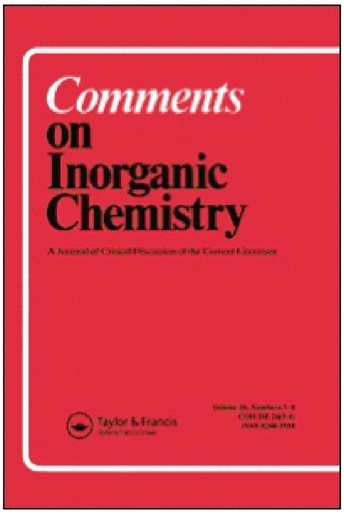

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Silylphosphanes

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Silylphosphanes

The chemistry of silylphosphanes has developed during the past 30 years. Silylphosphanes act as mild phosphorylating agents by means of Si–P bond cleavage and are finding increasing application in chemical syntheses involving the transfer of phosphido groups. Formation, cleavage and rearrangement reactions of silylphosphanes are described in this Comment.

1. FORMATION OF H_3Si-PH_2 AND ITS DERIVATIVES

The first hydrogen compound containing a Si–P bond was H_3Si-Ph_2 (bp = 12.7°C) prepared in 1953 by thermal decomposition of a mixture of SiH_4 and PH_3.[1] At 400°C SiH_4 decomposes through intermediates, yielding hydrogen and silicon, whereas thermal decomposition of PH_3 is observed only beyond 550°C. The first step in the decomposition of SiH_4 is

$$SiH_4 \longrightarrow SiH_3 + H. \qquad (1)$$

The following radical reactions

$$\begin{aligned} H \quad &+ PH_3 \longrightarrow PH_2 + H_2, \\ SiH_3 &+ PH_2 \longrightarrow H_3Si{-}PH_2 \end{aligned} \qquad (2)$$

determine the pyrochemical formation of H_3Si-PH_2 (450°C, reduced pressure). Formation of H_3Si-PH_2 from the hydrogen derivatives of the elements was later confirmed by electric discharge experiments using mixtures of gaseous SiH_4 and PH_3.[2] Formation of H_3Si-PI_2 and other silylphosphanes is reported from treating H_3SiI with white phosphorus.[3]

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As the preparation of larger product quantities by means of pyrochemical reactions is quite tedious, polar Si and P compounds were reacted in an attempt to favor formation of the Si–P bond by coincident salt precipitation:

$$\gtrdot\text{SiX} + \text{MP}\!\lessdot \longrightarrow \gtrdot\text{Si—P}\!\lessdot + \text{MX}; \qquad (3)$$

$$X = \text{Cl, Br, I}; \quad M = \text{alkali metal.}$$

In this manner $Me_3Si–P(C_6H_5)_2$ was prepared from Me_3SiCl and $NaP(C_6H_5)_2$.[4] However, reactions of H_3SiBr with KPH_2 yielded $(H_3Si)_3P$ due to stepwise proceeding metallation of all PH groups.[5] Silylphosphanes with functional groups at Si were first prepared as illustrated in Eq. (3) from silicon halides and $LiPEt_2$ ($Et = C_2H_5$)[6] which is soluble in ether and obtainable as a pure compound.[7] By this method $H_2MeSi–PEt_2$ ($Me = CH_3$), $H_3Si–PEt_2$, $Me_2ClSi–PEt_2$, $Cl_2Si(PEt_2)_2$, $Cl_3Si–PEt_2$, e.g., were generated which served for investigations of the reactivity of SiCl, SiH and SiP groups in silylphosphanes towards lithiating reagents.[8]

Silylphosphanes with one PEt_2 group which also contain the SiH moiety readily react on with the $LiPEt_2$ originally employed for the formation of the silylphosphane, yielding higher Si-phosphorylated compounds[8] without cleavage of Si–P bonds:

$$MeH_2SiPEt_2 + 2LiPEt_2 \longrightarrow MeSi[PEt_2]_3 + 2LiH. \qquad (4)$$

However, SiH containing silylphosphanes with several PEt_2 groups react differently: Li/H exchange and formation of $LiSi(PEt_2)_3$ occurs[8] as shown in Eq. (5):

$$HSi[PEt_2]_3 + LiPEt_2 \longrightarrow LiSi[PEt_2]_3 + HPEt_2. \qquad (5)$$

With Me_3SiCl this compound forms $Me_3Si–Si(PEt_2)_3$ quite as expected.

The demonstrated difficulties in the synthesis of PH-containing silylphosphanes arising from metallation of the PH group could be solved by developing a high-yield method for the preparation of $NaAl(PH_2)_4$[9] after $LiAl(PEt_2)_4$ had been found to be suitable for transferring PEt_2 groups to Si.[10] $NaAl(PH_2)_4$ may easily be prepared by reacting PH_3 with alkali metal in liquid NH_3 and after removal of NH_3 by treating the formed $NaPH_2$ with $AlCl_3$ in diglyme.[9] Quite correspondingly, $LiAl(PHMe)_4$[9] and $LiAl(PMe_2)_4$[11]

were obtained. These versatile compounds provided the prerequisites for the synthesis of PH-containing silylphosphanes. $H_3Si\text{-}PH_2$ was prepared from H_3SiBr and NaAl $(PH_2)_4$, $Me_3Si\text{-}PH_2$, $Me_xH_y\text{-}SiPH_2$, $Cl_xH_ySi\text{-}PH_2$ $(x + y = 3)$[9] were generated as well as $F_3Si\text{-}PH_2$.[12] Through $LiAl(PHMe)_4$, derivatives such as $Me_3\text{-}Si\text{-}PHMe$ became accessible which tend to rearrange, yielding $(Me_3\text{-}Si)_2PMe$ and $MePH_2$. This type of rearrangement occurs most easily with $H_3Si\text{-}PHMe$.[9] A convenient high-yield synthesis of $LiAl(PH_2)_4$ employs pure $LiPH_2 \cdot DME$[9] and $AlCl_3$ in diglyme, quite similar to the preparation of $NaAl(PH_2)_4$. Another less advantageous preparation of $LiAl(PH_2)_4$ is reported from reaction of $LiAlH_4$ with PH_3.[13]

2. CLEAVAGE OF THE Si-P BOND, AND APPLICATIONS OF THE CLEAVAGE IN SYNTHESIS

The chemistry of silylphosphanes is based on the methods of Si–P bond formation, of Si–P bond cleavage, and on the subsequent stabilizations by cyclization or rearrangement reactions.

A. Si–P Bond Cleavages

Due to the electronegativities of Si and P as well as to the high formation energies of Si–X (X = halogen), Si–O and Si–N bonds, silylphosphanes can be expected to exhibit facile cleavage of the Si–P bond and formation of the related silanes and phosphanes on treatment with HX and halides, H_2O and alcohols, NH_3 and amines, respectively. The reaction possibilities of $H_3Si\text{-}PH_2$ include the typical reactions of the Si–P bond, of the Si–H and P–H bonds. All silylphosphanes are sensitive to O_2. During the first investigations of $H_3Si\text{-}PH_2$ a variety of Si–P cleavage reactions was observed as depicted below:[1,14]

alkaline hydrolysis: $H_3Si—PH_2 + 4H_2O \xrightarrow{OH^-} Si(OH)_4 + 3H_2 + PH_3;$

acid hydrolysis: $H_3Si—PH_2 + H_2O \xrightarrow{H^+} H_3SiOH + PH_3,$

$H_3SiOH \xrightarrow{H^+} H_2$, Si oxihydrides, $SiH_4;$

alcoholysis: $\mathrm{H_3Si{-}PH_2 + C_2H_5OH \xrightarrow{OR^-} H_3Si{-}OC_2H_5 + PH_3}$,

$$\mathrm{H_3Si{-}OC_2H_5 + 3C_2H_5OH \xrightarrow{OR^-} Si(OC_2H_5)_4 + 3H_2}; \quad (6)$$

alcoholysis: (HCl) $\mathrm{H_3Si{-}PH_2 + C_2H_5OH \xrightarrow{HCl} H_3Si{-}OC_2H_5 + PH_3}$,

$\mathrm{H_3Si{-}OC_2H_5 \longrightarrow H_2, SiH_4}$,
SiH-containing alkoxypolysiloxanes;

liquid $\mathrm{NH_3}$: $\mathrm{H_3Si{-}PH_2 + NH_3 \longrightarrow}$ "$\mathrm{H_3Si{-}NH_2}$" + $\mathrm{PH_3}$,

"$\mathrm{H_3Si{-}NH_2}$" $\longrightarrow \mathrm{SiH_4}$
+ polymer SiH-containing SiN compounds;

HBr: $\mathrm{H_3Si{-}PH_2 + HBr \longrightarrow H_3SiBr + PH_3}$.

SiH- and SiCl-containing silylphosphanes rearrange[15] as shown in Eq. (7):

$$\begin{aligned} &\mathrm{2HClSi[PEt_2]_2 \longrightarrow H_2Si[PEt_2]_2 + Cl_2Si[PEt_2]_2},\\ &\mathrm{3H_2ClSi{-}PEt_2 \longrightarrow 2H_3Si{-}PEt_2 + Cl_3Si{-}PEt_2}. \end{aligned} \quad (7)$$

Because of Si–P bond cleavages

$$\mathrm{Cl_3Si{-}PEt_2 + H_3Si{-}PEt_2 \longrightarrow Cl_2Si[PEt_2]_2 + H_3SiCl}, \quad (8)$$

these are not reversible reactions. Also $\mathrm{HSiCl_3}$ may serve to cleave the Si–P bond[5]:

$$\mathrm{H_3Si{-}PEt_2 + HSiCl_3 \longrightarrow HCl_2Si{-}PEt_2 + H_3SiCl}. \quad (9)$$

B. Silylphosphane Adducts and Phosphonium Compounds; Formation of Cyclic B–P and Al–P Compounds

In organosubstituted silylphosphanes such as $\mathrm{Me_3Si{-}PEt_2}$ the Si–P bond is the only reactive bond. Reaction with EtI, and correspondingly with HI, occurs as shown in Eq. (10) if an excess of EtI is applied:

$$\mathrm{Me_3Si{-}PEt_2 + 2EtI \longrightarrow Me_3SiI + (Et_4P)I}. \quad (10)$$

With equimolar amounts at −78°C initially adducts such as $\mathrm{Me_3Si{-}PEt_2 \cdot EtI}$ are obtained which react by cleavage of the Si–P bond.[16] The ability to form phosphonium salts decreases with increasing electronegativity of the Si substituents. Thus $F_3Si{-}PH_2$ is found to form very weak adducts, and cleavage of the Si–P bond is possible only with certain strong Lewis acids.[12]

Formation of such adducts followed by Si–P bond cleavage provides a versatile method to generate new element–phosphorus compounds which could be demonstrated with adducts of $AlCl_3$, BF_3 or BCl_3, respectively.[17] The colorless crystals of $Me_3Si{-}PEt_2 \cdot AlCl_3$ decompose on warming to yield $Me_3SiCl + (Cl_2Al{-}PEt_2)_3$, and $Me_3Si{-}PEt_2 \cdot AlH_2Cl$ yields $Me_3SiH + (HClAl{-}PEt_2)_3$.[17] In an analogous manner $Me_3Si{-}PEt_2 \cdot BX_3$ generates $Me_3SiX + (Et_2P{-}BX_2)_3$ ($X = Cl, Br$).[18] Silylated transition metal complexes also were observed to yield silylphosphonium compounds such as $[Me_3SiPMe_3]^+ [Co(CO)_4]^-$ or $[(Me_3Si)_2PMe_2]^+ [Co(CO)_4]^-$ from $Me_3SiCo(CO)_4 + Me_3P$ or $Me_3Si{-}PMe_2$.[19]

C. Cleavages by Means of the C–Cl Group and by Acid Chlorides; Formation of P–C Multiple Bonds

Becker and Langer reported that $O{=}CCl_2$ at low temperatures cleaves $Me_3Si{-}Pph_2$ ($ph = C_6H_5$) to form carbonic acid bis(diphenylphosphide)[20]:

$$O{=}CCl_2 + 2Me_3Si{-}Pph_2 \longrightarrow O{=}C(Pph_2)_2 + 2Me_3SiCl. \qquad (11)$$

α-Chloroylidenemalonitrilediphenylphosphane may be obtained as reported by Issleib and Schmidt,[21]

$$(NC)_2C{=}CCl_2 + ph_2P{-}SiMe_3 \longrightarrow (NC)_2C{=}C(Cl)Pph_2 + Me_3SiCl, \qquad (12)$$

and α-aminoylidenemalonitrilephosphanes may be generated from 1-amino-1-chloro-2,2-dicyanoethylene and silylphosphanes[21]:

$$(NC)_2C{=}C(NH_2)Cl + Me_3Si{-}Pph_2 \longrightarrow (NC)_2C{=}C(NH_2){-}Pph_2 + Me_3SiCl. \qquad (13)$$

Transfer of a PR group also was used in the following reaction[21]:

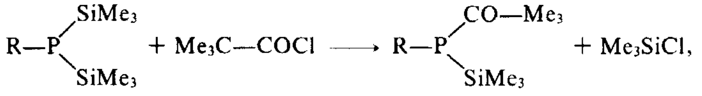
$$2(NC)_2C{=}C(R)Cl + phP(SiMe_3)_2 \longrightarrow [(NC)_2C{=}C(R)]_2Pph + 2Me_3SiCl. \qquad (14)$$

Cleavage of silylphosphanes by means of acid chlorides provides a method to prepare the related acid phosphides by transfer of the phosphido group[22] as shown in Eq. (15):

$$\text{aryl-COCl} + \text{Me}_3\text{Si—P(C}_6\text{H}_5)_2 \longrightarrow \text{aryl-CO—P(C}_6\text{H}_5)_2 + \text{Me}_3\text{SiCl}. \quad (15)$$

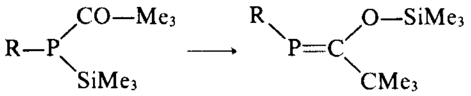
By treating Me_3Si–Pph_2 with oxalyl chloride, oxalic acid bis(diphenylphosphide) was generated, with phthalyl chloride also the related diphosphide, and in an analogous manner also squadric acid phosphide could be obtained.[23]

The versatility of the Si–P bond cleavage and the subsequent stabilization reactions was nicely demonstrated by Becker and co-workers.[24] Their synthesis of the P–C double bond starts with a Si–P cleavage in $RP(SiMe_3)_2$ with Me_3C–$COCl$,



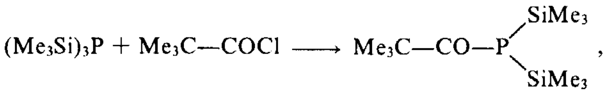
$$\text{R—P}(\text{SiMe}_3)_2 + \text{Me}_3\text{C—COCl} \longrightarrow \text{R—P}(\text{CO—Me}_3)(\text{SiMe}_3) + \text{Me}_3\text{SiCl}, \quad (16)$$

to generate the keto derivative which on warming rearranges to form the P–C double bond:



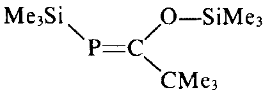
$$\text{R—P}(\text{CO—Me}_3)(\text{SiMe}_3) \longrightarrow \text{R—P=C}(\text{O—SiMe}_3)(\text{CMe}_3) \quad (17)$$

Quite similarly $(Me_3Si)_3P$ is cleaved:



$$(\text{Me}_3\text{Si})_3\text{P} + \text{Me}_3\text{C—COCl} \longrightarrow \text{Me}_3\text{C—CO—P}(\text{SiMe}_3)_2, \quad (18)$$

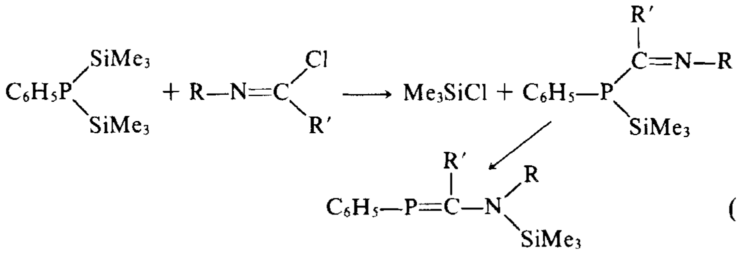
and rearrangement of the intermediate yields



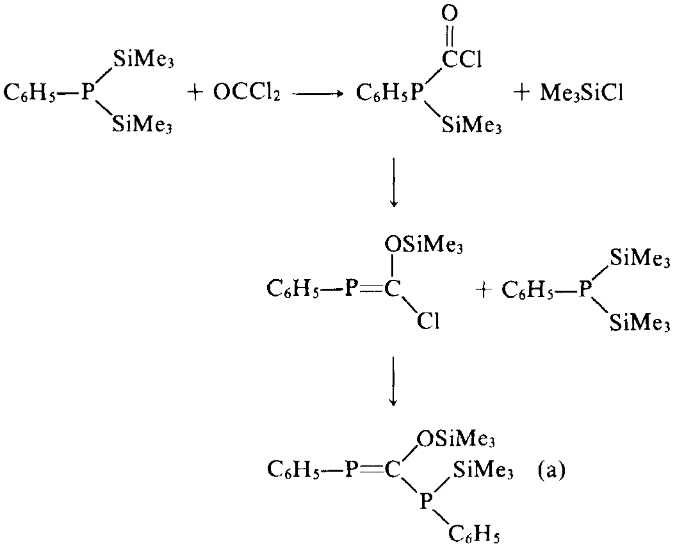
$$\text{Me}_3\text{Si—P=C}(\text{O—SiMe}_3)(\text{CMe}_3)$$

This derivative may eliminate $(Me_3Si)_2O$ (catalyzed by solid NaOH) to form Me_3C–C≡P according to recent investigations of Becker.[25]

A similar reaction principle was utilized by Issleib and co-workers[26] as well as by Appel and co-workers[27] in their investigations of the formation of molecules incorporating the P–C double bond. As reported by Issleib[26] the reaction of phP$(SiMe_3)_2$ with R-N=CR'Cl starts with cleavage of the Si-P bond which is followed by a rearrangement step:


(19)

The reaction of phP$(SiMe_3)_2$ with $COCl_2$ as reported by Appel[27] in its first steps takes place as depicted in Eq. (20) to yield (a) which reacts with $COCl_2$:


(20)

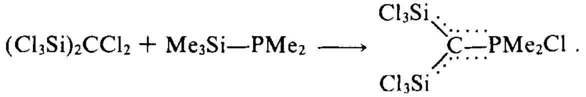
The reaction of phP$(SiMe_3)_2$ with R-N=CCl_2 proceeds through a similar cleavage and rearrangement mechanism.[29]

These cleavage reactions of the Si-P bond in silylphosphanes are caused by the favored formation of silylhalides. The observed rearrangements have to be attributed to the high stability of the newly formed Me_3Si-O or Me_3Si-N groups.

D. Cleavages by Means of Perchlorinated Carbosilanes; Formation of Ylides

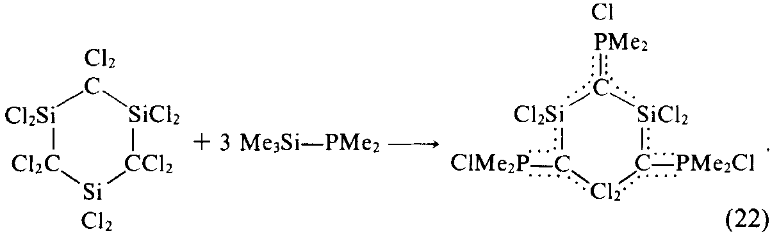
Further examples for the exploitation of Si–P bond cleavage and subsequent stabilization reactions of the initially formed intermediates are provided by the following reactions.

$(Cl_2Si\text{-}CH_2)_3$ can be phosphorylated by means of $Me_3Si\text{-}PMe_2$, and treatment of $(HBrSi\text{-}CH_2)_3$ with three moles of $Me_3Si\text{-}PMe_2$ produces $[(Me_3P)HSi\text{-}CH_2]_3$.[30] The Si–P cleavage proceeds from the SiCl group. In perchlorinated carbosilanes as $(Cl_3Si)_2CCl_2$ or $(Cl_2Si\text{-}CCl_2)_3$ the reactivity of the CCl group is considerably enhanced and can be used for a quantitative cleavage of the Si–P bond as was demonstrated in reactions of $Me_3Si\text{-}PMe_2$ with $(Cl_3Si)_2CCl_2$ and $(Cl_2Si\text{-}CCl_2)_3$[31]:



$$(Cl_3Si)_2CCl_2 + Me_3Si\text{—}PMe_2 \longrightarrow (Cl_3Si)_2C\text{—}PMe_2Cl\,. \qquad (21)$$

Instead of the initially formed intermediate containing a >C(Cl)-PMe_2 moiety (tetrahedral coordination of the C atom), which is not a stable compound, the ylide is generated by quantitative rearrangement. An x-ray structure determination as well as a ^{31}P NMR study show the planar arrangement of the molecule (sp^2 hybridization) and a significant shortening of the Si–C distance to 177 pm from a norm of 190 pm. Quite correspondingly, $(Cl_2Si\text{-}CCl_2)_3$ reacts as shown in Eq. (22):

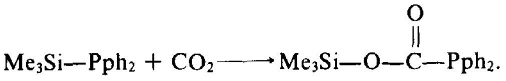


(22)

Formation of the ylide which occurs subsequent to the cleavage forces the six-membered ring of the starting molecule to rearrange from the chair form to the planar form.[31] The same products result from treating the appropriate starting substances with $LiPMe_2$. The above drawing was chosen to express the observed bond shortening and the missing ionic character of the product.

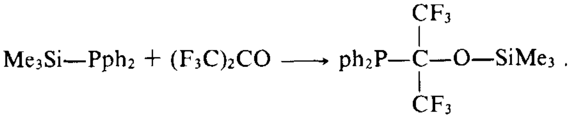
E. Insertions into the Si-P Bond

The reactivity of the Si-P bond allows for insertions of carbonyl compounds as demonstrated in Eq. (23)[32]:



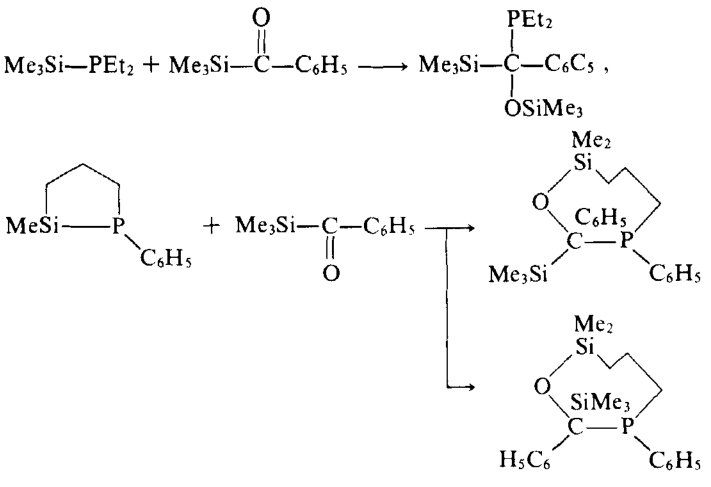
$$Me_3Si—Pph_2 + CO_2 \longrightarrow Me_3Si—O—\overset{\overset{\large O}{\|}}{C}—Pph_2. \qquad (23)$$

Also $H_2C{=}C{=}O$ may be inserted, and the reaction with $(F_3C)_2CO$ proceeds as shown in Eq. (24)[32]:



$$Me_3Si—Pph_2 + (F_3C)_2CO \longrightarrow ph_2P—\underset{\underset{\large CF_3}{|}}{\overset{\overset{\large CF_3}{|}}{C}}—O—SiMe_3 . \qquad (24)$$

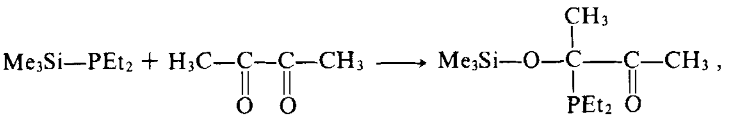
Further examples are given in Eq. (25)[33]:



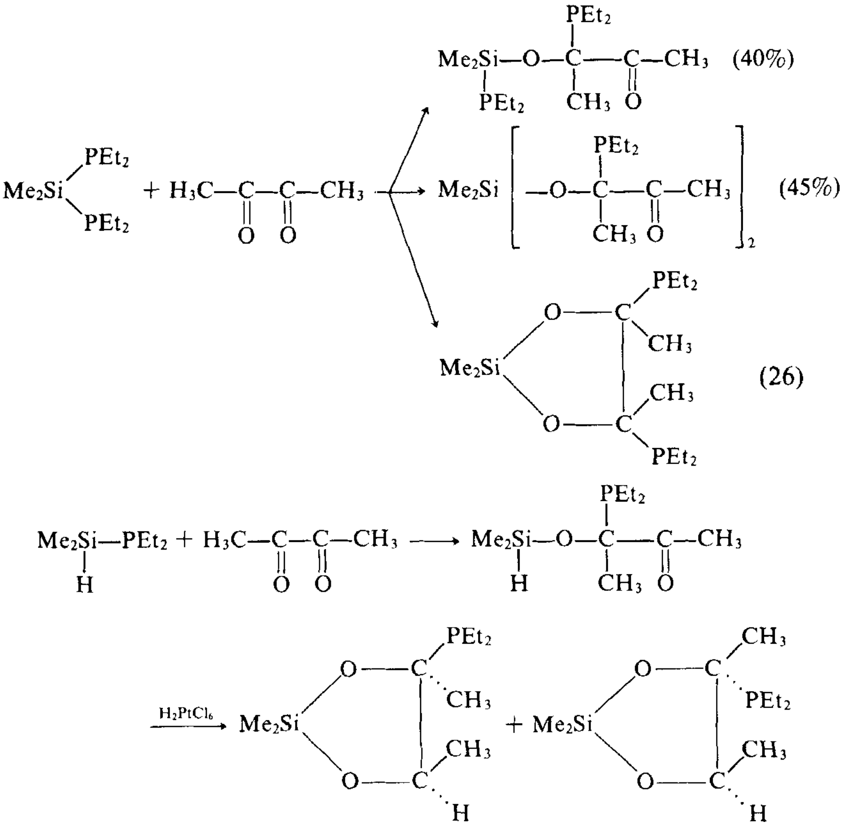
$$Me_3Si—PEt_2 + Me_3Si—\overset{\overset{\large O}{\|}}{C}—C_6H_5 \longrightarrow Me_3Si—\underset{\underset{\large OSiMe_3}{|}}{\overset{\overset{\large PEt_2}{|}}{C}}—C_6C_5 ,$$

(25)

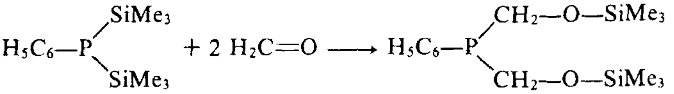
The following reactions of diketones have been reported[34]:



$$Me_3Si—PEt_2 + H_3C—\underset{\underset{\large O}{\|}}{C}—\underset{\underset{\large O}{\|}}{C}—CH_3 \longrightarrow Me_3Si—O—\underset{\underset{\large PEt_2}{|}}{\overset{\overset{\large CH_3}{|}}{C}}—\underset{\underset{\large O}{\|}}{C}—CH_3 ,$$

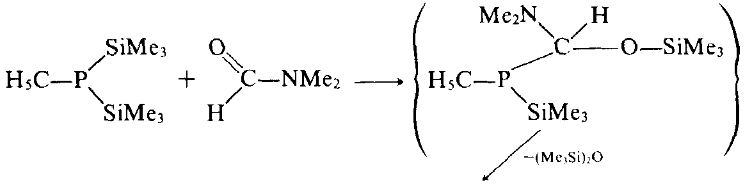

(26)

Formaldehyde reacts as shown in Eq. (27)[35]:

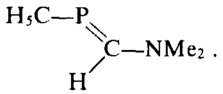


$$H_5C_6{-}P(SiMe_3)_2 + 2\,H_2C{=}O \longrightarrow H_5C_6{-}P(CH_2{-}O{-}SiMe_3)_2 \quad (27)$$

Dimethylformaldehyde undergoes a similar reaction as depicted in Eq. (28)[35]:



$$H_5C{-}P(SiMe_3)_2 + O{=}C(H){-}NMe_2 \longrightarrow \left(H_5C{-}P(SiMe_3){-}C(H)(NMe_2){-}O{-}SiMe_3 \right) \xrightarrow{-(Me_3Si)_2O}$$



(28)

3. P-METALLATED SILYLPHOSPHANES

A. Metallation of Silylphosphanes with PH Groups

Silylphosphanes with PH groups as Me_3SiPH_2 or $H_3Si{-}PH_2$ may be metallated by $LiPEt_2$ without cleavage of the Si–P bond,[36]

$$H_3Si{-}PH_2 + 2LiPEt_2 \longrightarrow H_3Si{-}PLi_2 + 2HPEt_2, \qquad (29)$$

and subsequently Li may be diplaced by CH_3Cl to yield $H_3Si{-}PMe_2$. Compounds of the type $H_{3-x}Me_xSi{-}PHLi$ are accessible by treating PH-containing derivatives with LiPHMe[36]:

$$H_3Si{-}PH_2 + LiPHMe \longrightarrow H_3Si{-}PHLi + MePH_2, \qquad (30)$$

which undergo disproportionation at room temperature in ether solutions as shown in Eq. (31):

$$2H_3Si{-}PHLi \longrightarrow (H_3Si)_2PLi + LiPH_2. \qquad (31)$$

With $AlCl_3$ the monolithiated derivatives produce compounds of the type shown in Eq. (32):

$$4H_3SiPHLi + AlCl_3 \longrightarrow LiAl(PHSiH_3)_4 + 3LiCl. \qquad (32)$$

B. Cleavage of the Si-P Bond

In silylphosphanes as H_3SiPEt_2 the SiH group may be substituted by $LiPEt_2$. Lithium alkyls, however, cleave the Si–P bond[8]:

$$HSi(PEt_2)_3 + LiMe \longrightarrow MeSiH(PEt_2)_2 + LiPEt_2. \qquad (33)$$

This Si–P cleavage by lithium alkyls may be applied to $(Me_3Si)_3P$ and goes fairly completely at −40°C in DME[37]:

$$(Me_3Si)_3P + BuLi \longrightarrow (Me_3Si)_2PLi \cdot DME + BuSiMe_3. \qquad (34)$$

A related cleavage of $(Me_3Si)_3P$ in DME is also possible with $LiPEt_2$ or LiPHMe at 0–20°C. Cleavage of a second Si–P bond to produce the dimetallated silylphosphane does not occur. The ether free lithium phosphide is accessible in hydrocarbon solution:

$$(Me_3Si)_2PH + BuLi \xrightarrow[\text{pentane}]{\text{cyclopentane}} (Me_3Si)_2PLi + BuH. \tag{35}$$

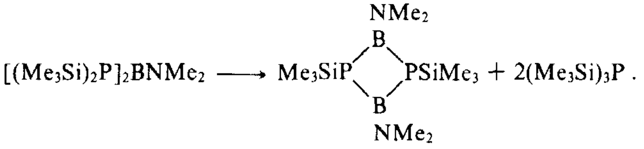
$(Me_3Si)_2PLi$ is a white crystalline compound which ignites spontaneously in air.

4. REACTIONS OF $(Me_3Si)_2PLi \cdot 2THF$ WITH HALIDES OF MAIN GROUP ELEMENTS, AND REARRANGEMENTS OF THE NOVEL PHOSPHANES

$(Me_3Si)_2PLi \cdot 2THF$ is a most versatile source of the $(Me_3Si)_2P$ group which may be transferred easily to halides of main group elements, and, by the various reaction possibilities of such novel phosphanes, provides many interesting opportunities in the chemistry of silylphosphanes. As an example the reactions with $(Me_2N)BCl_2$[38] are shown:

$$\begin{aligned} &(Me_3Si)_2PLi \cdot 2THF + (Me_2N)BCl_2 \longrightarrow \\ &\qquad (Me_3Si)_2P{-}B(NMe_2)Cl + LiCl + 2THF, \\ &2(Me_3Si)_2PLi \cdot 2THF + (Me_2N)BCl_2 \longrightarrow \\ &\qquad [(Me_3Si)_2P]_2BNMe_2 + 2LiCl + 4THF. \end{aligned} \tag{36}$$

The last product rearranges thermally:



(37)

Similar to the formation of $(Me_3Si)_2PLi \cdot 2THF$, derivatives with SiH groups such as $(Me_2HSi)_2PLi \cdot DME$ may be prepared. This substance was treated with $(Me_2N)_2BCl$:

$$\begin{aligned} &(Me_2HSi)_2PLi \cdot DME + (Me_2N)_2BCl \longrightarrow \\ &\qquad (Me_2HSi)_2P{-}B(NMe_2)_2 + LiCl + DME. \end{aligned} \tag{38}$$

At elevated temperatures the following rearrangement occurs[39]:

$$3(Me_2HSi)_2P{-}B(NMe_2)_2 \longrightarrow 2(Me_2HSi)_3P + [(Me_2N)_2B]_3P. \tag{39}$$

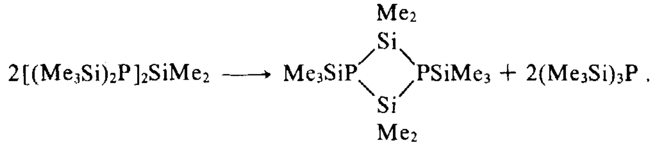
The reaction of $(Me_3Si)_2PLi \cdot 2THF$ with CH_2Cl_2 is shown in Eq. (40):

$$2(Me_3Si)_2PLi \cdot 2THF + CH_2Cl_2 \longrightarrow [(Me_3Si)_2P]_2CH_2 + 2LiCl; \quad (40)$$

and with Me_2SiCl_2 in Eq. (41):

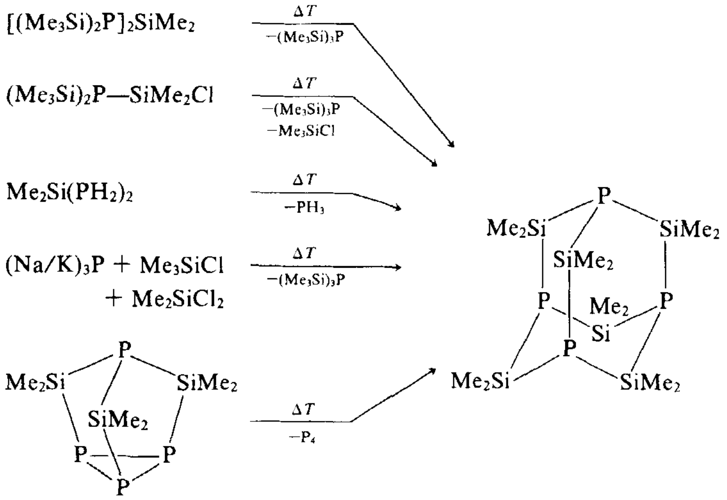
$$2(Me_2Si)_2PLi \cdot 2THF + Me_2SiCl_2 \longrightarrow [(Me_3Si)_2P]_2SiMe_2 + 2LiCl. \quad (41)$$

Slow formation of $(Me_3Si)_3P$ at 20–60°C indicates a gradual decomposition of the latter compound, whereas short-time thermolysis at about 220°C renders complete rearrangement:



$$2[(Me_3Si)_2P]_2SiMe_2 \longrightarrow Me_3SiP\overset{Me_2Si}{\underset{SiMe_2}{\diamond}}PSiMe_3 + 2(Me_3Si)_3P\,. \quad (42)$$

On prolonged thermolysis (38 h, 200°C, sealed tube) an additional rearrangement again eliminating $(Me_3Si)_3P$ yields $(Me_2Si)_6P_4$, a silylphosphane with adamantane structure.[40,41] This obviously very favored crystalline compound (stable beyond 400°C in a sealed tube) is very commonly generated in a number of similar reactions as demonstrated in Eq. (43):



(43)

Just as expected $(Me_3Si)_2PLi \cdot 2THF$ reacts also with phosphorus compounds such as $ClP(C_6H_5)_2$ and $ClPMe_2$ to produce $(Me_3Si)_2$-P-$P(C_6H_5)_2$ or $(Me_3Si)_2P$-PMe_2.[39]

Of particular interest are the reactions with $MePCl_2$, $C_6H_5PCl_2$ and $t\text{-}BuPCl_2$ ($t\text{-}Bu = t\text{-}C_4H_9$),[42] an example of which is shown in Eq. (44):

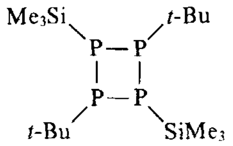
$$2(Me_3Si)_2PLi\cdot 2THF + MePCl_2 \longrightarrow [(Me_3Si)_2P]_2PMe + 2LiCl + 4THF. \quad (44)$$

Both $[(Me_3Si)_2P]_2PMe$ and $[(Me_3Si)_2P]_2PC_6H_5$ form colorless crystals, and tend to give cyclic phosphanes at 120–130°C. Thus, mixtures of $(Me_3Si)_3P$, $(Me_3Si)_2PH$ and of variously substituted five-membered P rings such as $P_5(SiMe_3)_3Me_2$, $P_5(SiMe_3)_2Me_3$ and $P_5(SiMe_3)Me_4$ may be obtained (120°C, 60 h) from $[(SiMe_3)_2P]_2PMe$, and at even higher temperature (170°C, 60 h) $P_7(SiMe_3)_3$ and $P_7(SiMe_3)_2Me$ are also generated. $[(Me_3Si)_2P]_2PC_6H_5$ reacts in quite an analogous manner.

The reaction of $(Me_3Si)_2PLi\cdot 2THF$ with $t\text{-}BuPCl_2$ in pentane proceeds as illustrated in Eq. (45):

$$4(Me_3Si)_2PLi\cdot 2THF + 2t\text{-}BuPCl_2 \longrightarrow$$

$$2(Me_3Si)_2P\text{—}P(t\text{-}Bu)\text{—}P(SiMe_3)_2 \longrightarrow$$

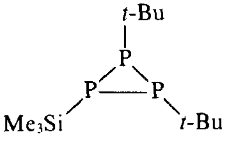


$$+ 2(Me_3Si)_3P. \quad (45)$$

Subsequent photolysis mainly produces mixtures of five-membered P rings such as $P_5(SiMe_3)_3(t\text{-}Bu)_2$, and prolonged irradiation produces both higher molecular compounds with even more P atoms, as $P_9(t\text{-}Bu)_3$, and $(Me_3Si)_3P$. In a mole ratio of 1:1 $(Me_3Si)_2PLi\cdot 2THF$ reacts with $t\text{-}BuPCl_2$ as depicted in Eq. (46)[42].

$$(Me_3Si)_2PLi\cdot 2THF + t\text{-}BuPCl_2 \longrightarrow$$

$$(Me_3Si)_2P\text{—}P(t\text{-}Bu)Cl + LiCl + 2THF \xrightarrow{20°C}$$



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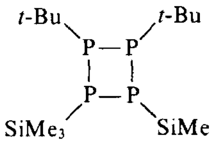

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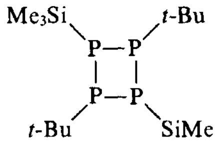
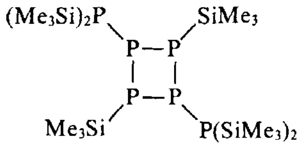

$+ (Me_3Si)_3P + Me_3SiCl\,. \qquad (46)$

Also the reaction with $Me_2N\text{-}PCl_2$[36] takes a similar course, and again $(Me_3Si)_3P$ is formed in side reactions.

$$2(Me_3Si)_2PLi \cdot 2THF + Me_2N\text{—}PCl_2 \longrightarrow$$

$$(Me_3Si)_2P\text{—}P(NMe_2)\text{—}P(SiMe_3)_2 + 2LiCl + 4THF \xrightarrow{20°C}$$


$+ 2Me_3Si\text{—}NMe_2\,. \qquad (47)$

Further P-functional silylphosphanes may be prepared from $(Me_3Si)_2PLi \cdot 2THF$ and PCl_3 at $-78°C$ in cyclopentane. The reaction sequence is given in Eqs. (48):

$$\begin{aligned}
&(Me_3Si)_2PLi \cdot 2THF + PCl_3 \longrightarrow (Me_3Si)_2P\text{—}PCl_2 + LiCl,\\
&(Me_3Si)_2P\text{—}PCl_2 + (Me_3Si)_2PLi \cdot 2THF \longrightarrow [(Me_3Si)_2P]_2PCl + LiCl,\\
&[(Me_3Si)_2P]_2PCl + (Me_3Si)_2PLi \cdot 2THF \longrightarrow \qquad (48)\\
&\qquad\qquad [(Me_3Si)_2P]_2P\text{—}P(SiMe_3)_2 + LiCl,\\
&[(Me_3Si)_2P]_2P\text{—}P(SiMe_3)_2 \xrightarrow{20°C} 2(Me_3Si)_3P + 2P.
\end{aligned}$$

Attempted trapping of products containing PCl groups by means of *t*-BuLi mainly results in the formation of $[(Me_3Si)_2P]_2PH$ which may be isolated as white crystals:

$$[(Me_3Si)_2P]_2PCl + Me_3CLi \longrightarrow [(Me_3Si)_2P]_2PH + Me_2C{=}CH_2 + LiCl. \qquad (49)$$

In a remarkably different reaction $(Me_3Si)_2PLi \cdot 2THF$ with PCl_3 and an excess of *t*-BuLi generates at 20°C among other compounds the four-membered ring $(Me_3C)_3P_4(SiMe_3)$, $(Me_3Si)_3P$ and Li_3P_7. The reactions of $(Me_3Si)_3P$ with PCl_3 as summarized in Eqs. (50)[43] start at $-78°C$ with cleavage of the Si–P bond:

$$
\begin{gathered}
(Me_3Si)_3P + PCl_3 \longrightarrow (Me_3Si)_2P{-}PCl_2 + Me_3SiCl,\\
(Me_3Si)_2P{-}PCl_2 + Me_3CLi \longrightarrow (Me_3Si)_2PLi + Me_3C{-}PCl_2,\\
(Me_3Si)_2PLi + (Me_3Si)_2P{-}PCl_2 \longrightarrow [(Me_3Si)_2P]_2PCl + LiCl, \qquad (50)\\
Me_3C{-}PCl_2 + (Me_3Si)_2PLi \longrightarrow (Me_3Si)_2P{-}PCl(CMe_3) + LiCl,\\
[(Me_3Si)_2P]_2PH + Me_3CLi + Me_3SiCl \longrightarrow\\
[(Me_3Si)_2P]_2PSiMe_3 + Me_3CH + LiCl.
\end{gathered}
$$

and on addition of *t*-BuLi also cleavage of the P–P bond occurs to give $(Me_3Si)_2PLi$ and Me_3CPCl_2. The following steps are quite common reactions and lead to the denoted compounds. The reactions of transition metal complexes with silylphosphanes are dealt with in Section 6.

5. REARRANGEMENT REACTIONS OF SILYLOLIGOPHOSPHANES INDUCED BY P METALLATION

The cleavage of $(Me_3Si)_3P$ with *t*-BuLi in THF yielding $(Me_3Si)_2PLi \cdot 2THF$ (isolable as colorless crystals)[37] delivers a most valuable synthetic intermediate. When this method is applied to $(Me_3Si)_2P{-}P(SiMe_3)_2$ the reaction takes the same course:

$$
\begin{gathered}
(Me_3Si)_2P{-}P(SiMe_3)_2 + t\text{-}BuLi \longrightarrow\\
(Me_3Si)_2P{-}P(Li)SiMe_3 + Me_3Si{-}t\text{-}Bu, \qquad (51)
\end{gathered}
$$

but the lithiated derivative cannot be isolated. Instead $(Me_3Si)_3P$, $(Me_3Si)_2PLi$, Li_3P_7 [45] and further, as yet not fully identified species appear as reaction products. A series of ^{31}P NMR spectra recorded at increasing temperatures from −80–20°C reveals the course of the reaction[44] which initially is determined by the lithiation step shown in Eq. (51). $(Me_3Si)_2P{-}P(Li)SiMe_3$ then reacts to form $(Me_3Si)_3P$, $(Me_3Si)_2PLi$ and Li_3P_7, and there are indications for another precursor of Li_3P_7. That indeed the lithiated diphosphane initiates the observed rearrangement is proven by the reaction of $(Me_3Si)_2P{-}PHSiMe_3$:

$$
(Me_3Si)_2P{-}P(H)SiMe_3 + t\text{-}BuLi \longrightarrow
$$

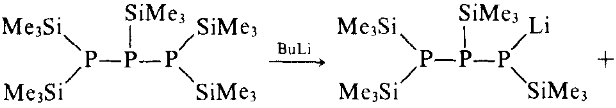
$$\begin{tikzcd}(\mathrm{Me_3Si})_2\mathrm{P{-}P(Li)SiMe_3} + t\text{-}\mathrm{BuH} \arrow[d] \\ (\mathrm{Me_3Si})_3\mathrm{P} + (\mathrm{Me_3Si})_2\mathrm{PLi} + \mathrm{Li_3P_7},\end{tikzcd} \tag{52}$$

which is found to proceed analogously.

It is interesting within this context to note that $[(\mathrm{Me_3Si})_2\mathrm{P}]_2\mathrm{PH}$ with t-BuLi in pentane solution generates conveniently isolable $[(\mathrm{Me_3Si})_2\mathrm{P}]_2\mathrm{PLi}$, which easily may be substituted by methylchloride or trimethylchlorosilane[44]:

$$\begin{tikzcd}[column sep=small] & {[(\mathrm{Me_2Si})_2\mathrm{P}]_2\mathrm{PH} + t\text{-}\mathrm{BuLi}} \arrow[d, "n\text{-pentane}"] & \\ & {[(\mathrm{Me_3Si})_2\mathrm{P}]_2\mathrm{PLi} + t\text{-}\mathrm{BuH}} \arrow[dl, "\mathrm{MeCl}"'] \arrow[dr, "\mathrm{Me_3SiCl}"] & \\ {[(\mathrm{Me_3Si})_2\mathrm{P}]_2\mathrm{PMe}} & & {[(\mathrm{Me_3Si})_2\mathrm{P}]_2\mathrm{P{-}SiMe_3}}\end{tikzcd} \tag{53}$$

A significantly different behavior is observed if polar solvents such as DME are employed.[44] Colorless crystals of $\mathrm{Li_3P_7}$ and of $(\mathrm{Me_3Si})_2\mathrm{PLi}\cdot\mathrm{DME}$ precipitate after concentrating the reaction mixture, and $(\mathrm{Me_3Si})_3\mathrm{P}$ as well as a red greasy residue remain. As indicated by variable-temperature ^{31}P NMR, $[(\mathrm{Me_3Si})_2\mathrm{P}]_2\mathrm{PH}$ initially is lithiated by t-BuLi in THF solution, e.g., to give $[(\mathrm{Me_3Si})_2\mathrm{P}]_2\mathrm{PLi}$. This rearranges to $(\mathrm{Me_3Si})_2\mathrm{P{-}PSiMe_3{-}P(Li)SiMe_3}$, which generates $(\mathrm{Me_3Si})_3\mathrm{P}$, $(\mathrm{Me_3Si})_2\mathrm{PLi}$ and an oligophosphorus species. This still unidentified intermediate eventually is used up to form $\mathrm{Li_3P_7}$, $(\mathrm{Me_3Si})_2\mathrm{PLi}$ and $(\mathrm{Me_3Si})_3\mathrm{P}$. Isomerization by Li/(SiMe$_3$) migration is deemed to be the determining reaction in the observed sequence. Another silylphosphane, $[(\mathrm{Me_3Si})_2\mathrm{P}]_2\mathrm{PSiMe_3}$ treated with n-BuLi under same conditions, provides certain proof for this reaction step.[44] For statistical and steric reasons at first a terminal P atom is lithiated:

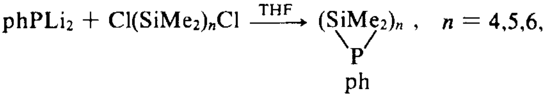

(54)

This intermediate reacts further as previously described to produce $(\mathrm{Me_3Si})_3\mathrm{P}$, $(\mathrm{Me_3Si})_2\mathrm{PLi}$ and $\mathrm{Li_3P_7}$. These results prompted investigation into whether the Me_3Si groups in $(Me_3Si)_3P_7$ might successively be displaced by *t*-BuLi to yield eventually Li_3P_7, i.e., without cleavage of the P_7 skeleton. Detailed studies hint at a quite complicated mechanism[44] and indicate that the primary lithiation product $Li(Me_3Si)_2P_7$ in a not yet fully elucidated manner reacts to yield eventually Li_3P_7 as well as $(Me_3Si)_2PLi$ and $(Me_3Si)_3P$.

Each of the oligophosphanes $(Me_3Si)_4P_2$, $[(Me_3Si)_2P]_2PH$, $[(Me_3Si)_2P]_2PSiMe_3$ and $(Me_3Si)_3P_7$ in DME solution with lithiating reagents finally yields Li_3P_7, $(Me_3Si)_2PLi$ and $(Me_3Si)_3P$ besides small amounts of a red solid which is mainly composed of red phosphorus. Obviously, the first lithiating attack determines the following rearrangement reactions via formation of in some cases short-lived intermediates. The formation of $(Me_3Si)_3P$ observed in any of the mentioned cases is due to desilylation of starting or intermediate compounds, and thus causes formation of new P–P bonds. $(Me_3Si)_2PLi$ is formed in lithium-exchange and cleavage reactions, both of which undoubtedly play a determining role. It should be emphasized that quite general importance has to be attributed to the above described reactions.

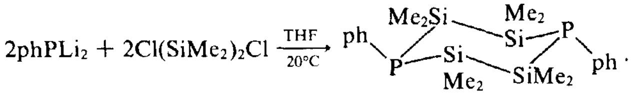
6. CYCLIC SILYLPHOSPHANES

Whereas the chemistry of simple silylphosphanes has been continuously developing for many years there is only relatively modest knowledge available on cyclic silylphosphanes. Even though as early as in 1959 the formation of cyclic silylphosphanes from the reaction of lithium phosphides with $(H_5C_2)_2SiCl_2$ was claimed,[46] investigations in this area cannot be regarded as complete. Schumann and Benda[47] reported the formation of $(ph_2Si{-}Pph)_2$ and $(ph_2Si{-}Pph)_3$ from ph_2SiCl_2 and K_2Pph ($ph = C_6H_5$). West and coworkers[48] extended this reaction principle to the preparation of novel cyclic compounds,

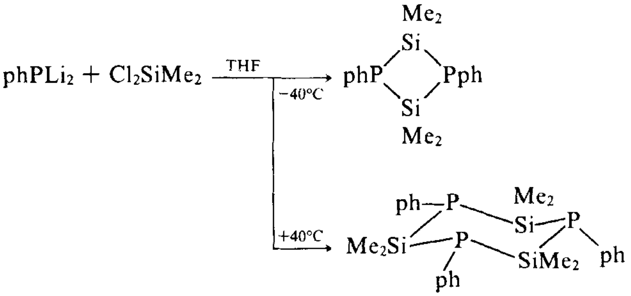


$$\mathrm{phPLi_2 + Cl(SiMe_2)_nCl \xrightarrow{THF} \underset{\underset{ph}{P}}{(SiMe_2)_n}}\ , \quad n = 4,5,6, \tag{55}$$

but found $Cl(SiMe_2)_2Cl$ and Cl_2SiMe_2 to react in a slightly different way:



(56)

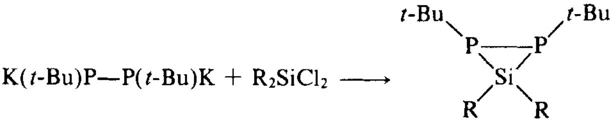


(57)

Elevated temperatures favor the formation of larger ring sizes. The following equilibrium reaction is reported to occur at 150°C:

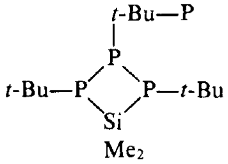
$$(phP—SiMe_2)_2 \xrightleftharpoons{150°C} (phP—SiMe_2)_3. \qquad (58)$$

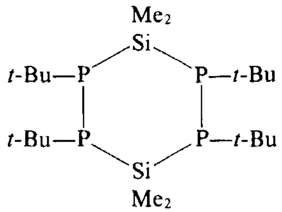
Baudler and co-workers[49] studied the synthesis of diphosphasiliranes which proceeds at −40–20°C as shown in Eq. (59),

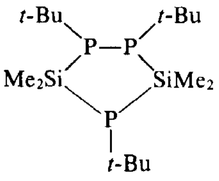


, R=Me, ph (59)

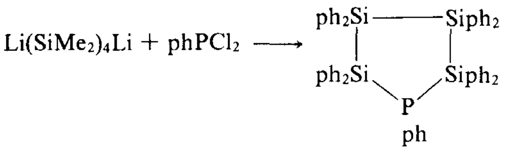
but which at slightly elevated temperature (up to 36°C) gives lower yields of the three-membered ring compound in favor of larger ring sizes as depicted below:







Another cyclic Si compound incorporating a hetero P atom may be prepared as demonstrated in Eq. (60):



(60)

Rearrangements of silylphosphanes containing the PHMe group[9]

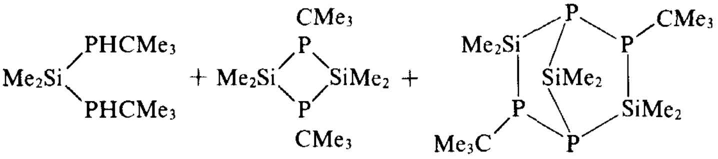
$$2Me_2HSi{-}PHMe \longrightarrow (Me_2HSi)_2PMe + MePH_2 \qquad (61)$$

provide a further entry into the chemistry of cyclic silylphosphanes. A four-center mechanism appears to account for the formation of these compounds. Introduction of two PHMe groups as in the attempted preparation of $Me_2Si(PHMe)_2$ results in such rearrangement reactions[51]:

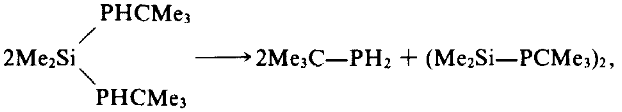
$$3Me_2SiCl_2 + 6LiPHMe \longrightarrow (Me_2Si{-}PMe)_3 + 3MePH_2 + 6LiCl. \qquad (62)$$

$(MeHSi{-}PMe)_3$ may be prepared similarly.

Bulky substituents apparently give rise to different reaction pathways. $(Me_3C)_2SiCl_2$ and LiPHMe generate the four-membered ring $[(Me_3C)_2Si{-}PMe]_2$ whereas Me_2SiCl_2 and $LiPHCMe_3$[51] produce $Me_3C{-}PH_2$ and



The bulky Me_3C group permits isolation of $Me_2Si(PHCMe_3)_2$ which is found to rearrange thermally:



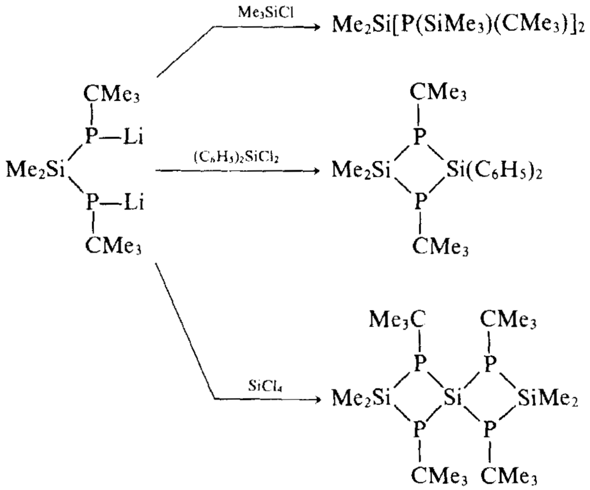
$$2Me_2Si(PHCMe_3)_2 \longrightarrow 2Me_3C{-}PH_2 + (Me_2Si{-}PCMe_3)_2, \qquad (63)$$

as was shown by a study of formation reactions of the cyclic compounds.

The dilithium derivative of $Me_2Si(PHCMe_3)_2$,

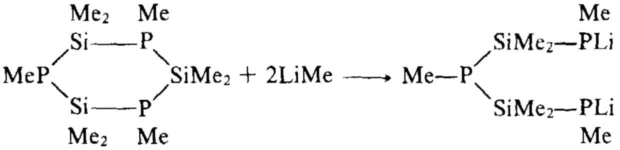
$$Me_2Si[PH(CMe_3)]_2 + 2n\text{-}C_4H_9Li \longrightarrow Me_2Si[PLi(CMe_3)]_2 + 2C_4H_{10}, \qquad (64)$$

may be employed in a variety of synthetic reactions.[51]



(65)

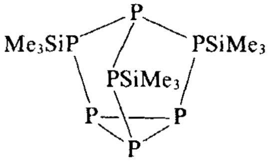
The well known cleavage reactions may be applied to the above described cyclic silylphosphanes,



(66)

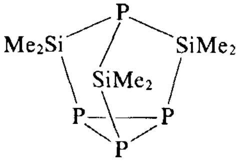
and the lithiated species may be isolated as crystals containing two moles of DME.

Dodecamethylhexasilatetraphosphaadamantane $(Me_2Si)_6P_4$ already was mentioned as an example of a polycyclic silylphosphane. $(Me_3Si)_3P_7$, another member of this class of compounds, is generated together with $(Me_3Si)_3P$ from white phosphorus, Na/K alloy and Me_3SiCl, and forms colorless crystals.[53]



The structure of this molecule is ascertained by ^{31}P NMR studies as well as by x-ray structure determination.[54] In the same reaction some higher order silylphosphanes are produced which to date have not been fully identified.

Cleavage of P_4 with Na/K alloy followed by addition of Me_2SiCl_2 to the reaction mixture yields hexamethyltrisilatetraphosphanortricyclene $(Me_2Si)_3P_4$ which also forms colorless crystals[55]:

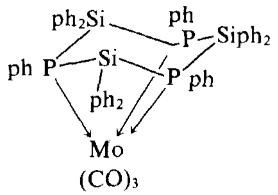


7. SILYLPHOSPHANES IN TRANSITION METAL COMPLEXES

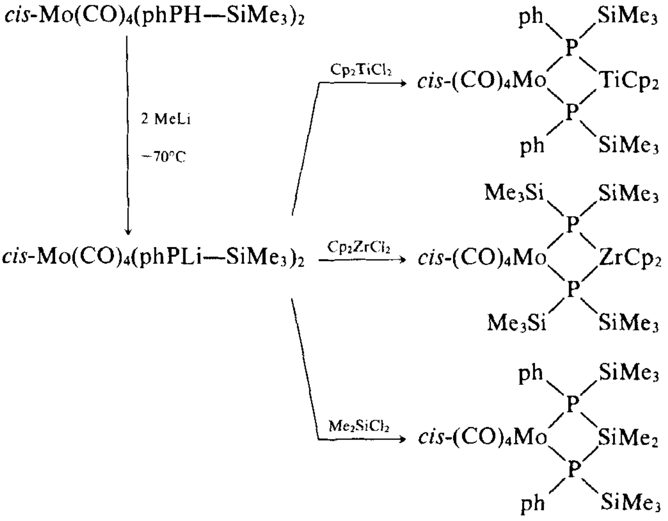
Of course, silylphosphanes are capable of reacting in various ways with transition metal complexes. One possibility is to employ the electron pair on the P atom of the silylphosphane directly to form the bond to the transition metal center. By reacting a transition metal complex halide with a silylphosphane through Si–P cleavage a phosphido group may be introduced. Furthermore, by treating complex halides with $LiP(SiMe_3)_2$ the $(Me_3Si)_2P$ group may be incorporated into the transition metal complex, which may be transferred to P-functional complex compounds by subsequent Si–P cleavage. All of these possibilities have been realized recently and offer further opportunities for development in the future.

A. Silylphosphanes as Ligands in Transition Metal Complexes

The first transition metal complexes incorporating silylphosphane ligands such as $(Me_3Si)_3P$ or $R_nP(SiMe_3)_{3-n}$ were reported by Schumann and Stelzer.[56] Further complex compounds with Si-substituted P-coordinated ligands such as $(CO)_5CrP(C_6H_5)(SiMe_3)_2$ [57] generated from $Cr(CO)_6$ and $(Me_3Si)_2PC_6H_5$, or $(CO)_3NiP(SiMe_3)_3$ generated from $Ni(CO)_4$ and $(Me_3Si)_3P$ [58] are known. Also the formation of the following compound was described[59]:



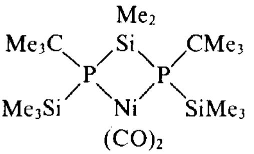
Johannsen and Stelzer[60] reported the preparation of *cis*-$Mo(CO)_4(phHP\text{-}SiMe_3)_2$ from *cis*-$Mo(CO)_4(phPH_2)_2$ by metallation with BuLi and subsequent treatment with Me_3SiCl, which could be transferred to the following cyclic phosphido complexes:



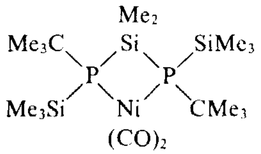
(67)

The behavior of the compounds $L = Me_2X\text{-}SiMe_2CH_2\text{-}XMe_2$ ($X = N,P$) as ligands in reactions with the transition metal complexes $Cr(CO)_6$ and $Mo(CO)_6$ was studied. $Me_2N\text{-}SiMe_2CH_2\text{-}PMe_2$ was found to form compounds as $(CO)_5CrPMe_2\text{-}CH_2SiMe_2\text{-}NMe_2$ (decrease in the basicity of the N atom due to interaction with the adjacent Si), whereas both $Me_2P\text{-}SiMe_2CH_2\text{-}NMe_2$ and $Me_2P\text{-}SiMe_2CH_2\text{-}PMe_2$ generate chelate complexes $(CO)_4ML$.[61]

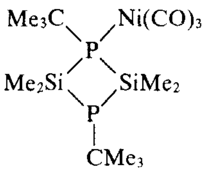
$Me_2Si[P(SiMe_3)CMe_3]_2$ with $Ni(CO)_4$ produces



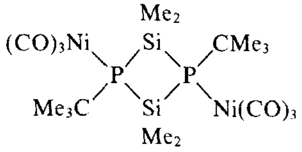
and



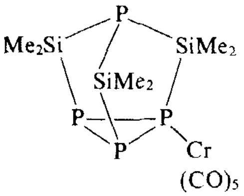
and the four-membered ring $(Me_2Si\text{-}PCMe_3)_2$ with $Ni(CO)_4$[62] generates



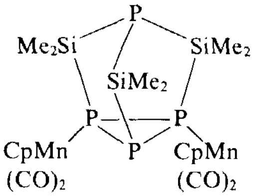
and



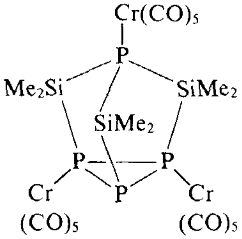
Hexamethyltrisilatetraphosphanortricyclene $(Me_2Si)_3P_4$ with $Mo(CO)_6$, $Cr(CO)_5THF$ or $Mn(n\text{-}C_5H_5)(CO)_2THF$ forms compounds of type A below, e.g.; however, with $Mn(n\text{-}C_5H_5)(CO)_2THF$ type B[63] also may be achieved. Type C is accessible with an excess of $Cr(CO)_5THF$[64]:



A

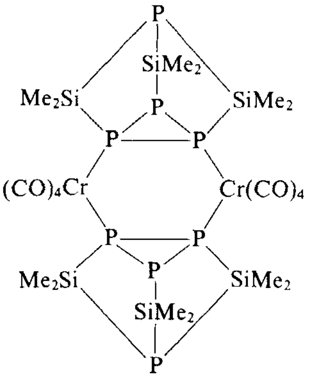


B

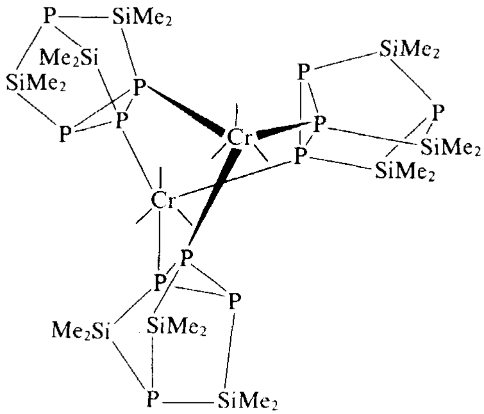


C

The reaction with tetracarbonylnorbornadienechromium(0) yields D.[63] $C_6H_6Cr(CO)_3$ or $(CHT)Cr(CO)_3$ (CHT = cycloheptatriene) yields E, which is also accessible by warming of A[65]:



D



E

It should be emphasized that under comparable experimental conditions no analogous compounds of $(Me_3Si)_3P_7$ can be obtained.

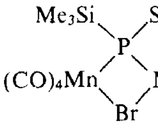
B. Reactions of Transition Metal Complex Halides with Silylphosphanes and $LiP(SiMe_3)_2$

$Me_3Si{-}P(C_6H_5)_2$ was utilized to transfer the phosphido group to $(CO)_5MBr$ (M = Mn,Re)[71]:

$$2(CO)_5MBr + 2Me_3SiP(C_6H_5)_2 \longrightarrow [(CO)_4MP(C_6H_5)_2]_2 + 2Me_3SiBr + CO. \quad (68)$$

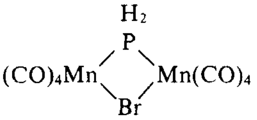
By treating $(CO)_5MnBr$ with $(Me_3Si)_3P$ Schäfer achieved the formation of bridged P-functional manganese carbonyl complexes[67]:

$$(CO)_5MnBr + (Me_3Si)_3P \longrightarrow$$



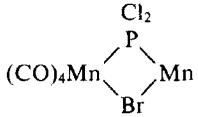
$$(CO)_4Mn(\mu\text{-}P(SiMe_3)_2)(\mu\text{-}Br)Mn(CO)_4 + Me_3SiBr + 2CO\,. \quad (69)$$

In this derivative CH_3OH cleaves the Si–P bonds to yield



$$(CO)_4Mn(\mu\text{-}PH_2)(\mu\text{-}Br)Mn(CO)_4$$

which may be prepared also directly from $(CO)_5MnBr$ and Me_3-$Si-PH_2$ and which is converted to

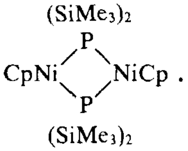


by CCl_4.

The reaction of $Cp(ph_3P)NiCl$ with $LiP(SiMe_3)_2$ produces a Ni complex compound incorporating a terminal phosphido group,

$$Cp(ph_3P)NiCl + LiP(SiMe_3)_2 \longrightarrow Cp(ph_3P)NiP(SiMe_3)_2, \qquad (70)$$

which in several steps reacts with $Ni(CO)_4$ (displacement of Pph_3 by CO) to form

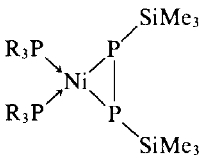


In a quite remarkable reaction this derivative is transformed by CH_3OH to $(CpNiPH_2)_3$,

$$3[CpNiP(SiMe_3)_2]_2 + 12CH_3OH \longrightarrow 2[CpNiPH_2]_3 + 12Me_3Si{-}OCH_3, \qquad (71)$$

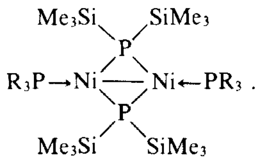
apparently through $(CpNiPH_2)_2$ as an intermediate.

$(R_3P)_2NiCl_2$ with $LiP(SiMe_3)_2$ initially produces $(R_3P)_2NiCl$ $P(SiMe_3)_2$ and $(R_3P)_2Ni[P(SiMe_3)_2]_2$ and after elimination of $(Me_3Si)_3P$ also crystals of



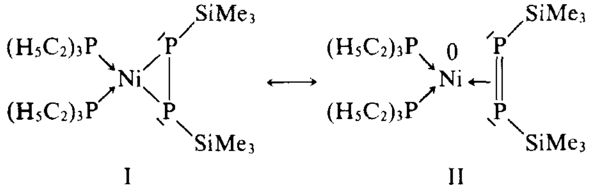
(a)

and



(b)

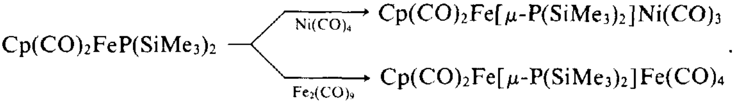
Both of these compounds are well established by NMR studies[69] and by x-ray structure determinations.[70] Compound (b) is one of the first unequivocally ascertained Ni(I)-phosphido-phosphane complexes. $P(n\text{-}Bu)_3$, PEt_3 and PMe_3 have been employed as ligands in such complex compounds.[69] In compound (a) Ni is nearly square planar coordinated, and an unusually short P–P distance of 214.8 pm was observed. This bond shortening may point to a small double bond contribution which can be rationalized by the following mesomeric formulas:



(72)

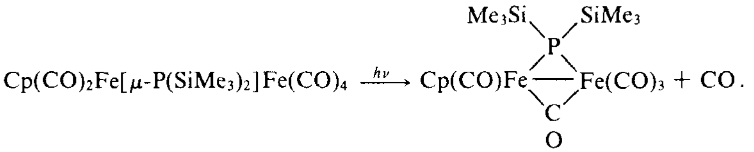
The structure of II corresponds to the analogous Ni(0)–ethylene complex $(ph_3P)_2NiC_2H_4$ which shows great similarity with respect to the coordination.[71]

The compounds $Cp(CO)_2FeX$ (X = Cl, Br) with $LiP(SiMe_3)_2$ form $Cp(CO)_2FeP(SiMe_3)_2$, which incorporates a terminal P-functional phosphido group.[66] With $Ni(CO)_4$ or $Fe_2(CO)_9$ this derivative yields, respectively, the products depicted in Eq. (73):



. (73)

UV irradiation initiates the transformation from a single bridged phosphido complex to a double bridged species (μ-CO):



(74)

Cleavage of the Si–P bonds in the single bridged derivatives with CH_3OH yields $Cp(CO)_2Fe(\mu\text{-}PH_2)Ni(CO)_3$ and $Cp(CO)_2Fe(\mu\text{-}PH_2)\text{-}Fe(CO)_4$.[72] Compounds of this type are also accessible as demonstrated in Eqs. (75) and (76).

$$Ni(CO)_4 + Me_3Si{-}PH_2 \longrightarrow (CO)_3NiPH_2{-}SiMe_3 + CO, \qquad (75)$$

$$(CO)_3NiPH_2{-}SiMe_3 + Cp(CO)_2FeBr \longrightarrow (CO)_3Ni(\mu\text{-}PH_2)Fe(CO)_2Cp. \qquad (76)$$

The latter reaction takes a more complicated course than indicated above involving several intermediates.[72]

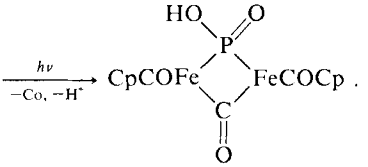
By treating Me_3SiPH_2 with $Cp(CO)_2FeX$ (X = Cl, Br) cationic PH_2-bridged iron complexes are accessible.

$$2\ Cp(CO)_2FeX + Me_3SiPH_2 \xrightarrow[\text{toluene}]{-Me_3SiX} [Cp(CO)_2Fe]_2PH_2^+Y^- \qquad (77)$$

$$Y = Cl,Br,PF_6,Bph_4.$$

These air-stable diferriophosphonium salts may be converted into P-halogenated derivatives by reactions of the PH_2 bridge with CCl_4 or CBr_4, which may be transferred to complex-stabilized phosphinic acid derivatives[73]:

$$[Cp(CO)_2Fe]_2PH_2^+ \xrightarrow[-CHBr_3\ -HBr]{+CBr_4\ +\ H_2O} [Cp(CO)_2Fe]_2P(OH)_2^+$$



(78)

In the solid state this organometallic substituted phosphinic acid is associated to dimers by means of hydrogen bridge bonds of the P(O)OH groups.[74]

$(CO)_5MnCl$ with Me_3SiPH_2 under appropriate conditions yields a mixture of $[(CO)_4MnPH_2]_2$ and $[(CO)_4MnPH_2]_3$, a four- and a six-membered ring system. In contrast to the analogous CpNi derivatives no changes of the ring skeleton are observed on heating both manganese complexes to their melting points. The four-membered as well as the six-membered ring may be chlorinated at room temperature in CCl_4:

$$[(CO)_4MnPH_2]_x \xrightarrow[-CHCl_3]{+CCl_4,\ 20°C} [(CO)_4MnPCl_2]_x \qquad (x = 2,3). \qquad (79)$$

Heating of a solution of the P-chlorinated six-membered ring

($x = 3$) causes rearrangement to the four-membered ring ($x = 2$). P fluorination can be achieved by halogen exchange by means of $AgBF_4$:

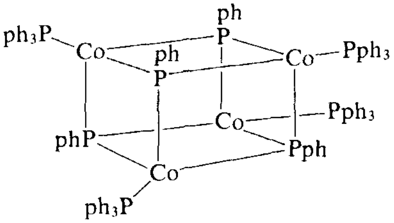
$$[(CO)_4MnPCl_2]_x \xrightarrow[-AgCl,\ -BF_3]{+AgBF_4} [(CO)_4MnPF_2]_x \qquad (x = 2,3). \qquad (80)$$

The P-fluorinated manganese complexes as well as the analogous PH_2 derivatives are thermally stable until their melting points. Complete P bromination is only possible with the four-membered ring[75]:

$$[(CO)_4MnPH_2]_2 \xrightarrow[-CHBr_3]{+CBr_4,\ toluene} [(CO)_4MnPBr_2]_2. \qquad (81)$$

The reactivity of the functional groups at phosphorus strongly depends on the ring size of the complexes.

Reactions of silylphosphanes with transition metal halides which yield cluster compounds according to investigations of Fenske[76] are of special interest. The compound $phP(SiMe_3)_2$ with $CoCl_2$ generates $Co_6(Pph)_8$, and $CoCl_2(Pph_3)_2$ with $phP(SiMe_3)_2$ yields $Co_4(Pph_3)_4$ (μ-Pph)$_4$ (cubane structure):



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