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Organometallic chemistry of hexanuclear carbonyl clusters*

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CONTENTS

ABSTRACT

Aspects of the synthesis, structures, and reactivity of hexanuclear metal carbonyl clusters that contain hydrocarbyl fragments as ligands are reviewed.

The synthesis of these compounds includes a wide range of techniques, but most rely on the production of reactive metal fragments which then aggregate into larger clusters. Typical methods include the treatment of metal carbonyls with a base, with heat, or both. These methods tend to lead to a range of product nuclearities, although in many cases the conditions can be optimized for a particular cluster. More rational syntheses, by ligand mediation in the coupling of smaller clusters or by capping reactions, are rarer, and they rely on the availability of suitable precursor compounds.

The structures of most hexanuclear metal complexes can be predicted by electron counting and application of the Wade–Mingos rules for cluster bonding. The commonest structures are the regular octahedron, the bicapped tetrahedron, and the trigonal prism, though less symmetrical and more open clusters are also known.

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* Dedicated to the memory of John C. Bailar, Jr., role-model, colleague, and friend.

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The reactivity of these clusters with organic fragments is reviewed according to the transition element. Specific reactions with alkenes, alkynes, and aromatic compounds are described and compared where possible. The most abundant information is available for ruthenium and osmium clusters. Ruthenium compounds tend to give products which retain the cluster geometry and have less bond activation in the ligands. Osmium compounds, in contrast, tend to lead to products with open geometries and a high degree of bond activation. The hexanuclear clusters of other transition elements are rarer, but examples involving rhodium, iridium, and rhenium are all described. The few compounds reported, however, allow no general conclusions to be drawn.

A growing area of interest has been heterometallic cluster compounds, and a variety of systems are described, including molybdenum–, cobalt–, and platinum–ruthenium, and osmium–platinum systems.

1. INTRODUCTION

Recent studies of transition metal carbonyl clusters have focused to an increasing degree on the chemistry of intermediate- to high-nuclearity clusters [1–5]. The synthesis and structural characterization of larger clusters has been developing steadily; the largest carbonyl-ligated cluster currently established is a mixed-metal compound with nuclearity of 44, i.e. $[Ni_{38}Pt_6(CO)_{48}H_2]^{4-}$ [6]. However, fundamental questions about the organometallic chemistry of known higher-nuclearity clusters have been much less addressed. Given that one of the driving forces for examining the chemistry of clusters is their potential as model systems for ligand adsorption and transformations on metal surfaces [7], it is important that the reactions of higher-nuclearity carbonyl clusters with hydrocarbon substrates be thoroughly examined.

In this article, the synthesis, structures, and reactivity of hexanuclear metal carbonyl clusters containing hydrocarbyl groups will be surveyed. Our attention will be focused on the transformations occurring in the cluster metal frameworks, as much less is known about the fate of the organic moieties after coordination. The survey is limited to hexanuclear clusters for three reasons: (1) hexanuclear compounds represent the first step across the threshold separating localized from delocalized bonding, in that one of the first applications of skeletal bonding models was to explain the deviation of octahedral clusters from "normal", i.e. localized 18-electron bonding models [2]; (2) by far the most information concerning organometallic derivatives is available for hexanuclear compounds at the present time; and (3) the structural motif of the octahedron, which represents the first known and most common structure for hexanuclear clusters, also represents the typical coordination shell of hexacoordinate mononuclear transition metal complexes, a topic that occupied the attention of John C. Bailar, Jr. throughout his research career [8].

2. GENERAL ASPECTS OF STRUCTURE, SYNTHESIS, AND REACTIVITY

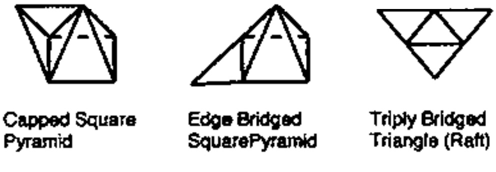
The entire range of structures displayed by hexanuclear cluster frameworks, with examples, has been reviewed [9]. The specific structures are generally consistent with the predictions based on Wade–Mingos skeletal electron pair bonding considerations. Thus, the octahedron is found for seven bonding pairs, the bicapped tetrahedron for six pairs, and the trigonal prism for nine pairs. Other, less symmetrical frameworks also occur for appropriate electron counts, such as face-capped and edge-bridged square pyramids and triply edge-bridged planar triangular arrays (see Scheme 1). Cases that do not obey the electron counting rules generally involve platinum centers; clusters that incorporate platinum atoms have been reviewed [10].

General strategies for cluster synthesis have also been reviewed recently [11]. In the particular context of constructing hexanuclear frameworks there are four distinguishable procedures that are worth highlighting. These are (a) pyrolysis of smaller carbonyl compounds; (b) reductive treatment of carbonyl precursors; (c) "capping" of preformed pentanuclear clusters; and (d) ligand-mediated coupling of trinuclear or smaller units.

Pyrolysis of a carbonyl precursor depends on the formation of small, reactive fragments, which aggregate into larger structures at a rate that is competitive with the ultimate aggregation into bulk metal. Perhaps the most notable example in this category is the pyrolysis of $Os_3(CO)_{12}$ without solvent in a sealed tube to give $Os_6(CO)_{18}$ as one component of a complex mixture of cluster products [12]. However, conditions can be optimized to give $Os_6(CO)_{18}$ in yields of 50–60% together with smaller amounts of other neutral products of nuclearity from Os_5 to Os_8 [13]. It is not clear whether the preponderance of the Os_6 product is due to dimerization of an Os_3 intermediate or to favored thermal stability under the reaction conditions.

Activation of metal carbonyls under reducing conditions has links back to Hieber's pioneering development of metal carbonyl chemistry. In many cases, such reactions tend to be more readily controlled than direct pyrolysis, since it is possible to vary the stoichiometric amounts of the reductant added as well as the temperature. It is likely that most of these reactions proceed by the process termed "redox condensation" by Chini et al. [14], in which a more highly reduced species interacts with a less highly reduced species to form a new metal–metal bonded aggregate (generally after carbonyl loss) with a charge-to-metal ratio at an intermediate level.

Bicapped Tetrahedron   Octahedron   Trigonal Prism



Capped Square Pyramid   Edge Bridged SquarePyramid   Triply Bridged Triangle (Raft)

Scheme 1. Some common structural types found in hexanuclear clusters.

Notable examples of hexanuclear compounds produced in this way include the synthesis of $[Ni_6(CO)_{12}]^{2-}$ by treatment of $Ni(CO)_4$ with $NaBH_4$ [15], the formation of $[Ir_6(CO)_{16}]^{2-}$ from $[Ir(CO)_4]^-$ and $Ir_4(CO)_{12}$ [16], and the synthesis of $[Ru_6C(CO)_{16}]^{2-}$ from $Ru_3(CO)_{12}$ by using either $[Mn(CO)_5]^-$ [17] or sodium dispersion [18] as reducing agents.

The reaction of a metal complex fragment with a preformed pentanuclear cluster to give a sixth vertex ("capping") is certainly a rational way to form a hexanuclear cluster, but it is really only useful if the pentanuclear cluster itself is relatively accessible synthetically. Furthermore, the new fragment will form a stable adduct only if the face that is capped is sufficiently electron-rich to form adequate metal–metal bonds and is not hindered by steric interactions. A seminal, very successful example is the demonstration by Muetterties and co-workers that $[Fe_5C(CO)_{14}]^{2-}$ can be capped by a variety of metal fragments to give hexanuclear mixed-metal carbide clusters [19]. The further advantage of using such a capping procedure is that the added fragment may contain a specific organic ligand, which therefore provides for very selective formation of a cluster hydrocarbyl derivative.

Finally, in certain cases it appears possible to utilize the properties of ligands attached to smaller metallic units in order to promote and control the metal–metal bond formation necessary to construct larger units. One such example involves the condensation of triruthenium sulfur clusters, where the sulfur atoms provide linkages in the cluster formation process [20]. Also, many examples are displayed in the work of Stone and co-workers where chains and clusters are formed via $M \equiv C$ coupling reactions [21].

Higher-nuclearity clusters that have relatively compact polyhedral geometries tend to be not only electronically saturated but also rather crowded within the coordination shell of the cluster framework. Reactivity studies of carbonyl substitution by tertiary phosphines have shown associative reaction profiles [22]. Since prospective organic ligands are not usually good nucleophiles, direct carbonyl substitution to form hydrocarbon derivatives is not intrinsically promising. However, substitution can be promoted by oxidative decarbonylation with trimethylamine oxide, as has been developed for smaller carbonyl complexes [23]. In certain cases, this process may lead to isolable intermediates with a more loosely bound ligand, such as acetonitrile [24], which may then be displaced by a hydrocarbon substrate. Finally, a very promising technique, for electroactive but structurally stable anionic clusters, is to oxidize the cluster by two electrons in the presence of a neutral ligand, thereby allowing incorporation of the ligand into the coordination shell [25].

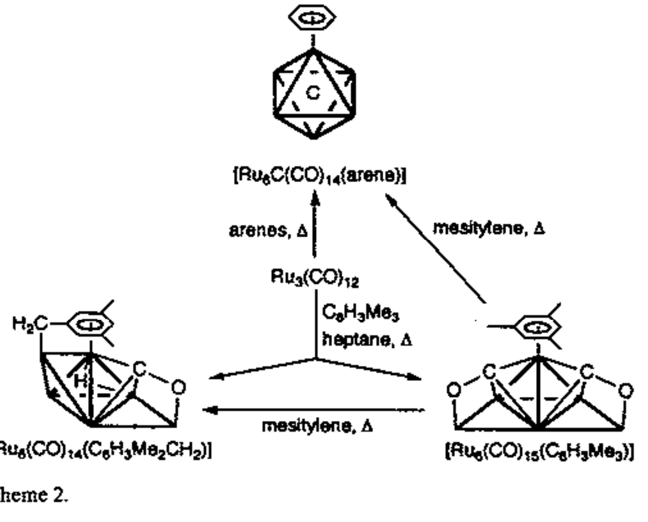
3. HOMOMETALLIC HEXANUCLEAR CLUSTERS

3.1 Carbido-hexaruthenium clusters

The carbido-hexaruthenium system represents the prototypical octahedral cluster framework, and the stability promoted by the encapsulated carbon ligand has allowed development of a diverse derivative organometallic chemistry in various forms. The first compounds in this class were the arene derivatives $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta^6\text{-arene})$, where arene = C_6H_6, C_6H_5Me, and $C_6H_3Me_3$, which were prepared in low yield by heating $Ru_3(CO)_{12}$ with the arene [26]. An extended range of arene derivatives has been explored more recently [27].

A re-investigation of the reaction forming the mesitylene-carbido cluster has given some useful insight into the pathways responsible. The cluster $Ru_6(\mu_4,\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$ is obtained from the heptane solution pyrolysis of $Ru_3(CO)_{12}$ and mesitylene, and it has a double edge-bridged tetrahedral core of ruthenium atoms with two quadruply bonded carbonyl ligands [28] (see Scheme 2). Thermolysis of this complex in mesitylene gives equal amounts of the octahedral $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$, described above, together with $HRu_6(\mu_4,\eta^2\text{-}CO)(CO)_{13}(\eta^1,\eta^6\text{-}CH_2(C_6H_3)Me_2)$. The latter has a metal core similar to $Ru_6(\mu_4,\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$; however, only one quadruply bonded carbonyl ligand remains. The other such carbonyl has been eliminated and replaced by a methylene group derived from the intramolecular C—H bond activation of one of the mesitylene methyl groups. This leads to formation of a Ru—Ru bond between the wing-tip and apical ruthenium atoms. It is apparent that this oxidative addition product is derived from an unsaturated "$Ru_6(\mu_4,\eta^2\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$" intermediate. The carbido co-product may also derive from this intermediate by C—O scission of the μ_4,η^2-CO ligand, loss of carbon dioxide, rearrangement to encapsulate the carbide, and trapping of carbon monoxide from solution.

The compound $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ can also be formed by the redox condensation of $[Ru_5C(CO)_{14}]^{2-}$ and $[Ru(\eta^6\text{-}C_6H_6)(PhCN)_3]^+$ [29]. This benzene cluster is reduced by Na_2CO_3/CH_3OH, and treatment of the intermediate dianion with additional $[Ru(\eta^6\text{-}C_6H_6)(PhCN)_3]^+$ does not result in net metal vertex expansion, although this may happen as an intermediate stage, but rather an overall redox

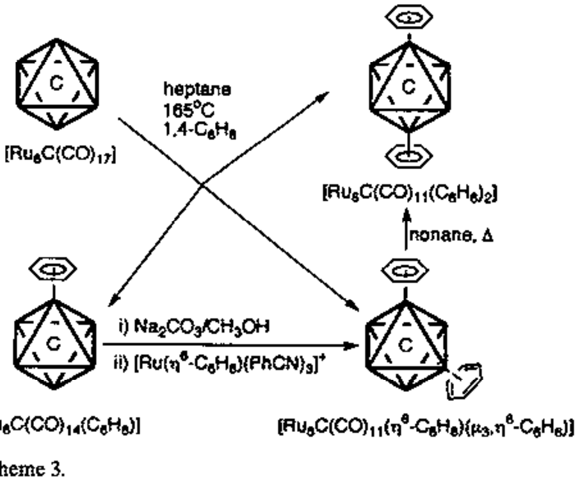


Scheme 2.

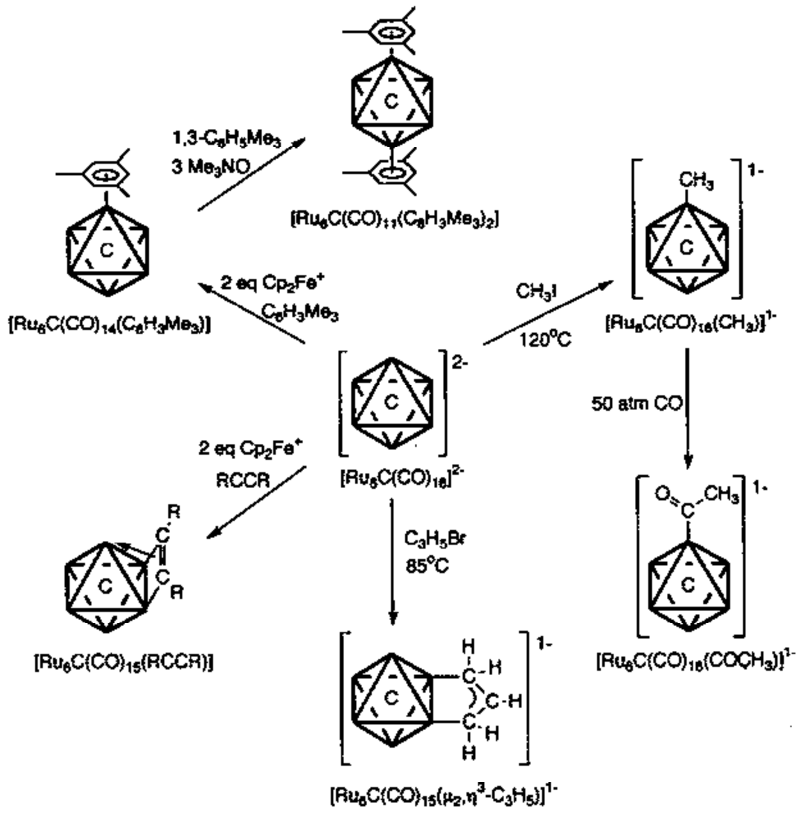
process to give $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3,\eta^2{:}\eta^2{:}\eta^2{:}\text{-}C_6H_6)$ as the major product (see Scheme 3). In this molecule, the second benzene ligand is coordinated to a metal triangle in a "cyclohexatriene" mode with the three coordinated C—C bonds shorter by 0.09 Å than the three uncoordinated ones. This compound represents the first example of an arene as a face-bridging ligand in a higher-nuclearity cluster.

Very recently, it was shown that heating $Ru_6C(CO)_{17}$ in the presence of 1,4-cyclohexadiene in heptane at 165°C is a direct route to two forms of the dibenzene-substituted cluster [30] (see Scheme 3). Upon being heated in nonane, the previously known $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3,\eta^2{:}\eta^2{:}\eta^2{:}\text{-}C_6H_6)$ could be converted to the new compound $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$, in which the two benzene ligands are bound to single metal centers on opposite vertices of the octahedron. An analogous "sandwich" compound $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)_2$ can be prepared by treating $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$ with three equivalents of Me_3NO and dihydromesitylene (1,3,5-trimethyl-1,3-cyclohexadiene) [31]. Although the original intention in forming the bis-mesitylene complex was to produce a face-capping arene ligand, the extra bulk of the mesitylene methyl groups may possibly preclude the face-capping bonding mode.

The reduced carbido cluster $[Ru_6C(CO)_{16}]^{2-}$ also shows possibilities for an extensive derivative chemistry (see Scheme 4). Reactions involving the formal replacement of the two negative charges by a two-electron donor are particularly successful [32,33]. A moderate oxidant, such as ferrocenium ion or ferric ion, can be used to generate, in situ, the formally unsaturated "$Ru_6C(CO)_{16}$" species, which attains stabilization by associating a two-electron donor ligand. A variety of alkynes have been used and these form, after loss of a carbonyl, the μ_3,η^2-face bridging adducts $Ru_6C(CO)_{15}(RCCR')$. Mesitylene also reacts with the unsaturated species, with loss of two carbonyls, to form the complex $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$. This type of



Scheme 3.



Scheme 4.

reaction was termed broadly as "oxidative addition" by Lewis and co-workers [33], but since this term is well-established as a reaction type in organometallic chemistry, the term "oxidative substitution" seems more appropriate.

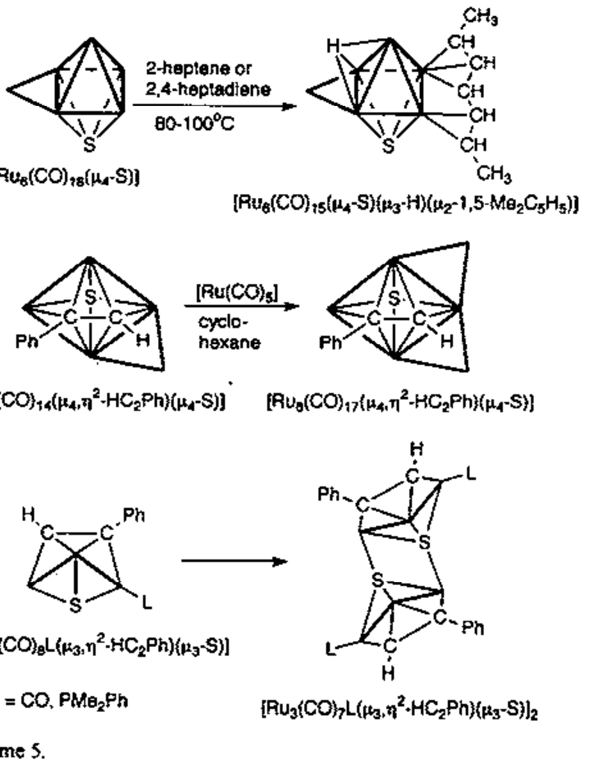
The cluster $[Ru_6C(CO)_{16}]^{2-}$ does undergo classical oxidative addition reactions [34,35], which illustrate the structural stability of the Ru_6C framework even under severe reaction conditions. Treatment with neat methyl iodide at 120°C for one hour gives $[Ru_6C(CO)_{16}(CH_3)]^-$ in 40% yield after chromatography over deactivated alumina. X-Ray crystallography shows that the octahedral metal framework is retained, with the methyl group attached to one ruthenium atom. Under carbon monoxide pressure (50 atm), carbonyl insertion occurs in $[Ru_6C(CO)_{16}(CH_3)]^-$ to give the η^1-acetyl cluster $[Ru_6C(CO)_{16}(COCH_3)]^-$, which retains the same metal and ligand arrangement. The cluster $[Ru_6C(CO)_{16}]^{2-}$ also reacts with neat allyl bromide at 85°C to give $[Ru_6C(CO)_{15}(\mu\text{-}C_3H_5)]^-$, in which the allyl group is coordinated to two ruthenium atoms in a μ,η^3-fashion. This was the first example of such a coordination mode in higher-nuclearity clusters. Interestingly, an analogous coordination mode is observed in the derivative

$Ru_6C(CO)_{14}(SePh)(\mu\text{-}C_3H_5)$, which is prepared by treating $[Ru_6C(CO)_{16}]^{2-}$ first with PhSeCl to produce $[RuC(CO)_{15}(SePh)]^-$, and then heating with allyl bromide to 110°C in a pressure bottle [35].

Although the complex $Ru_6C(CO)_{14}(\mu\text{-}CNMe_2)_2$ is formally a derivative of $[Ru_6C(CO)_{16}]^{2-}$, it is synthesized in low yield (6%) from the vacuum pyrolysis of $Ru_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$, rather than from a pre-assembled hexaruthenium cluster [36]. Its formation can be envisaged as proceeding through the coupling of two molecules of the planar trinuclear species. This process may be mediated by bridging of the (dimethylamino)carbyne ligands, with the thermodynamic stability of the carbon-centered octahedral structure responsible for the final product geometry.

3.2 *Heteroatom-stabilized hexaruthenium clusters*

The sulfido cluster $Ru_6(CO)_{18}(\mu_4\text{-}S)$, which has an edge-bridged octahedral structure with the sulfur atom occupying an apical position, reacts with either 2-heptene or 2,4-heptadiene to give $Ru_6(CO)_{15}(\mu_4\text{-}S)(\mu_3\text{-}H)(\mu\text{-}1,5\text{-}Me_2C_5H_5)$ [37] (see Scheme 5). The formation of the heptadienyl ligand requires C–H bond activation, and the ease with which this process occurs indicates the labile nature of the

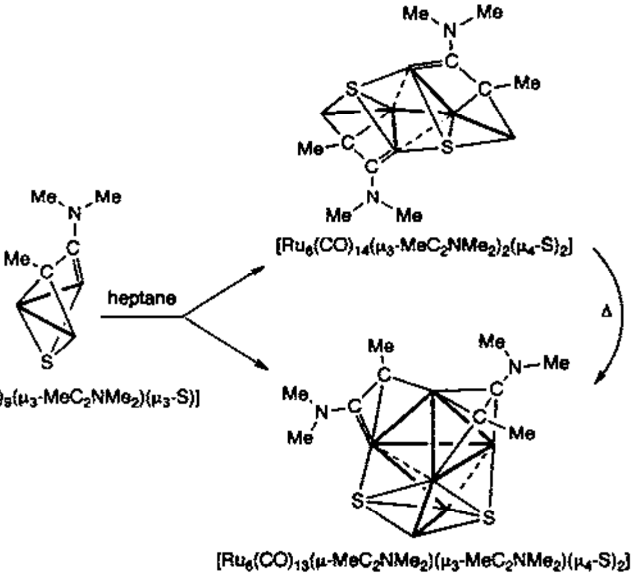


Scheme 5.

carbonyl ligands in the parent compound. This is also demonstrated by the reaction of $Ru_6(CO)_{18}(\mu_4\text{-}S)$ with dihydrogen at 80°C to form $Ru_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}H)_2$ in nearly quantitative yield [38].

Framework expansion via redox condensation allows the synthesis of $Ru_6(CO)_{17}(\mu_4,\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ from $Ru_5(CO)_{13}(\mu\text{-}CO)(\mu_4,\eta^2\text{-}HC_2Ph)(\mu_4\text{-}S)$ and $Ru(CO)_5$ [39] (Scheme 5). In this process a $Ru(CO)_4$ fragment formally replaces the bridging carbonyl ligand in the pentanuclear cluster. Since the latter compound itself is prepared in a stepwise fashion from $Ru_3(CO)_9(\mu_3,\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ by successive reaction with $Ru(CO)_5$ [20], such a growth process may find broader use for the synthesis of high-nuclearity clusters with organic ligands.

Another class of hexanuclear ruthenium clusters bearing hydrocarbon ligands can be synthesized from the dimerization of trinuclear compounds containing sulfur atoms, and their structures are based on cross-linking of the monomer units. For example, the decarbonylative coupling of $Ru_3(CO)_9(\mu_3,\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ and $Ru_3(CO)_8(PMe_2Ph)(\mu_3,\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ gives $[Ru_3(CO)_8(\mu_3,\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)]_2$ and $[Ru_3(CO)_7(PMe_2Ph)(\mu_3,\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)]_2$, respectively [40] (see Scheme 5). In both compounds, the trinuclear subunits are connected through a rhombic Ru_2S_2 linkage formed by the substitution of a carbonyl ligand on a ruthenium in one molecule by the sulfur lone pair in the other molecule. Similarly, $Ru_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ forms the dimer $[Ru_3(CO)_7(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)]_2$, which can undergo further decarbonylation and framework change to give $Ru_6(CO)_{13}(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)_2$ [41] (see Scheme 6). In these



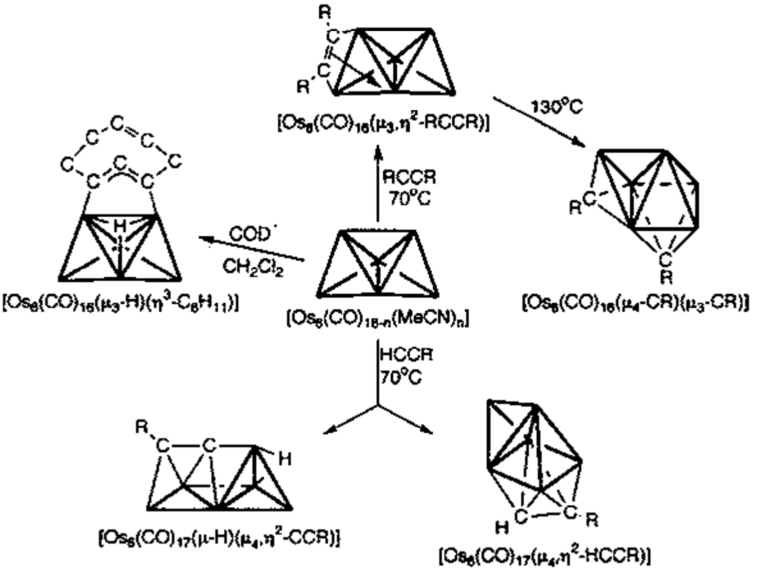
Scheme 6.

compounds, the ability of the sulfur atoms to adopt different coordination modes plays an important role in bringing the two trinuclear moieties together.

The coupling of a triruthenium cluster, mediated by phosphine ligands, leads to the formation of the bis-benzyne complex $Ru_6(CO)_{12}(\mu_4\text{-PMe})_2(\mu_3,\eta^2\text{-}C_6H_4)_2$ from $Ru_3(CO)_{11}(PPh_2Me)$ [42] (Scheme 7). It is interesting that an analogous compound is not formed with the PPh_3 derivative. The framework of this cluster is somewhat unusual in that it is related to a trigonal prism with the benzyne ligands, in a μ_3,η^2-bonding mode, capping the triangular faces. The phosphinidene groups cap two of the square faces, but the third square face shows a Ru—Ru bond across the diagonal, which distorts the framework from a true trigonal prism. A similar cluster framework is seen in the compound $Ru_6(CO)_{12}(\mu_4\text{-PPh})_2(\mu_3\text{-PPh})_2$ [43].

A hexaruthenium cluster with a cyclopentadienyl ligand has also been prepared [44] (Scheme 7). Treatment of the open pentaruthenium cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ with either C_5H_6 or C_5Me_5H in refluxing benzene leads to the octahedral cluster $Ru_6C(CO)_{10}(\mu\text{-}PPh_2)_2(\mu_3\text{-CH})(\eta^5\text{-}C_5R_5)$. The reaction mechanism is unclear as it must involve some cluster degradation to provide the extra metal center. It was suggested that the ligand C_2PPh_2 is the source of the carbido ligand as well as of the alkylidyne carbon. The alkylidyne proton is presumably derived from the cyclopentadiene ligand.

In an unusual reaction, heating $Ru_3(CO)_{12}$ in cyclohexane with stoichiometric amounts of phenol results in hexanuclear raft structure with a benzyne-like C_6H_4O ligand derived from the phenol [45]. Treatment of this product with $P(OMe)_3$ leads to carbonyl substitution by a phosphite ligand [46]. The X-ray crystal structures of



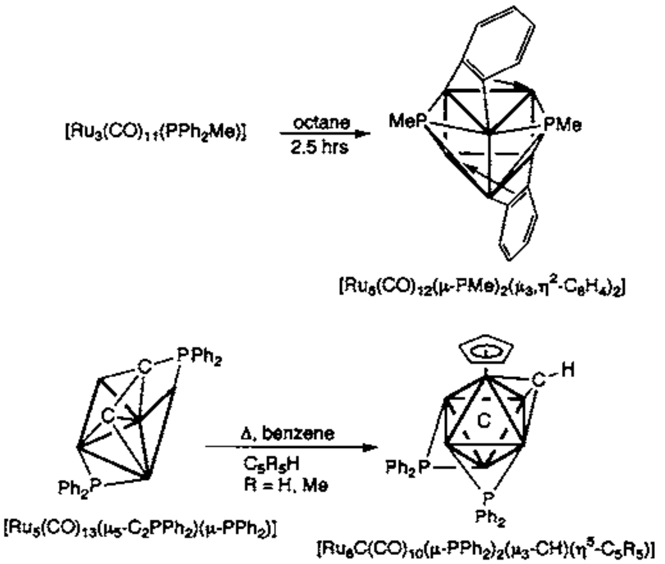
Scheme 7.

both products, $Ru_6H_2(CO)_{15}L(C_6H_4O)$ (L = CO, $P(OMe)_3$), show both triply and doubly bridging hydrides together with the C_6H_4O ligand bridging five of the metals via a number of different interactions. The most closely related complex is the cluster $[Ru_6H(\mu\text{-}OCNMe_2)_2(\mu\text{-}CO)_4(CO)_{14}]^-$ [47], which has a distorted ring of six ruthenium atoms but lacks the transannular Ru—Ru bonds seen in the raft complexes.

3.3 $Os_6(CO)_{18}$-derived clusters

The bicapped tetrahedral compound $Os_6(CO)_{18}$ has been shown to be a useful starting material for a variety of unique and interesting transformations, especially via the activated or "lightly-stabilized" derivatives $Os_6(CO)_{18-x}(MeCN)_x$ ($x = 1, 2$) [5]. A striking feature of the reactions of these clusters with organic substrates is the interplay between metal framework rearrangements and the cleavage of various bonds in the hydrocarbon moiety (see Scheme 8). For instance, the disubstituted cluster $Os_6(CO)_{16}(MeCN)_2$ reacts with 1,5-cyclooctadiene at ambient temperature to give $Os_6(CO)_{16}(\mu_3\text{-}H)(\eta^3\text{-}C_8H_{11})$, with the metal core geometry unchanged but one sp^2 C—H bond cleaved [48].

When $Os_6(CO)_{17}(MeCN)$ reacts with terminal alkynes HCCR, a mixture of two products is formed [49]. The first product, $Os_6(CO)_{17}(\mu\text{-}H)(\mu_4,\eta^2\text{-}CCR)$, has a metal core derived from the cleavage of two Os—Os bonds in the bicapped tetrahedron, which requires the addition of four electrons. As a result, the alkyne ligand has to donate a total of six electrons when it replaces the acetonitrile ligand, and the solution adopted at the mild temperature of the reaction (70°C) is C—H bond

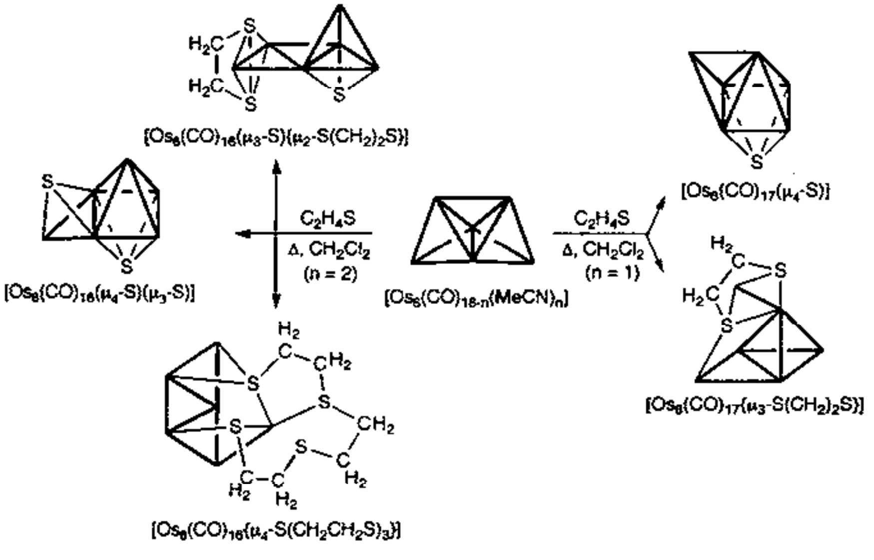


Scheme 8.

activation, resulting in a quadruply bridging acetylide ligand. The second product, $Os_6(CO)_{17}(\mu_4,\eta^2\text{-HCCR})$, has a capped square pyramidal structure, which arises from the cleavage of only one Os–Os bond due to alkyne insertion into the parent cluster. The required four electrons are provided by the alkyne ligand without bond activation. The reaction of $Os_6(CO)_{17}(MeCN)$ with the internal alkynes RCCR′ (R = Me, Ph; R′ = Me, Ph, or Et) at 70°C gives $Os_6(CO)_{16}(\mu_3,\eta^2\text{-RCCR}')$ as the major product, which retains the parent bicapped tetrahedral structure with a face-capping alkyne ligand. When $Os_6(CO)_{16}(\mu_3,\eta^2\text{-RCCR})$ (R = Me and Ph) is heated at 130°C for an extended period, C–C bond cleavage, accompanied by framework rearrangement to a capped square pyramidal structure, leads to $Os_6(CO)_{16}(\mu_4\text{-CR})(\mu_3\text{-CR})$ [49].

The reaction of $Os_6(CO)_{17}(MeCN)$ with excess thiirane, $(CH_2)_2S$, results in a higher degree of Os–Os bond cleavage (see Scheme 9), to form a tetrahedral cluster with both terminal and edge bridging osmium atoms, $Os_6(CO)_{17}(\mu\text{-S}(CH_2)_2S)$ [50]. A closely related opened structure is also observed in $Os_6(CO)_{19}(\mu_3,\eta^2\text{-NCMe})$ [51], which was prepared indirectly from $Os_6(CO)_{17}(MeCN)$ via an Os_6Pt species. The reaction of $Os_6(CO)_{16}(MeCN)_2$ with 10-fold excess of thiirane in refluxing dichloromethane gives two compounds with structures arising from multiple metal bond cleavage and thiirane ring-opening oligomerization [50].

Flattening $Os_6(CO)_{18}$ leads to the "raft" compound $Os_6(CO)_{21}$. In the activated form $Os_6(CO)_{20}(MeCN)$, it reacts with terminal alkynes to generate the compounds $Os_6(CO)_{20}(\mu_3,\eta^2\text{-C=C(H)(R)})$, whose metal core structure is that of a chain of four triangles [52]. The vinylidyne ligand forms from the terminal alkyne through a



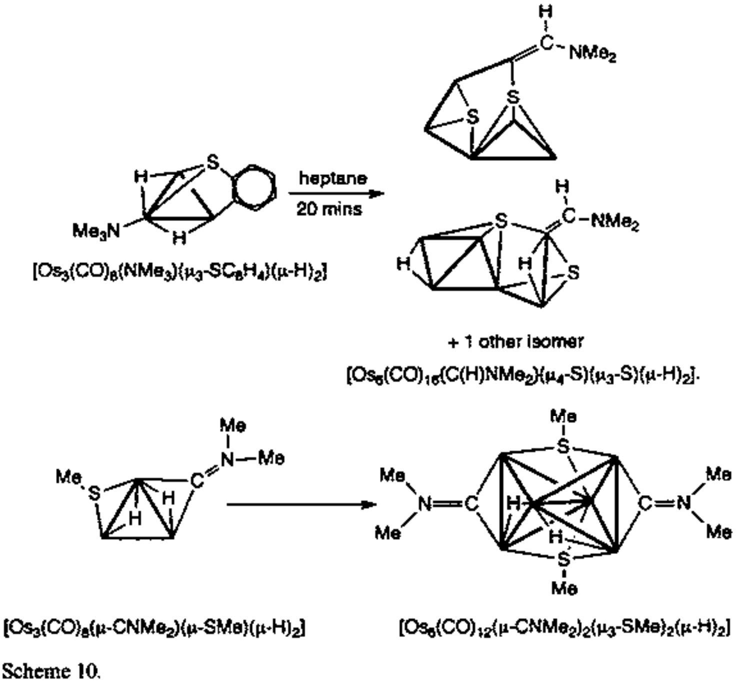
Scheme 9.

1,2-hydrogen shift. No reaction was observed with internal alkynes, indicating the nature of the reaction to be hydrogen assisted.

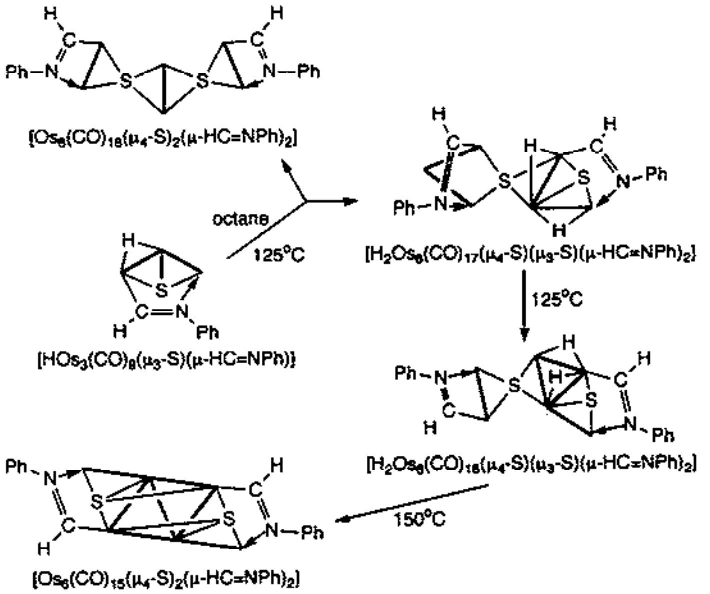
3.4 Heteroatom-stabilized hexaosmium clusters

Hexanuclear osmium clusters can be prepared, as in the case with ruthenium, from the coupling of trinuclear species containing hydrocarbyl ligands through assistance by heteroatoms. The resulting osmium clusters also do not possess compact polyhedral geometries. For instance, heating $Os_3(CO)_8(NMe_3)(\mu_3\text{-}SC_6H_4)(\mu\text{-}H)_2$ in refluxing heptane gives a mixture of three isomers, all having the formula $Os_6(CO)_{16}(C(H)NMe_2)(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)_2$ [53] (see Scheme 10). The structures are based on open and closed triangles linked by the sulfido ligands. Interconversion between two of the three isomers is assisted by carbon monoxide. Similarly, the decarbonylative coupling of $Os_3(CO)_8(\mu\text{-}CNMe_2)(\mu\text{-}SMe)(\mu\text{-}H)_2$ gives a structure with edge-sharing bitetrahedra [54].

More complex isomeric systems are encountered in the condensation of $HOs_3(\mu_3\text{-}S)(\mu\text{-}HC{=}NPh)(CO)_9$, from which $Os_6(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NPh)_2(CO)_{18}$, $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NPh)_2(CO)_{17}$, $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NPh)_2(CO)_{16}$, and $Os_6(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NPh)_2(CO)_{15}$ are formed [55] (see Scheme 11). In this reaction, the number of metal–metal bonds formed increases as the temperature is raised. Finally, the reaction of $Os_3(CO)_{10}(MeCN)_2$ with selenophene, C_4H_4Se, gives the



Scheme 10.



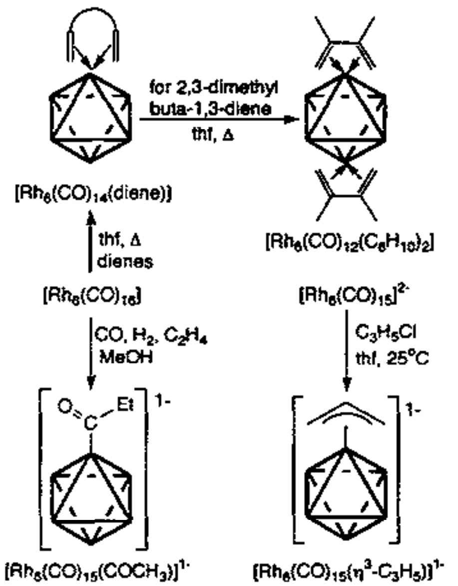
Scheme 11.

C–H and C–Se bond activated product $HOs_6(\mu_3\text{-}Se)(\mu_4,\eta^4\text{-}C_4H_3)(CO)_{20}$, which has an open-chain structure [56].

3.5 Hexarhodium clusters

The reactions of $Rh_6(CO)_{16}$ with various neutral and anionic ligands lead to carbonyl substitution products in which the Rh_6 framework is maintained [5]. Stable acyl derivatives are also known [57] (see Scheme 12). Reactions of $Rh_6(CO)_{16}$ with olefins have been examined [58]. No stable derivatives with simple olefins have been isolated, but in the cases of 1,5-cyclo-octadiene and 1,4-cyclohexadiene, the monodiene substituted products can be isolated and characterized. No metal core change occurs during the process, with the diene ligand replacing two terminal carbonyls on each rhodium center. The reaction with 2,3-dimethyl-1,3-butadiene gives both the mono- and di-substituted compounds, the former serving as the precursor for the latter. Up to three norbornadiene ligands can be incorporated to form $Rh_6(CO)_{10}(C_7H_8)_3$, which is the upper limit before cluster degradation takes place. Similar degradation to tetranuclear species occurs when cycloheptatriene and cyclooctatetraene are allowed to react with $Rh_6(CO)_{16}$.

The isoelectronic $[Rh_6(CO)_{15}]^{2-}$ reacts with allyl chloride to form the oxidative addition product $[Rh_6(CO)_{15}(\eta^3\text{-}C_3H_5)]^-$ in which the allyl group coordinates to a single rhodium atom in the η^3-coordination mode [59]. This bonding mode of the allyl ligand contrasts with that displayed in $[Ru_6C(CO)_{15}(\mu,\eta^3\text{-}C_3H_5)]^-$, as described



Scheme 12.

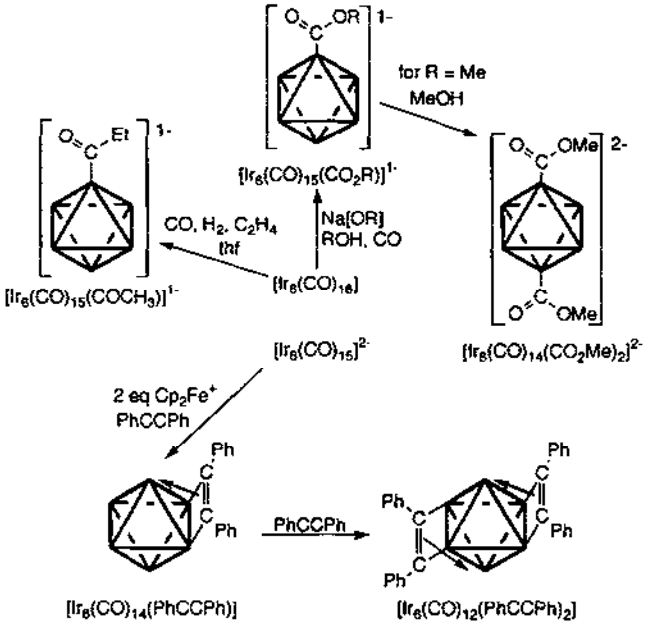
earlier. The octahedral core with the arrangement of the four face-bridging carbonyl groups, as in $Rh_6(CO)_{16}$, is retained.

There are two carbide-centered hexarhodium carbonyl clusters, namely, the octahedral $[Rh_6C(CO)_{13}]^{2-}$ [60] and the trigonal prismatic $[Rh_6C(CO)_{15}]^{2-}$ [61]. These two compounds can be readily interconverted by the addition/loss of two equivalents of carbon monoxide [60]. Despite the ease with which $[Rh_6C(CO)_{15}]^{2-}$ can be formed from $[Rh_6C(CO)_{13}]^{2-}$, reactions of the latter with diphosphines (P—P) give only the octahedral derivatives $[Rh_6C(CO)_{11}(P\text{—}P)]^{2-}$ [62]. No reactions with unsaturated hydrocarbons have been reported. It would be interesting to see whether association or substitution would occur if $[Rh_6C(CO)_{13}]^{2-}$ were treated with a diene.

3.6 Hexairidium clusters

The black isomer of $Ir_6(CO)_{16}$ is isostructural with $Rh_6(CO)_{16}$, with four μ_3-bridging carbonyl groups. Nucleophilic attack by methoxide and ethoxide anions at one carbonyl ligand affords the alkoyxcarbonyl derivative $[Ir_6(CO)_{15}(CO_2R)]^-$ (R = Me and Et) [63]. The solid state structure of $[Ir_6(CO)_{15}(CO_2Me)]^-$ is based on the parent octahedron. The methoxycarbonyl group is terminally bound to an iridium atom. When an excess of sodium methoxide is used, an equilibrium between $[Ir_6(CO)_{15}(CO_2Me)]^-$ and $[Ir_6(CO)_{14}(CO_2Me)_2]^{2-}$ is observable (Scheme 13).

The red isomer of $Ir_6(CO)_{16}$ is also reportedly reactive towards halides and



Scheme 13.

pseudohalides to form the ligand substituted products $[Ir_6(CO)_{15}(X)]^-$ and $[Ir_6(CO)_{14}(\mu_2\text{-}X)]^-$ [64,65]. This reactivity also suggests the possibility of replacing the carbonyl ligands with other donor ligands. However, reactions with dienes similar to those with $Rh_6(CO)_{16}$ have not been reported.

The dianion $[Ir_6(CO)_{15}]^{2-}$ behaves similarly to $[Ru_6C(CO)_{16}]^{2-}$ with respect to redox-assisted ligand association. When ferrocenium ion is used as the oxidant and a donor ligand such as diphenylacetylene is also present, the alkyne-substituted compound $Ir_6(CO)_{14}(\mu_3,\eta^2\text{-}C_2Ph_2)$ is formed in good yield [66]. Treatment with excess diphenylacetylene at 75°C gives the disubstituted cluster $Ir_6(CO)_{12}(\mu_3,\eta^2\text{-}C_2Ph_2)_2$, which has trans faces of the octahedron capped by the two alkyne ligands.

3.7 Other hexanuclear systems

There are a number of well-known homometallic hexanuclear compounds for which no hydrocarbyl derivatives have been reported. These include first-row analogs of some of the compounds discussed earlier, such as $[Fe_6C(CO)_{16}]^{2-}$ as well as $Co_6(CO)_{16}$, $[Co_6(CO)_{15}]^{2-}$, and $[Co_6C(CO)_{15}]^{2-}$ [14,32]. These compounds have a strong tendency to fragment to lower nuclearity clusters upon attempted substitution [67].

Similar lability of the metal–metal bonds is shown by the compounds

$[M_6(CO)_{12}]^{2-}$, M = Ni, Pt [68]. Although the polymerization of acetylene in the presence of the hexanickel cluster has been reported, no derivative of the cluster has been isolated [69].

On the other hand, the very stable carbido-hexarhenium clusters $[H_2Re_6C(CO)_{18}]^{2-}$ [70] and $[Re_6C(CO)_{19}]^{2-}$ [71] are known. The 19th carbonyl ligand in $[Re_6C(CO)_{19}]^{2-}$ causes a significant perturbation to the geometry of the ligand sphere. This unique situation brings added reactivity to this compound, i.e. the carbonyl ligand can be photochemically activated at room temperature, giving a formally unsaturated cluster species "$[Re_6C(CO)_{18}]^{2-}$", which can subsequently react with dihydrogen to give $[H_2Re_6C(CO)_{18}]^{2-}$. This species also reacts with diazomethane to form the methylene-bridged cluster $[Re_6C(CO)_{18}(\mu\text{-}CH_2)]^{2-}$; the latter compound is also formed by "decapping" $[Re_7C(CO)_{21}(\mu\text{-}CH_2)]^{1-}$ in acetonitrile [72].

4. SELECTED HETEROMETALLIC SYSTEMS

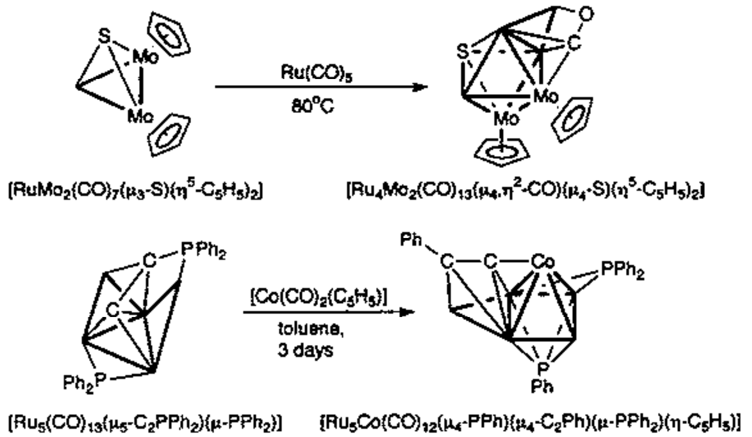
For mixed-metal cluster compounds, rich information about the synergic effect of different metals as well as the effect of metal specificity on hydrocarbyl ligand transformation can be anticipated. However, compared with the knowledge accumulated for homometallic clusters, information about heterometallic clusters is much scarcer. The majority of the studies on heterometallic hexanuclear carbonyl clusters has been concerned with their synthesis from smaller clusters using the methodologies discussed in Sect. 2. Ligand substitution and redox-assisted derivative formation have been very little explored.

4.1 Molybdenum–ruthenium

The mixed-metal cluster $Mo_2Ru_4(CO)_{13}(\mu_4,\eta^2\text{-}CO)(\mu_4\text{-}S)(\eta^5\text{-}C_5H_5)_2$ is obtained in 3% yield from the reaction of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ and $[CpMo(CO)_2]_2$ or in 23% yield from $Cp_2Mo_2Ru(CO)_7(\mu_3\text{-}S)$ and $Ru(CO)_5$ [73] (see Scheme 14). The structure of this compound is based on a sulfur-capped square pyramid, with one basal Ru—Ru bond being bridged by a $Ru(CO)_3$ unit. The formation of this cluster again demonstrates the usefulness of a main group heteroatom in the aggregation of smaller fragments of clusters. One particular point of interest about this complex is the existence of a μ_4,η^2-carbonyl ligand with a long C—O distance of 1.262(8) Å. The carbon atom in this carbonyl ligand triply bridges one Mo and two Ru atoms, and the oxygen atom is bound to the edge bridging Ru. It is noteworthy that oxygen atom is not connected to the expectedly more oxophilic Mo atom.

4.2 Ruthenium–cobalt

The condensation of $CpCo(CO)_2$ with the pentanuclear cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ affords the mixed-metal cluster $Ru_5Co(\eta^5\text{-}C_5H_5)(\mu_4\text{-}$



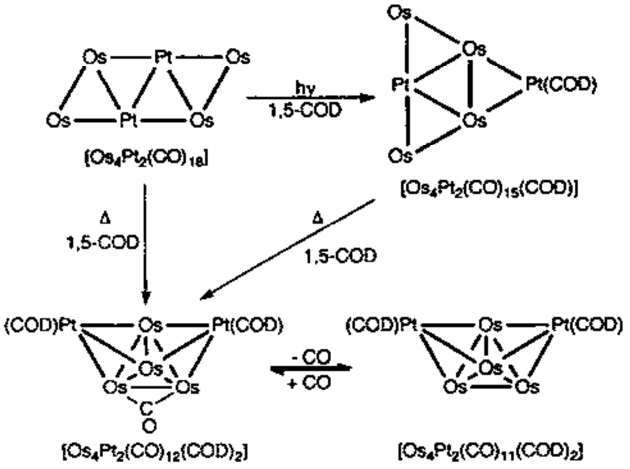
Scheme 14.

PPh)(μ_4-C_2Ph)(μ-PPh_2)$(CO)_{12}$ in 32% yield [74] (see Scheme 14). Both the metal core and the organophosphorus ligands undergo complex rearrangements during the cluster expansion. The overall ligand transformations are the formation of a phenylacetylide ligand, an edge-bridging diphenylphosphino group, and a μ_4-phenylphosphinidene moiety from a diphenylphosphinoacetylide ligand and an edge-bridging diphenylphosphino group. It was suggested that the phosphinidene ligand in the product actually originated from the phosphino group through cleavage of a P—C(Ph) bond rather than from the phosphinoacetylide ligand.

4.3 Ruthenium–platinum and osmium–platinum

Recent work has shown that $Pt(COD)_2$ and $Pt(COD)Cl_2$ (COD = 1,5 cyclooctadiene) are useful reagents for introducing platinum atoms and/or hydrocarbon ligands into heterometallic clusters. In most of the reported cases, reactions afford mixed-metal clusters having nuclearities higher than six, which are beyond the scope of this review. However, from the reaction between $[Ru_5C(CO)_{14}]^{2-}$ and $Pt(COD)Cl_2$, the cluster $Ru_5PtC(CO)_{14}(COD)$ is isolated in 41% yield [75]. The same compound also forms in the reaction of $Ru_5C(CO)_{15}$ and $Pt(COD)_2$. This compound reacts with carbon monoxide to displace the COD ligand and give $Ru_5PtC(CO)_{16}$, which has an octahedral metal core as required by the total electron count of 86.

In contrast to the previous compact structures, the structure of $Ru_4Pt_2(CO)_{18}$ is a puckered chain of four triangles in the form of a ladder with Pt–Pt interaction, and it can be formally viewed as a dimer of the hypothetical unsaturated complex "$Ru_2Pt(CO)_9$" [76]. Treatment of $Ru_4Pt_2(CO)_{18}$ with PhC≡CPh in refluxing heptane gives a higher-nuclearity compound $Ru_6Pt_3(CO)_{14}(\mu_3\text{-}C_2Ph_2)_3$, which is formally derived from the trimerization of "$Ru_2Pt(CO)_5(C_2Ph_2)$" with loss of a carbonyl. When $Ru_4Pt_2(CO)_{18}$ is allowed to react with 1,5-COD under UV irradi-



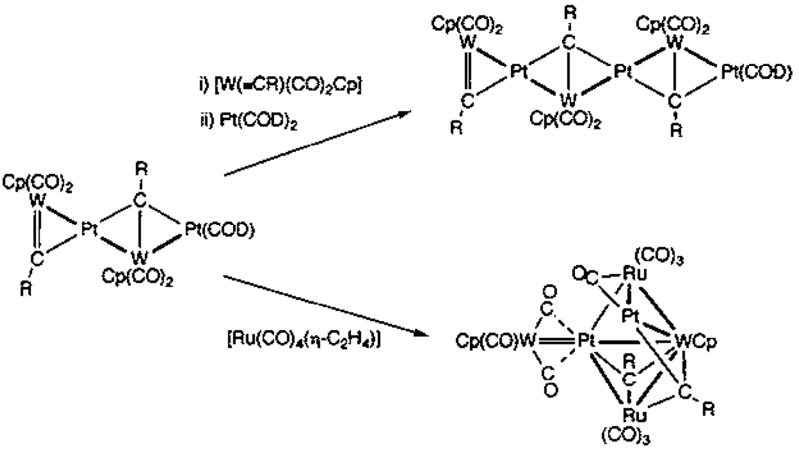
Scheme 15.

tion, both pentanuclear Ru_4Pt and nonanuclear Ru_5Pt_4 clusters are isolated. These results suggest the hexanuclear Ru_4Pt_2 cluster is not a very stable species and easily undergoes fragmentation and recombination to give bimetallic clusters of different metal ratios.

The compound $Os_4Pt_2(CO)_{18}$ (see Scheme 15) is isoelectronic and isostructural with $Ru_4Pt_2(CO)_{18}$. However, this structural unit seems to be more robust than its ruthenium analog. Under photolysis, $Os_4Pt_2(CO)_{18}$ reacts with 1,5-COD to give a substituted product, $Os_4Pt_2(CO)_{15}(COD)$, with the COD ligand bound to platinum [77]. However, it is noteworthy that $Os_4Pt_2(CO)_{15}(COD)$ is not a simple substituted complex of $Os_4Pt_2(CO)_{18}$, as the new compound has a "raft-like" non-planar structure with no Pt–Pt interaction. By electron counting rules, this new compound is four electrons short of the total of 90 electrons required by a planar structure. However, it is stable under UV irradiation. When $Os_4Pt_2(CO)_{18}$ is allowed to react thermally with 1,5-COD, two bicapped tetrahedron based compounds $Os_4Pt_2(CO)_{12}(COD)_2$ and $Os_4Pt_2(CO)_{11}(COD)_2$ form as the main products [78]. The former has all the electrons demanded by its structure and can be also obtained from the "raft-like" $Os_4Pt_2(CO)_{15}(COD)$. The latter compound forms by photochemical or thermal decarbonylation of the saturated compound.

4.4 *Tungsten–ruthenium–platinum*

The reagent $Pt(COD)_2$ has also been used to form hetero metallic clusters by reaction with Group 6 metal carbyne complexes. The reaction between these reagents yields stable complexes and a series of chain and star cluster complexes have been isolated. The platinum center can ligate either one carbyne, with retention of one COD ligand, or two carbynes alone. Likewise, the carbyne M≡C bond can ligate to



Scheme 16.

one or two platinum centers. This versatility allows chains of varying length to be constructed, with the odd-numbered chains being more commonly reported. Chains of seven or more metal atoms begin to encounter steric constraints and can form cyclic "star" clusters.

Four examples of six-membered chains have been reported with either W_3Pt_3 or WMo_2Pt_3 metal chains [79] (see Scheme 16). These complexes are all synthesized by the stepwise addition of $Pt(COD)_2$ and the carbyne complexes $Cp(OC)_2M(\equiv CR)$ to a trimetallic "bow tie" complex $PtM_2(\mu_2CR)_2Cp_2(CO)_4$.

The reactions between carbynes and platinum group metals are fairly general with a variety of carbyne complexes with different alkylidyne substituents and cyclopentadienyl ligands reacting with platinum, palladium, and nickel complexes with labile ligands [21]. Alternatively, the complex $W_2Ru_2Pt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_9(\eta^5\text{-}C_5H_5)_2$ is obtained from the reaction of $Ru(CO)_4(\eta\text{-}C_2H_4)$ with a tetranuclear chain compound of the type described above [80]. This reaction differs from those described previously as the ruthenium atoms do not extend the chain skeleton but instead bridge an interior Pt—W bond and cause alkylidyne migration. The final structure is an incomplete trigonal bipyramid with apical rutheniums and an equatorial plane of Pt—W—Pt atoms. The remaining tungsten atom is attached to a platinum via a double bond.

5. SUMMARY AND CONCLUSIONS

On the basis of the reactions discussed in this review, it is apparent that clusters possessing the compact octahedral geometry have greater structural integrity under reaction conditions suitable for substitution. This stability is found whether the cluster contains an interstitial carbide, as with the Ru_6C and Re_6C clusters, or not, as with the Rh_6 and Ir_6 clusters. Indeed, the octahedron seems to be an especially stable structure as it is frequently the result of cluster building reactions or the ultimate rearrangement product of more open hexanuclear clusters. It is important to note, however, that the octahedral structure is subject to steric constraints; when the steric interactions induced by substitution of larger ligands for carbonyls become too great, breakdown to smaller clusters or opening to less compact geometries ensues.

The chemistry of the Os_6 clusters is remarkably distinct at present. The lack of a predominantly stable cluster geometry allows metal framework rearrangement in many cases. This is particularly striking, given the mild conditions employed in most of the reported reactions. Furthermore, a frequent feature of the chemistry observed for the Os_6 clusters is bond activation in the coordinated hydrocarbon groups; both C—H and C≡C bond cleavage reactions have been seen. Although transformation of a hydrocarbyl group subsequent to its coordination is rare in the chemistry reported for other cluster systems, this will likely change as more systematic investigations of particular M_6 clusters develop.

The problem of "activating" the relatively robust M_6 clusters toward carbonyl substitution by hydrocarbon groups needs more attention. The formation and designed use of compounds with labile ligands has been limited largely to the Os_6 clusters, but oxidative decarbonylation with trimethylamine oxide should have much broader application. One of the most promising procedures for the initial introduction of a hydrocarbon ligand is "oxidative substitution" of anionic clusters. The limited work with Ru_6C and Ir_6 systems suggests a more general application of this technique will be quite successful.

The use of ligands with heteroatom substituents significantly widens the available chemistry. As has been shown, these substituents mediate in many cluster building reactions. Furthermore, bond scission within the ligand can produce hydrocarbyl fragments that remain as cluster ligands. A few examples have been discussed, such as the production of benzyne ligands from phosphine cyclometallation reactions and the use of selenophene to generate allyl type moieties. Many of these reactions employ relatively modest reaction conditions, although at the present time it is difficult to control either the nature of the resulting hydrocarbyl ligand or the nuclearity of the metal framework supporting it.

The area of heterometallic clusters offers an undoubtedly rich body of results that is relatively untapped at present. The ability to make these clusters in a rational manner by the addition of reactive metal fragments to a smaller cluster offers great promise for construction of specific hydrocarbyl derivatives. This approach also provides for the introduction of a wide range of transition metal centers into the clusters, and, therefore, a way to probe systematically the effects of metal substitution on the resulting organometallic chemistry.

Finally, the possibilities for developing new organometallic chemistry of metal cluster systems are certainly much broader than the restricted point of view that we have adopted here. In terms of hexanuclear, but non-carbonyl, clusters there are notable recent developments in the synthesis and characterization of alkyl derivatives of Mo_6 and W_6 halide clusters [81]. Furthermore, studies of the interaction of larger carbonyl clusters with hydrocarbon substrates raises the question of comparisons with the chemistry of M_6 systems in particular and the possibility of cluster size-specific reactions more generally [82]. Lastly, taking the question of cluster size to a distinct new level, we note the reported involvement of very large clusters/colloids in catalytic reactions [83] and wonder about the structures and reactivities of the hydrocarbyl groups on the "metal surfaces" of these species. It is clear that the organometallic chemistry of metal clusters continues to offer many intriguing challenges and compelling opportunities.

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