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Organometallic Chelate Complexes of the $\pi-\pi$ and $\pi-n$ Type

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Organometallic chelate complexes in which either organic fragments π-bonded to the metal (chelates of the $\pi-\pi$ type) or complexes where heteroatomic groups with an unshared electron pair (NR_2, PR_2, AsR_2, OR, etc.) linked to the metal via an n-type bond (chelates of the $\pi-n$ type) are present together with the π-bonded fragments are examined. Data on complexes with polydentate ligands, including different combinations of fragments π- and n-coordinated to the metal are also surveyed. The characteristic features of the formation of organometallic chelates of the $\pi-\pi$ and $\pi-n$ types, which depend on the properties of the chelating ligand and the nature of the metal, are discussed.
The bibliography includes 267 references.

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I. INTRODUCTION

Chelate complexes have found extensive applications in many fields of technology, medicine, and agriculture. The activity of complexones, pesticides, certain medicinal preparations, analytical reagents, etc. is based on their capacity for chelation. However, among such compounds, the so-called inorganic chelates, in which the bond between the metal and the ligand is achieved via a heteroatomic group, have been most widely and comprehensively investigated. Organometallic chelates in which at least one of the bonds of the chelating ligand and the metal atom or ion is a metal–carbon σ- or π-bond are much less well known and have been altogether very little investigated. These compounds are distinguished by a wide variety of types. At the same time the study of the problem of chelation in the chemistry of organometallic compounds of transition metals is important for a number of reasons. In the first place the increase of stability owing to the chelate effect makes it possible to synthesise and investigate new types of complexes. Furthermore, chelation is closely related to problems such as cyclisation, matrix synthesis, and the *cis*-effect. The chelate effect is also of practical importance; in particular, chelation is important in homogeneous catalytic reactions widely used in industry at the present time.

Studies on organometallic chelates began comparatively recently and have not so far been systematic. The main cause holding back the development of this field is lack of information about the characteristics of the formation of organometallic chelates. This review is an attempt at a survey of the data which have accumulated on the compounds indicated in order to discover both similarities between organometallic and inorganic chelates and differences due to the specific features of their coordinated organic ligands and the types of their bonds with the metal. The review analyses for the first time certain rules governing the formation as well as the characteristic features of the structures and geometries of organometallic chelates.

Since the significant differences between chelate compounds are determined by the nature of the coordinating group of the ligand and the bonds which they form with the metal, different chelate compounds can be classified in terms of the types of bond. Since three main types of bonds between the metal and the organic ligand are known [the n-bond (using the free electron pair of the heteroatom) and the σ- and π-bonds], in principle all chelates with bidentate ligands can form six types of complexes: $n-n$, $n-\sigma$, $n-\pi$, $\pi-\pi$, $\pi-\sigma$, and $\sigma-\sigma$ and the last five refer to organometallic chelates. In the present review attention has been concentrated on organometallic chelates with $\pi-\pi$ and $\pi-n$ bonds formed by bidentate chelating ligands containing two unsaturated fragments of the type C=C, C=X (X = N, O, or another heteroatom), C≡C, C≡N, , , , and  (chelates of the $\pi-\pi$ type) or, together with the unsaturated fragment, they contain a heteroatomic group with an unshared electron pair of the type NR_2, PR_2, AsR_2, SR_2, OR, etc.) (chelates of the $\pi-n$ type); complexes with polydentate ligands forming π- and n-bonds in different combinations are also considered (chelates of these types constitute the most complex and interesting case). The synthesis and certain properties of chelate complexes with σ-coordination (intramolecular) have been recently described in a series of reviews[1-6] and in the present review we shall therefore consider only data for chelates of the $\pi-\pi$ and $\pi-n$ types.

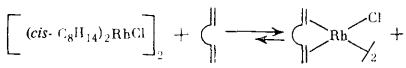
II. THERMODYNAMIC AND KINETIC CHELATE EFFECTS IN $\pi-\pi$ AND $\pi-n$ ORGANOMETALLIC CHELATES

There are no special grounds for the expectation of large differences between the thermodynamic and kinetic characteristics of the chelate effect (CE) in organometallic and inorganic chelates. However, a significant difference between the natures of the bond in organometallic compounds should lead to specific features which can be manifested in the properties of the bond between the metal atom and the coordinating group. Since the problem of stability is important in the chemistry of organometallic compounds of transition metals, the CE, as an effect involving an increase of stability, plays an important role. It is sufficient to state that the existence of many new types of compounds is due precisely to the CE. Furthermore, chelation and related phenomena, for example, synthesis in a matrix, are important for a homogeneous catalytic process. This is the reason for the importance of the analysis of the regularities and features characteristic of the CE in organometallic chelates.

Unfortunately, complexes with chelating ligands and the analogous complexes with related monodentate ligands are known in only a few instances. However, comparison of even

these scanty data shows that the complexes of monodentate ligands are as a rule less stable. For example, among the bismono-olefin complexes of metals, only rhodium(I) and iridium(I) complexes are stable, but their stability is again lower than that of the corresponding complexes with chelating diolefins. This is confirmed by the fact that, when a diolefin is added to complexes of this kind, a spontaneous reaction takes place with displacement of the mono-olefin and the formation of a diolefin complex. In complexes with volatile mono-olefins, the occurrence of such reactions can be explained (at least partially) by a shift of the equilibrium owing to the removal of the mono-olefin from the reaction sphere.

However, in the case of the complexes with cyclo-octene, one may claim, even in the absence of quantitative data, that the equilibrium in the reaction with cyclo-octa-1,5-diene[7] or cyclo-octatetraene[8] is almost wholly displaced to the right ($K \gg 1$) precisely as a result of the CE:



The question of the relative magnitudes of the CE in organometallic chelate complexes and of the dependence of this effect on various factors is much more complicated. Unfortunately there are very few quantitative data. Some of them are presented in Tables 1–4. The manifestation of the CE is supported by the formation constants of the silver complexes of unsaturated alcohols (of the π–n type) (Table 1).

Table 1. The formation constants (K, litre mol^{-1}) of Ag^+ complexes of unsaturated alcohols and their derivatives in water (partition method, 25 °C; reproducibility 10%)[9].

Olefin	K			
	X = H	X = OCOCH$_3$	X = OH	X = OCH$_3$
3-X-Prop-1-ene	—	0.35	12[a]; 22[b]	—
4-X-But-1-ene	—	0.31	26	—
5-X-Pent-1-ene	—	0.44	51	0.34
6-X-Hex-1-ene	0.095[a]	0.15	29	0.10
7-X-Hept-1-ene	—	<0.1	8.2	—
11-X-Undec-1-ene	—	<0.1	<0.1	—
5-X-5-Methylpent-1-ene	—	0.07	25	—
3-X-1-Methylenecyclohexane	0.096[c]	<0.1	19	—
3-(β-X-Ethyl)cyclopentene	0.119[c,d]	<0.1	38	—
5-X-Cyclo-octene	0.005[c]	<0.1	29	—

Note. $K = [\text{complex}]_{H_2O}/[\text{olefin}]_{CCl_4}[Ag]^+_{H_2O}$; [a] partition method[10]; [b] potentiometric method in water[11]; [c] value for cyclopentene[12]; [d] $K < 0.1$ for cyclo-octanol.

Thus the formation constant for *cis*-cyclo-oct-4-en-1-ol ($K = 29$) exceeds by several orders of magnitude the formation constants of the complexes with monodentate ligands of similar structure—*cis*-cyclo-octene ($K = 0.005$) and cyclo-octanol ($K < 0.1$). Analogous formation constants of the silver complexes of certain unsaturated alcohols have been obtained by the potentiometric method[13]. It is also noteworthy that, according to the data in Table 1 and Wilcox and Gaal[13], the character of the variation of the formation constants of chelate complexes as a function of the distances between the olefin and hydroxy-groups, considered in detail below, can be clearly traced. A similar trend in the variation of K has been observed[14] also for the reaction $Ag^+ + L \rightleftharpoons [AgL]^+$ (Table 2), where L are sulphur- and selenium-containing unsaturated ligands; however, the most interesting feature of this system is the fact that ΔH and not ΔS makes a decisive contribution to the CE.

Table 2. Thermodynamic parameters (kcal mol^{-1}) of the silver complexes[14]: $Ag^+ + L \rightarrow [AgL]^+$.

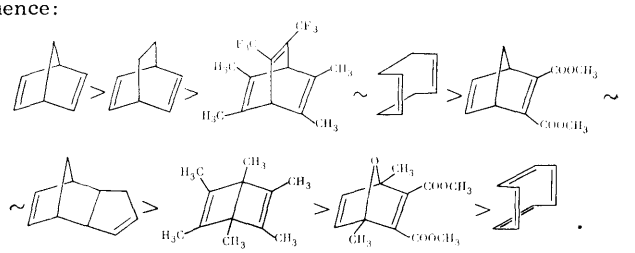
Ligand	$-\Delta G$	$-\Delta H$	$-T\Delta S$	$\delta(\Delta G)$	$\delta(\Delta H)$	$\Delta(T\Delta S)$
$C_4H_9SCH_2COO^-$	5.35	6.81	1.46	1.16	4.21	3.06
$CH_2{=}CH(CH_2)_2SCH_2COO^-$	6.51	11.02	4.52			
$CH_2{=}CH(CH_2)_3SCH_2COO^-$	5.71	8.39	2.68			
$C_4H_9SeCH_2COO^-$	6.24	7.79	1.55	0.78	5.23	4.42
$CH_2{=}CH(CH_2)_2SeCH_2COO^-$	7.05	13.03	5.97			
$CH_2{=}CH(CH_2)_3SeCH_2COO^-$	6.31	9.13	2.87			

The formation constants of silver complexes with various diolefins (complexes of the π–π type), listed in Table 3, illustrate the different contributions of the CE depending on the structure of the diolefin[15] (for comparison, Table 3 also includes complexes with mono-olefins of similar structure).

Table 3. The formation constants of the silver complexes of olefins in ethylene glycol at 40 °C[15] (gas–liquid chromatographic method).

Olefin	K, litre mol^{-1}	Olefin	K, litre mol^{-1}
But-1-ene	7.7	Cyclohexene	3.6
Buta-1,3-diene	4.2	Cyclohexa-1,4-diene	4.9
Penta-1,4-diene	10.2	1-Methyl-4-(2-propenyl)cyclo-hex-1-ene	5.9
Hexa-1,5-diene	28.8	4-Vinylcyclohex-1-ene	11.2
2-Methylhexa-1,5-diene	22.1	Norbornene	62
2,5-Dimethylhexa-1,5-diene	13.3	Norbornadiene	33.7
Hepta-1,6-diene	14.7	Cyclo-octa-1,3-diene	3.2
Octa-1,7-diene	11.3	Cyclo-octa-1,4-diene	14.4
Nona-1,8-diene	10.4	Cyclo-octa-1,5-diene	75
Deca-1,9-diene	7.8	Cyclo-octatetraene	91

The contribution of the CE is particularly large in the case of a cyclic diolefin—cyclo-octa-1,5-diene. For cyclic dienes, a marked dependence of the CE on the geometry of the chelating ligand has been observed and the equilibrium constants determined by the ^{1}H NMR method for the complexes [(diene)$RhCl_2$], vary by five orders of magnitude[16]. The chelating capacity of dienes diminishes in the following sequence:



Important results have been obtained by the direct determination of the enthalpies of formation (Table 4).[17]

The results show that in chelates of the π–*n* and π–π types both the entropy and enthalpy factors make an important contribution to the CE, as in inorganic chelates. The relative importance of these factors apparently varies as a function of the different features of the complexes.

The kinetic CE can be illustrated by data[18] obtained for the reaction

$$DQNi(diene) + P(OCH_3)_3 \rightleftarrows Ni[P(OCH_3)_3]_4 + DQ + diene,$$

where DQ is duroquinone and 'diene' is duroquinone, cyclo-octa-1,5-diene, *endo*-bicyclopentadiene, norbornadiene, and cyclo-octatetraene. It has been suggested that the first stage is the bimolecular reaction of trimethyl phosphite with the nickel complex in which one bond between the chelating diene and the metal is ruptured. The rate constants for this stage vary in the following sequence: DQ << cyclo-octadiene< bicyclopentadiene < norbornadiene < cyclo-octatetraene. The sequence obtained agrees with that found[19] on the basis of the ligand exchange reaction. Thus, in the given instance, the kinetic and thermodynamic CE act in the same direction.

Table 4. The heats of the reactions of chelating olefins and other ligands with $(CH_3CN)_2PdCl_2$ in methylene dichloride[17].

Ligand	$-\Delta H$, kcal mol^{-1}
Bicyclopentadiene	4.9±0.1
Cyclo-octatetraene	5.6±0.1
trans,trans,trans-Cyclododecatriene	5.9±0.1
1-Methyl-4-(2-propenyl)cyclohex-1-ene	6.8±0.3
Hexa-1,5-diene	8.0±0.4
Cyclo-octa-1,5-diene	13.0±0.4
Norbornadiene	13.3±0.8
Pyridine	26.0±0.7
Tetramethylethylenediamine	27.3±1.7
o-Phenylenebisdimethylarsine	35.2±0.7
Bis(diphenylphosphino)ethane	50.5±1.7

Together with quantitative thermodynamic and kinetic data, the decomposition temperatures as well as the results of physical methods of investigation and even qualitative chemical data are used to estimate the stabilities of the compounds. It is necessary to treat such results, particularly those of the last type, with caution. The overall stability of chelate π–π and π–*n* complexes is usually determined by the strength of the bond between the metal atom and the unsaturated fragment of the chelating ligand, since the heteroatom (possibly with the sole exception of oxygen) is usually more strongly bound to the metal (Table 4). However, this is true only when the complex does not contain other ligands bound still less strongly. The thermal stabilities of the compounds considered in terms of the thermodynamic and kinetic aspects should depend also on the mechanism of the decomposition reaction. In discussing the relative stabilities of the complexes on the basis of their decomposition temperatures (provided that these have been determined correctly), only data for isotypical complexes provide much information.

Physical methods as a rule give only indirect data about the metal–ligand bond strength. Infrared spectroscopy has been used most frequently for this purpose. For example, the shift of ν(C=C) on complex formation has been proposed[20–22] as a measure of metal–olefin bond strength. Since in the vast majority of cases the π–*n* and π–π chelates contain a double bond, one should note that this criterion can be used only to a first approximation. It has been found[23,24] that the vibration with the ν(C=C) frequency is not characteristic, since it is appreciably mixed with the δ(=C–H) deformation vibrations. It has therefore been suggested[25] that the overall percentage decrease of the ν(C=C) and δ(=C–H) frequencies in the coordination of an olefin be used. The frequency (or force constant) of the metal–olefin bond vibration can serve as another criterion[26]. However, few such data are available. Furthermore, the fact that the assignment of ν(C=C) on coordination (in many cases only tentative) has been carried out, with rare exceptions, only on the basis of infrared spectra without Raman spectroscopic data reduces the value of the results for the discussion of the stabilities of chelate complexes containing a double bond in the chelating ligand. Indeed it is difficult to discover a correlation between the character of the changes in the equilibrium constants[16] and the decrease of the vibrational frequency of the double bond on coordination in the complexes $[Rh(diene)Cl]_2$ (Table 5). On the basis of the values of ν(C=C), one can only assume that the strength of the M–$\overset{C}{\underset{C}{\|}}$ bond in the chelate complexes of this type is greater than that in the analogous complexes $[Rh(olefin)_2Cl]_2$ with monodentate olefins.

Table 5. The decomposition temperatures and changes in the stretching vibration frequencies of the double bond on coordination for complexes of the type $[Rh(diene)Cl]_2$ and $[Rh(mono\text{-}olefin)_2Cl]_2$.

Ligand	Decomp.temp.,°C	ν^{fl}(C=C)	ν^{c}(C=C)	$\Delta\nu$(C=C)
Norbornadiene	240 [27]	1550 [16]	1449 [16]	101 [16]
Norbornadiene	>170 [28]	—	—	150 [28]
Hexachloronorbornadiene	296—298* [29]	1604 [29]	1380 [29]	224
Bicyclo[2.2.2]octa-2,5-diene	—	1630 [16]	1430 [16]	200
Cyclo-octa-1,5-diene	>235 [30]	—	—	180 [28]
Tetrafluorobenzobarrelene	>270 [31]	—	—	—
Bicyclopentadiene	205 [32]	—	—	—
Hexamethylbicyclo[2.2.0]hexa-2,5-diene	—	1685 [16]	1505 [16]	180
Cyclo-octatetraene	145 [27]	1640 [16]	1412 [16]	228
Cyclo-octatetraene	—	1630 [8]	1410 [8]	220
Cyclodeca-1,6-diene	215—220 [32]	1650 [32]	1446 [32]	204
4-Vinylcyclohex-1-ene	>145 [33]	—	—	—
Hexa-1,5-diene	160 [34]	1642 [34]	1488, 1505 [34]	154, 137
2,5-Dimethylhexa-1,5-diene	>160 [28]	1646 [28]	1510 [28]	136
Cyclo-octene	>150 [28]	1650 [28]	1555 [28]	95
Cycloheptene	>115 [28]	1650 [28]	1560 [28]	90

Note. ν^{fl}(C=C) is the stretching vibration frequency of the double bond in the free ligand, ν^{c}(C=C) the stretching vibration frequency of the double bond in the coordinated ligand, and $\Delta\nu$(C=C) the shift of the stretching vibration frequency of the double bond on coordination.

* Melting point for fusion accompanied by decomposition.
Note. The numbers in square brackets denote references (Ed. of Translation).

Table 5 shows that the decomposition temperatures are in many instances better correlated with the strength of the bond between the metal and the ligand. Examination of the thermodynamic stabilities[16] (see above) and thermal stabilities (Table 5) of isotypical complexes leads to the same conclusion: complexes of norbornadiene and its analogues as well as those

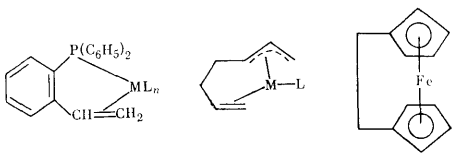
of cyclo-octa-1,5-diene are the most stable, while the complexes of *endo*-bicyclopentadiene and particularly cyclo-octatetraene are less stable.

In addition, the very fact of the formation of a chelate complex together with qualitative chemical reactivity data can be used to discuss various factors influencing the relative stabilities of the chelates.

III. THE INFLUENCE OF THE PROPERTIES OF THE CHELATING LIGAND ON THE STABILITY OF THE CHELATES

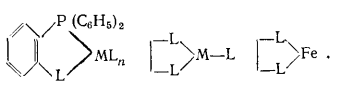
1. The Size of the Chelate Ring

The properties of chelate complexes are influenced most significantly by the nature of the chelating ligand, namely the nature of its coordinating groups, its geometry in the free state, the size and geometry of the bridging fragment separating the coordinating groups, and many other factors. However, before beginning the discussion of its influence, one must decide how to define the size of the chelate ring in π–n and π–π chelates. The point is that, in contrast to chelating ligands containing coordinating n- and σ-groups, ligands with π-fragments form chelate rings whose size is more difficult to define. We shall consider π–n and π–π chelates containing coordinating groups of different types:

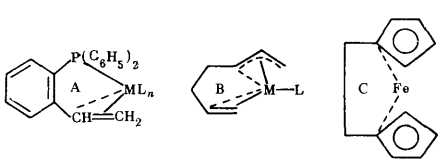


Even in the simplest case—in the chelate complex of diphenyl-*o*-styrylphosphine— the ring size can be defined in different ways. In the system of formulation for π-complexes usually employed a line connects the centre of the double bond with the metal atom. In this case one can assume that the size of the chelate ring amounts to 5.5 units[3,6]. When a metal–olefin bond is treated as a three-membered ring, we arrive at the conclusion that two rings are formed on chelation: a three-membered ring and a five-membered ring.

This treatment does not solve the problem in the case of more complex π-groups—allyl, butadiene, cyclopentadienyl, and arene, i.e. groups containing a system of conjugated bonds. However, one can propose a simple solution to this problem if one disregards the nature of the coordinating group and the latter is denoted by L, i.e. it is assumed that any coordinating group constitutes one unit in the ring. In this case the formulae of chelate complexes assumes the following form:

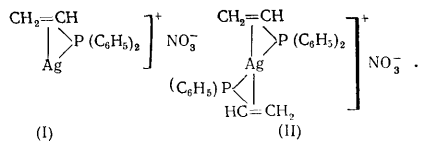


As a result, the chelate ring in the complexes considered must be regarded as five-membered. The activation of the chelate rings A, B, and C proper in these complexes leads to the same conclusion:



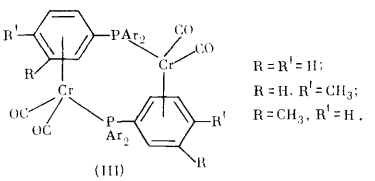
Despite the apparent arbitrary nature of this approximation, the latter "works" in most cases and, as will be seen from the foregoing, such calculations show that the greatest stability of the complexes and the maximum tendency towards their formation obtain in five- and six-membered rings, as for inorganic chelates.

For example, the simplest ligands which can form π–n chelates are heteroatomic substituted ethylenes. It is believed that diphenylvinylphosphine forms complexes (I) and (II) with silver cations[35]:



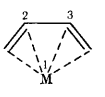
(I) (II)

Although the structure of the complexes has been assigned on the basis of a fairly broad set of data—analytical, spectroscopic (infrared, ^{1}H, and ^{31}P NMR), and cryoscopic—it cannot be regarded as finally established without resorting to X-ray diffraction analysis (XDA), particularly since chelation involving three-membered rings has not been observed in any one instance in the formation of metal complexes of heteroatomic substituted ethylenes. The fact that the formation of three-membered rings is unfavourable can sometimes lead to a dimeric product containing six-membered rings, as happens, for example, in the thermal interaction of $Cr(CO)_6$ with triarylphosphines. Here complexes (III) were isolated and acyclic compounds of the type arene. $Cr(CO)_2PAr_3$ were not detected[36].



(III)

Using the proposed method for the calculation of the number of units in the chelate ring, the numerous group of transition metal complexes with conjugated dienes should be classified as three-membered π–π chelates in terms of their formal features (see, for example, the relevant reviews[37–39]).



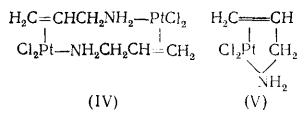
Indeed the term "chelates" is frequently used in the literature in relation to such compounds. However, we excluded them from consideration because the reduced energy of the antibonding π^* orbital of these ligands makes a significant contribution to the stability of complexes of this type (see, for example, Streitwieser[40] and Rybinskaya[41]), which masks the CE proper in these complexes.

Four-membered chelate rings are also relatively uncommon. Thus the high thermodynamic and kinetic stability of complexes of allyl alcohol, namely $[C_3H_5OH.PtCl_3]^-$,[42] can be explained by the additional coordination of the OH group to the platinum atom. This can also be indicated by the infrared spectra of compounds of the type of *trans*-$[C_3H_5OH.PtCl_2.amine]$ [a decrease of ν(OH) by 140–160 cm^{-1}].[43,44] An analogous situation has been noted for platinum complexes of β-hydroxyalkylacetylenes[43,44].

According to infrared spectroscopic data, in the 1:1 complex of C_3H_5OH with copper(I) chloride both the double bond [$\Delta\nu(C{=}C) \cong 95\ cm^{-1}$] and the OH group [$\Delta\nu(C{-}O) \cong 20\ cm^{-1}$] are coordinated. On this basis, a dimeric structure has been postulated for the chelating ligand $CH_2{=}CH{-}CH_2OH$.[45] The formation constant of the complex $C_3H_5OH.CuCl$ is higher than that of the complex of C_3H_5Cl with CuCl.[46] A significant difference between the formation constants of the complexes with the $AgNO_3$ in water has been observed for C_3H_5OH and alkylethylenes (Table 1).[8,9]

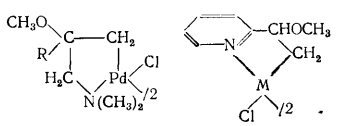
The higher heat of formation of complexes of the copper(I) halides CuCl and CuBr with allylamine compared with propylamine can also be explained by chelation[47] ($\Delta H_{C_3H_5NH_2} - \Delta H_{C_3H_7NH_2} = 10{-}12$ kcal mol^{-1}). Infrared spectroscopic data [the decrease of the frequencies $\nu(C{=}C)$, $\nu(NH_2)$, and $\delta(NH_2)$] also agree with the chelate structure of the complexes.

The question of the formation of platinum(II) chelate complexes of $C_3H_5NH_2$ cannot be regarded as finally solved. On the basis of infrared spectra, it has been suggested[48] that, together with the dimeric form (IV)[49,50], the monomeric form (V) is present, albeit in a smaller amount:



(IV) (V)

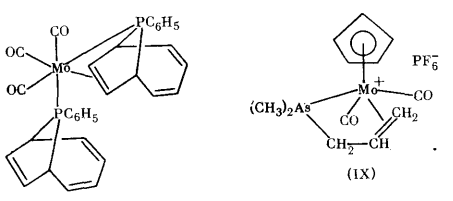
In addition, the intermediate formation of four-membered chelate rings of the $\pi{-}n$ type[51,52] has been suggested in the interaction of $C_3H_5NH_2$ with palladium(II) salts[53] and also of 2-vinylpyridine with palladium(II) and platinum(II)[54] in methanol with subsequent conversion into stable five-membered $n{-}\sigma$ chelate complexes (VI) and (VII)—the products of nucleophilic addition to the coordinated double bond:



(VI) (VII)

An analogous reaction of allyl- and propargyl-phosphines with platinum is also known[55].

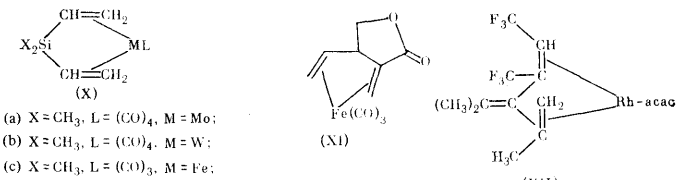
The structure of complexes (VIII) and (IX) with ligands containing a heteroatom in the allyl-position, namely 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene[56] and allyldimethylarsine[57], has been demonstrated more reliably:



(VIII) (IX)

The molecular weights were determined in these instances by osmometry or mass spectrometry. The relative stability of the four-membered chelate ring in compound (VIII) can be explained by the fact that the phosphorus atom is incorporated in a rigid bicyclic system. The formation of four-membered chelate rings is characteristic of bicyclic dienes (see below). The large radius of the arsenic atom in complexes (IX) can lead to the same result.

The formation of four-membered chelate rings with linear dienes is a fairly rare phenomenon. Such complexes of type (X) have been obtained from di- or tetra-vinylsilanes with molybdenum, tungsten[58,59], and iron[60,61] carbonyls [compounds (X, a–d)] and rhodium acetylacetonates[62] [compound (Xe)]:

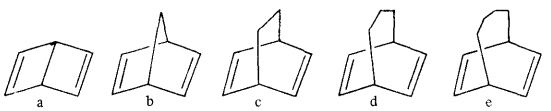


(X) (XI) (XII)

(a) X = CH_3, L = $(CO)_4$, M = Mo;
(b) X = CH_3, L = $(CO)_4$, M = W;
(c) X = CH_3, L = $(CO)_3$, M = Fe;
(d) X_2 = $(OC)_3Fe$ , L = $(CO)_3$, M = Fe;
(e) X = CH_3, L = acac, M = Rh.

Complexes (XI)[63] and (XII)[64] with linear 1,4-dienes, in which a carbon atom is a bridge separating olefinic groups, have been obtained recently. The structure of complexes (Xd), (XI), and (XII) has been demonstrated by X-ray diffraction.

Metal complexes with cyclic dienes in which the double bonds are also separated by carbon atoms are much more common. Cyclohexa-1,4-diene itself rarely behaves as a bidentate ligand (see, for example, Birch et al.[65])†, while its derivatives (XIII, a – e) with a bridge connecting the 1,4-positions have a geometry favouring chelation (see below).



a b c d e

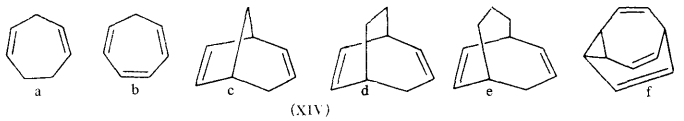
(XIII)

A single complex of palladium chloride with unsubstituted bicyclo[2.2.0]hexa-2,5-diene (Dewar benzene) (XIIIa) has been described[66], while complexes with the hexamethyl derivative of Dewar benzene are somewhat more common (see, for example, Huttner and Mills[67] and the references quoted therein).

Chelate complexes with bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) (XIIIb) are widely known. It is not possible to include these data in the present review and we shall therefore only refer to other surveys[37–39] and certain communications on X-ray diffraction studies[70–79]. Complexes based on bicyclo[2.2.2]octadiene (XIIIc)[16] or its derivatives[31,80,81] and bicyclo[2.2.3]nona-2,5-diene (XIIId) and its derivatives[82,83] have also been described. A complex of iron tricarbonyl with a ligand of type (XIIIe), in which the bridge consists of a conjugated diene coordinated to $Fe(CO)_3$, is known[84].

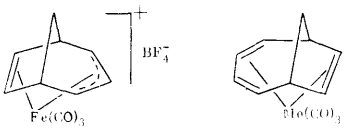
† The formation of stable complexes with quinones[68] and their isostructural analogues (1,4-difluoro-1,4-diboracyclohexa-2,5-dienes)[69] can be explained by a significant contribution of electronic factors (decrease of the energy of the π^* orbital of the ligand—see, for example, Rybin[68]). The geometrical factors are in this case apparently no less unfavourable than for cyclohexa-1,4-diene.

A four-membered ring is formed in chelates of cyclic 1,4-dienes and in the case of cyclohexa-1,4-dienes two four-membered rings are produced, while in other cases there is a possibility of the formation, together with a four-membered ring, of rings of another size, which happens in the case of cyclohepta-1,4-diene (XIVa)[85,86] and related compounds: cycloheptatriene (XIVb)[87], bicyclo[3.2.1]octadiene (XIVc)[88,89], and derivatives of bicyclo[3.2.2]nona-2,5-diene (XIVd)[83], bicyclo[2.3.3]deca-2,5-diene (XIVe)[90], and bullvalene (XIVf)[91].



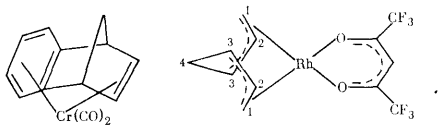
(XIV)

Several examples of chelate complexes of the $\pi-\pi$ type with four-membered rings in which ligands other than olefins are present as one or both coordinating groups are also known. These are allylolefin[83,88,89,92-94] and diene-mono-olefin chelates[59,95]—for example in complexes (XV) (its structure has been demonstrated by X-ray diffraction[88]) and (XVI)[95]:



(XV) (XVI)

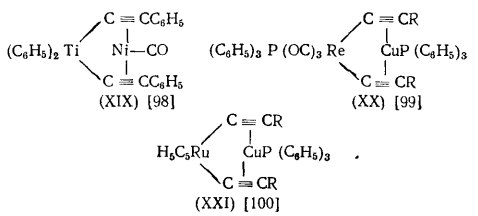
An arene ligand may function as one of the chelating groups, as happens in the chromium dicarbonyl complex of benzonorbornadiene (XVII)[96]. In compound (XVIII) both coordinating groups are π-allyl ligands[97]:



(XVII) (XVIII)

Here the chelating bis-π-allyl ligand is not incorporated in a bicyclic system, as in the cases described previously, and the chelate ring is therefore appreciably strained. The decrease of the Rh–C(1) and Rh–C(2) interatomic distances and partial rehybridisation of C(3) can be followed on the basis of X-ray diffraction data.

The increased stability of complexes (XIX)–(XXI)[98-100] with chelating diyne ligands# can be explained by the increased size of the atom separating the acetylenic groups, which should lead to a decrease of strain in chelate rings of this type. In addition, such strain depends also on the hybridisation of the atom indicated (see below):

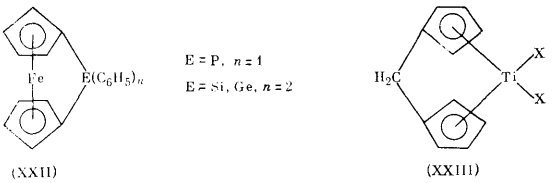


(XIX) [98] (XX) [99]

(XXI) [100]

Doubts have been expressed[102] about the results reported in a communication concerning dinitrile chelate complexes with the ligands $N\equiv C(CH_2)_nC\equiv N$ ($n = 1-3$)[101] involved in π-type coordination. See also Farona and Kraus[103].

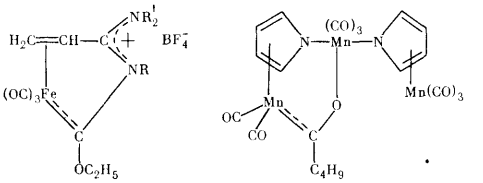
An analogous situation has been observed also in the case of ferrocenophanes, which can likewise be regarded as chelates. The replacement of a carbon atom by atoms with larger radii, namely silicon, germanium, and phosphorus, made it possible to obtain one-membered ferrocenophanes (XXII)[104], whose carbon analogues are unknown:



(XXII) (XXIII)

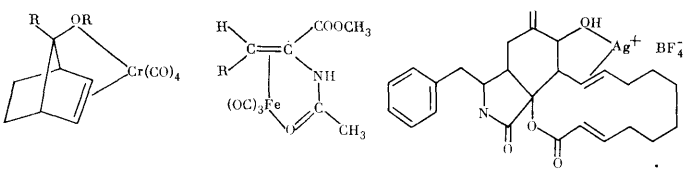
According to X-ray diffraction data, complexes (XXII) are appreciably strained[105]. On the other hand, the presence of a single carbon atom in the bridge is sufficient for wedge-shaped sandwich compounds—for example, compound (XXIII)[106].

Complexes containing five-membered rings are commonest among $\pi-n$ and $\pi-\pi$ chelates. In the case of $\pi-n$ chelates a double bond and allyl, cyclopentadienyl, and arene groups function as the unsaturated fragment, while the atoms providing the electron pair for coordination are those of C, O, S, Se, N, P, and As. Examples of chelates in which a carbon atom is involved in n-type coordination are provided by the carbene complexes (XXIV)[107] and (XXV)[108] obtained recently:



(XXIV) (XXV)

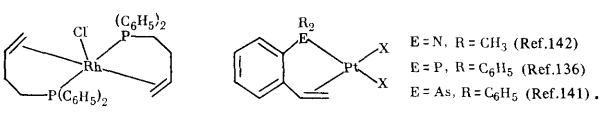
syn-Alkoxynorbornenes[109], acetamidoacrylates and acetamidocinnamates[110], and also the antibiotic Phomin[111], which form complexes (XXVI)–(XXVIII), have been used as oxygen-containing ligands:



(XXVI) (XXVII) (XXVIII)

The structure of compounds (XXIV), (XXV), (XXVII), and (XXVIII) has been established by X-ray diffraction.

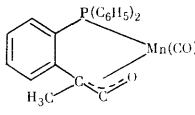
Ligands in which the 1-butenyl group is linked to oxygen[112], sulphur[113], selenium[114], and phosphorus[115-122] are fairly common. 2-Allylpyridine also has a geometry convenient for chelation[123,124], but ligands of the types considered which are most often employed are *o*-styryl derivatives of phosphorus[125-139], arsenic[137-141], or nitrogen[142]. Compounds (XXIX)[122] and (XXX), whose structure has been demonstrated by X-ray diffraction, have been quoted as examples:



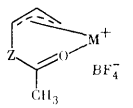
(XXIX) (XXX)

o-Styrylphosphine usually enters as such into the coordination sphere, but, on interaction with $CH_3Mn(CO)_5$, it is transformed into the oxoallylphosphine ligand [complex

(XXXI)][143]. Complexes with allyl [compound (XXXII)][144–146] or cyclobutadiene [compound (XXXIII)][147] and compound (XXXIV)[148]] fragments in the chelating ligand have also been obtained as a result of reactions in the coordination sphere of the metal and cyclobutadienes can be involved in the coordination of both η^2-type [compound (XXXIII)] and η^4-type [compound (XXXIV)].

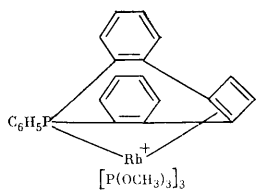


(XXXI)

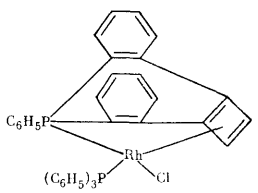


(XXXII)

Z = CH_2, M = $Fe(CO)_3$ (Ref.144)
Z = O, M = $Fe(CO)_3$ (Ref.145)
Z = CH_2, M = RhC_5H_5, IrC_5H_5 (Ref.146).

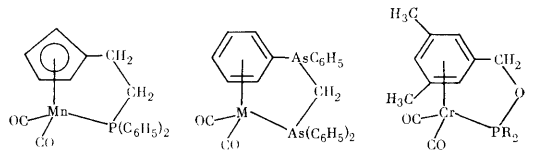


(XXXIII)



(XXXIV)

The following examples of cyclopentadienyl and arene chelate complexes of the π–n type are known: complexes (XXXV)[149], (XXXVI)[150], and (XXXVII)[151,152]:

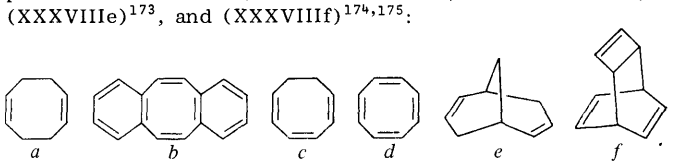


(XXXV) (XXXVI) (XXXVII)

(a) M = Cr; (b) M = Mo (a) R = C_6H_5; (b) R = OC_6H_5.

The structures of complexes (XXXI)[153], (XXXIII)[147], (XXXVIa)[154], and (XXXVIIb)[155] have been confirmed by X-ray diffraction.

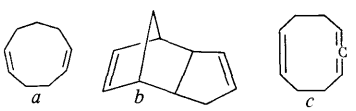
However, five-membered chelate complexes of the π–π type are undoubtedly the commonest. This applies primarily to complexes of cyclo-octa-1,5-diene (XXXVIIIa) (see, for example, Refs.37–39 and 156–169) and the related compounds (XXXVIIIb)[170], (XXXVIIIc)[171,172], (XXXVIIId)[37–39], (XXXVIIIe)[173], and (XXXVIIIf)[174,175]:



a b c d e f

(XXXVIII)

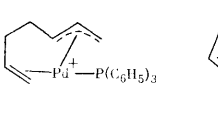
Complexes of cyclonona-1,5-diene (XXXIXa)[176] and compounds (XXXIX, b and c)[37–39,177–179] are close to this type of compound:



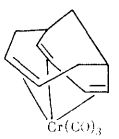
a b c

(XXXIX)

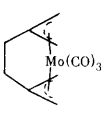
Complexes with linear dienes are fairly common among five-membered chelate complexes of the π–π type (see, for example, Refs.28, 34, and 180). The chain connecting the two double bonds can be incorporated in a six-membered ring[181,182]. One double bond can be endocyclic as, for example, in 4-vinylcyclohexene[183–185] or 5-methylenecyclopentene complexes[186]. Furthermore, various allylolefin [compound (XL)][187] (see also Lewis and Parkins[94]) or diene-olefin [compound (XLI)][188] (see also Ward and Pettit[189]), bisallyl [compound (XLII)][190], cyclopentadienylallyl [compound (XLIII)][191], cyclopentadienyldiene [compound (XLIV)][192], arene-olefin [compound (XLV)][193–195], arene-allene [compound (XLVI)][196], and arene-allyl [compound (XLVII)][197] chelates are known in addition:



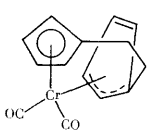
(XL)



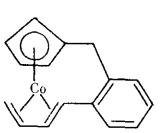
(XLI)



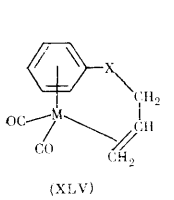
(XLII)



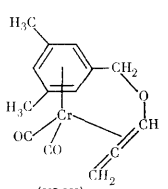
(XLIII)



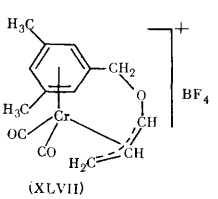
(XLIV)



(XLV)



(XLVI)

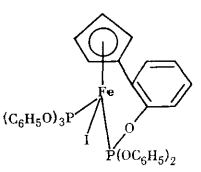


(XLVII)

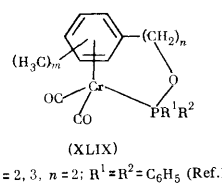
X = O, M = Cr; X = CH_2, M = Cr, Mo, W.

The structures of compounds (XLI) and (XLIV) have been established by X-ray diffraction. [2]Ferrocenophanes belong to chelates of the same type[5,198].

Although complexes with six-membered rings are encountered more rarely than those of five-membered rings, they are also fairly stable. As a rule, these are derivatives of platinum(II) and rhodium(I), which form the strongest bonds with olefins. The ligands of π–n type are mainly pentenyl derivatives of sulphur[113], selenium[114], phosphorus[116,120], and arsenic[199,200] as well as *o*-allylphenyl derivatives of phosphorus[128,129,201,202] or arsenic[201,202]. Complexes with *O*-alkyl-*N*-allyldithiocarbamates coordinated as bidentate ligands have been described[203–205]. Apart from olefin-containing six-membered π–n chelates, only the cyclopentadienyl chelate complexes (XLVIII)[206] and the arene chelate complexes (XLIX)[151,152,207–209] and (L)[210] are known. The structures of complexes (XLVIII)[211] and (L)[210] have been confirmed by X-ray diffraction:

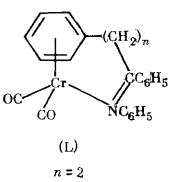


(XLVIII)



(XLIX)

m = 2, 3, n = 2; $R^1 = R^2 = C_6H_5$ (Ref.152)



(L)

n = 2

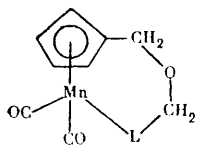
OC_6H_5 (Ref.151), F (Ref.205), ½  (Ref.206)

$R^1 = F$, $R^2 = OC_2H_5$ (Ref.207)

In some cases cyclodeca-1,6-diene does not exhibit chelating properties. Thus it forms a six-membered chelate with rhodium(I), gives rise to coordination polymers on reaction

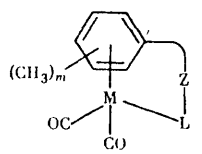
with palladium(II) salts, and does not react at all with platinum(II)[32,182,212]. The same can also be said of linear dienes, for example, diallyl ether[213-215]. The structure of some of its complexes has been established by X-ray diffraction[216,217].

Together with diene complexes, chelates containing one or two cyclic π-ligands of types (LI)[218], (LII)[193-196,219], and (LIII)[220] have been described:



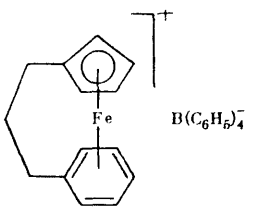
(LI)

L = CH=CH$_2$, C≡CH



(LIIa-e)

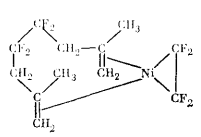
(a) M = Mo, W; Z—L = $(CH_2)_3CH{=}CH_2$;
(b) M = Cr; Z—L = $(CH_2)_3CH{=}CH_2$;
(c) M = Cr; Z—L = $CH_2OCH_2CH{=}CH_2$;
(d) M = Cr; Z—L = $CH_2OCH{=}C{=}CH_2$;
(e) M = Cr; Z—L = $CH_2OCH_2C{\equiv}CR$ (R = H, CH_3).



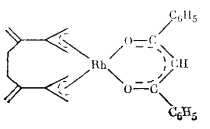
(LIII)

[3]Ferrocenophanes constitute the commonest type of six-membered π—π chelates[5,198].

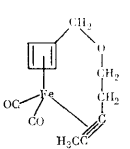
There are few data on compounds with seven-membered chelate rings. As examples, one may quote complexes (LIV)–(LVI)[221-223] (see also Refs. 224 and 225). The structure of compound (LV) has been confirmed by X-ray diffraction. Apart from these, compounds (XLIX, n = 3, R = C_6H_5, or OC_6H_5)[151,152], (L, n = 3)[210], and (LII, Z–L = $CH_2CH_2OCH_2$–C≡CR)[219], as well as [4]ferrocenophanes[5,198] and [4]dibenzenechromophanes[226] contain a seven-membered chelate ring:



(LIV) (Ref.221)

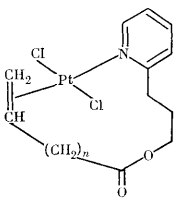


(LV) (Ref.222)



(LVI) (Ref.223)

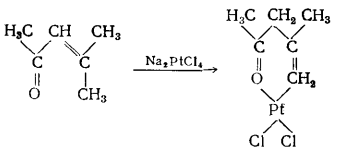
Chelates with medium and large rings are of special interest[152,198,227,228]. For example, complexes (XLIX, n = 4, R = C_6H_5 or OC_6H_5) contain eight-membered rings, while complexes (XLIX, n = 5, R = C_6H_5 or OC_6H_5) contain nine-membered chelate rings. The ease of formation of medium sized rings can be explained in this case[152] by the decrease of the extent of transannular interactions compared with hydrocarbon rings of the same size. Fairly large numbers of ferrocenophanes containing rings of medium size and macrorings have been synthesised[198] and [5]bisarenechromophanes have also been obtained[226,229]. However, the increase of the stability of such complexes as a result of the CE is apparently either small or zero. This is confirmed by the finding that the olefinic end of the ligand in complex (LVII) can be displaced by ethylene[228]:



(LVII)

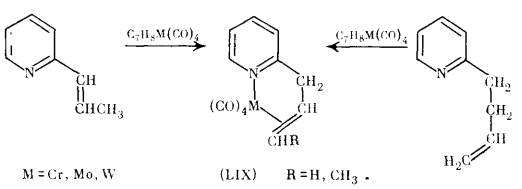
n = 1, 2, 4, 8.

Thus, despite the significant differences between the natures of the coordinating ligands, incorporating groups such as olefinic, allyl, cyclopentadienyl, etc., even a formal calculation of the number of units in the chelate ring reveals quite clearly a tendency towards the formation of the more stable five- and six-membered rings. Complexes (I) and (II) with three-membered rings are unique. Four-membered rings are also fairly rare with the exception of compounds with bicyclic dienes, which is due to the geometrical characteristic features of the latter. The lower stability of four-membered chelates compared with five-membered chelates is indicated by the fact that allyldiphenylphosphine forms chelate complexes neither with palladium(II) nor platinum(II), while butenyldiphenylphosphine forms them readily[117]. The use of divinyl ether was also unsuccessful, while hexa-1,5-diene gave a positive result[213]. The isomerisation of mesityl oxide under the influence of platinum(II) with formation of the mesityl iso-oxide complex (LVIII) containing a five-membered chelate ring is instructive. Even the loss of conjugation energy is compensated by the gain of chelate formation energy:



(LVIII).

The greater stability of five-membered chelate rings compared not only with four-membered but also with six-membered rings can be demonstrated by the reaction of 2-alkenylpyridines with norbornadiene complexes of Group VI metals[230]:

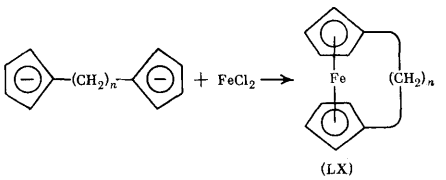


M = Cr, Mo, W (LIX) R = H, CH_3.

Isomerisation results only in the formation of complexes (LIX) containing five-membered chelate rings. The isomerisation of cyclo-octa-1,3-diene and cyclo-octa-1,4-diene under the influence of transition metals with formation of cyclo-octa-1,5-diene complexes is also consistent with these ideas[231-233]. The greater stability of five-membered rings compared with six-membered rings is also indicated by the interactions of 4-pentenyl and 3-butenyl derivatives of sulphur, selenium, and phosphorus with palladium(II). Only the 3-butenyl derivatives react with formation of five-membered chelates. It is of interest to note that platinum(II) forms chelates with both series of the above compounds[113,114,117]. The same can be said also of dienes, in which the double bonds are separated by two or three atoms[213]. The isomerisation of *o*-allylphenyldiphenylphosphine to the propenyl derivative[125,126] can also serve as evidence in support of the greater stability

of five-membered rings. This is also evident from a comparison of the relative reactivities of five- and six-membered chelates (see, for example, Garrow and Hartwell[117]).

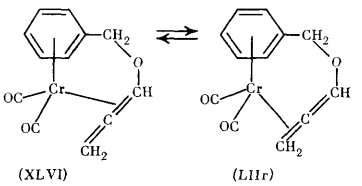
Yet another example illustrating the dependence of the CE on the size of the ring formed is provided by formation of ferrocenophanes in accordance with the following scheme:



(LX)

Thus the yield of a compound of type (LX) is 50% for $n = 2$, 2.5% for $n = 3$, 0.053% for $n = 4$, and 0.025% for $n = 5$.[198] The amount of polymeric products increases in the same sequence.

At the same time, chelates have been discovered in which the differences between the stabilities of the five- and six-membered rings are small. The chromium dicarbonyl complex with an arene-allene ligand gives rise in solution to an equilibrium mixture of the two forms corresponding to five-membered [compound XLVI)] and six-membered [compound (LIId)] chelates[196]. Unfortunately, this new instance of metallotropy has not been investigated adequately:



(XLVI) (LIIr)

The geometry of the ligand sometimes imposes a particular size on the chelate ring. Thus, in the case of arene-acetylene chelates of type (LIIe), six- and seven-membered rings are formed readily, while complexes with five-membered rings could not be obtained[219].

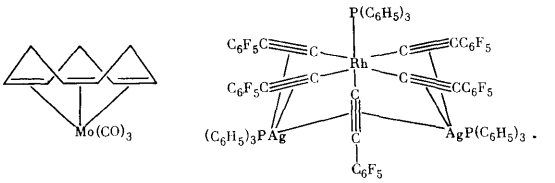
Quantitative data reflecting the dependence of thermodynamic stability on the size of the ring formed on chelation are available only for silver complexes[9,13-15,234], but they are satisfactorily correlated with qualitative data for other metals.

In conclusion of this Section one should note that approximately one-third of the known types of organometallic chelates have not been obtained as a result of specific synthesis but have been discovered accidentally as a result of the isomerisation of the ligand or its synthesis in the coordination sphere of the metal. In most cases this applies to five-membered chelates [compounds (XXIV), (XXV), (XXXI)–(XXXIV), (XL)–(XLIV), (XLVI), (XLVII), (LVIII), and (LIX)], but isolated examples of the synthesis of four-membered [compounds (XI), (XII), and (XVIII)], six-membered [compounds (XLVIII), and (LIId)], and seven-membered [compounds (LIV), and (LV)] complexes by this procedure are also known.

2. The Number of Rings

Studies on complexes with polydentate kn–$l\pi$- and $k\pi$-ligands were begun quite recently.

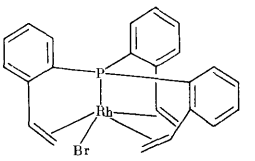
Complexes with polydentate $k\pi$-ligands ($k > 2$) have been little studied. Examples are provided by compounds (LXI)[235] and (LXII)[236] with ligands where three isolated double or triple bonds are coordinated to one metal atom. The structure of complex (LXII) has been established by X-ray diffraction:



(LXI) (LXII)

Ferrocenophanes with two, three, and four bridges[5,198] as well as bisarenechromophanes with two bridges[237,238] can be assigned to compounds of this type.

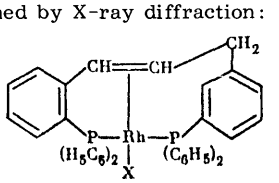
Complexes with kn–$l\pi$-ligands have been studied to a greater extent. Ligands potentially capable of forming five-membered rings have been synthesised for this purpose: tri(3-butenyl)phosphine[239], tri(4-pentenyl)phosphine[240], tri(*o*-vinylphenyl)phosphine[241,249], and tri(*o*-vinylphenyl)-arsine[242]. A rhodium(I) salt forms with these ligands penta-coordinate complexes of type (LXIII) whose structure, determined by X-ray diffraction[243,244], is trigonal-bipyramidal:



(LXIII)

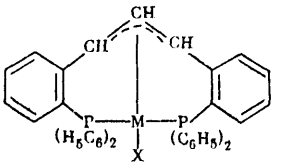
The double bonds are located approximately in the equatorial plane. Complexes with a similar structure have been obtained from phenyldi(*o*-vinylphenyl)phosphine[242] and dibutenyl-phenylphosphine[245]. On formation of complexes with Group VI metal[138,139], palladium(II)[246], and platinum(II)[246,247] carbonyls, these ligands react as bidentate species and in the case of palladium(II) and platinum(II) there is a rapid exchange of the coordinated and non-coordinated olefine groups according to ^{1}H NMR data. On the other hand, compounds containing two phosphorus atoms and one double bond [1,6-bis(diphenyl-phosphino)-*trans*-hexene and 1,6-bis(diphenylarsino)-*trans*-hexene] behave as tridentate ligands on formation of complexes with Group VI metal carbonyls[248].

Similar complexes with diphosphino-olefin ligands have been obtained also for other metals (see Bennett et al.[249] and the references therein and Clark[250]). The rhodium(I) complex (LXIV) has been quoted as an example[249]. Dehydrogenation of compounds (LXIV) leads to allyldiphosphinerhodium(I) complex of type (LXV). Other analogous derivatives (LXV) as well as complex (LXVI) with an allyl-dinitrogen ligand have also been obtained for other metals. The structures of compounds (LXV, M = Pd)[251] and (LXVI)[252] have been confirmed by X-ray diffraction:



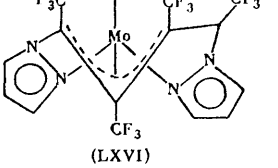
(LXIV)

X = Cl, Br



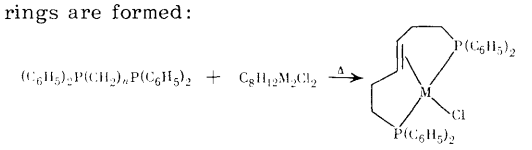
(LXV)

M = Pd; X = Cl; M = Rh, Ir, Ni; X = —



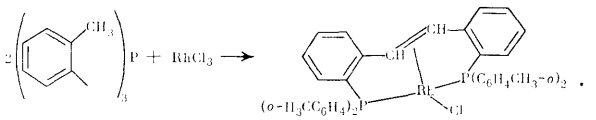
(LXVI)

It is noteworthy that, in the presence of a dehydrogenation catalyst, α,ω-bis(diphenylphosphino)alkanes form complexes (LXVII) with a tridentate diphosphino-olefin ligand only for $n = 6$,[250] i.e. only in the case where two five-membered chelate rings are formed:



M = Rh, Ir. (LXVII)

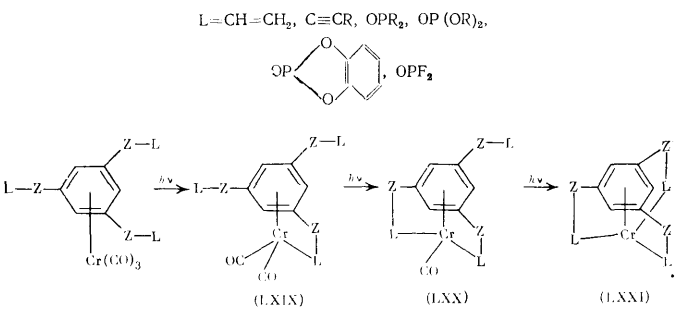
When $n = 5$, 7, or 8, complexes of type (LXVII) were not isolated. The tendency towards the formation of the analogous complex (LXVIII) with a conformationally more rigid chelating ligand [2,2′-bis(ditolylphosphino)stilbene] is so great that the ligand is generated in the coordination sphere of the metal from tri(*o*-tolyl)phosphine as a result of the dehydrogenation of the latter[253]:



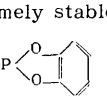
(LXVIII)

Similar reactions involving the formation of complexes with polydentate ligands as a result of dehydrogenation, isomerisation, and dimerisation have been investigated by Bennett and co-workers[135,253–258].

The characteristics of chelation with polydentate ligands have been studied systematically by Nesmeyanov and co-workers[259] in relation to arenechromium tricarbonyl complexes containing in the ω-position and in the side chain groups capable of coordination to metals:



(LXIX) (LXX) (LXXI)

Z are bridges consisting of $(CH_2)_n$ or various combinations of CH_2 and O. As a result, it has been found that the reaction is arrested at the single-bridge chelates (LXIX) when L = CH = CH_2 or $OPPh_2$ and at the two-bridge chelates (LXX) when L = $OP(OPh_2)$; all the CO ligands are substituted in succession with formation of extremely stable three-bridge ligands (LXXI) when L = OPF_2 or .

Whereas the electronic factors in chelation are determined by the nature of the group L, the steric factors are determined mainly by the size of the bridge Z. Thus single-bridge chelates of type (LXIX) are formed starting with a two-membered bridge, while the two- and three-bridge chelates (LXX) and (LXXI) are formed only starting with a three-membered bridge. The three-membered bridge (six-membered chelate ring) proved to be optimal in the synthesis of polycyclic chelates of this type. The structure of the three-bridge complex (LXXI, Z–L = $CH_2CH_2OPF_2$) has been established by X-ray diffraction[260].

Thus the nature of the ligand plays a significant role in the formation of polycyclic chelates.

3. The Conformation and Geometry of the Ligand

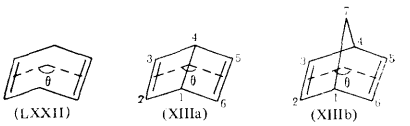
The question of the influence of the conformation of the ligand on the ease of formation of the chelates reduces to the elucidation of the number of possible conformations, their relative contributions, and, mainly, the conformation favourable for chelation. Apparently the greater the population of this favourable conformation, i.e. the conformation corresponding to the coordinated ligand, the greater the stability of the chelate complex. In the limiting case with a rigidly fixed conformation favourable for chelation, the contribution of this factor to the stability of the chelate complex should be a maximum. Indeed, a high stability has been observed in many cases for conformationally rigid ligands with a favourable disposition of the double bonds, such as, for example, norbornadiene and bicyclo[2.2.2]octa-2,5-diene[16] (Table 4).

Cyclo-octa-1,5-dienes[261] and cyclo-octatetraene[262], which have been shown to have the preferred boat conformation, form chelate complexes very readily; these have been obtained in large amounts with various metals. Cyclo-octadiene complexes are particularly stable (Tables 3 to 5).

The chair conformation of *cis*, *cis*-cyclodeca-1,6-diene is preferred to the boat conformation[263]. As a result, this ligand does not react with platinum(II) salts and its reaction with palladium(II) results in the formation of a polymeric complex[182]. On reaction with rhodium(I) derivatives at 80 °C, it gives rise to a chelate complex. This finding has been explained[32] by the fact that, at an elevated reaction temperature, the contribution of the boat conformation becomes considerable.

For linear ligands, the number of possible conformations is greater than for cyclic ligands and this number increases with increase in the length of the chain; the contribution of the favourable conformation therefore diminishes. Indeed, the stability of the complexes of linear ligands is lower (Tables 3 and 5). The decrease of the conformational mobility of the ligand results in an increase in the stability of the complexes formed. Thus *o*-allylphenyldimethylarsine and o-allylphenyldiphenylphosphine form chelate complexes with palladium(II) containing six-membered chelate rings[202], while pentenyldiphenylphosphine does not form such complexes[116]. This can be explained by the fact that, after the replacement of the C–C single bond in the chain by a multiple bond of the benzene ring, free rotation about this bond becomes impossible.

A significant change in geometry is observed in cyclic dienes, especially after the introduction of a bridge into the diene molecule. Only isolated examples of complexes have been described for cyclohexa-1,4-diene (LXXII) itself[65], but Dewar benzene[66,67] and norbornadiene[37–39,70–79] form complexes readily, which is probably due to the greater rigidity of the molecules owing to the presence of a bridge.



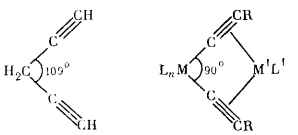
(LXXII) (XIIIa) (XIIIb)

The geometry of norbornadiene is particularly favourable for coordination to a metal, since in this compound the dihedral angle θ has the optimum value of approximately 115° and the

distance between C(1) and C(4) is increased to 2.24 Å, in contrast to Dewar benzene where it is approximately 1.55 Å; this reduces the extent of the non-bonding interactions of C(1) and C(4) with the metal atom on coordination[67]. It is interesting to note that an increase in the length of the bridge up to 2 and even 4 members causes little change in the geometry of the ligands[84,264] and the latter form stable complexes, like norbornadiene.

An important factor which diminishes the stability of chelate complexes with dienes is a non-parallel arrangement of the double bond. Such an arrangement is encountered in cyclic dienes with an odd number of atoms in the ring [the derivatives of cyclohepta-1,4-diene (XIV, a–f) and cyclonona-1,5-diene (XXXIX, a–c)], and also in dienes with an even number of atoms in the ring but with an asymmetric disposition of the double bonds (cyclo-octa-1,4-diene) or an asymmetric position of the bridge as in bicyclo[3.3.1]nona-2,6-diene (XXXVIIIe).

The geometry of the chelating ligand can depend on the nature of the atoms in the chain connecting two coordinating groups and also on their hybridisation. The replacement of a carbon atom in the chain of the diyne ligand (LXXIII) by the metal atom greatly reduces the angle between the acetylenic fragments which leads to a geometry of the ligand favourable for chelation. Complexes with ligands of type (LXXIV) are known[98–100], while no complexes have so far been obtained for the ligand (LXXIII). On the other hand, the formation of four-membered chelate rings by diolefin ligands requires an increase of the angle between the olefin fragments. This can be achieved by altering the hybridisation of the bridging carbon atom from sp^3 to sp^2, as shown in complex (XII)[64].



(LXXIII) (LXXIV)

4. The Nature of the Coordinating Groups

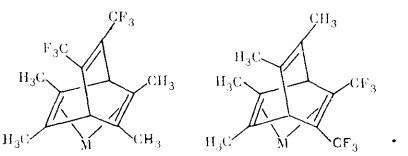
This problem has so far been little studied. In terms of the bond strength, the coordinating fragments can be arranged in the following sequence (for metals in a low oxidation state): P > As > N > unsaturated ligand > O; Se > S ≫ O (see also Table 4). Chelate complexes with a heteroatom can be arranged in the same sequence in terms of their stability. The data in Table 2 show that the stability of the selenium-containing chelate complexes of silver is higher than that of the corresponding sulphur-containing complexes. Chemical data are also consistent with this finding. Thus, in the case of alkenyl sulphide complexes of palladium(II) and platinum(II), *p*-toluidine fully substitutes the ligand, while in the alkenyl selenide derivatives only the double bond is displaced[113,114]. On the other hand, the substitution of the double bond C=C in the pentenylarsine complexes of platinum(II) by *p*-toluidine requires prolonged refluxing[200]. These complexes are as a rule more stable than the diene complexes. For example, diphenyl-*o*-styrylphosphine substitutes norbornadiene in Group VIB metal complexes with formation of complexes of type (XXX)[127].

The influence of substituents in the coordinating groups has not been studied systematically. It is evident from the available data that the introduction of even one alkyl substituent into a coordinating unsaturated group as a rule destabilises the chelate (Tables 1 and 3) and this is manifested even in the case of cationic silver complexes, the opposite behaviour being observed in the corresponding non-chelate mono-olefin complexes. Steric effects probably play a major role in organometallic chelates.

IV. THE INFLUENCE OF THE NATURE OF THE METAL ON THE STABILITY OF THE CHELATES

The stability of the chelate π–*n* and π–π complexes as a function of the nature of the metal varies as a rule in parallel with the stability of complexes of a similar structure containing non-chelating ligands. Thus the stability of the mono-olefin complexes of platinum(II) is greater than that of the analogous palladium(II) compounds. The same relative stabilities are observed also for chelate complexes with ligands containing a double bond. The CE does not as a rule alter the tendency in the variation of the stability but merely enhances it. The study of the dependence of the properties of the complexes on the metal is complicated by the fact that a sufficiently correct comparison is possible only for complexes containing the atoms of metals belonging to a single subgroup. Such a comparative study has been carried out by infrared and Raman spectroscopic methods for diene complexes of metals with the d^8 electron configuration and identical geometries of the compounds[30,34]. This led to the conclusion that the stability of the hexa-1,5-diene and cyclo-octadiene complexes of palladium(II), platinum(II), and rhodium(I) increases in the sequence indicated from palladium(II) to rhodium(I).

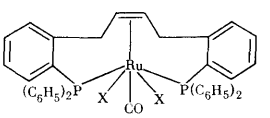
Depending on the nature of the metal, 2,3,5,6-tetramethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene can be coordinated in two ways: (LXXV) and (LXXVI):



(LXXV) (LXXVI)

A complex of type (LXXVI) is formed for M = $Mo(CO)_4$ or C_5H_5CO[80] and a complex of type (LXXV) for M = $[RhCl]_2$ or $Rh(Ph_3P)Cl$[16]; when M = $Fe(CO)_3$, complexes of both types are formed with the complex of type (LXXV) predominating[80].

It is noteworthy that in the case of chelates it is possible to obtain complexes with a metal–olefin bond in which the metal is in a higher oxidation state than is possible for non-chelate mono-olefin ligands. An example is provided by ruthenium(II) complexes of type (LXXVII)[156]:



(LXXVII)

X = Cl, Br.

The formation of such complexes is important primarily because the analogous compounds with monodentate and olefinic ligands occur as intermediates in catalytic processes and cannot be isolated because they are extremely unstable. Indeed, ruthenium(II) complexes of mono-olefins have not been isolated.

In contrast to inorganic chelates, the influence of metal atomic radius on chelate stability is low, since its variation for transition metals in Periods I–III in the zero oxidation state is insignificant (within the limits of 0.1 Å)[265]. The degree of oxidation exerts a major influence on the radius variation.

Specific valence angles α, which determine the geometry of the complex, are characteristic of each metal atom, depending on its nature, degree of oxidation, and ligand environment. It is interesting to examine this problem in relation to diene ligands used most frequently and forming the most stable complexes—norbornadiene and cyclo-octa-1,5-diene. Complexes of metals with square [for example, palladium(II), platinum(II), and rhodium(I)] and octahedral [for example, Group VI metals, ruthenium(II), etc.] configurations (α = 90°) form somewhat more stable compounds with norbornadiene[37–39] (see also Table 4). The stability of tetrahedral norbornadiene complexes {for example, the complex Ni(O)-[(duroquinone)Ni(diene)]}, is lower than that of complexes containing less rigid ligands—cyclo-octadiene and bicyclopentadiene[18,19]. Group IB metals (valence angles α = 109°, 120°, and 180°), characterised by a tendency towards linear hybridisation which increases from copper(I) to gold(I)[266], do not form cationic chelate complexes with norbornadiene§. Complexes in which norbornadiene behaves as a monodentate ligand were isolated later[267].

Not one chelate complex of the π–n or π–π type is known for gold(I). Only the powerful chelating ligand *o*-phenylenebisdimethylarsine forms a chelate complex with a tetrahedral configuration: $[(\text{diarsine})_2\text{Au}]^+\text{I}^-$.[266]

According to X-ray diffraction data, in complexes with a trigonal-bipyramidal configuration (valence angles 90° and 120°), ligands such as norbornadiene and cyclo-octadiene occupy one axial and one equatorial position (α = 90°) and not two equatorial positions (α = 120°), which also reflects the importance of the correspondence between the valence angles of the metal atoms and the geometry of the ligands.

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Summarising this review, one may say that organometallic chelate complexes constitute a new rapidly developing field in the chemistry of organometallic compounds. A large number of various chelate complexes of this type, among which polycyclic chelates are of special interest, have now been obtained. At the same time, the properties of organometallic chelates have so far been inadequately studied and the information available on this topic is in the main qualitative. Nevertheless, one may conclude that, in terms of many of their properties, organometallic chelates resemble inorganic chelates. This similarity is manifested primarily by the fact that in complexes of both types the five- and six-membered rings are the most stable, that the stability of the complexes increases with increase of the number of chelate rings in the molecule and with increase of the rigidity of the ligand, and also that both the entropy and enthalpy factors make an important contribution to the CE. At the same time, organometallic chelates have a whole series of characteristics associated primarily with the geometry of the organic ligand and the nature of the metal–carbon bond. Whereas the M = L bond in inorganic chelates is of the donor–acceptor type (n-type) and an increase of electron density at the heteroatom in the group L stabilises this bond, in organometallic chelates (where L is an organic π-ligand) the type of the metal–ligand bond is different. It is a combination of donor–acceptor and dative bonds. The nature of this π-bond makes its impression also on the geometry of the molecules of organometallic chelates. The metal atom in such complexes is as a rule located in a plane perpendicular to that of the π-ligand and not on the axis of the bond between the metal and the coordinating atom, as happens in inorganic chelates. Whereas the latter involve mainly metal cations, among organometallic chelates complexes of metals in a low oxidation state occupy a major place, which not only greatly extends the region of existence of chelate complexes in general but also makes it possible to expect that they will manifest new useful properties. For example, organometallic chelates with an increased electron density at the metal atom may prove to be active reductants or electron transferring agents, preserving at the same time the structure of the complex. The increase of stability as a result of the CE makes it possible to synthesise and investigate new types of organometallic complexes, information about the structure of which can throw light on the mechanisms of many catalytic processes. Finally, these complexes can themselves prove to be active catalysts, which has been confirmed by the isolation of some of them in catalytic reactions.

§ The only exception is that of the relatively unstable copper(I) complex of 7-t-butylnorbornadiene to which a chelate structure has been attributed solely on the basis of the ^{1}H NMR spectrum[267].

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