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Metallotropic Tautomeric Transformations of the σ,σ-Type in Organometallic and Complex Compounds

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The review is devoted to the consideration of studies in the field of metallotropy—a new type of tautomeric transformations of organometallic and complex compounds involving the intramolecular and intermolecular migration of metal-containing groups.
The bibliography includes 221 references.

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I. INTRODUCTION

The problems of tautomerism constitute one of the most important branches of theoretical chemistry and have attracted the constant attention of investigators throughout many years. The foundations of the science of tautomerism were laid as early as the end of the past century by A.M.Butlerov. Until the end of the 1950's, the most thoroughly investigated type of tautomerism involved prototropic transformations accompanied by the dissociation of σ-bonds and the migration of the hydrogen atom between cation-accepting centres. The study of these processes enabled M.I.Kabachnik to create a quantitative theory of prototropic equilibrium.

At the beginning of the 1960's a qualitative jump occurred in the study of tautomerism. It was caused, on the one hand, by the discovery of tautomeric processes associated with the dissociation of donor–acceptor σ- or π-bonds and processes involving the migration of groups containing a metal, metalloid, or carbon key atom and, on the other hand, the extensive application of the NMR method. All these factors led to the vigorous accumulation of qualitatively new facts and to the development of fundamentally new ideas in the theory of tautomeric processes.

This review deals with studies in the field of metallotropic transformations of organometallic and complex compounds. If the phenomenon under consideration is defined more vigorously, then one must assume that metallotropic transitions occur as a result of a change in the relative positions of two fragments of the compound—cationoid and anionoid, accompanied by the dissociation of some bonds and the formation of others between the metal and the ligand and in many instances also by a redistribution of the multiple bonds of the latter. Here the cationoid residue may be the metal or the organometallic group or another metal-containing species, where the metal forms a bond with the anionoid residue before and after the metallotropic transition. The anionoid residue can consist of a bifunctional (in the general case a polyfunctional) ligand capable, in principle, of forming several variants of the chemical bond with the same metal atom of the cationoid residue.

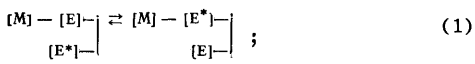
Initially[1-17] the problem of metallotropy was formulated and solved in relation to derivatives of prototropic tautomeric systems in which a "mobile" hydrogen atom has been replaced by an organometallic group. Among other features, in these studies the specific characteristics of the phenomenon, associated with the replacement of H by MR_n, were discovered. It was found that metallotropic systems are in all cases analogues of the corresponding prototropic models (as regards their structure and the process mechanism) and have many interesting, frequently fundamental, characteristic features.

It was subsequently discovered that, in principle, metallotropic transitions can occur in systems of very many types, including those very remote from the prototropic analogues. In particular, various types of metallotropic transformations in π-complexes of transition metals have been observed and in many cases investigated in detail.

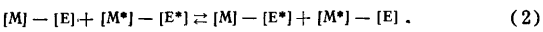
If this classification of the phenomenon of metallotropy is based on the nature of the bond formed by the metal, it is possible to distinguish three main types of metallotropic transitions: σ,σ- transitions, π,π-transitions, and σ,π-transitions. For tautomeric transformations of the σ,σ-type (sigmatropic transitions), it is postulated that before and after the rearrangement the metal forms localised (principle-valence or coordinate)σ-bonds with topologically different atoms of the anionoid residue of the given or another molecule. Transitions of the π,π-type consist in the migration of the metal from the system of multiple bonds, with which the π-bond had been formed initially, to a topologically different system in the given or another similar molecule. For transitions of the σ,π-type, it is suggested that in the initial and final states the metal forms bonds of different types with the ligand. The metallotropic π,π- and σ,π-transitions do not have prototropic analogues, while many (but not all) σ,σ-transitions are formally analogous to the corresponding prototropic systems. Studies on metallotropic π,π- and σ,π-transformations have been reviewed[18]. This review therefore deals mainly with the advances in recent years in the study of sigmatropic transitions of metal-containing groups.

A particular feature of the phenomenon considered must be emphasised. Metallotropic transitions can occur not only intramolecularly but are frequently also intermolecular. We shall adopt the convention that the intramolecular transformations are those in which the cationoid metal-containing group migrates between atoms of the same anionoid residue and which are not accompanied by the decomposition of the

given compound into kinetically independent species. On the other hand, in intermolecular metallotropic transitions the metal-containing species is separated for a short time from the anionoid residue and is attached to a "transferring agent" or passes into the bulk of the solution, as a result of which after the metallotropic transition the cationoid species is bound not to its "own" anionoid residue but to a "foreign" one. In terms of purely external features, the intermolecular metallotropic transitions may not differ from exchange processes in which the metal-containing species migrates from one anionoid residue to another. We shall therefore adopt the convention that metallotropic transitions will be assumed to be only those where the intermolecular migrations of the cationoid residues take place between bifunctional or polyfunctional ligands [process (I)]; and henceforth the symbol [M] denotes a metal-containing species, its organoelemental analogue, or a proton (cationoid residue), which is bound via the M–E σ-bond to the anionoid residue [E]. On the other hand, the transitions of metal-containing species between monofunctional ligands will be classified as exchange reactions [process (II)]:



(1)

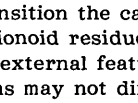
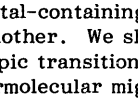


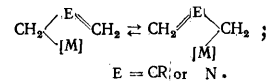
(2)

Mainly infrared and ultraviolet spectroscopic methods were used initially in studies of metallotropy and the equilibrium position in metallotropic systems[1–8]. However, subsequently high-resolution NMR, particularly dynamic NMR, began to be used on a wider scale for these purposes[9–17]. With the aid of the latter, it is often possible to obtain the kinetic characteristics of metallotropic processes, which permits a successful analysis of their mechanisms. This is because metallotropic transitions, like tautomeric transformations in general, frequently take place at rates comparable to the NMR time scale, which makes it possible to investigate not only the ratios of the possible tautomers but also the dynamics of their transformations. In view of these factors, a further consideration of the phenomenon of metallotropy will be based mainly on NMR results, but if necessary other data will also be employed.

The first experimental evidence in support of the occurrence of metallotropic transitions in organometallic compounds of non-transition metals was apparently obtained in 1960 by Nasmeyanov and Kravtsov[1] in an infrared and ultraviolet spectroscopic study of solutions of arylmercury derivatives of *p*-nitrosophenols in aprotic media. In a series of subsequent studies other instances of the migration of metal-containing groups between carbon atoms or heteroatoms of the corresponding molecule were investigated or simply discovered: however, one should note that these studies, including those by NMR, have been by no means systematic for all the models; the review of the relevant studies is therefore unfortunately somewhat fragmentary. In order to overcome this deficiency to some extent, in the analysis of certain model structures, for which the migration of metal-containing groups is as yet unknown, has been little studied, or may be impossible, we considered instances of E,E-transitions (E = C,N,O,S,etc.) with participation of cationoid species such as SiR_3 and GeR_3, which are organoelemental analogues of the groups R_3Sn and R_3Pb, as well as organometallic groups involving transition and light non-transition metals.

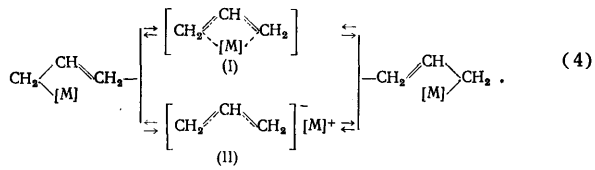
II. METALLOTROPIC C,C-TRANSITIONS

Among "purely carbon" systems, where there is a possibility of C,C-transitions of metal-containing groups accompanied by the dissociation of old and the formation of new metal–carbon bonds, one must first consider the simplest three carbon system , whose prototropic analogue has a relatively low mobility (as well as the related azomethine triad  with a central nitrogen atom, which has not been investigated at all from the standpoint of metallotropic transitions):



(3)

Although the occurrence of metallotropic 1,3-transitions [reaction (3)] with E=CR has usually been considered for a fairly wide range of allyl derivatives, we believe it is correct to discuss here only those examples in which the existence under specific conditions of a localised C_3H_5–[M] σ-bond has been demonstrated reliably. When the migration is retarded by the protons of the allyl group, the ^1H NMR spectrum shows the corresponding $AKLX_2$ system, which in a case of sufficiently rapid intramolecular or intermolecular C,C-transitions [reaction (4)], involving the C–M bond, degenerates to AX_4 (the corresponding spin systems are observed also for substituted allyl radicals). This phenomenon has been observed, in particular, in NMR studies of the compounds C_3H_5HgX[19,20], $(C_3H_5)_2Zn$[21,22], and $(C_3H_5)_3B$[23]:

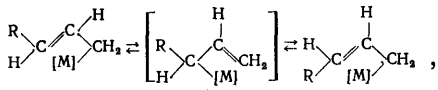


(4)

It has been suggested that the 1,3-transitions [reaction (4)] take place with the intermediate formation of either the transition state (I) or of ionic structures, for example of type (II). In the case of $(C_3H_5)_2Zn$[21,22] and asymmetric allyl derivatives of mercury[19,20], reaction (4) is intermolecular and that involving allyl derivatives of boron is intramolecular[23].

The occurrence of process (4) was first postulated in an attempt to explain the NMR spectra of allyl derivatives of magnesium[24]. However, one should note that the spectral pattern corresponding to the inhibition of the metallotropic transition has not so far been observed in the NMR spectra of the asymmetric derivatives C_3H_5MgX and $RCH{=}CHCH_2MgX$ even at very low temperatures[21–30], so that the question of the occurrence of migration processes in these systems has in essence remained open. In the study of the ^1H NMR spectra of the asymmetric compound $(t\text{-}C_4H_9CH_2CH{=}CHCH_2)_2Mg$ it was shown recently[31] that, at sufficiently low temperatures, both the *cis*- and *trans*-forms of this compound with C–Mg σ-bonds exist simultaneously in solvating media, while at higher temperatures they undergo an interconversion. These results suggested that the *cis–trans* isomerisation [reaction (5)] is preceded by the formation of structure (III)

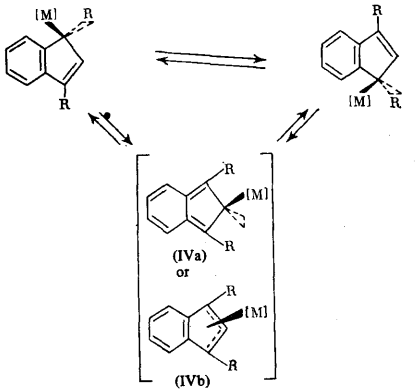
for a short time, evidently as a result of the metallotropic 1,3-transition



(III)
R = t-$C_4H_9CH_2$ (5)

where [M] = $MgCH_2CH{=}CHCH_2C(CH_3)_3$.

The indenyl organometallic compounds in which the C,C-metallotropic transformations [reaction (6)] can proceed not only via 1,3-transitions but also via two consecutive 1,2-shifts with formation of the intermediates (IVa) or (IVb), are an unusual example of a carbon triad:



(IVa) or (IVb) (6)

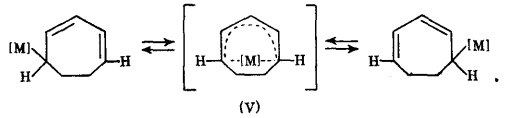
Changes in the ^1H and ^{13}C NMR spectra consistent with metallotropic C,C-transitions [reaction (6)] have been observed in the study of $(C_9H_7)_2Hg$,[10,32] $C_9H_7Sn(CH_3)_3$,[12,33-35] and other indenyl compounds[12,35-37], and it has been shown for a series of derivatives that this process takes place intramolecularly. The available NMR data for metallotropic transitions (6) indicate the dependence of the rate on the nature of [M] and make it possible to set up series based on the relative ease of metallotropic transformations as a function of the nature of the metal [series (7)] and the nature of the substituents in the group [M] [series (8)][35,38]:

$$R, H < Si(CH_3)_3 < Ge(CH_3)_3 < Sn(CH_3)_3 < HgC_9H_7; \quad (7)$$

$$Si(OCH_3)_3 < SiCl_3 < Si(CH_3)Cl_2 < Si(CH_3)_2Cl < Si(CH_3)_2C_6H_5 < Si(CH_3)_3. \quad (8)$$

As regards the mechanism of C,C-transitions (6), the results of the vast majority of the experimental and theoretical[39-41] studies support the view that they do not involve a 1,3-shift but proceed via consecutive 1,2-transitions. In particular, comparison of the energy characteristics of the C,C-transitions in indenyl and cyclopentadienyl (see below) organometallic compounds shows that in all cases the transition from $C_5H_5[M]$ to $C_9H_7[M]$ is accompanied by an increase of E_a by approximately 8.5 kcal mol^{-1}.[35] Bearing in mind that this quantity is close to the difference between the energies of the indenyl and isoindenyl structures, amounting to approximately 9 kcal mol^{-1} according to estimates[42], one can assume that the metallotropic transitions in indenyl derivatives take place via two consecutive 1,2-shifts with the intermediate formation of compound (IVa) or (IVb), which are not detectable by NMR.† Among other pieces of evidence in support of this mechanism, we may point to NMR data[12] for indenyl derivatives of tin with [M] = $Sn(CH_3)_2C_6H_5$ (R = H or CH_3). The authors[12] found that, in the absence of a dynamic system, the signals corresponding to the two CH_3Sn groups in [M] are shielded in different ways and can merge when the C,C-transitions are accelerated with increase of temperature. They interpreted this result as proof of the mechanism with a 1,2-shift, within the framework of which the intermediates (IVa) and (IVb) have a mirror symmetry plane, transforming one CH_3Sn group into the other, which is consistent with the averaging of their shielding (in the case of the 1,3-transition with inversion at the metal atom the two CH_3Sn groups should remain non-equivalent). The authors[12] noted, however, that the less probable 1,3-transition, with retention of the configuration at the tin atom and inversion of that at the asymmetric carbon atom, is also consistent with the experimental facts.

The occurrence of metallotropic C,C-transitions in allyl and indenyl derivatives is promoted by, among other things, appropriate geometrical factors. The detection of metallotropic transitions between more remote carbon atoms, particularly in pentad systems of type (9), is therefore important. The possibility of such transitions has been confirmed in an NMR study of the corresponding R_3Sn derivatives ($R = CH_3C_6H_5$).[49,50] The averaging of the shielding of the indicator nuclei in the 1- and 5-positions, associated with the acceleration of the C,C-transitions (9) via the 1,5-migration mechanism, apparently with the intermediate formation of the transition state (V), has been observed at fairly high temperatures in the ^1H and ^{13}C NMR spectra:

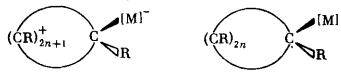


(V) (9)

The carbon systems with C,C-transitions (4), (6) and (9) can be conventionally referred to as "open" (in the sense used here they can evidently include also cyclic structures), because only "vibrational" transitions between two or more cation-accepting centres (degenerate or non-degenerate) are possible in them. Metallotropic systems of the "closed" type, in which there is a possibility of not only "vibrational" C,C-transitions but also of migrations of organometallic groups accompanied by the formation of a C–M bond in succession with all the carbon atoms of the system, have also been widely investigated. There is no point in considering the

† In making a choice between the two possible intermediates—the isoindenyl intermediate (IVa) and the π-allyl intermediates (IVb), one should apparently resort to the available NMR or other data concerning the structure of the σ-allyl derivatives of mercury, tin, germanium, and silicon[43-47]. Since tautomeric 1,3-transitions in these derivatives, accompanied by the intermediate formation of the π-structure (IVb), are unknown under non-catalytic conditions (the energy characteristics of the 1,3-transition in the π-allyl derivatives of silicon[48] show that the process is a rearrangement and not a tautomeric transformation), it is logical to give preference to the isoindenyl intermediate (IVa) when the 1,3-migration in indenyl organometallic compounds is considered.

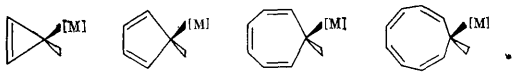
prototropic analogues of the "closed" systems because the relevant processes in such systems are clearly slow:



(VI) (VII)

(a) $n=1$, (b) $n=2$, (c) $n=3$, (d) $n=4$.

In the simplest "closed" systems the occurrence of metallotropic C,C-transitions appears to be most probable in even derivatives of type (VI) and in odd derivatives of type (VII).[18] Among structures (VII), σ-cyclopropenyl compounds (VIIa) ($n=1$, carbon triad) have so far not been investigated at all and the C,C-migration in σ-cycloheptatrienyl derivatives (VIIc) ($n=3$) and σ-cyclononatetraenyl derivatives (VIId) ($n=4$, R=H) of non-transition metals has been studied by NMR only for individual examples of organotin compounds[16, 50-52]. Thus the greatest number of publications deal with C,C-transitions in σ-cyclopentadienyl and related compounds (VIIb) ($n=2$, R=H or R≠H; carbon pentad)[11,32,35,41,53-81] (see also the relevant reviews concerning this problem[41,82,83]). The even charged structures (VI) have so far been investigated for the case with $n=1$ ($R=CH_3$)[84-86]:



(VIIa) (VIIb) (VIIc) (VIId)

The first convincing evidence in support of the occurrence of C,C-metallotropic transitions in σ-cyclopentadienyl compounds was obtained in 1965–1966 in a low-temperature NMR study of σ-cyclopentadienyl derivatives of iron[53], silicon, and germanium[54]. Subsequently analogous results were obtained in studies of compounds of a number of non-transition and transition metals[11,32,35,42,55-81]. In the ^1H NMR spectra of the C_5H_5 ligand in these compounds at fairly low temperatures a multiplet of the type AA'BB'X (or ABCDX for compounds with a lower symmetry) has been observed. The corresponding set of signals has been noted also in the ^{13}CNMR spectra. These results are consistent with the presence of a localised C_5H_5–M bond and have been confirmed in many instances in structural studies by diffraction methods[54, 59,87,88]. With increase of temperature, a number of patterns of an intermediate type are observed in the spectra and at still higher temperatures there is a single signal corresponding to the situation where all five ^1H or ^{13}C ring nuclei are equivalent as a consequence of the time averaging of their shielding.

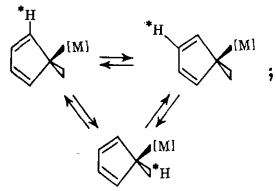
The change in the structure of the cyclopentadienyl compounds (VIIb) has an appreciable effect on the rates of metallotropic transitions in them. In particular, data referring to the derivatives of Group IVB elements[35,38,77] established the series (10)–(12) based on the relative changes in the rates of the processes as a function of the structure [M], which coincide with the corresponding series (7) and (8) established for indenyl organometallic derivatives:

$$R < Si(CH_3)_3 < Ge(CH_3)_3 < Sn(CH_3)_3, \quad (10)$$

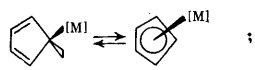
$$SiCl_3 < Si(CH_3)Cl_2 < Si(CH_3)_2Cl < Si(CH_3)_3, \quad (11)$$

$$Ge(OCH_3)_3 < GeCl_3 < Ge(GH_3)_3. \quad (12)$$

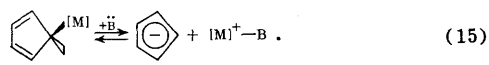
Three mechanisms for the migration of the organometallic group, leading to the averaging of the shielding of the nuclei in the NMR spectra, have been proposed: the intramolecular mechanisms (13) and (14) and the intermolecular mechanism (15) in highly basic media. Piper and Wilkinson[91], who were the first to suggest the possibility of sigmatropic C,C-transitions of the organometallic group in σ-cyclopentadienyl compounds of metals, pointed out that these transitions can proceed via the intramolecular migration of the metal along the perimeter of the ligand [reaction (13)]. Subsequently mechanism (14), postulating that the type of the C_5H_5–M bond changes in the course of intramolecular metallotropic transitions (σ,π-transitions[52]), was also proposed. Each of these mechanisms is consistent with the fundamental characteristics of the NMR spectra. The study of more detailed changes in the spectrum showed that the 1,2-shift mechanism (13) is preferable for intramolecular processes[53,60,61,92]; it presupposes the migration of the metal via the shortest path to a neighbouring carbon atom (and constitutes, as it were, a form of σ,π-conjugation: the opposed dynamic movement of electrons and the organometallic species). However, the available experimental data[52,63] do not allow the possibility of mechanism (14) to be rejected. The Woodward–Hoffmann rules have been extended to the study of the mechanism of sigmatropic migration in derivatives (VIIb)[39-41]:



(13)



(14)



(15)

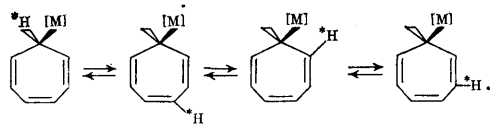
Certain factors complicating the analysis of the NMR spectra of the compounds C_5H_5–M must be emphasised. Firstly, in the study of the properties of cyclopentadienyl compounds of different metals the presence of the C_5H_5–[M] σ-bond is as a rule postulated in an explicit or implicit form (if, by virtue of its "electronic requirements", the metal can, in principle, form an M–C σ-bond) and hence a σ,σ-mechanism of the migration of metal-containing groups. However, the available data show that such hypotheses cannot be regarded as sufficiently correct in the absence of additional unambiguous confirmation (for example, the observation in the low-temperature ^1H NMR spectra of compounds C_5H_5-M of the spin system AA'BB'X, the observation of a localised bond in the study of compounds by diffraction methods, etc.). Secondly convincing evidence for the intramolecular character of the C,C-transitions of organometallic groups has been by no means obtained in all cases (the intramolecular nature of the transitions has been established, for example, for σ-cyclopentadienyl derivatives of Group IVB elements—Si, Ge, and Sn#)[35,62,69-73]. There are also more general difficulties associated with the existence of additional factors: the possibility of a change in the nature of the C_5H_5–M bond under the influence of solvents with a high solvating capacity[93-96], the ability of the cyclopentadienyl ligand to participate in the formation of a bridge bond with certain metals[97], the possibility of the retention of dynamic features in the C_5H_5–M fragment, even in a crystal[98], etc.

The fact that in organometallic derivatives of the type C_5H_5–M (in those compounds where the presence of a C,M σ-bond has been confirmed and in which the C,C-transitions

It has recently been found[92] that in highly basic media organotin groups can migrate also via the intermolecular mechanism (5).

are intramolecular) the existence of 1,2-transitions has been demonstrated led to an interesting theoretical problem. Indeed, among derivatives of type (VII) the mechanism of the C,C-migration satisfies two conditions simultaneously only in compounds (VIIb)—the intuitive idea that migration to the nearest atom (the 1,2-shift) is preferred and the orbital symmetry conservation rules (satisfied when the C,C-transition takes place via the 1,5-mechanism), because the 1,2- and 1,5-transitions are identical only in cyclopentadienyl compounds (VIIb).

Because of this, C,C-transitions have been investigated in some studies[16,50,99] in compounds (VIIc) with [M] = $Sn(C_6H_5)_3$, for which the 1,2- and 1,5-transitions do not coincide and can be fully distinguished by dynamic NMR:



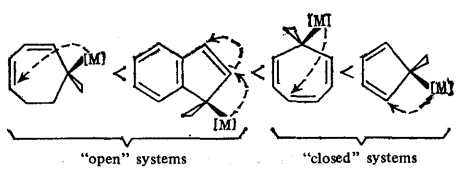
(16)

At low temperatures the ^1H and ^{13}C NMR spectra of this derivative correspond to a fixed structure with a localised C–M bond, which is consistent with data obtained in a study of this compound by a diffraction method in the crystalline state[99]. At higher temperatures the ^1H NMR spectrum shows a single signal corresponding to the seven protons of the cycloheptarrienyl ring with averaged chemical shifts. Analysis of the temperature-induced changes in the form of the NMR line led to the conclusion that the C,C-transitions within the limits of the seven-numbered ring take place via the 1,5-shift mechanism (16). Structure (VIII) has been proposed as a transition state in this process[49]. The possible formation of the centrally symmetrical structure (IX), at least at temperatures not exceeding 30 °C, has been rejected[16] on the grounds that the changes in the ^1H NMR spectrum are asymmetric. Thus the C,C-transitions of the organometallic group in derivatives (VIIc) do not take place in the direction of the shortest pathway (as in cyclopentadienyl compounds) but in the direction predicted by symmetry conditions. We may note, however, that, according to ^{13}C NMR data, the C,C-migrations of the organotin group in the σ-cyclononatetraenyl derivatives (VIId) take place preferentially in the direction of the shortest pathway[51].



(VIII) (IX)

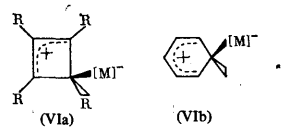
Summarising the data obtained hitherto for the C,C-transitions of organotin groups, we may quote the series (17), formulated by Curtis and Fink[49] and based on the increasing rates of metallotropic transformations as a function of the structure of the anionoid hydrocarbon residue:



"open" systems "closed" systems (17)

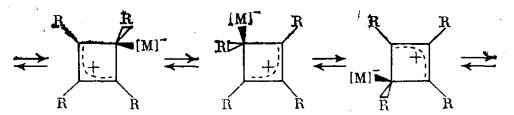
We may note that in all cases these are in essence sigmatropic 1,5-transitions (in terms of the classification of Woodward and Hoffmann[100]). In addition, the fact that the transitions in these systems are, from the point of view of their velocities, rearrangements rather than tautomeric transformations considered here when [M] = H appears to be significant. Thus the migration of organometallic groups in the systems analysed is promoted by additional factors, as a result of which the potential barrier is lower for heavier cationoid species. The principal factor appears to be the greater length of the C–M bond compared with the C–H bond and the presence in the metal atom of a vacant orbital, which is larger and has a lower energy than the potentially active vacant 2p orbitals of the hydrogen atom[101,102].

An analysis carried out as above in relation to the odd structures (VII) is in principle possible also for the even charged structures (VI):



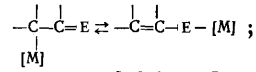
(VIa) (VIb)

Such analysis has been carried out hitherto only for the σ-complexes of cyclobutadiene–structure (VIa), $n = 1$, $R = CH_3$, $[M] = AlCl_3$.[84–86] Analysis of the ^1H and ^{13}C NMR spectra of the corresponding compounds over a wide range of conditions enabled a number of investigators[79–81] to find that in this case the intramolecular dynamics involves mainly (if not exclusively) the 1,2-shifts of the group $AlCl_3$ along the ring perimeter;



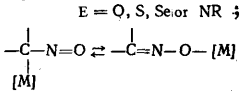
III. C,E-TRANSITIONS (E = O, S, Se, or NR)

Among non-degenerate C,E-triads, for which there is a possibility of the observation of metallotropic transitions, we shall point to two which are of particular interest—of the keto-enol type (18) and the nitroso-isonitroso type (19). In the corresponding non-metallated systems the reversible equilibrium prototropic transitions, which are rapid in terms of the NMR time scale, are as a rule observed extremely rarely[103]. However, in the study of the C,E-transitions in similar triads by procedures including the NMR method, certain advances have already been made, although in each individual case there is a probability of a shift of equilibrium (18) to one side, which precludes the simultaneous observation of both tautomeric forms in solution;



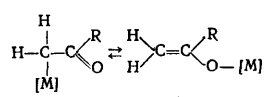
(18)

E = O, S, Se or NR;



(19)

The results of studies of keto-enol transformations (18) by procedures including infrared and NMR spectroscopy have been reported[14,104,105] for $[M] = R_3Sn$, R_3Ge, and E = O. The ratio of the tautomers in these systems depends on a number of factors, including the solvent and the presence of catalytic admixtures of certain compounds:

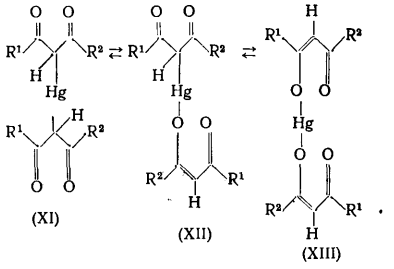


(Xa) (Xb) (20)

In the study of the ^1H NMR spectra of the $(CH_3)_3Sn$ derivative of acetone (X, $R = CH_3$)[14] the averaging of the signals due to the CH_2 groups of the O- and C-isomers was observed even in the absence of the catalysts, which indicates the

occurrence of fairly rapid C,O-transitions of the group $(CH_3)_3Sn$. The observed changes in the chemical shifts of the signals due to the CH_2 protons as a function of temperature permitted the conclusion that a change of temperature entails a displacement of tautomeric equilibrium (20) in the compound. The merging of the signals corresponding to different isomers and observed separately at lower temperatures has also been observed at 150 °C in chlorobenzene in the spectrum of the analogous derivative of acetophenone (X, $R = C_6H_5$).

C,O-Transitions of organomercury groups have been studied in connection with the analysis of the NMR spectra of a series of acetylacetonato-derivatives of mercury[15,106,107]:

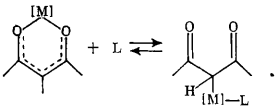


(21)

A study[15] of the keto-compound (XI, $R^1 = R^2 = t\text{-}C_4H_9$) in $CHCl_3$ showed that at room temperature the ^1H NMR spectrum does not exhibit signals corresponding to the $^{199}Hg-C-^1H$ spin–spin interaction, while at lower temperatures not only these satellites but also the methylidyne signal, corresponding to approximately a 3% content of one of the enol isomers (XII) or (XIII), are observed. This result can be explained by postulating that the organomercury group undergoes fairly rapid metallotropic C,O-transitions (21) in solution [in the crystal the compound exists only in the keto-form (XI)[106,108]]. It was subsequently found that[10] the C,O-transformations in this system are rapidly accelerated when ethanol-d_6 is used as the solvent.

A quantitative study of the keto–enol transitions (21) has been carried out[107] by dynamic NMR with the acac derivative of mercury, in which a high stabilisation of the enolic form ($R^1 = n\text{-}C_3F_7$ and $R^2 = t\text{-}C_4H_9$) has been achieved by introducing the electronegative group $n\text{-}C_3F_7$§. Apart from the main isomer (XI) in solution [in the crystal the compound exist only in the keto-form (XII)] comparable amounts have also been found of the enolic isomer (XII) and under certain conditions the two isomers are interconverted at a fairly high rate [isomer (XIII) with $R^1 = n\text{-}C_3F_7$ and $R^2 = t\text{-}C_4H_9$ is not formed, which facilitated the interpretation of the results by the authors[107]].

Analysis of the ^1H NMR line form of the compound in deuteroacetone in the temperature range from −60 °C, where the spectrum shows only the signal due to the proton of the methylidyne group of the keto-form (XI) and two signals due to the methylidyne protons of the enolic form (XII), to +40 °C, where all three signals merge into one, made it possible to determine the necessary thermodynamic parameters of the process ($E_a = 9.9$ kcal mol^{-1}).[107] Special experiments established that the metallotropic C,O-transitions take place intramolecularly in this instance (at least in the temperature range from −60° to +10 °C). It was noted that a change in the nature of the solvent influences the rate of the C,O-transitions but has almost no effect on the equilibrium position. Finally, analysis of the NMR data available for the acac derivatives of other metals capable of forming a C–M bond (platinum[110] and gold[111,112]) enabled the authors[107] to conclude that, among these metals, mercury is the most labile in relation to metallotropic C,O-transitions:

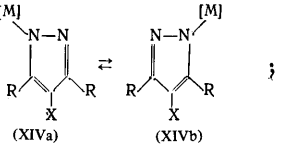


(22)

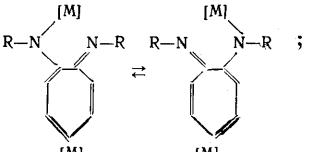
It has recently been reported[113] that the C,O-transition (22) has been detected by NMR in acetylacetonato-derivatives of gold with $[M] = Au(CH_3)_2$ and $L = PR_3$, in the course of which the acac ligand behaves either as a bidentate O-derivative or as a monodentate C-derivative. Reaction takes place when phosphines, which are necessary for the retention of the coordination number of the metal in the course of the process, are added to the solution.

IV. N,N-TRANSITIONS IN TRADITIONAL TAUTOMERIC SYSTEMS

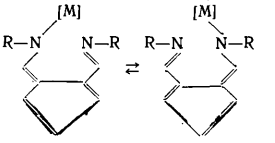
Among the traditional structures in which metallotropic N,N-transitions are possible, in principle, we may point in the first place to several even systems—the diad system (23), the tetrad system (24), and the hexad system (25).



(23)



(24)



(25)

Hypotheses concerning the possibility of the tautomeric transformations (23)–(25) for $[M] = H$ have been frequently put forward on the basis of various considerations including NMR data[114–122]. In particular, it has been possible[116] to "freeze" by dynamic NMR the prototropic N,N-transitions (25) and to discover the asymmetric structure of the fragment N...H–N. However, in terms of the phenomenon considered here the study of the N,N-transitions of the cationoid species $[M] \neq H$ has been developed to a definite extent only in the field of pyrazoles (23).

The occurrence of metallotropic N,N-transitions (23) has been demonstrated[17] in relation to *N*-arylmercury derivatives of pyrazoles and also[123–125] for $[M] = SiR_3$ and $Ge(CH_3)_3$. The case with $[M] = Sn(C_4H_9\text{-}n)_3$ has also been investigated recently[126].

N-Phenylmercury derivatives of 3,5-dimethyl-4-X-pyrazoles (XIV), where $[M] = HgC_6H_5$, $R = CH_3$, and X = Cl, Br, or NO_2, have been chosen[17] as model systems and the corresponding non-metallated compounds with $[M] = H$ were used

§ It must be emphasised that the acac derivatives of mercury can have, in principle, different and frequently unexpected structures[109], since kinetic study of their rearrangements, including C,O-transitions, is virtually impossible without a preliminary unambiguous determination of the structure of the substance.

for comparison. In the fixed isomers (XIVb), which are detected at fairly low temperatures, the degrees of shielding of the 3- and 5-CH_3 groups in the case of [M] = HgC_6H_5 differ appreciably. In contrast to organomercury derivatives, the separation of the signals due to the methyl protons is not observed in the ^1H NMR spectra of the initial pyrazoles {[M] = H} up to −110 °C.[17] This may be caused either by the higher mobility of the tautomeric system with [M] = H or by the unduly small difference between the degrees of shielding of the 3- and 5-methyl groups in the fixed tautomers. The data obtained in studies[121,122] where the splitting of the signals due to the $C_{(3)}$ and $C_{(5)}$ nuclei in compounds (XIV) with [M] = H and R = X = H, was observed in solvating solvents by ^{13}C-{^1H} NMR (at −110 °C in a mixture of diethylether and tetrahydrofuran[121] and at −17 °C in hexamethylphosphoramide[122]) apparently also support the first hypothesis.

Different mechanisms of the metallotropic transitions in the series of pyrazoles have been analysed[17]. In particular, the intermolecular N,N-transitions can occur in principle via both bimolecular and ionic mechanisms. However, the bimolecular mechanism of the formation of phenylmercury derivatives of pyrazoles tends to be disproved by the fact that the parameters of the ^1H NMR spectrum of compound (XIV, R = CH_3 and X = Cl) are independent of the concentration of this compound. Data concerning the influence of polar additives on the rate of the process may be evidence against the intermolecular transfer of the organometallic group via an ionic mechanism. It has been found that, when the polar nitromethane is added to a mixture of methylene chloride and chloroform, chosen as the main solvent, the migration of the phenylmercury group is accelerated slightly[17]. The use of a solvating agent such as pyridine as the additive also does not entail appreciable changes [which is analogous to the absence of a dependence of the rate of N,N-transitions on the solvent, observed in an NMR study of the $(CH_3)_3Si$ derivatives of pyrazole[125]].

Thus the most acceptable explanation of the ^1H NMR data obtained by Kravtsov et al.[17] is that the organomercury groups migrate between nitrogen atoms via the intramolecular 1,2-transitions (23). This mechanism presupposes the coordination of the mercury atom in its transition state to both nitrogen atoms of the heterocycle.

Solvating solvents exert different types of influence on the prototropic and metallotropic N,N-transitions in pyrazoles. Thus the addition of the polar nitromethane to a solution of compound (XIV) with [M] = H and X = Cl[116] as well as [M] = HgC_6H_5[17] has only an insignificant influence on the process. However, the addition of pyridine leads to a sharp acceleration of the prototropic process although this type of influence by pyridine has not been observed for [M] = HgC_6H_5. These findings apparently indicate a difference between the mechanisms of the N,N-transitions in the solvents employed. For cationoid species of other types, for example, [M] = SiR_3 and $Ge(CH_3)_3$, the results of studies by dynamic NMR[123-125] show that, as for [M] = HgC_6H_5, the N,N-transitions take place intramolecularly. These NMR data make it possible to set up sequences (26) and (27) based on the relative increase of the mobilities of the cationoid species in the series of pyrazoles as a function of their nature[26,27]:

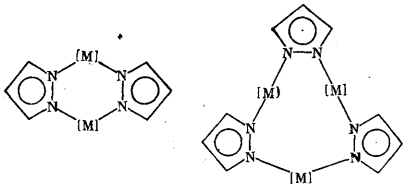
$$Si(OC_2H_5)_3 < Si(CH_3)_3 \sim Si(C_2H_5)_3 < Ge(CH_3)_3 < Sn(C_4H_{9}\text{-}n)_3 \quad (26)$$

$$SiR_3 < Ge(CH_3)_3 < HgC_6H_5 . \quad (27)$$

The available NMR data also permit certain inferences concerning the influence of substituents in the anionoid residue on the rates of the N,N-transitions. For example, an increase of the electron-donating capacity of the substituents in the 3- and 5-positions is accompanied by the acceleration of the 1,2-transitions of the organosilicon and organogermanium groups:

$$CF_3 < H < CH_3 . \quad (28)$$

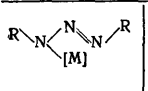
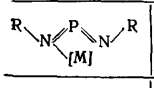
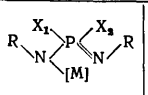
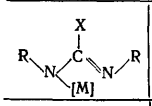
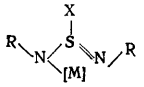
In conclusion we emphasise that the intramolecular mechanism formulated for the group of cationoid species considered, [M] = HgR, SnR_3, GeR_3, and SiR_3, for which the compounds (XIVa) are monomeric, cannot be transferred mechanically to pyrazoles with cationoid species of other types:



(XVa) (XVb)

The simplest example of explicit differences is provided by the case with [M] = H for which the trimeric structure (XVb) has been postulated[21], in the ground or transition states and for the description of the N,N-transitions of which one evidently cannot use mechanism (20). The pyrazole derivatives of univalent gold, [M] = Au, have an analogous structure in the ground state[127,128]. The dimeric structure (XVa) in the ground state has been established for yet another group of cationoid species with [M] = BR_2, AlR_2, GaR_2, or TlR_2,[129-132] and all the M–N bonds in these compounds are virtually equivalent[129].

Table 1. Certain degenerate metallotropic 1,3-transitions between nitrogen atoms in triad systems (according to NMR data).

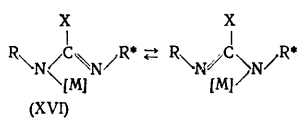
Tautometic system	X	[M]	R	Solvent	*t*, °C*	Refs.
	—	HgC_6H_5	FC_6H_4	Py + THF + $CHCl_3$ (3:2:2)	<−120	[139]
	—	$Si(CH_3)_3$	CH_3	C_6H_6	>80	[140]
	—	$Si(OCH_3)_3$	CH_3	CH_2Cl_2	18	[141]
	—	$Si(CH_3)Cl_2$	CH_3	CH_2Cl_2	−2	[141]
	—	$Si(CH_3)_3$	$C(CH_3)_3$	C_6H_6	0	[148]
	—	$Si(CH_3)_3$	$Si(CH_3)_3$	C_6H_{12}	77	[147]
	X_1=X_2=CH_3; X_2=$C(CH_3)_3$	$Sn(CH_3)_3$	CH_3	CCl_4	<−50	[145]
	X_1=CH_3; X_2=$C(CH_3)_3$	$Si(CH_3)_3$	CH_3	CCl_4	<−50	[145]
	X_1=X_2=OCH_3	$Si(CH_3)_3$	$Si(CH_3)_3$	decalin	98	[146]
	X_1=X_2=CH_3	$Si(CH_3)_3$	$Si(CH_3)_3$	$CDCl_3$	−20	[143]
	H	$HgCH_3$	n-$CH_3OC_6H_4$	CH_2Cl_2	<−100	[142]
	H	HgC_6H_5	n-$CH_3C_6H_4$	CH_2Cl_2	<−100	[142]
	C_6H_5	$Sn(CH_3)_3$	CH_3	$CDCl_3$	<−60	[9]
	C_6H_5	$Si(CH_3)_3$	CH_3	$CDCl_3$	<−60	[9]
	CH_3	$Si(CH_3)_3$	$Si(CH_3)_3$	$(C_2H_5)_2O$	<−50	[144]

* The temperature at which the signals of the indicator nuclei merge.

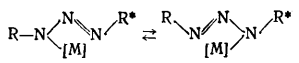
Among the odd systems, in which there is a possibility of N,N-transitions of organometallic species in principle, we shall point out, for example, the amidine triad (29) and the

diazoamine triad (30). The prototropic transformations (degenerate and non-degenerate) in the corresponding initial structures with [M] = H have so far been inadequately investigated by NMR[133-139]. There are also few data concerning the metallotropic transitions[9,139-142]. Table 1 gives a compilation of the available information about the degenerate metallotropic 1,3-transitions between nitrogen atoms in these and certain other triad systems, which have so far been established by NMR. It also includes data obtained for [M] = $Si(CH_3)_3$, because they make it possible to discover certain tendencies useful in the analysis of metallotropic transitions proper.

Degenerate metallotropic N,N-transitions of the amidine type were first observed in 1968[9] in the study of the ^1H NMR spectra of N,N-dimethylbenzamidine derivatives (XVI) with [M] = $Sn(CH_3)_3$ or $Si(CH_3)_3$, R = CH_3, and X = C_6H_5.[9]


(XVI)

(29)



(30)

It has been found that the signals of the non-equivalent *N*-methyl groups observed separately at −60 °C merge into a singlet with increase of temperature, which indicates acceleration of the N,N-transitions (29). This migration apparently takes place intramolecularly, which can be inferred from the absence of a dependence of the NMR spectra on the concentrations of the compounds and also from the observation in the case of [M] = $Sn(CH_3)_3$ even under fast dynamic conditions of satellites due to the spin–spin interaction of the ^{117}Sn and ^{119}Sn nuclei with the protons of the N–CH_3 groups[9]. For [M] = H, a singlet due to the indicator protons has also been observed at room temperature.

The results of a study[142] in which an attempt was made to observe N,N-transitions (29) of organomercury groups in compounds (XVI) with [M] = HgC_6H_5 or $HgCH_3$, X = H, and R = aryl permit additional conclusions. The ^1H NMR spectra of these compounds at temperatures up to −100 °C do not exhibit a splitting of the signals due to the indicator group protons (Table 1), which can be explained either by the unduly high rate of the N,N-transitions (29) or by the symmetrical structure of the compound in which the metal atom is linked simultaneously to both nitrogen atoms. Bearing in mind that the latter hypothesis conflicts with X-ray diffraction data[142], presumably the 1,3-N,N-transitions (29) of the organomercury groups in the amidine triad are appreciably faster than the transitions of the organotin groups.

The proton N,N-transitions in the open diazoamine systems (XVII) have been investigated frequently by NMR, but the majority of these studies refer to non-degenerate transformations with [M] = H and R ≠ R*. The retardation of the proton transitions (30) in the degenerate case has been noted in only one study[138].

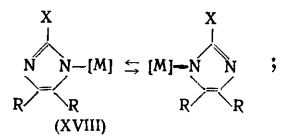
The study of degenerate metallotropic N,N-transitions (30) has begun only recently. Thus it has been observed[139] that, in contrast to di-(4-fluorophenyl)triazenes, the N,N-transitions (30) in their phenylmercury derivatives (XVII) with [M] = HgC_6H_5 and R = 4-FC_6H_5 are so fast that even in the temperature range from −90° to −120 °C only a consecutive broadening of the fluorine signal is observed, which may be evidence in support of some retardation of the intramolecular metallotropic transitions (the intermolecular migration of the phenylmercury groups takes place at higher temperatures). It is interesting to compare these results with data obtained for the N,N-transitions of organosilicon groups[140,141]. For [M] = SiR_3, the N,N-transitions (30) are also intramolecular and their rate depends significantly on the structure of the groups in [M]:

$$SiCH_3(C_2H_5)_2 < Si(CH_3)_3 < Si(CH_3)_2OCH_3 < SiCH_3(OCH_3)_2 < Si(OCH_3)_3 < \\ < Si(CH_3)_2Cl < Si(CH_3)Cl_2 < HgC_6H_5. \quad (31)$$

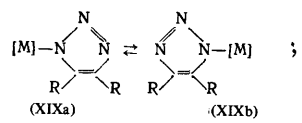
Presumably sequence (31) is associated with the increase in the same order of the coordinating capacity of the key element (Si or Hg), which facilitates the formation of the transition state.

The results of the NMR study of dynamic processes also in the series of derivatives of certain transition metals are available[149-153], but, bearing in mind the fact that the triazene ligand in transition metal complexes can behave not only (and not so much) as a monodentate species but also as a bidentate or bridging species[153-156], it is natural to suppose that the correct interpretation of these results requires the determination of independent data on the structure of the compounds, particularly on the type of bond between the organometallic group and the anionoid residue.

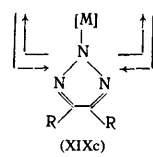
Among cyclic systems, imidazoles (XVIII) and vicinal 1,2,3-triazoles (XIX) are the simplest and most natural analogues of triads of the amidine and diazoamine types. As regards the possible metallotropic N,N-transitions, the most interesting feature of these nitrogen heterocycles is that, in contrast to the amidine and diazoamine triads (29) and (30), a planar four-unit cyclic transition state incorporating the M atom and three atoms of the triad cannot be formed in such systems:


(XVIII)

(32)


(XIXa) (XIXb)

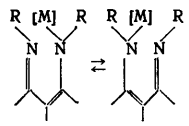
(33)


(XIXc)

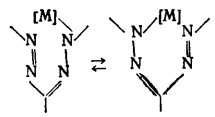
The question of the possible metallotropy in imidazoles can be considered in relation to cationoid groups such as $Si(CH_3)_3$ and $Ge(CH_3)_3$. Thus a study[157] of the ^{13}C NMR spectrum of trimethylsilyl derivatives of imidazole (X = CH_3, R = H) in the absence of a solvent demonstrated the non-equivalence of the $C_{(4)}$ and $C_{(5)}$ atoms even at room temperature. An analogous phenomenon has been observed in the study of the ^1H and ^{13}C NMR spectra of *N*-trimethylsilylimidazole and the ^{13}C NMR spectrum of an *N*-trimethylsilyl derivative of 2-methylimidazole in triethylamine. These results showed that, for [M] = $Si(CH_3)_3$, intramolecular 1,3-transitions (32) do not occur in imidazole. However, it has been established[157] that traces of water, usually present even in highly purified specimens of trimethylsilylimidazoles, catalyse intermolecular

N,N-transitions of the $(CH_3)_3Si$ groups¶. This conclusion was confirmed by the measurement of "frozen" ^1H and ^{13}C NMR spectra of trimethylsilyl derivatives of imidazoles and 2-methylimidazole in the study of each in triethylamine and by the acceleration of N,N-transitions following the addition of water. The intermolecular nature of the N,N-transitions was confirmed in the study of the ^{13}C NMR spectra of a mixture of trimethylsilyl derivatives of imidazole and 2-methylimidazole.

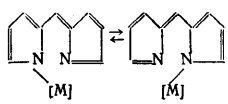
From the standpoint of metallotropic N,N-transitions, vicinal 1,2,3-triazoles (XIX) have yet another feature which distinguishes them from triazenes and is associated with the indefinite nature of the "instantaneous" structure of these compounds for different [M]. In particular, the fact that the ^{13}C NMR signals corresponding to the $C_{(4)}$ and $C_{(5)}$ nuclei are not resolved up to −50 °C for $[M]=SnR_3$[158] can be accounted for by the symmetrical structure of compound (XIXc) (all these compounds are monomeric in solution) and not by the rapid migration of the SnR_3 group between the nitrogen atoms via process (33). Although the authors themselves[158] are inclined towards the first hypothesis, the second explanation is no less ligitimate. Thus further study of the metallotropic transitions in the series of vicinal triazoles should be preceded by an unambiguous determination of their "instantaneous" structure:



(34)

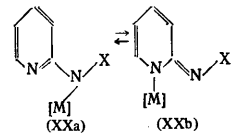


(35)



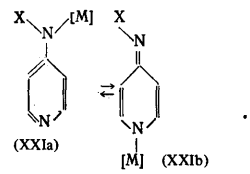
(36)

Only a few studies have been made on the question of the N,N-transitions of cationoid species in the pentads (34)–(36) and mainly for the case where [M] = H. In particular, low-temperature NMR measurements do not permit the detection of the prototropic transitions (36).[159] It has been suggested[160] on the basis of NMR data that, for $[M]=Tl(CH_3)_2$, the organometallic species is linked simultaneously to both nitrogen atoms. Although this conclusion is entirely likely, a more rigorous treatment requires the corresponding low-temperature measurements in order to throw more light on the question of the "instantaneous" structure of the compound with $[M]=Tl(CH_3)_2$: whether the metal in this derivative is tetracoordinate or tricoordinate and whether it executes rapid N,N-transitions:



(37)

An instance of non-degenerate N,N-transitions has been found[4,5] in an ultraviolet spectroscopic study of solutions of phenylmercury derivatives of 2- and 4-phenylsulphonylaminopyridines (representing respectively an aminopyridine triad and pentad). The simultaneous existence in solution in acetonitrile of the two possible tautomeric forms of these compounds—the aminopyridine form (XXa) or (XXIa) and the pyridone imine form (XXb) or (XXIb)—and their interconversion via non-degenerate metallotropic transitions of the amidine type (37) or (38) for $[M]=HgC_6H_5$ and $X=SO_2Ar$, has been demonstrated. A dependence of the tautomer ratio on the nature of the medium has been established. In particular, in dioxan equilibria (37) and (38) are almost wholly displaced towards the aminopyridine form:



(38)

The influences of various factors on the shifts of the tautomeric equilibria (37) and (38) have been compared for two different cationoid groups, namely [M] = H and HgC_6H_5.[4,5] It was found that, for [M] = H, the pyridone imine forms (XXb) and (XXIb) are more stable than for $[M]=HgC_6H_5$, particularly in solvents of low polarity. The substituents in the *para*-position of the benzene ring of the SOAr group have the same effect on the position of the tautomeric equilibrium involving both 2- or 4-arenesulphonylaminopyridines and their phenylmercury derivatives.

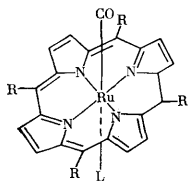
V. METALLOTROPIC N,N-TRANSITIONS IN SYSTEMS WITH M–N COORDINATE BONDS

In the tautomeric systems considered the metallotropic N,N-transitions of metal-containing species are accompanied by a rearrangement of the system of multiple bonds in the molecules. However, in principle, in organometallic derivatives one cannot rule out the possibility of the existence of tautomeric systems in which the metallotropic transition between two states does not require a redistribution of the multiple bonds. One of the types of structures of this kind can evidently consist of compounds in which [M] migrates between the heteroatoms N,O,S, etc., subject to the condition that the M–E bond is a coordinate linkage and that two or more equivalent or different atoms able to behave as donors of an unshared electron pair are available for its formation.

Such tautomeric systems have indeed been found in recent years. The first report of "non-traditional" metallotropic 1,3-transitions between nitrogen atoms appeared in 1967[161,162] and that of intramolecular 1,2-transitions was published in 1972.[163] Hitherto this phenomenon has been observed and investigated for an extremely wide variety of nitrogen-containing systems[164–183]. Several examples of degenerate

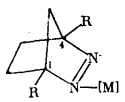
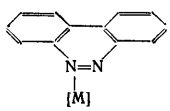
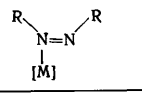
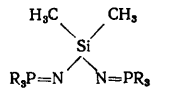
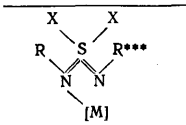
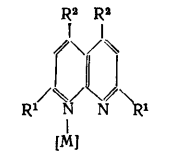
¶ In the light of these results, the results of a dynamic NMR study of imidazole derivatives, carried out for [M] = $Ge(CH_3)_3$, R = H or CH_3 and X = H by Cotton and Ciappenelli[124] and for $[M]=Si(CH_3)_3$ and R = X = H carried out by Torocheshnikov et al.,[125] apparently become more understandable. The studies were performed without taking into account the possibility of catalysis by traces of water and led the authors[124,125] to somewhat different conclusions, although they observed experimentally the same result—the identical shielding of the $H_{(4)}$ and $H_{(5)}$ nuclei as well as $C_{(4)}$ and $C_{(5)}$ nuclei over the entire temperature range accessible to investigation.

N,N-transitions of the 1,2- and 1,3-types in compounds with heterocyclic and other anionoid residues are presented in Table 2.



(XXII)

Table 2. Certain degenerate metallotropic 1,2- and 1,3-transitions between nitrogen atoms in non-traditional tautomeric systems (according to NMR data).

Tautomeric system	[M]	R	Solvent	t, °C*	Refs.
1,2-Transitions					
	$Cr(CO)_2Ar$	H	toluene-d_8	⩽50	[170]
	$Cr(CO)_5$**	—	$CDCl_3$	20	[176]
	$W(CO)_5$**	—	$CDCl_3$	20	[176]
	$Rh(CO)_2Cl$	—	$CDCl_3$	20	[178]
	$W(CO)_5$	iso-C_3H_7	$(CD_3)_2CO$	−30	[177]
1,3-Transitions					
	$Al(CH_3)_3$	CH_3	CH_2Cl_2	−60	[162]
	$Ga(CH_3)_3$	CH_3	CH_2Cl_2	−60	[162]
	$In(CH_3)_3$	CH_3	CH_2Cl_2	<−70	[162]
	$Al(CH_3)_3$	$Si(CH_3)_3$	CH_2Cl_2	−60	[166]
	$Al(CH_3)_3$	$Ge(CH_3)_3$	CH_2Cl_2	−60	[166]
	$Au(CH_3)_2X$****	R^1=CH_3, R^2=H	CH_2Cl_2	−90	[167]
	$Pt(PEt_3)Cl$	R_1 = R_2=H	$CD_2Cl_2/(CD_3)_2CO$	−70	[180]

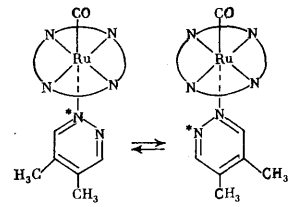
* Temperature at which the indicator nuclei are detected separately.

** ^{13}C NMR.

*** X = CH_3 or C_2H_5.

**** X = Hal, OCN, etc.

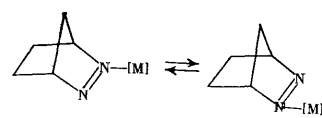
Eaton et al.[163] investigated by dynamic ^1H NMR several complexes of type (XXII), where R = iso-C_3H and L = mono- or di-nitrogen heterocyclic ligand. It was found that in the case where L = 4,5- or 3,6-dimethylpyridazine, 1,2-transitions can occur intramolecularly:



(39)

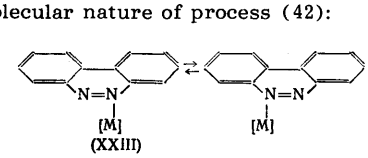
In particular, when L = 4,5-dimethylpyridazine at solution temperatures below approximately 12 °C, the signals corresponding to the indicator methyl groups are observed separately. With increase of temperature the signals broaden, approach one another, and finally merge into a single signal. The temperature dependence of the NMR line form for the complex in the presence of an excess of the free ligand permitted the conclusion that, in the range from −24° to +40 °C, process (39) is intramolecular, while at temperatures in the range 30–150 °C it also becomes intermolecular. Analogous results have been obtained in the study of the ruthenium complex of 3,6-dimethylpyridazine. In this case the process proceeds intramolecularly at lower temperatures, while above −43 °C it can also take place intermolecularly[163].

A study[170] of compounds of the type $CrAr(CO)_2L$, where L = 2,3-diazabicyclo[2,2,1]hept-2-ene, demonstrated a temperature dependence of the signal due to the 1,4-protons, which indicated the identical shielding of these protons at high temperatures and their different shielding at low temperatures. The authors suggested that these spectral changes are related to intramolecular 1,2-transitions (40) of the group [M] = $Cr(CO)_2Ar$ between the bicyclic nitrogen atoms. The study of process (40) using different aromatic ligands in [M] revealed a dependence of the free energy of activation for the process on the structure of the aromatic π-ring: $(CH_3)_6C < 1,3,5\text{-}(CH_3)_3C_6H_3 < C_6H_6 < 1,4\text{-}[CH_3OC(O)]_2.C_6H_4$.



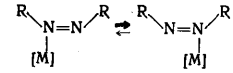
(40)

Additional information about the 1,2-transitions of groups containing transition metals has been obtained in a number of studies[176–179]. In particular, in a study of compounds (XXIII) by ^{13}C and ^1H NMR it was found that, for [M] = $Cr(CO)_5$ and $W(CO)_5$, process (41) takes place fairly rapidly at room temperature. The study of the $W(CO)_5$-complexes of the *cis*- and *trans*-isomers of 2-azopropane showed that N,N-transitions take place only in the *cis*-compounds {[M] = $W(CO)_5$, R = iso-C_3H_7; process (42)}. In this case the proximity of the neighbouring nitrogen atom reduces the activation energy for the intramolecular transition so much that the formation of a new W–N bond in the transition state requires a preliminary dissociation of the old bond. A series of pieces of evidence have been adduced in support of the intramolecular nature of process (42):

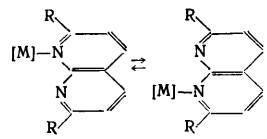


(XXIII)

(41)



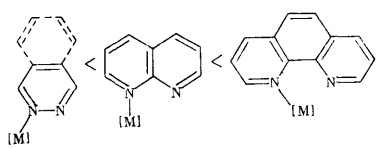
(42)



(43)

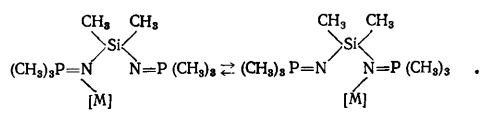
A thorough study has been made[167] of the metallotropic 1,3-N,N-transitions (43) in a series of 1,8-naphthyridine derivatives with $[M] = (CH_3)_2AuX$, X = Hal, OCN, or SeCN, and $R = CH_3$. At room temperature in weakly solvating solvents the ^1H NMR spectra of the compounds show that the non-equivalent methyl groups of the ligand are equally shielded, while at −90 °C their signals are converted into two separate singlets of equal intensity. The corresponding changes have been observed for aromatic protons in the 3,4- and 5,6-positions. Special experiments have established that the dynamic process is intramolecular (its characteristics are independent of the concentration of the test substance and of the addition of an excess of free 1,8-naphthyridine). This fact and also the monomeric nature of the compound permitted the conclusion that the changes in the NMR spectra are caused by metallotropic 1,3-transitions of the organogold group between the nitrogen atoms of the 1,8-naphthyridine ring. Yet another feature of process (43) should be noted: changes in the substituent X in the organogold group hardly alter the free energy of activation for the process.

Transitions of type (43) have also been studied for $[M] = MCl(PR_3)_2$, R = H, and M = Pt or Pd.[180-183] Furthermore, studies have been made of the 1,4-transitions of these metal-containing groups in a 1,10-phenanthroline complex and of the 1,2-transitions in the pyridazine and phthalazine complexes. Comparative analysis of the NMR data led to the conclusion that the rate of the N,N-transitions of the metal-containing group increases in the sequence:



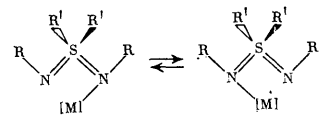
The increase takes place as the orientation of the unshared electron pair of the non-coordinated nitrogen atom becomes more favourable for the formation of a transition state in which both nitrogen atoms are linked simultaneously to the metal atom. In the palladium derivatives the rate of the process is higher than in the platinum compounds.

A comparative study has been made[161,162] of the 1,3-N,N-transitions (44) of the organometallic groups $[M] = Al(CH_3)_3$, $Ga(CH_3)_3$, and $In(CH_3)_3$:



(44)

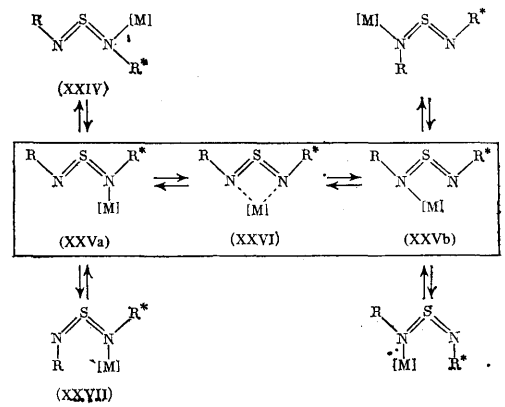
The ^1H NMR spectra of these derivatives at room temperature showed, as for the free ligand, a single doublet signal corresponding to the protons of the $(CH_3)_3P$ group. With decrease of temperature the signal broadens and in the case of the aluminium and gallium derivatives is split into two doublets of equal intensity; for the indium compound the splitting is not achieved even at −70 °C. The authors[152] concluded that they observed intramolecular 1,3-N,N-transitions (44) (their rate is independent of the addition of the non-coordinated ligand) of the groups $M(CH_3)_3$, whose rate increases in the sequence $Al(CH_3)_3 < Ga(CH_3)_3 < In(CH_3)_3$. Presumably this sequence is due to the increasing size of the vacant orbital of the metal with increase of its atomic number, which facilitates the formation of the transition state in which the metal forms a new bond before the dissociation of the old one:



(45)

Data have been published[166] on the metallotropic N,N-transitions (45) in bis-*S*-alkyl derivatives of sulphodi-imide, where $[M] = Al(CH_3)_3$, $R = (CH_3)_3Ge$ or $(CH_3)_3Si$ and $R' = CH_3$ or C_2H_5. At room temperature the ^1H NMR spectra exhibited a single signal corresponding to the indicator groups R; at lower temperatures the signal is split into two components of equal intensity. The authors[166] interpreted these results from the standpoint of fairly rapid N,N-transitions (45) of the organoaluminium group in the system. As regards the mechanism of these transitions, they occur mainly intramolecularly at fairly low temperatures, while at higher temperatures they can also take place intermolecularly.

A series of studies[171-175] have been devoted to the structure of and dynamic, including metallotropic, processes in sulphodi-imide derivatives of transition metals without substituents at the sulphur atom. Sulphodi-imides non-alkylated at the sulphur atom themselves undergo intramolecular dynamic transformations in the temperature range investigated by the authors (mainly as a result of the internal rotation about the S = N bond). This complicated the interpretation of the phenomena concerning the NMR spectra of the sulphodi-imide complexes of transition metals. Furthermore, one must take into account the fact that, on formation of these complexes, the sulphodi-imides can function not only as N-donors but also as S-donors or chelates, depending on the nature of the metal-containing group:



(46)

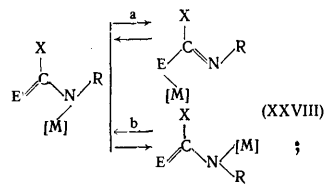
In the interpretation of the ^1H and ^{13}C NMR spectra of the sulphodi-imide derivatives of platinum(II), palladium(II), rhodium(I), and iridium(I) the authors considered several possible types of transformations, mainly intramolecular ones [the processes (XXIV) ⇌ (XXVa), (XXVII) ⇌ (XXVa), and (XXVa) ⇌ (XXVI) ⇌ (XXVb) via mechanism (46)]. Among these, only the reaction (XXVa) ⇌ (XXVb) is a metallotropic N,N-transition, which involves the intermediate formation of the transition state (XXVI) and which proved to be extremely sensitive to different structural factors. It has been found that the N,N-transitions depend appreciably on the properties of the metal and its environment and begin to be observed in the NMR spectra at temperatures from −45° to +60 °C; their rate decreases in the sequence Rh^I, Ir^I > neutral Pd^{II}, cationic Pt^{II} > neutral Pt^{II}.

A number of workers[172,174,175] were able to find several compounds in which the ligand exists mainly in the *trans, trans*-form (XXV) (and in which the dynamic processes observed by NMR can be explained exclusively by metallotropic N,N-transitions), in particular, a number of bivalent platinum complexes. A distinct separation of the signals corresponding to the indicator aryl groups is observed at −20 °C in the ^1H and ^{13}C NMR spectra of the complexes (XXV) with R = Ar and [M] = *trans*-$PtCl_2L$, while at 0 °C these signals have already merged. The N,N-transitions (46), whereby the authors[172] explained the observed spectral changes, proved to be intramolecular, because their rates were independent of either the concentration of the platinum complex or of the addition of the free ligand to the solution; however, above 30 °C the process was found to take place also via an intermolecular mechanism.

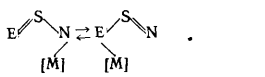
Among other features of reaction (46), the following have been noted. Firstly, it has been found that the rate of the N,N-transitions of platinum in diarylsulphodi-imides increases with decrease of the electron-donating capacity of the ligand L: $PR'_3 > AsR'_3 > SbR'_3$. Secondly, the rate of the process increases on enhancement of the electron-accepting properties of the aryl substituents and is therefore greater for R = Ar than for R = Alk. According to the authors, these results can be explained by the fact that the electron-accepting constituents are capable of stabilising the transition state (XXVI).

VI. N,E-TRANSITIONS (E = O, S, or Se)

Fairly numerous studies have been made of the dynamic transformations in the triads (47)[184-200] and (48)[201,202] (E = O or S). The interpretation of the results is in many instances difficult because of the possibility of dynamic changes of two types in these compounds—the 1,3-N,E-transition (47a) of the cationoid group and the internal rotation (47b) about the C–N bond in the amide(thioamide) form:



(XXVIII) ; (47)



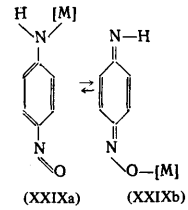
. (48)

In particular, when E = O, processes (47) were investigated in relation to different cationoid species and the occurrence of the amido-amidol N,O-tautomerism was noted for [M] = $Al(CH_3)_2$,[184] BR_2,[185] and SiR_3.[175]

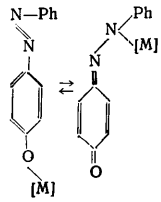
It has been shown for [M] = $Si(CH_3)_3$ and X = CH_3 that the N,O-transitions (47a) take place intramolecularly and that the *para*-substituents in R = aryl alter appreciably the ratio of the tautomers, promoting a shift of the equilibrium in the direction of the imidol form (XXVIII) in the sequence[197] $OCH_3 < CH_3 < H < Cl < NO_2$.

The 1,3-migration (47a) and the internal rotation (47b) have also been investigated for E = S, but in relation to a smaller number of examples.

A study has been made[2] of several potentially tautomeric systems in which there is a possibility of the metallotropic N,O-transitions (49) and (50)—nitrosoanilines (XXIX), hydroxyazo-compounds (XXX), and quinone phenylhydrazones:



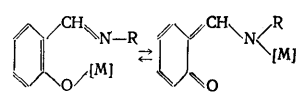
(XXIXa) (XXIXb) ; (49)



(XXXa) (XXXb) . (50)

In the study of nitrosoanilines, nitrosonaphthylamines, and their arylmercury derivatives a similarity was observed in the behaviour of cationoid species such as [M] = H and [M] = HgC_6H_5 from the standpoint of the tautomeric equilibrium (49); both organometallic derivatives and their unsubstituted analogues have the nitrosoamine structure (XXIXa) in solution (in contrast to nitrosophenols, for which the quinonoid form predominates). However, in the sodium salts of nitrosoanilines and nitrosonaphthylamines the anions exist in the quinonoid form. Similar results have been obtained in the study of hydroxyazo-compounds and their arylmercury derivatives (XXX). For cationoid species of both types—[M] = H and [M] = HgAr—the benzenoid structure (XXXa) is typical both in solution and in the solid state.

Yet another example of metallotropic tautomeric systems is provided by the organometallic derivatives of *o*- and *p*-hydroxyarylaldimines[203]. In particular, analysis of electronic and luminescence spectroscopic data for o-compounds of type (XXXI) with [M] = $HgCH_3$, HgC_6H_5, or $Tl(C_2H_5)_2$ led to the discovery of non-degenerate O,N-transitions (51). As for [M] = H, in non-polar solvents equilibrium (51) is almost wholly displaced towards the benzenoid O-form (XXXIa), while in solvating media the content of the quinonoid tautomers (XXXIb) also becomes appreciable. A shift towards the quinonoid form is likewise observed following a decrease of temperature. It is striking that in the crystalline state compound (XXXI) with [M] = HgC_6H_5 exists entirely in the quinonoid N-form[204]. The occurrence of O,N-transitions has also been observed in the phenylmercury derivative of *p*-hydroxyarylaldimine[203]:

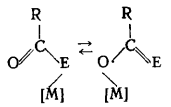


(XXXIa) (XXXIb) . (51)

VII. O,E-TRANSITIONS (E = O, S, or Se)

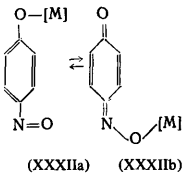
There are virtually no NMR data on degenerate metallotropic O,O-transitions in triads such as [M]–O–N=O and R–C(=O)–O–[M] and their determination will be limited by the

degree of development of the ^{17}O NMR method. It is methodologically simpler to investigate the non-degenerate tautomeric transitions (52) in triads of this kind, which can occur, for example, when $E \neq O$. Such a process has been investigated, in particular, for $E = Se$, $R = CH_3$, and $[M] = SiH_3$[205, 206]. By varying the conditions of the measurement, it was possible to observe in the ^1H NMR spectra both possible states of the system—either two sets of signals due to the SiH_3 group and the indicator group R, corresponding to slow O,Se-transitions of the SiH_3 group within the framework of non-degenerate interconversions of the O- and Se-isomers, or a single set of signals corresponding to the indistinguishability of the isomers owing to their rapid interconversion. Special experiments showed that reaction (52) is intramolecular:



(52)

An example of non-degenerate O,E-transitions can also be provided by the O,O-transitions in compounds with structurally non-equivalent oxygen atoms. Such compounds have been studied, in particular, in the investigation of Nesmeyanov and Kravtsov[1] mentioned above and in a subsequent investigation[7]. The authors studied the absorption spectra of organometallic derivatives of *p*-nitrosophenols (XXXII) with $[M] = HgC_6H_5$, $Sn(C_6H_5)_3$, or $Pb(C_6H_5)_3$. The set of infrared and ultraviolet spectroscopic data obtained showed that, in contrast to the solid state, where the organometallic derivatives of nitrosophenols have only the quinone oxime structure, in solution they exist in both forms—the quinone oxime form (XXXIIb) and the nitroso-form (XXXIIa). Thus the interconversion of the tautomeric forms of these compounds in solution takes place via the rapid non-degenerate metallotropic O,O-rearrangement (53):

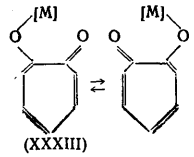


(XXXIIa) (XXXIIb)

(53)

The position of equilibrium (53) depends on a number of factors. In particular, for $[M] = Sn(C_6H_5)_3$ and $Pb(C_6H_5)_3$ in pyridine, THF, and acetone, the content of the nitroso-form is high, while in chloroform it is low. The nature of the organometallic group does not influence appreciably the position of equilibrium (53), which has been tested in relation to $[M] = HgAr$. On the other hand, the introduction of substituents into the aromatic ring of nitrosophenol lowers the content of the nitroso-form for derivatives with $[M] = Sn(C_6H_5)_3$ and $Pb(C_6H_5)_3$, as well as the initial nitrosophenols.

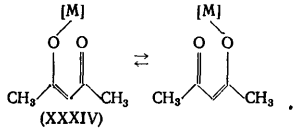
Among tetra- and penta-atomic systems, for which degenerate O,O-transitions of cationoid species have already been investigated by NMR, we shall mention the derivatives of tropolone and the enolic form of acetylacetone. However, these investigations are limited by the fact that, in relation to the majority of univalent organometallic groups, the anionoid residues of tropolone and acetylacetone behave as bidentate ligands. There are also structural difficulties associated with the inadequate knowledge about many potentially metallotropic systems. As a result, the data available at present about the O,O-dynamic processes (54) and (55) refer mainly to the case where $[M] = SiR_3$:[207-209]



(XXXIII)

(54)

Thus, in the study of compound (XXXIII) with $[M] = Si(CH_3)_2CH(CH_3)CH_2CH_3$ the $^{13}C-\{^1H\}$ NMR spectrum of the ring at 0 °C showed only four carbon signals instead of the expected seven. This result was interpreted as evidence for rapid O,O-transitions (54), which was confirmed in subsequent low-temperature measurements. Thus, for $[M] = SiR_3$ the enol–enol O,O-transitions in tropolones are comparatively rapid, in agreement with the conclusion already reached using the ^1H and ^{17}O NMR methods for $[M] = H$:[209]

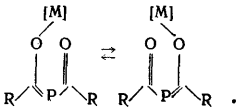


(XXXIV)

(55)

Analogous results were obtained in the study of the acetylacetonato-derivatives (XXXIV) with $[M] = Si(CH_3)_2R$[207] or $Si(CH_3)_2CH(CH_3)CH_2CH_3$.[208] Their ^1H or $^{13}C-\{^1H\}$ NMR spectra exhibit in the corresponding temperature ranges the entire set of spectral features corresponding to the dynamic process (55). The rate of transitions (55) in *cis*-acac-$Si(CH_3)_2R$ is higher than in tropolone and, depending on the nature of the group R, it increases in the sequence $CH(CH_3)CH_2CH_3 < n\text{-}C_4H_9 < C_2H_5 < CH_3 < CH_2=CH$, $C_6H_5 < CF_3CH_2CH_3$.

Certain observations have been made on the mechanism of degenerate enol–enol O,O-transitions (54) and (55) of organosilicon groups[208]. It has been found for $[M] = Si(CH_3)_2CH(CH_3)CH_2CH_3$ that both $SiCH_3$ groups give rise to separate signals in the $^{13}C-\{^1H\}$ NMR spectra in the temperature range where the occurrence of processes (54) and (55) was noted on the basis of NMR spectra. This enabled the authors[208] to conclude that the configuration at the silicon atom is preserved in the O,O-transitions of organosilicon groups and to postulate transition states for these processes. In our view, this result can also serve as evidence for the intramolecular mechanism of processes (54) and (55):



(56)

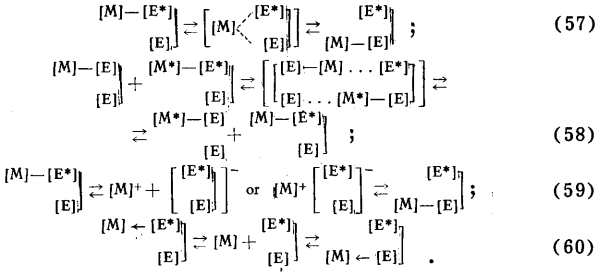
Finally, a recent communication[210] concerning the observation by NMR of O,O-transitions in a series of diacylphosphines should be mentioned {process (56), $[M] = Si(CH_3)_3$, $R = C(CH_3)_3$}.

VIII. THE MECHANISM OF METALLOTROPIC E,E-TRANSITIONS

The study of metallotropic tautomeric transformations is in essence only just beginning. It is therefore as yet difficult to expect a fairly complete understanding of the mechanism of this interesting and fairly unusual group of reactions. At present one can only attempt an initial survey of the available data, to assign them to certain most probable schemes, and to discover a series of common features of the influence of various factors on the rate of the process. Additional conclusions will evidently follow when the necessary

experimental data have been obtained. However, even the data already available on the metallotropic E,E-transitions are of theoretical value and can stimulate more far-reaching, including quantum-chemical, generalisations.

In considering the mechanism of metallotropic tautomeric transformations, one can restrict the treatment of a first approximation to four most suitable possibilities differing mainly in the characteristics of the elementary reaction steps and the form in which the cationoid and anionoid species exist:



(57)

(58)

(59)

(60)

Firstly, the metallotropic E,E-transitions can take place via the intramolecular mechanism (57). This variant of the reactions is observed in many systems with cation-accepting centres in close proximity in space, particularly in different triads.

The second possibility involves the intermolecular transfer of the cationoid species [M] in the synchronous transition in the course of the interaction of two or more molecules. This mechanism [for example, mechanism (58)] does not presuppose the dissociation of the molecules into individual cationoid and anionoid residues, but after the metallotropic transition step the species[M] is bound to the residue of the partner-molecule and not to its "own" anionoid residue.

Some derivatives can dissociate into kinetically independent species. For compounds with fairly ionic [M]–[E] bonds, these are usually the ions $[M]^+$ and $[\overline{E\ E}]^-$ or their ion pairs, including solvent separated pairs. In the latter case the metallotropic transition (59) consists in the fact that the cationoid species can be linked to an anionoid residue, but this time a "foreign" one and not its "own" residue.

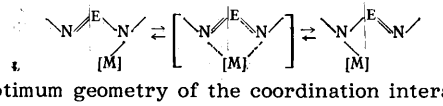
Finally the fourth possibility consists in the decomposition of the compound into neutral independent species, which are subsequently rejoined, and involves the metallotropic transition (60). This variant of the mechanism is characteristic of derivatives in which the coordinate bonds M ← E is formed between the groups [M] and $[\overline{E\ E}^*]$. In this case the anionoid and cationoid residues of the compound are stable neutral formations and can therefore exist independently in solution for a long time.

Within the framework of modern ideas[211,212], the first two mechanisms are of the associative type and the last two are of the dissociative type. We may note that the metallotropic transitions (59) are relatively atypical for the organometallic derivatives considered. On the other hand, the E,E-transitions (60) are already known in many instances (Section V). However, these data are so far insufficient for the interpretation of the characteristics of the decomposition of compounds into kinetically independent species, which is the rate-limiting stage of the metallotropic transition.

The structure of the compounds in which the intramolecular metallotropic transitions discovered hitherto take place in most cases is such that the metal atom forms a bond with one of the E atoms of the anionoid residue $[\overline{E\ E}^*]$ (E = N, O, S etc.) and is at the same time fairly close to the other E atom. Here it is envisaged that in the ground state of these compounds the distance between M and E* can be fairly large, but the relative positions of the three atoms in the given molecule—M, E, and E*—ensure the formation of a new M...E* bond and the transition state  even before the complete dissociation of the old M–E bond. In other words the elementary step of the intramolecular E,E-transition involves the virtually simultaneously dissociation of the old M–E bond and the formation of a new M–E* bond in which the potential barrier is overcome, but the system does not dissociate into kinetically independent species.

It must be emphasised that the "principle of geometrical proximity" formulated in this way, which presupposes the spatial proximity of the cation-accepting centres between which [M] migrates, constitutes a necessary but not sufficient condition for the intramolecular mechanism of metallotropic transitions. Apart from this, certain other factors, which also promote the transitions of the groups [M], are likewise important: the flexibility of the anionoid residue, facilitating the mutual approach of the cation-accepting centres, the marked electron-accepting properties of [M] and the electron-donating properties of E, and the correspondence between the geometry of the transition state and the optimum geometry of the coordination interactions for the given metal atom. However, ultimately all these factors are in some way related to the decrease of the barrier height on the potential energy curve for the E...M...E* system, which must be overcome in order to form the transition state without the dissociation of the system into kinetically independent species.

The postulate of a cyclic structure for the transition state may be adopted as one of the hypotheses concerning the elementary step in intramolecular metallotropic transitions. For example, the 1,2-transitions in pyrazoles and in general any 1,2-transitions, as well as many but by no means all 1,*n*-transitions satisfy this condition. In particular, the limitation may refer to systems of the triad type in which the atoms comprising the triad form part of the ring. This last refinement is associated with the virtual impossibility of ensuring the planarity of the transition state in small rings, as has been shown, for example, by a comparison of data for metallotropic transformations of the imidazole [reaction (32)] and amidine [reaction (29)] types. As mentioned above, in imidazoles the 1,3-transitions (32) take place only intermolecularly if at all[157], while in amidine derivatives the intramolecular process (29) takes place very readily[142], as in the case of the diazoamine triad (30). Evidently this clear difference is associated with the possibility of the formation in the latter case of a planar four-membered transition state, so that in this instance the fundamental step in the metallotropic transformation is a synchronous transformation of the bond system (E = N or CR):



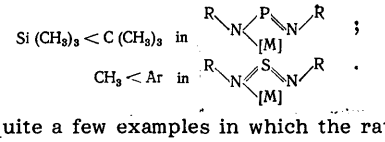
The optimum geometry of the coordination interactions for the given organometallic group may also be important[213]. Thus, the high migratory capacity of RHg groups compared with R_3Sn in intramolecular metallotropic processes can be partly attributed to the fact that a T-shaped geometry of the coordination interactions, close to the geometry of the coordination interactions in the formation of a cyclic transition state in intramolecular metallotropic processes, is optimum for the compounds RHgX,[214] while for the compounds R_3SnX the optimum geometry of coordination interactions is trigonal bipyramidal[215], in which the additional ligand occupies an axial position and which does not correspond to the coordination geometry of a cyclic transition state.

It must be emphasised that it is useful to consider metallotropic E,E-transitions only in structures where a mesomeric structure with delocalised bonds is not formed for geometrical or other reasons, as a result of which the potential of the E...M...E* system requires a single-well configuration in the structures considered, of the kind observed, for example, in dimeric derivatives of pyrazole $\{[M]-L\}_2$ with $[M]=TlR_2$, etc., and not a two-well configuration.

We shall consider in relation to known examples certain factors tending to accelerate the intramolecular metallotropic transitions.

In many instances the important factor determining the rate of E,E-transitions is the lability of the dissociating M–E bond, which increases with increase of its polarity and depends in its turn on the difference between the electronegativities of the atoms E and M and on the polar effects of the substituents. This is indicated, in particular, by the series characterising the influence of substituents attached directly to the metal in the cationoid species [M] on the rate of 1,2-transitions in pyrazoles and indenes (see Sections II and IV); $OCH_3 < Cl < C_6H_5 < CH_3$. In this case the σ-electron-accepting substituents, which reduce the polarity of the M–E bond, lower the capacity of the group [M] for migration, while electron-donating substituents increase it.

An analogous conclusion can apparently be reached by considering the influence of the substituents in the anionoid residue attached directly to the atom E. In contrast to the previous case, in the anionoid residue the polarity of the M–E bond decreases under the influence of electron-donating and not electron-accepting substituents. This influence of the substituents R has in fact been found experimentally[147, 148,171,172] for certain 1,3-transitions:



There are quite a few examples in which the rate of metallotropic E,E-transitions depends greatly on the ease of formation of the new bond. In this case the Lewis acidity of the metal in the cationoid species [M] and the basicity of the second cation-accepting centre can be regarded as the driving forces of the metallotropic tautomeric transformations. Indeed, data for the metallotropic C,C- and N,N-transitions in many organometallic systems have shown that the mobilities of different groups [M] in the E,E-transitions under consideration give rise to the following sequence: $R < SiR_3 < GeR_3 < SnR_3 < HgR$. Bearing in mind that the Lewis acidity of the metal atom in [M] increases in the same sequence, presumably the enhancement of the acidity of the metal tends to decrease the height of the potential barrier in the formation of the transition state and hence to facilitate the metallotropic transitions. An analogous conclusion follows from data for the influence of substituents in the cationoid residues of tautomeric systems such as triazenes and acetylacetonates[207,208]. In this case the substituent series, $C_4H_9 < C_2H_5 < CH_3 < OCH_3 < Cl$, is the opposite to that found for pyrazoles and indenes. An evident cause of this difference may be the difference between the geometries of these two groups of compounds. Whereas in the case of pyrazoles and indenes, which have a rigid geometry, the polarity of the dissociating M–E bond is more important, in compounds with a more flexible structure, such as, for example, triazenes and acetylacetonates, the rate of the process depends to a great extent on the ease of formation of the new M–E* bond. As a result, the enhancement of the electron-accepting properties of the substituents in [M], which renders the atom M more acid, is accompanied by the acceleration of the metallotropic transitions and not their retardation. It is natural to suppose that in this instance the substituent effects refer not so much to the M–E bonds as to a change in the acidity of the atom M, which facilitates or hinders the formation of the new M–E* bond.

Data concerning the ratio of the rates of the E,E-transitions of cationoid species such as $[M]\neq H$ and $[M]=H$ in related systems show that, whereas intramolecular tautomeric transformations are more characteristic of metallotropic transitions, intermolecular transformations of the synchronous type—bimolecular and in general n-molecular—are encountered much more frequently than in prototropic systems. In particular, O,O-transitions in acetylacetonate and tropolone derivatives with $[M]=H$ take place much faster than for $[M]=SiR_3$[207–209] {we may note that the C,C-transitions, which proceed via an intramolecular mechanism for both $[M]\neq H$ and $[M]=H$, are faster than the proton transitions for $[M]=HgR$, SnR_3, GeR_3, SiR_3, etc.}.

This may be caused also by the different capacities of the compounds considered for dimer formation and by their structural differences in the dimeric state. Many experimental data have shown that prototropic systems with bidentate anionoid residues form fairly frequently, if only for a short time, dimeric structures with non-equivalent bonds[216–218]:

$$\begin{bmatrix} [E]-H\ldots[E] \\ [E^*]\ldots H-[E^*] \end{bmatrix} \quad \begin{bmatrix} [E]\ldots H-[E] \\ [E^*]-H\ldots[E^*] \end{bmatrix}$$

These apparently include also tropolone and acetylacetonate derivatives, since prototropic transitions in these systems can proceed via an intermolecular mechanism, within the framework of the hydrogen bonds arising on formation of the dimer, and not via an intramolecular mechanism {as for $[M]=SiR_3$}. A similar explanation can be put forward in the interpretation of the results of the study of N,N-transitions in diaryltriazenes.

It is noteworthy that the capacity for the formation of associated species is characteristic also of the derivatives of certain metals among those considered here, in particular, tin, cadmium, and thallium, but in many instances, for example for $[M]=Tl$, the bonds are equivalent in the dimerisation process by virtue of geometrical and other causes, as a result of which the potential surface for the [E]–[M]–[E*] fragment is a single well:

$$\begin{bmatrix} [E]-[M]-[E^*] \\ [E^*]-[M]-[E] \end{bmatrix}$$

and the metallotropic transition considered here correspondingly loses its significance.

Certain preliminary considerations concerning the possible nature of the influence of the solvent on the rates of metallotropic processes can also be formulated. Thus it is to be expected that polar but weakly coordinating solvents will facilitate intramolecular and intermolecular metallotropic processes as a result of the polarisation, ionisation, or dissociation of the M–E bonds. Weakly polar coordinating solvents, which do not induce the ionisation or dissociation of the M–E bonds, should hinder intramolecular metallotropic processes and processes proceeding via a bimolecular mechanism by blocking the vacant orbitals of the metal atom. Finally, solvents exhibiting both a high coordinating capacity and a high polarity and capable of inducing the dissociation of the M–E bonds[219–221] should accelerate metallotropic processes, facilitating their occurrence via the intermolecular dissociative mechanism.

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