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Intramolecular Coordination in Organic Derivatives of the Elements

A.K.Prokof'ev, V.I.Bregadze, and O.Yu.Okhlobystin

For the first time, the data on the problem of intramolecular coordination in organic derivatives of the elements have been compiled and a systematic and critical account has been given. A definition of intramolecular coordination in its various forms is proposed. It has been shown that intramolecular coordination may constitute the driving force of a number of reactions of such organic derivatives (α-, β-, and γ-elimination).
The bibliography comprises 210 references

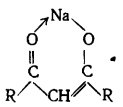
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I. INTRODUCTION

The concept of intramolecular coordination between a metal atom with vacant orbitals and an electron-donating atom in the same molecule has been recently put forward with increasing frequency to account for a number of physical anomalies associated with the structure of organometallic molecules and also in the interpretation of many of their reactions. Since the possibility of such coordination exists in principle, it is frequently postulated on the basis of purely intuitive considerations without more serious justification.

A typical example, dating back to as early as 1925, is the attribution of a chelate structure with covalent bonds to sodium enolates of β-dicarbonyl compounds on the basis of their relatively low melting points and appreciable solubility in aprotic solvents[1]:



Subsequently Brändström[2,3] attempted to use these concepts to explain the dual reactivity of alkali metal enolates.

The aim of the present review is to give a systematic account of the most important postulates put forward in connection with intramolecular coordination and to assess their possible role in organometallic reactions. It is scarcely useful to consider here also the numerous and well known cases of donor–acceptor interaction between two adjacent atoms (for instance, boron and nitrogen atoms in systems of the type of borazole, $d_\pi - p_\pi$ interaction in silylamines, etc.), although they can in fact be regarded as a special case of intramolecular coordination. Chelate compounds in which the electron-donating atom is in a side chain while the chain itself is separated from the metal by a heteroatom (acetylacetonates and related compounds) also will not be considered in detail if they are not truly organometallic compounds, i.e. do not contain at least one direct metal–carbon bond. Attention will be concentrated on compounds in which the carbon chain with the electron-donating atom is linked to the metal via a carbon atom:

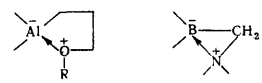


where D is the electron-donating atom.

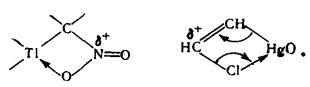
Frequently in cases where intramolecular coordination in a non-reacting molecule is rejected for some reason, a hypothesis of this kind is suggested for the transition state. Cases of this kind will also be considered briefly.

II. THE CONCEPT OF INTRAMOLECULAR COORDINATION

So far a serious theoretical basis for an intramolecular bond of this kind is lacking. Apparently the majority of investigators who postulated it agree that this is donor–acceptor interaction of the "hydrogen bond type". Nevertheless it is evident that in reality extreme cases are possible which could be regarded as qualitatively different. On the other hand, D → M interaction may be equivalent to almost complete charge transfer, i.e. the transfer of two electrons; we are then dealing with a stable intramolecular complex of the "reverse onium" type (ate-complex). In this class of intramolecular organometallic complexes, one may include, for example, the γ-alkoxy-derivatives of aluminium and certain amine complexes of boron, for example:

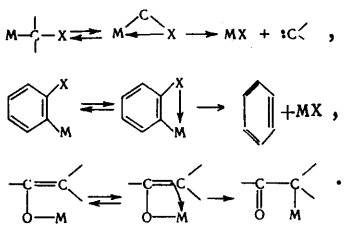


The charge transfer may not be quite so complete; such compounds resemble more the classical electron-deficient molecules (diborane, trimethylaluminium) containing three-centre bridge bonds, where the bond between the three nuclei is formed by two electrons. In this case a coordination-unsaturated metal atom and an atom with a considerable positive charge produced by its electronegative substituents serve as the electron-deficient centres. Such are, for example, the α-nitroalkyl derivatives of thallium and *cis*-β-chlorovinylmercury chloride:

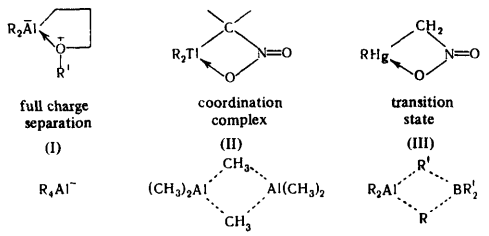


The similarity of these structures to the four-centre transition states in S_Ei reactions is not merely formal: there is finally a possibility of the case where a cyclic structure with a coordinate intramolecular bond is formed only as a transition state. These are the well known

reactions involving the formation of carbenes and dehydrobenzene and O–C rearrangements of non-ionic enolates.



Thus it is possible to distinguish three different types of intramolecular coordination reactions in organometallic compounds. Firstly, coordination interaction with full charge separation, as in compounds such as the tetraalkylaluminium salts, secondly, coordination complexes analogous to the trimethylaluminium dimer with bridge bonds, and, thirdly, intramolecular coordination occurring only in transition states, similar to the bridge type transition states in radical exchange reactions involving many organoaluminium and organoboron compounds:



However, it is important to remember that in all the above cases the driving force in the formation of bonds, possible rearrangements, or eliminations is the same: the coordination unsaturation of the metal atom which tends to make good its electron deficit at the expense of a donor in the same molecule, their interation (D → M) taking place through space in addition to a conjugation or induction chain.

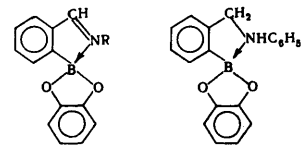
III. INTRAMOLECULAR COORDINATION AND PHYSICAL PROPERTIES OF THE MOLECULES

There is no doubt that the occurrence of intramolecular coordination may affect the physical properties of organometallic molecules. Indeed, in many cases the characteristic features of NMR and NQR spectra and dipole moments, the anomalous effects of *ortho*-substituents, etc. are attributed to such coordination interaction. Analysis of the literature data leads to the conclusion that in fact none of the usual methods can alone provide an answer as to the presence or absence of intramolecular coordination. Evidently such coordination can be reliably inferred only on the basis of consistent data derived by a number of methods. The situation is complicated also by the fact that factors such as intramolecular association (particularly in crystals), inductive and resonance effects, electrostatic attraction or attraction through space ("field effects"), etc. are superimposed on intramolecular coordination interaction.

Vibration Spectra

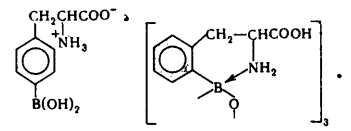
The presence of intramolecular coordination is frequently inferred from optical spectra of organic boron derivatives which show a distinct tendency towards the attainment of the tetrahedral sp^3 configuration.

B → N coordination interactions are therefore suggested for compounds of the type

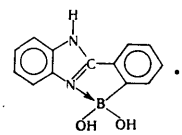


on the basis of a broad absorption band at 1220 cm^{-1}, which can be accounted for by B → N vibrations. The authors also postulate the possibility of intermolecular interaction.

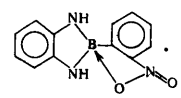
Comparison of the infrared spectra of boron-containing phenylalanines shows that the spectrum of the *ortho*-derivative exhibits, in contrast to the *para*-derivative, an intense broad band at 1710 cm^{-1}, which is characteristic of an unionised carboxylic acid:



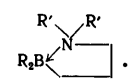
B → N intramolecular coordination has been proposed[6] for 2-(2-boronophenyl)benzimidazole on the basis of the high melting point (> 320°C) and the presence of $\lambda_{max} \simeq$ 310 nm in the ultraviolet spectrum (in 95% ethanol), while 2-(2′-methylphenyl)benzimidazole has λ_{max} = 277 nm. The absence of intense absorption in the region 7.2–7.8 μm is evidence that the boron atom is coordinated to four groups:



In view of the lower absorption intensity in the region of 350–400 nm of the ultraviolet spectra of 2-phenylbenzo-1,3,2-diazaborolines, compared with unsubstituted 2-(nitrophenyl)benzimidazoles, O → B intramolecular coordination, which is absent from the corresponding *meta*- and *para*-nitro-derivatives, is postulated[7]:

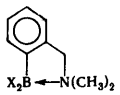


The dependence of the strength of the B → N coordinate bond on substitutents has been determined for γ-aminopropyl compounds[8,9]:



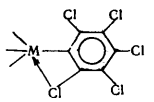
In the unsubstituted amine (R′ = H) coordination is postulated on the basis of the bathochromic shift of the NH_2 stretching vibration bands (3292 and 3350 cm^{-1}), which is characteristic of compounds with a B ← N coordinate bond. The occurrence of such interaction is supported also by the resistance to disproportionation (up to 200°C), which is high for asymmetric boron trialkyls, the relative stability in air, and high dipole moments (4.0–4.2 D). The substitution of a hydrogen atom at the nitrogen atom by dialkyl groups or the introduction of an alkoxy-group at the boron atom lowers the strength of the B ← N bond, while in the

compound $(EtO)_2BCH_2CH_2CH_2NEt_2$ there is probably no coordination at all (μ = 1.44 D). Similar coordination has been proposed[10] for compounds of the type

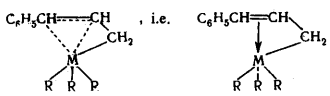


where X = OH or $N(CH_3)_2$. These compounds are relatively resistant to hydrolysis; furthermore, diamineboron distils in a vacuum (75–76°C/0.4 mmHg).

The ultraviolet spectra of pentachlorophenyl derivatives of silicon and tin show a much more intense absorption than the spectra of their hydrogen analogues; in view of this, intramolecular coordination was suggested as the explanation of many unusual properties of these compounds[11]:

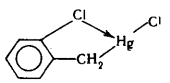


Substitution of the β-methyl proton in *trans*-β-methylstyrene by a $(C_2H_5)_3M$ group (where M = Si, Ge, or Sn) gives rise to a bathochromic shift, which has been explained[12] by an increase in the delocalisation of the π electrons of the allyl double bond through overlap with the vacant *d* orbitals of the metal



where M = Si, Ge, or Sn and R = C_2H_5.

A split Hg–Cl frequency (314, 364, and 251 cm^{-1}) in the infrared spectrum of *o*-chlorobenzylmercury chloride is accounted for by the existence of several rotational isomers[13]. The most intense band (314 cm^{-1}) is attributed to a conformation with possible intramolecular interaction:

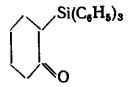


Recently, extensive experimental data have accumulated on the spectra of α-carbonyl organometallic compounds[14]. In the α-carbonyl derivatives of mercury and tin the carbonyl absorption in the infrared spectra is displaced towards lower frequencies (1686–1660 cm^{-1}) and in the ultraviolet spectra a slight displacement of the CO band towards longer wavelengths and a considerable increase of the intensity (by a factor of 200–300) compared with the carbon analogues has been observed, which suggests that these compounds have properties approaching those of conjugated systems. These data, together with the observed dual reactivity of α-metallated aldehydes and ketones, led to the conclusion that there is σ,π-conjugation in compounds of this kind[15,16]. However, Japanese investigators[17] believe that the considerable shift of the carbonyl frequency (ν_{CO} = 1645 cm^{-1}) in $Hg(CH_2CHO)_2$ and $ClHgCH_2CHO$ spectra can be explained by CO → Hg intramolecular coordination (the formation of a polymer is also possible), since in the spectra of acetaldehydemercury ν_{CH} = 2720 cm^{-1}, which corresponds to the normal vibrations in aldehydes; furthermore, this compound undergoes the usual reactions typical of the aldehyde group.

The lowering of ν_{CO} in the spectrum of $(C_6H_5)_3SiCH_2COC_6H_5$ (1667 cm^{-1}) compared with the carbon analogue (1698 cm^{-1}) has been explained by the inductive effect of silicon on the carbonyl group[18].

Thus the unusual spectroscopic properties of α-metallated ketones and aldehydes cannot be explained by any one effect. For this reason, attempts have been made in a number of investigations to discover the principal effect resposible for these anomalies. The significant difference between the observed and calculated frequencies of the carbonyl groups (the calculation was based on Thompson's equation $\nu_{CO} = 1720 + 15\Sigma\sigma^*$ cm^{-1}) [19] in $(CH_3)_3SiCH_2COCH_3$ (1698 and 1716 cm^{-1}) and $(CH_3)_3CCH_2COCH_3$ (1723 and 1717 cm^{-1}) suggested that intramolecular coordination in $(CH_3)_3SiCH_2COCH_3$ predominates over the inductive effect of silicon[20]. However, Thompson's relation was derived for compounds of the type CCl_3COCl, in which the field effect and other factors can be more important than inductive effects. Therefore this relation cannot be extended without modifications to the ketones considered above. The same workers later interpreted the higher intensity of the $n \rightarrow \pi^*$ transition (by a factor of 4–5) in α-silylketones relative to their carbon analogues as confirmation of the presence of intramolecular CO → Si coordination, since they believe that the intensity of this transition in related ketones cannot be accounted for by steric and inductive effects[21]. However, the study of β-substituted ketones shows that the exaltation of the $n \rightarrow \pi^*$ transition in these compounds can be explained by many factors and not necessarily the same ones which are responsible for the shift of the carbonyl frequency[22,23].

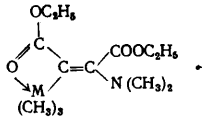
An attempt has been made to separate the inductive effects from other effects influencing the frequency of the carbonyl absorption in the spectrum of α-triphenylsilylcyclohexanone[24]:



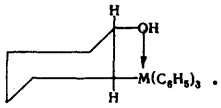
Since the frequency of the CO group in the spectrum of this compound in liquid paraffin is represented by a singlet at 1678 cm^{-1} and in the spectrum of the carbon analogue at 1709 cm^{-1}, it was concluded that Fermi resonance is unlikely. In carbon tetrachloride solution the singlet corresponding to the carbon compound is observed at 1720 cm^{-1}, while in the case of the silicon derivative it is split into two bands (1682 and 1692 cm^{-1}). The splitting is independent of concentration in the range 0.2–10%, which excludes intermolecular interaction. The splitting can be accounted for by a conformational equilibrium, since the relative intensities of the two peaks vary with temperature. The inductive effect of silicon should not depend on the conformation of the cyclohexane ring, whereas intramolecular coordination is possible only in the conformation where the silicon is equatorial. The results may be explained by the cooperative effect of the intramolecular CO → Si coordination and the inductive effect of silicon.

Intramolecular coordination has been proposed also for α-ethoxycarbonyl derivatives of Group IV elements, although it should be weaker than in the corresponding α-ketones. In organotin diazo-esters $R_{4-n}Sn[C(N_2)COOC_2H_5]_n$ (n = 1,2) it has been proposed on the basis that the dipole moment μ = 2.2 D (for n = 1 and R = CH_3) and also a considerable shift of the carbonyl (2070–2045 cm^{-1}) and diazo- (1675–1655 cm^{-1}) frequencies compared with the carbon analogues[25]. Intramolecular coordination is responsible for the splitting of the C=O bands (1735 and 1680 cm^{-1} for the silicon derivative, 1739 and 1698 cm^{-1} for the germanium derivative, and 1740 and 1705 cm^{-1} for the tin derivative) and the bands due to C=C vibrations (1570 and 1550 cm^{-1} for the silicon derivative, 1590 and 1555 cm^{-1} for the germanium derivative, and 1625 and 1590 cm^{-1} for the tin

derivative) in the infrared spectra of compounds of the type[26]:



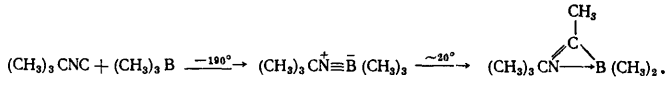
1,2-Disubstituted cyclohexanols of the type $2\text{-}(C_6H_5)_3MC_6H_{10}OH$ (M = Si or Ge) have been found to have a higher acidity[24] than 1-triphenylmethyl-2-cyclohexanol in view of the greater changes in the vibration frequencies of the hydroxy-group on addition of dimethyl sulphoxide and tetrahydrofuran. Since the electropositive effect of silicon and germanium should reduce the acid strength, the above anomalous increase of acidity is explained by an intramolecular interaction between oxygen and the metal



A similar interaction is postulated on the basis of the changes under analogous conditions in the infrared spectra of the silicon and germanium analogues of 1,1,1-triphenylethanol[27].

Radio-frequency Spectroscopy

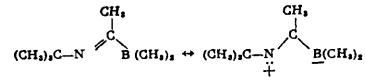
Attempts have often been made to demonstrate the presence of intramolecular coordination in organoboron compounds by proton resonance. The product of the addition of trimethylboron to t-butyl isocyanate isomerises at room temperature to a three-membered chelate complex which is resistant to the action of oxygen and moisture[28]:



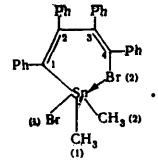
The PMR spectrum of the complex in benzene consists of three peaks δ: 2.57 p.p.m. (very broad), 1.18 p.p.m. (sharp), and 0.20 p.p.m. (broad) in proportions of 1 : 3 : 2, which correspond to the groups $=\overset{|}{C}-CH_3$, $-\overset{|}{C}-CH_3$, and $>B-CH_3$. In the infrared spectrum there is no frequency due to the stretching vibrations of the $\overset{+}{N}\equiv\overset{-}{C}$ group (2247 cm^{-1}) but there is a $\nu_{N=C}$ frequency at 1548 cm^{-1}. The mass spectrum of the complex corresponds to a monomeric structure†. The formation of a three-membered ring is undoubtedly caused by a steric factor, since less hindered isonitriles dimerise with formation of 2,5-dibora-2,5-dihydropyrazines[29].

Intramolecular (and intermolecular) coordination[30] is postulated in the molecule of dimethylaminomethylboron $(CH_3)_2BCH_2NH_2$. This compound is a weak acid and a weaker base than the corresponding monofunctional derivative; in the PMR spectra δ_{CH_2} is displaced towards stronger fields—0.24 p.p.m. (60 MHz) (δ_{CH_2} for cyclopropane is 0.20 p.p.m.).

† On the basis of the mass spectra, the authors believe that a preferable structure is the resonance hybrid:



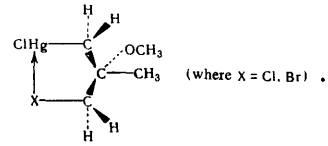
Intramolecular Sn ← Br interaction has been most convincingly demonstrated for 4-bromo-1,2,3,4-tetraphenyl-*cis*-*cis*-1,3-butadienyldimethyltin bromide[31]:



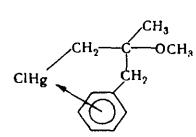
At 36°C the PMR spectra of this compound in carbon tetrachloride has a doublet with components of equal intensity due to the methyl protons (δ = 0.48 and 0.98 p.p.m.), which merges into a singlet at 87°C. There is a pronounced solvent effect: the addition of bases (pyridine, ethers, alcohols, etc.) to a solution of the compound in carbon tetrachloride gives rise to a singlet at δ = 0.73 p.p.m. At the same time in thionyl chloride (strongly ionising solvent) the temperature at which the doublet merges into a singlet is close to that for carbon tetrachloride. The non-equivalence of the methyl protons in the diene has been explained by intramolecular Sn ← Br interaction which stabilises the non-planar cisoid conformation and prevents rotation about the C(2)–C(3) bonds at low temperatures in non-basic solvents. The barrier to rotation about the C(2)–C(3) bonds, determined from the PMR spectra, is equivalent to 18.3 ± 0.23 kcal $mole^{-1}$. The hindered rotation of the diene and the non-equivalence of the methyl protons can be eliminated by breaking the weak coordinate bond Sn ← Br, which is observed experimentally on heating the specimen, the addition of a base competing with Br(2) in the coordination with Sn, and replacement of Br(2) by hydrogen. The suggested conformation of the diene has been confirmed by X-ray analysis[31].

The formation of an intramolecular complex in the Reformatskii reagent derived from $BrCH_2COOC_2H_5$ is suggested on the basis of the shift to higher fields of the signal due to CH_2 protons in the NMR spectrum with increasing solvating power of the solvent[32].

The formation of a ring by an intramolecular donor–acceptor interaction between mercury and halogen atoms in γ-halogenopropyl derivatives of mercury is the cause of the non-equivalence of the methylene protons [$\Delta\nu$ (CH_2Br) = 19.1 Hz, $\Delta\nu$ (CH_2Hg) = 13.6 Hz]:[33]



This non-equivalence diminishes sharply if a solvent such as pyridine, capable of breaking the coordinate bond, is employed. This entails also a decrease of the spin–spin coupling constant J_{HgCCCH_3} (36 Hz in deuterochloroform and 20 Hz in pyridine). The intromolecular π-coordination of the phenyl group with the mercury atom has been demonstrated for 2-methoxy-2-methyl-3-phenylpropylmercury chloride on the basis of the non-equivalence of the methylene protons, the J_{HgCCCH_3} constant, the effect of solvents, the temperature factor, and dilution[34]:

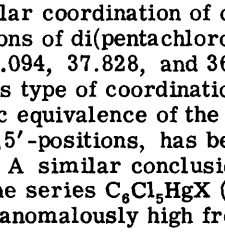


NMR spectroscopy has proved to be a powerful method for the investigation of intra- and inter-molecular coordination. The splitting of the lines due to the chlorine atoms in the CCl_3 group in the ^{35}Cl NMR spectra of the compounds Cl_3CHgBr (37.590, 37.893, 38.794, and 39.032 MHz), Cl_3CHgCl (37.604, 37.968, 39.032, and 39.172 MHz), and $(Cl_3C)_2Hg$ (37.037, 37.681, 38.675 MHz), which is considerable (> 2%), exceeding the limiting crystallographic splitting for molecular crystals with van der Waals interaction between molecules[35], has been explained by intramolecular interaction between one of the chlorine atoms of the CCl_3 group and the mercury atom[36,37]. However, this coordination, which has been confirmed by X-ray diffraction analysis[37], readily breaks down on formation of complexes of the above mercury compounds with dimethoxyethane (the appreciable line splitting vanishes from the ^{35}Cl NMR spectra)[38]. It is interesting that complexes are not formed with ethyl ether. Intramolecular coordination in Cl_3SnCH_2Cl has been proposed on the basis of spectroscopic data[39] and has been confirmed[40] by ^{35}Cl NMR spectra. The spectrum corresponding to the $SnCl_3$ group consists of two lines with intensity ratios of 1 : 2 and a splitting of 6% (23.072, 23.072, and 21.832 MHz), which is three times greater than the maximum possible crystallographic splitting. The non-equivalence of the chlorine atoms can be explained by the coordination interaction Cl → Sn in the Cl–Sn–CH_2–Cl plane.

The cryoscopic determination of the molecular weight in benzene shows that there is no association. Furthermore, the possibility of coordination is not inconsistent with the results of studies of the ^{35}Cl NMR spectra of Cl_3SnCH_2Cl in benzene and ether (1 : 1 and 1 : 2).[41] For test compound : solvent molar ratios of 1 : 1 and 1 : 2, the spectra of Cl_3SnCH_2Cl proved to be identical and therefore only 1 : 1 complexes are formed.

The complex $SnCl_4.2(C_2H_5)_2O$ consists of a tetragonal bipyramid in which four chlorine atoms are located at the base and the ether group are at the vertices[42]. The number of lines and their splitting, assigned to the $SnCl_3$ group in the complexes of Cl_3SnCH_2Cl with benzene and ether, is very similar to that in the spectrum of $SnCl_4.2(C_2H_5)_2O$. Therefore one may suppose that these complexes too have the structure of a tetragonal bipyramid in which three chlorine atoms are located at the base. Probably one of the vertices of the bipyramid is occupied by the coordinated chlorine of the CH_2Cl group and the other by a ligand molecule (Fig. 1).

The intramolecular coordination of chlorine atoms in the 2,2′- or 6,6′-positions of di(pentachlorophenyl)mercury (38.220, 38.220, 38.094, 37.828, and 36.421 MHz), where the evidence for this type of coordination comes also from the crystallographic equivalence of the chlorine atoms in the 3,4,5- and 3′,4′,5′-positions, has been demonstrated by the same method. A similar conclusion was reached also for compounds of the series C_6Cl_5HgX (X = Cl, C_6H_5, or CH_3) in view of the anomalously high frequency shifts in the ^{35}Cl NMR spectra compared with the usual substituents, of the *o*-chlorides compared with the *m*- and *p*-chlorides[43].



On the basis of ^{35}Cl NMR data[44], dipole moments[45], and the relative capacities for complex formation[46] of *cis*- and *trans*-β-chlorovinylmercury chlorides, it has been suggested that there is powerful intramolecular coordination in the *cis*-chloride molecule. Crystals of the *cis*-chloride (m.p. 55°C) are amorphous to X-rays and their ^{35}Cl NMR spectrum shows a single C–Cl frequency (33.132 MHz), which excludes the possibility of intramolecular coordination of the type occurring in the *trans*-chloride crystals. While the dipole moment of the *trans*-chloride (1.82 D in benzene at 25°C) agrees satisfactorily with the value calculated for the ideal model (1.92 D), for the *cis*-chloride there is a considerable discrepancy between the observed and calculated moments (2.92 and 3.57 D respectively). This last finding can be probably accounted for only by a considerable decrease in the angles ClCC and CCHg in consequence of intramolecular coordination. In contrast to the *trans*-analogue, the *cis*-chloride does not form a complex with pyridine, which shows that the mercury atom is coordination-saturated; the capacity of the *cis*-isomer to eliminate acetylene under the action of nucleophilic reagents is also sharply reduced[45].

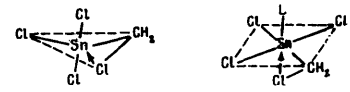
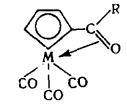


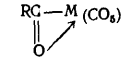
Figure 1. Structures proposed for Cl_3SnCH_2Cl and its ether and benzene complexes.

The conclusion that there is direct intramolecular interaction between the metal atom and the substituent is based[47] on the increase of the asymmetry parameter (η) in the ^{55}Mn, ^{187}Re, and ^{185}Re NMR spectra on introduction of a group COR (R = CH_3, CF_3, or C_6H_5) into the cyclopentadienyl ring of cyclopentadienylmetal tricarbonyls:



(M = Mn, Re).

Interaction of the same type between the oxygen of the acyl group and the metal has been postulated for acyl derivatives of manganese and rhenium pentacarbonyls on the basis of the infrared spectra[48] in combination with X-ray structural data[49,50]:



Structures

X-Ray diffraction analysis is used comparatively rarely to determine the structures of organometallic compounds with intramolecular coordination.

It has been found[51] that phenylsilatrane $C_6H_5Si(OCH_2CH_2)_3N$ consists of a distorted trigonal bipyramid with the nitrogen and carbon (from the phenyl group) atoms located at the vertices. The N–Si–C atoms lie almost on a straight line [deviation 0.016 Å (0.016°? Ed. of Translation)]. The silicon atom deviates from the plane of the oxygen atoms by 0.204 Å towards the phenyl carbon atom: ∠ C–Si–O (mean) = 97.1°; ∠ O–Si–O (mean) = 118.5°; l_{SiO} = 1.638–1.665 Å; l_{SiN} = 2.193 Å.

Ethylgermanatrane has a similar configuration[52]. The germanium atom deviates from the plane of the oxygen atoms by 0.23 Å towards the ethyl carbon atom: $\angle N-Ge-C = 176°$; $l_{GeN} = 2.25$ Å. In view of the experimentally established fact that the structures of the ethylgermanatrane and ethylsilatrane crystals are isomorphous, ethylsilatrane has a similar structure with corrections for the different covalent radius of silicon.

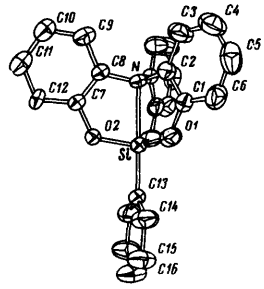


Figure 2. (2, 2′, 2″-Nitrilotriphenoxy)phenylsilane.

(2,2′,2″-Nitrilotriphenoxy)phenylsilane $C_6H_5Si(OC_6H_4)_3N$ also has the configuration of a distorted trigonal bipyramid[53]. The angle $\angle C-Si-O$ (mean) = 100.0° is much greater than the analogous angle for the triethoxy-analogue (97.3°) and lies approximately halfway between 90° (for the ideal trigonal bipyramid) and 109.5° (in the tetrahedron). The angle $\angle N-Si-C = 180°$ and the Si–N distance is 2.344 Å (2.179 Å in the triethoxy-analogue), which is 0.5 Å longer than the normal Si–N bond (Fig. 2).

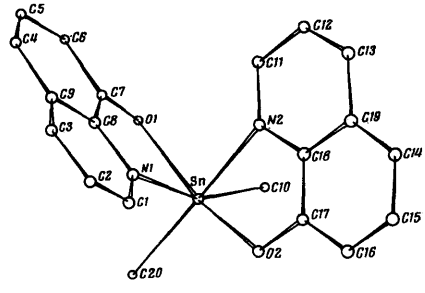


Figure 3. Di-(8-hydroxyquinolato)dimethyltin.

The configuration of di-(8-hydroxyquinolinato)dimethyltin $(CH_3)_2SnOx_2$ (Ox = 8-hydroxyquinoline) has also been determined[54] and found to be a highly distorted octahedron with the methyl groups in the *trans*-positions and the following bond lengths (Å): Sn–C 2.15 and 2.17, Sn–O 2.10 and 2.11, and Sn ← N 2.31 and 2.38; the angle $\angle CSnC$ is almost tetrahedral (110.7° ± 0.80°) (Fig. 3).

The intramolecular Sn ← Cl coordination interaction has been found unexpectedly in bipy$(OC)_3ClMoSnCH_3Cl_2$.[55] Tin in the crystals of this compound may be regarded as having a distorted trigonal bipyramidal environment in which Cl(1) and Cl(3) are linked to tin and molybdenum respectively; Cl(1)SnCl(3) = 168°. The chlorine atom linked to molybdenum is at a distance of 2.81 Å from the tin atom and is clearly linked to both metals (Fig. 4).

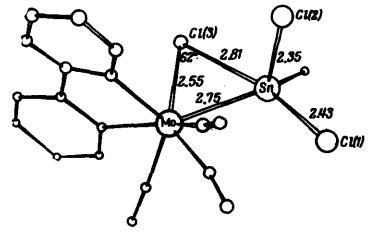


Figure 4. The structure of bipy$(OC)_3ClMoSnCH_3Cl_2$.

X-Ray diffraction analysis confirmed the occurrence of the intramolecular interaction Sn ← Br proposed for (4-bromo-1,2,3,4-tetraphenyl-*cis*-*cis*-buta-1,3-dienyl)dimethyltin bromide[31]. The presence of a weak coordinate Sn ← Br bond with a length of 3.769 ± 0.007 Å, which is shorter by 0.4 Å than the sum of the van der Waals radii of tin and bromine, has been demonstrated. For this interaction to be possible, the angle $\angle C(1)SnCH_3(1)$ has increased to 130.3° from the normal tetrahedral value of 109.5°.

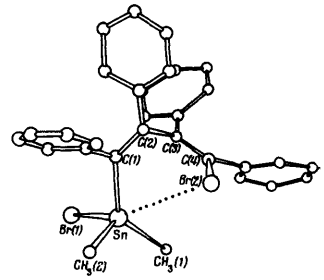
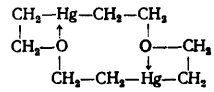


Figure 5. (4-Bromo-1,2,3,4-tetraphenyl-*cis*-*cis*-buta-1,3-dienyl)dimethyltin.

Furthermore, the lengths of the bonds involving Sn have increased from their normal values and also the bond C(4)–Br(2) has become appreciably longer. Normal bond lengths have also been observed (Å): Sn–Br(1) 2.507 ± 0.007 (2.46), Sn–C(1) 2.19 ± 0.04 (2.14); $Sn-CH_3(1) = Sn-CH_3(2)$ 2.24 ± 0.04 (2.18), and C(4)–Br(2) 2.01 ± 0.04 (1.89) (see Fig. 5).

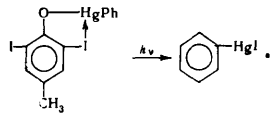
The crystal structures of α-substituted CCl_3HgBr, CCl_3HgCl,[37] $CBr_2ClHgBr$,[56] and CBr_3HgBr,[57] β-substituted (*trans*-ClCH=CHHgCl,[58] *trans*-ClCH=CHHgBr,[59] and $ClHgCH_2CHO$,[56] and γ-substituted $(CH_3)_2C(OC_2H_5)C(CH_3)_2.CH_3HgSCN$,[60] $(CH_3)_2C(OCH_3)C(CH_3)_2CH_2HgI$, $(CH_3)_2C(OCH_3)C(CH_3)_2CH_2HgSCN$,[61] *o*-$ClC_6H_4CH_2HgCl$,[56] and *p*-$CH_3C_6H_2(I_2)OHgC_6H_5$[62] derivatives of organomercury compounds have been investigated. It has been found that

in compounds with chlorine and oxygen atoms in the α-, β-, and γ-positions the Hg...X interaction does not usually result in Hg...X distances markedly different from those normally observed when different molecules come into contact. An exception is the dimeric molecule of $\beta\beta'$-oxidodiethylmercury[63], where the mercury atom is coordinated to an oxygen atom as well as two carbon atoms (Hg...O distance 2.21 Å):

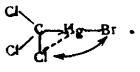


When the α-, β-, and γ-substituents are bromine, sulphur, and iodine atoms, intramolecular interaction in this case leads to a deviation of the Hg...X distances from the values corresponding to different molecules in contact: in CBr_3HgBr we have 3.00 Å for Hg...Br_I, 3.36 Å for Hg...Br_{II}, and 3.40 Å for Hg...Br_{III}; in derivatives of dithizone $Hg(C_{13}H_{12}N_4S)_2.2C_5H_5N$ the mercury atom has a nearly tetrahedral configuration: in the environment of the mercury atom there are two sulphur atoms at a distance of 2.4 Å and two sulphur atoms at a distance of 2.5–2.6 Å, with the valence angles SHgS = 155° and NHgN = 102°.

In the compound p-$CH_3C_6H_2(I)_2OHgC_6H_5$ the Hg...I intramolecular interaction leads to the photochemical decomposition of the crystals under the action of X-rays and the formation of phenylmercury iodide[62]:

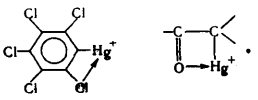


Under the action of X-rays, one of the chlorine atoms in the CCl_3 group in CCl_3HgBr crystals is replaced by bromine[37]:

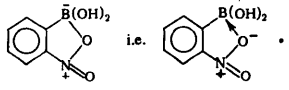


Other Methods

The low rate constants for the electrochemical reduction of β-carbonyl and pentachlorophenyl derivatives of mercury have been explained by the reduced positive charge at the mercury atom due to intramolecular coordination[64]:



The anomalously low acidity of o-nitrophenylboronic acid ($K_a = 0.56 \times 10^{-6}$) compared with the *meta*-isomer ($K_a = 6.9 \times 10^{-9}$) and the *para*-isomer ($K_a = 9.8 \times 10^{-9}$) has been explained[65] by the formation of the cyclic compound

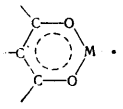


The possibility of intramolecular coordination, suggested in the compound $(C_2H_5)_3SnCH_2COCH_3$ in view of the appreciable quadrupole splitting in the GR spectrum (Moessbauer effect)[66–68], was investigated for different α- and β-carbonyl-containing stannanes[69]. Appreciable quadrupole splitting has been found for α-stannylcarbonyl compounds. It cannot be accounted for by the inductive effect of the halogenomethyl group, because it is absent even in the case of fluorine[70]. The enolate structure $R_3Sn-O-C$ is excluded by spectroscopic data. In addition the GR (Moessbauer) spectra of alkoxystannanes are significantly different. The mass spectra are also consistent with intramolecular CO → Sn coordination. There is no quadrupole splitting in the case of β-carbonyl derivatives of tin, in good agreement with infrared spectroscopic data, which show that, in contrast to stannyl ketones, the carbonyl frequency (1718 cm^{-1}) is the same as for the carbon analogues.

"Atranes" and Related Compounds

Organic derivatives of the elements in which the chain with the electron-donating atom is linked to the metal via a non-carbon atom constitute a somewhat distinct group. It includes diketone, diazene, dithiocarbamate, etc. derivatives. Data on compounds of this kind touch upon the main subject of the present review and are briefly described below.

X-Ray diffraction studies on acetylacetonates[71,72] have shown that the acetylacetonate rings are planar and that the pairs of M–O, C–O, and C–C bonds are of equal length:



It has been shown that these systems undergo a wide variety of electrophilic substitution reactions characteristic of aromatic systems[73].

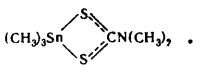
Intramolecular M ← N coordination interaction has been investigated in considerable detail for mono-, di-, and tri-ethanolamine derivatives of boron and silicon. Compounds of this kind were obtained for the first time in 1933[74] and in the course of 30 years boron compounds were investigated almost exclusively. The presence of the B ← N bond has been demonstrated on the basis of the monomeric structure[75], high dipole moments[76,77], high solubilities in water[78,79], and the absence of appreciable electron-donating properties of the nitrogen atom[80]. The presence of the Si ← N bond has been demonstrated using similar data[81] and also infrared[81,82] and PMR[81] spectroscopy and X-ray diffraction analysis[52,53]. The silicon compounds exhibit high biological activity: phenylsilatrane $C_6H_5Si(OCH_2CH_2)_3N$ proved to be several times more toxic than hydrocyanic acid[81]. The existence of the Sn ← N bond in stannatranes has been demonstrated by PMR and GR (Moessbauer) spectroscopy[83]. Exhaustive data on all known compounds of this type are presented by Prokof'ev[41].

The chelate salts of nitrilotriacetic acid of the type $X_{n-3}M(OCOCH_2)_3N$ should also be included in this class of compounds[84,85]. They have been found to have high biological activity[86].

The presence of the Sn ← N bond in the 8-hydroxyquinolinates $R_nSn(Ox)_{4-n}$, suggested because of the appearance of a yellow colour, the infrared, ultraviolet, and PMR spectrosopic data[87,88,89], and the monomeric nature of the compound[89], has been confirmed by X-ray diffraction analysis[54].

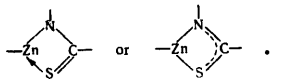
Organotin carboxylates of the type $R_2Sn(OCOR')_2$ exist in the fused and crystalline states as polymers with hexacoordinate tin atoms in which two carboxy-groups are located between adjacent tin atoms (according to infrared spectra)[90]. However, in non-polar solvents intermolecular coordination breaks down and the dicarboxylates form an asymmetric chelate structure with a non-linear skeleton (according to infrared and PMR spectra)[90,91]. Carboxylates of the type $R_3SnOCOR'$ also consist of polymers in crystalline and fused states[92-94]. However, in substituted carboxylates of the type $ClR_2SnOCOR'$ in solution intramolecular CO → Sn coordination is suggested (according to infrared spectroscopic data)[95].

A chelate structure has also been proposed for trimethyltin *NN*-dimethyldithiocarbamate on the basis of infrared spectroscopic studies in liquid paraffin and in solution and also in view of the monomeric form of the compound in benzene[96]:

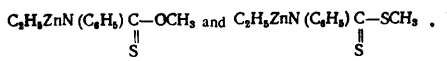


It is surprising that its oxygen analogue has a polymeric structure.

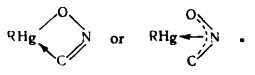
A similar difference between sulphur and oxygen in their capacity for forming an intramolecular coordinate bond was noted[97] in a comparison of the PMR spectra of *N*-(ethylzinc)acetanilide $C_2H_5ZnH(C_6H_5)COCH_3$ and its sulphur analogues. The considerably higher chemical shift of the methyl protons in *N*-(ethylzinc)thioacetanilide and its complexes with pyridine and *NNN'N'*-tetramethylethylenediamine constitutes, according to the authors, significant evidence in favour of the coordination of the thiocarbonyl groups to the zinc atom:



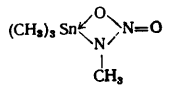
Similar coordination has also been proposed for other sulphur-containing compounds:



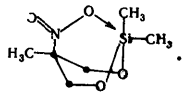
Interaction of this type has also been postulated for organomercury fulminates on the basis of preliminary structural data and characteristics of their chemical behaviour[98,99]:



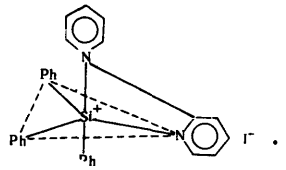
A transannular coordinate bond between one of the oxygen atoms of the nitro-group and the metal atom has been proposed for a number of organometallic nitro-compounds too. In organotin nitroamines $R_3SnN(NO_2)R'$ it is suggested in view of the pale brown colour, low melting points, stability in air, low conductivity in nitrobenzene, and infrared and Gr (Moessbauer) spectra[100]:



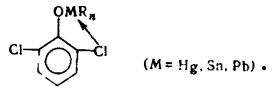
and in 2,2,5-trimethyl-5-nitro-2-sila-1,3-dioxan on the basis of the splitting of the signals due to the methylene protons in the PMR spectrum (in contrast to the analogous compounds without a nitro-group)[101]:



A chelate structure has been proposed for triphenyl(dipyridyl)siliconium iodide[102] and diphenyl(2,2'-dipyridyl)boronium perchlorate[103] but the proposed structures have not been adequately proved:



Intramolecular M ← Cl coordination interaction probably occurs also in organometallic derivatives of 2,6-dichlorophenol, since the ^{35}Cl NMR spectra showed two different signals for the chlorine atoms in the 2- and 6-positions in the aromatic ring and the splitting between these signals is 0.13–0.45 MHz for the tin and lead derivatives (i.e. is within the limits of the crystallographic effect), while for mercury it is 0.83–1.2 MHz (i.e. 2–3% of the measured quantity. If it is assumed that the splitting is proportional to the intensity of the coordination interaction, then it follows that in the above compound organotin groups exhibit a higher capacity for coordination[104]. However, the authors do not exclude completely the possibility of intermolecular interaction in these systems:



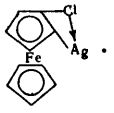
Similar coordination has been proposed also for organometallic derivatives of 2,6-dibromo-4-fluorophenol[105] in view of the increase of the chemical shift of fluorine-19 under the influence of the groups Et_3SnO and PhHgO in the ^{19}F NMR spectra compared with the spectra of 4-fluorophenol derivatives without bromine. In these systems too the coordination is more intense for the organomercury group.

IV. CHEMICAL CONSEQUENCES OF INTRAMOLECULAR COORDINATION

The chemical effects of intramolecular coordination may be extremely varied. It is logical to expect that it will be reflected mainly in anomalous reactions because of a different distribution of electron density in the molecule compared with "normal" reactions of related compounds where intramolecular coordination is known to be absent.

The first of the problems which arise here is the effect of intramolecular coordination on the strengths of metal–carbon bonds and hence the stability of the molecule as a whole. The views expressed in this connection reflect at least two, at first sight contradictory, trends. On the one hand, attempts are made to explain by intramolecular coordination the anomalous stability of many compounds which according to *a priori* estimates should not be so stable. The silver derivatives of chloroferrocene described by Nesmeyanov et al.[106] are typical examples of

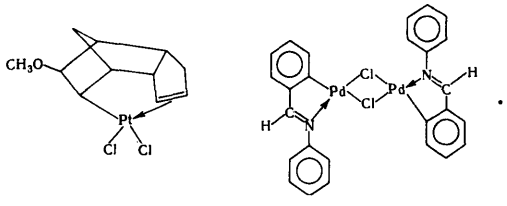
this kind; the authors explain their stability, unusual for organic silver σ-derivatives, by the Cl → Ag coordination:



On the other hand, the hypothesis of intramolecular coordination is being increasingly put forward to account for the thermal instability of organometallic compounds with functional substituents, particularly to account for the elimination reactions and the mechanism of metallotropic rearrangements [107,108].

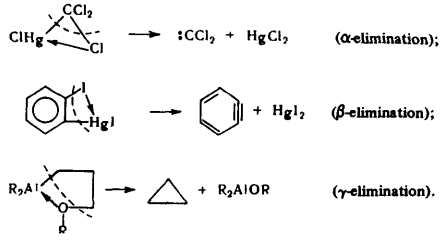
Apparently there is no contradiction between these two points of view. Among transition metals (or silver, copper, and gold which resemble them) intramolecular coordination, like intermolecular coordination, should indeed enhance the stability of the metal–carbon σ-bonds. The same bonds formed by a non-transition metal are polarised under the influence of coordination, which greatly increases their reactivity and hence makes the compound chemically more labile [109].

On the basis of X-ray diffraction [110] and infrared [111] and NMR [112] spectroscopic data, the stabilisation of the usually unstable σ-derivatives of transition metals as a result of intramolecular coordination interaction between the vacant orbitals of the metal atoms and the π-electron bonds or free electron pairs of other atoms is postulated, for example:



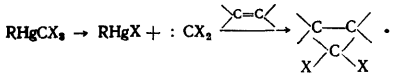
Similar intramolecular complexes or transition states corresponding to them are considered in Jones's review [113] and a number of later publications [114–117].

The presence of intramolecular coordination in the non-reacting molecule or its occurrence in the course of the incipient reaction may be regarded as a kind of "pre-existence" of the fragment to be eliminated:

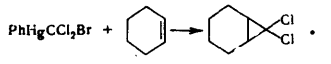


α-Elimination

As already mentioned (p. 200) the presence of intramolecular coordination in the trichloromethylmercury chloride molecules follows from X-ray diffraction analysis [37] and ^{35}Cl NMR spectra [38]. The capacity of compounds of this kind for α-elimination with the removal of a mercury halide and a dihalogenocarbene is not therefore surprising [118–138]:



Usually dihalogenocarbenes are readily formed in the thermolysis of trihalogenomethyl derivatives of mercury at 80°C in an inert solvent (benzene). However, some of them split off dihalogenocarbenes at a satisfactory rate even at room temperature. Thus the compounds $PhHgCCl_2Br$, $PhHgCClBr_2$, $PhHgCBr_3$, and $PhHgCCl_3$ decompose very slowly [132]:



The yields of 7,7-dichloronorcarane amount to 3, 12, and 66% after 3 h, 24 h, and 11 days respectively. Trihalogeno-derivatives of organomercury compounds, which are at least formally donors of dihalogenocarbenes, include also $PhHgCX_3$ (X = Cl or Br) [118–123], $Cl_3CHgCCl_3$, Cl_3CHgCl, [124] $PhHgCX_2Br$ (X = Cl or Br) [125], $PhHgCCl_2Br$, [120,121,126–136] $PhHgCClBr_2$, [121,127] $XC_6H_4HgCCl_2Br$, [137] and $Hg(CBr_3)_2$. [138]

Other α-halogenomethyl derivatives of organometallic compounds undergo the same type of thermal decomposition: ICH_2MgI, [139] $IZnCH_2I$, [140] $Zn(CH_2X)_2$ (X = Cl or I), [141,142] $Cd(CH_2I)_2$, [141] ICH_2HgI, $Hg(CH_2Br)_2$, [143] Et_2AlCH_2Cl, [144] and $In(CH_2I)_3$. [141] Monohalogenocarbenes CHX (X = Cl or Br) are eliminated in the decomposition of a number of organometallic compounds: $LiCHCl_2$, [145] $Zn(CHCl_2)$, [145] and $C_6H_5HgCHXBr$. [146,147]

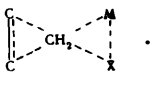
Under very mild conditions (−65°C), dichloronorcarane is formed from $LiCCl_3$ and cyclohexene [148–151] and at 80°C also from $(C_6H_5)_3PbCCl_3$. [143] The stability of organometallic compounds of this type depends on the metal. Dichlorocarbenes are formed in high yield on refluxing $(CH_3)_3SnCCl_3$ and $(CH_3)_3SnCCl_2Br$ in cyclo-octene [152], while trichloromethyltrichlorosilane gives rise to them only at 250°C. [153] Difluorocarbene is eliminated at 180–220°C from tris(trifluoromethyl)arsine and tris(trifluoromethyl)-stibine [154] and at 100–200°C from trifluoromethyl derivatives of pentavalent phosphorus: $(CF_3)_nPF_{5-n}$ ($n = 1–3$). [155,156]

Dihalogenocarbenes may be formed as a result of the exchange of a halogen for a metal in tetrahalogenomethanes, for example in the reaction between methyl-lithium and trifluoroiodomethane [157] or in the reaction of n-butyl-lithium and dibromodifluoromethane [158]. However, there are no reliable data about the intermediate formation of organometallic compounds in such reactions and therefore they will not be considered here.

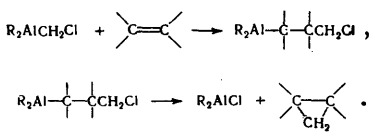
The interaction of the carbenes $:CZ_2$ (Z = H or halogen) with olefins, which leads to cyclopropanes, takes place stereospecifically and constitutes a *cis*-addition; this means that the carbenes entering into the reaction are in a singlet form.

Several different mechanisms have been proposed to account for the formation of cyclopropanes.

1. A bimolecular single-stage transfer of $:CZ_2$ in which the organometallic reagent reacts directly with the olefin via a five-centre transtion state [140,141]:

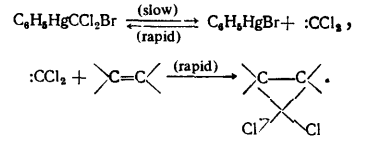


2. A bimolecular two-stage process via the addition of the organometallic reagent to the olefin with subsequent elimination of the metal halide [142]:

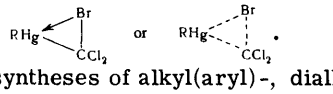


However, in this case it is difficult to reconcile the selectivity of the addition and elimination reactions and also the configurational stabilities of the intermediate organometallic compounds with the stereospecifity of the addition of carbenes to olefins.

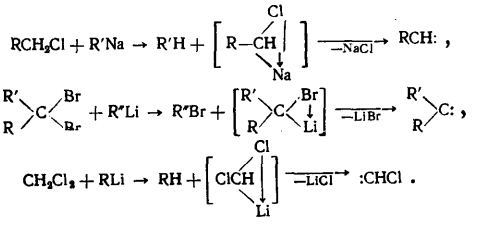
3. A process in which the rate-determining stage (possibly reversible) is the decomposition of the organometallic compound to the carbene with subsequent rapid reaction of the latter with the olefin and formation of the cyclopropane. The carbene mechanism proposed by a number of investigators [153,156,159] and investigated in detail by Seyferth and coworkers [132,137] can be represented by the following equations:



The intermediate formation of carbenes has been demonstrated by kinetic experiments in a number of cases. Thus carbene is formed as a result of α-elimination, which requires an internal nucleophilic attack by the halogen atom on the metal via the following transition state:

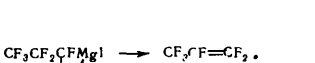


The principal syntheses of alkyl(aryl)-, dialkyl(diaryl)-, and monohalogeno-carbenes are based on the α-elimination of intermediate organometallic compounds, for example:

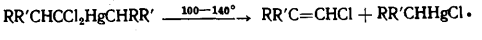


For a detailed account of the chemistry of carbenes, see the monographs by Kirmse [160] and Hine [161].

It is suggested that α-elimination from polyhalogenoalkyl compounds of various elements with expulsion of a carbene is a common reaction [153]. This is confirmed by the thermal instability of compounds of this kind. Trifluoromethylmagnesium iodide begins to decompose at a temperature as low as −60°C; [162] perfluoropropyl-lithium [157] and perfluoropropylmagnesium [163] and perfluoropropylzinc [164] iodides decompose at 40°, above 20°, and at 130–150°C respectively:

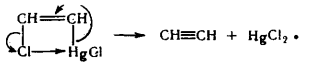


When any halogen except fluorine is in the α-position, the organometallic compounds of alkali and alkaline earth metals cannot be isolated at all [160,161,164]. Very slow decomposition of $\alpha\alpha$-dihalogenodialkyl compounds of mercury is observed even at room temperature, the process being sharply accelerated at 100°C: [165]



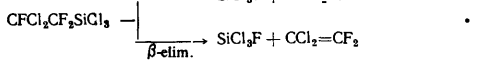
β-Elimination

The β-elimination reaction has been very thoroughly investigated among organomercury compounds [166]. If the reaction takes place under the influence of an extraneous reagent, β-elimination is usually explained by the Nesmeyanov mechanism [16] involving the transfer of the reaction centre along the σ, π- or σ,σ-conjugation chain. Until very recently, the possibility of coordination interaction through space, i.e. by-passing the conjugation chain, was not taken into account in such cases. Nevertheless the existence or formation of an intramolecular coordination bond is in some measure equivalent to nucleophilic attack on the metal atom, which results in a closed ring and the σ,σ- or σ,π-conjugation chain becomes "incorporated" as in the usual nucleophilic attack:

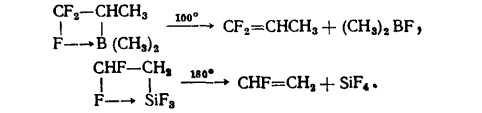


Evidently spontaneous and thermal β-elimination reactions should be treated in the same way. In those cases where coordination within the same molecule is impossible, a similar effect is achieved by intermolecular coordination, which occurs, for example, in the decomposition of *trans*-β-chlorovinylmercury chloride.

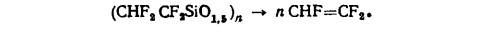
If the halogen in the polyhalogenoalkyl derivatives of silicon is present in both α- and β-positions, α-elimination is accompanied by simultaneous β-elimination, albeit to a much lesser extent, for example [153,167]:



At 185°C the yields of $CFCl{=}CFCl$ and $CCl_2{=}CF_2$ are 80 and 7% respectively. In the absence of a halogen in the α-position, β-elimination takes place, as shown for polyfluoroalkyl compounds of boron [168] and silicon [153]:

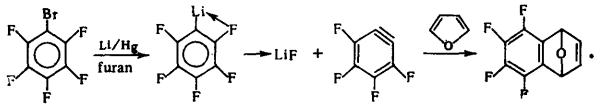


When the fluorine atom in polyfluoroalkylsilicones and polyfluoroalkylpolysiloxanes is present in both the α- and β-positions, thermal decomposition is accompanied by α- and β-elimination, both processes yielding an olefin [169]:



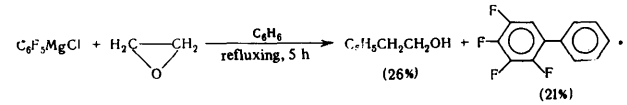
In contrast to the perfluoroalkyl organometallic compounds, the corresponding pentafluorophenyl derivatives are as a rule more stable. This applies particularly to lithium derivatives. Pentafluorophenyl-lithium [170] is an excellent starting material for the synthesis of other pentafluorophenyl metal derivatives. Being more stable than *o*-fluoro- and *o*-bromo-phenyl-lithium, pentafluorophenyl-lithium nevertheless decomposes with formation of tetrafluorodehydrobenzene, probably as a result of intramolecular coordination interaction between lithium and

fluorine atoms. The intermediate formation of tetrafluorodehydrobenzene has been demonstrated by the reaction with bromine and chlorine and also by the isolation of a Diels–Alder adduct in the reaction with furan:



The formation of 2-bromononafluorobiphenyl from bromopentafluorobenzene and pentafluorophenyl-lithium has also been explained[171] by the intermediate formation of tetrafluorodehydrobenzene, since usually direct attack on compounds of the type C_6F_5X by nucleophilic reagents leads to *para*- and not *ortho*-substitution. The intermediate formation of tetrafluorodehydrobenzene in this reaction has been confirmed also by other investigators[172].

The study of the products of the reaction of pentafluorophenyl organomagnesium derivatives also indicates the intermediate formation of tetrafluorodehydrobenzene. The interaction of pentafluorophenylmagnesium chloride with epoxyethane in benzene yields 2,3,4,5-tetrafluorobiphenyl, which is probably formed as a result of the abstraction of hydrogen from benzene[173]:



When cyclohexane is used as a solvent in this reaction and furan is added to the reaction mixture, the furan adduct mentioned above is formed. Pentafluorophenylmagnesium bromide refluxed in toluene also yields tetrafluorodehydrobenzene[174].

In trifluoromethyl derivatives of tin the tendency of the metal atom to enter into coordination interaction with the fluorine atom is considerable and trimethyltrifluoromethyltin is thermally unstable due to the migration of the fluorine to the tin atom[159]. However, pentafluorophenyl compounds of this type are much more stable; thus trimethylpentafluorophenyltin is stable at 250°C and decomposes only at 350°C.[175]

The unusual decomposition of potassium pentafluorophenyltrifluoroborate can also be explained by the coordination interaction between fluorine and boron atoms[176]:

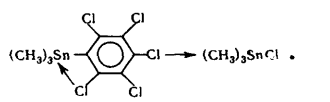
$$K^+[C_6F_5BF_3]^- \xrightarrow{300^\circ} KBF_4 + \text{perfluoropolyphenylenes.}$$

Perfluoropolyphenylenes are probably obtained as a result of the intermediate formation of tetrafluorodehydrobenzenes.

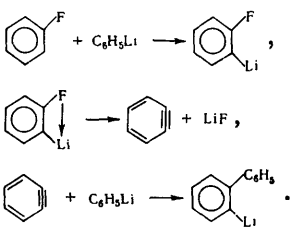
Prolonged pyrolysis of di-(π-cyclopentadienyl)di(pentafluorophenyl)titanium in a vacuum at 150°C leads to the migration of the fluorine atom to the titanium atom and partial decomposition of the substance:

$$(\pi\text{-}C_5H_5)_2\,Ti\,(C_6F_5)_2 \rightarrow (\pi\text{-}C_5H_5)_2\,Ti\,(C_6F_5)\,F.$$

Pentachlorophenyl organometallic compounds have not been investigated quite so widely as the pentafluorophenyl derivatives but here too results have been obtained which may be a consequence of the intramolecular coordination of the metal atom with the chlorine atom in the *ortho*-position. Thus pentachlorophenyltrimethyltin decomposes at 300°C with formation of trimethyltin chloride[177]:

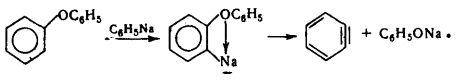


In all the above examples of coordination interaction between metal and halogen atoms the intermediate formation of dehydrobenzene derivatives has been demonstrated. Therefore such decomposition of pentafluoro- and pentachloro-phenyl derivatives of organometallic compounds may be regarded as a special case of a general tendency of aromatic compounds with metal and halogen atoms in the *ortho*-positions to decompose with formation of dehydrobenzenes. Wittig[178,179] was the first to postulate the formation of dehydrobenzene as an intermediate in the formation of 2-lithiumbiphenyl from fluorobenzene and phenyl-lithium:



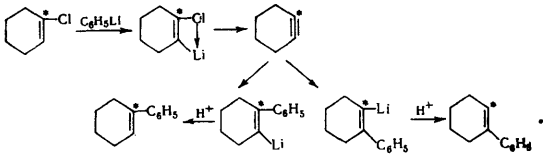
The rate-determining stage of the reaction is the elimination of lithium fluoride as a result of intramolecular coordination interaction leading to the formation of dehydrobenzene. The fact that, when labelled [^{14}C]-1-fluorobenzene is used, a mixture of almost equal amounts of the two isomeric biphenyls is obtained, suggests the intermediate formation of dehydrobenzene[180].

The existence of dehydrobenzene has also been demonstrated in the interaction of phenyl ether with phenylsodium[181,182]:



The elimination of sodium phenoxide in this reaction is probably caused by intramolecular coordination interaction of the ether oxygen with the sodium atom.

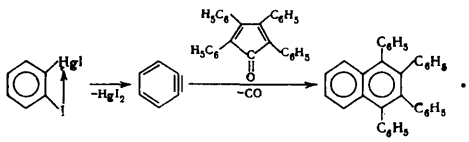
Similar elimination of MX fragments leading to analogues of dehydrobenzene is known also for the olefin series. Thus 1-phenylcyclohexene, which is obtained in the reaction between 1-chlorocyclohexene and phenyl-lithium in ether[183,184], and 1-phenylcyclopentene formed similarly from 1-chlorocyclopentene[185] are both probably produced via an intermediate cyclohexyne and cyclopentyne. This is confirmed by the finding that, when a labelled carbon atom in 1-chlorocyclohexene is employed, almost equal amounts of two phenylcyclohexenes, with substituents at both olefinic carbon atoms, are obtained[186]:



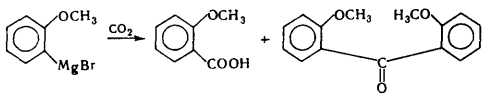
The coordination interaction between magnesium and bromine is probably responsible for the formation of cyclohexyne from the organomagnesium derivative of 1,2-dibromocyclohexene[187].

Irradiation with ultraviolet light leads to fairly intense coordination interaction between the mercury atom and the iodine atom in the *ortho*-position in 1-iodo-2-iodomercuribenzene. This results in the formation of mercury(II) iodide and dehydrobenzene, which was identified by the

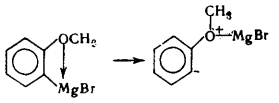
reaction with tetraphenylcyclopentadienone, giving a 25% yield of tetraphenylnaphthalene [188,189]:



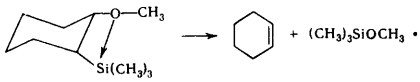
Reactions between carbon dioxide and Grignard reagents obtained from *o*-methoxybenzyl chloride, *o*-dimethylaminobromobenzene, and *o*-bromo(methylthio)benzene yielded both acids and ketones [190]. For example, *o*-methoxybenzoic acid and 2,2-dimethoxybenzophenone were obtained from *o*-methoxyphenylmagnesium bromide:



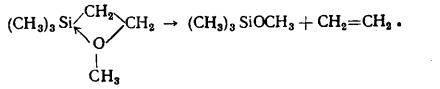
Under the same conditions, Grignard reagents obtained from *m*- or *p*-bromomethoxybenzene β-(*o*-methoxyphenyl)-ethyl chloride, *o*-bromomethylbenzene, and γ-methoxypropyl bromide give rise only to the corresponding acids. The anomalous reactions leading to the formation of ketones were accounted for by the formation of strained planar rings as a result of intramolecular coordination:



Thermal decomposition of the methyl ether derived from *cis*-2-trimethylsilylcyclohexanol (first-order reaction) [191] gives a quantitative yield of cyclohexene and methoxytrimethylsilane:



Ethylene is evolved in quantitative yield in the pyrolysis of ethylmethoxytrimethylsilane (first-order reaction) [191]:

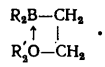


2-Alkoxyethyl derivatives of boron are thermally unstable and readily eliminate olefins [192]. Thus tri-(2-ethoxyethyl)boron begins to evolve ethylene at a temperature as low as −10°C:

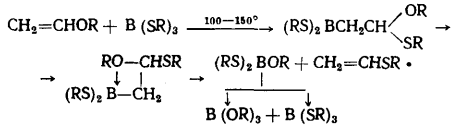
$$(C_2H_5OCH_2CH_2)_3B \rightarrow (C_2H_5OCH_2CH_2)_2BOC_2H_5 + CH_2{=}CH_2.$$

2-Ethoxyethyldiethoxyboron decomposes at a higher temperature (160–170°) than the butyl ester of di-(2-ethoxyethyl)boronic acid. Consequently thermal stability increases as 2-alkoxyethyl groups are replaced by alkoxy-groups.

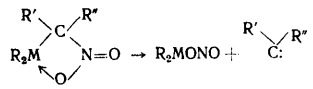
The reaction of dipropyldeuteroborane with *cis*-1-ethoxy-2-phenylethylene at 0°C gives a 40% yield of *trans*-β-deuterostyrene when the mixture is allowed to stand after the reaction at room temperature for 1 h. In this case *cis*-elimination takes place although the initial olefin does not isomerise on reaction with the normal borane [193]. It is interesting that, on replacing oxygen by sulphur in the initial olefin, the non-catalysed elimination reaction does not occur. The thermal instability of 2-alkoxyethyl derivatives of boron was explained by intramolecular coordination:



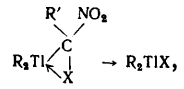
Similar coordination can account for the reaction of thioborates with vinyl ethers which yields alkyl vinyl sulphides and alkyl borates [194]:



Intramolecular coordination interaction is suggested for α-nitroalkyl derivatives of mercury and thallium, which decompose on heating with formation of nitrites and probably carbenes [195]:



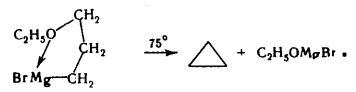
When halogen atoms are bonded to the α-carbon atoms of α-nitroalkyl derivatives of thallium, a competing intramolecular interaction takes place and in a number of cases the corresponding halide and not the nitrite is formed:



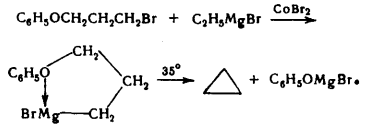
where X = F or Cl.

γ-Elimination

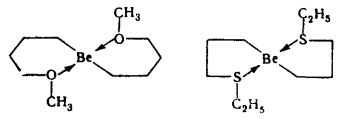
Intramolecular coordination can explain the thermal instability of 3-alkoxy-derivatives of Grignard reagents, as a result of which cyclopropane and its derivatives are readily formed [196,197]:



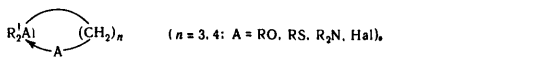
Cyclopropane is also formed in the double decomposition of Grignard reagents with 3-phenoxypropyl bromide in the presence of cobalt(II) salts (the Kharasch reaction) [198]:



Di-(δ-methoxybutyl)beryllium and di-(γ-ethylthiopropyl)-beryllium [199] are probably chelate salts, since they can be distilled in a vacuum:

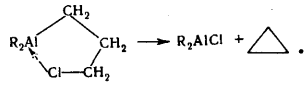


Convincing evidence has been adduced for intramolecular coordination in γ-amino-, γ-alkoxy-, γ-hydroxy-, γ-alkylthio-, γ-halogeno, and also δ-alkoxy-derivatives of aluminium [144,200,201]:



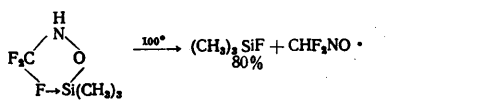
($n = 3, 4$; A = RO, RS, R_2N, Hal).

γ-Halogenalkyl derivatives of aluminium readily eliminate cyclopropane [144]:

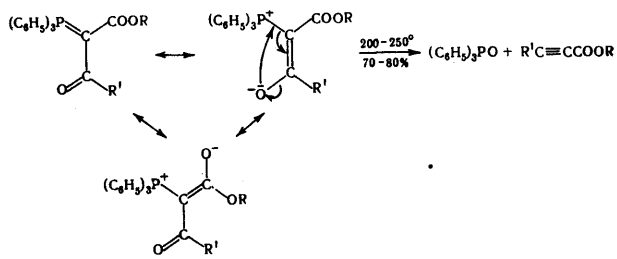


The evidence for coordination in the remaining compounds is based on their monomeric form in benzene and the absence of intermolecular coordination with ethyl ether; in the case of amines the evidence is based on the absence of electron-donating properties at the nitrogen atom (a quaternary compound is not formed with methyl iodide) [200,201]. When the fluorine atom is in the γ-position, the thermal and hydrolytic stability of the corresponding polysiloxanes is very high and $(CF_3CH_2CH_2SiO_{1.5})_n$ is not cleaved by alkalis at 20–80°C, while $(CF_3CH_2CH_2)_3B$ is stable at 100°C. [168]

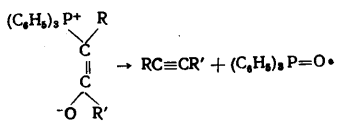
On the other hand, if the halogen atom is separated from the metal by a heteroatom (in *N*-trifluoromethyl-*O*-trimethylsilylhydroxylamine), γ-elimination can probably occur) [202]:



A surprising example of the effect of the possible intramolecular coordination on reactivity is provided by substituted phosphoranes [203]. Acylalkoxycarbonylmethylenetriphenylphosphoranes, the stability of which is explained by resonance, decompose at 220–250°C, yielding the corresponding propiolic esters and triphenylphosphine oxide:



On the basis of the resonance formulae, this reaction may be regarded as an intramolecular Wittig synthesis. In the reaction of betaines, in which R and R′ are not hydrogen atoms but any electron-accepting group, high yields of disubstituted acetylenes are obtained [204,205]:

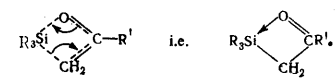


On the other hand, when R = $-C\equiv C-R'$, diacetylenes may be obtained in this way.

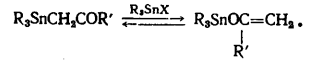
Metallotropy

Intense studies on various metallotropic rearrangements, including metallotropic photomerism, were begun recently. In all these investigations the concepts of intra- and intermolecular coordination, usually postulated for the transition state, are always employed. There is scarcely any sharp qualitative distinction between a transition complex of a clearly coordination type and coordination (intra- or inter-molecular) interaction in a system which has not yet reacted. The occurrence of such interaction, leading, for example, to the preferential formation of the conformation required for the rearrangement, should undoubtedly facilitate the rearrangement itself, lowering the required activation energy.

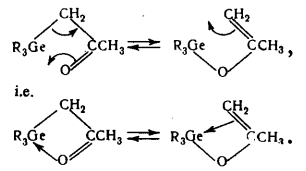
Such metallotropic rearrangements include, for example, the rearrangement of α-silylketones to silylenolates on heating [107,108] or in the presence of mercury and zinc salts and chlorosilanes [108,206]. The thermal rearrangement must be molecular, since, in the first place, the rearrangement of $(C_6H_5)_3SiCH_2COC_6H_5$ is a first-order reaction [107] and, in the second place, on heating mixtures of $(C_2H_5)_3SiCH_2COCH_3$ with $(CH_3)_3SiCH_2COC_6H_5$ and of $(C_2H_5)_3SiO(CH_3O)C=CH_2$ with $(CH_3)_3SiCH_2COC_6H_5$, it proved impossible to isolated intermolecular rearrangement products [108]. It is believed that the rearrangement proceeds via a four-centre activated complex [107,108], which is of the intramolecular coordination type:



The rapid catalytic rearrangement of a number of similar tin compounds is of the equilibrium type [207]:



The corresponding trialkylgermane derivatives constitute a true metallotropic tautomeric system with a relatively low (about 1 month) rate of attainment of equilibrium. It may be supposed that here too the rearrangement proceeds via a four-membered coordination complex [208,209]:



The explanation of the recently discovered metallotropic tautomerism of organometallic derivatives of *p*-nitrosophenols [210] is similarly based on the concept of intermolecular coordination.

The above review shows that the concept of intramolecular coordination is employed to account for a wide range of phenomena associated with the structure and reactivity of organometallic compounds. Nevertheless the experimental proof of the occurrence of intramolecular coordination interaction is in many cases clearly inadequate and the concept itself is frequently merely a useful hypothesis. However, this new trend in the chemistry of organic derivatives of the elements promises to become extremely fruitful and consequently deserves extensive and impartial development.

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