **96**[97] (Scheme 52).

The reaction of Cp*P=PMes* (**16**) with lithium phosphides provided a novel synthetic pathway to triphosphaallyl systems. The lithium salts **97a** and **97b** could not be isolated from the reaction mixture (Scheme 53) but were successfully quenched by water or methyl iodide to give the diphosphenes **98** and **99**.[98] An alternative approach to the triphosphaallyl system made use of methyl lithium instead of lithium supermesityl phosphide[91b] (Scheme 54).

Here the transient generation of the dianion $[Mes^*P]^{2-}$ was invoked, which eventually was trapped by the diphosphene **16** to yield the allylic system. With a stoichiometry of **16**/MeLi = 2:3 a nearly quantitative transformation of **16** to PMe_3, **97a**, and **97b** was observed. From a hexane solution violet-black crystals of the triphosphaallyl product were isolated. Their extreme sensitivity toward moisture, however, thwarted a structure analysis. Even under an inert atmosphere they spontaneously were protonated to the orange-colored solid compound **98**. Deprotonation of **98** with 1 equiv of butyllithium led to the mixture of **97a** and **97b** again.

The diphosphide Me_2P–PMes*Li, which was postulated as an intermediate, could be observed spectroscopically when equimolar amounts of **16** and methyllithium were employed in the reaction.

C. Cycloadditions

Like the carbon–carbon double bond in olefins the P=P double bond in diphosphenes is an appropriate candidate for a series of different cycloadditions.

1. [2 + 1] Cycloadditions

The addition of carbenes to the P=P functionality opened a new entry into the class of stable diphosphiranes. Useful precursors for the carbene moiety are diazoalkanes. In a formal sense this type of reaction may be envisaged as a [2 + 1] cycloaddition. However, it cannot be excluded that this transformation proceeded via an initial [2 + 3] dipolar cycloaddition, which is followed by a rapid N_2 extrusion. Usually the [2 + 3] cycloadducts cannot be detected. The first diazoalkane addition to a diphosphene was reported by Niecke et al.[99,91a] (Scheme 55).

Diphosphene **1** was converted by diazomethane (0 °C, 48 h) to a mixture of diphosphirane **101a** (80%) and phosphaalkene **102a** (10%)[100a,b] (Scheme 56).

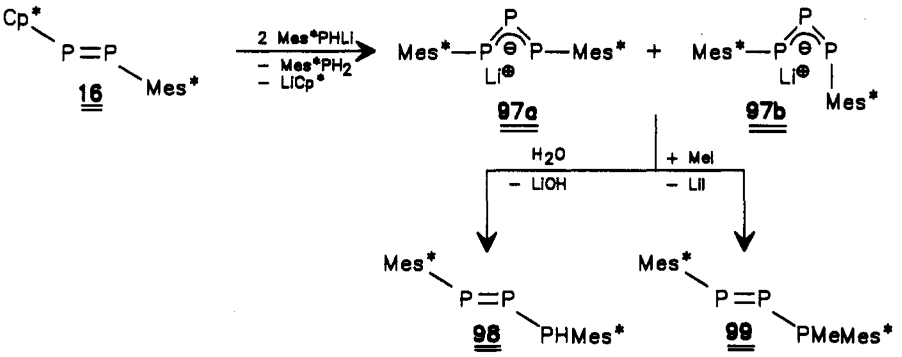
Diphenyldiazomethane Ph_2CN_2 is less reactive than CH_2N_2 and demanded a reaction temperature of 65 °C to give 80% of the diphosphirane **101b** and 20% of the phosphaalkene **102b**. Here the intermediate $\lambda^5\sigma^3$ phosphorane $Mes^*P^A{=}P^B(Mes^*){=}CPh_2$ was evidenced by ^{31}P NMR ($\delta(P_A) = 208.4$; $\delta(P_B) = 66.7$; $^1J_{PP} = 676$ Hz). The formation of ring **101c** from **1** and 9-diazofluorene was achieved photochemically.[100b]

The cyclopentadienyl-functionalized diphosphenes **11** and **16** were also prone to cyclopropanation by diazoalkanes[91b] (Scheme 57).

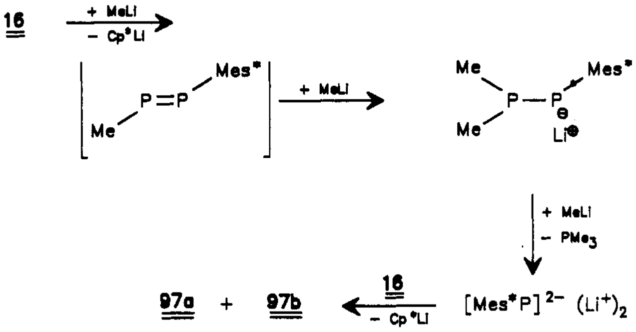
During the formation of **104c** the ^{31}P NMR spectra of the reaction mixture (Et_2O, −20 °C) showed two doublets at $\delta = 45$ and 68 ppm ($^1J_{PP} = 300$ Hz), which were tentatively assigned to a transient [2 + 3] cycloadduct.

A different approach to diphosphiranes, developed in the research groups of Koenig and Yoshifuji, made use of the stereoselective [2 + 1] cycloaddition of halogenated carbenes to the P=P bond of a number of diphosphenes (Scheme 58). The halocarbenes were generated by the reaction of KOtBu or nBuLi with an

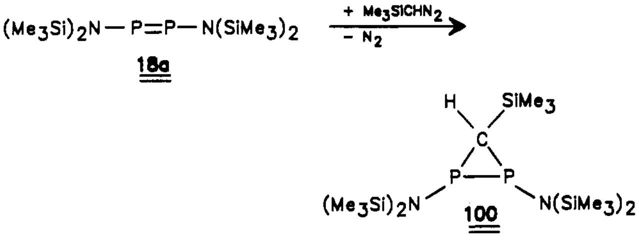
Scheme 53



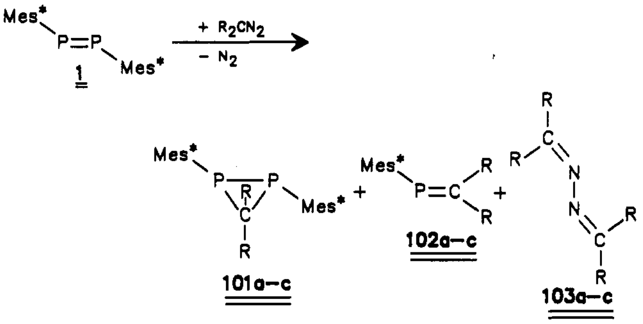
Scheme 54

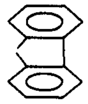


Scheme 55



Scheme 56

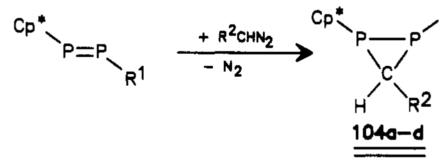


101–103	R_2
a	H, H
b	Ph, Ph
c	

excess of the corresponding haloform or alternatively from tetrahalomethanes and nBuLi at low temperatures.

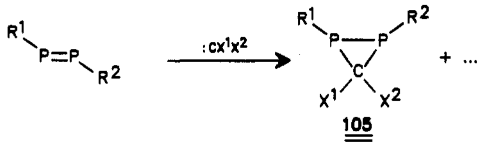
The reaction of the functionalized diphosphiranes **105** with organolithium compounds, Lewis acids as well as thermolysis or photolysis invariably led to ring

Scheme 57



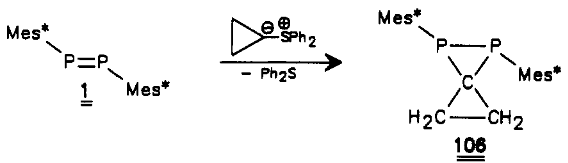
104	R^1	R^2
a	Cp*	H
b	Mes*	H
c	Cp*	Me_3Si
d	Mes*	Me_3Si

Scheme 58



105	R^1	R^2	X^1	X^2	Ref.
a	Mes*	Mes*	Cl	Cl	101, 102a,c
b	Mes*	Mes*	Br	Br	101, 102a,c
c	Mes*	Mes*	Ph	Br	102d
d	Mes*	Mes*	Ph	Cl	102c,d
e	Mes*	Mes*	Me	Cl	102c,d
f	$C(SiMe_3)_3$	Mes*	Cl	Cl	102b
g	$C(SiMe_3)_3$	Mes*	Br	Br	102b
h	Mes*	2,4,6-$tPn_3C_6H_2$	Cl	Cl	20a,b
i	2,4,6-$tPn_3C_6H_2$	2,4,6-$tPn_3C_6H_2$	Cl	Cl	20a,b
j	2,6-$tBu_2C_6H_3$	2,6-$tBu_2C_6H_3$	Cl	Cl	20a,c

Scheme 59

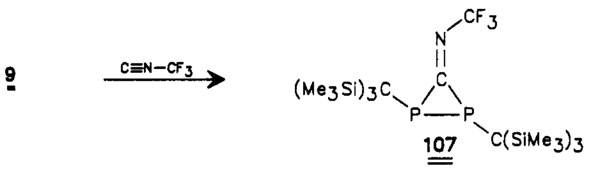


opening products such as 1,3-diphosphaallenes, 1,3-diphosphapropenes, and others.[20,101,102]

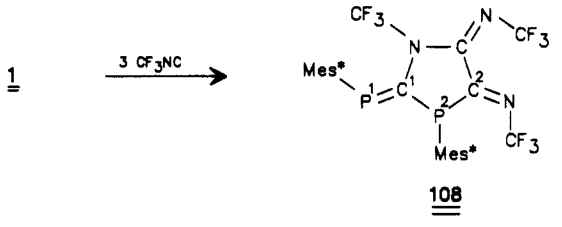
Sulfur Ylides. According to a method first devised by Weber,[103] Koenig et al. succeeded in the transformation of the diphosphene **1** into the 1,2-diphosphaspiro[2.2]pentane **106**.[102a] Diphenylsulfoniocyclopropanide served as the alkylidene transfer reagent (Scheme 59).

Isocyanides. A [2 + 1] cycloaddition was encountered in the reaction of equimolar amounts of diphosphene **9** and trifluoromethyl isocyanide.[104] This synthetic

Scheme 60



Scheme 61



pathway complements the [2 + 1] cyclocondensation approach earlier devised by Baudler et al. to the rare class of imino diphosphiranes[105] (Scheme 60).

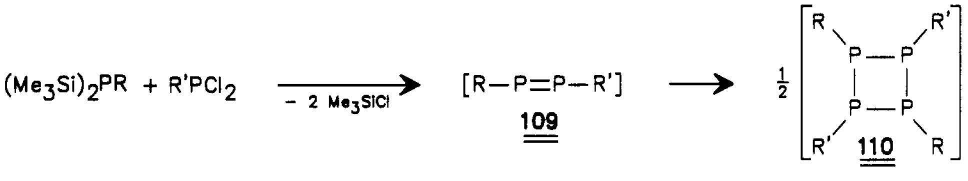
A different situation was met when diphosphene 1 was allowed to react with CF_3NC under similar conditions. The structure of product 108 was elucidated by X-ray crystallography, and it was ascertained that 108 was generated from three molecules of the isocyanide and one molecule of 1[104] (Scheme 61). The phosphorus carbon distances [1.683 (P1–C1), 1.842 (C1–P2), and 1.797 (P2–C2) Å] were in accord with a double bond and two single bonds, respectively.

2. [2 + 2] Cycloadditions

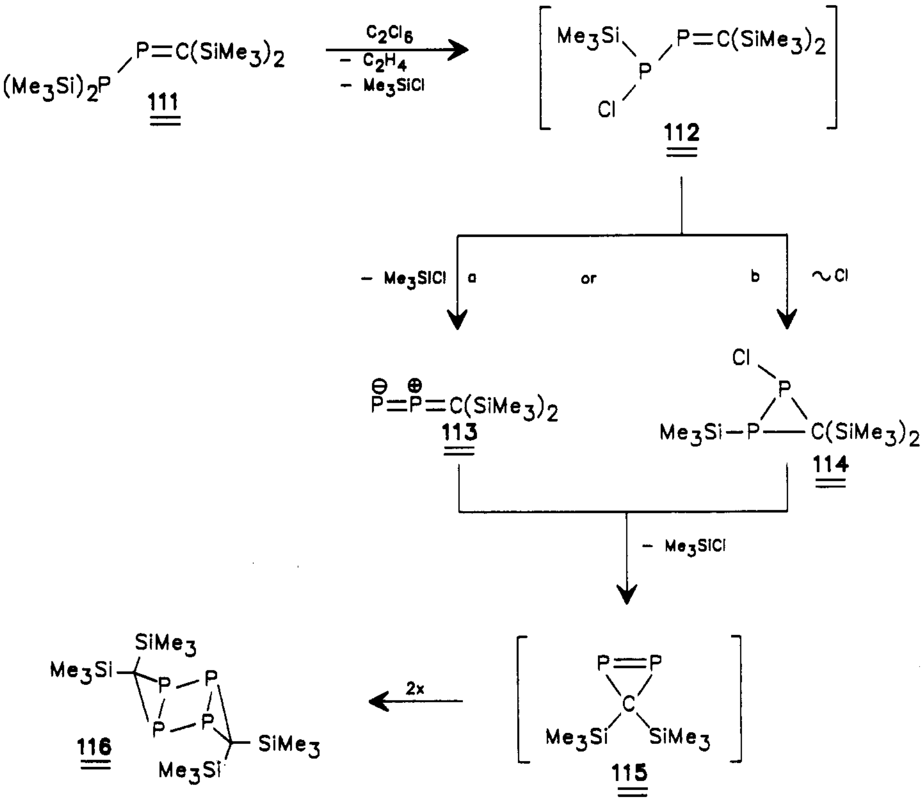
Cyclodimerizations. Diphosphenes which are not sufficiently protected by their substituents often undergo [2 + 2] self-dimerization to afford all-trans substituted cyclotetraphosphanes (Scheme 62).

The pronounced reactivity of 109[45c] and 115[106] precluded their observation by ^{31}P NMR techniques. The generation of the cyclotetraphosphanes **118a,b** from *tert*-butylbis(trimethylsilyl)phosphane and the respective aminodichlorophosphanes involved a [2 + 2] head-to-tail cyclodimerization of the transient diphosphenes 117. 117a could be detected by ^{31}P NMR (δ = 515 d, 585 d, $^1J_{PP}$ = 638 Hz) before it suffered from dimerization[50b] (Scheme 63).

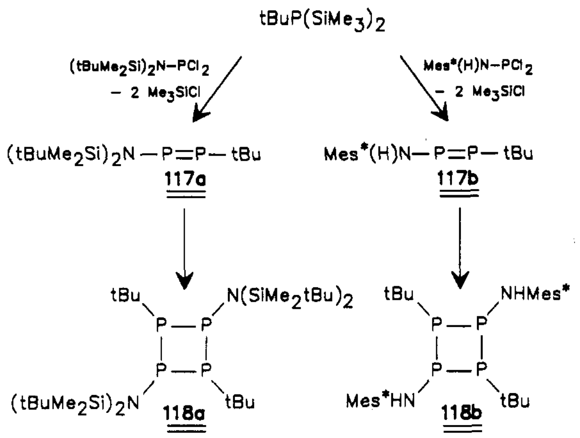
Scheme 62



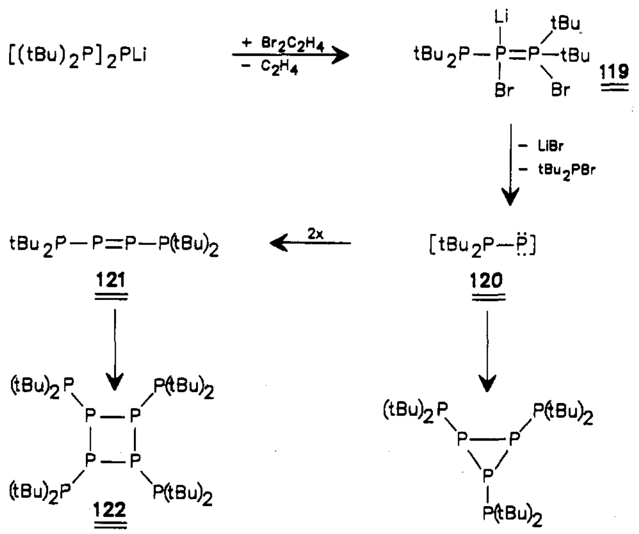
109, 110	R	R'
a	tBu	tBu
b	tBu	Mes



Scheme 63



Scheme 64

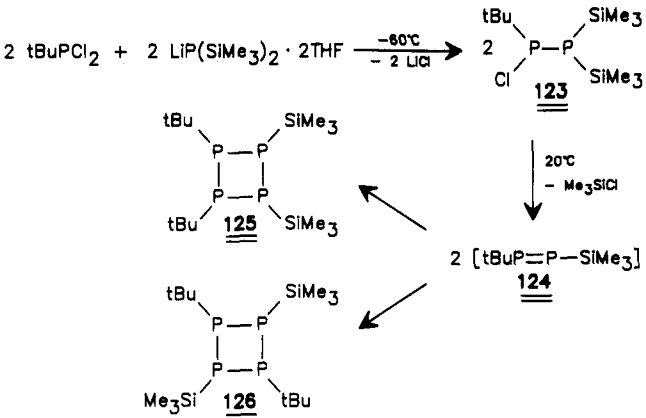


Fritz et al. described the synthesis of cyclotetraphosphanes **122** (in addition to cyclotriphosphanes) which might result from a sequence of dimerization processes of the phosphinidene moiety **120**. This species was freed from the phosphinidene phosphorane precursor **119** (Scheme 64). The transient nature of **120** and **121** was confirmed by trapping experiments.[107] Equimolar amounts of $tBuPCl_2$ and $LiP(SiMe_3)_2$ interacted at –60 °C to give the diphosphane **123**. Warming up the reaction mixture to ambient temperature led to the production of the reactive diphosphene **124**, which eventually experienced head-to-head and head-to-tail cyclodimerizations to give the cyclotetraphosphanes **125** and **126**[108] (Scheme 65).

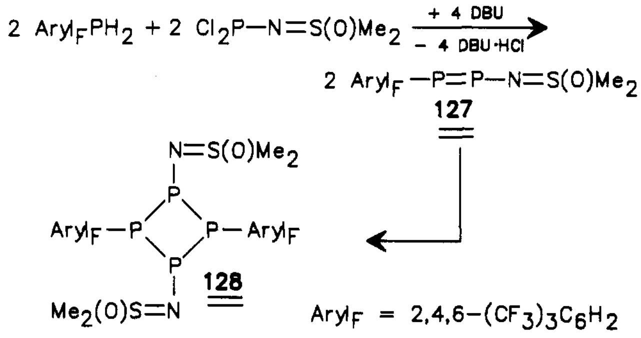
Again the intermediacy of diphosphene **124** was made plausible by trapping experiments. The thermolabile diphosphene **127** was produced during the condensation of $Aryl_FPH_2$ and an imino-substituted dichlorophosphane at –78 °C. At this temperature the double-bond system was successfully coordinated to a platinum complex. However, in the absence of trapping reagents dimerization to cyclotetraphosphane **128** occurred[31] (Scheme 66).

The magnesium reduction of a pyrrolyl dichlorophosphane afforded cyclotetraphosphane **130** via diphosphene **129**, which gave rise to a signal at $\delta = 454$ in the ^{31}P NMR spectrum of the reaction mixture[109] (Scheme 67).

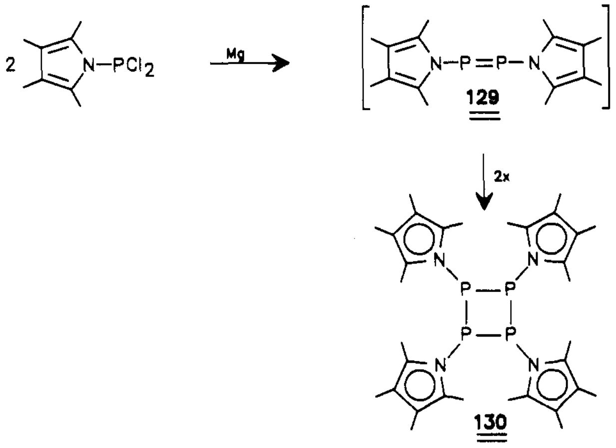
Scheme 65



Scheme 66



Scheme 67



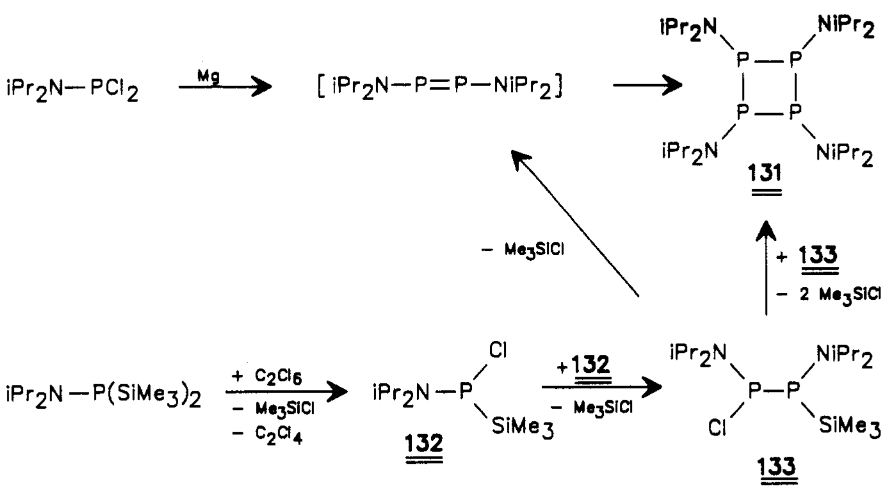
Similarly the synthesis of cyclotetraphosphane **131** may proceed via the transient diphosphene $iPr_2NP{=}PNiPr_2$.[110,111] Here, however, other mechanisms for the generation of the ring compound are also reasonable (Scheme 68).

Some isolable diphosphenes slowly cyclodimerized upon standing at room temperature. In the case of **17** the half-life time of this process was estimated to 1 week[34] (Scheme 69).

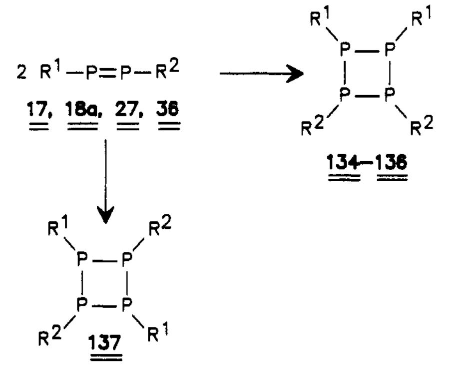
In some cases the dimerization of *Z*-configurated diphosphenes **24** was followed by cycloreversion and the subsequent cyclodimerization of the amino-substituted diphosphene fragment to yield cyclotetraphosphane **138** and diphosphene **1**[39] (Scheme 70).

Like the *Z*-configurated diphosphenes **24** the diphosphene **25b** slowly decomposed in solution at room temperature to the symmetrical diphosphenes **1** and $(Me_3Si)_3N_2P{=}PN_2(SiMe_3)_3$ (**140**). An explanation for

Scheme 68



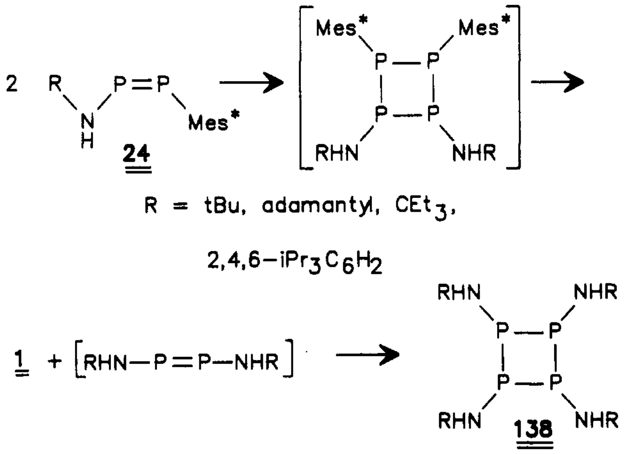
Scheme 69



R^1 = $P(NiPr_2)_2$ [44]
R^2 = $N(iPr_2)_2$

	R^1	R^2	Ref
17, 134	$CH(SiMe_3)_2$	$CH(SiMe_3)_2$	34
18a, 135	$N(SiMe_3)_2$	$N(SiMe_3)_2$	35
27, 136	Mes*	$SiPh_3$	41

Scheme 70

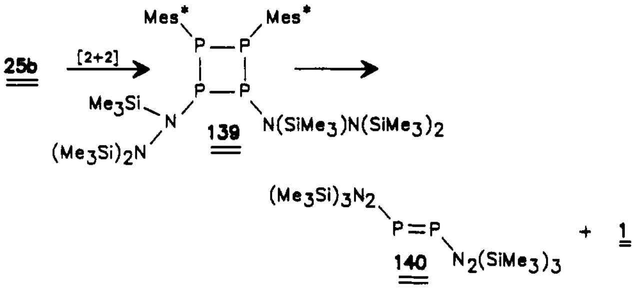


R = tBu, adamantyl, CEt_3, 2,4,6-$iPr_3C_6H_2$

this result invoked the transient appearance of the kinetically labile cyclotetraphosphane 139[40b,112] (Scheme 71).

An intramolecular electrocyclization process of the reactive 1,2,3-triphosphabutadienes **141a,b** was made responsible for the appearance of the bicyclic systems **142a,b** (Scheme 72).

Scheme 71



The P═P bond of **141a** was easily inserted into a P–C linkage of **142a** to give the bicyclic compound **143**. The insertion of reactive diphosphane into three-membered rings finds a precedence in the ring enlargement of silirane **144** to the 1,2,3-siladiphospholane **145**[45c] (Scheme 73).

The photochemically induced cyclodimerization of **11** to **146** was followed by the extrusion to two cyclopentadienyl fragments and the generation of bicyclotetraphosphane **147**. Under prolonged irradiation **147** degradated to white phosphorus[115] (Scheme 74).

Ether solutions of diphosphene **29b** decomposed upon standing for 5 days at −20 °C to give the bicyclotetraphosphane **148**[41] (Scheme 75).

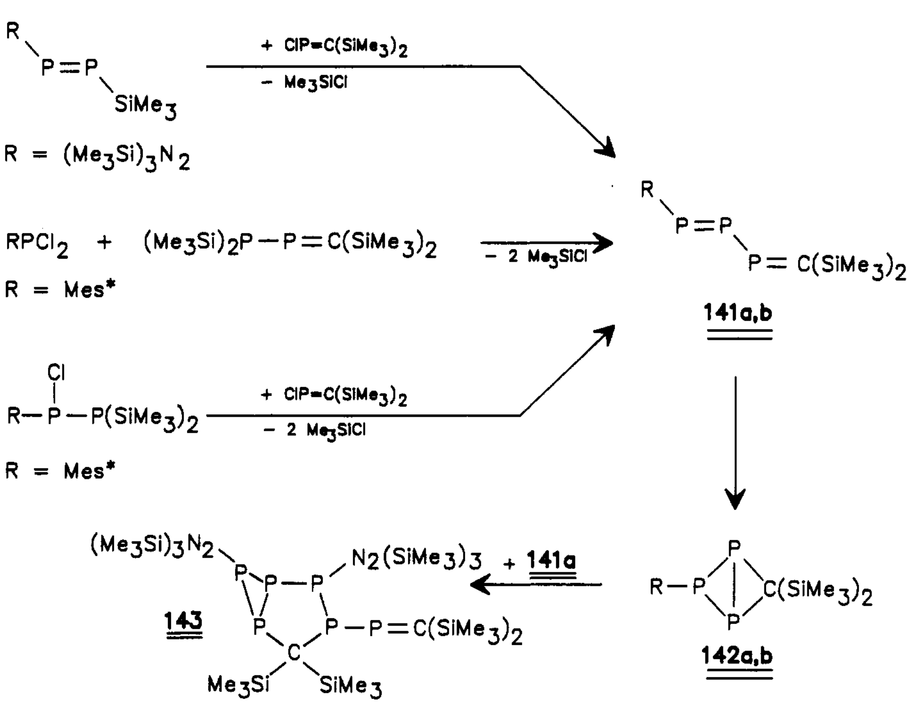
3. [2 + 3] Cycloadditions

Reactions with Azides. Diphosphene **18a** and the organic azides **149a–c** underwent a 1,3-dipolar cycloaddition to furnish the 1*H*-1,2,3-triaza-4,5-diphosphol-2-ene derivatives **150a–c**. The thermolability of **150a–c** precluded their isolation and confined their characterization to ^{31}P NMR evidence. Above ambient temperature the triazadiphospholenes decomposed to give the aminoiminophosphanes **151a–c** as the only nonpolymeric products. In the reaction with Me_3SiN_3 the diphosphene imide **152** was detected as an intermediate by ^{31}P NMR (δ = 62 d, 171 d, $^1J_{PP}$ = 881 Hz) (Scheme 76). The isolation of this compound failed.[91a,99]

4. [2 + 4] Cycloadditions

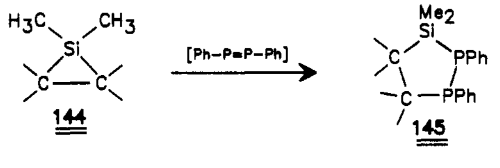
The close relationship of phosphorus and carbon chemistry is especially obvious in [2 + 4] cycloadditions of diphosphenes to 1,3-dienes, which parallel the

Scheme 72

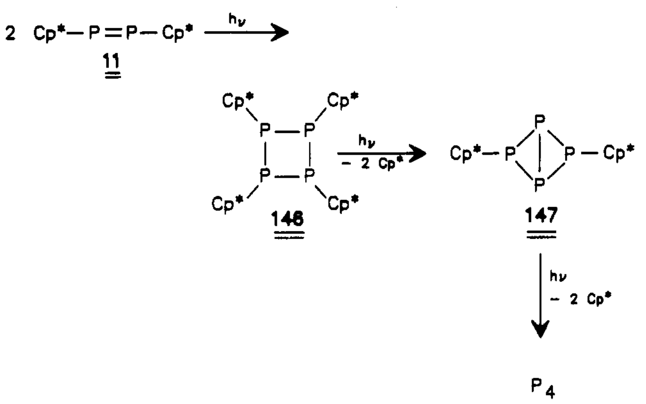


141, 142	R	Ref.
a	$(Me_3Si)_3N_2$	113
b	Mes*	114

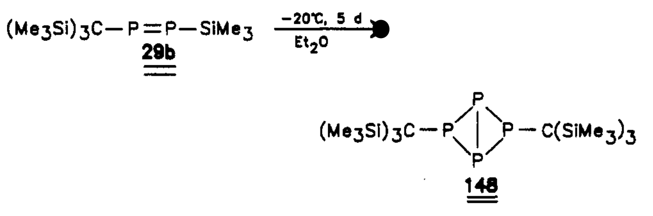
Scheme 73



Scheme 74



Scheme 75



prominent Diels–Alder reaction. This kind of transformation constituted a valuable tool for the interception of transient and highly reactive diphosphenes. Thus the intermediate appearance of diphosphenes such as tBuP=PtBu and tBuP=PMes was unambigiously demonstrated by the formation of the [2 + 4] cycloadducts 153 and 154[116] (Scheme 77).

The retro-Diels–Alder decomposition of 154 should liberate the diphosphene tBuP=PtBu. Thus heating 154 in the presence of 2,3-dimethylbuta-1,3-diene afforded 153a in good yields.[45b] The reactive diphosphene PhP=PPh, obtained from $Ph(H)PGeCl_3$ and DBU, was also efficiently trapped by 2,3-dimethylbuta-1,3-diene to give 153c[45b] (Scheme 78).

Analogously diphosphene $tBuP{=}PSiMe_3$ (124) could be transformed into 155 by treatment with the butadiene[108] (Scheme 79).

The reactive diphosphenes 156a,b were also intercepted via [2 + 4] cycloadditions[117] (Scheme 80).

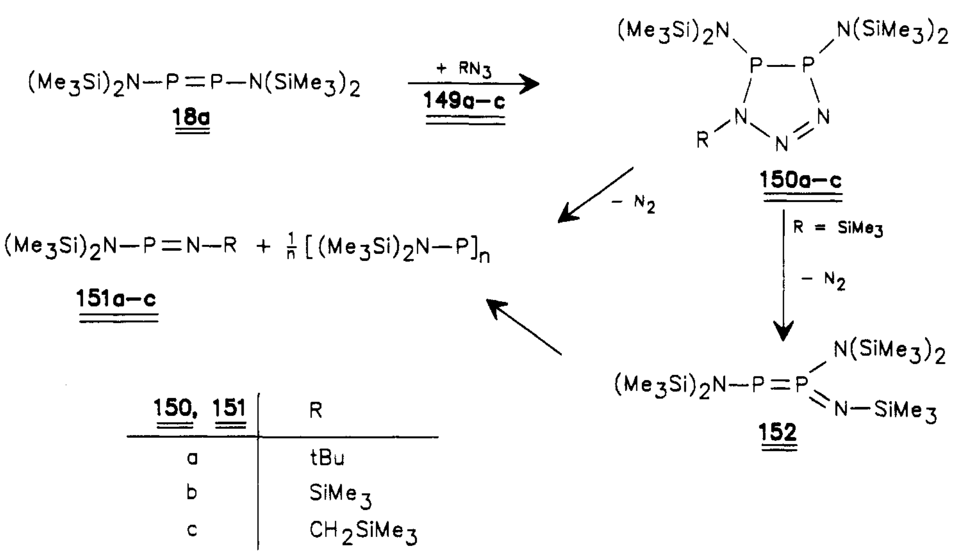
Grobe et al. have developed an elegant method for the production of instable CF_3-substituted diphosphenes, and again their evidence was based on [2 + 4] cycloaddition processes.

The symmetrical diphosphene 158 resulted from the dehalogenation of CF_3PI_2 by $SnCl_2$[118a] (Scheme 81). This transformation was found to be reversible and allowed the transfer of the diphosphene from one cycloadduct to another. Thus compound 160 is useful as a source of the reactive diphosphene 158 (Scheme 82).

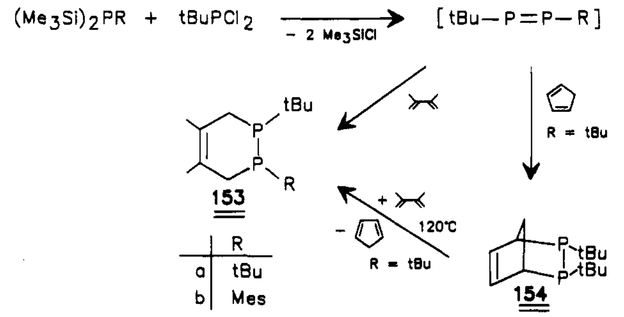
Unsymmetrical diphosphenes were available from distannylphosphanes 162 and (dimethylthio)phosphane 163. The thiophilicity of tin was assumed to be the driving force of this transformation. The in situ generated diphosphenes were trapped by various 1,3-dienes[118b] (Scheme 83). The influence of the groups R and R′ as well as that of the dienes upon this [2 + 4] cycloaddition has been discussed.

Diphosphenes with medium-sized substituents such as 17[35] and 18a[36,99] are also prone to [2 + 4] cycload-

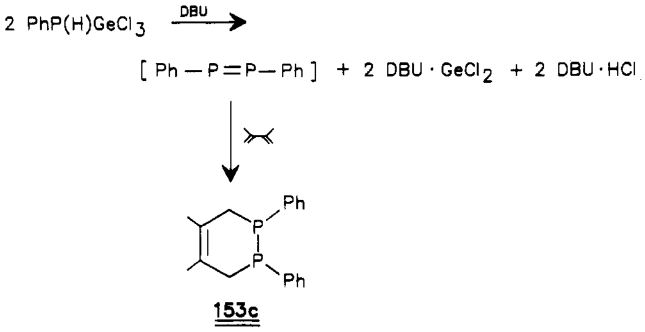
Scheme 76



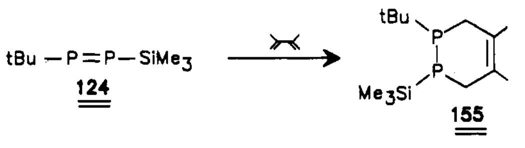
Scheme 77



Scheme 78



Scheme 79



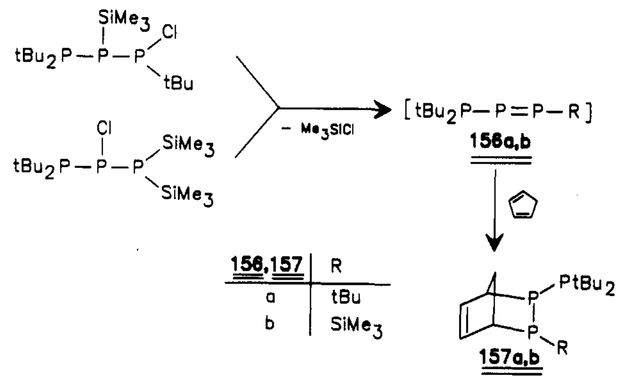
ditions with dienes (Scheme 84). Adduct **168** readily decomposes above 40 °C into its components and is thus useful as a storable source of diphosphene **18a**.

V. Transition Metal Diphosphene Complexes

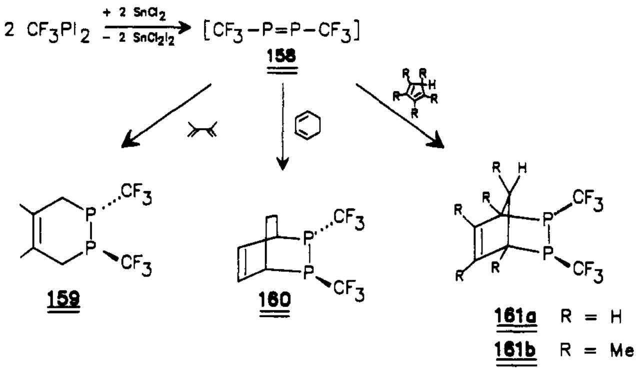
A. Coordination Modes of Diphosphenes

The rapid development of the chemistry of diphosphenes has also included the study of their ligand properties in transition metal complexes. Here at least seven modes of coordination of acyclic diphosphene ligands (A–G) are encountered to date[13] (Scheme 85).

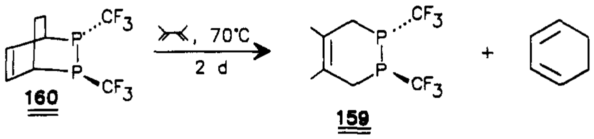
Scheme 80



Scheme 81



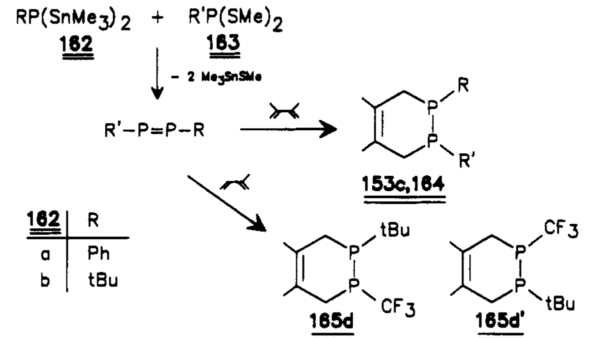
Scheme 82



π-Complexes of ring compounds with P–P fragments are not discussed here.

In compounds of type A the diphosphene acts as an η^1-ligand toward the metal center. Theoretical calculations on the model compound $(\eta^1\text{-}P_2H_2)Cr(CO)_5$ revealed that a realistic description of the ligand–metal interaction invokes a delocalized σ-donation from the HOMO of the ligand (the n_+ lone pair combination) and π-back-donation of a filled metal orbital into the

Scheme 83

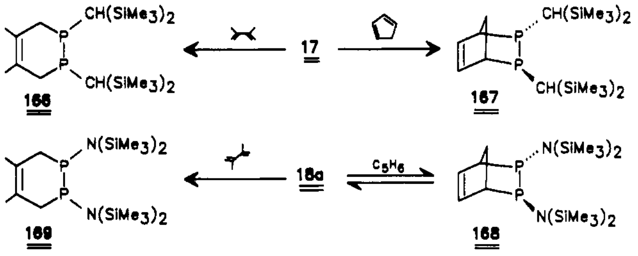


162	R
a	Ph
b	tBu

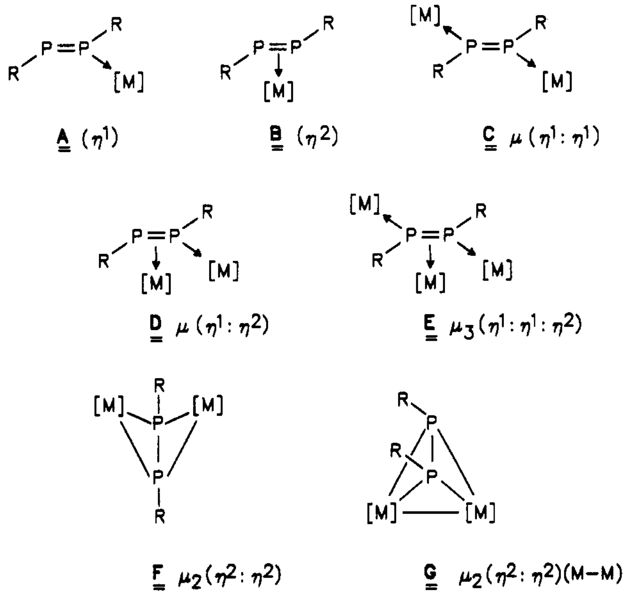
163	R'
a	CF_3
b	Me
c	tBu
d	Ph

164	R	R'
a	Ph	CF_3
b	Ph	Me
c	Ph	tBu
d	tBu	CF_3

Scheme 84

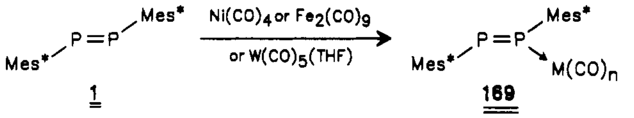


Scheme 85



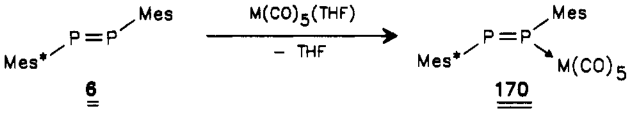
empty LUMO (the π^* orbital) of the ligand. The extent of the back-donation is quite large and comprises 0.30 electrons.[119] Formula B emphasizes a η^2-interaction of the P=P π-system with the metal atom. Like in olefin complexes donation from the filled π-orbital to an empty metal orbital transfers electron density from the ligand to the metal. π-Back-donation operates between filled metal orbitals and the LUMO (π^*) orbital of the diphosphene. In the coordination modes C–E a diphosphene is bridging two independant metal complex fragments. In C this is achieved by two η^1-interactions, whereas in types D and E a combination of η^1- and η^2-coordination is present. Formula F depicts a diphosphene incorporated in a butterfly molecule, whereas G is a representive of a cluster compound with a diphosphene building block. Other types of complexes with such a bonding situation are conceivable.

Scheme 86



169	$M(CO)_n$	Ref.
a	$Ni(CO)_3$	120
b	$Fe(CO)_4$	120
c	$W(CO)_5$	121

Scheme 87



170	a	b	c
M	Cr	Mo	W

Two main synthetic pathways lead to diphosphene complexes: At first a diphosphene ligand can be added to a coordinatively unsaturated complex or may replace labile ligands in suitable coordination compounds. Secondly the diphosphene ligand may be constructed from easily available and stable precursors in the coordination sphere of an organometallic complex. This method implies that the stability of the free diphosphene is not a prerequisite for its existence as a ligand in stable complexes.

The following section is organized by the respective coordination mode rather than by the method of preparation.

1. η^1-Diphosphene Complexes

Complexes with terminal diphosphene ligands, which are end-on bonded to the metal center via the lone pair of one phosphorus atom are often products of ligand displacement reactions. Thus the treatment of Mes*P=PMes* with $Ni(CO)_4$, $Fe_2(CO)_9$, and $W(CO)_5$-THF afforded species of the type under discussion (Scheme 86). The end-on coordination of a $Cr(CO)_5$ moiety to this diphosphene failed presumeably for steric reasons.

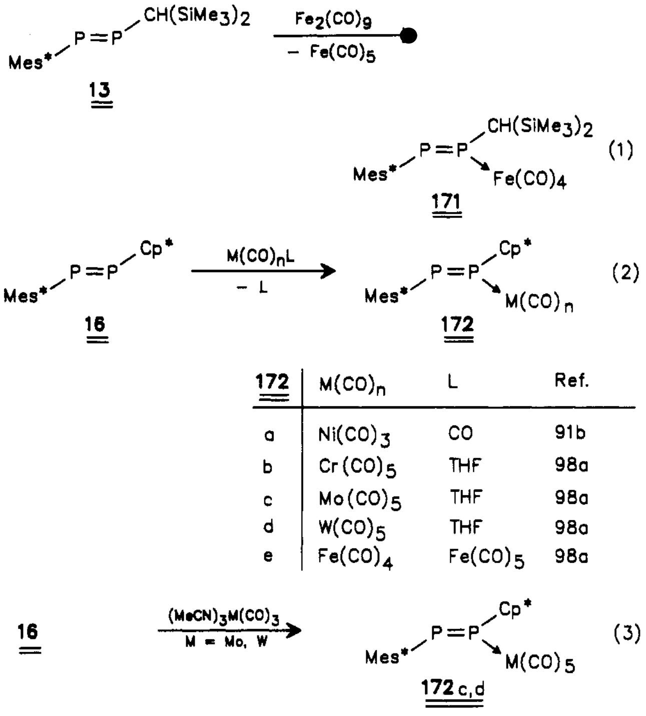
Consistently the treatment of the unsymmetrically substituted diphosphene Mes*P=PMes (**6**) with $M(CO)_5(THF)$ (M = Cr, Mo, W) leads to complexes with the metal carbonyl group at the less hindered phosphorus atom[61,121] (Scheme 87). The same is reflected in the transformations of Scheme 88.[120]

Attempts to prepare a $M(CO)_5$ complex of **6** with the metal at the more hindered phosphorus atom failed. Instead the rearranged products **170** and **173** with the metal at the sterically less congested site of the ligands were obtained[121a] (Scheme 89).

The interesting equilibrium **174a** ⇌ **174b**, which implies the migration of the $Ni(CO)_3$ group between the two phosphorus was observed by ^{31}P NMR spectroscopy (Scheme 90).

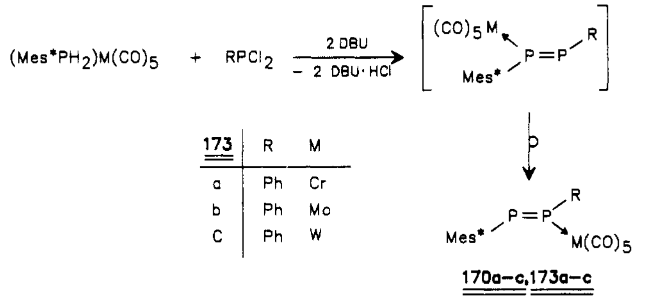
The fluoroaryl-substituted diphosphenes **14** and **41** obviously do not suffer from such the severe steric

Scheme 88



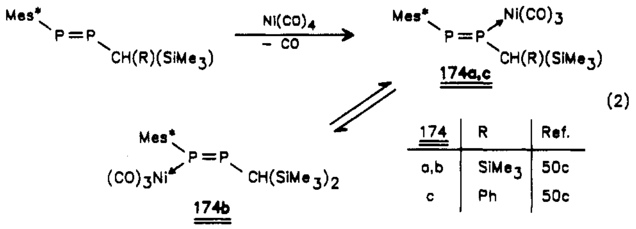
172	M(CO)$_n$	L	Ref.
a	Ni(CO)$_3$	CO	91b
b	Cr(CO)$_5$	THF	98a
c	Mo(CO)$_5$	THF	98a
d	W(CO)$_5$	THF	98a
e	Fe(CO)$_4$	Fe(CO)$_5$	98a

Scheme 89



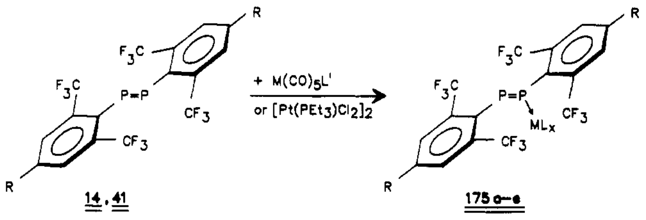
173	R	M
a	Ph	Cr
b	Ph	Mo
c	Ph	W

Scheme 90



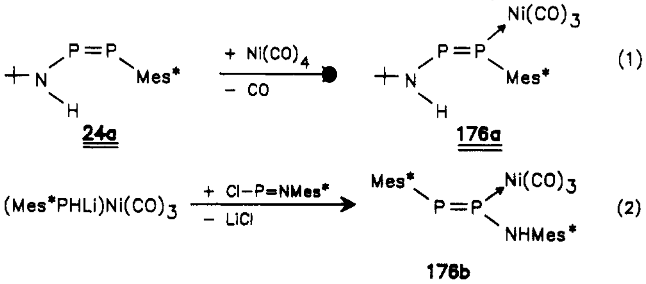
174	R	Ref.
a,b	SiMe$_3$	50c
c	Ph	50c

Scheme 91

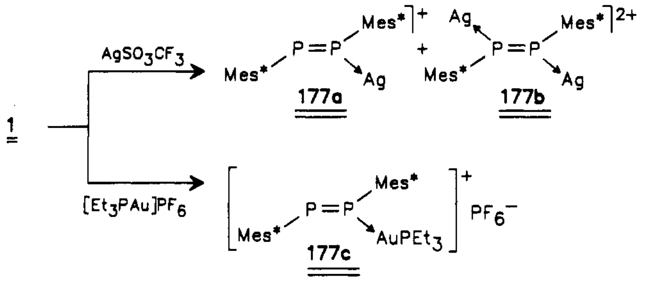


175	R	ML$_x$	L	Lit
a	H	Cr(CO)$_5$	C$_8$H$_{14}$	122a
b	CF$_3$	Cr(CO)$_5$	C$_8$H$_{14}$	122a
c	CF$_3$	Mo(CO)$_5$	CO	122b
d	CF$_3$	W(CO)$_5$	CO	122b
e	CF$_3$	Pt(PEt$_3$)Cl$_2$	—	122b

Scheme 92



Scheme 93



restrictions like 1 does[122] (Scheme 91). The reaction of the *Z*-configurated diphosphene **24a** with Ni(CO)$_4$ afforded the corresponding Ni(CO)$_3$ adduct with an end-on coordination of the ligand[39] (Scheme 92). Complex **176b** was synthesized via a substitution process and implied a 1,3-H shift from P to N.[50c]

The addition of AgSO$_3$CF$_3$ or of the coordinatively unsaturated gold compound (Et$_3$PAu)$^+$PF$_6^-$ to 1 furnished complexes **177a–c** with η^1-diphosphene ligands. These were observed by ^{31}P NMR spectroscopy in solution, but were not isolated[123] (Scheme 93).

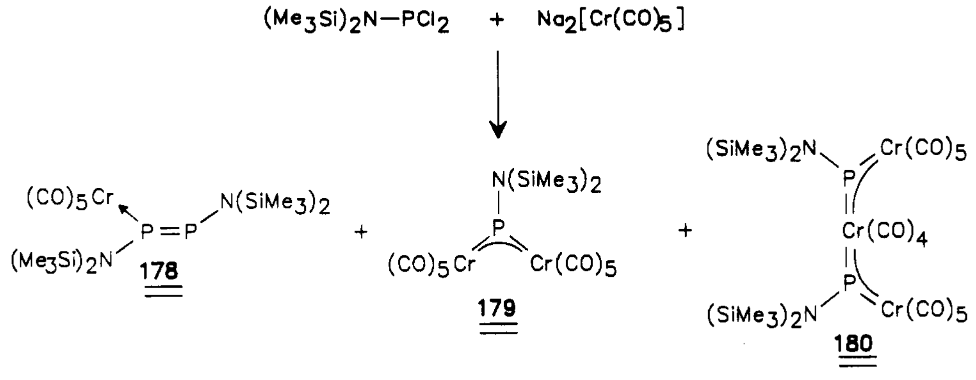
The reductive coupling of dichlorophosphanes by means of carbonyl metalates represents an interesting approach to diphosphene complexes. This type of reaction is not straightforward and leads to a number of products, depending on steric and electronic factors.

Power et al. studied the reaction of RPCl$_2$ with Na$_2$Cr(CO)$_5$ in different solvents and observed the formation of Cr(CO)$_5$ complexes with diphosphene, phosphinidene, phosphane, diphosphane, and cyclotriphosphane ligands.[124] The employment of (Me$_3$Si)$_2$NPCl$_2$ afforded the diphosphene complex **178** only as a minor product in 18% yield. The main product was the phosphinidene complex **179** (45%), whereas a trinuclear phosphinidene species **180** was generated in 10% yield[124c] (Scheme 94). The phosphane (Me$_3$Si)$_2$CHPCl$_2$ underwent a 45% conversion to **181a** when reacted with the chromate anion in ether[124b] (Scheme 95).

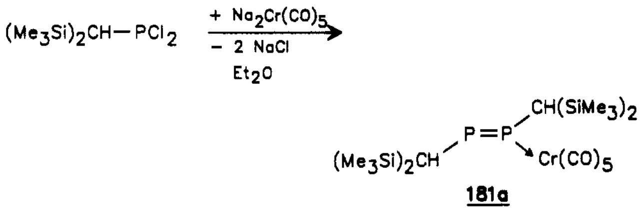
Huttner et al. carefully investigated the reactivity of Na$_2$M$_2$(CO)$_{10}$ toward various organodichlorophosphanes[125] (Scheme 96). He invoked phosphinidene complexes I as intermediates in the diphosphene complex synthesis via the dehalogenation of organodichlorophosphanes. Depending upon the steric requirement of the substituent R, one, two, or three M(CO)$_5$ fragments were ligated to the diphosphene. For R = C$_6$H$_5$, compounds of type V were formed, whereas with R = mesityl diphosphene complexes IV were generated in addition to phosphinidene species I.

Phosphinidene complexes and a phosphirane species accompanied the synthesis of {R[(CO)$_5$M]P=PR} (R

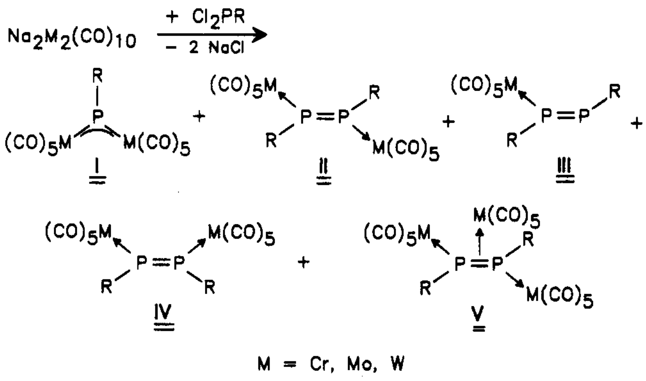
Scheme 94



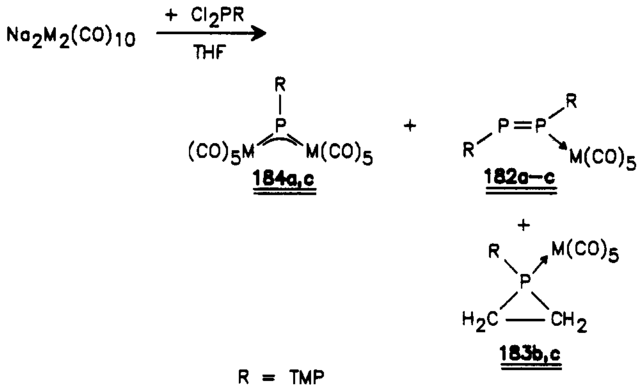
Scheme 95



Scheme 96



Scheme 97



182–184	M
a	Cr
b	Mo
c	W

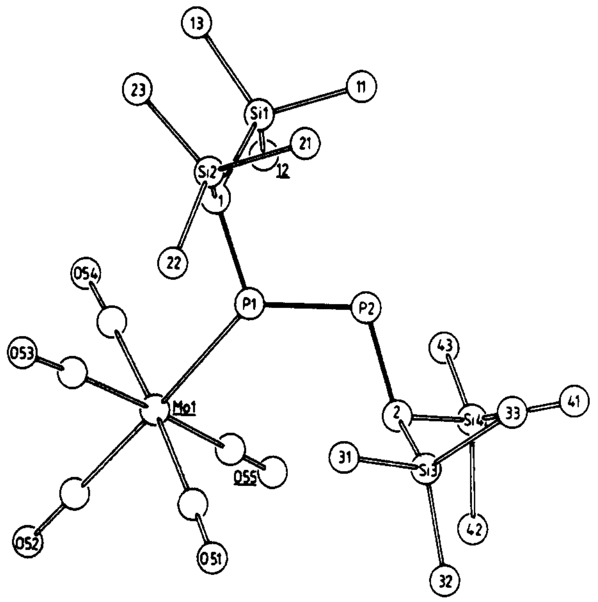
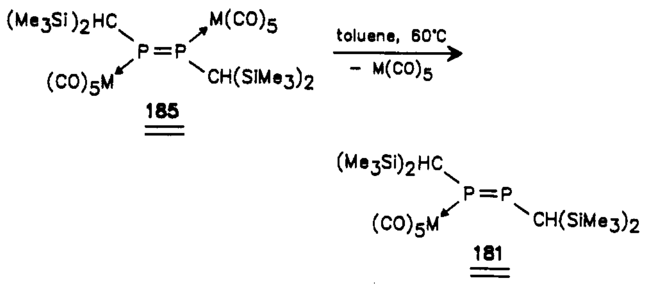


Figure 2. Molecular structure of (*E*)-{$(Me_3Si)_2CH$—P[Mo$(CO)_5$]=P—$CH(SiMe_3)_2$} (**181b**). Selected bond lengths (Å) and bond angles (deg): Mo(1)–P(1) 2.472 (2), P(1)–P(2) 2.006 (3), P(1)–C(1) 1.804 (6), P(2)–C(2) 1.813 (7); Mo(1)–P(1)–C(1) 119.3 (2), P(2)–P(1)–C(1) 106.9 (2), P(1)–P(2)–C(2) 104.5 (2), Mo(1)–P(1)–P(2) 133.8 (1). Reprinted from ref 125a. Copyright 1985, Elsevier Sequoia.

Scheme 98



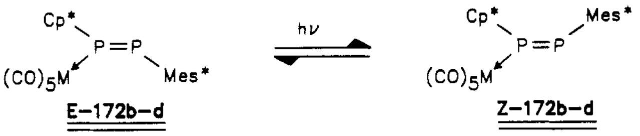
181,185	M
a	Cr
b	W

= TMP) **182**.[126] Complexes **183** were the result of a phosphinidene addition to ethylene, which was believed to originate from the solvent THF (Scheme 97).

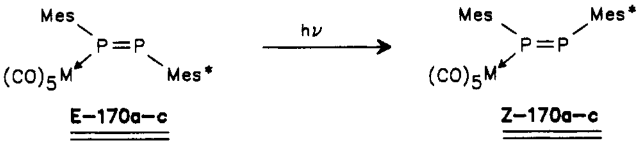
In the reaction of $(Me_3Si)_2CHPCl_2$ with $Na_2M_2(CO)_{10}$ (M = Cr, Mo, W) very short reaction times favored the occurrence of phosphinidene complexes, which were subsequently converted into complexes **185a–c**. Prolonged heating of **185** achieved the extrusion of one $M(CO)_5$ moiety to give compounds **181a–c** (Scheme 98).[125a] Figure 2 shows the molecular structure of **181b**.

The P=P bond length in the respective chromium complex **181a** was found to be 2.027 Å,[124c] which is in good agreement with other diphosphenes with unsupported P=P units. Obviously this bond distance is not affected significantly by the end-on coordination to a metal atom.

Scheme 99

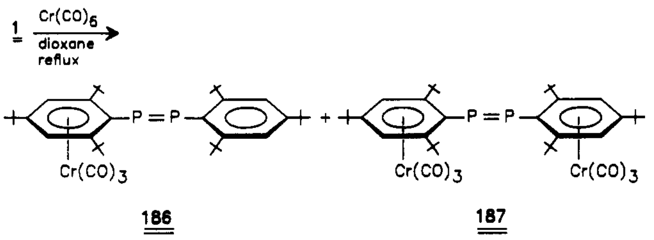


Scheme 100



M = Cr, Mo, W

Scheme 101



UV irradiation of the complexes *E*-**172b–d** led to an equilibrium mixture of the *E*- and *Z*-isomers[98a] (Scheme 99). On the other hand the compounds *E*-**170a–c** were quantitatively converted into the corresponding *Z*-isomers upon exposure to UV light[61] (Scheme 100).

The *E*/*Z* isomerization was accompanied by a high-field shift of the ^{31}P NMR resonances and an increase of the $^1J_{PP}$ coupling constant.

In light of the steric congestion in $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**9**) it is not surprising that all attempts to synthesize complexes thereof have failed.

The treatment of Mes*P=PMes* with $Cr(CO)_5(THF)$ did not lead to end-on coordination, but reacting $Cr(CO)_6$ with **1** in refluxing dioxane resulted in η^6-coordination of one or two $Cr(CO)_3$ fragments to the arene rings. The ^{31}P NMR spectrum of **187** exhibited a singlet at $\delta = 499.7$, whereas the spectrum of **186** was characterized by an AB pattern at $\delta = 503.2$ and 475.7 with a $^1J_{PP}$ constant of 590.8 Hz[127] (Scheme 101).

2. η^2-Diphosphene Complexes

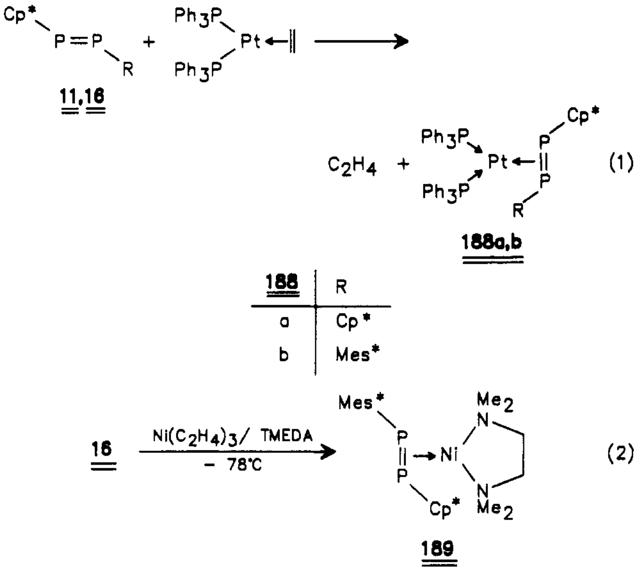
Only in a few cases were η^2-diphosphene complexes accessible by displacement reactions via the free diphosphene (Scheme 102). The diphosphenes **11** and **16** underwent reaction with ethylene–bis(triphenylphosphane)platinum to give the η^2-diphosphene complexes **188a,b** quantitatively.[98a]

Similarly a mixture of $Ni(C_2H_4)_3$, tetramethylethylenediamine (TMEDA), and **16** at −78 °C furnished the complex (η^2-Cp*P=PMes*)NiTMEDA **189** as violet platelets.[91b] The thermolabile complex **190** was obtained as a red solid from the reaction of $[nBu_3P]_2Ni(COD)$, nBu_3P, and **24a** in a toluene/hexane solution[39] (Scheme 103).

Trapping experiments with the labile diphosphene **127** at −60 °C led to η^2-diphosphene complex **191**[31] (Scheme 104).

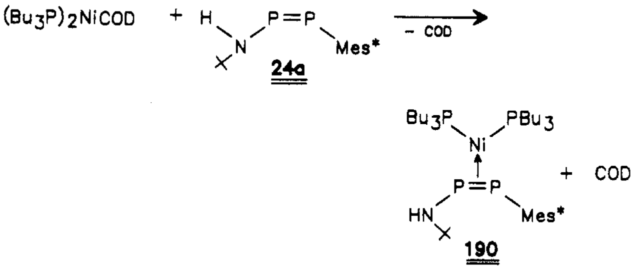
In the vast majority the η^2-ligated diphosphene was constructed from stable precursors in the coordination sphere of a metal center. Thus the degradation of the cyclotetraphosphane $(C_6F_5P)_4$ in the presence of $Pt(PPh_3)_4$[128a] or $Pd(PPh_3)_4$[129b] provided a method for the synthesis of the π-complexes **192a,b** (Scheme 105).

Scheme 102



188	R
a	Cp*
b	Mes*

Scheme 103



The *E* configuration of the diphosphene in **192b** was proved by X-ray analysis.[128a] The P=P bond distance of 2.156 (7) Å in this complex is significantly smaller than the standard value for a P–P single bond (2.22 Å).[77]

In a similar fashion, cyclotetraphosphane $(CF_3P)_4$ reacted with zerovalent Pt, Pd, and Ni complexes under refluxing conditions in benzene to give η^2-$CF_3P{=}PCF_3$ complexes **193a–f** (Scheme 106). Only **193a** was isolated and fully characterized.[128b]

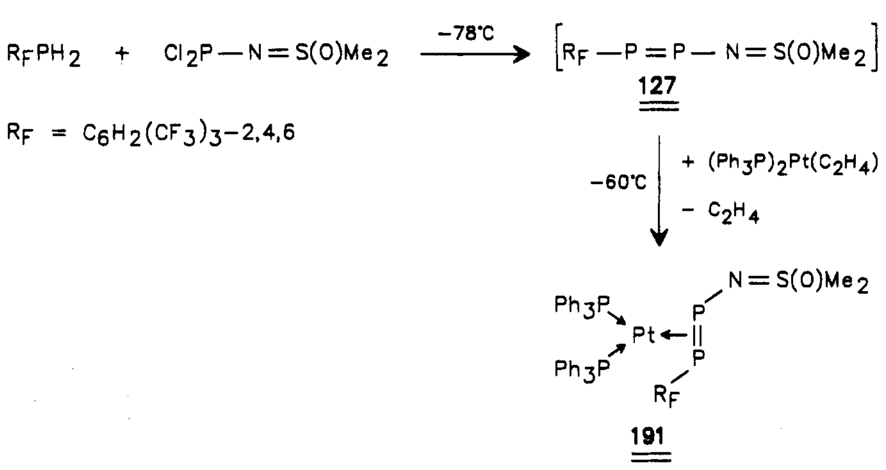
The fixation of reactive diphosphenes in the coordination sphere may be accompanied by a change in the oxidation state of the metal.

The first example of a η^2-diphosphene complex (**194**) was prepared by the reduction of white phosphorus with Cp_2MoH_2[130a] (Scheme 107). The X-ray structure analysis of **194** revealed a P–P bond distance of 2.146 (3) Å,[130b] which is markedly widened with respect to the calculated P–P bond length in free P_2H_2 (2.004 Å).[66]

Platinum and palladium complexes **195** with η^2-diphenyldiphosphene were the products of the reduction of *cis*- or *trans*-MCl_2L_2 with 1,2-dilithio-1,2-diphenyldiphosphane[129] (Scheme 108). In Pd complex **195a** a P–P bond of 2.121 (4) Å is present.

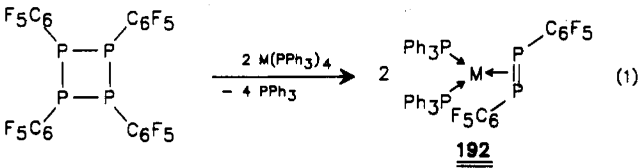
A similar type of reaction is reported from nickel chemistry: Treatment of $(PMe_3)_2NiCl_2$ with Li(tBu)P–P(tBu)Li gave the nickelatetraphosphacyclopentane **196** with an additional η^2-bonded diphosphene ligand. Presumably the heterocycle is formed by the coupling of two diphosphenes at the metal center[131] (Scheme

Scheme 104



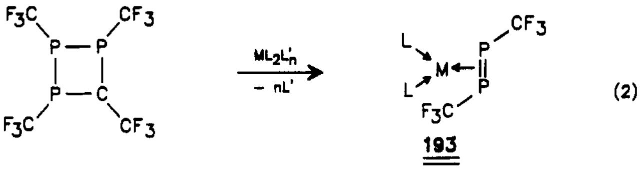
$R_F = C_6H_2(CF_3)_3$-2,4,6

Scheme 105



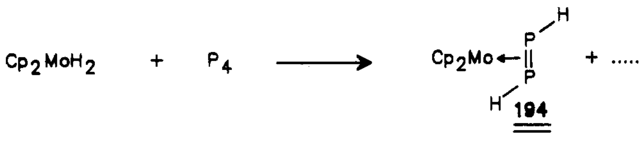
192	M
a	Pd
b	Pt

Scheme 106

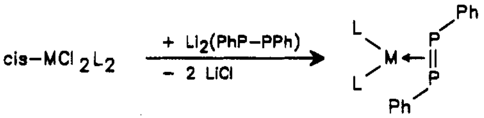


193	ML_2	nL'_n
a	$Pd(PPh_3)_2$	2 PPh_3
b	$Pt(PEt_3)_2$	PEt_3 or 2 PEt_3
c	$Pt(PMe_2Ph)_2$	2 PMe_2Ph
d	$Pt(PPh_3)_2$	C_2H_4or 2 PPh_3
e	Pd diphos	diphos
f	Ni diphos	diphos

Scheme 107

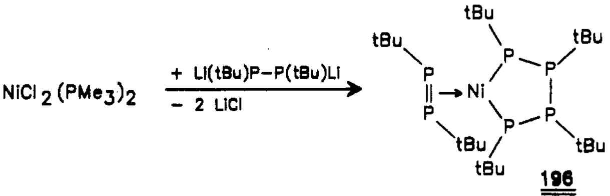


Scheme 108



195	M	L_2
a	Pd	diphos
b	Pt	$(PPh_3)_2$
c	Pt	diphos
d	Pt	$(PMe_2Ph)_2$

Scheme 109



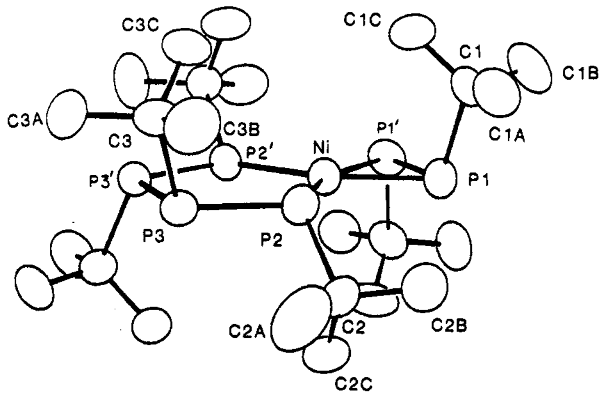


Figure 3. Molecular structure of **196**. Selected bond lengths (Å) and bond angles (deg): Ni-P(1) 2.257 (4), Ni-P(2) 2.149 (4), P(1)-P(1') 2.110 (5), P(2)-P(3) 2.237 (5), P(3)-P(3') 2.196 (4); P(2)-Ni-P(2') 101.2 (2), P(2)-Ni-P(1) 101.5 (1), Ni-P(1)-P(1') 82.1 (1), P(1)-Ni-P(1') 55.7 (1). Reprinted from ref 31. Copyright 1985 American Chemical Society.

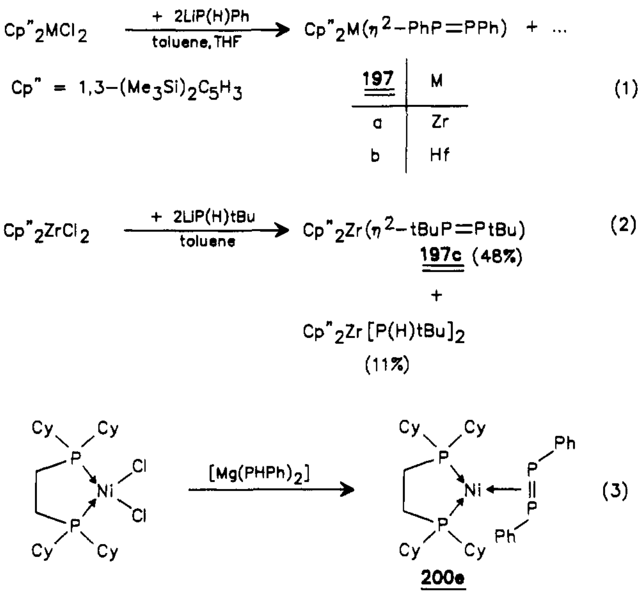
109). The NiP_6 unit is virtually planar as shown by a X-ray structure analysis. The molecular structure of **196** is shown in Figure 3.

Generally there is no need to employ dimetallodiphosphanes for this kind of synthesis. Primary metal phosphides such as LiPHR (R = Ph, tBu)[132] or $Mg(PHPh)_2$[133] react with complex metal dihalides to yield η^2-diphosphene complexes **197a–c** and **200e** (Scheme 110).

The synthesis of η^2-diphosphene complexes of Zr and Hf is of no general applicability. A study of the reaction of $(C_5H_5)_2MCl_2$, $(C_5Me_5)_2MCl_2$, and $[1,3\text{-}(Me_3Si)_2C_5H_3]MCl_2$ with primary lithium phosphides evidenced that the distribution of products depended upon (1) the metal and its reducibility, (2) the steric and electronic nature of the cyclopentadienyl ring, and (3) the bulk of the organic group at the phosphorus atom.[132]

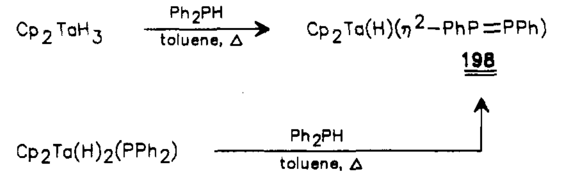
The first tantalum diphosphene complex resulted from the treatment of Cp_2TaH_3 with Ph_2PH in refluxing toluene[134] (Scheme 111). The diphosphene configu-

Scheme 110

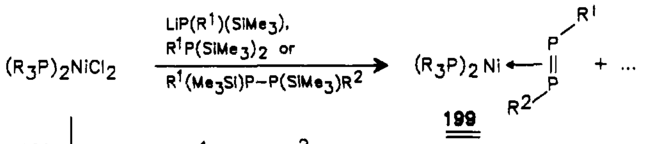


197	M
a	Zr
b	Hf

Scheme 111



Scheme 112



199	R	R^1	R^2
a	nBu	$SiMe_3$	$SiMe_3$
b	Et	$SiMe_3$	$SiMe_3$
c	Me	$SiMe_3$	$SiMe_3$
d	iBu	$SiMe_3$	$SiMe_3$
e	Ph	$SiMe_3$	$SiMe_3$
f	Et	tBu	tBu
g	Et	tBu	$SiMe_3$
h	Et	Ph	Ph

ration in the complex is uncertain. The mechanism of the formation of the diphosphene is unknown, but it was suggested that in a preliminary step the dihydride $Cp_2Ta(H)_2(PPh_2)$ is generated by insertion of the fragment $[Cp_2TaH]$ into the Ph_2P–H bond. The dihydride was synthesized independently and was readily converted into $Cp_2Ta(H)(\eta^2\text{-}PhP{=}PPh)$ by heating with Ph_2PH.[134]

Schäfer and co-workers carefully studied the reactivity of bisphosphane nickel dichlorides $(R_3P)_2NiCl_2$ toward silylphosphane derivatives such as $LiP(SiMe_3)R'$, $PR'(SiMe_3)_2$, and $P_2R'_2(SiMe_3)_2$.[135a,b]

The formation of diphosphene complexes of the types $(R_3P)_2Ni(\eta^2\text{-}Me_3SiP{=}PSiMe_3)$, $(R_3P)_2Ni(\eta^2\text{-}tBuP{=}PtBu)$ and $(R_3P)_2Ni(\eta^2\text{-}PhP{=}PPh)$ was favored by small Tolman cone angles of the phosphane ligands (<132° like in PMe_3, PEt_3, and $PnBu_3$) and low reaction temperatures (−30 to −10 °C). The employment of disilyldiphosphanes $P_2R'_2(SiMe_3)_2$ (R' = Ph, tBu, $SiMe_3$) gave the best yields of the η^2-diphosphene complexes **199a–h**, and the process formally may be considered as a [2 + 1] cyclocondensation[135b] (Scheme 112).

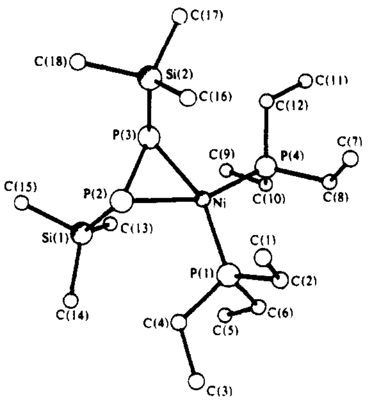
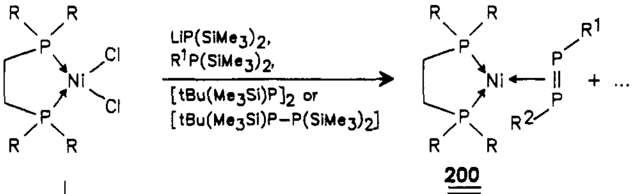


Figure 4. Molecular structure of **199b**. Selected bond lengths (Å) and bond angles (deg): Ni–P(2) 2.236 (2), Ni–P(3) 2.258 (2), P(2)–P(3) 2.149 (2), P(2)–Ni–P(3) 57.13 (5), Ni–P(2)–P(3) 61.95 (7), P(2)–P(3)–Ni 60.93 (6), Si(1)–P(2)–P(3) 97.87 (8), P(2)–P(3)–Si(2) 96.96 (8). Reprinted from ref 138. Copyright 1982 Munksgaard (Copenhagen).

Scheme 113



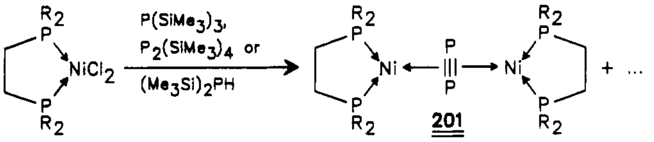
200	R	R^1	R^2
a	Et	$SiMe_3$	$SiMe_3$
b	Cy	$SiMe_3$	$SiMe_3$
c	Ph	$SiMe_3$	$SiMe_3$
d	Et	Ph	Ph
e	Cy	Ph	Ph
f	Ph	Ph	Ph
g	Cy	Me	Me
h	Et	tBu	tBu
i	Cy	tBu	tBu
j	Ph	tBu	tBu
k	Et	$SiMe_3$	tBu
l	Cy	$SiMe_3$	tBu
m	Ph	$SiMe_3$	tBu

The molecular structure of $(Et_3P)_2Ni\{\eta^2\text{-}[P(SiMe_3)]_2\}$ (**199b**, Figure 4) has been elucidated by X-ray analysis.[138] The structure shows an η^2-coordinated and trans-configurated diphosphene, the phosphorus centers of which are located in nearly the same plane as the nickel and the two remaining phosphorus atoms.

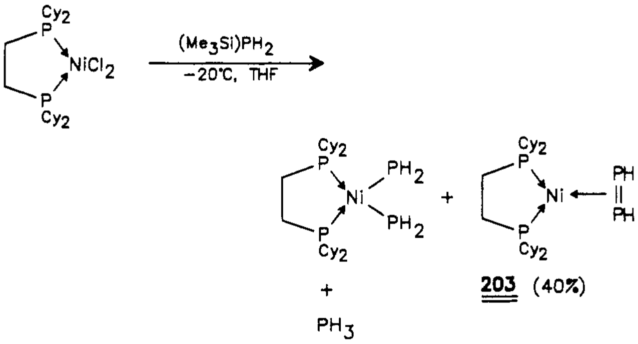
The reactions of $LiP(SiMe_3)_2$ with the square-planar chelate complexes $(R_2PCH_2CH_2PR_2)NiCl_2$ (R = Et, Cy, Ph) were more straightforward.[136] Here the bulky $Cy_2PCH_2CH_2PCy_2$ ligand even stabilized an η^2-MeP=PMe complex. When the silylphosphane components were of concern the best results were obtained with $LiP(SiMe_3)_2$, $PhP(SiMe_3)_2$, $MeP(SiMe_3)_2$, $[tBu(Me_3Si)_2P]_2$, and $(Me_3Si)_2PP(tBu)(SiMe_3)$ (Scheme 113).

The treatment of the chelate complexes with $P(SiMe_3)_3$ or $P_2(SiMe_3)_4$ did not furnish η^2-diphosphene

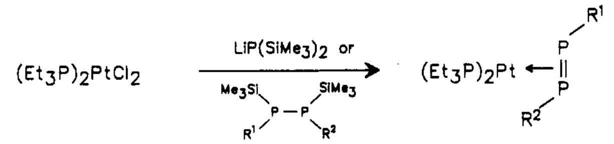
Scheme 114



Scheme 115



Scheme 116



	R^1	R^2
204	$SiMe_3$	$SiMe_3$
205	tBu	tBu
206	tBu	$SiMe_3$

complexes. Instead stable dinuclear complexes **201** with a bridging η^2:η^2-P_2 ligand were formed (Scheme 114). The same was observed when $(Me_3Si)_2PH$ was reacted with the respective nickel complexes. In the case of R = Cy the compounds $(Cy_2PCH_2CH_2PCy_2)Ni(\eta^2\text{-}HP{=}PSiMe_3)$ (**202**) and $(Cy_2PCH_2CH_2PCy_2)Ni(\eta^2\text{-}HP{=}PH)$ (**203**) were detected as intermediates by ^{31}P NMR spectroscopy[136c] (Scheme 115). The latter complex was isolated from the reaction of $(Cy_2PCH_2CH_2PCy_2)NiCl_2$ with Me_3SiPH_2 at -20 °C.[136c] Warming solid **203** or its solutions to 20 °C gave the diphosphorus complex **201**.

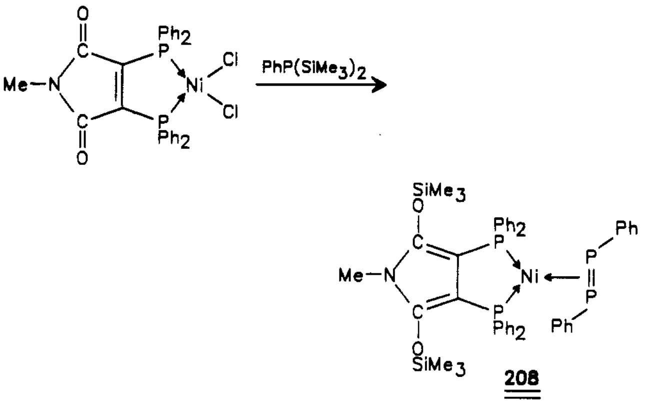
Schäfer extended the synthetic approach described here to the chemistry of platinum diphosphene complexes[137] (Scheme 116).

Under comparable conditions the use of $(Ph_3P)_2PtCl_2$ did not afford stable η^2-diphosphene complexes. The compounds $(Ph_3P)_2Pt(\eta^2\text{-}RP{=}PR)$ (**207**) (**a**, R = Me_3Si; **b**, R = tBu) were observed in the reaction mixture by ^{31}P NMR techniques, however.

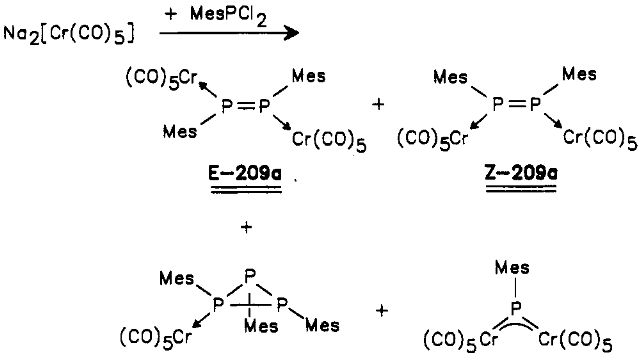
The same synthetic principle that was used for **199b** was used in the reaction of a 3,4-diphosphinomaleimidenickel complex with $PhP(SiMe_3)_2$. Here evidently the disilylphosphane first reduced the maleimide before the η^2-diphosphene complex **208** was built up[139] (Scheme 117).

An interesting question concerns the factors which govern the coordination mode of the diphosphene ligand. It is obvious that the η^2-mode is mainly realized with electron-rich complexes of the nickel triade. This may be an indication for the improved π-acceptor capacity when the diphosphene operates as an η^2-ligand.

Scheme 117



Scheme 118



The $(CO)_5Cr$ fragment is known as an electron-withdrawing group and therefore prefers the end-on coordination of a diphosphene where the donor abilities of the ligand predominate.

3. μ_2-(η^1:η^1)-Diphosphene Complexes

It was pointed out that the number of $M(CO)_5$ groups linked to a diphosphene P_2R_2 is highly dependant on the steric requirements of the substituents R. Thus, in order to obtain complexes with η^1:η^1 diphosphene bridges the size of these groups should be considerably smaller than that of a supermesityl unit.

Nearly all of the compounds under discussion were synthesized by the interaction of organodichlorophosphanes with carbonylmetalates.

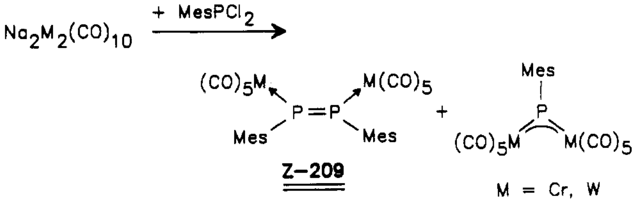
E- and *Z*-configurated complexes **209a** were the main products of the reaction of $MesPCl_2$ and $Na_2Cr(CO)_5$ in ether. A phosphinidene species and a cyclotriphosphane complex were observed as minor products[124c] (Scheme 118).

In contrast to these findings Huttner reported only the *Z*-configurated dinuclear diphosphene complexes in addition to a phosphinidene species as products of the dehalogenation of $MesPCl_2$ by $Na_2[M_2(CO)_{10}]$ (Scheme 119). The X-ray analysis of the molybdenum complex *Z*-**209b** revealed a P-P bond length of 2.026 (2) Å[125a] (Figure 5).

Other examples of this type of complexes are $[(E)\text{-}Me_3SiCH_2P{=}PCH_2SiMe_3][Cr(CO)_5]_2$ (**210**)[124c] and $[(E)\text{-}(Me_3Si)_2CHP{=}P{-}CH(SiMe_3)_2][M(CO)_5]_2$ (**185a,b**) (M = Cr, W)[125a] which were prepared from the corresponding organodichlorophosphane and $Na_2[Cr(CO)_5]$[124c] or $Na_2[M_2(CO)_{10}]$ (M = Cr, W).[125a]

The reduction of menthyldibromophosphane complexes **211a,b** to the dinuclear diphosphene complexes **212a,b** was effected by magnesium in THF[140] (Scheme 120).

Scheme 119



Z-209	M
a	Cr
b	Mo
c	W

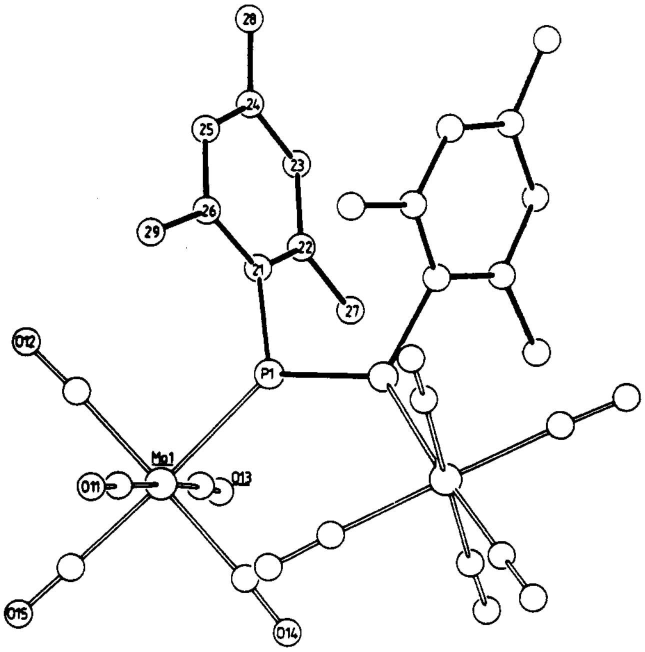
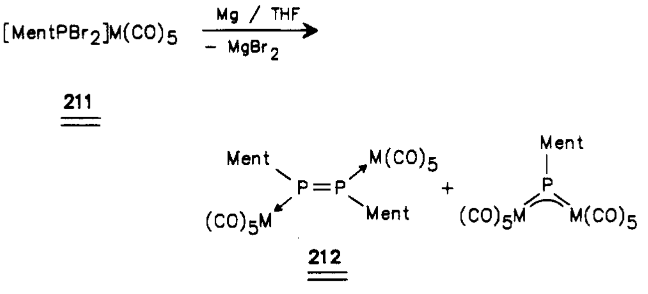


Figure 5. Molecular structure of **209b**. Selected bond lengths (Å) and bond angles (deg): Mo(1)-P(1) 2.454 (2), P(1)-P(1′) 2.026 (2), P(1)-C(21) 1.812 (4); Mo(1)-P(1)-C(21) 120.5 (1), Mo(1)-P(1)-P(1′) 132.3 (0), C(21)-P(1)-P(1′) 107.0 (1). Reprinted from ref 125a. Copyright 1985 Elsevier Sequoia.

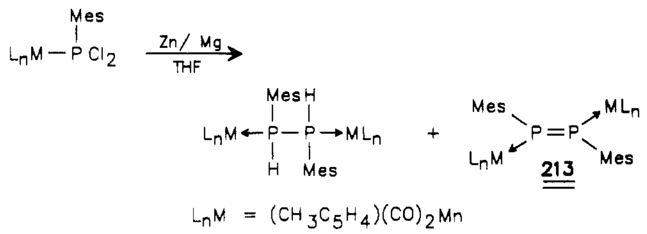
Scheme 120



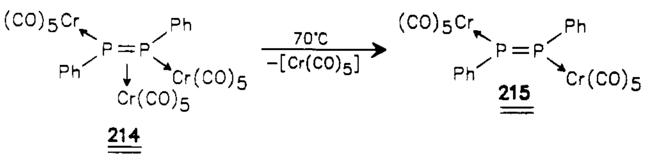
212	M
a	Cr
b	W

Again phosphinidene complexes accompanied the formation of the diphosphene species. The P–P distance in **212a** amounts to 2.040 Å.[140] Similarly the reduction of a manganese dichlorophosphane complex proceeded with the production of dinuclear diphosphane and diphosphene complexes[141] (Scheme 121).

Scheme 121



Scheme 122



The synthesis of compound **215** involved the thermal dissociation of one $Cr(CO)_5$ moiety from the trinuclear complex **214**[142a,b] (Scheme 122). The permanganate-like color of **215** was explained by a four-center, six π-electron system, which brought about a very small energy gap between the HOMO and the LUMO of the molecule (ca. 20 000 cm^{-1}).[143]

Since the $Fe(CO)_4$ fragment is smaller than the $M(CO)_5$ unit more diphosphenes tolerate the presence of two such groups. A viable synthetic pathway to the complexes under discussion was realized by the reductive dehalogenation of dichlorophosphanes by Collman's reagent[124a,144a,b] (Scheme 123). In **216** the P=P bond length was determined to 2.029 (1) Å, whereas **217** and **218** feature P=P bonds of 2.039 (1) and 2.053 (1) Å, respectively.[144]

The intermediacy of the phosphinidene species $RP=Fe(CO)_4$ was suggested in these transformations, but it has not been trapped by organic substrates as yet. Besides the course of the reaction between $RPCl_2$ and $Na_2Fe(CO)_4$ is highly dependent upon the nature of R and the solvent. Diphosphene complexes were favored by low concentrations of $Fe(CO)_4^{2-}$ in solution as it was realized in ether or hexane.[145]

A comparable synthetic approach, applied upon aryldichlorophosphanes and $Na_2[V(C_5H_5)(CO)_3]$ yielded diphosphene complex **219** for R = Mes[146] and vanadium phosphinidene complex $[Cp(CO)_2V]_2PMes^*$ in the case of the very bulky supermesityl group.[147] In several cases the treatment of Mes^*PCl_2 with carbonylmetalates gave diphosphene **1** in addition to phosphinidene complexes; however, no diphosphene complexes were detected among the products[148–150] (Scheme 124).

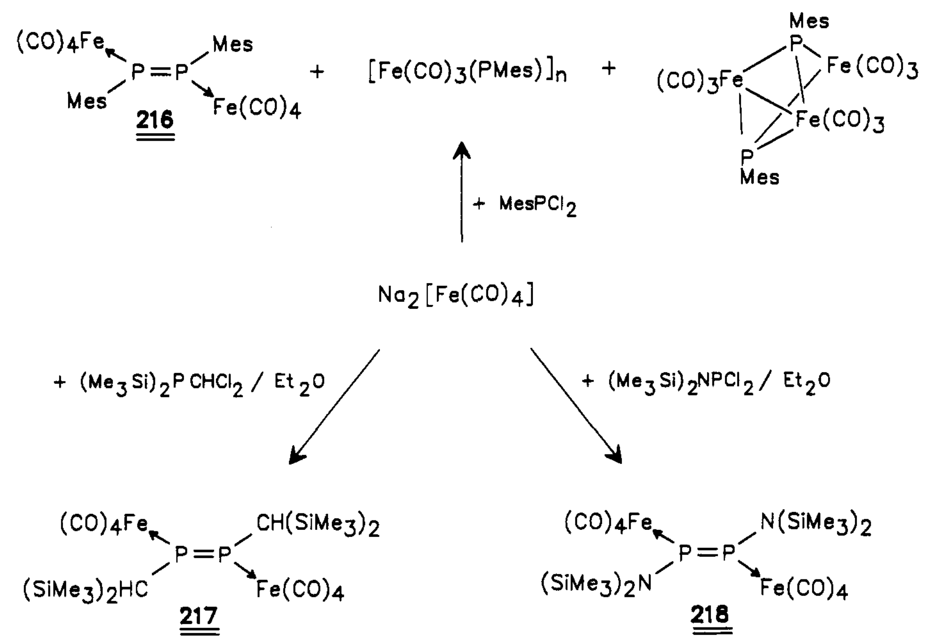
The addition of a second 16-electron fragment to a preformed η^1-diphosphene complex in order to synthesize μ-(η^1:η^1)-complexes was only realized for a small number of $Ni(CO)_3$ compounds[50c] (Scheme 125). The X-ray structure analysis of **220a** exhibited an *E*-configurated P=P bond of 2.029 Å.[50c]

4. μ_2-(η^1:η^2)-Diphosphene Complexes

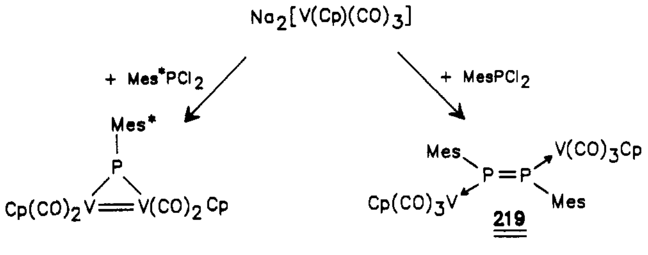
Dinuclear entities with η^1:η^2 diphosphene bridges of type D represent an interesting alternative to the complexes of type C discussed in the previous section.

The hydridocarbonylferrate $HFe(CO)_4^-$ reduced $PhPCl_2$ and diazaphospholyl dichlorophosphane to the complexes **221**[151] and **222**[152] with bridging η^1:η^2-diphosphene ligands. In addition the organochlorophosphane

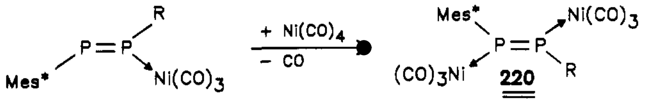
Scheme 123



Scheme 124



Scheme 125



220	R
a	$CH(SiMe_3)_2$
b	$CH(Ph)(SiMe_3)$
c	NHMes*

iron complex **223** was generated (Scheme 126). The ^{31}P NMR spectrum of **221** diplays an AB spin system with $\delta = 52.1$ and -34.5 ppm ($J_{AB} = 415$ Hz). The most interesting feature of the structure of complex **222** is the presence of a 1,3,4,6-tetraphosphahexatriene (1,3,5) unit which is η^1-bound to one $Fe(CO)_4$ and η^2-coordinated to another $Fe(CO)_4$ moiety[152] (Figure 6).

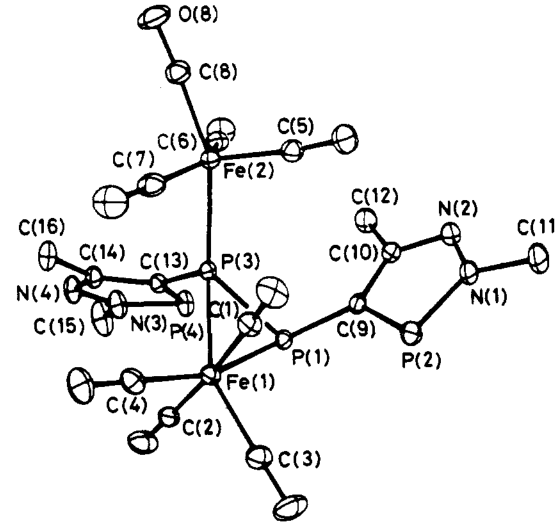
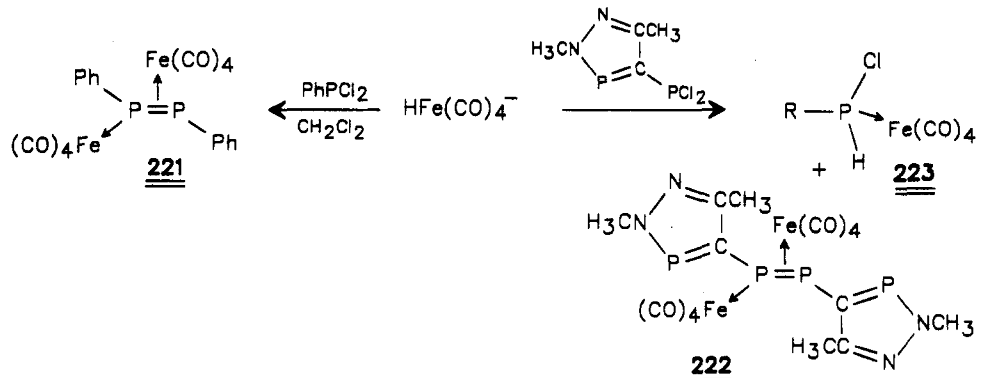


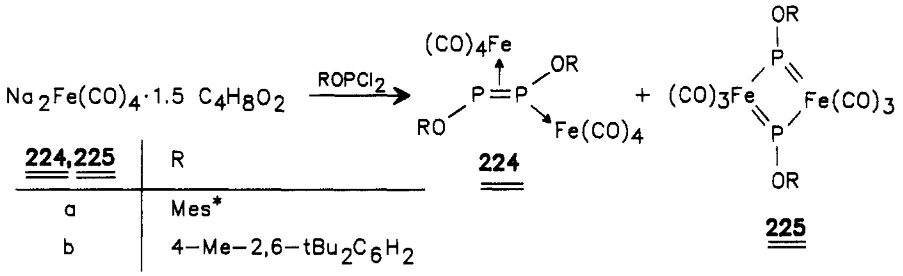
Figure 6. Molecular structure of **222**. Selected bond lengths (Å) and angles (deg): P(1)–P(3) 2.1504 (8), P(2)–C(9) 1.713 (2), P(4)–C(13) 1.714 (3), P(1)–C(9) 1.801 (2), P(3)–C(13) 1.802 (2); P(3)–P(1)–C(9) 105.6 (8), P(1)–P(3)–C(13) 101.2 (8). Reprinted from ref 152. Copyright 1988 Chemical Society, London.

Collman's reagent turned out to be a useful starting material for the synthesis of η^1:η^2-diphosphene iron complexes **224a,b** and the interesting bis(μ-phosphin-

Scheme 126

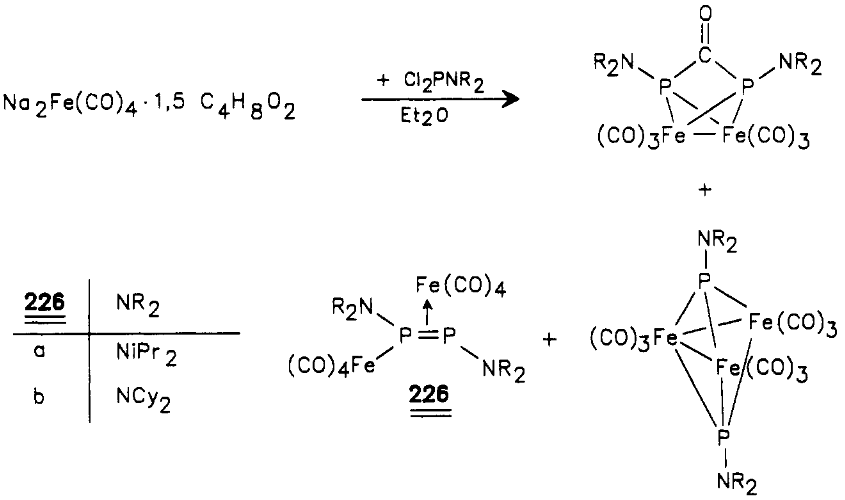


Scheme 127



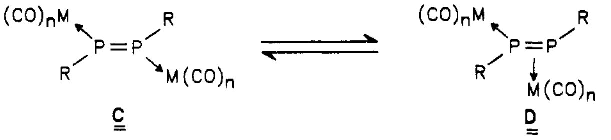
224,225	R
a	Mes*
b	$4\text{-}Me\text{-}2,6\text{-}tBu_2C_6H_2$

Scheme 128



226	NR_2
a	$NiPr_2$
b	NCy_2

Scheme 129



idene) species **225**[124b,144b] (Scheme 127). Complexes **224a,b** were converted into **225a,b** by gentle heating with concomitant loss of two CO ligands.

The X-ray structure analysis of **224a** revealed marked differences in bond lengths between the η^1(Fe–P) bond [2.226 (2) Å] and the η^2(P=P)Fe contacts [2.362 (2) and 2.347 (2) Å]. The P=P bond amounts to 2.184 (2) Å.[124b]

Diphosphene complexes **226** were among the minor products in the reaction of Collman's reagent with (dialkylamino)dichlorophosphanes in ether. Bulky substituents like iPr_2N, Cy_2N, or the TMP group were required for the success of this transformation[145] (Scheme 128).

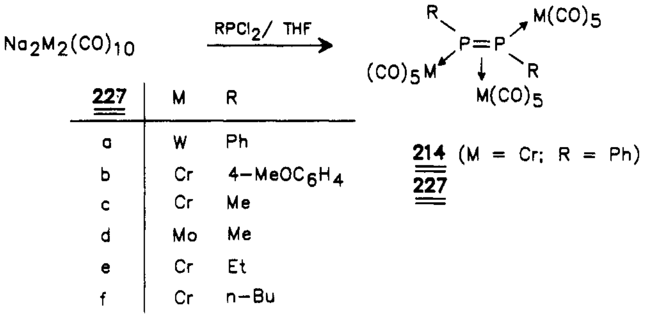
If one accepts a hypothetical equilibrium between the two isomers C and D, it is remarkable that both modes of coordination are realized in iron chemistry, whereas the pentacarbonyls of chromium, molybdenum, and tungsten clearly prefer structure C (Scheme 129).

5. μ_3-(η^1:η^1:η^2)-Diphosphene Complexes

Complexes of diphosphenes, where two metal centers are end-on-coordinated (η^1) via the lone pairs of the phosphorus atom and the third one is η^2-ligated to the π-system were mainly observed in the carbonyl chemistry of chromium, molybdenum, and tungsten.

An especially effective synthetic strategy involves dehalogenation and complexation steps which are operative in the mixture of $Na_2M_2(CO)_{10}$ with organodichlorophosphanes[142a,153] (Scheme 130). Again the formation of the diphosphene complexes is believed to proceed via the dimerization of the transient phosphinidene complexes $RP[M(CO)_5]_2$ or their THF adducts.

Scheme 130



227	M	R
a	W	Ph
b	Cr	$4\text{-}MeOC_6H_4$
c	Cr	Me
d	Mo	Me
e	Cr	Et
f	Cr	n-Bu

The X-ray analysis of **214** indicates significantly shorter Cr–P contacts for the η^1-bonded $Cr(CO)_5$ units than for the $Cr(CO)_5$ group engaged in the π-interaction (Figure 7). The P=P bond is considerably lengthened with respect to the unsupported P=P bond in **215** [d(P=P) = 2.021 (2) Å].[142a]

The dimerization of phosphinidene compounds into diphosphene derivates was examplified by the formation of compound **214** and **228**[154] (Scheme 131). In **228** a Z-configurated diphosphene is capping the triangular face of a cluster molecule. A chromium compound of this type is especially noticeable since only very few chromium clusters are known. The P–P bond in **228** amounts to 2.11 Å.[154] The ^{31}P resonance occurs at δ 352. The idea that diphosphene complexes are resulting from phosphinidene precursors is supported by the

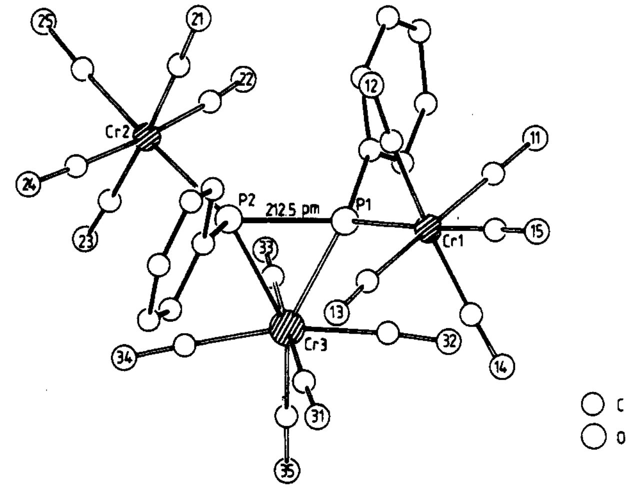
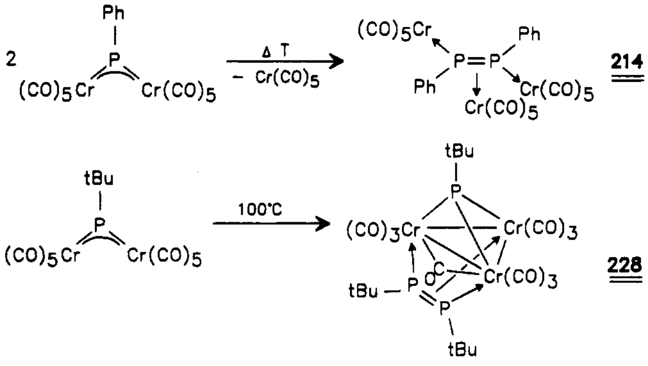
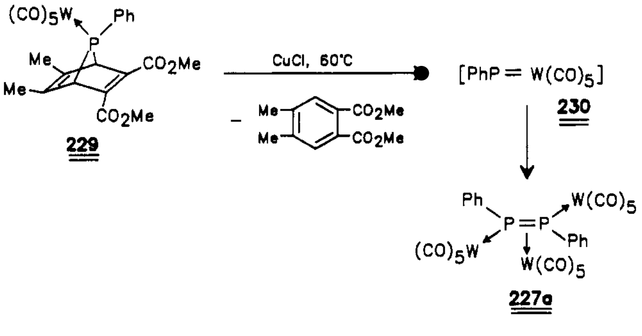


Figure 7. Molecular structure of **214**. Selected bond lengths (Å) and angles (deg): P(1)-P(2) 2.125 (6) [2.125 (4)], Cr(1)-P(1) 2.411 (4) [2.405 (5)], Cr(2)-P(2) 2.405 (4) [2.387 (4)], Cr(3)-P(1) 2.546 (5) [2.536 (5)], Cr(3)-P(2) 2.524 (3) [2.530 (5)]; P(2)-P(1)-Cr(1) 130.9 (2) [129.5 (2)], P(1)-P(2)-Cr(2) 130.3 [129.5 (1)]. Reprinted from ref 142a. Copyright 1983 VCH (Weinheim).

Scheme 131



Scheme 132



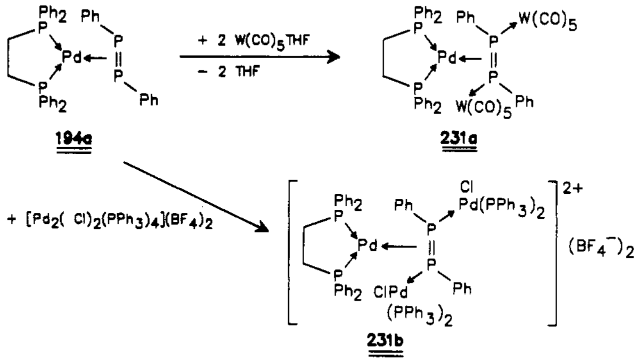
occurrence of **227a** as the main product in the thermal or catalytic decomposition of the appropriate 7-phosphanorbornadiene complex **229**. It is known that the latter serves as a source for the electrophilic phosphinidene complex **230**[155] (Scheme 132).

The lone pairs at the phosphorus atoms of the η^2-bound diphosphene in palladium complex **194a** still possess basic properties, which became evident by the addition of two $W(CO)_5$ groups[129b] (Scheme 133).

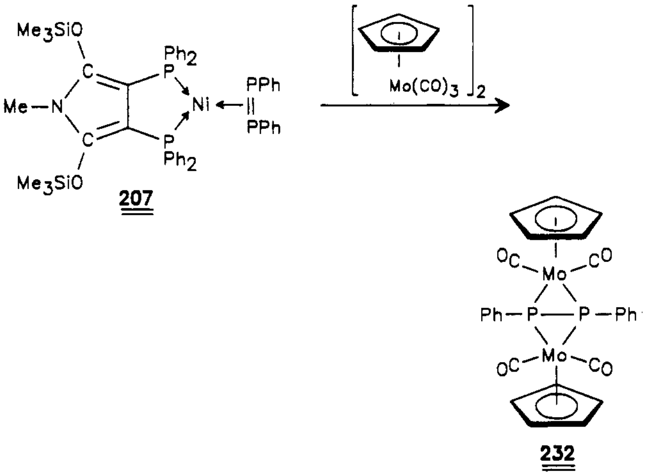
6. μ_2-(η^2:η^2)-Diphosphene Complexes

232 is the only well-documented complex, featuring a diphosphene as part of a butterfly arrangement. It was prepared in the course of a ligand transfer process (Scheme 134). According to the X-ray diffraction analysis, **232** displays a Mo_2P_2 skeleton with a P-P bond length of 2.136 Å and two short Mo-P bonds (2.466, 2.370 Å) as well as two long Mo-P contacts (2.542, 2.546 Å). Both MoP_2 triangles enclose a dihedral angle of 135°. Thus the *Z*-configurated diphosphene has to be considered as a six-electron ligand. A THF solution of **232** gave rise to a singlet at $\delta = -94$ ppm in the ^{31}P NMR spectrum.[156]

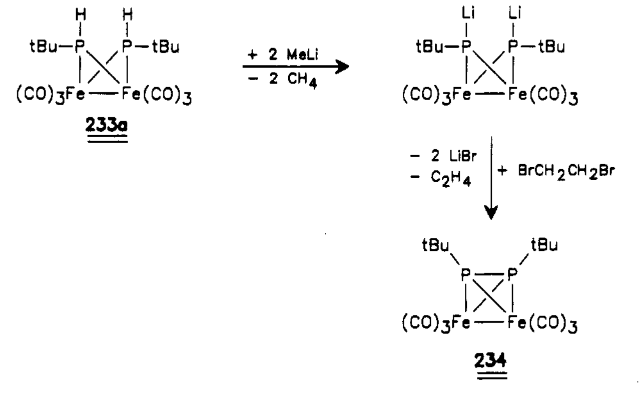
Scheme 133



Scheme 134



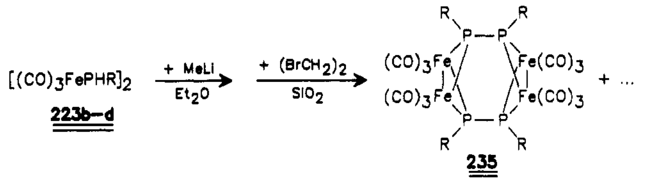
Scheme 135



7. Clusters with Diphosphene Units

The fusion of the sixth bond of the tetrahedrane **234** was accomplished by lithiation of the bridging *tert*-butylphosphido ligands in the butterfly complex **233a** and the subsequent oxidation of the dilithio compound with 1,2-dibromoethane[157a,b] (Scheme 135). The X-ray structure analysis of **234** demonstrates that the P=P bond in the diphosphene [2.059 (3) Å], which functions

Scheme 136



233,235	R
b	CH_3
c	Ph
d	p-Tol

Scheme 137

$$[\mathrm{Ir_4(CO)_{11}(PPhH)}]^-(\mathrm{DBU})^+ \xrightarrow[+\ [\mathrm{Au(PEt_3)}]\mathrm{ClO_4}]{+\ \mathrm{AgClO_4}} \mathbf{236}$$

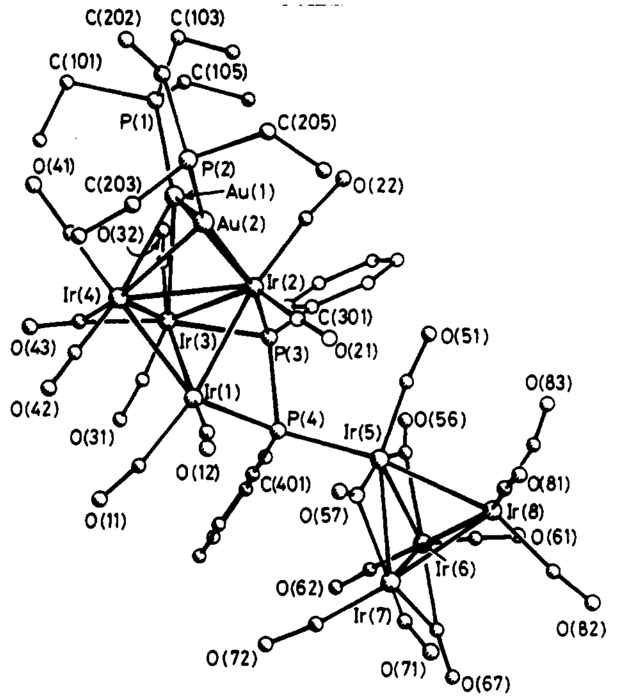


Figure 8. Molecular structure of **236**. Selected bond lengths (Å): Ir(2)–P(3) 2.302 (12), Ir(3)–P(3) 2.308 (9), Ir(1)–P(4) 2.434 (11), P(3)–P(4) 2.186 (13), Ir(5)–P(4) 2.375 (8). Reprinted from ref 159. Copyright 1986 Chemical Society, London.

as a six-electron ligand, is only marginally elongated by coordination. According to Hoffmann's isolobal analogy,[158] $[\mathrm{Fe(CO)_3^-}\leftrightsquigarrow\mathrm{CH}\leftrightsquigarrow\mathrm{RP^+}]$ complex **234** may be regarded as a derivative of the tetrahedrane C_4H_4.

The course of the dimetalation/oxidation sequence is sensitive to the steric requirements of the substituent at the μ-phosphido ligands in the butterfly precursor. The employment of the bis(μ_2-organylphosphido) complexes **233b–d** caused the formation of the organometallic analogs of octabisvalene **235b–d** instead of tetrahedranes.[157c,d] The P–P bond length of 2.23 Å in **235b** excludes the description of the cluster as a diphosphene complex. A μ_4-bridging dimethyldiphosphanediyl system seems to be a more appropriate characterization of the ligand (Scheme 136).

In cluster **236** [d(PP) = 2.186 (13) Å] the same problem is evident.[159] The author, however, admits that there are no clear-cut borderlines between these two extreme descriptions (Scheme 137, Figure 8).

Scheme 138

$$\mathrm{Na_2[Ni_6(CO)_{12}]} \xrightarrow[\mathrm{Et_2O,\ 20^\circ C}]{\mathrm{(Me_3Si)_2CHPCl_2}} \mathrm{Ni_5(CO)_6[(Me_3Si)_2CH{-}P{=}P{-}CH(SiMe_3)_2]Cl}\ \mathbf{237}$$

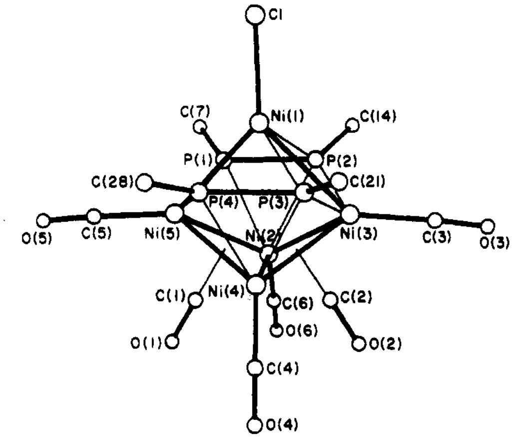


Figure 9. Molecular structure of **237**. Reprinted from ref 160. Copyright 1984 American Chemical Society.

The synthesis of the carbonyl nickel cluster **237** incorporating the $(Me_3Si)_2CHP{=}PCH(SiMe_3)_2$ ligand as a six-electron donor was achieved by dehalogenation of $(Me_3Si)_2CHPCl_2$ with $Na_2[Ni_6(CO)_{12}]$[160] (Scheme 138, Figure 9). The diphosphene ligands interact most closely with Ni(3) and Ni(5) as examplified by the short Ni–P distances (average ca. 2.18 Å). The distances between the phosphorus atoms and the other nickel atoms are almost 0.2 Å longer, averaging ca. 2.37 Å. The P(1)–P(2) and P(3)–P(4) bond lengths are 2.085 (4) and 2.098 (4) Å. Each of the diphosphene ligands obviously behaves as a σ-donor ligand toward Ni(3) and Ni(5), which results in fairly short Ni–P distances. The other Ni–P distances, which are considerably longer suggest that the diphosphenes are operating as very weak π-bonding ligands toward these three nickel atoms.[160]

B. ^{31}P NMR Spectroscopic Data of Diphosphene Complexes

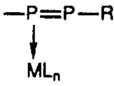
With a few exceptions the η^1-complexation of a diphosphene $R^1P^1{=}P^2R^2$ to give $R^1P^1(ML_n){=}P^2R^2$ is accompanied by the shielding of both nuclei P^1 and P^2 in the ^{31}P NMR spectrum. Usually the metal-bound atom P^1 experiences the more pronounced coordination shift (ca. $\Delta\delta = -30$ to -130 ppm) upon complexation. The amount of the screening depends on the nature of the group ML_n and within a homologous series it increases with the atomic number of the metal, e.g., $(Me_3Si)_2CHP_A[M(CO)_5]{=}P_BCH(SiMe_3)_2$ [$\Delta\delta$ P_A = -72.7 (M = Cr), -84.0 (M = Mo), -128.9 (M = W); $\Delta\delta$ $P_B = -41.2$ (M = Cr), -51.6 (M = Mo), -73.2 (M = W)].

In keeping with the idea that the prominent contribution for this chemical shifts stems from a paramagnetic term, which depends upon the HOMO/LUMO separation, one might suggest that in η^1-diphosphene complexes this energy gap increased.

This conclusion is underlined by the MO scheme for $H_2P_2Cr(CO)_5$ which indeed indicated an energy increase in the HOMO–LUMO separation (ca. 4.8 eV) in the complex as compared with the free ligand (ca. 3.6 eV).[119]

The same argumentation may be valid for complexes with μ_2-(η^1:η^1)-diphosphene ligands [e.g., $(Me_3Si)_2CHP[M(CO)_5]{=}P[M(CO)_5]CH(SiMe_3)_2$ ($\Delta\delta = -91.1$ ppm (M = Cr), -174.8 ppm (M = W))].

Table 4. ^{31}P NMR Data of η^1-Diphosphene Complexes



$$R^1{-}P{=}P{-}R^2 \quad (P \rightarrow ML_n)$$

compd	R^1	R^2	ML_n	δ ^{31}P	$^1J_{PP}$, Hz	solvent	ref(s)
169a	Mes*	Mes*	$Ni(CO)_3$	449.0; 422.0	540.3	Et_2O	120
169b	Mes*	Mes*	$Fe(CO)_4$	423.6; 396.4	578.0	CH_2Cl_2	120
169c	Mes*	Mes*	$W(CO)_5$	486.3; 357.4	561.5		12
E-**170a**	Mes	Mes*	$Cr(CO)_5$	500.9; 412.3	517.6	$CDCl_3$	61, 121
E-**170b**	Mes	Mes*	$Mo(CO)_5$	486.3; 395.0	518.8	$CDCl_3$	61, 121
E-**170c**	Mes	Mes*	$W(CO)_5$	461.9; 352.4	528.8	$CDCl_3$	61, 121
Z-**170a**	Mes	Mes*	$Cr(CO)_5$	393.9; 384.9	603.0		61, 121
Z-**170b**	Mes	Mes*	$Mo(CO)_5$	398.4; 359.0	585.9		61, 121
Z-**170c**	Mes	Mes*	$W(CO)_5$	393.1; 322.4	576.8		61, 121
171	$CH(SiMe_3)_2$	Mes*	$Fe(CO)_4$	424.0; 416.0	519.0	CH_2Cl_2	120
172a	Cp*	Mes*	$Ni(CO)_3$	443.3; 428.2	551	C_6D_6	91b
E-**172b**	Cp*	Mes*	$Cr(CO)_5$	498.2; 454.4	549	$CDCl_3$	98a
E-**172c**	Cp*	Mes*	$Mo(CO)_5$	485.6; 443.4	545	C_6D_6	98a
E-**172d**	Cp*	Mes*	$W(CO)_5$	465.1; 405.3	546	C_6D_6	98a
E-**172e**	Cp*	Mes*	$Fe(CO)_4$	462.3; 440.2	548	$CDCl_3$	98a
Z-**172b**	Cp*	Mes*	$Cr(CO)_5$	421; 385	603	n-C_6H_{14}	98a
Z-**172c**	Cp*	Mes*	$Mo(CO)_5$	396; 391	583	n-C_6H_{14}	98a
Z-**172d**	Cp*	Mes*	$W(CO)_5$	394; 362	581	n-C_6H_{14}	98a
173a	Ph	Mes*	$Cr(CO)_5$	498.9; 415.7	503.5	THF	121a
173b	Ph	Mes*	$Mo(CO)_5$	484.1; 399.5	500.5	THF	121a
173c	Ph	Mes*	$W(CO)_5$	458.8; 359.0	498.1	THF	121a
174a	$CH(SiMe_3)_2$	Mes*	$Ni(CO)_3$	434.8; 429.9	521.3		50c
174b	Mes*	$CH(SiMe_3)_2$	$Ni(CO)_3$	428.1; 422.3	521.3		50c
174c	$CH(Ph)(SiMe_3)$	Mes*	$Ni(CO)_3$	440.1; 425.2	514.2		50c
175a	2,6-$(CF_3)_2C_6H_3$	2,6-$(CF_3)_2C_6H_3$	$Cr(CO)_5$	438.7; 432.6	489	THF	122
175b	2,4,6-$(CF_3)_3C_6H_2$	2,4,6-$(CF_3)_3C_6H_2$	$Cr(CO)_5$	430.2; 427.6	501	THF	122
175c	2,4,6-$(CF_3)_3C_6H_2$	2,4,6-$(CF_3)_3C_6H_2$	$Mo(CO)_5$	412.7; 407.7	510	$CDCl_3$	122b
175d	2,4,6-$(CF_3)_3C_6H_2$	2,4,6-$(CF_3)_3C_6H_2$	$W(CO)_5$	386.5; 359.9	478	THF	122b
175e	2,4,6-$(CF_3)_3C_6H_2$	2,4,6-$(CF_3)_3C_6H_2$	$Pt(PEt_3)Cl_2$	346.6; 337.2	534	CH_2Cl_2	122b
176a	Mes*	NHtBu	$Ni(CO)_3$	341; 164	561	C_6D_6	39
176b	Mes*	NHMes*	$Ni(CO)_3$	416.5; 259.6	501.3	C_6D_6	50c
177a	Mes*	Mes*	Ag^+	435; 378	549	THF	123
177c	Mes*	Mes*	$AuPEt_3^+$	403; 358	555	THF	123
178	$(Me_3Si)_2N$	$(Me_3Si)_2N$	$Cr(CO)_5$	560.2; 540.4	631	C_6D_6	124c
181a	$(Me_3Si)_2CH$	$(Me_3Si)_2CH$	$Cr(CO)_5$	477.3; 446.2	510	C_6D_6	124b,c
				475.8, 444.3	516	$CDCl_3$	125a
181b	$(Me_3Si)_2CH$	$(Me_3Si)_2CH$	$Mo(CO)_5$	465.4; 433.0	515	$CDCl_3$	125a
181c	$(Me_3Si)_2CH$	$(Me_3Si)_2CH$	$W(CO)_5$	443.8, 388.1	514	$CDCl_3$	125a

In contrast to the η^1-ligand the η^2-ligated diphosphene experiences a dramatic shielding (ca. 450 ppm) relative to the free ligand. Thus the ^{31}P nuclei of Cp*P=PCp* (**11**) (δ = 504.0) are shifted by $\Delta\delta = -441.5$ ppm to δ = 62.5 in the π-complex [η^2-Cp*P=PCp*]Pt$(PPh_3)_2$ (**188a**).

In [η^2-Cp*P=PMes*]Pt$(PPh_3)_2$ (**188b**) similar coordination shifts ($\Delta\delta = -438.3$ and -455.6 ppm) were observed. Here doublets of doublets at δ = 52.3 ppm ($^1J_{PP}$ = 433 Hz and $^3J_{PPtP}$ = 36 Hz) and at δ = 28.9 ppm ($^1J_{PP}$ = 433 Hz and $^3J_{PPtP}$ = 46 Hz) were assigned to the diphosphene. The coupling constant $^1J_{PP}$ decreased from 584 Hz in **16** to only 433 Hz in the complex. The couplings of the P atoms of the diphosphene to the ^{195}Pt nucleus are 276 and 205 Hz. The resonances of the PPh_3 ligands show up as doublets of doublets at δ = 25.5 ($^3J_{PPtP}$ = 36 Hz) and δ = 21.9 ($^3J_{PPtP}$ = 46 Hz).[98a] Here the coupling constants $^1J_{PtP}$ increase by 1 order of magnitude (3094 and 3160 Hz). The small Pt–P coupling in the η^2-diphosphene–Pt ensemble and the small trans coupling, $^3J_{PPtP}$, to the phosphane ligands indicate that there is only a small 3s contribution in the bonding between the η^2-ligand and the metal.

The tremendous high-field shift of the phosphorus atoms of a diphosphene upon π-bonding demands an even greater HOMO–LUMO separation in such π-complexes. This invokes a destabilization of the π^*-orbital, a stabilization of the π-orbital and a more or less uneffected n_+-orbital as results from the η^2-ligation of the diphosphene to a transition metal center.

^{31}P NMR data of diphosphene complexes are compiled in the Tables 4–8.

VI. Reactivity of Transition Metal Diphosphene Complexes

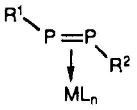
A. Transformation with Retainment of the P=P Double Bond

1. Substitutions

Methanolysis of the silylated η^2-diphosphene ligand in nickel complexes **200** furnished dinuclear complexes **201** with bridging $\mu_2(\eta^2{:}\eta^2)P_2$ units[136c] (Scheme 139).

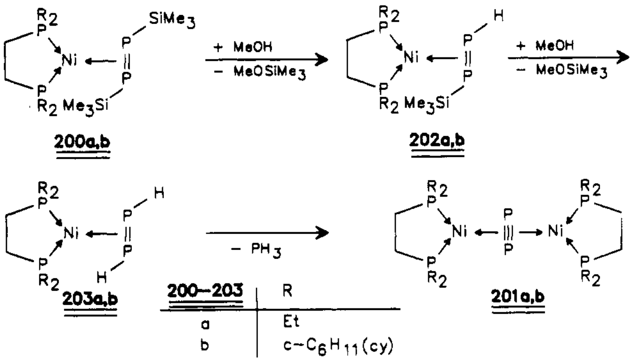
The steric bulk of the chelating $Cy_2PCH_2CH_2PCy_2$ provided enough kinetic stabilization to the transient compounds **202b** and **203b** to allow their detection by ^{31}P NMR. The methanolysis of $(Et_2PCH_2CH_2PEt_2)$-Ni(η^2-Me_3SiP=PtBu) (**200k**) also furnished the diphosphorus species **201a**, whereas **200l** afforded the η^2-HP=PtBu complex **238** in 80% isolated yield under comparable conditions. At 80 °C **238** decomposed to give **201b**[136c] (Scheme 140). The displacement of PPh_3 ligands in complex **192a** by a chelating diphosphane is also feasible[129b] (Scheme 141).

Table 5. ^{31}P-NMR-Data of η^2-Diphosphene Complexes

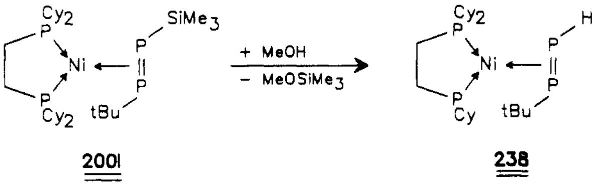


compd	R^1	R^2	ML_n	δ ^{31}P	$^1J_{PP}$, Hz	solvent	ref(s)
188a	Cp*	Cp*	$Pt(PPh_3)_2$	62.5		C_6D_6	98a
188b	Cp*	Mes*	$Pt(PPh_3)_2$	52.8; 29.0	435	C_6D_6	98a
189	Cp*	Mes*	Ni(TMEDA)	55.9; 51.0	440.8	THF-d_8	91b
190	tBuNH	Mes*	$Ni(PnBu_3)_2$	85.5; −55.1	427	toluene-d_8	39
191	2,4,6-$(CF_3)C_6H_2$	$N{=}S(O)Me_2$	$Pt(PPh_3)_2$	130.2; 29.5		C_6H_5Me/C_6D_6	31
192a	C_6F_5	C_6F_5	$Pd(PPh_3)_2$	32.0		C_6H_6	129b
192b	C_6F_5	C_6F_5	$Pt(PPh_3)_2$	−22.0		C_6H_6	129b
192c	C_6F_5	C_6F_5	Pd(diphos)	1.7		C_6H_6	129b
193a	CF_3	CF_3	$Pd(PPh_3)_2$	22.7		d_8-toluene	128b
193b	CF_3	CF_3	$Pt(PEt_3)_2$	−28.0		d_8-toluene	128b
193d	CF_3	CF_3	$Pt(PPh_3)_2$	−6.2		C_6D_6	128b
193e	CF_3	CF_3	Pd(diphos)	19.57		C_6H_5Me	128b.
193f	CF_3	CF_3	Ni(diphos)	19.42		C_6H_5Me	128b
194	H	H	$MoCp_2$	203		$(CD_3)_2SO$	130
195a	Ph	Ph	Pd(diphos)	34.3		C_6H_6	129b
195b	Ph	Ph	$Pt(PPh_3)_2$	18.1		C_6H_6	129b
195c	Ph	Ph	Pt(diphos)	−23.5		C_6H_6	129b
195d	Ph	Ph	$Pt(PMe_2Ph)_2$	4.5		C_6D_6	129b
196	tBu	tBu	$Ni(P\text{-}tBu)_4$	45.03	275	C_6D_6	131
197a	Ph	Ph	$[1,3\text{-}(Me_3Si)_2C_5H_3]_2Zr$	228.91		C_6D_6	132
197b	Ph	Ph	$[1,3\text{-}(Me_3Si)_2C_5H_3]_2Hf$	193.22		C_6D_6	132
197c	tBu	tBu	$[1,3\text{-}(Me_3Si)_2C_5H_3]_2Zr$	270.56		C_6D_6	132
198	Ph	Ph	$Cp_2Ta(H)$	−146; −164	327	C_6D_6	134
199a	$SiMe_3$	$SiMe_3$	$Ni[P(nBu)_3]_2$	−65		C_6D_6	135b
199b	$SiMe_3$	$SiMe_3$	$Ni(PEt_3)_2$	−67		C_6D_6	135b
199c	$SiMe_3$	$SiMe_3$	$Ni(PMe_3)_2$	−76		C_6D_6	135b
199d	$SiMe_3$	$SiMe_3$	$Ni[P(iBu)_3]_2$	−57		C_6H_5Me	135b
199e	$SiMe_3$	$SiMe_3$	$Ni(PPh_3)_2$	−22		C_6H_5Me	135b
199f	tBu	tBu	$Ni(PEt_3)_2$	54		C_6D_6	135b
199g	tBu	$SiMe_3$	$Ni(PEt_3)_2$	76; −86	384	C_6H_5Me	135b
199h	Ph	Ph	$Ni(PEt_3)_2$	−5		C_6D_6	135b
200a	$SiMe_3$	$SiMe_3$	$Ni[Et_2P(CH_2)_2PEt_2]$	−101		C_6D_6	136b
200b	$SiMe_3$	$SiMe_3$	$Ni[Cy_2P(CH_2)_2PCy_2]$	−103		C_6D_6	136b
200c	$SiMe_3$	$SiMe_3$	$Ni[Ph_2P(CH_2)_2PPh_2]$	−64		C_6H_5Me	136b
200d	Ph	Ph	$Ni[Et_2P(CH_2)_2PEt_2]$	−20		C_6D_6	136b
200e	Ph	Ph	$Ni[Cy_2P(CH_2)_2PCy_2]$	−34		C_6D_6	136b
200f	Ph	Ph	$Ni[Ph_2P(CH_2)_2PPh_2]$	−2		C_6D_6	136b
200g	Me	Me	$Ni[Cy_2P(CH_2)_2PCy_2]$	−28		C_6D_6	136b
200h	tBu	tBu	$Ni[Et_2P(CH_2)_2PEt_2]$	55		C_6D_6	136b
200i	tBu	tBu	$Ni[Cy_2P(CH_2)_2PCy_2]$	42		C_6D_6	136b
200j	tBu	tBu	$Ni[Ph_2P(CH_2)_2PPh_2]$	69		C_6D_6	136b
200k	$SiMe_3$	tBu	$Ni[Et_2P(CH_2)_2PEt_2]$	57; −107	382	C_6D_6	136c
200l	$SiMe_3$	tBu	$Ni[Cy_2P(CH_2)_2PCy_2]$	48; −110	369	C_6D_6	136c
200m	$SiMe_3$	tBu	$Ni[Ph_2P(CH_2)_2PPh_2]$	82; −78	392	C_6H_5Me	136c
202	$SiMe_3$	H	$Ni[Cy_2P(CH_2)_2PCy_2]$	−117; −126	315	C_6D_6	136c
203b	H	H	$Ni[Cy_2P(CH_2)_2PCy_2]$	−120		C_6H_5Me	136c
204	$SiMe_3$	$SiMe_3$	$Pt(PEt_3)_2$	−105		C_6D_6	137
205	tBu	tBu	$Pt(PEt_3)_2$	29		C_6D_6	137
206	tBu	$SiMe_3$	$Pt(PEt_3)_2$	46; −119	351	C_6H_5Me	137
207a	$SiMe_3$	$SiMe_3$	$Pt(PPh_3)_2$	−57		C_6H_5Me	137
207b	tBu	tBu	$Pt(PPh_3)_2$	54		C_6H_5Me	137
238	tBu	H	$Ni[Cy_2P(CH_2)_2PCy_2]$	41; −120	363	C_6D_6	136c

Scheme 139



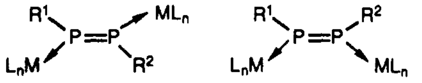
Scheme 140



2. Complexation and Decomplexation

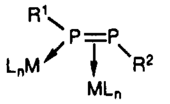
The addition of further complex fragments to the η^2-ligated diphosphene in (diphos)Pd(η^2-PhP=PPh) (**194a**) constitutes a pathway to complexes of higher nuclearity (Scheme 133). The transfer of the PhP=PPh

Table 6. ^{31}P NMR Data of μ-(η^1:η^1)-Diphosphene Complexes



compd	R¹	R²	ML$_n$	δ ^{31}P	$^1J_{PP}$, Hz	solvent	ref(s)
E-**185a**	$(Me_3Si)_2CH$	$(Me_3Si)_2CH$	$Cr(CO)_5$	425.9		CD_2Cl_2	125a
E-**185b**	$(Me_3Si)_2CH$	$(Me_3Si)_2CH$	$W(CO)_5$	342.2		CD_2Cl_2	125a
E-**209a**	Mes	Mes	$Cr(CO)_5$	419.9		C_6D_6	124c
Z-**209a**	Mes	Mes	$Cr(CO)_5$	396.7		C_6D_6	124c
Z-**209b**	Mes	Mes	$Mo(CO)_5$	367.7		CD_2Cl_2	125a
Z-**209c**	Mes	Mes	$W(CO)_5$	313.6		CD_2Cl_2	125a
E-**210**	Me_3SiCH_2	Me_3SiCH_2	$Cr(CO)_5$	189		C_6D_6	124c
E-**212a**	Ment	Ment	$Cr(CO)_5$	447.5		n-C_5H_{12}	140
E-**212b**	Ment	Ment	$W(CO)_5$	361.5		n-C_5H_{12}	140
E-**215**	Ph	Ph	$Cr(CO)_5$	369			125a,142
E-**216**	Mes	Mes	$Fe(CO)_4$	335.5		C_6H_6	144b
E-**217**	$(Me_3Si)_2CH$	$(Me_3Si)_2CH$	$Fe(CO)_4$	384.6		C_6H_6	144b
E-**218**	$(Me_3Si)_2N$	$(Me_3Si)_2N$	$Fe(CO)_4$	403.9		C_6H_6	144b
E-**219**	Mes	Mes	$(CO)_3CpV$	426		C_6D_6/THF	146
E-**220a**	Mes*	$(Me_3Si)_2CH$	$Ni(CO)_3$	367.2; 389.1	418.2		50c
E-**220b**	Mes*	$(Me_3Si)(Ph)CH$	$Ni(CO)_3$	378.1; 388.2	435.2		50c
E-**220c**	Mes*	NHMes*	$Ni(CO)_3$	214.2; 377.1	407.5		50c

Table 7. ^{31}P NMR Data of μ_2-(η^1:η^2)-Diphosphene Complexes



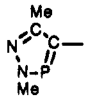
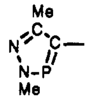
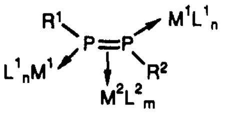
compd	R¹	R²	ML$_n$	δ ^{31}P	$^1J_{PP}$, Hz	solvent	ref(s)
221	Ph	Ph	$Fe(CO)_4$	52.1; −34.5	415	CD_2Cl_2	151
222			$Fe(CO)_4$	8.22; −52.38	384	CD_2Cl_2	152
224a	Mes*O	Mes*O	$Fe(CO)_4$	233.8; 193.4	532	C_6D_6	124b, 144b
226a	iPr_2N	iPr_2N	$Fe(CO)_4$	97.3; 61.7	477	Et_2O	145
226b	Cy_2N	Cy_2N	$Fe(CO)_4$	99.8; 63.2	488	Et_2O	145

Table 8. ^{31}P NMR Data of μ_3-(η^1:η^1:η^2)-Diphosphene Complexes



compd	R¹	R²	M¹L¹$_n$	M²L²$_m$	δ ^{31}P	solvent	ref(s)
214	Ph	Ph	$Cr(CO)_5$	$Cr(CO)_5$	97	CH_2Cl_2	142a,153
227a	Ph	Ph	$W(CO)_5$	$W(CO)_5$	−16.6	CH_2Cl_2	153
227b	4-MeO-C_6H_4	4-MeO-C_6H_4	$Cr(CO)_5$	$Cr(CO)_5$	108.5	CH_2Cl_2	153
227c	Me	Me	$Cr(CO)_5$	$Cr(CO)_5$	78.1	CH_2Cl_2	153
227d	Me	Me	$Mo(CO)_5$	$Mo(CO)_5$	27.2	CH_2Cl_2	153
227e	Et	Et	$Cr(CO)_5$	$Cr(CO)_5$	103.7	CH_2Cl_2	153
227f	nBu	nBu	$Cr(CO)_5$	$Cr(CO)_5$	99.9	CH_2Cl_2	153
231a	Ph	Ph	$W(CO)_5$	Pd(diphos)	17.0	C_6H_6	129b

ligand from **207** to **232** should also be referred to in this section (Scheme 134). A similar transfer of the diphosphene ligand was observed between $(Ph_3P)_2Pd(\eta^2$-$CF_3P{=}PCF_3)$ (**193a**) and its Pt homolog **193b** via $(Ph_3P)_2Pt(\eta^2$-$C_2H_4)$.[128b]

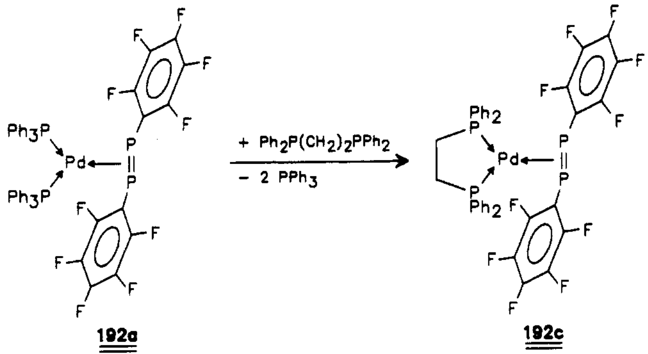
Thermally induced decomplexations of metal fragments from diphosphene ligands have also been illustrated before in the Schemes 98 and 122.

3. Thermolysis of the Coordinated Diphosphene

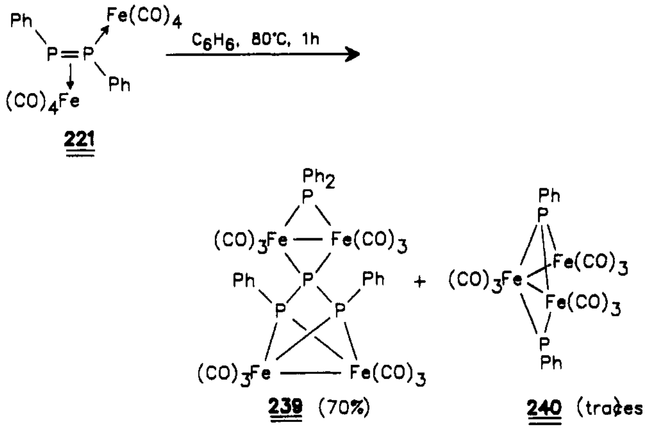
Thermolysis of the η^1:η^2-diphosphene complex **221** took a different course. Heating a benzene solution of **221** for 1 h at 80 °C led to the disintegration of the diphosphene unit (Scheme 142). An X-ray structure analysis of **239** revealed the main product of the thermolysis as a tetranuclear complex with a μ_4-bridging η^3-PhPPPPh ligand. Another fragment of the former PhP=PPh ligand constitutes a μ_2-PPh_2 bridge.[161]

At elevated temperatures compounds **221** as well as **239** experienced another rearrangement with the result of the tetranuclear cluster **241** (Figure 10). This complex features an μ_4-(η^2:η^1)-diphosphenyl ligand which unsymmetrically caps a square of iron atoms; μ_4-PPh and μ_2-PPh_2 bridges are also present in the molecule[161] (Scheme 143). The ^{31}P NMR resonances of the phosphorus nuclei of the diphosphenyl fragment were assigned to signals at δ = 117.3 (ddd, $^1J_{PP}$ = 357 Hz) and δ = 169.5 ppm (ddd, $^1J_{PP}$ = 357 Hz).

Scheme 141



Scheme 142



4. 1,2-Additions to the P=P Double Bond in Diphosphene Complexes

The permanganate-colored compound **215** reacted stereoselectively with alcohols, amines, and acids to the expected yellow diphosphane complexes **242a–d**. They were found exclusively in the threo form due to a trans addition of HX to the multiple bond. The trinuclear complex **214** was also employed in these reactions as it cleanly liberates **215**, when heated to 70 °C[142b] (Scheme 144). The P–P bond in **242d** was not affected by additional HCl. This is remarkable with respect to the smooth stepwise cleavage of the P=P bond in $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**9**).[23b,92c]

In contrast to this the bromination of **215** at 65 °C yielded a 1:1 mixture of the meso and racemic dibromo products **243**[142b] (Scheme 145). The reverse reaction was effected by treatment of **243** with zinc. The η^1:η^1:η^2-complexes **214** and **227** also exhibited the reactivity of P–P double bonds, even without the prior release of the η^2-ligated $Cr(CO)_5$ moiety. The addition of acetic acid to the phenyl derivative or that of methanol to the anisyl compound proceeded stereoselectively in a trans fashion, whereas with the ethyl derivative and methanol two stereoisomers were produced[153] (Scheme 146).

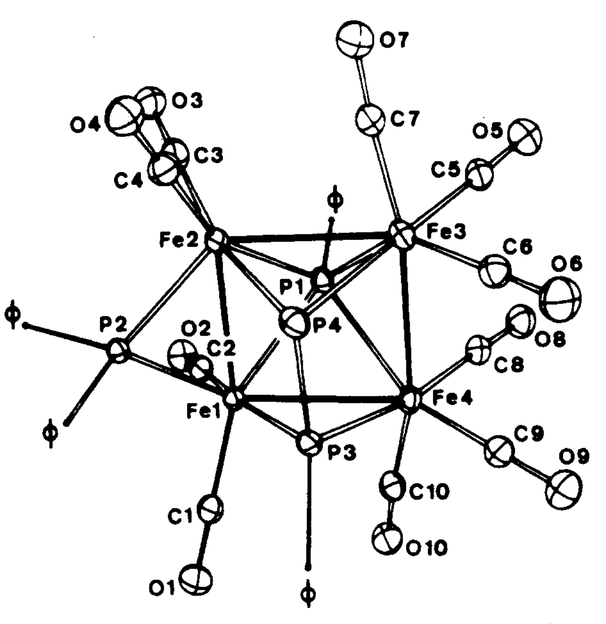
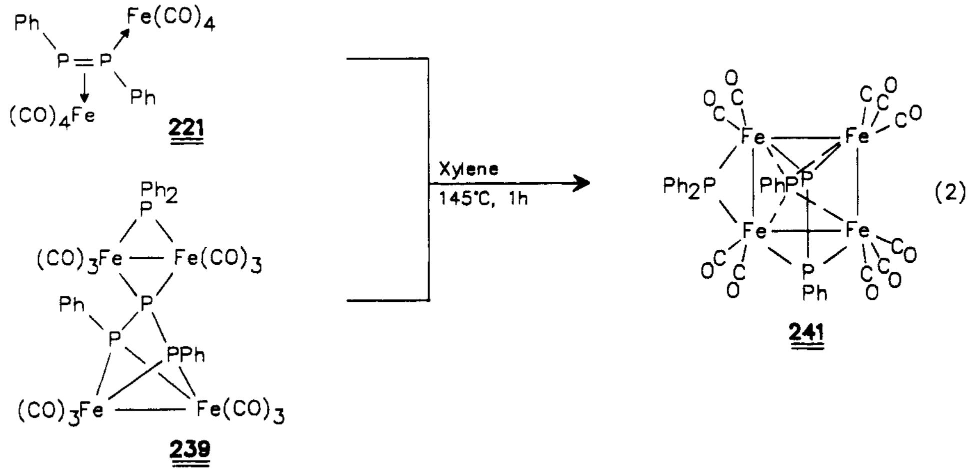


Figure 10. Structure of **241**. Selected bond lengths (Å) and bond angles (deg): Fe(1)–P(3) 2.205 (2), Fe(4)–P(3) 2.247 (2), Fe(2)–P(4) 2.297 (2), Fe(3)–P(4) 2.342 (2), P(3)–P(4) 2.126 (2); Fe(1)–P(3)–Fe(4) 76.64 (6), Fe(2)–P(4)–Fe(3) 71.95 (6), C(29)–P(3)–P(4) 113.1 (1). Reprinted from ref 161. Copyright 1988 American Chemical Society.

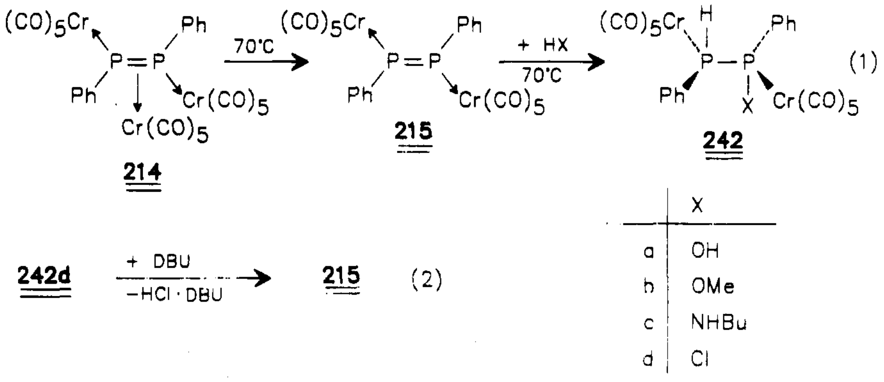
A mixture of the meso and racemic forms of complex **246** was synthesized by the $LiAlH_4$ reduction of diphosphene complex **212a**[140] (Scheme 147).

A hydrometalation process was responsible for the conversion of the μ-(η^1:η^2)-diphosphene diiron compound **221** into trinuclear complexes **247a,b** with a bridging diphosphane-1,1-diido ligand. The constitution of the products invoked an α-addition of the metal hydride to P_B with a subsequent migration of a $Fe(CO)_4$ moiety[151] (Scheme 148).

Scheme 143

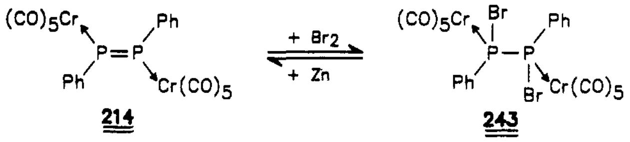


Scheme 144

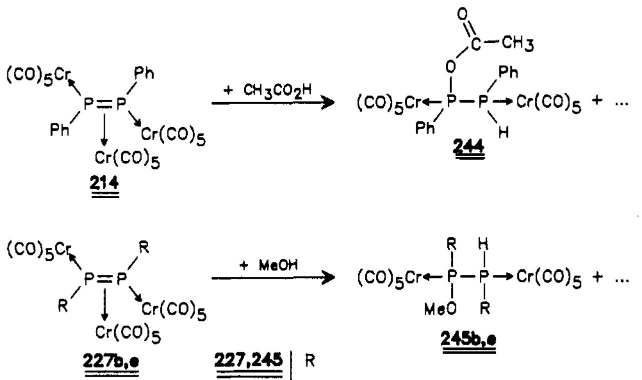


	X
a	OH
b	OMe
c	NHBu
d	Cl

Scheme 145

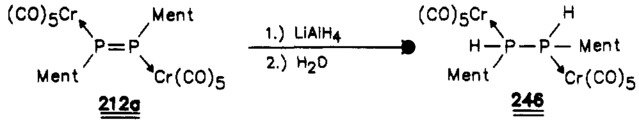


Scheme 146

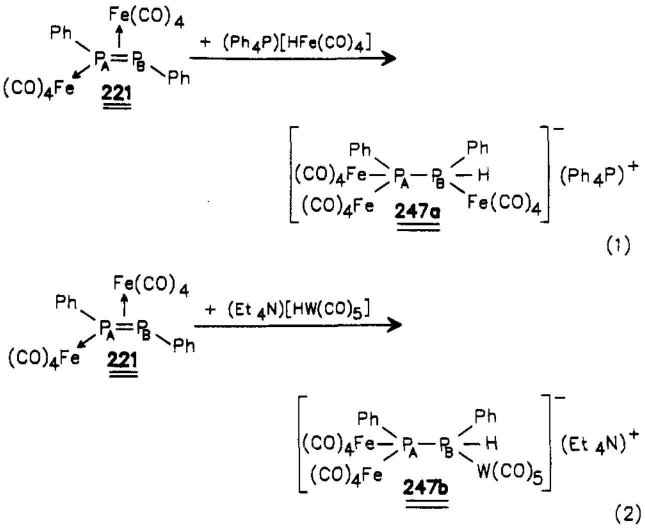


227,245	R
b	4−MeO−C6H4
e	Et

Scheme 147



Scheme 148



5. Cycloadditions to Diphosphene Complexes

A number of cycloadditions to the unsupported as well as supported P=P double bond in complexes of the type **215** or **214** were reported by Huttner et al. The oxidation of **215** or **227g** (R = p-MeOC$_6$H$_4$) with 1 equiv of sulfur yielded the corresponding thiadiphosphirane complexes **248a,b**[126a,142b] (Scheme 149). The related diphosphirane complex **249** was formed when the violet solution of **215** in toluene was allowed to react with diazomethane[142b] (Scheme 150). In a formal sense the azadiphosphirane complex **250** was the product of a [2 + 1] cycloaddition of phenylnitrene to the P=P bond of **214**. The intermediacy of a [3 + 2] cycloadduct with a subsequent N$_2$ elimination, however, could not be excluded.[126a]

[2 + 4] cycloaddition reactions of the diphosphene complexes **215**[142b] or alternatively **227f**[153] with cyclopentadiene or 2,3-dimethylbutadiene furnished complexes of cyclic diphosphanes (Scheme 151). According to ^{31}P NMR analysis these [2 + 4] cycloadditions proceeded stereoselectively and only one diastereoisomer was observed.

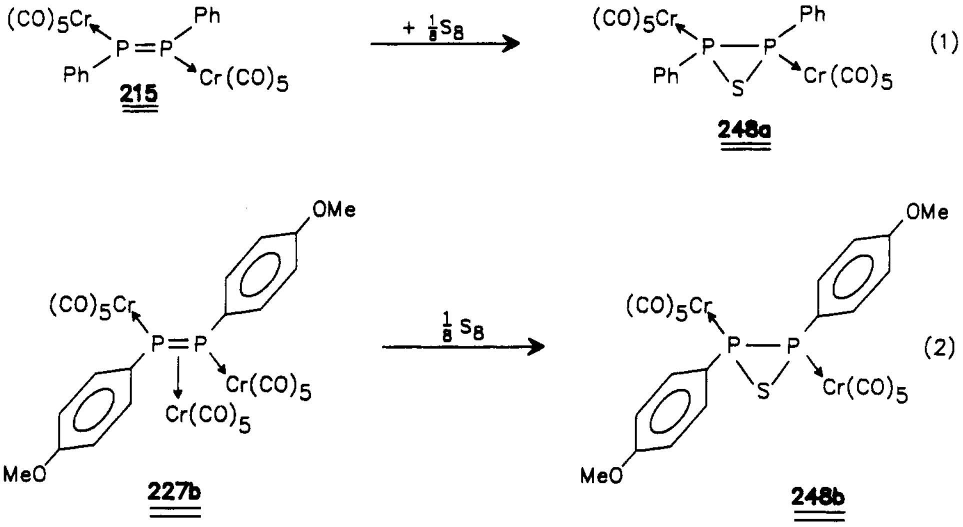
6. Insertion Reactions into the P=P Double Bond of Diphosphene Complexes

During the attempted purification by chromatography on a silica column the (η^1:η^2)-diphosphene iron complexes **226a–c** experienced hydrolysis of the PP bond, and the dinuclear diphosphine oxide complexes **253a–e** were isolated[145] (Scheme 152).

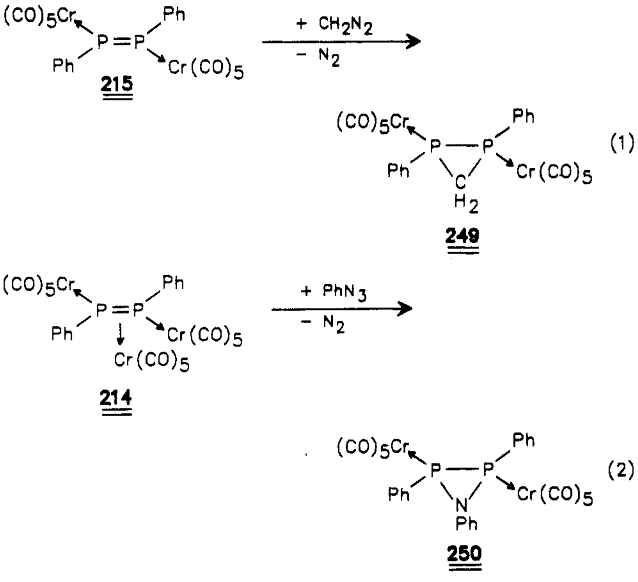
Vahrenkamp described insertion and cleavage reactions of the P–P bond in the diferradiphosphatetrahedrane **234**[157b] (Scheme 153). CO insertion into the P=P multiple bond of **234** occurred when a benzene solution of the tetrahedrane was exposed to a 50-bar CO pressure at 80 °C. The most remarkable structural feature of the resulting diphospho urea **254** is the acute angle PC(O)P (84.6°) at the carbonyl bridge (Figure 11). Complex **255** was the result of the insertion of ethylene into the P–P bond of **234**.

The hydrogenation of **234** with elemental H$_2$ (50 bar, 80 °C) led to an isomeric mixture of the butterfly molecule **233** containing μ_2-(PHtBu) ligands. The same result was obtained by superhydride reduction of **234** and subsequent methanolysis of the reaction mixture[157b] (Scheme 154).

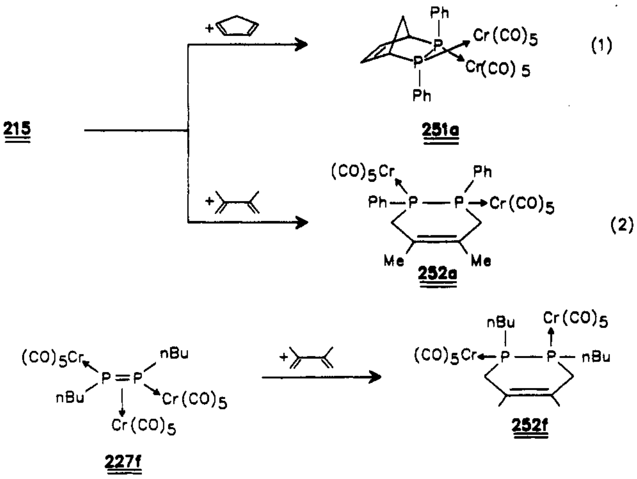
Scheme 149



Scheme 150

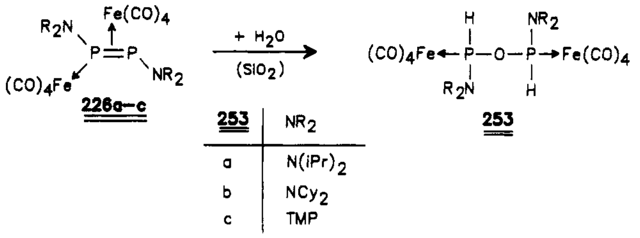


Scheme 151



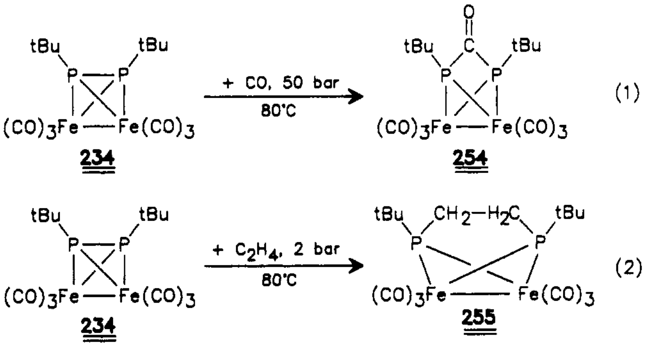
The P–P bond of **234** was also cleaved when the cluster was allowed to react with anhydrous hydrogen chloride in benzene (Scheme 155). The tetrahedrane was not affected by S_8 or diazomethane in boiling benzene, whereas decomposition took place with Cl_2, $SOCl_2$, and PCl_5.

Scheme 152



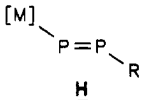
253	NR2
a	N(iPr)2
b	NCy2
c	TMP

Scheme 153

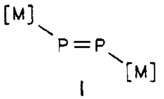


VII. Metallodiphosphenes (Diphosphenyl Complexes)

A common feature of the complexes of the types A–G in Scheme 85 is that the structural integrity of the diphosphene entity is mainly preserved. There are other diphosphenes conceivable where one or both of the organic substituents are replaced by metal complex fragments (H or I):



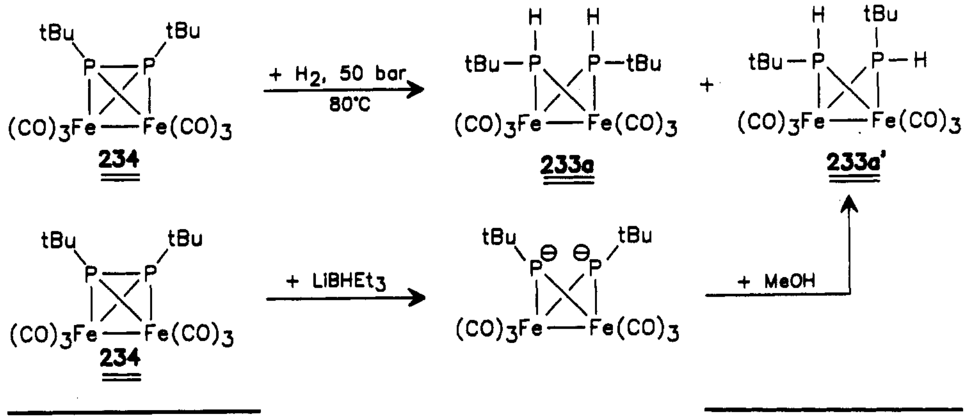
H



I

Because of the electronic and structural influences the metal fragment imposes upon the P═P moiety compounds H and I should display a different chemistry as the type of complexes already described, and therefore they merit discussion in a separate section.

Scheme 154



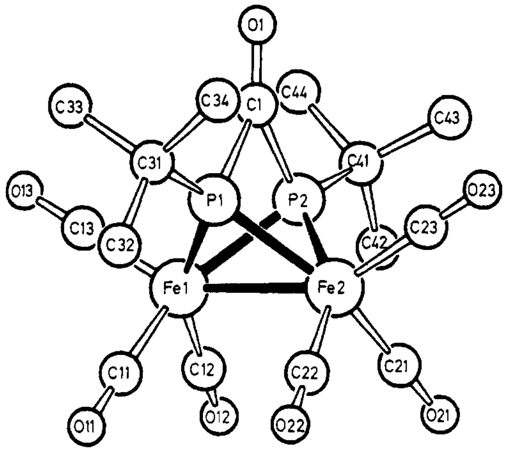
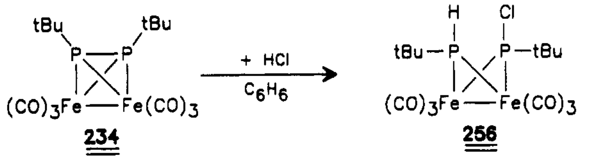


Figure 11. Molecular structure of **254**. Selected bond lengths (Å) and bond angles (deg): Fe(1)–Fe(2) 2.623 (2), Fe(1)–P(1) 2.228 (4), Fe(1)–P(2) 2.228 (4), Fe(2)–P(1) 2.228 (4), Fe(2)–P(2) 2.236 (4), P(1)–P(2) 2.525 (4), P(1)–C(1) 1.875 (9), P(2)–C(1) 1.878 (9), C(1)–O(1) 1.172 (9); Fe–P–Fe 72.1/72.0 (1), P–Fe–P 69.0/68.9 (1), P(1)–C(1)–P(2) 84.6 (6). Reprinted from ref 157. Copyright 1986 Verlag der Zeitschrift fuer Naturforschung.

Scheme 155



A. Synthesis, Structures, and Spectra

The first representative of a transition metal substituted diphosphene, the complex (E)-(η^5-C_5Me_5)$(CO)_2$FeP=PMes* (**257**) (Figure 12) was synthesized by the reaction of a disilylphosphidoiron complex with Mes*PCl_2 in THF (Scheme 156). The orange crystalline solid was obtained in yields up to 70%.[162] In the ^{31}P NMR spectrum of **257** two doublets (δ = 553.5 and 715.2, Table 9) were observed in the characteristic region of unsymmetric diphosphene with a large $^1J_{PP}$ coupling constant of 594.2 Hz. The X-ray structure analysis ascertained the presence of an unsupported P=P bond [2.027 (3) Å] which compares well with the corresponding bond length in Mes*P=PMes* (**1**). The same is true for the angle P–P–C_{Aryl} [102.4 (1)°] at the organically substituted phosphorus atom, which is considerably smaller as the valence angle at the metalated phosphorus [109.8 (1)°].

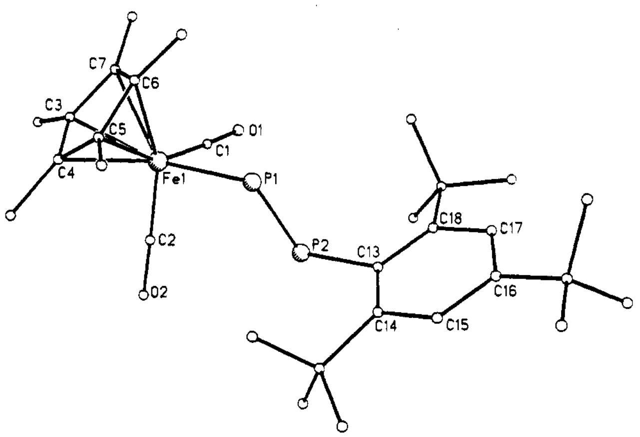
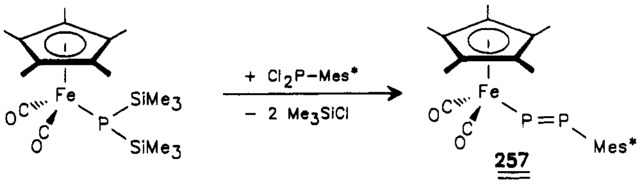


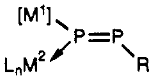
Figure 12. Molecular structure of **257**. Selected bond lengths (Å) and bond angles (deg): Fe(1)–P(1) 2.260 (1), P(1)–P(2) 2.027 (3), P(2)–C(13) 1.873 (3); Fe(1)–P(1)–P(2) 109.8 (1), P(1)–P(2)–C(13) 102.4 (1). Reprinted from ref 162b. Copyright 1987 American Chemical Society.

Scheme 156



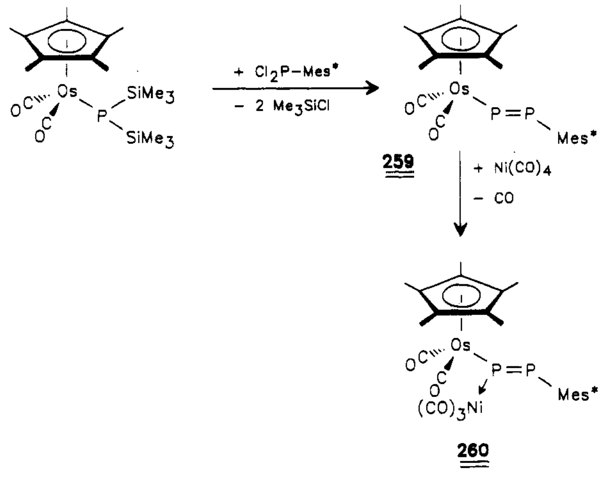
In order to explore the scope and the limits of the synthetic principle performed here, the homologous ruthenium and osmium disilylphosphido complexes were allowed to react with Mes*PCl_2 under comparable conditions. Whereas the preparation of the orange-red crystalline $(C_5Me_5)(CO)_2$RuP=PMes* **258** proceeded without difficulties, the isolation of the analogous osmium complex **259** failed. Its formation was inferred from two doublets in the ^{31}P NMR spectrum at δ = 543.2 and 632.0 with a P–P coupling of 583.9 Hz and from the conversion of **259** into the $Ni(CO)_3$ adduct **260** upon treatment with an excess of $Ni(CO)_4$[162b] (Scheme 157). The decreased stability of the diphosphenyl complex **259** with the 5d metal osmium, as opposed to the 3d and 4d congeners, was also met in the chemistry of manganese[163] and rhenium[164] (Scheme 158). Without any problems the manganese complex **261** was synthesized by the reaction of the respective disilylphosphido complex with supermesityl dichlorophosphane in THF. When a similar synthetic procedure was applied to the analogous rhenium disilylphosphido complex the isolation of any stable diphosphenyl

Table 9. ^{31}P NMR Data of Metallodiphosphenes [M]P = PR and their η^1-Complexes



compd	[M¹]	R	M^2L_n	$\delta\ ^{31}P_M$	$\delta\ ^{31}P_R$	$^1J_{PP}$, Hz	solvent	ref(s)
257	$Cp^*(CO)_2Fe$	Mes*		715.2	553.5	594.2	C_6D_6	162a,b
258	$Cp^*(CO)_2Ru$	Mes*		676.5	551.6	597.1	C_6D_6	162a,b
259	$Cp^*(CO)_2Os$	Mes*		632.0	543.2	583.9	THF	162b
261	$Cp^*(CO)(NO)Mn$	Mes*		728.5	535.7	597.4	C_6D_6	163
262	$Cp^*(CO)(NO)Re$	Mes*		637.2	532.1	583.1	THF	164
268a	$Cp(CO)(PPh_3)Fe$	$2,6\text{-}(CF_3)_2C_6H_3$		861.8	487.0	615	THF	122a
268b	$Cp(CO)(PPh_3)Fe$	$2,4,6\text{-}(CF_3)_3C_6H_2$		877.9	475.2	599	THF	122a
269a	$Cp^*(CO)_2Fe$	$2,6\text{-}(CF_3)_2C_6H_3$		797.1	488.9	594	THF	122a
269b	$Cp^*(CO)_2Fe$	$2,4,6\text{-}(CF_3)_3C_6H_2$		812.3	475.5	592	THF	122a
272a	$(C_5Me_4Et)(CO)_2Fe$	Mes*		719.7	553.4	596	THF	166a
272b	$(C_5Me_4nBu)(CO)_2Fe$	Mes*		719.6	553.7	597	THF	166a
273	$(1,3\text{-}tBu_2C_5H_3)(CO)_2Fe$	Mes*		678.1	559.1	598	THF	166a
274	$Cp(CO)_2Fe$	Mes*		671	563	600	THF	91b,d
275	$Cp(CO)(PPh_3)Fe$	Mes*		765.4	562.0	621.2	C_6D_6	162b
276	$Cp^*(CO)_3Cr$	Mes*		653.0	559.6	610.1	$CDCl_3$	98a, 167
277a	$Cp^*(PPh_3)Ni$	Mes*		754	543	623	toluene/C_6H_6	98a
277b	$Cp^*[P(nBu)_3]Ni$	Mes*		784	538	632	toluene/C_6H_6	98a
278	$Cp^*(CO)_2Fe$	Cp*		690	559	625	THF	91b,d
285	$Cp^*(CO)_2Fe$	$C(SiMe_3)_3$		788.2	602.3	654.8	C_6D_6	169
270a	$Cp(CO)(PPh_3)Fe$	$2,6\text{-}(CF_3)_2C_6H_3$	$Cr(CO)_5$	665.7	473.6	605	THF	122a
270b	$Cp(CO)(PPh_3)Fe$	$2,4,6\text{-}(CF_3)_3C_6H_2$	$Cr(CO)_5$	676.0	461.7	624	CD_2Cl_2	122a
271a	$Cp^*(CO)_2Fe$	$2,6\text{-}(CF_3)_2C_6H_3$	$Cr(CO)_5$	650.9	491.5	585	THF	122a
271b	$Cp^*(CO)_2Fe$	$2,4,6\text{-}(CF_3)_3C_6H_2$	$Cr(CO)_5$	661.5	477.3	587	THF	122a
263	$Cp^*(CO)(NO)Re$	Mes*	$Cr(CO)_5$	562.7	509.6	560.9	C_6D_6	164
289	$Cp^*(CO)_2Fe$	Mes*	$Cr(CO)_5$	599.6	572.0	593.4	C_6D_6	164
290	$Cp^*(CO)_2Fe$	Mes*	$Fe(CO)_4$	546.3	514.6	581.9	C_6D_6	171
291	$Cp^*(CO)_2Fe$	Mes*	$Ni(CO)_3$	591.7	509.9	576.6	C_6D_6	172
292	$(C_5Me_4Et)(CO)_2Fe$	Mes*	$Cr(CO)_5$	597	573	595	THF	166b
293	$(C_5Me_4nBu)(CO)_2Fe$	Mes*	$Cr(CO)_5$	597.5	572.8	594	THF	166b
294	$(1,3\text{-}tBu_2C_5H_3)(CO)_2Fe$	Mes*	$Cr(CO)_5$	574.8	565.7	589	THF	166b
295	$Cp^*(CO)_2Ru$	Mes*	$Fe(CO)_4$	503.9	495.9	571.6	C_6D_6	171
296	$Cp^*(CO)_2Ru$	Mes*	$Ni(CO)_3$	556.7	503.7	564.1	C_6D_6	172
297	$Cp^*(CO)_2Os$	Mes*	$Fe(CO)_4$	437.5	491.8	553.3	C_6D_6	171b
298	$Cp^*(CO)_2Os$	Mes*	$Ni(CO)_3$	500.1	495.6	545.8	C_6D_6	162b
299	$Cp^*(CO)(NO)Mn$	Mes*	$Cr(CO)_5$	603.6	562.1	593.1	C_6D_6	164

Scheme 157



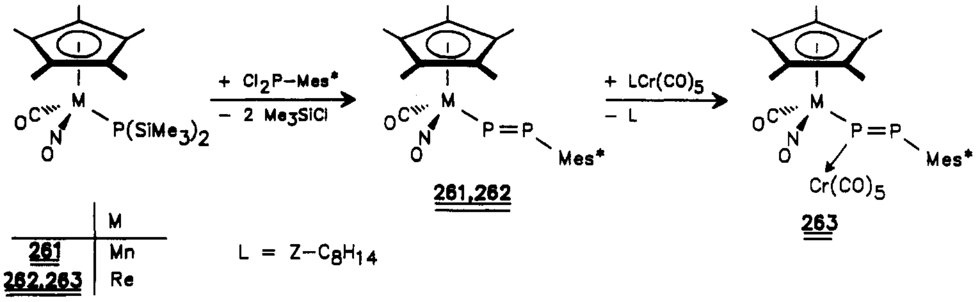
complex was hampered. The presence of two doublets at δ = 637.2 and 532.1 ppm with the characteristic J_{PP} constant of 538.1 Hz in the ^{31}P NMR spectrum of the reaction mixture indicated the transient appearance of diphosphenyl complex **262**. Trapping the thermolabile **262** was accomplished by its conversion in the $Cr(CO)_5$ adduct **263**, which was isolated by column chromatography as a stable crystalline solid.[164]

Attempts to extend the same synthetic approach to diphosphenyl complexes to the early transition metals zirconium and hafnium clearly showed the limitation of this concept.[42] The reaction of the $Cp_2M(CH_3)[P(SiMe_3)_2]$ **264** (M = Zr, Hf) with Mes^*PCl_2 resulted in the production of $Cp_2M(CH_3)Cl$ and thermolabile $Mes^*P{=}PSiMe_3$ (**29a**) instead of the expected metallodiphosphenes. Obviously complexes **264a,b** functioned as disilylphosphido transfer reagents.[42]

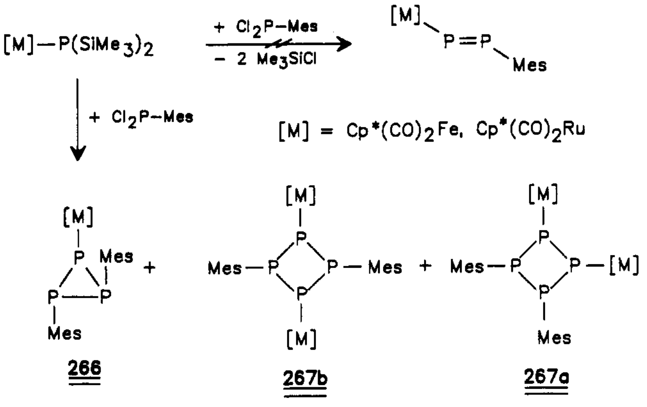
The synthesis of metallodiphosphenes is also governed by sterical restrictions as known from other diphosphenes. This became especially evident when the complexes $Cp^*(CO)_2MP(SiMe_3)_2$ (M = Fe, Ru) were allowed to react with mesityldichlorophosphane. No diphosphenyl complexes were detected in the reaction solution. Instead a mixture of metal-functionalized cyclotriphosphanes and cyclotetraphosphanes (**266** and **267**) were obtained[165] (Scheme 159).

The size of the nonafluoromesityl- and the hexafluoro-*o*-xylyl groups should be somewhere among those of the supermesityl and the mesityl substituents (Scheme 160). Therefore it was interesting to test the reactivity of (nonafluoromesityl)dichlorophosphane ($2,4,6\text{-}(CF_3)_3C_6H_2PCl_2$) and (hexafluoro-*o*-xylyl)dichlorophosphane [$2,6\text{-}(CF_3)_2C_6H_3PCl_2$] toward several disilylphosphido complexes of iron.[122] In addition to small amounts of the symmetric diphosphenes **14** and **41** the thermolabile diphosphenyl complexes **268**, **269a,b** were formed in these reactions. Their isolation failed. Trapping experiments with [(*Z*)-cyclooctene]$Cr(CO)_5$ furnished the corresponding $Cr(CO)_5$ adducts **270a,b** and **271a,b**.[122]

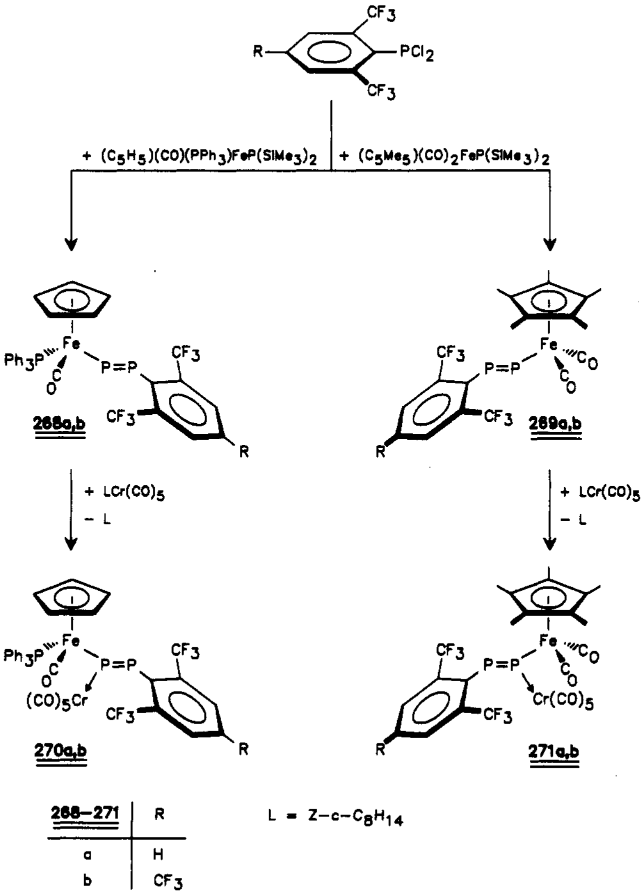
Scheme 158



Scheme 159



Scheme 160



The influence of the η^5-ring at the metal center on the course of the diphosphenyl complex formation was also studied. With the bulky ligands η^5-C_5Me_4Et, η^5-C_5Me_4n-Bu, and 1,3-$tBu_2C_5H_3$ the preparation of stable diphosphenyl complexes was also feasable.[166a]

With $(C_5H_5)(CO)_2FeP(SiMe_3)_2$, which contains the parent cyclopentadienyl ring the synthesis of a stable diphosphenyl complex failed. However, the replacement of a CO group by the more bulky and electron-rich triphenylphosphane ligand constitutes a situation, where the preparation of the isolable diphosphenyl complex **275** proceeds without difficulty[162b] (Scheme 161).

A complementary access to diphosphenyl complexes involves the oxidative addition of the pentamethylcyclopentadienyl-derived diphosphene **16** to transition metal complexes containing labile ligands. Stirring a suspension of $(CH_3CN)_3Cr(CO)_3$ and **16** for 3 days in toluene gave the corresponding chromium diphosphenyl complex **276**[98a,167] (Scheme 162). An analogous molybdenum complex was detected by ^{31}P NMR spectroscopy as a minor product in the reaction of $(CH_3CN)_3Mo(CO)_3$ and **16**, but could not be isolated.

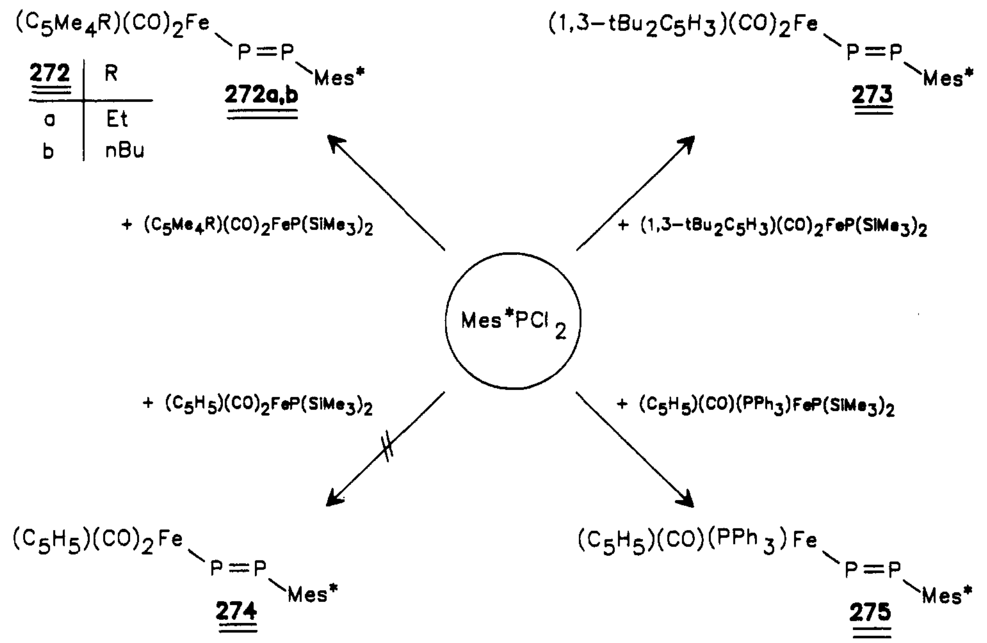
Unstable nickel diphosphenyl complexes **277a,b** were formed when **16** was allowed to react with (ethylene)-bisphosphane nickel species.[91b,98a] This was inferred from the spectroscopic data showing doublets at δ = 543 and δ = 754 ($^1J_{PP}$ = 623 Hz) for the ^{31}P nuclei of the P=P group in **277a**. In the transformation leading to **277a** a η^1-complex such as $[\eta^1$-Cp*P=PMes*](Ph_3P)-Ni was invoked as intermediate, whereas the generation of **277b** was believed to proceed via the π-complex $[\eta^2$-Cp*P=PMes*]$(nBu_3P)_2$Ni.

As shown in section II.C, the pentamethylcyclopentadienyl group in diphosphenes **11** and **16** is prone to nucleophilic substitution. In keeping with this, Cp*P=PMes* (**16**) underwent reaction with NaFe-$(CO)_2$Cp* to produce diphosphenyl complex **257** (Scheme 163). The analogous reaction with the less bulky Na[Fe$(CO)_2$Cp] afforded the thermolabile complex **274**, which was characterized by doublets at δ = 671 and 563 ppm ($^1J_{PP}$ = 600 Hz) in the ^{31}P NMR spectrum.[91b,d]

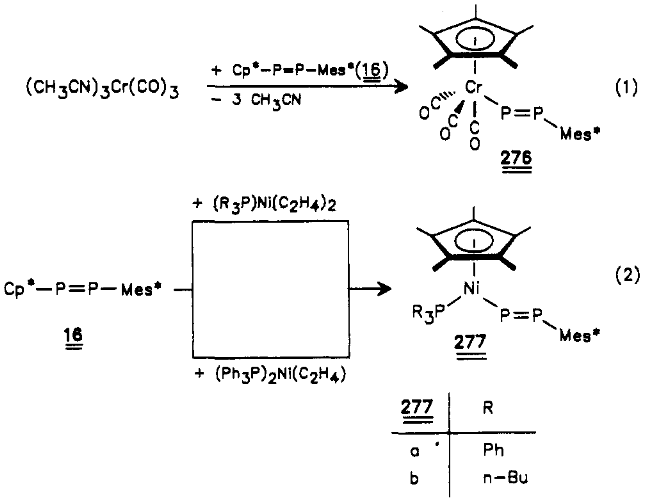
Attempts to synthesize pentamethylcyclopentadienyl-functionalized diphosphenyl complexes such as **278** led to the organometallic tetraphospha[1.1.0]-bicyclobutane **280**[91b,d] (Scheme 164). The formation of **280** involved the head-to-tail cyclodimerization of transient **278** and subsequent loss of two Cp* fragments from cyclotetraphosphane **279**, as evidenced by ^{31}P NMR studies.

The loss of pentamethylcyclopentadienyl rings from phosphorus atoms was impressively demonstrated by the conversion of **11** into the P_6 ligand of the triple-decker complex **281**[168] (Scheme 165). The crucial step in the synthesis of the metallodiphosphene **285** is the 1,3-Me_3Si shift from phosphorus to carbon in the metal-functionalized 1,2-diphospha-2-propene **282**. This mi-

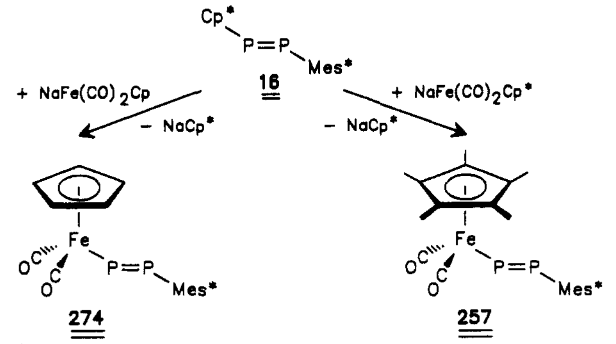
Scheme 161



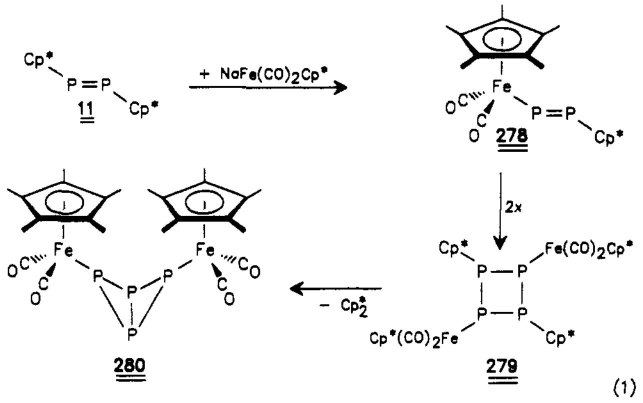
Scheme 162



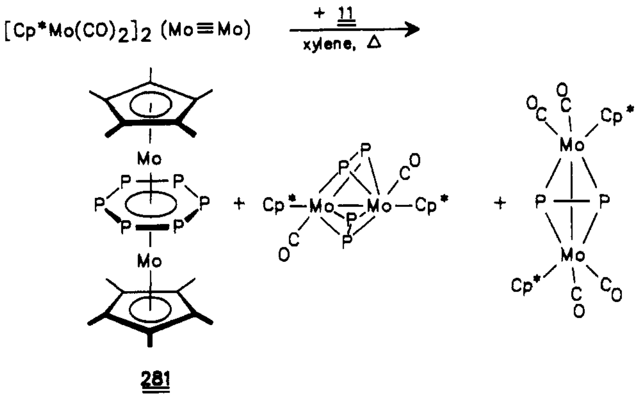
Scheme 163



Scheme 164



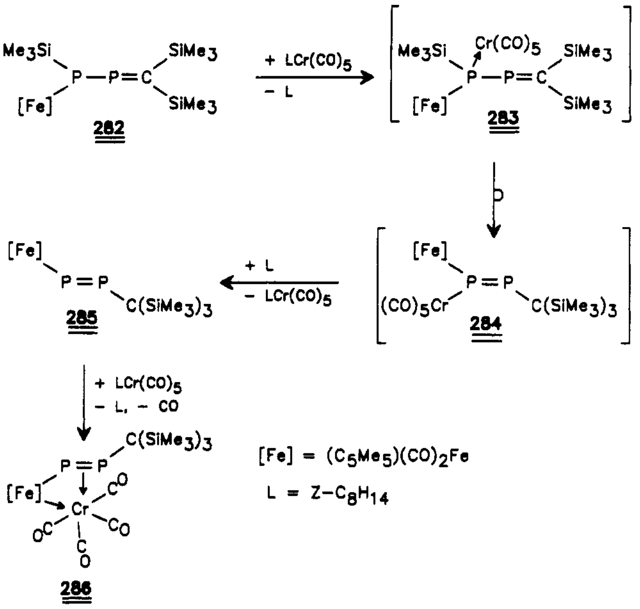
Scheme 165



gration was induced by catalytical amounts of [(*Z*)-cyclooctene]Cr(CO)$_5$. The coordination compound **286**, where the metallodiphosphene is functioning as an η^3-ligand toward the Cr(CO)$_4$ moiety was observed as a byproduct. An alternative description of **286** as a 42 VE butterfly (arachno complex) makes use of the Wade–Mingos rules. The employment of equimolar amounts of [(*Z*)-cyclooctene]Cr(CO)$_5$ resulted in the predominant generation of **286**. It is conceivable that the steric congestion in the intermediate η^1-complex **284** led to dissociation and that the formation of final product **286** was induced by the attack of a Cr(CO)$_5$ group at the P=P π-system[169] (Scheme 166).

The ^{31}P NMR spectrum of **285** comprises two doublets at δ = 788.2 and 602.3 ppm with a $^1J_{PP}$ couplings constant of 654.8 Hz. On the other hand complex **286** (Figure 13) is characterized by two doublets at considerably higher field (δ = 431.5, 134.9 ppm; $^1J_{PP}$ = 524 Hz). The molecular structures of both compounds were elucidated by X-ray diffraction analysis. The P=P

Scheme 166



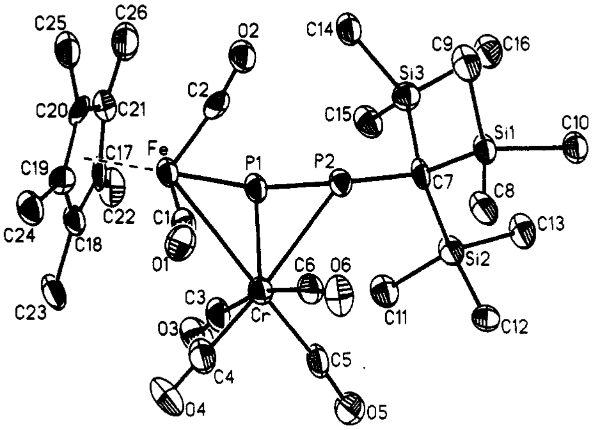


Figure 13. Molecular structure of **286**. Selected bond lengths (Å) and bond angles (deg): Cr–Fe 2.945 (3), Cr–P(1) 2.395 (4), Cr–P(2) 2.635 (4), Fe–P(1) 2.313 (3), P(1)–P(2) 2.090 (4); Fe–P(1)–P(2) 101.5 (1), P(1)–P(2)–C(7) 110.1 (3). Reprinted from ref 169. Copyright 1991 Chemical Society, London.

bond distances of *E*-configurated **285** [2.017 (3) Å] is significantly widened when **285** is coordinated to the $Cr(CO)_4$ moiety in **286**.

All attempts to synthesize diphosphenes with two organometallic groups as substituents at the P═P unit failed. Upon reduction with elemental magnesium or when reacted with $Cp^*(CO)_2FeP(SiMe_3)_2$ the dichlorophosphido complex $Cp^*(CO)_2FePCl_2$ was converted into a mixture of the permetalated cyclotriphosphane $[\eta^5\text{-}C_5Me_5)(CO)_2FeP]_3$ (**288**) and the bicyclotetraphosphane **280**.

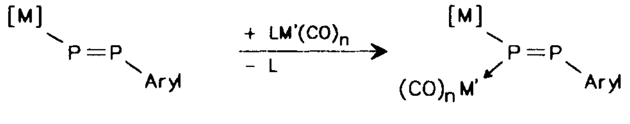
There was no spectroscopic evidence for the diphosphene $Cp^*(CO)_2Fe—P═P—Fe(CO)_2Cp^*$.[170]

VIII. Reactivity of Metallodiphosphenes

A. Ligand Properties

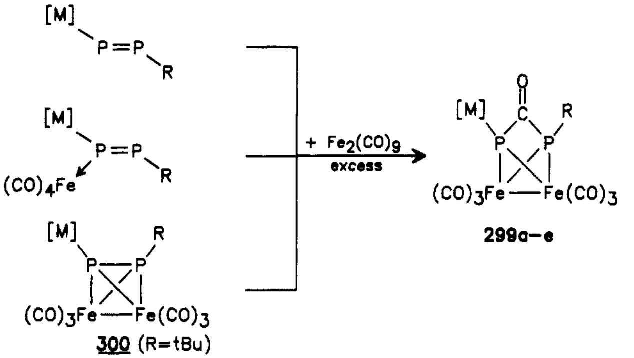
In almost all coordination compounds with metal carbonyls the metallodiphosphenes function as η^1-ligands via the lone pair at the metalated phosphorus atom. Thus the 16-electron fragments $Cr(CO)_5$, $Fe(CO)_4$, and $Ni(CO)_3$ can easily be attached to the diphosphenyl complexes by reaction with $[(Z)\text{-cyclooctene}]Cr(CO)_5$, $Fe_2(CO)_9$, and $Ni(CO)_4$ respectively (Scheme 167). In the ^{31}P NMR spectra the η^1-coordination of the diphosphenyl complexes is generally reflected in a marked high-field shift of the doublets for the metalated phosphorus atom ($\Delta\delta$ ca. −100 to −200 ppm). The coordination shift of the arylated phosphorus is less pronounced (+26 to −56 ppm).

Scheme 167



compd	[M]	Aryl	$M(CO)_n$	L	ref(s)
289	$Cp^*(CO)_2Fe$	Mes*	$Cr(CO)_5$	$(Z)\text{-}C_8H_{14}$	164
290	$Cp^*(CO)_2Fe$	Mes*	$Fe(CO)_4$	$Fe(CO)_5$	171
291	$Cp^*(CO)_2Fe$	Mes*	$Ni(CO)_3$	CO	172
292	$(Me_4EtC_5)(CO)_2Fe$	Mes*	$Cr(CO)_5$	$(Z)\text{-}C_8H_{14}$	166b
293	$(Me_4nBuC_5)(CO)_2Fe$	Mes*	$Cr(CO)_5$	$(Z)\text{-}C_8H_{14}$	166b
294	$(1,3\text{-}tBu_2C_5H_3)(CO)_2Fe$	Mes*	$Cr(CO)_5$	$(Z)\text{-}C_8H_{14}$	166b
295	$Cp^*(CO)_2Ru$	Mes*	$Fe(CO)_4$	$Fe(CO)_5$	171
296	$Cp^*(CO)_2Ru$	Mes*	$Ni(CO)_3$	CO	172
297	$Cp^*(CO)_2Os$	Mes*	$Fe(CO)_4$	$Fe(CO)_5$	171b
298	$Cp^*(CO)_2Os$	Mes*	$Ni(CO)_3$	CO	162b
270a	$Cp(CO)(PPh_3)Fe$	$2,6\text{-}(CF_3)_2C_6H_3$	$Cr(CO)_5$	$(Z)\text{-}C_8H_{14}$	122a
271a	$Cp^*(CO)_2Fe$	$2,6\text{-}(CF_3)_2C_6H_3$	$Cr(CO)_5$	$(Z)\text{-}C_8H_{14}$	122a
270b	$Cp(CO)(PPh_3)Fe$	$2,4,6\text{-}(CF_3)_3C_6H_2$	$Cr(CO)_5$	$(Z)\text{-}C_8H_{14}$	122a
271b	$Cp^*(CO)_2Fe$	$2,4,6\text{-}(CF_3)_3C_6H_2$	$Cr(CO)_5$	$(Z)\text{-}C_8H_{14}$	122a
299	$Cp^*(CO)(NO)Mn$	Mes*	$Cr(CO)_5$	$(Z)\text{-}C_8H_{14}$	164
263	$Cp^*(CO)(NO)Re$	Mes*	$Cr(CO)_5$	$(Z)\text{-}C_8H_{14}$	164

Scheme 168

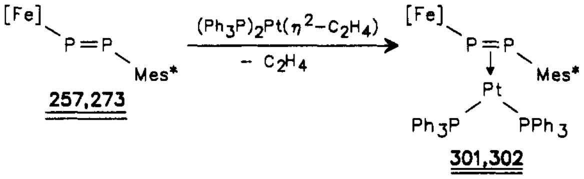


299	[M]	Aryl	Ref.
a	$Cp^*(CO)_2Fe$	Mes*	171
b	$Cp^*(CO)_2Ru$	Mes*	171
c	$Cp^*(CO)_2Os$	Mes*	171b
d	$Cp^*(CO)_2Fe$	$2,4,6\text{-}(CF_3)_3C_6H_2$	173
e	$Cp^*(CO)_2Fe$	tBu	173

The reaction of the diphosphenyl complexes $(C_5Me_5)(CO)_2MP═P—Mes^*$ (M = Fe, Ru, Os) with a large excess of $Fe_2(CO)_9$ took a different course. Here $Fe_2(CO)_6$ complexes **299a–c** with bridging 2-oxo-1,3-diphosphapropanediyl ligands were obtained (Scheme 168). Obviously a carbonyl group from decomposing $Fe_2(CO)_9$ had been inserted into the P═P bond.[171]

The same result was observed when $(C_5Me_5)(CO)_2FeP═PC_6H_2(CF_3)_3\text{-}2,4,6$ **269b** was reacted with an excess of $Fe_2(CO)_9$.[173] It was demonstrated that η^1-complexes of the type $[M]P[Fe(CO)_4]═PAryl$ **290**, **295**, and **297** were smoothly converted to the insertion products by excess of $Fe_2(CO)_9$ and thus have to be regarded as intermediates in this transformation.

Scheme 169



	[Fe]
257,301a	$(C_5Me_5)(CO)_2Fe$
272a,301b	$(C_5Me_4Et)(CO)_2Fe$
272b,301c	$(C_5Me_4nBu)(CO)_2Fe$
273,302	$(1,3tBu_2C_5H_3)(CO)_2Fe$

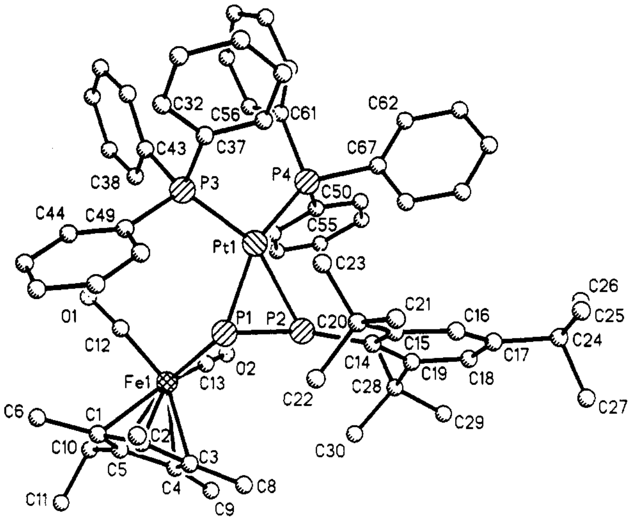


Figure 14. Molecular structure of **301b**. Selected bond lengths (Å) and bond angles (deg): Pt–P(1) 2.374 (2), Pt–P(2) 2.400 (3), Pt–P(3) 2.276 (3), Pt–P(4) 2.310 (2), P(1)–P(2) 2.140 (4), Fe–P(1) 2.368 (3); P(1)–Pt–P(2) 53.3 (1), P(1)–Pt–P(3) 97.0 (1), P(3)–Pt–P(4) 104.5 (1), P(2)–Pt–P(4) 105.2 (1). From ref 166b, in press.

Likewise the tetrahedrane **300** yielded **299e** upon treatment with $Fe_2(CO)_9$.

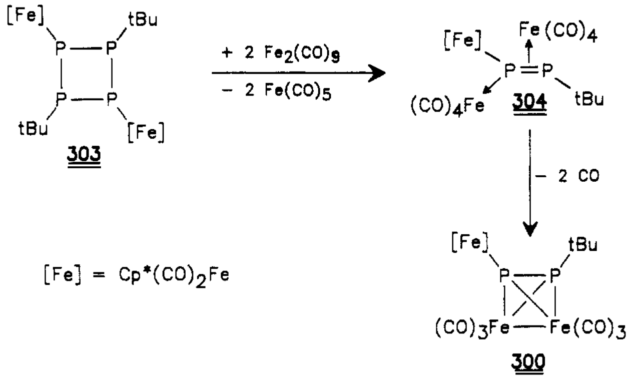
A different strategy for the synthesis of such complexes involved the treatment of bulky (dialkylamino)dichlorophosphanes with $Na_2Fe(CO)_4 \cdot 1,5$-dioxane in ether.[145,174]

Only in six cases did diphosphenyl complexes show a different coordination mode than the well-known η^1-ligation. As mentioned before the reaction of the 1,2-diphosphapropene **282** with $[(Z)\text{-}C_8H_{14}]Cr(CO)_5$ furnished complex **286** in which the metallodiphosphene **285** is functioning as an η^3-ferradiphosphaallyl ligand.[169]

Equimolar amounts of the metallodiphosphenes **257a–c**, **273**, and $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ underwent reaction to give the η^2-complexes **301a–c** and **302**[166b] (Scheme 169). The ^{31}P NMR spectra of **301a–c** and **302** comprise resonances at δ = 93.4–128.5 and 63.7–72.3 (J_{PP} = 428–440 Hz) for the η^2-diphosphene moiety. The X-ray structure analysis of **301b** features the metallodiphosphene unsymmetrically coordinated to the platinum (Figure 14).

The sixth example, the tetrahedrane **300**, was isolated from the reaction of the metalated cyclotetraphosphane **303** with an excess of $Fe_2(CO)_9$[173] (Scheme 170). In the ^{31}P NMR spectrum compound **300** gives rise to doublets at δ = −88.8 and 45.3 with a coupling constant of 491 Hz. It was proposed that the cyclotetraphosphane is attacked by $Fe(CO)_4$ fragments to afford the η^1:η^2-complex **304**. The removal of two carbonyl ligands from **304** completed the tetrahedrane formation.

Scheme 170



B. Reactions of Metallodiphosphenes with Chalcogens

The reaction of equivalent amounts of **257** and sulfur in THF at ambient temperature led to the isolation of the red crystalline thioxo-λ^5-diphosphenyl complex **305** (Scheme 171). Heating a benzene solution of **305** to 80 °C ended in the rearrangement of the metalated thiadiphosphirane **306**.[175] The addition of second equivalent of sulfur to **305** gave a mixture of Mes^*PS_2 **308** and the thiadiphosphirane sulfide **307**. The X-ray structure analysis of **305** shows a trigonal planar phosphorus atom with double bonds to the neighboring phosphorus and sulfur[175] (Figure 15).

The ligand in this molecule can be interpreted as a congener of the still unknown metaphosphite ligand $[P(=O)_2]^-$, which formally is an analog of the well-known nitro ligand.

The diphosphenyl iron complex **257** was oxidized by gray selenium to the metalated selenadiphosphirane **310**. The selenoxo-λ^5-diphosphenyl complex **309** was detected as an intermediate by its two doublets at $\delta^{31}P$ = 383.8 and 335.0 with satellite couplings $^1J(^{31}P^{77}Se)$ of 753.0 and 121.2 Hz, respectively.[175]

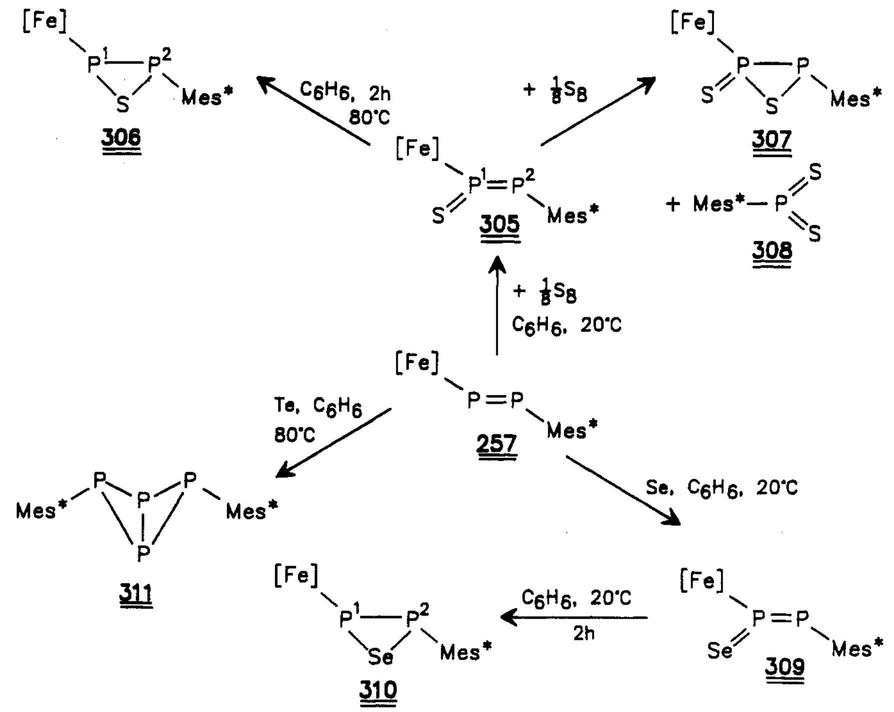
A different situation was encountered when **257** was allowed to react with tellurium. Here 24 h of heating at 80 °C were needed to bring the reaction to completion. The bicyclotetraphosphane **311** was isolated as the only phosphorus containing product.[175]

C. Reactions of Metallodiphosphenes with Alkylidene Transfer Reagents

In looking at the products, the formation of thia- and selenadiphosphiranes may be considered as [2 + 1] cycloadditions regardless of the real reaction mechanism. The same formalism may be applied to the conversions diphosphenyl complexes undergo when allowed to react with sulfur ylides and diazomethane.

The iron and ruthenium compounds, **257** and **258**, smoothly reacted with an excess of the sulfur ylide $Me_2S(O){=}CH_2$ to give the orange diphosphiranes **312a,b** in 45 and 32% yield, respectively. The same compounds were also accessible by treatment of the

Scheme 171



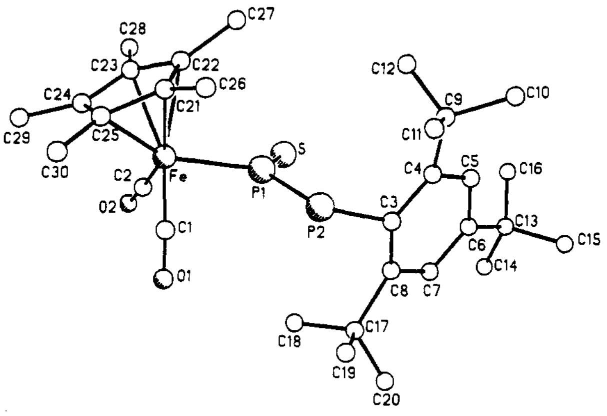


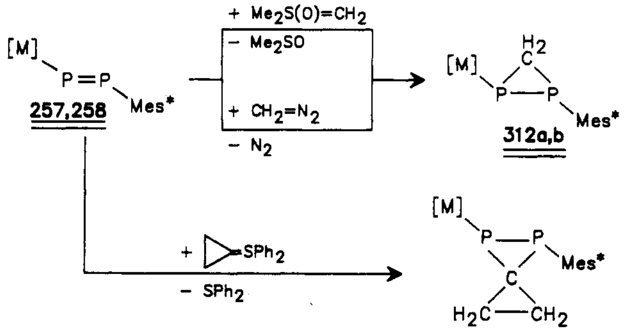
Figure 15. Molecular structure of (η^5-C_5Me_5)$(CO)_2$FeP(S)=PMes* **305**. Selected bond lengths (Å) and angles (deg): Fe–P(1) 2.227 (1), P(1)–P(2) 2.041 (1), P(1)–S 1.936 (2), P(2)–C(3) 1.885 (3); Fe–P(1)–S 121.1 (1), Fe–P(1)–P(2) 114.2 (1), P(2)–P(1)–S 124.4 (1), P(1)–P(2)–C(3) 104.8 (1). From ref 175. Copyright 1987 American Chemical Society.

diphosphenyl complexes with an excess of diazomethane albeit in smaller yields[103,176] (Scheme 172). The synthesis of the first 1,2-diphosphaspiro[2.2]pentanes **313a,b** was based upon the reaction of **257** and **258** with equimolar amounts of diphenylsulfonio cyclopropanide. The X-ray structure determination of **313a** confirmed the presence of a 1,2-diphosphaspiro[2.2]pentane system linked to the metal through an Fe–P bond[103] (Figure 16).

D. Reactions of Metallodiphosphenes with Isocyanides

The metallodiphosphenes **257** and **285** were cleanly reacted with equimolar amounts of trifluoromethyl isocyanide to give the iminodiphosphiranes **314** and **315**[177] (Scheme 173). The ^{31}P NMR spectra of the [2 + 1] cycloadducts **314** and **315** correspond well with those of the iminodiphosphiranes obtained by Baudler et al.[105]

Scheme 172



313a,b

Compound	[M]
257,312a,313a	Cp*(CO)$_2$Fe
258,312b,313b	Cp*(CO)$_2$Ru

E. Reactions of Metallodiphosphenes with Electron-Deficient Alkenes

Metalated diphosphenes can be regarded as electron-rich heteroolefins, and the quest for [2 + 2] cycloadditions with electron-poor alkenes to give 1,2-diphosphetanes seems intriguing. In order to provide insight into this problem diphosphenyl complexes were subjected to the reaction with a number of acyclic α,β-unsaturated aldehydes and ketones, which are well known as powerful Michael acceptors.

The diphosphenyl complexes **257** and **258** smoothly reacted with equimolar amounts of acrolein, methacrolein, and but-3-en-2-one to give the dark violet dihydro-1,2-λ^5-oxaphospholenes **317a–e** instead of the expected 1,2-diphosphetanes **316** (Scheme 174). Obviously the five-membered heterocycles are the products of a cheletropic [1 + 4] cycloaddition.[178] This result can be rationalized by the fact that the introduction of an electron-releasing and highly nucleophilic transition metal fragment raises the energy of the n^+ orbital

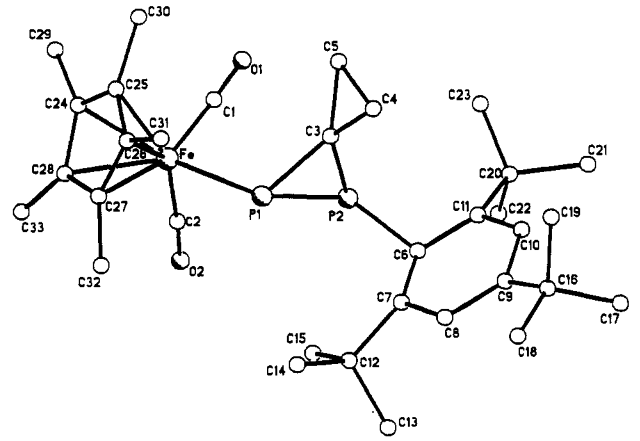
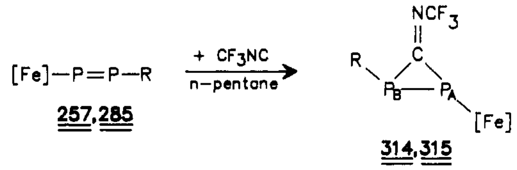


Figure 16. Molecular structure of **313a**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.310 (1), P(1)–P(2) 2.206 (2), P(1)–C(3) 1.799 (5), P(2)–C(3) 1.824 (5), C(3)–C(4) 1.510 (6), C(3)–C(5) 1.489 (7), C(4)–C(5) 1.485 (8), P(2)–C(6) 1.921 (3); Fe–P(1)–P(2) 109.3 (1), P(1)–P(2)–C(6) 107.1 (1), P(2)–P(1)–C(3) 53.0 (2), P(1)–P(2)–C(3) 52.0, P(1)–C(3)–P(2) 75.0 (2). From ref 103. Copyright 1988 American Chemical Society.

Scheme 173



257,285

314,315

Comp	[Fe]	R	δ P_A	δ P_B	$^1J_{PP}$/ Hz
314	Cp*(CO)$_2$Fe	Mes*	−71.5	−169.8	32.5
315	Cp*(CO)$_2$Fe	C(SiMe$_3$)$_3$	−66.7	−156.8	56.0

relative to the π-MO, making "carbene-like" reactions feasible. This is reflected in the oxidation potential of **257** of only $E_{ox} = +0.45$ V (in THF vs SCE),[179] whereas for $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ the potential $E_{ox} = +1.14$ V (in CH_3CN vs SCE) was reported.[73]

The molecular structure of **317a** was established by a single crystal X-ray analysis. The analysis shows the presence of a dihydrooxaphospholene ligand with an exocyclic P=P bond. The ring ligand is attached to the iron via a tetracoordinate phosphorus atom in an η^1-fashion (Figure 17).

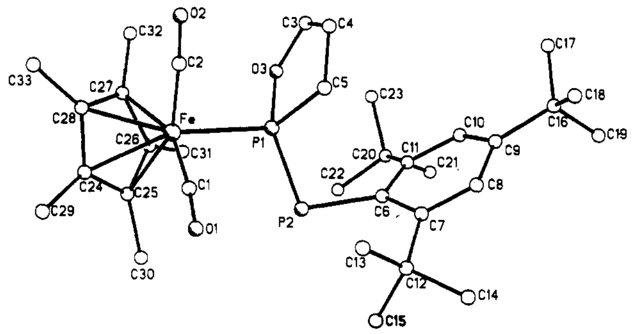


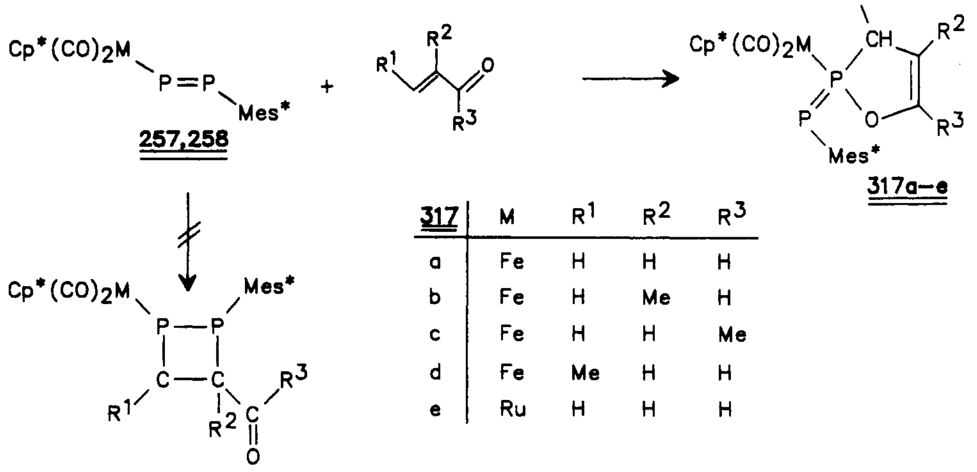
Figure 17. Molecular structure of **317a**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.243 (2), P(1)–P(2) 2.064 (2), P(1)–O(3) 1.703 (5), P(1)–C(5) 1.852 (7), P(2)–C(6) 1.850 (5), O(3)–C(3) 1.388 (11), C(3)–C(4) 1.268 (12), C(4)–C(5) 1.455 (11); Fe–P(1)–P(2) 111.2 (1), Fe–P(1)–O(3) 105.9 (2), Fe–P(1)–C(5) 114.2 (2), O(3)–P(1)–C(5) 92.0 (3), P(1)–P(2)–C(6) 100.3 (2). From ref 178b. Copyright 1989 American Chemical Society.

A [2 + 2] cycloaddition also took place, when Cp*(CO)$_2$FeP=PMes* **257** was subjected to the reaction with fumarodinitrile, which yielded the all-trans-oriented 1,2-diphosphetane **318**. Similarly, **257** was converted by either dimethyl fumarate or dimethyl maleate into the all-trans-configurated 1,2-diphosphetane **319**. In the latter case considerable amounts of the maleate were catalytically isomerized to the fumarate. These observations account for a two-step mechanism, which allows rotation around the C–C bond in the zwitterionic intermediate[180] (Scheme 175).

Heating a 1:1 mixture of **257** and maleimide or *N*-methylmaleimide in benzene at 75 °C afforded the transition metal functionalized 1,2-diphosphetanes **320** and **321** as a 1:3 mixture of two diastereoisomers.[181] They are derived from an endo and/or exo [2 + 2] cycloaddition of the P=P bond of **257** to the C=C functionality of the imides (Scheme 176). The molecular structure of the major isomer **321b** confirmed the presence of a 4,5-diphospha-2-azabicyclo[3.2.0]heptane-1,3-dione system linked to the metal through a Fe–P bond [2.319 (2) Å] at the endo face of the bicycle.

The reaction of **257** and with an excess of *N*-methylmaleimide took a different course.[182] Here the

Scheme 174



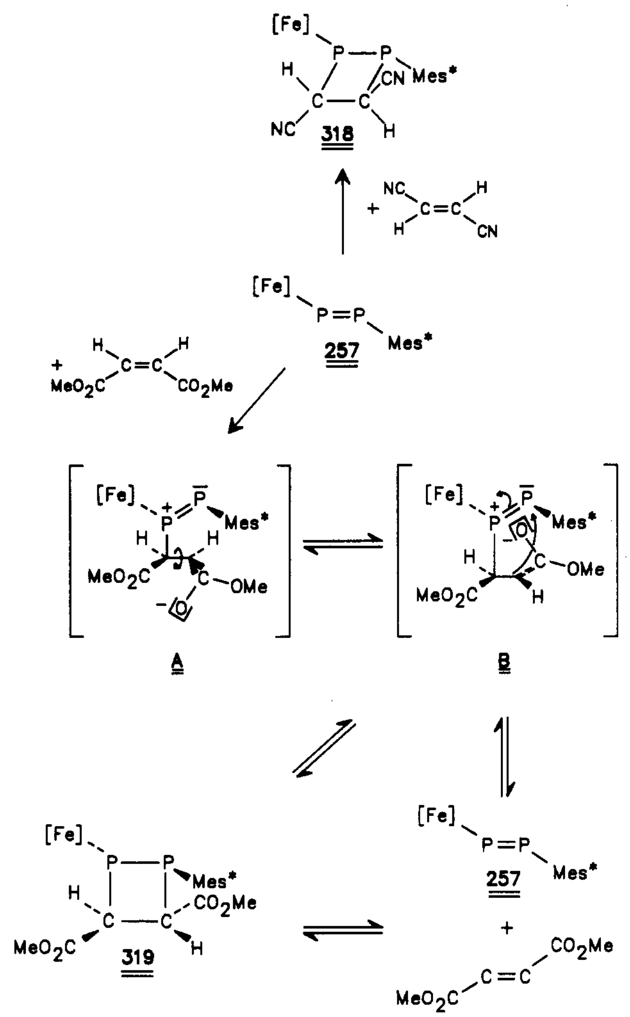
257,258

317a–e

316

317	M	R^1	R^2	R^3
a	Fe	H	H	H
b	Fe	H	Me	H
c	Fe	H	H	Me
d	Fe	Me	H	H
e	Ru	H	H	H

Scheme 175



cleavage of the P=P bond was observed to give iron complex **322** (Figure 18) with a chiral phosphido ligand. One substituent at this ligand can be described as a bicyclo[3.1.0]1-aza-4-phosphahexane-2,6-dione.

It is worth mentioning that the 1:1 adduct **321** did not react with additional maleimide.

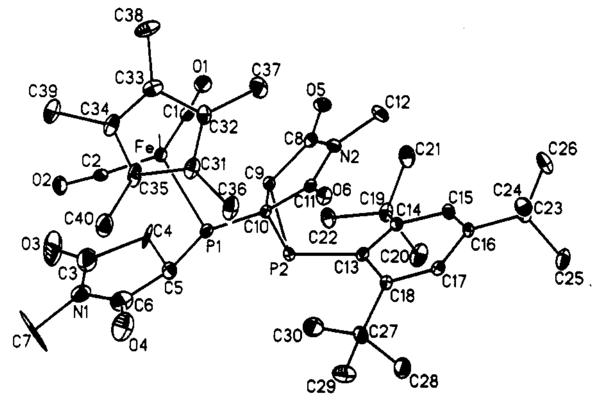


Figure 18. Molecular structure of **322**. Selected bond lengths (Å) and angles (deg): Fe–P(1) 2.318 (2), P(1)–C(10) 1.875 (6), C(9)–C(10) 1.522 (8), P(2)–C(9) 1.854 (5), P(2)–C(13) 1.846 (7); Fe–P(1)–C(10) 109.4 (2), P(1)–C(10)–C(9) 131.1 (4), P(1)–C(10)–P(2) 121.2 (3), P(2)–C(9)–C(10) 67.0 (3), C(9)–P(2)–C(10) 48.0 (3), C(9)–P(2)–C(13) 105.5 (3), C(10)–P(2)–C(13) 104.5 (3). Reprinted from ref 182. Copyright 1992 Barth (Leipzig).

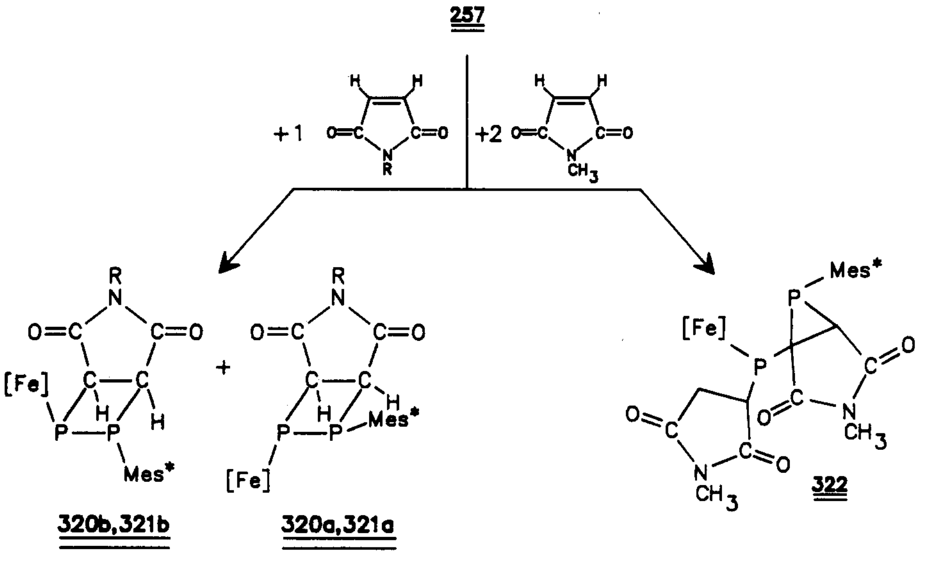
F. Reactions of Metallodiphosphenes with Azo Compounds

The step from electron-poor alkenes to azo compounds with electron-withdrawing substituents is obvious. In principal a [2 + 2] cycloaddition with diphosphenes should provide a synthetic route to the still unknown 1,2-diaza-3,4-diphosphetidines **323** (Scheme 177).

Indeed the addition of diazodicarboxylates to a THF solution of **257** gave rise to the formation of 1:1 adducts but from spectroscopic evidence (e.g. $\delta^{31}P$ = 184.1 d; –0.1 d, J = 731 Hz) the structure of a four-membered ring had to be discarded. The X-ray structure analysis revealed **324a** as oxadiazaphospholene, which was generated by a cheletropic [1 + 4] cycloaddition[183,184] (Figure 19).

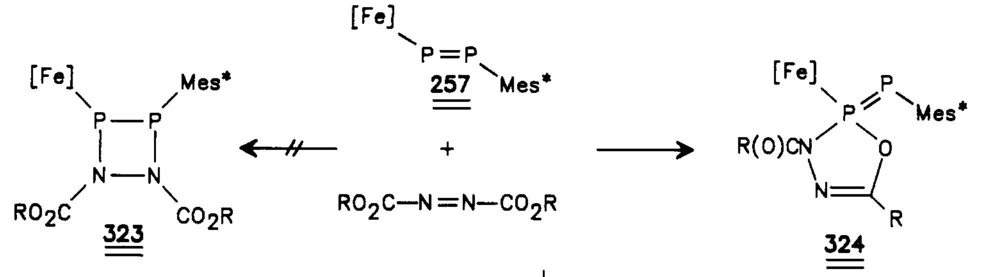
This mode of cycloaddition should be avoided when the N=N bond is incorporated in a rigid system with

Scheme 176



[Fe] = $Cp^*(CO)_2Fe$; 320 (R=H), 321 ($R=CH_3$)

Scheme 177



324	R
a	OEt
b	O–tBu
c	OCH_2Ph
d	NC_5H_{10}

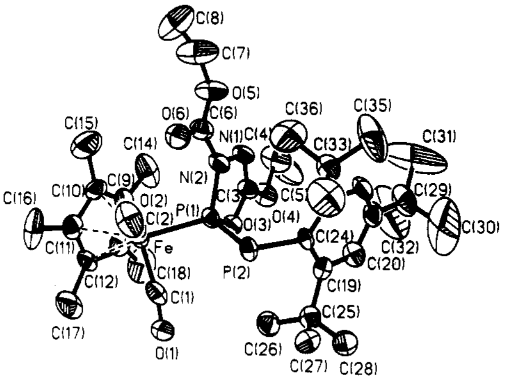


Figure 19. Molecular structure of **324a**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.241 (2), P(1)–P(2) 2.074 (3), P(1)–N(2) 1.744 (6), P(1)–O(3) 1.709 (5), P(2)–C(24) 1.870 (7); Fe–P(1)–P(2) 111.6 (1), Fe–P(1)–N(2) 114.9 (2), Fe–P(1)–O(3) 112.3 (2), P(2)–P(1)–N(2) 118.1 (2), P(2)–P(1)–O(3) 111.9 (2), N(2)–P(1)–O(3) 85.3 (3), P(1)–P(2)–C(24) 101.1 (2). Reprinted from ref 183. Copyright 1991 American Chemical Society.

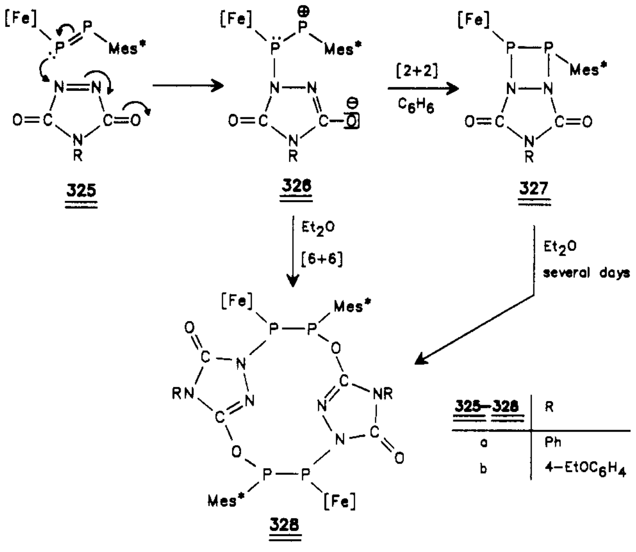
exocyclic CO functions as it is given in the 1,3,4-triazoline-2,5-diones **325**. In keeping with this the reaction of **325a,b** with $Cp^*(CO)_2FeP{=}PMes^*$ **257** in benzene furnished the first 1,2-diaza-3,4-diphosphetidines **327a,b** as yellow crystals[185] (Scheme 178).

When, however, the same reaction was performed in ether as a solvent a different situation was encountered. Here the twelve-membered macrocycles **328a,b** were isolated as products. Their formation invokes the [6 + 6] head-to-tail cyclodimerization of the zwitterionic intermediate **326**. In the unpolar benzene these zwitterions may be not sufficiently stabilized so that the addition was followed by a rapid intramolecular cyclization to give **327a,b**.[185] Evidence for the zwitterionic intermediate was inferred from a ^{31}P NMR spectrum of the fresh reaction mixture. At −40 °C doublets at δ = 143 and 345 ($^1J_{PP}$ = 635 Hz) were registered.[185]

The X-ray structure analysis of **327a** features a tilted 1,2-diaza-3,4-diphosphetidine (dihedral angle = 164°) which is fused to a 1,2,4-triazolidine-3,5-dione system via the adjacent nitrogen atoms (Figure 20).

In the crystal, the macrocycle **328**, containing four P, four N, two O and two C atoms, adopts a crown conformation in which two boatlike halves are connected via the nitrogen atoms N2 and N5 (Figure 21).

Scheme 178



325–328	R
a	Ph
b	$4\text{-}EtOC_6H_4$

G. Reactions of Metallodiphosphenes with Hexafluoroacetone

An electron-poor double bond is also present in hexafluoroacetone. When the diphosphenyl iron complex **257** is exposed to an excess of the ketone in pentane solution, one observes the formation of the five-membered metallocycle **330**[186] (Scheme 179). At −40 °C in pentane solution **330** is slowly transformed into the 1-oxa-2,3-diphosphetane **331**. It is assumed that the generation of **330** proceeds via the transient [2 + 1] cycloadduct **329**, involving heterolytic opening of the P–C bond and attack of the $C(CF_3)_2^-$ unit at a carbonyl ligand. On the other hand, opening of the P–O bond in **329** and oxygen attack at the arylated phosphorus atom may afford **331**.

The most interesting feature of the molecular structure of **330** is the geometry of the nearly planar five-membered metalloheterocycle (Figure 22). The Fe–P bond is remarkably short and suggests multiple bond contributions.

H. Reactions of Metallodiphosphenes with Electron-Deficient Alkynes

Having in mind of the rich chemistry that diphosphenyl complexes display with electron-poor double-

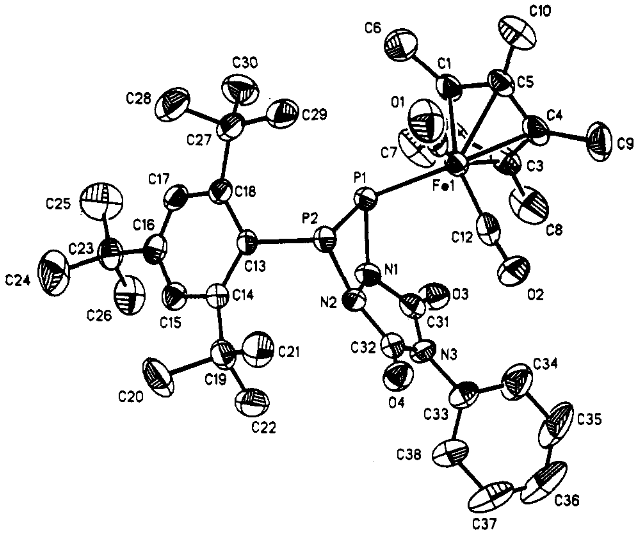


Figure 20. Molecular structure of **327a**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.296 (2), P(1)–P(2) 2.275 (2), P(1)–N(1) 1.825 (5), P(2)–N(2) 1.777 (5), P(2)–C(13) 1.881 (5), N(1)–N(2) 1.429 (6); Fe–P(1)–P(2) 108.4 (1), P(1)–P(2)–C(13) 97.9 (2), Fe(1)–P(1)–N(1) 111.3 (1), P(2)–P(1)–N(1) 75.4 (1), P(1)–N(1)–N(2) 101.9 (3), N(1)–N(2)–P(2) 103.9 (3), P(1)–P(2)–N(2) 76.5 (2), N(2)–P(2)–C(13) 98.7 (2). Reprinted from ref 185a. Copyright 1991 Chemical Society, London.

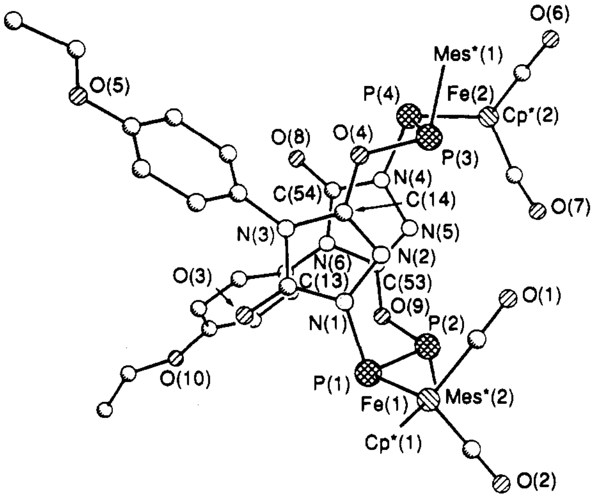
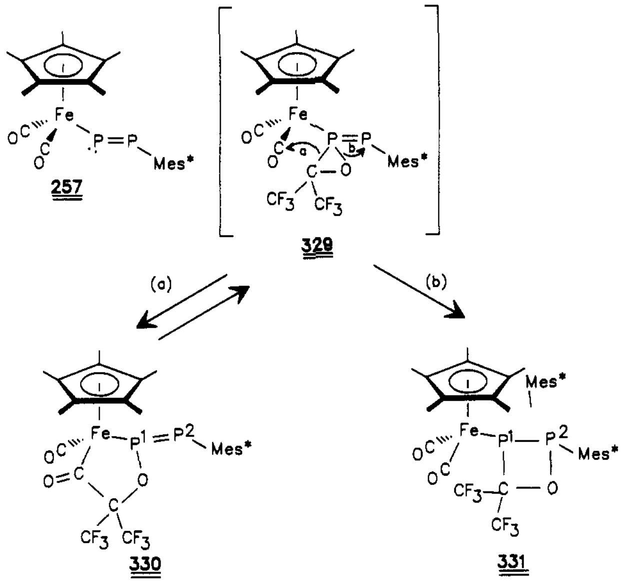


Figure 21. Molecular structure of **328b**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.277 (3), Fe(2)–P(2) 2.250 (4), P(1)–P(2) 2.235 (4), P(3)–P(4) 2.250 (4), N(1)–N(2) 1.417 (11), N(4)–N(5) 1.422 (11), P(1)–N(1) 1.772 (9), P(4)–N(4) 1.771 (8), P(2)–O(9) 1.737 (7), P(3)–O(4) 1.733 (7); N(1)–P(1)–P(2) 93.5 (3), P(1)–P(2)–O(9) 101.0 (3), N(4)–P(4)–P(3) 92.6 (3), P(4)–P(3)–O(4) 99.6 (3), Fe(1)–P(1)–P(2) 105.0 (1), Fe(2)–P(4)–P(3) 105.6 (1). From ref 185a. Copyright 1991 Chemical Society, London.

bond systems, it is obvious to investigate their chemical behavior toward electron-deficient alkynes.

The reaction of Cp*(CO)$_2$FeP=PMes* (**257**) with equimolar amounts of HC≡CCO$_2$Me (**332a**), and MeC≡CCO$_2$Me (**332b**) in benzene regiospecifically afforded the dark green crystalline metallocycles **333a**,**b**. The low-field resonances and the large coupling constants in the ^{31}P NMR spectra of **333a** (δ = 439.0 d, 299.5 d, $^1J_{PP}$ = 614.0 Hz) and **330b** (δ = 420.1 d, 279.9 d, $^1J_{PP}$ = 664.2 Hz) are characteristic for diphosphene ligands in the η^1-coordination mode. Both compounds possess an *E*-configurated P=P bond like **257**. On the other hand dimethyl acetylenedicarboxylate **332c** and the acetylenic ketones **332d**,**e** underwent reaction with **257** to yield the metalloheterocycles **334c–e** with *Z*-configurated double bonds (Scheme 180). Presumably severe steric interactions between the supermesityl ring and R^1 were responsible for the isomerization.[187] Compounds **333** and **334** can be regarded as chelate complexes of the novel 1,2-diphosphabutadiene ligand system.

Scheme 179



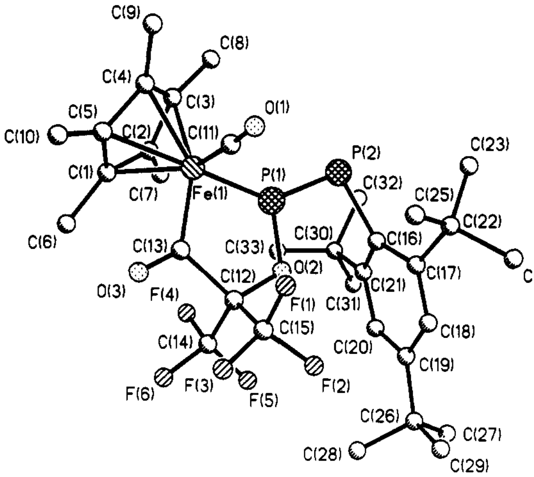
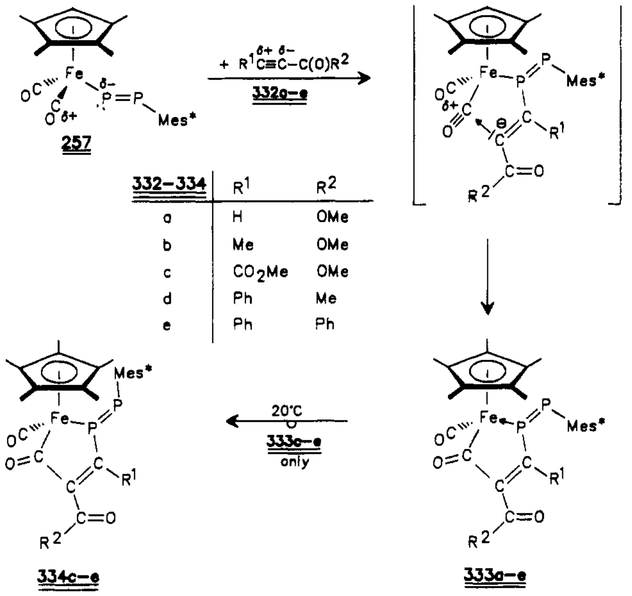


Figure 22. Molecular structure of **330**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.084 (4), Fe–C(13) 1.937 (14), P(1)–P(2) 2.014 (5), P(1)–O(2) 1.647 (9), P(2)–C(16) 1.860 (13), O(2)–C(12) 1.427 (15), O(3)–C(13) 1.191 (16), C(12)–C(13) 1.640 (19); Fe–P(1)–P(2) 140.3 (2), Fe–P(1)–O(2) 109.5 (3), P(2)–P(1)–O(2) 109.9 (3), P(1)–P(2)–C(16) 99.0 (4). Reprinted from ref 186. Copyright 1992 American Chemical Society.

It was assumed that the formation of the metalloheterocycles proceeded via a dipolar [2 + 3] cycloaddition. The negative charge of the 1,3 dipole is centered at the metalated phosphorus atom of **257**, whereas its positive charge is located at the carbon atom of a terminal carbonyl ligand. The X-ray structure analyses of **333b**[187] (Figure 23) and **334d**[188] underline the structural assignments based on spectroscopic data.

The special role of the transition metal in the [2 + 3] cycloaddition between diphosphenyl complexes and alkynes was tested in going from **257** to ruthenium

Scheme 180



332–334	R¹	R²
a	H	OMe
b	Me	OMe
c	CO₂Me	OMe
d	Ph	Me
e	Ph	Ph

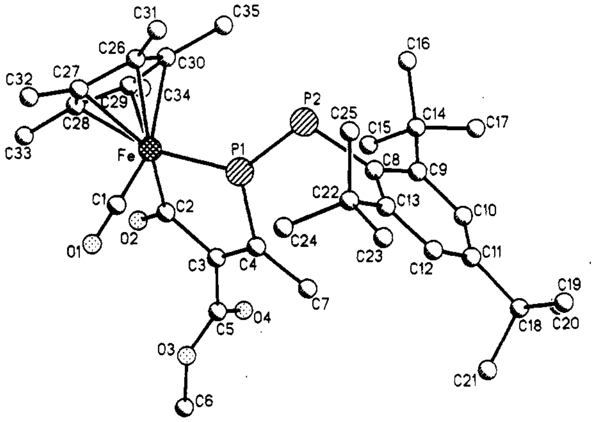
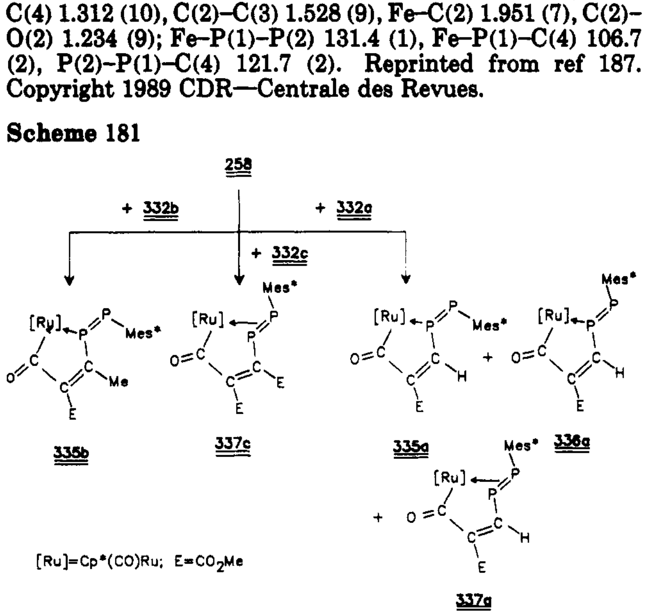


Figure 23. Molecular structure of **333b**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.117 (2), P(1)–P(2) 2.031 (3), P(2)–C(8) 1.847 (6), P(1)–C(4) 1.819 (6), C(3)–C(4) 1.312 (10), C(2)–C(3) 1.528 (9), Fe–C(2) 1.951 (7), C(2)–O(2) 1.234 (9); Fe–P(1)–P(2) 131.4 (1), Fe–P(1)–C(4) 106.7 (2), P(2)–P(1)–C(4) 121.7 (2). Reprinted from ref 187. Copyright 1989 CDR—Centrale des Revues.

Scheme 181



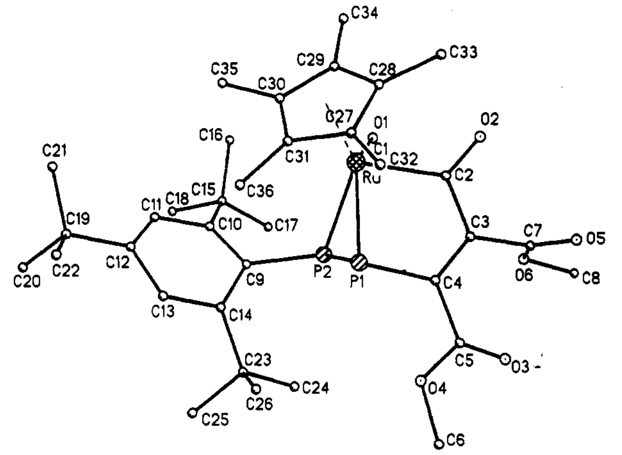


Figure 24. Molecular structure of **337c**. Selected bond lengths (Å) and bond angles (deg): Ru–P(1) 2.383 (1), Ru–P(2) 2.572 (1), P(1)–P(2) 2.121 (1), Ru–C(2) 2.093 (3), C(2)–C(3) 1.493 (5), C(3)–C(4) 1.340 (5), P(1)–C(4) 1.837 (3), P(2)–C(9) 1.864 (3); Ru–P(1)–P(2) 69.4 (1), Ru–P(2)–P(1) 98.9, P(1)–Ru–P(2) 50.5 (1), P(1)–P(2)–C(9) 103.7 (1), P(2)–P(1)–C(4) 96.5 (1). Reprinted from ref 189. Copyright 1989 VCH (Weinheim).

homolog **258**. The complex **258** and **332b** underwent reaction to yield the olive green crystalline **335b** with an *E* configuration at the P=P bond as the product of a [2 + 3] cycloaddition[189] (Scheme 181). The phosphorus atom at the olefinic double bond is η^1-coordinated to the metal. This was reflected in the ^{31}P NMR spectrum where two doublets (δ = 394.9 and 270.9 ppm) with a large coupling ($^1J_{PP}$ = 657.3 Hz) were registered.

An analogous behavior was observed in the reaction of **258** with **332a**. After 90 min, dark green crystalline **335a** was isolated from the benzene solution. Prolonged stirring resulted in the isomerization of **335a** to the *Z*-configurated **336a** and the η^2-diphosphene complex **337a**. The three isomers were formed in a **335a**/**336a**/**337a** 74:16:10 ratio. Their separation was not possible.

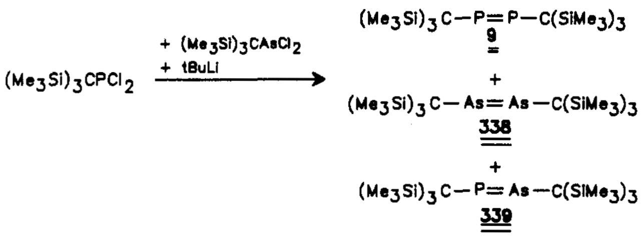
A dark red color change was observed upon addition of dimethyl acetylenedicarboxylate to a benzene solution of **258**. The reaction appeared to be straightforward, affording ruby-red crystalline **337c**, in which the ruthenium atom is involved in π-bonding to the P=P bond. This is reflected in the ^{31}P NMR spectrum by resonances at δ = 104.5 and 50.8 ppm ($^1J_{AB}$ = 439.0 Hz). From IR evidence in the region of the stretching vibrations of the terminal carbonyl ligands in **335**–**337** it is clear that the η^2-P=P ligand is a much better acceptor than the η^1-P=P alternative (**335a**, ν(CO) = 1962 cm^{-1}; **337c**, ν(CO) = 1993 cm^{-1}). The formation of **337c** from **335c** or **336c** invokes the first σ-/π-rearrangement of a diphosphene ligand.[189] The single-crystal X-ray analysis of **337c** features the situation of a transition metal complex with an unsymmetrically coordinated η^2-diphosphene ligand[189] (Figure 24).

IX. Phosphaarsenes, Diarsenes, and Phosphastibenes

A. Synthesis, Structures, and Spectra

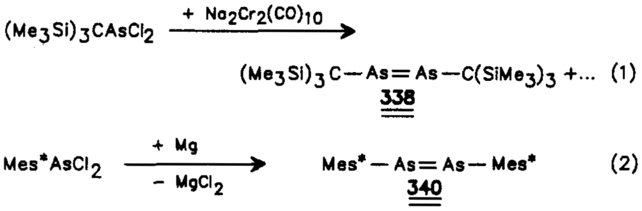
The same strategies, which proved to be valid for the synthesis of diphosphenes may be also be applied for their higher congeners. A reductive coupling with the formation of phosphaarsene **339** occurred when *tert*-butyllithium was added to a mixture of $(Me_3Si)_3CPCl_2$ and $(Me_3Si)_3CAsCl_2$.[190a] In addition comparable amounts of diphosphene **9** and diarsene **338** were also generated (Scheme 182). Of course the reduction of pure $(Me_3Si)_3CAsCl_2$ with *tert*-butyllithium also gave **338**.[190b] The same diarsene was isolated from the

Scheme 182



$$(Me_3Si)_3CPCl_2 \xrightarrow[+\ tBuLi]{+\ (Me_3Si)_3CAsCl_2} \underset{\underline{\underline{9}}}{(Me_3Si)_3C{-}P{=}P{-}C(SiMe_3)_3} + \underset{\underline{\underline{338}}}{(Me_3Si)_3C{-}As{=}As{-}C(SiMe_3)_3} + \underset{\underline{\underline{339}}}{(Me_3Si)_3C{-}P{=}As{-}C(SiMe_3)_3}$$

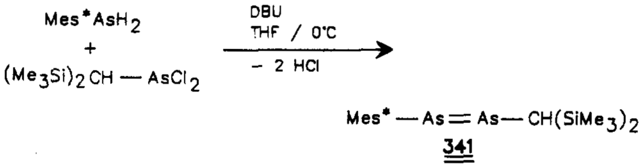
Scheme 183



$$(Me_3Si)_3CAsCl_2 \xrightarrow{+\ Na_2Cr_2(CO)_{10}} \underset{\underline{\underline{338}}}{(Me_3Si)_3C{-}As{=}As{-}C(SiMe_3)_3} + \ldots \quad (1)$$

$$Mes^*AsCl_2 \xrightarrow[-\ MgCl_2]{+\ Mg} \underset{\underline{\underline{340}}}{Mes^*{-}As{=}As{-}Mes^*} \quad (2)$$

Scheme 184



$$Mes^*AsH_2 + (Me_3Si)_2CH{-}AsCl_2 \xrightarrow[-\ 2\ HCl]{DBU,\ THF\ /\ 0°C} \underset{\underline{\underline{341}}}{Mes^*{-}As{=}As{-}CH(SiMe_3)_2}$$

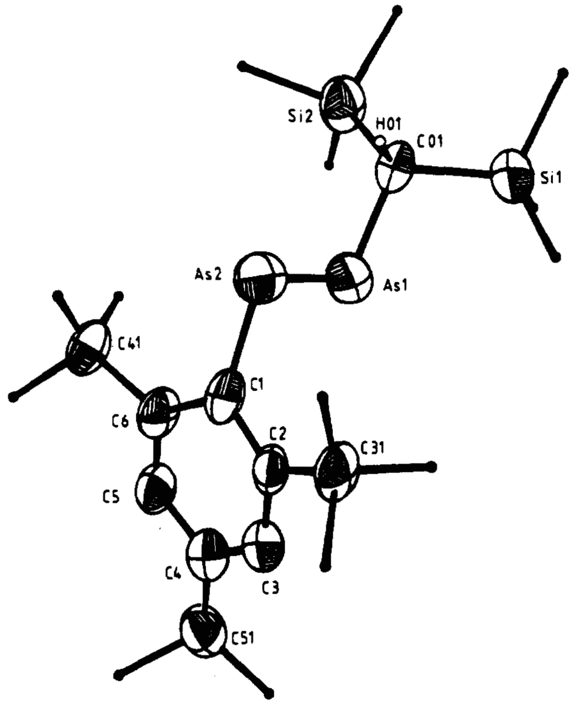


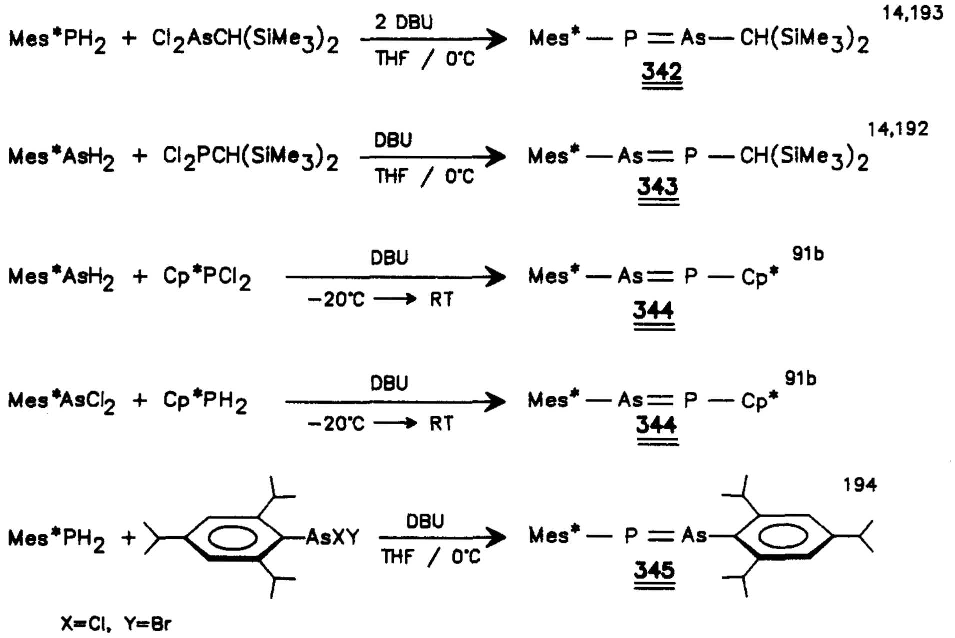
Figure 25. Molecular structure of (*E*)-$(Me_3Si)_2CHAs{=}AsMes^*$ (**341**). Selected bond lengths (Å) and bond angles (deg): As(1)-As(2) 2.224 (2), As(1)-C(01) 1.976 (10), As(2)-C(1) 1.946 (1); As(2)-As(1)-C(01) 99.9 (3), As(1)-As(2)-C(1) 93.6 (3). Reprinted from ref 192. Copyright 1983 American Chemical Society.

reaction of $(Me_3Si)_3CAsCl_2$ with $Na_2Cr_2(CO)_{10}$.[143] The preparation of the yellow crystalline diarsene **340** with two aryl substituents was accomplished by the treatment of Mes^*AsCl_2 with magnesium at 0 °C[191] (Scheme 183). Diarsene **340** was also produced in small amounts during the reaction of $Cp^*(CO)_2FeP(SiMe_3)_2$ with Mes^*AsCl_2 (see section XII).

The only other stable diarsene (**341**), reported in the literature, was synthesized in the base-catalyzed condensation of Mes^*AsH_2 and $(Me_3Si)_2CHAsCl_2$[14,192] (Scheme 184). The X-ray crystal structure determination of **341** exhibited an *E*-configurated molecule with an As=As bond length of 2.224 (2) Å (Figure 25). The bond angles at the arsenic atoms of 93.6 (3)° and 99.9 (3)° are appreciably smaller than the bond angles at phosphorus in the diphosphenes RP=PR [R = $(Me_3Si)_3C$, 108.5 (4)° av; R = Mes*, 102.8 (1)°], reflecting both the tendency to an increasing p character in going from P to As and possibly a decrease in steric encumbrance resulting from the longer bond As=As and As—C bonds.

The same approach was useful for the straightforward synthesis of stable phosphaarsenes, as illustrated in Scheme 185. From ^{31}P NMR monitoring it was deduced that the condensation to give **345** proceeded stepwise

Scheme 185



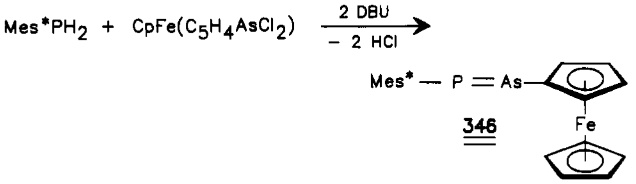
$$Mes^*PH_2 + Cl_2AsCH(SiMe_3)_2 \xrightarrow[THF\ /\ 0°C]{2\ DBU} \underset{\underline{\underline{342}}}{Mes^*{-}P{=}As{-}CH(SiMe_3)_2} \quad ^{14,193}$$

$$Mes^*AsH_2 + Cl_2PCH(SiMe_3)_2 \xrightarrow[THF\ /\ 0°C]{DBU} \underset{\underline{\underline{343}}}{Mes^*{-}As{=}P{-}CH(SiMe_3)_2} \quad ^{14,192}$$

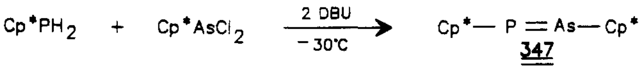
$$Mes^*AsH_2 + Cp^*PCl_2 \xrightarrow[-20°C\ \longrightarrow\ RT]{DBU} \underset{\underline{\underline{344}}}{Mes^*{-}As{=}P{-}Cp^*} \quad ^{91b}$$

$$Mes^*AsCl_2 + Cp^*PH_2 \xrightarrow[-20°C\ \longrightarrow\ RT]{DBU} \underset{\underline{\underline{344}}}{Mes^*{-}As{=}P{-}Cp^*} \quad ^{91b}$$

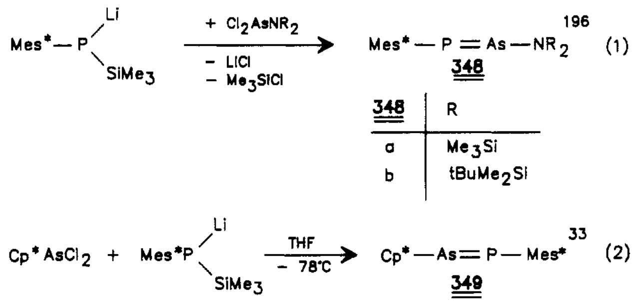
Scheme 186



Scheme 187

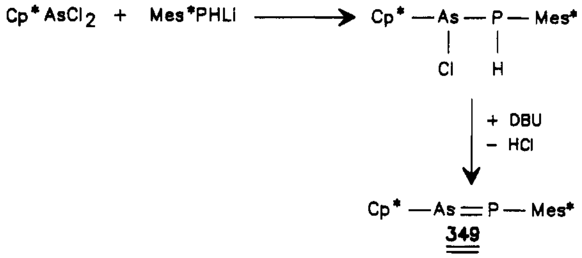


Scheme 188



via the phosphino arsane Mes*PHAsX$C_6H_2(iPr)_3$-2,4,6.[194] The phosphaarsene **346** with a ferrocenyl substituent, which formed readily in THF, decomposed when the solution was concentrated[195] (Scheme 186).

Scheme 189



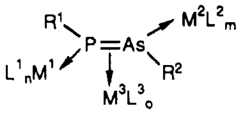
A similar instability was reported from phosphaarsene Cp*As=PCp* (**347**)[91b] (Scheme 187). Both phosphaarsenes were trapped as ligands in platinum complexes (see section XI).

A somewhat different synthetic pathway took advantage from the ready 1,2 elimination of LiCl and Me_3SiCl (Scheme 188). Here a stepwise synthesis via a functionalized phosphinoarsane with subsequent HCl elimination was also feasible[33] (Scheme 189).

There are only two accounts in the literature which are concerned with the successful synthesis of phosphastibenes.

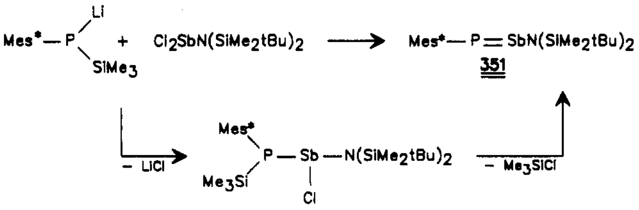
In the reaction mixture of $(Me_3Si)_2CHSbCl_2$, supermesitylphosphane, and DBU at 0 °C, phosphastibene Mes*P=SbCH$(SiMe_3)_2$ (**350**) was detected by its ^{31}P NMR resonances at $\delta = 620.0$. At ambient temperature the compound completely decomposed within 2 hours.

Table 10. ^{31}P NMR Data of Phosphaarsenes, η^1-Phosphaarsene Complexes, Metallophosphaarsenes, and η^1-Complexes of Metallophosphaarsenes



compd	R^1	R^2	$M^1L^1_n$	$M^2L^2_m$	$M^3L^3_o$	$\delta\ ^{31}P$	solvent	ref(s)
339	$C(SiMe_3)_3$	$C(SiMe_3)_3$				668	not given	190a
342	Mes*	$CH(SiMe_3)_2$				575	CH_2Cl_2	14, 193
343	$CH(SiMe_3)_2$	Mes*				533	CH_2Cl_2	14, 192
344	Cp*	Mes*				541	C_6D_6	91b
345	Mes*	2,4,6-$iPr_3C_6H_2$				580	C_6D_6	194
346	Mes*	1-ferrocenyl				492.8	THF	195
347	Cp*	Cp*				568.3	THF	91b
348a	Mes*	$N(SiMe_3)_2$				540.6		196
348b	Mes*	$N(SitBuMe_2)_2$				543.5		196
349	Mes*	Cp*				536.8	C_6D_6	98a
366	$CH(SiMe_3)_2$	Mes*		$Fe(CO)_4$		429		120b
367	$CH(SiMe_3)_2$	Mes*	$Fe(CO)_4$			390		120b
368	Mes*	Cp*		$Cr(CO)_5$		554.5	C_6D_6	98a
372	Mes*	Cp*			$Pt(PPh_3)_2$	66.3	C_6D_6	98a
373	Mes*	1-ferrocenyl			$Pt(PPh_3)_2$	62.4		195
374	Cp*	Cp*			$Pt(PPh_3)_2$	105.4	THF	91b
375	Cp*	Mes*			$Pt(PPh_3)_2$	89.6	C_6H_6	91b
402a	Mes*	$Cp^*(CO)_2Fe$				603	THF	211, 212
402b	Mes*	$Cp(CO)(PPh_3)Fe$				605.3	C_6D_6	211, 212
402c	Mes*	$MeCp(CO)(PPh_3)Fe$				603.3	C_6D_6	211, 212
403a	Mes*	$Cp^*(CO)_2Fe$		$Cr(CO)_5$		628.8	C_6D_6	212
403b	Mes*	$Cp(CO)(PPh_3)Fe$		$Cr(CO)_5$		608.7	C_6D_6	212
403c	Mes*	$MeCp(CO)(PPh_3)Fe$		$Cr(CO)_5$		607.4	C_6D_6	212
406a	$Cp^*(CO)_2Fe$	Mes*				765.7	THF	213
406b	$Cp^*(CO)_2Ru$	Mes*				724.9	THF	213
406c	$Cp^*(PPh_3)(CO)Fe$	Mes*				821.3	THF	213
410a	$Cp^*(CO)_2Fe$	Mes*	$Cr(CO)_5$			616.3	C_6D_6	213
410b	$Cp^*(CO)_2Ru$	Mes*	$Cr(CO)_5$			579.0	C_6D_6	213
410c	$Cp^*(PPh_3)(CO)Fe$	Mes*	$Cr(CO)_5$			618.4	C_6D_6	213
411a	Mes*	$Cp^*(CO)_3Cr$				608.2	C_6D_6	167
411b	Mes*	$Cp^*(CO)_3Mo$				586.9	$CDCl_3$	167
412a	Mes*	$Cp^*(PPh_3)Ni$				587	C_6H_6/toluene	98a
412b	Mes*	$Cp^*(Pn\text{-}Bu_3)Ni$				588	C_6H_6/toluene	98a

Scheme 190



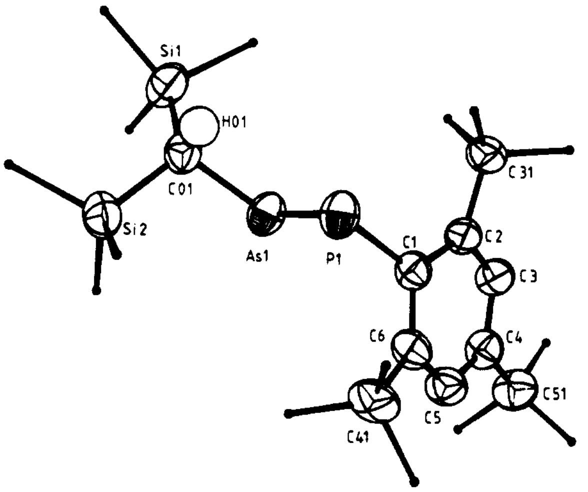
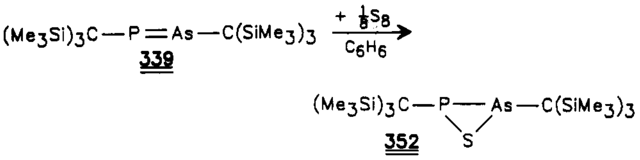


Figure 26. Molecular structure of (*E*)-$(Me_3Si)_2CHAs{=}PMes^*$ (**342**). Selected bond lengths (Å) and bond angles (deg): As(1)-P(1) 2.124 (2), As(1)-C(01) 1.995 (5), P(1)-C(1) 1.847 (5); C(01)-As(1)-P(1) 101.2 (2), As(1)-P(1)-C(1) 96.4 (2). Reprinted from ref 193. Copyright 1983 Chemical Society, London.

Scheme 191



A more promising approach was based upon the coupling of an aminodichlorostibane with $LiP(SiMe_3)$-Mes*. The product **351** was obtained as a dark red oil[196] (Scheme 190).

In the ^{31}P NMR spectra, the phosphaarsenes (Table 10) gave rise to resonances at even lower fields than those of the related diphosphenes [for example, $(Me_3Si)_3CAs{=}PC(SiMe_3)_3$, $\delta = 668$, versus $(Me_3Si)_3CP{=}PC(SiMe_3)_3$, $\delta = 599$].

The As=P bond in $Mes^*P{=}AsCH(SiMe_3)_2$ (**342**) amounts to 2.124 (2) Å.[193] Here the bond angle at phosphorus [96.4 (2)°] is much smaller than in **1** [102.8 (1)°] (Figure 26).

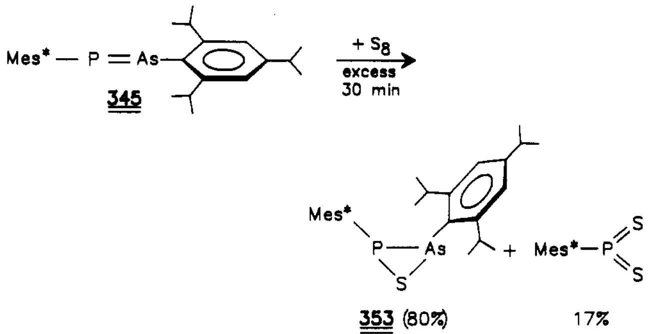
X. Reactivity of Phosphaarsenes and Diarsenes

A. Reactions with Sulfur and Selenium

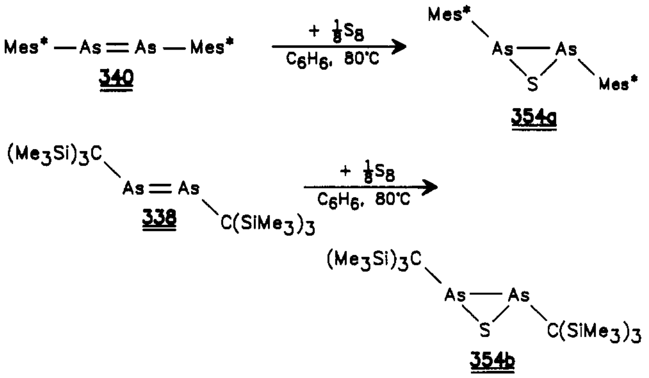
Phosphaarsenes such as **339** are prone to reaction with sulfur, usually producing thiaphosphaarsiranes like **352**[190,194] (Scheme 191).

The treatment of **345** with crystalline sulfur in benzene at ambient temperature led to the corresponding heterocycle **353** as the main product (Scheme 192).

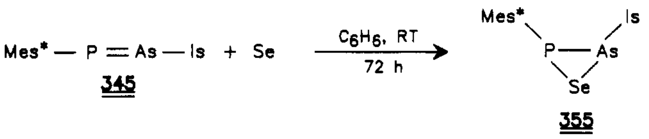
Scheme 192



Scheme 193



Scheme 194



Thiadiarsiranes **354a** and **354b** were accessible by reaction of the diarsenes **340**[191] and **338**[190b] with sulfur (Scheme 193).

Phosphaarsene **345** and gray selenium underwent reaction to yield selenaphosphaarsirane **355** as indicated by a singlet in the ^{31}P NMR spectrum at $\delta = -48.1$ ppm [$^{31}J(P^{77}Se) = 147$ Hz]. The isolation of pure **355** has been thwarted by decomposition[194] (Scheme 194).

B. Reactions with Diazomethane

The interaction of phosphaarsenes and diarsenes with CH_2N_2 opened a synthetic route to three-membered heterocycles containing phosphorus, arsenic, and carbon atoms.

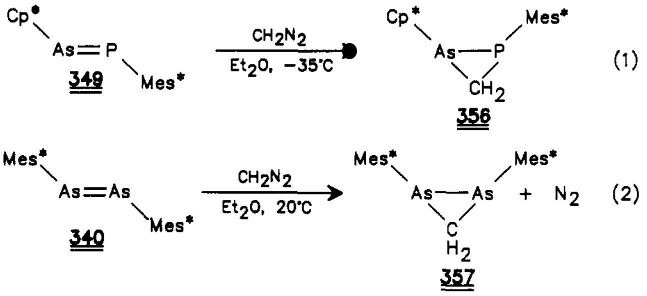
The phosphaarsene **349** experienced a clean conversion to the corresponding phosphaarsirane **356** when treated with diazomethane[91b] (Scheme 195). The yellow crystalline product gave rise to a singlet at $\delta = -148$ ppm in the ^{31}P NMR experiment.

The synthesis of diarsirane **357** was accomplished by exposing diarsene **340** to an ethereal solution of diazomethane[191] (Scheme 195).

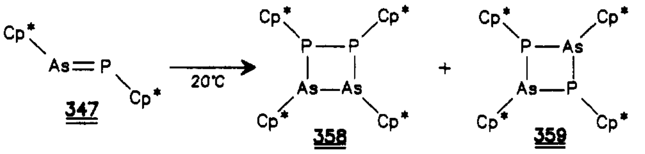
C. [2 + 2] Dimerizations and Subsequent Reactions

The phosphaarsene **347** dimerized in solution at temperatures above 0 °C to give a mixture of the two isomeric diphosphadiarsetanes **358** and **359**[91b] (Scheme 196).

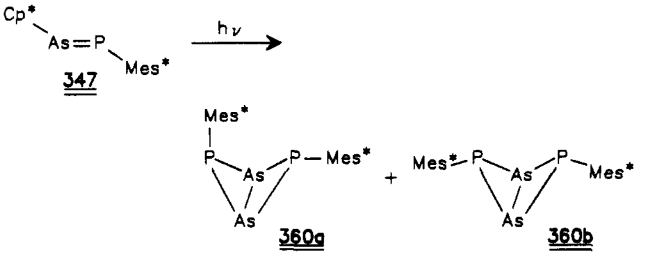
Scheme 195



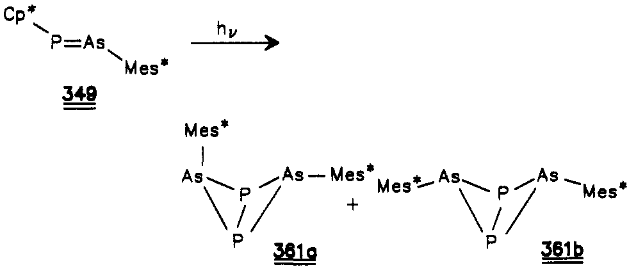
Scheme 196



Scheme 197



Scheme 198



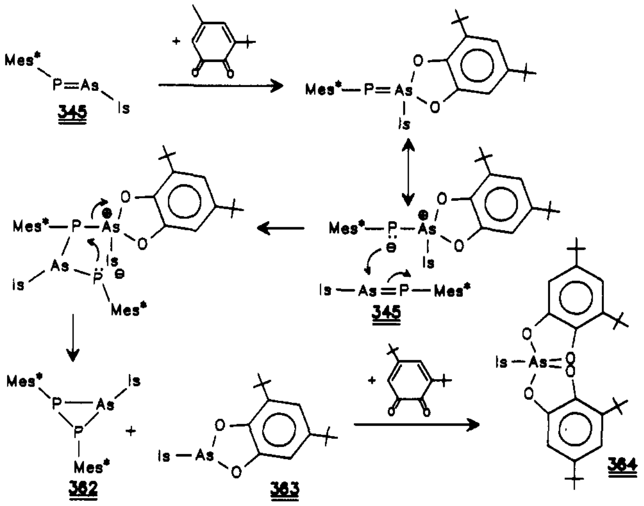
Photolysis of **347** furnished a mixture of the 1,3-diarsa-2,4-diphosphabicyclo[1.1.0]butane isomers **360**[115] (Scheme 197).

The analogous photoirradiation of a solution of **349** afforded a mixture of the thermolabile 2,4-diarsa-1,3-diphosphabicyclo[1.1.0]butanes **361**, as taken from ^{31}P NMR data of the reaction solution (Scheme 198). The decreased stability of **361** as compared to the constitutional isomers **360** was rationalized by the capability of arsenic to tolerate more acute valence angles than phosphorus.[91b]

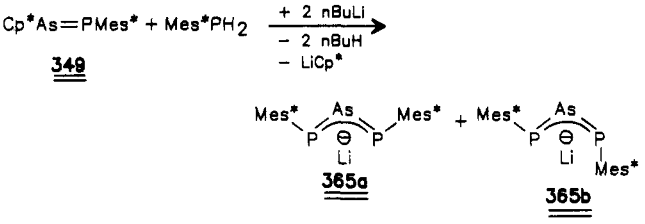
D. Reaction of Phosphaarsenes with Ortho Quinones

The reaction of an ortho quinone with Mes*P=AsIs **345** did not furnish the expected [4 + 2] cycloadduct. Instead the formation of diphosphaarsirane **362** and arsorane **364** were encountered[194] (Scheme 199). In the first step the ortho quinone attacks the phosphaarsene at the arsenic atom, which is expected to be more accessible than the phosphorus atom. The intermediate arsonium phosphanide attacks another molecule of **345** with the generation of the diphosphaarsirane **362** and arsane **363**. The latter is further oxidized by the ortho quinone to afford **364**.

Scheme 199



Scheme 200



E. Substitutions

Like the analogous diphosphene Cp*P=PMes* (**16**) phosphaarsene **349** underwent a substitution reaction when treated with lithium supermesitylphosphide. Thereby two isomeric 2-arsa-1,3-diphosphaallyl anions (**365a,b**) were generated (Scheme 200). In the ^{31}P NMR spectrum of the deep blue reaction mixture a singlet at $\delta = 252$ was assigned to the symmetric anion **365a**, whereas **365b** gave rise to doublets at $\delta = 194$ and $\delta = 284$ ppm ($^1J_{PP} = 116$ Hz). Both isomers are present in a **a**/**b** = 2:1 ratio. Attempts to isolate compounds **365** resulted in decomposition.[98a]

XI. Transition Metal Complexes of Phosphaarsenes, Diarsenes, and Distibenes

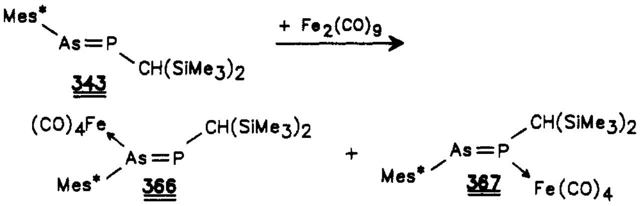
Generally the same modes of coordination as discussed with diphosphene ligands are conceivable in the complex chemistry of phosphaarsenes, diarsenes, and distibenes. To date, however, only transition metal complexes of the types A–E (section V) were described in the literature.

When treated with $Fe_2(CO)_9$ the arsaphosphene **343** was transformed into a mixture of the isomeric η^1-complexes **366** and **367**, which differ in the site of ligation of the $Fe(CO)_4$ moiety[120b] (Scheme 201).

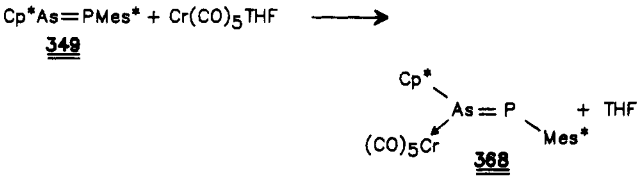
The reaction of the arsaphosphene **349** with $Cr(CO)_5THF$ gave rise to the pentacarbonylchromium adduct **368**[98a] (Scheme 202).

A carbonyliron complex with an η^1-bonded diarsene resulted from **341** and $Fe_2(CO)_9$,[120b] whereas an analogous $Cr(CO)_5$ complex was isolated from the reaction of the diarsene with $Cr(CO)_5THF$[120b,197] (Scheme 203).

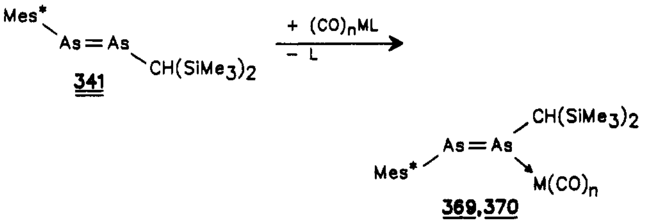
Scheme 201



Scheme 202



Scheme 203



	M	n	L
369	Fe	4	$Fe(CO)_5$
370	Cr	5	THF

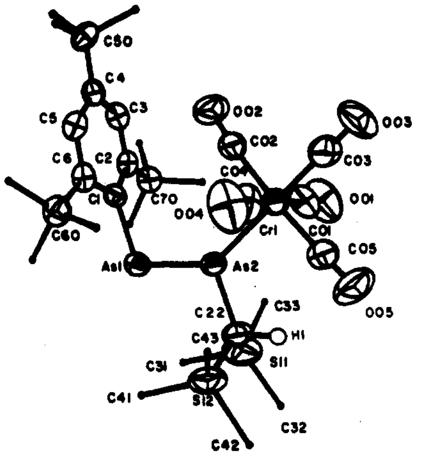
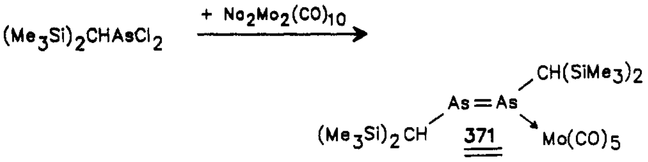
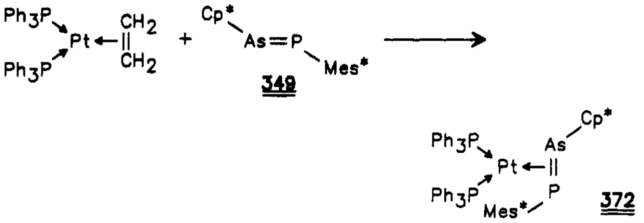


Figure 27. Molecular structure of **370**. Selected bond lengths (Å) and bond angles (deg): As(1)–As(2) 2.246 (1), As(1)–C(1) 1.978 (5), As(2)–C(22) 1.981 (5), As(2)–Cr(1) 2.454 (1); As(2)–As(1)–C(1) 104.0 (1), As(1)–As(2)–C(22) 103.9 (2), As(1)–As(2)–Cr(1) 138.51 (3), Cr(1)–As(2)–C(22) 117.6 (2). Reprinted from ref 120b. Copyright 1984 American Chemical Society.

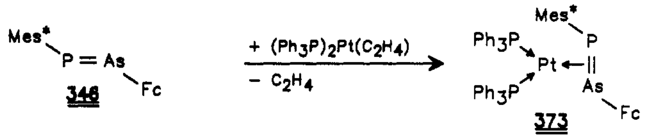
Scheme 204



Scheme 205



Scheme 206



$Fc = (\eta^5\text{-}C_5H_5)(\eta^5C\text{-}_5H_4)Fe$

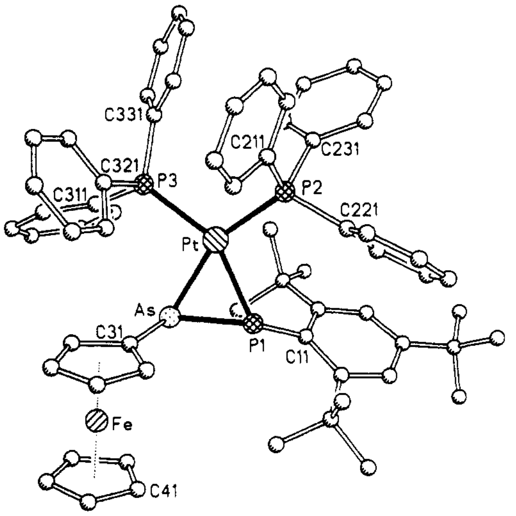


Figure 28. Molecular structure of **373**. Selected bond lengths (Å) and bond angles (deg): Pt–As 2.515 (1), Pt–P(1) 2.364 (2), Pt–P(2) 2.295 (3), Pt–P(3) 2.300 (2), As–P(1) 2.289 (3); As–Pt–P(1) 55.9 (1), As–Pt–P(2) 156.9 (1), As–Pt–P(3) 97.4 (1), P(1)–Pt–P(2) 101.1 (1), P(1)–Pt–P(3) 151.4 (1), P(2)–Pt–P(3) 105.2 (1), Pt–As–P(1) 58.7 (1), As–P(1)–Pt 65.4 (1). Reprinted from ref 195. Copyright 1988 Verlag der Zeitschrift fuer Naturforschung.

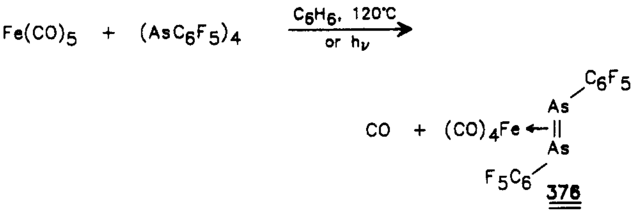
The X-ray analysis of **370** features an *E*-configurated diarsene, where the $Cr(CO)_5$ unit is linked to the arsenic center of less steric hinderance (Figure 27). The previous reactions involved free phosphaarsenes and diarsenes which obviously experienced sufficient kinetical stabilization from bulky substituents.

A different synthetic pathway to η^1-diarsene complexes is based on the reductive coupling of organodichloroarsanes by carbonyl metalate anions. The molybdenum–pentacarbonyl complex **371** was isolated when $(Me_3Si)_2CHAsCl_2$ was allowed to interact with $Na_2Mo_2(CO)_{10}$ (Scheme 204). It was assumed that for steric reasons only one $Mo(CO)_5$ fragment was accommodated at this ligand.[143]

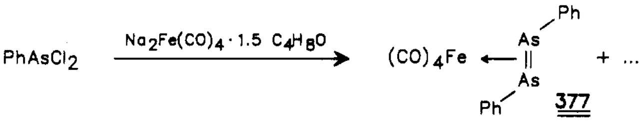
There are a few reports in the literature dealing with side-on-coordinated phosphaarsenes and diarsenes in platinum and iron complexes.

The stable phosphaarsene **349** displaced the ethylene ligand in $(C_2H_4)Pt(PPh_3)_2$ to give the expected η^2-phosphaarsene complex, which was isolated as a stable solid[98a] (Scheme 205). The interception of the thermolabile ferrocenyl-substituted phosphaarsene **346** as η^2-ligand led to the formation of platinum complex **373**[195] (Scheme 206, Figure 28). The molecular structure of **373**, as ascertained by X-ray analysis, displays a three-membered ring of the elements Pt, P, and As.

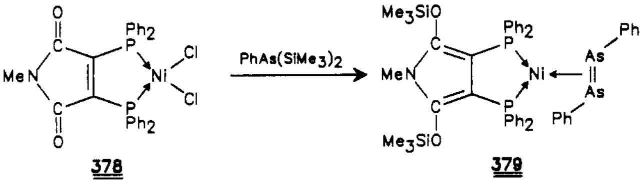
Scheme 207



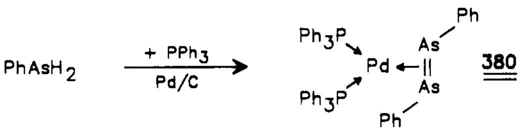
Scheme 208



Scheme 209



Scheme 210



The same synthetic approach was utilized for the preparation of the thermolabile complexes $Pt(\eta^2Cp^*{-}P{=}AsCp^*)(PPh_3)_2$ (**374**) and $Pt(\eta^2{-}Cp^*P{=}As{-}Mes^*)(PPh_3)_2$ (**375**).[91b]

The first η^2-diarsene complex was synthesized by using tetrakis-(pentafluorophenyl)cyclotetraarsane as a source for the ligand. The four-membered ring reacted with $Fe(CO)_5$ in benzene to afford **376** as yellow plates[198] (Scheme 207). In the η^2-coordinated diarsene a As–As bond distance of 2.388 Å was determined, which is somewhere between the corresponding bond lengths in $Mes^*As{=}AsCH(SiMe_3)_2$ (2.22 Å) and $(AsMe)_5$ (2.428 (8) Å).[199]

The related compound $(CO)_4Fe(\eta^2\text{-}PhAs_2Ph)$ (**377**) resulted from the dechlorination of $PhAsCl_2$ by means of $Na_2Fe(CO)_4$·1,5-dioxane[200] (Scheme 208). The diarsene ligand in this complex occupies an equatorial position in a distorted trigonal bipyramide with an As–As bond distance of 2.365 (2) Å.

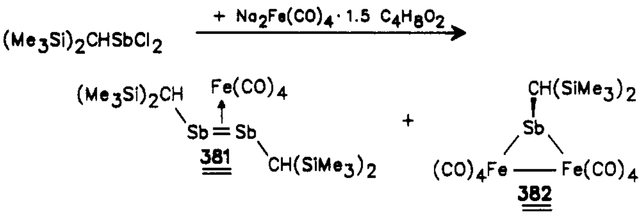
The same η^2-As_2Ph_2 ligand is constructed at a Ni center from precursor **378** and a phenyldisilylarsane[139] (Scheme 209).

The catalytic dehydrogenation of $PhAsH_2$ on palladium in the presence of PPh_3 provided another entry into the chemistry of η^2-diarsene complexes[201] (Scheme 210).

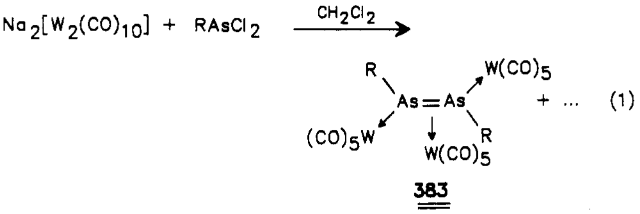
Collman's reagent reacted with $(Me_3Si)_2CHSbCl_2$ to give of a mixture of a η^2-distibene complex **381** and the cyclic diferrastibirane **382**[202,203] (Scheme 211).

According to the X-ray structure analysis compound **381** may be viewed as a complex in which the distibene $(Me_3Si)_2CHSb{=}SbCH(SiMe_3)_2$ is operating as a η^2-ligand. The Sb–Sb bond length [2.774 (1) Å] is consistent with a multiple bond, being markedly shorter than a typical Sb–Sb bond [e.g. Ph_4Sb_2 2.837 (1) Å].[204]

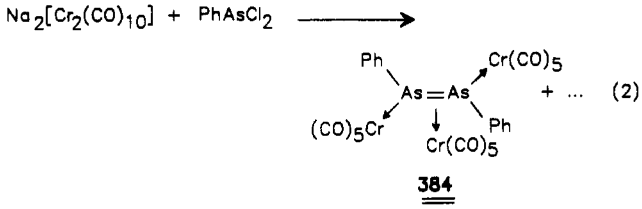
Scheme 211



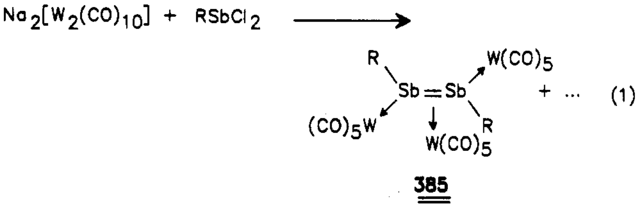
Scheme 212



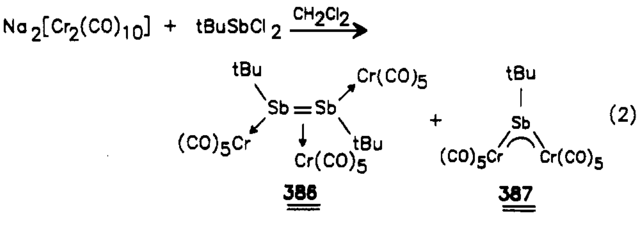
383	R	Ref.
a	Ph	143
b	CH=CClPh	143



Scheme 213

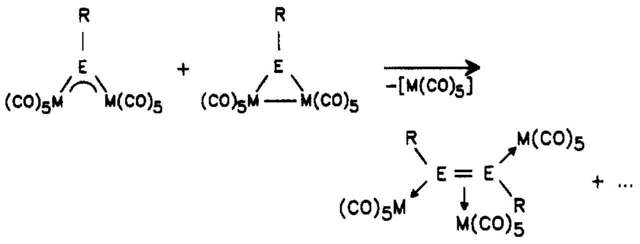


385	R	Ref.
a	tBu	207,208
b	Me	208
c	Ph	208



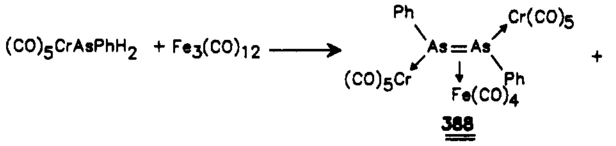
Complexes of the type E with two end-on- and one side-on-coordinated metal fragments at a As=As or Sb=Sb bond are elegantly accessible by the reaction of carbonylmetalates with organodichlorarsanes or -stibanes (Schemes 212 and 213, respectively). This reductive coupling was especially sensitive to the solvent. In CH_2Cl_2 good yields of diarsene and distibene complexes were obtained.[143,205-209] In THF solution such reactions usually furnished arsinidene or stibinidene complexes. This was explained by the donor ability of the THF molecule which stabilizes transient arsinidene and stibinidene species. In the absence of the donor solvent a dimerization of the latter species is invoked

Scheme 214

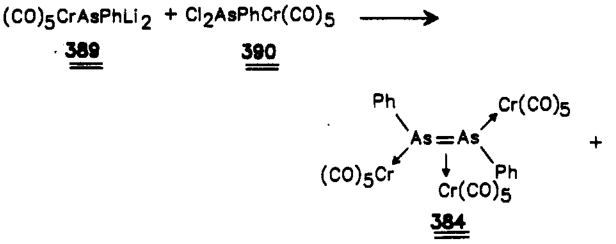


E = P,As,Sb; M = Cr,M,W; R = alkyl, aryl

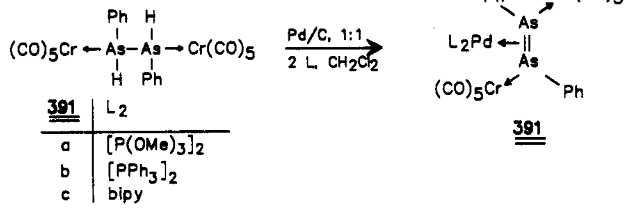
Scheme 215



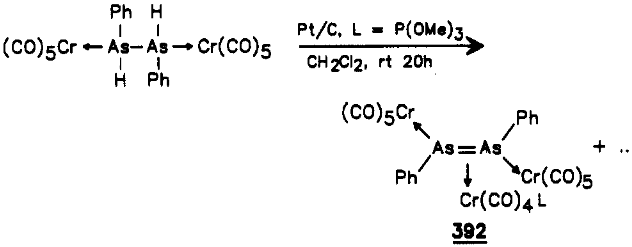
Scheme 216



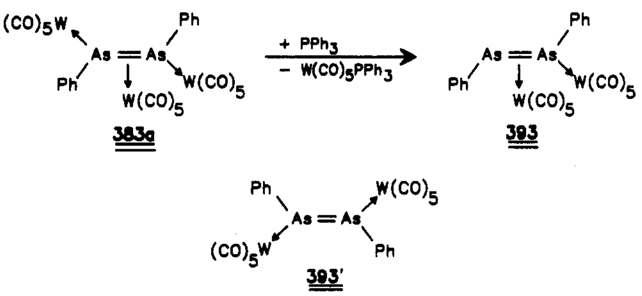
Scheme 217



Scheme 218



Scheme 219



to explain the preferred formation of the double-bond species[143,208] (Scheme 214).

Alternative procedures for the preparation of diarsene complexes such as **388** took advantage of the dehydrogenation of $(CO)_5Cr(PhAsH_2)$ in the presence of $Fe_3(CO)_{12}$ (Scheme 215).[143]

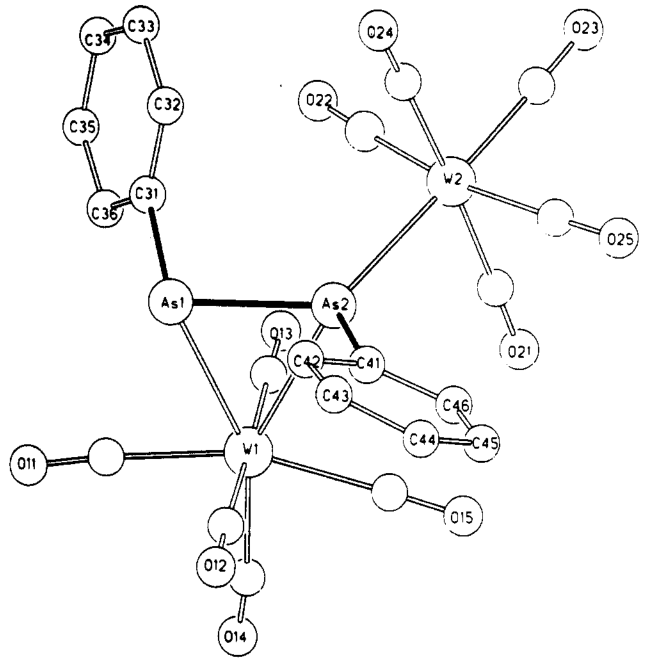


Figure 29. Molecular structure of **393**. Selected bond lengths (Å) and bond angles (deg): As(1)–As(2) 2.342 (4), W(1)–As(1) 2.769 (4), W(1)–As(2) 2.728 (4), W(2)–As(2) 2.622 (4), As(1)–C(31) 1.96 (2), As(2)–C(41) 1.96 (2); C(31)–As(1)–As(2) 99.3 (6), As(1)–As(2)–C(41) 102.3 (6), As(1)–W(1)–As(2) 50.4 (1), W(1)–As(1)–As(2) 63.9 (1), W(1)–As(2)–As(1) 65.7 (1). Reprinted from ref 143. Copyright 1986 Verlag der Zeitschrift fuer Naturforschung.

The reaction of dilithioarsenide complex **389** with dichloroarsane complex **390** also afforded the diarsene complex **384** (Scheme 216).[205]

An interesting entry into diarsene chemistry consisted in the catalytic dihydrogenation of a dinuclear diarsane complex in the presence of auxiliary ligands[201,210] (Schemes 217 and 218).

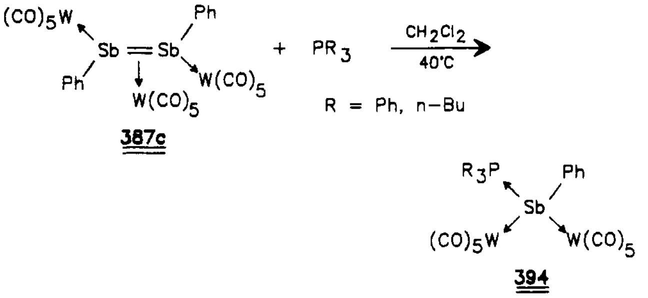
The identity of coordination compounds with μ-(η^1:η^1:η^2)-diarsene and -distibene ligands was manifested by several X-ray structure analyses.

XII. Reactivity of Diarsene and Distibene Complexes

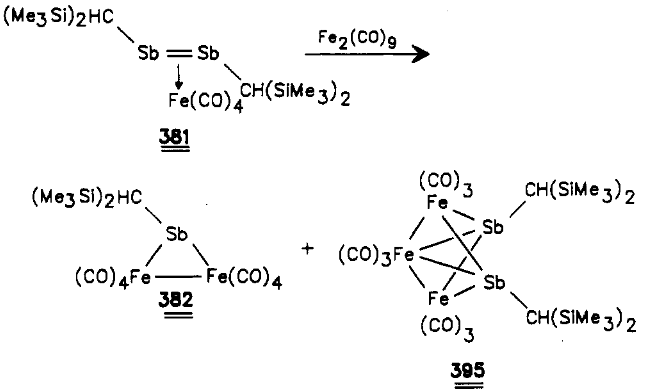
As already mentioned before, heating a solution of $[Cr(CO)_5]_3(PhP{=}PPh)$ (**214**) yielded deep violet $[Cr(CO)_5]_2(PhP{=}PPh)$ (**215**) with an unsupported P=P bond.[142b] In contrast to this finding the removal of a $W(CO)_5$ group from $[W(CO)_5]_3(PhAs{=}AsPh)$ (**383a**) with PPh_3 led to the dinuclear (η^1:η^2)-diarsene complex **393** (Scheme 219, Figure 29). Obviously this mode of coordination is more stable than the arrangement in the (η^1:η^1)-diarsene complex **393'**.[143]

A completely different behavior was encountered when the analogous distibene moiety was treated with tertiary phosphanes. Here the cleavage of the Sb=Sb bond under generation of a base-stabilized stibinidene complex was observed. One half of the distibene was quantitatively converted into the stibinidene complex **394**, whereas the fate of the second half was unclear[208] (Scheme 220). This reaction establishes a chemical proof for the proposal that stibinidene and distibene complexes are closely related to each other. The η^2-distibene iron complex **381** served as precursor for the polynuclear compounds **382** and **395** when treated with $Fe_2(CO)_9$[202] (Scheme 221).

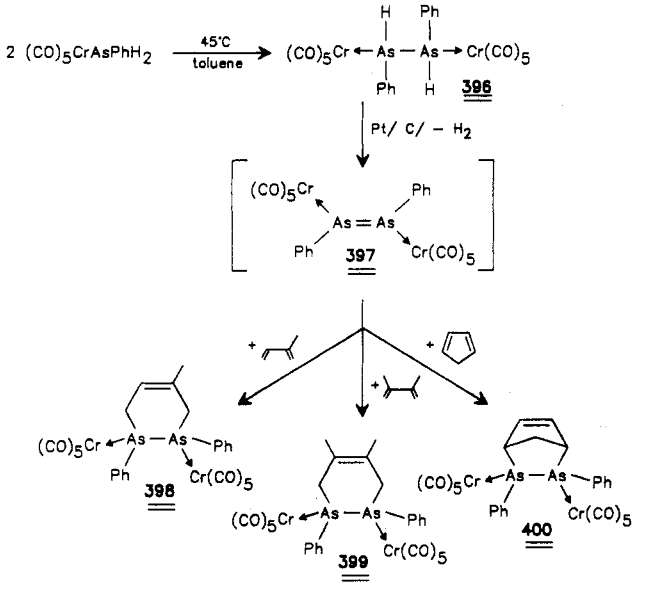
Scheme 220



Scheme 221



Scheme 222

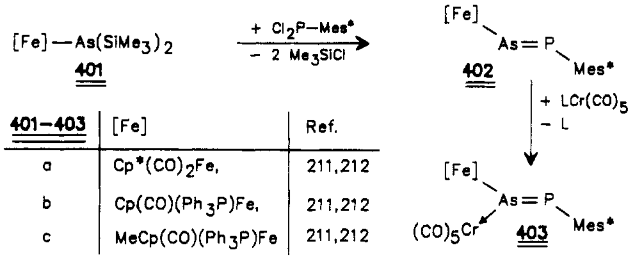


Despite the instability of complex $(CO)_5WAs(Ph){=}As(Ph)W(CO)_5$ (**393′**) with respect to its (η^1:η^2)-isomer **393** it was possible to generate reactive $(CO)_5CrAs(Ph){=}As(Ph)Cr(CO)_5$ (**397**) from the diarsane complex **396** by catalytic dehydrogenation. Trapping experiments proved the existence of this transient species[201,210] (Scheme 222). An *E* stereochemistry was present in the Diels–Alder-adducts **398–400**.

XIII. Phosphaarsenyl and Diarsenyl Complexes

A short extra section for metallophosphaarsenes and metallodiarsenes seems to be justified for the same reasons as given before for metallodiphosphenes.

Scheme 223



401–403	[Fe]	Ref.
a	Cp*(CO)2Fe,	211,212
b	Cp(CO)(Ph3P)Fe,	211,212
c	MeCp(CO)(Ph3P)Fe	211,212

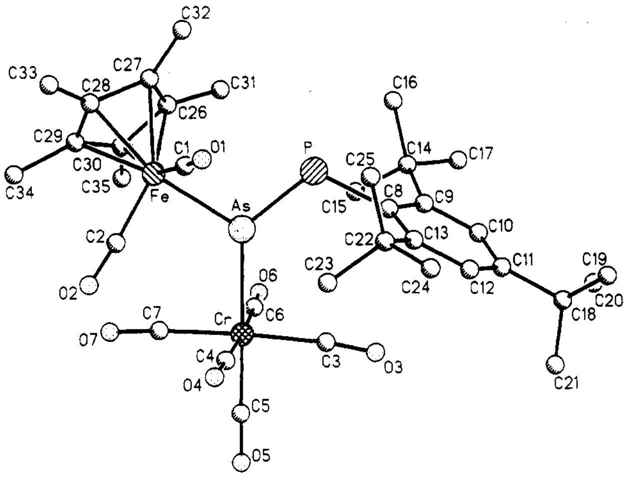
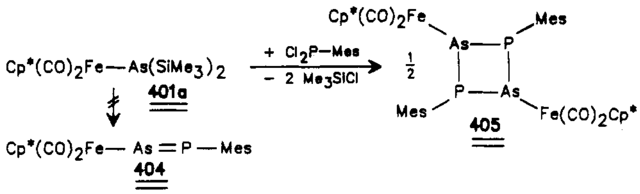


Figure 30. Molecular structure of (η^5-C_5Me_5)$(CO)_2FeAs[Cr(CO)_5]{=}PMes^*$ (**403a**). Selected bond lengths (Å) and angles (deg): Fe–As 2.389 (1), As–P 2.155 (1), As–Cr 2.494 (1), P–C(8) 1.855 (5); Fe–As–P 102.2 (1), Fe–As–Cr 125.3 (1), Cr–As–P 131.4 (1), As–P–C(8) 112.1 (1). Reprinted from ref 212. Copyright 1988 VCH (Weinheim).

Scheme 224

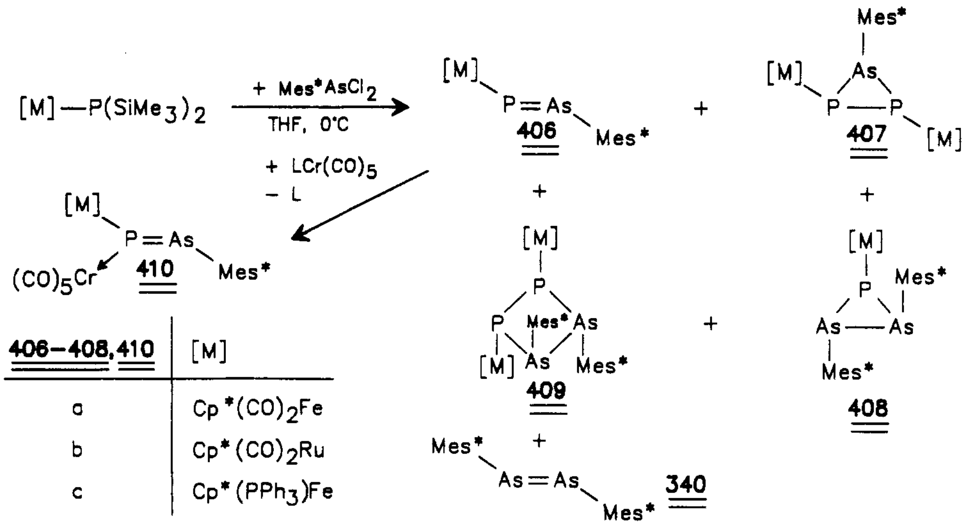


The synthetic strategy developed for the preparation of diphosphenyl complexes is also valid for the generation of the two isomeric forms of phosphaarsenyl complexes [M]As=PR and [M]P=AsR (Scheme 223). The disilylarsenido iron complexes **401a–c** were converted by Mes^*PCl_2 into the corresponding phosphaarsenyl complexes **402a–c** with a Fe–As linkage. The derivatives containing a PPh_3 group as ancilliary ligands **402b,c** are stable dark-red solids. The complex $Cp^*(CO)_2FeAs{=}PMes^*$ (**402a**), however, suffered from rapid decomposition to $Mes^*P{=}PMes^*$ and other unidentified species.[211] Trapping experiments with [(*Z*)-cyclooctene]$Cr(CO)_5$ provided the stable dark-red $Cr(CO)_5$ adduct **403a** which was subjected to an X-ray structure analysis.[212]

The molecular structure of **403a** (Figure 30) in the crystal turned out to be analogous to the corresponding diphosphene derivate $Cp^*(CO)_2FeP[Cr(CO)_5]{=}PMes^*$ (**289**). The compound features an *E*-configurated unsupported As=P double bond with the $Cr(CO)_5$ unit attached to the arsenic atom.

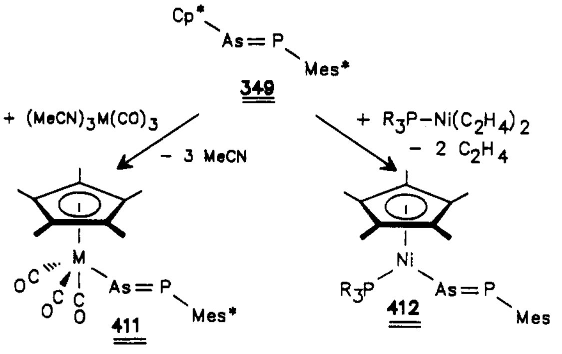
At this point it should be emphasized that the formation and stability of the metallophosphaarsenes [M]As=PR crucially depends upon the steric situation of the organic group R. This became evident, when compound **401a** was treated with mesityldichlorophosphane. Here no monomeric phosphaarsenyl complex

Scheme 225



406–408,410	[M]
a	$Cp^*(CO)_2Fe$
b	$Cp^*(CO)_2Ru$
c	$Cp^*(PPh_3)Fe$

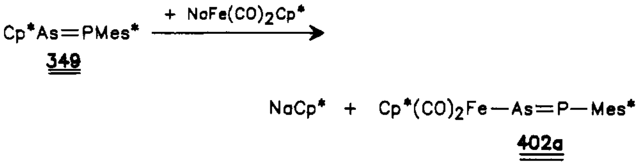
Scheme 226



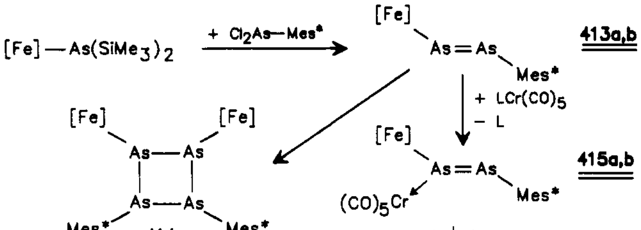
a) M=Cr; b) M=Mo

a) R=Ph; b) R=nBu

Scheme 227



Scheme 228



413,415	[Fe]
a	$Cp^*(CO)_2Fe$
b	$Cp(CO)(PPh_3)Fe$

such as **404** was detected. Instead 1,3-diphospha-2,4-diarsetane (**405**) was isolated[211] (Scheme 224).

Disilylphosphido complexes of iron and ruthenium underwent reaction with Mes^*AsCl_2 to give phosphaarsenyl complexes **406** with a metal–phosphorus linkage. In addition the diphosphaarsiranes **407**, phosphadiarsiranes **408**, 1,2-diphospha-3,4-diarsetanes **409**, and the diarsene **340** were formed[213] (Scheme 225).

The phosphaarsenyl complexes **406a,b** could not be isolated from the reaction mixture. But again the interception with [(*Z*)-cyclooctene]$Cr(CO)_5$ provided the stable $Cr(CO)_5$ derivatives **410a,b**.[213]

Phosphaarsenyl complexes of chromium and molybdenum **411a,b** were synthesized by a different method, utilizing the lability of the Cp*–As σ-bond in phosphaarsene **349**. This molecule experienced an oxidative addition to the metals with low coordinate numbers[167] (Scheme 226). The phosphaarsenyl complexes of nickel **412a,b**, which were prepared analogously, resisted isolation due to their ready decomposition.[98a]

A third approach to a phosphaarsenyl metal complex was based upon the nucleophilic substitution of the pentamethylcyclopentadienyl ring in **349** by $NaFe(CO)_2Cp^*$ [91b] (Scheme 227).

Only the two diarsenyl complexes **413a,b** have been reported in the literature up to now. They were synthesized according to the general procedure from disilylarsenido iron complexes **401a,b** and Mes^*AsCl_2 in THF. Upon workup the cyclotetraarsane **414a** was the only tractable product (Scheme 228). The interception of the diarsenyl complexes as their $Cr(CO)_5$ derivatives **415a,b** was achieved by treatment of the freshly prepared reaction mixture with [(*Z*)-cyclooctene]$Cr(CO)_5$. A control reaction between cyclotetraarsane **414a** and [(*Z*)-cyclooctene]$Cr(CO)_5$ failed to produce the adduct **415a**.[214a,b]

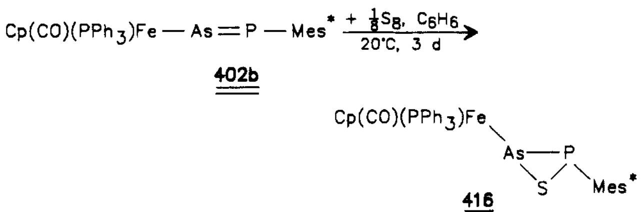
The X-ray structure analysis of **415a** shows an *E*-configurated diarsene with a free As=As bond of 2.259 (1) Å, where the $Cr(CO)_5$ unit is attached to the metalated arsenic atom, a situation well known from the analogous diphosphenyl- and phosphaarsenyl system.[214b] The chromium arsenic bond distance of 2.492 (1) Å corresponds to a single bond.

XIV. Reactivity of Phosphaarsenyl Complexes

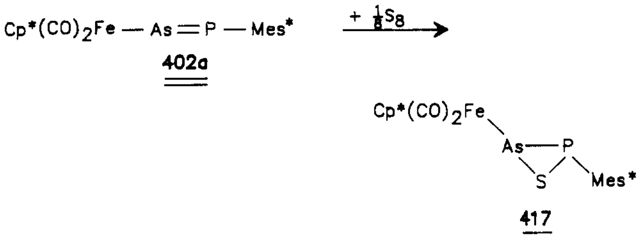
Essentially there exists only one account in the literature that is concerned with the chemical reactivity of phosphaarsenyl complexes.[170]

The phosphaarsenyl complex **402b** reacted with 1 equiv of sulfur to give the red microcrystalline metal-functionalized phosphathiaarsirane **416** (Scheme 229). A conceivable intermediate with an As=S function could not be detected by ^{31}P NMR spectroscopy. The thermolability of $Cp^*(CO)_2FeAs{=}PMes^*$ (**402a**) made

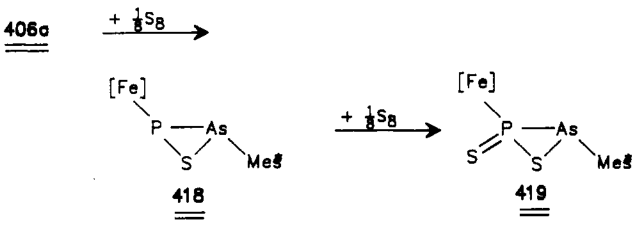
Scheme 229



Scheme 230



Scheme 231



it necessary to perform the sulfurization with the in situ generated complex (Scheme 230). The same was true for the preparation of the phosphathiaarsirane 418 starting from instable 406a (Scheme 231). The subsequent treatment of 418 with a second equivalent of sulfur furnished the phosphathiaarsirane *P*-sulfide 419.

It is remarkable that in spite of the thiophilicity of iron the metal fragment kept its position at the pnicogen atom, and that the sulfur refused to insert into the Fe–P or Fe–As bonds.

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