METALLAIMINES >M=N-, METALLAPHOSPHENES >M=P- AND METALLAARSENES >M=As-

A. Kandri Rodi[1], H. Ranaivonjatovo[1], J. Escudié*[1] and A. Kerbal[2]
[1] Heterochimie Fondamentale et Appliquee, URA 477, Universite P. Sabatier, 118, route de Narbonne, F-31062 Toulouse cedex, France
[2] Laboratoire de Chimie Organique, Faculté des Sciences Dhar El Mahraz, Universite Sidi Mohamed Ben Abdellah, BP 1796, Fes, Maroc

Abstract

All the stable metallaimines >M=N-, metallaphosphenes >M=P- and metallaarsenes >M=As- (M: Si, Ge, Sn) prepared until now are reported with their synthetic routes and their characteristic physicochemical data (^{29}Si, ^{31}P, ^{119}Sn NMR, double bond lengths). The routes to transient species are also summarized.

Introduction

Many researches have been devoted to low coordinated species of groups 14 and 15 in the last 30 years. However, in the field of compounds with a double bond between two heavy elements of these groups, thus derivatives of the type $>M_{14}=M_{15}-$ (M_{14}: Si, Ge, Sn; M_{15}: N, P, As), it is only in 1984 that the first stable example of such new organometallic functions, the phosphasilene $Mes_2Si=PAr$ [1] (Ar: 2,4,6-tri-tert-butylphenyl), has been reported by Bickelhaupt. Since this date, many other $>M_{14}=M_{15}-$ derivatives have been successfully synthesized, and some of them stabilized owing to the use of bulky groups which prevent their oligomerisation (for reviews on Si=X see ref 2-4, on Ge=X see ref 4-6).

The main purpose of this review is to report in schemes, with only very brief comments, all the possible routes to such transient or stable compounds, and to present in the form of tables all the stable derivatives prepared until now with their characteristic physicochemical data (^{29}Si, ^{31}P, ^{119}Sn NMR, double bond lengths).

The reactivity of these species is not reviewed in this paper.

I TRANSIENT METALLAIMINES

a) Silaimines

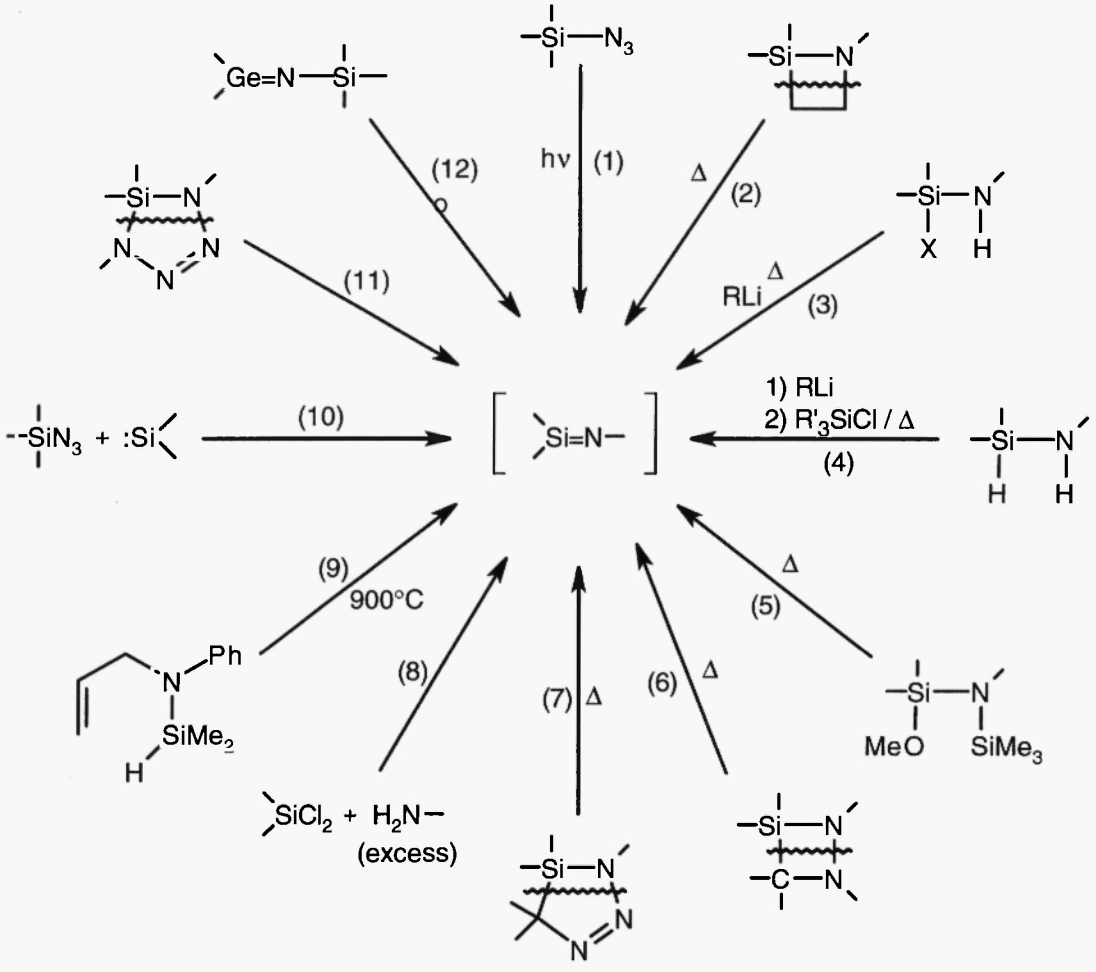
Many reactions have been described for the synthesis of transient silaimines. These species have only been characterized by trapping. The next scheme summarizes all the routes to these derivatives. Many of these reactions have already been reported in the very well documented review by G. Raabe and J. Michl [2]. Thus, in this paper, we give only the references corresponding to the papers published after this review.

(1) Curtius rearrangement with loss of nitrogen [2, 7-12].
(2) thermal decomposition of a silaazetidine [13-14].
(3) reaction of an alkyllithium with a halogenosilylamine, and elimination of LiX [2, 15].
(4) reaction of an alkyllithium with a silylamine, followed by addition of chlorosilane in non polar solvents producing cyclodisilazanes via a silaimine intermediate [16, 17].
(5) thermal elimination of trimethyl(methoxy)silane [2].
(6) thermal elimination of imine from a siladiazetidine [2].
(7) reaction of an azide with a transient silene leading to a silatriazole followed by a [2+3] decomposition [18, 19].
(8) intermolecular dehydrochlorination between a dichlorosilane and a primary amine by an excess of amine [20].
(9) elimination of propene from a hydrosilyl(allyl)amine by a retro-ene reaction [21].
(10) reaction of a silylazide with a transient silylene, with intermediate formation of a silatriazetidine

and elimination of nitrogen [22].

(11) [2+3] decomposition of a silatetrazole [23].

(12) rearrangement of a germaimine involving the migration of the double bond [19].



b) Germa- and stannaimines

Some routes used for the synthesis of transient silaimines are also successful for transient germaimines and two of them for stannaimines; moreover, specific routes have also been found.

(1) thermal decomposition of a germaazetidine: first route to a transient germaimine [24].

(2) reaction of a germylene or a stannylene with an azide, followed by loss of nitrogen [25].

(3) Curtius rearrangement in a germylazide under photolysis followed by loss of nitrogen [26].

(4) reaction of a cyclodigermazane with two moles of phenylisocyanate finally leading to a germadiazetidine in equilibrium with a germaimine and phenylisocyanate [27].

(5) monomerisation of a dimer or a trimer of a germaimine (digermazane or trigermazane) by a Lewis base or a Lewis acid [27-30].

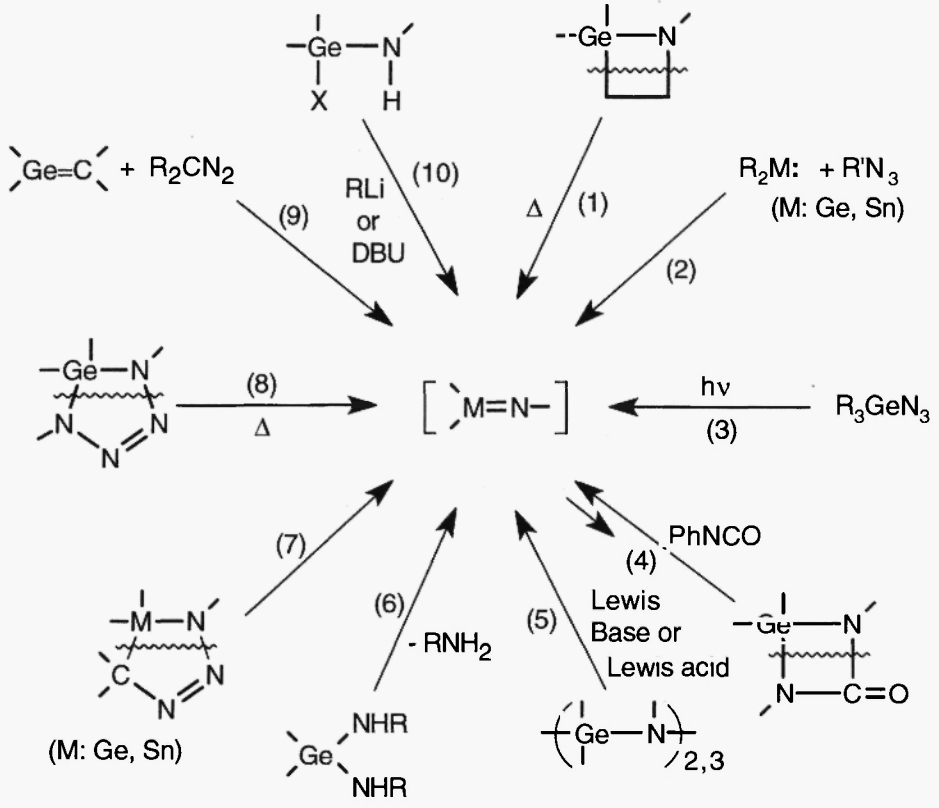
(6) elimination of RNH_2 from a diaminogermane obtained by intermolecular dehydrochlorination between a dichlorogermane and a primary amine [27].

(7) [2+3] decomposition of a germa- or stannatriazole obtained by reaction of an azide with a transient germene or stannene [19, 31].

(8) [2+3] decomposition of a germatetrazole [32, 33].

(9) reaction of a germene with diazofluorene or diphenyldiazomethane leading to a transient germaimine and fluorenyl- or diphenylcarbene [36].

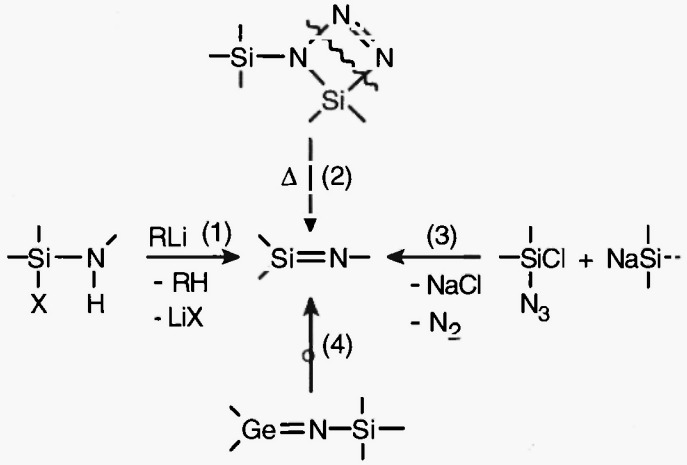
(10) dehydrochlorination of a chlorogermylamine by an alkyllithium or by DBU [34, 35].



II STABLE METALLAIMINES

a) Silaimines

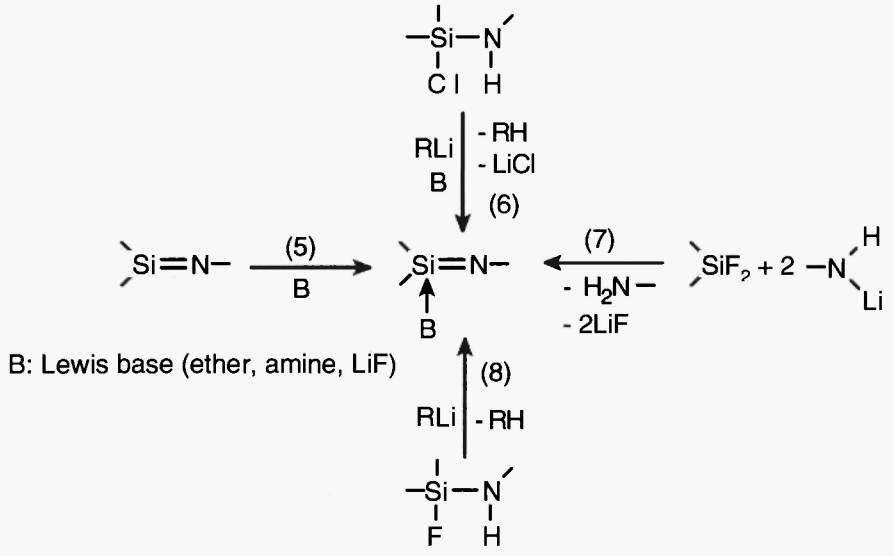
(1) dehydrochlorination (or fluorination) from a chloro- (or fluoro)silylamine by a lithio compound.
(2) decomposition (loss of nitrogen) from a silatriazetidine.
(3) reaction between a silylsodium and a chlorosilylazide with rearrangement involving the migration of a silyl group on a nitrogen.
(4) multi-step rearrangement of a germaimine >Ge=N- substituted on nitrogen by a silicon group.



Transient or stable silaimines can be stabilized by inter- or intramolecular coordination with Lewis bases:

(5) direct complexation of a stable silaimine by a Lewis base.
(6) dehydrochlorination of a chlorosilylamine by an alkyllithium in the presence of a Lewis base. Without complexation, silaimines substituted on silicon by methyl groups are not stable.

(7) reaction of 2 equivalents of a lithium amide with a difluorosilane substituted by a CH_2NMe_2 group involving an intramolecular coordination of silicon by nitrogen.
(8) reaction of methyllithium with a fluorosilylamine leading to a silaimine complexed by lithium fluoride.



The transient silaimine $Me_2Si{=}NtBu$ has been stabilized by complexation with a transition metal according to the two following processes:
(9) elimination of tetramethylsilane from a N-zirconium silylamine.
(10) exchange of ligand on zirconium from a complexed silaimine.

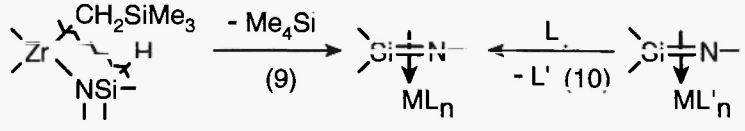
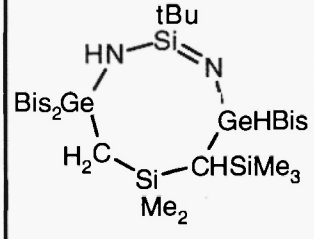


Table 1: stable silaimines

Silaimines	Synthetic routes	$\delta^{29}Si$ (ppm)	d(Si=N)(Å)	Ref.
$tBu_2Si{=}NSitBu_3$	2,3	+78.3	1.568(3)	22,37,38
$iPr_2Si{=}NAr$	1	+60.3		39,40
	4	+38.4		41

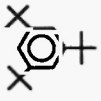
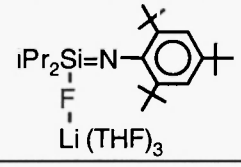
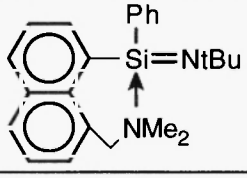
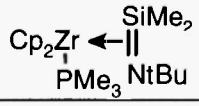
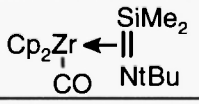
Bis: $(Me_3Si)_2CH$, Ar: 

Table 2: complexed silaimines

complexed silaimines	Synthetic routes	$\delta\,^{29}Si$ (ppm)	d(Si=N)(Å)	Ref.
$tBu_2Si{=}NSitBu_3$ ↑ THF	5	+1.0	1.588(9)	38
$tBu_2Si{=}NSitBu_3$ ↑ NMe_2Et	5	+18.1		42
$tBu_2Si{=}NSitBu_3$ ↑ $O{=}CPh_2$	5	+54.2	1.601(2)	43
$Me_2Si{=}NSitBu_3$ ↑ B (B: Et_2O, THF, NEt_3, NMe_2Et)	6	B: Et_2O δ: -1.5; THF: -4.4; NMe_2Et: -8.8; NEt_3: -11.2		44
	8	-26.9	1.619(5)	40
	7	-9.6		45
$tBu_2Si{=}NSiMetBu_2$ ↑ THF	6	-14.6; ^{14}N: -329.08	1.596(2)	46
	9		1.687(3)	47
	10	-69.9		47

b) Germaimines

(1) reaction of a germylene with a diazomalonic ester. This was the first route to a stable germaimine.
(2) reaction of a germylene with an azide, followed by loss of nitrogen with, in some cases, complexation by a Lewis base.
(3) photolysis of a germylazide involving a Curtius rearrangement.
(4) intermolecular dehydration between GeH_4 and RNO.
(5) reaction of an hydrogermaimine with HCl or bis(trifluoromethyl)nitroxyl R_2NO involving the replacement of hydrogen by Cl or R_2NO.

(6) dehydrohalogenation of a halogenogermylamine by an alkyllithium.

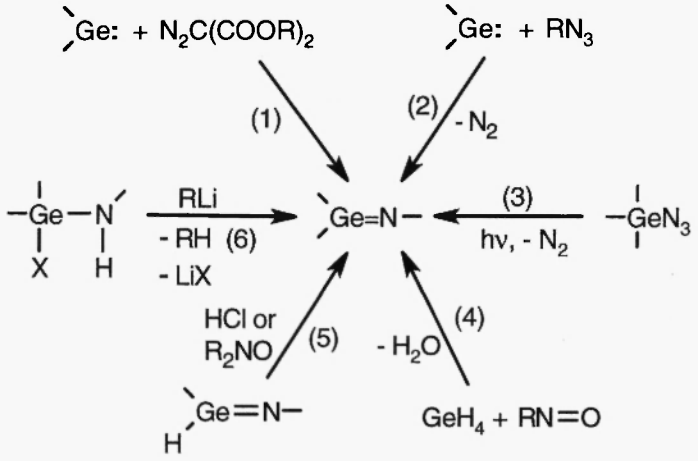
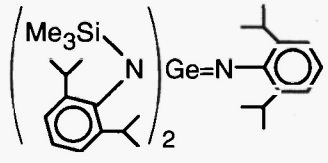


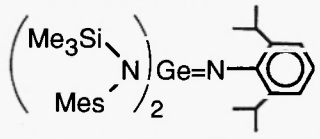
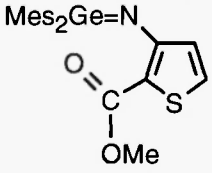
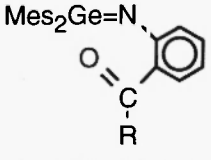
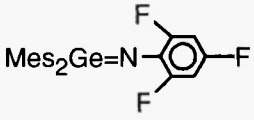
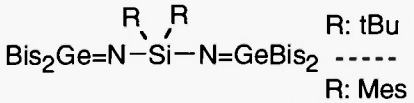
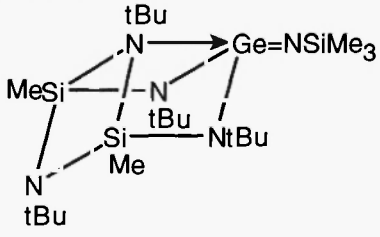
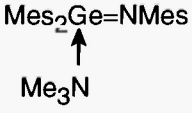
Table 3: stable germaimines

Germaimines	Synthetic routes	d(Ge=N) (Å)	Ref.
$[(Me_3Si)_2N]_2Ge=N-N=CRR'$ * R=R': COOMe --- ** R: COOMe, R': COOEt, SO_2Tol, COPh R, R': $COCH_2CMe_2CH_2CO$	1		48 --- 49
$[Me_3Si)_2N]_2Ge=NSiX_3$ X: C_2H_5; OtBu	2		50b
$Mes_2Ge=NMes$	3		51,52
$CF_3N=GeH_2$	4		53,54
$CF_3N=Ge(H)ON(CF_3)_2$	5		
$CF_3N=Ge[ON(CF_3)_2]_2$	5		
$(CF_3)_2NO-N=GeH_2$	4		
$(CF_3)_2NO-N=Ge(H)Cl$	5		
$(CF_3)_2NO-N=Ge(H)ON(CF_3)_2$	5		
$CF_3N=Ge(H)Cl$	5		
$CF_3N=GeCl_2$	5		
	2	1.703(2)	55

*However, in this reaction Meller *et al.* did not observe this free germaimine but do not exclude its formation as a short-lived intermediate [50a].

**The germaimines formed in this case are not stable and rearrange due to the presence of an enolisable function on the diazo compound.

Table 3 followed

	2		55
$[(Me_3Si)(Mes)N]_2Ge{=}NMes$	2	1.691(3)	55
	6		56
 (R: OMe, NMe_2)	6		57,58
	6		59
$Bis_2Ge{=}NSi(N_3)R_2$ R: tBu ----- R: Mes	2	1.704(3) ----------	41
 R: tBu ----- R: Mes	2	---------- 1.681(8)	41
	2	1.688(9)	60
	2		51

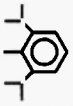
Bis: $(Me_3Si)_2CH$

c) Metastable stannaimine

reaction of a stannylene with an azide with loss of nitrogen. The stannaimine obtained by this route is stable only below -30°C, but has nevertheless been characterized by ^{119}Sn NMR and X-ray diffraction.

$$>Sn: + N_3R \xrightarrow[-N_2]{} \backslash Sn{=}N-$$

Table 4: stannaimine

Stannaimine	δ^{119}Sn(ppm)	d(Sn=N)(Å)	Ref.
$[(Me_3Si)_2N]_2Sn{=}N$– 	-3.5	1.921(2)	61

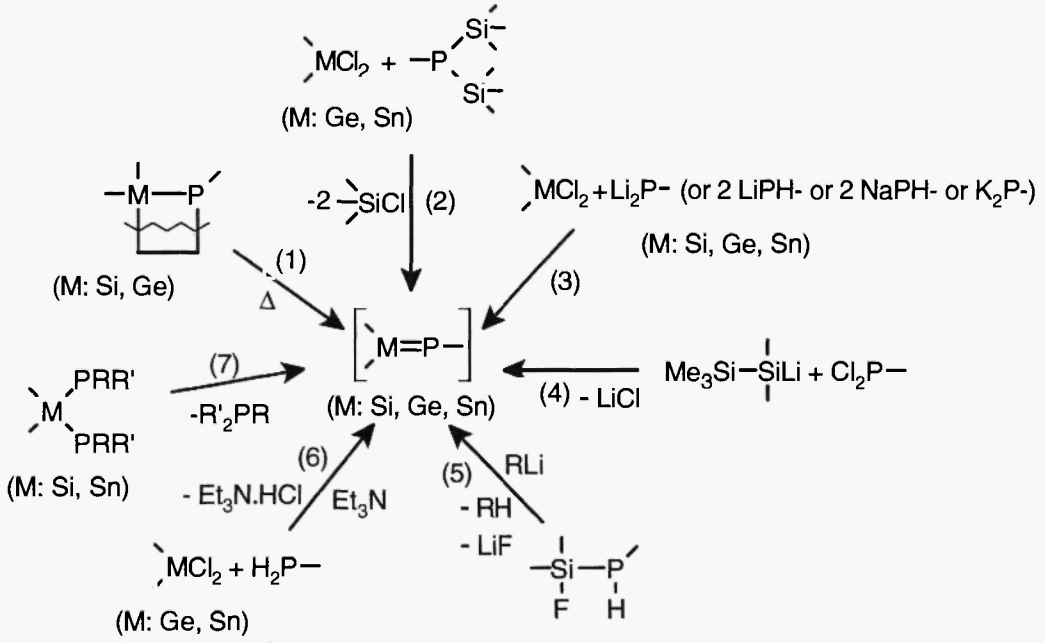
III TRANSIENT METALLAPHOSPHENES >M=P-

(1) thermal decomposition of a sila- [62] or germaphosphetane [63].
(2) dechlorosilylation reaction of a compound obtained by reacting a dichlorogermane or a dichlorostannane with a disilylphosphane [64, 65].

Transient sila-, germa- and stannaphosphenes obtained by routes (1) and (2) have been characterized by trapping [62-64] or by formation of their dimers [65].

Routes (3) to (7) could also involve the transient formation of metallaphosphenes, but only their dimers or trimers are obtained:

(3) reaction of a dilithium (or dipotassium) phosphanide or of a twofold excess of lithium phosphanide or sodium phosphanide with a dihalogenosilane [66-72], -germane [67, 73, 74] or -stannane [75].
(4) reaction between a disilanyllithium and a dichlorophosphane followed by elimination of trimethylchlorosilane [76].
(5) dehydrofluorination of a fluorosilylphosphane by an alkyllithium [77-83].
(6) intermolecular dehydrochlorination between a primary phosphane and a dichlorogermane or -stannane by an amine [67, 84].
(7) thermal elimination of R'_2PR from a diphosphasilane [85, 86] or -stannane [87, 88].



IV STABLE METALLAPHOSPHENES

Derivatives of the type >M=P- (M: Si, Ge, Sn) are called metallaphosphenes (for ex: germaphosphenes). However, since phosphorus has an atomic number greater than silicon, derivatives with a Si=P double bond are named phosphasilenes.

a) Phosphasilenes

(1) dehydrochlorination of a chlorosilylphosphane by an alkyllithium.
(2) dehydrofluorination of a fluorosilylphosphane by an alkyllithium.
(Routes (1) and (2) are the most widely used).
(3) reaction of water or of an alkyl halide with a diphosphasilaallylanion.
(4) addition of two equivalents of butyllithium to a mixture of primary phosphane and dichlorosilane.
(5) reaction of a dilithium phosphanide with a dichlorosilane substituted by a CH_2NMe_2 group, involving an intramolecular coordination of silicon by nitrogen.

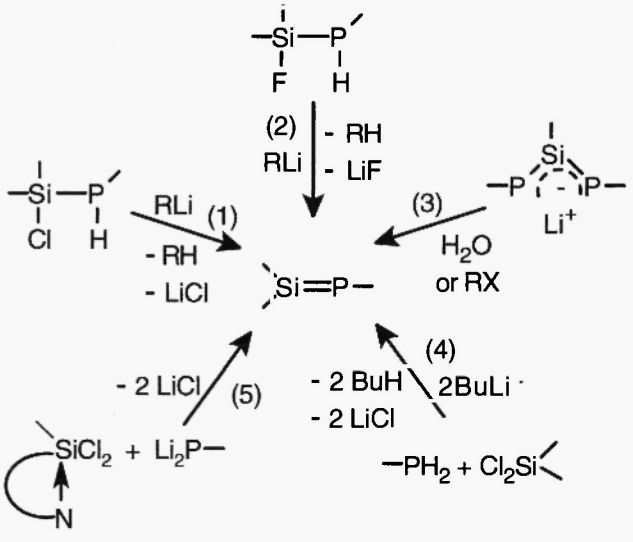


Table 5: stable phosphasilenes

Phosphasilenes	Synthetic routes	$\delta^{29}Si$ (ppm) ($^1J_{P-Si}$ Hz)	$\delta^{31}P$ (ppm)	d(Si=P) (Å)	Ref
Mes_2Si=PAr	1	151.0 (149)	136		1
Es_2Si=PAr	1	150.1 (152)	133.7		89
Is(Ph)Si=PAr	1	153.0 (E) (151)	93.5		89
Is(Mes)Si=PAr	1	148.7 (E) (152)	122.7		89
Is(tBu)Si=PAr	1, 4	175.9 (E) (155)	105.7		89
[Ar(H)P](tBu)Si=PAr	3		142		90
[Ar($SiMe_3$)P](tBu)Si=PAr	3		83.3		90
Es(dep)Si=PAr Z and E	1	149.2 (153) 149.0 (153)	134.2 135.8		91

Table 5 followed

Is(tBu)Si=PIs	1	190.3 (E) (153)	66.2		91
Is(tBu)Si=PEs	1	194.1 (E) (153)	65.8		91
Is(tBu)Si=PMes	1	196.8 (E) (153)	69.0		91
Is(tBu)Si=P-C$_6$H$_3$-OOct	1	199.0 (E) (154)	69.7		91
Is(tBu)Si=PSi(iPr)$_3$	2	213.2 (Z) (161)	-29.9	2.062(1)	92
[Ar(PPh$_2$)P](tBu)Si=PAr	3	180.2 (203.0)	128.7	2.094(3)	93
Is$_2$Si=P-SiMe$_2$tBu	2	178.4 (149)	17.7		94
Is$_2$Si=P-P(tBu)$_2$	2	184.6 (158)	72.2		94
Is(tBu)Si=P-C$_6$H$_3$(Ph)$_2$-Ph	1	180.0 (E) (151)	86.7		91
Is$_2$Si=P-Si(iPr)$_3$	2	167.8 (160)	11.1		94
C$_6$H$_4$(Si=PPh)(CH$_2$NMe$_2$)	5	-6.4 (Z) (24.1) -2.7 (E) (9.2)	-116.5 (Z) -97.2 (E)		45

Is: dep: Es: Ar:

b) Germaphosphenes

1) dehydrofluorination of a fluorogermylphosphane by tert-butyllithium: the best route to germaphosphenes giving nearly quantitative yields.
(2) dehydrochlorination of a chlorogermylphosphane by a phosphorus ylide.
(3) dehydrochlorination of a chlorogermylphosphane by DBU. (2) and (3) give the corresponding germaphosphene in low yields (< 20%).
(4) thermal Z/E isomerisation of a germaphosphene.
(5) reaction of a difluorogermane with a dilithium phosphanide.

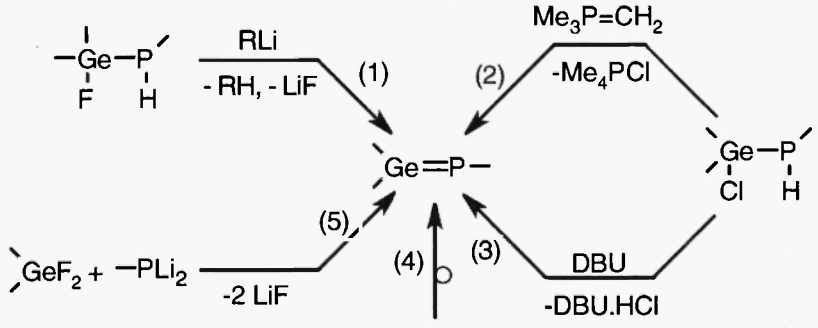
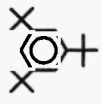
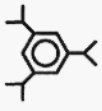


Table 6: stable germaphosphenes

Germaphosphenes	Synthetic routes	$\delta^{31}P$(ppm)	d(Ge=P) (Å)	Ref.
Mes, Ar / Ge=P / Mes	1, 2, 3	175.4		95, 96
			2.139(3)	97
Mes, Ar / Ge=P / tBu	1	169.2	2.143(4)	98
tBu, Ar / Ge=P / Mes	4	157.4		98
tBu, Ar / Ge=P / tBu	1	156.6		98
Mes, Is / Ge=P / Mes	5	145.3		99, 102

Ar:  , Is: 

c) Stannaphosphenes

(1) dehydrofluorination of a fluorostannylphosphane by tert-butyllithium: nearly quantitative route to stannaphosphenes.

(2) defluorosilylation of a fluorostannyl(silyl)phosphane.

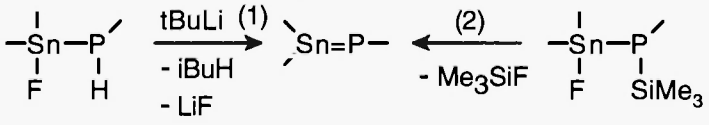
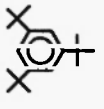
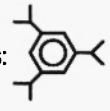


Table 7: stable stannaphosphenes

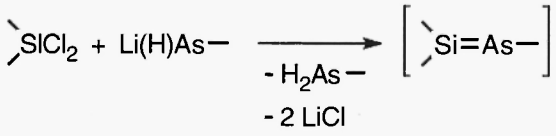
Stannaphosphenes	Synthetic routes	$\delta^{31}P$ (ppm)	$\delta^{119}Sn$ (ppm)	$^1J_{P\text{-}119Sn}$ $^1J_{P\text{-}117Sn}$ (Hz)	Ref.
$Bis_2Sn{=}PAr$	1	204.7	658.3	2295 2191	96, 100
$Is_2Sn{=}PAr$	1	170.7	499.5	2208 2110	101, 102
$Is_2Sn{=}PIs$*	2	124.6 at - 80°C	600.6 at - 80°C	2182 2110	103
$Is_2Sn{=}PBis$	2	168.9	606.0	2264 2163	103

* decomposes at room temperature

Bis: $(Me_3Si)_2CH$, Ar:  , Is: 

V TRANSIENT ARSASILENES

The reaction of a dichlorosilane with an excess of lithium arsanide leads to the four-membered ring 1,3-disiladiarsetane, probably via an arsasilene intermediate [104].



VI STABLE ARSASILENES

(1) The reaction of butyllithium with a fluorosilyl(silyl)arsane followed by elimination of lithium fluoride leads to stable arsasilenes.

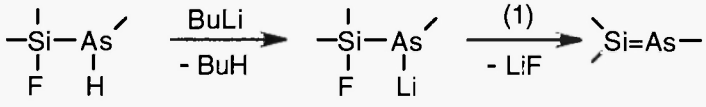
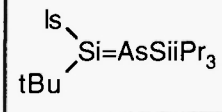
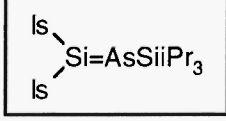
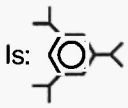


Table 8: stable arsasilenes

Arsasilenes	Synthetic routes	δ ^{29}Si (ppm)	d(Si=As) (A)	Ref.
	1	228.8 (Z)	2.164 (1) (Z)	92, 105
	1	179.1		92, 105



Conclusion

As one can see from the tables, many M_{14}=M_{15} derivatives have now been prepared and isolated. Most of them are stabilized by the large steric hindrance by the use on both sides of the double bond of very bulky groups which prevent the oligomerisation. Substituted aryl groups appear to be as the best ones for the stabilization, probably because of a conjugation between the aromatic rings and the M_{14}=M_{15} double bond. In contrast, germaimines prepared by Ang and Lee do not dimerize although substituted by very small groups: this very surprising behaviour is probably due to the important electronic effect of the CF_3 groups.

Some metallaimines or metallaphosphenes have also been stabilized by complexation by a Lewis base or a transition metal.

Doubly-bonded silicon compounds are of course more abundant than doubly-bonded germanium (except for germaimines) or tin derivatives (see table 9). For the latter, isolable stannaphosphenes have been obtained whereas the sole stannaimine prepared was characterized only below -30°C.

In the series M_{14}=M_{15}, no compounds of lead or antimony are known and only two arsasilenes have been obtained, whereas compounds with a double bond between arsenic and germanium or tin are still unknown.

The doubly-bonded derivatives of phosphorus, silicon and tin can be easily evidenced by their characteristic low field shifts in ^{31}P, ^{29}Si and ^{119}Sn NMR, except when the metal is complexed: in this case much higher field shifts are observed closer to those found in trivalent phosphorus or tetravalent silicon compounds.

The M_{14}=M_{15} double bond is much shorter than the corresponding single bond (7-9%). Structural determinations by X-ray diffraction show that the double bond skeleton is generally completely planar.

All these derivatives present, despite the large steric hindrance, a very important reactivity. Thus, besides their interest in academic research, these new organometallic functions should be useful in organic and organometallic synthesis.

Table 9: number of stable (or at least characterized by ^{29}Si or ^{119}Sn NMR) >M_{14}=M_{15}- derivatives, including complexed compounds. Z and E isomers are considered as different compounds

metallaimines	>M=N-	>Si=N- >Ge=N- >Sn=N-	15 24 1
metallaphosphenes	>M=P-	>Si=P- >Ge=P- >Sn=P-	21 5 4
metallaarsenes	>M=As-	>Si=As-	2

References

1. C.N. Smit, F.M. Lock and F. Bickelhaupt, *Tetrahedron Lett.*, 1984, **25**, 3011.
2a. G. Raabe and J. Michl, *Chem. Rev.*, 1985, **85**, 419.
b. G. Raabe and J. Michl, in *The Chemistry of Organic Silicon Compounds*, Edited by S. Patai and Z. Rappoport, 1989, chapter 17, p 1015.
3. M. Driess and R. Janoschek, *THEOCHEM*, 1994, **119**, 129.
4. N. Wiberg, *J. Organomet. Chem.*, 1984, **273**, 141.
5a. J. Satgé, *Adv. Organomet. Chem.*, 1982, **21**, 241.
b. J. Barrau, J. Escudié and J. Satgé, *Chem. Rev.*, 1990, **90**, 283.
6. J. Escudié, C. Couret, H. Ranaivonjatovo and J. Satge, *Coordination Chem. Rev.*, 1994, **130**, 427.
7. K.M. Welsh, J. Michl and R. West, *J. Am. Chem. Soc.*, 1988, **110**, 6689.
8. S.S. Zigler, K.M. Welsh, R. West and J. Michl, *J. Am. Chem. Soc.*, 1987, **109**, 4392.
9. J.G. Radziszewski, P. Kaszynski, D. Littmann, V. Balaji, B.A. Hess Jr. and J. Michl, *J. Am. Chem. Soc.*, 1993, **115**, 8401.
10. S.S. Zigler, L.M. Johnson and R. West, *J. Organomet. Chem.*, 1988, **341**, 187.
11. G. Maier and J. Glatthaar, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 473.
12. A. Sekiguchi, W. Ando and K. Honda, *Chem. Lett.*, 1986, 1029.
13. K. Tamao, Y. Nakagawa and Y. Ito, *J. Am. Chem. Soc.*, 1992, **114**, 218.
14. N. Auner, A.W. Weingartner and G. Bertrand, *Chem. Ber.*, 1993, **126**, 581.
15. S. Vollbrecht, U. Klingebiel and D. Schmidt-Baese, *Z. Naturforsch. B*, 1991, **46**, 709.
16. W. Fink, *Helv. Chim. Acta*, 1966, **49**, 1408.
17. G.H. Wiseman, D.R. Wheeler and D. Seyferth, *Organometallics*, 1986, **5**, 146.
18. N. Wiberg, G. Preiner, G. Wagner and H. Köpf, *Z. Naturforsch. B*, 1987, **42**, 1062.
19. N. Wiberg, P. Karampatses and Ch.-K. Kim, *Chem. Ber.*, 1987, **120**, 1203.
20. A. Kienzle, A. Obermeyer, R. Riedel, F. Aldinger and A. Simon, *Chem. Ber.*, 1993, **126**, 2569.

21. J.M. Denis, P. Guenot, M. Letulle, B. Pellerin and J.L. Ripoll, *Chem. Ber.*, 1992, **125**, 1397.
22. M. Weidenbruch, B. Brand-Roth, S. Pohl and W. Saak, *J. Organomet. Chem.*, 1989, **379**, 217.
23. N. Wiberg, G. Preiner and K. Schurz, *Chem. Ber.*, 1988, **121**, 1407.
24. M. Riviere-Baudet, P. Riviere and J. Satge, *J. Organomet. Chem.*, 1978, **154**, C23.
25. P. Riviere, A. Cazes, A. Castel, M. Riviere-Baudet and J. Satge, *J. Organomet. Chem.*, 1978, **155**, C58.
26. G. Bertrand, J.P. Majoral and A. Baceiredo, *Acc. Chem. Res.*, 1986, **19**, 17.
27. G. Lacrampe, H. Lavayssiere, M. Riviere-Baudet and J. Satge, *Rec. Trav. Chim. Pays-Bas* 1983, **102**, 21.
28. M. Riviere-Baudet, G. Lacrampe and J. Satge, *C. R. Acad. Sci . Paris (Ser. C)* , 1979, **289**, 223.
29. M. Riviere-Baudet, P. Riviere, A. Castel, G. Lacrampe and J. Satge, *Rec. Trav. Chim. Pays-Bas* , 1983, **102**, 65.
30. M. Riviere-Baudet, A. Khallaayoun and J. Satge, *Rec. Trav. Chim. Pays-Bas* , 1988, **107**, 152.
31. N. Wiberg and Ch.-K. Kim, *Chem. Ber.*, 1986, **119**, 2980.
32. T. Ohtaki and W. Ando, *Chem. Lett.*, 1994, 1061.
33. N. Wiberg, P. Karampatses and Ch.-K. Kim., *Chem. Ber.*, 1987, **120**, 1213.
34. M. Riviere-Baudet, A. Khallaayoun, J. Satge and M. Ahra, *Synth. React. Inorg. Met-Org. Chem.*, 1992, **22**, 683.
35. M. Riviere-Baudet, P. Riviere, A. Khallaayoun, J. Satge and K. Rauzy, *J. Organomet. Chem.*, 1988, **358**, 77.
36. M. Lazraq, C. Couret, J-P. Declercq, A. Dubourg, J. Escudie and M. Riviere-Baudet, *Organometallics*, 1990, **9**, 845.
37. N. Wiberg, K. Schurz and G. Fischer, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 1053.
38. N. Wiberg, K. Schurz, G. Reber and G. Müller, *J. Chem. Soc. Chem. Commun.*, 1986, 591.
39. M. Hesse and U. Klingebiel, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 649.
40. R. Boese and U. Klingebiel, *J. Organomet. Chem.*, 1986, **315**, C 17.
41. W. Ando, T. Ohtaki and Y. Kabe, *Organometallics*, 1994, **13**, 434.
42. N. Wiberg and K. Schurz, *Chem. Ber.*, 1988, **121**, 581.
43. N. Wiberg, K. Schurz, G. Müller and J. Riede, *Angew. Chem. Int. Ed. Engl.*, 1988, **27**, 935.
44. N. Wiberg and K. Schurz, *J. Organomet. Chem.*, 1988, **341**, 145.
45. R. Corriu, G. Lanneau and C. Priou, *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 1130.
46. S. Walter, U. Klingebiel and D. Schmidt-Bäse, *J. Organomet. Chem*, 1991, **412**, 319.
47. L.J. Procopio, P.J. Carroll and D.H. Berry, *J. Am. Chem. Soc.*, 1991, **113**, 1870.
48. C. Glidewell, D. Lloyd, K.W. Lumbard and J.S. McKechnie, *Tetrahedron Lett.*, 1987, **28**, 343.
49. C. Glidewell, D. Lloyd and K.W. Lumbard, *J. Chem. Soc. Dalton Trans.*, 1987, 501.
50a. G. Ossig, A. Meiler, S. Freitag, O. Müller, H. Gornitzka and R. Herbst-Irmer, *Organometallics*, 1996, **15**, 408.
b. J. Pfeiffer, W. Maringgele, M. Noltemeyer and A. Melier, *Chem. Ber.*, 1989, **122**, 245.
51. M. Riviere-Baudet, J. Satge and A. Morere, *J. Organomet. Chem.*, 1990, **386**, C7.
52. T. Tsumuraya and W. Ando, *Chem. Lett.*, 1989, 1043.
53. H.G. Ang and F.K. Lee, *J. Chem. Soc. Chem. Commun.*, 1989, 310.
54. H.G. Ang and F.K. Lee, *Fluorine Chem.*, 1989, **43**, 345.
55. A. Meller, G. Ossig, W. Maringgele, D. Stalke, R. Herbst-Irmer, S. Freitag and G.M. Sheldrick, *J. Chem. Soc. Chem. Commun.*, 1991, 1123.
56. M. Riviere-Baudet and A. Morere, *J. Organomet. Chem.*, 1992, **431**, 17.
57. M. Riviere-Baudet, A. Khallaayoun and J. Satge, *Organometallics*, 1993, **12**, 1003.
58. M. Riviere-Baudet, A. Khallaayoun and J. Satgé, *J. Organomet. Chem.*, 1993, **462**, 89.
59. M. Riviere-Baudet, J. Satge and F. El Baz, *J. Chem. Soc. Commun.*, 1995, 1687.
60. M. Veith, S. Becker and V. Huch, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 216.
61. G. Ossig, A. Meller, S. Freitag and R. Herbst-Irmer, *J. Chem. Soc. Chem. Commun.*, 1993, 497.
62. C. Couret, J. Escudié, J. Satge, J.D. Andriamizaka, and B. Salnt-Roch, *J. Organomet. Chem.*, 1979, **182**, 9.
63. J. Escudie, C. Couret, J. Satge and J.D. Andriamizaka, *Organometallics*, 1982, **1**, 1261.

64. C. Couret, J. Satge, J.D. Andriamizaka and J. Escudié, *J. Organomet. Chem.*, 1978, **157**, C35.
65. D. Hänssgen and H. Aldenhoven, *Chem. Ber.*, 1990, **123**, 1833.
66. R.T. Oakley, D.A. Stanislawski and R. West, *J. Organomet. Chem.*, 1978, 57, 389.
67. H. Schumann and H. Benda, *Chem. Ber.*, 1971, **104**, 333.
68. M. Driess, R. Gleiter, R. Janoschek, H. Pritzkow and M. Reisgys, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 1484.
69. M. Driess, *Phosphorus, Sulfur and Silicon*, 1992, **64**, 39.
70. M. Driess, H. Pritzkow and M. Reisgys, *Chem. Ber.*, 1991, **124**, 1931.
71. G. Fritz and R. Biastoch, *Z. Anorg. Allg. Chem.*, 1986, **535**, 63.
72. G. Fritz and P. Amann, *Z. Anorg. Allg. Chem.*, 1986, **535**, 106.
73. M. Driess, H. Pritzkow and U. Winkler, *Chem. Ber.*, 1992, **125**, 1541.
74. M. Driess and H. Pritzkow, *Chem. Ber.*, 1993, **126**, 1131.
75. D. Hänssgen, H. Aldenhoven and M. Nieger, *Chem. Ber.*, 1990, **123**, 1837.
76. A.H. Cowley and T. H. Newman, *Organometallics*, 1982, **1**, 1412.
77. U. Klingebiel and N. Vater, *Angew. Chem. Int. Ed. Engl.*, 1982, **21**, 857.
78. W. Clegg, M. Haase, U. Klingebiel and G.M. Sheldrick, *Chem. Ber.*, 1983, **116**, 146.
79. M. Andrianarison, U. Klingebiel, D. Stalke and G.M. Sheldrick, *Phosphorus, Sulfur and Silicon*, 1989, **46**, 183.
80. M. Driess, U. Winkler, W. Imhof, L. Zsolnai and G. Huttner, *Chem. Ber.*, 1994, **127**, 1031.
81. U. Klingebiel, N. Vater, W. Clegg, M. Haase and G. M. Sheldrick, *Z. Naturforsch B*, 1983, **38**, 1557.
82. D. Stalke, M. Meyer, M. Andrianarison, U. Klingebiel and G. M. Sheldrick, *J. Organomet. Chem.*, 1989, **366**, C15.
83. N. Wiberg and H. Schuster, *Chem. Ber.*, 1991, **124**, 93.
84. H. Schumann and H. Benda, *Angew. Chem. Int. Ed. Engl.*, 1968, **7**, 812.
85. G. Fritz and R. Uhlman, *Z. Anorg. Allg. Chem.*, 1978, **442**, 95.
86. G. Fritz and W. Hölderich, *Z. Anorg. Allg. Chem.*, 1977, **431**, 76.
87. D. Hänssgen, H.Aldenhoven and M. Nieger, *J. Organomet . Chem.*, 1989, **367**, 47.
88. D. Hänssgen, A. Dörr, H. Dens and R. Jeske, *J. Organomet . Chem.*, 1995, **487**, 17.
89. C.N. Smit and F. Bickelhaupt, *Organometallics*, 1987, **6**, 1156.
90. E. Niecke, E. Klein and M. Nieger, *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 751.
91. Y. Van Den Winkel, H.M.M. Bastiaans and F. Bickelhaupt, *J. Organomet. Chem.*, 1991, **405**, 183.
92. M. Driess, S. Rell and H. Pritzkow, *J. Chem. Soc. Chem. Commun.*, 1995, 253.
93. H.R.G. Bender, E. Niecke and M. Nieger, *J. Am. Chem. Soc.*, 1993, **115**, 3314.
94. M. Driess, *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 1022.
95a. J. Escudie, C. Couret, J. Satgé, M. Andrianarison and J.D. Andriamizaka, *J. Am. Chem. Soc.*, 1985, **107**, 3378.
b. J. Escudié, C. Couret, M. Andrianarison and J. Satgé, *J. Am. Chem. Soc.*, 1987, **109**, 386.
96. J. Escudie, C. Couret, M. Andrianarison, A. Raharinirina and J. Satgé, *Phosphorus and Sulfur* , 1987, **30**, 377.
97. M. Dräger, J. Escudie, C. Couret, H. Ranaivonjatovo and J. Satgé, *Organometallics*, 1988, **7**, 1010.
98. H. Ranaivonjatovo, J. Escudie, C. Couret, J. Satge and M. Dräger, *New J. Chem.*, 1989, **13**, 389.
99. H. Ranaivonjatovo, J. Escudie, C. Couret and J. Satgé, *J. Organomet. Chem.*, 1991, **415**, 327.
100. C. Couret, J. Escudié, J. Satgé, A. Raharinirina and J. D. Andriamizaka, *J. Am. Chem. Soc.*, 1985, **107**, 8280.
101. H. Ranaivonjatovo, J. Escudie, C. Couret and J. Satgé, *J. Chem. Soc. Chem. Commun.*, 1992, 1047.
102. H. Ranaivonjatovo, J. Escudie, C. Couret, A. Kandri Rodi and J. Satgé, *Phosphorus, Sulfur and Silicon*, 1993, **76**, 61.
103. A. Kandri Rodi, Thesis, Toulouse, 1995.
104. M. Driess, R. Janoschek and H. Pritzkow, *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 460.
105. M. Driess and H. Pritzkow, *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 316.

Received: January 22, 1996 - Accepted in revised camera-ready form: January 26, 1996