STABLE METALLA-ALKENES >M=C< AND DIMETALLA-ALKENES >M=M< (M : Si, Ge, Sn)

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Abstract

All the stable doubly-bonded derivatives of the type >M=C<, >M=M< (M : Si, Ge, Sn) and their transition metal complexes prepared until now are described as well as their synthetic routes; some of their typical physicochemical data such as ^{29}Si and ^{119}Sn NMR chemical shifts and the M=C or M=M double bond lengths are also reported.

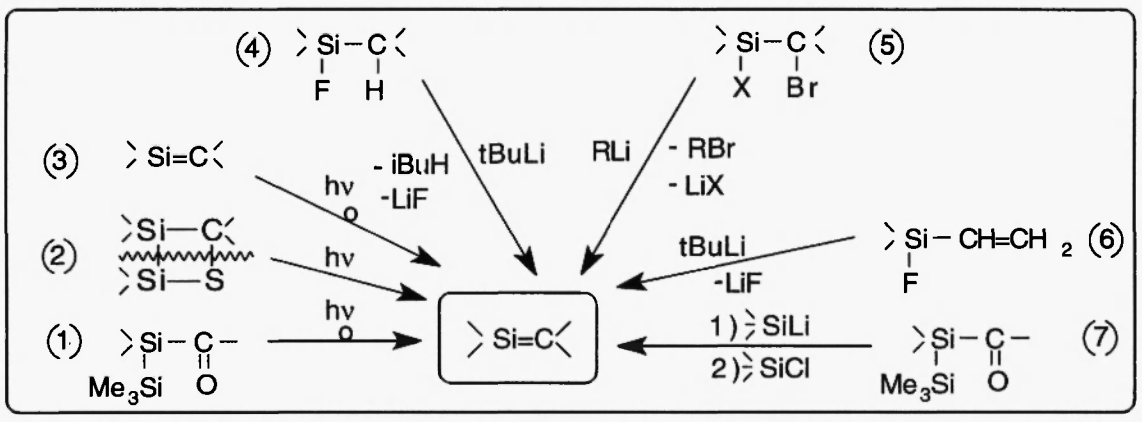
Introduction

The synthesis of doubly-bonded species of group 14 elements such as metalla-alkenes >M=C< and dimetalla-alkenes >M=M< (M : Si, Ge, Sn) has been during a long time a great challenge for organometallic synthetic chemists. Since the isolation, in 1981, of the first stable silene by Brook [1] and disilene by West [2], exciting progress has been made in this field and now many species which were thought to exist only as intermediates have been prepared and isolated. The previous reviews published in this field (silicon [3-12], germanium [12-17] and tin [14]) were generally devoted to only one group 14 element or to one type of doubly-bonded species (>M=C< or >M=M<).

Thus, the purpose of this paper is to collect in a sole short review, presented in the form of tables and with brief comments, the information on the synthesis and the characteristic physicochemical data (^{29}Si, ^{119}Sn NMR, double bond lengths) of all the doubly-bonded silicon, germanium and tin derivatives of the type metalla-alkenes >M=C< and dimetalla-alkenes >M=M< prepared until the end of 1995. The synthetic routes to these derivatives are summarized in schemes. As the synthesis and the reactivity of transient species of this type are particularly well documented, we will limit our study to stable derivatives or to derivatives at least characterized by physicochemical methods such as NMR or UV. The reactivity of such compounds is not reviewed in this paper.

I - METALLA-ALKENES

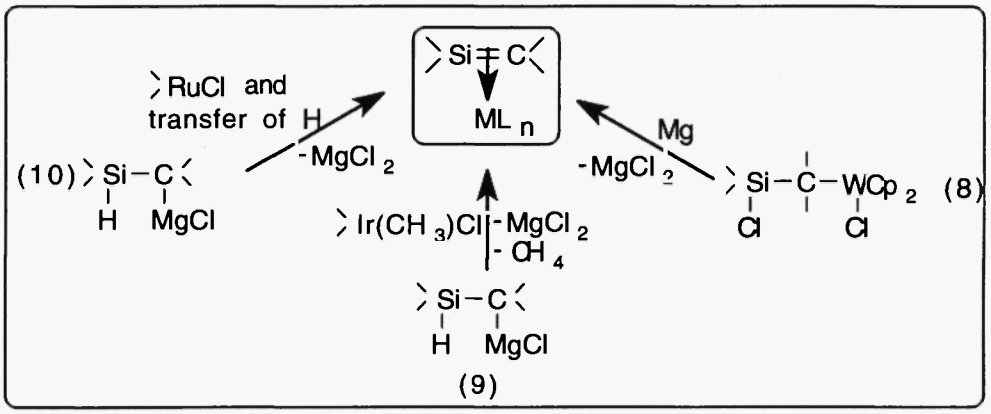
1) Silenes



(1) the photolysis of an acylsilane, involving a migration of the Me_3Si group onto oxygen, was the

first route to stable silenes [1] ; many silenes have been obtained by this route.
(2) [2+2] decomposition of a four-membered heterocycle under irradiation.
(3) rearrangement of a silene to another silene.
(4) dehydrofluorination of a fluorosilane by a lithio compound followed in some cases by complexation with a Lewis base.
(5) exchange Li/Br, followed by elimination of LiX.
(6) addition of tBuLi on the vinyl double bond, followed by elimination of LiF. This route was initiated by Jones [18] ; many transient silenes have been obtained by Auner by this process [19].
(7) action of a silyllithio compound on an acylsilane followed by reaction with a chlorosilane.

In some cases silenes have been stabilized owing to the complexation of silicon by Lewis bases such as ethers or amines [24, 28, 29].



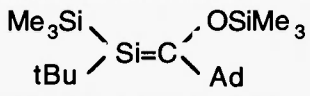
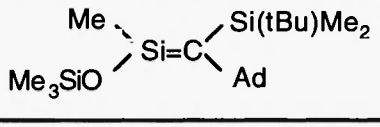
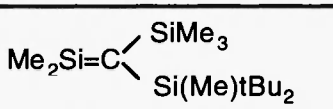
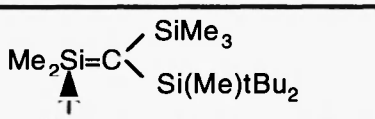
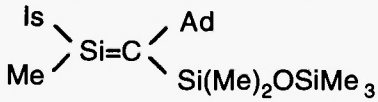
Routes (8), (9) and (10) afford silenes stabilized by complexation with transition metals.
(8) reaction of magnesium with a complex of tungsten.
(9) reaction of a Grignard compound with $(Me_3P)Cp^*Ir(Me)Cl$ followed by loss of methane.
(10) reaction of a Grignard compound with a complex of Ru, followed by a transfer of hydrogen.

In contrast to free silenes, which are easily characterized by their low field chemical shifts in ^{29}Si NMR, complexed silenes present shifts at much higher field, close to those of tetracoordinated silanes. Thus, such compounds can be considered as intermediate structures between silenes and three-membered ring heterocycles.

Table 1 : SILENES

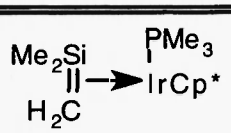
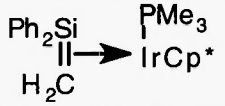
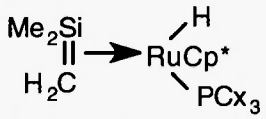
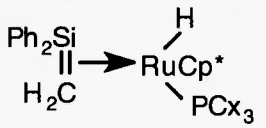
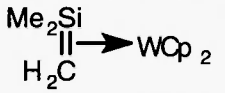
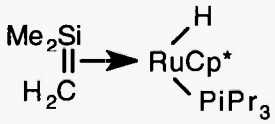
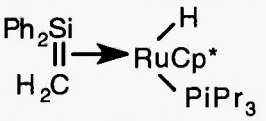
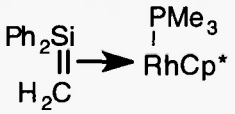
SILENES	synthetic routes	$\delta\ ^{29}Si$ (ppm)	d(Si=C) (Å)	ref.
$(Me_3Si)_2Si=C(OSiMe_3)(Ad)$	1	+ 41. 80	1.764	1 20
$(Me_3Si)_2Si=C(OSiMe_3)(CEt_3)$	1	+ 54. 30		20

Table 1 : followed

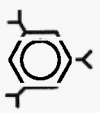
SILENES	synthetic routes	$\delta^{29}Si$ (ppm)	d(Si=C) (Å)	ref.
$(Me_3Si)_2Si=C(tBu)OSiMe_3$ †	1	+ 41. 44		1
$(Me_3Si)_2Si=C(Mes)OSiMe_3$ †	1	+ 37.70		21
$(Me_3Si)_2Si=C(Mes)OSiEt_3$	7	+ 34.30		22
	1	+ 73.70		21 b, 23
 †	3	+ 126.5		21 b, 23
	4	+ 144.2	---------- 1.702	24 - 27 ---------- 28
	4		1.747 ----------	28 ---------- 24
$Me_2Si=C(SiMe_2Ph)_2$  $EtNMe_2$	5		1.761	29
$Me_3Si(Ph)Si=C(CEt_3)OSiMe_3$	1	+ 61.60		21 b, 30 a
$Me_3Si(Mes)Si=C(Ad)OSiMe_3$	1	+ 44.05 (Z) + 41.84 (E)		30 b
$(Me_3Si)_2Si=C(bco)OSiMe_3$	1	+ 42.40		30 a
$Mes_2Si=CPh_2$	2	+ 76.68		31
$Mes_2Si=CHCH_2tBu$	6	+ 77.60		32
$Me_3Si(Is)Si=C(Ad)OSiMe_3$	1	+ 43.31 (Z) + 40.33 (E)		33
	3	+ 108.08		33

† dimerize slowly at room temperature

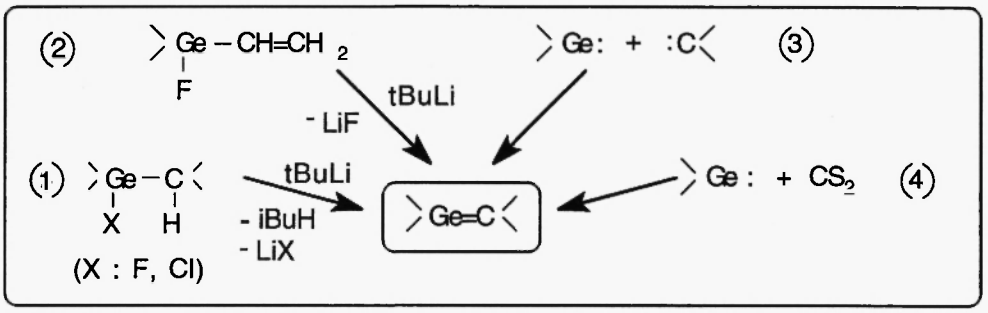
Table 1 : followed

COMPLEXED SILENES	synthetic routes	$\delta\ ^{29}Si$ (ppm)	d(Si=C) (Å)	ref.
	9			34
	9	- 20.77	1.810	34, 37
	10			35, 37
	10			35, 37
	8	- 15.77	1.800	36, 37
	10			37
	10	+ 6.14	1.782	37
	9			34

bco : (2,2,2)bicyclooctyl , Cx : Cyclohexyl , Cp* : pentamethylcyclopentadienyl

Is :  Ad :  Mes : 

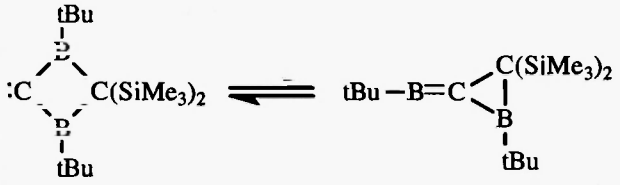
2) Germenes



(1) reaction of tBuLi on a chloro- or fluorogermane substituted by a fluorenyl group, followed by elimination of LiF.

(2) addition of tBuLi on the $CH=CH_2$ double bond, followed by elimination of LiF.

(3) coupling reaction between a stable germylene and a carbene. This route, used by Berndt, involves the following "cryptocarbene" which can, depending on the substrate, behave as a boron-carbon doubly-bonded compound.



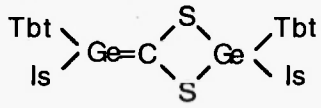
(4) reaction of a stable germylene with CS_2, giving initially the ylide Tbt(Tip)Ge^--S^+=C=S, followed by cyclisation to a germathiirane and reaction with a second molecule of germylene.

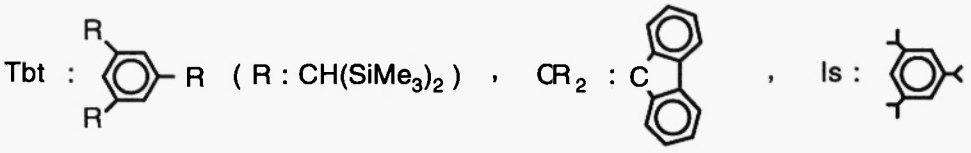
Table 2 : GERMENES

GERMENES	synthetic routes	δ ^{13}C of sp^2 C (ppm)	d(Ge=C) (Å)	ref.
$Mes_2Ge=CR_2$	1		---------- 1.801, 1.808 (*)	38 ---- 39
$(Me_3Si)_2N$, $(Me_3Si)_2N$, Ge=C, tBu, B, C, B, tBu, $SiMe_3$, $SiMe_3$	3	+ 115	1.827	40, 41
Me_2Si, N, tBu, N, tBu, Ge =C, tBu, B, tBu, B, tBu, C, $SiMe_3$, $SiMe_3$	3	+ 93		40, 41
$[(Me_3Si)_2CH]_2Ge=CR_2$	1			42
$(Me_3Si)_2CH$, Mes, $Ge=CR_2$	1			42

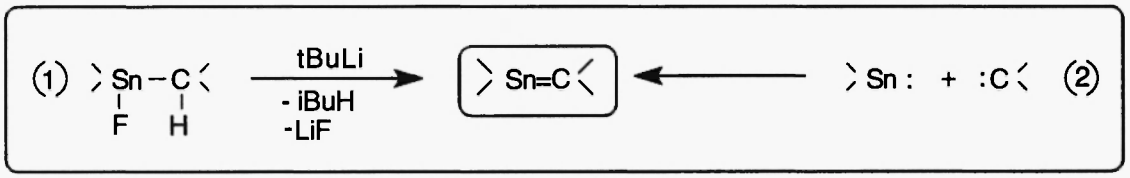
(*) two independent molecules in the unit cell

Table 2 : followed

GERMENES	synthetic routes	$\delta^{13}C$ of sp^2 C (ppm)	d(Ge=C) (Å)	ref.
$(R_2CH)_2Ge=CR_2$	1			43
$R_2CH(tBu)Ge=CR_2$	1	+ 79.80		43
$Mes_2Ge=CHCH_2tBu$	2	+ 124		44
	4		1.771	45



3) Stannenes



(1) reaction of tBuLi with a fluorostannane substituted by a fluorenyl group, then elimination of LiF. This stannene slowly dimerizes at room temperature.
(2) coupling reaction between a stable stannylene and a stable carbene or the "cryptocarbene" already used for the synthesis of stable germenes.

Table 3 : STANNENES

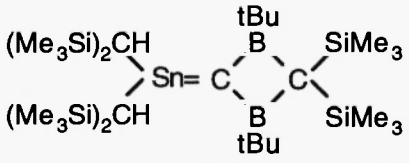
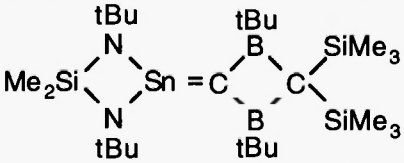
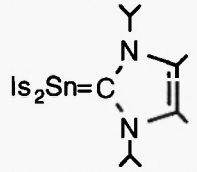
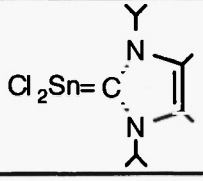
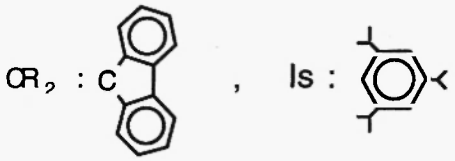
STANNENES	synthetic routes	$\delta^{119}Sn$ (ppm)	d(Sn=C) (Å)	ref.
	2	+ 835	2.025	41, 46
	2	+ 647		41, 46
$Is_2Sn=CR_2$	1	+ 288		47

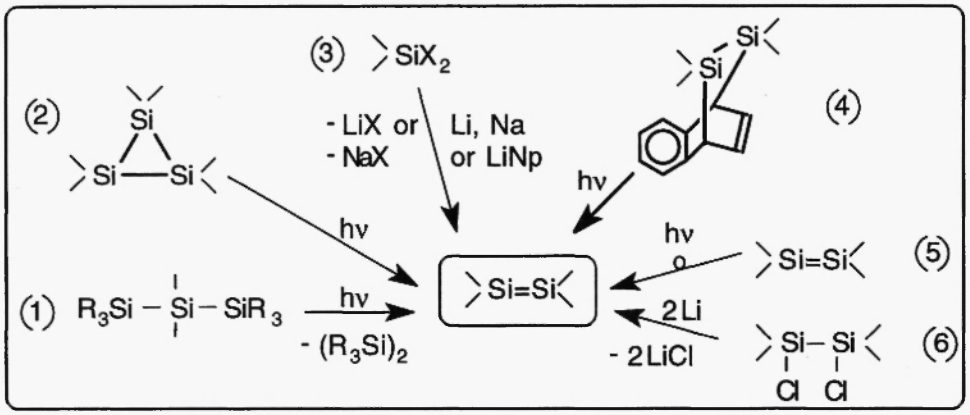
Table 3 : followed

STANNENES	synthetic routes	$\delta^{119}Sn$ (ppm)	d(Sn=C) (Å)	ref.
	2	+ 710	2.379	48
	2	- 59.4	2.290	49

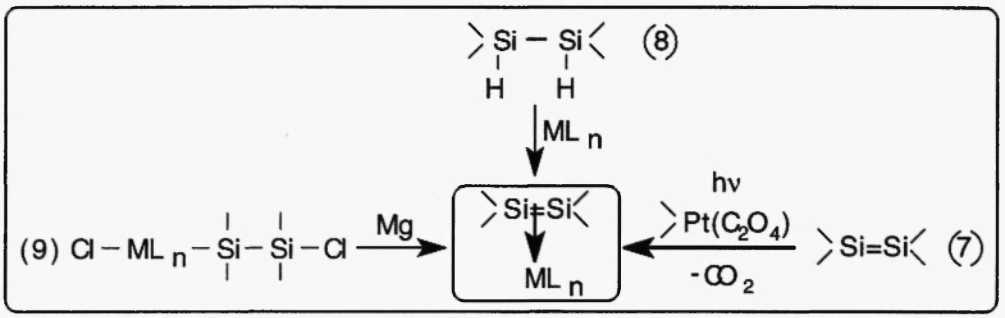


II - DIMETALLA-ALKENES

1) Disilenes



(1) photolysis of an acyclic trisilane, with dimerization of a silylene intermediate. The first disilene was obtained by this route [2] which also allowed the formation of unsymmetrical disilenes by photolysis of two different trisilanes.
(2) the photolysis of a cyclic trisilane is also a route widely used.
(3) reaction of lithium, sodium or lithium naphthalenide (most of the cases) with a dihalo (dialkyl- or diaryl)silane.
(4) this route (retro Diels-Alder reaction by photolysis) was only used for the synthesis of metastable $tBu_2Si{=}SitBu_2$, which was characterized by UV [55].
(5) cis-trans isomerisation (by photolysis or not) or rearrangement of a disilene involving an exchange of substituents between two silicon atoms.
(6) reaction of lithium with a dichlorodisilane.



(7) direct complexation of a stable disilene by a transition metal. Some less sterically congested, and thus transient disilenes, have also been stabilized by complexation with transition metals.
(8) reaction of a disilane with a transition metal with loss of hydrogen.
(9) reaction of magnesium with $Cl-ML_n-\underset{|}{\overset{|}{Si}}-\underset{|}{\overset{|}{Si}}-Cl$

As for silenes, the complexed disilenes obtained in routes (7) and (8) present generally in ^{29}Si NMR high-field chemical shifts very different of those of free disilenes.

Table 4 : DISILENES

DISILENES	synthetic routes	$\delta\,^{29}Si$ (ppm) ($^1J_{SiSi}$, Hz)	d(Si=Si) (Å)	ref.
$Mes_2Si=SiMes_2$	1, 3	+ 63.6	2.160	2, 50, 62
$dmp_2Si=Sidmp_2$	1, 5	+ 64.06		51, 52
$Mes_2Si=Sidmp_2$	1, 5	+ 65.19 + 62.56 (155)		51
dmp(Mes)Si=Si(Mes)dmp	1, 5	+ 63.87 (Z) + 63.86 (E)		51
$Mes_2Si=Si(Mes)dmp$	1	+ 63.14, + 64.42 (158)		51 b
$(dmp)_2Si=Si(Mes)dmp$	1	+ 63.30, + 64.63 (156)		51 b
$dmt_2Si=Sidmt_2$	1, 5	+ 65.15		51 c
$Mes_2Si=Sidmt_2$	1, 5	+ 64.22, + 64.11		51 c
Mes(dmt)Si=Si(dmt)Mes	1, 5	+ 64.37 (E), + 64.15 (Z)		51 c
$dmp_2Si=Sidmt_2$	1, 5	+ 65. 82, + 63.24		51 c
tBu(Mes)Si=Si(Mes)tBu	1, 2	+ 94.7 (Z) + 90.3 (E)	2.143 (E)	57, 58, 62
R(Mes)Si=Si(Mes)R (R : $N(SiMe_3)_2$)	1	+ 61.9 (E) + 49.4 (Z)		59
Ad(Mes)Si=Si(Mes)Ad	1	+ 92.6 (Z) + 87.1 (E)	2.138 (E)	62, 63
$dep_2Si=Sidep_2$	2		2.140	64, 65

Table 4 : followed

DISILENES	synthetic routes	δ ^{29}Si (ppm) ($^{1}J_{SiSi}$, Hz)	d(Si=Si) (Å)	ref.
$Is_2Si=SiIs_2$	3	+ 53.41	2.144	66
$[(Me_3Si)_2CH]_2Si=Si[CH(SiMe_3)_2]_2$	3			67
$(Et_3Si)_2Si=Si(SiEt_3)_2$	2			68
Tbt(Mes)Si=Si(Mes)Tbt	3	+ 56.16, + 56.74, + 57.12, + 58.12 (Z)* + 66.49 (E)	2.228 (E)	69, 70
$[iPr_2(Me)Si]_2Si=Si[Si(Me)iPr_2]_2$	3	+ 144.5		71
$[tBu(Me)_2Si]_2Si=Si[Si(Me)_2tBu]_2$	2	+ 142.1		71
$(iPr_3Si)_2Si=Si(SiiPr_3)_2$	3	+ 154.5		71
$Mes_2Si=SiIs_2$	6	+ 57.86,+ 59.40 (159.5)		72
Is(Mes)Si=Si(Mes)Is	1	+ 58.44 (Z) + 58.19 (E)		73
tBu(Is)Si=Si(Is)tBu	5 (Z) 1 (E)	+ 96.93 (Z) + 87.39 (E)	2.157 (E)	74
$Me_3Si(Is)Si=Si(Is)SiMe_3$	5 (Z) 1 (E)	+ 97.68 (Z) + 97.75 (E)	2.152 (E)	74
$(tBuCH_2)_2Si=Si(CH_2tBu)_2$ †	2			53
$tBu_2Si=SitBu_2$ †	2, 4			54 - 55
$(Et_2CH)_2Si=Si(CHEt_2)_2$ †	2			56
$(Me_3SiCH_2)_2Si=Si(CH_2SiMe_3)_2$ †	2			60
$(iBu)_2Si=Si(iBu)_2$ †	2			60
$(sBu)_2Si=Si(sBu)_2$ †	2			60
Pr(tBu)Si=Si(tBu)Pr †	2 (Z)			60
Me(tBu)Si=Si(tBu)Me †	2 (Z)			60
$(iPr)_2Si=Si(iPr)_2$ †	2			61

* 4 signals due to conformational isomers

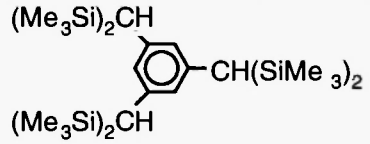
† unstable at room temperature, characterized by UV (~ 420-430 nm); see also for UV ref [14]

Table 4 : followed

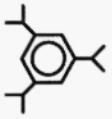
COMPLEXED DISILENES	synthetic routes	$\delta\,^{29}Si$ (ppm) ($^1J_{SiSi}$, Hz)	d(Si=Si) (Å)	ref.
Me_2Si ⇉ MCp_2 Me_2Si	9	- 20.3 (M : Mo) - 48.1 (M : W)	2.260	75
Mes_2Si ⇉ $Pt(PR_3)_2$ Mes_2Si	7	- 23.9 (R : Et) - 29.1 (R : Ph)		76
R'_2Si ⇉ Pt(P,P = PR_2, PR_2) R'_2Si	8	+ 19.60 (R : Ph, R' : iPr) + 23.47 (R : Ph, R' : Me) - 7.84 (R : Cx, R' : Ph)		76

dmp : 

Mes : 

Tbt : 

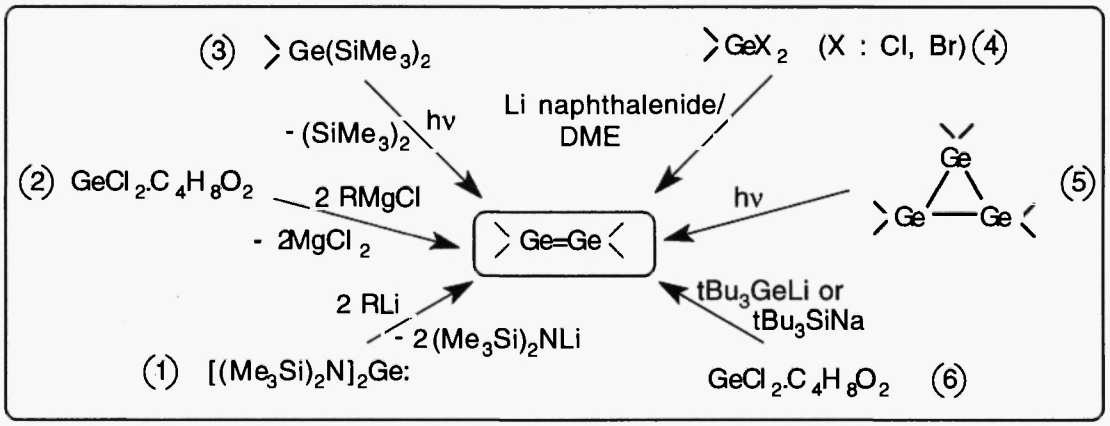
dep : 

Is : 

dmt : 

Cx : Cyclohexyl

2) Digermenes



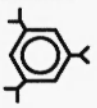
(1) reaction of a lithio compound with a germylene ; this route allowed the synthesis of the first compound with a germanium-germanium double bond in the solid state by Lappert (R : $(Me_3Si)_2CH$) [78]. This compound behaves as two germylenes in solution.
(2) reaction of a Grignard reagent with the dichlorogermylene-dioxane complex.
(3) coupling of two germylenes obtained by irradiation of a disilylgermane.
(4) reaction of lithium naphthalenide with a dichloro- or dibromogermane.
(5) photolysis of a trigermirane leading to germylenes which dimerize ; this route is also widely used.
(6) reaction of a germyllithium or a silylsodium derivative with the dichlorogermylene-dioxane

complex. The trigermirene, first compound with an intracyclic germanium-germanium double bond, is formed via a multi-step mechanism [87].

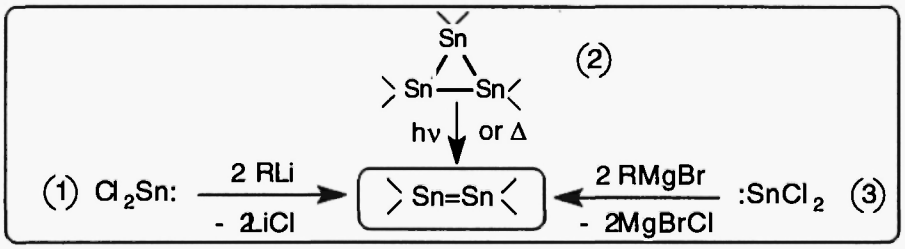
Table 5 : DIGERMENES

DIGERMENES	synthetic routes	d(Ge=Ge) (Å)	ref.
$dmp_2Ge{=}Gedmp_2$ *	3		77 a
$Mes_2Ge{=}GeMes_2$ *	3		77 b, 77c
Mes(tBu)Ge=Ge(tBu)Mes *	3 (Z/E)		14
Mes(dep)Ge=Ge(dep)Mes *	3 (Z/E)		14
$[(Me_3Si)_2CH]_2Ge{=}Ge[CH(SiMe_3)_2]_2$ **	1, 2	2.347	78 - 81
$dip_2Ge{=}Gedip_2$	1, 4		82
$dep_2Ge{=}Gedep_2$	3, 5	2.213	83, 84
$ls_2Ge{=}Gels_2$	3		85, 86
dip(Mes)Ge=Ge(Mes)dip	4, 5 (Z/E)	2.301 (Z)	84
tBu_3M, $MtBu_3$ Ge, tBu_3MGe ═ $GeMtBu_3$ (M : Si, Ge	6	2.239 (M : Si)	87

* not isolated ; characterized by UV
** behaves as two germylenes in solution

dep :  , dip :  , dmp :  , ls : 

3) Distannenes

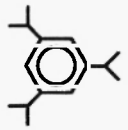


(1) reaction of a lithio compound with a stannylene ; this route gave the first compound with a tin-tin double bond in the solid state with R : $(Me_3Si)_2CH$ [81, 89]. However, in solution, this compound behaves as two stannylenes.
(2) thermolysis or photolysis of a tristannirane (same route than for disilenes or digermenes).
(3) reaction of a Grignard compound with dichlorostannylene.

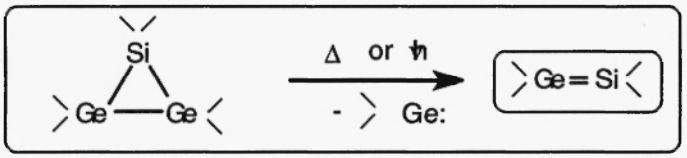
Table 6 : DISTANNENES

DISTANNENES	synthetic routes	δ ^{119}Sn (ppm) ($^{1}J_{SnSn}$, Hz)	d(Sn=Sn) (Å)	ref.
$[(Me_3Si)_3Si]_2Sn=Sn[Si(SiMe_3)_3]_2$ *	1		2.8247	88
$[(Me_3Si)_2CH]_2Sn=Sn[CH(SiMe_3)_2]_2$ **	1	---------- 725 and 740 at 165 K ---------- 735 (3317) and 750 (1784) at 183 K	2.764 ---------- ----------	81, 89 ---------- 90 ---------- 67
$Is_2Sn=SnIs_2$	2	427.3 (2930) at 205 K		91, 92
$Ar'_2Sn=SnAr'_2$ *	3	1330* at 298 K 1401* at 373 K	2.910	93

* in solution, only the stannylene is observed
** the NMR results suggest that this compound exists, at least partially, in a distannene form in solution at low temperatures

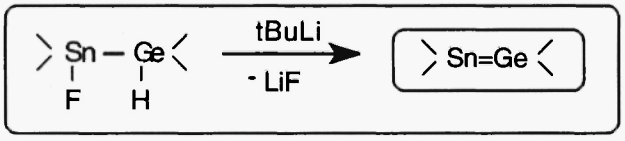
Is :  , Ar' : 

4) Germasilenes



thermolysis or photolysis of a digermasilirane with the formation of a germylene. The germasilene $Mes_2Ge=SiMes_2$ [94, 95] is not stable at room temperature and rearranges to silylgermylene :Ge(Mes)-$SiMes_3$, but can be evidenced by trapping reactions and by its low field ^{29}Si chemical shift (δ : + 80.6 ppm).

5) Stannagermenes



reaction of tBuLi with a fluorostannylgermane in Et_2O/toluene 30/70. Above 0°C, the stannagermene $Is_2Sn=GeMes_2$ (Is : 2,4,6-triisopropylphenyl) (δ ^{119}Sn : + 360 ppm) affords a distannagermirane. The synthesis and reactivity of this stannagermene will be described soon [96].

Conclusion

Doubly-bonded compounds of silicon and tin can generally be characterized by their low-field shifts in ^{29}Si and ^{119}Sn NMR and some of them by X-ray, which shows, at least for silicon and germaniun compounds, a significant shortening of the double bond in relation to the corresponding single bond (~ 7-10 %). However, for tin derivatives, the shortening is generally extremely small (~ 2-4 %), which explains the particular behaviour of these derivatives.

All these compounds present a high reactivity despite the large steric hindrance necessary for their stabilization.

As shown on table 7, the number of stable doubly-bonded derivatives decreases drastically by going down in the group 14, from silicon to tin. If many silenes or disilenes have now been synthesized, stannenes or distannenes are still very rare and no doubly-bonded compounds of lead have so yet been described ; moreover, most of the doubly-bonded tin compounds which are reported here slowly dimerize or behave as stannylenes in solution.

We can also note that dimetalla-alkenes of the type >M=M'< with two different heavy group 14 elements, probably because their synthesis is more difficult, are still very rare : only two metastable derivatives of this type have been evidenced by NMR at low temperature.

In conclusion, even if this field of doubly-bonded elements of group 14 has been widely studied during the last fifteen years, a great progress can still be made, particularly to find new synthetic routes, novel stabilizing groups and to better understand the influence of electronic factors on the stabilization.

table 7

METALLA-ALKENES	>M=C<	>Si=C< >Ge=C< >Sn=C<	27 * 9 5
DIMETALLA-ALKENES	>M=M<	>Si=Si< >Ge=Ge< >Sn=Sn<	41 ** 7 4
		>Ge=Si< >Sn=Ge<	1 1

* including 8 complexed silenes ; ** including 7 complexed disilenes
Z and E isomers are considered as different compounds

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