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Intramolecular Coordination in Organic Derivatives of Non-transition Elements

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The problem of intramolecular coordination in organic derivatives of non-transition elements is surveyed and critically considered. Only those inner complexes (in an unreacting molecule or in the transition state)where the chain with the donor atom is linked to the element only via carbon atoms are considered. The data are treated systematically on the basis of the type of ligand. It is shown that intramolecular coordination is the driving force in various molecular rearrangements and many elimination reactions involving organic derivatives of the elements.
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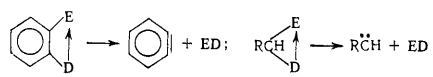
I. INTRODUCTION

Twenty years have elapsed since the synthesis of the first stable organic derivatives of the elements with intramolecular coordinate bonding in which the chain containing the donor atom is linked to the non-transition acceptor element only via carbon atoms. They have been called inner complex organic derivatives of the elements [1]. The comparatively sluggish development of this field can be explained both by the lack of clear-cut criteria concerning the understanding of the very concept of intramolecular coordination (IAMC) and by the defects of the current physical and physicochemical methods for the determination of the structure of matter and the consequent serious difficulties in the detection and demonstration of IAMC.

IAMC should be understood as a donor–acceptor interaction with charge transfer within the limits of a single molecule taking place through space, by-passing the conjugation chain, and involving the formation of a new single D–E bond in the limiting case (D is the electron-donating atom and E the non-transition acceptor element). Naturally one excludes from consideration a similar interaction between two adjacent atoms of the type of $d_{\pi}-p_{\pi}$ conjugation, for example in aminoboranes and silylamines, which might be regarded as a special case of IAMC resulting in only an increase of bond order.

The strength of IAMC in a non-reacting molecule is unknown, since no inner complex for which the conformational equilibrium constant has been determined has so far been described. Nevertheless most investigators suggest that intramolecular coordination interaction is energetically close to hydrogen bonding. The limits of its manifestation are fairly wide: from complete charge transfer, as, for example, in γ-aminopropyl compounds of boron, to closed structures in which IAMC occurs only in the transition state.

The available data on the properties of organic derivatives of the elements with IAMC were reviewed for the first time in 1970 [2]. Their importance for theory and practice in the chemistry of organic derivatives of the elements was already noted at the time. In subsequent years these compounds were successfully used in the synthesis of reactive and unstable species such as carbenes and arynes, the synthesis of which by other methods is in many instances impossible. Reactions of this kind, proceeding via IAMC, have been described by Nefedov et al. [3]:



In the present review we shall therefore not consider β-elimination in aromatic systems with formation of arynes and α-elimination in aliphatic systems with formation of carbenes.

The aim of the present review is to survey data on the physical and chemical properties of organic derivatives of non-transition elements with IAMC. We shall consider only compounds in which the chain containing the donor atom is linked to the acceptor element via carbon atoms, i.e. true organic derivatives of the elements with IAMC:



The data reviewed are arranged systematically on the basis of the type of ligand, which we believe to be most convenient for the detection of differences in the acceptor properties of elements, and are dealt with in order of decreasing electron-donating capacity of the ligand subgroups in the sequence $\geqslant$N $>$–O– $>$–Hal π-systems. This series is purely conventional and changes markedly as a function of the element and the reaction conditions for ligand atoms, belonging to different subgroups, linked to the same hydrocarbon groups. At the same time practice has shown that the ease of formation and the stabilities of many organic derivatives of the elements increase in this sequence. Each type of ligand is discussed in order of increasing size of the rings formed in IAMC, the elements being considered in order of their increasing valence within a Period and downwards within the limits of a single subgroup. The chemical consequences of IAMC are surveyed after coordination in non-reacting molecules has been examined.

Particular attention is devoted in this review to X-ray diffraction studies of compounds with IAMC, since the geometrical criterion—the distance between the donor and acceptor atoms—is one of the most clear-cut pieces of evidence for the presence or absence of coordination.

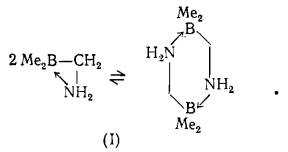
However, this criterion cannot be always justified experimentally owing to the lack of the exact values of the van der Waals radii of the elements in their organic compounds[4]. Furthermore, the radius depends on the hybridisation of the element and can therefore change. Naturally experimental accuracy is frequently the decisive factor and for this reason all studies where it is not indicated have been excluded from this review.

II. INNER COMPLEXES WITH NITROGEN-SUBGROUP LIGANDS

The synthesis of nitrogen-containing organic derivatives of the elements frequently presents considerable difficulties because of the electron-donating capacity of amine and nitrogen and its tendency to form intermolecular complexes. Their number and variety are therefore greatly inferior to similar derivatives of the oxygen and fluorine subgroups.

The presence of IAMC has a significant influence on the physical and spectroscopic properties of organic derivatives of the elements. It is very important to have at ones disposal consistent data obtained by different methods, since only then can one decide sufficiently unambiguously whether or not IAMC is present. This is also associated with the necessity to separate interfering factors such as intermolecular coordination (IRMC), crystal and field effects, solvation, inductive and resonance effects, etc.

Measurements of the molecular weight in the gas phase (13.8% of the dimer at 0°C and pure monomer at temperature exceeding 40°C up to 75°C) and the temperature variation of the ^{11}B NMR spectrum in the liquid phase (decrease of the degree of dimerisation from 84.3% at −25°C to 24.3% at 35°C with a heat of dimerisation of about 9 kcal mole^{-1}) have shown that aminomethylboron (I) is involved in a dimer–monomer equilibrium, the amount of monomer increasing with temperature[5]:

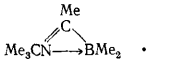


(I)

The study of the dissociation of complexes (I) with trimethylboron and ammonia has shown unambiguously that complex (I) is a weaker acid and a weaker Lewis base than the corresponding monofunctional derivatives. According to ^{11}B and ^{1}H NMR spectroscopic data, the electron density at the boron atom in complex (I) is enhanced compared with trialkylboron and the δ_{CH_2} signal is strongly displaced towards a lower field (by 0.24 p.p.m.; 0.20 p.p.m. in cyclopropane). The combined data quoted above provide serious grounds for the assumption that B ← N intramolecular coordination obtains in the monomeric state of compound (I).

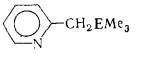
It is noteworthy that[6] dimethylaminomethylboron exists only in the dimeric form up to 170°C. The authors explain this difference from compound (I) by the greater electron-donating capacity of nitrogen in $RNMe_2$ compared with RNH_2, which is in turn manifested by a decrease of the acid properties of dimethylaminoboranes.

The three-membered inner complex obtained in a quantitative yield at room temperature when the product of the addition of trimethylboron to t-butyl isocyanide $Me_3CN{\equiv}C\bar{B}Me_3$ isomerises proved to be resistant to the action of oxygen and moisture[7]. The ^{1}H NMR spectrum of the complex was found to contain three signals of the CH_3 group with the line intensity ratios 1 : 2 : 3, while the infrared spectrum contains a band with $\nu(N{=}C) = 1548\ cm^{-1}$, but there is no band with $\nu(N{\equiv}C) = 2247\ cm^{-1}$. Furthermore, it has been established (by mass spectrometry) that the gas phase contains only the monomeric form of the complex. All these findings confirm the proposed structure[7]:

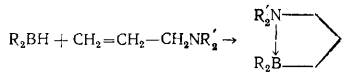


The steric factor is the decisive cause of the formation of the three-membered ring, since the reaction between less hindered isonitriles and boranes leads to the formation of dimeric products—2,5-dibora-2,5-dihydropyrazines[8].

The coordination capacity of the element E in the R_2ECH_2X system (X = Si, Ge, or Sn and X = N, O, S, or a halogen) is extremely low and only one complex, formed by trifluoromethyltrimethyltin with hexamethylphosphoramide[9], has been isolated and weak adduct formed by chloromethyltrimethyltin with dimethylformamide in solution has been described[10]. The latter complex was detected by Mössbauer spectroscopy, although in the organotin compound itself there is no Sn ← Cl intramolecular coordination, as can be seen from the nuclear quadrupole resonance (NQR) spectra[11], Mössbauer spectra[12], and dipole moments[13]. Furthermore, the basicity sequence of the amino-derivatives (Ge > Sn > Si) is consistent with the adopted electronegativity scale of the elements E [14] and there is therefore no coordination even in these compounds. For this reason, the claim[15,16] concerning the occurrence of IAMC in the above system (or the "α-effect") is invalid. According to infrared and ultraviolet spectra, IAMC is also absent from 2-substituted pyridines (E = Si, Ge, or Sn) [17]:

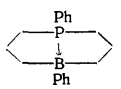


γ-Aminopropyl derivatives of Group III elements cyclise extremely readily to five-membered rings via E ← N intramolecular coordination; in most cases they are obtained by the addition of hydrides to allylamines[18–24]:



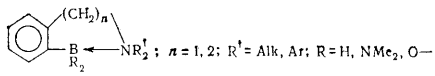
These complexes are relatively resistant to cold water[18], solutions of alkalis[24], disproportionation[22], peroxides[21], mercaptans[23], and heat[22]. Furthermore, they are stable in air and do not react with ammonia and phosphine[21]. In the gas phase, they exist as monomers[21]. The high dipole moments (4.0–4.2 D)[23], high refractions[21], infrared spectroscopic data [$\nu(B \leftarrow N) = 1266\ cm^{-1}$][19], ^{11}B and ^{1}H NMR data[19–21,24], and mass spectra[19,20,24] also indicate the occurrence of IAMC. When the hydrogen atom attached to nitrogen is replaced by alkyl groups or when an alkoxy-group is attached to a boron atom, the strength of the B ← N bond decreases appreciably and in the compound $(EtO)_2BCH_2CH_2CH_2NEt_2$ ($\mu = 1.44$ D) the bond probably does not exist at all[23].

The phosphorus analogue probably also exists in a cyclic form[25]:



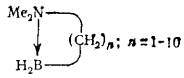
This is shown by its stability in air and on heating and by ^{11}B and ^{1}H NMR data.

Compounds of the type



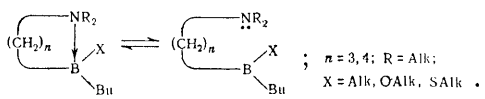
have also been described[26-28]. They too are relatively resistant to hydrolysis and, when R = H, do not react with olefins, which is characteristic of complexes with an intermolecular N → B bond[28].

It has been suggested[29] that all compounds of the type



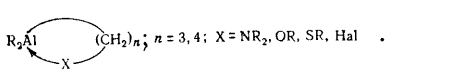
in general involve intramolecular coordination, since their dipole moments are approximately 4 D and the fragments $(M - 1)^+$, where M is the molecular weight, give rise to high intensities in the mass-spectra, this being characteristic of compounds having such a structure; the expected infrared and ^{1}H NMR spectroscopic properties have also been obtained.

A detailed study of compounds of this class by the ^{11}B and ^{1}H NMR methods showed that, both in the pure state and in solutions, they consist of an equilibrium mixture of cyclic and linear forms[30-32]:

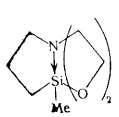


The breakdown and occurrence of intramolecular coordination take place at a rate exceeding 10^3 s^{-1}, which enabled the authors[30] to call these compounds a "pulsating" system. The equilibrium position depends on n, R, and X as well as temperature. With increase of temperature, the equilibrium is displaced towards the linear form (as shown by the temperature variation of the ^{11}B NMR spectra and the dipole moments). The equilibrium constants and heats of reaction were calculated from these results.

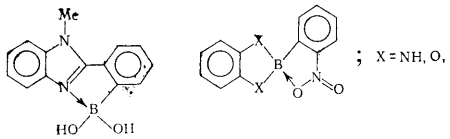
Similar aluminium compounds are also inner complexes[1,33-35], which are monomeric in hydrocarbons, distil *in vacuo* without decomposition, do not form adducts with ether (for X = OR), and do not form quaternary compounds with methyl iodide (for X = NR_2)[1]:



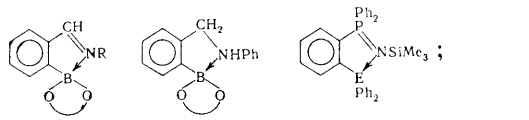
X-Ray diffraction analysis of methyl(2,2′,3-nitrilodiethoxypropyl)silane confirms the occurrence of IAMC in γ-aminopropyl compounds of non-transition elements even for a relatively poor acceptor such as the silicon atom (reliability index $R = 4.6\%$).[36] The molecule of this compound consists of a distorted trigonal bypyramid with the nitrogen atom and the methyl group at the vertices. The Si–N bond length (2.336 Å) is much smaller than the sum of the van der Waals radii (3.5 Å), but greatly exceeds the length of the covalent bond (1.74–1.78 Å). Steric factors decrease the CNSi angle from the tetrahedral value to 102°, which makes the N → Si linkage relatively long.



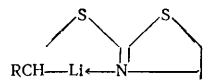
Inner-complex coordination has been put forward to account for the anomalous ultraviolet spectra of the compounds[37,38]



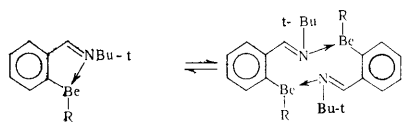
the infrared[39-41] and ^{1}H NMR spectra[40,41] of the compounds



and for the formation of the anomalous products of the reactions of lithiothiazoline[42]:

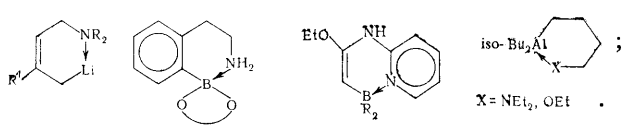


Such coordination is apparently the cause of the *ortho*-metallation of azomethines by dialkylberyllium[43]; in this case, when R = t-Bu, the degree of association of the reaction product in benzene is 1.55–1.65, which suggests the equilibrium

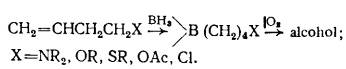


It is also responsible for the *ortho*-metallation of azobenzenes by mercury acetate[44]. These compounds are widely used in the chemistry of transition metals[45].

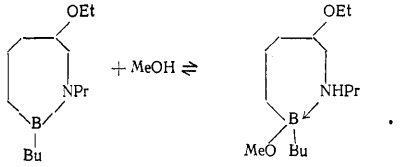
The formation of six-membered rings as a result of N → E intramolecular coordination takes place with much greater difficulty because of the appreciable angular ring strain. Such ring structures have been proposed for compounds of lithium[46] (on the basis of the stereoselectivity of the reaction products), boron [ν(N → B) = 1240 cm^{-1} [47] on the basis of infrared and ^{11}B NMR spectroscopic data[48,49]], and aluminium[34]; they are monomeric in benzene solution and thermally stable:



The instability of the coordinate bond in six- and even seven-membered rings is illustrated by the fact that stable products of the hydroboration of but-3-enyl derivatives containing functional substituents are readily oxidised to alcohols[50]:

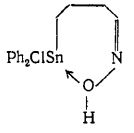


The rapid dissociation and formation of the N → B intramolecular coordinate bond in substituted 1,2-azaborepanes are reversible and depend both on the concentration of methanol in hexane solutions of the compound and on temperature, as shown[51] by the signal shifts in the ^{11}B NMR spectrum:



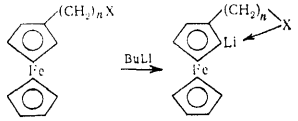
Similar aluminium compounds, iso-$Bu_2Al(CH_2)_5X$ (X = NEt_2 or OEt), contain associated species with intermolecular bonds together with seven-membered IAMC structures[34].

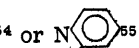
A seven-membered ring is probably formed in δ-stannyloximes, whose infrared spectra, both in the solid state and in solution, contain a ν(OH) = 3475 cm^{-1} band, and none due to the hydroxy-groups involved in hydrogen bonding are present. Furthermore, when treated with PCl_5, they undergo a Beckmann rearrangement with exchange of the hydroxy- and stannylpropyl groups, which should therefore be located in the *syn*-positions relative to one another:



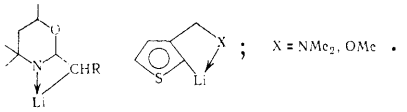
When chlorine attached to tin is replaced by a phenyl group, the compounds behave as the usual ketoximes and do not exhibit the above anomalies[52].

The *ortho*-metallation reactions of ferrocenes and benzenes, with substituents containing atoms having unshared electron pairs (X), and also of heterocycles with the aid of alkyl derivatives of lithium, sodium, and magnesium are of great practical importance from the synthetic standpoint. The high selectivity and high yields of the reaction products can probably be accounted for by the formation of a strong M ← X intermolecular coordinate bond in the initial stages with subsequent metallation in the *ortho*-position and stabilisation of the resulting complexes by an M ← X intramolecular coordinate bond. In most cases lithium alkyls are used as the metallating agents.

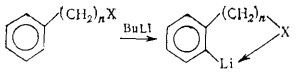


Direct metallation has been investigated in detail for the following amino-derivatives of ferrocene: $n = 1$, X = NMe_2,[53]  (m = 4 or 5),[54] or [55]; $n = 2$, X = NMe_2.[56] The reactions proceed much more readily than for unsubstituted ferrocene[53]. The evidence for coordination is provided indirectly by the condensation products. These reactions are described in greater detail elsewhere[57,58].

Dihydro-1,3-oxazines[59] and thiophens[60] are just as readily metallated[60]:



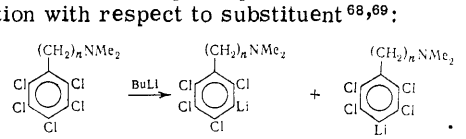
Aminobenzenes are metallated in the *ortho*-position much more slowly and under much more severe conditions than the ferrocene analogues in consequence of the reduced acidity of the protons:



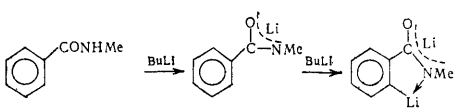
Substituted benzenes have been investigated: $n = 0$, X = NMe_2 [61,62]; $n = 1$, X = NMe_2 [63]; X = AsR_2 [64]; $n = 2$, X = NMe_2.[65,66]

The presence of the N → Li intramolecular coordinate bond in such compounds is confirmed by the infrared spectroscopic study[67] of the ^6Li- and ^7Li-labelled benzene complexes ($n = 1$, X = NMe_2) in addition to the isolation of *ortho*-substituted reaction products. The ν(C – Li) = 355 cm^{-1} and ν(N → Li) = 494 cm^{-1} bands in the spectrum of the compound with ^7Li were displaced to 370 and 500 cm^{-1} respectively following the introduction of ^6Li. This isotopic shift is characteristic of the N → Li intermolecular coordinate bond and the Li–C bond in ordinary lithium alkyls. Cryoscopic determination of the molecular weight in DMSO showed that at minimal concentrations the degree of association of these complexes is less than 1 but at high concentrations it exceeds 4. An N → Li intermolecular bond is probably formed in the compounds together with the intramolecular coordinate bond. The coordination is confirmed also by the ready removal of DMSO, a powerful solvating solvent, at room temperature *in vacuo*, while ordinary lithium alkyls form stable complexes under these conditions even with ether.

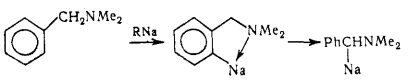
The sharp decrease of the Lewis basicity of the amino-group in *NN*-dimethylamino(alkyl)perchlorobenzenes as a result of the strong electronegativity of the perchlorophenyl group and the impossibility of the formation of an intermolecular coordinate bond with butyl-lithium (particularly in the presence of solvating solvents) lead to their metallation only in the *meta*- and *para*-positions and not the *ortho*-position with respect to substituent[68,69]:



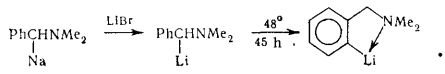
Secondary amines[70], amides[71], and sulphonamides[72] are metallated initially at the nitrogen and only then in the *ortho*-position (in the presence of an excess butyl-lithium), for example:



Sodium alkyls metallate *NN*-dimethylbenzylamine in the *ortho*-position with subsequent spontaneous isomerisation to the derivative with the metal in the α-position with respect to the amino-group[73]:

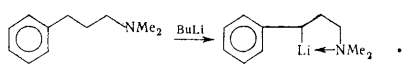


When sodium in the last compound is replaced by lithium, the *ortho*-metallated product can be reformed after prolonged heat treatment, although at room temperature the α-lithio-compound is stable:

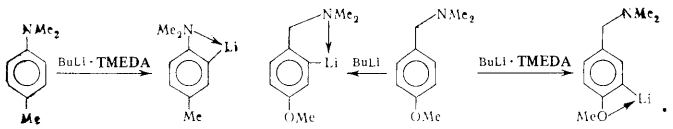


The reasons for these isomerisations are obscure.

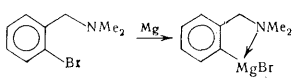
The metallation of *NN*-dimethyl-3-phenylpropylamine proceeds in the chain with formation of a five-membered ring [74]:



One should note that *ortho*-metallation by butyl-lithium proceeds comparatively slowly (11–21 h), but is sharply accelerated (1–2 h) when its complex with tetramethylethylenediamine (TMEDA) is used [75]. On the other hand, the lithium atom in the complex BuLi.TMEDA lacks electron-accepting properties and cannot therefore be involved in an intermolecular coordinate bond with the nitrogen atom of the amino-derivatives of benzene, ferrocene, and heterocycles, which is the main cause of the metallation of the 2-position, and not of the more acidic methylprotons in *NN*-dimethyl-*p*-toluidine [75], and of the *ortho*-position relative to the methoxy-group in *p*-methoxy-*NN*-dimethylbenzylamine. [76] In these compounds the *ortho*- and *para*-directing effects of the dimethylamino- and methoxy-groups exceed respectively those of the methyl and dimethylaminomethyl groups:

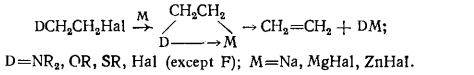


Grignard reagents are also formed very readily (in quantitative yields) from 2-bromobenzyl-*NN*-dimethylamine, while the 3- and 4-bromo-derivatives do not react under analogous conditions [77]:



The chemical manifestations of intramolecular coordination are extremely varied and frequently involve "anomalous" elimination reactions and rearrangements, which do not occur with related compounds where coordination is known to be absent. Furthermore, the metal–carbon σ-bond is polarised under the influence of coordination and therefore becomes more reactive. Such processes are particularly frequent in aliphatic systems.

When alkyl halides containing a heteroatom in the β-position are acted upon by reactive metals, extremely unstable organometallic compounds are formed and decompose at the instant of formation as a result of easy β-elimination [78,79]:

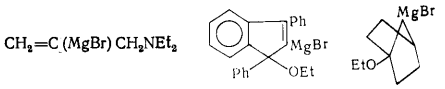


D=NR_2, OR, SR, Hal (except F); M=Na, MgHal, ZnHal.

The reason for the instability of such compounds is probably a D → M intramolecular coordinate bond, although this has not been specially investigated.

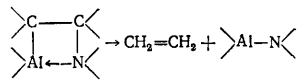
Numerous studies have shown that β-elimination in Grignard reagents cannot be prevented either by very low temperatures or by the protection of functional groups [79].

There are only a few instances of the successful formation of Grignard reagents of this type where either the activation energy for the formation of allenes is unduly high [80,81] or the elimination reaction is forbidden by Bredt's rule [82]:

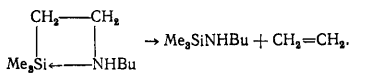


Halogenoamines $R_2N(CH_2)_nHal$ form organomagnesium compounds in THF with $n \geqslant 3$. [79,83]

The β-aminoethyl derivatives of aluminium, which begin to decompose with formation of ethylene already during their formation when vinylamines add to aluminium hydrides (at 20–60°C), are also unstable [84]:

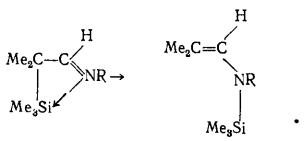


The similar silicon compounds are much more stable, and silanes with tertiary amino-groups are not decomposed on prolonged heat treatment up to 300°C, while those with secondary amino-groups eliminate ethylene at this temperature with a 30% yield [85]:



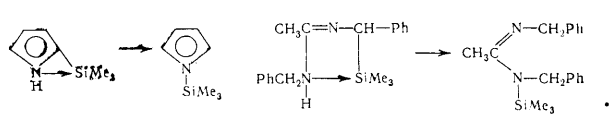
Quaternary salts decompose in the same way, but silylamines with alkoxy-groups at the silicon atom are stable.

Organosilicon derivatives of aldimines rearrange very slowly at room temperature to the corresponding *N*-derivatives [86]:

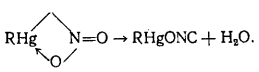


The isomerisation is sharply accelerated in the presence of 10 mole % of trimethylsilyl bromide and depends markedly on steric factors; for example, with R = t-Bu or iso-Pr there is no isomerisation. It is very probable that the non-catalysed rearrangement takes place intramolecularly, by analogy with the keto–enol isomerisation (see Section III).

Diatropic rearrangements with exchange of the trimethylsilyl group for hydrogen in 2-trimethylsilylpyrrole at room temperature [87] and in silylacetamidines at 95–200°C [88] apparently take place in the same way, although their mechanism has not been investigated (these rearrangements are considered in greater detail in Section III):



Kashutina and Okhlobystin [89] suggest that this is why α-nitromethyl derivatives of mercury decompose at the instant of formation to fulminate and water:



It is interesting to note that trinitromethyl compounds of mercury are fairly stable and it is believed[89] that the possibility of dehydration is a necessary condition for the rearrangement.

III. COMPLEXES WITH OXYGEN-SUBGROUP LIGANDS

1. Aldehydes and Ketones

The carbonyl group in α-carbonyl organic derivatives of the elements has "anomalous" spectroscopic properties compared with carbon analogues—its absorption in the infrared and ultraviolet spectra is displaced towards longer wavelengths and the band intensities are greatly enhanced. These findings have been explained by σ,π conjugation[90]. However, the even greater shift of the ν(CO) wavenumber (to 1645 cm^{-1}), while ν(CH) retains its normal value in the $RHgCH_2CHO$ ($R = Cl$ or CH_2CHO) spectra would be difficult to understand in terms of conjugation, which led to the hypothesis[91] that both intramolecular and intermolecular CO → Hg coordinate bonds are formed in these compounds. The IAMC hypothesis, leading to a decrease of the positive charge on the metal, was put forward to explain the low rate constant for the electrochemical reduction of α-carbonyl derivatives of mercury[92]:



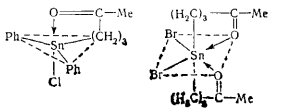
Attempts have been made in a number of studies to determine the main effect responsible for these anomalies. The increase of the intensity of the $n \rightarrow \pi^*$ transition band by a factor of 4–5 in the spectra of α-silylketones compared with the carbon analogues confirmed, according to Musker and Ashby[93], the presence of a CO → Si intramolecular coordinate bond and could not be explained by steric and inductive effects. However, the exaltation of the $n \rightarrow \pi^*$ transition is observed in many other ketones and may be due to factors which do not affect the absorption by the carbonyl group. The significant difference between the observed and calculated wavenumbers of the carbonyl group in the spectra of α-silylketones and their carbon analogues cannot serve as proof of a greater contribution by IAMC compared with the inductive effect of the trialkylsilyl group, since no account was taken in the calculations of the influence of the field and other factors which may be more important than the inductive effects[94]. Furthermore, it follows from the infrared spectra of α-silylketones in the gas phase [the bathochromic shift of ν(CO)][95] that there is no intermolecular coordination in these compounds.

There are probably concerted effects of the CO → Si intramolecular coordinate bond and the inductive effect of the R_2Si-group in α-silylketones, since the ν(CO) band in the spectrum of α-triphenylsilylcyclohexanone is split in carbon tetrachloride into two components, the intensities of which vary with temperature, but the splitting itself is independent of concentration and can therefore be accounted for by a conformational equilibrium[94]. Intramolecular coordination probably obtains also in α-stannylketones, since an appreciable quadrupole splitting (Δ) is observed in their Mössbauer spectra and furthermore such interaction is not inconsistent with mass-spectrometric data[10].

Coordination of this kind is absent from β- and γ-stannylketones[10,96] but becomes appreciable when the hydrocarbon groups at the tin atom in these compounds are replaced by powerful electronegative groups—halogens (see Table)[96].

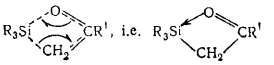
The values of ν(CO) permit the existence of an Sn ← OC intramolecular coordinate bond in compounds (III), (IV), and (VII) but not in (II) and (V), since the tin atom in compounds of the latter type does not usually exhibit coordinating properties.

When complexes (IV), (VI), and (VII) with bipyridyl are formed, the intramolecular coordinate bond is ruptured and the ν(CO) wavenumbers become characteristic of the free carbonyl group. The occurrence of intramolecular coordination is confirmed also by the analysis of the chemical shifts of the protons in the methylene group linked to the carbonyl group. The signals of compounds (II) and (V) are located in the region of $\tau = 7.55$ p.p.m. The replacement of the phenyl group by a halogen in these compounds causes their downfield shift in consequence of the appearance of IAMC, which reduces magnetic shielding. On the other hand, in the bipyridyl complexes (IV), (VI), and (VII) the carbonyl group is liberated and the proton signals again appear in the region of $\tau = 7.55$ p.p.m. There is no intermolecular coordination in these compounds, since compounds (III) and (VII) are monomeric in benzene. There is no splitting Δ in the Mössbauer spectra of compounds (II) and (V), which is as a rule a characteristic feature of tetracoordinate organotin compounds, but it is appreciable in the spectra of compounds (III) and (VII). The magnitude and sign of Δ suggest the following structure of these compounds:



The occurrence of intramolecular or intermolecular coordination in non-reacting organic derivatives of the elements with α-carbonyl groups should facilitate the possible elementotropic rearrangements, since such interaction lowers the activation energy for the transition complex. Indeed α-silylketones rearrange to the isomeric siloxyalkenes on heating to 160–180°C for 2–3 h [97] or on standing in the presence of catalytic amounts of mercury and zinc salts and halogenosilanes[98]: $R_3SiCH_2COR' \rightarrow R_3SiOC(R') = CH_2$, where R and R' = alkyl or aryl.

The thermal rearrangement is a process common to these compounds and takes place intramolecularly via a four-membered transition state[97]:



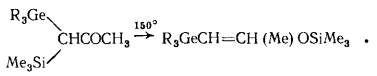
This is proved by the following findings: (a) the retention of configuration in the thermolysis of the optically active ketone (+)-α-(methylphenyl-1-naphthylsilyl)benzophenone [97]; (b) the absence of intermolecular interaction products in the thermolysis of a mixture of α-trimethylsilylacetophenone and triethylsilylacetone [98]; (c) the first order of the reaction[97]. The activation energy for the rearrangement is 26–33 kcal $mole^{-1}$ depending on R and R'.[99] On the other hand, catalytic isomerisation is an intermolecular process[98].

Silylmethyl sulphoxides, which are heteroanalogues of α-silylketones, undergo a remarkable rearrangement[100]:

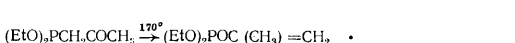
$$Me_3SiCH_2\underset{\underset{O}{\|}}{S}R \xrightarrow{60^\circ} Me_2SiOCH_2SR.$$

Its mechanism is obscure. The germanium analogue does not isomerise under these conditions and the phosphorus analogue $Me_3SiCH_2P(O)Ph_2$ is stable even at 180°C.

$\alpha\alpha$-Dimetallated ketones also isomerise on heating. Thus germyl silyl ketones are converted into C-silylated germyl-substituted enols[101] at a higher rate than α-monosilylketones:



A phosphonate ester rearranges similarly (to the extent of 50% in the presence of 2% orthophosphoric acid and to the extent of only 1% in the absence of a catalyst)[102]:



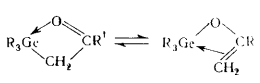
It is believed that the rearrangement proceeds intramolecularly, since it is unaffected by the addition of 2-butanone.

Spectroscopic properties of γ-stannylketones.[96]

Compound	ν(CO), cm^{-1} (in liq. paraffin)	τCH$_2$CO, p.p.m. (in CDCl$_3$)	δ for SnO$_2$, mm s^{-1}	Δ, mm s^{-1}
(II) $Ph_3Sn(CH_2)_3COMe$	1705	7.55	1.73	0
(III) $Ph_2ClSn(CH_2)_3COMe$	1669	7.46	1.38	−3.30
(IV) $PhCl_2Sn(CH_2)_3COMe$	1670	7.30	—	—
$PhCl_2Sn(CH_2)_3COMe$·bipy *	1710	7.55	—	—
(V) $Ph_2Sn[(CH_2)_3COMe]_2$	1709	7.55	1.41	0
(VI) $Cl_2Sn[(CH_2)_3COMe]_2$	1680	7.23	—	—
$Cl_2Sn[(CH_2)_3COMe]_2$·bipy	1705	7.42	—	—
(VII) $Br_2Sn[(CH_2)_3COMe]_2$	1675	7.27	1.66	+3.83
$Br_2Sn[(CH_2)_3COMe]_2$·bipy	1703	7.55	1.56	+3.80

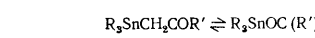
*bipy = 2,2′-bipyridyl.

True elementotropic tautomerism occurs in the case of α-germylketones[103], the equilibrium position depending strongly on temperature, an increase of which increases the content of the O-isomer. The equilibrium between the isomers is established slowly (in about one month)[104] at room temperature and much faster following the addition of bromogermanes. Presumably this reversible rearrangement proceeds via a coordination complex:

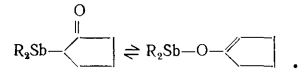


The contents of the C- and O-isomers depend strongly on the substituent linked to the keto-group. Thus, at 20°C and with R = CH_3, the equilibrium mixture contains 3% of the O-isomer for R′ = CH_3 [105] and 33.7% for R′ = p-ClC_6H_4.[106] The germanotropic equilibrium constant is satisfactorily correlated with Hammett's σ constant (ρ = 1.67). Consequently electron-donating substituents in the aromatic ring decrease and electron-accepting substituents increase the concentration of the O-isomer in the equilibrium mixture, which occurs in prototropic keto–enol systems, but in a series of organic derivatives of the elements, this influence is much stronger. The thermodynamic parameters of the isomerisation reaction have been calculated from the temperature variation of the equilibrium constants; for example ΔH = 2.64 ± 0.05 kcal mole^{-1} and ΔS = 2.1 ± 0.1 kcal mole^{-1} K^{-1} for R = R′ = CH_3.[106] Fractionation of the mixture of isomers can displace the equilibrium almost completely towards the more volatile O-isomer.

Stannylmethyl ketones and the corresponding O-stannylenols undergo interconversions at much higher rates than their germanium analogues. The rearrangement is also reversible but proceeds intermolecularly[105,107] and is greatly accelerated following the addition of trialkyltin halides (the average lifetime of the isomers is 10^{-1}–10^{-3} s). Depending on the substituents R and R′, the equilibrium mixture may contain 6–23% of the O-isomers, the amount of which is frequently independent of temperature.

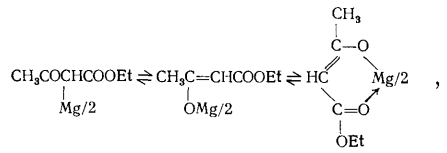


In the series of similar antimony compounds, the rate of equilibration depends on the structure of the ketone. In the antimony derivatives of cyclohexanone, the rate is approximately the same as for stannylmethyl ketones, while the cyclopentanone compound of antimony isomerises much more slowly. With increase of temperature, the content of the O-isomer in the equilibrium mixture rises: for example from 20% at 20°C to 30% at 113°C for the latter compound[108]:

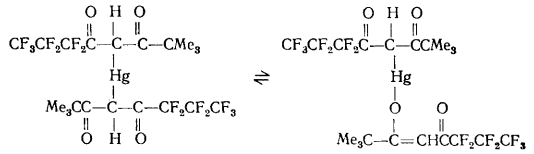


The mechanism of this rearrangement is unknown.

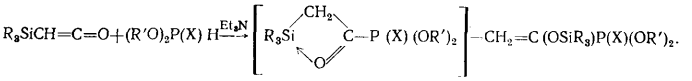
Keto–enol tautomerism probably occurs in the magnesium derivatives of acetoacetic ester, the infrared spectra of which depend markedly on the solvent and concentration[109]:



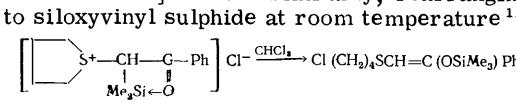
and also in the mercury derivatives of β-diketones (two different constants $J_{^1H-C-^{199}Hg}$ have been obtained in acetone at −75°C, namely 257 and 273 Hz):[110]



It is believed that the interaction of trialkylsilylketens with trialkyl phosphites and phosphorothioites (X = O or S) proceeds via intermediate ketophosphinate esters, which then isomerise intramolecularly to the corresponding siloxyvinyl compounds with 70–85% yields[111]:

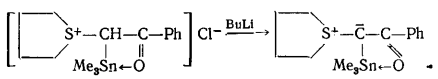


Silylmethylsulphonium chloride [ν(CO) = 1675 cm^{-1} in carbon tetrachloride] behaves similarly, rearranging slowly to siloxyvinyl sulphide at room temperature[112]:

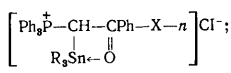


The tin analogue is stable, but the marked decrease of ν(CO) (to 1524 and 1487 cm^{-1} in KBr) suggests the existence of an Sn ← OC〈 intramolecular coordinate linkage in this compound. When it is acted upon by butyl-lithium

in THF, butane is evolved: the former coordination is probably regained in the resulting ylid [ν(CO) = 1528 cm^{-1}][112]:

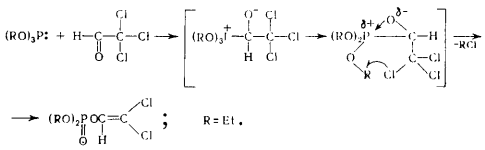


The same type of interaction has been suggested also for phosphoranes [ν(CO) = 1470–1495 cm^{-1} in KBr]. Furthermore, these compounds are resistant to hydrolysis and methanolysis and are not quaternised by methyl iodide[113].

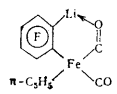


X=H, Me, OMe, Cl, Br.

A remarkable example of the influence of the possible intramolecular coordination on reactivity is the Perkow reaction—the interaction of triethyl phosphite with chloral to form $\beta\beta$-dichlorovinyl diethyl phosphate. According to one of the proposed mechanisms, the reaction proceeds via phosphonium salts[114]:

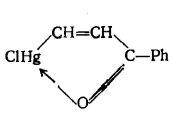


Intramolecular coordination is the cause of the unusually high stability of complex (VIII)[115]:



ortho-Fluorolithio-derivatives of aromatic compounds are known to be thermally unstable and to form arynes readily[3]. However the corresponding aryne has not been observed (the Diels–Alder reaction with furan leads to the *ortho*-hydrotetrafluorophenyl derivative in quantitative yield) for compound (VIII) (containing an iron atom in the *ortho*-position), while the *meta*- and *para*-isomers give rise to the normal addition products. A similar difference has been observed also between the exchange reactions involving (π-C_5H_5)$(CO)_2$FeI. The coordination in this compound breaks down following the addition of D_2O (the *o*-deutero-isomer has been isolated quantitatively).

The higher stability of *cis*-β-oxovinylmercury halides compared with the *trans*-analogues has been explained similarly[116]. X-Ray diffraction analysis of *cis*-β-benzoylvinylmercury chloride demonstrated a cisoid conformation of the molecule in which the oxygen atom is directed towards the mercury atom (R = 13.6%; $l_{Hg...O}$ = 2.88 Å). The Hg...O distance and the sum of the van der Waals radii (2.9–3.1 Å) are within the limits of experimental accuracy. However, the decrease of the ClHgC angle, located opposite the oxygen atom, to 173° ± 2° and the conformation of the molecule suggest the following coordination[117]:



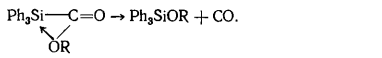
2. Acids and Their Derivatives

Silylacetic acids rearrange to the isomeric acyloxysilanes at the melting point and also under very mild conditions, frequently at 25°C, in the presence of basic catalysts, for example triethylamine[118]:

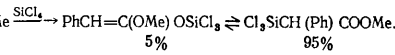


The thermal isomerisation proceeds intermolecularly while the catalytic isomerisation can be both intermolecular and intramolecular. However, in highly dilute solutions, where the extent of bimolecular reactions is reduced to a minimum, only the intramolecular pathway operates, since optically active vinylacetic acids are converted into the corresponding acetoxysilanes with retention of configuration at the silicon atom[119].

Silyl derivatives of carboxylic acids and their esters are readily decarboxylated at 150–230°C via an intramolecular mechanism, which has been demonstrated by kinetic data and also by the finding that the thermolysis of a mixture of the esters does not lead to intermolecular interaction products[99]:

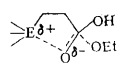


The ester of stannylated phenylacetic acid reacts with $SiCl_4$ to form a keten acetal, which readily isomerises in 2–3 days at room temperature to the carbon derivative until the attainment of equilibrium[120]:



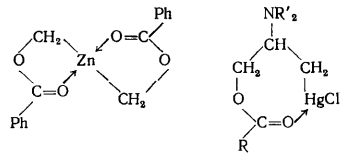
This is the first instance of silylotropism. Distillation of the equilibrium mixture leads to a slight shift of equilibrium towards the *O*-isomer, but the initial equilibrium position is restored after the period stated above.

The esters $Et_3E(CH_2)_2COOEt$ (E = Si, Ge, or Sn) hydrolyse much faster than ethyl butyrate or $Et_3E(CH_2)_3$. .COOEt, which cannot be accounted for solely by the inductive effect of the Et_3E groups. It is believed[121] that the higher rate of hydrolysis can be explained by the formation of intermediate complexes:



Such stabilisation of the transition state is absent for $Et_3Sn(CH_2)_3COOEt$, since five-membered rings are frequently formed at a higher rate than six-membered rings.

In view of the reduced values of ν(CO), intramolecular coordination has been suggested for bis(benzoyloxymethyl)-zinc [ν(CO) = 1645 cm^{-1}][122] and carboxypropyl derivatives of mercury [ν(CO) = 1680–1710 cm^{-1}][123]:



and also in compounds of the type $Me_nX_mSn(CH_2)_2COOMe$ (n = 1 or 2; m = 1 or 2; X = Cl or Br) [ν(CO) = 1656 to 1680 cm^{-1} in KBr][124], the τMeO signal in the ^{1}H NMR spectra of which undergoes a downfield shift. It is suggested that a trigonal bypyramidal structure occurs in these compounds, one of its vertices being occupied by the acetoxy-group[124].

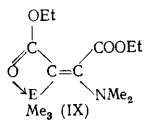
It is noteworthy that intramolecular coordination occurs in R_3SnCH_2COOMe but not in R_3SnCH_2OCOMe (according to Mössbauer spectra) [95], which is probably associated with the greater inductive effect of the methoxycarbonyl group compared with the acetoxy-group.

Internal coordination has been suggested also for diazoesters:

$$R_{4-n}Sn\,[C(N_2)COOEt]_n \text{ (where } n=1,2) \text{ and } YC(N_2)COOEt\,,$$

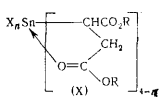
where Y = Me_3Si, Me_3Ge, Me_3Pb, or RHg, in view of the high dipole moment μ = 2.2 D (for n = 1 and R = Me), the monomeric state of the compounds in benzene (for tin compounds), and the appreciably reduced values of ν(CO) (1640–1675 cm^{-1}) and ν(N≡N) (2045–2070 cm^{-1}) compared with the carbon analogues [125]. The coordination in diazoesters is probably stronger than in α-ketones and α-carboxyesters, since the shift of ν(CO) in the latter compounds is smaller.

The occurrence of intramolecular coordination is the cause of the splitting of the ν(CO) bands (1735 and 1680 cm^{-1} for E = Si, 1739 and 1698 cm^{-1} for E = Ge, and 1740 and 1705 cm^{-1} for E = Sn) and ν(C=C) bands (1570 and 1550 cm^{-1} for E = Si, 1590 and 1555 cm^{-1} for E = Ge, and 1625 and 1590 cm^{-1} for E = Sn) in the infrared spectra of compounds of type (IX) [126] (see also Riviera-Boudet and Satge [127]):



(IX)

The difference between the coordinated and covalently linked carbonyl groups is manifested particularly clearly in organotin diethoxycarbonylethyl derivatives (X),



(X)

X = Hal; n = 2, 3

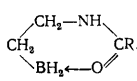
the spectra of which contain ν(CO) bands in the ranges 1634–1660 and 1692–1718 cm^{-1}. [128,129] A trigonal bipyramid with the ethoxycarbonyl group at one of the vertices has been proposed for n = 3. [129] Two isomers have been isolated for n = 2 and X = Br and their crystal structures have been determined [130,131]. They both (R = 9.8 and 16.7%) have distorted octahedral structures. The two bromine atoms are in the *cis*-positions and the 1,2-di(ethoxycarbonyl)ethyl groups are linked to the tin atom via oxygen and carbon atoms with formation of five-membered rings. The Sn–O bond length (2.44–2.49 Å) greatly exceeds the sum of the covalent radii (2.06 Å) and the Sn ← OC coordination is therefore fairly weak.

In consequence of amide conjugation, the organic acid amide derivatives of the elements are much more labile than the corresponding α-ketones and α-acids and therefore rearrange under more severe conditions [132–134]; secondary amides rearrange to the *N*-isomers, while acylated *N*-alkylamides rearrange to the *O*-isomers. These isomerisations probably also proceed via an intramolecular mechanism:

$$R_3ECH_2CONHR' \xrightarrow{140-200^\circ} R_3EN(R')COCH_3;\ E=Si,\ Ge,$$

$$Et_3SiCH_2CON(Me)COR \xrightarrow{160-180^\circ} Et_3SiOC[N(Me)COR]=CH_2.$$

It is believed that intermediates with intramolecular coordination of the type

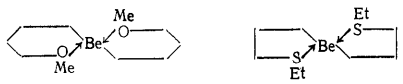


are formed in the hydroboration of *N*-alkenylureas and *N*-alkenylcarbamates, which reduces the reactivity of H_2B groups, prevents further hydroboration, and after hydrolysis leads to high yields of the corresponding alkylboronic acids, while in the case of terminal olefins trialkylboron compounds are formed exclusively [135].

3. Alcohols and Ethers

Alcohol and ether derivatives of the elements frequently exhibit reduced thermal stability as a result of O → E intermolecular coordination and evolve comparatively readily ethylene and cyclopropane (CP) or their derivatives, particularly in those cases where the functional group is in the β- and γ-positions with respect to the element. Such ready β- and γ-elimination is undoubtedly associated with the higher strength (energy) of E–O bonds compared with E–C bonds. In some cases such compounds could be isolated under mild conditions.

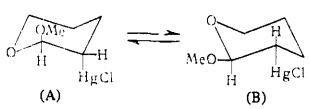
The stability of di-(δ-methoxybutyl)- and di-(γ-ethylthiopropyl)-beryllium on distillation in a high vacuum suggested that these compounds exist as inner-complex salts [136]:



In solutions *cis*-β-mercurated alicyclic alcohols are probably also involved in intramolecular coordination, since the OH absorption band in the infrared spectra is displaced towards longer wavelengths by 18–22 cm^{-1} compared with the carbon analogues [137], while the shift for the *trans*-isomers is only 6–10 cm^{-1}. However, it is not altogether clear whether this approach can be used for open-chain compounds or compounds with conformationally mobile rings. The study of the conformation equilibria of the mercury derivatives of tetrahydropyran in acetonitrile,

$$(A) \rightleftharpoons (B)$$

showed that the strength of the coordinate bond in these compounds is low [138]. It has been found from ^1H NMR spectra that the equilibrium mixture contains at least 56% of conformation (B) (ΔG = −0.14 kcal $mole^{-1}$):



(A) (B)

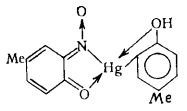
Since ΔG for HgX groups is equal or close to zero, intramolecular coordination stabilises conformation (B) with an energy of about 1 kcal $mole^{-1}$. It has been suggested [138] that the intramolecular stabilisation of unstable conformations is common to all compounds with substituents between which appreciable coordination interaction is possible.

This conclusion was confirmed in a study of the dipole moments of β-substituted mercury compounds of the type $HalHgCH_2CH_2X$ [Hal = Cl, Br, or I; X = OMe, OCOMe, CF_3, or $C(NO_2)_3$]. [139] In the series of these compounds, intramolecular coordination occurs in benzene only for X = OMe or OCOMe and in the former case is so weak that it breaks down following the addition of ethyl acetate. The capacity for intramolecular coordination decreases in

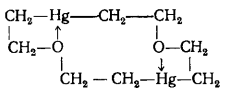
the following sequence of substituents X: MeOCO > MeO ≫ CF_3 > $C(NO_2)_3$. For the last two substituents, this conclusion had been made earlier on the grounds that, when these compounds are acted upon by nucleophiles, ethylene is not evolved owing to the absence of electron-donating groups capable of coordination, while the presence in the β-position of substituents with an unshared electron pair (OR, OCOR, and NR_2) leads under the same conditions to complete β-elimination. Furthermore, when X = CF_3, the constant $^{J}(CF_3...Hg)$ for the ^{19}F NMR spectrum in carbon tetrachloride is extremely low [140, 141].

However, in the crystalline state there is no intramolecular coordination at all in the mercury compounds, which has been shown convincingly by X-ray diffraction. Thus the mutual orientation of the substituents relative to the cyclohexane ring in the α(*dd*, *ll*) and β(*dl*, *dl*) diastereoisomers of 2-methoxycyclohexylmercury chloride proved to be different, the intramolecular Hg...O distances in the α-isomer (4.06 Å) and in the β-isomer (3.06 Å) virtually ruling out intramolecular coordination [142].

The Hg...O distance in the 2-hydroxy-5-methylphenylmercury derivative of 5-methylnitrosophenol is 3.00 Å, the C–N and N–O linkages are close to double bonds, and the mercury atom is joined covalently to the carbon atoms of the phenolic ring and the nitrogen atom of benzoquinone (R = 11%). [143] However, in this case the very weak Hg ← O interaction is largely determined by the rigidity of the molecular geometry:

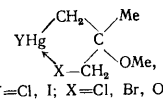


Hg ← N intermolecular coordination (2.77 Å) with almost planar conformation of the –Hg–C–C–N group (R = 5.6%) obtains even in *N*-[2-(chloromercuri)ethyl]-diethylamine [144]. An exception is the dimeric molecule of ββ′-oxidodiethylmercury [145]:



Here intramolecular coordination leads to the formation of a tricyclic structure (l_{HgO} = 2.21 ± 0.06 Å). However, following a slight decrease of the CHgC angle (to 176°), the hybrisation of the mercury atom remains virtually unchanged, which indicates a low accuracy of the above investigation.

When organomercury compounds contain an atom with a free electron pair in both β- and γ-positions, intramolecular coordination occurs with formation of a five-membered ring in consequence of smaller angular strain. This is the cause of the non-equivalence of the methylene protons in the ^1H NMR spectra of compound (XI):

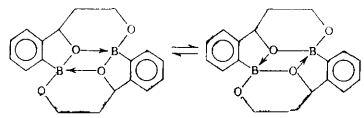


Y=Cl, I; X=Cl, Br, OH.

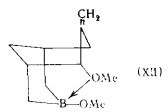
(XI)

[Y = Cl; X = Cl or Br; $\Delta\nu(CH_2Br)$ = 19.1 Hz; $\Delta\nu(CH_2Hg)$ = 13.6 Hz]; the non-equivalence diminishes sharply in the presence of solvents which break the coordinate bond, for example pyridine, and this leads in its turn to a decrease of J_{HgCCCH_3} (it amounts to 36 Hz in $CDCl_3$ and 20 Hz in pyridine) [146]. When Y = I and X = OH, a temperature variation of J_{HCOH} is observed in $CDCl_3$ and ν(OH) in the infrared spectrum falls to 3584 cm^{-1}. [147] The non-equivalence of the methylene protons in compounds of the type $BrHgCH_2CR(OR')COX$ (R = Me, Ph, **O**Bu-t, or Me and X = Me or OMe) is even more pronounced [$\nu(CH_2Hg)$ = 8.7–29.7 Hz in carbon tetrachloride]. However, it is difficult to determine in this instance which oxygen atom is involved in the Hg ← O intramolecular coordination: peroxide, carbonyl, or ester oxygen [148].

Internal coordination is responsible for the enhanced hydrolytic and chemical stability (there is no reaction with 2-aminoethanol and *o*-phenylenediamine under mild conditions) of the boronate diester [149]:



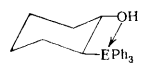
The doublet of signals in the ^{11}B NMR spectrum (with chemical shifts of –30.5 and –51.3 p.p.m. relative to $Et_2O.BF_3$) corresponds to the coordinated and free boron atoms in the bicyclic ester (XII),



(XII)

which evidently exists in the form of an equilibrium mixture of chair-boat and chair-chair conformers, the proportions of which have been found to be 65 : 35. [150]

The enhanced acidity of silyl (germyl)-substituted cyclohexanols (XIII)

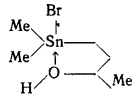


(XIII)

(E = Si, Ge)

relative to carbon analogues, which has been established on the basis of the large shifts of the ν(OH) bands in the infrared spectra following the addition of DMSO and THF, can be accounted for by E ← O intramolecular coordination, since the electropositive influence of silicon and germanium should reduce the acidity of these alcohols [94]. On the other hand, the acidity of 1,1,1-triphenylethanol derivatives of silicon and germanium is normal [151]. The large difference clearly demonstrates the influence of conformation on the proximity of the electron-donating and electron-accepting atoms.

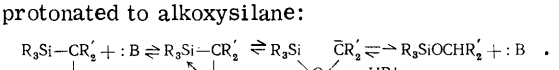
The coordination in γ-stannylethanol (XIV)



(XIV)

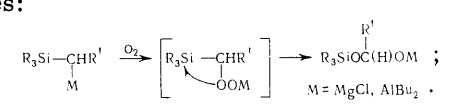
probably takes place as a result of the very high value of $J_{^{117}/^{119}Sn-CH_3}$ in the ^1H NMR spectrum, which amounts to 60.6/63.4 Hz in 0.32 M solution in carbon tetrachloride in the presence of added tris(dipivaloylmethanato)europium [152].

In the presence of basic catalysts (active metals, organometallic compounds, or amines), silylmethanols readily rearrange to alkoxysilanes [153-156] via a pseudo-first-order reaction [157]. Its rate is very sensitive to the nature of the group at the methanol centre and the activation energy is 8–11 kcal mole^{-1}. The basic catalyst removes the acid proton and the resulting α-hydroxy-ion then undergoes an intramolecular rearrangement with formation of a stronger Si–O bond and the fixation of the negative charge at the carbon atom. The carbanion formed is rapidly protonated to alkoxysilane:

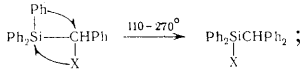


This isomerisation proceeds with retention of configuration at the chiral Si centre [158] and with its inversion at the chiral carbinol centre [159].

The products of the oxidation of the Si–C bond in α-trialkylsilyl organometallic compounds, i.e. hydroperoxy-salts [160], undergo a similar rearrangement and are converted as a result of hydrolysis into silanols and siloxanes:

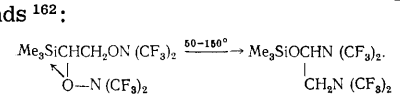


The thermal rearrangements of α-substituted benzyltriphenylsilanes probably proceed via an intramolecular mechanism with migration of the substituent X to the silicon atom accompanied by the transfer of the phenyl group from silicon to carbon [161]:

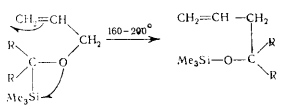


X = OAc, OTs, F, Cl .

This also happens in the thermal rearrangement of trifluoromethylaminoxyalkylsilanes with dissociation of the Si–C and N–O bonds and the formation of stronger Si–O and N–C bonds [162]:



These isomerisations, which take place almost quantitatively (the latter is a first-order reaction), are examples of diatropic rearrangements in which two σ bonds change places as a result of the cyclic process. A study of the kinetics of the conversion of allyl silylmethyl ether to a silylether [163]

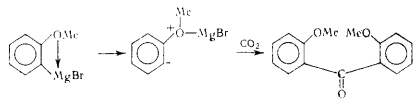


(R + R = o,o'-biphenylene, R = Ph;)

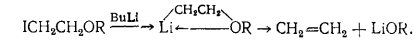
showed that the rearrangement does not proceed via a single mechanism. For example, when R + R = *oo'*-biphenylene, the silyl group migrates intramolecularly to the extent of 100%, while the allyl group migrates via this mechanism only to the extent of 72%. The isomerisation proceed via a first-order reaction and depends only slightly on the solvent. The activation parameters (in benzene) are $E_a = 32.3 \pm 0.6$ kcal mole^{-1}, $\Delta H^{\neq} = 31.4 \pm 0.6$ kcal mole^{-1}, and $\Delta S^{\neq} = -8.9 \pm 0.8$ cal K^{-1}.

β-Metallated alcohols and ethers are fairly stable in solution in aromatic compounds. Like aminoferrocenes (aminobenzenes), alkoxyferrocenes (alkoxybenzenes) are therefore metallated by butyl-lithium only at the site adjoining the substituent owing to Li ← OR intramolecular coordination, benzene derivatives reacting much more slowly. Substituted ferrocenes with X = CPh_2OH, [164] OMe, [165,166] CH_2OR, [167] or Cl [166] and benzenes with X = OMe [168] or SO_2CMe_3 [169] have been used. In the case of thioanisole [170], the α-position of the ring is metallated with subsequent transfer of the lithium atom to the methyl group, probably as a result of *trans*-metallation.

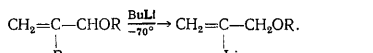
Internal coordination has also been proposed to account for the anomalous reactions between CO_2 and Grignard reagents derived from *o*-bromomethoxy(methylthio-, dimethylamino-)benzenes, as a result of which both acids and ketones have been obtained [171-173]. The formation of the latter can be understood on the basis of this scheme



Aliphatic β-lithioethers very readily eliminate lithium alkoxides owing to the Li ← OR intramolecular coordination and can therefore be obtained only at very low temperatures [174,175]. For example, when β-iodoethers are acted upon by butyl-lithium, the main product is ethylene with only a 5% yield of the desired product [174]:



Similar α-vinyl-lithium compounds are much more stable and can be obtained in a preparative yield, for example [176,177]:



β-Alkoxyethylmagnesium compounds are extremely unstable (see Section II).

It is interesting to note that ethers [and sulphides] of the type $ROCH_2MgCl$ and $PhCH_2SCH_2MgCl$ are stable at −30° and 0°C respectively, but [at higher temperatures?] decompose with elimination of ethylene [178]:

However, in the presence of cyclohexene their decomposition does not lead to the formation of norcarane [178], so that the elimination of ethylene most probably proceeds via intermolecular coordination.

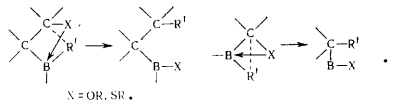
β-Alkoxyethyl derivatives of boron are also thermally unstable. For example, tris-(2-alkoxyethyl)boron begins to evolve ethylene at a temperature as low as −10°C. However, the stability of these compounds increases as the 2-alkoxyethyl groups are substituted by alkoxy-groups and 2-alkoxydiethoxyboron decomposes only at 160–170°C. [179]

It has been shown that the ease of elimination of olefins from the compounds R_2BC-CX depends on X. When

X = OTs, OBz, OAc, or Cl, the decomposition takes place below 0°C, while for X = OAlk(Ar) the compound can be isolated [180,181].

It has been shown for deuterated [182] and cyclohexane [183] derivatives of boron that thermal β-elimination takes place via an intramolecular mechanism. Under comparable conditions, β-alkoxylethylboron compounds form olefins more readily than the analogous sulphur derivatives [182, 184].

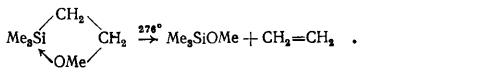
β-Elimination may be accompanied also by a β-transition (a new type of diatropic rearrangement), which likewise proceeds intramolecularly [185,186]. α-Transition reactions proceed similarly [183,185]:



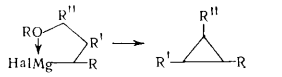
X = OR, SR.

Al ← OR intramolecular coordination is probably the cause of the thermal instability also of β-alkoxyethyl derivatives of aluminium [33,187].

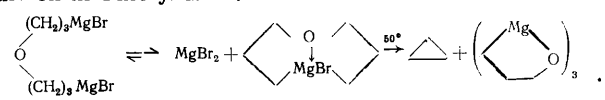
Similar silicon compounds decompose only under severe conditions and eliminate olefins quantitatively via a first-order reaction [188] (see also Tsurugi et al. [189]), for example:



There is no doubt that the thermal instability of 3-alkoxy(aryloxy)-derivatives of Grignard reagents can be accounted for by Mg ← OR intramolecular coordination [190-193]. This reaction can serve as a preparative method for the preparation of substituted cyclopropanes (yield of about 50%):

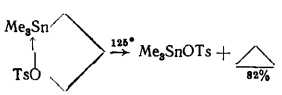


Bifunctional Grignard reagents disproportionate fully in THF into cyclic monomeric compounds (their degrees of association have been determined), which eliminate cyclopropane on thermolysis [194]:



On thermolysis, the compounds iso-$Bu_2Al(CH_2)_2OR$ (n = 3 or 4) form cyclopropane [34,195,196] and cyclobutane [34] respectively.

Tin compounds $Me_3Sn(CH_2)_nOTs$ (n = 3 or 4) behave in different ways depending on the value of n. [197] When n = 3, the thermolysis leads to cyclopropane, while in the case of n = 4–6 olefins are mainly produced, although 10% of cyclopentane has been obtained for n = 5:

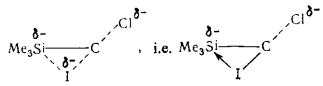


Presumably compounds of the type $E(CH_2)_nOR$ ($n > 3$) do not form cyclic products on thermolysis even when they contain reactive metals. For example, γ-ethoxybutylmagnesium bromide decomposes only with elimination of butyl ethyl ether [191].

IV. COMPLEXES WITH HALIDE LIGANDS

The extensive employment of many types of alkyl (aryl) halides and their derivatives in direct metallation reaction has led to the synthesis of numerous classes of organic derivatives of the elements with possible Hal – M intramolecular coordination and in the case of reactive metals most of them are extremely unstable at room temperature and readily decompose as a result of α- and β-elimination with formation of carbenes and arynes respectively [3]. In this part of the review we shall consider only compounds where intramolecular coordination is postulated in a non-reacting molecule, the transition state, or in thermolysis with formation of olefins and cycloalkanes.

Such coordination was postulated for the first time in the transition state to account for the sharp acceleration of the exchange (by a factor of 13) of the chlorine atom in trialkylchloromethylsilanes for an iodine atom in dry acetone (the Finkelstein reaction) in relation to the carbon analogues [198,199]:



This concept was subsequently used to explain the unusually easy nucleophilic substitution of the chlorine atom for I, OR, and SR in α-chloromethyl derivatives of mercury (the exchange is accelerated by a factor of 10^6 compared with n-BuCl) [200], boron [201], germanium, and tin [202]. It is noteworthy that there is no intramolecular coordination of this type in a non-reacting molecule (see Section I).

When alkyl substituents at the central atom are replaced by powerful electronegative groups capable of exciting the vacant orbitals of the central atom, intramolecular coordination takes place, as shown for trichloromethyl derivatives of mercury Cl_3CHgX (X = Cl, Br, or CCl_3). In ^{35}Cl NQR spectra there is appreciable (>2%) splitting of the lines due to the chlorine atoms in the CCl_3 group, which has been explained by an intramolecular interaction of one of the chlorine atoms with the mercury atom [203]. The authors believe [203] that such coordination has been confirmed by the X-ray diffraction analysis of Cl_3CHgBr in which Hg...Cl distances proved to be different—two of them are 3.21 Å and one is 3.15 Å. However, since the difference is within the limits of experimental error, the above conclusion cannot be regarded as reliable. Coordination in the above compounds breaks down when dimethoxyethane is added (the pronounced line splitting disappears), but not in the presence of ether [204].

Cl → Sn intermolecular coordination probably also occurs in chloromethyltrichlorotin. Thus its mass spectrum [205] reveals the presence of rearranged fragments formed as a result of the ejection of carbene via a three-membered transition state, while the ^{35}Cl NQR spectrum of the $SnCl_3$ group [206] was found to consist of two lines with an intensity ratio of 1 : 2 and a splitting of about 6%, which exceeds by a factor of three the maximum possible crystallographic splitting. The non-equivalence of chlorine atoms has been explained by the possible coordination interaction between chlorine and tin, which can be both intermolecular and intramolecular. Cryoscopic determination of the molecular weight in benzene showed that there is no association. Furthermore, on reaction with an excess of relatively weak electron donors such as ether and benzene, the compound forms 1 : 1 (and not 1 : 2) complexes, existing only in solution (according to ^{35}Cl NQR spectra), which is not a characteristic feature of organotin compounds with powerful electronegative groups. This shows that the intramolecular coordination is stronger than the intermolecular coordination with ether and benzene. It was therefore assumed that these complexes have the configuration of a trigonal bipyramid with the tin atom in the centre and the three chlorine atoms in the equatorial plane; one of the vertices is occupied by the chlorine atom of the chloromethyl group and the other by a molecule of ether or benzene [2].

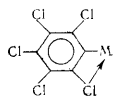
Ethyl acetate causes only a partial breakdown coordination in Cl_3SnCH_2Cl (according to dipole moment measurements),

while pyridine destroys it completely with formation of a 1 : 2 complex; calorimetric data made it possible to estimate the energy of the intermolecular coordination as approximately 5 kcal mole^{-1}, which is typical for a hydrogen bond[13].

Finally, electron diffraction study of this compound in the vapour phase (R = 12.3%)[207] showed that its molecule is a distorted octahedron with hindered rotation about the Sn–C bond. However, one cannot conclude directly from these data that the Cl → Sn intramolecular coordinate bond is present.

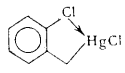
It is interesting to note that dichlorobis(chloromethyl)tin consists in the crystalline state of infinite chains with intermolecular Sn ← Cl bonds (X-ray diffraction analysis, R = 17.7%).[208]

The pentachlorophenyl derivatives of the number of metals have anomalous spectroscopic properties, which suggested the occurrence of intermolecular coordination:



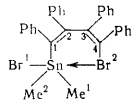
The compound with M = HgC_6Cl_5 melts at a much higher temperature than the corresponding pentafluorophenyl derivative[209]. The splitting of the frequencies of the *ortho*-chlorine atoms and their appreciable shift relative to the *meta*- and *para*-atoms have been observed in the ^{35}Cl NQR spectrum. The same characteristics have been found also for M = HgR (R = Cl, Me, or Ph).[210] Furthermore, low electrochemical reduction rate constants have been obtained for these compounds[92]. According to ultraviolet spectroscopic data, the pentafluorophenyl derivatives of silicon and tin have $\lambda_{max} \simeq 200$ nm, and a much higher molar absorption than their hydrogen-containing analogues[211]. *o*-Halogenophenyl derivatives of alkali and alkaline earth metals are extremely unstable owing to intramolecular coordination and the ease of formation of arynes, which is of great importance for synthesis[3]. The corresponding ferrocene derivatives are entirely stable (see Section III).

The absorption band corresponding to the vibrations of the Hg–Cl bond in the infrared spectrum of *o*-chlorobenzylmercury chloride is split into three components owing to the existence of several rotational isomers. The most intense component at 314 cm^{-1} has been attributed to the conformation with possible intramolecular coordination[212]:



A very interesting variation of the influence of substituents on intramolecular coordination has been observed in butadienyltin derivatives[213]. A doublet of equally intense signals due to the methyl protons (δ = 0.48 and 0.98 p.p.m., 36°C), merging into a singlet on heating to 87°C, has been found in the ^{1}H NMR spectrum of 4-bromo-1,2,3,4-tetraphenyl-*cis*,*cis*-buta-1,3-dienyldimethyltin bromide (XV). The addition of basic solvents, for example ether or pyridine, has a similar influence. To explain the non-equivalence of the methyl protons in the diene, Sn ← Br intramolecular coordination was postulated: it stabilises the non-planar distorted cisoid conformation and hinders the rotation about the $C_{(2)}$–$C_{(3)}$ bond with a barrier of 18.3 ± 0.23 kcal mole^{-1} (according to ^{1}H NMR spectra) at room temperature and in non-basic solvents. Consequently intramolecular coordination can be disrupted by heating the specimen or by adding basic solvents.

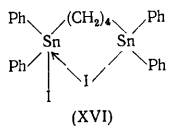
The proposed conformation of the diene (XV) in solution proved to be the same as in the crystalline state, as shown by X-ray diffraction (R = 10.7%).[213,214] The Sn ← Br bond length is 3.77 Å, which is smaller by 0.4 Å than the sum of the van der Waals radii of tin and bromine atoms. To ensure such coordination, the $C_{(1)}$–Sn–Me^1 angle has increased to 129° (from the tetrahedral angle of 109.5°) and the torsional angle in the butadiene fragment has increased to 68.1°:



(XV)

The introduction of the phenyl group in place of bromine and tin atoms should cause the breakdown of intramolecular coordination, since a tin atom linked to four carbon atoms does not usually exhibit coordinating properties. X-Ray diffraction analysis of this compound[215] confirmed this hypothesis: the Sn ← Br bond length is 4.346 Å and the $C_{(1)}$–Sn–Me^1 angle is 117.1°.

The conformation of the molecule can be very different in the crystalline state and in solution. For example, 1,4-bis(iododiphenylstannyl)butane has a high dipole moment in benzene (5.24 D), which is believed[216] to be associated with the existence of the inner complex (XVI):



(XVI)

However, in the crystalline state the molecule proved to be symmetrical with a tetrahedral configuration of the tin atom (X-ray diffraction analysis; R = 9.6%).[217] At the same time, when iodine in compound (XVI) is replaced by hydroxy- and acetoxy-groups, the compounds probably exist in the crystalline state as inner complexes—their Mössbauer spectra show appreciable quadrupole splittings compared with the iodine analogue and the tin atom is undoubtedly pentacoordinate[218].

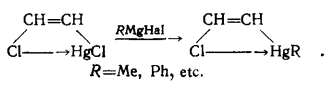
The influence of intramolecular coordination on the physical and chemical properties of organic derivatives of the elements has been studied in particularly great detail in relation to *cis*-β-chlorovinylmercury chloride. A singlet at 33.132 MHz was observed in the ^{35}Cl NQR spectrum, its position apparently indicating the absence of intermolecular coordination, as happens in the *trans*-isomer[219]. Whereas the dipole moment of the *trans*-isomer agrees well with the calculation, for the *cis*-isomer there is a sharp discrepancy between the observed and calculated moments in benzene (2.92 and 3.57 D respectively), which is believed[220] to be caused solely by the appreciable decrease of the ClCC and CCHg angles in consequence of the intramolecular coordination. Using different solvents (benzene, dioxan, and ethyl acetate), it has been shown by the same method that the strength of the Cl → Hg intramolecular coordinate bond in *cis*-ClCH = CHHgHal decreases in the sequence Cl > Br > I,[221] while strong intermolecular Hal → Hg bonds have been observed in the corresponding *trans*-analogues (on the basis of Hal NQR spectra)[222]. Intramolecular coordination probably occurs also in di(*cis*-β-chlorovinyl)mercury, since $J_{^{13}C-^{199}Hg}$ in the ^{13}C NMR spectrum is appreciably higher than for symmetrical mercury compounds, where coordination is known to be ruled out[223].

Finally, the *cis*-β-chlorovinylmercury chloride molecule has been investigated by gas electron diffraction (R = 11.5%)[224]. The intramolecular non-valent Hg...Cl distance proved to be 3.27 Å, while the sum of the van der Waals radii is 3.3–3.5 Å. Consequently the electron-diffraction data are consistent with the occurrence of extremely weak intramolecular coordination, but cannot be regarded as unambiguous proof. The decrease of the CHgCl angle, located opposite the additional chlorine atom, to 168.5° might also indicate intramolecular coordination, but it is not clear in which direction the Hg–Cl bond is "bent". Presumably the intramolecular coordination is largely determined by the rigidity of the molecular geometry:



Nevertheless the mercury atom in the *cis*-isomer is coordination-saturated and the *cis*-chloride does not therefore form complexes with pyridine[225], TMEDA, and di(mercaptomethyl)ethane[226], in contrast to the *trans*-chloride. For this reason, nucleophilic attack on the mercury atom should be hindered in the *cis*-isomer, which in turn hinders the nucleophilic cooperation in electrophilic substitution at the carbon atom.

Apart from considerable resistance to electrophilic substitution, *cis*-β-chlorovinylmercury chloride does not eliminate acetylene even when acted upon by powerful nucleophilic agents, i.e. lacks completely the capacity to transfer the reaction centre and therefore lacks "dual" reactivity. For example, whereas the *trans*-isomer immediately evolves acetylene even when acted upon by a weak nucleophilic agent such as dibutylmercury, the *cis*-isomer is readily alkylated by Grignard reagents[226–228]:

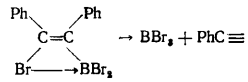


R=Me, Ph, etc.

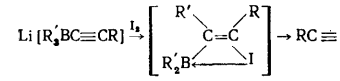
It has been shown that the *cis*-compound is also smoothly symmetrised on treatment with iodide ions, in contrast to the *trans*-compound, which immediately evolves acetylene[227,228]. Both stereoisomers react with diazomethane without the evolution of acetylene and with formation of the corresponding β-chlorovinyl(chloromethyl)mercury compound, which then eliminates acetylene under thermodynamically-controlled conditions[226–228].

The study of the thermolysis of β-chlorovinyl derivatives of mercury has shown[229] that the stability of *cis*-ClCH=CHHgHal decreases in the sequence Cl > Br > I, while the inverse series holds for the *trans*-isomers. However, this behaviour in the case of the *cis*-compounds is inconsistent with the decrease of the strength of intramolecular coordination in the sequence observed in the measurement of dipole moments[221]. The mass spectra of the *cis*- and *trans*-compounds are qualitatively the same, but the *cis*-isomers are more stable under electron impact.

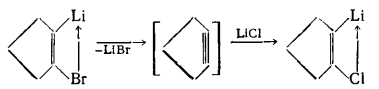
Unfortunately the strength of intramolecular coordination has not been investigated for different halogens in the halogenovinyl group, since such compounds could not be synthesised despite numerous attempts. Nevertheless the strength of intramolecular coordination should presumably increase in the sequence Cl < Br < I, by analogy with boron derivatives. The series is fairly clear for the latter. Indeed *cis*-β-chlorovinylboron distills *in vacuo* without decomposition and is smoothly arylated by di-(*p*-anisyl)mercury to *cis*-β-chlorovinyl(dianisyl)boron.[226] β-Bromovinyl compounds decompose to acetylenes on slow heating *in vacuo*[230]:



while β-iodovinyl compounds cannot be isolated at all because they are converted quantitatively into acetylenes even under mild conditions (–78°C)[231]:

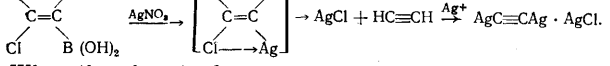


β-Halogenovinyl derivatives of alkali and alkaline earth metals are still less stable. Thus 2-bromo-1-lithiocyclopentane eliminates a very unstable monomolecular cyclopentyne at a temperature as low as 20°C (this has been established on the basis of the concentration variation of the salt effects and the reversibility of the formation of lithium bromide) via a first-order reaction with an activation energy of 24 kcal mole^{-1} (± 10%). In its thermolysis in the presence of 2,5-diphenyl-3,4-benzofuran, the product of addition to cyclopentyne, the formation of which in the course of the reaction had been demonstrated kinetically, was isolated. Lithium chloride adds to cyclopentyne with formation of 2-chloro-1-lithiocyclopentene:[232]

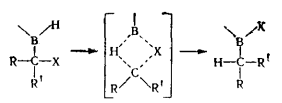


Cyclohexyne and cycloheptyne have been obtained under mild conditions from 2-fluoro-1-lithiocyclohexene and a Grignard reagent, based on 1,2-dibromocycloheptene, respectively[233,234]. Their formation has been demonstrated by condensation and trimerisation reactions and is undoubtedly due to M ← Hal intramolecular coordination (M = Li or MgHal).

β-Chlorovinyl derivatives of silver are also extremely unstable. When an attempt was made to obtain them by treating stereochemically pure *cis*- and *trans*-β-chlorovinylboronic acids with aqueous silver nitrate solution, only the complex of silver carbide with silver chloride AgC≡CAg.AgCl was isolated. The initial state probably involves the formation of *cis*- and *trans*-β-chlorovinyl derivatives of silver, which eliminate acetylene as a result of Ag ← Cl intramolecular or intermolecular coordination, and the acetylene is metallated by the excess silver ions[235]:

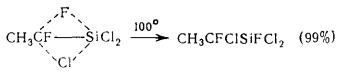


When the chemical consequences of intramolecular coordination in aliphatic systems are considered, one must remember the spontaneous diatropic intramolecular rearrangement of α-halogeno-organoboranes with hydride substitution of halogen and the formation of alkylhalogenoboranes, which proceeds via a first-order reaction with inversion of configuration[236,237]:

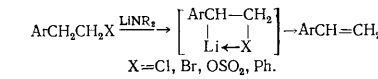


An analogous exchange involving organosilicon compounds takes place similarly (with a virtually quantitative yield) but under severe conditions (100–160°C) when there

are different halogens at the silicon and α-carbon atoms, for example[238] (see also Brook and Jones[161]):

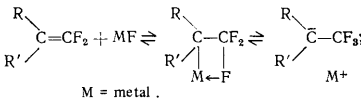


β-Halogeno-derivatives of alkali metals are extremely unstable and readily eliminate olefins[239,240], for example:



These compounds can be obtained at very low temperatures with a yield not exceeding several per cent[174].

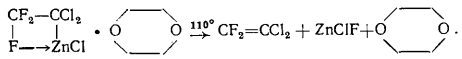
In the case of organofluorine compounds β-elimination may be in equilibrium with the reaction involving the addition of the metal fluoride to the olefin:



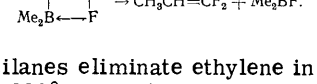
The position of such equilibrium depends on many factors, but probably mainly on the M–F bond energy. In fact LiF and NaF, which hardly add to fluoro-olefins, have a much higher M–F bond energy than KF and CsF, which readily form carbanions on interaction with perfluoro-isobutene and perfluoropropene.

Aliphatic Grignard reagents can be obtained only when there is no heteroatom other than fluorine in the β-position (see Section I and also Ballard and Gilman[241]).

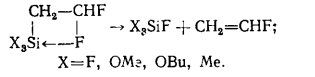
Organozinc compounds possess the same properties[242,243]; one should note that β-elimination takes place much more readily than α-elimination even in the case of relatively unreactive halogens[243]:



β-Halogenoboron compounds are extremely unstable and usually decompose already at the instant of formation[244–249]. Even the most stable of the compounds described remain stable only at –78°C and begins to decompose slowly at room temperature and rapidly at 100°C [246]:

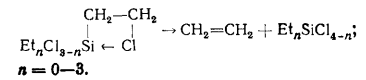


β-Fluoroethylsilanes eliminate ethylene in the gas phase only at 150–320°C via a first-order reaction. The rate of reaction is independent of the surface to volume ratio of the reaction vessel, pressure, and the presence of radical traps—cyclohexene and nitric oxide[250–254]:

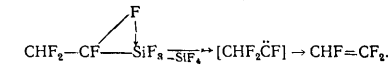


The liquid-phase decomposition of siloxane with X = OBu in a silicone oil proceeds via the same mechanism[255]. β-Fluoroethylpolysiloxanes of the type $[CHF_2CH_2SiO_{1.5}]_n$ behave similarly[255–256].

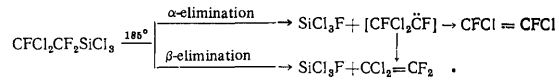
β-Chloroethylsilanes decompose in the gas phase at 300–400°C also via a first-order reaction, the rate of reaction increasing on replacement of alkyl substituents at the silicon atom by chlorine[257–260]:



When fluorine atoms are present simultaneously in the α- and β-positions with respect to silicon, α-elimination takes place exclusively[251,261–263], for example;

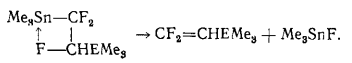


On the other hand, when different halogens are present in the α- and β-positions in the molecule, α-elimination clearly predominates over the possible β-elimination or the 1,2-shift of the fluorine atom in the carbene formed (the yields of olefins are 80 and 7% respectively)[263,264]:



It is difficult to account for this mode of thermolysis. Purely conformational factors probably play a decisive role here.

Mixed polyfluoroethyl derivatives of the type $Me_3SnCF_2CFHEMe_3$ (E = Si, Ge, or Sn) decompose at much lower temperatures (55°C, 20°C, and at the instant of preparation) and exclusively via β-elimination[265,266]:

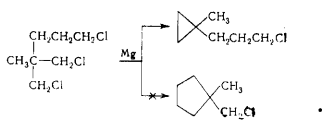


These findings can be accounted for both by a decrease of the E–C bond energy in the sequence Si > Ge > Sn and by the sharp increase of the coordinating capacity of E in the reverse sequence. Conformational factors probably also play a significant role, since $^1J_{Sn-F_\alpha} > {}^1J_{Sn-F_\beta}$.

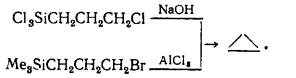
Compounds of the type $Me_3ECF_2CHFM(CO)_5$ (where E = Ge or Sn and M = Mn or Re) also decompose similarly at the instant of formation[267–269].

If the fluorine atom is in the γ-position, then organic derivatives of the elements (for example, derivatives of magnesium[270], boron[270], and silicon[271]) acquire enhanced stability and decompose via a radical-chain mechanism[271]. The lack of coordinating capacity by the fluorine atom in the γ-position has not been satisfactorily explained.

On the other hand, other halogens in the γ-position decrease sharply the stability of organometallic compounds and it is actually impossible to isolate them in the case of reactive metals. For example, magnesium[272–275], zinc[276], and aluminium[245] compounds readily eliminate substituted cyclopropanes. The tendency towards intramolecular 1,3-interaction is very great and clearly predominates over 1,4- and 1,5-interactions, for example[274]:

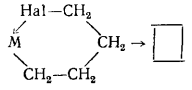


It is interesting that γ-halogenopropyl derivatives of boron[244] and silicon[277] are thermally stable. Nevertheless cyclopropane is readily formed from the silicon compounds[277] either as a result of a base-catalysed elimination (in which the carbanion formed in the ionisation of the Si–C bond undergoes intramolecular nucleophilic substitution) or under the influence of aluminium chloride, which involves the intramolecular electrophilic substitution of the carbonium ion formed on ionisation of the C–Hal bond:



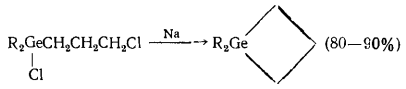
Cyclopropane is not formed in reactions involving the exchange of the reactants.

δ-Halogenobutyl derivatives of reactive metals (sodium, lithium, magnesium[278], and aluminium[196]) decompose only at elevated temperatures with slight (11–13%) elimination of cyclobutane (CB):

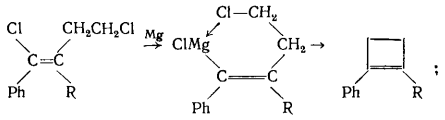


However, similar aluminium compounds have been found[245] to give rise on decomposition exclusively to methylcyclopropane and but-1-ene, but not cyclobutane.

An exception to this rule is the cyclisation of γ-halogenopropyl-silanes and -germanes[279,280] under the influence of sodium in boiling toluene, for example:

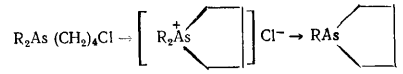


and of an unusual Grignard reagent formed from 1,4-dichlorobut-1-enes in ether (the yield of cyclobutene reaches 90%) where magnesium reacts with the vinyl chlorine and not the primary chlorine[281]:

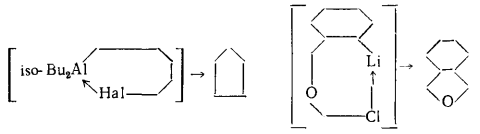


R=H, Ph.

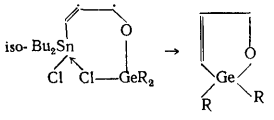
δ-Cyclobutyl derivatives of arsenic form five-membered rings at 160–170°C in 80% yield[282,283], while compounds with longer or shorter aliphatic chains are thermally stable:



Cyclisation reactions of ε-halogeno-derivatives of lithium[284], and aluminium[196] have also been described; these have not been isolated, but a Hal → M linkage has been postulated on the basis of the high yields of reaction products (70 and 75% respectively):



The reactions of γ-siloxy(germyloxy)chlorostannanes at temperatures exceeding 130°C with formation of oxametallocyclo-alkanes and -alkenes[285] have also been described, for example:

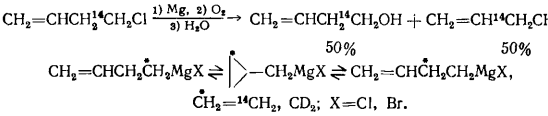


V. COMPLEXES WITH π-LIGANDS

In contrast to transition metals, which readily form stable π-complexes playing an extremely important role in modern chemistry, particularly in the stereochemically controlled reactions of π-electron systems, such complexes of non-transition metals have been obtained only recently for bivalent germanium, tin, and lead (see, for example, the paper by Doe et al.[286] and the references quoted there). At the same time, it has been shown in numerous investigations that, although many ω-unsaturated organometallic compounds derived from Group IA–IIIA metals cannot in fact be isolated in a pure state, they are undoubtedly formed as intermediates in solutions and cyclise very rapidly as a result of M ← π-ligand intramolecular coordination.

1. Olefins

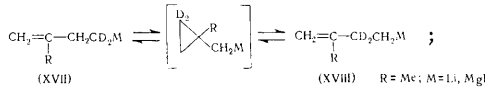
This new branch of the chemistry of organometallic compounds was begun by a study[287] in which the Grignard reagent obtained from the deuterium-labelled or [^{14}C] allylmethyl chlorde (bromide) was oxidised by oxygen in ethereal solution. The distribution of the label along the chain in the unsaturated alcohols obtained demonstrated unambiguously that the Grignard reagent cyclises before its oxidation to the alcohol:



The ^{1}H NMR spectra show that ≥ 99% of the Grignard reagent from arylmethyl chloride (bromide) and from cyclopropylmethyl chloride has the allylmethyl structure. This had been established by the author in an earlier study[288]. The time of 50% equilibration between the isomeric acyclic forms of the Grignard reagent is 30 h at 27°C and 40 h at 55°C and corresponds to an activation energy of 23 kcal mole^{-1}.

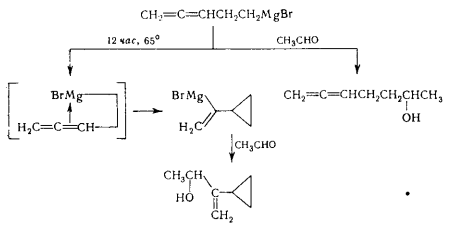
The existence of the cyclic form has been demonstrated by the fact that treatment of cyclopropylmethyl bromide (chloride) with magnesium in methyl ether (–24°C) or in ethyl ether (36°C) in the presence of traces of benzoic acid yielded methylcyclopropane, the content of which reached 55% in the case of the bromide[289]. This amount should correspond to the initial cyclic form, whose protonation is much faster than its rearrangement. The rearrangement proceeds via a first-order reaction and its 50% reaction time is about 2 h at –24°C, which corresponds to a free energy of activation of 19 kcal mole^{-1}.

The study of the influence of substituents in the γ- and δ-positions on the rearrangement of allylmethyl Grignard reagents showed that the vinyl group or two phenyl groups in the δ-position appreciably accelerate the rearrangement in consequence of the stabilisation of the partial negative charge in the cyclic forms. Thus, when phenyl groups are present, the distribution of the deuterium label between the α- and β-positions was completed in 5 h at room temperature, the content of the cyclic form being less than 0.3%.[290] Conversely, the phenyl group in the γ-position appreciably retards the formation of the cyclic form, probably in consequence of the destabilisation of the cyclopropane ring. According to ^{1}H NMR spectra, compound (XVII) is stable in ethers at room temperature and rearranges to (XVIII) only after 8 h at 100°C.[291] The study of the reversible isomerisation (XVII) ⇌ (XVIII), i.e.

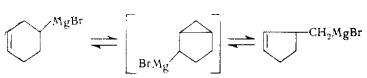


by ^{1}H NMR [292] showed that the rate of equilibration depends on the following factors: (1) the structure of the organic group; (2) temperature; (3) the electronegativity of the metal (it decreases in the sequence Li $\gg$ R_2Mg > RMgX); (4) the solvent (in more polar solvents, the isomerisation is retarded for magnesium compounds but accelerated for lithium compounds); (5) the concentration (it increases linearly for Grignard reagents, the proportionality constant depending particularly strongly on the temperature, solvent, and substituents; on the other hand, for the lithium compound it depends appreciably on the concentration); (6) the presence of salts in solution [$MgBr_2$ accelerates the rearrangement of (XVII), while lithium alkoxides retard it]. Furthermore, compounds (XVIII) predominate in the equilibrium mixture in consequence of the very pronounced thermodynamic secondary isotope effect and the (XVII) $\rightleftharpoons$ (XVIII) equilibrium constant depends on the physical conditions. The authors explain [292] the results by the existence of two different mechanisms of the reversible isomerisation (XVII) $\rightleftharpoons$ (XVIII): an ionisation-recombination process for lithium compounds and a bimolecular process for organomagnesium compounds, probably via an *at* complex.

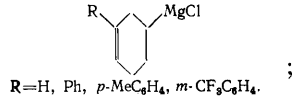
The allene system apparently constitutes the limiting case of the stabilisation of the cyclic form (because of the absence of decyclisation) and it is therefore of preparative importance for the synthesis of vinylcyclopropanes. For example, the yields of the Grignard reagent from 5-bromopenta-1,2-diene in THF and of the cyclic and straight-chain alcohols derived from it (respectively after refluxing for 12 h and without heating, with subsequent treatment with acetaldehyde) proved to be 25%, which indicates a quantitative cyclisation reaction with a 50% decomposition period of about 4 days at 25°C [293]:



The rearrangements of cyclic allylmethyl Grignard reagents have also been investigated. While the cyclopentene compound decomposes on heating without change in ring size, the cyclohexene and methylcyclopentene Grignard reagents undergo interconversions, the latter greatly predominating in the equilibrium mixture (about 90% after several hours at 80°C) [294-296]:



It has been shown with the aid of deuterium labels that the rearrangement proceeds via a bicyclic intermediate, which, however, cannot be determined in the equilibrium mixture. The authors believe that the driving force of the ring contraction process [294-296] is the difference between the stabilities of the primary and secondary Grignard reagent, which they estimated as 3.7 kcal $mole^{-1}$. The equilibrium constant depends strongly on the solvent and concentration, and a secondary entropy-controlled isotope effect is observed for the deuterated compounds:

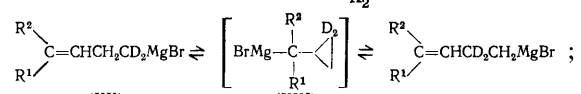


R=H, Ph, *p*-MeC_6H_4, *m*-$CF_3C_6H_4$.

(XIX)

Comparison of the rates of rearrangement to compound (XIX) showed that an aryl group decreases and electronegative substituents slightly increase the rate. These results correspond best to isomerisation with ClMg ← ‖ intramolecular coordination via a bicyclic intermediate, which is formed at a lower rate than that of its decomposition to the cyclopentene ring [297]. Furthermore, the signals of the olefinic protons in the ^{1}H NMR spectra of the initial Grignard reagents are located in a lower field compared with the corresponding hydrocarbons, which the authors [297] believe may serve as evidence for the formation of π-complexes.

This mechanism was confirmed in a study of the kinetics of the reversible isomerisation (XX) $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ (XXII), i.e.



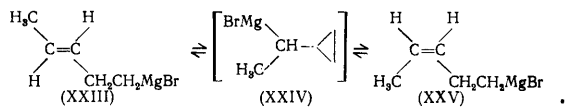
(XX) (XXI)

(a) R^1=H, R^2=Me; (b) R^1=R^2=Me ,

(XXII)

by ^{1}H NMR in ether [298]. It was found that compound (XXa) (*cis* : *trans* = 42 : 58) is in equilibrium with compound (XXII) only after 775 h at 100°C. The rearrangement is retarded even more after the introduction of a second methyl group in the δ-position: compound (XXb) gives rise to (XXIIb) after 900 h at this temperature with a yield of only 20%. These results conflict with a radical mechanism. To demonstrate the involvement of the intermediate (XXI), which cannot be detected in the equilibrium mixture, a study was made of the kinetics of the *cis–trans* isomerisation (XXIII) $\rightleftharpoons$ (XXV) with gas–liquid chromatographic identification of the carboxylated reaction products in the form of their methyl esters. Regardless of the initial compound, (XIII) or (XXV), the isomerisation was described by a first-order equation and always led to the same mixture of *cis*- and *trans*-products (21 : 79). Since the sums $k_1 + k_2$ for the equilibria (XXa) (XXIIa) and (XXIII) (XXV) are of the same order of magnitude, (XXI) and (XXIV) are true intermediates, in which the single bond between the carbanionic centre and the cyclopropane ring has sufficient time for free rotation. The *cis-trans* isomerisation

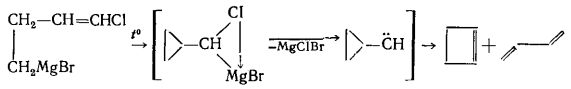
(XXIII) $\overset{k_1}{\rightleftharpoons}$ (XXV) therefore proceeds via the same mechanism as the reversible isomerisation involving the α- and β-positions in the (XX) $\rightleftharpoons$ (XXII) process [298]:



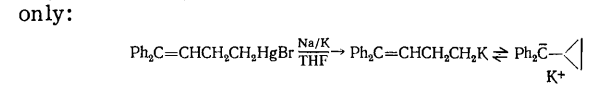
(XXIII) (XXIV) (XXV)

When a chlorine atom is introduced into the δ-position, the Cl → Mg intramolecular coordination occurs with formation of cyclopropylcarbene, since thermolysis of the Grignard reagent in ethers yielded cyclobutene in 80% yield together with a small amount of buta-1,3-diene (detected by ^{1}H NMR) [299]. The 50% decomposition period of the initial compound in THF is 500 h at 61.5°C and 2 h at

107°C, which corresponds to an activation energy of 30 kcal mole^{-1}:

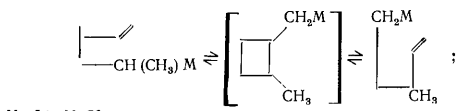


The dependence of the cyclisation–decyclisation reaction on the amount of ionic character of the metal–carbon bond has been investigated [300]. When the allylmethyl compound of mercury is added to the sodium–potassium alloy in THF, a dark cherry-red solution of the cyclic anion is formed immediately, giving rise after carboxylation to phenylcyclopropylacetic acid in 80% yield. The replacement of potassium by sodium also leads to the cyclic product only:



Its stability is explained by the stabilisation of the electron pair by the benzene rings. On the other hand, when the potassium in ether is replaced by lithium or magnesium, which form stronger covalent bonds with carbon, there is an immediate reverse rearrangement to the corresponding acyclic products. These rearrangements are reversible. For example, diphenylcyclopropylmethyllithium is stable in THF, while in ether it isomerises completely to $\gamma\gamma$-diphenylallylmethyl-lithium. The reverse rearrangement can be induced by the simple addition of THF to an ethereal solution the compound.

In systems containing a four-membered ring there is also equilibrium between the acyclic and cyclic forms of the organometallic compounds, for example [301]:



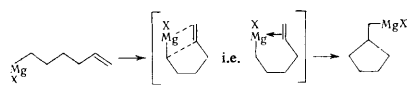
M=Li, MgCl.

In THF, the Grignard reagent rearranges much more slowly than the sodium and lithium compounds, despite the use of less polar hydrocarbons as solvents for the latter. The equilibrium mixture obtained for the organolithium derivative contains more than 99% of the primary compound, which indicates its higher stability compared with the isomeric secondary compounds. It is believed that this isomerisation proceeds via a four-membered cyclic intermediate.

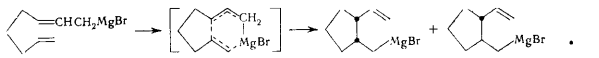
Equilibrium is established in such systems at a very high rate. For example, it is 3×10^{-6} s^{-1} at 140°C and 3.5×10^{-5} s^{-1} at 160°C (obtained from the rate of appearance of α-protons in the ^{1}H NMR spectrum) for deuterated organomagnesium compounds, the isomer concentrations at equilibrium being in proportions of 3 : 2. [302]

It is important to note that cyclobutane does not form even in trace amounts in the isomerisation of allylmethyl compounds [290,291].

Because of the low angular ring strain, cyclopentyl derivatives of metals are fairly stable, but their stability depends strongly on the nature of the organic group. Thus the primary Grignard reagent obtained from 7-bromohept-1-ene forms 7% of methylcyclohexane [303], while the secondary Grignard reagent (from 6-chlorohept-1-ene) gives after hydrolysis a mixture of *cis*- and *trans*-1,2-dimethylcyclopentanes in proportions of 1 : 4 with a yield of 88% [304]:

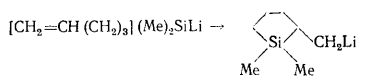


The secondary Grignard cyclises faster than the primary or tertiary reagent in THF at 100°C, all the rearrangements proceeding via first-order reactions. The observed ratios of the *cis*- and *trans*-products undoubtedly indicate an intramolecular mechanism of these reactions (an intermolecular interaction of a Grignard reagent with an isolated double bond is unknown with the exception of the addition of ethylene to allylmagnesium chloride) [305]:

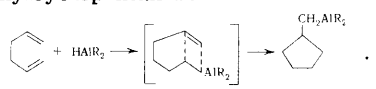


The isomerisation is highly stereoselective. Thus, when an ethereal solution of diene was refluxed, it cyclised smoothly with formation of *cis*- and *trans*-products in yields of 90 and 3% respectively and a 50% decomposition period of 2 h. [306]

Cyclisation involving the formation of cyclopentanes also occurs in the series of organolithium compounds, for example with $CH_2 = CH(CH_2)_3CHRLi$ (R = H or Me) [307], norbornene systems [308], and silicon-lithium derivatives [309], the process being quantitative in the last instance:

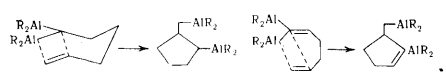


Organic derivatives of Group III metals, particularly aluminium compounds, play an important role in the formation of cyclopentanes. Using these, Ziegler [310] achieved for the first time the cyclisation reaction in the chemistry of ω-unsaturated organometallic compounds. He showed that the interaction of dialkylaluminium hydride with hexa 1,5-dienes gives a quantitative yield of α-aluminomethylcyclopentanes:



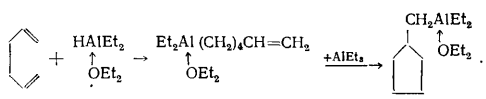
Subsequently this reaction was extended to strained 1,5-dienes [311].

The mode of hydroalumination of vinylacetylenes with subsequent cyclisation can be controlled by choosing an appropriate solvent. For example, the reaction involving hex-1-en-5-yne in ether with subsequent hydrolysis gave the cyclopentane derivative an 80% yield, while in triethylamine the reaction leads to cyclopentenes with the same yield [312]:



The reaction of trialkylaluminium with buta-1,3-dienes also leads to cyclopentanes (yield 27%). [313]

All the reactions described above proved to be feasible only because the cyclisation is faster, even at low temperatures, than the intramolecular addition of dialkylaluminium hydrides to the terminal double bonds. However, such cyclisation can be prevented with the aid of specific coordination. For example, it does not occur with the $Et_2AlH \leftarrow OEt_2$ ether adduct, the acyclic product being formed in 93% yield (>Al ← || intramolecular coordination is impossible), but the adduct can cyclise quantitatively following the addition of a catalytic amount of triethylaluminium, which decomposes the complex and liberates the ω-unsaturated organoaluminium compound [314]:



A general method has been proposed for the cyclisation of hex-5-enyl organometallic compounds based on the exchange reaction between dihex-5-enylmercury and the corresponding metal[315]:

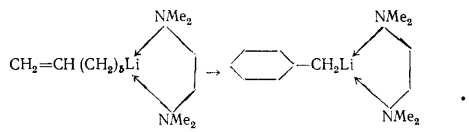
$$\frac{n}{2}\,Hg[(CH_2)_4CH{=}CH_2]_2 + mM \rightarrow mM[(CH_2)_4CH{=}CH_2]_n \rightarrow$$
$$\rightarrow mM[CH_2(\text{cyclo-}\,C_5H_{12})]_n;$$
$$M{=}Li,\ Mg,\ Al,\ Ga,\ In.$$

In non-coordinating solvents, the formation of a ring requires between 1 h and 8 days at 25°C for M = Li (depending on the solvent; 1 h in ether), 24 h at 110°C for M = Mg, 48 h at 40°C for M = Al, 3 weeks at 95°C for M = Ga, and 3 weeks at 110°C for M = In (the reaction times were determined from ^{1}H NMR spectra). The solvent plays a major role in determining the rate of exchange and cyclisation[316]. For lithium, the rate increases in the sequence cyclopentane < benzene ≪ ethyl ether (8 days, 96 h, and 1 h respectively); the aluminium compound could not be isolated from hydrocarbons, while in THF the reaction does not proceed at all and in ethyl and phenyl ethers it occurs to the extent of 4.9 and 95% respectively. These results are consistent with the known behaviour of organolithium compounds in basic media, where intermolecular linkages are broken, which leads to an increase of their reactivity. The opposite effect is observed for aluminium compounds.

It is remarkable that these rearrangements proceed much more readily than the analogous intermolecular reactions. However, they do not occur with but-3-enyl and pent-4-enyl derivatives of metals because of the high strain in the three- and four-membered rings[315].

The ease of cyclisation of hexenyl derivatives of metals decreases in the sequence Al > Mg > Li > Zn ≫ Hg [317] (for zinc, the cyclisation takes place to a very slight extent). This sequence is probably determined by the presence of vacant orbitals in the metal and the polarity of the M–C bond.

On the other hand, the heptenyl derivatives of lithium and magnesium do not form six-membered rings either in ether or in THF, but in the presence of TMEDA, which greatly increases the polarity of the M–C bond, they cyclise readily and irreversibly (special experiments showed that the cyclopentylmethyl and cyclohexylmethyl derivatives of lithium and magnesium are not decyclised in the presence of TMEDA) [307]:



Similar aluminium compounds form cyclohexanes at an elevated temperature[318] in yields up to 70% [316], while octenyl derivatives of aluminium do not cyclise to cycloheptanes.[316]

The comparatively ready cyclisation of ω-unsaturated organometallic compounds should be preceded in many instances by M ← || intramolecular coordination in non-reacting molecules, which has been studied in a number of investigations using various physicochemical methods.

Weak Li ← || intramolecular coordination has been postulated in but-3-enyl-lithium[319] on the basis of ^{7}Li and ^{1}H NMR and infrared and ultraviolet spectroscopic data, which indicate anomalous properties of the double bond.

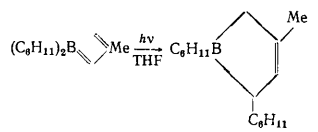
The chain length in olefins has little influence on the electronic environment of the double bond, but the introduction of groups in the terminal positions alters the chemical shifts of the olefinic protons, which are in general correlated with the electron-donating or electron-accepting properties of the substituents. For example, dibut-3-enyl- and dihex-5-enyl-zinc have the normal parameters of the ^{1}H NMR spectrum (the signals of the olefinic protons are located in the same region as for the corresponding pure alkenes) and there is no coordination interaction in these compounds. On the other hand, the spectrum of dipent-4-enylzinc is anomalous: compared with pent-1-ene, the chemical shifts due to the protons of the olefinic and α-carbon atoms are displaced downfield owing to the decreased electron density at the double bond. Furthermore, the signals due to the α-protons are displaced downfield even more at −70°C or on formation of a complex with 2,2′-bipyridyl. These data suggested the existence of weak Zn ← || intramolecular coordination[317,320]. It was impossible to study dipent-4-enylmagnesium by a similar procedure because of its insolubility in coordinating solvents, and in the analogous mercury compound there is no such coordination[320].

Alkenyl derivatives of Group III metals exhibit the same characteristics. For example, in the infrared spectra of alk-4-enyl derivatives of aluminium the band due to the ν(CH) deformation vibrations of the olefinic linkage is displaced by 30–38 cm^{-1} towards shorter wavelengths and the band due to the ν(C=C) vibrations is displaced by 22–23 cm^{-1} towards longer wavelengths compared with the initial olefins. The compounds are monomeric in benzene and their spectra change following dilution by hydrocarbons. However, the >Al ← || intramolecular coordinate linkage is ruptured under the influence of Lewis acids, since ether adducts, for example, have the normal ν(CH) and ν(C=C) frequencies. Intramolecular coordination in non-reacting alk-4-enylaluminium compounds (cyclisation occurs only at elevated temperatures) is confirmed additionally by ^{1}H NMR spectra where the $\delta_{CH=CH}$ signals are displaced downfield by 0.3 p.p.m., while the δ_{CH_2} signals of the isobutyl groups are displaced upfield by 0.15 p.p.m., compared with the 6- and 7-enyl homologues of aluminium, in which there is no coordination (no frequency shifts were observed in the spectra)[321].

It is interesting to note that the signals of the olefinic protons are displaced upfield also on formation of a complex with trimethylamine, and the shifts are independent of concentration. This clearly indicates an intramolecular mechanism of these processes. The energy of the >Al ← || intramolecular coordinate bond has been estimated as at least 2–5 kcal mole^{-1}.[322]

^{1}H, ^{13}C, and ^{119}Sn NMR and infrared and Mössbauer spectra have shown[323,324] that there is no M ← || coordination in the alkenyl derivatives of Group IV elements of type >M(CH$_2$)$_n$CH = CHR (M = Si, Ge, or Sn; n = 1 or 2; R = H or Ph).

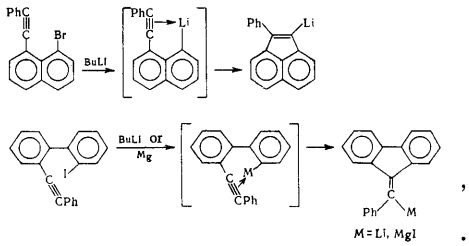
The photochemical cyclisation of dienylboranes to boracyclopent-3-ene is exceptional [ν(C=C) = 1635 cm^{-1}; monomeric state in benzene[325]] and probably proceeds via intramolecular coordination:



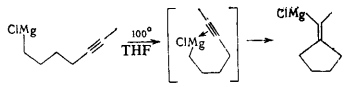
2. Acetylenes

The intramolecular addition of organometallic compounds to an isolated acetylenic bond has been little investigated, but is of considerable practical interest for the synthesis

of various classes of vinyl compounds. It has been shown that such interaction in rigidly fixed systems depends on the relative positions of the C≡C triple bond and the M–C bond.[326,327] For example, when 8-bromo-1-phenylethynylnaphthalene is metallated with butyl-lithium, it cyclises, but the cyclisation reaction does not proceed with the corresponding Grignard reagent. The difference is undoubtedly associated with the much higher polarity of the C–Li bond compared with C–Mg. The carbon skeleton of 2-chloro-1-phenylethynylbenzene does not change when chlorine is replaced by lithium or magnesium, while treatment of 2-iodo-2′-phenylethynylbiphenyl with butyl-lithium or magnesium results in cyclisation to a five-membered ring:



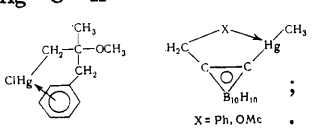
Aliphatic systems with triple bonds may be of preparative importance for the synthesis of ethylidenecyclopentanes. For example, when the Grignard reagent derived from 7-chlorohept-2-yne is refluxed for 6 days at 100°C with subsequent hydrolysis, the yield is 90%; however, the yield falls to several per cent in the absence of refluxing. There is no doubt that the isomerisation takes place after the formation of the Grignard reagent, the 50% cyclisation period of which is 50 h at 100°C:[328]



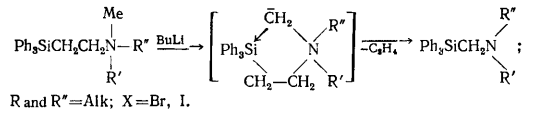
Similar reactions with 7-halogeno-oct-2-ynes yield substituted ethylidenecyclopentanes, the 50% cyclisation period for the bromide, amounting to about 15 h at 100°C. Like the alkenyl derivatives, secondary alkynyl Grignard reagents cyclise faster than the primary reagents, the smaller of the two possible rings being formed, i.e. ethylidenecyclopentanes and not the more stable methylcyclohexenes.[305,328]

3. Aromatic Compounds and Carbanions

According to ^{1}H NMR spectra, Hg<C6H5 intramolecular coordination probably occurs in 2-methoxy-2-methyl-3-phenylpropylmercury, since the methylene protons are found to be non-equivalent, the non-equivalence diminishing sharply when strong solvating solvents, for example pyridine, capable of breaking the coordinate linkage, are used[329]. J_{HgCCCH_3} changes in the same way. A similar interaction has also been proposed for methylmercury derivatives of carboranes in view of the similar influence of solvents on $J^{199}Hg-C-^1H$.[330]



A very rare instance of possible intramolecular coordination with a carbanion has been described recently. Three base-catalysed rearrangements of quaternary ammonium salts are known—the Stevens, Sommelet-Hauser, and Hofmann rearrangements. On the other hand, a specific rearrangement of the molecular skeleton of silicon derivatives takes place. When silylethylammonium salts were treated with an excess of butyl-lithium and then with water, silylmethylamines were obtained as the main product[331] and the Stevens rearrangement was not observed:



R and R″=Alk; X=Br, I.

The amines are probably formed as a result of intramolecular attack by the negative charge on the silicon atom in the intermediate carbanion, which leads to the ejection of ethylene. In the case of R″ = Ph, there is no rearrangement and only *NN*-dimethylaniline has been isolated.

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The data described demonstrate convincingly the increasing importance of intramolecular coordination for the understanding of many aspects of the structure and reactivity of organic derivatives of the elements, and particularly its decisive involvement in preparative syntheses of many classes of organic compounds, the preparation of which by other methods is either difficult or impossible. On the other hand, the concept of intramolecular coordination has not been justified theoretically and it is often difficult to demonstrate it experimentally. However, this field of the chemistry of organic derivatives of the elements began to develop vigorously only recently and holds out much promise for the immediate future.

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