Translated from *Uspekhi Khimii*, **43**, 1035-1049 (1974) U.D.C. 543.51 : 547 : 186; 547.402

Mass Spectrometry of Transition Metal π-Complexes

P.E.Gaivoronskii and N.V.Larin

The problems of the fragmentation of transition metal π-complexes under the influence of electron impact are examined. The mass spectra of this class of compounds reflect fairly well the differences in the nature and stability of the metal-ligand bond as well as structural and other differences. Together with the rupture of the metal-ligand bond, electron impact results in the partial fragmentation of the ligands linked to the metal atom by π-bonds, the nature and degree of fragmentation depending on the nature and molecular weight of the ligand.
The bibliography includes 131 references.

CONTENTS

I. Introduction 466
II. Metal π-complexes with aromatic ligands 466
III. Metal π-complexes with aromatic and π-acceptor ligands 469
IV. Complexes containing groups linked by σ-bonds 470
V. Characteristics of the mass spectra of metal π-complexes and problems of the isotopic analysis of elements in the form of their π-complexes 471

I. INTRODUCTION

Volatile transition metal compounds can be conventionally divided into the following groups in terms of the type of the metal–ligand bond.

A. Chelate complexes, for example acetylacetonates.

B. Complexes with ligands of the π-acceptor type (carbon monoxide, nitric oxide, phosphines, arsines, nitriles, etc.).

C. Complexes with ligands linked by π-bonds. The ligands in such complexes are organic substances with double, triple, and conjugated bonds.

Studies on the mass-spectrometry of organometallic alkyl and phenyl compounds and metal complexes with ligands such as carbon monoxide have been described fairly completely in recently published reviews [1,2] and other reviews [3-5] deal with the mass spectra of certain transition metal π-complexes.

The present review deals with studies on the mass-spectrometry of transition metal π-complexes. The problems of the fragmentation of π-complexes and the correlation between the fundamental characteristics of the mass-spectra and the metal–ligand bond energies are considered initially. The review is also concerned with problems relating to the identification of ions containing the atoms of polyisotopic elements and with the occurrence of ion–molecule reactions in the mass spectrometer. The problems associated with the measurement of appearance potentials and the calculations on their basis of the average metal–ligand bond dissociation energy are not discussed, since they have been dealt with in detail in other reviews [2,6]. The mass-spectra of the π-complexes have been classified in accordance with the nature of the ligands, since the latter are in fact responsible for the main characteristics of the mass-spectra of the π-complexes.

II. METAL π-COMPLEXES WITH AROMATIC LIGANDS

The mass-spectra of the π-complexes of transition metals having the general formula L_1ML_2 (L = C_7H_7, C_5H_5, or C_6H_6) reflect the differences between the electron-donating capacities of the ligands but at the same time have many features in common.

Dicyclopentadienyl Compounds

Compounds of this class have been frequently investigated mass-spectrometrically [7-11]. The molecular ion peaks in the mass spectra of such complexes are as a rule the most intense and successive dissociation of the cyclopentadienyl groups from the molecular ion leads to the formation of metal ions and the fragment $C_5H_5M^+$, the peaks of which are also fairly intense. The cyclopentadienyl groups are also to a considerable degree fragmented. The group C_3H_3 and ethylene and acetylene molecules are mainly split off. When hydrogen atoms and methyl or other radicals are split off from the molecular ion, a series of ions are formed whose peak intensities are low. On fragmentation of molecular ions, the charge as a rule remains on the metal-containing fragment. The majority of fragmentation processes are accompanied by metastable transitions, with intense and distinct peaks [9].

The ionisation potentials of dicyclopentadienyl complexes are lower or equal to those of the atoms of the complex-forming elements [8,9,12,13]. This permitted the conclusion [8,9] that, in the ionisation of compounds such as ferrocene, an electron is removed from a non-bonding orbital localised at the metal atom. This conclusion is satisfactorily consistent with data calculated for ferrocene by the molecular orbital method [14].

The intensity of the metal ion peaks in the mass-spectra of the isoelectronic dicyclopentadienyl complexes of iron, ruthenium, and osmium (Table 1) decreases on passing from ferrocene to osmocene. This indicates an increase in the strength of the metal–cyclopentadienyl bond with increase of the atomic number of the complex-forming element. The metal–ligand bond energies for ferrocene and ruthenocene quoted in Table 1, calculated from the appearance potentials of iron and ruthenium ions, confirm this. An analogous correlation between the mass spectra and the appearance potentials was observed for chromium, molybdenum, and tungsten hexacarbonyls [15-18].

The relative intensity of the metal ion peaks in the spectra of a series of dicyclopentadienyl compounds of vanadium, iron, nickel, and chromium increases, amounting respectively to 12.5, 16.1, 18.9, and 28.2% of the overall intensity of the peaks [8]. The increase is due to the decrease of the average metal–ligand bond dissociation energy, which is 88, [19] 74, [20] 62, [20] and 54 [21] kcal $mole^{-1}$ respectively.

The substitution of hydrogen atoms in the ligands can have a significant influence on the nature of the fragmentation. The study of the mass-spectra of substituted ferrocenes [22-28] showed that simple substituents (methyl and ethyl groups and halogen atoms) hardly affect the nature and degree of fragmentation. More complex substituents give rise to a number of characteristic features associated with the fragmentation of the substituent itself. In compounds containing alkyl and vinyl substituents in the same ring, cyclopentadienyl (Cp) groups without substituents are split off preferentially [25].

Table 1. Relative peak intensities of the principal ions in the mass-spectra and the metal–ligand bond dissociation energies in the dicyclopentadienyl complexes of iron, ruthenium, and osmium (%).

Ion	Fe	Ru	Os
$(C_5H_5)_2M^+$	100	100	100
$C_5H_5M^+$	36	21.7	2.7
M^+	27	2.8	0.5
D_{M-L}, kcal mole^{-1}	78	112	—

The mass-spectra of cyclopentadienyl compounds also reflect satisfactorily the degree of polarity of the metal–cyclopentadienyl bond. In order to demonstrate the influence of the nature of the metal–cyclopentadienyl bond on the characteristics of the fragmentation and the nature of the mass-spectrum, it is useful to compare the mass-spectra of dicyclopentadienyl π-complexes with those of ionic and σ-linked dicyclopentadienyl compounds. Thus the fragmentation of ionic dicyclopentadienyl magnesium and manganese compounds † [8,9] proceeds in the same way as in compounds of the ferrocene type. However, an increase in the amount of ionic character of the metal–cyclopentadienyl bond reduces the relative intensity of the molecular ion peaks and increases the intensity of the fragment ion peaks (Table 2).

Table 2. Relative peak intensities of the principal ions in the mass-spectra of the dicyclopentadienyl complexes of iron, magnesium, and manganese (%).

Ion	Fe	Mg	Mn
$(C_5H_5)_2M^+$	100	100	100
$C_5H_5M^+$	36	171	157
M^+	27	139	136

† In contrast to ferrocene and other dicyclopentadienyl transition metal compounds, Cp_2Mn is an ionic compound. Detailed information about studies dealing with the demonstration of the ionic character of the metal–cyclopentadienyl bonds in this compound can be found in other reviews [29,30].

Under the influence of electron impact, thallium cyclopentadienide splits off the cyclopentadienyl group, giving rise to a metal ion whose peak intensity is a maximum in the spectrum [31,32].

The mass-spectra of metal dicyclopentadienyl complexes with σ linkages (see, for example, the mass-spectrum of Cp_2Pb) [33] are close to the mass-spectra of ionic dicyclopentadienyl compounds.

Tricyclopentadienyl Compounds

Tricyclopentadienyl complexes of the lanthanides, which are partly ionic and partly of the π-complex type, constitute an extremely interesting class. The relative intensity of the molecular ion peaks in the mass-spectra of these compounds is fairly high [34-37]. The elimination of the first cyclopentadienyl group leads to the formation of the ions Cp_2M^+, the relative intensity of whose peaks is as a rule maximal in the spectrum. Further fragmentation leads to the pattern which is well known for ferrocene.

In contrast to the dicyclopentadienyl compounds of transition metals, the ionisation potentials of the tricyclopentadienyl complexes exceed by 1–2 eV the ionisation potentials of the lanthanide atoms, which can probably be accounted for by the removal on ionisation of an electron which is not localised at the atom of the complex-forming element but at the ligand, as in chelated chromium acetylacetonates [38].

Tetracyclopentadienyl Compounds

The mass-spectra of the tetracyclopentadienyl π-complexes of uranium and thorium [34,39] have intense peaks due to the molecular ion and the ions formed as a result of the elimination of cyclopentadienyl groups from the latter. The peaks due to the Cp_3M^+ ions are the most intense in the spectra. As for the di- and tricyclopentadienyl complexes, in the mass-spectra of the tetracyclopentadienyl complexes of uranium and thorium contain fairly intense peaks due to ions associated with the partial fragmentation of the ligands.

Table 3. Relative peak intensities of the principal ions in the mass-spectra of bisbenzenechromium and bisbenzenevanadium (%). [40]

Ion	Cr	V
$(C_6H_6)_2M^+$	28.5	85.6
$C_6H_6M^+$	37.6	83.5
M^+	100	100
$(C_6H_6)_2M^+$	6.2	18.0

Bisarene Compounds

The intensities of the molecular ion peaks in the mass-spectra of bisbenzenevanadium [40] and bisbenzenechromium [7,13,40,41] are much higher (Table 3), which is evidence for a fairly high stability of the metal–benzene bond. However, in contrast to the dicyclopentadienyl

compounds, in the mass spectra of the bisarene complexes the peaks due to the metal ions and not the molecular ions are the most intense. This difference is evidence that the stability of the metal–ligand bond in compounds of the type LML decreases following the replacement of cyclopentadienyl groups by benzene molecules. On the other hand, comparison of the relative intensities of the molecular ion peaks in the mass-spectra of bisbenzenechromium and bisbenzenevanadium leads to the conclusion that the benzene–vanadium bond is stronger than the benzene–chromium bond. These conclusions are satisfactorily consistent with thermochemical measurements[42].

The fragmentation of bisarene compounds is extremely simple and leads to the successive elimination of benzene molecules from the molecular ion with retention of the charge on the metal-containing fragments, which is confirmed by the presence in the mass-spectra of intense and distinct peaks due to metastable transitions.

The intensities of the peaks due to the $MC_5H_5^+$, $MC_4H_4^+$, $MC_3H_3^+$, MC_2H^+, and other ions in the mass-spectra of the bisarene compounds are extremely low. This shows that the fragmentation of the π-linked ligands in the bisarene compounds hardly occurs, in contrast to the cyclopentadienyl complexes, which is related to the greater stability of the benzene ring compared with other aromatic systems and the low metal–ligand bond energy.

The study of the mass-spectra of methyl, isopropyl, and phenyl derivatives of bisbenzenechromium [43–45] showed that the nature of the mass-spectra and the fragmentation of the molecular ions in these compounds and in bisbenzenechromium are similar. In the mass-spectra of the bisarene compounds of chromium with asymmetric ligands—benzenecumenechromium and diethylbenzeneethylbenzenechromium [44,45]—the relative intensities of the peaks due to the CrL_1^+ and CrL_2^+ ions differ appreciably, which is evidence for the preferential elimination of ligands containing a smaller number of alkyl substituents. A mass-spectrometric study of benzenehexamethylbenzenemanganese[46] also showed that benzene is split off from the molecular ion more readily than hexamethylbenzene.

The peaks due to molecular ions and not the metal ion, as for bisarenechromium compounds, are the most intense in the mass-spectra of bisbenzenemolybdenum and its ethyl derivatives[47]. The sharp increase of the relative intensity of the molecular ion peaks on passing from bisbenzenechromium to bisbenzenemolybdenum is evidence, as for cyclopentadienyl and carbonyl complexes, for an increase in the strength of the metal–ligand bond with increase of the atomic number of the complex-forming element.

The ionisation potentials of the bisarene compounds are somewhat lower, as for the dicyclopentadienyl complexes, than the ionisation potentials of the complex-forming elements. The introduction of methyl substituents into bisbenzenechromium reduces the ionisation potential, but the decrease is not quite so distinct as for the free ligands[43].

A characteristic feature of the bisarene compounds is the permanent presence in their mass-spectra of fairly intense peaks due to the hydrocarbon ions of the ligands. The complete agreement of the relative intensities of the peaks due to these ions with the relative intensities of the corresponding ions in the mass-spectra of the free ligands, the formation of metallic films on the components of the ion source, the increase of the intensity of the peaks of these ions with increase of the temperature of the ion source, and the equality of the appearance potentials of the corresponding hydrocarbon ions in the mass-spectra of the bisarene compounds and the free ligands led to the conclusion[40,44] that the formation of the hydrocarbon ions is associated with the presence of free ligands in the ion source of the mass-spectrometer. The latter are formed as a result of the partial thermal decomposition of the bisarene compounds in the ion source.

Transition Metal Complexes with Asymmetric Aromatic Ligands

The mass-spectra of compounds of the type $C_5H_5MC_7H_7$, where M = V, Cr, Mo, or W, and compounds of the type $C_5H_5MC_6H_6$, where M = Mn or Cr,[7,40,48–50] reflect satisfactorily the differences between the electron-donating capacities of the C_5H_5, C_7H_7, and C_6H_6 groups. The elimination of the cyclopentadienyl group from the molecular ions of these complexes takes place after the C_7H_7 and C_6H_6 groups have been split off.

A characteristic feature of the fragmentation of the complexes containing the C_7H_7 group is the elimination from the latter of an acetylene molecule with formation of the ion Cp_2M^+ via the mechanism

$$C_5H_5MC_7H_7^+ \rightarrow (C_5H_5)_2M^+ + C_2H_2 ,$$

and the ion in its turn splits off in succession cyclopentadienyl groups with formation of the $C_5H_5M^+$ fragment and metal ions, so that the fragmentation of the C_5H_5 and C_6H_6 groups joined by π-bonds to the complex-forming atom is analogous to that of the dicyclopentadienyl and bisarene compounds.

Thus, comparison of the mass-spectra of compounds of the type $(C_5H_5)_2M$, $C_5H_5MC_7H_7$, $C_5H_5MC_6H_6$, and $(C_6H_6)_2M$, for example the mass-spectra of the isoelectronic iron, chromium, and manganese compounds (Table 4), readily demonstrates the decrease of the relative intensity of the molecular ion peak on passing from ferrocene to bisbenzenechromium. This decrease is evidence for the weakening of the metal–ligand bond due to the decrease of the electron-donating activity of the ligands in the series $C_5H_5 > C_7H_7 > C_6H_6$.

Table 4. Relative peak intensities of the principal ions in the mass-spectra of the isoelectronic complexes of chromium, manganese, iron with aromatic ligands (%)*.

Ion	$(C_5H_5)_2Fe$	$C_7H_7CrC_5H_5$	$C_5H_5MnC_6H_6$	$(C_6H_6)_2Cr$
$L_1ML_2^+$	61.5	50.4	22.6	17.2
$MC_5H_5^+$	22.4	9.5	45.1	
$C_6H_6M^+$	—	—	—	22.6
M^+	16.1	40.1	32.3	60.2

*The overall intensity of the peaks due to the ions $L_1ML_2^+$, L_1M^+, L_2M^+, and M^+ was adopted as 100%.

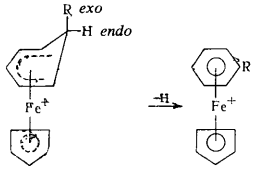
Complexes Containing Olefins Linked by π-bonds

The molecular ions of complexes containing, apart from the cyclopentadienyl group, π-linked olefins[50–53] split off the cyclopentadienyl group after the complete or

partial elimination of the olefin. Thus in the molecular ion of the $CpRh(C_2H_4)_2$ complex[50,52] the rupture of the metal–cyclopentadienyl bond is preceded by the stepwise elimination of the ethylene ligand species:

$$CpRh(C_2H_4)_2^+ \rightarrow CpRhC_2H_4^+ \rightarrow CpRh^+ \rightarrow Rh^+.$$

In complexes containing cyclo-olefins linked by π-bonds to the metal atom there is appreciable dehydrogenation of the olefin apart from the dissociation of the metal–ligand bond and partial fragmentation of the ligand species consisting in the elimination of the neutral C_2H_4, C_2H_2, and C_3H_3 groups. In a number of cases there is a stereoselective formation of aromatic fragments[54,69]:



The replacement of one cyclopentadienyl group in ferrocene by the indenyl ligand greatly complicates the nature of the fragmentation[51]. The molecular ion in the complex $CpFeC_9H_7$ loses the cyclopentadienyl group, simultaneously with the elimination of the indenyl ligand and the formation of the $CpFe^+$ ion, giving rise to the $C_9H_7Fe^+$ ion. In contrast to $CpFe^+$, the latter does not split off the indenyl ligand with formation of a metal ion but eliminates the iron atom, forming the ion $C_9H_7^+$, with a high intensity spectral peak.

The fragmentation mechanism becomes even more complicated when the indenyl group is replaced by its hydrogenation product C_9H_9 and C_9H_{11}. Dehydrogenation with formation of the $FeC_9H_8^+$ ion, which in turn loses the metal atom simultaneously with the elimination of the C_9H_8 group giving rise to the ion $C_9H_8^+$ and the products of its further fragmentation, is characteristic of these complexes. Fragmentation processes leading to the contraction of the ring with formation of the aromatic fragments $CpFeC_7H_7^+$, Cp_2Fe^+, and $CpFeC_6H_6^+$ are also characteristic of compounds containing the indenyl ligand and its hydrogenation products.

Table 5. The ionisation potentials of chromium, vanadium, manganese, and cobalt and of their complexes with benzene, the cyclopentadienyl group, and carbon monoxide.

Ion	V	Cr	Mn	Co	References
$(C_6H_6)_2M$	7.56	6.91	7.25	6.2	8
$C_6H_6MC_7H_7$	7.24	5.96	—	—	40
$(C_6H_6)_2M$	6.26	5.91	—	—	40
$C_6H_6MC_5H_5$	—	6.13	6.92		40
M	6.74	6.764	7.432	7.86	72
$C_6H_6M(CO)_3$	—	7.30	—	—	64
$C_5H_5M(CO)_4$	8.2				59
$C_5H_5M(CO)_3$	—	—	8.3	—	59
$C_5H_5M(CO_2)$	—	—	—	8.3	59
$M(CO)_6$	7.53	8.48			16
$M_2(CO)_{10}$	—	—	8.5	—	73
$M_2(CO)_4$	—	—	—	8.1	73

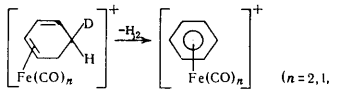
The olefin–metal complexes not containing the cyclopentadienyl group have been comparatively less well investigated by mass-spectrometry. The study of the mass-spectra of biscyclo-octa-1,5-dieneplatinum and biscyclo-octa-1,5-dienenickel[55], cycloheptadienylcycloheptatrienyltitanium[56], cyclo-octenylcyclo-octa-1,5-dienecobalt[57], and biscyclo-octatetraenethorium[58] showed that the fragmentation of complexes of this kind is analogous to that of the bisarene compounds, but the fragmentation of the π-linked hydrocarbon ligands takes place to a greater extent. The replacement of both cyclopentadienyl groups in ferrocene by indenyl groups leads to the elimination of the iron atoms from the molecular fragment ions $C_9H_7Fe^+$, which results in the presence in the mass spectrum of ions due to the indenyl ligand apart from the peaks due to metal-containing ions[51].

III. METAL π-COMPLEXES WITH AROMATIC AND π-ACCEPTOR LIGANDS

Mononuclear Complexes

The mass-spectra of the cyclopentadienyl complexes of cobalt[59], manganese[10,59–61], vanadium[59,61], rhenium[61], and iron[62] having the general formula $CpM(CO)_n$, cyclobutadienyltricarbonyliron[63], and benzenetricarbonylchromium[13,64,65] reflect satisfactorily the differences between the strengths of the metal–ligand bonds and the donor-acceptor properties of carbon monoxide, benzene, and the cyclopentadienyl group. The hydrocarbon ligands in these compounds are split off only after the complete loss of all the carbonyl groups from the molecular ion. Under these conditions, the CpM^+ ions also loses C_2H_2, C_2H_4, and other neutral groups, while there is hardly any fragmentation of the benzene ring with dissociation of carbon–carbon bonds.

The peaks due to the CpM^+ ion are the most intense in the mass-spectra of cyclopentadienyl derivatives of metal carbonyls, while the peaks of the metal ion are the most intense in the spectrum of benzenetricarbonylchromium. The carbonyl complexes with cyclic olefins behave similarly[60,62,66–69]. However, in this case the elimination of the carbonyl group and the olefin may prove to be equally probable, as has been observed for complexes of the type $C_5H_5M(CO)_2$(cyclo-olefin).[60] Moreover, dehydrogenation processes with subsequent aromatisation of the six-membered ring are characteristic of metal carbonyl complexes containing olefins, particularly those with adjacent CH_2 groups[54,69]:



The stereoselective formation of aromatic fragments proceeds in parallel with the decarbonylation of the molecular and fragment ions.

The fragmentation of substituted benzenetricarbonylchromium complexes $(CO)_3CrC_6H_5X$[64,70] depends significantly on the nature of the substituent X. The mass-spectra of the complexes with X = CH_3 and C_6H_5 hardly differ from the mass spectrum of benzenetricarbonylchromium. For electronegative substituents (Cl, F), the peaks of the rearranged ions CrX^+, the formation of which proceeds via the mechanism

$$CrC_6H_5X^+ \rightarrow CrX^+ + C_6H_5,$$

and is accompanied by a peak due to a metastable transition, exhibit an appreciable intensity in the mass spectra. The ions $CrC_6H_5X^+$ and $CrC_6H_4X^+$ lose an HX molecule with formation of the ions $CrC_6H_4^+$ and $CrC_6H_3^+$.

In the presence of more complex substituents (OCH_3, $COCH_3$, $OCOCH_3$, etc.) the peaks of the ions formed as a result of the fragmentation of the group X appear in the mass-spectra. The fragmentation of substituted cycloheptatriene and π-benzyl complexes of chromium tricarbonyl takes place similarly [71].

The ionisation potentials of benzenecarbonyl and cyclopentadienylcarbonyl complexes of transition metals (Table 5) are somewhat higher than those of the bisarene and dicyclopentadienyl compounds, but are lower than the ionisation potentials of the corresponding carbonyls.

The ionisation potential of benzenetricarbonylchromium decreases following the introduction of electron-donating substituents and increases following the introduction of electron-accepting substituents into the benzene ring [74]. However, a linear relation between the ionisation potentials of the arenetricarbonylchromium complexes and those of the free arenes, as in the case of the carbonylphosphine complexes of chromium, molybdenum, and tungsten[75], is not observed.

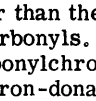
In cyclopentadienyl- and benzene-carbonyl-nitrosyl complexes of the type $CpM(NO)_x(CO)_y$ and $C_6H_6N(NO)_x(CO)_y$ [68,76-78] nitric oxide and carbon monoxide are eliminated with equal probabilities. Fragmentation with dissociation of the Cp–M and C_6H_6–M bonds begins only after the complete elimination of the carbonyl and nitrosyl groups. A very unusual rearrangement has been observed by Müller [77] in the mass-spectrum of $CpV(NO)_2$. .CO. The ion $CpVNO^+$, formed after the elimination of the NO and CO groups, decomposes with formation of pyridine.

Whereas the loss of CO and NO groups from the carbonylnitrosyl complexes is equally probable, the mass-spectra of complexes with phosphines, arsines, and sulphur-containing and other ligands reflect the differences between the donor–acceptor capacities of carbon monoxide, nitric oxide, sulphur, and phosphines. Thus a study of the mass-spectrum of $CpMn(CO)_2N_2$ showed [79] that, for example, molecular nitrogen is a more powerful electron donor than carbon monoxide. The elimination of ligand species from the molecular ions derived from the carbonylphosphine complexes of the type $CpM(CO)_m(PX_3)_n$ and $C_6H_6M(CO)_m(PX)_n$ (X = H, Cl, Me, Et, etc.) [80-84] proceeds in the following sequence: the carbonyl groups are split off first, the phosphine molecules next, and only then does the elimination of the Cp and C_6H_6 groups begin. The elimination of the phosphine group is accompanied by its partial fragmentation, which leads to the presence in the mass-spectra of lines due to the ions $CpMPX_2^+$, $CpMPX^+$, and $CpMP^+$. The lines due to the CpM^+ ion in the spectra of the cyclopentadienyl complexes and due to the metal ion in the spectra of the benzene complexes show the greatest intensity. In the olefin complexes of manganese of the type $C_4H_4Mn(CO)_2EPh_3$ (E = P, As, or Sb) [85] the olefins are split off after the elimination of the CO and EPh_3 groups and there is a steady decrease of the strength of the bond between the metal and phosphine, arsine, and stibine.

The substitution of a hydrogen atom in the ligands PH_3, AsH_3, H_2S, H_2Se, etc. influences significantly the ionisation potential of the complex, the dependence of the latter on the ionisation potential of the corresponding ligand being linear [86].

Dinuclear and Polynuclear Complexes

Certain cyclopentadienyl complexes exist as dimers in the gas phase. Molecular ions and ions formed by their fragmentation have been detected in the mass-spectra of such compounds {see, for example, the mass-spectrum of $[PtCp]_2$}. [87] Simultaneously with the elimination of the cyclopentadienyl group and the formation of the M_2^+ cluster, the metal–metal bond is broken with formation of metal ions and the fragment CpM^+. Partial fragmentation of the π-linked cyclopentadienyl group is also observed.

In complexes containing ligands of the π-acceptor type apart from cyclopentadienyl groups the metal atoms can be joined both by a usual metal–metal bond and by bridge-type bonds:  Carbon monoxide, nitric oxide, phosphines, and other two- and three-electron ligands can serve as bridging groups.

Under the influence of electron impact, complexes with bridge-type bonds $CpMX_nMCp$ (where X = carbon monoxide, phosphines, and other ligands) [88-91] split off Cp groups forming the ions MX_nM^+ with fairly intense peaks. The removal of bridging groups leads to the breakdown of the cluster with formation of the ions M^+, CpM^+, $C_3H_3M^+$, etc. There are no peaks for M_2^+ ions in the mass-spectra of complexes of this kind. It is striking that the bridging ligands are linked to the metal atoms much more strongly than the same ligands occupying terminal positions.

In complexes with a usual metal–metal bond or with one such bond and several bridge-type bonds [90,92-97] the successive removal of ligand species from the molecular ion leads to the formation of the ion M_2^+. There is a simultaneous rupture of the metal–metal bond with subsequent further fragmentation of the resulting fragments.

Structural differences are shown particularly clearly by the mass-spectra of $[CpFe(CO)_2]_2$ and $[CpMo(CO)_3]_2$. [90] Thus in the mass-spectrum of $[CpMo(CO)_3]_2$, which has a metal–metal bond, the peaks of the ion $CpMoMoCp^+$ have the maximum intensity, while in the mass-spectrum of $[CpFe(CO)_2]_2$, where the linkage between the iron atoms in the molecule is formed by CO bridging groups, the intensity of the peaks due to ions containing two iron atoms is low and the peak for the $CpFe^+$ ion is the most intense. A similar difference has been observed [98] for the molybdenum and chromium complexes $[CpM(CO)_3]_2$, although in this case the reason for the difference is in all probability the thermal instability of the chromium complex.

A similar behaviour has been observed for complexes containing different transition metal atoms [97,99,100].

IV. COMPLEX-CONTAINING GROUPS LINKED BY σ-BONDS

Certain transitions metals form complexes containing, apart from π-linked ligands and ligands of the π-acceptor type, also groups linked to the atom of the complex-forming element by σ-bonds, namely hydrogen and halogen atoms, organic groups, etc.

Dicyclopentadienylmetal Hydrides and Halides

Studies on the dicyclopentadienyl complexes of rhenium, tungsten, tantalum, and molybdenum hydrides showed [8,9,101,102] that there are no significant differences between the mass-spectra of the dicyclopentadienyl complexes and the dicyclopentadienylmetal hydrides. After the elimination of hydrogen atoms from the molecular

ions, the Cp_2M^+ ions undergo fragmentation, which gives rise to the pattern well known for compounds of the ferrocene type.

In the cyclopentadienyl complexes of titanium, zirconium, hafnium, and niobium halides [11,103-105] the halogen atoms are retained somewhat more strongly by the molecular ions than are hydrogen atoms in the dicyclopentadienylmetal hydrides, but the type of fragmentation of both classes of compounds is similar. This can also be said of the uranium and thorium complexes Cp_3MF and Cp_3MI. [34,38]

Complexes with σ-Linked Organic Groups

The mass-spectra of cyclopentadienyl complexes with σ-linked organic groups are in many cases complicated by the fragmentation of the latter. The nature and degree of fragmentation of complexes of the type $CpM(CO)_xR_y$, [61,106-111] $Cp_2M(CO)_xR_y$, [11,112-115] and $CpMX_xR$ [116,117] (where X = fluorine, chlorine, bromine, or iodine atoms and R = organic or inorganic groups) are largely determined by the dimensions and stability of the organic groups linked by σ-bonds to the metal atom and also by the amount of ionic character of the metal–group and metal–halogen bonds [117]. The ion $CpMC_7H_7^+$, containing a π-linked tropylium cation, which is absent from the mass-spectrum of the corresponding fluorinated complex, has been detected in the mass-spectra of complexes containing the $CH_2C_6H_5$ group [110].

Heteronuclear Complexes

The so called heteronuclear metal complexes, namely compounds with σ-bonds between atoms of a transition metal and elements of the main Groups, exhibit somewhat unusual behaviour.

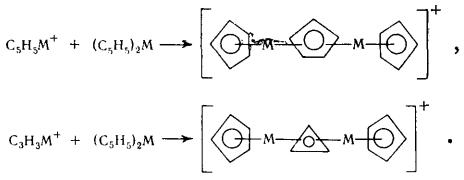
Under electron impact, extensive rupture of the metal–element bond takes place in such compounds simultaneously with the elimination of the ligand species. The charge is then retained preferentially by the fragment containing atoms of the elements of the main Groups. Thus in the mass-spectra of compounds of the type $CpM(CO)_mEX_n$ (where E = mercury, silicon, germanium, or tin; X = halogen atoms or organic groups) [62,90,118,119] and the compounds $CpRu(AsPh_3)_2SnCl_3$ [120] and $[HgM(CO)_nCp]_2$ [90,119] (M = Co or Fe) the peaks of ions containing a mercury, germanium, silicon, or tin atom are the most intense, while in the mass-spectra of the molybdenum and tungsten complexes $Et_2GeM(CO)_3Cp$ [121] the peaks of ions containing the M–Ge groups have the highest intensity.

Thus the mass-spectra of the metal complexes reflect the differences in the strength and nature of the metal–ligand and metal–metal bonds as well as structural and other differences. The principal characteristics of the mass-spectra of compounds of this class are a function of the electron-donating activity of the ligand and the atomic number of the complex-forming element. On the other hand, compounds of this type have features which will be discussed in the next section.

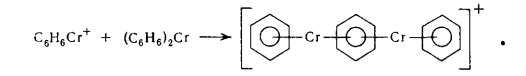
V. CHARACTERISTICS OF THE MASS-SPECTRA OF METAL π-COMPLEXES AND PROBLEMS OF THE ISOTOPIC ANALYSIS OF ELEMENTS IN THE FORM OF THEIR π-COMPLEXES

Ion–Molecule Reactions

One of the distinctive features of the complexes under consideration is their capacity to enter into ion–molecule reactions. At a pressure in the region of the ion source of $10^{-5}-10^{-6}$ mmHg, the mass-spectra of metal π-complexes can show peaks due to ions with a mass number exceeding the molecular weight of the complex. Thus, in a study of the mass-spectra of ferrocene and a mixture of ferrocene and nickelocene peaks due to the ions $Cp_3Fe_2^+$ and Cp_3FeNi^+ as well as peaks due to ions formed on their fragmentation with ejection of the cyclopentadienyl group were observed [122]. These ions, for which a double sandwich structure was suggested, are formed in the ion source of the mass-spectrometer as a result of the ion–molecule reactions



Similar reactions are characteristic also of other dicyclopentadienyl compounds, in particular of dicyclopentadienylchromium [123]. Bisbenzenechromium is also capable of forming ion–molecule association complexes [123]:



Both consecutive loss of ligand species and partial fragmentation of the cyclopentadienyl groups, mainly the elimination of ethylene and acetylene molecules with formation of the fragments $Cp_2C_3H_3M^+$, $CpC_3H_3M^+$, etc., are characteristic of the secondary ions Cp_3M^+, while the ion $(C_6H_6)_3Cr_2^+$ splits off only benzene molecules and there is virtually no partial fragmentation of the ligand species.

The mass-spectra of $CpM(CO)_n$ (M = V, Mn, or Co) [124] and $CpCr(NO)(CO)_2$ [123] contain peaks due to the ions $Cp_2M_2(CO)_n^+$ and $Cp_2M_2(CO)_n(NO)^+$ (formed as a result of reactions between ions and neutral molecules), which successively lose CO, NO, and cyclopentadienyl groups. As for the ions Cp_3M^+, a characteristic feature of these ions is the fragmentation of the cyclopentadienyl ligand species π-linked to the metal atom. The secondary ion $(C_6H_6)_2Cr(CO)_3^+$ behaves similarly in the mass-spectrum of benzenetricarbonylchromium [123], but there is no partial fragmentation of the C_6H_6 groups. Clusters containing three and more metal atoms are observed. Ion–molecule association complexes of this kind are characteristic also of trinuclear complexes [125].

Ion–molecule reactions of another type involve the addition of fluorides (PF_3, AsF_3, SbF_3, SF_4, and NF_4) to the metal-containing ions in the mass-spectrum of $CpMn(CO)_3$. [126]

Rearranged and Metastable Ions

Another characteristic feature of metal π-complexes is their capacity to form rearranged ions with fairly intense mass-spectral peaks.

Thus the rearranged ions MH^+ are as a rule absent from the mass-spectra of metal complexes with aromatic and π-acceptor ligands. However, in the mass-spectra of complexes containing σ-linked organic groups the intensity of peaks of ions of this kind is high, particularly in the case of fluorinated groups [91,109]. This can be explained by the higher strength of the metal–fluorine bond compared with the metal–hydrogen bond.

Another type of rearrangement processes characteristic of metal π-complexes are those involving the migration of cyclopentadienyl groups. In the mass-spectra of dinuclear compounds with one cyclopentadienyl group at each metal atom there are peaks due to the Cp_2M^+ ions [94,127]:

$$CpCr_2S_2Cp^+ \rightarrow Cr_2Cp^+ \ .$$

The cyclopentadienyl group can migrate also to a heteroatom σ-linked to the atom of the complex-forming element. Thus in the mass spectrum of $Cp(CO)_2FeSn.Cl_2Fe(CO)_2Cp$ the intensity of the peaks of the rearranged ion $CpSnCl^+$ is maximal [90]. Trialkylgermylmolybdenum and trialkylgermyltungsten complexes $Cp(CO)_3MGePh_3$, the mass-spectra of which show the presence of the $CpGe^+$ ion, behave analogously.

In many instances rearrangement processes lead to the formation of ions containing a metal–metal bond [128,129]:

$$Cp(CO)Fe(CO_2)Fe(CO)Cp^+ \rightarrow Cp_2Fe_2^+ \ ,$$
$$(CO)_5MnHgMn(CO)_5^+ \rightarrow Mn_2(CO)_n^+ \ .$$

A characteristic feature of the mass-spectra of π-complexes is also the unusually great abundance of peaks due to metastable transitions. Intense, distinct peaks accompany processes involving the abstraction from the molecular ions of cyclopentadienyl and carbonyl groups and benzene molecules:

$$CpM(CO)_n^+ \rightarrow CpM(CO)_{n-1}^+ + CO \ ,$$
$$C_6H_6M(CO)_n^+ \rightarrow C_6H_6M(CO)_{n-1}^+ + CO \ ,$$
$$Cp_2M^+ \rightarrow CpM^+ + Cp \ ,$$
$$(C_6H_6)_2M^+ \rightarrow C_6H_6M^+ + C_6H_6 \ .$$

Very intense peaks are observed also for metastable transitions accompanying the fragmentation of the cyclopentadienyl groups:

$$Cp_2M^+ \rightarrow CpMC_3H_3^+ + C_2H_2 \ ,$$
$$CpM^+ \rightarrow C_3H_3M^+ + C_2H_2 \ .$$

Still more intense metastable transition peaks accompany the decomposition of the fragment ions:

$$C_6H_6M^+ \rightarrow M^+ + C_6H_6 \ ,$$
$$C_5H_5M^+ \rightarrow M^+ + C_5H_5 \ .$$

The metastable transition peaks are diffuse and the corresponding apparent mass is determined from the relation [6]

$$m^* = \frac{m_2^2}{m_1} \ ,$$
$$m_1^+ = m_2^+ + (m_1 - m_2) \ .$$

Characteristics of the Mass-spectra of Polyisotopic Metal Complexes

Acton was the first to employ volatile metal carbonyls and their derivatives to investigate the natural abundance of metal isotopes [130]. (Acton's studies have been reviewed in detail by Bruce [1].) Transition metal π-complexes also constitute a convenient means for the investigation of isotope composition. Using cyclopentadienyl compounds, the natural abundance of ruthenium isotopes was investigated [131] and the relative amounts of vanadium and rhenium isotopes were checked. The presence in the mass-spectra of π-complexes of intense peaks due to the metal ion and the satisfactory agreement of these peaks with the isotope ratio make it possible to employ π-complexes for the isotopic analysis of metals.

No less important is the problem of the identification of ions in the mass-spectra of π-complexes. The identification of ions in the mass-spectra obtained on low-resolution apparatus is frequently extremely difficult. Such difficulties are somewhat diminished in the case of organometallic compounds. The differences between the relative concentrations of isotopes in the π-complexes of polyisotopic transition metals lead to the formation of different characteristic molecular and fragment ions, represented by a group of peaks the intensities of which agree satisfactorily with the isotope ratio. This greatly facilitates the identification of the metal-containing ions in low-resolution mass-spectra.

REFERENCES

1. M. I. Bruce, Adv. Organomet. Chem., 6, 273 (1968).
2. D. B. Chambers, E. Glockling, and J. C. Light, Quart. Rev., 22, 317 (1968).
3. M. Cais and M. S. Lupin, Adv. Organomet. Chem., 82, 211 (1970).
4. R. W. Kiser, in "Characterisation of Organometallic Compounds" (Edited by M. Tsutsui), Interscience, 1969, p. 137.
5. J. Müller, Angew. Chem. Int. Ed., 11, 653 (1972).
6. R. I. Reed, Quart. Rev., 20, 527 (1966).
7. R. G. Denning and R. A. Wentworth, J. Amer. Chem. Soc., 88, 4619 (1966).
8. L. Friedman, J. P. Irsa, and G. Wilkinson, J. Amer. Chem. Soc., 77, 3689 (1955).
9. J. Müller and I. D'or, J. Organomet. Chem., 10, 313 (1967).
10. N. V. Zakurin, S. P. Gubin, and Y. P. Bochin, J. Organomet. Chem., 23, 535 (1970).
11. Y. Takegami, T. Ueno, T. Suzuki, and Y. Fuchizaki, Bull. Chem. Soc. Japan, 41, 2637 (1968).
12. A. Foffani, S. Pignataro, G. Distefano, and G. Innorta, J. Organomet. Chem., 7, 473 (1967).
13. S. Pignataro and F. P. Lossing, J. Organomet. Chem., 10, 531 (1967).
14. E. Ruch, Z. phys. Chem. (Frankfurt), 6, 356 (1956).
15. D. R. Bidinosti and N. S. McInture, Canad. J. Chem., 45, 641 (1967).
16. A. Foffani, S. Pignataro, B. Cantone, and F. Grasso, Z. phys. Chem. (Frankfurt), 45, 79 (1965).
17. R. E. Winters and R. W. Kiser, Inorg. Chem., 4, 157 (1965).
18. G. A. Junk and H. J. Svec, Z. Naturforsch., 23b, 1 (1968).

19. V. I. Tel'noi, I. B. Rabinovich, V. N. Latyaeva, and A. N. Lineva, Dokl. Akad. Nauk SSSR, 197, 1348 (1971).
20. G. Wilkinson, P. L. Pauson, and F. A. Cotton, J. Amer. Chem. Soc., 76, 1970 (1954).
21. A. Reckzigel, Dissertation Universität, München, 1962.
22. D. W. Slocum, R. Lewis, and G. J. Mains, Chem. Ind. (London), 50, 2095 (1966).
23. M. Cais, M. S. Lupin, and J. Sharvit, "Proceedings of the 10th International Conference on Coordination Chemistry, Tokyo–Nikko, 1967, Abstracts of Papers", the Chemical Society of Japan, Tokyo, 1967, pp. 26–28.
24. G. E. Herberich, G. Greiss, H. F. Heil, and J. Müller, Chem. Comm., 1328 (1971).
25. M. Cais, M. S. Lupin, and J. Sharvit, Israel J. Chem., 7, 73 (1969).
26. L. D. Smithson, A. K. Bhattacharya, and F. L. Hedberg, "Organic Mass Spectrometry", Vol. 4, Supplement, 1970, p. 383.
27. A. Mandelbaum and M. Cais, Tetrahedron Letters, 3847 (1964).
28. I. J. Spilners and J. G. Larson, Org. Mass. Spectrom., 3, 915 (1970).
29. D. Wilkinson and F. Cotton, Progr. Inorg. Chem., 1, 1 (1959).
30. M. L. H. Green, "Organometallic Compounds", Vol. 2, "The Transition Elements" (Translated into Russian), Moscow, 1972.
31. M. I. Bruce, Org. Mass. Spectrom., 2, 1037 (1969).
32. J. M. Lalancette and A. Lachance, Canad. J. Chem., 49, 2996 (1971).
33. V. Mikulaj, Z. Naturforsch., 26a, 1104 (1971).
34. J. Müller, Chem. Ber., 102, 152 (1969).
35. G. G. Devyatykh, S. G. Krasnova, G. K. Borisov, N. V. Larin, and P. E. Gaivoronskii, Dokl. Akad. Nauk SSSR, 193, 1069 (1970).
36. J. L. Thomas and R. G. Hayes, J. Organomet. Chem., 23, 487 (1970)
37. G. G. Devyatykh, N. V. Larin, P. E. Gaivoronskii, G. K. Borisov, S. G. Krasnova, and L. F. Zyuzina, Dokl. Akad. Nauk SSSR, 208, 1094 (1973).
38. G. M. Bancroft, G. Reichert, J. B. Westmore, and H. D. Gesser, Inorg. Chem., 8, 474 (1969).
39. M. L. Anderson and L. R. Crisler, J. Organomet. Chem., 17, 345 (1969).
40. J. Müller and P. Göser, J. Organomet. Chem., 12, 163 (1968).
41. G. G. Devyatykh, N. V. Larin, and P. E. Gaivoronskii, Zhur. Obshch. Khim., 39, 1823 (1969).
42. H. A. Skinner, Adv. Organomet. Chem., 2, 49 (1964).
43. G. E. Herberich and J. Müller, J. Organomet. Chem., 16, 111 (1969).
44. N. V. Larin, G. G. Devyatykh, and P. E. Gaivoronskii, Zhur. Neorg. Khim., 17, 1626 (1972) [Russ. J. Inorg. Chem., No. 6 (1972)].
45. G. G. Devyatykh, N. V. Larin, and P. E. Gaivoronskii, Dokl. Akad. Nauk SSSR, 198, 585 (1971).
46. E. O. Fischer and M. W. Schmidt, Chem. Ber., 100, 3782 (1967).
47. G. G. Devyatykh, P. E. Gaivoronskii, and N. V. Larin, Zhur. Obshch. Khim., 43, 1130 (1973).
48. H. W. Wehner, E. O. Fischer, and J. Müller, Chem. Ber., 103, 2258 (1970).
49. E. O. Fischer and H. W. Wehner, J. Organomet. Chem., 11, P29 (1968).
50. R. B. King, Appl. Spectrosc., 23, 148 (1969).
51. R. B. King, Canad. J. Chem., 47, 559 (1969).
52. R. B. King, J. Organomet. Chem., 14, P19 (1968).
53. K. W. Barnett, F. D. Mando, and C. A. Reilly, J. Amer. Chem. Soc., 91, 3387 (1969).
54. R. W. Arhart, Tetrahedron Letters, 297 (1972).
55. J. Müller and P. Göser, Angew. Chem., 79, 980 (1967).
56. H. O. Oven and M. H. J. Liefde, J. Organomet. Chem., 31, 71 (1971).
57. S. Otsuka and M. Rossi, J. Chem. Soc. (A), 2630 (1968).
58. A. Streitwieser, Jnr. and N. Yoshida, J. Amer. Chem. Soc., 91, 7528 (1969).
59. R. E. Winters and R. W. Kiser, J. Organomet. Chem., 4, 190 (1965).
60. J. Müller and M. Herberhold, J. Organomet. Chem., 13, 399 (1968).
61. R. B. King, J. Amer. Chem. Soc., 90, 1417 (1968).
62. P. E. Gross, M. A. Haas, and J. M. Wilson, "Some Newer Physical Methods in Structural Chemistry", United Trade Press, London, 1967, p. 90.
63. R. G. Amiet, P. C. Reeves, and R. Pettit, Chem. Comm., 1208 (1967).
64. J. Müller and P. Göser, Chem. Ber., 102, 3314 (1969).
65. N. Maoz, A. Mondelbaum, and M. Cais, Tetrahedron Letters, 2087 (1965).
66. M. I. Bruce, Internat. J. Mass Spectrom. Ion Phys., 2, 349 (1969).
67. R. B. King, Appl. Spectrosc., 23, 536 (1969).
68. R. E. Winters and R. W. Kiser, J. Phys. Chem., 69, 3198 (1965).
69. C. C. Lee, R. G. Sutherland, and B. J. Thomson, Tetrahedron Letters, 2625 (1972).
70. P. Göser, Diss. Doct. Naturwiss. Fak. Allgem. Wiss. Techn. Hochschule, München, 1969.
71. J. Müller and K. Fenderl, Chem. Ber., 103, 3128 (1970).
72. "Spravochnik Khimika" (The Chemist's Handbook), 1963, Vol. 1, p. 325.
73. R. E. Winters and R. W. Kiser, J. Phys. Chem., 69, 1618 (1965).
74. J. Müller, J. Organomet. Chem., 18, 321 (1969).
75. G. Distefano, G. Innorta, S. Pignataro, and A. Foffani, J. Organomet. Chem., 14, 165 (1968).
76. M. A. Haas and J. M. Wilson, J. Chem. Soc. (B), 104 (1968).
77. J. Müller, J. Organomet. Chem., 23, C38 (1970).
78. E. O. Fischer, R. J. J. Schneider, and J. Müller, J. Organomet. Chem., 14, P4 (1968).
79. D. Sellmann, Angew. Chem., 83, 1017 (1971).
80. E. O. Fischer, E. Louis, W. Bathelt, and J. Müller, Chem. Ber., 102, 2547 (1969).
81. M. Hofler and M. Schnitzler, Chem. Ber., 104, 3117 (1971).
82. R. B. King, J. Amer. Chem. Soc., 90, 1412 (1968).
83. M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, J. Chem. Soc. (A), 2929 (1971).
84. J. Müller and K. Fenderl, J. Organomet. Chem., 19, 123 (1969).
85. R. B. King and A. Efraty, Org. Mass Spectrom., 3, 1227 (1970).
86. G. Distefano, A. Foffani, G. Innorta, and S. Pignataro, Adv. Mass Spectrom. London, 696 (1971).
87. E. O. Fischer and H. S. Woldan, Chem. Ber., 100, 705 (1967).

88. A. N. Nesmeyanov, A. Chapovsky, and Yu. A. Ustynyuk, J. Organomet. Chem., 9, 345 (1967).
89. E. O. Fischer, W. Berngruber, and C. G. Kreiter, J. Organomet. Chem., 14, P25 (1968).
90. J. Lewis, A. R. Manning, J. R. Miller, and J. M. Wilson, J. Chem. Soc. (A), 1663 (1966).
91. R. B. King, J. Amer. Chem. Soc., 90, 1429 (1968).
92. H. Brunner and S. Loskot, Z. Naturforsch., 26b, 757 (1971).
93. E. O. Fischer and R. J. J. Schneider, Angew. Chem., 79, 537 (1967).
94. R. C. Dobbie, M. Green, and F. G. Stone, J. Chem. Soc. (A), 1881 (1969).
95. H. Brunner, J. Organomet. Chem., 14, 173 (1968).
96. N. Flitcroft, J. Organomet. Chem., 15, 254 (1968).
97. A. R. Dias and M. L. Green, Rev. port. quim., 11, Nos. 4–6, 61 (1969).
98. R. B. King, J. Amer. Chem. Soc., 88, 2075 (1966).
99. K. Yasufuku and H. Yamazaki, Bull. Chem. Soc. Japan, 43, 1588 (1970).
100. K. Yasufuku and H. Yamazaki, J. Organomet. Chem., 35, 367 (1972).
101. J. Lewis and B. F. G. Johnson, Acc. Chem. Res., 1, 245 (1968).
102. F. Macaŝek, V. Mikulaj, and P. Drienovsky, Coll. Czech. Chem. Comm., 35, 993 (1970).
103. J. G. Dillard and R. W. Kiser, J. Organomet. Chem., 16, 265 (1969).
104. P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding, and R. C. Srivastava, J. Chem. Soc. (A), 2106 (1969).
105. F. W. Siegert and M. H. J. Liefde, J. Organomet. Chem., 23, 177 (1970).
106. M. I. Bruce, and C. H. Davies, J. Chem. Soc. (A), 1077 (1969).
107. M. L. H. Green and W. E. Lindsell, J. Chem. Soc. (A), 2215 (1969).
108. M. I. Bruce, Org. Mass Spectrom., 2, 63 (1969).
109. R. B. King, Appl. Spectrosc., 23, 137 (1969).
110. M. I. Bruce, Inorg. Nuclear Chem. Letters, 3, 157 (1967).
111. M. I. Bruce and C. H. Davies, Inorg. Nuclear Chem. Letters, 4, 675 (1968).
112. J. H. Teuben and H. J. Maijer, J. Organomet. Chem., 17, 87 (1969).
113. J. L. Burmeister, E. A. Deardorff, A. Jensen, and V. H. Christiansen, Inorg. Chem., 9, 58 (1970).
114. M. I. Bruce and M. Thomas, Org. Mass Spectrom., 1, 835 (1968).
115. R. S. P. Coutts and P. C. Wailes, Austral. J. Chem., 20, 1579 (1967).
116. J. D. Hawthorne, M. J. Mays, and R. N. F. Simpson, J. Organomet. Chem., 12, 407 (1968).
117. A. N. Nesmeyanov, V. A. Dubovitskii, O. V. Nogina, and V. N. Bochkarev, Dokl. Akad. Nauk SSSR, 165, 125 (1965).
118. B. M. Kingston and M. F. Lappert, J. Chem. Soc., Dalton Trans., 69 (1972).
119. R. B. King, Org. Mass Spectrom., 2, 657 (1969).
120. T. Blackmore, M. I. Bruce, and F. G. A. Stone, J. Chem. Soc. (A), 2376 (1971).
121. A. Carrick and F. Glockling, J. Chem. Soc. (B), 104 (1968).
122. E. Schumacher and R. Taubenest, Helv. Chim. Acta, 47, 1525 (1964).
123. J. Müller and K. Fenderl, Chem. Ber., 104, 2199 (1971).
124. J. Müller and K. Fenderl, Chem. Ber., 103, 3141 (1970).
125. E. Schumacher and R. Taubenest, Helv. Chim. Acta, 49, 1447 (1966).
126. J. Müller and K. Fenderl, Chem. Ber., 104, 2207 (1971).
127. F. A. Cotton, A. K. Fischer, and G. Wilkinson, J. Amer. Chem. Soc., 81, 800 (1959).
128. M. J. Mays and R. N. F. Simpson, J. Chem. Soc. (A), 1936 (1967).
129. P. Brown and C. Djerassi, Angew. Chem. Int. Ed., 6, 477 (1966).
130. F. W. Acton, "Mass-spectra and Isotopes", Edward Arnold and Co., London, 1942.
131. L. Friedman and I. P. Irsa, J. Amer. Chem. Soc., 75, 5741 (1953).

Institute of Chemistry,
USSR Academy of
Sciences, Gorky