

The chemistry of heterometallic carbidocarbonyl clusters

Sergei P. Gubin

N.S. Kurnakov Institute of General and Inorganic Chemistry,
USSR Academy of Sciences, Moscow 117907 USSR

Abstract - The general preparative route to the synthesis of mixed-metals carbidocarbonyl clusters with two- and three different metal are discussed. New reactions of penta- and hexanuclear clusters are described: in particular the reaction of oxidative polyhedral contraction and expansion, thermal degradation and direct substitution one to another metals. The structure of heterometallic clusters is discussed.

INTRODUCTION

There is at present considerable interest in the chemistry of mixed-metal clusters which contain of all kinds of metals (ref.1,2). Such mixed-metal clusters might prove useful e.g. for the relationships between molecular clusters and alloy surfaces with respect to chemisorption and polymetallic catalysis, for the synthesis of catalyst precursors, for the stereochemistry of compounds with asymmetric metal core, for the preparation of alloys with the precise composition etc.

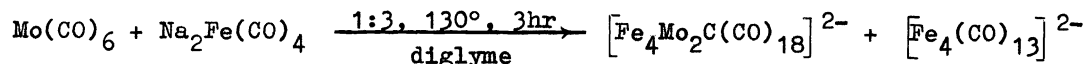
A substantial subgroup of mixed-metal clusters is comprised of the carbide clusters, that have a carbon atom bonded only to cluster framework metal atoms (ref.3). These clusters may be taken as molecular models of the type of bonding that occurs in the bulk carbide, fragments of mixed-metal carbide surrounded by carbonyl ligands and also surface carbides, formed from dissociative chemisorption of CO on relatively electropositive metals like iron. Sometimes the carbidic carbon atom in metal clusters has a significant chemical reactivity especially when they are exposed to reactive molecules in the clusters with open face.

In this paper we shall describe some preparative routes to mixed-metal carbide clusters having two and three different metals, and report some reactions of these species which depend on their multimetal character.

SYNTHETIC PROCEDURES

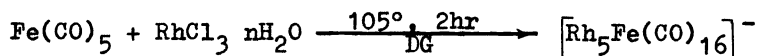
In spite of the evident indications that mixed-metal carbide clusters have a rich and interesting chemistry, there are few known rational synthetic procedures for preparing compounds with two different metal atoms, and virtually none for tri- or tetra-metal clusters. Although most of the known bimetallic compounds in these categories have been obtained by designed synthesis (ref.4), the preparative methods were inconvenient. For example, the treatment of $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$ with $\text{Mo}(\text{CO})_3(\text{THF})_3$ affords two bimetallic clusters where the octahedral product $[\text{Fe}_4\text{Mo}_2\text{C}(\text{CO})_{18}]^{2-}$ 1 prevailed. However, the key starting reagent for such synthesis - the four atom carbide cluster $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$ was prepared in several steps from iron pentacarbonyl (ref.4).

We reported a convenient, one reaction flask synthesis of bimetallic 1 by direct interaction of $[\text{Fe}(\text{CO})_4]^{2-}$ with $\text{Mo}(\text{CO})_6$ (yield 60%) (ref.5).



Diglyme (DG) is the preferred solvent for such reactions which required high temperature for they to occur at convenient rates. More selective

synthesis is direct interaction of $\text{Fe}(\text{CO})_5$ with RhCl_3 , yield 80% (ref.6)

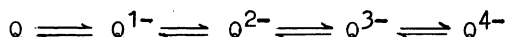


We have shown that the $[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$ 2 and $[\text{Fe}_5\text{C}(\text{CO})_{14}]^{2-}$ 3 species and many their bimetallic analogs are now accessible in bench (multigram) quantities via the direct high-temperature reaction of $\text{Fe}(\text{CO})_5$ in diglyme (ref. 7).

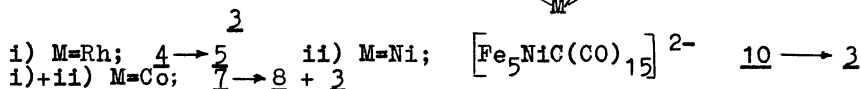
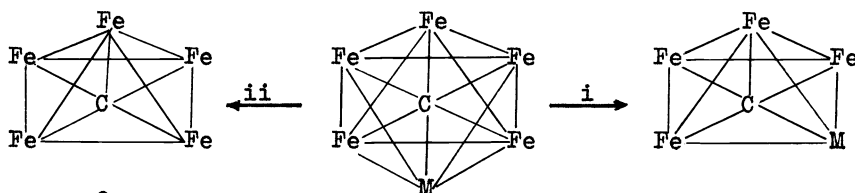
Four main pathway to mixed-metal carbide clusters have been investigated, namely, (1) oxidative polyhedral contraction, (2) thermal degradation, (3) polyhedral expansion reaction, and (4) direct substitution one to another metals.

REDOX REACTIONS OF HETEROMETALLIC CARBIDOCARBONYL CLUSTERS

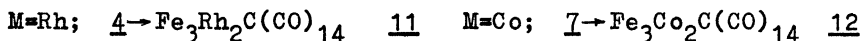
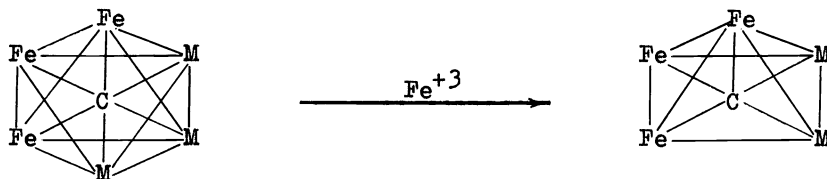
Cluster compounds are expected to have the ability to undergo multielectron transfer processes and thus to act as an "electron reservoir" (ref.9). Indeed, the cyclic voltammetry ($v=4$ V/sec) and polarography of clusters 2 - 9 (Table 1) showed two, three or four one-electron reversible couples according to



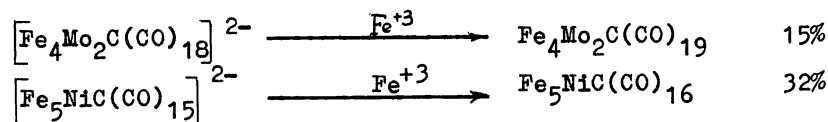
These results show that clusters 2 - 9 (Q) undergo a series of one-electron reductions, each step (on dropping mercury electrode, Table 1) being diffusion controlled and reversible. It seems likely that the LUMO involved in reduction is in most cases a nonbonding orbital. However, it was found that all clusters in Table 1 undergo an irreversible one-(or two-) electron oxidation (at Pt) even at high scan rates ($v=20$ V/sec). The chemical oxidation corresponds to an electrochemical one. Firstly, oxidation of hexanuclear Fe_5M -clusters with ferric ion gives the products of polyhedral contraction (Note a).



The trinuclear Fe_3M_3 -clusters undergo the same degradations with removal of one M-apex



Interestingly, we observed a nontrivial way of oxidation of dianion clusters



The formal results of these reactions is the electron-pair replacement by CO-ligand. Such reactions give also some amounts of side products and must be mechanistically complex.

Note a: Throughout this paper CO-ligands omitted for clarity.

TABLE 1. Redox Potentials^a of mixed-metal carbidocarbonyl clusters

Compound		<u>reduction</u>		<u>oxidation</u>	
		$E_{1/2}^b, V$	n	$E_{1/2}^c, V$	n
$[\text{Fe}_5\text{C}(\text{CO})_{14}]^{2-}$	<u>3</u>	-1.94 ^d	1	-0.22	2
		-2.39 ^d	1		
$[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$	<u>2</u>	-1.74 ^d	1	-0.06	2
		-2.04 ^d	1		
		-2.65 ^d	2		
$[\text{Fe}_5\text{RhC}(\text{CO})_{16}]^-$	<u>4</u>	-1.07 ^d	1	+0.42	1
		-2.36 ^d	1		
		-2.66 ^d	2		
$[\text{Fe}_4\text{RhC}(\text{CO})_{14}]^-$	<u>5</u>	-1.07 ^d	1	+0.42	1
		-1.66 ^d	1		
		-2.15 ^d	1		
$[\text{Fe}_3\text{Rh}_3\text{C}(\text{CO})_{15}]^-$	<u>6</u>	-1.20 ^d	1	+0.65	1
		-2.28	1		
$[\text{Fe}_5\text{CoC}(\text{CO})_{16}]^-$	<u>7</u>	-1.07 ^d	1	+0.42	1
		-1.44 ^d	1		
		-1.82 ^d	1		
		-2.42	1		
$[\text{Fe}_4\text{CoC}(\text{CO})_{14}]^-$	<u>8</u>	-1.07 ^d	1	+0.45	1
		-1.75 ^d	1		
		-2.52 ^d	1		
		-2.70	1		
$[\text{Fe}_3\text{Co}_3\text{C}(\text{CO})_{15}]^-$	<u>9</u>	-0.97 ^d	1	+0.55	1
		-1.55 ^d	1		
		-2.22 ^d	1		
		-2.67 ^d	1		

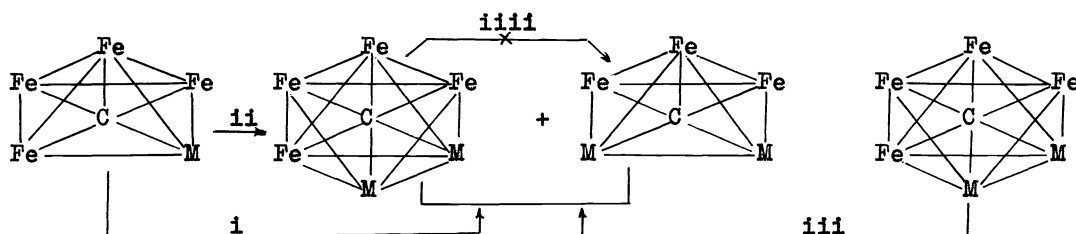
^a CH_3CN , Et_4NBF_4 , $1 \cdot 10^{-3} \text{ M}$

^b The dropping mercury electrode vs. Ag/Ag^+

^c The rotating disc electrode vs Ag/Ag^+

^d reversible wave

The oxidation of pentanuclear clusters yields a mixture of products



I $\text{M}=\text{Rh}$ 5

i) Fe^{+3} or CF_3COOH , CH_2Cl_2 , 25°C , 30 min
 $[\text{Fe}_4\text{Rh}_2\text{C}(\text{CO})_{16}]^{2-}$ 13 + 11 (1:1) yield 80%

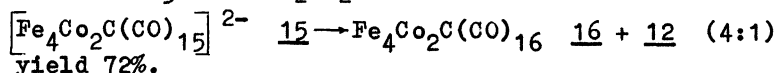
ii) $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, CH_2Cl_2 , 25°C , 2 hr, 13 yield 60%

iii) Fe^{+3} or CF_3COOH , CH_2Cl_2 , 25°C , 30 min
 $[\text{Fe}_4\text{Rh}_2\text{C}(\text{CO})_{15}]^{2-}$ 14 \rightarrow 13 + 11 (2:1)

iiii) Fe^{+3} , no reaction

II $\text{M}=\text{Co}$; 8 i) Fe^{+3} or CF_3COOH , CH_2Cl_2 , 25°C , 30 min only 12 yield 60%

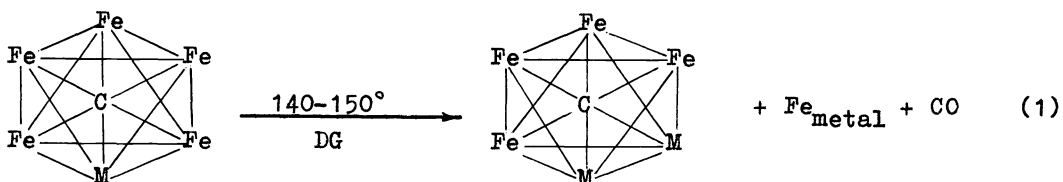
iii) Fe^{+3} or CF_3COOH , CH_2Cl_2 , 25°C , 30 min



These results show once more the influence of the condition in the redox reactivity of mixed-metal carbidocarbonyl clusters. It is clear that the controlled oxidative polyhedral contraction is the difficult and complex process.

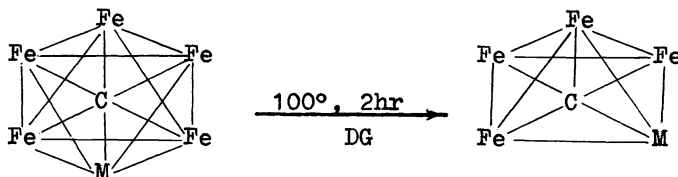
THERMAL DEGRADATION

Pyrolysis reaction of a small clusters has long been known to give a cluster of higher nuclearity (ref.1). We have shown that hexanuclear mixed-metal carbide clusters undergo thermal degradation. The summary reaction can be represented as



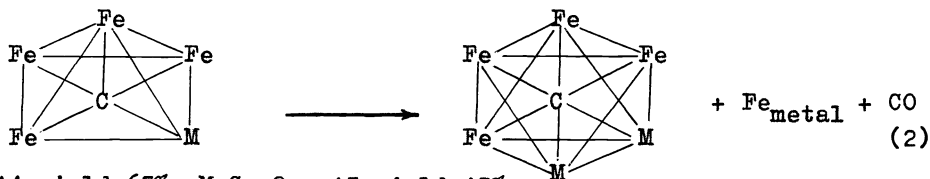
$\text{M}=\text{Rh}$; 4 \rightarrow 14 yield 60% $\text{M}=\text{Co}$; 7 \rightarrow 15 yield 55%

although this is oversimplified. As shown in reaction (eq.1) Fe_4M_2 - product can be envisioned to form via formal displacement of an apex $\text{Fe}(\text{CO})$ -unit in 4 by M^- ($\text{M}=\text{Rh}, \text{Co}$). If we assume that the attack of M^- on a cluster anion occurs at an open face then the abundance of Fe_4M_2 -clusters is explainable only in term of the presence of pentanuclear nido-species in solution. We are directing our attention to the reactivity of Fe_5M -clusters under more mild conditions. When the temperature of the reaction was decreased to 100° hexanuclear clusters were not produced. At these temperature the reaction can be represented as



$\text{M}=\text{Rh}$; 4 \rightarrow 5 yield 80% $\text{M}=\text{Co}$; 7 \rightarrow 8 yield 70% $\text{M}=\text{Fe}$; $140-150^\circ$, 10hr, DG
2 \rightarrow 3 yield 60%

Therefore, five-atom mixed-metal carbide clusters are readily prepared by thermal degradation of hexanuclear compounds. The formation of Fe_4M -clusters can be describe as a thermal ejection of $\text{Fe}(\text{CO})_2$ -unit. The pyrolysis of homometallic 2 occurs in more rigid condition. ² Although thermal degradation of mixed-metal clusters offers large synthetic possibilities it requires a careful screening of the experimental conditions, because the composition of the reaction mixture is dependent on small experimental changes. Thus the behaviour of pentanuclear Fe_4M -clusters are strikingly temperature-dependent: when the reaction is conducted at $145-150^\circ\text{C}$, the product is principally hexanuclear cluster (eq.2)

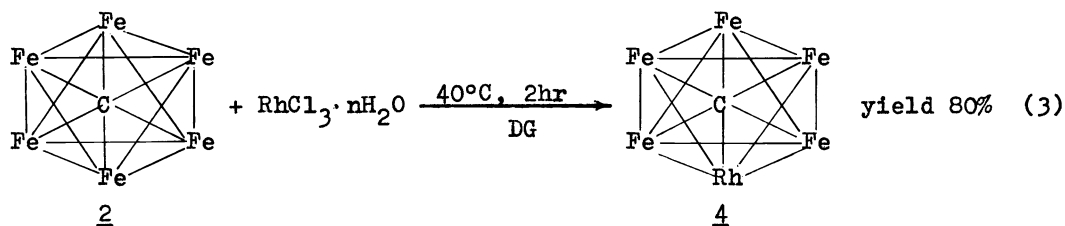


$\text{M}=\text{Rh}$; 5 \rightarrow 14 yield 65%; $\text{M}=\text{Co}$; 8 \rightarrow 15 yield 45%

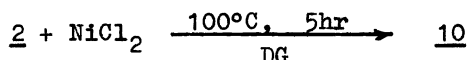
It seems likely that reaction (eq.1) proceed via a pentanuclear species.

DIRECT METAL SUBSTITUTION INTO CARBIDE CLUSTERS

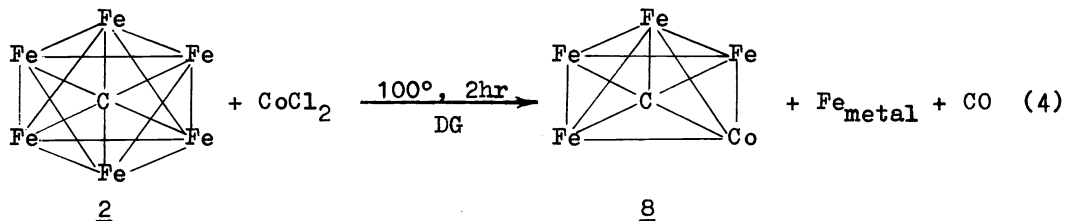
Treatment of 2 in solution with rhodium(III) chloride at elevated temperature affords a heterometallic cluster



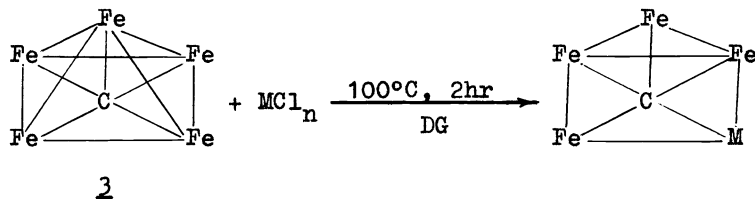
The reaction proceeds under relatively mild conditions and affords excellent yield of mixed-metal cluster (ref.6). It was a first example of direct metal substitution in cluster molecule. Under more vigorous reaction conditions NiCl_2 yields only 36% of monosubstituted compounds



Attempts to carry out reaction such as (eq.3) with CoCl_2 have been without success. Cobalt(II) chloride does not exhibit as high a reactivity as RhCl_3 . The interaction of 2 with CoCl_2 may occur under more rigorous conditions



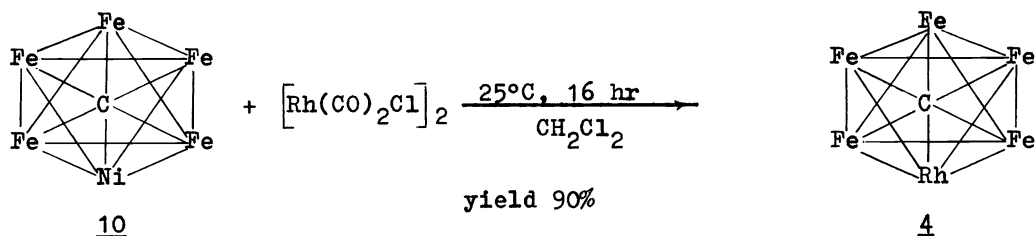
There is an important difference between two reactions as shown in Eqs.(3) and (4). First of all it has been suggested that the initial step of reaction (eq.3) appears to be a substitution of one Fe-apex in 2 by CoCl_2 leading to formation of 7 in which loss of one Fe-apex takes place as result of thermal degradation of framework. However, there is some question whether only such a way would inevitably lead to Fe_4Co -cluster. We consider separately the behaviour of pentanuclear clusters in condition of metal-substitution reaction. Treatment of 3 in solution with metal chlorides affords also a substitution product.



$\text{M}=\text{Co}$; $n=2$; 8 yield 60%; $\text{M}=\text{Rh}$; $n=3$; 5 yield 70%

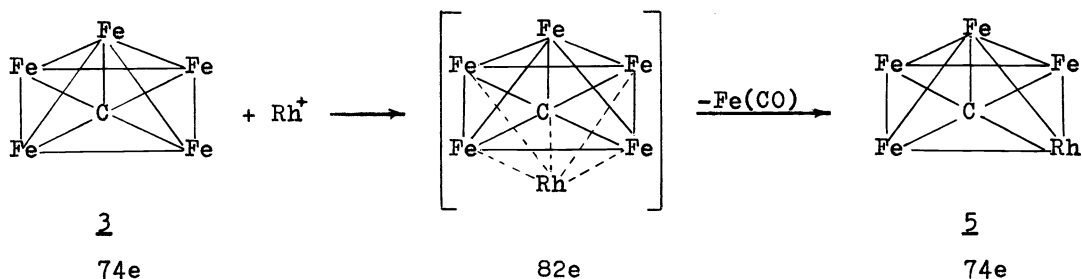
The formation of Fe_4M -clusters can be formally described as a replacement of Fe^0 -apex in 3 by M^+ -unit ($\text{M}=\text{Co}, \text{Rh}$). Consequently, there is another way to Fe_4M -clusters in reaction (eq.4) which cannot be neglected.

We have also shown that hexanuclear mixed-metal cluster 10 undergo metal substitution; the reaction can be represented as



This reaction is very selective and can be formally described as a replacement of Ni^0 -apex in 10 by $\text{Rh}(\text{CO})^+$ -unit. All investigated replacements of one to another metals in both hexa- and pentanuclear clusters are accomplished in accordance with the Wade's rule and isolobal relationship.

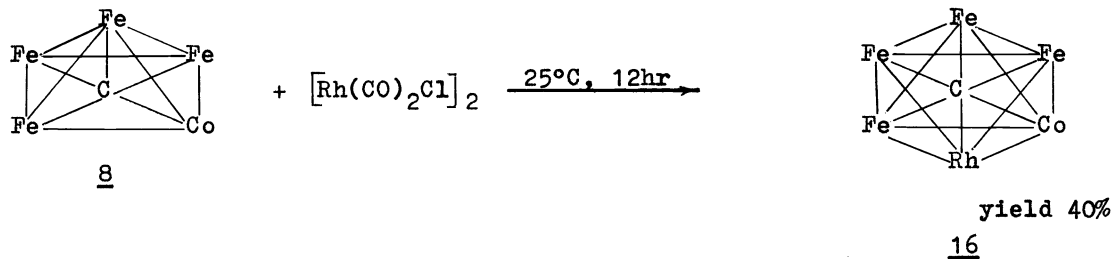
Now we are far from a detailed understanding of the mechanism of metal-substitution. However, a number of facts have been established concerning redox properties, thermal degradation and reactivity of mixed-metal clusters. The initial step in substitution reaction is the rapid electron transfer between cluster anion and metal cation. There seems little doubt that substitution occurs by initial coupling of the cluster anion (nucleophile) with metal cation (electrophile). In case of pentanuclear clusters the resulting intermediate is structurally equivalent to the products of nido-cluster expansion reactions, for example,



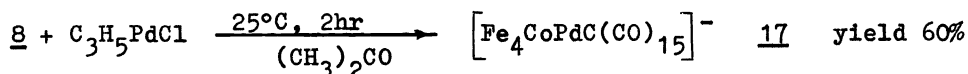
However, this intermediate is electronically unsaturated and converts very quickly in the substituted cluster. This reaction scheme clearly parallels that for aromatic substitution.

CLUSTER WITH THREE DIFFERENT METALS

In continuation of our investigation of heteronuclear clusters, we report here the new synthetic route to octahedral clusters with two or three "hetero" vertices. The Fe_4M -clusters can further add the lacking vertex producing clusters with three different metals in the octahedron. Thus, the reaction of 8 and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ gives the neutral cluster $\text{Fe}_4\text{CoRhC}(\text{CO})_{16}$ 16.



Similarly, 8 with $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ forms the Fe,Co,Pd -cluster (ref.8)



The "hole" in nido Fe_4M -clusters ($\text{M}=\text{Rh}, \text{Co}$) can be filled by a wide variety of atomic units including Rh, Co, Pd, Ni etc. The obtained clusters of this type are $[\text{Fe}_4\text{RhPdC}(\text{CO})_{15}]^-$, $[\text{Fe}_4\text{NiRhC}(\text{CO})_{15}]^-$ and $[\text{Fe}_4\text{NiCoC}(\text{CO})_{15}]^-$.

THE STRUCTURAL STUDIES

All clusters were fully characterized by analysis, i.r. and mass-spectrum. The structures of compounds 2, 4, 5, 6, 8, 9, 10 and 16 have determined by x-ray analysis. The structure of anion 16 is shown in Fig.1. Both Rh and Co atoms in cluster 16 are disordered over the M(1), M(2) and M(3), M(5) pairs of vertices respectively. Thus in 16 heterometal atoms are in cis-position to each other in agreement with the preferable cleavage of a cis-vertex in monosubstituted octahedron confirmed with the structure of 8 and 5.

Due to the disordering of metal atoms, the geometrical parameters of the metal polyhedron in 16 are mainly averaged values. The bond distance Fe-Rh M(1) - M(2) of 2.809 Å is longer than the length of basal edge Rh-Fe of 2.779 Å in the Fe_4Rh -cluster- (ref.4) but slightly shorter than the Rh-Fe distance of 2.823 Å in the disordered octahedral Fe_5Rh -cluster (ref.10). The average distances $C_{in}-(\text{Rh}, \text{Fe})$ 1.959 Å, $C_{in}-(\text{Co}, \text{Fe})$ 1.899 Å and $C_{in}-\text{Fe}$ 1.898 Å can be compared with the distance $C_{in}-(\text{Rh}, \text{Fe})$ 1.94 Å and $C_{in}-\text{Fe}$ 1.98 Å (av.) in Fe_4Rh -cluster 5 and $C_{in}-(\text{Co}, \text{Fe})$ 1.87 Å, $C_{in}-\text{Fe}$ 1.97 Å (av.) in Fe_4Co -cluster 8. The length of M(4) - M(6) edge of 2.690 Å corresponding to the Fe-Fe bond, is equal, within accuracy limits, to the average Fe-Fe distance of 2.695 Å in the heteronuclear octahedral

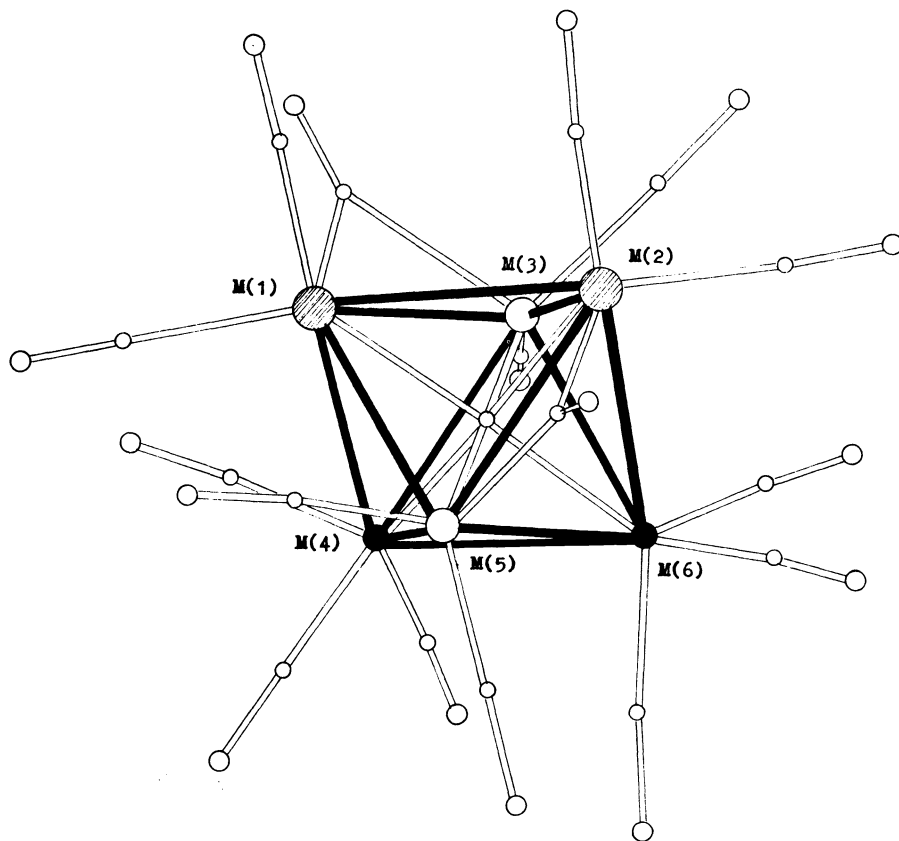


Fig. 1. Structure of $\text{Fe}_4\text{CoRhC}(\text{CO})_{16}^{16-}$; M(1)-2/3Rh+1/3Fe; M(2)-1/3Rh+2/3Fe; M(3), M(4)-Co, Fe; M(4), M(6)-Fe.

Fe_5Rh -cluster 4 and considerably longer than the average Fe-Fe distance of 2.616 Å in Fe_4Rh -cluster 5 and of 2.618 Å in 8. This is probably a result of cluster expansion caused by the interstitial carbon atom (ref.3).

In the molecule 16 there are 14 terminal and two μ_2 -CO ligands. A general configuration of the ligand envelope corresponds to the minimum of interligand repulsion and (in Johnson and Benfield's notation) may be described as 1:6:3:(3):3 (ref.11). The same configuration of ligand polyhedron exists also in Fe_5Rh - 4 (12 terminal and 4 semibridging μ_2 -CO groups) and $[\text{FeRh}_5(\text{CO})_{16}]^-$ -clusters (12 terminal and 4 μ_3 -CO groups) (ref.10). The relative orientation of the cluster core and the ligand shell as well the character of disordering of metal atoms over octahedral vertices inside the ordered ligand polyhedron are, however, different in all three cases. Noteworthy, in the disordered metal cluster considered here, heterometal atoms are statistically distributed over the vertices with an identical ligand environment.

In conclusion it should be stressed that direct metal substitution parallel with vertex cleavage in octahedral carbide clusters and subsequent apex-addition open a possibility of construction of multimetallic heteronuclear polyhedra. The next step along this path represent a very promising class of heterometallic clusters with four (or even more) different metals in polyhedron. Among clusters of this type we are especially looking for the compounds with asymmetric metal core which can exhibit chirality and other related interesting features.

Acknowledgements

Research results of my capable co-workers Dr V.E.Lopatin and post-graduate students M.Ts.Tsybenov and G.V.Burmakina are discussed in this article. The structural studies are collaborative with Drs. Yu.T.Struchkov and Yu.L.Slovokhotov. I would like to acknowledge and express my appreciation to them. I wish to thank also of Drs. V.A.Trukhacheva and L.A.Shelydjakova and Mrs N.M.Mikova and V.A.Ershova for their contributions to this work.

REFERENCES

1. W.L.Gladfelter, G.L.Geoffroy, Adv.Organomet.Chem., 18, 207-273 (1980).
2. H.Vahrenkamp, Adv.Organomet.Chem., 22, 169-208 (1983).
3. J.S.Bradley, Adv.Organomet.Chem., 22, 1-59 (1983)
4. M.Tachikawa, R.L.Geerts, E.L.Muettterties J.Organomet.Chem., 213, 11-24 (1981).
5. V.E.Lopatin, N.M.Mikova, S.P.Gubin, Koord.Khim., 10, 715-716 (1984).
6. S.P.Gubin, N.M.Mikova, M.Ts.Tsybenov, V.E.Lopatin, Koord.Khim., 10, 625-633 (1984).
7. V.E.Lopatin, N.M.Mikova, S.P.Gubin Izv.Akad.Nauk USSR, Ser.Khim., 1925-1926 (1981).
8. V.E.Lopatin, N.M.Mikova, S.P.Gubin, Izv.Akad.Nauk USSR, Ser.Khim., 2170 (1983).
9. P.Lemoine, Coord.Chem.Rev., 47, 55-88 (1982).
10. Yu.L.Slovokhotov, Yu.T.Struchkov, V.E.Lopatin, S.P.Gubin, J.Organomet.Chem., 266, 139-146 (1984).
11. R.E.Benfield, B.F.G.Johnson, Trans.Met.Chem., 6, 131-144 (1981).