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Reviews

Reactions of ruthenium and osmium cluster carbonyls with heteroatom-substituted and functionalized alkynes

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The results of studies of the reactions of ruthenium and osmium cluster carbonyls with metal alkynes, silylalkynes, propargyl alcohols and their derivatives, diynes, enynes, and ferrocenylacetylene are summarized. Intramolecular rearrangements in the cluster complexes including migrations of carbonyl, hydride, and hydrocarbon ligands as well as the metal core reorganization are considered.

Key words: ruthenium carbonyl clusters; osmium carbonyl clusters; alkyne derivatives; intramolecular rearrangements.

The ability of transition-metal cluster complexes to bind ligands to several metal atoms is a distinctive feature of these compounds. Such ligand modification results in their activation under mild conditions. The chemistry of ruthenium and osmium clusters seems to be the most rich compared to the chemistry of other metal carbonyl clusters. Particular diversity is observed for the products of reactions of $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and their derivatives with alkynes.[1,2]

In this review, the results obtained by the author and his co-workers in studies of transformations of ~~heteroatom-substituted and functionalized alkynes on ruthenium~~ and osmium clusters are generalized. Investigations of transformations of these alkynes made it possible to obtain new types of complexes that cannot be isolated using conventional alkynes and to observe new reactions of carbon—carbon, carbon—hydrogen, and carbon—heteroatom bond formation and cleavage under extremely mild conditions. Here, only a brief mention is made of our previous studies on cluster chemistry,[3,4] whereas the results obtained recently are reported in detail.

Stereochemical nonrigidity of cluster complexes due to migration of carbonyl, hydride, and hydrocarbon ligands and the metal core as well[5,6] is yet another remarkable feature of these compounds. It was the establishment of the mechanism of intramolecular rearrangement of highly symmetric $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ clusters that was the subject of our first study on metal clusters.[7,8] At that time, the problem of establishing the exchange mode of CO groups in these complexes seemed ~~to be unsolved.[9,10] To solve it, we used two approaches.~~ The first of them was based on ^{13}C NMR spectroscopic study of the $^{187}Os_3(CO)_{12}$ cluster enriched with the magnetic isotope of osmium, whereas the second approach was based on studying the heteronuclear $Ru_2Os(CO)_{12}$ and $RuOs_2(CO)_{12}$ clusters. Both approaches made it possible to obtain unambiguous proofs of internuclear exchange of CO groups in $M_3(CO)_{12}$ (M = Ru, Os) clusters.[7,8] Further, as will be shown

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below, the stereochemical nonrigidity of cluster systems has been the focus of our interest and we succeeded in finding various novel rearrangements for organometallic ruthenium and osmium complexes.

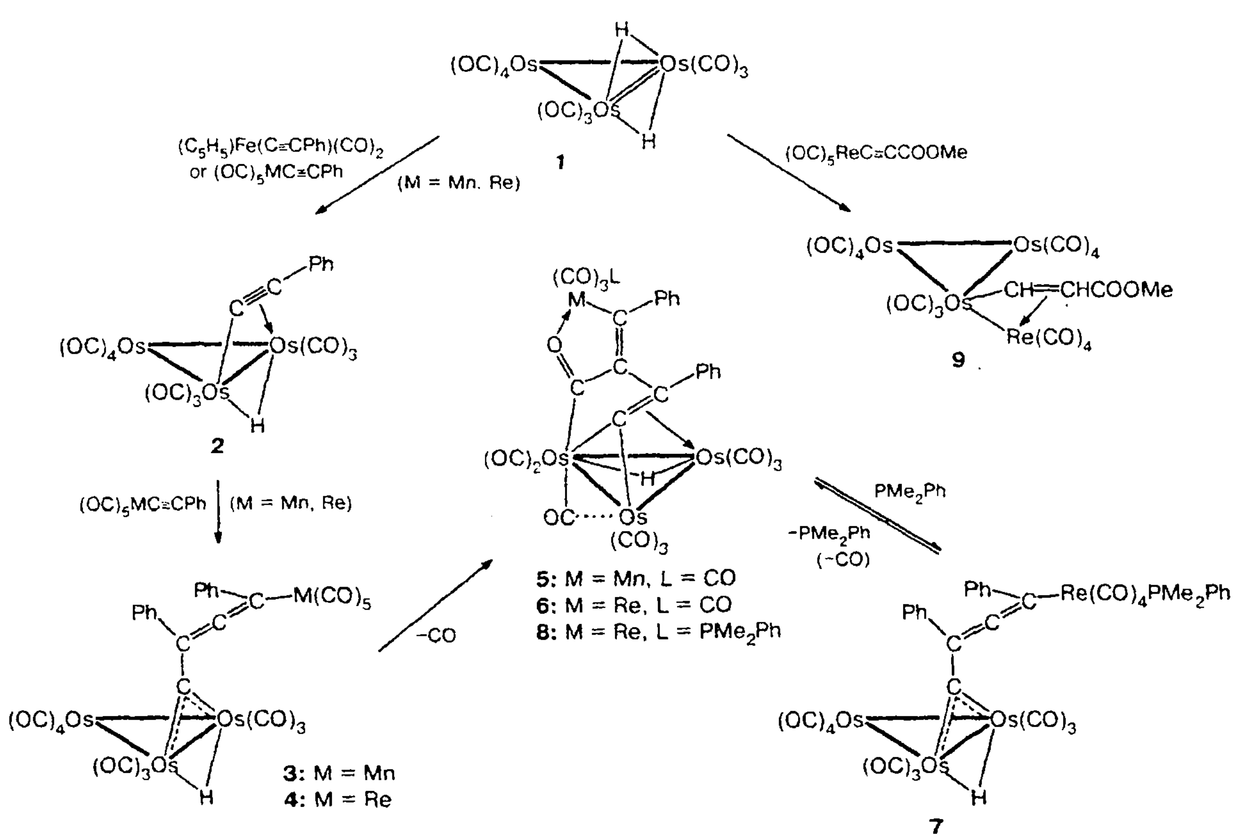
Reactions of osmium clusters with metal alkynes

Scheme 1 summarizes the results of the studies of the reactions of the dihydride cluster $Os_3H_2(CO)_{10}$ (**1**) with σ-acetylene derivatives of manganese, rhenium, and iron.[11–14] The reactions of cluster **1** with $(OC)_5MC{\equiv}CPh$ (where M = Mn, Re) and $(\eta^5\text{-}C_5H_5)Fe(C{\equiv}CPh)(CO)_2$ are accompanied by the cleavage of the bond between the metal atom and the acetylene carbon atom and by transfer of the $PhC{\equiv}C$ group to the triosmium cluster with the formation of the complex $Os_3H(\mu\text{-}C{\equiv}CPh)(CO)_{10}$ (**2**). In the reactions with manganese and rhenium derivatives the second alkyne molecule $(OC)_5MC{\equiv}CPh$ (M = Mn, Re) can be added to the acetylide ligand of complex **2** that formed, thus resulting in labile $Os_3H\{\mu\text{-}C(Ph){=}C{=}C(Ph){-}M(CO)_5\}(CO)_{10}$ (M = Mn (**3**), Re (**4**)) clusters with a bridging allenyl-substituted carbyne ligand.[13] These carbyne clusters readily lose a CO group at the Mn or Re atom to give clusters **5** and **6** containing a μ_3-vinylidene ligand each, respectively.[11–13] The formation of clusters **5** and **6** is accompanied by coupling of one of the CO groups at the Os atom with the hydrocarbon ligand, so the terminal carbonyl group becomes the σ-acyl group. It is noteworthy that all these reactions proceed at room temperature and at lower temperatures as well.

In the reaction of PMe_2Ph with cluster **6** the phosphine ligand is added to the Re atom. This is accompanied by the cleavage of the O—Re and C—C bonds, thus resulting in complex **7**, a phosphine derivative of cluster **4**. Complex **7** appeared to be more thermally stable than cluster **4** and was characterized by single-crystal X-ray diffraction analysis.[12] Heating of cluster **7** in warm hexane results in losing the PMe_2Ph ligand or a CO group at the Re atom to give the initial complex **6** or its phosphine derivative **8** (see Scheme 1).

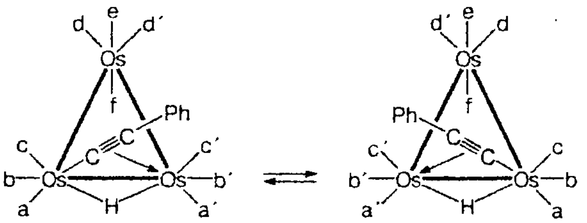
The ease of C—C bond formation and cleavage in the reactions of noncharged substrates occurring in the course of the transformations considered above is assumed to be due to the fact that these reactions proceed by a polar mechanism,[3] which is favored by the carbocationic character of the carbon atom of the acetylide ligand in cluster **2**.[15]

Scheme 1



It was found that the nature of the substituent in the metal alkyne has a strong effect on the structure of the products of its reaction with cluster **1**. For instance, unlike $(OC)_5ReC{\equiv}CPh$, the alkyne $(OC)_5ReC{\equiv}CCOOMe$ reacts with complex **1** to give the tetranuclear cluster $Os_3Re(\mu\text{-}CH{=}CHCOOMe)(CO)_{15}$ (**9**) with a bridging alkenyl ligand.[14]

^{1}H and ^{13}C NMR studies of the $Os_3H(\mu\text{-}C{\equiv}C{-}Ph)(CO)_{10}$ cluster in the hydride region (the $J_{^{187}Os-^{1}H}$ satellite spectrum) and in the carbonyl region, respectively, have led to the discovery of acetylide ligand fluctuation.[16,17] This rearrangement includes fast exchange of σ- and π-bonds of the ligand with two bridging metal atoms and is accompanied by pairwise averaging of the signals of a,a′-; b,b′-; c,c′-; and d,d′-CO groups in the ^{13}C NMR spectrum, whereas two axial CO groups (e and f) appear as single resonances.



We have also developed another procedure for the synthesis of cluster **2** and related complexes, which includes the replacement of the bridging chlorine atom in $Os_3H(Cl)(CO)_9(L)$ (L = CO, PR_3) clusters by bridging acetylide group in reactions with lithium acetylides.[17] We have also discovered that $Os_3H(Cl)(CO)_9(L)$ complexes can be synthesized in the reactions of corresponding dihydrides $Os_3H_2(CO)_9(L)$ with chloromethanes under solar light.[18]

The reaction of $Os_3H(Cl)(CO)_9(PMe_2Ph)$ with $LiC{\equiv}CPh$ results in two isomeric complexes $Os_3H(\mu\text{-}C{\equiv}CPh)(CO)_9(PMe_2Ph)$ (**10** and **11**, Scheme 2). The structure of complex **10** was established by single-crystal X-ray diffraction analysis.[17] Initially, isomer **11** was assumed to have a structure with the PMe_2Ph ligand at the osmium atom that is π-bonded to the $PhC{\equiv}C$ group. However, recently reported data of X-ray study of isomeric $Os_3H(\mu\text{-}CH{=}CH_2)(CO)_9(PPh_3)$ vinyl complexes[19] suggest that the structure shown in Scheme 2 is more plausible for compound **11**. On heating of cluster **11** in toluene the σ-bond of the $PhC{\equiv}C$ group migrates to the osmium atom of the $Os(PMe_2Ph)(CO)_3$ fragment and internuclear exchange of one of the CO groups occurs to give isomer **10**.

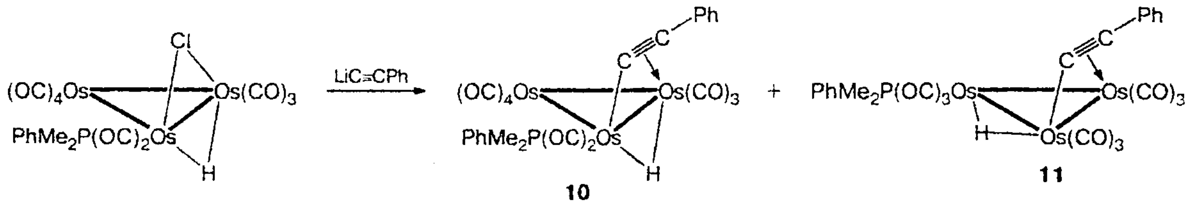
Reactions of ruthenium and osmium clusters with silylalkynes

The $Ru_3H(\mu\text{-}O{=}CNMe_2)(CO)_{10}$ cluster reacts with excess $Me_3SiC{\equiv}CH$ in hexane at 22 °C to give a colorless complex $Ru\{\eta^5\text{-}C_5H_2(SiMe_3)_2OH\}(\eta^1\text{-}COMe)(CO)_2$ (**12**). In this complex the hydroxyl group forms an intramolecular hydrogen bond with the oxygen atom of the σ-acyl ligand.[20] It is assumed that the acyl ligand is generated from the initial alkyne molecule which undergoes acetylene-vinylidene rearrangement *via* the 1,2-shift of the Me_3Si group followed by desilylation and hydration within the coordination sphere of the Ru atom.[21,22] The low-yield formation of complex **12** is also observed in the reaction of $Ru_3(CO)_{12}$ with $Me_3SiC{\equiv}CH$. This reaction results in the yellow-orange $Ru_3H(\mu_3\text{-}C{\equiv}CSiMe_3)(CO)_9$ trinuclear acetylide cluster (**13**) as the major product.[21,22]

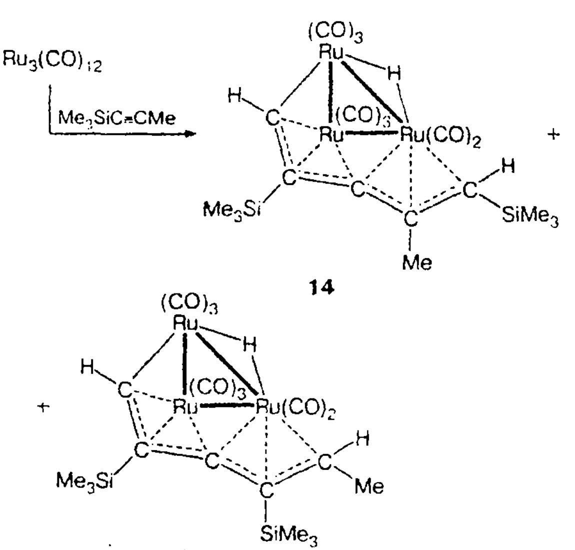
The reaction of $Ru_3(CO)_{12}$ with $Me_3SiC{\equiv}CMe$ in hot hexane results in unusual products, the $Ru_3H\{\mu_3\text{-}CHC(SiMe_3)CC(Me)C(H)SiMe_3\}(CO)_8$ (**14**) and $Ru_3H\{\mu_3\text{-}CHC(SiMe_3)CC(SiMe_3)C(H)Me\}(CO)_8$ (**15**) hydride complexes (Scheme 3), that were obtained in equal yields.[21,22] The structure of the former was established by single-crystal X-ray diffraction analysis (Fig. 1). In this complex five carbon atoms of the organic ligand are bonded to the Ru_3 core. The bonding of the C(9)—C(10) fragment with the Ru(1) and Ru(2) atoms can be considered as σ,π-alkenyl bonds, whereas the C(11)C(12)C(13) fragment is the allylidene group π-bonded to the Ru(3) atom and σ-bonded to the Ru(2) atom. Obviously, the formation of an organic ligand from two alkyne molecules involves the 1,2-shift of the Me_3Si group and double dehydrogenation of the Me group in one of the alkyne molecules (with migration of H atoms to the Ru_3 core and to the second alkyne molecule).

The mechanism of linear dimerization of silylalkynes was investigated by studying their transformations on the Os_3 cluster.[23–26] To this end, the alkyne cluster $Os_3(\mu_3\text{-}Me_3SiC_2Me)(\mu\text{-}CO)(CO)_9$ (**16**) was obtained in the re-

Scheme 2



Scheme 3



action of $Os_3(CO)_{10}(NCMe)_2$ with $Me_3SiC{\equiv}CMe$ at 22 °C. It was established that the alkyne ligand in cluster **16** does not undergo the acetylene-vinylidene rearrangement by 1,2-shift of the Me_3Si group.[23] Thus, heating of complex **16** in refluxing heptane results only in the methyl group dehydrogenation to give the cluster $Os_3H\{\mu_3\text{-}C(SiMe_3){=}C{=}CH_2\}(CO)_9$ (**17**) with the allenyl ligand.

The alkyne cluster **16** reacts with $Me_3SiC{\equiv}CMe$ in hexane at 60 °C to give the intermediate red complex $Os_3\{\mu_3\text{-}C(SiMe_3){=}C(Me)C{=}C(SiMe_3)Me\}(CO)_9$ (**18**), which undergoes fast decarbonylation under conditions of the reaction to give the yellow hydride $Os_3H\{\mu_3\text{-}C(SiMe_3)C(Me)CC(SiMe_3)CH_2\}(CO)_8$ (**19**), which was characterized by single-crystal X-ray diffraction analysis.[23,24] Unfortunately, we failed to grow crystals of the red complex **18** suitable for X-ray study.

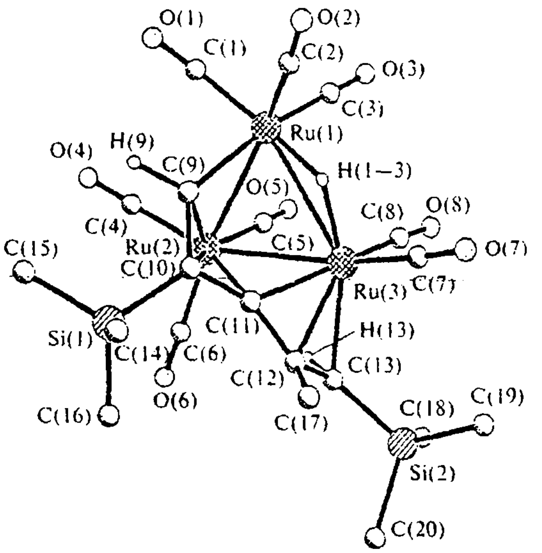
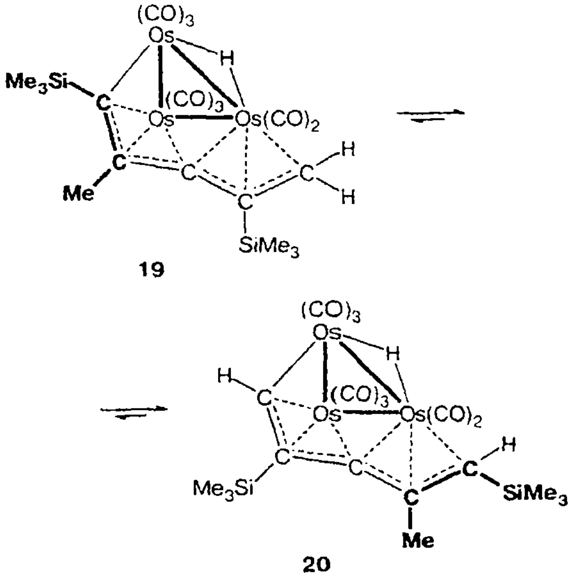
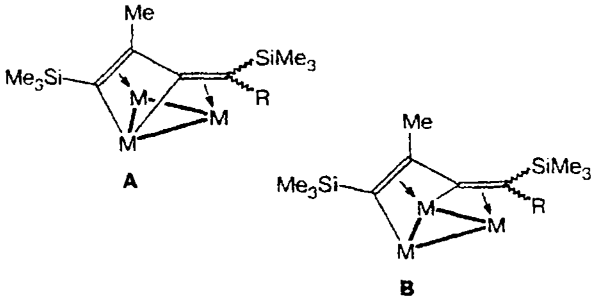


Fig. 1. Molecular structure of cluster $Ru_3H\{\mu_3\text{-}CHC(SiMe_3)\text{—}CC(Me)C(H)SiMe_3\}(CO)_8$ (**14**).

Being performed under more severe conditions or on heating of complex **19** in refluxing heptane, the above-mentioned reaction results in the formation of the hydride $Os_3H\{\mu_3\text{-}C(SiMe_3)C(Me)CC(Me)C(H)SiMe_3\}(CO)_8$ (**20**),[23,24] the osmium analog of ruthenium complex **14**. This new rearrangement **19** → **20** involves the exchange of the bonding modes of the σ,π-alkenyl and π-allyl fragments of the hydrocarbon ligand and can formally be considered a 1,5-hydrogen shift. Obviously, the rearrangement must include interchange of H atoms between the ligand and the Os_3 core and the internuclear exchange of one of the CO groups.



Two modes of bonding the organic ligand to the metal triangle are possible for the red complex **18** (see structures **A** and **B**). The structure of type **A** containing the metallacyclobutene moiety was not described earlier in cluster chemistry, whereas the structure of type **B** was found for the triruthenium complex $Ru_3H\{\mu_3\text{-}CH{=}C(Pr^i)C{=}CH_2\}(\mu\text{-}PPh_2)(CO)_7$ containing the diene-diyl ligand, terminal CO groups, and the hydride and phosphide bridging ligands.[27]



Since only terminal CO groups are present in complex **18** (IR spectral data), the possibility for each metal atom to have the 18$\bar{e}$-shell can only be provided by structure **A**. However, such a uniform electron distribution is not always observed in cluster complexes. Therefore we have continued with our attempts to isolate compounds related to the red complex **18** in order to unambiguously establish their structure by single-crystal X-ray diffraction analysis.

To this end, reactions of $Me_3SiC{\equiv}CMe$ with the alkyne clusters $Os_3(\mu\text{-}PhC_2Ph)(CO)_{10}$ and $Os_3(\mu_3\text{-}FcC_2CH{=}CHFc)(\mu\text{-}CO)(CO)_9$ (Fc is ferrocenyl) were carried out.[4] However, we failed to isolate the red intermediates of these reactions, related to complex **18**, since they undergo fast decarbonylation to give the corresponding yellow hydride complexes, namely, the $Os_3H\{\mu_3\text{-}C(Ph)C(Ph)CC(SiMe_3)CH_2\}(CO)_8$ complex and a mixture of two isomers: $Os_3H\{\mu_3\text{-}C(Fc){-}C(CH{=}CHFc)CC(SiMe_3)CH_2\}(CO)_8$ and $Os_3H\{\mu_3\text{-}C(CH{=}CHFc)C(Fc)CC(SiMe_3)CH_2\}(CO)_8$. The structure of the hydrocarbon ligand in the compounds obtained indicates that it is the second alkyne molecule reacting with the alkyne complex that undergoes the acetylene-vinylidene rearrangement.

Eventually, the reaction of cluster **16** with $Me_3SiC{\equiv}CBu^n$ (Scheme 4) resulted in a corresponding red complex, which was isolated and characterized by single-crystal X-ray diffraction analysis[25,26] (Fig. 2). In cluster $Os_3\{\mu_3\text{-}C(SiMe_3){=}C(Me)C{=}C(SiMe_3)Bu^n\}(CO)_9$ (**21**), each metal atom of the Os_3 triangle coordinates three terminal CO groups. The organic ligand is coordinated to three osmium atoms: the C(10)=C(11) and C(12)=C(13) double bonds of dienediyl are π-coordinated to the Os(2) and Os(3) atoms, respectively, whereas the Os(1) atom forms two σ-bonds with the C(10) and C(12) atoms to give the osmacyclobutene moiety. The four-membered heterocycle is nonplanar, and the angle of folding along the C(10)...C(12) line is equal to 17°. Thus, cluster **21** contains the osmacyclobutene moiety and has the structure of type **A**.

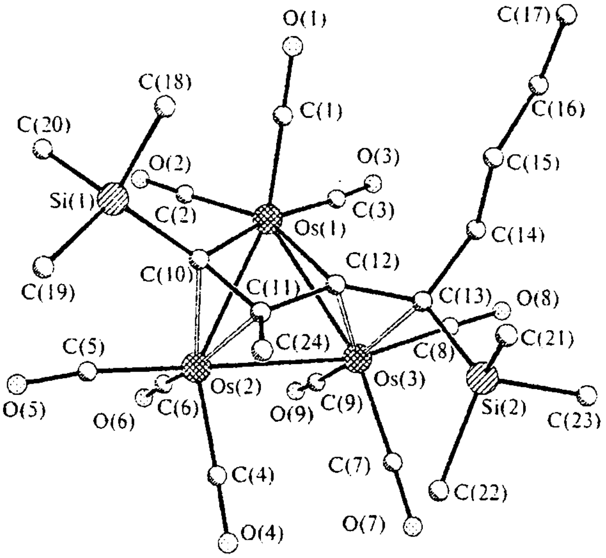
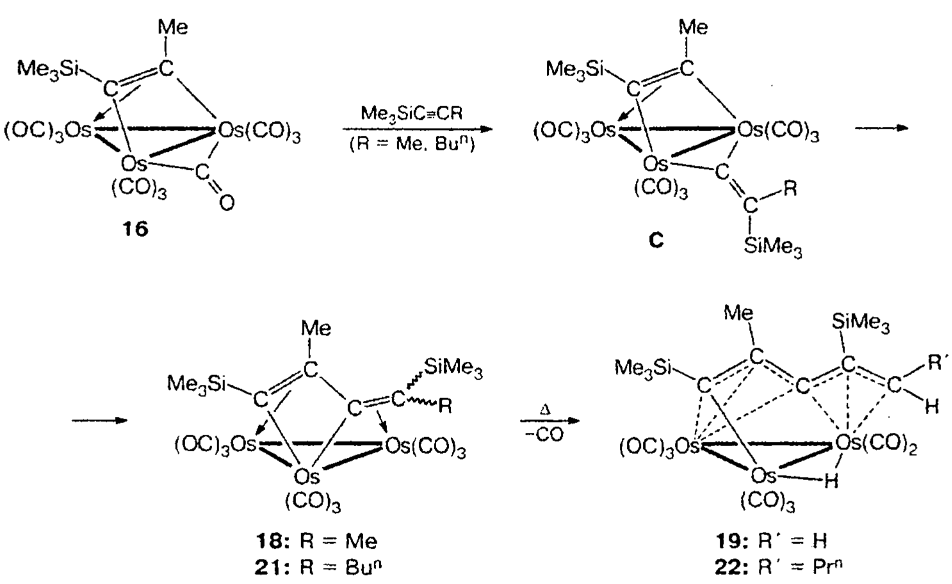


Fig. 2. Molecular structure of cluster $Os_3\{\mu_3\text{-}C(SiMe_3){=}C(Me){-}C{=}C(SiMe_3)Bu^n\}(CO)_9$ (**21**).

Scheme 4



Data of IR, ^{1}H NMR, and ^{13}C NMR spectroscopy indicate that the red clusters **18** and **21** are structural analogs. Similarly to the former, the latter undergoes decarbonylation on heating to give the yellow hydride complex $Os_3H\{\mu_3\text{-}C(SiMe_3)C(Me)CC(SiMe_3)C(H)\text{—}Pr^n\}(CO)_8$ (**22**) (see Scheme 4).

Investigations of temperature dependences of the ^{1}H and ^{13}C NMR spectra of clusters **18** and **21** showed that these molecules are stereochemically nonrigid due to the exchange of both the hydrocarbon and carbonyl ligands.[26]

Thus, we succeeded in establishing the fact that complexes containing a metallacyclobutene moiety are key intermediates of linear dimerization of silylalkynes and their co-dimerization with other alkynes on the Ru_3 and Os_3 clusters. The organic ligand in these complexes is formed *via* the alkyne—vinylidene coupling (see intermediate **C** in Scheme 4), the $:C{=}C(SiMe_3)R$ vinylidene being generated from the second (incoming) alkyne molecule to be coupled with the μ_3-coordinated alkyne due to 1,2-shift of the Me_3Si group.

As is known, not only silylalkynes but also terminal alkynes can undergo acetylene-vinylidene rearrangement within the coordination sphere of the metal atom.[28] Moreover, it is terminal alkynes that are the subject of most of the reported studies of the above-mentioned rearrangements. It could be expected that terminal alkynes will undergo acetylene-vinylidene rearrangement *via* a 1,2-hydrogen shift in reactions with the alkyne cluster **16** to give corresponding clusters containing the osmacyclobutene moiety and related to the red complexes **18** and **21**.

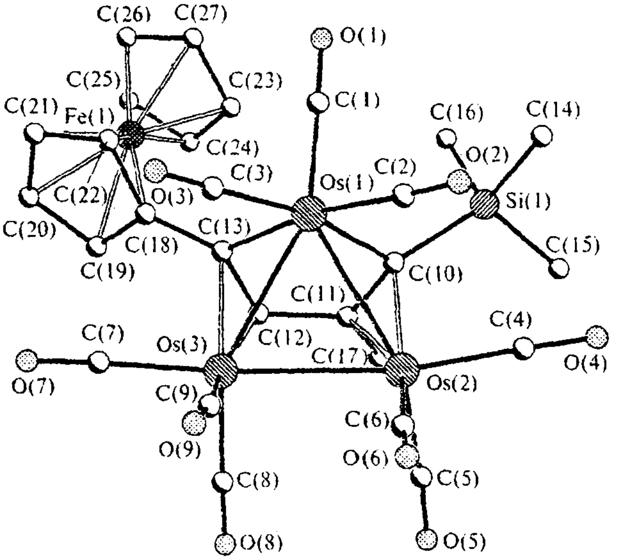
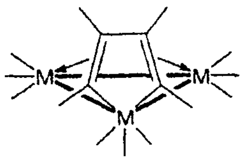
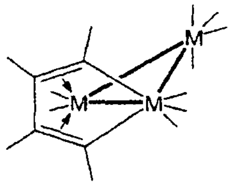


Fig. 3. Molecular structure of cluster $Os_3\{\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}C(SiMe_3)C(Me)CHC(Fc)\}(CO)_9$ (**24**).

However, the reactions of cluster **16** with terminal alkynes in hot hexane result in the products of alkyne—alkyne coupling, *i.e.*, in complexes containing the metallacyclopentadiene moiety. Unusual is the structure of the major products of these reactions, in which the dienediyl ligands have "face-on" coordination (structure **D**), which was previously unknown for carbonyl clusters. The reactions of **16** with phenylacetylene[29,30] and ferrocenylacetylene[31] resulted in the $Os_3\{\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}C(SiMe_3)C(Me)CHC(Ph)\}(CO)_9$ (**23**) and $Os_3\{\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}C(SiMe_3)C(Me)CHC(Fc)\}(CO)_9$ (**24**) clusters, respectively (Fig. 3). The isomeric clusters $Os_3\{\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{-}C(SiMe_3)C(Me)C(Ph)CH\}(CO)_9$ (**25**) and $Os_3\{\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{-}C(SiMe_3)C(Me)C(Fc)CH\}(CO)_9$ (**26**) of the known structure **E** with "side-on" coordination of the organic ligand are formed in low yields (Scheme 5).



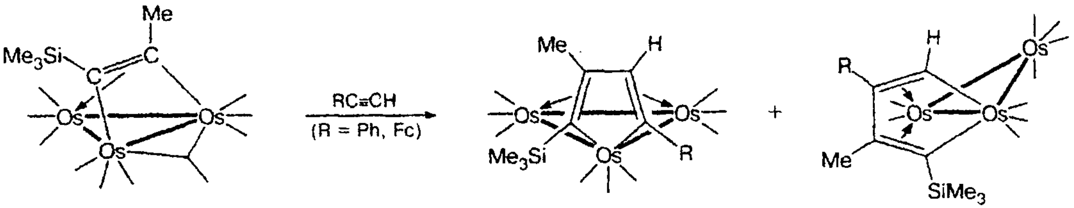
D



E

The unit cell of cluster **24** contains two independent molecules with virtually the same parameters. The structure of one of the molecules is shown in Fig. 3. In molecule **24**, as well as in the previously studied com-

Scheme 5



16

23: R = Ph
24: R = Fc

25: R = Ph
26: R = Fc

plex **23**, the osmacyclopentadiene ring has an envelope conformation: the angle of folding along the C(10)...C(13) line is 27.5° and 26.0° for two independent molecules of **24** (this angle is 28.8° for **23**).

A remarkable feature of the structure of cluster **24** and all clusters of structure **D** we have studied is asymmetry of π-bonds formed by the Os(2) and Os(3) atoms with olefin fragments of the metallacyclopentadiene moiety. For instance, as the Os(3) atom is equidistant from the C atoms of the olefin bond (the Os(3)—C(12) distances are 2.26(1) and 2.27(1) Å while the Os(3)—C(13) distances are 2.25(1) and 2.25(1) Å for two independent molecules), the Os(2) atom forms essentially nonequivalent bonds with C atoms of the second olefin fragment (the Os(2)—C(10) distances are 2.17(1) and 2.17(1) Å while the Os(2)—C(11) distances are 2.43(1) and 2.48(1) Å for two independent molecules).

Unlike the well-known trimetallic clusters of structure **E**, which are typical products of reactions of iron subgroup metal carbonyl clusters with acetylenes,[32–35] clusters of structure **D** were not characterized earlier, though the possibility of their formation has been repeatedly discussed.[33,36,37]

Heating of clusters **23** and **24** in benzene results in their decarbonylation and the formation of corresponding hydride complexes $Os_3H\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^4{:}\eta^1\text{-}C(SiMe_3)C(Me)CHC(R')\}(CO)_8$ ($R' = C_6H_4$ (**27**), $C_5H_3FeC_5H_5$ (**28**)) containing *ortho*-metallated phenyl[29] and ferrocenyl[31] substituents. Hydride **27** reacts with PPh_3 to give the cluster $Os_3\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^4\text{-}C(SiMe_3)C(Me)CHC(Ph)\}(CO)_8(PPh_3)$ (**29**).[29]

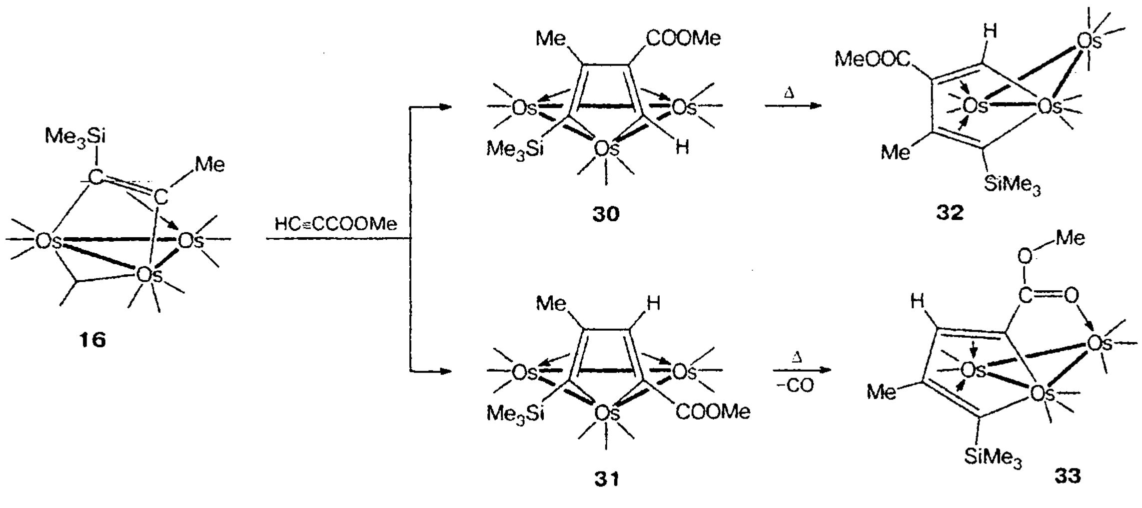
After we had synthesized complexes of structure **D** with the new mode of the dienediyl moiety coordination to the Os_3 core, it could be expected that complexes belonging to this type can be precursors of isomeric compounds of structure **E**, *i.e.*, the well-known products of alkyne dimerization.

As was mentioned above, heating of clusters **23** and **24** results in their decarbonylation to give the corresponding hydride complexes **27** and **28**. Similar hydride complexes are also obtained in the thermolysis of triosmium clusters of structure **E** with an aryl group as substituent in the α-position of the osmacyclopentadiene ring.[38] In these clusters the five-membered heterocycle is tilted with respect to the plane of the Os_3 triangle and is in intermediate position between those observed in the limiting cases (structures **D** and **E**).

In a continuation of the studies of heteroalkyne dimerization on the Os_3 cluster we synthesized a novel complex of structure **D** and first observed its **D** → **E** intramolecular rearrangement, which was unknown previously.[39,40] The reaction of complex **16** with $HC{\equiv}CCOOMe$ results in the clusters $Os_3\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C(SiMe_3)C(Me)C(COOMe)CH\}(CO)_9$ (**30**), $Os_3\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C(SiMe_3)C(Me)CHC(COOMe)\}(CO)_9$ (**31**), $Os_3\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^4\text{-}C(SiMe_3)C(Me)C(COOMe)CH\}(CO)_9$ (**32**), and $Os_3\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^4{:}\eta^1\text{-}C(SiMe_3)C(Me)CHC(COOMe)\}(CO)_8$ (**33**) (Scheme 6). The structure of clusters **30** and **33** was confirmed by single-crystal X-ray diffraction analysis.[40]

It was shown that the octacarbonyl cluster **33** is obtained as a result of decarbonylation of cluster **31**. After elimination of a CO group the vacant coordination position in this cluster is occupied by the acyl oxygen atom of the ester group. Because of the tightening effect of the MeOOC group, the osmacyclopentadiene ring is tilted with respect to the plane of the Os_3 triangle as in

Scheme 6



the case of hydride clusters with an *ortho*-metallated α-substituent in the metallacyclopentadiene moiety, in which the angle between the plane of the five-membered metallacycle and the plane of the Os_3 triangle is 64.7°.

Unlike complexes **23**, **24**, or **31**, neither a substituent capable of undergoing *ortho*-metallation nor a functional group capable of coordinating the metal atom is attached to α-position of the metallacyclopentadiene moiety of cluster **30**. Because of this, the **30** → **32** rearrangement occurs under mild conditions at 45—50 °C. This isomerization, never observed previously, involves the μ_3-η^1:η^1:η^2:η^2 → μ-η^1:η^1:η^4-rearrangement of the hydrocarbon ligand and internuclear migration of one of the CO groups.

Thus, we have shown[39,40] that clusters of type **E**, in which the hydrocarbon ligand forms a η^4-diene bond with one of the osmium atoms, are thermodynamically more stable than their precursors, clusters of type **D** containing two η^2-olefin bonds. We believe that this is the reason why clusters of type **D** have remained "elusive" for such a long time.

Reactions of ruthenium and osmium clusters with functionalized alkynes

We also studied the reactions of 1,4-diferrocenylbuta-1,3-diyne and 1,4-diphenylbut-1-en-3-yne with $Ru_3(CO)_{12}$ and $Ru_3(\mu\text{-dppm})(CO)_{10}$ (dppm = $Ph_2PCH_2PPh_2$), 1,4-diferrocenylbut-1-en-3-yne with $Os_3(CO)_{10}(NCMe)_2$, and those of alkynes of the propargyl series with the triosmium clusters. Under conditions of our experiments (thermal reactions at moderate temperatures of 60 to 80 °C), the reactions of diynes and enynes containing ferrocenyl substituents result in the clusters of known structural types. It is likely that only specific products can be formed in this case because of the presence of two bulky ferrocenyl groups in the ligand. On the contrary, the less sterically hindered enyne PhC≡CCH=CHPh enters into unusual reactions, undergoes unexpected rearrangements, and forms complexes of previously unknown structure.

Studies of propargyl systems were carried out to generate cationic triosmium clusters with 5ē- and 6ē-propargyl ligands and to investigate their structure and reactivity toward P-nucleophiles.

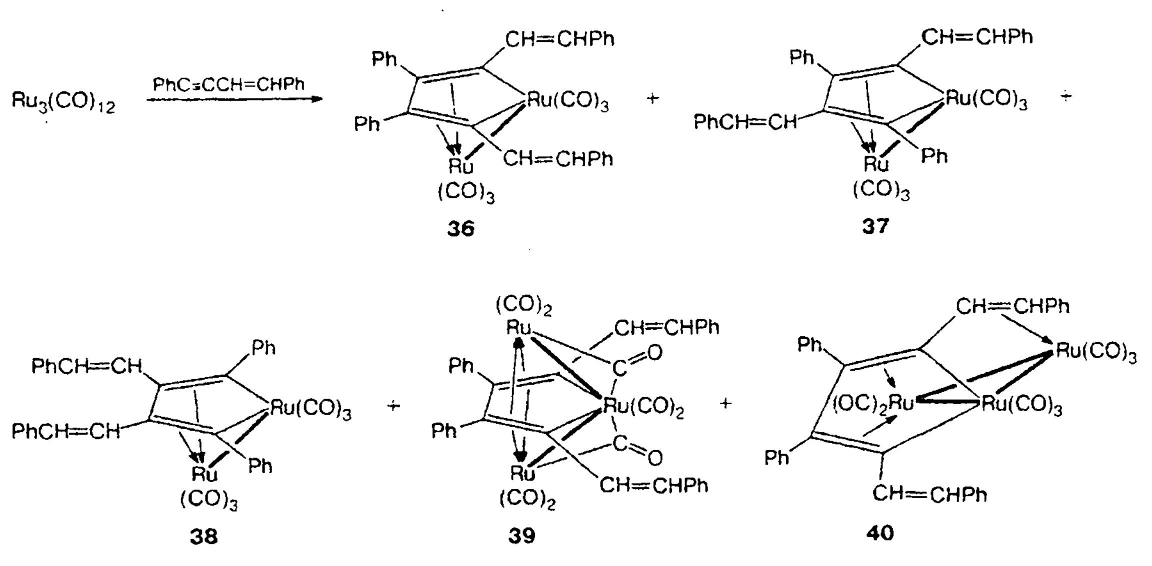
Reactions with diynes and enynes

The reaction of diyne FcC≡CC≡CFc with $Ru_3(CO)_{12}$ in refluxing hexane results in isomeric binuclear complexes $Ru_2\{\mu\text{-}C_4Fc_2(C{\equiv}CFc)_2\}(CO)_6$ (**34a—c**) with the ruthenacyclopentadiene moiety and in the complex $Ru_2\{\mu\text{-}C_4Fc_2(C{\equiv}CFc)_2CO\}(CO)_6$ (**35**) with the diruthenacycloheptadienone moiety.[41]

The reaction of enyne PhC≡CCH=CHPh with $Ru_3(CO)_{12}$ in refluxing hexane results in a complex mixture of isomeric complexes from which the isomers $Ru_2\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}(CO)_6$ (**36—38**), the orange complex $Ru_3\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}(\mu\text{-}CO)_2(CO)_6$ (**39**), and the brown complex $Ru_3\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^4{:}\eta^2\text{-}C_4Ph_2(CH{=}CHph)_2\}(CO)_8$ (**40**) of a previously unknown type were isolated as individual compounds (Scheme 7).[41,42] The structure of complex **40** was established by single-crystal X-ray diffraction analysis (Fig. 4).

The molecule **40** has a Ru_3 triangle; two out of the three Ru atoms coordinate three CO groups, while the

Scheme 7



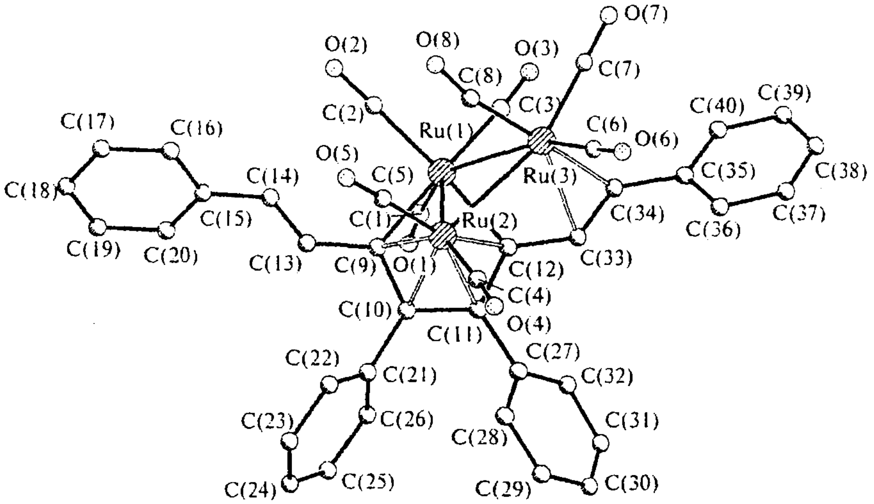


Fig. 4. Molecular structure of cluster $Ru_3\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^4{:}\eta^2\text{-}C_4Ph_2(CH{=}CHPh)_2\}(CO)_8$ (**40**).

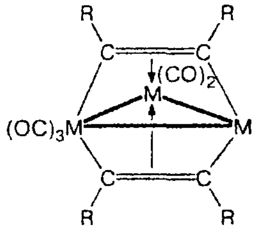
third Ru atom coordinates two CO ligands and the hydrocarbon ligand formed by "head-to-head" coupling of two enyne molecules. The mode of the hydrocarbon ligand bonding to the Ru_3 core is complicated, namely, the C(9) and C(12) atoms form σ-bonds with the Ru(1) atom to give the ruthenacyclopentadiene ring, whereas the C(9)C(10)C(11)C(12) diene fragment of this ring is π-coordinated to the Ru(2) atom; in the end, the C(33) and C(34) atoms of the alkenyl substituent form π-bonds with the Ru(3) atom.

In complex **40** the five-membered heterocycle is tilted with respect to the Ru_3 plane due to the tightening effect of the coordinated alkenyl group, and the dihedral angle between the C(9)Ru(1)C(12) and Ru_3 planes is equal to 54.1°.

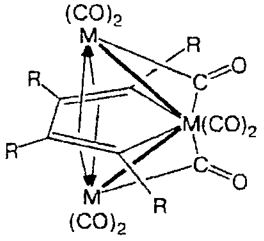
In the course of studying the pathways of the formation of cluster **40** we have found that it is formed in high yield when the orange complex **39** is heated in refluxing hexane. In this case, the binuclear complex **36**, a fragmentation product of the trinuclear cluster, was also isolated in low yield.[43]

As is known,[44–46] the thermal reaction of PhC≡CPh with $M_3(CO)_{12}$ (M = Fe, Ru) results in two types of isomeric $M_3(PhC_2Ph)_2(CO)_8$ complexes, namely, in the violet (M = Fe, Ru) and in black (M = Fe) or orange (M = Ru) ones. The first type of compounds contains two 2σ,π-coordinated alkyne ligands situated on the opposite sides of the plane of the metal triangle. When heated, these compounds are converted into isomeric black (M = Fe) and orange (M = Ru) complexes in which one of the M—M bonds in the initial M_3 triangle is cleaved while two alkyne ligands are coupled to form a metallacyclopentadiene ring. In addition, two of the eight CO ligands are bridging ligands. The orange complex **39** belongs to the second type.

The above-mentioned $M_3(RC_2R)_2(CO)_8 \rightarrow M_3(RC_2R)_2(\mu\text{-}CO)_2(CO)_6$ isomerization of the known



M = Fe (violet)
M = Ru (violet)



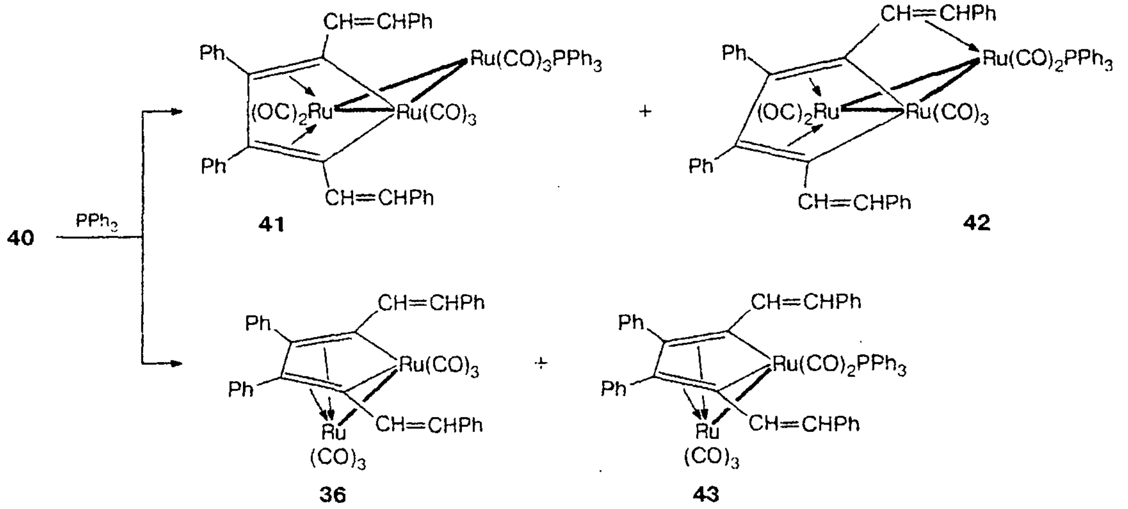
M = Fe (black)
M = Ru (orange)

complexes proceeds in refluxing benzene. However, no information was reported on further conversion of the black (M = Fe) and orange (M = Ru) isomers into compounds containing a reformed M_3 triangle, as we observed in the **39** → **40** isomerization. Thus, the presence of alkenyl substituents in the metallacyclopentadiene ring of cluster **39** provides a way for the third isomer of composition $M_3(RC_2R)_2(CO)_8$ of the type of brown cluster **40** to exist. The mechanism of the **39** → **40** isomerization remains unclear. Likely, it does not involve a pre-fragmentation of complex **39** with the formation of binuclear compound **36** followed by addition of a ruthenium carbonyl particle. This is confirmed by the fact that no cluster **40** is formed on heating of complex **36** with $Ru_3(CO)_{12}$ in refluxing hexane.

Reactions of cluster **40** with PPh_3, $P(OPr^i)_3$, and CO have been studied.[43] The reaction with PPh_3 (benzene, at 22 °C) is accompanied by displacement of the alkenyl group out of the coordination sphere of the Ru atom and the formation of a labile green cluster $Ru_3\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^4\text{-}C_4Ph_2(CH{=}CHPh)_2\}(CO)_8(PPh_3)$ (**41**) (Scheme 8). Complex **41** readily undergoes decarbonylation to give the red complex $Ru_3\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^4{:}\eta^2\text{-}C_4Ph_2(CH{=}CHPh)_2\}(CO)_7(PPh_3)$ (**42**), a phosphine

Scheme 8

$$\underset{\mathbf{39}}{Ru_3\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}(\mu\text{-}CO)_2(CO)_6} \xrightarrow{\Delta} \underset{\mathbf{40}}{Ru_3\{\mu_3\text{-}C_4Ph_2(CH{=}CHPh)_2\}(CO)_8}$$



derivative of cluster **40**. In addition to clusters **41** and **42**, binuclear complexes **36** and $Ru_2\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}(CO)_5(PPh_3)$ (**43**) were found among the products; the yield of complexes **36** and **43** increases as the duration of the reaction increases.

The structure of cluster **41** was established by single-crystal X-ray diffraction analysis. The molecule has a pseudomirror plane passing through the Ru_3 plane, the P atom, and the midpoint of the diene fragment, whose plane forms an angle of 88° with the plane of the Ru_3 triangle.

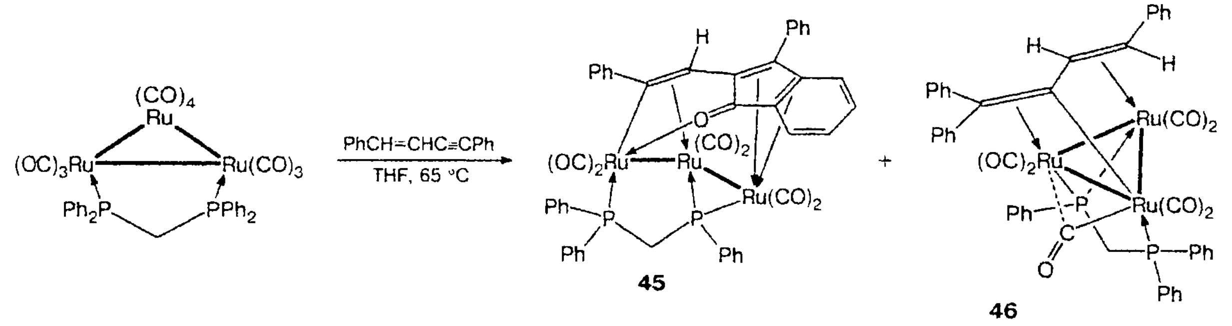
Reaction of complex **40** with triisopropylphosphite (see Scheme 8) results in the green cluster $Ru_3\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}(CO)_8\{P(OPr^i)_3\}$ (**44**), which is more stable towards fragmentation than complex **41**. This is likely explained by differences in steric characteristics of the phosphorus-containing ligands (the Tolman cone angle for PPh_3 and $P(OPr^i)_3$ is 145° and 130°, respectively).

When carbon monoxide is bubbled through a benzene solution of cluster **40**, the starting brown solution gradually turns yellow because of the formation of complex **36**. The intermediate cluster $Ru_3\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}(CO)_9$ that formed is likely less stable than its phosphorus-containing derivatives **41** and **44** and undergoes fast fragmentation.

To establish the position of the PPh_3 ligand in complex **43** and related isomers, these compounds were studied by IR, ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy, while the products of reaction between cluster $Ru_2\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}(CO)_6$ and triphenylphosphine in refluxing toluene, the $Ru_2\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}(CO)_{6-n}(PPh_3)_n$ ($n = 1, 2$) complexes, were characterized by single-crystal X-ray diffraction analysis.[47] As a result, we established that in the monophosphine derivatives of binuclear complexes of the ruthenole type, obtained both by $Ru_3\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}(CO)_8(PPh_3)$ fragmentation and by replacement of a CO group by PPh_3 in the binuclear complex $Ru_2\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}(CO)_6$, the PPh_3 ligand is bound to the ruthenium atom of the ruthenacyclopentadiene ring.

Thermal reaction of $PhC{\equiv}CCH{=}CHPh$ with cluster $Ru_3(\mu\text{-}dppm)(CO)_{10}$ proceeds in a manner quite different from that of the reaction with $Ru_3(CO)_{12}$ (Scheme 9). Two out of the three complexes isolated in this case were characterized by single-crystal X-ray diffraction analysis. According to the data of ^1H NMR, ^{31}P NMR, and X-ray diffraction studies, the organic ligands in the products of reactions of $PhC{\equiv}CCH{=}CHPh$ with $Ru_3(\mu\text{-}dppm)(CO)_{10}$ and $Ru_3(CO)_{12}$ are distinctly different. The reaction of $Ru_3(\mu\text{-}dppm)(CO)_{10}$ with $PhC{\equiv}C{-}CH{=}CHPh$ results in the red cluster $Ru_3\{\mu_3\text{-}C(Ph){=}CH{-}\overline{CC(Ph)(1{,}2\text{-}C_6H_4)C}({=}O)\}\{\mu_3\text{-}P(Ph)CH_2PPh_2\}(CO)_6$ (**45**) containing only two Ru—Ru bonds as one of the major products. At the formation of complex **45** the dppm ligand is transformed into a phosphine-phosphide ligand because of the loss of a Ph group. In this case the newly formed organic ligand is an indenone derivative

Scheme 9



45

46

resulting from a three-component coupling of dehydrobenzene (with dppm as its source), CO, and metallated enyne.[48]

Yet another completely characterized product of this reaction is the yellow cluster $Ru_3\{\mu_3\text{-}C(=CPh_2)\text{—}CH=CHPh\}\{\mu_3\text{-}P(Ph)CH_2PPh_2\}(\mu\text{-}CO)(CO)_6$ (**46**) whose precursor is complex **45**. Heating of the latter results in elimination of the indenone acyl group followed by its transfer to the Ru_3 core in the form of a CO ligand. Eventually, the starting enyne molecule is phenylated by diphosphine dppm *via* cleavage of the C—C bond in the indenone ligand and the addition of a hydrogen atom to the organic ligand to form the 1,1,4-triphenylbutadienyl ligand. In molecule **46**, the 1,1,4-triphenylbutadienyl ligand forms two π-bonds and one σ-bond with ruthenium atoms of the reformed Ru_3 triangle.

The structure of the third product isolated in this reaction has not been established as yet. The parameters of the ^1H NMR spectrum indicate that in this complex the ethylene fragment of the hydrocarbon ligand is also π-coordinated to the ruthenium atom.

It is noteworthy that the formation of compounds similar to **45** and **46** was never observed though the reactions of $Ru_3(\mu\text{-dppm})(CO)_{10}$ with alkynes and diynes were studied earlier.

The different types of the products of the reactions of $Ru_3(CO)_{12}$ and its diphosphine derivative, complex $Ru_3(\mu\text{-dppm})(CO)_{10}$, with $PhC{\equiv}CCH{=}CHPh$ indicate how drastically the course of reaction can be changed by such ligand modification of the starting metal carbonyl cluster.

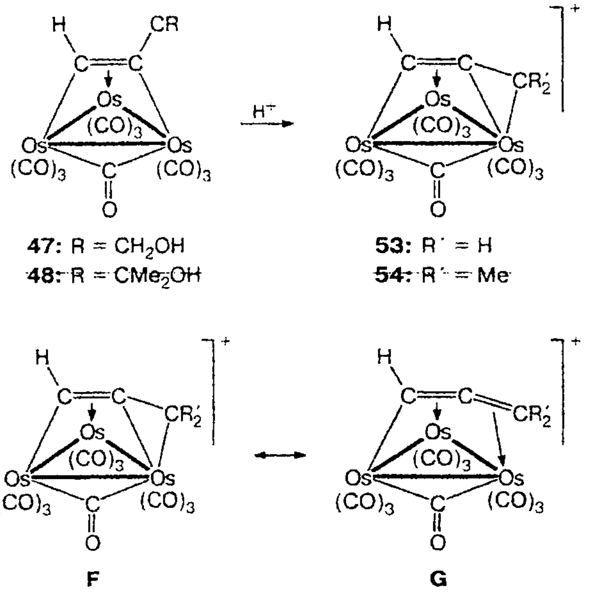
Reactions with propargyl alcohols and their derivatives

Recently, intensive studies of complexes with the η^3-propargyl ligand have been carried out. Mono-[49,50] and binuclear[51] complexes were studied in detail, whereas almost no data on η^3-coordination of the propargyl ligand were reported for trinuclear systems.

For this reason, we synthesized the alkyne clusters $Os_3(\mu_3\text{-}HC_2R)(\mu\text{-}CO)(CO)_9$ (R = CH_2OH (**47**), CMe_2OH (**48**), and $C(Me){=}CH_2$ (**49**)) using known approaches. Thermolysis of these clusters in refluxing octane gave the corresponding acetylide derivatives $Os_3H(\mu_3\text{-}C{\equiv}CR)(CO)_9$ (R = CH_2OH (**50**), CMe_2OH (**51**), and $C(Me){=}CH_2$ (**52**)).[52,53] Compounds **48** and **51** were reported previously.[54] Low-temperature protonation of the clusters obtained with CF_3COOH, CF_3SO_3H, and $HBF_4 \cdot OEt_2$ was studied by ^1H and ^{13}C NMR spectroscopy.

Protonation of complexes **47** and **48** containing the 4ē-alkyne ligand results in the corresponding cationic complexes $[Os_3(\mu_3\text{-}HC_2CR'_2)(\mu\text{-}CO)(CO)_9]^+$ (R′ = H (**53**), Me (**54**))[52] (Scheme 10), in which the propargyl ligand donates five electrons. According to ^{13}C NMR spectroscopy data, bonding of the hydrocarbon ligand in clusters **53** and **54** can be best described as a resonance hybrid of structures **F** and **G** with the predominant contribution coming from structure **F**. The signal of the $\underline{C}Me_2$ carbon atom in complex **54** is observed in a rather high field (at δ 37), which best corresponds to structure **F** with the 3σ,π-coordinated ligand.

Scheme 10



47: R = CH_2OH
48: R = CMe_2OH

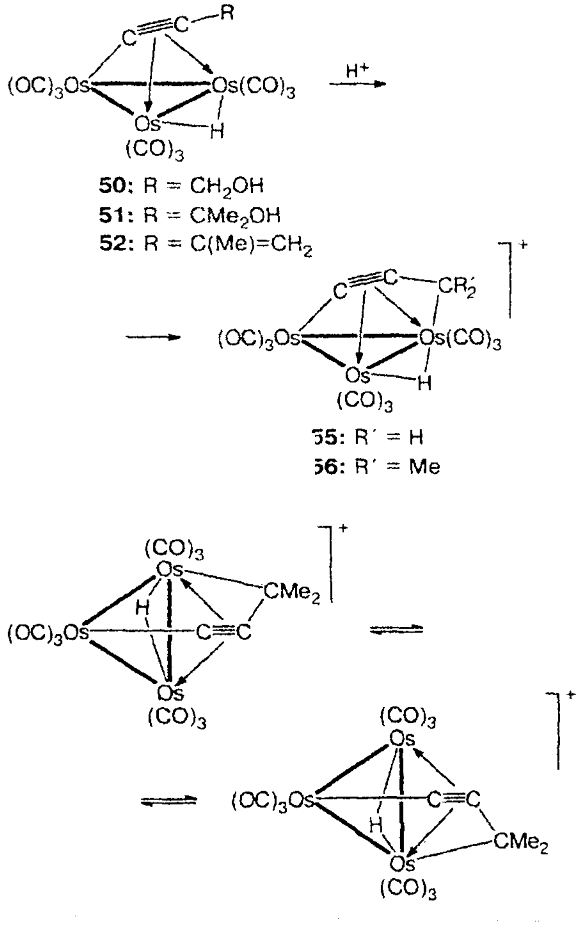
53: R′ = H
54: R′ = Me

F

G

Protonation of acetylide clusters **50**—**52** with CF_3SO_3H at -50 °C results in cationic complexes $[Os_3H(\mu_3\text{-}C{\equiv}CCR'_2)(CO)_9]^+$ (R′ = H (**55**), Me (**56**)) with the 6ē-propargyl ligand (Scheme 11). Complex **55** is much less stable than cluster **56**, though even the latter cannot be isolated as a salt.[52,53] Data of ^1H NMR spectroscopy indicate an exchange process in complex **56** (see Scheme 11).

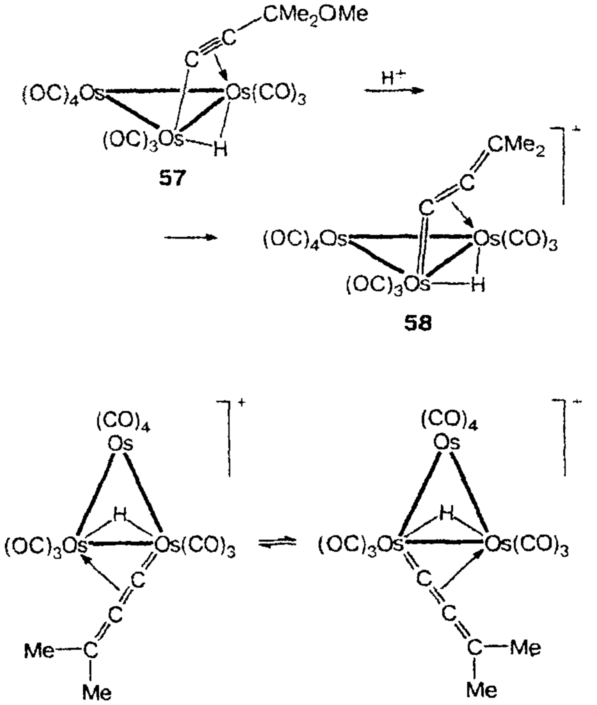
Scheme 11



The above-mentioned examples of protonation of alkyne and acetylide triosmium clusters show that the carbocationic center generated at the β-position with respect to the osmium atom is stabilized by direct participation of the metal atom, which also occurs in α-metallocenyl carbocations and in related cationic organometallic complexes.[55]

Unlike protonation of clusters $Os_3(\mu_3\text{-}HC_2R)(\mu\text{-}CO)(CO)_9$ and $Os_3H(\mu_3\text{-}C{\equiv}CR)(CO)_9$ (R = CH_2OH, CMe_2OH, $C(Me){=}CH_2$) resulting in cationic clusters with the μ_3-propargyl ligand, protonation of cluster $Os_3H(\mu\text{-}C{\equiv}CCMe_2OMe)(CO)_{10}$ (**57**), which we have synthesized using an original procedure by the reaction of $Os_3H(Cl)(CO)_{10}$ with $LiC{\equiv}CCMe_2OMe$,[56] gives the cationic allenylidene complex $[Os_3H(\mu\text{-}C{=}C{=}CMe_2)(CO)_{10}]^+$ (**58**) (Scheme 12).

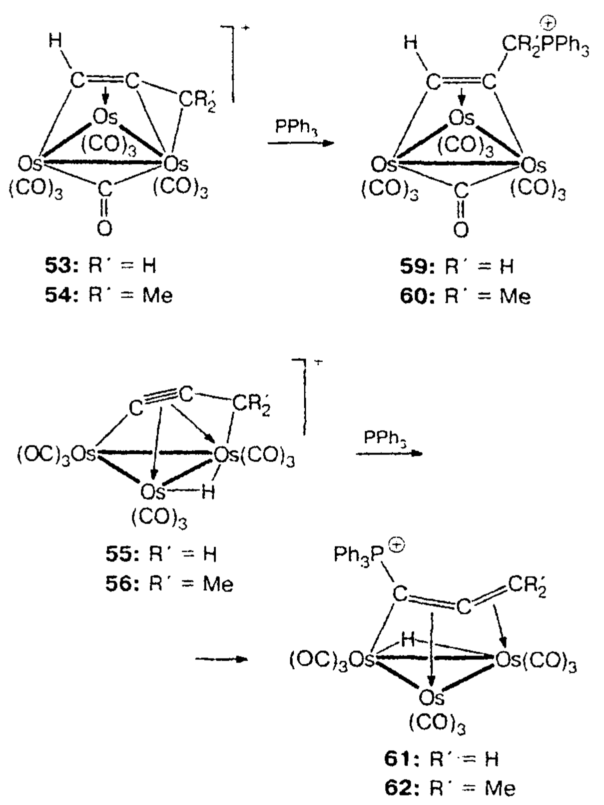
Scheme 12



Cluster **58** is stable only at low temperatures. Its ^1H and ^{13}C NMR spectra indicate exchange processes, one of which is the exchange of the hydrocarbon ligand between two osmium atoms.

Reactions of these cationic clusters with triphenylphosphine[52] (Scheme 13) have been studied. Complexes $[Os_3(\mu_3\text{-}HC_2CR'_2)(\mu\text{-}CO)(CO)_9]^+$ (R′ = H (**53**), Me **54**)) and $[Os_3H(\mu_3\text{-}C{\equiv}CCR'_2)(CO)_9]^+$ (R′ = H (**55**), Me (**56**)) react with PPh_3 at low temperatures and the phosphine attacks at the β-C or α-C atom of the ligand, respectively, to give the corresponding phosphonium complexes $[Os_3\{\mu_3\text{-}HC_2C(PPh_3)R'_2\}(\mu\text{-}CO)(CO)_9]^+$ (R′ = H (**59**), Me (**60**)) and $[Os_3H\{\mu_3\text{-}C(PPh_3){=}C{=}CR'_2\}(CO)_9]^+$ (R′ = H (**61**), Me (**62**)).

Scheme 13



53: R' = H
54: R' = Me

59: R' = H
60: R' = Me

55: R' = H
56: R' = Me

61: R' = H
62: R' = Me

Reactions of ruthenium and osmium clusters with ferrocenylacetylene

Only a few examples of ferrocenylacetylene reactions with metal carbonyl clusters have been reported.[57–62] Though ferrocenylacetylene does not belong to heteroatom-substituted or functionalized alkynes, in some instances the presence of an organometallic ferrocenyl substituent at the acetylene carbon atom results in the formation of complexes of unique structure in reactions with metal carbonyls.

Ferrocenylacetylene derivatives of a metal carbonyl cluster were first synthesized in the reaction of the $Os_3H_2(CO)_{10}$ dihydride with FcC≡CH,[57,58] which gave known types of complexes, *e.g.*, the alkenyl $Os_3H(\mu\text{-}CH=CHFc)(CO)_{10}$ (**63**) and alkyne $Os_3(\mu_3\text{-}HC_2Fc)(\mu\text{-}CO)(CO)_9$ (**64**) clusters. Their thermolysis also gave the expected products, namely, the vinylidene $Os_3H_2\{\mu_3\text{-}C=C(H)Fc\}(CO)_9$ (**65**) and acetylide $Os_3H(\mu_3\text{-}C\equiv CFc)(CO)_9$ (**66**) clusters, respectively. The results in the case of low-temperature protonation of cluster **65** with trifluoroacetic acid[57,58] appeared to be somewhat unexpected. Unlike the vinylidene complex $Os_3H_2(\mu_3\text{-}C=CH_2)(CO)_9$ (**67**), whose protonation results in the trihydride cationic complex $[Os_3H_3(\mu_3\text{-}C=CH_2)(CO)_9]^+$, complex **65** reacts with CF_3COOH to give the alkenyl complex $Os_3H_2(\mu\text{-}CH=CHFc)(CO)_9(OCOCF_3)$. It was shown that cluster **65** reacts with CF_3COOD in such a manner that the electrophile adds to the carbene carbon atom of complex **65**. Different behavior of clusters **65** and **67** in the protonation reactions is explained by intermediate formation of the structures with a C—H···Os agostic bond and by the known enhanced ability of the Fc group to delocalize the positive charge. Heating of an $Os_3H_2(\mu\text{-}CH=CHFc)(CO)_9(OCOCF_3)$ solution to room temperature results in intramolecular activation of the α-C—H bond by the alkenyl group to give the trihydride cationic cluster $[Os_3H_3(\mu_3\text{-}C=CHFc)(CO)_9]^+$. ¹H NMR study of $[Os_3H_3(\mu_3\text{-}C=CHR)(CO)_9]^+$ (R = H, Ph, Fc) clusters ($J_{^{187}Os-^{1}H}$ satellite spectra) showed that the stereochemical nonrigidity of these complexes is due to rotation of the vinylidene ligand above the plane of the Os_3 triangle rather than to migration of hydride ligands along the perimeter of the Os_3 triangle.

Interesting results were obtained in studies of the ferrocenylacetylene reaction with $Ru_3(CO)_{12}$.[59,60,63,64] The reaction in refluxing hexane (Scheme 14) results in five products, namely, in the red-brown $Ru_2(\mu\text{-}C_4H_2Fc_2)(CO)_6$ (**68**), dark-red $Ru_2\{\mu\text{-}C(H)=C(Fc)\text{—}COC(H)=C(Fc)\}(CO)_6$ (**69**), red-orange $Ru_3H(\mu_3\text{-}C\equiv CFc)(CO)_9$ (**70**),[59] crimson $Ru_3H(\mu\text{-}CFc)(CO)_{10}$ (**71**),[60] and dark-green $Ru_4H(\mu_4\text{-}C_2Fc)(CO)_{12}$ (**72**) complexes.[63,44] The last two complexes have no analogs; their structure, as well as that of complex **68**, was established by single-crystal X-ray diffraction analysis. The remarkable feature of the structure of complex **68** is that it contains no semibridging CO group. This is the first example of the ruthenole type complex with such a

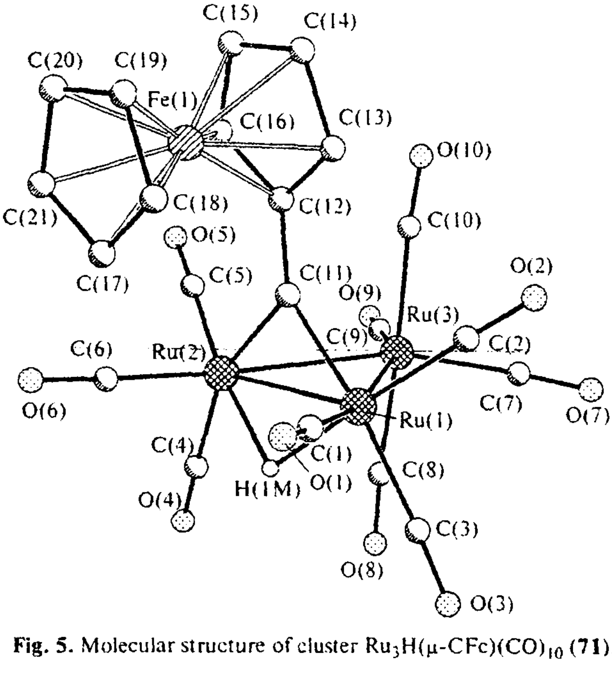
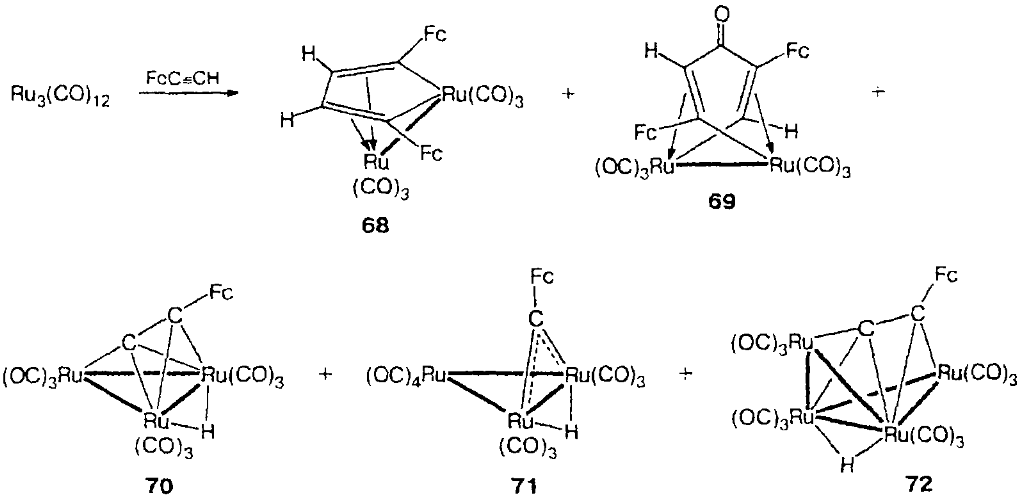


Fig. 5. Molecular structure of cluster $Ru_3H(\mu\text{-}CFc)(CO)_{10}$ (**71**).

Scheme 14

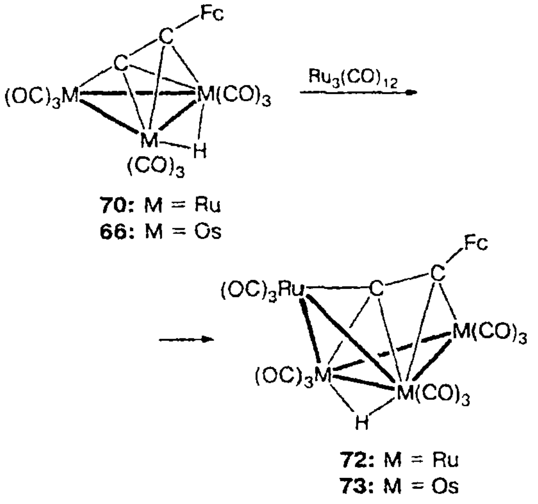


conformation.[59] As is known, most of the related iron and ruthenium complexes of composition $M_2(\mu\text{-}C_4R_4)(CO)_6$ (M = Fe, Ru) are compounds for which the alternative structure with one semibridging CO group is observed in the crystal. Recently,[65] rotational isomerism of related diruthenium and dirhenium complexes with the metallacyclopentadiene ring was studied by IR spectroscopy in a wide temperature range (165—293 K).

The formation of carbyne cluster **71** in the above-mentioned reaction indicates cleavage of the C≡C triple bond of the alkyne. This is the first example of cleavage of terminal alkyne under the action of ruthenium carbonyl.[60] X-Ray diffraction study of cluster **71** (Fig. 5) revealed an interesting feature of its structure.

The dihedral angle between the Ru(1)Ru(2)C(11) and Ru_3 triangle planes is 91.9° while the C(11)...Ru(3) distance between the carbyne carbon atom and the ruthenium atom of the $Ru(CO)_4$ unit is 2.78(1) Å. This distance is rather long to allow for the formation of a normal bond between these atoms. Despite this fact, the clearly seen rotation of the $Ru(CO)_4$ unit with respect to the Ru(3) atom is observed, so the C(10)O(10) axial ligand makes a Ru(mdpt)...Ru(3)—C(10) angle of 100.0°, while the other axial ligand, C(8)O(8), makes a Ru(mdpt)...Ru(3)—C(8) angle of 76.8°. Similar distortion of the $Os(CO)_4$ unit due to its donor-acceptor interaction with the carbyne carbon atom is observed in the $Os_3H(CH)(CO)_{10}$,[66] $Os_3H(CPh)(CO)_{10}$,[67] and $Os_3H(CCH_2CHMe_2)(CO)_{10}$ [68] triosmium clusters and successively decreases in the same order; however, no distortion is observed in cluster **7**,[12] which indicates that the degree of distortion of the $Os(CO)_4$ unit is dependent on the electronic properties of the substituent at the carbyne carbon atom. The results of the study of cluster **71** in the crystal showed that a weak bonding interaction is possible even at a distance of 2.78(1) Å between the C(11) and Ru(3) atoms.

Complex **70** reacts with ruthenium carbonyl[63] to give the green cluster $Ru_4H(\mu_4\text{-}C_2Fc)(CO)_{12}$ (**72**) in a yield >50%. The latter slowly decomposes both in solution and in the solid state to give the trinuclear acetylide complex **70** and $Ru_3(CO)_{12}$. Analogously, the reaction of cluster $Os_3H(\mu_3\text{-}C{\equiv}CFc)(CO)_9$ (**66**) with $Ru_3(CO)_{12}$ results in the green heteronuclear cluster $RuOs_3H(\mu_4\text{-}C_2Fc)(CO)_{12}$ (**73**).[63]



According to the data of X-ray study (Figs. 6 and 7), molecule **72** contains four ruthenium atoms in a "butterfly" configuration. Each Ru atom is bonded to three terminal CO groups while two ruthenium atoms at the "hinge" positions are bonded by a bridging hydride ligand.

A remarkable feature of the structure of cluster **72** is the coordination mode of the organic ligand, which is bound to four ruthenium atoms in a rather complicated

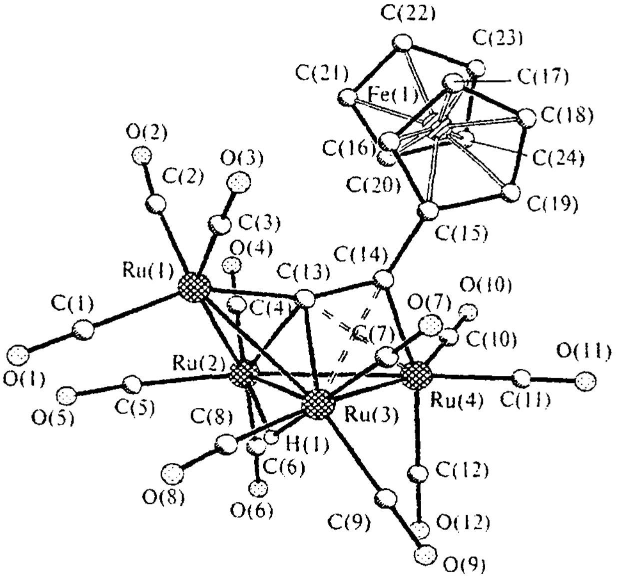


Fig. 6. General view of molecule $Ru_4H(\mu_4\text{-}C_2Fc)(CO)_{12}$ (72).

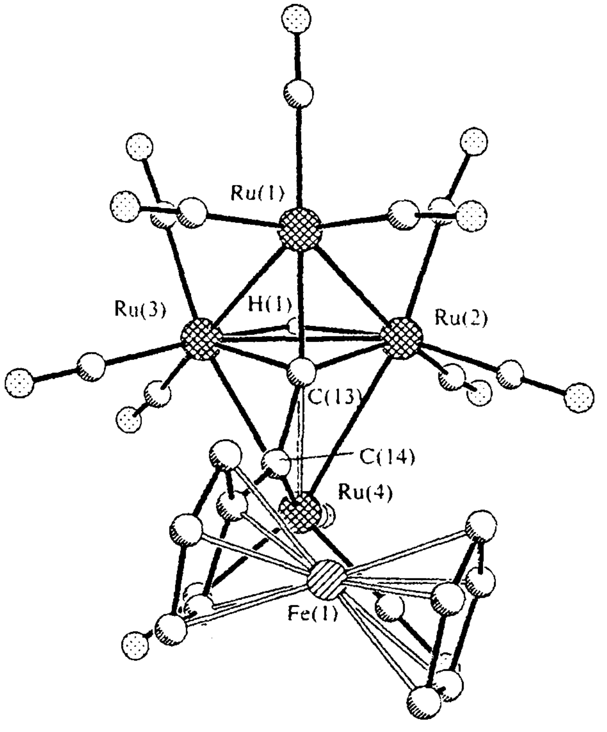
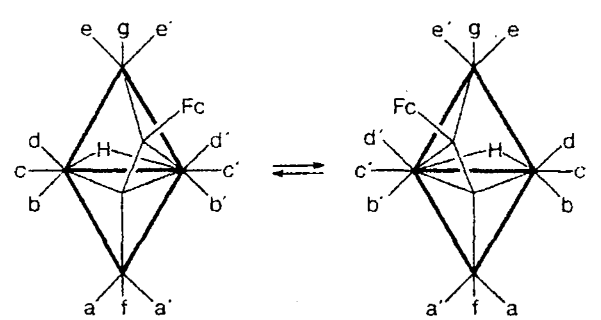


Fig. 7. Projection of molecule $Ru_4H(\mu_4\text{-}C_2Fc)(CO)_{12}$ (72) on the Ru(2)Ru(3)Ru(4) plane.

manner. The C(13) atom is located nearly symmetrically above the plane of the Ru(1)Ru(2)Ru(3) equilateral triangle and is bonded to all its vertices. The other acetylene carbon atom, C(14), is bonded to the Ru(4) atom. There are also two additional contacts between the carbon and metal atoms, namely, the C(13)...Ru(4) and C(14)...Ru(3) distances equal to 2.58(1) and 2.76(1) Å, respectively. The distance between the C(14) and Ru(2) atoms (3.10(1) Å) is too long to suggest an interaction. The C(13)—C(14) bond length is 1.34(1) Å and the C(14)—C(15) bond makes an angle of 6.8° with the substituted cyclopentadienyl ring of the ferrocene moiety. As is known, such a deviation of the exocyclic bond toward the iron atom is characteristic of α-ferrocenyl carbocations.[55]

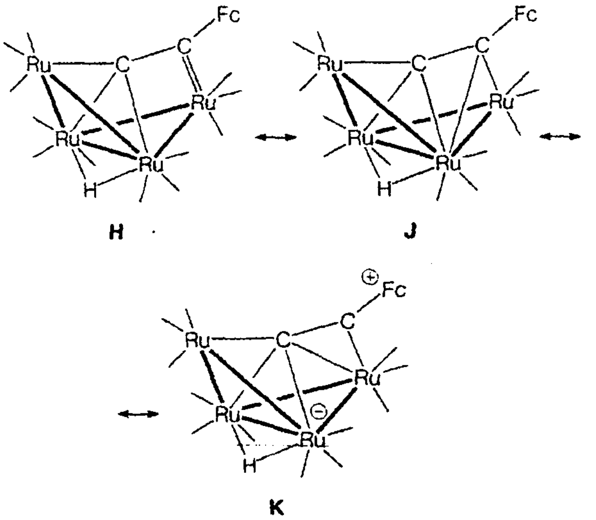
To gain a better insight into the bonding of the acetylide ligand in cluster **72**, the results of ^1H and ^{13}C NMR studies of this compound at variable temperature[63] should also be considered. At −60 °C, the protons of the substituted cyclopentadienyl ring of the ferrocenyl moiety are pairwise diastereotopic and appear in the ^1H NMR spectrum as four signals at δ 5.83, 5.23, 4.70, and 4.56. Heating of the solution is accompanied by broadening of the signals and at 50 °C the H(2), H(5) and H(3), H(4) protons appear at δ 5.56 and 4.76. These changes in the spectral pattern are explained by the rearrangement of the μ_4-acetylide ligand, which in essence is enantiomerization of the cluster. The rearrangement consists of the π,σ-exchange of the hydrocarbon ligand between the two ruthenium atoms at the "hinge" positions and results in pairwise averaging of all CO groups except for the f and g ones (Scheme 15).

Scheme 15



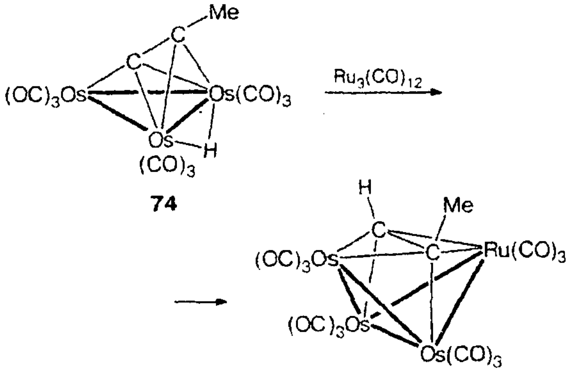
Twelve signals of CO groups are observed in the ^{13}C NMR spectrum of cluster **72** at −73 °C, which is in agreement with the nonsymmetrical structure of the molecule. Several dynamic processes are observed on raising the solution temperature, among which the localized exchange of three CO groups at one of the two ruthenium atoms at the base of the "butterfly" wings, $(OC)_3Ru(\mu\text{-}H)Ru(CO)_3$, has the lowest activation energy. This result, which is in agreement with the data of X-ray study, must indicate that these ruthenium atoms are nonequivalent or, in other words, that the interaction between the C(14) and Ru(3) atoms occurs despite the rather long distance between them (2.76(1) Å). In this connection it should be remembered that the data of X-ray study of the carbyne cluster **71** suggest an interaction between the carbon and ruthenium atoms separated by 2.78(1) Å.

Adequate description of the mode of bonding the organic ligand to the metal core in complex **72** requires consideration of the resonance structures **H**, **J**, and **K**. Structure **H** with the carbene-carbyne ligand seems to be reasonable if the relatively long C(13)...Ru(4) and C(14)...Ru(3) distances are considered as nonbonding ones. In this case the temperature dependence of the ^{1}H NMR spectrum should be due to hindered rotation with respect to the exocyclic C—C bond at the ferrocenyl group. However, the ^{13}C NMR spectral pattern at −40 °C, namely, a localized exchange of three CO groups at one of the ruthenium atoms at the "hinge" positions (in the absence of nonbonding contacts between the Fc group and CO ligands, as follows from the data of X-ray study) cannot be explained by invoking the carbene-carbyne structure **H**. Therefore the contribution of structure **J** in which one of the ruthenium atoms at the "hinge" positions is π-bonded to the FcC$_2$ ligand, whereas the other Ru atom at the "hinge" position is σ-bonded to the FcC$_2$ ligand, should also be taken into account; such a structure is in agreement the ^{13}C NMR spectral pattern. Finally, the bipolar charge-transfer structure **K** should also make a contribution; in this structure, the electron density is transferred from the ferrocenyl group to the Ru$_4$ cluster, which is indicated by the tilt of the C(14)—C(15) exocyclic bond toward the iron atom (not observed in the crystal structure of the trinuclear cluster **70** [63]) and by relatively strong deshielding of the cyclopentadienyl protons of the ferrocene moiety in the ^{1}H NMR spectrum.



H **J** **K**

The uniqueness of complex **72** and its heteronuclear analog **73** can indirectly indicate that structure **K** makes a contribution to the bonding of the ligand to the Ru$_4$ core in the former. No formation of clusters of such a structure was observed previously in the studies of the reactions between acetylenes and metal carbonyls, which indicates a decisive role of the ferrocenyl group in the formation (stabilization) of green clusters **72** and **73**. In this connection mention may be made that, unlike Os$_3$H(μ_3-C≡CFc)(CO)$_9$, the reaction of isostructural acetylide complex Os$_3$H(μ_3-C≡CMe)(CO)$_9$ (**74**) with Ru$_3$(CO)$_{12}$ results in the red *alkyne* cluster RuOs$_3$(μ_4-HC$_2$Me)(CO)$_{12}$ (**75**) of the known type with the "butterfly" core[69] rather than in the hydride-acetylide cluster related to compounds **72** and **73**.



74 **75**

The Ru$_3$(CO)$_{12}$, Ru$_3$H(μ_3-C≡CFc)(CO)$_9$, Os$_3$H(μ_3-C≡CFc)(CO)$_9$, Ru$_4$H(μ_4-C$_2$Fc)(CO)$_{12}$, and RuOs$_3$H(μ_4-C$_2$Fc)(CO)$_{12}$ clusters were studied by cyclic voltammetry.[70] It was established that reversible one-electron oxidation of the ferrocene moiety in the acetylide clusters proceeds at more positive potentials than the ferrocene and ferrocenylacetylene oxidation does. This indicates that the cluster core is an electron acceptor toward the ferrocenylacetylide group. Tetranuclear clusters are stronger acceptors than trinuclear ones, which is in agreement with the relative shielding of the protons of the ferrocenyl units in the ^{1}H NMR spectra of these complexes.

* * *

Our investigations of the transformations of heteroatom-substituted and functionalized alkynes on the ruthenium and osmium carbonyl clusters made it possible to obtain various new organometallic complexes, to discover new reactions of carbon—carbon, carbon—hydrogen, and carbon—heteroatom bond formation and cleavage, and to find various novel intramolecular rearrangements. Many of the reactions and rearrangements we found can be considered as homogeneous models for both the conversion of hydrocarbons and exchange processes with participation of C—C and C—H bonds occurring on the surface of heterogeneous catalysts. It is believed that the results obtained will be useful for targeted search for new reactions and catalytic systems.

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