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Stereochemical Non-rigidity (Internal Rotation and Metallotropy) of Organic Derivatives of Transition Metals Investigated by Nuclear Magnetic Resonance Spectroscopy

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Types of stereochemical non-rigidity of organic derivatives of transition metals, which have been widely studied by nuclear magnetic resonance during recent years, are classified. Two types of process—internal rotation in complexes of transition metals and intramolecular transfers of metal-containing groups (metallotropy)—are examined in greater detail. The discussion of the most characteristic structural situations met in π-complexes of transition metals covers not only the dynamic processes already observed by the n.m.r. method but also examples of compounds for which such processes have not yet been observed but may in principle be found. A list of 256 references is included.

CONTENTS

I. Introduction	678
1. Types of intramolecular transitions	678
2. Equivalence of nuclei in static molecule	679
3. Dynamic equivalence of nuclei—dynamic n.m.r. (d.n.m.r.)	679
II. Internal rotation in complexes of transition metals	680
1. Rotation about metal-ligand π-bonds	680
2. Rotation about multiple π-bonds	683
III. Intramolecular migrations of metal-containing groups (metallotropy)	684
1. σ-σ-Transitions	684
2. σ-π-Transitions	686
3. π-π-Transitions	686

I. INTRODUCTION

With many organometallic structures two aspects—static and dynamic—must be considered. The dynamic aspect implies possible activation of molecular rearrangements which cannot be classified as oscillations. Although this problem has been posed and solved for organic chemistry during the past few decades, for organometallic and inorganic chemistry it has become urgent only during recent years.

Many of the known types of dynamic processes can be examined by nuclear magnetic resonance. Some of them are intermolecular, and n.m.r. is widely used for their study (see e.g. reviews on intermolecular dynamics† in organometallic derivatives[1-6]). Other types of processes are intramolecular, and are a kind of manifestation of the "stereochemical non-rigidity" of the compounds (this term was proposed by Muetterties[7]). In several organometallic compounds transitions occur between non-equilibrium states of the system (non-degenerate conversions). In other compounds the intramolecular conversions are degenerate, so that the final state is indistinguishable from the initial state of the system. Nuclear magnetic resonance is an especially fertile approach to such systems, since the actual fact of conversion and also its mechanism cannot always be detected and studied by other methods.

† In the papers under discussion the word "dynamics" is applied to any processes which either lead to or are accompanied by a change in the relative equilibrium arrangement of the atoms in the molecule.

1. Types of Intramolecular Transitions

Nuclear magnetic resonance has been used to study many types of intramolecular processes in organic derivatives of transition metals. However, certain especially characteristic and quite frequent processes—internal rotation, tautomeric transitions, allogonic rearrangements (pseudorotation), reconstruction of organometallic rings, etc.—can be distinguished. Nevertheless, "purely" intramolecular processes are almost impossible under the actual conditions of an n.m.r. experiment, owing to the effect of the solvent and similar factors. It is therefore necessary to determine which processes can be regarded as intramolecular. We shall apply the term *intramolecular* to processes which do not involve breakdown of the compound into two or more kinetically independent species or entry of the compound into other kinetically independent species (stable solvates, complexes.

With internal rotation a change in the orientation of one fragment relative to another in a compound is accomplished by turning about an axis coinciding in direction with a chemical bond. In contrast to traditional organic compounds, internal rotation in transition-metal complexes can occur not only about a localised (σ or coordinate) bond but also about delocalised π-bonds, including bonds of order exceeding unity.

Tautomeric processes in organometallic compounds of transition metals involving intramolecular rearrangements

of metal-containing groups (metallotropic transitions) are fundamentally novel and therefore especially interesting. Metallotropic transitions occur in any change in the relative positions of two fragments of the compound—the metal (or metal-containing group) and the remainder of the molecule—which is accompanied by a redistribution of its bond system. Metallotropy was first studied by Nesmeyanov and Kravtsov on the intramolecular migration of a transition metal between σ-bonds in a compound [8]. Since then examples have also been found of various migrations of metal-containing groups on π-complexes of transition metals. The richness and variety of the structural possibilities characteristic of transition-metal complexes result in a multiplicity of types of metallotropic transitions.

Allogonic rearrangements (pseudorotation) cover all processes occurring in coordination polyhedra (including square planar complexes and complexes containing *inter alia* different kinds of π-bonds). They include also rearrangements of the skeleton of coordination compounds in which a polyhedron different from the original is formed as transition state (pseudorotation, a term proposed by Berry [9]) or intermediate (allogonic rearrangements, a term proposed by Bennett et al. [10]).

The stereochemical non-rigidity of organometallic rings containing the metal in the main skeleton of the ring may involve both the dynamic aspects that are investigated on the usual organic rings and several questions specific to organometallic compounds, such as the possibility of intermediate opening of the ring, etc.

The history of the problem is comparatively brief. During the "preparatory" decade 1956–1966 the efforts of various workers [7-27] led to the discovery and the investigation of several types of intramolecular conversions in organometallic compounds, and also in a series of compounds which can be regarded as models for organometallic structures. Thus the main outlines of the problem were revealed, and certain hypotheses formulated on the mechanisms of the molecular reorientations. A period of "attack and charge" began in 1967, characterised by an avalanche of fresh information. No tendency is yet evident for this process to level off on a plateau.

Thus, in spite of the relative novelty of the problem, the literature on the stereochemical non-rigidity of organometallic compounds is so large that it is already quite difficult to cover in a short survey (Cotton's review was published in 1968, [28] and that of Vrieze et al. in 1969 [5]). Only the first two types of intramolecular dynamics—internal rotation and tautomerism—will therefore be discussed in the present Review. However, we must not ignore the formality of any such (including the suggested) classification of these processes and hence the difficulty of deciding in several cases what type of transition takes place in a particular molecular system.

2. Equivalence of Nuclei in Static Molecule

Following Abragam's suggestion [29] comparable nuclei are termed *isochronous* if they have the same shielding, and *anisochronous* if their shielding differs. Nuclei may be either regularly or accidentally isochronous. Isochronous nuclei are equivalent only if their equivalence is due to considerations of symmetry (static or dynamic). Otherwise they are non-equivalent even if a spectroscopic experiment indicates identity of shielding (accidentally isochronous).

Depending on their relative arrangement in the molecule any comparable groups—by which we shall henceforward imply comparable nuclei or groups of nuclei in some fragment—may be either chemically equivalent, enantiotopic, or diastereotopic. Groups which are coupled by a simple axis of rotation C_n ($1 < n < \infty$) are chemically equivalent [30]. Groups that are defined as chemically equivalent, and hence isochronous "from the viewpoint" of nuclear magnetic resonance spectroscopy, are in fact equivalent in chemical terms: i.e. they cannot be distinguished by their behaviour in any chemical reaction [31] and they cannot become spectroscopically distinguishable in a chiral medium. Enantiotopic groups possess an enantiomeric environment and hence are coupled by a reflection–rotation axis S_n (rotation about axis C_n followed by reflection in the plane of symmetry, $1 \leq n < \infty$). [32] Enantiotopic groups are isochronous in achiral (optically inactive) solvents, but may become anisochronous in chiral media. Finally, diastereotopic groups cannot be interchanged by any symmetry operation, and thus are geometrically non-equivalent [32]. As a consequence, diastereotopic groups should in principle be anisochronous in any solvent. Although the diastereotopy (geometrical non-equivalence) of groups is in principle a necessary condition for the spectroscopic non-equivalence of their nuclei, this condition is not sufficient. Differences in the shielding of diastereotopic nuclei depend on the structure of the molecules, the solvent, and several other factors. In individual cases these differences may become so small that they cannot be observed, and the groups can then be regarded as accidentally isochronous (but not equivalent).

3. Dynamic Equivalence of Nuclei—Dynamic n.m.r. (d.n.m.r.)

The above definitions apply to molecular statics, in which molecules are considered in fixed structural situations with the mutual arrangement of their atoms and bonds unchanged. Actually the investigator is usually dealing not with static but with dynamic stereochemistry. Various intramolecular movements in compounds produce an averaging of the shielding and other spectral parameters of the groups. The symmetry of the molecule seems to improve, and hence the spectrum to degenerate. As a consequence of the degeneracy diastereotopic groups may become "dynamically chemically equivalent" or "dynamically enantiotopic". Several factors—temperature, nature of solvent, concentration of compound, etc.—may in principle be the averaging agent, introducing dynamic equivalence (in the n.m.r. sense) into the molecular system, but the temperature has the greatest importance for intramolecular processes.

The relative character of the "dynamic" behaviour of molecular systems must be emphasised: particular groups may be diastereotopic for some methods, but chemically equivalent or enantiotopic (dynamically) for others. Thus a spectroscopic examination of a compound usually yields not its absolute but its effective (average) symmetry, and hence the effective equivalence of its groups—equivalence "in terms of" the method of investigation used.

The relative character of the boundary between the static and the dynamic behaviour of a molecular system is governed also by the individual features of the compound (or process) and by the possibilities—the time scale—of the physical method used. A compound may "appear" static, immobile for some methods and dynamic for

others, and the process may correspondingly be "slow" for some methods and "rapid" for others.

The time scale of a spectroscopic method (the time necessary for the observation of discrete spectra) is directly related to the energy of the transitions observed: the smaller the energy of transitions between states of the system, the slower the processes "visible" by this method. A comparison made by Muetterties [7] shows that microwave spectroscopy, particularly high-resolution nuclear magnetic resonance, is substantially "slower" than diffraction methods of analysis, or electronic and vibrational spectroscopy. With processes so rapid that the system remains for $10^{-13}-10^{-15}$ s in each state vibrational spectroscopy, for example, enables the spectrum of each state to be observed, whereas n.m.r. spectroscopy reveals only spectra averaged over several states of the molecular system. On the other hand, n.m.r. spectroscopy enables processes having a lifetime of $10^{-1}-10^{-9}$ s to be observed, and is quite rapid in comparison with any method involving direct isolation of molecular systems in any discrete states (if these states are non-degenerate, and such separation is feasible).

Thus n.m.r. spectroscopy is a fortunate method of investigation for chemistry, since it is able to cover a range of processes and problems which are often inaccessible to other methods. These include various states of organometallic compounds and their reactions having activation energies of 5–25 kcal mole^{-1}. This is especially important because the molecular structure of these compounds in the liquid phase may differ from their structure in the crystal [7]. The branch of n.m.r. spectroscopy used to investigate the inter- and intra-molecular dynamics of molecules is termed dynamic nuclear magnetic resonance (d.n.m.r.). Beginning with the classic work of Gutowsky and his collaborators [33–35], this branch underwent serious theoretical development and has found many applications (see reviews [36,37]).

Information on the dynamics of a molecule can in principle be obtained also by examining a "frozen" spectrum ("slow dynamics", the indicator groups being dynamically chemically non-equivalent or enantiotopic). However, investigation of a compound is especially fruitful and informative in a critical region, in which a small perturbation (change in temperature, introduction of a somewhat different substituent, etc.) will reveal the whole sequence of changes in the spectrum—from the "frozen" spectrum, through a series of intermediate spectra, to the degenerate spectrum.

Several d.n.m.r. approaches, including the stereochemical non-rigidity of compounds, have been worked out in the investigation of dynamic phenomena. The simplest approach is to study the merging of the signals. The kinetic and thermodynamic parameters are obtained by finding experimentally the coalescence temperature T_c. However, this approach will give acceptable results only for the simplest systems, in particular for a two-centre exchange without spin–spin interaction between the nuclei of diastereotopic groups.

However, complete analysis (usually by means of an electric computer) of the changes in spectral line form accompanying effective averaging of the environments of the diastereotopic groups is required for accurate investigation. Importance attaches both to the "limiting" spectra (the discrete, "static" spectrum, and also the averaged, "dynamic" spectrum) and to all intermediate spectra produced as the averaging process gradually becomes more intense. With intramolecular processes, as already mentioned, only changes in the temperature of the solution can act as such an averaging agent.

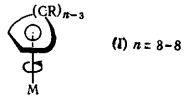
II. INTERNAL ROTATION IN COMPLEXES OF TRANSITION METALS

Rotation about σ-bonds has been relatively well studied on various organic models (e.g. review [38]). This type of dynamics applied to coordinate bonds and metal–ligand σ-bonds has also become the object of n.m.r. investigations during recent years [39–46], although it evidently possesses no special theoretical features.

Studies of two "new" types of rotation—about metal–ligand π-bonds and also in the ligands themselves having a π-type of coordination to a transition-metal atom—give especially interesting structural information. Investigation of this type of dynamics enables the problem of the electronic structure of π-bonds to be discussed from a fresh point of view [47].

1. Rotation about Metal–Ligand π-Bonds

Internal rotation about the n-fold axis in complexes in which a π-C_nR_n–M bond is formed (where C_nR_n is a cyclic ligand in which the multiple bonds are all equivalent and all involved in complex formation, $n = 3-8$, and R = H or R ≠ H—structure I)

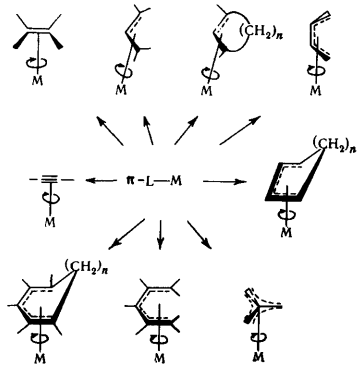


(I) $n = 3-8$

is opposed by such low barriers that its rate evidently cannot be measured by high-resolution n.m.r. in solution (see e.g. Refs. 48–51 for $n = 5$ and 6). With complexes in which the multiple-bond system coordinated with the transition-metal atom is not continuous, or else is continuous but non-uniform, on the other hand, examination of internal rotation is in many cases "permitted" by the high-resolution n.m.r. time scale. The first study of this kind was made by Cramer [15].

Scheme 1

Some possible types of internal rotation about metal–ligand π-bonds



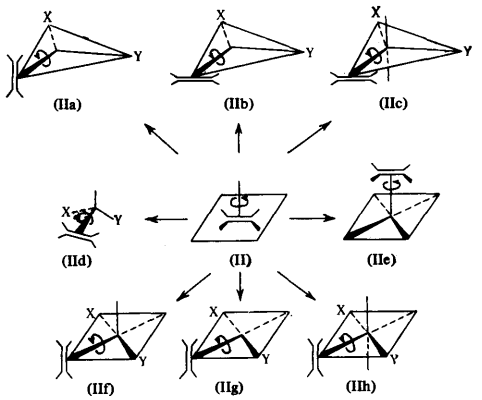
Among the main types of structures (Scheme 1) that can be examined in connection with the problem of internal rotation about a metal–ligand π-bond, π-ethylenic and π-allylic derivatives have been most studied.

(*a*) Internal rotation in π-ethylenic complexes

Various criteria can be used in examining internal rotation about a π-alkene–metal bond in π-ethylenic derivatives (structure II), the choice of which depends on the symmetry of the whole complex (i.e. on whether its rotational isomers are equivalent or non-equivalent). Scheme 2 assembles several types of π-ethylenic complexes, on which the problem of internal rotation can conveniently be considered.

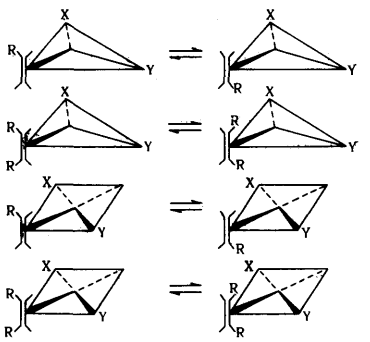
Scheme 2

Some types of structures in which internal rotation about a π-alkene–M bond is possible



Complexes containing highly symmetrical ethylenic ligands [C_2H_4, C_2F_4, $C_2(CH_3)_4$, etc.] and different groups X and Y (structures II—a, g, h), for example, form equivalent rotational isomers. Changes in the rate of degenerate internal rotation in derivatives of this type can conveniently be assessed from the temperature dependence of the ^1H and ^{19}F n.m.r. spectra of the olefinic ligand. At sufficiently low temperatures with "slow" rotation the indicator groups of this ligand (the ^1H and ^{19}F nuclei) separate into two types of diastereotopic nuclei according to their environment and hence shielding. Thus the low-temperature limiting spectrum of the ethylenic ligand does not exhibit a solitary signal (as in the spectrum of the uncomplexed unsaturated compound—the spin system A_4 for ethylene and tetrafluoroethylene, and A_{12} for 2,3-dimethylbut-2-ene) but a set of signals of the system AA'BB' or AA'KK' for the first two compounds, and also the doublet $A_6 + K_6$ for the third compound. Rise in temperature and acceleration of rotation are accompanied by more rapid exchange of the environments of the diastereotopic nuclei and degeneration of the n.m.r. spectrum of the ethylenic ligand (AA'KK' $\rightarrow A_4$, $A_6 + K_6 \rightarrow A_{12}$, etc.).

Rotational isomers of compounds having a ligand of low degree of symmetry (monosubstituted or *cis*-disubstituted ethylene and X = Y are non-equivalent, and each has its own low-temperature boundary n.m.r. spectrum of corresponding intensity. Examination of the temperature dependence of the spectra of such complexes may reveal the interconversion of rotational isomers throughout the range of possible rates—from "slow" to "rapid" dynamics—processes (1)–(4), etc.



The largest number of papers have appeared on internal rotation in complexes of types (IIa) [15,52–58] and (IIg).[59–61] Very few data have yet been obtained on intramolecular dynamics in the other π-ethylenic derivatives—tetrahedral (IId), octahedral (IIh), trigonal bipyramidal (IIc), etc.—included in Scheme 2.[62–67] Low-resolution n.m.r. has also been used for this purpose[68,69].

Application of n.m.r. to rhodium and iridium derivatives of type (IIa) with highly symmetrical π-ethylenic ligands (X = C_5H_5, C_6H_6, etc. and Y = C_2H_4, C_2F_4, SO_2, etc.) shows that the rate of degenerate rotation of the alkene depends significantly on the nature of the metal and on the structure of the rest of the complex. Rotation is appreciably more rapid with M = Rh and Y = SO_2 or C_2F_4 than when Y = C_2H_4. An ethylene ligand (Y = C_2H_4) rotates more slowly in an iridium than in a rhodium complex. A tetrafluoroethylene group rotates much more slowly than does ethylene.

Study of degenerate rotation in platinum complexes PtXAlkeneChelate (X = Cl, Br) of type (IIg) reveals a slight dependence of the rate of rotation of ethylene on the structure of the remainder of the compound. Derivatives of this type also show non-degenerate rotation in the interconversion of isomers obtained from monosubstituted and *cis*-disubstituted ethylenes (reactions (3) and (4) respectively). It is significant that neither substitution of the *cis*-substituent X (Cl by Br) nor replacement of an acetylacetonate by a hexafluoroacetylacetonate ligand produces a definite change in the rate of rotation of the alkene. The very fact of observing geometrical isomers of (IIa) and (IIg) is an unambiguous n.m.r. proof that the axis of the alkene is oriented perpendicular to the plane of the complex both in solution and in the crystal[70,71].

The choice of transition state in the discussion of internal rotation about an alkene–metal π-bond is directly connected with the structure of the complexes. Diffraction data show that in several compounds an ethylenic ligand is oriented perpendicular to the plane of the molecule if such can be distinguished (IIa,[70] IIg,[71] etc.). In these complexes the state in which the ligand lies in the plane of the complex is obviously more favourable energetically, and is observed in the n.m.r. spectrum with slow dynamics, whereas the less favourable transition state is almost unobservable, since its contribution to the spectral parameters is negligible because of its short lifetime. The given dynamics applied to the complexes (IIg) can than be represented by[59]



An attempt was made[59] to assess the effect of electronic and structural factors on the rate of this process and on the stability of its transition state. Since, however, the axis of an ethylenic ligand in a π-complex may be not only perpendicular to but also coplanar with the complex (IIb),[72] the transition state in process (5) may actually be an intermediate complex having an appreciable lifetime and hence making an appreciable contribution to the special parameters.

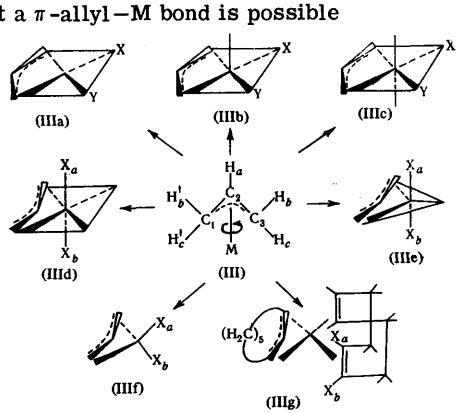
The observation of intramolecular rotation in ethylenic π-complexes by d.n.m.r. may in principle be complicated by a contribution from intermolecular dynamics, connected with the lability of certain alkene–metal π-bonds[73–83]. In several cases, however, experimental conditions can be distinguished which eliminate almost completely the intermolecular component of the process. Criteria of this are, for instance, that the parameters of the n.m.r. spectrum should be independent of the concentration of the compound, additions of the free ligand, etc.[53,76] The observation of spin–spin interaction between nuclei of the ethylenic ligand (hydrogen-1, fluorine-19, carbon-13, etc.) and nuclei of the metal (rhodium-103, platinum-195, etc.) or other ligands (phosphorus-31, etc.) in the π-alkene–metal fragment throughout the range of rates is convincing evidence that the process is intramolecular[15,54,59].

(*b*) Internal rotation in π-allylic complexes

Internal rotation about a π-allyl–metal axis (structure III) can in principle occur quite slowly (on the n.m.r. time scale) in a wide range of compounds in which the metal is attached to a three-electron ligand. Several examples are combined in Scheme 3.

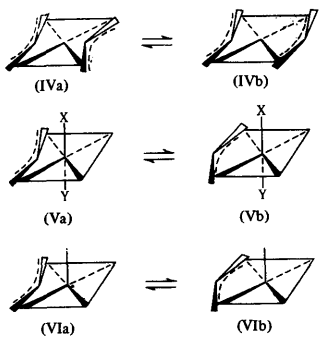
Scheme 3

Some types of structures in which internal rotation about a π-allyl–M bond is possible



Asymmetry in π-allylic complexes with a non-degenerate ligand spectrum of type AGKPX [square planar (IIIa),[84,85] octahedral (IIIc),[86–93] etc.—for terminology see Refs. 91 and 94] originates in the inequality between the substituents X and Y. Slowness of internal rotation in complexes of this type is indicated by the anisochronous behaviour of the terminal methylene groups (structure III)—of the $C_{(1)}$ and $C_{(3)}$ nuclei in the ^{13}C n.m.r. spectrum, and of the *cis*-protons H(b) and H(b′) and also the *trans*-protons H(c) and H(c′) in the ^1H n.m.r. spectrum. With symmetrical complexes (IIId–g), possessing a degenerate spectrum AK_2X_2, slowness of internal rotation is evidenced by anisochronous behaviour of the structurally identical indicator substituents $X_{(a)}$ and $X_{(b)}$, e.g. in the niobium complex (IIIf) [$X_{(a)} = X_{(b)} = \pi\text{-}C_5H_5$ [95]], in the cobalt and rhodium complexes (IIIg),[96,97] etc. [the non-equivalence of the groups $X_{(a)}$ and $X_{(b)}$ is due to the non-coplanarity of the $C_{(1)}–C_{(2)}–C_{(3)}$ and $C_{(1)}–M–C_{(3)}$ planes of the π-allyl–metal bond].

Slowness of rotation about a π-allyl–metal bond may be indicated also by the spectral observation in an appropriate temperature range (and the theoretical possibility of physical separation) of rotational isomers in those types of compounds whose rotamers are non-equivalent from considerations of symmetry. In particular, the isomeric pairs (IV)–(VI) (processes 6–8)



(6)

(7)

(8)

have been observed by ^1H n.m.r. Investigation of the temperature dependence of the ^1H n.m.r. spectrum for several π-allyl compounds of transition metals has shown that internal rotation about the π-allyl–metal bond may occur at rates that can be conveniently recorded by n.m.r. methods. The effect has been examined in greatest detail in a study of molecules of two types—asymmetric π-allylic compounds (IIIc), and also symmetrical compounds forming isomeric pairs (IV)–(VI).

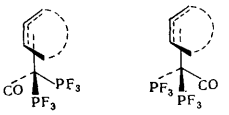
With rise in temperature (dynamic) symmetry appears in the spectrum of the asymmetric complexes (IIIc) (AGKPX → AK_2X_2): anisochronicity of the two terminal methylene groups is replaced by their isochronicity and hence dynamic equivalence. This effect is observed between −20° and 90°C with $[RhCl(\pi\text{-}C_3H_5)_2]_2$,[91] from −67° to 20°C with $Fe(CO)_2(\pi\text{-}C_3H_5)_2$,[88,89] from 60° to 120°C with $Ru(CO)_2(\pi\text{-}C_3H_5)_2$,[93] etc. In the spectra of compounds (IV)–(VI) forming isomeric pairs, interconversion of the rotational isomers (a) and (b) begins to become more rapid with rise in temperature. As a result, the two spin systems AK_2X_2 coalesce into a single system (and the rotational isomers thus become indistinguishable by n.m.r. spectroscopy) or the ratio of the isomers changes[98–102].

With both types of compounds the observed spectral changes are satisfactorily explained on the assumption that the allyl group swings at an appropriate frequency about the metal–ligand axis (process III). The π-allyl ligand thus occupies successively first one and then another orientation relative to the remainder of the molecule, so that the terminal methylene groups exchange their environments [$C_{(1)} \rightleftharpoons C_{(3)}$, H(b) ⇌ H(b′), H(c) ⇌ H(c′)]. A similar explanation applies to the temperature dependence of the spectrum of tri-π-allylrhodium, which probably has a trigonal prism structure[21,22,90]. Becconsall and O'Brien first described intramolecular rotation of type (III) in this particular compound[22]. It must be stressed, however, that the observed spectral changes can in principle be

explained, not by transitions between rotational isomers, but by some other intermolecular (e.g. exchange) or intramolecular (pseudorotation) mechanisms [103]. Thus the most informative spectroscopic methods must be employed to elucidate the true mechanism of stereochemical non-rigidity in these compounds.

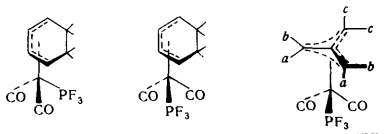
(*c*) Internal rotation in derivatives having four- and five-electron ligands

Internal rotation about the π-C_4H_6–M bond in compounds having four-electron ligands has been investigated on π-butadiene, π-cyclohexadiene, and π-trimethylenemethane complexes of the type π-L–$Fe(CO)_n(PF_3)_{3-n}$. [104-108] The π-butadiene and π-cyclohexadiene derivatives π-$C_4H_6Fe(CO)(PF_3)_2$ and π-$C_6H_8Fe(CO)(PF_3)_2$ can be most conveniently investigated by ^{19}F n.m.r. because of their low degree of symmetry. At sufficiently low temperatures the two trifluorophosphine groups are diastereotopic, but become dynamically equivalent with rise in temperature. These results are consistent with the hypothesis that, of the two non-equivalent rotational isomers



(VIIa) (VIIb)

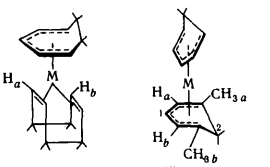
the energetically more favourable isomer (VIIa) is stabilised at low temperatures [104,107]. Investigation of the analogous complex π-$C_6H_8Fe(CO)_2PF_3$ has shown, however, that at low temperatures both rotational isomers—(VIIIa) and (VIIIb)—may exist with closely similar probabilities [107].



(VIIIa) (VIIIb) (IX)

The highly symmetrical π-trimethylenemethane ligand enables the interconversion of rotational isomers to be investigated by proton magnetic resonance. The spectrum of π-$C_4H_6Fe(CO)_2PF_3$ below −73°C contains three equally intense groups of signals corresponding to three types of ligand protons—$H_{(a)}$, $H_{(b)}$, and $H_{(c)}$—in each of the three equivalent rotational isomers (IX). At sufficiently high temperatures, however, the spectrum is a doublet, which indicates the appearance of dynamic equivalence among these protons and the intramolecular character of the dynamics ($^{31}P-^1H$ spin–spin interaction is observed throughout the temperature range). These spectral changes are attributed [108] to acceleration of rotation about the π-C_4H_6–Fe bond, as a result of which the rotational isomers undergo more rapid interconversion, while the protons $H_{(a)}$, $H_{(b)}$, and $H_{(c)}$ interchange their environments.

A few papers have appeared on intramolecular rotation in complexes containing five-electron ligands. In the cobalt complex which according to n.m.r. data [106] has the "transverse" structure (Xa), the diene protons $H_{(a)}$ and $H_{(b)}$ of the π-cyclo-octa-1,5-diene ligand are diastereotopic owing to the low degree of symmetry of the π-cycloheptadienyl ligand. The temperature dependence of the n.m.r. spectrum shows that these protons are anisochronous at −25°C, but become isochronous at 70°C, obviously as a consequence of dynamic equivalence. These changes in the spectrum were attributed [106] to acceleration of internal rotation about the π-1,5-diene–cobalt bond. However, this is not the only hypothesis, for similar spectral changes should be observed with more rapid rotation about the π-cycloheptadienyl–cobalt bond:



(Xa) (Xb)

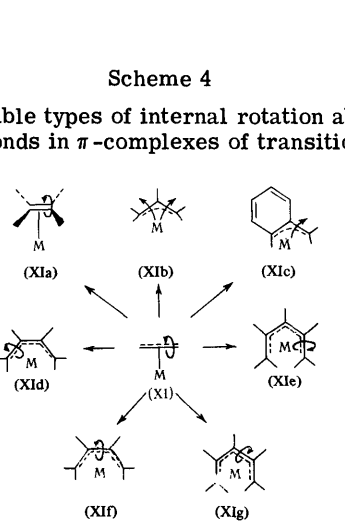
This latter explanation is supported by the temperature dependence of the spectrum of the biscyclohexadienyliron derivative [105]. The low-temperature spectrum of this compound is consistent with the transverse structure (Xb): groups lying outside the plane passing through positions 1, 2, and Fe [$H_{(a)}$ and $H_{(b)}$, $CH_{3(a)}$ and $CH_{3(b)}$] are diastereotopic and anisochronous in the n.m.r. spectrum (the authors [105] interpreted their results somewhat differently). With rise in temperature the shielding of the (*a*) and (*b*) groups averages out, and this is obviously an effect of internal rotation about the metal–pentadienyl π-bond.

2. Rotation about Multiple π-Bonds

In most organic compounds rotation about ethylenic bonds is opposed by considerable barriers, so that n.m.r. has not usually been employed to investigate this type of dynamics (see e.g. review [38]). However, several examples of compounds are known in which these barriers were lowered by certain structural changes, so that internal rotation could be observed by the n.m.r. method [109-118]. Nor is the dynamics associated with rotation about π-bonds with barriers accessible to n.m.r. investigation fundamentally impossible in organic derivatives of transition metals. However, whether or not such dynamics is observable may be determined not only by the structure of the organic ligand but also in considerable measure by the "electronic requirements" of the transition metal. Scheme 4 assembles examples of several structures in which dynamics of type (XI) is theoretically possible.

Scheme 4

Some possible types of internal rotation about multiple bonds in π-complexes of transition metals

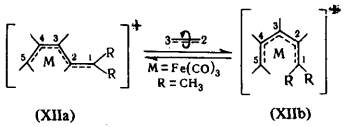


(XIa) (XIb) (XIc) (XId) (XI) (XIe) (XIf) (XIg)

Rotation of type (XIa–e), involving the terminal fragment of a system of multiple bonds, has so far been discussed in connection with n.m.r. data on certain π-allyl (XIb) and π-benzyl (XIc) derivatives. Thus examination of the spectrum of tetra-allylzirconium reveals that the diastereotopic (and anisochronous) *cis*- and *trans*-protons $H_{(b)}$ and $H_{(c)}$, added to each of the terminal carbon atoms (structure III), become isochronous with rise in temperature: whereas the spectrum is of AK_2X_2 type at −74°, it degenerates to AX_4 when the temperature rises to −10°C.[20,98,99,119] A similar spectral pattern is found with tetra-allylthorium (AK_2X_2 at 10° and AX_4 at 80°C).[119] A reversible change in the allylic portion of the spectrum has been found also with π-benzyl derivatives of molybdenum, tungsten, and palladium[19,120,121].

Even in the π-allyl derivatives, however, dynamic equivalence of *cis*- and *trans*-protons has so far been observed only in a limited number of examples. Attempts to detect it in several other π-allylic complexes have proved unsuccessful[91,122,123]. Nor have publications appeared on the dynamics (XI—a, d, e) in other types of π-complexes.

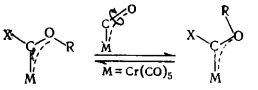
King and Fronzaglia[19], who were the first to observe process (XI) in a π-benzyl compound of molybdenum, suggested that the appearance of isochronicity of the methylene protons with rise in temperature was due to acceleration of rotation about a carbon–carbon bond of order 1.5 in the ligand. The temperature dependence of the spectrum of tetra-allylzirconium has been explained similarly[98]. However, the results obtained are consistent also with alternative mechanisms, including intermediate formation of a σ-type compound[120]:



(XIIa) (XIIb) (9)

The process (XIf, g), involving the central fragment of the system of multiple bonds in the ligand, has been observed only in the derivatives (XIg). Ionic π-pentadienyl complexes of iron exist as two isomers (XII), of which the *cis*-isomer (XIIb) is the more stable[124–127]. Nuclear magnetic resonance has revealed[125] *cis*- and *trans*-interconversions (9) of these isomers at all rates over the whole range, which confirms the possibility that rotation about the 1.5 bond $C_{(2)}–C_{(3)}$ may be accelerated. It is significant that the rate of rotation about the $C_{(1)}–C_{(2)}$ bond is much lower.

Internal rotation in carbene derivatives has been investigated on compounds of type (XIII). At sufficiently low temperatures they exist as two rotational isomers (*trans* and *cis*—XIIIa and XIIIb), each having its own n.m.r. spectrum, including the spectrum of the indicator groups OR (R = CH_3, C_2H_5) and X (X = CH_3, Ar). The relative intensities of the OR (or X) signals show that the mixture contains unequal amounts of the two isomers, which depend on the structure of the compound and the solvating power of the solvent. With rise in temperature the signals of both indicator groups gradually broaden, and then coalesce, at a temperature depending on the nature both of R and of X. An obvious explanation of the observed temperature dependence is that *cis*- and *trans*-isomers may be converted one into the other by internal rotation about the 1.5 bond C·····O:[128–131]



(XIIIa) (XIIIb)

III. INTRAMOLECULAR MIGRATIONS OF METAL-CONTAINING GROUPS (METALLOTROPY)

Processes of several kinds—transition of $\sigma–\sigma$, $\pi–\pi$, and $\sigma–\pi$ types—are included in metallotropy. Migrations of $\sigma–\sigma$ type (sigmatropic transitions) presuppose that the metal forms a localised coordinate or σ-bond with topologically distinguishable ligand atoms before and after the regrouping, during which its system of multiple bonds undergoes rearrangement. Metallotropic systems of this type reproduce formally the corresponding prototropic systems, and transitions can occur both between equivalent and between non-equivalent positions. Transitions of $\pi–\pi$ type consist in transfer of the metal from the system of multiple bonds with which the π-bond was originally formed to another—equivalent or non-equivalent—system. With $\sigma–\pi$ transitions the metal-containing group forms bonds of fundamentally different types with the ligand in initial and final states of the molecule. Transitions of $\pi–\pi$ and $\sigma–\pi$ types have no prototropic analogues.

Metallotropic transitions may be accompanied by either preservation of or change in the "connectedness"‡ of metal and ligand in the metal–ligand fragment of the molecule. The "connectedness" of this fragment is maintained in $\sigma–\sigma$ transitions, but changes during $\sigma–\pi$ transitions. Conversions of $\pi–\pi$ type are more varied: they can take place either with maintenance of or change in the "connectedness" of the given fragment.

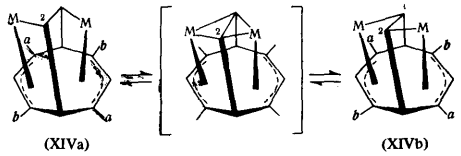
Metallotropic transitions of all the above types will be discussed below with the use of several examples. It must be stressed, however, that there are many organometallic compounds, in particular cluster structures, in which the dynamics is so complicated that it is often difficult to assign to one of the simple types[133–145]. Furthermore, the term "metallotropy" merely indicates the final result of the process—migration of a metal-containing group in space—not its cause or mechanism. These may include the flexibility of the ligand, the ease of formation of the transition state, the spatial proximity of the two energy minima between which the metal-containing group migrates, etc.

1. $\sigma–\sigma$ Transitions

Intramolecular transitions of $\sigma–\sigma$ type, accompanied by rupture of an M–El σ-bond (El = N, O, S, etc.) and formation of a similar or some other σ-bond, have been little studied in the chemistry of transition metals. Only occasional examples are known[146,147]. Intramolecular

‡ The term "connectedness" is the [translation of] the Russian equivalent of *hapto* (proposed by Cotton[132])—the number h^n of the adjacent n atoms of the ligand involved in forming a bond with the metal. This term differs from "denticity" in sense and in range of use, and its application to π-complexes seems justified.

equilibrium $\sigma-\sigma$ transitions of metal-containing groups involving metal–carbon M–C bonds

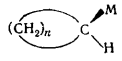


(XIVa) (XIVb)

are obviously of fundamental interest.

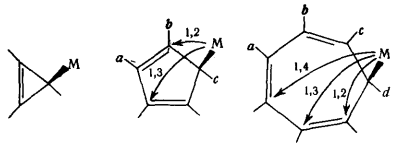
The transformations observed in the n.m.r. spectra of the derivative (XIV) with M = $Fe(CO)_3$ provide an example of such dynamics. Two types of bonds—π-allylic and σ—are formed by each metal atom in this compound. At 0°C the spectrum of the complex corresponds to the low-temperature limiting structure with diastereotopic (and anisochronous) protons $H_{(a)}$ and $H_{(b)}$ in both indicator π-allyl fragments. Gradual changes are observed with rise in temperature, and at 45°C the $H_{(a)}$ and $H_{(b)}$ protons become dynamically equivalent. The cause of these spectral changes is acceleration of the synchronous degenerate transitions of the metal atoms between two possible positions, as a result of which each atom forms a σ-bond alternately with the $C_{(1)}$ atom and with the $C_{(2)}$ atom [148].

In cyclic compounds $\sigma-\sigma$ transitions are most probable in derivatives of the type [28]



(XV) n: a) 1; b) 2; c) 3.

The position of the metal-containing group with respect to the system of double bonds in these compounds is favourable (though in different degrees) for both dynamic and static $\sigma-\pi$ conjugation. This may in principle promote significant activation of the M–C σ-bond, and hence facilitate its dynamics. Among specific examples with $n = 1-3$ σ-cyclopropenyl compounds (XVa) have so far remained completely unstudied, while the largest number of publications are concerned with σ-cyclopentadienyl compounds (XVb):

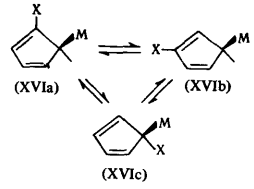


(XVa) (XVb) (XVc)

Dynamic n.m.r. investigation of σ-cyclopentadienyl derivatives of certain transition metals of the iron and chromium subgroups shows that at sufficiently low temperatures the spectrum of the cyclopentadienyl ligand contains a multiplet due to the five-spin system of protons AA'BB'X [10,149–154] (or ABCDX with compounds of lower symmetry [155]; a corresponding set of signals is observed in the ^{13}C n.m.r. spectrum [156]). Such spectra correspond to the presence in these compounds of a localised C_5H_5-M bond, and in several cases this has been confirmed independently by structural investigations by diffraction methods [10,157,158]. A series of patterns of intermediate type is observed with gradual rise in temperature, and at still higher temperatures a single signal representing a situation in which all five ring protons are isochronous owing to the time averaging of their shielding (or for some other reason).

Two main mechanisms have been suggested for the intramolecular migration of a metal-containing group resulting in such averaging: Piper and Wilkinson, the first to meet this phenomenon, pointed to the possibility of $\sigma-\sigma$ transfers of the metal-containing group along the perimeter of the cyclopentadienyl ligand [11]; more recently a mechanism involving a change in type of the C_5H_5-M bond ($\sigma-\pi$ transitions) has been proposed [159]. Either mechanism explains the main features of the ^1H n.m.r. spectra of these compounds. Study of the finer spectral changes shows that, depending on the structure of the compounds and several other factors, both the first [10,152,153] and the second [160–163] (Section III, 2) mechanisms may operate.

Certain features of the mechanisms of $\sigma-\sigma$ transitions in σ-cyclopentadienyl compounds ($\sigma-\pi$ transitions will be considered in Section III, 2) have been studied on derivatives of two types: in compounds containing C_5H_5M fragments (and C_5X_5M in general) migration of the metal-containing group reduces to the degenerate processes



(XVIa) (XVIb) (XVIc) (10)

(where X = H); in derivatives having a substituted ligand (C_5H_4XM, etc.) degeneracy is eliminated, and the process reduces to the interconversion of the isomers (XVI) (X ≠ H). In both cases, however, the $\sigma-\sigma$ transition can in principle involve 1–2 and/or 1–3 migration of the metal-containing group within the cyclic fragment (structure XVb). [10]

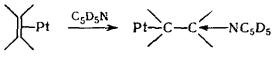
The forms of the $H_{(a)}$ and $H_{(b)}$ signals in derivatives containing a C_5H_5M fragment are found to vary in different rates with rise in temperature (their assignment was based on analysis of the multiplicity of the main signals and their ^{13}C satellites, on the ^{13}C spectra, and also on the proton spectra of corresponding deuteriated derivatives [10,152,153]). The interconversion of isomers of (XVI) has been examined also on a σ-$C_5H_4CH_3$ derivative of ruthenium [153]. These spectral features agree best with 1–2 displacement. Thus a choice could be made in favour of one of the forms of sigmatropic rearrangement—that involving migration of the metal along the shortest path to the adjacent carbon atom (and representing a form of $\sigma-\pi$ conjugation—"counter" dynamics of electrons and metal-containing group). The Woodward–Hoffman rules have also been extended [164] to the mechanism of sigmatropic migration in the derivatives (XVb).

It must be emphasised that a C_5H_5-M σ-bond and hence a $\sigma-\sigma$ mechanism of migration have beem assumed also for many other derivatives—$C_5H_5AuP(C_6H_5)_3$, [165] $C_5H_5(CH_3)_2AuP(C_6H_5)_3$, [166] $C_5H_5(C_6H_5)Pt[P(C_2H_5)_3]_2$, [167] etc. The initial premise in all cases is that the "electronic requirements" of the transition or post-transition metal enable it in principle to form a metal–carbon σ-bond. However, such presuppositions are not sufficieintly convincing by themselves in the absence of other unambiguous confirmation. Such support could come from the detection of the AA'BB'X spin system in the low-temperature ^1H n.m.r. spectrum, the detection of a localised bond when the compounds are examined by difiraction, etc. In any specific case, moreover, additional investigations are

necessary which would reveal some disregarded factors—intermolecular dynamics involving the C_5H_5-M bond [168,169], change in character of this bond under the influence of strongly solvating solvents [169-172], bridge formation by the cyclopentadienyl ligand [173], maintenance of some form of dynamics in the crystal [174], etc.

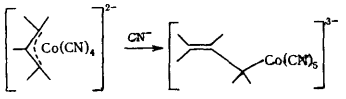
2. $\sigma-\pi$ Transitions

The $\sigma-\pi$ transitions often encountered in organometallic chemistry are investigated by various physicochemical methods, including nuclear magnetic resonance (available information on this topic has been reviewed [175]). $\sigma\pi$-Reactions are usually intermolecular. Thus n.m.r. observations have been reported on irreversible



(11)

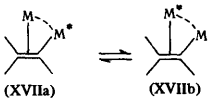
and reversible $\sigma-\pi$ transformations in ethylenic complexes of platinum [176,177]. Papers have appeared on irreversible and reversible $\sigma-\pi$ transitions in π-allylic complexes [178-181], in particular on the reversible reaction



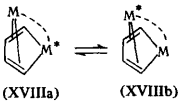
(12)

investigated by n.m.r. [182,183] (such transitions in π-allylic complexes gave rise to a lively controversy—see reviews [5,94] and subsequent communications [184,185]).

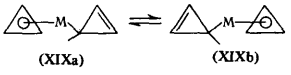
However, there are very few examples of $\sigma-\pi$ transitions that are actually intramolecular. Change in the valency state of the metal in the direction of the given ligand (change in the "connectedness" of the metal–ligand fragment) in compounds possessing stereochemical nonrigidity of this type should, of course, be balanced by the "internal resources" of the molecule. This condition can be realised (at least for degenerate $\sigma-\pi$ transitions) by e.g. combining in one molecule two formally identical metal–ligand fragments, two metals attached to a single ligand by different bonds (structures XVII and XVIII), or two ligands attached in different ways to one metal (structures XIX–XXI):



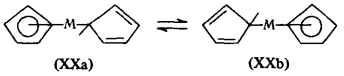
(XVIIa) (XVIIb) (13)



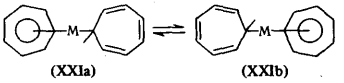
(XVIIIa) (XVIIIb) (14)



(XIXa) (XIXb) (15)



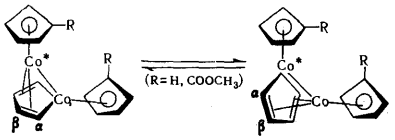
(XXa) (XXb) (16)



(XXIa) (XXIb) (17)

The two metals or ligands may be either structurally isolated or have some additional bond to form a kind of "cluster". Under appropriate temperature conditions the metal–ligand fragments may be expected to interchange functions, and the rates of certain of these degenerate processes may lie in a range suitable for n.m.r. observation.

Examples are known of dimetal compounds of type (XVII), [186-190] but there are at present no reports of the observation of degenerate $\sigma-\pi$ reactions (13) in them. Among dimetal complexes (XVIII) [191,192] "dynamic" derivatives—the dicobalt compounds (XXII: R = H, $COOCH_3$)—are known [193,194]. In these compounds one metal atom is attached to the butadiene fragment by two metal–carbon σ-bonds, and the other by a π-C_4H_4-M π-bond. The two π-cyclopentadienyl ligands are then situated in different environments, and are therefore diastereotopic. Dynamic n.m.r. investigation of solutions of (XXII) indicates that the indicator groups (π-C_5H_5 and CH_3 respectively with R = H and $COOCH_3$) are anisochronous at room temperature, but become isochronous at higher temperatures. However, shielding of the diastereotopic α- and β-diene protons is maintained when dynamic equivalence of the indicator groups appears in the high-temperature spectra. These temperature changes correspond most probably to intramolecular reactions (18) (their rates are independent of concentration), in which each metal atom occupies alternately one of two nonequivalent positions—that in which it forms a π-butadiene bond or the position in which it is attached to the ends of the butadiene fragment by two σ-bonds:



(XXIIa) (XXIIb) (18)

Degenerate $\sigma-\pi$ transitions (15)–(17) are possible between the rings in compounds having $M(\pi\text{-}C_nH_n)(\sigma\text{-}C_nH_n)$ as principal fragment. Processes (15) and (17) for $n = 3$ and 7 respectively have not yet been investigated. With $n = 5$ process (16) has been observed in the n.m.r. examination of the compounds $(C_5H_5)_4M$, $(C_5H_5)_3MX$, $(C_5H_5)_2MXY$, etc. [150,151,154,155,160-163], and can be expected over a wider range of structures. In particular, the low-temperature n.m.r. spectra of certain $(C_5H_5)_4M$ derivatives [160-163] and $(C_5H_5)_3MoNO$, [150,151] together with X-ray examination of crystalline specimens [157,158,161,195,196], show that a C_5H_5-M bond occurs in two forms—delocalised π-bond (spectrum A_5) and localised M–C σ-bond (spectrum AA'BB'X)—within the same molecule. At higher temperatures the set of signals corresponding to the σ-C_5H_5 group degenerates into a single A_5 signal, so that two singlets can be observed, corresponding respectively to protons of the π-C_5H_5 group and the averaged signal due to protons of the σ-C_5H_5 group. At still higher temperatures further changes are observed in the spectrum, accompanied by coalescence of the two signals into one. Thus not only endocyclic $\sigma-\sigma$ transitions (10) take place in these compounds but also $\sigma-\pi$ conversions (16), in which the metal is attached to each cyclopentadienyl ligand alternately by a σ-bond and by a π-bond.

3. $\pi-\pi$ Transitions

Dynamic n.m.r. spectral study of $\pi-\pi$ transitions—dynamic processes of a fundamentally novel type for chemistry—began only during 1966–1967. However, the

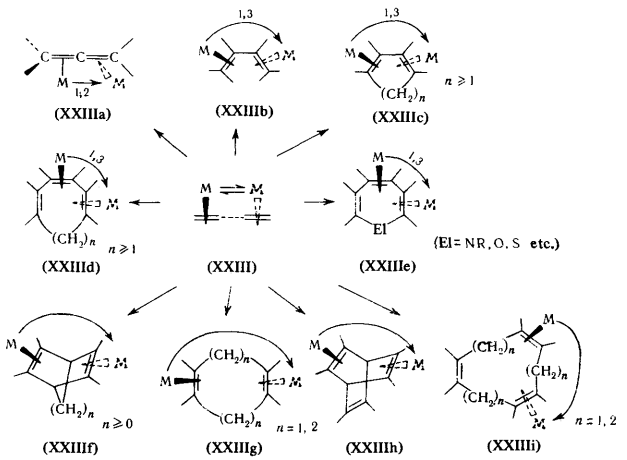
number of known examples is already fairly large, and research is extending to ever new classes of organometallic compounds.

(*a*) $\pi-\pi$ Transitions in derivatives with a ligand having an open system of π-electrons

Schemes 5 and 6 show several types of complexes in which $\pi-\pi$ migration of one metal-containing group is theoretically possible with maintenance of the "connectedness" of the π-metal–ligand fragment in the ground state. The main feature of these structures is the open chain of π-electrons in the carbon skeleton of the ligand.

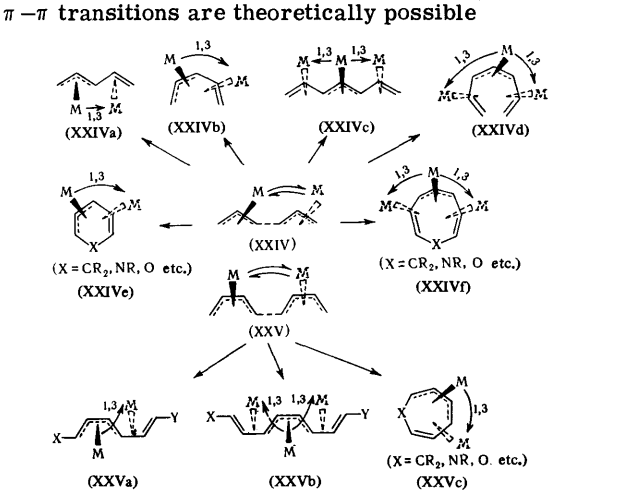
Scheme 5

Some types of ethylenic π-complexes in systems in which the ligand has an open chain of π-electrons and in which $\pi-\pi$ transitions are theoretically possible



Scheme 6

Some types of π-allylic and π-butadiene complexes in systems with an open chain of π-electrons, in which $\pi-\pi$ transitions are theoretically possible

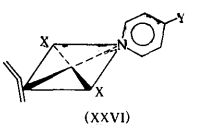


As a consequence, movements of the metal-containing group directed to one side along the perimeter of the unsaturated chain are excluded, and only "vibrational" transitions (degenerate or non-degenerate) between two or more centres are possible. The selection of systems assembled in Schemes 5 and 6 is obviously in considerable measure formal, so that each requires special examination of the conditions under which transitions can actually occur. 1,2-Transitions, involving migration of the metal-containing group to an adjacent C–C bond, are obviously possible only in a limited number of systems. The 1,3- and 1,4-types of migration, as well as more complicated transitions, are formally possible in a wider range of systems. It must be noted that not all the types of organometallic compounds in Schemes 5 and 6 are known at present. Even among those structures which have already been prepared [192,197–200], however, metallotropic $\pi-\pi$ transitions have been investigated so far in isolated cases.

The first investigation of metallotropic $\pi-\pi$ transitions in π-complexes having an open system of π-electrons was made by Ben-Shoshan and Pettit [201] on an allene derivative of iron (structure XXIIIa). In compounds of this type the metal is coordinated with only one multiple bond of the ligand [201–206]. Dynamic n.m.r. investigations have since been extended to compounds of other metals [204,205].

At sufficiently low temperatures the proton n.m.r. spectra of the tetramethylallene complexes π-$C_7H_{12}Fe(CO)_4$ and π-$C_7H_{12}PtCl_2py$ contain three singlet signals corresponding to the "frozen" structure of the compounds—two non-equivalent non-coordinated methyl groups and two equivalent coordinated groups—of relative intensities 1 : 1 : 2. With rise in temperature all the signals coalesce into a single signal, the effect being unaffected by the addition of free tetramethylallene and pyridine to the solution (at temperatures not exceeding $-40°C$). In the spectrum of $(\pi$-$C_7H_{12}PtCl_2)_2$, a compound of lower symmetry, four methyl singlets of equal intensity are observed at $-70°C$, which merge into one signal when the solution warms up to room temperature. Here $^{195}Pt-{}^{1}H$ spin–spin interaction is observed throughout the temperature range. The effect is independent of the concentration of the complex and of the addition of free tetramethylallene or another tetramethylallene complex [201,204,205].

These experimental facts are explained by intramolecular $\pi-\pi$ 1,2-transitions of the metal atom from one double bond to the other (XXIIIa). [201] The rate of migration of the metal depends significantly on the structure of the complex. Thus it varies appreciably in the compounds

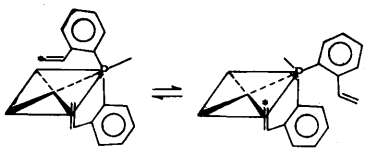


(where X = Cl and M = Pt) on such slight perturbations as changing the substituent Y. [204] The effect is still more striking with more profound structural changes: whereas the process is observed in the spectrum of tetramethylallene derivatives of iron and platinum, it has not yet been detected in allene and 1,1-dimethylallene derivatives of platinum, nor in the allene complex of nickel and the tetramethylallene complex of rhodium [201–206].

Investigation of the dynamic behaviour of other ethylenic π-complexes shown in Scheme 5 and also of other analogous systems awaits our research workers. We will mention certain specific types of $\pi-\pi$ migration studied in ethylenic complexes. Thus the dynamic behaviour of the compound

$Co(\pi\text{-}C_8H_8)\pi\text{-}C_5H_5$, in which the cyclo-octatetraene ligand has 1,5-attachment to the cobalt atom, has been examined[27]. Rise in temperature produces reversible spectral changes, confirming the occurrence of a $\pi-\pi$ transition in the system.

A peculiar example of a $\pi-\pi$ transition in an ethylenic system has been established[207] in an investigation of the proton n.m.r. spectra of tri-*o*-styrylphosphineplatinum and the corresponding arsine and stibine complexes. These compounds obviously have a square planar structure. A single ABX set of signals, corresponding to the two types of ethylenic groups—both uncomplexed and coordinated with the platinum atom—is observed in their n.m.r. spectra at room temperature. Signs of complex formation (displacement of the ethylenic signals towards higher fields relative to the initial ligands and decrease in the proton–proton interaction constants J_{cis} and J_{trans}) are appreciably less marked than in other known π-ethylenic derivatives of platinum[208-211]. The splitting constant $J_{^{195}Pt-^{1}H}$ with one of the protons in the given phosphine complex is about one-third of its value in the usual π-ethylenic complexes of bivalent platinum[208-211]. All these spectral peculiarities are consistent with quite rapid $\pi-\pi$ transitions



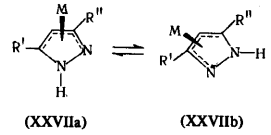
(19)

as a result of which all the spectral characteristics of coordinated and uncoordinated double bonds are averaged out. The process is assumed to be intramolecular with a five-coordinated transition stage.

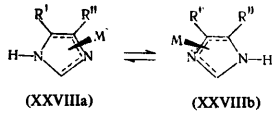
Papers on migration in π-allylic systems (XXIV) have not yet appeared, whereas corresponding n.m.r. data are already known for several π-butadiene structures (XXV). It is found in particular that, in the open systems (XXVa) and (XXVb), $\pi-\pi$ transitions between isomers having somewhat different properties (X ≠ Y) are slow on the n.m.r. time scale. Because of the non-equilibrium character of the process, the n.m.r. recording of such transitions involves merely analytical measurement of the ratio of the isomers. The path of migration of the group M = $Fe(CO)_3$ in compounds (XXVa) and (XXVb) is more or less obvious: only 1,3-transitions, which require no rearrangement of the system of valency bonds, are possible. The "connectedness" of the fragment is assumed to diminish in the transition state, with formation of a π-ethylenic structure ($h^4 \rightarrow [h^2] \rightarrow h^4$).[212-214]

A unique route for intermolecular transformations—$\pi-\pi$ 1,3-transfers of the metal-containing group from one diene fragment to another—is possible also in carbocyclic and heterocyclic compounds (XXVc) having an acyclic system of multiple bonds. Among compounds (XXVc) that have been studied by n.m.r.,[192,200] however, this dynamics has hitherto been observed only in derivatives having X = NR.[215,216] At 0°C the spectrum of the ethylenic portion of the ^{1}H-azepine derivative corresponds to the instantaneous structure in which the tricarbonyliron group is coordinated with only one diene fragment; at room temperature the signals become blurred; and at 65–85°C the spectrum degenerates into a spin system corresponding to dynamic equivalence of the two diene fragments. These spectral changes were interpreted as evidence of the speeding up of transfers of the group M = $Fe(CO)_3$ between two structurally possible positions (another type of dynamics—acceleration of rotation about the N–R bond—is also possible, and appropriate spectral changes have been attributed to it; inversion of the nitrogen atom in this compound is probably quite rapid).

Tricarbonyliron derivatives of pyrazole and imidazole have been prepared[217], and most probably have a π-butadiene structure (XXVII and XXVIII). Their d.n.m.r. investigation showed significant differences between high- and low-temperature spectra: whereas at sufficiently low temperatures the indicator groups R′ and R″ (CH_3 or H) are anisochronous and hence diastereotopic, they become isochronous as the temperature gradually rises. The observed spectral changes might be explained by acceleration of the $\pi-\pi$ transitions a ⇌ b (1,2-transitions for the pyrazole derivatives (XXVII), and 1,3-transitions for the imidazole derivatives (XXVIII); a "counter" rearrangement of the system of double bonds is assumed in both cases) associated with intermolecular and/or intramolecular $\sigma-\sigma$ migration of NH protons:



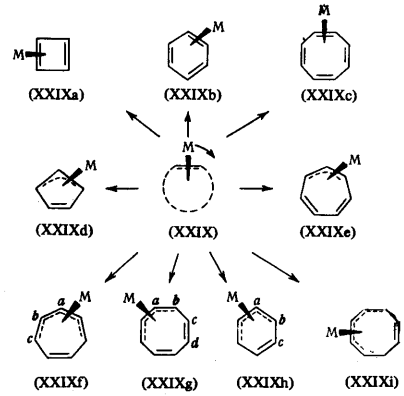
(XXVIIa) (XXVIIb) (20)



(XXVIIIa) (XXVIIIb) (21)

Scheme 7

Some types of compounds with a cyclic system of π-electrons in the ligand, where $\pi-\pi$ transitions are possible



(XXIXa) (XXIXb) (XXIXc) (XXIXd) (XXIX) (XXIXe) (XXIXf) (XXIXg) (XXIXh) (XXIXi)

(*b*) $\pi-\pi$ Transitions in systems with a ligand having a closed chain of π-electrons

Scheme 7 assembles several types of organometallic π-complexes in which a carbocyclic ligand has a cyclic system of π-electrons. The transition metal, because of its "electronic requirements", is unable to coordinate with all the π-electrons simultaneously, but only with an individual segment of the carbon ring. In contrast to the

derivatives discussed in the preceding subsection, the complexes (XXIX) may in principle possess more intense and varied $\pi-\pi$ dynamics: not only "vibrational" but also unidirectional translational movements of metal-containing groups are possible in them; and the π-bond in the transition state of complexex (XXIX) can assume the energetically unforbidden form (I), which is formally similar to the structure of the ground state in many π-complexes. However, these features of the derivatives (XXIX) complicate substantially discussion of the mechanisms of their $\pi-\pi$ transformations because of the multiplicity of the latter.

Among the mono-olefinic π-complexes (XXIXa–c) $\pi-\pi$ transitions have so far been detected in the platinum derivative (XXIXb). The process is intramolecular, since spin–spin interaction between platinum-195 and the ring nuclei is observed throughout the temperature range. The n.m.r. spectrum of the compound in the "frozen" state is consistent with X-ray data [218].

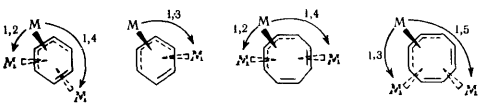
Information is available on the π-allylic complexes (XXIXd, e). The complex (XXIXd) has been prepared [219], and an aluminium derivative of this type has been studied by gas-phase electron diffraction [220]. Cycloheptatrienyl complexes of molybdenum, tungsten, cobalt, and iron of the type (XXIXe) have been described [19,221–229], and their stereochemical non-rigidity has been investigated by d.n.m.r. on several examples. Unfortunately, the structure (XXIXe) (based on the "electronic requirements" of the metal taking into account its bonds in the rest of the complex) is not uniquely possible. Low-temperature n.m.r. investigations of these complexes indicate the possibility not of a π-allylic but of a C_7H_7-M σ-bond [94,224], although in the fairly specific pyrazolylborate derivative of molybdenum the bond in the crystal is actually π-allylic [226]. Thus a more exact discussion of the mechanism of metallotropic transitions in the complexes (XXIXe) ($\pi-\pi$, $\sigma-\sigma$, or more complicated) will evidently be possible only after their "instantaneous" structure has been elucidated both in solution and in the crystal.

The preparation and the n.m.r. investigation of the derivatives $[C_7H_7Fe(CO)_3]^+$ and $C_7H_7Mn(CO)_3$ have been reported [16,219]. The low-temperature limiting spectrum of these compounds corresponds to the "frozen" structure (XXIXf) with anisochronous protons of the diastereotopic groups $a-d$. Degeneration of the spectrum into A_7 at higher temperatures indicates that the ligand nuclei become dynamically equivalent. The observed spectral changes are due to acceleration of $\pi-\pi$ transitions of the metal-containing group, but insufficient data are yet available for assessment of the more detailed mechanism of these transitions.

The largest number of papers are concerned with $\pi-\pi$ transitions in butadiene π-complexes (XXIXh) and (XXIXg), and much of the information on their dynamic behaviour has been obtained only during most recent years. The protons of the diastereotopic indicator groups ($a-d$ in XXIXg, and $a-c$ in XXIXh) are anisochronous at sufficiently low temperatures, but become isochronous at higher temperatures. The temperature dependence of the line form has been investigated experimentally, and the theoretical form of the line has been calculated for various lifetimes of the molecules in the "frozen" state.

The history of the d.n.m.r. study of the cyclo-octatetraene derivatives (XXIXg) is extremely dramatic. Originally it was known only that the protons of the cyclo-octatetraene ligand were isochronous in solutions of $\pi-C_8H_8Fe(CO)_3$ and similar compounds: the proton n.m.r. spectrum contained a narrow singlet independently of the choice of solvent or of solution temperature right down to $-60°C$. [230–232] As a result it was suggested that this ligand has a planar structure and that all its eight protons are equivalent (structure I: $n = 8$). [230,231,233] However, this hypothesis was not confirmed by a structural examination of $\pi-C_8H_8M(CO)_3$ molecules (M = Fe, [13] Ru [234]). Dickens and Lipscomb [13] found that, at least in the crystal, the $M(CO)_3$ group forms a π-bond with only one conjugated diene unit (structure XXIXg). These workers suggested that the equivalence of the protons of the $\pi-C_8H_8-M$ bond in a solution of the iron complex, in contrast to the crystal, was for the n.m.r. observer not static but dynamic in origin, and resulted from the rapid movement of the metal-containing group between several possible 1,3-diene positions. During 1966–1967 several groups of workers were able to reach sufficiently low temperatures to "freeze" the n.m.r. spectral pattern for both complexes and several related compounds [23,25,26,235–239]. The instantaneous structure of these compounds in solution was actually found to be identical with their structure in the crystal: as the temperature fell the spectrum of the π-cyclo-octatetraene ligand revealed four anisochronous indicator groups, corresponding to four types of diastereotopic nuclei in the ligand. Similar results have since been obtained in investigations of these and analogous derivatives of type (XXIXg) (M = Fe, Ru, Os) by proton [240–244] and carbon-13 [245] nuclear magnetic resonance. Evidence has also been obtained in support of the intramolecular character of the observed dynamics. For example, study of a solution of a mixture of cyclo-octatetraene and the complex $\pi-C_8H_8Fe(CO)_3$ at room temperature revealed no interaction between them: the ring protons of both compounds were anisochronous in the n.m.r. spectrum [231]. Finally, it has been found [246,247] that in these and related compounds $\pi-\pi$ dynamics is maintained even in the crystal. Only lowering the temperature of the crystal led to an (apparent) arrest of the process, i.e. to a decrease in the frequency of transitions to around 1 kHz (limit of sensitivity of the method employed).

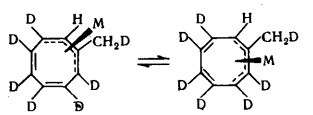
Consideration of the detailed mechanism of $\pi-\pi$ processes in π-cyclo-octatetraene derivatives (XXIXg) involves a choice [244] between several possibilities—1,2-, 1,3-, 1,4-, or 1,5-transitions (structures XXXc and XXXd)—with formation of a non-planar transition state or a $\pi-\pi$ transition via a planar transition state (I: $n = 8$) with a statistical distribution of products. Analogous mechanisms (XXXa, b) are suggested for the derivatives (XXIXh). [248] With 1,2- and 1,4-transitions (XXXa, c), of course, spatial displacement of the metal (if it occurs at all) must be accompanied by redistribution of the system of multiple bonds in the ligand (valency tautomerism), but with 1,3- and 1,5-transitions (XXXb, d) the bond system will be unchanged:



(XXXa) (XXXb) (XXXc) (XXXd)

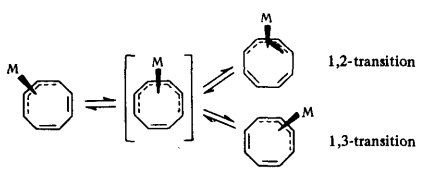
The experimental results are discussed on the basis of these possible mechanisms. Thus comparison of experimental and theoretical n.m.r. line forms indicates [244] that, in derivatives (XXIXg) of metals of the iron subgroup, both experimental and theoretical patterns are least consistent with 1,4- and 1,5-transitions, and also with the statistical mechanism involving the transition state (I: $n = 8$). The temperature dependence of the spectrum of $\pi-C_8H_8Ru(CO)_3$ led to the conclusion [237] that $\pi-\pi$ transitions

in systems such as (XXIXg) are effected by successive 1,2-shifts of the metal-containing group, and that a mechanism involving $\pi-\pi$ 1,3-transitions is unacceptable. A similar conclusion has been reached for compounds of type (XXIXh).[248] This is consistent with Anet's experimental results on the compound (XXXI),[236] which may in principle exist as very many structures, although contributions by structures other than (XXXIa, b) to the high-temperature spectrum are extremely small. Only two equivalent structures—(XXXIa) and (XXXIb)—are observed in the low-temperature boundary spectrum. Thus the intramolecular dynamics in this compound reduces to degenerate $\pi-\pi$ 1,2-transitions:



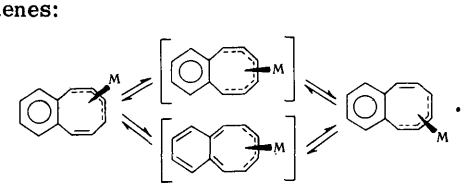
(XXXIa) (XXXIb) (22)

However, conclusions on 1,2-migration have since become somewhat less categorical. Thus the theoretical pattern of migration of the metal in π-$C_8H_8Ru(CO)_3$ agrees best with experiment only on the assumption of definite contamination of 1,2-transitions by a 1,3-type of mechanism[244]. On the other hand, study of the temperature dependence of the spectrum of π-$C_8H_8Os(CO)_3$ reveals several additional difficulties connected with the complexity of obtaining the theoretical n.m.r. line form for such multispin systems[243]:

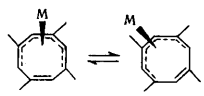


(23)

It is probable that $\pi-\pi$ transitions in the derivatives (XXIXg) and (XXIXh) can be accomplished both by one of the suggested mechanisms (1,2-, 1,3-, 1,4-, and 1,5-transitions or the statistical mechanism) and by some other mechanism. For cyclo-octatetraene derivatives, in particular, mechanism (23) can be suggested as a hypothesis. Vibrations of the ring in the transition state would then be accompanied by an increase in the "connectedness" of the metal ($h^4 \rightarrow [h^6] \rightarrow h^4$), which allows for the objective result[244] that each step in the reaction involves formation of a mixture of 1,2- and 1,3-transition products. A mechanism with intermediate increase in the "connectedness" of the metal—as an alternative to a mechanism involving intermediate formation of a quinoid structure[249]—is useful in considering $\pi-\pi$ transitions of the tricarbonyliron group in benzo- and naphtho-cyclo-octatetraenes:



Stereochemical non-rigidity has been investigated[23,24,222,240,241,250,251] in the cyclo-octatetraene derivatives (XXIXi) of metals of the chromium and iron subgroups. However, the difficulties of interpreting the low-temperature boundary spectrum prevented sufficiently detailed information from being obtained on the mechanism of dynamics in the cyclo-octatetraene derivatives themselves[23,222]. These difficulties were overcome to a certain extent by using 1,3,5,7-tetramethylcyclo-octatetraene as ligand[24,251]. Over the range adjacent to the temperature at which the low-temperature boundary spectrum is observed the process is effected by 1,2-transitions:

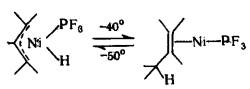


(24)

However, the spectral changes observed on further heating indicate that the process becomes more complicated. Under these conditions the stereochemical non-rigidity is probably due also to the formation in the transition state of the planar structure (I) with enhancement of "connectedness" ($h^6 \rightarrow [h^8] \rightarrow h^6$).

(*c*) $\pi-\pi$ Transitions accompanied by change in the "connectedness" of the metal in the metal–ligand fragment

Little study has yet been made of $\pi-\pi$ transitions of this type. An illustration is the reversible reaction

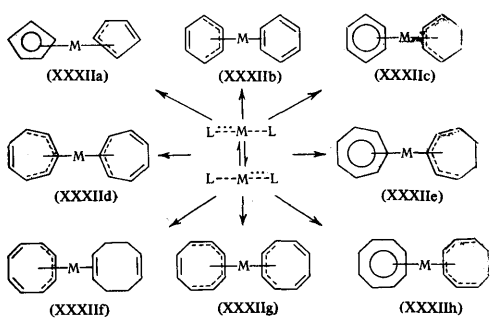


(25)

which has been investigated by n.m.r.[252] However, this reaction involves a $\sigma-\sigma$ transfer of a proton as well as a $\pi-\pi$ transfer of the metal, so that the composition of the metal–ligand fragment itself changes.

Scheme 8

Some types of π-complexes containing a $(\pi$-$C_nH_n)_2M$ fragment in which intercyclic $\pi-\pi$ transitions are fundamentally possible



A "purer" case of these processes is provided by degenerate intramolecular transitions of like ligands between non-equivalent states. Several types of complexes having $(\pi$-$C_nH_n)_2M$ as the main fragment are assembled systematically in Scheme 8. Dynamics of this kind can in principle occur in such compounds, provided that the variation in "connectedness" of each metal–ligand unit is produced by the "internal resources" of the other unit. Intercyclic $\pi-\pi$ exchanges are not yet known for rings containing an odd number of carbon atoms. Only one of the possible types of these reactions has been

investigated by n.m.r. for each of the "even" rings. Such reactions can in principle occur both in dicyclic compounds $(\pi\text{-}C_nH_n)_2M$ not containing any other ligands and in more complicated compounds—$(\pi\text{-}C_nH_n)_2MR$, $(\pi\text{-}C_nH_n)_2.MCO$, $(\pi\text{-}C_nH_n)_2MNO$, $(\pi\text{-}C_nH_n)_2M(CO)_2$, etc.

Structural data [253] indicate that one ring in the compound $(\pi\text{-}C_8H_8)_2Fe$ forms a diene π-bond, and the other a triene π-bond (structure XXXIIg). A d.n.m.r. investigation [240] suggests that, at temperatures below $-84°C$, the metal undergoes vigorous migration in the "diene" ring (all its protons are isochronous) and is "frozen" with respect to the triene ring (four types of protons are anisochronous). At higher temperatures the metal migrates rapidly inside both cyclo-octatetraene ligands—diene and triene (the protons in each of them become isochronous)— and above $-35°C$ the averaged signals due to the two rings coalesce into one. Thus cyclo-octatetraene ligands attached to an iron atom by unequal π-bonds exchange the types of bonds quite rapidly and entirely synchronously.

Similar conclusions follow from d.n.m.r. data on the ruthenium complex (XXXIIc). Two types of bonds—π-diene and π-arene—are present in the crystal [254]. Nevertheless, the temperature dependence of the n.m.r. spectrum of this complex reveals changes indicating the occurrence of quite rapid intercyclic $\pi-\pi$ transitions [255]. Finally, yet another type of dynamics, not shown in Scheme 8, has been observed in $(C_8H_8)_2M$ derivatives [256].

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