Journal of Organometallic Chemistry 573 (1999) 139–155

Complexes of transition metal carbonyls with alkynes. Closo- and nido-pentagonal bipyramidal clusters[1]

Enrico Sappa *

Dipartimento di Chimica IFM, Universita di Torino, Via Pietro Giuria 7, I-10125 Turin, Italy

Received 26 March 1998

Abstract

A short review of the synthetic methods, structures and isolobal relationships of the closo $M_3(CO)_8(RC_2R')_2$ and of the nido $M_2(CO)_6(RC_2R')_2$ pentagonal bipyramidal complexes (M = Fe, Ru, Os) and of some related compounds is given. The role of these complexes in organic synthesis and in catalysis is discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Metal carbonyl clusters; Alkynes; Metallacyclic complexes; Isolobal relationships; Organic syntheses

1. Introduction

Metal carbonyl complexes and clusters, in particular those belonging to the iron triad, react easily with alkynes to afford various substituted derivatives [1]; among them worthy of note are the closo-pentagonal bipyramidal 'open clusters' $Fe_3(CO)_6(\mu_2\text{-}CO)_2(RC_2R')_2$ {**I**}, and the nido diferracyclopentadienyl, or 'iron-ferrole', complexes $Fe_2(CO)_6(RC_2R')_2$ {**II**}.

Complexes **I** show interesting isolobal relationships with respect to each other and to boranes or carboranes; they were also found among the organometallic products from catalytic hydrogenation experiments. Complexes **II** (and ferrole-like structures) were proposed as intermediates in several catalytic or stoichiometric processes under homogeneous or heterogeneous conditions; among them we can mention metathesis ([2]a,b) and alkyne cycloaddition reactions ([2]c), hydro-olygomerization of alkynes ([2]d) and rearrangement of small-ring organic molecules ([2]e). They can also play a role as intermediates in Ziegler–Natta catalysis ([2]f) or in olefin polymerization with chromocene supported on alumina ([2]g). Their intermediacy in alkyne cyclotrimerization or in the synthesis of tropones will be discussed in this paper. Ferrole-estradiol complexes have been used in 'carbonylmetallo immunoassay' tests [3]. Last but not least, bis(cyclopentadienyl)diiron alkenylidyne complexes have shown some activity as NLO materials [4].

Iron–ferrole complexes **II** may undergo further thermal degradation, with loss of $M(CO)_n$ fragments to form arachno $Fe(CO)_4(C_2RR')_2$ complexes **III**. The latter will not be discussed in detail in this paper. The structures of complexes **I**, **II** and **III** are shown in Fig. 1.

Abbreviations: Bu^t, *t*-butyl; Cp, C_5H_5, cyclopentadienyl; Cp*, C_5Me_5, pentamethyl cyclopentadienyl; Dppm, bis(diphenylphosphino)methane; Et, ethyl; HPLC, high performance liquid chromatography; Me, methyl; NLO, non linear optics; Ph, phenyl; UV-PES, ultra violet photo electronic spectroscopy.

* Fax: +39 11 6707855; e-mail: sappa@ch.unito.it

[1] Dedicated to Professor B.F.G. Johnson on the occasion of his 60th birthday.

PII S0022-328X(98)00706-2

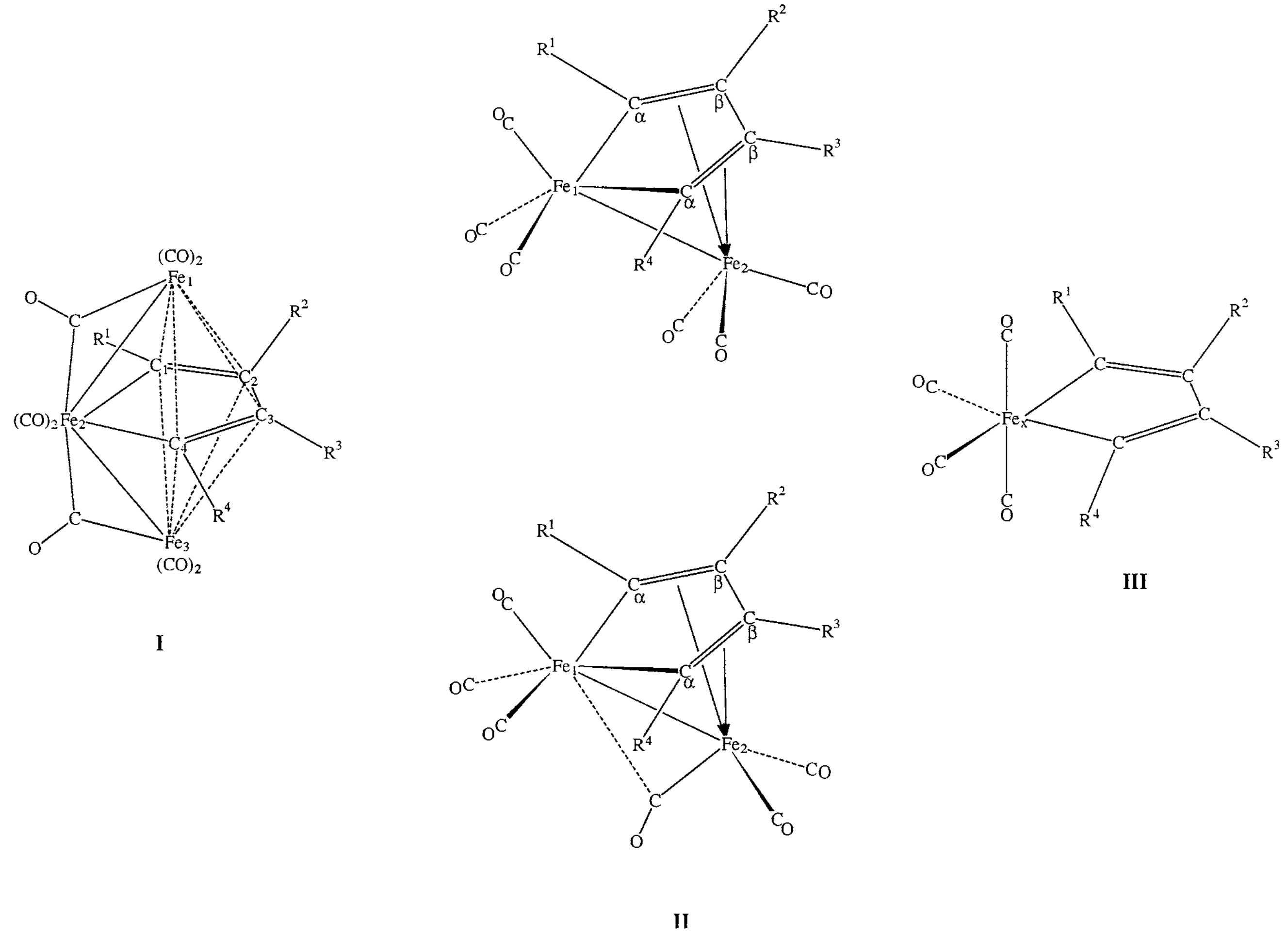


Fig. 1. Structures of complexes **I**, **II** (top sawhorse arrangement, bottom non-sawhorse arrangement) and **III**.

2. Synthetic methods for complexes I and II

2.1. Synthesis of complexes *I*

Complexes $Fe_3(CO)_8(RC_2R')_2$ (**I**) were at first obtained upon reaction of $Fe_3(CO)_{12}$ with alkynes; this led to $Fe_3(CO)_9(RC_2R')$ clusters containing a 'perpendicular alkyne', which further react with another alkyne molecule to form the disubstituted $Fe_3(CO)_8(RC_2R')_2$ 'violet isomers', having two independent alkynes coordinated in 'parallel' fashion to the same cluster edge [5]. The latter isomerize to complexes **I**, 'green isomers', which in turn fragment to give nido ferrole derivatives **II**. Presumably, the formation of the violet isomers is the fundamental reaction step that may explain the substitutional isomerism observed for complexes **I** and **II** and discussed in Section 3. Unfortunately only two complexes of such kind, both containing the symmetrical C_2Ph_2 ligand, have been fully characterized [6].

By contrast, for $Ru_3(CO)_{12}$ the first step would be the formation of trinuclear complexes with parallel alkynes. A slightly different reaction mechanism leads to triosmium derivatives with metallacycles on one edge or on the face of the triangular cluster frame (complexes **IA**, **IB** below). The above reaction sequences have been discussed in Refs. ([1]a, [5]).

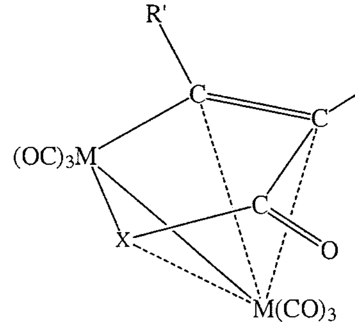
2.1.1. Cyclo-oligomerization reactions

Dimerization of alkynes may occur under thermal [1] or photochemical conditions with or without loss of dihydrogen [7]. Cyclotrimerization generally occurs with loss of dihydrogen [8] or hydrogen shift [9]. When propargyl alcohols are reacted, loss of water may also be observed [10]. Cyclization of a single molecule of dipropargylamine may lead to complexes **I** [11]. Finally, thermal cyclization and orthometalation of coordinated phenylacetylide accompanied by metal fragment condensation leads to heterometallic complexes **I** [12].

2.1.2. Coupling and rearrangement of ligands

Coupling and/or rearrangement of coordinated ligands may also lead to the aforementioned structures. Examples are:

1. Coordination of an alkyne as an allylic ligand, followed by insertion of another alkyne [13].



M = Fe, R = R' = Et	X = O	Ref. [35]
M = Fe, R = Me, R' = Et	X = O	[35]
M = Fe, R = Ph, R' = Et	X = O	[35]
M = Fe, R = R' = Ph	X = O	[34]
M = Fe, R = H, R' = Bu^t	X = O	[34]
M = Fe, R = C(Ph)H, R' = Ha	X = O	[36]$*^b$
M = Fe, R = H, R' = Ph	X = S	[37]
M = Fe, R = Me, R' = $\mathrm{NEt}_2{}^c$	X = SPh	[38]
M = Fe, R = Me, R' NEt_2	X = NPh	[38]
M = Fe, R-R' = $\mathrm{CH{=}CHNMe}_2$	X = NPh	[39]*
M = Fe, R-R' = CH=CHS	X = NPh	[39]*
M = Ru, R = R' = Ph	X = NPh	[40]
M = Fe, R = Me, R' = NEt_2	X = NEt	[38]
M = Fe, R-R' = $\mathrm{C_4H_3R}$	X = N-N=CHR'	[41]*

(a) C-OMe instead of C=O. (b) The symbol * indicates a sawhorse structure. (c) C=S instead of C=O.

Scheme 1.

2. Coupling of cluster-bound methylidynes with alkynes [14] or phospha-alkynes [15].

2.1.3. Skeletal expansion reactions

Finally, complexes **I** can be formed through skeletal expansion reactions, via insertion of alkynes into M–M or M–X bonds; X = P [16], X = N [17], X = S [18], X = Se, Te [19]. The structures of such complexes are reported in Fig. 3, below. The complex with X = P ([16]b,c) can also be obtained through a reaction involving coordination, rearrangement and metal fragment condensation, starting from $\mathrm{Ru_3(CO)_{12}}$ and triphenylphosphirene [20]. Another type of skeletal expansion is represented by the insertion of metal fragments into M–C bonds of hydrocarbyl-substituted clusters [21]. A skeletal expansion reaction involving alkynes is also the one that leads from the square-planar, electronically unsaturated, $\mathrm{Fe_4(CO)_{11}(\mu_4\text{-}PR)_2}$ to $\mathrm{Fe_4(CO)_4(\mu_4\text{-}CO)(\mu_3\text{-}PBu^t)\{Bu^tPCHCMe\}}$, containing a bridging phosphinidene in place of a bridging CO [22]. This reaction represents the reverse of the observed 'degradation' processes for complexes **I**, which leads to square-planar derivatives (Section 3.1.2.1).

*2.1.4. Synthesis of structural isomers of complexes **I***

Trinuclear derivatives with the metallacycle disposed along a cluster edge {**IA**} (Fig. 4, below), or sitting on the cluster face {**IB**}, are obtained by direct reaction of $\mathrm{Os_3(CO)_{12}}$ with alkynes [23] or by cooligomerization of alkynes coordinated in parallel fashion with incoming acetylenes, with or without orthometalation products. Osmium–ferrole derivatives are obtained in the same reactions [24].

The reactions of $\mathrm{(Cp)_2Ru_3(CO)_3(\mu\text{-}CO)_2[C_2(CF_3)_2]}$ (containing a 'parallel' alkyne), or of its MeCN-substituted derivative, with other alkynes leads to complexes **I** with cyclopentadienyl substituants in 'apical' position and to bis-cyclopentadienyl ferrole derivatives. In such reactions the formation of complexes with a metallacyclic ring sitting on a cluster face, but acting as a: μ-σ-(π-allyl) ligand, has also been reported (Complexes **IC**); an example is $\mathrm{Cp_2Ru_3(\mu\text{-}CO)_2\{C_2(CF_3)_2\}\{C_2Ph_2\}}$ [25]. During these reactions, fragmentation of alkynes into methylidyne groups does occur with effects on the isomerism of the products.

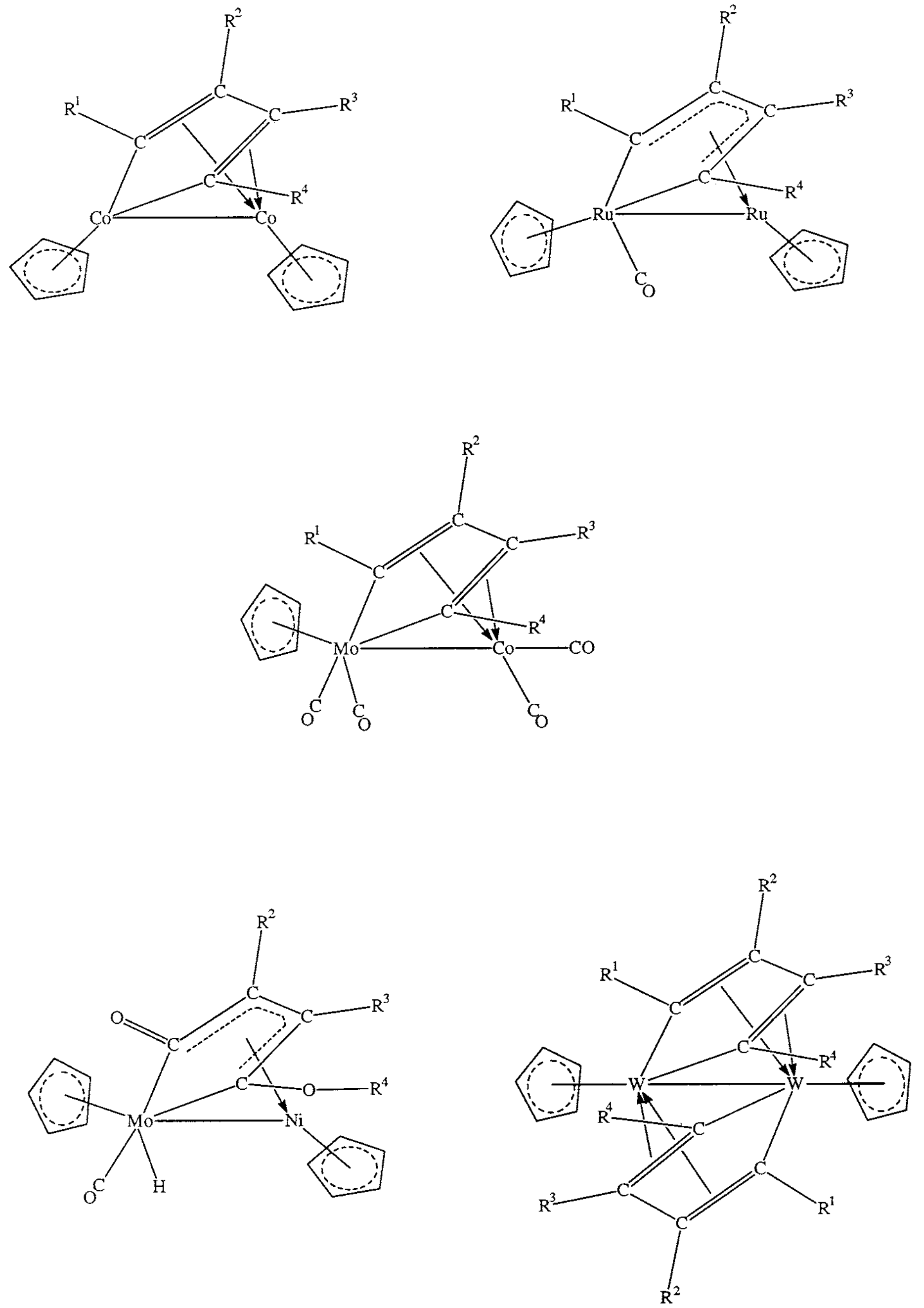


Fig. 2. Examples of dicobalt {$R^1 = R^2 = R^3 = R^4 = \mathrm{Cl}$} [45], diruthenium {$R^1 = R^2 = R^3 = R^4 = \mathrm{Ph}, \mathrm{CF_3}$} [25], cobalt–molybdenum {$R^1 = R^4 = \mathrm{Ph}$, $R^2 = R^3 = \mathrm{H}$} [47], nickel–molybdenum {$R^1 = R^2 = R^3 = \mathrm{Me}$} [48] ferrole structures and of an unusual 'bis-ferrole' complex {$R^1 = R^2 = R^3 = R^4 = \mathrm{Me}$} [49].

2.2. Synthesis of complexes **II**

These complexes are among the main products from the reactions of the iron triad metal carbonyls with alkynes and are obtained upon thermal degradation of complexes **I**. There exist, however, some 'independent' syntheses for complexes **II**; one is the desulfurization of thiophene on $Fe_3(CO)_{12}$ [26] to give $Fe_2(CO)_6(C_4H_4)$. Others are the reactions of $Fe(CO)_5$ [27] or of $[HFe(CO)_4]^-$ with alkynes [28]; interestingly, in the latter reaction non-sawhorse (see Fig. 1 and Section 3.3) complexes with two OH on the α-carbon atoms were obtained [29]. By contrast, sawhorse derivatives with OH groups on the α-carbons were obtained by reacting $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with C_2Et_2 in alkaline solution (and/or in hydrocarbons) [30].

Ferrole complexes have also been obtained by reacting the acetylides $Fe_2(CO)_6(\mu\text{-SEt})(\mu\text{-}\eta\text{-}C_2R)$ (R = Me, Ph) with alkynes [31]. To our knowledge similar reactions for diiron phosphido-bridged acetylides $Fe_2(CO)_6$

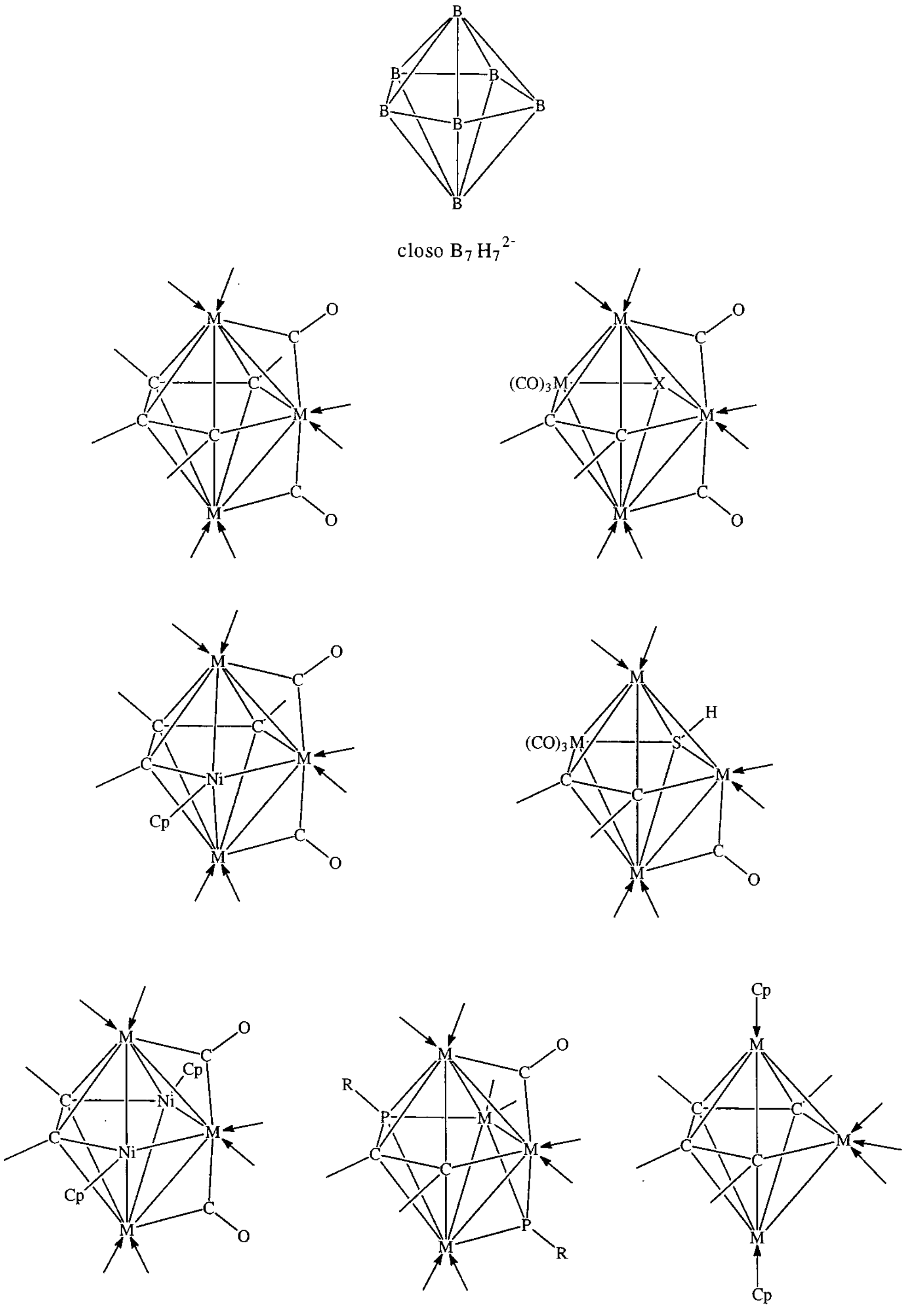


Fig. 3. Comparison of the skeletal structure of $[B_7H_7]^{2-}$ and of those of complexes **I**. Isolobal relationships for pentagonal bipyramidal structures containing a different number of metal atoms and/or heteroatoms. M = Fe, Ru, Os. X = P, N, S, Se, Te. Ligands omitted for clarity. See Section 2.1.1 and Refs. [16–22,25].

(μ-PPh$_2$)(μ-η-C$_2$R) have not been reported [32]. Unusual metallacyclic arrangements are also observed when coordinated diynes react with carbenes ([33]a) or when complexes with coordinated diynes undergo metal fragment condensation ([33]b).

2.3. Ferrole derivatives containing 'heteroelements' in the organic ring

As previously said, the reaction of $Fe_3(CO)_{12}$ with C_2Et_2 in hydrocarbons, or that of $Fe(CO)_5$ with C_2Et_2

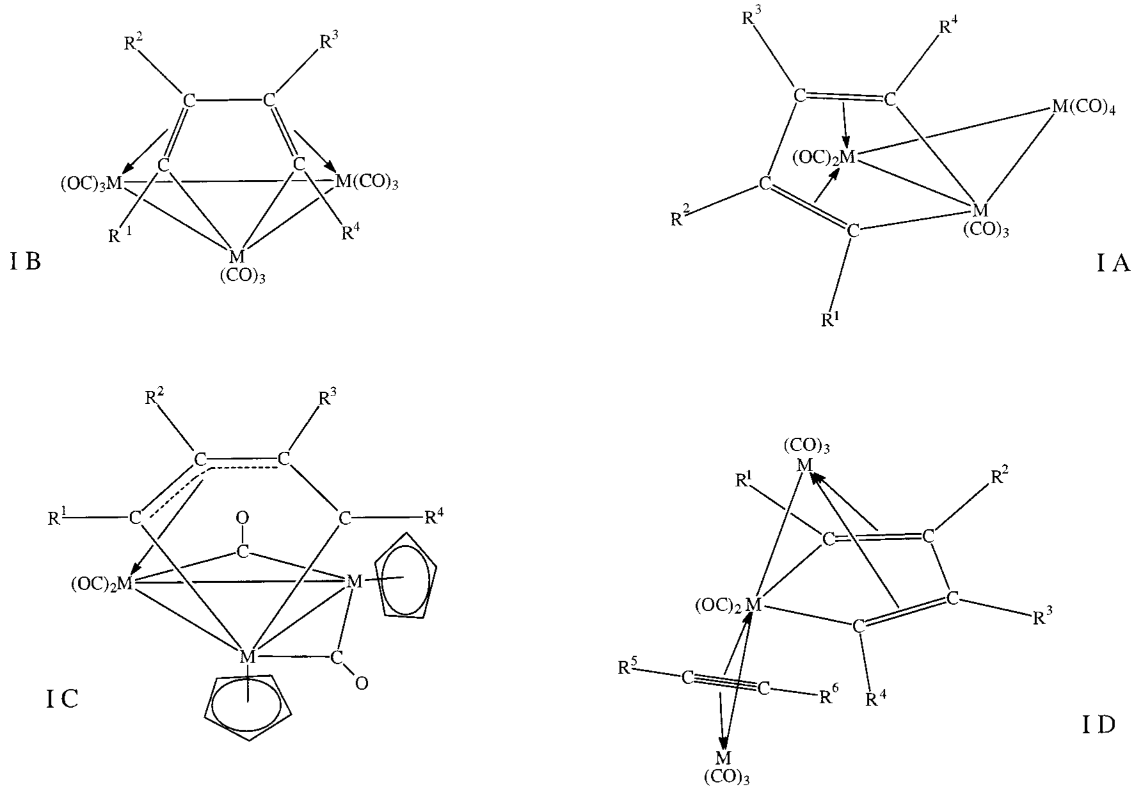


Fig. 4. Structures of complexes **IA** (top, right), **IB** (top, left), **IC** (bottom, left) and **ID** (bottom, right).

in CH_3OH/KOH, lead to maleoyliron and hydroxyferrole derivatives and to the carboxylato complex $Fe_2(CO)_6\{C_2Et_2(COO)\}$ [30]. For the latter complex a formation mechanisms requiring water was proposed [34]. Recently it was found that the complex is formed upon splitting of water, a process favoured by TLC silica [35]. A related reaction is that of the allenylidene iron derivative $Fe_3(CO)_9(\mu\text{-}CO)\{C{=}C{=}C(H)Ph\}$, where splitting of methanol does occur to form the ferrole complex $Fe_2(CO)_6\{Ph(H)CCCH(OMe)O\}$ (see Scheme 1) [36].

These complexes represent examples of structures with ‘heteroelements’ that replace carbon in the ferrole ring. Other compounds containing oxygen, nitrogen or sulphur in the metallacyclic ring are shown in Scheme 1 [34–41].

2.4. Synthesis of binuclear derivatives containing metals not belonging to the iron triad

The majority of complexes **II** contain iron triad metals. However, these structures can also be obtained from other transition metals [42]. For instance, ‘cobalt ferrolet’ complexes have been obtained by reacting $CO_2(CO)_8$ with alkynes [43]. Cobalt ferroles have also been obtained from terminal diynes with geminal methyl groups in α-position with respect to the triple bonds [44]. Bis-(cyclopentadienyl) dicobalt ferrole complexes have been reported [45]: one should keep in mind the isolobal relationships between $M(CO)_3$ and M(Cp) fragments [46].

A cobalt–molybdenum ferrole has also been obtained from the reaction of $(Cp)(PPh_3)(CO)_2MoCo(CO)_3(PPh_3)$ with phenylacetylene, after loss of the two phosphine ligands [47]; worthy of note is that, among six possibilities, only the α,α-isomer has been selectively obtained. Other molybdenum containing derivatives are discussed in Section 4.4.

A nickel–molybdenum complex, $(Cp^*Ni)\{C(OMe)C(Me)C(Me)\ C(O)\}\{CpMo(H)CO\}$ is found among the final products of the reaction between $(Cp^*Ni)Mo(CO)_3(Cp)$ and 2-butyne, which follows a complex pathway [48].

An unprecedented bis(metallacyclopentadiene) structure is obtained by treating $\{W(NCMe)(MeC_2\text{-}Me)_2(Cp)\}PF_6$ with sodium amalgam in a reductive dimerization process [49]. The structures of the above complexes are shown in Fig. 2.

3. Structures, isolobal relationships and isomerism of complexes I and II

3.1. Structural features and isolobal relationships

*3.1.1. Complexes **I***

The more common structure for these complexes is shown in Fig. 1 and consists of an open bimetallic frame

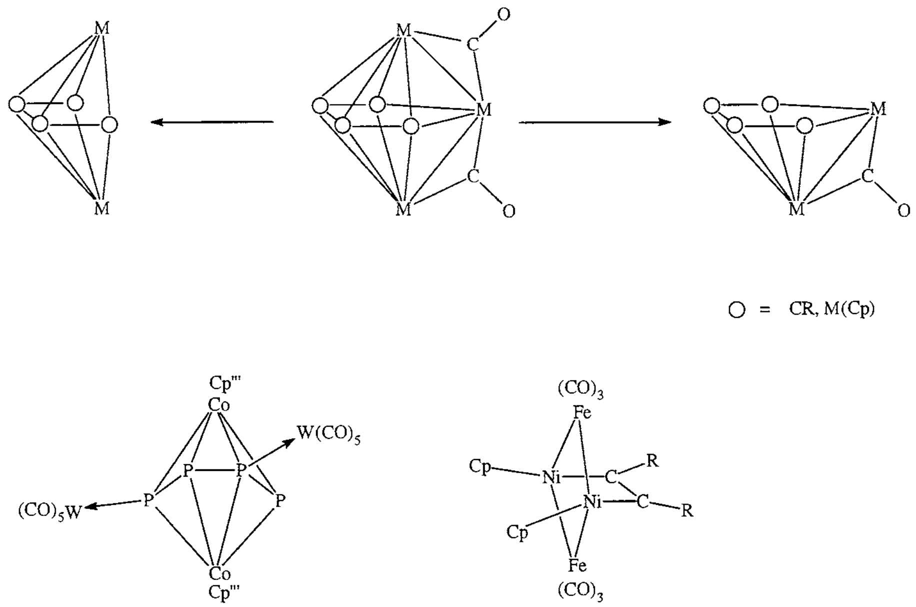


Fig. 5. Alternative degradation pathways for complexes **I** leading to complexes **II** (right) or to 'square planar' structures (left) and examples of square planar derivatives [55,56].

with two bridging CO and a metallacyclic ring linked (via σ-bonds) to the equatorial metal, and (via π-bonds) to the apical metal atoms. All of the iron complexes, except one [50], adopt this kind of structure. This should be particularly stable because of its PSEPT relationship [51] with the closo $[B_7H_7]^{2-}$ anion [52]. The stability of this structural arrangement is also reflected by the fact that there are several clusters with a butterfly or square pyramidal metal core containing heteroatoms (P, N, S...), which are related each to the other and to complexes **I** by isolobal relationships [46], as shown in Fig. 3.

*3.1.2. Complexes **IA**, **IB**, **IC***

For ruthenium and osmium, however, there are some structural alternatives, as follows:

1. The five-membered metallacyclic ring involves one of the (closed triangular) cluster edges with a bonding interaction typical of nuclear ferroles, complexes **IA**. Additional features may consist in the orthometalation of a phenyl group belonging to a C_2Ph_2 ligand on a cluster metal atom or in the presence of a third (independent) alkyne coordinated to the cluster [23].
2. The five-membered ring is sitting on the face of a closed triangular cluster, as found for $Os_3(CO)_9(RC_2R')_2$ [23,24], complexes **IB**. Reorientation from structure **IB** to **IA** has been observed upon orthometalation of Ph or $Fe(Cp)_2$ substituants [53]. Finally, the metallacyclic ring sitting on the face of the triangular frame may act as a μ-σ-(π-allylic) ligand as in $Cp_2Ru_3(\mu\text{-}CO)_2\{C_2(CF_3)_2\}\{C_2Ph_2)$ [25], complexes **IC**.

An intermediate situation between trinuclear and binuclear derivatives is that found in the open cluster $Os_3(CO)_8(C_2Me_2)_3$ {**ID**}in which a metallacyclic ring formed by two alkynes is linked to two metal atoms, and the third alkyne is independently coordinated to the other Os–Os bond [54]. Examples of structures **IA**–**ID** are reported in Fig. 4.

*3.1.2.1. 'Degradation' of complexes **I**.* 'Degradation' of complexes **I** (usually under thermal conditions) leads to nido-structures and may occur in two alternative ways:

1. Loss of an apical metal fragment, leading to the binuclear ferroles **II**.
2. Loss of an equatorial fragment. These pathways are shown in Fig. 5.

The latter is apparently less common; it has been observed (or hypothesized) for iron-nickel clusters [55]. Isolobally related systems are the heterometallic $[(1,2,4\text{-}Bu^t_3C_5H_2)CO_2(P_4)\{M(CO)_5\}_n]$ complexes (M = Cr, Mo, W; $n = 1$, 2) containing (equatorial) P_4 chains [56].

In some instances (and with alkynes containing 'exotic' substituants) decomposition of complexes **I** leads to nonplanar arachno ferrole structures [57].

The isolobal relationships between the nido-ferrole structures **II** and those of boranes or carboranes are well exemplified by the reactions of diborylcarbenes with bis(cyclooctadiene)platinum to give ferrole-like structures [58], Fig. 6.

3.2. Substitutional isomerism

*3.2.1. In complexes **I***

It occurs when alkynes RC_2R' (R = / = R') take part in the formation of metallacycles in complexes **I**. Sub-

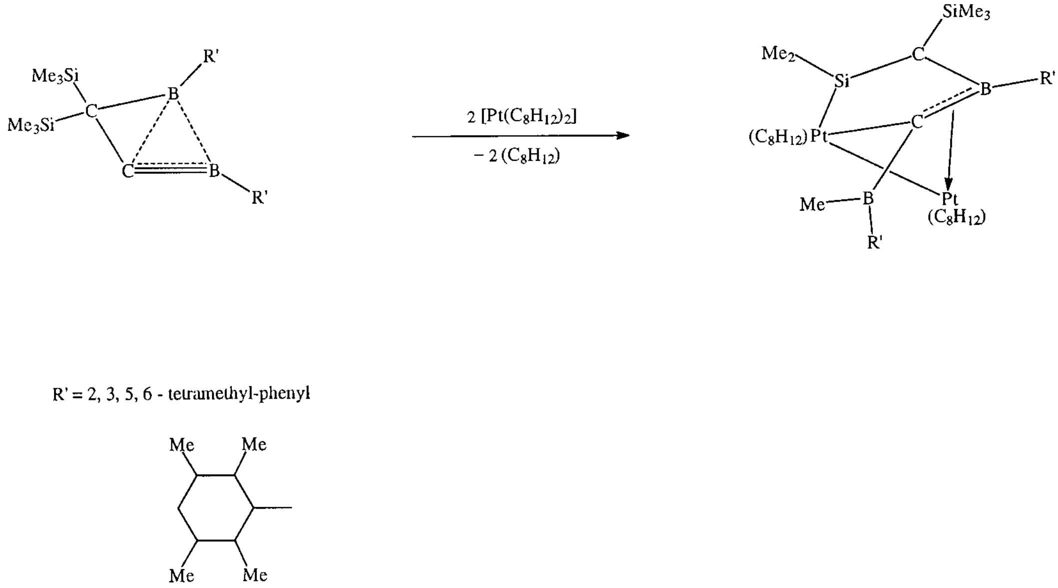


Fig. 6. Reactions of diboryl-carbenes with bis(cyclooctadiene)platinum to form ferrole-like structures.

stitutional isomers are obtained upon head-to-tail or tail-to-tail coupling of asymmetrical alkynes, presumably following the reaction path discussed in Section 2.1. Other formation mechanisms for complexes **I**, starting for example from bismethylidyne parents (Section 2.4), may lead to isomers; the number of isomers for each combination is listed in Scheme 2.

Fenske–Hall calculations on $M_3(CO)_8(C_4H_4)$ (M = Fe, Ru) complexes, taking into account the interactions between C_4H_4 and $M_3(CO)_8$ fragments were performed [59]. The interaction of the iron-containing fragment is stronger than that of ruthenium; the bridging CO's exert only minor effects. An UV-PES study on complexes **I** and on non-sawhorse ferroles indicates that the high stability of the metallacyclic rings can be due to strong Fe–C(σ) interactions; the semibridging carbonyl contributes to stabilization by helping with charge transfer to the ring metal atom [60]. Anyhow, substitutional isomerism has not been taken into account.

3.2.2. *In complexes* ***II***

Extended Hueckel 'CACAO' calculations [61] showed that the energy differences between substitutional iron–ferrole isomers are small. NMR data show considerable differences in the chemical shifts of the ferrole ring carbons [62].

The reaction of $Ru_3(CO)_{12}$ with ferrocenylacetylene $(Fc)C_2H$ yields a mixture of the hydrido-acetylide $HRu_3(CO)_9(C_2Fc)$, of the ferrole $Ru_2(CO)_6(HC_2Fc)_2$ [α,α-isomer] and of the flyover $Ru_2(CO)_6(HC_2Fc)_2CO)$ [α,β-isomer] [63,64]. The reaction of $Ru_3(CO)_{12}$ with 1,4-diphenylbuta-1,3-diyne affords ruthenium ferrole [α,β-isomer] and flyover [α,α-isomer] derivatives, whereas from $Ru_3(CO)_{11}(MeCN)$ the ferrole $Ru_2(CO)_5(MeCN)(L)$ [α,α-isomer, MeCN on Ru(σ)] is obtained, together with tri- and tetra-nuclear alkyne derivatives [65].

Modelling studies by Osella and coworkers [3] indicate that the sterically favoured isomers for ferroles **II** are the α,β-ones; the observed predominance of the α-α-isomers has been ascribed to a kinetic rather than thermodynamic control of the formation reactions. They hypothesized that 'independent' formation of ferroles occurs starting from mononuclear complexes with two coordinated alkynes, followed by condensation of another metal fragment; this mechanism would account for the observed isomerism and is similar to the one proposed for the formation of $(Cp)Co(RC_2R')_2$ [66]. The recent isolation and structural characterization of the 'tweezer' complex $\{(Cp^*)(PEt_3)Ir(C_2Ph)_2\}Pt(C_6F_5)_2$ accords with this hypothesis [67].

Hoffmann and coworkers have proposed a different formation mechanism starting from binuclear iron-alkyne derivatives; again coupling with less sterically encumbered substituants would be favoured [68] (Fig. 7).

Most of the ferrole complexes are however obtained upon thermal degradation of clusters **I**; therefore the question arises whether substitutional isomerism can be maintained during loss of $Fe(CO)_2$ fragments. This point has not been clarified yet, to our knowledge. However, it has been shown that condensation of metal fragments with ferroles leads to complexes **I** with isomerism retention [69].

3.3. *Structural isomerism*

As discussed in Section 3.1, complexes **I** may show different structural arrangements due to the orientation

Substitutional isomers of complexes I obtainable following different synthetic patterns.

Synthetic method	number of isomers
Coupling of alkynes	
a) Two symmetrical (RC_2R) alkynes	one
b) One symmetrical (RC_2R) alkyne one asymmetrical ($R^1C_2R^2$) alkyne	two
c) Two asymmetrical, identical ($R^1C_2R^2$) alkynes	three
d) Two different asymmetrical alkynes ($R^1C_2R^2$) ($R^3C_2R^4$)	three
Coupling of alkynes and methylidynes	
e) One symmetrical alkyne (RC_2R) and two identical methylidynes (CR^1)	two
f) One asymmetrical alkyne (RC_2R^1) and two identical methylidynes (CR^2)	four
g) One asymmetrical alkyne (RC_2R^1) and two different methylidynes (CR^2)(CR^3)	eight

Scheme 2.

of the metallacyclic ring with respect to the cluster frame (Complexes **IA**, **IB**, **IC**).

For the iron–ferrole derivatives **II**, another type of structural isomerism has been observed. Almost 100 ferrole derivatives have been reported in the literature [70], and they mostly belong to the 'non sawhorse'; arrangement [71] (Fig. 1), as shown by the X-ray structural studies available.

The above mentioned thermal degradation of closo-complexes **I** {containing two bridging carbonyls} to nido-complexes **II** would require the formation of non-sawhorse structures, retaining a semi-bridging CO. The formation of sawhorse isomers would be expected to follow one of the mechanisms discussed in Section 3.2.2. The already mentioned theoretical study on the $Fe_2(CO)_6$ frame substituted with various ligands {including alkyne olygomers} [68] has shown that formation of ferrole complexes is favoured by electronic reasons and distortion effects and that ligands inhibiting the electron acceptor ability of the C_4H_4 ring (e.g. OH groups) make the ferrole structures less stable. In addition, it has been shown that the non-sawhorse structure is favoured (about 0.3 eV) with respect to the sawhorse one. In this paper unusual syntheses of ferrole complexes and isolobal relationships between them and carboranes are also discussed.

3.4. NMR fluxionality and chromatographic studies

Solution fluxionality has been found for ferrole complexes as indicated by variable temperature NMR studies; 'ring slippage' is the most common process, as observed for diiron [70], dirhodium [72] and cobalt–tungsten [73] complexes. Attempts to separate the substitutional isomers of the diiron ferrole [74] or flyover [75] complexes via HPLC were successful.

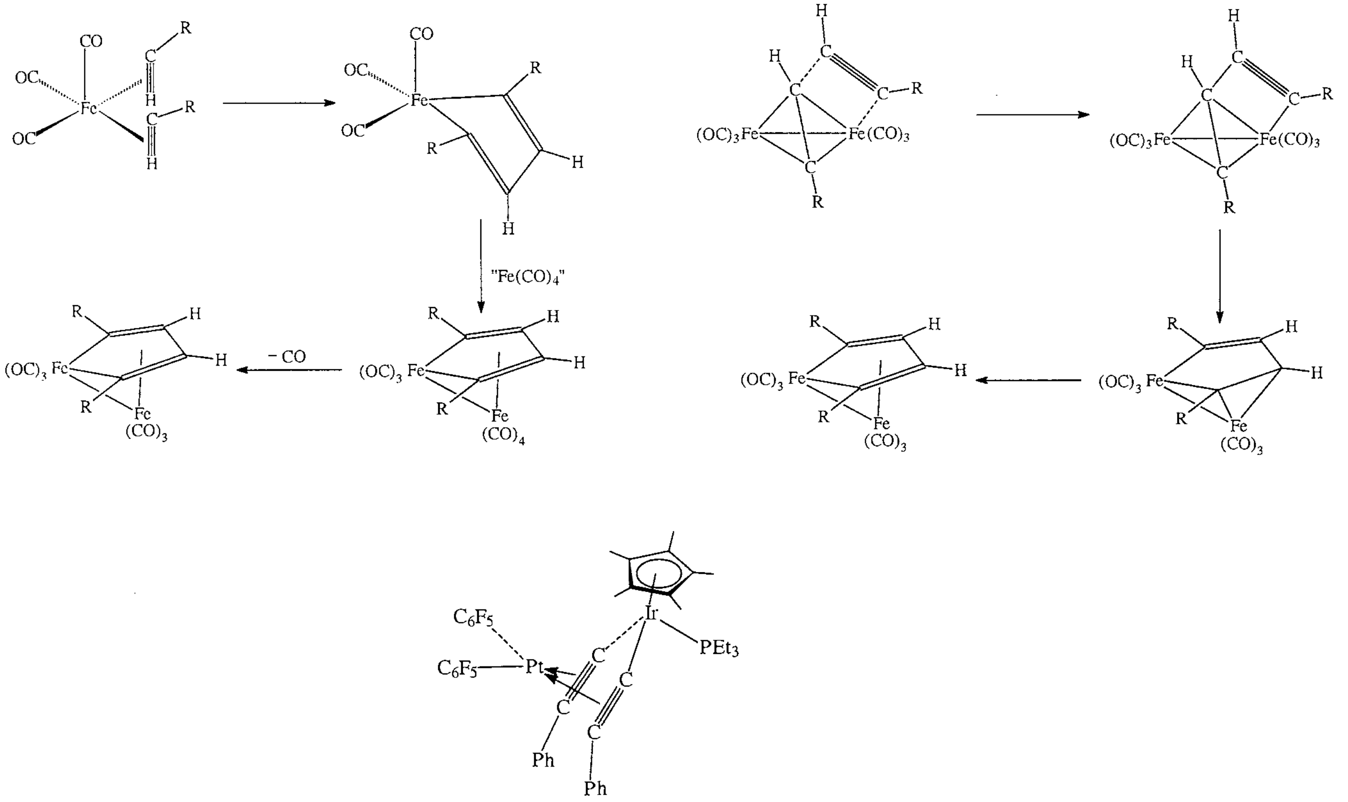


Fig. 7. 'Independent' formation mechanisms proposed for complexes **II**. Top, left, Osella and coworkers [3], right Hoffmann and coworkers [68]. Bottom, a Pt–Ir 'tweezer' complex [67].

4. Reactivity of the complexes

As previously pointed out, the interest in complexes **I** is justified by their structural features and by the isolobal relationships with other clusters. Their reactivity, however, is not particularly interesting; in the light of the actual knowledge, they do not participate in organic syntheses and have only a minor importance in catalytic reactions. By contrast, the binuclear complexes **II** are found as intermediates in a considerable variety of stoichiometric and catalytic reactions [2]. Examples of organic products obtained through the intermediacy of complexes **II** are reported in Fig. 8.

4.1. Ferrole derivatives as intermediates in the formation of substituted benzenes

Cobalt-containing complexes **II** play a key role as intermediates in the homogeneous reactions of cobalt carbonyls with alkynes leading to organic products [44,76]. In particular, alkyne cyclotrimers {1,2,4- or 1,3,5-substituted benzenes} may be easily obtained; a summary of these reactions is given in Ref. [77]. The formation of ferrole complexes occurs before that of dicobalt flyover derivatives {Complexes **IVA**, Fig. 11}; the latter are formed by three alkynes whose head-to-tail or tail-to-tail coupling is responsible for benzene isomerism [76]. A similar reaction sequence has been observed in the reactions of $CO_2(CO)_8$ with phenylacetylene [43]. Worthy of note is that the structure of the above flyover derivatives is different from that of the diiron complexes (**IVB**), obtained from type **II** structures.

Complex $CO_2(CO)_5\{(HC_2CCMe_2)_2NMe\}$, obtained from a terminal diyne [44], reacts with phenylacetylene to form benzene cyclotrimers in high yields, together with a nitrogen-containing product. It also reacts with nitrils to produce nitrogen-containing heterocycles and a cyclopentenone derivative obtained upon insertion of CO into the cobaltacyclopentadiene parent complex (Fig. 9).

It is worth noting that flyover structures of type **IVA** have also been reported in the case of diruthenium bis(cyclopentadienyl) frames [78].

Last but not least, ruthenium ferrole complexes {type **II**} and a triruthenium cluster with a metallacyclopentadienic ring on a cluster edge {type **IA**} have been suggested as intermediates in the cyclization of terminal diynes to give unexpected heterocyclic derivatives [79] (Fig. 10).

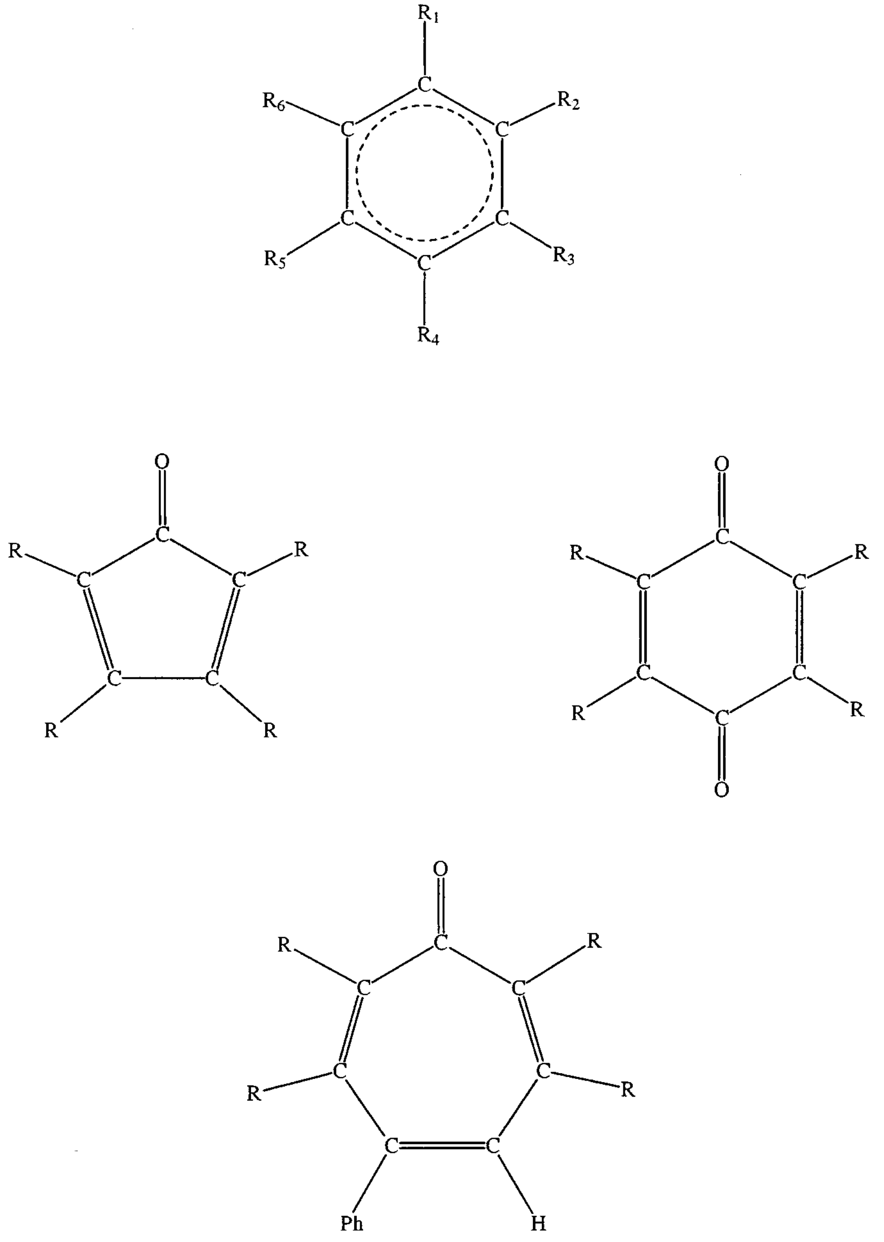


Fig. 8. Alkyne oligomers obtained through the intermediacy of structures **II** (see text).

4.2. Formation and role of iron or ruthenium flyover derivatives

Iron {or ruthenium} flyover derivatives with structures different from those observed with cobalt (**IVA**) are also known; these complexes are formed through cyclization of three alkynes, one of which uses only one carbon atom. More common is the structure formed by only two alkynes and a CO inserted in between [80] {Complexes **IVB**}. The structures of complexes **IV** are shown in Fig. 11 [80–87]. These flyover complexes are considered intermediates in the formation of cyclopentadienone derivatives and of tropones. However, their formation pathways and isomerism have not been fully elucidated.

Apparently the presence of Me_3NO and/or of dppm ligands favours ferrole-flyover transformations, presumably by making the insertion of CO between coordinated alkynes easier. For example, (non sawhorse) $Fe_2(CO)_6(C_2Et_2)_2$ [88], when treated with dppm in the presence of Me_3NO inserts CO to form the ‘flyover’ derivative $Fe_2(CO)_5(dppm)[(C_2Et_2)_2CO]$; the latter, in the presence of HC_2Ph and Me_3NO, gives the tropone precursor $Fe_2(CO)_5[(C_2Et_2)_2(CO)(HC_2Ph)]$ [82] shown in Fig. 13. Stepwise formation of coordinated tropones in the photochemical reactions of $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)$ with alkynes, through the intermediacy of type **IVB** complexes, has been recently observed [89].

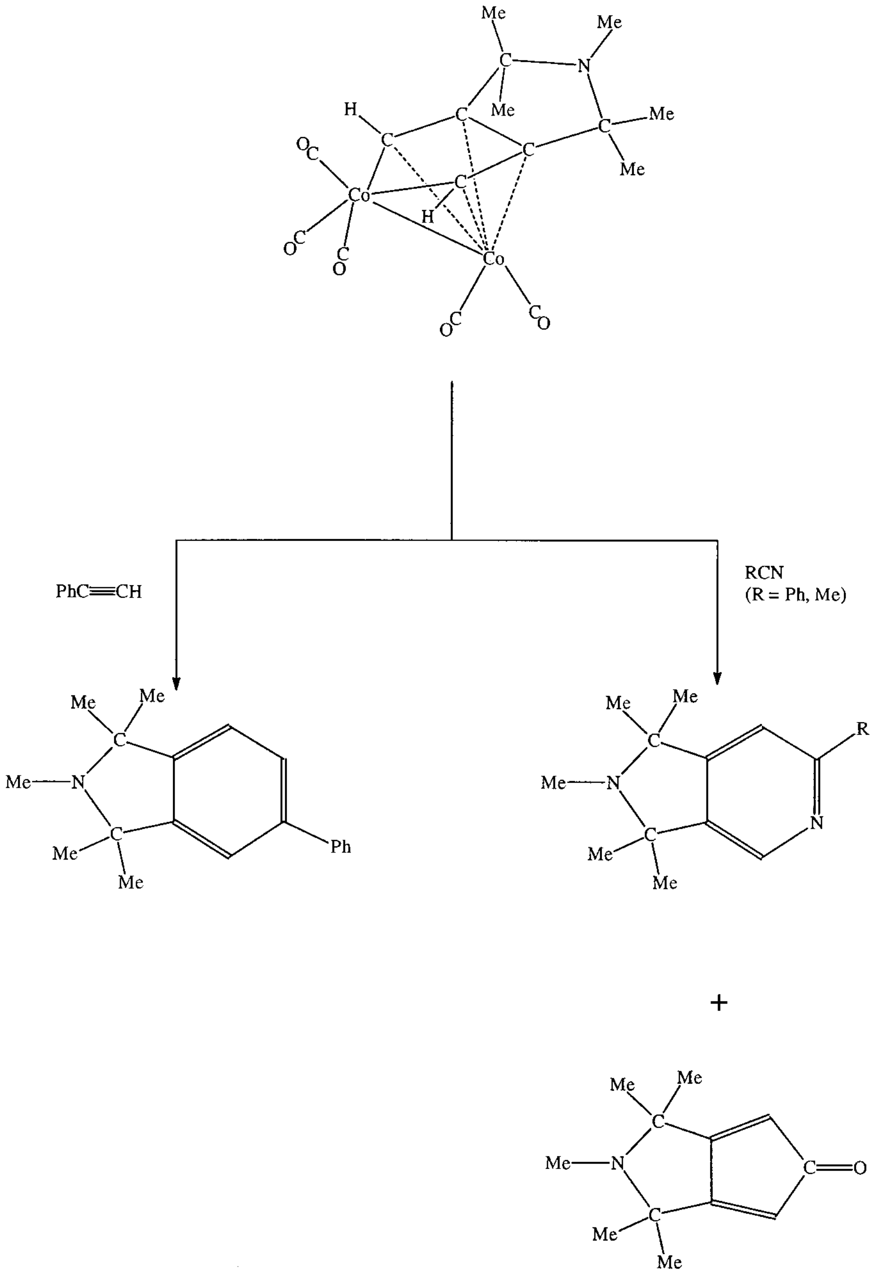


Fig. 9. Reactions of a dicobaltacyclopentadiene with alkynes and nitrils (for details see Section 4.1).

Diruthenium flyover complexes have been obtained by reacting $Ru_3(CO)_9(C_{16}H_{16})$ {$C_{16}H_{16}$ = 2,2-paracyclophane} with C_2Ph_2 and Me_3NO in dichloromethane [90]. Other diruthenium flyover derivatives have been obtained upon thermal degradation of trinuclear dppm-substituted clusters [86].

As previously pointed out, there is no certain evidence for the formation mechanisms of and the isomerism for these derivatives. Several mechanisms {all of them evidenced in the literature} could be invoked: (a) insertion of CO during 'ring slippage'; (b) formation of a 'tweezer' intermediate [91] followed by CO insertion; (c) partial opening of the ferrole ring and CO insertion; (d) Fe–Fe bond cleavage in the presence of CO [92]. Recent work on dirhodium derivatives has provided some evidence for the formation of coordinated 'butadienes' which could then undergo cyclization and CO insertion and/or coupling of a coordinated cyclopentadiene with a coordinated CO/alkyne ligand (Fig. 12) [93].

Labelling experiments indicate that the ferrole $Fe_2(CO)_6(C_2Et_2)_2$ can be selectively enriched with ^{13}CO on the Fe_1 atom (Fig. 1). No ^{13}CO enrichment of the ketonic carbonyl was observed in the corresponding **IVB** flyover complex; this behaviour could indicate that this carbonyl ligand comes from the ferrole Fe_2 atom [94].

4.3. Binuclear complexes as precursors of tropones

The reaction of diiron flyover complexes (**IVB**) with alkynes may lead to the formation of binuclear ‘precursors’ of tropones [82]. So far, only three complexes with this structural features have been characterized by X-ray diffraction {Complexes **V**}; they show a different chain isomerism, as shown in Fig. 13 [82,95,96]. The substitutional isomerism of the C_1–C_4 part of the chain formed by two alkynes with a CO inserted between them corresponds to the one found in the case of the parent flyovers; the entering HC_2R alkyne (C_5–C_6) undergoes a side-on attack at the Fe–C(σ-π) bond and forms a new C–C bond by using the C–H end.

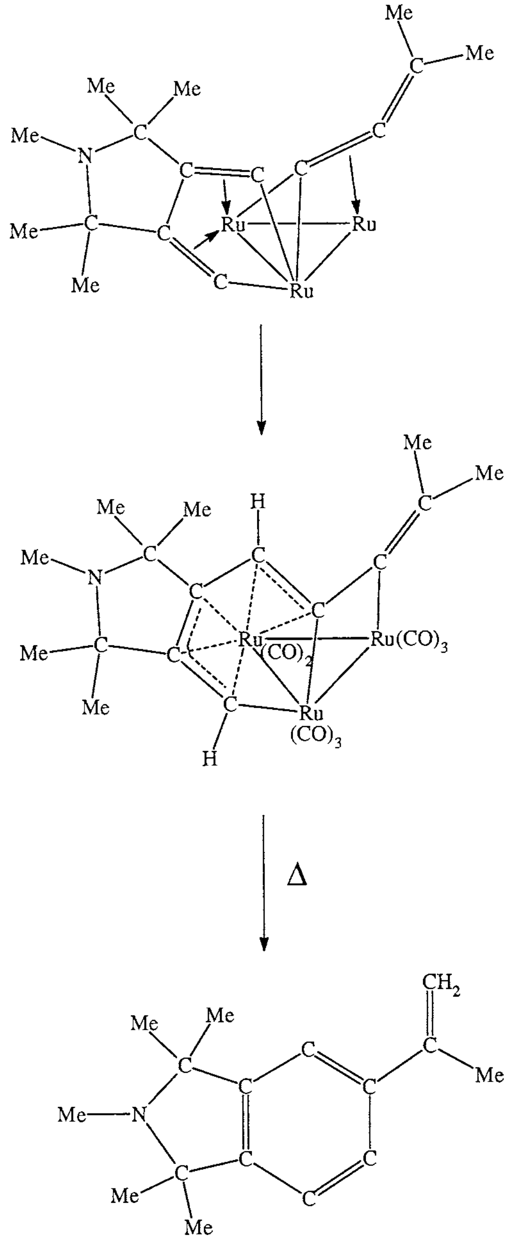


Fig. 10. Reaction sequence leading to an unexpected cyclic product from functionalized diynes. Top, proposed metallacyclic intermediate (CO’s omitted for clarity); centre X-ray structure of a metallacyclic complex which releases the organic product (bottom) upon thermal treatment.

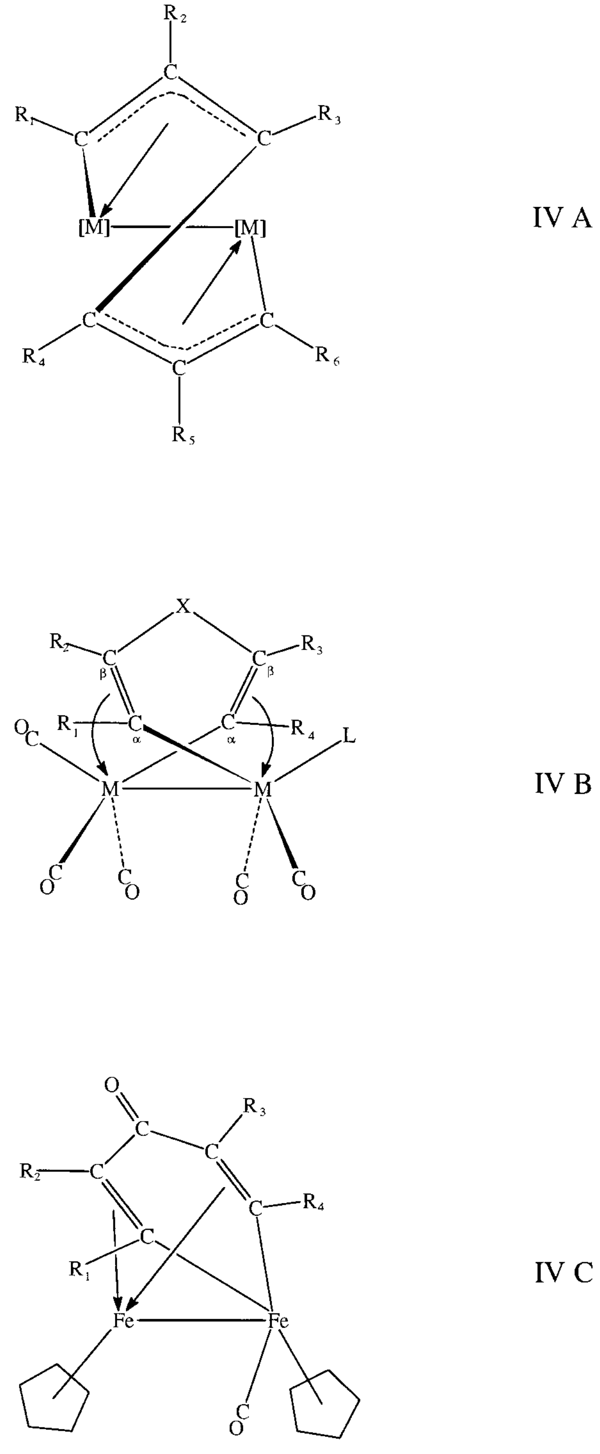


Fig. 11. Structures of flyover complexes: top, **IVA** {M = Co(CO)$_2$ [76], M = CpRu [78]}; centre **IVB** {M = Fe, L = CO, X = CO, R = Ph [80], C_2SiMe/SiMe [85]; L = PPh_3, dppm, X = CO, R = Me, Et, Me/Ph(isomers) [81,82]; L = CO, X = C=CH_2, R = H [83]; L = CO, X = $SiPh_2$, R = Me [84]; M = Ru, L = CO, X = CO, R = Ph, H [86]; M = CpCo, X = CO, R = Cl [45]}; bottom, the unique example reported for a “side-on” structure (**IVC**, R = CF_3) [87].

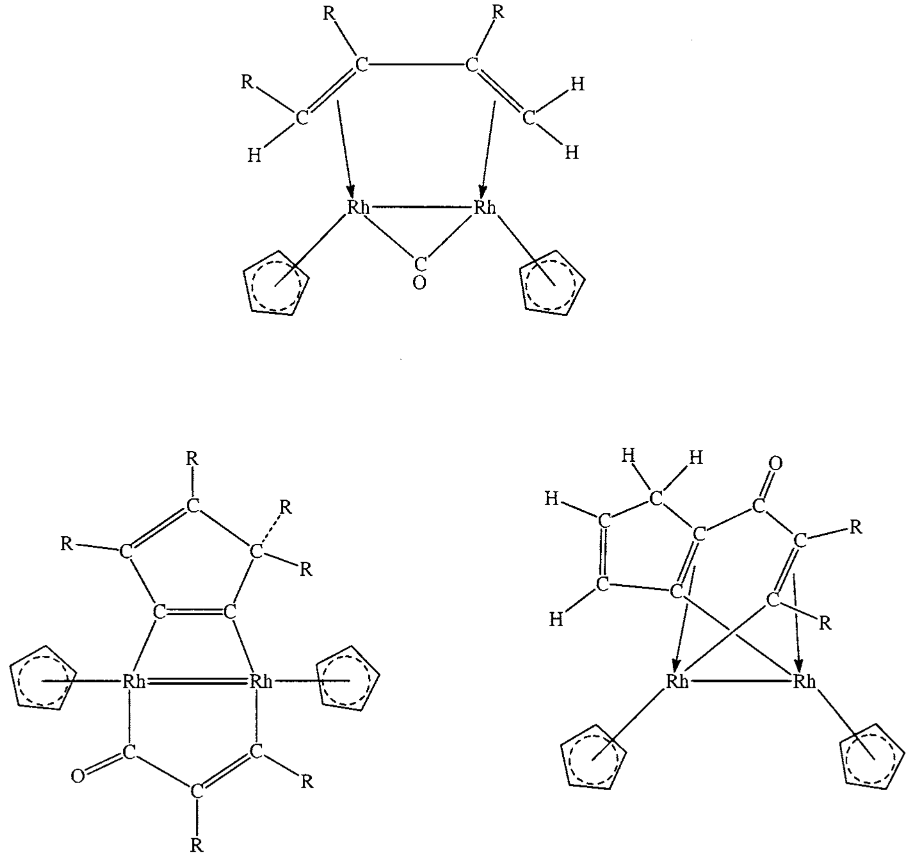


Fig. 12. Dirhodium complexes which could be involved in the formation of flyover structures [93].

A reaction sequence leading to alkyne cyclotrimers and tropones has been found when (Cp)Co(CO)$_2$ was reacted with C_2Cl_2 (dichloroacetylene) in diethylether; hexachlorobenzene was formed together with bis(cyclopentadienyl)dicobalt ferrole and flyover complexes, type **III** mononuclear complexes and π-substituted hexachlorotropone derivatives [45].

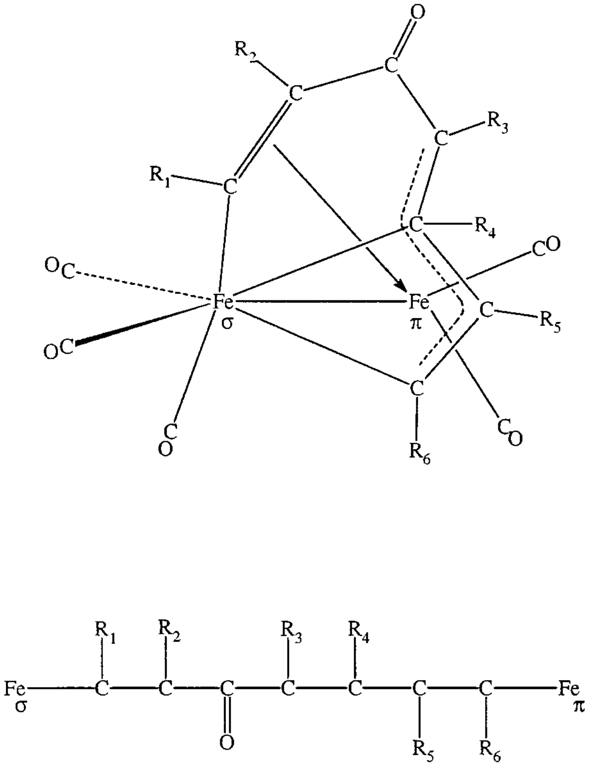
4.4. Reactions leading to ferrole ring cleavage

'Dismantling' of a metallacyclopentadiene ring may also occur. Examples are: (a) butterfly alkyne-methylidyne derivatives of cobalt and molybdenum have been obtained by reacting $Co_2(CO)_8$ with the ferrole $(Cp)_2(CO)Mo(C_2Ph_2)_2$ [97]. The same complex reacts with oxygen giving an oxoferrole species which further reacts with $Ru_3(CO)_{12}$ or $Co_2(CO)_8$ to form a pentanuclear ruthenium–molybdenum alkylidyne oxo complex or a cobalt–molybdenum ferrole derivative [98]. These reactions could represent the reverse process to that leading to the formation of complexes **I** starting from bismethylidyne clusters (Section 2.1.2). This behaviour could also be of some interest when considering that metallacyclic species have been suggested as intermediates in alkene and alkyne metathesis reactions.

4.5. Pentagonal bipyramidal complexes in catalysis

Type **I** and **II** iron and ruthenium complexes have been found among the organometallic products recovered after the homogeneous and solid-gas catalytic hydrogenation of alkynes on iron-, ruthenium- and iron–ruthenium clusters [99,100]. These complexes are unreactive byproducts formed upon condensation of metal fragments promoted by (excess) alkynic substrates.

A triruthenium complex {type **IB**} with a metallacyclic ring formed by two C_2Ph_2 molecules has also been reported [99]. Finally, type **I** complexes have been obtained during the hydrogenation of alkynes in the presence of phosphinidene-substituted ruthenium clusters [101]. Bis(cyclopentadienyl)-diruthenium ferrole-like complexes have also been isolated and characterized during the homogeneous hydrogenation of alkynes on $(Cp)_2Ru_3(CO)_5(C_2Ph_2)$; once again, they were inactive reaction byproducts [102]. Finally, during the hydrogenation of C_2Et_2 in the presence of $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ supported on inorganic oxydes the formation of 'parallel' $H_2Ru_3CO)_9(C_2Et_2)$ {active intermediate} and of $Ru_3(CO)_8(C_2Et_2)_2$ {side product} was observed [94]; the same products were found when hydrogenation was



R_1=H, R_2=Ph, R_3=H, R_4=Ph, R_5*=H, R_6=Ph	Ref. [95]
R_1=H, R_2=Bu^t, R_3=Bu^t, R_4=H, R_5*=H, R_6=Bu^t	[96]
R_1=R_2=R_3=R_4=Et, R_5*=H, R_6=Ph	[82]
R_1=R_2=R_3=R_4=Et, R_5*=H, R_6=Bu^t	[82]

Fig. 13. Structure and isomerism for complexes **V**.

performed in homogeneous conditions [99] or when $Ru_3(CO)_{12}$ was reacted with C_2Ph_2 in CH_3OH/KOH solution [103,104].

5. Concluding remarks

Closo- and nido-pentagonal bipyramidal structures **I** and **II**, which are formed upon reaction of metal carbonyls with alkynes, show a very high stability and similarity with borane structures. These derivatives, particularly complexes **II**, play important roles in the cyclo-oligomerization and co-oligomerization of alkynes with different substrates under homogeneous stoichiometric or catalytic conditions.

Several reaction pathways have been elucidated, but there are still some unknown aspects in this field of chemistry, in particular those concerning the formation mechanisms of the flyover and 'tropone' derivatives.

Acknowledgements

Financial support to this work came from MURST (Rome). Dr Domenica Marabello is ackowledged for the execution of drawings.

References

[1] (a) W. Hubel, in: I. Wender, P. Pino (Eds), Organic Syntheses via Metal Carbonyls, vol. 1, Wiley-Interscience, New York, 1968, p. 273. (b) E. Sappa, A. Tiripicchio, P. Braunstein, Chem. Rev. 83 (1983) 203. (c) E. Sappa, J. Cluster Sci. 5 (1994) 211.

[2] (a) N. Calderon, J.P. Lawrence, F.A. Ofstead, Adv. Organomet. Chem. 17 (1979) 449. (b) R.R. Schrock, J. Organomet. Chem. 300 (1986) 249. (c) N.E. Schore, Chem. Rev. 88 (1988) 1081. (d) F. Biagini, A.M. Caporusso, T. Funaioli, C. Fachinetti, Angew. Chem. Int. Ed. Engl. 28 (1989) 1009. (e) K.O. Bishop, Chem. Rev. 76 (1976) 461. (f) R.J. Mc Kinney, J. Chem. Soc. Chem. Commun. (1980) 490. (g) C. Otero Arean, E. Escalona Platero, G. Spoto, A. Zecchina, J. Mol. Catal. 56 (1989) 211.

[3] D. Osella, G. Dutto, C. Nervi, M.J. McGlinchey, A. Vessieres, G. Jaouen, J. Organomet. Chem. 533 (1997) 97.

[4] J.A. Bandy, H.E. Bunting, M.H. Garcia, M.L.H. Green, S.R. Marder, M.E. Thompson, D. Bloor, P.V. Kolinsky, R.J. Jones, J.W. Perry, Polyhedron 11 (1992) 1429.

[5] A discussion of clusters with alkynes coordinated in parallel or perpendicular fashion is in: S. Deabate, R. Giordano, E. Sappa, J. Cluster Sci. 8 (1997) 407.

[6] Iron derivative: (a) R.P. Dodge, V. Shomaker, J. Organomet. Chem. 3 (1965) 274. Ruthenium derivative: (b) S. Rivomanana, G. Lavigne, N. Lugan, J.-J. Bonnet, Organometallics 10 (1991) 2285.

[7] R. Victor, V. Usieli, S. Sarel, J. Organomet. Chem. 129 (1977) 387.

[8] (a) E. Rosenberg, S. Aime, L. Milone, E. Sappa, A. Tiripicchio, A.M. Manotti Lanfredi, J. Chem. Soc. Dalton Trans. (1981) 2023. (b) S.A.R. Knox, J. Cluster Sci. 3 (1992) 385.

[9] E. Sappa, A.M. Manotti Lanfredi, A. Tiripicchio, Inorg. Chim. Acta 42 (1980) 255.

[10] E. Sappa, G. Predieri, A. Tiripicchio, F. Ugozzoli, Gazz. Chim. Ital. 125 (1995) 51.

[11] G. Gervasio, R. Giordano, E. Sappa, M. Costa, G. Predieri, A. Tiripicchio, J. Cluster Sci. 4 (1993) 33.

[12] A.D. Shaposhnikova, G.L. Kamalov, R.A. Stadnichenko, A.A. Pasynskii, I.L. Eremenko, S.E. Nefedov, Yu. T. Struchov, A.I. Yanovsky, J. Organomet. Chem. 405 (1991) 111.

[13] (a) O. Gambino, M. Valle, S. Aime, G.A. Vaglio, Inorg. Chim. Acta 8 (1974) 71. (b) R.P. Ferrari, G.A. Vaglio, O.Gambino, M. Valle, G. Cetini, J. Chem. Soc. Dalton Trans. (1972) 1998. (c) S. Aime, L. Milone, D. Osella, M. Valle, J. Chem. Res (S) (1978) 77; ibid (M) (1978) 785.

[14] D. Nuel, F. Dahan, R. Mathieu, J. Am. Chem. Soc. 107 (1985) 1658.

[15] (a) D. Lentz, H. Michael, Angew. Chem. Int. Ed. Engl. 28 (1989) 321. (b) Idem, Chem. Ber. 121 (1988) 1413; J. Organomet. Chem. 327 (1989) 109.

[16] (a) F. Van Gastel, A.J. Carty, M.A. Pellinghelli, A. Tiripicchio, E. Sappa, J. Organomet. Chem. 385 (1990) C50. (b) J. Lunniss, S.A. MacLaughlin, N.J. Taylor, A.J. Carty, E. Sappa, Organometallics 4 (1985) 2066. (c) J.F. Corrigan, S. Doherty, N.J. Taylor, A.J. Carty, Organometallics 12 (1993) 1365. (d) K. Knoll, Th. Fassler, G. Huttner, J. Organomet. Chem. 332 (1987) 309. (e) D. Buchholz, G. Huttner, L. Zsolnai, J. Organomet. Chem. 381 (1990) 97.

[17] (a) M.L. Blohm, W.L. Gladfelter, Organometallics 5 (1986) 1049. (b) J.S. Song, S.H. Han, N.T. Nguyen, G.L.Geoffroy, A.L. Rheingold, Organometallics 9 (1990) 2386.

[18] (a) R.D. Adams, S. Wang, J. Am. Chem. Soc. 109 (1987) 924. (b) R.D. Adams, J.E. Babin, M. Tasi, T.A. Wolf, Organometallics 6 (1987) 2228. (c) Th. Fassler, G. Huttner, J. Organomet. Chem. 381 (1990) 391.

[19] B. Eber, D. Buchholz, G. Huttner, Th. Fassler, W. Imhof, M. Fritz, J.C. Jochims, J.C. Daran, J. Jeannin, J. Organomet. Chem. 401 (1991) 49.

[20] A.J. Arce, Y. De Sanctis, R. Machado, M.V. Capparelli, J. Manzur, A.J. Deeming, Organometallics 14 (1995) 3592.

[21] (a) D. Osella, E. Sappa, A. Tiripicchio, M. Tiripicchio Camellini, Inorg. Chim. Acta 42 (1980) 183. (b) A. Tiripicchio, M. Tiripicchio Camellini, E. Sappa, J. Chem. Soc. Dalton Trans. (1984) 627.

[22] J.T. Jaeger, A.K. Powell, H. Vahrenkamp, Chem. Ber. 121 (1988) 1729.

[23] First structural determinations on osmium derivatives (**IA**): G. Ferraris, G. Gervasio, J. Chem. Soc. Dalton Trans. (1972) 1057; (1973) 1933; (1974) 1813.

[24] Complexes **IB**: A.A. Koridze, N.M. Astakhova, F.M. Dolgushin, A.I. Yanovsky, Yu. T. Struchov, P.V. Petrovskii, Organometallics 14 (1995) 2167.

[25] K.J. Adams, J.J. Barker, S.A.R. Knox, A.G. Orpen, J. Chem. Soc. Dalton Trans. (1996) 975.

[26] H.D. Kaesz, R.B. King, T.A. Manuel, L.D. Nichols, F.G.A. Stone, J. Am. Chem. Soc. 82 (1960) 4749.

[27] (a) G.N. Schrauzer, J. Am. Chem. Soc. 81 (1959) 5307. (b) E.H. Braye, W. Hubel, J. Organomet. Chem. 3 (1965) 25. (c) W. Hubel, E.H. Braye, J. Inorg. Nucl. Chem. 10 (1959) 250 {ibid. p. 204}. See also: (d) G.E. Coates, M.L.H. Green, K.Wade, Organometallic Compounds, vol. II, Methuen, London, 1968, p. 303.

[28] (a) H.W. Sternberg, R.A. Friedel, R.Markby, I. Wender, J. Am. Chem. Soc. 78 (1956) 3621. (b) R. Clarkson, E.R.H. Jones, P.C. Wailes, M.C. Whiting, J. Am. Chem. Soc. 78 (1956) 6206. See also Ref. [26].

[29] (a) A.A. Hock, O.S. Mills, Proc. Chem. Soc. (1958) 233. (b) A.A. Hock, O.S. Mills, Acta Cryst. 14 (1961) 139.

[30] S. Aime, L. Milone, E. Sappa, A. Tiripicchio, A.M. Manotti Lanfredi, J. Chem. Soc. Dalton Trans. (1979) 1664.

[31] C. Rosenberger, N. Steunou, S. Jeannin, Y. Jeannin, J.Organomet.Chem. 494 (1995) 17.

[32] P. Blenkiron, A.J. Carty, E. Sappa. (manuscript in preparation).

[33] (a) P. Blenkiron, G.D. Enright, N.J. Taylor, A.J. Carty, Organometallics 15 (1996) 2855. (b) P. Blenkiron, G.D. Enright, A.J. Carty, J. Chem. Soc. Chem. Commun. (1997) 483.

[34] L. Milone, D. Osella, M. Ravera, P.L. Stanghellini, E. Stein, Gazz. Chim. Ital. 122 (1992) 451.

[35] G. Gervasio, E. Sappa, J. Organomet. Chem. 498 (1995) 73.

[36] G. Gervasio, D. Marabello, E. Sappa, J. Chem. Soc. Dalton Trans. (1997) 1851.

[37] T. Fassler, G. Huttner, J. Organomet. Chem. 376 (1989) 367.

[38] V. Crocq, J.C. Daran, Y. Jeannin, J. Organomet. Chem. 373 (1989) 85.

[39] W. Imhof, J. Organomet. Chem. 533 (1997) 31.

[40] S.H. Han, G.L. Geoffroy, A.L. Rheingold, Organometallics 5 (1986) 2561.

[41] A. Zimniak, J. Zachara, J. Organomet. Chem. 533 (1997) 45.

[42] So far complexes **I** containing entirely metals not belonging to the iron triad have not been reported.

[43] I. Moldes, T. Papworth, J. Ros, A. Alvarez-Larena, J.F. Piniella, J. Organomet.Chem. 489 (1995) 65.

[44] G. Predieri, A. Tiripicchio, M. Tiripicchio Camellini, M. Costa, E. Sappa, J. Organomet. Chem. 423 (1992) 129.

[45] K. Sunkel, J. Organomet. Chem. 391 (1990) 247.

[46] R. Hoffmann, Angew. Chem. Int. Ed. Engl. 21 (1982) 711.

[47] F.-E. Hong, I.-R. Lue, S.-C. Lo, C.-C. Lin, J. Organomet. Chem. 495 (1995) 97.

[48] M.J. Chetcuti, B.E. Grant, P.E. Fanwick, Organometallics 14 (1995) 2937.

[49] N.G. Connelly, T. Escher, A.J. Martin, B. Metz, A.G. Orpen, J. Cluster Sci. 6 (1995) 125.

[50] E. Cabrera, J.-C. Daran, Y. Jeannin, O. Kristiansson, J. Organomet. Chem. 310 (1986) 367.

[51] K. Wade, Adv. Inorg. Chem. Radiochem. 1 (1976) 18.

[52] A concise but useful exposition on the relationships between boron hydrides, metal clusters is in: K.F. Purcell, J.C. Kotz, Inorganic Chemistry, Chapter 18, W.B. Saunders Company, Philadelphia, 1977, p. 980 and references therein.

[53] A.A. Khoridze, A.M. Shaloumov, F.M. Dolgoushin, A.I. Ivanovskj, Yu. T. Struchov, P.V. Petrovskii, Russian Chem. Bull. 45 (1966) 702. See also Refs. [23,24].

[54] B.F.G. Johnson, R. Khattar, J. Lewis, P.R. Raithby, J. Organomet. Chem. 335 (1987) 17.

[55] (a) E. Sappa, A.M. Manotti Lanfredi, G. Predieri, A. Tiripicchio, A.J. Carty, J. Organomet. Chem. 288 (1985) 365. (b) A. Sironi, G. Gervasio, E. Sappa, J. Cluster Sci. 5 (1994) 535. See also ref. ([1]c).
[56] O.J. Scherer, G. Berg, G. Wolmershauser, Chem. Ber. 128 (1995) 635.
[57] J.C. Daran, E. Gilbert, M. Gouygou, S. Halut, B. Heim, Y. Jeannin, J. Cluster Sci. 5 (1994) 373.
[58] A. Gunale, H. Pritzkow, W. Siebert, D. Steiner, A. Berndt, Angew. Chem. Int. Ed. Engl. 34 (1995) 1111.
[59] D. Osella, G. Arman, R. Gobetto, F. Laschi, P. Zanello, S. Ayrton, V. Goodfellow, C.E. Housecroft, S.M. Owen, Organometallics 8 (1989) 2689.
[60] M. Casarin, D. Ajo, G. Granozzi, E. Tondello, S. Aime, Inorg. Chem. 24 (1985) 1241. See also: (b) F.A. Cotton, Prog. Inorg. Chem. 21 (1976) 1. (c) M. Bernard, A. Dedieu, S. Nakamura, New J. Chem. 8 (1984) 149.
[61] C. Mealli, D.M. Proserpio, J. Chem. Educ. 67 (1990) 399.
[62] E. Sappa. (unpublished results).
[63] A.A. Koridze, A.I.Yanovski Yu., T. Struchov, J. Organomet. Chem. 441 (1992) 277.
[64] In discussing the substitutional isomerism we take into account the more bulky substituants thus, an α-α-isomer is the one containing two bulky substituants on the C(σ) carbons of the ferrole ring (Fig. 1).
[65] M.I. Bruce, N.M. Zaitseva, B.W. Skelton, A.H. White, Inorg.Chim. Acta 250 (1996) 129.
[66] J.P. Collman, L.S. Hegedus, Principles, Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley Cal, 1995, pp. 525–529 and references therein.
[67] J.R. Berenguer, J. Fornies, E. Lalinde, F. Martinez, J. Chem. Soc. Chem. Commun. (1995) 1227.
[68] D.L. Thorn, R. Hoffmann, Inorg. Chem. 17 (1978) 126.
[69] S. Jeannin, Y. Jeannin, F. Robert, C. Rosenberger, J. Organomet. Chem. 480 (1994) 111.
[70] W.P. Fehlhammer, M. Stolzenberg, in G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, 1st ed., vol. 4, Pergamon, Oxford, 1982, p. 548.
[71] F.A. Cotton, J.M. Troup, J. Am. Chem. Soc. 96 (1974) 1233.
[72] R.S. Dickson, Polyhedron 10 (1991) 1995.
[73] M.J. Chetcuti, P.E. Fanwick, J.C. Gordon, Inorg.Chem. 30 (1991) 4710.
[74] (a) A. Mangia, G. Predieri, E. Sappa, Anal. Chim. Acta 152 (1983) 289. (b) M. Careri, A. Mangia, P. Manini, G. Predieri, E. Sappa, J. Organomet. Chem. 476 (1994) 127.
[75] D. Osella, O. Gambino, C. Nervi, M. Ravera, J. Organomet. Chem. 433 (1992) 287.
[76] G. Gervasio, E. Sappa, L. Marko, J. Organomet. Chem. 444 (1993) 203. See also ref. [11].
[77] R. Giordano, E. Sappa, G. Predieri, Inorg. Chim. Acta 228 (1995) 139.
[78] L.A. Brady, A.F. Dyke, S.E. Garner, S.A.R. Knox, A. Irving, S.M. Nicholls, A.G. Orpen, J. Chem. Soc. Dalton Trans. (1993) 487.
[79] E. Boroni, M. Costa, G. Predieri, E. Sappa, A. Tiripicchio, J. Chem. Soc. Dalton Trans. (1992) 2585.
[80] (a) R.J.P. Corriu, J.J.E. Moreau, J. Chem. Soc. Chem. Commun. (1980) 278. (b) F.A.Cotton, D.L.Hunter, J.M.Troup, Inorg.Chem., 15 (1976) 63.
[81] D. Osella, M. Botta, R. Gobetto, R. Amadelli, V. Carassiti, J. Chem. Soc. Dalton Trans. (1988) 2519.
[82] (a) E. Sappa, D. Cauzzi, G. Predieri, A. Tiripicchio, M. Tiripicchio Camellini, J. Organomet. Chem. 412 (1991) C14. (b) R. Giordano, E. Sappa, D. Cauzzi, G. Predieri, M. Tiripicchio, J. Organomet. Chem. 511 (1996) 263. See also ref. 11.
[83] (a) J. Piron, P. Piret, J. Meunier-Piret, M. van Meerssche, Bull. Soc. Chim. Belg. 78 (1969) 121. (b) P. Piret, J. Meunier-Piret, M. van Meerssche, G.S.D. King, Acta Cryst. 19 (1965) 78.
[84] M.H. Carre, J.J.E. Moreau, Inorg.Chem. 21 (1982) 3099.
[85] R.C. Pettersen, C.G. Cash, Inorg. Chim. Acta 34 (1979) 261.
[86] S. Rivomanana, C. Mongin, G. Lavigne, Organometallics 15 (1996) 1195.
[87] J.L. Davidson, M. Green, F.G.A. Stone, A.J. Welch, J. Chem. Soc. Dalton Trans. (1976) 2044.
[88] Synthesis: (a) S. Aime, L. Milone, E. Sappa, A. Tiripicchio, M. Tiripicchio Camellini, J. Chem. Soc. Dalton Trans. (1979) 1155, references therein. Structure: (b) A. Marzotto, M. Biagini Cingi, A. Ciccarese, D.A. Clemente, Acta Cryst. 96 (1991) C 47.
[89] S.A.R. Knox, B.R. Lloyd, D.A.V. Morton, A.G. Orpen, M.L. Turner, G. Hogarth, Polyhedron 14 (1995) 2723.
[90] A.J. Blake, P.J. Dyson, S.L. Ingham, B.F.G. Johnson, C.M. Martin, Organometallics 14 (1995) 862.
[91] W. Hirpo, M.D. Curtis, J.W. Kamp, Organometallics 11 (1994) 3360.
[92] A.C. Cano, N. Zuniga-Villareal, C. Alvarez Toledano, R.A. Toscano, M. Cervantes, A. Diaz, H. Rudler, J. Organomet. Chem. 464 (1994) 23.
[93] R.S. Dickson, B.C. Greaves, Organometallics 12 (1993) 3249.
[94] R. Giordano, E. Sappa. (unpublished results).
[95] J. Meunier-Piret, P. Piret, M. Van Meerssche, Acta Cryst. 19 (1965) 85.
[96] E. Sappa, L. Milone, G.D. Andreetti, Inorg. Chim. Acta 13 (1975) 67.
[97] H. Adams, L.J. Gill, M.J. Morris, J. Chem. Soc. Dalton Trans. (1996) 3909.
[98] H. Adams, L.J. Gill, M.J. Morris, J. Organomet. Chem. 533 (1997) 117.
[99] R. Giordano, E. Sappa, J. Organomet. Chem. 448 (1993) 157.
[100] (a) D. Campagnola, M. Castiglioni, W. Dastru, S. Deabate, R. Giordano, P.J. King, E. Sappa, Inorg. Chim. Acta 262 (1997) 157. (b) D. Campagnola, S. Deabate, R. Giordano, E. Sappa, J. Cluster Sci. 9 (1998) in press.
[101] M. Castiglioni, R. Giordano, E. Sappa, J. Organomet. Chem. 407 (1991) 377 and references therein.
[102] R. Giordano, E. Sappa, S.A.R. Knox, J. Cluster Sci. 7 (1996) 179.
[103] O. Gambino, E. Sappa, G. Cetini, J. Organomet. Chem. 44 (1972) 185.
[104] A discussion of these, other reactions involving cluster anions is in the forthcoming ESF book P. Braunstein, L. Oro, P.R. Raithby (Eds.), Metal Clusters in Chemistry, Wiley-VCH, New York.