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Three-membered Metallocycles

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The results of structural and theoretical studies on cluster compounds with a framework in the form of a triangle made up of metal atoms are examined, a systematic account is given of the types of three-membered metallocycles in which the number of electrons is different from the "magic" number, and the causes of their stability are analysed. The influence of the ligand shell and of the formation of multiple bonds on the stability of three-membered metallocycles is demonstrated.
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I. INTRODUCTION

The chemistry of cluster compounds, a field undergoing vigorous development at the present time,[1] is at the junction between a number of other fields of science: inorganic chemistry, organoelemental chemistry, catalysis, biochemistry, colloidal chemistry, the physics of ultradisperse systems, the physics of surfaces, and electronic materials science†.

†In the USSR two All-Union Discussion Seminars were held on the chemistry and physics of cluster compounds (1979 and 1981) as well as the Ist All-Union Conference on the chemistry of clusters together with the Ist All-Union Seminar on "clusters in catalysis" (1983). The proceedings of the seminar and the conference have been published in special issues of the journals Izv.Sirbir.Akad.Nauk SSSR, Ser. Khim. (Bulletin of the Siberian Division of the USSR Academy of Sciences, Chemistry Series), 1982, Issue 4, No.9, and Koord.Khim. (Coordination Chemistry), 1984, **10**, No.5.

The term cluster compounds is given to those metal compounds whose molecules contain a framework of metal atoms at distances permitting a direct metal–metal interaction, surrounded by a framework of ligands;[2] the characteristics of the electronic structure of two-centre metal–metal bonds of different multiplicity have been investigated in detail in relation to a series of dinuclear metal complexes[3] (see also other communications[4-9]). Cluster compounds are divided into small (N = 3–12)#,[10-13] medium (N = 13–40),[14-15] large (N = 41–100),[16] and ultralarge or "giant" (N > 100). The framework in cluster molecules can consist of metal chains of different lengths and with different degrees of branching,[17-19] metallocycles,[20] metalloskeletons,[21] metallopolyhedra, as well as combinations of the above structural elements. Cluster

#Here and henceforth N represents the nuclearity of the cluster, i.e. the number of metal atoms constituting the framework of the cluster compound.

compounds are characteristic of transition metals,[22] lanthanides and actinides,[23] and the majority of non-transition metals.[24,25] Heterometallic cluster compounds containing two,[27-30] three,[31] and more different kinds of metal atoms in the molecular skeleton are being vigorously investigated.[26] The metal framework in cluster compounds is as a rule coated by a dense layer of ligands, both terminal and bridging§, which may consist of individual atoms (H,[32,33] Cl, Br, I,[34-36] S, Se, Te [37,38]), groups of atoms (CR,[39] EL [40]), or molecules (CO,[41,42] NO,[43] olefins, arenes [44-47]), etc. Monoatomic ligands (H, C, N, S, P, etc.) can sometimes be located within the metallic framework surrounded on the outside by other ligands.[48-51] On the other hand, the so-called "ligand-free" metal clusters can exist under specific specially created conditions in both condensed and gas phases in the form of ultradisperse metallic systems[52,53] or "naked" cluster ions.[24]

A profound analogy between cluster compounds of metals and skeletal and polyhedral compounds of non-metallic elements such as boron, phosphorus, arsenic, etc. has been noted.[54] The principle of isolobal correspondence[55] makes it possible, for example, to "substitute" boron atoms in the polyhedron by metal-containing groups with formation of polyhedral metalloboranes[56]—compounds which occupy an intermediate position between the skeletons of non-metallic elements and cluster compounds of metals.

Analysis of the trends in the development of the chemistry of cluster compounds permits the conclusion that for each element in the Periodic System it is probably possible to obtain molecular compounds with frameworks in the form of chains, rings, skeletons, or polyhedra made up of atoms of the given element. In other words, examination of the geometrical structure,[57] electronic structure,[58,59] and the energy relations[60] of the known cluster compounds does not reveal any fundamental factors prohibiting the formation, on the basis of any element of the Periodic System, of molecular compounds having the simplest structural elements specified above. In this sense the chemistry of cluster compounds is the "organic" chemistry of non-carbon elements.

The synthesis,[61] reactivity,[62] electrochemistry,[63,64] dynamics,[65,66] and stereochemistry[67,68] of cluster compounds of metals have been examined in a series of review articles. It has been shown that the coordination of the ligands to several metal centres in the cluster¶ as a rule differs significantly from the coordination of the same ligands in mononuclear complexes.[69,70] In this connection the use of cluster compounds and materials as catalysts, both homogeneous and heterogeneous, constitutes one of the leading trends in research into catalysis.[71-74] Clusters enter into the composition of a new class of biocatalysts—polynuclear oxidation-reduction enzymes (ferredoxins,[75] ferritins,[76] etc.) and play a key role in a series of most important biological processes, such as oxidation,[77] the fixation of atmospheric nitrogen, etc.[78,79]

It has been established that, together with the cluster compounds of metals, many solids (materials) without molecular structure also contain discrete cluster groups made up of metal atoms separated from one another by non-metallic elements (ligands). For example, cluster groups are the principal structural elements of the so-called "Chevrel phases", which are ultraconducting materials with high critical fields;[80,81] chains made up of metal atoms are the principal structural element of quasi-one-dimensional conducting materials;[82] materials of the type "claspol" containing metal clusters in polymer matrices have been produced.[83]

The intermediate position of cluster compounds between the thoroughly investigated mononuclear and coordination compounds, on the one hand, and compact metals, which have been just as thoroughly investigated, on the other, and the fact that they possess a set of properties differing from both the former and the latter[84] necessitates a vigorous development of theoretical ideas concerning the nature of the bonds in cluster molecules.[85-92] However, despite considerable advances, the questions of the electronic structure of cluster compounds are actually the most controversial at the present time†.

In order to deduce the general rules, extensive experimental data are necessary; although the number of cluster compounds which have been isolated and characterised is fairly large, for many types of clusters, in particular those of moderate and high nuclearity, only 1–2 examples are known, as a rule comprising one metal and ligands of one type.[93]

In contrast to this, cluster compounds having a framework in the form of three-membered metallocycles are widely distributed, have been obtained for the majority of metals, and have ligands of different types. Furthermore, in cluster compounds with a high nuclearity most of the faces of the polyhedra in the metal framework are triangular and three-membered metallocycles can therefore model to some extent the properties of more complex clusters. Within the framework of the rule of skeletal electron pairs,[85] the triangle made up of metal atoms is the principal structural element in the group of polyhedra (the tetrahedron, the trigonal bipyramid, etc.), each having 12 skeletal electrons and in this sense, can be regarded as the *nido*-structure in relation to the tetrahedron and the *arachno*-structure in relation to the trigonal bipyramid.[94] Furthermore, a triangle made up of metal atoms is the simplest element of close packing on the surface of certain faces of metallic crystals; here there is also a possibility of modelling properties, in particular in problems of the interaction of adsorbed substrates with the surfaces of metals.[95,96]

Accordingly, the possible relations between the structure of cluster compounds, the number of cluster valence electrons (CVE), the number and nature of the ligands, and the position of the element in the Periodic System are analysed in this review in relation to the widely distributed "simplest" cluster molecules, having a framework made up of three-membered metallocycles, which have been studied in detail. The relevant conclusions are compared with the results of quantum-chemical calculations on the electronic structures of triangular clusters.

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§ In designating the bridging character of a bond, the Greek letter μ is placed before the symbol representing the given ligand; if the number of metal atoms to which the ligand is bound is greater than two, numerical designations are used, for example μ_3-H, μ_4-PPh, etc.

¶ Henceforth cluster compounds will be referred to for brevity as "clusters" and in those cases where it will be necessary to note the properties of clusters as representatives of the class of coordination compounds, we shall employ the term "complexes".

† A detailed critical examination of various approaches to the description of the electronic structure of cluster compounds has been carried out in the review of Yu.L.Slovokhotov and Yu.T.Struchkov (in this issue of the Journal).

II. THREE-MEMBERED METALLOCYCLES HAVING THE "MAGIC" NUMBER OF VALENCE ELECTRONS

The electronic structure of triangular molecular systems has been frequently investigated as the simplest case of cluster interactions. The "magic" number of cluster valence electrons for three-membered metallocycles is 48; here each metal atom at the apex of the triangle assumes the 18-electron configuration.

The absence of bridging ligands and a high symmetry make the trinuclear cluster ruthenium and osmium carbonyls convenient reference compounds for structural, spectroscopic, and theoretical studies on three-membered metallocycles. The $M_3(CO)_{12}$ molecules, where M = Ru or Os, have the structure of an equilateral triangle with D_{3h} symmetry:[97,98] each metal atom is linked to four terminal CO groups; two of these are equatorial and are located in the plane of the ring, while the other two are perpendicular to this plane (Fig.1). The carbonyl groups are almost linear; the deviation of the axial CO groups from linearity is appreciably greater than for the equatorial groups, probably owing to the repulsion of the oxygen atoms of the neighbouring ligands, whose van der Waals radius is greater than that of carbon. The M–C bond lengths also differ somewhat: the axial CO ligands are in the *trans*-positions relative to one another and have longer M–C bonds, while the equatorial CO groups are in the *trans*-position relative to the metal–metal bond and, as a consequence of the π-acceptance, they can shorten somewhat the M–C bond. Overall, 12 CO ligands are distributed in such a way that the resulting ligand polyhedron is an anticubo-octahedron (Fig.1*b*).[94]

The selection rules for the $Os_3(CO)_{12}$ molecule (D_{3h} symmetry space group) predict two vibrational modes for the metal–metal bond: A_1 (fully symmetrical vibration) and E (doubly degenerate vibration). Analysis of the Raman spectra of $Os_3(CO)_{12}$ in the low-frequency range (30–200 cm^{-1}) showed[99] that, among the 12 frequencies active in the Raman spectrum, the two most intense frequencies can be assigned to ν(M–M): A'_1 at 158 cm^{-1} and E' at 117 cm^{-1}; the contribution of the deformations of the M–C bond to the

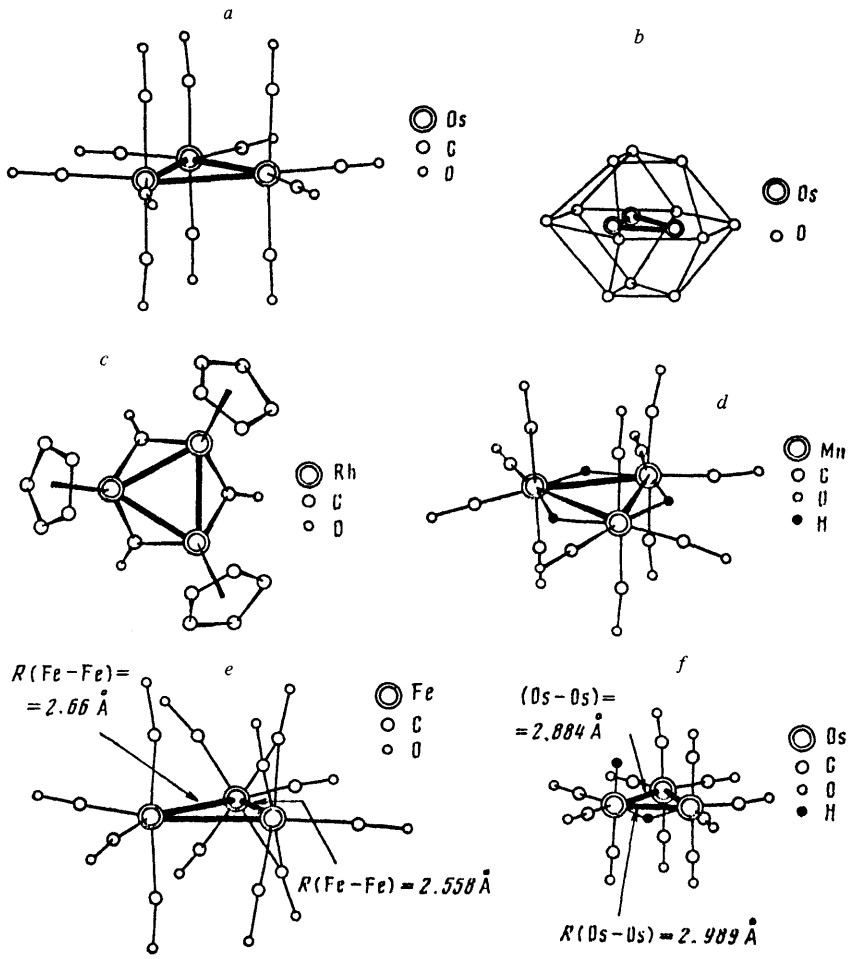


Figure 1. The structure of three-membered metallocycles with 48 CVE and having no μ_3-ligands: *a*) $Os_3(CO)_{12}$; R(Os–Os) = 2.877 Å; R(Os–C_{ax}) = 1.946 Å; R(Os–C_{eq}) = 1.912 Å;[98] *b*) the anticubo-octahedron as the ligand polyhedron of the $M_3(CO)_{12}$ molecule;[94] *c*) $Rh_3(\mu\text{-}CO)_3(Cp)_3$; R(Rh–Rh) = 2.62 Å; R(Rh–C_{Cp}) = 2.24 Å; R(Rh–C_{CO}) = 2.00 Å;[102] *d*) $Mn_3(\mu\text{-}H)_3(CO)_{12}$; R(Mn–Mn) = 3.111 Å; R(Mn–H) = 1.72 Å; R(Mn–C_{ax}) = 1.854 Å; R(Mn–C_{eq}) = 1.789 Å;[101] *e*) $Fe_3(\mu\text{-}CO)_2(CO)_{10}$;[120] *f*) $Os_3(CO)_{11}(\mu\text{-}H)(H)$.[124]

potential energy of these vibrational modes has been estimated at 20% (A_1') and 50% (E'). It is striking that calculation of the force constants for the Os–Os bond yielded two very similar values: $f_{Os-Os} = 0.91 \times 10^{-3}$ dyn A^{-1} when account is taken of the contribution of all the ligands and $f_{Os-Os} = 0.93 \times 10^{-3}$ dyn A^{-1} when no account is taken of the ligands. The analogous calculation for $Ru_3(CO)_{12}$ yielded $f_{Ru-Ru} = 0.82 \times 10^{-3}$ dyn A^{-1} in full agreement with the general tendency towards the weakening of the M–M bond on moving along the Groups of the Periodic System from below upwards. We may also note that $\nu_{A_1'}/\nu_{E'} \cong \sqrt{2}$, which agrees well with the theory for the vibrations of the M_3 triangle as a whole without taking into account the interaction with the ligands.

In the region of the stretching vibration frequencies of the CO ligand (1800–2100 cm^{-1}) the spectra of $M_3(CO)_{12}$, where M = Ru or Os, show absorption bands due solely to the terminal CO ligands;[99] on dissolution, only slight changes take place in the positions and intensities of the CO vibration bands, which indicates the preservation in solution of the principal symmetry elements of these molecules, found for crystalline specimens.

It is possible to detect rapid exchange processes in solutions of the above compounds on the NMR time scale, but the rates of these processes for ruthenium and osmium carbonyls differ very significantly. At 10 °C the ^{13}C NMR spectrum of a solution of $Os_3(CO)_{12}$ consists of two lines (due to the axial and equatorial CO ligands) with a 1 : 1 intensity ratio and corresponds to a structure of this compound in the crystal with D_{3h} symmetry. On heating, the above signals are broadened; the coalescence point is at ~70 °C; at 100 °C a single broad signal corresponding to the positional exchange of the CO ligands (axial–equatorial) is observed.[100] It is striking that in $Ru_3(CO)_{12}$ solutions this type of exchange is observed over the entire experimental temperature range down to −100 °C. Several hypotheses concerning the mechanism of the exchange process have been put forward.[65,66]

Table 1. Three-membered homoelemental metallocycles without μ_3-ligands (48 CVE).

Formula	Refs.
$Mn_3(\mu\text{-}H)_3(CO)_{12}$	[101]
$Tc_3(\mu\text{-}H)_3(CO)_{12}$	[57]
$Re_3(\mu\text{-}H)_3(CO)_{12}$	[57]
$[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$	[112]
$[Re_3(\mu\text{-}H)(CO)_{12}]^{2-}$	[116]
$Re_3(\mu\text{-}H)_3(CO)_{10}(Py)_2$	[118]
$Re_3(\mu\text{-}H)_3(CO)_{11}PPh_3$	[119]
$Fe_3(\mu\text{-}CO)_2(CO)_{10}$	[103, 120]
$[Fe_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$	[121]
$Fe_3(\mu\text{-}CO)_2(CO)_9ER_3(E = P, As)$	[122]
$Fe_3(\mu\text{-}CO)_2(CO)_7L_3(L = PR_3; P(OR)_3)$	[123]
$Ru_3(CO)_{12}$	[97]
$Ru_3(CO)_{10}L_2$	[57]
$Ru_3(\mu\text{-}GeMe_2)_3(CO)_9$	[57]
$Os_3(CO)_{12}$	[98]
$Os_3(CO)_{11}P(OMe)_3$	[104]
$Os_3(\mu\text{-}H)(CO)_{11}(H)$	[124]
$Rh_3(\mu\text{-}CO)_3(Cp)_3$	[102]

Tables 1–4 list the main types of the homo- and heteroelement and three-membered metallocycles, each containing 48 CVE. Evidently, the ruthenium and osmium carbonyls examined above are in essence compounds with identical structural characteristics in which the metal-containing fragments are linked to one another by metal–metal bonds. In all the remaining cases there is a certain number of bridging ligands in the ring. Typical examples of the cluster structures listed in Table 1 are illustrated in Fig. 1.

The hydride $Mn_3(\mu\text{-}H)_3(CO)_{12}$ has a structure closest to the $M_3(CO)_{12}$ structures, where M = Ru or Os. Six axial and six equatorial CO ligands are linked to the equilateral triangle of Mn atoms.[101] The difference consists only in the fact that three bridging hydrogen atoms are located along the metal–metal bonds in the plane of the triangle#. The rhodium compound $Rh_3(\mu\text{-}CO)_3(Cp)_3$ is less symmetrical, although it does possess an idealised threefold symmetry axis; the bridging CO ligands and $\eta^5\text{-}C_5H_5$ groups are located on different sides relative to the equilateral Rh_3 triangle.[102] In the equilateral triangle of Fe atoms in the $Fe_3(CO)_{12}$ molecule, one metal atom has the same geometry (two axial and two equatorial CO ligands) as the metal atoms in $M_3(CO)_{12}$, where M = Ru or Os. However, the other two metal atoms are linked by strongly asymmetric bridges made up of CO ligands.[103] Despite this, the CO ligands are close packed on the surface of the Fe_3 ring and form an idealised cubo-octahedron.[66]

Table 2. Three-membered heteroelemental metallocycles without μ_3-ligands (48 CVE).

Formula	Refs.
$[MnFe_2(\mu\text{-}CO)_2(CO)_{10}]^-$	[46]
$[MnOs_2(CO)_{12}]^-$	[46]
$[TcFe_2(\mu\text{-}CO)_2(CO)_{10}]^-$	[26]
$[ReFe_2(\mu\text{-}CO)_2(CO)_{10}]^-$	[26]
$[ReOs_2(CO)_{12}]^-$	[46]
$Re_2Ru(H)_2(CO)_{12}$	[26]
$MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta^5\text{-}C_5Me_5)_2$	[148]
$FeRu_2(CO)_{12}$	[26]
$FeOs_2(CO)_{12}$	[26]
$Fe_2Ru(\mu\text{-}CO)_2(CO)_{10}$	[46]
$Fe_2Os(\mu\text{-}CO)_2(CO)_{10}$	[26]
$Fe_2Co(\mu\text{-}CO)_2(CO)_7Cp$	[26]
$Fe_2Rh(\mu\text{-}CO)_2(CO)_7Cp$	[46]
$FeRh_2(\mu\text{-}CO)_2(CO)_4(Cp)_2$	[46]
$RuOs_2(CO)_{12}$	[26]
$Ru_2Os(CO)_{12}$	[26]
$Co_2Os(\mu\text{-}CO)(CO)_{10}$	[26]

The $Os_3(CO)_{11}(\mu\text{-}H)(H)$ cluster is the least symmetrical among those examined above. One axial CO group has been replaced by the H ligand, while the second hydrogen atom is of the bridging type and is located in the equatorial plane. The corresponding Os–Os distance is greater by 0.112 Å than the lengths of the other two Os–Os bonds.[104]

#The lengthening of the Mn–Mn bond is typical of clusters where no bridging groups other than μ-H are present along the edge.

Many stable 48-electron three-membered metallocycles are centred on one or two sides on various μ_3-ligands (Tables 3 and 4) in which the key atom can be both a carbon atom and the atoms of other elements. The structures of the most typical compounds of this type are presented in Figs.2 and 3.

A series of clusters with a μ_3-CR ligand are illustrated in Fig.2*a* by means of the two most typical examples. In the $Co_3(CO)_9(\mu_3\text{-}CCH_3)$ cluster an sp^3-hybridised carbon atom is located above the three cobalt atoms of the equilateral Co_3 triangle; the three cobalt atoms are linked to it via single Co–C bonds directed at a 60° angle relative to the plane of the triangle. The tetrahedral environment of the carbon atom is somewhat distorted because the Co–C–Co angles are on average only ~80°. All the atoms are electronically and coordinatively saturated, so that the $Co_3(CO)_9CR$ cluster group is always diamagnetic.[105]

The formation of the frontier orbitals of the $Co_3(CO)_9(\mu_3\text{-}CH)$ cluster from the orbitals of the $Co_3(CO)_9$ and CH fragments is shown schematically in Fig.4, the scheme having been taken from Schilling and Hoffman.[106] The frontier orbitals of the planar $Co_3(CO)_9$ fragment with C_{3v} symmetry have been obtained by adding three electrons to the frontier molecular orbitals of the $Fe_3(CO)_9$ fragment; it is assumed that this does not entail significant changes in the electronic structure except for the alteration of the order of the orbitals with $2a_1$ and $1a_2$ symmetry, which have similar energies. The three orbitals of the CH group are hybridised in such a way that one-low-lying orbital, having an electron pair, is directed towards the side opposite to that of the C–H bond, while the other two orbitals, which are degenerate *p*-type orbitals, are perpendicular to the C–H bond and have one electron. It is striking that the orbital with a_1 symmetry, which is unsuitable for bonding to the group located over the centre of the ring, becomes the highest occupied orbital in the cluster.

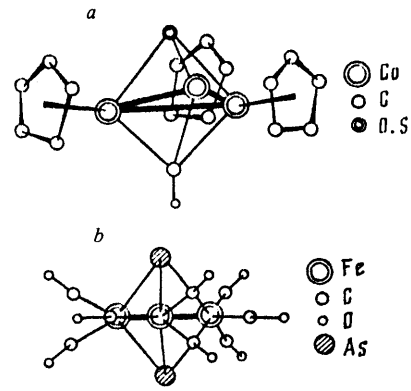


Figure 3. The structure of three-membered metallocycles with 48 CVE each having two μ_3-ligands: *a*) $Co_3(Cp)_3(\mu_3\text{-}CO)(\mu_3\text{-}E)$ [113,114] [E = O: R(Co–Co) = 2.37 Å, R(Co–C_{CO}) = 1.78 Å, R(Co–O) = 2.00 Å; E = S: R(Co–Co) = 2.452 Å]; *b*) $Fe_3(CO)_9(\mu_3\text{-}As)_2$;[115] R(Fe–Fe) = 2.62 Å; R(Fe–C) = 1.80 Å; R(Fe–As) = 2.348 Å.

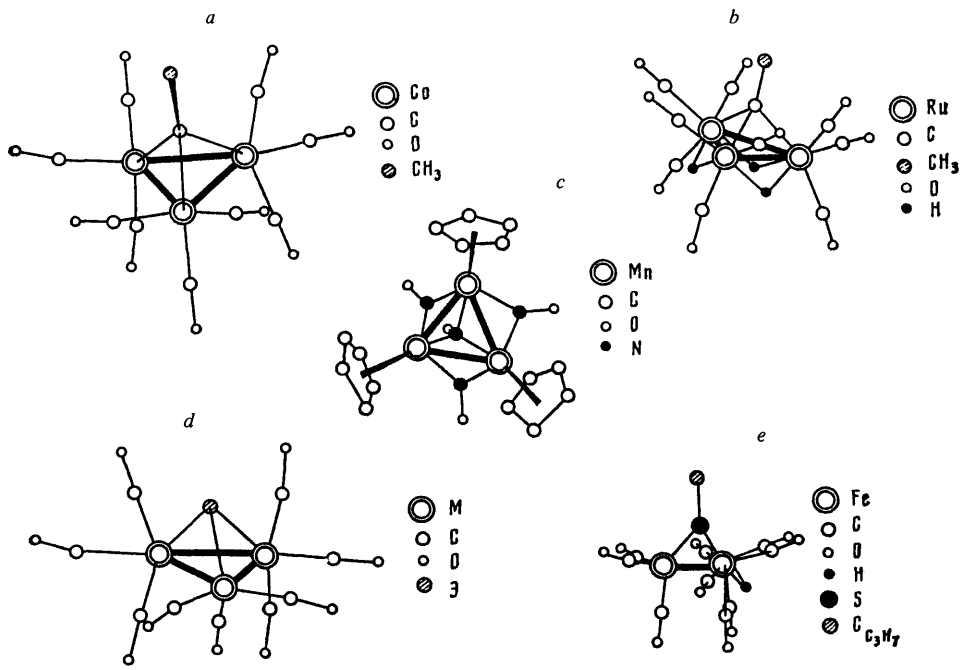


Figure 2. The structure of three membered metallocycles with 48 CVE each having one μ_3-ligand: *a*) $Co_3(\mu_3\text{-}CCH_3)(CO)_9$;[39] R(Co–Co) = 2.467 Å; R(Co–C_{apic}) = 1.90 Å; R(Co–C_{CO}) = 1.80 Å; R(C–CH_3) = 1.53 Å; *b*) $Ru_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CCH_3)$;[127] R(Ru–Ru) = 2.842 Å; R(Ru–C_{apic}) = 2.083 Å; R(Ru–H) = 1.72 Å; *c*) $Mn_3(\mu\text{-}NO)_3(Cp)_3(\mu_3\text{-}NO)$;[108] R(Mn–Mn) = 2.506 Å; R(Mn–N_{μ_3}) = 1.929 Å; R(Mn–N_{μ}) = 1.848 Å; *d*) $FeCo_2(CO)_9(\mu_3\text{-}E)$ [57] [E = S: R(M–M) = 2.55 Å, R(M–E) 2.16 Å; E = Se: R(M–M) = 2.58 Å, R(M–E) = 2.29 Å; E = Te: R(M–M) = 2.60 Å, R(M–E) = 2.47 Å]; *e*) $Fe_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}SC_3H_7\text{-iso})$;[46] R(Fe–Fe) = 2.657 Å; R(Fe–S) = 2.143 Å; R(Fe–H) = 1.80 Å.

Many compounds with the $(CO)_9Co_3C$ fragment, linked to various groups R such as H, halogen, alkyl, arylalkyl, halogenoalkyl, alkoxy, etc., as well as organometallic and other analogous groups are known.[40] The "organic chemistry" of the μ_3-C atom linked to the $Co_3(CO)_9$ fragment has been studied in detail.[39] Tables 3 and 4 show that the μ_3-C bridges are widely distributed in the chemistry of three-membered metallocycles. Fig.2 illustrates the structure of the $Ru_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CCH_3)$ cluster, whose composition differs from that of the cobalt cluster examined above by the presence of three bridging hydrogen atoms; the latter are not located in the plane of the Ru_3 ring, as happens, for example, in the structure of the hydride $Mn_3(\mu\text{-}H_3(CO)_{12}$, but deviate in the direction opposite to that of the side of the metallocycle centred on the μ_3-CCH_3 group. The molecule has approximately the C_{3v} symmetry.[107]

Table 3. Three-membered homo- and hetero-elemental metallocycles each having one μ_3-ligand (48 CVE).

Formula	Refs.
$Co_3(CO)_9(\mu_3\text{-}B\text{-}NEt_2)$	[40]
$Co_3(\mu\text{-}CO)_3(CO)_6(\mu_3\text{-}Al)$	[40]
$Co_3(CO)_9(\mu_3\text{-}CR)$	[39]
$Fe_2(\mu\text{-}CO)_3(Cp)_2(\mu_3\text{-}CR)$	[128]
$FeWPt(\mu\text{-}CO)(CO)_5(PMe_2Ph_2)_2(Cp)(\mu_3\text{-}CR)$	[125]
$Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CH)$	[126]
$Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CCH_3)$	[46]
$Ru_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CCH_3)$	[127]
$Fe_2Ni(CO)_7(Cp)(\mu_3\text{-}CCH_2CH_3)$	[26]
$Co_2W(CO)_8(Cp)(\mu_3\text{-}CC_6H_4CH_3)$	[130]
$Ni_3(Cp)_3(\mu_3\text{-}CC_6H_5)$	[129]
$FeRhW(\mu\text{-}CO)(CO)_5(Cp)(\eta^5\text{-}C_9H_7)(\mu_3\text{-}CC_6H_4CH_3)$	[125]
$Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NC_6H_5)$	[131]
$Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NC_6H_5)$	[132]
$Fe_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NSiMe_3)$	[133, 134]
$Mn_3(\mu\text{-}NO)_3(Cp)_3(\mu_3\text{-}NO)$	[108]
$Ir_3(PF_3)_9(\mu_3\text{-}P)$	[135]
$Co_8(CO)_9(\mu_3\text{-}PS)$	[129]
$Fe_2Cr(\mu\text{-}CO)_2(CO)_9(\mu_3\text{-}PC_6H_5)$	[26]
$Fe_2Mn(\mu\text{-}CO)_2(CO)_6(Cp)(\mu_3\text{-}PC_6H_5)$	[136]
$Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}S)$	[129]
$Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}S)$	[57]
$FeCo_2(CO)_9(\mu_3\text{-}S)$	[57]
$FeCo_2(CO)_9[\mu_3\text{-}S\text{-}Cr(CO)_5]$	[111]
$Fe_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}SR)$	[46]
$Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}Se)$	[129]
$FeCo_2(CO)_9(\mu_3\text{-}Se)$	[57]
$Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}Te)$	[129]
$FeCo_2(CO)_9(\mu_3\text{-}Te)$	[57]
$Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}SBu\text{-}t)$	[137]

Clusters with NO ligands are so far comparatively rare (see, for example, Feltham and Enemark[43]). Fig.2*c* illustrates the structure of the compound $Mn_3(\mu\text{-}NO)_3(Cp)_3.(\mu_3\text{-}NO)$.[108] The molecule has the C_{3v} symmetry; in its base is located the equalateral Mn_3 triangle, each side of which is spanned by a bridging NO group which is not located in the plane of the ring: the deviation of the NO group from the plane of the ring is ~47°. On the opposite side, the ring is centred on the μ_3-NO ligand. The planar Cp rings deviate from the plane of the triangle by an angle of ~17° towards the side opposite to that of the μ-NO ligands. Overall, this arrangement results in a fairly close symmetrical packing of the ligands around the Mn_3 triangle.

The centering of the three- and four-carbon faces in clusters with a high nuclearity on chalocogenide ligands is very common; three-membered metallocycles with μ_3-chalcogenide ligands are therefore of special interest. Fig.2*d* presents the structures of the most typical representatives of these compounds. The structure of the clusters $Co_2Fe(CO)_9(\mu_3\text{-}X)$, where X = S, Se, or Te, are isotypical; the molecules have approximately the C_{3v} symmetry, and one of the sides of the Co_2Fe ring is centred on the X group; the ring is in essence an equalateral triangle. The differences in the M–M bond length are within the limits of the accuracy of the method, which is not surprising bearing in mind that the covalent radii of the Fe and Co atoms are virtually identical (1.165 and 1.162 Å).[109,110] Fig.2 shows that the metal–metal distances depend on the nature of the chalogen and increase with the increase of the radius or the μ_3-X group. We may note that the chalcogen atom in the μ_3-arrangement provides only four electrons for the formation of bonds with the metal atoms; it retains a free electron pair located in an orbital directed to the "outside" at right angles to the plane of the ring. It can be detected experimentally: such clusters behave like the usual two-electron-donating ligands and are capable, for example, of substituting the CO group in chromium carbonyl with formation of a derivative of the usual type—cyclo-$FeCo_2(CO)_9[\mu_3\text{-}S.Cr(CO)_5]$.[111]

Table 4. Three-membered homo- and hetero-elemental metallocycles each having two μ_3-ligands (48 CVE).

Formula	Refs.
$Ru_3(CO)_9(\mu_3\text{-}CO)[\mu_3\text{-}NSi(CH_3)_3]$	[46]
$Fe_3(CO)_9(\mu_3\text{-}CO)[\mu_3\text{-}NSi(CH_3)_3]$	[133]
$Co_3(Cp)_3(\mu_3\text{-}CO)[\mu_3\text{-}NSi(CH_3)_3]$	[46]
$Rh_3(Cp)_3(\mu_3\text{-}CO)[\mu_3\text{-}NSi(CH_3)_3]$	[46]
$Co_3(Cp)_3(\mu_3\text{-}CO)(\mu_3\text{-}N{-}N{=}CPh_2)$	[138]
$Co_3(Cp)_3(\mu_3\text{-}CO)(\mu_3\text{-}S)$	[114]
$Co_3(Cp)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$	[113]
$Ni_2Co(Cp)_3(\mu_3\text{-}CO)_2$	[26]
$Ni_2Fe(Cp)_2(CO)_5(\mu_3\text{-}CO)_2$	[26]
$[Ni_2Mn(Cp)_2(CO)_3(\mu_3\text{-}CO)_2]^-$	[26]
$Co_3(Cp)_3[\mu_3\text{-}CN(C_2H_5)_2]_2$	[126]
$Rh_3(Cp)_3[\mu_3\text{-}CN(C_2H_5)_2]_2$	[126]
$Co_3(Cp)_3(\mu_3\text{-}NO)_2$	[43]
$Fe_3(CO)_9(\mu_3\text{-}As)_2$	[115]
$Fe_3(CO)_9[\mu_3\text{-}SnFe(CO)_2(Cp)]_2$	[57]

In contrast to this, the μ_3-SR group (where R is an organic substituent) provides five electrons for the formation of bonds with metal atoms. Fig.2*e* illustrates the structure of the cluster compound $Fe_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}SC_3H_7\text{-iso})$; the Fe atoms form an almost equilateral triangle, the bridging hydride being directed to the side opposite to that of the μ_3-SR group and linking symmetrically two Fe atoms.[112]

The centering of the three-membered rings on the μ_3-ligands on two sides renders the ligand shells in such cluster molecules more compact and probably increases their stability. Examples of triangular clusters with two μ_3-ligands are presented in Table 4; certain structures are illustrated in Fig.3.

The centering of the triangular face on μ_3-CO ligands is frequently observed in cluster compounds with high nuclearity; such examples are encountered much more rarely among the triangular clusters considered in this review. A rare structurally characterised example of the coordination of the oxygen atom as a μ_3-ligand, which provides four electrons for the formation of bonds with metal atoms, occurs in the $Co_3Cp_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$ cluster. Owing to the small radius of the oxygen atom, the principal Co–O, Co–Co, and Co–C_{CO} bond lengths in the molecule are somewhat shortened.[113]

This can be seen fairly clearly from a comparison of the corresponding distances in the isoelectronic and isostructural cluster $Co_3Cp_3(\mu_3\text{-}CO)(\mu_3\text{-}S)$,[114] in which the Co–Co bond length is greater almost by 0.1 Å.

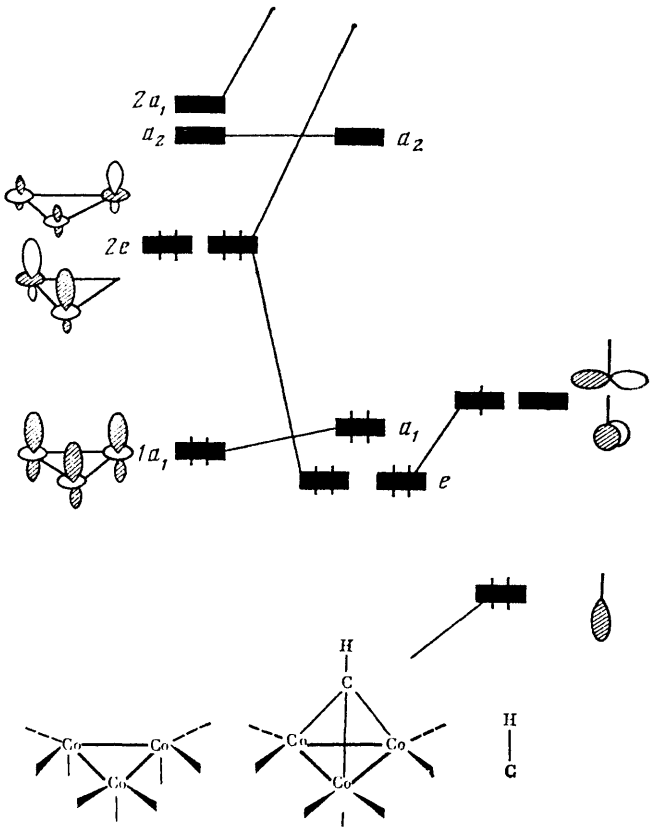


Figure 4. The frontier orbitals of the $Co_3(CO)_9(\mu_3\text{-}CH)$ cluster.[106]

Finally in the last of the structures considered (Fig. 3*b*), namely that of the $Fe_3(CO)_9(\mu_3\text{-}As)_2$ cluster, each of the two arsenic atoms behaves as a three-electron ligand and the Fe_3 triangle is centred on them on two sides.[115]

Thus three-membered metallocycles, each having 48 CVE, are fairly common; the homometallic compounds are characteristic of transition elements with the d^7–d^9 electronic configuration; in heterometallic clusters the range of elements is wider—they can incorporate Pt(d^{10}), W, or Cr(d^6). The metal framework in cluster compounds of this type can be surrounded by ligands differing significantly in both their electronic and steric properties. The majority of the cluster compounds presented in Tables 1–4 possess π-acceptor linear carbonyl ligands; together with these, π-donor ligands are also present, namely ligands such as S, Cp, Sr, NR, etc., as well as ligands incapable of additional π-interaction with the metal framework, of the type of CR, B-NEt_3, etc.

It is noteworthy that Tables 1–4 list clusters without CO ligands, for example, $Co_3Cp_3(\mu_3\text{-}NO)_2$ and $Rh_3Cp_3[\mu_3\text{-}CN.(C_2H_5)_2]_2$, as well as the $Ir_3(PF_3)_9(\mu_3\text{-}P)$ cluster in which there are no M–C bonds at all. A definite preference for either ligands or metals in the formation of compounds of this type should probably not be expected. The existence of a large number of cluster compounds with carbonyl ligands, which have been synthesised and investigated, is not due to their special properties but apparently arises because in the initial stages of the development in this field metal carbonyls were most often employed as the starting compounds in the synthesis of clusters.

Table 5. Three-membered metallocycles each having 49 CVE.

Formula	Refs.
$Co_3(CO)_9(\mu_3\text{-}S)$	[109]
$Co_3(CO)_9(\mu_3\text{-}Se)$	[110]
$Ni_3(Cp)_3[\mu_3\text{-}NC(CH_3)_3]$	[139]
$Co_3(CO)_9(\mu_3\text{-}PR)$	[46]
$Ni_3(Cp)_3(\mu_3\text{-}CO)_2$	[57]
$[Co_3(Cp)_3(\mu_3\text{-}S)_2]^+$	[114]

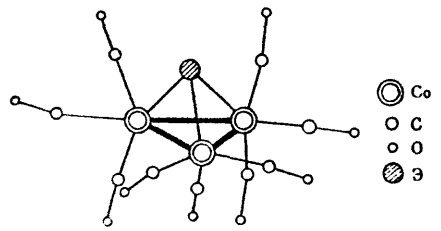


Figure 5. The structure of the $Co_3(CO)_9(\mu_3\text{-}E)$ clusters;[109,110] E = S: R(Co–Co) = 2.64 Å, R(Co–E) = 2.14 Å; E = Se: R(Co–Co) = 2.62 Å, R(Co–E) = 2.28 Å.

III. TRIANGULAR CLUSTERS WITH AN EXCESS OF VALENCE ELECTRONS

Several examples of entirely stable structurally characterised triangular metallocycles containing more than the magic number of valence electrons are known. Examples of such compounds are presented in Table 5. It is striking that they all have at least one μ_3-ligand.

In the first place we shall consider paramagnetic compounds, each having 49 CVE. The structure of the $Co_3(CO)_9(\mu_3\text{-}E)$ clusters, where E = S or Se [109,110] (Fig. 5), is based, like that of the diamagnetic 48-electron analogues $Co_2Fe(CO)_9.(\mu_3\text{-}E)$, where E = S or Se, on an equilateral triangle made up of metal atoms and centred on an apical chalcogenide ligand in accordance with a tetrahedral motif. The molecules have the idealised C_{3v} symmetry. The larger radius of the selenium atom compared with that of the sulphur atom increases the Co–E distance, but hardly affects the length of the Co–Co bond. However, it has been noted[110] that the metal–metal distances in the 49-electron clusters are greater (by 0.08 Å for E = S and 0.04 Å for E = Se) than in the isostructural 48-electron clusters $Co_2Fe(CO)_9(\mu_3\text{-}E)$, where E = S or Se. Consequently the appearance of an unpaired electron entails an appreciable increase of the metal–metal bond length. It has been concluded[110] that the highest

half-filled MO in the $Co_3(CO)_9(\mu_3\text{-}E)$ cluster, where E = S or Se, has a strongly antibonding character in relation to the metal–metal bonds of the Co_3 triangle.

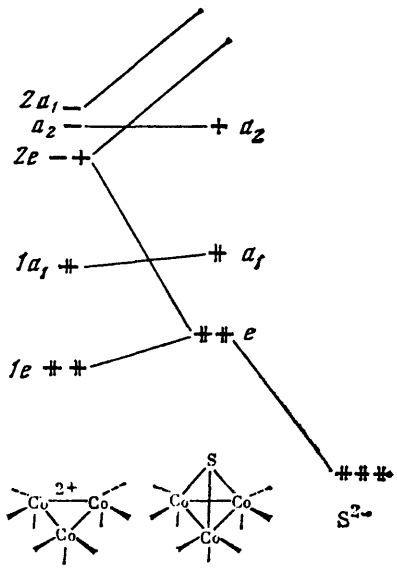


Figure 6. Diagram illustrating the interaction of the orbitals in the formation of the $Co_3(CO)_9(\mu_3\text{-}S)$ cluster.[106]

Fig. 6 illustrates a scheme for the construction of the frontier molecular orbitals of the $Co_3(CO)_9(\mu_3\text{-}S)$ cluster from the orbitals of the $[Co_3(CO)_9]^{2+}$ and S^{2-} fragments.[106] The low-lying fully occupied *p* orbitals of the S^{2-} group interact strongly with the 1*e* orbitals of the $[Co_3(CO)_9]^{2+}$ fragment and conversely the $1a_1$ and a_2 orbitals hardly undergo a change in their positions on formation of the cluster. Apparently the unpaired electron is located in the a_2 orbital of the cluster, which is antibonding in relation to the metal–metal bonds (Fig. 6). Calculations have shown that, when an electron enters this orbital, the overlap populations between the cobalt atoms diminish by a factor greater than 2, which in fact leads to the observed increase of the metal–metal distance.

More detailed experimental information about the nature and spatial orientation of this orbital has been obtained from EPR spectra;[110] the spectra of both solutions of the $Co_3(CO)_9.(\mu_3\text{-}E)$ clusters, where E = S or Se, and the single crystals of the diamagnetic isostructural compounds $FeCo_2(CO)_9(\mu_3\text{-}E)$, containing 0.5% of the isomorphous paramagnetic $Co_3(CO)_9.(\mu_3\text{-}E)$ clusters, have been investigated. The EPR spectrum of a single crystal with E = Se consists of 22 lines due to the hyperfine interactions of the unpaired electron with the three ^{59}Co nuclei ($J = 7/2$). Detailed analysis of the EPR spectra[110] showed that the unpaired electron is located in the non-degenerate antibonding MO disposed in the plane of the Co_3 triangle and made up predominantly of the $3d_{xz}$ orbitals of the Co atom without an appreciable contribution by the *s* orbitals. The hyperfine splitting constant $[A_{11}] = 77.0$ G calculated on this basis is in good agreement with the experimental value $[A_{11}] = 74.3$ G. The hyperfine splitting constant for the $Co_3(CO)_9(\mu_3\text{-}S)$ cluster is smaller by only 2%, i.e. $[A_{11}] = 72.8$ G, than for the selenium compound, which undoubtedly demonstrates yet again the strongly antibonding character of the a_2 orbital and its location in the plane of the ring orthogonally in relation to the *s*, *p*, and *d* orbitals of the apical chalcogen atom.

The compound $Cp_3Ni_3(\mu_3\text{-}S)_2$ [159] having 53 CVE also belongs to the group of paramagnetic triangular clusters. Here the Ni–Ni distances have been increased to 2.80 Å. The stability of the cluster is determined by the density of the ligand packing and the two μ_3-S bridges spanning the metal atoms. The same causes are apparently responsible for the stability of the analogous cobalt cluster $Co_3Cp_3(\mu_3\text{-}S)_2$, which has three electrons less; the Co...Co distances have likewise been increased, to 2.687 Å.[114]

If the μ_3-bridges spanning the metal atoms to form a triangle cannot be formed for one reason or another under the conditions of the synthesis, the presence of 50 CVE in the molecule leads to the rupture of one M–M bond and the conversion of the framework of the cluster from a metallocycle into a metallochain; as a rule, this is not a linear chain but a "wedge" with the angle at the central atom in the range 80–100°; as it were, a slightly open triangle is obtained. A detailed discussion of such molecules is outside the framework of this review.

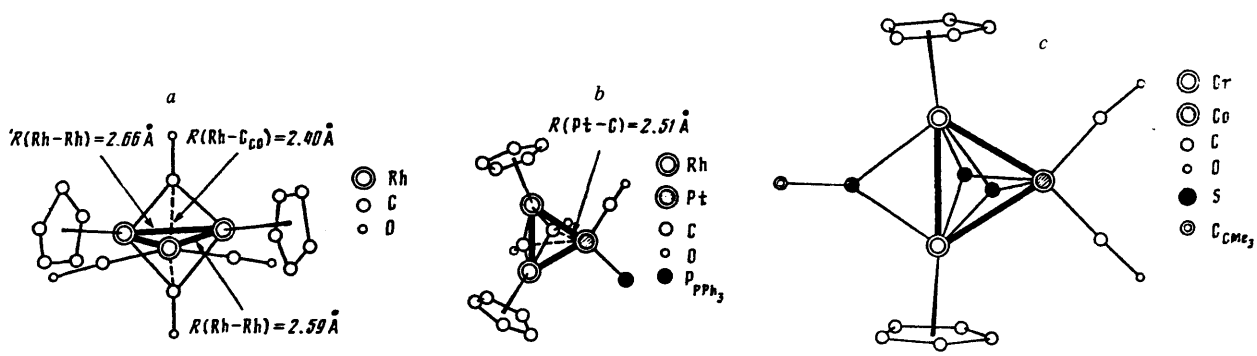


Figure 7. The structure of clusters each having 46 CVE: *a*) $Rh_3(\mu\text{-}CO)_2(CO)_2(Cp)_2$;[144] *b*) $Rh_2Pt(\mu\text{-}CO)_2(CO)(Cp)_2(PPh_3)$;[142] $R(Rh–Rh) = 2.65$ Å; $R(Rh–Pt) = 2.65$ Å; *c*) $Cr_2Co(Cp)_2(CO)_2[\mu\text{-}SC(CH_3)_3](\mu_3\text{-}S)_2$;[143] $R(Cr–Cr) = 2.62$ Å; $R(Cr–Co) = 2.59$ Å; $R(Co–S) = 2.20$ Å; $R(Cr–S_{\mu_3}) = 2.30$ Å.

IV. STABLE THREE-MEMBERED METALLOCYCLES WITH A DEFICIENCY OF VALENCE ELECTRONS

Analysis of structurally characterised triangular clusters has shown that three-membered metallocycles with less than 48 CVE are encountered no more rarely than clusters with the magic number of CVE. In order to discover the cause of the stability of such compounds, we shall examine in greater detail their abundance and the characteristics of their structure.

1. Three-Membered Metallocycles having 46 CVE

Table 6 presents examples of triangular clusters, each having 46 CVE. The homoelemental compounds are represented by rhodium clusters, but most of the compounds are heterometallic clusters each containing two metal atoms with the d^7–d^9 configuration and one Pt atom. In all cases the molecules contain bulky phosphine or Cp ligands together with the CO groups.

Table 6. Homo- and hetero-elemental three-membered metallocycles each having 46 CVE.

Formula	Refs.
$Rh_3(\mu\text{-}PPh_2)_3(CO)_5$	[140]
$Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2$	[141]
$[Rh_3(\mu\text{-}CO)_2(CO)_2(Cp)_2]^-$	[144]
$Mo_2Fe(Cp)_2(CO)_8$	[26]
$Cr_2Co(Cp)_2(CO)_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2$	[143]
$PtFeW(CO)_6(\mu_3\text{-}CR)(Cp)(PEt_3)$	[125]
$Pt_2W[\mu\text{-}C(OMe)Ph](CO_6[P(t\text{-}Bu)_2Me]_3$	[57]
$PtFe_2(CO)_8(PR_3)_2$	[125]
$PtFe_2(CO)_9(PR_3)$	[145]
$PtFe_2(CO)_8COD$	[125]
$PtCo_2(CO)_7L_2$	[46, 146]
$PtRu_2(CO)_8(diphos)$	[125]
$PtOs_2(CO)_7(PMePh_2)_3$	[26]
$PtRu_2(CO)_7(PPh_3)_3$	[26]
$PtRh_2(\mu\text{-}CO)_2(COD)(\eta^5\text{-}C_5Me_5)_2$	[142]
$PtRe_2(\mu\text{-}H)_2(CO)_9(PRh_3)$	[26]
$AuRe_2(\mu\text{-}H)(CO)_9(PPh_3)$	[26]
$PtRh_2(\mu\text{-}CO)(\mu_3\text{-}CO)(PPh_3)(\eta^5\text{-}C_5Me_5)_2$	[142]

The cluster species $[Rh_3(\mu\text{-}CO)_2(CO)_2Cp_2]^-$ and $Rh_2Pt.(\mu\text{-}CO)_2(CO)Cp_2(PPh_3)$ can be regarded as the products of the addition of the isoelectronic groups $[Rh(CO)_2]^-$ and $Pt(CO)PPh_3$ to the double bond of the dimer $Cp_2Rh_2(\mu\text{-}CO)_2$ (Figs. 7*a* and 7*b*). Both structures have definite features in common: the CO bridging ligands are not in the same plane with the rhodium atoms in both cases and are inclined in the direction of the third metal atom, so that, for example, the angle between the Rh(1)–Rh(2)–C(5) plane and the plane of the ring is 77.5°; an analogous situation has been observed in a Pt cluster (Fig. 7).

Formally the same result, i.e. the presence of 46 CVE, can be achieved when the framework of the cluster contains one metal atom with the d^8–d^9 configuration and two metal atoms with the d^6 configuration, the structure of one such compound being illustrated in Fig. 7*c*. This is also a product of addition, in this instance of the $Co(CO)_2$ fragment, to a dimeric chromium complex; it is believed[143] that the high exchange interaction parameter ($-2J = 530$ cm^{-1}) is satisfactorily correlated with the shortening of the Cr–Cr distance (2.617 Å).[143] Fig. 7*c* shows that the Cr_2Co triangle is surround by a shell of adjoining ligands; whereby a more complete shielding of the metallic framework against the possible (under the conditions of synthesis) attachment of additional ligands is apparently achieved.

We may note that the appearance of the 47th electron in the cluster $Cr_2Fe(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2(CO)_3$ with an analogous composition leads to a significant "loosening" of one Fe–Cr bond in the triangle (the distances are 2.726 and 3.010 Å respectively).[160]

Furthermore, 46-electron clusters can also be achieved when the triangle contains two Pt atoms and one W atom[57] and also three different atoms (Pt, Fe, and W).[125] The number of such combinations is likely to become fairly large in the future.

2. Three-Membered Metallocycles having 44 CVE

The decrease of the number of CVE in triangular cluster compounds is achieved in two ways—by a gradual accumulation in the framework of atoms of elements lying to the right or to the left of metals with the d^8 electronic configuration. The homoelemental cluster compounds each containing 44 CVE are represented by the Pd and Pt as well as Ir triangular metallocycles (Table 7). The 42-electron triangles considered in the next subsection, are typical for the first two elements; sometimes the reversible addition of yet another two-electron ligand with formation of 44-electron three-membered metallocycles is possible.[161] The very fact of the existence of the equilibrium of the type $Q_{42}CVE + L \rightleftharpoons Q_{44}CVE$ shows that the number of CVE is not the only factor determining the stability of cluster compounds of this type.

Table 7. Homo- and hetero-elemental three-membered metallocycles each having 44 CVE.

Formula	Refs.
$Cr_2Fe(\mu\text{-}OR)_2(CO)_4(Cp)_2$	[149]
$Mo_2Pt(CO)_4(Cp)_2(PPh_3)_2$	[125]
$[Ir_3(H)_6(\mu\text{-}H)\{P(C_6H_{11})_3\}_3Py_3]^{2+}$	[57]
$Pt_2Fe(CO)_5[P(OPh)_3]_3$	[57]
$Pt_2Ru(CO)_5(PR_3)_3$	[147]
$Pt_2Ru(CO)_4(PR_3)_4$	[26]
$Pt_2Os(CO)_5(PR_3)_3$	[26]
$Pt_2Cr[\mu\text{-}C(OMe)Ph](CO)_6(PR_3)_2$	[150]
$Pt_2W[\mu\text{-}C(OMe)Ph](CO)_6(PR_3)_2$	[150]
$Pt_3(\mu\text{-}CO)_3(PR_3)_4$	[57]
$[Pt_3(CO)_3(\mu\text{-}CO)_3]^{2-}$	[57]
$Pd_3[CNC(CH_3)_3]_5(\mu\text{-}SO_2)_2$	[57, 46]
$Pd_3(\mu\text{-}CO)_3(PPh_3)_4$	[46]

Heterometallic triangular clusters are presented in Table 7. A characteristic example of such compounds is the $Pt_2W.[\mu\text{-}C(OMe)Ph])CO)_6[P(t\text{-}Bu)_2Me]_2$ cluster, whose structure is illustrated in Fig. 8*a*. The Pt_2W triangle is equilateral; the planar carbene ligand lies in a plane perpendicular to that of the Pt_2W ring and passing through the W atom and the centre of the Pt–Pt bond; the CO ligands are of the semi-bridging type with markedly different distances to the Pt and W atoms; overall, the metallic framework of the cluster is strongly shielded against external influences by virtue of the branched ligand environment.

If is of interest to compare the structures of two clusters—$FeCr_2(\mu\text{-}OR)_2(CO)_4(Cp)_2$ and $FePt_2(CO)_5[P(OPh)_3$ (Figs. 8*b* and 8*c*). Both compounds contain the electronically saturated $Fe(CO)_4$ group symmetrically linked to the corresponding bimetallic fragments. Evidently, formally the same result (44 CVE) can be achieved via two significantly different pathways. The qualitative schemes for the distribution of electrons among the MO in the clusters indicated have been examined by Eremenko et al.[149] and Johnson and Benfield[94] respectively. The fact that both the Fe atom in the $Fe(CO)_4$ group and the M–M bonds opposite it are strongly sterically shielded owing to the close packing of branched ligands, which is clearly seen from a projection of the structure of the cluster illustrated in Fig. 8*d*, is striking.

One must note that, although the majority of the triangular metallocycles presented in Table 7 contain CO groups as ligands, there exists an example of a cluster compound without CO ligands, namely $Pd_3[CNC(CH_3)_3]_5(SO_2)_2$ [155] as well as a cluster which altogether lacks M–C bonds, namely $\{Ir_3(H)_6 .(\mu\text{-}H)[P(C_6H_{11})_3]_3Py_3\}^{2+}$. [57]

3. Three-Membered Metallocycles having 42 CVE

Table 8 presents examples of cluster compounds which each have 42 CVE; evidently these compounds can be divided into two groups—the cluster compounds of Group VI and VII transition elements and the larger group of platinum, palladium, and rhodium compounds. Fig. 9 illustrates the structures of some of the cluster compounds having 42 CVE each.

The cluster cation $[Mo_3(Cp)_3(\mu\text{-}S)_2(\mu_3\text{-}S)]^+$ is very compact; one side of the Mo_3 triangle is shielded by the μ_3-S ligand, while the other is shielded by three μ-S groups, which deviate markedly from the plane of the ring; from the outside, each Mo atom is coordinated to a planar Cp ring (Fig. 9*a*). On the other hand, the formation of a stable 42-electron platinum cluster apparently does not require the complete shielding of the metallic triangle by a close-packed ligand shell; it is sufficient that the bulky substituents should prevent the mutual approach of the two Pt_3 rings, along the three-fold axis passing through the centre of the ring, to distances sufficient for the formation of prismatic structures with weak metal–metal bonds between the rings.

Table 8. Three-membered metallocycles each having 42 CVE.

Formula	Refs.
$[Re_3(\mu\text{-}Cl)_3Cl_9]^{3-}$	[151]
$[W_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]^{4+}$	[152]
$[Mo_3(\mu\text{-}S)_3(\mu_3\text{-}S)(Cp)_3]^+$	[156]
$Pt_3[\mu\text{-}CNC(CH_3)_3][CNC(CH_3)_3]_5$	[154]
$Pt_3(\mu\text{-}CO)_3(PR_3)_3$	[46]
$Pt_3[\mu\text{-}C(OCH_3)C_6H_4CH_3]_3(CO)_3$	[157]
$Pt_3[\mu\text{-}C(OCH_3)C_6H_5]_3[P(CH_3)_3]_3$	[157]
$Pt_3(H)_6[P(Bu\text{-}tper)_3]_3$	[153]
$Pd_3(\mu\text{-}CO)_3(PPh_3)_3$	[46]
$Rh_3(\mu\text{-}H)_3[P(OCH_3)_3]_6$	[158]

A typical example of such compounds is illustrated in Fig. 9*c*. Each platinum atom has one terminal CO ligand and is linked to its neighbours by a bridging carbene ligand; the carbene ligands are almost planar and each such plane is

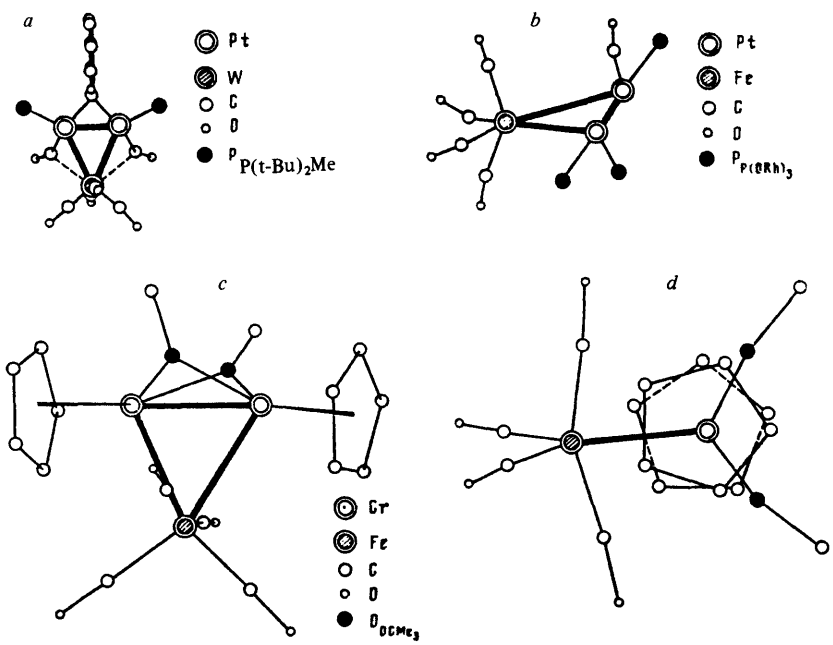


Figure 8. The structure of clusters each having 44 CVE: *a*) $Pt_2W[\mu\text{-}C(OCH_3)C_6H_5](\mu\text{-}CO)_2(CO)_4\{P[C(CH_3)_3]_2CH_3\}_2$;[150] R(Pt–Pt) = 2.63 Å; R(Pt–W) = 2.83 Å; R(Pt–C_{CO}) = 1.87 Å; R(W–C_{CO}) = 2.43 Å; α-(Pt–C–O) = 148°; *b*) $Pt_2Fe(CO)_5[P(OC_6H_5)_3]_3$;[57] R(Pt–Pt) = 2.63 Å; R(Pt–Fe) = 2.57 Å; *c*) $Cr_2Fe[\mu\text{-}OC(CH_3)_3]_2(CO)_4(Cp)_2$;[149] R(Cr–Cr) = 2.64 Å; R(Cr–Fe) = 2.70 Å; *d*) projection along the Cr–Cr axis.

perpendicular to that of the Pt_3 ring and passes through the centre of the Pt–Pt bond.

The only 42-electron rhodium cluster listed in Table 8 is an example of a compound in which the electronically unsaturated metallic triangle is fully shielded by highly branched ligands (Fig. 9*b*). The Rh–Rh distance is increased owing to the presence of the bridging hydrogen atoms.

One must note that, among the three-membered metallocycles listed in Table 8, there are many examples of compounds without M–C bonds: here we encounter for the first time triangular clusters having only typical acido-ligands, which are characteristic of "inorganic" complexes. As an example, we shall consider the $Re_3(\mu\text{-}Cl)_3Cl_9$ cluster, whose structure is illustrated in Fig. 9*d*. Evidently the Re–Re distances are greatly diminished compared with, for example, the length of this bond in $Re_2(CO)_{10}$ (3.02 Å). It has been suggested that multiple M–M bonds are present in this and analogous compounds.[162]

It is striking that the chloride ligands in the above cluster compounds, like the carbonyl groups in compounds of the type $M_3(CO)_{12}$, where M = Ru or Os, give rise to a close-packed configuration and a ligand polyhedron analogous to that shown in Fig. 1 with the sole difference that the central hexagon has been rotated by an angle of 60° relative to the axis passing through the centre of the Re_3 triangle.

The question whether three-membered metallocycles having less than 42 CVE can exist should apparently be answered in the affirmative. The organometallic compound $Re_3(CH_3)_9$, containing 30 CVE and the product of the addition to the latter of phosphine ligands, namely $Re_3(CH_3)_9(PEt_2Ph)_3$, which has 36 CVE, are known.[163]

Thus the following conclusions characterising the relation between the structure and the number of CVE in triangular cluster compounds can be drawn from the data examined above:

1. Stable three-membered cluster compounds of transition metals with the d^6–d^{10} configuration and 48, 46, 44, 42, or fewer CVE are known. The close packing of the bulky ligands on the surface of the metallic framework, which results in the shielding of the M–M bond against the influence of external agents, becomes increasingly pronounced with decrease of the number of CVE.
2. No specific ligand preference in the formation of triangular cluster compounds has been discovered; among the examples listed in Tables 1–8, ligands of virtually all known types are encountered.
3. The smaller the number of CVE in the compound, the shorter the M–M bond; this conclusion is valid for metals with the d^6–d^7 configuration but does not extend to the triangular Pd and Pt clusters.
4. In the cluster compounds with 49 CVE the unpaired electron is located in a highly antibonding (in relation to the M–M bond of the metallic framework) non-degenerate MO. Such compounds have at least one μ_3-bridging ligand, which maintains the metal atoms at short distances from one another.
5. In cluster compounds with 50 CVE a second electron enters the antibonding non-degenerate MO, which leads to the rupture of one metal–metal bond; the triangle is opened and the metallic framework assumes the form of a bent chain made up of three metal atoms.
6. In a cluster having 53 CVE all three Ni...Ni bonds are greatly extended compared with the normal Ni–Ni distance. The stability of such a cluster is determined by the close packing of the ligands in the presence of two μ_3-S bridges spanning the metal atoms.
7. The presence in the cluster framework of each Pt, Pd, and Au atom as a rule reduces the number of CVE by two. A typical number of CVE in the triangle of Pt or Pd atoms is 42 (sometimes 44). In the presence of a greater number

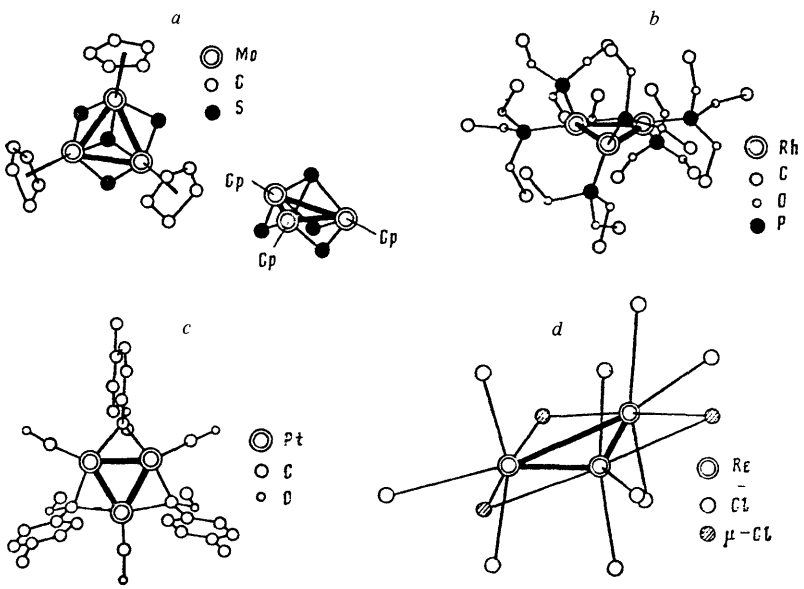


Figure 9. The structure of clusters each having 42 CVE: *a*) $[Mo_3(\mu\text{-}S)_3(\mu_3\text{-}S)(Cp)_3]^+$;[156] R(Mo–Mo) = 2.81 Å; R(Mo–S_μ) = 2.29 Å; R(Mo–S_{μ_3}) = 2.31 Å; *b*) $Rh_3(\mu\text{-}H)_3[P(OCH_3)_3]_6$;[158] R(Rh–Rh) = 2.82 Å; *c*) $Pt_3[\mu\text{-}C(OCH_3)C_6H_4CH_3\text{-}p]_3(CO)_3$;[157] R(Pt–Pt) = 2.62 Å; *d*) $[Re_3(\mu\text{-}Cl)_3Cl_9]^{3-}$; R(Re–Re) = 2.47 Å.[151]

of CVE the homometallic triangle made up of Pt or Pd atoms is open.

V. THE ELECTRONIC STRUCTURE OF THREE-MEMBERED METALLOCYCLES

In the formation of a metallocycle with a framework in the form of a regular triangle the three transition metal atoms each provide nine orbitals ($5d + 1s + 3p$), which results in a set of 27 MO (Fig.10); three of these (a_2' and e') have unduly high energies and are unsuitable for bonding.[164] Consequently in the metallic triangles there are only 24 cluster valence molecular orbitals (CVMO). In the three-membered metallocycles considered this set of MO is occupied in different ways by the electrons provided by the metal atoms and the ligands.

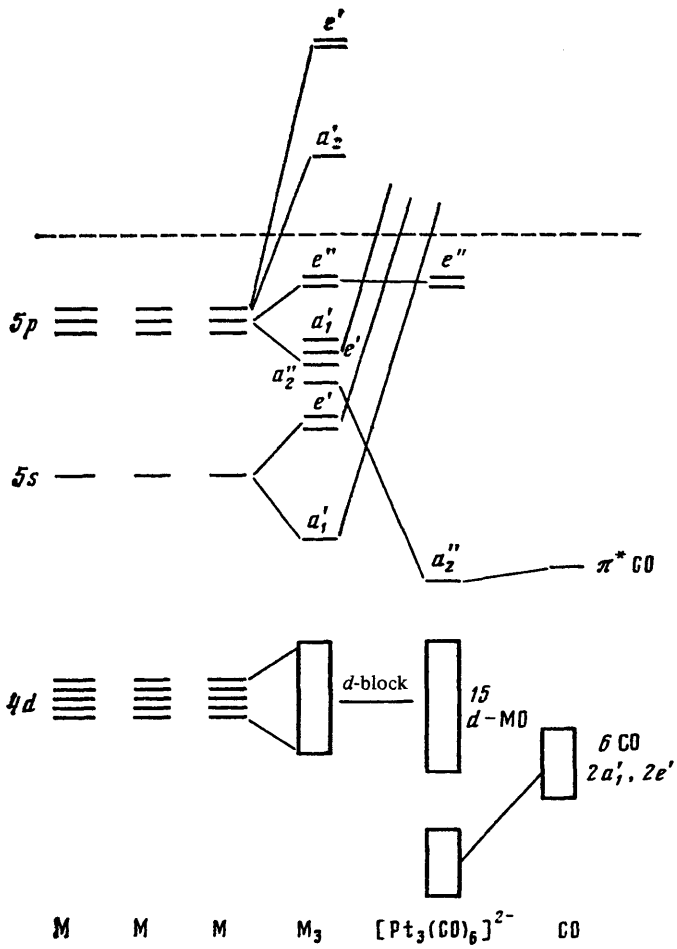


Figure 10 A qualitative scheme for the interaction of the AO of metals in the formation of a ligand-free M_3 triangle;[164] the changes occurring on formation of the anion $[Pt_3(CO)_6]^{2-}$ are shown on the right.

In the cluster compounds with 48 CVE all 24 CVMO are occupied, while in compounds of other types the situation is more complex. When the metallic triangle of the framework interacts with ligands (for example, with CO ligands) the cluster MO made up of the *s* and *p* AO undergo the greatest changes. Although the relative order in which the individual *d* orbitals are arranged changes somewhat on interaction with ligands (Figs.10 and 11), these changes are comparatively small, probably owing to the relatively small integrals, i.e. $[S] \leq 0.1$, for the overlap of the *d* orbitals of the metal with the orbitals of ligands such as the CO group.[165] Calculations have shown that the entire set of 27 MO of triangular clusters can be divided into four main groups, boundaries between which are approximate and vary as a function of the nature of the metals and the ligands. The molecular orbitals with the lowest energies are used mainly for bonding with the ligands because the combination of three *s* and nine *p* orbitals has the symmetry and directional properties suitable for bonding with ligands. The remaining five *d* orbitals form a set of MO having similar energies (the *d* block), through which the direct metal–metal interaction takes place. Next follow the so-called frontier orbitals, both HOMO and LUMO. Finally the antibonding orbitals with the highest energy belong to the fourth group.

This subdivision can be seen clearly in relation to the MO obtained as a result of EHM calculations for the $Ru_3(CO)_{12}$ molecule (Fig.11).[165] Examination of the character of the frontier orbitals of greatest importance for chemistry led to the conclusion that 48-electron metallocycles of the type of $M_3(CO)_{12}$ with D_{3h} symmetry are "inorganic" analogues of cyclopropane;[106] this analogy does not apply solely to the topological correspondence of the structures and the nature of the frontier orbitals; it is more profound and embraces also chemical behaviour: the similarity of $M_3(CO)_{12}$ to cyclopropane in the ring opening and closure reactions has been established in relation to $Os_3(CO)_{12}$.[167]

The $M_3(CO)_{12}$ clusters can be constructed by combining three octahedral $M(CO)_4$ fragments; the frontier orbitals of such fragments are illustrated in Fig.12. Two hybrid frontier orbitals of the a_1 and b_2 types, analogous to the σ and p orbitals of methylene, are located over a low-lying weakly split level mostly corresponding to the t_{2g} level in octahedral complexes. The $Fe(CO)_4$ and CH_2 fragments are isolobal and each has at least one pair of electrons in the two frontier orbitals indicated. The formation of the frontier orbitals of $Fe_3(CO)_{12}$ by combining the orbitals of the three $Fe(CO)_4$ groups, analogous to the formation of the orbitals of cyclopropane from those of the three CH_2 groups, is illustrated in Fig.12.[106] Evidently the orbitals of the t_{2g} level interact weakly with one another, forming the orbitals of the cluster *d* block, while the a_1 and b_2 orbitals give rise to a set of MO of the Walsh type. The difference from cyclopropane consists in the fact that both in the initial $Fe(CO)_4$ fragments and in the $Fe_3(CO)_{12}$ cluster the orbitals of the a_1 type have a higher energy than the b_2 orbitals, while in the cyclopropane the opposite situation obtains. It is believed[106] that this order in the arrangement of the orbitals is confirmed by the results of the investigation of the electronic and photoelectron spectra of $M_3(CO)_{12}$, where M = Ru or Os,[59] indicating the non-degenerate character of the HOMO in these compounds.

An analogous set of frontier orbitals of another 48-electron metallocycle, namely $Co_3(CO)_9(\mu_3\text{-}CH)$, is obtained by combining the orbitals of the $Co_3(CO)_9$ and CH fragments (Fig.4). It can be assumed that in other 48-electron triangular cluster compounds the qualitative scheme for the arrangement of the MO and their occupation by electrons is the same as for the molecules examined above. Information about the

character of the LUMO in such systems has been obtained in studies of the EPR spectra of certain 49-electron compounds presented in Table 5. Unfortunately there are as yet no experimental data which would permit the estimation of the energy gap between the HOMO and LUMO. The entry of a second electron into the LUMO results in the rupture of one metal–metal bond in the triangle.

Thus the scheme for the electronic structure of 48-electron triangular clusters put forward in a number of studies explains satisfactorily the existing experimental data. From this scheme, it follows without a doubt that triangular cluster compounds in which the number of CVE is greater than 48 should have greatly "loosened" metal–metal bonds up to an appreciable weakening of the direct interaction between the metal atoms. The stability of such cluster compounds is determined mainly by the μ_3-ligands which span the metallic triangle. For example, there are 53 CVE in the $Ni_3(\mu_3\text{-}S)_2.(Cp)_3$ cluster; the Ni–Ni bond length in this cluster is 2.80 Å,[159] which is greater by 0.4 Å than in the compound $Ni_3(\mu_3\text{-}CO)_2(Cp_3)$ with an analogous structure,[57] which has 4 CVE less [R(Ni–Ni) = 2.39 Å]; the five excess electrons in the $Ni_3(\mu_3\text{-}S)_3(Cp)_3$ cluster occupy three antibonding orbitals, while the weak Ni...Ni bonding is determined mainly by the exchange interaction involving the single unpaired electron ($\mu_{eff} = 1.7\ \mu_B$).

The data examined in Section II show that three-membered metallocycles with 48 CVE are characteristic of metals with the d^8 configuration or one close to it. However, clusters with fewer CVE are just as common; they can be divided into two groups—three-membered metallocycles made up of the atoms of the metal at the beginning of the transition series and triangles made up of the atoms of platinum group metals. It is striking that sometimes formally the same number of CVE can be attained by a different pathway—by introducing platinum metals or Group VI metals (Cr, Mo, and W). However, the electronic structure of the metallic framework in such cluster compounds is different. In platinum metallocycles the Pt–Pt distances (2.65–2.79 Å) differ little from the metal–metal distance in metallic platinum (2.77 Å), while in triangles made up of Group VI metal atoms the metal–metal distances are significantly shortened.

It might have been supposed that multiple metal–metal bonds are formed in triangles made up of atoms of metals having the d^6 or lower configuration, particularly since the existence of multiple bonds in dinuclear compounds of the same metals is a well established fact. For example, the results of quantum-calculations for model Cr, Mo, Ru, and Rh dimers, in which the metal atoms are linked by four identical planar bridges (O_2CH) located in pairs in mutually perpendicular planes and shielding fairly densely the space between the metal atoms, have been described;[3] the real molecules can each have in addition two two-electron axial ligands L. In the rhodium dimer each metal atom has a filled electron shell (taking into account the two electrons from the axial ligands L). The metal–metal bond orders are unity. In the isostructural ruthenium dimers there are two fewer electrons, while in the chromium and molybdenum dimers there are six fewer electrons. The rigid configuration of the dimers makes it impossible to attach additional ligands and make good from outside this electron deficit. The 18-electron shell in each metal atom in these compounds is therefore produced as a result of the formation of metal–metal multiple bonds; the bond multiplicity is 2 in the ruthenium dimer and 4 in the chromium and molybdenum dimers. In terms of the chosen coordinate system,[3] in the rhodium dimer the HOMO with $2b_{1u}$ symmetry is at the same time the antibonding δ^* orbital in relation to the metal–metal δ-bond; when it is filled with electrons, the δ-bond is ruptured and, conversely, a decrease of the number of electrons in this orbital leads to the appearance of a δ-bond

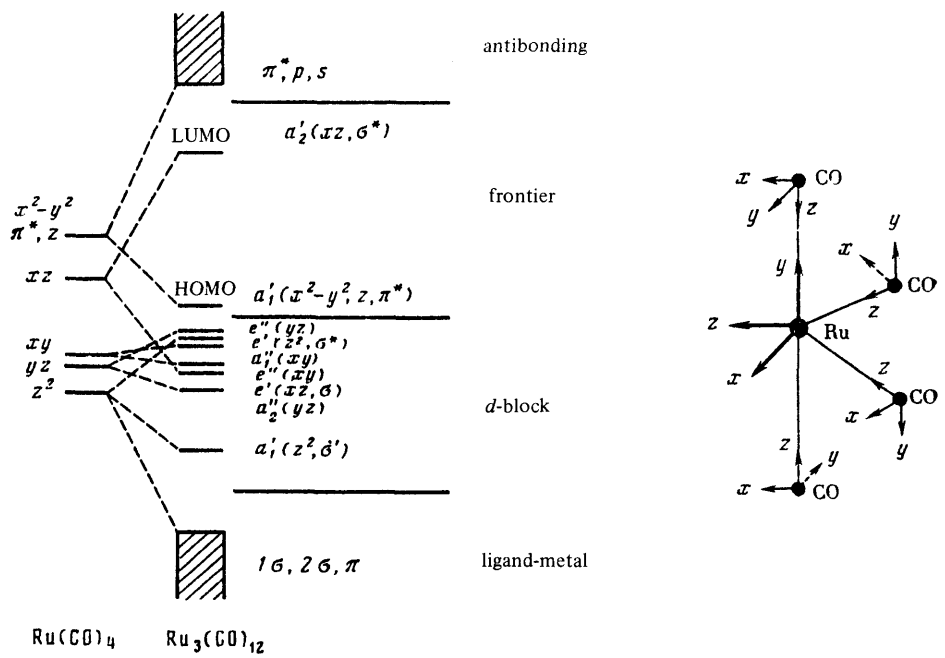


Figure 11. The formation of the molecular orbitals of $Ru_3(CO)_{12}$ from the MO of the $Ru(CO)_4$ fragment; HOMO = xz and LUMO = π^*, z for the $Ru(CO)_4$ fragment; the coordinate system for the $Ru(CO)_4$ fragment is shown on the right.[165]

between the metal atoms on moving along the above series of dimers from right to left; the same considerations are applicable to the π orbital which follows the δ^* orbital (see Cotton and Walton[3], pp.366–382).

One cannot rule out the possibility of a similar approach to the consideration of the electronic structures of three-membered metallocycles. The decrease of the number of intrinsic *d* electrons in the metal atoms and the impossibility of making good this deficit by attaching ligands should result in the occurrence of additional interaction between the AO of the metals with formation of multiple bonds.

Among electron-deficient clusters, quantum-chemical calculations have been made mainly for the Re_3 metallocycle;[59] they agree well with the hypothesis that multiple bonds are present in this and similar compounds. For example, the results of EHM calculations for the $(Re_3Cl_{12})^{3-}$ ion led the authors[166] to the conclusion that the two-centre bonds between the rhenium atoms can be described as double bonds.

Thus there are grounds for the assumption that, for the majority of the compounds listed in Tables 6–8 subject to the condition that the normal geometry of the framework and of the ligand environment is conserved, a decrease of the number of CVE compared with 48 for metals to the left of the iron group in the Periodic System can involve the formation of metal–metal multiple bonds in the metallocycle.

The normal multiplicity of each metal–metal bond (q) in a three-membered metallocycle can be calculated from the formula

$$q = \frac{54 - n}{6}$$

where 54 is the maximum number of electrons when all the 27 MO of the trinuclear cluster are occupied, n the number of CVE in the given three-membered metallocycle, and 6 the number of electrons capable of being accommodated in the three residual vacant CVMO in clusters with a filled shell having 48 CVE and a metal–metal bond multiplicity of unity.

Thus in the presence of 46 CVE the multiplicity of each metal–metal bond is 1 + 1/3, when all the bonds are equalised, or two M–M bonds have a multiplicity of unity and a third a multiplicity of two. This situation obtains, for example, in the 46-electron cluster $Os_3(\mu\text{-}H)_2(CO)_{10}$, where the bond between the two Os atoms spanned by two μ-H bridges has a multiplicity of 2, while the other two bonds have a multiplicity of unity; see also Cotton.[162]

From general considerations, it is understandable that the decrease of the bond lengths with increasing multiplity of the metal–metal bond in trinuclear metallocycles should be relatively smaller than in dimers. The difference between

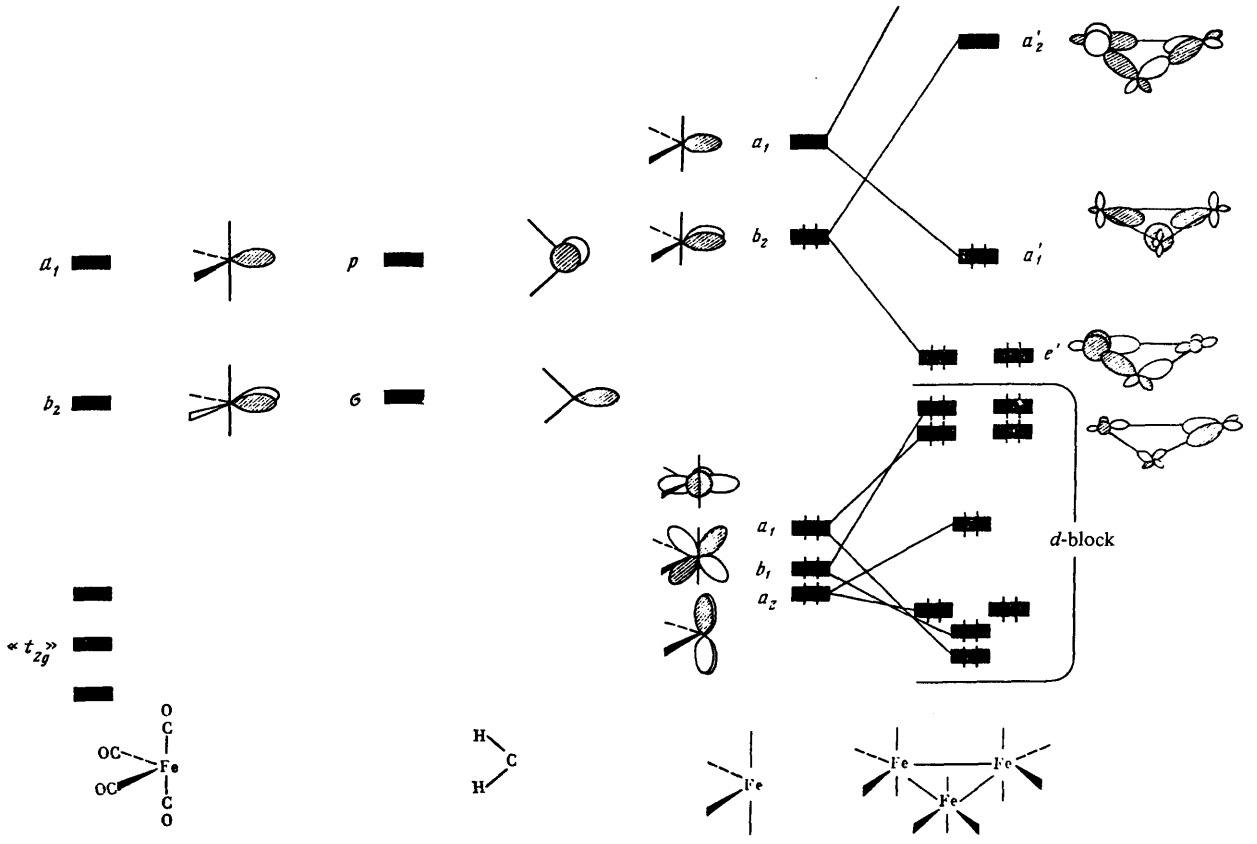


Figure 12. The group orbitals of the $Fe(CO)_4$ and CH_2 fragments; the formation of the MO of the $Fe_3(CO)_{12}$ molecule (idealised geometry with D_{3h} symmetry) from the orbitals of the $Fe(CO)_4$ fragments is shown on the right-hand side.[106]

the lengths of bonds of different multiplicity probably becomes increasingly less appreciable with increasing nuclearity of the clusters.

It follows from the calculated and experimental results presented above that triangular clusters based on platinum and palladium with a deficiency of electrons are as a rule coordination unsaturated and it would appear that they could combine with one or two more ligands in order to build up their electron shell to a stable state, but this does not occur in reality. In other words a triangle of Pt or Pd atoms can combine with a smaller number of ligands than the triangles made up of atoms of the other metals examined above. Furthermore, in heterometallic triangles each Pt or Pd atom reduces the total number of two-electron ligands by unity.

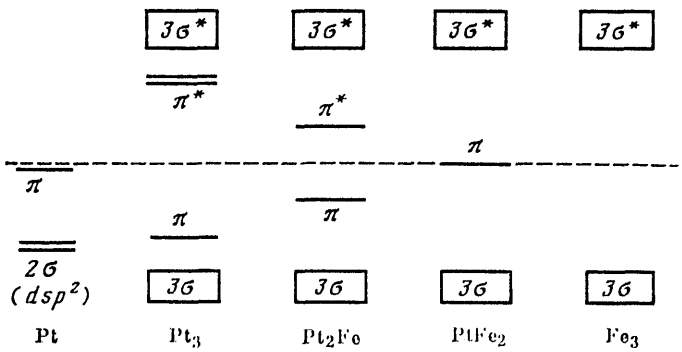


Figure 13. A qualitative scheme for the π-interactions in three-membered metallocycles with participation of platinum.[94]

It has come to be assumed that the energy of one of the *p* orbitals of the Pt or Pd atoms is unduly high and the orbital cannot participate in the formation of a bond with the ligand. Three such orbitals, extended along an axis perpendicular to the plane of the M_3 ring form as a rule in such cases the set of three MO illustrated schematically in Fig.13.[94] It is believed that these orbitals should have energies within the energy gap between the HOMO and LUMO for clusters with a filled electron shell. The changes occurring in the region of the frontier orbitals in the regular transition from Fe_3 to Pt_3 clusters are shown schematically in Fig.13. As a result of this interaction, one of the π MO becomes weakly bonding and two others become weakly antibonding.

This qualitative scheme agrees in the main with the results of an EHM calculation for the planar dianion $[Pt_3(CO)_6]^{2-}$, which are presented in Fig.10. Evidently all the 15 MO of the *d* block are occupied and the two excess electrons are in the a_2'' orbital, which has predominantly the π^*_{CO} character. The unoccupied non-bonding orbitals of the e'' set are in essence the almost unchanged *p* orbitals of the M_3 framework; calculations have shown that, in compounds with 42 CVE, all the orbitals having the *p* character ($a_2'' + e''$) are unoccupied.[164]

Thus an additional interaction of the π type also occurs in triangles based on platinum and its analogues, however, it does not involve the *d* orbitals, as in the previous case, but the MO made up of orbitals of the *p* type. However, in connection with the weakly bonding character of these MO, an appreciable decrease of the metal–metal distances does not as a rule occur.

The ability of platinum triangles to be coordinated to one another with formation of prismatic structures of different lengths, which are characterised by a weak interaction between the rings (the Pt–Pt bond length is greater than 3 Å) has been explained by the presence of orbitals of this type.

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Thus comparison of the structures and numbers of CVE in a wide range of three-membered metallocycles permits the conclusion that the magic number of 48 CVE for triangular clusters means merely that in the presence of a large number of CVE, the triangular structure of the framework with short metal–metal bonds cannot be retained; on the other hand, experience has shown that, when the number of CVE is reduced, the extent by which it differs from the magic number for triangular clusters can vary within fairly broad limits.

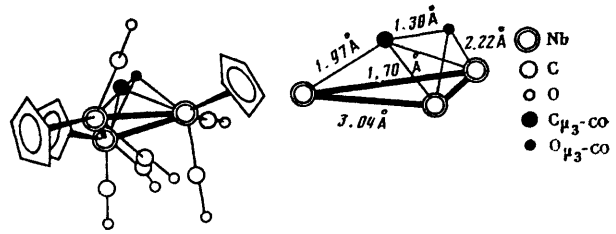


Figure 14. The structure of the $Nb_3(\mu_3\text{-}CO)(CO)_6(Cp)_3$ cluster.[168]

On the other hand, one should note that in the chemistry of cluster compounds there is apparently no rigid specification whatsoever of the numbers of CVE for particular types of metals and ligands. It was noted above that, as one moves to the left along the Periodic System and the number of electrons in the valence shell of the metal atom falls, the number of CVE in the corresponding triangular compound differs to an increasing extent from the magic number. However, the $Cp_3Nb_3(CO)_7$ triangular niobium cluster with 48 CVE has been obtained, its structure being shown in Fig.14.[168] For this compound to have 48 CVE, the seventh CO group must supply six electrons for the formation of bonds with the metal atoms and for this to happen it must be located parallel to the plane of the Nb_3 ring. Fig.14 shows that this condition is fulfilled with adequate precision. The stretching vibration frequency of the seventh CO group is then displaced so much (to 1330 cm^{-1}) that in this case one can apparently envisage two ligands (C and O) weakly interacting with one another on the surface of the metallocycle. Consequently, if the ligand environment, occupying almost the same volume around the M_3 ring, can supply a greater number of electrons, a configuration with a filled electron shell obtains even for an element such as niobium, which has only five *d* electrons.

The same picture has been observed for the cluster compounds of metals having a filled *d* shell. Although triangular Pd and Pt clusters having 48 CVE have not so far been

obtained, one may quote an example from the chemistry of tetrahedral clusters. The magic number for the tetrahedron is 60 CVE; the majority of tetrahedral Pd and Pt compounds have, like the corresponding triangles, a significantly smaller number of CVE, but the $Pd_4(\mu\text{-}CO)_6(PBu_3)_4$ cluster with a tetrahedral structure of the framework has 60 CVE.[169]

In the formation of each given cluster compound there probably exist limited possibilities for the selection of ligands; a tendency is observed towards the construction of the most compact molecule with a preferential filling of the space around the metallic framework. Since the metallic framework itself is fairly stable, for example, in the form of ultradisperse metallic particles,[52] the electronic requirements which must be met by the ligand in the formation of a cluster on its basis are not rigorous, permitting deviations from the magic numbers. The number of examples in which the number of CVE differs from the magic number will apparently increase in the future as experimental data accumulate, particularly for cluster compounds with a high nuclearity.

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