Reviews

Acetylide derivatives of transition metal cluster carbonyls

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Modes of formation, structural features, reactivities, and stereochemical nonrigidity of cluster carbonyl complexes with acetylide ligands are considered.

Key words: acetylide derivatives of transition metals, metal cluster carbonyls, structures, intramolecular rearrangements.

1. Introduction

Acetylide derivatives of transition metals belong to an important class of organometallic compounds, which have attracted growing interest in recent years. In addition to the rich and diversified chemistry of acetylide groups as ligands,[1] an intimate relationship between the chemistry of acetylide derivatives of transition metals and the organometallic chemistry of vinylidene complexes is also worthy of note.[2] Besides, acetylide complexes attract attention in connection with the prospects for preparing new materials exhibiting nonlinear optical properties, liquid crystals, and metal-containing polymers.

Acetylide derivatives of transition metal cluster carbonyls possess interesting characteristic features.[1] A distinguishing feature of these systems is the versatility of modes of bonding of the acetylide group with the metal core. In this respect, the acetylide group is unrivaled among organic ligands. An adequate description of the character of the acetylide—metal core coordination in clusters and of the types of bonding (and sometimes even estimation of the number of electrons donated) often presents difficulties because of the complexity of modes of bonding of acetylide ligands with several (up to six!) metal atoms. The reasons for variations in the C≡C bond length of coordinated acetylide in such a wide range from 1.19 Å (the value typical of a noncoordinated C≡C bond) to 1.49(3) Å are not quite clear.

Yet another interesting feature of acetylide complexes is their stereochemical nonrigidity, which allows the acetylide ligand to be involved in a great diversity of modes of exchange in the course of intramolecular rearrangements.

In this review, approaches to the preparation and the structural features of acetylide derivatives of cluster carbonyls are surveyed. Modes of exchange of acetylide groups in cluster complexes are discussed and the main typical reactions involving these groups are considered.

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2. Modes of bonding of acetylide groups in metal cluster carbonyls

The known modes of coordination of acetylide ligands in metal complexes are shown in Fig. 1. These modes are considered below in order of increasing number of metal atoms in the cluster with which the acetylide ligand forms σ- or π-bonds. Simultaneously, an approach to the preparation of a particular complex will be described. It should be noted that several general methods are available for the synthesis of compounds under consideration. These methods involve oxidative addition of terminal alkyne or heteroatom-substituted alkyne to the metal atom with the participation of $H-C_{sp}$ or $X-C_{sp}$ (X = P, Cl, or another heteroatom) bonds, respectively. Reactions of mononuclear acetylide derivatives of transition metals with cluster carbonyl complexes are also rather widely used. Approaches involving the transfer of the acetylide group from the mononuclear complex to the cluster and the replacement of

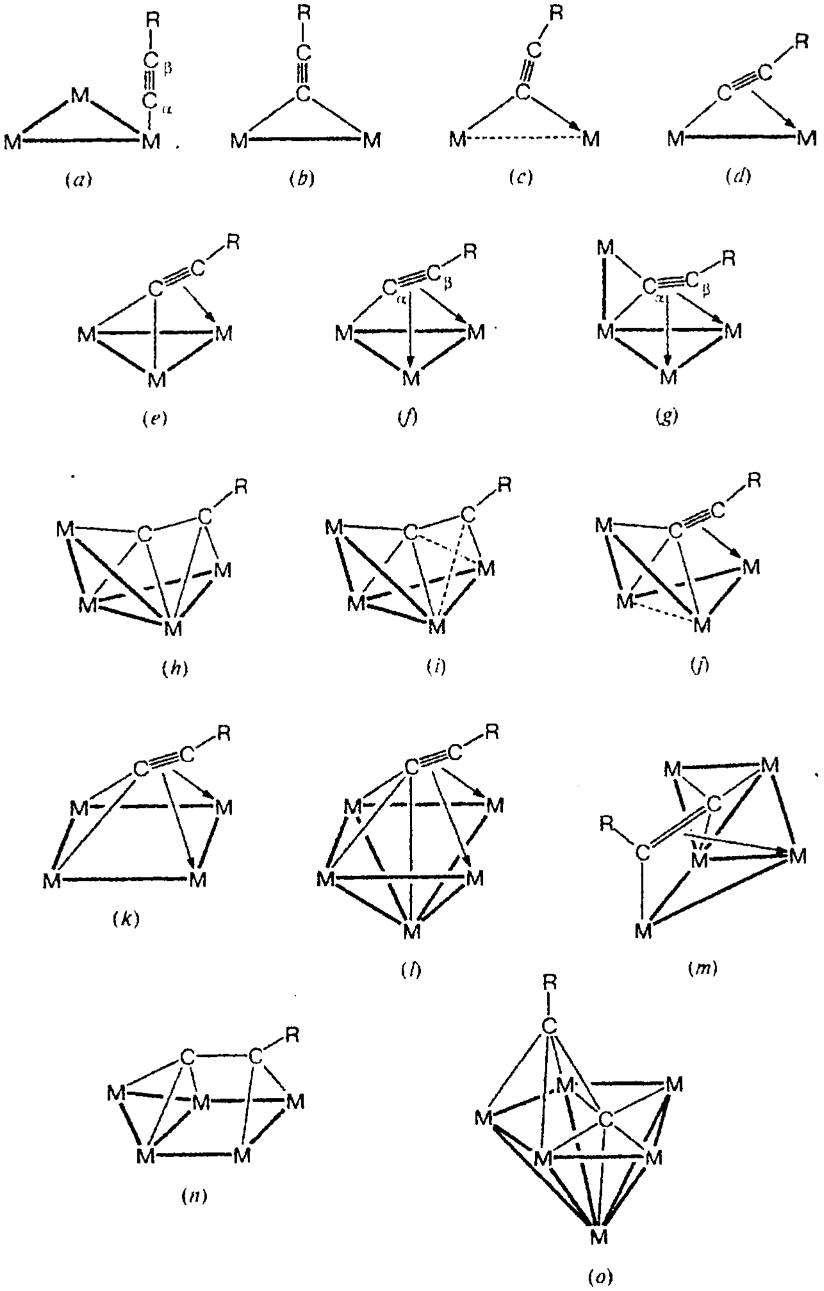


Fig. 1. Modes of coordination of acetylide groups in metal cluster carbonyls.

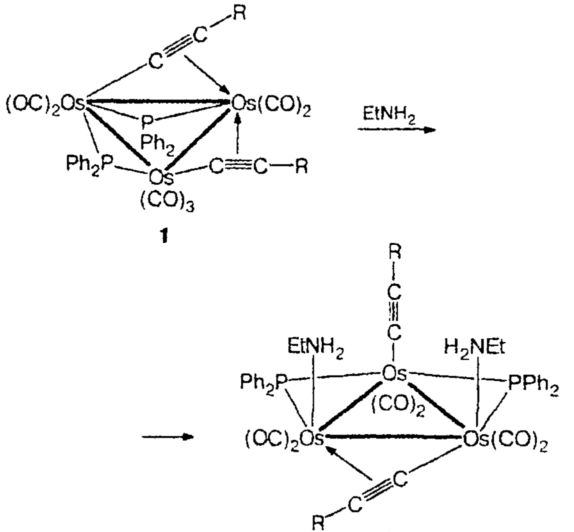
the bridging halide ligand of the cluster by the acetylide group under the action of lithium acetylide are less common.

2.1. Acetylide groups as terminal ligands (*a*)*

Only two examples of the preparation of trinuclear clusters with a terminal acetylide ligand of the σ type are known (see Fig. 1, *a*). In these cases, the compounds cannot be isolated in the direct reactions of alkynes with cluster complexes. All these compounds were synthesized from complexes containing the bridging σ,π-coordinated acetylide ligand. Thus, the clusters $Os_3(CO)_7(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C_2R)_2$ (**1**: R = Ph (**a**) or Pr^i (**b**)), which were prepared by thermolysis of diphosphine derivatives of osmium carbonyl $Os_3(CO)_{10}(Ph_2PC{\equiv}CR)_2$ in refluxing decalin, contain two $\mu\text{-}\eta^2$-acetylide ligands.[3] In the reaction of **1a** with ethylamine, one of these ligands became terminal (σ-coordinated) and one CO group was simultaneously displaced giving rise to a complex of composition $Os_3(CO)_6(\mu\text{-}PPh_2)_2(NH_2Et)_2(\mu\text{-}\eta^2\text{-}C_2Ph)(\eta^1\text{-}C_2Ph)$ (**2a**) (according to the data of X-ray diffraction analysis).[3]

Taking into account the carbocationic character of the carbon atoms of bridging acetylide groups (see Section 3), it was expected that reactions of clusters **1** with phosphines would afford products of addition at the acetylide ligand. However, the reactions of **1a** with $PR^1_2R^2$ ($R^1 = R^2 = Et$; or $R^1 = Ph$ and $R^2 = C_2Ph$, C_2Pr^i, or C_2Bu^t) yielded only products of replacement of the CO group, *viz.*, complexes of composition $Os_3(CO)_6(PR^1_2R^2)(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C_2Ph)_2$.

The reaction of $HBF_4 \cdot OEt_2$ with the acetylide cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}C_2CMe_2OMe)$ (**3**) at low temperature gave rise to the cationic allenylidene complex $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}C{=}C{=}CMe_2)][BF_4]$ (**4**). Treatment of the latter with an excess of triphenylphosphine afforded the cluster $[Os_3(\mu\text{-}H)(CO)_{10}(PPh_3)\{\eta^1\text{-}C_2CMe_2PPh_3\}][BF_4]$ (**5**) (Scheme 1). In the course of formation of complex **5**, one of the PPh_3 molecules added to the allenylidene ligand, which was transformed into the η^1-coordinated acetylidephosphonium group. The second phosphine molecule occupied the vacant position at the Os atom, which appeared as a result of displacement of the π-coordinated ligand.**



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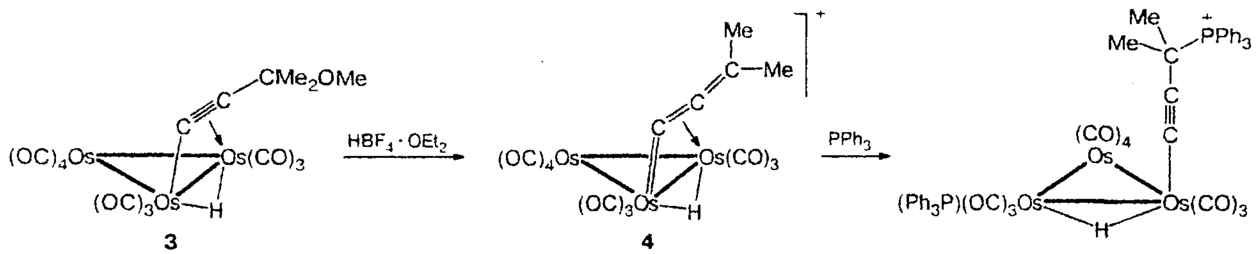
Whereas the photochemical reaction of $Re_2(CO)_{10}$ with phenylacetylene afforded dirhenium complexes containing the bridging acetylide ligand,[4,5] a number of dirhenium complexes with the η^1-acetylide ligand were obtained by photochemical reactions of $Re_2(CO)_8\{\mu\text{-}(L{-}L)\}$ (L—L = $Ph_2PCH_2PPh_2$ (dppm) or $Me_2PCH_2PMe_2$ (dmpm)) with terminal alkynes RC≡CH (R = H or Ph).[5] However, these reactions yielded compounds of compositions $Re_2(\mu\text{-}H)(CO)_6\{\mu\text{-}(L{-}L)\}(\mu\text{-}\eta^2\text{-}C_2R)$, $Re_2(CO)_5(L{-}L)\{\mu\text{-}\eta^2\text{-}C(R){=}CH_2\}(\mu_2\text{-}\eta^2\text{-}C_2R)$, and $Re_2(CO)_6\{\mu\text{-}(L{-}L)\}\{\mu_2\text{-}\eta^2\text{-}C(R){=}CH_2\}(\mu\text{-}\eta^2\text{-}C_2R)$ along with the complexes $Re_2(\mu\text{-}H)(CO)_7\{\mu\text{-}(L{-}L)\}(\eta^1\text{-}C_2R)$ (**6**: L = dppm, R = H (**a**); L = dppm, R = Ph (**b**); or L = dmpm, R = Ph (**c**)). The yields of these products depend on the reaction time and the nature of the diphosphine ligand. The reaction of $Re_2(CO)_7\{\mu\text{-}(L{-}L)\}(NCMe)$ with

Scheme 1



3 **4** **5**

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* Hereinafter, the letters given in parentheses in subtitles correspond to notations used in Fig. 1.

** O. A. Kizas, E. V. Vorontsov, V. V. Krivykh, O. L. Tok, F. M. Dolgushin, A. I. Yanovskii, and A. A. Koridze, unpublished results.

phenylacetylene at 40 °C afforded complexes **6a** and **6b**, in which the η^1-acetylide group is in the *cis* position with respect to the phosphorus atom. The thermal reaction of $Re_2(CO)_7(\mu\text{-dppm})(NCMe)$ with PhC≡CH produced complex **7b**, which is isomeric to complex **6b** and contains the acetylide group in the *trans* position with respect to the phosphorus atom.

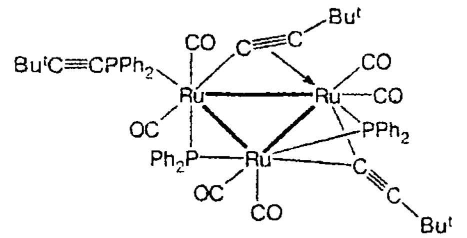
In the complex $Re_2(\mu\text{-H})(CO)_7(\mu\text{-dmpm})(\eta^1\text{-}C_2Ph)$ (**6c**), the C≡C bond length (1.200(9) Å) is virtually equal to the corresponding bond length in free alkyne (1.204(2) Å).

2.2. Acetylide groups as bridging ligands

Among compounds of the class under consideration, clusters with bridging acetylide ligands occur most frequently. The acetylide group in these compounds can be coordinated with up to six metal atoms. Note that modes of bonding may be substantially different even if the same number of metal atoms are coordinated by this group (see Fig. 1).

2.2.1. Symmetrical $\mu\text{-}\eta^1$-bridges (*b*)

If this mode of coordination is realized, the linear acetylide ligand forms a three-center one-electron bond between one carbon atom and two metal atoms (see Fig. 1, *b*). Thus, the triruthenium cluster $Ru_3(CO)_5(\mu\text{-}PPh_2)_2(Ph_2PC{\equiv}CBu^t)(\mu\text{-}\eta^2\text{-}C_2Bu^t)(\mu\text{-}\eta^1\text{-}C_2Bu^t)$ (**8**) simultaneously contains the $\mu\text{-}\eta^1$- and $\mu\text{-}\eta^2$-acetylide groups. These groups are formed as a result of oxidative addition of phosphinoalkyne.[6] The C≡C distance in the first group (1.19(1) Å) is virtually identical to the length of the noncoordinated triple bond in the initial ligand $Ph_2PC{\equiv}CBu^t$, whereas the C≡C bond length in the $\mu\text{-}\eta^2$-coordinated group (1.24(3) Å) is noticeably larger.



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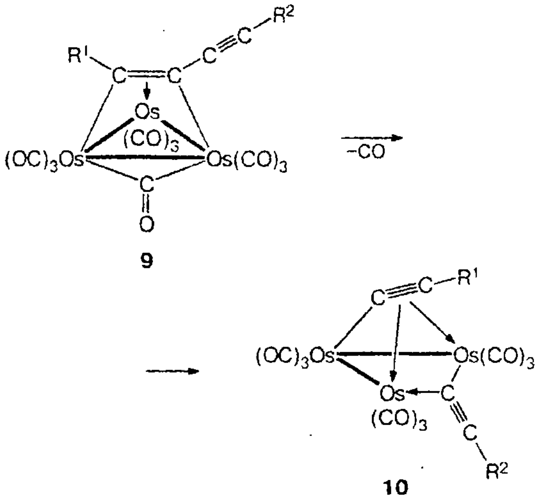
2.2.2. Unsymmetrical $\mu\text{-}\eta^1$-bridges (*c*)

Thermal decarbonylation of the decacarbonyl clusters $Os_3(CO)_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-}R^1C_2C{\equiv}CR^2)$ (**9**: $R^1 = R^2 = Ph$ (**a**); $R^1 = SiMe_3$, $R^2 = Ph$ (**b**); $R^1 = Ph$, $R^2 = SiMe_3$ (**c**); or $R^1 = SiMe_3$, $R^2 = Bu^t$ (**d**)) containing the $2\sigma,\pi$-coordinated diyne was accompanied by the cleavage of the central C—C bond of the ligand[7] to form the corresponding nonacarbonyl clusters $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2\text{-}C_2R^1)(\mu\text{-}\eta^1\text{-}C_2R^2)$ (**10**) in which the distances between the unbound Os atoms are 3.257(4) and 3.2[illegible](2) Å for **10a** and **10b**, respectively. The $\mu_3\text{-}2\eta^2\text{-}C_2R^1$ and $\mu\text{-}\eta^1\text{-}C_2R^2$ ligands in these complexes serve as donors of five and three electrons, respectively. In complexes **10a** and **10b**, the $\mu\text{-}\eta^1$-acetylide ligand is nonlinear and the distances between the β-carbon atom and the nearest osmium atom are 2.77(2) and 2.66(3) Å, respectively, which is indicative of weak interactions between these atoms.



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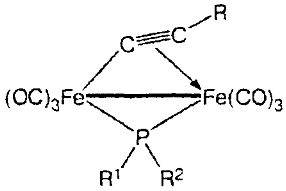
Thermolysis of $Os_3(CO)_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-}EtC_2C{\equiv}CEt)$ (**9e**) in refluxing octane afforded the hydridoallenyl complex of composition $Os_3(\mu\text{-H})(CO)_9\{\mu_3\text{-}\eta^1\text{-}\eta^2{:}\eta^2\text{-}C(C{\equiv}CEt){=}C{=}C(H)Me\}$ of the well-known type instead of the bis-acetylide cluster. Under analogous conditions, the complex $Os_3(CO)_9(CMe)(C_2CMe)$ with an unknown structure was prepared from the cluster $Os_3(CO)_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-}MeC_2C{\equiv}CMe)$.[7] These data indicate that the mechanism of thermolysis of the clusters depends on the structure and the electronic properties of the substituent in the alkyne.

2.2.3. $\mu\text{-}\eta^2\text{-}(\sigma,\pi)$-Bridges (*d*)

Much of the known complexes containing the σ,π-coordinated acetylide ligand belong to binuclear derivatives of transition metals. Many of these complexes were synthesized by oxidative addition of phosphinoalkyne to the metal core of carbonyl complexes. The resulting compounds contain the acetylide and phosphide bridges.

A series of the complexes $Fe_2(CO)_6(\mu\text{-}PR^1R^2)(\mu_2\text{-}\eta^2\text{-}C_2R)$ (**11**: $R = R^1 = R^2 = Ph$; $R = R^1 = Ph$, $R^2 = C_2Ph$; $R = Ph$, $R^1 = Bu^t$, $R^2 = C_2Ph$; $R = Bu^t$, $R^1 = R^2 = Ph$; $R = Pr^i$, $R^1 = R^2 = Ph$; or $R = Cy$ (Cy is cyclohexyl), $R^1 = R^2 = Ph$) were prepared[8,9] by reactions of $Fe_2(CO)_9$ with the corresponding phosphines $RC{\equiv}CPR^1R^2$. These reactions are believed to proceed through the intermediate formation of complexes which do not contain the Fe—Fe bond, because the binuclear complex of composition $(OC)_4Fe(Ph_2PC{\equiv}CBu^t)Fe(CO)_4$ was obtained as one of the reaction products. This complex was characterized by X-ray diffraction analysis. It was suggested that compounds of this type are intermediates in the synthesis of complexes with the Fe—Fe bond.



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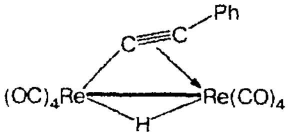
Thermolysis of trinuclear carbonyl phosphines $M_3(CO)_{11}(Ph_2PC{\equiv}CR)$ (M = Fe, Ru, or Os; R = Ph, Bu^t, or Pr^i) performed under rather drastic conditions afforded complexes of composition $M_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2R)$ (M = Fe (**11**), Ru (**12**), or Os (**13**); R = Ph (**a**), Bu^t (**b**), or Pr^i (**c**)).[9a] When thermolysis is carried out under milder conditions, the trinuclear clusters $M_3(CO)_9(\mu\text{-}PPh_2)(\mu_3\text{-}2\eta^2\text{-}C_2R)$ (M = Ru, Os) can be isolated from the reaction mixture (see Section 2.2.5).

Heating of the clusters $Ru_3(CO)_{11}(PPh_2C{\equiv}C{-}C{\equiv}CR)$ (R = Bu^t or Ph) in refluxing THF gave rise to the $\mu\text{-}\eta^2_{\alpha,\beta}$-butadiynyl complexes $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C{-}C{\equiv}CR)$.[9b]

The binuclear iron complexes $Fe_2(CO)_6(\mu\text{-}SR)(\mu\text{-}\eta^2\text{-}C_2R^1)$ (**14:** R = Bu^t, R^1 = Ph; R = R^1 = Bu^t; R = Bu^t, R^1 = $SiMe_3$; R = Et, R^1 = Ph; R = Et, R^1 = Bu^t; or R = Ph, R^1 = Bu^t) were prepared[10] by the reactions of $[Et_3NH][Fe_2(CO)_6(\mu\text{-}SR)]$ with bromoacetylenes $BrC{\equiv}CR^1$.

Photochemical reactions[4,5] of $Re_2(CO)_{10}$ with alkynes $RC{\equiv}CH$ (R = H or Ph) yielded the complexes $Re_2(\mu\text{-}H)(CO)_8(\mu\text{-}\eta^2\text{-}C_2R)$ (R = H (**15**) or Ph (**16**)). For the reactions of the carbonyl phosphines $Re_2(CO)_8[\mu\text{-}(L{-}L)]$ (L—L = dppm or dmpm) with alkynes[5] see above.



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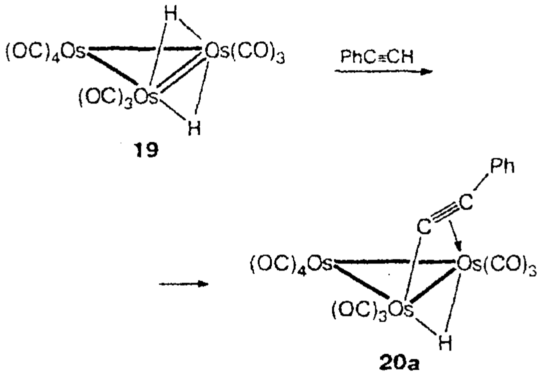
Complex **16** was also prepared by the reaction of $Re_2(\mu\text{-}H)(CO)_8(\mu\text{-}\eta^2\text{-}CH{=}CHMe)$ with an excess of phenylacetylene.[11] The reactions of $Re_2(CO)_8(NCMe)_2$ with phenylacetylene and 17α-ethynylestradiol yielded the complexes $Re_2(\mu\text{-}H)(CO)_7(NCMe)(\mu\text{-}\eta^2\text{-}C_2R)$ (**17:** R = Ph (**a**) or $C_{18}H_{25}O_2$ (**b**), respectively).[12]

The addition of $RC{\equiv}CLi$ (R = Alk or Ar) to $[Mo_2(CO)_4L_2]$ (L = η^5-Cp or $\eta^5\text{-}C_9H_7$ (Cp = C_5H_5)) afforded acetylide anionic complexes of composition $Li[Mo_2(CO)_4(L_2)(\mu\text{-}\eta^2\text{-}C_2R)]$ (**18**).[13]

Unsaturated carbonyl hydride $Os_3(\mu\text{-}H)_2(CO)_{10}$ (**19**) reacted with terminal alkynes at room temperature to form several products. However, only reactions with phenyl- and *tert*-butylacetylene yielded the clusters $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}C_2R)$ (**20:** R = Ph (**a**) or Bu^t (**b**), respectively) with the mode of acetylide-ligand coordination under consideration.[14,15]

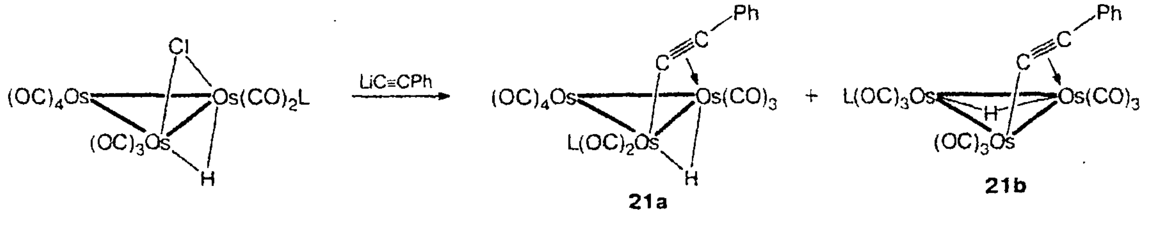


Cluster **20a** was also prepared as a result of the transfer of the acetylide ligand to the triosmium cluster in reactions of dihydride **19** with metallaalkynes $(OC)_5MC{\equiv}CPh$ (M = Mn or Re) or $(\eta\text{-}Cp)Fe(CO)_2(C{\equiv}CPh)$.[16,17]

The reaction of cluster **19** with $(OC)_5ReC{\equiv}CCOOMe$ proceeded differently to form the tetranuclear alkenyl complex $Os_3Re(CO)_{15}(\mu\text{-}\eta^2\text{-}CH{=}CHCOOMe)$.[18]

A method was developed[19] for the synthesis of triosmium clusters with the σ,π-acetylide ligand. The method involves the replacement of the bridging chlorine atom in the complexes $Os_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_9(L)$ (L = CO or PMe_2Ph) by the acetylide group under the action of lithium acetylide. This method was used for the preparation of complexes **3**[20] and **20** (**20:** R = Ph[19] (**a**) or $SiMe_3$[21] (**c**)) and isomeric complexes **21a** and **21b** of composition $Os_3(\mu\text{-}H)(CO)_9(PMe_2Ph)(\mu\text{-}\eta^2\text{-}C_2Ph)$ (Scheme 2).[19]

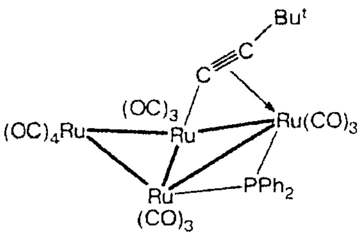
Scheme 2



Another method for the synthesis of triosmium clusters with the σ,π-acetylide ligand is based on the use of the complex $Os_3(CO)_{11}(NCMe)$ containing the labile acetonitrile ligand. Thus, the reaction of $Os_3(CO)_{11}(NCMe)$ with $Me_3SiC{\equiv}CH$ yielded complex **20c**.[21]

Goldphosphine analogs of hydride cluster **20a**, *viz.*, the complexes of composition $Os_3(AuL)(CO)_{10}(\mu\text{-}\eta^2\text{-}C_2Ph)$ (**22**: L = PPh_3 (**a**) or PMe_2Ph (**b**)), were prepared[22] by oxidative addition of goldalkynes $LAu(C{\equiv}CPh)$ to $Os_3(CO)_{10}(NCMe)_2$.

The tetraruthenium clusters of compositions $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2Bu^t)$ (**23**) and $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu_3\text{-}\eta^2\text{-}C_2Bu^t)(\mu\text{-}\eta^2\text{-}C_2Bu^t)(Ph_2PC{\equiv}CBu^t)$ (**24**) containing the μ-η²-acetylide ligand were formed upon thermolysis of $Ru_3(CO)_{11}(Ph_2PC{\equiv}CBu^t)$ and $Ru_3(CO)_9(Ph_2PC{\equiv}CBu^t)_3$, respectively.[23] These electron-rich 64-electron clusters possess a strongly flattened "butterfly" Ru_4 core containing two or three elongated Ru—Ru bonds.



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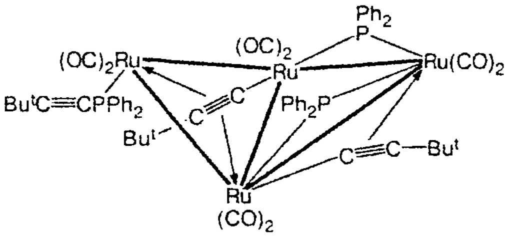

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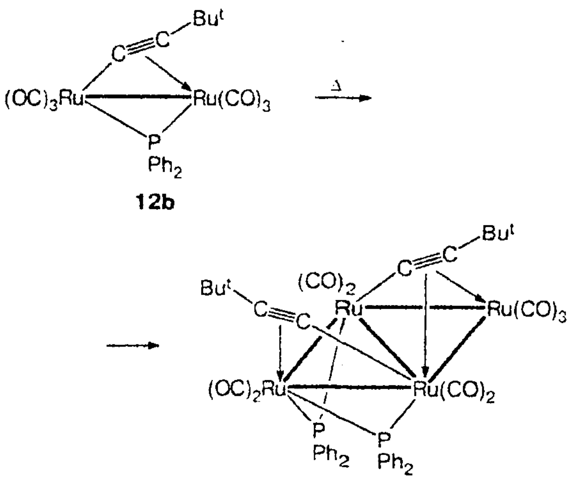
In cluster **23**, the metal core is almost planar and the dihedral angle between the Ru_3 triangles is 176.93°. In cluster **24**, the corresponding dihedral angle is 167.04°. In complex **23**, the C—Ru distances for the π-coordinated acetylenic α- and β-carbon atoms are substantially different (2.285(8) and 2.509(8) Å, respectively). In cluster **24**, the difference in the C—Ru bond lengths for the α- and β-carbon atoms of the μ-η²-acetylide ligand (2.292(7) and 2.620(8) Å, respectively) is even larger, which is indicative of a substantial weakening of the π-bond between the ligand and the ruthenium atom.

Thermolysis of the binuclear complex $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2Bu^t)$ (**12b**) in refluxing toluene afforded $Ru_4(CO)_9(\mu\text{-}PPh_2)_2(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-}C_2Bu^t)(\mu\text{-}\eta^2\text{-}C_2Bu^t)$ (**25**).[24] In this 64-electron cluster, the metal core is virtually planar. Only two Ru—Ru bond lengths have standard values (2.782(4)—2.858(4) Å), whereas the remaining three Ru—Ru bonds are noticeably elongated (3.021—3.097 Å). The C≡C bond lengths in the μ_3-η²:η²- and μ-η²-acetylide groups are 1.296(6) and 1.209(6) Å, respectively.



12b

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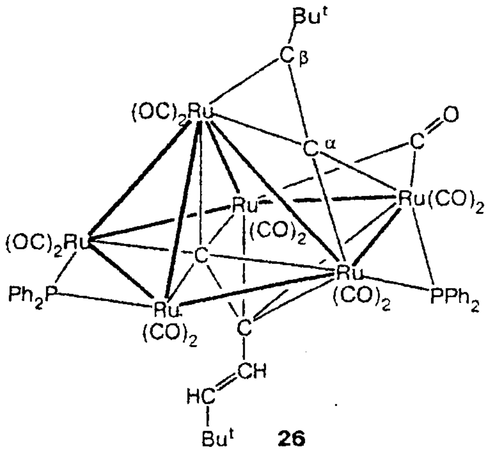
The structures of the metal cores in clusters **23**—**25** show a tendency to flattening of the "butterfly" and elongation of the Ru—Ru bond as the number of electrons donated by the ligands increases.

2.2.4. μ_3-η²-(σ,σ,π)-Bridges (*e*)

This rare mode of bonding of the acetylide ligand was found in the hexanuclear cluster $Ru_6(CO)_{12}(\mu\text{-}CO)(\mu\text{-}PPh_2)_2(\mu_6\text{-}C_2CH{=}CHBu^t)(\mu_3\text{-}C_2Bu^t)$ (**26**), which was obtained as one of the products upon thermolysis of the complex $\{Ru_3(\mu\text{-}H)(CO)_8(\mu_3\text{-}C_2Bu^t)\}_2(\mu\text{-}Ph_2PC{\equiv}CPPh_2)$ (**27**).[25] In cluster **26**, the Ru_6 core adopts a pentagonal-pyramidal configuration with the C_2Bu^t group being inserted at the $Ru_{(ap)}$—$Ru_{(basal)}$ edge. This group is bound only to three of four Ru atoms that form the "butterfly." The multiple bond length in the acetylide ligands is 1.245(8) Å and the distances from the C_α and C_β atoms to the π-bonded Ru atom are 2.211(6) and 2.269(6) Å, respectively.



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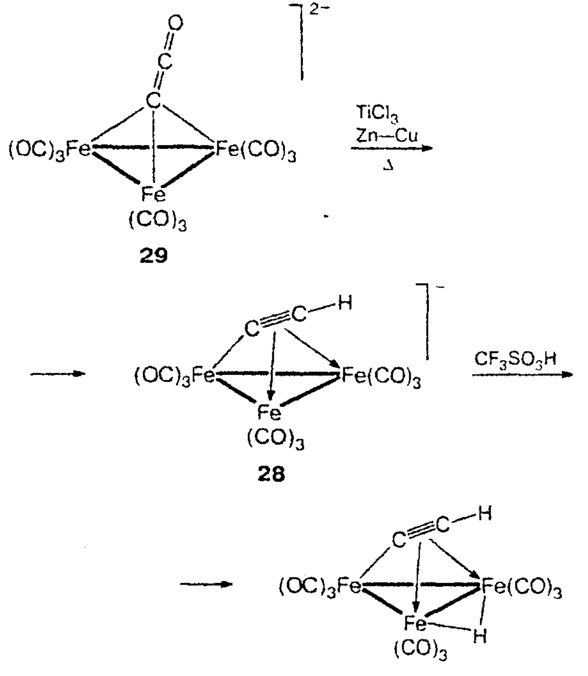
2.2.5. μ_3-η^2-(σ,π,π)-Bridges (*f*)

This mode of coordination is often observed in acetylide derivatives of cluster carbonyls and prevails in trinuclear 48-electron complexes. In this case, the acetylide ligand forms one σ-bond and two π-bonds with the metal core, thus acting as a donor of five electrons.

Hydridoacetylide complexes of composition $M_3(\mu\text{-H})(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2R)$ (M = Ru or Os) serve as classical examples of complexes with the mode of ligand coordination under consideration. These complexes were prepared in the early investigations on the chemistry of rutheniun and osmium carbonyls. These clusters are formed as a result of oxidative addition of terminal alkynes to the metal core. Interestingly, the reactions of $Fe_3(CO)_{12}$ with terminal alkynes did not afford $Fe_3(\mu\text{-H})(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2R)$. Hence, iron complexes of this type were prepared by indirect methods. For example, the anionic cluster $[Fe_3(CO)_9(C_2H)]^-$ (**28**) was synthesized by the reaction of ethoxyacetylene with the dianionic complex $[PPh_4]_2[Fe_3(CO)_{11}]$.[26a] More recently, this compound was synthesized by treatment of the ketenylidene dianionic complex of composition $[(Ph_3P)_2N]_2[Fe_3(CO)_9(CCO)]$ (**29**) with low-valence titanium compounds.[26b] The reaction of CF_3SO_3H with cluster **28** afforded $Fe_3(\mu\text{-H})(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2H)$ (**30**) in quantitative yield.



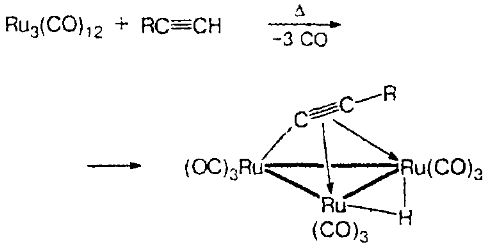
29

28

30

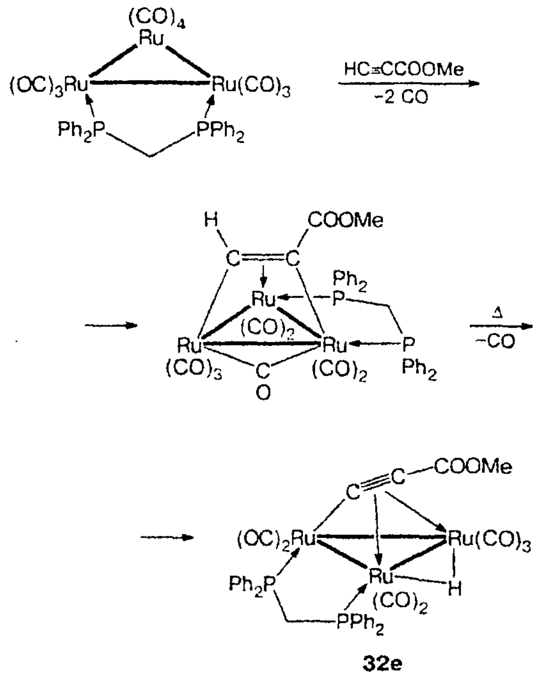
The cluster $Fe_3(\mu\text{-H})(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2SiMe_3)$ was unexpectedly obtained[27] upon condensation of a nickel vapor into a methylcyclohexane solution containing bis(trimethylsilyl)acetylene and $Fe(CO)_5$ at −120 °C. The reaction mechanism and the fate of metallic nickel remain unclear.

As mentioned above, the general method for the synthesis of the complexes $M_3(\mu\text{-H})(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2R)$ (M = Ru or Os) involves thermal reactions of trinuclear metal carbonyls with alkynes RC≡CH.[28] the yields of acetylide complexes depending substantially on the nature of both the R group in alkyne and the metal atom in the cluster. The procedure did not always afford the desired products in preparative yields, particularly, in the case of osmium complexes. This procedure was used for the synthesis of the ruthenium clusters $Ru_3(\mu\text{-H})(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2R)$ (**31**: R = Bu^t (**a**), Ph (**b**), CMe$_2$OH (**c**), C(Me)(Et)OH (**d**), C(Me)(Ph)OH (**e**), SiMe$_3$ (**f**), or Fc (**g**)).



31

The reactions of $Ru_3(CO)_{10}(\mu\text{-dppm})$ with terminal alkynes proceeded more selectively than those of $Ru_3(CO)_{12}$ to give the clusters $Ru_3(\mu\text{-H})(CO)_7(\mu\text{-dppm})(\mu_3\text{-}2\eta^2\text{-}C_2R)$ (**32**: R = Bu^t (**a**), Ph (**b**), C$_6$F$_5$ (**c**), SiMe$_3$ (**d**), or COOMe (**e**)) in high yields.[29] When the reaction was performed with methyl propiolate,[42] the intermediate alkyne complex $Ru_3(CO)_7(\mu\text{-CO})(\mu\text{-dppm})(\mu_3\text{-}\eta^2\text{-}HC_2COOMe)$ was isolated. Subsequent heating of the latter in THF afforded cluster **32e**.



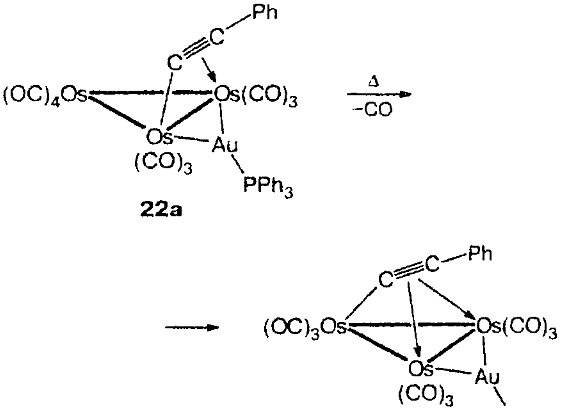
32e

The reaction of $Ru_3(CO)_{10}(\mu\text{-dpam})$ (dpam = $Ph_2AsCH_2AsPh_2$) with phenylacetylene afforded two isomeric complexes of composition $Ru_3(\mu\text{-H})(CO)_7(\mu\text{-dpam})(\mu_3\text{-}2\eta^2\text{-}C_2Ph)$ (**33** and **34**) in which the hydride ligand forms a bridge at different Ru—Ru edges of the metal triangle. These complexes do not undergo interconversion.[29]

The tetranuclear clusters $Ru_3(AuPR_3)(CO)_7(\mu\text{-dppm})(\mu_3\text{-}2\eta^2\text{-}C_2Ph)$ (**35**: R = Ph (**a**) or *p*-Tol (**b**)) were prepared[29] by the reaction of $Ru_3(CO)_{10}(\mu\text{-dppm})$ with $(PR_3)Au(C{\equiv}CPh)$.

In the early investigations of the chemistry of triosmium clusters, $Os_3(CO)_{12}$ was used as the starting compound for the preparation of acetylide derivatives. In these studies, the complexes $Os_3(\mu\text{-H})(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2R)$ (**36**: R = Bu^t (**a**), Ph (**b**), Me (**c**), or Et (**d**)) were synthesized for the first time.[30] The reactions involving osmium carbonyl proceed under drastic conditions and are characterized by low selectivity, except, probably, for alkyne Bu^{t}C≡CH (as in the case of the reaction with $Ru_3(CO)_{12}$). In a more efficient and convenient procedure for the synthesis of osmium clusters, dihydride **19** is used as the starting compound. Reactions of this dihydride with alkynes afforded the intermediate complexes $Os_3(CO)_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-}HC_2R)$ and then acetylides of composition $Os_3(\mu\text{-H})(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2R)$ (**36**: R = H (**e**), CH_2OH (**f**), CMe_2OH (**g**), $C(Me){=}CH_2$ (**h**), or Fc (**i**)[14,31–33]).

Nonacarbonyl hydride complexes of type **36** or their goldphosphine analogs were prepared by thermolysis of decacarbonyl complexes with the $\mu\text{-}\eta^2$-acetylide ligand. For example, the clusters $Os_3(\mu\text{-H})(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2SiMe_3)$[21] (**36k**) and $Os_3(AuL)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2Ph)$[22] (L = PPh_3 (**a**) or PMe_2Ph (**b**)) were prepared by the reactions of **20a**, **22a**, and **22b**, respectively. The related compounds with the ferrocenylacetylide ligand $M_3(AuPPh_3)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2Fc)$ (M = Ru or Os) were synthesized by the reactions of the anionic complex $[Ru_3(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2Fc)]^-$ with $ClAuPPh_3$ and of $Os_3(CO)_{10}(NCMe)_2$ with $FcC{\equiv}CAuPPh_3$, respectively.[34]

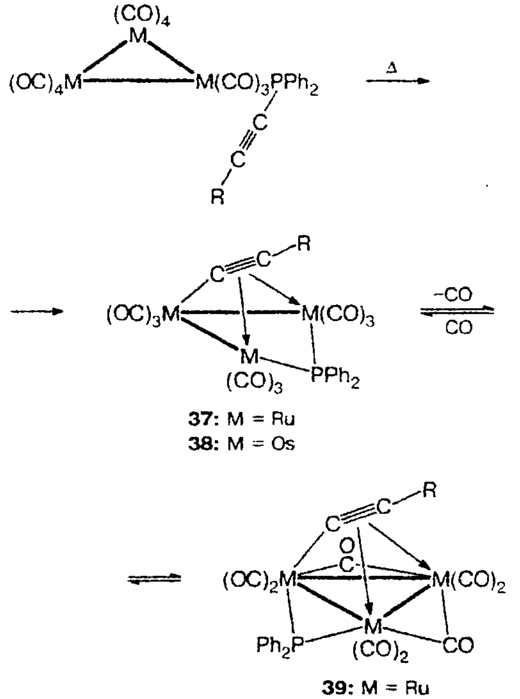

22a

The formation of the acetylide clusters $M_3(\mu\text{-H})(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2CPh_2OH)$ (M = Ru or Os)[35] in the reaction of $M_3(CO)_{12}$ with internal alkyne $HOPh_2CC{\equiv}CCPh_2OH$ involves the cleavage of the C_{sp}—C_{sp^3} bond.

The alkyne molecule can be very readily introduced into trimetallic ruthenium or osmium clusters using the acetonitrile derivatives $M_3(CO)_{12-n}(NCMe)_n$ (*n* = 1 or 2). The osmium derivatives are more stable and convenient for handling. Generally, the reactions are carried out at room temperature and alkyne clusters are obtained as primary products.[36–38] As mentioned above, decarbonylation of the latter afforded the acetylide complexes $M_3(\mu\text{-H})(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2R)$. This procedure was used for the preparation of ruthenium derivatives **31b,c** and **31h** (R = CH_2OMe)[34,36] and osmium derivatives **36a,c,d,h,i,k** and **36l** (R = CH_2CH_2OH).[31,34,38,39]

The reactions of $Ru_3(CO)_{12}$ with $XC{\equiv}CPh$ (X = Cl or Br) accompanied by the cleavage of the C—X bond afforded the complexes $Ru_3(\mu\text{-X})(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2Ph)$,[40] in which the bridging halogen atom donates three electrons resulting in the opening of the Ru_3 core, *i.e.*, the latter contains only two Ru—Ru bonds.

Complexes of composition $M_3(CO)_9(\mu\text{-}PPh_2)(\mu_3\text{-}2\eta^2\text{-}C_2R)$[9,41,42] (M = Ru (**37**) or Os (**38**); R = Pr^i (**a**) or Bu^t (**b**)) have analogous structures. These compounds were prepared upon controlled thermolysis of the carbonyl phosphine clusters $M_3(CO)_{11}(Ph_2PC{\equiv}CR)$. Thermolysis under more drastic conditions afforded complexes of composition $M_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^2{:}\eta^2\text{-}C_2R)$ (M = Ru (**39**) or Os (**40**); R = Pr^i (**a**) or Bu^t (**b**)). In these clusters, two bridging CO groups are located at the nonequivalent M—M edges of the newly formed M_3 triangle.[42]


37: M = Ru
38: M = Os
39: M = Ru
40: M = Os

The reactions of $M_3(CO)_{12}$ (M = Ru or Os) with $P(C{\equiv}CBu^t)_3$ gave rise[43] to complexes of composition $M_3(CO)_9\{\mu\text{-}P(C{\equiv}CBu^t)_2\}(\mu_3\text{-}2\eta^2\text{-}C_2Bu^t)$ isostructural to compounds **37** and **38**.

A series of heterometallic complexes with the μ_3-acetylide ligand were synthesized by reactions of mononuclear acetylides with metal carbonyls or their derivatives. Thus, the reaction of $(\eta\text{-}Cp)Fe(CO)_2(C{\equiv}CR)$ with $Co_2(CO)_8$ yielded the trinuclear complexes $Co_2\{\mu\text{-}2\eta^2\text{-}RC_2Fe(CO)_2(\eta\text{-}Cp)\}(CO)_6$ (R = Me or Ph).[44a–c] The reactions of $(\eta\text{-}Cp')Fe(CO)_2(C{\equiv}CH)$ ($Cp' = C_5H_5$ or C_5Me_5) with cobalt carbonyl proceed analogously.[44d] The ruthenium analog of the phenylacetylide complex was also prepared.[44e] The reaction of $Fe_2(CO)_6(\mu\text{-}SBu^t)(\mu\text{-}\eta^2\text{-}C_2SiMe_3)$ with $Co_2(CO)_8$ afforded the cluster $Fe_2Co(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2SiMe_3)$.[45] The compounds $(\eta\text{-}Cp)NiFe_2(CO)_6(\mu_3\text{-}2\eta^2\text{-}C_2R)$ (R = Pr^i or Bu^t) were synthesized by the reaction of $[(\eta\text{-}Cp)Ni(CO)]_2$ with $Ph_2PC{\equiv}CR$ and $Fe_2(CO)_9$ in refluxing heptane.[46a,b] The reactions of $Re_2(\mu\text{-}H)(CO)_8(\mu\text{-}\eta^2\text{-}C_2Ph)$ with $Co_2(CO)_8$ and $Cp_2Mo_2(CO)_6$ produced the clusters $ReCo_2(CO)_{11}(\mu_3\text{-}2\eta^2\text{-}C_2Ph)$ and $ReMo_2Cp_2(CO)_7(\mu_3\text{-}\eta^2{:}\eta^2\text{-}C_2Ph)$, respectively.[46c,d]

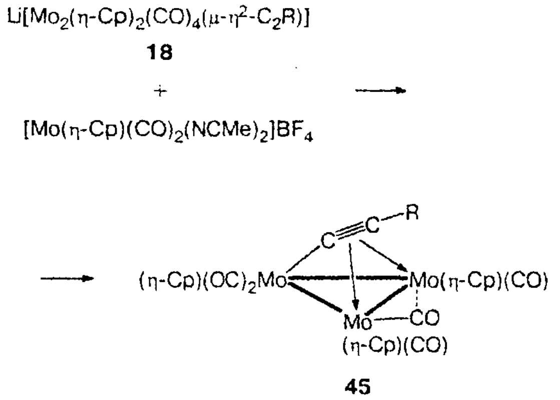
Heating of $(Ph_3P)_2(OC)_2IrC{\equiv}CPh$ with $Fe_2(CO)_9$ in refluxing heptane afforded a mixture of four complexes, *viz.*, $Fe(CO)_4(PPh_3)$, the acetylide clusters of compositions $Fe_2Ir(CO)_8(PPh_3)(\mu_3\text{-}2\eta^2\text{-}C_2Ph)$ and $Fe_2Ir(CO)_7(PPh_3)_2(\mu_3\text{-}2\eta^2\text{-}C_2Ph)$, and the alkyne cluster $FeIr_2(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)$, whose diyne ligand is formed as a result of coupling of two PhC_2 groups.[47]

The clusters $(\eta\text{-}Cp^*)WRe_2(CO)_8(\mu\text{-}CO)(\mu_3\text{-}2\eta^2\text{-}C_2R)$ ($Cp^* = C_5Me_5$; R = Ph or $C(Me){=}CH_2$) were prepared by the reactions of $(\eta\text{-}Cp^*)W(CO)_3(C{\equiv}CR)$ with $Re_2(CO)_8(NCMe)_2$.[48]

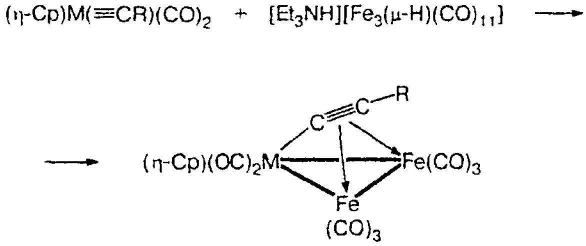
The reactions of $(\eta\text{-}Cp')W(CO)_3(C{\equiv}CPh)$ ($Cp' = C_5H_5$ or C_5Me_5) with $Ru_3(CO)_{12}$ and $Os_3(CO)_{10}(NCMe)_2$ yielded the trinuclear clusters $(\eta\text{-}Cp')WM_2(CO)_8(\mu_3\text{-}2\eta^2\text{-}C_2Ph)$ (M = Ru, $Cp' = C_5H_5$ (**41**) or C_5Me_5 (**42**); M = Os, $Cp' = C_5H_5$ (**43**) or C_5Me_5 (**44**)).[49] The reaction with the osmium complex afforded also the tetranuclear clusters $(\eta\text{-}Cp')WOs_3(CO)_{11}(\mu_4\text{-}C_2Ph)$.

Treatment of $[Mo(\eta\text{-}Cp)(CO)_2(NCMe)_2][BF_4]$ with the anionic acetylide complex $Li[Mo_2(\eta\text{-}Cp)_2(CO)_4(\mu\text{-}\eta^2\text{-}C_2R)]$ (**18**: R = Ph or Bu^t) gave rise to the trimolybdenum clusters $Mo_3(\eta\text{-}Cp)_3(CO)_4(\mu\text{-}CO)(\mu_3\text{-}\eta^2{:}\eta^2\text{-}C_2R)$ (**45**). This method can be used for the synthesis of heterometallic clusters. Thus, the reaction of $[Rh(NCMe)_2(nbd)][BF_4]$ (nbd is norbornadiene) with $Li[Mo_2(\eta\text{-}Cp)(CO)_4(\mu\text{-}\eta^2\text{-}C_2Ph)]$ yielded $Mo_2Rh(\eta\text{-}Cp)_2(nbd)(CO)_4(\mu_3\text{-}\eta^2{:}\eta^2\text{-}C_2Ph)$, whereas the analogous reaction of $[Ru(\eta\text{-}Cp)(CO)(NCMe)_2]^+$ with $Li[Mo_2(\eta\text{-}Cp)_2(CO)_4(\mu\text{-}\eta^2\text{-}C_2Bu^t)$ gave $Mo_2Ru(\eta\text{-}Cp)_3(CO)_4(\mu_3\text{-}\eta^2{:}\eta^2\text{-}C_2Bu^t)$.[13c]

Heating of a mixture of $(\eta\text{-}Cp)Mo(CO)_3(C{\equiv}CPh)$ and $Ru_3(CO)_{12}$ afforded the trinuclear cluster $(\eta\text{-}Cp)MoRu_2(CO)_8(\mu_3\text{-}2\eta^2\text{-}C_2Ph)$ (**46**) and the pentanuclear cluster $(\eta\text{-}Cp)_2Mo_2Ru_3(CO)_8(\mu\text{-}CO)_5(\mu_4\text{-}C_2Ph)$ (**47**) in 42 and 5% yields, respectively.[50]



The clusters $Fe_2M(\eta\text{-}Cp)(CO)_2(\mu_3\text{-}2\eta^2\text{-}C_2R)$ (M = Mo, R = Me (**48**); M = W, R = Me (**49**); or M = W, R = *p*-Tol (**50**)) were prepared upon heating of the carbyne complexes $M({\equiv}CR)(CO)_2(\eta\text{-}Cp)$ with the anionic cluster $[Et_3NH][Fe_3(\mu\text{-}H)(CO)_{11}]$.[51] The use of a ^{13}C-enriched $W({\equiv}{}^*CMe)({}^*CO)_2(\eta\text{-}Cp)$ sample in this reaction demonstrated that the carbonyl ligand served as a source of the α-carbon atom for the acetylide ligand in cluster **49**.

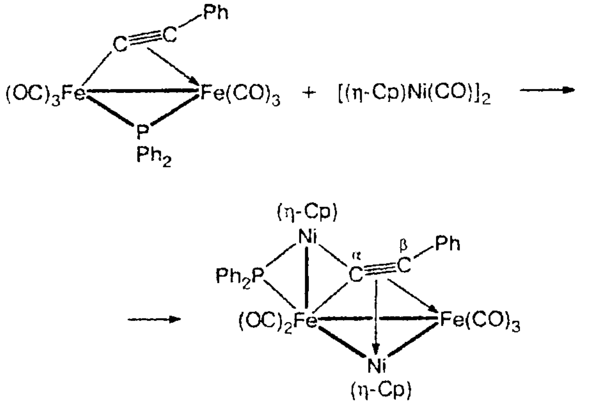


48: M = Mo, R = Me
49: M = W, R = Me
50: M = W, R = *p*-Tol

2.2.6. μ_4-η^2-(σ,σ,π,π)-Bridges (*g*)

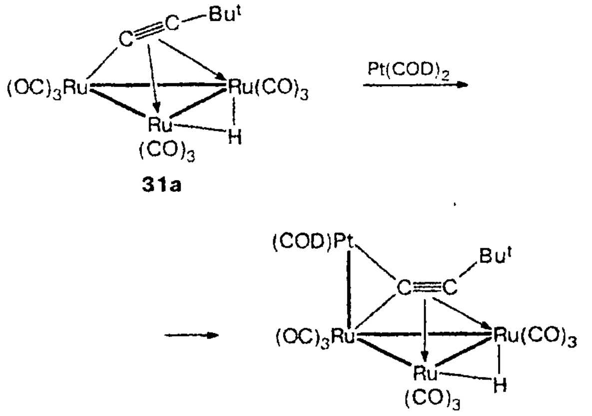
Generally, in clusters with an acetylide ligand of this type, the latter is coordinated not only to three atoms of the metal triangle, but also to the fourth metal atom, which is axially coordinated at one of the atoms of the metal triangle, through the acetylene C_α atom. The acetylide ligand in these complexes donates five electrons. In this case, the idealized bonding of the acetylide ligand can be considered as μ_4-η^2-(⊥)-coordination with the C_α—C_β bond being perpendicular to the M—M bond of the metal triangle. However, the strictly orthogonal mode of coordination of the acetylide ligand is generally disturbed. As a result, the carbon atoms of the acetylene group are located at different distances from the π-bonded metal atoms. An alternative situation involves the parallel configuration with the C_α—C_β bond of the acetylide being parallel to one of the M—M edges of the metal triangle resulting in the μ_4-η^2-(||)-σ,σ,σ,π-mode of coordination. However, in the case of clusters containing four or more metal atoms, these structures can not always be unambiguously distinguished.

The μ_4-η^2-(⊥)-mode of coordination of the acetylide ligand was observed in the complex $Cp_2Ni_2Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C_2Ph)$ (**51**), which was prepared by the reaction of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2Ph)$ with $[CpNi(CO)]_2$.[52]



51

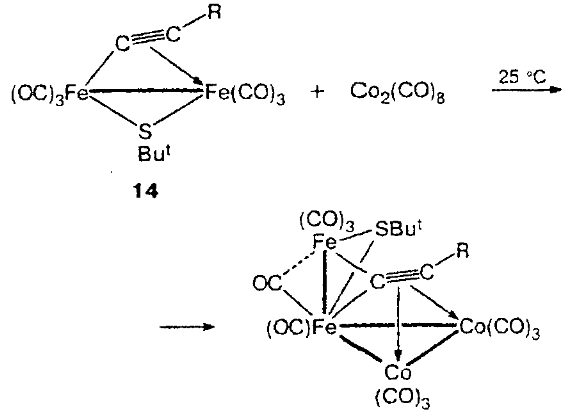
In the cluster $(COD)PtRu_3(\mu\text{-}H)(CO)_9(\mu_4\text{-}\eta^2\text{-}C_2Bu^t)$ (**52**), prepared[53] by the reaction of $Pt(COD)_2$ (COD is cycloocta-1,5-diene) with $Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2Bu^t)$ (**31a**), the angle between the directions of the C_α—C_β and Ru—Ru bonds is 98.5°. As a result, the C_α atom is located at different distances from the above-mentioned ruthenium atoms (2.291(5) and 2.484(5) Å).



52

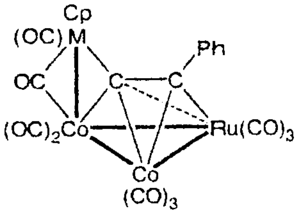
Treatment of cluster **52** with bis(diphenylphosphino)ethane (dppe) afforded the hydridoacetylide complex $Ru_3Pt(\mu\text{-}H)(CO)_9(dppe)(\mu_4\text{-}\eta^2\text{-}C_2Bu^t)$ (**53**) and the tautomeric vinylidene complex $Ru_3Pt(CO)_9(dppe)(\mu_4\text{-}\eta^2\text{-}C{=}C(H)Bu^t)$ (**54**).[53] In cluster **53**, the distances from the C_α atom to the ruthenium atoms bound through the hydride bridge differ only slightly (2.396(6) and 2.427(6) Å). As a result, the angle between the C_α—C_β vector and the Ru—Ru bond is 91.3°, and the conformation is closer to strictly orthogonal geometry than that observed in complex **52**.

The reactions of $Fe_2(CO)_6(\mu\text{-}SBu^t)(\mu\text{-}\eta^2\text{-}C_2R)$ (**14**: R = Ph or Bu^t) with $Co_2(CO)_8$ (THF, 25 °C) afforded heterometallic clusters of composition $Fe_2Co_2(CO)_{10}(\mu\text{-}CO)(\mu\text{-}SBu^t)(\mu_4\text{-}\eta^2\text{-}C_2R)$ (**55**).[45]

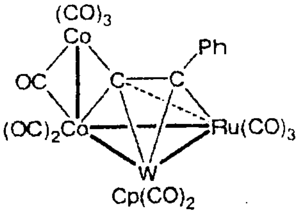


55

The reactions of $CpM(CO)_2(C{\equiv}CPh)$ (M = Fe or Ru) or $CpW(CO)_3(C{\equiv}CPh)$ with $RuCo_2(CO)_{11}$ yielded the corresponding tetranuclear clusters $CpMRuCo_2(CO)_9(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}C_2Ph)$ (M = Fe (**56**) or Ru (**57**)) and $CpWRuCo_2(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}C_2Ph)$ (**58**). According to the results of X-ray diffraction analysis, the orientation of the PhC_2 group in these compounds is such that the C_α atom is located at distances of 2.60(1) and 2.39(1) Å from the Ru and W atoms, respectively. The coordination of the PhC_2 group in these complexes is believed to deviate from μ_4-η^2-(⊥)-coordination, approximating the parallel μ_4-η^2-(||)-coordination.[54]

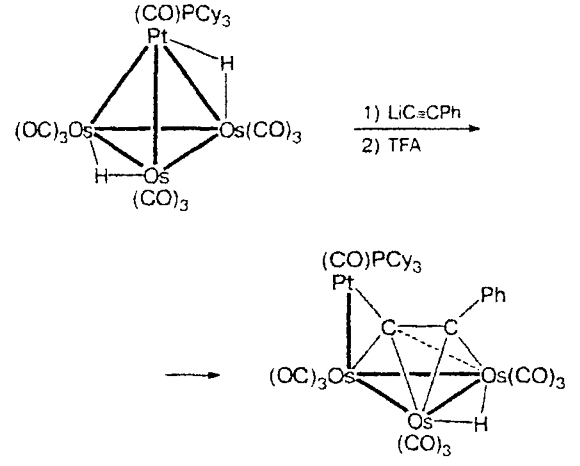


56: M = Fe
57: M = Ru



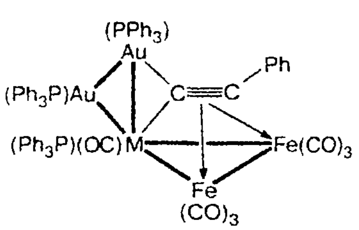
58

Treatment of the tetrahedral electron-deficient cluster $Os_3Pt(\mu-H)_2(CO)_{10}(PCy_3)$ with lithium phenylacetylide followed by acidification of the reaction mixture with an excess of CF_3COOH afforded the complex $Os_3Pt(\mu-H)(CO)_{10}(PCy_3)(\mu_4-\eta^2-C_2Ph)$ (**59**).[55] In this complex, the C_α—C_β vector is not perpendicular to the opposite Os—Os axis and deviates from orthogonal alignment by 10°. As a result, the C_α atom is located at distances of 2.59(1) and 2.40(1) Å from two Os atoms.



59

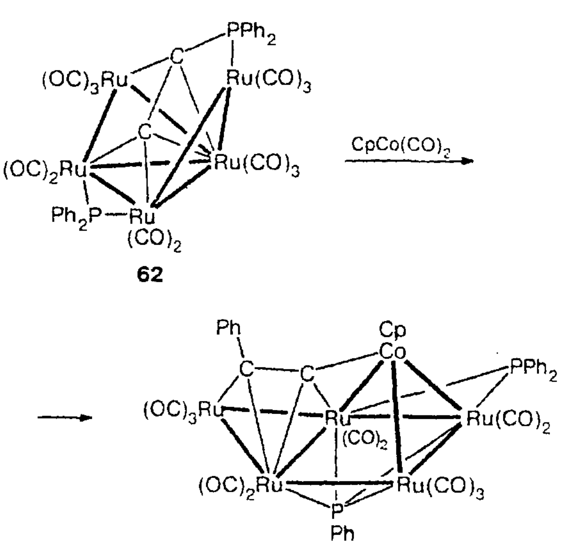
The pentanuclear clusters $Au_2Fe_2M(CO)_7(PPh_3)_3(\mu_4-\eta^2-C_2Ph)$[56] (**60**: M = Rh (**a**) or Ir (**b**)) were synthesized by auration of the clusters $Fe_2M(CO)_8(PPh_3)(\mu_3-2\eta^2-C_2Ph)$ (M = Rh, Ir) under the action of $[O\{Au(PPh_3)_3\}_3][BF_4]$ in the presence of $[(Ph_3P)_2N][Co(CO)_4]$. The mode of coordination of the acetylide ligand in **60b** may be considered as a distorted $\mu_4-\eta^2-(\perp)$-coordination, the angle between the C_α—C_β axis and the Fe—Fe bond being equal to 103°.



60a,b

M = Rh (**a**), Ir (**b**)

An analogous mode of coordination of the acetylide ligand was observed in the clusters $CpCoRu_5(CO)_{12}(\mu-PPh_2)(\mu_4-PPh)(\mu_4-\eta^2-C_2Ph)$ (**61**) (prepared by the reaction of $Ru_5(CO)_{13}(\mu-PPh_2)(\mu_5-C_2PPh_2)$ (**62**) with $CpCo(CO)_2$)),[57a] $Co_2Ru_3(\mu-CO)_2(CO)_9(\mu-dppm)(\mu_4-C_2Ph)(\mu_3-C_2Ph)$ (generated by the reaction of complex $Ru_3(CO)_8(\mu-dppm)(\mu_3-\eta^2-PhC_2C{\equiv}CPh)$ with $Co_2(CO)_8$)),[57b] and $Mo_2Ru_3(CO)_{11}(\mu_3-S)(\mu_4-C_2Ph)Cp_2$.[57c]

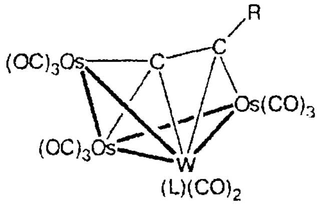


61

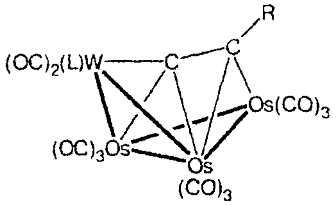
2.2.7. $\mu_4-\eta^2-(\sigma,\sigma,\sigma,\pi)$-Bridges (*h*)

This mode of coordination of acetylide ligands is usually observed in clusters with the metal core adopting the "butterfly" configuration. The C_α atom forms two σ-bonds with two metal atoms of one of the wings of the "butterfly" and the C_β atom forms an identical bond with the metal atom located in the wingtip position of the second wing. The multiple bond of the RC_2 ligand forms a π-bond with one of the metal atoms occupying the hinge positions of the "butterfly" core. Generally, the ligand in this case is assumed to donate five electrons.

The reactions of $CpW(CO)_3(C{\equiv}CR)$ (R = Ph or Bu^t) with $Os_3(CO)_{10}(NCMe)_2$ afforded the tetranuclear complexes $CpWOs_3(CO)_{11}(\mu_4-\eta^2-C_2R)$ (R = Ph (**63a**) or Bu^n (**64a**))[58] along with the trinuclear clusters $CpWOs_2(CO)_8(\mu_3-\eta^2:\eta^2-C_2R)$.



63a: L = Cp, R = Ph
64a: L = Cp, R = Bu^n
65: L = Cp*, R = CH_2OMe

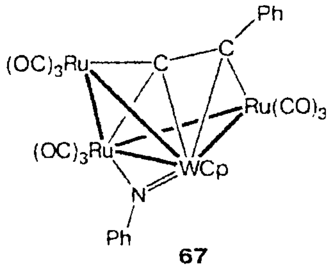


66: L = Cp*, R = CH_2OMe

In cluster **63**, the W atom occupies the hinge position of the "butterfly" and is π-coordinated to the acetylide group. This coordination may be considered as σ,σ,π-parallel (the mode of coordination typical of μ_3-alkyne trinuclear clusters) with respect to the WOs_2 triangle.[58]

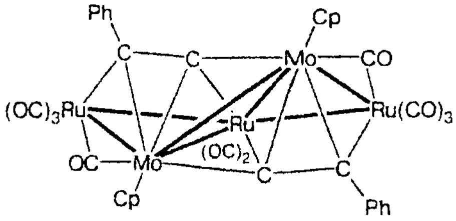
The reaction of $Cp^*W(CO)_3(C{\equiv}CCH_2OMe)$ with $Os_3(CO)_{10}(NCMe)_2$ yielded two isomeric complexes of composition $Cp^*WOs_3(CO)_{11}(C_2CH_2OMe)$[59] (**65** and **66**). The metal core in these complexes adopts the "butterfly" configuration. However, these complexes differ in the position of the W atom in the core, *viz.*, this atom occupies the hinge and wingtip positions of the wing in **65** and **66**, respectively.

The reaction of $CpW(CO)_3(C{\equiv}CPh)$ with complex $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$ afforded the cluster $CpWRu_3(CO)_9(\mu\text{-}NPh)(\mu_4\text{-}\eta^2\text{-}C_2Ph)$ (**67**) containing the bridging imide and acetylide ligands.[60] The $C_\alpha{-}C_\beta$ distance in the acetylide ligand (1.20(1) Å) is unusual for a μ_4-η^2-coordinated group.



67

The Mo_2Ru_3 core in the pentanuclear cluster $Cp_2Mo_2Ru_3(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}\eta^2\text{-}C_2Ph)_2$ (**47**), which was prepared by the reaction of $CpMo(CO)_3(C{\equiv}CPh)$ with $Ru_3(CO)_{12}$, possesses the double "butterfly" geometry with two equivalent acetylide ligands coordinated at opposite sides.[50]

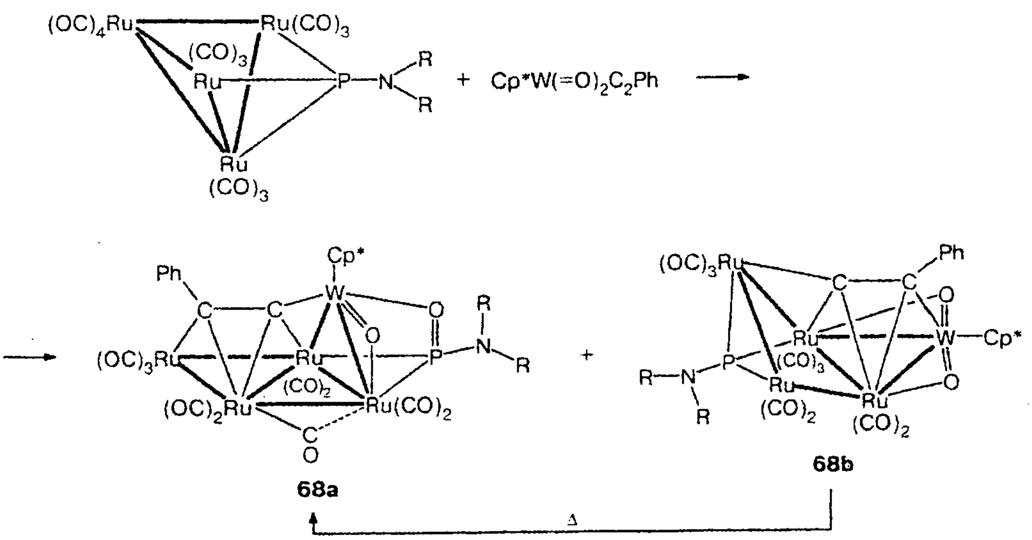


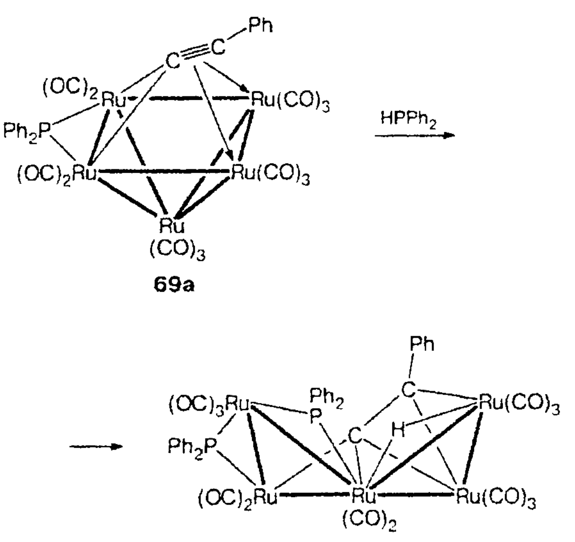
47

The reactions of the aminophosphinide cluster $Ru_4(CO)_{13}(\mu_3\text{-}PNR_2)$ (R = Pr^i or Cy)[61] with $Cp^*W(O)_2(C{\equiv}CPh)$ afforded complexes of compositions $Cp^*W(\mu\text{-}O)Ru_4(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{-}P(O)NR_2\}(\mu_4\text{-}\eta^2\text{-}C_2Ph)$ (**68a**) and $Cp^*W(\mu\text{-}O)_2Ru_4(CO)_{10}(\mu_3\text{-}PNR_2)(\mu_4\text{-}\eta^2\text{-}C_2Ph)$ (**68b**), respectively. The rearrangement **68b→68a** was observed upon heating in refluxing heptane (Scheme 3).[62]

Oxidative addition of $HPPh_2$ to the pentanuclear complex $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_4\text{-}2\eta^2\text{-}C_2R)$ (**69a**, R = Ph) containing the tetragonal-pyramidal metal core afforded the cluster $Ru_5(\mu\text{-}H)(CO)_{13}(\mu\text{-}PPh_2)_2(\mu_4\text{-}\eta^2\text{-}C_2R)$ (**70**). The metal core of the latter adopts a "bow tie" conformation and the acetylide ligand forms three σ-bonds and one π-bond with the core.[63]

Scheme 3

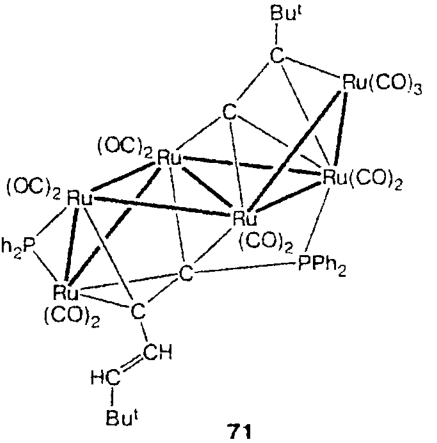




69a

70

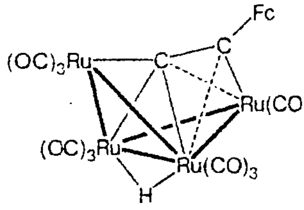
The ruthenium cluster $Ru_6(CO)_{13}(\mu\text{-}PPh_2)(\mu_5\text{-}Bu^tCH{=}CHC_2PPh_2)(\mu_4\text{-}C_2Bu^t)$ (**71**) was prepared along with complex **26** upon thermolysis of cluster **27**.[25]



71

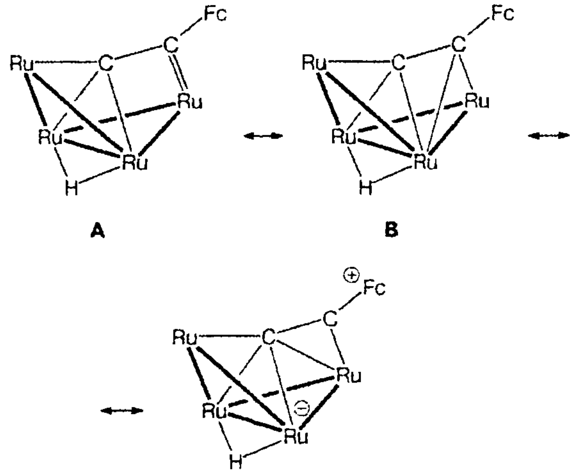
2.2.8. μ_4-Bridges (*i*)

The reaction of $Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2Fc)$ (**31g**) with $Ru_3(CO)_{12}$ yielded the cluster $Ru_4(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}C_2Fc)$ (**72**). The heterometallic analog $RuOs_3(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}C_2Fc)$ (**73**) was synthesized starting from $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2Fc)$ (**36i**). The metal core of complex **72** adopts a "butterfly" configuration with the dihedral angle between the Ru_3 wings of 127.6°. The acetylide C_α atom is symmetrically located above the plane of the Ru_3 isosceles triangle of one of the wings and forms bonds with all vertices of this triangle. The C_β atom is bound to the Ru atom located in the wingtip position of the second Ru_3 wing of the "butterfly." Two additional contacts between the ligand and the metal core with $C_\alpha{-}Ru_{top}$ and $C_\beta{-}Ru_{nod}$ distances of 2.58(1) and 2.76(1) Å, respectively, are observed (these distances are indicated by dashed lines in Fig. 1, *i*).[64]



72

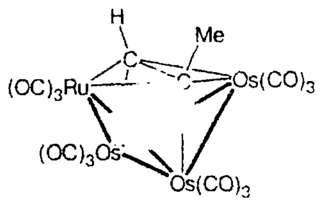
Based on the data of ^1H and ^{13}C NMR spectroscopy and X-ray diffraction analysis, it was suggested[65] that the coordination of the acetylide ligand in complex **72** should be described by three resonance structures **A**, **B**, and **C**. Structure **A** containing the carbyne-carbene ligand seems to be reasonable if the above-mentioned distances (2.58(1) and 2.76(1) Å) are considered as nonbonded. The validity of structure **B** follows from the ^{13}C NMR spectral data, which demonstrated that the ruthenium atoms of the $Ru(\mu\text{-}H)Ru$ fragment are nonequivalent (at −40 °C, the localized exchange was observed only for three CO groups at one of the Ru atoms). The contribution of bipolar structure **C** is evident from the inclination of the exocyclic bond at the ferrocene unit toward the iron atom (which is typical of α-ferrocenyl carbocations) as well as from a rather substantial deshielding of the protons of the ferrocenyl group in the ^1H NMR spectrum.



A **B**

C

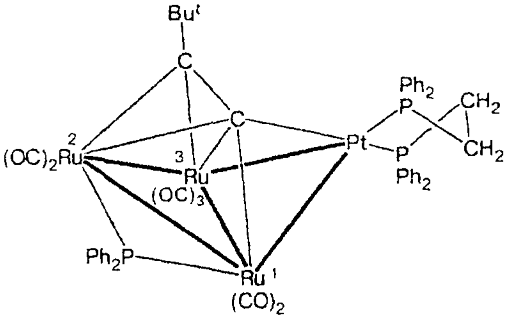
The unique features of these compounds indicate that the ferrocenyl group is of importance in the formation/stabilization of clusters **72** and **73**. Thus, unlike **36i**, the isostructural cluster $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2Me)$ (**36c**) reacted with $Ru_3(CO)_{12}$ to form the alkyne cluster of composition $RuOs_3(CO)_{12}(\mu_4\text{-}HC_2Me)$ (**74**) with the "butterfly"-type core rather than the hydridoacetylide cluster related to compounds **72** and **73**.[66] Apparently, the hypothetical hydridoacetylide complex of composition $RuOs_3(\mu-H)(CO)_{12}(\mu_4-C_2Me)$ should be the precursor of cluster **74**.



74

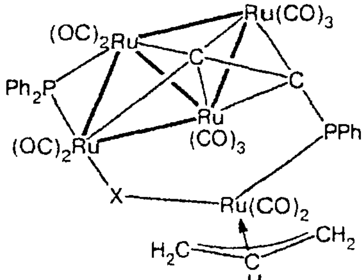
The synthesis of the cluster $Ru_3Pt(CO)_7(\mu-PPh_2)(dppe)(\mu_4-\eta^2-C_2Bu^t)$ (**75**) by the reaction of $Ru_3Pt(\mu-H)(CO)_9(dppe)(\mu_4-\eta^2-C_2Bu^t)$ (**53**) with $Ph_2PC{\equiv}CPPh_2$ was reported.[67] In cluster **75**, the acetylide ligand is rotated so that the angle between the $C_\alpha-C_\beta$ and Ru(2)—Ru(3) bonds is 99.8°. The dihedral angle between the wings of the "butterfly" is 126.7(1)°. It is believed that the acetylide ligand in this cluster donates five electrons.[67]

In cluster **75**, the geometry of the acetylide ligand relative to the metal core can be considered as a model of an intermediate not only for tautomerization **53** $\rightleftharpoons$ **54** (Scheme 4) (see Section 2.2.6), but also for the hydridoacetylide cluster → alkyne cluster isomerization pathway of the clusters with the "butterfly" core.



75

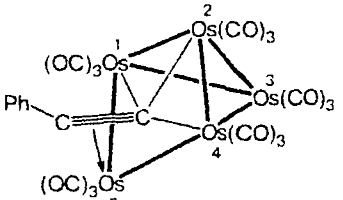
A configuration of the acetylide ligand similar to that observed in cluster **75** was found in the complex $Ru_4(CO)_{10}(\mu-PPh_2)(\mu-Cl)\{\mu_4-C_2PPh_2Ru(CO)_2(\eta-C_3H_5)\}$ (**76a**).[68] This compound and its analog (**76b**, X = Br) were prepared by reactions of $Ru_5(CO)_{13}(\mu-PPh_2)(\mu_5-C_2PPh_2)$ (**62**) with $CH_2{=}CHCH_2X$ (X = Cl or Br, respectively).



76

2.2.9. μ_4-η^2-(σ,σ,σ,π)-Bridges (*j*)

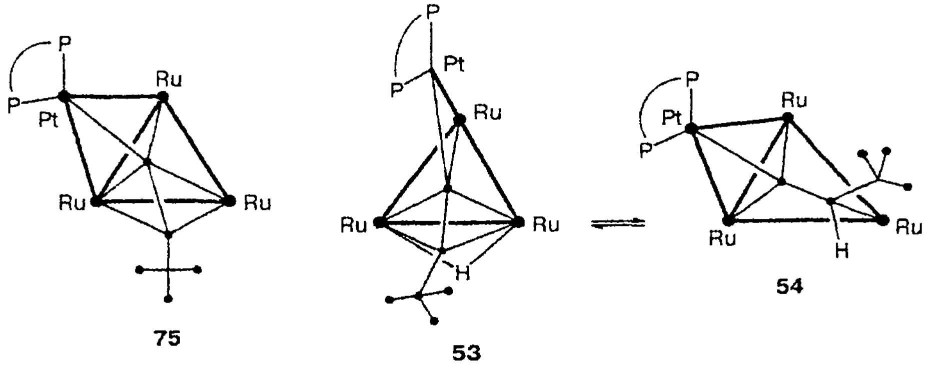
The pentanuclear cluster $Os_5(\mu-H)_2(CO)_{15}$ reacted with phenylacetylene to form $Os_5(\mu-H)_2(CO)_{15}(\mu_4-\eta^2-C_2Ph)$ (**77**).[69] The hydride ligands in complex **77** were not directly located by X-ray diffraction analysis. However, it was suggested that these ligands bridge the elongated Os(1)—Os(3) and Os(3)—Os(4) edges. The distance between the acetylene carbon atoms (1.49(3) Å) indicates that the order of the acetylene bond substantially decreases upon coordination. It is believed that the PhC_2 ligand in cluster **77** serves as a donor of four electrons.

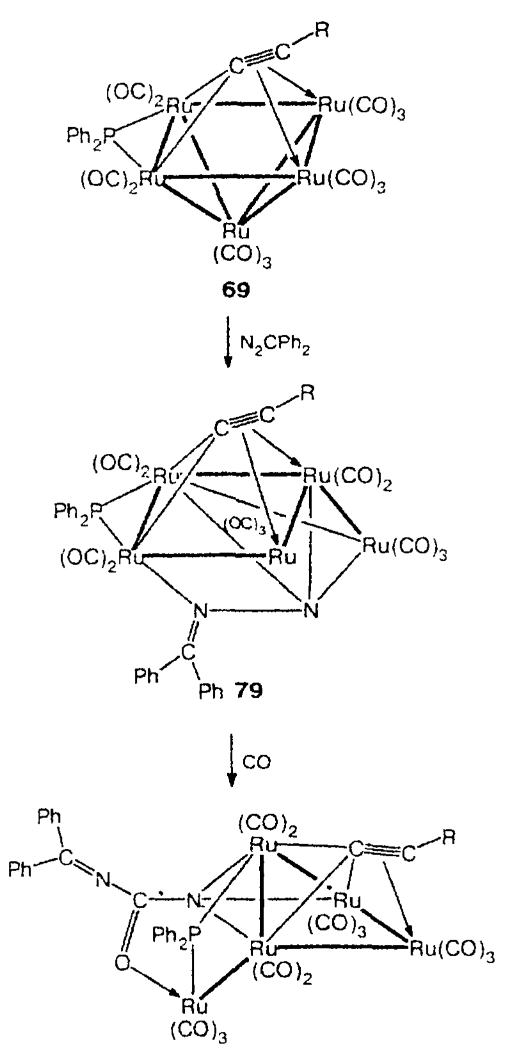


77

An analogous mode of coordination of the acetylide ligand was also observed in the ruthenium complexes of

Scheme 4





69

79

78

composition $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C_2R)\{\mu_4\text{-}NC(O)NCPh_2\}$ (**78**: R = Ph (**a**) or Pr^i (**b**)).[70] These compounds were formed by the reactions of the clusters $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_4\text{-}2\eta^2\text{-}C_2R)$ (**69a,b**) with diphenyldiazomethane N_2CPh_2 followed by carbonylation of the resulting complexes of composition $Ru_5(CO)_{12}(\mu\text{-}PPh_2)(\mu_4\text{-}2\eta^2\text{-}C_2R)(\mu_4\text{-}N_2CPh_2)$ (**79a,b**). The acetylene bond length in cluster **78b** is 1.32 Å.

2.2.10. μ_4-η^2-(σ,σ,π,π)-Bridges (*k*)

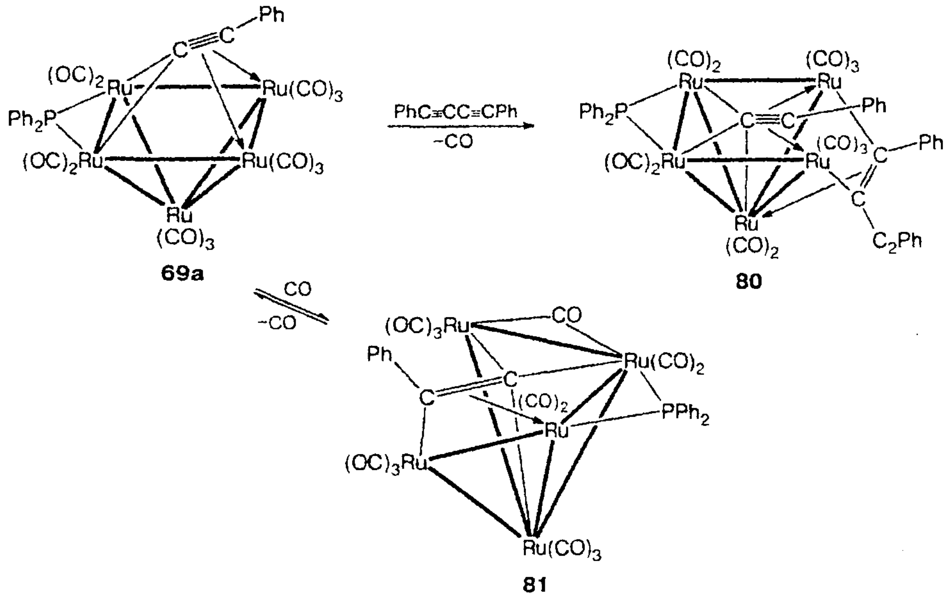
The geometry of clusters with this type of bonding differs from that considered in Section 2.2.6 in that four metal atoms coordinated by the acetylide ligand form a square.

The square-pyramidal pentaruthenium clusters $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_4\text{-}2\eta^2\text{-}C_2R)$ (**69**: R = Ph (**a**), Pr^i (**b**), or Bu^t (**c**)) were prepared upon heating of $Ru_3(CO)_{11}(Ph_2PC{\equiv}CR)$ in refluxing heptane.[71] X-ray diffraction study of complex **69a** demonstrated that the five-electron acetylide ligand is located above the square plane of the cluster.[71b] The rather large C_α—C_β bond length (1.342(11) Å) in this complex is close to the length of the multiple bond in olefins. This mode of bonding of the acetylide ligand was also observed in the nickel-ruthenium cluster $NiRu_4(CO)_9(\mu\text{-}PPh_2)_2(\mu_4\text{-}\eta^2\text{:}\eta^2\text{-}C_2Pr^i)_2$ in spite of the fact that it contains the "butterfly" Ru_4 core tightened by the Ni(CO) group.[71c]

2.2.11. μ_5-η^2-(σ,σ,σ,π,π)-Bridges (*l*)

The reaction of the pentanuclear cluster $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_4\text{-}2\eta^2\text{-}C_2Ph)$ (**69a**) (Scheme 5) with

Scheme 5



69a

80

81

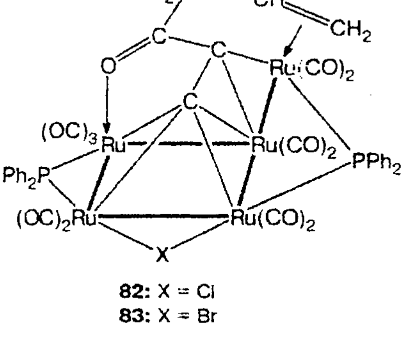
diphenylbutadiyne afforded the cluster $Ru_5(CO)_{12}(\mu$-$PPh_2)(\mu_3$-η^2-$PhC_2C{\equiv}CPh)(\mu_5$-η^2-$C_2Ph)$ (**80**).[72] In the course of the synthesis of **80**, one of the Ru—Ru bonds in the starting complex is cleaved due to donation of four electrons upon the addition of the diyne ligand. In this case, the acetylide C_α atom is coordinated to all five metal atoms of the cluster. The C_α—C_β bond length is 1.34[illegible](9) Å.

2.2.12. μ_5-η^2-($\sigma,\sigma,\sigma,\sigma,\pi$)-Bridges (*m*)

Treatment of a solution of cluster **69a** in THF with carbon monoxide yielded the adduct $Ru_5(CO)_{13}(\mu$-$CO)(\mu$-$PPh_2)(\mu_5$-η^2-$C_2Ph)$ (**81**); the reaction was reversible (Scheme 5).[71] Lewis bases, such as MeCN, PhCN, $Pr^i{}_2NH_2$, Bu^sNH_2, or Py, also added to **69a** to form structurally similar adducts.

The pentanuclear metal core of complex **81** consists of three Ru_3 triangles. The central triangle shares two vertices with the other two triangles. Alternatively, this core can be considered as a double "butterfly." The acetylide ligand is coordinated to five ruthenium atoms of the cluster. The α-carbon atom is coordinated to three metal atoms of the inner surface of one of the Ru_3 triangles and the β-carbon atom is involved in the formation of both a π-bond with the fourth hinge Ru atom and a simple σ-bond with the fifth metal atom. The "acetylene" bond in cluster **81** is noticeably longer (1.39(1) Å) than that in its precursor **69a** (1.342(9) Å).

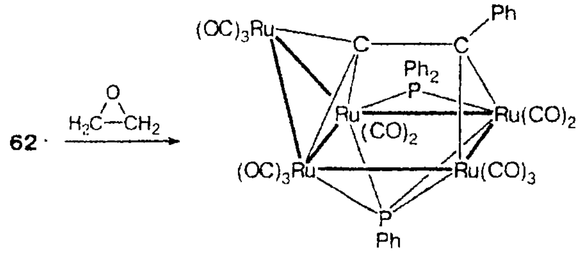
Yet another example of this type of bonding of the acetylide ligand was found in the clusters $Ru_5(CO)_{11}(\mu$-$PPh_2)_2(\mu$-$X)\{\mu_5$-$CCC(O)CH_2CH{=}CH_2\}$ (X = Cl (**82**) or Br (**83**)).[68] The latter were formed along with clusters **76a,b** by the above-described (Section 2.2.8) reactions of $Ru_5(CO)_{13}(\mu$-$PPh_2)(\mu_5$-$C_2PPh_2)$ (**62**) with allyl halides. X-ray diffraction study of cluster **83** demonstrated that the C_α atom is bound to all ruthenium atoms of the Ru_4 rhombus. Strong bonds between the C_α atom and three Ru atoms may be indicative of a somewhat carbyne character of the former. The acetylide ligand forms a π-bond with one of the metal atoms of the Ru_4 rhombus and the C_β atom forms a σ-bond with the fifth ruthenium atom. The C_α—C_β distance in the "acetylide" ligand of this complex is 1.47(5) Å.



82: X = Cl
83: X = Br

2.2.13. μ_5-Bridges (*n*)

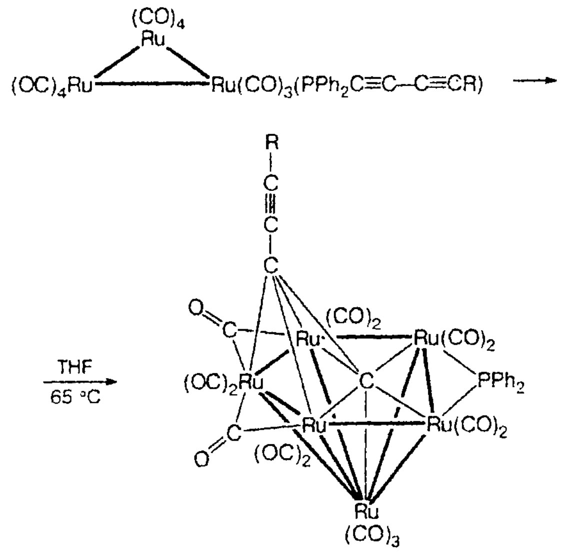
The reaction of $Ru_5(CO)_{13}(\mu$-$PPh_2)(\mu_5$-$C_2PPh_2)$ (**62**) with ethylene oxide (benzene, 100 °C, a Carius tube) afforded the cluster $Ru_5(CO)_{13}(\mu$-$PPh_2)(\mu_4$-$PPh)(\mu_5$-$C_2Ph)$ (**84**) as the major compound. The rhombic metal core of this complex is formed by four ruthenium atoms. One edge of the rhombus is bound *via* the bridging ruthenium atom.[73] One of the acetylide atoms, *viz.*, C_α, is coordinated to three atoms of the Ru_3 triangle and the second carbon atom, *viz.*, C_β, is coordinated to two other ruthenium atoms of the opposite edge of the metal rhombus. The distance between the "bridging" ruthenium atom and the C_α atom is 1.965(6) Å, which is indicative of some degree of double-bond character of these atoms (the carbenoid character). The C_α—C_β bond length in cluster **84** is 1.395(8) Å.



84

2.2.14. μ_6-Bridges (*o*)

The hexaruthenium clusters $Ru_6(CO)_{13}(\mu$-$CO)_2(\mu$-$PPh_2)(\mu_6$-$C_2C{\equiv}CR)$ (R = Bu^t (**85**) or Ph (**86**)) were isolated from products of thermolysis of the complexes $Ru_3(CO)_{11}(PPh_2C{\equiv}C$-$C{\equiv}CR)$ in 3.2 and 1.2% yields, respectively.[74] According to the results of X-ray diffraction study, complex **85** contains a pentagonal-pyramidal metal core, a geometry being hitherto unknown for Ru_6 clusters. The $C_\alpha{\equiv}C_\beta$—$C_\gamma{\equiv}CBu^t$ fragment resulting from the cleavage of the P—C bond in the starting complex is bound to the Ru_6 core through the C_α and C_β atoms in a very complex mode. The C_α atom is coordinated to five ruthenium atoms in a manner similar to the mode of coordination of the carbide atom in the cluster $Ru_5C(CO)_{15}$ and is located above the basal plane (at a distance of 0.26 Å) passing through four ruthenium atoms. The ^{13}C NMR spectra of complexes **85** and **86** have a signal of the C_α atom at very low field (δ ≅ 303), *i.e.*, in the region more commonly associated with an interstitial carbon atom in transition metal clusters, which is indicative of the carbide character of this atom. The C_β atom of the hydrocarbon ligand, like the alkylidyne group, forms σ-bonds with three ruthenium atoms. These interactions cause an elongation of the $C_\alpha{\equiv}C_\beta$ bond to 1.458(7) Å, *i.e.*, this distance is greater than the length of the formally single C_β—$C\gamma$ bond (1.435(6) Å).



85: R = Bu^t
86: R = Ph

The authors[74] believed that the bonding of the diynyl ligand observed in cluster **85** can be considered as that of the alkylidyne-carbide type. In this case "carbide" (μ_5-C$_\alpha$, 4ē) and "alkylidyne" (μ_3-C$_\beta$, 3ē) donate a total of seven electrons, but the ligand retains the C—C bond.

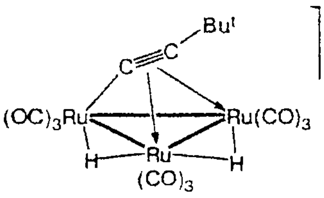
3. Reactivity of cluster acetylides

It is known that mononuclear η^1-acetylide complexes react with electrophiles at the acetylenic β-carbon atom to form cationic vinylidene complexes.[2] The nucleophilic addition is typical of multidentate acetylide ligands in cluster complexes, unlike mononuclear systems. In the complexes under consideration, the carbon atoms of the acetylide ligand have the *carbocationic* character,[1b] which is manifested in the fact that uncharged P-, N-, O-, or C-nucleophiles can readily add to these atoms.

Below are considered reactions of different reagents with acetylide ligands, except for reactions of coordinatively unsaturated metal fragments (such as Pt(COD), *etc.*) with the participation of the M—C$_\alpha$ bond of the acetylide ligand discussed in the preceding section. Examples of the cleavage of the C≡C bond to form the carbide atom and the alkylidyne ligand are also considered.

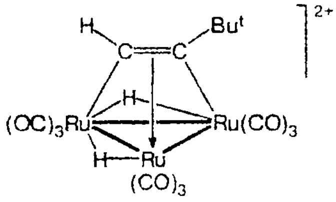
3.1. Protonation

Using the reaction of carbonyl $Os_3(CO)_{12}$ with concentrated H_2SO_4 as an example, it was demonstrated that the hydride ligand in the cationic complexes $[M_3H(CO)_{12}]^+$ (M = Ru or Os) bridges two metal atoms and lies in the plane of the M$_3$ triangle.[75] When a solution of the cluster $Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2Bu^t)$ (**31a**) in dichloromethane was treated with trifluoroacetic acid, the proton also added at the metal—metal edge of the cluster to give the cationic dihydride complex $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}C_2Bu^t)]^+$ (**87**).[76]



87

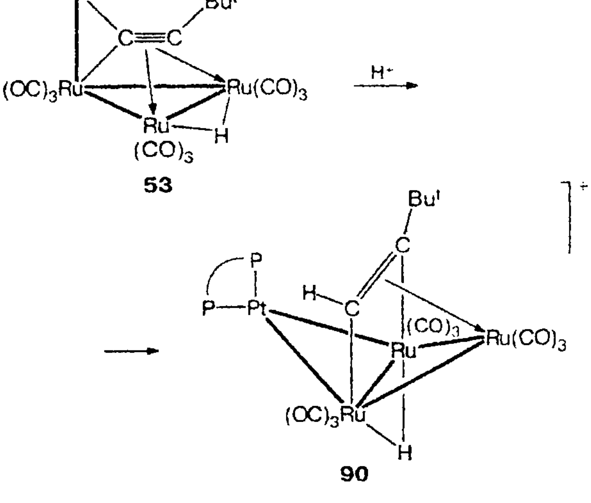
Dissolution of cluster **31a** in 98% H_2SO_4 or HSO_3Cl was accompanied by two-step protonation and the second proton added at the C$_\alpha$ atom of the acetylide ligand to form the dicationic alkyne complex $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}HC_2Bu^t)]^{2+}$ (**88**). Analogous two-step protonation was also observed in the reactions of the clusters $Ru_3(\mu\text{-}H)(CO)_8(PR_3)(\mu_3\text{-}2\eta^2\text{-}C_2Bu^t)$ (R = Ph or OMe) to form isomeric dicationic complexes.[76]



88

Treatment of a solution of the cluster $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2H)$ (**36e**) in chloroform with an excess of $HBF_4\cdot OEt_2$ afforded the ionic complex $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}C_2H)]^+$ (**89**).[77]

Unlike the above-considered examples, the reaction of the tetranuclear cluster $Ru_3Pt(\mu\text{-}H)(CO)_9(dppe)(\mu_4\text{-}\eta^2\text{-}C_2Bu^t)$ (**53**) with an excess of $HBF_4\cdot OEt_2$ was accompanied by the addition of the proton at the C$_\alpha$ atom of the acetylide to give the cationic alkyne complex $[Ru_3Pt(\mu\text{-}H)(CO)_9(dppe)(\mu_3\text{-}HC_2Bu^t)]^+$ (**90**) with a "butterfly" core.[53]

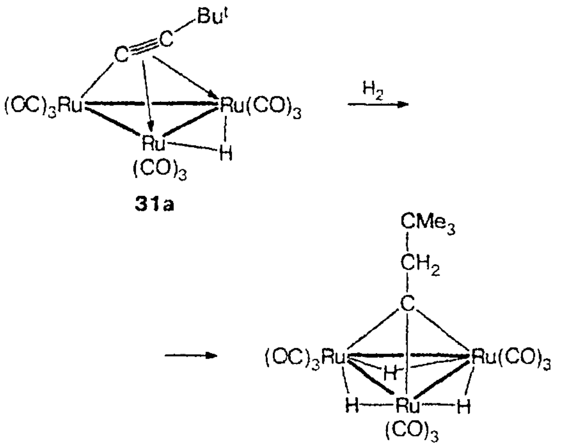


53

90

3.2. Reduction

Treatment of a solution of cluster **31a** in hydrocarbon solvents with molecular hydrogen afforded the trihydride complex with the carbyne ligand, *viz.*, $Ru_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCH_2CMe_3)$ (**91**).[78] It was suggested that in the course of hydrogenation, the dihydride alkyne complex $Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Bu^t)$ and the dihydride vinylidene complex $Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}C(H)Bu^t)$ were formed as intermediates.



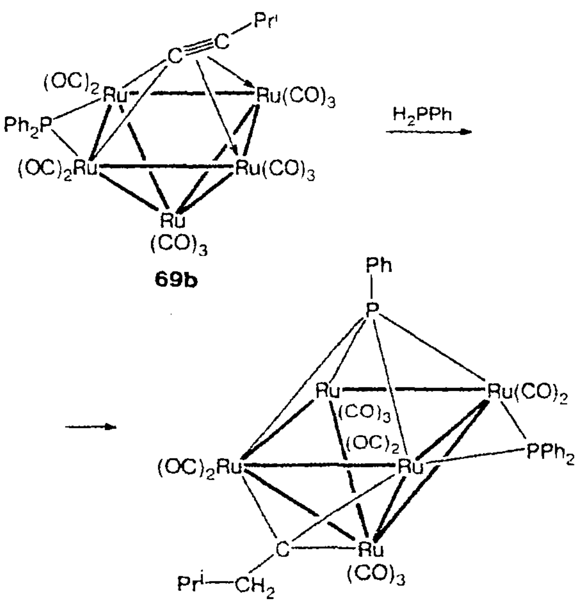
31a

91

Hydrogenation of the reactive cluster $Ru_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu_3\text{-}2\eta^2\text{-}C_2Bu^t)$ (**39b**) was studied.[1b] The reaction proceeded through the formation of the vinylidene complex $Ru_3(\mu\text{-}H)(CO)_8(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^2\text{-}C{=}C(H)Bu^t)$ to form the alkenyl complex $Ru_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}HC{=}C(H)Bu^t)$ as the final product.[1b] The phosphinide cluster of composition $Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PPh)$ and *tert*-butylethylene were also detected among the reaction products.

Treatment of the cluster $Fe_2Ir(CO)_8(PPh_3)(\mu_3\text{-}2\eta^2\text{-}C_2Ph)$ with molecular hydrogen afforded the vinylidene hydride complex $Fe_2Ir(\mu\text{-}H)(CO)_8(PPh_3)\{\mu_3\text{-}\eta^2\text{-}C{=}C(H)Ph\}$ (**92**).[47] This complex along with the alkyne cluster $Fe_2Ir(\mu\text{-}H)(CO)_8(PPh_3)(\mu_3\text{-}\eta^2\text{-}HC_2Ph)$ (**93**) was also formed as a result of addition of the hydride ion to $Fe_2Ir(CO)_8(PPh_3)(\mu_3\text{-}2\eta^2\text{-}C_2Ph)$ followed by its protonation.

The reaction of $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_4\text{-}2\eta^2\text{-}C_2R)$ (**69b**, R = Pr^i) with phenylphosphine gave rise to complexes of compositions $Ru_5(CO)_{12}(\mu\text{-}PPh_2)(\mu_4\text{-}PPh)(\mu_3\text{-}CCH_2R)$ (**94**) and $Ru_5(\mu_3\text{-}H)(CO)_{10}(\mu\text{-}PPh_2)(\mu_3\text{-}PPh)(\mu_4\text{-}PPh)$ (**95**) in 20 and 60% yields, respectively.[79] The metal core in cluster **94** can be described as a square bipyramid formed by five Ru atoms and the P atom with the C_α atom of the alkylidyne group CCH_2Pr^i located above one of the Ru_3 faces. Thus, reduction of the acetylide group of complex **69b** is accompanied by the simultaneous formation of the μ_4-PPh and μ_3-CCH_2Pr^i groups and migration of the C_α atom of the hydrocarbon ligand from the square face of the metal core to the triangular face. Conversion **69b** → **95** involves, apparently, the stage of formation of the unstable alkyl complex of composition $Ru_5(CO)_{11}(PPh_2)(PPh)_2(CH_2CH_2Pr^i)$ (**96**). However, the latter has not been isolated.



69b

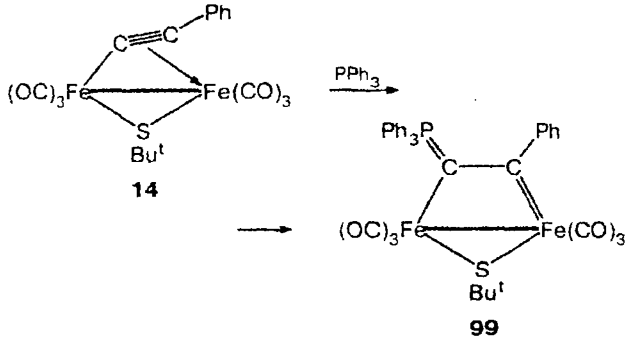
94

3.3. Reactions with Lewis bases

For the acetylide ligands, reactions with uncharged P-, N-, and O-nucleophiles were carried out. Studies of the reactivities of different acetylide clusters demonstrated that the regioselectivity of nucleophilic attack is determined not only by the mode of coordination of the acetylide ligand and the charge density distribution at the C_α and C_β atoms, but also by steric factors.

3.3.1. Reactions with P-nucleophiles

The binuclear complex $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2R)$ (**11a**) reacted with phosphites $P(OR')_3$ (R′ = Me, Et, or Bu^n) in a benzene solution at room temperature to form the corresponding complexes $Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}C[P(OR')_3]CPh\}$ (**97**). In these compounds, the phosphorus atom forms a bond with the C_α atom of the initial acetylide ligand.[80]



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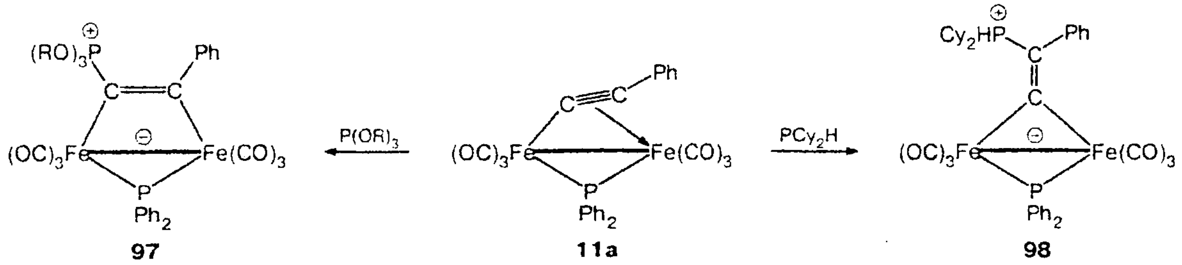
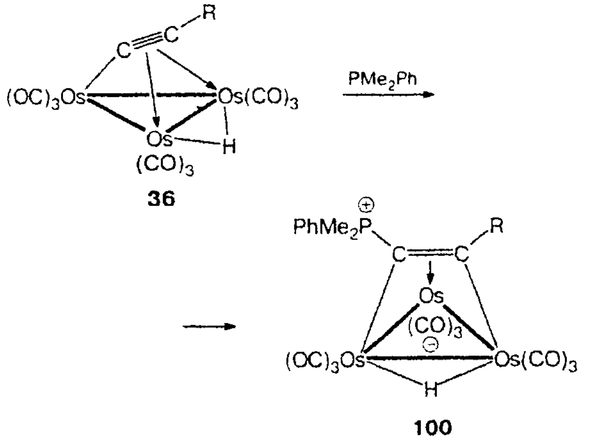
Scheme 6

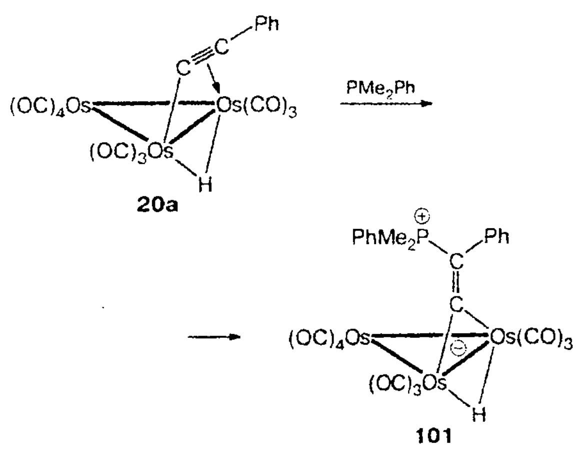


In the reaction of complex **11a** with bulky dicyclohexylphosphine (Scheme 6), the β-carbon atom of the acetylide ligand is subject to attack giving rise to $\mathrm{Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}C{=}C(Ph)PCy_2H\}}$ (**98**).[81]

As a result of the attack of $\mathrm{PPh_3}$ at the $\mathrm{C_\alpha}$ atom, the complex $\mathrm{Fe_2(CO)_6(\mu\text{-}SR)(\mu\text{-}\eta^2\text{-}C_2R')}$ (**14**, R = Bu^t, R' = Ph) gave a phosphonium ylide-carbene complex of composition $\mathrm{Fe_2(CO)_6(\mu\text{-}SBu^t)(\mu\text{-}Ph_3PC_2Ph)}$ (**99**).[10]

The clusters $\mathrm{Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2R)}$ (**36**, R = H, Me, Ph, or CMe$_2$OH) readily reacted with PMe$_2$Ph to form the corresponding zwitterionic complexes $\mathrm{Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}RC_2PMe_2Ph)}$ (**100**),[82] whereas the cluster $\mathrm{Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}C_2Ph)}$ (**20a**), in which the acetylide ligand is coordinated to two osmium atoms, added PMe$_2$Ph through the β-carbon atom to give the zwitterionic complex of composition $\mathrm{Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}C{=}C(Ph)PMe_2Ph\}}$ (**101**).



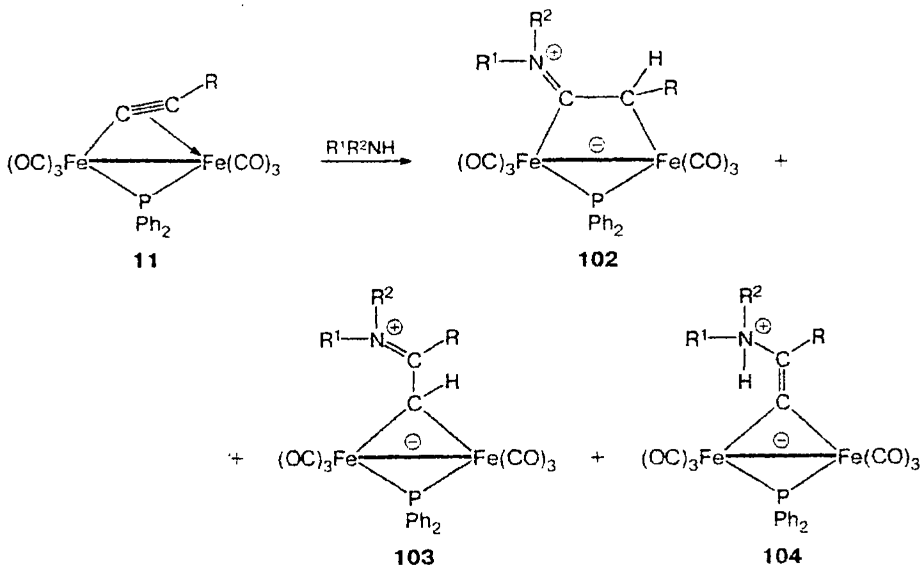


3.3.2. Reactions with N-nucleophiles

The reactions of the acetylide iron complexes $\mathrm{Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2R)}$ (**11**, R = Ph, *p*-MeOC$_6$H$_4$, *p*-BrC$_6$H$_4$, Cy, or Bu^t) with primary, secondary, and tertiary amines were described.[83] The reactions with primary and secondary amines afforded the zwitterionic μ-η^2- (**102**) and μ-η^1-alkylidene (**103**) complexes, which were formed as a result of nucleophilic attack of acetylide and the migration of the hydrogen atom, and the μ-η^1-vinylidene complexes (**104**) as the final products (Scheme 7).

The regioselectivity of the nucleophilic addition depends on the electronic and steric properties of the R group as well as on the size of the amino group. Thus, amines with minor and moderate steric requirements (for example, CyNH$_2$) reacted with compound **11** (R = Ph) to form $\mathrm{Fe_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^2\text{-}C\{NR^1R^2\}C(H)R]}$ (**102**) and $\mathrm{Fe_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1\text{-}CHC\{NR^1R^2\}R]}$ (**103**: R^1 = H, R^2 = Cy) in good yields. Bulkier primary amines, for example, Bu^{t}NH$_2$, gave only addition products at the β-carbon atom (**103**: R = Ph, R^1 = H, R^2 = Bu^t). The reactions of small-volume secondary amines (such as Me$_2$NH or Et$_2$NH) at 40 °C afforded complexes structurally similar to those obtained by the reactions of primary amines containing bulky substituents (**103**: R = Ph; R^1 = R^2 = Me or Et). However, the reactions of **11** (R = Ph) with secondary amines at 0 °C gave rise to amine-acetylide adducts, which subsequently underwent smooth isomerization to form complexes **103**. Complexes **11** did not react with bulky secondary (Pr$^i_2$NH or Cy$_2$NH) or tertiary amines. The course of the reactions of amines is also affected by the size of the R substituent in binuclear carbonyl complexes **11**. Thus, in going from Ph to Bu^t and Cy, the reactivity of acetylide with respect to primary amines noticeably changes. Actually, the reactions of complexes **11** containing R = Cy with primary amines afforded only compounds **102**, whereas the complexes containing R =

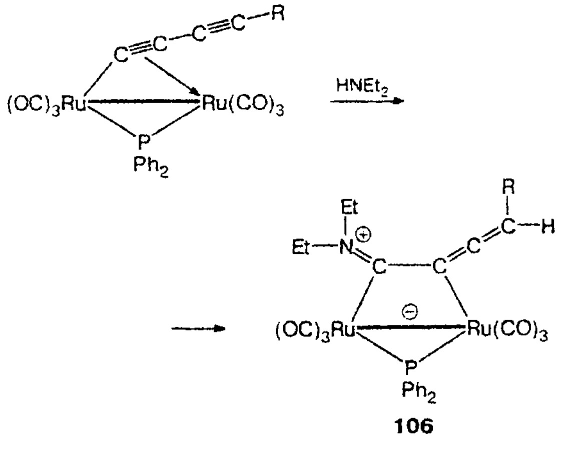
Scheme 7



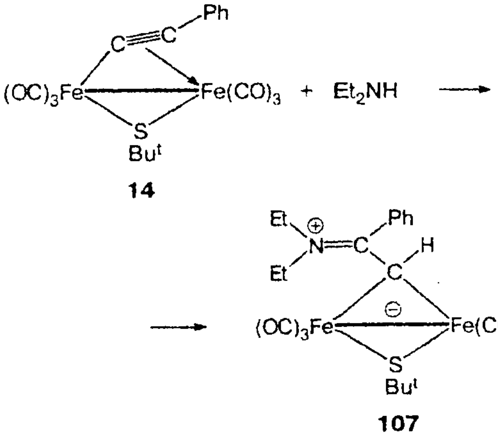
Bu^t did not react with primary, secondary, and tertiary amines at all.

A comparative study of the reactivities of the acetylide complexes $M_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2Ph)$ (M = Fe (**11**), Ru (**12**), or Os (**13**)) with respect to amines, *viz.*, diethylamine, isopropylamine, and cyclohexylamine, was carried out.[84] The reactions of all three acetylides with cyclohexylamine involved attack at the α-carbon atom accompanied by proton transfer along the triple bond of the acetylide ligand to form a dicarbon bridge in the iminium complex $M_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^2\text{-}C\{NHR\}CH(Ph)](\mu\text{-}PPh_2)$ (**105**, R = Cy). In the case of complex **11**, a product of nucleophilic attack at the β-carbon atom of acetylide also formed.

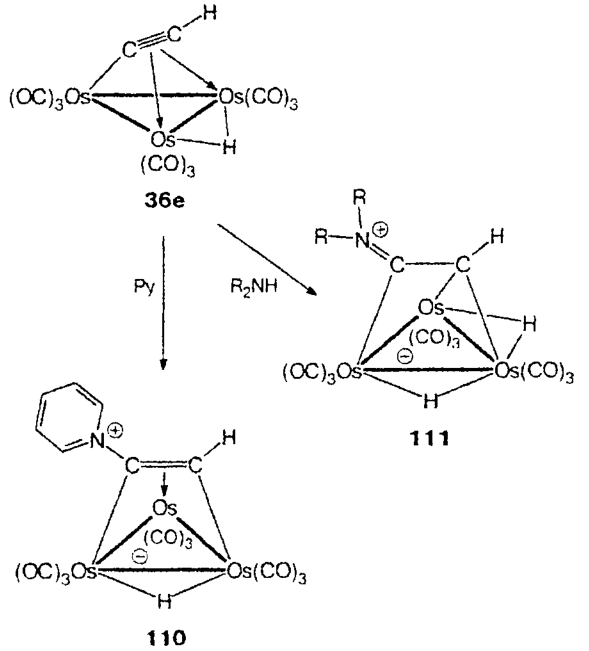
The binuclear butadiynyl compounds $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}C{\equiv}CR)$ (R = Bu^t or Ph) reacted with $HNEt_2$ to form the diethylaminobutatriene complexes $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1,\eta^1\text{-}Et_2N{=}CC{=}C{=}C(H)R]$ (**106**: R = Bu^t (**a**) or Ph (**b**), respectively).[9b]



Reactions of $Fe_2(CO)_9(\mu\text{-}SR)(\mu\text{-}\eta^2\text{-}C_2R^1)$ (**14**) with amines afforded zwitterionic adducts.[10] However, even in the case of R = Ph these reactions proceeded less smoothly than those with complex **11** containing the same substituent. Reactions of complex **14** (R = R^1 = Bu^t) with $(Me_3Si)_2NH$, Ph_2NH, $MeNH_2$, $PrNH_2$, Me_2NH, or Pr^i_2NH yielded only products of decomposition of the starting complex. Complex **14** (R = Bu^t, R^1 = Ph) reacted with diethylamine to form the zwitterionic iminium complex $Fe_2(CO)_6(\mu\text{-}SBu^t)\{\mu\text{-}\eta^1\text{-}CHC(=NEt_2)Ph\}$ (**107**) in 70% yield, whereas the reaction of **14** with aniline gave the complex of composition $Fe_2(CO)_6(\mu\text{-}SBu^t)(\mu\text{-}CH_2C(Ph){=}NPh)$ (**108**) containing the iminoethyl bridging ligand in 80% yield. The reaction with *tert*-butylamine afforded the α,β-unsaturated acyl complex of composition $Fe_2(CO)_6(\mu\text{-}SBu^t)(\mu\text{-}O{=}CCH{=}C(Ph)NHBu^t)$ (**109**).

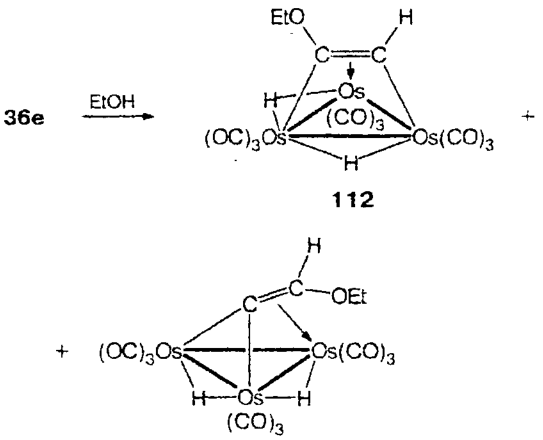


Pyridine, ammonia, and diethylamine gave the corresponding adducts as a result of nucleophilic attack at the α-carbon atom of acetylide in the trinuclear cluster $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2H)$ (**36e**).[77a,85] The zwitterionic pyridine adduct $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_5H_5NC_2H)$ (**110**) readily eliminated pyridine to recover complex **36e**, whereas the amine derivatives $Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}R_2NC_2H)$ (**111**: R = H (**a**) or Et (**b**)) did not eliminate R_2NH even in an acidic medium.



3.3.3. Reactions with O-nucleophiles

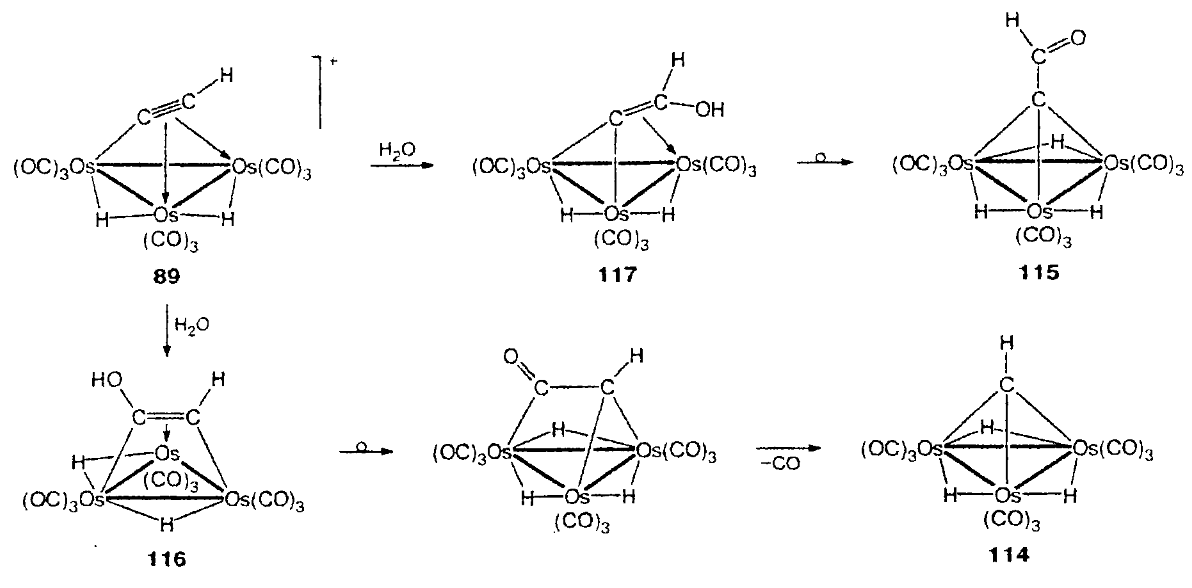
The reaction of ethanol with the cluster $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2H)$ (**36e**) was accompanied by nucleophilic attack at both the C_α and C_β atoms of the acetylide ligand to form the alkyne complex $Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}EtOC_2H)$ (**112**) and the vinylidene complex $Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}C{=}C(H)OEt\}$ (**113**), respectively.[77]



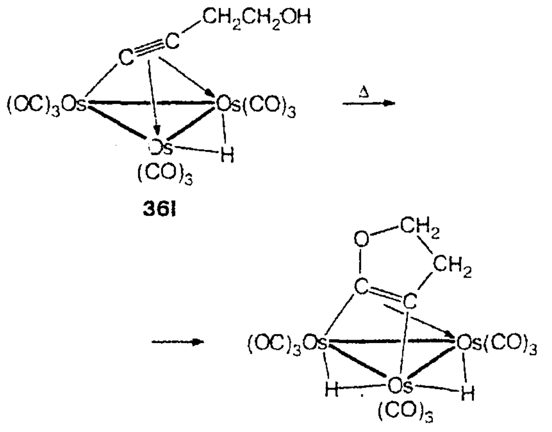
Previous protonation of cluster **36e** giving rise to cationic dihydride **89** (see Section 3.1) was carried out to enhance the carbocationic properties of the carbon atoms of the acetylide ligand. The reaction of this complex with water in a strongly acidic medium afforded the trihydride carbyne clusters $Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CH)$ (**114**) and $Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCHO)$ (**115**). Hydrolysis products **114** and **115** were suggested[77] to be formed from hydroxy derivatives **116** and **117**, respectively (Scheme 8).

Heating of the cluster $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2CH_2CH_2OH)$ (**36l**) was accompanied by its isomerization to form the dihydride alkyne complex $Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}\overline{C{=}CCH_2CH_2O})$ (**118**). It was sug-

Scheme 8



gested that the conversion involved intramolecular nucleophilic attack of the hydroxyl group at the C_α atom of the acetylide ligand.[38]



36l

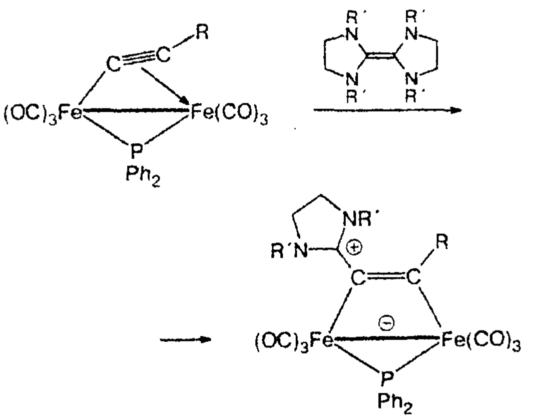
118

3.4. Formation of carbon—carbon bonds

The electrophilic character of the carbon atoms of the acetylide ligands in clusters is manifested in the fact that not only uncharged P-, N-, and O-nucleophiles but also (which is particularly remarkable) nucleophilic carbenes, isonitriles, and alkynes readily add to the acetylide ligands, which is accompanied by the formation of carbon—carbon bonds at room or lower temperatures.

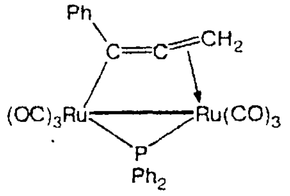
3.4.1. Reactions with carbenes

Reactions of electron-rich olefins $[\overline{=CNR'(CH_2)_2NR'}]_2$ (R' = Me, Et, or CH_2Ph) with the complexes $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2R)$ (**11**, R = Ph or Bu^t) afforded the mesionic compounds $Fe_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}C\{\overline{CN(R')CH_2CH_2N(R')}\}CPh]$ (**119**) through carbene—acetylide coupling.[86]



119

Diazoalkanes react with bi- and trinuclear clusters to form complexes containing the allenyl ligand $C(R^1)=C=CR^2R^3$. The latter is generated by the insertion of carbene $:CR^2R^3$ into the $M-C_\alpha$ bond of the acetylide ligand. In the bi- and trinuclear complexes, the allenyl ligand serves as a donor of three and five electrons, respectively. Two modes of coordination are possible for three-electron ligands, *viz.*, $\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}$ and $\mu\text{-}\eta^1\text{:}\eta^2_{\beta,\gamma}$, which are determined by the sizes of the substituents at the C_γ atom of the allenyl group.[87] Thus, the reactions of N_2CR_2' (R' = H, Me, or Ph) with the complexes $M_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2Ph)$ (M = Ru (**12**) or Os (**13**)) afforded compounds of composition $M_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}C(Ph)=C=CR_2'\}$.[87] However, X-ray diffraction study revealed different modes of coordination of the allenyl ligand in the complexes $Ru_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2_{\beta,\gamma}\text{-}C(Ph)=C=CH_2\}$ (**120**) and $Ru_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}\text{-}C(Ph)=C=CPh_2\}$ (**121**).



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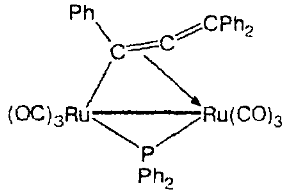
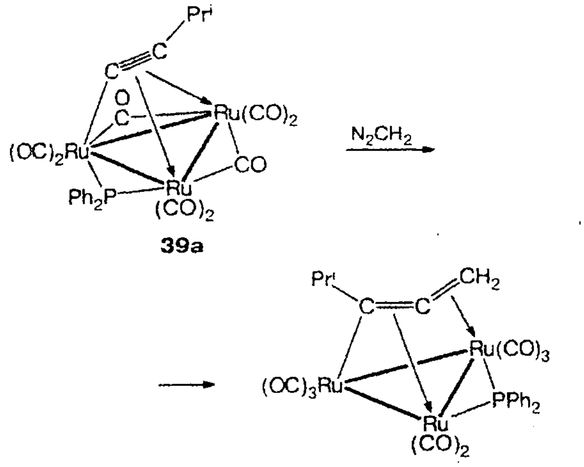


121

Attack of carbene on the α-carbon atom of the butadiynyl ligand in the complexes $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C\equiv CC\equiv CR)$ (R = Bu^t or Ph) in the reactions with N_2CR_2' afforded the corresponding 1-ynylallenyl complexes of composition $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}\text{-}C(C\equiv CR)=C=CR_2')$.[87] In the case of N_2CPh_2, the addition of carbene occurred also at the C_β atom to form the η^1-indenyl derivatives $Ru_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH(C_6H_4)C(Ph)=CC\equiv CBu^t\}$ and $Ru_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C=C(Ph)C=C(Ph)(C_6H_4)CH\}$.

The reaction of the trinuclear cluster $Ru_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-}C_2Pr^i)$ (**39a**) with diazomethane gave the complex $Ru_3(CO)_8(\mu\text{-}PPh_2)\{\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}C(Pr^i)=C=CH_2\}$ (**122**).[41]

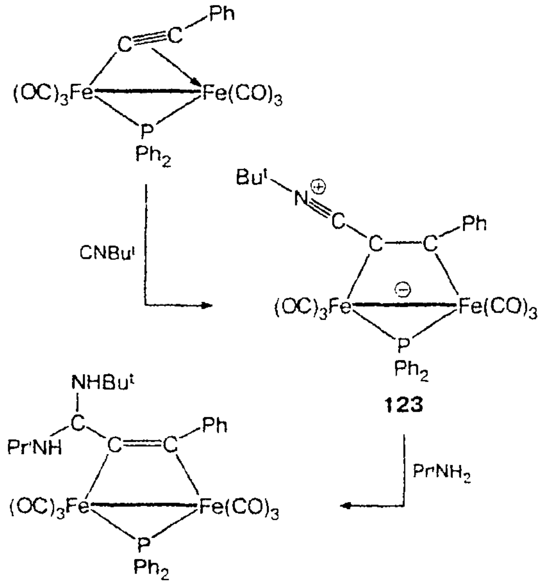


39a

122

3.4.2. Reactions with isonitriles

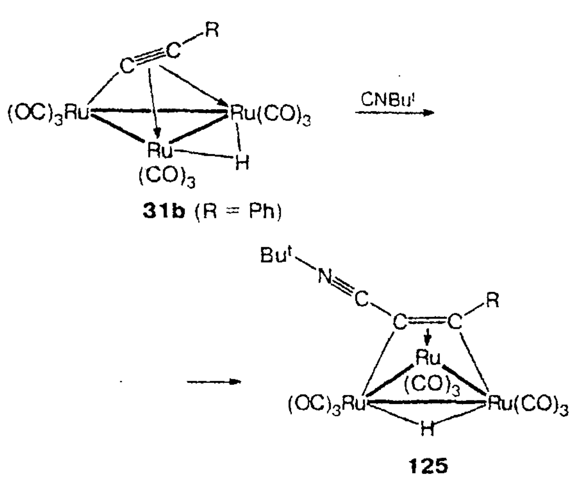
The complex $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2Ph)$ reacted with CNBu^t in benzene at room temperature to form the zwitterionic compound $Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}C(CNBu^t)CPh\}$ (**123**) as a result of nucleophilic attack of the C_α atom of the acetylide ligand.[88] Amination of complex **123** with isopropylamine afforded the cluster $Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}C[C(NHPr^i)(NHBu^t)]C(Ph)\}$ (**124**).



123

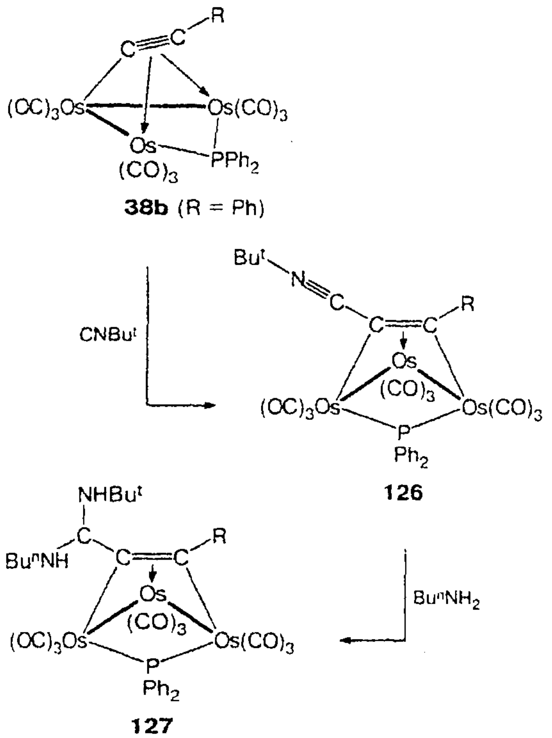
124

Regiospecific addition at the α-carbon atom was observed in the reactions of CNBu^t with the clusters $Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2R)$ (**31b**) and $Os_3(CO)_9(\mu\text{-}PPh_2)(\mu_3\text{-}2\eta^2\text{-}C_2R)$ (**38**) to form the zwitterionic complexes $Ru_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}C(CNBu^t)CR\}$ (**125**) and $Os_3(CO)_9(\mu\text{-}PPh_2)\{\mu_3\text{-}C(CNBu^t)CR\}$ (**126**), respectively. Treatment of complex **126** with butylamine gave rise to $Os_3(CO)_9(\mu\text{-}PPh_2)[\mu_3\text{-}CC\{NH(Bu^n)NH(Bu^t)\}CR]$ (**127**) in quantitative yield.[89]



31b (R = Ph)

125



38b (R = Ph)

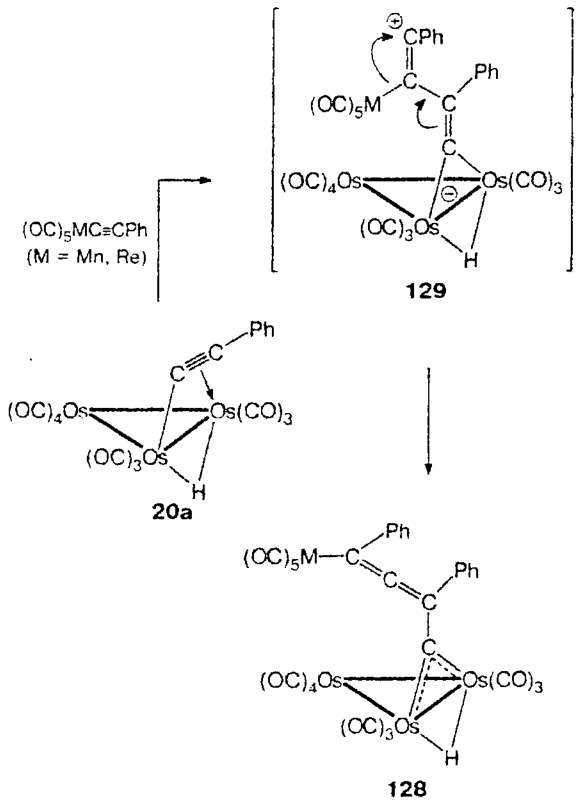
126

127

3.4.3. Reactions with alkynes

The formation of C—C bonds through interactions of alkynes with the acetylide ligand in the complexes $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2R)$ (**11**, R = Ph or Bu^t) and $Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}C_2Bu^t)$ (**31a**) was described.[1] Mechanisms of these multicomponent reactions remain unclear. However, it was suggested that these bonds are formed through the insertion of CO into the Fe—C and Fe—P bonds in the case of complexes **11** and migration of hydride to the hydrocarbon ligand and oligomerization of alkynes in the case of complex **31a**.

Reactions of the cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}C_2Ph)$ (**20a**) with metallaalkynes $(OC)_5MC{\equiv}CPh$ (M = Mn or Re) are better understood and are consistent with the polar mechanism.[16,17] These reactions proceeded at room temperature to form the clusters $Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}CC(Ph){=}C{=}C(Ph)M(CO)_5\}$ (**128**: M = Mn (**a**) or Re (**b**)) with allenyl-substituted carbyne ligand.[16,17,90] It is remarkable that the formation of the C—C bond was accompanied by the addition of metallaalkyne at the β-carbon atom of acetylide in cluster **20a**, *i.e.*, at the site of nucleophilic attack of the phosphine in the reaction of **20a** with PMe_2Ph. It was suggested that the corresponding zwitterionic complexes **129** generated as a result of nucleophilic attack of alkyne $(OC)_5MC{\equiv}CPh$ at the β-carbon atom of cluster **20a** appeared as intermediates upon the formation of carbyne clusters **128**.



3.5. Cleavage of C≡C bonds

The fact that acetylide clusters readily add nucleophiles suggests[87b] that these molecules can be considered, at least partially, as alkylidyne carbides in which the naked carbide carbon atom and the alkylidyne fragment CR form of the $M_n(C)(CR)$ core. The structures of some acetylide clusters provide evidence in favor of the validity this suggestion and the structure of the above-considered (see Section 2.2.14) complex $Ru_6(CO)_{13}(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu_6\text{-}C_2C{\equiv}CBu^t)$[74] (**85**) provides the most impressive example. The relationship between coordinated acetylides and carbide-alkylidynes was discussed in the literature.[46,87b]

In this connection, the reversible formation of carbide and alkylidyne from acetylide clusters is of interest. Several examples of these reactions involving the cleavage of the C≡C bond in acetylide are known.

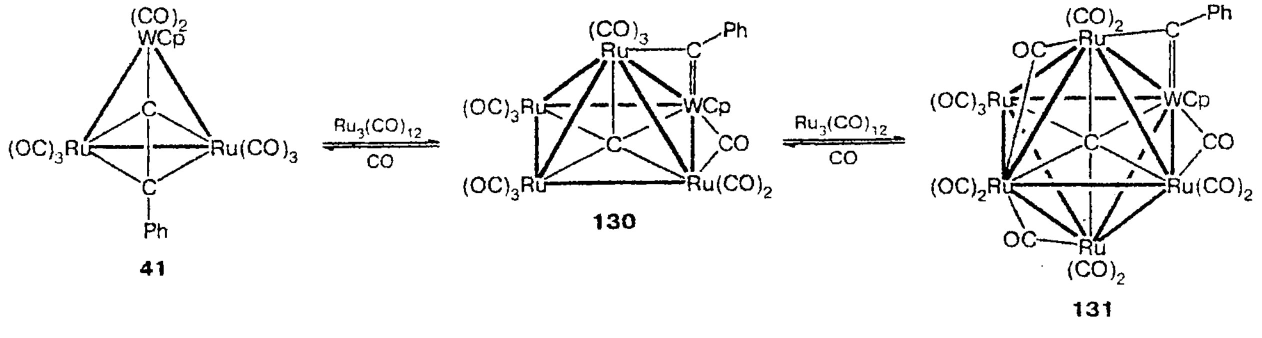
Heating of $(\eta\text{-}Cp)WRu_2(CO)_8(\mu_3\text{-}2\eta^2\text{-}C_2Ph)$ (**41**) with $Ru_3(CO)_{12}$ in refluxing heptane afforded two carbide clusters.[91] *viz.*, the pentanuclear complex of composition $CpWRu_4(\mu_5\text{-}C)(CO)_{11}(\mu\text{-}CO)(\mu\text{-}CPh)$ (**130**) and the hexanuclear complex of composition $CpWRu_5(\mu_6\text{-}C)(CO)_{11}(\mu\text{-}CO)_3(\mu\text{-}CPh)$ (**131**) (Scheme 9). In molecule **130**, the WRu_4 metal core adopts the square-pyramidal configuration with the Ru atom in the apical position. The carbide atom deviates from the WRu_3 plane by 0.177(6) Å and the unsymmetrical phenylalkylidyne ligand forms a bridge along the W—Ru_{ap} edge.

Hexanuclear complex **131** has a slightly distorted octahedral WRu_5 core containing the alkylidyne ligand at the W—Ru edge. Cluster **131** was prepared from compound **130** in 60% yield upon heating with $Ru_3(CO)_{12}$ in boiling toluene. This sequence of the reactions is reversible. Thus, treatment of cluster **131** with carbon monoxide (14 atm) in toluene at 78 °C afforded complex **130** in 94% yield.

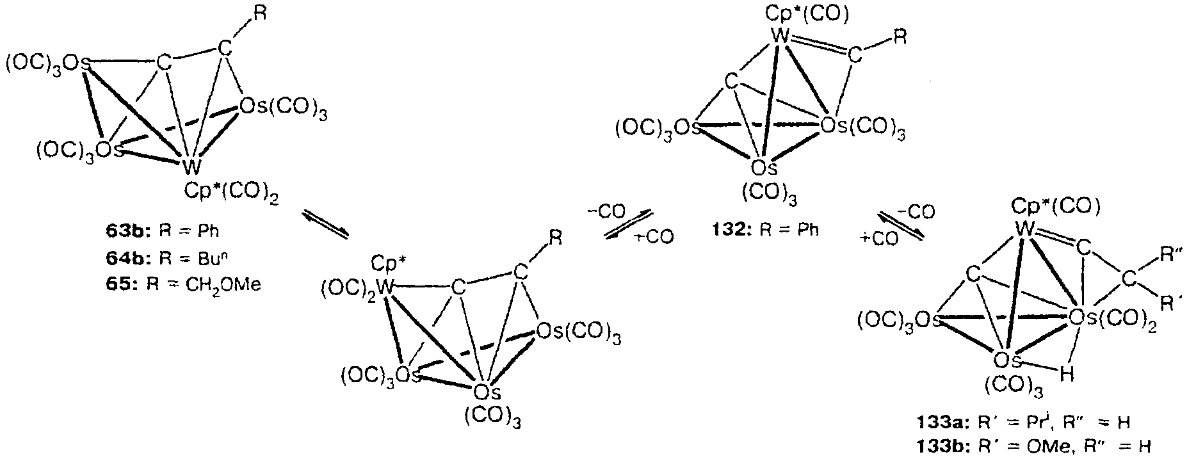
Depending on the R substituent in the acetylide ligand, the tetranuclear acetylide clusters $Cp^*WOs_3(CO)_{11}(\mu_4\text{-}C_2R)$ (R = Ph (**63b**), Bu^n (**64b**), or CH_2OMe (**65**)) underwent reversible cleavage of the C≡C bond and activation of the C—H bond to form the carbide alkylidyne cluster $Cp^*WOs_3(CO)_{10}(\mu_4\text{-}C)(\mu\text{-}CPh)$ (**132**) and the carbide vinylidene clusters $Cp^*WOs_3(CO)_9(\mu_4\text{-}C)(\mu\text{-}H)(\mu\text{-}CCHCR')$ (**133**: R′ = Pr (**a**) or OMe (**b**)), respectively (Scheme 10).[92]

The reactions of the complexes $LW(CO)_3(C{\equiv}CPh)$ (L = Cp or Cp*) with the alkyne clusters $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}RC_2R)$ (R = *p*-Tol or Me) in refluxing toluene yielded heterometallic clusters of composition $LWOs_3(CO)_9(\mu_3\text{-}CPh)(\mu_4\text{-}CCRCR)$ (L = Cp, R = *p*-Tol (**134a**); or L = Cp*, R = Me (**134b**)). These clusters contain a metal core assuming the form of a planar triangulated rhombus.[93] The alkylidyne ligand μ_3-CPh forms a bridge with the atoms of the WOs_2 triangle, and the α-carbon atom formed upon the cleavage of the C≡C bond of acetylide is coupled with the alkyne ligand to form the C_3-hydrocarbon ligand.

Scheme 9



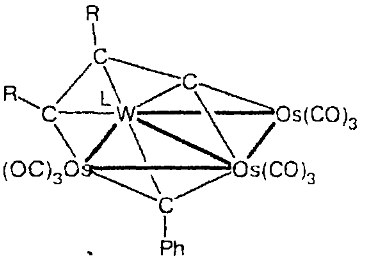
Scheme 10



63b: R = Ph
64b: R = Bu^n
65: R = CH$_2$OMe

132: R = Ph

133a: R' = Pr^i, R" = H
133b: R' = OMe, R" = H



134a: L = Cp, R = Tol
134b: L = Cp*, R = Me

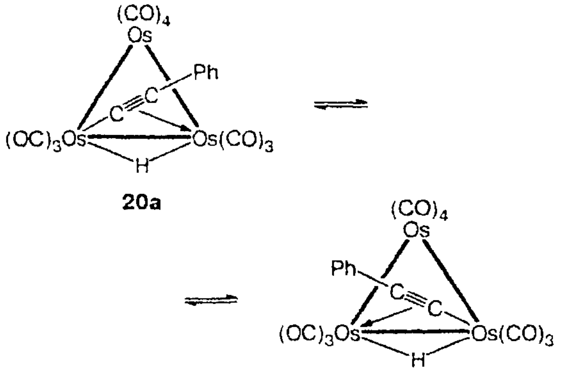
The above-considered reactions of cleavage and formation of the C—C bonds with the participation of the carbide and C$_2$ ligands are of interest for elucidation of processes involving reduction of CO and activation of hydrocarbons on the catalyst surface.

4. Intramolecular rearrangements of acetylide clusters

In this section, we consider intramolecular rearrangements with the participation of acetylide ligands. These rearrangements involve different modes of exchange of acetylide groups and hydridoacetylide—vinylidene rearrangements.

4.1. Fluxional behavior of acetylide ligands

The fluxional behavior of the acetylide ligand was discovered in 1984 simultaneously for the triosmium cluster Os$_3$(μ-H)(CO)$_{10}$(μ-η^2-C$_2$Ph)^{94} (**20a**) and the dirhenium complex Re$_2$(μ-H)(CO)$_8$(μ-η^2-C$_2$Ph)^{11} (**16**). The rearrangement involves rapid interchange of the σ- and π-bonds of the bridging acetylide ligand between two metal atoms.

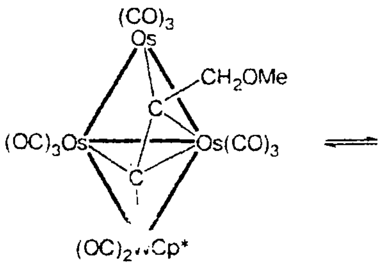


20a

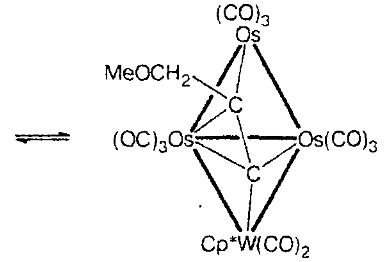
20a

The results of NMR spectral studies of a number of complexes with bridging μ-η^2-acetylide ligands demonstrated that the above-mentioned phenomenon has a rather general character. Thus, the rearrangement of the acetylide ligand was observed in the complexes Re$_2$(μ-H)(CO)$_6$(μ-dppm)(μ-η^2-C$_2$H)^5 (**6a**), Re$_2$(μ-H)(CO)$_7$(NCMe)(μ-η^2-C$_2$Ph)^{12} (**17a**), M$_2$(CO)$_6$(μ-PPh$_2$)(μ-η^2-C$_2$R)^{9a} (M = Fe (**11**), Ru (**12**), or Os (**13**); R = Ph (**a**), Bu^t (**b**), or Pr^i (**c**)), Fe$_2$(CO)$_6$(μ-SR)(μ-η^2-C$_2$R^1)^{10} (**14**: R = Bu^t or Ph; R^1 = Bu^t, Ph, or SiMe$_3$), and Os$_3$(μ-H)(CO)$_{10}$(μ-η^2-C$_2$CMe$_2$OMe)^{20} (**3**).

Yet another type of σ→π,π→σ exchange has been found recently for the μ$_4$-acetylide groups in tetranuclear clusters with the "butterfly" core. In the clusters Ru$_4$(μ-H)(CO)$_{12}$(μ$_4$-C$_2$Fc) (**72**)^{64} and Cp*WOs$_3$(CO)$_{11}$(μ$_4$-C$_2$CH$_2$OMe)^{59} (**66**), σ-π exchange of the acetylide ligand occurs between two hinge atoms of the metal core.



66

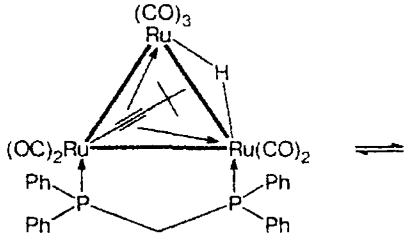


66

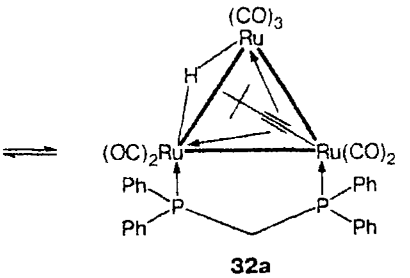
It is worthy of note that cluster **66** was formed from isomeric cluster **65** through skeletal rearrangement involving the migration of the fragment $Cp^*W(CO)_2$ from the hinge to the wingtip position of the butterfly wing.

4.2. Rotation of acetylide ligands

Studies of the temperature dependence of the ^1H, ^{13}C, and ^{31}P NMR spectra of the cluster $Ru_3(\mu\text{-}H)(CO)_7(\mu\text{-dppm})(\mu_3\text{-}\eta^2{:}\eta^2\text{-}C_2Bu^t)$ (**32a**) revealed the rotation of the acetylide ligand accompanied by the concerted jump of the hydride from one Ru—Ru edge to another.[95]



32a



32a

Studies of the cluster $Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}2\eta^2\text{-}CBu^t)$ (**31a**) by ^{13}C NMR spectroscopy at variable temperature revealed three exchange processes.[96] The lowest-energy process is governed by the localized exchange of three CO groups at the unique $Ru(CO)_3$ unit. Two other higher-energy processes afford complete averaging of the CO groups without internuclear exchange. These processes involve the rotation of the acetylide ligand about the Ru_3 triangle accompanied by hydride migration and the localized exchange of the carbonyl groups in the $Ru(CO)_3$ units.

The rotation of the acetylide ligand was also observed in the trimolybdenum complex $Mo_3(\eta\text{-}Cp)_3(\mu\text{-}CO)(CO)_4(\mu_3\text{-}\eta^2{:}\eta^2\text{-}C_2Ph)$ (**45**).[13] In the heterometallic clusters $(\eta\text{-}Cp')WRu_2(CO)_8(\mu_3\text{-}\eta^2{:}\eta^2\text{-}C_2Ph)$ ($Cp' = C_5H_5$ (**41**) or C_5Me_5 (**42**)), the acetylide ligand undergoes rotation by 360° on the surface of the WRu_2 triangle.[49] In analogs of these complexes with the WOs_2 core, this exchange was not observed.

Similar rotation of the hydrocarbon ligand on the surface of the metal triangle was observed in the vinylidene osmium clusters $[Os_3(\mu\text{-}H)_3(CO)_9\{\mu_3\text{-}\eta^2\text{-}C{=}C(R)H\}][BF_4]$.[97]

4.3. Hydridoacetylide—vinylidene interconversion

The hydridoacetylide cluster $Ru_3Pt(\mu\text{-}H)(CO)_9(dppe)(\mu_4\text{-}\eta^2\text{-}C_2Bu^t)$ (**53**) and the vinylidene cluster $Ru_3Pt(CO)_9(dppe)\{\mu_4\text{-}\eta^2\text{-}C{=}C(H)Bu^t\}$ (**54**) exist in solutions in tautomeric equilibrium.[53] However, these clusters can be separated by chromatography or low-temperature recrystallization. Vinylidene complex **54** is a thermodynamically favorable product, and the equilibrium constant $K = 12(\pm 1)$ at 298 K. The rate of conversion of **53** into **54** follows first-order kinetics. The kinetics remains unchanged in the presence of additives, such as diethylamine or pyridine, which is indicative of the intramolecular character of the exchange process. Therefore, the interconversion of **53** and **54** involves the reversible formal migration of the hydrogen atom from the metal—metal edge to the β-carbon atom of the acetylide ligand.

The conversion of $Cp(L)W_2Os_2(\mu\text{-}H)(CO)_9(\mu_4\text{-}\eta^2\text{-}C_2Ph)$ (**135**, L = Cp or Cp*) into $Cp(L)_2W_2Os_2(CO)_7(\mu\text{-}CO)_2\{\mu_3\text{-}\eta^2\text{-}C{=}C(H)Ph\}$ (**136**)[98] provides yet another example of the reversible rearrangement of an acetylide complex into a vinylidene complex. Heating of the acetylide or vinylidene complex in refluxing toluene affords a mixture of both isomeric complexes. This conversion involves also a change of the configuration of the metal core from "butterfly" to tetrahedral.

The relationship between the fluxionality of the ligands and their reactivity is an interesting aspect of the stereochemical nonrigidity of cluster complexes. Thus, to account for the ease of formation of the C—C bond in the reactions of the cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}C_2Ph)$ (**20a**) with alkynes $(OC)_5MC{\equiv}CPh$ (M = Mn or Re), it was postulated[90] that the carbocationic character of the β-carbon atom of the acetylide group should be enhanced in the transition state of the rearrangement of the acetylide ligand. The involvement of the zwitterionic transition state was also assumed for the rearrangement of the allenyl ligand in the complex $Ru_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2{}_{\alpha,\beta}\text{-}C(Ph)=C=CPh_2\}$ (**121**).[87b] However, the relationship between the fluxional behavior and the reactivity of the organic ligand calls for further investigation.

5. Conclusion

To summarize, it can be stated that the acetylide group is actually an unexcelled organic ligand as regards the diversity of modes of coordination to metals. Multisite bonding with several metal centers is responsible for the high reactivity of the acetylide groups in the formation of the carbon—carbon bond and makes them highly susceptible to nucleophilic attack. In addition, the coordination to several metal atoms of the cluster favors the cleavage of the C≡C bond, yielding carbides and carbynes. The C≡CR and C≡O ligands are similar in that they are able to form terminal and various types of bridging bonds and to generate carbides.[1] These two ligands are also characterized by the ability to participate in dynamic exchange processes.

Evidently, investigations of acetylide derivatives of metal clusters as models make it possible to throw light on the reactivity of C_1 and C_2 ligands coordinated to several metal atoms in the reactions of formation of carbon—carbon bonds and are of interest for elucidation of some catalytic processes, for example, the Fischer—Tropsch synthesis. Moreover, there is some hope that a search for unusual reactions of formation and cleavage of C—C bonds in acetylide metal clusters will be helpful for the design of new catalytic systems.

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