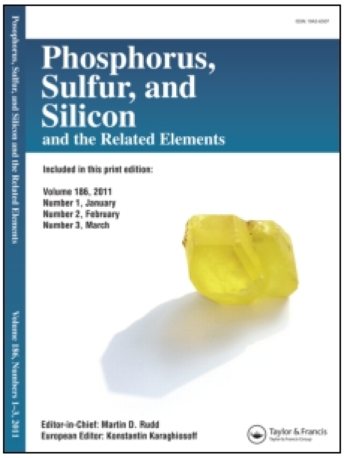

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METALLAPHOSPHENES AND DIPHOSPHENES

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METALLAPHOSPHENES AND DIPHOSPHENES

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Transient metallaphosphenes ($\rangle$M=P—) have been obtained by exchange reactions between disilylphosphines and organometaldihalides (M = Ge, Sn), or by thermolysis of 2-metallaphosphetanes (M = Si, Ge). They are characterized by trapping reactions with strained heterocycles. The first stable germaphosphene **12** has been synthesized by dehydrohalogenation from the parent halogermylphosphine and isolated in form of orange crystals. It is very reactive toward compounds with active hydrogen.

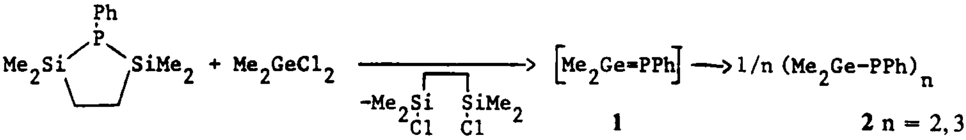
Transient diphosphenes (—P=P—) have been prepared by the same type of exchange reactions between disilylphosphines and dichlorophosphines and characterized by trapping reactions on dienes. The second stable diphosphene **18** has been obtained by addition of *t*-BuLi on trisyldichlorophosphine. Its structure has been determined by X-ray diffraction and some aspects of its reactivity are described. The reaction of bisyltrichlorogermylphosphine with DBU affords the new stable and potentially reactive diphosphene **30**.

RESULTS AND DISCUSSION

There has been much recent interest in compounds in low coordination states, and particularly those having a double bond between two main group atoms other than carbon.[1] In this paper, we describe the synthesis and characterization of compounds with a dicoordinated trivalent phosphorus atom bonded to an element of group 14[2] (metallaphosphenes $R_2M{=}PR'$, M = Si, Ge, Sn) or to another phosphorus atom (diphosphenes $RP{=}PR'$).

I. Metallaphosphenes

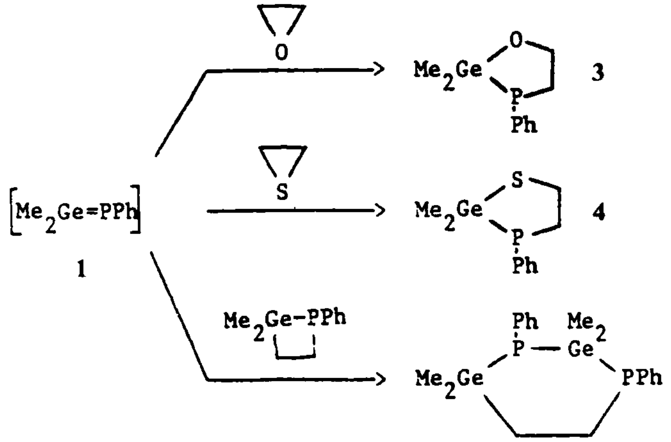
1. Transient metallaphosphenes. The first derivative obtained in the field of metallaphosphenes was the transient germaphosphene $Me_2Ge{=}PPh$ **1**. This species was obtained in an exchange reaction between the dimethyldichlorogermane and a 2,5-disilaphospholane (or an acyclic disilylated phosphine)[3]:



1 **2** n = 2,3

These exchange reactions occur in very mild conditions (from −45°C) with a good yield, and give only the cyclic dimer and trimer forms in the absence of trapping reagent.

Nevertheless the transient germaphosphene **1** has been clearly characterized by insertion and ring expansion reactions with ethylene oxide, ethylene sulfide and a 2-germaphosphetane leading to the germoxyphospholane **3**, the germathiaphospholane **4** and the digermadiphosphorinane **5** respectively[3]:



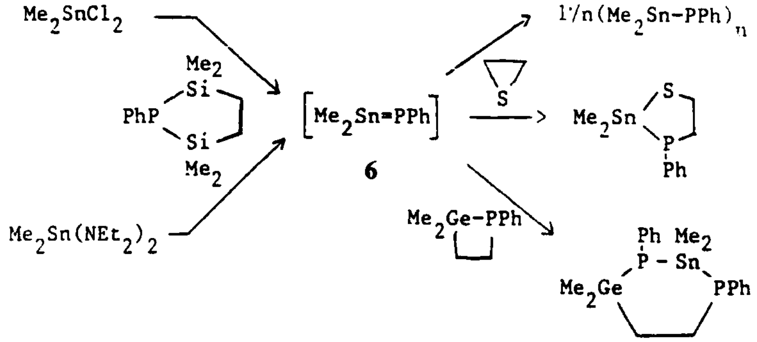
$\delta\ ^{31}P$: −101.8[4]

$\delta\ ^{31}P$: −73.2

2 diastereoisomers:

5a $\delta\ ^{31}P$:	P(Ge): −126.2
90%	P(C) : −74.3
5b	P(Ge): −126.0
10%	P(C) : −69.2

The isolog stannaphosphene $Me_2Sn{=}PPh$ **6** has been obtained by the same type of exchange reactions (from dialkyldihalotin or dialkyldiaminotin) and also characterized by similar trapping reactions[5]:

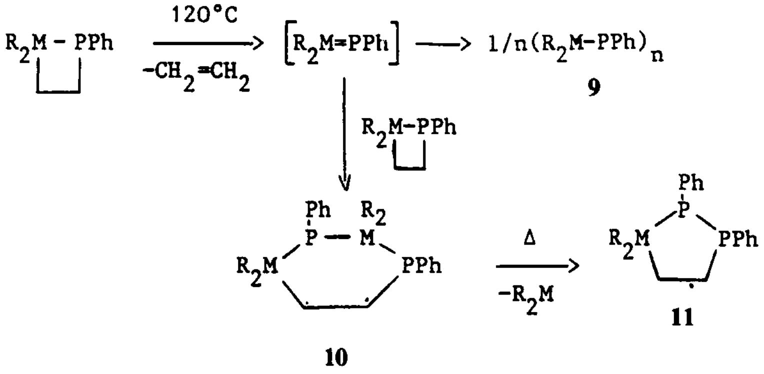


7 $\delta\ ^{31}P$: −86.3

2 diastereoisomers:

8a $\delta\ ^{31}P$:	P(Ge): −144.0
60%	P(Sn): −69.8
8b	P(Ge): −150.8
40%	P(Sn): −81.5

The thermal decomposition of 4-membered 2-sila- and 2-germaphosphetanes is also a good source of silaphosphenes[6] and germaphosphenes[7]; these species have been characterized by formation of oligomers **9** and by insertion into the metal-phosphorus bond of the precursor:

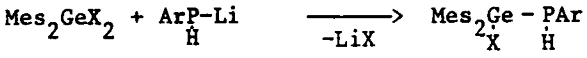


M = Si, R = Me	**11a** δ ^{31}P: P(Si): −105.0, P(C): −0.4,	^1J(PP): 253 Hz
M = Ge, R = Me	**11b** δ ^{31}P: P(Ge): −101.2, P(C): +3.5,	^1J(PP): 270 Hz
M = Ge, R = Et	**11c** δ ^{31}P: P(Ge): −103.7. P(C): +1.5,	^1J(PP): 270 Hz

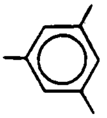
In the experimental conditions heterocycles **10** decompose by loss of silylene or germylene R_2M to afford a 3-sila or 3-germa 1,2-diphospholane **11**.

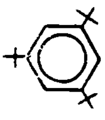
2. *Stable germaphosphene.* After these first results, it seemed quite evident that the instability of these compounds was intimately related to the easy accessibility of the double bond. Indeed we thought that such compounds could be stabilized when reactive sites are protected by steric hindrance. Owing to bulky substituents on metal and phosphorus, the first stable silaphosphene has been characterized[8] and we have isolated the first stable germaphosphene.[9]

The initial step in the synthesis of 2,2-dimesityl-1-1-(2,4,6-tri-tert-butyl-phenyl)-germaphosphene **12** involves the preparation of fluoro- or chloro-germylphosphines **13** by action of the lithiophosphine on dimesityldihalogermanes:



$$\mathrm{Mes_2GeX_2} + \mathrm{Ar}\underset{\mathrm{H}}{\mathrm{P}}\mathrm{-Li} \xrightarrow[-\mathrm{LiX}]{} \mathrm{Mes_2}\underset{\mathrm{X}}{\mathrm{Ge}}-\underset{\mathrm{H}}{\mathrm{P}}\mathrm{Ar} \qquad \mathbf{13}$$

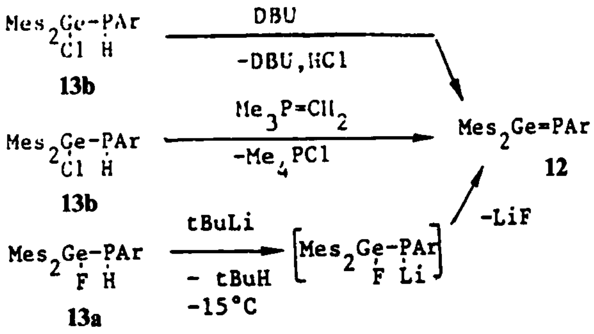
Mes: 

Ar: 

X = F	**13a** δ ^{31}P: −110.6 ^2J(PF): 9Hz ^1J(PH): 209 Hz
X = Cl	**13b** δ ^{31}P: −90.9, ^1J(PH): 215 Hz

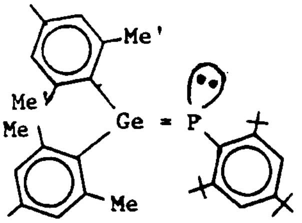
Dehydrochlorination of chlorogermylphosphine **13b** is obtained by action of strong bases such as DBU (1,5-diazabicyclo [5.4.0]undec-5-ene) or trimethyl-methylenephosphorane. The yields in **12** are respectively 15% and 30%.

But germaphosphene **12** can be obtained in nearly quantitative yield by reaction between tert-butyllithium and **13a**:



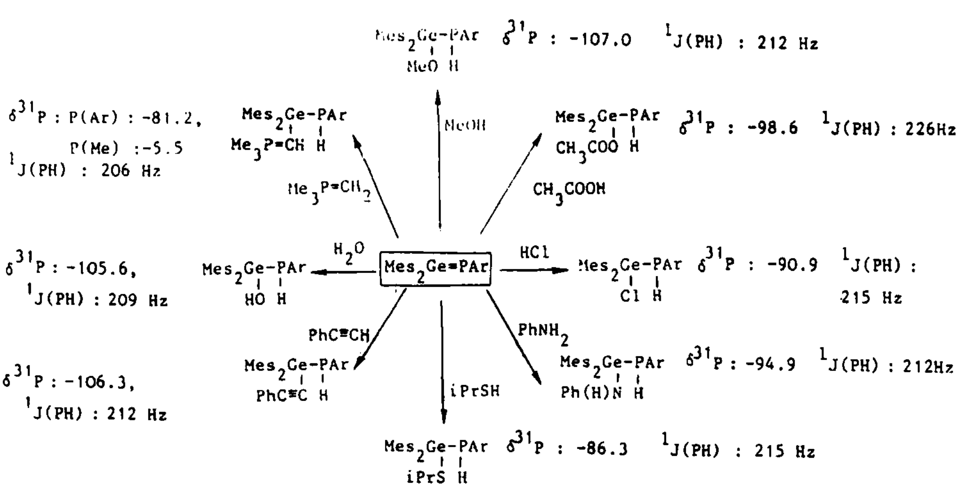
The very air-sensitive germaphosphene **12** has been recrystallized from pentane and isolated in pure form (mp: 155–160°C). A striking feature of this germaphosphene is its thermochromism which is characterized by a change in color from orange-red at +100°C, to orange at room temperature and yellow at −100°C.

12 has been characterized by its physico-chemical data, particularly by ^{31}P NMR (δ + 175.4 ppm) and by ^{1}H NMR: in this last case we observe a different chemical shift for the inequivalent ortho methyl groups (Me: 2.12, Me′: 2.60 ppm) of the mesityl because of the absence of rotation around the germanium-phosphorus double bond:



12

The structure of **12** was corroborated by its chemical behavior. Its reactivity is very high toward compounds with active hydrogens such as water, alcohols, organic and mineral acids, amines, thiols, acetylenic compounds and phosphorus ylides:



In each case we have observed a regiospecific reaction with the formation of the secondary phosphine. These preliminary results confirm the expected polarity of the $>Ge{=}P-$ bond, with germanium as the more positive partner, already predicted by calculations made in collaboration with J. C. Barthelat.[10]

II. Diphosphenes

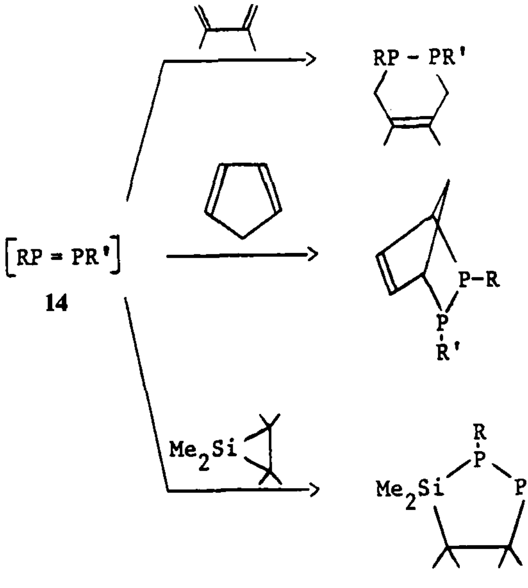
Among phosphorus compounds in low coordination states, diphosphenes have been of current interest since 1981. As in the case of metallaphosphenes, transient or stable diphosphenes can be obtained depending on the bulkiness of substituents on phosphorus.

1. Transient diphosphenes. The same type of exchange reactions performed for the synthesis of germa- and stannaphosphenes can be extended to the preparation of little hindered diphosphenes.[11] So the reactions between disilylphosphines and dichlorophosphines lead to diphosphenes, which give immediately cyclic oligomeric forms $(RP{-}PR')_n$ in the absence of trapping reagent:

$$(Me_3Si)_2PR + R'PCl_2 \xrightarrow[-2Me_3SiCl]{} \underset{\mathbf{14}}{[RP{=}PR']} \longrightarrow (RP{-}PR')_n$$

14a R = Ph, R′ = Ph
14b R = tBu, R′ = tBu
14c R = tBu, R′ = Mes

Diphosphenes can be characterized by cycloaddition reactions with conjugated dienes, such as 2,3-dimethylbutadiene[11] or cyclopentadiene, or insertion into an intracyclic silicon-carbon bond of a strained heterocycle such as hexamethylsilirane:

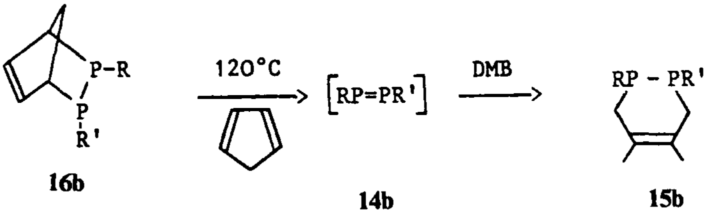


15b $\delta\ ^{31}P$: −11.4
15c P(tBu): −12.5
P(Mes): −58.8
$^1J(PP)$: 229 Hz

16b $\delta\ ^{31}P$: −1.8 and 6.1
(AB system)
$^1J(PP)$: 272 Hz

17a $\delta\ ^{31}P$: P(Si): −133.3
P(C): +12.6
$^1J(PP)$: 177 Hz

The cycloadduct **16b** is a good precursor of di-tert-butyldiphosphene by a thermal reversible reaction at about 120°C; the regenerated diphosphene **14b** can be trapped, for example on 2,3-dimethylbutadiene to give **15b**:



All these results show that exchange reactions appear as a very convenient route for the synthesis of short lived and reactive diphosphenes substituted by a small group.

2. *Stable diphosphenes*

*a. Ditrisyldiphosphene **18**.* After the synthesis of the first stable diphosphene by Yoshifuji and coll.,[12] we have synthesized the second stable diphosphene, the bis[tris(trimethylsilyl)methyl]diphosphene **18**;[13] this diphosphene, stabilized owing to the very bulky trisyl group $(Me_3Si)_3C$, was obtained by a new synthetic method using tert-butyllithium and the corresponding dichlorophosphine **19** (let us note that magnesium does not react with **19**):

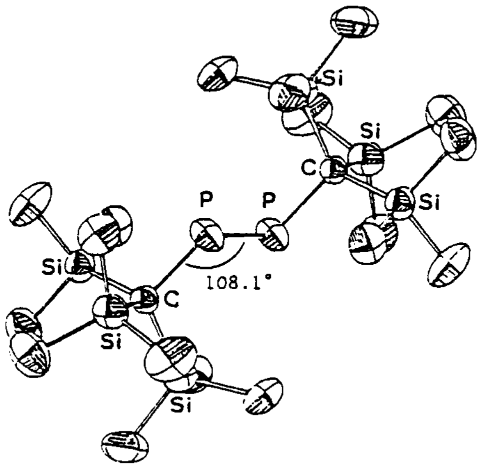
$$\underset{\mathbf{19}}{2\,(Me_3Si)_3CPCl_2} \xrightarrow{tBuLi} \underset{\mathbf{18}}{(Me_3Si)_3C\text{-}P{=}P\text{-}C(SiMe_3)_3}$$

The same diphosphene has been prepared, at nearly the same time, by Cowley (action of sodium naphthalenide on dichlorophosphine **19**)[14] and Issleib (action of lithium metal on **19**).[15]

18 has been purified by column chromatography on silica and presents after crystallization from pentane air stable orange-pink crystals. It has been characterized by its very low field chemical shift at 598.6 ppm in ^{31}P NMR and by its UV absorptions at 486 nm ($n \rightarrow \pi^*$) and 353 nm ($\pi \rightarrow \pi^*$). Structure of **18** was confirmed by X-ray diffraction.[13b,16] It crystallizes in the triclinic space group; two independent centro-symmetric molecules exist in the unit cell, one of them presents a rotation of 35° round the phosphorus—carbon bond. The two trisyl groups are in trans position; the P=P double bond has a normal length (2.003 and 2.001 Å).

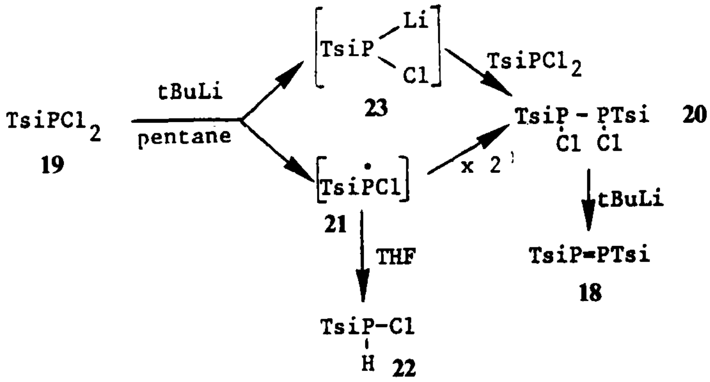
The mechanism of formation of **18** is difficult to prove unambiguously. However, it seems that its immediate precursor is the dichlorodiphosphine **20** which is obtained nearly pure when an equivalent of *t*-BuLi is added to the dichlorophosphine **19**. Further addition of *t*-BuLi to **19** affords the quantitative formation of the diphosphene **18**.

The precursor of **20** seems to be the radical **21** since in THF we have observed the formation of the chlorophosphine **22**, obtained by hydrogen abstraction from the

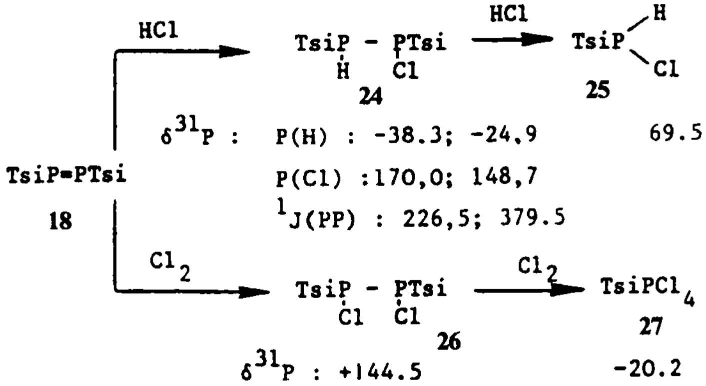


P—C: 1.866 Å C—Si: 1.924 Å P=P: 2.003 Å and 2.001 Å

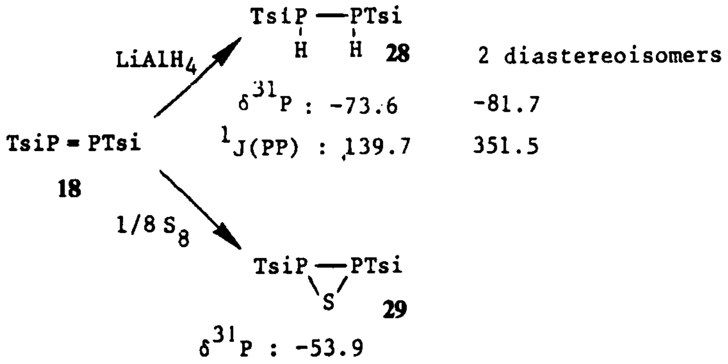
solvent. But it is also possible to postulate an intermediate **23** after intermolecular lithium-chlorine exchange:



We have studied a few aspects of the chemical reactivity of the diphosphene **18**.[13b] We have observed addition reactions on the P=P double bond of strong electrophilic reagents such as hydrogen chloride or chlorine:



The reduction of **18** by lithium aluminium hydride leads to the diphosphine **28**. Sulfur also reacts with **18** with formation of the diphosphathiirane **29** after three hours at 120°C. All these reactions are nearly quantitative:



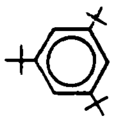
The great interest of using the very bulky trisyl group is to stabilize well adducts **24**, **25**, **26**, **28**, such structures being generally unstable.

b. Dibisyldiphosphene 30. However, as the ditrisyldiphosphene **18** is not very reactive because of the bulkiness of substituents on phosphorus, we have tried to synthesize a less hindered both stable and reactive diphosphene substituted by the bis(trimethylsilyl)methyl group (called bisyl).[17] Classical methods of synthesis of diphosphenes such as action of magnesium[18] or lithio compounds[17] on bisyldichlorophosphine **31** do not lead to the expected diphosphene but only to oligomers or alkylation reactions.

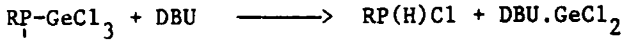
It was thus clear that a new synthetic route was necessary. It appeared to us that chlorophosphines RP(H)Cl were good precursors of diphosphenes by dehydrochlorination with DBU:

$$2\ RP(H)Cl \xrightarrow{DBU} RP{=}PR$$

R =



However, as chlorophosphines are stable only with very bulky substituents, it was necessary, in our case, to use precursors of these compounds such as trichlorogermylphosphines **32** which lead, by addition of DBU, to the corresponding chlorophosphines **33** and the complex DBU · $GeCl_2$:



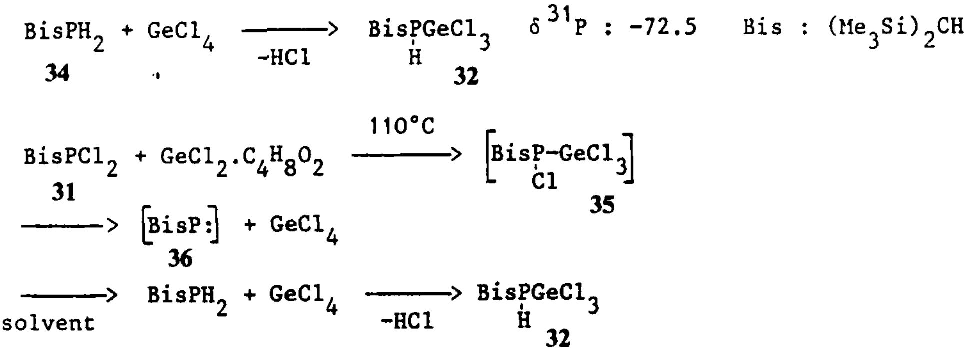
$$\underset{\substack{|\\H}}{RP}\text{-}GeCl_3 + DBU \longrightarrow RP(H)Cl + DBU.GeCl_2$$

32 **33**

32 has been easily prepared by two routes:

—direct action of germanium tetrachloride on bisylphosphine **34**

—action of the dichlorogermylene-dioxane complex on **31**:



$$\underset{\mathbf{34}}{\mathrm{BisPH_2}} + \mathrm{GeCl_4} \xrightarrow[-\mathrm{HCl}]{} \underset{\mathbf{32}}{\mathrm{Bis}\underset{\mathrm{H}}{\mathrm{P}}\mathrm{GeCl_3}} \quad \delta\,^{31}\mathrm{P} : -72.5 \quad \mathrm{Bis} : (\mathrm{Me_3Si})_2\mathrm{CH}$$

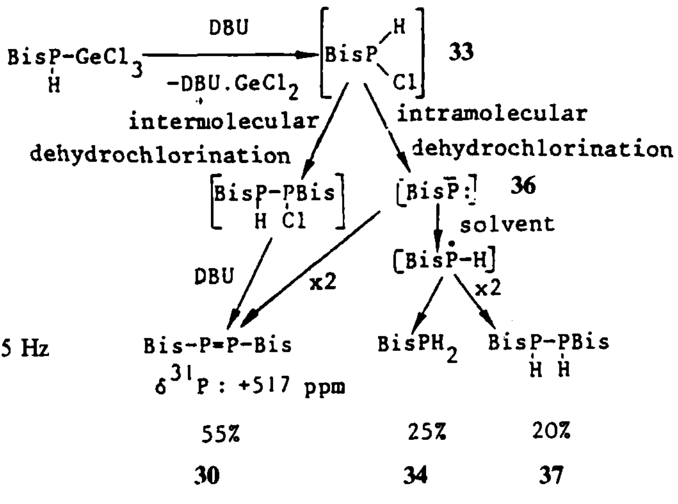
$$\underset{\mathbf{31}}{\mathrm{BisPCl_2}} + \mathrm{GeCl_2.C_4H_8O_2} \xrightarrow{110^\circ\mathrm{C}} \underset{\mathbf{35}}{\left[\mathrm{Bis}\underset{\mathrm{Cl}}{\mathrm{P}}\mathrm{-GeCl_3}\right]}$$

$$\longrightarrow \underset{\mathbf{36}}{\left[\mathrm{BisP:}\right]} + \mathrm{GeCl_4}$$

$$\xrightarrow[\mathrm{solvent}]{} \mathrm{BisPH_2} + \mathrm{GeCl_4} \xrightarrow[-\mathrm{HCl}]{} \underset{\mathbf{32}}{\mathrm{Bis}\underset{\mathrm{H}}{\mathrm{P}}\mathrm{GeCl_3}}$$

In the second reaction process, the synthesis of **32** involves the preliminary insertion of dichlorogermylene into a phosphorus–chlorine bond of **31** followed by α-elimination from the adduct **35** and intermediate formation of triplet phosphinidene **36** which abstracts two hydrogens from the solvent. Then **34** reacts with germanium tetrachloride as in the first route.

Addition of a twofold excess of DBU to **32**, leads to the expected diphosphene **30**, the primary phosphine **34** and the diphosphine **37** in the relative percentage 55/25/20:



34 $\delta\,^{31}\mathrm{P}$: −149 $^1J(\mathrm{PH})$: 185 Hz
37 2 diastereoisomers
$\delta\,^{31}\mathrm{P}$: −90.2 and −97.9

30 can be purified by a rapid distillation using a short column (bp: 80–85°C/10^{-2} mm Hg). It exhibits in ^{31}P NMR a characteristic low field chemical shift (517 ppm) and was also identified by mass spectrometry. **30** is an orange-yellow liquid, which polymerizes to $(\mathrm{BisP})_3$ after about three days at room temperature and two months at −25°C.

The formation of the compounds **34** and **37** involves, after the initial formation of the chlorophosphine **33**, two competitive reactions a and b:

a) intermolecular dehydrochlorination with formation of **30**

b) intramolecular dehydrochlorination leading to **34** and **37** probably via a phosphinidene intermediate **36**. However, dimerization of **36** to give diphosphene **30** cannot be completely excluded.

Diphosphene **30**, less hindered than most of the other stable diphosphenes, seems very reactive (it cannot be purified by column chromatography and slight exposure to air results immediately in its disappearance) and may serve as a good model for thorough studies of the phosphorus–phosphorus double bond reactivity which is not very developed until now.

All our results confirm that using very bulky substituents can stabilize and allow isolation of new species with multiple bonds between heavier main group elements known until now only as transient species.

The great interest of kinetically stabilized and reactive derivatives such as germaphosphene and diphosphene is to allow a large study of the reactivity of germanium–phosphorus and phosphorus–phosphorus double bonds.

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