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ALKYNE-SUBSTITUTED TRANSITION METAL CLUSTERS

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I. Introduction

The area of organometallic chemistry concerned with the interactions between transition metal cluster complexes and small molecules has expanded greatly over the last decade. One of the major reasons for this interest has stemmed from the need to understand the role of both homogeneous and heterogeneous catalysts in a variety of important industrial processes (*1*). Particularly in heterogeneous catalysis, there is an appealing analogy between the interaction of an organic absorbate on a catalytic metal surface and that of an organic ligand bonded to a transition metal cluster, which may itself be viewed as a small fragment of metal. One advantage of the latter situation is that the cluster complex may be probed readily by a number of techniques which give a more detailed view of the chemistry of such species than could be obtained by a study of the surfaces themselves. This use of cluster complexes as structural models for surface chemistry has proved helpful in the understanding of these systems, and the area of the cluster–surface analogy has been the subject of a number of review articles (*2–8*).

Perhaps another reason for the development of the organometallic chemistry of homonuclear and heteronuclear cluster complexes is the sheer academic fascination at the great synthetic and structural diversity of these molecules. Various aspects of the chemistry of these species, particularly those involving interactions with unsaturated organic molecules, have been discussed in a number of recent publications (*9–15*).

This article is concerned with one specific aspect of cluster organometallic chemistry, and describes the synthesis, characterization, structure, and reactivity of transition metal clusters containing alkyne, or alkyne-derived ligands. Alkynes display a diverse reactivity in their reactions with carbonyl clusters, and exhibit a wider range of coordination modes than any other simple, unsaturated molecule. It is this compelling diversity that has prompted the authors to undertake this review.

The area of alkyne–cluster chemistry has been the subject of two previous review articles. The first is concerned largely with alkyne–cobalt chemistry (*16*), while the second provides a comprehensive, systematic review of alkyne-substituted homo- and heterometallic carbonyl clusters of the iron, cobalt, and nickel triads (*17*). This latter review covers the literature up to the end of 1981. The present work does not set out to be fully comprehensive, but rather reflects the authors' own interests in the subject. A number of key examples are given in each subsection to illustrate points in the discussion, and, where possible, these examples have been taken from the recent literature, covering the period to the middle of 1984.

Before commencing the discussion, it is advisable to define what is meant by an alkyne or alkyne-derived ligand. The problem arises because the reaction between a cluster and an alkyne or alkene may lead to the same product, and it is difficult to decide whether the ligand is derived from an alkyne or an alkene. It is also possible that an alkyne may fragment upon coordination, or that several alkynes may link together, via C—C bond formation, to give a larger, coordinated organic group. For the purposes of this review molecules are considered which have been formed by the reaction of a cluster complex with an alkyne, or where the bonding and coordination geometry of the coordinated ligand is reminiscent of that of related alkyne-substituted clusters. However, two areas which obey these general conditions are not discussed in great detail. These are the clusters containing capping alkylidyne ligands, derived from alkynes by the rupture of the C—C triple bond, and those in which alkynes have linked together to form complex organic units. These types of complex will only be mentioned where they are relevant to the discussion. Both these areas have been featured in other review articles (*11, 15–17*).

II. Reactions of Clusters with Unsaturated Ligands

Several factors affect the nature of the products in a reaction between a transition metal cluster and an alkyne or alkene. In this section, the various synthetic routes to alkyne or alkene-substituted clusters will be presented, and these will be used to analyze the changes in reactivity of the cluster systems when one or more of the important reaction parameters is altered. In order to simplify the discussion, tri-, tetra-, and higher nuclearity clusters will be treated separately. Finally, in this section, there is a brief description of the chemistry of alkylidyne-substituted clusters since synthetic routes to alkyne-containing complexes may involve these species.

A. TRINUCLEAR CLUSTERS

1. *Thermal Activation*

a. Alkynes. The reaction between alkynes or alkenes and binary carbonyl complexes of iron, ruthenium, and osmium has been extensively studied. The quantity of data now available makes it possible to

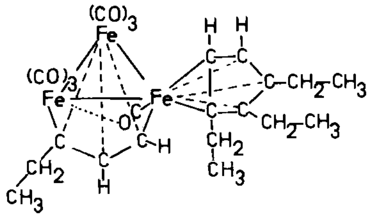


FIG. 1. A triiron cluster containing a larger organic fragment built up from a combination of alkene-based units.

draw some conclusions about the reactivity of the clusters with these unsaturated organic molecules.

The reactions of $M_3(CO)_{12}$ (M = Fe, Ru, Os) with disubstituted alkynes (RC≡CR) produce mononuclear (*18, 19*), dinuclear (*18–25*), trinuclear (*19–22, 26–36*), and tetranuclear species (*37–40*), as illustrated by Eq. (1). Some of the products involve polymerization of the alkyne (*22, 27, 34–36*) and interaction with one or more of the carbonyls already bonded to the cluster (*20–22*). In these reactions, metal–metal bond cleavage occurs more frequently in the case of iron clusters, although the formation of tetranuclear clusters in several of the reactions with $Ru_3(CO)_{12}$ must involve rupture of metal–metal bonds. In the case of osmium, where the metal–metal bonds are stronger, most of the high-yield products are trinuclear. It is also important to mention that some of the reaction products contain larger organic units (Fig. 1), and the formation of these ligands requires the rupture of acetylenic C≡C triple bonds (*41*). There are also examples where the nuclearity of the starting material is retained but the bonds between the metal atoms are broken (*42*).

$$Ru_3(CO)_{12} + PhCCPh \longrightarrow Ru_4(CO)_{12}(PhCCPh) \qquad (1)$$

In many cases the use of mono-substituted alkynes in reactions with $M_3(CO)_{12}$ (M = Fe, Ru, Os) gives products very similar to those obtained with disubstituted alkynes (*43–48*). Nevertheless, the hydrogen atoms α to the triple bond may undergo a transfer from the ligand to the metal framework (*49–52*). Another interesting chemical transformation occurs in the reaction of $Fe_3(CO)_{12}$ with 1-pentyne (*53*). One of the products obtained, in very low yield, is the pentanuclear carbide $Fe_5C(CO)_{15}$ [Eq. (2)].

$$Fe_3(CO)_{12} + MeCCEt \longrightarrow Fe_5C(CO)_{15} \qquad (2)$$

There are few reports of reactions between alkynes and trinuclear clusters of metals other than iron, ruthenium, or osmium. Some rhodium, platinum, and mixed-metal clusters undergo metal–metal bond rupture in reactions with alkynes (*54–56*), while in other cases the alkyne coordinates to the trinuclear unit without causing any major changes in framework geometry (*56–59*), as illustrated in Eq. (3).

$$\mathrm{RuC0_2(CO)_{11}} + \mathrm{HCCBu^t} \xrightarrow[n\text{-pentane}]{4\ \mathrm{hr}/15^\circ\mathrm{C}} \mathrm{RuCo_2(CO)_9}(\mu^3 - \eta^2\text{-}\mathrm{HCCBu^t}) \qquad (3)$$

b. Alkenes. The thermal reactions between $M_3(CO)_{12}$ (M = Ru, Os) and alkenes have also been extensively studied, and there are some interesting differences in their reactivity when compared to alkynes. In the reaction of $Ru_3(CO)_{12}$ with mono-substituted alkenes cluster growth is a common feature (*60, 61*) although trinuclear products are also obtained (*62*). An example of this type of reaction is shown in Fig. 2. When a high pressure of ethylene is used (*60*) a carbido cluster is formed in high yield, and ethylene oligomerization is observed in some of the other products. In contrast, the reaction of $Os_3(CO)_{12}$ with mono-substituted alkenes gives mostly one type of product $Os_3H_2(RCCR)(CO)_9$, where hydrogen transfer has occurred (*63–66*). However, in some cases, under similar conditions, cluster growth does take place.

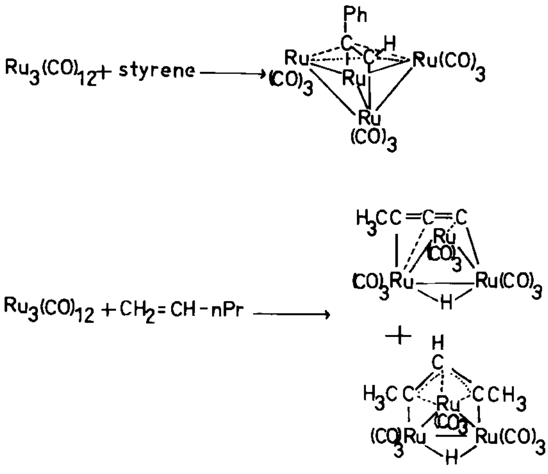


FIG. 2. Reaction of $Ru_3(CO)_{12}$ with mono-substituted alkenes.

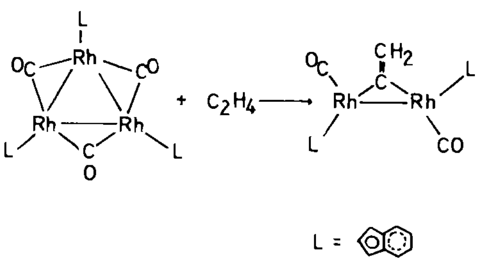


FIG. 3. Cluster breakdown of a trirhodium cluster.

The reaction of $M_3(CO)_{12}$ with both open-chain and cyclic polyalkenes has attracted some attention, especially in the case of $Ru_3(CO)_{12}$. In most of the examples reported, the organic fragment bonds to the metal framework in such a way as to interact with more than one of the three metal atoms (*68–77*). There are some exceptions to this general statement, however. One is the reaction of $Ru_3(CO)_{12}$ with cyclopentadiene, in which a mononuclear complex is obtained (*78*). In other cases, tetranuclear and hexanuclear compounds are obtained (*79–81*). Cluster breakdown has also been observed in the case of a rhodium complex upon reaction with ethylene (*55*) as shown in Fig. 3.

It is important at this stage to mention that most reactions involving the use of alkynes or alkenes have been carried out in hydrocarbon solvents, such as hexane or octane, or in aromatic ones, such as benzene. When polar solvents are employed there are sometimes variations in the number of products and in the yields obtained (*28, 31*). For example, in hydrocarbon solvents, the reaction between $Ru_3(CO)_{12}$ and diphenylacetylene leads to the isolation of $Ru_3(CO)_9(PhCCPh)$ as the major product. When the same reaction is carried out in basic aqueous methanol, the hydrido complex $Ru_3H_2(CO)_9(PhCCPh)$ is obtained in reasonable yield.

c. *Importance of Other Substituents in a Cluster.* The nature of the starting cluster also affects the type and characteristics of the products obtained from reactions with alkynes and alkenes. A good example of this is the chemistry of the unsaturated cluster $Os_3H_2(CO)_{10}$ as opposed to that of $Os_3(CO)_{12}$ (Fig. 4). It is known that complexes with the general formula $Os_3(CO)_{10}$ (organic ligand) may be obtained under much milder conditions when $Os_3H_2(CO)_{10}$ is used as the starting material (*82–90*), although other types of compound can also be obtained (*91–97*), but in which oligomerization of the ligand does not occur. Other substituted compounds have been made to react with alkynes and alkenes, and the type of product obtained depends, to a

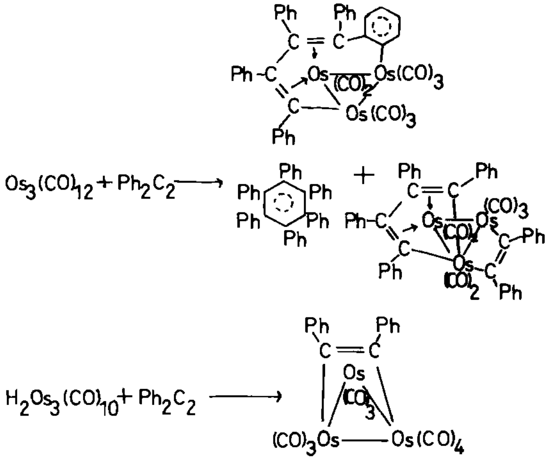


FIG. 4. Contrast in reactivity between $Os_3(CO)_{12}$ and $Os_3H_2(CO)_{10}$.

great extent, on whether the substituent is a good leaving group or can modify its mode of bonding (*98–104*). The alkyne or alkene may interact with the *other* substituents of the cluster as well as with the metal framework as has been observed in the chemistry of some binuclear compounds (*105*).

d. Importance of Substituents in Organic Fragment. The type of substituents on the alkyne or alkene is also important in determining the kind of complex obtained in a given reaction. If one or both of the substituents are functional groups which can also coordinate to the metal atoms it is possible that the whole organic fragment may act as a polydentate ligand (*106, 107*), as shown in Fig. 5. Alternatively, the functional group may separate from the rest of the ligand and bond independently (*108*). In some examples the ligand can behave in several different ways, as has been observed in the chemistry of phosphino-alkynes (*109–114*). Other types of ligand such as amino-alkynes (*115–118*), hydroxyalkynes (*119–124*), and other groups (*125,*

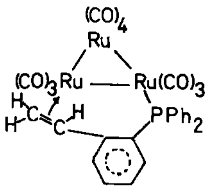


FIG. 5. An alkene-derived ligand acting in a polydentate mode.

126) have also been treated with cluster compounds. The products obtained from these reactions vary widely, and depend on the donor–acceptor properties of the substituents, and on the availability of groups which can be eliminated from the organic ligand.

2. *Photolytic or Chemical Activation*

Photolytic and chemical methods of activation have also been employed in the reactions of clusters with unsaturated organic ligands. The photochemical activation of compounds containing metal–metal bonds has not received much attention until relatively recently (*127*). However, it is now being investigated in some detail. In some cases the photochemical products differ from those obtained by thermal activation alone (*127*). The reaction of $Ru_3(CO)_{12}$ with ethylene is an example of such behavior (*128*).

The best example of chemical activation in cluster chemistry is the use of Me_3NO which results in CO replacement under mild conditions (*129*). In an interesting example taken from alkyne–cluster chemistry, when Me_3NO is used dry a monosubstituted cluster derivative is obtained, but with damp Me_3NO a tetranuclear vinylidene complex is isolated (*130, 131*), as illustrated in Eqs. (4) and (5), respectively.

$$M_3(CO)_{12} + Ph_2PCCPh + 2Me_3NO \longrightarrow Ru_3(CO)_{11}Ph_2PCCPh \qquad (M = Ru, Os) \tag{4}$$

$$Ru_3(CO)_{12} + Ph_2PCCPh + Me_3NO + H_2O \longrightarrow$$
$$Ru_4(CO)_{10}(CCHPh)(OH)(PPh_2) + Ru_3(CO)_9(CCPh)(PPh_2) + Ru_3(CO)_8(CCPh)(PPh_2) \tag{5}$$

3. *Reactions between Different Metallic Species Which Form Trinuclear Clusters*

a. With Alkyne Ligands. The reactions between different metallic species when one or both contain coordinated alkyne ligands are particularly useful in the synthesis of mixed-metal clusters. The alkyne can serve as a link which places two kinds of metal atoms at a distance where bond formation can occur. Several nickel–iron and nickel–ruthenium compounds have been prepared by this technique (*132–139*), although, in some examples, the reaction has resulted in the fusion of ligands (*140*) or the polymerization of alkynes (*141, 142*). Reactions between two complexes of the same element have also been

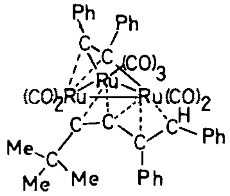


FIG. 6. Polymerization of alkenes on triruthenium clusters.

described (*55*), and similar reaction processes are observed (Fig. 6). Combinations of complexes of other metals have made it possible to obtain a whole range of mixed-metal clusters containing organic ligands (*143*–*154*), although the ligand does not always coordinate through the unsaturated fragment (*155*), and in some cases no new metal–metal bonds are formed (*156*).

b. With Other Ligands. Another three types of complexes that have been or are being extensively studied are those containing carbyne, carbene, and acetylide ligands. Their reactions with other metallic species have produced a wide range of products (*157*–*166*). For example, carbene complexes are formed by reactions of the type shown in Eq. (6), while carbynes may be obtained by the route illustrated in Eq. (7).

$$\mathrm{W(CO)_5C(OMe)Ph + Pt(C_2H_4)_2(PR_3) \longrightarrow WPt_2[\mu\text{-}C(OMe)Ph](CO)_6(PR_3)_2} \quad (6)$$

$$\mathrm{W(CTol)(CO)_2Cp + Co_2(CO)_8 \longrightarrow Co_2W(\mu_3\text{-}CTol)(CO)_8Cp} \quad (7)$$

$$\mathrm{Tol,\ C_6H_4Me;\ Cp,\ \eta^5\text{-}C_5H_5)}$$

4. *Other Reactions That Produce Unsaturated Organic Fragments*

Although the reactions between alkynes or alkenes and metal clusters are the main source of alkyne-substituted complexes, there are other reagents which can produce similar products. Two such reagents are tetraphenylcyclopentadienone, which in the reaction with $Ru_3(CO)_{12}$ produces $Ru_3(CO)_{10}(PhCCPh)$ (*167*), and dimethylvinylarsine, which has been made to react with several carbonyl clusters [Eq. (8)] (*168, 169*). In the reaction of $M_3(CO)_{12}$ (M = Ru, Os) with a number of tertiary phosphines and aromatic alcohols, an oxidative addition takes place and benzyne–triosmium compounds are obtained (*170*–*176*). The fact that $Os_3(CO)_{11}PEt_3$ can be converted into an alkyne compound (*177*) suggests that the conversion goes through substituted intermediates. Carbene derivatives of clusters have also been shown to undergo changes that produce clusters with unsaturated organic ligands (*178, 179*), as illustrated by Eq. (9).

$$\begin{tikzcd}
\mathrm{Os_3(CO)_{11}[AsMe_2(CHCH_2)]} \arrow[r, "-\mathrm{CO}", "96^\circ\mathrm{C}"'] & \mathrm{Os_3(CO)_{10}(CHCH_2)(AsMe_2)} \arrow[d, "-\mathrm{CO}"', "125^\circ\mathrm{C}"] \\
\mathrm{Os_3H(CO)_9(HCCH)(AsMe_2)} & \mathrm{Os_3H(CO)_9(CCH_2)(AsMe_2)} \arrow[l, "150^\circ\mathrm{C}"', "\text{isomerization}"]
\end{tikzcd} \tag{8}$$

$$\begin{aligned}
&[\mathrm{Ru_3H(CO)_9(C(O)Me)(\eta^2{-}C(O)Me)}]^- \xrightarrow{\mathrm{EtOSO_2CF_3}} \\
&\quad [\mathrm{Ru_3H(CO)_9(C(Me)OEt)(\eta^2{-}C(OMe))}]^{\ddagger} \xrightarrow{-\mathrm{MeCHO}} \mathrm{Ru_3H_2(CO)_9(EtOCCH)}
\end{aligned} \tag{9}$$

B. TETRANUCLEAR CLUSTERS

There have been far fewer studies on the reactions between tetranuclear clusters and alkynes or alkenes than have been reported for trinuclear systems. The reactions that have been investigated have largely been with alkenes. Both $Ru_4H_4(CO)_{12}$ and $Os_4H_4(CO)_{12}$ react with mono- and polyalkenes, and substitution of hydrides and carbon monoxide ligands is observed in most cases (*180–187*), as shown by Eq. (10). There are a few examples, however, where metal–metal bond cleavage does occur and trinuclear clusters are isolated (*181–183, 188*). In contrast, when $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$ are treated with dienes, cluster growth occurs (*189–193*).

$$\mathrm{OS_4H_4(CO)_{12} + RHCCHR'} \xrightarrow{h\nu} \mathrm{Os_4H_3(CO)_{11}(RCC(H)R')} \tag{10}$$

Most of the reported reactions between tetranuclear clusters and alkynes involve mixed-metal cluster species. In these systems hydride and carbon monoxide substitution generally occurs [Eq. (11)] (*194–200*), although in some cases Me_3NO has been used to activate the starting material (*201, 202*), and in still others cluster breakdown takes place even under mild reaction conditions (*203*). $Rh_4(CO)_{12}$ (*204*) and $Ir_4(CO)_{12}$ (*205*) retain their nuclearity in reactions with alkynes, but in the latter case the metal framework geometry is altered (Fig. 7). The use of $[Ir_4(CO)_{11}Br]^-$ instead of $Ir_4(CO)_{12}$ in reactions with alkenes produces alkene-substituted tetranuclear complexes (*189*), as shown in Fig. 7. Few other homonuclear clusters have been found to react with alkynes (*206–208*). In the reaction between the tetranuclear cluster $Cp_2W_2Ir_2(CO)_{10}$ and diphenylacetylene two independent processes

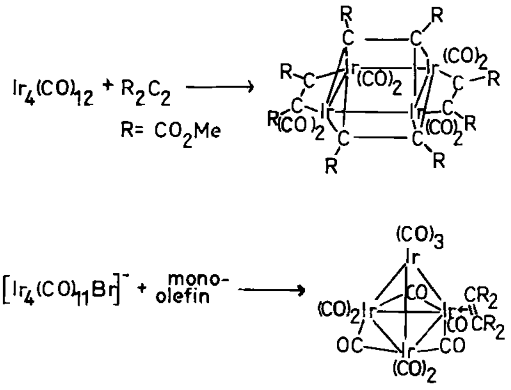


FIG. 7. Reactions of tetrairidium clusters with alkynes and alkenes.

occur. These involve cleavage of either a W—W bond or a W—Ir bond giving rise to two different modes of coordination of the alkyne ligand (*209*).

$$NEt_4[RuCo_3(CO)_{12}] + PhCCPh \xrightarrow[\text{reflux}]{\text{acetone}} NEt_4[RuCo_3(CO)_{10}PhCCPh] \quad (11)$$

The reaction between two metal-containing species, one of which also contains a coordinated alkyne, has produced several tetranuclear species (*210–223*), such as that shown in Eq. (12).

$$Fe_3(CO)_9(RCCR) + [CpNi(CO)]_2 \longrightarrow Cp_2Ni_2Fe_2(CO)_6(RCCR) \quad (12)$$

C. HIGHER CLUSTERS

The chemistry of clusters containing more than four metal atoms has only been studied in detail over the last few years, and at the present time there are few reports of reactions of these higher clusters with alkynes or alkenes.

In osmium chemistry, the reaction between $Os_5H_2(CO)_{15}$ and some mono- and disubstituted alkynes gives rise to products in which the metal framework geometry differs from that of a trigonal bipyramid, as proposed for the parent hydrido carbonyl. This geometry change requires the rupture of metal–metal bonds (*224*). In one product of the reaction, $Os_5(CO)_{13}(PhCCPh)_2$, the two alkyne groups adopt different bonding modes, a characteristic which has been observed in only a few compounds (*27, 37, 55, 205, 225*). On the other hand, $Os_5(CO)_{19}$, which is a cluster with an open "bow-tie" framework (*226*), undergoes CO substitution when acetylene is added [Eq. (13)] (*227*).

$$Os_5(CO)_{19} + HCCH \xrightarrow[\text{reflux}]{\text{heptane}} Os_5(CO)_{17}(HCCH) + Os_4(CO)_{12}(HCCH) \qquad (13)$$

Three effects are observed in the reactions of $Os_6(CO)_{18}$ with diphenylacetylene and ethylene. There is modification of the metal framework, rupture of a C≡C triple bond, and dimerization of ethylene (*228–230*). When the activated clusters $Os_6(CO)_{17}(MeCN)$ (*230*) and $Os_6(CO)_{20}(MeCN)$ (*231*) react with mono- and disubstituted alkynes, different penta- and hexanuclear framework geometries are obtained, and the alkyne-derived ligands adopt a range of coordination modes (Fig. 8).

Few other reactions between higher clusters and unsaturated organic ligands have been carried out (*231, 232*), but there are a number of studies which involve group IB organometallic derivatives (*233–236*). There are also a few high-nuclearity mixed-metal cluster alkynes which are the products of reactions between two heterometal complexes (*237–242*).

The main difference between the reactions of high-nuclearity clusters with alkynes and alkenes and those of the smaller clusters is that

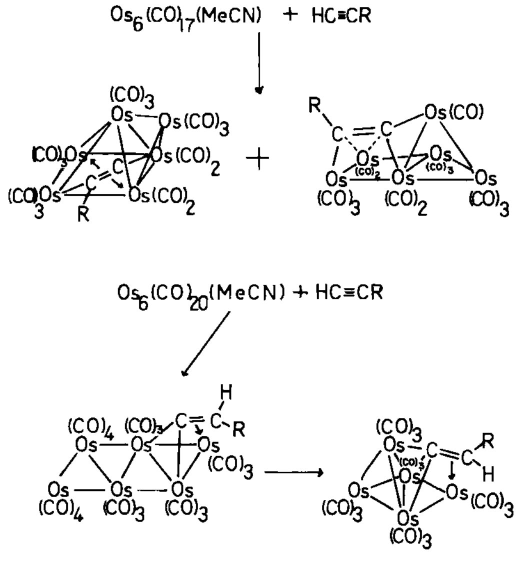


FIG. 8. Reactions of activated hexanuclear osmium clusters with alkynes.

the addition of the organic fragment can produce the rupture of metal–metal bonds without cluster breakdown.

D. REACTIONS THAT INVOLVE CLUSTER BUILD-UP

Several reactions have been reported in which alkyne- or carbyne-substituted clusters have been obtained from mono- or dinuclear complexes, or from the metal in the gas phase. The reagents with which the metallic species are treated range from alkynes, with functionalized substituents in most cases (*243–251*), to Grignard salts (*252, 253*) or halogen-substituted cycloalkanes (*254*). In some cases, the starting metal complex already contains an unsaturated organic fragment which, upon reaction with H_2 [Eq. (14)] (*255*) or an acid (*256*), might favor cluster growth.

$$\begin{array}{l} Cp_2Rh_2(CO)(CF_3CCCF_3) + H_2 \longrightarrow \\ \quad CF_3CH_2CH_2CF_3 + Cp_3Rh_3(CO)(CF_3CCCF_3) + Cp_3Rh_3(CO)_3 + Cp_4Rh_4(CO)_2 \end{array} \tag{14}$$

In some reactions of this type, the increase in nuclearity of the complex does not necessarily involve cluster formation because metal–metal bonds need not be formed if the metals are bridged by ligands (*257–260*) or if an open structure is adopted (*261–263*).

E. ALKYLIDYNE CLUSTERS

Although it may be said that alkylidyne clusters do not contain an unsaturated organic fragment, the chemistry of these compounds is related to that of the alkyne and alkene derivatives, and their synthesis will be discussed briefly.

One of the most important links between alkylidyne and alkyne compounds is that one of the first synthetic routes for cobalt alkylidynes involved alkynes as reagents (*264–268*). In later studies, several other synthetic routes to cobalt (*269–280*), rhodium (*281, 282*), iron (*283–285*), molybdenum (*286, 287*), ruthenium (*288–292*), osmium (*293, 294*), nickel (*295, 296*), and some mixed-metal (*165, 297–302*) clusters have been developed. Reagents employed include carbynes (*166, 277, 280*), alkali metals (*269*), carbon disulfide (*275*), dithioesters (*276, 282*), $RCCl_3$, and acids (*281, 282*).

The reactivity of alkylidyne compounds has also been widely studied, particularly by Seyferth and co-workers who have carried out a great variety of reactions with cobalt complexes (*303–312*). Other groups have shown interest in this area (*313–340*). It is important to note that reactions of halomethylidene clusters can produce alkyne complexes (*341–344*).

Alkylidyne clusters may be considered as precursors to carbido species, and a number of studies on iron, ruthenium, and osmium systems have been carried out to investigate this relationship (*345–362*).

III. Methods of Characterization of Alkyne-Substituted Clusters

A. INTRODUCTION

Alkyne-substituted cluster compounds are amenable to and, indeed, have been subjected to all of the standard techniques for structural characterization. The rather more "sporting techniques" of infrared and NMR spectroscopy have been employed to good effect in solution, while definitive structural data in the solid state is obtained by single-crystal X-ray and neutron diffraction studies. Mass spectroscopic data also give useful information on the molecular weight of the complex. Within the last few years ultraviolet photoelectron spectroscopy has been used successfully in the analysis of bonding in clusters although it is not suited as a direct structural probe. In related work on the adsorption of alkynes on metal surfaces a number of other spectroscopic and diffraction techniques have been used, and this area of research has been the subject of a recent review (*2*). In this section we will discuss the advantages and disadvantages of each of the standard structural probes, and show to what extent they may be applied to transition metal clusters containing alkyne ligands.

B. INFRARED SPECTROSCOPY

For free acetylene the ν(C—C) stretching mode occurs at 2100 cm^{-1} while for ethylene, where the formal bond order is reduced from three to two, the ν(C—C) stretch is lowered to 1623 cm^{-1} (*363*). It might be expected that alkyne molecules coordinated to metal clusters would exhibit stretching frequencies in the range ca. 2100–1600 cm^{-1}, the region where ν(C—O) stretching modes for terminal, edge bridging, and face capping carbon monoxide ligands are observed. Unfortunately, in practice, the C—C vibrational modes are very difficult to detect because they are very weak, and because a majority of alkyne-substituted clusters also contain carbonyl groups so that any absorptions from the alkyne may be swamped by or confused with the stronger carbonyl absorptions.

It is possible to overcome this problem partially by investigating the structures of cluster complexes which do not have carbonyl groups bonded to them, or at least those which contain only a small number of terminal carbonyls. These ligands give rise to absorption bands at the higher end of the frequency range, and are less likely to overlap with the weaker alkyne vibrations. An early example of such an investigation is the report of the $\nu(C{\equiv}C)$ stretching frequencies in the hexacopper alkyne clusters $Ar_4Cu_6R_2$ [Ar = aryl; R = "PhC≡C" (*1*), "*p*—$MeC_6H_4C{\equiv}C$" (*2*), "2,4,6—$Me_3C_6H_2C{\equiv}C$" (*3*)] (*234*). The observed $\nu(C{\equiv}C)$ vibrations lie in the range 2051–2037 cm^{-1}, and are consistent with the alkynes σ bonding to the two Cu atoms causing little reduction in C≡C bond strength. These values may be compared with the $\nu(C{\equiv}C)$ stretching frequency of 1933 cm^{-1} in the polymeric copper arylacetylides, $(PhC{\equiv}CCu)_n$, in which π interactions cause a reduction in C–C bond order (*364*). In the tetranuclear cluster $Ni_4(CO)_4(CF_3CCCF_3)_3$ (*365*), where the alkyne ligands adopt the μ_3–η^2 bonding mode (Fig. 9), the $\nu(C{\equiv}C)$ stretch, being observed as a weak band at 1564 cm^{-1}, is greatly reduced from the free ligand value, and from the value of 1905 cm^{-1} in the mononuclear complex $Ni(CO)_2(CF_3CCCF_3)$. This reduction in stretching frequency is consistent with significant electron donation from the ligands to the metal framework.

In the last few years the interest in the modes of bonding of unsaturated organic fragments to metal surfaces (*4*), to aid in the understanding of reactions which occur in catalytic processes, has been a major cause of the redoubling of effort to obtain good quality infrared spectra of discrete, model alkene and alkyne cluster compounds. The vibrational frequencies of the coordinated organic groups in the cluster compounds, where the bonding mode is known, may be related to the infrared spectra of the surface coordinated species. It is assumed that local environments in the two cases are similar, and the mode of coordination on the surface may be established in this way. A number of studies on triosmium alkene and alkyne clusters, involving solution

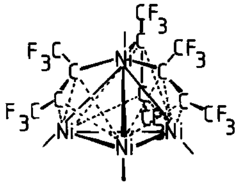


FIG. 9. Structure of $Ni_4(CO)_4(F_3CC_2CF_3)_3$.

and solid-state infrared and Raman spectra, and using deuterium substitution, have been carried out. For a comparison with the spectra of surface coordinated species an accurate analysis of all the ν(CC), ν(CH), $\delta(CH_2)$, and $\rho(CH_2)$ modes is required, but since this review is more concerned with the nature of the C–C interaction, and that of the organic fragment within the cluster framework, the ν(C—C) mode is the most relevant. Table I summarizes the value of this parameter for the clusters studied (*366–369*). All these complexes show a major reduction in the stretching frequency compared to the free acetylene ligand, and are also lower than for free ethylene, suggesting that there is considerable electron donation to the metal framework. There is a significant reduction in frequency in going from $Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CCH)$, where the ligand retains a greater amount of alkyne character, to any of the next four complexes, in which the stretching frequencies are similar despite the varying modes of coordination of the ligands. These four complexes display greater alkene character. The two final complexes $Os_3(CO)_{11}(\eta^2\text{-}C_2H_4)$ and $Os_3(CO)_9(\mu\text{-}H)(\mu\text{-}SPr^n)(\eta^2\text{-}C_2H_4)$ show the expected reduction in frequency for π-bound alkenes. In general, with a little care, it seems that the values are transferable from one complex to another, and it is possible to draw up a table of expected ranges for the various alkyne and alkene vibrations (*366*).

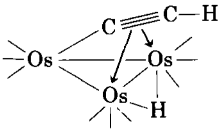
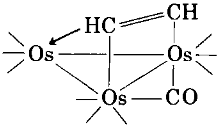
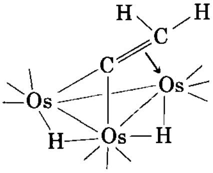
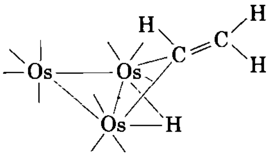
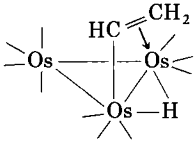
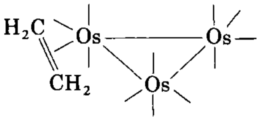
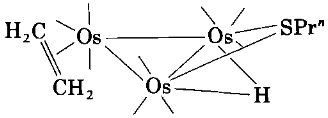
Generally, infrared spectroscopy gives fairly detailed and useful information on the overall symmetry of the molecule under investigation, particularly if the complex contains carbonyl ligands as well as alkyne groups, since the pattern and number of carbonyl stretching bands are related to the molecular symmetry of the complex (*370*). It is also relatively quick to establish the presence of isomers in solution, if the structure of the complex is known, if more ν(C–O) stretching bands are observed than would be expected from group theoretical calculations for a molecule of that symmetry. A case in point is that of $(Cp)_2NiRu_2(CO)_3(\mu_3\text{-}CO)(PhCCPh)$, whose solution spectrum shows one more carbonyl absorption in the bridging region than would be expected for the single capping CO group observed in the solid-state structure (*136*). A second isomer with two bridging CO groups is present in solution.

C. ^{1}H NMR Spectroscopy

^{1}H NMR spectroscopy plays an important role in the identification of all organometallic compounds. In cluster complexes this technique has been particularly useful for establishing the presence of hydride ligands

TABLE I

INFRARED ν(C–C) STRETCHING FREQUENCIES IN TRIOSMIUM ALKYNE AND ALKENE CLUSTERS

Complex	ν(C–C) cm^{-1}	Reference
$Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}CCH)$  	1533	*366*
$Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}HCCH)$  	1301	*367, 368*
$Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)$  	1331	*368, 369*
$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$  	1311	*368*
$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$  	1310	*369*
$Os_3(CO)_{11}(\eta^2\text{-}C_2H_4)$  	1190	*366*
$Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}SPr^n)(\eta^2\text{-}C_2H_4)$  	1194	*366*

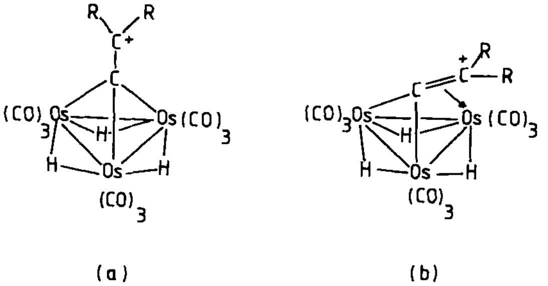


FIG. 10. Possible structures for the $[Os_3H_3(CO)_9CCR_2]^+$ cation.

(*371*), and by studying the coupling to active metallic elements, such as ^{103}Rh (*372*) or ^{187}Os (*373, 374*), it is often possible to find the exact location of the hydride with respect to the cluster framework. The observation of ^{187}Os–^{1}H couplings has proved useful in the elucidation of the structures of two clusters containing alkyne-derived ligands. In the mixed-metal cluster $Os_3M(\mu\text{-}H)(CO)_{14}(PhCCPh)_2$ (M = Mn, Re) (*375*), which contains an organic ligand derived from the coupling of two "PhC≡C" groups, ^{187}Os–^{1}H couplings clearly indicate that the hydride bridges an Os–Os edge of the Os_3 triangle. In the cationic cluster $[Os_3H_3(CO)_9(CCR_2)]^+$, the singlet hydride resonance has two sets of satellites of equal intensity caused by ^{187}Os–^{1}H spin–spin coupling (*376*). This rules out the upright carbenium ion structure for the cation (Fig. 10a), and is consistent with the fluxional process involving hydrocarbon ligand rotation about the C—CR_2 axis in a tilted structure (Fig. 10b), and concomitant rotation of the $Os_3H_3(CO)_9$ unit.*

For any cluster complex which incorporates an organic-based ligand, ^{1}H NMR is one of the most powerful tools for characterizing the organic species, investigating the existence of isomers in solution (*216*), or determining the nature of any fluxional processes which may occur (*294, 377*). Aspects of the use of this technique may be found in most research papers on organometallic and cluster chemistry.

Of special relevance to the investigation of alkyne-substituted clusters is the observation of a low-field resonance, generally in the range -1 to $+1.5\tau$, for a proton attached to a carbon atom which is either σ or π bonded to the metals. Values of the chemical shift for this signal for 23 tri- and tetranuclear osmium clusters were presented by

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* Recent work by Shapley has led him to propose an alternative explanation for the observed data which does not differentiate between the two possible ligand orientations. See Holmgren *et al.*, *J. Organomet. Chem.* **284**, p. C5, (1985).

Sappa *et al.* in their review (*17*). This constitutes quite a powerful diagnostic probe for such complexes. The reason for the appearance of this signal at such a low field may be due to the fact that the proton is bonded to a carbon which is partially carbenic in character.

D. ^{13}C NMR Spectroscopy

^{13}C NMR is generally applicable to organometallic and organo cluster compounds, but has the advantage of giving a direct probe on the acetylenic carbon atoms in alkyne-substituted clusters. With the development of more powerful NMR instruments, this technique has been used extensively to characterize organo-substituted cluster complexes in solution. For smaller clusters, the combination of ^{13}C NMR with ^{31}P NMR and resonance studies from metallic nuclei, where appropriate, frequently leads to complete structure elucidation.

However, there are a number of disadvantages in the use of ^{13}C NMR. These include the requirement of a relatively large sample, and the problems of solubility, particularly with larger molecular units. In order to establish the nature of fluxional processes which may occur, it is necessary to run the spectrum at various temperatures. This may again increase experimental complexity. The spectra are not always simple to interpret, which is also true for ^{1}H NMR results. This problem may sometimes be overcome by means of labeling experiments. For ^{1}H NMR, specific exchange of some of the hydrogens by deuterium atoms is relatively straightforward, and a comparison of the partially deuterated and nondeuterated spectra frequently leads to the assignment of a majority of the signals. For ^{13}C NMR, treatment of the alkyne-substituted carbonyl cluster with ^{13}C-enriched carbon monoxide will increase the intensity of the signals of the carbonyl carbons compared to those of the alkyne groups, which do not generally exchange, and thus permit assignment of the signals. A number of studies on alkyne-substituted clusters do involve both the fluxionality of the carbonyl ligands and of the alkyne groups and these will be discussed in Section V.

As with the low-field signal for the proton bonded to alkyne carbons coordinated to the metal, the ^{13}C signals often prove a useful diagnostic tool. These ^{13}C signals also tend to be at low field, but the position of the signal may vary by several hundred ppm depending on the environment of the carbon atom. There are a number of important steric and electronic factors which have a major influence on the interaction between the alkyne carbons and the metal framework that prevent the maximum use of this data.

Carty (*13*) has indicated that for a closely related group of complexes there is a workable correlation between the observed positions of the signals and the reactivity of the carbons with which they are associated. The acetylenic ^{13}C NMR resonances for a number of tri- and tretranuclear clusters have been collected in Table II; the relevant bonding types for the alkyne-derived ligands are also illustrated in this Table (*13, 203, 285, 366, 378–380*). The shifts for the trinuclear clusters are generally to higher field than the shifts of carbene carbon resonances in carbene complexes, which lie in the range 200–350 ppm. The resonance for the C_α atom in the tetranuclear cluster $FeCo_3(CO)_9(Cp)(\mu_4\text{-}\eta^3\text{-}CCH_2)$ (*285*) is within this range, and suggests a more carbenic nature for this carbon. Within a structurally related series of molecules the variations of the C_α and C_β resonances are dependent on the metal atoms to which they are bonded and on the nature of the substituent R groups, and may be indicative of the differences in polarization in the $C{\equiv}C$ triple bond. If it is assumed that a change in $\delta(^{13}C)$ is mainly associated with a change in charge on the carbon atom (*381*), then $\delta(C_\alpha) + \delta(C_\beta)$ gives an idea of the total charge alteration in the $C{\equiv}C$ bond while $\delta(C_\alpha) - \delta(C_\beta)$ is a measure of the polarization of that bond (Table II). In the complexes of types A and B the value for the C_β resonance shows a much smaller variation than that for C_α, except in the case of the triosmium cluster $Os_3H(CO)_9(\mu_3\text{-}\eta^2 \perp CCH)$ (*366*), in which the C_β resonance is abnormally low. The data suggest that the overall change in charge is greater for the type A structures than for type B, and that polarization of the C–C bond in type A shows a greater variation than for type B.

The single resonance for the π-bonded alkene ligand in $Os_3(CO)_{11}(C_2H_4)$ (*366*) lies considerably upfield of the equivalent C_α resonance in the type D complexes, in which σ bonding between the metals and the alkene ligand is important. These C_α resonances are interestingly quite similar to those in the type A and B complexes.

It should be pointed out that the sample considered in this discussion is very small, and a great deal more experimental work is required before any generalization can be made about the relationship between the position of the ^{13}C resonances and the reactivity of the systems.

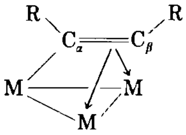
The observation of $^{13}C–^{13}C$ coupling constants in μ_2- and $\mu_4\text{-}\eta^2$-alkyne cobalt clusters has also shed some light on the nature of bonding in these complexes (*382*). There is a drastic decrease in the $^1J(CC)$ coupling constant on going from the free alkyne to complexes where the ligand is bonded to two or four cobalt atoms. In $Co_4(CO)_{10}(\mu_4\text{-}\eta^2\text{-}HCCH)$, the $^1J(CC)$ constant is 21 Hz, compared to that of 171.5 Hz in HCCH, and theoretical calculations indicate that this is consistent with a rehybridization of the formally *sp* hybridized acetylenic C atoms toward sp^3 hybridization.

TABLE II

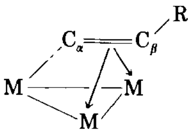
^{13}CNMR RESONANCES FOR SOME ALKYNE- AND ALKENE-SUBSTITUTED TRI- AND TETRANUCLEAR CLUSTERS

Complex	Type[a]	ppm				Reference
		$\delta(C_\alpha)$	$\delta(C_\beta)$	$\delta(C_\alpha) - \delta(C_\beta)$	$\delta(C_\alpha) + \delta(C_\beta)$	
$Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}EtC_2Et)$	A	221.9	106.8	115.1	328.7	*378*
$Fe_2Mo(CO)_8Cp(\mu_3\text{-}\eta^2\text{-}\perp\text{-}CCMe)$	B	181.8	95.9	85.9	277.7	*379*
$Fe_2W(CO)_8Cp(\mu_3\text{-}\eta^2\text{-}\perp\text{-}CCMe)$	B	165.7	108.3	57.4	274.0	*379*
$Fe_2W(CO)_8Cp(\mu_3\text{-}\eta^2\text{-}\perp\text{-}CCTol)$	B	172.9	112.7	60.2	285.6	*379*
$FeW_2(CO)_6Cp_2(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_2Tol_2)$	A	168.5	153.8	14.7	322.3	*380*
$Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}CCPr^i)(PPh_2)$	B	134.4	103.8	30.6	238.2	*13*
$Ru_3H(CO)_8(\mu_3\text{-}\eta^2\text{-}\perp\text{-}CCBu^t)(PPh_2OEt)$	B	140.5	112.2	28.3	252.7	*13*
$Ru_3H(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}CCBu^t)$	B	164.2	110.6	53.6	274.8	*13*
$RuW_2(CO)_7Cp_2(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_2Tol_2)$	A	153.1–128.0				*380*
$Os_3(CO)_{11}(\mu\text{-}C_2H_4)$	C	22.4				*366*
$Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}\parallel\text{-}HCCH)$	D	123.4				*366*
$Os_3H(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}CCH)$	B	134.4	41.6	92.8	176.0	*366*
$OsPt_2(CO)_5(\mu_3\text{-}\eta^2\text{-}\parallel\text{-}MeC_2Me)(PPh_3)_2$	D	155.5				*203*
$FeCo_3(CO)_9Cp(\mu_4\text{-}\eta^3\text{-}CCH_2)$	E	304.0				*285*

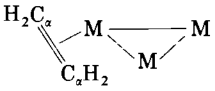
[a]



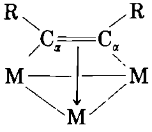
A



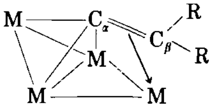
B



C



D



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E. MASS SPECTROMETRY

Mass spectrometry is widely used in organometallic and cluster chemistry as a rapid means of determining the molecular weight, the number of carbonyl and other ligands present, and even the number of metal atoms present. In the case of relatively small molecules it is also possible to detect hydrogen loss.

There are, however, a number of limitations to the technique. First, the complex must be volatile. The presence of ligands such as phosphines or phosphidoalkynes greatly reduces the volatility as does the presence of anionic or large polynuclear cluster frameworks. The results obtained are dependent on the instrument and on the experimental conditions used. In order to increase the volatility it is often necessary to increase the temperature at the probe. This temperature increase may not always be carefully controlled, and can lead to deposition of metal within the instrument, which reduces its sensitivity and produces erroneous molecular weight peaks. At elevated temperatures, cluster breakdown is common, and in the publications on $Ir_4(CO)_8[C_2(COOMe)_2]_4$ (*205*) and $Os_5(CO)_{17}(HCCH)$ (*227*), the molecular ion peak obtained from the mass spectrum does not correspond to the molecular formula established by X-ray crystallography. Molecular rearrangements may also occur within the instrument without apparent loss of molecular fragments, and this has been observed in a number of Co–Rh derivatives (*383*).

A number of developments of the technique are now available but have not been widely used. These include chemical ionization, field ionization or desorption, and negative ionization. The techniques of fast atom bombardment (FAB) and field desorption appear the most promising for detecting the molecular ions in compounds that would otherwise break up in the instrument (*9*).

Regrettably, alkyne-substituted cluster complexes seem particularly prone to fragmentation and very few accurate mass spectroscopic studies have been reported. A recent exception has been the field-desorption and electron-impact mass spectral investigation of mono- and oligo-nuclear ferracyclic ring systems of the from $Fe_x(CO)_y(C_2R_2)_2$ ($x = 1, 2, 3$; $y = 6, 8$) (*384*). These species show intense molecular ion peaks, which enable ready recognition of the molecular composition.

F. X-RAY CRYSTALLOGRAPHIC AND NEUTRON DIFFRACTION STUDIES

It is probably fair to say that up to the present time single-crystal X-ray diffraction studies have done more to further the development of cluster chemistry than any other method of structure characterization.

The main reason is that all the systems are relatively complex and, while spectroscopic techniques may give part of the answer as to the nature and stereochemistry of the compound, a full crystallographic study will in a vast majority of cases give a definitive answer. In the reviews on alkyne-substituted clusters and related compounds, a large proportion of the discussion of the chemistry has been based on solid-state structural data, and this review is no exception. The variety of structural cluster types incorporating alkyne ligands will be presented in Section IV.

However, there are a number of limitations and criticisms which may be leveled at the crystallographic technique, and it is worth bearing these in mind when looking at the available structural data. Perhaps, most importantly, the technique deals with the solid state, and a vast majority of reaction chemistry occurs in solution. Also, it is frequently the case that the structural analysis is performed on one crystal, and one crystal only, and this crystal may not be representative of the molecules in the bulk sample. Careful work on a number of ruthenium cluster systems has shown the existence of a number of different solid-state isomers and different crystalline modifications (*380, 385*). It is probable that in solution there is more than one structural form but that one crystallizes out preferentially.

Another problem involves the accuracy of the data obtained. Particularly with cluster compounds of the second and third row transition metal elements, absorption effects and the like may introduce quite large uncertainties into the positions of the lighter atoms. The estimated standard deviations obtained from most crystallographic programs tend to rather underestimate the errors, and while good, accurate absorption corrections are routinely carried out, the true error on a C–C bond length in, say, a tetranuclear osmium cluster alkyne is probably of the order of ± 0.05 Å. This makes comparisons between bond parameters for the lighter atoms rather less meaningful than some authors would have us believe, and a formal assignment of "bond order" for an acetylenic bond far from certain. The problem is even more severe when the location of hydrogen atoms is being discussed, and in larger clusters these atoms are seldom located directly because the scattering is dominated by the heavy metal atom contribution. A variety of very useful indirect methods (*386*) have been developed for the location of hydrides, but these have not been applied to the location of acetylenic hydrogen atoms.

The problem of hydrogen atom location may be overcome, and a reduction in the uncertainties in the positions of the lighter atoms obtained, by the use of neutron diffraction. This method is generally similar to X-ray diffraction except that neutrons are diffracted by the atomic nuclei rather than by the surrounding electron cloud. The scattering power of the nucleus is not dependent on the number of subatomic particles that it contains and it varies almost randomly throughout the periodic table. The difference in neutron scattering power of a hydrogen atom and a third row transition element is far smaller than the difference in X-ray scattering power. Absorption effects for neutrons are also much smaller. So light atoms are located with considerable precision, and it is possible to observe significant variations in bond parameters for these atoms which are consistent with current bonding theories.

Unfortunately, neutron diffraction brings its own problems. These include the requirement of a large single crystal, weighing of the order of 30 mg (which may be larger than the total yield of a typical cluster synthesis), and access to a nuclear reactor for a period of several weeks for a single experimental run. Present day neutron fluxes are an order of magnitude weaker than X-ray sources so that it requires a much longer time to measure the intensity of each reflection.

So far only one alkyne-substituted (*387*) and two vinylic cluster derivatives (*186, 388*) have been analyzed by neutron diffraction. Hopefully, the development of high-energy neutron sources and two-dimensional detectors over the next few years will see an advance in this area of structural chemistry.

G. ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY

This technique is not a direct structural probe, but has been used as an experimental method to augment theoretical calculations on the bonding in cluster systems, including a number of alkyne-substituted complexes (*389–391*). The basis of the technique is that photons in the vacuum ultraviolet region of the spectrum, whose energy is about 10 eV, interact with molecules in the gas phase to cause either promotion of electrons from one bound state to another or their ejection as free electrons. Photoelectron spectroscopy is only concerned with processes that liberate electrons, either by direct ionization [Eq. (15)],

$$\mathrm{M} \xrightarrow{h\nu} \mathrm{M}^{+} + e^{-} \tag{15}$$

or possibly by autoionization [Eq. (16)],

$$\mathrm{M} \xrightarrow{h\nu} \mathrm{M}^{*} \longrightarrow \mathrm{M}^{+} + e^{-} \tag{16}$$

where M* may be in a stable, metastable, or unstable state (*392*). The source of radiation for the experiment is obtained from the helium emission spectrum in which the He(I) line (21.22 eV) predominates, accounting for 98% of the emission, so that for the majority of substances which have ionization potentials of 5 eV or greater, essentially the only ionization caused is due to the He(I) resonance line. The spectra obtained in this way are compared with orbital energy diagrams, and the orbitals from which the electrons are ionized may be identified. This is possible because of close adherence to the precepts of Koopmans' Theorem, which postulates the equality of the negative of an ionization energy to a one-electron orbital energy.

This technique has been used extensively as an experimental comparison for one or other of the types of theoretical molecular orbital calculations for organic and some nonmetallic inorganic compounds. However, for transition metal complexes and cluster compounds, their lower volatility presents some difficulties, and for the photoelectron spectra of the cluster alkyne complexes that have been recorded a heated inlet probe has been used to overcome this problem.

In order to ease the interpretation of the photoelectron spectra, and to obtain the best correlation between experimental data and related theoretical calculations, it is advisable to consider a series of related molecules. In the case of alkyne-substituted clusters He(I)-excited vapor-phase photoelectron spectra have been obtained on the series of molecules $Co_2(CO)_6(PhCCH)$ (**1**) (*389*), $Fe_3(CO)_9(EtCCEt)$ (**2**) (*390*), $M_3(CO)_9(\mu\text{-}H)(CCR)$ (M = Ru, Os) (**3**) (*391*), and $Co_4(CO)_{10}(PhCCH)$ (**4**) (*389*), which exhibit the range of bonding modes illustrated in Fig. 11.

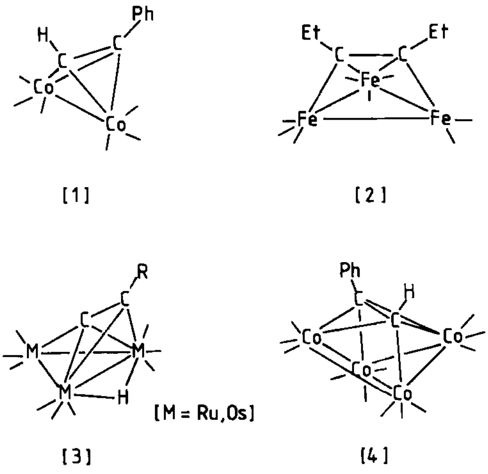

FIG. 11. Alkyne clusters for which photoelectron spectroscopic data are available.

The combined experimental and theoretical results emphasize the carbynic nature of the acetylenic carbon atoms bonded to the cluster, as indicated by NMR experiments (Sections III,C and D), and show that there is an increase in negative charge on the acetylenic carbon as the number of metal atoms to which it is coordinated increases and the C–C bond order decreases. The highest negative charge on these carbons would be obtained by cleaving the C–C bond to form μ_3-alkylidyne systems. The calculations indicate that the normally accepted model for metal alkyne bonding (Section IV, A) is correct, and that there is a net back donation into ligand π^* orbitals, which increases as the number of metal alkyne bonding (Section IV,A) is correct, and that there is a net describe the alkyne bonding in **2** in terms of two σ bonds and one π bond, and in **3** as one σ bond and two weaker π interactions.

If these results are transferable to other alkyne cluster systems it appears that, in general, the ideas on cluster alkyne bonding developed over the last two decades from the work of Dahl and co-workers (*26*) are correct.

IV. Types of Bonding of Alkynes in Cluster Complexes

A. BONDING MODES OF ALKYNES

Before considering the bonding of alkynes in cluster complexes it is worth discussing the rather simpler cases of mononuclear alkyne complexes and the free ligand itself.

The molecular orbital energy stacking diagram for free acetylene is shown in Fig. 12. It can be seen that all the available bonding molecular orbitals are filled and that the free ligand has formal triple bond character. Upon coordination to a metal atom, the C–C vector lies perpendicular to the σ-bonding orbital on the metal and donates electron density from a filled π-bonding orbital, as illustrated in Fig. 13.

The bonding in monometal alkyne complexes is usually interpreted in terms of the Dewar–Chatt–Duncanson model (*293*), since the alkyne molecule has a pair of π and π^* molecular orbitals which lie in the plane of the metal and the two carbon atoms. These two orbitals are denoted $\pi_{\parallel}$ and $\pi_{\parallel}{}^*$, and are analogous to those in π-bonded alkene complexes (*394*). There is also a pair of π and π^* molecular orbitals which lie perpendicular to the metal–carbon plane, denoted $\pi_{\perp}$ and $\pi_{\perp}{}^*$. These orbitals are illustrated in Fig. 14. Both sets of π and π^* orbitals have the correct symmetry to interact with metal d orbitals. The interaction

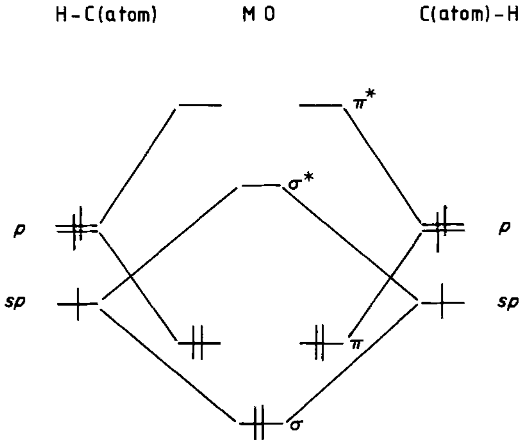

FIG. 12. MO stacking diagram for free acetylene.

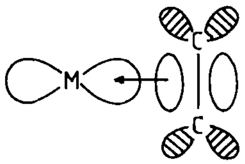

FIG. 13. π-Bonding overlap between acetylene and metal σ bond.

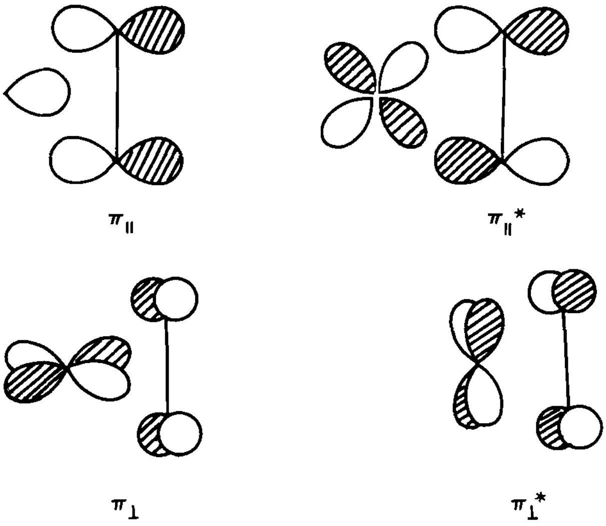

FIG. 14. Interactions between the π and π* molecular orbitals of an alkyne with metal orbitals of appropriate symmetry.

involving the $\pi_{\perp}{}^{*}$ orbital is not energetically significant because only a δ type overlap is involved. The overlap which involves the filled $\pi_{\perp}$ molecular orbital is important, and has a magnitude similar to that involving the $\pi_{\parallel}{}^{*}$ orbital. The addition π-donor interaction possible for an alkyne means that it may function simultaneously as a π-acceptor and a π-donor ligand. In terms of electron counting it may formally act as a two- (using $\pi_{\parallel}$) or a four-electron (using $\pi_{\parallel}$ and $\pi_{\perp}$) donor. Recent theoretical calculations confirm the importance of the $\pi_{\perp}$ orbital in bonding to monometal complexes and indicate that the observed orientation of the alkyne is at least partially dependent on the strength of the interaction from this orbital (*395*).

The bonding scheme described above is consistent with the change in the C–C bond length and the C–C–R bond angle. In free acetylene the C–C bond length is 1.21 Å while upon complexation it is lengthened to a value typically in the range 1.3–1.45 Å. For free alkynes, the C–C–R angle is approximately 180°, but in complexes, a cis bending occurs giving angles in the range 120–150°. Hoffmann and co-workers (*396*) have made a thorough study of the variation of these parameters in a range of dinuclear alkyne-substituted complexes. For dimetallic systems, the acetylenic C–C bond may lie essentially parallel or perpendicular to the metal–metal vector. The interactions between molecular orbitals which participate in these two stereochemistries are different, and this explains differences in the observed C–C–R angles for the two groups: 120–130° for the parallel bonded alkynes and 130–150° for the perpendicular bonded alkynes. Because of the use of different orbital arrangements there is expected to be a relatively high barrier to rotation between the two orientations which makes fluxionality in these systems less likely at lower temperatures.

For higher cluster complexes containing coordinated alkyne-derived ligands the situation with regard to modes of bonding of the organic fragment is considerably more complicated. A single alkyne may donate between two and six electrons to a cluster depending upon the mode of coordination. Unlike a carbonyl group, an alkyne may fragment upon coordination to a cluster, and in this way, increase the number of electrons which it formally donates. Particularly in the case of acetylene itself, or with mono-substituted alkynes, an acetylenic hydrogen may either transfer to the metal framework to give a hydride, which formally donates one electron to the cluster, or undergo a shift to the other acetylenic carbon, which results in a coordinated organic ligand more reminiscent of an alkene. A "naked C–C" unit, in which all the organic substituents have been lost, would formally donate six electrons. For disubstituted alkynes the nature of the bonded R group may also have an influence on the mode of bonding, particularly if the group is bulky and exerts a strong steric influence. In all cases fragmentation of the alkyne may result in one of the fragments not appearing in the cluster complex at all, but forming part of another product in the reaction. Alternatively, it is possible that, upon coordination to the cluster, alkynes may link together or with other cluster ligands via C–C bond formation to give extended organic based units bonded to the cluster. A discussion of the variety of bonding modes of such groups is beyond the scope of this review, and only specific examples of direct relevance to the structural chemistry of cluster alkynes will be described. Neither will structures containing capping alkylidyne ligands, obtained by alkyne fragmentation, be discussed in detail since these have been comprehensively reviewed elsewhere (*16*, *17*). The modes of bonding of alkyne ligands, and of ligands derived from alkynes, coordinated to three, four, or five metal atoms in clusters are illustrated in Fig. 15. It is sometimes difficult to decide whether the coordinated ligands in Fig. 15 are derived from alkynes or alkenes, since there are a number of reactions in which the use of either species leads to the same product. However, an examination of these bonding modes suggests that only the ligands in structural types M3, M6, M7, M11, M15, M16, and M17 are truely acetylenic, the remainder may be described as acetylides or ethylenic substituents. Each type of bonding mode will be discussed in Section IV,C.

B. ELECTRON COUNTING AND BONDING CONSIDERATIONS

For alkynes bonded to higher nuclearity clusters no overall molecular orbital treatment encompassing all the variations in geometry has appeared yet.* However, there are a small number of examples of specific alkyne-substituted clusters which have been analyzed by one type of molecular orbital treatment or another, and a number of these have been mentioned in Section III,G because photoelectron spectroscopy has been used as an aid to assignments. CNDO calculations (*397*) on $Fe_3(CO)_9(EtCCEt)$ (*390*) and $M_3(CO)_9(\mu\text{-}H)(CCR)$ (M = Ru, Os) (*391*) and Fenske–Hall calculations (*398*) on $Co_4(CO)_{10}(PhCCH)$ (*389*) indicate that there is net back donation into alkyne π^* orbitals, which increases as the number of metal atoms to which the ligand is bonded increases. The normally accepted view of considering the interaction

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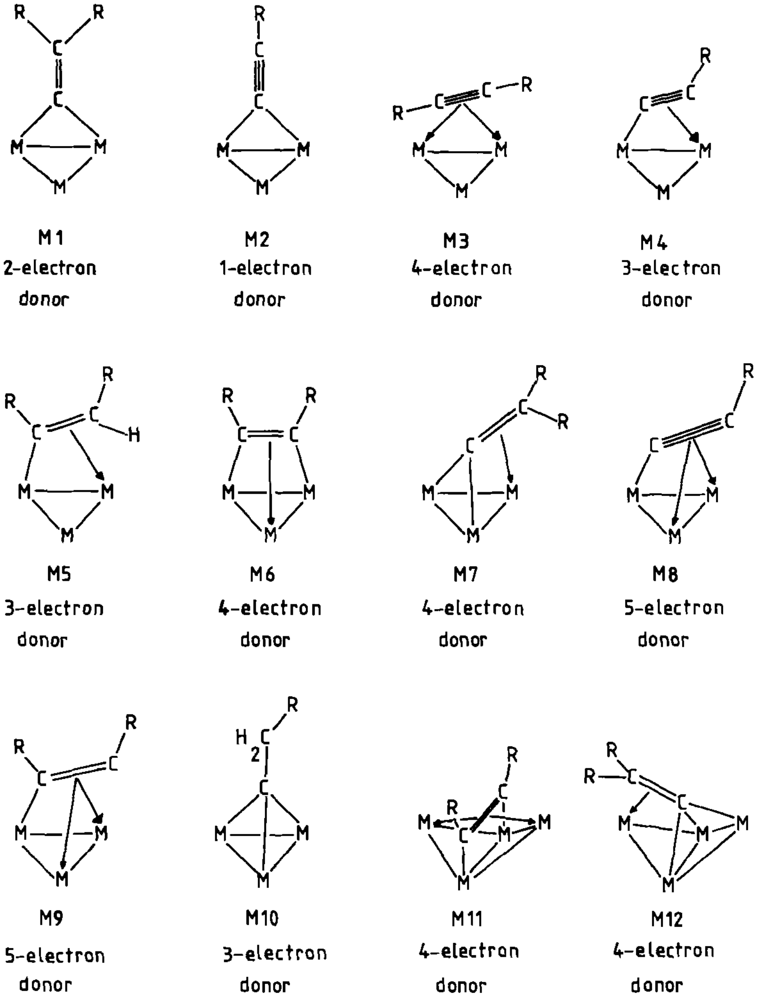
* A more comprehensive molecular orbital treatment of the bonding in alkyne-substituted trimetallic clusters has recently appeared. See Halet *et al.*, *Inorg. Chem* **24**, p. 218 (1985).



M1 2-electron donor

M2 1-electron donor

M3 4-electron donor

M4 3-electron donor

M5 3-electron donor

M6 4-electron donor

M7 4-electron donor

M8 5-electron donor

M9 5-electron donor

M10 3-electron donor

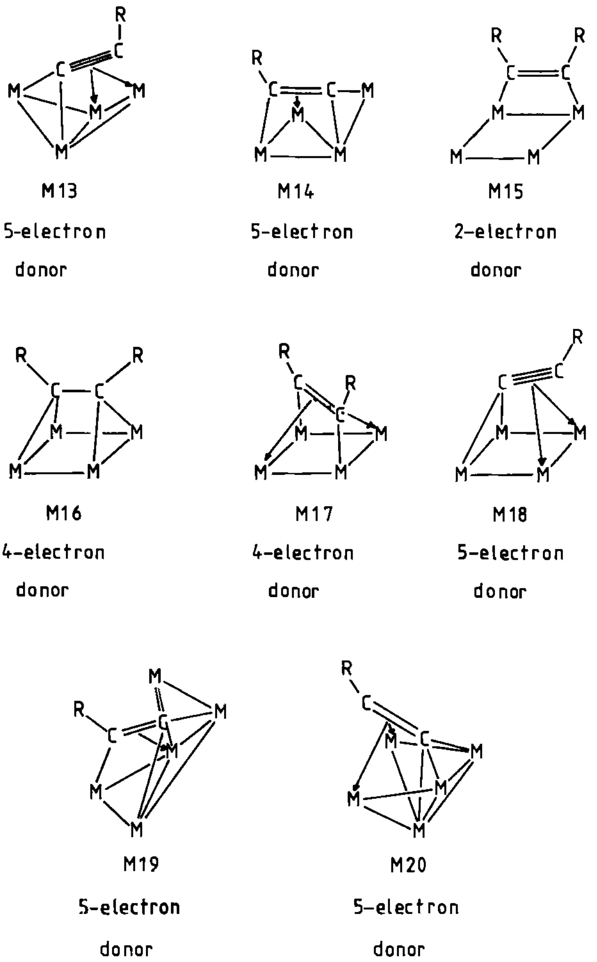
M11 4-electron donor

M12 4-electron donor

FIG. 15. Observed bonding modes of alkyne and alkyne-derived ligands in cluster complexes.

between the alkyne ligand and the metals in terms of σ and π bonds seems correct, at least for tri- and tetranuclear systems.

More generally, in terms of electron counting, alkyne-substituted clusters may be treated in a manner similar to other cluster systems. In these schemes the ligands are considered primarily as species which donate electrons to the cluster framework and do not have specific donor and acceptor properties of their own. Because of possible



M13 5-electron donor

M14 5-electron donor

M15 2-electron donor

M16 4-electron donor

M17 4-electron donor

M18 5-electron donor

M19 5-electron donor

M20 5-electron donor

FIG. 15 (*Continued*)

confusion as to the number of electrons that the alkyne-derived ligand may donate, particularly in the case in which a hydrogen splits off the ligand and bonds to the metal framework independently, it is better to include the electron donated by this hydride in the electron count from the parent, organic free ligand. The simplest of these counting schemes is the "18-Electron Rule" or the "Effective Atomic Number Rule" where the skeletal metal framework is held together by a network of two-centre two-electron bonds (*399*). This scheme works reasonably well for relatively small systems such as $Co_2(CO)_6(RCCR)$, which is a 34-electron system, and indicates the presence of a single metal–metal bond. However, this rule frequently breaks down for larger clusters.

A theory which shows greater applicability to bonding in cluster compounds is the "Polyhedral Skeletal Electron Pair Theory" (PSEPT) which allows the probable structure to be deduced from the total number of skeletal bond pairs (*400*). Molecular orbital calculations show that a *closed* polyhedron with n vertex atoms is held together by a total of $(n + 1)$ skeletal bond pairs. A *nido* polyhedron, with one vertex vacant, is held together by $(n + 2)$ skeletal bond pairs, and an *arachno* polyhedron, with two vacant vertices, by $(n + 3)$ skeletal bond pairs. Further, more open structures are obtainable by adding additional pairs of electrons. This discussion of these polyhedral shapes is normally confined to metal atoms, but it is possible to consider an alkyne, $RC{\equiv}CR$, either as an external ligand or as a source of two skeletal CR units. So that, for example, the cluster skeleton in the complex $Co_4(CO)_{10}(RCCR)$, shown in Fig. 16, may be considered as a *nido* trigonal bipyramid (a "butterfly" cluster) with a coordinated alkyne or as a *closo* octahedron with two carbon atoms in the core.

The disadvantages of this approach are twofold. With higher nuclearity clusters the number of geometric possibilities for the same electron count increases, and while the PSEPT may be used to rationalize a number of the observed configurations it is not predictive. Secondly, unlike boranes, for which the theory was originally developed, increasing the nuclearity of the cluster does not always result in a larger *closo* polyhedron, but the observed structure is often best described in terms of a smaller polyhedron where some of the faces are capped. The result of this is that a monocapped polyhedron with n skeletal atoms has n electron pairs available for cluster bonding. This may be thought of as being equivalent to adding a capping group to a *closo* cluster polyhedron without formally adding an electron pair. For a transition metal

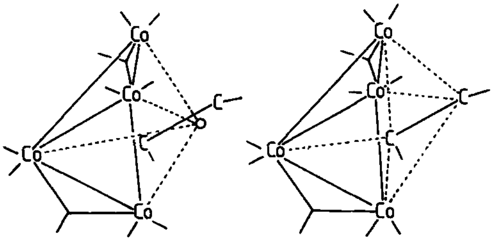


FIG. 16. Two different bonding descriptions of the cluster $Co_4(CO)_{10}(RCCR)$.

cluster with n skeletal metal atoms the total number of skeletal electron pairs (P) is given by Eq. (17).

$$P = 0.5\,(\text{total valence electrons} - 12n). \tag{17}$$

Several groups have performed calculations on the possible geometries adopted by higher nuclearity clusters but these have generally considered the arrangement of the atoms in the metal core only (*401*). Mingos developed an extension of the PSEPT to include nonconical fragments (*402*), and has given some general principles for electron counting in condensed polyhedra (*403*). With these developments it is possible to rationalize all platinum-group metal condensed polyhedral cluster structures.

In practice, specific cluster metal framework geometries are associated with particular electron counts and the number of formal metal–metal bonds present. It is often simplest to analyze structures in terms of these electron counts. Some of the possible metal framework geometries associated with the more common electron counts are illustrated in Fig. 17, and these metal arrays, along with the mode of coordination of the alkyne-substituted ligands, will be used in Section IV,C to order the discussion of the structural types.

C. The Structures of Alkyne-Substituted Clusters

In alkyne-substituted cluster complexes neither the "side-on" π bond nor the "end-on" acetylide type bond to a single metal center is observed, unlike the situation in mononuclear systems where these are the only modes possible. It is possible to explain the absence of simple π-bound alkynes in a manner similar to that used to rationalize the occurrence of bridging carbonyls in carbonyl clusters. The alkyne is capable of acting as a strong π-acceptor ligand, and with two or three metal atoms available it may be favorable to maximize the back donation by coordinating to all of them. However, it would be interesting to see if an activated cluster, such as $Os_3(CO)_{11}(MeCN)$, would react with alkynes to give a simple π-bound substitution product. At present, the absence of single-center acetylide interactions in clusters is also generally explained in terms of maximized back donation. This rationalization is supported by the structures of copper acetylides (*364*), which are polymeric, with the acetylide σ bonded to one metal and π bonded to another (Fig. 18). Similar simultaneous metal–acetylide σ and π bonding occurs in the mixed-metal cluster derivatives $Cu_4Ir_2(PPh_3)_2(CCPh)_8$ (*237*), $RhAg_2(CCC_6F_5)_5(PPh_3)$ (*164*), and

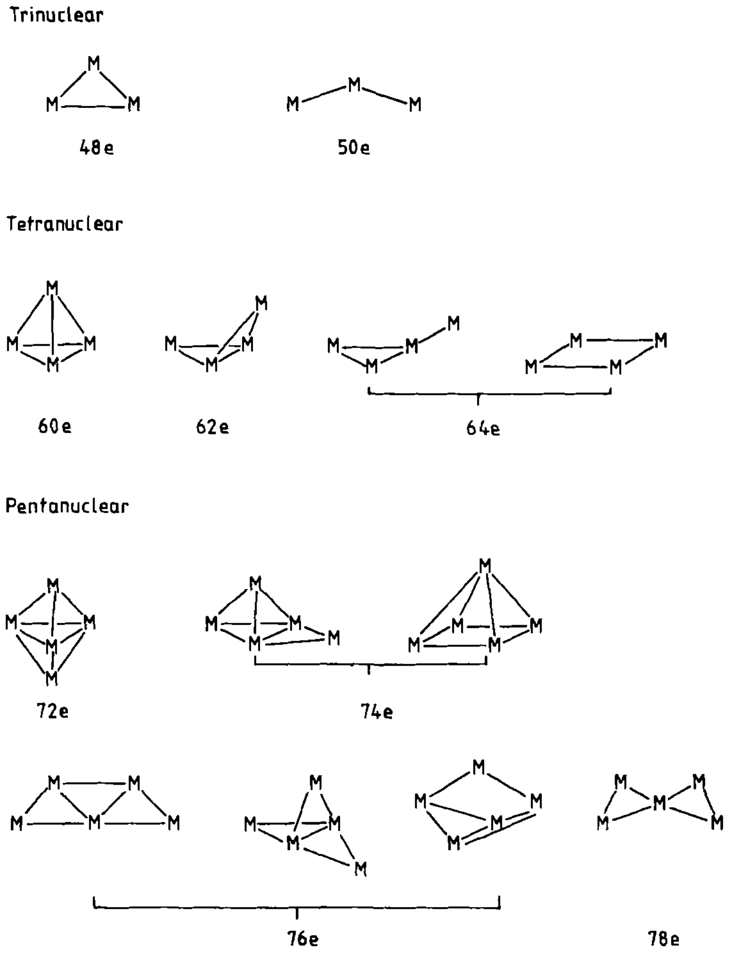


FIG. 17. Possible metal cluster framework geometries.

$[CpFe(CO)_2(CCPh)CuCl]_2$ (*404*), and where the acetylenic C–C bond lengths lie in the range 1.18–1.29 Å. In $[CpFe(CO)_2(CCPh)CuCl]_2$ (Fig. 19), the C–C–Fe angles both show a marked deviation from linearity, each with a value of 162(2)°.

In contrast to alkyne ligands, alkenes are observed to bond "side-on" to one metal center in a cluster complex. This may reflect the poorer π-acceptor properties of an alkene compared to an alkyne. In all cases reported for single alkene units the ligand has been coordinated to a metal atom in a trinuclear cluster unit, and in the majority of cases the

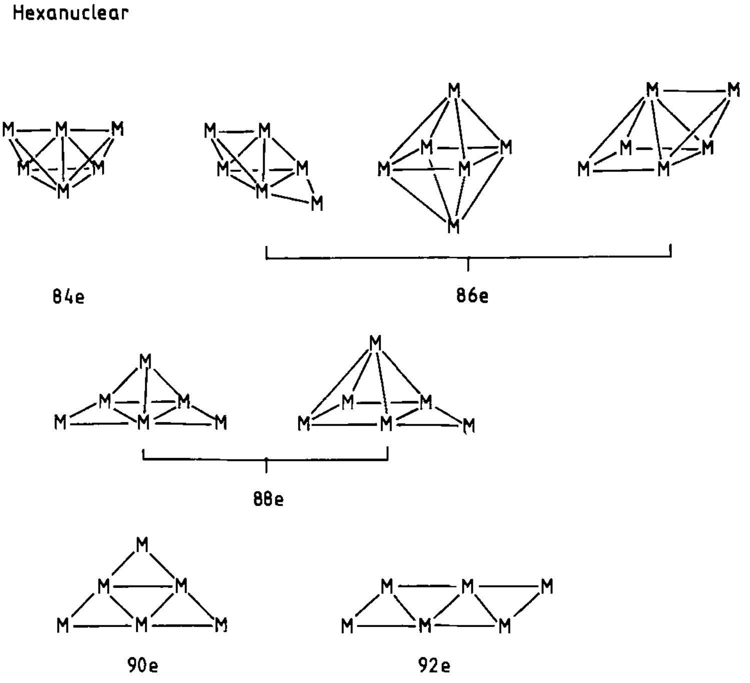


FIG. 17 (*Continued*)

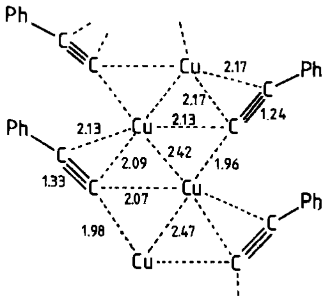


FIG. 18. Structure of phenylethynyl copper. (Bond lengths in Å.)

olefinic C=C bond lies in the plane of the metal triangle (*106, 263, 405–408*). In these clusters the substituents range from hydrogen to CF_3 groups, and in the case of $Ru_3(CO)_{10}(\mu\text{-P-}\eta^2\text{-}CH_2{=}CHC_6H_4PPh_2)$ (*106*), a substituted phenyl group; the olefinic C–C distances lie in the range 1.36(4)–1.51(4) Å. The plane defined by the olefinic carbons and the atoms of the substituent groups lie approximately perpendicular to the

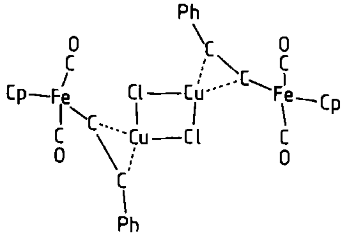


FIG. 19. Structure of $[CpFe(CO)_2(C{\equiv}CPh)CuCl]_2$.

plane of the metal triangle. The C–C–X (substituent) angles show only small deviations from the idealized value of 120°, the largest being in the case of $Ru_3(CO)_{10}(\mu\text{-P-}\eta^2\text{-}CH_2{=}CHC_6H_4PPh_2)$ (*106*), in which the substituent is linked to another coordinating ligand.

A different orientation of the coordinated alkene is observed in the structure of $Ir_3(CO)_7(\mu\text{-}PPhCH{=}CHPPh_2)$ (*244*). The alkene ligand lies above the metal triangle coordinating to one Ir atom while the two substituent P atoms bond to one and two metals, respectively (Fig. 20). The olefinic C–C distance is 1.44(2) Å, and the average C–C–P angle is 118(1)°. The difference in orientation of the alkene presumably results from the interactions of the P substituents with the cluster which are not present in the other alkene-substituted molecules.

Related to the clusters with coordinated alkenes are the diene-substituted complexes $Os_3(CO)_{10}(cis\text{-}C_4H_6)$, $Os_3(CO)_{10}(trans\text{-}C_4H_6)$ (*409*), and $Ru_6C(CO)_{15}(MeCH{=}CH{-}CH{=}CHMe)$ (*60*). In these clusters the mode of bonding of the individual olefinic C–C bonds is similar to that of a simple alkene, although in the two latter cases the ligand spans two adjacent metal centers.

1. *Interactions of Alkyne Ligands with Two Metal Centers*

The simplest type of interaction between an alkyne-derived ligand and two metal centers is mode M1 in Fig. 15. This alkenylidene ligand, which formally donates two electrons to the cluster, has been observed

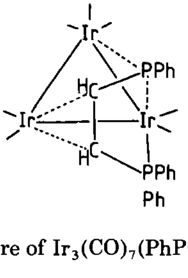


FIG. 20. Structure of $Ir_3(CO)_7(PhPCH{=}CHPPh_2)$.

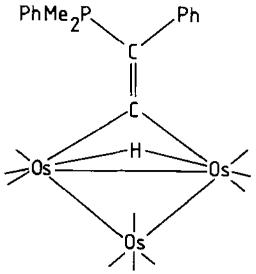


FIG. 21. Structure of $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}C{=}CPhPMe_2Ph)$.

in a number of dinuclear complexes (*410*) but is relatively uncommon in polynuclear species. A recent example appears in the structure of $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}C{=}CPhPMe_2Ph)$ (*411*), which is shown in Fig. 21. The C–C vector lies approximately perpendicular to the metal–metal bond which it spans. The ligand appears to have a strong bond-shortening influence on the bridged metal–metal bond, since this Os—Os bond is ca. 0.07 Å shorter, at 2.802(1) Å, than the two unbridged Os—Os bonds, despite the presence of a bridging hydride along the same Os—Os vector. A hydride bridge normally lengthens a metal–metal bond.

The mode M2, in which an acetylide ligand spans a metal–metal edge and lies perpendicular to the metal–metal vector, has been observed in the trinuclear cluster $Ru_3(CO)_6(\mu\text{-}CCBu^t)(\mu\text{-}\eta^2\text{-}CCBu^t)(PPh_2)_2$ (*113*) (Fig. 22). A second $C{\equiv}CBu^t$ alkyne ligand adopts bonding mode M4. The Ru—Ru bond bridged by the M2 mode $C{\equiv}CBu^t$ group and a PPh_2 ligand is relatively short, at 2.863(1) Å, and the C–C bond length of 1.19(1) Å is indicative of the retention of triple bond character. The same mode of acetylide bonding is observed in the hexanuclear cluster $Cu_6(C_6H_4NMe_2)_4(CCC_6H_4Me)_3$ (*263*), in which C–C multiple bonding is also retained; C–C 1.18(1) Å.

Bonding mode M3 is truly acetylenic in character, and is common in dinuclear complexes (*17*). It has been observed in the trinuclear platinum cluster $Pt_3((PEt_3)_4(PhCCPh)_2$ (*151*). The three Pt atoms adopt

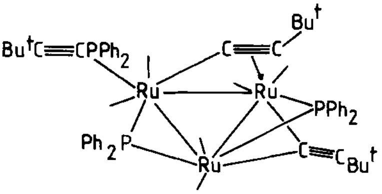


FIG. 22. Structure of $Ru_3(CO)_6(PPh_2)_2(\mu\text{-}CCBu^t)(\mu\text{-}\eta^2\text{-}CCBu^t)(Ph_2PCCBu^t)$.

an open V-shaped arrangement while the acetylenic units form transverse bridges across the two Pt–Pt vectors on the convex side of the metal V. The C–C bond length is 1.34(3) Å, and the phenyl groups bend away from the metal atoms to give a C–C–Ph angle of 139(1)°.

The bonding mode M4 is again more common for dinuclear species than for polynuclear ones, however, this is the mode of bonding that best describes the coordination of the acetylides in the mixed-metal clusters $Cu_4Ir_2(PPh_3)(CCPh)_8$ (*237*), $RhAg_2(CCC_6F_5)_5(PPh_3)_3$ (*164*), and $[CpFe(CO)_2(CCPh)CuCl]_2$ (*412*), which were discussed previously. Examples are also found in ruthenium chemistry. The cluster $Ru_3(CO)_6(\mu\text{-}CCBu^t)(\mu\text{-}\eta^2\text{-}CCBu^t)(Ph_2PCCBu^t)(PPh_2)_2$ (*113*) contains a ligand bonded in this mode, as do the complexes $Ru_4(CO)_{13}(\mu\text{-}\eta^2\text{-}CCBu^t)(\mu\text{-}PPh_2)$ and $Ru_4(CO)_8(\mu\text{-}\eta^2\text{-}CCBu^t)(\mu_3\text{-}\eta^2\text{-}CCBu^t)(Ph_2PC{\equiv}CBu^t)(\mu\text{-}PPh_2)_2$ (*404*). The structures of these two compounds are illustrated in Fig. 23. The $\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t$ ligands act as three-electron donors so that the two complexes are 64-electron systems. This results in an almost planar "butterfly" metal framework with a dihedral angle in the range 167–178°, and contrasts with the 62-electron alkyne-substituted "butterfly" clusters which will be discussed in Section IV,C,2. A 64-electron cluster, by normal electron counting rules, would be expected to have four metal–metal bonds. In this case there appears to be a lengthening of all five metal–metal bonds in the "butterfly" framework.

There are eight cluster complexes that exhibit bonding mode M5. The ligand may be described as an alkenyl group and formally donates three electrons to the cluster via one σ and one π bond. The reported structures include neutron diffraction studies on $Os_3(\mu\text{-}H)(CO)_{10}(HC{=}CH_2)$ (*388*) and $Os_4(\mu\text{-}H)_3(CO)_{11}[HC{=}C(H)Ph]$ (*186*), and relevant bond parameters are displayed in Table III (*52, 91, 186, 192, 195, 338, 413, 414*).

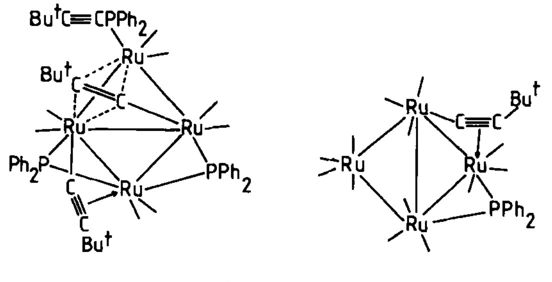


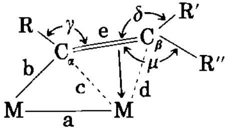
FIG. 23. Structures of $Ru_4(CO)_{13}(\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t)(\mu\text{-}PPh_2)$ and $Ru_4(CO)_8(\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)(Ph_2PC{\equiv}CBu^t)(\mu\text{-}PPh_2)_2$.

TABLE III

PARAMETERS IN CLUSTERS CONTAINING LIGANDS WHICH DISPLAY BONDING MODE M5[a]

Compound	a (Å)	b (Å)	c (Å)	d (Å)	e (Å)	γ (degrees)	δ (degrees)	μ (degrees)	Reference
$Os_3H(CO)_{10}(HC{=}CH_2)$	2.845(2)	2.107(3)	2.273(3)	2.362(3)	1.396(4)	113.9(3)	121.0(4)	121.6(3)	*388*
$Os_4H_3(CO)_{11}(HC{=}CHPh)$	2.830(3)	2.15(1)	2.15(1)	2.30(1)	1.36(2)	113(1)	122(1)	122(1)	*186*
$Os_3H(CO)_{10}(HC{=}CHEt)$	2.834(1)	2.15(2)	2.28(2)	2.46(3)	1.40(3)	—	121(4)	—	*413*
$Os_3H(CO)_{10}(HC{=}CHBu^t)$	2.814(2)	2.10(2)	2.27(2)	2.43(2)	1.38(4)	—	122(2)	—	*52*
$Os_3H(CO)_{10}(PhC{=}CHPh)$	2.820(3)	2.11(4)	2.34(4)	2.44(4)	1.40(5)	117(3)	131(3)	—	*91*
$Os_3H(CO)_{11}(PEt_3)$ $(F_3CC{=}CCF_3)$	2.848(2)	2.16(3)	2.24(3)	2.20(3)	1.41(4)	—	—	—	*414*
$FeCo_3(CO)_9(PhC{=}CHPh)$ (PhC_2Ph)	2.369(4)	1.98(1)	2.00(1)	2.13(1)	1.42(2)	121(1)	126(1)	—	*195*
$Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})$ (C_8H_{10})	2.665(2)	2.02(3)	2.18(3)	2.29(4)	1.51(5)	—	—	—	*192*

[a] Parameters refer to:



In all the complexes the vinylic C–C distances indicate a formal bond order of less than two, consistent with π donation to the cluster. For the six compounds which also contain a hydrido bridge the complexes may be considered as derived from the interaction of a nonhydrido cluster with an alkene HRC=CR′R″, with resultant migration of an alkene hydrogen to the cluster cage. The orientation of the stilbenyl ligand in $Os_3H(CO)_{10}(PhC{=}CHPh)$ (*91*) differs from that in the vinyl complexes where the hydrogen atom on the α carbon of the ligand is syn with respect to the σ-bonded Os atom. The phenyl substituent on the α carbon is anti with respect to the same metal atom. Therefore, in the vinyl derivatives with the α carbon bridging one side of the metal triangle, the β carbon points outside the triangle, whereas in the stilbenyl derivative (*91*), the β carbon points inside the triangle. This is not the case with the "butterfly" cluster $FeCo_3(CO)_9(PhC{=}CHPh)(PhCCPh)$ (*195*), in which the stilbenyl group adopts the same orientation with respect to the $FeCo_2$ face as the vinyl.

The molecule $Ru_3(CO)_7[(CCBu^t)(PhC{=}CHPh)](PhCCPh)$ (*141*) contains a stilbenyl ligand related to that just described, except that the group is σ bonded to a C atom of the $CCBu^t$ group rather than a metal; this C–C distance is 1.45(2) Å. A *t*-butylacetylene derivative is also known (*46*).

For alkyne-derived ligands the only other type of coordination involving only two metal centers in a cluster is mode M15. Here the ligand bridges a metal–metal vector by forming a σ bond to each metal, and formally acts as a two-electron donor. This alkyne-derived ligand closely resembles an alkene with two cis substituents replaced by metal atoms. The bonding arrangement has been observed in the planar cluster $Ir_4(CO)_8[C_2(COOMe)_2]_4$ (*205*), whose structure is illustrated in Fig. 24. The acetylenic C atoms of the M15 bonded ligands lie in the Ir_4 plane with the C–C bond parallel to the bridged Ir–Ir bonds. The acetylenic C–C bond lengths of 1.28(1) Å suggests a relatively high bond order, and the bridged Ir–Ir bonds, at 2.715(1) Å, are shorter than the other two Ir–Ir bonds [2.810(1) Å]. The cluster is a 64-electron complex and the planar metal arrangement is consistent with this electron count. The complex also contains two M16 bonded ligands.

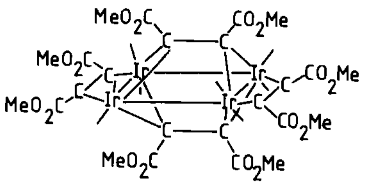


FIG. 24. Structure of $Ir_4(CO)_8[C_2(COOMe)_2]_4$.

2. *Interactions of Alkyne Ligands with Three Metal Centers*

There are more examples of alkyne-derived ligands interacting with a triangle of metal atoms in a cluster than with any other metal arrangement. The triangles may be held together by direct metal–metal interactions or there may be relatively little bonding between them, and the nuclearity of the cluster containing the alkyne-capped unit may range from three to seven.

The first of these bonding modes is denoted M6 and is illustrated in Fig. 15. In this case the alkyne bonds to two different metal atoms via σ bonds, one from each acetylenic carbon, and to the third metal via a π bond. It is generally considered to donate four electrons to the cluster. This mode of bonding causes the acetylenic C–C bond to lie approximately parallel to an edge of the metal triangle, and for this reason it is often given the notation μ_3-(η^2-$\|$) when the ligand arrangement is discussed.

The mode M6 has been reported in a variety of homo- and heteronuclear clusters and is one of the most common modes to have been observed. Both mono- and disubstituted alkynes adopt this geometry and the hydrogen is not transferred to the cluster framework. Not only is this geometry found in simple alkyne-substituted clusters but the coordinated ligand may form part of a cyclodienyl or aromatic ring system, such as in $Ru_3(\mu\text{-}H)_2(CO)_9(C_8H_{12})$ (*415*) or $Os_3(\mu\text{-}H)_2(CO)_9(C_6H_4)$ (*416*). Table IV lists a number of the structurally characterized clusters of this general type together with some relevant bond lengths. The structures of a few examples of complexes exhibiting this bonding mode are illustrated in Fig. 25. A number of trends are evident from these results. The acetylenic C–C bond lengths lie in the range 1.33–1.47 Å, which suggests that the formal bond order is less than two. The two acetylenic carbons and their substituent atoms remain approximately planar in all the complexes despite the asymmetry of the coordination of the alkyne, which may in some cases be attributed to the heterometallic character of the triangle which it caps. As expected, in general, the metal–carbon σ bonds are slightly shorter than the metal–carbon π bonds. It is interesting to note that in a number of the homonuclear clusters, where there are no other groups bridging metal–metal vectors, one of the metal–metal bonds involving the unique metal atom is particularly short. This suggests that the coordination of the alkyne is placing electrons in an orbital which is strongly bonding between this pair of metal atoms.

The bonding mode M7 may be considered as derived from M6 by a shift of one of the substituent groups so that both are coordinated to the

TABLE IV

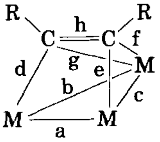
BOND LENGTHS IN μ_3-(η^2-$\|$)-ALKYNE SUBSTITUTED CLUSTERS

Compound	Bond lengths (Å)[a]				Ref.
	a	b	c	h	
	d	e	f	g	
$Cp_3Rh_3(CO)(PhCCPh)$	2.674(1)	2.655(1)	2.638(1)	1.39(1)	*59*
	2.022(8)	2.040(7)	2.110(7)	2.154(8)	
$Cp_3Rh_3(CO)[(C_6F_5)CC(C_6F_5)$	2.672(1)	2.599(2)	2.588(1)	1.41(2)	*59*
	2.03(1)	2.02(1)	2.09(1)	2.09(1)	
$Fe_3(CO)_8(PhCCPh)_2$[b]	2.469(5)	2.457(5)	2.592(5)	1.39(3)	*27*
	2.04(2)	2.06(2)	1.98(2)	1.97(2)	
$Ru_3(CO)_7[(C_2Bu^t)(PhC_2HPh)$	2.839(5)	2.682(7)	2.812(3)	1.37(2)	*141*
$[(PhCCPh)$	2.33(2)	2.07(2)	2.10(2)	2.21(2)	
$Ru_3H_2(CO)_8(HCCC_6H_4PPh_2)$	3.021(1)	2.874(1)	2.731(1)	—	*106*
	2.098(7)	2.085(6)	2.262(7)	2.289(7)	
$Ru_3H(CO)_9(PPh_2)(PhCCPh)$	3.838(1)	2.813(1)	2.908(1)	1.415(11)	*104*
	2.118(8)	2.168(7)	2.274(7)	2.341(8)	
$Os_3(CO)_{10}(PhCCPh)$	2.888(1)	2.844(1)	2.711(1)	1.44(1)	*417*
	2.182(8)	2.070(9)	2.188(8)	2.293(9)	
$Os_3(CO)_7(C_2Ph_2)_2(PhC_2Ph)$	2.680(2)	2.814(2)	2.744(2)	1.33(3)	*34*
	2.16(2)	2.08(2)	2.22(2)	2.28(2)	
$Os_3(CO)_9(CH_2)(PhCCPh)$	2.763(1)	2.765(1)	2.738(1)	1.37(3)	*418*
	2.13(2)	2.14(2)	2.27(2)	2.28(2)	
$Os_3H(CO)_9(HCCPMe_2Ph)$	2.980(1)	2.795(1)	2.766(1)	1.41(2)	*411*
	2.13(1)	2.06(2)	2.27(2)	2.25(2)	
$Os_3H(CO)_9(MeCCCH_2PMe_2Ph)$	2.987(1)	2.749(1)	2.761(1)	1.42(3)	*411*
	2.13(2)	2.13(2)	2.25(2)	2.29(2)	
$Ni_3(CO)_3(C_8H_8)(F_3CCCCF_3)$	2.703(2)	2.458(2)	2.458(2)	1.38(1)	*365*
	1.901(8)	1.895(9)	—	—	
$MnFe_2(CO)_8Cp(HCCCOOMe)$	2.679(1)	2.561(1)	2.577(1)	1.362(4)	*152*
	1.973(3)	1.967(3)	2.063(3)	2.094(3)	
$NiFe_2(CO)_6Cp(PhCCPh)^-$	2.474(1)	2.453(1)	2.506(1)	1.383(7)	*135*
	1.918(5)	1.970(5)	2.014(5)	2.104(6)	
$FeCo_2(CO)_9(EtCCEt)$	2.576(1)	2.479(1)	2.489(1)	1.37(1)	*56*
	1.961(6)	1.957(6)	2.047(6)	2.035(7)	
$NiCoFe(CO)_5Cp(PPh_3)(PhCCPh)$	2.486(4)	2.467(4)	2.390(4)	—	*148*
	1.93(2)	2.03(2)	—	—	
$NiFeMo(CO)_5Cp_2(PhCCCO_2C_3H_7)$[c]					*419*
$NiFeCo(CO)_6Cp(PhCCCO_2C_3H_7)$[c]					*419*
$Ni_2Fe(CO)_3Cp_2(PhCCCO_2C_3H_7)$[c]					*419*
$Co_2Ru(CO)_9(HCCMe)$	2.699(1)	2.591(2)	2.459(2)	1.34(1)	*57*
	—	—	—	—	
$Co_2Ru(CO)_9(PhCCPh)$	2.688(1)	2.587(1)	2.454(1)	1.370(3)	*199*
	2.124(2)	1.976(2)	2.080(2)	2.072(2)	
$Ru_2Ni(CO)_4Cp_2(PhCCPh)$	2.553(2)	2.550(3)	2.712(3)	1.383(7)	*136*
	1.926(5)	2.075(5)	2.148(6)	2.091(7)	
$OsW_2(CO)_7Cp_2(TolCCTol)$[d]	3.159(2)	2.863(2)	2.839(2)	1.47(3)	*166*
	2.117(19)	2.111(24)	2.320(20)	2.306(21)	

TABLE IV (*Continued*)

	Bond lengths (Å)[a]				
	a	b	c	h	
Compound	d	e	f	g	Ref.
Two isomers	2.981(2)	2.981(2)	3.017(2)	1.43(3)	
	2.198(18)	2.052(20)	2.208(21)	2.304(18)	
$OsW_2(CO)_7Cp_2(TolCCTol)$[d]	3.158(1)	2.857(1)	2.836(1)	1.46(3)	*162*
	2.187(18)	2.180(20)	2.229(19)	2.268(19)	
Two isomers	2.987(1)	2.817(1)	3.016(1)	1.42(3)	
(separate determinations)	2.202(18)	2.090(21)	2.284(21)	2.365(19)	
$OsPt_2(CO)_5(PPh_3)_2(MeCCMe)$	3.033(2)	2.662(2)	2.662(2)	1.40(1)	*203*
	2.060(8)	2.055(7)	2.22(1)	2.23(1)	
$Os_3WH(CO)_{10}(TolCCTol)$	2.922(3)	2.823(3)	2.775(3)	—	*201*
	2.21(5)	2.17(4)	2.18(4)	2.13(4)	
$Os_5(CO)_{17}(HCCH)$	2.957(3)	2.908(3)	2.715(3)	1.39(4)	*227*
	2.23(3)	2.09(3)	2.13(3)	2.29(3)	
$Os_5(CO)_{13}(PhCCPh)_2$	2.664(2)	2.768(2)	2.747(2)	1.39(4)	*224*
	2.09(2)	2.15(2)	2.21(2)	2.24(2)	
$Os_6(CO)_{16}(MeCCEt)$	2.817(2)	2.780(2)	2.769(2)	1.35(6)	*230*
	2.25(4)	2.16(4)	2.25(4)	2.09(5)	

[a] Bond lengths refer to the following structure:

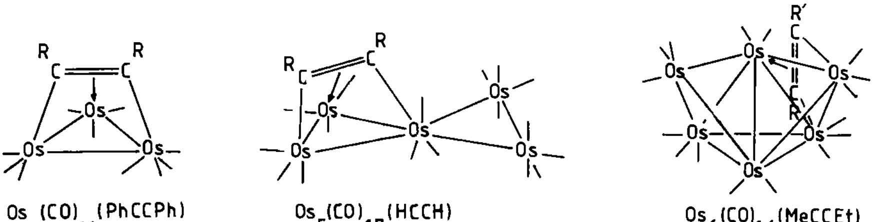


[b] Values averaged over two alkynes in the same cluster.

[c] Bond parameters not available.

[d] Two independent determinations of the same structure.

same acetylenic carbon atom. The α carbon of the alkyne-derived ligand then bonds to two metal atoms via σ interactions, and the unsaturated C–C bond formally donates a pair of electrons to a third metal atom via a π interaction. This type of coordinated ligand has been characterized spectroscopically in a variety of complexes (*420*) but there have been a relatively small number of crystal structures showing this feature. Four examples are $Os_3H_2(CO)_9(C{=}CH_2)$ (*66*), $Co_2Ru(CO)_9(C{=}CHMe)$ (*57*)



$Os_3(CO)_{10}(PhCCPh)$ $Os_5(CO)_{17}(HCCH)$ $Os_6(CO)_{16}(MeCCEt)$

FIG. 25. Structures of clusters containing μ_3-(η^2-||)-alkyne ligands.

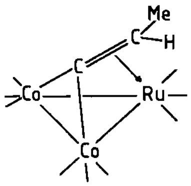


FIG. 26. Structure of $Co_2Ru(CO)_9(C{=}CHMe)$.

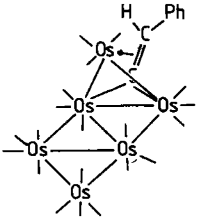


FIG. 27. Structure of $Os_6(CO)_{20}(C{=}CHPh)$.

(Fig. 26), $Os_6(CO)_{20}(C{=}CHPh)$ (*231*) (Fig. 27), and $Ru_3(CO)_9(AuPPh_3)_2$ $(C{=}CHBu^t)$ (*15*). In these structures the acetylenic C–C bond lengths lie in the range 1.32–1.42 Å, and the metal–carbon σ bonds are slightly shorter than the π interactions. The C=CHR plane lies approximately parallel to the capped metal triangle, and the C–C–R angles show only small deviations from the expected angle of 120° for an sp^2-hybridized carbon atom.

The ligands which adopt bonding mode M8 are best considered as acetylides. They formally donate five electrons to the metal framework via one σ and two π bonds. The orientation of the C–C multiple bond is approximately perpendicular to one side of the capped triangle and is often described by the notation μ_3-(η^2-$\perp$). Some examples of clusters containing this mode of coordination are listed in Table V together with

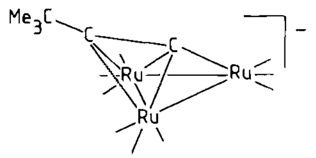


FIG. 28. Structure of the anion $[Ru_3(CO)_9(C{\equiv}CBu^t)]^-$.

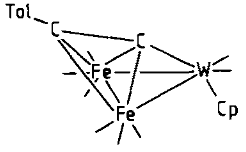


FIG. 29. Structure of $CpWFe_2(CO)_6(C{\equiv}CTol)$.

some relevant bond distances. Two examples of these clusters are illustrated in Figs. 28 and 29. Despite the high formal donation of electrons to the cluster from the unsaturated C–C bond, these bond lengths remain relatively short, lying in the range 1.27–1.32 Å, in comparison with distances in complexes having ligands which adopt bonding modes M6 and M7. As in related clusters the metal–carbon σ bond is significantly shorter than the π distances, and in this case the distances to the β carbon atom are longer than the distances to the α carbon atom. This generally results in the unsaturated C–C bond leaning away from the netal triangle which it caps. The average acetylide C–C–R angle of 140° in these complexes is significantly greater than the equivalent angle in ligands which adopt the related mode M7. This is consistent with a different formal hybridization on the β carbon atom.

There are four clusters which contain the related μ_3-(η^2-$\perp$)-alkyne ligand in which the alkyne-derived ligand is coordinated to a metal triangle via one σ and two π bonds (bonding mode M9). In the complexes $Fe_3(CO)_9(PhCCPh)$ (*26*) (Fig. 30), $Ni_4(NCBu^t)_4(PhCCPh)_3$ (*424*), $Ni_4(CO)_4(CF_3CCCF_3)_3$ (*365*), and $Cp_2W_2Fe(CO)_6(MeC_6H_4CCC_6H_4Me)$ (*166*), the acetylenic C–C bonds range from 1.27 to 1.41 Å, but, in

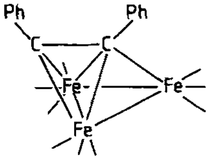


FIG. 30. Structure of $Fe_3(CO)_9(PhC{\equiv}CPh)$.

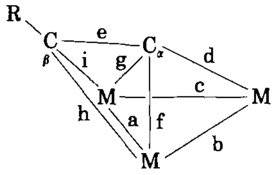
TABLE V

Bond Lengths in μ_3-(η^2-$\perp$)-Alkyne Substituted Clusters

	Bond lengths (Å)^a					
	a	b	c	d	e	
Compound	f	g	h	i		Reference
$\mathrm{CpFe_3(CO)_7(C{\equiv}CPh)}$	2.524(1)	2.632(1)	2.639(1)	1.829(6)	1.299(9)	*421*
	2.040(4)	2.081(5)	2.006(5)	2.031(5)		
$\mathrm{Ru_3H(CO)_9(C{\equiv}CBu^t)}$	2.792(3)	2.795(3)	2.799(3)	1.947(3)	1.315(3)	*387*
	2.207(3)	2.214(3)	2.268(3)	2.271(3)		
$\mathrm{Ru_3(CO)_9Cl(C{\equiv}CPh)}$	3.277(4)	2.805(5)	2.815(5)	1.95(2)	1.29(3)	*108*
	2.25(2)	2.30(2)	2.32(2)	2.28(2)		
$\mathrm{[Ru_3(CO)_9(C{\equiv}CBu^t)]^-}$	2.665(3)	2.790(3)	2.800(3)	1.95(2)	1.27(3)	*422*
	2.18(2)	2.16(2)	2.24(2)	2.24(2)		
$\mathrm{Ru_3H(CO)_8(PPh_2OEt)(C{\equiv}CBu^t)}$	2.7988(5)	2.8212(4)	2.8407(5)	1.946(4)	1.320(6)	*114*
	2.209(4)	2.194(4)	2.243(4)	2.252(4)		
$\mathrm{Ru_3(CO)_9(PPh_2)(C{\equiv}CPr^i)}$	3.466(1)	av. 2.839		—	1.284(8)	*130*
	—	—	—	—		

$Os_3(CO)_9(PPh_2)(C{\equiv}CPr^i)$	3.508(1)	av. 2.879		—	1.28(1)	*130*
	—	—	—	—		
$Ru_3(CO)_8(PPh_2)(C{\equiv}CBu^t)$	2.8257(4)	2.8151(4)	2.7084(4)	—	—	*130*
	—	—	—	—		
$Os_3H(CO)_9(C{\equiv}CCF_3)$	2.828(1)	2.872(1)	2.874(1)	2.179(10)	1.331(13)	*423*
	2.262(10)	2.271(10)	2.179(10)	2.181(9)		
$[Ru_3(CO)_9(C{\equiv}CBu^t)(HgBr)]_2$	2.900(3)	2.813(3)	2.806(2)	1.96(2)	1.31(3)	*146*
	2.19(2)	2.20(2)	2.25(2)	2.26(2)		
$Ru_3H(CO)_9[CCC(CH_2)Ph]$	2.791(2)	2.810(2)	2.812(2)	1.904(14)	1.27(2)	*119*
	2.18(2)	2.19(2)	2.19(1)	2.28(1)		
$CpNiFe_2(CO)_6(C{\equiv}CBu^t)$	2.378(3)	2.564(3)	2.610(3)	1.813(10)	1.28(1)	*134*
	2.010(10)	1.929(10)	2.060(10)	2.034(10)		
$CpWFe_2(CO)_8(C{\equiv}CTol)$	2.503(3)	2.874(3)	2.897(2)	1.999(15)	1.30(2)	*426*
	2.025(11)	2.011(11)	2.091(13)	2.086(12)		

[a] Bond lengths refer to the following structure:



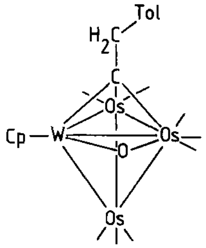


FIG. 31. Structure of $CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$.

contrast to compounds containing ligands which exhibit bonding mode M8, the metal–carbon π interactions are shorter than or similar in length to the metal–carbon σ bonds.

Clusters which contain ligands that adopt bonding mode M10 are closely related to the capped alkylidyne clusters which have been structurally reviewed elsewhere (*16, 17*). There are, however, three complexes in which the β carbon atom carries two hydrogen and an organic group, and may be considered as derived from an alkyne without fragmentation of the acetylenic C–C bond. In $Ru_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCH_2Bu^t)$ (*425*), the Ru–C(α) distances show slight asymmetry [2.091(5)–2.116(5) Å], and the C(α)–C(β) bond length of 1.525(9) Å indicates a reduction in the formal bond order to close to unity. Similar trends are observed in $CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3CCH_2Tol)$, shown in Fig. 31, where the metal–carbon(α) distances are W–C 2.030(12), Os–C 2.100(10) and 2.291(12) Å (*427*), and in $Ru_5(CO)_{12}(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)(\mu_3\text{-}CH_2Pr^i)$ (*428*).

It is interesting to note the change in angle between the capped metal triangle and the unsaturated C–C bond vector as the mode of coordination of the organic group to the cluster changes. For example, the C–C bond in M7 type clusters is approximately parallel to the plane of the triangle. In M8 type clusters the β carbon is significantly further from the triangle than the α carbon but remains bonded to it. In M10 type clusters the C–C vector is approximately perpendicular to the plane of the triangle. This progressive change of orientation of the organic ligand may perhaps reflect steps in a reaction pathway which could be related to the catalytic adsorption of alkyne ligands on a metal surface.

3. *Interactions of Alkyne Ligands with Four-Metal Centers*

There are now quite a number of examples of alkyne-derived ligands interacting with four-metal centers. It is sterically difficult for an alkyne to interact with all four metal atoms of a closed tetrahedral arrangement, but it is possible for an alkyne to interact with an open "butterfly" cluster or with a planar rectangle of metal atoms. In terms of formal electron counting a closed tetrahedron is normally associated with 60 electrons, a "butterfly" arrangement with 62 electrons, and a rectangular arrangement with 64 electrons. As with trinuclear clusters, while the alkyne, in this case, interacts with four metal atoms, the nuclearity of the cluster may be higher, and examples with five or six metals are known.

The bonding mode M11, in which the acetylenic C≡C bond lies approximately parallel to the "hinge" metal–metal bond of the "butterfly" to give a distorted M_4C_2 octahedron, is one of the most commonly observed modes for tetrametal clusters. This view of the cluster core as an octahedron allows the structures of these complexes to be rationalized in terms of Wade's Rules (*400*). The alkyne is coordinated to the two "hinge" metal atoms via what may be considered as σ bonds, and to the two "wingtip" metal atoms via π bonds. A number of clusters exhibiting this bonding mode are listed in Table VI together with some relevant structural parameters. It will be noted that the dihedral angle between the "wings" of the "butterfly" remains approximately constant despite the variations in metallic types and nuclearity of the clusters. The acetylenic C–C lengths in this group of compounds show considerable variations, ranging from 1.34(1) to 1.55(4) Å. However, the estimated standard deviations on $Os_4(CO)_{12}(HCCH)$ (Fig. 32) and $Os_4(CO)_{12}(HCCEt)$ (*67*) are rather high and a shorter distance would be more consistent with the other structures.

A related molecule to those listed in Table VI is $Ru_4(CO)_{11}(C_8H_{10})$ (*182*), in which one unsaturated bond of the octadiene occupies the capping site to make up the octahedron while the other π bonds to one Ru atom (Fig. 33).

The bonding mode M12 may be considered to be related to M7 except that the α carbon of the acetylide coordinates to three metal atoms rather than two. In both types the plane defined by the acetylide carbons and the two substituent atoms bonded to the β carbon is approximately

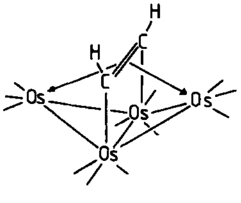


FIG. 32. Structure of $Os_4(CO)_{12}(HCCH)$.

TABLE VI

Structural Parameters in Alkyne-Substituted "Butterfly" Clusters Which Adopt Bonding Mode M11

	M–M bond lengths (Å)		Acetylenic	Dihedral	
Compound	av. Hinge–wingtip	Hinge–hinge	C–C length (Å)	angle (degrees)	Reference
$Co_4(CO)_{10}(EtCCEt)$	2.434	2.522	1.44	118	*207*
$Ru_4(CO)_{12}(MeCCMe)$	2.719	2.880(1)	1.45(1)	116.9	*60*
$Ru_4(CO)_{12}(PhCCPh)$	2.73	2.85(1)	1.46(2)	115.5	*40*
$Os_4(CO)_{12}(HCCH)$	2.793	2.847(2)	1.55(4)	—	*67*
$Os_4(CO)_{12}(HCCEt)$	2.756	2.849(2)	1.54(3)	—	*67*
$Os_5(CO)_{13}(PhCCPh)_2$	2.734	2.910(2)	1.46(3)	115	*224*
$Os_6(CO)_{16}C(MeCCMe)$	2.826	2.745(4)	1.36(2)	—	*229*
$FeRu_3(CO)_{12}(PhCCPh)$(1st isomer)	2.681[a]	2.780(1)	1.460(3)	112.7	*198*
$FeRu_3(CO)_{12}(PhCCPh)$(2nd isomer)	2.678[a]	2.849(1)	1.458(4)	117	*198*
$Ru_2Co_2(CO)_{11}(PhCCPh)$	2.595[a]	2.757(1)	1.432(5)	—	*196*
$RuCo_3(CO)_9(PPh_2)(HCCBu^t)$	2.505[a]	2.776(1)	1.424(5)	115.2	*221*
$[RuCo_3(CO)_{10}(PhCCPh)]^-$	2.505[a]	2.725(2)	1.34(1)	115.2	*199*
$FeCo_3(CO)_9[PhC_2(H)Ph](PhCCPh)$	2.432[a]	2.670(4)	1.41(2)	118	*195*
$Ru_4(CO)_{11}(HCCC_6H_4PPh_2)$	2.744	2.823(1)	1.455(11)	—	*429*

[a] Averaged M–M bond lengths in mixed-metal clusters.

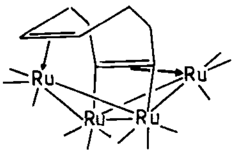
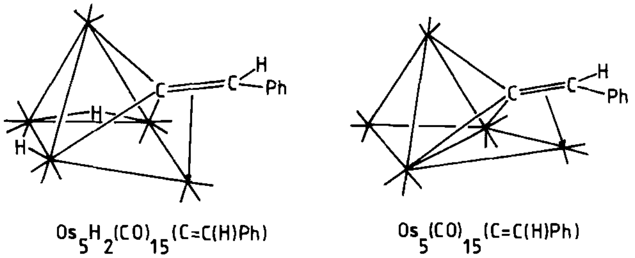


FIG. 33. Structure of $Ru_4(CO)_{11}(C_8H_{10})$.

parallel to that of the metal triangle over which it lies and with which there is an interaction. This type of ligand is considered to be a four-electron donor although the interaction with the three metal atoms that are capped by the α carbon must be delocalized. This mode of bonding is observed most frequently in mixed-metal clusters, and a number of examples of homo- and heterometal clusters are presented in Table VII. The acetylide C–C lengths in these clusters indicate a reduction in the formal bond order to less than two, and on average these distances are shorter than those found for ligands which adopt bonding mode M7. This suggests a greater donation to the metal framework in the former case. However, the most interesting feature of these compounds is the increase in dihedral angle of the "butterfly wings" and the lengthening of the two hinge metal atoms on the addition of two more electrons, thus indicating a progression toward a planar metal arrangement. Examples of the 74- and 76-electron complexes are shown in Fig. 34.

Related to bonding mode M12 is mode M13 where a ligand, best described as an acetylide, bonds to a "butterfly" metal framework by forming what may be considered σ bonds to one "hinge" and one "wingtip" metal atom and π bonds to the other two metal atoms. This mode of coordination has been observed in the pentanuclear mixed-metal cluster $NiRu_4(CO)_9(\mu\text{-}PPh_2)_2(C{\equiv}CPr^i)_2$ (*242*), in which the dihedral angle between the "wings" of the Ru_4 "butterfly" is only 95.6°,



$Os_5H_2(CO)_{15}(C{=}C(H)Ph)$ $Os_5(CO)_{15}(C{=}C(H)Ph)$

FIG. 34. Structures of $Os_5(CO)_{15}[C{=}C(H)Ph]$ and $Os_5H_2(CO)_{15}[C{=}C(H)Ph]$.

TABLE VII

ALKYNE-SUBSTITUTED CLUSTERS WHICH ADOPT BONDING MODE M12

Compound	Electron count	M–M Bond Lengths (Å) av. Wingtip–hinge	M–M Bond Lengths (Å) Hinge–hinge	C–C bond lengths (Å)	"Butterfly" dihedral angle (degrees)	Reference
$CpCo_3Fe(CO)_9(C{=}CH_2)$[a]	62	2.540	2.456(3)	1.431(12)	—	*285*
$CpRu_3Ni(CO)_9[C{=}C(H)Bu^t]$[a,b]	61	2.687	2.825(2)	1.436(13)	116.6	*215*
$CpRu_3Ni(CO)_9H[C{=}C(H)Pr^i]$[a]	62	2.692	2.843(1)	1.417(8)	118.3	*217*
$CpOs_3Ni(CO)_9H[C{=}C(H)Bu^t]$[a]	62	2.699	2.855(2)	1.44(3)	117.1	*211*
$Ru_4(CO)_{10}(OH)(PPh_2)[C{=}C(H)Pr^i]$	64	2.766	3.456(1)	1.415(2)	141.5	*131*
$Ru_4(CO)_{10}(OEt)(PPh_2)[C{=}C(H)Pr^i]$	64	2.758	3.455(1)	—	143.7	*131*
$Os_5H_2(CO)_{15}[C{=}C(H)Ph]$[c]	76	2.872	3.783(2)	1.49(3)	144.1	*224*
$Os_5(CO)_{15}[C{=}C(H)Ph]$	74	2.844	2.830(1)	1.51(3)	115.2	*231*

[a] Averaged mixed-metal bond lengths.

[b] Reformulated as $CpRu_3Ni(CO)_9H[C{=}C(H)Bu^t]$(*217*).

[c] Averaged over two independent molecules.

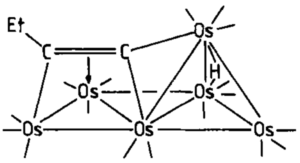


FIG. 35. Structure of $Os_6(\mu\text{-}H)(CO)_{17}(C{=}CEt)$.

and the two independent acetylenic C–C distances are 1.34(3) and 1.38(4) Å, respectively.

Another mode of coordination of an alkyne to four-metal centers which may be considered as derived from a "butterfly" geometry is bonding mode M14. In this case it is not the "hinge" bond which has lengthened to form a rectangular arrangement but a "hinge–wingtip" bond which results in a "spiked-triangular" array of metal atoms. This arrangement has been observed in several clusters which contain organic ligands derived from alkynes. These include $Cp_2Ni_2Ru_2(CO)_6[C_2(H)C({=}CH_2)CH_3]$ (*218*) and $Cp_2Ni_2Fe_2(CO)_6[C_2(H)C({=}CH_2)CH_3]$ (*213*). There is also one example of an alkyne-substituted cluster with this geometry, $Os_6(\mu\text{-}H)(CO)_{17}(CCEt)$ (*230*), shown in Fig. 35. The coordination of the alykne is reminiscient of bonding mode M6, except that one of the R groups has been replaced by a bond to a metal. The relevant C–C–Et and C–C–Os angles do not differ significantly from those in M6-bonded complexes.

In the context of these structures it is interesting to compare the geometries of alkynes bonded to metal clusters and those bound to metal surfaces. While the more common bonding modes such as M6 and M11 may represent models of acetylenes bonded to well-defined metal planes, the less common modes such as M14 and M19 may be representative of the type of bonding that occurs at dislocations on the metal surface.

Turning to modes of alkyne coordination where the metal arrangement is considered to be essentially planar, the structure of $Ir_4(CO)_8[C_2(COOMe)_2]_4$ (*205*) contains two alkyne ligands which exhibit bonding mode M16. The structure was shown in Fig. 24, and it is interesting to note that the acetylenic C–C bond lengths for the two tetracoordinated ligands are significantly longer [1.446(9) Å] than for the two edge-bridging alkynes [1.278(11) Å], which display bonding mode M15. This complex is a rare example of a cluster where the same ligand adopts two different bonding modes in the same molecule.

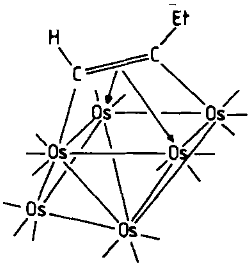


FIG. 36. Structure of $Os_6(CO)_{17}(HCCEt)$.

A number of tetra-, penta-, and hexanuclear clusters have been characterized, in which the alkyne-derived ligand adopts bonding mode M17. This mode may be considered a derivative of mode M11 in that addition of further electron pairs has lengthened the "butterfly hinge" bond and increased the dihedral angle to such an extent that the metal framework is approximately planar. In all these complexes there is a small tetrahedral distortion of the rectangle. The acetylenic C–C bond now lies across the diagonal of the rectangle and forms σ bonds to two opposite corners and π bonds with the other two. The structure of one such cluster, $Os_6(CO)_{17}(HCCEt)$ (*230*), is shown in Fig. 36. Some structural parameters for this type of complex are listed in Table VIII. The acetylenic C–C bond length lies in the range found for bonding mode M11 ligands (Table VI), and it is unlikely that the strength of electron donation to the cluster is substantially different.

Bonding mode M18 is found in the pentanuclear cluster $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(C{\equiv}CPh)$ (*431*), shown in Fig. 37. The alkyne-derived ligand which may be considered to be an acetylide is formally σ bonded to two adjacent Ru atoms of the rectangle and involved in a π interaction with the other two; the acetylide C–C bond length is 1.34(1) Å. The acetylide

TABLE VIII

STRUCTURAL PARAMETERS FOR CLUSTERS WHICH CONTAIN ALKYNE-DERIVED LIGANDS ADOPTING BONDING MODE M17

Compound	Average M–M bond length	Acetylenic C–C length	Reference
$Cp_2Ni_2Fe_2(CO)_6(EtCCEt)$[a]	2.420	1.43(2)	*210, 419*
$Ru_4(CO)_{11}(MeCCPh)_2$	2.786	1.40(1)	*430*
$Cp_2Ni_2Ru_3(CO)_8(PhCCPh)$[a]	2.570	1.41(1)	*431*
$Os_6(CO)_{17}(HCCEt)$	2.862	1.45(2)	*230*

[a] Averaged mixed-metal bond length.

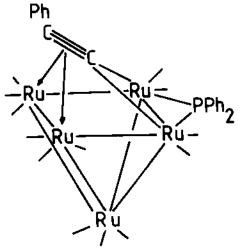


FIG. 37. Structure of $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(C{\equiv}CPh)$.

C–C–C(Ph) angle of 141.4(4)° is similar to the average value of 140° found for ligands that adopt the acetylide bonding mode M8.

As has been noted elsewhere (*17*) the environment of the α carbon atom of the acetylide type ligands such as those observed in bonding modes M8, M13, and M18 resembles, to an extent, that of a carbido carbon. As the nuclearity of the cluster with which the acetylene interacts increases, the similarity between the environments also increases. In the case of $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(C{\equiv}CPh)$ (*431*), the structure is closely related to the carbido complex $Ru_5C(CO)_{15}$ (*432*).

4. Interactions of Alkyne Ligands with Five-Metal Centers

There are two examples of alkyne-substituted clusters in which there is an interaction between the alkyne and five-metal centers. Both occurrences are found in the related pentanuclear ruthenium complexes $Ru_5(CO)_{14}(\mu\text{-}PPh_2)(C{\equiv}CPh)$ (*431*) and $Ru_5(CO)_{12}(\mu\text{-}PPh_2)(PhC{\equiv}CC{\equiv}CPh)(C{\equiv}CPh)$ (*104*). The ligand in the former complex (Fig. 38) adopts the bonding mode M19 in which the acetylide α carbon caps an Ru_3 triangle, while the β carbons forms a σ bond with a fourth Ru atom, and both acetylide carbons are involved in a π bond to a fifth metal. The acetylide C–C bond length is 1.39(1) Å, which is longer than the value observed in the cluster $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)$ (*431*), from which it is prepared. The C–C–C(Ph) angle is 123.6(4)°, which is similar to that of a coordinated alkyne and ca. 17° less than the

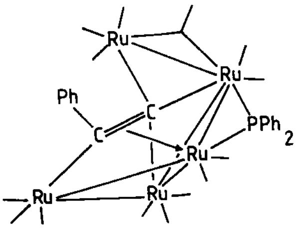


FIG. 38. Structure of $Ru_5(CO)_{14}(\mu\text{-}PPh_2)(C{\equiv}CPh)$.

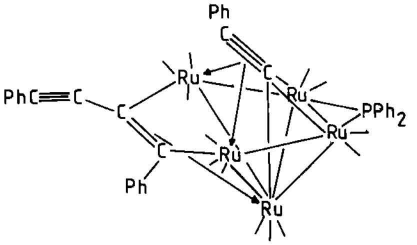


FIG. 39. Structure of $Ru_5(CO)_{12}(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(\mu_5\text{-}\eta^2\text{-}C{\equiv}CPh)$.

acetylide type angle observed in the precursor. The cluster may be considered as a 76-electron species, with the alkyne donating five electrons. The observed "double butterfly" metal framework, with eight formal Ru–Ru bonds, is then consistent with this count.

In the cluster $Ru_5(CO)_{12}(\mu\text{-}PPh_2)(PhC{\equiv}CC{\equiv}CPh)(C{\equiv}CPh)$ the α carbon atom of the alkyne caps three metal atoms and the acetylenic C–C bond donates π-electron density to the other two metal atoms. This mode of coordination is denoted M20, and the structure of the complex is illustrated in Fig. 39. The μ_5-C≡C bond length of 1.340(9) Å is shorter than that in $Ru_5(CO)_{14}(\mu\text{-}PPh_2)(\mu_5\text{-}\eta^2\text{-}C{\equiv}CPh)$ but similar to that found in the precursor $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)$. The μ_5-C≡C—C(Ph) angle is 131.6°. The cluster also contains a $\mu_3\text{-}\eta^2$-PhC≡CC≡CPh ligand which coordinates through one unsaturated C—C bond in bonding mode M6.

5. *Interactions between Clusters and Dicarbide Units*

Encapsulated dicarbide clusters of two types have been characterized. Those in which the carbon atoms remain within bonding distance of each other, and those in which the carbon atoms are well separated and occupy separate cavities of a closed metal polyhedron. The former type may be considered to contain an alkyne C–C unit from which all organic substituents have been removed. The closed polyhedral clusters $Rh_{12}(C_2)(CO)_{25}$ (*433*) and $[Co_{11}(C_2)(CO)_{22}]^{3-}$ (*434*), and the open "boat-shaped" cluster $Co_6(C_2)(CO)_{14}(S)$ (*435*), contain this unit. In $Rh_{12}(C_2)(CO)_{25}$ (*433*), the metals adopt a regular polyhedral geometry which may be described in terms of layer packing of atoms. The carbide carbon atoms occupy an irregular cavity with a C–C separation of 1.48(2) Å. There are 14 Rh–C contacts, 9 short and 5 long, with average values of 2.22 and 2.58 Å, respectively. In the anion $[Co_{11}(C_2)(CO)_{22}]^{3-}$ (*434*), the Co polyhedron may be described as a tricapped cube. The C–C separation is 1.62(5) Å, and the Co–C contacts lie in the range 1.86–

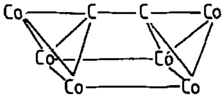


FIG. 40. Core geometry of $Co_6(\mu_6\text{-}C_2)(\mu\text{-}CO)_6(CO)_8(\mu_4\text{-}S)$.

2.37(3) Å. The peripheral dicarbide cluster $Co_6(C_2)(CO)_{14}(S)$ (*435*) contains a "boat" array of Co atoms, of which the four basal ones form an essentially regular square. The two apical Co atoms are connected through a Co–C–C–Co link; the C–C separation is 1.37(2) Å. These two carbon atoms are also bonded to the four basal Co atoms. The core geometry of the cluster is illustrated in Fig. 40.

V. Fluxionality in Solution

As was mentioned in Section III,C the majority of cluster carbonyls are fluxional molecules. Frequently the nature of the fluxional process is dependent on the temperature, and may involve a varying number of carbonyl groups and hydride ligands, if the latter are present. Examples of alkyne ligands themselves becoming involved in the fluxional processes, however, are comparatively rare. This may stem from the fact that when an alkyne coordinates to two, three, or four metal atoms, there is an extensive formal rehybridization of the carbon atomic orbitals in order to form relatively strong metal–carbon σ bonds. This contrasts with the case of an alkyne bonded to a single metal center. Facile migration would not be expected if terminal and bridging sites differ substantially in energy. Also, if the ligand is a two-electron donor in one coordination mode and a greater-than-two-electron donor in another, facile migration of this ligand is unlikely because of the electronic pertubation at the various metal centers produced in the transition states (*4*). This argument has been confirmed by the calculations by Hoffman *et al.* (*396*) on perpendicular and parallel orientations of alkynes in binuclear complexes, which show that interconversions between the modes require a relatively high activation energy.

However, ^1H and ^{13}C NMR studies on a number of alkyne-substituted clusters do show that the alkyne ligand is involved in fluxional processes. ^1H NMR experiments on a range of complexes indicate that a variety of dynamic processes involving hydrogens occur. These include rapid hydride exchange between bridging and terminal positions (*41*), rotation of the organic fragment bound to the cluster (*377*), and flipping of the alkyne or alkene (*128, 181*). A combination of these processes may take place in a single system (*436*). The observation of the relative rates of exchange in different dynamic processes taking place within a single molecule may help to discriminate between two possible structures in solution. An example where this has been helpful is in the elucidation of the structure of $Os_3H_2(CO)_9(C{=}CH_2)$ (*65*), in which the rate of exchange of the two vinylidene protons is faster than that of the two hydride ligands, and is consistent with the two latter ligands bridging different Os–Os bonds.

^{13}C NMR has been used to confirm the existence of fluxional processes involving the carbonyl ligands in polynuclear alkyne complexes (*40, 330, 339, 437*). It is apparent that in the limited number of complexes studied the nature of the dynamic processes is related to the modes of bonding of the organic group (*21, 438, 439*). It appears that the greater the number of ligands coordinated to a particular metal the higher is the energy barrier that has to be overcome before these ligands become fluxional. For example, in the molecule $Fe_3(CO)_8(PhCCPh)$, one $Fe(CO)_2$ unit does not participate in the CO scrambling, and this is believed to be connected with the high formal coordination number for that Fe atom (*440*).

^{13}C NMR may be used to establish the nature of exchange processes which involve the redistribution of σ and π bonds between the organic group and the metal atoms (*441*). Flipping (*20*) and rocking (*174*) of the coordinated organic group has also been observed, and in some cases enantiomerization of the cluster may be caused by rotation of the ligand about a molecular axis (*329*).

Combined ^1H and ^{13}C NMR studies indicate that several of the above-mentioned processes may occur simultaneously within a single molecule (*442–444*). In some instances the solvent appears to have an influence on which dynamic processes predominate under a particular set of conditions (*58*).

VI. The Reactivity of Alkyne-Substituted Clusters

The reactivity of clusters containing coordinated alkyne or alkyne-derived ligands has not been widely investigated. This review has indicated that quite a significant number of complexes of this type have now been synthesized, but it is important to remember that quite a large proportion of these clusters are obtained in relatively low yield, and it is perhaps this aspect that has hindered further research into their reaction chemistry. However, over the last several years, an increasing number of publications reporting the reactions of alkyne-substituted clusters have appeared. Common reagents that have been used to investigate the reactivity of these species include carbon monoxide, hydrogen, phosphines, and an excess of the alkynes themselves. These reaction types are discussed below.

A. PYROLYSIS REACTIONS

Thermal activation of alkyne-substituted clusters frequently results in the loss of one or more carbon monoxide ligands (*418, 445, 446*). Concomitant with this loss is an alteration in the bonding mode of the organic ligand in order to retain the electron balance within the molecule (*107*). Such a reaction is shown in Fig. 41, where an osmacyclopentadiene ring is transformed into a trisubstituted-η^5-cyclopentadienyl system. Metal–metal bond formation may take place in some examples (*446, 447*).

There have also been reports of cluster growth, from trinuclear to tetra- (*429*) or pentanuclear (*448*) complexes. However, in these two reactions it is important to note that the clusters involved contain functionalized alkynes. These phosphidoacetylenes show a considerable versatility in their modes of bonding. This is particularly true in the example illustrated in Fig. 42 where different reaction temperatures

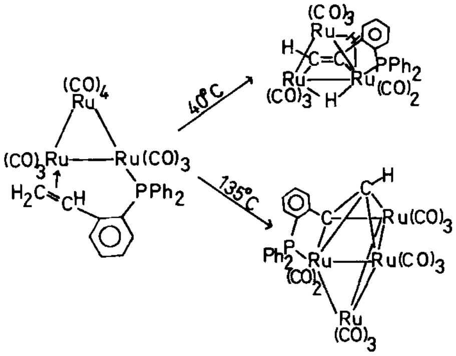


FIG. 41. Reactions of functionalized alkynes.

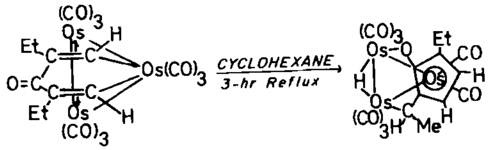


FIG. 42. Thermal activation of alkyne-substituted clusters.

lead to different coordination modes of the ligand and to different nuclearity of the resulting cluster.

Alkyne scission also occurs when a rhodium or iridium trimetallic cluster is heated under vacuum (*449*).

Photochemical activation of an allyl complex results in the loss of carbon monoxide, which leads to the formation of a coordinatively unsaturated species (*450*).

B. REACTIONS WITH CARBON MONOXIDE AND DIHYDROGEN

Carbonylation reactions may result in the modification of the coordination mode of the organic ligand (*407, 451–453*). This is sometimes caused by the transfer of hydrides bonded to the metal framework to the unsaturated organic fragment (*407, 452, 453*), as illustrated by Eq. (18).

$$\mathrm{Os_4H_3(CO)_{11}[HC{=}C(H)Me] + HCCH \longrightarrow Os_4H_2(CO)_{11}[\mu_1\text{-}\eta^3\text{-}CHCHC(H)Me]} \qquad (18)$$

Reaction with hydrogen may also result in the hydrogenation of the organic unit (*425*), but if an excess is used, the acetylenic ligand may be lost [Eq. (19)] (*425*). A similar process has been observed in the reactions of dinuclear species (*454*). The nature of the products obtained from the coordinated organic fragment in these reactions seems to depend on the extent of unsaturation in the cluster as a whole or in the organic group itself (*455*).

$$\mathrm{Ru_3H(CO)_9(CCBu^t) \xrightarrow{H_2} Ru_3H_3(CO)_9CCH_2Bu^t \xrightarrow{H_2} Ru_4H_4(CO)_{12} + MeCH_2Bu^t} \qquad (19)$$

C. REACTIONS WITH PROTIC ACIDS

Variable-temperature ^{1}H NMR studies of the reactions between alkyne-substituted clusters and protic acids indicate that protonation takes place initially at a metal center in the cluster framework with inter- and intramolecular hydride exchange. If a second protonation takes place, as happens in some cases, the site of the reaction is the organic ligand (*118, 456, 457*).

D. REACTIONS WITH PHOSPHINES AND PHOSPHITES

The reactions of alkyne-substituted clusters with trialkylphosphines or phosphites that have been reported can be divided into two groups. In one group the phosphine or phosphite forms a bond with one of the metal atoms, and in the second it adds to the ligand.

Examples of the first type of these reactions are found in several systems but the reaction mechanisms may follow different pathways. One route is substitution of one of the carbonyl ligands as has been observed in some osmium and ruthenium complexes (*458, 459*). The other mechanism involves metal–metal bond fission (*414, 428*), and in some cases this means the formation of cluster compounds with a smaller number of metal atoms [Eq. (20)] (*460*).

$$\mathrm{Cp_2Ni_2Fe_2(CO)_6(\mu_4\text{-}PhCCPh) + PR_3 \longrightarrow CpNi(PR_3)_2][CpNiFe_2(CO)_6(\mu_3\text{-}PhCCPh)]} \quad (20)$$

The addition of a phosphine group to the organic fragment has been studied in some detail in compounds with cluster-bound vinyl ligands. The zwitterionic adducts which are formed can then undergo nucleophilic addition reactions (*411, 461, 462*). A reaction of this type also occurs with amine-substituted alkynes coordinated to osmium and ruthenium complexes (*117*).

E. REACTIONS WITH ALKYNES

The reaction between clusters containing alkyne ligands and an excess of the same or a different alkyne, in most cases, result in the formation of new C–C bonds by combination of the new organic ligand with the previously coordinated one (*141, 147, 430, 463–466*). The mechanisms followed by these reactions are not known but the range of products obtained indicates that there are important differences in going from one reaction to another. While in some examples the complexes formed have two distinct, well-separated organic groups bonded to the metal framework (*430, 466*), in others metal–metal bond rupture occurs [Eq. (21)] (*465*).

$$\mathrm{Ru_3H(CO)_9(CCBu^t) + HCCPr^i \longrightarrow Ru_3(CO)_8(C_{16}H_{22})} \quad (21)$$

F. REACTIONS WITH OTHER METALLIC SPECIES

Reactions between alkyne-substituted clusters and other metallic species have been used frequently as synthetic routes to mixed-metal clusters, particularly for Ru–Ni (*214–217*), as exemplified by Eq. (22), and Ru–Fe (*220*) complexes. In all these reactions the new metallic group forms bonds with the organic unit and with the metallic framework. It is possible that the first step in these reactions is the coordination of the organic fragment to the incoming metallic unit, and this is followed by the formation of metal–metal bonds to the metals in the cluster cage. In some cases insertion of a metal–hydride bond into a metal acetylide linkage occurs (*467*).

$$\mathrm{Ru_3H(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPr^i) + [CpNi(CO)]_2 \longrightarrow CpNiRu_3H(CO)_9(\mu_4\text{-}\eta^2\text{-}C{=}CHPr^i)} \qquad (22)$$

There are syntheses where the new metallic species enhances a different type of reactivity. This has been observed in the reactions between alkyne-substituted ruthenium clusters and compounds of mercury (*145, 146*). In most of the characterized products a mercury atom or an HgX_2 (X = halogen) fragment serves as a bridge between two ruthenium cluster frameworks which retain the coordinated alkyne.

Carbon–carbon bond formation has been observed in the reaction of an alkyne-substituted osmiun cluster with manganese and rhenium

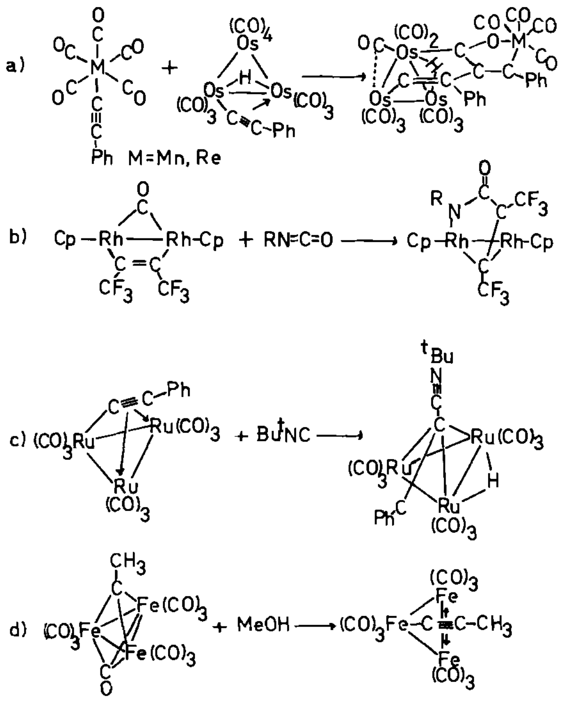


FIG. 43. Reactions of alkyne-substituted clusters with mononuclear complexes and other groups.

acetylides. The C–C bonds are formed by acetylide–alkyne and alkyne–CO couplings, and the manganese or rhenium atom does not form direct metal–metal bonds with the osmium atoms (Fig. 43a) (*375*).

G. OTHER REACTIONS

Coordinated alkyne and alkylidyne groups can form new C–C bonds by reactions with other compounds such as isocyanates (*468*), isocyanides (*469*), or by a reduction mechanism (*470*) (Fig. 43).

Other reactions of alkyne-substituted clusters include those in which parts of the complex other than the organic ligand itself are modified. However, the bonding mode of the latter may also be altered because of the new electronic requirements of the metallic cage. This occurs in some deprotonation reactions with OH^- (*422*), $[Me_3O]^+$ (*423*), or by nucleophilic attack of a halide (*406, 408*). Fragmentation and recombination of the metal framework in $Ru_3(CO)_{11}(Ph_2PC{\equiv}CPr^i)$ in the presence of water result in the formation of a tetranuclear complex which contains a face-bridging hydroxo group (*131*).

Recently, a series of triruthenium clusters containing allenyl or alkynyl ligands have been investigated electrochemically, and two, subsequent one-electron reduction steps have been observed (*471*). Further studies of this kind should provide a new insight into the electronic processes which take place in alkyne-substituted cluster systems.

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