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Heavy Allenes and Cumulenes E═C═E′ and E═C═C═E′ (E = P, As, Si, Ge, Sn; E′ = C, N, P, As, O, S)

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Jean Escudié was born in Decazeville (south of France) in 1946. He received his Ph.D. degree from the University Paul Sabatier, Toulouse, in 1978 under the supervision of Professor J. Satgé. After postdoctoral studies with Professor D. Seyferth at MIT in 1979–1980, he joined again the University Paul Sabatier where he is currently "Directeur de Recherche au Centre National de la Recherche Scientifique (CNRS)". His main research interests involve the chemistry of heavy group 14 and 15 elements such as silicon, germanium, tin, phosphorus, and arsenic. He is particularly interested in multiple bonding of these elements.

Native of Toliary—Southern Madagascar—Henri Ranaivonjatovo ran his first experiment in chemistry at the University of Madagascar in Antananarivo, where he completed his "Diplôme Universitaire d′Etudes Scientifiques". He then flew north to France and joined the research group of Professor Jacques Satgé. In 1984 he received his "Doctorat du 3e Cycle" and in 1986 his "Doctorat de l′Université Paul Sabatier" (Ph.D.) from the University of Toulouse. As a recipient of a research fellowship from the Alexander Von Humboldt Foundation, he enjoyed a postdoctoral stay in Bonn, Germany, with the research group of Professor Dr. Edgar Niecke. He currently holds a position at the "Centre National de la Recherche Scientifique". His research interests focus on multiple bonding in main-group metal chemistry.

Leslie Rigon was born in 1972 in France. She received her Masters degree from the University of Bordeaux and her Ph.D. degree in 1999 from the University Paul Sabatier, Toulouse, under the supervision of Dr. Jean Escudié. Her Ph.D. research was devoted to low-coordinated species of silicon, tin, and phosphorus involving cumulated double bonds (phosphasilaallenes and stannaphosphaallenes) and to the synthesis of new huge stabilizing groups.

I. Introduction

Since the pioneer work of Yoshifuji, Brook, and West who synthesized in 1981 the first stable diphosphene $ArP{=}PAr$ (Ar = 2,4,6-tri-*tert*-butylphenyl),[1] silene $(Me_3Si)_2Si{=}C(Ad)OSiMe_3$,[2] and disilene $Mes_2Si{=}SiMes_2$,[3] respectively, low-coordinate species of group 14 and 15 elements have been extensively studied. Almost all the possible combinations of E_{14} (C, Si, Ge, Sn), E_{15} (N, P, As), and E_{16} (O, S, Se, Te) elements have been achieved, and derivatives such as $E_{14}{=}E_{14}$, $E_{14}{=}E_{15}$, $E_{15}{=}E_{15}$, and $E_{14}{=}E_{16}$ have been prepared and isolated or at least characterized by their physicochemical data for the metastable species. It appeared that the stabilization of unsaturated derivatives of main-group elements was mainly permitted by using bulky groups, preventing their dimerization or oligomerization. Another way to stabilize such low-coordinate species is by complexation with transition metals; electronic effects are less important. Synthesis, theoretical aspects, physicochemical studies, and the reactivity of these doubly bonded derivatives which are heavy homologues of alkenes, imines, azo compounds, etc., is now well-documented.

Therefore, a new and exciting challenge was the synthesis and the stabilization of other important organic functions such as allenes or cumulenes containing doubly bonded heavy elements. Due to the presence of two adjacent double bonds, their stabilization is less trivial than that of compounds with only one isolated double bond. However, owing to the use of judicious substituents, some $-P{=}C{=}Y$ (Y = C, N, P, As, O, S) derivatives have been isolated or trapped and studied. Recent progress has been made on $>E{=}C{=}Y$ compounds (E = Si, Ge, Sn; Y = C, N, P), which were still unknown 6 years ago.

Some derivatives with three cumulative double bonds of the type $-P{=}C{=}C{=}X$ (X = C, P) or $-As{=}C{=}C{=}X$ have also been synthesized and several derivatives isolated.

All of these allenic or cumulenic compounds are interesting from a theoretical point of view for their physicochemical data and their chemical behavior which show several peculiarities. The purpose of this paper is to review the progress reported on transient or stable compounds of the general formulas $E{=}C{=}E'$ and $E{=}C{=}C{=}E'$ (E = P, As, Si, Ge, Sn; E′ = C, N, P, As, O, S). In the case of phosphorus or arsenic derivatives, only those with a $\lambda^3\sigma^2$ P or As will be reviewed. Thus, we will describe successively the following types of derivatives with their usual names (other names also found in the literature are given in parentheses): $-P{=}C{=}C<$, 1-phosphaallene (ethenylidenephosphine, λ^3-phosphaallene); $-P{=}C{=}N-$, 1-phospha-3-azaallene (1-aza-3-phosphaallene, phos-

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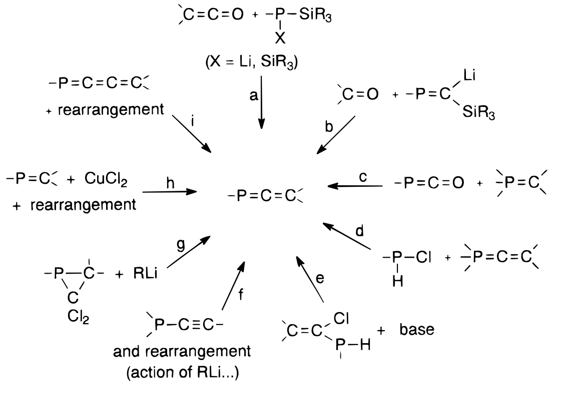
phacarbodiimide, carboimidophosphene, iminomethylidenephosphine, iminomethylenephosphine); −P=C=P−, 1,3-diphosphaallene (carbodiphosphene); As=C=C<, 1-arsaallene; −P=C=As−, 1-arsa-3-phosphaallene; −As=C=As−, 1,3-diarsaallene; −P=C=O, phosphaketene; −P=C=S, phosphatioketene; −P=C=C=C<, 1-phosphabutatriene; −P=C=C=P−, 1,4-diphosphabutatriene; −As=C=C=C<, 1-arsabutatriene; >Si=C=C<, 1-silaallene (1-silapropadiene); >Si=C=C=C<, 1-silabutatriene; >Si=C=N−, silaketenimine (silylene-isocyanide complex); >Si=C=P−, 1-phospha-3-silaallene; >Si=C=O, silaketene (silylene-carbon monoxide complex); >Ge=C=C<, 1-germaallene (1-germapropadiene); >Ge=C=P−, 1-germa-3-phosphaallene; >Sn=C=N−, stannaketenimine (stannylene-isocyanide complex). In this review, Ar is always the 2,4,6-tri-*tert*-butylphenyl group ("supermesityl").

For reviews related to the subject, see particularly those on E=C compounds, E = Si,[4−14] Ge,[12,14−16] Sn,[12,14,15g,16] P,[14,18,19] As.[17] In these reviews, some >Si=C=C<,[4b,13] >Ge=C=E′ (E′ = C, P[15g]), and particularly −P=C=E″[19] (E″ = C, N, P, O, S) derivatives are described. For other reviews on doubly bonded derivatives of silicon, germanium, tin, phosphorus, and arsenic, see also refs 20 and 21.

II. 1-Phosphaallenes −P=C=C<

The most extensively studied allenic phosphorus compounds are the 1-phosphaallenes −P=C=C<. Various types of synthetic routes to these compounds have been reported. The most commonly used methods are phospha−Wittig reactions, Peterson-type reactions, dehydrohalogenation of 1-chlorovinylphosphines, rearrangement of alkynylphosphines, and ring opening of phosphiranes (Scheme 1).

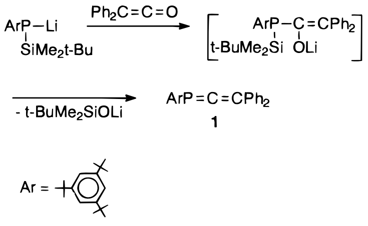
Scheme 1



A. Synthesis

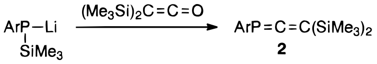
1. Reactions of Ketenes with Lithium Silylphosphides (Route a)

The reaction of diphenylketene with a lithium silylphosphide performed by Yoshifuji was the first route to a phosphaallene[22,23] (eq 1). **1** is extraordinarily stable toward heat, light, and atmospheric moisture or oxygen.



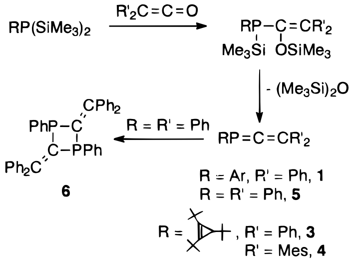
(1)

The bis(trimethylsilyl)phosphaallene **2** was synthesized by Märkl[24] by the same route, with the bis(trimethylsilyl)ketene and a lithium trimethylsilylphosphide as the starting material (eq 2). A similar



$$\underset{\text{SiMe}_3}{\text{ArP}-\text{Li}} \xrightarrow{(\text{Me}_3\text{Si})_2\text{C}=\text{C}=\text{O}} \underset{\mathbf{2}}{\text{ArP}=\text{C}=\text{C}(\text{SiMe}_3)_2} \qquad (2)$$

procedure, using disilylphosphines instead of lithium phosphides and small amounts of sodium hydroxyde to catalyze the elimination of hexamethyldisiloxane, allowed the synthesis of stable **1**,[25] **3**,[26] and **4**[26] but also transient **5**,[25] which gives the corresponding head-to-tail dimer **6**: the reason for this dimerization is the absence of steric hindrance on the phosphorus atom (eq 3). Only one isomer of **6** is obtained with

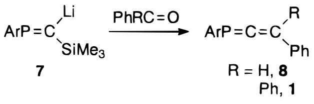


(3)

the phenyl groups on phosphorus anti.[25] This stereospecific reaction may be due to a thermally induced symmetry allowed [$2\pi s + 2\pi a$] process, which is only possible with linear systems exhibiting low substitution.

2. Reactions of Aldehydes or Ketones with a Phosphavinyllithium (Route b)

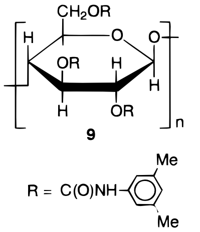
The 1-silyl-2-phosphavinyllithium **7**, obtained from dichlorophosphaethene ArP=CCl$_2$ by successive reaction with n-BuLi, Me$_3$SiCl, and then t-BuLi, is a convenient and direct reagent for introducing a ArP=C unit. Thus, reaction of **7** with benzophenone or benzaldehyde gives the phosphaallenes **1**[27] and **8**[27] by a Peterson-type reaction (eq 4).



(4)

In a chiral solvent such as (+)-phenylethylamine, the ^{31}P NMR of **8** displayed two signals centered at 75 ppm separated by 2 Hz.[19,28] The two enantiomers of **8** were completely separated[29] by a chiral HPLC column of cellulose tris(3,5-dimethylphenylcarbamate) **9** (Chart 1). It should be noted that when amylase tris(3,5-dimethylphenylcarbamate) was used instead of **9**, the resolution of **8** failed, indicating that chiral recognition is very sensitive to small changes.

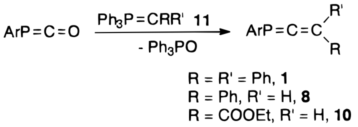
Chart 1



The racemization, which might involve either the inversion at the phosphorus atom or the rotation around the P=C or C=C bond, occurs upon photolysis but was reluctant in the dark or by thermolysis since an optically active sample did not lose its activity even at 50 °C for 15 h.[29] This phenomenon is very similar to those reported on other doubly bonded phosphorus compounds such as diphosphenes −P=P−[30,31] and phosphaalkenes −P=C<[32,33] which isomerize on photolysis.

3. Wittig Reactions (Route c)

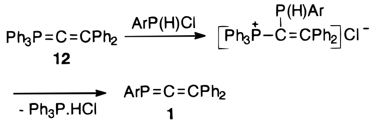
An approach based on an analogy with the Wittig reaction allowed the synthesis of **1**,[34] **8**,[25] and **10**[25] using phosphaketene ArP=C=O and the appropriate alkylidenetriphenylphosphorane **11** (eq 5). Despite the relative low steric hindrance, **10**, isolated as colorless crystals, is stable and can be purified by column chromatography on silica.



(5)

4. Reaction of a λ^5-Phosphaallene with a Chlorophosphine (Route d)

The reaction of λ^5-phosphaallene **12** with chlorophosphine ArP(H)Cl was another route to the λ^3-phosphaallene **1**[35] (eq 6). This method is similar to that previously described by the same authors for the synthesis of phosphaalkenes −P=C<[36] using alkylidenetriphenylphosphorane $Ph_3P{=}CR_2$ instead of **12**.

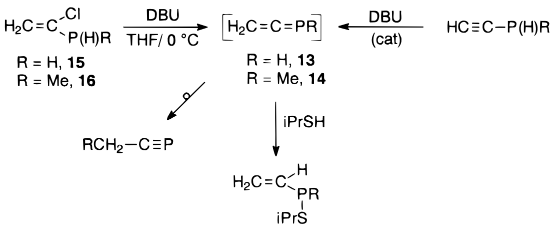


(6)

5. Dehydrochlorination (Route e)

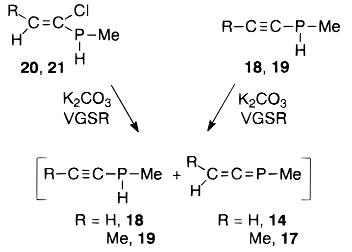
Transient phosphaallenes **13**[37] and **14**[38] have been prepared by base-induced dehydrohalogenation of the 1-chlorovinylphosphine **15** and the 1-chlorovinylmethylphosphine **16** (Scheme 2). In solution, the dehydrochlorination with DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene) occurs at −90 °C for **15** and at 0 °C for **16**, but **13** and **14** are too unstable to permit characterization by ^{31}P NMR; their transient formation was proven chemically by addition of 2-propanethiol. In the absence of trapping reagents, **13** and **14** isomerize to the transient phosphaalkyne $RCH_2{-}C{\equiv}P$ which can be characterized at low temperature.

Scheme 2

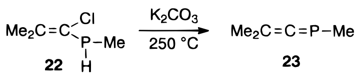


Transients **14** and **17** have been obtained in the gas phase using K_2CO_3 at 250 °C as a solid base[38] (VGSR) (Scheme 3). A mixture of phosphaallene **14** (or **17**) and 1-alkynylphosphine **18** (or **19**) is observed. Some products are obtained from **18**/**19** by a rearrangement alkyne−allene. A tautomeric equilibrium **14**/**18** or **17**/**19** can rationalize these results.

Scheme 3



In the absence of hydrogen on the vinyl group, as in **22**, gas-phase dehydrochlorination provides an efficient synthesis of pure phosphaallene **23**[38] (eq 7).



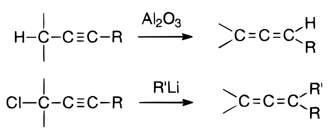
(7)

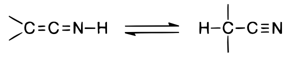
Phosphaallenes **14**, **17**, and **23** slowly oligomerize on warming to −20 °C. The structures of **14** and **17** have been determined from their low-temperature ^1H, ^{13}C, and ^{31}P NMR, IR, and mass spectra.

6. From Alkynylphosphines (Route f)

The reaction alkyne → allene is well-known in carbon chemistry since allenes can be synthesized from alkynes[39] (Scheme 4). Ketenimines >C=C=N−, analogues of phosphaallenes, can also be obtained from nitriles containing α-hydrogens, although the tautomeric equilibrium normally favors the nitrile[40] (eq 8). This type of rearrangement of a triple bond to two cumulative double bonds has been largely used in phosphaallene chemistry. Thus, transient phosphaallenes **13** and **14** have been obtained by a rearrangement from alkynylphosphines[38] catalyzed by a small amount of DBU (Scheme 2).

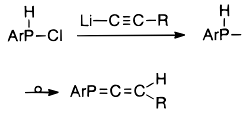
Scheme 4



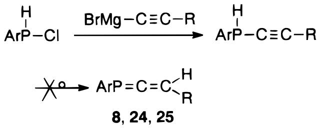


(8)

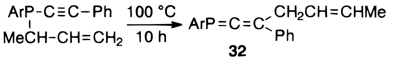
Many stable phosphaallenes **8** and **24**–**31** have been prepared from alkynylphosphines obtained from LiC≡CR and ArP(H)Cl (eq 9).[41] When R = CPh_2-$OSiMe_3$, the phosphaallene ArP═C═C(H)CPh_2OSiMe_3 is not stable and easily loses Me_3SiOH to lead to the phosphabutatriene ArP═C═C═CPh_2[41b] (see section X). **30** and **31** also lose Me_3SiOH, but the corresponding phosphabutatrienes were not isolated in pure form. By contrast, when the Grignard reagent BrMg–C≡C–R (R = Ph, t-Bu, Me) is used instead of LiC≡CR, the expected phosphaallenes **8**, **24**, and **25** are not formed: the corresponding alkynylphosphines are stable and do not isomerize because the Grignard reagent is not as basic as the lithium compound LiC≡CR and does not induce the rearrangement[41a] (eq 10). Phosphaallenes **8** and **26**–**28** are obtained as racemates and phosphaallenes **29**–**31** exist in the form of diastereoisomers.


(9)

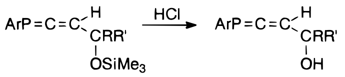
R = Ph, **8**; t-Bu, **24**; Me, **25**; CH_2OSiMe_3, **26**; CMe_2OSiMe_3, **27**; C(2,2'-diphenyl)$OSiMe_3$, **28**; CMe(Ph)$OSiMe_3$, **29**; CPh(4-MeC_6H_4)$OSiMe_3$, **30**; CPh(α-naphthyl)$OSiMe_3$, **31**


(10)

The rearrangement alkynylphosphine–phosphaallene can also be thermally induced to give **32**[42] (eq 11).


(11)

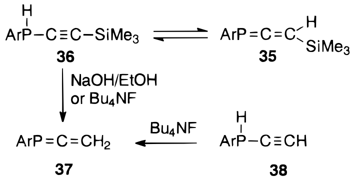
The reaction of **26** and **27** with a solution HCl (2 N)/MeOH affords the phosphaallenes **33** and **34** by cleavage of the Si–O bond without reaction on the P═C or C═C bonds[41b] (eq 12). The synthesis of **33** and **34** corresponds to the formation of a phosphaallene from another phosphaallene.


(12)

R = R' = H, **26** R = R' = H, **33**
R = R' = Me, **27** R = R' = Me, **34**

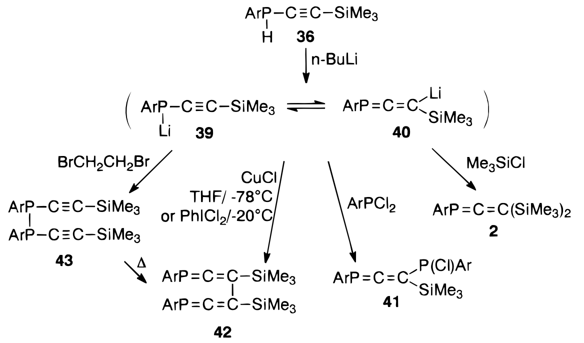
An equilibrium is observed between the phosphaallene **35** and the corresponding alkynylphosphine **36** in which the Si–C bond is easily cleaved by NaOH/EtOH or by reaction with tetrabutylammonium fluoride to afford **37**[41a] (Scheme 5). **37** was also obtained by the Bu_4NF-induced isomerization of the ethynylphosphine **38** but not by heating **38** in refluxing toluene for 1 h.[43] Although substituted by only two hydrogens on the carbon and not by bulky groups, **37** is perfectly stable. Thus, it seems necessary to use bulky groups on phosphorus and not necessary on carbon to stabilize phosphaallenes.

Scheme 5



Lithiation of the alkynylphosphine **36** by MeLi/TMEDA[24] or n-BuLi[44] affords the lithium phosphide **39** which is expected to exist in metallotropic equilibrium with the lithiated allene **40** (Scheme 6).

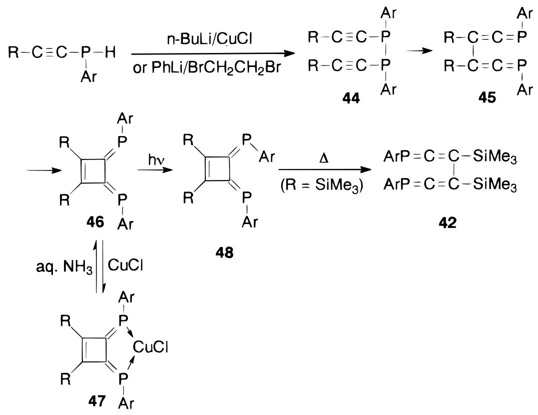
Scheme 6



Quenching with chlorotrimethylsilane or a dichlorophosphine leads to the phosphaallenes **2**[24] and **41**,[24] respectively. In the reaction of **39**/**40** with CuCl, a radical coupling reaction occurs and the new compound **42** with two phosphaallene moieties was formed;[44] the latter was also obtained in a ionic coupling reaction using $PhICl_2$[44] and by reaction with $BrCH_2CH_2Br$[45] via intermediate **43**, followed by a thermally induced Cope reaction.

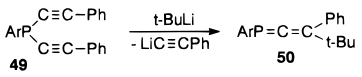
The study of the reactivity of R–C≡C–P(H)Ar with n-BuLi,[46] n-BuLi and CuCl,[47] or PhLi and $BrCH_2CH_2$-Br[48] has been performed for a variety of groups R (R = Me, t-Bu, *n*-pentyl, *p*-tolyl, $SiMe_3$, Si(t-Bu)Me_2 and α-furyl,[47] Ph,[46,47] CH_2Ph[48]) (Scheme 7) to determine the influence of this substituent R on the outcome of the reaction. Due to the presence of a bulky Ar group, only racemic diphosphines **44** or, as in the case of less bulky R groups, racemic diphosphaallenes **45** are formed by a Cope rearrangement. With bulky R (t-Bu, $SiMe_3$, Si(t-Bu)Me_2), the diphosphines **44** can be isolated.[47] A conrotatory electrocyclization of **45** leads to the *E*,*E*-configured cyclobutene **46** and the corre-

Scheme 7



sponding complexes **47** with excess CuCl. The photochemical isomerization of **46** leads to **48**.[47] Derivative **46** (R = $SiMe_3$) remains unchanged after heating to 150 °C,[44] whereas a slow electrocyclic ring opening of **48** (R = $SiMe_3$) occurs at 120 °C to afford the bis(phosphaallene) **42**[44] (Scheme 7). **39**/**40** has also been largely used as precursor of 1-phosphabutatrienes (see section X).[44, 49,50]

Owing to the good leaving-group property of the phenylethynyl substituent, the phosphaallene **50** has been obtained by addition of t-BuLi to the corresponding bis(phenylethynyl)phosphine **49**[19,51] (eq 13).

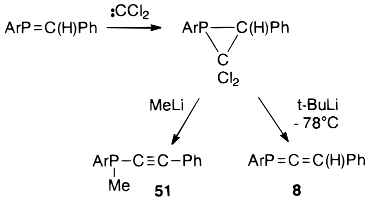


(13)

7. From a Dichlorophosphirane (Route g)

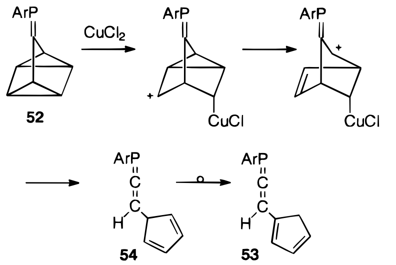
Addition of t-BuLi to a solution of 2,2-dichlorophosphirane obtained by addition of dichlorocarbene to *E*- and *Z*-2-phenyl-(2,4,6-tri-*tert*-butylphenyl)phosphaethylene leads to the phosphaallene **8**[52] in 62% yield (Scheme 8). This reaction is a formal insertion of a carbon atom into the $P{=}C$ double bond of the starting phosphaalkene. With methyllithium, only the alkynylphosphine **51** was formed. These results indicate that t-BuLi is a more suitable reagent than MeLi which is often used for the synthesis of allenes.

Scheme 8



8. From a Phosphinylidene Quadricyclane (Route h)

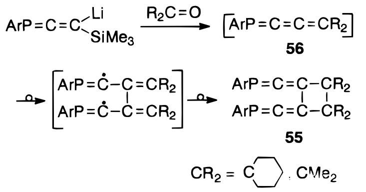
When the 3-(2,4,6-tri-*tert*-butylphenylphosphinylidene)quadricyclane **52** was reacted with $CuCl_2$, the phosphaallene **53** was formed according to a four-step mechanism[53] (eq 14). **54** rearranges to **53** by a 1,5-hydrogen shift: the driving force for this reaction must be the conjugation between the cyclopentadienyl system and the phosphaallene carbon−carbon double bond, making **53** more stable than **54**.[53]



(14)

9. Rearrangement from a 1,3-Phosphabutatriene (Route i)

Reaction of cyclohexanone or acetone with $ArP{=}C{=}C(Li)SiMe_3$ gives the bis(phosphaallenes) **55**, probably via the expected phosphabutatriene intermediates **56** followed by a radicalar dimerization[50a] (eq 15).



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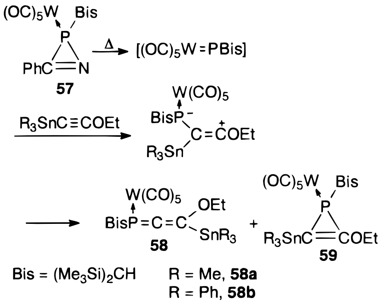
10. Transition-Metal-Complexed Phosphaallenes

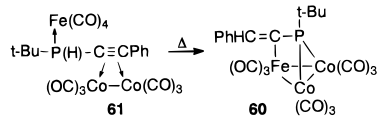
Two types of reactions have been performed: (a) direct complexation of a stable phosphaallene by a transition metal (such a route is developed in section II.D.8 devoted to the reactivity of phosphaallenes) and (b) formation of transition-metal-substituted phosphaallenes from other phosphorus derivatives or transition-metal complexes. Three phosphaallenes complexes were obtained according to this route.

Heating the azaphosphirene complex **57** in the presence of alkynylstannane $R_3Sn{-}C{\equiv}C{-}OEt$ leads, via the phosphinidene complex $BisP{=}W(CO)_5$, to a mixture of η^1-phosphaallene complex **58**[54,55] and phosphirene **59** (eq 16). Using $Me_3Si{-}C{\equiv}C{-}OEt$ instead of $R_3Sn{-}C{\equiv}C{-}OEt$ does not give any phosphaallene[55] but instead exclusively a phosphirene-like compound **59** substituted by a Me_3Si group instead of R_3Sn.



(16)

The cluster-stabilized phosphaallene **60**[56] has been obtained in low yield from $t\text{-}BuP(Cl)C{\equiv}CPh$ by successive addition of $HFe(CO)_4^-$ and $Co_2(CO)_8$ giving **61** followed by refluxing in *n*-hexane (eq 17). The structure of **60** consists of a metallic triangle coordinated to the $t\text{-}BuP{=}C$ moiety of the $t\text{-}BuP{=}C{=}CHPh$ fragment. A similar type of bonding has been reported in the triiron complex $Fe_3(\mu^3\text{-}PPh)(\mu\text{-}PhPC(OEt)Ph)(CO)_9$.[57]



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B. Physicochemical Studies

Although phosphaallenes are generally crystalline derivatives, only $ArP{=}C{=}CPh_2$ has been characterized by single-crystal X-ray diffraction.[34,58] The $P{=}C$ bond length (1.63[34] or 1.625(4) Å[58]) is in the lower limit for such a double bond, probably due to the presence of the sp carbon. The $C{=}C$ distance is also

Table 1. Phosphaallenes R^{1}P=C=CR^{2}R^3: Synthetic Routes and Physicochemical Data (For methods, see Scheme 1.)

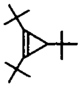
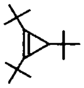
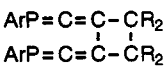
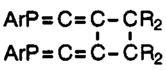
n°	R^1	R^2	R^3	δ ^{31}P ppm ($^3J_{PH}$) Hz	δ ^{13}C$_1$ ($^1J_{PC}$)	δ ^{13}C$_2$ ($^2J_{PC}$)	mp (°C)	color	method	ref
1[a]	Ar	Ph	Ph	71.7[27] (23)	237.6 (26.6)	128.3 (6.4)	160-161.5[22] 165[34] 157-160[27]	colorless[22]	a, b, c, d	22, 34, 58, 27, 36
2	Ar	TMS	TMS	3.84			oil	yellow	a	24
3		Ph	Ph	92.7	241 (24.4)	127.5 (10.8)	96	yellow	a	26
4		Mes	Mes	93.2	243.4 (28.0)		99	yellow	a	26
8	Ar	H	Ph	75.6[25] (27) 78.64[41a] (26.6) 75.2[27] (24.4)	240.5 (25.7) 239.3 (25)	113.4 (10.5) 112.9 (10)	100-103[41a] 118[25] 109-114	orange[41a] colorless[25] colorless	b, c, g	25, 27, 41a, 52a
10[b]	Ar	H	CO$_2$Et	71.4 (26)	243.8 (24)	104.3 (13)	93	colorless	c	25
13	H	H	H						e, f	38
14[c]	Me	H	H	42 (26)	250.4 (24.6)	95.2 (13.6)			e, f	38
17	Me	H	Me	45.3 (23)	247.2 (24.5)	107.6 (11.3)			e, f	38
23	Me	Me	Me	39	209 (23.8)	118.6 (10)			e	38
24	Ar	H	t-Bu	77.8 (28)	236.8 (28.7)	122.9 (12.5)	86-87.5	colorless	f	41a
25	Ar	H	Me	66.6 (27.9)	240.3 (27.9)	105.7 (12.5)	69-70.5	colorless	f	41a
26	Ar	H	CH$_2$OTMS	68.9 (26.4)	237 (27.2)	110.6 (13.28)	oil	colorless	f	41b
27	Ar	H	CMe$_2$OTMS	77.6 (27.0)	235.6 (23.67)	119.9 (13.97)	oil	colorless	f	41b

Table 1 (Continued)

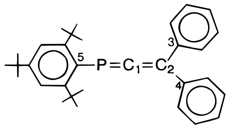
28	Ar	H	C2,2-diphenylOTMS	82.3 (27.03)	236.7 (26.47)	116.6 (12.5)	54-56	yellow	f	41b
29	Ar	H	CMePhOTMS	80.2 (26.28) 79.46 (25.51)	236.4 (29.41)	118.9 (13.97)	108-110	colorless	f	41b
30	Ar	H	$C(C_6H_5)(4\text{-}Me\text{-}C_6H_4)(OTMS)$	80.04 (15) 80.19 (15.1)					f	41b
31	Ar	H	$C(C_6H_5)(\alpha$-naphthyl)OTMS	80.63 (27.14) 82.06 (27.63)					f	41b
32	Ar	Ph	$CH_2CH{=}CHCH_3$	(E) 67.5 (Z) 67.2	236.9 (27)	124.0 (8)	138	colorless	f	42
37	Ar	H	H	62.2 (29.1)	244.1 (27.9)	93.2 (14.7)	119-121[41a]	colorless	f	41a, 43
41	Ar	TMS	P(Cl)Ar				impure solid	pale yellow	f	24
42	Ar	TMS	C(TMS)=C=PAr	42.9[45a] 45.07[44]	233.63 (36.9) 234.02 (37.6)	115 49 (13.2, 13.3) 115.6 (18.7)	131-133[44]	colorless	f	44, 45a
53	Ar	H	C_5H_5	75 (28.7)	242.1 (23)				h	53
55a	 $ArP{=}C{=}C{-}CR_2$ $ArP{=}C{=}C{-}CR_2$		$CR_2 = Cx$	90.6	234.9 (25.7)	127.6 (14.0)	194	pale yellow	i	50a
55b	 $ArP{=}C{=}C{-}CR_2$ $ArP{=}C{=}C{-}CR_2$		$CR_2 = CMe_2$	92.0	233.3 (29.9)	128.2 (14.0)	184	pale yellow	i	50a

[a] d(P=P) (Å): 1.625(4),[58] 1.63.[34] d(C=C) (Å): 1.327(5),[58] 1.31.[34] PCC (deg): 168.0(3),[58] 167.[34] [b] ν(C=O) (cm^{-1}): 1710. [c] IR (cm^{-1}): ν(C=C), 1715; ν(C=P), 869.

short (1.31[34] or 1.327(5) Å[58]) and is almost the same as that of allene itself. The P=C=C bond angle (168.0(3)°)[58] deviates by 12° from 180°: this bending appears to be caused not only by steric repulsion, but also by electronic effects. C_1, C_2, C_3, and C_4 atoms are coplanar within 0.01 Å, and the phosphorus atom deviates by 0.35 Å from this plane[58] (Chart 2). The interplanar angle between the two planes $C_1C_2C_3C_4$ and $C_1C_2PC_5$ is 87.2°, very close to the ideal 90°.[58]

This structure is in good agreement with those calculated on $HP{=}C{=}CH_2$ (see section II.C.1). It should be noted that as in all the ArP=X compounds,

Chart 2



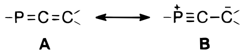
the aromatic ring is distorted to a boat form.

Compared with phosphaalkenes $-P{=}C<$, the chemical shift of the phosphorus atom (39−93 ppm) is at much higher field (Table 1).

The ^{13}C chemical shifts of the sp-hybridized carbon appear at very low field (209−250 ppm), as expected for an allenic carbon. The observed ^{1}J and ^{2}J coupling constants between the phosphorus atom and the carbon atoms (23−30 and 10−18 Hz, respectively) are unexpectedly small (Table 1).

In the infrared spectrum, there is no significant band in the 1600−2300 cm^{-1} region where many antisymmetric $X{=}C{=}Y$ stretchings are observed.[59] There is little, if any, contribution of form **B** (Chart 3).

Chart 3



Phosphaallenes are generally colorless, sometimes pale yellow. The λ_{max} in the UV−Vis spectrum is generally between 305 and 337 nm, the lowest value being 275 nm for $ArP{=}C{=}CH_2$[41a] (Table 2).

Table 2. UV Data of Phosphaallenes

compound	λ_{max} (nm) (ϵ)	ref
1	337 (4100); 263 (27 300); 242 (30 000)	22
8	330 (1500); 258 (23 700); 222 (17 400)	41a
24	308 (740); 275 (2500); 222 (21 200)	41a
25	300 (1100); 222 (24 300)	41a
26	305 (1450); 280 (3200); 220 (35 500)	41b
27	310 (1400); 280 (3700); 220 (51 300)	41b
28	307 (10 000); 270 (39 800); 230 (123 000); 215 (100 000)	41b
29	310 (2500); 285 (5000); 227 (43 300); 215 (40 700)	41b
37	275 (1500); 227 (1700)	41a
42	310 (10 233); 263 (31 000); 260 (34 674); 218 (48 978)	44

C. Theoretical Studies

1. Geometry

The geometry of phosphaallene $HP{=}C{=}CH_2$ has been calculated as having C_s symmetry by various methods including (top) or not including (bottom) the correlation effects[58,60−62] (Table 3). This is in good agreement with the X-ray structure determination performed on $ArP{=}C{=}CPh_2$.[34,58]

Calculations at the HF/6-31G** level on $XP{=}C{=}CH_2$ ($X = Cl, F$)[61a] predict a slight shortening of the $P{=}C$ bond length (Table 4).

Calculations on the phosphaallene radical anion $(HP{=}C{=}CH_2)^{\bullet-}$ [62] showed two minimum energy conformations, cis- and trans-like (more stable by about 1.8−3.0 kcal/mol). The formation of the anion leads to an increase of the $P{=}C$ (1.688−1.769 Å) and $C{=}C$ (1.323−1.343 Å) bond lengths, larger for $P{=}C$ than for $C{=}C$.[62]

Table 3. Geometry in $HP{=}C{=}CH_2$

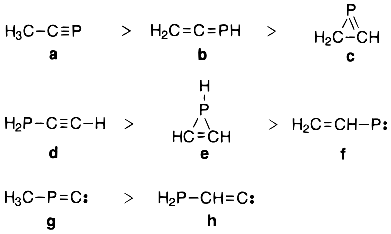
method	P=C (Å)	C=C (Å)	P−C−C (deg)	H−P−C (deg)	C−C−H (deg)	ref
B3LYP/6-311G**	1.646	1.304	173.84	95.95	121.42	62
MCSCF/6-311G**	1.655	1.319	174.96	96.93	121.18	62
MP2/6-311G**	1.646	1.316	173.36	94.92	121.01	62
CCSD/DZP	1.655	1.327	174.3	94.9	109.1	60a
CISD/DZP	1.643	1.316	174.8	95.3	108.6	60b
MP2/6-31G**	1.648	1.314	173.6	95.4	121.2	61a
HF/DZP	1.635	1.301	175.6	96.5	108.0	60b
HF/6.31G*	1.634	1.295	175.6	97.1	121.2	58
HF/3-21G*	1.624	1.292	176.47	97.05	121.44	62
HF/4-31G	1.657	1.290		96.3	107.4	61b

Table 4. Geometry in $XP{=}C{=}CH_2$ (HF/6-31G)[61a]**

	P=C (Å)	C=C (Å)	P−C−C (deg)	X−P−C (deg)	C−C−H (deg)
X = Cl	1.621	1.296	176.6	101.9	121.2
X = F	1.618	1.297	175.8	103.5	121.2

2. Relative Stability of C_2H_3P Isomers

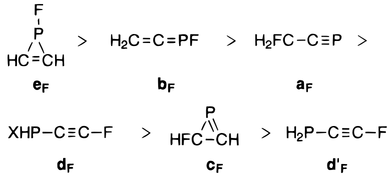
Chart 4



Calculations performed on the C_2H_3P isomers **a**−**h**[60,61a] (Chart 4) showed that 1-phosphapropyne **a** is the most stable derivative. The phosphaallene **b** lies about 20 kcal/mol (between 18 and 23 kcal/mol depending on the method used) higher in energy followed by 2*H*-phosphirene **c** (∼20−21 kcal/mol), ethynylphosphine **d** (∼31 kcal/mol) and the 1*H*-phosphirene **e** (∼35 kcal/mol).[60,61a] Phosphinidene **f** and double-bonded carbenes **g** and **h** are much less stable (respectively, ∼52,[60b] 70−80,[60] and 87[60b] kcal/mol). A similar energy ordering has been found for the isovalent C_2H_3N species.[63]

The energy diagram is dramatically modified in the fluorinated and chlorinated derivatives, particularly in the fluorinated species since the fluorophosphaallene $\mathbf{b_f}$ becomes energetically more favorable than $H_2FC{-}C{\equiv}P$ $\mathbf{a_f}$ by about 4.5 kcal/mol.[61a] The preference of $\mathbf{b_f}$ over $\mathbf{a_f}$ arises essentially from a difference between the energies of the P−F and C−F bonds.[61a] In fluorinated compounds the energy ordering is displayed in Chart 5.[61a] When the halogen is a

Chart 5

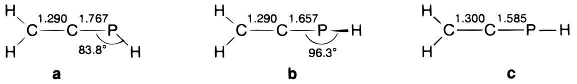


chlorine, the energy ordering is **a** > **b** > **e** > **d** > **c** > **d′**.

3. Configurational Stability

The phosphaallenes are rather stable toward configurational change. The barrier to rotation was calculated to be 47−49 kcal/mol[61b] and the barrier to inversion 78−84 kcal/mol.[61b] Thus, the interconversion process via the rotation transition structure **a** is noticeably favored relative to the inversion transition structure **c** by about 30−36 kcal/mol (Chart 6). For comparison, the difference between the two processes is much lower in $H_2C{=}PH$ (6 kcal/mol)[64] and in HP=PH (10 kcal/mol).[65] By contrast, in the ketenimine $H_2C{=}C{=}NH$, the interconversion process involves, as expected, an inversion of nitrogen with a much lower barrier, generally close to 10 kcal/mol.[66]

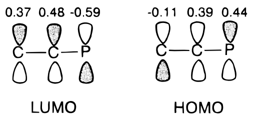
Chart 6



4. Electronic Structure

The HOMO in $H_2C{=}C{=}PH$ as well as in $H_2C{=}PH$ is the π-orbital of the C=P bond with the largest coefficient on the P atom. There is only a small difference of energy to the lower n-orbitals of the phosphorus atom.[61b] Both the LUMO and HOMO appear to be dominated by the C=P bond, which possesses the largest orbital coefficient[61b] (Chart 7).

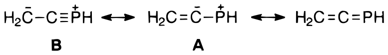
Chart 7 [a]



This explains the similar chemical behavior between phosphaallenes and phosphaalkenes. The n−π separation of 0.6 eV in $H_2C{=}C{=}PH$ is much smaller than that in $H_2C{=}C{=}NH$ (3.15 eV). The sp² carbon is the most negatively charged, which is a great difference with the ketenimines[61b] (Table 5). Note in this table that the formal charge at (P)H may vary according to the quality of the starting geometry (supposed to be best described by using DZP//6-31G*), illustrating the high polarizability of the P−H bond.

The resonance structures **A** and **B** appear to be only minor contributors to the overall structure of the $HP{=}C{=}CH_2$ molecule[61b] (Chart 8).

Chart 8


$$H_2\overset{-}{C}{-}C{\equiv}\overset{+}{P}H \longleftrightarrow H_2C{=}\overset{-}{C}{-}\overset{+}{P}H \longleftrightarrow H_2C{=}C{=}PH$$

The dipole moment was estimated to be 1.44[61b]−1.66 D,[58] bigger than in phosphaalkene $HP{=}CH_2$ (1.289 D)[58] but smaller than in ketenimine $H_2C{=}C{=}NH$ (1.74 or 1.97 D).[63]

Table 5. Charges in Phosphaalkenes, Phosphaallenes, and Ketenimines

	$H_2C^1{=}PH$		$H_2C^2{=}C^1{=}PH$		$H_2C^2{=}C^1{=}NH$
atom	DZP// 4.31G[61b]	DZP// 6-31G*[58]	DZP// 4.31G[61b]	DZP// 6-31G*[58]	DZP// 4.31G[61b]
C^1	−0.49	−0.54	−0.10	−0.09	−0.24
C^2			−0.34	−0.41	0.06
P (or N)	0.17	0.19	0.13	0.11	−0.27
H(P or N)	0.01	−0.01	0.05	−0.05	0.20

5. Vibrational Frequencies

As said previously, the most striking feature is that there are no significant bands in the region 1600−2300 cm^{-1}, in clear contrast to other cumulenes. Calculations display two stretching frequencies belonging to the C=C=P skeleton at 1788 (stretching of the C=C bond) and 789 cm^{-1} (stretching of the C=P bond).[61b] For comparison, the C=C=N stretching frequency is in the 2000−2050 cm^{-1} range (for example 2011 cm^{-1} in $Mes_2Ge(F)C{=}C{=}N{-}CPh_3$)[67] and is a very strong band. Such results prove the great difference between the two molecules since no stretching mode involves the C=C=P group: C=P and C=C stretching are nearly independent of each other due to the nongeometric and electronic interactions between C=C and C=P bonds.

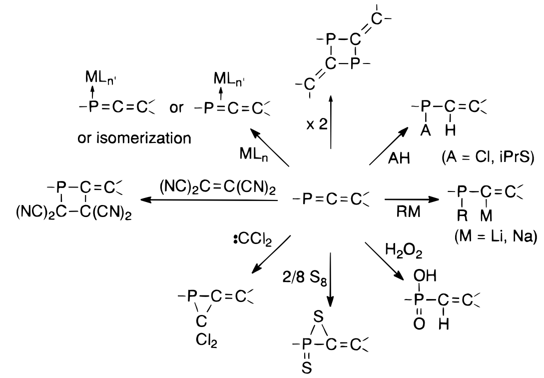
6. Proton Affinity

The carbon double bonded to phosphorus is the preferred site of protonation followed by phosphorus and the sp² carbon,[61b] in contrast to the case of ketenimine in which the ordering is sp²-C, N and then sp-C.[68]

D. Reactivity

Three reactive centers are present in phosphaallenes: the P=C double bond, the C=C double bond, although this bond is expected to be less reactive, and the phosphorus atom, mainly for complexation with transition metals (Scheme 9). The reactivity of phosphaallenes is in fact very similar to that of phosphaalkenes −P=C<,[18,19] since the adjacent C=C double bond does not interfere with the P=C unsaturation. One exception is the formation of cyclobutene[44−48] (see section II.A.6 and Scheme 7) from bis(phosphaallenes) by dimerization between two C=C double bonds.

Scheme 9



1. Dimerization (Scheme 9)

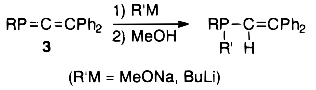
A large steric hindrance on phosphorus is necessary for the stabilization in a monomeric state, explaining why the bulky 2,4,6-tri-*tert*-butylphenyl ("supermesityl") group has been generally used. Only two phosphaallenes have been stabilized by another group, the tri-*tert*-butylcyclopropenyl group.[26] With a phenyl group on phosphorus, $PhP{=}C{=}CPh_2$ is not stable enough for a physicochemical characterization and head-to-tail dimerizes.[25]

2. Reaction with Protic Reagents

HCl and ^{i}PrSH add to the P═C double bond of $ArP{=}C{=}CHPh$[19] and $RP{=}C{=}CH_2$ (R = H, Me),[37,38] respectively (Schemes 2 and 9). In all cases the hydrogen goes to the central carbon atom in agreement with calculations.

3. Reaction with Alkoxide or Lithium Compounds

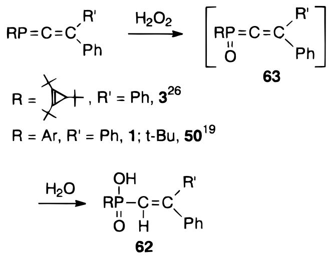
Methanol does not react with **3**. In contrast, the nucleophilic sodium methoxide adds, as well as *n*-butyllithium, to the P═C double bond of phosphaallene $RP{=}C{=}CPh_2$ (R = tri-*tert*-butylcyclopropenyl) to afford after methanolysis the corresponding phosphine[26] (eq 18).



(18)

4. Reaction with H_2O_2

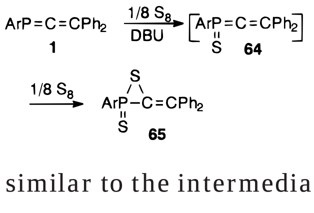
The "oxidative" addition of oxygen to the P═C double bond via treatment of the phosphaallenes **1**, **3**, and **50** with aqueous hydrogen peroxide and subsequent addition of water gives the phosphinic acids **62**[19,26] (eq 19). It is assumed that, in view of the resistance of phosphaallenes to solvolysis, the first step of the reaction is the formation of the highly reactive oxovinylidene-phosphoranes **63** followed by the 1,2-addition of water.[26] (It is known that methyleneoxophosphoranes O═P(R)═C< easily add water to yield phosphinic acids.[69])



(19)

5. Reaction with Sulfur

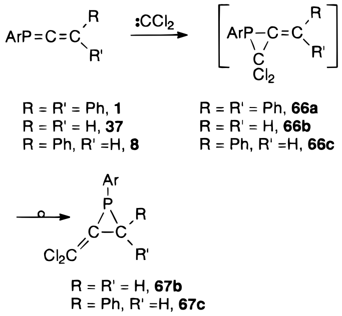
An intermediate similar to **63**, the 1-phosphaallene-1-sulfide **64**, was postulated in the reaction of sulfur with $ArP{=}C{=}CPh_2$ in the presence of DBU, finally leading to the thiaphosphirane sulfide **65**[70,71] (eq 20). **64** was observed in ^{31}P NMR (δ $^{31}P = 79$ ppm)[70] and is similar to the intermediate postulated in sulfurization reactions of other types of doubly bonded phosphorus compounds such as phosphaalkenes[72,73] and diphosphenes.[74]



(20)

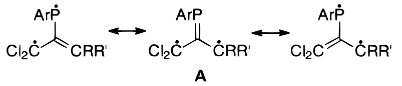
6. Reaction with Carbenes

A [2+1]-cycloaddition reaction to the P═C double bond was observed in the reaction of phosphaallenes **1**, **8**, and **37** with dichlorocarbenes (generated by the Makosza method[75] using benzyltriethylammonium chloride as a phase-transfer catalyst) leading to **66**[43,52b,76] (eq 21). Whereas **66a** is stable, methylene–phosphiranes with less bulky substituents at the terminal carbon isomerize to **67b** and **67c**,[43] probably via intermediate **A** in which the steric bulk is operating in determining the regiochemistry of the reaction product[43] (Chart 9). A molecular mechanics calculation (MM2 method) predicted that **67b** was more stable than **66b** by 2.47 kcal/mol,[43] in agreement with experiment.



(21)

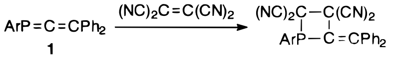
Chart 9



Heterocycles **66** and **67** present the expected upfield chemical shifts (−93.4 to −126.7 ppm) characteristic of phosphorus-containing small-ring compounds.[78] **66a** appears to be an excellent precursor of 1-phosphabutatriene by reaction with a lithium compound (see section X.A) and of $ArP{=}CCl_2$ and allene $Ph_2C{=}C{=}CCl_2$[77] with an excess CCl_2.

7. Reaction with $(NC)_2C{=}C(CN)_2$

A [2+2]-cycloadditition between **1** and tetracyanoethylene gives the corresponding four-membered ring compound[19] (eq 22).



(22)

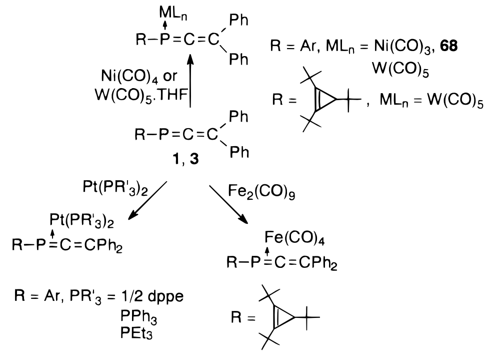
8. Reaction with Transition-Metal Complexes (Scheme 10)

The reactions of phosphaallenes with transition-metal complexes give various results depending on the metal used and on the experimental conditions (Scheme 10).

An η^1-coordination was observed in the complexation of **1** with $W(CO)_5{\cdot}THF$[79a] or $Ni(CO)_4$[79b] and of **3** with $W(CO)_5{\cdot}THF$.[26] Complex **68**[79b] is labile since it reverts to **1** by dissolution in toluene.

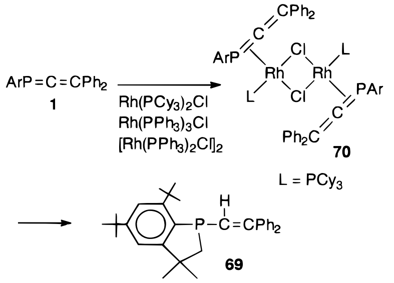
With $Fe_2(CO)_9$ and **3**, an η^2-coordination occurs,[26] as proved by the dramatic shift to higher field of the

Scheme 10



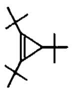
δ ^{31}P (−103.9 ppm) relative to the parent **3** (δ = 92.7 ppm) or to the complexes with an η^1-coordination (δ = 53−87 ppm) (Table 6). An η^2-coordination was also observed between **1** and platinum complexes.[80,81]

With phosphaallene **1** and some rhodium complexes, a quantitative isomerization to the phosphaindane **69** was observed[81,82] (eq 23). The catalytically active intermediate **70** was isolated when L = PCy_3. An isomerization of **1** to phosphaindane **69** occurs also with $Pt(PCy_3)_2$.[81]



(23)

Table 6. Phosphaallene Complexes

η	RP=C=C(R1)R2			ML_n	δ ^{31}P (ppm)	δ $^{13}C_1$ ($^1J_{CP}$)	δ $^{13}C_2$ ($^2J_{CP}$)	d P=C (Å)	d C=C (Å)	$P-C_1-C_2$ (deg)	method[e]	ref
	R	R_1	R_2									
η^1	Ar[a]	Ph	Ph	$Ni(CO)_3$	78.1			1.615(5)	1.318(6)	171.5	a	79b
η^1	Ar	Ph	Ph	$W(CO)_5$	53.78 ($^1J_{PW}$: 268.6)			1.625(4) 1.632(7)	1.327(5) 1.311(10)	168.0(3) 171.2(6)	a	79a
η^1	 [b]	Ph	Ph	$W(CO)_5$	81.7 ($^1J_{PW}$:110.8)	226.3 (18.0)					a	26
η^2	 [c]	Ph	Ph	$Fe(CO)_4$	-103.9	156.8 (26.5)	140.1 (20.1)				a	26
η^2	Ar	Ph	Ph	(dppe)Pt	-96.3						a	80b, 81
η^2	Ar	Ph	Ph	$(Ph_3P)_2Pt$	-70.6						a	80b, 81
η^2	Ar	Ph	Ph	$(Et_3P)_2Pt$	-105.1						a	80b, 81
η^2	Ar[d]	Ph	Ph	$[Cy_3PRhCl]_2$	-38.8 (J_{PRh}: 37)	179.6 (99.0)					a	82
η^2	Ar	Ph	Ph	$[Ph_3PRhCl]_2$	-59.3 (J_{PRh}: 37)						a	82
η^1	$(Me_3Si)_2CH$	OEt	$SnMe_3$	$W(CO)_5$	76.4 (J_{PW}:262.6)	226.5 (90.9)	156.1				b	54
η^1	$(Me_3Si)_2CH$	OEt	$SnPh_3$	$W(CO)_5$	87.4 (J_{PW}:265.5)	227.8 (90.4)	154.5 (2.0)				b	54
η^2	t-Bu	H	Ph	$(CO)_3FeCo_2(CO)_6$				1.753(9)	1.33(1)	130.3(7)	c	56

[a] mp: 129 °C, colorless crystals. [b] Yellow-brown resin. [c] Red-brown crystals. [d] IR: ν(C=C): 1586 cm^{-1}, red crystals. [e] Methods: (a) Direct complexation of a phosphaallene by a transition metal. (b) Reaction of an azaphosphirene complex with an acetylenic. (c) Reaction of a chlorophosphine with $H(CO)_4Fe^-$ and $Co_2(CO)_8$.

By studying group 6 metal carbonyl complexes of $-P{=}P-$, $-P{=}C<$, $-P{=}C{=}C<$, and $-P{=}C{=}P-$, Yoshifuji found that their ^{31}P chemical shifts correlate to one another so that their structures in solution could be determined.[83]

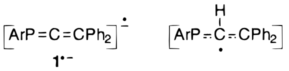
9. Electrochemical Reduction of Phosphaallenes

A cyclic voltammetry study has been performed on the phosphaallenes **1** and the ^{13}C-enriched **1′** and **1″**[62] (Chart 10), which have been synthesized by route b (Scheme 1) using $H^{13}CCl_3$ (for **1′**) and $O{=}^{13}CPh_2$ (for **1″**).[84] **1** undergoes irreversible reduction at 2266 mV in THF and 1965 mV in DMF. Although the EPR parameters are not inconsistent with the formation of the radical anion $\mathbf{1}^{\bullet-}$ (isotropic coupling with P in solution, 262 MHz for **1**, **1′**, **1″**; with ^{13}C, 33 MHz for **1′**, 34 MHz for **1″**), calculations show that the hyperfine interactions are more in accordance with the neutral allylic structure $[ArPCHCPh_2]^\bullet$ than with the radical anion $\mathbf{1}^{\bullet-}$[62] (Chart 11).

Chart 10

$ArP{=}C{=}CPh_2$ **1** $ArP{=}^{13}C{=}CPh_2$ **1'** $ArP{=}C{=}^{13}CPh_2$ **1"**

Chart 11



10. Phosphaallenes as Precursors of Phospha- and Diphosphabutatrienes

Reactions of phosphaallenes such as **26**−**31**, **40**, and **41**, leading to 1-phosphabutatrienes or 1,4-diphosphabutatrienes $-P{=}C{=}C{=}X$ (X = C, P) and thus not involving the $P{=}C{=}C$ moiety, have also been reported. They are described in sections X and XII devoted to the synthesis of these derivatives.

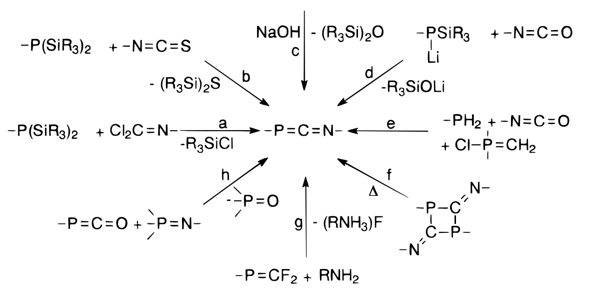
III. 1,3-Phosphaazaallenes –P=C=N–

A. Synthesis

1. Reactions Leading To Dimers of Phosphaazaallenes (Routes a, b, c)

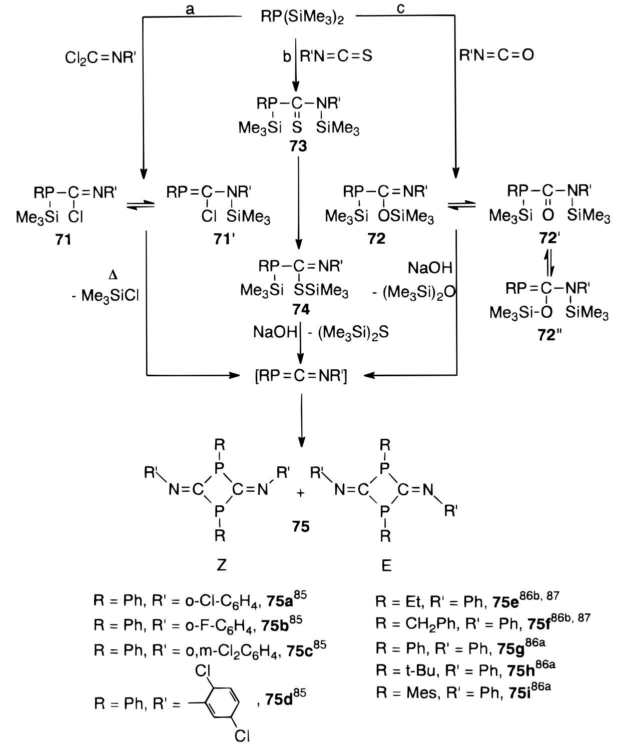
The first attempts to synthesize phosphaazallenes were performed in 1980 (Scheme 11). However, when steric hindrance is not large enough, only their head-to-tail dimers by P=C bonds, the 2,4-diimino-1,3-diphosphetanes, were obtained.[85−87]

Scheme 11



The three similar routes a, b, c, starting from a bis(trimethylsilyl)phosphine $RP(SiMe_3)_2$,[85−87] have been used (Scheme 12). Reactions with various isocyanide dichlorides $R'N{=}CCl_2$ lead first to the tautomeric forms **71**/**71′**[85] (route a). With phenylisocyanate $PhN{=}C{=}O$, the iminomethylphosphines **72**[86] exist in equilibrium with the carbamoylphosphines **72′** and smaller amounts of alkylidenephosphines **72″**[88] (route c). With phenylisothiocyanate, the thiocarbamoylphosphines **73**[86] are characterized in solution as well as in the solid state. However, after some days at room temperature, they rearrange to **74**[86a] (route b). Heating **71**/**71′**[85] or addition of small amounts of sodium hydroxyde to **73**/**74**[86] or **72**/**72′**/**72″**[86] leads to transient phosphaazaallenes which then dimerize.

Scheme 12



R = Ph, R' = o-Cl-C$_6$H$_4$, **75a**[85]
R = Ph, R' = o-F-C$_6$H$_4$, **75b**[85]
R = Ph, R' = o,m-Cl$_2$C$_6$H$_4$, **75c**[85]
R = Ph, R' = , **75d**[85]
R = Et, R' = Ph, **75e**[86b, 87]
R = CH$_2$Ph, R' = Ph, **75f**[86b, 87]
R = Ph, R' = Ph, **75g**[86a]
R = t-Bu, R' = Ph, **75h**[86a]
R = Mes, R' = Ph, **75i**[86a]

The expected phosphaazaallenes could not be characterized by physicochemical methods or by trapping reactions, but their intermediate formations can be reasonably postulated. An intermolecular elimination of Me_3SiCl, $(Me_3Si)_2O$, or $(Me_3Si)_2S$, even if it cannot be completely excluded, is very unlikely.

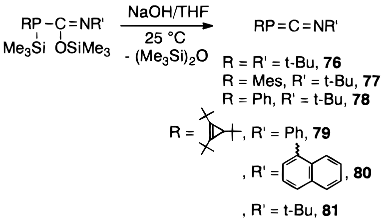
A mixture of *E* and *Z* isomers is obtained for the dimers **75**, displaying as expected three groups of signals in the ^{31}P NMR, one singlet for the *E* isomer and two doublets for the unequivalent phosphorus atoms of *Z* isomer. When the group on phosphorus is the small ethyl group, two trimers are also obtained[86b] besides the dimers.

2. Reactions Leading To Stable or Marginally Stable Phosphaazaallenes

By marginally stable, we mean stable enough to be physicochemically characterized by at least IR or NMR.

a. From Silylphosphines and Isocyanates (Route c). The first stable phosphaallenic compound

$-P{=}C{=}E$ to be prepared was the phosphaazaallene t-BuP=C=Nt-Bu obtained by Kolodiazhnyi by route c[89] (eq 24). **76** is very stable since it can be purified



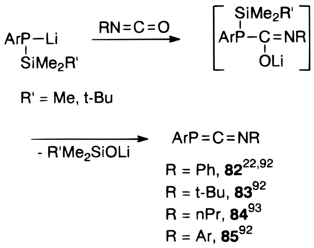
(24)

by distillation at 65−66 °C/10 mmHg. Two other stable phosphaazaallenes **77** and **78** have been obtained by this route.[90]

Such a result proves that the choice of substituents is very important for the stabilization of doubly bonded phosphorus compounds and that a small change in the substituents drastically modifies the stability of these species: for example, **76** is stable whereas the phosphaazaallene with a Ph instead of a t-Bu on nitrogen dimerizes rapidly.[86a]

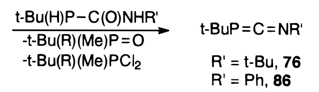
This route was also employed by Regitz to prepare the three stable phosphaazaallenes **79**, **80**, and **81** substituted on phosphorus by the very bulky tri-*tert*-butylcyclopropenyl group.[91]

b. From Lithium Silylphosphides and Isocyanates (Route d). A similar route starting from the lithium silylphosphide ArP(Li)SiMe$_3$ instead of the disilylphosphine RP(SiMe$_3$)$_2$ involving the elimination of Me$_3$SiOLi was used by Yoshifuji[22,92] and Appel.[93] This phospha−Peterson reaction allowed the synthesis of the four stable phosphaazaallenes **82**−**85** (eq 25).



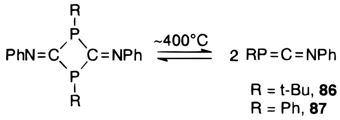
(25)

c. Dehydration of Phosphaureas (Route e). The di-*tert*-butylphosphaazaallene **76** has also been synthesized by Kolodiazhnyi[90b] by dehydration of a phosphauree by a *P*-chloroylide,[94] the latter being obtained from CCl$_4$ and the corresponding phosphine (eq 26). When R′ is a phenyl, the dimer of **86** was formed rapidly.



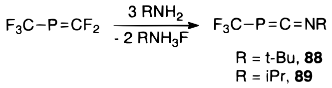
(26)

d. Monomerization (Route f). The phosphaazaallenes **86** and **87** can be generated from their dimers by flash vacuum pyrolysis at 400 °C[95] and trapped at low temperature (eq 27). The reaction was monitored by IR. On warming the pyrolysate above −55 (R = Ph) or −25 °C (R = t-Bu), the strong bands at, respectively, 1853 and 1839 cm^{-1} ascribable to the P=C=N moiety decreased due to the dimerization of **86** and **87** to the diphosphetanes.



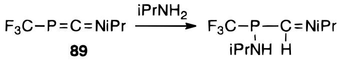
(27)

e. From an Amine and a *C,C*-Difluorophosphaalkene (Route g). The reaction of *P*-trifluoromethyldifluorophosphaalkene F$_3$C−P=CF$_2$[96] with primary amines such as *tert*-butyl- or isopropylamines in a 1/3 molar ratio leads to the phosphaazaallenes **88**[97] and **89**[97] (eq 28). **89** is obtained in a very low



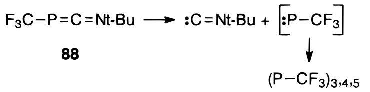
(28)

yield (5%) because it reacts with the starting ^{i}PrNH$_2$ to give the corresponding imine (eq 29).



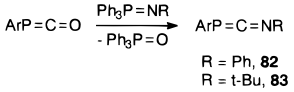
(29)

Due to the strong electronic effect of the CF$_3$ group, **88** presents a behavior completely different from other phosphaazaallenes since it does not give a dimer but slowly decomposes at room temperature by cleavage of the P=C double bond leading to *tert*-butylisonitrile and cyclopolyphosphines[97] (eq 30).



(30)

f. Wittig-Type Reaction (Route h). A Wittig-type reaction of a phosphaketene with an iminophosphorane has also been successfully used to prepare phosphaazaallenes **82** and **83**[19,28] (eq 31).



(31)

B. Physicochemical Studies

1. IR (Table 7)

Whereas no significant band in the 1600−2200 cm^{-1} region was observed for phosphaallenes $-P{=}C{=}C{<}$, one of the main characteristics in the IR of the phosphaazaallenes is the strong band between 1830 and 1915 cm^{-1} due to the asymmetric stretching vibration (Table 7). A large contribution of the dipolar forms **a** and **b** is probably responsible for this band (Chart 12). The absorption was exceptionally found at 1948 cm^{-1} in F$_3$C−P=C=Nt-Bu **(88)**[97] due to the electronic effect of the CF$_3$ group. Surprisingly, three absorptions at 2020, 2040, and 2060 cm^{-1} were given for the phosphaazaallene ArP=C=NAr[92] substituted by two extremely bulky Ar groups. The latter also has another special characteristic compared to other

Chart 12

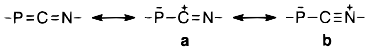
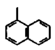


Table 7. Phosphaazaallenes: Synthetic Routes and Physicochemical Data (For methods, see Scheme 11)

n°	R (P)	R¹(N)	ν P=C=N (cm^{-1})	δ ³¹P	δ ¹³C (ppm) J_{PC} (Hz)	mp (°C) or Eb (mm Hg)	color	method	ref
76	t-Bu	t-Bu	1895	-64.47	199.96 (76)	Eb: 65/10	yellow oil	b,e	89, 90
77	Mes	t-Bu	1905	-127				b, e	90
78	Ph	t-Bu	1915	-99				b, e	90b, 95
79		Ph	1830	-104.5	206.8 (61.6)	172	yellow	b	91
80			1840	-101.4	205.9 (63.5)	Eb: 140/10^{-2}	yellow oil	b	91
81		t-Bu	1870	-115.0	198.4 (78.1)	Eb: 110/10^{-3}	yellow oil	b	91
82[a]	Ar	Ph	1845	-106.2	209.4 (27.4)	90-92	yellow	d, h	19, 22, 28, 92
83[b]	Ar	t-Bu	1885	-101.9	192.2 (76.2)	166-168	yellow	d, h	19, 28, 92
84	Ar	nPr	1890	-112	196.9 (74)	59-60		d	93
85	Ar	Ar	2060 2040 2020	-135.3	171.8 (91.4)	82-84	red	d	92
86	t-Bu	Ph	1839					b, c, f	90b, 95
87	Ph	Ph	1853					c, f	95
88[c]	CF_3	t-Bu	1948	-87.3	172.5 (89.2)			g	97
89	CF_3	iPr		-93.5				g	97

[a] UV: 415 nm (ϵ 490), 288 (8700), 258 (32 600), 202 (73 500), X-ray: d(P=C) 1.651 Å, d(C=N) 1.209 Å; P−C−N 171.1°; dihedral angle CPCN 128°, CNCP 134°. [b] UV: 376 (490), 291 (9600), 250 (7200), 203 (49 600). [c] $\delta(^{15}N)$: −130.8.

phosphaazaallenes since it is red[92] whereas such derivatives are generally yellow.

2. NMR (Table 7)

In ^{31}P NMR, chemical shifts between −64 and −135 ppm are observed. Such unusual high-field chemical shifts, since low-coordinate phosphorus atoms generally give signals at low field (200−500 ppm), prove the contribution of the forms **a** and **b** (Chart 12).

In ^{13}C NMR, the signal of the sp carbon is as expected at very low field, between 170 and 210 ppm with generally large $^1J_{PC}$ coupling in the range 70−90 Hz. Such a large coupling compared to the 25−30 Hz observed for $^1J_{PC}$ in phosphaallenes −P=C=C< reflects the great difference between the two structures.

3. X-ray Studies

The X-ray study[98] of ArP=C=NPh displays a P−C−N angle (171.2°) distorted from linearity (wider angles are found by calculations (see section III.C.1)) and a slightly compressed value for the C=N bond length (1.209 Å) compared to carbodiimides RN=C=NR (R = p-MeOC$_6$H$_4$, 1.213 and 1.226 Å;[99a] R = p-Tol, 1.204 and 1.223 Å).[99b] A slight elongation of the P=C bond length is observed (1.651 Å vs, for example, 1.635(8) and 1.630(8) Å in the diphosphaallene ArP=C=PAr[100]). Thus, from the X-ray, IR, and ^{31}P analyses, there seems to be some contribution from the canonical form of type **b** (Chart 12).

C. Theoretical Studies

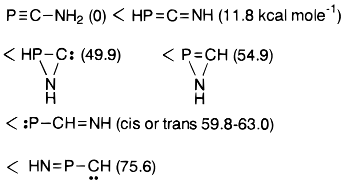
1. Geometry

The fully optimized geometries determined by ab initio calculations exhibit a nonlinear P=C=N frame with a P−C−N angle of 174.8° [98] (HF/6-31G) (up to 176.7° with less complete basis sets).[98,101] However, the energy difference between nonlinear and linear P=C=N configurations is not significant (0.5 kcal/mol).[101]

2. Relative Stability of PCNH$_2$ Isomers

Calculations (HF/4-31G) on the structure and energy of PCNH$_2$ isomers produced by a hydrogen shift reveal that the aminophosphaalkyne P≡C−NH$_2$ is more stable than HP=C=NH by about 11.8 kcal/mol[102] (Chart 13).

Chart 13



3. Configurational Stability

The isomerization process occurs by an inversion at the C=N bond and by a rotation around the C=P bond. The calculated energy barrier (DZP//4-31G) for the racemization of HP=C=NH is very low (~ 4.2 kcal/mol),[101] similar to that found in carbodiimides HN=C=NH (8 kcal/mol).[103]

4. Electronic Structure

The structure of HP=C=NH can be understood as clearly showing the electron-withdrawing effect of the C=N group, which is well correlated with the calculated overlap populations[101] (P=C: 0.85, N=C: 1.51). This confers a partial double-bond character onto the P=C double bond, which favors a rotation around this bond and a partial triple-bond character onto the C=N bond which favors the inversion.[101]

In comparing the charges on phosphorus, carbon, and nitrogen atoms in HP=C=NH, as well as in HP=CH$_2$, HP=C=PH, and HN=C=NH (Table 8), we can note a charge transfer toward the phosphorus atom in HP=C=NH. This is reflected in its ^{31}P NMR signal at low field (~−100 ppm) whereas HP=CH$_2$ and HP=C=PH give signals around 200−400 and 150 ppm, respectively.

5. Proton Affinity and Chemical Reactivity

The protonation occurs preferentially at the phosphorus atom in HP=C=NH.[101] By comparison, other

Table 8. Charges on C, P, and N Atoms in Phosphaalkenes, Diphosphaallenes, Phosphaazaallenes, and Carbodiimides (HF/DZP)[101]

atom	$HP{=}CH_2$	$HP{=}C{=}PH$	$HP{=}C{=}NH$	$HN{=}C{=}NH$
C	−0.49	−0.14	−0.06	0.28
P	0.17	0.02	−0.01	
N			−0.25	−0.40

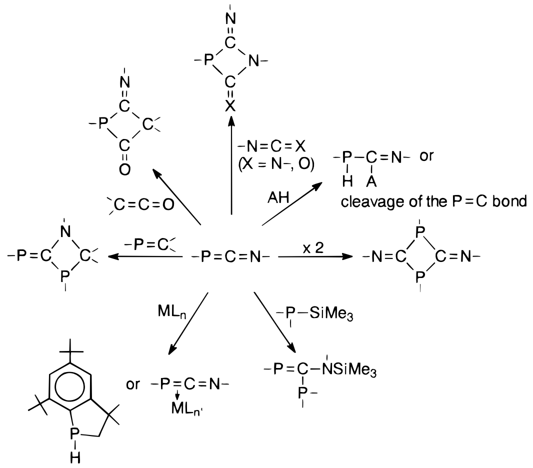
$-P{=}C{=}E$ compounds such as $HP{=}C{=}O$[104] also display a P-protonation but a C-protonation is predicted for $HP{=}C{=}CH_2$[61b] and $HP{=}C{=}PH$.[101] The preference for reactions to occur at the C=P bond is consistent with the polar character of the bond and the electrophilic center situated at the phosphorus atom.

D. Reactivity

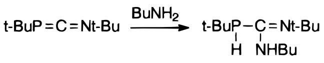
1. Protic Reagents

Most of the reactions of phosphaazaallenes are observed on the P=C double bond, but some also occur on the C=N moiety (Scheme 13).

Scheme 13



Addition of butylamine to t-BuP=C=Nt-Bu is slow at room temperature, giving, after about 10 days, the adduct **90** with the nucleophile part added to the carbon atom and the proton to the phosphorus atom[89,90] (eq 32).

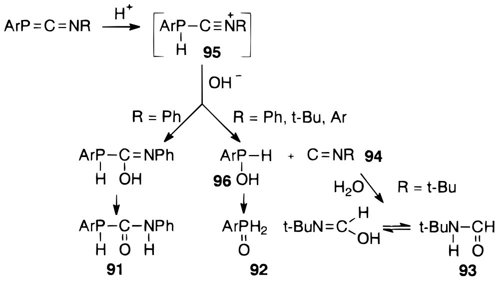


$$t\text{-BuP}{=}C{=}Nt\text{-Bu} \xrightarrow{BuNH_2} t\text{-BuP(H)}{-}C(NHBu){=}Nt\text{-Bu} \qquad (32)$$

90

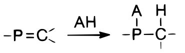
With water, various products **91**−**94** are obtained depending on the steric hindrance of the group on nitrogen;[92] in each reaction the phosphine oxide $ArP(O)H_2$ was obtained (Scheme 14). The formation of **91**−**94** can be understood by the following mechanism postulated by Yoshifuji:[92] the first step of the reaction could be the formation of the intermediate **95** obtained by protonation of the phosphorus atom followed by cleavage of the P−C bond with formation of **94** and **96** which then gives **92**. When R is the bulky Ar group, the isocyanide **94** is stable toward water. When R is a *tert*-butyl, the isocyanide t-BuN=C hydrolyzes to give the *N*-*tert*-butylformamide HC(O)NHt-Bu. When the substituent on nitrogen is not bulky enough (such as a phenyl) to prevent nucleophilic attack on carbon, compound **91** was obtained as the major product.

Scheme 14



Protonation of the phosphorus atom and nucleophilic attack on the carbon atom in phosphaazaallenes can also be understood by the largest HOMO coefficient on P and a rather large LUMO coefficient on C.

A reversed reactivity of phosphaalkenes toward proton-acidic reagents has been established (eq 33).[18,19]



$$-P{=}C\langle \xrightarrow{AH} -P(A){-}C(H)\langle \qquad (33)$$

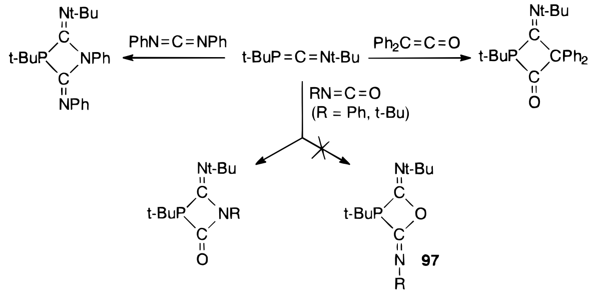
A = RO, RS

This difference in the regiochemistry of this addition can be interpreted by both charges and orbital considerations. In phosphaalkenes, the strongly positive charge on the phosphorus atom induces exclusive fixation of anionic X^- to phosphorus whereas in phosphaazaallenes the shift of the electronic density to the phosphorus atom gives it a certain nucleophilic character making it able to capture the proton.

2. Diphenylketene, Carbodiimides, and Isocyanates

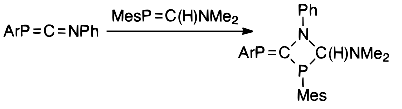
[2+2]-Cycloadditions occur between $Ph_2C{=}C{=}O$,[90] $PhN{=}C{=}NPh$,[89a,90] $RN{=}C{=}O$ (R = Ph,[89,90] t-Bu[89b,90]), and the P=C double bond of t-BuP=C=Nt-Bu generally at −70 °C (Scheme 15). These reactions are regiospecific involving an addition to the C=C double bond of $Ph_2C{=}C{=}O$ and the C=N double bond of $RN{=}C{=}O$. In the reaction with isocyanates, the absence of compound **97** is not surprising since C=N additions have been generally demonstrated to be more favorable.[105]

Scheme 15



3. Phosphaalkenes

Another type of [2+2]-cycloaddition has been reported between phosphaazaallene ArP=C=NPh and the phosphaalkene $MesP{=}C(H)NMe_2$: in contrast to cumulenes which give [2+2]-cycloadducts with the P═C double bond of the phosphaazaallene, it is the C═N unsaturation which is involved in this case (eq 34).[19,28]

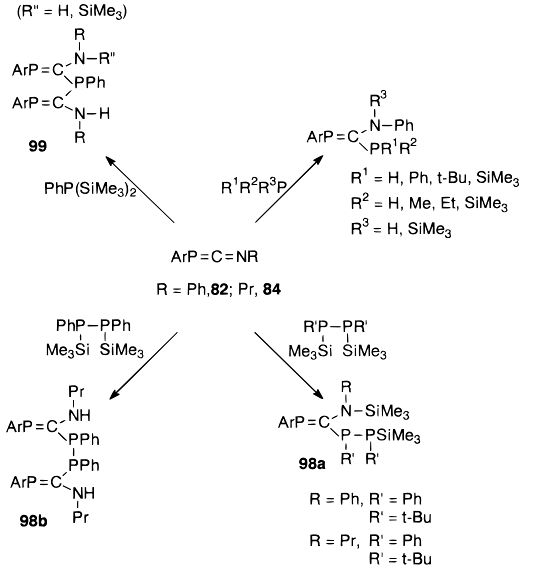


(34)

4. Silylphosphines

The addition of various silylphosphines having one, two, or three Si−P bonds to phosphaazaallenes ArP═C═NR (R = Ph, Pr) occurs only by the C═N double bond.[93] The driving force for this reaction could be the formation of the strong Si−N bond (Scheme 16).

Scheme 16

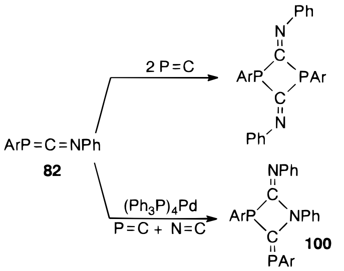


In nonpolar solvents, **82** and **84** give with disilyldiphosphines compounds **98a** whereas in acetonitrile solvolysis products **98b** and **99** were exclusively obtained from **82** and **84** and disilylphosphines or disilyldiphosphines.[93] In contrast to less hindered compounds, **99** undergoes no Cope rearrangement.

5. Dimerization

When the steric hindrance is not important enough, the main reaction of phosphaazaallene is a very easy head-to-tail dimerization by the P═C double bonds[85,86,95] (eq 27, Schemes 12 and 13). This is well understood from the large difference in the HOMO−LUMO energy separation between the P═C and C═N bonds, which induces a strong stabilizing interaction when the two C═P double bonds approach each other.[101] For example, ArP═C═NPh slowly dimerizes on standing at room temperature in solution or even in the solid state via the two P═C double bonds to give the corresponding diphosphetane[81] (Scheme 17). Due to the large steric hindrance proved by the restricted rotation around the P−C(Ar) bond observed in ^{1}H NMR, only the *E* isomer was obtained whereas generally both *E* and *Z* isomers are formed in the dimerization of other phosphaazaallenes.[85,86]

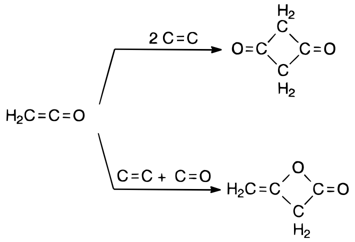
Scheme 17



$(Ph_3P)_4Pd$ catalyzes the dimerization of ArP═C═NPh but give another type of dimer involving a P═C and a C═N double bond.[81] **100** can be characterized in ^{31}P NMR by an AX system at δ: 111 (ArP═C) and 32 ppm (ArP) with a coupling constant $^2J_{PP}$ of 124 Hz.[81] We should note that it is rather unusual to find a compound such as **82** which exists in three isolable different forms, a monomer and two types of dimers.

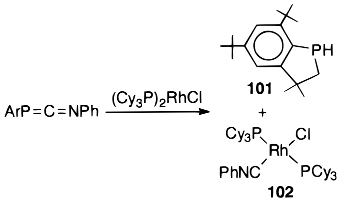
A similar type of symmetrical and unsymmetrical dimerization is observed with transient metallacumulenes such as metallaphosphaallenes RR′E═C═PAr (E = Si[106a] and Ge,[106b] see sections XVI and XIX) and even with ketene (Scheme 18).

Scheme 18



6. Transition-Metal Complexes (Table 9)

Reactions of phosphaazallenes with transition-metal complexes give various derivatives depending on the metal used. With $(Cy_3P)_2RhCl$ and ArP═C═NPh, only derivatives **101** and **102** are obtained (eq 35).[82] This result suggests that the rhodium-induced extrusion of CNPh moiety from the phosphacumulene gives the intermediate phosphinidene ArP which is known to undergo intramolecular cyclization due to an insertion of the phosphorus atom into a CH bond of an *o*-t-Bu group forming **101**.[107] The presence of the isocyanide fragment on Rh is clearly demonstrated by the IR spectrum (Table 9; ν(CN) 1991 cm^{-1}).



(35)

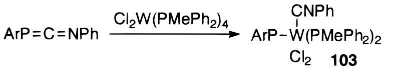
In the reaction between $Cl_2W(PMePh_2)_4$ and ArP═C═NPh (eq 36), the ^{31}P NMR analysis immediately after reaction shows a spectrum very similar to that obtained for the adduct between this same transition-metal complex and ArP═C═O,[108] which has been characterized by X-ray. Thus, by comparison, this

Table 9. Physicochemical Data of Transition-Metal Complexes[a] of Phosphaazaallene ArP=C=NPh

ML_n	η^2 on P=C or N=C	δ ^{31}P	δ ^{13}C	color	ref
$(Me_3SiC_5H_4)_2NbCl$ [b]	N=C	14.3	171.5 (J_{PC} = 155.3)	red	109
dppePt [c]	P=C	−146.5[d] −144[e] (broad signal)	196	orange	81
$(Ph_3P)_2Pt$	P=C	−140.2			81
$(Cy_3P)_2Pt$	P=C	−162.9			81

[a] Obtained by direct complexation of ArP=C=NPh. [b] IR: ν(P=C) 1505 cm^{-1}. X-ray: d(P=C) 1.688(19) Å, d(C=N) 1.301(23) Å; P−C−N 156.2(13)°. [c] IR: ν(C=N) 1577 cm^{-1}. [d] Toluene. [e] THF-d_8.

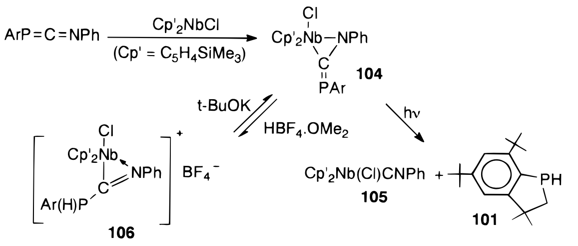
NMR is indicative of a compound of type **103**[108] which is not thermally stable and decomposes in a few hours at 25 °C.



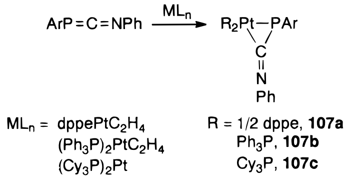
$$ArP{=}C{=}NPh \xrightarrow{Cl_2W(PMePh_2)_4} ArP{-}\overset{CNPh}{\underset{Cl_2}{W}}(PMePh_2)_2 \quad \textbf{103} \tag{36}$$

With a substituted cyclopentadienyl niobium complex, the first phosphaazaallene complex **104** has been obtained in the form of red air-stable crystals, thermally stable in solution at 80 °C (Scheme 19).

Scheme 19



IR (ν(P=C) = 1505 cm^{-1}), ^{31}P NMR (δ = 14.3 ppm), and X-ray confirm the η^2-coordination on the C=N double bond which was predicted from the Pearson theory. Photolysis of **104** gives the phosphaindane **101** and the niobium complex **105**, whereas addition of HBF$_4$·OMe$_2$ affords the phosphaimino complex **106**.[109] In contrast with the results reported with niobium, η^2-complexes on the P=C double bond are observed with platinum complexes and the same phosphaazaallene[81] (eq 37). **107a** is stable and can be isolated, whereas **107b** and **107c** are unstable in solution.

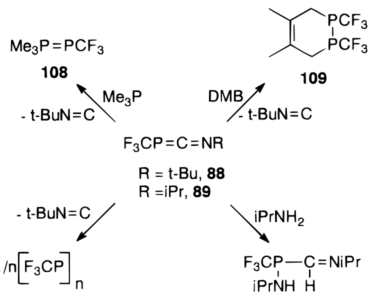


(37)

7. Reactivity of F_3C–P=C=NR

Due to the presence of the CF_3 group on the phosphorus atom, the phosphaazaallenes F_3C−P=C=N−R (R = ^{i}Pr, t-Bu) present a very special reactivity compared to the other known phosphaazaallenes (Scheme 20). For example, the regiochemistry of the addition of an amine (^{i}PrNH$_2$) to the P=C double bond of **89**, involving protonation of the sp carbon,[97] is the reverse of that observed for t-BuP=C=Nt-Bu in which the protonation of the phosphorus atom occurs.[89a] The very easy dissociation of the P=C double bond of **88** is observed with formation of *tert*-butylisonitrile and the phosphinidene F_3C−P giving oligomers $(CF_3P)_n$.[97]

Scheme 20



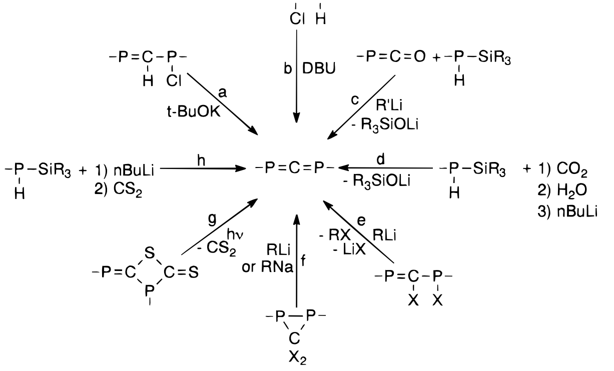
The reaction of **88** with the trimethylphosphine yields the phosphorus ylide **108** previously described by Burg.[110a,b] With 2,3-dimethylbutadiene, the six-membered ring compound **109** was obtained corresponding to the cycloaddition of the DMB with the diphosphene F_3C−P=P−CF_3[111] formed from the phosphinidene F_3C−P (**109** has previously been prepared from F_3C−PI_2, $SnCl_2$, and DMB).[112]

IV. 1,3-Diphosphaallenes –P=C=P–

A. Synthesis

Very few 1,3-diphosphaallenes have been synthesized until now: three “symmetrical” ones (bearing the same group on the two phosphorus atoms) and two “unsymmetrical” ones. The first diphosphaallene isolated was ArP=C=PAr, prepared simultaneously by Appel,[34] Karsch,[113] and Yoshifuji[114] by three different routes (see Scheme 21 for the general methods).

Scheme 21

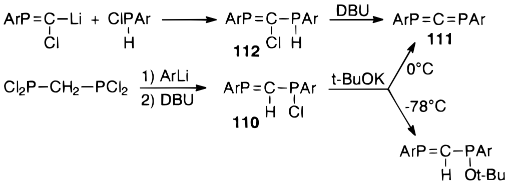


1. Dehydrohalogenation (Routes a, b)

Dehydrohalogenation of **110** (prepared from Cl_2P−CH_2−PCl_2 and successive reactions with ArLi and

DBU) by t-BuOK at 0 °C afforded the first diphosphaallene **111**[113] (Scheme 22). At lower temperature, only the substitution of chlorine by the Ot-Bu group occurs.[113]

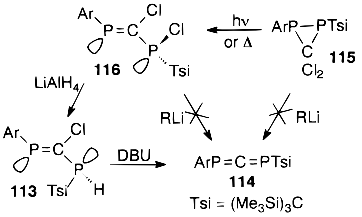
Scheme 22



111 was also obtained by dehydrochlorination by DBU from phosphaalkenylphosphine **112**.[27] (**112** was prepared by reaction between ArP(H)Cl and the carbenoid ArP═C(Cl)Li, which is a very useful synthon in low-coordinate phosphorus chemistry[115−117]). ArP═C═PAr is an air- and moisture-stable compound which can be purified by column chromatography.

A similar dehydrohalogenation with DBU from the derivative **113** afforded the unsymmetrical diphosphaallene **114**[118] bearing the Ar group and the overcrowded trisyl group (trisyl = $(Me_3Si)_3C$) (Scheme 23).

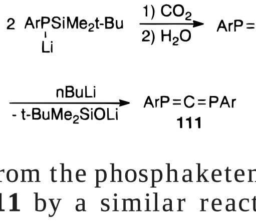
Scheme 23



114 cannot be obtained from diphosphirane **115** (prepared from diphosphene ArP═PTsi and CCl_2)[119] nor from **116** by reaction with lithium compounds as its symmetrical isologue ArP═C═PAr since only unidentified products are obtained in these cases.[118] A mechanistic study shows that a suitable conformation of the diphosphapropene is necessary for the formation of the diphosphaallene. Reduction of **116** to **113** involves a change in the conformation, as proved by the great variation of $^2J_{PP}$ from 457 to 89 Hz. Thus, it seems that the allene **114** can be prepared only from a diphosphapropene in the suitable conformation **113** close to that of allene.[118]

2. Elimination of R3SiOLi (Routes c, d)

Bubbling dry carbon dioxide in a solution of ArP(Li)SiMe$_2$t-Bu followed by hydrolysis afforded the phosphaalkenylphosphine **117** (eq 38). Treatment with butyllithium followed by stirring at 35 °C gave **111**[114] in an excellent yield.



$$2\ \mathrm{ArP(Li)SiMe_2t\text{-}Bu} \xrightarrow[2)\ H_2O]{1)\ CO_2} \mathrm{ArP{=}C(OSiMe_2t\text{-}Bu){-}PHAr}\ (\mathbf{117}) \xrightarrow[-\ t\text{-}BuMe_2SiOLi]{nBuLi} \mathrm{ArP{=}C{=}PAr}\ (\mathbf{111}) \qquad (38)$$

Starting from the phosphaketene ArP═C═O, Appel prepared **111** by a similar reaction[34] involving the phosphaalkenylphosphine intermediate **118** (Scheme 24); alternatively, addition of ArP(Li)SiMe$_3$ to ArP═C═O gave directly ArP═C═PAr via a Peterson olefination. In the reaction of the phosphaketene with lithium phosphide, the lithium salt **119a** (Chart 14) has been characterized by a triplet in ^7Li NMR ($\delta = -1.44$ ppm, $J_{PLi} = 42.5$ Hz) and a quartet 1,1,1,1 in ^{31}P NMR at −15.6 ppm.[19] Similar NMR spectra were observed for other diphosphaallyl anions such as **119b** and **119c** (**119b**, $J_{PLi} = 41$ Hz; **119c**, $J_{PLi} = 48$ Hz).[120]

Scheme 24

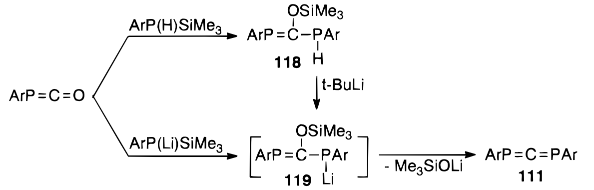
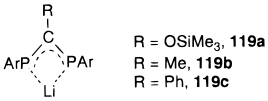


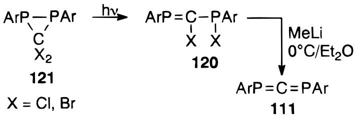
Chart 14



The transient ArP═C═PR (R = 2,4,6-$^iPr_3C_6H_2$) has also been obtained by this route (see section IV.C.7) from a *C*-siloxysubstituted diphosphapropene.

3. Dehalogenation (Route e)

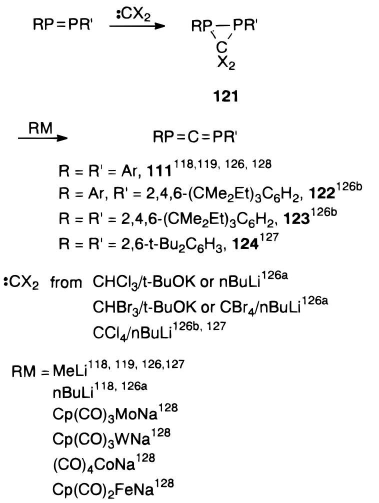
The 2,3-dihalodiphosphapropenes **120** obtained by photolysis of the corresponding 3,3-dihalo-1,2-diphosphiranes **121** are good precursors of the diphosphaallene **111** by reaction with methyllithium in Et$_2$O[118,119] (eq 39). The mechanism of ring opening of diphosphiranes **121** (thermal,[121] photolytic,[122] with Grignard reagents,[123] or with Lewis acids[124]) and the stereochemistry of this reaction, leading to 2,3-dihalo-1,3-diphosphapropenes **120**, have been very well studied by Koenig. The diphosphaallene ArP═C═PAr was obtained from the diphosphapropene **120** formed in a trans-gauche conformation after photolysis.[118] This result explains why the unsymmetrical diphosphaallene ArP═C═PTsi was not obtained with MeLi from the corresponding diphosphapropene **116** (Scheme 23) since this compound was obtained by thermolysis or photolysis of the corresponding diphosphirane **115** in a trans-syn conformation.[118]



(39)

4. From a Diphosphirane (Route f)

The most often used route to diphosphaallene was the reaction of *C*,*C*-dihalodiphosphiranes **121** with lithium compounds (eq 40). This route was convenient for the synthesis of both symmetrical and unsymmetrical diphosphaallenes (a similar ring opening of *C*,*C*-dihalocyclopropanes has been often used for the preparation of allenes[125]). The first step was generally the synthesis of the diphosphiranes **121** by



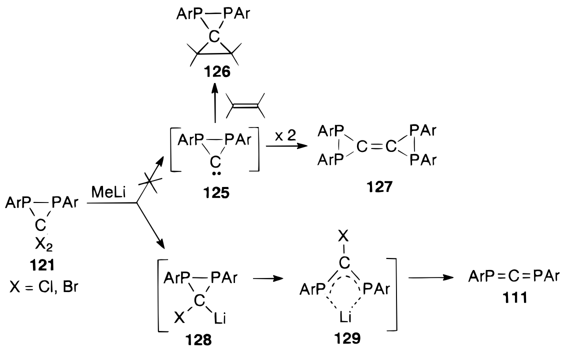
(40)

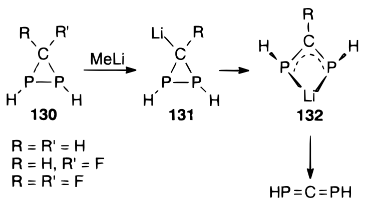
reaction of CCl_2 with the corresponding diphosphenes,[119,126] then their ring opening by alkyllithium reagents[118,119,126,127] or anionic transition-metal complexes.[128]

The ^{13}C-enriched diphosphaallene $ArP{=}^{13}C{=}PAr$[129] has been obtained by this route starting from ^{13}-$CHCl_3$.

Compound **122**[126b] was the first unsymmetrical diphosphaallene to be synthesized. The mechanism of formation of diphosphaallenes from *C*,*C*-dihalodiphosphiranes has been experimentally studied by Koenig[118,119] and theoretically by Bachrach[130] (Scheme 25). The intermediate formation of the carbene **125** followed by a carbenic insertion into the P−P bond has been ruled out[119] since the spiranic derivative **126** was not obtained when the reaction was performed in the presence of excess of cyclohexene or tetramethylethylene nor was the alkene **127**: by analogy with the chemistry of carbenic cyclopropane,[131] such a dimer **127** should be obtained. Thus, the probable intermediates in the formation of the diphosphaallenes are the 2,2-lithio(chloro)-1,3-diphosphiranes **128** and then the diphosphaallyl anions **129**. Such a mechanism was confirmed by examination of the energetics[130] and calculations (HF/6-31G*) performed on the model **130** (eq 41). The first step of the reaction is the formation of **131** followed by a ring opening to give the stable allyl anion **132** driven by two exothermic processes: relief of the ring strain (~14.8 kcal/mol) and formation of a Li^+/diphosphaallyl$^-$ pair.[130] The next step, which is the formation of the diphosphaallene, is endothermic.

Scheme 25



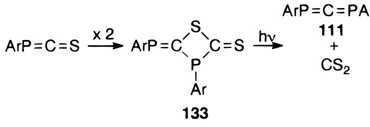


(41)

The fact that the formation of **131** (R = H) is exothermic and that **132** is much lower in energy (18.8 kcal/mol) is consistent with the experimental inability to detect the diphosphiranyl anion.[130]

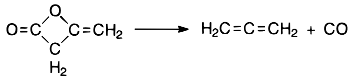
5. Decomposition of a Thiophosphetane (Route g)

The four-membered ring compound **133**, formed by the dimerization of the phosphathioketene $ArP{=}C{=}S$ (see section VIII), decomposed under UV irradiation to give the diphosphaallene **111** and CS_2[132] and not the monomer $ArP{=}C{=}S$ (eq 42).



(42)

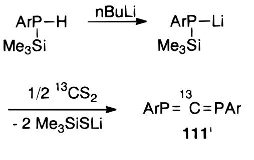
A similar [2+2]-decomposition was observed from diketene, which gives allene and CO_2 and does not afford the monomer $H_2C{=}C{=}O$ (eq 43).[133]



(43)

6. Elimination of Me_3Si–SLi (Route h)

To perform physicochemical studies, particularly EPR, Geoffroy also synthesized the ^{13}C-enriched diphosphaallene **111′** but by another method than that used by Alberti[129] (see section IV.A.4). Starting from $ArP(H)SiMe_3$, addition of BuLi and then 0.5 equiv of $^{13}CS_2$ led to **111′** after warming to room temperature[134] (eq 44). The same method was used by Appel to obtain $ArP{=}C{=}PAr$.[19]



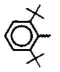
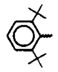
(44)

B. Physicochemical Studies

1. Stereochemical Studies

Attempts to observe the enantiomers of $ArP{=}C{=}PAr$ by ^1H or ^{31}P NMR using a chiral solvent (D-(+)-α-Ph(Et)NH) or a chiral NMR shift reagent such as an europium derivative failed.[135] The enantiomers of **111** could be separated by HPLC using a chiral column of (+)-polytriphenylmethyl methacrylate. The estimated $[\alpha]_D$ for the optically pure (−)-diphosphaallene **111** was −470°.[135] The racemization was very low in the dark but occurred rapidly upon irradiation at 370 nm.[135]

Table 10. Diphosphaallenes RP=C=PR′: Synthetic Routes and Physicochemical Data (For methods, see Scheme 21; Ar′ = 2,4,6-(EtMe$_2$C)$_3$C$_6$H$_2$)

n°	R	R’	δ ^{31}P (J_{PP})	δ ^{13}C (J_{PC})	mp (°C)	method	ref
111[a]	Ar	Ar	141.6	277.08 (58.5)	177-179	a	113, 153
[b]			141.7	276.2 (58.1)	206-207	b f	27 118, 119, 126, 128
						g	132
						e	118, 119
[c]					202-204	c	34
						d	23, 114
111’[d]	Ar	Ar	141		202-204	h	134
			140.20			f	129
114	Ar	Tsi	169.0, 145.7 (4.6)			b	118
122[e]	Ar	Ar’	142.5, 142.4 (18.5)		126.9-132	f	126b
123	Ar’	Ar’	142.2		64.5-78.0	f	126b
124			142.4	275.6 (58.0)	126-129	f	127

[a] Colorless crystals. [b] UV: 358 nm (e: 1300), 262 (4860). [c] X-ray:[100] d(P=C) 1.635(8) and 1.630(8) Å; P−C−P 172.6(5)°. [d] ^{13}C-sp-enriched. [e] Colorless crystals.

It should be noted that there are no reports on optically active carbodiimides −N=C=N− analogues because the activation energies for racemization are probably too low to allow isolation of enantiomers.

2. NMR (Table 10)

The expected low-field shifts (between 141 and 169 ppm) are observed in the ^{31}P NMR for diphosphaallenes (Table 10). Signals are deshielded compared to those of phosphaallenes −P=C=C< (39−93 ppm) and particularly phosphaazaallenes −P=C=N− (−64 to −135 ppm), and are close to those reported for phosphaalkenes (200−400 ppm).[18]

The ^{13}C NMR spectra display the classical very low field signal generally observed for allenic carbon (∼270−280 ppm) with the expected rather large magnitude of the P−C coupling constant ($^1J_{PC}$ = ∼58 Hz).

3. X-ray Study

The X-ray structure determination has been performed for the sole ArP=C=PAr compound.[100] The P=C bonds (1.635(8) and 1.630(8) Å) are shorter than classical P=C bonds with an sp^2-hybridized carbon atom (1.68−1.72 Å). This shortening is probably due to both the electronic characteristics of the P=C=P system and to the smaller bond radius of the sp-hybridized carbon atom. A significant deviation from linearity is observed for the P−C−P angle (172.6(5)°). This angular contraction reduces the interaction between the very bulky Ar groups, but it seems that this nonlinearity, which is reproduced by calculations, is mainly due to an electronic character within the P−C−P backbone.[136] The substitution by halogens accentuates this bending.[136] The orientation of the two Ar groups is almost orthogonal in relation to the P−P axis,[100] like in the allenes which exhibit a comparable geometry.

4. UV−Visible and IR

Diphosphaallenes are colorless solids. The UV−visible spectrum of ArP=C=PAr displays absorptions at 358 and 262 nm.[114]

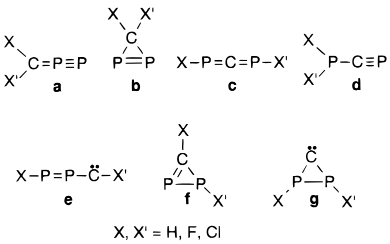
No characteristic band for the PCP unit has been observed by IR, contrary to the case of phosphaazaallenes −P=C=N−. This lack of PCP bending mode was also predicted by calculations.[136]

C. Theoretical Studies

1. Relative Stability of XX′CP$_2$ Isomers

A theoretical study has been performed on the XX′CP$_2$ isomers **a**−**g** (X,X′ = H, F, Cl) to determine the effect of halogen atoms on their energy and geometry[136] (Chart 15). Great differences are observed in the stability of **a**−**g** depending on the nature of X and X′. For example, in the H_2CP_2 series, the energy ordering (in kcal/mol) is as follows: **b** (0) < **d** (10.2) < **f** (14.5) < **c** (23.4) < **a** (41.2). Carbenic compounds **e** and **g** are less stable.

Chart 15



Halogen substitution drastically changes this ordering; for $HFCP_2$ and F_2CP_2, it is, respectively, **f** (F on P) (0) < **d** (6.9) < **b** (16.5) < **c** (24.3) < **f** ′ (F on C) (33.5) < **a** (72.5) and **d** (0) < **c** (19.7) < **f** (29.1) < **b** (37.3) < **a** (89.7).

Only small differences are observed between chlorine- and fluorine-substituted derivatives. It should be noted that the phosphorus−halogen moiety behaves as the main stabilizing factor since a great difference is, for example, observed between **f** with F on phosphorus and **f** ′ with F on carbon.

A theoretical study on $XX'CN_2$ compounds gives quite different results,[137] since the ordering is for H_2CN_2 $\mathbf{a_n} < \mathbf{b_n}$ (Chart 15, with N instead of P); for $HFCN_2$ $\mathbf{b_n} < \mathbf{a_n}$; and for F_2CN_2 $\mathbf{b_n} < \mathbf{a_n} < \mathbf{d_n} < \mathbf{f_n} < \mathbf{e_n}$. These findings are in agreement with experimental observations since diazomethane is more stable than diazirine while difluorodiazirine is known but not difluorodiazomethane.

2. Geometries and Configurational Stability

The fully optimized geometries (HF/4-31G) have been calculated for four configurations of HP=C=PH.[101] The most stable form compares well with the X-ray data found in ArP=C=PAr, with a P=C bond length (1.644 Å) compressed by 0.03 Å in relation to that of $HP{=}CH_2$.

In great contrast with phosphaazaallenes, diphosphaallenes are calculated to have a rather high isomerization barrier (42 kcal mol^{-1}).[101] Thus, it is expected that diphosphaallenes are stable toward configurational changes.

3. Proton Affinity and Chemical Reactivity

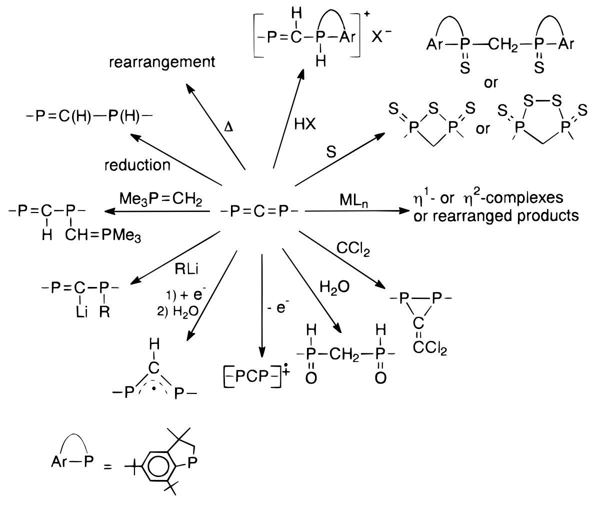
The protonation occurs preferentially at the C atom in diphosphaallenes, whereas, as said previously, it is the phosphorus atom in phosphaazaallenes.[101] This is in good agreement with the calculated charges which indicate a negative carbon.

Whereas phosphaazaallenes are predicted to give preferentially π-complexes with metal, the theoretical behavior of diphosphaallenes is more confusing.[101]

D. Reactivity

Scheme 26 summarizes the reactivity observed.

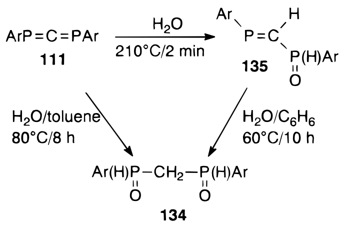
Scheme 26



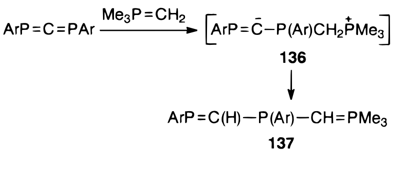
1. Protic Reagents

The diphosphaallene ArP=C=PAr reacts with water only after heating: the diphosphine oxide **134** was obtained quantitatively in the form of the meso isomer,[138] as proved by an X-ray structure[139] (Scheme 27). A very large coupling constant ($^2J_{PP}$ = 510 Hz) was observed between the two phosphorus atoms. **134** was also obtained from **135** after 10 h at 60 °C in benzene and **135** from ArP=C=PAr after heating for 2 min at 210 °C.[138] As postulated by calculations, the protonation occurred on the central carbon.

Scheme 27



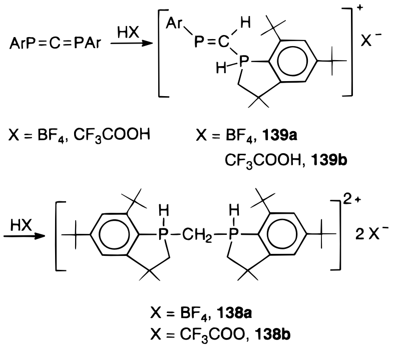
The ylide $Me_3P{=}CH_2$ reacts much more easily (at room temperature) with ArP=C=PAr to afford adduct **137**, probably via the intermediate **136**[140] (eq 45). This addition of $Me_3P{=}CH_2$ to the P=C double bond was similar to that observed on the P=Ge unsaturation of germaphosphene $Mes_2Ge{=}PAr$.[141]



(45)

Reaction of 2 equiv of HBF_4 or F_3CCOOH with ArP=C=PAr proceeds at the phosphorus atoms, with subsequent cyclization of an *o*-*tert*-butyl group to afford **138a** and **138b** in the form of a mixture of diastereoisomers meso and rac in a 1/1 ratio via the intermediates **139a** and **139b**[142a] (eq 46).

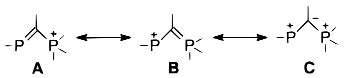
The 2-phosphonio-1-phosphaalkene **139a**[142b] was isolated as a yellow crystalline compound (which dissolves surprisingly well in toluene) and presents a resonance signal of the P(II) atom at 365.8 ppm; this signal at unusually low field is in the range



(46)

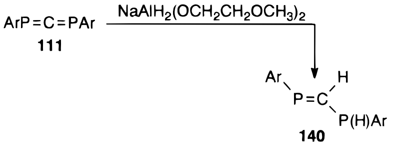
observed for phosphenium ions.[143] On the other hand, the ^{13}C NMR signal of the central carbon is at relatively high field (116.25 ppm) for a sp^2 carbon of phosphaalkene with a small coupling constant with the P(II) atom (11.0 Hz) and a much higher one with the P(V) atom (116.3 Hz).[142a] All these data indicate that a resonance relationship as described in Chart 16 can be postulated for **139a** and that the resonance structures **B** and **C** are of considerable importance in describing its actual structure.

Chart 16



2. Reduction

The attempted reduction of $\mathrm{ArP{=}C{=}PAr}$ with $LiAlH_4$ failed. In contrast, sodium bis(methoxyethoxy)aluminum hydride reacted with **111** to give the phosphinophosphaethylene **140**[144] (eq 47). Only one



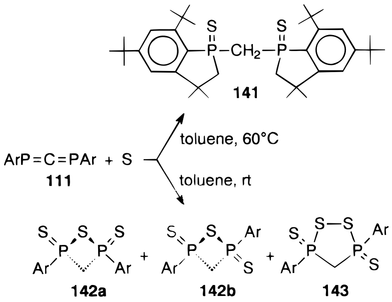
(47)

P=C double bond could be reduced. Because of the large $^2J_{PP}$ coupling constant (100.1 Hz), the configuration of **140** appeared to be *E*;[144] this configuration was determined by an empirical rule postulated by Becker and Regitz:[145] the $^2J_{PX}$ coupling constant is larger when X is syn to the lone pair of P than when it is anti. In isomer *Z*, the $^2J_{PP}$ coupling constants should be of about 10–30 Hz.

3. Sulfur

Various results have been observed in the reaction of $\mathrm{ArP{=}C{=}PAr}$ with sulfur depending on the reaction conditions. By heating a toluene solution of **111** at 60 °C for 24 h, Karsch observed the formation of **141** in which the cyclization involving the C–H bond of two *o*-*tert*-butyl groups occurred[142a] (Scheme 28). In contrast, when the reaction was performed in toluene at room temperature in the presence of DBU, Yoshifuji obtained the three derivatives **142a**, **142b**, and **143**; **142a** is by far the most abundant (yield 35%), whereas **142b** and **143** are obtained in only very low yield (respectively, 0.5% and 2.2%).[146] The structures of **142a**[146a] and **143**[146b] have been established by a X-ray crystallographic analysis and the trans configuration of **142b** by a ^1H NMR analysis which displays magnetically equivalent protons for the methylene group.[146b]

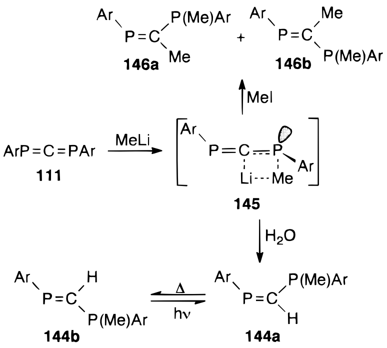
Scheme 28



4. Lithium Compounds

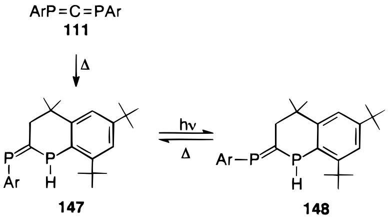
Methyllithium adds to one P=C double bond of $\mathrm{ArP{=}C{=}PAr}$ to give after hydrolysis the compound **144a** (Scheme 29); after some hours at room temperature, the formation of **144b** was observed ($t_{1/2}$ (25 °C) ~8 h); **144b** gives again **144a** by photolysis. Quenching the lithium adduct **145** with methyl iodide affords the two isomers **146a** and **146b** in the ratio 40/60.[140] The *Z* or *E* configuration of **146a** and **146b** was established on the basis of the magnitude of the PP coupling constants (**146a** (*E*), $^2J_{PP} = 150$ Hz; **146b** (*Z*), $^2J_{PP} = 18$ Hz).[140]

Scheme 29



5. Thermolysis

The thermolysis of $\mathrm{ArP{=}C{=}PAr}$ (110 °C/15 h) resulted in the formation of tetrahydro-1-phosphanaphthalene **147** via C–C bond formation involving a C–H addition of an *o*-*tert*-butyl group to the P=C double bond[144] (eq 48). NMR data, particularly the



(48)

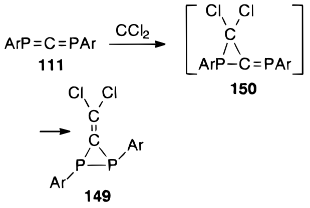
small $^2J_{PP}$ coupling constant (23.2 Hz), shows that

147 is the *Z* isomer. On irradiation, an equilibrium mixture *Z*/*E* 1/1 was obtained (**148** (*E*), ${}^2J_{PP}$ =105.0 Hz).

It should be noted that such a cyclization to a six-membered ring involving an *o*-t-Bu group is unusual since generally five-membered ring derivatives are obtained.

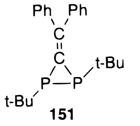
6. Dichlorocarbene

Reaction of ArP=C=PAr with dichlorocarbene gives the methylenediphosphirane **149**, probably via the initial formation of the phosphinidenephosphirane **150** followed by cleavage of the P−CCl$_2$ bond[76] (eq 49). The X-ray structure determination of **149** displays very different P−P−C(Ar) bond angles (87.4(2)° and 124.3(2)°),[76] indicating that the structure of **149** is completely different from that of the related compound **151**[147] (Chart 17) in which an approximate crystallographic 2-fold axis bisects the three-membered ring and the P−P bond (P−P−C(t-Bu) bond angles: 99.9(2)° and 104.8(3)°). The special structure of **149** is due to short contacts between the diphosphirane ring and one of the Ar groups as well as to steric repulsion between a chlorine and *o-tert*-butyl groups.[76]



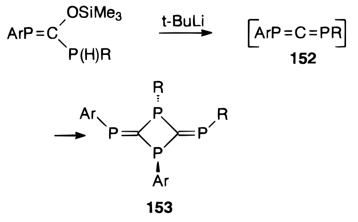
(49)

Chart 17



7. Dimerization

When the steric protection is not important enough, a head-to-tail dimerization occurs by two P=C bonds, for example, in the unsymmetrical diphosphaallene **152**, substituted by Ar and 2,4,6-triisopropylphenyl groups[19,148] (eq 50). The structure of dimer **153** has been proved by X-ray investigations which show that the ring structure is nearly planar (sum of angles 358.3°), with groups on the ring in a trans position and groups on the P=C double bond *Z*-configurated.[19,148]



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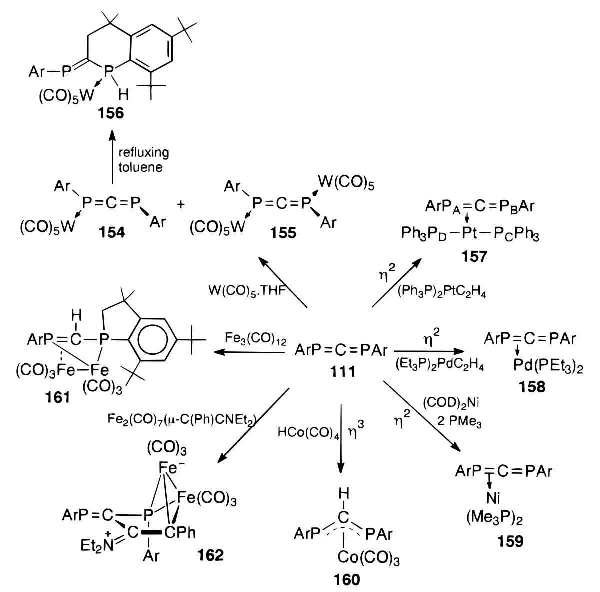
R = 2,4,6-triisopropylphenyl

Scheme 30



8. Transition-Metal Complexes (Scheme 30, Table 11)

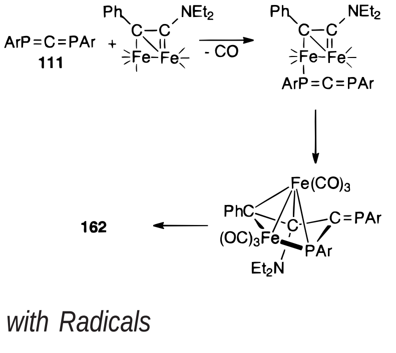
Various reactions have been reported (Scheme 30; Table 11) between diphosphaallene ArP=C=PAr and transition-metal complexes giving the following (1) η^1-complexes **154**[149] and **155**[150] via one or two phosphorus atoms (in refluxing toluene **154** rearranges to tetrahydro-1-phosphanaphthalene complex **156**[149] by a formal addition of a CH bond of a t-Bu group to one P=C double bond. The diphosphaallene part in **155** has a similar configuration to noncoordinated **111**); (2) η^2-complexes **157**,[151] **158**,[152] and **159**[153] via one P=C double bond exclusively with platinum, palladium, and nickel complexes (**158** and **159** are fluxional in solutions at 25 °C, the metal moving between the two P=C bonds.[152,153] By contrast, no evidence for a fluxional behavior was found in **157**,[151] since the four expected distinct phosphorus resonances are observed in ^{31}P NMR above room temperature. Due to the nonmagnetic equivalence of the two PPh$_3$ ligands, it seems that the diphosphaallene moiety lies in the plane containing platinum and the two PPh$_3$ ligands[151] according to a mode of bonding similar to that reported in the related allene complexes (Ph$_3$P)$_2$Mallene (M = Pt, allene = CH$_2$=C=CRR′ (RR′ = H$_2$, HMe, Me$_2$); M = Pd, allene = CH$_2$=C=CH$_2$).[154] A perpendicular mode of bonding established for some rhenium allene complexes seems less likely[155]); (3) η^3-diphosphaallyl complexes **160**[140] using HCo(CO)$_4$, with preliminary addition of the CoH to a P=C double bond; (4) more complicated structures with various diiron complexes to form **161**[149] (involving a cyclization with an *o-tert*-butyl group) or **162**[156] (a possible mechanism for the formation of **162** involves in a first step the fixation of the diphosphaallene at one iron atom with elimination of CO followed by a [2+2]-cycloaddition between P=C and Fe=C bonds with a C−C coupling (eq 51). A subsequent donation of the nitrogen lone pair would then cleave a C−Fe bond to form **162**[156]). All these results

Table 11. Physicochemical Data of Complexed Diphosphaallenes (see Scheme 30)

no.	δ P$_A$ (ppm)	δ P$_B$ (ppm)	$J_{P_AP_B}$ (Hz)	d(PC) (Å)	ref
154	151.9	132.8 (J_{PW} = 273)	39		149
155[a]	144.3 ($^1J_{PW}$ = 285.0; $^3J_{PW}$ = 17.0)	144.3 ($^1J_{PW}$ = 285.0; $^3J_{PW}$ = 17.0)	97.7	1.62(2)	150
157[b]	−187.2	−97.2	10.9		151
158				1.67(3) 1.73(3)	152

[a] Dihedral angle C(Ar)P$_A$P$_B$C(Ar): 71.4(8)° (83° in ArP=C=PAr). [b] δ P$_D$, −119.0; δ P$_C$,: −114.5; J_{PtP_D}, 3457; J_{PtP_C}, 3127; J_{PtP_B}, 318; J_{PtP_A}, 239; $J_{P_CP_D}$, 26.3; $J_{P_DP_B}$, 72.5; $J_{P_BP_C}$, 75.6; $J_{P_CP_A}$, 52.8.

show that ArP=C=PAr offers considerable potential as ligand.

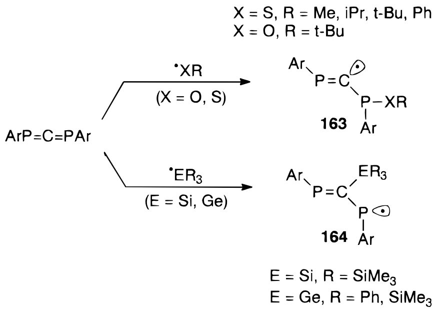


(51)

9. Reaction with Radicals

The regioselectivity of the addition of radicals to diphosphaallene is very dependent on the nature of the attacking radical:[129] electrophilic •OR and •SR radicals attack one of the phosphorus atoms giving short-lived phosphavinyl radical adducts, while silyl and germyl radicals •ER$_3$ (E = Si, Ge) add to the carbon atom to afford relatively persistent phosphinyl radicals (Scheme 31).

Scheme 31



163 has very low g factors (2.0014−2.0017) compatible with a radical centered at the carbon atom (radicals centered at the phosphorus atom have larger values of g factors).[157] The assignment of the two phosphorus splittings in **163** (aP(II), 91.78−105.25 G; aP(III),: 7.97−18.00 G) and in **164** (aP(II), 63.60−88.31 G; aP(III), 42.54−45.02 G) has been confirmed by ab initio calculations (UMP2/DZP//TZP).

10. Diphosphaallene Radical, Radical Cation, and Radical Anion

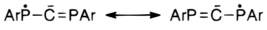
The radical cation ArPCPAr$^{•+}$ was obtained from ArP=C=PAr by chemical oxidation[158a] or electrochemical oxidation[134,158a] and was investigated through EPR spectroscopy,[134,158a] cyclic voltammetry (oxidation potential of 2.0 eV),[158a] and pulse radiolysis.[158a] Its UV spectrum displays bands centered at 320 (overlapping of three different transitions) and 410 nm[158a] (transition from the SOMO to the second LUMO). The EPR study allowed the determination of the two ^{31}P and ^{13}C coupling constants which are close (between 3.02 and 3.70 mT depending on the experimental conditions[134,158a]).

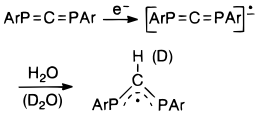
Whereas the HPPH dihedral angle is 90° in the neutral molecule, ab initio calculations performed on the radical compound HPCPH[134] or on PhPCPPh[158a] predict that they can adopt cis- and trans-like conformations.

The study of the radical anion has been the subject of some investigations[84,158] which are controversial. It is particularly the case for the electrochemical reduction of ArP=C=PAr in THF giving an EPR spectrum consisting of a 7.6 mT triplet[158b] (coupling of the unpaired electron with two equivalent or nearly so phosphorus atoms) with an additional 0.328 mT doublet[158c] (coupling with a hydrogen atom) and a g-factor close to 2.009.[158b,c]

It appears that the spectrum does not correspond to the expected diphosphaallenyl radical anion (Chart 18) but to the corresponding diphosphaallyl radical which would originate through its protonation immediately after its formation by traces of water remaining in the solvent[158c] (eq 52). This identification was supported by DFT calculations (UB3LYP/VTZP) performed on the diphenyl-1,3-diphosphaallyl radical.

Chart 18

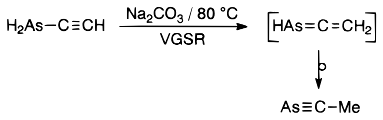




(52)

V. 1-Arsaallenes –As=C=C<

Arsaalkyne MeC≡As was obtained by rearrangement of the alkynylarsane HC≡CAsH$_2$ on solid sodium carbonate heated at 80 °C (VGSR conditions). By analogy with the phosphorus analogues[37,38] a plausible mechanism for this rearrangement involves the arsaallene HAs=C=CH$_2$ as intermediate, but in contrast to the case of the phosphorus analogues,[37,38] all attempts to characterize it have been unsuccessful[159] (eq 53).



(53)

Table 12. −P=C=As−, −As=C=As−, −P=C=O, −P=C=S, and − P=C=C=P− Derivatives: Synthetic Routes and Physicochemical Data

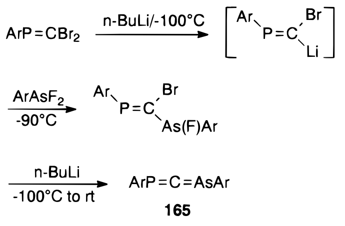
no.	compound	δ ^{31}P (J_{PC})	δ ^{13}C	mp (°C)	color	method[e]	ref
165[a]	ArP=C=AsAr	159.7 (75.1)	299.54	198 (dec)	yellow	a	106a
166[b]	ArAs=C=AsAr		297.47	164−166 (dec)	yellow	a	160b
167	t-BuP=C=O	−180				b, c	162
168[c]	ArP=C=O	−207.4		115−117	orange	b	163
178	ArP=C=S					d	132
181	(η^5-$\mathrm{C_5Me_5}$)$\mathrm{(CO)_2}$FeP=C=S					e	175
202	TsiAs=C=C=$\mathrm{CPh_2}$					f	186
204[d]	ArP=C=C=PAr	180(E),170.6(Z)		224−226 (dec)	yellow-orange	g	24
						h	168
				250	yellow	i	190b

[a] UV nm (ϵ): 374 (1267), 274 (45634). [b] UV nm (ϵ): 388 (838), 282 (97674). [c] IR: 1953 cm^{-1}. [d] UV nm (ϵ): [24] 465 (1850), 387 (14700), 314 (3600), 244 (29700), 213 (19700). [e] Methods: (a) Dehalogenation of a dihalodiarsa(or phosphaarsa)propene. (b) Reaction between phosgene and a disilylphosphine. (c) Reaction between phosgene and a silylphosphine. (d) Reaction between thiophosgene and a disilylphosphine. (e) Reaction between $\mathrm{CS_2}$ and a ferrio(disilyl)phosphine. (f) Dehydrohalogenation or dehydromethoxylation of an allenylarsane. (g) Wittig−Peterson reaction. (h) From a dichloromethylenediphosphirane. (i) From a halophosphaethenyllithium.

VI. 1,3-Arsaphosphaallenes −As=C=P−

A. Synthesis

Whereas many cumulenic compounds of phosphorus have been synthesized, only two allenic derivatives of arsenic, the arsaphosphaallene ArAs=C=PAr **165** and the diarsaallene ArAs=C=AsAr **166** (see section VII), have been isolated. **165**[160a] has been prepared in an excellent yield (88%) by debromofluorination at −100 °C of the corresponding (phosphaalkenyl)fluoroarsane obtained from ArP=C(Li)-Br[115] and $\mathrm{ArAsF_2}$[161] (eq 54). **165** was obtained after crystallization from pentane as air- and moisture-stable hexagonal light-yellow crystals.



(54)

B. Physicochemical Studies

1. NMR (Table 12)

The NMR spectra of **165**[160a] are consistent with the assigned structure, particularly the δ ^{13}C at very low field (299.54 ppm, d, $^1J_{CP}$ = 75.1 Hz) characteristic of an allenic carbon and the δ ^{31}P at 159.7 ppm, in the range previously determined for diphosphaallene ArP=C=PAr. At room temperature, a broad signal was observed in ^{1}H NMR for the *o-tert*-butyl groups due to a slow rotation of the Ar groups because of the steric congestion (a similar broad signal was reported for the Ar groups in ArP=C=PAr).[34] A dynamic ^{1}H NMR allowed the determination of their rotation barrier by following the coalescence of *o-tert*-butyl groups and also of aromatic protons. The surprisingly high value calculated (13.6 kcal/mol) shows the great steric congestion in **165**.[160a]

2. UV Spectrum

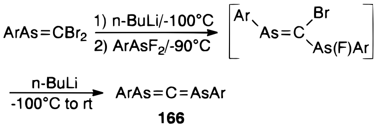
n → π* and π → π* absorptions were observed at, respectively, 374 (ϵ = 1267) and 274 nm (ϵ = 45634),[160a] close to those determined in ArP=C=PAr.[27]

3. X-ray Study

The X-ray structure of **165** could not be refined satisfactorily due to a peak height of more than 1.9 eÅ^{-3} remaining on the difference electron density map which may be interpreted as an alternative position of a phosphorus atom or an arsenic atom.[160a] However, despite the poor refinement, the allenic structure of **165** was proved unambiguously.

VII. 1,3-Diarsaallenes −As=C=As−

The diarsaallene ArAs=C=AsAr **166**[160b] has been prepared in a good yield from $\mathrm{ArAs{=}CBr_2}$ using the same procedure as for the arsaphosphaallene ArAs=C=PAr[160a] (eq 55) and was obtained after crystallization from pentane as light-yellow crystals. Owing to the great steric hindrance caused by the Ar groups, it appeared thermally and air and moisture stable and was characterized by NMR, particularly by the extremely low-field ^{13}C chemical shift (297.5 ppm) (Table 12).



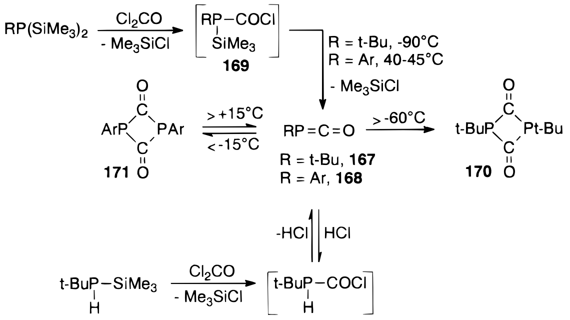
(55)

VIII. Phosphaketenes −P=C=O

A. Synthesis

Only two phosphaketenes **167**[162] and **168**[163] have been obtained until now by reaction of phosgene with a disilylphosphine via the intermediate formation of **169** and further elimination of $\mathrm{Me_3SiCl}$ (Scheme 32). **169a** (R = t-Bu) could be detected[162] but not **169b** (R = Ar), probably because of a more drastic reaction condition.[163] t-BuP=C=O has also been obtained from silylphosphine t-BuP(H)$\mathrm{SiMe_3}$ and phosgene.[162] It is stable in solution only below −60 °C and gives above −60 °C the head-to-tail dimer **170** via the two P=C double bonds.[162]

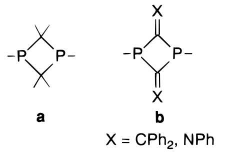
Scheme 32



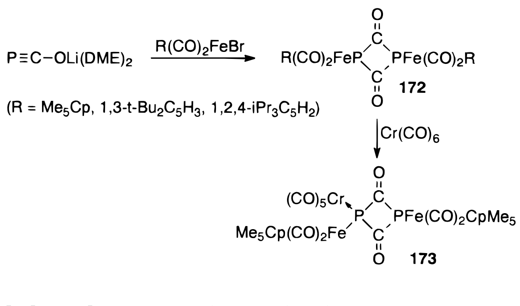
Orange crystals of ArP=C=O obtained upon cooling are stable at room temperature and above (mp 115−117 °C). By contrast with t-BuP=C=O, its dimeric form **171** crystallized from CH_2Cl_2 solutions below −20 °C.[19] The equilibrium between ArP=C=O and its dimer **171** is completely shifted to ArP=C=O between +50 and +60 °C.

171 presents a planar P_2C_2 ring with trans orientation of the Ar groups and the shortest intracyclic P−C bonds (1.796− 1.838 Å)[19] ever observed for 1,3-diphosphetanes. Such bond lengths are generally in the range 1.87−1.91 Å in **a**[164] and 1.83−1.89 in **b**[25,86b] (Chart 19). This is probably partly due in **171** and **b** to the reduced covalent radius of the sp^2 ring carbons compared to the sp^3-hybridized carbon atoms.

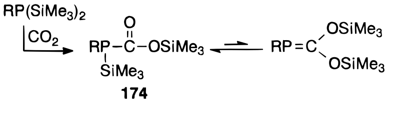
Chart 19



Other similar diphosphetanes such as the diferriodiphosphetane diones **172**[165] and the chromium complex of one of them **173**[165] have been prepared by Weber starting from lithoxyphosphaalkyne and bromoiron complexes, but phosphaketenes R(CO)$_2$FeP=C=O could not be detected during the course of the reaction (eq 56). Note that the addition of CO$_2$ to the disilylphosphines RP(SiMe$_3$)$_2$ (R = Me, t-Bu, Ph) leads to derivatives **174**,[166] which are potential precursors of phosphaketenes by elimination of hexamethyldisiloxane (eq 57).



(56)



(57)

Table 13. Phosphaalkene, Phosphaketene and Isocyanate: Net Charges, Overlap Populations, and Dipole Moment (ab initio DZP//4-31G)[101]

		$HP=CH_2$	HP=C=O	HN=C=O
net charges	P	0.17	−0.06	−0.45
	C	−0.49	0.10	0.47
	O		−0.11	−0.34
overlap population	P=C	1.08	0.73	
	C=O		1.49	1.45
	C=N			1.61
dipole moment		1.02	0.67	3.21

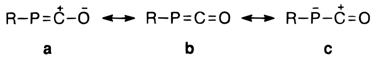
B. Physicochemical and Theoretical Studies

1. NMR (Table 12) and Charge Distribution (Table 13)

The ^{31}P NMR signals of **167** and **168** appear at very high field, respectively, −180[162] and −207.4[163] ppm, and are rather comparable to those observed for −P=C=N− derivatives. Such strongly negative values are in good agreement with the net charge calculations which show that the phosphorus atom has a negative charge and that the P=C bond polarity is in −P=C=O (P$^{\delta-}$−C$^{\delta+}$) the opposite of that in phosphaalkenes −P=C< (P$^{\delta+}$−C$^{\delta-}$) (Table 13).

The mesomeric structures **a**−**c** can be written (Chart 20). As a result, the carbon atom is the electropositive center for a nucleophilic attack and, due to the rather small differences between the negative charges on P and O, both centers can be in competition for attracting electrophilic agents.[104]

Chart 20

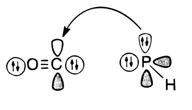


The overlap population of the CP bond in HPCO is calculated to be smaller than that in phosphaalkenes, in agreement with its longer bond length.[104]

2. Geometry

HPCO is calculated (ab initio, 4-31G*) to possess a planar *E*-bent structure (HPC, 88.7°; PCO, 176.7°)[104] with a slightly stretched P=C bond (1.685 Å)[104] compared to the P=C bond in H$_2$C=PH (1.672 Å),[101] H$_2$C=C=PH (1.657 Å),[61b] and HP=C=PH (1.644 Å),[101] under the action of the C=O bond. A similar stretching of the P=C bond (1.718 Å)[101] was observed in HP=C=NH. The geometry of HP=C=O can be considered as a result of a stabilizing interaction between PH and CO fragments[104] (Chart 21).

Chart 21



In contrast to HNCO, in which the barrier to linearity is very low (<5 kcal/mol), the barrier in HPCO is extremely high[104] (73 kcal/mol) and arises essentially from the inversion at the phosphorus atom.

3. IR and Vibrational Frequencies

The asymmetric stretching vibration of the P=C=O group in ArPCO lies at 1953 cm^{-1} [163] and is roughly comparable to the calculated one (2167 cm^{-1}, 4-31G value[104]). As in other cumulenes, there is a symmetric stretching calculated at 630 cm^{-1}.[104]

4. Electronic Structure

The HOMO is the π-orbital as in HNCO.[104] Unlike other cumulenes, the LUMO can be described as a n*-orbital of P rather than the usual π*-orbital.

From all the theoretical data it can be concluded that the carbon−phosphorus bond in HPCO is essentially a dative single bond enforced by a π-backdonation.[104]

5. Protonation Site

Calculations have been performed on five possible structures of protonated HPCO species. It appears that P-protonation is unambiguously preferred.[104] It should be noted that a consideration based only on the charge distribution failed to predict this behavior.

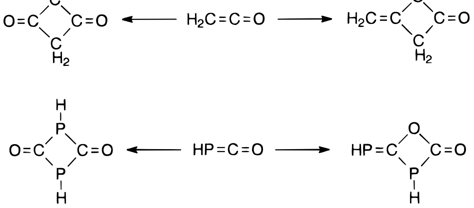
6. Dissociation

The dissociation of HPCO and of its protonated species have been examined to provide further insight into their stability. At the MP4/6-31G** level using 4-31G-optimized geometries, HPCO lies only 20 kcal/mol below the PH and CO fragments in their ground states: this relatively small value does not ensure the stability of the HPCO molecule.[104] Such a theoretical result has been proved experimentally with the frequent loss of CO (see section VIII.C). By contrast, the protonated HPCO lies 46 kcal/mol below the fragments PH_2^+ and CO.

7. Dimerization

Ab initio studies have been performed on the dimerization of phosphaketene HPCO and ketene at the same level of theory (MP2/6-31G*).[167] In the dimerization of ketene, the preferred lactone formation is due to kinetic control. However, this preference for lactone over dione formation is small and dependent on the computational method. For HP═C═O the dione derivative is more stable than the lactone compound which is in fact less stable than two isolated phosphaketenes.[167] Both reactions occur via the classical $[2\pi_s + 2\pi_a]$-pathway, and surprisingly, the dimerization is only slightly exothermic (Scheme 33). The difference in the reaction pathways between $H_2C{=}C{=}O$ and HP═C═O can be attributed, among other factors, both to ring strain and steric effects.

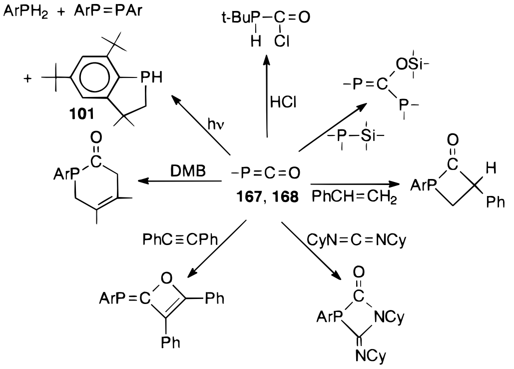
Scheme 33



C. Reactivity

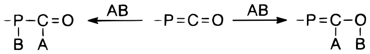
A summary of the reactivity is given in Scheme 34.

Scheme 34



From the mesomeric structures previously shown (Chart 20), two possibilities can occur depending on the AB reagent (Scheme 35). In fact, the chemistry of phosphaketenes has a close relationship with that of isocyanates.

Scheme 35



1. Photolysis

A slow decomposition with loss of CO[19] occurs upon photolysis by a mercury lamp which is not surprising from the results of the calculations.[104] The formation of $ArPH_2$, of the diphosphene ArP═PAr, and of the cyclization product **101** arises probably from a phosphinidene intermediate which has not been detected (Scheme 34).

2. Addition of HCl

As expected from the P═C bond polarity and from calculations, hydrochloric acid adds to t-BuP═C═O with H on phosphorus and Cl on the carbon atom[162] (Scheme 34).

3. Reaction with Silylphosphines

Phosphaketenes **167** and **168** react via the CO bond with silylphosphines, leading to phosphaalkenes. Depending on the starting silylphosphines used (mono-, di-, or trisilylphosphines and monosilyl- or disilyldiphosphines), various phosphaalkenes or polyphosphaalkenes have been obtained.[162,168] Some of these reactions are displayed in Scheme 36. As said previously, the addition of a lithium silylphosphide to phosphaketene ArP═C═O is a good route to diphosphaallene ArP═C═PAr[34] (Scheme 24).

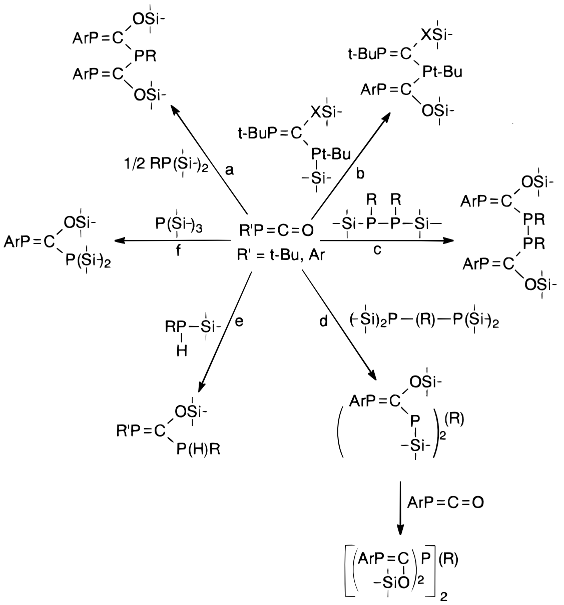
4. Phosphorus Ylide

By reaction with phosphorus ylides, phosphaketene ArP═C═O is also a good precursor of other phosphacumulenes such as the phosphaallenes $ArP{=}C{=}CR_2$ (R_2 = Ph_2;[34] H, Ph;[25] H, COOEt[25]) (see section II, eq 5).

5. [2+2]-Cycloadditions

Two types of [2+2]-cycloadditions have been reported:[19] (1) involving the P═C moiety with styrene[19]

Scheme 36



a) R = Me, t-Bu, Cy, Ph, Mes, Tip, Me_3Si, $(Me_3Si)_3C$[168a]
b) X = O, N, p-$C_6H_4CF_3$[168a]
c) R = Me_3Si, Ph, iPr[168c]
d) R = 1,4-Ph, $(CH_2)_3$, cis $CH_2CH{=}CHCH_2$[168a]
e) R = R' = t-Bu[162], Ar[168a]
f) ref 168b

and a carbodiimide[19,148] and (2) involving the CO moiety with diphenylacetylene.[19,148]

6. [2+4]-Cycloaddition

A Diels–Alder reaction has been observed between ArP═C═O and 2,3-dimethylbutadiene leading to the corresponding phosphorinene.[19,148] This reaction proceeds only via the P═C double bond (Scheme 34).

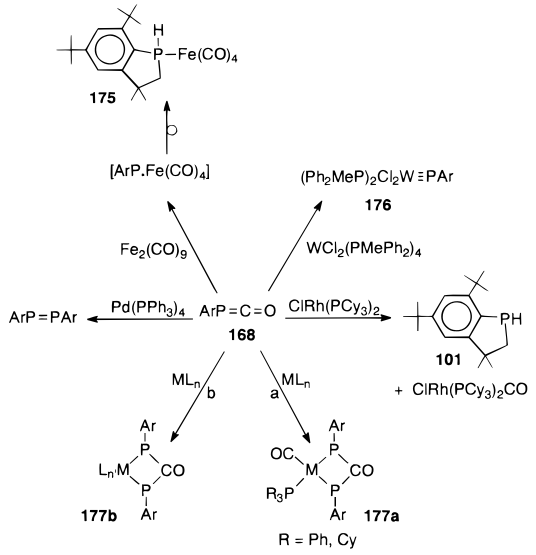
7. Transition-Metal Complexes

Various reactions have been reported between ArP═C═O and transition-metal complexes[82,108,169–171] (Scheme 37). Generally they involve a P═C bond cleavage resulting in the decarbonylation of the phosphaketene and yield products derived from the phosphinidene ArP. Thus, the phosphaindane **101** was obtained with a rhodium complex[82] and the phosphaindane complex **175** with $Fe_2(CO)_9$.[169] Formation of **175** probably involves the terminal phosphinidene complex $ArPFe(CO)_4$ intermediate.

With a tungsten derivative compound **176**[108] was formed. Its ^{31}P NMR data ($\delta = 193.0$ ppm, $^1J_{PW} = 649$ Hz)[108] are completely different from those of Cp_2WPAr (δ $^{31}P = 661.1$ ppm, $^1J_{PW} = 153.5$ Hz),[172] which was the first angular terminal phosphinidene complex (type **A**) (Chart 22) to be reported.[173] An X-ray investigation showed that **176** was the first linear terminal phosphinidene complex (type **B**) with a C–P–W angle of 168.2(2)°. The very short P–W distance (2.169(1) Å) is consistent with a triple-bond description, which also explains the $\delta^{31}P$ at a relatively upfield shift since the phosphorus atoms of –P═C< are more deshielded than those of P≡C–.[18]

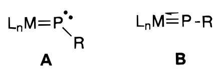
Diphosphaureylene complexes **177a**[170] and **177b**[171] were obtained from ArP═C═O and Pt or Pd derivatives. They result formally from decarbonylation of the phosphaketene and coupling of the resulting phosphinidene intermediate with another molecule of the cumulene. (Note that such a diphosphaureylene ligand was previously known only to bridge two metal centers[174]). The ^{31}P chemical shifts of **177a** and **177b** vary from 14.0 to 176.8 ppm.[170,171]

Scheme 37



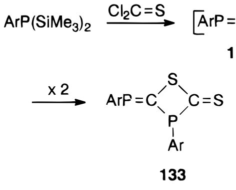
a) ML_n[170] = $(Ph_3P)_2PtC_2H_4$, $(Cy_3P)_2Pt$
b) ML_n[171] = η^2-triphosPt, dppePt (dppe = $Ph_2PCH_2CH_2PPh_2$)
dppePd, dcpePd (dcpe = $Cy_2PCH_2CH_2PCy_2$), dpppPd
(dppp = $Ph_2P(CH_2)_3PPh_2$), dmpePd (dmpe = $Me_2PCH_2CH_2PMe_2$),
η^2-triphosPd

Chart 22



IX. Phosphathioketenes –P═C═S

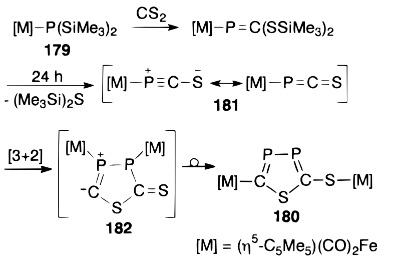
Much less work has been performed on phosphathioketenes since only two papers report the formation of transient –P═C═S derivatives.[132,175] The reaction of the disilylphosphine $ArP(SiMe_3)_2$ with thiophosgene gives the four-membered ring derivative **133**, which is assumed to be formed via phosphathioketene ArP═C═S intermediate **178** which dimerizes in a unsymmetrical [2 + 2]-cycloaddition[132] (eq 58). As stated previously, **133** is (by photolysis) a precursor of the corresponding diphosphaallene ArP═C═PAr[132] (eq 42).



(58)

A similar type of dimerization was observed for ArP═C═NPh in the presence of a palladium complex and also for Ph(Tip)Si═C═PAr[106a] (see section XVIII) and Mes_2Ge═C═PAr[106b] (see section XIX).

When ferrio(disilyl)phosphine **179** was reacted with CS_2, compound **180**, the first example of a 1,3,4-thiadiphosphole,[175] was obtained in 29% yield probably via the phosphathioketene **181** which, contrary to ArP═C═S, gives a [3 + 2]-self-dimerization to the zwitterionic heterocycle **182** and then finally a sigmatropic [1,2]- and [1,3]-migration (eq 59). Neither the hypothetical metallophosphathioketene **181** nor the heterocycle **182** could be detected spectroscopically.



(59)

The same reaction with the ruthenium complex (η^5-C_5Me_5)$(CO)_2$Ru gives only poor yields of the ruthenium analogue of **180**.[175]

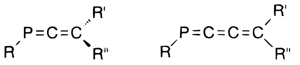
In the arsenic field, the reaction between the metallodisilylarsane [M]As$(SiMe_3)_2$ and CS_2 furnished the metalloarsaalkene [M]As═C$(SSiMe_3)_2$,[175] which is more stable than its phosphorus analogue and does not decompose to the hypothetical arsathioketene [M]As═C═S.

X. 1-Phosphabutatrienes –P═C═C═C<

The first phosphabutatriene −P═C═C═C<, a derivative with three cumulative double bonds, has been synthesized by Märkl in 1986.[176] Since this date, some other derivatives of this type have been prepared and stabilized owing to the use of bulky groups: all of them are substituted on phosphorus by the huge 2,4,6-tri-*tert*-butylphenyl.

One of the differences between phosphaallenes and phosphabutatrienes is that when the groups on carbon are different and if phosphorus is stable to inversion, phosphaallenes are chiral whereas *Z*/*E* isomers are expected for phosphabutatrienes (Chart 23).

Chart 23

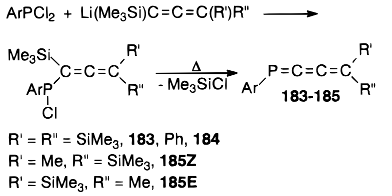


A. Synthesis

A summary of the synthesis reactions is given in Scheme 38.

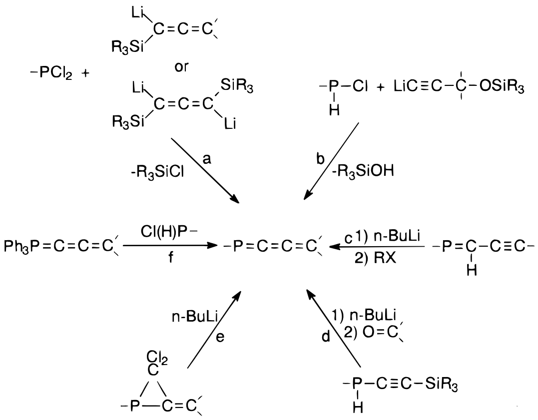
1. From Lithiated Allenes or Acetylenes (Routes a, b, c)

Refluxing a THF mixture of $ArPCl_2$ and the lithium salt of alkynes $Me_3Si{-}C{\equiv}C{-}CH(R')R''$ leads to **183**–**185** through Me_3SiCl elimination[176] (eq 60). In this case the P═C double bond is formed in the final step. Such phosphabutatrienes, as for all the isolable derivatives of this type, are air and moisture stable. In the case of **185**, the *Z* and *E* isomers were cleanly separated by chromatography on silica gel.[176]

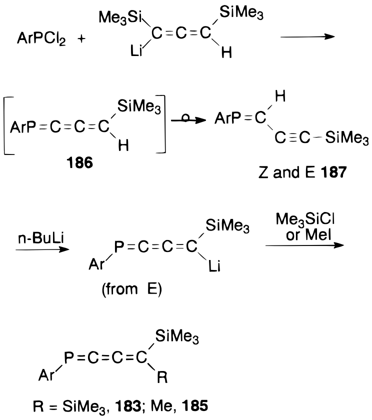


(60)

Scheme 38



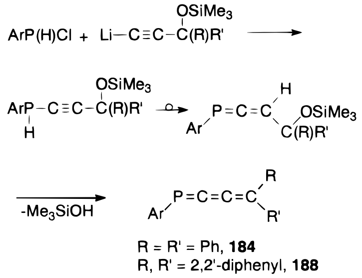
Addition of $ArPCl_2$ to a less encumbered lithiated allene gives the transient phosphabutatriene **186** which spontaneously rearranges to **187**[177] (eq 61).



(61)

Addition of BuLi to **187** affords a lithium-substituted phosphabutatriene and then phosphabutatrienes **183** and **185** upon quenching with chlorotrimethylsilane or methyl iodide.

Elimination of Me_3SiOH from the adequate phosphaallene was also a good route to phosphabutatrienes **184** and **188**, the last step being the formation of a C═C double bond[41b] (eq 62).

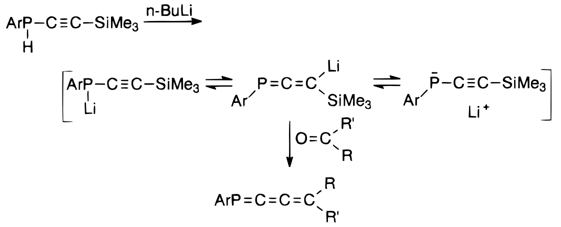


(62)

2. Wittig–Peterson Reactions (Route d)

As said previously (section II.A), Wittig−Peterson reactions are good routes to phosphaallenes. They have also been applied successfully to the synthesis of phosphabutatrienes **184** and **189**−**193**[50a,178] (eq 63).

When R and R′ are not bulky enough, such as hydrogen, methyl, or cyclohexyl, the phosphabutatrienes are not stable and a dimerization occurs[50a] (see section X.C.1).

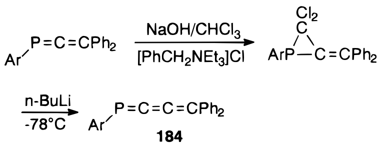


(63)

R = R′ = Ph, **184**; 4-Me_2N-C_6H_4, **189**; 2-adamantylidene, **190**
R = Ph; R′ = 4-Cl-C_6H_4, **191**; 4-MeO-C_6H_4, **192**; 4-Me_2N-C_6H_4, **193**

3. From Methylenephosphiranes (Route e)

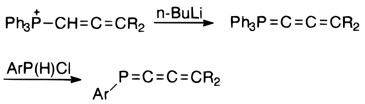
Some phosphaallenes have been obtained by addition of a lithium compound to *C*,*C*-dichlorophosphiranes (see section II.A). A similar route from a methylene (*C*,*C*-dichloro)phosphirane afforded phosphabutatriene **184**[76] (eq 64). One carbon atom was formally inserted into the P=C double bond of the starting phosphaallene to extend the cumulative double-bond system.



(64)

4. From λ^5-Phosphabutatrienes (Route f)

The phosphabutatrienes **184**, **194**, and **195** were obtained by the reaction previously used by Märkl to synthesize phosphaalkenes[36] or phosphaallenes (see section II.A), i.e., the reaction between chlorophosphine ArPHCl and λ^5-phosphabutatrienes[35] (eq 65).



(65)

R = Ph, **184**; Et, **194**; iPr, **195**

B. Physicochemical Studies

The color of phosphabutatrienes varies from colorless to yellow (the most often found color) and sometimes to orange or red. λ_{max} is observed at 412 nm for $ArP{=}C{=}C{=}CPh_2$[176] (420 nm in $Ph_2C{=}C{=}C{=}CPh_2$) and 474 nm for the red **193**.[178]

Oils or crystals are generally remarkably stable, both thermally (melting points up to 196° are generally observed without decomposition) and toward air and moisture.

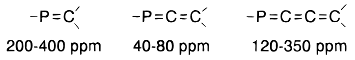
1. ^{31}P NMR (Table 14)

Chemical shifts between ca. 120 and 350 ppm are registered for phosphabutatrienes. They are very dependent on the groups on the terminal carbon, since they are in the range 120−160 ppm with two alkyl or aryl groups, 288.6 and 322.3 ppm with one $SiMe_3$ group, and 343.3 ppm with two $SiMe_3$ groups. They are close to the chemical shifts observed for the phosphaalkene analogues[179−181] (Chart 24). By contrast, phosphaallenes $-P{=}C{=}C<$ display chemical shifts at much higher field, generally between 40 and 80 ppm (Chart 25). Thus, it seems there is an alternation of chemical shifts between phosphaalkenes, phosphaallenes, and phosphabutatrienes probably caused by the different orbital geometries. If the chemical shifts for *Z* and *E* isomers are very close (1 or 2 ppm of difference) when the two groups on the carbon atom are rather similar,[176,178] large $\Delta\delta$ is observed in the case of $ArP{=}C{=}C{=}C(Me)SiMe_3$ (43.7 ppm),[176] in agreement with the results reported for phosphaalkenes.

Chart 24

$MesP{=}CPh_2$	$ArP{=}C(Ph)SiMe_3$	$ArP{=}C(SiMe_3)_2$
233 ppm[179]	293 ppm[180]	393 ppm[181]

Chart 25



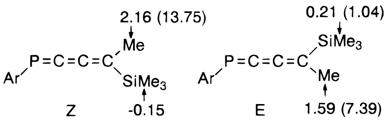
2. ^{13}C NMR (Table 14)

A similar alternation of the chemical shift for the sp carbon bonded to phosphorus is observed in the ^{13}C NMR of phosphabutatrienes with signals in the range 170−190 ppm, exactly like in phosphaalkenes ($MesP{=}CPh_2 = 193.7$ ppm)[179] but very different from those of phosphaallenes (generally 230−250 ppm). β- and γ-carbons resonate at higher field than α-carbon, the γ-carbon generally being the most upfield shifted.

3. ^1H NMR

In the ^1H NMR spectrum of *Z*/*E* isomers of $ArP{=}C{=}C{=}C(Me)SiMe_3$, Me and $SiMe_3$ display signals at lower field and exhibit larger ^5J or $^6J_{PH}$ couplings when they are cis to the phosphorus lone pair, as previously observed for phosphaalkenes[182] (Chart 26).

Chart 26



δ ^1H (^5J or $^6J_{PH}$) for **185** Z and E

4. X-ray Studies

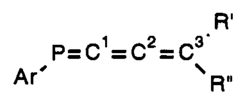
Only one X-ray structure investigation has been performed on $ArP{=}C{=}C{=}CPh_2$.[176] Classical P=C and C=C bond lengths are determined with PC_1C_2 and $C_1C_2C_3$ bond angles very close to 180° (Table 14).

From the physicochemical data reported for phosphabutatrienes, it seems that these derivatives have a closer relationship to phosphaalkenes than to phosphaallenes both in ^1H, ^{13}C, or ^{31}P NMR and also from a stereochemistry point of view, since they can exist as *Z*/*E* isomers.

C. Reactivity

A summary of the reactivity is given in Scheme 39. The reactivity of phosphabutatrienes is still relatively

Table 14. Phosphabutatrienes: Synthetic Routes and Physicochemical Data (For methods, see Scheme 38)

n°	R'	R"	δ ^{31}P	δ ^{13}C C^1 (J_{PC})	C^2 (J_{PC})	C^3 (J_{PC})	color	mp (°C)	method	ref
										
183	SiMe$_3$	SiMe$_3$	343.3		106.5	114.9			a, c	176,
					(21.8)	(10.6)				177
184	Ph	Ph	156.7				yellow	156-8	a	176
[a]			157.1	178.7	164.8	122.3	yellow	155-7	b	41b
				(25.22)	(35.80)	(45.57)				
								149-50	d	50a
								153-4	c	76
			158.0	178.69	164.84	122.32		148-150	f	36
				(24.55)	(36.82)	(45.77)				
185a Z	Me	SiMe$_3$	288.6				colorless oil		a	176
185b E[b]	SiMe$_3$	Me	332.3	170.5	82.3	108.2	colorless oil		a	176
				(71.8)	(23.1)	(9.7)				
188	2,2'-diphenyl		182.3						b	41b
189	4-Me$_2$N-C$_6$H$_4$	4-Me$_2$N-C$_6$H$_4$	123.8	175.6	157.3	123.9	intense red	175-9	d	50a
				(25.8)	(35.2)	(43.8)				
190	2-Ad		119.5	185.4	157.9	135.4	yellow	124-6	d	50a
				(21.2)	(26.5)	(39.1)				
191	Ph	4-Cl-C$_6$H$_4$					yellow	193-6	d	50a
192 E,Z	Ph	4-MeO-C$_6$H$_4$	150.6	178.2	163.2	136.8	orange	110-6	d	50a
			149.2	178.0	162.9	136.5				
				(25.87)	(35.82)	(59.05)				
193 Z/E[c]	Ph	4-Me$_2$N-C$_6$H$_4$	139.9 (E)	177.0	160.4	123.0	red	135-9	d	178
				(24.90)	(35.9)	(45.0)				
			137.3 (Z)	177.3	161.1					
				(25.52)	(35.85)					
194	Et	Et	119.69	189.67	162.29	130.60	yellow red		f	36
				(23.88)	(28.53)	(41.13)				
195	iPr	iPr	118.50	191.67	160.73	140.67	light yellow		f	36
				(25.21)	(19.19)	(41.80)				

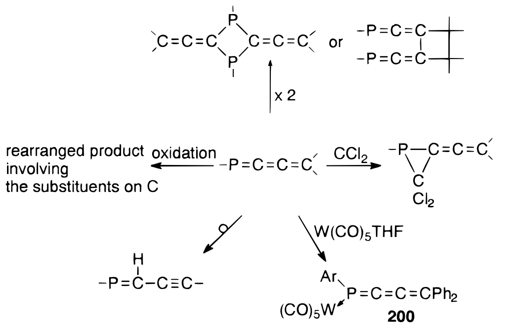
[a] P−C$_1$, 1.647(8) Å; C$_1$C$_2$, 1.253(10) Å; C$_2$C$_3$, 1.348(10) Å; PC$_1$C$_2$,178.4(5)°; C$_1$C$_2$C$_3$, 178.3(6)°. UV nm (ε): 412 (20 200), 396 (19 400), 305 (7000), 268 (19 800), 238 (26 700). IR (cm^{-1}): 1940. [b] IR (cm^{-1}): 2095. [c] UV (nm): 474 (31 700), 355 (9100), 309 (14 100).

undeveloped, compared to that of phosphaallenes, diphosphaallenes, or phosphaazaallenes.

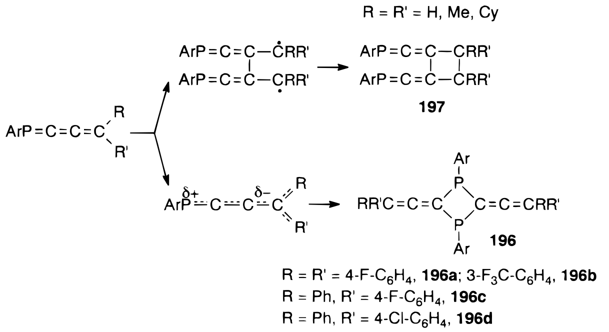
1. Dimerization

Two types of dimerization occur leading to cyclobutanes or to 1,3-diphosphetanes depending on the substituents on the carbon atom. With electron-withdrawing groups, such as halogen-substituted groups, diphosphetanes **196** are obtained,[50b] whereas with less electronegative groups, such as H, Me, or Cy, only cyclobutanes **197** are formed[50] (Scheme 40). We should note the great difference of stability

Scheme 39



Scheme 40

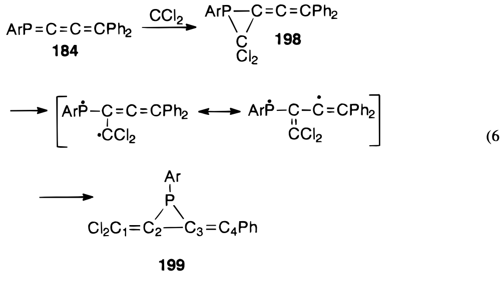


between ArP=C=C=CPh$_2$ and the corresponding phosphabutatrienes in which the phenyl groups have been substituted in the 3- or 4-position by an halogen:[50b] the former is thermally very stable whereas the latter head-to-tail dimerize spontaneously by the P=C bonds after their synthesis by the Wittig–Peterson reaction to give diphosphetanes **196** in the form of yellow crystals. The X-ray structure of **196a** shows a planar four-membered ring with P–C bond lengths between 1.816(4) and 1.863(4) Å. In the case of **196d**, *Z*/*E* derivatives are obtained (δ ^{31}P = 27.92 and 30.40 ppm ($^2J_{PP}$ = 45.7 Hz) for *Z* isomers and 29.21 ppm for *E* isomers)[50b] whereas the dimerization of **196c** is stereoselective giving only one isomer (the question of *Z* or *E* isomer is not resolved).

Heterocycles **196** have the characteristic absorptions of allenes close to 1900 cm^{-1} in the IR spectra.[50b]

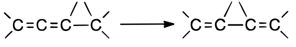
2. Reaction with Dichlorocarbene

Addition of CCl$_2$ to the phosphabutatriene **184** leads to the corresponding ethenylidenephosphirane **198** which rearranges on warming to the stable phospha[3]radialene **199**[77] according to a radicalar mechanism (eq 66); a similar rearrangement was observed with *C*,*C*-dichlorophosphiranes obtained from phosphaallenes (see section II.C.6) (eq 21). This



(66)

type of isomerization leading to radialenes has also been observed in other ethenylidenephosphiranes[183] and ethenylidenethiiranes[184] (eq 67). The X-ray in-



M = S, PR

(67)

vestigation of **199**[185] displays a planar structure (C^1–C^4 atoms, the two Cl, P, and the ipso-C of phenyl groups being approximately in the same plane) and a short C^{2}C^3 central bond (1.422(2) Å).

3. Rearrangement

As stated previously[177] (eq 61), transient phosphabutatrienes rearrange to C-alkynylphosphaalkenes.

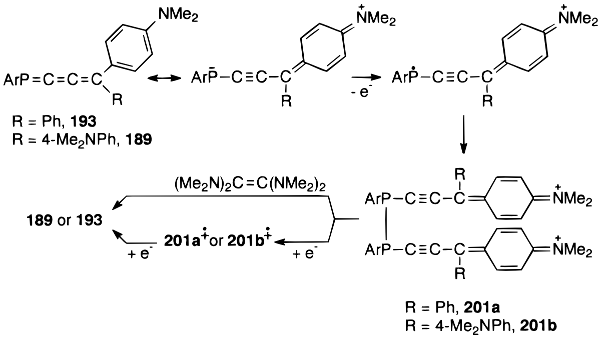
4. Complexation

ArP=C=C=CPh$_2$ reacts with W(CO)$_5$·THF to give the η^1-complex **200**[49] (Scheme 39). The overall conformation of the ligand phosphabutatriene in the complex is quite similar to that of free ligand with no appreciable change in the corresponding bond lengths and angles of the P=C=C=C frame: P=C, 1.664(6) Å; C$_1$=C$_2$, 1.222(9) Å; C$_2$=C$_3$, 1.363(9) Å; PC$_1$C$_2$, 175.7(6)°; C$_1$C$_2$C$_3$, 175.0(7)°.

The ^{31}P chemical shift of **200** is, as expected, dramatically upfield shifted (91.6[49] vs 157.1 ppm in the free ArP=C=C=CPh$_2$[41b]), but δ ^{13}C values for the three carbon atoms are, respectively, about the same (C$_1$, 175.79 ppm; C$_2$, 154.94 ppm; C$_3$, 138.33 ppm). The only important difference is the PC$_1$ coupling constant: 104.5 Hz in **200**[49] vs 25.22 Hz in ArP=C=C=CPh$_2$.[41b]

5. Oxidation

The electrochemical study of phosphabutatrienes **189** and **193** shows an irreversible oxidation at 0.50 V and an irreversible reduction at 0.06 V; however, the total cycle is reversible.[178] The oxidation of **189** and **193** gives the diphosphines **201a** and **201b** via the corresponding phosphinyl radicals[178] (eq 68).



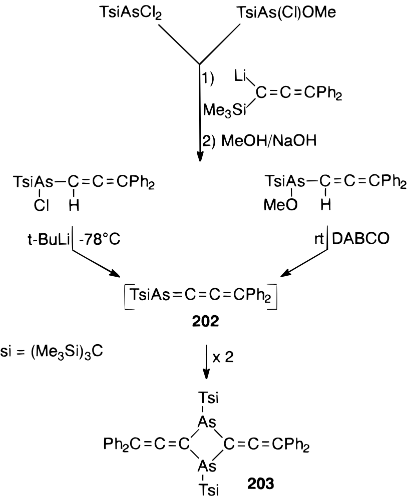
(68)

XI. 1-Arsabutatrienes –As=C=C=C<

Due to the larger size of arsenic compared to phosphorus, the stabilization of doubly bonded arsenic derivatives is, of course, more difficult. One characteristic example is the head-to-tail dimerization, via two As=C bonds, of the transient arsabutatriene TsiAs=C=C=CPh$_2$,[186] the sole derivative of this type, whereas the phosphorus analogue ArP=

$C{=}C{=}CPh_2$ is very stable; **202**, with the same phenyl groups on carbon and the extremely bulky Tsi group (bulkier than Ar) on arsenic, is only an intermediate in the reaction starting from $TsiAsCl_2$[187] or TsiAs(Cl)OMe (Scheme 41). The type of dimerization of **202**, leading to diarsetane **203**, occurred for phosphabutatrienes[50b] substituted on the carbon atom by electron-withdrawing groups.

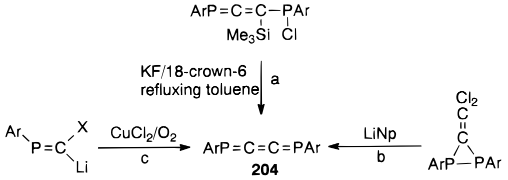
Scheme 41



XII. 1,4-Diphosphabutatrienes –P=C=C=P–

Only one compound of this type, the 1,4-diphosphabutatriene $ArP{=}C{=}C{=}PAr$ **204**, has been synthesized until now by three different routes (Scheme 42).

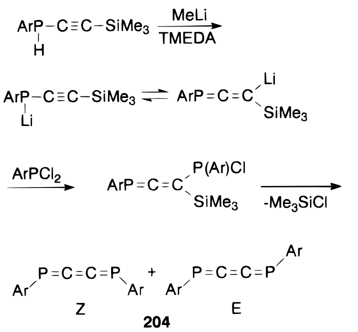
Scheme 42



A. Synthesis

1. Wittig–Peterson-Like Reaction (Route a)

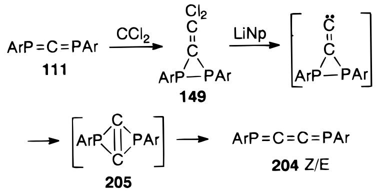
Märkl was the first to synthesize such a derivative[24] by a Wittig–Peterson-like condensation, starting from a silylethynylphosphine (eq 69). Addition of methyllithium followed by reaction with $ArPCl_2$ gave the coupling product phosphinylphosphaallene, which partially loses Me_3SiCl at room temperature. Complete elimination of Me_3SiCl was achieved by treatment with KF/18-crown-6 in refluxing toluene to give **204** as an *E*/*Z* isomeric mixture 78/22.[24]



(69)

2. From a Dichloromethylenediphosphirane (Route b)

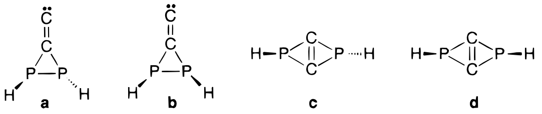
Addition of lithium naphthalenide to the diphosphirane **149**,[76] obtained from the 1,3-diphosphaallene $ArP{=}C{=}PAr$ and CCl_2, led in 40% yield to **204**[188] (eq 70): the mechanism giving **204** was supposed to involve a vinylidene–carbene intermediate through an electron-transfer process from lithium naphthalenide and then the highly strained 2,4-diphosphabicyclo[1,1,0]butene **205**.



(70)

Calculations have been performed by Bachrach[189] on the four model compounds **a**–**d** (Chart 27) to determine the mechanism leading from diphosphirane **149** to the diphosphabutatriene **204** (eq 70); **c** is a transition structure on the energy surface, whereas its cis isomer **d** is a local minimum; **d** lies 13–15 kcal/mol above **a** and is unlikely to be an intermediate in the conversion of **149** to **204**.

Chart 27



3. From a Halophosphaethenyllithium (Route c)

A convenient preparation of **204** in about 50–60% yield[190] was the reaction of halophosphaethenyllithium $ArP{=}C(X)Li$ (X = Br, Cl)[115] (easily obtained by halogen/lithium exchange from $ArP{=}CX_2$) with copper(II) chloride in the presence of oxygen (Scheme 43). However this reaction is extremely dependent on the reaction conditions: the diphosphabutatriene **204** or the diphosphabutadiene **207** were almost selectively formed depending on the temperature of the reaction and, in the absence of $CuCl_2/O_2$, the diphosphacyclobutadiene **206** was obtained[191] (Table 15).

Scheme 43

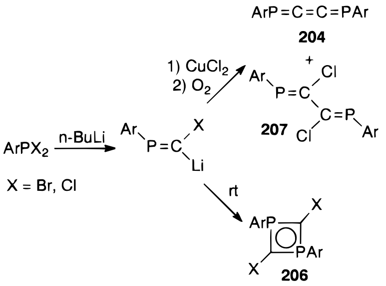


Table 15. Copper-Mediated Coupling Reaction of ArP=C(X)Li Giving Diphosphabutadiene 204 or Diphosphabutatriene 207 (isolated yields)[190]

compound	T (°C)	**204**	**207**
ArP=C(Cl)Li	0	54	7
	−78	0	46
ArP=C(Br)Li	−78	47	13
	−95	0	22

B. Physicochemical Studies

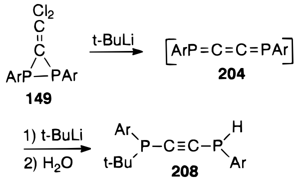
ArP=C=C=PAr is obtained in the form of yellow crystals (dec 224−226,[24] 250 °C[190b]) only sparingly soluble in usual organic solvents.

1. NMR (Table 12)

The E/Z structures (E major compound in the ratio 4/1 in all types of syntheses) have been assigned on the basis of NMR. In ^{1}H NMR, the signals of the E isomer (o- and p-t-Bu, aromatic H) are at lower field than those of the Z isomer. The same phenomenon is observed in ^{31}P NMR (E 180.6, Z 170.6 ppm).[24] A similar low-field shift on going from Z to E isomer was also found in the diphosphene ArP=PAr (E 492,[1] Z 369 ppm[30]). The δ ^{31}P values for ArP=C=C=PAr are deshielded by about 30 ppm compared to those found for diphosphaallenes −P=C=P−.

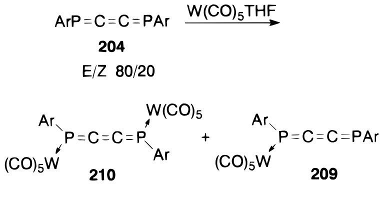
C. Reactivity

The reactivity of diphosphabutatriene **204** is relatively unknown since only two reactions have been performed, addition of *tert*-butyllithium[188] and complexation by tungsten pentacarbonyl.[190b] When t-BuLi (instead of naphthalene lithium) was added to the methylenediphosphirane, the expected diphosphabutatriene **204** could not be isolated: the diphosphaalkyne **208** was obtained exclusively as a mixture of diastereoisomers, probably by addition of t-BuLi to the previously formed **204**[188] (eq 71).



(71)

When **204** was allowed to react with 1 equiv of W(CO)$_5$·THF, monocoordinated complex **209** (δ ^{31}P = 105.3 and 181.5 ppm, $^{3}J_{PP}$ = 315.1 Hz) was obtained, together with the dicoordinated complex **210**, but could not be isolated[190b] (eq 72). With an



(72)

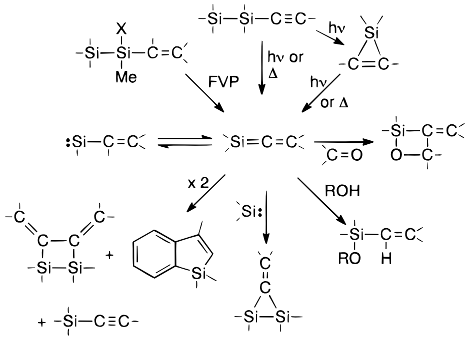
excess of W(CO)$_5$·THF, **210** in the form of deep blue crystals (UV−vis, λ_{max} = 609 nm (log ϵ = 4.83), 318 nm (log ϵ = 4.05)) was obtained. Surprisingly, even starting from a 80/20 mixture of E/Z isomers of **204**, the sole isomer **210** E was formed and characterized by ^{31}P NMR (δ = 105.0 ppm, $^{1}J_{PW}$ = 169.6, $^{4}J_{PW}$ = 109.0 Hz) and ^{13}C NMR (δ =175.0, $^{1}J_{PC}$ = 30.0, $^{2}J_{PC}$ = 26.0 Hz). The X-ray structure determination proved the end-on-type coordination at both phosphorus atoms and displayed a planar WPCCPW framework.[190b]

XIII. 1-Silaallenes >Si=C=C<

A. Transient Uncomplexed 1-Silaallenes

Before the synthesis and isolation of the first stable silaallenes by West in 1993,[192] very important work was performed by Ishikawa on transient-free or nickel-complexed silaallenes. Photolysis and thermolysis of silirenes or ethynyldisilanes were the main route to these transient silaallenes formed in relatively poor yields, generally less than 25%, due to a competitive formation of dimethylsilylene obtained by extrusion from the ethynyldisilanes and of other byproducts (Scheme 44).

Scheme 44



Transient silaallenes were evidenced by trapping reactions, by the formation of their rearrangement products, and also in some cases by their physicochemical data.

1. Physicochemical Data

Silaallene Me$_2$Si=C=C(SiMe$_3$)Ph exhibits a pseudo-first-order lifetime of about 25 μs at room temperature in nitrogen-saturated hexane solution,[193] compare to that of silylene Me$_2$Si (100 ns) and of the corresponding silirene (100 ms).

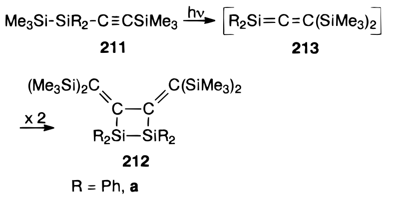
Its UV absorption (λ_{max} = 268 nm with a shoulder at 305 nm) corresponds to a superposition of a benzenoid absorption (268 nm) with the $\pi-\pi^*$ absorption of the Si=C double bond (305 nm)[193] and is significantly blue-shifted compared to that observed in Me$_2$Si=C=C(SiMe$_3$)$_2$ (λ_{max} = 275 nm, shoulder = 325 nm).[194] There is a great difference with Me$_2$Si=CH$_2$, which absorbs at 244 nm.[195] This difference can most likely be attributed to hyperconjugative interactions between the Si=C double bond and the C−SiMe$_3$ bond which are expected to be the most important in the bis(trimethylsilyl)-substituted silaallene. Such interactions analogous to the β-silyl effect in carbocation chemistry[196,197] generally strongly affect the electronic spectra of alkenes[198] as well as their reactivity.

2. Dimerization

When alkynyldisilanes **211**[199,200] were photolyzed by irradiation with a low-pressure mercury lamp, the 1,2-disilacyclobutanes **212** and $Me_3SiC{\equiv}CSiMe_3$ were obtained (eq 73). Their formation can be best understood in terms of head-to-head dimerization of transiently formed silaallenes **213**. The yield in disilacyclobutanes **212** is generally close to 20%, except when the substituents on silicon are *o*-tolyl groups: the very low yield obtained in this case is probably due to the steric hindrance which prevents the dimerization and gives rearrangement products.[200]

A similar head-to-head dimerization has previously been observed in some silenes, particularly those substituted on carbon by a $OSiMe_3$ group, although the general mode of dimerization of such compounds is a head-to-tail mode.[11]

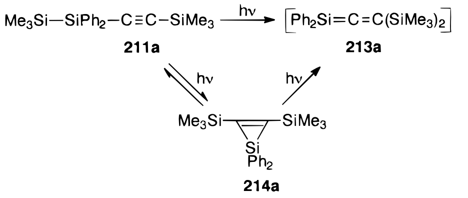
A higher yield of **212a** (29%) was obtained when **211a** was photolyzed in the presence of bis(trimethylsilyl)acetylene[199b] (eq 73).This result indicates that the silylene Ph_2Si produced during photolysis adds to this alkyne to give silirene **214a**, which can be transformed photochemically into **211a** and silaallene **213a** (Scheme 45).



R = Ph, **a**
R = o-Tol, **b**; m-Tol, **c**; p-Tol, **d**

(73)

Scheme 45

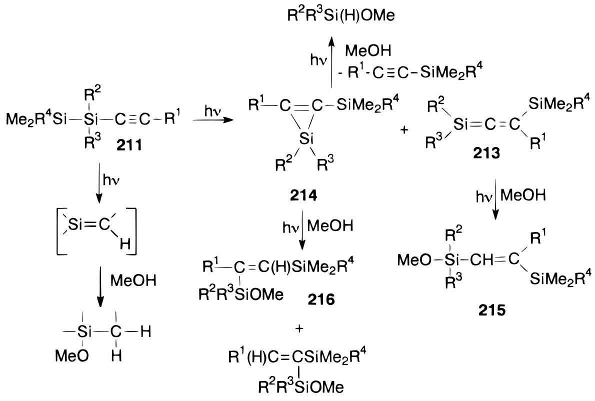


3. Reaction with Protic Reagents

We have reported in the Scheme 46 all the reactions which have been found to occur in the photolysis of disilanes in the presence of methanol. However, in the other trapping reactions reported in the following paragraphs, we will describe only the reactivity of transient silaallenes, i.e, the topics of this review; it is, of course, necessary to remember that many trapping products of other reactive species are also formed.

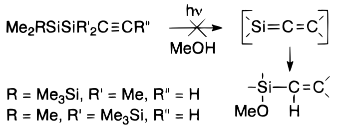
When photolysis of disilanes **211** was performed in the presence of methanol, methoxysilanes **215** were obtained in low yields, generally as a mixture of *Z*/*E* isomers due to a photochemical isomerization, proving the transient formation of silaallenes **213** and a regioselective addition of the methanol to the Si=C double bond.[193,194,199b,201−203] In some cases methoxysilanes **215** are not obtained from **211** because the silaallenes **213** are not transiently formed[199] (eq 74).

Scheme 46



Silaallenes **213** characterized:

a $R^1 = SiMe_3$, $R^2 = R^3 = Ph$, $R^4 = Me$[199b]
e $R^1 = Ph$, $R^2 = R^3 = R^4 = Me$[193,201]
f $R^1 = SiMe_3$, $R^2 = R^3 = Mes$, $R^4 = Me$[202]
g $R^1 = SiMe_3$, $R^2 = R^3 = R^4 = Me$[194]
h $R^1 = H$, $R^2 = R^3 = Me$, $R^4 = Ph$[203]
i $R^1 = H$, $R^2 = R^4 = Me$, $R^3 = Ph$[203]
j $R^1 = H$, $R^2 = R^3 = Ph$, $R^4 = Me$[203]
k $R^1 = H$, $R^2 = R^4 = Me$, $R^3 = SiMe_3$[203]

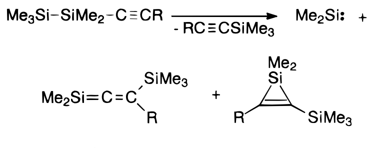


R = Me_3Si, R' = Me, R" = H
R = Me, R' = Me_3Si, R" = H

(74)

Silirenes **214** are produced generally in higher yield than silaallenes **213**. The less hindered Si−C bond of the silirene is cleaved preferentially,[204] but sometimes both Si−C bonds are cleaved and other transient species such as silylenes or silenes are also generated during the photolysis of disilanes and react with methanol. Thus, these reactions are rather complicated, which explains the low yields in trapping adducts of silaallenes.

a. Case of 213e and 213g. Interesting work has been made by Leigh on silaallenes $Me_2Si{=}C{=}C(Ph)SiMe_3$ **(213e)**[193] and $Me_2Si{=}C{=}C(SiMe_3)_2$ **(213g)**[194] generated by laser flash pyrolysis of the corresponding ethynyldisilanes (eq 75). This author determined the rate constants of the reaction of **213e** and **213g** with MeOH (the corresponding adducts **215g** and **216g** (Scheme 46) have been characterized), t-BuOH, CH_3COOH, as well as acetone and oxygen.



R = Ph, **213e**
R = $SiMe_3$, **213g**

(75)

As expected, the substitution of the phenyl group in **213e** by a trimethylsilyl group (**213g**) results in a 20−1000-fold decrease in reactivity toward the same reagents (MeOH, *t*-BuOH, CH_3COOH, acetone, O_2).[193,194] The more important steric effect of Me_3Si

Table 16. Bimolecular Rate Constants for Reactions of 213e and 213g at 23 °C[193] ($k_q/10^7$ M^{-1} s^{-1})

reagent	**213e**	**213g**
MeOH	$k_{\mathrm{MeOH}} = 2.4 \pm 0.6\ 10^6$ M^{-1} s^{-1}	$k_{\mathrm{MeOH}} = 5.3 \pm 2.0\ 10^7$ M^{-1} s^{-1} $k_{\mathrm{2MeOH}} = 9.9 \pm 1.8\ 10^9$ M^{-2} s^{-1}
t-BuOH	$k_{\mathrm{t-BuOH}} = 2 \pm 1\ 10^4$ M^{-1} s^{-1}	$k_{\mathrm{t-BuOH}} = 1.6 \pm 0.5\ 10^7$ M^{-1} s^{-1} $k_{\mathrm{2t-BuOH}} = 2.2 \pm 0.9\ 10^8$ M^{-2} s^{-1}
CH_3COOH	9.8 ± 0.6	511 ± 50
CH_3COCH_3	0.18 ± 0.01	5.8 ± 0.6
Oxygen	11 ± 2	1.5 ± 0.7

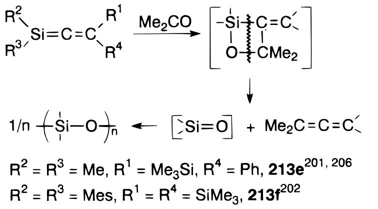
than Ph also explains this difference in reactivity between these two silaallenes.

As indicated in Table 16, the reactivity of **213e** and **213g** is much more important with CH_3COOH than with MeOH and particularly *t*-BuOH.[193] The rate law for the reaction with alcohols contains both first- and second-order terms in alcohol concentration, indicating a complex mechanism comparable to the one determined for silenes.

Thus, although these two silaallenes exhibit a characteristic silene reactivity, they react much more slowly than silenes studied by similar methods.[205]

4. Reaction with Acetone

Silaallenes **213e**[201,206]and **213f**[202] generated by photolysis of ethynyldisilanes react with acetone to give transient [2+2]-cycloadducts which decompose in the conditions of the reaction with formation of polysiloxanes and of the corresponding allenes[201,202,206] in low yields, generally less than 20% (eq 76).



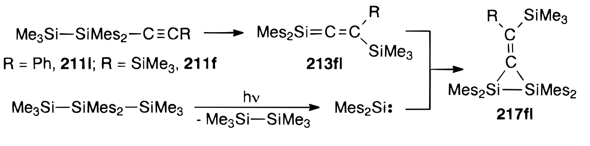
(76)

A reaction of the enol form of acetone has not been observed in this case, whereas depending on the reaction conditions (thermolysis, photolysis) and on the substituents on silicon and carbon, ene reactions, [2+2]-cycloadditions, or sometimes both are observed between enolizable ketones and silenes $>Si{=}C<$.[4,5,11]

5. Reaction with Silylene

Irradiation of the corresponding alkynyldisilanes in hexane between −20 and −40 °C in the presence of trisilane $Mes_2Si(SiMe_3)_2$ affords disiliranes **217f** and **217l** in, respectively, 14% and 25% yield[207] (Scheme 47). The formation of these two derivatives

Scheme 47



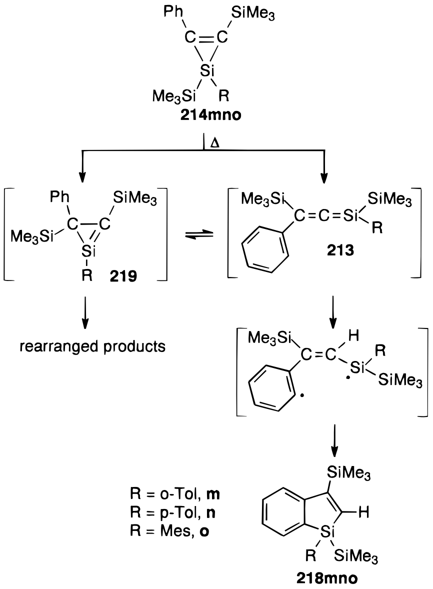
is best explained by a [2+1]-cycloaddition between dimesitylsilylene and the silaallenes **213**. The photolysis of **211l** alone also gave **217l** but in low yield (7%): this experiment proves that **211l** rearranges to **213l** but also decomposes by loss of silylene Mes_2Si.[207a]

Yellow crystals of disiliranes **217f** and **217l** can be purified by column chromatography because they are stable toward atmospheric oxygen and moisture,[207] which is not generally the case for other disiliranes with less bulky groups on silicon.

6. Thermal Rearrangement

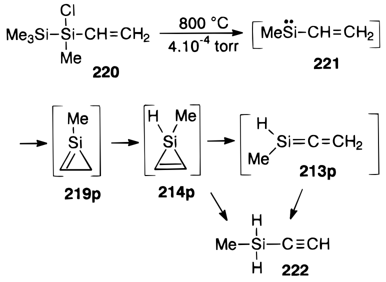
Thermolysis of silirenes **214m, 214n**, and **214o** affords silaindenes **218m**, **218n**, and **218o** (Scheme 48).[208] The yield in **218** depends on the temperature

Scheme 48



since it is, respectively, of 58% and 36% for **218m** and **218n** at 130 °C[208a] but decreases at temperature higher than 150 °C. Thermolysis of **214o** at 280 °C gave **218o** in 28%.[208bc] The formation of **218** can be explained by isomerization of the silirenes **214** to silaallenes **213**, followed by a hydrogen shift from the ortho position of the phenyl ring to the central carbon of the silaallene and then coupling of the resulting diradical. Some other products were formed in this reaction arising probably from silirenes **219** formed by a 1,2-trimethylsilyl shift from the ring silicon atom to the sp[2] carbon.

Silaallene $Me(H)Si{=}C{=}CH_2$[209] has been postulated to be a possible intermediate in the formation of ethynylsilane $MeSiH_2C{\equiv}CH$ by thermolysis of disilane **220** (eq 77). It seems likely that the silylene **221** is initially formed and isomerizes to silirene **219p** by intramolecular π-addition followed by hydrogen migration to silicon to form **214p**. Rearrangement of



(77)

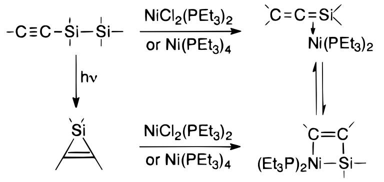
214p could give the ethynylsilane **222** directly or via the silaallene **213p**.

B. Transient Complexed 1-Silaallenes

1. Dimerization or Rearrangement

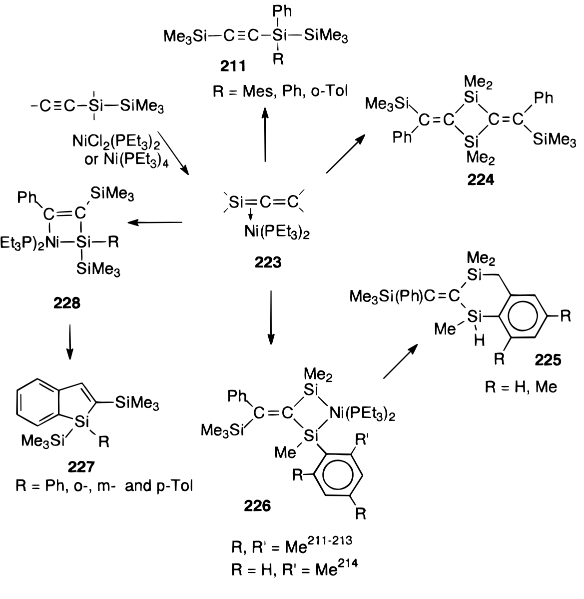
The nickel-catalyzed reaction of alkynylpolysilanes affords silaallene–nickel complexes and nickelasilacyclobutenes as reactive intermediates (Scheme 49).

Scheme 49



These two derivatives are in equilibrium. The nickelasilacyclobutenes can also be obtained by preliminary photolysis of alkynyldisilanes leading to silirenes followed by addition of nickel complexes. The reaction course leading to the final products from these intermediates is remarkably dependent on the substituents on silicon and carbon as well as on the trapping agent. Thus, all these reactions generally give many derivatives, and trapping products arising from silaallenes are generally obtained in low yields, except in some special cases.

Scheme 50



In the absence of trapping reagent, nickel-complexed silaallenes **223** give derivatives **211**, **224**, **225**, and **227** depending on the substituents (Scheme 50). Contrary to the case of silaallenes $R_2Si{=}C{=}C(SiMe_3)_2$ (R = Ph, *o*-, *m*-, *p*-tolyl)[199,200] which give head-to-head dimers, silaallene $Me_2Si{=}C{=}C(Ph)SiMe_3$ complexed by nickel leads to **224**, head-to-tail dimer of the free silaallene in the form of only one stereoisomer in 64–78% yield.[210] The active catalyst is probably a Ni(0) species.

When the silicon is substituted by a mesityl group, the cyclization products **225** were obtained, probably via the intermediates **226**.[211–214] Without nickel catalyst, compounds **225** are not formed from the alkynyldisilanes. These results indicate that the nickel atom plays an important role for the C–H activation of the *o*-mesityl methyl group and that **225** compounds are produced via the silaallene–nickel complex **223**. Similar thermal cyclization involving a mesityl or a 2,6-dimethylphenyl group on an sp^2 silicon atom has already been reported.[215]

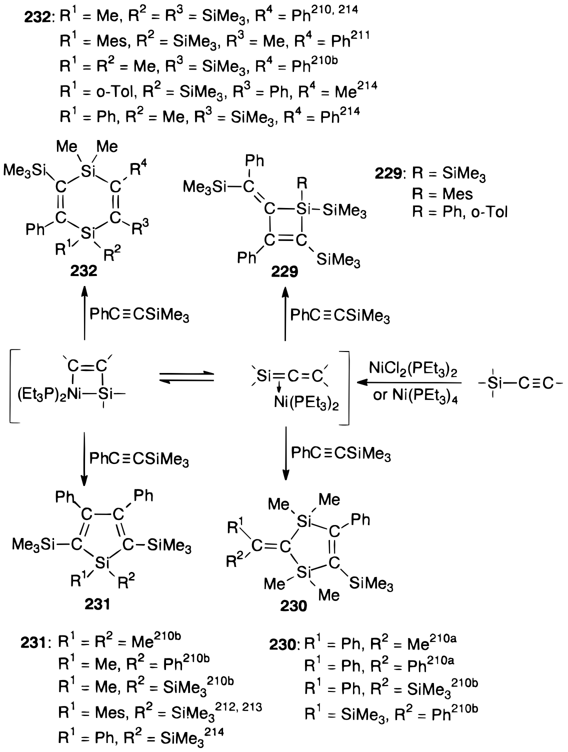
Ethynylsilanes **211** are also obtained with a catalytic amount of nickel(0) complex,[211,214] probably by the isomerization of the silaallene–nickel complex by a 1,3-phenyl shift from a sp^2 carbon onto a sp^2 silicon atom.

Silaindenes **227**[216] are formed by a C–H activation of the phenyl group of the nickelasilacyclobutene intermediate **228** followed by a reductive elimination of the nickel species.

2. Reaction with Acetylenic Derivatives

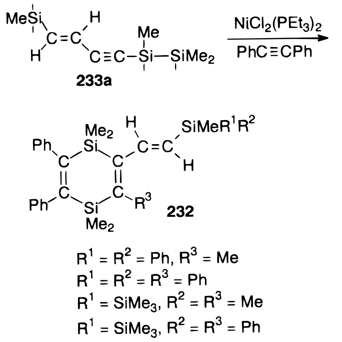
When the reactions of alkynylsilanes with nickel complex were performed in the presence of an excess of $PhC{\equiv}CSiMe_3$[210–214] or $PhC{\equiv}CPh$,[217] various four-, five-, and six-membered ring heterocycles **229**–**232** were obtained (Scheme 51). The formation of **229** and

Scheme 51

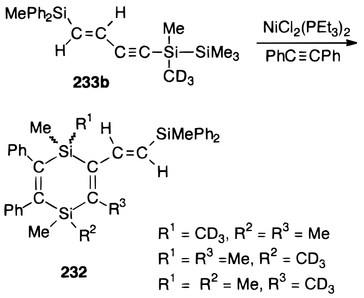


230 can be best explained in terms of the reaction of the silaallene–nickel complex with the acetylenic compound. A nickelasilacyclobutene intermediate, in equilibrium with the silaallene complex, is probably involved in the formation of siloles **231** and disilacyclohexadienes **232**.

In the special case of alkynyldisilanes **233a** substituted on one acetylenic carbon by a vinyl group (eq 78), no trapping product was obtained with $PhC\equiv CSiMe_3$. However, with diphenylacetylene, disilacyclohexadienes **232** were formed from the corresponding silaallene–nickel complexes.[217] Surprisingly, the same compounds **232** were obtained starting from alkynyldisilanes having the two different $SiMe_2SiMe_2Ph$ and $SiMePhSiMe_3$ moieties.[217] Moreover, starting from **233b**, the three derivatives **232** with the group CD_3 in R^1, R^2, or R^3 position were obtained[217] (eq 79). These results indicate that the key intermediate, the structure of which is unknown, must have a fluxional behavior.[217]

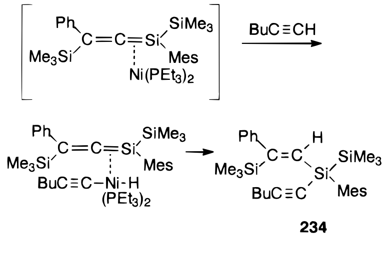


(78)



(79)

By contrast, reaction of the transient silaallene–nickel complex with butylacetylene does not afford any cyclic compound but the derivative **234**[213] (eq 80).

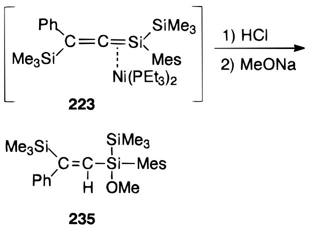


(80)

The formation of **234** can be explained by the oxidative addition of the ethynyl C–H bond to the Ni atom followed by the addition to the Si–C bond. Such C–H bond activation of an acetylenic derivative by a nickel complex has previously been reported.[218]

3. Reaction with Hydrochloric Acid

Addition of $Ni(PEt_3)_4$ to $PhC\equiv CSi(Mes)(SiMe_3)_2$ followed by addition of HCl then MeONa leads to compound **235** via the silaallene–nickel complex intermediate **223**[218] (eq 81).



(81)

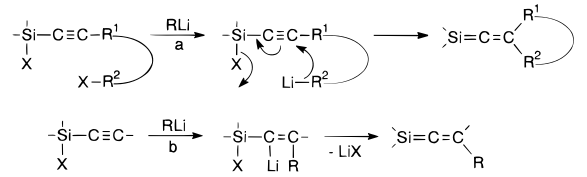
C. Stable 1-Silaallenes

1. Synthesis

As stated previously, the first stable silaallene was obtained by West in 1993.[192] It was stabilized by an extremely large steric hindrance around the Si=C=C moiety. Since this date, six other stable silaallenes have been obtained.[219–221]

Two routes allowed the synthesis of such derivatives (Scheme 52): (1) dehalogenative intramolecular carbometalation–elimination (route a) and (2) addition of organolithium reagents at the carbon triple bond of fluoroalkynylsilanes followed by LiF elimination of the intermediate vinyllithium compounds (route b).

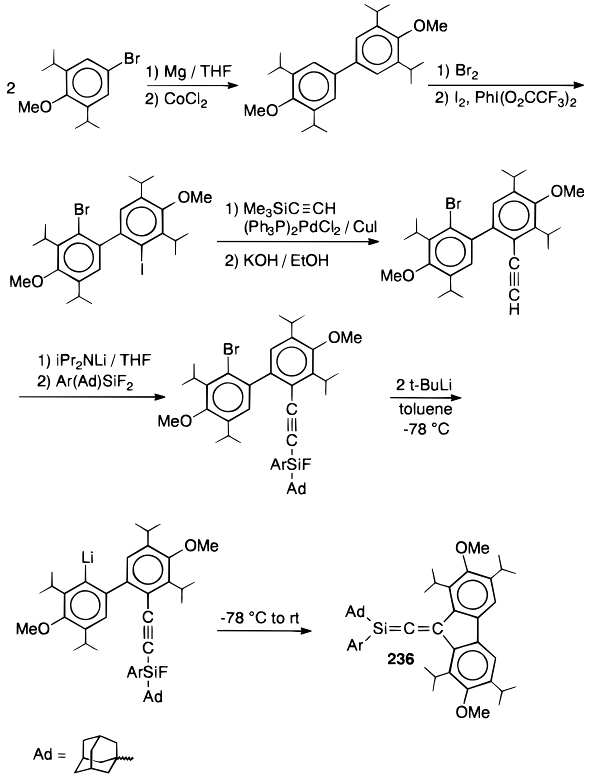
Scheme 52

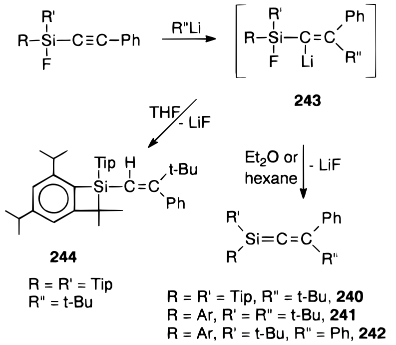


a. Intramolecular (Symphoric) Method. The symphoric method (by symphoric the authors mean “the bringing together of reactants into the proper spatial relationship”[219]) was the first to be explored; it allowed the synthesis of silaallenes with the terminal carbon included in a fluorenyl group.[192,219,221] However, although the last step occurs in a nearly quantitative yield, the precursors can only be prepared in a multistep synthesis with great efforts. For example, the synthetic process leading to the first stable silaallene **236** is described in Scheme 53.[192,219] The two silaallenes **237** and **238** (Table 17) with a substituted fluorenylidene have also been obtained by a similar route.[221] For silaallene **239**, the final step involved the use of an excess of magnesium turnings in refluxing ether instead of t-BuLi.[219]

b. Intermolecular (Steric) Method. Route b[219,220] allowed for the choice of one of the substituents on the terminal carbon, which depends on the organolithium used; it was successful for the synthesis of silaallenes **240**, **241**, and **242** (eq 82). This route is related to the well-known addition–elimination reaction of chlorovinylsilanes (addition of t-BuLi to the C=C double bond followed by loss of LiX) first described by Jones[222] and later widely used in the synthesis of silenes >Si=C<, particularly by Auner[223] but also by some other groups;[224,225] such a route also allowed the synthesis of a stable germene from the corresponding fluorogermane.[226]

Scheme 53





(82)

The addition of organometallic reagent to the β-carbon atom of haloalkynylsilanes could compete with the attack at silicon, but it is possible to block this attack by using very bulky groups on silicon. The t-BuLi added stereo- and regiospecifically to the carbon–carbon triple bond of the alkynylfluorosilane to form the vinyllithium compound **243** in the sterically less-hindered cis conformation. When R = R′ = Tip and R″ = t-Bu, the intermediate **243** complexed by tetramethylethylenediamine could be isolated and structurally characterized proving the mechanism of this reaction. The rate of elimination of LiF from **243** significantly increased when Et_2O was replaced by a nonpolar solvent like hexane: at room temperature, the silaallene **240** was formed within few hours in Et_2O but only in a few seconds in hexane due to an increased destabilization of **243** by the nonpolar solvent. Using THF as solvent, the cyclic product **244** was obtained instead of the silaallene **240**.

In the case of silaallene **241**, an intermediate such as **243** was not observed: the rapid elimination of LiF was probably driven by significantly greater steric hindrance in the vinylic intermediate. The reaction of the fluoroalkynylsilane with PhLi to give the silaallene **242** occurred much more slowly than the reaction with t-BuLi, requiring 3 days at room temperature. In all cases, nearly quantitative yields in silaallenes were obtained by route a or b.

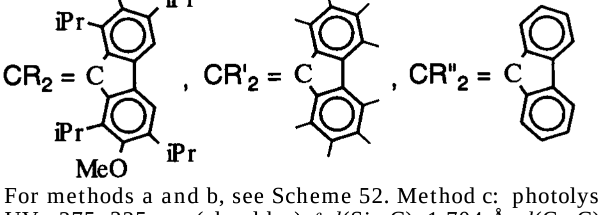
2. Physicochemical and Theoretical Studies

a. Geometry. The silaallenes **236**[192] and **240**[220] have been structurally characterized by X-ray crystallography. The geometry of the Si=C=C skeleton is very similar in the two silaallenes with extremely short Si=C double bonds (1.693(3) Å in **240**[220] and 1.704(4) Å in **236**[192]). Such a short distance was expected since silicon is bonded to an sp-hybridized carbon atom. The slightly longer Si=C distance in **236** probably reflects a greater steric repulsion.[192] The Si=C bond length in silaallenes is very close to that determined in silene $Me_2Si{=}C(SiMe_3)SiMe($t-

Table 17. 1-Silaallenes: Synthetic Routes and Physicochemical Data[a]

no.	silaallene	^{29}Si (ppm)	^{13}C (ppm)	color	method[b]	ref
213e[c]	$Me_2Si{=}C{=}C(Ph)SiMe_3$				c	193
213g[d]	$Me_2Si{=}C{=}C(SiMe_3)_2$				c	194
236[e]	$Ad(Ar)Si{=}C{=}CR_2$	48.4	225.7	orange	a	192
237	t-Bu(Ar)$Si{=}C{=}CR'_2$	48.0	228.2	bright yellow	a	221
238	$Tip_2Si{=}C{=}CR'_2$	16.2	237.1	bright yellow	a	221
239	t-$Bu_2Si{=}C{=}CR''_2$	44.0		red	a	219
240[f]	$Tip_2Si{=}C{=}C(Ph)$t-Bu	13.1	223.6	colorless	b	220
241[g]	t-Bu(Ar)$Si{=}C{=}C(Ph)$t-Bu	55.1	216.3 (J_{CSi}: 142.4)		b	219, 220
242	t-Bu(Ar)$Si{=}C{=}CPh_2$	58.6	227.9		b	219, 220

[a] Ad = 1-adamantyl, Tip = 2,4,6-$^iPr_3C_6H_2$, Ar = 2,4,6-t-$Bu_3C_6H_2$.



[b] For methods a and b, see Scheme 52. Method c: photolysis of alkynyldisilane. [c] UV: 268, 305 nm (shoulder). Lifetime τ: 25 μs. [d] UV: 275, 325 nm (shoulder). [e] d(Si=C), 1.704 Å; d(C=C), 1.324 Å; SiCC, 173.5°. UV: 267, 276 (max), 297, 318, 334 tailing up to 540 nm. IR: 800 (s), 1030 (br), 1090 (br), 1260 (s), 1400 (s), 1450 (br), 1600 (br), 2960 (br) cm^{-1}. [f] d(Si=C), 1.693(3) Å; d(C=C), 1.325(4); SiCC, 172.0(3)°. [g] δ ^{29}Si: 52.8 in ref 219.

Table 18. Expected Structure[a] for Allenes, Silaallenes, Silenes, and Germenes (ab initio calculations)[235]

compound	$f(E_{\sigma+\pi})$ (kcal/mol)	$\Sigma\Delta E_{S\to T}$ (kcal/mol)	expected structure
$H_2Si{=}C{=}CH_2$	52−56	65	NL
$H_2C{=}Si{=}CH_2$	52−56	30−50	L
$F_2C{=}Si{=}CH_2$	59−64	90−110	NL
$H_2C{=}C{=}CH_2$	86	36	L
$F_2C{=}C{=}CH_2$	97	96	L
$H_2C{=}SiH_2$	52−56	9	P
$H_2Ge{=}GeH_2$	42−52	12.5	P

[a] L, linear; NL, nonlinear; P, planar. $\Sigma\Delta E_{S\to T}$: sum of the singlet−triplet separation for the two fragments. $f(E_{\sigma+\pi}) = {}_{1/2}E_{\sigma+\pi}[1 + (q_1 + q_2)/2] + 200\, q_1q_2$. q_1 and q_2 are the possible π net charges on the two "carbene" centers forming the double bond. $E_{\sigma+\pi}$: $\sigma+\pi$ bond energies.

Bu)$_2$ (1.702(5) Å)[227] but is shorter than in the other silenes structurally characterized $(Me_3Si)_2Si{=}C(Ad)OSiMe_3$ (Ad = 1-adamantyl) (1.764 Å)[228a] and $Me_3Si(Me_2Si\text{-t-Bu})Si{=}Ad'$ (Ad′ = 2-adamantylidene) (1.741 Å)[228b] which exhibit a significant elongation.

The Si=C double bond lengths in **236** and **240** agree closely with those found by calculations in silaallenes $H_2Si{=}C{=}CH_2$: 1.702[229] and 1.703 Å[230] (SCF/3.21G). The Si=C distance in **236** and **240** fits well with the calculated Si=C bond length predicted by calculations on $H_2Si{=}CH_2$ by Apeloig (1.718 Å)[231,232] and Schaefer (1.703 Å).[233a] Note that numerous calculations have been reported for the predictions of the Si−C double bond length in the parent silene $H_2Si{=}CH_2$ (for a review on this subject, see ref 233b).

The carbon−carbon double bond is predicted to be shorter (1.296,[230] 1.29 Å[206]) than that experimentally found (1.324[192] and 1.325 Å[220]). The C=C bond length lies in the normal range in both **236** and **240**, and the Si−C−C bond angle is relatively close to 180° (173.5°[192] and 172.0°[220]). The silicon atom in **240** is slightly pyramidalized (sum of angles 357.2(2)°),[220] whereas the terminal sp^2 carbon is essentially planar.

Both experiments and calculations display cases where double bonds between main-group elements deviate from planarity and cumulenes or triple bonds deviate from linearity. Carter and Goddard suggested a simple correlation between the strength of typical $\sigma + \pi$ planar double bonds and the $\Delta E_{S\to T}$ of their fragments[234] ($\Delta E_{S\to T}$ = singlet−triplet separation of the interacting fragments forming the multiple bond). The contribution of Trinquier and Malrieu[235] may be considered as a structural extension of this kind of argument to the occurrence of nonplanar (or nonlinear) minima on potential surfaces. When $f(E_{\sigma+\pi})$ ($E_{\sigma+\pi}$ = strength of typical $\sigma + \pi$ planar double bonds) is smaller than $\Sigma\Delta E_{S\to T}$, the system is expected to be nonplanar or nonlinear; otherwise it is expected to be planar or linear. Some examples are given in the Table 18 for 1- and 2-silaallenes, allenes, silenes, and digermenes. As seen from this table, calculations predict nonlinear 1-silaallenes in good agreement with the experiment (Si−C−C = 173.5° in **236**[192] and 172° in **240**[220])

b. NMR (Table 17). In ^{13}C NMR, a strong deshielding is observed as expected for the sp carbon atoms (216−237 ppm). In ^{29}Si NMR, signals are observed between 13.1 and 58.6 ppm.

Table 19. Charges on 1-Silaallenes and Silenes

compound	Si	sp C	sp^2 C	ref
$H_2Si{=}C{=}CH_2$[a]	+0.17	−0.10	−0.35	229, 230
$H_2Si{=}CH_2$	+0.46		−0.67	231
$H_2Si{=}CHOH$	+0.26		−0.06	231

[a] HF(6-31G**//3-21G).

The ^{13}C and ^{29}Si chemical shifts for **236, 237**, **239**, **241**, and **242** are close to those of stable silenes $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$,[228a] which bears an electron-donating oxygen substituent at carbon (respectively, 214.2 and 41.4 ppm), and $Me_3Si(Me_2Si\text{-t-Bu})Si{=}Ad'$ (respectively, 196.8 and 51.7 ppm).[228b] However, they are relatively different from those of the Wiberg's stable silene $Me_2Si{=}C(SiMe_3)Si(Me)\text{t-Bu}_2$,[227] which are strongly deshielded at Si (144.2 ppm) and shielded at C (77.2 ppm) suggesting a much more polar double bond which is electron deficient at Si and electron rich at C.

The silaallenes **238** and **240** substituted by two aryl groups have the most shielded ^{29}Si NMR signals for compounds with a doubly bonded silicon. For example, silenes with two aryl groups on Si give signals at about 60 ppm higher field: $Mes_2Si{=}CPh_2$, 76.68 ppm;[236] $Mes_2Si{=}CHCH_2\text{t-Bu}$, 77.60 ppm.[224] (For a review on δ ^{29}Si chemical shifts of Si=C derivatives, see refs 4, 5, and 11).

c. Charges. Net atomic charges on Si and C have been determined for $H_2Si{=}C{=}CH_2$ by ab initio calculations and compared to those of $H_2Si{=}CH_2$ and $H_2Si{=}CHOH$ (Table 19). The partial charges on Si and C are much more important in the parent silene $H_2Si{=}CH_2$ (+0.46 and −0.67)[231] than in the silaallene $H_2Si{=}C{=}CH_2$ (+0.17 and −0.10).[229,230]

In the silaallene the charges on H are +0.198 (H on C) and −0.055 (H on Si).[230]

The charges on the silaallene are closer to those of silene $H_2Si{=}CHOH$[231] (+0.26 and −0.06) than those of silene $H_2Si{=}CH_2$. Thus, it can be postulated that 1-silaallenes exhibit a partial "reversed polarity" of the silicon−carbon double bond, comparable in effect to that of an electron-donating oxygen substituent on carbon. This "reversed polarity" is believed to be the most important factor to explain the low reactivity of silaallenes. The dipolar moment in $H_2Si{=}C{=}CH_2$ is estimated to be 0.09 D.[230]

d. Stability of C_2SiH_4 Isomers. The relative stability of C_2SiH_4 isomers has been examined by some groups on 5 isomers (including 2-silaallenes but not 1-silaallenes),[237] 8 isomers,[238] 9 isomers,[239] and 15 isomers[230] and is reported in Table 20 with the high-level calculations in column 1. The relative stability of C_2SiH_4 and $C_2Si_2H_6$ isomers, including some singlet or triplet diradical forms,[206] has also been examined.

Three silylenes **b**, **c**, and **e** are among the most stable isomers. In contrast, the carbenes are generally found to be rather unstable, with the exception of **g**.[230] There is about 20 kcal/mol between 1-silaallene and 2-silaallene[230,239] illustrating the unstability conferred on the system by having an additional multiple bond between carbon and silicon.

The calculations show that silirene **d** is more stable than 1-silaallene **f**. Moreover, calculations performed

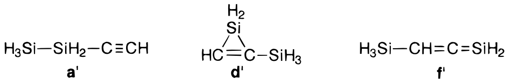
Table 20. Relative C_2SiH_4 Isomer Energies (kcal/mol)

	compound	ref 238[a]	ref 230[b]	ref 239[c]	ref 237[d]
a	$H_3Si-C{\equiv}CH$	0	0	0	0
b	$HSiCH{=}CH_2$	20.0[e]	13.4	15.4	
c	H_2CCH_2Si	14.8	14.7	17.2	17.0
d	$HC{=}CHSiH_2$	11.9	14.8	15.2	16.6
e	$Si{=}CHCH_3$	16.8	15.9	18.0	
f	$H_2Si{=}C{=}CH_2$	25.7	28.9	29.8	
g	$H_3Si-CH{=}C$		35.4		
h	$H_2C{=}Si{=}CH_2$		50.1	49.0	45.7
i	$HC{\equiv}SiCH_3$		61.9	63.3	60.7
j	$HSi{=}CHCH_2$	49.8	65.2		
k	$HSi{\equiv}CCH_3$		66.3	68.9	
l	H_2SiCH_2CH		75.4		
m	H_2SiCH_2C		84.3		
n	$H_2C{=}SiHCH$		90.7		
o	$C{=}SiHCH_3$		90.8		

[a] MP2/6-31G**//MP2/6-31G**. [b] SCF/6-31G*//SCF/3-21G. [c] SCF/DZP//SCF/DZ. [d] SCF/DZd//SCF/DZd. [e] syn.

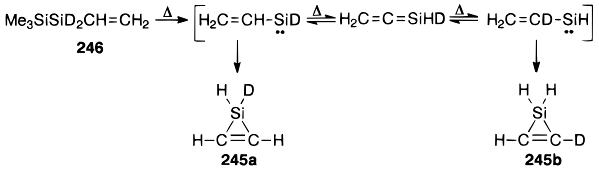
on $C_2Si_2H_6$ isomers show that the silirene **d′** is lower in energy by 30 kcal/mol than 1-silaallene **f ′**[206] (Chart 28). This is consistent with the experimental results since the silirenes are obtained as the major products from alkynyldisilanes **a′**. These stabilities differ significantly from those of the carbon compounds analogues: propyne > allene > cyclopropene ≫ cyclopropylidene.

Chart 28



Maier studied the thermolysis of $Me_3SiSiD_2CH{=}CH_2$[238] (Scheme 54). Interestingly, about equivalent amounts of silirenes **245a** and **245b** were obtained. This is probably due to an equilibrium between two silylenes (generated from **246**) via the silaallene $H_2C{=}C{=}SiHD$.[238] According to Gordon,[230] the similar isomerization of $H_2C{=}CH-SiH$ to $H_2C{=}C{=}SiH_2$ requires 15.5 kcal/mol. The rearrangement silylene → silirene could be initiated by the addition of the silylene center to the C=C double bond leading to a 1-silacycloprop-1-ene followed by a 1,2-H (D) shift or directly by insertion of the silylene center in the CH bond of the olefinic CH_2 group.[238]

Scheme 54



The rotational barrier has been calculated for 1- and 2-silaallenes. Depending on the type of calculations, very different values are obtained: according to Krogh-Jespersen,[229] the barrier to internal rotation was predicted at 35 kcal/mol for $H_2Si{=}C{=}CH_2$ and 20 kcal/mol for $H_2C{=}Si{=}CH_2$ (53 kcal/mol in allene) The transition state should possess bent geometries in all three molecules, with open-shell singlet states with one electron localized in a carbene-type σ-orbital and three delocalized π-electrons (case of $H_2Si{=}C{=}CH_2$) or a closed-shell singlet state with two electrons in a silylene type σ-orbital and only two π-electrons (case of $H_2C{=}Si{=}CH_2$). Much greater rotational barriers have been predicted by Lien and Hopkinson[239] (76.2 kcal/mol for $H_2Si{=}C{=}CH_2$ and 29.2 kcal/mol for $H_2C{=}Si{=}CH_2$), probably by taking into account transition states with four π-electrons. Considering the reluctance of silicon to engage in multiple bonding if alternatives are available, such results are probably less likely.

The bond separation reactions for both 1- and 2-silaallenes are exothermic, indicating that the parent molecule has been destabilized relative to the separated bonds;[230] thus, placing double bonds adjacent to each other has a destabilizing effect (Chart 29). Apparently the effect is greater for two cumulated Si=C double bonds than for adjacent C=C and Si=C double bonds. The corresponding bond-separation energy for allene is −4.4 kcal/mol.[230]

Chart 29

$$H_2Si{=}C{=}CH_2 + CH_4 \longrightarrow H_2Si{=}CH_2 + H_2C{=}CH_2 \quad (-3.12\ \text{kcal/mol})$$

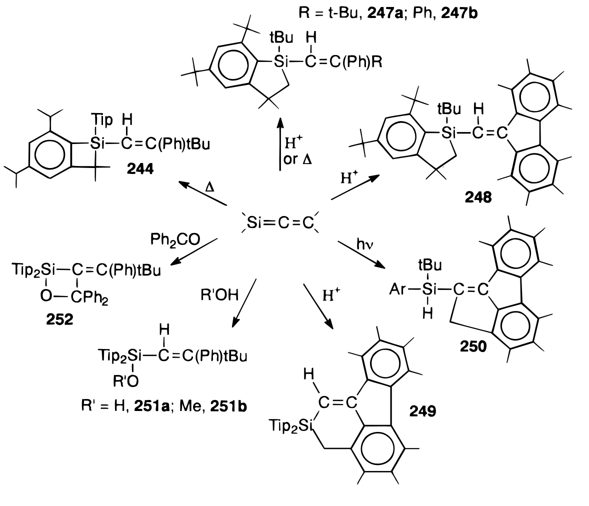
$$H_2C{=}Si{=}CH_2 + SiH_4 \longrightarrow 2\ H_2Si{=}CH_2 \quad (-8.60\ \text{kcal/mol})$$

3. Reactivity

A summary of the reactivity is given in Scheme 55.

a. Acidic Rearrangement. Silaallenes **236** and **237** are stable for days under neutral or slightly basic conditions and in the presence of air, water, and even in refluxing ethanol. This is in striking contrast to all other multiply bonded silicon compounds, particularly silenes.[4,5,11,13] **242**, with two phenyl groups on carbon, is more sensitive to decomposition.[220] Silaallene **241** is very stable in the presence of oxygen. It does not react with benzaldehyde, 2,3-dimethylbutadiene, or trimethylchlorosilane, but heated in a sealed tube at 90 °C, it gives the rearrangement product **247a**.[220] Surprisingly, the same rearrangement was observed at room temperature in ethanol after some hours and very rapidly even at −78 °C when 0.05 equiv of H_2SO_4 was added.[220] With D_2SO_4 instead of H_2SO_4, the compound **247a** with incorporation of deuterium in the

Scheme 55



vinylic position was formed. This suggests that the mechanism of this acid-catalyzed rearrangement occurs via protonation of the sp carbon to give a silicenium ion which undergoes an electrophilic substitution by a proton from a Me group. Only the isomer with the vinylic proton cis to the t-Bu group is obtained.

A similar rearrangement reaction occurred with silaallenes **237** and **242** to give compounds **247b**[220] and **248**.[221]

Silaallene **238** was nearly stable for 1 month in Et_2O in a sealed tube: less than 10% decomposition occurred leading to an unidentifiable product.[221] However, when any proton source was added to a solution containing **238**, a surprising rearrangement took place immediately to give compound **249**.[221] It is postulated that the proton adds to the central sp carbon leading to a cationic intermediate, then the silicon inserts into a CH bond of one of the methyl group on the fluorenylidene forming a new SiC bond.[221] This type of rearrangement has never been observed previously in doubly bonded species of silicon, germanium, or tin.

b. Photolytic Rearrangement. Yellow silaallene **237** became red when exposed to light, under an argon atmosphere, for a period of some months. A single red crystal of this new derivative showed it to be **250**,[219,221] due to a cyclization involving the proximal methyl group on the substituted fluorenylidene.

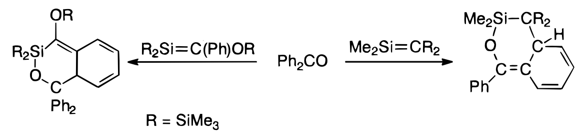
c. Thermal Rearrangement. Another type of cyclization, leading to the four-membered ring silicon derivative **244**,[220] has been observed with silaallene **240**. This intramolecular insertion of the Si=C double bond into one of the adjoining tertiary aliphatic C−H bonds of the ^{i}Pr groups occurred when **240** was heated at 135 °C for several hours. This insertion reaction does not proceed stereospecifically, leading to a 4.5/1 mixture of *Z* (Si and Ph on the same side) and *E* isomers. Surprisingly, the sole **244** *Z* was obtained from the lithium compound **243** and THF after warming to room temperature[220] (eq 82). In this case the stereospecificity of the reaction excludes the intermediate formation of **240**: this reaction should occur by intramolecular deprotonation of a benzylic C−H bond (the basicity of the vinyl anion in THF is strong enough to abstract a benzylic proton) followed by ring closure of this benzyllithium derivative intermediate.

d. Water, Methanol, Benzophenone. The silaallene **240** is the most reactive silaallene. It reacts instantly with water and methanol to give the derivatives **251**[220] in almost quantitative yield. *Z* and *E* isomers are obtained, but the major products are the less strained cis isomers (Si and Ph on the same side).

Despite the steric hindrance, benzophenone also reacts with **240**[220] via a formal [2+2]-cycloaddition to give the corresponding *Z* and *E* four-membered ring derivatives **252**. The structure of the major *E* product (Ph and CPh_2 in cis position) was solved by X-ray diffraction methods.

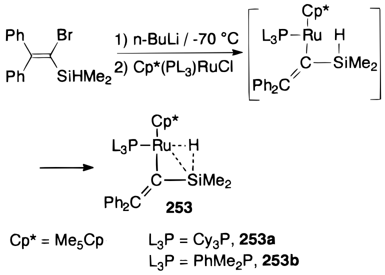
It is interesting to compare the reactivity of **240** toward benzophenone with the chemical behavior of silenes with the same ketone: a [2+4]-cycloaddition involving a Ph group of the benzophenone occurs with $Me_2Si{=}C(SiMe_3)_2$,[240] while the [2+4]-cycloaddition observed with $(Me_3Si)_2Si{=}C(Ph)OSiMe_3$ involves the phenyl group of the silene[241] (Scheme 56). These six-membered ring derivatives thermally or photochemically isomerize to the corresponding four-membered ring silaoxetanes.

Scheme 56



In conclusion, the silaallenes do not seem to be very reactive; this is partly due to the large steric hindrance necessary to stabilize the Si=C moiety, but this low reactivity is also in agreement with calculations which predict a "reversed polarity" of the Si=C double bond compared to silenes.

e. Ruthenium Complex of a 1-Silaallene. A stable ruthenium complex of a 1-silaallene has been recently reported by Jones[242] (eq 83). Due to the presence of nonequivalent methyl groups, of a metal hydride doublet at −11.53 ppm in the ^1H NMR, and of a doublet in the ^{29}Si NMR spectrum (δ, −81.89; J_{SiH}, 66 Hz), it seems that only a partial transfer of the hydride from silicon to ruthenium has occurred.[242]



(83)

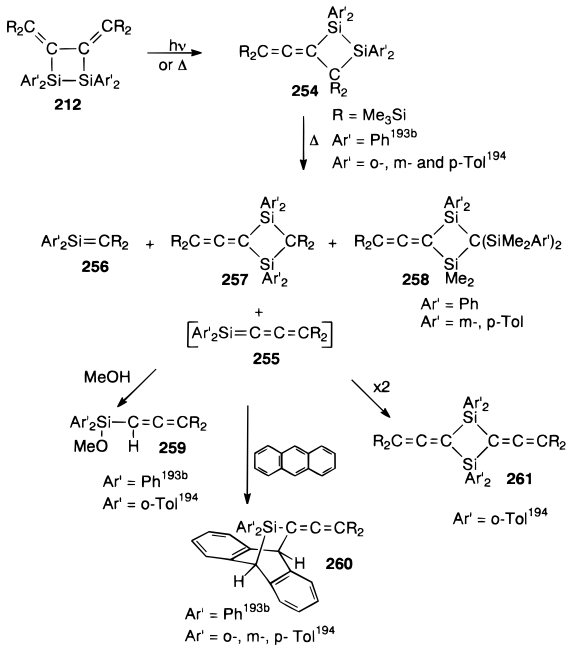
The mass spectrum exhibits the molecular peak and the loss of silaallene ligand. The Si=C bond length in **253a** (1.805(6) Å) corresponds to the bonding in silene complex (1.800(8) Å in $Cp_2W(\eta^2\text{-}Me_2Si{=}CH_2)$,[243] 1.810(6) Å in $Cp^*(PMe_3)Ir(\eta^2\text{-}Ph_2Si{=}CH_2)$[244]). As expected, this bond is longer than the corresponding bond in free silaallenes **236** and **240** (1.704[192] and 1.693 Å[220]) but shorter than standard Si−C single bonds which are in the range 1.85−1.90 Å. The C−C bond length (1.351(6) Å) corresponds to a typical localized C=C double bond.

An exchange of ligand occurs in **253a** when it is heated in the presence of $PhMe_2P$, leading to **253b** (from J_{SiH} = 57 Hz, the bonding apparently has not changed). Note that **253a** has the interesting chemical property of catalyzing the dimerization of phenylacetylene (head-to-head, 62%) and 1-hexyne (head-to-tail, 57%) to give butenynes.

XIV. 1-Silabutatrienes >Si=C=C=C<

1,2-Disilacyclobutanes **212**[193,194] gave, by thermolysis at 200 °C or by photolysis, 1,2-disilacyclobutanes

Scheme 57



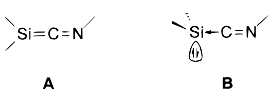
254 (Scheme 57). Heating them at 250 °C afforded transient silabutatrienes **255**[193b,194] with silenes **256** and 1,3-disilacyclobutanes **257** and **258**. The latter derivatives were not formed when Ar′ is a bulky group such as *o*-tolyl.

The formation of 1-silabutatriene **255** could be evidenced when the thermolysis was performed in the presence of methanol or anthracene, leading, respectively, to **259** and **260**.[193b,194] In the absence of trapping reagent, thermolysis of **254** (Ar′ = *o*-Tol) afforded the 1,3-disilacyclobutane **261**,[194] dimer of the silabutatriene intermediate **255**. Much larger groups will be necessary, particularly on the silicon atom, to stabilize such species.

XV. >SiCN− Species

Studies on >SiCN− species, obtained by the reactions of a silylene with an isocyanide, have been performed by the two groups of Weidenbruch[245] and Okazaki.[246] Two types of compounds could be obtained (Chart 30): (1) a silaazallene (silaketenimine) **A** and (2) a silylene−isocyanide complex **B**.

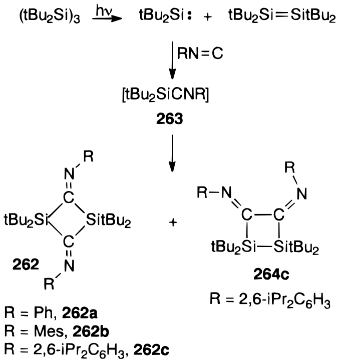
Chart 30



A. Synthesis

1. From (t-Bu$_2$Si)$_3$ and an Isocyanide

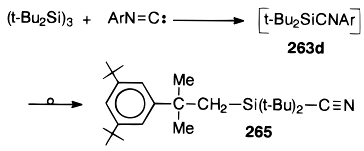
Hexa-*tert*-butylcyclotrisilane[247] is known to give photochemically di-*tert*-butylsilylene and tetra-*tert*-butyldisilene which can be trapped by various reagents. When (t-Bu$_2$Si)$_3$ was photolyzed in the presence of arylisocyanides, 2,4-disilacyclobutanes-1,3-diimines **262** were obtained[245] (eq 84). It is suggested that the first step is a reaction between the silylene and the isocyanide to give a silaazaallene (type **A**) or a Lewis-acid−base product (type **B**) **263** followed by a dimerization to afford the four-membered ring compounds **262**. When R is the bulky 2,6-diisopropylphenyl, a small amount of 3,4-disilacyclobutane-1,2-diimine **264c** was also obtained. Compounds **262** and **264c** could result from the reaction of the isocyanide with a disilacyclopropanimine intermediate (such a compound would be formed by a [2+1]-cycloaddition between the isocyanide and the disilene t-Bu$_2$Si═Si-t-Bu$_2$). However, as such insertion reactions of isocyanides into Si−Si single bonds only take place in the presence of palladium catalysts,[248] they can be ruled out. As both **262c** and **264c** are formed simultaneously, it is likely that they arise from a common intermediate **263c** followed by a head-to-head or a head-to-tail dimerization.



(84)

The X-ray structure analysis of **262a** and **262c** shows that the two aryl rings are trans to each other and that the four-membered ring atoms are almost in a plane.[245] The most striking feature in compounds **262** is their color: ruby red (**262a**[245a]), red (**262b**[245b]), and violet (**262c**[245b]) which is reflected in the wavelength absorption up to 520 (**262a**) and 560 nm (**262c**). The observed red shift of **262c** seems to correspond with an increase of ring strain within this series; such an argument was proposed by West[249] to explain the red color of a disilacyclopropanimine.

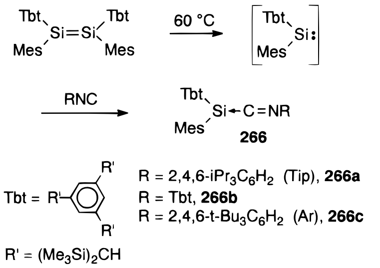
When (t-Bu$_2$Si)$_3$ was photolyzed in the presence of the isocyanide ArN═C bearing the very bulky 2,4,6-tri-*tert*-butylphenyl group, the adduct **265** was obtained as the sole product,[245] probably from an intermediate **263d** (eq 85). Other examples of such aryl−alkyl isomerizations of the Ar group have previously been observed,[250] but their mechanism is still not understood. From all these reactions, it was impossible to determine if intermediate **263** had a structure of type **A** or **B**.



(85)

2. From a Disilene and an Isocyanide

Using extremely bulky groups on silicon, the first silylene−isocyanide adducts (type **B**) were recently isolated.[246] The silylene was obtained from the very hindered disilene Mes(Tbt)Si═Si(Tbt)Mes bearing the huge Tbt group (2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl); this disilene is thermally labile and gives the corresponding silylene under mild conditions (60 °C)[251,252] (eq 86). Reactions with bulky isocyanides lead to the almost quantitative formation of the silylene−isocyanide adducts **266**[246] as blue-green (**266a**), green-blue (**266b**), or deep blue (**266c**) powders. **266a**−**c** are stable but highly air and moisture sensitive.



(86)

B. Physicochemical and Theoretical Studies

The physicochemical data of these derivatives agree with a structure of type **B** (silylene−isocyanide adduct) rather than with a silaazaallene structure **A**[246] (Table 21).

Table 21. NMR and UV Data for Silylene−Isocyanide Adducts[246]

compound	δ ^{29}Si THF	δ ^{29}Si C_6D_6/rt	δ ^{29}Si C_6D_6/60 °C	δ ^{13}C SiCN	δ ^{13}C J_{SiC}	UV (ϵ)
266a	−55.7	−53.6	−53.2	209.2	38.6	596 (400)
266b	−57.9	−57.4	−56.5	196.6	22.1	632 (100) 397 (3000)
266c	−48.9	−48.6	−47.9	178.5	1.0	671 (200) 390 (2000)

The ^{29}Si NMR spectra of **266** showed signals at high field very different from those obtained in West's silaallenes or in silenes.[11] The Si−C coupling constants in the SiCN unit are smaller than in Si−C single bonds (generally close to 50 Hz) or in Si═C double bonds (83−85 Hz),[253] indicating that these Si−C bonds are weak; their strength decreases in the order **266a** > **266b** > **266c** with increasing bulkiness of the substituents.

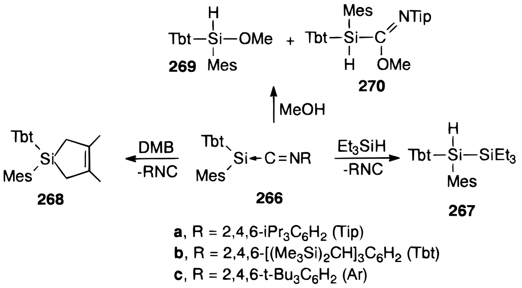
The ^{29}Si NMR chemical shifts were about the same at room temperature or at 60 °C, indicating that the rate of interconversion between **266** and the silylene plus the isocyanide must be too slow to be observed by NMR spectroscopy. A very different phenomenon was observed for the "stannaazaallene" synthesized by Grützmacher[254] since the variable-temperature ^{119}Sn experiments show a low-field shift with increasing temperature due to an increase of the ratio of the stannylene in the equilibrium mixture (see section XX).

B3LYP/6-31G(d) calculations on $Ph_2SiCNPh$ predicted clearly a silylene−Lewis-base complex with a bent Si−C−N bond (163.4°) and a long Si−C distance (1.882 Å) comparable to a Si−C single bond. The calculated chemical shifts at Si (−38.9) and C (178.0) are in good agreement with the experimental data.

C. Reactivity

The reactivity of **266** shows a weak Si−C bond and confirms the silylene−isocyanide structure since reactions with Et_3SiH, DMB, or MeOH afforded mainly the starting isocyanides and the compounds **267**−**269** corresponding to the trapping of silylene Tbt(Mes)Si[246] (Scheme 58). Within the series **266a**−**c**, the reaction rates increased as expected with the bulkiness of the substituents from **266a** to **266c**. The formation of a minor amount of adduct **270** was only obtained in the reaction of **266a** with methanol, probably by an initial protonation of the silicon atom followed by an attack of MeO$^-$ on the carbon of the SiCN unit.

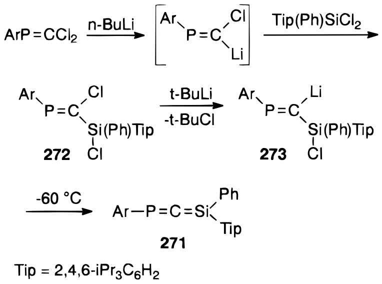
Scheme 58



XVI. 1,3-Phosphasilaallenes >Si═C═P−

A. Synthesis

The first metastable phosphasilaallene **271**,[106a] an allenic compound with doubly bonded silicon and phosphorus, has recently been prepared by dehalogenation from the corresponding precursor **272** (eq 87). **272** was prepared according to a procedure described by Bickelhaupt for the synthesis of ArP═C(Cl)SiMe$_3$[115] from ArP═CCl$_2$. The reaction of **272** with t-BuLi followed by ^{31}P NMR between −80 °C and room temperature showed the immediate formation of the lithium compound **273** formed by Cl/Li exchange (δ ^{31}P = 417.6 ppm) and the elimination of LiCl around −60 °C. The phosphasilaallene **271** was stable up to −30 °C but slowly dimerized above. However, if the temperature was increased rather rapidly between −80 °C and room temperature, signals of the phosphasilaallene could be observed up to 0 °C.



(87)

B. Physicochemical Studies

1. NMR Studies (Table 22)

271 was characterized by ^{13}C, ^{29}Si, and ^{31}P NMR with signals at very low field, as expected for such a structure: δ ^{13}C = 269.1 ppm, δ ^{29}Si = 75.7 ppm, δ ^{31}P = 288.7 ppm.[106a] Comparable ^{13}C and ^{31}P low-field

Table 22. >Si=C=P−, >Ge=C=C<, >Ge=C=P−, and >Sn=C=N− Derivatives: Synthetic Routes and Physicochemical Data

no.	compound[a]	^{31}P (J_{PC})	^{13}C	mp (°C)	color	method[b]	ref
271[c]	Ph(Tip)Si=C=PAr	288.7 (45.8)	269.1			a	106a
278[d]	$Tip_2Ge=C=C(Ph)t\text{-}Bu$		235.1	125	colorless	b	272
281	$Tbt(Mes)Ge=C=CR_2$		243.5		colorless	c, d	273
288	$Mes_2Ge=C=PAr$	240.0 (54.3)	280.9			a	106b
293[e]	$R'_2SnCNMes$			88	yellow	e	254

[a] Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$. Tbt = 2,4,6-[(Me$_3$Si)$_2$CH]$_3$C$_6$H$_2$. CR$_2$ = fluorenylidene. R′ = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$. [b] Methods: (a) Dehalogenation of >E(X)−C(X)=PAr. (b) Addition of RLi on an alkynylfluorogermane. (c) Dehalogenation of a haloalkenylgermane. (d) From a telluragermirane. (e) Reaction between a stannylene and an isocyanide. [c] δ ^{29}Si: 75.7 ppm. [d] d Ge=C: 1.783 Å, C=C: 1.314(2) Å. [e] d(Sn=C), 2.397(3) Å; d(C=N), 1.158(3) Å. IR: 2166 cm^{-1}. δ ^{119}Sn (extrapolated): −150 ppm.

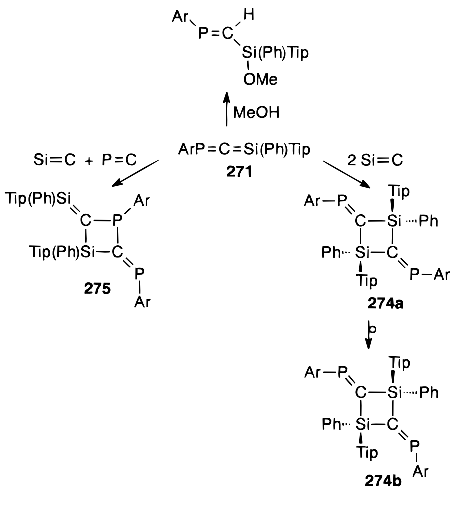
chemical shifts were observed for phosphaallenes and diphosphaallenes (see Tables 1 and 10).

The ^{29}Si chemical shift is also relatively close to those of silaallenes prepared by West (Table 17) but very different from those of the silylene−isocyanide complexes Tbt(Mes)SiCNR (−48 to −58 ppm).[246]

C. Reactivity

According to its physicochemical data and reactivity, a real structure of allene can be postulated for **271**: the intermediate formation of a silylene has never been observed like in the reactivity of >SiCN− species or >SiCO derivatives (see section XVII). For example, the regioselective addition of methanol leads to the exclusive formation of the adduct on the Si=C double bond with oxygen bonded to silicon (Scheme 59).

Scheme 59



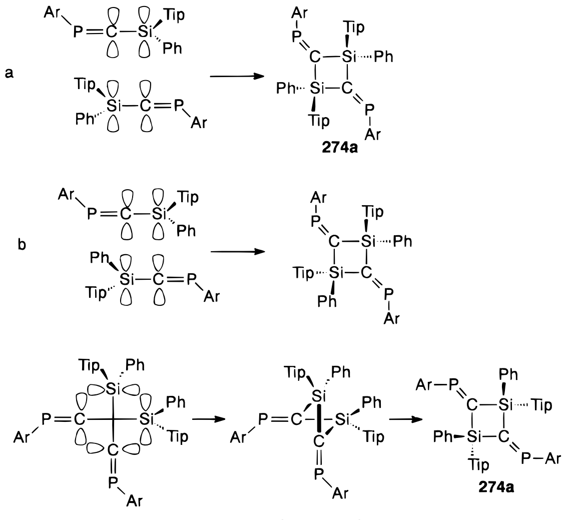
Above −20 °C, two types of dimerization occurred: the minor one (40%) involves two Si=C double bonds leading to 1,3-disilacyclobutane **274a**, and the major one (60%) occurs by one Si=C and one P=C double bond to afford the unsymmetrical heterocycle **275**[106a] (Scheme 59). Due to the large $^2J_{PP}$ coupling constant (224 Hz), it seems that the structure of **275** involves the two Ar groups in a trans position, which allows a relief of the steric hindrance. In a cis structure, the coupling constant is generally around 15−30 Hz.[29,144,255]

The dimer **274a** (δ ^{31}P = 431.9 ppm) formed immediately after reaction isomerizes to the dimer **274b** (δ ^{31}P = 425.4 ppm)[106a] after a few days in solution at room temperature. The structure of **274b**, with the two Tip groups on the same side of the nearly planar Si$_2$C$_2$ four-membered ring and the two Ar groups in a cis position relative to the PCCP axis, has been proved by an X-ray structure determination.

1. Mechanism of the Dimerization

The mechanistic aspects of the dimerization of silenes to form 1,3-disilacyclobutanes have been the subject of many theoretical and experimental studies which are sometimes controversial between concerted mechanism or stepwise mechanism involving a biradical intermediate.[11,256−259] Although the concerted supra−supra process [2πs + 2πs] is forbidden according to the Woodward Hoffmann rules, the polarization of the double bond is supposed to lead to their relaxation: thus, due to the large difference of steric hindrance between Tip and Ph groups in **271**, a cycloaddition between the two same enantiomers could lead to **274a** (Scheme 60, a) whereas a cycloaddition between two different isomers should give the disilacyclobutane with Tip in a trans position (Scheme 60, b). Specific effects due to the nature of the frontier orbitals could favor such a coupling

Scheme 60



[a] Reprinted with permission from ref 106a. Copyright 1999 Wiley-VCH.

between the two same enantiomers in this concerted mechanism.

A concerted supra−antara process [2πs + 2πa] is generally considered the most probable in the case of allenes or ketenes[260] and could also occur to give **274a** according to the sterically most favorable approach shown in Scheme 60 c. However, although the stereospecificity of this dimerization suggests a concerted mechanism, a two-stage mechanism leading also to stereospecificity due to the large steric hindrance caused by Ar and Tip groups cannot be excluded.[106a]

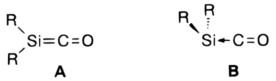
XVII. >SiCO species

A. Synthesis

Silaketenes RR′Si═C═O have not yet been isolated as stable species at room temperature: of course the stabilization of such derivatives is rather difficult since only silicon can be substituted, and thus, special extremely bulky groups should be used.

Two types of RR′SiCO species could be obtained: a silaketene form (**A**) and a complex between silylene and CO (**B**) (Chart 31). Two approaches have been used to generate RR′SiCO species (Scheme 61): (a) the reaction between formaldehyde generated from paraformaldehyde at 100 °C and silicon atoms obtained by vaporization of silicon at 1500 °C[261] and (b) the reaction between carbon monoxide and silylenes.[262−264] Transient silylenes were obtained by photolysis of dodecamethylcyclohexasilane,[262,263] dimethyldiazidosilane,[263] or various trisilanes.[262] For Cp*$_2$SiCO, the reaction was performed between CO and stable decamethylsilicocene Cp*$_2$Si.[264]

Chart 31



Scheme 61

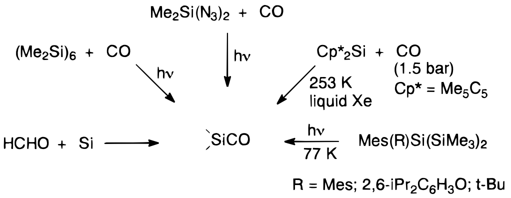


Table 24. λ_{Max} (cm^{-1}) for Silylenes, RR′SiCO Species, and Disilenes

R, R′	RR′Si	RR′SiCO	RR′Si═SiRR′	ref
Mes$_2$	580, 330	354, 284	420	262
Mes, t-Bu	505, 290	338, 290	330	262
Mes, OR[a]	398	328	380, 342	262
Me$_2$	454	345		262
Me$_2$	450	342		263
H$_2$		296		261

[a] OR = 2,6-^{i}Pr$_2$C$_6$H$_3$O.

All the RR′SiCO derivatives were studied in matrixes or glasses of argon at 12 K,[261] 3-methylpentane at 77 K,[262,263] or xenon at 235 K[264] by IR or UV (Tables 23 and 24). The complexation of CO to Cp*$_2$Si was found to be reversible since the silylene was recovered after evaporation of the xenon. However, this complex is more stable than the other RR′SiCO complexes since it can be observed up to the moderate temperature of 253 K.

The absolute rate constants have been determined for the gas-phase reactions of silylene SiH$_2$ with a series of diatomic molecules (HCl, Cl$_2$, NO, O$_2$, and CO):[265] silylene is found to be almost unreactive with CO and significantly less reactive than singlet methylene but somewhat more reactive than halogenated silylene.

B. Physicochemical and Theoretical Studies

1. IR (Table 23)

The CO stretching vibration was observed at 1962 (Me$_2$SiCO),[263] 2065 (Cp*$_2$SiCO),[264] and 2043 or 2051/2054 cm^{-1} (H$_2$SiCO).[261] In the case of H$_2$SiCO, these bands also correspond to the SiH stretching vibration. Experiments were also made with carbon monoxide labeled with ^{13}C [261,263,264] and separately with ^{18}O[263,264] or with deuterium for D$_2$SiCO.[261] The isotopic shift data are in good agreement with those expected.

In calculations to predict the ν(CO) in H$_2$SiCO,[261,266] the best accordance with experiment is found at the B3LYP/6-311G** level[261] (2116 cm^{-1}). Small band shifts are observed between free H$_2$Si and CO and the complex H$_2$Si·CO. They reflect the small changes in geometry between the fragments and the complex. For Me$_2$SiCO, the calculated value of 2073 cm^{-1} [261] (B3LYP/6-31G**) compares favorably with experiment. Higher values were found by previous calculations at a lower level.[263]

Table 23. Experimental IR Data of CO and SiH Bands in R$_2$SiCO Compounds

compound	IR (cm^{-1}) ν CO	ref	compound	IR (cm^{-1}) ν CO and SiH	ref
Me$_2$Si^{12}C^{16}O	1962	263	H$_2$SiCO	2043[a] 2051/2054[b]	261
Me$_2$Si^{13}C^{16}O	1918	263			
Me$_2$Si^{12}C^{18}O	1915	263	H$_2$Si^{13}CO	1996.0 (CO)[c] 2044.9 (SiH)	261
Cp$^*{}_2$Si^{12}C^{16}O	2065	264			
Cp$^*{}_2$Si^{13}C^{16}O	2017	264	D$_2$SiCO	2043.9 (CO) 1479.1/1490.9 (SiD)	261
Cp$^*{}_2$Si^{13}C^{18}O	1970	264			

[a] Mean value of CO and SiH$_2$ stretching observed bands from Si and HCHO. [b] From photolysis of H$_2$Si(N$_3$)$_2$ and CO at 254 nm. [c] The two stretching SiH bands overlap.

2. UV (Table 24)

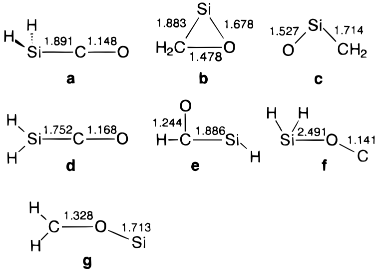
Table 24 reports the absorptions found for RR′SiCO compounds as well as those obtained for silylenes RR′Si and disilenes RR′Si═SiRR′.[262]

The interaction between silylenes and CO has been monitored by UV−vis spectroscopy both at 77 K and upon warming.[262] In the rigid 3-methylpentane matrix at 77 K, only silylenes were identified by their absorption. Annealing of the matrix resulted in the growth of new bands attributed to RR′SiCO species. Upon further warming, these bands disappeared to give those of the corresponding disilenes.[262] Such behavior looks like that of other acid−base complexes of silylenes with donor molecules which give disilenes when the matrix is melted.[267] Thus, the results observed are consistent with formulation of the RR′SiCO species as acid−base complexes **B** in which both fragments keep their identity rather than silaketenes **A**.[235]

3. Relative Energies

The relative energies and the calculated geometries have been determined for the planar silaketene form[261,263,266] and for the silylene•CO complex,[261,263,266] but also for several CH_2OSi isomers[261] (B3LYP/6-31G**) (Chart 32). The bond lengths are also reported on the formulas **a**−**g**.

Chart 32



It appears, as expected from the experiments, that the global minimum is the $H_2Si•CO$ complex **a**.[261] This is in contrast with the carbon series in which the planar ketene $H_2C═C═O$ is the most stable isomer.[268] The silaoxirane **b** with a divalent silicon atom is very close to **a** (0.6 kcal/mol).[261] The slightly bent 1-silaketene **c** is 15.8 kcal/mol less stable than **a**.[261] The planar silaketene **d** with a C_{2v} symmetry represents, as predicted by various calculations,[261,263,266] the transition structure for the inversion reaction of **a** and lies about 16.6 kcal/mol above **a**.[261] Higher values of 17−23[266] and 23[235] kcal/mol are found at a lower level of theory. Formylsilylene **e** is less stable (22.1 kcal/mol), as well as the two complexes H_2SiOC **f** and H_2COSi **g**, which are complexes by the oxygen atom[261] (respectively, 24.8 and 33.7 kcal/mol). Other CH_2OSi species with a carbenic carbon are, as expected, the least stable ones.[261] Calculations on planar Me_2SiCO and $Me_2Si•CO$ complex give similar results with the silaketene less stable by 17−20 kcal/mol.[263,266]

4. Geometry

The geometry of planar silaketene **d**, silylene•CO complex **a**, and other H_2SiCO isomers have been determined by calculations (B3LYP/6-31G**)[261] (Chart 32). **a** and **b** have also been calculated at various other levels,[235,261,263,266] particularly B3LYP/6-31G**, which probably gives the most accurate values (Si−C and CO bond lengths at 1.895 and 1.939 Å are slightly shortened[261]). The CO bond distance is very close to the distance found in the carbon monoxide. The SiCO bond angle is 167.6°[261] (B3LYP/6-311G**).

Table 25. GAPT Atomic Charges in H_2SiCO and Me_2SiCO[269]

	H_2SiCO			Me_2SiCO
	DZP, SCF	DZP, CISD		DZP/DZ, SCF
	complex **a**[a]			
H	−0.22	−0.19	C(H_3)	−0.18
Si	0.32	0.20	Si	0.43
C	0.81	0.81	C	0.76
O	−0.68	−0.63	O	−0.70
	planar form **d**[a]			
H	−0.05		C(H_3)	−0.10
Si	−0.05		Si	0.31
C	1.27		C	1.05
O	−1.13		O	−1.15

[a] Complex **a** and planar form **d**, see Chart 32.

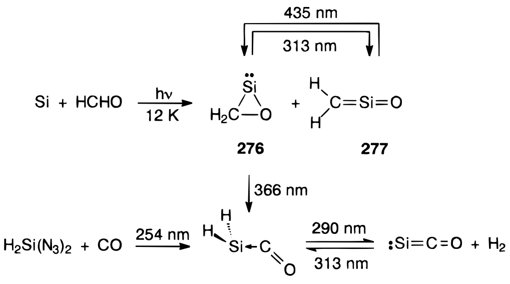
5. Atomic Charges

The atomic charges in the planar form silaketene **d** and in the silylene•CO complex **a** have been determined for H_2SiCO and Me_2SiCO species by application of the GAPT (generalized atomic polar tensor) population analysis[269] (Table 25). The polarity of the SiH bond in complex **a** and in the starting silylene are very similar, and the CO bond in **a** is less polarized than that in the ketene molecule; the polarity decreases (although slightly) upon inclusion of electron correlation.

6. Mechanistic Studies

A very important study has been made by Maier to determine the mechanism of the reaction between $H_2Si(N_3)_2$ and CO or between Si and HCHO.[261] Depending on the wavelength of irradiation, silirane **276**, planar form **277**, or $H_2Si•CO$ complex and SiCO (after elimination of H_2) have been characterized (Scheme 62).

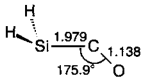
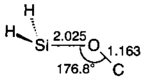
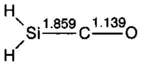
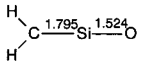
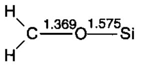
Scheme 62



C. Radical Cation $H_2CSiO^{•+}$

The radical cation of elemental composition $[H_2CSiO]^{•+}$ was obtained by electron impact ionization of $(MeO)_4Si$,[270,271] and its geometry, electronic structure, and relative stability have been determined[270] (Table 26).

Table 26. Geometry and Relative Energies (kcal/mol) for $[H_2CSiO]^{\bullet +}$ Isomers[270]

		MP2/6-31G**//MP2/6-31G** + ZPVE
a		1.1
b		24.5
c		10.1
d		23.4
e		0.0

Like in the neutral H_2SiCO species,[235,261,266] the ketene-like planar structure **c** is not a minimum but corresponds to a transition state of the isomerization between the two forms **a**; the energy difference between **a** and **c** is only 9 kcal/mol[270] (about 16 kcal/mol for the neutral species).[261] The CO stretching is calculated at 2124 cm^{-1} [270] (2210 cm^{-1} for the neutral species). [261]

The Si−C bond can be understood in terms of an interaction between the empty p orbital of the silicon and the pair of electrons on the carbon. A relatively long Si−C bond (1.979 Å) results. As expected, the unpaired electron occupies the sp^2-hybridized orbital of $SiH_2^{\bullet +}$ and Si is both the radical site and the center of charge. [270]

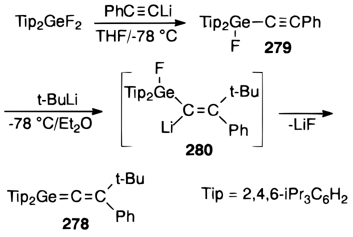
XVIII. 1-Germaallenes >Ge=C=C<

A. Synthesis

It was only in 1998 that the first compounds with a Ge=C=C unit were reported by the groups of West[272] and Okazaki.[273] Only two germaallenes have been obtained so far.

1. From a Fluoroalkynylgermane

Germaallene **278** was synthesized by addition of *tert*-butyllithium to the carbon−carbon triple bond of fluoroalkynylgermane **279** at −78 °C (eq 88). The presumed lithium intermediate **280** rapidly eliminated lithium fluoride at low temperature to give **278** in approximately 85% yield.[272]



(88)

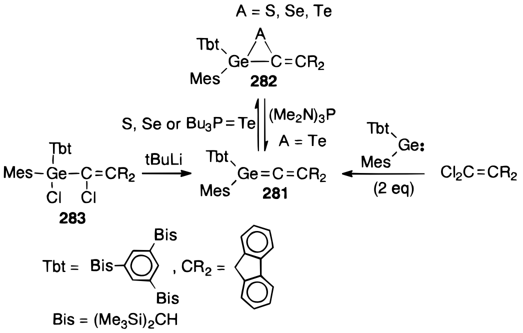
The synthetic process was the same as that used for the preparation of isostructural silaallene **240**,[220] but in this case the intermediate lithium compound was stable up to 0 °C and could be isolated and studied by crystallography. This important difference in the stability of the intermediates is of course due in the case of germanium to the weaker Ge−F bond which favors LiF elimination. This low-temperature elimination of LiF has previously been observed in the synthesis of a germaphosphaallene[106b] (see section XIX) and germenes >Ge=C<.[274]

Germaallene **278**, obtained as colorless plates, is stable up to 0 °C in Et_2O solution and was isolated by crystallization at −20 °C.

2. From a Haloalkenylgermane, a Germylene, or a Telluragermirane

The stable germaallene **281**,[273] with the carbon atom included in a fluorenylidene group and substituted on germanium by a mesityl group and the huge Tbt group, has been obtained by addition of a very large excess of $(Me_2N)_3P$ (50 equiv) to telluragermirane **282** (A = Te) at room temperature (Scheme 63). The yield of germaallene **281** depends on the quantity of $(Me_2N)_3P$: with 10 equiv of phosphorus triamide a mixture **281**/**282** in a 1/2 ratio was obtained, and with 1.2 equiv a mixture in a 2/7 ratio was obtained.[273] These results suggest an equilibrium between **282** + $(Me_2N)_3P$ and **281** + $(Me_2N)_3PTe$, slow enough on the NMR time scale to be observed. Thus, it is difficult to isolate the germaallene by this method, even if trapping experiments show that it is formed in nearly quantitative yield with a large excess of $(Me_2N)_3P$.

Scheme 63



By contrast, the dechlorination of **283** by t-BuLi (2.2 equiv) at −72 °C allowed the isolation of germaallene **281** as a colorless solid and appeared to be the best route to this compound.[273]

The formation of **281** as a reactive intermediate was previously postulated in the reaction between 2 equiv of the germylene Tbt(Mes)Ge: and $Cl_2C=CR_2$ in the presence of selenium, sulfur, or $Bu_3P=Te$ leading to the alkylidenechalcogenogermirane **282** (A = S, Se, Te);[275] the first step of this reaction should be the initial insertion of germylene into the C−Cl bond of $Cl_2C=CR_2$ followed by dechlorination leading to the germaallene **281** and subsequent chalcogenation.

B, Physicochemical Studies

1. ^{13}C NMR (Table 22)

278 and **281** have characteristic low-field chemical shifts for the central allenic carbon: 235.1 ppm for

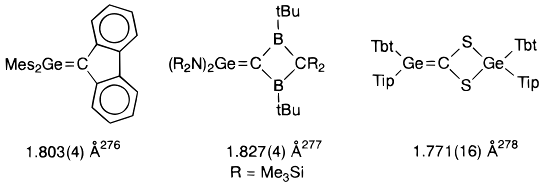
278[272] and 243.5 ppm for **281**.[273] Similar low-field shifts have been observed for silaallenes[192,219–221] and germaphosphaallene Mes$_2$Ge=C=PAr.[106b]

2. X-ray Structure Investigation

It is of interest to compare the structure of **278**[272] with that of the isostructural silaallene **240**.[220] In both derivatives the E=C=C skeleton is nonlinear, but the bending is much more important in the germanium compound than in the silicon derivative: 159.2° instead of 172.0°. The Ge atom is more pyramidalized than the Si atom: sum of angles on Ge = 348.4° and on Si = 357.2°. The angle between the plane including the two ipso carbons of the Tip groups and the Ge atom and the vector made by the Ge=C bond (147.4°)[272] is more bent than the corresponding angle in the silaallene (163.8°).

The Ge=C bond length (1.783 (2) Å) is among the shortest Ge=C bond length since distances between 1.77 and 1.81 Å are found in germenes >Ge=C<[276–278] (Chart 33).

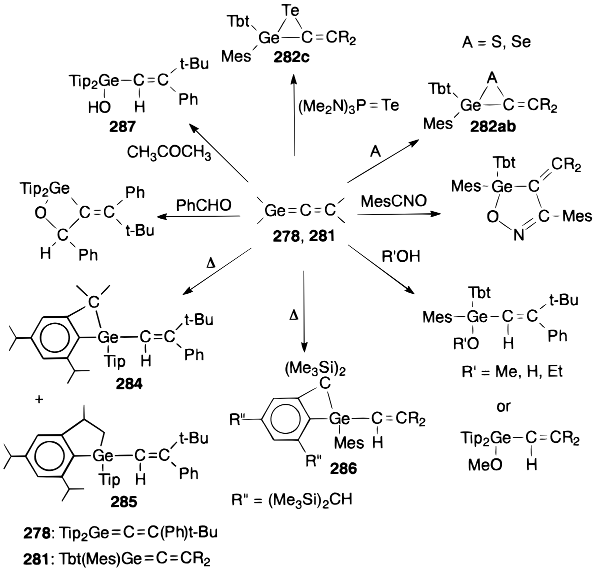
Chart 33



C. Reactivity

A summary of the reactivity is given in Scheme 64

Scheme 64



1. Action of Protic Reagents and Rearrangements

At 0 °C in solution or above 90 °C in the solid state, **278** rearranges to heterocycles **284** and **285**.[279] Similarly, germaallene **281** gives derivative **286**.[273] This type of CH insertion–cyclization reaction seems to be a significant route for doubly bonded silicon or germanium compounds as well as for germylenes[280] since under mild conditions the Ge–C double bond forms strained four- and five-membered rings rather than remaining as a double bond.

Water, methanol, or ethanol adds easily to the Ge=C double bond of **281**[279] and methanol to the Ge=C unsaturation of **278**,[273] with in all cases oxygen bonded to Ge.

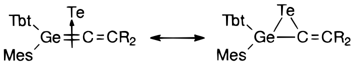
A surprising reaction was observed between **278** and carefully dried acetone leading to **287**, which seems to be the water adduct of the starting germaallene. The initial formation of a germyl enol ether, previously found in the reaction of acetone with Ge=C double bonds of germenes,[281] followed by hydrolysis has been ruled out.[279] In this case, acetone probably dimerizes to form diacetone alcohol which decomposes to mesityl oxide and water. Thus, it seems likely that **278** may serve to dehydrate acetone directly.

2. Cycloadditions

Various types of cycloadditions have been observed: [2+1] between **281** and sulfur, selenium, or (Me$_2$N)$_3$P=Te to give **282a**, **282b**, and **282c**,[273] [2+2] between **278** and benzaldehyde leading to a germaoxetane,[279] and a [2+3]-cycloaddition between **281** and mesitonitrile to form the corresponding five-membered ring heterocycle.[273]

The X-ray structure determination of **282c** showed a short Ge–C bond in the three-membered ring (1.88(2) Å)[275] (generally such Ge–C single bonds are in the range 1.95–1.98 Å)[282] and a sum of angles of 354.4° around the germanium, suggesting a considerable sp^2 character for this atom. It seems that such phenomena can be explained by using the π-complex binding model of a tellurium atom with a Ge=C double bond of a germaallene (Chart 34). These types of structures have already been reported in three-membered ring derivatives of germanium with a Ge–Ge–X (X = S,[283] C,[284] N,[284] and Te[285]) or Ge–P–S[286] linkage.

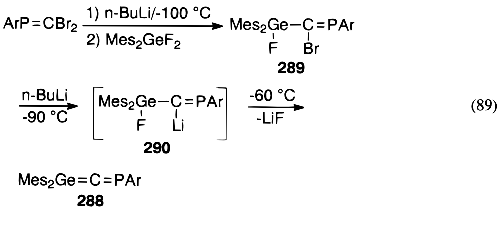
Chart 34



XIX. 1,3-Germaphosphaallenes >Ge=C=P–

A. Synthesis and Physicochemical Studies

The germaphosphaallene Mes$_2$Ge=C=PAr **(288)**[106b] was the first allenic compound of germanium to be physicochemically characterized. It was obtained by a debromofluorination by *n*-butyllithium of the corresponding precursor **289**, a procedure very similar to that used for the synthesis of phosphasilaallene Ph(Tip)Si=C=PAr[106a] (eq 89). The lithium derivative

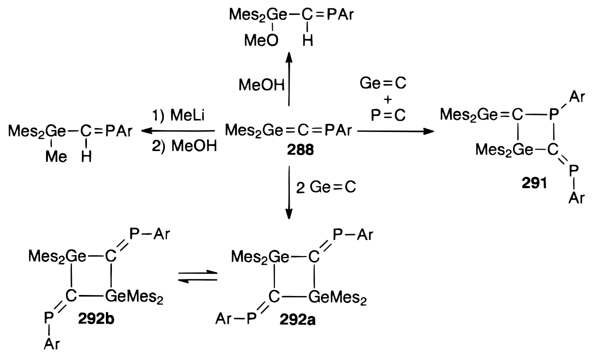


intermediate **290** was formed immediately at −90 °C as evidenced in ^{31}P NMR by a signal at 397.4 ppm ($^{3}J_{PF}$ = 16.9 Hz). Elimination of LiF occurred at −60 °C to give orange solutions of germaphosphaallene **288**; **288** was characterized by low-field shifts in the ^{31}P NMR (δ = 240.0 ppm) and in the ^{13}C NMR for the central sp carbon (δ = 280.9 ppm, $^{1}J_{PC}$ = 54.3 Hz). Such chemical shifts (Table 22) are close to those observed in phosphasilaallene **271**[106a] and in diphosphaallenes.

B. Reactivity

288 was also characterized by its chemical reactivity[106b] (Scheme 65): addition of methanol and methyllithium followed by methanolysis gave the corresponding adducts on the sole Ge═C double bond; the P═C double bond is unreactive toward air and moisture and even methyllithium. In the absence of trapping reagent, the germaphosphaallene dimerized above −30 °C: two types of dimerization occurred (like in phosphasilaallene **271**[106a]) by a Ge═C and a P═C double bond (to give **291**) and by two Ge═C double bonds (to give **292a**) in a 88/12 ratio. The heterocycle **291** has an AX spectrum in ^{31}P NMR (δ P(II) = 269.5 ppm, δ P(III) = 61.3 ppm, $^{2}J_{PP}$ = 225.4 Hz); from the large $^{2}J_{PP}$ coupling constant, it seems that the trans isomer **291** with Ar (on P(II)) and P(III) in a trans position is obtained since, as previously stated, the literature data show that this coupling constant is around 15−30 Hz in cis structures.

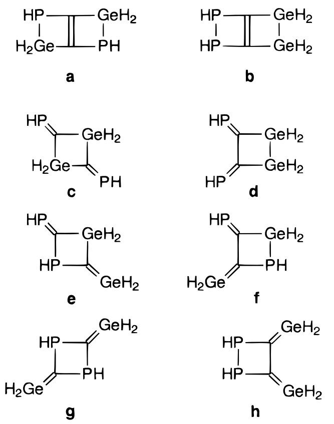
Scheme 65



Immediately after reaction, the only dimer **292** obtained was the isomer **292a**, with the two Ar groups in a trans position relative to the PCCP axis. After 1 week at room temperature, in solution, a mixture of isomers **292a**/**292b** in a 48/52 ratio was obtained corresponding to the thermodynamic equilibrium.

Preliminary calculations (restricted Hartree−Fock calculations with the GAUSSIAN 92 package) have been performed on model dimers **a**−**h**[106b] resulting from the couplings of the two molecules of germaphosphaallene H_2Ge═C═PH (Chart 35). The more stable dimers are the "butterfly" structures **a** and **b** about 15 kcal/mol below **c** and **d**. The latter are, in turn, favored by about 18 kcal/mol with respect to **e** and **f**; **g** and **h** corresponding to the coupling of two P═C double bonds are the least favorable. Very small differences are found between head-to-head and head-to-tail dimers for each series and for the cis or trans PH arrangement in agreement with the thermodynamic equilibrium observed experimentally between **292a** and **292b**. The discrepancies observed with experiment are of course due to the large groups used.

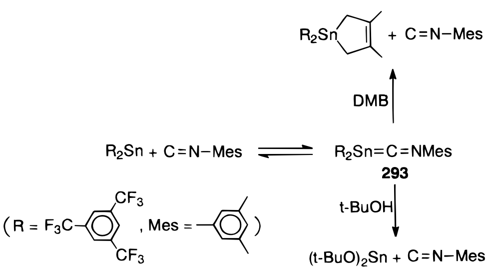
Chart 35



XX. >SnCN− Species

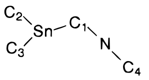
It is well-known that the stabilization of doubly bonded species is more and more difficult when going down in a group. For example, whereas many doubly bonded derivatives of silicon and germanium have been synthesized and isolated,[14] very few doubly bonded derivatives of tin, particularly those with the Sn═C moiety, are known.[287−290] Thus, it is not surprising that only one compound with a formal cumulative Sn═C═E bond has been prepared. This derivative of the type R_2SnCNR', which is a formal stannaazaallene, has been reported by Grützmacher in the reaction between a diarylstannylene and the mesitylisocyanide[254] (Scheme 66).

Scheme 66



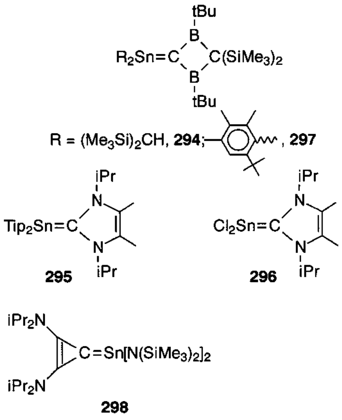
The X-ray study of **293** shows that the $C_2C_3SnC_1$-NC_4 atoms which should lie in a plane in an idealized stannaazaallene structure form a skeleton with a very bent orientation (Chart 36); such a bent molecular structure was predicted by the model of Trinquier and Malrieu.[235] The bond angles C_3SnC_1 and C_2SnC_1 (respectively, 104.9(1)° and 83.4(1)°)[254] are far from the theoretical 120° value. The most striking feature is the very long SnC_1 bond (2.397(3) Å), even longer than the SnC_2 or SnC_3 bonds (2.314(3) and

Chart 36



2.306(2) Å) and the standard Sn−C single bond (generally 2.15−2.20 Å[291]) corresponding better to the Sn−C distances in very encumbered systems (2.20−2.30 Å).[292] Shorter Sn−C distances than Sn−C_1 are observed in stannenes (for example, 2.025 Å in **294**[293]) and in compounds **295**−**298** (**295**, 2.379 Å;[287a] **296**, 2.290 Å;[288] **297**, 2.032 (5) Å;[287b] and **298**, 2.303 (9) Å[289]) which can be considered as complexes between stannylenes and carbenes (Chart 37). The C_1N distance (1.158(3) Å) is typical for isocyanides.

Chart 37



In the IR, the CN stretching vibration was observed at 2166 cm^{-1} [254] (2118 cm^{-1} in the starting MesNC) (Table 22).

The ^{119}Sn NMR chemical shift of **293** is very dependent on the temperature and was extrapolated at −150 ppm. The measurement of this temperature-dependent chemical shift allowed for the determination of the dissociation enthalpy between stannylene and isocyanide, which is 7.08 kcal/mol.

293 reacts with t-BuOH and with dimethylbutadiene to afford exclusively trapping products of the stannylene R_2Sn and the starting isocyanide.

From all these data, it seems that the Sn−C1 interaction in **293** may be best described as a double π-donor−acceptor interaction similar to that reported in other unsaturated compounds of tin such as distannene $R_2Sn{=}SnR_2$ (R = $(Me_3Si)_2CH$).[294] Thus, the structure of **293** is similar to that found in R_2SiCNR compounds.[245,246] It must be noted that completely different structures were observed in the case of phosphaazaallenes, which have an allenic geometry.

XXI. Conclusion

As it can be seen from Table 27, the most important work on allenic compounds of groups 14 and 15 has been performed on phosphorus derivatives. The chemistry of low-coordinate arsenic derivatives is much less developed since only two allenic compounds have been isolated until now. Such a difference with phosphorus is of course due to the greater difficulty to stabilize As(II) than P(II) derivatives because of, among other factors, longer bond lengths for which the dimerization is easier and also to the toxicity of arsenic and to the absence of NMR signals, very useful in the case of phosphorus, which does not prompt research groups to work on this element.

Table 27. Allenic and Cumulenic Derivatives Isolated or Characterized[a]

compound	no.			compound	no.		
P=C=C	**21**	[3]	1	Si=C=C	**7**	[2]	17
P=C=N	**8**	[6]	9**	Si=C=N	**3***		3**
P=C=P	**5**			Si=C=P		[1]	
P=C=O	**1**	[1]		Si=C=O		[6]*	
P=C=S			2	Si=C=C=C			4
P=C=As	**1**			Ge=C=C	**2**		
As=C=As	**1**			Ge=C=P		[1]	
P=C=C=C	**11**			Sn=C=N	**1***		
P=C=C=P	**1**						
As=C=C=As			1**				

[a] Bold numbers indicate compounds which were actually isolated. Numbers in square brackets indicate compounds unstable at room temperature which were characterized by their physicochemical data. Italic numbers indicate compounds which were characterized only by trapping reactions. Numbers followed by an asterisk indicate compounds which should be considered as complexes rather than allenic derivatives. Numbers followed by two asterisks indicate dimers which were obtained probably via transient monomers. E=C=E′ derivatives complexed by transition metal are not registered.

As expected, the number of isolated allenic compounds decreases going down in the group 14, 15, or 16. Allenic derivatives of antimony, selenium, and tellurium are still unknown. Very bulky groups will probably be necessary to stabilize such species, for example, the Tbt group (2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl) used by Okazaki and Tokitoh[295] and the huge terphenyl group used by Power[296] (R = 2,6-bis(2,4,6-triisopropylphenyl)phenyl) which recently allowed the stabilization of the doubly bonded antimony or bismuth compounds $RSb{=}E_{15}R$ or $RBi{=}E_{15}R$.

In the field of $E_{14}{=}C{=}E'$ derivatives, the stabilization and isolation is difficult due to the very reactive $E_{14}{=}C$ bond. Thus, such a double bond must be created after the C=E′ unsaturation, limiting the number of synthetic routes available. Moreover, contrary to the case of −P=C=E′ derivatives, complexes of silylenes (germylenes or stannylenes) with the C=E′ moiety (E′ = O, N) seem to be more favorable than allenic structures. Thus, substituents on group 14 elements having a very special steric or electronic influence must be found to allow the isolation of derivatives $E_{14}{=}C{=}N$ (O) having an allenic behavior. Complexation by transition metals is also a solution for the stabilization of such species.

Compounds with three cumulated double bonds are very rare, since only phosphabutatrienes or diphosphabutatrienes have been isolated whereas arsenic or silicon derivatives of this type have only been evidenced by trapping.

Even if the reactivity of E=C=E′ derivatives begins to be well-known, many reactions can still be performed. It is particularly true for $E_{14}{=}C{=}E'$ compounds for which the chemical behavior is rather unknown, although they seem less reactive than expected.

Due to the presence of two cumulated double bonds, the E=C=E′ derivatives possess a very special structure which should confer them promising properties. A great development will probably occur in the next few years in this field.

To conclude, we can mention, even if it is not the topic of this review, that allenic derivatives with a heavy group 14 element in the central position (instead of carbon), such as $X{=}E_{14}{=}X'$ (X, X′= group 14, 15, and 16 elements) are extremely rare. Some of them, such as 2-silaallenes $>C{=}Si{=}C<$,[223,297−299] 2-silaketenes $>C{=}Si{=}O$,[299] silanediimines $-N{=}Si{=}N-$,[300−302] and silicon dioxide $O{=}Si{=}O$,[299,303] have only been evidenced by trapping reactions. A tin derivative with an allenic structure, the "tristanna-allene" $R_2Sn{=}Sn{=}SnR_2$, has been recently reported by Wiberg.[304] As predicted by calculations, the stabilization of $X{=}E_{14}{=}X'$ species with two cumulated double bonds on the central E_{14} element appears to be more difficult than the stabilization of $>E_{14}{=}C{=}X$ derivatives. However, great progress will also most likely be made in this field in the following years.

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