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New Contribution to the Development of Organoelementary and Organic Chemistry

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I. INTRODUCTION

Twenty years ago, in a review of the achievements of the chemistry of organoelementary compounds, it was necessary to begin by defining the concept of "organoelementary chemistry", to formulate the region embraced by this science, and to specify its borderline position between organic and inorganic chemistry. Nowadays there is no need of this: organoelementary chemistry has become firmly established as a large and important branch of chemistry, covering a multiplicity of types of compounds, possessing numerous and well developed synthetic methods, specific reactions, and laws of reactivity, and having found diverse and important practical applications—from organoelementary medicinals, the industrial manufacture of which constitutes a typical example of fine organic synthesis, to organoelementary polymeric materials, combustion regulators, agricultural chemicals, and many other products of large-scale, so called heavy organic synthesis.

Organoelementary chemistry occupied a strong position in the development of general and theoretical aspects of chemistry, by providing extremely convenient materials for study by theoreticians and experimentalists. Not only in the USSR, which contains the first Institute of Organoelementary Compounds to be founded in the world, but also in other countries institutes and major laboratories appeared, specialising in the study of organoelementary chemistry, and publication of an international journal on the chemistry of organometallic compounds was started, while more than half the papers in the "Journal of General Chemistry" were devoted to organoelementary compounds.

An outstanding part in this birth and vigorous development of organoelementary chemistry as an independent branch of science was played by A. N. Nesmeyanov, in whose works and those of his many pupils organoelementary and especially organometallic chemistry found its greatest development. Ten years ago we gave in this journal a brief review of Nesmeyanov's scientific activities [1]. While referring readers to this review, in the present paper we shall concentrate our attention on the results of investigations made during recent years.

Nesmeyanov had an unusually broad range of scientific interests. He and his school undertook the leading fundamental researches in several fields of organometallic, organoelementary, and organic chemistry.

In spite of the diversity of subjects investigated by Nesmeyanov, they show a profound inner relationship in the logic with which the questions were posed and with which the investigation was developed. As example we may point to the logical and methodological connection existing between his diazo-method (1929) and his synthesis in 1955 of diarylchloronium salts, which greatly enriched one of the oldest branches of organic chemistry, that of chlorinated organic compounds. Just as at one time the diazo-method, originally proposed for synthesising organomercury compounds, was then developed by him in a comprehensive series of researches, leading to methods for the synthesis of organic compounds of several non-transition elements, so the "onium" synthesis was extended to the preparation of aromatic and heterocyclic diarylchloronium, diarylbromonium, triaryloxonium, sulphoxonium, and completely aromatic ammonium salts.

A profound inner connection exists between such apparently remote lines of research by Nesmeyanov as the investigation of β(and α)-substituted organometallic compounds (quasi-complex compounds), β-chlorovinyl ketones, and the tautomerism and dual reactivity of organic and organometallic compounds.

Using the popular definition of academics as romantics and classicists, we can say that Nesmeyanov is a romantic in the breadth of his interests and in his thirst for new discoveries, and a classicist in the accuracy of the expanded interests, the depth and comprehensiveness with which he works out problems.

During the past ten to fifteen years Nesmeyanov and his students have conducted researches in several completely new fields. Examples are the comprehensive and extraordinarily intensive investigation of organometallic compounds of transition metals, the discovery and investigation of the phenomenon of metallotropy, and the already mentioned investigations of onium and β-chlorovinyl compounds. He initiated and directed researches on synthetic foodstuffs, this work being reviewed in the present issue by V. M. Belikov, R. V. Golovnya, S. V. Rogozhin, G. L. Slonimskii, and B. V. Tolstoguzov.

A brief survey is given below of some new investigations by Nesmeyanov in the chemistry of organometallic compounds of transition and non-transition metals and on general aspects of organic chemistry.

II. ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS

The past two decades have seen a vigorous growth of research on the organic compounds of transition metals. Not so very long—twenty years—ago it was considered that the transition metals did not form organometallic compounds. The few substances of this type then known, such as tetramethylplatinum, were regarded as a typical, exceptions to the rule. Nevertheless, an extremely characteristic feature of transition metals was the formation of numerous complex compounds of the Werner type, which had been widely studied in the chemistry of inorganic complexes and metal carbonyls, these forming a very peculiar, isolated "island" of chemical compounds marked off from the "continents" of inorganic and organic substances.

Fundamental changes have occurred in this field during recent years. Transition metals have been found to be capable of forming exceptionally numerous organometallic compounds of sandwich type, as well as π- and σ-complexes, which are sometimes extremely stable, as e.g. ferrocene, on the basis of which it has proved possible to construct new families of organic derivatives—not only metal–hydrocarbons but also halogeno-derivatives, alcohols, aldehydes, ketones, nitro- and amino-derivatives, carboxylic and organoelementary acids, and many others—a vast region of mixed structures, including sandwiches, π-complexes, and carbonyls, being found also between inorganic complex compounds and the new organic derivatives of transition metals. The carbonyl "island" has proved to form part of an immense new "mainland".

The chemistry of organic compounds of transition metals has proved exceptionally rich in new types of chemical bond, new laws, and new reactions. The Soviet school of organometallic chemists, with Nesmeyanov at its head, has made an exceptionally important contribution to the development of this field.

1. Metallocene and Arene Compounds of Iron (Ferrocene)

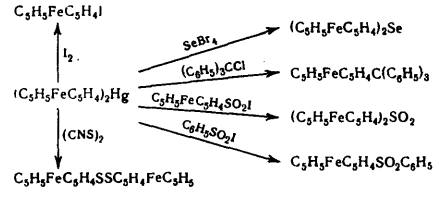
The main theme of this work was at first the development of the chemistry of ferrocene [2]. Nesmeyanov and his pupils have now carried out wide researches on the organic compounds of a large group of transition metals—iron, cobalt, manganese, rhenium, chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, zirconium, hafnium—and certain other elements.

In investigating ferrocene and its derivatives, Nesmeyanov and his coworkers solved a large group of general problems in this branch of chemistry. Examples are the determination of the reactivity of ferrocene compounds as non-benzenoid aromatic systems, the establishment of specific differences in the reactivity of ferrocene and aromatic benzenoid compounds, rules of orientation in substitution reactions in ferrocene and its derivatives, the magnitude of polar effects in the reactions of ferrocene compounds, the polar characteristics of the ferrocenyl group as a substituent, the effect of ferrocenyl on the stability of adjacent cationic, radical, and anionic centres, electronic effects in the ferrocene series, the development of methods for demonstrating the structure of ferrocene derivatives, and the transition from ferrocene to compounds of other types. The list of problems can easily be extended.

In the solution of these problems Nesmeyanov made wide use of the whole available range of chemical, physical, and physicochemical methods of investigation. Only a brief survey of some of the results obtained can, of course, be given in this paper.

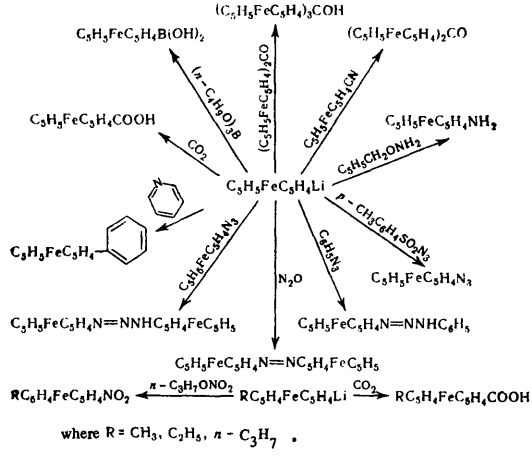
In order to solve the problems it was first necessary to develop synthetic methods for, and examine the chemical reactions of, various derivatives of ferrocene. At the start of this series of investigations only a single substitution in the cyclopentadienyl ring of ferrocene was known, this being the reaction with acid halides and anhydrides to form ketones [3]. Since the classical electrophilic substitution reactions—halogenation, nitration, sulphonation, etc.—are difficult in the ferrocene series (because of the ease of oxidation of ferrocene), Fischer and Jira [4] spoke against an analogy between ferrocene and aromatic compounds.

Scheme 1



In the very first paper of this series, Nesmeyanov and his coworkers [5] showed this view to be incorrect, by effecting the mercuration of ferrocene with mercury acetate and its metallation with butyl-lithium. Mercury and lithium derivatives of ferrocene have since been widely used in the preparation of other ferrocene compounds (Scheme 1). In particular it has proved possible for the first time, with mercury derivatives of ferrocene as starting material, to obtain halogenated derivatives [6], and ferrocenylamine from ferrocenyl-lithium [7] (Scheme 2).

Scheme 2



The lithium compounds can be converted into carboxylic and boronic acids, ketones, alcohols, amines, azides, and nitro-, azo-, and diazamino-derivatives of the ferrocene series (Scheme 2).

The direct alkylation of ferrocene [8,9] by alkyl halides and alkenes in the presence of aluminium chloride was accomplished by Nesmeyanov and Kochetkova during 1956–1958. Introduction of the first alkyl group into the ferrocene molecule favours further alkylation. Nesmeyanov et al. have since shown by gas–liquid chromatography that

all possible isomeric di- and tri-alkylated ferrocenes are thus formed [10-12]. Use of a mixture of anhydrous aluminium chloride and lithium tetrahydroaluminate increases the yield so greatly that alkylation becomes a method for preparing certain homologues of ferrocene.

Study of the absorption spectra of monoalkylated and heteroannular dialkylated ferrocenes and comparison with those of the corresponding acyl derivatives have permitted an assignment of the absorption bands of ferrocene itself [10-12]. The agreement of the change in the spectra predicted theoretically (by calculation based on the molecular orbital method to the Hückel approximation) on passing from ferrocene to its substituted derivatives with the experimental data has confirmed the correctness of this assignment [13].

Investigation of the nuclear magnetic resonance spectra of homologues of ferrocene containing primary, secondary, and tertiary alkyl groups indicates hyperconjugation of the alkyl substituent with a cyclopentadienyl ring of the ferrocene system [14].

Nesmeyanov and his students have discovered many new reactions—acylation [15,16], sulphonation [17], phosphorylation [18]—of electrophilic substitution. Together with Kursanov, Setkina, and their coworkers a study was made of the deuteriation of ferrocene and its substituted derivatives [19-23]. Investigations have been made of the nucleophilic substitution of halogen in ferrocenyl halides [24-26], of radical substitution—arylation by aromatic diazo-compounds [5,7,27]—and many other reactions [2,28], e.g. the condensation of ferrocene with aldehydes [29].

o-Carboxybenzoylferrocene undergoes reactions of a peculiar type [30-33]. By ring–chain tautomerisation in its cyclic form it exhibits several reactions of the α-ferrocenylcarbonium ion, e.g. extremely readily occurring nucleophilic substitutions initiated by acids. The ferrocene analogue of anthraquinone—"ferrocoanthraquinone"—has been obtained by a series of transformations of the "open" acyclic form of *o*-carboxybenzoylferrocene.

Nesmeyanov, Vil'chevskaya, Kochetkova, and their coworkers accomplished the phosphorylation of ferrocene with phosphorus trichloride, obtaining triferrocenylphosphine oxide. This reaction has considerable value for alkyl, aralkyl, and aryl derivatives of ferrocene. The peculiar behaviour of these compounds towards nucleophilic and electrophilic reagents distinguishes them from the corresponding aromatic and aliphatic organophosphorus compounds [34,35].

The investigation by Nesmeyanov, Sazonova, and Drozd of ferrocenylboronic acids has proved extremely fruitful for synthetic purposes [36-40]. In particular, monochloro- and 1,1′-dichloro-ferrocene were obtained for the first time by replacement of the $B(OH)_2$ group in these acids, and hydroxy- and amino-ferrocenes have been prepared by the same method (Scheme 3).

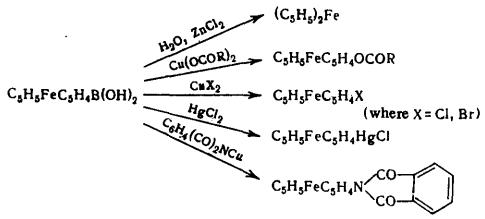
The synthesis of chlorinated ferrocenes made it possible to obtain various compounds by a nucleophilic substitution of the chlorine by other groups. It was shown [24,25,41,42] that the halogen in halogenated ferrocenes is easily exchanged in the presence of copper salts; amino- and hydroxy-derivatives of ferrocene, as well as azides, nitriles, and other derivatives, have been obtained in this way (Scheme 4).

Without attempting to exhaust all the methods of preparing ferrocene compounds developed by Nesmeyanov and his students, we may mention a series of papers on preparations involving the use of *NNN*-trialkylammonium derivatives of ferrocene (Scheme 5) (together with Perevalova, Shilovtseva, Ustynyuk, et al. [43-48])

A specific "ricochet" substitution (cyanation) involving iron has been discovered [49-51]. Ferricinium salts (or ferrocene in the presence of aluminium chloride) on treatment with hydrocyanic acid yield ferrocenecarbonitrile:

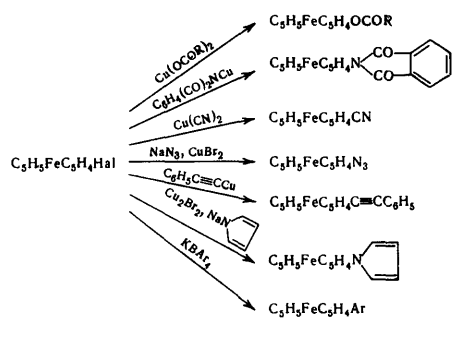
$$(C_5H_5)_2Fe \xrightarrow[FeCl_3]{HCN} C_5H_5FeC_5H_4CN\ .$$

Scheme 3

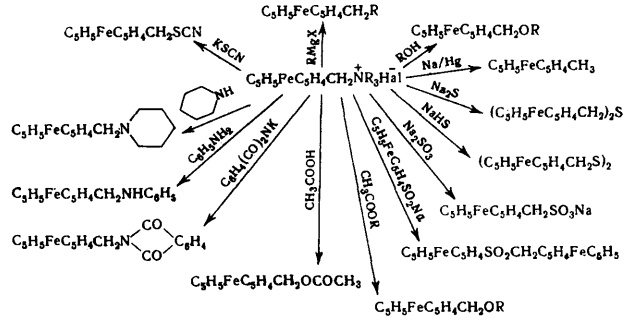


This is not a bimolecular nucleophilic substitution, since it does not obey the rules of orientation for nucleophilic substitution. Thus electron-acceptor substituents (*p*-nitrophenyl, phenylsulphonyl, acetyl, and chloro-, bromo-, cyano-, and nitro-groups) make cyanation more difficult and favour the formation of heteroannular isomers [50]. The cyanide anion probably first attacks the iron atom of the ferricinium cation with liberation of the proton from the hydrocyanic acid molecule (the pH of the medium decreases). The cyano-group then migrates into the five-membered ring with simultaneous reduction of the iron.

Scheme 4



Scheme 5



Representatives of the principal types of compounds of the ferrocene series have been obtained by the above reactions and several others, in most cases the mechanism of

their formation (electrophilic, nucleophilic, radical substitution) has been established, and their chemical properties have been studied.

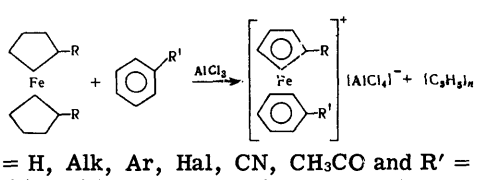
The reactions of many functional derivatives of ferrocene are analogous to those of the corresponding aromatic compounds. Several fundamental differences in chemical reactivity have been observed between ferrocene compounds and their aromatic analogues. Thus the former are incapable of the typical rearrangements of aromatic compounds: azoferrocene, for example, cannot undergo the benzidine rearrangement[52], and the allyl ether of ferrocenol is unable to rearrange into allylferrocenol[53]. This is explained by the inability of the ferrocene ring system to transmit *T*-effects requiring quinoid transition states.

A series of papers by Nesmeyanov, Gubin, and Perevalova has been devoted to electronic effects in ferrocene compounds[54-57]. The formal oxidation potentials of a large number of derivatives of ferrocene[54,55], the dissociation constants of acids and phenols, and the basic dissociation constants of amines of the ferrocene series[56] have been determined, and the infrared and ultraviolet spectra of several substituted ferrocenes studied. The application of correlation equations to an analysis of the results revealed the difference between the interaction of substituents with the phenyl and with the ferrocenyl ring systems, and enabled ferrocenyl to be characterised as a substituent[57].

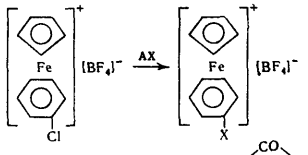
Both in the ferrocene system and in the benzene ring a ferrocenyl substituent exhibits electron-donor properties, the effect of the ferrocenyl being determined by the combination of a strong positive inductive effect with a fairly weak positive conjugative effect.

The effect of ferrocenyl on the stability of a neighbouring cationic centre is consistent with the above description of ferrocenyl as a substituent: it stabilises a neighbouring carbonium centre, carbonium salts containing ferrocenyl residues in the α-position being extremely stable[58,59]. The triferrocenylmethyl cation is also stable at room temperature[60].

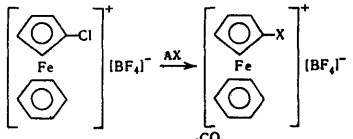
A remarkable type of ligand exchange was discovered in ferrocene by Nesmeyanov and Vol'kenau[61,62]. When ferrocene interacts with benzene and its derivatives in the presence of aluminium chloride, one five-membered ring is exchanged for an arene ring with the formation of arenecyclopentadienyl derivatives of iron:



where R = H, Alk, Ar, Hal, CN, CH_3CO and R′ = H, Alk, Ar, Hal, OAlk, OAr, CH_3, CH_3CONH. The effect on this reaction of substituent groups both in the ferrocene and in the arene has been investigated. The reactivity of the arenecyclopentadienyl compounds of iron thus made available has been studied. In particular, the replacement of halogen in the five-membered and six-membered rings by other groups has been investigated:



where X = OAlk, OAr, SAr, SAlk, C_6H_4(CO)(CO)N, NH_2, NHK, $C_5H_{10}N$; A = Na, K, H



where X = OAlk, C_6H_5S, C_6H_4(CO)(CO)N, NH_2, NHC_6H_{11}, $C_5H_{10}N$.
A = Na, K, H

2. Carbonyls and Organometallic Derivatives of Metal Carbonyls

In a long series of papers Nesmeyanov, Anisimov, Kolobova, Makarov, Pasynskii, and Ioganson have elaborated methods for the synthesis of organometallic compounds of manganese, rhenium, niobium, tantalum, vanadium, and several other transition metals, and have studied their chemical reactions, physicochemical properties, comparative reactivity, the nature of the bond, the mutual influence of groups, and many other aspects of their chemistry[63,64].

Mixed compounds have been investigated, in which the metal is bound to cyclopentadienyl and carbonyl groups, as well as aromatic derivatives of manganese and rhenium carbonyls containing a metal–carbon σ-bond, and polymetallic derivatives of molybdenum and tungsten carbonyls containing a direct metal–metal bond with elements of Group IVb.

A method has been developed for the synthesis of cyclopentadienyl derivatives of carbonyls of metals in Group VII:[63,64]

$$C_5H_5Na + ClM(CO)_5 \rightarrow C_5H_5M(CO)_3 + 2CO + NaCl$$

where M = Mn, Re.

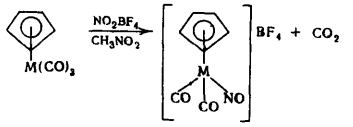
The acylation[65], mercuration[65], chloromethylation[65], phosphorylation[65], and deuteriation of tricarbonylcyclopentadienylmanganese (TCCM) and to some extent of its homologues[66-68] have been accomplished, as well as the deuteriation[66-68], sulphonation[69], and mercuration[69] of tricarbonylcyclopentadienylrhenium (TCCR). The cyclopentadienyl derivatives of Group VII metals have been shown to resemble ferrocene in possessing aromatic properties, the above rhenium compound being less active in electrophilic substitutions, but more active in protophilic substitutions, than is the corresponding manganese derivative.

It has been discovered[70,71] that the ring in TCCM and TCCR can be metallated.

The transformations of the lithium, mercury, and chloroderivatives of TCCM and TCCR have been studied[70,71]. Methods have been worked out for synthesising various compounds containing in the cyclopentadiene ring such groups as COOH, NH_2, $B(OH)_2$, HgCl, Cl, Br, RCO, and many others. These reactions are set out in Scheme 6.

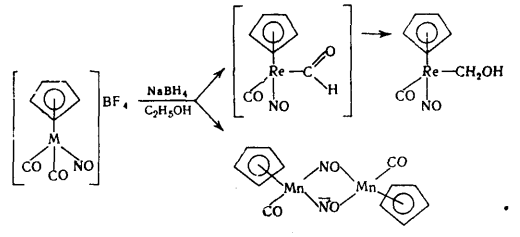
The chloromethylation of TCCM and the chemical reactions of the chloromethyl derivatives have been studied[65].

TCCM and TCCR react in very peculiar fashion with nitryl tetrafluoroborate. Instead of the expected nitration of the ring the reaction involves simultaneous oxidation–reduction and ligand exchange with the formation of nitrosyl complexes:

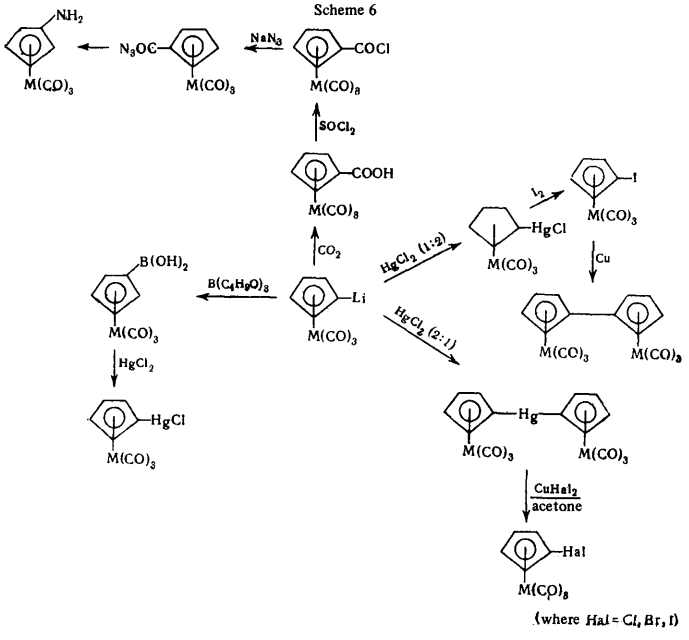


(where M = Mn, Re)

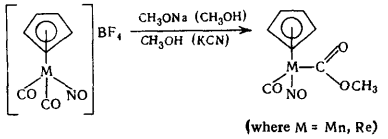
Several differences in chemical behaviour have been established between the cyclopentadienyl–carbonyl complexes of manganese and of rhenium. When the fluoroborate complexes are reduced with sodium tetrahydroborate in ethanol, the manganese derivative yields a dimeric product, but the rhenium analogue gives an alcohol:



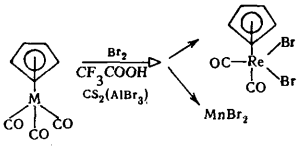
Scheme 6



The action on the fluoroborate complexes of a sodium alkoxide in methanol, or of methanol in the presence of potassium cyanide, results in esters (reaction at the carbonyl group):

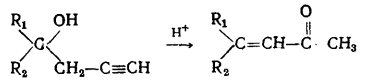


Bromination under conditions of electrophilic substitution goes in different ways with TCCR and TCCM:



The chemical behaviour of ketones of TCCM has been investigated. Reduction of the ketones [72], hydration of the carbonyls, and interaction of the former with Grignard and Iotsich reagents have been accomplished, and the rearrangement of tertiary α-acetylenic alcohols has been studied [73,74].

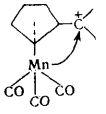
The rearrangement of β-acetylenic alcohols has been discovered [75]:



where R_1 = TCCM, $C_5H_4FeC_5H_5$ and R_2 = CH_3, C_2H_5, C_6H_5.

Ketones of TCCM on treatment with bromine yield α-bromoketones [76]. A study has been made of the mobility of halogen in the α-position with respect to the carbonyl group in nucleophilic substitutions and condensations.

The TCCM residue is more efficient than phenyl in stabilising an adjacent carbonium centre. Yet it also surpasses phenyl in reactions involving a neighbouring α-anionic centre. Thus a TCCM residue possesses stronger negative and positive mesomeric effects than does phenyl. Its stronger positive mesomeric effect (+M) is obviously due to the part played by the electronic environment of manganese in stabilising the α-carbonium centre:



Investigation of TCCM, TCCR, and their derivatives by physical methods (infrared, nuclear magnetic resonance, nuclear quadrupole resonance spectra, etc.) has enabled differences in the fine structure of the manganese and rhenium compounds to be formulated (relative electron density of the cyclopentadienyl rings, order of the metal–carbonyl bond, etc.).

The reactions of the carbonyl–cyclopentadienyl complexes of vanadium, niobium, and tantalum with *p*- and π-donor ligands have been examined [77], and new types of complexes of these metals obtained containing cyclopentadienyl, carbonyl, and substituted acetylenic groups. For example, products of the successive incorporation of one, two, and three diphenylacetylene molecules with one niobium atom have been isolated, the final product being hexaphenylbenzene. This process can be regarded as a model of the trimerisation of acetylenic hydrocarbons on complexes of transition metals.

Methods have been worked out for preparing derivatives of manganese and rhenium carbonyls containing metal–carbon σ-bonds [78], of the types $XC_6H_4COM(CO)_5$ and $XC_6H_4M(CO)_5$, where X is a substituent in the aromatic ring. The way in which the electronic effect of the substituent X in these compounds is transmitted via the metal atom to the carbonyl groups has been examined by various physical methods [79].

3. Heteropolymetallic Derivatives of Metal Carbonyls

It is well known that, unlike π-complexes of transition metals, the organic σ-derivatives are unstable if they contain no other stabilising ligands. When ligands (CO, π-C_5H_5, etc.) capable of accepting electron density from the metal into vacant π-orbitals are introduced into the coordination sphere of the metal atom, the metal–carbon σ-bond is considerably stabilised. The preparation of several stable organic σ-derivatives of metal carbonyls has opened up the possibility of synthesising stable compounds containing σ-bonds between atoms of transition metals and of elements in Group IVb other than carbon.

The researches of Nesmeyanov and his students showed that compounds containing covalent bonds between atoms of

transition metals and of Group IVb elements can be obtained by several methods—(1) exchange interaction of salts of metal carbonyls with organic halides of silicon, germanium, tin, or lead [80-93], e.g.

$$R_3MX + NaRe(CO)_5 \rightarrow R_3MRe(CO)_5$$
$$R_2MX_2 + 2NaMo(CO)_3C_5H_5 \rightarrow R_2M[Mo(CO)_3C_5H_5]_2$$
$$RMX_3 + 3NaCo(CO)_4 \rightarrow RM[Co(CO)_4]_3$$
$$SnX_4 + 4NaFe(CO)_2C_5H_5 \rightarrow Sn[Fe(CO)_2C_5H_5]_4$$

where M = Si, Ge, Sn, Pb, R = Alk, Ar, and X = Cl, Br.

(2) Reactions involving "insertion" of germanium dichloride at metal–halogen bonds [84]:

$$Cl-Fe(CO)_2C_5H_5 + GeCl_2 \xrightarrow{\text{dioxan}} Cl_3Ge-Fe(CO)_2C_5H_5$$
$$Cl-M'(CO)_3C_5H_5 + GeCl_2 \rightarrow Cl_3Ge-M'(CO)_3C_5H_5$$

where M′ = Mo, W; or at a metal–carbon bond:

$$R-Fe(CO)_2C_5H_5 + GeCl_2 \xrightarrow{\text{dioxan}} RCl_2Ge-Fe(CO)_2C_5H_5$$

where R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, $C_6H_5CH_2$. It is also possible for germanium dichloride to be inserted into metal–metal bonds under mild conditions:

$$C_6H_5(OC)_2Fe_2 + GeCl_2 \xrightarrow[\text{dioxan}]{} Cl_2Ge[Fe(CO_2)C_5H_5]_2 .$$

Insertions of tin dihalides into dinuclear carbonyls in which the two parts are linked by a direct metal–metal bond, e.g. $[C_6H_5(CO)_3M']_2$ (M′ = Mo, W) or $M'_2(CO)_{10}$(M′ = Mn, Re), takes place at high temperatures or on ultraviolet irradiation:

$$M'_2(CO)_{10} + SnCl_2 \rightarrow Cl_2Sn[M'(CO)_5]_2$$
$$[C_5H_5(CO)_3M']_2 + SnCl_2 \rightarrow Cl_2Sn[M'(CO)_3C_5H_5]_2 .$$

With molybdenum and tungsten derivatives, compounds containing one metal–carbonyl group, such as $Cl_3SnM'(CO)_3C_5H_5$, have been isolated together with the above insertion products.

(3) Trichlorogermyl derivatives of the carbonyls of molybdenum, tungsten, iron, and manganese have been obtained by reaction between trichlorogermane and the corresponding carbonyl halides [85,86]:

$$ClMn(CO)_5 + Cl_3GeH \rightarrow Cl_3GeMn(CO)_5 + HCl .$$

(4) Compounds containing bonds between cobalt and a Group IVb element have been prepared also directly from octacarbonyldicobalt and organic halides of germanium, tin, or lead [87]:

$$R_nMX_{4-n} + Co_2(CO)_8 \rightarrow R_nX_nM[Co(CO)_4]_{4-m-n}$$

where R = Alk, Ar, n = 1–3, m = 2–0, and M = Ge, Sn, Pb. The number of carbonylcobalt groups linked directly to the atom of the non-transition element is determined by the ratio of the reactants, but does not exceed three.

The methods enumerated above have been used to obtain many new compounds containing atoms of Group IVb elements together with 1–6 identical or differing atoms of transition metals.

Derivatives, containing a metal–metal σ-bond, of Group IVb elements and metal carbonyls are mostly crystalline substances, soluble in the usual organic solvents, and insoluble in water. A considerable proportion of them are coloured, varying from pale yellow to red.

In the solid state compounds containing metal–metal bonds (with the exception of certain derivatives of cobalt) are stable to the action of oxygen and atmospheric moisture. Depending on the nature of the transition metal the thermal and oxidative stability of the complexes increases in the sequence

$$Co < Cr < Mo < W < Mn < Re < Fe .$$

The most stable compounds are those containing a tin–transition metal bond. Derivatives containing germanium and especially lead atoms are less stable. Among compounds containing transition metal–silicon bonds derivatives of carbonyls of Group VII metals (manganese, rhenium) are the most stable, withstanding prolonged heating (at 160–170°C for 35 h) without appreciable decomposition. As the number of carbonylmetal groups combined with the non-transition metals increases, the thermal and oxidative stability diminishes. Derivatives containing three or four metal atoms, of the types $R_2M[M'(CO)_mL]_2$ and $RM[M'(CO)_mL]_3$, are the least stable. Tetrametallic derivatives have been obtained mainly with tin and silicon.

The chemical properties of compounds containing metal–metal bonds with two or more metal-bound fragments depend in considerable measure on the nature of the stabilising ligands, the electronegativity of the substituents combined with the non-transition metals, and several other factors.

Three types of reaction—at metal–metal, metal–carbon, and metal–carbonyl group bonds—are possible with compounds of the given type, containing R–M–M′–CO bonds, where R = Alk, Ar, Hal. The action of halogens, halogen hydrides, hydrohalic acids, and several other reagents has been investigated.

The reactions of derivatives containing two metal atoms are specific, depending on the conditions, the nature of the transition metal, and the ligands attached to it.

The action of chlorine or bromine on tin derivatives of manganese and rhenium carbonyls at temperatures from 0° to 70°C is accompanied by cleavage of carbon–tin bonds, while the metal–metal bonds are preserved. The replacement of phenyl groups may be successive:

$$(C_6H_5)_2Sn[M'(CO)_5]_2 \xrightarrow{+2Hal_2} C_6H_5Hal_2Sn-M'(CO)_5 \rightarrow Hal_3Sn-M'(CO)_5$$

where M′ = Mn, Re and Hal = Cl, Br.

In cobalt-containing complexes a metal–metal bond always undergoes cleavage on treatment with halogens under any conditions.

Germyl derivatives of Group VII metal carbonyls do not react with halogen hydrides, whereas the stannyl derivatives do interact with them, the carbon–tin bonds being cleaved while the metal–metal bonds are maintained. The replacement of phenyl groups may be partial or complete depending on the reaction conditions. The above reactions of the dimetallic derivatives are analogous to those of classical organotin compounds.

Reactions between trimetallic complexes and hydrogen halides also involve replacement of phenyl groups and preservation of metal–metal bonds, e.g.

$$(C_6H_5)_2Sn[Mn(CO)_5]_2 \xrightarrow{+2HCl} Cl_2Sn[Mn(CO)_5]_2 .$$

A metal–metal bond is considerably stabilised by the presence of electronegative substituents attached to the non-transition metal. Thus the interaction of $(C_6H_5)_3SnFe(CO)_2C_5H_5$ with mercuric chloride is accompanied by cleavage of the tin–iron bond, whereas the corresponding chloro-derivative does not react:

$$(C_6H_5)_3SnFe(CO)_2C_5H_5 + HgCl_2 \rightarrow (C_6H_5)_3SnCl + ClHgFe(CO)_2C_5H_5 .$$

On interaction with nucleophilic agents, halogen-containing germyl and stannyl derivatives of metal carbonyls, like

ordinary organometallic halides of Group IV elements, exchange halogens for the corresponding anions to form derivatives having different functional substituents attached to the non-transition metal atom, the metal–metal bonds being preserved [88–90]:

$$[L(CO)_mM']_2MCl_2 + 2R^- \rightarrow [L(CO)_mM']_2MR_2$$

where R = NO_2, NO_3, C_2H_3S, C_5H_5, NCS, etc.

From these reactions it has been possible to ascertain the behaviour of metal–metal bonds in these complexes towards various nucleophilic reagents and different reaction media, and to prepare several derivatives containing donor or acceptor substituents attached to the non-transition metal atom. Under these conditions the stannyl derivatives of carbonyls of Groups VII and VIII metals have proved to be the most stable. Derivatives of Group VI metals readily break down in alkaline media. On the other hand, derivatives of iron carbonyl show exceptional stability towards both acidic and alkaline reagents. Derivatives of manganese and rhenium carbonyls occupy an intermediate position, the former being the less stable. Derivatives of cobalt carbonyl are the most sensitive to conditions in the exchange reactions.

The germyl and stannyl derivatives of manganese, rhenium, and iron react with Grignard reagents in the normal fashion:

$$Br_3GeMn(CO)_5 + 3C_6H_5MgBr \rightarrow (C_6H_5)_3GeMn(CO)_5$$

$$[C_5H_5(CO)_2Fe]_2MCl_2 + 2RMgX \rightarrow [C_5H_5(CO)_2Fe]_2MR_2$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5 and M = Ge, Sn.

The carbonylmetal portions of dinuclear and polynuclear derivatives exhibit all the properties characteristic of ordinary metal carbonyls: they are able to exchange the carbonyl groups for other ligands, e.g. triphenyl-phosphine, -arsine, and -stibine, without cleavage of metal–metal bonds:

$$R_3SnM'(CO)_5 + P(C_6H_5)_3 \rightarrow R_3Sn{-}M'(CO)_4P(C_6H_5)_3 .$$

Investigation of these reactions has shown that the ease of exchange is largely governed by the electronegativity of the substituents attached to the non-transition metal atom. The presence of electron-acceptor substituents facilitates exchange; electron-donor substituents, on the other hand, make exchange more difficult.

Derivatives containing two metal atoms undergo extremely interesting photochemical reactions with π-donor ligands. Thus the ultraviolet irradiation of $(C_6H_5)_3Sn{-}Fe(CO)_2C_5H_5$ in the presence of ethylene at atmospheric pressure results in the detachment of one carbonyl group with the formation of a π-ethylene complex:

$$(C_6H_5)_3Sn{-}Fe(CO)_2C_5H_5 + CH_2{=}CH_2 \xrightarrow[\text{benzene}]{h\nu} (C_6H_5)_3Sn{-}Fe(CO)(CH_2{=}CH_2)C_5H_5 + CO .$$

An X-ray study of the crystalline structure of compounds [91] containing tin–iron, tin–manganese, and tin–cobalt bonds has shown that the metal–metal bonds are always shorter than the sums of the singly bound covalent radii of the metals and are very sensitive to the nature of substituents attached to the Group IVb atom. Thus in compounds of the type $X_2Sn[Fe(CO)_2C_5H_5]_2$ increase in the electronegativity of X is accompanied by an appreciable shortening of the tin–iron bonds together with an increase in the iron–tin–iron angles (see Table).

In the same series of compounds there is observed a parallel increase in the frequency νCO, which indicates an increase in the carbon–oxygen bond order:

$$X{-}Sn{-}M{=}C{=}O \leftrightarrow \bar{X}{-}Sn{-}M{-}C{\equiv}\overset{+}{O} .$$

Compound	Bond lengths, Å			Fe–Sn–Fe angle, °	ν_{CO}, cm^{-1}	$\sigma_{C_5H_5}$,* p.p.m.
	Sn–Fe	Fe–CO	C–O			
$(CH_3)_2Sn[Fe(CO)_2C_5H_5]_2$	2.60	1.72	1.20	124	1981	4.91
$(ONO)_2Sn[Fe(CO)_2C_5H_5]_2$	2.56	1.72	1.19	126	2027	4.93
$Cl_2Sn[Fe(CO)_2C_5H_5]_2$	2.49	1.76	1.08	128.6	2022	5.19

*These are apparently τ-values (Ed. of Translation).

All these changes have been explained by the hypothesis of $d_\pi{-}d_\pi$ interaction between completed *d*-orbitals of the transition metal and vacant *d*-orbitals of the tin atom, with a consequent increase in order of the tin–iron bond. Further support for the occurrence of such interaction has been obtained from an analysis of the infrared spectra [79], the most convenient for investigation being those of manganese carbonyl derivatives of the type $X_3MMn(CO)_5$. These compounds have an approximately octahedral structure, with a substituent other than carbonyl at one of the vertices of the octahedron. The presence of two types of carbonyl groups (equatorial and axial) in these molecules enables us to delimit the transmission of electronic effects of MX_3 substituents through the metal atom to the carbonyl groups.

Analysis of the infrared spectra reveals that the frequency of the vibrational band due to equatorial carbonyl groups varies linearly with the Taft inductive σ^*-parameter for the MX_3 groups, whereas the vibrational frequency of the axial group is influenced by both inductive and mesomeric effects of the substituent.

All compounds containing a bond between a manganese atom and a non-transition element of Group IVb exhibit a considerable contribution of $d_\pi{-}d_\pi$ interaction to the metal–metal bond.

The infrared spectra of π-cyclopentadienyl derivatives of the carbonyls of molybdenum, tungsten [92], and iron [93] containing M–Ge or M–Sn bonds, of the types $[C_5H_5(CO)_3M']_2MX_2$ and $[C_5H_5(CO)_2Fe]_2MX_2$, exhibit satisfactory correlation between the frequencies νCO and the σ^*-values for the substituents X, which indicates a predominantly inductive transfer of electronic effects from substituents of the non-transition metal to carbonyl groups located at an angle to the metal–metal bond.

In a study of the infrared spectra of compounds of the type $X_2M[Fe(CO)_2C_5H_5]_2$, where M = Ge or Sn, it has been suggested that rotational isomers of these compounds are present in solutions, as a consequence of rotation about the germanium–iron or tin–iron bonds [94]. Analogous isomers are possible also with molecules containing one metal–metal bond, in which several different substituents are attached to the non-transition metal atom. This hypothesis has been confirmed for the compound $CH_3Cl_2GeFe(CO)_2C_5H_5$ by determining the relative intensities of the νCO bands in the infrared spectra in various solvents and at various temperatures.

4. Organometallic Compounds of Titanium, Zirconium, and Hafnium

Nesmeyanov, Nogina, and their coworkers have investigated cyclopentadienyl derivatives of titanium, which exhibit several fundamental differences from ferrocene and its derivatives. They have established that cyclopentadienyl compounds of titanium readily decompose under the action of nucleophilic reagents [95-97]. In several cases, for example $C_5H_5Ti(OC_2H_5)_3$ and $(C_5H_5)_2Ti(OCOCH_3)_2$, the Ti–C_5H_5 bond is cleaved even by treatment with ethanol at 20°C. Furthermore, mono- and di-cyclopentadienyl derivatives of quadrivalent titanium, unlike ferrocene, undergo no substitution reactions (acylation, alkylation, mercuration, cyanation, and probably radical substitution reactions). In this connection Nesmeyanov concerned himself mainly, in the chemistry of the cyclopentadienyl derivatives of titanium, with the exchange of ligands on the titanium and the accompanying change in the properties of the Ti–C_5H_5 bond. Several convenient and accessible methods were developed for preparing various types of mono- and di-cyclopentadienyl derivatives of titanium [98-101]. Examples are methods for synthesising trialkoxides, trihalides, and also cyclopentadienyl derivatives of titanium which are at the same time inner-complex compounds, as well as compounds containing different atomic groupings (alkoxy-, aryloxy-, and acyloxy-groups, halogen atoms, and several others) attached simultaneously to the titanium atom.

Chemical and physical methods have been used to investigate the way in which the effect of various ligands is transmitted through the titanium atom to the cyclopentadienyl ring [102-104]. It was found that, as the number of electron-acceptor halogen atoms in the molecule decreases, the yield of cyclopentadiene produced by the alcoholysis and hydrolysis of the above substances increases, as also the yield of ferrocene on reaction with the iron(II) ion [102-104]. This chemical behaviour, combined with the results of comprehensive physical investigations of these compounds by infrared, mass, and nuclear magnetic resonance spectroscopy and conductivity measurements on several substances, has led to the conclusion that the bond between titanium and the cyclopentadienyl ring becomes more polar as the electron-acceptor properties of the ligands diminish [102-104].

The nature of the ligands combined with the titanium affects also the type of rotation of the cyclopentadienyl rings in its dicyclopentadienyl derivatives, as has been shown by nuclear magnetic resonance. The presence of bulky ligands on the titanium impedes rotation of the rings, probably owing to the "catching" of hydrogen atoms in rings located at an angle to one another [105].

Investigation of a large number of monocyclopentadienyl derivatives of titanium by infrared spectroscopy over the range 200–500 cm^{-1} has enabled an assignment to be made of the titanium–cyclopentadienyl ring and titanium–halogen stretching vibrations [106].

Nesmeyanov, Brainina, and their coworkers [107-109] developed several new methods for synthesising cyclopentadienyl compounds of zirconium and hafnium. They prepared and made a detailed investigation of novel types of compounds, such as cyclopentadienyl-oxans containing two metal atoms, mixed compounds containing zirconium (or hafnium), cyclopentadienyl rings, and chelate groups.

Nesmeyanov and Kritskaya studied π-allyl complexes of iron of the type tricarbonyl-π-allyliron halides and di-π-allyliron and carbonyl. In particular, they showed that the π-allyl groups underwent rotation about an axis passing through the centre of the plane of the allyl ligand and the iron atom. The magnitude of the rotational barrier depends on the nature of other groups present in the molecule [110-113].

The same workers have shown that complexes of π-benzyl type are formed comparatively easily with iron by fused aromatic systems starting with naphthalene. Several compounds have been prepared in which naphthylmethyl groups are simultaneously attached to iron by both π- and σ-bonds. π-Benzyls represent a novel type of ligands—the benzologues of π-allyl. [114]

III. ORGANOMETALLIC COMPOUNDS OF NON-TRANSITION METALS AND PROBLEMS OF CONJUGATION, DUAL REACTIVITY, AND TAUTOMERISM

During recent years Nesmeyanov's researches have been concentrated mainly on expanding the chemistry of organometallic compounds of the transition metals. Investigations on compounds of non-transition metals, which are still going on, represent mainly an extension of previously established lines of research, described in detail in a previous review [1]. Therefore they will be only briefly discussed below. During recent years these lines of research have already been independently continued by Nesmeyanov's students. They include the work by O. A. Reutov and his coworkers on the stereochemistry of the electrophilic substitution of a metal at saturated and ethylenic carbon atoms, a series of papers by I. F. Lutsenko et al. on organometallic derivatives of oxo-compounds, and several others.

In studying the properties, structural peculiarities, and effect of atoms and groups on the reactivity of organometallic compounds Nesmeyanov made a big contribution to the solution of important theoretical questions of general significance for chemical science. For example, the investigation by Nesmeyanov, Freidlina, and Borisov of β- and α-alkylated organometallic compounds ("quasi-complex" compounds) led not only to several general methods for the preparation of various compounds of this class and the solution of the hitherto controversial question of their structure but also to new ideas on the dual reactivity of substances, on the "transfer of the reactive centre" along a chain of $\sigma\pi$-, $\sigma\delta$-, $p\pi$-, and $p\sigma$-conjugation in a molecule, and to distinguishing these phenomena from those of tautomerism as equilibrium isomerisation. Many of these ideas have entered widely into the general practice of chemical research.

Nesmeyanov and Lutsenko expanded the investigation of this field by developing a method for the preparation of α-mercurated aldehydes and ketones as well as carboxylic esters, and studying their properties. Compounds having this structure were also found to exhibit dual reactivity.

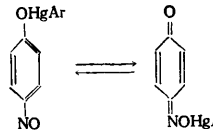
These investigations by Nesmeyanov and Borisov also laid the foundations of the stereochemistry of unsaturated organometallic and organoelementary compounds. They developed methods for the synthesis, separation, and identification of various β-substituted *cis*- and *trans*-unsaturated organometallic compounds, and established the main stereochemical laws in exchange reactions and the reduction of such compounds. These workers formulated the general rule that the geometrical configuration is maintained during electrophilic and radical substitutions at an ethylenic carbon atom [2]. The value of this rule is fully comparable with the well known rules of inversion and non-inversion of stereochemical configuration in the chemistry of optical isomers.

A series of papers by Nesmeyanov and Sazonova on the dual reactivity of metal (magnesium, lithium, sodium, etc.) derivatives of diphenylpropiomesitylene are closely related in concept to the investigation of quasi-complex compounds and α-mercurated oxo-compounds. These enolates were obtained in two stereoisomeric forms—*cis* and *trans*—which under certain conditions were incapable of mutual conversion, i.e. of tautomeric transitions [2]. The investigation under these conditions of the dual reactivity of these enolates served as the experimental basis for extending concepts of dual reactivity and migration of the reactive centre, developed in the study mainly of covalent mercury compounds, to the reactions of ordinary metallic derivatives of keto-enolic and other tautomeric systems and for generalising them throughout the field of tautomerism. Over this period Nesmeyanov has published a series of summary papers [115-117], devoted to problems of tautomerism and dual reactivity.

During recent years the further development of work on vinyl compounds of metals has led Nesmeyanov and Borisov to the synthesis of those of antimony, arsenic, tin, and germanium, and the preparation of ethylene derivatives containing two organometallic groups attached to the ethylenic bond, in which the metal atoms are either like or unlike [118-121]. The structure of β-chlorovinyl compounds of mercury has been confirmed by nuclear magnetic resonance, and the rate of acidolysis of the *cis*-isomer shown to be lower than that of the *trans*-isomer, in confirmation of Nesmeyanov's earlier concept of σπ-conjugation in these compounds and of a link between the geometric configuration of their molecules and their reactivity [122-124].

Nesmeyanov and his coworkers have developed a method for the synthesis of trichloromethyl- and polyhalogenomethyl-mercury salts and trichloromethylarylmercury, which are of interest as a source of halogenated carbenes which cannot be obtained in alkaline medium [125].

Nesmeyanov and Kravtsov have used spectroscopic methods in a broad investigation of the structure of organometallic derivatives of tautomeric and potentially tautomeric systems in which the bonds between metal and cation-acceptor centre are of low polarity. They have established that in most cases the organometallic derivatives have the structure of one of the two possible tautomeric forms, the nature of which depends on the character of the metal atom and the atom of the tautomeric substance [126-129]. Nevertheless, in the cases of the organomercury, organolead, and organotin derivatives of nitrosophenols this work resulted in the discovery of the phenomenon of metallotropy, i.e. the reversible migration of the organometallic grouping in the tautomeric system, and the position of tautomeric equilibrium was shown to depend on the nature of the solvent, of the organometallic grouping, and of substituents in the system, e.g. nitrosophenol [130]. Similar results were obtained for the *N*-organomercury derivatives of arylsulphonylaminopyridines [131]. It was then established for *N*-organomercury derivatives of halogenoimidazoles that intermolecular coordination in the crystalline state can lead to intermolecular mesomerism, in which the metal is simultaneously bound to both possible cation-acceptor centres in the tautomeric system [132]:



An analogous structure, intermediate between two possible states, is possible in intramolecular mesomerism, which is characteristic of the mercury and organomercury derivatives of cyclopentadiene [133]. Thus it has been shown that, depending on the character of the tautomeric system, the nature of the metal, and the physical state, every possible type of structure—(1) one of the extreme forms, (2) tautomeric equilibrium of the two forms, and (3) inter- and intra-molecular mesomerism—can be found in the metal derivatives of tautomeric systems. Thus to the only known form of cationotropy—prototropy—is added a new type—metallotropy.

Nesmeyanov's investigations on the structure of organometallic derivatives of tautomeric systems made it necessary to clear up several related questions of theoretical organometallic chemistry. In the course of this work it was established that the electronic effect of mercury-containing substituents is inductive in character, being markedly dependent on the nature of the solvent, and it was also demonstrated that organomercury, organolead, and organotin groups are capable of intramolecular coordination with halogen atoms [134-136].

IV. INVESTIGATIONS ON ORGANIC COMPOUNDS

Studies of dual reactivity and tautomerism belong equally to organometallic and to organic chemistry. Passing now to a brief account of certain new results of Nesmeyanov's researches in the field of organic chemistry, we may mention a series of papers (with R. Kh. Freidlina, E. I. Vasil'eva, F. K. Velichko, L. I. Zakharkin, Sh. A. Karapet'yan, V. N. Kost, R. G. Petrova, E. Ts. Chukovskaya, and others) on radical telomerisation and rearrangements of radicals, which have been partly described above [1]. At the present time investigations in this field are being conducted over a broad front by Nesmeyanov's students.

1. Investigations on β-Substituted Vinyl Ketones

A characteristic feature of Nesmeyanov's research activity is the close interlinking of three branches of chemistry—theoretical, organic, and organoelementary—which can be especially clearly traced in his work on β-substituted vinyl ketones [137,138].

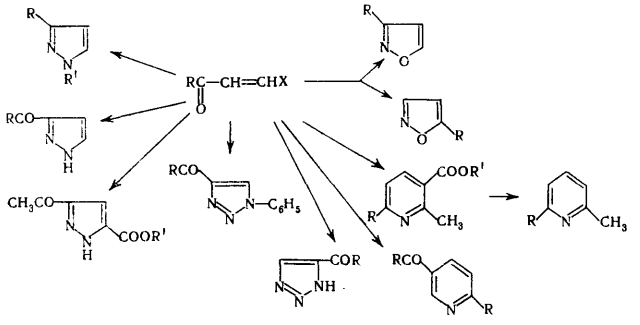
The high activity of the carbonyl group together with the mobility of the β-substituent in compounds of the type RCOCH : CHX was successfully exploited by Nesmeyanov Kochetkov, and Rybinskaya to develop methods for the synthesis of various five-membered nitrogen-containing heterocycles. Nesmeyanov, Kochetkov, and their coworkers used the same compounds to develop methods for the synthesis of pyridine derivatives (see Scheme 7).

Especially interesting examples of these heterocycles were cations isoelectronic with naphthalene and phenanthrene and containing an onium heteroatom $\dot{O}=$ or $>\dot{N}=$. Thus the reaction of β-chlorovinyl ketones with phenols and 2-naphthol was used to develop a method for the synthesis of benzopyrylium, flavylium, and naphthopyrylium salts. Subsequently the synthesis has been accomplished of heterocyclic cations containing an ammonium nitrogen atom in a bridge, so called dehydroquinolizinium salts and their 1-aza- and 1,9-diaza-analogues [138] (see Scheme 8).

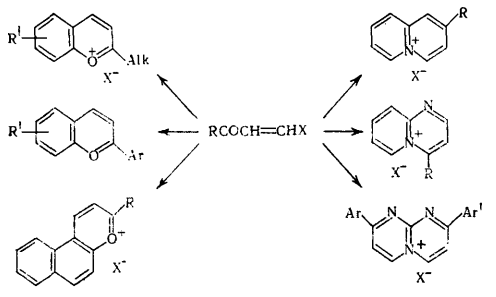
After the rule that geometrical configuration is maintained during electrophilic and homolytic substitution at an ethylenic carbon atom had been formulated, Nesmeyanov, Kochetkov, and Rybinskaya undertook a study of the

stereochemistry of nucleophilic substitution, choosing β-substituted vinyl ketones as model compounds. This investigation required a great amount of preliminary work, which involved developing a broad synthetic method, termed β-ketovinylation [138]. The reaction of β-ketovinylation, which is now taken to imply the introduction of a ready made RCOCH : CH group into a molecule, has permitted the preparation of the most diverse *cis*- and *trans*-β-substituted vinyl ketones. The ketovinyl fragment in these compounds was combined with atoms of various elements, such as carbon, nitrogen, oxygen, sulphur, hydrogen, iron, cobalt, and tungsten. Development of the method of ketovinylation resulted in the synthesis of organic compounds of various classes. In the course of this investigation the choice of ketovinylating agent was shown to be very important, and basic principles for such choice were formulated. For example, β-chlorovinyl ketones can be used for the ketovinylation of weakly basic and strongly polarised anions such as SCN^-, $SC_6H_5^-$, $SO_2C_6H_5^-$, N_3^-, etc., whereas in the case of strongly basic and relatively unpolarised nucleophiles (Alk, Ar^-, H^-, NH_2NH_2) the reaction leads to an addition product involving the carbonyl group [138]. This example thus provides evidence that, in the choice of ketovinylating agent, the selectivity of nucleophilic reagents towards a definite reaction centre has to be taken into account. For the ketovinylation of strongly basic and weakly polarised nucleophiles, therefore, the use of β-dimethylaminovinyl ketones was recommended. Furthermore, very active quaternary β-acylvinyltrimethylammonium salts were proposed [138] for very weakly nucleophilic anions ($OCOCH_3$, NO_2, etc.).

Scheme 7

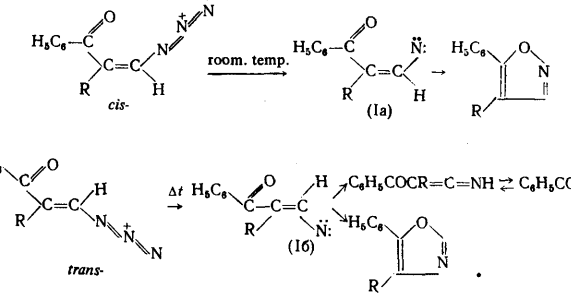


Scheme 8



As a result of this large amount of synthetic work it was found that the most convenient model reaction for studying the stereochemistry of nucleophilic substitution at an ethylenic reaction centre is the reaction of compounds C_6H_5COCR : CHX with the azide ion in various media.

Nesmeyanov and Rybinskaya showed by means of this reaction that the stereochemical course of nucleophilic substitution at an ethylenic carbon atom depends on the nature of the group X which is eliminated. For substrates having X groups (such as the chloride anion) which are "readily removable" as anions it was found that the geometrical configuration was preserved. In the case of "slowly removable" groups X (such as $C_6H_5SO_2$) the reaction resulted mainly in formation of the thermodynamically more stable isomer; and with "very difficultly removable" groups (X = CN, SO_3^-), reaction with the azide ion yields, instead of β-azidovinyl ketones, the isomeric 4-acyl-1,2,3-triazoles. The stereochemical results obtained in this way enabled a mechanism of direct substitution with intermediate formation of carbanions to be suggested for nucleophilic substitution at an activated double bond, and this is supported also by kinetic investigations [138]. A very interesting rearrangement was studied on β-azidovinyl ketones as example, which showed that stabilisation of the intermediate nitren species (Ia and Ib) depends mainly on its configuration:



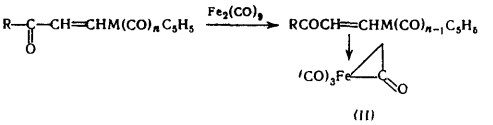
Very interesting compounds, β-aminovinyl ketones, were prepared by β-ketovinylation, and these exhibited a new type of tautomerism, ketiminol ⇌ enamineketone [138].

Another line of research deriving from the study of ketovinylation reactions was concerned with determining the orientation of nucleophilic attack in XCH : CHY systems, where X and Y are strong electron-acceptor groups. The kinetic investigation by Nesmeyanov, Rybinskaya, and Rybin led to a hypothesis which enabled the orientation of nucleophilic attack for systems of this type to be predicted by comparing data on the kinetic or thermodynamic acidities of the corresponding methyl derivatives CH_3X and CH_3Y. These workers started from the view that the orientation of nucleophilic attack should depend on the relative stability of the intermediate carbanions XCH–CHYZ and XZHCH–CHY (where Z is the nucleophilic reagent) [137].

The chemistry of β-substituted vinyl ketones has recently been considerably added to by the investigations of Nesmeyanov and his coworkers on σ- and π-complexes of transition metals, in which β-substituted vinyl ketones were used as ligands. The employment of complex anions $[Fe(CO)_2C_5H_5\text{-}\pi]^-$, $[W(CO)_3C_5H_5\text{-}\pi]^-$ (pyridinatocobaloxime)$^-$ in ketovinylation led to synthesis of the complexes σ-RCOCH : CH.ML_n (where M is a transition metal and L a unidentate ligand). [138]

However, β-substituted vinyl ketones have been most widely used for the preparation of σ-complexes with iron carbonyls [139–142], in which it was possible to trace qualitatively the variation in the complexing power of RCOCH : CHX with the nature of the substituent X. This investigation showed that π-complexes are not formed from ligands containing strongly electron-donor groups (e.g. X = $NAlk_2$) or from RCOCH : CHX in which X = CN, NO_2. In the

latter two cases polymers were isolated having a non-stoichiometric iron content. Stable complexes were obtained only from ligands having X = Cl, SO_2R, COOR, COC_6H_5. Comparison of these results with the calculated energies of antibonding orbitals for the corresponding ligands showed that this energy is too high for a stable π-complex to be formed in the case of RCOCH : $CHNAlk_2$ and too low for the ligands RCOCH : CHX (X = CN, NO_2). The formation of polymers having a non-stoichiometric iron content was explained by the possibility of complete transfer of an electron from the metal to the ligand. The radical-anion obtained $(RCOCH : CHX)^{\cdot -}$ could in turn give rise to a polymeric chain. It is interesting that on π-coordination with metals the ligands maintained their original configuration. Investigation of σ-ketovinyl complexes in reactions with $Fe_2(CO)_9$ enabled Nesmeyanov and his coworkers to obtain a series of novel mixed dinuclear $\sigma\pi$-complexes of type (II), characterised by a metal–metal bond and a bridging carbonyl group:



(II)

where M = Fe, $n = 2$ and M = W, $n = 3$.

2. Onium Compounds

The first investigation of this series was made in 1929, when Nesmeyanov examined the decomposition of the double salts formed by diazonium compounds with mercury(II) iodide, and established the formation of iodonium salts [143]:

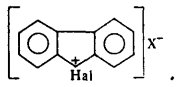
$$C_6H_5N_2HgI_3 \text{ and } (C_6H_5N_2)_2HgI_4 \rightarrow [(C_6H_5)_2HgI_4] + N_2 \ .$$

Some of the most recent (1967) work on these lines is described in a paper on the reactions of arenediazonium fluoroborates with substituted iodobenzenes, which showed the effect of the nature of nuclear substituents both in the diazonium salt and in the iodobenzene on the yield of diaryliodonium salts [144].

A set of methods was developed constituting the onium synthesis [2], based on transfer of the aryl radical or aryl cation of the onium compounds to a metal atom, salts, unsaturated compounds, and substances containing atoms having a lone pair of electrons—O, S, Se, N, P, As, Sb, Cl, Br, I.

The most general results of these investigations include firstly the establishment of two types of decomposition of diazonium, iodonium, and certain other onium salts with transfer of aryl cations or aryl radicals [145]. Conditions which determine the type of decomposition have been worked out (effect of structure of aromatic nucleus of onium compound, nature of salt anion, nature of substrate (aryl acceptor), nature of solvent, presence of catalyst, etc.). The rules established by Nesmeyanov together with Makarova, Tolstaya, et al. for the directed synthesis of various compounds from diazonium or other onium salts are now widely used in synthetic practice (e.g. the synthesis of arylisothiuronium salts by the reaction of arenediazonium fluoroborates with thiourea [146,147]).

Another most important result of this work was the contribution of the onium method to the synthesis of previously unknown types of compounds of multivalent chlorine, bromine, oxygen, nitrogen, and sulphur. Thus, in contrast to compounds of multivalent iodine, which have been known for a long time, the simplest compounds of multivalent chlorine and bromine—diarylchloronium and diarylbromonium salts—were unknown before the work of Nesmeyanov, Tolskaya, and their coworkers [148,149]. Only heterocyclic compounds of this type were known previously [150]:



It appeared that a heterocyclic position of the halogenonium grouping was a necessary condition for the existence of sufficiently stable halogenonium compounds. However, Nesmeyanov, Tolstaya, and their coworkers obtained numerous symmetrical and unsymmetrical diaryliodonium and diarylbromonium salts, as well as heterocyclic compounds of this type. The synthesis of diarylchloronium and diarylbromonium salts was accomplished by the reaction of arenediazonium fluoroborates with aryl halides:

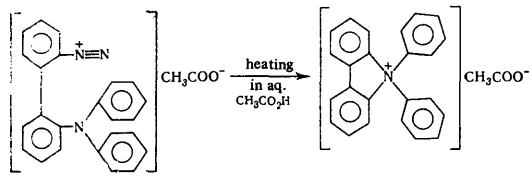
$$ArN_2BF_4 + Ar'Hal \rightarrow [ArAr'Hal]^+BF_4^- \xrightarrow{+X^-} [ArAr'Hal]^+X^- \ .$$

It proved possible to prepare the hitherto unknown triaryloxonium salts by the same method [151]:

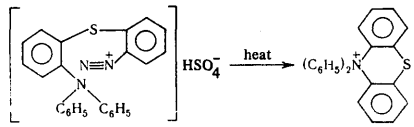
$$ArN_2BF_4 + Ar_2O \rightarrow [Ar_3O^+]\,BF_4^- \xrightarrow{X^-} [Ar_3O^+]\,X^- .$$

In contrast to Meerwein's trialkyloxonium salts [152,153], triphenyloxonium salts are extremely stable compounds, decomposing only when heated above 150°C.

Completely aromatic onium compounds had been known for all elements other than nitrogen in the main subgroup of Group V of the Periodic System. Tetra-arylammonium salts could not be obtained by the arylation of triphenylamine with diphenyliodonium fluoroborate. Compounds of this type, namely *NN*-diphenylcarbazolium salts, could be prepared [154] by the reaction



The same workers have recently described the preparation and properties of another fully aromatic ammonium cation, *NN*-diphenylphenothiazinium [155]:



When benzenediazonium fluoroborate decomposes in a mixture of dimethyl sulphoxide and chlorobenzene, bromobenzene, or acetone, the sulphoxide sulphur undergoes arylation with the formation of hitherto unknown onium salts of dimethyl phenyl sulphoxide [156]:



Nesmeyanov and his coworkers have made a broad investigation of the reactions of the newly prepared onium compounds. They have shown, for example, that diphenylchloronium and diphenylbromonium salts are nitrated in the *meta*-position, thus conforming to the general rule of orientation in the nitration of aromatic onium compounds. On the other hand, the nitration of triphenyloxonium fluoroborate, which could be accomplished only under severe

conditions (with a mixture of anhydrous nitric and concentrated sulphuric acids at 100°C), yields tri-*p*-nitrophenyloxonium fluoroborate. The nitration of triphenyloxonium fluoroborate by means of nitryl tetrafluoroborate takes place even at room temperature and also leads to the same tri-*p*-nitrophenyloxonium fluoroborate.

The explanation given for the unusual behaviour of the triphenyloxonium cation was that the strong negative inductive effect of the oxonium oxygen, which inactivated the phenyl rings, was nevertheless associated, as in the halogenobenzenes, with conjugation of the lone pair of electrons on the oxygen atom with the π-electrons of the phenyl (+ *T*-effect). [157]

Tri-*p*-nitrophenyloxonium fluoroborate was reduced to the corresponding amino-derivative. The basic properties of the amino-groups in tri-*p*-aminophenyloxonium salts are appreciably weakened under the influence of the oxonium oxygen. These amino-groups are diazotised only under conditions for the diazotisation of weakly basic amines, e.g. by the action of nitrosylsulphuric acid. The tri-*p*-aminophenyloxonium cation is formally analogous in structure to the parafuchsine cation, but, unlike the latter, is colourless [158]. Explanations are given for this difference. For the infrared spectra of diphenylhalogenonium and triphenyloxonium compounds see Ref. 159.

Quite recently Nesmeyanov has shown, together with Makarova, Chapovskii, and Ustynyuk, that a rylation by diazonium and other onium compounds can be used for the synthesis of σ-aryl derivatives of transition metals. The action of benzenediazonium, diaryliodonium, and triphenylsulphonium salts on the anions of cyclopentadienylcarbonyl-iron [160,161], -tungsten [162], and -molybdenum [163] has yielded their σ-aryl derivatives. Thus the σ-phenyl derivative has been obtained by the interaction of triphenylsulphonium fluoroborate with the sodium salt of π-cyclopentadienyldicarbonyliron:

$$\pi\text{-}C_5H_5Fe(CO)_2Na + [(C_6H_5)_3S^+]\,BF_4^- \rightarrow \pi\text{-}C_5H_5Fe(CO)_2C_6H_5 \ .$$

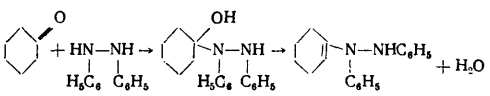
Let us make a brief mention of Nesmeyanov's work on hydride migration. In 1960 Nesmeyanov and Golovnya showed for the first time that the nitrogen atom in the azo- and diazo-groups of organic compounds can act as an acceptor for hydridic hydrogen, being more vigorous than the carbonium cation [164]. Salts of azobenzene with electrophilic reagents such as boron trifluoride, sulphuric acid, hydrobromic acid, hydrochloric acid, orthophosphoric acid, zinc chloride, etc. were able to remove hydride hydrogen from most organic solvents.

The surprising ability of azobenzene to abstract hydrogen from compounds which are so stable to oxidation as benzene, nitrobenzene, cyclohexane, and n-hexane, the ease of occurrence of the reaction with cycloheptatriene, and also the absence of reaction with chloroform and nitromethane led these workers to suggest the following reaction mechanism

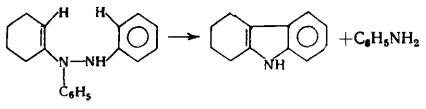
$$[C_6H_5{-}NH{=}N{-}C_6H_5]^+HSO_4^- + H{:}\,C\!\!<\!\!\rightarrow C_6H_5NH{-}NH{-}C_6H_5 + \overset{+}{C}\!\!<\!\!\rightarrow + HSO_4^-$$

$$C_6H_5NH{-}NH{-}C_6H_5 + H_2SO_4 {-} (NH_3^+C_6H_4)_2SO_4^{2-} \ .$$

In the course of their investigation [164] Nesmeyanov and Golovnya discovered a new variant of the classical Fischer–Arbuzov synthesis of indoles. They showed that in the presence of boron trifluoride azobenzene reacts with cyclohexanone to form tetrahydrocarbazole. The reaction takes place also with homologues of cyclohexanone. The first stage is reduction of the azobenzene by hydride hydrogen abstracted from the cyclohexanone, the resulting hydrazobenzene reacts with the ketone to give the corresponding one–hydrazine:



and this cyclises to tetrahydrocarbazole with the elimination of aniline (not ammonia, as in the usual indole ring-closure):



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