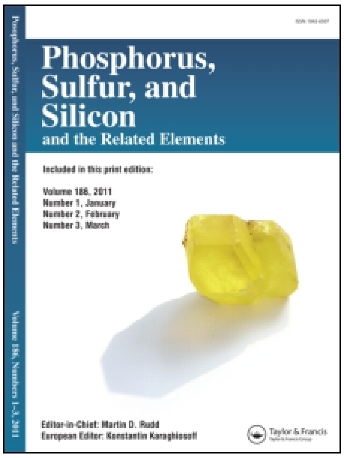

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METALLOLES-14 CHEMISTRY

J. Dubac[a]; A. Laporterie[a]; G. Manuel[a]; H. Iloughmane[a]
[a] Laboratoire des Organométalliques, Equipe de Recherche Associée au C.N.R.S., Université Paul-Sabatier, Toulouse Cédex, France

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METALLOLES-14 CHEMISTRY

J. DUBAC,* A. LAPORTERIE, G. MANUEL and H. ILOUGHMANE

Laboratoire des Organométalliques, Equipe de Recherche Associée au C.N.R.S., U.A. n° 477, Université Paul-Sabatier, 118 route de Narbonne, 31062 Toulouse Cédex, France

In order to obtain β-functionalized 1-sila (or germa)-cyclopent-2-enes $R^1R^2\overline{MCH = CR^3{-}CR^4(X)CH_2}$ (M = Si, Ge; R^1, R^2 = Me or Ph; R^3, R^4 = H or Me) (I) various oxidation methods of metallacyclopent-3-enes have been examinated. The resulting metallacyclopent-4-ene-3-ols (I, X = OH) were converted into phenylcarbamates (I = OC(O)NHPh) or S-methylxanthates (I = OC(S)SMe) and their utility as intermediates in the synthesis of metalloles (siloles and germoles) was investigated.

Depending on the experimental conditions, catalytic dehydration of metallacyclopentenols or thermolysis of carbamates or xanthates give various dienes via four different reaction processes: i) β-elimination C—M; ii) β-elimination C—H; iii) isomerization of C-methylated metalloles; iv) catalytic demetallation.

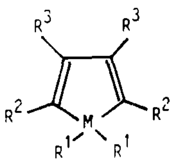
The thermolysis of arylcarbamates is the best method for conversion of I to metalloles, specially for the synthesis of remarkably dimerization-stable 1,1-R^1R^2-3,4-dimethylmetalloles ($\geq$ 80% yield). A one pot synthesis of these stable metalloles from the corresponding alcohol and phenyl isocyanate is proposed.

Unstable monomeric metalloles are stabilized by transition metal complexes or trapped by a (4 + 2) cycloaddition.

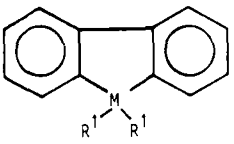
INTRODUCTION

Although the chemistry of the cyclopentadienes and heterocyclopentadienes (phospholes and thiophenes) is one of the most attractive and productive, the chemistry of the group 14 metalloles is one of the least known in organometallic chemistry. Since 1981, it does seem to have been considerably developed.

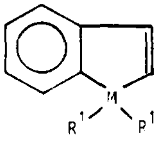
The synthesis of metalloles-14 derivatives, isologs of cyclopentadienes, do not present any particular difficulties in the case of the C-phenylated compounds (**1**, M = Si, Ge, Sn; $R^2 = R^3$ = Ph; R^2 (ou R^3) = H, R^3 (ou R^2) = Ph) [Braye[1], Leavitt's,[2] Gilman's[3] or Seyferth's[4] methods] or in the analogous fluorene (**2**)[5] or indene (**3**)[6] derivatives.



(1)



(2)



(3)

On the other hand, the C-unsubstituted metalloles-14, unstable as monomers, have only been identified in recent years. The first 1,1-dimethylsilole (**6a**)[7,8] synthesis

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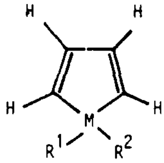
*Author to whom all correspondence should be addressed.

proved to be impossible to reproduce.[9] The formation of the silole itself (**4**) has been proposed[10,11] during the reaction of ^{31}Si atoms on butadiene, but the doubtful chemical identification seems to be contested.[12] The synthesis of this compound has in fact been the object of contradictory publications.[13]



M = Si, $R^1 = R^2 = H$ (**4**)
$R^1 = Me, R^2 = H$ (**5**)
$R^1 = R^2 = Me$ (**6a**)
M = Ge, $R^1 = R^2 = Me$ (**6b**)

Since 1981, the first C-unsubstituted metalloles of group 14, the 1,1-dimethylsilole (**6a**)[14,15] and -germole (**6b**),[16] were identified in monomeric form, and derivatized by cycloadditions[14-16] and metal complexations.[17] Only the dimeric form of 1-methylsilole (**5**) can be observed.[9]

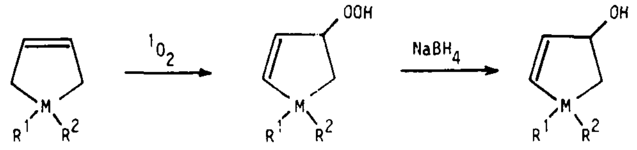
The synthesis of this type of compound is now evolving towards those of the C-alkylated derivatives due to the possible stabilization of the monomeric forms in the series of siloles,[18-23] germoles[18,19,24] and stannoles.[25]

This review is intended to summarize the work done in this field by our team in Toulouse since 1981.

1. SYNTHESIS OF 1-METALLACYCLOPENT-4-ENE-3-OLS

We thought that the *β*-functionalized metallacyclopent-2-enes could produce metalloles-14 by a *β*-elimination reaction. The synthesis of the starting alcohols was envisaged by an oxidation of the metallacyclopent-3-enes (**7**).

The action of molecular oxygen (in the triplet state) gives alcohols of this type with a very low yield,[26] even with catalysts, but singlet oxygen produces, by an ene-reaction mechanism,* a migration of the carbon-carbon double bond and after reduction gives the expected metallacyclopentenols **9**.[14,16,28] The intermediate hydroperoxide **8** can be characterized.



M = Si, $R^1 = R^2 = Me$	**7a**	**8a**	**9a**
M = Ge, $R^1 = R^2 = Me$	**7b**	**8b**	**9b**

Excellent yields are observed with methylated ($R^1 = R^2 = Me$),[14,16] phenylated ($R^1 = Me$, $R^2 = Ph$; $R^1 = R^2 = Ph$),[28] vinylated or allylated[29] derivatives (for the

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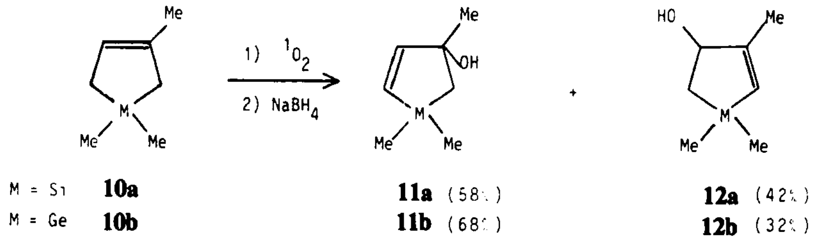
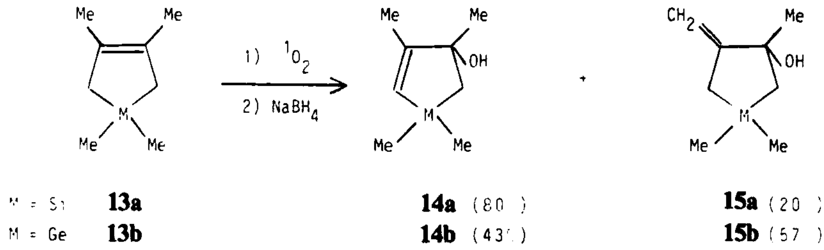
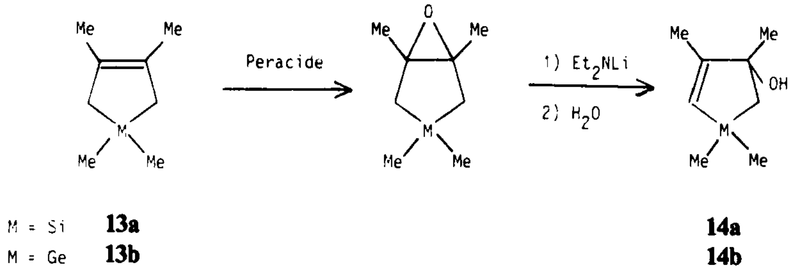
* For details of this reaction in the case of alkenylsilanes, see reference 27 (and ref. therein).



SCHEME 1



SCHEME 2



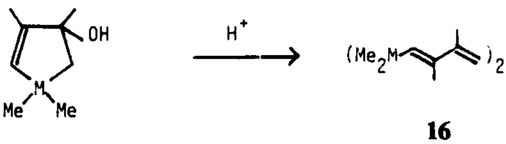
SCHEME 3

latter compound, the exocyclic allylic function is not oxidized). With the C-methylated metallacyclopentenes, the photooxygenation is not regiospecific (Schemes 1 and 2).

The same alcohols **9**, **11**, **12** and **14** are also prepared by a base-promoted rearrangement of the epoxides corresponding to the metallacyclopentenes **7**, **10** and **13**.[30] This second method is particularly interesting in the case of the metallacyclopentenes from group 14 because it gives the alcohols **14** regiospecifically (Scheme 3).

2. DEHYDRATION OF 1-METALLACYCLOPENT-4-ENE-3-OLS

When treated by a protonic acid, the 1-metallacyclopent-4-ene-3-ols decompose at room temperature to form the siloxane or the gemoxane **16** by βC—M elimination.



16

Other aprotic dehydration agents of allylic alcohols give the same results.[28]

The βC—H elimination was obtained by a catalytic dehydration (Al_2O_3 or ThO_2) of these alcohols in the gas phase (Table I). The 1,1-dimethylsilole (**6a**) and the 1,1-dimethylgermole (**6b**), unstable as monomers, are trapped at low temperature, identified by nmr spectroscopy, and chemically characterized by their [4 + 2] adducts and their tricarbonyliron complex (Scheme 4).[14,16,17]

The formation of C-methylated metalloles **17** and **19**, in lesser yield with respect to the transoid isomers **18** and **20**, from the alcohol mixture used, could correspond to a Hofmann-type dehydration. We have shown[19,28] (Table I) that the ratios of dienes thus formed are thermodynamic and correspond to a catalytic isomerization of the metalloles **17** and **19**:

i) the dehydration of isomerically pure alcohols (**14a, b**) gives the same ratios of dienes as the **14** + **15** mixtures;

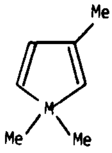
ii) the dehydration of C-methylated silacyclopentanols (**24, 25**) corresponds to a Saytzeff-type elimination on the two catalysts Al_2O_3 (87 and 84%) or ThO_2 (70 and 77%);

iii) pure 1,1,3,4-tetramethylsilole (**19a**) isomerizes to transoid diene on the same catalysts (Scheme 5).

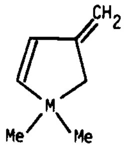
TABLE I

Catalytic dehydration of metallacyclopentenols and metallacyclopentanols

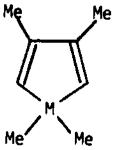
Alcohols	Catalyst and experimental conditions	Products (%) Saytzeff elimination	Products (%) Hofmann elimination	References
9a	Al_2O_3; 300°C/0.01 mmHg	**6a**		14
	Al_2O_3; 220°C/atm.p.(cyclopentane)	**6a**		17
9b	Al_2O_3; 300°C/0.01 mmHg	**6b**		16
	Al_2O_3; 220°C/atm.p.(cyclopentane)	**6b**		17
11a/**12a** (58/42)	Al_2O_3; 300°C/0.01 mmHg	**17a** (35%)	**18a** (65%)	18
	ThO_2; 300°C/atm.p.(cyclopentane)	**17a** (25%)	**18a** (75%)	19
11b/**12b** (68/32)	Al_2O_3; 300°C/0.01 mmHg	**17b** (42%)	**18b** (58%)	18
14a/**15a** (80/20)	Al_2O_3; 300°C/0.01 mmHg	**19a** (15%)	**20a** (85%)	18
	Al_2O_3; 230°C/atm.p.(cyclopentane)	**19a** (18%)	**20a** (82%)	19
	ThO_2; 300°C/atm.p.(cyclopentane)	**19a** (25%)	**20a** (75%)	19
14a	Al_2O_3; 230°C/atm.p.(cyclopentane)	**19a** (18%)	**20a** (82%)	19
14b/**15b** (43/57)	Al_2O_3; 300°C/0.01 mmHg	**19b** (20%)	**20b** (80%)	18
14b	Al_2O_3; 223°C/atm.p.(cyclopentane)	**19b** (17%)	**20b** (83%)	19
	ThO_2; 356°C/atm.p.(cyclopentane)	**19b** (35%)	**20b** (65%)	19
24	Al_2O_3; 200°C/atm.p.(cyclopentane)	**26** (58%), **27** (29%)	**28** (13%)	28, 41
	ThO_2; 355°C/atm.p.(cyclopentane)	**26** (45%), **27** (25%)	**28** (30%)	28
25	Al_2O_3; 200°C/atm.p.(cyclopentane)	**29** (68%), **30** (16%)	**31** (16%)	28, 41
	ThO_2; 350°C/atm.p.(cyclopentane)	**29** (71%), **30** (6%)	**31** (23%)	28



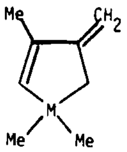
17a
17b



18a
18b

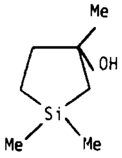


19a
19b

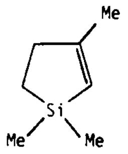


20a
20b

M=Si
M=Ge



24



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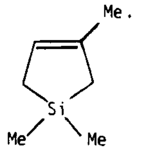

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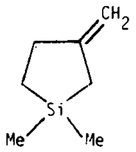

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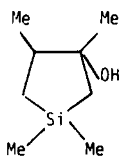

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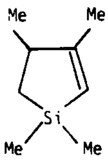

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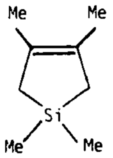

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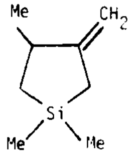
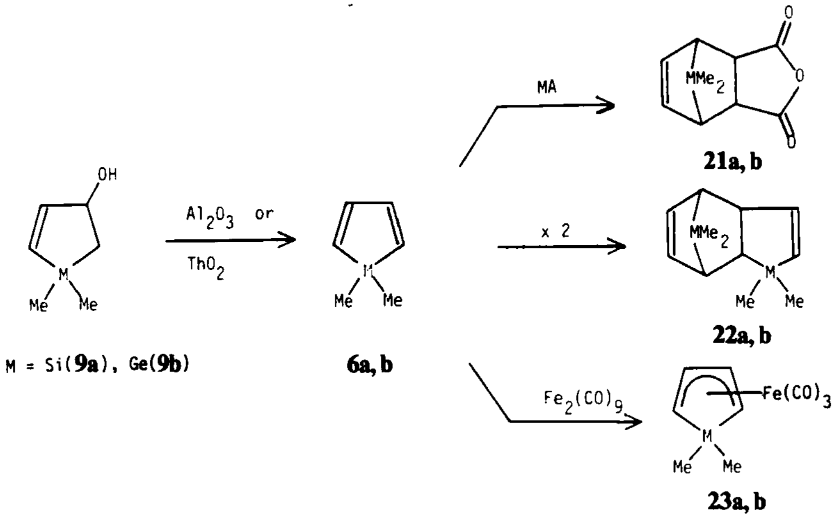


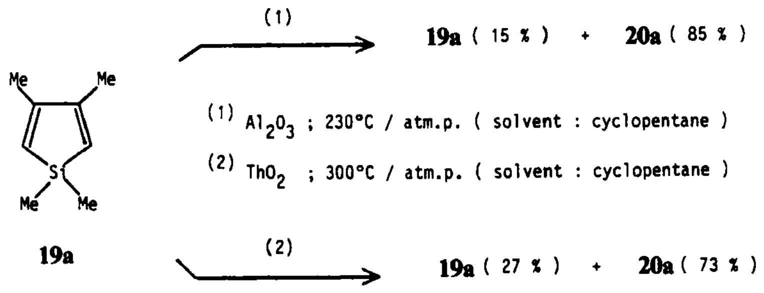
3

Consequently, the dehydration method of the metallacyclopentenols which allows us to obtain the first monomeric C-unsubstituted metalloles-14 is not as good for the synthesis of the C-methylated derivatives.

Furthermore, the catalysts have to be treated thermally and chemically to prevent the demetallation reaction of the metallole[19] which gives the butadiene from **6**, the isoprene from **17** and the 2,3-dimethylbutadiene from **19**.



SCHEME 4



19a

(1) Al_2O_3 ; 230°C / atm.p. (solvent : cyclopentane)

(2) ThO_2 ; 300°C / atm.p. (solvent : cyclopentane)

(1) → **19a** (15 %) + **20a** (85 %)

(2) → **19a** (27 %) + **20a** (73 %)

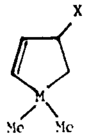
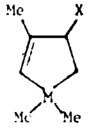
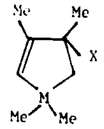
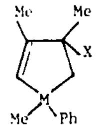
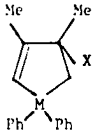
SCHEME 5

3. THERMOLYSIS OF ESTERS OF 1-METALLACYCLOPENT-4-ENE-3-OLS

While we were obtaining the 1,1-dimethylsilole (**6a**)[14] from the catalytic dehydration of the 1,1-dimethyl-1-silacyclopent-4-ene-3-ol (**9a**), Burns and Barton[15] were preparing the same silole by thermolysis of the corresponding benzoic ester at 540°C.

TABLE II

Thermolysis of esters of metallacyclopentenols

	M	X	T(°C)	Yield*	Selectivity (%) βC—H	Selectivity (%) βC—M
	Si	OC(O)Ph	540°	60[15]	**6a**	(**)
	Si	OC(O)NHPh (36a)	310°	80	**6a**	(**)
	Ge	OC(O)NHPh (36b)	310°	80	**6b**	(**)
	Si	OC(S)SMe (32)	unst.	92	**6a** (60)	**34** (40)
	Si	OC(O)NHPh (38a)	310°	72	**17a**	(**)
	Ge	OC(O)NHPh (38b)	310°	60	**17b**	(**)
	Si	OC(O)NHPh (42a)	70°	83	**19a** (95) **20a** (5)	(**)
	Ge	OC(O)NHPh (42b)	70°	86	**19b** (90) **20b** (10)	(**)
	Si	OC(S)SMe (33)	unst.	90	**19a** (42) **20a** (28)	**35** (30)
	Si	OC(O)NHPh	70°	88	**51** (90) **53** (10)	(**)
	Si	OC(O)NHPh	70°	80	**52** (85) **54** (15)	(**)

*In isolated product; **Non-identified.

In order to get an elimination reaction at lower temperature and in a homogenous liquid phase, we have envisaged substituting the hydroxy group in the metallacyclopentenols by a better leaving group.

Since by thermolysis, the β-halogenoalkyltrimethylsilanes give the preferential elimination of the $SiMe_3$ group (βC-Si),[31] it seemed that the *S*-methylxanthates (Chugaev elimination) or the *N*-phenylcarbamates could be suitable precursors.[32]

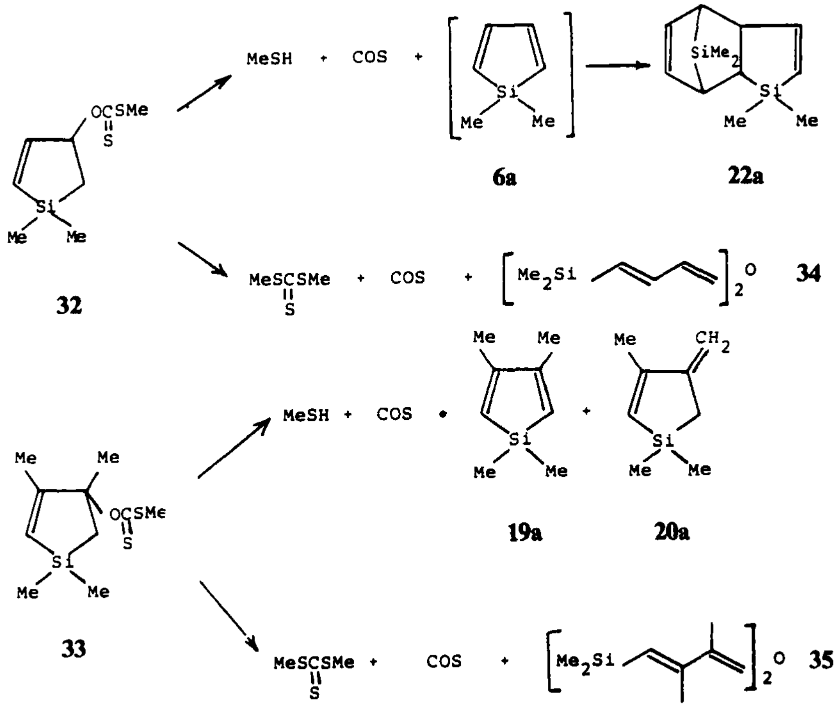
3.1 Synthesis and decomposition of 1-metallacyclopent-4-ene-3-S-methylxanthates[22]

The *S*-methylxanthates **32** and **33**, prepared in ether in the usual way, are thermally unstable. Their decomposition (Table II, Scheme 6) even though not regiospecific gives a predominance of siloles **6a** and **19a**. The presence of siloxanes **34** and **35** (30%), due to a βC—Si elimination, makes the method less interesting.

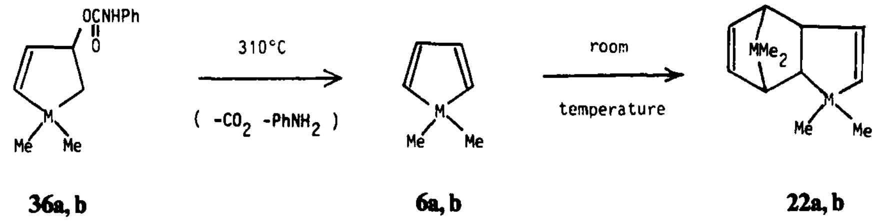
3.2 Synthesis and thermolysis of 1-metallacyclopent-4-ene-3-N-phenylcarbamates[22]

3.2.1 Metalloles unstable as monomers. The *N*-phenylcarbamates **36**, obtained by the addition of alcohols **9** on phenyl isocyanate are stable at the reflux of usual solvents. Their thermolysis at 310°C (Scheme 7) gives the 1,1-dimethylmetalloles (**6**) which are collected in a dry ice trap, identified immediately after reaction by nmr and trapped by maleic anhydride or nonacarbonyl iron.[22]

The mixture of two carbamate isomers **37** and **38** corresponding to the alcohols **11** and **12** are refluxed in carbon tetrachloride for 10 hrs. We isolated the dimer **39** from the metallole **17**, coming from the tertiary carbamate **37** (Scheme 8a). The secondary



SCHEME 6

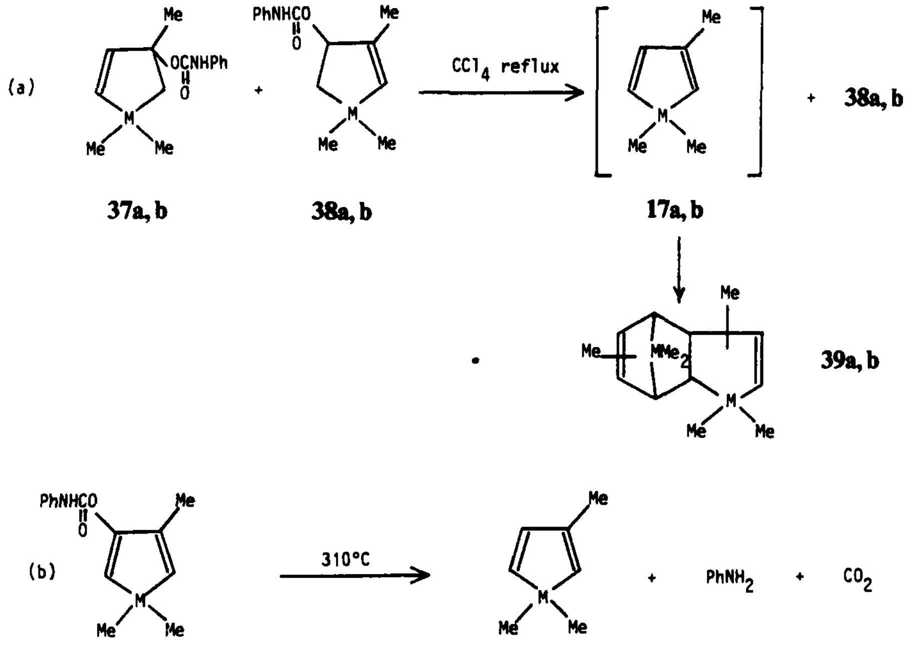


36a, b **6a, b** **22a, b**

SCHEME 7

carbamate **38**, non-decomposed under these conditions, is isolated pure and thermolyzed at 310°C (Scheme 8b). The 1,1,3-trimethylmetallole (**17**) is collected in a dry ice trap as before, identified by nmr and trapped by maleic anhydride or nonacarbonyl iron[22] (Scheme 8c).

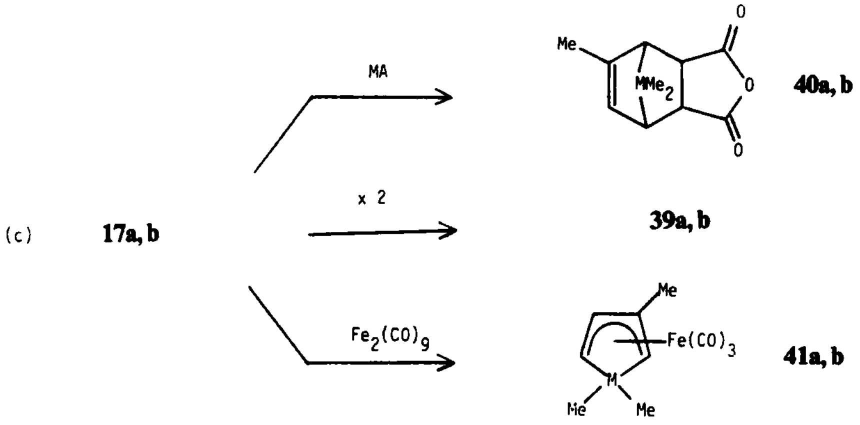
3.2.2 Metalloles stable as monomers. The 1,1,3,4-tetramethylsilole (TMSI, **19a**) and -germole (TMGE, **19b**) are prepared from the 1,1,3,4-tetramethylsila (or germa)-cyclopentenols (**14**) and phenyl isocyanate. The synthesis of tertiary carbamates **42**, unstable at 70°C is done in pentane or ether, in the presence of a catalyst (stannous octanoate).[22] The carbamate **42** decomposes slowly at carbon tetrachloride or benzene reflux giving the metallole **19**, stable in these conditions, and isolated by vacuum distillation.



37a, b **38a, b** **17a, b** **39a, b**

38a, b **17a, b**

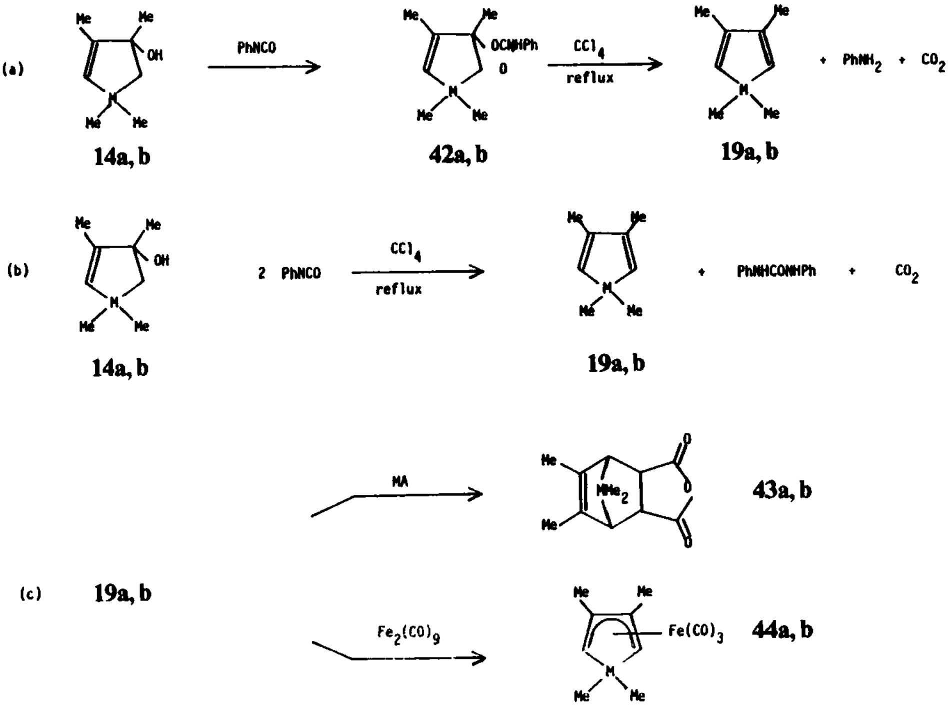
SCHEME 8



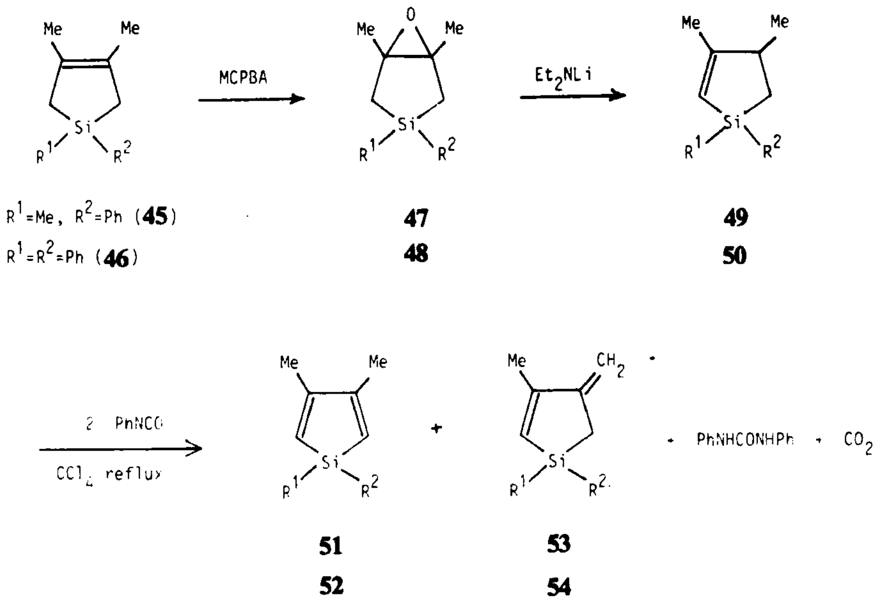
SCHEME 8 (Continued)

A two step, one pot synthesis of TMSI or TMGE is possible from these alcohols and phenyl isocyanate in the same solvents. The aniline is trapped by PhNCO in excess giving diphenylurea (Scheme 9b). The yields exceed 80%, and the isomeric purity of the metallole is high (Table II).

These two metalloles also react with maleic anhydride and nonacarbonyliron (Scheme 9c).



SCHEME 9



R^1=Me, R^2=Ph (**45**)
R^1=R^2=Ph (**46**)

47
48

49
50

51
52

53
54

SCHEME 10

This method of synthesis is now extended to other metallole-14 compounds bearing various substituents on the heteroatom. For example, we give (Scheme 10) the synthesis of two new siloles, stable as monomers, the 1,3,4-trimethyl-1-phenylsilole (**51**) and the 3,4-dimethyl-1,1-diphenylsilole (**52**). The yield of each of these three steps is between 80 and 98%.

4. STABILITY OF THE METALLOLES-14

The C-phenylated metalloles, stable as monomers, have been the subject of much work such as the studies of complexation reactions[33-35] or of functionalization of the heteroatom.[36]

The polymethylmetalloles described here behave quite differently:

–the metalloles unstable as monomers such as the 1,1-dimethylmetalloles or the 1,1,3-trimethylmetalloles dimerize at room temperature;

–the metalloles stable as monomers, bearing two methylated groups on the 3 and 4 carbon atoms of the ring easily isomerize to give the transoid isomer dienes.*

By analogy with the stability of the isoelectronic phospholium ions of the **6a**, **17a** and **19a** methylsiloles, and those of the cyclodienes, it seems that the stability of the metalloles-14 as monomers is mainly under electronic control.[22] The isomerization into transoid dienes could involve a [1,3]-hydrogen migration.[19]

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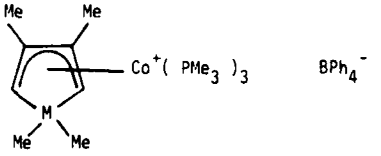
*For the precautions to be taken for the synthesis of these metalloles, see ref. 22.

5. NEW GROUP 14 METALLOLES AS LIGANDS IN TRANSITION-METAL CHEMISTRY

The first π-silole complexes were described by Brunet and al. in 1969.[33] The carbonyl irons often need a high temperature (60°C → 200°C) or irradiation to react with the C-phenylated siloles.[35] The C-unsubstituted or C-methylated metalloles-14 have a higher reactivity towards these compounds. The tricarbonyliron complexes are easily obtained from the reaction of nonacarbonyliron between 0°C and 60°C (Table III). They are air stable yellow liquids or solids with low melting points.



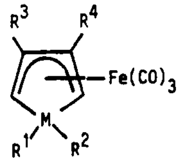
M = Si **(55a)** , Ge **(55b)**

A study of their electronic structure,[14] as well as a crystallographic analysis[40] of the cationic cobalt complexes **55** have been presented.

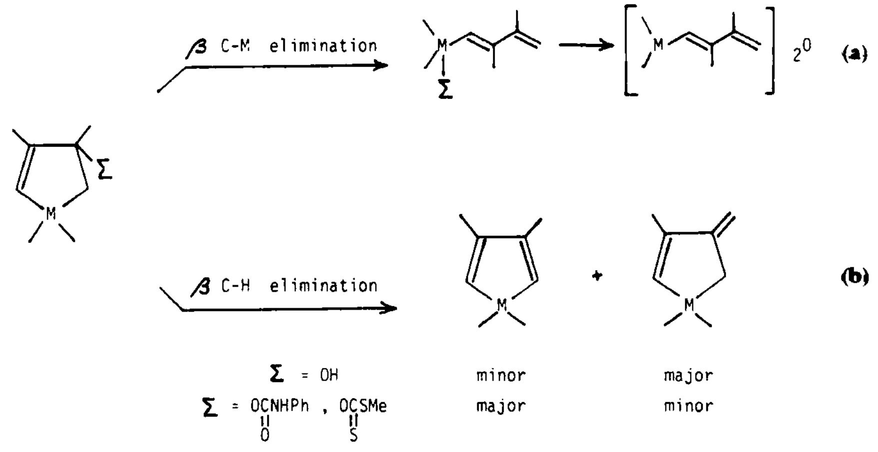
Other cobalt, molybdenum, chromium and nickel π-complexes have recently been synthesized.[38,39]

TABLE III

Group 14 (η^4-metallole) tricarbonyliron complexes (C-unsubstituted or C-methylated metalloles)



M	R^1	R^2	R^3	R^4	References
Si	Me	Me	H	H	17, 22, 38
	Me	Me	Me	H	22
	Me	Me	Me	Me	20, 22
	Me	*n*Bu	Me	Me	21
	Me	Ph	Me	Me	29
	*n*Bu	*n*Bu	Me	Me	21
	Ph	Ph	Me	Me	29
Ge	Me	Me	H	H	17
	Me	Me	Me	H	24
	Me	Me	Me	Me	24
	Me	*n*Bu	Me	Me	21



SCHEME 11

CONCLUSION

The dehydration of 1-metallacyclopent-4-ene-3-ols and the thermolysis of their esters (*S*-methylxanthates, *N*-phenylcarbamates) can give two competitive elimination reactions, the functional groups (OH, OC(O)NHPh, OC(S)SMe) being eliminated by a βC—H cleavage or a βC—M (Si, Ge) cleavage (Scheme 11).

With the alcohols, the usual dehydration agents (i.e. the acids) give exclusively a βC—M elimination (Scheme 11a); catalytic dehydration in gas phase involves βC—H elimination but results in a thermodynamic equilibrium of the dienes, where the metallole is always the minor product (Scheme 11b).

With the xanthates, both eliminations occur. With the carbamates, only the βC—H elimination is observed. The metallole is, in this case, the major and the kinetic product of the elimination reaction.

From the metallacyclopentenols and phenyl isocyanate the one-pot synthesis method of the group 14 metalloles, stable as monomers, is presently the best synthetic method of this type of compound. Furthermore, it seems that this method could be extended to other series of heterocycloalkenes or -alkadienes.

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