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CYCLOPENTADIENYL COMPOUNDS OF SILICON, GERMANIUM, TIN AND LEAD

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CONTENTS

I. INTRODUCTION

Although the first metal derivatives of cyclopentadiene were prepared by Thiele[1, 2] at the turn of the century, the current interest in these compounds originates from the independent discoveries of ferrocene by two groups of workers in 1951[3, 4]. Following this work and the establishment of the now well-known sandwich structure[5, 6], cyclopentadienyl compounds of most of the transition metals and of many main group elements were soon discovered. Several reviews have been published on various aspects of metal cyclopentadienyl chemistry. Birmingham[7] has reviewed the synthesis of these compounds, Fritz[8] their infrared spectra, and Wilkinson[9] their preparation and properties. The present review, however, is concerned with cyclopentadienyl, indenyl and fluorenyl derivatives of the Group IVB elements and includes their preparation and their physical and chemical properties.

II. METHODS OF PREPARATION

A. Cyclopentadienyls of Groups IA, IIA and IIIB as reagents

Reaction of Group IA and IIA metal cyclopentadienyl compounds with Group IVB halides has been the most widely used method for the synthesis of the compounds under review. Potassium is sufficiently active to react with cyclopentadiene when the latter is added to a suspension of potassium shot in toluene. Sodium, however, fails to react under similar conditions and must first be dispersed into particles of 1 to $3 \cdot 10^{-6}$m in diameter. Lithium cyclopentadienide is generally prepared from n-BuLi or PhLi. These are the most common intermediates. In addition, magnesium and thallium cyclopentadienides have been used. Magnesium reacts readily with cyclopentadiene vapour at 500°, to form magnesium cyclopentadienide. The thallium compound is more conveniently prepared by the reaction of thallium hydroxide with cyclopentadiene. Of these compounds, only thallium cyclopentadienide is air stable, so that the others must be prepared in an inert atmosphere. Substituted cyclopentadienes also form metallic derivatives. Thus methylcyclopentadiene, pentamethylcyclopentadiene, indene and fluorene* all react with Li, Na or K[7].

These compounds react with Group IVB halides according to the equation:

$$R_nMX_{4-n} + (4\text{-}n)\,M'C_5H_5 \rightarrow R_nM(C_5H_5)_{4\text{-}n} + (4\text{-}n)\,M'X$$

(M = Si, Ge, Sn, Pb; M′ = Na, K, Li; X = halogen)

By far the best solvents for this reaction are tetrahydrofuran and 1,2-dimethoxyethane. In these solvents, most reactions are rapid and complete, and the reaction may be run conveniently at temperatures between 25° and reflux.

The dicyclopentadienyl compounds of tin and lead have been prepared by this method from the anhydrous metal salts in tetrahydrofuran and other solvents[10, 11].

B. Cyclopentadienyl Grignards

C_5H_5MgBr reacts with Group IVB halides to give the desired compounds:

$$R_nMX_{4\text{-}n} + (4\text{-}n)\,C_5H_5MgBr \rightarrow R_nMC_5H_{5(4\text{-}n)} + (4\text{-}n)\,MgBrX$$

(M = Si, Ge, Sn; X = halogen)

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* Abbreviated as ind and fluor.

No lead compound has been prepared using this method.

Although this was the first method used to prepare a Group IVB cyclopentadiene derivative[12], the method is now little used, due to several disadvantages. The cyclopentadienyl Grignard is not prepared directly, but must be prepared by a displacement reaction between cyclopentadiene and an alkyl Grignard reagent. High yields in this replacement reaction are achieved only when the diethyl ether is partially replaced by a higher boiling solvent such as benzene or toluene. Also it is often necessary to reflux the reaction mixture for 12–24 hours to achieve better yields of the desired compound, but even then yields are generally less than 50%. The method has been used, however, to prepare a series of cyclopentadienyl tin compounds[13], but only a few silicon and germanium compounds have been prepared by this method.

1-Indenylmagnesium bromide has been used to prepare several indenyl tin compounds[13], and 2-indenylmagnesium bromide, prepared from 2-bromoindene, has been used to prepare 2-trimethylsilylindene, unobtainable by other methods[14].

9-Fluorenylmagnesium bromide is known[15], but has not been used to prepare fluorenyl derivatives of the Group IVB metals.

C. Tin–amine method

Another preparative route to the tin derivatives was discovered during studies of aminostannanes of the type $R_3Sn{-}NR'_2$[16,17]. These compounds react with acidic protons, displacing free amine:

$$R_3Sn{-}NR'_2 + HA \rightarrow R_3SnA + R'_2NH$$

$$(A = OH, OR, SR, Cl, NH_2, NHR, NR_2, PR_2, AsR_2, C{\equiv}CR, C_5H_5)$$

Cyclopentadienyl and indenyl derivatives have been formed by this reaction using $R_3Sn{-}NMe_2$:

$$R_3Sn{-}NMe_2 + C_5H_6 \rightarrow C_5H_5SnR_3 + Me_2NH$$

$$R_3Sn{-}NMe_2 + C_9H_8 \rightarrow \text{ind}{-}SnR_3 + Me_2NH$$

(R = Alkyl or aryl)

The dimethylamine boils off at room temperature to give good yields of the products.

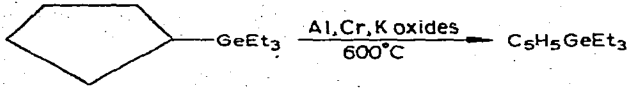
The 9-hydrogen in fluorene has been found to be insufficiently acidic to react with these compounds[18].

This method may be used to prepare derivatives, which have mixed metal substituents on the cyclopentadiene ring[18, 19], *e.g.* $C_5H_4(SiMe_3)(SnMe_3)$ prepared from $C_5H_5SiMe_3$ and $Me_3Sn{-}NMe_2$.

D. *Miscellaneous methods*

There has been one report of a cyclopentadienylsilane being prepared directly from dicyclopentadiene. Passing $HSiCl_3$ and dicyclopentadiene through a quartz tube at 600°, gives $C_5H_5SiCl_3$ in unstated yield[20].

Also, $n\text{-}Bu_2Sn(OMe)_2$ is reported to react directly with indene to give $ind_2Sn(n\text{-}Bu)_2$[21]. $C_5H_5GeEt_3$ has been prepared by dehydrogenation of the corresponding cyclopentane derivative[22].



E. *Preparation from other Group IVB cyclopendatienyl compounds*

In general, Group IVB cyclopentadienyl compounds are reactive species, resulting in the cleavage of the metal–cyclopentadiene bond (*cf.* Section IV). However, compounds which have other functional groups present (especially halogen) may react with retention of the metal cyclopentadiene bond. Thus, these compounds react with Grignard reagents:

$$C_5H_5SiCl_3 + 3MeMgBr \rightarrow C_5H_5SiMe_3 + 3MgBrCl \qquad \text{(Ref. 20)}$$

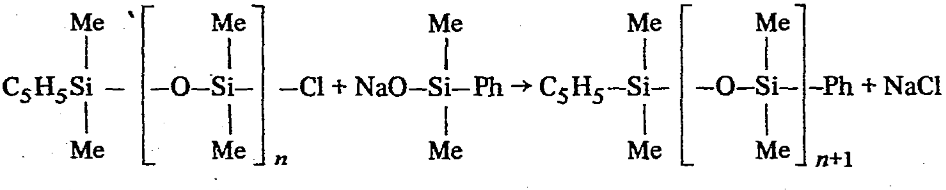
$$(C_5H_5)_3SnCl + CH_2{=}CHMgCl \rightarrow (C_5H_5)_3Sn{-}CH{=}CH_2 + MgCl_2 \qquad \text{(Ref. 23)}$$

$$C_5H_5SnCl_3 + CH_2{=}CHMgCl \rightarrow C_5H_5Sn(CH{=}CH_2)Cl_2 + MgCl_2 \qquad \text{(Ref. 23)}$$

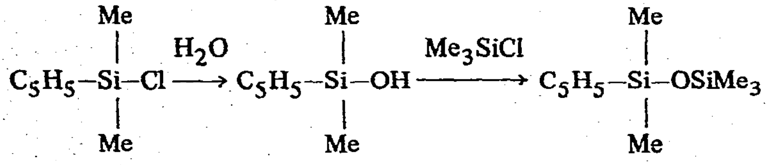
They also react with alcohols to give alkoxy derivatives:

$$C_5H_5SiMe_2Cl + HOEt \rightarrow C_5H_5SiMe_2OEt + HCl \qquad \text{(Ref. 24)}$$

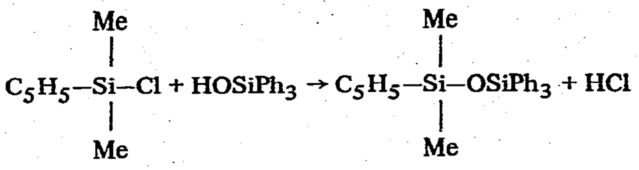
In a study of siloxylferrocenes, three similar methods were used to prepare the cyclopentadienylsiloxanes[25]:



$$C_5H_5\underset{Me}{\overset{Me}{Si}} - \left[-O-\underset{Me}{\overset{Me}{Si}}-\right]_n -Cl + NaO-\underset{Me}{\overset{Me}{Si}}-Ph \rightarrow C_5H_5-\underset{Me}{\overset{Me}{Si}}-\left[-O-\underset{Me}{\overset{Me}{Si}}-\right]_{n+1}-Ph + NaCl$$



$$C_5H_5-\underset{Me}{\overset{Me}{Si}}-Cl \xrightarrow{H_2O} C_5H_5-\underset{Me}{\overset{Me}{Si}}-OH \xrightarrow{Me_3SiCl} C_5H_5-\underset{Me}{\overset{Me}{Si}}-OSiMe_3$$

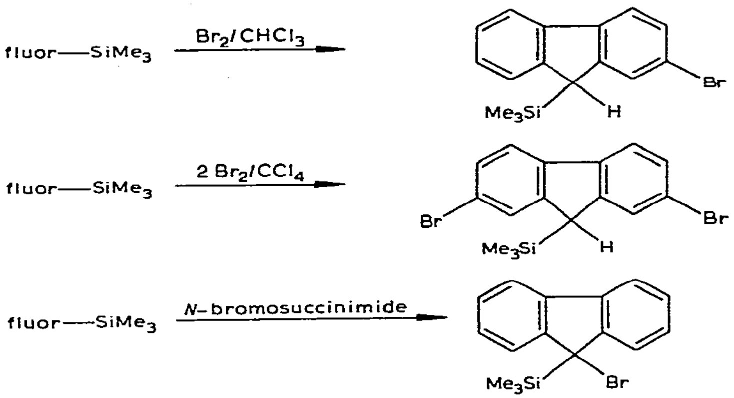


$$C_5H_5\text{–}\underset{Me}{\overset{Me}{Si}}\text{–Cl} + HOSiPh_3 \rightarrow C_5H_5\text{–}\underset{Me}{\overset{Me}{Si}}\text{–}OSiPh_3 + HCl$$

The tin–fluorene bond in fluor–$SnPh_3$ is reported to be stable to HCl in benzene[26]. However, one of the phenyl groups is cleaved:

$$\text{fluor–}SnPh_3 \xrightarrow[C_6H_6]{HCl} \text{fluor–}Sn(Cl)Ph_2$$

The silicon–fluorene bond is stable to Br_2 and *N*-bromosuccinimide[27]. Thus various brominated fluorene derivatives may be prepared with retention of the silicon–fluorene bond *e.g.*



III. PHYSICAL PROPERTIES AND STRUCTURES

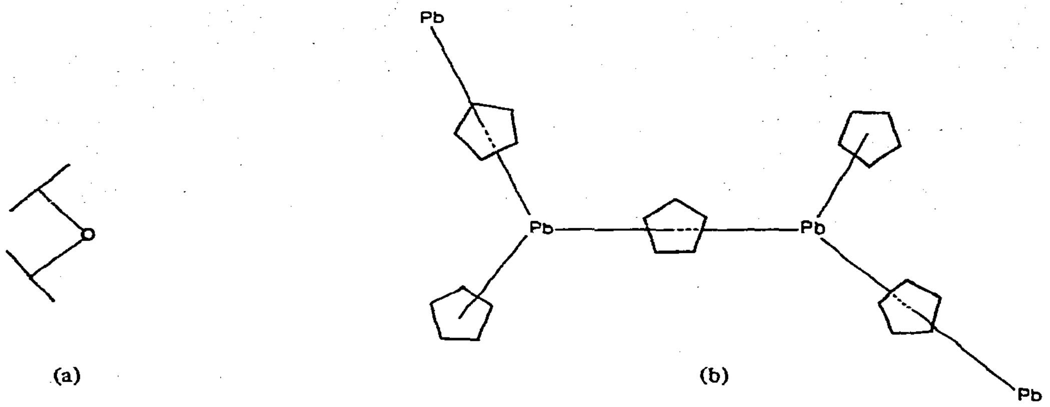
A. Infrared, Raman and ultraviolet spectra, and diffraction methods

1. Divalent derivatives

The infrared spectra of $(C_5H_5)_2Sn$, $(C_5H_5)_2Pb$ and the methylcyclopentadienyl derivatives have been recorded in various media[28, 29, 30] and shown to be similar to that of ferrocene[5, 6]. The UV spectra, however, showed a band not found in metalcyclopentadienides or cyclopentadienylmetal derivatives with a ferrocene-type structure[29]. In addition, these compounds have permanent dipole moments: $\mu(Sn)$ 0.96 ± 0.10D; $\mu(Pb)$ 1.29 ± 0.04D[29].

For $(C_5H_5)_2Sn$, the angle between the C_5 planes is 45 ± 15°, and for $(C_5H_5)_2Pb$ is approximately 55°[31]. The bonding in these compounds is assumed to be predominantly σ bonding, with some additional π bonding between the metal and the cyclopentadienyl rings[29, 30].

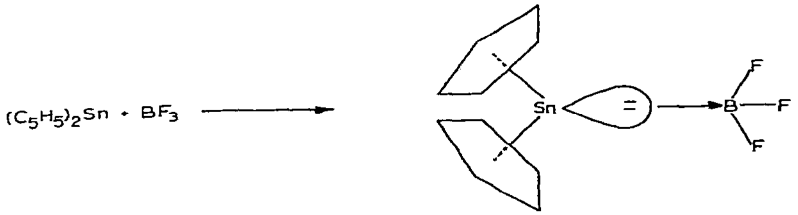
Gas phase electron diffraction studies of dicyclopentadienyllead[31] show it to have an



(a) (b)

Fig. 1.

angular sandwich structure (Fig. 1a). NMR studies (*cf.* Section III.B.1) and the observed dipole moment are consistent with this result. Mössbauer studies on dicyclopentadienyltin have confirmed the presence of Sn^{II} in this compound[32]. Further, the "carbenoid" properties of the species have been demonstrated by the formation of a complex with boron trifluoride[33].



Two crystalline forms of $(C_5H_5)_2Pb$ are known[34]. In the orthorhombic form (Fig. 1b), each lead atom is attached to two bridging cyclopentadienyl groups and one terminal cyclopentadienyl group. The lead to ring bonds are all at approximately 120°, and the polymer may be considered to arise by the lone pair of electrons on each monomer interacting with the cyclopentadienyl ring of another monomer.

A monoclinic form of $(C_5H_5)_2Pb$ is of unknown structure.

2. *Tetravalent derivatives*

The first reported infrared spectrum of a cyclopentadienyl–Group IVB compound, that for $C_5H_5SiMe_3$[35], was recorded in conjunction with those of $C_5H_5CuPEt_3$ and $(C_5H_5)_2Hg$, during a study of the nature of the metal–carbon bond present in these compounds. The spectra showed little similarity except in so far as they all possessed a band at 1610–1640 cm^{-1}, attributable to the carbon–carbon double bond stretching mode ($\nu(C{=}C)$). Furthermore the ultraviolet spectrum of $C_5H_5SiMe_3$ was found to be quite similar to that of cyclopentadiene itself, since they both showed absorptions at λ_{max} = 242 nm, characteristic of conjugated diene system. In contrast, ferrocene and other π-bonded metal cyclopentadienyls were found to show no intense absorption bands in this region. On the basis of these observations, together with the nature of its reaction with maleic anhydride (*cf.* Section IV, D), $C_5H_5SiMe_3$ was assumed to have a σ Si—C bond. Similarly, the IR and Raman spectra of cyclopentadienylgermanium compounds indicate the presence of a covalent metal—carbon bond[36].

Although the IR spectra of methylcyclopentadienyllead compounds have been well documented[37], the nature of the metal—carbon bonding was studied using NMR data (*cf.* Section III, B).

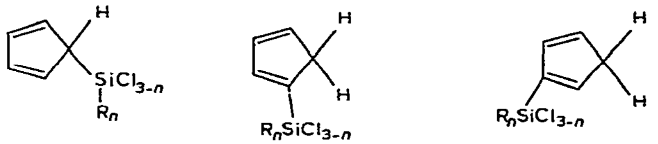
Further evidence to support a σ metal—carbon bond description for this type of compound has been obtained from a study of the IR spectra of cyclopentadienylchlorosilanes, which have been interpreted[38] in terms of the three isomers illustrated in Fig. 2.

The primary product of the reaction between sodium cyclopentadienide and a chlorosilane is a 5-(chlorosilyl)cyclopentadiene (I), because, as a result of the equivalence of all the carbon atoms in the cyclopentadienide ion, this isomer will be formed on the addition of the chlorosilane group to any of the carbon atoms of this anion. The interconversion of (I), (II) and (III) is possible through a series of proton shifts, as has been observed for several related substituted cyclopentadienes[39].

Theoretically, this isomerization is expected to be more rapid for cyclopentadienylchlorosilane derivatives than for alkyl substituted cyclopentadienes, due to the polarization of the carbon—hydrogen bond. The transformation (I) → (II) is also favoured energetically since the chlorosilane group is in conjugation with both of the double bonds of the cyclopentadiene ring for the latter isomer.

The IR spectra of these compounds showed peaks in the regions 2950—2860 cm^{-1} and 1379—1375 cm^{-1} which are assigned to the stretching and deformation vibrations respectively of CH_2 groups in the cyclopentadiene ring. As expected, the introduction of a chlorosilyl group into the 1-position of the cyclopentadiene ring, caused the frequencies of the symmetric and asymmetric vibrations of the double bonds to fall from 1505 and 1595 cm^{-1} respectively in cyclopentadiene, to 1498 and 1580 – 1569 cm^{-1} in these compounds. The intensity of the bands due to the symmetric vibrations of the double bonds increased as the number of polar substituents (Cl, Ph) increased. This was explained by the occurrence of conjugation between the double bonds of the ring and the chlorosilane group. On this evidence, isomer (I) was excluded, and isomer (II) favoured on thermodynamic grounds to isomer (III), due to the conjugation effect already mentioned.

An equilibrium mixture between (II) and (III) and excluding (I), was considered, but rejected on the grounds that, under gas liquid chromatography, the compounds were prac-



(I) (II) (III)

Fig. 2.

tically homogeneous. NMR studies (*cf.* Section III, B) on analogous compounds indicate that an equilibrium mixture of (I), (II) and (III) is obtained.

Fritz[8] has reviewed the IR spectra of cyclopentadienylmetal derivatives, and has assigned the IR active fundamentals in these compounds. From spectroscopic (and chemical) evidence, it is known that bonding in metal cyclopentadienyls can be of four different types:

(a) ionic bonding; assumed for those compounds which show essentially the spectrum of the $C_5H_5^-$ anion.

(b) localized σ bonding; assumed for those compounds where the ligands still have, according to their absorptions, diene character, as in cyclopentadiene itself (Fig. 3a).

(c) complex bonding; assumed for those compounds which show a ligand spectrum corresponding to local C_{5v} symmetry (Fig. 3b). This group is subdivided into two subsets according to whether the ligand is bonded by: (i) a genuine π bond or (ii) a central σ bond (from the metal to the centre of the symmetrical C_5H_5 ring).

There are, of course intermediate stages between the four classes, and a strict classification of some compounds is impossible.

Cyclopentadienyl–Group IVB compounds correspond spectroscopically to cyclopentadiene with one of the methylenic protons substituted by a metal (class (b) above). Accordingly, due to the lower local symmetry, spectra will be observed having a greater number of bands compared with those of symmetrically bound cyclopentadienyl ligands. Absorption bands always appear in the eight frequency ranges given in Table 1.

The C–H stretching region in the IR has been used[40] as a "fingerprint" region to allow a clear choice to be made between σ and π bonded cyclopentadiene rings. For the symmetrically bonded ring (Fig. 3b), only two bands are allowed in the C–H stretching region of the IR on the basis of local C_{5v} symmetry, corresponding to the totally symmetric A_1 mode and the doubly degenerate E_1 mode. On the other hand, five C – H stretching modes are expected in the IR for the σ bonded species (Fig. 3a) as all vibrations will be IR active. The four associated with the olefinic protons would be expected to occur at frequencies greater than 3000 cm^{-1}. Thus this region offers a clear and simple choice to be made regarding the mode of bonding of the cyclopentadiene ring. As compounds of the type $C_5H_5MMe_3$ (M = Si, Ge, Sn, Pb) all show several absorptions above 3000 cm^{-1} it may be concluded that these compounds have a σ structure.

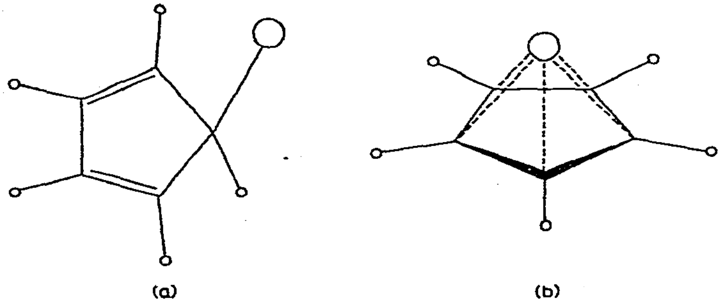

(a) (b)

Fig. 3.

TABLE 1

TYPICAL INFRARED BANDS FOR "DIENE–C_5H_5" LIGANDS

Frequency No.	*Frequency range (cm^{-1})*	*Number of bands*	*Intensity* [a]
1	1529 – 1610	1	w, m
2	1359 – 1389	1	m, s
3	1029 – 1079	1 - 2	m, s
4	967 – 1002	1 - 2	m, s
5	876 – 917	1 - 2	m, s
6	809 – 841	1 - 3	s
7	690 – 750	1 - 4	s, vs
8	610 – 620	1	m

[a] The most frequent intensities are underlined.

B. Nuclear magnetic resonance spectra

1. Divalent derivatives

The NMR spectra of $(C_5H_5)_2Sn$ and $(C_5H_5)_2Pb$ show only one main proton line at 175 cps and 193 cps, respectively, relative to cyclohexane on the low field side[29]. The methylcyclopentadienyl derivatives show only two main lines, with intensity ratio[29] 4/3. These observations are in agreement with the angular sandwich structure proposed for these compounds.

2. Tetravalent derivatives

Much of the interest shown in Group IVB cyclopentadienyl compounds arises from their proton magnetic resonance spectra, many of which show a marked dependence on temperature.

The NMR spectra of σ-cyclopentadienyl derivatives of tin[40] and lead[37] show only one resonance signal for the five protons of the σ-cyclopentadienyl ring. By contrast, in the spectra of σ-cyclopentadienyl compounds of silicon and germanium[41, 42, 43], separate signals are given by the saturated and unsaturated protons at approximately $\tau 3$ and $\tau 7$ respectively. Fritz and Kreiter[41, 43], who studied the spectra of these latter two compounds over a temperature range of $-50°$ to $+150°$, found that with increasing temperature, the signals from the different protons of the cyclopentadiene ring broadened and merged, finally coalescing into one sharp singlet at τ 4.25. Other spectroscopic and chemical evidence indicated that in these compounds the cyclopentadienyl ring was bonded to the central atom by a localized metal-to-carbon bond, rather than one similar to that found in either ferrocene or other π-cyclopentadienyl compounds. Recently[44], the ^{13}C NMR spectra of cyclopentadienyl compounds of Si, Ge and Sn have been reported. The chemical shifts and coupling constants, $J\,(^{13}C–H)$, were found to differ significantly from those in most π-bonded cyclopentadienyl compounds[45], and this evidence was used to substantiate the σ nature of the metal–cyclopentadienyl bond.

These compounds were recognised, therefore, to be further examples of a special class of compound, in which, due to some mechanism, all of the protons became equivalent with respect to the time scale for NMR measurements, *cf.* π-$C_5H_5Fe(CO)_2\sigma$-C_5H_5[46].

Two mechanisms have been proposed to account for this behaviour: metallotropic and prototropic rearrangements.

The metallotropic rearrangement, which has been termed "fluxional", "stereo-chemical non-rigidity", or "ring-whizzing", is illustrated in Fig. 4. Theoretical consideration has been given[47] to the migration of the metal in these compounds. However, the possible transition states[48] were discussed on the basis of a planar ring of the molecule in the ground state. Recent electron diffraction studies have been shown that the ring is in fact bent in an envelope configuration[49, 50].

The structural data suggest that the bond distribution is as illustrated in Fig. 5b. An alternative mechanism, that of a series of 1,2 and/or 1,3 proton shifts (Fig. 6) has been proposed[51] on the strength of the isolation of Diels–Alder adducts of both structures IV and VI.

In the case of a proton migration, it is impossible[47] for a transition complex to be formed in which the migrating proton is equidistant from all five carbon atoms, unless the

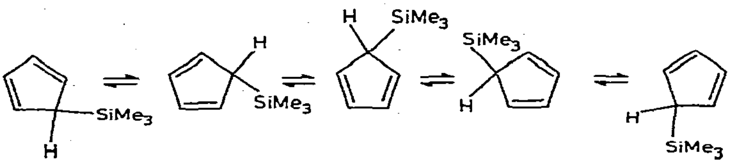
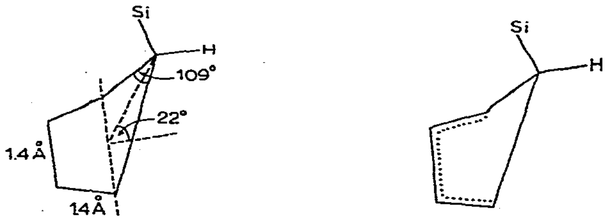
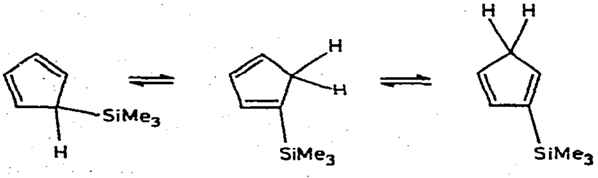


Fig. 4.



(a) (b)

Fig. 5. Gas phase structure of $Me_3SiC_5H_5$.



(IV) (V) (VI)

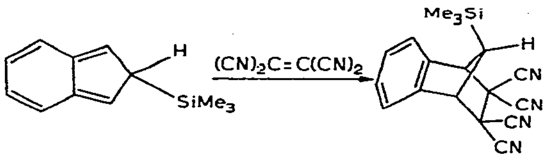
Fig. 6. Isomers of $Me_3SiC_5H_5$.

carbon–hydrogen bonds are considerably longer than is normal. Thus migration will probably take place through the form of a C_1HC_2 (or C_1HC_5) three centre bond, and will therefore be a 1, 2 migration.

Further consideration of possible transition states[47] has indicated that the isomerization by proton migration would be slower than that for trimethylsilyl migration, and, in fact, a factor of 10^6 has been quoted[40].

The interpretation of the variable temperature NMR spectra of $C_5H_5SiMe_3$ in terms of both metallotropic and prototropic rearrangements[52] has further been confirmed by the work of Davison and Rakita[40]. They have suggested that the proton migration, responsible for the vinylsilane Diels–Alder product, cannot be sufficiently rapid to account for the reversible temperature NMR results. Lifetimes for proton migration in cyclopentadiene and alkylcyclopentadienes[39] vary from several minutes to a few hours and a comparable value would be expected for the trimethylsilyl derivative. Thus, for cyclopentadienylsilanes, both metallotropic and prototropic rearrangements occur simultaneously, the intramolecular rearrangement (Fig. 4), giving rise to the reversible NMR spectrum and the isomerization (Fig. 6) giving structures which do not have temperature-dependent NMR spectra. Facile hydrogen migration does not appear to take place in the case of the Ge or Sn compounds, although additional signals appear in the NMR spectra of samples stored for several months at room temperature[38].

Metal migration is degenerate in the case of monosubstituted cyclopentadienyls. The indenyl system, however, enables a natural extension to be made of the concept of fluxional behaviour[53]. The overall 1, 3-shift passes through a short-lived, iso-indenyl derivative designated A* below, and therefore migration of the metal in the indenyl derivative may be considered to be a quasi degenerate process. The low concentrations of A* may be detected by trapping with a reactive dienophile such as tetracyanoethylene[54] (see Table 2).

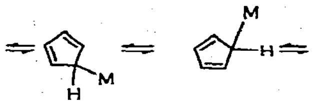
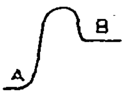
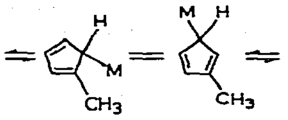
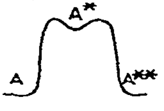
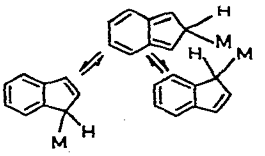


In principle, parameters for metallotropic rearrangements in monosubstituted cyclopentadienyl derivatives may be compared with the parameters obtained for indenyl systems (quasi-degenerate processes), and polymetallated or alkylcyclopentadienes (non-degenerate processes).

In particular, when the parameters for the metallotropic rearrangement of Group IVB cyclopentadienyls and indenyls are compared[53], it can be seen that for both of the systems, the activation energy increases in the series, Sn, Ge and Si. This process proceeds in cyclopentadienyls with an activation energy which is on average 9 kcal • $mole^{-1}$ lower than that for the corresponding indenyls (this is consistent with the energy difference between the indene and iso-indene structures). In addition, indenyl systems migrate at temperatures 150–180° higher than the corresponding cyclopentadienyl systems.

The NMR spectrum[52] of $C_5H_5SiMe_3$ at several temperatures is reproduced in Fig. 7, and the corresponding peak assignments are given in Table 3. These results, which indicate

TABLE 2

Rearrangement type	Kinetic pattern	Potential energy curve	Example
Degenerate	$A \rightleftharpoons A^*$ $[A] \equiv [A^*]$		
Non-degenerate	$A \rightleftharpoons B$ $[A] \neq [B]$		
Quasi-degenerate	$A \rightleftharpoons A^* \rightleftharpoons A^{**}$ $[A] \equiv [A^{**}]$ $A \gg A^*$		

that, at 20°, an equilibrium mixture contains about 13.5% of the isomers V and VI, have also been confirmed by other workers[40, 42, 43]. Very recently, the compositions of equilibrated mixtures of the isomers of $C_5H_5SiMe_3$ have been determined at various temperatures in the range 60 – 200°[54a]. As the temperature was increased the equilibrium (Fig. 6) was displaced to the right. From these data various thermodynamic functions concerning the prototropic shifts have been deduced. The kinetics of the isomeric conversions are based purely upon the integration of the ^1H resonances of the trimethylsilyl groups of the three isomers in the various isomeric mixtures. We experienced certain difficulty in a complete separation of the three resonances on a 100 MHz instrument, and found it impossible on the 60 MHz instrument on which this work is reported to have been performed!

High concentrations (> 50%) of the vinylic isomers may be obtained by flow vacuum pyrolysis of trimethylsilylcyclopentadiene in the gas phase[55]. The isomeric mixture reverts to the room temperature equilibrium on standing. The reversion, which is clearly followed by UV spectroscopy, also appears to be temperature dependent, being much faster at 40° than at 20°.

In pure $C_5H_5SiMe_3$, the signal (b) was first observed by Strohmeier and Lemmon[42], who explained it on the basis of the inequivalence of one of the three *Si*-methyl groups. Kreiter[43], however, explained signals (b) and (c) by the presence of impurity which neither affected the results of a micro-analysis nor was separable by distillation. He showed that, in a freshly distilled sample, the intensity of these signals was low, but increased with both heat and time. These observations may be rationalised by the following explanation. As it

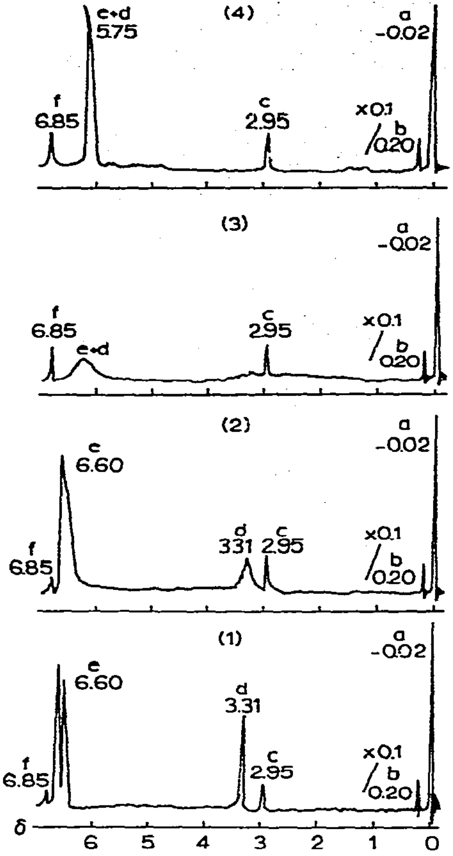


Fig. 7. NMR spectra of cyclopentadienyltrimethylsilane determined at various temperatures: (1) at −30°; (2) at 20°; (3) at 60°; (4) at 120° (From ref. 52).

TABLE 3

ASSIGNMENT OF PEAKS IN THE NMR SPECTRA (FIG. 7) OF $C_5H_5SiMe_3$

Peak	*Chemical shift (ppm.)*	*Assignment (cf. Fig. 6)*	
a	0.02	Me_3Si	isomer IV
d	3.31	saturated CH	
e	6.60	unsaturated CH	
b	0.20	Me_3Si	isomers V, VI
c	2.95	saturated CH	
f	6.85	unsaturated CH	

is known that 5-substituted cyclopentadienes are the lowest boiling isomers[56], then on distillation the mixture will be enriched with isomer IV. It is probable therefore that Kreiter[43] observed the slow establishment of thermodynamic equilibrium among the isomers IV, V and VI.

At −30°, the fine structures of the signals (d) and (e) may be resolved[45] to give a spectrum typical of an A_2B_2X system, as expected for a localized structure (IV). As the temperature is increased, metallotropic rearrangement occurs, until at 120° (Fig. 7), the protons of the cyclopentadiene ring become equivalent.

$C_5H_5GeMe_3$ shows the same variable temperature behaviour[40]. The NMR spectra at various temperatures are reproduced in Fig. 8. At +93° two peaks are observed at τ4.13 and 9.95 (integrated ratio 5/9) corresponding to the five cyclopentadiene ring protons and the nine methyl protons. At lower temperatures, the low field resonance first broadens and then changes into two signals at τ6.53 and 3.5 (integrated ratio 1/4), the latter of which corresponds to the A_2B_2 part of the A_2B_2X pattern (*cf.* $C_5H_5SiMe_3$). The slow exchange limit is reached at −57°.

The variable temperature proton NMR spectra of $C_5H_5SiMe_3$ [40] *(vide supra)* show that as the temperature is increased, the upfield portion of the A_2B_2 pattern for the four olefinic protons collapses more rapidly than the lowfield portion. The metallotropic rearrange-

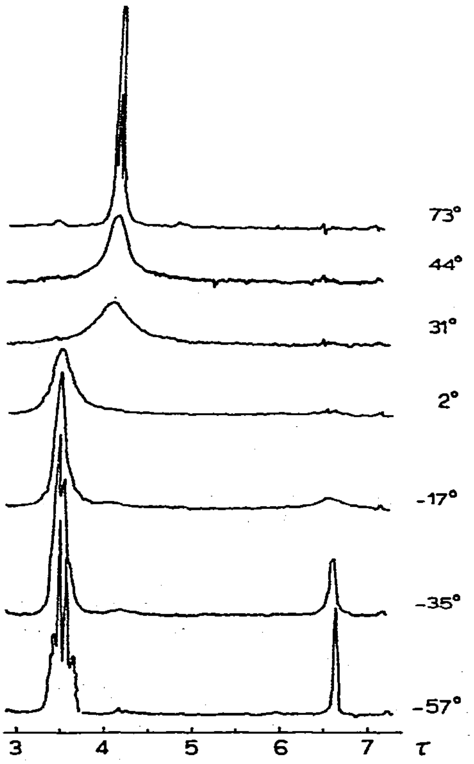


Fig. 8. The proton magnetic resonance spectra of cyclopentadienyltrimethylgermane, $(CH_3)_3GeC_5H_5$, in the region τ 3−7 at several temperatures (ref. 40).

ment, therefore, cannot be one of dissociation – recombination, which would result in a symmetrical collapse of all the protons, and must be a non-dissociative one[57]. The presence of tin satellites in the fast exchange spectra of the cyclopentadienyl stannanes[40] is further evidence for an intramolecular rearrangement. A random rearrangement process would also give rise to a symmetrical collapse, hence the process must involve predominantly 1, 2 or 1, 3 shifts.

The saturation transfer technique (INDOR) and other related methods have been utilized to afford a complete analysis of all of the isomers in trimethylsilylcyclopentadiene. In addition, the spectra of $C_5H_5SiMe_2Cl$ and $C_5H_5SiCl_3$ have been partially analysed[58, 58a]. The main vinylic isomer in the series $C_5H_5SiMe_nCl_{3-n}$ (n = 0,1,2 and 3) is the 1-substituted species, while the 5-substituted isomers are subject to the usual metallotropic rearrangement.

As the electronegativity of the substituents attached to the silicon atom increases, the equilibrium associated with the prototropic rearrangement is shifted towards the formation of the vinylic isomers, whilst the corresponding metal migration rate decreases.

	Isomer content (%) (*cf.* Fig. 2)			B.p. (°C/mm)
n	I	II	III	
0	(35	59	6)	(59/15)
	(50	45	5)	(58/15)
1	75	26	3	62/15
2	79	19	2	54/15
3	90	9	1	54/15

By exact analogy with the work on π-$C_5H_5Fe(CO)_2$-σ-C_5H_5 [57], it is possible to determine how the environment changes for each proton during either 1, 2 or 1, 3 shifts (Fig. 9).

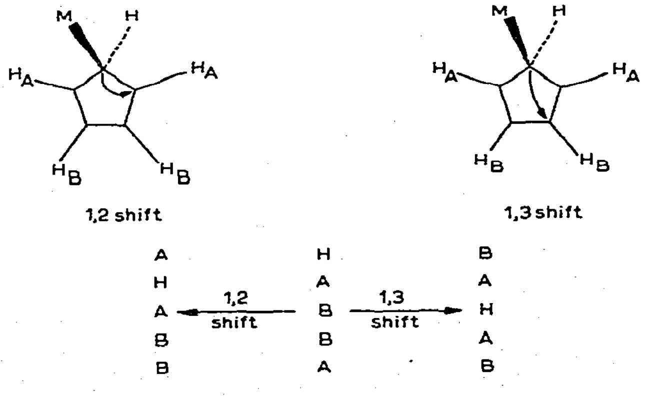


Fig. 9. Proton environment changes by 1, 2 and 1, 3 shifts.

In each case all protons, except one, change environment. The difference lies in the fact that for a 1,2 shift the unchanged environment is of type B, while for a 1,3 shift it is of type A. Thus for a 1,2 shift the A resonance should collapse most rapidly with increasing temperature, whereas for a 1,3 shift the B resonance should collapse most rapidly, since the averaging depends inversely on the lifetime of a nucleus in a given environment. Thus to distinguish between the two mechanisms it is necessary to assign the two parts of the A_2B_2 multiplet in the limiting low temperature spectrum to the correct olefinic protons.

The criteria which have been used for this assignment are[59]:

(a) comparison of chemical shifts with the analogous indenyl compounds where the assignment has been rigorously established by deuteration and multiple resonance experiments[60, 61]
(b) correlation of observed fine structure with that expected from empirical values of coupling constants[62]
(c) the relative sensitivities of the two kinds of olefinic protons to the effects of diamagnetic anisotropies, *e.g.* in $(C_5H_5)_3MoNO$[63]
(d) the splitting pattern of the ^{13}C satellites of the lines corresponding to the H_A and H_B protons[64].

Davison and Rakita[40, 61, 65] have studied cyclopentadienyl and indenyl derivatives of Si, Ge and Sn, and employing the first criteria above only, adopted an assignment for the A_2B_2 multiplet in the $C_5H_5MMe_3$ compounds which led to 1,2 shifts. This assignment placed the A protons at higher field than the B protons, in contrast to transition metal derivatives, where the opposite assignment is put forward (ref. 59 and references cited therein). However, Cotton[66] has demonstrated that the relative values for the chemical shifts of protons A and B are sensitive to the nature of the group to which the cyclopentadienyl or indenyl group is attached. Thus Davison and Rakita's conclusion that 1,2 shifts prevail in the non transition-metal derivatives as well as in the transition-metal derivatives is entirely credible, although it rests on only one line of indirect argument.

Recently, however, Sergeyev, Avramenko and Ustynyuk[67, 68], on the basis of a spin tickling experiment on $C_5H_5SiMe_2Cl$, deduced an opposite assignment to Davison and Rakita, leading, necessarily to a 1,3 shift mechanism. The NMR spectrum[67] of $C_5H_5SiMe_2Cl$ is temperature dependent in the same way as $C_5H_5SiMe_3$ above. The results of the spin tickling experiment[68] have been scrutinised by Cotton[59], and he showed that the experimental results were misinterpreted in the first place, and that they in fact lead to the assignment of the upfield portion of the multiplet to the A protons and hence, as before, 1,2 shifts predominate.

As has already been mentioned, $C_5H_5SnMe_3$ and $C_5H_5PbMe_3$ show only a single resonance in their NMR spectra, due to the cyclopentadiene protons, even over a wide range of temperatures. Below −60°, some broadening is observed[40] in the case of $C_5H_5SnMe_3$, but at no temperature could separate signals be obtained due to protons in different environments. Thus, in these compounds, the barrier to migration of the Me_3M (M = Sn or Pb) group is so low that even at −80°, metallotropic rearrangement still occurs.

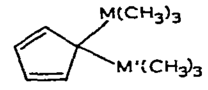
It has been reported[37, 41] that substitution of a methyl group into the cyclopentadienyl ring causes the compound to assume a static configuration. (This assertion has also been adopted for the compound $MeC_5H_4Au \cdot PPh_3$[69].) Davison and Rakita, however, in their systematic study[40] of these Group IVB compounds, have shown that this is not the case and in fact the original data were precisely those expected for a dynamic σ-methylcyclopentadiene group. Methylcyclopentadienyltrimethyl-silane and -germane, show variable temperature NMR spectra analogous to the unsubstituted cyclopentadienyl compounds. In the case of the tin compound, broadening of the fast-exchange spectrum occurs at temperatures below −60°, but as for $C_5H_5SnMe_3$, no fine structure is observed. The pentamethylcyclopentadiene compound of germanium and tin were also studied[40], and showed the expected fluxional behaviour. These compounds are examples of molecules which cannot rearrange by proton migration, and this is further evidence that the variable temperature NMR spectra are the result of metal migration.

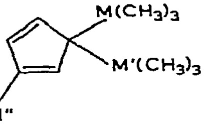
Russian workers in a series of NMR studies on Group IV cyclopentadienyl and related systems have obtained the ^1H spectra of trimethylgermylcyclopentadiene and trimethylstannylcyclopentadiene at 100 MHz over a wide temperature range[44, 53, 58, 67, 68].

By following the unsymmetrical collapse of the olefin multiplet, the cyclopentadienyl group in the germanium compound has been conclusively shown to migrate through a series of 1,2 shifts. Even at −100° → −150° a complete analysis of the tin system was not possible, due to the anisotropic effects at these temperatures.

3. Polymetallated Group IVB cyclopentadienes

Recently cyclopentadienes with two and three Group IVB groups attached have been synthesised[18, 19]. These are summarized below:





Also $C_5H_2[Sn(CH_3)_3]_4$ is reported, and all structures have been established by NMR and mass spectrometry[19, 70]. Their fluxional behaviour has been studied by both ^1H and ^{13}C spectroscopy, and some detailed results have been published[70a].

IV. CHEMICAL PROPERTIES

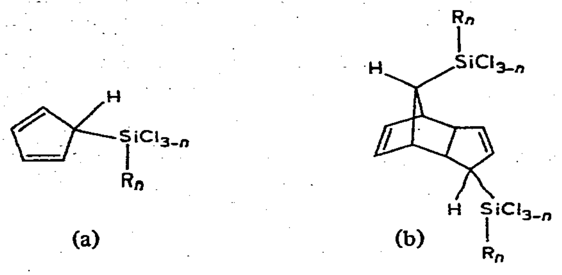
A. Divalent derivatives

The structures of dicyclopentadienyltin and dicyclopentadienyllead have been discussed above. These compounds are white air-sensitive solids, and as already mentioned[32], the "lone pair" of electrons on tin in $(C_5H_5)_2Sn$ has been utilized in the formation of the complex $(C_5H_5)_2Sn \rightarrow BF_3$.

B. Tetravalent derivatives

1. Stability

Like cyclopentadiene, cyclopentadienylchlorosilanes dimerize at room temperature[71].



(a) (b)

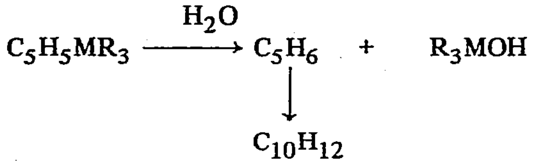
Fig. 10.

The rate of dimerization increases with the number of electronegative atoms and groups on the Si atom, and decreases with the number of electron-donating groups. Thus a molecular weight corresponding to the dimer of $C_5H_5SiCl_3$ is attained after seven days, and for $C_5H_5SiMe_2Cl$ after approximately 100 days. The dimers are cracked at higher temperatures to give the monomer and some polymeric material.

Cyclopentadienylgermane derivatives appear to be relatively air stable[18], but the tin derivatives decompose on standing at room temperature as a result of oxidation and polymerization[13]. $(C_5H_5)_4Sn$ is spontaneously inflammable in air[13].

2. Protonic fissions of metal–ring bonds

Cyclopentadienyl-, indenyl-, and fluorenyl-tin and -lead derivatives are all easily hydrolysed by water, to give the metal hydroxide[13, 26, 72, 73]:



$$\begin{array}{cccc} C_5H_5MR_3 & \xrightarrow{H_2O} & C_5H_6 & + \quad R_3MOH \\ & & \downarrow & \\ & & C_{10}H_{12} & \end{array}$$

(M = Sn, Pb)

Cyclopentadienylsilane derivatives are stable to water at room temperature (the preparation of these compounds involves digestion with water!). However, indenylsilane derivatives react with H_2SO_4 or NaOH to give a siloxane[74]:

$$\text{ind-SiMe}_3 \xrightarrow{NaOH} (Me_3Si)_2O$$

1, 1-Bis (trimethylsilyl) indene is partially converted to 1-trimethylsilylindene when treated with alcohol[74].

The rates of cleavage of various fluorenyl derivatives of Si, Ge and Sn, by aqueous ethanol have been measured[75], and the results interpreted in terms of steric effects in the transition state. The transition state is visualised in Fig. 11. In this intermediate, the Si–R bonds are at right angles to the HO–Si–C line, and there is thus the possibility of interference between the R groups and the fluorenyl group. Fluor-$SiEt_3$ is found to be less reactive than fluor-$SiMe_3$ by a factor of 10^3. It is postulated that this is due to the increased steric hindrance of the ethyl groups compared with the methyl groups, rather than the small difference in electron release by the methyl and ethyl groups. The steric effects appear to be markedly smaller in the germanium compounds compared with the silicon compounds, such that the Me_3Si- compound is now only 2.5 times as reactive as the Me_3Ge- compound, while with the Et_3M- compounds, the considerable increase in hindrance with the silicon compound causes it to be three times less reactive than its germanium analogue.

Rates of cleavage for the tin analogues were difficult to measure due to the insolubility of the tin compounds in the solvent used. However, approximate rates showed the tin compounds to be extremely reactive compared with the silicon compounds, and again it is postulated that this is due to the steric effects in the silicon compounds, rather than a reflection of the relative inherent ease of cleavage of the C–Sn bond compared with the C–Si bond.

3. Halide fissions of metal–ring bonds

(a) HCl

Cyclopentadienyl derivatives of silicon and tin are cleaved by HCl to give the corresponding metal chlorides:

$$C_5H_5SnR_3 + HCl \rightarrow R_3SnCl + [C_5H_6] \qquad \text{(Ref. 73)}$$

$$C_5H_5SiH_3 + HCl \rightarrow H_3SiCl + [C_5H_6] \qquad \text{(Ref. 76)}$$

Similar behaviour is observed for indenyltin derivatives[72]. Arylfluorenyl derivatives of tin and lead, however, react with HCl, with retention of the metal–fluorene bond[26, 72]. In these compounds the phenyl groups are cleaved first:

$$\text{fluor-PbPh}_3 \xrightarrow[\text{benzene}]{\text{HCl}} \text{fluor-PbPh}_2\text{Cl}$$

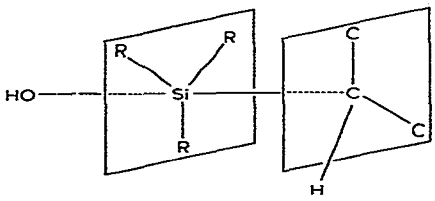


Fig. 11.

Tetraindenyltin and tetrafluorenyltin are both reported to be stable to HCl[72, 77].

(b) Bromine. Bromine reacts with various metal derivatives to give the expected organometal bromide[13, 40, 78].

$$e.g.\ C_5H_5SnPh_3 \xrightarrow{Br_2} BrSnPh_3$$

In the case of $(C_5H_5)_4Sn$, no identifiable products are obtained[73].

(c) Metal halides. Indenylsilane derivatives are cleaved by stannic chloride to give the corresponding chlorosilane[74]:

$$\text{ind-SiMe}_3 \xrightarrow{SnCl_4} Me_3SiCl$$

The organotin compound was not isolated. $(C_5H_5)_4Sn$ reacts with $SnCl_4$[73], but again no identifiable products were isolated.

4. *Diels—Alder reactions*

Cyclopentadienyl derivatives of silicon, germanium and tin all undergo Diels—Alder reactions with dienophiles such as maleic acid, diethyl maleate, diethyl acetylenedicarboxylate and *N*-phenylmaleimide[12, 13, 36, 55, 79]. On the basis of this evidence, together with spectroscopic evidence, cyclopentadientyl Group IVB derivatives are assumed to have a σ metal—carbon bond.

The structures of the adducts obtained between $C_5H_5SiMe_3$ and acetylenic dienophiles have been determined using NMR techniques[80]. Two isomers were obtained, represented by structures VII and VIII (Fig. 12).

1-Trimethylsilylcyclopentadiene, however, would be expected to give the *syn*- and *anti*-7-trimethylsilylbicyclo[2.2.1]heptadienes, structures IX and X (Fig. 13).

(VII) (VIII)

R = Me_3Si; R' = H, COOEt, COOMe

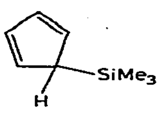
Fig. 12.

(IX) (X)

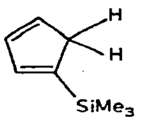
Fig. 13.

Thermal rearrangement between VII and VIII was shown not to occur, and therefore on this basis, the rearrangement involving prototropic shifts (Fig. 6) was proposed.

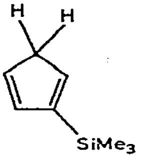
At the temperature of the reactions (200°), it was assumed that isomer VI would be favoured in the equilibrium between IV and VI.



(IV)



(V)

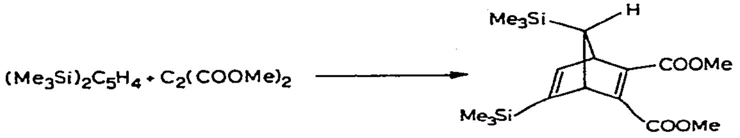


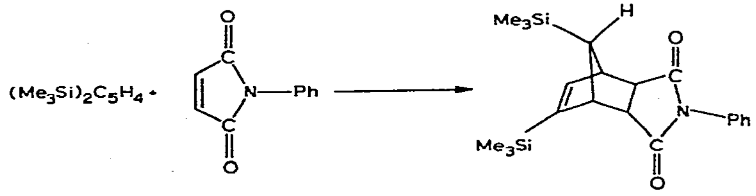
(VI)

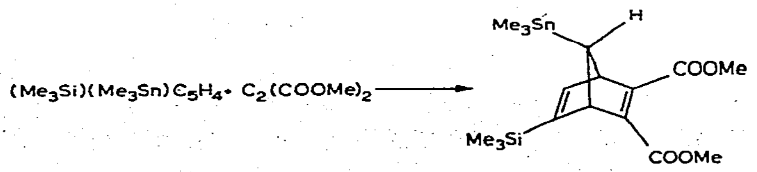
Upon treatment of a gas phase thermolysed mixture, which was shown to contain large amounts of V and VI, with dimethylacetylene-dicarboxylate, adducts derived from only IV and VI were observed[55]. The large trimethylsilyl group at the dieneophile coordination position is assumed to prohibit the formation of this adduct, since the rate of reaction is likely to be considerably slower than the observed isomerisation to IV. Nevertheless, there has been a claim[81] of a small amount of an adduct derived from V.

Further, there are two ways that an unsymmetrical dienophile, RC≡CR′, may add at the 2 and 5 positions of VI. With the Me_3Si group at position 3, it would be expected that the steric interaction with R or R′ would favour the addition of the smaller of the two groups at position 2. The experimental results are in complete agreement with this prediction as structure VII, in which the two Me_3Si groups are in the 2, 5 positions, is found to predominate over VIII, for the products obtained with the unsymmetrical acetylenes.

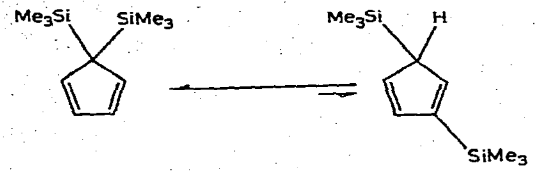
Cycloaddition reactions of bis-metallated systems with dienophiles, such as dimethylacetylenedicarboxylate and *N*-phenylmaleimide yield interesting products, in that at room temperature overall 1, 3-metallotropic shifts appear to occur[82].







Steric hindrance to the approaching dienophile due to two bulky metal groups in the 5 position of the cyclopentadiene ring is presumably responsible for these shifts. It has been stated that the following equilibrium exists in bis-metallated cyclopentadienes.



5. Formation of metallocene derivatives

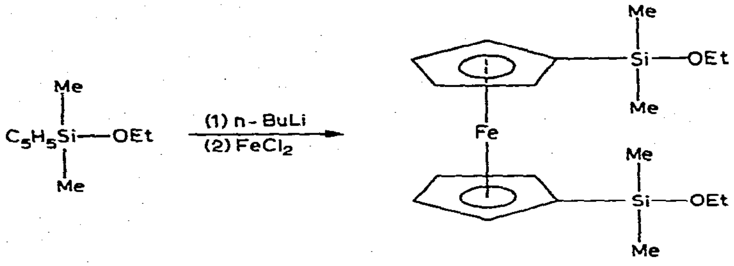
Metallocene derivatives containing R_3M (M = Group IVB metal) groups may be obtained by two general methods:

(1) reaction of Group IVB organo-halide with a metallated derivative of a metallocene. Examples will not be considered further as they do not directly involve a cyclopentadienyl Group IVB derivative.

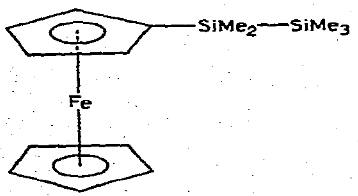
(2) reaction of a metal halide with metallated cyclopentadienyl Group IVB derivative.

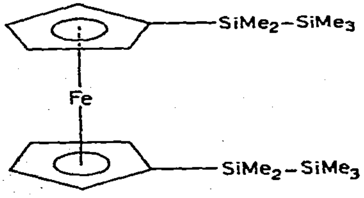
Thus, 1, 1′-bis(trimethylsilyl)ferrocene is obtained from the reaction of $FeCl_2$ and the lithium salt of $C_5H_5SiMe_3$ [83].

Various silicon-substituted ferrocenes with hydrolyzable functional groups have been prepared[24, 74], *e.g.*



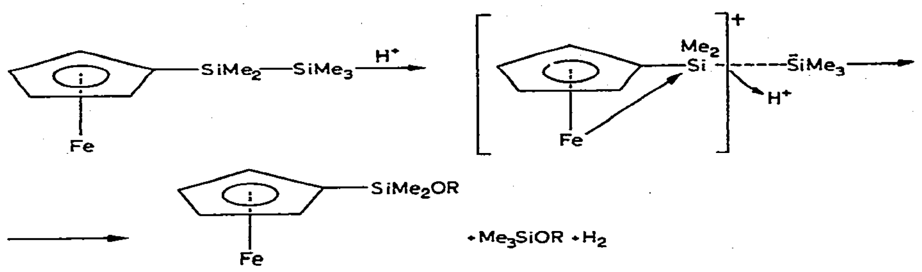
Two disilanyl-substituted ferrocenes have been reported[84]:



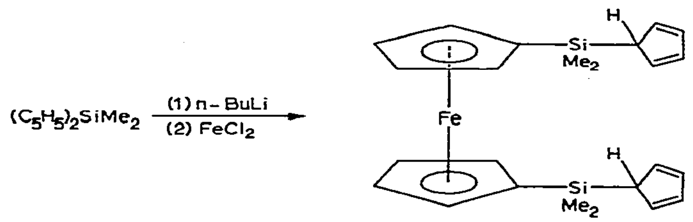


Both compounds are cleaved by extremely dilute alcoholic HCl to give products corresponding to cleavage of the Si–Si bond, as well as ferrocene, resulting from the cleavage of the

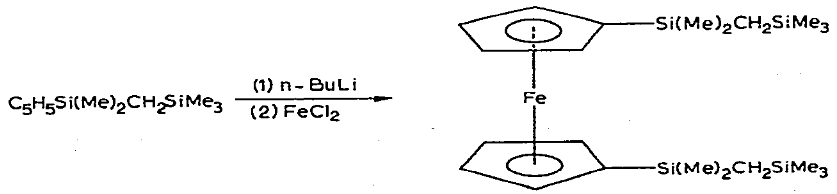
Si—ring bond. Under the same conditions, cyclopentadienylpentamethyldisilane is recovered unchanged. Therefore this cleavage of the Si—Si bond adjacent to a ferrocenyl group is explained by stabilization of the transition state, resulting from overlap of filled *d*-orbitals of iron with the electron deficient *p*-orbitals of silicon:



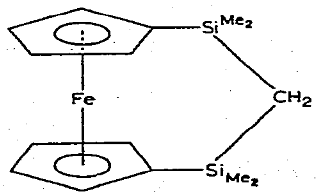
An interesting derivative is formed, together with polymeric material, when FeCl$_2$ reacts with the monolithium salt of $(C_5H_5)_2SiMe_2$[85]:



A ferrocene derivative, containing the $SiCH_2Si$ grouping has been prepared from $C_5H_5Si(Me)_2CH_2SiMe_3$[98].



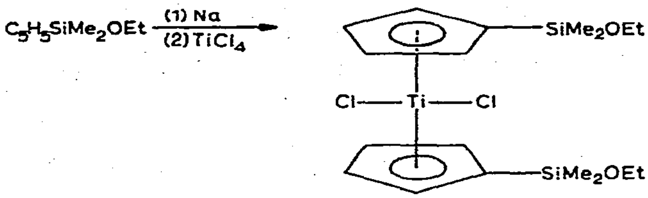
Attempts to prepare



in an analogous way, from bis(cyclopentadienyldimethylsilyl)methane, were unsuccessful.

Triphenylgermyl-substituted ferrocenes have also been prepared from $C_5H_5GePh_3$ and $FeCl_2$[86].

Several titanocene derivatives have been prepared from cyclopentadienylsilanes[87, 88], *e.g.*:

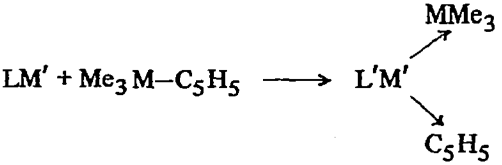


(ref. 74)

6. *Reactions with metal carbonyls*

The reaction of cyclopentadienyl Group IVB derivatives with transition metal carbonyls may be classified into three types:

Type 1 (oxidative addition): In this case, the cyclopentadienyl compound adds oxidatively to a single transition metal centre[89].



$$LM' + Me_3M{-}C_5H_5 \longrightarrow L'M' \begin{cases} \nearrow MMe_3 \\ \searrow C_5H_5 \end{cases}$$

M = Si, Ge, Sn. M′ = transition metal. L, L′L″ ligands attached to M′ *e.g.*:

$$(MeCN)_3W(CO)_3 + Me_3SnC_5H_5 \rightarrow \pi\text{-}C_5H_5(CO)_3W\text{-}SnMe_3$$

Type 2 (oxidative cleavage): In this case, the Me_3M and C_5H_5 fragments become attached to different metal sites[90].

$$LM'{-}M'L + Me_3M{-}C_5H_5 \rightarrow L'M'{-}C_5H_5 + L''M'{-}MMe_3$$

e.g. $$Mn_2(CO)_{10} + Me_3Sn{-}C_5H_5 \rightarrow \pi\text{-}C_5H_5Mn(CO)_3 + Me_3Sn{-}Mn(CO)_5$$

$$Co_2(CO)_8 + Me_3Sn{-}C_5H_5 \rightarrow \pi\text{-}C_5H_5Co(CO)_2 + Me_3Sn{-}Co(CO)_4$$

The reactions of the iron carbonyls are more complex. With $Fe_2(CO)_9$, the primary reaction path appears to be:

$$Fe_2(CO)_9 + 2Me_3Sn - C_5H_5 \rightarrow (Me_3Sn)_2Fe(CO)_4 + (\pi\text{-}C_5H_5)_2Fe + 5CO$$

One important product decomposition route is

$$2(Me_3Sn)_2Fe(CO)_4 \rightarrow [Me_2SnFe(CO)_4]_2 + 2Me_4Sn$$

Type 3: In this case, the integrity of the Group IVB molecule is maintained. This behaviour is particularly characteristic of $C_5H_5SiMe_3$[91]

$$LM' + Me_3M{-}C_5H_5 \rightarrow \pi\text{-}Me_3MC_5H_4{-}M'L'$$

e.g. $$Re_2(CO)_{10} + 2Me_3SiC_5H_5 \rightarrow 2(\pi\text{-}Me_3SiC_5H_4)Re(CO)_3 + 4CO + H_2$$

The corresponding reaction with dimanganese decacarbonyl, however, takes two paths[91]: one in which the silicon-ring bond remains intact:

$$Mn_2(CO)_{10} + 2Me_3SiC_5H_5 \rightarrow 2(\pi\text{-}Me_3SiC_5H_4)Mn(CO)_3 + 4CO + H_2$$

and the other in which silicon-ring fission takes place:

$$Mn_2(CO)_{10} + Me_3SiC_5H_5 \rightarrow Me_3SiMn(CO)_5 + (\pi\text{-}C_5H_5)Mn(CO)_3 + 2CO$$

Why manganese carbonyl should be unique in causing such a fission reaction under these conditions is not clear at this time.

In the case of the metal carbonyl halides, ring-metal fission invariably takes place[91, 92].

$$Me_3MC_5H_5 + M'(CO)_5Br \rightarrow (\pi\text{-}C_5H_5)M'(CO)_3 + Me_3MBr + 2CO$$

(M = Si, Sn; M′ = Mn, Re)

Methylcyclopentadienyl, indenyl and fluorenyl derivatives of tin react similarly[92].

$$CH_3C_5H_4SnMe_3 + M'(CO)_5Br \rightarrow (\pi\text{-}CH_3C_5H_4)M'(CO)_3$$

(M′ = Mn, Re)

$$\text{ind-}SnMe_3 + M'(CO)_5Br \rightarrow (\pi\text{-}C_9H_7)M'(CO)_3$$

(M′ = Mn, Re)

$$\text{fluor}{-}SnMe_3 + Mn(CO)_5Br \rightarrow (\pi\text{-}C_{13}H_9)Mn(CO)_3$$

This work has been extended to compounds which have both silicon and tin groups on the cyclopentadienyl ring[93]. In these cases exclusive cleavage of the organotin group occurs.

$$C_5H_4(SiMe_3)(SnMe_3) + Mn(CO)_5Br \rightarrow (\pi\text{-}Me_3SiC_5H_4)Mn(CO)_3 + Me_3SnBr$$

The following compounds react similarly[93]: $C_5H_4[Si(Me_2)SiMe_3](SnMe_3)$, $C_5H_4(CH_2SiMe_3)(SnMe_3)$ and $Me_2Si(C_5H_4SnMe_3)_2$.

7. Miscellaneous reactions

Silylcyclopentadiene reacts with trimethylamine at room temperature to give $H_3Si{-}NMe_2$[76].

$$H_3Si{-}C_5H_5 \xrightarrow{Me_3N} H_3Si{-}NMe_2$$

The reaction between $C_5H_5SnPh_3$ and n-BuLi does not give the expected lithium cyclopentadienide derivative, but instead gives Ph_4Sn[13].

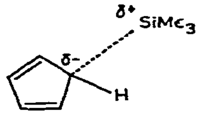
The cyclopentadienyl ring in $C_5H_5GeEt_3$ is reduced using Raney nickel as a catalyst to the corresponding cyclopentane derivative[94].

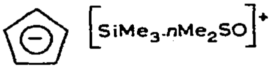
$$C_5H_5GeEt_3 \xrightarrow[\text{Raney nickel}]{H_2} C_5H_9GeEt_3$$

The indenyl ring in silylindenes is similarly reduced[74].

$$\text{ind-SiMe}_3 \xrightarrow[\text{Raney nickel}]{H_2} C_9H_9SiMe_3$$

Recently[95] it has been reported that $C_5H_5SiMe_3$ reacts with dimethylsulphoxide with cleavage of the silicon–cyclopentadiene bond to give hexamethyldisiloxane and cyclopentadienylidenedimethylsulphurane. The NMR spectrum of a mixture of $C_5H_5SiMe_3$ and dimethylsulphoxide has been interpreted[52] in terms of polarized complexes and partially dissociated molecules of the type:





V. TABULAR SURVEY OF CYCLOPENTADIENYL, INDENYL AND FLUORENYL COMPOUNDS OF THE GROUP IVB ELEMENTS

The preparative method, yield, melting point or boiling point and any physical data contained in the reference are detailed in the tabular survey under the appropriate compound.

The synthetic methods are as described in Section II:

A, Group IA, IIA and IIIB metal cyclopentadienyl method.
B, Cyclopentadienyl Grignard method.
C, Metal amine method.
D, Direct method.
E, Preparation from other Group IVB cyclopentadienyl compounds.

SILICON

Compound	*Synthetic method*	*Yield (%)*	*B.p. (°C/mm) m.p. (°C)*	*Data*	*References*
$C_5H_5SiH_3$	A	89	59–61	IR, NMR	76
$MeC_5H_5SiH_3$	A	99	(-144 to -148)	IR, NMR	76
$C_5H_5SiMe_3$	A	40	43–44/19	n_D^{20} 1.4608 NMR	45, 52
	A	15	138–140	n_D^{20} 1.4622	96
	A	71	32/12	NMR	41
	A	73	41–43/16	-	51
	A	-	-	IR, UV	35
	A	-	-	IR, NMR	40
	A	-	-	NMR	42
	A	-	-	^{13}C NMR	44
	B	45	43–44/19	-	12, 97
	E	-	138–140	n_D^{20} 1.4610 IR, R	20
$C_5H_5Si(Me)_2CH_2SiMe_3$	B	56	58–59/6	n_D^{20} 1.4780	98
$C_5H_4(SiMe_3)_2$	A	51	44.5/0.2	-	18
	A	60	45/3	-	19
$MeC_5H_5SiMe_3$	A	-	54–56/16	IR, NMR	40
$(C_5H_5)_2SiMe_2$	B	40	73/25	-	12, 97
$(C_5H_5SiMe_2)_2CH_2$	B	50	84–86/0.4	n_D^{20} 1.5245	98
$C_5H_5SiEt_2H$	A	-	74/25	n_D^{20} 1.4732	99
$C_5H_5Si_2Me_5$	B	65	86/22	n_D^{20} 1.4913	84
$C_5H_5SiMe_2$(1-piperidyl)	E	82	56–60/0.3	n_D^{25} 1.4984	24
$(C_5H_5SiMe_2)_2O$	E	53	65/0.15	n_D^{25} 1.4852	24
$C_5H_5(SiMe_2O)_3Et$	E	82	70–72/0.5	n_D^{25} 1.4268	24
$C_5H_5(SiMe_2O)_2SiMe_2C_5H_5$	E	49	89–94/0.2	n_D^{25} 1.4708	24
$C_5H_5SiMe_2OSiMe_2Ph$	E	80	83–86/0.03	-	25
$C_5H_5SiMe_2(OSiMe_2)_2Ph$	E	76	107–112/0.04	-	25
$C_5H_5SiMe_2(OSiMe_2)_3Ph$	E	61	116–144/0.09	-	25
$C_5H_5SiMe_2OSiMe_3$	E	66	82–83/21	-	25
$C_5H_5SiMe_2OSiMe_2C_6H_3Cl_2$	E	46	102/0.03	-	25
$C_5H_5SiMe_2OSiPh_3$	E	57	156–159/0.05	-	25
$MeC_5H_5SiMe_2OSiMe_2Ph$	E	79	82–85/0.16	-	25
$C_5H_5SiCl_3$	A	58	46–48/4	n_D^{20} 1.5100 d^{20} 1.3632 IR	38, 100
	A	56	58/10	n_D^{25} 1.5212	101
	D	25	72/30	n_D^{20} 1.4972 d^{20} 1.2338	20
$C_5H_5SiMeCl_2$	A	73	47–49/8	n_D^{20} 1.4920 d^{20} 1.1622 IR	38, 100
	A	-	51/10	NMR	67, 68
	A	55	36–50/3	-	25
	B	-	-	-	12
$C_5H_5SiEtCl_2$	A	64	76–78/10	n_D^{20} 1.4982 d^{20} 1.1530 IR	38, 100

(continued on next page)

Compound	*Synthetic method*	*Yield (%)*	*B.p. (°C/mm)* *m.p. (°C)*	*Data*	*References*
$C_5H_5SiPhCl_2$	A	70	135–136/6	n_D^{20} 1.5666 d^{20} 1.2266 IR	38,100
	A	55	83/0.5	n_D^{25} 1.6822	101
$C_5H_5Si(Pr)Cl_2$	-	-	-	IR	38
$C_5H_5Si(i\text{-}Pr)Cl_2$	-	-	-	IR	38
$C_5H_5Si(n\text{-}Bu)Cl_2$	-	-	-	IR	38
$C_5H_5Si(i\text{-}Bu)Cl_2$	-	-	-	IR	38
$C_5H_5Si(CH{=}CH_2)Cl_2$	A	37	63–65/8	n_D^{20} 1.5070 d^{20} 1.1710 IR	38, 100
	A	-	30–35/1	n_D^{25} 1.5150	101
$C_5H_5SiMe_2Cl$	A	60	54–56/14	n_D^{20} 1.4870 d^{20} 1.0048 IR	38, 100
	A	69	37–40/7	-	25
	B	-	80–83/0.7	-	12, 97
$MeC_5H_5SiMe_2Cl$	A	71	75–90/20	-	25
$C_5H_5SiEt_2Cl$	A	62	78–80/17	n_D^{20} 1.4875 d^{20} 0.9986	38, 100
$C_5H_5Si(Me)PhCl$	-	-	-	IR	38
$C_5H_5Si(Me)(CH{=}CH_2)Cl$	A	60	74–75/23	n_D^{20} 1.4970 d^{20} 1.0139 IR	38, 100
$C_5H_5SiMe_2OSiMe_2Cl$	A	57	62–82/3–4	-	25
$C_5H_5SiMe_2(OSiMe_2)_2Cl$	A	40	62–100/1.5–2	-	25
$C_5H_5CH_2SiMe_2H$	A	41	39–40/11	n_D^{20} 1.4804	102
$C_5H_5CH_2SiMe_3$	A	16	40–43/6	n_D^{20} 1.4840	103
$C_5H_5CH_2SiMe_2OBu$	A	58	40/0.4	n_D^{20} 1.4539	102
$C_5H_5Si(OEt)_3$	A	-	94–95/2	-	104
$C_5H_5Si(O\text{- }n\text{-}Bu)_3$	A	-	103/0.4	-	104
$C_5H_5Si(Me)OEt_2$	E	86	40–45/0.8	n_D^{25} 1.4452	24
$C_5H_5Si(Me)_2OEt$	E	86	34–38/2.5	n_D^{25} 1.4564	24
ind-$SiMe_3$	A	55	87/4	$n_D^{25\ 5}$ 1.5404 NMR	61, 105
	A	55	87/4	n_D^{20} 1.5423 d^{20} 0.9450	74
2-ind-$SiMe_3$	B	43	72–74/0.8	n_D^{29} 1.5476 NMR	14
$C_9H_6(SiMe_3)_2$ [a]	A	17	106/3	n_D^{20} 1.5307 d^{20} 0.9300	74
	A	-	116/3.5	n_D^{25} 1.5284 NMR	14
$C_9H_6(SiMe_3)_2$ [b]	A	60	(68–69)	NMR	14
3-Me-ind-$SiMe_3$	A	53	76/1	n_D^{28} 1.5310 NMR	14
ind_2SiMe_2	A	24	155/4	n_D^{20} 1.6110 d^{20} 1.0600	74

[a] Mixture of 1, 1- and 1, 3-isomers. [b] 1,2-Isomer.

Compound	*Synthetic method*	*Yield (%)*	*B.p. (°C/mm)* *m.p. (°C)*	*Data*	*References*
ind-$SiEt_3$	A	49	121/3	n_D^{20} 1.5420 d^{20} 0.9500	74
$C_9H_6(SiEt_3)_2$	A	27	170/3	n_D^{20} 1.5335 d^{20} 0.9300	74
ind-$SiMe_2Ph$	A	78	112/0.2	NMR	14
ind-$SiMeCl_2$	A	74	92/3	d^{20} 1.2010	74
ind-$SiMe_2Cl$	A	64	92/3	n_D^{20} 1.5525 d^{20} 1.0760	74
$ind_2SiMeCl$	A	11	179/2	d^{20} 1.1310	74
ind-Si(O-n-Bu)Me_2	A	49	113/3	n_D^{20} 1.5165 d^{20} 0.9640	74
ind-Si$(O\text{-}n\text{-}Bu)_2$Me	A	54	130/1.5	n_D^{20} 1.5015 d^{20} 0.9760	74
fluor-$SiMe_3$	A	-	-	-	75
	A	60	(97.5)	-	27
	A	74	(96–97)	-	28
$fluor_2SiMe_2$	A	3	(178–179)	-	27
$(9\text{-}Brfluor)_2SiMe_2$	E	-	(220–230)	-	27
$C_{13}H_8(SiMe_3)_2$	E	17	(110)	-	27
	E	84	(109–110)	-	106
9-Me-fluor-Me_3	E	31	(118)	-	27
9-Br-fluor-Me_3	E	98	(134.5)	-	27
9-Cl-fluor-Me_3	E	27	(122)	-	27
2-Br-fluor-Me_3	E	23	(116.5)	-	27
2, 7-Br_2-fluor-Me_3	E	46	(149)	-	27
fluor-$SiEt_3$	E	60	167.5/1.2	n_D^{20} 1.5960	75

GERMANIUM

Compound	*Synthetic method*	*Yield (%)*	*B.p. (°C/mm)* *m.p. (°C)*	*Data*	*References*
$C_5H_5GeMe_3$	A	-	48/13.5	n_D^{28} 1.4805 NMR, IR	40
				^{13}C NMR	44
				Gas phase electron diffraction	107
	A	30	44/10.5	-	18
$MeC_5H_5GeMe_3$	A	-	58–59/10	n_D^{23} 1.5605 NMR, IR	40
$(C_5H_4)(GeMe_3)_2$	A	21	98/10.5	-	18
$Me_5C_5GeMe_3$	A	-	74/2.1	NMR, IR	40
$(C_5H_5)_2GeMe_2$	A	61	130/14	NMR	14
	B	31	71–73/4	n_D^{20} 1.5490 d^{20} 1.1629 IR, R	36

(continued on next page)

Compound	*Synthetic method*	*Yield (%)*	*B.p. (°C/mm) m.p. (°C)*	*Data*	*References*
$C_5H_5GeEt_3$	A	-	105/16	n_D^{20} 1.5029 d^{20} 1.0740	94
	B	67	59–60/4	n_D^{20} 1.5005 d^{20} 1.0773 IR, R	36
$C_5H_5GeMe_2Et$	B	23	31–32/4	n_D^{20} 1.4930 d^{20} 1.0931 IR, Raman	36
$C_5H_5Ge(n\text{-}Bu)_3$	A	-	109/0.4	n_D^{20} 1.4942 d^{20} 1.0115	94
$C_5H_5GePh_3$	A	-	(176–177)	-	86, 94
ind-$GeMe_3$	A	-	72/0.8	n_D^{23} 1.5605 NMR	61
ind-$GeEt_3$	A	-	161/4	n_D^{20} 1.5589 d^{20} 1.1230	94
ind-$GePh_3$	A	-	(126)	-	94
ind_2GePh_2	A	-	(144–145)	-	94
ind_4Ge	A	-	(196–198)	-	94
fluor-$GeMe_3$	A	73	147–150/2.2 (92)	-	75
fluor-$GeEt_3$	A	64	170/1	n_D^{20} 1.6060	75
	A	-	165/0.5	n_D^{20} 1.6071 d^{20} 1.1761	94
fluor-$GePh_3$	A	-	(214)	-	94

TIN

Compound	*Synthetic method*	*Yield (%)*	*B.p. (°C/mm) m.p. (°C)*	*Data*	*References*
$C_5H_5SnMe_3$	A	-	85/10	NMR	108
	A	-	54/2.9	n_D^{26} 1.5189 NMR, IR	40
	C	50	56–60/1	-	16, 17
				^{13}C NMR	44
$MeC_5H_4SnMe_3$	A	-	50/2.3	n_D^{22} 1.5283 NMR, IR	40
$Me_5C_5SnMe_3$	A	-	92/2	NMR, IR	40
$C_5H_4(SnMe_3)_2$	-	-	-	^{13}C NMR	44
$(C_5H_5)_2SnMe_2$	A	-	85/0.001	NMR	108
$(C_5H_5)_3SnMe$	A	-	115/0.001	NMR	108
$(C_5H_5)_4Sn$	A	53	(81–82)	NMR	41
	A	67	(76–77)	-	73
	A	-	-	NMR	108
$(MeC_5H_4)_4Sn$	B	42	(71–73)	-	13
	A	82	-	NMR	41
$C_5H_5SnEt_3$	A	-	65/0.001	NMR	108
	A	-	92–93.5/4	n_D^{30} 1.5192	73, 109

Compound	*Synthetic method*	*Yield (%)*	*B.p. (°C/mm)* *m.p. (°C)*	*Data*	*References*
$(C_5H_5)_2SnEt_2$	A	-	90/0.001	NMR	108
	A	58	121–123/2.5	n_D^{30} 1.5890	73
$C_5H_5Sn(n\text{-}Bu)_3$	A	-	90/0.001	NMR	108
	C	-	134/0.8	n_D^{20} 1.5047	17
$(C_5H_5)_2Sn(n\text{-}Bu)_2$	A	67	105/0.001	NMR	108
$(C_5H_5)_3Sn(n\text{-}Bu)$	A	-	150/0.001	NMR	108
$C_5H_5SnPh_3$	A	-	-	NMR	108
	A	-	(120)	-	110
	B	72	(130–131)	-	13
	B	-	(130–131)	-	111
	C	70	(129)	-	16, 17
$(C_5H_5)_2SnPh_2$	A	-	-	NMR	108
	A	-	(106)	-	109
	A	-	(290dec.)	-	110
	B	70	(105–106)	-	13
$(C_5H_5)_3SnPh$	A	-	-	NMR	108
	B	40	(64–65)	-	13
$(C_5H_5)_3SnCl$	-	-	-	-	23
$(C_5H_5)_3Sn(CH{=}CH_2)$	-	-	-	-	23
$(C_5H_5)SnCl_3$	-	-	-	-	23
$C_5H_5SnCl_2(CH{=}CH_2)$	-	-	-	-	23
ind-$SnMe_3$	A	-	64/0.15	n_D^{21} 1.5941 NMR	61
	A	-	-	NMR	105
	C	-	(129)	-	16
	C	53	74/0.01	-	18
3-Me-ind-$SnMe_3$	A	72	74.5–75/0.1	n_D^{28} 1.5817	14
1,2-Me_2-ind-$SnMe_3$	A	34	69/0.17	-	14
2-Br-ind-$SnMe_3$	A	-	95–97/0.1	-	14
ind-$SnEt_3$	A	30	100–102/0.15	n_D^{30} 1.5752	73
ind-$Sn(nBu)_3$	A	-	-	-	112, 113, 114
$ind_2Sn(nBu)_2$	-	-	-	-	20
ind-$SnPh_3$	A	-	(128–129)	-	72, 77
	B	46	(129–130)	-	13
	C	74	(129)	-	16, 17
ind_2SnPh_2	A	-	(116–117)	-	72
	B	30	(108–110)	-	13
ind-$Sn(Me)_2Ph$	A	-	107/0.06	n_D^{23} 1.6242 NMR	14
ind_4Sn	A	-	(215)	-	72, 77
fluor-$SnMe_3$	A	-	-	-	18, 75
fluor-$SnEt_3$	A	47	151/0.15	n_D^{20} 1.6229	75
fluor-$SnPh_3$	A	-	(129–130)	-	72, 77
	A	44	(126–130)	-	78
2-Me_2N-fluor-$SnPh_3$	A	-	(150–151)	-	72, 77
$fluor_2SnPh_2$	A	-	(179)	-	72
$fluor_3SnPh$	A	-	(262dec.)	-	72

(continued on next page)

Compound	*Synthetic method*	*Yield (%)*	*B.p. (°C/mm)* *m.p. (°C)*	*Data*	*References*
fluor-Sn (cyclopentyl)$_3$	A	44	(95–97)	-	78
fluor$_2$Sn(cyclopentyl)$_2$	A	57	(217–220)	-	78
fluor$_3$Sn(cyclopentyl)	A	83	(214–220)	-	78
fluor-Sn(cyclohexyl)$_3$	A	78	(133–136)	-	78
fluor$_2$Sn-(cyclohexyl)$_2$	A	76	(235–240)	-	78
fluor$_3$Sn-(cyclohexyl)	A	56	(247–249)	-	78
fluor-Sn(naphthyl)$_3$	A	49	(243–245)	-	78
fluor$_2$Sn(naphthyl)$_2$	A	80	(288–292dec.)	-	78
fluor$_3$Sn(naphthyl)	A	68	(291–293dec.)	-	78
fluor-Sn(Ph)$_2$Cl	A	-	(140–141)	-	72
fluor$_2$SnPhCl	A	-	(143)	-	72
(fluor)$_4$Sn	A	41	(310dec.)	-	72
	A	-	(210)	-	77
$(C_5H_5)_2Sn$	A	50	(104–105)	IR, UV	
				NMR	10, 11
				gas phase	28, 29
				electron diffraction	30, 31
$(MeC_5H_4)_2Sn$	A	-	-	IR, NMR	29
$(C_5H_4)(SnMe_3)_2$	C	90	80/3	-	19
$(C_5H_3)(SnMe_3)_3$	C	86	80/3	-	19
$(C_5H_2)[Sn(Me_3)]_4$	C	60	122/1 (60–61)	-	19

LEAD

Compound	*Synthetic method*	*Yield (%)*	*B.p. (°C/mm)* *m.p. (°C)*	*Data*	*References*
$C_5H_5PbMe_3$	A	-	-	NMR	18, 37
$MeC_5H_4PbMe_3$	A	-	-	NMR, IR	37
$(C_5H_5)_2PbMe_2$	A	-	-	NMR, IR	37
$(MeC_5H_4)_2PbMe_2$	A	-	-	NMR, IR	37
$C_5H_5PbEt_3$	A	-	-	NMR	37
$MeC_5H_4PbEt_3$	A	-	-	NMR, IR	37
$(C_5H_5)_2PbEt_2$	A	-	-	NMR, IR	37
$(MeC_5H_4)_2PbEt_2$	A	-	-	NMR, IR	37
ind-PbPh$_3$	A	75	(122)	-	26
ind$_2$PbPh$_2$	A	-	(107–110)	-	26
fluor-PbPh$_3$	A	75	(118–120)	-	26
fluor$_2$PbPh$_2$	A	30	(138–140)	-	26
fluor-Pb(Ph)$_2$Cl	E	-	(>160dec.)	-	26
$(C_5H_5)_2Pb$	A	25	(132–135)	IR, UV	
				NMR	10, 11
				Gas phase	28, 29
				electron diffraction	30, 31
$(MeC_5H_4)_2Pb$	A	-	-	IR, NMR	79

MIXED

Compound	*Synthetic method*	*Yield (%)*	*B.p. (°C/mm)* *m.p. (°C)*	*Data*	*References*
$C_5H_4(SiMe_3)(SnMe_3)$	C	60	45/0.02	-	18
		22	42/1.0	-	19
$C_5H_4[SiMe_2SiMe_3]SnMe_3$	C	58	90/0.1	-	18
$C_5H_4(CH_2SiMe_3)SnMe_3$	C	26	72/0.2	-	18
$Me_2Si(C_5H_4SnMe_3)_2$	C	-	-	-	18
$(Me_3Si)_2C_5H_3(SnMe_3)$	C	64	102/4	-	6
$(C_5H_3)SiMe_3(SnMe_3)_2$	C	80	84/3	-	19
$(C_5H_4)(GeMe_3)(SnMe_3)$	C	84	82/3	-	19
$(C_5H_3)(SiMe_3)(GeMe_3)(SnMe_3)$	C	77	68/1	-	19

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