

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

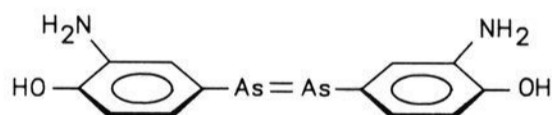


Lothar Weber was born in Langenöls/Silesia in 1944. He studied chemistry at the Philipps Universität in Marburg, where he received his "Doctor Rerum Naturalium" in 1973. For the year 1974 to 1975, he carried out postdoctoral studies with Prof. B. M. Trost in Madison/Wisconsin. In 1982 he accomplished 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 PhPCl₂ and PhPH₂, 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



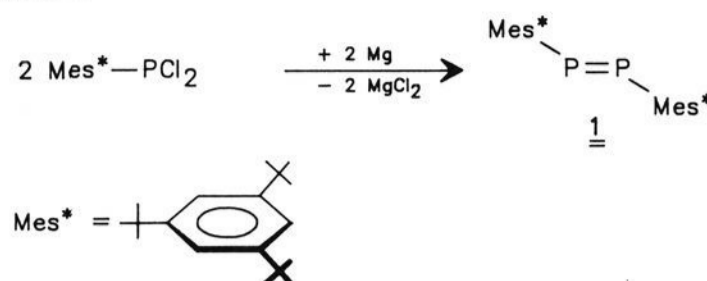
Later X-ray crystallographic work on compounds of the empirical composition C₆H₅As revealed their oligomeric character.⁷

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

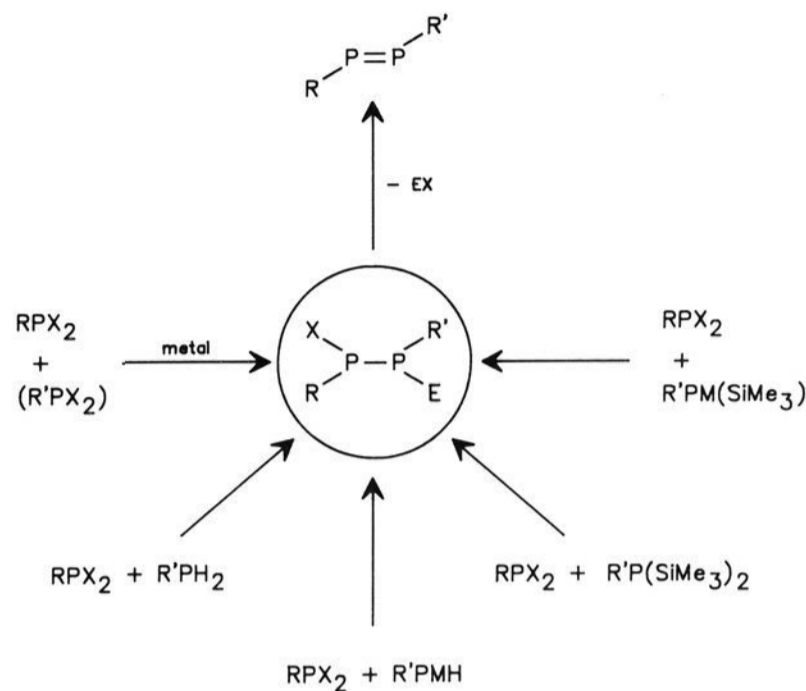
The reduction of (2,4,6-tri-*tert*-butylphenyl)dichlorophosphane with elemental magnesium in THF led to the orange-red crystalline diphosphene 1 (Scheme 1).

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 articles⁹⁻¹³ 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: *n*Bu (*n*-butyl), *t*Bu (*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), *i*Pr (isopropyl), *t*Pn (*tert*-pentyl), THF (tetrahydrofuran), TMEDA (*N,N,N',N'*-tetramethylethylenediamine), and TMP (2,2,6,6-tetramethylpiperidyl).

II. Preparations of Diphosphenes

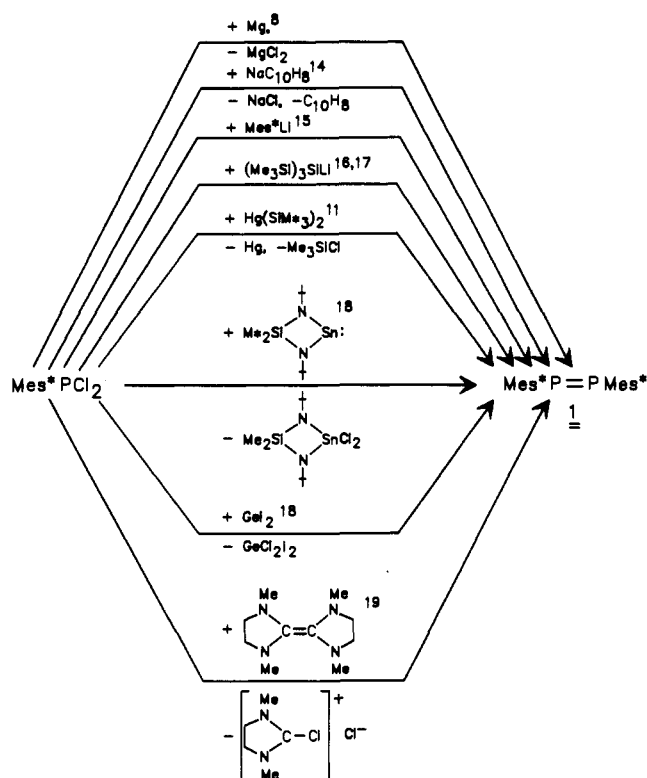
A. Eliminations and/or Condensations

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 unambiguous 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 unambiguously shown by ^{31}P NMR spectroscopy.

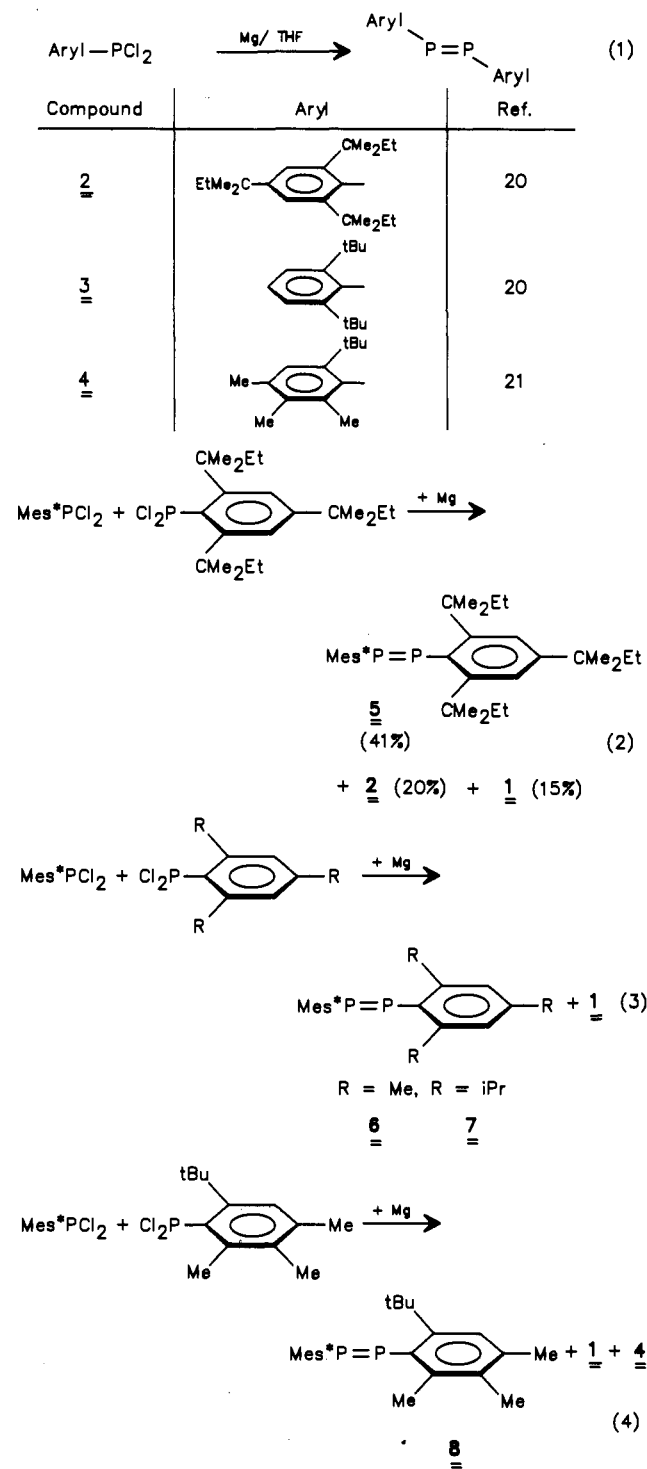
The reductive coupling of aryldichlorophosphanes by magnesium metal was utilized to furnish other symmetrically^{20,21} and unsymmetrically substituted diphosphenes²¹ (Schemes 3 and 4).

Diphosphene 1 is also available from the reduction of a 1,3,5-trithia-2,4,6-triphosphinane with triphenylphosphane¹⁵ (Scheme 5).

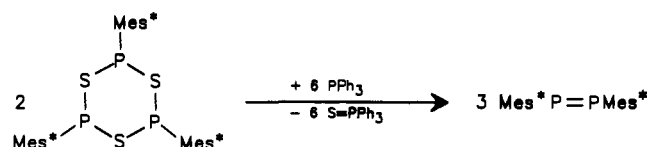
The first dialkyldiphosphene $(\text{Me}_3\text{Si})_3\text{CP}=\text{PC}(\text{SiMe}_3)_3$ (9) was obtained from the reaction of dichlorophosphane $(\text{Me}_3\text{Si})_3\text{CPCl}_2$ with sodium naphthalenide.^{14,22} Alternative syntheses of 9 made use of organolithium reagents such as $(\text{Me}_3\text{Si})_3\text{CLi}$,¹⁴ $t\text{BuLi}$,²³ as well as lithium metal²⁴ or $\text{Hg}(\text{SiMe}_3)_2$ ¹¹ as reducing agents (Scheme 6).

When the sodium naphthalenide reduction was carried out with equimolar amounts of Mes^*PCl_2 and

Scheme 4



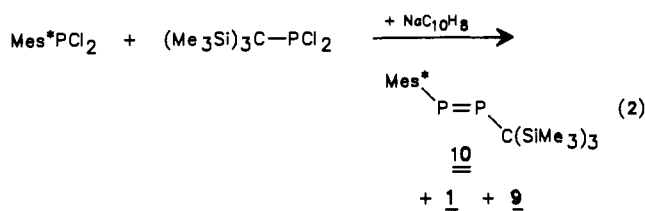
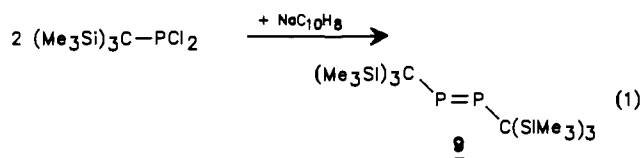
Scheme 5



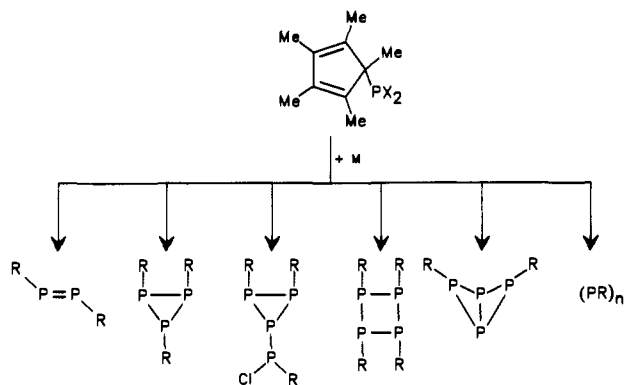
$(\text{Me}_3\text{Si})_3\text{CPCl}_2$ the predominant formation of the symmetrical diphosphenes 1 and 9 was observed. In addition the unsymmetrical diphosphene 10 was produced in 20% yield.²⁵

Bis(pentamethylcyclopentadienyl)diphosphene (11) was detected among a number of products when $(\text{C}_5\text{Me}_5)\text{PCl}_2$ was reduced by metals such as Mg, Li, and

Scheme 6

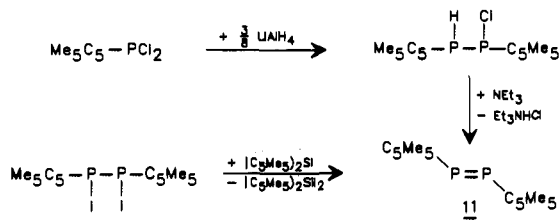


Scheme 7



M = Mg, Li, K, $\text{Li}_2\text{C}_{10}\text{H}_8$

R = C_5Me_5



K or alternatively dilithium naphthalenediide.²⁶ The dehalogenation of $[(\text{C}_5\text{Me}_5)\text{PI}]_2$ with decamethylsilocene also afforded 11.²⁷ A more convenient and straightforward synthesis of 11 was accomplished by the reduction of $(\text{C}_5\text{Me}_5)\text{PCl}_2$ with LiAlH_4 and the subsequent elimination of hydrogen chloride from the chlorodiphosphane by means of triethylamine²⁸ (Scheme 7).

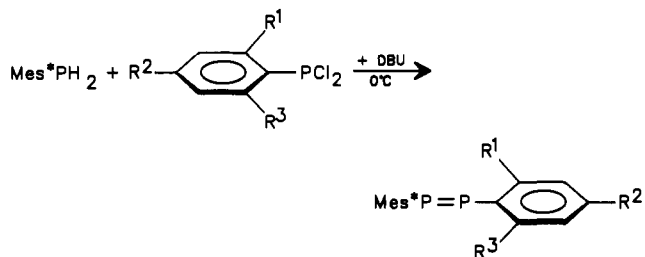
It is conceivable that the intermediate diphosphane resulted from the coupling of $(\text{C}_5\text{Me}_5)\text{PCl}_2$ with $(\text{C}_5\text{Me}_5)\text{PH}_2$.

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 diphosphenes²⁹ (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

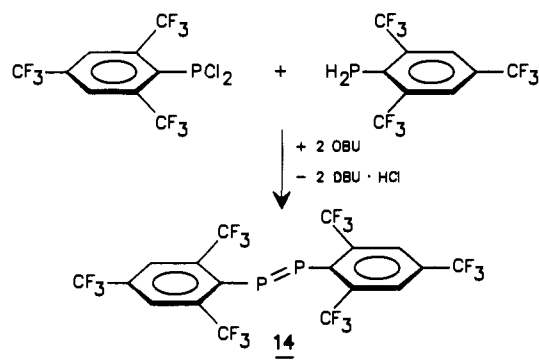
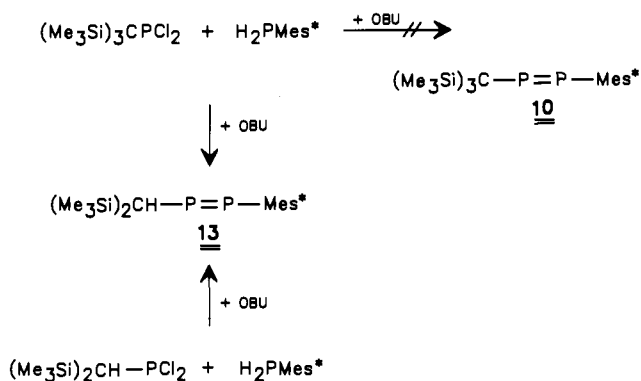
Surprisingly the attempted condensation of $(\text{Me}_3\text{Si})_3\text{CPCl}_2$ with Mes^*PH_2 in the presence of DBU did not afford the expected diphosphene 10. Instead the unsymmetrical diphosphene $(\text{Me}_3\text{Si})_2\text{CHP}=\text{PMes}^*$

Scheme 8



Compound	R ¹	R ²	R ³	yield
<u>1</u>	tBu	tBu	tBu	-
<u>8</u>	Me	Me	Me	76%
<u>12a</u>	tBu	tBu	Me	31%
<u>12b</u>	H	H	H	-

Scheme 9



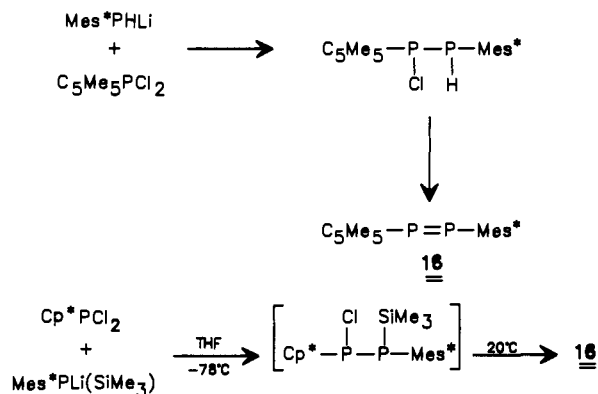
(13) was obtained.³⁰ Presumably one Me_3Si group at the trisilylmethyl substituent was removed by the nucleophilic attack of chloride during the course of the reaction. A more straightforward access to 13 was realized by the reaction of $(\text{Me}_3\text{Si})_2\text{CHPCl}_2$ with Mes^*PH_2 under similar conditions³⁰ (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 solid³¹ (Scheme 9b).

A mixture of $2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_2\text{PCl}_2$ and Mes^*PH_2 was dehydrochlorinated to give the unsymmetrical thermolabile diphosphene $2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_2\text{P}=\text{PMes}^*$ (15).³² Instead of primary phosphanes the respective phosphides or organosilylphosphides were also successfully employed for diphosphene syntheses (Scheme 10). The intermediate diphosphane $\text{Cp}^*\text{P}(\text{Cl})-\text{P}(\text{H})\text{Mes}^*$ was not identified.³³

An efficient synthesis of $(\text{Me}_3\text{Si})_2\text{CHP}=\text{PCH}(\text{SiMe}_3)_2$ made use of HX or Me_3SiX eliminations from diphos-

Scheme 10

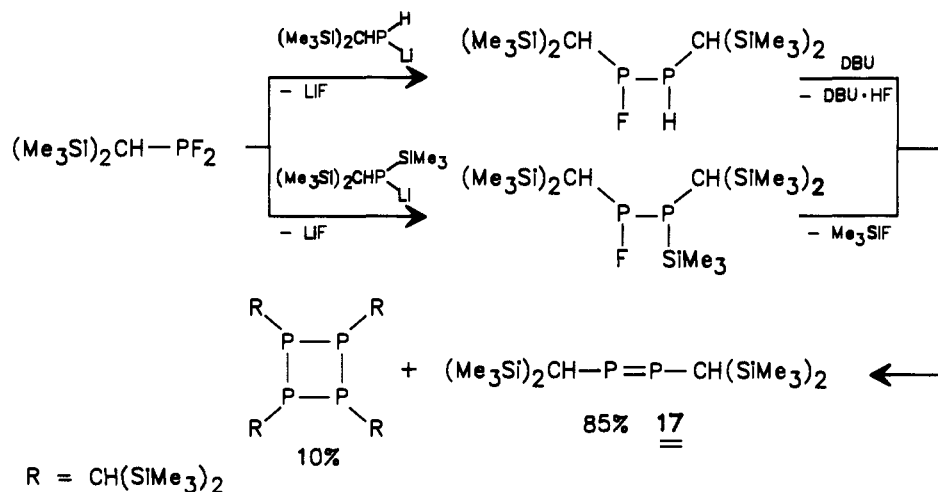


phanes as the crucial step of the process³⁴ (Scheme 11).

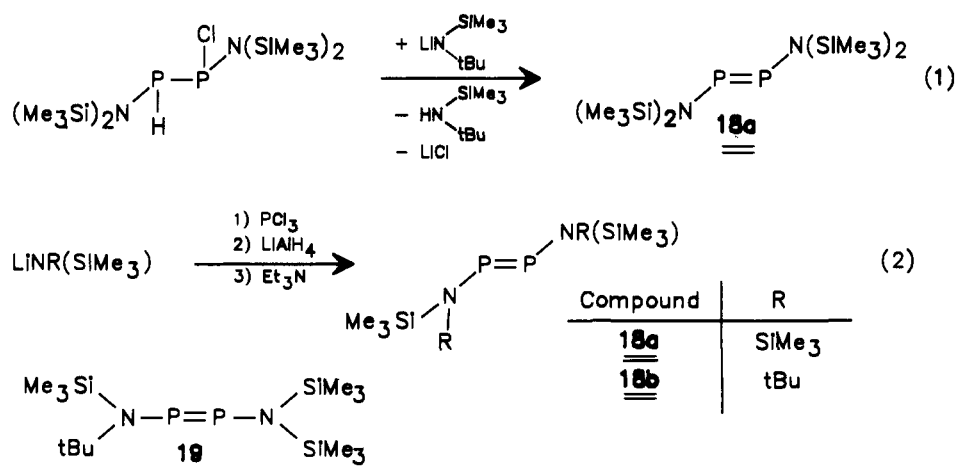
The cyclotetraphosphane stemmed from the [2 + 2] self-dimerization of **17**. This reaction possesses a half-life time of one week at ambient temperature. Obviously diphosphene **17** is at the borderline of kinetic stability.

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)SiMe₃ to give diphosphene **18a**³⁵ (Scheme 12, eq 1).

Scheme 11



Scheme 12



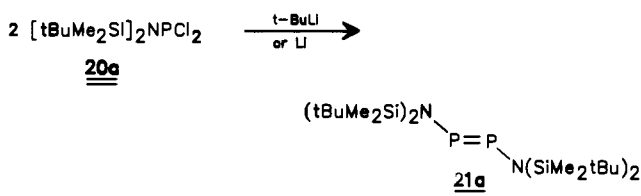
Compound **18a** was a ruby red liquid which dimerized to a cyclotetraphosphane within a few hours. The syntheses of similar diaminodiphosphenes were performed in a one-pot reaction involving the subsequent treatment of the lithium amides LiNR(SiMe₃) with PCl₃, LiAlH₄, and NEt₃³⁶ (Scheme 12, eq 2).

If a mixture of the amides LiN(SiMe₃)₂ and LiN(tBu)(SiMe₃) 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

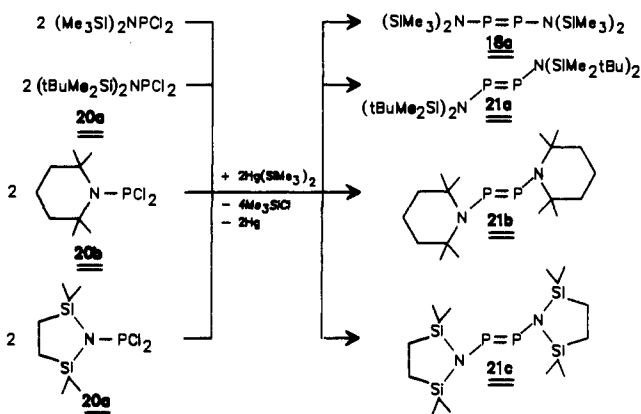
Other synthetic approaches discussed earlier were also operating well in the generation of symmetrical aminodiphosphenes. Thus the sterically well protected diphosphene **21a** was available by the reductive coupling of **20a** with lithium metal,³⁶ *tert*-butyllithium,³⁶ or Hg(SiMe₃)₂¹¹ (Scheme 13). 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

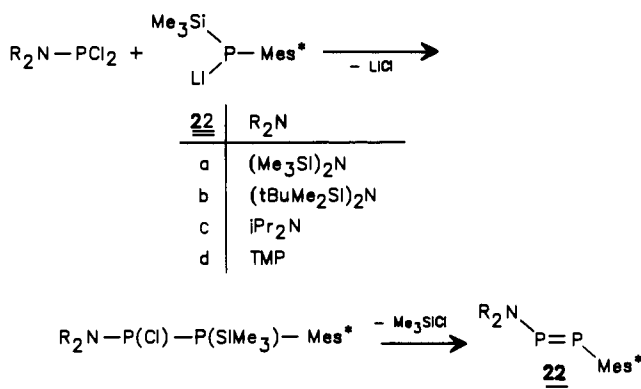
Scheme 13



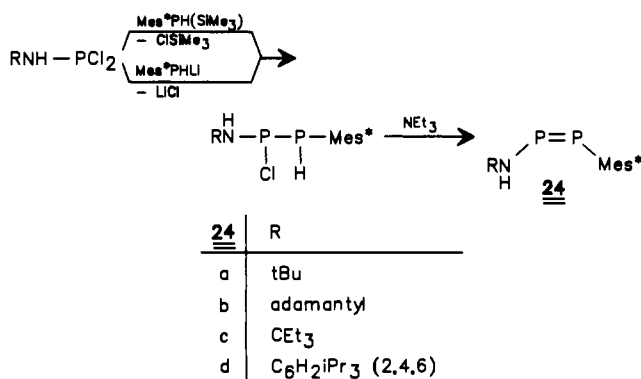
Scheme 14



Scheme 15



Scheme 16



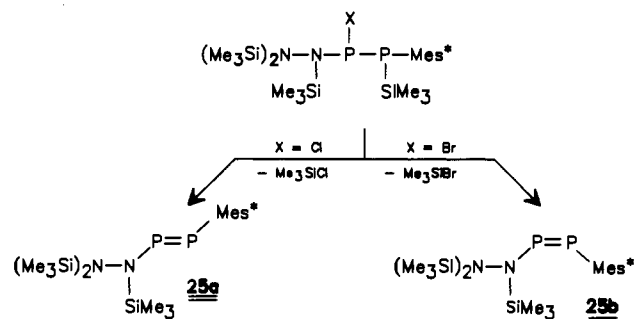
Mes*PLi(SiMe₃), Mes*PH(SiMe₃), or Mes*PHLi^{11,38} (Scheme 15).

A similar reaction between aminodichlorophosphane **20b** and LiP(tBu)(SiMe₃) furnished thermolabile TMPP=PtBu (**23**).^{37b}

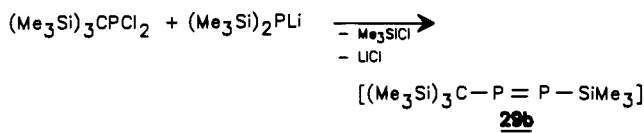
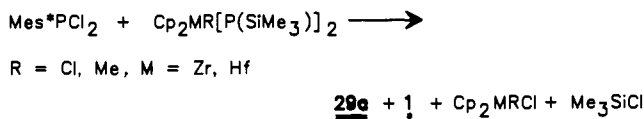
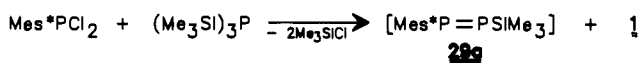
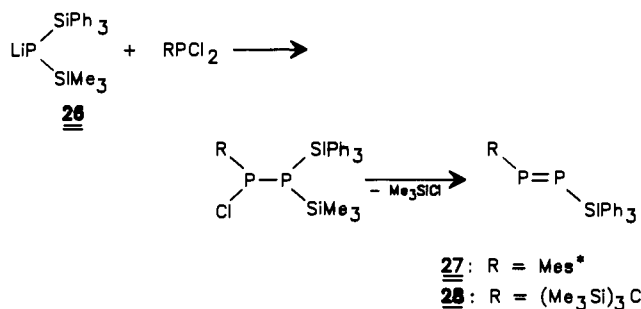
The presence of a primary amino substituent led to the rare class of the *Z*-configured diphosphenes **24**³⁹ (Scheme 16).

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

Scheme 17



Scheme 18

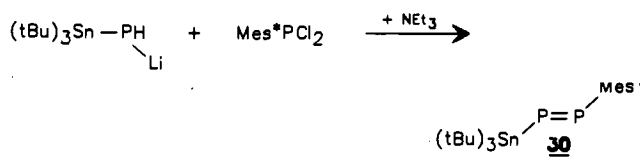


which were stable and could be synthesized selectively.^{40a,b} Thus (*E*)-(Me₃Si)₂NN(SiMe₃)P=P Mes* (**25a**) was obtained as the only product after elimination of Me₃SiCl from a functionalized 1-chlorodiphosphane, whereas the analogous reaction of the bromo derivative cleanly afforded the *Z*-isomer **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 Δ*G*_{(293)E/Z} = 25.5 (5) and Δ*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 (Δ*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*PCl₂ or (Me₃Si)₃CPCI₂ in ether solution afforded the diphosphenes **27** and **28** quantitatively. In both cases the intermediate functionalized diphosphanes were detected by ³¹P NMR spectroscopy⁴¹ (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 $\text{P}(\text{SiMe}_3)_3$ were heated in CDCl_3 the formation of $\text{Mes}^*\text{P}=\text{PMes}^*$ (**1**) took place. The unsymmetrical and thermolabile diphosphene **29a** was observed as byproduct by ^{31}P NMR techniques.²¹ A

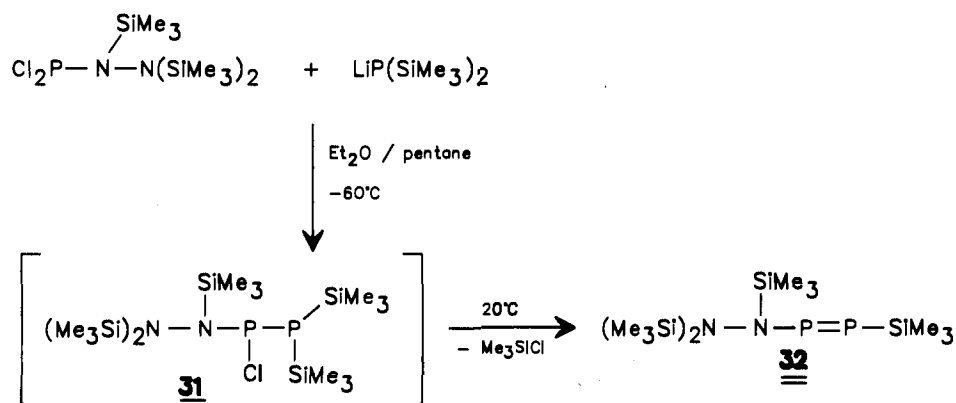
similar result was obtained when Mes^*PCl_2 was treated with bis(trimethylsilyl)phosphido complexes of zirconium and hafnium⁴² (Scheme 18b).

The formation of **1** was rationalized by a rapid $\text{Me}_3\text{Si}-\text{Si}/\text{Cl}$ exchange between the educts. **29b** was produced by coupling $(\text{Me}_3\text{Si})_3\text{CPCl}_2$ with $\text{LiP}(\text{SiMe}_3)_2$. It decomposed to a bicyclic tetraphosphane (see section IV.C.2).

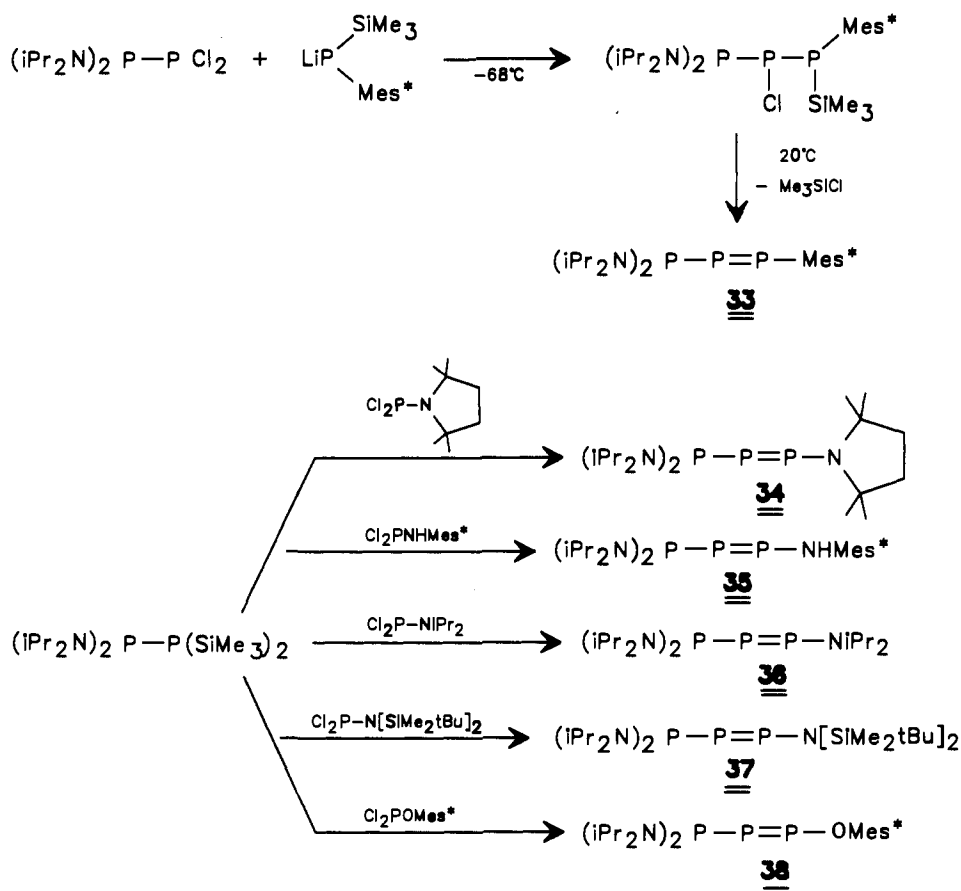
The synthesis of the first stable stannyl-substituted diphosphene **30** was also based on condensation and 1,2-elimination processes⁴³ (Scheme 19). Violet crystalline **30** was isolated in 62% yield.

When a solution of $\text{Cl}_2\text{PN}(\text{SiMe}_3)\text{N}(\text{SiMe}_3)_2$ in pentane was reacted at -60°C with a solution of $\text{LiP}(\text{SiMe}_3)_2$ in ether and the resulting solution was stirred for 3 h at room temperature the intermediate diphosphane **31**

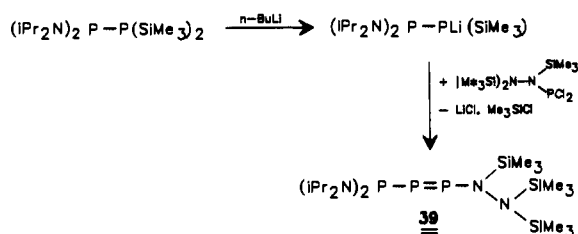
Scheme 20



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 $(\text{iPr}_2\text{N})_2\text{P}-\text{P}(\text{SiMe}_3)_2$ into a lithium derivative previous to the reaction with the hydrazidodichlorophosphane $(\text{Me}_3\text{Si})_2\text{N}_2\text{PCl}_2$ 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 Chloro-

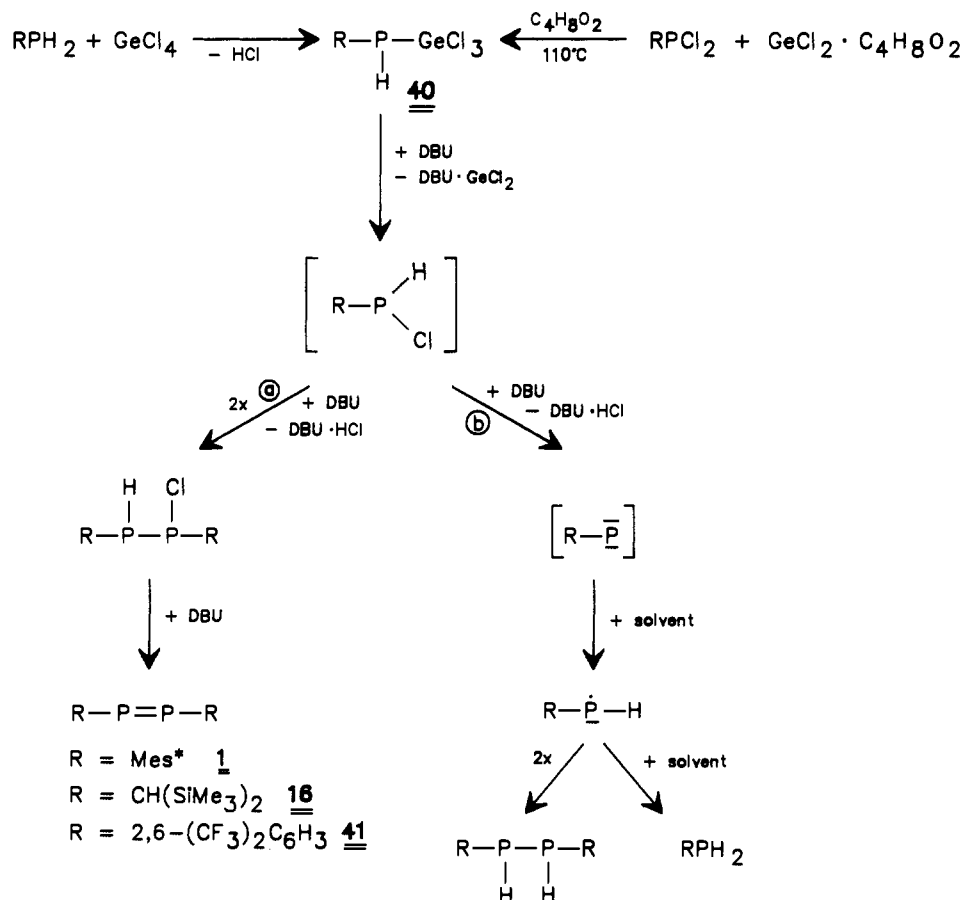
phosphanes are only sufficiently stable with bulky substituents. However the easily available (trichlorogermyl)phosphanes **40** can be utilized as in situ reagents for these reactive species. They are conveniently accessible by the treatment of a primary phosphane with GeCl_4 and the subsequent removal 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 dioxane⁴⁵ (Scheme 23).

There are two mechanisms invoked to account for diphosphene formation as well as for the occurrence of RPH_2 and $\text{RPH}-\text{PHR}$ [$\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$] 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 $\text{RPH}-\text{PHR}$ via radical intermediates. When the DBU-induced elimination was carried out with a mixture of $\text{Mes}^*\text{P}(\text{H})\text{GeCl}_3$ and $2,6\text{-(CF}_3)_2\text{C}_6\text{H}_3\text{P}(\text{H})\text{GeCl}_3$ 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).

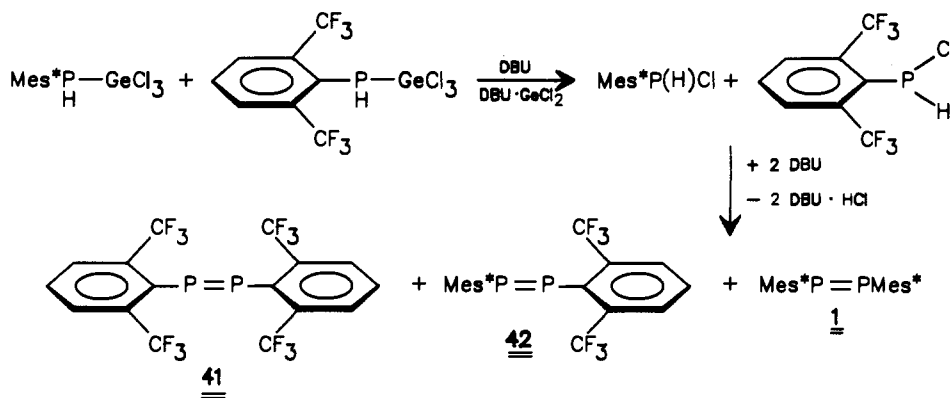
B. Rearrangement Reactions

1,3-Shift reactions of silyl substituents are of great importance for the synthesis of phosphalkenes,⁴⁶ but there are only a few examples for the formation of $\text{P}=\text{P}$

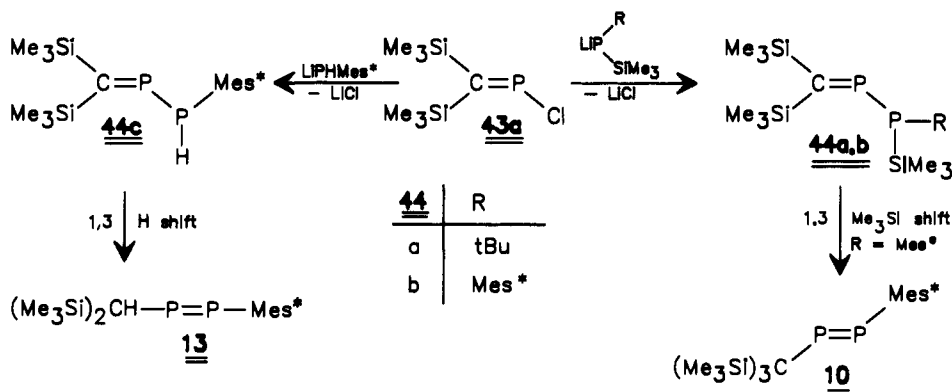
Scheme 23



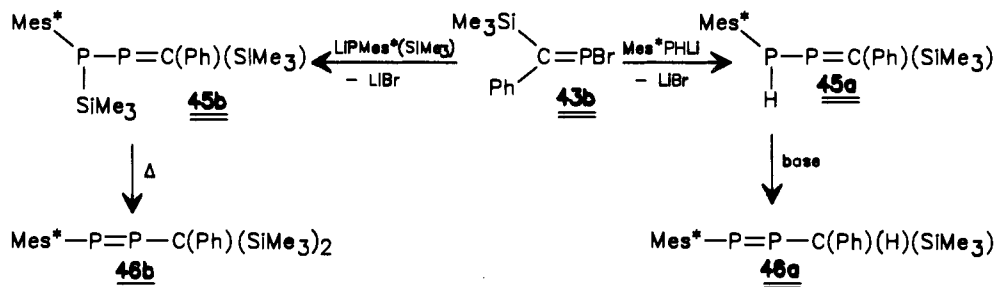
Scheme 24



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 shift⁴⁷ (Scheme 25).

The phosphino-substituted phosphalkene 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.

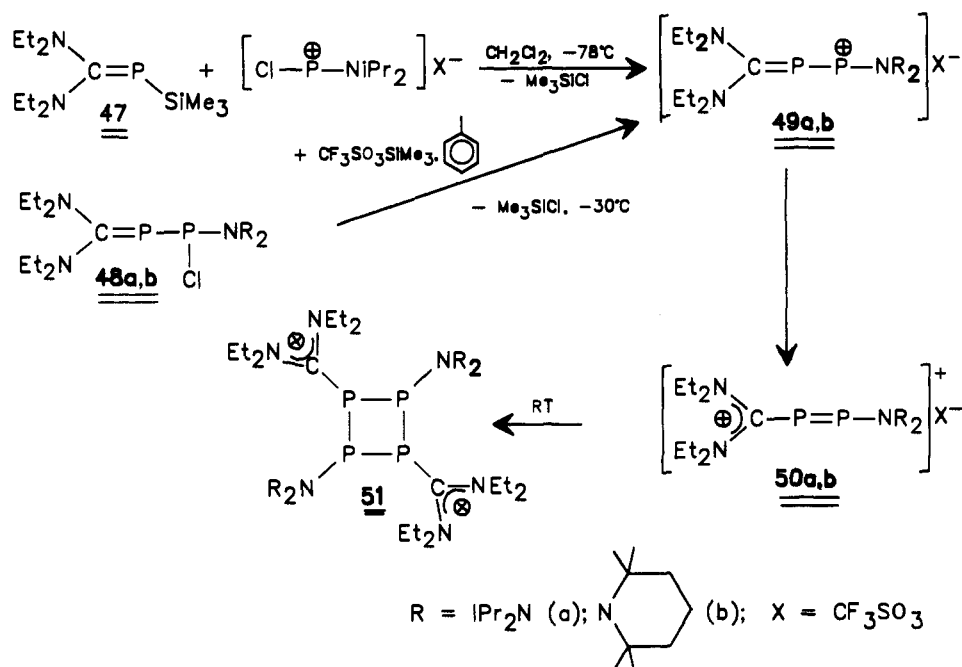
Diphosphenes 46a,b were synthesized similarly from the *P*-bromomethylenephosphane 43b and the respective lithium phosphides via the phosphalkenes 45a and 45b^{50c} (Scheme 26).

The phosphonium ions 49a,b could neither be detected in the coupling reaction of $(\text{Et}_2\text{N})_2\text{C}=\text{PSiMe}_3$

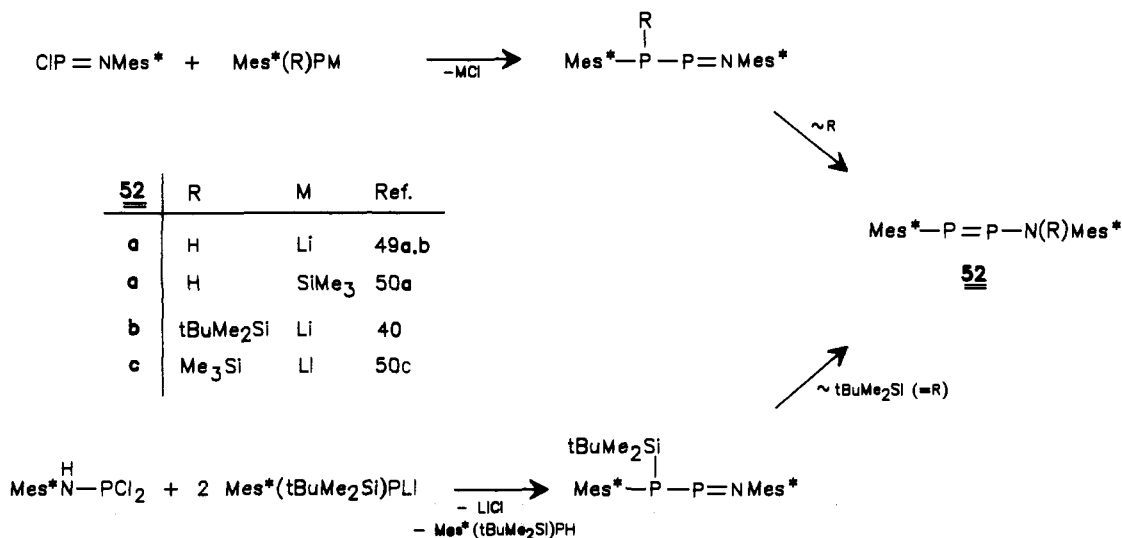
(47) with the phosphonium moiety $[\text{ClPN}(\text{iPr})_2]^+\text{SO}_3\text{CF}_3^-$ nor in the halide abstraction process from $(\text{Et}_2\text{N})_2\text{C}=\text{P}(\text{Cl})\text{NR}_2$ (48a,b). Instead at -78°C the carbenium ion-substituted diphosphenes 50a,b were observed by ^{31}P NMR (50a, $\delta = 493.5$ d, 200.0 d, $^1J_{\text{PP}} = 520$ Hz; 50b, $\delta = 465$ d, 210 d, $J_{\text{PP}} = 525$ Hz). It was obvious that the formation of the diphosphenes 50a,b was due to the extremely fast isomerization 49 \rightarrow 50, favored by the higher stability of 50a,b in comparison to the phosphonium ions 49a,b. The delocalization of the positive charge on the $(\text{Et}_2\text{N})_2\text{C}$ 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 51⁴⁸ (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 $\text{ClP}=\text{NMe}^*$ 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



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 $\text{XP}=\text{PR}'$ 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 diisopropylamide⁵¹ (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 $\text{Mes}^*\text{P}=\text{PNu}$. Diphosphene **54**, which

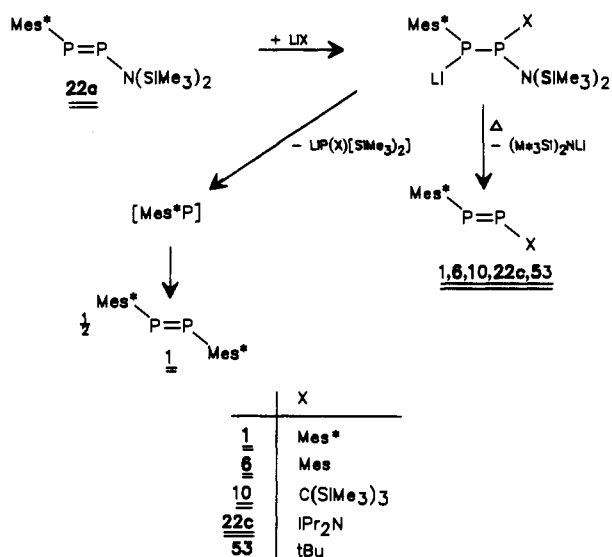
is stable in solution up to -30°C , was conveniently synthesized by the exposure of **22c** to an excess of gaseous HCl in ether solution at -78°C ⁵² (Scheme 30).

The tendency of the diphosphene $\text{Cp}^*\text{P}=\text{PCp}^*$ (**11**) to undergo facile substitution reactions could be inferred from the remarkably long $\text{P}-\text{C}$ 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 failed²⁸ (Scheme 31).

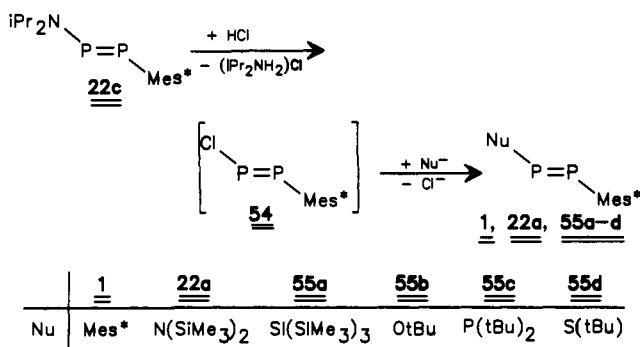
D. Miscellaneous Methods

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).

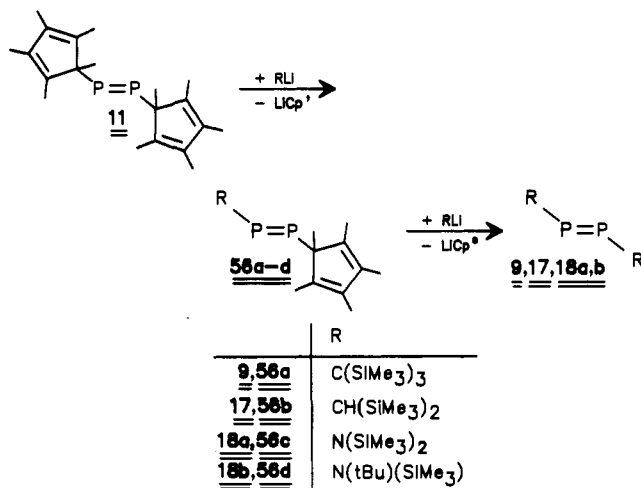
Scheme 29



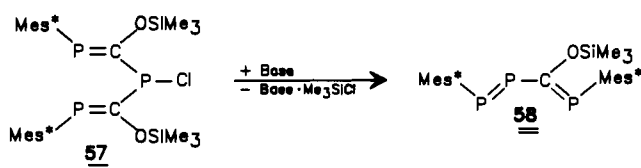
Scheme 30



Scheme 31

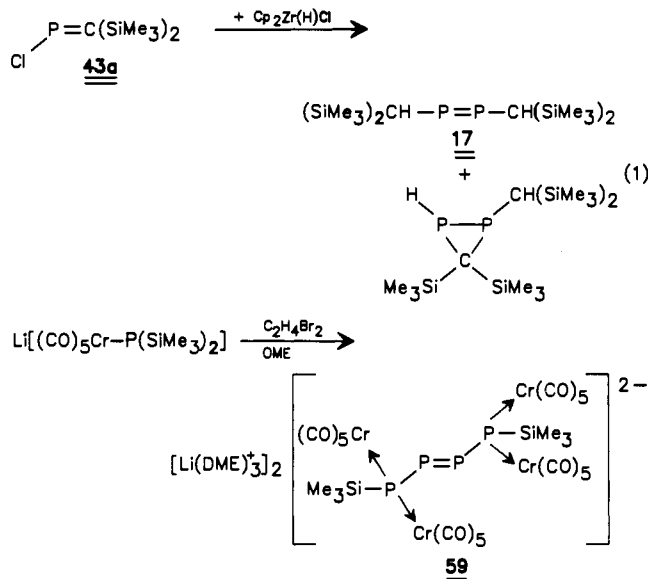


Scheme 32



The hydrozirconation reagent Cp₂Z(H)Cl reduces the phosphalkene **43a** to give a mixture of diphosphene **17** and diphosphirane PH-P[CH(SiMe₃)₂]C(SiMe₃)₂^{54a} (Scheme 33).

Scheme 33



Unexpectedly the reaction of the anionic phosphido complex Li[(CO)₅Cr-P(SiMe₃)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 be 34 kcal/mol. For an inversion process 66 kcal/mol were necessary.⁶⁶ An experimental study by laser irradiation 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 P₂H₄ 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] **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, whereas the n_+ MO is the HOMO according to the presumably more accurate CI and Davidson-corrected energies.⁶⁶ The latter conclusion is in accord with the results of X_α studies on trans HP=PH.^{9b,63}

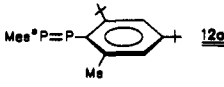
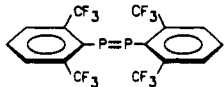
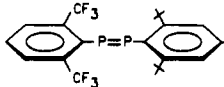
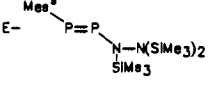
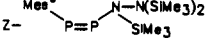
B. Electric and Electron-Spectroscopic Studies

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 $[Mes^*P-PMes^*]^-$ which were stable for several days under an inert gas atmosphere.⁷²

The triplet appearance of the ESR spectrum of the radical anion (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 (1)⁻ and (9)⁻ 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

As shown in Table 1 each diphosphene exhibits two electronic absorptions in the range of 300 to 500 nm.

Table 1. UV/Vis Data of Selected Diphosphenes

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

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)
<i>trans</i> -Diphosphenes							
Mes*P = PMes* (1)	2.034 (2)	1.862 (2)		102.8 (1)		172.2 (1)	8
(Me ₃ Si) ₃ CP = 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 ₂ Si) ₂ NP = PN(SiMe ₂ tBu) 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 ₃ Si) ₃ CP = PSiPh ₃ (28)	2.005 (2)	1.868 (6) ^a	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 ₂ N) ₂ PP = 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 ₂ N) ₂ PP = 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 ₂ N) ₂ PP = PN(SiMe ₂ tBu) ₂ (37)	2.011 (2)	1.736 (4) ^h	2.228 (1) ^h	110.5 (1) ^h	89.8 (<0.1) ^h	-179.8 (1)	44b
(LiL ₃) ₂ {[M] ₂ RPP + PPR[M] ₂ } (59) ^h	2.025 (3)	2.219 (2)		105.9 (1)			54c
<i>cis</i> -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)₆; R = Me₃Si.

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 sp³ to sp². 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 [Mes₂B(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. In spite 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 P₂H₂. In the symmetrical diphosphenes the bond angles range from 102.2 (1)° in (tBuMe₂Si)₂NP=PN(SiMe₂tBu)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 (Me₃Si)₃CP=PSiPh₃ (28) the difference between the angles SiPP = 98.65 (8)° and CPP = 110.5 (1)° considerably decrease,⁴¹ while in Mes*P=PSntBu₃ 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*-configured 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, P, and Y. A similar observation was made in the bisaminodiphosphene 21a³⁶ where the lone pairs at nitrogen are directed perpendicularly to the π -bond. The same holds for diphosphene (iPr₂N)₂PP=PN(SiMe₂tBu)₂ (37)^{44b} and is in sharp contrast to (iPr₂N)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*-configured diphosphenes 24a and 24b³⁹ 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(SiMe₃)N(SiMe₃)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*-configured 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}

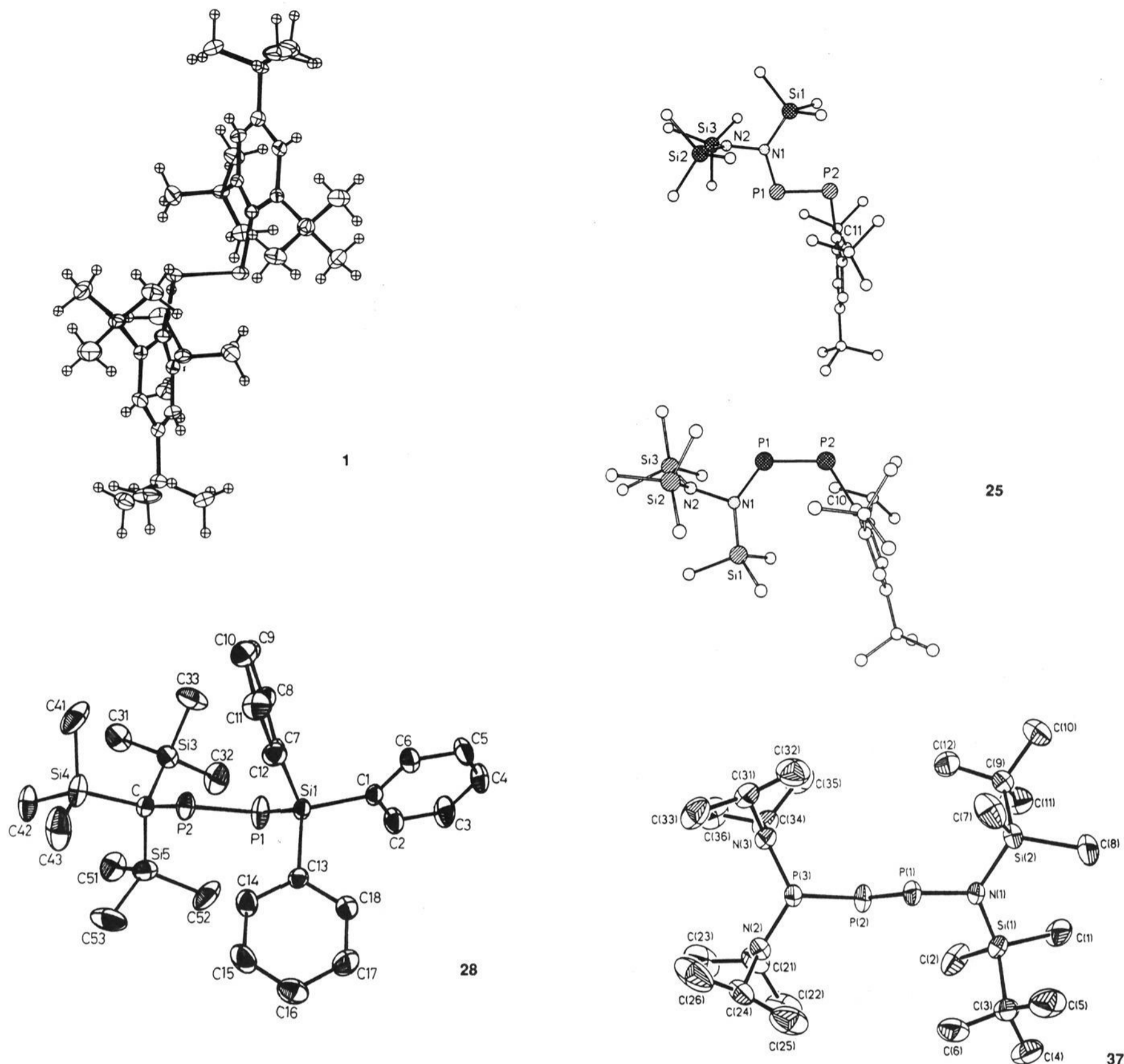


Figure 1. Molecular structures of $\text{Mes}^*\text{P}=\text{PMe}^*$ (1), $\text{Mes}^*\text{P}=\text{PSiPh}_3$ (28), $(i\text{Pr}_2\text{N})_2\text{PP}=\text{PN}[\text{SiMe}_2\text{tBu}]_2$ (37), and (*E*)- and (*Z*)- $\text{Mes}^*\text{P}=\text{PN}_2(\text{SiMe}_3)_3$ (25a,b). Reprinted from refs 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 $\text{tBuP}[\text{Cr}(\text{CO})_5]_2$.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.

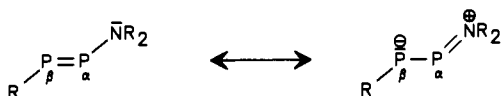
Indeed Huttner succeeded in finding a linear correlation between the absorbance in the UV/vis spectra λ_{max} and the chemical shifts $\delta^{31}\text{P}$ of a series of phosphinidene complexes.⁸¹ The situation, however, is more complicated in the case of *E*-configured diphosphenes with a coordination 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 $\text{Mes}^*\text{P}=\text{PC}(\text{SiMe}_3)_3$ (**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 $(\text{Me}_3\text{Si})_3\text{CP}^A=\text{P}^B\text{SiMe}_3$ (**29b**)⁴¹ ($\delta_A = 544.1$, $\delta_B = 686.9$, $^1J_{\text{PP}} = 633.2$ Hz) or $(\text{Me}_3\text{Si})_3\text{CP}^A=\text{P}^B\text{SiPh}_3$ (**28**)⁴¹ ($\delta_A = 511.8$, $\delta_B = 711.4$, $^1J_{\text{PP}} = 633.1$ 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: $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{FeP}^A=\text{P}^B\text{Aryl}_F$ ($\text{Aryl}_F = 2,4,6\text{-}(\text{CF}_3)_3\text{C}_6\text{H}_2$), ($\delta_A = 877.9\text{d}$, $\delta_B = 487.0\text{d}$; $^1J_{\text{PP}} = 615$ 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 $\text{Mes}^*\text{P}=\text{PN}(\text{iPr})_2$ (**22c**), $\text{Mes}^*\text{P}=\text{PTMP}$ (**22d**), or $(\text{iPr}_2\text{N})_2\text{PP}=\text{PTMP}$ (**34**), where π -conjugation of the nitrogen lone pair with the $\text{P}=\text{P}$ 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 $\delta_{\text{P}\alpha} = 446.9$ and $\delta_{\text{P}\beta} = 276.4$ ($^1J_{\text{PP}} = 537$ Hz). For comparison in $\text{Mes}^*\text{P}=\text{PN}(\text{SiMe}_3)_2$, 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 ($^1J_{\text{PP}} = 584.2$ Hz).

In sharp contrast to their *E*-isomers *Z*-configured 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*)- $\text{Mes}^*\text{P}=\text{PNH}(\text{tBu})$ (**24a**) two doublets are registered at $\delta = 214$ and 377 ppm ($^1J_{\text{PP}} = 526.0$ Hz).

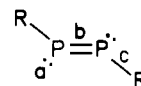
Especially interesting is the comparison of the spectra of (*E*)- and (*Z*)- $\text{Mes}^*\text{P}=\text{PN}(\text{SiMe}_3)\text{N}(\text{SiMe}_3)_2$ **25a** and **25b**, respectively. The spectrum of **25a** features doublets at $\delta = 311$ (P_β) and $\delta = 481$ (P_α) ($J_{\text{PP}} = 554$ Hz) which agrees with the presence 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), $J_{\text{PP}} = 516$ Hz]. The differences in chemical shifts between the *E*- and *Z*-isomers amount to $\Delta\delta_{\text{P}\alpha} = 123$ ppm and $\Delta\delta_{\text{P}\beta} = 121$ ppm.

The values of $^1J_{\text{PP}}$ 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 $^1J_{\text{PP}}$ values for

$\text{P}=\text{P}'$ 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 $\text{P}=\text{P}$ 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 $\text{P}=\text{P}$ double bond according to the respective organic model obvious.

Reactions at the P-R bond (c) involve substitutions with retainment of the $\text{P}=\text{P}$ 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 $\text{P}=\text{O}$ functionality into the C-H bond (Scheme 34).

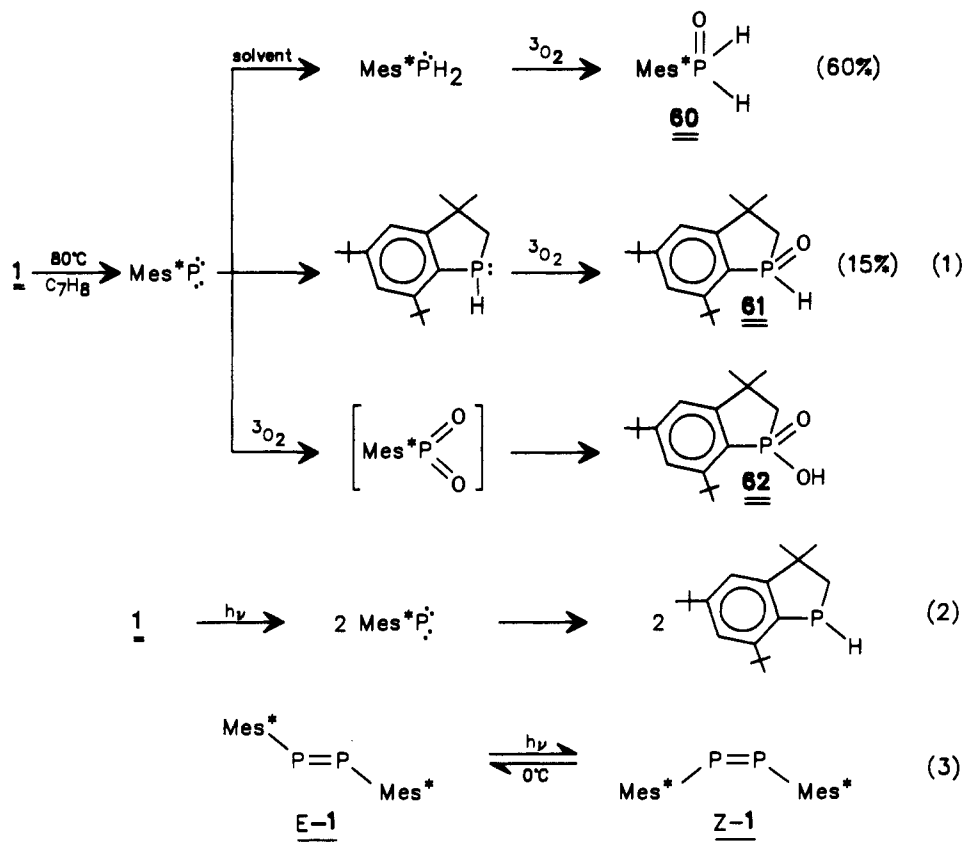
This assumption was supported by the thermal decomposition of **1** in a $\text{THF}/\text{C}_6\text{H}_6$ mixture at +120 °C which eventually afforded Mes^*PH_2 .¹⁶ Photoirradiation of **1** with a medium-pressure mercury lamp without a pyrex filter gave a phosphaindan derivative via the believed intermediacy 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 trioxophetanes (phosphorus ozonides) **63** led to the formation

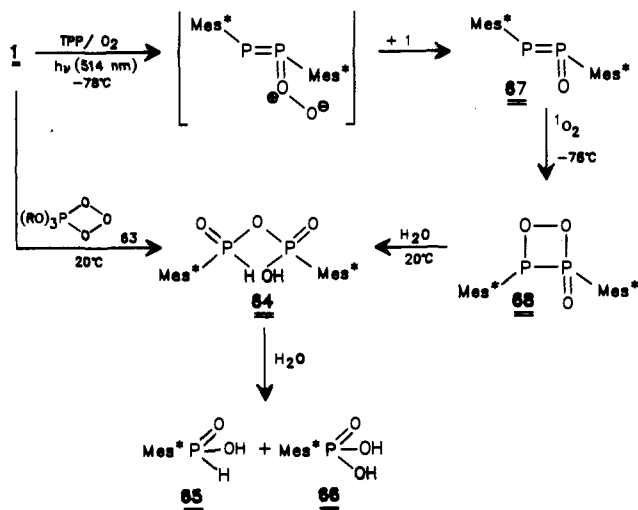
Table 3. ^{31}P NMR Data of Diphosphenes $\text{R}^1\text{P}=\text{P}\text{R}^2$

compd	R ¹	R ²	^{31}P NMR: δ , ppm	$^1J_{\text{PP}}$, Hz	ref(s)	compd	R ¹	R ²	^{31}P NMR: δ , ppm	$^1J_{\text{PP}}$, Hz	ref(s)
Z-1	Mes*	Mes*	368	70		29b	(Me ₂ Si) ₃ C	SiMe ₃	544.1; 686.9	633.2	41
E-1	Mes*	Mes* (1)	492.4	82		30	Mes*	SntBu ₃	446.5; 465.71	607.9	43
2	2,4,6-tPr ₃ C ₆ H ₂	2,4,6-tPr ₃ C ₆ H ₂	490.8	20b		32	(Me ₂ Si) ₃ N ₂	SiMe ₃	210.3; 542	540	44a
3	2,6-tBu ₂ C ₆ H ₃	2,6-tBu ₂ C ₆ H ₃	488.7	20a		33	Mes*	P(NiPr ₂) ₂	502.7; 554.0	574	44b
4	2-tBu-4,5,6-Me ₃ C ₆ H	2-tBu-4,5,6-Me ₃ C ₆ H	509.8	21		34	TMP	P(NiPr ₂) ₂	320.1; 496.5	574	44b
5	Mes*	2,4,6-tPr ₃ C ₆ H ₂	489.9; 491.2	582.9	20b	35	NHMe [*]	P(NiPr ₂) ₂	407.4; 544.0	570	44b
6	Mes*	Mes	467.6; 540.4	573.7	29	36	N-iPr ₂	P(NiPr ₂) ₂	245.7; 483.9	534	44b
7	Mes*	2,4,6-iPr ₃ C ₆ H ₂	470, 535	572	21	37	N(SiMe ₂ tBu) ₂	P(NiPr ₂) ₂	442.9; 577.6	602	44b
8	Mes*	2-tBu-4,5,6-Me ₃ C ₆ H	478, 512	580	21	38	OMes*	P(NiPr ₂) ₂	386.2; 590.2	564	44b
9	(Me ₃ Si) ₃ C	(Me ₃ Si) ₃ C	599.6 [598.6]	14, 22 [23]		39	(Me ₃ Si) ₃ N ₂	P(NiPr ₂) ₂	298.7; 522.3	522	44b
10	Mes*	(Me ₃ Si) ₃ C	530.0; 533.1	619.7	25	41	2,6-(CF ₃) ₂ C ₆ H ₃	2,6-(CF ₃) ₂ C ₆ H ₃	477.1		45d
11	C ₂ Me ₅	C ₂ Me ₅	504.0	28		42	Mes*	2,6-(CF ₃) ₂ C ₆ H ₃	422.1; 533.0	574.3	45d
12a	Mes*	2,4-tBu ₂ -6-MeC ₆ H ₂	480.1; 517.0	583.5	29	46a	Mes*	C(Ph)(H)(SiMe ₃)	486.6; 522.8	569.9	50c
12b	Mes*	Ph	455.5; 525.5	548.7	29	46b	Mes*	CPh(SiMe ₃) ₂	510.8; 530.1	598.0	50c
13	Mes*	CH(SiMe ₃) ₂	493.0; 513.0	577.5	30	50a	(Et ₂ N) ₂ C ⁺	N(iPr) ₂	200; 493.5	520	48
14	2,4,6-(CF ₃) ₃ C ₆ H ₂	2,4,6-(CF ₃) ₃ C ₆ H ₂	474	31		50b	(Et ₂ N) ₂ C ⁺	TMP	210; 465	525	48
15	2,4,6-(CF ₃) ₃ C ₆ H ₂	Mes*	416.8; 537.6	572	32	52a	Mes*	NHMe [*]	314; 455	537	49a
16	Mes*	C ₂ Me ₅	484.8; 491.1	584	33				316.2; 450	532	50a
17	(Me ₃ Si) ₂ CH	(Me ₃ Si) ₂ CH	517	34		52b	Mes*	N[SiMe ₂ (tBu)]Mes*	350.1; 480.8	578.2	50c
18a	(Me ₃ Si) ₂ N	(Me ₃ Si) ₂ N	572	35		52c	Mes*	N(SiMe ₃)Mes*	343.1; 483.2	571.4	50c
18b	(Me ₃ Si)(tBu)N	(Me ₃ Si)(tBu)N	499	36		53	Mes*	tBu	524.7; 531.9	576.6	51, 11
19	(Me ₃ Si)(tBu)N	(Me ₃ Si) ₂ N	507; 544	670	36	54	Mes*	Cl	473.4; 522.8	598	52a
21a	(tBuMe ₂ Si) ₂ N	(tBuMe ₂ Si) ₂ N	561	36		55a	Mes*	Si(SiMe ₃) ₃	501.2; 610.6	598	52a
21b	TMP	TMP	471.1	37a		55b	Mes*	OtBu	397.6; 524.3	573.7	52a
22a	Mes*	(Me ₃ Si) ₂ N	409.3; 501.5	584.2	38	55c	Mes*	P(tBu) ₂	487.1; 600.9	586	52a
22b	Mes*	(tBuMe ₂ Si) ₂ N	389.6; 501.2	537.1	11	55d	Mes*	StBu	448.1; 468.0	549.3	52a
22c	Mes*	iPr ₂ N	276.4; 446.9	537	52a	56a	C ₂ Me ₅	C(SiMe ₃) ₃	522.2; 545.8	635	28
22d	Mes*	TMP	336.1; 460.7	579.9	38	56b	C ₂ Me ₅	CH(SiMe ₃) ₂	492.6; 522.8	599	28
23	tBu	TMP	383; 508	611	37b	56c	C ₂ Me ₅	N(SiMe ₃) ₂	478.3; 546.2	632	28
Z-24a	Mes*	tBuNH	214; 377	526	39	56d	C ₂ Me ₅	N(tBu)(SiMe ₃)	529.1; 440.1	640	28
Z-24b	Mes*	1-AdNH	213; 375	524.5	39	58	Mes*	C(OSiMe ₃) = PMes*	414.6; 394.3	510	53
Z-24c	Mes*	Et ₃ CNH	212.3; 379.0	527.2	39	59	[(CO) ₅ Cr] ₂ (Me ₃ Si)P	[(CO) ₅ Cr] ₂ (Me ₃ Si)P	552	640	54c
Z-24d	Mes*	2,4,6-iPr ₃ C ₆ H ₂ NH	209.3; 379.7	523	39	98	Mes*	PHMes*	500; 552	571	98a
E-25a	Mes*	(Me ₃ Si) ₃ N ₂	311, 481	554	40b	99	Mes*	PMesMes*	473; 493	558	98a
Z-25b	Mes*	(Me ₃ Si) ₃ N ₂	190; 358	516	40b	140	(Me ₃ Si) ₃ N ₂	N ₂ (SiMe ₃) ₃	325		40b,
27	Mes*	SiPh ₃	457.7; 641.9	588.7	41						112
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						

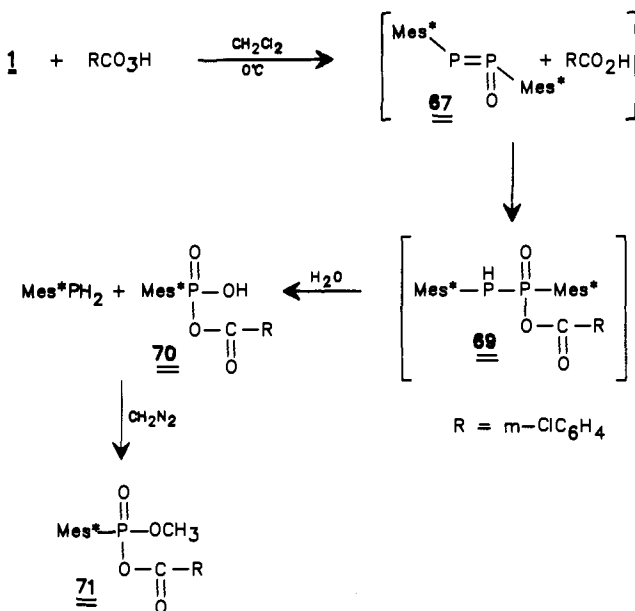
Scheme 34



Scheme 35



Scheme 36



Scheme 37



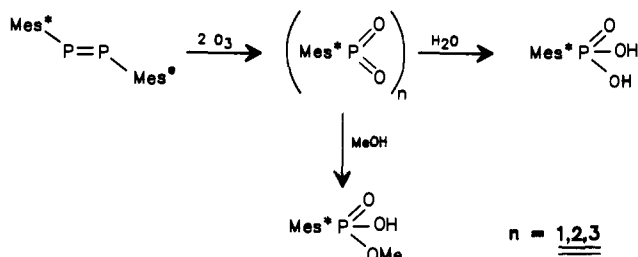
of anhydride **64**. Compound **64** was easily hydrolyzed to a mixture of phosphonic acid **65** and phosphonic acid **66**.^{83,85}

Photochemically produced ¹O₂ (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).

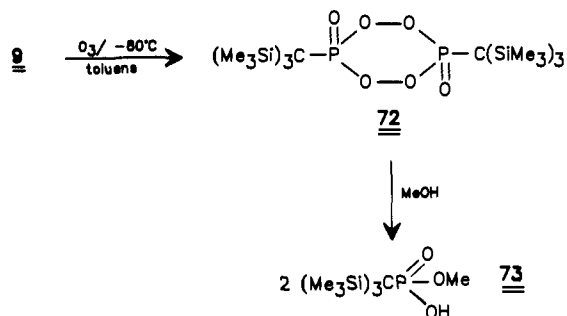
The transient production of diphosphene oxide **67** was also invoked in the reaction of **1** with *m*-chlorobenzoic acid in CH₂Cl₂ and subsequent treatment of the reaction mixture with ethereal diazomethane. The mixed ester anhydride **71** was obtained in 58% yield⁸⁶ (Scheme 36).

Compound **67** was available as a stable product (71%) from the ultrasonic irradiation of a mixture of super-

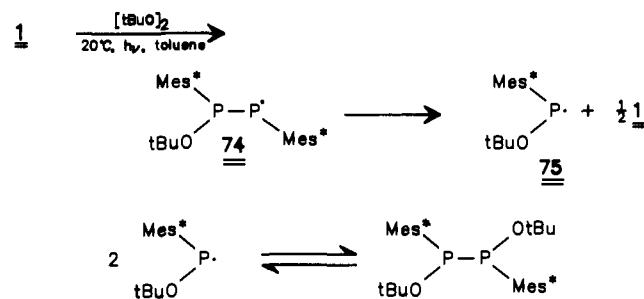
Scheme 38



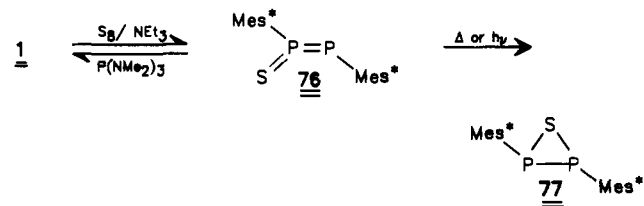
Scheme 39



Scheme 40



Scheme 41



mesityl phosphonic dichloride and magnesium at 0 °C⁸⁶ (Scheme 37).

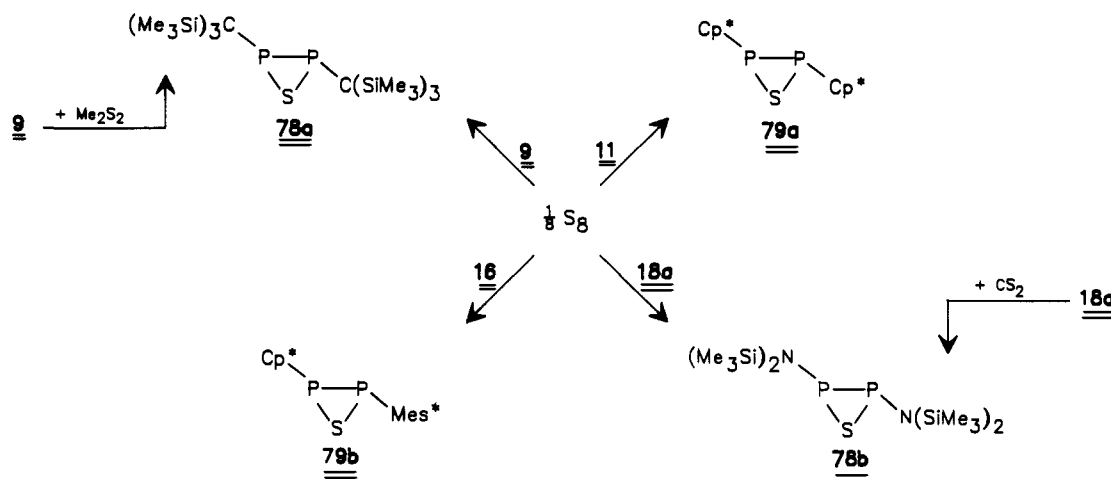
In the ³¹P NMR spectrum compound **67** exhibited an AB pattern centered at δ = 206.5 (Mes*P=) and 69.8 (Mes*P(O)=) with a large coupling constant ¹J_{PP} = 638.6 Hz.

Ozonolysis of **1** in CH₂Cl₂ or toluene at -96 °C produced the monomer, dimer, and trimer of Mes*P(O)₂ (³¹P NMR control) which reacted with methanol or water to the methyl ester and the acid respectively⁸⁷ (Scheme 38).

The ozonolysis of **9** in toluene at -70 °C yielded the cyclic dimer **72**, characterized by a ³¹P NMR signal at δ = 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 spectroscopy⁷⁴ (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 $\delta = 247.8$ and 255.8 . The large coupling constant $^1J_{\text{PP}} = 629.9$ 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*-configured diphosphene with a P=P double bond of 2.054 (2) Å. The sulfur atom is attached to a trigonal-planarly configured phosphorus atom via a P=S double bond [1.931 (2) Å]. Desulfurization of **76** was achieved by $\text{P}(\text{NMe}_2)_3$.⁸⁹ Heating **76** in boiling toluene or its photoirradiation with a mercury lamp led to thiadiphosphirane **77**. This species was also accessible by the reduction of $\text{Mes}^*\text{P}(\text{S})\text{Cl}_2$ 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).

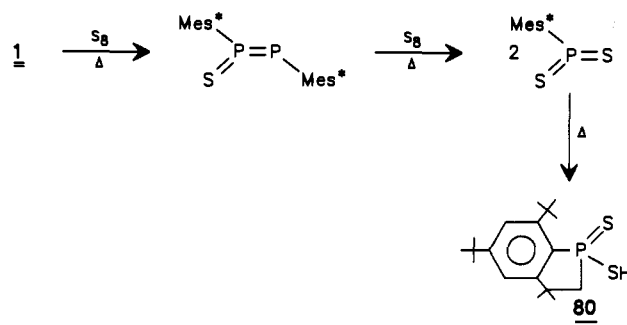
When **1** was reacted with sulfur and DBU in refluxing toluene the P=P bond was broken and the dithiophosphinic acid **80** was obtained. **80** was believed to be the product of a P=S insertion of transient Mes^*PS_2 into the CH bond of an *o*-*tert*-butyl group.^{92a-c} This assumption was underlined 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 $\text{Mes}^*\text{P}(\text{Se})_2$. The ^{31}P NMR spectrum of **81** displayed a singlet at $\delta^{31}\text{P} = -47.4$ with a selenium coupling of $^1J(^{31}\text{P}^{77}\text{Se}) = 131.8$ Hz.⁹³ The large P–Se coupling of 854.5 Hz in the ^{31}P NMR spectrum of $\text{Mes}^*\text{P}(\text{Se})_2$ ($\delta = 273.0$) is indicative of P=Se double bonds (Scheme 44).

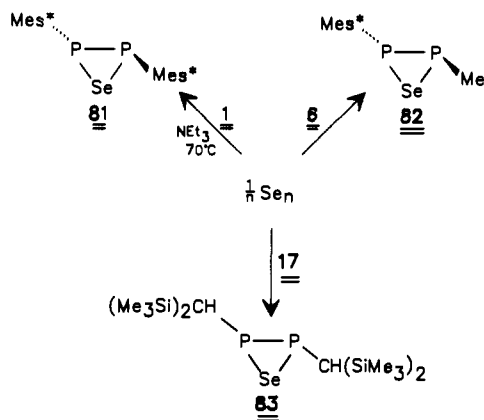
3. Halogenations

The 1,2-dichlorodiphosphane **84** was produced in the reaction of **9** with equimolar amounts of chlorine in

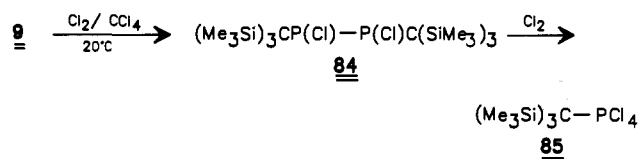
Scheme 43



Scheme 44



Scheme 45

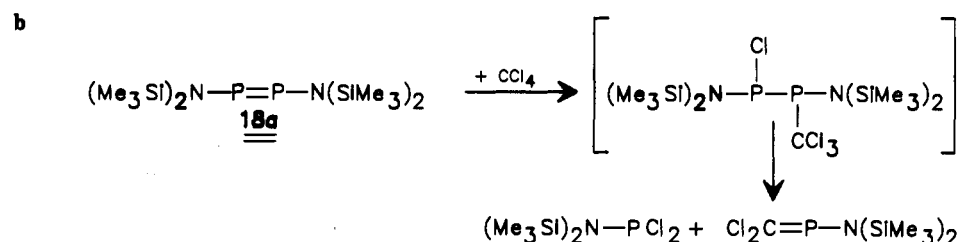
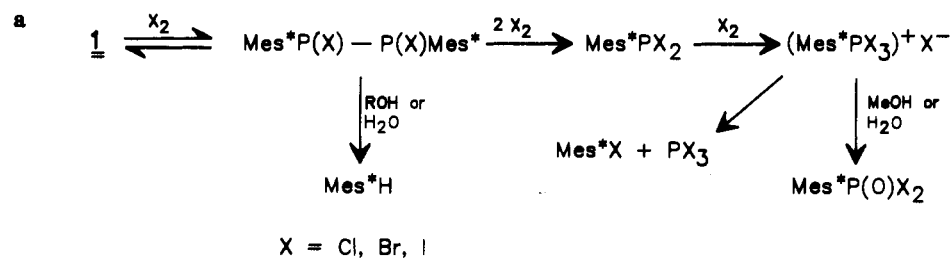


CCl_4 at ambient temperature. An excess of the halogen furnished the alkyl phosphorus tetrachloride **85**^{23b} (Scheme 45).

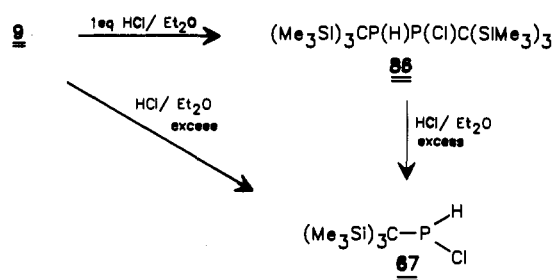
Diphosphene **1** was attacked by various halogens to give products such as phosphinic dihalides, phosphorus trihalides, haloarenes, and supermesitylene dependent upon the nature of the halogen and the reaction conditions. The Scheme 46a gives a rationale for the observed pattern of products.

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).

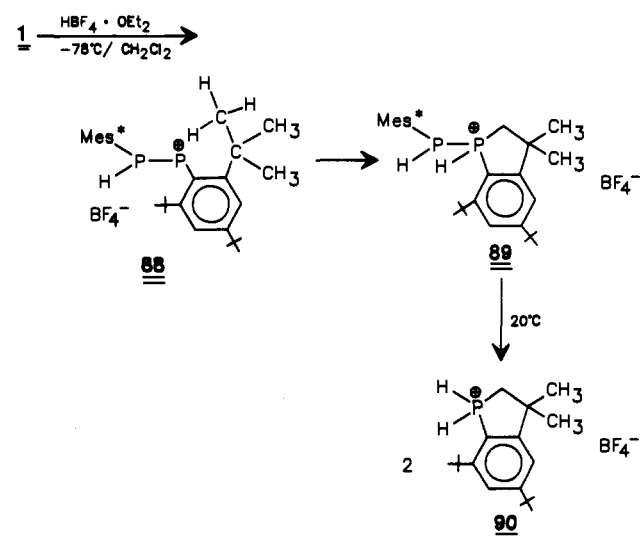
9 and **86** suffered from cleavage of the P-P bond when an excess of ethereal HCl was employed in the reaction. Compound **87** is a representative of the rare class of organochlorophosphanes $\text{RP}(\text{H})\text{Cl}$.^{23b,92b} The P=P double bond of **9** was also cleaved by an excess of ethereal HBF_4 in CH_2Cl_2 solution at -78°C . Phosphonium salt $[(\text{Me}_3\text{Si})_3\text{CPH}_3]^+\text{BF}_4^-$ was the sole product. The protonation of **1** by an excess of $\text{HBF}_4\cdot\text{OEt}_2$ at -78°C took a different course. The intermediate phosphonium 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

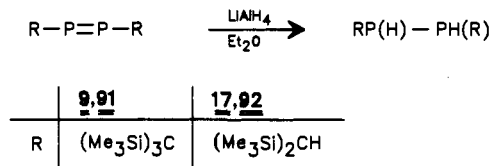
1. Hydrogenations

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

Scheme 48



Scheme 49

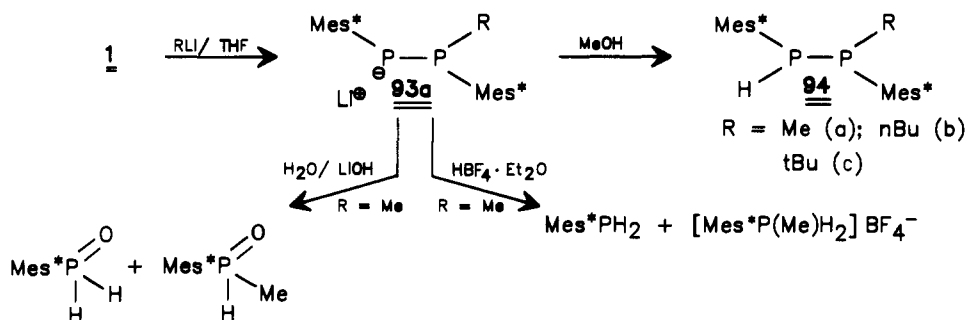


synthesis of **1** from Mes^*PCl_2 and an excess of magnesium in THF was accompanied by a considerable amount of the diphosphane $\text{Mes}^*\text{P}(\text{H})\text{P}(\text{H})\text{Mes}^*$, which might result from the reduction of **1** with subsequent proton abstraction.²² A clean reduction of **1** to give a mixture of *dl*- and *meso*-diphosphanes was accomplished by treatment with LiAlH_4 ⁹⁵ or $\text{K}[\text{sBu}_3\text{BH}]$.^{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).

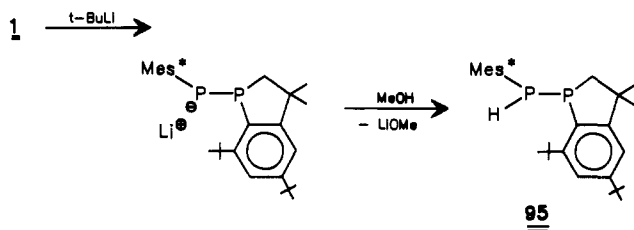
2. Reactions with Lithium Alkyls

Independently Cowley^{92b,96} and Yoshifuji⁹⁷ 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).

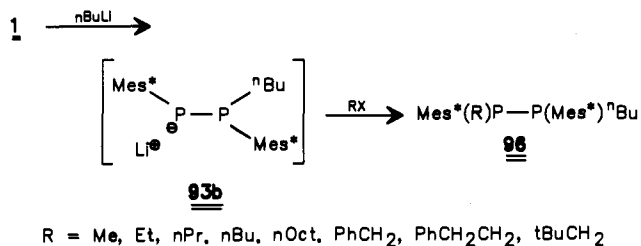
Scheme 50



Scheme 51



Scheme 52



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 $\text{Mes}^*\text{P}(\text{O})(\text{H})_2$ and $\text{Mes}^*\text{P}(\text{O})(\text{H})\text{Me}$, or alternatively by ethereal HBF_4 to produce Mes^*PH_2 and $[\text{Mes}^*\text{P}(\text{Me})\text{H}_2]^+\text{BF}_4^-$. In the reaction of **1** with $t\text{BuLi}$ 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 $\text{Cp}^*\text{P}=\text{PMes}^*$ (**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 $[\text{Mes}^*\text{P}]^{2-}$ was invoked, which eventually was trapped by the diphosphene **16** to yield the allylic system. With a stoichiometry of $16/\text{MeLi} = 2:3$ 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 $\text{Me}_2\text{P}-\text{PMes}^*\text{Li}$, 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 $\text{P}=\text{P}$ double bond in diphosphenes is an appropriate candidate for a series of different cycloadditions.

1. [2 + 1] Cycloadditions

The addition of carbenes to the $\text{P}=\text{P}$ 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 phosphalkene **102a** (10%)^{100a,b} (Scheme 56).

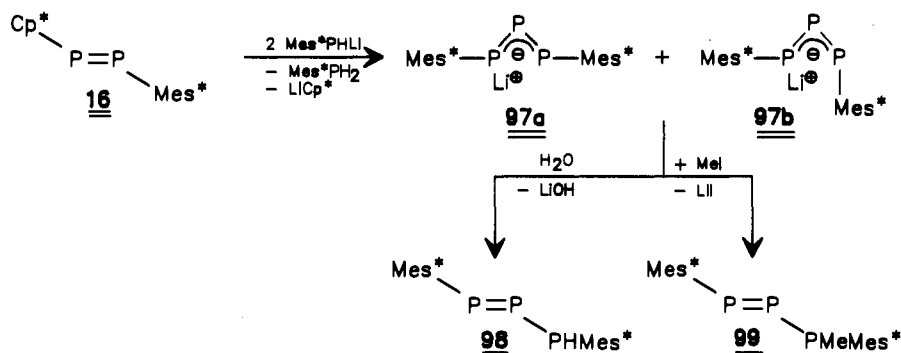
Diphenyldiazomethane Ph_2CN_2 is less reactive than CH_2N_2 and demanded a reaction temperature of 65 °C to give 80% of the diphosphirane **101b** and 20% of the phosphalkene **102b**. Here the intermediate $\lambda^5 \sigma^3$ phosphorane $\text{Mes}^*\text{P}^{\text{A}}=\text{P}^{\text{B}}(\text{Mes}^*)=\text{CPh}_2$ was evidenced by ³¹P NMR ($\delta(\text{P}_\text{A}) = 208.4$; $\delta(\text{P}_\text{B}) = 66.7$; $^1J_{\text{PP}} = 676$ Hz). The formation of ring **101c** from **1** and 9-diazo-fluorene was achieved photochemically.^{100b}

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

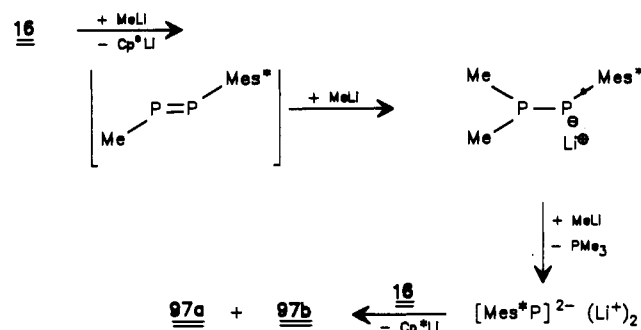
During the formation of **104c** the ³¹P NMR spectra of the reaction mixture (Et_2O , -20 °C) showed two doublets at $\delta = 45$ and 68 ppm ($^1J_{\text{PP}} = 300$ Hz), which were tentatively assigned to a transient [2 + 3] cycloadduct.

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 $\text{P}=\text{P}$ bond of a number of diphosphenes (Scheme 58). The halocarbenes were generated by the reaction of KOtBu or $n\text{BuLi}$ with an

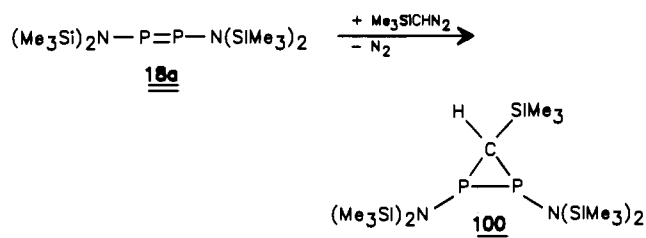
Scheme 53



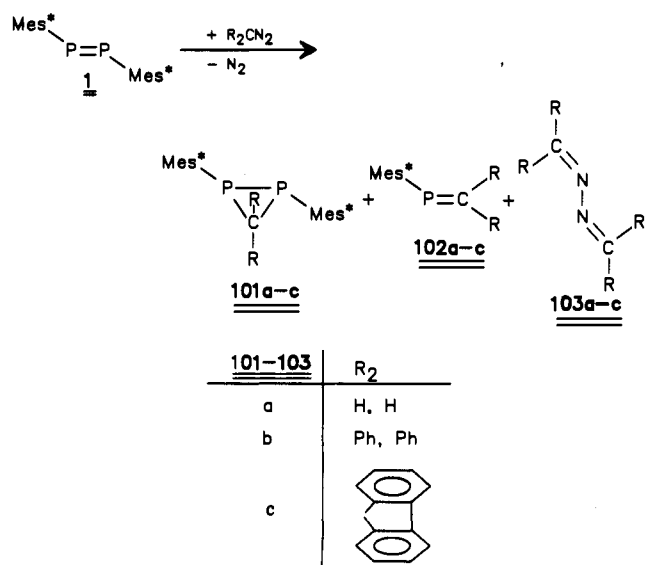
Scheme 54



Scheme 55



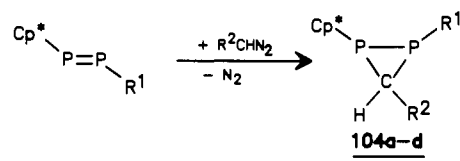
Scheme 56



excess of the corresponding haloform or alternatively from tetrahalomethanes and $n\text{BuLi}$ at low temperatures.

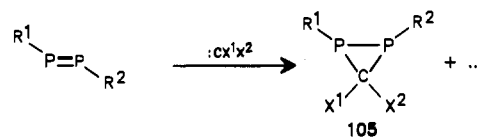
The reaction of the functionalized diphosphiranes **105** with organolithium compounds, Lewis acids as well as thermolysis or photolysis invariably led to ring

Scheme 57



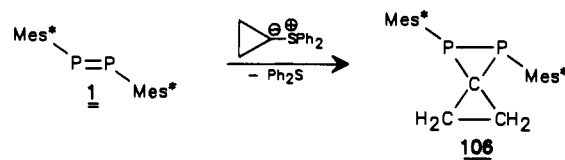
104	R^1	R^2
a	Cp^*	H
b	Mes^*	H
c	Cp^*	Me_3Si
d	Mes^*	Me_3Si

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	$\text{C}(\text{SiMe}_3)_3$	Mes^*	Cl	Cl	102b
g	$\text{C}(\text{SiMe}_3)_3$	Mes^*	Br	Br	102b
h	Mes^*	2,4,6- $\text{tPn}_3\text{C}_6\text{H}_2$	Cl	Cl	20a,b
i	2,4,6- $\text{tPn}_3\text{C}_6\text{H}_2$	2,4,6- $\text{tPn}_3\text{C}_6\text{H}_2$	Cl	Cl	20a,b
j	2,6- $\text{tBu}_2\text{C}_6\text{H}_3$	2,6- $\text{tBu}_2\text{C}_6\text{H}_3$	Cl	Cl	20a,c

Scheme 59

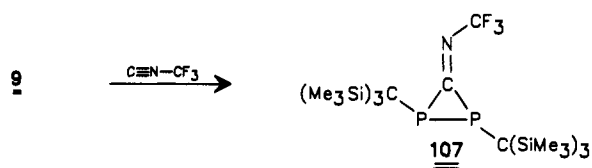


opening products such as 1,3-diphosphaallenes, 1,3-diphosphapropenes, and others.^{20,101,102}

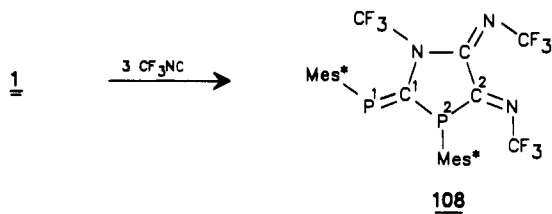
Sulfur Ylides. According to a method first devised by Weber,¹⁰³ Koenig et al. succeeded in the transformation of the diphosphene **1** into the 1,2-diphosphaspiro[2.2]pentane **106**.^{102a} Diphenylsulfoniocyclopropanide served as the alkylidene transfer reagent (Scheme 59).

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

Scheme 60



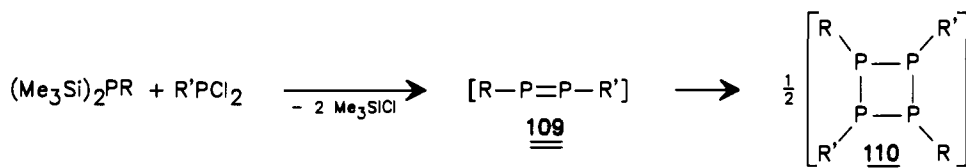
Scheme 61



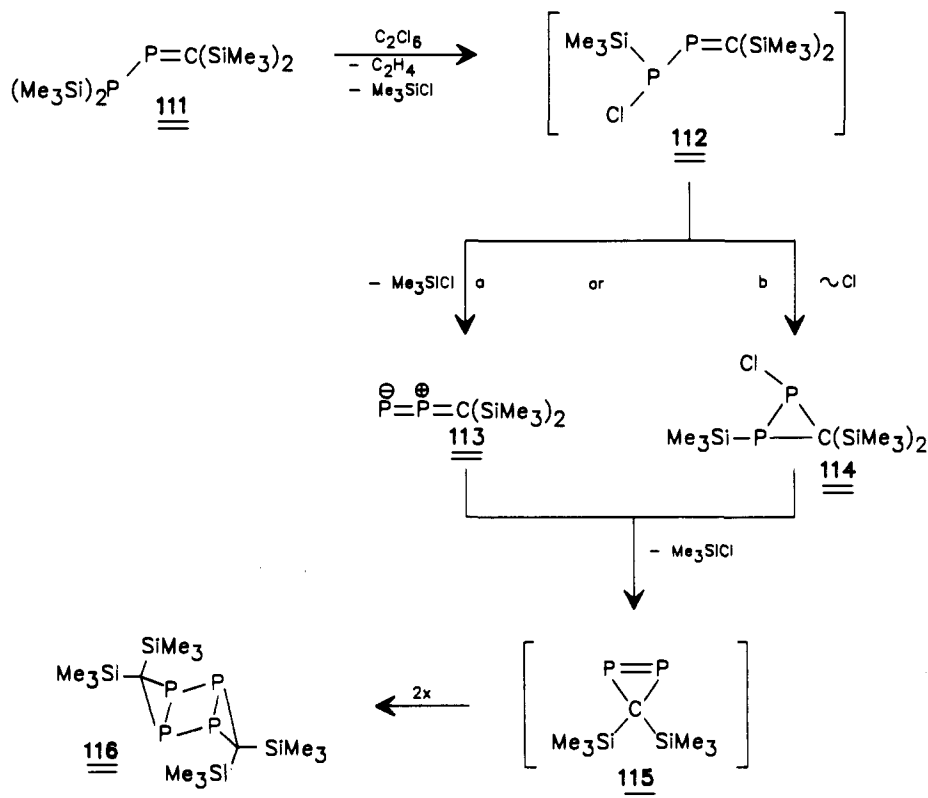
pathway complements the [2 + 1] cyclocondensation approach earlier devised by Baudler et al. to the rare class of imino diphosphiranes¹⁰⁵ (Scheme 60).

A different situation was met when diphosphene 1 was allowed to react with CF₃NC under similar con-

Scheme 62



<u>109</u> , <u>110</u>	R	R'
a	tBu	tBu
b	tBu	Mes



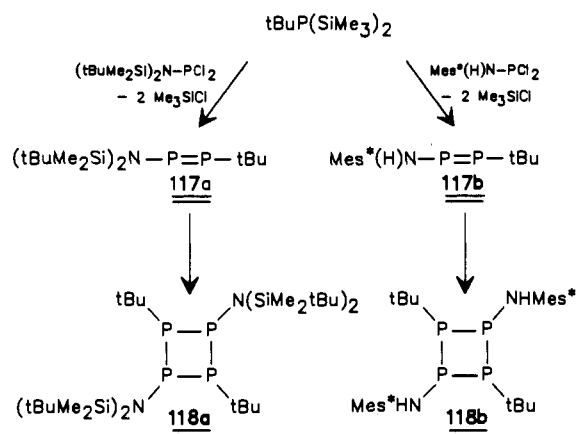
ditions. The structure of product 108 was elucidated by X-ray crystallography, and it was ascertained that 108 was generated from three molecules of the isocyanide and one molecule of 1¹⁰⁴ (Scheme 61). The phosphorus carbon distances [1.683 (P1-C1), 1.842 (C1-P2), and 1.797 (P2-C2) Å] were in accord with a double bond and two single bonds, respectively.

2. [2 + 2] Cycloadditions

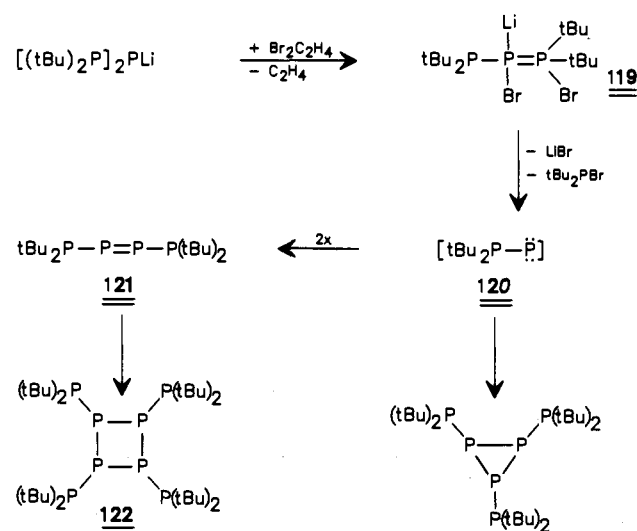
Cyclodimerizations. Diphosphenes which are not sufficiently protected by their substituents often undergo [2 + 2] self-dimerization to afford all-trans substituted cyclotetraphosphanes (Scheme 62).

The pronounced reactivity of 109^{45c} and 115¹⁰⁶ precluded their observation by ³¹P 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 ³¹P NMR ($\delta = 515$ d, 585 d, $^1J_{PP} = 638$ Hz) before it suffered from dimerization^{50b} (Scheme 63).

Scheme 63



Scheme 64

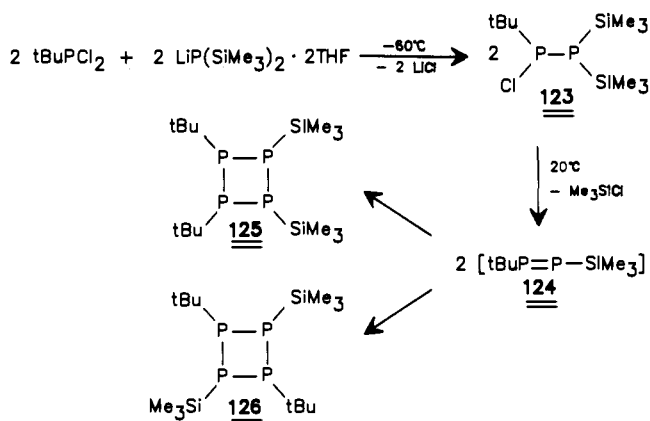


Fritz et al. described the synthesis of cyclotetraphosphanes **122** (in addition to cyclotriphosphanes) which might result from a sequence of dimerization processes of the phosphinidene moiety **120**. This species was freed from the phosphinidene phosphorane precursor **119** (Scheme 64). The transient nature of **120** and **121** was confirmed by trapping experiments.¹⁰⁷ Equimolar amounts of $t\text{BuPCl}_2$ and $\text{LiP}(\text{SiMe}_3)_2$ 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).

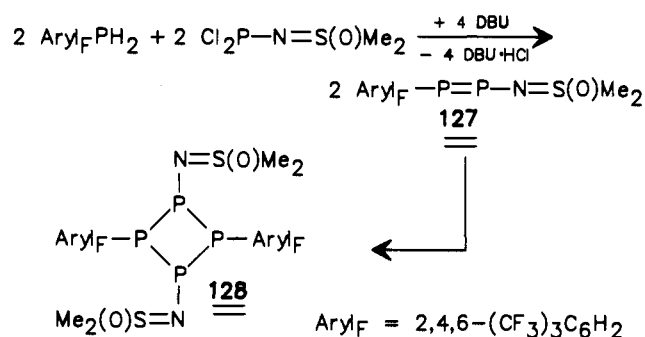
Again the intermediacy of diphosphene **124** was made plausible by trapping experiments. The thermolabile diphosphene **127** was produced during the condensation of Aryl_FPH_2 and an imino-substituted dichlorophosphane at -78°C . At this temperature the double-bond system was successfully coordinated to a platinum complex. However, in the absence of trapping reagents dimerization to cyclotetraphosphane **128** occurred³¹ (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 mixture¹⁰⁹ (Scheme 67).

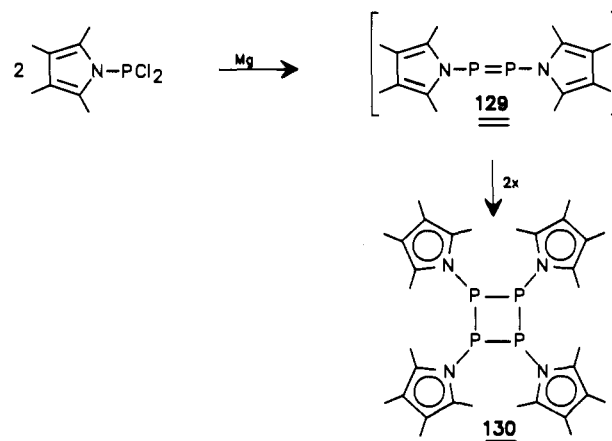
Scheme 65



Scheme 66



Scheme 67



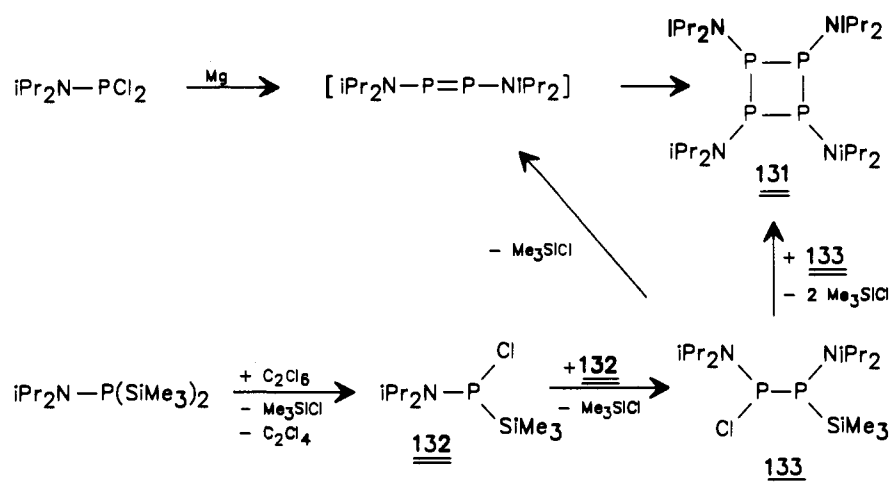
Similarly the synthesis of cyclotetraphosphane **131** may proceed via the transient diphosphene $i\text{Pr}_2\text{NP}=\text{PNiPr}_2$.^{110,111} Here, however, other mechanisms for the generation of the ring compound are also reasonable (Scheme 68).

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 week³⁴ (Scheme 69).

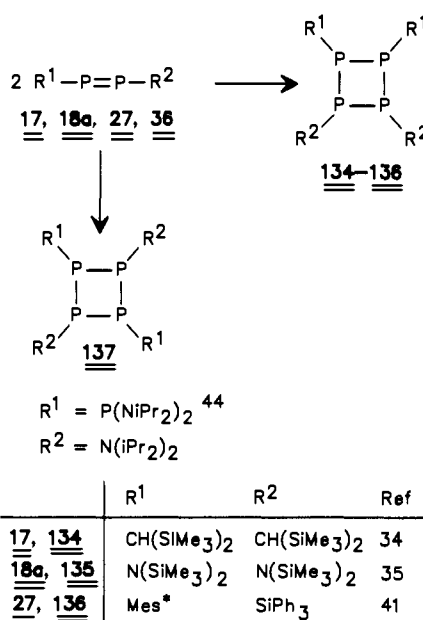
In some cases the dimerization of *Z*-configured diphosphenes **24** was followed by cycloreversion and the subsequent cyclodimerization of the amino-substituted diphosphene fragment to yield cyclotetraphosphane **138** and diphosphene **139** (Scheme 70).

Like the *Z*-configured diphosphenes **24** the diphosphene **25b** slowly decomposed in solution at room temperature to the symmetrical diphosphenes **1** and $(\text{Me}_3\text{Si})_3\text{N}_2\text{P}=\text{PN}_2(\text{SiMe}_3)_3$ (**140**). An explanation for

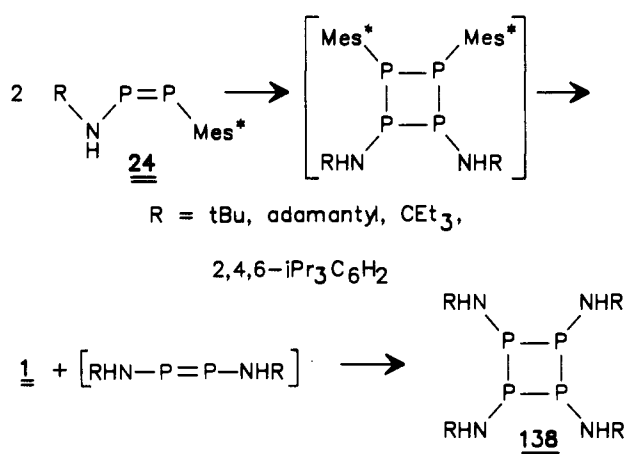
Scheme 68



Scheme 69



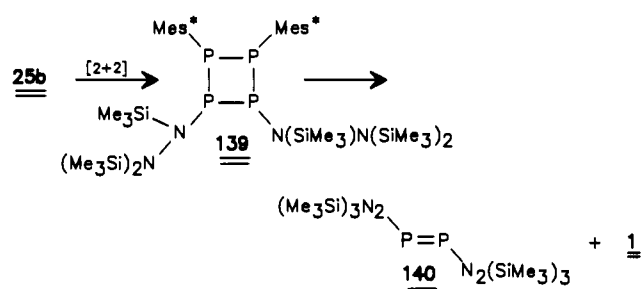
Scheme 70



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

An intramolecular electrocyclozation 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 of two cyclopentadienyl fragments and the generation of bicyclic tetraphosphane 147. Under prolonged irradiation 147 degraded to white phosphorus¹¹⁵ (Scheme 74).

Ether solutions of diphosphene 29b decomposed upon standing for 5 days at -20 °C to give the bicyclic tetraphosphane 148⁴¹ (Scheme 75).

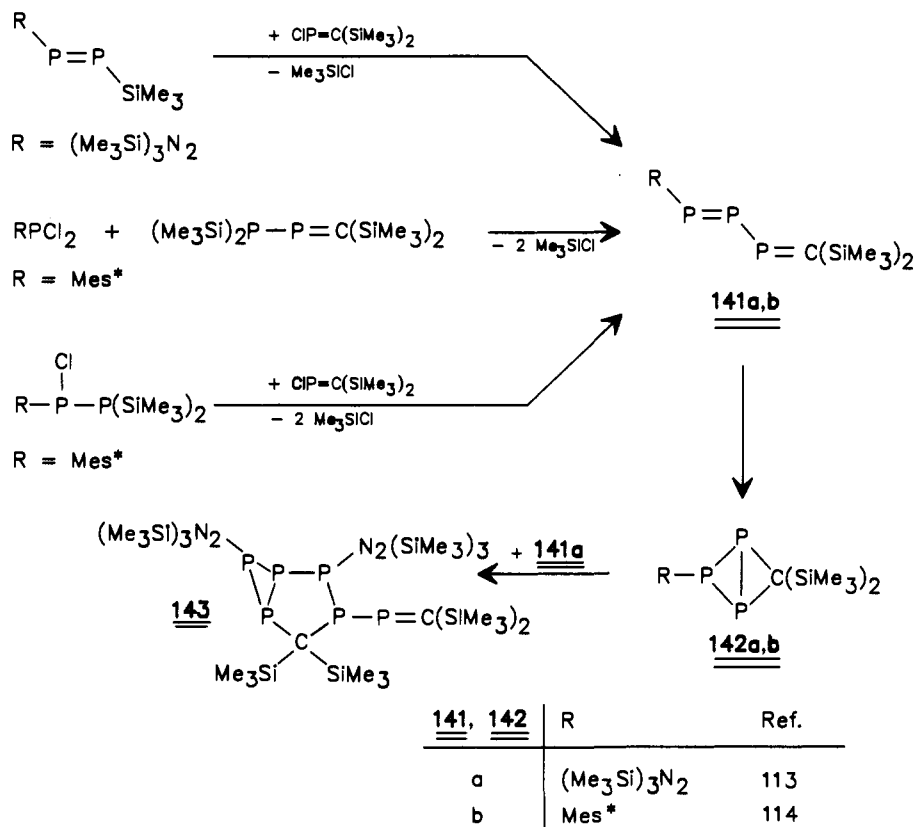
3. [2 + 3] Cycloadditions

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 ³¹P NMR evidence. Above ambient temperature the triazadiphospholenes decomposed to give the aminoiminophosphanes 151a-c as the only nonpolymeric products. In the reaction with Me₃SiN₃ the diphosphene imide 152 was detected as an intermediate by ³¹P NMR (δ = 62 d, 171 d, ¹J_{PP} = 881 Hz) (Scheme 76). The isolation of this compound failed.^{91a,99}

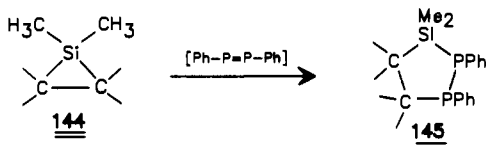
4. [2 + 4] Cycloadditions

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

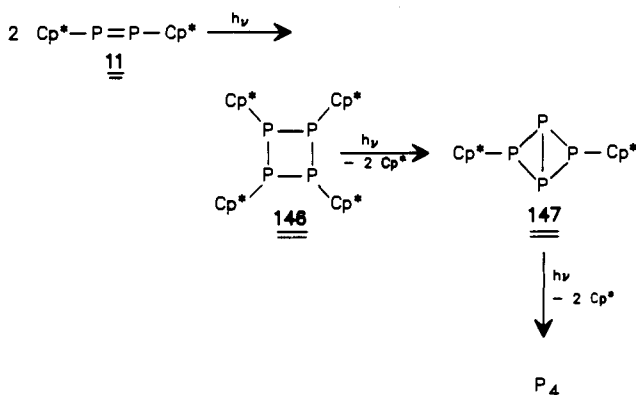
Scheme 72



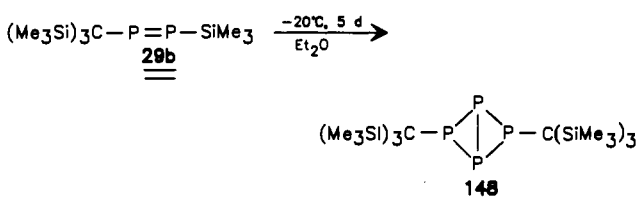
Scheme 73



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 unambiguously 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)PGeCl₃ and DBU, was also efficiently trapped by 2,3-dimethylbuta-1,3-diene to give **153c**^{45b} (Scheme 78).

Analogously diphosphene tBuP=PSiMe₃ (**124**) could be transformed into **155** by treatment with the butadiene¹⁰⁸ (Scheme 79).

The reactive diphosphenes **156a,b** were also intercepted via [2 + 4] cycloadditions¹¹⁷ (Scheme 80).

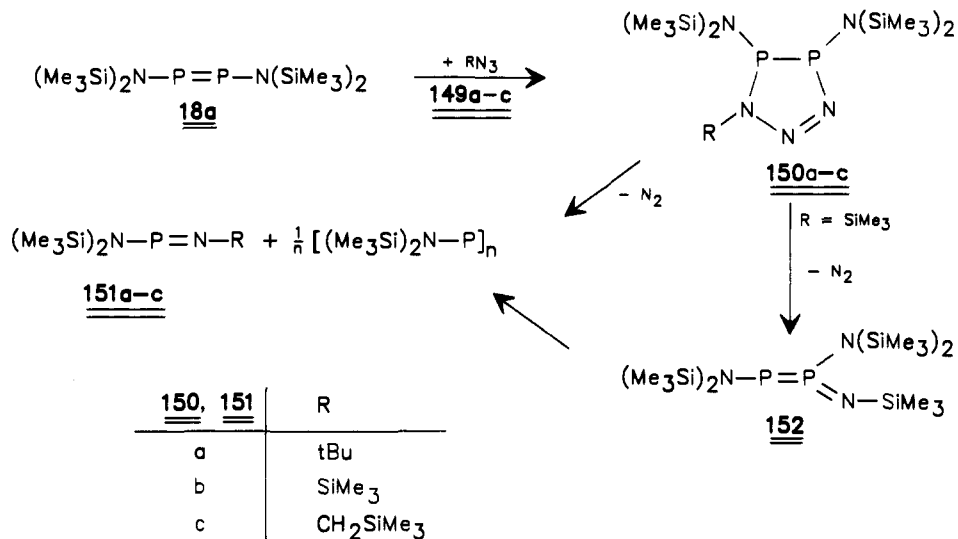
Grobe et al. have developed an elegant method for the production of instable CF₃-substituted diphosphenes, and again their evidence was based on [2 + 4] cycloaddition processes.

The symmetrical diphosphene **158** resulted from the dehalogenation of CF₃PI₂ by SnCl₂^{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).

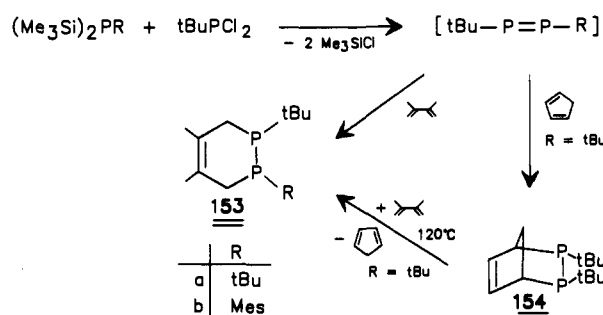
Unsymmetrical diphosphenes were available from distannyldiphosphanes **162** and (dimethylthio)phosphane **163**. The philicity of tin was assumed to be the driving force of this transformation. The in situ generated diphosphenes were trapped by various 1,3-dienes^{118b} (Scheme 83). The influence of 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 **173**⁵ and **18a**^{36,99} are also prone to [2 + 4] cycloadd-

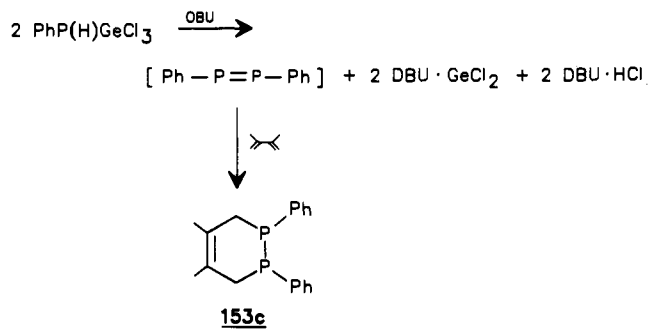
Scheme 76



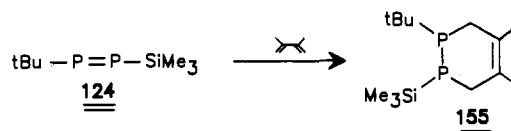
Scheme 77



Scheme 78



Scheme 79



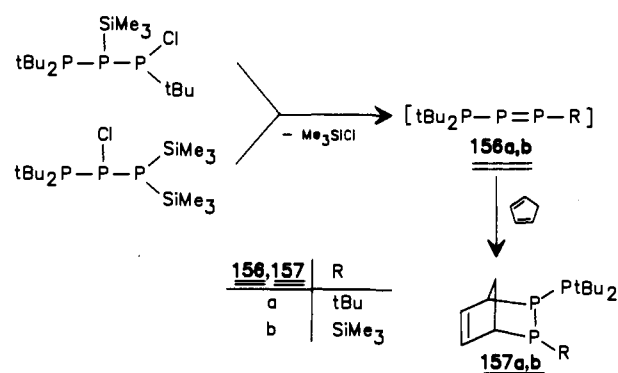
ditions with dienes (Scheme 84). Adduct 168 readily decomposes above 40 °C into its components and is thus useful as a storable source of diphosphene 18a.

V. Transition Metal Diphosphene Complexes

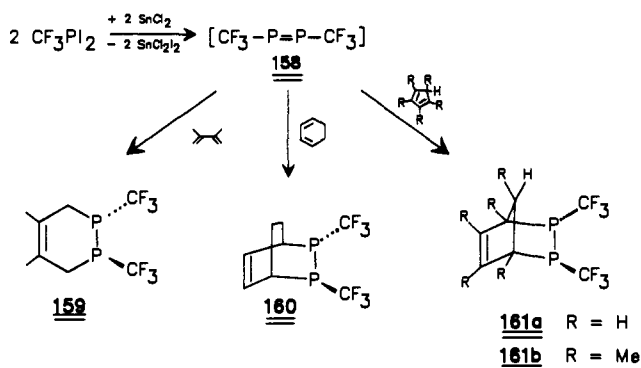
A. Coordination Modes of Diphosphenes

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 date¹³ (Scheme 85).

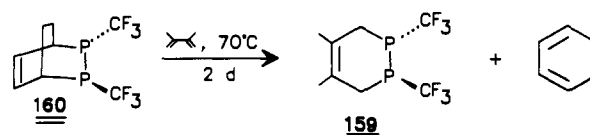
Scheme 80



Scheme 81



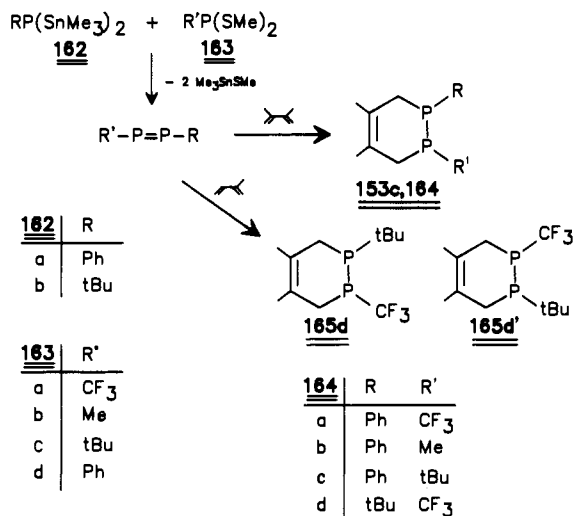
Scheme 82



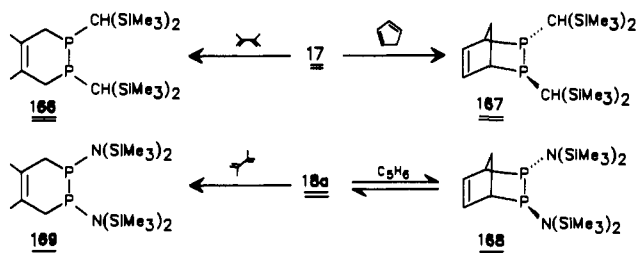
π -Complexes of ring compounds with P-P fragments are not discussed here.

In compounds of type A the diphosphene acts as an η^1 -ligand toward the metal center. Theoretical calculations on the model compound $(\eta^1\text{-P}_2\text{H}_2)\text{Cr}(\text{CO})_5$ 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

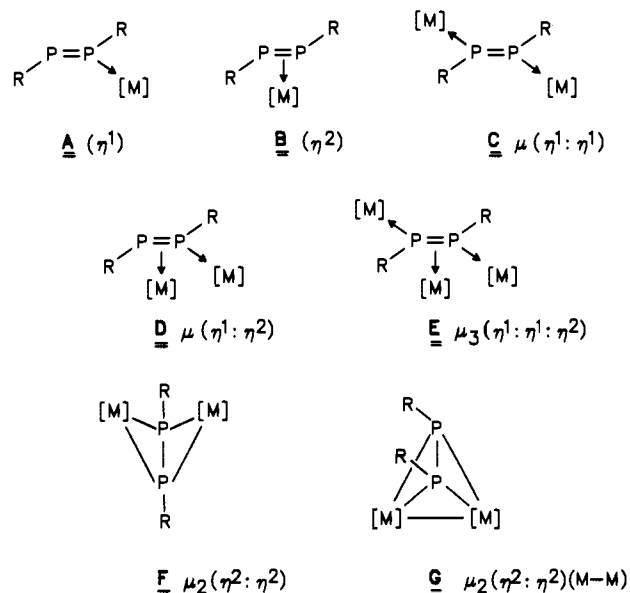
Scheme 83



Scheme 84

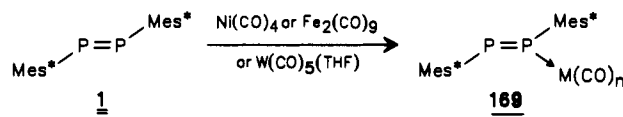


Scheme 85



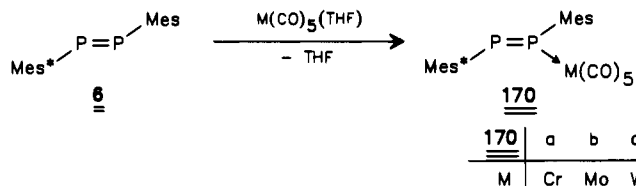
empty LUMO (the π^* orbital) of the ligand. The extent of the back-donation is quite large and comprises 0.30 electrons.¹¹⁹ Formula B emphasizes a η^2 -interaction of the $\text{P}=\text{P}$ π -system with the metal atom. Like in olefin complexes donation from the filled π -orbital to an empty metal 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 independent 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 diphos-

Scheme 86



169	M(CO) _n	Ref.
a	Ni(CO) ₃	120
b	Fe(CO) ₄	120
c	W(CO) ₅	121

Scheme 87



phene incorporated in a butterfly molecule, whereas G is a representative of a cluster compound with a diphosphene building block. Other types of complexes with such a bonding situation are conceivable.

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 $\text{Mes}^*\text{P}=\text{PMes}^*$ with $\text{Ni}(\text{CO})_4$, $\text{Fe}_2(\text{CO})_9$, and $\text{W}(\text{CO})_5(\text{THF})$ afforded species of the type under discussion (Scheme 86). The end-on coordination of a $\text{Cr}(\text{CO})_5$ moiety to this diphosphene failed presumably for steric reasons.

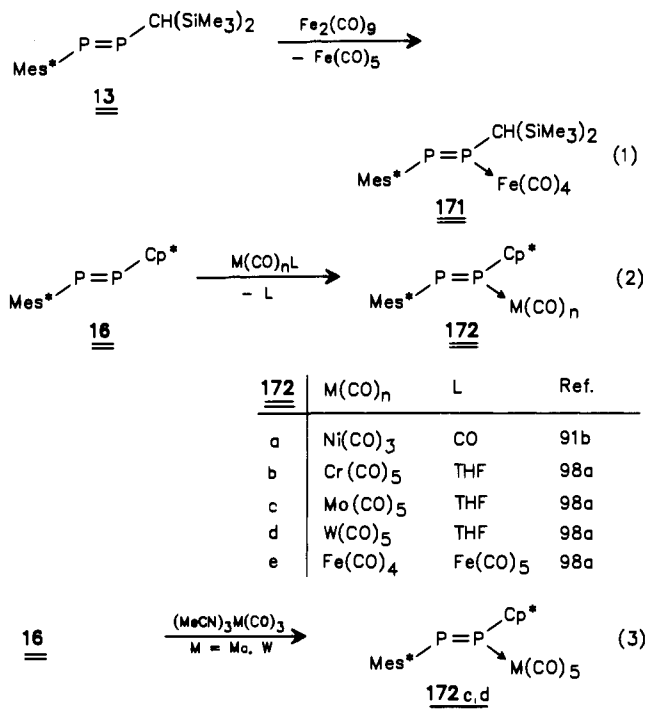
Consistently the treatment of the unsymmetrically substituted diphosphene $\text{Mes}^*\text{P}=\text{PMes}$ (6) with $\text{M}(\text{CO})_5(\text{THF})$ (M = Cr, Mo, W) leads to complexes with the metal carbonyl group at the less hindered phosphorus atom^{61,121} (Scheme 87). The same is reflected in the transformations of Scheme 88.¹²⁰

Attempts to prepare a $\text{M}(\text{CO})_5$ 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).

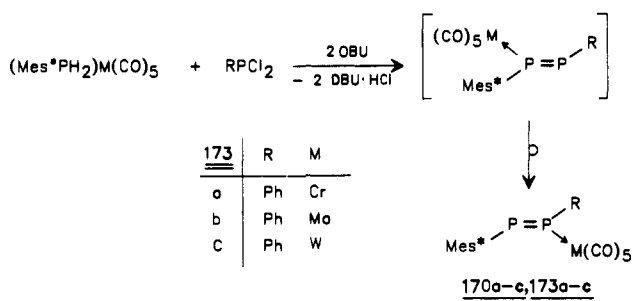
The interesting equilibrium $174a \rightleftharpoons 174b$, which implies the migration of the $\text{Ni}(\text{CO})_3$ group between the two phosphorus was observed by ³¹P NMR spectroscopy (Scheme 90).

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

Scheme 88



Scheme 89



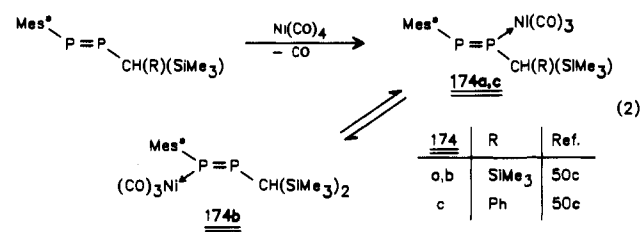
restrictions like 1 does¹²² (Scheme 91). The reaction of the *Z*-configured diphosphene 24a with Ni(CO)₄ afforded the corresponding Ni(CO)₃ adduct with an end-on coordination of the ligand³⁹ (Scheme 92). Complex 176b was synthesized via a substitution process and involved a 1,3-H shift from P to N.^{50c}

The addition of AgSO₃CF₃ or of the coordinatively unsaturated gold compound (Et₃PAu)⁺PF₆⁻ to 1 furnished complexes 177a-c with η¹-diphosphene ligands. These were observed by ³¹P NMR spectroscopy in solution, but were not isolated¹²³ (Scheme 93).

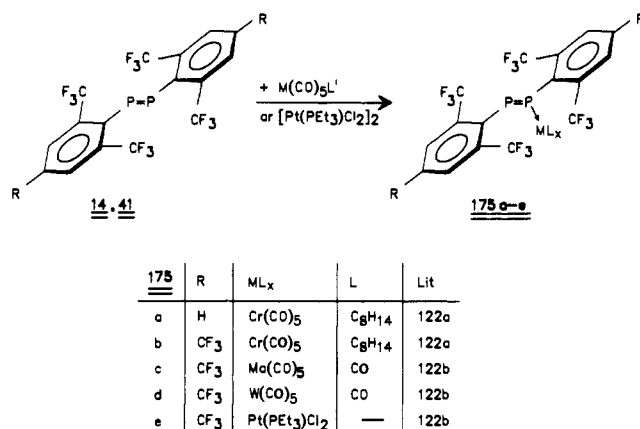
The reductive coupling of dichlorophosphanes by means of carbonyl metalates represents an interesting approach to diphosphene complexes. This type of reaction is not straightforward and leads to a number of products, depending on steric and electronic factors.

Power et al. studied the reaction of RPCl₂ with Na₂Cr(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 (Me₃Si)₂NPCl₂ 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 (Me₃-

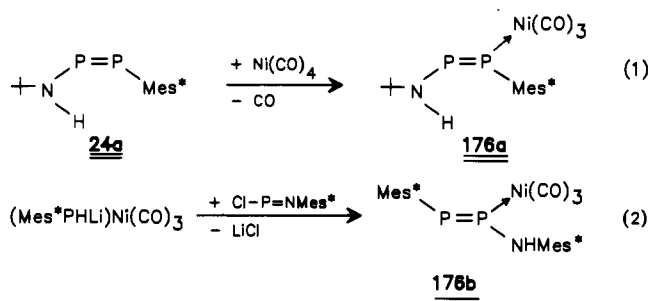
Scheme 90



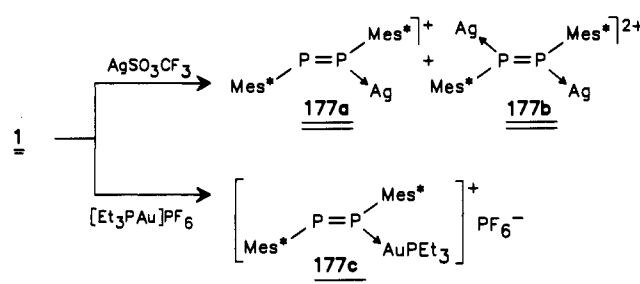
Scheme 91



Scheme 92



Scheme 93

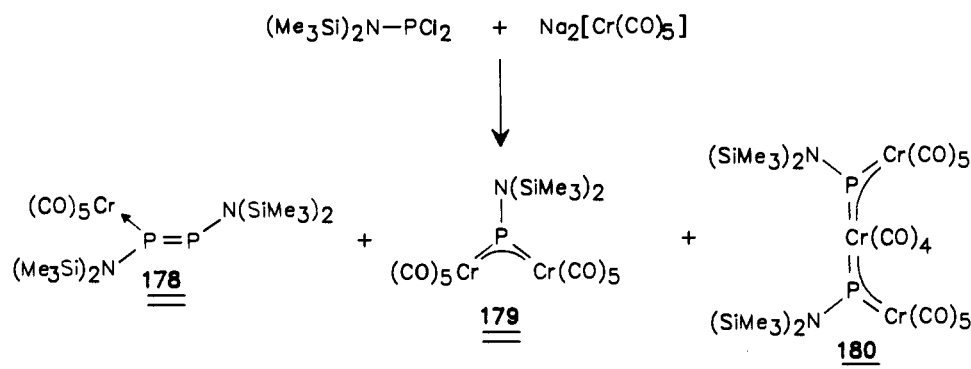


Si)₂CHPCl₂ underwent a 45% conversion to 181a when reacted with the chromate anion in ether^{124b} (Scheme 95).

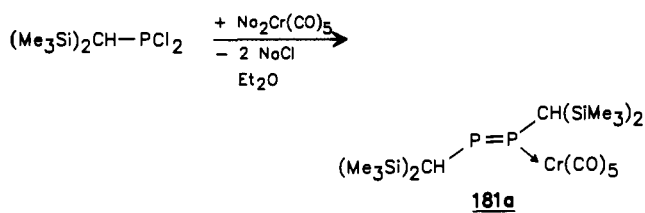
Huttner et al. carefully investigated the reactivity of Na₂M₂(CO)₁₀ toward various organodichlorophosphanes¹²⁵ (Scheme 96). He invoked phosphinidene complexes I as intermediates in the diphosphene complex synthesis via the dehalogenation of organodichlorophosphanes. Depending upon the steric requirement of the substituent R, one, two, or three M(CO)₅ fragments were ligated to the diphosphene. For R = C₆H₅, 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)₅M]P=PR} (R

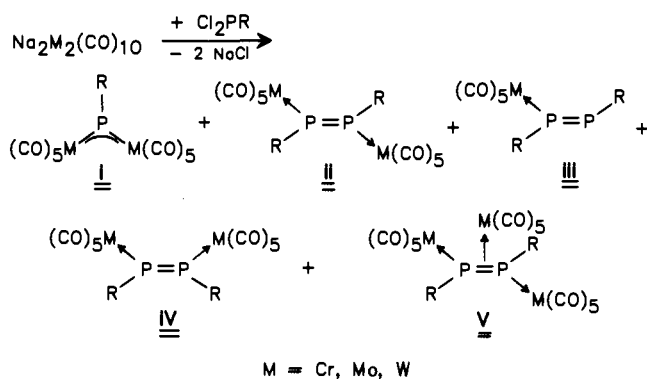
Scheme 94



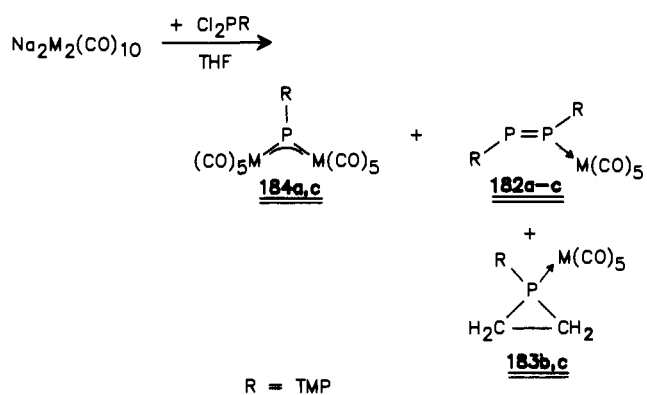
Scheme 95



Scheme 96



Scheme 97



<u>182-184</u>	M
a	Cr
b	Mo
c	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 $(\text{Me}_3\text{Si})_2\text{CHPCl}_2$ with $\text{Na}_2\text{M}_2(\text{CO})_{10}$ (M = Cr, Mo, W) very short reaction times favored the occurrence of phosphinidene complexes, which were subsequently converted into complexes 185a-c. Pro-

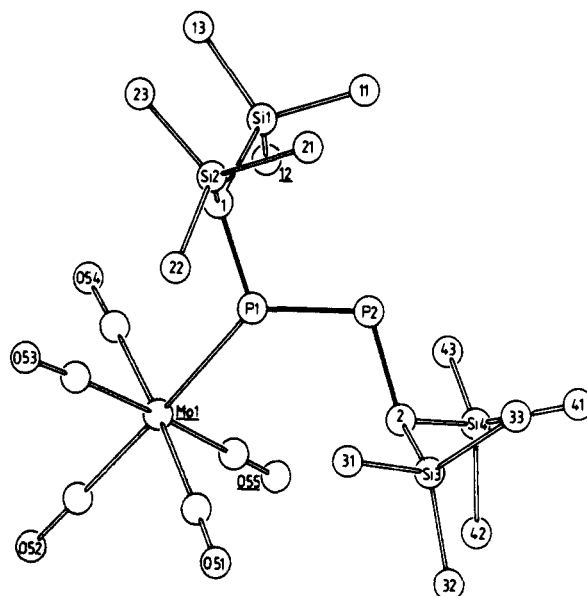
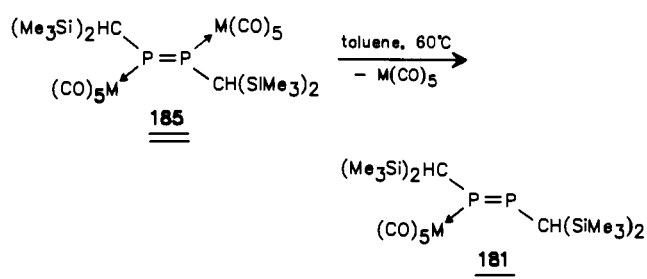


Figure 2. Molecular structure of (E) - $\{(\text{Me}_3\text{Si})_2\text{CH}-\text{P}[\text{Mo}(\text{CO})_5]=\text{P}-\text{CH}(\text{SiMe}_3)_2\}$ (181b). Selected bond lengths (Å) and bond angles (deg): Mo(1)-P(1) 2.472 (2), P(1)-P(2) 2.006 (3), P(1)-C(1) 1.804 (6), P(2)-C(2) 1.813 (7); Mo(1)-P(1)-C(1) 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



<u>181,185</u>	M
a	Cr
b	W

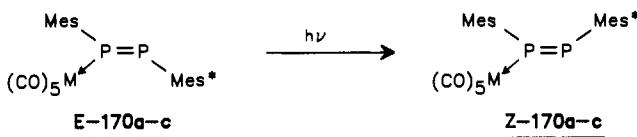
longed heating of 185 achieved the extrusion of one $\text{M}(\text{CO})_5$ moiety to give compounds 181a-c (Scheme 98).^{125a} Figure 2 shows the molecular structure of 181b.

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

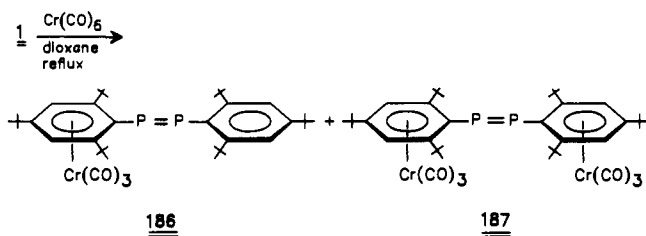


Scheme 100



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 light⁶¹ (Scheme 100).

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

In light of the steric congestion in (Me₃Si)₃CP=PC-(SiMe₃)₃ (**9**) it is not surprising that all attempts to synthesize complexes thereof have failed.

The treatment of Mes*P=PMe* with Cr(CO)₆ (THF) did not lead to end-on coordination, but reacting Cr(CO)₆ with **1** in refluxing dioxane resulted in η⁶-coordination of one or two Cr(CO)₃ fragments to the arene rings. The ³¹P NMR spectrum of **187** exhibited a singlet at δ = 499.7, whereas the spectrum of **186** was characterized by an AB pattern at δ = 503.2 and 475.7 with a ¹J_{PP} constant of 590.8 Hz¹²⁷ (Scheme 101).

2. η²-Diphosphene Complexes

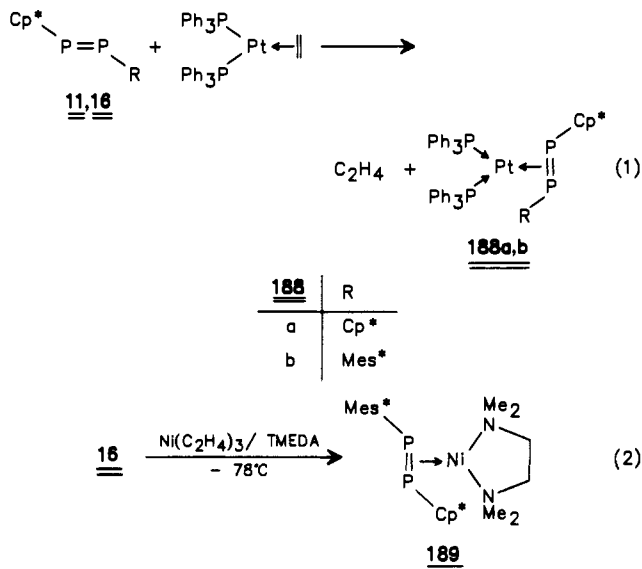
Only in a few cases were η²-diphosphene complexes accessible by displacement reactions via the free diphosphene (Scheme 102). The diphosphenes **11** and **16** underwent reaction with ethylene-bis(triphenylphosphane)platinum to give the η²-diphosphene complexes **188a,b** quantitatively.^{98a}

Similarly a mixture of Ni(C₂H₄)₃, tetramethylethylenediamine (TMEDA), and **16** at -78 °C furnished the complex (η²-Cp*P=PMe*)NiTMEDA **189** as violet platelets.^{91b} The thermolabile complex **190** was obtained as a red solid from the reaction of [nBu₃P]₂Ni(COD), nBu₃P, and **24a** in a toluene/hexane solution⁹⁹ (Scheme 103).

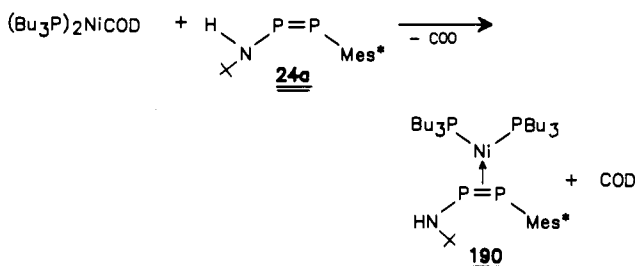
Trapping experiments with the labile diphosphene **127** at -60 °C led to η²-diphosphene complex **191**³¹ (Scheme 104).

In the vast majority the η²-ligated diphosphene was constructed from stable precursors in the coordination sphere of a metal center. Thus the degradation of the

Scheme 102



Scheme 103



cyclotetraphosphane (C₆F₅P)₄ in the presence of Pt-(PPh₃)₄^{128a} or Pd(PPh₃)₄^{129b} provided a method for the synthesis of the π-complexes **192a,b** (Scheme 105).

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 (CF₃P)₄ reacted with zerovalent Pt, Pd, and Ni complexes under refluxing conditions in benzene to give η²-CF₃P=PCF₃ complexes **193a-f** (Scheme 106). Only **193a** was isolated and fully characterized.^{128b}

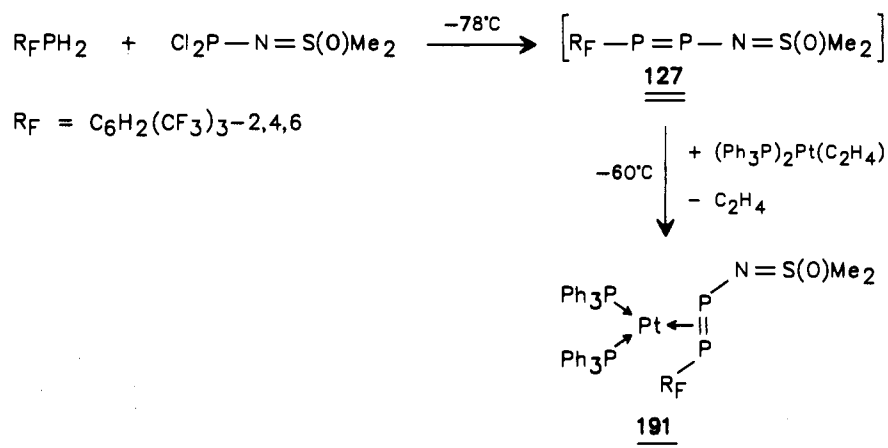
The fixation of reactive diphosphenes in the coordination sphere may be accompanied by a change in the oxidation state of the metal.

The first example of a η²-diphosphene complex (**194**) was prepared by the reduction of white phosphorus with C₂P₂MoH₂^{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 P₂H₂ (2.004 Å).⁶⁶

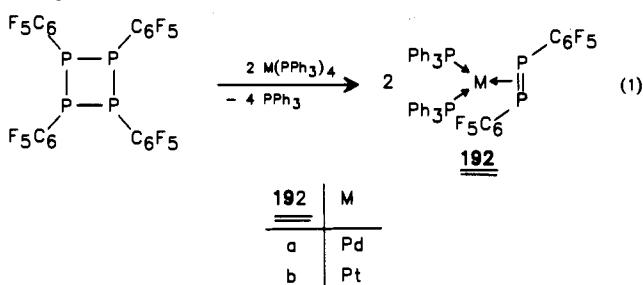
Platinum and palladium complexes **195** with η²-diphenyldiphosphene were the products of the reduction of *cis*- or *trans*-MCl₂L₂ with 1,2-dithio-1,2-diphenyldiphosphane¹²⁹ (Scheme 108). In Pd complex **195a** a P-P bond of 2.121 (4) Å is present.

A similar type of reaction is reported from nickel chemistry: Treatment of (PMe₃)₂NiCl₂ with Li(tBu)P-P(tBu)Li gave the nickelatetraphosphacyclopentane **196** with an additional η²-bonded diphosphene ligand. Presumably the heterocycle is formed by the coupling of two diphosphenes at the metal center¹³¹ (Scheme

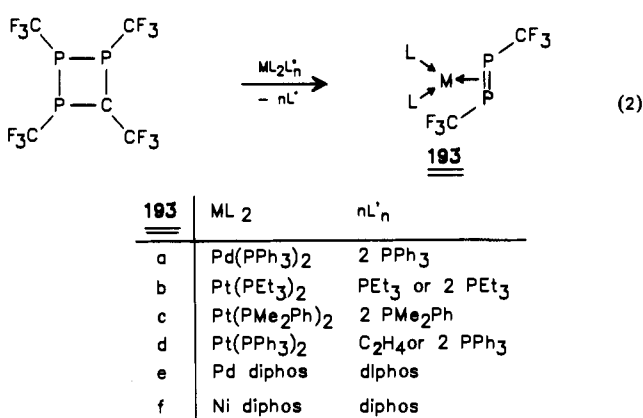
Scheme 104



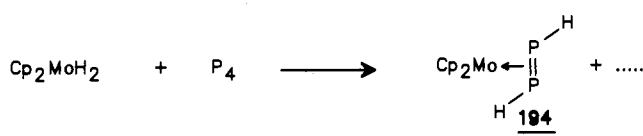
Scheme 105



Scheme 106



Scheme 107

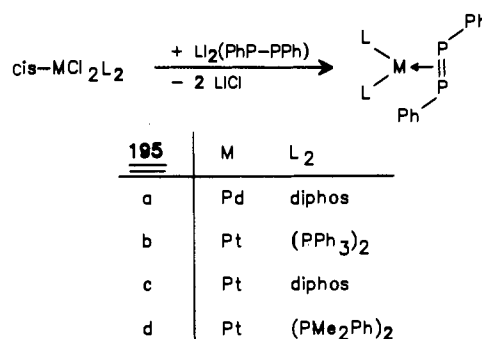


109). The NiP₆ unit is virtually planar as shown by a X-ray structure analysis. The molecular structure of 196 is shown in Figure 3.

Generally there is no need to employ dimetallo-diphosphanes for this kind of synthesis. Primary metal phosphides such as LiPHR (R = Ph, tBu)¹³² or Mg-(PPh)₂¹³³ react with complex metal dihalides to yield η²-diphosphene complexes 197a-c and 200e (Scheme 110).

The synthesis of η²-diphosphene complexes of Zr and Hf is of no general applicability. A study of the reaction of (C₅H₅)₂MCl₂, (C₅Me₅)₂MCl₂, and [1,3-(Me₃Si)₂C₅H₃]-MCl₂ with primary lithium phosphides evidenced that the distribution of products depended upon (1) the

Scheme 108



Scheme 109

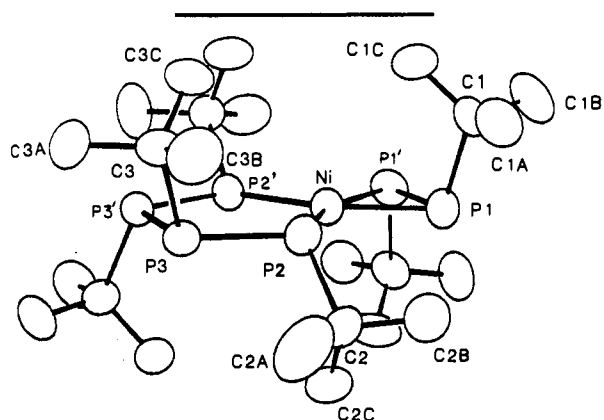
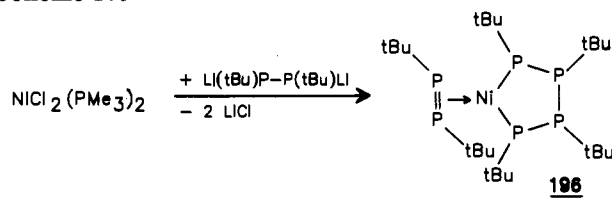
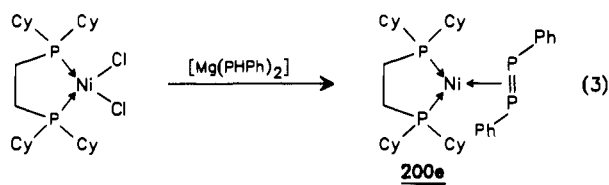
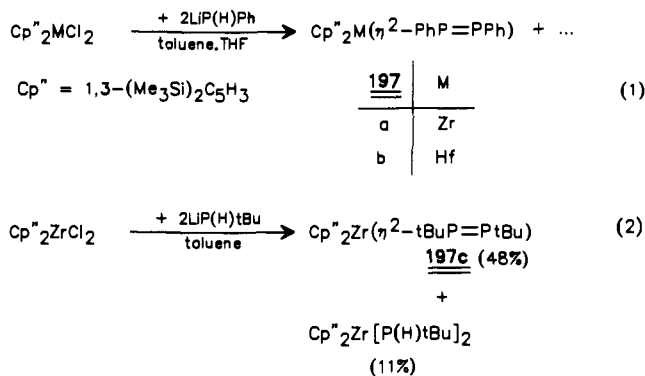


Figure 3. Molecular structure of 196. Selected bond lengths (Å) and bond angles (deg): Ni-P(1) 2.257 (4), Ni-P(2) 2.149 (4), P(1)-P(1') 2.110 (5), P(2)-P(3) 2.237 (5), P(3)-P(3') 2.196 (4); P(2)-Ni-P(2') 101.2 (2), P(2)-Ni-P(1) 101.5 (1), Ni-P(1)-P(1') 82.1 (1), P(1)-Ni-P(1') 55.7 (1). Reprinted from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

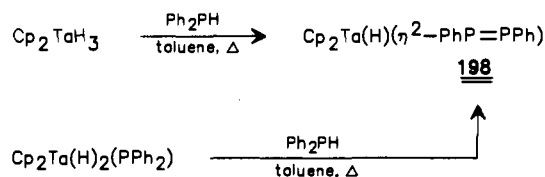
metal and its reducibility, (2) the steric and electronic nature of the cyclopentadienyl ring, and (3) the bulk of the organic group at the phosphorus atom.¹³²

The first tantalum diphosphene complex resulted from the treatment of Cp₂TaH₃ with Ph₂PH in refluxing toluene¹³⁴ (Scheme 111). The diphosphene configu-

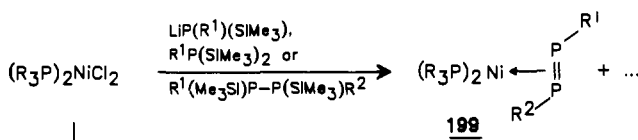
Scheme 110



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 $\text{Cp}_2\text{Ta(H)}_2(\text{PPh}_2)$ is generated by insertion of the fragment $[\text{Cp}_2\text{TaH}]$ into the $\text{Ph}_2\text{P-H}$ bond. The dihydride was synthesized independently and was readily converted into $\text{Cp}_2\text{Ta(H)}(\eta^2\text{-PhP=PPh})$ by heating with Ph_2PH .¹³⁴

Schäfer and co-workers carefully studied the reactivity of bisphosphane nickel dichlorides $(\text{R}_3\text{P})_2\text{NiCl}_2$ toward silylphosphane derivatives such as $\text{LiP}(\text{SiMe}_3)_2$, $\text{R}^1\text{P}(\text{SiMe}_3)_2$, and $\text{P}_2\text{R}'_2(\text{SiMe}_3)_2$.^{135a,b}

The formation of diphosphene complexes of the types $(\text{R}_3\text{P})_2\text{Ni}(\eta^2\text{-Me}_3\text{SiP=PSiMe}_3)$, $(\text{R}_3\text{P})_2\text{Ni}(\eta^2\text{-tBuP=PtBu})$ and $(\text{R}_3\text{P})_2\text{Ni}(\eta^2\text{-PhP=PPh})$ 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

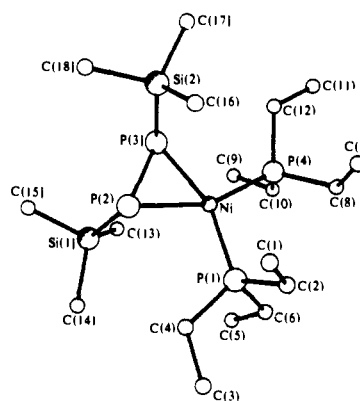
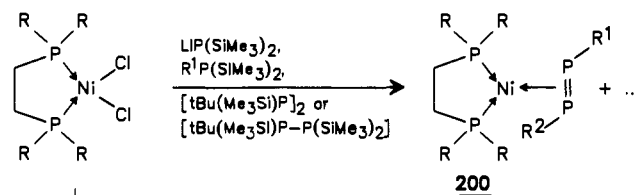


Figure 4. Molecular structure of **199b**. Selected bond lengths (Å) and bond angles (deg): Ni-P(2) 2.236 (2), Ni-P(3) 2.258 (2), P(2)-P(3) 2.149 (2), P(2)-Ni-P(3) 57.13 (5), Ni-P(2)-P(3) 61.95 (7), P(2)-P(3)-Ni 60.93 (6), Si(1)-P(2)-P(3) 97.87 (8), P(2)-P(3)-Si(2) 96.96 (8). Reprinted from ref 138.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

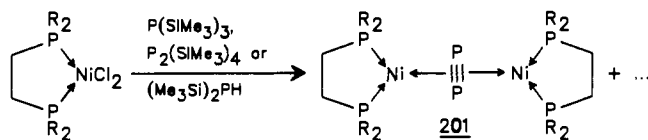
disilyldiphosphanes $\text{P}_2\text{R}'_2(\text{SiMe}_3)_2$ ($\text{R}' = \text{Ph}$, tBu, SiMe₃) gave the best yields of the η^2 -diphosphene complexes **199a-h**, and the process formally may be considered as a [2 + 1] cyclocondensation^{135b} (Scheme 112).

The molecular structure of $(\text{Et}_3\text{P})_2\text{Ni}(\eta^2\text{-[P}(\text{SiMe}_3)_2])_2$ (**199b**, Figure 4) has been elucidated by X-ray analysis.¹³⁸ The structure shows an η^2 -coordinated and trans-configured diphosphene, the phosphorus centers of which are located in nearly the same plane as the nickel and the two remaining phosphorus atoms.

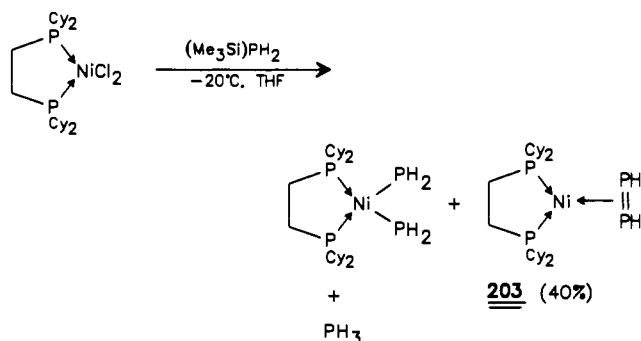
The reactions of $\text{LiP}(\text{SiMe}_3)_2$ with the square-planar chelate complexes $(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)\text{NiCl}_2$ ($\text{R} = \text{Et}$, Cy, Ph) were more straightforward.¹³⁶ Here the bulky $\text{Cy}_2\text{-PCH}_2\text{CH}_2\text{PCy}_2$ ligand even stabilized an $\eta^2\text{-MeP=PMe}$ complex. When the silylphosphane components were of concern the best results were obtained with $\text{LiP}(\text{SiMe}_3)_2$, $\text{PhP}(\text{SiMe}_3)_2$, $\text{MeP}(\text{SiMe}_3)_2$, $[\text{tBu}(\text{Me}_3\text{Si})_2\text{P}]_2$, and $(\text{Me}_3\text{Si})_2\text{PP}(\text{tBu})(\text{SiMe}_3)$ (Scheme 113).

The treatment of the chelate complexes with $\text{P}(\text{SiMe}_3)_3$ or $\text{P}_2(\text{SiMe}_3)_4$ did not furnish η^2 -diphosphene

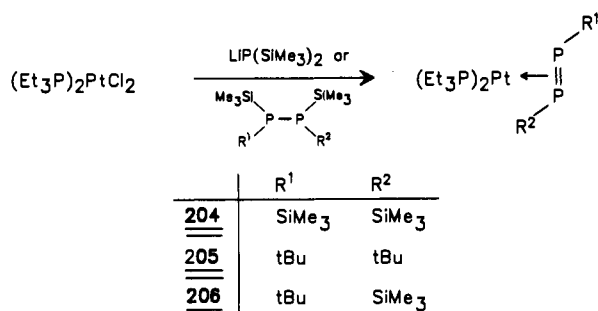
Scheme 114



Scheme 115



Scheme 116



complexes. Instead stable dinuclear complexes 201 with a bridging $\eta^2:\eta^2$ -P₂ ligand were formed (Scheme 114). The same was observed when (Me₃Si)₂PH was reacted with the respective nickel complexes. In the case of R = Cy the compounds (Cy₂PCH₂CH₂PCy₂)-Ni(η^2 -HP=PSiMe₃) (202) and (Cy₂PCH₂CH₂PCy₂)-Ni(η^2 -HP=PH) (203) were detected as intermediates by ³¹P NMR spectroscopy^{136c} (Scheme 115). The latter complex was isolated from the reaction of (Cy₂PCH₂CH₂PCy₂)-NiCl₂ with Me₃SiPH₂ at -20 °C.^{136c} Warming solid 203 or its solutions to 20 °C gave the diphosphorus complex 201.

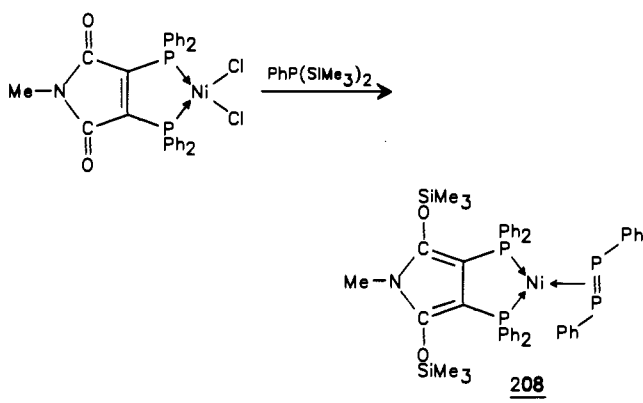
Schäfer extended the synthetic approach described here to the chemistry of platinum diphosphene complexes¹³⁷ (Scheme 116).

Under comparable conditions the use of (Ph₃P)₂PtCl₂ did not afford stable η^2 -diphosphene complexes. The compounds (Ph₃P)₂Pt(η^2 -RP=PR) (207) (a, R = Me₃Si; b, R = tBu) were observed in the reaction mixture by ³¹P NMR techniques, however.

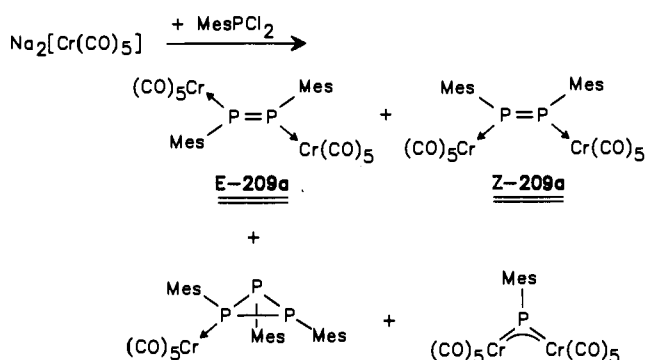
The same synthetic principle that was used for 199b was used in the reaction of a 3,4-diphosphinomaleimidenickel complex with PhP(SiMe₃)₂. Here evidently the disilylphosphane first reduced the maleimide before the η^2 -diphosphene complex 208 was built up¹³⁹ (Scheme 117).

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. $\mu_2(\eta^1:\eta^1)$ -Diphosphene Complexes

It was pointed out that the number of M(CO)₅ groups linked to a diphosphene P₂R₂ is highly dependant on the steric requirements of the substituents R. Thus, in order to obtain complexes with $\eta^1:\eta^1$ 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.

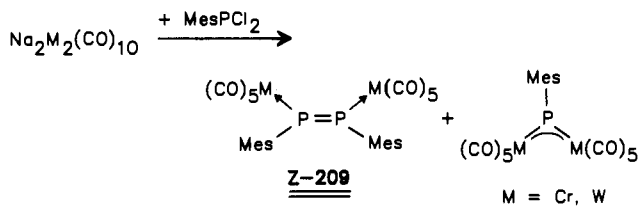
E- and *Z*-configured complexes 209a were the main products of the reaction of MesPCL₂ and Na₂Cr(CO)₅ in ether. A phosphinidene species and a cyclotriphosphane complex were observed as minor products^{124c} (Scheme 118).

In contrast to these findings Huttner reported only the *Z*-configured dinuclear diphosphene complexes in addition to a phosphinidene species as products of the dehalogenation of MesPCL₂ by Na₂[M₂(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*)-Me₃SiCH₂P=PCH₂SiMe₃][Cr(CO)₅]₂ (210)^{124c} and [(*E*)-(Me₃Si)₂CHP=P-CH(SiMe₃)₂][M(CO)₅]₂ (185a,b) (M = Cr, W)^{125a} which were prepared from the corresponding organodichlorophosphane and Na₂[Cr(CO)₅]^{124c} or Na₂[M₂(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 THF¹⁴⁰ (Scheme 120).

Scheme 119



<u>Z-209</u>	M
a	Cr
b	Mo
c	W

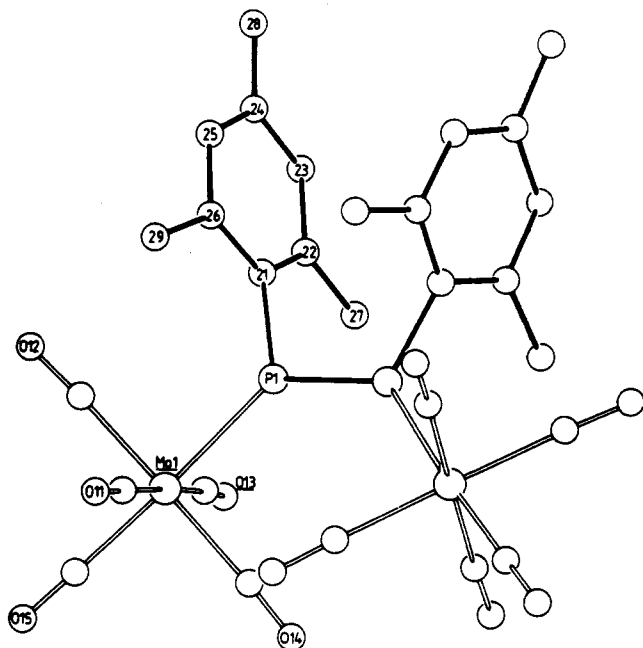
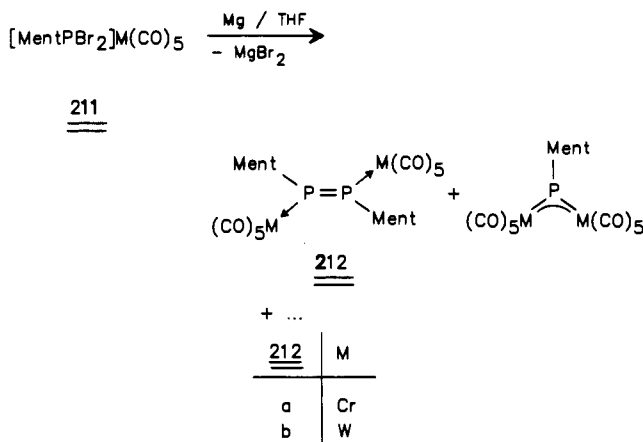


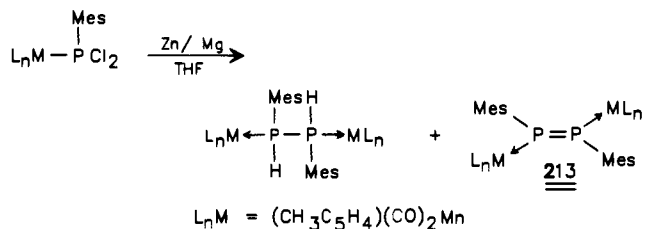
Figure 5. Molecular structure of 209b. Selected bond lengths (Å) and bond angles (deg): Mo(1)–P(1) 2.454 (2), P(1)–P(1′) 2.026 (2), P(1)–C(21) 1.812 (4); Mo(1)–P(1)–C(21) 120.5 (1), Mo(1)–P(1)–P(1′) 132.3 (0), C(21)–P(1)–P(1′) 107.0 (1). Reprinted from ref 125a. Copyright 1985 Elsevier Sequoia.

Scheme 120

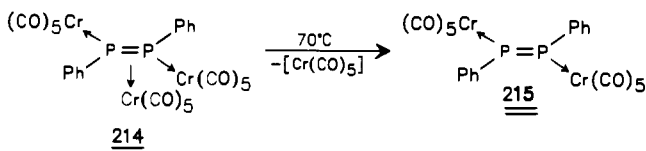


Again phosphinidene complexes accompanied the formation of the diphosphene species. The P–P distance in 212a amounts to 2.040 Å.¹⁴⁰ Similarly the reduction of a manganese dichlorophosphate complex proceeded with the production of dinuclear diphosphene and diphosphene complexes¹⁴¹ (Scheme 121).

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 RPCl₂ and Na₂Fe(CO)₄ is highly dependent upon the nature of R and the solvent. Diphosphene complexes were favored by low concentrations of Fe(CO)₄²⁻ in solution as it was realized in ether or hexane.¹⁴⁵

A comparable synthetic approach, applied upon aryldichlorophosphanes and Na₂[V(C₅H₅)(CO)₃] yielded diphosphene complex 219 for R = Mes¹⁴⁶ 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*PCl₂ with carbonylmetalates gave diphosphene 1 in addition to phosphinidene complexes; however, no diphosphene complexes were detected among the products¹⁴⁸⁻¹⁵⁰ (Scheme 124).

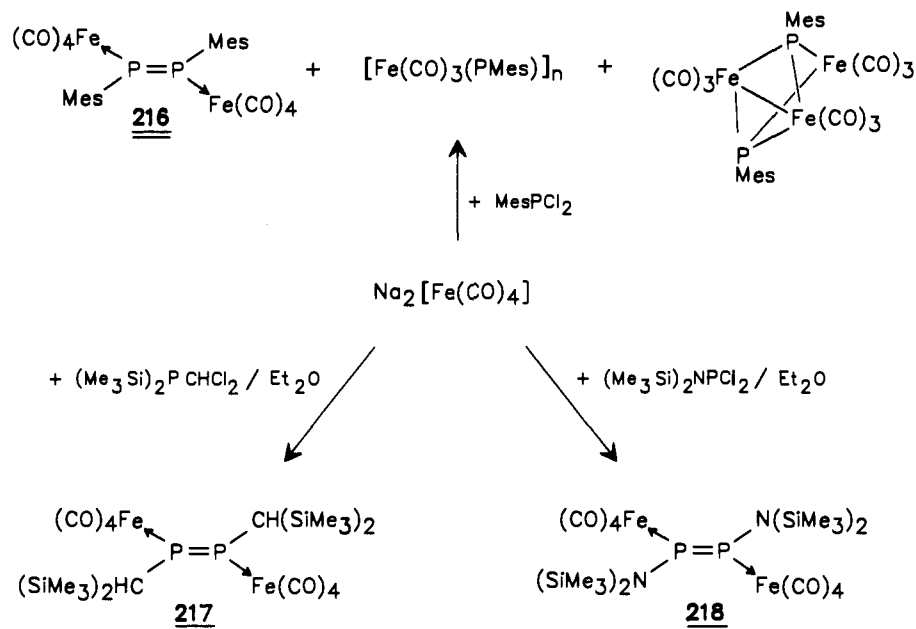
The addition of a second 16-electron fragment to a preformed η¹-diphosphene complex in order to synthesize μ-(η¹:η¹)-complexes was only realized for a small number of Ni(CO)₃ compounds^{50c} (Scheme 125). The X-ray structure analysis of 220a exhibited an E-configured P=P bond of 2.029 Å.^{50c}

4. μ₂(η¹:η²)-Diphosphene Complexes

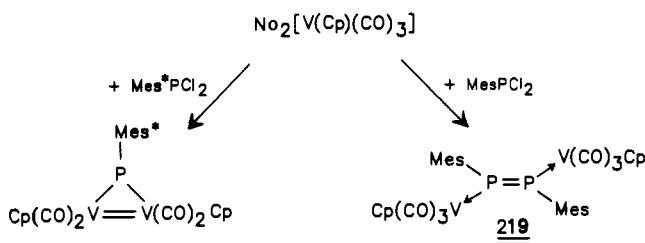
Dinuclear entities with η¹:η² diphosphene bridges of type D represent an interesting alternative to the complexes of type C discussed in the previous section.

The hydridocarbonylferrate HFe(CO)₄⁻ reduced Ph-PCl₂ and diazaphospholyl dichlorophosphate to the complexes 221¹⁵¹ and 222¹⁵² with bridging η¹:η²-diphosphene ligands. In addition the organochlorophosphate

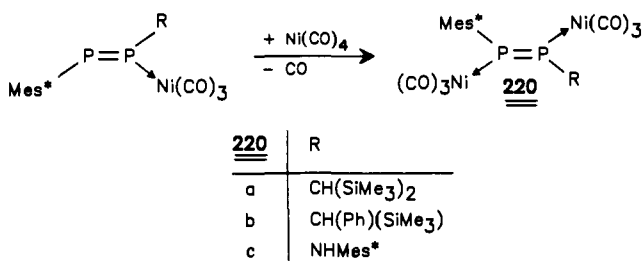
Scheme 123



Scheme 124



Scheme 125



iron complex **223** was generated (Scheme 126). The ^{31}P NMR spectrum of **221** displays an AB spin system with $\delta = 52.1$ and -34.5 ppm ($J_{\text{AB}} = 415$ 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 $\text{Fe}(\text{CO})_4$ and η^2 -coordinated to another $\text{Fe}(\text{CO})_4$ moiety¹⁵² (Figure 6).

Scheme 126

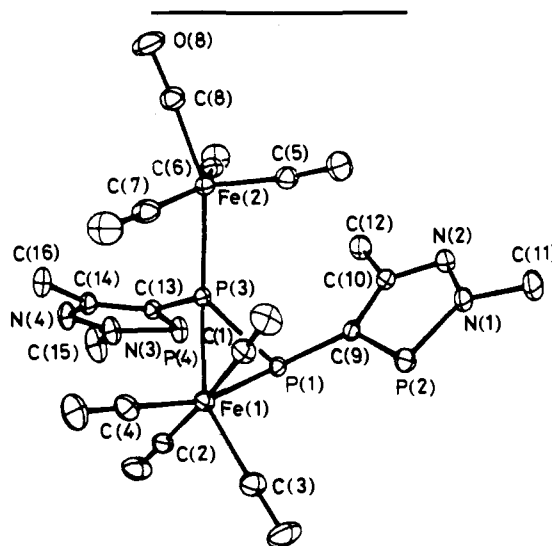
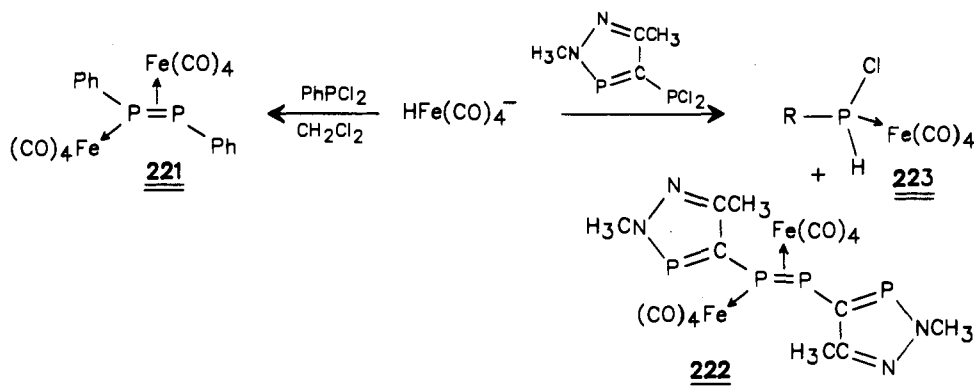
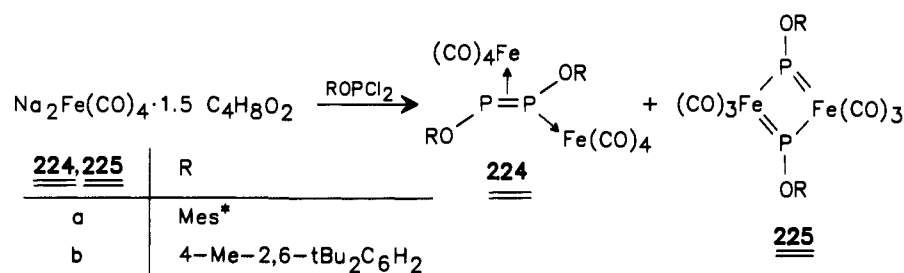


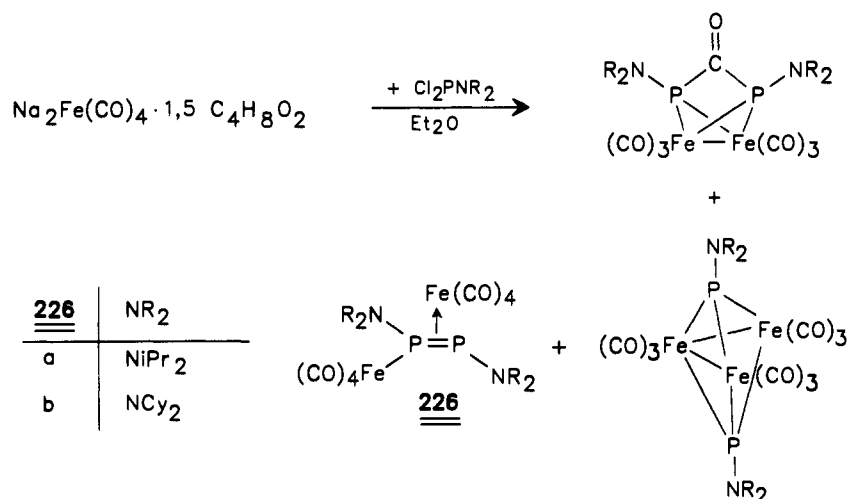
Figure 6. Molecular structure of **222**. Selected bond lengths (Å) and angles (deg): P(1)–P(3) 2.1504 (8), P(2)–C(9) 1.713 (2), P(4)–C(13) 1.714 (3), P(1)–C(9) 1.801 (2), P(3)–C(13) 1.802 (2); P(3)–P(1)–C(9) 105.6 (8), P(1)–P(3)–C(13) 101.2 (8). Reprinted from ref 152. Copyright 1988 Chemical Society,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

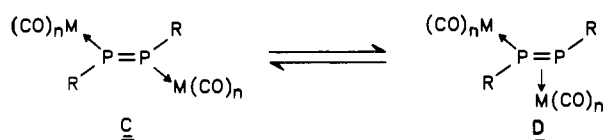
Scheme 127



Scheme 128



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 $\eta^1(\text{Fe}-\text{P})$ bond [2.226 (2) Å] and the $\eta^2(\text{P}=\text{P})\text{Fe}$ 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 *i*Pr₂N, Cy₂N, or the TMP group were required for the success of this transformation¹⁴⁵ (Scheme 128).

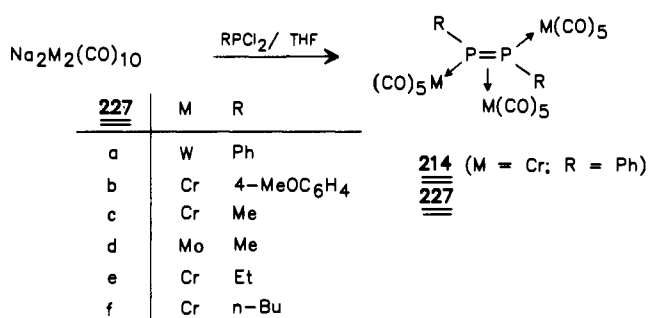
If one accepts a hypothetical equilibrium between the two isomers C and D, it is remarkable that both modes of coordination are realized in iron chemistry, whereas the pentacarbonyls of chromium, molybdenum, and tungsten clearly prefer structure C (Scheme 129).

5. $\mu_3(\eta^1:\eta^1:\eta^2)$ -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

Scheme 130



operative in the mixture of $\text{Na}_2\text{M}_2(\text{CO})_{10}$ 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 $\text{RP}[\text{M}(\text{CO})_5]_2$ or their THF adducts.

The X-ray analysis of **214** indicates significantly shorter Cr-P contacts for the η^1 -bonded $\text{Cr}(\text{CO})_5$ units than for the $\text{Cr}(\text{CO})_5$ 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** [$d(\text{P}=\text{P}) = 2.021$ (2) Å].^{142a}

The dimerization of phosphinidene compounds into diphosphene derivatives was exemplified by the formation of compound **214** and **228**¹⁵⁴ (Scheme 131). In **228** a Z-configured 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 ³¹P resonance occurs at δ 352. The idea that diphosphene complexes are resulting from phosphinidene precursors is supported by the

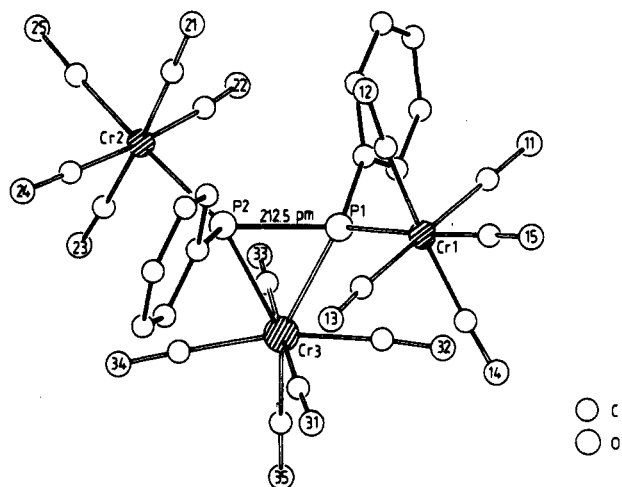
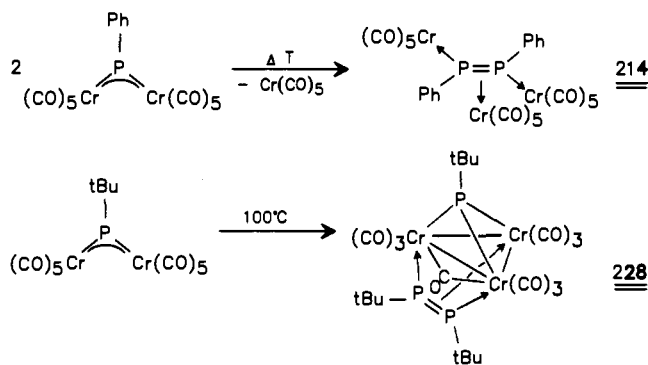
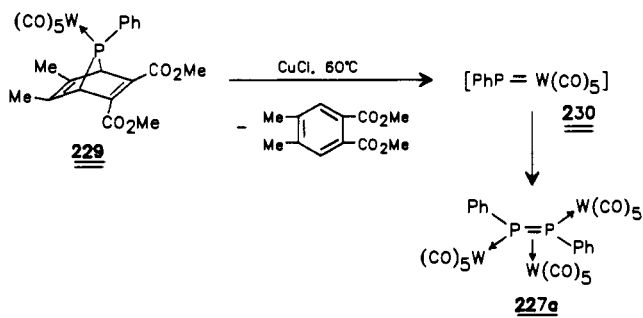


Figure 7. Molecular structure of **214**. Selected bond lengths (Å) and angles (deg): P(1)–P(2) 2.125 (6) [2.125 (4)], Cr(1)–P(1) 2.411 (4) [2.405 (5)], Cr(2)–P(2) 2.405 (4) [2.387 (4)], Cr(3)–P(1) 2.546 (5) [2.536 (5)], Cr(3)–P(2) 2.524 (3) [2.530 (5)]; P(2)–P(1)–Cr(1) 130.9 (2) [129.5 (2)], P(1)–P(2)–Cr(2)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

Scheme 131



Scheme 132



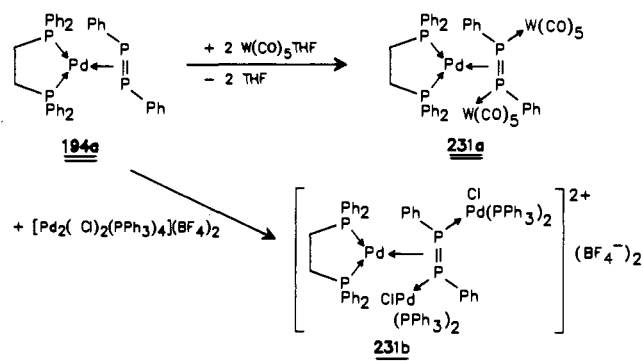
occurrence of **227a** as the main product in the thermal or catalytic decomposition of the appropriate 7-phosphanorbornadiene complex **229**. It is known that the latter serves as a source for the electrophilic phosphinidene complex **230**¹⁵⁵ (Scheme 132).

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).

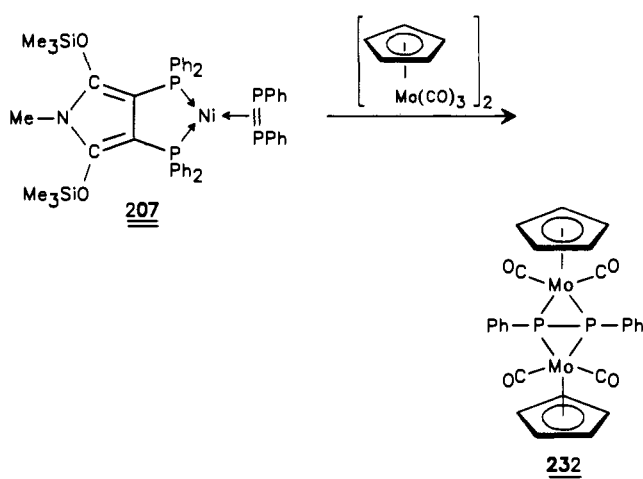
6. $\mu_2(\eta^2:\eta^2)$ -Diphosphene Complexes

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

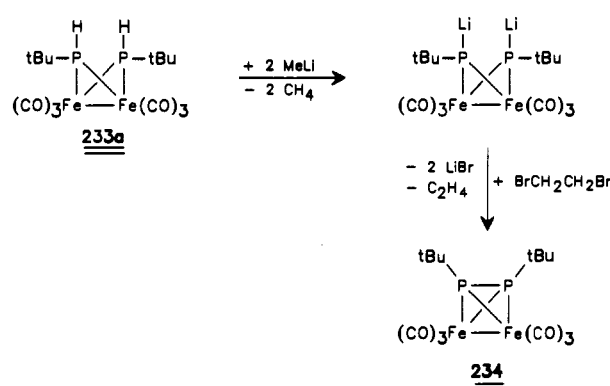
Scheme 133



Scheme 134



Scheme 135

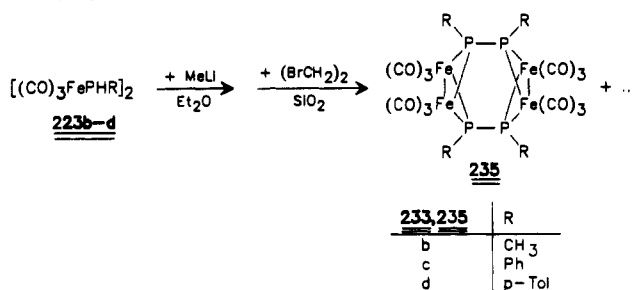


(Scheme 134). According to the X-ray diffraction analysis, **232** displays a Mo_2P_2 skeleton with a P–P bond length of 2.136 Å and two short Mo–P bonds (2.466, 2.370 Å) as well as two long Mo–P contacts (2.542, 2.546 Å). Both MoP_2 triangles enclose a dihedral angle of 135°. Thus the *Z*-configured 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 ³¹P NMR spectrum.¹⁵⁶

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



Scheme 137

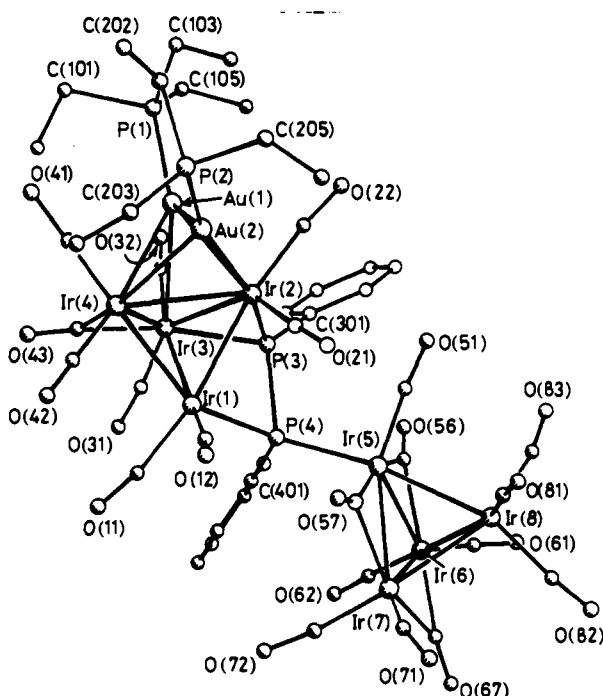
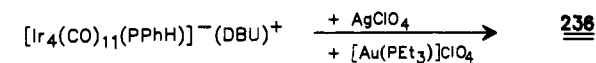


Figure 8. Molecular structure of **236**. Selected bond lengths (Å): Ir(2)–P(3) 2.302 (12), Ir(3)–P(3) 2.308 (9), Ir(1)–P(4) 2.434 (11), P(3)–P(4) 2.186 (13), Ir(5)–P(4) 2.375 (8). Reprinted from ref 159. Copyright 1986 Chemical Society, London.

as a six-electron ligand, is only marginally elongated by coordination. According to Hoffmann's isolobal analogy,¹⁵⁸ $[\text{Fe}(\text{CO})_3 \leftrightarrow \text{CH} \leftrightarrow \text{RP}^+]$ 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** [$d(\text{PP}) = 2.186$ (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).

The synthesis of the carbonyl nickel cluster **237** incorporating the $(\text{Me}_3\text{Si})_2\text{CHP}=\text{PCH}(\text{SiMe}_3)_2$ ligand as a six-electron donor was achieved by dehalogenation

Scheme 138

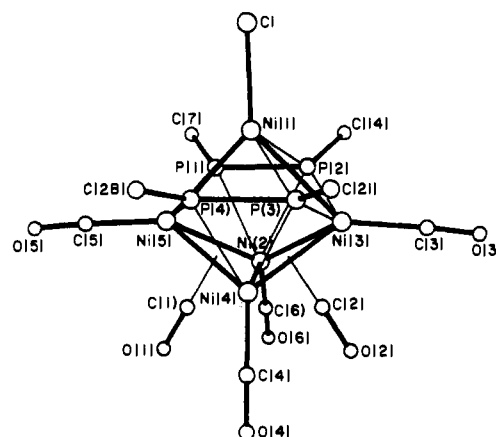
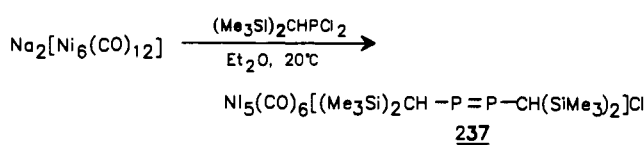


Figure 9. Molecular structure of **237**. Reprinted from ref 160. Copyright 1984 American Chemical Society.

of $(\text{Me}_3\text{Si})_2\text{CHPCl}_2$ with $\text{Na}_2[\text{Ni}_6(\text{CO})_{12}]$ ¹⁶⁰ (Scheme 138, Figure 9). The diphosphene ligands interact most closely with Ni(3) and Ni(5) as exemplified 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. ³¹P NMR Spectroscopic Data of Diphosphene Complexes

With a few exceptions the η^1 -complexation of a diphosphene $\text{R}^1\text{P}^1=\text{P}^2\text{R}^2$ to give $\text{R}^1\text{P}^1(\text{ML}_n)=\text{P}^2\text{R}^2$ is accompanied by the shielding of both nuclei P^1 and P^2 in the ³¹P 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., $(\text{Me}_3\text{Si})_2\text{CHP}_A[\text{M}(\text{CO})_5]=\text{P}_B\text{CH}(\text{SiMe}_3)_2$ [$\Delta\delta \text{ P}_A = -72.7$ (M = Cr), -84.0 (M = Mo), -128.9 (M = W); $\Delta\delta \text{ P}_B = -41.2$ (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 $\text{H}_2\text{P}_2\text{Cr}(\text{CO})_5$ 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., $(\text{Me}_3\text{Si})_2\text{CHP}[\text{M}(\text{CO})_5]=\text{P}[\text{M}(\text{CO})_5]\text{CH}(\text{SiMe}_3)_2$ ($\Delta\delta = -91.1$ ppm (M = Cr), -174.8 ppm (M = W))].

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

$$\begin{array}{c} \text{R}^1-\text{P}=\text{P}-\text{R}^2 \\ \downarrow \\ \text{ML}_n \end{array}$$

compd	R ¹	R ²	ML _n	δ ^{31}P	$^1J_{\text{PP}}$, Hz	solvent	ref(s)
169a	Mes*	Mes*	Ni(CO) ₃	449.0; 422.0	540.3	Et ₂ O	120
169b	Mes*	Mes*	Fe(CO) ₄	423.6; 396.4	578.0	CH ₂ Cl 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 ₂ Cl ₂	120
172a	Cp*	Mes*	Ni(CO) ₃	443.3; 428.2	551	C ₆ D 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 ₆ D ₆	98a
E-172d	Cp*	Mes*	W(CO) ₅	465.1; 405.3	546	C ₆ D 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 ₆ H ₁₄	98a
Z-172c	Cp*	Mes*	Mo(CO) ₅	396; 391	583	n-C ₆ H ₁₄	98a
Z-172d	Cp*	Mes*	W(CO) ₅	394; 362	581	n-C ₆ H 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) ₂ C ₆ H ₃	2,4,6-(CF ₃) ₃ C ₆ H ₂	Cr(CO) ₅	438.7; 432.6	489	THF	122
175b	2,4,6-(CF ₃) ₃ C ₆ H ₂	2,4,6-(CF ₃) ₃ C ₆ H ₂	Cr(CO) ₅	430.2; 427.6	501	THF	122
175c	2,4,6-(CF ₃) ₃ C ₆ H ₂	2,4,6-(CF ₃) ₃ C ₆ H ₂	Mo(CO) ₅	412.7; 407.7	510	CDCl ₃	122b
175d	2,4,6-(CF ₃) ₃ C ₆ H ₂	2,4,6-(CF ₃) ₃ C ₆ H ₂	W(CO) ₅	386.5; 359.9	478	THF	122b
175e	2,4,6-(CF ₃) ₃ C ₆ H ₂	2,4,6-(CF ₃) ₃ C ₆ H ₂	Pt(PET ₃)Cl ₂	346.6; 337.2	534	CH ₂ Cl ₂	122b
176a	Mes*	NHtBu	Ni(CO) ₃	341; 164	561	C ₆ D ₆	39
176b	Mes*	NHMes*	Ni(CO) ₃	416.5; 259.6	501.3	C ₆ D ₆	50c
177a	Mes*	Mes*	Ag ⁺	435; 378	549	THF	123
177c	Mes*	Mes*	AuPEt ₃ ⁺	403; 358	555	THF	123
178	(Me ₃ Si) ₂ N	(Me ₃ Si) ₂ N	Cr(CO) ₅	560.2; 540.4	631	C ₆ D ₆	124c
181a	(Me ₃ Si) ₂ CH	(Me ₃ Si) ₂ CH	Cr(CO) ₅	477.3; 446.2	510	C ₆ D ₆	124b,c
				475.8, 444.3	516	CDCl ₃	125a
181b	(Me ₃ Si) ₂ CH	(Me ₃ Si) ₂ CH	Mo(CO) ₅	465.4; 433.0	515	CDCl ₃	125a
181c	(Me ₃ Si) ₂ CH	(Me ₃ Si) ₂ CH	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) ($\delta = 504.0$) are shifted by $\Delta\delta = -441.5$ ppm to $\delta = 62.5$ in the π -complex [η^2 -Cp*P=PcP*]Pt(PPh₃)₂ (188a).

In [η^2 -Cp*P=PMes*]Pt(PPh₃)₂ (188b) similar coordination shifts ($\Delta\delta = -438.3$ and -455.6 ppm) were observed. Here doublets of doublets at $\delta = 52.3$ ppm ($^1J_{\text{PP}} = 433$ Hz and $^3J_{\text{PPtP}} = 36$ Hz) and at $\delta = 28.9$ ppm ($^1J_{\text{PP}} = 433$ Hz and $^3J_{\text{PPtP}} = 46$ Hz) were assigned to the diphosphene. The coupling constant $^1J_{\text{PP}}$ 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 PPh₃ ligands show up as doublets of doublets at $\delta = 25.5$ ($^3J_{\text{PPtP}} = 36$ Hz) and $\delta = 21.9$ ($^3J_{\text{PPtP}} = 46$ Hz).^{98a} Here the coupling constants $^1J_{\text{PtP}}$ 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, $^3J_{\text{PPtP}}$, 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

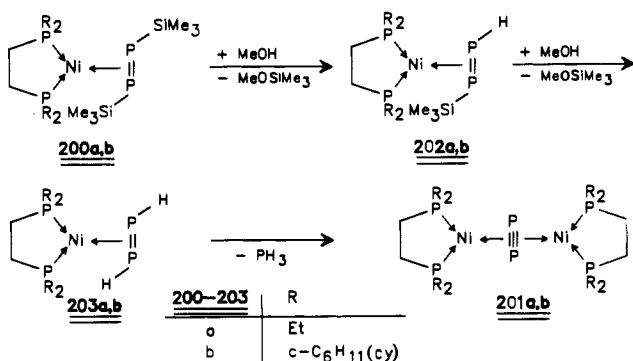
Methanolysis of the silylated η^2 -diphosphene ligand in nickel complexes 200 furnished dinuclear complexes 201 with bridging $\mu_2(\eta^2:\eta^2)\text{P}_2$ units^{136c} (Scheme 139).

The steric bulk of the chelating Cy₂PCH₂CH₂PCy₂ provided enough kinetic stabilization to the transient compounds 202b and 203b to allow their detection by ^{31}P NMR. The methanolysis of (Et₂PCH₂CH₂PET₂)-Ni(η^2 -Me₃SiP=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 PPh₃ ligands in complex 192a by a chelating diphosphene is also feasible^{129b} (Scheme 141).

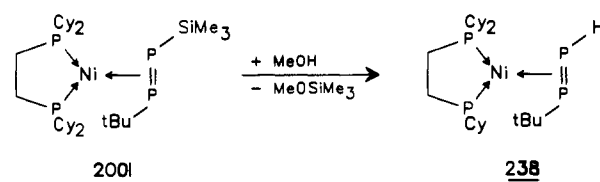
Table 5. ^{31}P -NMR-Data of η^2 -Diphosphene Complexes

compd	R ¹	R ²	ML _n	$\delta^{31}\text{P}$	$^1J_{\text{PP}}$, Hz	solvent	ref(s)
188a	Cp*	Cp*	Pt(PPh ₃) ₂	62.5		C ₆ D ₆	98a
188b	Cp*	Mes*	Pt(PPh ₃) ₂	52.8; 29.0	435	C ₆ D ₆	98a
189	Cp*	Mes*	Ni(TMEDA)	55.9; 51.0	440.8	THF- <i>d</i> ₈	91b
190	tBuNH	Mes*	Ni(PnBu ₃) ₂	85.5; -55.1	427	toluene- <i>d</i> ₈	39
191	2,4,6-(CF ₃) ₃ C ₆ H ₂	N=S(O)Me ₂	Pt(PPh ₃) ₂	130.2; 29.5		C ₆ H ₅ Me/C ₆ D ₆	31
192a	C ₆ F ₅	C ₆ F ₅	Pd(PPh ₃) ₂	32.0		C ₆ H ₆	129b
192b	C ₆ F ₅	C ₆ F ₅	Pt(PPh ₃) ₂	-22.0		C ₆ H ₆	129b
192c	C ₆ F ₅	C ₆ F ₅	Pd(diphos)	1.7		C ₆ H ₆	129b
193a	CF ₃	CF ₃	Pd(PPh ₃) ₂	22.7		<i>d</i> ₈ -toluene	128b
193b	CF ₃	CF ₃	Pt(PEt ₃) ₂	-28.0		<i>d</i> ₈ -toluene	128b
193d	CF ₃	CF ₃	Pt(PPh ₃) ₂	-6.2		C ₆ D ₆	128b
193e	CF ₃	CF ₃	Pd(diphos)	19.57		C ₆ H ₅ Me	128b
193f	CF ₃	CF ₃	Ni(diphos)	19.42		C ₆ H ₅ Me	128b
194	H	H	MoCp ₂	203		(CD ₃) ₂ SO	130
195a	Ph	Ph	Pd(diphos)	34.3		C ₆ H ₆	129b
195b	Ph	Ph	Pt(PPh ₃) ₂	18.1		C ₆ H ₆	129b
195c	Ph	Ph	Pt(diphos)	-23.5		C ₆ H ₆	129b
195d	Ph	Ph	Pt(PMe ₂ Ph) ₂	4.5		C ₆ D ₆	129b
196	tBu	tBu	Ni(P-tBu) ₄	45.03	275	C ₆ D ₆	131
197a	Ph	Ph	[1,3-(Me ₃ Si) ₂ C ₅ H ₃] ₂ Zr	228.91		C ₆ D ₆	132
197b	Ph	Ph	[1,3-(Me ₃ Si) ₂ C ₅ H ₃] ₂ Hf	193.22		C ₆ D ₆	132
197c	tBu	tBu	[1,3-(Me ₃ Si) ₂ C ₅ H ₃] ₂ Zr	270.56		C ₆ D ₆	132
198	Ph	Ph	Cp ₂ Ta(H)	-146; -164	327	C ₆ D ₆	134
199a	SiMe ₃	SiMe ₃	Ni[P(nBu) ₃] ₂	-65		C ₆ D ₆	135b
199b	SiMe ₃	SiMe ₃	Ni(PEt ₃) ₂	-67		C ₆ D ₆	135b
199c	SiMe ₃	SiMe ₃	Ni(PMe ₃) ₂	-76		C ₆ D ₆	135b
199d	SiMe ₃	SiMe ₃	Ni[P(iBu) ₃] ₂	-57		C ₆ H ₅ Me	135b
199e	SiMe ₃	SiMe ₃	Ni(PPh ₃) ₂	-22		C ₆ H ₅ Me	135b
199f	tBu	tBu	Ni(PEt ₃) ₂	54		C ₆ D ₆	135b
199g	tBu	SiMe ₃	Ni(PEt ₃) ₂	76; -86	384	C ₆ H ₅ Me	135b
199h	Ph	Ph	Ni(PEt ₃) ₂	-5		C ₆ D ₆	135b
200a	SiMe ₃	SiMe ₃	Ni[Et ₂ P(CH ₂) ₂ PEt ₂]	-101		C ₆ D ₆	136b
200b	SiMe ₃	SiMe ₃	Ni[Cy ₂ P(CH ₂) ₂ PCy ₂]	-103		C ₆ D ₆	136b
200c	SiMe ₃	SiMe ₃	Ni[Ph ₂ P(CH ₂) ₂ PPh ₂]	-64		C ₆ H ₅ Me	136b
200d	Ph	Ph	Ni[Et ₂ P(CH ₂) ₂ PEt ₂]	-20		C ₆ D ₆	136b
200e	Ph	Ph	Ni[Cy ₂ P(CH ₂) ₂ PCy ₂]	-34		C ₆ D ₆	136b
200f	Ph	Ph	Ni[Ph ₂ P(CH ₂) ₂ PPh ₂]	-2		C ₆ D ₆	136b
200g	Me	Me	Ni[Cy ₂ P(CH ₂) ₂ PCy ₂]	-28		C ₆ D ₆	136b
200h	tBu	tBu	Ni[Et ₂ P(CH ₂) ₂ PEt ₂]	55		C ₆ D ₆	136b
200i	tBu	tBu	Ni[Cy ₂ P(CH ₂) ₂ PCy ₂]	42		C ₆ D ₆	136b
200j	tBu	tBu	Ni[Ph ₂ P(CH ₂) ₂ PPh ₂]	69		C ₆ D ₆	136b
200k	SiMe ₃	tBu	Ni[Et ₂ P(CH ₂) ₂ PEt ₂]	57; -107	382	C ₆ D ₆	136c
200l	SiMe ₃	tBu	Ni[Cy ₂ P(CH ₂) ₂ PCy ₂]	48; -110	369	C ₆ D ₆	136c
200m	SiMe ₃	tBu	Ni[Ph ₂ P(CH ₂) ₂ PPh ₂]	82; -78	392	C ₆ H ₅ Me	136c
202	SiMe ₃	H	Ni[Cy ₂ P(CH ₂) ₂ PCy ₂]	-117; -126	315	C ₆ D ₆	136c
203b	H	H	Ni[Cy ₂ P(CH ₂) ₂ PCy ₂]	-120		C ₆ H ₅ Me	136c
204	SiMe ₃	SiMe ₃	Pt(PEt ₃) ₂	-105		C ₆ D ₆	137
205	tBu	tBu	Pt(PEt ₃) ₂	29		C ₆ D ₆	137
206	tBu	SiMe ₃	Pt(PEt ₃) ₂	46; -119	351	C ₆ H ₅ Me	137
207a	SiMe ₃	SiMe ₃	Pt(PPh ₃) ₂	-57		C ₆ H ₅ Me	137
207b	tBu	tBu	Pt(PPh ₃) ₂	54		C ₆ H ₅ Me	137
238	tBu	H	Ni[Cy ₂ P(CH ₂) ₂ PCy ₂]	41; -120	363	C ₆ D ₆	136c

Scheme 139

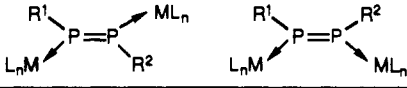


Scheme 140

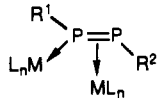


2. Complexation and Decomplexation

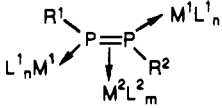
The addition of further complex fragments to the η^2 -ligated diphosphene in (diphos)Pd(η^2 -PhP=PPh) (194a) constitutes a pathway to complexes of higher nuclearity (Scheme 133). The transfer of the PhP=PPh

Table 6. ^{31}P NMR Data of $\mu\text{-}(\eta^1:\eta^1)$ -Diphosphene Complexes


compd	R ¹	R ²	ML _n	δ ^{31}P	$^1J_{\text{PP}}$, Hz	solvent	ref(s)
E-185a	(Me ₃ Si) ₂ CH	(Me ₃ Si) ₂ CH	Cr(CO) ₅	425.9		CD ₂ Cl ₂	125a
E-185b	(Me ₃ Si) ₂ CH	(Me ₃ Si) ₂ CH	W(CO) ₅	342.2		CD ₂ Cl ₂	125a
E-209a	Mes	Mes	Cr(CO) ₅	419.9		C ₆ D ₆	124c
Z-209a	Mes	Mes	Cr(CO) ₅	396.7		C ₆ D ₆	124c
Z-209b	Mes	Mes	Mo(CO) ₅	367.7		CD ₂ Cl ₂	125a
Z-209c	Mes	Mes	W(CO) ₅	313.6		CD ₂ Cl ₂	125a
E-210	Me ₃ SiCH ₂	Me ₃ SiCH ₂	Cr(CO) ₅	189		C ₆ D ₆	124c
E-212a	Ment	Ment	Cr(CO) ₅	447.5		n-C ₅ H ₁₂	140
E-212b	Ment	Ment	W(CO) ₅	361.5		n-C ₅ H ₁₂	140
E-215	Ph	Ph	Cr(CO) ₅	369			125a,142
E-216	Mes	Mes	Fe(CO) ₄	335.5		C ₆ H ₆	144b
E-217	(Me ₃ Si) ₂ CH	(Me ₃ Si) ₂ CH	Fe(CO) ₄	384.6		C ₆ H ₆	144b
E-218	(Me ₃ Si) ₂ N	(Me ₃ Si) ₂ N	Fe(CO) ₄	403.9		C ₆ H ₆	144b
E-219	Mes	Mes	(CO) ₃ CpV	426		C ₆ D ₆ /THF	146
E-220a	Mes*	(Me ₃ Si) ₂ CH	Ni(CO) ₃	367.2; 389.1	418.2		50c
E-220b	Mes*	(Me ₃ Si)(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 $\mu_2\text{-}(\eta^1:\eta^2)$ -Diphosphene Complexes


compd	R ¹	R ²	ML _n	δ ^{31}P	$^1J_{\text{PP}}$, Hz	solvent	ref(s)
221	Ph	Ph	Fe(CO) ₄	52.1; -34.5	415	CD ₂ Cl ₂	151
222	Me	Me	Fe(CO) ₄	8.22; -52.38	384	CD ₂ Cl ₂	152
224a	Mes*O	Mes*O	Fe(CO) ₄	233.8; 193.4	532	C ₆ D ₆	124b, 144b
226a	iPr ₂ N	iPr ₂ N	Fe(CO) ₄	97.3; 61.7	477	Et ₂ O	145
226b	Cy ₂ N	Cy ₂ N	Fe(CO) ₄	99.8; 63.2	488	Et ₂ O	145

Table 8. ^{31}P NMR Data of $\mu_3\text{-}(\eta^1:\eta^1:\eta^2)$ -Diphosphene Complexes


compd	R ¹	R ²	M ¹ L ¹ _n	M ² L ² _m	δ ^{31}P	solvent	ref(s)
214	Ph	Ph	Cr(CO) ₅	Cr(CO) ₅	97	CH ₂ Cl ₂	142a,153
227a	Ph	Ph	W(CO) ₅	W(CO) ₅	-16.6	CH ₂ Cl ₂	153
227b	4-MeO-C ₆ H ₄	4-MeO-C ₆ H ₄	Cr(CO) ₅	Cr(CO) ₅	108.5	CH ₂ Cl ₂	153
227c	Me	Me	Cr(CO) ₅	Cr(CO) ₅	78.1	CH ₂ Cl ₂	153
227d	Me	Me	Mo(CO) ₅	Mo(CO) ₅	27.2	CH ₂ Cl ₂	153
227e	Et	Et	Cr(CO) ₅	Cr(CO) ₅	103.7	CH ₂ Cl ₂	153
227f	nBu	nBu	Cr(CO) ₅	Cr(CO) ₅	99.9	CH ₂ Cl ₂	153
231a	Ph	Ph	W(CO) ₅	Pd(diphos)	17.0	C ₆ H 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 (Ph₃P)₂Pd(η^2 -CF₃P=PCF₃) (193a) and its Pt homolog 193b via (Ph₃P)₂Pt(η^2 -C₂H₄).^{128b}

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

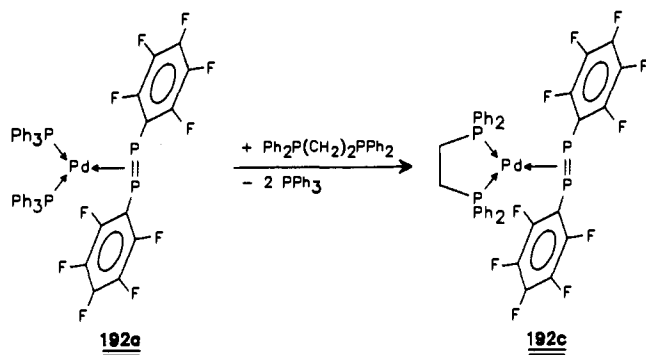
3. Thermolysis of the Coordinated Diphosphene

Thermolysis of the $\eta^1:\eta^2$ -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

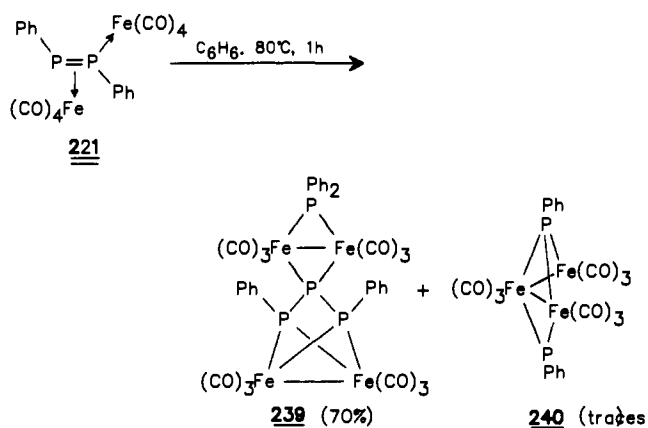
analysis of 239 revealed the main product of the thermolysis as a tetranuclear complex with a μ_4 -bridging η^3 -PhPPPh ligand. Another fragment of the former PhP=PPh ligand constitutes a μ_2 -PPh₂ bridge.¹⁶¹

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 $\mu_4\text{-}(\eta^2:\eta^1)$ -diphosphene ligand which unsymmetrically caps a square of iron atoms; μ_4 -PPh and μ_2 -PPh₂ bridges are also present in the molecule¹⁶¹ (Scheme 143). The ^{31}P NMR resonances of the phosphorus nuclei of the diphosphene fragment were assigned to signals at $\delta = 117.3$ (ddd, $^1J_{\text{PP}} = 357$ Hz) and $\delta = 169.5$ ppm (ddd, $^1J_{\text{PP}} = 357$ Hz).

Scheme 141



Scheme 142

4. 1,2-Additions to the $\text{P}=\text{P}$ 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 $\text{P}-\text{P}$ bond in 242d was not affected by additional HCl . This is remarkable with respect to the smooth stepwise cleavage of the $\text{P}=\text{P}$ bond in $(\text{Me}_3\text{Si})_3\text{CP}=\text{PC}(\text{SiMe}_3)_3$ (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

Scheme 143

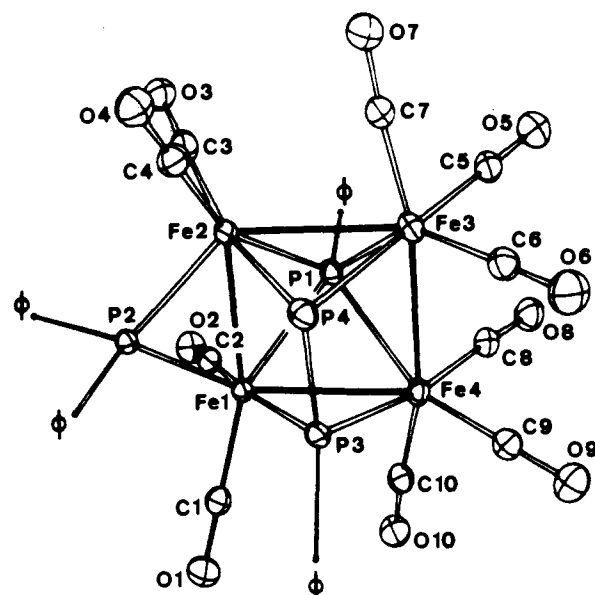
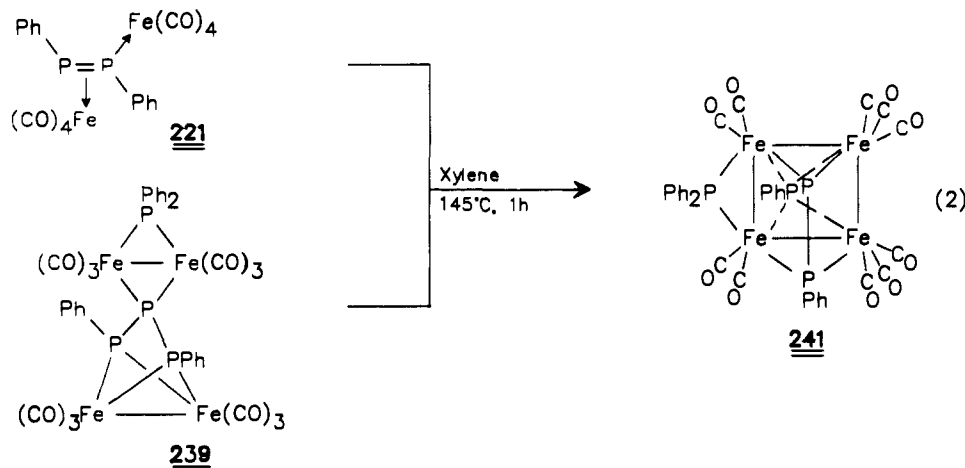


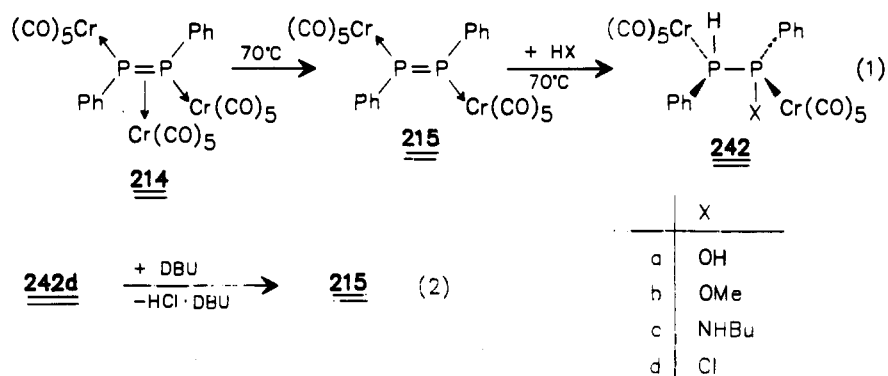
Figure 10. Structure of 241. Selected bond lengths (Å) and bond angles (deg): $\text{Fe}(1)-\text{P}(3)$ 2.205 (2), $\text{Fe}(4)-\text{P}(3)$ 2.247 (2), $\text{Fe}(2)-\text{P}(4)$ 2.297 (2), $\text{Fe}(3)-\text{P}(4)$ 2.342 (2), $\text{P}(3)-\text{P}(4)$ 2.126 (2); $\text{Fe}(1)-\text{P}(3)-\text{Fe}(4)$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

products 243^{142b} (Scheme 145). The reverse reaction was effected by treatment of 243 with zinc. The η^1 : η^2 -complexes 214 and 227 also exhibited the reactivity of $\text{P}-\text{P}$ double bonds, even without the prior release of the η^2 -ligated $\text{Cr}(\text{CO})_5$ 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 produced¹⁵³ (Scheme 146).

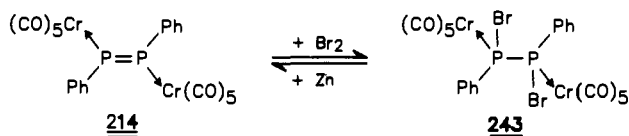
A mixture of the meso and racemic forms of complex 246 was synthesized by the LiAlH_4 reduction of diphosphane complex 212a¹⁴⁰ (Scheme 147).

A hydrometalation process was responsible for the conversion of the μ -(η^1 : η^2)-diphosphane 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 $\text{Fe}(\text{CO})_4$ moiety¹⁵¹ (Scheme 148).

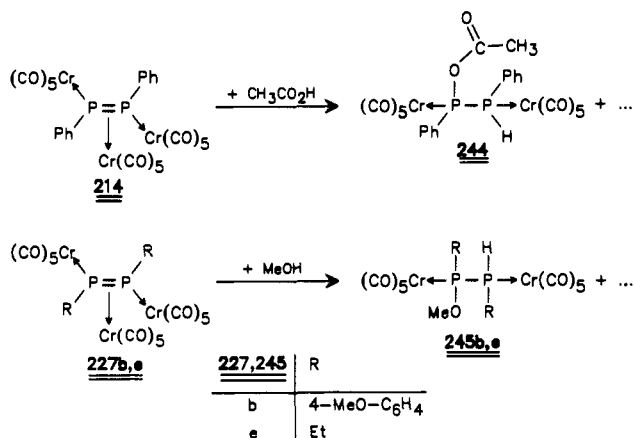
Scheme 144



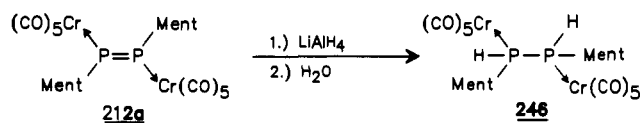
Scheme 145



Scheme 146



Scheme 147

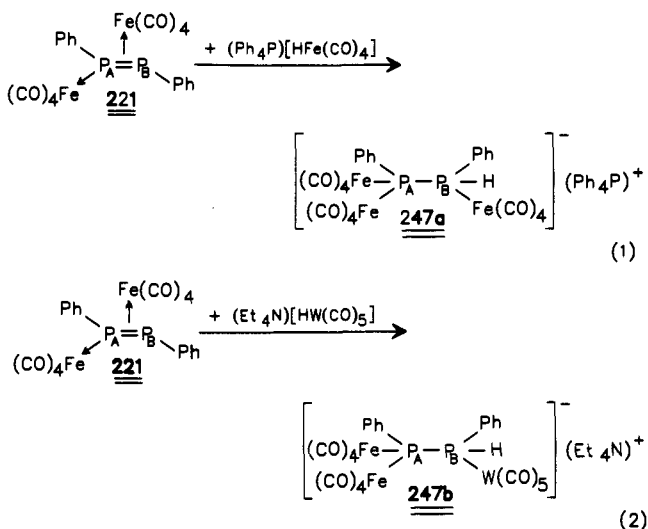


5. Cycloadditions to Diphosphene Complexes

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*-MeOC₆H₄) 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 N₂ elimination, however, could not be excluded.^{126a}

[2 + 4] cycloaddition reactions of the diphosphene complexes 215^{142b} or alternatively 227f¹⁵³ with cyclopentadiene or 2,3-dimethylbutadiene furnished complexes of cyclic diphosphanes (Scheme 151). According

Scheme 148



to ³¹P NMR analysis these [2 + 4] cycloadditions proceeded stereoselectively and only one diastereoisomer was observed.

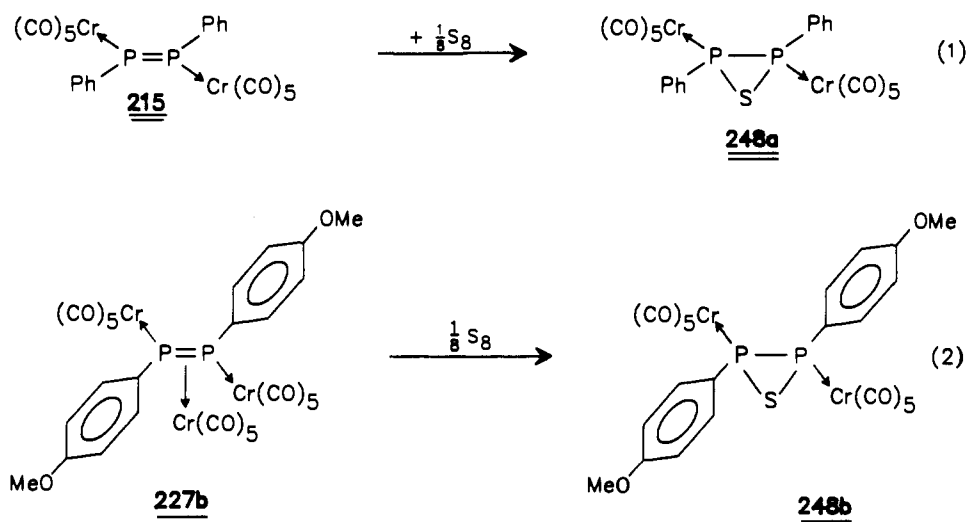
6. Insertion Reactions into the P=P Double Bond of Diphosphene Complexes

During the attempted purification by chromatography on a silica column the (η¹:η²)-diphosphene iron complexes 226a-c experienced hydrolysis of the PP bond, and the dinuclear diphosphine oxide complexes 253a-e were isolated¹⁴⁵ (Scheme 152).

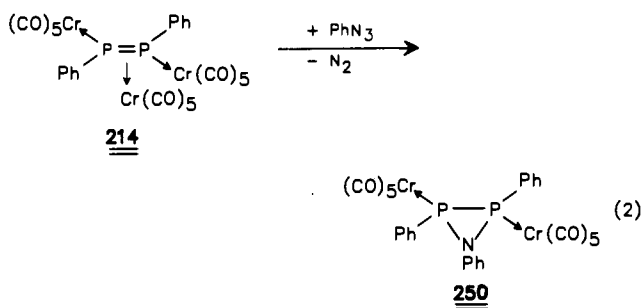
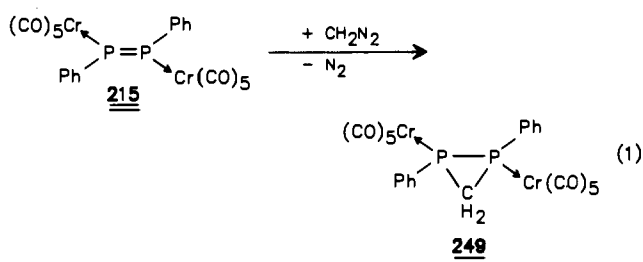
Vahrenkamp described insertion and cleavage reactions of the P-P bond in the diferradiphosphatetrahedrane 234^{157b} (Scheme 153). CO insertion into the P=P multiple bond of 234 occurred when a benzene solution of the tetrahedrane was exposed to a 50-bar CO pressure at 80 °C. The most remarkable structural 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 H₂ (50 bar, 80 °C) led to an isomeric mixture of the butterfly molecule 233 containing μ₂-(PHTBu) ligands. The same result was obtained by superhydride reduction of 234 and subsequent methanolysis of the reaction mixture^{157b} (Scheme 154).

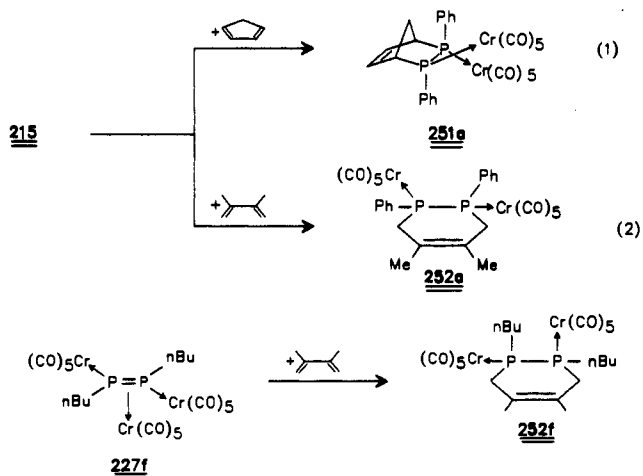
Scheme 149



Scheme 150

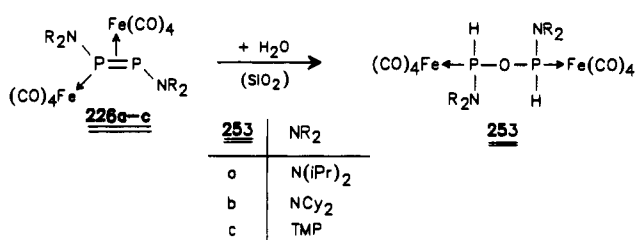


Scheme 151

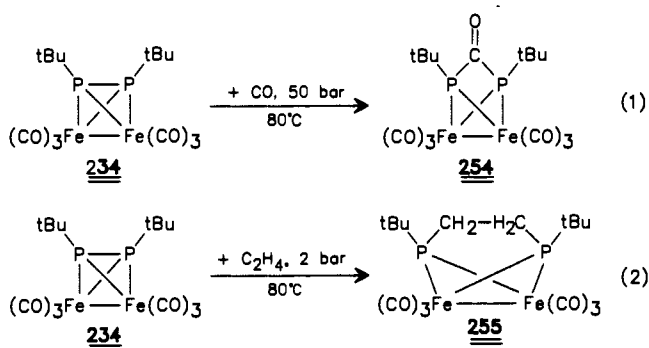


The P-P bond of 234 was also cleaved when the cluster was allowed to react with anhydrous hydrogen chloride in benzene (Scheme 155). The tetrahedrane was not affected by S₈ or diazomethane in boiling benzene, whereas decomposition took place with Cl₂, SOCl₂, and PCl₅.

Scheme 152



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):



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

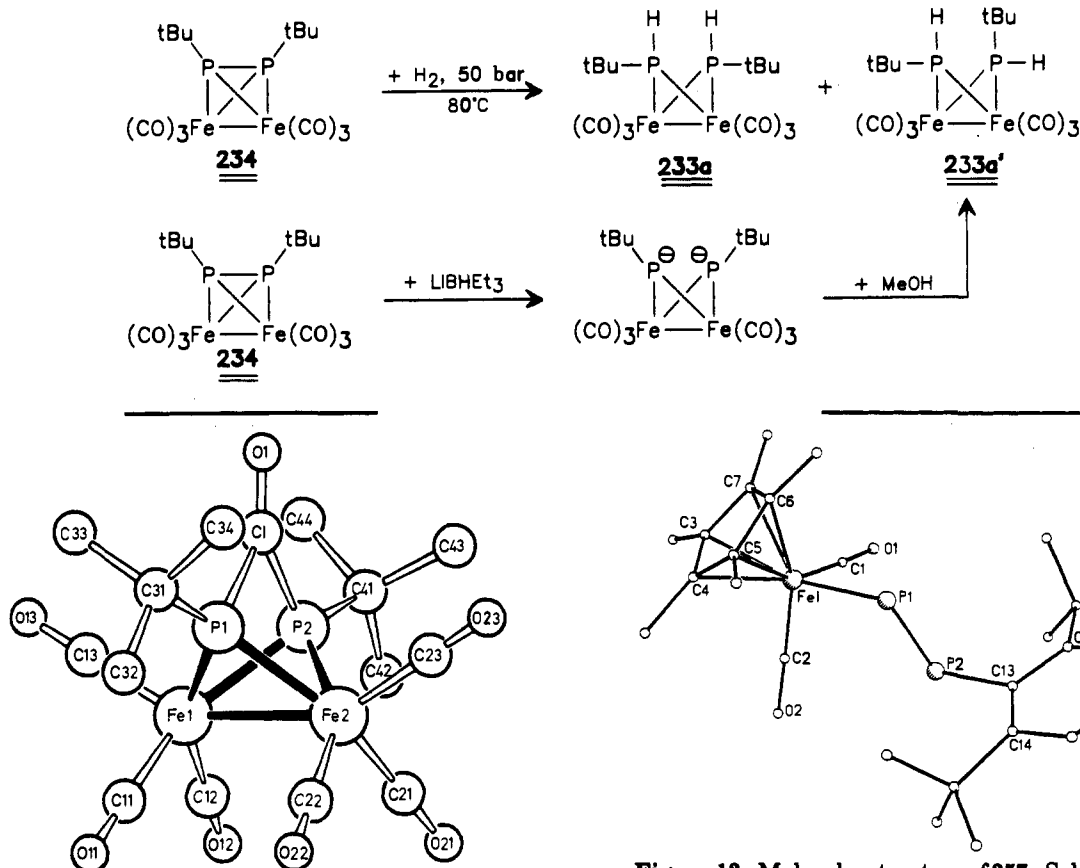
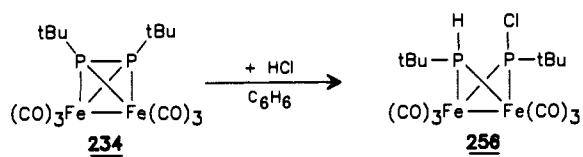


Figure 11. Molecular structure of **254**. Selected bond lengths (Å) and bond angles (deg): Fe(1)–Fe(2) 2.623 (2), Fe(1)–P(1) 2.228 (4), Fe(1)–P(2) 2.228 (4), Fe(2)–P(1) 2.228 (4), Fe(2)–P(2) 2.236 (4), P(1)–P(2) 2.525 (4), P(1)–C(1) 1.875 (9), P(2)–C(1) 1.878 (9), C(1)–O(1) 1.172 (9); Fe–P–Fe 72.1/72.0 (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*)-(η⁵-C₅Me₅)(CO)₂-FeP=PMe^{*} (**257**) (Figure 12) was synthesized by the reaction of a disilylphosphidoiron complex with Me^{*}PCl₂ in THF (Scheme 156). The orange crystalline solid was obtained in yields up to 70%.¹⁶² In the ³¹P 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 Me^{*}P=PMe^{*} (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)°].

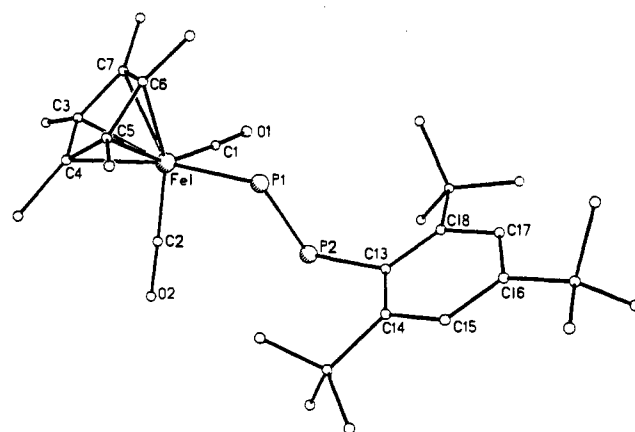
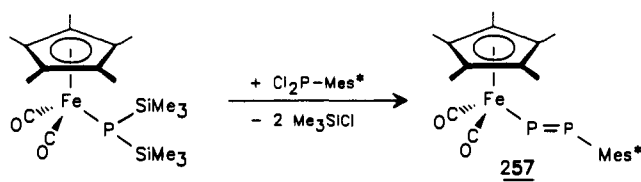


Figure 12. Molecular structure of **257**. Selected bond lengths (Å) and bond angles (deg): Fe(1)–P(1) 2.260 (1), P(1)–P(2) 2.027 (3), P(2)–C(13) 1.873 (3); Fe(1)–P(1)–P(2) 109.8 (1), P(1)–P(2)–C(13) 102.4 (1). Reprinted from ref 162b. Copyright 1987 American Chemical Society.

Scheme 156

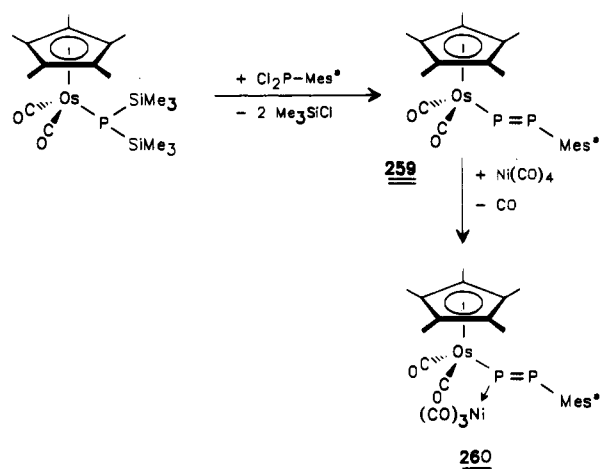


In order to explore the scope and the limits of the synthetic principle performed here, the homologous ruthenium and osmium disilylphosphido complexes were allowed to react with Me^{*}PCl₂ under comparable conditions. Whereas the preparation of the orange-red crystalline (C₅Me₅)(CO)₂RuP=PMe^{*} **258** proceeded without difficulties, the isolation of the analogous osmium complex **259** failed. Its formation was inferred from two doublets in the ³¹P 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)₄ adduct **260** upon treatment with an excess of Ni(CO)₄.^{162b} (Scheme 157). The decreased stability of the diphosphényl complex **259** with the 5d metal osmium, as opposed to the 3d and 4d congeners, was also met in the chemistry of manganese¹⁶³ and rhenium¹⁶⁴ (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 diphosphényl

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

compd	$[\text{M}^1]$	R	M^2L_n	$\delta^{31}\text{P}_\text{M}$	$\delta^{31}\text{P}_\text{R}$	$^1J_{\text{PP}}$, Hz	solvent	ref(s)
257	$\text{Cp}^*(\text{CO})_2\text{Fe}$	Mes*		715.2	553.5	594.2	C_6D_6	162a,b
258	$\text{Cp}^*(\text{CO})_2\text{Ru}$	Mes*		676.5	551.6	597.1	C_6D_6	162a,b
259	$\text{Cp}^*(\text{CO})_2\text{Os}$	Mes*		632.0	543.2	583.9	THF	162b
261	$\text{Cp}^*(\text{CO})(\text{NO})\text{Mn}$	Mes*		728.5	535.7	597.4	C_6D_6	163
262	$\text{Cp}^*(\text{CO})(\text{NO})\text{Re}$	Mes*		637.2	532.1	583.1	THF	164
268a	$\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}$	2,6-(CF_3) $_2\text{C}_6\text{H}_3$		861.8	487.0	615	THF	122a
268b	$\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}$	2,4,6-(CF_3) $_3\text{C}_6\text{H}_2$		877.9	475.2	599	THF	122a
269a	$\text{Cp}^*(\text{CO})_2\text{Fe}$	2,6-(CF_3) $_2\text{C}_6\text{H}_3$		797.1	488.9	594	THF	122a
269b	$\text{Cp}^*(\text{CO})_2\text{Fe}$	2,4,6-(CF_3) $_3\text{C}_6\text{H}_2$		812.3	475.5	592	THF	122a
272a	$(\text{C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Fe}$	Mes*		719.7	553.4	596	THF	166a
272b	$(\text{C}_5\text{Me}_4\text{nBu})(\text{CO})_2\text{Fe}$	Mes*		719.6	553.7	597	THF	166a
273	$(1,3\text{-tBu}_2\text{C}_5\text{H}_3)(\text{CO})_2\text{Fe}$	Mes*		678.1	559.1	598	THF	166a
274	$\text{Cp}(\text{CO})_2\text{Fe}$	Mes*		671	563	600	THF	91b,d
275	$\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}$	Mes*		765.4	562.0	621.2	C_6D_6	162b
276	$\text{Cp}^*(\text{CO})_3\text{Cr}$	Mes*		653.0	559.6	610.1	CDCl_3	98a, 167
277a	$\text{Cp}^*(\text{PPh}_3)\text{Ni}$	Mes*		754	543	623	toluene/ C_6H_6	98a
277b	$\text{Cp}^*[\text{P}(\text{nBu})_3]\text{Ni}$	Mes*		784	538	632	toluene/ C_6H_6	98a
278	$\text{Cp}^*(\text{CO})_2\text{Fe}$	Cp^*		690	559	625	THF	91b,d
285	$\text{Cp}^*(\text{CO})_2\text{Fe}$	$\text{C}(\text{SiMe}_3)_3$		788.2	602.3	654.8	C_6D_6	169
270a	$\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}$	2,6-(CF_3) $_2\text{C}_6\text{H}_3$	$\text{Cr}(\text{CO})_5$	665.7	473.6	605	THF	122a
270b	$\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}$	2,4,6-(CF_3) $_3\text{C}_6\text{H}_2$	$\text{Cr}(\text{CO})_5$	676.0	461.7	624	CD_2Cl_2	122a
271a	$\text{Cp}^*(\text{CO})_2\text{Fe}$	2,6-(CF_3) $_2\text{C}_6\text{H}_3$	$\text{Cr}(\text{CO})_5$	650.9	491.5	585	THF	122a
271b	$\text{Cp}^*(\text{CO})_2\text{Fe}$	2,4,6-(CF_3) $_3\text{C}_6\text{H}_2$	$\text{Cr}(\text{CO})_5$	661.5	477.3	587	THF	122a
263	$\text{Cp}^*(\text{CO})(\text{NO})\text{Re}$	Mes*	$\text{Cr}(\text{CO})_5$	562.7	509.6	560.9	C_6D_6	164
289	$\text{Cp}^*(\text{CO})_2\text{Fe}$	Mes*	$\text{Cr}(\text{CO})_5$	599.6	572.0	593.4	C_6D_6	164
290	$\text{Cp}^*(\text{CO})_2\text{Fe}$	Mes*	$\text{Fe}(\text{CO})_4$	546.3	514.6	581.9	C_6D_6	171
291	$\text{Cp}^*(\text{CO})_2\text{Fe}$	Mes*	$\text{Ni}(\text{CO})_3$	591.7	509.9	576.6	C_6D_6	172
292	$(\text{C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Fe}$	Mes*	$\text{Cr}(\text{CO})_5$	597	573	595	THF	166b
293	$(\text{C}_5\text{Me}_4\text{nBu})(\text{CO})_2\text{Fe}$	Mes*	$\text{Cr}(\text{CO})_5$	597.5	572.8	594	THF	166b
294	$(1,3\text{-tBu}_2\text{C}_5\text{H}_3)(\text{CO})_2\text{Fe}$	Mes*	$\text{Cr}(\text{CO})_5$	574.8	565.7	589	THF	166b
295	$\text{Cp}^*(\text{CO})_2\text{Ru}$	Mes*	$\text{Fe}(\text{CO})_4$	503.9	495.9	571.6	C_6D_6	171
296	$\text{Cp}^*(\text{CO})_2\text{Ru}$	Mes*	$\text{Ni}(\text{CO})_3$	556.7	503.7	564.1	C_6D_6	172
297	$\text{Cp}^*(\text{CO})_2\text{Os}$	Mes*	$\text{Fe}(\text{CO})_4$	437.5	491.8	553.3	C_6D_6	171b
298	$\text{Cp}^*(\text{CO})_2\text{Os}$	Mes*	$\text{Ni}(\text{CO})_3$	500.1	495.6	545.8	C_6D_6	162b
299	$\text{Cp}^*(\text{CO})(\text{NO})\text{Mn}$	Mes*	$\text{Cr}(\text{CO})_5$	603.6	562.1	593.1	C_6D_6	164

Scheme 157



complex was hampered. The presence of two doublets at $\delta = 637.2$ 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 $\text{Cr}(\text{CO})_5$ adduct 263, which was isolated by column chromatography as a stable crystalline solid.¹⁶⁴

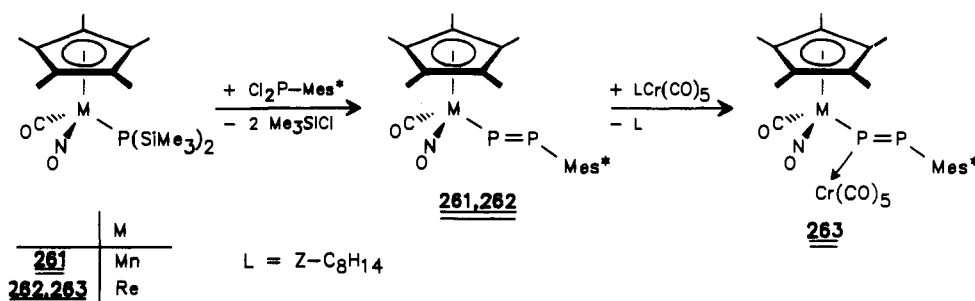
Attempts to extend the same synthetic approach to diphosphenyl complexes to the early transition metals zirconium and hafnium clearly showed the limitation

of this concept.⁴² The reaction of the $\text{Cp}_2\text{M}(\text{CH}_3)\text{P}(\text{SiMe}_3)_2$ 264 ($\text{M} = \text{Zr}, \text{Hf}$) with Mes^*PCl_2 resulted in the production of $\text{Cp}_2\text{M}(\text{CH}_3)\text{Cl}$ and thermolabile $\text{Mes}^*\text{P}=\text{PSiMe}_3$ (29a) instead of the expected metallodiphosphenes. Obviously complexes 264a,b functioned as disilylphosphido transfer reagents.⁴²

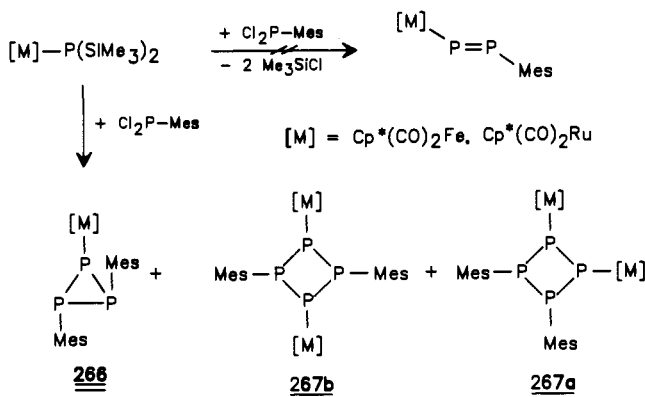
The synthesis of metallodiphosphenes is also governed by sterical restrictions as known from other diphosphenes. This became especially evident when the complexes $\text{Cp}^*(\text{CO})_2\text{MP}(\text{SiMe}_3)_2$ ($\text{M} = \text{Fe}, \text{Ru}$) were allowed to react with mesityldichlorophosphate. No diphosphenyl complexes were detected in the reaction solution. Instead a mixture of metal-functionalized cyclotriphosphanes and cyclo-tetraphosphanes (266 and 267) were obtained¹⁶⁵ (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)dichlorophosphate (2,4,6-(CF_3) $_3\text{C}_6\text{H}_2\text{PCl}_2$) and (hexafluoro-*o*-xylyl)dichlorophosphate [2,6-(CF_3) $_2\text{C}_6\text{H}_3\text{PCl}_2$] 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] $\text{Cr}(\text{CO})_5$ furnished the corresponding $\text{Cr}(\text{CO})_5$ adducts 270a,b and 271a,b.¹²²

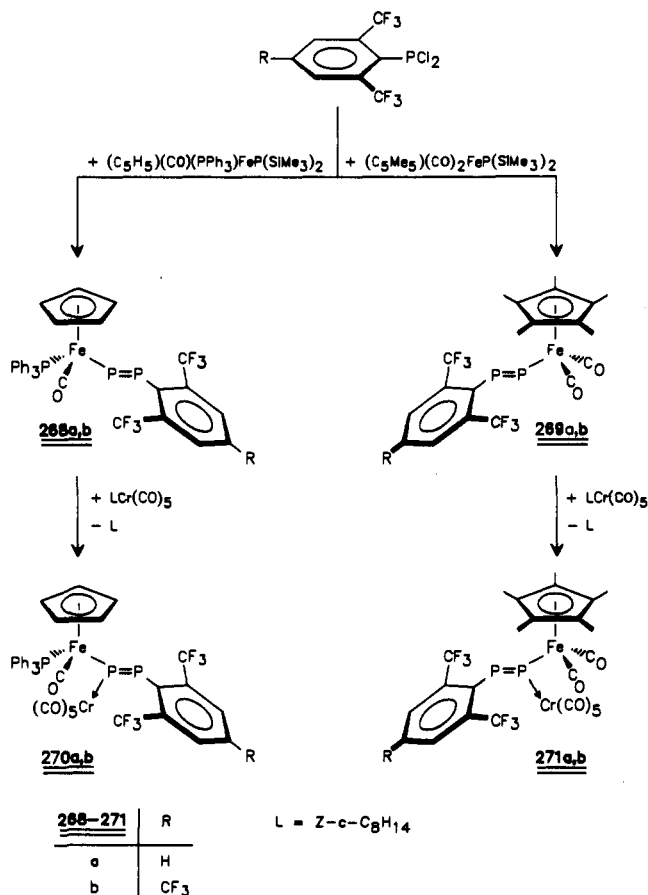
Scheme 158



Scheme 159



Scheme 160



The influence of the η^5 -ring at the metal center on the course of the diphosphene complex formation was also studied. With the bulky ligands η^5 -C₅Me₄Et, η^5 -C₅Me₄n-Bu, and 1,3-tBu₂C₅H₃ the preparation of stable diphosphene complexes was also feasible.^{166a}

With (C₅H₅)(CO)₂FeP(SiMe₃)₂, which contains the parent cyclopentadienyl ring the synthesis of a stable diphosphene 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 diphosphene complex 275 proceeds without difficulty^{162b} (Scheme 161).

A complementary access to diphosphene complexes involves the oxidative addition of the pentamethylcyclopentadienyl-derived diphosphene 16 to transition metal complexes containing labile ligands. Stirring a suspension of (CH₃CN)₃Cr(CO)₃ and 16 for 3 days in toluene gave the corresponding chromium diphosphene complex 276^{98a,167} (Scheme 162). An analogous molybdenum complex was detected by ³¹P NMR spectroscopy as a minor product in the reaction of (CH₃CN)₃Mo(CO)₃ and 16, but could not be isolated.

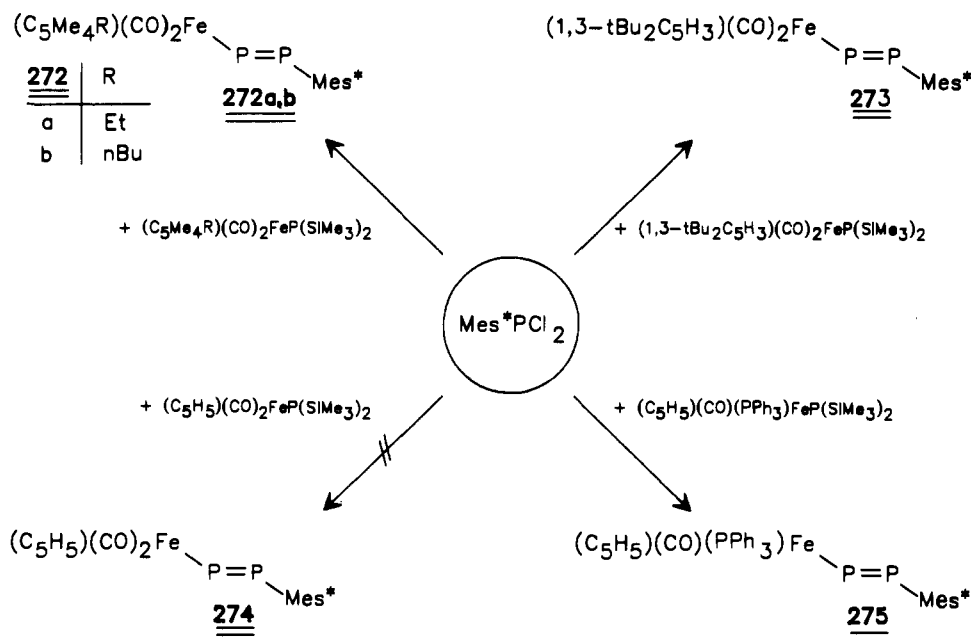
Unstable nickel diphosphene complexes 277a,b were formed when 16 was allowed to react with (ethylene)-bisphosphane nickel species.^{91b,98a} This was inferred from the spectroscopic data showing doublets at $\delta = 543$ and $\delta = 754$ (¹J_{PP} = 623 Hz) for the ³¹P nuclei of the P=P group in 277a. In the transformation leading to 277a a η^1 -complex such as [η^1 -Cp*P=PMe₃](Ph₃P)-Ni was invoked as intermediate, whereas the generation of 277b was believed to proceed via the π -complex [η^2 -Cp*P=PMe₃](nBu₃P)₂Ni.

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=PMe₃ (16) underwent reaction with NaFe(CO)₂Cp* to produce diphosphene complex 257 (Scheme 163). The analogous reaction with the less bulky Na[Fe(CO)₂Cp] afforded the thermolabile complex 274, which was characterized by doublets at $\delta = 671$ and 563 ppm (¹J_{PP} = 600 Hz) in the ³¹P NMR spectrum.^{91b,d}

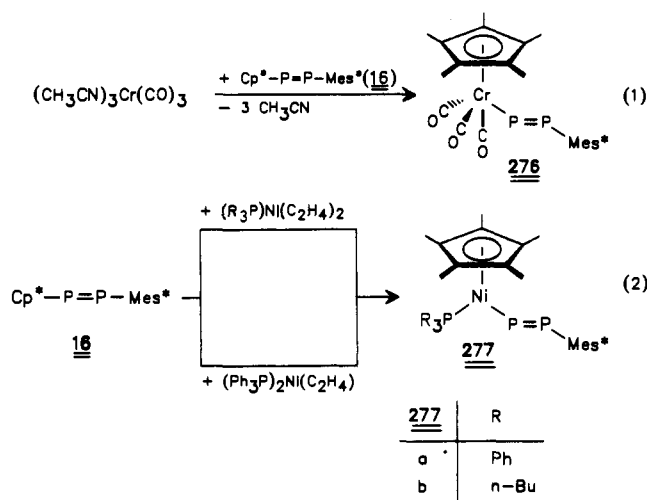
Attempts to synthesize pentamethylcyclopentadienyl-functionalized diphosphene complexes such as 278 led to the organometallic tetraphospha[1.1.0]-bicyclobutane 280^{91b,d} (Scheme 164). The formation of 280 involved the head-to-tail cyclodimerization of transient 278 and subsequent loss of two Cp* fragments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

The loss of pentamethylcyclopentadienyl rings from phosphorus atoms was impressively demonstrated by the conversion of 11 into the P₆ ligand of the triple-decker complex 281¹⁶⁸ (Scheme 165). The crucial step in the synthesis of the metallodiphosphene 285 is the 1,3-Me₃Si shift from phosphorus to carbon in the metal-functionalized 1,2-diphospha-2-propene 282. This mi-

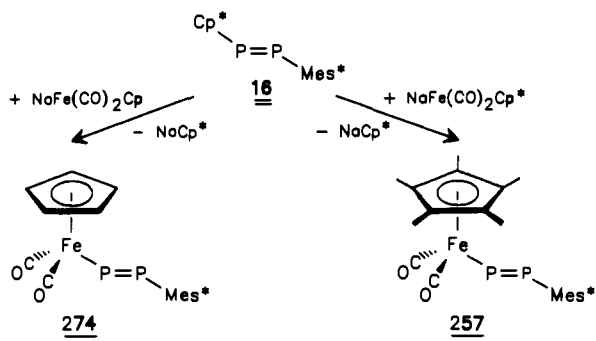
Scheme 161



Scheme 162

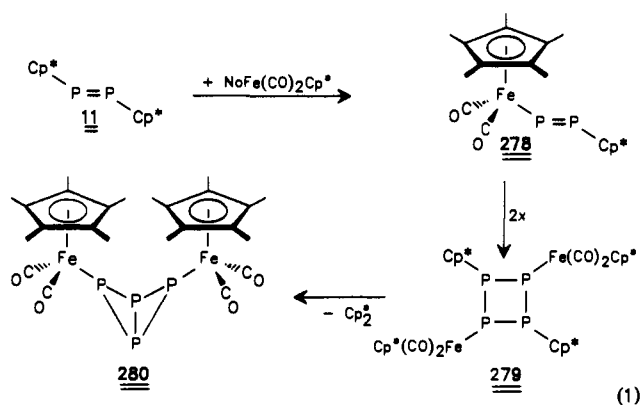


Scheme 163

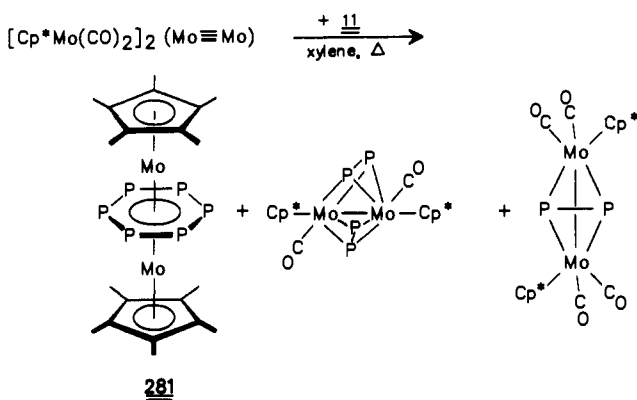


gration was induced by catalytical amounts of [(*Z*-cyclooctene)Cr(CO)₅]. The coordination compound 286, where the metallodiphosphene is functioning as an η³-ligand toward the Cr(CO)₄ moiety was observed as a byproduct. An alternative description of 286 as a 42 VE butterfly (arachno complex) makes use 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

Scheme 164



Scheme 165



congestion in the intermediate η¹-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-system¹⁶⁹ (Scheme 166).

The ³¹P 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

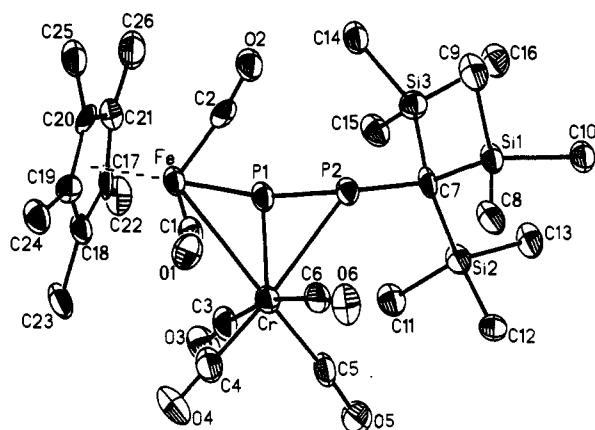
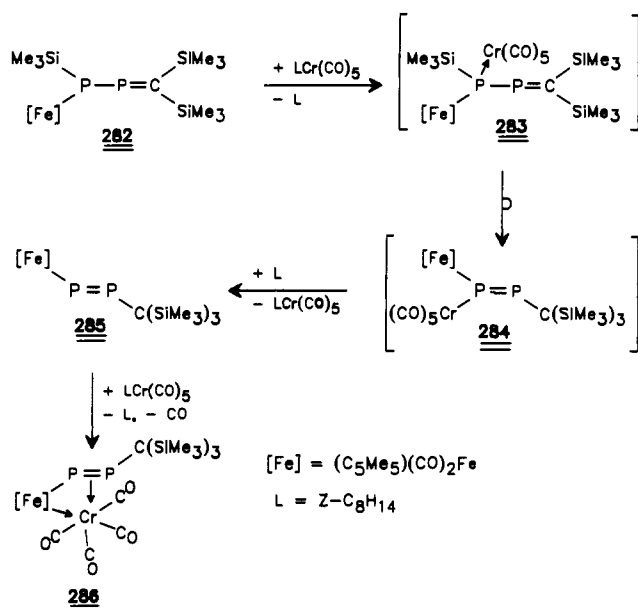


Figure 13. Molecular structure of **286**. Selected bond lengths (Å) and bond angles (deg): Cr-Fe 2.945 (3), Cr-P(1) 2.395 (4), Cr-P(2) 2.635 (4), Fe-P(1) 2.313 (3), P(1)-P(2) 2.090 (4); Fe-P(1)-P(2) 101.5 (1), P(1)-P(2)-C(7) 110.1 (3). Reprinted from ref 169. Copyright 1991 Chemical Society, London.

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

All attempts to synthesize diphosphenes with two organometallic groups as substituents at the $\text{P}=\text{P}$ unit failed. Upon reduction with elemental magnesium or when reacted with $\text{Cp}^*(\text{CO})_2\text{FeP}(\text{SiMe}_3)_2$ the dichlorophosphido complex $\text{Cp}^*(\text{CO})_2\text{FeP}(\text{SiMe}_3)_2$ was converted into a mixture of the permetalated cyclotriphosphane $[\eta^5\text{-C}_5\text{Me}_5](\text{CO})_2\text{FeP}]_3$ (**288**) and the bicyclotetraphosphane **280**.

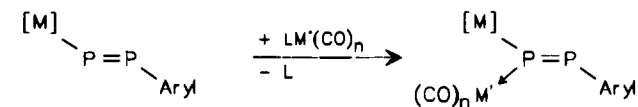
There was no spectroscopic evidence for the diphosphene $\text{Cp}^*(\text{CO})_2\text{Fe}-\text{P}=\text{P}-\text{Fe}(\text{CO})_2\text{Cp}^*$.¹⁷⁰

VIII. Reactivity of Metallodiphosphenes

A. Ligand Properties

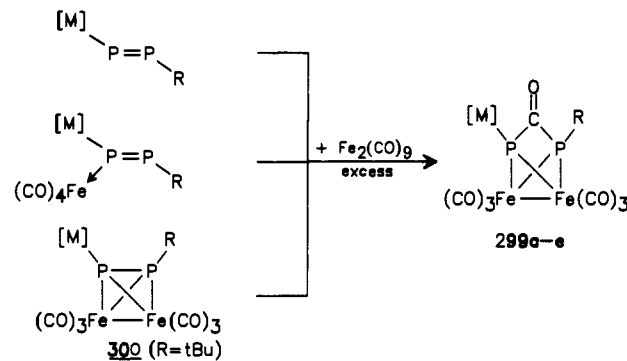
In almost all coordination compounds with metal carbonyls the metallodiphosphenes function as η^1 -ligands via the lone pair at the metalated phosphorus atom. Thus the 16-electron fragments $\text{Cr}(\text{CO})_5$, $\text{Fe}(\text{CO})_4$, and $\text{Ni}(\text{CO})_3$ can easily be attached to the

Scheme 167



compd	[M]	Aryl	M(CO) _n	L	ref(s)
289	$\text{Cp}^*(\text{CO})_2\text{Fe}$	Mes*	$\text{Cr}(\text{CO})_5$	(<i>Z</i>)- C_6H_{14}	164
290	$\text{Cp}^*(\text{CO})_2\text{Fe}$	Mes*	$\text{Fe}(\text{CO})_4$	$\text{Fe}(\text{CO})_5$	171
291	$\text{Cp}^*(\text{CO})_2\text{Fe}$	Mes*	$\text{Ni}(\text{CO})_3$	CO	172
292	$(\text{Me}_n\text{EtC}_n)(\text{CO})_2\text{Fe}$	Mes*	$\text{Cr}(\text{CO})_5$	(<i>Z</i>)- C_6H_{14}	166b
293	$(\text{Me}_n\text{BuC}_n)(\text{CO})_2\text{Fe}$	Mes*	$\text{Cr}(\text{CO})_5$	(<i>Z</i>)- C_6H_{14}	166b
294	$(1,3\text{-tBu}_2\text{C}_2\text{H}_3)(\text{CO})_2\text{Fe}$	Mes*	$\text{Cr}(\text{CO})_5$	(<i>Z</i>)- C_6H_{14}	186b
295	$\text{Cp}^*(\text{CO})_2\text{Ru}$	Mes*	$\text{Fe}(\text{CO})_4$	$\text{Fe}(\text{CO})_5$	171
296	$\text{Cp}^*(\text{CO})_2\text{Ru}$	Mes*	$\text{Ni}(\text{CO})_3$	CO	172
297	$\text{Cp}^*(\text{CO})_2\text{Os}$	Mes*	$\text{Fe}(\text{CO})_4$	$\text{Fe}(\text{CO})_5$	171b
298	$\text{Cp}^*(\text{CO})_2\text{Os}$	Mes*	$\text{Ni}(\text{CO})_3$	CO	162b
270a	$\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}$	2,6-(CF_3) ₂ C_6H_3	$\text{Cr}(\text{CO})_5$	(<i>Z</i>)- C_6H_{14}	122a
271a	$\text{Cp}^*(\text{CO})_2\text{Fe}$	2,6-(CF_3) ₂ C_6H_3	$\text{Cr}(\text{CO})_5$	(<i>Z</i>)- C_6H_{14}	122a
270b	$\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}$	2,4,6-(CF_3) ₃ C_6H_2	$\text{Cr}(\text{CO})_5$	(<i>Z</i>)- C_6H_{14}	122a
271b	$\text{Cp}^*(\text{CO})_2\text{Fe}$	2,4,6-(CF_3) ₃ C_6H_2	$\text{Cr}(\text{CO})_5$	(<i>Z</i>)- C_6H_{14}	122a
299	$\text{Cp}^*(\text{CO})(\text{NO})\text{Mn}$	Mes*	$\text{Cr}(\text{CO})_5$	(<i>Z</i>)- C_6H_{14}	164
263	$\text{Cp}^*(\text{CO})(\text{NO})\text{Re}$	Mes*	$\text{Cr}(\text{CO})_5$	(<i>Z</i>)- C_6H_{14}	164

Scheme 168



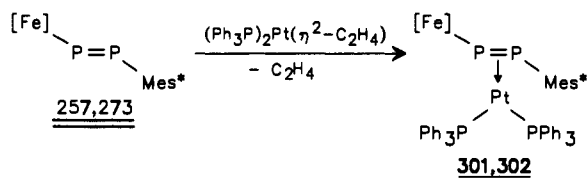
<u>299</u>	[M]	Aryl	Ref.
a	$\text{Cp}^*(\text{CO})_2\text{Fe}$	Mes*	171
b	$\text{Cp}^*(\text{CO})_2\text{Ru}$	Mes*	171
c	$\text{Cp}^*(\text{CO})_2\text{Os}$	Mes*	171b
d	$\text{Cp}^*(\text{CO})_2\text{Fe}$	2,4,6-(CF_3) ₃ C_6H_2	173
e	$\text{Cp}^*(\text{CO})_2\text{Fe}$	tBu	173

diphosphene complexes by reaction with [(*Z*-cyclooctene) $\text{Cr}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, and $\text{Ni}(\text{CO})_4$ respectively (Scheme 167). In the ^{31}P NMR spectra the η^1 -coordination of the diphosphene 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).

The reaction of the diphosphene complexes $(\text{C}_5\text{Me}_5)(\text{CO})_2\text{MP}=\text{P}-\text{Mes}^*$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) with a large excess of $\text{Fe}_2(\text{CO})_9$ took a different course. Here $\text{Fe}_2(\text{CO})_9$ complexes **299a-c** with bridging 2-oxo-1,3-diphosphapropanediyl ligands were obtained (Scheme 168). Obviously a carbonyl group from decomposing $\text{Fe}_2(\text{CO})_9$ had been inserted into the $\text{P}=\text{P}$ bond.¹⁷¹

The same result was observed when $(\text{C}_5\text{Me}_5)(\text{CO})_2\text{FeP}=\text{PC}_6\text{H}_2(\text{CF}_3)_3$ -2,4,6 **269b** was reacted with an excess of $\text{Fe}_2(\text{CO})_9$.¹⁷³ It was demonstrated that η^1 -complexes of the type $[\text{M}]\text{P}[\text{Fe}(\text{CO})_4]=\text{PAr}$ **290**, **295**, and **297** were smoothly converted to the insertion products by excess of $\text{Fe}_2(\text{CO})_9$ and thus have to be regarded as intermediates in this transformation.

Scheme 169



	[Fe]
<u>257,301a</u>	(C ₅ Me ₅)(CO) ₂ Fe
<u>272a,301b</u>	(C ₅ Me ₄ Et)(CO) ₂ Fe
<u>272b,301c</u>	(C ₅ Me ₄ nBu)(CO) ₂ Fe
<u>273,302</u>	(1,3tBu ₂ C ₅ H ₃)(CO) ₂ Fe

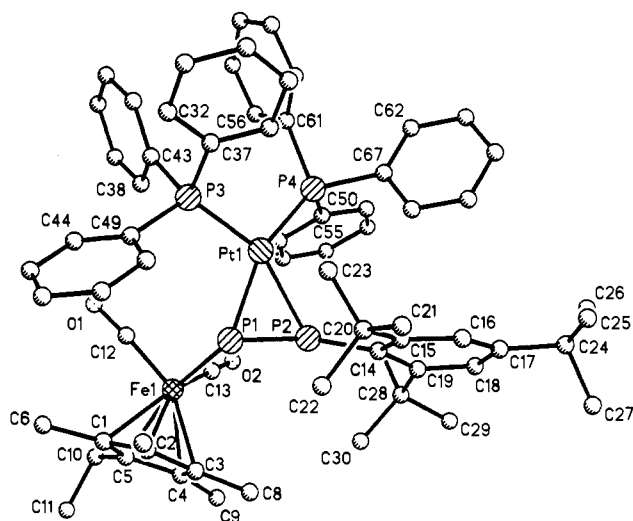


Figure 14. Molecular structure of **301b**. Selected bond lengths (Å) and bond angles (deg): Pt-P(1) 2.374 (2), Pt-P(2) 2.400 (3), Pt-P(3) 2.276 (3), Pt-P(4) 2.310 (2), P(1)-P(2) 2.140 (4), Fe-P(1) 2.368 (3); P(1)-Pt-P(2) 53.3 (1), P(1)-Pt-P(3) 97.0 (1), P(3)-Pt-P(4) 104.5 (1), P(2)-Pt-P(4) 105.2 (1).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

Likewise the tetrahedrane **300** yielded **299e** upon treatment with Fe₂(CO)₉.

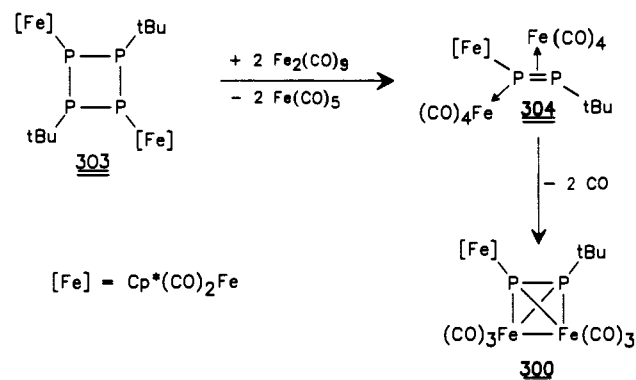
A different strategy for the synthesis of such complexes involved the treatment of bulky (dialkylamino)-dichlorophosphanes with Na₂Fe(CO)₄·1,5-dioxane in ether.^{145,174}

Only in six cases did diphosphenyl complexes show a different coordination mode than the well-known η¹-ligation. As mentioned before the reaction of the 1,2-diphosphapropene **282** with [(Z)-C₈H₁₄]Cr(CO)₅ furnished complex **286** in which the metallodiphosphene **285** is functioning as an η³-ferradiphosphaallyl ligand.¹⁶⁹

Equimolar amounts of the metallodiphosphenes **257a-c**, **273**, and (η²-C₂H₄)Pt(PPh₃)₂ underwent reaction to give the η²-complexes **301a-c** and **302**^{166b} (Scheme 169). The ³¹P 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 η²-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 Fe₂(CO)₉¹⁷³ (Scheme 170). In the

Scheme 170



³¹P 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 η¹:η²-complex **304**. The removal of two carbonyl ligands from **304** completed the tetrahedrane formation.

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-λ⁵-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*PS₂ **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 sulfur¹⁷⁵ (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-λ⁵-diphosphenyl complex **309** was detected as an intermediate by its two doublets at δ³¹P = 383.8 and 335.0 with satellite couplings ¹J(³¹P⁷⁷Se) 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 Me₂S(O)=CH₂ 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

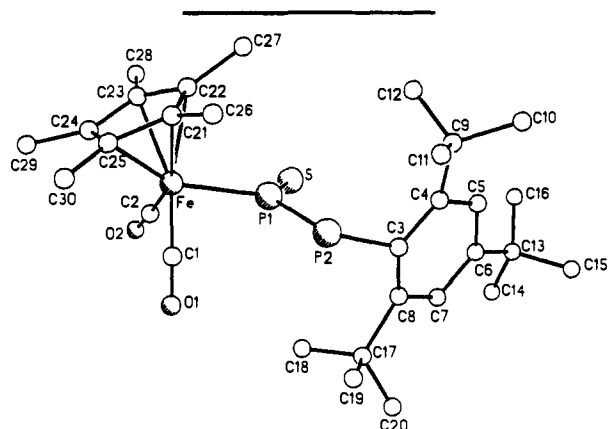
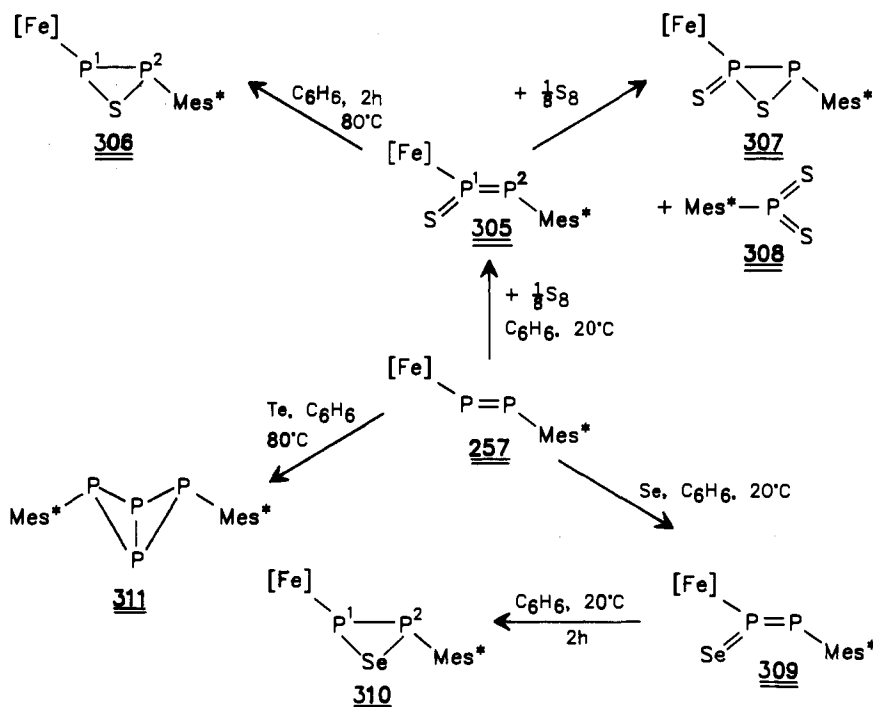


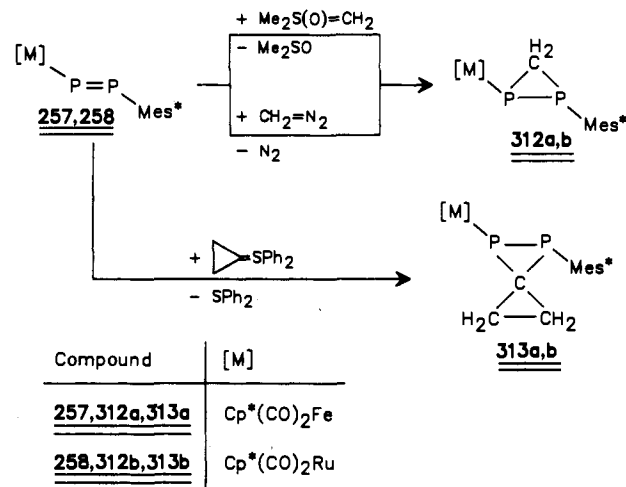
Figure 15. Molecular structure of $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP}(\text{S})=\text{PMes}^*$ **305**. Selected bond lengths (Å) and angles (deg): Fe–P(1) 2.227 (1), P(1)–P(2) 2.041 (1), P(1)–S 1.936 (2), P(2)–C(3) 1.885 (3); Fe–P(1)–S 121.1 (1), Fe–P(1)–P(2) 114.2 (1), P(2)–P(1)–S 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 bond¹⁰³ (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 ³¹P 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



E. Reactions of Metallodiphosphenes with Electron-Deficient Alkenes

Metallated diphosphenes can be regarded as electron-rich heterolefins, 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

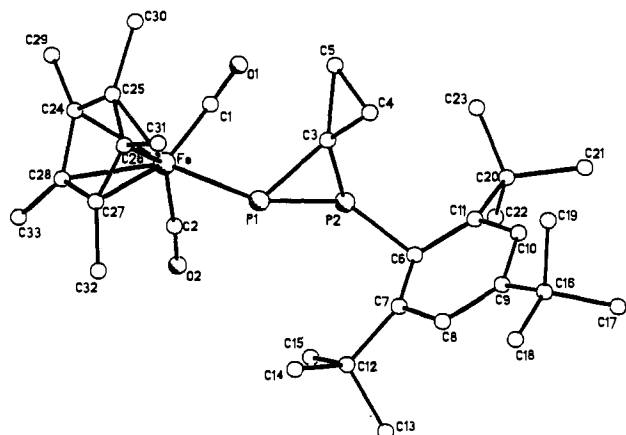
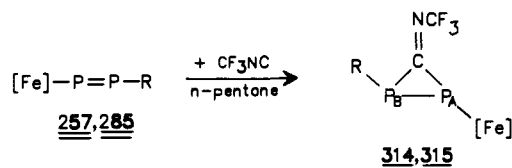


Figure 16. Molecular structure of **313a**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.310 (1), P(1)–P(2) 2.206 (2), P(1)–C(3) 1.799 (5), P(2)–C(3) 1.824 (5), C(3)–C(4) 1.510 (6), C(3)–C(5) 1.489 (7), C(4)–C(5) 1.485 (8), P(2)–C(6) 1.921 (3); Fe–P(1)–P(2) 109.3 (1), P(1)–P(2)–C(6) 107.1 (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



Comp	[Fe]	R	δ_{P_A}	δ_{P_B}	J_{PP} / Hz
<u>314</u>	Cp*(CO) ₂ Fe	Mes*	-71.5	-169.8	32.5
<u>315</u>	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 (Me₃Si)₃CP=PC(SiMe₃)₃ the potential $E_{ox} = +1.14$ V (in CH₃CN 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

Scheme 174

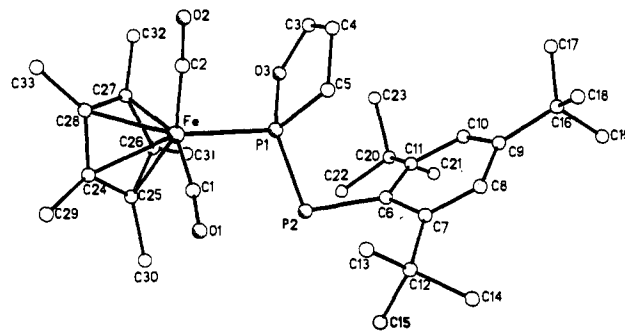
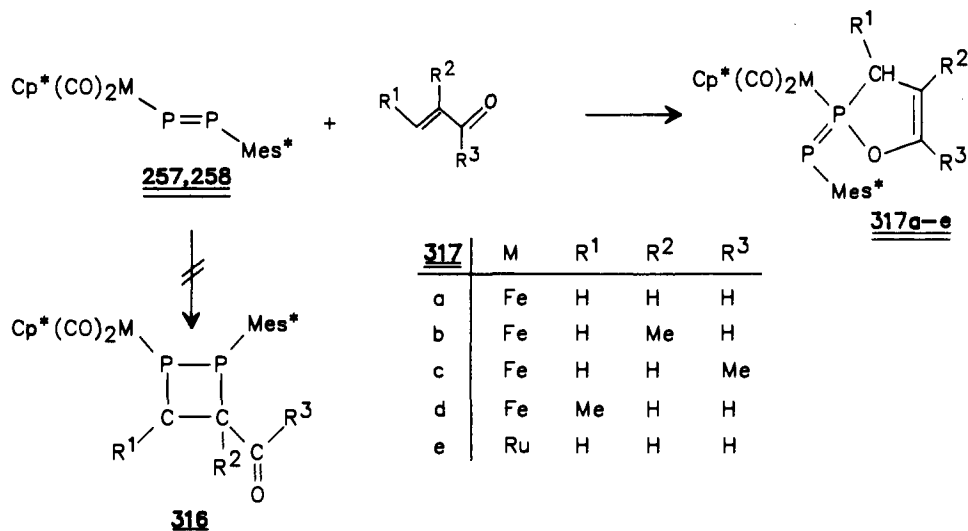


Figure 17. Molecular structure of **317a**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.243 (2), P(1)–P(2) 2.064 (2), P(1)–O(3) 1.703 (5), P(1)–C(5) 1.852 (7), P(2)–C(6) 1.850 (5), O(3)–C(3) 1.388 (11), C(3)–C(4) 1.268 (12), C(4)–C(5) 1.455 (11); Fe–P(1)–P(2) 111.2 (1), Fe–P(1)–O(3) 105.9 (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.

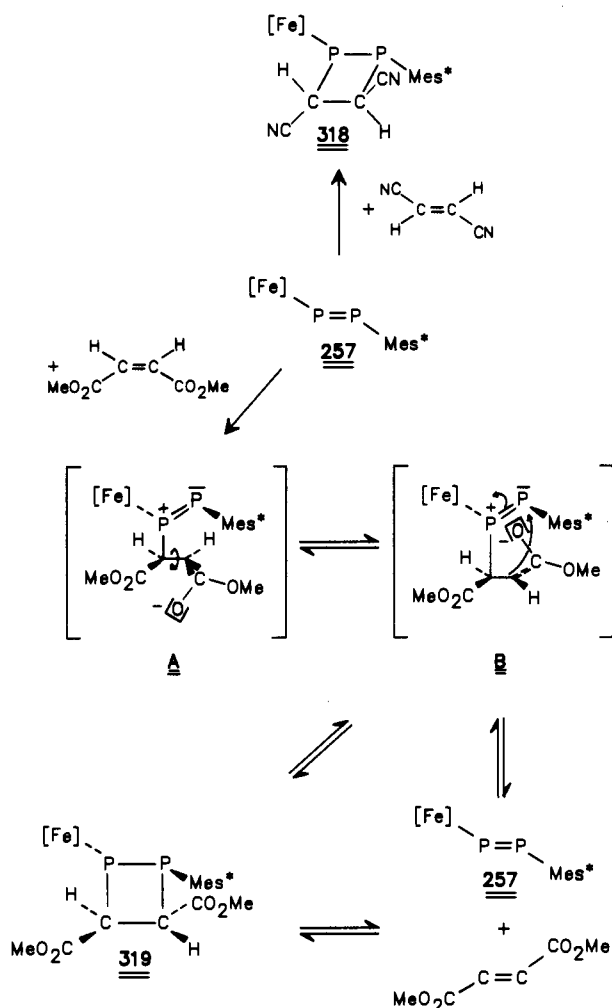
the iron via a tetracoordinate phosphorus atom in an η^1 -fashion (Figure 17).

A [2 + 2] cycloaddition also took place, when Cp*(CO)₂FeP=PMe^{s*} **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-configured 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 intermediate¹⁸⁰ (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

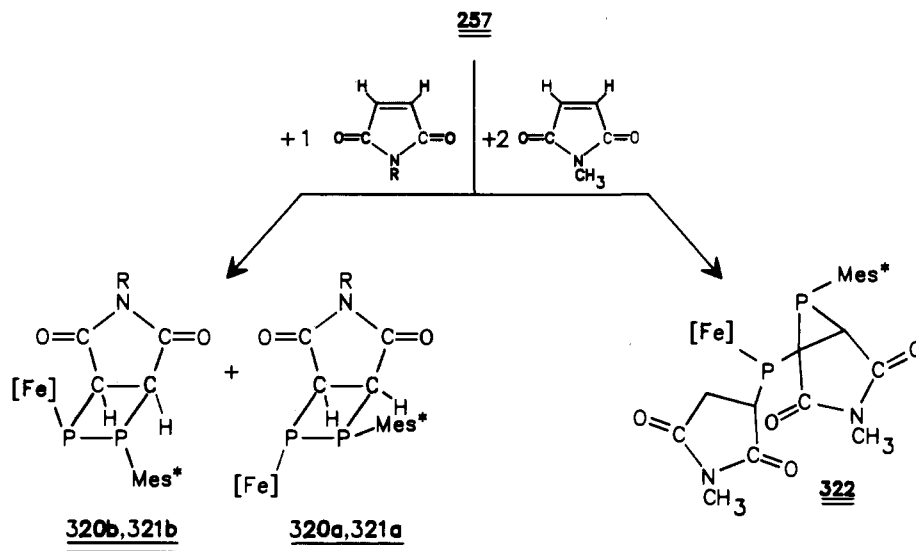
Scheme 175



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.

Scheme 176



$[Fe] = Cp^*(CO)_2Fe$; **320** (R=H), **321** (R=CH₃)

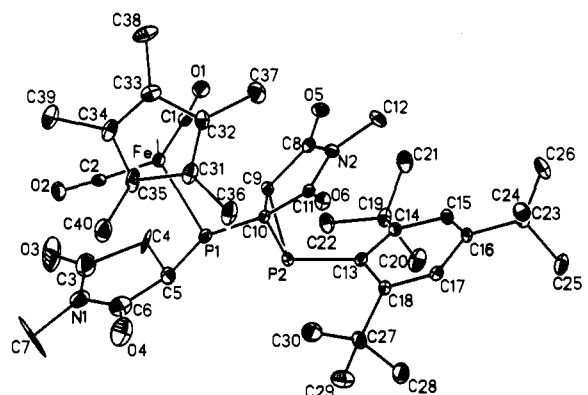


Figure 18. Molecular structure of **322**. Selected bond lengths (Å) and angles (deg): Fe–P(1) 2.318 (2), P(1)–C(10) 1.875 (6), C(9)–C(10) 1.522 (8), P(2)–C(9) 1.854 (5), P(2)–C(13) 1.846 (7); Fe–P(1)–C(10) 109.4 (2), P(1)–C(10)–C(9) 131.1 (4), P(1)–C(10)–P(2) 121.2 (3), P(2)–C(9)–C(10) 67.0 (3), C(9)–P(2)–C(10) 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 177

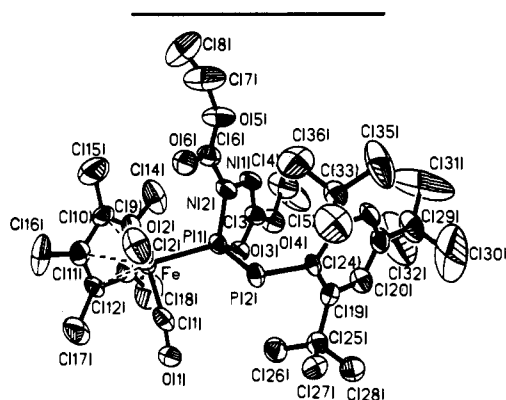
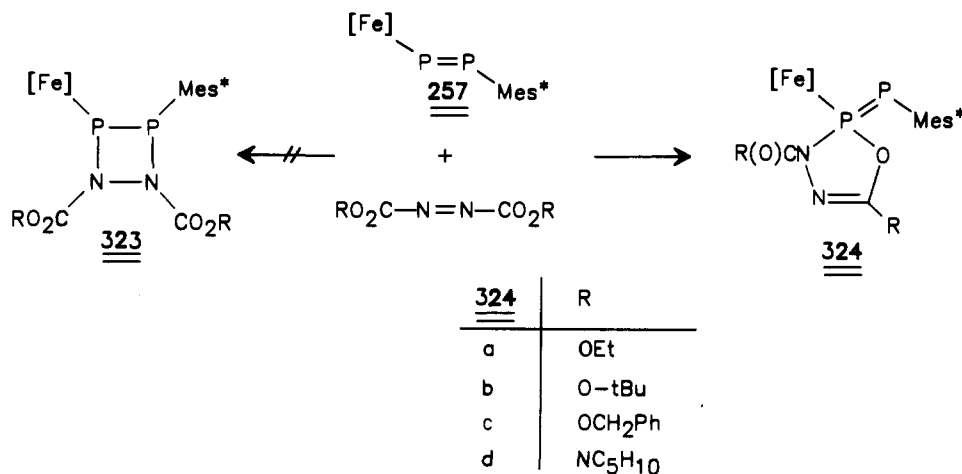


Figure 19. Molecular structure of **324a**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.241 (2), P(1)–P(2) 2.074 (3), P(1)–N(2) 1.744 (6), P(1)–O(3) 1.709 (5), P(2)–C(24) 1.870 (7); Fe–P(1)–P(2) 111.6 (1), Fe–P(1)–N(2) 114.9 (2), Fe–P(1)–O(3) 112.3 (2), P(2)–P(1)–N(2) 118.1 (2), P(2)–P(1)–O(3) 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.

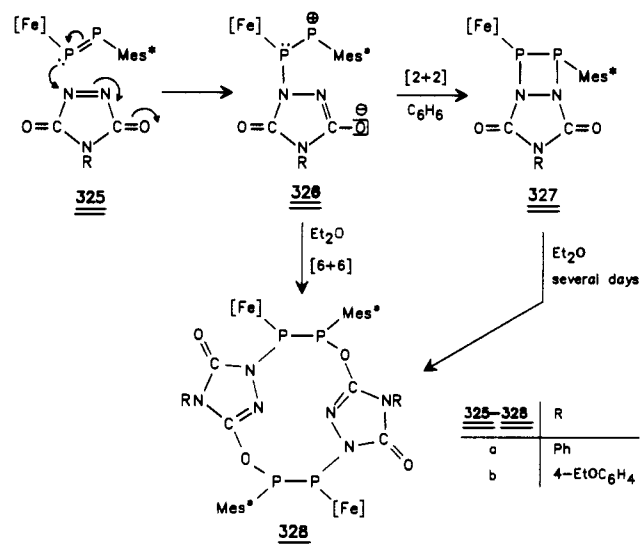
exocyclic CO functions as it is given in the 1,3,4-triazoline-2,5-diones **325**. In keeping with this the reaction of **325a,b** with Cp*(CO)₂FeP=PMes* **257** in benzene furnished the first 1,2-diaza-3,4-diphosphetidines **327a,b** as yellow crystals¹⁸⁵ (Scheme 178).

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 ³¹P NMR spectrum of the fresh reaction mixture. At –40 °C doublets at $\delta = 143$ 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



G. Reactions of Metallodiphosphenes with Hexafluoroacetone

An electron-poor double bond is also present in hexafluoroacetone. When the diphosphanyl 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(CF₃)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 metallocycle (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 diphosphanyl complexes display with electron-poor double-

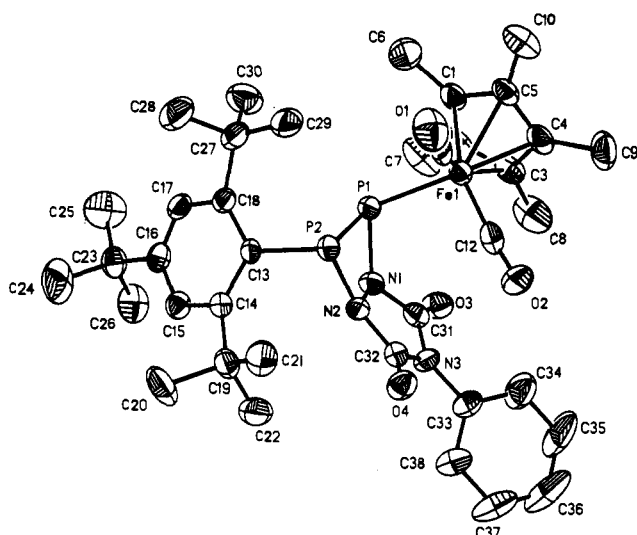


Figure 20. Molecular structure of **327a**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.296 (2), P(1)–P(2) 2.275 (2), P(1)–N(1) 1.825 (5), P(2)–N(2) 1.777 (5), P(2)–C(13) 1.881 (5), N(1)–N(2) 1.429 (6); Fe–P(1)–P(2) 108.4 (1), P(1)–P(2)–C(13) 97.9 (2), Fe(1)–P(1)–N(1) 111.3 (1), P(2)–P(1)–N(1) 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.

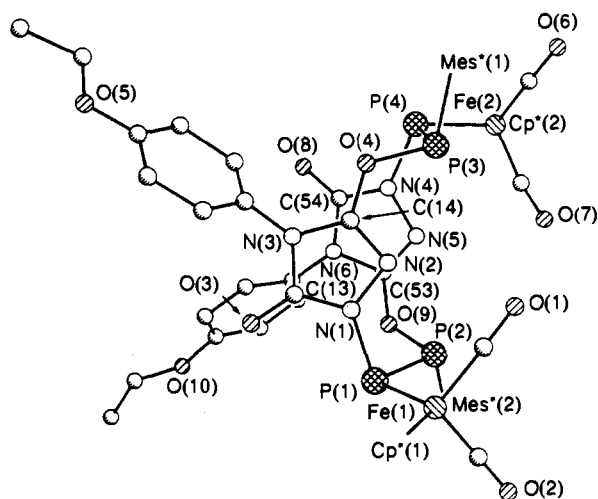


Figure 21. Molecular structure of **328b**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.277 (3), Fe(2)–P(2) 2.250 (4), P(1)–P(2) 2.235 (4), P(3)–P(4) 2.250 (4), N(1)–N(2) 1.417 (11), N(4)–N(5) 1.422 (11), P(1)–N(1) 1.772 (9), P(4)–N(4) 1.771 (8), P(2)–O(9) 1.737 (7), P(3)–O(4) 1.733 (7); 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 $\text{Cp}^*(\text{CO})_2\text{FeP}=\text{PMes}^*$ (**257**) with equimolar amounts of $\text{HC}\equiv\text{CCO}_2\text{Me}$ (**332a**), and $\text{MeC}\equiv\text{CCO}_2\text{Me}$ (**332b**) in benzene regiospecifically afforded the dark green crystalline metalocycles **333a,b**. The low-field resonances and the large coupling constants in the ^{31}P NMR spectra of **333a** ($\delta = 439.0$ d, 299.5 d, $^1J_{\text{PP}} = 614.0$ Hz) and **330b** ($\delta = 420.1$ d, 279.9 d, $^1J_{\text{PP}} = 664.2$ Hz) are characteristic for diphosphene ligands in the η^1 -coordination mode. Both compounds possess an *E*-configured P=P bond like **257**. On the other hand dimethyl acetylenedicarboxylate **332c** and

Scheme 179

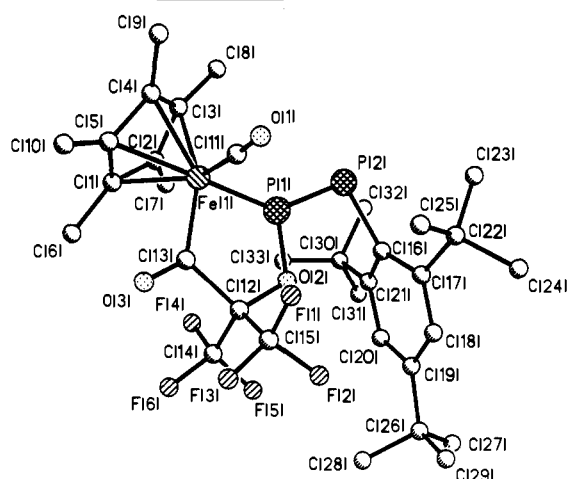
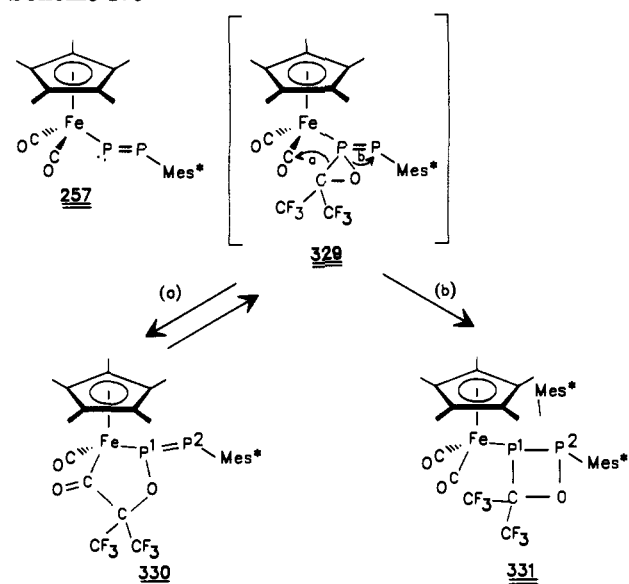


Figure 22. Molecular structure of **330**. Selected bond lengths (Å) and bond angles (deg): Fe–P(1) 2.084 (4), Fe–C(13) 1.937 (14), P(1)–P(2) 2.014 (5), P(1)–O(2) 1.647 (9), P(2)–C(16) 1.860 (13), O(2)–C(12) 1.427 (15), O(3)–C(13) 1.191 (16), C(12)–C(13) 1.640 (19); Fe–P(1)–P(2) 140.3 (2), Fe–P(1)–O(2) 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.

the acetylenic ketones **332d,e** underwent reaction with **257** to yield the metaloheterocycles **334c–e** with *Z*-configured 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.

It was assumed that the formation of the metaloheterocycles 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 diphosphene complexes and alkynes was tested in going from **257** to ruthenium

Scheme 180

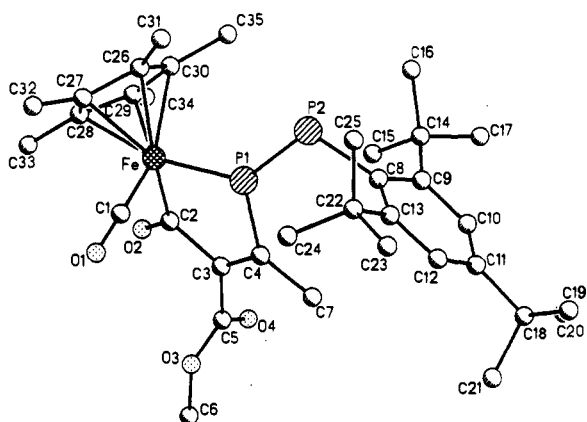
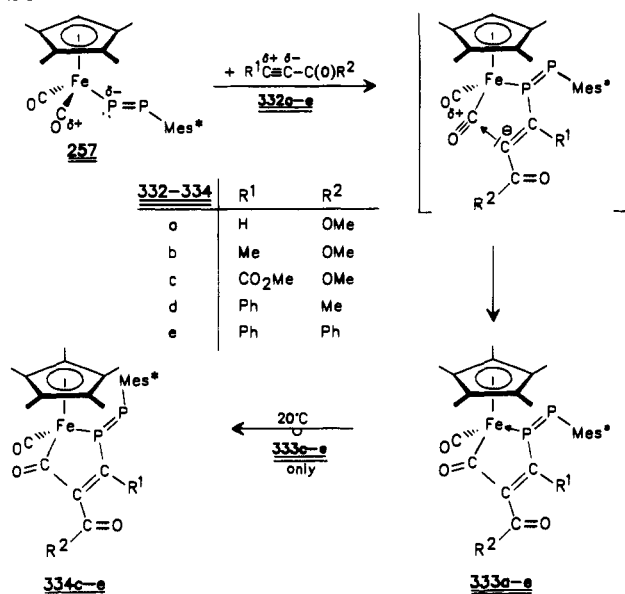
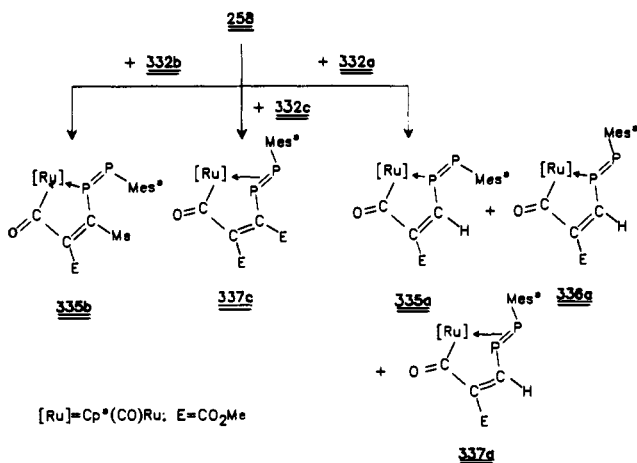


Figure 23. Molecular structure of 333b. Selected bond lengths (Å) and bond angles (deg): Fe-P(1) 2.117 (2), P(1)-P(2) 2.031 (3), P(2)-C(8) 1.847 (6), P(1)-C(4) 1.819 (6), C(3)-C(4) 1.312 (10), C(2)-C(3) 1.528 (9), Fe-C(2) 1.951 (7), C(2)-O(2) 1.234 (9); Fe-P(1)-P(2) 131.4 (1), Fe-P(1)-C(4) 106.7 (2),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

Scheme 181



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] cycloaddition¹⁸⁹ (Scheme 181). The phos-

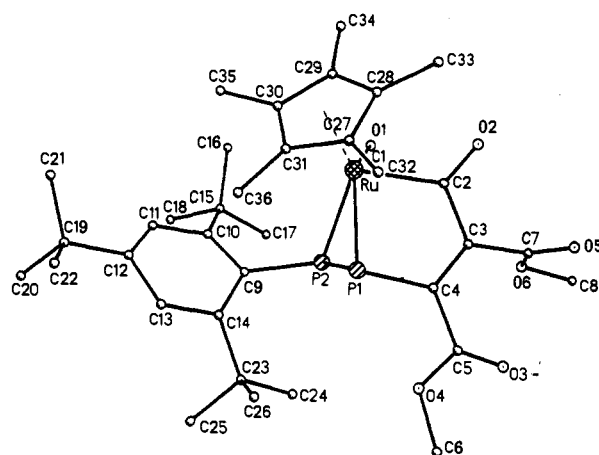


Figure 24. Molecular structure of 337c. Selected bond lengths (Å) and bond angles (deg): Ru-P(1) 2.383 (1), Ru-P(2) 2.572 (1), P(1)-P(2) 2.121 (1), Ru-C(2) 2.093 (3), C(2)-C(3) 1.493 (5), C(3)-C(4) 1.340 (5), P(1)-C(4) 1.837 (3), P(2)-C(9) 1.864 (3); Ru-P(1)-P(2) 69.4 (1), Ru-P(2)-P(1) 98.9, P(1)-Ru-P(2) 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).

phorus atom at the olefinic double bond is η^1 -coordinated to the metal. This was reflected in the ³¹P NMR spectrum where two doublets ($\delta = 394.9$ 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*-configured 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.

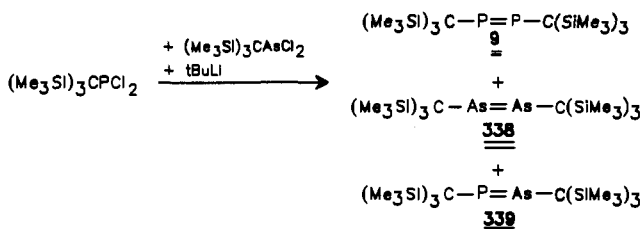
A dark red color change was observed upon addition of dimethyl acetylenedicarboxylate to a benzene solution of 258. The reaction appeared to be straightforward, affording ruby-red crystalline 337c, in which the ruthenium atom is involved in π -bonding to the P=P bond. This is reflected in the ³¹P NMR spectrum by resonances at $\delta = 104.5$ 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, $\nu(\text{CO}) = 1962$ cm⁻¹; 337c, $\nu(\text{CO}) = 1993$ 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 ligand¹⁸⁹ (Figure 24).

IX. Phosphaarsenes, Diarsenes, and Phosphaalbenes

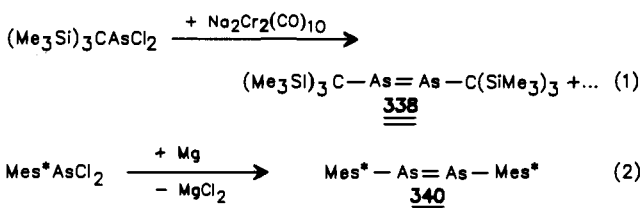
A. Synthesis, Structures, and Spectra

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 (Me₃Si)₃CPCl₂ and (Me₃Si)₃CAsCl₂.^{190a} In addition comparable amounts of diphosphene 9 and diarsene 338 were also generated (Scheme 182). Of course the reduction of pure (Me₃Si)₃CAsCl₂ with *tert*-butyllithium also gave 338.^{190b} The same diarsene was isolated from the

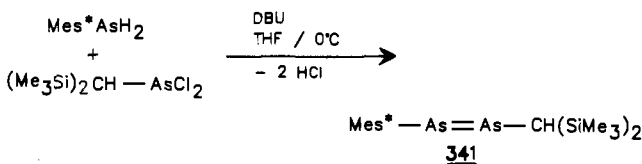
Scheme 182



Scheme 183



Scheme 184



reaction of $(\text{Me}_3\text{Si})_3\text{CAsCl}_2$ with $\text{Na}_2\text{Cr}_2(\text{CO})_{10}$.¹⁴³ The preparation of the yellow crystalline diarsene **340** with two aryl substituents was accomplished by the treatment of $\text{Mes}^*\text{AsCl}_2$ with magnesium at 0°C ¹⁹¹ (Scheme 183). Diarsene **340** was also produced in small amounts during the reaction of $\text{Cp}^*(\text{CO})_2\text{FeP}(\text{SiMe}_3)_2$ with $\text{Mes}^*\text{AsCl}_2$ (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 $(\text{Me}_3\text{Si})_2\text{CHAsCl}_2$.^{14,192} (Scheme 184). The X-ray crystal structure determination of **341** exhibited an *E*-configured molecule with an $\text{As}=\text{As}$ bond length of 2.224 (2) Å (Figure 25). The bond angles at the arsenic atoms of $93.6(3)^\circ$ and $99.9(3)^\circ$

Scheme 185

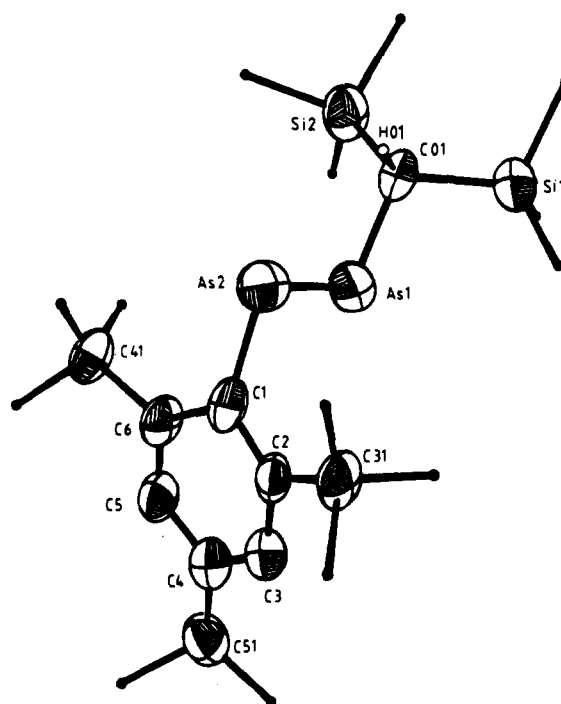
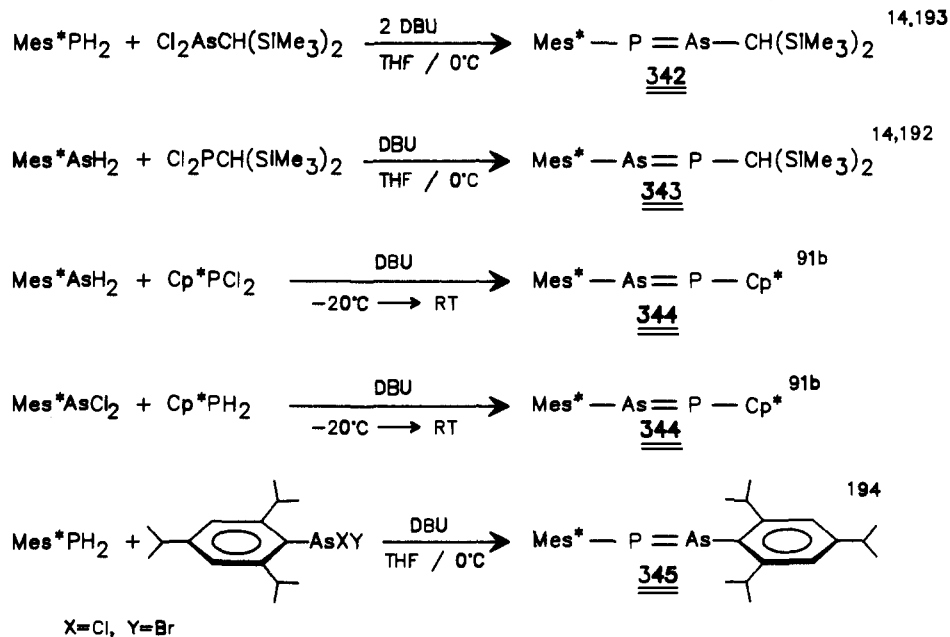
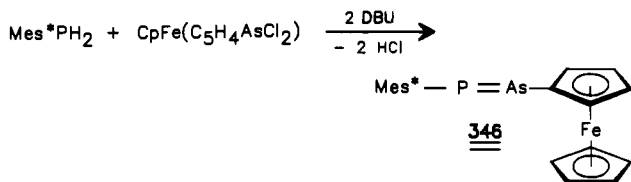


Figure 25. Molecular structure of (*E*)- $(\text{Me}_3\text{Si})_2\text{-CHAs}=\text{AsMes}^*$ (**341**). Selected bond lengths (Å) and bond angles (deg): $\text{As}(1)-\text{As}(2)$ 2.224 (2), $\text{As}(1)-\text{C}(01)$ 1.976 (10), $\text{As}(2)-\text{C}(1)$ 1.946 (1); $\text{As}(2)-\text{As}(1)-\text{C}(01)$ $99.9(3)^\circ$, $\text{As}(1)-\text{As}(2)-\text{C}(1)$ $93.6(3)^\circ$. Reprinted from ref 192. Copyright 1983 American Chemical Society.

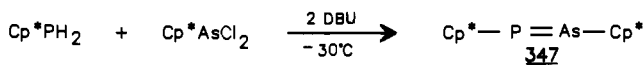
$(3)^\circ$ are appreciably smaller than the bond angles at phosphorus in the diphosphenes $\text{RP}=\text{PR}$ [$\text{R} = (\text{Me}_3\text{Si})_3\text{C}$, $108.5(4)^\circ$ av; $\text{R} = \text{Mes}^*$, $102.8(1)^\circ$], reflecting both the tendency to an increasing p character in going from P to As and possibly a decrease in steric encumbrance resulting from the longer bond $\text{As}=\text{As}$ and $\text{As}-\text{C}$ bonds.

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

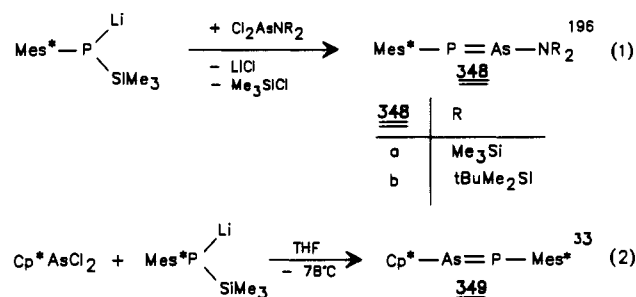
Scheme 186



Scheme 187

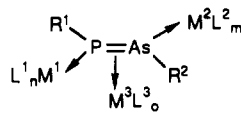


Scheme 188



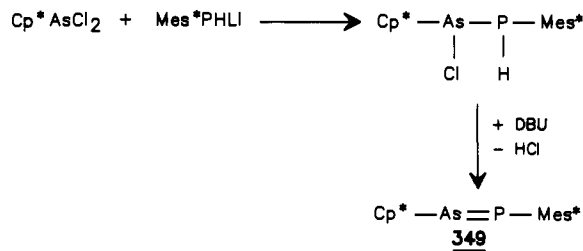
via the phosphino arsane $\text{Mes}^*\text{PHAsXC}_6\text{H}_2(\text{iPr})_3$ -2,4,6.¹⁹⁴ The phospharsene **346** with a ferrocenyl substituent, which formed readily in THF, decomposed when the solution was concentrated¹⁹⁵ (Scheme 186).

Table 10. ³¹P NMR Data of Phospharsenes, η¹-Phospharsene Complexes, Metallophospharsenes, and η¹-Complexes of Metallophospharsenes



compd	R ¹	R ²	M ¹ L ¹ _n	M ² L ² _m	M ³ L ³ _o	δ 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 ₂ Cl ₂	14, 193
343	CH(SiMe ₃) ₂	Mes*				533	CH ₂ Cl ₂	14, 192
344	Cp*	Mes*				541	C ₆ D ₆	91b
345	Mes*	2,4,6-iPr ₃ C ₆ H ₂				580	C ₆ D 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 ₆ D 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 ₆ D ₆	98a
372	Mes*	Cp*			Pt(PPh ₃) ₂	66.3	C ₆ D 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 ₆ H ₆	91b
402a	Mes*	Cp*(CO) ₂ Fe				603	THF	211, 212
402b	Mes*	Cp(CO)(PPh ₃)Fe				605.3	C ₆ D ₆	211, 212
402c	Mes*	MeCp(CO)(PPh ₃)Fe				603.3	C ₆ D ₆	211, 212
403a	Mes*	Cp*(CO) ₂ Fe		Cr(CO) ₅		628.8	C ₆ D ₆	212
403b	Mes*	Cp(CO)(PPh ₃)Fe		Cr(CO) ₅		608.7	C ₆ D ₆	212
403c	Mes*	MeCp(CO)(PPh ₃)Fe		Cr(CO) ₅		607.4	C ₆ D ₆	212
406a	Cp*(CO) ₂ Fe	Mes*				765.7	THF	213
406b	Cp*(CO) ₂ Ru	Mes*				724.9	THF	213
406c	Cp*(PPh ₃)(CO)Fe	Mes*				821.3	THF	213
410a	Cp*(CO) ₂ Fe	Mes*	Cr(CO) ₅			616.3	C ₆ D ₆	213
410b	Cp*(CO) ₂ Ru	Mes*	Cr(CO) ₅			579.0	C ₆ D ₆	213
410c	Cp*(PPh ₃)(CO)Fe	Mes*	Cr(CO) ₅			618.4	C ₆ D ₆	213
411a	Mes*	Cp*(CO) ₃ Cr				608.2	C ₆ D ₆	167
411b	Mes*	Cp*(CO) ₃ Mo				586.9	CDCl ₃	167
412a	Mes*	Cp*(PPh ₃)Ni				587	C ₆ H ₆ /toluene	98a
412b	Mes*	Cp*(Pn-Bu ₃)Ni				588	C ₆ H ₆ /toluene	98a

Scheme 189



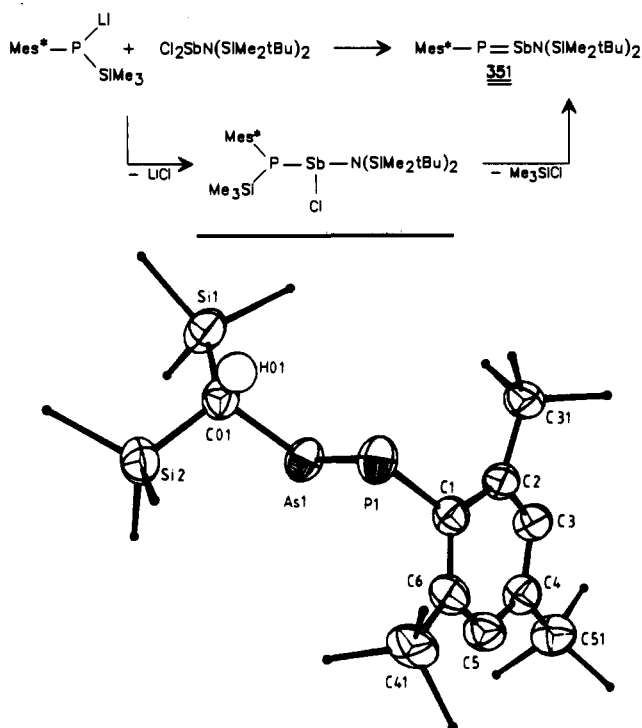
A similar instability was reported from phospharsene $\text{Cp}^*\text{As}=\text{PCp}^*$ (**347**)^{91b} (Scheme 187). Both phospharsenes were trapped as ligands in platinum complexes (see section XI).

A somewhat different synthetic pathway took advantage from the ready 1,2 elimination of LiCl and Me₃SiCl (Scheme 188). Here a stepwise synthesis via a functionalized phosphinoarsane with subsequent HCl elimination was also feasible³³ (Scheme 189).

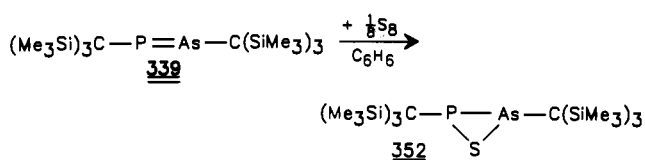
There are only two accounts in the literature which are concerned with the successful synthesis of phosphastibenes.

In the reaction mixture of (Me₃Si)₂CHSbCl₂, supermesitylphosphane, and DBU at 0 °C, phosphastibene $\text{Mes}^*\text{P}=\text{SbCH}(\text{SiMe}_3)_2$ (**350**) was detected by its ³¹P NMR resonances at δ = 620.0. At ambient temperature the compound completely decomposed within 2 hours.

Scheme 190



Scheme 191



A more promising approach was based upon the coupling of an amidodichlorostibane with LiP(SiMe₃)—Mes*. The product **351** was obtained as a dark red oil¹⁹⁶ (Scheme 190).

In the ³¹P NMR spectra, the phospharsenes (Table 10) gave rise to resonances at even lower fields than those of the related diphosphenes [for example, (Me₃Si)₃CP=As—PC(SiMe₃)₃, δ = 668, versus (Me₃Si)₃CP=PC(SiMe₃)₃, δ = 599].

The As=P bond in Mes*P=AsCH(SiMe₃)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).

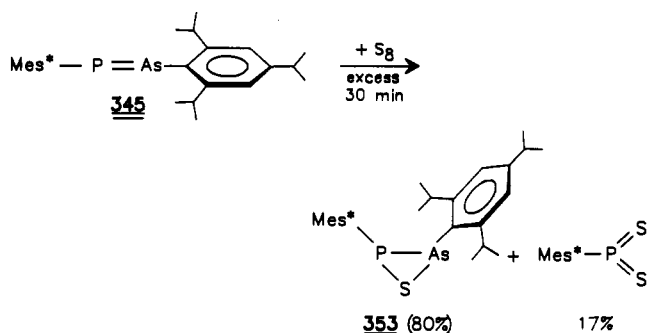
X. Reactivity of Phospharsenes and Diarsenes

A. Reactions with Sulfur and Selenium

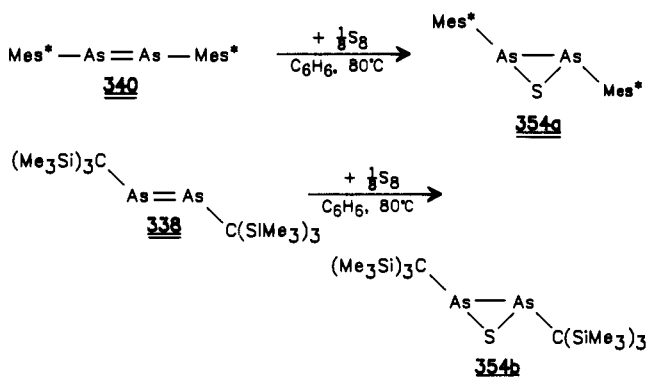
Phospharsenes such as **339** are prone to reaction with sulfur, usually producing thiophospharsiranes like **352**^{190,194} (Scheme 191).

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

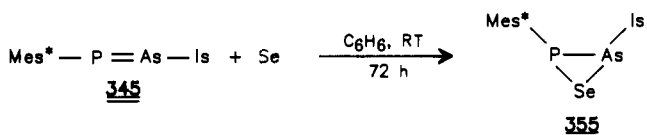
Scheme 192



Scheme 193



Scheme 194



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

Phospharsene **345** and gray selenium underwent reaction to yield selenophospharsirane **355** as indicated by a singlet in the ³¹P NMR spectrum at δ = -48.1 ppm [³¹J(P⁷⁷Se) = 147 Hz]. The isolation of pure **355** has been thwarted by decomposition¹⁹⁴ (Scheme 194).

B. Reactions with Diazomethane

The interaction of phospharsenes and diarsenes with CH₂N₂ opened a synthetic route to three-membered heterocycles containing phosphorus, arsenic, and carbon atoms.

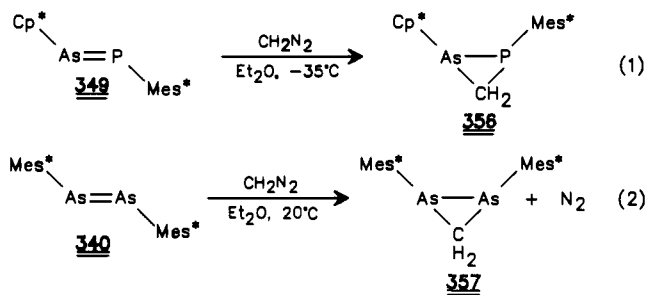
The phospharsene **349** experienced a clean conversion to the corresponding phospharsirane **356** when treated with diazomethane^{91b} (Scheme 195). The yellow crystalline product gave rise to a singlet at δ = -148 ppm in the ³¹P NMR experiment.

The synthesis of diarsirane **357** was accomplished by exposing diarsene **340** to an ethereal solution of diazomethane¹⁹¹ (Scheme 195).

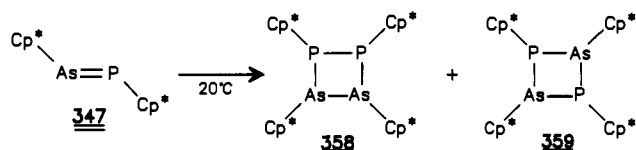
C. [2 + 2] Dimerizations and Subsequent Reactions

The phospharsene **347** dimerized in solution at temperatures above 0 °C to give a mixture of the two isomeric diphosphadiarsenes **358** and **359**^{91b} (Scheme 196).

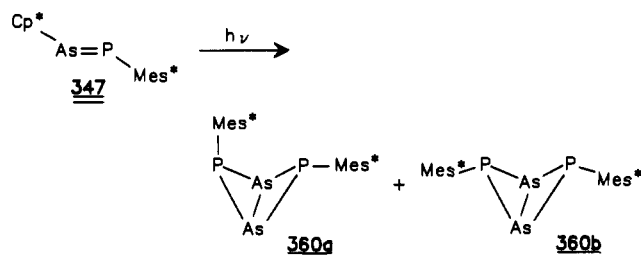
Scheme 195



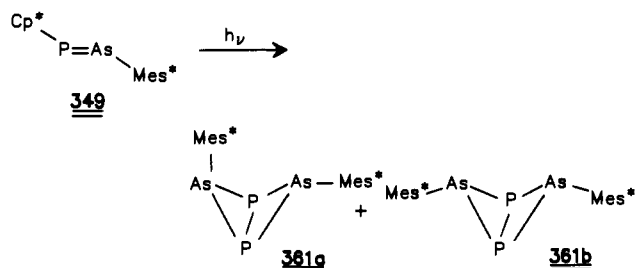
Scheme 196



Scheme 197



Scheme 198



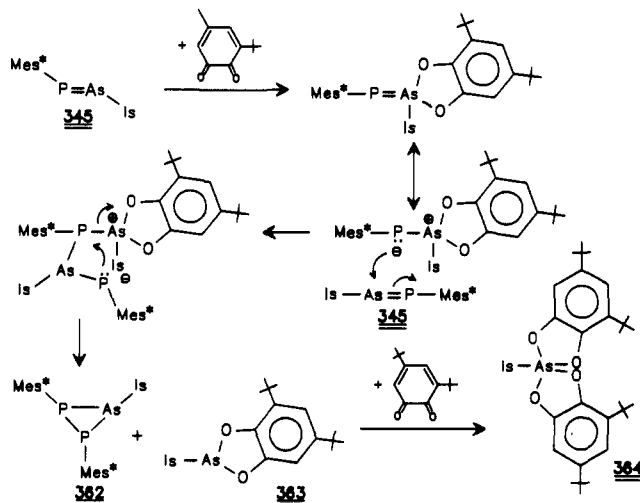
Photolysis of **347** furnished a mixture of the 1,3-diarsa-2,4-diphosphabicyclo[1.1.0]butane isomers **360**¹¹⁵ (Scheme 197).

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 ³¹P 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}

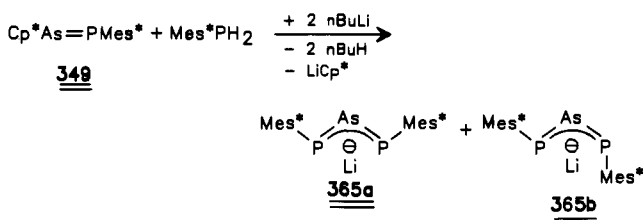
D. Reaction of Phosphaarsenes with Ortho Quinones

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 encountered¹⁹⁴ (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

Scheme 199



Scheme 200



arsane **363**. The latter is further oxidized by the ortho quinone to afford **364**.

E. Substitutions

Like the analogous diphosphene Cp*P=P Mes* (**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 ³¹P 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

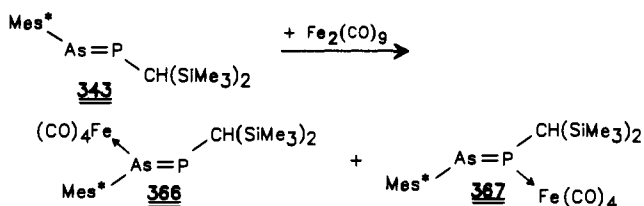
Generally the same modes of coordination as discussed with diphosphene ligands are conceivable in the complex chemistry of phosphaarsenes, diarsenes, and distibenes. To date, however, only transition metal complexes of the types A–E (section V) were described in the literature.

When treated with Fe₂(CO)₉ the arsaphosphene **343** was transformed into a mixture of the isomeric η¹-complexes **366** and **367**, which differ in the site of ligation of the Fe(CO)₄ moiety^{120b} (Scheme 201).

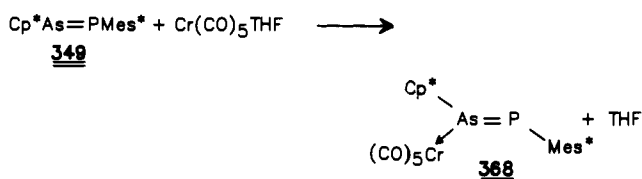
The reaction of the arsaphosphene **349** with Cr(CO)₅THF gave rise to the pentacarbonylchromium adduct **368**^{98a} (Scheme 202).

A carbonyliron complex with an η¹-bonded diarsene resulted from **341** and Fe₂(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).

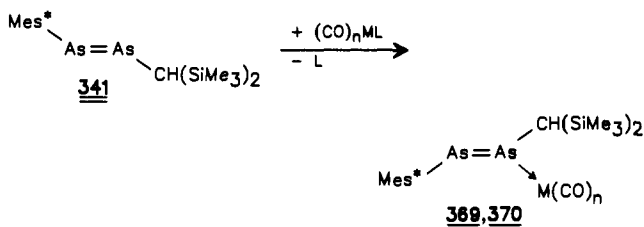
Scheme 201



Scheme 202



Scheme 203



	M	n	L
<u>369</u>	Fe	4	Fe(CO) ₅
<u>370</u>	Cr	5	THF

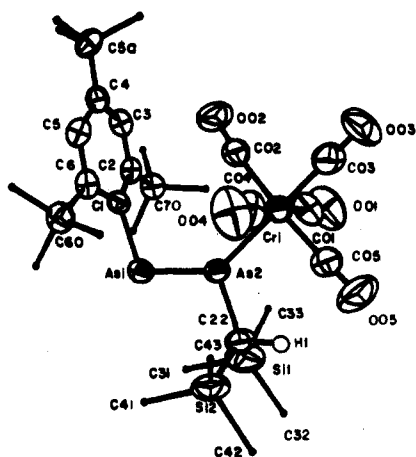
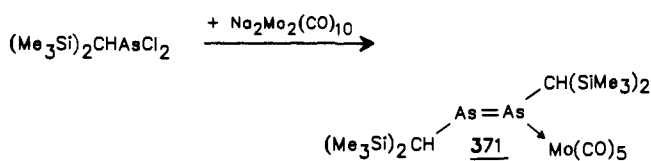


Figure 27. Molecular structure of 370. Selected bond lengths (Å) and bond angles (deg): As(1)–As(2) 2.246 (1), As(1)–C(1) 1.978 (5), As(2)–C(22) 1.981 (5), As(2)–Cr(1) 2.454 (1); As(2)–As(1)–C(1) 104.0 (1), As(1)–As(2)–C(22) 103.9 (2), As(1)–As(2)–Cr(1) 138.51 (3), Cr(1)–As(2)–C(22) 117.6 (2). Reprinted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

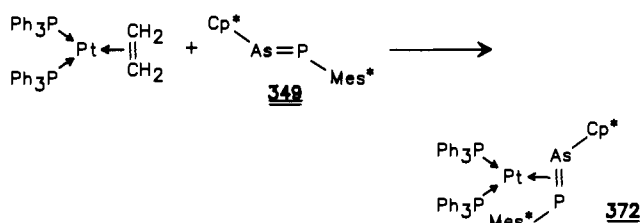
The X-ray analysis of 370 features an *E*-configured diarsene, where the Cr(CO)₅ unit is linked to the arsenic center of less steric hindrance (Figure 27). The previous reactions involved free phospharsenes and diarsenes which obviously experienced sufficient kinetical stabilization from bulky substituents.

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 (Me₃Si)₂CHAsCl₂ was allowed to interact with

Scheme 204



Scheme 205



Scheme 206

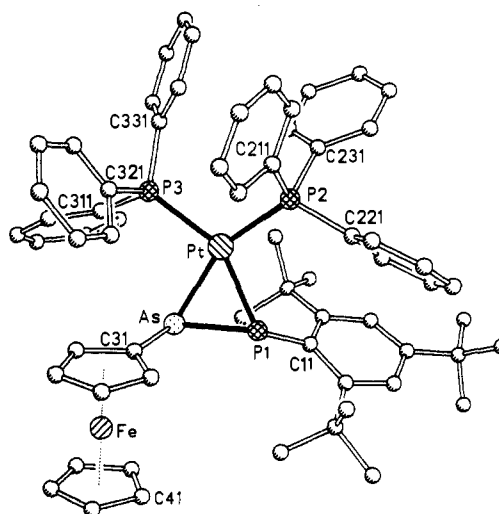
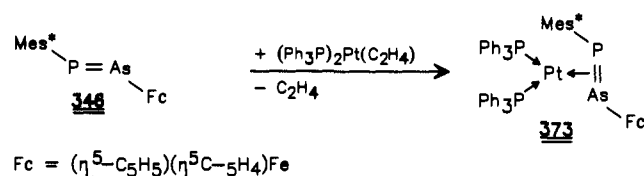


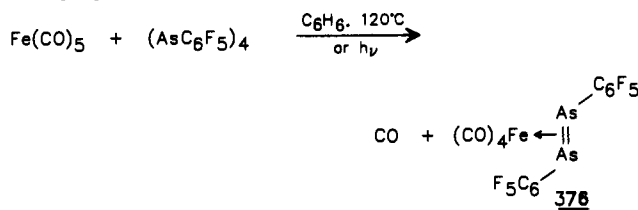
Figure 28. Molecular structure of 373. Selected bond lengths (Å) and bond angles (deg): Pt–As 2.515 (1), Pt–P(1) 2.364 (2), Pt–P(2) 2.295 (3), Pt–P(3) 2.300 (2), As–P(1) 2.289 (3); As–Pt–P(1) 55.9 (1), As–Pt–P(2) 156.9 (1), As–Pt–P(3) 97.4 (1), P(1)–Pt–P(2) 101.1 (1), P(1)–Pt–P(3) 151.4 (1), P(2)–Pt–P(3) 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.

Na₂Mo₂(CO)₁₀ (Scheme 204). It was assumed that for steric reasons only one Mo(CO)₅ fragment was accommodated at this ligand.¹⁴³

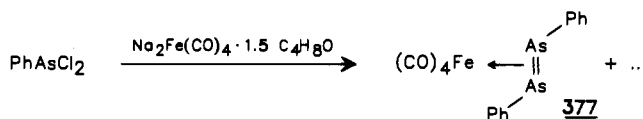
There are a few reports in the literature dealing with side-on-coordinated phospharsenes and diarsenes in platinum and iron complexes.

The stable phospharsene 349 displaced the ethylene ligand in (C₂H₄)Pt(PPh₃)₂ to give the expected η^2 -phospharsene complex, which was isolated as a stable solid^{98a} (Scheme 205). The interception of the thermolabile ferrocenyl-substituted phospharsene 346 as η^2 -ligand led to the formation of platinum complex 373¹⁹⁵ (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.

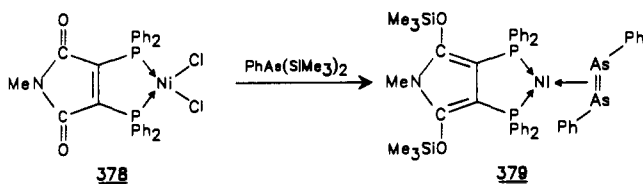
Scheme 207



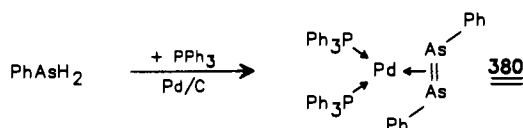
Scheme 208



Scheme 209



Scheme 210



The same synthetic approach was utilized for the preparation of the thermolabile complexes $\text{Pt}(\eta^2\text{Cp}^*\text{-P=AsCp}^*)(\text{PPh}_3)_2$ (374) and $\text{Pt}(\eta^2\text{-Cp}^*\text{P=As-Mes}^*)(\text{PPh}_3)_2$ (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 $\text{Fe}(\text{CO})_5$ in benzene to afford 376 as yellow plates¹⁹⁸ (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 $\text{Mes}^*\text{As=AsCH}(\text{SiMe}_3)_2$ (2.22 Å) and $(\text{AsMe})_5$ (2.428 (8) Å).¹⁹⁹

The related compound $(\text{CO})_4\text{Fe}(\eta^2\text{-PhAs}_2\text{Ph})$ (377) resulted from the dechlorination of PhAsCl_2 by means of $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1,5\text{-dioxane}$ ²⁰⁰ (Scheme 208). The diarsene ligand in this complex occupies an equatorial position in a distorted trigonal bipyramid with an As-As bond distance of 2.365 (2) Å.

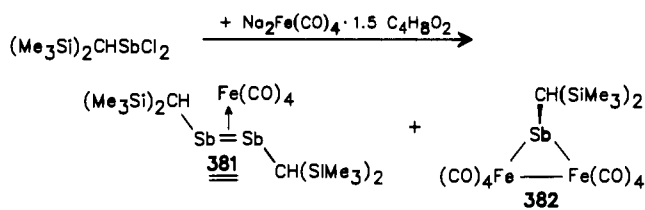
The same $\eta^2\text{-As}_2\text{Ph}_2$ ligand is constructed at a Ni center from precursor 378 and a phenyldisilylarsane¹³⁹ (Scheme 209).

The catalytic dehydrogenation of PhAsH_2 on palladium in the presence of PPh_3 provided another entry into the chemistry of η^2 -diarsene complexes²⁰¹ (Scheme 210).

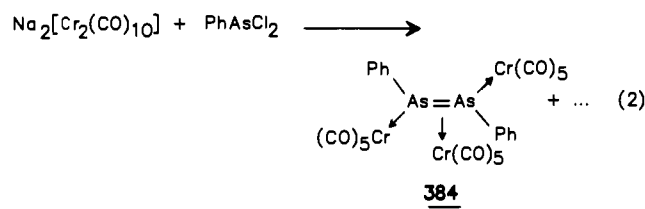
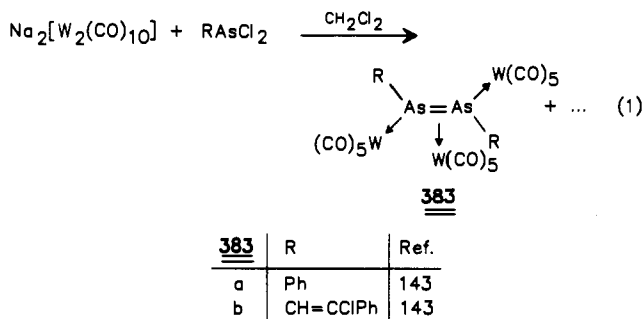
Collman's reagent reacted with $(\text{Me}_3\text{Si})_2\text{CHSbCl}_2$ to give of a mixture of a η^2 -distibene complex 381 and the cyclic diferrastibirane 382^{202,203} (Scheme 211).

According to the X-ray structure analysis compound 381 may be viewed as a complex in which the distibene $(\text{Me}_3\text{Si})_2\text{CHSb}=\text{SbCH}(\text{SiMe}_3)_2$ 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

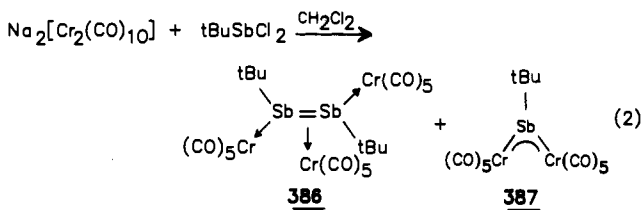
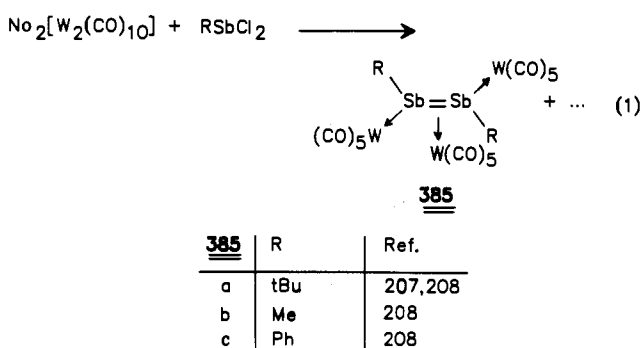
Scheme 211



Scheme 212



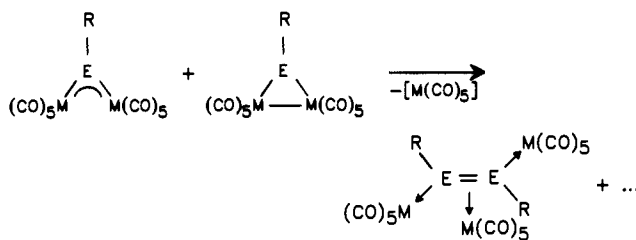
Scheme 213



than a typical Sb-Sb bond [e.g. Ph_4Sb_2 2.837 (1) Å].²⁰⁴

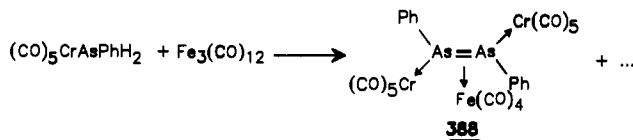
Complexes of the type E with two end-on- and one side-on-coordinated metal fragments at a As=As or Sb=Sb bond are elegantly accessible by the reaction of carbonylmetalates with organodichlorarsanes or -stibanes (Schemes 212 and 213, respectively). This reductive coupling was especially sensitive to the 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

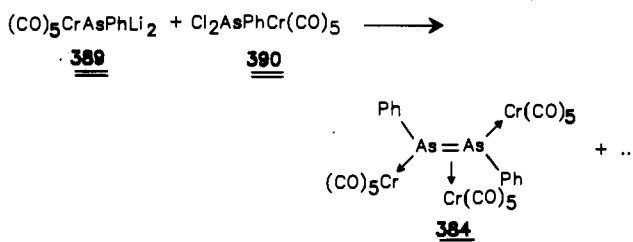


E = P, As, Sb; M = Cr, Mo, W; R = alkyl, aryl

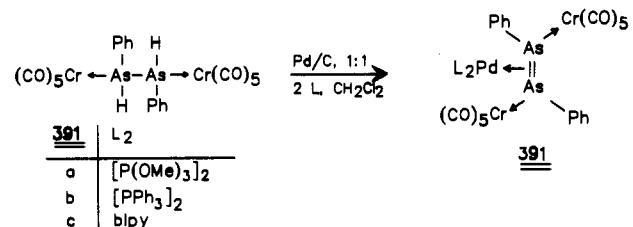
Scheme 215



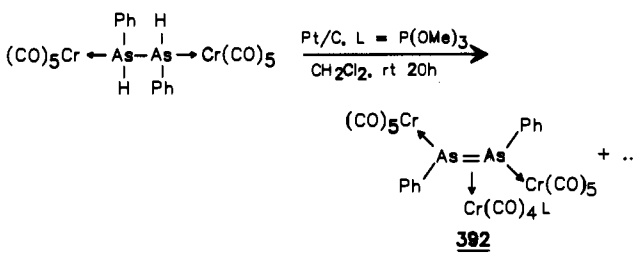
Scheme 216



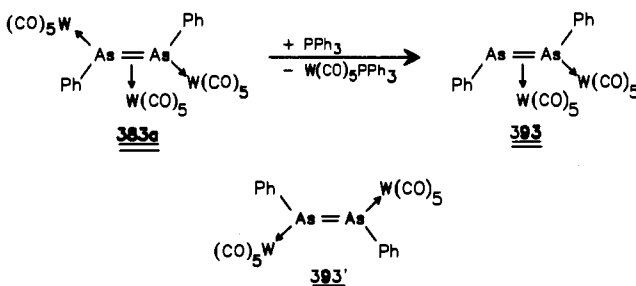
Scheme 217



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 $(\text{CO})_5\text{Cr}(\text{PhAsH}_2)$ in the presence of $\text{Fe}_3(\text{CO})_{12}$ (Scheme 215).¹⁴³

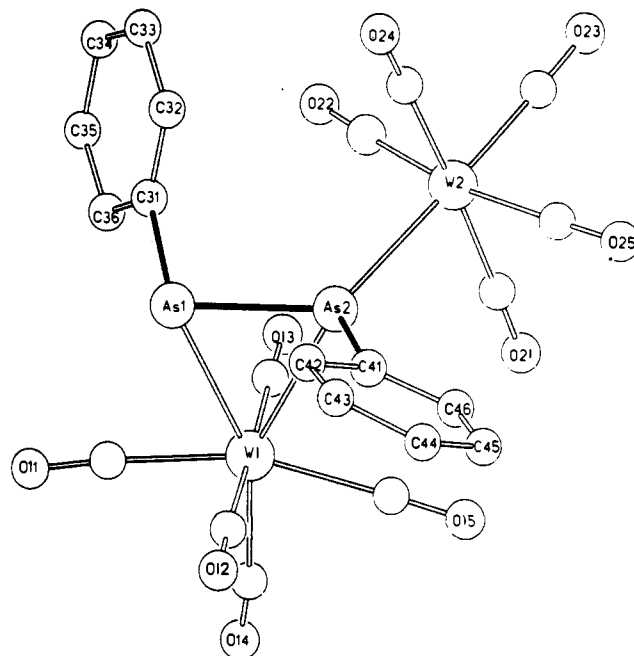


Figure 29. Molecular structure of 393. Selected bond lengths (Å) and bond angles (deg): As(1)–As(2) 2.342 (4), W(1)–As(1) 2.769 (4), W(1)–As(2) 2.728 (4), W(2)–As(2) 2.622 (4), As(1)–C(31) 1.96 (2), As(2)–C(41) 1.96 (2); C(31)–As(1)–As(2) 99.3 (6), As(1)–As(2)–C(41) 102.3 (6), As(1)–W(1)–As(2) 50.4 (1), 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).

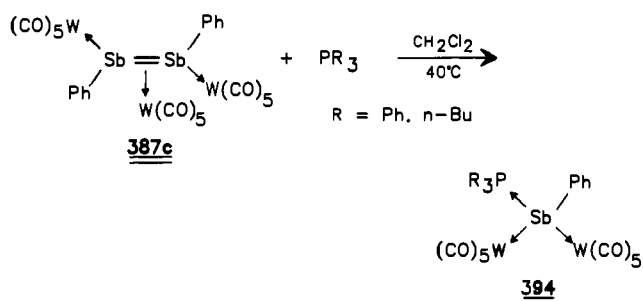
The identity of coordination compounds with μ -(η^1 : η^1 : η^2)-diarsene and -distibene ligands was manifested by several X-ray structure analyses.

XII. Reactivity of Diarsene and Distibene Complexes

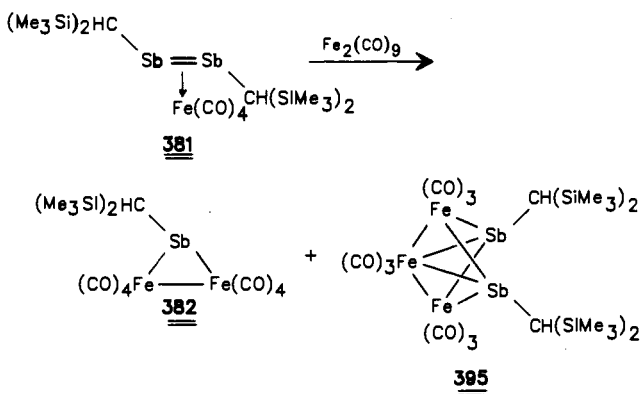
As already mentioned before, heating a solution of $[\text{Cr}(\text{CO})_5]_3(\text{PhP}=\text{PPh})$ (214) yielded deep violet $[\text{Cr}(\text{CO})_5]_2(\text{PhP}=\text{PPh})$ (215) with an unsupported P=P bond.^{142b} In contrast to this finding the removal of a $\text{W}(\text{CO})_5$ group from $[\text{W}(\text{CO})_5]_3(\text{PhAs}=\text{AsPh})$ (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 $\text{Fe}_2(\text{CO})_9$.²⁰² (Scheme 221).

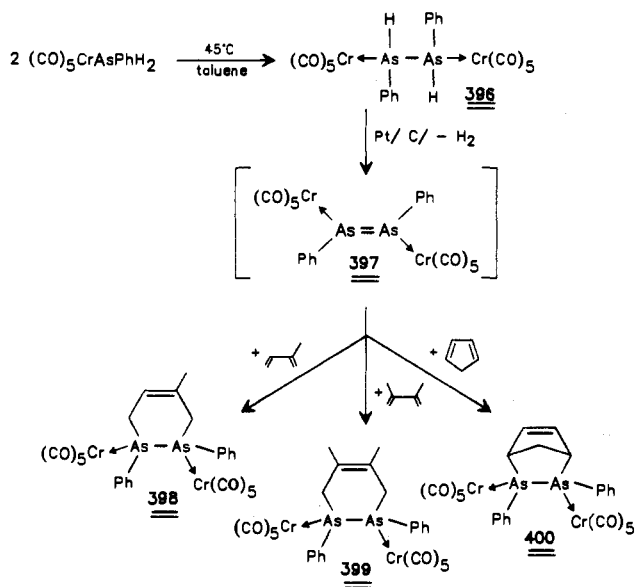
Scheme 220



Scheme 221



Scheme 222



Despite the instability of complex $(\text{CO})_5\text{WAs}(\text{Ph})=\text{As}(\text{Ph})\text{W}(\text{CO})_5$ (**393'**) with respect to its $(\eta^1:\eta^2)$ -isomer **393** it was possible to generate reactive $(\text{CO})_5\text{CrAs}(\text{Ph})=\text{As}(\text{Ph})\text{Cr}(\text{CO})_5$ (**397**) from the diarsene 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.

The synthetic strategy developed for the preparation of diphosphenyl complexes is also valid for the generation of the two isomeric forms of phosphaarsenyl

Scheme 223

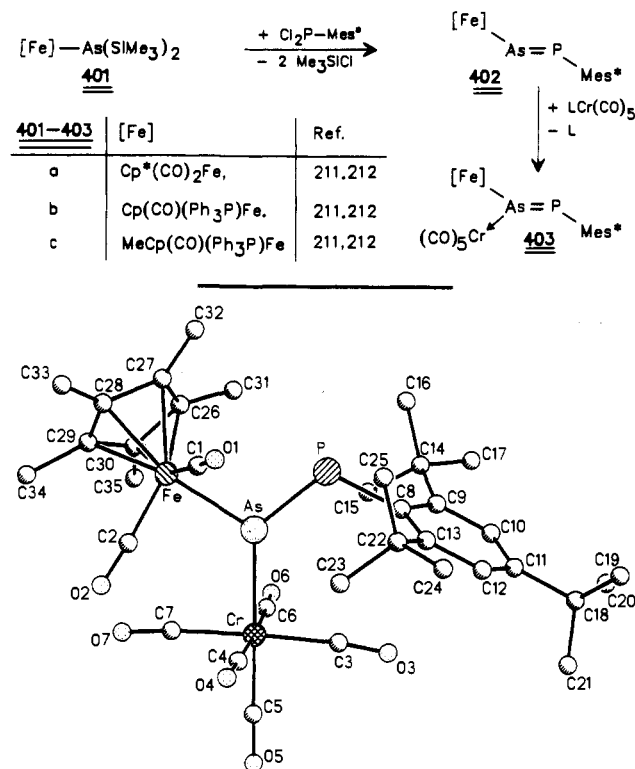
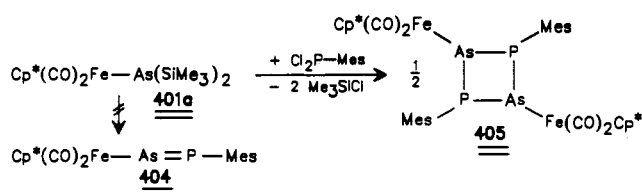


Figure 30. Molecular structure of $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeAs}[\text{Cr}(\text{CO})_5]=\text{PMes}^*$ (**403a**). Selected bond lengths (Å) and angles (deg): Fe–As 2.389 (1), As–P 2.155 (1), As–Cr 2.494 (1), P–C(8) 1.855 (5); Fe–As–P 102.2 (1), Fe–As–Cr 125.3 (1), Cr–As–P 131.4 (1), As–P–C(8) 112.1 (1). Reprinted from ref 212. Copyright 1988 VCH (Weinheim).

Scheme 224

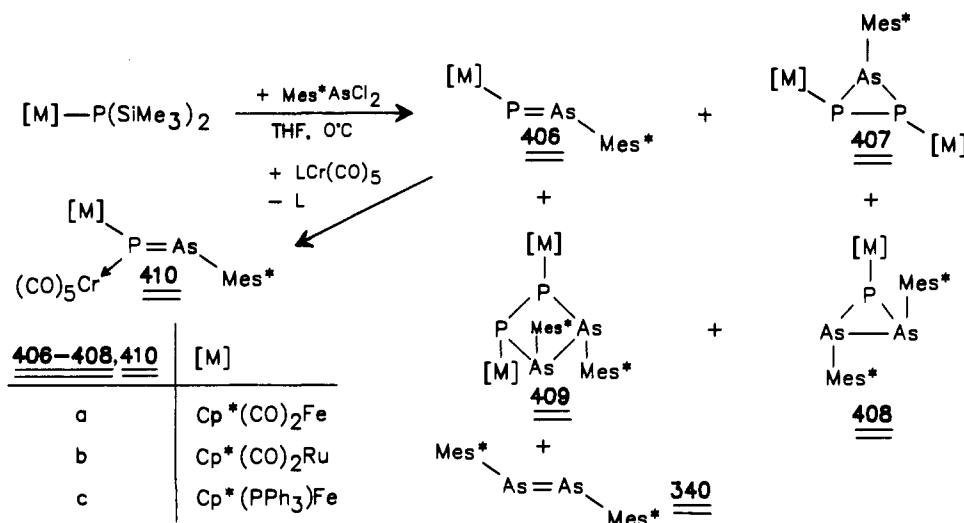


complexes $[\text{M}]\text{As}=\text{PR}$ and $[\text{M}]\text{P}=\text{AsR}$ (Scheme 223). The disilylarsenido iron complexes **401a**–**c** were converted by Mes^*PCl_2 into the corresponding phosphaarsenyl complexes **402a**–**c** with a Fe–As linkage. The derivatives containing a PPh_3 group as ancillary ligands **402b,c** are stable dark-red solids. The complex $\text{Cp}^*(\text{CO})_2\text{FeAs}=\text{PMes}^*$ (**402a**), however, suffered from rapid decomposition to $\text{Mes}^*\text{P}=\text{PMes}^*$ and other unidentified species.²¹¹ Trapping experiments with $[(Z)\text{-cyclooctene}]\text{Cr}(\text{CO})_5$ provided the stable dark-red $\text{Cr}(\text{CO})_5$ adduct **403a** which was subjected to an X-ray structure analysis.²¹²

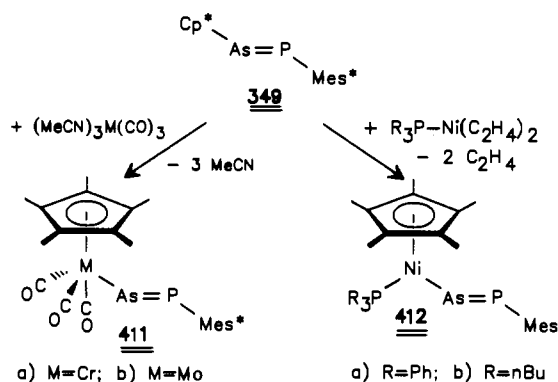
The molecular structure of **403a** (Figure 30) in the crystal turned out to be analogous to the corresponding diphosphenyl derivative $\text{Cp}^*(\text{CO})_2\text{FeP}[\text{Cr}(\text{CO})_5]=\text{PMes}^*$ (**289**). The compound features an *E*-configured unsupported $\text{As}=\text{P}$ double bond with the $\text{Cr}(\text{CO})_5$ unit attached to the arsenic atom.

At this point it should be emphasized that the formation and stability of the metallophosphaarsenes $[\text{M}]\text{As}=\text{PR}$ 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



Scheme 226



such as 404 was detected. Instead 1,3-diphospha-2,4-diarsetane (405) was isolated²¹¹ (Scheme 224).

Disilylphosphido complexes of iron and ruthenium underwent reaction with Mes*AsCl₂ to give phosphoarsenyl 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 formed²¹³ (Scheme 225).

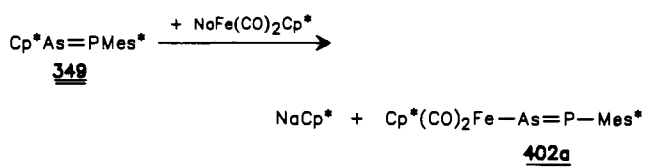
The phosphoarsenyl complexes 406a,b could not be isolated from the reaction mixture. But again the interception with [(Z)-cyclooctene]Cr(CO)₅ provided the stable Cr(CO)₅ derivatives 410a,b.²¹³

Phosphoarsenyl complexes of chromium and molybdenum 411a,b were synthesized by a different method, utilizing the lability of the Cp*-As σ-bond in phosphoarsene 349. This molecule experienced an oxidative addition to the metals with low coordinate numbers¹⁶⁷ (Scheme 226). The phosphoarsenyl complexes of nickel 412a,b, which were prepared analogously, resisted isolation due to their ready decomposition.^{98a}

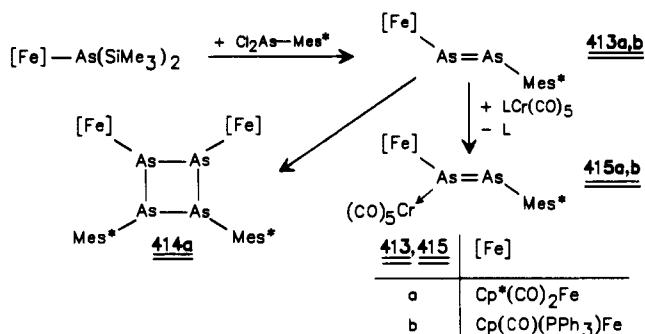
A third approach to a phosphoarsenyl metal complex was based upon the nucleophilic substitution of the pentamethylcyclooctadienyl ring in 349 by NaFe(CO)₂Cp*^{91b} (Scheme 227).

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*AsCl₂ in THF. Upon workup the cyclooctaarsane 414a was the only tractable product (Scheme 228). The inter-

Scheme 227



Scheme 228



ception 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 cyclooctaarsane 414a and [(Z)-cyclooctene]Cr(CO)₅ failed to produce the adduct 415a.^{214a,b}

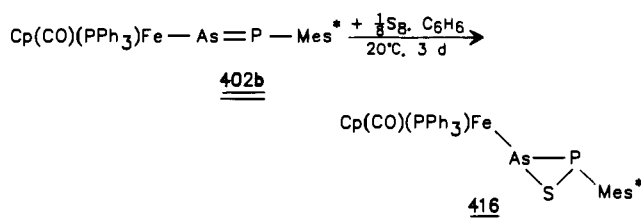
The X-ray structure analysis of 415a shows an *E*-configured diarsene with a free As=As bond of 2.259 (1) Å, where the Cr(CO)₅ unit is attached to the metalated arsenic atom, a situation well known from the analogous dipospheno- and phosphoarsenyl system.^{214b} The chromium arsenic bond distance of 2.492 (1) Å corresponds to a single bond.

XIV. Reactivity of Phosphoarsenyl Complexes

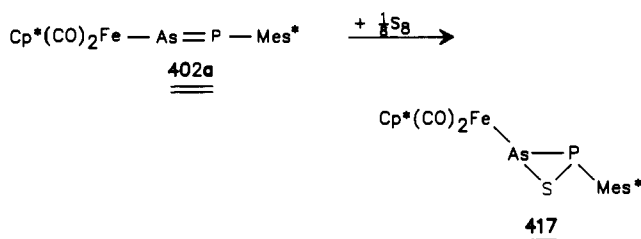
Essentially there exists only one account in the literature that is concerned with the chemical reactivity of phosphoarsenyl complexes.¹⁷⁰

The phosphoarsenyl 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 ³¹P NMR spectroscopy. The thermolability of Cp*(CO)₂FeAs=PMes* (402a) made

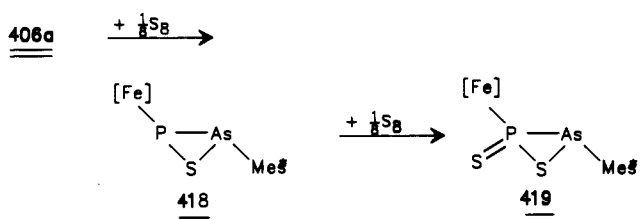
Scheme 229



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 pnictogen atom, and that the sulfur refused to insert into the Fe–P or Fe–As bonds.

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