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Group 14 Metalloles. 1. Synthesis, Organic Chemistry, and Physicochemical Data

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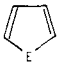
Abbreviations

The following abbreviations are used throughout the text: DTB, 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene; DDB, 1,4-dilithio-1,4-diphenyl-1,3-butadiene; DPSI, 2,5-diphenylsilole; DPGE, 2,5-diphenylgermole; DPSN, 2,5-diphenylstannole; TPSI, 2,3,4,5-tetraphenylsilole; TPGE, 2,3,4,5-tetraphenylgermole; TPSN, 2,3,4,5-tetraphenylstannole; TMSI, 1,1,3,4-tetramethylsilole; TMGE, 1,1,3,4-tetramethylgermole.

Introduction

The five-membered heterocyclic dienes 1 such as furan, thiophene, and pyrrole represent an important domain of heterocyclic chemistry. Some are found in living organisms (porphyrins), some are used in chemical processes for biomass exploitation (furan derivatives), and others are used as precursors of new electrical conductors (polypyrroles, polythiophenes).



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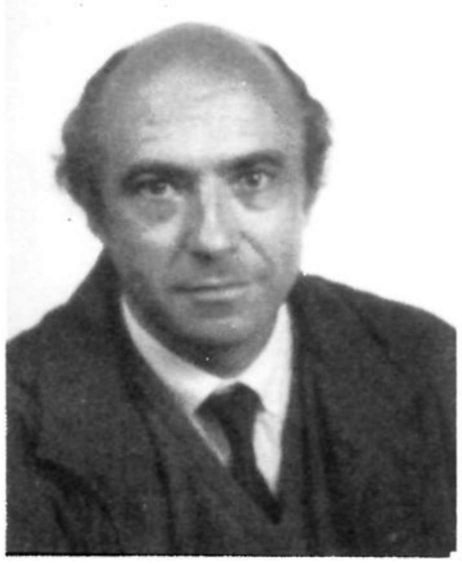
Jacques Dubac was born in 1938 in Grenade-sur-Garonne, France. His graduate work (Doctorat d'Etat ès Sciences Physiques) was performed at the Université Paul Sabatier in Toulouse under the direction of Professors M. Lesbre and P. Mazerolles. He became Professor of Chemistry at the same univeristy in 1980. Dr. Dubac's principal research interests are in synthetic and mechanistic organometallic chemistry, especially that of silicon and germanium compounds.

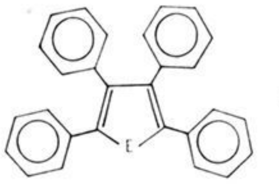


André Laporterie was born in 1944 in Caussade-Rivière (Hautes-Pyrénées), France. He obtained his Licence ès Sciences Physiques in 1965, the Doctorat de 3° Cycle in 1968, and the Doctorat d'Etat degree in 1976 at the Université Paul Sabatier. His principal research deals with cycloadditions and ene and retro-ene reactions in group 14 organometallic chemistry. He is Maître de Conférences in Organic Chemistry at the same University.

Georges Manuel is Professor of Chemistry at the Université Paul Sabatier, Toulouse, France. He was born in Toulouse in 1937, and studied at the Ecole Nationale Supérieure de Chimie de Toulouse, where he received a degree in engineering in 1959. He also obtained the diploma Licence ès Sciences Physiques and then the Doctorat d'Etat de Sciences Physiques in 1970 from the Université Paul Sabatier in the laboratory of Professor M. Lesbre and Dr. P. Mazerolles. Professor Manuel's principal research interest is devoted to sila- and germacycloalkene compounds as synthons for organometallic derivatives, polymeric materials, and carbide deposits. He used to fly to Los Angeles, where a joint program was developed with Professor W. P. Weber at the University of Southern California.

A large number of compounds are now known where E may be a main-group or a transition element. Of the heterocyclopentadienes, or *heteroles*, containing an element other than oxygen, sulfur, or nitrogen, the chemistry of phospholes has been most extensively developed.[1]

The development of group 14 heterole chemistry[2] (also called *metalloles* due to the metallic nature of the elements E = Si, Ge, Sn, and Pb) is not unlike that of the group 15 heteroles: the discovery of siloles, germoles, and stannoles coincides with that of phospholes, arsoles, and stiboles (**2**);[3] the synthesis of simple het-

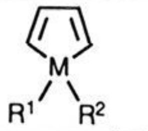


(2)

eroles (**1**) proved to be more difficult, and measurable progress in this area has only been achieved in recent years, especially in the case of the group 14 heteroles. Noteworthy events include the synthesis of 1-methylphosphole (E = PMe),[4] 1-methylsilole (E = SiHMe),[5] 1,1-dimethylsilole (E = $SiMe_2$),[6,7] 1,1-dimethylgermole (E = $GeMe_2$),[8] and phosphole (E = PH).[9]

In this review, we present the methods of group 14 metallole synthesis including benzometalloles (metallafluorenes and metallaindenes), their organic chemical properties, and their physicochemical data. Colomer, Corriu, and Lheureux (companion paper in this issue; part 2) deal with ionic species and the transition-metal complexes of group 14 metalloles.

TABLE 1. C-Unsubstituted Group 14 Metalloles

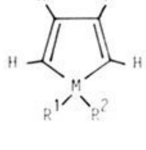


M	R^1	R^2	remarks	ref
Si	H	H	dimer (low yield)	16
Si	Me	H	monomer (unstable): adduct with MA, HFB; dimer: bp 42–44 °C/0.1 Torr, MS, NMR (^1H)	5
Si	Me	Me	monomer (unstable): NMR (^1H, ^{13}C), adduct with MA; dimer: bp 110 °C/28 mmHg, NMR (^1H, ^{29}Si), MS	6, 7, 20
Ge	Me	Me	monomer (unstable): NMR (^1H), adduct with MA;	8, 17
			dimer: NMR (^1H)	17a
Sn	^nBu	^nBu	monomer (stable): bp 80 °C/0.01 Torr, NMR (^1H, ^{13}C), MS	21b

I. *Synthesis*

A. C-Unsubstituted Metalloles (Table 1)

The synthesis of C-unsubstituted group 14 metalloles has been one of the most interesting challenges, pursued by a number of research groups between 1960 and 1980.

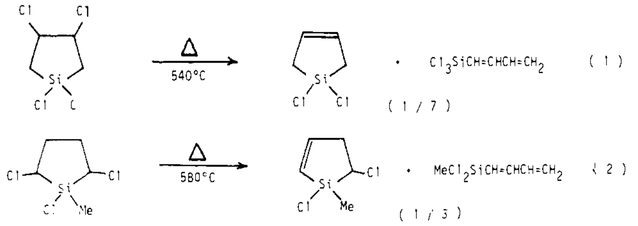


M = Si, $R^1 = R^2 = H$ (**3**)
$R^1 = H$, $R^2 = Me$ (**4**)
$R^1 = R^2 = Me$ (**5a**)
M = Ge, $R^1 = R^2 = Me$ (**5b**)

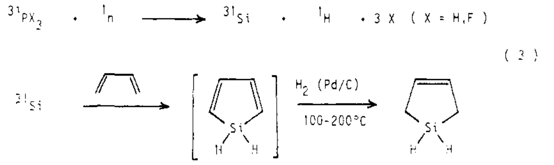
Attempts at catalytic dehydrogenation of metallacyclopentanes[10] or metallacyclopentenes[11] failed or proved impossible to reproduce. Goubeau et al.,[10b] on the one hand, and Nefedov et al.,[10c] on the other, reported having identified 1,1-dimethylsilole (**5a**) during dehydrogenation of 1,1-dimethylsilacyclopentane (3–9% yield) after having separated the products by gas-phase chromatography. It is now beyond doubt, based on studies by Dubac[6] and Barton,[7] that this compound, which is unstable as a monomer, could not be present in the mixture obtained. The catalytic dehydrogenation of 1,1-dimethylgermacyclopent-3-ene occurs but 1,1-dimethylgermole (**5b**) could not be identified among the reaction products.[11]

Other attempts to synthesize these metalloles by dehydrohalogenation of polychloro(or bromo)metallacyclopentanes also met with failure.

Thermolysis of chlorinated silacyclopentanes does not yield 1,1-dichlorosilole as originally reported[12a,b] but butadienylsilanes and silacyclopentenes[12c,d] (eqs 1 and 2). 1,1-Dichlorosilole was not identified but the authors proposed its transient existence in the pyrolysate.[12d] Although not supported by experimental data, this hypothesis remains intriguing, as it has recently been observed (cf. section I.E.1.b) that 1-chloro-1,3,4-trimethylsilole is unstable. Consequently, all attempts to synthesize these compounds could only meet with failure. In the germole series, dehydrobromination of 1,1,3,4-tetrabromogermacyclopentane or 1,1-dimethyl-2-bromogermacyclopent-3-ene also failed.[13]



Synthesis of $[^{31}\text{Si}]$silole (**3**) was attempted by the reaction of recoil silicon-31 atoms with butadiene[14] (eq 3). The chemical identification (high-temperature catalytic hydrogenation) is probably erroneous because both 1-methylsilole (**4**)[5] and 1,1-dimethylsilole (**5a**) are unstable[6,7] and dimerize instantly. Indeed, this method has already been criticized.[15]

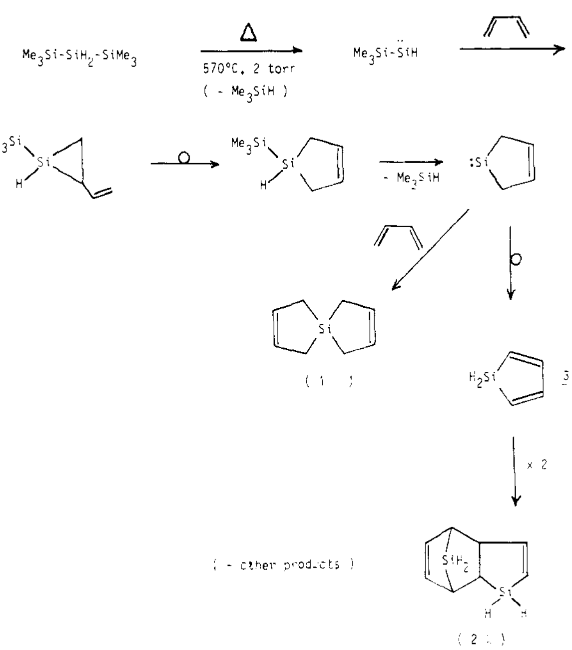


In 1986, Boo and Gaspar[16] reported the formation of the silole dimer (2% yield) during the pyrolysis of 1,1,1,3,3,3-hexamethyltrisilane with butadiene (Scheme 1).

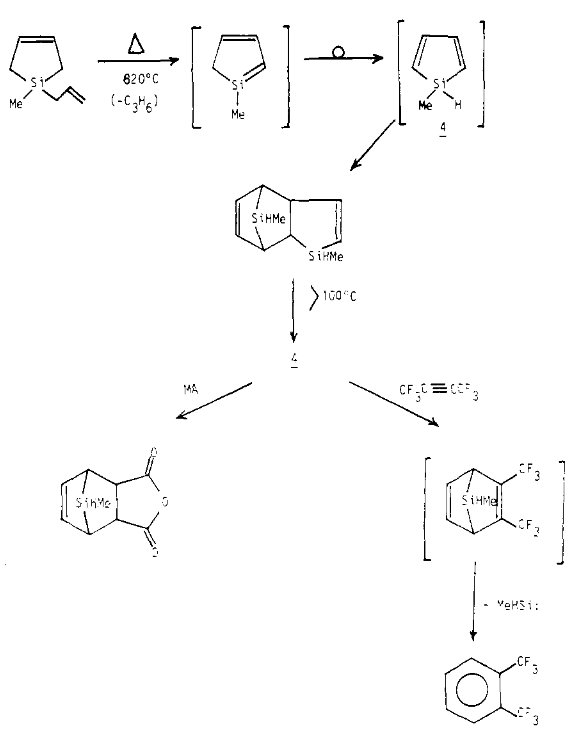
The first C-unsubstituted silole, 1-methylsilole (**4**), was obtained by flash vacuum pyrolysis of 1-allyl-1-methyl-1-silacyclopent-3-ene (Barton, 1979)[5] (Scheme 2) and identified as its dimer. 1-Methylsilole undergoes in situ Diels–Alder reaction with various dienophiles to yield a stable adduct.

The first *monomeric* C-unsubstituted silole, 1,1-dimethylsilole (**5a**), was prepared simultaneously by Burns and Barton[7] and ourselves[6] in 1981. It is produced by dehydration, either direct[6] or indirect,[17–19] of 1,1-dimethyl-1-silacyclopent-4-en-3-ol (Scheme 3). Direct dehydration (β C–H elimination) takes place in the gas phase on alumina at 300 °C/0.01 mmHg[6] or in cyclopentane at 220 °C at atmospheric pressure.[17] Dehydration in the liquid phase by acidic reagents results in β C–Si cleavage with formation of a dienic siloxane.

SCHEME 1



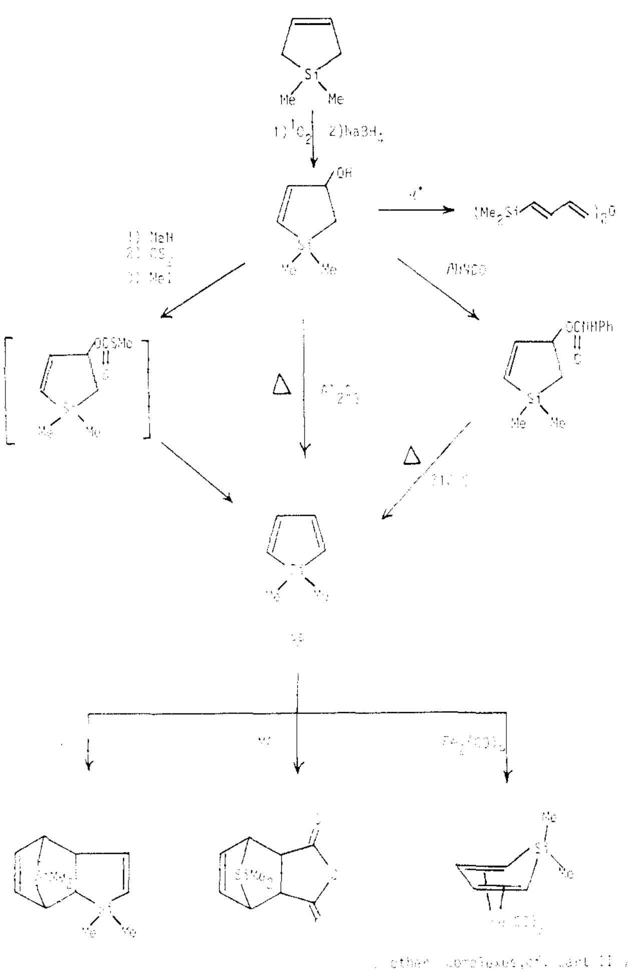
SCHEME 2



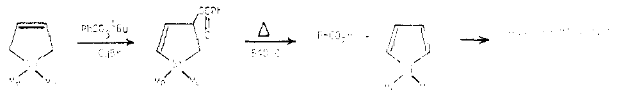
Flash pyrolysis of 3-(benzoyloxy)-1,1-dimethyl-1-silacyclopent-4-ene also affords 1,1-dimethylsilole by a specific β C–H elimination[7] (Scheme 4).

While the *S*-methylxanthate ester of the dimethylsilacyclopentenol is unstable, this method is unsuitable since this decomposition gives the dimer of silole **5a** together with siloxane $(Me_2SiC_4H_5)_2O$ (30%) due to a β C–Si elimination.[19] On the other hand, the corresponding *N*-phenylcarbamate, obtained by reaction of

SCHEME 3

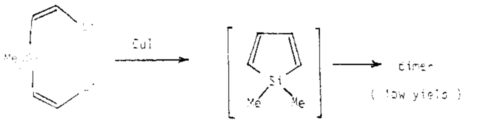


SCHEME 4



this alcohol with phenyl isocyanate, is stable. Its thermolysis at 310 °C gives regiospecifically 1,1-dimethylsilole, identified immediately after reaction by NMR or by trapping with maleic anhydride or diiron nonacarbonyl (Scheme 3).

Sakurai et al. have also prepared in low yield the dimer of 1,1-dimethylsilole by an entirely different method (eq 4), copper iodide catalyzed coupling of bis(2-lithiovinyl)dimethylsilane.[20]

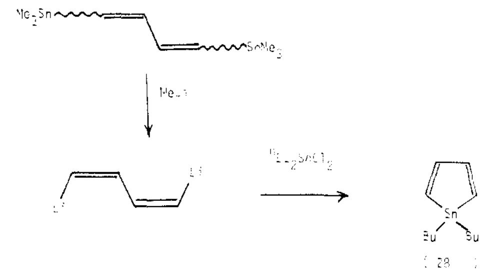


(4)

The method of synthesis, previously described for 1,1-dimethylsilole, has been successfully applied to the preparation of the first C-unsubstituted germole, 1,1-dimethylgermole (**5b**), obtained by dehydration of 1,1-dimethyl-1-germacyclopent-4-en-3-ol[8] and by thermolysis of the corresponding N-phenylcarbamate.[17]

Attempts to produce C-unsubstituted stannoles through closure of 1,4-dichlorobuta-1,3-diene with diorganotin dichlorides failed;[21a] however, the 1,1-dibutylstannole was obtained recently by Ashe and Mahmoud via the 1,4-dilithio-1,3-butadiene[21b] (Scheme 5).

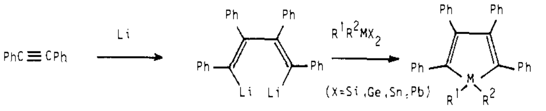
SCHEME 5



B. C-Substituted Metalloles

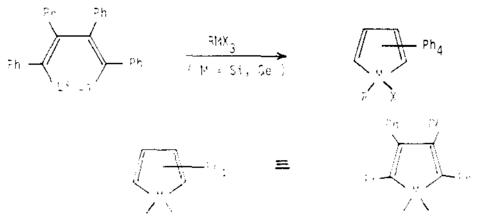
1. Synthetic Methods Involving Direct Formation of the Dienic Ring

(*a*) *Cyclization of 1,4-Dilithio-1,3-butadienes by a Polyfunctional Compound* R_nMX_{4-n} *(n = 0–2).* (*i*) *Cyclization of 1,4-Dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (DTB).* The first group 14 heterocyclopentadienes to be obtained were the 2,3,4,5-tetraphenylmetalloles, synthesized in 1959. The method described by Leavitt, Manuel, and Johnson[3c] for the preparation of cyclopentadienes containing Ge or Sn involves the condensation of the corresponding metal dihalides with DTB[22] (eq 5). Hübel and Braye[23] prepared hexaphenylsilole using the same method. It has been shown that this reaction can be accelerated by ultrasound for M = Si, R^1 = H, R^2 = Me.[48] This method, which has since received much development, has allowed the synthesis of a whole series of group 14 metalloles with a diversely substituted heteroatom.[2b,3b,24–49,233] The 2,3,4,5-tetraphenylmetalloles known to date are shown in Table 2.



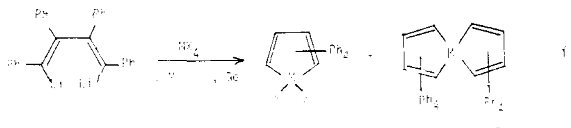
(5)

When DTB is added to the halide, the cyclization takes place in good yield with trihalogenosilanes or -germanes (eq 6).



(6)

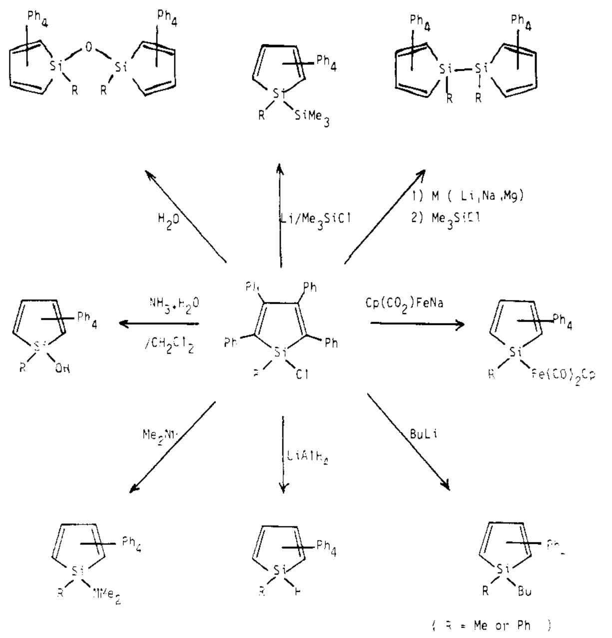
The use of tetrahalogenated derivatives MX_4 yields heteroatom-dihalogenated metalloles and the corresponding spirometalloles. 1,1-Dichloro-TPSI and -TPGE are obtained with yields of roughly 70%,[35,41] whereas the corresponding spiro derivatives are isolated in lower yield[3b,d,35] (eq 7).



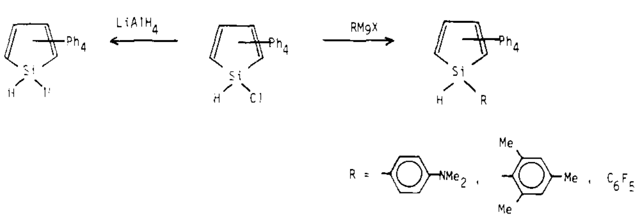
(7)

In the stannic series, octaphenyl-1,1′-spirobistannole may be obtained from $SnCl_4$ as well as from R_2SnCl_2 or R_3SnCl (R = Me, Et, ^{n}Bu),[36,47] the exocyclic Sn–C

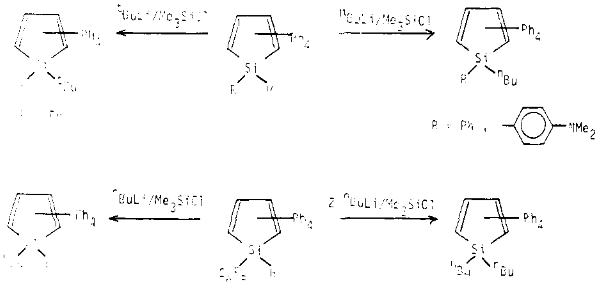
SCHEME 6



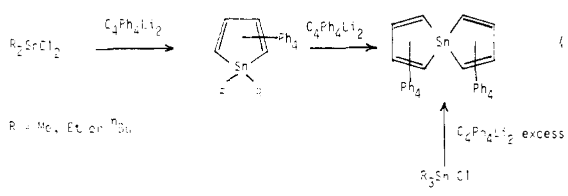
SCHEME 7



SCHEME 8



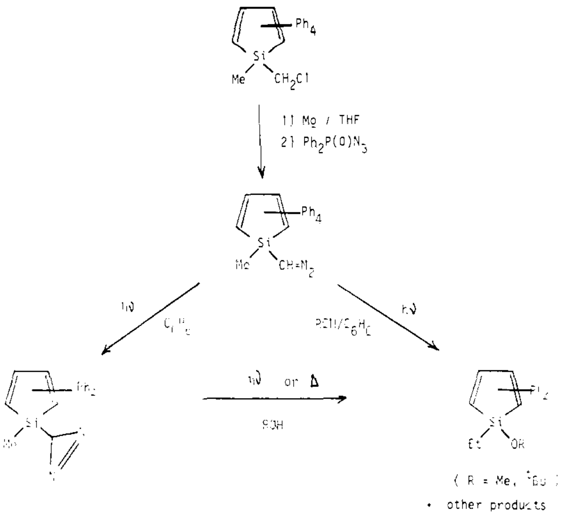
bond being easily broken by the dilithio derivative (eq 8).



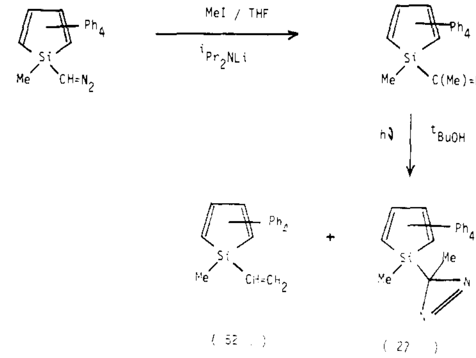
(8)

Due to the ease of substitution of a halogen atom on silicon (nucleophilic substitution), chlorosiloles are precursors of other functional siloles containing Si–H, Si–O, or Si–N bonds, saturated or unsaturated hydrocarbons on the heteroatom, or Si–metal (Fe) bonds[26–28,35,41] (Schemes 6 and 7). TPSI was thus prepared by reduction of 1-chloro-TPSI,[31] itself obtained by cyclization of DTB with the trichlorosilane.

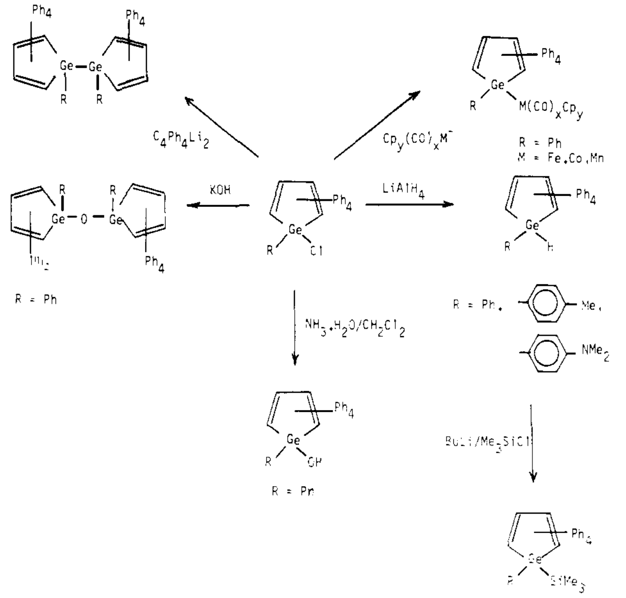
SCHEME 9



SCHEME 10



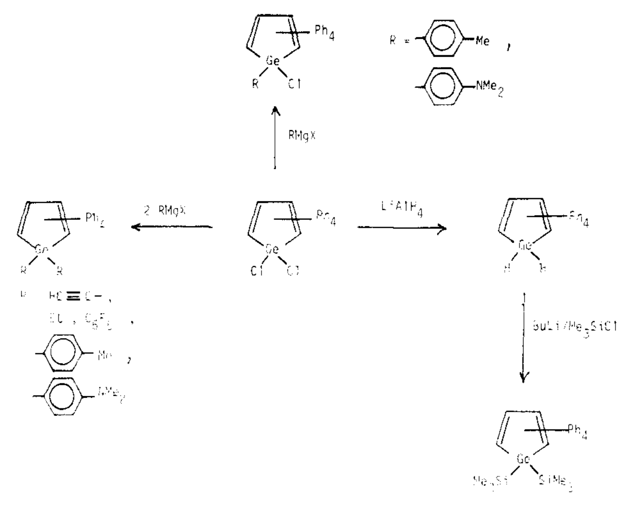
SCHEME 11



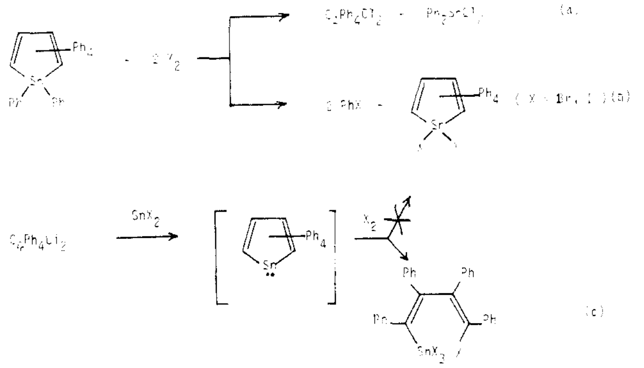
Organolithium reagents (RLi, R = ^{n}Bu, ^{t}Bu) allow the alkylation of a hydrogenosilole but substitute the C_6F_5 group in preference to a hydrogen atom[41] (Scheme 8). The Grignard reagent prepared from 1-methyl-1-(chloromethyl)-TPSI reacts with diphenylphosphoryl azide to give (1-methyl-2,3,4,5-tetraphenylsilacyclopentadienyl)diazomethane, which on photolysis in the presence of an alcohol yields the rearranged alkoxysilole[46] (Scheme 9). Photolysis in ^{t}BuOH of the diazoethane derivative gives a mixture of a diazirine and a vinylsilole (Scheme 10).

Similarly, in the germole series, mono- and dichloro derivatives are the precursors of functional and other substituted germoles[27,35,43] (Schemes 11 and 12).

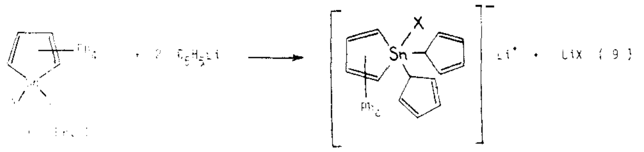
SCHEME 12

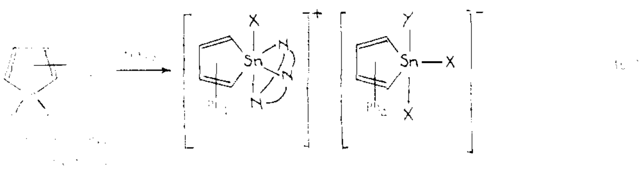


SCHEME 13

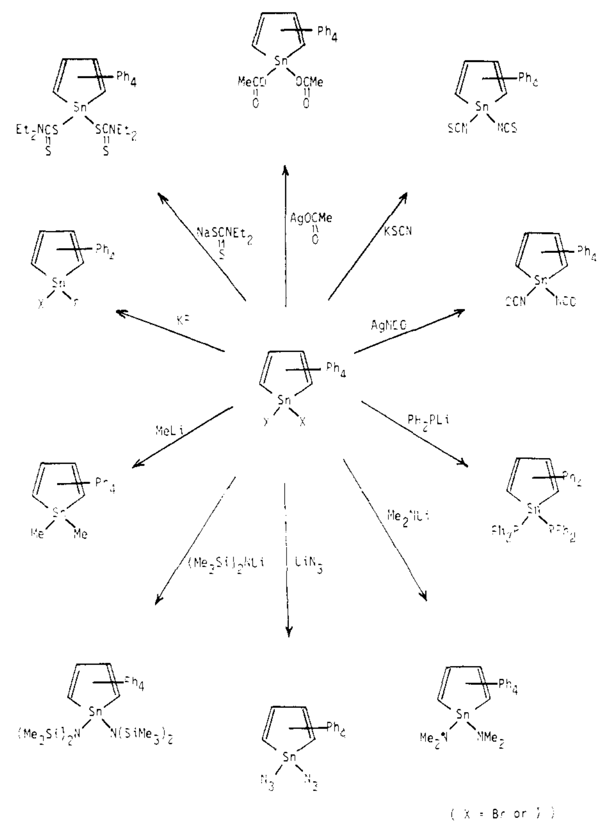


The key intermediate in the development of the derivative chemistry of the stannoles is the dibromostannole. Zuckerman's synthesis of this dihalide (Scheme 13) proceeds by cleavage with molecular bromine[39,45] of the phenyl–tin bonds of hexaphenylstannole. Iodine gives the same reaction,[45] but chlorination of hexaphenylstannole by molecular chlorine cleaves the Sn–C ring bonds.[44] Attempted synthesis of the dihalostannoles by halogenation of the intermediate tin(II) stannole from DTB and SnX_2 yields only the ring-opened products (Scheme 13). Dihalotetraphenylstannoles can be derivatized to form a series of disubstituted stannoles[44] (Scheme 14). The dihalostannoles form neutral or ionic adducts in which the tin atom is five- or six-coordinated.[44,45] Alkylation of $C_4Ph_4SnX_2$ (X = Br, I) by lithium cyclopentadienide yields ionic compounds with pseudorotating axial- and equatorial-fluxional η^1-cyclopentadienyl groups in a single tin(V) anion[45] (eq 9). With 2,2′,2″-terpyridine (terpy) dihalostannoles form double salts with a trigonal-bipyramidal anion and an octahedral cation[44] (eq 10).

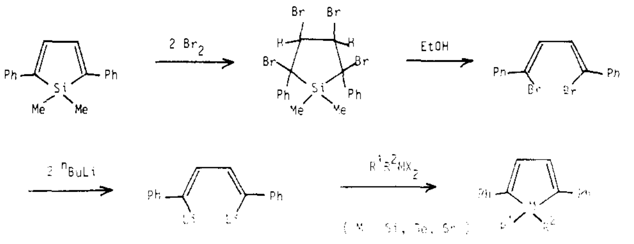




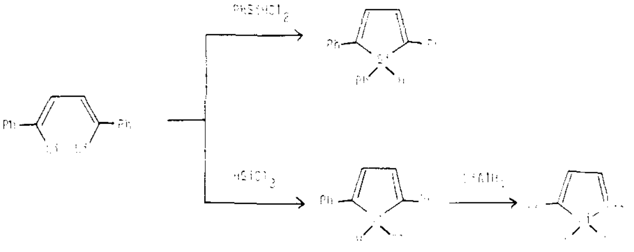
SCHEME 14



SCHEME 15



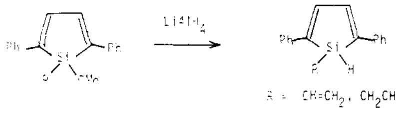
SCHEME 16



(*ii*) *Cyclization of 1,4-Dilithio-1,4-diphenyl-1,3-butadiene* (*DDB*). We owe this method of synthesis to Gilman et al.,[50] who proposed an interesting preparation of DDB from 1,1-dimethyl-DPSI, which is obtained as in eq 21. The dilithium reagent cyclizes with a dihalide $R^1R^2MX_2$ (M = Si,[50,52a] Ge,[52b] Sn[50]) (Scheme 15), or a halo hydride (Scheme 16) to yield Si-functional 2,5-diphenylsiloles.[30]

In recent work, Corriu et al.[53,54] have developed this method and shown that the use of alkoxysilanes, particularly $RSi(OMe)_3$ (R = Me, CH_2=CH, CH_2=$CHCH_2$, Me_3Si, OMe) is preferable to that of chlorosilanes for the cyclization of DDB (Scheme 15, X = Cl; R^1, R^2 = H, Me; Me, CH=CH_2; X = OMe, R^1, R^2 = Me, OMe; CH_2=CH, OMe; CH_2=$CHCH_2$) (40–70% yield). The preparation in one step of 1-R-2,5-diphenylsiloles (R = Me, Ph) is also possible from the reaction of anionic pentacoordinated silicon complexes [RSi(O$_2$C$_6$H$_4$-o)$_2$]$^-$Na$^+$ with DDB followed by reduction with LiAlH$_4$.[55]

The same authors have shown that these functional siloles may be transformed without ring cleavage in various ways, such as the reduction of methoxysiloles (eq 11) and the chlorination or alkylation of hydrogenosiloles (eq 12). They observed, too, that 2,5-diphenylsiloles appear to be less stable than the 2,3,4,5-tetraphenylsiloles, or were at least more difficult to obtain, particularly the mono- and dichlorinated as well as the spiro derivatives.



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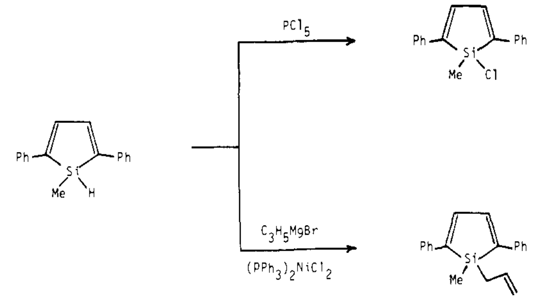
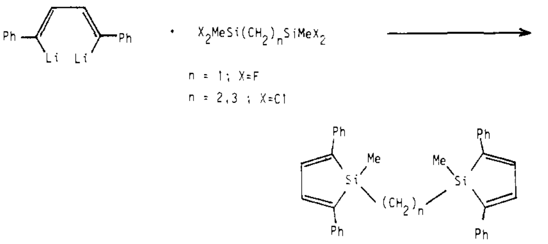


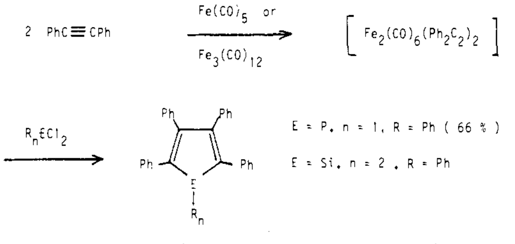
(12)

The reaction of DDB with α,ω-bis(dihalomethylsilyl)alkanes gives 1,n-bis(1-methyl-2,5-diphenyl-1-silacyclopentadien-1-yl)alkanes[42] (eq 13). The group 14 2,5-diphenylmetalloles are assembled in Table 3.



(13)

(b) *Reaction of Two Acetylenic Molecules with a R$_2$M Fragment.* (i) *Reaction between an Alkyne and a Dihalosilane via a Transition-Metal Acetylenic Complex.* In 1959, Braye and Hübel[3a] (eq 14) reported that reaction of diphenylacetylene and iron carbonyls with phenylphosphorous dichloride gave pentaphenylphosphole (140 °C, 66% yield). Hexaphenylsilole is mentioned in their paper as an analogous compound.

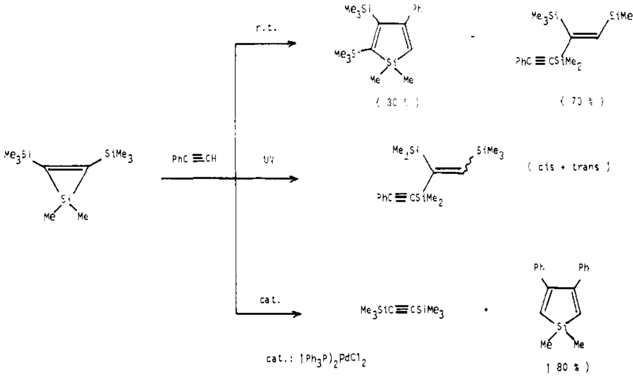


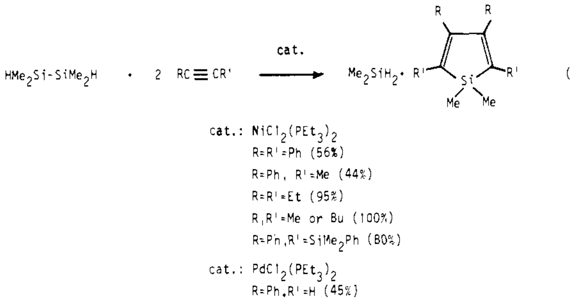
(14)

As the reaction of diphenylacetylene with iron carbonyls gives a ferracyclopentadiene complex,[125] this synthetic approach is the same as the one reported in section I.B.4.

(ii) *Reaction between an Alkyne and a Disilane.* Dichlorobis(triethylphosphine)nickel(II) or -palladium(II) catalyzes the reaction of *sym*-tetramethyldisilane with bisubstituted acetylenic compounds to give C-substituted siloles in good yield[56,59a,234] (eq 15). This reaction corresponds to the addition of dimethylsilylene (Me$_2$Si:) to two molecules of alkyne.

SCHEME 17



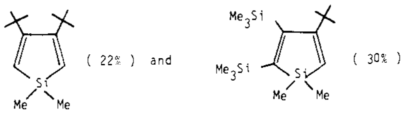


(15)

(iii) *Action of an Alkyne on a Silirene (1-Silacyclopropene).* A similar synthetic method uses a silirene, which may be an intermediate in the preceding reaction, which reacts with an alkyne in the presence of a catalyst [(Ph$_3$P)$_2$PdCl$_2$,[57,58] (Et$_3$P)$_2$NiCl$_2$,[59] (Et$_3$P)$_4$Ni[60]].

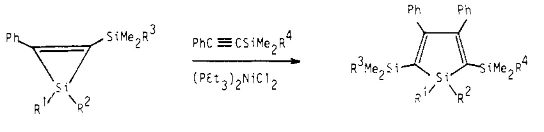
For example, reaction of phenylacetylene with 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene catalyzed by (PPh$_3$)$_2$PdCl$_2$ yields 1,1-dimethyl-3,4-diphenylsilole (80%)[57] (Scheme 17). This reaction corresponds to the addition of dimethylsilylene to two molecules of phenylacetylene; bis(trimethylsilyl)acetylene is eliminated. When repeated at room temperature without catalyst, this reaction yields another silole (30%). Under UV irradiation, no silole is formed.

The results of this reaction vary depending on the acetylenic compound used. With *tert*-butylacetylene and (Ph$_3$P)$_2$PdCl$_2$ as catalyst, simultaneous formation of the following siloles is observed:[57b]



With acetylene, no 1,1-dimethylsilole is produced. Rather a bicyclic compound[57d] is formed.

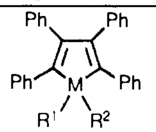
Many siloles with a variety of substituents on carbon have been obtained by this method; among these are 2,5-disilylsiloles[59a] (42–99%) (eq 16).



(16)

The reaction mechanism appears to be rather complex. Many authors propose the existence of a silacyclobutene intermediate.[57-60] Recently, Ishikawa et al.[60]

TABLE 2. **Group 14 2,3,4,5-Tetraphenylmetalloles**



M	R¹	R²	prep method[a] (% yield)	mp[b]	remarks	ref
Si	H	H	B	209–210		31
Si	H	Me	A	225–226		26
			B (70–90)	223–224	IR	27, 35
			A (68)		ultrasonically accelerated	48
Si	H	^{n}Bu	B (72)	109	NMR (^{1}H), MS	41
Si	H	Ph	A	200		26
			B (70–90)	198–199		27, 28, 35
Si	H	C_6F_5	B (74)	181	NMR (^{1}H, ^{19}F)	41
Si	H	Mes	B (71)	179	NMR (^{1}H), IR	41
Si	H	p-$Me_2NC_6H_4$	B	217	NMR (^{1}H), IR	41
Si	H	Cl	A (44)	212–216	NMR (^{1}H), IR	30, 41
Si	Cl	Cl	A (68)	197	NMR (^{1}H), IR	41
Si	Cl	Me	A (58)	194–195	reverse addition	27, 35
Si	Cl	Ph	A (70)	181–183	reverse addition	27, 35
			A (55)	177–178		28
Si	OH	Me	B	210–215	IR	28
			B	199–202	IR	35
Si	OMe	Et	B (19–42)	137	NMR (^{1}H), IR, MS	46
Si	O^{t}Bu	Et	B (15–31)	117–118	NMR (^{1}H, ^{13}C), IR	46
Si	NMe_2	Me	B	144		28
Si	Me	Me	A (72)	181–182	IR, UV	25
			H (56)	178–179		37
Si	Me	CH_2Cl	A (32)	152–153		33
Si	Me	CHN_2	C (78)	154–156	NMR (^{1}H), MS, IR, UV	46
Si	Me	c-CHN_2	C (64)	>78	NMR (^{1}H), IR, MS	46
Si	Me	Et	A (55)	145	IR, UV	34
Si	Me	$CH{=}CH_2$	C (52)	170		46
Si	Me	$C(Me)N_2$	C (83)	130–132	NMR (^{1}H), MS, IR	46
Si	Me	c-$C(Me)N_2$	C (27)	142 (dec)	NMR (^{1}H, ^{13}C), MS, IR	46
Si	Me	^{n}Pr	A (25)	116	IR, UV	34
Si	Me	^{n}Bu	A (52)	126	IR, UV	34
Si	Me	Ph	A	173–174		28
			A (76)	172	IR, UV	34
Si	Me	o-MeC_6H_4	A (32)	136	IR, UV	34
Si	Me	p-MeC_6H_4	A (45)	186	IR, UV	34
Si	Me	$CH_2C_6H_5$	A (33)	149	IR, UV	34
Si	Et	Et	A (45)	135–136	IR, UV	34
Si	$C{\equiv}CH$	$C{\equiv}CH$	B	170–172	IR	40
Si	Et	Ph	A (24)	129	IR, UV	34
Si	^{n}Pr	^{n}Pr	A (42)	105	IR, UV	34
Si	^{n}Pr	Ph	A (64)	146	IR, UV	34
Si	^{n}Bu	^{n}Bu	A (44)	89	IR, UV	34
			B (80)	81	NMR (^{1}H), MS	41
Si	^{n}Bu	Ph	B (93)	156	NMR (^{1}H), MS	41
			B (65)	145–148	IR	35
Si	^{n}Bu	p-$Me_2NC_6H_4$	B (89)	126	NMR (^{1}H), MS	41
Si	^{t}Bu	Ph	B (64)	160	NMR (^{1}H), MS	41
Si	Ph	Ph	A (50)	191	UV	3b, 23
Si	Ph	C_6H_{11}	A (24)	159	IR, UV	34
Si	Ph	o-MeC_6H_4	A (30)	231–235	IR, UV	34
Si	Ph	m-MeC_6H_4	A (41)	175	IR, UV	34
Si	Ph	p-MeC_6H_4	A (27)	170–175	IR, UV	34
Si	Ph	$CH_2C_6H_5$	A (15)	218	IR, UV	34
Si	p-MeC_6H_4	p-MeC_6H_4	A (15)	212–213	IR, UV	34
Si	$CH_2C_6H_5$	$CH_2C_6H_5$	A (29)	145	IR, UV	34
Si	$(C{\equiv}C)_n$	$(C{\equiv}C)_n$	B		high-resistance semiconductors	40
Si	Ph	$SiMe_3$	B (37)	185	NMR (^{1}H), MS	41
Si	Me	$(CH_2)_2Si(Me)C_4Ph_4$	A (2)	261–264	NMR (^{1}H), MS	42
Si	Ph	$Si(Ph)C_4Ph_4$	B (87)	223	MS	41
			B (63–92)	237–238		30
Si	Me	$OSi(Ph)C_4Ph_4$	B	267–268		28
Si	Ph	$OSi(Ph)C_4Ph_4$	B	239–240		28
Si	Me	$Fe(CO)_2C_5H_5$	B (70)	200	NMR (^{1}H, ^{13}C, ^{29}Si), MS, IR	49
Si	Ph	$Fe(CO)_2C_5H_5$	B (60)	201–203	IR	35
Si	$(CH_2)_4$		A (50)	222	IR, UV	29, 34
Si	$(CH_2)_5$		A (87)	212	IR, UV	29, 34
Si	C_4Ph_4[d]		A (1)	288–295		3b
Si	Ph	Ph	A (30)	220–221	2,3,4,5-tetratolylsilole, IR, UV, NMR (^{1}H)	38
Si	Ph	Ph	A (65)		2,3-diphenyl-4,5-ditolylsilole, IR, UV, NMR (^{1}H)	38
Ge	H	H	D (70–90)	192–193	IR	27, 35
Ge	H	Ph	D (70–90)	187–188	IR	27, 35

TABLE 2 (Continued)

M	R^1	R^2	prep method[a] (% yield)	mp[b]	remarks	ref
Ge	H	p-MeC_6H_4	D (86)	175	NMR (^1H), IR	43
Ge	H	p-$Me_2NC_6H_4$	D (80)	214	NMR (^1H), IR	43
Ge	Cl	Cl	A (70)	197–199	reverse addition	27, 35
			I (90)			236
Ge	Cl	Ph	A (47)	210–211	reverse addition	27, 35
Ge	Cl	p-MeC_6H_4	D (86)	172	NMR (^1H)	43
Ge	Cl	p-$Me_2NC_6H_4$	D (84)	252	NMR (^1H)	43
Ge	OH	Ph	D	256–257	IR	35
Ge	Ph	$OGe(Ph)C_4Ph_4$	D	255–257	IR	35
Ge	Me	Me	A	179–181	NMR (^1H), IR	32
			A	183–184	MS, IR	36
Ge	Et	Et	D (79)	145	NMR (^1H)	43
Ge	$C{\equiv}CH$	$C{\equiv}CH$	D (65)	194–196	IR	40
Ge	Ph	Ph	D	198–199		35
Ge	C_6F_5	C_6F_5	D (35)	196	NMR (^1H)	43
Ge	Ph	$SiMe_3$	A (97)	181		43
			D (80)	178–180	IR	27, 35
Ge	Ph	$Ge(Ph)C_4Ph_4$	D (25)	235–236		35
Ge	p-MeC_6H_4	p-MeC_6H_4	D (95)	196	NMR (^1H)	43
Ge	p-MeC_6H_4	$SiMe_3$	D (94)	186	NMR (^1H), IR	43
Ge	p-$Me_2NC_6H_4$	$SiMe_3$	D (93)	175	NMR (^1H), IR	43
Ge	p-$Me_2NC_6H_4$	p-$Me_2NC_6H_4$	D (66)	233	NMR (^1H)	43
Ge	$SiMe_3$	$SiMe_3$	D (87)	114	NMR (^1H), IR	43
Ge	Ph	$Fe(CO)_2C_5H_5$	D (74)	191–193	IR	35
Ge	Ph	$Co(CO)_4$	D (65)	165	IR	35
Ge	Ph	$Mn(CO)_5$	D (89)	144	IR	35
Ge	$(C{\equiv}C)_n$	$(C{\equiv}C)_n$	D		high-resistance semiconductors	40
Ge	C_4Ph_4[d]		A (22)	258–260		3d
Sn	F	Br	F (45)	189	IR, MB[c]	44
Sn	F	I	F (43)	182–184	IR, MB	44
Sn	Br	Br	E (95)	167.5	IR, MB	45
					adducts with N derivatives	44
Sn	I	I	E (74)	168	IR, MB	45
					adducts with N derivatives	44
Sn	Br	$N(SiMe_3)_2$	F (24)	178	IR, MB	44
Sn	OC(O)Me	OC(O)Me	F (64)	182–183	IR, MB	44
Sn	N_3	N_3	F (58)	153–154	IR, MB	44
Sn	NCO	NCO	F (42)	163–165	IR, MB	44
Sn	NCS	NCS	F (12)	153	IR, MB	44
Sn	NMe_2	NMe_2	F (69)	158–159	IR, MB	44
Sn	PPh_2	PPh_2	F (57)	165–167	IR, MB	44
Sn	$SC(S)NEt_2$	$SC(S)NEt_2$	F (19)	146	IR, MB	44
Sn	Me	Me	A (77)	193–195		24
			A (80)	185–187	NMR (^1H)	47
			A (67)	192–193		3d
			A	191.5–192.5	MB	36
			F (38)	189	NMR (^1H, ^{119}Sn), IR	45
Sn	Me	Me	A (51)	202–204	2,3,4,5-tetra-p-tolylstannole, NMR (^1H)	47
Sn	$CH{=}CH_2$	$CH{=}CH_2$	A (69)	158–159		3d
			A (42)	154–156	IR, MS	36
Sn	Ph	Ph	A (40)	174		3b
			A (20)	173–174		3d
Sn	C_4Ph_4[d]		A (40)	275–280	from $SnCl_4$	3b
			A (62)	280–282		3d
			A (67)	263	from Me_2SnCl_2	36
			G (64)	275–277	from $C_4Ph_4Li_2$	47
Pb	Ph	Ph	A (15)	153–155	IR	36

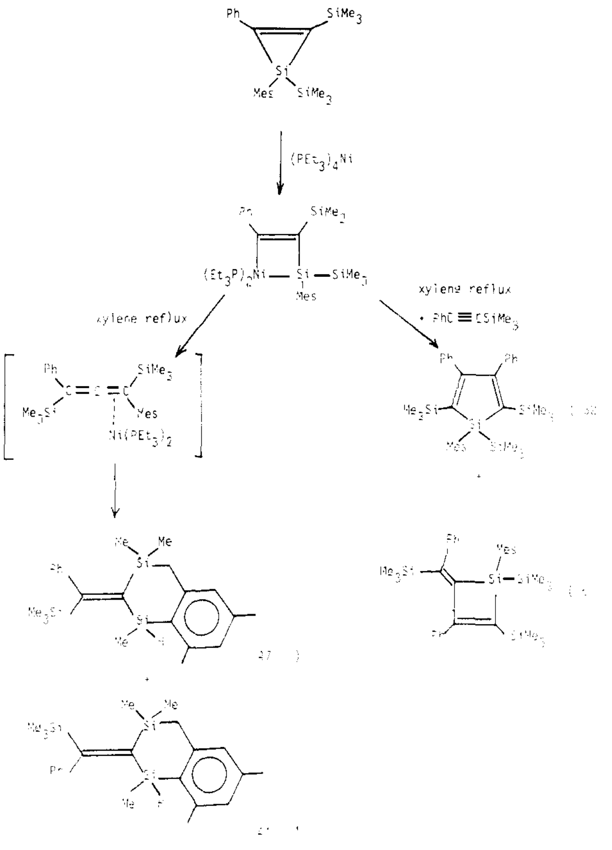
[a] Methods: (A) section I.B.1.a.i (eqs 5–7); (B) Schemes 6–8; (C) Schemes 9 and 10; (D) Schemes 11 and 12; (E) Scheme 13; (F) Scheme 14; (G) eq 8; (H) section I.B.1.b.i (eq 15); (I) Section I.B.4. [b] °C. [c] Mössbauer effect. [d] Spirobimetallole.

identified a nickelasilacyclobutene in solution, which on reaction with an acetylenic compound gave the expected silole together with other minor products (Scheme 18). This nickelasilacyclobutene is degraded on refluxing in xylene, probably via a silapropadiene–nickel complex. Several transformations of metallasilacyclobutenes to metallasilacyclohexadienes or metalladisilacyclopentenes are also possible.[57d,60] Seyferth et al.[57d] have suggested that $(Ph_3P)_2Pd^0$ is the active catalyst that reacts with the silirene to form the palladasilacyclobutene. Two distinct pathways, one involving a silylene complex, could explain the formation of a silole (Scheme 19).

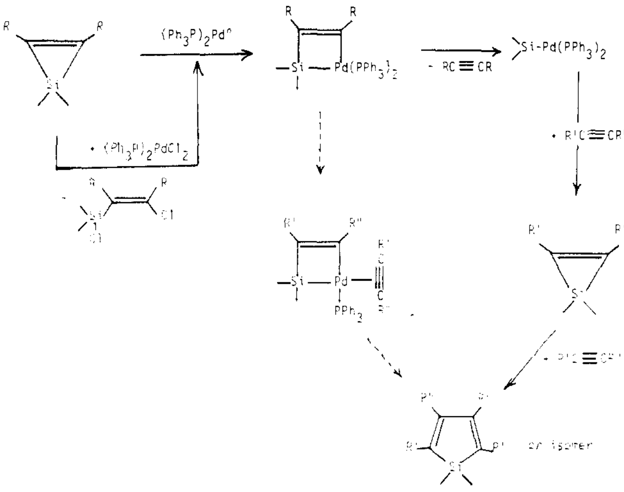
A cyclotrisilane, hexa-*tert*-butylcyclotrisilane, reacts with phenylacetylene catalyzed by $(PPh_3)_2PdCl_2$ to yield 1,1-di-*tert*-butyl-3,5-diphenylsilole (49%).[61]

(*iv*) *Thermolysis of Silirenes.* Thermolysis of silirenes at 250 °C can give various products:[62] 1,2-disilacyclobutenes, 1,4-disilacyclohexa-2,5-dienes, and siloles. This reaction has been found to proceed simultaneously by two different pathways, one of which involves a concerted $[2\sigma + 2\sigma]$ dimerization; the other involves the silylene extrusion. The former reaction is suppressed when a bulkier substituent is introduced onto the carbon atom in the silacyclopropene ring. Consequently, the silylene extrusion takes place predominantly and

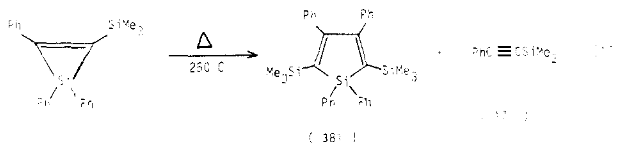
SCHEME 18



SCHEME 19

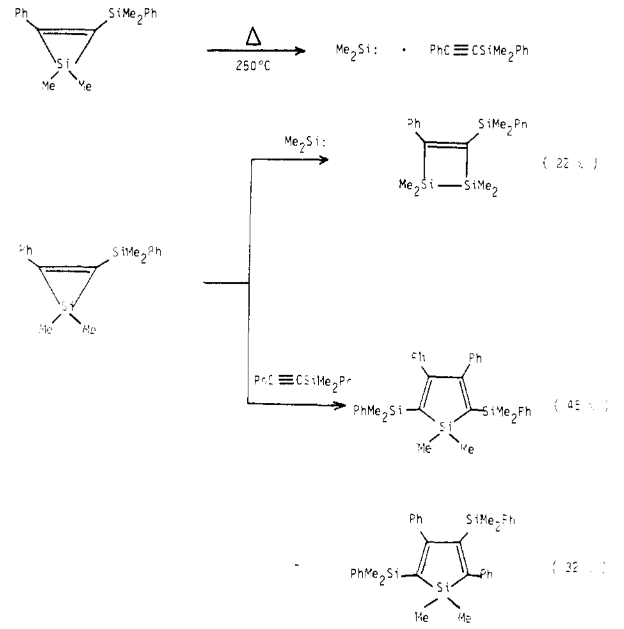


1,2-disilacyclobutenes and siloles are obtained (Scheme 20). When substituents on the ring silicon atom are changed from methyl to phenyl, no 1,2-disilacyclobutenes are produced, but siloles are formed as the predominant products (eq 17).



(*v*) *Reaction between a 7-Metallanorbornadiene and an Alkyne.* Trapping of a silylene generated by pyrolytic or photochemical decomposition of a 7-silanorbornadiene by an acetylenic compound does not give the expected silole but rather a 1,4-disilacyclohexadiene.

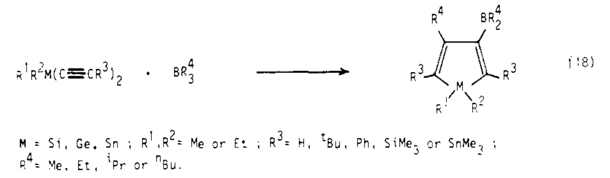
SCHEME 20



The only known example of this reaction was reported by Marinetti-Mignani and West.[49] However, the silole isolated is identical with the one used. It appears that iron atoms may catalyze the insertion reaction of diphenylacetylene into the intermediate silirene ring. In this case, the silirene ring does not undergo dimerization to yield the 1,4-disilacyclohexadiene (eq 71).

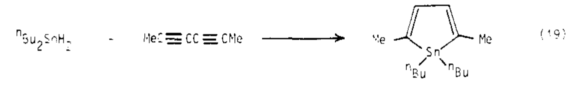
The products resulting from cycloadditions of alkynes RC≡CR′ with free singlet dimethylgermylene depend on R, R′, and the RC≡CR′/Me_2Ge molar ratio.[215] A large excess of phenylacetylene, diethyl acetylenedicarboxylate, or cyclooctyne leads to the corresponding germole (cf. section II.B.2.b.ii and Scheme 34).

(*c*) *Action of Trialkylboranes on Bis((trimethylstannyl)ethynyl)dimethylsilane.* The reaction of two acetylenic groups bonded to the same heteroatom M to yield a metallole was achieved by Wrackmeyer,[63] who cyclized a bis(alkynyl)silane, -germane, or -stannane using trialkylboranes (eq 18).



If the substituents carried on the ring carbons (C–Sn, C–B) could be replaced by functional groups, this method would prove to be very interesting.

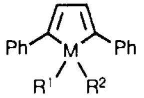
(*d*) *Action of a Dihydride R_2MH_2 on a 1,3-Diyne.* To our knowledge, a single metallole has been prepared in this way. Thus, condensation of dibutylstannane with 2,4-hexadiyne yields 1,1-di-*n*-butyl-2,5-dimethylstannole (15%)[64] (eq 19).



2. Synthetic Methods Involving Saturated Heterocycles (Metallacyclopentanes)

(*a*) *Dehydrogenation.* Attempts at catalytic dehydrogenation of silacyclopentanes have either failed or

TABLE 3. Group 14 2,5-Diphenylmetalloles

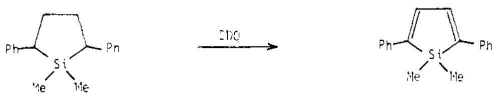


M	R^1	R^2	prep method^a (% yield)	mp^b	remarks	ref
Si	H	H	F	151–153	IR, UV	31
			F (60)	145–146	NMR (^{1}H), IR	53
Si	H	Cl	A		not isolated	31
			F (75)			53a
Si	H	Me	A (42)	97–98	dec slowly at room temp, NMR (^{1}H) IR	53
			A^d (51)	97–99		55
Si	H	$CH{=}CH_2$	F (90)	63–65	NMR (^{1}H)	53
Si	H	$CH_2CH{=}CH_2$	F (60)	65–67	NMR (^{1}H)	53
Si	H	Ph	A	180–181		31
			A^d (50)	176–178		55
Si	H	$SiMe_3$	F (5)	114–115	NMR (^{1}H), IR	53
Si	F	F	F (60)			53a
Si	Cl	Me	F (75)	136–137	NMR (^{1}H)	53
Si	OMe	OMe	A (70)	103–104	NMR (^{1}H)	53
Si	OMe	Me	A (70)	122–124	NMR (^{1}H)	53
Si	OMe	$CH{=}CH_2$	A (50)	86–90	NMR (^{1}H)	53
Si	OMe	$CH_2CH{=}CH_2$	A (40)	62–64	NMR (^{1}H)	53
Si	OMe	$SiMe_3$	A		unstable	53
Si	Me	Me	A (68)	130–133	NMR (^{1}H), UV	50, 51
Si	Me	Et	B (62)	60–61	UV, IR	66
Si	Et	Et	B (48)	82–83	UV, IR	66
Si	^{n}Bu	^{n}Bu	B (60)	64–65	UV, IR	66
Si	Me	$CH{=}CH_2$	A (51)	51	NMR (^{1}H)	53
Si	Me	$CH_2CH{=}CH_2$	F (67)	58–59	NMR (^{1}H)	53
Si	Me	Ph	A (40)	99	NMR (^{1}H)	51
			B (65)	105–106	UV, IR	66
Si	Ph	Ph	A (27)	164.5		51
Si	Me	$SiMe_3$	A (51)	95–96	NMR (^{1}H)	52, 53b
Si	Me	$CH_2Si(Me)C_4H_2Ph_2{}^c$	A (25)	174–175	NMR (^{1}H, ^{13}C, ^{29}Si)	42
Si	Me	$(CH_2)_2Si(Me)C_4H_2Ph_2{}^c$	A (54)	241–242	NMR (^{1}H, ^{13}C)	42
Si	Me	$(CH_2)_3Si(Me)C_4H_2Ph_2{}^c$	A (58)	113–115	NMR (^{1}H, ^{13}C, ^{29}Si)	42
Si	Me	Me	D (45–80)	98–99	3,4-diphenylsilole, NMR (^{1}H)	56b, 57a,d, 58
			E (78.5)	96.5–97	NMR (^{1}H, ^{13}C, ^{29}Si), IR	78
Si	^{t}Bu	^{t}Bu	D (49)	109	2,4-diphenylsilole, NMR (^{1}H), MS, IR	61
Ge	Me	Me	A (65)	128	NMR (^{1}H), MS	52b
			B (48)	132–133	NMR (^{1}H), UV	67
			C (80)			69
Sn	Me	Me	A (38)	120–121	NMR (^{1}H), UV	50

^{a} Methods: (A) section I.B.1.a; (B) section I.B.2.b; (C) section I.B.3.a; (D) section I.B.1.b; (E) section I.B.3.b; (F) substitution reaction at M. ^{b} °C ^{c} See eq 13. ^{d} $[RSiO_2(C_6H_4\text{-}o)_2]^-Na^+$ (R = Me or Ph) + DDB + $LiAlH_4$.

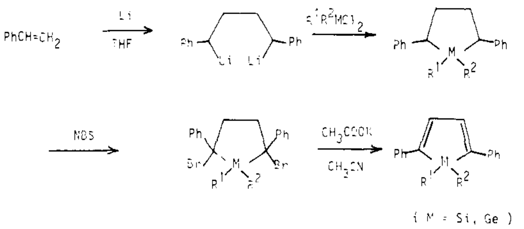
proved impossible to reproduce (cf. section I.A).

Benzylic activation in 1,1-dimethyl-2,5-diphenylsilacyclopentane (cf. section I.2.b) makes this compound reactive toward 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).[65] The dehydrogenation can be achieved either at room temperature (2 days) or in refluxing benzene (16 h) with a high yield (86%) (eq 20).



(20)

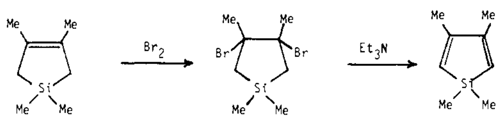
(*b*) *Dehydrohalogenation.* The transformation of a 2,5-diphenylsilacyclopentane to a 2,5-diphenylsilole by the bromination/dehydrobromination reaction sequence was achieve by Gilman et al.[50] in 1967 (eq 21, M = Si, $R^1 = R^2 =$ Me). This method is doubly interesting: (1) it provides a straightforward synthesis of a 2,5-diphenylsilacyclopentane by cyclization of 1,4-dilithio-1,4-diphenylbutane, obtained by dimerization of styrene in the presence of lithium, together with a dichlorosilane; (2) it opens the possibility of preparing 1,4-dilithio-1,4-diphenyl-1,3-butadiene from 1,1-dimethyl-DPSI (Scheme 15), and the subsequent use of this dilithium reagent to obtain 2,5-diphenylmetalloles, especially functionalized ones (cf. section I.B.1.a).



(21)

The method has been applied to other 2,5-diphenylsiloles ($R^1 = R^2 =$ Et, ^{n}Bu; $R^1 =$ Me, $R^2 =$ Et; $R^1 =$ Me, $R^2 =$ Ph)[66] and also to the synthesis of 1,1-dimethyl-2,5-diphenylgermole.[67]

Numerous attempts at synthesizing C-unsubstituted germoles and siloles by dehydrohalogenation of polyhalogenosila(or germa)cyclopentanes have met with failure (cf. section I.A). Recently, Joo et al.[68] obtained TMSI together with its dimer (48% of the mixture) by bromination/dehydrobromination of 1,1,3,4-tetramethylsilacyclopent-3-ene (eq 22). By comparison we have obtained this silole[19,80] as a monomer in higher yield (cf. section I.B.3b).

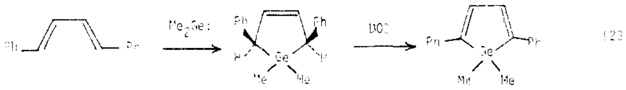


(22)

3. Synthetic Methods Involving Unsaturated Heterocycles (Metallacyclopentenes)

(*a*) *Dehydrogenation.* In 1964, Nefedov et al.[11] attempted the catalytic dehydrogenation (450 °C/$Al_2O_3 \cdot CrO_3 \cdot K_2O$ or 350–400 °C/10% Pt–C) of 1,1-dimethylgermacyclopent-3-ene. 1,1-Dimethylgermole could not be identified among the reaction products.[17]

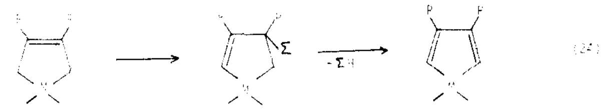
The *cis*-2,5-diphenylgermacyclopent-3-ene, obtained from dimethylgermylene and (*E*,*E*)-1,4-diphenylbutadiene, can be dehydrogenated smoothly by DDQ to form 1,1-dimethyl-DPGE[69] (eq 23).



(23)

Unfortunately, direct dehydrogenation of metallacyclopentenes is not a general method. Dehydrogenation of 3,4-dimethylmetallacyclopentenes would yield 3,4-dimethylmetalloles, which are known to be stable as monomers. Unfortunately, reaction of DDQ with 1,1,3,4-tetramethylsilacyclopent-3-ene gave only the transoid isomer **7c** of TMSI (**7a**).[79a] Similar results were obtained with 1,1,3-trimethylsilacyclopent-3-ene and DDQ.[52c] No reaction is observed between DDQ and 1,1-dimethylsilacyclopent-3-ene in refluxing benzene.[79a]

(*b*) *Dehydration of 1-Metallacyclopent-4-en-3-ols.* The sila- or germacyclopent-3-enes are easily obtained. In our opinion, they could be excellent precursors to siloles and germoles, provided that they could be transformed into functional derivatives (eq 24, Σ ≠ halogen; cf. section I.A).

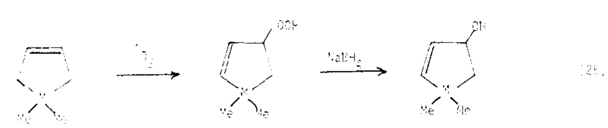


(24)

The ene reaction[70] was investigated in order to achieve the functionalization, especially with singlet oxygen as enophile.

(*i*) *Synthesis of 1-Metallacyclopent-4-en-3-ols.* The reaction of molecular oxygen ($^3O_2$) with silacyclopentenes gives alcohols in low yield.[71] 1,1,3,4-Tetramethylsilacyclopentene is more easily oxidized by $^3O_2$ than 1,1-dimethylsilacyclopentene (Table 6).

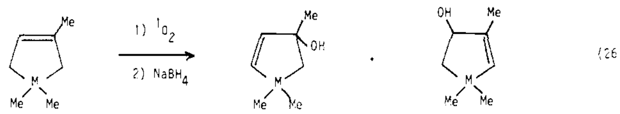
On the other hand, singlet oxygen reacts with metallacyclopentenes via an ene reaction.[70] This involves migration of the carbon–carbon double bond and, after reduction of the intermediate hydroperoxide, gives the expected 1-metallacyclopent-4-en-3-ols[6,18,73,74a,75] (eq 25).



M = Si(8a), Ge(8b)

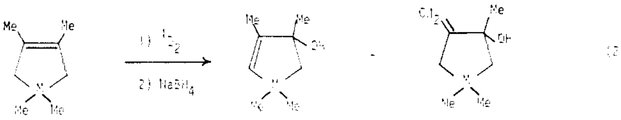
(25)

Good yields are observed with various substituents at silicon: methyl,[6,73,74a] phenyl,[75] vinyl,[18b] or allyl.[75] The photooxidation is not regiospecific in the case of C-methylated metallacyclopentenes (eqs 26–28). The same metallacyclopentenols (**8**–**11**) can be prepared by a base-promoted rearrangement of the corresponding epoxides.[76] This method is useful in the case of 3,4-dimethylated derivatives because it gives the corresponding alcohols regiospecifically[75,76] (eq 29). This method is, however, not applicable to M–vinyl or M–allyl derivatives.[18,75]



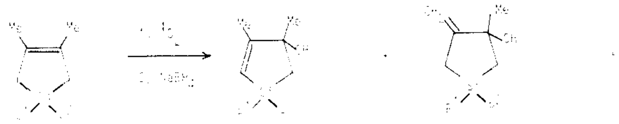
M = Si , 9a 10a
M = Ge , 9b 10b

(26)



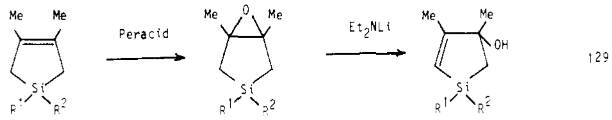
M = Si , 11a 12a
M = Ge , 11b 12b

(27)



R^1=Me, R^2=Ph 13 14
R^1=Me, R^2= allyl 15 17
R^1=R^2= allyl 18 19

(28)



(29)

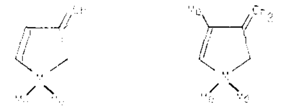
R^1=R^2=Me, M=Si(11a), Ge(11b)
R^1=Me,R^2=Ph, M=Si(13)
R^1=R^2=Ph, M=Si(15)

(*ii*) *Direct Dehydration of Metallacyclopent-4-en-3-ols.* Metallacyclopent-4-en-3-ols decompose on treatment by a protonic acid at room temperature to form the siloxane or the germoxane corresponding to a β C–M elimination[6,18] (Scheme 3).

The catalytic dehydration of these alcohols in the gas phase gives the expected β C–H elimination and produces 1,1-dimethylsilole (**5a**) and -germole (**5b**) (Scheme 3). This method has been applied to C-methylated metallacyclopentenols in an attempt to obtain C-methylated metalloles **6** and **7** (Table 7).

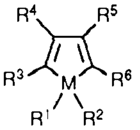
M = Si 6a 7a
M = Ge 6b 7b

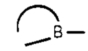
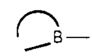
With alumina or thoria, dehydration of isomeric mixtures of allylic heterocyclic alcohols **9** + **10** and **11** + **12** gives the corresponding C-methylated metalloles **6a**,**b** and **7a**,**b** (minor products) and the exocyclic isomeric dienes **6c**,**d** and **7c**,**d** (major products) (Table 7). The dienes are formed in the thermodynamic ratios



and correspond to a catalytic isomerization of the metalloles **6a**,**b** and **7a**,**b**: dehydration of isomerically pure alcohols **11a**,**b** gives the same ratios of dienes as the **11** + **12** mixtures; the dehydration of C-methylated silacyclopentanols over Al_2O_3 or ThO_2 corresponds to a Saytzeff-type elimination;[77] pure tetramethylsilole (**7a**)

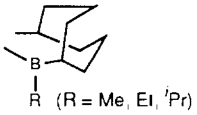
TABLE 4. C-Substituted Group 14 Metalloles



M	R^1	R^2	R^3	R^4	R^5	R^6	prep method[a] (% yield)	mp[b]	remarks	ref
Si	Me	Me	H	^{t}Bu	^{t}Bu	H	B (22)		NMR (^{1}H), n^{25}_{D}	57b,d
Si	Me	Me	H	CMe=CH$_2$	CMe=CH$_2$	H	B (42)		NMR (^{1}H) n^{25}_{D}	57b,d
Si	Me	Me	Et	Et	Et	Et	A (95)			56a
Si	Me	Me	Me	^{n}Bu	^{n}Bu	Me	A (100)		*R* alternate (3 isomers)	56a
Si	Me	Me	H	Ph	Ph	H	B (45–80)	98–99	NMR (^{1}H)	56b, 57a,d, 58
							F (78.5)	96.5–97	NMR (^{1}H, ^{13}C, ^{29}Si), IR	78
Si	^{t}Bu	^{t}Bu	Ph	H	Ph	H	B (49)	109	NMR (^{1}H), MS, IR	61
Si	Me	Me	Me	Ph	Ph	Me	A (44)		NMR (^{1}H), UV	56a
Si	Me	^{t}Bu	H	Me	CH$_2$SiMe$_3$	H	G	110–112/13[e]	NMR (^{1}H)	166
Si	^{n}Bu	^{n}Bu	H	Me	CH$_2$SiMe$_3$	H	G	105–107/0.07[e]	NMR (^{1}H)	166
Si	Me	Me	SiMe$_3$	SiMe$_3$	^{t}Bu	H	B (30)	42–42.5	NMR (^{1}H)	57b,d
Si	Me	Me	SiMe$_3$	SiMe$_3$	CMe=CH$_2$	H	B (34)	48.5–49.5	NMR (^{1}H)	57b,c
Si	Me	Me	SiMe$_3$	SiMe$_3$	Ph	H	B (22)		NMR (^{1}H)	57a,c
Si	Me	Me	SiMe$_3$	Ph	Ph	SiMe$_3$	B (94)	96–97	NMR (^{1}H), IR	59
Si	Me	Me	SiMe$_3$	Ph	Ph	SiMe$_2$Et	B (86)	95–96	NMR (^{1}H), IR	59
Si	Me	Me	SiMe$_2$Et	Ph	Ph	SiMe$_2$Et	C (19)	103	NMR (^{1}H)	62
Si	Me	Me	SiMe$_2$Ph	Ph	Ph	SiMe$_2$Ph	B (80)		NMR (^{1}H), IR	59
							C (45)			62
Si	Me	Me	SiMe$_2$Ph	Ph	SiMe$_2$Ph	Ph	C (32)		NMR (^{1}H)	62
Si	Me	Me	CO$_2$Me	CO$_2$Me	Ph	SiMe$_3$	B			58
Si	Me	Ph	SiMe$_3$	Ph	Ph	SiMe$_3$	B (73)	150	NMR (^{1}H), IR	59
							C (42)			62
Si	Me	Ph	Ph	SiMe$_3$	SiMe$_3$	Ph	C (17)		NMR (^{1}H)	62
Si	Ph	Ph	SiMe$_3$	Ph	Ph	SiMe$_3$	B (99)	209–210	NMR (^{1}H), IR	59a
							C (38)	208		62b
Si	Me	Mes	SiMe$_3$	Ph	Ph	SiMe$_3$	B (86)	128–130	NMR (^{1}H), IR	59a
Si	Me	SiMe$_3$	SiMe$_3$	Ph	Ph	SiMe$_3$	B (42)	62	NMR (^{1}H) IR	59a,b
Si	Mes	SiMe$_3$	SiMe$_3$	Ph	Ph	SiMe$_3$	B (32)	180.6	NMR (^{1}H, ^{13}C)	60
Si	Me	Me	SnMe$_3$	Me	BMe$_2$	SnMe$_3$	E (q)[c]		NMR[d]	63a,b
Si	Me	Me	SnMe$_3$	Et	BEt$_2$	SnMe$_3$	E (q)[c]		NMR[d]	63a,b
Si	Me	Me	SnMe$_3$	^{i}Pr	B^{i}Pr$_2$	SnMe$_3$	E (q)[c]		NMR[d]	63a,b
Ge	Me	Me	Ph	H	Ph	H	D (82)	150–170/0.01[e]	NMR (^{1}H), MS	215
Ge	Me	Me	SnMe$_3$	Me	BMe$_2$	SnMe$_3$	E (q)[c]		NMR[d]	63a,b
Ge	Me	Me	SnMe$_3$	Et	BEt$_2$	SnMe$_3$	E (q)[c]		NMR[d]	63a,b
Ge	Me	Me	Ph	CF$_3$	CF$_3$	Ph	G		NMR (^{1}H), IR	32
Ge	Me	Me	CO$_2$Me	CO$_2$Me	CO$_2$Me	CO$_2$Me	G[f]		NMR (^{1}H), IR	32
Ge	Me	Me	COOEt	COOEt	COOEt	COOEt	D (65)			215
Sn	Me	Me	H	Et	BEt$_2$	H	E (46)	51–52/0.01[e]	NMR[d]	63c
Sn	Me	Me	H	^{i}Pr	B^{i}Pr$_2$	H	E (55)	63–64/0.01[e]	NMR[d]	63c
Sn	Me	Me	H	^{n}Bu	B^{n}Bu$_2$	H	E (40)	105–110/0.01[e]	NMR[d]	63c
Sn	Et	Et	H	Et	BEt$_2$	H	E (65)	66–67/0.01[e]	NMR[d]	63c
Sn	Me	Me	^{t}Bu	Me	BMe$_2$	^{t}Bu	E (q)[c]	45–46		63d
Sn	Me	Me	^{t}Bu	Et	BEt$_2$	^{t}Bu	E (92)	96–98/0.01[e]	NMR[d]	63d
Sn	Me	Me	Me	Et	BEt$_2$	^{t}Bu	E (81)	82/0.01[e]	NMR[d]	63d
Sn	Me	Me	Ph	Et	BEt$_2$	Ph	E		NMR (^{13}C, ^{119}Sn)	63e
Sn	Me	Me	SiMe$_3$	Et	BEt$_2$	SiMe$_3$	E	105–108/0.01[e]	NMR[d]	63d
Sn	Me	Me	H	 [g]		H	E (>80)		NMR[d]	63f
Sn	Me	Me	H	 [g]		H	E (>80)		NMR[d]	63f
Sn	Me	Me	H	 [g]		H	E (>80)		NMR[d]	63f
Sn	Me	Me	H	^{i}Pr	*h*	H	E		NMR[d]	63f

[a] Methods: (A) section I.B.1.b.ii; (B) section I.B.1.b.iii; (C) section I.B.1.b.iv; (D) section I.B.1.b.v; (E) section I.B.1.c; (F) section I.B.3.b; (G) other method. [b] °C. [c] q = quantitative yield. [d] Multinuclear NMR (H, ^{13}C, ^{11}B, ^{29}Si, ^{19}Sn). [e] bp (°C/Torr). [f] The result of this reaction is perhaps different.[140]

g



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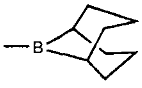
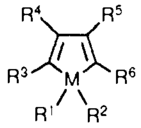


isomerizes to transoid diene **7c** on the same catalysts.[74b]

Consequently, the dehydration of the metallacyclopentenols, which allowed access to the first monomeric C-unsubstituted group 14 metalloles (cf. I.A), is not suitable for the synthesis of C-methylated derivatives, which are important as the double C-methylation (7) increases stability of the monomeric metallole (cf. section II.A).

Furthermore, the catalysts have to be treated thermally and chemically to prevent the demetalation re-

TABLE 5. **C-Methylated Group 14 Metalloles**

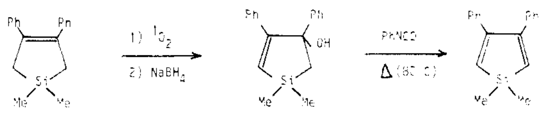


M	R^1	R^2	R^3	R^4	R^5	R^6	prep method[a] (% yield)	bp[b]	remarks	ref
Si	H	H	H	Me	Me	H	A		NMR (^{1}H, ^{13}C, ^{29}Si), MS, adduct with MA	79
Si	H	Me	H	Me	Me	H	A (80)	60–63/45	NMR (^{1}H, ^{13}C, ^{29}Si), MS, IR, PES, adduct with MA	79b, 82
Si	H	Ph	H	Me	Me	H	A (25–40)	70–72/0.1	NMR (^{1}H, ^{13}C, ^{29}Si), MS, IR, adduct with MA	79b, 82
Si	F	Me	H	Me	Me	H	E		unstable, NMR (^{1}H, ^{13}C, ^{29}Si), MS	79
Si	OMe	Me	H	Me	Me	H	E (80)	66–68/20	NMR (^{1}H, ^{13}C, ^{29}Si), MS	79
Si	O^{i}Pr	Me	H	Me	Me	Me	E (60)	77–80/15	NMR (^{1}H)	79
Si	OMe	Ph	H	Me	Me	H	E		not pure, NMR (^{1}H)	79
Si	NEt$_2$	Me	H	Me	Me	H	E (85)	80/10	NMR (^{1}H, ^{13}C, ^{29}Si)	79
Si	Me	Me	H	H	Me	H	B		monomer (unstable): NMR (^{1}H), adduct with MA	74a
							C (72)		monomer; dimer: bp 112–115/15, NMR (^{1}H), MS	19
Si	Me	Me	H	Me	Me	H	B		NMR (^{1}H), adduct with MA	74a
							C (80)	58/30		80
							C (83)		one-pot synthesis; NMR (^{1}H, ^{13}C, ^{29}Si), MS, IR, UV	19
							D (48)		monomer–dimer mixture	68
Si	Me	^{n}Bu	H	Me	Me	H	E (70)	96–98/13	NMR (^{1}H), MS, adduct with MA	166
Si	Me	^{t}Bu	H	Me	Me	H	E	74–6/15	essentially transoid isomer	166
Si	^{n}Bu	^{n}Bu	H	Me	Me	H	E (65)	122–125/13	NMR (^{1}H), MS, adduct with MA	166
Si	Me	$CH_2CH{=}CH_2$	H	Me	Me	H	C (88)	80–82/15	NMR (^{1}H), adduct with MA	75
							E (88)			79
Si	$CH_2CH{=}CH_2$	$CH_2CH{=}CH_2$	H	Me	Me	H	C (82)	54–57/0.55	NMR (^{1}H), adduct with MA	75
Si	Me	Ph	H	Me	Me	H	E (9)		NMR (^{1}H)	166
							C (90)	81–83/0.1	NMR (^{1}H), adduct with MA	75
							E (90)			79
Si	Ph	Ph	H	Me	Me	H	C (73)	135–140/0.05	NMR (^{1}H), adduct with MA	75
Ge	H	H	Me	Me	Me	Me	E		MS	236
Ge	Me	H	Me	Me	Me	Me	E		MS	236
Ge	Ph	H	Me	Me	Me	Me	E (80)	102/0.52	NMR (^{1}H, ^{13}C), MS	236
Ge	Cl	Cl	Me	Me	Me	Me	G (83)		NMR (^{1}H, ^{13}C), MS	110a, 236
Ge	Br	Br	Me	Me	Me	Me	G (80)		NMR (^{1}H)	236
Ge	Ph	Cl	Me	Me	Me	Me	E		NMR (^{1}H)	236
Ge	Me	Me	Me	Me	Me	Me	G(60)	90/23	NMR (^{1}H, ^{13}C), MS	236
Ge	Me	Me	H	H	Me	H	B		monomer (unstable): NMR (^{1}H), adduct with MA	74a
							C			17b
Ge	Me	Me	H	Me	Me	H	B		NMR (^{1}H), adduct with MA	74a
							C (85)	75/30		17b
							C (86)		one-pot synthesis; NMR (^{1}H, ^{13}C), MS, IR, UV	19
Ge	Me	^{n}Bu	H	Me	Me	H	E (70)	50/0.07	NMR (^{1}H), adduct with MA	166
Ge	Ph	Ph	Me	Me	Me	Me	G		MS	236
Sn	^{n}Bu	^{n}Bu	Me	H	H	Me	F (15)		NMR (^{1}H), MS	64

[a] Methods: (A) section I.B.3.d; (B) section I.B.3.b; (C) section I.B.3.c; (D) section I.B.2.b; (E) substitution reaction at M; (F) section I.B.1.d; (G) section I.B.4.

action of the metallole[74b] which leads to $(Me_2MO)_n$ and butadiene from **5**, isoprene from **6**, and 2,3-dimethylbutadiene from **7**.

The above method was recently applied to synthesize a silole unable to isomerize into a transoid diene, 1,1-dimethyl-3,4-diphenylsilole[78] (eq 30).



(30)

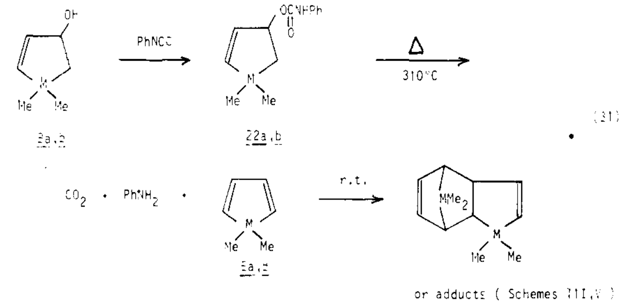
(c) *Thermolysis of Esters of 1-Metallacyclopent-4-en-3-ols.* As has already been said (cf. section I.A), 1,1-dimethylsilole was prepared in 1981 by catalytic dehydration of 1,1-dimethylsilacyclopent-4-en-3-ol[6] and by thermolysis of the corresponding benzoate ester.[7]

In order to avoid the isomerization of C-methylated metalloles into transoid dienes, mild conditions for the elimination reactions have been sought (Table 8).

The *S*-methylxanthates **20** and **21** are thermally unstable. They decompose during their synthesis by two competitive elimination pathways, β C–H and β C–Si (3/2)[19] (Scheme 21). The presence of dienic siloxanes makes the Chugaev reaction of no great value.

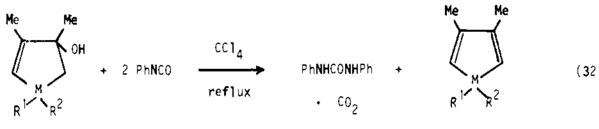
With the *N*-phenylcarbamates, only the β C–H elimination is observed, and the metallole is the major product of the elimination reaction (Table 8).

In the case of the secondary carbamates, the thermolysis reaction takes place at 310 °C to yield 1,1-dimethylmetalloles (**5a,b**) (eq 31) and 1,1,3-trimethylmetalloles (**6a,b**). These unstable monomers were identified by ^{1}H NMR spectroscopy and trapped as Diels–Alder adducts (dimer, maleic anhydride) or as



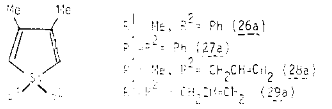
tricarbonyliron complexes[17,19] (Scheme 22).

With tertiary carbamates, the reaction is far more useful.[79a] These are stable enough to be isolated. They decompose regiospecifically at about 70 °C in solution. If the reaction is carried out in carbon tetrachloride, one can check the reaction progress by NMR spectroscopy. This method made it possible to prepare the first lower alkyl substituted group 14 metalloles, stable in the monomeric state, 1,1,3,4-tetramethylsilole (**7a**)[19,80] and -germole (**7b**)[17b,19] (Scheme 23). A one-pot synthesis is possible in the same solvents[79a] (eq 32). The yields and the isomeric purity of the metallole are high (Table 8).

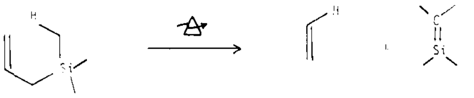


(32)

This method has been recently applied to pseudofunctional siloles with phenyl or allyl groups (**26**–**29**).[75]



(*d*) *Flash Vacuum Pyrolysis of 1-Allylsilacyclopent-3-enes.* Flash vacuum pyrolysis (FVP) of allylsilanes gives, by a retroene reaction process,[70,81] propene and an unstable silene which dimerizes or undergoes rearrangement (eq 33). Totally new organosilicon compounds (e.g., silabenzene) have been obtained in this way.[70,81] Barton and Burns applied this reaction to the synthesis of siloles.[5]

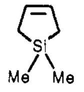
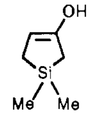
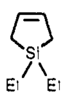
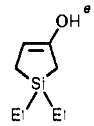
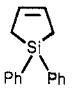
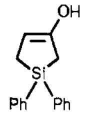
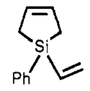
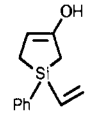
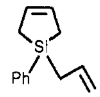
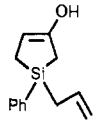
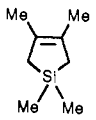
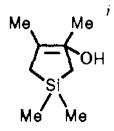


(33)

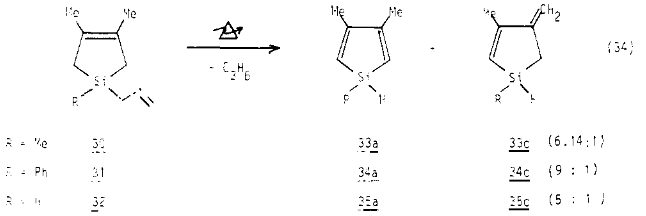
Thermolysis at 820 °C under low pressure of 1-allyl-1-methylsilacyclopent-3-ene gave the dimer of the first C-unsubstituted silole to be identified (Scheme 2). A disadvantage of this method is the requirement for 1-allylsilacyclopent-3-enes, whose synthesis by reaction of allyldichlorosilanes, 1,3-dienes, and magnesium gives low yields.[5] However, since a new method of synthesis that can be utilized to prepare a number of silacyclopentenes,[75,79] particularly ones in which an allyl group is bonded to silicon, has recently been developed, Barton's method for the synthesis of 3,4-dimethylsiloles with a Si–H bond, stable as monomers, is more practical.

FVP of 1-allyl-1,3,4-trimethylsilacyclopent-3-ene (**30**) and 1-allyl-1-phenyl-3,4-dimethylsilacyclopent-3-ene (**31**) gives 1,3,4-trimethylsilole (**33a**) and 1-phenyl-3,4-dimethylsilole (**34a**), respectively, together with their transoid isomers, the latter as minor products[82] (eq 34).

TABLE 6. Methods of Oxidation of Some Silacyclopentenes into Silacyclopentenols

		% yield			
silacyclopentene	silacyclopentenol	*a*	*b*	*c*	*d*
		75[73]	86[76]		
	 [e]			8[71b]	
		91[18]	78[76]		12[71c]
		66[18b]	*f*		
		32[18b]	*f*		
	 [i]	80[74a g]	80[76]		60[18b,72a h]

[a] Photooxidation ($^1O_2$)/reduction. [b] Base-promoted rearrangement of the epoxides. [c] Catalytic oxidation ($^3O_2$). [d] Triplet oxygen oxidation. [e] +other products. [f] Inoperative method. [g] +isomer. [h] The $^3O_2$ oxidation reaction was carried out at 60 °C like that of 1,2-dimethylcyclohexene:[72b] 40% of untransformed silacyclopentene and 60% of the expected alcohol are obtained. When this reaction takes place in refluxing MeOH with the same concentrations as for the photooxidation ($^1O_2$), nothing is observed after 5 h, whereas $^1O_2$ reacts within minutes with the tetramethylsilacyclopentene.[74a] [i] Some 1-allyl- or 1-phenyl-3,4-dimethylsilacyclopentenols have been recently reported (method *a*).[75]

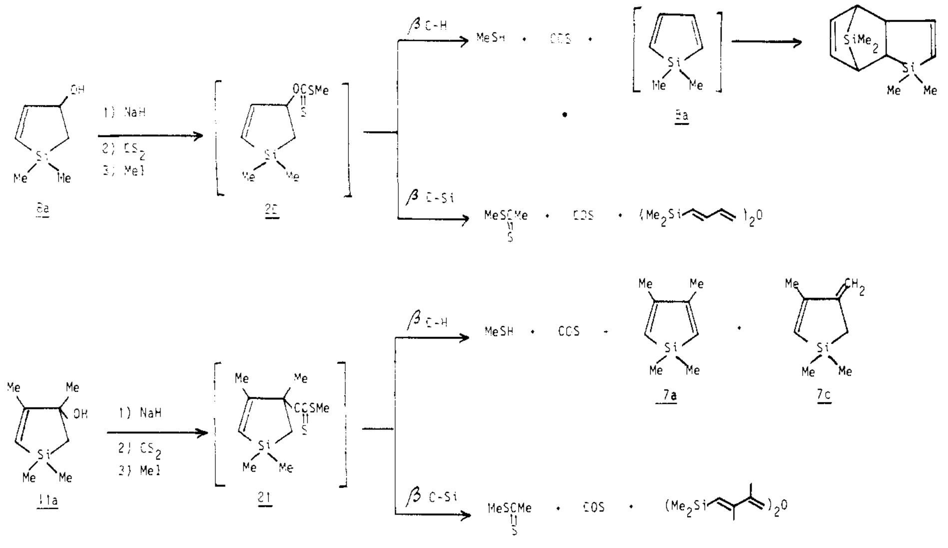


(34)

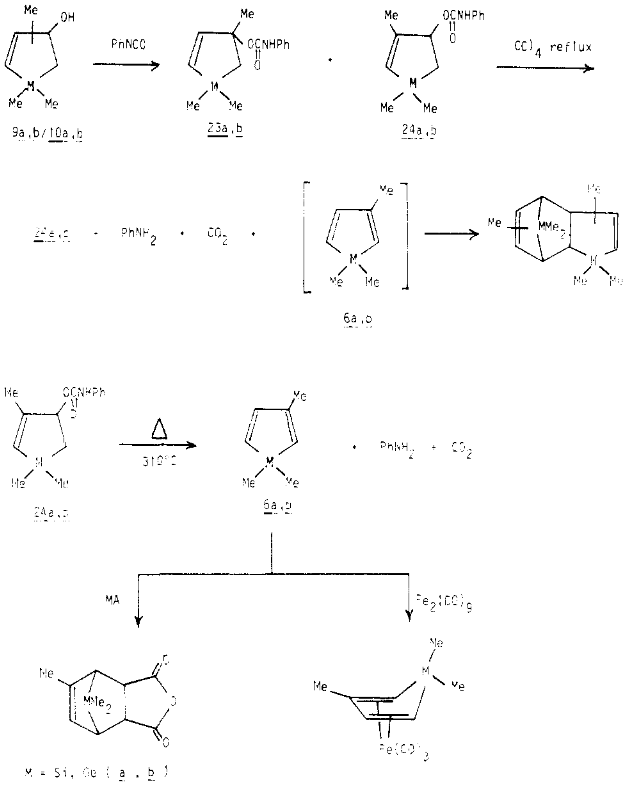
3,4-Dimethylsilole (**35a**), a metallole having two Si–H bonds, has been also prepared by the same method,[79] but the yield is low and, together with dienes **35a** and **35c**, other products are formed.

A kinetic study (SFR technique)[83] of the retroene reaction of 1-allylsilacyclopent-3-enes has recently shown that the *A* factor is similar to, but the activation energy is lower than, that with acyclic allylsilanes[84] (Table 9). Moreover, as this energy is higher in the case of allyltrimethylsilane (cleavage of a C–H bond of a methyl group),[84] it is clear that exocyclic loss of propene is insignificant in the pyrolysis of 1-allylsilacyclopent-3-enes. In spite of the very fast [1,5]-H rearrangement

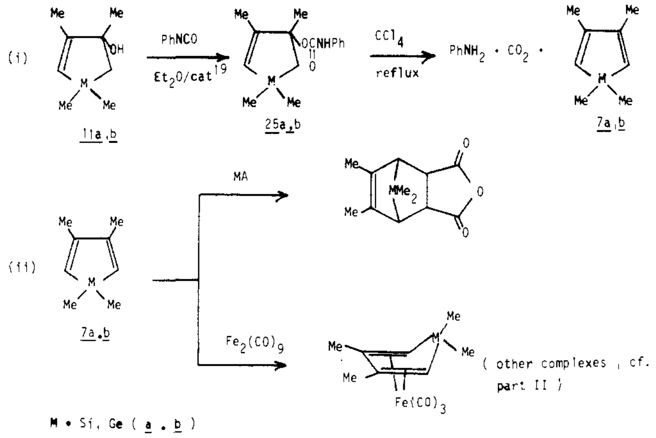
SCHEME 21



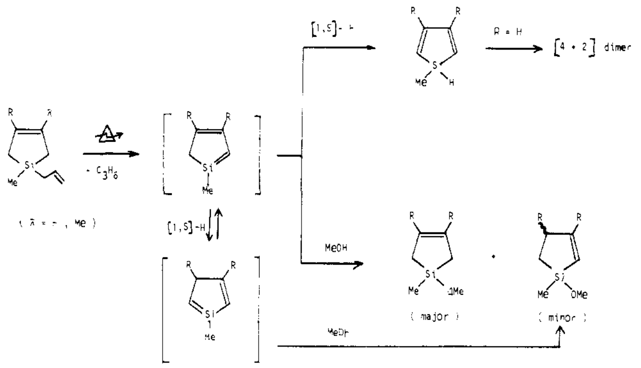
SCHEME 22



SCHEME 23



SCHEME 24



of 2*H*-silole and/or 3*H*-silole intermediates, the latter has been trapped with an excess of MeOH to give a mixture of 1-methoxysilacyclopent-3-ene and 1-methoxysilacyclopent-2-ene[83] (Scheme 24). FVP of a silacyclopent-3-ene with a substituted allyl group shows that an exocyclic 1,3-silyl shift is in competition with the endocyclic retroene reaction in these compounds[83] (Table 9).

In marked contrast, the FVP of the germanium analogue of **30** did not give the corresponding germole; the only identifiable product was 2,3-dimethylbutadiene formed by a cheleotropic elimination.[82]

The C-substituted group 14 metalloles are assembled in Tables 4 and 5.

4. Exchange Reactions (Transmetalation) with Other Heterocyclopentadienes

Although transmetalation reactions in heterocyclic chemistry are well-known reactions, no systematic synthesis of group 14 metalloles by this process has yet been described.

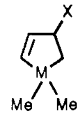
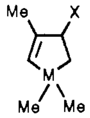
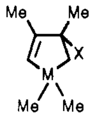
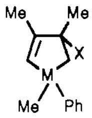
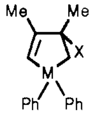
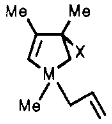
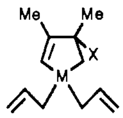
The stannoles, owing to the lability of the Sn–C bond, have already been used for the preparation of other heteroles (cf. section II.J and eq 112). However, since their synthesis is presently less developed for the C-unsubstituted or lower alkyl substituted derivatives than that of the corresponding siloles or germoles, they are not useful for the preparation of the latter.

TABLE 7. Catalytic Dehydration of Metallacyclopentenols

alcohols	cat. and exptl conditions (°C/mmHg)	products 		rel %	ref
8a	Al_2O_3; 300/0.01	**5a**			6
	Al_2O_3; 220/atm press. (CP[a])	**5a**			17
8b	Al_2O_3; 300/0.01	**5b**			8
	Al_2O_3; 220/atm press. (CP)	**5b**			17
9a/**10a** (58/42)	Al_2O_3; 300/0.01	**6a**	**6c**	35/65	74
	ThO_2; 300/atm press. (CP)	**6a**	**6c**	25/75	74
9b/**10b** (68/32)	Al_2O_3; 300/0.01	**6b**	**6d**	42/58	74
11a/**12a** (80/20)	Al_2O_3; 300/0.01	**7a**	**7c**	15/85	74
	Al_2O_3: 230/atm press. (CP)	**7a**	**7c**	18/82	74
	ThO_2; 300/atm press. (CP)	**7a**	**7c**	25/75	74
11a	Al_2O_3; 230/atm press. (CP)	**7a**	**7c**	18/82	74
11b/**12b** (43/57)	Al_2O_3; 300/0.01	**7b**	**7d**	20/80	74
11b	Al_2O_3; 223/atm press. (CP)	**7b**	**7d**	17/83	74
	ThO_2; 356/atm press. (CP)	**7b**	**7d**	35/65	74

[a] CP = cyclopentane.

TABLE 8. Thermolysis of Esters of Metallacyclopentenols

ester	M	X	T, °C	% yield	selectivity (%) β C-H	β C-M	ref
	Si	OC(O)Ph	540	60	**5a**		7
		OC(S)SMe (**20**)	unstable	92	**5a** (60)	**26** (40)	19
		OC(O)NHPh (**22a**)	310	80	**5a**		17, 19
	Ge	OC(O)NHPh (**22b**)	310	80	**5b**		17
	Si	OC(O)NHPh (**24a**)	310	72	**6a**		19
	Ge	OC(O)NHPh (**24b**)	310	60	**6b**		17b
	Si	OC(S)SMe (**21**)	unstable	90	**7a** (42) **7c** (28)	**27** (30)	19
	Si	OC(O)NHPh (**25a**)	75	83	**7a** (95) **7c** (5)		19, 80
	Ge	OC(O)NHPh (**25b**)	75	86	**7b** (90) **7d** (10)		17b, 19
	Si	OC(O)NHPh	75	90	**26a** (90) **26c** (10)		75
	Si	OC(O)NHPh	75	73	**27a** (82) **27c** (18)		75
	Si	OC(O)NHPh	75	88	**28a** (50)[a] **28c** (50)		75
	Si	OC(O)NHPh	75	82	**29a** (50)[a] **29c** (50)		75

[a] Reactions carried out from isomeric mixtures of carbamates (50:50 endocyclic:exocyclic C=C double bond).

Recently, Fagan and Nugent obtained some heteroles containing elements of groups 13–16 by transmetalation reactions with various zirconacyclopentadienes.[110] Among them, two group 14 metalloles have been reported, 1,1-dichloro-2,3,4,5-tetramethylgermole and a stannole[110a] (Scheme 25).

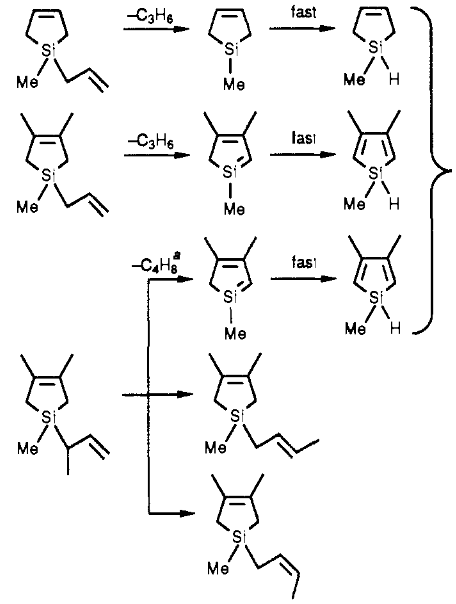
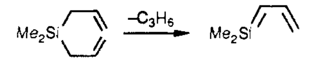
Transmetalations using some transition element heteroles ($Cp_2EC_4R_4$; E = Ti, Zr, Hf; R = Ph, Me) and halogermanes have been recently reported.[236]

C. Dibenzometalloles or 9-Metallafluorenes

1. Cyclization of 2,2'-Difunctional Biphenyls

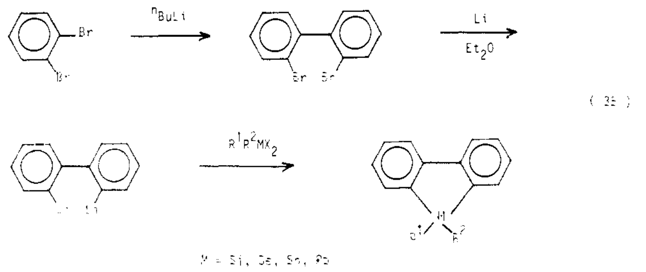
(*a*) *2,2'-Dilithiobiphenyl.* The predominant method for the synthesis of 9-metallafluorenes described by

TABLE 9. Arrhenius Parameters and Rate Constants for Pyrolysis of Some Allylsilanes

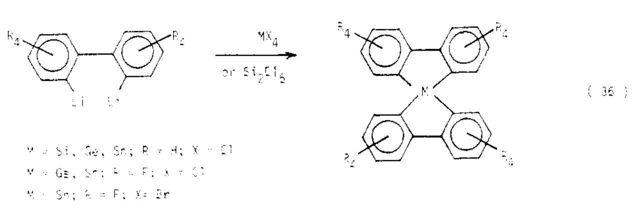
reaction	log A	E_a, kJ·mol^{-1}	$k_{500\,°C}$, s^{-1}	ref
	11.0 ± 0.1	179 ± 2	8.01 × 10^{-2}	83
	11.6 ± 0.3	176 ± 4	5.09 × 10^{-1}	83
	11.3 ± 0.2	173 ± 3	4.07 × 10^{-1}	83
$Me_3Si\text{–}CH_2CH{=}CH_2 \xrightarrow{-C_3H_6} Me_2Si{=}CH_2$	11.6 ± 0.5	230 ± 8	1.14 × 10^{-4}	84a
	11.2 ± 0.1	199 ± 2	5.65 × 10^{-3}	84b

[a] In this case the values are estimated (see ref 83).

Gilman in 1955[85] is the one-step reaction of 2,2′-dilithiobiphenyl with various organometallic halides (eq 35). This method easily provides numerous sila-, germa-, stanna-, and plumbafluorenes with alkyl, aryl, halogeno, hydrogen, or silyl groups on the heteroatom (Table 10).

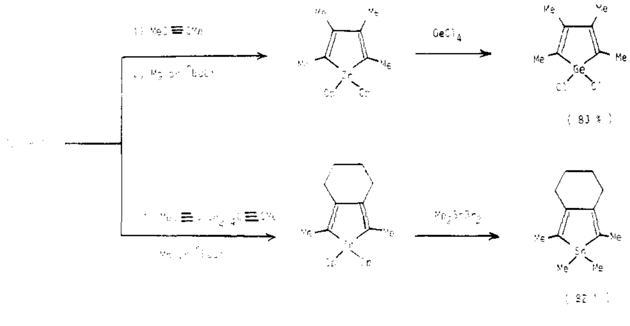


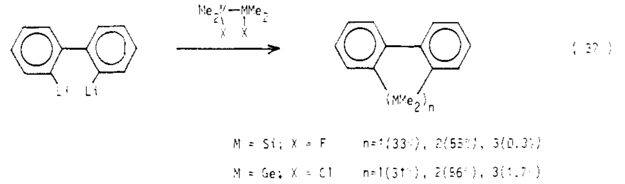
2,2′-Dilithiobiphenyl also reacts with tetrahalides of Si, Ge, and Sn and with hexachlorodisilane to give 5,5′-spirobi[dibenzometalloles][85b,d,86] (eq 36). 2,2′-Dilithiooctafluorobiphenyl leads to polyfluorospirogerma(and stanna)fluorenes.[87a–c]



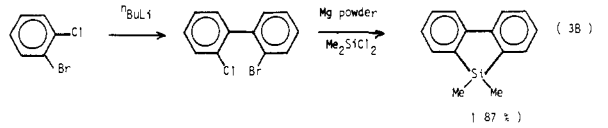
1,2-Difluoro-1,1,2,2-tetramethyldisilane and 1,2-dichloro-1,1,2,2-tetramethyldigermane react with 2,2′-dilithiobiphenyl (eq 37). In each case, two main products have been characterized: dibenzo-1,1,2,2-tetramethyl-1,2-disila(or digerma)cyclohexa-3,5-diene and 9,9-dimethyl-9-sila(or germa)fluorene.[88]

SCHEME 25



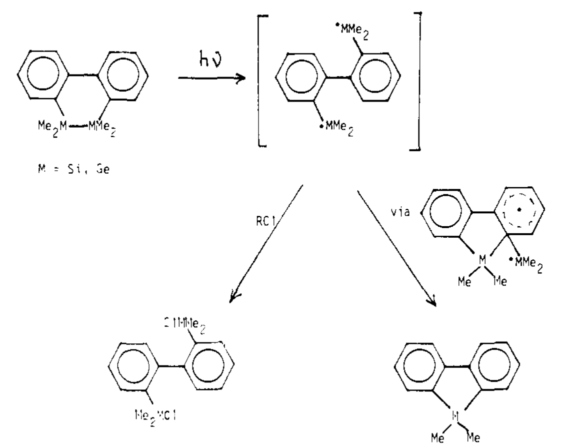


(*b*) *2,2′-Dihalogenobiphenyl.* Reaction of 2-chloro-2′-bromobiphenyl with magnesium powder followed by addition of Me_2SiCl_2 yields 9,9-dimethyl-9-silafluorene[89] (eq 38).

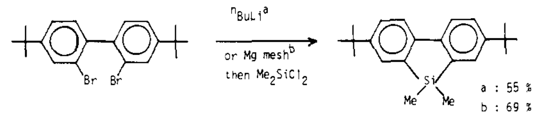


2,2′-Dibromo-4,4′-di-*tert*-butylbiphenyl reacts with *n*-butyllithium or with magnesium mesh. The bis(organometallic) compound thus obtained on treatment

SCHEME 26

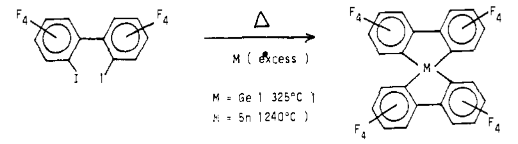


with Me_2SiCl_2 leads to the corresponding silafluorene[89] (eq 39).



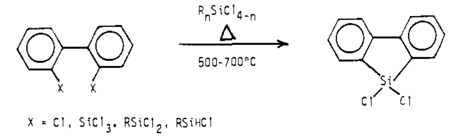
(39)

2,2′-Diiodooctafluorobiphenyl reacts at high temperatures with Ge or Sn metal powder to produce the corresponding polyfluorometallaspirofluorenes[87d] (eq 40).



(40)

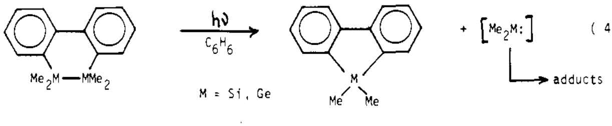
When 2,2′-dichlorobiphenyl and various 2,2′-bis(chlorosilyl)biphenyls are pyrolyzed with organochlorosilanes, 9,9-dichloro-9-silafluorene is produced[90] (eq 41).



(41)

2. *Irradiation of Dibenzo-1,1,2,2-tetramethyl-1,2-disila(or digerma)cyclohexa-3,5-diene*

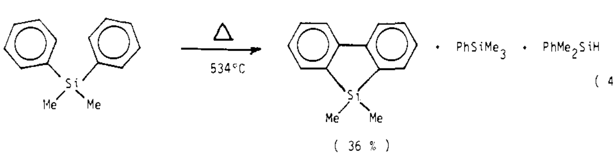
Photolysis of dibenzo-1,1,2,2-tetramethyl-1,2-disila(or germa)cyclohexa-3,5-diene results in extrusion of dimethylsilylene (or germylene) and formation of 9,9-dimethyl-9-sila(or germa)fluorene (eq 42). This irradiation occurs by a diradical process[88a] (Scheme 26).



(42)

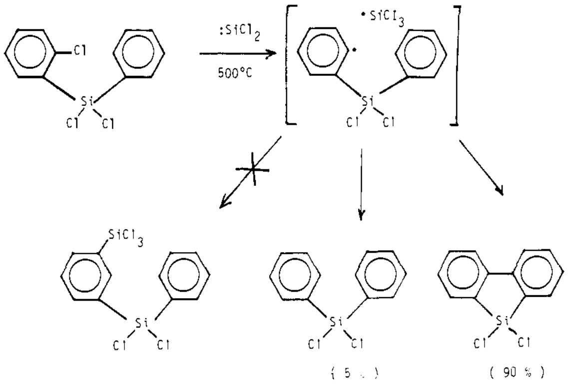
3. *Thermolytic Reactions*

Pyrolysis of dimethyldiphenylsilane leads to several products; among these is 9,9-dimethyl-9-silafluorene, produced by loss of hydrogen and intramolecular cyclization[91] (eq 43).

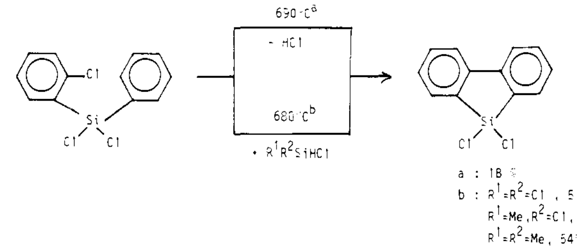


(43)

Thermal interaction of (o-chlorophenyl)phenyldichlorosilane with hexachlorodisilane or other organochlorosilanes gives 9,9-dichloro-9-silafluorene in high yield (eqs 44 and 45). This may be due to the high tendency of the (phenyldichlorosilyl)phenyl radical to cyclize intramolecularly.[92,93]



(44)



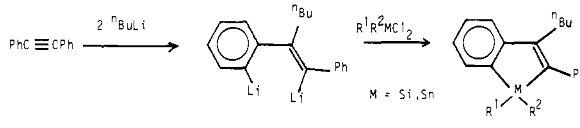
(45)

The various group 14 metallafluorenes known to date are assembled in Table 10.

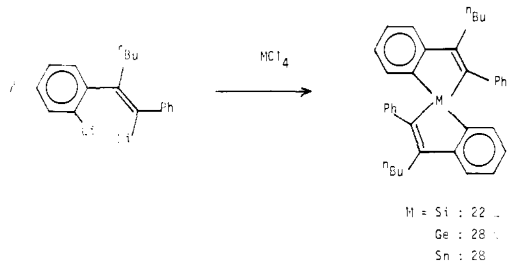
D. Benzometalloles or 1-Metallaindenes

1. *Cyclization of a 1-Lithio-2-(2′-lithiophenyl)ethylene*

Several metallaindenes, listed in Table 11, are obtained by the reaction of organometallic dihalides of Si and Sn with the title dilithio reagent[106] (eq 46). When tetrahalides of Si, Ge, and Sn are used, spirometallaindenes are obtained (eq 47).



(46)



(47)

2. *Thermolytic Reactions*

The copyrolysis of chlorinated phenylvinylchlorosilanes and hexachlorodisilane, a source of dichlorosilylene, gives 1,1-dichloro-1-silaindene with a moderate yield, as shown in eq 48.[92a]

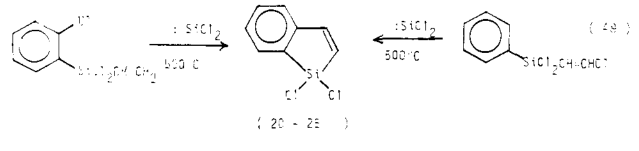
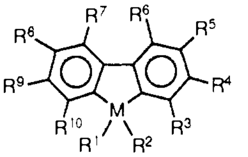


TABLE 10. **Group 14 9-Metallafluorenes**



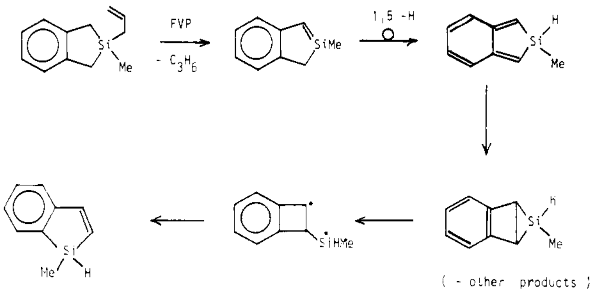
M	R^1	R^2	prep method[a] (% yield)	bp[b]	mp[c]	remarks[d]	ref
Si	H	Me	A (60)		41–42	NMR (^1H, ^{29}Si), IR	94
			D (23–53)			NMR (^1H), MS, IR	95, 98
Si	H	Ph	D (55–88)	130–131/0.005		NMR (^1H), MS, IR	85d, 95
Si	H	CH_2Ph	D (72)	135–138/0.005	68.5–69.5		85d
Si	Cl	Cl	A (38)	108–110/0.01			85b
			C (60–90)				92a, 93a, 99a,b
Si	Me	Cl	A (83)	98–100/0.007			85b,d
Si	Ph	Cl	A (73)	172–175/0.005			85b,d
Si	CH_2Ph	Cl	A (47)	150–157/0.01			85b,d
Si	$C_{12}H_{25}$	Cl	A (86)	180–182			85b,d
Si	Me	Me	A (33–87)	89–110/0.4–0.8	55–58	NMR (^1H)	88a, 89
			B (11–85)				88a,b
			C (36)			MS, IR	91
			D (36–100)	87–90/0.005	55–57		85b,c,d, 100
					58–59		
					59–61		
Si	Me	Et			42.5–43	UV	102b
Si	Me	$CH{=}CH_2$	A (41)	134–136/0.5	58–59	UV	102b
Si	Me	$CHBrCH_2Br$			71–72	UV	102b
Si	Me	${}^nBu$	D (36–63)			NMR (^1H), IR	100, 101a,b
Si	Me	${}^tBu$	D (18)		68–70	NMR (^1H), MS, IR	100
Si	$(CH_2)_5$		A	144–145		IR	85b
Si	Me	Ph	D (75)		66	NMR (^1H), MS, IR	100
Si	Me	*e*	D (65)		115–116		85b
Si	Me	$SiMe_3$	A (94)		57	NMR (^1H), MS, IR	100
Si	Me	$SiMe_2Et$	D (64)			NMR (^1H), MS	98
Si	Me	$SiR^1C_{12}H_8$[h]	(43)		185–186		85d
Si	Me	$OSiR^1C_{12}H_8$[h]	D (77)		127–128	IR	85d
Si	Me	$SSiR^1C_{12}H_8$[h]	D (90)		114–115	NMR (^1H, ^{29}Si), MS, RX	94
Si	Et	Et	A (23)	95–105/0.02	60–61		88a
Si	${}^nBu$	${}^nBu$	D (100)			NMR (^1H), MS, IR	100, 101a,b
Si	${}^nBu$	Ph	D (40)			NMR (^1H), MS, IR	100
Si	$C_{12}H_{25}$	$C_{12}H_{25}$	A (28)	240–243/0.01		*n*, *d*	85b
Si	$C_{12}H_{25}$	Ph	D (73)	196–198/0.012		*n*, *d*	85b
Si	$C_{12}H_{25}$	$C_{16}H_{33}$	(66)	230–232/0.005		*n*, *d*	85b
Si	$C_{12}H_{25}$	*f*	D (82)	242–247/0.008		*n*	85b
Si	$C_{12}H_{25}$	*g*	D (80)	250–251/0.005		*n*, *d*	85b
Si	$C_{12}H_{25}$	$SiR^1C_{12}H_8$[h]	D (53)		59–61	IR	85d
Si	$C_{12}H_{25}$	$OSiR^1C_{12}H_8$[h]	D (46)	190–200/0.03	74–75	IR	85d
Si	$C_{14}H_{29}$	$C_{14}H_{29}$	D (36)	245–250/0.003		*n*, *d*	85b
Si	Ph	Ph	A (31)		148–149		85a, 102a
			D (25–81)		147–149	NMR (^1H), MS, IR, UV	85b,d, 100, 102a
Si	Ph	$OSiR^1C_{12}H_8$[h]	D (21)		203–204	IR	85d
Si	Ph	$SiMe_3$	A (92)		54	NMR (^1H), MS, IR	100
Si	Ph	*e*	D (87)		137–138		85d
Si	$SiMe_3$	$SiMe_3$	A (96)		60–61	NMR (^1H), MS, IR	100
Si	Me	${}^iBu$	(10)			$R^3 = SiMe_3$; NMR (^1H, ^{13}C), MS, IR	95
Si	Me	O^iPr	D (28)			$R^3 = SiMe_3$; NMR (^1H), MS, IR	95
Si	Me	$SiMe_3$	(16)			$R^5 = SiPh_2Me$; NMR (^1H, ^{13}C), MS	101a
Si	Ph	${}^iBu$	(20)			$R^3 = SiMe_3$; NMR (^1H), MS	95
Si	Ph	O^iPr	D (44)			$R^3 = SiMe_3$; NMR (^1H), MS	95
Si	Me	Me	A (69)			$R^4 = R^9 = {}^tBu$; NMR (^1H, ^{13}C), MS	89
Si	Me	Me	(44)			$R^5–R^8 = Me$	88c
Si	Ph	Ph	A (20)		147–149	$R^3–R^{10} = F$; IR	87c
Si	$C_{12}H_8$[i]		A (56)		226–227		85b
			A (20)		230–231		85d
			D (38)		225–227		85c,d
Ge	Me	Me	A (31–77)		85–87	NMR (^1H)	88a
Ge	Ph	Ph	A (75)		152–153	UV	102a
Ge	Ph	Ph	A (30)		138–141	$R^3–R^{10} = F$; IR	87a–c
Ge	$C_{12}H_8$[i]		A (29)		244–246		85b
Ge	$C_{12}F_8$[i]		A (48)		230–232	$R^3–R^{10} = F$; IR	87a–d
Sn	Me	Me	A (72)		123–125	NMR (^1H)	106b
						stabilizer, insecticide	103
Sn	Cl	*e*	D (84)		230–232		86
Sn	Et	Et	A (56)		73	UV	86
Sn	${}^nBu$	${}^nBu$	A (65)		56	IR	86
Sn	$c\text{-}C_6H_{11}$	$c\text{-}C_6H_{11}$	A (64)		104	IR	86
Sn	Ph	Ph	A (58)		141.5	IR, UV	86, 104
Sn	*e*	*e*	A (72)	196		IR	86

TABLE 10 (Continued)

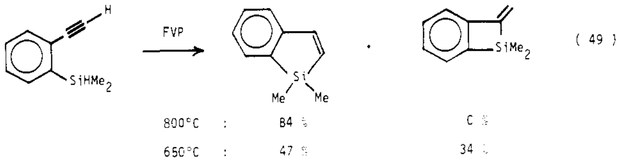
M	R^1	R^2	prep method[a] (% yield)	bp[b]	mp[c]	remarks[d]	ref
Sn	p-MeC_6H_4	p-MeC_6H_4	A (55)		108	IR	86
Sn	Me	Me	A			R^3-R^{10} = F	87c
Sn	Ph	Ph	A (24)		131-133	R^3-R^{10} = F; IR	87c
Sn	$C_{12}H_8$[i]		A (23)		320-322		86
Sn	$C_{12}F_8$[i]		A (17)		227-229	R^3-R^{10} = F; IR	87c,d
Pb	Ph	Ph	A (30)		136-137	UV	104

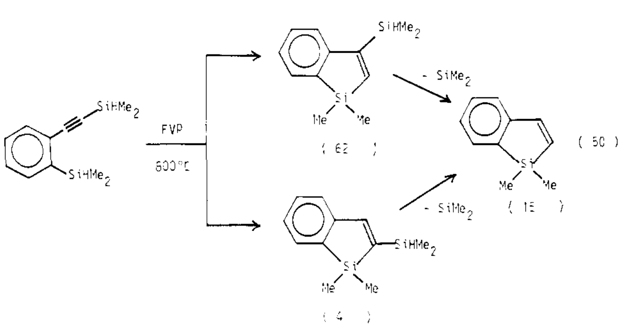
[a] Methods: (A) section I.C.1.a or I.C.1.b; (B) section I.C.2; (C) section I.C.3; (D) substitution reaction at M. [b] °C/mmHg. [c] °C. [d] Unless otherwise indicated R^1-R^{10} = H. [e] 2-Biphenylyl. [f] 3-Biphenylyl. [g] $(PhCH_2)_2MeSiCH_2$. [h] $MR^1C_{12}H_8$ = 9-R^1-9-metallafluorenyl. [i] Spirobimetallafluorene.

SCHEME 27

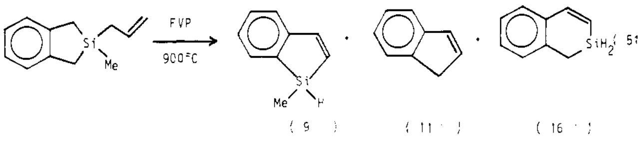


By FVP of (o-dimethylsilylphenyl)acetylene at 800 °C, Barton obtained 1,1-dimethyl-1-silaindene in high yield[107a] (eq 49) via insertion of an intermediate vinylidene into the Si-H bond. At 650 °C the reaction affords the silaindene and the isomeric 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene arising from an initial [1,5]-H shift from silicon. Deuterium labeling revealed that there are two pathways leading to silaindene, via a carbene or via a diradical. FVP of a disilylated derivative of phenylacetylene also provides mechanistic data concerning the formation of 1,1-dimethyl-1-silaindene[107a] (eq 50).

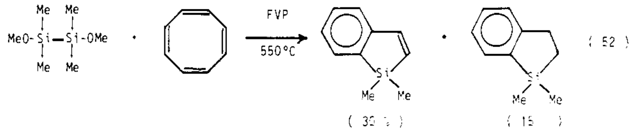




FVP of 2-allyl-2-methyl-2-silaindane leads to 1-methyl-1H-1-silaindene, 2-sila-1,2-dihydronaphthalene, and indene[96] (eq 51). Barton explained the formation of these products by a rearrangement of an initially formed 1H-2-silaindene via a retroene reaction. Trapping reactions established the intermediacy of the 1H-2-silaindene and an isobenzosilole (Scheme 27).

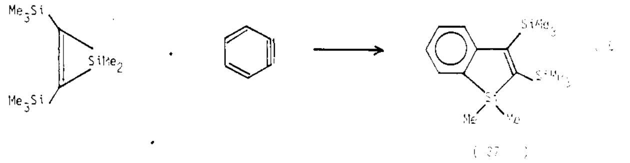


Addition of dimethylsilylene to cyclooctatetraene affords 1,1-dimethyl-1-silaindene and -indane[107b] (eq 52).



3. *Other Reactions*

A very interesting "two-atom" insertion reaction of a silirene into the C≡C bond of benzyne leading to a silaindene has been observed by Seyferth[108] (eq 53).



Photolysis of disilacyclohexadienes leads to silaindene structures via a 1-silabicyclo[2.1.0]pent-3-ene intermediate, which could be trapped with methanol.[97]

E. Functional Metalloles and Benzometalloles

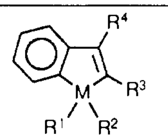
We shall define a "functional group" as one that is capable of being replaced by another one. In group 14 chemistry, such functional groups are H, X, OR, SR, NR_2, etc. Some hydrocarbon groups (phenyl, allyl, etc.) that can be replaced (M-C cleavage) are considered as "pseudofunctional groups". The latter become more labile when the group 14 organometallic compounds are complexed by a transition metal; this is exemplified in the group 14 metallole chemistry (cf. part 2 in this issue).

Functional derivatives of C-unsubstituted group 14 metalloles are unknown, except for 1-methylsilole,[5] which is unstable (cf. section I.A and Scheme 2).

1. *Functional C-Substituted Metalloles*

(*a*) *Functional C-Phenylated Metalloles.* 2,3,4,5-Tetraphenyl- and 2,5-diphenylmetalloles carrying functional groups may be obtained (cf. section I.B.1.a) by direct cyclization of 1,4-dilithio-1,3-butadiene (eqs 6 and 7; Schemes 15 and 16) and substitution of a group on the heteroatom (eqs 11 and 12; Schemes 6, 7, and 11-14).

TABLE 11. **Group 14 1-Metallaindenes**



M	R^1	R^2	R^3	R^4	prep method[a] (% yield)	mp[b]	remarks	ref
Si	Me	H	H	H	B (9)		NMR (^{1}H)	96
Si	Me	Me	H	H	B (84)		NMR (^{1}H, ^{13}C), MS	107
Si	Cl	Cl	H	H	B (25)			92a
Si	Me	Me	$SiHMe_2$	H	B (4)			107a
Si	Me	Me	H	$SiHMe_2$	B (62)			107a
Si	Me	Me	$SiMe_3$	$SiMe_3$	C (37)		NMR (^{1}H), *n*	108
Si	Me	Me	Ph	^{n}Bu	A (92)		bp 133 °C/0.02 mmHg; NMR (^{1}H)	106b
Si	Ph	Ph	Ph	^{n}Bu	A (55)	81.5-84.5	NMR (^{1}H)	106
Si	H	$SiMe_3$	$PhC{=}C(SiMe_3)_2$	$SiMe_3$	(70)	158	NMR (^{1}H, ^{13}C, ^{29}Si), MS, IR, RX	97
Si	$C_8H_4R^3R^4$ [c]		Ph	^{n}Bu	A (22)	125-126	NMR (^{1}H)	106
Ge	$C_8H_4R^3R^4$ [c]		Ph	^{n}Bu	A (28)	128-129	NMR (^{1}H)	106
Sn	Me	Me	Ph	^{n}Bu	A (73)		bp 133-140 °C/0.005 mmHg; NMR (^{1}H)	106b
Sn	$C_8H_4R^3R^4$ [c]		Ph	^{n}Bu	A (28)	139.5-142.5	NMR (^{1}H)	106

[a] Methods: (A) section I.D.1; (B) section I.D.2; (C) section I.D.3. [b] °C. [c] Spirobimetallaindene.

(*b*) *Functional C-Methylated Metalloles.* The lower alkyl substituted metalloles have been at the center of recent research work in our laboratory[79b] since the first C-methylated siloles having a Si–H bond were synthesized.[82]

Pseudofunctional siloles with Si–C bonds (phenyl or allyl) were obtained[75] by thermolysis of metallacyclopentenol esters (cf. section I.B.3.c).

Attempts to functionalize 1-phenyl- or 1-allylsiloles by cleavage of the exocyclic Si–C bond were not successful.[18b,82]

All attempts at chlorinating 1,3,4-trimethylsilole (**33a**) have failed.[109] Not only does the reducing power of **33a** seem low (no reaction in CCl_4 reflux in the presence of Bz_2O_2), but also the attempted chlorination by more efficient agents (Ph_3CCl; $PdCl_2$; CCl_4, Pd–C, etc.) under milder conditions (room temperature) did not produce 1-chloro-1,3,4-trimethylsilole. The latter, which is apparently formed (NMR), decomposes at room temperature. However, the iron tricarbonyl complex is stable (cf. part 2).

The more stable 1-fluoro-1,3,4-trimethylsilole (**36a**) has been identified spectroscopically (^{1}H, ^{13}C, ^{19}F NMR; MS) and chemically. **36a** has been prepared by fluorination of either 1,3,4-trimethylsilole (**33a**) or 1-methoxy-1,3,4-trimethylsilole (**37a**) (Scheme 28). The latter is very stable and is easily obtained by the exothermic reaction of methoxytributyltin with **33a**.

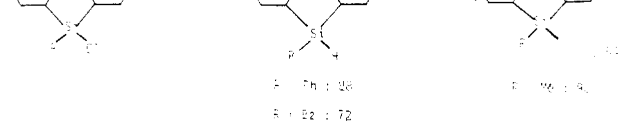
The amination of **33a** by R_2NLi proceeds in excellent yield to give the stable 1-(dialkylamino)-1,3,4-trimethylsilole (Scheme 28). Similarly, substitution of the Si-bonded hydrogen in **33a** by a hydrocarbon group can be performed by use of an organolithium reagent and is another method that may lead to pseudofunctional siloles.

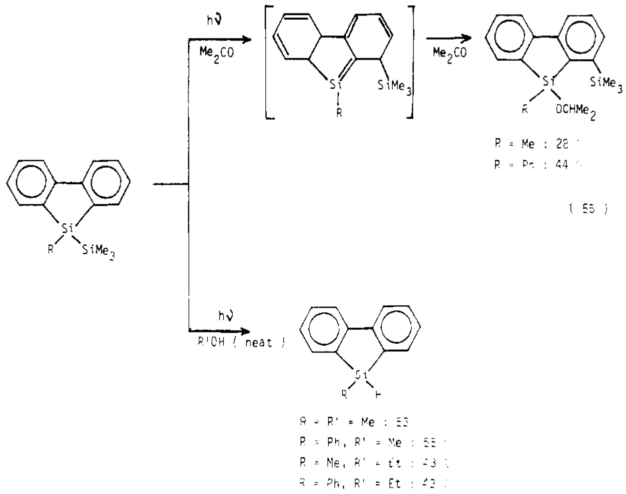
The stability of group 14 metalloles is discussed later (cf. section II.A), but the instability of lower alkyl substituted halogenosiloles, especially the chloro derivatives, is probably the reason for the failure of attempts to synthesize C-unsubstituted halogenometalloles such as 1,1-dichlorosilole (cf. section II.A).

2. *Functional Benzo- and Dibenzometalloles*

Cyclization of 2,2′-dilithiobiphenyl leads directly to some functional dibenzometalloles (metallafluorenes) (eq 35) with one or two Si–Cl bonds[85b] or a Si–H bond.[94] Pseudofunctional silafluorenes are also produced in the same reaction with vinyl, aryl, benzyl, or trimethylsilyl groups on the silicon atom (Table 10).

Functional metallafluorenes are also obtained by substitution reactions on the metal. The chloro compounds are reduced by $LiAlH_4$ to hydrogeno derivatives[85d] (eq 54). The Si–Si bond of 9-(trimethylsilyl)-9-silafluorenes reacts on photolysis (eq 55) with acetone to give a Si–O(C) bond via a Si=C double bond[95] and with neat alcohol (MeOH, EtOH) to give Si–H bonded fluorenes. Hydrolysis of the silafluorenyl anion also leads to a Si–H group.[98]



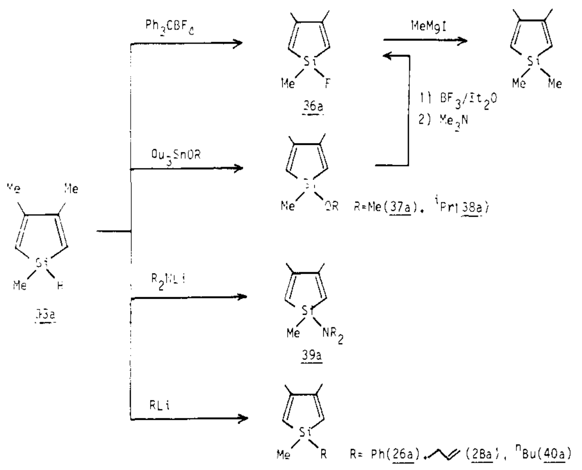


The Si–H bond of silafluorene reacts with sulfur (eq 54) to give a Si–S–Si bond.[94]

The Si–Cl bond interacts with sodium or lithium to give a Si–Si bond.[85d] The Si–Li intermediate reacts with Me_2SO_4 to produce 9,9-dimethyl-9-silafluorene.[85d]

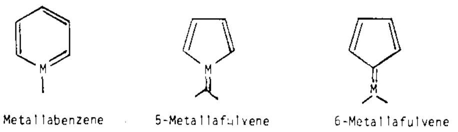
Functional 1-metallaindenes with Si–H[96,97] (eq 51) or with Si–Cl bonds[92a] (eq 48) are obtained in direct thermolytic reactions.

SCHEME 28



F. 5-Metallafulvenes and Analogues

Silabenzene and silafulvene are very reactive organometallic compounds[81] due to the sp^2-hybridized silicon. Like most silenes, those compounds are unstable and have been identified either by the matrix isolation method at low temperature or by trapping with alcohols, carbonyl compounds, or dienes.



With regard to the group 14 metallafulvenes, the more numerous studies concen the 6-metallafulvenes.[111-114] Dibenzo-6-germafulvene (Ge=C) has been recently isolated.[114]

By analogy with the heteroles, we shall consider here the 5-metallafulvenes and their analogues (metallacyclopentadienone, etc.), as well as the benzo forms, which have been the subject of some work.

It has already been noted (cf. section I.B.1.a and Scheme 9) that photolysis or thermolysis of (silacyclopentadienyl)diazomethane 41 or -diaziridine 42 in the presence of an alcohol yields, among other compounds, alkoxysiloles. According to Ando et al.,[46] the carbene 43 may rearrange to two intermediates: the 1-silatoluene 44 by ring expansion or 5-silafulvene 45 by 1,2-migration of a methyl group (Scheme 29). These sp^2-hybridized silicon species were trapped by alcohols, ketones, and dienes. In the presence of alcohols (MeOH, ^{t}BuOH), 5-silafulvene 45 gives the 1-alkoxysiloles 47 (R = Me, ^{t}Bu), while in the presence of benzophenone, it decomposes into 1,1-diphenylpropene and probably the silacyclopentadienone 46.

More recently, Terunuma et al.[115] thermolyzed (FVP) spiro[silacyclobutane-1,9-'[9*H*-9]silafluorene] (48), which, like other silacyclobutanes, decomposes by [2 + 2] cycloreversion to give ethene and 2-silafluorene (49), which dimerizes in a head-to-tail manner (50), whereas copyrolysis of 48 with benzophenone produces 1,1-diphenylethene and a siloxane oligomer, whose formation may be ascribed to fragmentation of the initial adduct 51 to dibenzosilacyclopentadienone 52 and the alkene (Scheme 30).

II. Organic Chemical Properties of Group 14 Metalloles

A. Stability. Isomerizations

1. Diels–Alder [4 + 2] Dimerization

In the case of C-phenylated group 14 metalloles, the presence of aromatic groups on the ring carbon atoms decreases the reactivity of the diene system. Diels–Alder cycloadditions (cf. section II.B) as well as formation of transition-metal complexes (cf. part 2) are more difficult to achieve than similar reactions with C-unsubstituted or C-methylated metalloles. These C-phenylated metalloles are stable monomers. A comparable difference in reactivity is found with phospholes.[1a]

As with cyclopentadiene and its 5-substituted derivatives, especially 5,5-dimethylcyclopentadiene,[116] the

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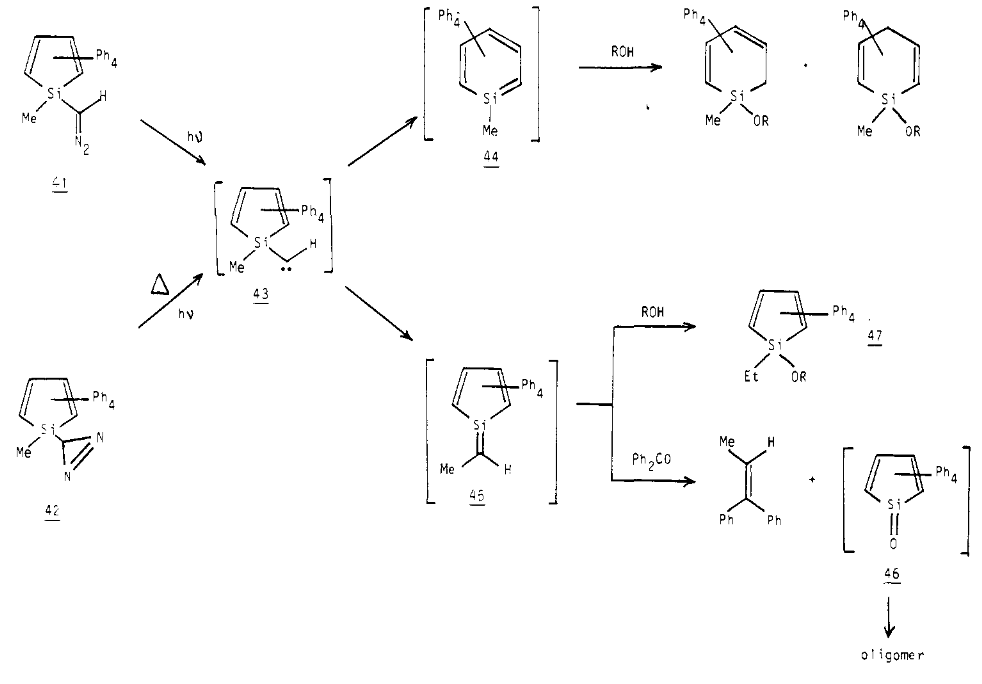
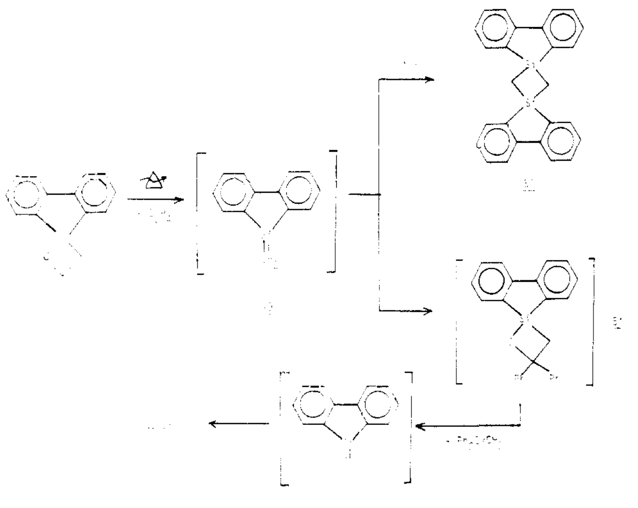


SCHEME 30



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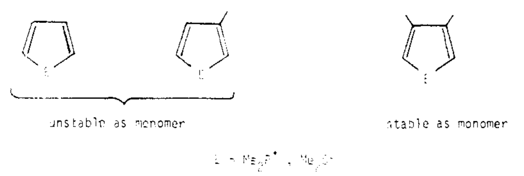


group 14 1,1-dimethylmetalloles dimerize at room temperature; the germole is less reactive than the silole.[8] Methyl group substitution on carbons 3 and 4 stabilized these monomers (3,4-dimethylmetalloles).[17b,19,80] The inhibition to dimerization of polymethylcyclopentadienes, which dimerize far less readily than cyclopentadiene,[117] may be attributed to an increase in frontier orbital energy-level differences. The polymethylcyclopentadienes become weaker dienophiles as their LUMO levels increase.[118] The close correspondence between the stability of siloles and that of the isoelectronic phospholium ions[1a,119] has been established[19] (Scheme 31).

Steric hindrance between a heteroatom-bonded substituent and a *C*-methyl group in the transition state has been proposed.[18] However, the stability of 3,4-dimethylsiloles with Si–H bonds (**33a**–**35a**),[79,82] especially **35a**, which present no hindrance in the [4 + 2] transition state, must result from electronic factors.

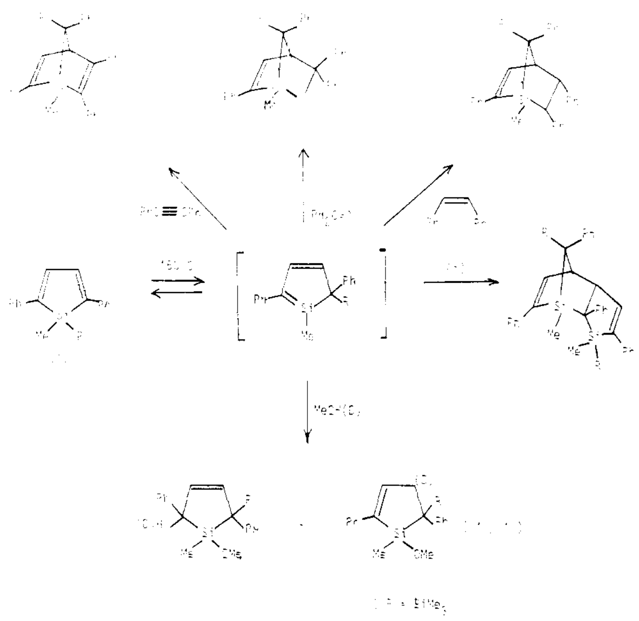
The insertion of a C or Si atom into the ring is sufficient to stabilize the system: 1,1-dimethyl-1-silacyclohexa-2,4-diene[120a] and 1,1,2,2-tetramethyl-1-silacyclohexa-3,5-diene,[120b] which have no ring-carbon substituents, are nevertheless stable as monomers.

The recent work of Ashe and Mahmoud[21b] is particularly interesting in two respects: the synthesis of the first C-unsubstituted stannole (Scheme 5), and its surprising stability as the monomer. This result is related to the previous observation[8] that 1,1-dimethylgermole is more stable as the monomer than 1,1-dimethylsilole. The kinetic stability toward [4 + 2] dimerization increases from siloles to stannoles with the size of the heteroatom.

2. Geometric Isomerization of the C-Substituted Metalloles into Transoid Dienes

The transoid dienes (**c**, **d**) are the thermodynamic isomers of the methylsiloles (**a**) and germoles (**b**) (Table 6).[74] Isomerizations of this type are known in the case of methylcyclopentadienes[121] or methylphospholes[122] and are promoted by catalysts, particularly acids. The catalytic influences of alumina and of thoria in the case of siloles and germoles have been demonstrated.[74b] Basic lithium reagents also catalyze this isomerization (cf. section II.G) by forming an allylic carbanion.[166]

SCHEME 32



Under noncatalytic synthesis conditions, a partial isomerization (≤10–15%) of C-methylated siloles and germoles is observed (cf. section I.B.3.c,d). To minimize the formation of transoid dienes, storage at −20 °C or lower is needed. The isomerization at room temperature is, however, slow, and several months are necessary before the transoid isomer becomes predominant.[18,19] The mechanism of this noncatalytic isomerization implies a thermally allowed [1,3]-H antarafacial migration.[123]

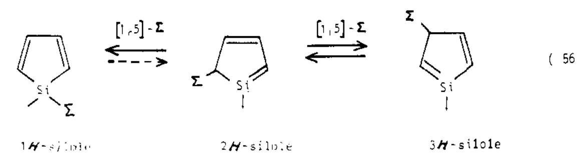
In the case of some of the known 3,4-disubstituted derivatives, such as 1,1-dimethyl-3,4-di-*tert*-butylsilole[57b,d] or 1,1-dimethyl-3,4-diphenylsilole,[56b,57a,58] this type of isomerization is impossible. The 2,5-dimethylmetalloles, which would lose the carbon–carbon double-bond conjugation by isomerization, are probably more stable in the metallole form than 3,4-dimethyl derivatives. Only one such derivative is known, 1,1-di-*n*-butyl-2,5-dimethylstannole.[64]

3. Isomerization by [1,5]-Shifts. Relative Stability of the 1H-Metalloles (1-Metallacyclopenta-2,4-dienes) and of the 2H-Metalloles (1-Metallacyclopenta-1,3-dienes)

The 2*H*-metalloles possessing a tricoordinate heteroatom M and a M=C bond, are unstable. In 1979, Barton et al.[52a] isolated the trapping products (methanol etc.) of a 2*H*-silole produced by 1,5-isomerization of the trimethylsilyl group of 1-methyl-1-(trimethylsilyl)-2,5-diphenylsilole (Scheme 32).

2*H*-Siloles are the reaction intermediates in the FVP of 1-allylsilacyclopent-3-enes[5,79b,82,83] (cf. section I.B.3.d, Scheme 24). Following a 1,5-H shift, they yield the 1*H*-silole isomers (eq 56). A similar intermediate species has also been postulated in the case of a benzosilole[96] (Scheme 27).

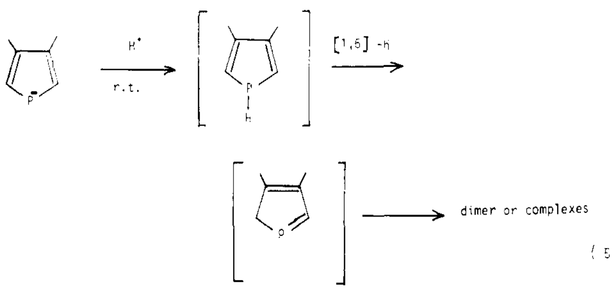
In another study, Mathey et al. showed that 1*H*-phospholes isomerize into 2*H*-phospholes which then



(56)

(The migrating group Σ can be an hydrogen atom [5,87], a trimethylsilyl group [52a] or another substituent)

spontaneously dimerize, but may be trapped by complexation (eq 57). The relative stabilities of the $1H$-



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and $2H$-heteroles is thus reversed between the phosphorus and silicon series. This result may be explained by reference to the relative stabilities of the σ bonds in silanes and phosphines (Si > P) and that of the π bonds in silenes and phosphenes (Si < P).[124]

No $2H$-germoles or stannoles are as yet known. The FVP of 1-allylgermacyclopent-3-enes does not lead to a germole[82] (cf. section I.B.3.d).

To date, no group 14 $3H$-metallole has been identified. It is, however, possible that $3H$-siloles are formed by isomerization of $2H$-siloles at high temperatures[83] (Scheme 24). Under these conditions, the possibility of reaction intermediates of the Dewar type cannot be ruled out.

4. *Stability of Functional and Spiro Derivatives*

The instability of the 1-halo-3,4-dimethylsiloles (cf. section I.E.1.b) may seem surprising in view of the high energy of the bonds between Si and the halogens.

With cyclopentadiene, although polyhalogenated derivatives are well-known (hexachlorocyclopentadiene), 5-halocyclopentadienes have proved to be kinetically less stable than cyclopentadiene.[182-184] An effect similar to *spiroconjugation* has been proposed (interaction between two perpendicular π systems joined by a central tetrahedral atom)[185] as being responsible for modifications in the electronic spectra and chemical reactivity of halocyclopentadienes, cyclopentadienone ketals (dialkoxycyclopentadienes), and 1,1-dioxothiophene.[184-186]

The thermal instability of 1-halo-3,4-dimethylsiloles could be the result of a more complex phenomenon. It must be noted that halosiloles are stabilized via transition-metal complexation [e.g., (η^4-1-chloro-3,4-dimethylsilole)carbonyliron][187] or if the ring carbons carry phenyl substituents (cf. section I.E.1.a). The observations that 1-halo-3,4-dimethylphospholes (stabilized as σ tungsten pentacarbonyl complexes),[188] 1-chloro-2,3,4,5-tetramethylstibole, and 1-chloro-2,3,4,5-tetramethylbismole[110a] are thermally unstable suggest that this phenomenon is common to many heterocyclopentadienes, although, 1,1-dichloro-2,3,4,5-tetramethylgermole is more stable.[110a]

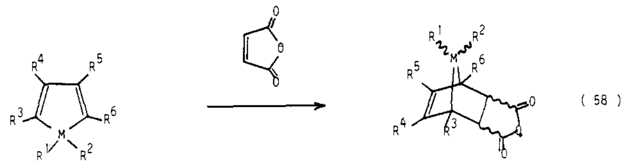
Similarly, results concerning the synthesis of group 14 spirobimetalloles deserve comment. The synthesis of these compounds is extremely easy with tin, less so with germanium, and virtually impossible with silicon (cf. section I.B., Table 2); indeed, octaphenylspirobisilole was isolated in only 1%.[2b] Attempts to synthesize tetraphenylspirobisilole have proved unsuccessful.[53b] It would not be surprising if, as in spirodienes of this type,[185] a HOMO destabilization due to spiroconjugation occurred in spirobisiloles. This interaction would be considerably decreased in spirobigermoles and -stannoles due to increased lengths of Ge–C and Sn–C bonds.

B. Cycloaddition Reactions

1. *Diels–Alder [4 + 2] Cycloadditions with Ethylenic Dienophiles*

C-Unsubstituted monomer group 14 metalloles are not stable and spontaneously dimerize by a [4 + 2] Diels–Alder reaction (cf. section II.A.1). They have, however, been trapped as stable adducts with ethylenic dienophiles.

(*a*) *Reactions.* Maleic anhydride (MA) reacts in situ with 1-methylsilole generated from the dimer in solution in toluene (>100 °C)[5] (Scheme 2). The 1,1-dimethylmetalloles and 1,1,3-trimethylmetalloles, observable but unstable as monomers, readily yield stable MA adducts at room temperature (Schemes 3 and 22).[6,7,18,74a] The same applies to other lower alkyl C-substituted metalloles (eq 58 ($R^4 = R^5 =$ Me; $R^3 = R^6 =$ H; R^1, $R^2 =$ Me, Ph, ^{n}Bu, or $CH_2CH{=}CH_2$),[74a,75,166] Table 5). For C-phenylated metalloles, the cycloaddition with MA takes place at a higher temperature (eq 58). Numerous 2,5-diphenylated,[66,67] 3,4-diphenylated,[78] or 2,3,4,5-tetraphenylated[29,32,126-128] derivatives with alkyl, alkenyl, or aryl groups at the heteroatom (Si, Ge) have been described.



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Recently, Weber et al.[78] reported a kinetic study of the Diels–Alder reactions of three C-phenylated siloles with MA. For 1,1-dimethyl-TPSI the activation energy is higher (60.25 kJ·mol^{-1}) than with 1,1-dimethyl-DPSI or 1,1-dimethyl-3,4-diphenylsilole (39.33 and 34.73 kJ·mol^{-1} respectively), the latter values are very close to that observed for the reaction of cyclopentadiene with MA. The large negative activation entropy values ($\Delta S = -30$ to -40 eu) are consistent with those previously found for Diels–Alder reactions.

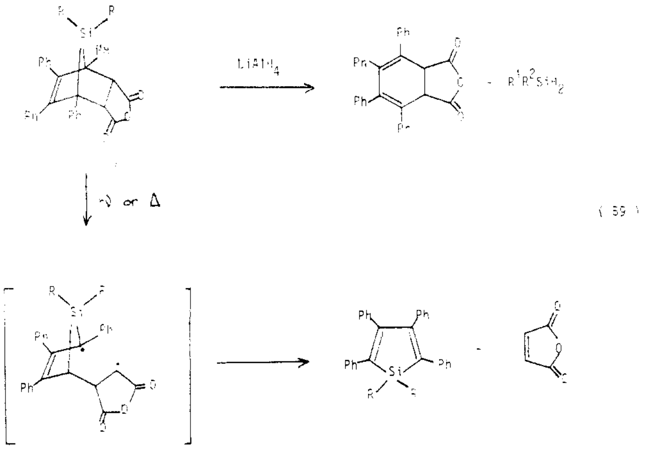
Other ethylenic dienophiles, vinyltrichlorosilane,[129] methyl acrylate,[128] acrylonitrile,[128] dimethyl fumarate,[78] and cyclopropene,[130] react with C-phenylated siloles to give stable adducts.

There is only one report of the formation of cycloadducts from a $2H$-silole.[52a] With $Ph_2C{=}O$ and PhCH=CHPh, the [4 + 2] cycloadducts of the conjugated diene system are formed rather than the expected [2 + 2] cycloadducts with the Si=C double bond (Scheme 32).

(*b*) *Stereochemistry of the Adducts.* ^{1}H NMR studies show that in [4 + 2] cycloadditions of siloles with ethyl acrylate, the ester group in the adduct is in the *endo* position.[128] The preferential *endo* configuration in substituted 7-silanorbornenes has also been shown, after methylation, in the case of a trichlorosilyl substituent.[129] Similarly, according to Alder's rule, the *endo* configuration has been attributed to the adducts with MA[128] and cyclopropene.[130]

When two different groups R^1 and R^2 are present on the heteroatom of the silole, two adducts (*syn*/*anti*) can be formed. In the ^1H NMR, a Si–Me group or a Si–H proton *syn* with respect to the double bond (*anti* with respect to the branched dienophile) is shielded and appears upfield compared to the shift of the analogous proton(s) in the *anti* isomer.[75,82,83,128] For C-unsubstituted or C-methylated siloles with Me and H substituents at the silicon, the two *syn*/*anti* MA adducts are formed in approximately equal amounts.[5,82,83] When the two substituents at the silicon are Ph, H; Me, $CH_2CH{=}CH_2$; or Me, Ph, the major adduct results from the approach of the dienophile on the less hindered side of the unsymmetrical silole; thus, the more bulky group is preferentially *syn* with respect to the C=C bond of the bicycloheptene structure.[75,83] With C-tetraphenylated siloles and various dienophiles, the same result is generally observed (except for the adduct with acrylonitrile when $R^1 = CH{=}CH_2$, $R^2 = Me$[128]).

(*c*) *Properties of the Adducts.* The MA adducts of siloles, when treated with $LiAlH_4$, undergo degradation with loss of the silyl group (eq 59).[29,127] Thermolysis or photolysis of these adducts leads to the retro-Diels–Alder reaction (eq 59).[131]



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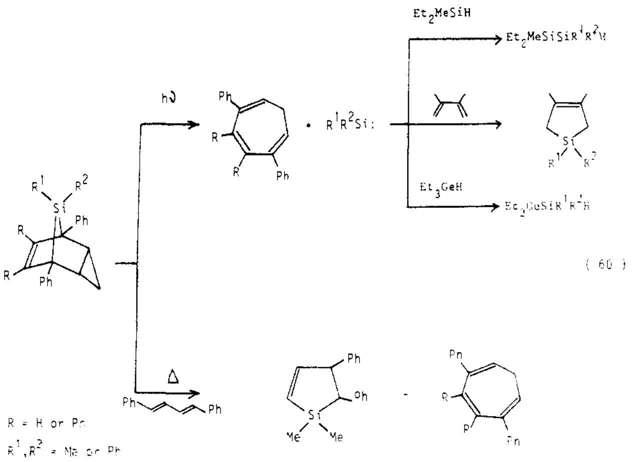
Cyclopropene adducts of siloles on irradiation or thermolysis extrude silylene, which can be trapped by dienes or a hydrogenosilane (or -germane) (eq 60).[130,146]



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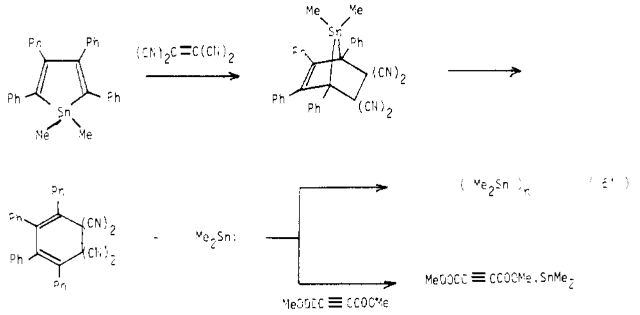
In the tin series, the [4 + 2] cycloadduct 5,5,6,6-tetracyano-7,7-dimethyl-1,2,3,4-tetraphenyl-7-stannanorbornene could be isolated at −30 °C but decomposed above −20 °C to give free stannylene by a concerted mechanism (eq 61).[139]



(61)

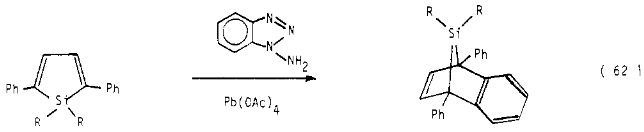
2. Diels–Alder [4 + 2] Cycloadditions with Acetylenic Dienophiles

(*a*) *Reactions.* Siloles, germoles, and stannoles usually react with alkynes (methyl acetylenedicarboxylate, hexafluorobutyne, benzyne, phenylacetylene, etc.) to give 7-metallabicyclo[2.2.1]heptadienes. Their stability is variable, depending on the metal and on the various substituents present on the ring and heteroatom (Table 12).

For C-unsubstituted metalloles, only one such reaction has been described. Barton and Burns[5] produced 1-methylsilole in the presence of hexafluorobutyne and obtained o-bis(trifluoromethyl)benzene. They proposed the transient formation of the cycloaddition derivative (Scheme 2).

The cycloadditions of C-phenylated metalloles to hexafluorobutyne or methyl acetylenedicarboxylate take place under mild conditions (see references in Table 12). With ethynyltrichlorogermane in CCl_4 reflux, the yield may reach 95%.[129]

Benzyne, produced by oxidation of 1-aminobenzotriazole with lead tetraacetate, reacts with siloles to give a series of 2,3-benzo-1,4-diphenyl-7-silanorbornadienes[135] (eq 62).



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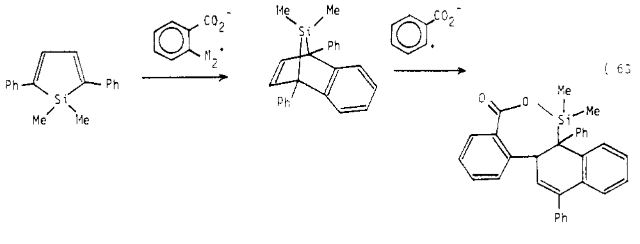
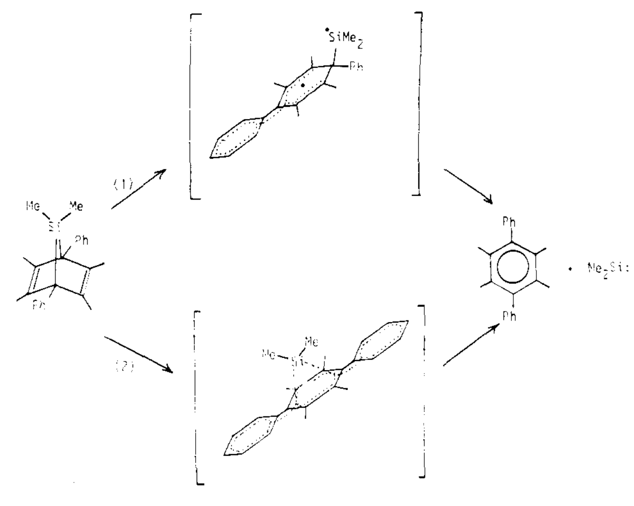
However, reaction of benzyne, produced thermally from benzenediazonium-2-carboxylate, to 1,1-dimethyl-DPSI did not yield the Diels–Alder adduct. Instead, a further reaction of the initial adduct with benzenediazonium-2-carboxylate is observed[52b] (eq 63).



(63)

The reaction of 1,1-dimethyl-2,5-diphenylsilole and tolan at room temperature was reported to produce a 7-silanorbornadiene.[134] This product was later shown to be a 1:1 crystal complex of the two reactants.[143] The

SCHEME 33



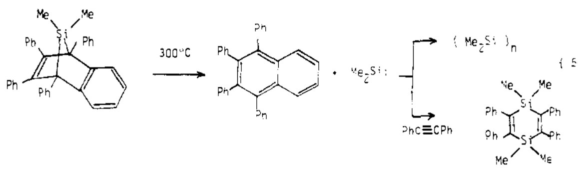
formation of the Diels–Alder adduct is nonetheless observed when the reaction is conducted in a sealed tube at 150 °C for 7 days.[133]

(*b*) *Thermal Decomposition of Metallanorbornadienes* (*i*) *Silanorbornadienes.* Table 12 reveals that decreasing substitution on the six-membered ring of the silanorbornadienes results in decreased thermal stability. The mechanism and the factors governing the ease of 7-silabicyclo[2.2.1]heptadiene thermolysis to generate free silylene and the corresponding benzene derivatives have been investigated (refs 132 and 133 and references therein). In all cases, a first-order degradation was observed.

The classification of the 7-silanorbornadienes into two groups a and b according to the main-ring substituents simplifies the presentation of their stability and decomposition reaction mechanism.[132]

Group a. The substituents bonded onto the 7-silanorbornadiene structure of these compounds include alkyl, cycloalkyl, or aryl groups. The latter sometimes includes condensed rings.

As early as 1964, Gilman noted that thermolysis of such 7-silanorbornadienes produces silylenes.[25,126] For example, 2,3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene decomposes at 300 °C to give 1,2,3,4-tetraphenylnaphthalene and a dimethylsilylene polymer (eq 64). This silylene can be trapped by reaction with diphenylacetylene.

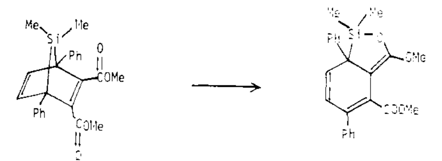


(64)

Appler, Neumann, et al.[132] in a study of this type of decomposition into silylene and aromatic derivatives of a series of diversely substituted 7-silanorbornadienes concluded that a benzene ring condensed on positions 5 and 6 or phenyl groups on positions 2 and 3 of the basal structure increased the thermal stability of these norbornadienes. On the other hand, decomposition is promoted by phenyl groups at the bridgehead carbon atoms (C-1 and C-4) if a conformation coplanar to the basic ring is allowed by the neighboring substituents (Scheme 33). The authors present two possible pathways 1 and 2 for the silylene formation. They favor the latter as the existence of a biradical intermediate was not proven.[132] It was also noted that the presence of chlorine atoms on the silicon atom greatly enhances this reaction. The activation enthalpy of these decompositions is around 125 kJ·mol^{-1} and the decomposition temperature is generally above 150 °C.

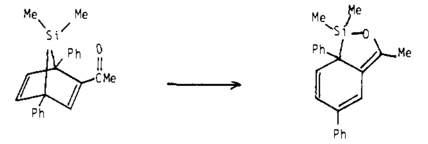
Group b. In this group are included all 7-silanorbornadienes bearing a C=O or CF_3 group.

The silanorbornadiene adduct of methyl acetylenedicarboxylate with 1,1-dimethyl-DPSI could not be isolated. This adduct decomposes via a 1,5-sigmatropic rearrangement of silicon to oxygen to form a silyl enol ether[133] (eq 65). This 1,5-migration of silicon to oxygen



(65)

appears to be general and occurs with other norbornadienes substituted by a carbonyl group[132,133] (eqs 66 and 67). The silyl enol ether is subsequently transformed into polysiloxane and a benzene derivative.[132]



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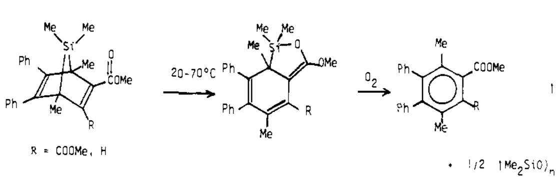

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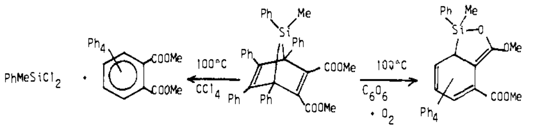
Rearrangements of Diels–Alder adducts of siloles and dimethyl acetylenedicarboxylate find precedent in the work of Gilman, who reported 2,3-dicarbomethoxy-1,4,5,6-tetraphenylsilanorbornadiene rapidly rearranges in the presence of ethanol.[25,126] The products obtained from thermolysis of such norbornadienes vary according to the solvent used. With hexadeuteriobenzene, in the presence of oxygen, the formation of silyl enol ether is noted, while with carbon tetrachloride, formation of a dichlorosilane occurs[133] (eq 68).



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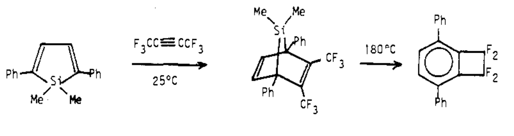
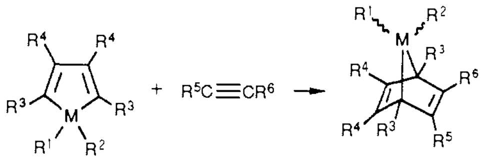
Dimethyldifluorosilane is formed via a radical pathway on thermolysis of the Diels–Alder adduct of 1,1-dimethyl-DPSI and hexafluorobutyne[133] (eq 69). With



(69)

dimethyltetraphenylsilole two different adducts were obtained by Hota[32] and Barton.[133] These adducts on thermolysis also give dimethyldifluorosilane. On pho-

TABLE 12. Cycloadditions of Group 14 Metalloles with Acetylenic Dienophiles

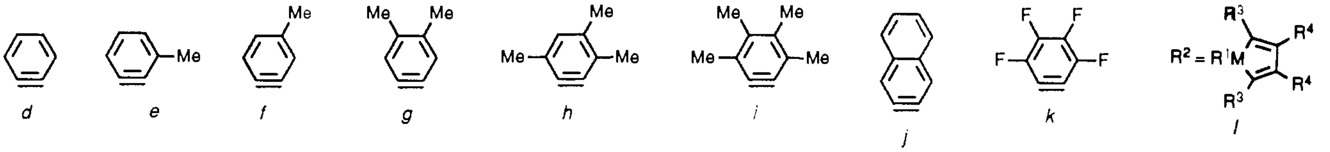


R^1	R^2	R^5	R^6	mp[a]	remarks[b]	ref
From C-Unsubstituted Siloles (M = Si, $R^3 = R^4 = H$)						
Me	H	CF_3	CF_3		*c*	5
From 2,5-Diphenylsiloles (M = Si, R^3 = Ph, R^4 = H)						
Me	Me	CF_3	CF_3		$T_d = 180$	133
				95–100 (dec)	$T_d < 70$	137
				100–104		52b
Me	Me	C(O)Me	H		*c*	133
Me	Me	COOMe	H			132
Me	Me	COOMe	COOMe		*c*	66, 133
				80–90	$t_{28} = 35–135$	132
Me	Me	Ph	Ph	175–188		133, 134
Me	Me	$GeCl_3$	H		$k_{37} = 0.085$	67, 129
Me	Me	*d*			*c*	52b, 134
				108–109	$T_d = 220$	135
				114	$t_{215} = 24$	132
Me	Me	*e*		151		132
Me	Me	*h*		128		132
Me	Me	*i*		199	$t_{215} = 135$	132
Me	Me	$(CH_2)_6$		123	$t_{160} = 540$	132
Me	Et	COOMe	COOMe		*c*	66
Me	Ph	COOMe	COOMe		*c*	66
Me	$SiMe_3$	*d*		113–115	$T_d = 220$	135
Me	$SiMe_2Ph$	*d*		138–139	$T_d = 220$	135
Me	Si_2Me_5	*d*		115–116	$T_d = 220$	135
Et	Et	COOMe	COOMe		*c*	66
^{n}Bu	^{n}Bu	COOMe	COOMe		*c*	66
$SiMe_3$	$SiMe_3$	*d*		153–154	$T_d = 220$	135
From 3,4-Diphenylsiloles (M = Si, R^3 = Me, R^4 = Ph)						
Me	Me	COOMe	H			132
Me	Me	COOMe	COOMe		$t_{22} = 1800$	132
Me	Me	*d*				132
Me	Me	*i*		156	$t_{215} = 65$	132
Me	Me	$(CH_2)_6$		137	$t_{200} = 110$	132
Me	Me[m]	*d*		106	$t_{215} = 205$	132
From 2,3,4,5-Tetraphenylsiloles (M = Si, $R^3 = R^4$ = Ph)						
Me	Me	CF_3	CF_3	143–145	$T_d = 300$	32
				124–126	$T_d = 233$	133
					$k_{250} = 0.7$	137
Me	Me	COOMe	COOMe	200	$t_{115} = 115$	132
					$T_d = 218–221$	25
Me	Me	Ph	H	148–150	$T_d = 300$	25
					$k_{200} = 6$	137
Me	Me[n]	Ph	Ph		*c*	62
Me	Me	C(O)Ph	C(O)Ph	163–164		128
Me	Me	*d*		233–234	$T_d = 300$	25
				234	$t_{250} = 300$	132
					$k_{250} = 0.84$	137
Me	Me	*e*		212		132
Me	Me	*f*		119		132
Me	Me	*g*		189		132
Me	Me	*h*		178		132
Me	Me	*i*		223		132
Me	Me	*j*		250		132
Me	Me	$(CH_2)_6$		195	$t_{215} = 146$	132
Me	Ph	COOMe	COOMe	209		132
Me	Ph	C(O)Ph	C(O)Ph	244–245		128
Me	*p*-MeC_6H_4	*d*		>270		132
Me	*p*-MeC_6H_4	$(CH_2)_6$		250		132
Cl	Me	COOMe	COOMe	178		132
Cl	Me	$(CH_2)_6$		197	$t_{150} = 50$	132
Me	*l*	*d*		281–285	$T_d = 350$	141
Me	$Cp(CO)_2Fe$	COOMe	COOMe		$T_d = 144$	49
Me	$Cp(CO)_2Fe$	*d*			$T_d = 180$	49
Et	Et	COOMe	COOMe	183–192		127
Et	Et	*d*		163		127
^{n}Pr	^{n}Pr	COOMe	COOMe	182–190		127
^{n}Pr	^{n}Pr	*d*		189		127

TABLE 12 (Continued)

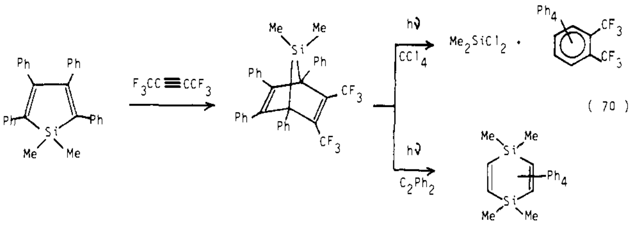
R^1	R^2	R^5	R^6	mp[a]	remarks[b]	ref
^{n}Bu	^{n}Bu	COOMe	COOMe	191-236		127
^{n}Bu	^{n}Bu	*d*		159		127
Ph	c-C_3H_5	*d*		226-227	T_d = 540	138
Ph	Ph	COOMe	COOMe	208-211 (dec)		126
Ph	Ph	C(O)Ph	C(O)Ph	263-264 (dec)		128
Ph	Ph	*d*		238-240	T_d = 300	126
p-MeC_6H_4	*p*-MeC_6H_4	COOMe	COOMe	188-216		127
p-MeC_6H_4	*p*-MeC_6H_4	*d*		248		127
p-MeC_6H_4	*p*-MeC_6H_4	$(CH_2)_8$		127		132
CH_2Ph	CH_2Ph	COOMe	COOMe		*c*	127
CH_2Ph	CH_2Ph	Ph	H	209		127
$(CH_2)_4$		COOMe	COOMe		*c*	127
$(CH_2)_4$		Ph	H		*c*	29, 127
$(CH_2)_4$		*d*		200		29, 127
$(CH_2)_5$		COOMe	COOMe	199-211		127
$(CH_2)_5$		Ph	H	178-179		29, 127
$(CH_2)_5$		*d*		234		29, 127
Cl	Cl	$(CH_2)_6$		225		132
From 2,5-diphenylgermoles (M = Ge, R^3 = Ph, R^4 = H)						
Me	Me	$GeCl_3$	H		*c*	67
Me	Me	COOMe	COOMe		*c*	67
From 2,3,4,5-Tetraphenylgermoles (M = Ge, R^3 = R^4 = Ph)						
Me	Me	CF_3	CF_3		*c*	32
Me	Me	COOMe	COOMe		*c*	32
					T_d = room temp	140
Me	Me	Ph	H		*c*	32
Me	Me	*d*			t_{138} = 42	136
Me	Me	*e*			t_{152} = 420	136
Me	Me	*f*			t_{120} = 42	136
Me	Me	*g*			t_{140} = 42	136
Me	Me	*h*			t_{165} = 4200	136
Me	Me	*i*			t_{180} = 7200	136
Ph	Ph	*h*			t_{160} = 240	136
From 2,3,4,5-Tetraphenylstannoles (M = Sn, R^3 = R^4 = Ph)						
Me	Me	COOMe	COOMe		*c*	142
Me	Me	*d*			*c*	139
Me	Me	*k*			*c*	139

[a] Melting point (°C) of the adduct. [b] T_d = decomposition temperature (°C) of the adduct; t_T = half-decomposition time at the temperature T (°C); k_T = rate constant (10^{-3} min^{-1}) for a first-order decomposition. [c] Adduct not isolated. [d-k] $R^5C{\equiv}CR^6$:



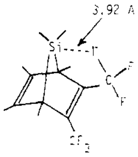
[m] R^4 = $R^{5,6}$ (benzo). [n] R^3 = Ph and $SiMe_3$.

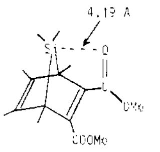
tolysis in CCl_4 or in the presence of diphenylacetylene, dimethylsilylene may be trapped[133] (eq 70).



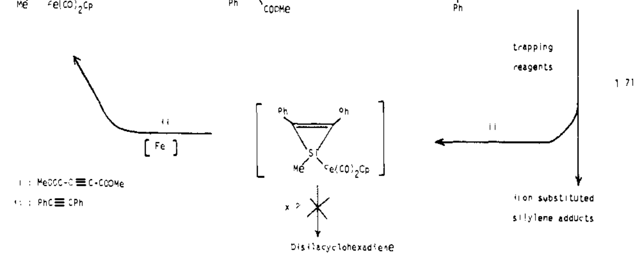
(70)

It has been shown[132] in such 2,3-disubstituted silanorbornadienes that the silicon–oxygen and silicon–fluorine distances are less than the sum of the van der Waals radii. Thus, the silicon atom may induce the decomposition of the strained bicyclic compounds by formation of intramolecular Si–O or Si–F bonds.



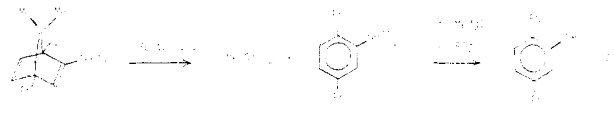


Some silanorbornadienes, however, although bearing CF_3, COOMe, or $GeCl_3$ groups on the basic ring, yield silylene and the corresponding aromatic compound by decomposition. This type of decomposition has been noted by Barton for an adduct of hexafluorobutyne[5] (Scheme 2). An iron-substituted silylene [Cp(CO)$_2$FeSiMe] has been generated and trapped by various reagents[49] (eq 71).

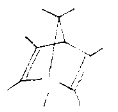


(71)

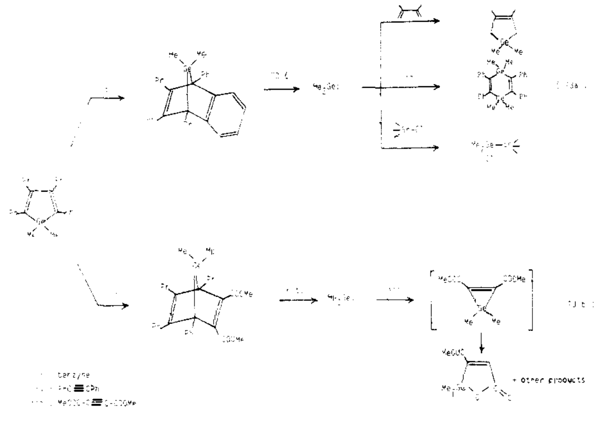
A silanorbornadiene with a $GeCl_3$ group on its basic ring slowly decomposes at room temperature following a first-order rate of reaction, giving the aromatic derivative resulting from the loss of dimethylsilylene[67,129] (eq 72).



The first and only example of the 1-silanorbornadiene ring system (**53**) derived from a 2H-silole proved to be remarkably stable, in contrast to the 7-silanorbornadienes.[52a] The adduct resulting from the [4 + 2] Diels–Alder reaction of a 2H-silole with diphenylacetylene (Scheme 32) did not decompose by heating to 150 °C. Further, no acetylene exchange was observed with an excess of di-p-tolylacetylene. The 1-silanorbornadiene system is probably less strained than that of the 7-sila isomer and, moreover, the decomposition by loss of the bridge would give an unstable silabenzene (Si=C) compound.



(*ii*) *Germa(or stanna)norbornadienes.* It has been shown by Neumann and Schriewer[69] that free singlet dimethylgermylene (Me_2Ge:) is formed directly from 7-germanorbornadienes rather than via a two-step mechanism with an intermediate biradical.[136] This germylene has been trapped in the presence of various reagents (eq 73a).

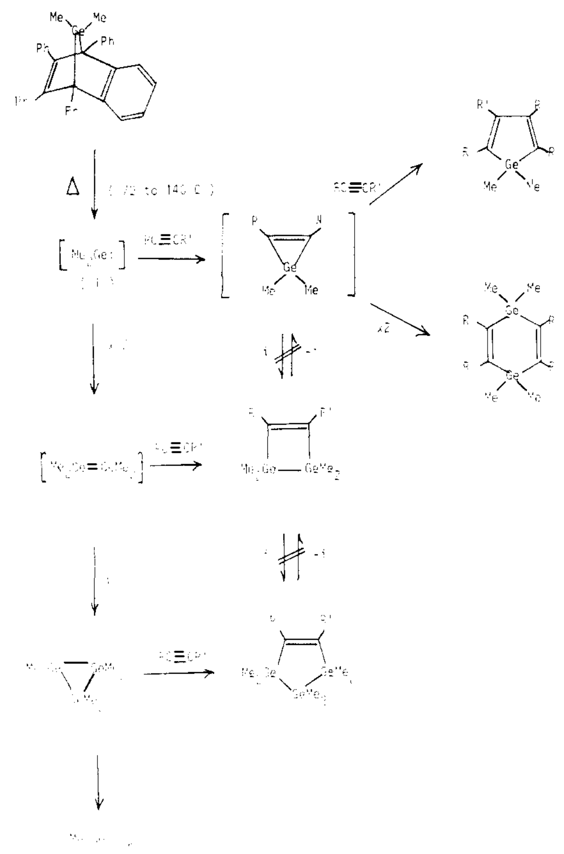


Neumann et al.[215] have recently trapped the intermediates resulting from the pyrolytic decomposition of a 7-germanorbornadiene by alkynes (Scheme 34). Cyclooctyne, diethyl acetylenedicarboxylate, and phenylacetylene lead to the corresponding germole and digermacyclohexadiene. Some alkynes (e.g., R/R′ = Bu/H, ^{t}Bu/CN, Ph/Ph) give exclusively the digermacyclohexadiene, and some others do not react with Me_2Ge (e.g., R/R′ = ^{t}Bu/H, Ph/Et, Pr/Me).

Whereas the 1,1-dimethyl-TPSI adduct with dimethyl acetylenedicarboxylate is stable, the germanium analogue slowly decomposes at room temperature.[140] Pyrolysis in the presence of excess dimethyl acetylenedicarboxylate gives many products.[32,140] The major is probably formed by decomposition (not dimerization to 1,4-digermacyclohexadiene) of the germirene intermediate (eq 73b).

Comparable differences in stability between sila- and germanorbornadienes have been observed during cycloadditions. For example, ethynyltrichlorosilane (or -germane) and 1,1-dimethyl-DPSI give a stable adduct, while similar reaction with 1,1-dimethyl-DPGE gives only decomposition products.[67,129] Similar results have been observed with hexafluorobutyne[32] and phenylacetylene.[32,140,235]

SCHEME 34



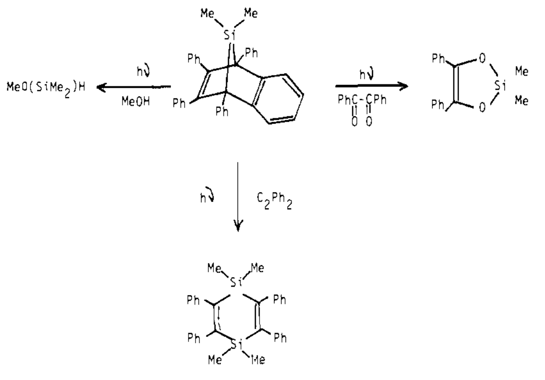
No stable stannanorbornadienes are known. Attempted Diels–Alder reaction of 1,1-dimethyl-TPSN with acetylenic dienophiles failed to give the expected adducts. Instead, the aromatic hydrocarbon and products apparently resulting from a transient stannylene were isolated.[139,142]

The relative instability of stanna(and germa)norbornadienes has been attributed to the larger size of the heteroatom, which sufficiently distorts the ring system to the point where elimination of stannylene (or germylene) readily occurs.[32]

(*c*) *Photochemical Decomposition of Metallanorbornadienes.* It has been reported that 7-silanorbornadienes with two different substituents on silicon undergo both thermally and photochemically induced epimerization at silicon.[155] Photo-induced decomposition of analogues to yield dimethyl tetraphenylphthalate has also been observed.[131,133] Photolysis of tetraphenylated silanorbornadienes results in rapid extrusion of the corresponding substituted benzene.

While dimethylsilylene is produced at 300 °C by pyrolysis of 2,3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene,[25] photolysis (λ = 250 nm) of the same product at room temperature proved to be an excellent source of dimethylsilylene, probably in its singlet state[145] (eq 74).

Recently, methylphenylsilylene has been generated by the same method and trapped by ethanol, triethylsilane, and 2,3-dimethylbutadiene with the fol-



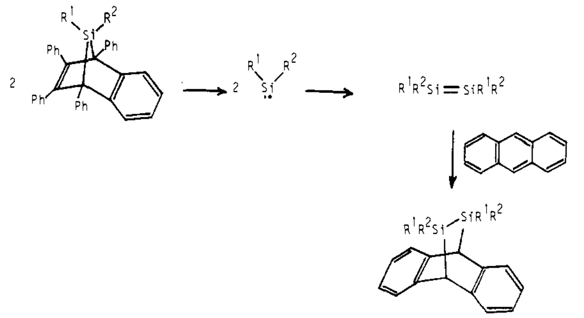
(74)

lowing relative rate constants: $k_{\mathrm{EtOH}}/k_{\mathrm{Et_3SiH}} = 4.8$ and $k_{\mathrm{DMB}}/k_{\mathrm{Et_3SiH}} = 3.0$ at 298 K.[157]

The photolysis of 7-germanorbornadienes in a hydrocarbon matrix at 77 K leads to germylenes R_2Ge: (R = Me, Et, Ph), stable at this temperature, which show an electronic absorption band at 420–466 nm.[158]

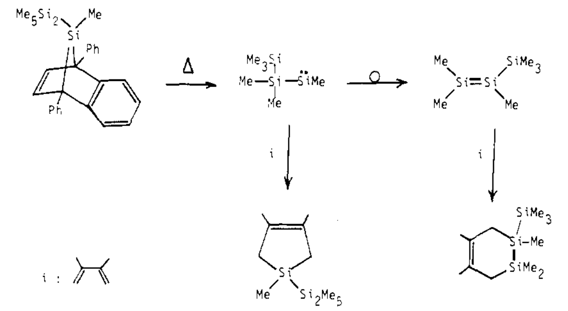
(*d*) *7-Silanorbornadienes as Precursors of Species with Multiple Bonding to Silicon.* The chemistry of compounds containing multiple bonds to silicon atoms has been reviewed.[81] We report here some reactions from group 14 metallole cycloadducts yield such reactive species.

In 1979, Sakurai et al.[144] suggested that variously substituted silylenes generated by thermolysis of 7-silanorbornadienes dimerize to disilenes which are then trapped by anthracene (eq 75).



(75)

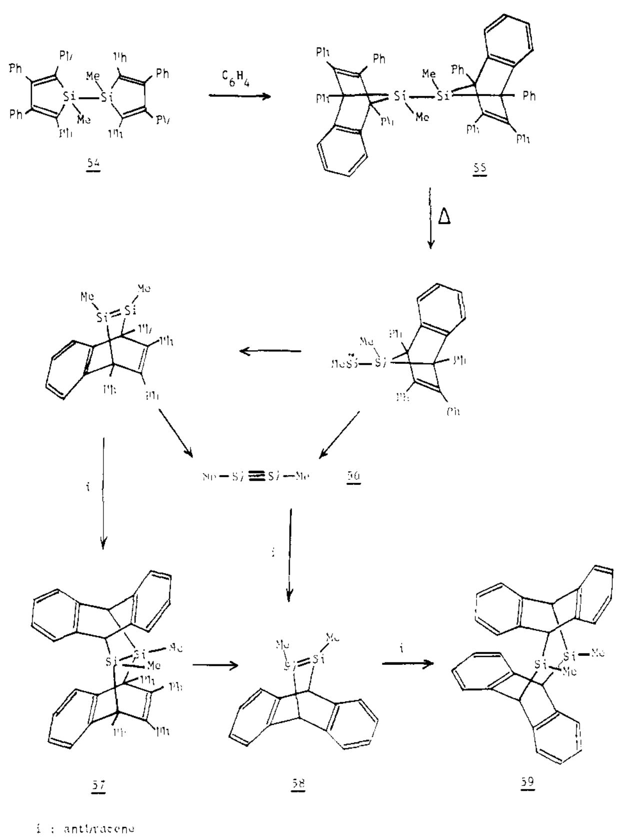
Thermal rearrangement of a silylsilylene to disilene has also been detected in the thermolysis of a 2,3-benzo-1,4-diphenyl-7-silanorbornadiene derivative which gave in the presence of 2,3-dimethylbutadiene the cycloadducts (silacyclopentene and disilacyclohexane) corresponding to trapping of the silylene and disilene[135] (eq 76). Photochemical generation of these species is also possible from the same silanorbornadiene.[156]



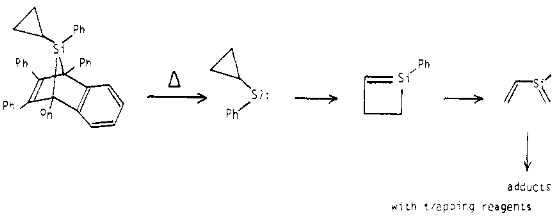
(76)

An interesting 7-silanorbornadiene has been obtained by Ando et al.[138] from 1-cyclopropyl-1,2,3,4,5-pentaphenylsilole and benzyne. Its pyrolysis at 540 °C gives cyclopropylphenylsilylene, which can expand the ring to form 1-phenyl-1-silacyclobutene. This is followed by ring opening to 2-phenyl-2-silabutadiene, which can be trapped with ROH or Ph_2CO (eq 77).

SCHEME 35



i : anthracene



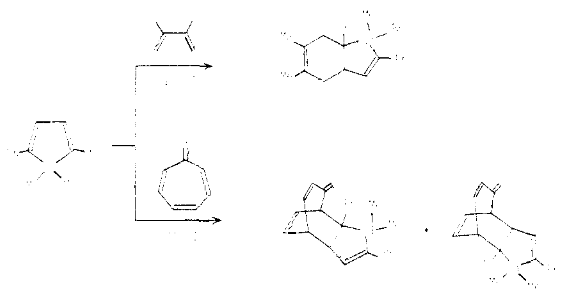
(77)

West et al.[141] have taken advantage of the thermal lability of group 14 metallole cycloadducts in an attempt to obtain a triply bonded silicon derivative. The benzyne adduct **55** of the bisilole **54** (Scheme 35) upon thermolysis serves as a disilyne **56** synthon. The product **59** obtained by copyrolysis of **55** with anthracene could result either from the diaddition of anthracene[141a] to the dimethyldisilyne (**56**) or from another intermediate compound (**57**).

The copyrolysis of **55** with diphenylacetylene or 3-hexyne produces the 1,4-disilabarrelenes (12 and 2% yield, respectively) corresponding to the addition of three alkyne molecules to the dimethyldisilyne **56**. The probable immediate precursor is a 1,4-disilabenzene.[141b]

3. Group 14 Metalloles as Dienophiles

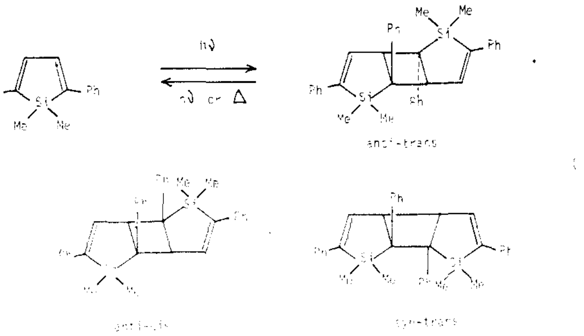
When 1,1-dimethyl-DPSI is heated in the presence of 2,3-dimethylbutadiene[134] or tropone,[154] [4 + 2] cycloadducts are obtained in good yields (eq 78). In these reactions, the silole reacts as the dienophile.



A 2*H*-silole can give a [4 + 2] cycloadduct with the isomeric 1*H*-silole, the latter being the dienophile.[52a]

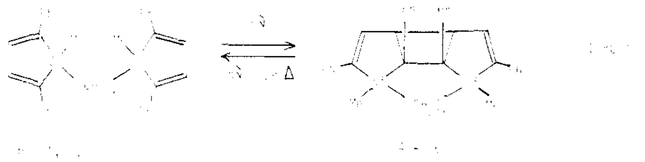
4. [2 + 2] Cycloadditions

It has been reported by Barton and Nelson[150] and by Nakadaira and Sakurai[151] that low-energy irradiation of 1,1-dimethyl-DPSI yields [2 + 2] photodimers (eq 79). The major isomer formed under irradiation with a high-pressure mercury lamp is the *anti-trans* dimer. The *anti-cis* and *syn-trans* dimers are obtained as minor products under a variety of conditions.[151] A mechanistic study showed that this photodimerization occurs through the excited singlet state of the silole.[42]



(79)

Under the same conditions, α,ω-bis(1-methyl-2,5-diphenylsilacyclopentadienyl) alkanes undergo intramolecular [2 + 2] cycloaddition (eq 80).[42]



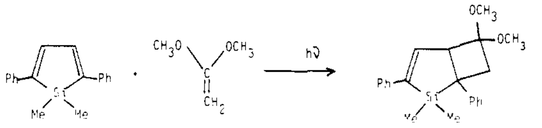
These photodimers give a cycloreversion reaction to the monomer silole by irradiation with a low-pressure mercury lamp or by thermolysis.[42,50,151]

C-Tetraphenylated siloles are photochemically inert.[42,150,151]

A similar [2 + 2] dimerization reaction occurs with 1,1-dimethyl-DPSI; however, under the same conditions, the tin analogue suffers Sn–C cleavage, leading to polymeric products.[150]

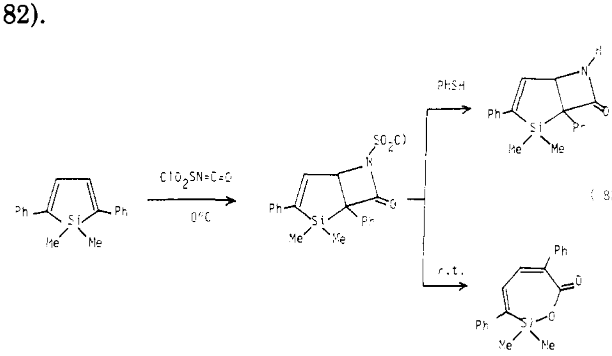
A mixed dimer is formed upon irradiation of an equimolecular solution of 1,1-dimethyl-DPSI and 1,2,5-triphenylphosphole.[150]

Photoaddition of 1,1-dimethoxyethene to 1,1-dimethyl-DPSI yields a ketal in 70% yield (eq 81), which can serve as the starting point for the synthesis of 1,1-dimethyl-2,7-diphenylsilacyclohepta-2,4,6-triene.[152]



(81)

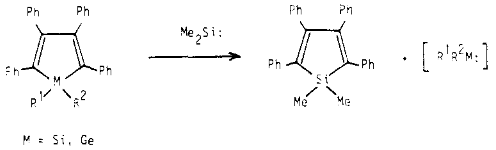
A β-lactam is obtained when *N*-chlorosulfonyl isocyanate is added at 0 °C to 1,1-dimethyl-DPSI.[153] The lactam can immediately be quenched via thiophenol–pyridine reduction, but it undergoes further transformation when allowed to stand at room temperature (eq 82).



(82)

5. Reactions with Unstable Low-Coordinated Metalated Species

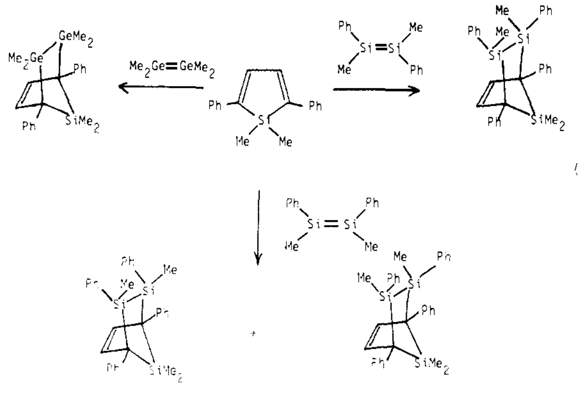
(*a*) *Silylenes and Germylenes.* Thermally or photochemically generated dimethylsilylene undergoes an exchange reaction with 1-methyl-1,2,3,4,5-pentaphenylsilole[146] and 1,1-dimethyl-2,3,4,5-tetraphenylgermole (eq 83).[147] This exchange could proceed by the initial formation of a vinylcyclopropane ([2 + 2] cycloaddition of the silylene with the metallole), which subsequently rearranges and extrudes silylene (or germylene), or by a diradical process.



M = Si, Ge

(83)

(*b*) *Disilenes and Digermenes.* *cis-* and *trans-*1,2-dimethyl-1,2-diphenyldisilenes give [4 + 2] Diels–Alder adducts with 1,1-dimethyl-DPSI in 90% yield.[148] The stereospecificity of the addition demonstrates that the Si=Si bond is a true double bond, like C=C with slow *cis-trans* isomerization in the range 300–350 °C. Tetramethyldigermene reacts in a similar way (eq 84).[149]

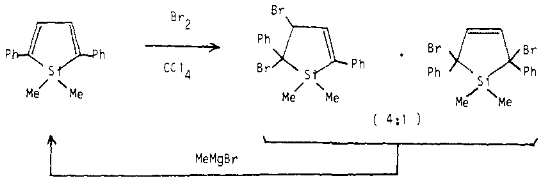


(84)

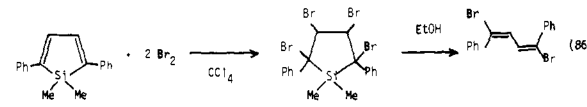
C. Reactions with Halogens

In the presence of halogens the group 14 metalloles can react in three different ways: (i) addition of 1 or 2 equiv of halogen to the diene system, with preservation of the cyclic structure; (ii) cleavage of one or two endocyclic M–C bonds, with destruction of the cyclic structure; (iii) substitution of one or two exocyclic substituents, with preservation of the metallole structure.

In the silole series, Gilman et al.[50] reported the action of bromine on 1,1-dimethyl-DPSI. This compound rapidly absorbs 1 equiv of bromine to give a mixture of silacyclopentenes in which the bromines are in *trans* positions (eq 85). Treatment of this mixture with methylmagnesium bromide regenerates the starting silole. Reaction with a second equivalent of bromine takes place slowly to give the corresponding tetrabromosilacyclopentane (eq 86). This derivative reacts with refluxing ethanol to give an almost quantitative yield of (*E,E*)-1,4-dibromo-1,4-diphenylbutadiene via a double β elimination. With MeMgBr it reacts in the same way as the dibromide.

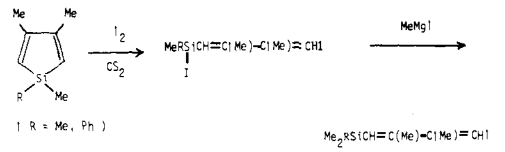


(85)



(86)

The strength of the Si–C endocyclic bond in siloles is also illustrated by the addition of bromine to the vinyl C=C bond of 5-methyl-5-vinyldibenzosilole without ring opening.[102b] However, iodine cleaves the C-methylated silole ring (eq 87), and an excess of iodine gives a complex mixture instead of the expected 1,4-diiodo-2,3-dimethylbutadiene.[18b]

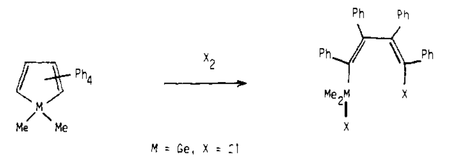


$MeRSi(I)CH{=}C(Me){-}C(Me){=}CHI$

$Me_2RSiCH{=}C(Me){-}C(Me){=}CHI$

(87)

In the 2,3,4,5-tetraphenylated germole series, Freedman[159] indicated that reaction with chlorine occurred with ring opening. Similar reactions are observed with bromine in the case of analogous stannole and plumbole (eq 88); [(*Z,Z*)-butadienyl] metal halides are formed in quantitative yield. A dibenzogermole is slowly cleaved by iodine at high temperature.[87c]

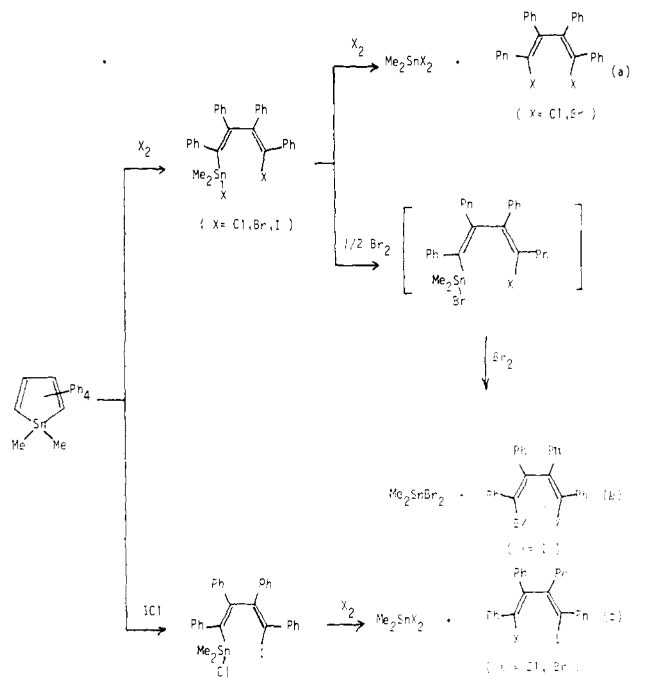


(88)

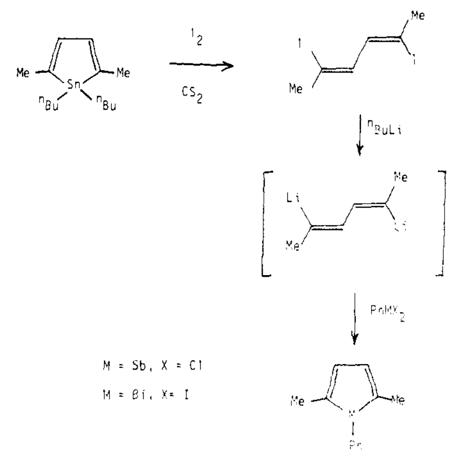
M = Ge, X = Cl
M = Sn, X = Br

Halogenation of a variety of stannoles has been extensively studied. Freedman[24,160a,161] demonstrated that halogenation of 1,1-dimethyl-TPSN occurs with ring cleavage. The methyl–tin bonds remain intact. Further chlorination or bromination led to dimethyltin dihalide and dihalobutadiene (Scheme 36a). With the weaker electrophile iodine, further reaction of the stannyl dihalides does not occur up to temperatures of 100 °C, and hence mixed dihalobutadienes can be synthesized according to Scheme 36b. Similarly, iodine monochloride allows the conversion of the stannole to the mixed dihalobutadienes (Scheme 36c). The stannyldihalobutadienes formed by ring cleavage of stannoles have been shown to undergo other interesting reactions.[160-162]

SCHEME 36



SCHEME 37

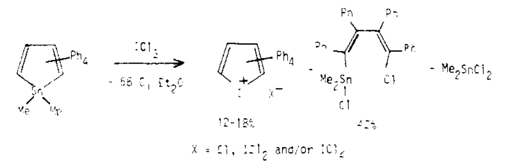


Ashe and Drone[64b] have discussed the reaction of 1,1-dibutyl-2,5-dimethylstannole with iodine leading to (*Z,Z*)-2,5-diiodohexa-2,4-diene, which on further treatment with *n*-butyllithium followed by phenylbismuth diiodide affords 1-phenyl-2,5-dimethylbismole. 1-Phenyl-2,5-dimethylstibole can be obtained by this method (Scheme 37).

By contrast, Zuckerman et al.[39,45] have found that controlled bromination or iodination of hexaphenylstannole occurs with cleavage of the exocyclic tin–phenyl bonds to give 1,1-dihalostannoles (Scheme 13b), which can be derivatized to form numerous interesting substituted stannoles[44] as indicated in Scheme 14, as well as the only known group 14 metalloles having a five- or six-coordinated heteroatom[44,45] in the shape of anionic or cationic species (eqs 9 and 10).

On the other hand, mild chlorination by chlorine cleaves endocyclic Sn–C bonds, thereby leading to (*Z,Z*)-1,4-dichloro-1,2,3,4-tetraphenylbutadiene and diphenyltin dichloride[44] (Scheme 13a).

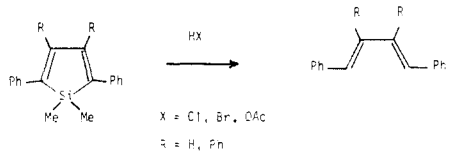
Related to the reactions of halogens toward stannoles, Sandel et al.[163] reported that treatment of a tetraphenylstannole with iodine trichloride led to cleavage products and the Hückel aromatic 2,3,4,5-tetraphenyliodolium ion (eq 89).



(89)

D. Reactions with Acids

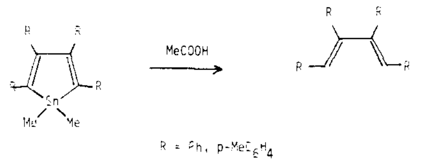
Several authors have described the action of acids on siloles leading to cleavage of two endocyclic Si–C bonds. The corresponding butadienes in which the geometry of the parent silole is retained are produced in high yields (eq 90). Thus, Gilman et al.[50] observed that



(90)

hydrogen bromide in refluxing ethanol reacts with 1,1-dimethyl-DPSI to produce *trans,trans-* or (*E,E*)-1,4-diphenylbutadiene. A similar reaction occurs with glacial acetic acid on prolonged reflux and with concentrated hydrochloric acid on prolonged reflux and with concentrated hydrochloric acid in DME. In analogous reactions 1,1-dimethyl-TPSI gives the *cis,cis-* or (*E,E*)-1,2,3,4-tetraphenylbutadiene.[164] The structure of the substituted butadiene formed by this acidic cleavage allows the determination of the location of the substituents in the silole ring.[59a]

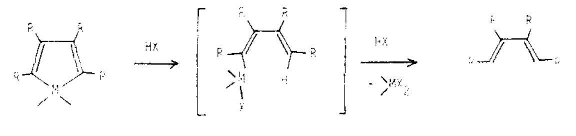
Stannoles are more easily cleaved by acids than siloles. Freedman[24] reported that 1,1-dimethyl-TPSN on brief exposure to a dilute solution of acetic acid in alcohol underwent rapid cleavage of the unsaturated ring carbon to tin bonds with the quantitative formation of (*E,E*)-1,2,3,4-tetraphenylbutadiene; tetra-*p*-tolylbutadiene is obtained from the corresponding tetratolylstannole[47] (eq 91). Ring opening also occurs with a dibenzostannole and HCl.[86]



(91)

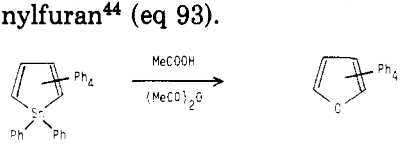
With stannoles the cleavage mechanism is probably a two-step protodestannylation. The product of the first cleavage [halodimethyl((*E,E*)-1,2,3,4-tetraaryl-1,3-butadienyl)tin] has been isolated in one case.[47]

In the reaction of acids with siloles, addition to the carbon–carbon double bonds (cf. section II.C) and substitution (protodesilylation) are both possible. The double-addition product can subsequently undergo double β elimination to give the same products as those from the double substitution. However, since the geometry of the parent silole, as of the parent stannole, is retained in the diene formed, the mechanism is probably the same in the two cases (eq 92).



(92)

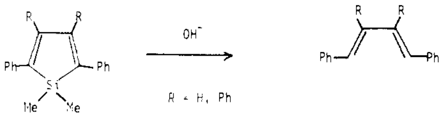
On the other hand, the reaction of acetic acid with hexaphenylstannole in acetic anhydride leads to tetraphenylfuran[44] (eq 93).



(93)

E. Reactions with Bases

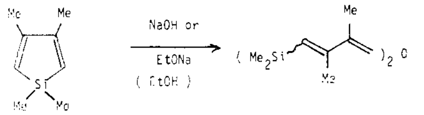
The product formed in the alkaline cleavage of siloles (ammonia,[35] potassium or sodium hydroxide[35,164]) is the same butadiene compound as that from the acid decomposition (eq 94). The reaction probably proceeds



(94)

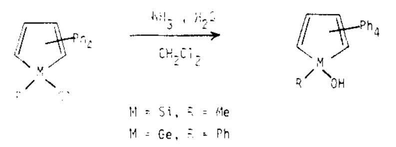
by nucleophilic attack of the hydroxide ion on silicon and subsequent ring opening with retention of the geometry of the starting silole.[164]

In the case of 1,1,3,4-tetramethylsilole the reaction stops after the first Si–C cleavage, giving a dienyl siloxane (eq 95).



(95)

However, a two-phase reaction mixture consisting of dilute NH_4OH and a solution of 1-chloro-TPSI or -TPGE in methylene chloride gives the corresponding 1-hydroxysilole and -germole (eq 96).[35]



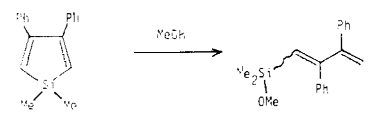
(96)

Zuckerman et al.[44] observed that several dihalostannoles form neutral complexes with bases such as pyridine, 2,2′-bipyridyl, and 1,10-phenanthroline and double salts (eq 10) with 2,2′,2″-terpyridine.

F. Reactions with Alcohols

A few reports treat the reactivity of group 14 metalloles toward alcohols.

Methanol cleaves one endocyclic Si–C bond of 1,1-dimethyl-3,4-diphenylsilole and gives an 80% yield of silylated diene[57d] (eq 97). On the other hand, 2 equiv of methanol or ethanol reacts with 1,1-dimethyl-2,5-bis(trimethylstannyl)-3-(dialkylboryl)-4-alkylsiloles or -germoles to give quantitatively 1,1-dimethyl-3,4-dialkylsila(or germa)cyclopent-3-enes[63b] (eq 98).



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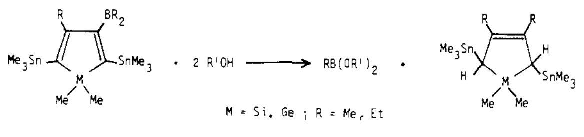
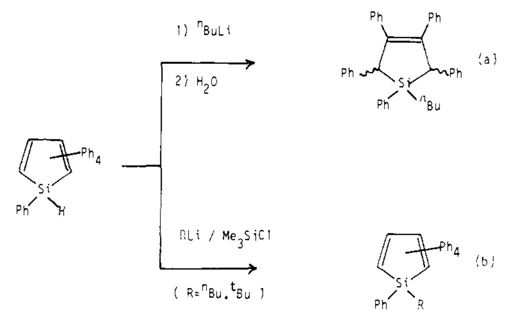


(98)

G. Reactions with Grignard and Lithium Reagents

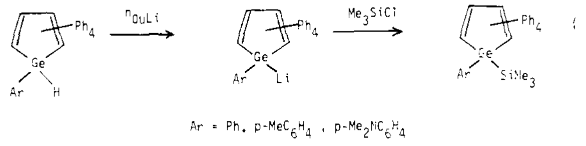
These reagents are among those most often used in group 14 chemistry for substitution reactions (S_N2-M)[165] of various groups bonded to the heteroatom. The metalloles of the same group are no exception to this (cf. section I.E and the schemes, and equations therein). However, the reactivity of organolithium reagents often leads to unexpected results, and distinct differences between individual metalloles deserve further discussion.

A study of the reactivity of simple hydrosiloles (1-hydro-3,4-dimethylsiloles) toward lithium reagents has recently been undertaken[79b,109] (Scheme 28). Though these siloles lead to a classical S_N2-Si substitution, the hydrosiloles with *C*-phenyl substituents behave differently. Pentaphenylsilole suffers substitution of the Si-bonded hydrogen together with a secondary reaction: the reduction of the diene ring to a cyclopentene ring by 1,4-addition of the lithium hydride that is produced during the S_N2-Si reaction[41] (eq 99a). This secondary reaction, not observed with 1-hydro-3,4-dimethylsiloles, may be avoided by scavenging LiH in situ with Me_3SiCl[41] (eq 99b; Scheme 8).



(99)

The hydrogermoles, like the hydrogermanes, show different behavior toward the lithium reagents. They undergo metalation of the germanium[35,43] (eq 100), a

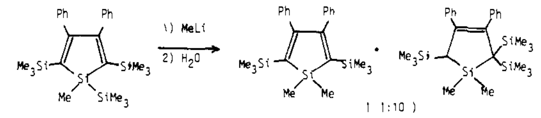


(100)

reaction that remains the only known method for obtaining germacyclopentadienide anions (cf. part 2). These anions, though unstable, can be trapped in situ by Me_3SiCl.[43]

The reactivity of lithium reagents on metalloles devoid of leaving groups on the heteroatom, e.g., 1-alkylsiloles, has proved to be very interesting.

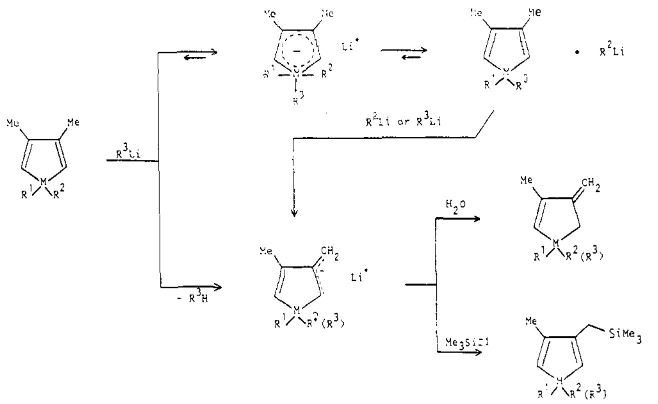
n-Butyllithium reacts with 1-*n*-butylpentaphenylsilole by a 1,4-addition reaction to the π system,[41] as does methyllithium with 1-silylsiloles, leading essentially to the rearranged addition product together with a small proportion of the trimethylsilyl group substitution product[100] (eq 101).

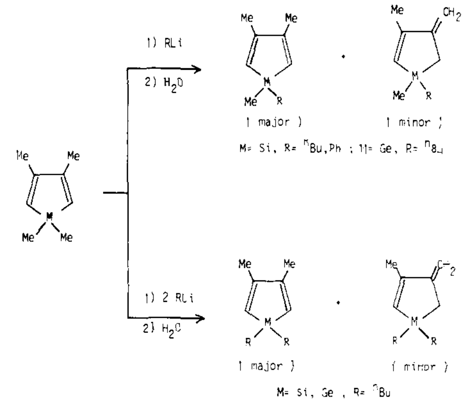


(101)

In marked contrast, the reaction of RLi (R = ⁿBu, ᵗBu, Ph) at -70 °C in THF with TMSI or TMGE gives the 1-R-1,3,4-trimethylmetalloles or the 1,1-di-R-3,4-dimethylmetalloles[18b,166] (eq 102). Phenyllithium is less

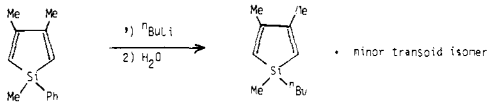
SCHEME 38





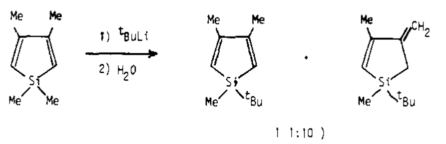
(102)

reactive than *n*-butyllithium (9% and 70% yield, respectively, with TMSI),[166] and the phenyl group is displaced in preference to the methyl group by ⁿBuLi in 1-phenyl-1,3,4-trimethylsilole[18b] (eq 103). Metalation



(103)

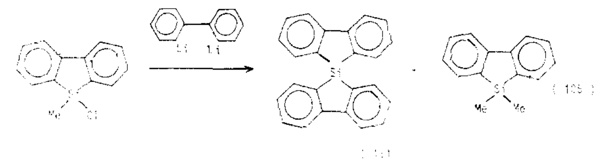
of the SiMe or GeMe groups (MCH_2Li) is not observed but a partial (ⁿBuLi, PhLi) or predominant (ᵗBuLi) (eq 104) isomerization of metalloles into transoid dienes



(104)

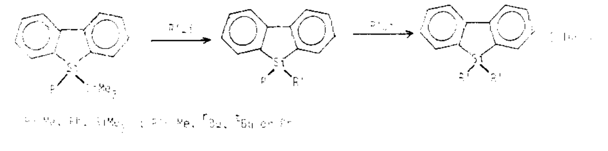
occurs. This isomerization involves the formation of an allylic carbanion (Scheme 38), especially with a basic lithium reagent (ᵗBuLi), which is protonated by water α to Si (or Ge) and is silylated on the exocyclic carbon by Me_3SiCl. Substitution reactions,[166] as well as certain rearrangements,[100] on exocyclic groups bonded to the heteroatom may occur via a five-coordinated anionic complex (Scheme 38).

Cleavage of an Si–C bond by a lithium reagent is rarely observed.[167] While working on the dibenzosilole series, Gilman and Gorsich[85d] in 1958 had already attributed the formation of 5,5′-spirobi[dibenzosilole] from 5-chloro-5-methyldibenzosilole and 2,2′-biphenylenedilithium (eq 105) to the reaction of the latter with the Si–Cl bond and then with the starting dibenzosilole Si–Me bond; the formation of 5,5′-dimethyldibenzosilole is a result of the action of me-



thyllithium, produced in the former reaction, on the untransformed chlorodibenzosilole. These authors also observed the cleavage of 5,5′-spiro[dibenzosilole] by the phenyllithium.

More recently, Kumada et al.[100,101b] investigated the reaction of RLi (R = Me, ^nBu, ^tBu, Ph) on various dibenzosiloles (eq 106). The reaction of MeLi and



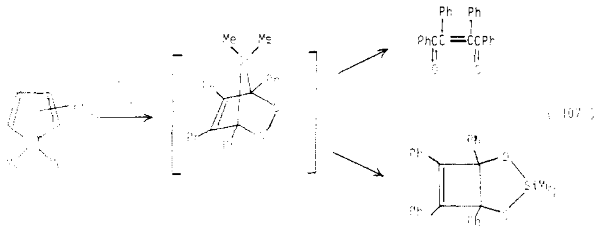
^nBuLi produces 1,1-dialkyldibenzosiloles in quantitative yields, while PhLi, and particularly ^tBuLi, are less reactive. The authors propose an anionic five-coordinated silicon species as a key intermediate for these substitution reactions.

In the stannole series, various reactions that appear surprising at first may be explained by the extraordinary reactivity of the exocyclic tin–carbon bonds with regard to lithium reagents. Thus, the reaction of DTB on 1,1-dialkyl-TPSN leads to alkyl–tin bond cleavage–cyclization by the dilithium reagent[36] (eq 8).

H. Oxidation

Various reactions described earlier (e.g., halogenation) may be considered as oxidation reactions. We will now consider only the oxidation reactions with oxygen or peracids.

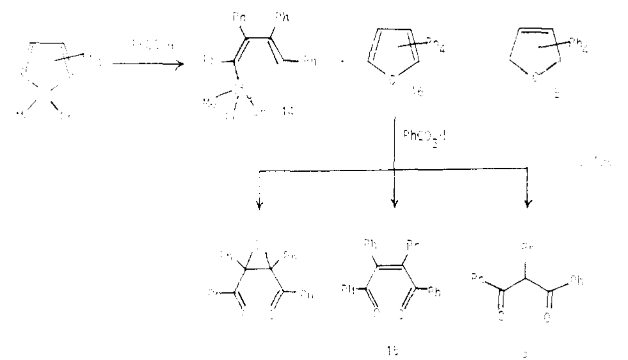
Photooxygenation of 1,1-dimethyl-TPSI was first described by Sato et al.[168] and reinvestigated by Sakurai et al.[169] *cis*- and *trans*-dibenzostilbenes (found in the photooxygenation of tetraphenylfuran and -thiophene[170]) are formed (eq 107), in addition to the major



product (1:1.45), 3,3-dimethyl-1,5,6,7-tetraphenyl-2,4-dioxa-3-silabicyclo[3.2.0]heptene. These are obtained from the intermediate endoperoxide, which is produced by the 1,4-addition of singlet oxygen to the cyclic diene. The formation of isodidesyl in this reaction[168] seems due to subsequent hydrolytic cleavage of the dioxasilabicycloheptane[169] rather than to hydrogen abstraction from the SiMe groups by the oxy radical derived from the endoperoxide.

Under the same conditions as previously described,[168] the photooxygenation of 1-methyl-1-vinyl-TPSI leads to analogous products.[171]

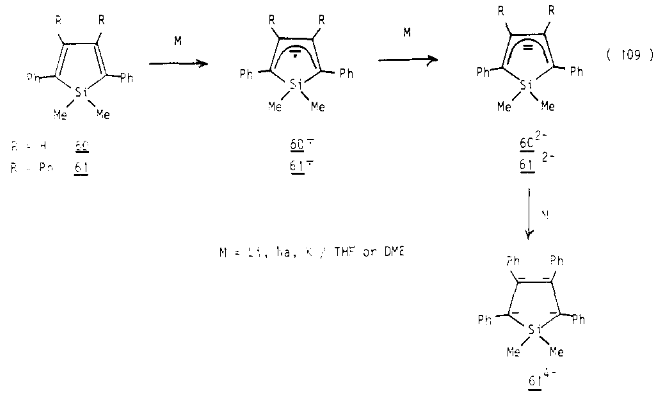
1-Methyl-1,2,3,4,5-pentaphenylsilole when treated with perbenzoic acid yielded a mixture of products (eq 108) resulting from the oxidation of the diene system, various cleavages, and rearrangements.[171] Hexaphenylsilole gives a mixture comprising tetraphenylfuran and *cis*-dibenzoylstilbene. Tetraphenylfuran is also produced with a low yield in the reaction of peracetic acid with 1,1-dimethyl-TPSN.[161]



I. Reduction

1. Alkali Metal Reduction

The alkali metal reductions of 1,1-dimethyl-DPSI (**60**) and 1,1-dimethyl-TPSI (**61**) have been followed by electron spin resonance and UV–visible spectrometry.[172] Observations consistent with the formation of the radical anions $\mathbf{60}^{\bullet-}$ and $\mathbf{61}^{\bullet-}$, which are further reduced to the dianions $\mathbf{60}^{2-}$ and $\mathbf{61}^{2-}$, have been reported (eq 109).



The presence of these dianions was also shown by aqueous quenching and the isolation of *cis*-dibenzylstilbene.[164]

More recently, using lithium as reductant, O'Brien and Breeden[173] have reported the ^{13}C NMR characterization of these anions and of the highly charged tetraanion $\mathbf{61}^{4-}$ (eq 109). The lithium dianion $\mathbf{60}^{2-}$ in THF or DME and the sodium and potassium dianions in THF are all remarkably stable even in the presence of an excess of alkali metal. Addition of metal to a solution of $\mathbf{61}^{2-}$ results in the formation of the new species $\mathbf{61}^{4-}$. In this case, after the addition of two electrons, loss of MeLi would result in 1-methyl-2,3,4,5-tetraphenylsilacyclopentadienide anion (cf. part 2); no evidence for the formation of MeLi was found. ^{13}C NMR chemical shifts provide strong evidence that this new species is indeed the tetraanion $\mathbf{61}^{4-}$.

In the ENDOR spectra of some C-phenylated silole anion radicals in solution, a temperature dependence of line widths and line positions was observed.[181] This dynamic behavior has been interpreted as being due to hindered rotation of substituted phenyl rings. From Arrhenius parameters one may conclude that the main part of the potential barrier stems from π conjugation effects. Moreover, the proton hyperfine couplings of the various siloles, which are very similar despite the different substituents on the silicon, may indicate that π conjugation is interrupted at the silicon.

The emitter in the chemiluminescent electron-transfer oxidation of the radical anions and dianions of **60** and **61** has been shown to be the parent compound:[174]

$$A^{2-} \xrightarrow{O_2} A^{\bullet-} \xrightarrow{O_2} A$$

In the case of 9,9-diphenylsilafluorene the alkali reduction products apparently decompose by phenyl- or aryl-silicon bond cleavage.[174a] With a bisilafluorene, the lithium attacks the Si–Si bond and yields 9-lithiosilafluorene.[85d]

In an attempt to prepare 1-hydro-3,4-dimetylsiloles via a silacyclopentadienide anion, we tried to cleave an exocyclic bond of 1-phenyl-1,3,4-trimethylsilole with lithium.[79b,82] We found that lithium attacked the diene system of this silole, resulting in the formation of 1-phenyl-1,3,4-trimethylsilacyclopent-3-ene after hydrolysis.

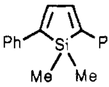
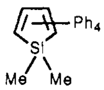
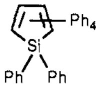
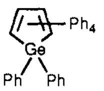
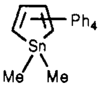
Reaction with an alkali metal gives substitution instead of reduction if the metallole possesses an exocyclic Si–Cl or Ge–Cl bond.[41,43]

2. *Electrode Reactions*

The electrochemical behavior of some group 14 metalloles has been explored.[175,176] Evidence for stable anion radical and dianion formation has been found.

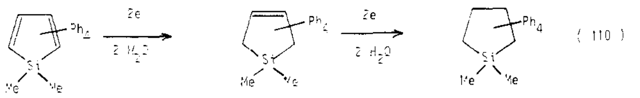
Metalloles **60**–**64** show two reduction waves (Table 13) which indicate that the metallole is reduced to a radical anion ($A^{\bullet -}$) at the potential of the first wave and to a dianion (A^{2-}) at the potential of the second. The ESR spectra of some of these radical anions have been reported (Table 13).

TABLE 13. Electrochemical Data for Metalloles 60–64 and ESR Spectra for the Corresponding Radical Anions

metallole	$-E_{1/2}$, V 1[a]	2[a]	ΔH, G	g	comments	ref
 **60**	1.94	2.26				176
 **61**	1.94	2.18				176
 **62**	2.5	2.9	4.5	2.0016	radical anion blue; five lines observed at 5×10^{-5} M separated by 0.9 G	175
 **63**	3.2		10	2.0037	radical anion blue (half-life ~1 min); extreme modulation broadening	175
 **64**	2.6	3.0	7	2.0020	stable blue radical anion formed if 1 e/molecule added; one main line with two small satellites, $\Delta H_{\mathrm{Sn}^{117,119}}$ = 35 G	175

[a] Half-wave potentials at the first and second polarographic waves. In MeCN containing Et_4NClO_4 as supporting electrolyte, vs aqueous SCE (**60**, **61**); in DME containing Bu_4NClO_4 vs $Ag/AgClO_4$/0.1 M Bu_4NClO_4 (**62**–**64**).

Electrode reaction of **61** in acetonitrile solution in the presence of water resulted in a two-step saturation of the diene ring (ECE mechanism)[176] (eq 110). However, controlled-potential electrolysis of **61** did not give the expected compound but decomposition products.



3. *Reactions with Hydrides*

$LiAlH_4$ is widely used for the synthesis of metalloles or benzometalloles with M–H bonds (cf. section I.E and equations and schemes therein). This hydride does not attack the diene ring.

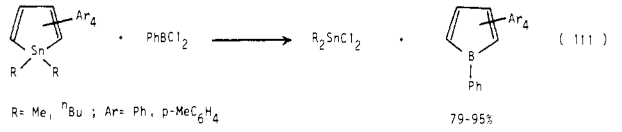
Lithium hydride formed in situ may, however, give an addition reaction with the diene system.[41]

J. Transmetalation Reactions

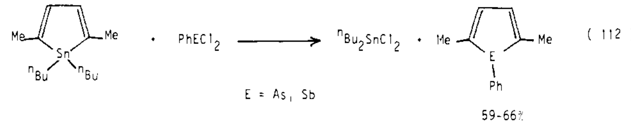
Transmetalation reactions that produce group 14 metalloles have recently been described (cf. section I.B.4).

Stannoles differ significantly from other group 14 metalloles in their ability to be transmetalated by boron, arsenic, and antimony halides. The transmetalation reaction allows one to obtain with high yields the corresponding heterocyclopentadienes: boroles, arsoles, and stiboles.

Eisch et al.[177] and Herberich et al.[178] obtained by this method pentaphenylborole and 1-phenyl-2,3,4,5-tetra-*p*-tolylborole following eq 111. Other boroles were described by Wrackmeyer et al. following similar reactions.[63c,d]



Ashe et al.[64a,179] successfully prepared an arsole and a stibole using the same method (eq 112).



Usón et al.[180] investigated the possibility of obtaining auroles from 2,3,4,5-tetraphenylstannoles. Whereas the reaction between $AuCl_3$ and DTB gives low yields of 1-hydroxy-2,3,4,5-tetraphenylaurole dimer,[3b] the use of the stannole compound offers a clear advantage since the yields obtained are not only higher, but the reactions are also more straightforward (eq 113).

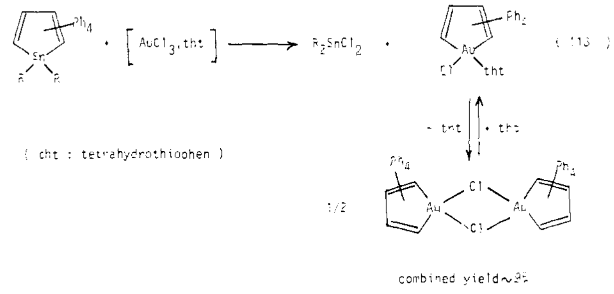
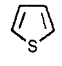
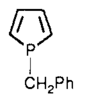
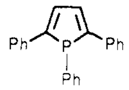
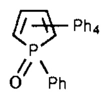
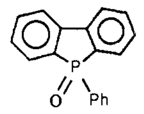
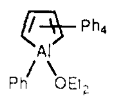
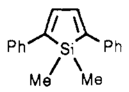
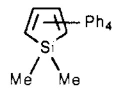
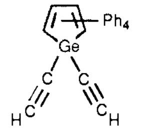
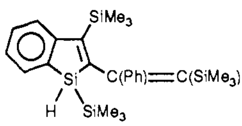
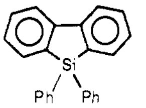
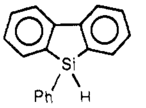
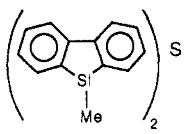
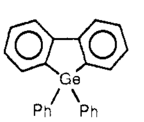
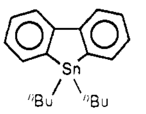


TABLE 14. **Structural Data for Some Group 14 Metalloles and Related Heterocyclopentadienes**

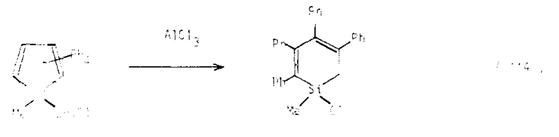
	α,	bond lengths,^{a} Å			
	deg	E—C	C=C	C—C	ref
 65	102.8	1.509	1.342	1.469	193
 66	92.2	1.714	1.370	1.423	194
 67	90.7	1.783	1.343	1.438	195
 68		1.822	1.349	1.440	196
 69	93.3	1.810	1.355	1.505	197
 70	93.4	1.790	1.398	1.479	198
 71	91.6	1.966	1.360	1.516	199
 60		1.878	1.345	1.466	189
 61	92.6^a	1.868	1.358	1.511	190
 72	91.4^a	1.927	1.353	1.510	191
 73		1.899 1.847^b	1.354 1.406^c	1.484	97
 74	91.8	1.863	1.406^c	1.482	192b
 75	91.5	1.865	1.401^c	1.492	192b
 76	91.9^a	1.862	1.414^c	1.483	94
 77	90	1.98	1.42^c	1.45	192a
 78	83.0	2.135	1.400^c	1.496	192c

^{a} Mean values. ^{b} Si–C$_{ar}$. ^{c} C$_{ar}$–C$_{ar}$.

K. Ring Expansion

Ring expansion of a silacyclopentadienylcarbene generated from thermolysis or photolysis of (1-methyl-2,3,4,5-tetraphenylsilacyclopentadienyl)diazomethane and -diazirine to silabenzene is known[46] (cf. section I.F and Scheme 29).

With $AlCl_3$, 1-(chloromethyl)-1-methyl-TPSI undergoes ring expansion leading to 1-chloro-1-methyl-2,3,4,5-tetraphenylsilacyclohexa-2,4-diene[33] (eq 114).



III. Physicochemical Properties of Group 14 Metalloles

A. Structural Data

Known structural analyses of group 14 metalloles have been undertaken using X-ray diffraction of C-phenylated metalloles[189-191] and benzometalloles.[94,97,192]

1,1-Dimethyl-DPSI (**60**) crystallizes in the orthorhombic $Pmn2_1$ space group, $Z = 2$, with cell constants $a = 15.669$ Å, $b = 7.500$ Å, and $c = 6.548$ Å.[189] Molecules of **60** possess exact C_s symmetry; the mirror plane passes through the silicon atom and is normal to the plane of the silole ring. The carbon–carbon bond lengths within this ring (Table 14) are similar to those in cyclopentadiene and rather different from those found in thiophene (**66**) and 1,2,5-triphenylphosphole (**68**). The bond lengths are 1.466 and 1.345 Å for C–C and C=C bonds, respectively. This indicates a low degree of double-bond delocalization, in agreement with the lack of aromaticity and in contrast with phosphole P^{III} **68** and thiophene. In **60**, the butadiene unit is perfectly planar, whereas the silicon atom is displaced from this plane by 0.08 Å, thus forming a dihedral angle between the two Si–C bonds and the butadiene unit of 3.7°. The phenyl rings are almost coplanar with the butadiene unit.

1,1-Dimethyl-TPSI (**61**) crystallizes in the monoclinic $P2_1/c$ space group, $Z = 8$, with cell dimensions $a = 9.103$

Å, b = 18.674 Å, c = 30.603 Å, and β = 113.22°.[190] The two molecules in the asymmetric unit differ mainly in the rotations of the phenyl groups with respect to the silole ring, presumably as a result of crystal packing forces.[190] Moreover, the silole ring geometry is considerably different from that observed in **60**. The central carbon–carbon single bond is significantly longer (1.511 Å) in **61** than in **60** (1.466 Å) (Table 14), which suggests a strong carbon–carbon double-bond localization. In the phosphole P^{IV} **69**, in which the phosphorus electron pair is involved in a bond with an oxygen atom, one finds, by comparison to the phosphole P^{III} **68**, a lengthening of the central C–C bond. This bond length (1.505 Å) is close to that found in silole **61**. The same is true for the aluminole **71** (1.516 Å). This bond lengthening may be compared with that observed in heteroles **60** and **68** as well as in 1,2,3,4-tetraphenyl-*cis,cis*-butadiene (1.49 Å).[200] This may be attributed to steric interactions between the phenyls on the β carbons as these groups are constrained to a cisoid geometry.[199]

1,1-Diethynyl-TPGE (**71**) also crystallizes as two independent molecules in the triclinic system (space group $P\bar{1}$, a = 11.238 Å, b = 12.855 Å, c = 18.428 Å, α = 107.20°, β = 99.79°, γ = 90.72°, Z = 4). The geometric characteristics are similar to those of silole **61** (Table 14), particularly the C–C and C=C bond lengths.[191] The dihedral angles between the planes of the phenyl substituents and the plane of the heterocycle range from 30° to 70°.

In the benzometallole **73**[97] and the dibenzometalloles **74–78**,[94,192] the rings are planar, or almost so. The C=C bonds of these five-membered rings are longer than in the corresponding metalloles (Table 14).

To summarize, one can say that in all these five-membered rings (i) the ring is planar or almost planar, (ii) the bonding around the heteroatom can be viewed as a distorted tetrahedron where the endocyclic bond angle α is ca. 83–94°, (iii) the phenyl substituents on the carbon atoms are arranged in a propeller-like fashion, and (iv) the bond lengths, particularly in the case of C(3)–C(4), vary depending on the substituents carried by the ring carbons, although no structural data are available on lower alkyl substituted metalloles. It seems likely that these parameters would be directly linked to the reactivity in cycloadditions (cf. section II.B) and complexation reactions (cf. part 2).

B. Infrared Spectroscopy

Analysis of the infrared spectrum of cyclopentadiene has been the subject of contradictory interpretations,[201] especially in the region of 1600 cm^{-1}. The C=C stretching band (B_1 mode), which would be expected to appear around 1580 cm^{-1},[201a] is masked by two bands of greater intensity. These bands, apparently, are not due to fundamental vibrations but to combination bands. For pyrrole, furan, and thiophene the ring stretching bands occur in the 1600–1400-cm^{-1} range.[202] Their positions as well as their intensities are very sensitive to changes in substituents.

In the case of phenyl-substituted siloles, some bands appear between 1500 and 1600 cm^{-1},[59,66,203] but the ring stretching bands have not been clearly defined. The highest frequency C=C band is situated between 1578 and 1600 cm^{-1}.[204] This would suggest, based on the position of the C=C band of silacyclopent-2-enes,[205] low delocalization of the two C=C bonds (cf. section III.A).

No bands appear in the region of 1600 cm^{-1} in C-methylated silole or germole spectra, whereas a band at 1520 cm^{-1} of medium or low intensity is found in the spectra of 3,4-dimethylsiloles and -germoles.[18,79b,82] We believe that this band is due to the antisymmetric stretching vibration (B_1 mode) of the C=C bonds.

This band's extremely low frequency is due to the following: (i) the vinylic position of the C=C bonds (the ν(C=C) vibration in sila- and germacyclopent-2-enes is found below 1600 cm^{-1} [205]); (ii) conjugation of the two C=C bonds is apparently more intense in C-methylated metalloles than in C-phenylated metalloles.

The transoid isomers (**c**, **d**) of 3,4-dimethylmetalloles (**a**, **b**) show two intense bands.[18] The first is at 1615 cm^{-1} (exocyclic ν(C=C)); the second, at 1555 cm^{-1} (endocyclic ν(C=C)), is the more intense of the two.

In the case of 1-hydrosiloles or -germoles, the stretching band ν(M–H) (M = Si, Ge) is to be found between 2105 and 2165 cm^{-1} [27,31,41,53b,82] and between 2020 and 2060 cm^{-1},[27,43] respectively. This band's position is weakly influenced by the type of substituents (Ph, Me) on the carbon ring. For example, the ν(Si–H) frequency is observed between 2120 and 2130 cm^{-1} in the case of 1-methylsiloles whether the ring is methylated[82] or phenylated[27,53b] as well as in the case of 9-methylsilafluorene.[94,98]

However, the frequency ν(M–H) greatly varies with the type of substituent carried on the heteroatom. Thus, the substitution of a phenyl group by a *p*-(dimethylamino)phenyl group of +M effect lowers the acidity of the corresponding tetraphenylgermole and decreases the ν(Ge–H) frequency by 32 cm^{-1}.[43]

Zuckermann et al.[44,45] studied the IR absorption bands of some 1,1-disubstituted stannoles. The absorption of groups bonded to the tin was determined, notably the ν_{asym} and ν_{sym} Sn–X modes in 1,1-dihalostannoles. 1-Fluoro-1-halostannoles show two ν(Sn–F) bands at ca. 570 and 350 cm^{-1}. The first is assigned to the stretching mode, while the second belongs to the ν(Sn←F) mode. It arises from the dative bridging interaction in an associated structure.

All of the IR spectra of 9-silafluorenes show an absorption band at 1124 cm^{-1}, which appears to be characteristic of the dibenzosilole nucleus.[85b,d] In addition, the alkyl- or aryl-substituted derivatives exhibit other bands between 1060 and 1080 cm^{-1}.

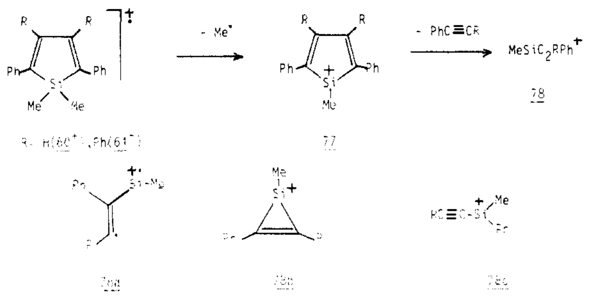
C. Ultraviolet Spectroscopy

The maximum of the absorption for cyclopentadiene and its C-methylated derivatives is to be found between 238 and 250 nm.[206] For the 1-alkylphospholes and their C-methylated derivatives, it is around 286 nm.[1a,207] TMSI (**7a**) and TMGE (**7b**) possess a maximum in the same region (285 and 280 nm, respectively) of low intensity (ϵ = 1700 and 1900, respectively).[18,19] The short-wavelength region is masked by the intense absorption of minor transoid isomers: **7c**, λ_{max} = 242 nm, ϵ = 13000; **7d**, λ_{max} = 243 nm, ϵ = 18500.[19]

The C-phenylated group 14 metalloles, like the C-phenylated cyclopentadienes,[208] show absorption maxima at 220–270 and at 350–380 nm (cf. references in Tables 2–5).

A comparison between the spectra of 1,4-diphenyl-

SCHEME 39



cyclopentadiene[208a,b] and 1,1-dimethyl-2,5-diphenylmetalloles (Si,[42,67] Ge,[67,209] Sn[50]) shows no influence by the heteroatom. The UV maxima are practically at the same position (λ_{max} = 230 and 370 nm) and have comparable intensities (ϵ = 10 000–15 000 and ϵ = 20 000–21 000, respectively) regardless of the metallole. We do, however, notice a bathochromic shift for the longest wavelength maximum when comparing the metallole value (370 nm) with that of the cyclopentadiene derivatives (350, 359 nm).[108a,b]

Nelson[209] compared several C-phenylated group 14, 15, and 16 heteroles. He noted that the compounds that are not aromatic in nature (group 14 metalloles) have the longest λ_{max} absorption, ca. 350–370 nm, whereas those compounds that are aromatic have this absorption at ca. 300–320 nm.

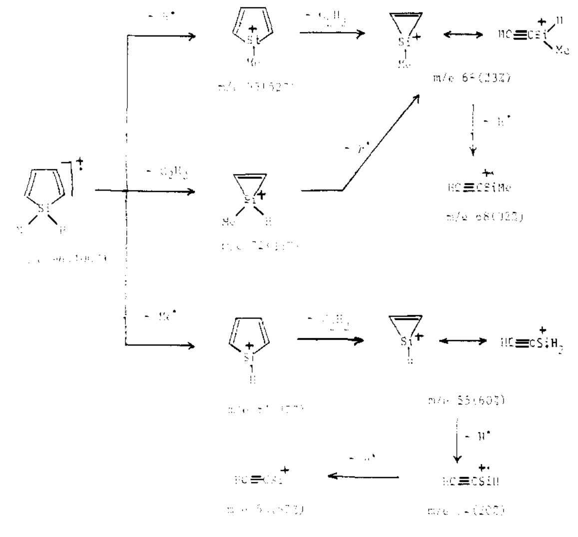
The intensity of this band is relatively lower in the case of 2,3,4,5-tetraphenylsiloles than for 2,5-diphenylsiloles, which implies a decrease in the conjugation between the phenyl groups and the silole cycle.[204] For 1,1-dimethyl-DPSI, the absorption at 370 nm is of high intensity (ϵ = 20 000–20 400).[42,67] This may result from the coplanar disposition of the phenyl groups (cf. section III.A). For 1,1-dimethyl-TPSI, the absorption at 357 nm has a lower intensity (ϵ = 8570–10 000).[25,42,204] This may be due to the propeller-like conformation of the four C-phenyl groups that cannot simultaneously all be coplanar with the five-membered ring.

In an interesting study concerning the photochemistry of siloles, Sakurai et al.[42] compared the quantum yields of fluorescence and photochemical cycloaddition of 2,5-diphenylsiloles. His results suggest that intermolecular (1,1-dimethyl-DPSI) or intramolecular (α,ω-bis(1-methyl-2,5-diphenylsilacyclopentadienyl)alkanes) photocycloaddition occurs through the excited state and competes with fluorescence. The fluorescence emission wavelength is higher in the case of 2,3,4,5-tetraphenylsiloles (490–530 nm)[210] than for 2,5-diphenylsiloles (455–465 nm);[42] 1,1-dimethyl-DPSI emits at 455 nm and 1,1-dimethyl-TPSI at 489 nm.

D. Mass Spectrometry

1,1-Dimethyl-DPSI (**60**) and 1,1-dimethyl-TPSI (**61**) give mass spectra that have very few intense peaks, and, in both cases, the molecular ion is the most abundant.[211] For these two compounds, the fragment ions have similar structures: M – 15$^+$, resulting from loss of a silicon-bonded methyl radical, expulsion of neutral acetylenic fragments corresponding to carbons C(2) and C(3) or C(4) and C(5), MeSi$^+$, PhSi$^+$, and PhMeHSi$^+$ ions. The fragmentation pattern of Scheme 39 was supported by observation of appropriate metastable peaks. Instead of the silacyclopropenium structure **78b**$^+$, the structure of **78**$^+$ may correspond to an acetylenic form **78c**$^+$, which would result from migration of a phenyl group of **78a**$^+$ from the α-carbon atom to the silicon atom. Indeed, metastable peaks are observed in the spectra of **60** and **61** for the fragmentation of **78** to both PhSi$^+$ (m/e 105) and MeSi$^+$ (m/e 43). Furthermore, close examination of metastable transitions shows that various other rearrangements occur during fragmentation of **60** and **61**, in particular the migration of hydrogen atoms from phenyl or methyl groups to the silicon.

SCHEME 40



A program for the structural analysis of siloles by mass spectrometry has been put forward.[212]

The spectra of some simple siloles have recently been published: 1-methylsilole (**4**),[83] 1,3,4-trimethylsilole (**33a**),[82,83] 1-phenyl-3,4-dimethylsilole (**34a**),[82,83] TMSI (**7a**), and TMGE (**7b**).[19] Detailed study of the fragmentation mechanisms of these metalloles has not yet been reported. A few speculative mechanisms have been proposed.[18b,79b]

The molecular peak is strong in all instances; it is the base peak for compounds 4 and **34a**. The (M – 1)$^+$ ion that originates from the loss of a hydrogen atom appears for the three hydrosiloles but is most intense for 4 (52%). The (M - Me)$^+$ ion is also abundant for 4 (37%) and **33a** (base peak). The MeSi$^+$ and PhSi$^+$ ions appear as strong peaks (40–50%) for siloles with methyl or phenyl groups, respectively, bonded to the silicon atom. Ions formed by the loss of an acetylenic fragment are also abundant in the case of simple siloles (loss of acetylene or propyne) as for **60** and **61**. A hypothetical fragmentation mechanism for 1-methylsilole (4) is proposed in Scheme 40.

E. NMR Spectrometry

1. ^1H NMR

(*a*) *Ethylenic Protons.* With group 14 metalloles, the relative positions of the signals of the ethylenic protons Hα (C(2) and C(5)-H) and Hβ (C(3) and C(4)-H) are reversed when compared to heterocyclopentadienes containing an electronegative atom (furan, pyrrole):[213] the Hα atoms resonate at higher fields than the Hβ

atoms (Table 15). Furthermore, these protons resonate at higher fields than in the case of thiophene[213] or 1-alkylphospholes.[1a,214] This denotes a lower ring current in group 14 metalloles, which are nonaromatic heterocyclopentadienes.

The vicinal coupling constant between the Hα and Hβ protons is roughly 10 Hz, as measured for 1,1-dimethyl- and 1,1,3-trimethylsilole and -germole.[17b,19] This is greater than the coupling observed in 1-methylphosphole (7.2 Hz),[214] thiophene (4.7 Hz),[213] furan (1.4 Hz), or pyrrole (2.6 Hz).[213]

The signals of these Hα and Hβ protons are extremely useful probes for the NMR analysis of the transition-metal complexation reactions of metalloles (cf. part 2).

In 2,5-diphenylsiloles, the Hβ signal is masked by the phenyl group signals.[53b] The same is true for the Hα signal of silaindenes, which is found at 6.2 ppm.[96,107]

(*b*) *Proton Bonded to the Heteroatom.* A proton bonded to the silicon in siloles is deshielded when compared to the same proton in alkylsilanes, but it resonates at a position similar to that found in silacyclopentenes. For example, δ(SiH) = 4.40 ppm for 1,3,4-trimethylsilacyclopent-3-ene (C_6D_6) and 4.55 ppm for 1,3,4-trimethylsilole (C_6D_6).[79b] The presence of phenyl groups on α ring carbons causes a deshielding: δ(SiH) = 5.00 ppm for the 1-methyl-DPSI (CCl_4).[53b] Phenyl groups at the β positions have no further effect: δ = 5.02 ppm for 1-methyl-TPSI.[204]

Two hydrogen atoms bonded to the silicon atom of siloles resonate at higher field signal than a single hydrogen atom: δ = 4.36 ppm for 3,4-dimethylsilole (C_6D_6)[79b] and 4.80 ppm for 2,5-diphenylsilole (CCl_4).[53b]

For benzosiloles, the Si–H signal is found at similar values, δ = 4.6 ppm for 1-methylsilaindene[96] and 4.9 ppm for 9-methylsilafluorene.[98]

(*c*) *Groups Bonded to the Heteroatom.* In the phosphorus series (1-methylphosphole and 1-methylphospholene),[214] the chemical shifts of the methyl groups are very different (Δδ = 0.92 ppm) according to whether the ring is a heterocyclopentene or a heterocyclopentadiene.

The chemical shifts of the methyl groups bonded to silicon in methylsiloles (Table 15), and methylsilacyclopentenes[216] are almost identical, which is in agreement with a lack of ring current in the case of siloles. The same holds true for methylgermoles and methylgermacyclopentenes.[217]

Nonequivalence of identical groups bonded to the heteroatom has been found for some stannoles capable of an expansion of coordination at the tin atom. The variable-temperature proton NMR spectra of lithium 1,1-bis(η^1-cyclopentadienyl)-1-halo-TPSN have been interpreted as resulting from a five-coordinated stannole containing a fluxional η^1-C_5H_5 group, which is also undergoing pseudorotation. This interconverts axial and equatorial positions in a $[C_4Ph_4Sn(\eta^1\text{-}C_5H_5)_2X]^-$ anion.[39,45]

2. ^{13}C NMR

The relative chemical shifts of ethylenic carbons Cα and Cβ in group 14 metalloles (Table 16) are reversed when compared to furan or pyrrole.[218] They are very close in the case of thiophene[218] or 1-alkylphospholes.[1a,219] As in all heterocyclopentadienes[220] the presence of *C*-methyl substituents causes a deshielding of bonded carbons and an opposite effect for adjacent carbons: **5a** → **7a**, Δδ(Cβ) = 11.4 ppm, Δδ(Cα) = −4.8 ppm.

3. ^{29}Si and ^{119}Sn NMR

The ^{29}Si resonance signal in a silacycle is found at lower field than for a similar acyclic compound. This difference is roughly Δδ = 11–17 ppm. The following are several examples: diethyldimethylsilane (δ = 5.0 ppm)[221] and 1,1-dimethylsilacyclopentane (δ = 16.8 ppm);[222] allyltrimethylsilane (δ = 0.4 ppm)[221] and 1,1-dimethylsilacyclopent-3-ene (δ = 16.5 ppm);[223] dimethyldivinylsilane (δ = 13.7 ppm)[221] and TMSI (δ = −0.5 ppm) (Table 16). These chemical shift differences may be due to C–Si–C angle differences between the silacycles and linear compounds.[223] The endocyclic C(2)–Si–C(5) angle, measured by X-ray diffraction (cf. section III.A) was found to be 92° for 1,1-dimethyl-TPSI,[190] a value similar to that found for silacyclopentanes[224] and silacyclopentenes[225] (92–98°). The geometry of the bonds around the silicon atom and the hybridization of this atom (angle strain induces p character in the endocyclic Si–C bonds and increases the s character in the exocyclic bonds) are similar in five-membered silacycles. One must remember that silacyclopent-3-enes are planar[225] like siloles. However, the chemical shift of the ^{29}Si nucleus in silacycles does not change in a regular fashion with increasing ring size from three- to six-membered.[221]

A deshielding of the ^{31}P nucleus has also been noted and discussed in phospholes.[1a] Our conclusions confirm that this deshielding is not due to the aromaticity of phospholes as it is also found in nonaromatic compounds such as siloles.

The effects of substituents bonded to the silicon atom of siloles on the chemical shift of the ^{29}Si nucleus are similar to those observed in organosilanes[221] (Table 16).

Replacement of a methyl group bonded to silicon by a vinyl group produces a shielding of 7 or 8 ppm,[221,223] whereas an allyl group has little influence. It follows that the ^{29}Si signal in siloles is found at higher field than in silacyclopentanes and silacyclopent-3-enes.

In C-phenylated siloles, the ^{29}Si resonances lie between δ = 2 and δ = 8 ppm for the 1,1-dimethylated derivatives: 2.3 ppm for 1,1-dimethyl-DPSI,[78b,226] 2.8 ppm for 1,1-dimethyl-3,4-diphenylsilole,[78b] and 8 ppm for 1,1-dimethyl-TPSI.[78b,226] For siloles that carry trimethylstannyl groups on α carbons, the ^{29}Si signal is found at 25–30 ppm.[63a,b]

The ^{29}Si nucleus of 9-methyl-9-silafluorene has a chemical shift of −20.1 ppm,[94] close to that of 1,3,4-trimethylsilole (−20.6 ppm).[79b]

Very few ^{119}Sn chemical shift values for stannoles have been reported (δ = 5–30 ppm/Me_4Sn).[63c–e]

F. Mössbauer Spectroscopy

Mössbauer spectroscopy, applicable to the ^{119}Sn nucleus, is a fundamental analytical technique for tin derivatives.[227] Various parameters such as the oxidation state, the electron density, or the coordination number of the tin atom as well as the stereochemistry around it, contribute to the IS (isomer shift) and the QS (quadrupole splitting) values. Five- or six-coordination is to be expected for $\rho > 2.1$ and four-coordination for

TABLE 15. ^{1}H NMR Spectra of C-Unsubstituted or C-Methylated Group 14 Metalloles

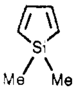
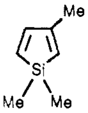
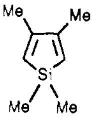
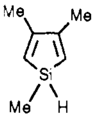
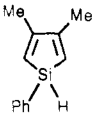
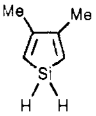
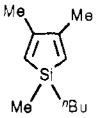
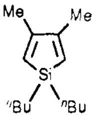
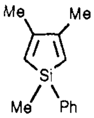
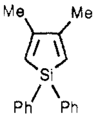
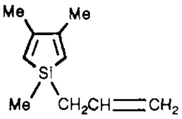
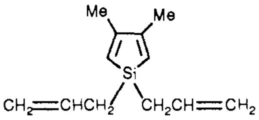
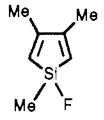
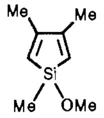
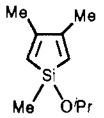
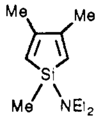
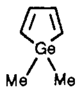
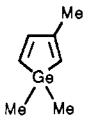
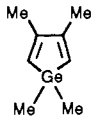
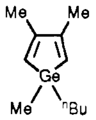
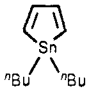
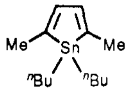
compd	solvent	δ_{M-Me} and/or δ_{M-H}	$\delta_{C=CH}$	δ_{C-Me}	ref
 5a	CCl_4	0.17	6.05 (H_α), 6.95 (H_β)^a		6, 19
	$CDCl_3$	0.72	6.02, 6.78		7
 6a	CCl_4	0.16	5.47, 6.01 (H_α), 6.68 (H_β)^b	1.98	19, 74
 7a	CCl_4	0.10	5.46	1.96	19, 80
 33a	C_6D_6	0.15 4.55^c	5.71	1.82	82, 83
 34a	C_6D_6	5.10^c	5.79	1.82	82, 83
 35a	C_6D_6	4.36^c	5.62	1.74	79b
	CCl_4	0.08	5.50	1.95	166
	CCl_4		5.50	1.96	166
 26a	CCl_4	0.45	5.80	2.03	75
 27a	CCl_4		5.95	2.03	75
 28a	CCl_4	0.10	5.48	1.93	75
 29a	$CDCl_3$		5.66	2.03	75

TABLE 15 (Continued)

compd	solvent	$\delta_{M\text{-}Me}$ and/or $\delta_{M\text{-}H}$	$\delta_{C{=}CH}$	$\delta_{C\text{-}Me}$	ref
 **36a**	C_6D_6	0.25	5.36	1.66	79b, 109
 **37a**	C_6D_6	0.29	5.42	1.79	79b, 109
 **38a**	C_6D_6	0.30	5.50	1.90	79b, 109
 **39a**	C_6D_6	0.31	5.58	1.84	79b, 109
 **5a**	CCl_4	0.38	6.20 (H_α), 6.85 (H_β)		8
 **6a**	CCl_4	0.35	5.66, 6.20 (H_α), 6.65 (H_β)	1.97	17b
 **7a**	CCl_4	0.30	5.71	1.97	17b
	CCl_4	0.25	5.80	1.80	166
	$CDCl_3$	0.87–1.55[d]	6.50 (H_α), 7.16 (H_β)[e]		21b
	$CDCl_3$		6.60	2.10	64a

[a] Degenerate AA′XX′ system; neighboring theoretical spectrum: $J^{2,4} = J^{3,5} = 1.65$ Hz, $J^{2,5} = 2.29$ Hz, $J^{2,3} = J^{4,5} = 9.75$ Hz.[19] [b] System analyzed by double resonance: $J^{2,4} = 1.50$ Hz, $J^{2,5} = 1.0$ Hz, $J^{4,5} = 10$ Hz, J(C(2)H-CMe) = 1.50 Hz. [c] SiH signal; weak coupling constant of this SiH proton with H_α ($^3J < 1$ Hz) and C-Me ($^5J < 1$ Hz). [d] ^{n}Bu. [e] $J_{^{119}SnH}$ = 156.8 and 147.2 Hz.

$\rho < 1.8$ (ρ = QS/IS). Variable-temperature Mössbauer spectroscopy can give further information on the structure of organotin compounds.[228]

The spectra of 1,1-dibromo(or diiodo)-TPSN are doublets with IS and QS values (ρ = 1.50 and 1.44)[44] consistent with four-coordinated diorganotin(IV) dihalides.[45] On the other hand, the Mössbauer spectral data for 1-fluoro-1-bromo(or iodo)-TPSN (ρ = 2.41 and 2.25, respectively) is consistent with a polymeric structure with unsymmetrical F–Sn···F bonds between adjacent stannoles.[44]

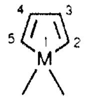
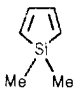
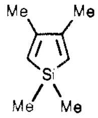
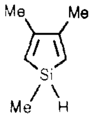
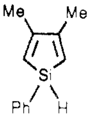
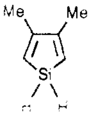
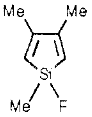
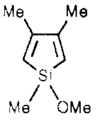
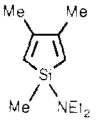
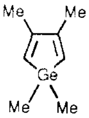
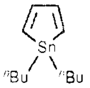
Many stannoles that are substituted by functional groups possessing unshared electron pairs (N_3, NCO, NCS, OC(O)R, SC(S)NR_2) show Mössbauer QS and ρ values in good agreement with an octahedral geometry for the tin atoms.[44]

Dihalostannoles give neutral or ionic complexes (cf. section I.B.a.i, eqs 9 and 10), the structures of which have been deduced from Mössbauer, IR, and NMR data.[44,45]

G. Photoelectron Spectroscopy and Theoretical Calculations

The photoelectron spectra of TMSI and TMGE (Table 17)[17b] show three bands between 8 and 12 eV.

TABLE 16. ^{29}Si and ^{13}C NMR Spectra of Simple Group 14 Metalloles

	solvent	δ(^{29}Si) (from TMS)	δ(^{13}C) (from TMS)				ref
			Si*Me*	C(2,5)	C(3,4)	C*Me*	
 **5a**	$CDCl_3$		-5.5	131.3	145.6		7
 **7a**	$CDCl_3$	-0.5	-5.1	126.5	157.0	20.6	19
 **33a**	C_6D_6	-20.6	-7.7	123.9	159.0	20.8	79b, 83
 **34a**	C_6D_6	-21.6		125.9	160.1	20.6	79b, 83
 **35a**	C_6D_6	-49.5		119.6	161.0	20.7	79b
 **36a**	C_6D_6		-5.0	120.1	159.7	20.3	79b, 109
 **37a**	C_6D_6	8.1	-5.4	122.0	158.8	20.5	79b, 109
 **39a**	C_6D_6	-3.7	-6.0	125.2	158.5	20.3	79b, 109
 **7b**	$CDCl_3$		-4.6	127.5	153.3	20.6	19
	$CDCl_3$		29.6[a] 26.9 13.5 11.4	131.6	145.6		21b

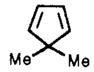
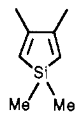
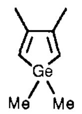
[a] ^{n}Bu.

The first band (8.20 eV) is shifted slightly toward lower energy in comparison with cyclopentadiene and 5,5-dimethylcyclopentadiene. It corresponds to ionization of the $1a_2$ (π) orbital. This shift is in agreement with the inductive effect of the silicon or germanium atom.

The second band corresponds to the other $2b_1$ (π) orbital of the diene system. The potential ionization of this orbital is significantly lower than that for cyclopentadiene: 9.8 eV for TMSI and 9.55 eV for TMGE. This destabilization is due to the fact that this orbital is localized on the metal. The σb_2 and σa_1 orbitals corresponding to Si–C or Ge–C bonds appear in the same region.

The third band includes two partially overlapping bands due to an ionization of the $1b_1$ (π) and the σ orbitals.

TABLE 17. **Vertical Ionization Potentials of Cyclopentadienes and Group 14 Metalloles**

compd	$\pi(a_2)$	$\pi(b_1)$	$\sigma(b_2)$	$\sigma(a_1)$	$\pi(b_1)$	σ	ref
	8.55	10.7	12.2	12.6	14.8	13.5	230
	8.45	10.55	11.3	11.6	12.5	12.6	17b
 7a	8.20	9.8	10.15[a]	10.15[a]	11.15	11.45	17b
 7b	8.20	9.55	9.85	10	11	11.45	17b

[a] Approximate value (overlapping of corresponding bands).

The PE spectrum of 1,3,4-trimethylphosphole[229] exhibits a first band at 8.25 eV, corresponding both to the ionization of the n pair and the πa_2 orbital, and a second band at 10.35 eV (πb_1/P–C). The position of the first band is similar to that found for TMSI and TMGE, but the position of the second band reflects a more stable orbital for the phosphole.

The geometry of the parent silole has been predicted by using a STO-2G basis set,[231] and the theoretical valence ionization potentials of this molecule have been calculated;[232] however, this silole remains unknown.

The molecular orbitals of 1,1-dimethylsilole and TMSI have also been calculated by the MNDO method.[17b]

IV. Conclusions and Perspectives

The synthesis of group 14 metalloles has undergone continuous development over the past 30 years, and the literature now offers a wide range of preparative methods. The C-substituted derivatives, stable as monomers, and the dibenzometalloles (metallafluorenes) are the easiest to obtain. Among these are a large number of derivatives with functional groups on the heteroatom.

In the past few years, siloles and germoles lacking C-substitution have been identified, although they are kinetically unstable. Nevertheless, the parent compounds are still unknown. The recent discovery of a convenient preparation of 1,4-dilithio-1,3-butadiene has allowed the synthesis, by cyclization, of a C-unsubstituted stannole that is stable.[238] This route opens the way to the parent stannoles and can be expected to lead to further progress in the synthesis of other heterocyclopentadienes without C-substitution. The gas-phase pyrolysis methods of synthesis of unstable monomeric compounds that can be trapped at low temperature and spectroscopically identified seem to be more convenient than the condensed-phase methods.

The use of heterocyclopentadienes of transition elements in the synthesis of metalloles of group 14 (and other groups) is not yet very widespread. This route should become more important as exchange reactions (transmetalation) and catalytic processes are developed.

Some of the chemical properties of the group 14 metalloles are similar to those of cyclopentadiene (cycloaddition reactions) but the presence of a heteroatom M results in a number of specific properties: (i) the extension of coordination at M (stannoles); (ii) unstable isomers with M=C double bonds (2*H*- and 3*H*-metalloles); (iii) transmetalation reactions (the synthesis of heteroles from stannoles); (iv) reactions that result in ring opening by cleavage of one (or two) M–C bond(s); (v) substitution reactions at M, very common in the DPSI and TPSN series.

In addition to recent studies of ionic derivatives and transition-metal complexes of new siloles and germoles (cf. part 2), much research has been directed to the synthesis of analogues of carbenes (silylenes, germylenes) as well as of species with multiply bonded heteroatoms, by pyrolysis or photolysis of Diels–Alder cycloadducts (formation of disilenes and of disilynes) prepared from group 14 metalloles, or of metallacyclopentadienylcarbenes (formation of silabenzenes and of silafulvenes).

Besides the presence of an unshared pair on the heteroatom, which bestows on the heteroles of the neighboring group 15 the possibility of further coordination,[1] some notable differences in properties have been revealed: the kinetic instability of the C-unsubstituted siloles and germoles with respect to Diels–Alder dimerization, and the different stability of the various isomeric sigmatropic forms (1*H*-, 2*H*-, and 3*H*-siloles and -phospholes).

If the methods of synthesis of the group 14 metalloles can be further developed, our knowledge of their chemical properties seems now to be sufficiently extensive that the search for applications may be envisaged.

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