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NMR Study of Equilibrium Intermolecular Exchange Processes Involving Univalent Organometallic Groups of the Type R_nM, Containing an Atom of a Heavy Non-transition Metal from Periods V and VI

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The results of NMR studies of intermolecular exchange reactions accompanied by the rupture of a metal - carbon or metal - heteroatom bond for the case where the role of the metal is played by a univalent organometallic group containing a heavy non-transition metal as central atom have been systematised. The bibliography contains 146 references.

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I. INTRODUCTION

Exchange reactions of type (1) represent one of the most widely encountered types of chemical transformation, characteristic of inorganic, organic, and organometallic compounds:

$$AX + BY \rightleftarrows BX + AY \ . \qquad (1)$$

In the field of organic compounds, the exchange reactions include replacement at a carbon atom, and hydrogen exchange[1-5]. In the field of inorganic compounds, exchange reactions include ligand exchange at a metal or non-metal atom, where the ligands may be anions or neutral molecules[3]. A specific feature of exchange reactions in inorganic compounds is that, since many metal compounds are insoluble in aprotic organic solvents, ligand exchange is studied in an aqueous medium, and the materials studied have been mainly complex compounds[6-9]. Finally, for organometallic compounds of non-transition and transition metals, exchange reactions (1) involve chiefly intermolecular transfer of the organometallic groups from one ligand to another with the rupture of metal–carbon or metal–heteroatom σ- or (π-) bonds.

The present review deals chiefly with exchange reactions of the type:

$$R_nMX + R_nM^*Y \rightleftarrows R_nM^*X + R_nMY \ , \qquad (2)$$

where R_nM and R_n^*M are univalent organometallic groups.

The choice of this process is determined by the following considerations. Exchange reactions of type (2) in organometallic derivatives of EH-acids (where the anionic residue E contains as connecting atom the elements C, N, O, S, etc.) formally resemble hydrogen exchange in the EH-acids themselves:

$$HX + H^*Y \rightleftarrows H^*X + HY \ . \qquad (3)$$

In both cases there is intermolecular exchange of species of cationic type. The specific feature of this exchange is that both R_nM and H are able to act as unshared electron pair acceptors, exhibiting a greater or lesser coordinating power, depending on the nature of the partner. The lability of M–X bonds usually decreases with decrease in their polarity. It is therefore appropriate to determine the specific features of the migrating power of organometallic groups compared with the hydrogen atom with the minimum difference in the polarity of the corresponding bonds. This condition is satisfied to the greatest extent by the heavy non-transition metals of periods V and VI. Unlike the metals of periods II–IV, the heavy non-transition metals form bonds of low polarity, and the electronegativity differences between them and the hydrogen atom are appreciably smaller than those between the hydrogen atom and the metals of the higher periods.

In this connection, the present review deals with the intermolecular exchange of univalent particles of cationic type, containing heavy non-transition metals of periods V and VI.

In the analysis of reactions of type (2) it is possible to concentrate attention on the dynamics of either the anionic or the cationic groups. In the first case, the exchange reactions (2) and (3) can be divided into three types[10]:

metal–metal (M–M*) exchange;
metal–proton (M–H) exchange;
proton–proton (H–H*) exchange.

In the second case, reactions (2) can be classified as follows:

exchange of the carbon–carbon type (C,C-exchange of organometallic groups);
heteroatom–heteroatom exchange (N,N-, O,O-, S,S-, etc. exchange);
carbon–heteroatom exchange (C,N-, C,O-, C,S-, etc. exchange).

The chief method of studying exchange processes in many cases is by NMR[11-15], which makes it possible to obtain the quantitative characteristics of exchange reactions and to analyse the mechanism by which they take place. The "popularity" of NMR is related to the fact that exchange reactions of the type being considered often take place at rates commensurate with the time scale of this method. Even in those cases where the rate of exchange is low on the NMR time scale, the method makes it possible to determine the composition of the reaction mixture without resorting to preparative isolation of the components.

In recent years, NMR has been widely used to study the migrating power of organometallic groups in exchange reactions of type (2), and in particular to study exchange in which $R_nM = R_n^*M$. In this case the NMR method makes it possible to study exchange reactions both for non-degenerate exchange ($X \neq Y$) and for degenerate exchange ($X = Y$). In the case of non-degenerate exchange (2), evidence of the process may be provided by the changes in the shielding of the groups R of R_nM, which should in principle be different. In the study of degenerate exchange, the shielding of the groups of the group R will not change in the course of the exchange. If however the metal contains isotopes having half-integral spin, and the substituent contains indicator atoms or groups of atoms, it is possible to reach conclusions regarding the characteristic features of the exchange (2) from the presence or absence of spin–spin coupling between them and the nucleus of the metal atom.

Most discussion in the literature has dealt with the spin–spin coupling of the nuclei of the metal with a proton in the fragment M–E–C–H (where E = O, S, N) in organometallic derivatives in which the M–E bond is the most labile part of this fragment. However, although the existence of spin–spin coupling in this fragment makes it possible to conclude that intermolecular exchange is slow (on the NMR time scale), the absence of this type of interaction in the NMR spectrum (without special search for it under conditions of slow exchange) is not a strict indication of a fast reaction.

II. INTERMOLECULAR EXCHANGE OF THE METAL–METAL TYPE TAKING PLACE WITH THE RUPTURE OF METAL–CARBON BONDS (C,C-EXCHANGE OF ORGANOMETALLIC GROUPS)

Intermolecular exchange processes accompanied by the rupture of an R_nM-C bond and the formation of a new bond of this type have been most widely studied for M = Cd[16–25] and Tl[26–31] and to a lesser extent for M = Hg[32–35]. For other metals, only fragmentary data are available.

1. Exchange in Derivatives of Metals of Group IIb

In a series of organic compounds of the group IIb metals, the exchange reactions being considered can be represented in general form as follows:

$$RM_1{-}R' + RM_2{-}R'' \rightleftarrows RM_1{-}R'' + RM_2{-}R' \quad . \qquad (4)$$

Degenerate intermolecular exchange ($M_1 \neq M_2$, $R' = R''$), accompanied by the rupture of M–C bonds, has been most widely studied for the methyl derivatives of cadmium (reaction (4), $M_1 = M_2 = Cd$ and $R = R' = R'' = CH_3$)[18,19,21,24,36–39]. It has been shown that under certain conditions (medium, temperature, concentration) the exchange reaction (4) in $(CH_3)_2Cd$ takes place at rates comparable with the NMR time scale, that this reaction shows second-order kinetics (in ether), and that its activation energy is 15.6–17.0 kcal mole^{-1} (in toluene) or 5.6–7.0 kcal mole^{-1} (in THF, triethylamine, ether). The reaction rate increases considerably when basic compounds are added to solutions of $(CH_3)_2Cd$ in inert media.

A study of the ^1H NMR spectra of diethyl- and di-isobutylcadmium in toluene and pyridine[14] revealed $^{111/113}Cd$ satellites, which became slightly broader with increase in temperature, again possibly indicating that the exchange reaction (4) takes place in these compounds.

In contrast to the case of the dialkyl compounds of cadmium, the ^1H NMR spectrum of $(H_2C{=}CH)_2Cd$, because of rapid exchange, does not show $^{111/113}Cd{-}C{-}^1H$ spin–spin coupling in ether and hydrocarbon media[32]. At the same time, $^{111/113}Cd{-}C{-}^{19}F$ satellites are observed for solutions of $(CF_3)_2Cd$ in THF, indicating fairly slow exchange (4) in this compound[23].

In contrast to the cadmium compounds, the complete organometallic mercury compounds R_2Hg and $RHgR'$ show $^{199}Hg{-}C{-}^1H$ (R = CH_3, C_2H_5, $C_6H_5CH_2$, $H_2C{=}CH$, etc.)[40–44], $^{199}Hg{-}^{13}C$,[45–47] and $^{199}Hg{-}C{-}^{19}F$ (R = CF_3, C_2F_5, $F_2C{=}CF$, etc.)[48–51] spin–spin coupling over a wide range of conditions. This feature is evidently related to the high stability of the Hg–C bonds with respect to exchange in these compounds.

The Hg–C bond is activated by including, in symmetrical organo-mercury compounds, multiple bonds in the β-position relative to the Hg–C bond[52]. A ^1H NMR study of $(C_5H_5)_2Hg$ at room temperature and lower temperatures in weakly solvating solvents revealed rapid intermolecular exchange of C_5H_5Hg groups from one C_5H_5 group to another[35]. The rate of the process increases sharply with increase in temperature and (or) increase in the solvating power of the solvent:

$$C_6H_6 < R_2O < C_5H_5N < DMF < DMSO \ .$$

The earliest studies of non-degenerate exchange reactions in organic derivatives of group IIb metals by NMR were carried out by Allred and McCoy[16,17] for various mixtures of the type (4) (M_1 = Cd, M_2 = Zn or Hg, R = R′ = R″ = CH_3). These and subsequent studies[18,20,22,24,25] revealed the main characteristics of these non-degenerate C,C-exchanges of organometallic groups. It was suggested[16,17] that the averaging of the shielding of the methyl groups, observed in mixtures of dimethylcadmium and dimethylzinc, is due to the rapid exchange of CH_3M groups from one methyl group to another. The order of this reaction in all solvents except ethyl ether is 1.7 ± 0.3, and its rate is independent of the dielectric constant of the solvent, but depends on its donor power. This indicated that ionisation is not the rate-determining stage of the exchange reaction (4). When one of the components of the system is dimethylmercury, the exchange is slow on the NMR time scale[17,18].

Thus in alkyl derivatives of the group IIb metals, the reactivity of the M–C bonds in intermolecular exchange increases in the order: Hg–C ≪ Cd–C < Zn–C.

Another illustration supporting this conclusion is provided by data for $R_2'M + R_2''M$ mixtures (M = Cd and Hg). Thus a ^{113}Cd NMR study of an equimolar $(CH_3)_2Cd + (CH_3CH_2)_2Cd$ mixture showed[25] that the spectrum contains three $^{113}Cd\{^1H\}$ signals with intensity ratio 1 : 2 : 1; the central signal corresponds to the mixed derivative $CH_3CdC_2H_5$. This indicates that the rupture of the Cd–C bond is slow on the NMR time scale.

The NMR data for $R_2'Hg + R_2''Hg$ mixtures ($R' = C_6H_5CH_2$, $R'' = CH_3$ or C_6H_5; $R' = CH_3$, $R'' = C_6H_5$ or CF_3, etc.) indicate that the exchange leading to the formation of the compounds R′HgR″ can take place only when the corresponding mixtures are heated for a long time at a high temperature[43].

The dependence of the reactivity of the Cd–C bond in non-degenerate exchange (4) on the nature of R has been studied[20]. Thus for M_1 = Cd, M_2 = Zn, and $R = R' = R'' = CH_2{=}CH$, the $M{-}CH{=}CH_2$ σ-bond is more labile than the $M{-}CH_3$ bond. A similar conclusion follows from the study of this reaction for $M_1 = M_2$ = Cd and $R = R' = CH_3$;

$R'' = CH_2{=}CH$; or $R = R' = H_2C{=}CH$; $R'' = CH_3$.

2. Exchange in Derivatives of Group III Metals

Exchange reactions in organic derivatives of group III metals can be represented in general form as follows

$$R_2M{-}R + R_2M^*{-}R^* \rightleftarrows R_2M{-}R^* + R_2M^*{-}R \quad . \qquad (5)$$

Degenerate exchange in compounds of this type has been studied in most detail for trimethylthallium [26,27]. At low temperatures the ^1H NMR spectra of solutions of $(CH_3)_3Tl$ in CH_2Cl_2 or $C_6D_5CD_3$ show two signals of equal intensity, due to the splitting of the methyl protons on the thallium isotopes. With increase in temperature these signals become broader and merge, indicating that Tl–C bond rupture is fairly frequent on the time scale of the method. The reaction is of approximately second order, and its activation energy is 6 ± 1 kcal mole^{-1} in CH_2Cl_2 and 6.3 ± 0.5 kcal mole^{-1} in $C_6D_5CD_3$. When $C_6D_5CD_3$ is replaced by the solvating solvents $(CH_3)_2O$ and $(CH_3)_3N$, the rate of exchange decreases slightly [27]. It is suggested [27] that the mechanism of this intermolecular exchange involves the formation of a dimeric transition state.

Reaction (5) was also studied by ^1H NMR for $(C_2H_5)_3Tl$ and $(C_6H_5)_3Tl$. [26,27] For $(C_6H_5)_3Tl$, the following order of decrease in the exchange rate with increase in the solvating power of the medium was established:

$$CH_2Cl_2 > C_6D_6,\ (CH_3)_2O > (CH_3)_3N \quad .$$

Non-degenerate C,C-exchange involving groups containing indium or thallium has been comparatively little studied. Thus the formation of compounds of the type R_2TlR' and $RTlR'_2$ in R_3Tl and R'_3Tl mixtures has been detected by ^1H NMR for $R = CH_3$ and $R' = C_2H_5$. At room temperature, the exchange is rapid on the NMR time scale, whereas at low temperatures in CH_2Cl_2 the individual spectra of all possible compounds are observed [26]. NMR data have also been obtained for the exchange of groups in the system $(CH_3)_3Tl + (CH_3)_2Tl(HC{=}CH_2) + CH_3Tl(HC{=}CH_2)_2$. [27] The study of the last process established that the exchange of vinyl groups is more rapid than that of methyl groups.

NMR data [54–61] make it possible to reach conclusions regarding the limits of stability of Tl–C bonds in exchange reactions. Thus the ^1H NMR spectra of R_2TlX, where X represents electronegative substituents, at room temperature in different media show $^{203/205}Tl{-}C{-}^1H$, $^{203/205}Tl{-}C{-}C^1H$, and $^{203/205}Tl{-}^{13}C$ splitting, indicating that the Tl–C bond is stable under these conditions. This was confirmed [28] by a study of $(CH_3)_2TlX + (C_2H_5)TlX$ mixtures, which showed that the system does not contain mixed derivatives $(CH_3)(C_2H_5)TlX$.

Exchange with rupture of Tl–C bonds is not observed in various compounds of the type $(CH_3)_2Tl{-}R$, where $R = C{\equiv}CC_6H_5$ or C_5H_5. [30,31] There are few data on exchange reactions in derivatives of other group III metals. The intermolecular exchange (5) for M_1 = In and M_2 = Ga ($R = R' = R'' = CH_3$) is rapid on the NMR time scale even at −65° in toluene [62]. A study of exchange in a $(CH_3)_3In + (CH_3)_6Al_2$ mixture in toluene [62] showed that the rate of this process depends on the reagent ratio but is independent of the concentration. This indicates that the reaction is not bimolecular, and that the exchange is preceded by the conversion of the $(CH_3)_6Al$ dimers into monomers, which limits the overall process.

3. Exchange in Mixtures of Derivatives of the Metals of Groups II and III

C,C-exchange of organometallic groups in mixtures of the alkyl derivatives of metals of groups IIb and III by NMR was first studied by McCoy and Allred [17]. In mixtures of $(CH_3)_2Cd$ and $(CH_3)_3Al$ in benzene at room temperature, methyl groups are exchanged (reaction (6), $M_1 = Cd$, $M_2 = Al$, $R = R' = R'' = CH_3$):

$$RM_1{-}R' + R_2M_2{-}R'' \rightleftarrows RM_1{-}R'' + RM_2{-}R' \quad . \qquad (6)$$

Important kinetic and thermodynamic data were obtained [20,24] for the case where $R = R' = R'' = CH_3$, $M_1 = Cd$, and $M_2 = In$ or Ga. In most cases the reaction is bimolecular, and $(CH_3)_2Cd$ exchanges with $(CH_3)_3In$ more slowly than with $(CH_3)_3Ga$. For $R = R' = R'' = CH_3$ and $M_1 = Cd$, $M_2 = Ga$ or $M_1 = Zn$, $M_2 = In$, [24] the rate of exchange decreases with increase in the coordinating power of the solvent.

4. Exchange in Derivatives of Group IVb Metals

M–C bonds, where M = Sn and Pb, are much more stable than the bonds formed by these metals with heteroatoms. Intermolecular C,C-exchange of organometallic groups in a series of organotin and organolead compounds has been detected by NMR only under catalytic conditions [63].

Under ordinary conditions, the NMR spectra of organotin and organolead compounds show $^*M{-}C{-}^1H$ ($^*M = {}^{119}Sn$ [64–67] and ^{207}Pb, [68,69]) $^*M{-}^{13}C$ (^{119}Sn, [70–72] ^{207}Pb [70,73,74]), $^*M{-}C{-}^{19}F$ (^{119}Sn, [65] ^{207}Pb [75]), etc. spin–spin coupling, indicating that the M–C bonds are stable on the NMR time scale.

One example of exchange accompanied by the rupture of an Sn–C bond is known, however: broadening of the signals of the $^{117/119}Sn$ satellites is observed [76] when $(CH_3)_3SnC{\equiv}CCF_3$ is dissolved in hexamethylphosphortriamide.

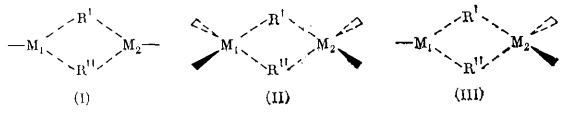
5. Mechanism of Intermolecular C,C-Exchange

The available data on exchange reactions accompanied by the rupture of metal–carbon bonds and subsequent intermolecular C,C-exchange of organometallic groups from one group to another can be summarised briefly as follows (Table 1).

1. All C,C-exchange reactions studied are bimolecular for derivatives of metals in groups IIb and III and for mixtures of group IIb and III derivatives [15,16,18,20,22,25,33]. The only exception is exchange in the $(CH_3)_3In + (CH_3)_6Al_2$ system, in which one of the reagents is a dimer [62].

2. C,C-exchange takes place in derivatives of metals of groups IIb (Cd) and III (In, Tl) and is practically unknown for metals of group IVb (Sn, Pb). For isostructural compounds in non-solvating solvents, the reaction rate is greatest for group III derivatives and lowest for derivatives of group IIb metals, and is intermediate in mixtures of compounds of metals of groups IIb and III. [20]

3. The rate of C,C-exchange is increased by solvating solvents of basic character in the case of group IIb metals (Cd) and decreased for group III metals (In, Tl) or mixtures containing a group III metal [18,21,24,20,27].



4. For organometallic derivatives of metals of groups IIb and III with identical groups but different metals, the rate of C,C-exchange decreases on going from compounds of metals of period V (Cd or In) to compounds of metals of period VI (Hg or Tl)[17,18,24,27,20]. For derivatives with identical metals but different groups, the rate of C,C-exchange increases on going to groups with more nucleophilic carbon atoms[27,22].

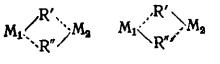
Table 1. Data on the intermolecular C,C-exchange of organometallic groups in a series of methyl derivatives of non-transition metals of periods V and VI: $(CH_3)_{n-1}M_1^*CH_3 + (CH_3)_{m-1}M_2CH_3 \rightleftharpoons (CH_3)_{n-1}M_1CH_3 + (CH_3)_{m-1}M_2^*CH_3$.

M_1	M_2	n	m	Solvent	E_a, kcal mole^{-1}	$\Delta H^{\neq}$, kcal mole^{-1}	$S^{\neq}$, e.u.	Refs.
Cd	Cd	2	2	—	15.7	—	−9.8	21
Cd	Cd	2	2	THF	6.8	—	−28.3	21
Cd	Cd	2	2	$(C_2H_5)_3N$	6.9	—	—	24
Cd	Cd	2	2	$(C_2H_5)_2O$	5.6	—	−38	24
Cd	Zn	2	2	cyclo-$C_6H_{11}CH_3$	17.0	16.4	−3	20
Cd	Ga	2	3	cyclo-C_5H_{10}	6.7	8.1	−17	20
Cd	Ga	2	3	CH_2Cl_2	7.3	6.7	−19	20
Cd	Ga	2	3	toluene	7.0	6.4	−23	20
Cd	In	2	3	CH_2Cl_2	8.4	7.8	−14	20
Zn	In	2	3	CH_2Cl_2	5	—	—	24
Zn	In	2	3	$(C_2H_5)_2O$	9.1	8.5	−14	24
Zn	In	2	3	$(C_2H_5)_3$	16.3	15.7	+2	24
In	Ga	3	3		5	—	—	62
Tl	Tl	3	3	CH_2Cl_2	6	—	—	27
Tl	Tl	3	3	toluene-α-d_3	6.3	—	—	27

The basic hypothesis regarding the mechanism of intermolecular C,C-exchange in the reactions being considered usually assumes that the transition state has a four-unit structure[17,18,20,22,24,27,35].

Evidence in support of this suggestion is provided by the bimolecular character of all reactions for which the concentration dependence has been studied, and also by the negative entropy of activation of most exchange reactions (Table 1)[20,24].

The ease of formation of a cyclic transition state with delocalised bonds should be influenced significantly by the coordinating power of the metal atom and in particular by its ability to form cyclic associates. This is due to the fact that the organic groups R′ and R″ and the non-transition metals M_1 and M_2, following Henold and coworkers[20], can be regarded as Lewis bases and acids. On the other hand, a cyclic transition state is a structure intermediate between real or hypothetical cyclic associates:



Exchange between them must involve the overcoming of an energy barrier, the height of which determines the ease of formation of a cyclic transition state with delocalised bonds. For hydrogen-bonded associates, increase in the energy of the hydrogen bonds is accompanied by a decrease in the height of the barrier, and the state of the system approaches a state with delocalised bonds[77,78]. An analogous phenomenon should be observed for organometallic associates with increase in the intensity of coordination interactions. Thus the stable dimer of trimethylaluminium corresponds structurally to a cyclic transition state with delocalised bonds for exchange between two trimethylaluminium molecules[79].

It may therefore be expected that the ease of formation of the transition states (I)–(III) and the rate of exchange reactions will increase with increase in the coordinating power of the metal atom and the donor power of the groups R, including the case where associates are not formed in the solution of the compound R_mM.[17,80] Thus for example the order of change in the rate of exchange:

$$Zn + Cd > Cd + Cd \gg Zn + Hg,\ Cd + Hg,\ Hg + Hg;$$
$$In + Zn > In + Cd;$$
$$Ga + In > Tl + Tl$$

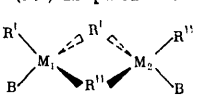
in methyl derivatives $(CH_3)_mM$ (m = 2 or 3) corresponds to the decrease in the acidity of the non-transition metals in isostructural compounds with increase in the period number[81,82] and also to the decrease in the ability of the structure to change from the normal configuration to that realised in the transition state[83]. The increase in the rate of exchange on going from methyl to vinyl compounds (M = Cd[22] or Tl[27]) is due to the greater ease of formation of transition states in the case of vinyl compounds due to the participation of the π-electrons of the vinyl group.

The available data on the influence of the medium on the rate of exchange reactions can also be explained if account is taken of the fact that in solvating media the compounds R_2M (M = Cd, Hg) and R_3M (M = In, Tl) are in the solvated state. The fundamental differences found in the analysis of C,C-exchange between compounds of the metals of groups IIb and III are evidently related to the following feature.

As a result of solvation (B is a unidentate solvent of basic character)

$$R_2M + 2B \rightleftarrows R_2M \cdot B + B \rightleftarrows R_2M \cdot 2B$$
$$R_3M + B \rightleftarrows R_3M \cdot B$$

derivatives of group IIb metals, which have two vacant orbitals, form solvates of two types, whereas compounds of group III metals with one vacant orbital form only one. The solvates $R_2M.2B$ and $R_2M.B$ with completely blocked vacant metal orbitals evidently cannot undergo exchange reactions because of the negligibly low acid strength of the metals†. At the same time the solvate $R_2M.B$[84] may be more reactive than R_2M, since solvation leads to an increase in the basic strength of the group R,[85] and in addition the vacant metal orbital required for the formation of the transition state (IV) is preserved:



(IV)

Thus in solvating media the rate of exchange is limited by the formation of the transition state (IV) in the case of R_2M, and by the decomposition of the solvated species $R_3M.B$ in the case of R_3M. This last feature also applies to exchange in mixtures of derivatives of the metals of groups IIb and III, where the rate decreases in solvating solvents[24].

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†An example is provided by the complex $(CH_3)_2Cd.[(C_2H_5)_2NCH_2CH_2N(C_2H_5)_2]$, in which both vacant orbitals of cadmium are blocked, and which, because of its stability, can be isolated in the crystalline state[81]. These features explain why the ^1H NMR spectrum of a solution of $(CH_3)_2Cd$ in tetramethylethylenediamine clearly shows satellites due to $^{117/119}Cd$–C–H spin–spin coupling, indicating slow exchange of the methyl groups[37].

III. INTERMOLECULAR EXCHANGE OF ORGANOMETALLIC GROUPS TAKING PLACE WITH METAL–HETEROATOM BOND RUPTURE

1. N,N-Exchange of Organometallic Groups

For most metals except mercury [10,87,88] and tin [89-94], there are comparatively few published data on the NMR spectra of compounds containing the fragment $R_nM-N<$ which might give an indication of the range of lability of these bonds in exchange reactions of the type

$$R_nM-NR'R'' + R_nM^*-N^*R'R' \rightleftarrows R_nM-N^*R'R'' + R_nM^*-NR'R'' \quad (7)$$

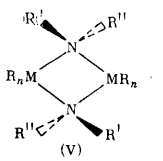
For mercury derivatives, there were until recently only fragmentary data on N,N-exchange of organomercury groups. Thus for $CH_3HgN(CF_3)_2$, $^{199}Hg-N-C-^{19}F$ spin–spin coupling was not detected, and this can be be attributed to exchange of methylmercury groups between different $N(CF_3)_2$ groups [87].

Exchange reactions have been studied [10] in organomercury derivatives of substituted N-methylbenzenesulphonamides. In these compounds there is relatively rapid N,N-exchange of arylmercury groups (7) (R_nM = ArHg, $NR'R'' = N(CH_3)SO_2Ar'$). The reaction rate increases considerably with increase in the concentration of the organomercury derivative and decreases slightly when the solvent chloroform or chlorobenzene is replaced by the solvating pyridine.

Electron-accepting substituents in the arylmercury group increase the rate of the N,N-exchange of the arylmercury groups, and electron-donating substituents decrease it:

$$4\text{-}(CH_3)_2NC_6H_4 < 2,4,6\text{-}(CH_3)_3C_6H_2 < 4\text{-}CH_3OC_6H_4 < C_6H_5 < 4\text{-}ClC_6H_4 < 3,4,5\text{-}Cl_3C_6H_2.$$

These results indicate [10] that in sufficiently inert media, the mechanism of the N,N-exchange of arylmercury groups (7) is associative in character and is accompanied by the formation of a cyclic transition state (structure (V), R_nM = ArHg, $R' = CH_3$, $R'' = SO_2Ar'$).


(V)

In the ^1H NMR spectra of various compounds of the type $R_2TlN(CH_3)_2$, the $N(CH_3)_2$ group corresponds to a triplet signal, indicating splitting of the methyl protons not on one but simultaneously on two equivalent thallium nuclei [95,96]. This proves that this compound is dimeric in solution (structure (V), $R_nM = R_2Tl$, $R' = CH_3$) and that the Tl–N bonds are stable on the ^1H NMR time scale.

The N,N-exchange of organometallic groups has been studied to a slightly greater extent in organotin derivatives. A study of the ^1H NMR spectra of 20% solutions of organotin derivatives of diethylamine $R_3SnN(C_2H_5)_2$ in CCl_4 at room temperature revealed spin–spin coupling of the $^{117/119}Sn$ nuclei with the CH_2 protons in the diethylamino-group, indicating that the Sn–N bond has a fairly long lifetime [89,90]. It was later found, however, that the ^1H NMR spectrum of $(CH_3)_3SnN(CH_3)_2$, studied in the absence of solvent, does not show $^{117/119}Sn-N-C-^1H$ spin-spin coupling either at room temperature or at −50° [91] (or even at −68° [92]). The most acceptable explanation of these results is that there is rapid exchange of the organotin groups between the dimethylamino-groups (reaction (7), $R_nM = (CH_3)_3Sn$, $NR'R'' = N(CH_3)_2$). $^{117/119}Sn-N-C-^1H$ spin–spin coupling was subsequently observed [93] in the ^1H NMR spectra of 20% solutions of $R_3SnN(CH_3)_2$ in benzene.

The temperature dependence of the form of the signals due to $^{117/119}Sn-N-C-^1H$ coupling has been studied [92]. Comparison of the temperatures at which the signals of the tin satellites merge for different compounds revealed the influence of the nature of the organic group, attached to the tin atom, on the rate of exchange:

$$(C_4H_9)_3SnN(CH_3)_2 < (C_2H_5)_3SnN(CH_3)_2 < (CH_3)_3SnN(CH_3)_2 .$$

In the compounds $(CH_3)_3SnN(CH_2)_n$ with heterocyclic $N(CH_2)_n$ groups, $^{119}Sn-N-^{13}C$ spin–spin coupling was observed [94] only for $n = 5$ or 6, but not for $n = 2-4$, indicating that the Sn–N bonds have a comparatively short lifetime.

In a discussion of the mechanism of exchange accompanied by the rupture of Sn–N bonds [94], it was suggested that this exchange is a bimolecular process, involving the formation of intermediates of type (V) ($R_nM = R_3Sn$). Evidence in support of this is provided, for example, by the dimeric structure of the compound $(CH_3)_3SnN(CH_2)_2$ in solution [94].

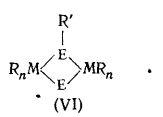
2. O,O-, S,S-, and O,S-Exchange of Organometallic Groups

Reactions of this type in the series of compounds being considered can be expressed as follows (E = O or S):

$$R_nM-ER' + R_nM^*-E^*R' \rightleftarrows R_nM-E^*R' + R_nM^*-ER' \quad (8)$$

They have been studied in most detail for organotin compounds [90,97-102] and less fully for derivatives of mercury [102-105], thallium [28,96,106-108], and lead [102,109,110].

Thus a study of solutions of the compounds C_6H_5HgOR' did not detect $^{199}Hg-O-C-^1H$ spin–spin coupling in any case [103], indicating that in CH_2Cl_2 at 33.5°, O,O-exchange of phenylmercury groups from one OR′ group to another is fairly rapid on the ^1H NMR time scale (reaction (8), $R_nM = C_6H_5Hg$, E = O). It was suggested that the reaction mechanism involves an associative scheme with the intermediate formation of dimers of type (VI), where E = O and $R_nM = C_6H_5Hg$.


(VI)

A ^1H NMR study of the phenylmercury derivative of toluene-ω-thiol [102] showed that the spectrum of solutions of this compound does not show $^{199}Hg-S-C-^1H$ spin–spin coupling at −40° (in chlorobenzene or pyridine) or even at −110° (in a $CH_2Cl_2 + CHCl_3$ mixture), indicating fairly rapid S,S-exchange of the phenylmercury groups (reaction (8), $R_nM = C_6H_5Hg$, $ER' = SCH_2C_6H_5$). Similar results were obtained in a study of the S,S-exchange of organomercury groups in mixtures of the compounds $t\text{-}C_4H_9HgSCH_3 + t\text{-}C_4H_9HgSCH(CH_3)C_6H_5$. [104] In this case the rate of the S,S-exchange of the organomercury groups in relatively inert media is so great that the rate of this bimolecular process can be decreased only at ~ −140°.

Data on the O,O- and S,S-exchange of organothallium groups R_2Tl have been published [28,96,106-108]. At room temperature the ^1H NMR spectra of many compounds of the type $(R_2TlX)_2$ (structure (VI), $R_nM = R_2Tl$), the signals due

to the spin–spin coupling of the protons of the R groups with ^{203}Tl and ^{205}Tl nuclei are broadened considerably and often are not resolved.

With decrease in the temperature of a solution of $[(CH_3)_2TlOC_2H_5]$ in $C_6D_5CD_3$,[108] the ^1H NMR spectrum shows broadening of the signals of the CH_3Tl groups. With further cooling of the solution below −10°, however, the signals of the methyl protons again become narrow and at −60° acquire the same form and width as at room temperature. A characteristic feature is that the $^{203/205}Tl-C-^1H$ spin–spin coupling constant is the same at +39° and at −60°. In the discussion of this phenomenon, the authors of Refs. 96 and 103 examined several possible associative exchange mechanisms, which reduce to the same form of exchange between the dimeric and monomeric state of the derivative being analysed.

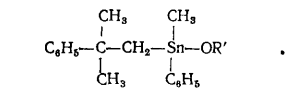
For the compounds R_3MER' (M = Pb, Sn; E = O, S) the exchange reactions with the rupture of M–O bonds have been least studied for the lead derivatives. Thus the ^1H NMR spectra of solutions of R_3PbOR' in CCl_4[109] do not show $^{207}Pb-O-C-^1H$ spin–spin coupling. Similar results were obtained in Ref. 110. Davies and Puddephat[109] suggested that this phenomenon is related to rapid exchange of organometallic groups from one OR′ group to another.

A study of the ^1H NMR spectra of organotin alkoxides of the type R_3SnOR' in CCl_4 at room temperature[90] did not detect $^{117/119}Sn-O-C-^1H$ spin–spin coupling. It was suggested that this result is due not to exchange but to the ionic character of the Sn–O bonds. Subsequent temperature studies of the ^1H NMR spectra of a number of organotin compounds containing an Sn–O bond[99–101] made it possible to observe this spin–spin coupling and hence to establish that the absence of $^{117/119}Sn$ satellites from the NMR spectra of R_3SnOR' derivatives in a number of cases is due not to the ionic character of the Sn–O bond but to the rapid exchange of the organotin groups from one oxygen atom to another (reaction (8), $R_nM = R_3Sn$, E = O). The rate of exchange increases in the order[99]:

$$CH_2C(CH_3)_3,\ CH(C_6H_5)_2,\ CH(CH_3)_2 < CH_2C_6H_5 < C_2H_5 < CH_3.$$

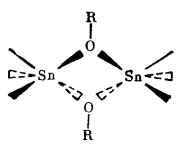
It was suggested that the exchange involves a bridged dimer (VI) ($R_nM = R_3Sn$, E = O).

The influence of a number of factors on the mechanism of exchange accompanied by the rupture of Sn–O bonds has been studied[100]. A study was made of the exchange reactions in compounds (VII); in solutions of these compounds in benzene, exchange of OR′ groups may be accompanied by inversion of the configuration of the tin atom[101].



R=CH₃, i-C₃H₇, t-C₄H₉, C₆H₅ (VII)

The rate of exchange of OR′ groups is not equal to the rate of inversion, that is not every exchange act is accompanied by inversion of the configuration of the metal atom. The nature of the group R′ has a greater influence on the rate of exchange than on the rate of inversion. A probable transition state for both processes may be the dimeric cyclic intermediate (VIII), the formation and decomposition of which take place with preservation of the configuration of the metal atom.

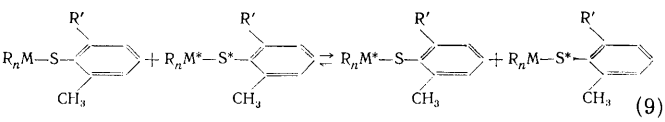


(VIII)

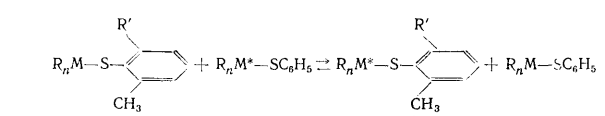
A study of the ^1H NMR spectra of the compound $(CH_3)_3SnSCH_3$ in chloroform[111] showed that the signals due to $^{117}Sn-S-C-^1H$ and $^{119}Sn-S-C-^1H$ spin–spin coupling are not resolved. Abel and Brady[112], in a study of this compound in a 30% solution in CCl_4, on the contrary, observed these signals separately; when even very small quantities of impurity (such as, for example, acids and thiols) are present in the solutions, however, the ^{117}Sn and ^{119}Sn satellites are not resolved; this is due to the catalysis of reaction (8) ($R_nM = (CH_3)_3Sn$, E = S, R′ = CH_3) by the impurities.

A number of subsequent papers give data on the values of $^3J(^{119}Sn-S-C-^1H)$[113] and $^2J(^{119}Sn-S-^{13}C)$[94] in R_3SnSR' compounds; the very fact that these data were obtained indicates that the Sn–N bonds in them have a fairly long lifetime. In particular, the study of the ^1H NMR spectra of the individual compounds $R_nMSCH_2C_6H_5$ or their mixtures in chlorobenzene and pyridine at different temperatures ($R_nM = (C_6H_5)_3Pb$ or $(C_6H_5)_3Sn$) did not detect any signs of exchange reactions of type (8).[102] Available data on the lability of the bonds M–O and M–S are too fragmentary to permit a comparison of the mobility of univalent organometallic groups with different metals for a fixed element E or to estimate the influence of the nature of the element E on the mobility of the organometallic groups of each type. A systematic examination of this problem was begun only recently[10,102,114–117].

Thus the dependence of the lability of the M–S bonds in thiophenol derivatives on the nature of the organometallic group has been studied[102,114,115] for the reactions



(9)



R′ = H or CH_3; $R_nM \neq R_nM^*R_nM$ and $R_nM^* = C_6H_5Hg$, $(C_6H_5)_3Pb$, $(C_6H_5)_3Sn$, $(C_6H_5)_2Sb$, $(C_6H_5)_4Sb$. (10)

The data[102,114,115] on the S,S-exchange of organometallic groups in these mixtures established the following regular features: a) the rate of the S,S-exchange increases when chlorobenzene is replaced by pyridine; b) the increase in the steric hindrance when a proton as R′ is replaced by a methyl group is accompanied by a decrease in the rate of exchange; c) the ability of organometallic groups to undergo intermolecular exchange in chlorobenzene increases in the order:

$$(C_6H_5)_3Sn < (C_6H_5)_2Sb \sim (C_6H_5)_3Pb < C_6H_5Hg < (C_6H_5)_4Sb .$$

These regular features are for the most part preserved[117] for O,O-exchange of organometallic groups in substituted phenols:

$$R_nM-OAr + R_nM^*-O^*Ar \rightleftarrows R_nM-O^*Ar + R_nM^*-OAr$$
$$R_nM \neq R_nM';\ R_nM \text{ and } R_nM^* = C_6H_5Hg,\ (C_6H_5)_3Pb,\ (C_6H_5)_3Sn,\ (C_2H_5)_3Sn . \quad (11)$$

As in the case of thiophenols, the C_6H_5Hg group has the highest mobility, and the $(C_6H_5)_3Sn$ group the lowest mobility in the exchange reaction (11). The rate of the process increases both with increase in the electron-acceptor

properties of the group Ar and when chloroform as solvent is replaced by pyridine. Steric hindrance, and also the presence, in the ortho-positions, of substances capable of intramolecular coordination interaction with the metal, on the other hand, decrease the rate of the O,O-exchange.

Data obtained by Kravtsov and coworkers [102] were interpreted on the basis of an associative exchange mechanism with the intermediate formation of cyclic four-unit transition states with delocalised bonds:



3. Exchange of Organometallic Groups Between Halogen Atoms

In the study of dynamic processes accompanied by the rupture of metal–halogen bonds, it is only in the case of Hal = F that it is possible to use NMR, which can be used successfully for derivatives of the type M–ER where E = O or S, and M–NR′R″, where E = N or P (analysis of the form of the signals corresponding to the spin–spin coupling *M–*E, *M–E–C–^{1}H, *M–E–^{13}C, *M–E–^{1}H, etc.). Thus in a study of the ^{1}H NMR of the compounds R_3SnF (R = CH_3, C_2H_5) in methanol solution [108], ^{1}H–C–Sn–^{19}F spin–spin coupling was not reported, although its value in $[C_6H_5CH(CH_3)_2CH]_3SnF$, measured later [119], was fairly high (~ 5 Hz). The absence of splitting can be attributed to F,F-exchange of organotin groups:

$$R_nM{-}X + R_nM^*{-}Y \rightleftarrows R_nM^*{-}X - R_nM{-}Y$$

$$R_nM = [C_6H_5CH(CH_3)_2CH_2]_3Sn,\ X = Y = F \quad , \qquad (12)$$

In this connection, in the study of halogen exchange in series of organometallic compounds, extensive use is made of the examination of the non-degenerate exchange of organometallic groups in mixtures of compounds with different halogen atoms (reaction (12), X ≠ Y = Hal, R_nM = RHg [42,43,120–122] or R_3Sn [123–128]). Another method makes it possible to study degenerate exchange in the case where the compound being studied contains a chiral (or prochiral) atom, inversion at which, detected by NMR, can in principle be related to reaction (12) (X = Y = Hal, R_nM = R_3Sn, etc. [125,129–134]).

In the ^{1}H NMR spectra of solutions of individual compounds of the type RHgI and RHgBr (R = CH_3,[42,43] $C_6H_5CH_2$,[43] $H_2C{=}CH$,[120] etc.), the satellites due to ^{199}Hg–C–^{1}H spin–spin coupling are either broadened or completely absent [42,43,120]. To explain this phenomenon it was first suggested [42,43,120] that in solutions of these compounds, fast exchange with rupture of C–Hg bonds takes place. Subsequent studies showed, however, that there is insufficient evidence for these suggestions. In particular, it has been found [53] that the C–Hg bond in alkyl derivatives of mercury is fairly stable and that exchange accompanied by its rupture cannot take place in fractions of a second.

The study of compounds RHgI [32,121,135] shows that the broadening in the NMR spectra of mercury satellites is due not to exchange but to relaxation effects‡. Thus in later studies [121,122] of exchange in organomercury layers, the results were interpreted in terms of halogen exchange.

Thus Hatton and coworkers [42], in a study of the ^{1}H NMR spectra of an equimolar mixture of methylmercury halides (X = Cl, Y = I) in pyridine at room temperature observed an averaged picture. Similar results were obtained in a study of the NMR spectra of ternary mixtures (RHgCl + RHgBr + RHgI; R = CH_3 or $C_6H_5CH_2$).[43] In mixtures of type (12) for R_nM = CH_3Hg, X = Cl or Br, and Y = I in DMF, exchange is rapid even at −71°.[122]

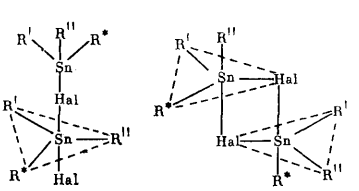
The reactivity of organotin compounds R_3SnX in halogen exchange reactions has been studied fairly frequently in recent years. In discussion relating to the interpretation of NMR data on halogen exchange in a series of organotin derivatives, many aspects of the problem became evident—the complexity of this reaction, and also a number of characteristic features of the compounds R_3SnX, which distinguish them from other derivatives R_nMX. Up to the present, however, there is still lack of agreement regarding the mechanism of this process.

A number of studies of the degenerate exchange of organotin groups between halogen atoms have been carried out for compounds of the type R′R″R*SnHal, in which the tin atom is chiral (R′ ≠ R″ ≠ R*) and the carbon group R* has a prochiral centre containing groups suitable for NMR study [$(CH_3)_2CH$, $C_6H_5(CH_3)_3CCH_2$, $C_6H_5CH_2$, $(CH_3)_2CHCH_2$, etc.] [129–131,192]. For these compounds in solution there is ready rapid inversion of the geometric configuration of the tin atom. There may be several reasons for this inversion: intermolecular exchange of organotin groups between halogen atoms is the most probable, but not the only explanation (reaction (12), R_nM = R′R″R*Sn, X = Y = Hal).

The conclusion that the observed phenomenon is of intermolecular origin is confirmed by the fact that in all cases, increase in concentration is accompanied by an increase in the rate of the process. The exchange involves the tin–halogen bond, since when the halogen atom in R′R″R*SnHal is replaced by a carbon group the dynamics are no longer recorded by NMR [130,131,137–139].

Direct proof has been obtained [131] for the relationship between the inversion of the tin atom and the exchange of the halogen atom in the compounds R′R″R*SnHal. The NMR study of the compounds (Hal = Cl and I, R* = C_6H_5·$(CH_3)_2CCH_2$, R′ = CH_3 and R″ = $C_6H_5CH_2$) showed that the rates of intermolecular exchange are exactly equal to the rates of inversion at the tin atom, and these two processes possibly take place by the same mechanism.

In a more detailed discussion of the associative mechanism of the exchange of halogens in the compound R′R″R*SnHal, accompanied by racemisation of the asymmetric tin atom, two versions were considered [131], with one or two bridging halogen atoms:



which agree with the bimolecular character of the process.

The non-degenerate exchange of anionic residues in the compounds R_3SnX (reaction (12), X ≠ Y, R_nM = R_3Sn) including the case where at least one of the substituents X or Y is a halogen atom, has been studied by NMR chiefly for systems with R = CH_3. [123–128,140] A NMR study of mixtures of these compounds (Y = Cl, Br, I) [123] showed that the rate of reaction (12) for the organotin halides

‡ The broadening of the mercury satellites in CH_3HgSCN has been shown [136] to be due to the presence of traces of CH_3HgI, used [42] to prepare methylmercury thiocyanate. The ^{1}H NMR spectrum of the compound CH_3HgSCN, obtained from methylmercury chloride, did not contain any sign of broadening of the mercury satellites [136].

changes in the order:

$$Cl + I < Br + I < Cl + Br \ .$$

Subsequently, several groups of workers made more detailed studies of the exchange reaction (12) in trimethyltin derivatives [124-126]. Thus Redl and Winokur [124], in a study of this reaction in cyclohexane (X = Cl, Y = I) found that with increase in temperature from 33° to 95°, the apparent rate constant of the reaction does not increase, but decreases§. Moreover, the order of the reaction with respect to each of the components is different, is not integral, and changes considerably with change in temperature. These results [124] indicate that in mixtures of organotin compounds, the kinetics of reaction (12) are complex. The authors cited believe that different types of associative equilibria, preceding the actual exchange, may be established in the solution:

$$2\,(CH_3)_3SnBr \overset{K}{\rightleftarrows} [(CH_3)_3SnBr]_2$$
$$(CH_3)_3Sn^*I + [(CH_3)_3SnBr]_2 \rightleftarrows (CH_3)_3Sn^*Br + (CH_3)_3SnBr + (CH_3)_3SnI \ . \quad (13)$$

The rate of exchange is given by the expression:

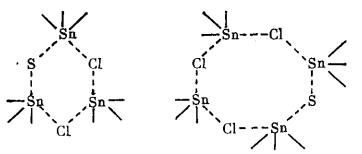
$$v = k_{app}[(CH_3)_3SnI]\,[(CH_3)_3SnBr]^2 = kK\,[(CH_3)_3SnI] \cdot [(CH_3)_3SnBr]^2 \quad (14)$$

Since the experimentally determined order of the reaction with respect to $(CH_3)_2SnBr$ is 2.6, it is possible that the exchange act is preceded by the formation of not only dimers but also associates with a larger number of units. Increase in temperature on the one hand should increase the rate of exchange by increasing k, but on the other hand will lead to a decrease in the concentration of associates (decrease in K in Eqn. [14]). If the absolute magnitude of the last effect is greater than that of the first, the overall rate of the reaction should decrease with increase in temperature.

Later, a ^1H NMR study for $R_nM = (CH_3)_3Sn$, X = Cl, and Y = I in toluene [125] showed that the overall order of reaction (12) at 27° is approximately three, again indicating a possible associative mechanism, although the rate of this reaction in the range from −70° to 30° does not decrease with increase in temperature, as shown in Ref. 124, but increases. At higher temperatures, however, the ^1H NMR spectrum did not show temperature reproducibility. The rate of exchange increases considerably on going from toluene to pyridine, whereas when Y = I is replaced by $Y = SC_6H_5$ or $C{\equiv}CC_6H_5$, the rate of exchange decreases. Reaction (12) was subsequently studied for the case where one of the anionic groups contains a sulphur atom ($Y = SCH_3$ [127] and SC_6H_5 [140,141]).

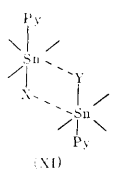
When X = Cl and $Y = SCH_3$, [127] the exchange reaction (12) in methylene chloride is rapid not only on the ^1H NMR time scale but also on the ^{119}Sn NMR time scale, and with decrease in the temperature of the solution there is only a slight broadening of the ^1H NMR signal. Unfortunately, the concentrations of the compounds studied were not reported [127], so that the results cannot be compared with earlier [123] and later (X = Cl, $Y = SC_6H_5$) [140,141] data.

A study of the regular features of the exchange reaction (12) for $R_nM = (CH_3)_3Sn$, X = Cl, and $Y = SC_6H_5$ [141] gave additional information on the mechanism of exchange reactions involving organotin halides. When the reaction was carried out in toluene, the "inverse" temperature dependence of the rate of exchange was observed, and the activation energy had a negative value (−2.3 kcal mole^{-1}). The calculated orders of the reaction (2.8 with respect to $(CH_3)_3SnCl$ and 1.0 with respect to $(CH_3)_3SnSC_6H_5$) do not depend significantly on temperature; the entropy of activation of the process has a high negative value (−62.0 kcal mole^{-1} K^{-1}). These results indicated that in relatively inert media the reaction takes place by an associative mechanism with the intermediate formation of cyclic transition states:



(IX) (X)

Since the decisive factor determining the characteristic features of the associative mechanism of exchange is the ability of the compounds R_3SnX to undergo association in inert media, a cardinal change might be expected when the reaction is studied in solvating solvents. In this case the elementary act of the reaction may involve solvated organotin molecules:



(XI)

These considerations explain the sharp increase in the rate of the exchange reaction (12) ($R_nM = (CH_3)_3Sn$, X = Cl, and Y = I) in pyridine [125], for which the transition state (XX) was proposed.

The mechanism of the exchange (12) may be even more complex in solvents of medium solvating power. In this case the equilibrium $R_3SnX + B \rightleftharpoons R_3SnX.B$ may not be displaced very far to the right, and the elementary act may involve both solvated and non-solvated molecules. This apparently explains the two-stage character of the changes observed on going from toluene to tetrahydrofuran for the exchange reaction (12) with X = Cl and $Y = SC_6H_5$ ($R_nM = (CH_3)_3Sn$); in THF the rate of the reaction decreases below −30° and increases at higher temperatures [140].

The associative mechanism has been assumed to be the most probable mechanism of the exchange reaction (12) for organotin compounds [124,125]. Two recent papers [126,128] dealing with exchange reactions (12) ($R_nM = (CH_3)_3Sn$; X, Y = Hal, X ≠ Y) explain the results by assuming a dissociative mechanism, including preliminary dissociation of the organotin halide and subsequent attack by the halide anion on an undissociated molecule:

$$(CH_3)_3SnX \rightleftarrows (CH_3)_3Sn^+ + X^-$$
$$(CH_3)_3SnY + X^- \rightleftarrows (CH_3)_3SnX + Y^- \ . \quad (15)$$

Reaction (12) has been studied in toluene [126]. Unfortunately, a detailed kinetic analysis was not carried out, and the conclusion that mechanism (15) is preferred is based only on the fact that when small quantities (~ 2×10^{-4} M) of molecular iodine are added to the solutions being studied a decrease in the rate of exchange is observed, and the pseudo-first-order rate constant is linearly dependent on $[I_2]^{-1/2}$. It is assumed [126] that molecular iodine binds the halide ions formed on dissociation (15), thus decreasing

§As already noted, a similar phenomenon was observed [108] in a study of exchange reactions in the compounds $(R_2TlOR')_2$.

their effective concentration in the solution and hence lowering the rate of the exchange reaction (the greater inhibiting action of I_2 on the exchanging systems containing $(CH_3)_3SnI$, in the authors' opinion [126], agrees with the increase in the stability constants of the ionic complexes $[I_2X]^-$ in the order $I_3^- > I_2Br^- > I_2Cl^-$).

Ladd and Glasberg [128], who studied reaction (12) in chloroform and methylene chloride, favour the ionic mechanism on the basis of the fact that with increase in the polarity of the medium there is an increase in the pseudo-first-order rate constant. In their opinion, within the framework of the associative mechanism of exchange, change in the polarity of the medium should not have such a marked influence. Various thermodynamic characteristics of this reaction have also been determined [128]. In particular, it has been shown that the exchange has a large negative entropy of activation and fairly low activation energies. Moreover, the quantity τ_A^{-1} is linearly dependent on the square of the concentration of the components of the reaction. This last fact was interpreted as indicating that the exchange is of second order not only in the cases which they studied but also for system (12) for X = Cl and Y = I; the overall order of this reaction was found to be three [125].

It may be suggested, however, that the discrepancy in the conclusions in Refs. 124, 125 and Refs. 126, 128 is due to misunderstanding and is related to the fact that the authors of Refs. 126 and 128 used pseudo-first-order rate constants in the kinetic calculations. Simple analysis¶ shows that detection of a linear relationship between τ_A^{-1} and $[A]^2$ by NMR spectroscopy unavoidably leads to the conclusion that the reaction being studied is of third order, as confirmed experimentally [125].

Proceeding to the discussion of the observations [136,138] used as arguments in support of the ionic mechanism of the exchange reactions (12), it should be noted that these observations also agree with an associative mechanism for these reactions. Thus for example the reason for the inhibiting action of small quantities of molecular iodine may be that the I_2 molecules, by coordinating to the organotin halides, prevent the formation of associates of type (IX) and (X). As far as the influence of large quantities of molecular iodine are concerned, they will act as ordinary basic additives.

The observed [128] effect of increase in the exchange rate in the study of the reaction in more polar media, within the framework of the associative mechanism, can be attributed to an increase in the polarity of the Sn–X bond. In this case there is an increase in the electrophilic character of the metal atom and the nucleophilic character of the anionic residue and hence an increase in the ability of the molecules of the organometallic halide to form associates (IX) and (X). Thus the apparent rate of exchange should increase in polar media. It should be emphasised that the suggested [126] ionisation of organotin halides is unlikely in inert media. Finally, the ionic mechanism does not explain either the high and non-integral orders observed in a number of cases for the reaction being considered or the inverse temperature dependence of the apparent reaction rate [124,141].

Thus the available facts indicate that an associative mechanism is more probable for reaction (12) for organotin compounds. It is clear, however, that more rigorous confirmation of this suggestion requires additional studies, in particular for the case where the anionic residues X and Y are halogens.

IV. C,E-EXCHANGE OF ORGANOMETALLIC GROUPS

A number of papers describe the study of the exchange of organometallic groups between anionic residues, including both carbon (R) and heteroatom groups [19,37,143,144]:

$$R_nM^*-R' + R_nM-X \rightleftarrows R_nM^*-X + R_nM-R' \quad (16)$$

Thus the ^1H NMR spectrum of an equimolar mixture of diphenylmercury and phenylmercury bromide (R = R′ = C_6H_5, M = Hg, X = Br) in dimethyl sulphoxide [143] even at 34° shows broadening of the signals of the *ortho*- and *meta*-protons corresponding to both compounds, and also of the signals due to vicinal $^{199}Hg-C-C-^1H$ spin–spin coupling. Since this effect is not observed in the study of either of these compounds individually, it was concluded that it is due to fairly intensive C,Br-exchange of phenylmercury groups in the solution.

In a number of organocadmium compounds, reactions of type (16) can be assumed on the basis of familiar results of the study of two types of compound—aryl and methyl. In particular, data on reaction (16) were obtained [144] by ^{19}F NMR for perfluoroaryl derivatives of Cd (R = R′ = C_6F_5, X = I). The study of this reaction in various solvating solvents (DMSO, DMF, etc.) showed that its rate depends on the nature of the medium.

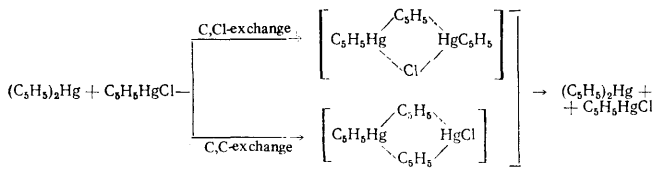
In connection with the discovery that the rate of exchange of methyl groups in dimethylcadmium is increased catalytic quantities of CH_3CdOCH_3 and in general CH_3CdOR'',[19] reaction (16) for R = R′ = CH_3 and X = OR″ was studied by ^1H NMR [19,37]. It was found, however, that the mechanism is extremely complex and that the tetrameric molecules CH_3CdOR'' [145] exert practically no catalytic influence†. It was suggested [19,37] that this exchange process is catalysed not by tetrameric CH_3CdOR'' molecules but by small quantities of dimeric or monomeric molecules. The rate of the process in the presence of added CH_3CdOR'' increases in the order [37]: C_6H_5O, $C_2H_5O > CH_3O >$ iso-C_3H_7O.

The problem of the dual character of the possible reaction mechanism also arises in the analysis of the NMR spectroscopic data obtained [35] for cyclopentadienyl derivatives of mercury. The data [35] indicated that in a mixture of the compounds $(C_5H_5)_2Hg$ and C_5H_5HgCl there is intensive intermolecular exchange. In view of the familiar lability

¶ The rate of an exchange reaction involving both molecules of reagent A and molecules of reagent B is given by the equation: $d[A]/dt = k[A]^n[B]^m$. The lifetime of the exchanging particle in position A (τ_A) in turn is related to the reaction rate by the expression [142]: $d[A]/dt = \tau_A^{-1}[A]$. Thus $\tau_A^{-1} = k[A]^{n-1}[B]^m$. Similarly, for τ_B: $\tau_B^{-1} = k[A]^n[B]^{m-1}$. Thus the experimental determination of the values of τ_A and τ_B for different values of [A] and [B] makes it possible to find the values of m and n. For the case where [A] = [B], it is possible to determine only the overall order of the reaction $m + n$: $\tau_A^{-1} = k[A]^{m+n-1}$.

† Evidence in support of this is provided, in particular, by the detection, in the ^1H NMR spectrum of a $(CH_3)_2Cd + CH_3CdOCH_3$ mixture, of satellites of the signal of the OCH_3 group, due to $^{111/113}Cd-O-C-^1H$ vicinal spin–spin coupling [37].

of the C_5H_5Hg bond, however, there are at least two fundamentally different processes which satisfactorily explain the observed results:



In the system studied, C,Cl-exchange evidently takes place. The specific features of C_5H_5–Hg σ-bonds suggest, however, that the corresponding C,C-exchange takes place simultaneously in the system [35].

For R = CN, the exchange in mixtures (16) is of the C,E-type only from formal indications. However, since in the organic derivatives of the transition metals being considered the R_nM–CN bond is appreciably covalent, it is also appropriate to examine C,E-exchange for R = CN in this section also.

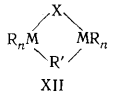
The C,E-exchange of the groups $R_nM = CH_3Hg$ [see Eqn. (16)] has been studied [104,122] for R′ = CN and X = Hal or SR″. In the case where X = Hal, the systems studied can be arranged in the following order of increasing rate of exchange with change in the halogen atom: I < Cl < Br. A study of the concentration dependence of the rate of this exchange for X = Cl [122] or SR″ [116,104] in DMF showed that the reaction is bimolecular and of first order with respect to each of the components. The reaction rate also increases sharply when DMF as solvent is replaced by pyridine [122].

Reaction (16) for $R_nM = CH_3Hg$ was also studied in aqueous solutions for R′ = CN and anionic residues X with different properties [121]. Kinetic NMR measurements showed that for X = OH (at pH > 9), Cl, SO_3^{2-}, and $S_2O_3^{2-}$, a mechanism of anion attack is possible

$$CH_3HgCN + X^{\ominus} \rightleftarrows CH_3HgX + CN^- \qquad (17)$$

whereas for exchange in the systems with X = OH (at pH < 9) and CH_3COO^-, the direct exchange reaction (16) apparently takes place.

From the data obtained, two fundamentally different routes for the exchange reaction (16) for $R_nM = CH_3Hg$ were examined [104]. The first assumes the formation of a cyclic transition state (XII) ($R_nM = CH_3Hg$, R′ = CN):



XII

whereas the second assumes that the reaction involves pre-exchange equilibria, in which ions or ion pairs separated by solvent are formed. The question of the mechanism was examined in a quantitative study [104] of exchange in system (16) ($R_nM = CH_3Hg$, R′ = CN) in DMF for a wide range of substituents X. The observed order of change in the rate of exchange:

$$Cl < OCOOH_3 < Br < SCN < SCH_3 < SC_6H_5 < SC_6H_4Cl\text{-}p < SC(CH_3)_3$$

does not coincide with the familiar order of increase in the ionic character of the bonds Hg–X (RS < CN < Br < SCN < Cl < $OCOCH_3$). Moreover, it was found that the rate constants of the exchange reactions, calculated from the ionisation constants of the compounds RHgX, are appreciably smaller than the experimental values, particularly for the case of compounds in which the Hg–S bond is highly covalent.

Thus the most probable mechanism of exchange in the compounds CH_3HgX in aprotic solvents is an associative mechanism, accompanied by the intermediate formation of cyclic transition states (XII). When both X and R′ in (XII) are substituents containing unshared pairs of electrons (Hal, SCN, SR″), the rate of exchange is too high to be observed on the NMR time scale. The replacement of one anionic group R′ by the SCN group, which is sufficiently polar but which has less tendency to coordinate to the metal atom, is accompanied by a decrease in the reaction rate constant by at least four orders of magnitude, so that the study of exchange in these systems becomes possible on the ^1H NMR time scale. When the second anionic group is replaced by the SCN group, however, the exchange reaction becomes slow on the same scale.

V. EXCHANGE BETWEEN ORGANOMETALLIC GROUPS AND A PROTON, TAKING PLACE WITH RUPTURE OF A CATIONIC PARTICLE–HETEROATOM BOND (E,E-EXCHANGE WITHIN THE FRAMEWORK OF EXCHANGE OF THE METAL–PROTON TYPE)

Among the different types of intermolecular dynamics, the least extensively studied is non-degenerate E,E-exchange, in which there is equilibrium exchange of a proton and an organometallic group:

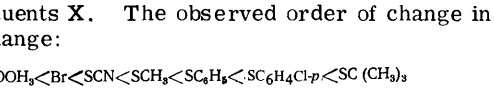
$$R_nM{-}ER'_m + H{-}E^*R'_m \rightleftarrows R_nM{-}E^*R'_m + H{-}ER'_m \ . \qquad (18)$$

Dynamics of this kind were apparently first observed by Alcock and Timms [146], when the existence of reaction (18), rapid on the PMR time scale, was assumed on the basis of an NMR study of mixtures of acetic acid and organotin or organolead acetates. It was also pointed out [146] that the replacement of phenyl groups in $R_nM = R_3Sn$ by cyclohexyl and isopropyl groups is accompanied by a decrease in the rate of exchange.

Analysis of published data shows few examples of the observation of reaction (18) by NMR. For example, the ^1H NMR spectrum of a $CH_3CdOCH_3 + HOCH_3$ mixture did not show two separate OCH_3 group signals corresponding to the individual compounds, and this result was interpreted as indicating that there is intermolecular exchange of the OCH_3 groups [37].

It should be noted that special NMR study of exchange processes of the metal–proton type in mixtures of EH-acids and their organometallic derivatives began relatively recently, and these reactions have been studied chiefly in a comparison with proton–proton reactions in EH-acids and metal–metal reactions in their organometallic derivatives.

In particular, a comparison of this kind, which made it possible to estimate the relative mobility of the hydrogen atom and organometallic groups for the case where E = N and M = Hg was carried out [10] for the case of N-methylbenzenesulphonamides and their N-phenylmercury derivatives:



(19)

a) $M_1 = M_2 = H$, proton–proton exchange;
b) $M_1 = M_2 = C_6H_5Hg$, metal–metal exchange;
c) $M_1 = H$, $M_2 = C_6H_5Hg$, metal–proton exchange.

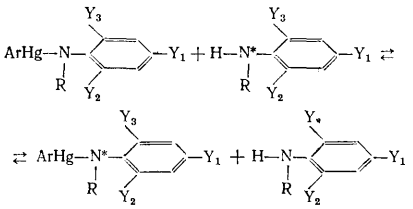
Analysis of the results showed that in a mixture of pyridine solutions of these NH-acids and their N-phenylmercury derivatives, the degenerate exchange (19a) and (19b) characteristic of the individual compounds is accompanied by another type of exchange involving the mutual

exchange of hydrogen atoms and phenylmercury groups between the same sulphonamide residues (reaction 19c). The rate of this exchange is extremely sensitive to the nature of the substituent in the benzenesulphonamide group; the rate of exchange (19c) increases in the order:

$$o\text{-Cl} < p\text{-}C_6H_5 < p\text{-}NH_2 < p\text{-}NO_2 < p\text{-Cl}\ .$$

For the system with Y = *p*-Cl it was found that this exchange is slightly slower in nitromethane than in pyridine, and much slower in chloroform than in pyridine and nitromethane. It was established[10] that under certain conditions the HgC_6H_5 group is more mobile in intermolecular exchange than the hydrogen atom.

A quantitative study of metal–proton exchange accompanied by the exchange of an arylmercury group by a hydrogen atom was carried out[116] for benzenesulphonanilides and their N-arylmercury derivatives in a pyridine–chlorobenzene (2 : 3) mixture:



(20)

R = $C_6H_5SO_2$;

a) $Y_2 = CH_3$; Ar = C_6H_5; Y_3 = H; Y_1 = H, Br, NO_2, $N(CH_3)_2$;

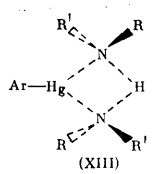
b) $Y_2 = Y_3 = CH_3$; Ar = C_6H_5; Y_1 = Br;

c) $Y_3 = CH_3$; Ar = C_6H_5; $Y_1 = Y_2$ = Br;

d) $Y_2 = CH_3$; Y_3 = H; Y_1 = Br; Ar = *p*-XC_6H_4, X = OCH_3 Cl, $N(CH_3)_2$.

The results show that the rate of reaction (20a) is increased by electron-acceptor substituents in the aryl group Y_1 on the nitrogen atom and is decreased by electron-donor substituents. At the same time, both electron-acceptor and electron-donor substituents in the arylmercury group increase the rate of this exchange process. It was shown for system (20b)[116] that reaction (20) is of first order with respect to each reagent, and its activation energy is 11.3 ± 1.3 kcal mole^{-1}. It was also demonstrated that steric hindrance, which increases on going from reaction (20a) to reaction (20b), and to a greater extent intramolecular coordination [possible on going from reaction (20b) to reaction (20c)], increase the rate of metal–metal exchange.

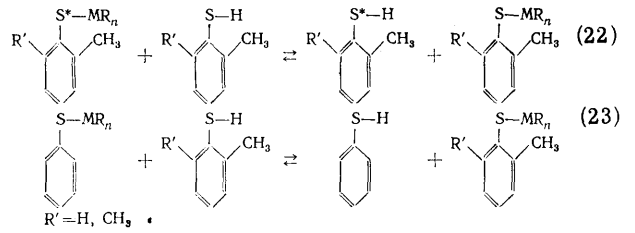
All the results indicated that the exchange reaction (19) is bimolecular and involves the intermediate formation of the cyclic transition state (**XIII**):



(XIII)

In a study of exchange between organometallic groups and a proton, accompanied by the rupture and redistribution of the bonds M–S and H–S, toluene-ω-thiol[102] or substituted thiophenols and the corresponding organometallic derivatives[102,114,115] were used as model systems:

$$C_6H_5CH_2S^*MR_n + C_6H_5CH_2SH \rightleftarrows C_6H_5CH_2S^*H + C_6H_5CH_2SMR_n \qquad (21)$$



(22)

(23)

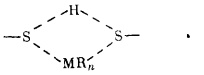
R′ = H, CH_3.

It was found that exchange (21) is slow on the NMR time scale. This feature, and also the fact that the degenerate exchange of PhHg groups in solutions of $C_6H_5CH_2SHgPh$ in chlorobenzene (8) is rapid, indicate that, as in the case of compounds containing N–H and N–Hg bonds, the PhHg group has a greater ability to undergo intermolecular exchange than the hydrogen atom.

The PMR spectra of the mixtures (22) in chlorobenzene showed[114] that metal–proton exchange is rapid only for $R_nM = SbPh_4$. In all other systems, reaction (22) is slow on the classical NMR time scale even at high temperatures. The PMR spectra of the mixtures (23) in chlorobenzene showed that the organometallic groups and the proton can be arranged in the following order of increasing ability of these cationic groups to undergo intermolecular exchange:

$$Ph_3Sn < H < Ph_3Pb \approx Ph_2Sb < PhHg < Ph_4Sb.$$

The concentration dependence of the rate of reaction (23) ($R_nM = SnPh_3$, R′ = H) showed that it is of first order with respect to each component. In addition, the steric hindrance arising on going from 2-methylthiophenol and its derivatives to 2,6-dimethylthiophenol and its derivatives decreases the rate of exchange. A study of the effect on the rate of reaction (23) of various factors which influence radical reactions (ultraviolet radiation, atmospheric oxygen, the addition of phenothiazine as inhibitor) showed fairly conclusively that this reaction does not take place by a radical mechanism. It was suggested that metal–proton exchange takes place by an associative mechanism including the formation of a cyclic transition state with delocalised bonds.



The change from solutions of systems (22) and (23) in the relatively inert chlorobenzene to solutions of the same systems in pyridine leads to an increase in the rate of metal–proton exchange (22) only in one case, namely for R′ = H, R_nM = PhHg. In all other systems, the reaction remains slow on the PMR time scale. Thus in pyridine also, the PhHg group is more mobile than the Ph_3Sn, Ph_3Pb, and Ph_2Sb groups. The effect of an increase in the rate of metal–proton exchange under the influence of pyridine in the case of other R_nM groups was shown for the case of reaction (23) (R_nM = Ph_3Sn or Ph_3Pb).

Metal–proton exchange taking place with the rupture of M–O and H–O bonds was studied for mixtures of substituted phenols and their organometallic derivatives[117]:

$$ArO^*\text{—}H + ArO\text{—}MR_n \rightleftarrows ArO^*\text{—}MR_n + ArO\text{—}H$$

Ar = 2,6-$(CH_3)_2$-4-BrC_6H_2, 2-CH_3-4-BrC_6H_3, 2-CH_3-4,6-$Br_2C_6H_2$, 2,6-$(CH_3)_2$-4-$NO_2C_6H_2$. (24)

Reaction (24) showed the following principal characteristic features at 33°: a) the PhHg group is the most mobile, and the Ph_3Sn group the least mobile in intermolecular exchange both in chloroform and in pyridine; b) increase in the

electron-acceptor properties of Ar leads to an increase in the rate of exchange; and c) the change from solutions of the corresponding systems in chloroform to solutions in pyridine also increases the rate of reaction (24).

The common features in these relationships and those previously obtained for M–N and H–N bonds on the one hand and M–S and H–S bonds on the other suggested that in the case of M–O and H–O bonds also, metal–proton exchange takes place by an associative mechanism with the formation of cyclic transition states with delocalised bonds, although additional quantitative data are required for a more detailed study of the mechanism of this reaction.

REFERENCES

1. C.K.Ingold, "Structure and Mechanism in Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1973.
2. O.A.Reutov, I.P.Beletskaya, and V.I.Sokolov, "Mekhanismy Reaktsii Metallorganicheskikh Soedinenii" (Mechanisms of the Reactions of Organometallic Compounds), Izd.Khimiya, Moscow, 1972.
3. A.I.Yurodskii, "Khimiya Izotopov" (Isotope Chemistry), Izd.Akad.Nauk SSSR, Moscow, 1957.
4. A.I.Shatenshtein, "Izotopnyi Obmen i Zameshchenie Vodoroda v Organicheskikh Soedineniyakh" (The Isotopic Exchange and Replacement of Hydrogen in Organic Compounds), Izd.Akad.Nauk SSSR, Moscow, 1960.
5. V.K.Pogorelyi and I.P.Gragerov, Uspekhi Khim., 39, 1856 (1970) [Russ.Chem.Rev., No.10 (1970)].
6. F.A.Cotton and G.Wilkinson, "Advanced Inorganic Chemistry" (Translated into Russian), Part 1, Izd. Mir, Moscow, 1969.
7. F.Basolo and R.G.Pearson, "Mechanisms of Inorganic Reactions" (Translated into Russian), Izd.Mir, Moscow, 1971.
8. J.P.Candlin, K.A.Taylor, and D.T.Thompson, "Reactions of Transition Metal Complexes" (Translated into Russian), Izd.Mir, Moscow, 1970.
9. L.I.Budarin and K.B.Yatsimirskii, Uspekhi Khim., 37, 469 (1968) [Russ.Chem.Rev.No.3 (1968)].
10. L.A.Fedorov, A.S.Peregudov, and D.N.Kravtsov, J.Organometal.Chem., 40, 251 (1972).
11. C.S.Johnson, in "Advances in Magnetic Resonance", Vol.1 (edited by J.S.Waugh), Acad.Press, New York, 1965, p.33.
12. T.L.Brown, Accounts Chem.Research, 1, 23 (1968).
13. N.S.Ham and T.Mole, in "Progress in NMR", Vol.4 (edited by J.W.Emsley, J.Feeney, and L.H.Sutcliffe), 1969, p.91.
14. J.P.Oliver, in "Advances of Organometal.Chem.", Vol.8 (edited by F.G.A.Stone and R.West), 1970, p.167.
15. N.M.Sergeev, Uspekhi Khim., 42, 769 (1973) [Russ.Chem.Rev., No.5 (1973)].
16. A.L.Allred and C.R.McCoy, Tetrahedron Letters, 25 (1960).
17. C.R.McCoy and A.L.Allred, J.Amer.Chem.Soc., 84, 912 (1962).
18. R.E.Dessy, F.Kaplan, G.R.Coe, and R.M.Salinger, J.Amer.Chem.Soc., 85, 1191 (1963).
19. N.S.Ham, E.A.Jeffery, T.Mole, J.K.Saunders, and S.N.Stuart, J.Organometal.Chem., 8, 17 (1967).
20. K.L.Henold, J.Soulati, and J.P.Oliver, J.Amer. Chem.Soc., 91, 3171 (1969).
21. W.Bremser, M.Winokur, and J.D.Roberts, J.Amer.Chem.Soc., 92, 1080 (1970).
22. H.D.Visser, L.P.Stodulski, and J.P.Oliver, J.Organometal.Chem., 24, 563 (1970).
23. B.L.Dyatkin, B.I.Martynov, I.L.Knunyants, S.R.Sterlin, L.A.Fedorov, and Z.Stumbreviciute, Tetrahedron Letters, 1345 (1971).
24. J.Soulati, K.L.Henold, and J.P.Oliver, J.Amer. Chem.Soc., 93, 5694 (1971).
25. A.D.Cardin, P.D.Ellis, J.D.Odom, and J.W.Howard, J.Amer.Chem.Soc., 97, 1672 (1975).
26. J.P.Maher and D.F.Evans, Proc.Chem.Soc., 208 (1961).
27. J.P.Maher and D.F.Evans, J.Chem.Soc., 5534 (1963).
28. J.V.Hatton, J.Chem.Soc., 40, 933 (1964).
29. A.G.Lee and G.M.Sheldrick, J.Chem.Soc., A,1055 (1969).
30. A.G.Lee and G.M.Sheldrick, Chem.Communs, 441 (1969).
31. A.G.Lee, J.Chem.Soc., A,2157 (1970).
32. N.S.Ham, E.A.Jeffery, T.Mole, and S.N.Stuart, Chem.Communs, 254 (1967).
33. E.M.Seitz and S.D.Hall, J.Organometal Chem., 15, P7 (1968).
34. K.Flatau and H.Musso, Angew.Chem., Int.Ed., 9, 379 (1970).
35. A.N.Nesmeyanov, N.S.Kochetkova, L.A.Fedorov, and R.B.Materikova, Dokl.Akad.Nauk SSSR, 199, 361 (1971).
36. G.Klose, Ann.Phys., 8, 220 (1961).
37. E.A.Jeffery and T.Mole, Austral.J.Chem., 21, 1187 (1968).
38. H.Dreeskamp and K.Hildenbrand, Z.Naturforsch., 23a, 940 (1968).
39. F.Huet, E.Henry-Basch, and P.Freon, Bull.soc. chim.France, 1426 (1970).
40. R.E.Dessy, T.J.Flautt, H.H.Jaffé, and G.F.Reynolds, J.Chem.Phys., 30, 1422 (1959).
41. D.W.Moore and J.A.Happe, J.Phys.Chem., 65, 224 (1961).
42. J.V.Hatton, W.G.Schneider, and W.Siebrand, J.Chem.Phys., 39, 1330 (1963).
43. M.D.Rausch and J.R.Van Wazer, Inorg.Chem., 3, 761 (1964).
44. L.A.Fedorov, E.I.Fedin, B.A.Kvasov, and I.P.Beletskaya, Zhur.Strukt.Khim., 10, 247 (1969).
45. K.A.McLauchlan, D.H.Whiffen, and L.W.Reeves, Mol.Phys., 10, 131 (1966).
46. L.A.Fedorov, Z.Stumbreviciute, A.K.Prokof'ev, and E.I.Fedin, Dokl.Akad.Nauk SSSR, 209, 134 (1973).
47. F.J.Weigert and J.D.Roberts, Inorg.Chem., 12, 313 (1973).
48. C.G.Krespan, J.Org.Chem., 25, 105 (1960).
49. T.D.Coyle, S.L.Stafford, and F.G.A.Stone, Spectrochim.Acta, 17, 968 (1961).
50. A.J.Downs, J.Chem.Soc., 5273 (1963).
51. L.A.Fedorov, Z.Stumbreviciute, B.L.Dyatkin, B.I.Martynov, and S.R.Sterlin, Dokl.Akad.Nauk SSSR, 204, 1135 (1972).
52. A.N.Nesmeyanov, Uch.Zap.Moskov.Gos.Univ., 132, 5 (1950).
53. G.F.Reynolds and S.R.Daniel, Inorg.Chem., 6, 480 (1967).

54. J.P.Maher and D.F.Evans, Proc.Chem.Soc., 176 (1963).
55. J.P.Maher and D.F.Evans, J.Chem.Soc., 637 (1965).
56. G.D.Shier and R.S.Drago, J.Organometal.Chem., 5, 330 (1966).
57. H.Kurosawa and R.Okawara, J.Organometal. Chem., 14, 226 (1968).
58. H.Kurosawa, M.Tanaka, and R.Okawara, J. Organometal.Chem., 12, 241 (1968).
59. J.P.Maher, M.Evans, and M.Harrison, J.Chem. Soc., Dalton Trans., 199 (1972).
60. H.C.Bell, J.R.Kalman, J.T.Pinhey, and S.Sternhell, Tetrahedron Letters, 3391 (1974).
61. L.Ernst, J.Organometal.Chem., 82, 319 (1974).
62. K.C.Williams and T.L.Brown, J.Amer.Chem.Soc., 88, 5460 (1966).
63. K.Moedritzer, Organometal.Chem.Rev., 1, 179 (1966).
64. J.J.Burke and P.C.Lauterbur, J.Amer.Chem.Soc., 83, 326 (1961).
65. H.C.Clark, J.T.Kwon, L.W.Reeves, and E.J.Walls, Canad.J.Chem., 41, 3005 (1963).
66. L.A.Fedorov and E.I.Fedin, Izv.Akad.Nauk SSSR, Ser.Khim., 787 (1971).
67. M.Gielen, M.De Clercq, and B.De Poorter, J.Organometal.Chem., 34, 305 (1972).
68. H.Zimmer and O.A.Homberg, J.Org.Chem., 31, 947 (1966).
69. G.Singh, J.Organometal.Chem., 11, 133 (1968).
70. H.Dreeskamp and G.Stegmeier, Z.Naturforsch., 22a, 1458 (1967).
71. H.G.Kuivila, J.L.Considine, R.J.Mynott, and R.H.Sarma, J.Organometal.Chem., 55, C 11 (1973).
72. T.N.Mitchell, J.Organometal.Chem., 59, 189 (1973).
73. M.J.Cooper, A.K.Holliday, P.H.Makin, R.J.Puddephat, and P.J.Smith, J.Organometal. Chem., 65, 377 (1974).
74. D.de Vos, J.Organometal.Chem., 104, 193 (1976).
75. D.Seyferth, G.J.Murphy, R.L.Lambert, and R.E.Mammarella, J.Organometal.Chem., 90, 173 (1975).
76. E.T.Bogoradovskii, V.S.Zavgorodnyi, and A.A.Petrov, Zhur.Obshch.Khim., 45, 2564 (1975).
77. D.Hadzi and A.Novak, Ber.Bunsenges.Phys.Chem., 64, 567 (1960).
78. M.L.Huggins, Angew.Chem., 83, 163 (1971).
79. N.Muller and D.E.Pritchard, J.Amer.Chem.Soc., 82, 248 (1960).
80. K.Yasuda and R.Okawara, Organometal.Chem. Rev., 2, 255 (1967).
81. D.P.N.Satchell and R.S.Satchell, Chem.Rev., 69, 251 (1969).
82. D.P.N.Satchell and R.S.Satchell, Uspekhi Khim., 42, 1009 (1973).
83. R.J.Gillespie, "Molecular Geometry" (Translated into Russian), Izd.Mir, Moscow, 1975.
84. L.A.Fedorov, Z.Stumbreviciute, B.I.Martynov, and B.L.Dyatkin, Zhur.Org.Khim., 11, 489 (1975).
85. L.A.Fedorov and E.I.Fedin, Dokl.Akad.Nauk SSSR, 195, 856 (1970).
86. K.H.Thile, Z.anorg.Chem., 330, 8 (1964).
87. R.C.Dobbie and H.J.Emeléus, J.Chem.Soc., A, 367 (1966).
88. D.Breitinger, K.Geske, and W.Beitelschmidt, Angew.Chem., Int.Ed., 10, 555 (1971).
89. M.R.Kula, C.G.Kreiter, and J.Lorberth, Chem. Ber., 77, 1294 (1964).
90. J.Lorberth and M.R.Kula, Chem.Ber., 97, 3444 (1964).
91. J.Lorberth and M.R.Kula, Chem.Ber., 98, 520 (1965).
92. E.W.Randall, C.H.Yoder, and J.J.Zuckerman, J.Amer.Chem.Soc., 89, 3438 (1967).
93. J.Lorberth, J.Organometal.Chem., 16, 235 (1969).
94. M.E.Bishop, C.D.Schaeffer, and J.J.Zuckerman, J.Organometal.Chem., 101, C19 (1975).
95. B.Walther and K.Thiede, J.Organometal.Chem., 32, C7 (1971).
96. G.M.Sheldrick and J.P.Yesinowski, J.Chem.Soc., Dalton Trans., 870 (1975).
97. A.G.Davies and W.R.Symes, J.Chem.Soc., C, 1009 (1967).
98. A.J.Leusink, H.A.Budding, and J.W.Marsman, J.Organometal.Chem., 13, 155 (1968).
99. A.G.Davies, D.C.Kleinschmidt, P.R.Palan, and S.C.Vasishtha, J.Chem.Soc., C,3972 (1971).
100. U.Folli, D.Iarossi, and F.Taddei, J.Chem.Soc., Perkin Trans.II, 1284 (1973).
101. U.Folli, D.Iarossi, and F.Taddei, J.Chem.Soc., Perkin Trans.II, 638 (1973).
102. D.N.Kravtsov, A.S.Peregudov, E.M.Rokhlina, and L.A.Fedorov, J.Organometal.Chem., 77, 199 (1974).
103. A.J.Bloodworth, J.Chem.Soc., C,2051 (1970).
104. R.D.Bach and A.T.Weibel, J.Amer.Chem.Soc., 97, 2575 (1975).
105. R.D.Bach and A.T.Weibel, J.Amer.Chem.Soc., 98, 6241 (1975).
106. H.Kurosawa, K.Yasuda, and R.Okawara, Bull. Chem.Soc.Japan, 40, 861 (1967).
107. A.G.Lee, J.Chem.Soc., A,467 (1970).
108. A.G.Lee and G.M.Sheldrick, Trans.Faraday Soc., 67, 7 (1971).
109. A.G.Davies and R.J.Puddephat, J.Chem.Soc., C, 2663 (1967).
110. R.Honigschmidt-Grossich and E.Amberger, Chem.Ber., 102, 3589 (1969).
111. E.V.Van den Berghe, D.F.Van de Vondel, and G.P.Van der Kelen, Inorg.Chim.Acta, 1, 97, (1967).
112. E.W.Abel and D.B.Brady, J.Organometal.Chem., 11, 145 (1968).
113. E.V.Van den Berghe and G.P.Van der Kelen, J.Organometal.Chem., 26, 207 (1971).
114. D.N.Kravtsov, A.S.Peregudov, S.I.Pombrik, E.M.Rokhlina, and L.A.Fedorov, J.Organometal. Chem., 72, 153 (1974).
115. L.A.Fedorov, D.N.Kravtsov, A.S.Peregudov, S.I.Pombrik, and E.M.Rokhlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1512 (1975).
116. A.S.Peregudov, D.N.Kravtsov, and L.A.Fedorov, J.Organometal.Chem., 71, 347 (1974).
117. A.S.Peregudov, D.N.Kravtsov, L.A.Fedorov, and V.M.Pachevskaya, Izv.Akad.Nauk SSSR, Ser. Khim., 1811 (1978).
118. J.Lorberth and H.Vahrenkamp, J.Organometal. Chem., 11, 111 (1968).
119. W.McFarlane and R.J.Wood, Chem.Communs., 262 (1969).
120. P.R.Wells, W.Kitching, and R.F.Henzell, Tetrahedron Letters, 1029 (1964).
121. R.B.Simpson, J.Chem.Phys., 46, 4775 (1967).
122. L.L.Murrell and T.L.Brown, J.Organometal. Chem., 13, 301 (1968).
123. E.V.Van den Berghe, G.P.Van der Kelen, and Z.Eeckhaut, Bull.Soc.Chim.Belg., 76, 79 (1967).

124. G.Redl and M.Winokur, J.Organometal.Chem., 26, C 36 (1971).
125. A.S.Peregudov, L.A.Fedorov, D.N.Kravtsov, and E.M.Rokhlina, Zhur.Obshch.Khim., **42**, 2194 (1972).
126. S.O.Chan and L.W.Reeves, Inorg.Chem., **12**, 1704 (1973).
127. E.V.Van den Berghe and G.P.Van der Kelen, J.Organometal.Chem., **72**, 65 (1974).
128. J.A.Ladd and B.R.Glasberg, J.Chem.Soc., Dalton Trans., 2378 (1975).
129. G.J.D.Peddle and G.Redl, Chem.Communs., 626 (1968).
130. G.J.D.Peddle and G.Redl, J.Amer.Chem.Soc., 92, 365 (1970).
131. D.V.Stynes and A.L.Allred, J.Amer.Chem.Soc., 93, 2666 (1971).
132. F.P.Boer, J.J.Flynn, H.H.Freedman, S.V.McKinley, and V.R.Sandel, J.Amer.Chem. Soc., 89, 5068 (1967).
133. F.P.Boer, G.A.Doorakian, H.H.Freedman, and S.V.McKinley, J.Amer.Chem.Soc., **92**, 1225 (1970).
134. F.P.Boer, F.P.Van Remoortere, P.P.North, and G.N.Reeke, Inorg.Chem., 10, 529 (1971).
135. P.L.Goggin, R.J.Goodfellow, and S.R.Haddock, J.Chem.Soc., Dalton Trans., 647 (1972).
136. M.Gielen, M.R.Barthels, M.De Clercq, C.Dehouck, and G.Mayence, J.Organometal.Chem., 34, 315 (1972).
137. M.Leguan, Y.Besace, and J.P.Ballaquet, J. Organometal.Chem., **144**, C 39 (1978).
138. S.A.Kandil and C.E.Holloway, J.Chem.Soc., Dalton Trans., 1421 (1973).
139. M.Gielen, S.Simon, Y.Tondeur, M.Van de Steen, and C.Hoogzand, Bull.Soc.Chim.Belg., 83, 337 (1974).
140. E.D.Korniets, L.A.Fedorov, D.N.Kravtsov, and E.I.Fedin, Izv.Akad.Nauk SSSR, Ser.Khim., 2401 (1976).
141. E.D.Korniets, L.A.Fedorov, E.I.Fedin, and D.I.Kravtsov, Izv.Akad.Nauk SSSR, Ser.Khim., 1526 (1977).
142. J.J.Delpuech, Bull.soc.chim.France, 2696 (1964).
143. L.A.Fedorov, I.P.Beletskaya, E.I.Fedin, B.A.Kvasov, and O.A.Reutov, Teor.Eksper.Khim., 550 (1967).
144. D.F.Evans and R.F.Phillips, J.Chem.Soc., Dalton Trans., 978 (1973).
145. G.E.Coates and A.Lauder, J.Chem.Soc., A, 264 (1966).
146. N.W.Alcock and R.E.Timms, J.Chem.Soc., A, 1873 (1968).

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