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Metallacyclopentadienes: structural features and coordination in transition metal complexes †

F M Dolgushin, A I Yanovsky, M Yu Antipin

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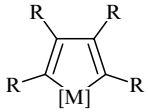
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Abstract. Results of structural studies of polynuclear transition metal complexes containing the metallacyclopentadiene fragment are overviewed. The structural features of the complexes in relation to the nature of the substituents in the organic moiety of the metallacycles, the nature of the transition metals and their ligand environment are analysed. The main structural characteristics corresponding to different modes of coordination of metallacyclopentadienes to one or two additional metal centres are revealed. The bibliography includes 154 references.

I. Introduction

Metallacycles and their complexes occupy a special place in modern organometallic chemistry because of their higher stability compared to acyclic analogues (the so-called chelating effect) as well as the diverse applications of metallacyclic compounds in both fundamental and applied investigations. The formation of metallacyclic fragments is observed in many reactions of organic substrates with transition metal complexes, for example, in cycloaddition, insertion of metal atoms into C–H bonds, reactions accompanied by dimerisation of unsaturated molecules through C–C coupling or reactions involving carbonyl, nitrile and other ligands of the starting complex. Methods for the synthesis of compounds containing metallacyclic fragments and their chemical properties were described in general reviews [1,2] as well as in reviews devoted to special problems.[3–5] Transition metal complexes containing metallacyclic fragments play an important role in metal-catalysed chemical transformations, such as alkene and acetylene metathesis, isomerisation of strained rings, cycloaddition of alkenes, oligomerisation of dienes and polymerisation.

Coupling of alkenes or alkynes in the coordination sphere of metal atoms is widely used in the synthesis of metallacyclic compounds giving rise primarily to five-membered metallacycles.[1,2] Of particular interest are five-membered unsaturated metallacycles, the so-called metallacyclopentadienes (MCPs).



The MCP fragment is considered as an important intermediate in the synthesis of organic compounds from alkynes,[5–10] for example, in cyclotrimerisation of alkynes to form benzene derivatives and in the synthesis of quinones and tropones. Synthesis methods and studies of the chemical properties and structural features of transformation products of alkynes involved in transition metal complexes, including investigations of polynuclear complexes with the MCP fragment, were covered in the reviews.[11–14] In these complexes, the metallacycle generally serves as a π ligand with respect to transition metal atoms. Investigation of the coordination ability of the MCP fragment, particularly, taking into account its close analogy to the cyclopentadienyl ligand, is of interest not only for the development of the chemistry of certain systems but also for solution of more general problems of organometallic chemistry associated with a search for new 'non-classical' π ligands. Single-crystal X-ray diffraction is used as the main experimental method for studying the structures of MCP complexes.

Extensive experimental data on the structures of polynuclear transition metal complexes, in which the MCP fragment is involved in binding to one or several metal atoms, are available. According to the Cambridge Structural Database (CSD),[15] more than 350 structures of such compounds were characterised. For some series of related compounds, the results of structural studies were systematised (see, for example, the reviews [13,16,17]). However, abundant data on the structures of complexes with the MCP fragment have remained beyond the scope of these publications.

The present review covers the results of structural studies of polynuclear complexes containing the MCP fragment with special emphasis on comparative analysis of the structure of the MCP fragment and the modes of its coordination in transition metal complexes depending on the ligand environment, electronic state, the type and number of metal atoms, electronic and steric characteristics of substituents in the organic moiety of the metallacycle. We have restricted ourselves to complexes containing

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† The present review completes a series of publications covering main fields of research of the A N Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences [see *Russian Chemical Reviews* **73** (5) (2004)].

more than three metal atoms. Prominence is given to bi- and trinuclear complexes of metals for which most representative data are available in the CSD (metals of the iron and cobalt subgroups). The structure of the uncoordinated MCP fragment has been discussed in detail earlier.[2,18] Hence, we do not consider mononuclear complexes. Complexes with metallacycles, in which one or several carbon atoms are replaced with heteroatoms (N, O, S, *etc.*), are also beyond the scope of our review.

II. Dinuclear complexes with the metallacyclopentadiene fragment

The first structure of an MCP-containing dinuclear complex with composition $Fe_2(CO)_6\{C(OH)C(Me)C(Me)C(OH)\}$ (**1**) was published in 1961.[19] The structure of complex **1** is shown in Fig. 1. The authors believed that the Fe(1) and Fe(2) atoms are in different oxidation states (0 and 2+, respectively); the diene fragment is coordinated to the Fe(2) and Fe(1) atoms through two σ-bonds and two π-bonds, respectively. Equalisation of the C–C bond lengths in the ring is indicative of strong conjugation. One of the six carbonyl groups, *viz.*, C(10)O(10), is apparently semibridging with the Fe(1)–C(10)–O(10) angle of 168°. However, in the authors' opinion, the Fe(2)···C(10) distance (2.48 Å) is too large to be indicative of interaction between these atoms.

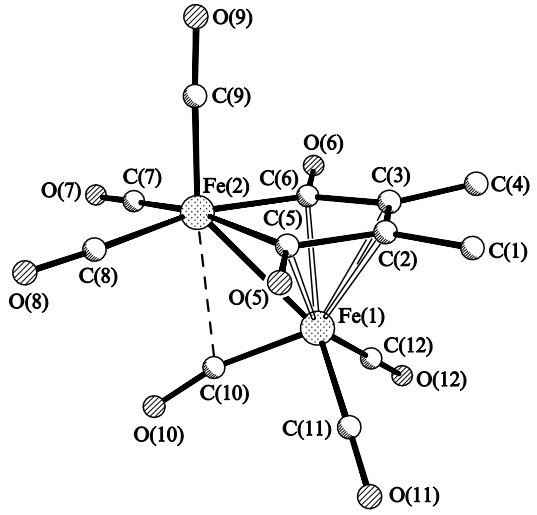


Figure 1. Structure of the $Fe_2(CO)_6\{C(OH)C(Me)C(Me)C(OH)\}$ complex (**1**).[19]
The hydrogen atoms are omitted, the atomic numbering scheme corresponds to that used in the original paper.

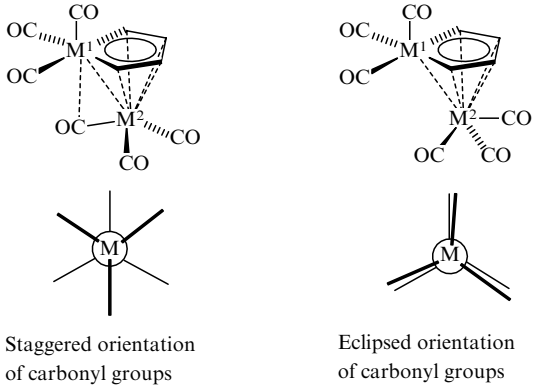
In the above-described compound, the structural motif, which proved to be typical of many bi- and polynuclear transition metal complexes, was found for the first time. Later on, the ferracyclopentadienyl fragment in complex **1** was given the short name ferrole. Nowadays all structurally similar dinuclear complexes are called complexes of the ferrole type regardless of the metal atoms involved in such complexes.

The structures of 158 dinuclear complexes of this type with different transition metals are included in the CSD. For convenience of comparison and discussion, typical compounds are shown in Fig. 2. The compounds are divided into five groups according to which subgroup of the Periodic Table the metal atom of the MCP fragment belongs. Each column in Fig. 2 begins with homometallic complexes with identical ligands (in most cases, these are carbonyl complexes) followed by heterometallic complexes (two different metal atoms, M^1 and M^2) and complexes with metal atoms in a non-equivalent ligand environment.

All compounds can formally be divided into two types according to the modes of distribution of electrons donated by an organic ligand between the metal atoms depending on the external ligand environment. In complexes of one type, the butadiene fragment forms two σ-bonds with one metal atom giving rise to a five-membered metallacycle, which is coordinated to the second metal atom through the metal–metal σ-bond and π-coordination of two alkene bonds of the diene fragment (η^1-η^4-coordination of the MCP fragment). For both metal atoms, the effective atomic number (EAN) rule is fulfilled, *i.e.*, the metal atoms have the filled 18-electron configuration (**A2**, **B1**, **B2**, **C4**, **D1** – **D3** in Fig. 2). In complexes of another type (**A1**, **C1** – **C3**, **D4**, **D5**, **E1**, **E2**), this description of coordination leads to non-equivalence of the electronic states of the metal atoms, which can be remedied by considering the metallacycle as a completely delocalised π-system (η^5-coordination of the MCP fragment). It should be emphasised that the use of these two limiting forms for the description of binding of the MCP fragments in dinuclear transition metal complexes of the ferrole type is based only on the formal application of the EAN rule. Nevertheless, as will be demonstrated below, the predominant contribution of one particular form was confirmed by the experimentally observed differences in the geometric parameters of ferrole complexes of different types.

1. Carbonyl complexes with metals of the iron subgroup

In crystals, dinuclear ferrole-type carbonyl complexes with metal atoms of the iron subgroup exist as one of two conformers, which differ in the orientation of the $M(CO)_3$ fragments with respect to the M–M bond. In most structures, like in complex **1**, the carbonyl groups have a staggered conformation giving rise to a shortened intramolecular contact between the endocyclic metal atom and one of the carbonyl groups at the exocyclic metal atom (this carbonyl group will be called semibridging). The second conformer is characterised by the eclipsed orientation of the carbonyl groups with the result that semibridging interaction is absent. In the general form, the structures of two conformers can be represented by the following scheme:



Dinuclear iron, ruthenium and osmium carbonyl complexes containing the MCP fragment are listed in Table 1 (structures available in the CSD and two compounds **31** and **32**, which were not deposited with CSD). Analogous complexes in which one or several carbonyl groups are replaced with other ligands (phosphine, alkene, *etc.*) are not considered. Polynuclear (containing more than two metal atoms) complexes bearing a ferrole-type fragment are also not included in Table 1. Selected compounds of this type are described below.

Analysis of the data from Table 1 shows that, first, isomers with a staggered conformation of carbonyl groups occur much more frequently than those with an eclipsed conformation of these groups (except for complexes of osmium for which only three structures of the type under consideration are known, and all these complexes have carbonyl groups in an eclipsed orientation). Second, for all compounds containing the semibridging carbonyl

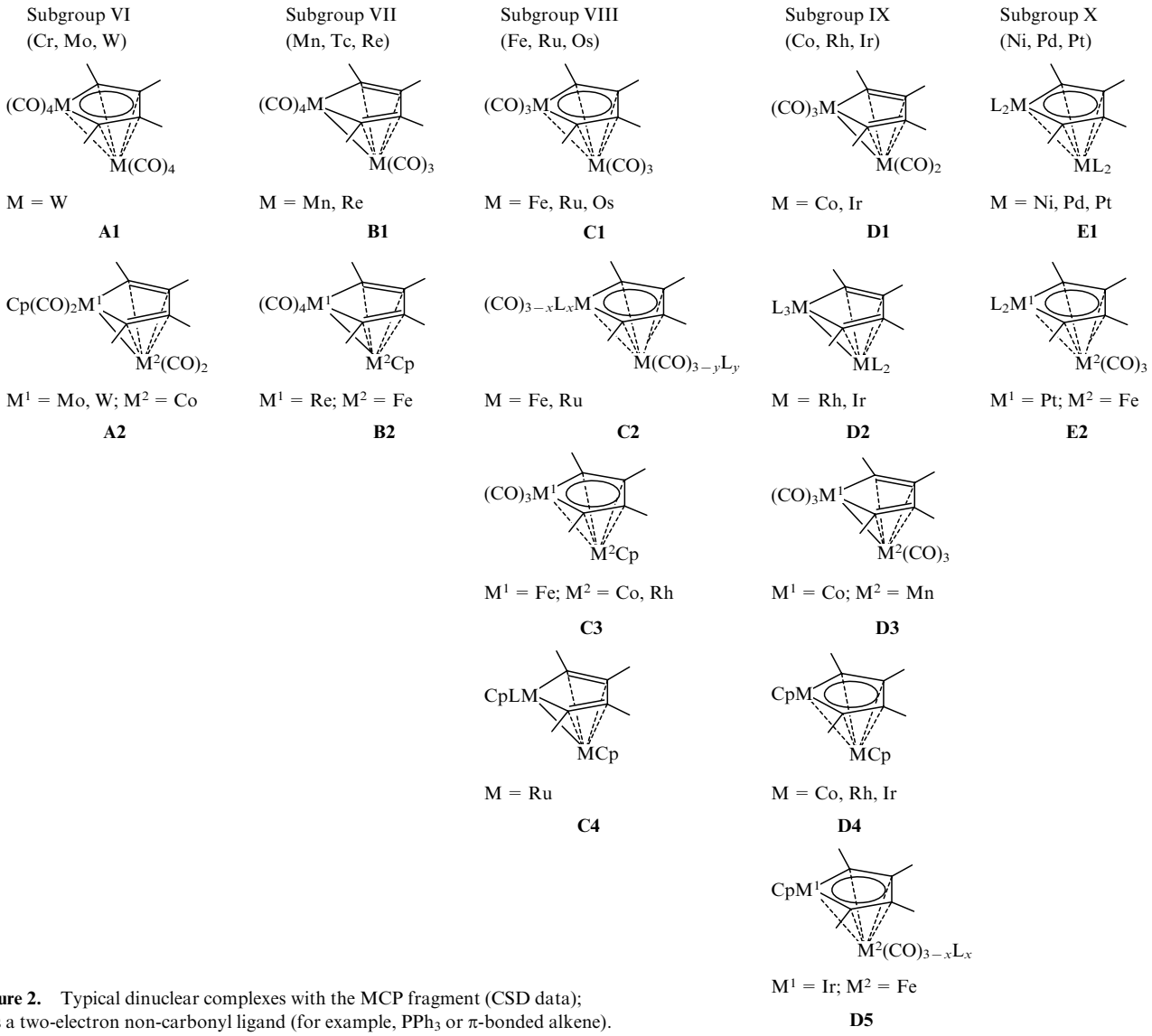
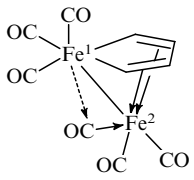


Figure 2. Typical dinuclear complexes with the MCP fragment (CSD data); L is a two-electron non-carbonyl ligand (for example, PPh_3 or π-bonded alkene).

group, there is a clear correlation between the $M^1\cdots CO(4)$ distance and the deviation of the metal carbonyl group $M^2-C-O(4)$ from linearity. These parameters vary over rather wide ranges, whereas the M^1-M^2 bond lengths are in a relatively narrow range. For example, the $M^1\cdots CO(4)$ distances in the iron complexes with a staggered conformation of carbonyl groups vary from 2.281 to 2.596 Å, whereas the M^1-M^2 distances are in the range of 2.463–2.533 Å, which is apparently indicative of high mobility of the carbonyl ligands at the M^2 atom relative to the relatively rigid metal–metal bond and a very weak interaction between the M^1 atom and the semibridging carbonyl group. It should be noted that the iron complexes with an eclipsed conformation of carbonyl ligands (compounds **21**, **22** and **23**) are characterised by somewhat larger metal–metal bond lengths (2.538, 2.544 and 2.568 Å, respectively). However, such a correlation is not observed for ruthenium complexes.

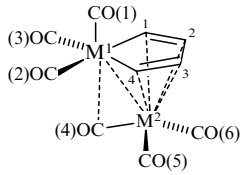
The nature of the metal–semibridging CO group interaction, its role in stabilisation of the molecule, the reasons for the existence of one of two possible conformers and other problems associated with this interesting characteristic feature of dinuclear ferrole-type carbonyl complexes with metals of the iron subgroup were discussed in numerous structural and theoretical studies. In particular, the following scheme of charge redistribution in complex **2** with unsubstituted ferrole was proposed [20] (the formal description assumes a negative charge on the metal atom involved in the metallacycle and a positive charge on the second metal atom): back donation from the occupied d orbitals of Fe^1 to the π* orbital of the semibridging CO group, which, in turn, leads to an increase in σ-donation from this carbonyl group to the electron-deficient Fe^2 atom.



This scheme of charge density redistribution in transition metal complexes involving semibridging carbonyl ligands was proposed in the studies by Cotton (see, for example, Refs 50 and 51).

An alternative description was proposed in the publication,[46] where two ruthenium complexes (**31** and **32**) were considered. The authors of the cited study noted that the lengths of the $M^1-C(1)$ and $M^1-C(4)$ σ-bonds in these complexes and a number of other analogous compounds are close to the M=C double bond lengths in carbene complexes (the same fact was also mentioned in the study [20]). It is therefore concluded that there is a substantial additional π-contribution to binding of the metal atom M^1 in the ring. Hence, the charge redistribution in such complexes can occur as follows: $M^2 \rightarrow M^1 \rightarrow$ π electrons of the ring $\rightarrow M^2$. Therefore,

Table 1. Main geometric parameters for the dinuclear carbonyl complexes with general composition $(C_4R_4)M_2(CO)_6$ containing the MCP fragment (M^1, M^2 = Fe, Ru, Os; distances are given in Å, angles are given in degrees).



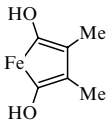
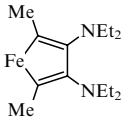
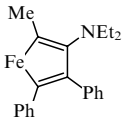
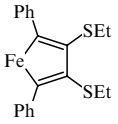
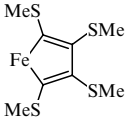
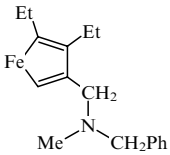
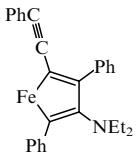
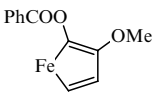
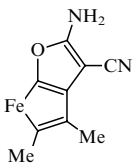
Compound [a]	MCP fragment	M^1-M^2	$M^1\cdots CO(4)$	$M^2-C-O(4)$ angle	$M^1-CO(1)$	$M^1-CO(2)$, $M^1-CO(3)$	$M^1-C(1)$, $M^1-C(4)$	C(1)–C(2), C(2)–C(3), C(3)–C(4)	ω [b]	τ [c]	Ref.
1		2.494	2.484	167.9	1.744	1.809 1.799	1.944 1.947	1.413 1.430 1.424	0.4	7.1	19
2		2.515	2.509	167.2	1.744	1.814 1.822	1.938 1.953	1.406 1.413 1.368	0.3	8.7	20
3		2.506	2.386	162.0	1.719	1.817 1.805	2.000 2.033	1.440 1.457 1.415	2.1	16.0	21
4		2.497	2.398	162.8	1.747	1.808 1.818	1.978 1.972	1.421 1.442 1.431	5.6	15.6	22
5		2.496	2.414	164.3	1.753	1.798 1.789	1.974 1.975	1.410 1.454 1.433	5.0	12.8	23
6		2.533	2.505	166.5	1.764	1.824 1.804	1.965 1.970	1.429 1.436 1.439	0.6	12.3	24
7		2.488	2.406	165.3	1.775	1.798 1.808	1.992 1.950	1.409 1.430 1.431	0.3	9.3	25
8		2.500	2.479	166.5	1.757	1.807 1.825	2.016 1.956	1.425 1.441 1.429	9.3	14.0	26
9		2.522	2.596	169.5	1.757	1.814 1.830	1.955 1.921	1.410 1.429 1.410	5.1	11.7	27
10		2.510	2.545	167.8	1.761	1.809 1.818	1.911 2.007	1.413 1.417 1.414	2.5	11.3	28

Table 1 (continued).

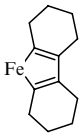
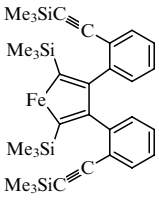
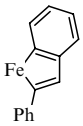
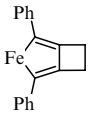
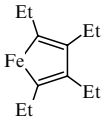
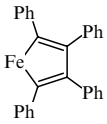
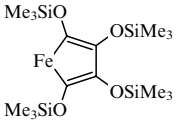
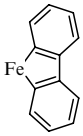
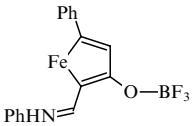
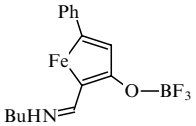
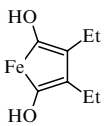
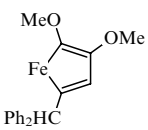
Compound [a]	MCP fragment	M^1-M^2	$M^1\cdots CO(4)$	$M^2-C-O(4)$ angle	$M^1-CO(1)$	$M^1-CO(2)$, $M^1-CO(3)$	$M^1-C(1)$, $M^1-C(4)$	$C(1)-C(2)$, $C(2)-C(3)$, $C(3)-C(4)$	ω [b]	τ [c]	Ref.
11		2.463	2.321	161.9	1.722	1.787 1.739	1.936 1.987	1.413 1.429 1.403	0.2	10.1	29
12		2.494	2.281	156.9	1.772	1.807 1.803	2.018 2.012	1.414 1.439 1.428	1.0	12.9	30
13		2.520	2.472	164.8	1.765	1.749 1.778	1.970 1.978	1.386 1.440 1.442	5.4	7.3	31
14		2.490	2.436	163.8	1.760	1.804 1.817	2.041 2.030	1.403 1.408 1.397	0.1	15.0	32
15		2.504	2.483	166.9	1.764	1.805 1.819	1.970 1.982	1.433 1.435 1.423	0.05	9.6	33
16		2.503	2.374	162.1	1.777	1.827 1.824	1.981 1.956	1.418 1.439 1.427	2.9	9.7	34
17		2.500	—	—	$\langle M^1-CO\rangle$ = 1.83		$\langle 1.92\rangle$	—	—	—	35
18		2.468	2.320	158.4	1.773	1.786 1.807	2.002 2.004	1.409 1.455 1.424	0.1	8.1	36
19		2.505	2.552	169.8	1.782	1.836 1.832	1.989 1.992	1.438 1.420 1.422	6.9	14.9	37
20		2.498	2.501	167.4	1.802	1.816 1.829	2.002 1.989	1.435 1.434 1.413	9.1	12.8	37
21		2.544	eclipsed orientation of carbonyl groups		1.734	1.795 1.809	1.930 1.935	1.419 1.436 1.411	0.7	−1.2	38
22		2.538	the same		1.745	1.786 1.749	1.885 1.953	1.414 1.392 1.392	5.4	5.9	39

Table 1 (continued).

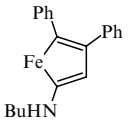
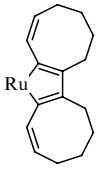
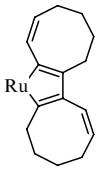
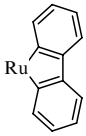
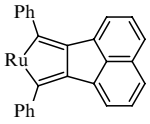
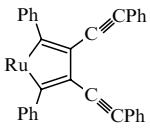
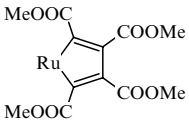
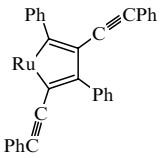
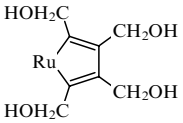
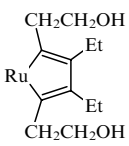
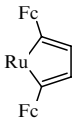
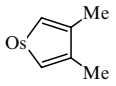
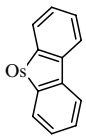
Compound [a]	MCP fragment	M^1-M^2	$M^1\cdots CO(4)$	$M^2-C-O(4)$ angle	$M^1-CO(1)$	$M^1-CO(2)$, $M^1-CO(3)$	$M^1-C(1)$, $M^1-C(4)$	$C(1)-C(2)$, $C(2)-C(3)$, $C(3)-C(4)$	ω [b]	τ [c]	Ref.
23		2.568	eclipsed orientation of carbonyl groups		1.773	1.816 1.792	1.956 1.988	1.416 1.436 1.414	16.9	−8.5	37
24		2.632	2.565	164.6	1.877	1.962 1.980	2.072 2.100	1.397 1.449 1.388	1.1	10.6	40
25		2.706	2.666	166.0	1.888	1.951 1.964	2.115 2.032	1.415 1.411 1.457	1.9	12.1	40
26		2.700	2.326	148.7	1.910	1.920 1.937	2.125 2.137	1.425 1.474 1.433	2.7	11.4	41
27		2.712	2.549	161.5	1.889	1.964 1.956	2.114 2.123	1.412 1.460 1.424	0.6	13.3	42
28 [d]		2.714 2.728	2.49 2.69	157 161	1.84 1.83	1.94 1.91 1.97 1.93	2.11 2.08 2.12 2.08	1.41 1.46 1.47 1.38 1.45 1.48	4.0 6.0	14.7 13.4	43
29 [d]		2.735 2.753	2.853 2.968	174.2 173.0	1.872 1.867	1.943 1.968 1.981 1.939	2.068 2.070 2.052 2.076	1.413 1.433 1.401 1.441 1.417 1.421	0.7 0.7	8.6 10.1	44
30		2.703	2.700	166.2	1.790	1.930 1.959	2.064 2.063	1.386 1.461 1.405	1.3	10.1	45
31 [e]		2.743	2.76	169	1.90	1.97 2.00	2.08 2.06	1.43 1.42 1.44	—	10.0	46
32 [e]		2.717	2.762	169.0	1.874	1.967 1.950	2.101 2.089	1.42 1.44 1.42	—	9.2	46

Table 1 (continued).

Compound [a]	MCP fragment	M^1-M^2	$M^1\cdots CO(4)$	$M^2-C-O(4)$ angle	$M^1-CO(1)$	$M^1-CO(2)$, $M^1-CO(3)$	$M^1-C(1)$, $M^1-C(4)$	$C(1)-C(2)$, $C(2)-C(3)$, $C(3)-C(4)$	ω [b]	τ [c]	Ref.
33		2.720	eclipsed orientation of carbonyl groups		1.892	1.949 1.949	2.074 2.074	1.410 1.397 1.410	0	−4.8	47
34		2.74	the same		–	–	–	–	–	–	48
35		2.754	"		1.891	1.902 1.958	2.054 2.116	1.404 1.415 1.455	5.7	4.6	49
36		2.725	"		1.897	1.937 1.921	2.124 2.087	1.460 1.485 1.462	1.3	2.8	41

[a] M^2 = Fe (**1**–**24**), Ru (**25**–**33**), Os (**34**–**36**). [b] The C(1)−C(2)−C(3)−C(4) torsion angle. [c] The dihedral angle between the C(1)C(2)C(3)C(4) and C(1)M^1C(4) planes; the positive value corresponds to the deviation of the M^1 atom from the plane of the diene fragment in the direction opposite to the M^2 atom, the negative value corresponds to the deviation of the M^1 atom toward the M^2 atom. [d] Values are given for two independent molecules in the crystal. [e] The structures are unavailable in the CSD.

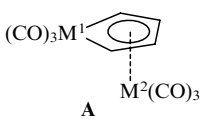
this process can take place without the involvement of a semibridging carbonyl group.

The contributions of Fe atoms and the diene fragment to the molecular orbitals of the ferrole complex $Fe_2(CO)_6(C_4H_4)$ were analysed in detail in the systematic study of the electronic structures of complexes containing the dinuclear fragment $M_2(CO)_6$, which is bound to various organic ligands.[52] It was demonstrated that there is an insignificant (0.2 eV) difference in the energy of two conformers of the complex with carbonyl ligands in eclipsed and staggered orientations. In the former case, there is a better overlap between the orbitals of the Fe^2 atom and the diene fragment. In the latter case, bonding interaction occurs between the Fe^1 atom and the semibridging carbonyl group.

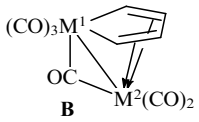
It should be emphasised that the interaction between the M^1 atom and the semibridging carbonyl group is weak in both cases. The results of ^{13}C NMR and IR spectroscopic studies of dinuclear complexes of the ferrole type at low temperatures (below −125 °C)[53–55] provide evidence for free rotation of the $M^2(CO)_3$ fragment in solution.

An interesting observation was made in the study of ruthenium complex **29**.[44] There are two independent molecules in the crystal. These molecules have similar geometry, except for the orientation of the semibridging carbonyl group (CO_{sb}); the $Ru(1)\cdots CO_{sb}$ distances in two independent molecules are 2.852(9) and 2.968(8) Å. An even larger difference in the $Ru(1)\cdots CO_{sb}$ distances [2.49(3) and 2.69(3) Å] was observed in two crystallographically independent molecules of complex **28**,[43] although the molecules differ only in the angle of rotation of the phenyl substituents with respect to the plane of the MCP fragment. Such substantial differences in the length of the $Ru(1)\cdots CO_{sb}$ contact, which are caused only by the crystal packing effects, confirm the conclusion as to a fine balance between forces responsible for the existence of one of two possible conformers.

Consequently, the structures of dinuclear ferrole-type carbonyl complexes with metals of the iron subgroup should be described with consideration for the contribution of two possible limiting forms (**A** and **B**):



A



B

In the first case (**A**), it is presumed that the endocyclic metal atom M^1 is completely integrated into the common π system of the MCP fragment through which the charge redistribution between two metal atoms occurs. For another limiting form (**B**), the charge redistribution occurs through the bridging carbonyl group, and the M^1 atom is not involved in the interaction with the π system of the butadiene unit of the metallacycle. However, the fact that the interaction between the endocyclic metal atom and the semibridging carbonyl group is weak as well as the flattened structure of the MCP fragment are indicative of the predominant contribution of the form **A**.

It can be assumed that the semibridging interaction characterises the degree of involvement of the endocyclic metal atom in the common π system of the MCP fragment. This assumption is supported by analysis of the structure of the MCP fragment in complexes **1**–**36** (see Table 1). With rare exceptions, the butadiene fragment in the metallacycles retains a planar structure (see the ω torsion angles in Table 1), whereas the endocyclic metal atom generally deviates from the plane of the butadiene system in the direction opposite to the second metal atom (parameter τ in Table 1). An interesting exception is compound **33**, which provides the only example of ruthenium complexes with carbonyl ligands in an eclipsed orientation.[47] The structure of this complex is shown in Fig. 3.

In the crystal, the molecule occupies a special position on the symmetry plane passing through both ruthenium atoms and the midpoint of the C(6)−C(6A) bond. Four carbon atoms of the metallacycle are coplanar, whereas the endocyclic Ru(1) atom deviates from the plane of the butadiene fragment by 0.134(1) Å toward the second metal atom Ru(2), *i.e.*, there is 'negative' folding ($\tau = -4.8°$) of the metallacycle along the C(5)···C(5A) line. It should be noted that the presence of two bulky ferrocenyl substituents in the α positions of the metallacycle in complex **33** has apparently only a slight effect on the structure of the MCP fragment, as evidenced by the absence of shortened intramolecu-

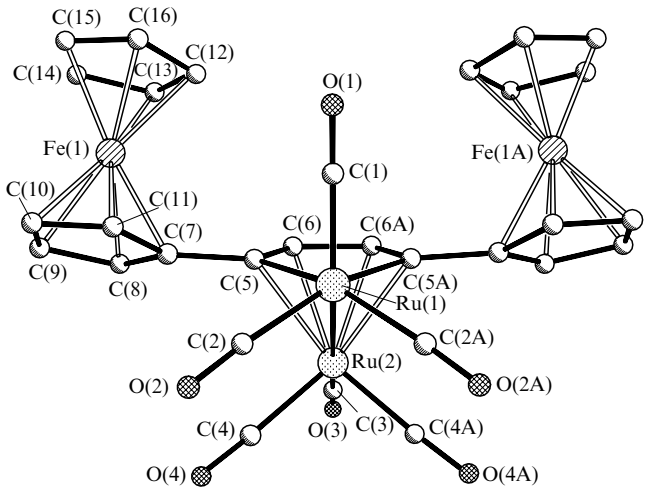


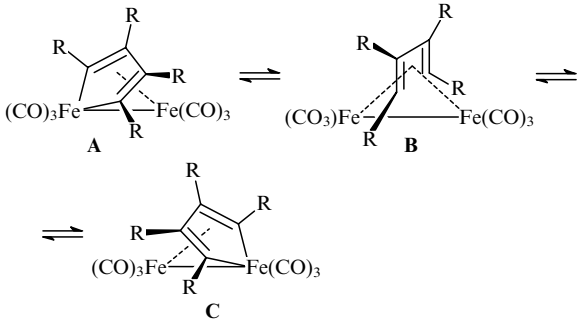
Figure 3. Structure of complex **33**.[47]

lar contacts. Besides, the negative value of the parameter τ is observed in two iron complexes (**21** and **23**), which also contain carbonyl ligands in an eclipsed orientation (see Table 1) and are devoid of sterically crowded substituents in the MCP fragment. In all other complexes with an eclipsed conformation of carbonyl ligands (**22**, **35** and **36**, see Table 1), the endocyclic metal atom deviates from the mean plane through four carbon atoms of the metallacycle in the direction opposite to the second metal atom. Nevertheless, in all complexes with eclipsed carbonyl ligands, folding of the MCP fragment is substantially smaller (the average angle $\tau = 4^\circ$) than that in complexes with staggered ligands and the semibridging carbonyl group (the average angle $\tau = 11^\circ$). Therefore, the MCP fragment is substantially flattened in complexes which contain carbonyl ligands in an eclipsed orientation and in which, correspondingly, additional interactions with the semibridging carbonyl group are absent.

The surprising thing is that the crystal structures of three dinuclear osmium complexes of the ferrole type (compounds **34**, **35** and **36**) are characterised by the eclipsed orientation of carbonyl ligands, whereas the staggered orientation (with the formation of the semibridging CO group) is typical of iron and ruthenium complexes. This fact was explained on the basis of *ab initio* calculations for $M_2(CO)_6(C_4H_4)$ (M = Fe, Ru, Os) complexes and comparison of these results with the data from UV photoelectron spectroscopy.[56] The authors proposed two mechanisms of charge redistribution in the dinuclear system: the direct metal–metal interaction and back donation from the d orbitals of the endocyclic metal atom to the π orbitals of the butadiene fragment and the semibridging carbonyl group. The absence of osmium complexes with staggered carbonyl ligands was accounted [56] for by substantial strengthening of the metal–metal interaction in the series Fe, Ru, Os, because the charge balance in such complexes can be established without the involvement of the semibridging carbonyl group.

It should be noted that derivatives containing only carbonyl ligands (**A1**, **B1**, **C1**, **D1**) were found for almost all dinuclear complexes with the MCP fragment (with the exception of Ni, Pd and Pt complexes; see Fig. 2). However, the existence of complexes as two conformers, *viz*., with the semibridging carbonyl group and without this group, is typical only of metals of the iron subgroup. In none of the complexes with other metals does a shortened contact between the endocyclic metal atom and one of the carbonyl groups coordinated to the second metal atom occur.

Yet another interesting characteristic feature of ferrole-type complexes is the rapid ferrole ring exchange **A** $\rightleftharpoons$ **C** characterised by the transition state **B** with the symmetry C_{2v}. This exchange was exemplified by optically active alkoxy- and hydroxy-substituted ferroles, which undergo racemisation at high temperatures.[57] The transformation from the hypothetical intermediate state **B** with the symmetry C_{2v} into ferrole was theoretically considered in the study.[52]



A remarkable example of the equilibrium transition between ferroles **A** and **C** was reported in the study,[58] where two isomers **37** and **38** (Fig. 4) were prepared in 18% and 57% yields, respectively, by thermolysis of the trimetallic cluster $Fe_3(CO)_9(N_2Et_2)$ with phenylacetylene. Heating of the pure isomers in solution afforded an equilibrium mixture of two complexes, which clearly confirms the occurrence of the dynamic transition **A** $\rightleftharpoons$ **C**. The enthalpy of isomerisation determined from the temperature dependence of the equilibrium constant is 90 ± 20 kJ mol^{-1} (low accuracy is related to slow decomposition of the compounds at high temperatures). The structures of both isomers were established by X-ray diffraction analysis.[59]

Both clusters contain the linear trimetallic core [the Fe(1)–Fe(2)–Fe(3) angle is 162° and 167° in isomers **37** and **38**, respectively]. The central iron atom is coordinated by both the

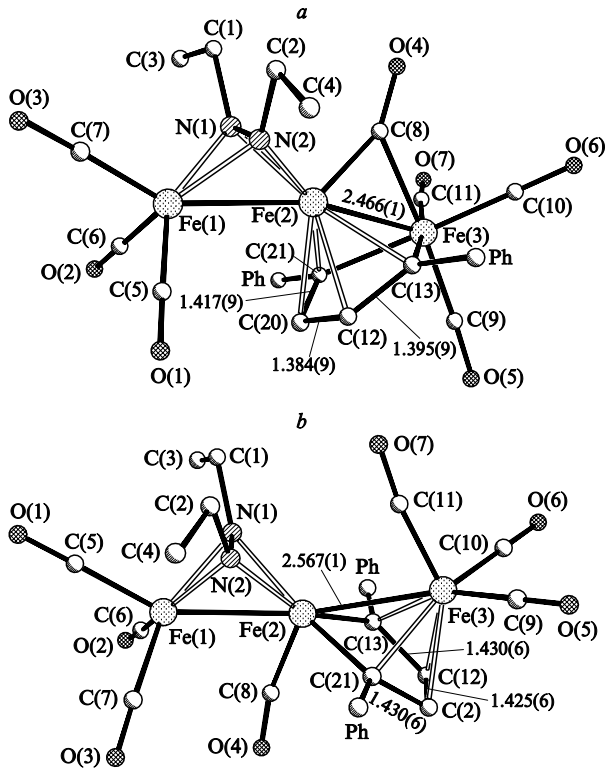


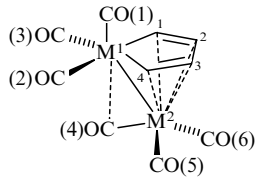
Figure 4. Structures of isomers **37** (*a*) and **38** (*b*) with composition $Fe_2(CO)_7(\mu\text{-}N_2Et_2)(\mu\text{-}HCCPh)_2$.[59]
Hereinafter, the bond lengths are given in Å. The phenyl substituents at the C(13) and C(21) atoms are omitted. The average Fe–C distances in the metallacycle are 2.02 and 1.93 Å, the Fe–C_{MCP} distances (π-coordination) are 2.09 and 2.11 Å in isomers **37** and **38**, respectively.

μ-azoalkane and μ-butadienyl ligands, which are located on opposite sides of the metal chain. The MCP fragments in both isomers are structurally similar to those in dinuclear ferrole complexes. The C—C bond lengths are equalised and the endocyclic metal atom deviates from the plane of the butadiene fragment in the direction opposite to the π-coordinated metal atom [the folding angle along the C(13)···C(21) line in the metallacycle is 15.2° and 12.9° for complexes **37** and **38**, respectively].

An analogous structure was described also for several homo- and heterometallic trinuclear complexes [60–65] containing an open metal chain and the MCP fragment. Only in one complex,[60] is the central metal atom involved in the metallacycle (like in isomer **38**). In other cases, the metallacycle is formed by the terminal metal atom (analogously to isomer **37**). In all compounds, the structure of the dinuclear fragment with the metallacycle is similar to that observed in dinuclear complexes of the ferrole type.

2. Phosphine derivatives

A characteristic feature of dinuclear carbonyl complexes of the ferrole type (see Table 1) is a shorter bond between the metal atom M^1 and the carbonyl group CO(1) located perpendicular to the plane of the metallacycle compared to two other bonds [M^1—CO(2) and M^1—CO(3)] involving the carbonyl groups in *trans* positions with respect to the M^1—C(1) and M^1—C(4) σ-bonds. For example, the average M^1—CO(1) and M^1—CO(2,3) bond lengths in the iron complexes are 1.76 and 1.81 Å, respectively.



A noticeable shortening of the M^1—CO(1) bond can be explained by two alternative hypotheses:[17] (a) an increase in the electron density on the M^1 atom due to the $M^2 \rightarrow M^1$ dative bond, which, in turn, leads to an increase in back donation from the M^1 atom to the CO(1) group; (b) the electron deficiency on the metal atom M^1 is compensated by an increase in electron donation by the CO(1) group. The second hypothesis was confirmed by the fact that it is this carbonyl group that is replaced with a stronger σ-donor, for example, with the phosphine ligand.[54,66–68] For instance, prolonged refluxing of $(C_4Ph_4)Fe_2(CO)_6$ with triphenylphosphine in toluene afforded the only product $(C_4Ph_4)Fe_2(CO)_5PPh_3$ (**39**). Its structure was established by X-ray diffraction analysis [54] and is shown in Fig. 5 (prior to this study, it was believed that the phosphine ligand is coordinated to the exocyclic iron atom [69]).

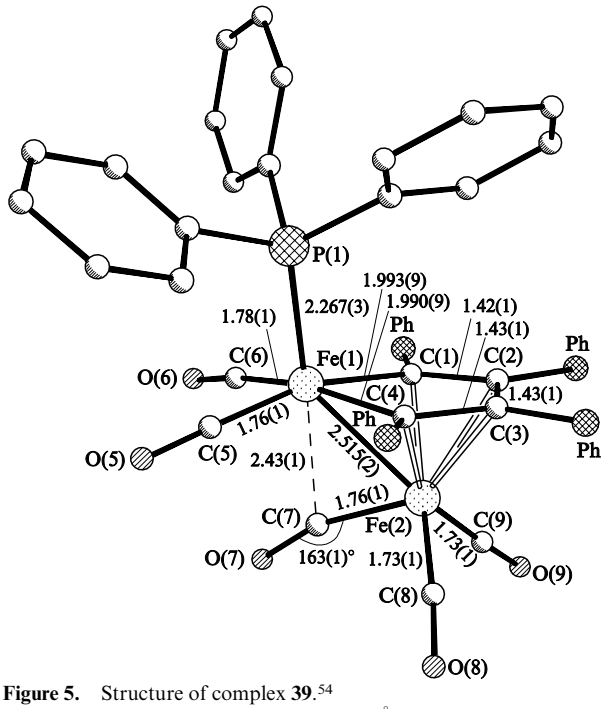


Figure 5. Structure of complex **39**.[54]
The average Fe(2)—C_{MCP} distance is 2.14 Å.

A comparison of the geometric parameters of complex **39** and its carbonyl analogue (compound **16**, Table 1) reveals no substantial differences in their structures. By contrast, the shortest $M^1 \cdots CO_{sb}$ distances [2.223(8) Å for Fe (see Ref. 66) and 2.236(3) Å for Ru (see Ref. 67)] in the series of ferrole-type carbonyl complexes (see Table 1) are observed in iron and ruthenium complexes with the trimethylphosphine ligand,[66,67] which is a stronger donor compared to the triphenylphosphine ligand.

It should be noted that in all monophosphine derivatives whose structures were established, the phosphine ligand is coordinated to the metal atom of the MCP fragment. Apparently, this isomer is thermodynamically more stable than the isomer in which this ligand is coordinated to the second metal atom (M^2). Coordination of the phosphine ligand to the M^2 atom was found only in diphosphine derivatives prepared by successive substitution of two CO groups in dinuclear hexacarbonyl complexes.[67,68]

3. Complexes with η^5- and η^1-η^4-coordination of the metallacyclopentadiene fragment

When describing complexes of the ferrole type, many authors (see, for example, Refs 61 and 63) invoked the analogy between the MCP fragment and the cyclopentadienyl ligand. This analogy is supported by the geometry of the metallacycle (a nearly planar structure, equalisation of the C—C bond lengths), the data from spectroscopic and electrochemical studies [70] and results of theoretical calculations.[18,52] A series of homo- and heteronuclear complexes of the ferrole type in which the exocyclic metal atom is coordinated simultaneously to the metallacycle and the cyclopentadienyl ligand (**B2**, **C3**, **C4**, **D4** in Fig. 2) belong to a peculiar type of metallametallocenes.[70–73] The structures of two ruthenium complexes **40** [74] and **41** [75] (see Fig. 6) are of interest.

Unlike homometallic dinuclear carbonyl complexes with metals of the iron subgroup characterised by η^5-coordination of the MCP fragment (**C1** and **C2** in Fig. 2), complexes **40** and **41** contain the η^1-η^4-coordinated metallacycle. This is related to the difference in the number of electrons donated to the metal atoms from the external ligand environment. In carbonyl complexes, each metal atom acquires six electrons, whereas the endocyclic ruthenium atom in complexes **40** and **41** has seven electrons and the exocyclic ruthenium atom has five electrons. Two different descriptions of the coordination modes of the MCP fragment in dinuclear complexes assume different electronic structures of the metallacycles. We proposed these descriptions based on the formal application of the EAN rule (see description of Fig. 2). The validity of this approach is supported also by the differences in the geometric structure of the complexes under consideration.

In complex **40**, the Ru(1)—Ru(2) bond is substantially elongated [2.831(1) Å)] compared to the Ru—Ru bonds in ruthenium carbonyl complexes **25**–**33** (the average bond length is 2.721 Å, see Table 1). In addition, the structure of the MCP fragment in complex **40** is non-planar, the folding angle of the metallacycle along the C(1)···C(4) line is 18.2°, which is also substantially larger than the average value (10.7°) for carbonyl complexes **25**–**33** (parameter τ in Table 1). It can be assumed that these changes in complex **40** are caused only by steric repulsions between the methyl groups of the pentamethylcyclopentadienyl ligands located in *cis* positions relative to the metal—metal bond. However, a comparison with complex **41**, in which the cyclopentadienyl ligands are in *trans* positions with respect to the metal—metal bond and steric hindrance is absent, provides

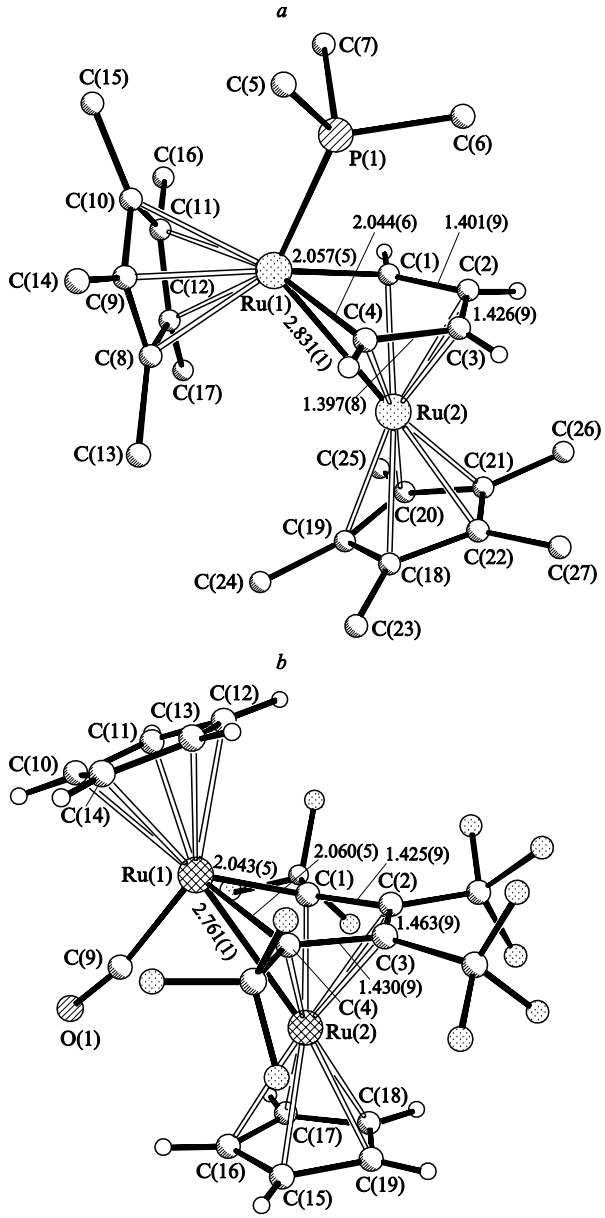


Figure 6. Structures of the complexes (η^5-C_5Me_5)Ru(PMe_3)(μ-η^4-C_4H_4)Ru(η^5-C_5Me_5) (**40**)[74] (*a*) and (η^5-C_5H_5)Ru(CO)(μ-η^4-$C_4(CF_3)_4$)Ru(η^5-C_5H_5) (**41**)[75] (*b*).

evidence for the predominant influence of the electronic properties of the ligand environment about the ruthenium atoms on the structure of the dinuclear fragment containing the metallacycle. The Ru(1)—Ru(2) bond length in complex **41** is smaller [2.761(1) Å] than that in complex **40** but it is noticeably larger than the average bond length in ruthenium carbonyl complexes **25**–**33**. The structure of the MCP fragment in complex **41**, where steric hindrance is absent, is analogous to that observed in complex **40**. The folding angle of the metallacycle is 23.1°. In both complexes, the C—C bonds are equalised. The Ru—C bond lengths in the metallacycles are close to the values typical of other ruthenacyclopentadienyl fragments.

In addition to complexes **40** and **41**, a number of analogous ruthenium compounds with cyclopentadienyl ligands and various ligands of another nature at the Ru(1) atom were also described.[76–78] In all complexes, the Ru—Ru bond is elongated and the MCP fragment shows greater deviations from planarity compared to those observed in ruthenium hexacarbonyl complexes of the ferrole type. In this connection, it is of interest to compare these compounds with the dinuclear cobalt carbonyl complexes $Co_2(CO)_5(C_4R_4)$ (**D1** in Fig. 2), whose formal consideration also reveals the η^1-η^4-coordination of the MCP fragment. The structures of all known dinuclear cobalt carbonyl complexes with the MCP fragment were described in the publication.[8] The authors noted that the structures of the complexes are independent of the nature of substituents in the organic moiety of the metallacycle and are characterised by equalisation of the C—C bond lengths in the diene fragment, a substantial deviation of the metallacycle from planarity (the average folding angle of the metallacycle is 16.5°) and a slight shortening of the Co—C bonds in the metallacycle (1.973 Å) compared to the values typical of the Co—C σ-bonds. Therefore, in the authors' opinion,[8] the use of the analogy between the MCP fragment and the cyclopentadienyl ligand in these complexes is not quite correct.

To compare complexes with different coordination modes of the MCP fragment (η^1-η^4- or η^5-coordination of the metallacycle) in more detail, we chose compounds with the same metal atoms and different ligand environments. In addition to the above-described ruthenium complexes, such pairs are known for cobalt and rhodium. The structures of these compounds are shown in Fig. 7 and their main geometric parameters are given in Table 2.

Table 2. Selected average geometric parameters for complexes with different coordination modes of the MCP fragment.

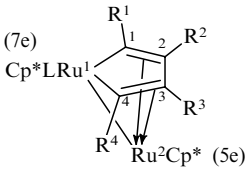
Metal	Coordination mode of the MCP fragment	M^1-M^2 /Å	$M^1-C(1,4)$ /Å	τ [a] /deg	Compounds
Ru	η^1-η^4	2.806	2.060	21.8	**40**–**44**
	η^5	2.725	2.073	9.3	**25**–**33**
Co	η^1-η^4	2.488	1.973	16.5	**45**–**49**
	η^5	2.451	1.889	5.7	**50**–**52**
Rh	η^1-η^4	2.708	2.048	16.5	**53**, **54**
	η^5	2.648	1.991	4.2	**55**–**58**

[a] The folding angle of the metallacycle along the C(1)···C(4) line.

The numbers of electrons donated by the external ligand environment to the metal atoms M^1 and M^2 are given in parentheses in Fig. 7. For complexes in which the numbers of electrons donated to the M^1 and M^2 atoms differ from each other (compounds at the left of Fig. 7), the fulfillment of the EAN rule assumes the formation of two σ-bonds between the organic ligand and the M^1 atom giving rise to the MCP fragment, which, in turn, is η^1-η^4-coordinated to the M^2 atom (the metal—metal σ-bond and π-coordination of the butadiene fragment). For complexes containing the M^1 and M^2 atoms in the same ligand environment (compounds at the right of Fig. 7), this consideration leads to non-equivalence of the metal atoms and, consequently, the electron density redistribution occurs apparently through the common π system of the metallacycle (η^5-coordination of the MCP fragment).

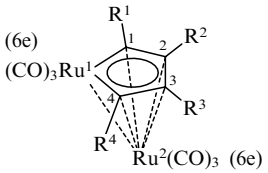
As can be seen from Table 2, the metal—metal bonds in the compounds with η^5-coordination of the MCP fragment are 0.03–0.08 Å shorter than those in the compounds with η^1-η^4-coordination. The structure of the MCP fragment also depends on its coordination mode. In the complexes with η^5-coordination, the metallacycle is more flattened than that in the complexes with η^1-η^4-coordination (parameter τ). In addition, the $M^1-C(1)$ and $M^1-C(4)$ bonds in the metallacycles are substantially shortened in the cobalt and rhodium complexes with η^5-coordination of the MCP fragment. This situation is not observed in ruthenium complexes.

Therefore, two coordination modes of the metallacycle occur in dinuclear complexes containing the MCP fragment depending on the number of electrons donated by the ligand environment

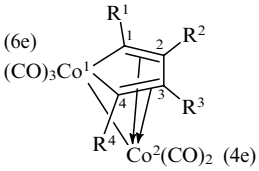


40–**44**

Compounds	L	Substituents	Ref.
40	PMe_3	R^1, R^2, R^3, R^4 = H	74
41	CO	R^1, R^2, R^3, R^4 = CF_3; Cp* = C_5H_5	75
42	C_2H_4	R^1, R^4 = Me; R^2, R^3 = H	76
43	2{Cl}	R^1, R^2, R^3, R^4 = H	77
44	2{Me}	R^1, R^3 = COOMe; R^2, R^4 = H	78

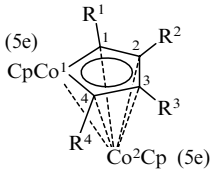


25–**33** (see Table 1)



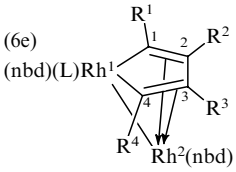
45–**49**

Compounds	Substituents	Ref.
45	$R^1-R^2=R^3-R^4=(CH_2)_6$	8
46	R^1, R^4 = SF_5; R^2, R^3 = H	8
47	R^1, R^4 = H; R^2-R^3 = $CMe_2N(Me)CMe_2$	8
48	R^1, R^4 = Ph; R^2, R^3 = H	8
49	R^1 = Ph; R^2 = H; R^3, R^4 = Me	8



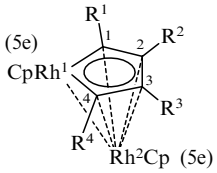
50–**52**

Compounds	Substituents	Ref.
50	R^1, R^2, R^3, R^4 = Cl	79
51	$R^1-R^2=R^3-R^4=C_4H_4$, Cp = C_5Me_5	80
52	$R^1-R^2=C_4H_4$, R^3 = Me, R^4 = H	81



53, **54** (nbd is norbornadiene)

Compounds	L	Substituents	Ref.
53	PMe_3	R^1, R^4 = H; R^2, R^3 = Me	82
54	PPh_3	R^1 = C≡CPh; R^2, R^4 = Ph; R^3 = H	83



55–**58**

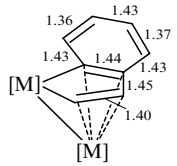
Compounds	Substituents	Ref.
55	R^1 = COOMe; R^2 = Me; R^3, R^4 = CF_3	84
56	$R^1-R^2=R^3-R^4=C_4H_4$; Cp = C_5Me_5	80
57	$R^1-R^2=C_4H_4$, R^3 = Ph, R^4 = H	85
58	$R^1-R^2=C_4H_4$, R^3 = Me, R^4 = H	85

Figure 7. Dinuclear complexes with the η^1-η^4- and η^5-coordinated MCP fragment.

about each metal atom. These coordination modes differ in the geometric parameters (see Tables 1 and 2). Complexes with η^1-η^4-coordination of the MCP fragment are characterised by a non-planar structure of the metallacycle with the endocyclic metal atom deviating from the plane of the butadiene unit in the direction opposite to the second metal atom (the folding angle of the metallacycle is close to 20°). Complexes with η^5-coordination of the MCP fragment are characterised by a more flattened structure of the metallacycle with an insignificant deviation of the endocyclic metal atom from the plane of the butadiene unit (the folding angle of the metallacycle is close to 5°). In this case, it is apparently more reasonable to assign the metallacycle to aromatic heterocycles. Shortening of the metal–metal bond is also typical of complexes with η^5-coordination. In some cases, shorter metal–carbon bonds were found in the metallacycle. In dinuclear carbonyl complexes with metals of the iron subgroup and carbonyl ligands in a staggered orientation, the structure of the MCP fragments is intermediate between the η^1-η^4 and η^5-coordination modes (the average folding angle of the metallacycles is 11°). This is attributable to an additional interaction between the metal atoms through the semibridging carbonyl group. Apparently, this additional interaction provides an alternative electron density redistribution between the metal atoms and results in a smaller contribution of the π system of the metallacycle to this process. The above analysis demonstrates that the folding angle of the metallacycle, which characterises the deviation of the endocyclic metal atom from the plane of the butadiene fragment, is most sensitive to a change in the coordination mode of the MCP fragment in dinuclear transition metal complexes.

III. Coordination of the metallaindene fragment

Among transition metal complexes involving the MCP fragment, many bi- and polynuclear compounds contain the five-membered metallacycle fused to the benzene ring to form the metallaindene system.



The above scheme gives the average C–C bond lengths (in Å) in dinuclear complexes with the metallaindene fragment.[31,49,67,80,81,85–89] We did not take into account polynuclear complexes (because the presence of additional metal atoms complicates the consideration) as well as complexes in which the six-membered ring is fused at the C–C single bond of the MCP fragment or the five-membered metallacycle is fused to two six-membered rings (as, for example, in complex **18** [36]).

The distribution of the bond lengths in the metallaindene system is indicative of a noticeable difference in the double and single C–C bonds and also of a decrease in the order of the double bond at which two rings are fused. It should be noted that a planar structure is typical of the metallaindene fragments (the average dihedral angle between the planes of the five- and six-membered rings is 6.4°; if the metal atom is ignored, this angle is 3.6°).

The fact that the common π system of the metallaindene fragment is divided into two butadiene units was clearly demonstrated in the study,[90] where the structure of trinuclear complex **59** was described (Fig. 8).

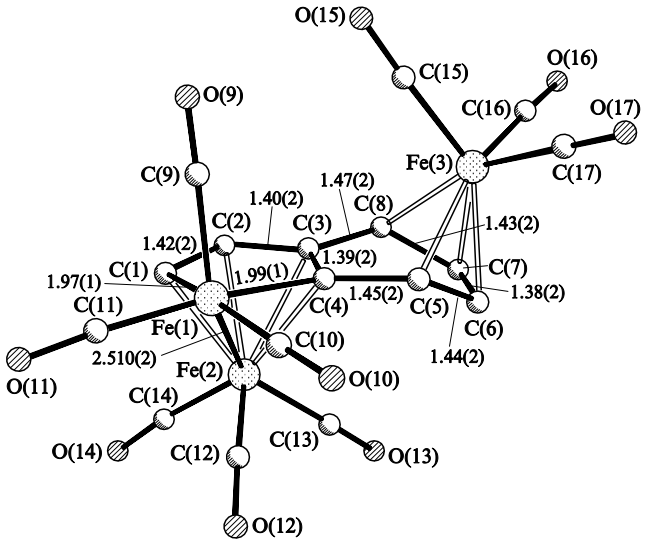


Figure 8. Structure of the ferraindene complex $Fe_3(CO)_9(C_8H_6)$ (**59**).[90]

As can be seen from Fig. 8, the Fe(2) and Fe(3) atoms are located on opposite sides of the bicyclic fragment, whose structure is essentially non-planar. There are two planar fragments, *viz*., C(1)C(2)C(3)C(4)C(5)C(8) and C(5)C(6)C(7)C(8). The dihedral angle between these planes is 32.5°. Hence, molecule **59** can be considered as consisting of two isolated fragments, *viz*., *cis*-butadienetricarbonyliron and the dinuclear ferrole complex. The latter has a structure typical of such complexes. The carbon–carbon bonds in the MCP fragment are equalised. The Fe(1) atom deviates from the plane through four carbon atoms by 0.16 Å in the direction opposite to the Fe(2) atom; the folding angle of the metallacycle along the C(1)···C(4) line is 8.0°. The carbonyl groups in the $Fe_2(CO)_6$ fragment are in a staggered orientation [the semibridging carbonyl group C(12)O(12) deviates from the linear coordination by 11°, the Fe(1)···C(12) distance is 2.53 Å]. The C(3)–C(8) and C(4)–C(5) bond lengths have values typical of the $C(sp^2)–C(sp^2)$ single bond within experimental error. Later on, an analogous complex containing the *p*-tolyl substituent at the C(2) atom and the methyl substituent at the C(7) atom was described.[91]

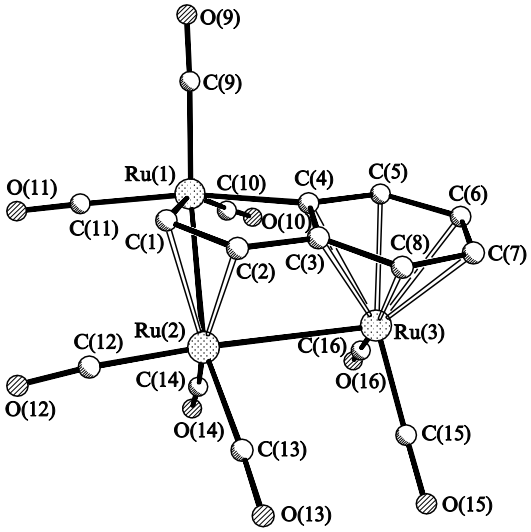


Figure 9. Structure of the ruthenaindene complex $Ru_3(CO)_8(C_8H_6)$ (**60**).[92]

Even more interesting results were obtained in the study,[92] where benzothiophene was subjected to desulfurisation in the reaction with $Ru_3(CO)_{12}$. The structure of trinuclear complex **60** (Fig. 9, Table 3) containing the metallaindene system was described. However, the coordination mode in this complex differs from that observed in compound **59**.

Table 3. Main geometric parameters for complexes **61**–**63** (bond lengths are given in Å, angles are given in degrees).

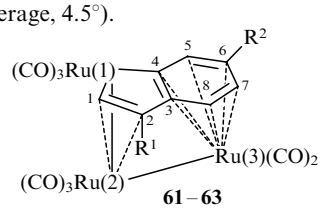
Parameter	Compound			
	60	**61**	**62**	**63**
Ru(1)–Ru(2)	2.781	2.774	2.781	2.783
Ru(2)–Ru(3)	2.946	2.951	2.951	2.958
Ru(1)–C(1)	2.058	2.042	2.052	2.057
Ru(1)–C(4)	2.088	2.093	2.106	2.096
Ru(2)–C(1)	2.237	2.246	2.252	2.233
Ru(2)–C(2)	2.257	2.266	2.280	2.249
Ru(3)–C(3)	2.351	2.374	2.342	2.352
Ru(3)–C(4)	2.322	2.335	2.316	2.356
Ru(3)–C(5–8)	2.248–2.295	2.244–2.305	2.261–2.299	2.275–2.280
C(1)–C(2)	1.400	1.394	1.394	1.394
C(2)–C(3)	1.458	1.445	1.478	1.453
C(3)–C(4)	1.454	1.450	1.449	1.440
C–C (in benzene ring)	1.399–1.430	1.384–1.432	1.400–1.438	1.392–1.438
Ru(1)–Ru(2)–Ru(3)	83.5	85.2	84.8	86.8

In complex **60**, both additional ruthenium atoms are located on the same side of the bicyclic system. The five-membered metallacycle coordinates the second ruthenium atom, Ru(2), through one C(1)=C(2) double bond, whereas two other carbon atoms of the metallacycle, *viz*., C(3) and C(4), are involved in η^6-coordination to the third ruthenium atom, Ru(3). Taking into account the planar structure of the metallaindene system (the dihedral angle between the mean planes of the five-membered metallacycle and the six-membered benzene ring is 7.6°), the

authors considered the $C_8H_6Ru(CO)_3$ fragment as the 8-electron ligand π-coordinated to the $Ru_2(CO)_5$ group.

Three structurally similar ruthenaindene complexes **61**–**63** were described in studies of the products obtained in reactions of $Ru_3(CO)_{12}$ with substituted benzenes.[93–95] Main geometric parameters of complexes **61**–**63** are given in Table 3.

The metallaindene system in complexes **61**–**63**, like that in complex **60**, is planar (the dihedral angle between the planes of the five-membered metallacycle and the six-membered ring is, on average, 4.5°).



61–**63**

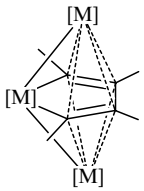
Compound	R^1	R^2	Ref.
61	Me	H	93
62	Me	$C(CH_2)Me$	94
63	H	Me	95

Evidently, the coordination mode of the MCP fragment in these four complexes differs radically from that observed in all the above-described compounds in which the metallacycle is symmetrically η^5-coordinated to one additional metal centre. In complexes **60**–**63**, the five-membered metallacycle is bound to two additional metal centres, one metal atom, Ru(2), being η^3-coordinated [the free C(1)=C(2) double bond and the Ru(1) atom are involved in coordination], whereas another metal atom, Ru(3), is η^2-coordinated [coordination by the C(3)=C(4) double bond involved in fusion to the six-membered ring]. The coordination is accompanied by localisation of the carbon–carbon bonds in the five-membered metallacycle. This is particularly clearly manifested in the C(2)–C(3) bond length. In all complexes, this bond corresponds to the length of the $C(sp^2)-C(sp^2)$ single bond. An interesting structural feature of the MCP fragment in complexes **60**–**63** is the deviation of the Ru(1) atom from the plane through four carbon atoms [C(1), C(2), C(3) and C(4)] toward two other metal atoms [Ru(2) and Ru(3)]. The mean folding angle of the metallacycle along the C(1)···C(4) line is 9.4°. The C(1)–C(2)–C(3)–C(4) torsion angle is 2.5°. It should also be noted that none of the complexes has an additional semibridging interaction between the ruthenium atoms involving carbonyl ligands, which is typical of ruthenium complexes of the ferrole type.

As is evident from the foregoing, the presence of the second additional metal centre in complexes containing the MCP fragment can lead to a substantial change in the coordination mode of the metallacycle. The main coordination modes of the MCP fragment in polynuclear transition metal complexes are described below.

IV. Trimetallic clusters with a pentagonal-bipyramidal geometry

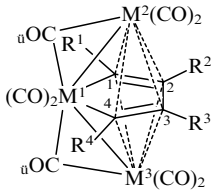
In addition to the above-described dinuclear complexes with the MCP fragment, there is one more large class of related compounds with a pentagonal-bipyramidal geometry.



In these compounds, the MCP fragment is η^5-coordinated to two metal atoms located symmetrically on opposite sides of the plane of the metallacycle. Such complexes are often produced in reactions which also give dinuclear complexes of the ferrole type. This is particularly typical of reactions of metal carbonyls of the iron subgroup with alkynes.[12,13]

The first structure of the trinuclear iron complex $Fe_3(CO)_8(PhC_2Ph)_2$ characterised by pentagonal-bipyramidal geometry was described almost 40 years ago.[96] Later on, the structures of a series of analogous homonuclear iron and ruthenium clusters were studied. Their main geometric parameters are given in Table 4.

Table 4. Main geometric parameters (distances are given in Å, angles are given in degrees) of trinuclear iron and ruthenium complexes with a pentagonal-bipyramidal geometry.



Compound [a]	Substituents	M^1-M^2, M^1-M^3	$M^2-M^1-M^3$ angle	$M^1-C(1)$, $M^1-C(4)$	C(1)–C(2), C(2)–C(3), C(3)–C(4)	τ [b]	M^1-CO_M	M^2-CO_M, M^3-CO_M	Ref.
64	$R^1=R^2=R^3=R^4=Ph$	2.428 2.435	87.6	2.062 2.031	1.457 1.458 1.434	1.3	1.991 1.988	1.841 1.770	96
65	$R^1=R^3=NEt_2$, $R^2=R^4=Me$	2.430 2.437	88.1	2.093 2.067	1.447 1.466 1.467	1.1	2.061 2.061	1.865 1.869	97
66	$R^1=R^4=F$, $R^2=R^3=H$	2.436 2.433	88.4	1.986 1.971	1.414 1.420 1.436	0.2	2.097 2.078	1.850 1.860	98
67	$R^1=R^2=F$, $R^3=R^4=H$	2.433 2.433	88.4	1.988 2.054	1.418 1.414 1.427	0	2.081 2.081	1.876 1.876	98

Table 4 (continued).

Compound [a]	Substituents	M^1-M^2, M^1-M^3	$M^2-M^1-M^3$ angle	$M^1-C(1)$, $M^1-C(4)$	$C(1)-C(2)$, $C(2)-C(3)$, $C(3)-C(4)$	τ [b]	M^1-CO_M	M^2-CO_M, M^3-CO_M	Ref.
68	$R^1 = R^4 = F$, $R^2 = Ph$, $R^3 = Me$	2.425 2.426	88.8	2.007 1.948	1.422 1.457 1.459	1.9	1.964 2.127	1.902 1.828	98
69	$R^1 = R^2 = Ph$, $R^3 = Me$, $R^4 = OEt$	2.440 2.440	87.8	2.061 2.053	1.441 1.438 1.444	1.7	2.046 2.072	1.861 1.849	99
70	$R^1 = R^2 = SiMe_3$, $R^3 = OEt$, $R^4 = Me$	2.426 2.439	87.2	2.118 2.012	1.465 1.465 1.425	3.4	2.087 2.003	1.846 1.884	99
71	$R^1 = R^3 = Ph$, $R^2 = NEt_2$, $R^4 = CCPh$	2.442 2.422	88.4	2.058 1.996	1.476 1.468 1.445	0.6	2.061 2.066	1.754 1.825	26
72	$R^1 = Ph$, $R^2 = R^3 = NEt_2$, $R^4 = CHCHMe$	2.429 2.420	88.7	2.076 2.075	1.431 1.477 1.440	1.2	2.085 2.005	1.841 1.854	100
73 [c]	$R^1 = R^4 = H$, $R^2-R^3 = =CMe_2NHCMe_2$	2.427 2.411	88.1	2.053 2.073	1.428 1.443 1.436	0.3	2.044 2.006	1.860 1.856	101
		2.419 2.406	88.7	2.062 2.064	1.431 1.439 1.423	0.6	2.056 2.001	1.865 1.859	
74	$R^1 = R^2 = Et$, $R^3 = H$, $R^4 = CH_2N(Me)CH_2Ph$	2.431 2.440	87.3	2.058 2.036	1.443 1.445 1.432	0.7	2.085 2.046	1.845 1.859	25
75	$R^1 = R^2 = R^3 = R^4 = Ph$	2.670 2.672	89.1	2.218 2.216	1.460 1.472 1.451	0.9	2.158 2.156	2.028 2.008	102
76	$R^1 = R^4 = Ph$, $R^2-R^3 = C_5H_4FeC_5H_4$	2.669 2.652	89.1	2.198 2.243	1.436 1.471 1.439	1.4	2.155 2.096	2.000 1.988	103
77	$R^1 = R^3 = Bu^t$, $R^2 = H$, $R^4 = CHCHBu^t$	2.661 2.669	88.8	2.172 2.226	1.425 1.450 1.419	0.6	2.117 2.142	2.008 1.976	104
78	$R^1 = R^2 = R^3 = R^4 = Me$	2.651 2.651	88.6	2.207 2.219	1.450 1.460 1.441	0	2.190 2.190	1.999 1.999	105
79	$R^1 = R^4 = Ph$, $R^2 = R^3 = H$	2.683 2.683	89.0	2.209 2.209	1.442 1.454 1.442	0.4	2.169 2.169	2.014 2.014	106
80	$R^1-R^2 = C_{10}H_{16}$, $R^3 = R^4 = Ph$	2.668 2.664	88.7	2.203 2.220	1.427 1.493 1.469	1.0	2.196 2.136	1.964 1.998	107

[a] M = Fe (**64**–**74**), Ru (**75**–**80**). [b] The folding angle of the metallacycle along the C(1)···C(4) line. [c] Two crystallographically independent molecules.

Complexes **64**–**80** contain an open trimetallic core with two nearly equal-length metal–metal bonds; the angle between these bonds is close to 90°. Each metal atom is coordinated by two terminal CO groups. Two other carbonyl groups form bridges between the central and peripheral metal atoms. The bridging CO groups are slightly shifted to the peripheral metal atoms (the M^1-CO_M distances are, on average, 0.2 Å longer than the M^2-CO_M and M^3-CO_M distances). The central metal atom is involved in two σ-bonds with the butadiene moiety to form the MCP fragment, which is, in turn, symmetrically π-coordinated to both peripheral metal atoms at the vertices of the bipyramid.

The metallacycle is planar (parameter τ in Table 4) and dissects the structure into two equivalent moieties, each moiety being structurally similar to dinuclear iron and ruthenium complexes of the ferrole type. The common symmetry of these complexes is particularly pronounced in the crystal structures of compounds **67**, **78** and **79**. Molecules of these compounds occupy special positions on the mirror symmetry plane passing through the plane of the metallacycle. The carbon–carbon bonds in the MCP fragments of complexes **64**–**80** are equalised, whereas the metal–metal distances (the average values are 2.429 and 2.666 Å for the iron and ruthenium complexes, respectively) are noticeably shortened compared to the corresponding bonds in dinuclear complexes of the ferrole type (see Table 1).

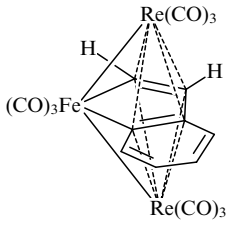
The structures of the trinuclear complexes listed in Table 4 are often described using polyhedral clusters (see, for example, the

studies [26, 100] and the review [13]), for which the number of skeletal electrons (*i.e.*, electrons involved in bonding in the polyhedron) is counted according to the so-called Wade's rule (or the '$2n+2$' rule).[108]

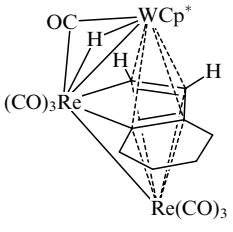
In complexes **64**–**80**, the M_3C_4 system can be considered as a *closo*-pentagonal-bipyramidal structure. According to Wade's rules, 16 skeletal electrons are required for a seven-vertex polyhedron. It is easy to demonstrate that this rule is fulfilled for all compounds listed in Table 4. After the removal of one vertex of the bipyramid occupied by the $Fe(CO)_2$ or $Ru(CO)_2$ group, which donates no skeletal electrons, the seven-vertex *closo* system is transformed into a six-vertex pyramidal cluster with a *nido* structure, the total number of skeletal electrons remaining unchanged. The six-vertex clusters thus obtained represent the above-described dinuclear carbonyl complexes of the ferrole type. It should be noted that all dinuclear complexes which are presented in Fig. 2 and contain different transition metal atoms with different ligand environments, can be described as *nido*-pentagonal-pyramidal systems bearing 16 skeletal electrons.

The possibility of the transformation of trinuclear complexes with composition $M_3(CO)_8(RC_2R)_2$ into the dinuclear complexes $M_2(CO)_6(RC_2R)_2$ has been demonstrated in the pioneering studies on the chemical behaviour of these clusters [109, 110] and was subsequently confirmed in many investigations (see, for example, Refs 98 and 111). This transformation occurs in the course of thermolysis under severe conditions, no other products being formed, which is indicative of high stability of ferrole complexes and the MCP fragment. Investigation of the electronic structures of ferracyclopentadiene derivatives (dinuclear and trinuclear complexes) by photoelectron spectroscopy and *ab initio* calculations [112] demonstrated a high degree of electron density delocalisation in these clusters as well as the strong Fe–C σ-interaction in the metallacycle, which accounts for the stability of the MCP fragment in chemical reaction. Substantial delocalisation of the electron density in trinuclear iron and ruthenium clusters with a pentagonal-bipyramidal geometry is also evidenced by the data from spectroscopic (^1H and ^{13}C NMR and IR) and electrochemical studies of a large number of compounds containing various substituents at the carbon atoms of the metallacycles.[111, 113]

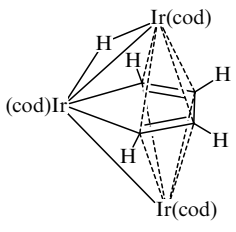
In addition to the above-mentioned pentagonal-bipyramidal trinuclear iron and ruthenium carbonyl complexes **64**–**80**, six structurally similar compounds with other transition metal atoms and/or with another ligand environment were described. These are two heteronuclear complexes with composition $Re_2Fe(CO)_9(CH=CHC_6H_4)$ (**81**)[114] and $Cp^*WRe_2(CO)_7$.$(\mu\text{-}H)(CH=CHC_6H_8)$ (**82**),[115] the trinuclear iridium complex $Ir_3(2\eta^2\text{-cod})_3(\mu\text{-}H)(C_4H_4)$ (cod is cyclooctadiene) (**83**)[82] and the trinuclear ruthenium complexes $Ru_3(CO)_6(dppm)(C_4H_2Ph_2)$ [dppm is bis(diphenylphosphine)methane] (**84**),[116] $Cp^*_3Ru_3$.$(H)(C_4H_3Et)$ (**85a**)[117] and $Cp_2Ru_3(CO)_3\{C_2(CF_3)_2$.$C_2(CO_2Me)_2\}$ (**86b**),[118] the latter two complexes having an unusual triple-decker sandwich structure. All complexes satisfy the '$2n+2$' rule for the number of skeletal electrons in the *closo*-pentagonal-bipyramidal polyhedron. The structure of the MCP fragments in complexes **81**–**85** is analogous to that observed in trinuclear iron and ruthenium carbonyl complexes **64**–**80**.



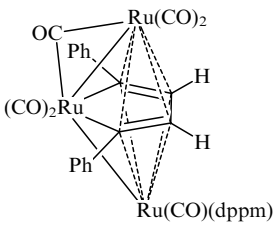
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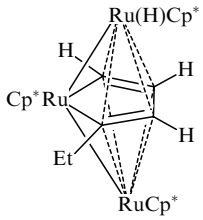
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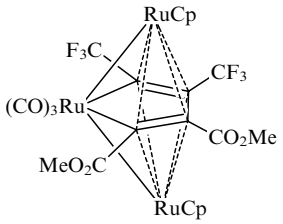
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84



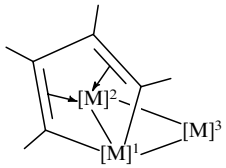
85a



85b

V. Coordination of the metallacyclopentadiene fragment to transition metal clusters

Many trinuclear and polynuclear complexes with the MCP fragment include the structural motif presented in the following scheme:



The lateral or $\mu_2\text{-}2\eta^1\text{-}\eta^4$-coordination of an organic ligand to the triangular metal core is typical of trimetallic iron, ruthenium and osmium clusters.[97, 119–137] The formation of such complexes was observed in the reactions of metal carbonyl clusters of the iron subgroup with alkynes and their functional derivatives. The complexes contain the dinuclear ferrole-type fragment and the third metal atom, which is not directly bound to the organic moiety of the metallacycle.

The structural formulae and selected geometric parameters of the triangular metal complexes of the iron subgroup with this coordination mode of the MCP fragment are given in Table 5. All complexes contain the MCP fragment, whose diene moiety is π-coordinated to the M^2 atom. Besides, in some complexes (**86**, **87**, **92**–**99** and **107**–**109**), the functional group at one of the α-carbon atoms of the metallacycle is coordinated to the third metal atom (M^3), which is not involved in a direct bond with the MCP fragment. This additional interaction results in inclination of the MCP fragment relative to the plane of the triangle formed by the metal atoms (the average angle between the planes is 63°). In complexes in which an additional coordination to the third metal atom is absent, the metallacycle is located almost perpendicular to the $M^1M^2M^3$ plane (the average angle between the planes is 83°).

In complexes listed in Table 5, the metal–metal bond lengths are non-equivalent. The M^1-M^2 bond lengths are close to the values observed in the dinuclear complexes of the ferrole type (see Table 1, complexes **1**–**36**). The M^2-M^3 bonds have similar or even somewhat larger lengths, whereas the M^1-M^3 bond between the endocyclic metal atom and the metal atom which is not directly bound to the MCP fragment, is noticeably elongated in most complexes. This tendency is most pronounced in complexes **91** and **100**–**103** bearing no bridging ligands, whose tightening effect may substantially influence the M–M bond lengths. For this reason, it is of interest to compare two related ruthenium complexes $Ru_3(CO)_8(PPh_3)\{C_4Ph_2(CH=CHPh)_2\}$ (**91**)[123] and $Ru_3(CO)_8\{C_4Ph_2(CH=CHPh)_2\}$ (**92**)[124] containing, along with the MCP fragment, only terminal two-electron ligands (CO or PPh_3). Complex **92** was prepared by the thermal reaction of enyne $PhCH=CHC\equiv CPh$ with $Ru_3(CO)_{12}$. The reaction of complex **92**

Table 5. Selected geometric parameters (bond lengths are given in Å, angles are given in degrees) for trinuclear iron, ruthenium and osmium clusters with the laterally coordinated MCP fragment.

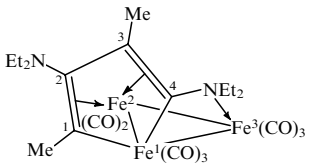
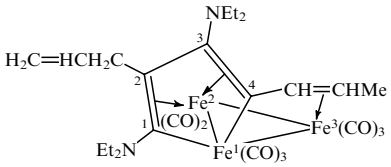
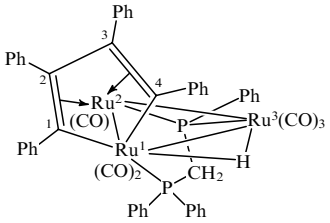
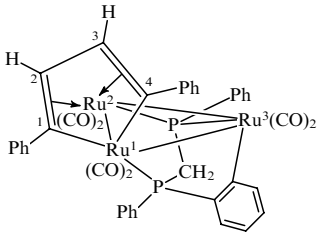
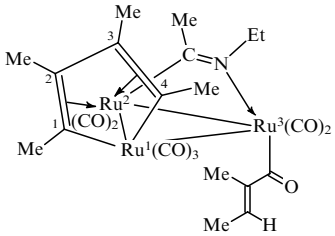
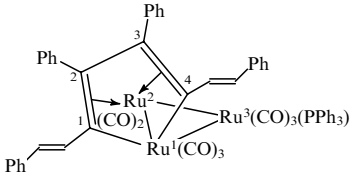
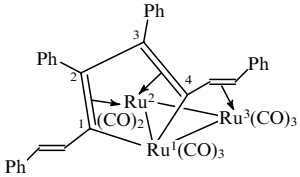
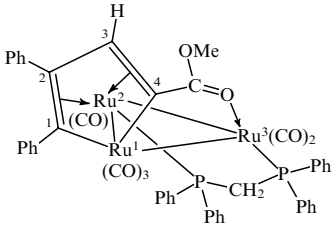
Compound	Formula	M^1-M^2, M^2-M^3, M^1-M^3	$M^1-C(1)$, $M^1-C(4)$	C(1)–C(2), C(2)–C(3), C(3)–C(4)	ω [a]	τ [b]	θ [c]	Ref.
86		2.506 2.604 2.564	2.006 1.970	1.419 1.440 1.418	1.8	12.4	55.4	97
87		2.557 2.590 2.642	2.136 1.965	1.453 1.453 1.444	3.6	16.3	58.9	119
88		2.663 2.800 3.034	2.168 2.114	1.400 1.443 1.384	1.1	6.2	75.6	120
89		2.714 2.827 2.982	2.21 2.07	1.33 1.41 1.46	7.0	3.5	78.4	121
90		2.779 2.897 3.073	2.053 2.060	1.388 1.450 1.374	3.5	10.9	89.5	122
91		2.757 2.732 2.927	2.128 2.137	1.409 1.438 1.428	0.1	9.6	88.4	123
92		2.733 2.802 2.823	2.146 2.082	1.432 1.443 1.430	4.7	14.6	58.5	124
93		2.701 2.697 2.830	2.174 2.083	1.426 1.404 1.403	4.4	14.5	66.1	120

Table 5 (continued).

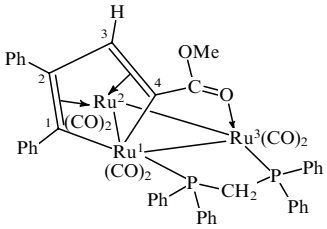
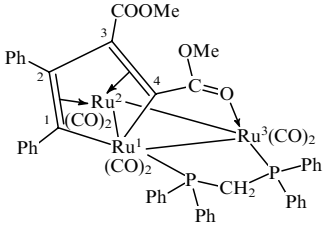
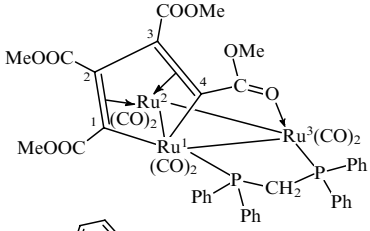
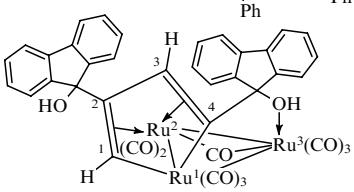
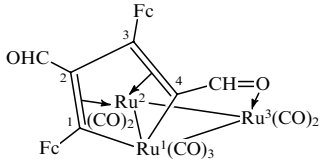
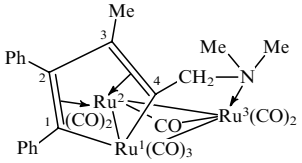
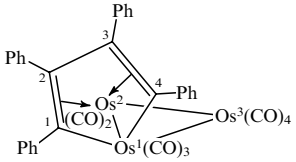
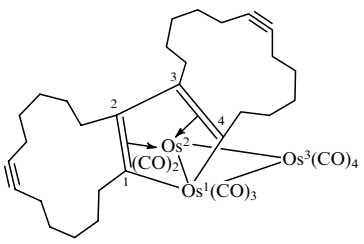
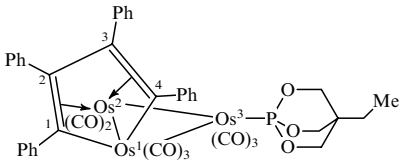
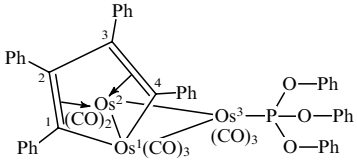
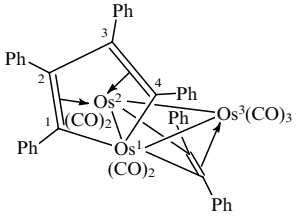
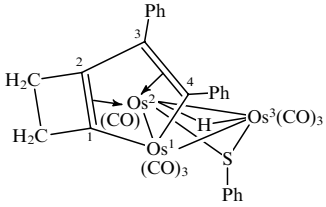
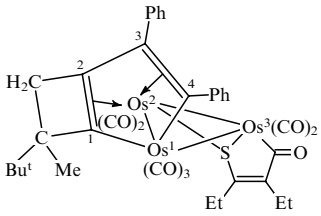
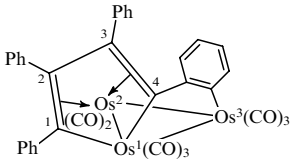
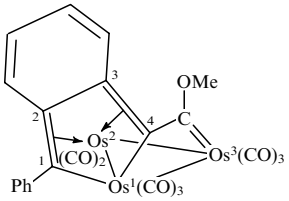
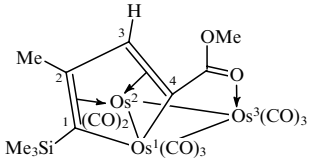
Compound	Formula	M^1-M^2, M^2-M^3, M^1-M^3	$M^1-C(1)$, $M^1-C(4)$	$C(1)-C(2)$, $C(2)-C(3)$, $C(3)-C(4)$	ω [a]	τ [b]	θ [c]	Ref.
94		2.730 2.679 2.880	2.154 2.108	1.432 1.435 1.408	3.2	13.3	64.6	120
95		2.744 2.683 2.860	2.141 2.111	1.457 1.428 1.417	5.7	15.0	65.3	120
96		2.739 2.698 2.863	2.116 2.115	1.418 1.439 1.419	5.8	13.3	64.2	125
97		2.777 2.879 2.833	2.069 2.111	1.386 1.425 1.395	0.4	9.5	63.1	126
98		2.712 2.701 2.822	2.185 2.086	1.455 1.417 1.449	0.9	14.6	64.4	127
99 [d]		2.771 2.884 2.855 2.773 2.850 2.829	2.09 2.10 2.07 2.09	1.40 1.45 1.37 1.46 1.45 1.38	2.6 1.2	8.0 8.1	61.9 62.8	128
100 [e]		2.739 2.741 2.894 2.729 2.723 2.917	2.14 2.13 2.01 2.14	1.37 1.42 1.47 1.37 1.47 1.40	4.0 0.5	9.8 9.1	85.9 84.9	129
101		2.743 2.731 2.928	2.183 2.183	1.402 1.472 1.402	0	9.3	90.0	130

Table 5 (continued).

Compound	Formula	M^1-M^2, M^2-M^3, M^1-M^3	$M^1-C(1)$, $M^1-C(4)$	C(1)–C(2), C(2)–C(3), C(3)–C(4)	ω [a]	τ [b]	θ [c]	Ref.
102		2.752 2.739 2.905	2.132 2.149	1.400 1.442 1.439	0.3	7.9	89.9	131
103		2.761 2.732 2.921	2.182 2.054	1.269 1.509 1.521	2.4	6.4	87.4	131
104		2.677 2.794 2.737	2.150 2.097	1.361 1.475 1.437	4.9	−9.0	80.4	132
105		2.725 2.722 3.017	2.11 2.23	1.41 1.44 1.42	4.0	11.7	78.5	133
106		2.747 2.770 3.054	2.06 2.14	1.41 1.44 1.45	4.6	2.3	77.9	134
107		2.747 2.873 2.943	2.247 2.158	1.561 1.269 1.514	8.8	19.6	66.7	135
108		2.720 2.754 2.903	2.16 2.12	1.41 1.44 1.40	3.8	13.9	59.9	136
109		2.718 2.722 2.854	2.202 2.108	1.440 1.458 1.401	4.8	12.5	64.7	137

[a] The C(1)–C(2)–C(3)–C(4) torsion angle. [b] The dihedral angle between the C(1)C(2)C(3)C(4) and C(1)M^1C(4) planes. [c] The dihedral angle between the mean plane of the MCP fragment and the plane of the $M^1M^2M^3$ triangle. [d] Two crystallographically independent molecules. [e] Two crystal modifications: monoclinic $P2_1/c$ and orthorhombic *Iba*2.

with triphenylphosphine led to the displacement of the alkenyl ligand π-coordinated to the Ru(3) atom giving rise to complex **91**.[123] The triphenylphosphine ligand in complex **91** occupies an equatorial position at the Ru(3) atom in the *trans* position with respect to the Ru(1)–Ru(3) bond.

The Ru(1)–Ru(2) bond length in complexes **92** and **91** [2.733(1) and 2.757(1) Å, respectively] remains virtually unchanged and is typical of the Ru–Ru bonds in dinuclear ruthenium complexes of the ferrole type (2.703–2.753 Å, see Table 1). This fact is indicative of structural rigidity of the fragment regardless of the type of the complex, the ligand environment about the metal atoms and substituents at the carbon atoms of the metallacycle.

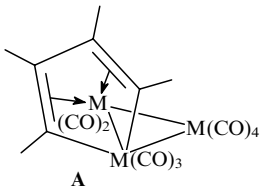
It is noteworthy that two other metal–metal bond lengths in complexes **92** and **91** are different. The Ru(1)–Ru(3) bond in complex **91** [2.927(1) Å] is substantially elongated compared to the analogous bond in complex **92** [2.823(1) Å]. Apparently, this is associated with the influence of the phosphine ligand in the *trans* position with respect to the Ru(1)–Ru(3) bond and can also be attributable to the lack of the tightening effect which occurs in the case of additional coordination by the alkenyl group of an organic ligand. The latter explanation seems to be more reasonable because an analogous change in the Ru(1)–Ru(3) bond length is observed in complexes **88**–**90** (2.982–3.073 Å) compared to complexes **93**–**99** (2.822–2.880 Å), in which an additional coordination to the Ru(3) atom is respectively absent and present (see Table 5).

The shortening of the Ru(2)–Ru(3) bond in complex **91** [2.732(1) Å] compared to that in complex **92** [2.802(1) Å] is less pronounced. A comparison of complexes **88**–**90** and **93**–**99** from Table 5 reveals no changes in the Ru(2)–Ru(3) bond length. Presumably, the mode of electron density redistribution in the cluster plays an important role in establishing electron balance on metal atoms. For example, the bridging ligands have a dominant role in complexes **88**–**90**, whereas the role of the direct metal–metal interaction increases significantly in complex **91** in which bridging interactions are absent (all carbonyl ligands are terminal). In this connection, it should be emphasised that the distribution of the bond lengths in the triangle formed by the metal atoms in analogous osmium complexes (**100**–**103**, Table 5), which also have no bridging ligands, is similar to that observed in complex **91**.

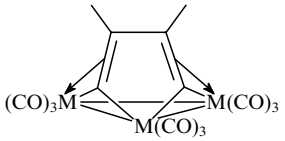
Reversible dissociation of the π-coordinated alkenyl group was exemplified by complexes **91** and **92**.[123] The transformation of one triruthenium cluster into another cluster is accompanied by migration of the MCP fragment relative to the plane of the Ru_3 triangle. In addition, the transformation is accompanied by the redistribution of the Ru(1)–Ru(3) and Ru(2)–Ru(3) bond lengths, which is indicative of high lability of the third metal centre bound to the dinuclear ferrole-type fragment. Apparently, it is this metal atom through which the electron density in the triangular clusters is redistributed to establish charge balance in a similar way to that observed in dinuclear ferrole-type complexes with staggered carbonyl ligands involving the semibridging carbonyl group. For example, the structure of complex **96** was described [125] as a result of the formal substitution of the semibridging carbonyl group in compound **29** (see Table 1) with the isolobal $Ru(CO)_3(PR_3)$ group. A comparison of complexes **96** and **29** demonstrates that there is a complete analogy in the structure of the dinuclear fragment with the metallacycle.

In addition to the triangular iron, ruthenium and osmium complexes with the laterally coordinated MCP fragment, there are also a number of heteronuclear complexes with more complicated structures (this is often associated with the presence of additional metal centres), which have a trimetallic core analogous to that of the metallacycle. The commonly used reactions of acetylide clusters with alkynes or alkyne complexes afford tri-, tetra- and polynuclear mixed complexes with the MCP fragment [WOs_3,[138–140] WRe_2,[115] Mo_2Re_2 (see Ref. 141)]. Since the structure of the metallacycle and its coordination are analogous to those described above for complexes **86**–**109**, we will not consider them in more detail.

An alternative mode of coordination of the MCP fragment to triangular transition metal clusters can be described as the μ_3-2η^1-2η^2 interaction between the organic ligand and the metal core. Symmetrical binding of the diene moiety to the triangle consisting of metal atoms is referred to as facial coordination, unlike the above-described lateral coordination. The assumption about the possibility of this coordination mode was made when studying the reactions between metal carbonyl complexes of the iron subgroup and an excess of alkynes giving rise to the $M_3(CO)_9(RC_2R)_2$ clusters, for which two structures (**A** and **B**) with the μ-2η^1-η^4- and μ_3-2η^1-2η^2-coordinated organic ligand were considered.[142, 143]



A



B

X-Ray diffraction study of one of the first $Os_3(PhC_2Ph)_2(CO)_9$ clusters demonstrated that it has the structure **A**.[129] Later on, analogous structures were assigned to all related compounds.[144, 145] Until recently, there was no convincing evidence for the existence of complexes with the structure **B**.

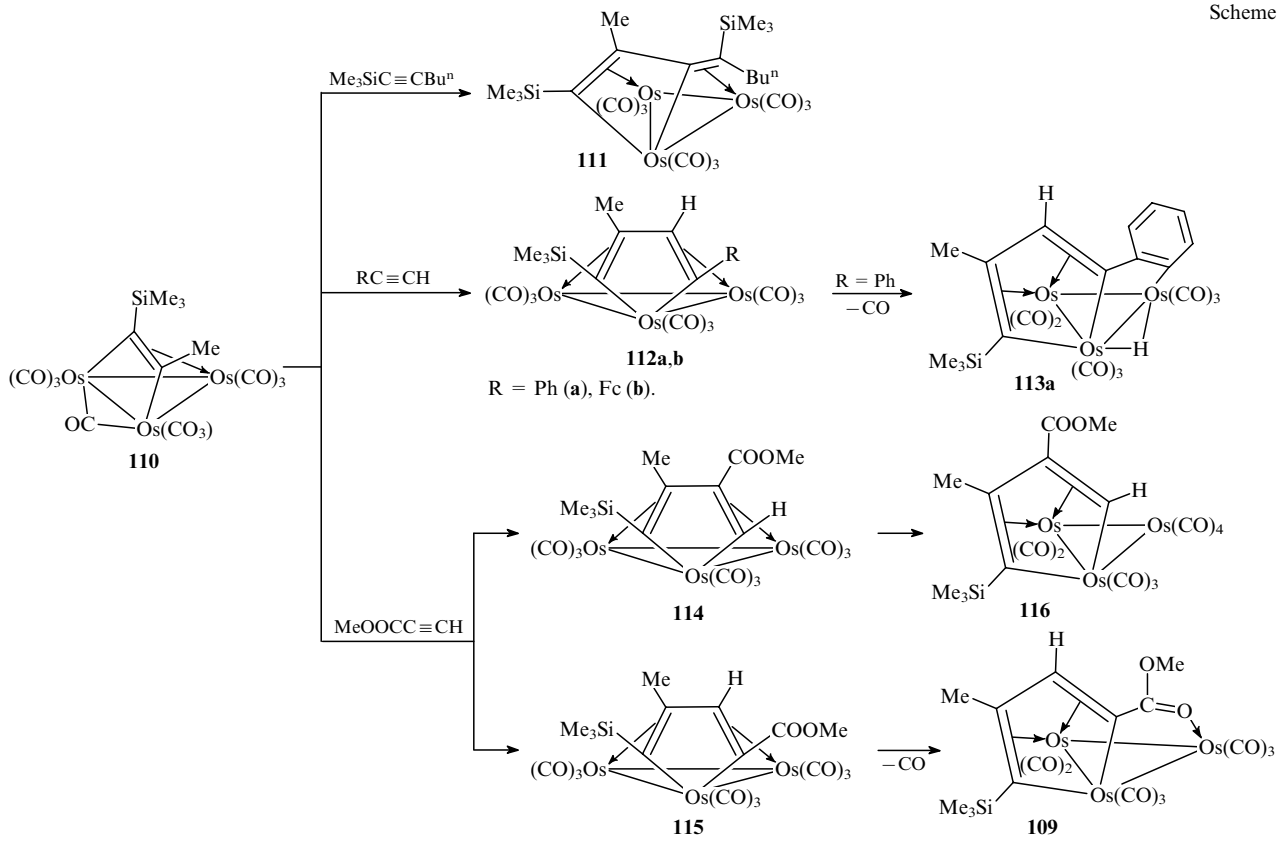
The experimental proof of the existence of isomers with the structure **B** was obtained for the first time in studies of the reactions of the alkyne cluster Os_3(μ-CO)$(CO)_9$(μ-2η^1-η^2-Me_3SiC_2Me) (**110**) with phenylacetylene [146, 147] as well as with other monosubstituted alkynes, *viz*., ferrocenylacetylene [148] and methyl propiolate.[137] The reactions involve alkyne–alkyne coupling and afford triosmium clusters with the facially coordinated osmacyclopentadiene fragment (complexes **112a**,**b**, **114** and **115** in Scheme 1). It should be noted that an analogous reaction with silyl-substituted alkyne $Me_3SiC{\equiv}CBu^n$ is accompanied by the acetylene–vinylidene rearrangement to give a cluster with the osmacyclobutadiene unit $Os_3(CO)_9\{\mu_3$-2η^1-2η^2-C$(SiMe_3)$=C.$(Me)C=C(SiMe_3)Bu^n\}$ (**111**).[149]

As can be seen from Scheme 1, thermolysis of the complexes with the facially coordinated MCP fragment gives rise to trinuclear complexes with the laterally coordinated MCP fragment. For example, complexes **112a**,**b** are transformed into hydride clusters with the *ortho*-metallated phenyl (**113a**) [146, 147] or ferrocenyl (**113b**) [148] fragment, respectively. The reaction of alkyne cluster **110** with methyl propiolate produces two isomeric complexes **114** and **115** with the facially coordinated MCP fragment, which differ in the mode of coupling of unsymmetrical alkynes.[137] Subsequent thermolysis of complex **115** containing the ester group in the α position of the osmacyclopentadiene ring affords complex **109**.[137]

Cluster **114** was studied by IR and NMR spectroscopy. In this cluster, the α position of the metallacycle contains no groups which are susceptible to *ortho*-metallation, or functional substituents capable of being coordinated to the metal atom. It was demonstrated that cluster **114** can undergo an intramolecular rearrangement and is a precursor of cluster **116**.[150] This previously unknown intramolecular rearrangement involves a change in the coordination mode of the dienediyl ligand (μ_3-2η^1-2η^2 → μ-2η^1-η^4) and the internuclear migration of one CO group. The trimetallic cluster with the facially coordinated MCP fragment, in which the hydrocarbon ligand forms η^2-bonds with two metal atoms, was demonstrated [150] to be thermodynamically less stable than the isomer in which the ligand forms the diene η^4-bond with one metal atom (lateral coordination of the MCP fragment).

The structures of three complexes (**112a**,[147] **112b** [148] and **114** [137]) with the facially coordinated MCP fragment were estab-

Scheme 1



lished by X-ray diffraction analysis. The molecular structure of complex **112a** is shown in Fig. 10. Main geometric parameters for complexes **112a**,**b** and **114** are given in Table 6.

The formation of complexes **112a**,**b** involves coupling of monosubstituted alkyne (phenyl- or ferrocenylacetylene, respectively) with the already coordinated silyl-substituted alkyne, which proceeds in such a way that the hydrogen atom is bound to the β-carbon atom of the MCP fragment. In complex **114**, the hydrogen atom is bound to the α-carbon atom of the MCP fragment. Otherwise complexes **112a**,**b** and **114** are structurally similar and the presence of different substituents in the MCP fragments has no noticeable effect on the geometry of the coordination unit of the complexes.

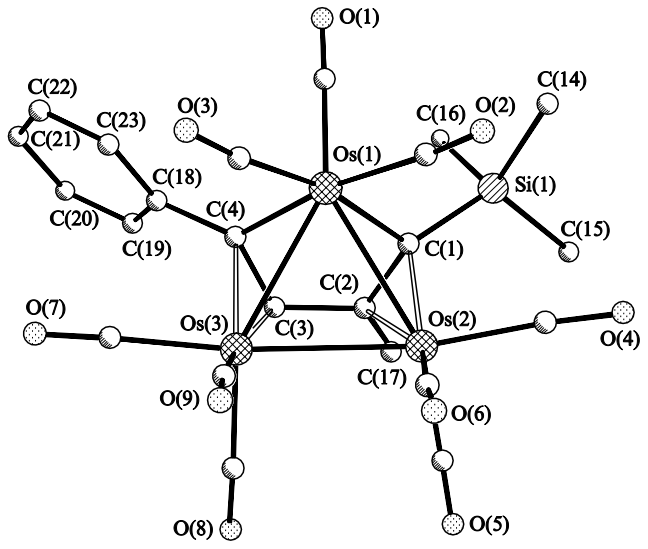


Figure 10. Molecular structure of the triangular osmium cluster $Os_3(CO)_9\{\mu_3\text{-}2\eta^1\text{-}2\eta_2\text{-}C(SiMe_3)C(Me)C(H)C(Ph)\}$ (**112a**) with the facially coordinated MCP fragment.[147]

In the complexes under consideration, the osmacyclopentadiene ring is substantially non-planar due to the deviation of the endocyclic osmium atom from the plane of the butadiene fragment toward two other metal atoms. The folding angle of the metallacycle along the C(1)···C(4) line is 30° (parameter τ in Table 6) and is substantially larger than the values typical of the MCP fragments coordinated to one metal atom (in dinuclear complexes of the ferrole type and trinuclear complexes with the laterally coordinated MCP fragment).

In complexes **112** and **114**, the C−C bond lengths in the butadiene moiety of the metallacycle are more differentiated than those in the complexes with the η^5-coordinated metallacycle. Although the differences in the bond lengths are only slightly larger than the experimental error, the tendency to an increase in the C(2)−C(3) bond length compared to the C(1)−C(2) and C(3)−C(4) alkene bond lengths is observed in all cases (the average values are 1.48, 1.41 and 1.42 Å, respectively). On the other hand, the lengths of the endocyclic σ-bonds involving the Os(1) atom are in the range typical of analogous bonds in complexes with the η^5-coordinated osmacyclopentadienyl fragment (2.01–2.25 Å; dinuclear complexes **35** and **36** listed in Table 1 and trinuclear complexes **100**–**109** presented in Table 5). However, it should be noted that the Os(1)−C(1) and Os(1)−C(4) bonds in complexes **112** and **114** are non-equivalent. In all cases, the distance to the C(1) atom bearing the trimethylsilyl substituent is somewhat larger than the Os(1)−C(4) bond length (the average values are 2.18 and 2.13 Å, respectively). The reasons for this non-equivalence are not quite clear. It can be assumed that an elongation of the Os(1)−C(1) distance eliminates unfavourable contacts between the trimethylsilyl group and the carbonyl groups at the Os(1) atom. It cannot also be excluded that some geometric distortions are related to the positive inductive effect of the trimethylsilyl group. Presumably, this is responsible for another structural feature of these complexes, *viz*., asymmetry of

Table 6. Selected geometric parameters for trinuclear osmium complexes with the facially coordinated MCP fragment (distances are given in Å, angles are given in degrees).[a]

Compound	Os(1)–Os(2), Os(1)–Os(3), Os(2)–Os(3)	Os(1)–C(1), Os(1)–C(4)	C(1)–C(2), C(2)–C(3), C(3)–C(4)	ω [b]	τ [c]	θ [d]	Os(2)–C(1), Os(2)–C(2)	Os(3)–C(4), Os(3)–C(3)
112a	2.811(1) 2.811(1) 2.825(1)	2.19(2) 2.12(1)	1.44(2) 1.46(2) 1.48(2)	4.3	28.8	32.9	2.18(1) 2.42(2)	2.22(1) 2.25(1)
112b (see [e])	2.819(1) 2.818(1) 2.804(1)	2.19(1) 2.15(1)	1.39(2) 1.49(2) 1.41(2)	5.1	27.5	34.0	2.17(1) 2.43(1)	2.25(1) 2.26(1)
	2.831(1) 2.825(1) 2.815(1)	2.18(1) 2.15(1)	1.41(2) 1.47(2) 1.41(2)	4.3	26.0	35.1	2.17(1) 2.48(1)	2.25(1) 2.27(1)
114	2.8248(7) 2.8254(7) 2.7932(7)	2.174(7) 2.099(8)	1.42(1) 1.49(1) 1.42(1)	3.2	23.8	36.4	2.167(9) 2.441(9)	2.178(8) 2.277(9)

[a] For the atomic numbering scheme, see Fig. 10. [b] The C(1)–C(2)–C(3)–C(4) torsion angle. [c] The folding angle of the metallacycle along the C(1)···C(4) line [the dihedral angle between the C(1)C(2)C(3)C(4) and C(1)Os(1)C(4) planes]. [d] The dihedral angle between the C(1)C(2)C(3)C(4) and Os(1)Os(2)Os(3) planes. [e] Two crystallographically independent molecules.

π-coordination of the Os(2) and Os(3) atoms to the corresponding alkene bonds in the metallacycle. One osmium atom [Os(3)] is located at virtually equal distances from the carbon atoms of the C(3)–C(4) alkene bond [the average Os(3)–C(3) and Os(3)–C(4) bond lengths are 2.27 and 2.23 Å, respectively], whereas another osmium atom [Os(2)] forms non-equivalent bonds with the carbon atoms of the C(1)–C(2) alkene bond [the average Os(2)–C(1) and Os(2)–C(2) bond lengths are 2.17 and 2.44 Å, respectively].

The osmacyclopentadiene ring in complexes **112** and **114**, unlike that in the trinuclear complexes with the laterally coordinated MCP fragment, is located above the plane of the triangular metal core (facial coordination of the MCP fragment). The averaged dihedral angle between the plane passing through four carbon atoms of the butadiene moiety of the metallacycle and the plane of the triangle formed by the osmium atoms (parameter θ in Table 6) is 34.5°.

The trinuclear complexes with the laterally coordinated MCP fragment differ from those with the facially coordinated MCP fragment also in that the metal–metal bond lengths in the latter are equalised. All Os–Os bond lengths in complexes **112** and **114** vary within a narrow range (2.793–2.834 Å).

In addition to the above-described compounds **112** and **114**, only one compound belonging to trimetallic clusters with the facially coordinated MCP fragment, *viz*., trinuclear molybdenum cyclopentadienyl complex **117**, was structurally characterised.[151] The structure of complex **117** is shown in Fig. 11.

The metal core in complex **117** is V-shaped. The bond between the Mo(1) and Mo(2) atoms is absent, although they are linked through the bridging chlorine atom. All Mo atoms are linked by the μ_3-bridging oxygen atom. In the study,[151] the μ_3-O, μ-Cl and $C_4(CF_3)_4$ groups in complex **117** were considered as four-, three- and six-electron ligands, respectively, and consequently, the complex as a whole has 46 valence electrons, which implies the presence of four metal–metal bonds (in this case, the molybdenum atoms have an 18-electron configuration). Based on this analysis and the results of theoretical calculations, the Mo(1)–Mo(3) and Mo(2)–Mo(3) bonds in complex **117** were assumed to be double and it was postulated that there is no direct interaction between the Mo(1) and Mo(2) atoms. The structure of the MCP fragment in complex **117** is analogous to that described for complexes **112** and **114** and differs substantially from that observed in complexes with η^5-coordination of the metallacycle. For example, the carbon–carbon distances in the metallacycle

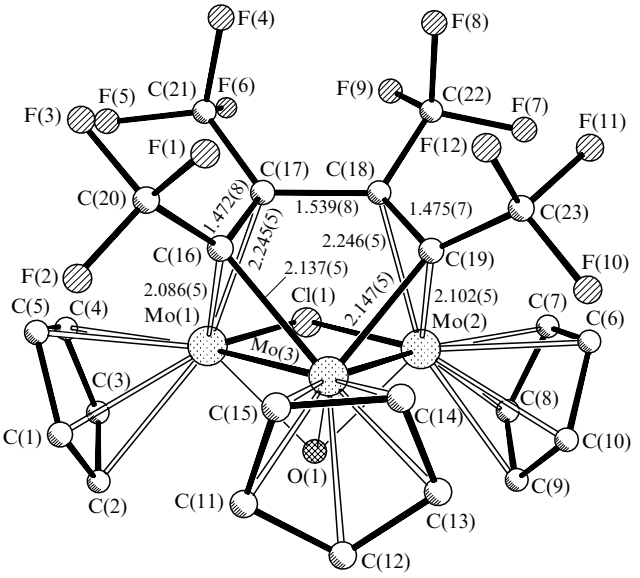


Figure 11. Structure of the $Mo_3(\mu\text{-Cl})(\mu_3\text{-O})(C_5H_5)_3\{C_4(CF_3)_4\}$ complex (**117**).[151]
The Mo(1)–Mo(3) and Mo(2)–Mo(3) bond lengths are 2.5723(7) and 2.5790(7) Å, respectively; the Mo(1)···Mo(2) distance is 2.8930(7) Å.

are noticeably differentiated (short–long–short) and the metallacycle is significantly folded (38.9°) along the C(16)···C(19) line.

VI. Conclusion

In conclusion of the description of complexes containing the MCP fragment, is should be emphasised once again that this metallacycle exhibits various coordination modes with transition metal atoms. The most commonly observed coordination mode is described as the symmetrical η^5-coordination to an additional metal centre (dinuclear complexes of the ferrole type and trimetallic clusters with the laterally coordinated MCP fragment). In these complexes, the MCP fragment is nearly planar. The equalisation of the carbon–carbon bond lengths in the diene moiety is indicative of strong conjugation in the carbon chain. The degree of deviation of the metallacycle from planarity can serve as a

criterion of the involvement of the endocyclic metal atom in the interaction with the π system of the diene moiety and, in the case of dinuclear complexes, corresponds to two different modes of coordination of the MCP fragment to an additional metal centre (η^1-η^4- or η^5-coordination). The symmetrical η^5-coordination of the MCP fragment to two additional metal centres is observed also in trimetallic clusters with a pentagonal-bipyramidal geometry. The presence of additional metal centres can substantially influence the coordination properties of the MCP fragment, as demonstrated for trimetallic complexes with the metallaindene system or clusters with the facially coordinated metallacycle. In the latter case, the MCP fragment is η^3-coordinated to two additional metal centres, which excludes the formation of the common π system. The structure of the MCP fragment is characterised by a substantial deviation from planarity and localisation of the carbon–carbon bonds in the diene moiety. However, it should be noted that complexes of this type are observed much more rarely than complexes with the η^5-coordinated MCP fragment.

Polynuclear complexes with the MCP fragment are most often formed in the reactions of metal derivatives with acyclic organic molecules, *i.e.*, the metallacyclic ligand is formed simultaneously with the complex as such. The analogy between the MCP fragment and the cyclopentadienyl ligand is invoked many times in discussions of the structures of particular compounds, *i.e.*, in the 'post-factum' analysis of the already formed MCP complexes. However, examples of the use of mononuclear complexes with the MCP fragment as ligands in reactions with other transition metal complexes are scarce (see, for instance, Ref. 152).

A growing number of publications devoted to investigations of metal-containing fragments as potential representatives of a new class of π ligands demonstrates that this problem has attracted increasing interest. Many aspects of these studies were covered in reviews on aromaticity of metallacycles [153] and investigations of the structures and chemical properties of six-membered metallabenzenes.[154]

Undoubtedly, the use of metallacyclic fragments, including metallacyclopentadienes, as non-classical ligands is a promising area of modern chemistry of transition metal π-complexes.

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